Visible-Light-Induced [3+2] Cycloadditions of Donor/Donor Diazo Intermediates with Alkenes to Achieve (Spiro)-Pyrazolines and Pyrazoles

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1. General information

Commercial reagents were used without purification and reactions were run under Ar atmosphere with the exclusion of moisture from reagents using standard techniques for manipulating air-sensitive compounds. All reactions, unless noted, were performed in oven-dried glassware with magnetic stirring under an inert atmosphere of dry argon.

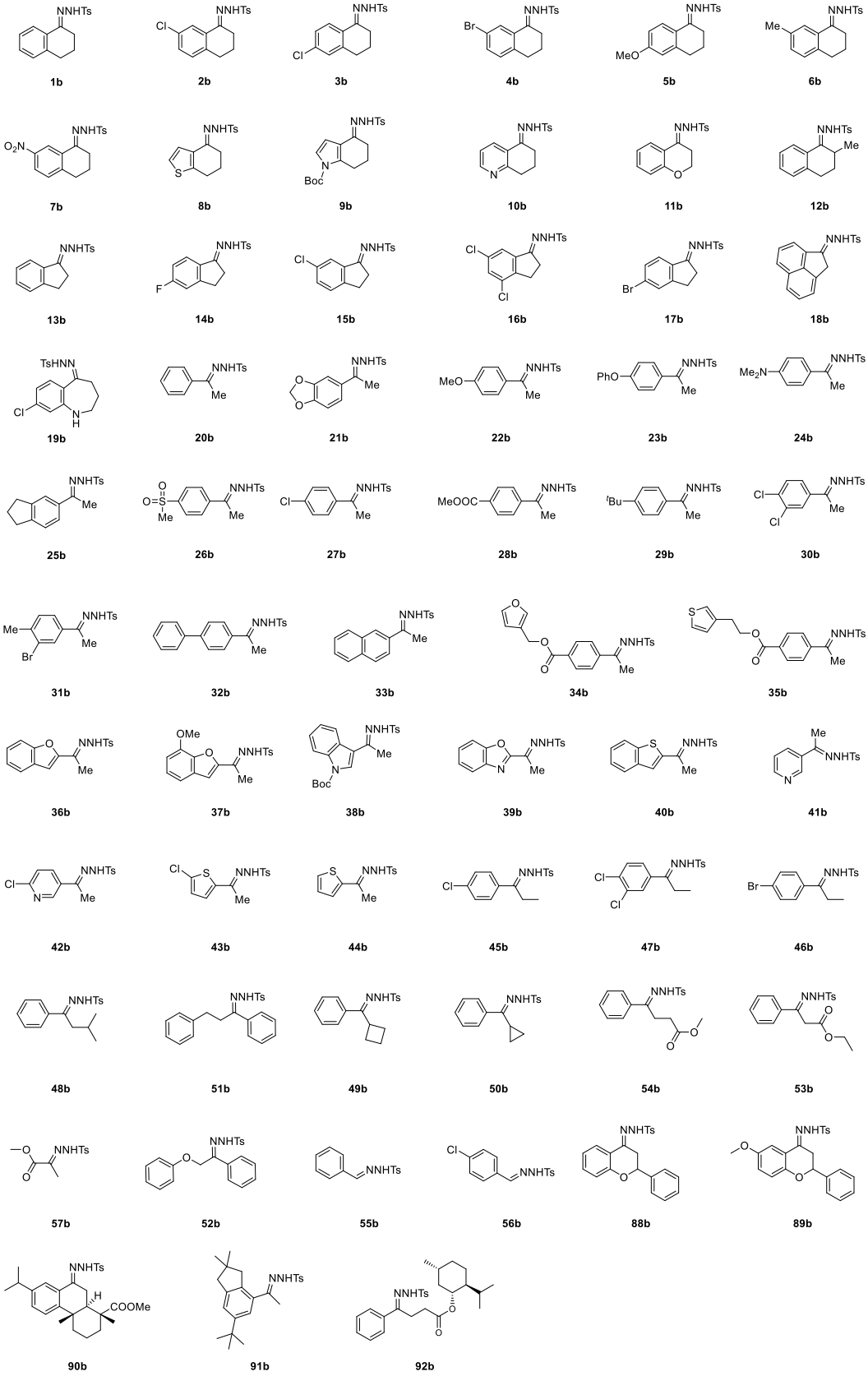
^{1}H NMR spectra (500 MHz) and ^{13}C NMR spectra (126 MHz) were recorded using Bruker Avance 500 spectrometer with $CDCl_3$ or CD_3OD as solvent. NMR spectra were calibrated using the solvent residual signals ($CDCl_3$: δ $^{1}H = 7.26$, δ $^{13}C = 77.16$; CD_3OD: δ $^{1}H = 3.34$, δ $^{13}C = 49.86$). The following abbreviations were used to describe peak splitting patterns when appropriate: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, comp = composite of magnetically non-equivalent protons, dd = doublet of doublets), coupling constants (Hz), integration and assignment. ^{13}C NMR spectra were acquired with broad-band proton decoupling, therefore the assignment of C, CH, CH_2 or CH_3 groups was based on additional HSQC experiments. The assignments of individual NMR signals were based on additional 2D NMR experiments (COSY, NOESY, HSQC, HMBC). High-resolution mass spectra (HRMS) were recorded on an Agilent MSD-Trap-XCT or Q-Tof micro mass spectrometer.

Thin layer chromatography (TLC) was performed using MilliporeSigma glass TLC plates (silica gel 60 coated with F_{254}, 250 μm) and spots were visualized using UV light (254 nm). SiliaFlash® P60 silica gel (particle size: 40-63 μm, pore size: 60 Å) was used for flash column chromatography. A petroleum ether/EtOAc solvent system was used as mobile phase and commercial silica cartridges (12-80 g, Grace®) as stationary phase.

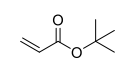
Kessil lamps were purchased from Tansoole, with precise wavelengths (456 nm).

Alpha-tetralone **1a**, Butyl acrylate **1c**, 1,8-Diazabicyclo[5.4.0]undec-7-ene (**DBU**) were purchased from TCI. Anhydrous THF & 2-MeTHF were purchased from Tansoole. Alkene compounds **61c**, **64c**, **65c**, **66c**, **68c**, **71c**, **93c**, **94c**, **95c**, **96c**, **97c** and **98c** were prepared using reported literature procedures. Other alkene compounds were purchased from Bide Pharm, Tansoole, Fisher, TCI or Energy Chemical and used without further purification. *N*-tosylhydrazones **1b-92b** were prepared using reported procedures.

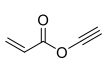
N-tosylhydrazones included in the manuscript



Alkenes included in the manuscript



58c



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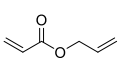
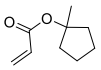


60c



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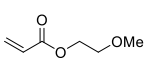
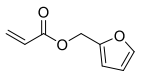


62c

63c



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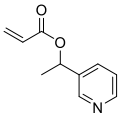

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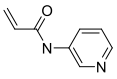

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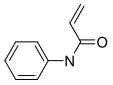
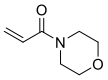
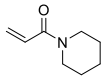


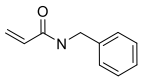
69c



70c



71c



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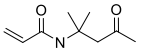
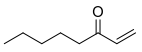
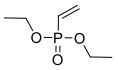


73c



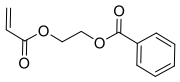
74c



75c

76c

77c



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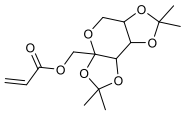
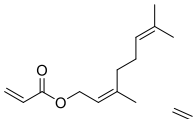
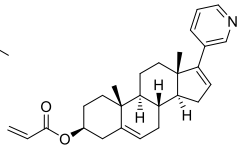


93c



94c



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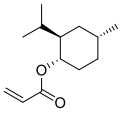

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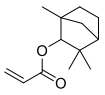

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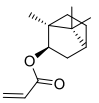


98c

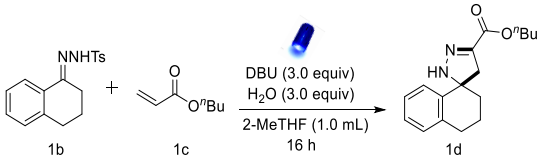
2. Setup for photochemical reactions

The reaction setup is depicted in **Figure S1**. The reaction setup consists of 4 commercially available Kessil lamps which were purchased from Tansoole, with precise wavelengths (456 nm), cooling of the setup was performed by two commercially available fans to keep the temperature around 30 °C.

Figure S1: Photochemical reaction setup using 456 nm Kessil Lamps.

3. Optimization of reaction conditions

Table S1. Optimization of synthesizing sipropyrazolines.

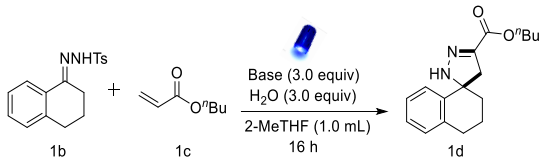


1b 1c 1d

Entry[a]	Changes from standard conditions	Yield[b]
1	None	90%
2	DBN instead of DBU	76%
3	DTHP instead of DBU	10%
4	Cs_2CO_3 instead of DBU	N.D.
5	Et_3N instead of DBU	N.D.
6	THF instead of 2-MeTHF	89%
7	MeCN instead of 2-MeTHF	50%
8	2.0 equiv of **1c** was used	80%
9	Without H_2O	76%
10	3.0 equiv PTC[c] instead of H_2O	82%
11	In the Dark	N.D.
12	Without base	N.D.

[a]Reaction conditions: **1b** (0.2 mmol), butyl acrylate (0.3 mmol, 1.5 equiv.), base (0.6 mmol, 3.0 equiv.), H_2O (0.6 mmol, 3.0 equiv.), solvent (1.0 mL), irradiation with 40 W blue Kessil lamp (λ = 456 nm), r.t., argon atmosphere, 16 h., n.d. = not detected. [b]Yields were determined by ^1H NMR analysis of the crude reaction mixture using 1,3,5-trimethoxybenzene as the internal standard. [c]PTC: tetrabutylammonium bromide.

Table S2. Screening of bases

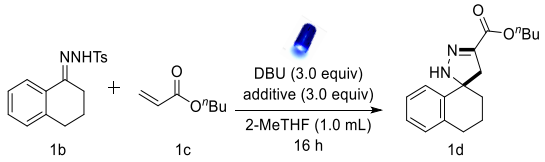


1b 1c 1d

Entry[a]	Base	Yield[b]
1	DBU	90%
2	DBN	76%
3	DTHP	10%
4	Cs_2CO_3	N.D.
5	TBD	N.D.
6	DIPEA	N.D.
7	TMEDA	N.D.
8	Et_3N	N.D.

[a]Reaction conditions: compound **1b** (0.2 mmol, 1.0 equiv), butyl acrylate (0.3 mmol, 1.5 equiv), Base (0.6 mmol, 3.0 equiv), H_2O (0.6 mmol, 3.0 equiv), 2-MeTHF (1.0 mL), irradiation with 40 W blue Kessil lamp (λ = 456 nm), r.t., argon atmosphere, 16 h., n.d. = not detected. [b]Yields were determined by ^{1}H NMR analysis of the crude reaction mixture using 1,3,5-trimethoxybenzene as the internal standard.

Table S3. Screening of additive

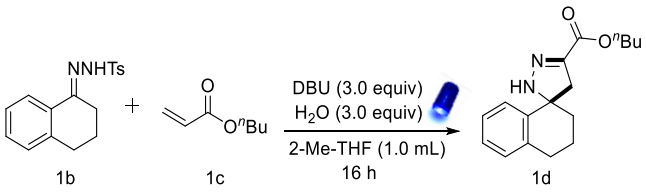


1b 1c 1d

Entry[a]	additive	Yield[b]
1	Without additive	76%
2	H_2O	90%
3	pyridine	51%
4	Tetrabutylammonium chloride	56%
5	Tetrabutylammonium bromide	82%
6	Tetrabutylammonium bromide (10 mol%)	61%

[a]Reaction conditions: compound **1b** (0.2 mmol, 1.0 equiv), butyl acrylate (0.3 mmol, 1.5 equiv), DBU (0.6 mmol, 3.0 equiv), additive (0.6 mmol, 3.0 equiv), 2-MeTHF (1.0 mL), irradiation with 40 W blue Kessil lamp (λ = 456 nm), r.t., argon atmosphere, 16 h. [b]Yields were determined by ^{1}H NMR analysis of the crude reaction mixture using 1,3,5-trimethoxybenzene as the internal standard.

Table S4. Screening different wavelengths.

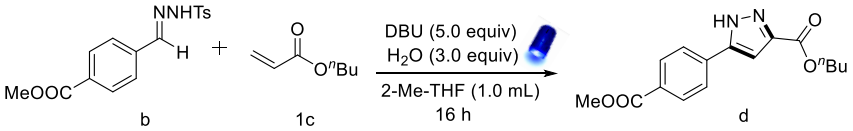


1b 1c 1d

Entry[a]	Variations	Yield [%][b]
1	None	90%
2	390 nm instead of 456 nm	85%
3	405 nm instead of 456 nm	77%
4	427 nm instead of 456 nm	66%

[a]Reaction conditions: compound **1b** (0.2 mmol, 1.0 equiv), butyl acrylate (0.3 mmol, 1.5 equiv), DBU (0.6 mmol, 3.0 equiv), H_2O (0.6 mmol, 3.0 equiv), 2-MeTHF (1.0 mL), irradiation with 40 W blue Kessil lamp (456 nm), r.t., argon atmosphere, 16 h. [b]Yields were determined by ^{1}H NMR analysis of the crude reaction mixture using 1,3,5-trimethoxybenzene as the internal standard.

Table S5. Optimization of synthezising pyrazoles.



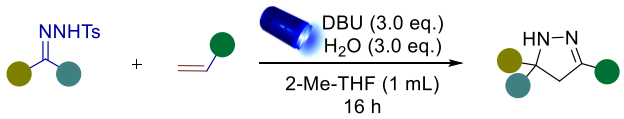
b 1c d

Entry[a]	Changes from standard conditions	Yield[b]
1	None	65%
2	O_2 instead of Ar	56%
3	3.0 equiv of DDQ was added	36%
4	3.0 equiv of NaOH was added	53%
5	10 h instead of 16 h	54%
6	24 h instead of 16 h	58%

[a]Reaction conditions: [a]Reaction conditions: compound **b** (0.2 mmol, 1.0 equiv), butyl acrylate (0.3 mmol, 1.5 equiv), DBU (1.0 mmol, 5.0 equiv), H_2O (0.6 mmol, 3.0 equiv), 2-MeTHF (1.0 mL), irradiation with 40 W blue Kessil lamp (λ = 456 nm), r.t., argon atmosphere, 16 h. [b]Yields were determined by ^{1}H NMR analysis of the crude reaction mixture using 1,3,5-trimethoxybenzene as the internal standard.

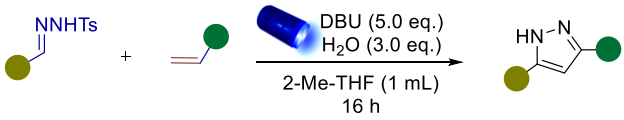
4. Procedures of synthesizing products and characterization data

General procedure A of synthesizing (spiro)-pyrazolines



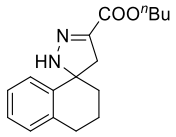
A dry 5 mL Schlenk tube containing a stirring bar was charged with 0.2 mmol of *N*-tosylhydrazone (1.0 equiv), 0.3 mmol of alkene (1.5 equiv), 0.6 mmol of DBU (3.0 equiv) and 0.6 mmol (3.0 equiv) of H_2O. After purging the flask for three times under vacuum and three times under argon, it was charged with 2-Methyltetrahydrofuran (1.0 mL). The reaction was kept for 16 h under 40 W Kessil lamp reaction setup (the progress can be monitored *via* TLC). Then, the resulting mixture underwent an aqueous workup (using distilled water; or brine in case of slurry phase separation) and was extracted three times with dichloromethane[1]. The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo*. Products were purified *via* flash column chromatography with ethyl acetate and hexane as solvents.

General procedure B of synthesizing pyrazoles



A dry 5 mL Schlenk tube containing a stirring bar was charged with 0.2 mmol of *N*-tosylhydrazone (1.0 equiv), 0.3 mmol of alkene (1.5 equiv), 1.0 mmol of DBU (5.0 equiv) and 0.6 mmol (3.0 equiv) of H_2O. After purging the flask for three times under vacuum and three times under argon, it was charged with 2-Methyltetrahydrofuran (1.0 mL). The reaction was kept for 16 h under 40 W Kessil lamp reaction setup (the progress can be monitored *via* TLC). Then, the resulting mixture underwent an aqueous workup (using distilled water; or brine in case of slurry phase separation) and was extracted three times with dichloromethane. The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo*. Products were purified *via* flash column chromatography with ethyl acetate and hexane as solvents.

Characterization data of the pyrazolines and pyrazoles

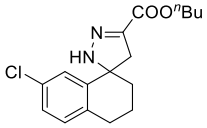


Butyl 2',3,4,4'-tetrahydro-2*H*-spiro[naphthalene-1,3'-pyrazole]-5'-carboxylate (1d): Prepared according to the general procedure A, the title compound was prepared from *N*-tosylhydrazone (**1b**) (62.8 mg, 0.2 mmol, 1.0 equiv) and butyl acrylate (**1c**) (44.0 µl, 0.3 mmol, 1.5 equiv). Spiropyrazoline **1d** was obtained after column chromatography (hexane: EtOAc, 3:1) as a colourless oil (51.5 mg, 0.18 mmol, 90%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42–7.25 (m, 1H), 7.17–7.07 (m, 2H), 7.07–6.95 (m, 1H), 6.27 (s, 1H), 4.24–4.11 (m, 2H), 3.06 (s, 2H), 2.74 (d, *J* = 5.9 Hz, 2H), 1.99 (dd, *J* = 10.8, 7.1 Hz, 1H), 1.86–1.74 (m, 3H), 1.64 (dt, *J* = 14.6, 6.9 Hz, 2H), 1.36 (dq, *J* = 14.8, 7.4 Hz, 2H), 0.88 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 162.6, 139.8, 138.6, 136.0, 128.5, 127.1, 126.4, 126.3, 68.4, 64.5, 46.7, 35.7, 30.3, 28.7, 19.5, 18.7, 13.3.

HRMS (ESI+), *m/z* calculated for $C_{17}H_{22}N_2O_2$ $[M + Na]^+$: 309.1573, found: 309.1565.

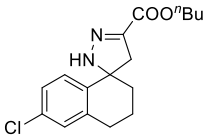


Butyl 7-chloro-2',3,4,4'-tetrahydro-2*H*-spiro[naphthalene-1,3'-pyrazole]-5'-carboxylate (2d): Prepared according to the general procedure A, the title compound was prepared from *N*-tosylhydrazone (**2b**) (69.7 mg, 0.2 mmol, 1.0 equiv) and butyl acrylate (**1c**) (44.0 µl, 0.3 mmol, 1.5 equiv). Spiropyrazoline **2d** was obtained after column chromatography (hexane: EtOAc, 3:1) as a colourless oil (51.3 mg, 0.16 mmol, 80%).

^{1}H NMR (500 MHz, CD_3OD) δ 7.31 (d, *J* = 2.2 Hz, 1H), 7.13 (dd, *J* = 8.2, 2.2 Hz, 1H), 7.06 (d, *J* = 8.3 Hz, 1H), 4.20 (t, *J* = 6.7 Hz, 2H), 3.13 (d, *J* = 17.5 Hz, 1H), 2.96 (d, *J* = 17.5 Hz, 1H), 2.77 (t, *J* = 5.7 Hz, 2H), 2.02–1.80 (m, 4H), 1.72–1.62 (m, 2H), 1.42 (dq, *J* = 14.8, 7.4 Hz, 2H), 0.96 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (126 MHz, CD_3OD) δ 164.7, 144.1, 137.6, 136.5, 133.0, 131.7, 128.5, 127.8, 69.8, 65.7, 47.9, 36.2, 31.9, 29.6, 20.7, 20.3, 14.2.

HRMS (ESI+), *m/z*: calculated for $C_{17}H_{21}ClN_2O_2$ $[M + H]^+$: 321.1364, found: 321.1388.

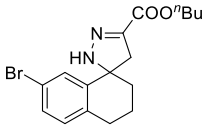


Butyl 6-chloro-2',3,4,4'-tetrahydro-2*H*-spiro[naphthalene-1,3'-pyrazole]-5'-carboxylate (3d): Prepared according to the general procedure A, the title compound was prepared from *N*-tosylhydrazone (**3b**) (69.7 mg, 0.2 mmol, 1.0 equiv) and butyl acrylate (**1c**) (44.0 µl, 0.3 mmol, 1.5 equiv). Spiropyrazoline **3d** was obtained after column chromatography (hexane: EtOAc, 3:1) as a colourless oil (52.6 mg, 0.164 mmol, 82%)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 (d, *J* = 8.4 Hz, 1H), 7.13 (dd, *J* = 8.5, 2.3 Hz, 1H), 7.10–6.99 (m, 1H), 6.31 (s, 1H), 4.23 (td, *J* = 6.8, 1.6 Hz, 2H), 3.13 (d, *J* = 17.7 Hz, 1H), 3.04 (d, *J* = 17.6 Hz, 1H), 2.77 (t, *J* = 6.2 Hz, 2H), 2.05 (dd, *J* = 11.2, 5.3 Hz, 1H), 1.93–1.76 (m, 3H), 1.70 (dt, *J* = 14.7, 6.8 Hz, 2H), 1.41 (h, *J* = 7.4 Hz, 2H), 0.94 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 162.4, 138.7, 138.3, 137.9, 132.7, 128.1, 128.0, 126.4, 68.0, 64.5, 46.7, 35.3, 30.2, 28.6, 19.2, 18.7, 13.3.

HRMS (ESI+), *m/z*: calculated for $C_{17}H_{21}ClN_2O_2$ $[M + H]^+$: 321.1364, found: 321.1350.

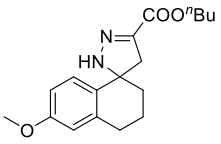


Butyl 7-bromo-2',3,4,4'-tetrahydro-2*H*-spiro[naphthalene-1,3'-pyrazole]-5'-carboxylate (4d): Prepared according to the general procedure A, the title compound was prepared from *N*-tosylhydrazone (**4b**) (78.4 mg, 0.2 mmol, 1.0 equiv) and butyl acrylate (**1c**) (44.0 µl, 0.3 mmol, 1.5 equiv). Spiropyrazoline **4d** was obtained after column chromatography (hexane: EtOAc, 3:1) as a colourless oil (59.2 mg, 0.162 mmol, 81%)

^{1}H NMR (500 MHz, CD_3OD) δ 7.46 (d, *J* = 2.2 Hz, 1H), 7.28 (dd, *J* = 8.2, 2.2 Hz, 1H), 7.05–6.96 (m, 1H), 4.22 (t, *J* = 6.7 Hz, 2H), 3.14 (d, *J* = 17.5 Hz, 1H), 2.97 (d, *J* = 17.5 Hz, 1H), 2.76 (d, *J* = 4.7 Hz, 2H), 2.03–1.79 (m, 4H), 1.69 (dt, *J* = 14.5, 6.7 Hz, 2H), 1.43 (dq, *J* = 14.8, 7.4 Hz, 2H), 0.96 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (126 MHz, CD_3OD) δ 162.8, 142.5, 135.7, 135.1, 130.1, 129.5, 128.9, 118.9, 67.9, 63.9, 46.0, 34.3, 30.0, 27.7, 18.8, 18.3, 12.2.

HRMS (ESI+), *m/z*: calculated for $C_{17}H_{21}BrN_2O_2$ $[M + Na]^+$: 387.0679, found: 387.0703.

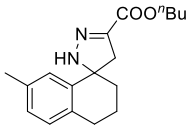


Butyl 6-methoxy-2',3,4,4'-tetrahydro-2*H*-spiro[naphthalene-1,3'-pyrazole]-5'-carboxylate (5d): Prepared according to the general procedure A, the title compound was prepared from *N*-tosylhydrazone (**5b**) (68.9 mg, 0.2 mmol, 1.0 equiv) and butyl acrylate (**1c**) (44.0 µl, 0.3 mmol, 1.5 equiv). Spiropyrazoline **5d** was obtained after column chromatography (hexane: EtOAc, 3:1) as a colourless oil (39.2 mg, 0.124 mmol, 62%)

^{1}H NMR (500 MHz, CD_3OD) δ 7.22 (d, *J* = 8.7 Hz, 1H), 6.73 (d, *J* = 10.6 Hz, 1H), 6.60 (d, *J* = 1.9 Hz, 1H), 4.20 (t, *J* = 6.7 Hz, 2H), 3.73 (s, 3H), 3.07 (d, *J* = 17.4 Hz, 1H), 2.98 (d, *J* = 17.4 Hz, 1H), 2.77 (d, *J* = 10.4 Hz, 2H), 2.02 – 1.79 (m, 4H), 1.67 (p, *J* = 6.9 Hz, 2H), 1.42 (m, 2H), 0.96 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (126 MHz, CD_3OD) δ 163.0, 158.3, 137.2, 135.5, 132.2, 127.3, 112.2, 112.1, 67.8, 63.7, 53.7, 45.8, 35.4, 30.0, 28.8, 19.2, 18.3, 12.2.

HRMS (ESI+), *m/z*: calculated for $C_{18}H_{24}N_2O_3$ $[M + Na]^+$: 339.1679, found: 339.1705.

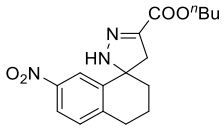


Butyl 7-methyl-2',3,4,4'-tetrahydro-2*H*-spiro[naphthalene-1,3'-pyrazole]-5'-carboxylate (6d): Prepared according to the general procedure A, the title compound was prepared from *N*-tosylhydrazone (**6b**) (65.6 mg, 0.2 mmol, 1.0 equiv) and butyl acrylate (**1c**) (44.0 µl, 0.3 mmol, 1.5 equiv). Spiropyrazoline **6d** was obtained after column chromatography (hexane: EtOAc, 3:1) as a colourless oil (45.6 mg, 0.152 mmol, 76%).

^{1}H NMR (500 MHz, CD_3OD) δ 7.12 (d, *J* = 1.6 Hz, 1H), 7.03 – 6.88 (m, 2H), 4.20 (t, *J* = 6.6 Hz, 2H), 3.09 (d, *J* = 17.4 Hz, 1H), 2.99 (d, *J* = 17.4 Hz, 1H), 2.74 (s, 2H), 2.25 (s, 3H), 2.06–1.73 (m, 4H), 1.75–1.61 (m, 2H), 1.52–1.34 (m, 2H), 0.96 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (126 MHz, CD_3OD) δ 164.9, 141.7, 137.2, 137.1, 134.6, 129.9, 129.3, 128.2, 69.9, 65.6, 47.9, 37.1, 31.9, 29.9, 21.3, 21.1, 20.2, 14.1.

HRMS (ESI+), *m/z*: calculated for $C_{18}H_{25}N_2O_2$ $[M + H]^+$: 301.1911, found: 301.1882.

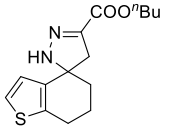


Butyl 7-nitro-2',3,4,4'-tetrahydro-2*H*-spiro[naphthalene-1,3'-pyrazole]-5'-carboxylate (7d): Prepared according to the general procedure A, the title compound was prepared from *N*-tosylhydrazone (**7b**) (70.8 mg, 0.2 mmol, 1.0 equiv) and butyl acrylate (**1c**) (44.0 µl, 0.3 mmol, 1.5 equiv). Spiropyrazoline **7d** was obtained after column chromatography (hexane: EtOAc, 3:1) as a colourless oil (60.9 mg, 0.194 mmol, 97%)

^{1}H NMR (500 MHz, CD_3OD) δ 8.24 (d, *J* = 2.4 Hz, 1H), 8.01 (dd, *J* = 8.5, 2.4 Hz, 1H), 7.34 (dd, *J* = 8.5, 1.0 Hz, 1H), 4.23 (t, *J* = 6.7 Hz, 2H), 3.21 (d, *J* = 17.6 Hz, 1H), 3.02 (d, *J* = 17.6 Hz, 1H), 2.93 (q, *J* = 8.1, 6.4 Hz, 2H), 2.11–1.86 (m, 4H), 1.69 (dt, *J* = 14.5, 6.7 Hz, 2H), 1.44 (m, 2H), 0.96 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (126 MHz, CD_3OD) δ 164.5, 148.1, 145.8, 143.9, 138.1, 131.4, 123.2, 122.9, 69.8, 65.8, 47.9, 35.7, 31.9, 30.2, 20.3, 20.2, 14.1.

HRMS (ESI+), *m/z*: calculated for $C_{17}H_{22}N_3O_4$ $[M + H]^+$: 332.1605, found: 332.1588.

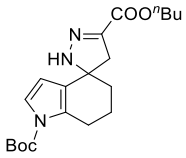


Butyl 2',4',6,7-tetrahydro-5*H*-spiro[benzo[b]thiophene-4,3'-pyrazole]-5'-carboxylate (8d): Prepared according to the general procedure A, the title compound was prepared from *N*-tosylhydrazone (**8b**) (64.0 mg, 0.2 mmol, 1.0 equiv) and butyl acrylate (**1c**) (44.0 µl, 0.3 mmol, 1.5 equiv). Spiropyrazoline **8d** was obtained after column chromatography (hexane: EtOAc, 3:1) as a colourless oil (38.0 mg, 0.13 mmol, 65%)

^{1}H NMR (500 MHz, CD_3OD) δ 7.14 (d, *J* = 5.3 Hz, 1H), 6.88 (d, *J* = 5.3 Hz, 1H), 4.22 (t, *J* = 6.7 Hz, 2H), 3.06 (d, *J* = 17.3 Hz, 1H), 2.99 (d, *J* = 17.3 Hz, 1H), 2.79 (d, *J* = 9.0 Hz, 2H), 2.07–1.83 (m, 4H), 1.75–1.62 (m, 2H), 1.43 (m, 2H), 0.97 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (126 MHz, CD_3OD) δ 162.8, 138.0, 137.3, 137.1, 124.1, 122.2, 66.4, 63.8, 43.6, 35.0, 30.0, 23.7, 20.3, 18.3, 12.2.

HRMS (ESI+), *m/z*: calculated for $C_{15}H_{20}N_2O_2S$ $[M + H]^+$: 293.1318, found: 293.1289.

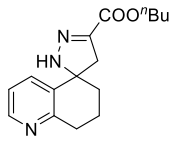


1-(tert-butyl) 5'-butyl 2',4',6,7-tetrahydrospiro[indole-4,3'-pyrazole]-1,5'(5*H*)-dicarboxylate (9d): Prepared according to the general procedure A, the title compound was prepared from *N*-tosylhydrazone (**9b**) (80.6 mg, 0.2 mmol, 1.0 equiv) and butyl acrylate (**1c**) (44.0 µl, 0.3 mmol, 1.5 equiv). Spiropyrazoline **9d** was obtained after column chromatography (hexane: EtOAc, 3:1) as a colourless oil (55.6 mg, 0.148 mmol, 74%)

^{1}H NMR (500 MHz, CD_3OD) δ 7.16 (s, 1H), 6.12 (s, 1H), 4.25 (t, *J* = 6.6 Hz, 2H), 3.06 (d, *J* = 17.1 Hz, 1H), 2.95 (d, *J* = 17.2 Hz, 1H), 2.87 (d, *J* = 11.0 Hz, 2H), 2.05–1.81 (m, 4H), 1.73 (dt, *J* = 14.5, 6.7 Hz, 2H), 1.62 (s, 9H), 1.53–1.42 (m, 2H), 1.01 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (126 MHz, CD_3OD) δ 164.8, 150.9, 139.5, 131.7, 126.9, 121.4, 109.1, 84.8, 67.2, 65.6, 44.7, 36.5, 31.9, 28.2, 25.4, 21.5, 20.2, 14.1.

HRMS (ESI+), *m/z*: calculated for $C_{20}H_{29}N_3O_4$ $[M + H]^+$: 376.2231, found: 376.2258.

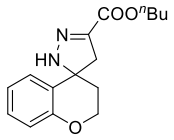


Butyl 2,4,7',8'-tetrahydro-6'*H*-spiro[pyrazole-3,5'-quinoline]-5-carboxylate (10d): Prepared according to the general procedure A, the title compound was prepared from *N*-tosylhydrazone (**10b**) (63.0 mg, 0.2 mmol, 1.0 equiv) and butyl acrylate (**1c**) (44.0 µl, 0.3 mmol, 1.5 equiv). Spiropyrazoline **10d** was obtained after column chromatography (hexane: EtOAc, 3:1) as a colourless oil (39.1 mg, 0.136 mmol, 68%)

^{1}H NMR (500 MHz, CD_3OD) δ 8.34 (dd, *J* = 4.8, 1.6 Hz, 1H), 7.84 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.28 (dd, *J* = 8.0, 4.8 Hz, 1H), 4.21 (t, *J* = 6.6 Hz, 2H), 3.18 (d, *J* = 17.5 Hz, 1H), 3.03 (d, *J* = 17.5 Hz, 1H), 2.94 (t, *J* = 6.5 Hz, 2H), 2.09–1.84 (m, 4H), 1.68 (dt, *J* = 14.6, 6.7 Hz, 2H), 1.43 (dq, *J* = 14.7, 7.4 Hz, 2H), 0.96 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (126 MHz, CD_3OD) δ 162.7, 155.3, 147.0, 136.6, 136.2, 135.5, 121.7, 67.7, 63.9, 45.7, 33.8, 30.8, 30.0, 18.3, 18.3, 12.2.

HRMS (ESI+), *m/z*: calculated for $C_{16}H_{21}N_3O_2$ $[M + Na]^+$: 310.1526, found: 310.1491.

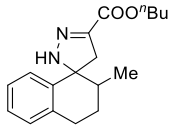


Butyl 2',4'-dihydrospiro[chromane-4,3'-pyrazole]-5'-carboxylate (11d): Prepared according to the general procedure A, the title compound was prepared from *N*-tosylhydrazone (**11b**) (63.2mg, 0.2 mmol, 1.0 equiv) and butyl acrylate (**1c**) (44.0 µl, 0.3 mmol, 1.5 equiv). Spiropyrazoline **11d** was obtained after column chromatography (hexane: EtOAc, 3:1) as a colourless oil (52.9 mg, 0.18 mmol, 90%)

^{1}H NMR (500 MHz, CD_3OD) δ 7.29 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.11 (ddd, *J* = 8.3, 7.2, 1.7 Hz, 1H), 6.87 (ddd, *J* = 7.8, 7.2, 1.2 Hz, 1H), 6.74 (dd, *J* = 8.2, 1.2 Hz, 1H), 4.33–4.12 (m, 4H), 3.16 (d, *J* = 17.5 Hz, 1H), 3.07 (d, *J* = 17.5 Hz, 1H), 2.12–2.04 (m, 2H), 1.70–1.62 (m, 2H), 1.46–1.38 (m, 2H), 0.95 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (126 MHz, CD_3OD) δ 164.6, 155.5, 138.4, 130.2, 128.4, 127.7, 122.1, 118.0, 66.0, 65.8, 64.6, 47.4, 35.7, 31.9, 20.3, 14.3.

HRMS (ESI+), *m/z*: calculated for $C_{16}H_{20}N_2O_3$ $[M + H]^+$: 289.1547, found: 289.1589.

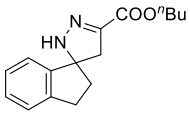


Butyl 2-methyl-2',3,4,4'-tetrahydro-2*H*-spiro[naphthalene-1,3'-pyrazole]-5'-carboxylate (12d): Prepared according to the general procedure A, the title compound was prepared from *N*-tosylhydrazone (**12b**) (65.6 mg, 0.2 mmol, 1.0 equiv) and butyl acrylate (**1c**) (44.0 µl, 0.3 mmol, 1.5 equiv). Spiropyrazoline **12d** was obtained after column chromatography (hexane: EtOAc, 3:1) as a colourless oil (32.5 mg, 0.108 mmol, 54%, dr = 1:1).

^{1}H NMR (500 MHz, CD_3OD) δ 7.25–7.12 (m, 3H), 7.08 (d, *J* = 8.5 Hz, 1H), 4.20 (td, *J* = 6.6, 4.9 Hz, 2H), 3.22–3.20 (m, 1H), 2.91–2.75 (m, 2H), 2.69 (d, *J* = 17.9 Hz, 1H), 2.03–1.82 (m, 2H), 1.78–1.61 (m, 3H), 1.49–1.37 (m, 2H), 1.05–0.92 (m, 6H).

^{13}C NMR (126 MHz, CD_3OD) δ 164.9, 141.9, 137.0, 136.7, 130.0, 129.9, 128.4, 128.2, 128.0, 127.8, 127.7, 127.6, 72.5, 65.6, 47.4, 41.9, 40.7, 39.2, 31.9, 29.7, 28.3, 28.3, 28.0, 20.2, 15.9, 15.2, 14.1.

HRMS (ESI+), *m/z*: calculated for $C_{18}H_{24}N_2O_2$ $[M + H]^+$: 301.1911, found: 301.1934.

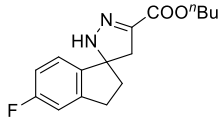


Butyl 2,2',3,4'-tetrahydrospiro[indene-1,3'-pyrazole]-5'-carboxylate (13d): Prepared according to the general procedure A, the title compound was prepared from *N*-tosylhydrazone (**13b**) (60.0 mg, 0.2 mmol, 1.0 equiv) and butyl acrylate (**1c**) (44.0 µl, 0.3 mmol, 1.5 equiv). Spiropyrazoline **13d** was obtained after column chromatography (hexane: EtOAc, 3:1) as a colourless oil (28.9 mg, 0.106 mmol, 53%).

^{1}H NMR (500 MHz, CD_3OD) δ 7.31–7.17 (m, 4H), 4.22 (t, *J* = 6.6 Hz, 2H), 3.15 (d, *J* = 17.3 Hz, 1H), 3.03 (d, *J* = 17.3 Hz, 1H), 3.01–2.84 (m, 2H), 2.37–2.15 (m, 2H), 1.74–1.60 (m, 2H), 1.44 (h, *J* = 7.4 Hz, 2H), 0.97 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (126 MHz, CD_3OD) δ 162.8, 145.1, 142.0, 137.6, 127.5, 126.3, 123.9, 121.8, 76.6, 63.8, 42.5, 39.5, 30.0, 28.3, 18.3, 12.2.

HRMS (ESI+), *m/z*: calculated for $C_{16}H_{20}N_2O_2$ $[M + H]^+$: 273.1598, found: 273.1634.



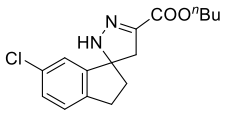
Butyl 5-fluoro-2,2',3,4'-tetrahydrospiro[indene-1,3'-pyrazole]-5'-carboxylate (14d): Prepared according to the general procedure A, the title compound was prepared from *N*-tosylhydrazone (**14b**) (63.6 mg, 0.2 mmol, 1.0 equiv) and butyl acrylate (**1c**) (44.0 µl, 0.3 mmol, 1.5 equiv). Spiropyrazoline **14d** was obtained after column chromatography (hexane: EtOAc, 3:1) as a colourless oil (32.5 mg, 0.112 mmol, 56%).

^{1}H NMR (500 MHz, CD_3OD) δ 7.29 (dd, *J* = 8.3, 5.2 Hz, 1H), 7.11–6.85 (m, 2H), 4.25 (t, *J* = 6.6 Hz, 2H), 3.24–3.02 (m, 2H), 2.94 (dd, *J* = 39.8, 8.0 Hz, 2H), 2.38 (dd, *J* = 12.9, 7.9 Hz, 1H), 2.35–2.24 (m, 1H), 1.79–1.63 (m, 2H), 1.57–1.38 (m, 2H), 1.00 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (126 MHz, MeOD) δ 164.7 (d, *J* = 243.9 Hz), 164.6, 146.6 (d, *J* = 8.5 Hz), 142.9 (d, *J* = 2.5 Hz), 139.6, 125.3 (d, *J* = 9.5 Hz), 115.1 (d, *J* = 23.3 Hz), 112.5 (d, *J* = 22.3 Hz), 77.8, 65.7, 44.4, 41.7, 31.9, 30.2 (d, *J* = 2.1 Hz). 20.2, 14.1.

^{19}F NMR (282 MHz, CD_3OD) δ -118.37.

HRMS (ESI+), *m/z*: calculated for $C_{16}H_{19}FN_2O_2$ $[M + H]^+$: 291.1503, found: 291.1538.

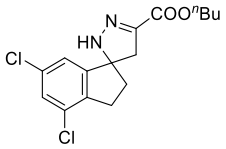


Butyl 6-chloro-2,2',3,4'-tetrahydrospiro[indene-1,3'-pyrazole]-5'-carboxylate (15d): Prepared according to the general procedure A, the title compound was prepared from *N*-tosylhydrazone (**15b**) (66.8 mg, 0.2 mmol, 1.0 equiv) and butyl acrylate (**1c**) (44.0 µl, 0.3 mmol, 1.5 equiv). Spiropyrazoline **15d** was obtained after column chromatography (hexane: EtOAc, 3:1) as a colourless oil (27.6 mg, 0.09 mmol, 45%).

^{1}H NMR (500 MHz, CD$_3$OD) δ 7.28–7.17 (m, 3H), 4.22 (t, *J* = 6.6 Hz, 2H), 3.17 (d, *J* = 17.3 Hz, 1H), 3.00 (d, *J* = 17.4 Hz, 1H), 2.98–2.81 (m, 2H), 2.41–2.30 (m, 1H), 2.30–2.18 (m, 1H), 1.68 (dq, *J* = 8.5, 6.7 Hz, 2H), 1.49–1.39 (m, 2H), 0.96 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (126 MHz, CD$_3$OD) δ 164.5, 149.3, 142.7, 139.8, 133.7, 129.5, 127.3, 124.0, 78.3, 65.8, 44.4, 41.5, 31.9, 29.7, 20.2, 14.1.

HRMS (ESI+), *m/z*: calculated for $C_{16}H_{19}ClN_2O_2$ $[M + Na]^+$: 329.1027, found: 329.1056.

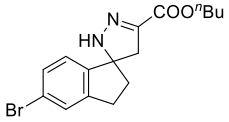


Butyl 4,6-dichloro-2,2',3,4'-tetrahydrospiro[indene-1,3'-pyrazole]-5'-carboxylate (16d): Prepared according to the general procedure A, the title compound was prepared from *N*-tosylhydrazone (**16b**) (73.9 mg, 0.2 mmol, 1.0 equiv) and butyl acrylate (**1c**) (44.0 µl, 0.3 mmol, 1.5 equiv). Spiropyrazoline **16d** was obtained after column chromatography (hexane: EtOAc, 3:1) as a colourless oil (25.9 mg, 0.076 mmol, 38%).

^{1}H NMR (500 MHz, CD$_3$OD) δ 7.32 (d, *J* = 1.8 Hz, 1H), 7.22 (d, *J* = 1.8 Hz, 1H), 4.22 (t, *J* = 6.7 Hz, 2H), 3.20 (d, *J* = 17.5 Hz, 1H), 3.03 (d, *J* = 17.4 Hz, 1H), 2.97 (dd, *J* = 8.6, 4.2 Hz, 1H), 2.93–2.83 (m, 1H), 2.39 (ddd, *J* = 12.2, 7.9, 4.2 Hz, 1H), 2.33–2.19 (m, 1H), 1.68 (dt, *J* = 14.5, 6.7 Hz, 2H), 1.43 (dq, *J* = 14.8, 7.4 Hz, 2H), 0.96 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (126 MHz, CD$_3$OD) δ 164.3, 151.0, 141.0, 140.0, 134.7, 132.5, 129.1, 122.9, 78.9, 65.8, 44.6, 40.6, 31.9, 29.1, 20.2, 14.1.

HRMS (ESI+), *m/z*: calculated for $C_{16}H_{18}Cl_2N_2O_2$ $[M + H]^+$: 341.0818, found: 341.0832.

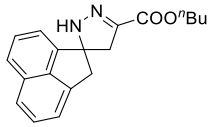


Butyl 5-bromo-2,2',3,4'-tetrahydrospiro[indene-1,3'-pyrazole]-5'-carboxylate (17d): Prepared according to the general procedure A, the title compound was prepared from *N*-tosylhydrazone (**17b**) (76.0 mg, 0.2 mmol, 1.0 equiv) and butyl acrylate (**1c**) (44.0 µl, 0.3 mmol, 1.5 equiv). Spiropyrazoline **17d** was obtained after column chromatography (hexane: EtOAc, 3:1) as a colourless oil (33.7 mg, 0.096 mmol, 48%).

^{1}H NMR (500 MHz, CD$_3$OD) δ 7.45–7.28 (m, 2H), 7.19 (d, *J* = 8.1 Hz, 1H), 4.21 (t, *J* = 6.6 Hz, 2H), 3.16 (d, *J* = 17.3 Hz, 1H), 3.02 (d, *J* = 17.4 Hz, 1H), 2.98–2.84 (m, 2H), 2.31 (dd, *J* = 7.8, 4.7 Hz, 1H), 2.27–2.17 (m, 1H), 1.74–1.63 (m, 2H), 1.46–1.38 (m, 2H), 0.96 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (126 MHz, CD$_3$OD) δ 164.5, 146.6, 146.4, 139.7, 131.3, 129.0, 125.6, 123.1, 78.0, 65.7, 44.3, 41.3, 31.9, 30.0, 20.2, 14.1.

HRMS (ESI+), *m/z*: calculated for $C_{16}H_{19}BrN_2O_2$ $[M + H]^+$: 351.0703, found: 351.0735.

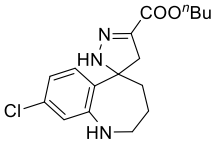


Butyl 2',4'-dihydro-2*H*-spiro[acenaphthylene-1,3'-pyrazole]-5'-carboxylate (18d): Prepared according to the general procedure A, the title compound was prepared from *N*-tosylhydrazone (**18b**) (67.2 mg, 0.2 mmol, 1.0 equiv) and butyl acrylate (**1c**) (44.0 µl, 0.3 mmol, 1.5 equiv). Spiropyrazoline **18d** was obtained after column chromatography (hexane: EtOAc, 3:1) as a colourless oil (45.0 mg, 0.146 mmol, 73%).

^{1}H NMR (500 MHz, CD$_3$OD) δ 7.70 (d, *J* = 8.2 Hz, 1H), 7.63 (d, *J* = 8.3 Hz, 1H), 7.49 (dt, *J* = 14.7, 7.6 Hz, 2H), 7.39 (d, *J* = 7.0 Hz, 1H), 7.27 (d, *J* = 6.8 Hz, 1H), 4.21 (t, *J* = 6.7 Hz, 2H), 3.67–3.50 (m, 2H), 3.25 (s, 2H), 1.67 (p, *J* = 6.9 Hz, 2H), 1.42 (h, *J* = 7.5 Hz, 2H), 0.95 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (126 MHz, CD$_3$OD) δ 164.5, 148.3, 141.7, 139.9, 138.0, 132.5, 129.5, 129.5, 125.9, 123.9, 120.9, 119.8, 77.1, 65.8, 48.6, 47.0, 31.9, 20.2, 14.1.

HRMS (ESI+), *m/z*: calculated for $C_{19}H_{20}N_2O_2$ $[M + H]^+$: 309.1598, found: 309.1604.

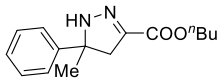


Butyl 8-chloro-1,2,2',3,4,4'-hexahydrospiro[benzo[b]azepine-5,3'-pyrazole]-5'-carboxylate (19d): Prepared according to the general procedure A, the title compound was prepared from *N*-tosylhydrazone (**19b**) (72.6 mg, 0.2 mmol, 1.0 equiv) and butyl acrylate (**1c**) (44.0 µl, 0.3 mmol, 1.5 equiv). Spiropyrazoline **19d** was obtained after column chromatography (hexane: EtOAc, 3:1) as a colourless oil (38.9 mg, 0.116 mmol, 58%).

^{1}H NMR (500 MHz, CD_3OD) δ 7.29 (d, *J* = 2.5 Hz, 1H), 7.00 (dd, *J* = 8.3, 2.5 Hz, 1H), 6.79 (d, *J* = 8.3 Hz, 1H), 4.16 (t, *J* = 6.7 Hz, 2H), 3.29 (d, *J* = 17.4 Hz, 1H), 3.26–3.18 (m, 1H), 2.81 (d, *J* = 17.4 Hz, 1H), 2.74 (m, 1H), 2.03–1.75 (m, 4H), 1.72–1.60 (m, 2H), 1.47–1.34 (m, 2H), 0.94 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (126 MHz, CD_3OD) δ 164.7, 149.4, 139.9, 137.9, 128.6, 127.8, 126.8, 123.3, 74.8, 65.7, 48.8, 42.1, 37.2, 31.9, 27.0, 20.2, 14.1.

HRMS (ESI+), *m/z*: calculated for $C_{17}H_{22}ClN_3O_2$ $[M + H]^+$: 336.1473, found: 336.1498.

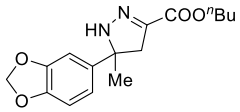


Butyl 5-methyl-5-phenyl-4,5-dihydro-1*H*-pyrazole-3-carboxylate (20d): Prepared according to the general procedure A, the title compound was prepared from *N*-tosylhydrazone (**20b**) (57.2mg, 0.2 mmol, 1.0 equiv) and butyl acrylate (**1c**) (44.0 µl, 0.3 mmol, 1.5 equiv). Spiropyrazoline **20d** was obtained after column chromatography (hexane: EtOAc, 3:1) as a colourless oil (43.2 mg, 0.166 mmol, 83%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45–7.31 (m, 4H), 7.28 (d, *J* = 7.0 Hz, 1H), 6.32 (s, 1H), 4.24 (t, *J* = 6.8 Hz, 2H), 3.18–3.01 (m, 2H), 1.70 (dt, *J* = 14.7, 6.9 Hz, 2H), 1.62 (s, 3H), 1.42 (dq, *J* = 14.8, 7.4 Hz, 2H), 0.94 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 162.4, 144.9, 140.4, 128.2, 126.8, 124.7, 69.4, 64.5, 45.9, 30.2, 27.0, 18.7, 13.3.

HRMS (ESI+), *m/z*: calculated for $C_{15}H_{20}N_2O_2$ $[M + H]^+$: 261.1598, found: 261.1559.

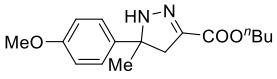


Butyl 5-(benzo[d][1,3]dioxol-5-yl)-5-methyl-4,5-dihydro-1*H*-pyrazole-3-carboxylate (21d): Prepared according to the general procedure A, the title compound was prepared from *N*-tosylhydrazone (**21b**) (66.4 mg, 0.2 mmol, 1.0 equiv) and butyl acrylate (**1c**) (44.0 µl, 0.3 mmol, 1.5 equiv). Spiropyrazoline **21d** was obtained after column chromatography (hexane: EtOAc, 3:1) as a colourless oil (35.2 mg, 0.116 mmol, 58%).

^{1}H NMR (500 MHz, CD_3OD) δ 6.91–6.82 (m, 2H), 6.76 (d, *J* = 8.1 Hz, 1H), 5.91 (s, 2H), 4.19 (t, *J* = 6.6 Hz, 2H), 3.04 (d, *J* = 16.9 Hz, 1H), 2.93 (d, *J* = 17.0 Hz, 1H), 1.66 (dt, *J* = 14.5, 6.6 Hz, 2H), 1.50 (s, 3H), 1.45–1.36 (m, 2H), 0.95 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (126 MHz, CD_3OD) δ 164.7, 149.3, 147.9, 141.5, 139.8, 119.4, 109.0, 107.2, 102.4, 71.2, 65.7, 46.8, 31.9, 28.0, 20.2, 14.1.

HRMS (ESI+), *m/z*: calculated for $C_{16}H_{20}N_2O_4$ $[M + H]^+$: 305.1496, found: 305.1515.

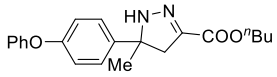


Butyl 5-(4-methoxyphenyl)-5-methyl-4,5-dihydro-1*H*-pyrazole-3-carboxylate (22d): Prepared according to the general procedure A, the title compound was prepared from *N*-tosylhydrazone (**22b**) (63.6 mg, 0.2 mmol, 1.0 equiv) and butyl acrylate (**1c**) (44.0 µl, 0.3 mmol, 1.5 equiv). Spiropyrazoline **22d** was obtained after column chromatography (hexane: EtOAc, 3:1) as a colourless oil (38.9 mg, 0.134 mmol, 67%).

^{1}H NMR (500 MHz, CD_3OD) δ 7.30 (d, *J* = 8.8 Hz, 2H), 6.88 (d, *J* = 8.9 Hz, 2H), 4.19 (t, *J* = 6.6 Hz, 2H), 3.76 (s, 3H), 3.05 (d, *J* = 16.9 Hz, 1H), 2.94 (d, *J* = 16.9 Hz, 1H), 1.66 (dt, *J* = 14.5, 6.7 Hz, 2H), 1.52 (s, 3H), 1.46–1.37 (m, 2H), 0.95 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (126 MHz, CD_3OD) δ 164.7, 160.1, 139.7, 139.4, 127.5, 114.9, 70.8, 65.7, 55.7, 46.7, 31.9, 27.9, 20.2, 14.1.

HRMS (ESI+), *m/z*: calculated for $C_{16}H_{22}N_2O_3$ $[M + H]^+$: 291.1703, found: 291.1716

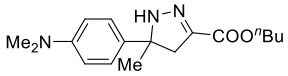


Butyl 5-methyl-5-(4-phenoxyphenyl)-4,5-dihydro-1*H*-pyrazole-3-carboxylate (23d): Prepared according to the general procedure A, the title compound was prepared from *N*-tosylhydrazone (**23b**) (76.0 mg, 0.2 mmol, 1.0 equiv) and butyl acrylate (**1c**) (44.0 µl, 0.3 mmol, 1.5 equiv). Pyrazoline **23d** was obtained after column chromatography (hexane: EtOAc, 3:1) as a colourless oil (54.3 mg, 0.154 mmol, 77%).

^{1}H NMR (500 MHz, CD_3OD) δ 7.40–7.31 (m, 4H), 7.10 (tt, *J* = 7.4, 1.1 Hz, 1H), 6.99–6.93 (m, 4H), 4.20 (t, *J* = 6.6 Hz, 2H), 3.10 (d, *J* = 16.9 Hz, 1H), 2.98 (d, *J* = 17.0 Hz, 1H), 1.67 (dt, *J* = 14.5, 6.7 Hz, 2H), 1.55 (s, 3H), 1.42 (h, *J* = 7.4 Hz, 2H), 0.96 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (126 MHz, CD_3OD) δ 164.7, 158.6, 157.7, 142.4, 139.8, 130.9, 127.9, 124.5, 119.9, 119.7, 70.9, 65.7, 46.7, 31.9, 27.9, 20.2, 14.1.

HRMS (ESI+), *m/z*: calculated for $C_{21}H_{25}N_2O_3$ $[M + H]^+$: 353.1860, found: 353.1875.

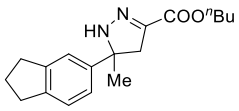


Butyl 5-(4-(dimethylamino)phenyl)-5-methyl-4,5-dihydro-1*H*-pyrazole-3-carboxylate butyl 5-(4-methoxyphenyl)-5-methyl-4,5-dihydro-1H-pyrazole-3-carboxylate (24d): Prepared according to the general procedure A, the title compound was prepared from *N*-tosylhydrazone (**24b**) (66.2 mg, 0.2 mmol, 1.0 equiv) and butyl acrylate (**1c**) (44.0 µl, 0.3 mmol, 1.5 equiv). Pyrazoline **24d** was obtained after column chromatography (hexane: EtOAc, 3:1) as a colourless oil (46.7 mg, 0.154 mmol, 77%).

^{1}H NMR (500 MHz, CD_3OD) δ 7.22 (d, *J* = 8.9 Hz, 2H), 6.75 (d, *J* = 8.8 Hz, 2H), 4.19 (t, *J* = 6.6 Hz, 2H), 3.02 (d, *J* = 16.8 Hz, 1H), 2.95 (d, *J* = 16.9 Hz, 1H), 2.90 (s, 6H), 1.67 (dt, *J* = 14.6, 6.7 Hz, 2H), 1.52 (s, 3H), 1.48–1.37 (m, 2H), 0.96 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (126 MHz, CD_3OD) δ 164.8, 151.3, 139.5, 135.5, 126.9, 114.1, 70.8, 65.6, 46.7, 41.1, 31.9, 27.7, 20.2, 14.1.

HRMS (ESI+), *m/z*: calculated for $C_{17}H_{26}N_3O_2$ $[M + H]^+$: 304.2020, found: 304.2036.

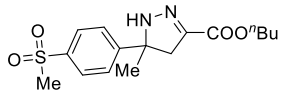


Butyl 5-(2,3-dihydro-1H-inden-5-yl)-5-methyl-4,5-dihydro-1*H*-pyrazole-3-carboxylate (25d): Prepared according to the general procedure A, the title compound was prepared from *N*-tosylhydrazone (**25b**) (65.6 mg, 0.2 mmol, 1.0 equiv) and butyl acrylate (**1c**) (44.0 µl, 0.3 mmol, 1.5 equiv). Pyrazoline **25d** was obtained after column chromatography (hexane: EtOAc, 3:1) as a colourless oil (49.8 mg, 0.166 mmol, 83%).

^{1}H NMR (500 MHz, CD$_3$OD) δ 7.23 (d, *J* = 1.7 Hz, 1H), 7.19 – 7.10 (m, 2H), 4.19 (t, *J* = 6.7 Hz, 2H), 3.07 (d, *J* = 16.8 Hz, 1H), 2.95 (d, *J* = 16.9 Hz, 1H), 2.87 (dt, *J* = 12.0, 7.4 Hz, 4H), 2.06 (p, *J* = 7.4 Hz, 2H), 1.74–1.61 (m, 2H), 1.53 (s, 3H), 1.49–1.35 (m, 2H), 0.96 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (126 MHz, CD$_3$OD) δ 162.9, 143.8, 143.5, 142.0, 137.8, 123.3, 122.3, 120.2, 69.5, 63.8, 44.8, 31.9, 31.5, 30.0, 26.3, 24.8, 18.3, 12.2.

HRMS (ESI+), *m/z*: calculated for $C_{18}H_{24}N_2O_2$ [M + H]$^+$: 301.1911, found: 301.1889.

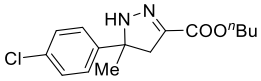


Butyl 5-methyl-5-(4-(methylsulfonyl)phenyl)-4,5-dihydro-1*H*-pyrazole-3-carboxylate (26d): Prepared according to the general procedure A, the title compound was prepared from *N*-tosylhydrazone (**26b**) (73.0 mg, 0.2 mmol, 1.0 equiv) and butyl acrylate (**1c**) (44.0 µl, 0.3 mmol, 1.5 equiv). Pyrazoline **26d** was obtained after column chromatography (hexane: EtOAc, 3:1) as a colourless oil (61.5 mg, 0.182 mmol, 91%).

^{1}H NMR (500 MHz, CD$_3$OD) δ 7.94 (d, *J* = 8.5 Hz, 2H), 7.69 (d, *J* = 8.6 Hz, 2H), 4.21 (t, *J* = 6.6 Hz, 2H), 3.20 (d, *J* = 17.0 Hz, 1H), 3.11 (s, 3H), 2.99 (d, *J* = 17.0 Hz, 1H), 1.68 (dt, *J* = 14.5, 6.6 Hz, 2H), 1.59 (s, 3H), 1.43 (dq, *J* = 14.8, 7.4 Hz, 2H), 0.96 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (126 MHz, CD$_3$OD) δ 164.4, 153.8, 140.7, 140.3, 128.8, 127.7, 71.2, 65.8, 46.5, 44.4, 31.9, 27.8, 20.2, 14.1.

HRMS (ESI+), *m/z*: calculated for $C_{16}H_{22}N_2O_4S$ [M + H]$^+$: 339.1371, found: 339.1350.

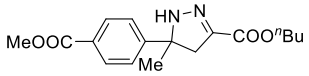


Butyl 5-(4-chlorophenyl)-5-methyl-4,5-dihydro-1*H*-pyrazole-3-carboxylate (27d): Prepared according to the general procedure A, the title compound was prepared from *N*-tosylhydrazone (**27b**) (65.7 mg, 0.2 mmol, 1.0 equiv) and butyl acrylate (**1c**) (44.0 µl, 0.3 mmol, 1.5 equiv). Pyrazoline **27d** was obtained after column chromatography (hexane: EtOAc, 3:1) as a colourless oil (57.7 mg, 0.196 mmol, 98%).

^{1}H NMR (500 MHz, CD_3OD) δ 7.39 (d, *J* = 8.7 Hz, 2H), 7.34 (d, *J* = 8.7 Hz, 2H), 4.20 (t, *J* = 6.6 Hz, 2H), 3.11 (d, *J* = 16.9 Hz, 1H), 2.95 (d, *J* = 17.0 Hz, 1H), 1.76–1.62 (m, 2H), 1.54 (s, 3H), 1.49–1.35 (m, 2H), 0.96 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (126 MHz, CD_3OD) δ 162.7, 144.4, 138.1, 132.0, 127.7, 126.3, 69.0, 63.9, 44.7, 30.0, 25.8, 18.3, 12.2.

HRMS (ESI+), *m/z*: calculated for $C_{15}H_{19}ClN_2O_2$ $[M + H]^+$: 295.1208, found: 295.1220.

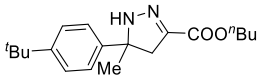


Butyl 5-(4-(methoxycarbonyl)phenyl)-5-methyl-4,5-dihydro-1*H*-pyrazole-3-carboxylate (28d): Prepared according to the general procedure A, the title compound was prepared from *N*-tosylhydrazone (**28b**) (69.2 mg, 0.2 mmol, 1.0 equiv) and butyl acrylate (**1c**) (44.0 µl, 0.3 mmol, 1.5 equiv). Pyrazoline **28d** was obtained after column chromatography (hexane: EtOAc, 3:1) as a colourless oil (47.7 mg, 0.15 mmol, 75%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.5 Hz, 2H), 7.46 (d, *J* = 8.5 Hz, 2H), 6.32 (s, 1H), 4.24 (t, *J* = 6.8 Hz, 2H), 3.92 (s, 3H), 3.15 (d, *J* = 17.1 Hz, 1H), 3.05 (d, *J* = 17.1 Hz, 1H), 1.77–1.66 (m, 2H), 1.63 (s, 3H), 1.54–1.36 (m, 2H), 0.94 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 166.2, 162.2, 149.9, 140.6, 129.6, 128.7, 124.8, 69.4, 64.7, 51.7, 45.9, 30.2, 27.0, 18.7, 13.3.

HRMS (ESI+), *m/z*: calculated for $C_{17}H_{22}N_2O_4$ $[M + H]^+$: 319.1652, found: 319.1665.

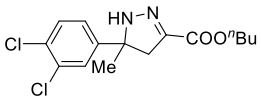


Butyl 5-(4-(tert-butyl)phenyl)-5-methyl-4,5-dihydro-1*H*-pyrazole-3-carboxylate (29d): Prepared according to the general procedure A, the title compound was prepared from *N*-tosylhydrazone (**29b**) (68.8 mg, 0.2 mmol, 1.0 equiv) and butyl acrylate (**1c**) (44.0 µl, 0.3 mmol, 1.5 equiv). Pyrazoline **29d** was obtained after column chromatography (hexane: EtOAc, 3:1) as a colourless oil (60.7 mg, 0.192 mmol, 96%).

^{1}H NMR (500 MHz, CD_3OD) δ 7.37 (d, *J* = 8.5 Hz, 2H), 7.30 (d, *J* = 8.5 Hz, 2H), 4.19 (s, 2H), 3.05 (s, 1H), 2.98 (s, 1H), 1.67 (dq, *J* = 8.7, 6.7 Hz, 2H), 1.53 (s, 3H), 1.47–1.38 (m, 2H), 1.30 (s, 9H), 0.95 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (126 MHz, CD_3OD) δ 164.7, 151.0, 144.4, 139.7, 126.5, 126.0, 71.1, 65.7, 46.6, 35.3, 31.9, 31.8, 27.9, 20.2, 14.1.

HRMS (ESI+), *m/z*: calculated for $C_{19}H_{28}N_2O_2$ $[M + H]^+$: 317.2224, found: 317.2230.

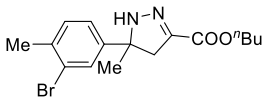


Butyl 5-(3,4-dichlorophenyl)-5-methyl-4,5-dihydro-1*H*-pyrazole-3-carboxylate (30d): Prepared according to the general procedure A, the title compound was prepared from *N*-tosylhydrazone (**30b**) (71.3 mg, 0.2 mmol, 1.0 equiv) and butyl acrylate (**1c**) (44.0 µl, 0.3 mmol, 1.5 equiv). Pyrazoline **30d** was obtained after column chromatography (hexane: EtOAc, 3:1) as a colourless oil (38.8 mg, 0.118 mmol, 59%).

^{1}H NMR (500 MHz, CD_3OD) δ 7.58 (d, *J* = 2.2 Hz, 1H), 7.49 (d, *J* = 8.4 Hz, 1H), 7.34 (dd, *J* = 8.4, 2.2 Hz, 1H), 4.20 (t, *J* = 6.6 Hz, 2H), 3.13 (d, *J* = 17.0 Hz, 1H), 2.95 (d, *J* = 17.0 Hz, 1H), 1.74–1.62 (m, 2H), 1.54 (s, 3H), 1.47–1.37 (m, 2H), 0.95 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (126 MHz, CD_3OD) δ 162.5, 146.5, 138.4, 131.5, 130.0, 129.8, 126.9, 124.7, 68.7, 63.9, 44.7, 30.0, 25.7, 18.3, 12.2.

HRMS (ESI+), *m/z*: calculated for $C_{15}H_{18}Cl_2N_2O_2$ $[M + Na]^+$: 351.0638, found: 351.0654.

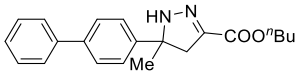


Butyl 5-(3-bromo-4-methylphenyl)-5-methyl-4,5-dihydro-1*H*-pyrazole-3-carboxylate (31d): Prepared according to the general procedure A, the title compound was prepared from *N*-tosylhydrazone (**31b**) (76.3 mg, 0.2 mmol, 1.0 equiv) and butyl acrylate (**1c**) (44.0 µl, 0.3 mmol, 1.5 equiv). Pyrazoline **31d** was obtained after column chromatography (hexane: EtOAc, 3:1) as a colourless oil (40.2 mg, 0.114 mmol, 57%).

^{1}H NMR (500 MHz, CD_3OD) δ 7.57 (d, *J* = 1.3 Hz, 1H), 7.25 (d, *J* = 1.6 Hz, 2H), 4.19 (t, *J* = 6.6 Hz, 2H), 3.08 (d, *J* = 17.0 Hz, 1H), 2.93 (d, *J* = 16.9 Hz, 1H), 2.34 (s, 3H), 1.74–1.61 (m, 2H), 1.52 (s, 3H), 1.49–1.38 (m, 2H), 0.94 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (126 MHz, CD_3OD) δ 162.6, 145.4, 138.1, 135.7, 130.2, 128.4, 123.9, 123.8, 68.7, 63.9, 44.7, 30.0, 25.9, 20.7, 18.3, 12.2.

HRMS (ESI+), *m/z*: calculated for $C_{16}H_{21}BrN_2O_2$ $[M + Na]^+$: 375.0679, found: 375.0680.

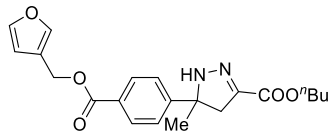


Butyl 5-([1,1'-biphenyl]-4-yl)-5-methyl-4,5-dihydro-1*H*-pyrazole-3-carboxylate (32d): Prepared according to the general procedure A, the title compound was prepared from *N*-tosylhydrazone (**32b**) (72.9 mg, 0.2 mmol, 1.0 equiv) and butyl acrylate (**1c**) (44.0 µl, 0.3 mmol, 1.5 equiv). Pyrazoline **32d** was obtained after column chromatography (hexane: EtOAc, 3:1) as a colourless oil (58.5 mg, 0.174 mmol, 87%).

^{1}H NMR (500 MHz, CD_3OD) δ 7.59 (dd, *J* = 8.3, 2.4 Hz, 5H), 7.46 (dd, *J* = 8.3, 2.3 Hz, 2H), 7.41 (td, *J* = 6.8, 3.6 Hz, 2H), 7.31 (d, *J* = 2.4 Hz, 1H), 4.20 (td, *J* = 6.7, 2.3 Hz, 2H), 3.12 (dd, *J* = 17.0, 2.3 Hz, 1H), 3.00 (dd, *J* = 17.0, 2.3 Hz, 1H), 1.72–1.64 (m, 2H), 1.58 (d, *J* = 2.3 Hz, 3H), 1.46–1.37 (m, 2H), 0.95 (td, *J* = 7.5, 2.5 Hz, 3H).

^{13}C NMR (126 MHz, CD_3OD) δ 162.8, 144.6, 140.0, 139.3, 137.9, 128.0, 126.5, 126.3, 126.0, 125.0, 69.2, 63.8, 44.7, 30.0, 26.0, 18.3, 12.2.

HRMS (ESI+), *m/z*: calculated for $C_{21}H_{24}N_2O_2$ $[M + H]^+$: 337.1911, found: 337.1917.

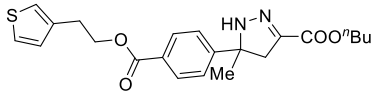


Butyl 5-(4-((furan-3-ylmethoxy)carbonyl)phenyl)-5-methyl-4,5-dihydro-1*H*-pyrazole-3 carboxylate (33d): Prepared according to the general procedure A, the title compound was prepared from *N*-tosylhydrazone (**33b**) (82.4 mg, 0.2 mmol, 1.0 equiv) and butyl acrylate (**1c**) (44.0 µl, 0.3 mmol, 1.5 equiv). Pyrazoline **33d** was obtained after column chromatography (hexane: EtOAc, 3:1) as a colourless oil (48.4 mg, 0.126 mmol, 63%).

^{1}H NMR (500 MHz, CD_3OD) δ 8.06–7.92 (m, 2H), 7.52 (dd, *J* = 8.4, 1.8 Hz, 3H), 6.53 (dd, *J* = 3.3, 0.7 Hz, 1H), 6.42 (dd, *J* = 3.3, 1.9 Hz, 1H), 5.30 (s, 2H), 4.20 (t, *J* = 6.6 Hz, 2H), 3.15 (d, *J* = 16.9 Hz, 1H), 2.97 (d, *J* = 17.0 Hz, 1H), 1.77–1.61 (m, 2H), 1.56 (s, 3H), 1.50–1.35 (m, 2H), 0.95 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (126 MHz, CD_3OD) δ 167.3, 164.5, 153.0, 151.1, 144.7, 140.0, 130.9, 129.9, 126.7, 111.8, 111.7, 71.3, 65.8, 59.5, 46.4, 31.9, 27.8, 20.2, 14.1.

HRMS (ESI+), *m/z*: calculated for $C_{21}H_{24}N_2O_5$ $[M + H]^+$: 385.1758, found: 385.1765.

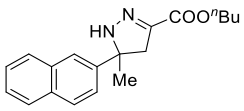


Butyl 5-methyl-5-(4-((2-(thiophen-3-yl)ethoxy)carbonyl)phenyl)-4,5-dihydro-1*H*-pyrazole-3-carboxylate (34d): Prepared according to the general procedure A, the title compound was prepared from *N*-tosylhydrazone (**34b**) (88.4 mg, 0.2 mmol, 1.0 equiv) and butyl acrylate (**1c**) (44.0 µl, 0.3 mmol, 1.5 equiv). Pyrazoline **34d** was obtained after column chromatography (hexane: EtOAc, 3:1) as a colourless oil (54.7 mg, 0.132 mmol, 66%).

^{1}H NMR (500 MHz, CD_3OD) δ 8.00 (d, *J* = 8.5 Hz, 2H), 7.51 (d, *J* = 8.5 Hz, 2H), 7.28–7.13 (m, 1H), 6.92 (d, *J* = 3.6 Hz, 2H), 4.48 (t, *J* = 6.5 Hz, 2H), 4.19 (t, *J* = 6.6 Hz, 2H), 3.28 (t, *J* = 6.4 Hz, 2H), 3.15 (d, *J* = 17.0 Hz, 1H), 2.97 (d, *J* = 17.0 Hz, 1H), 1.66 (dt, *J* = 14.5, 6.7 Hz, 2H), 1.56 (s, 3H), 1.41 (h, *J* = 7.4 Hz, 2H), 0.95 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (126 MHz, CD_3OD) δ 167.5, 164.5, 152.9, 141.4, 140.1, 131.0, 130.1, 127.9, 126.8, 126.7, 125.1, 71.3, 66.6, 65.8, 46.5, 31.9, 30.3, 27.8, 20.2, 14.1.

HRMS (ESI+), *m/z*: calculated for $C_{22}H_{24}N_2O_6S$ $[M + H]^+$: 415.1573, found: 415.1537.

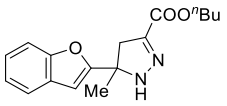


Butyl 5-methyl-5-(naphthalen-2-yl)-4,5-dihydro-1*H*-pyrazole-3-carboxylate (35d): Prepared according to the general procedure A, the title compound was prepared from *N*-tosylhydrazone (**35b**) (67.7 mg, 0.2 mmol, 1.0 equiv) and butyl acrylate (**1c**) (44.0 µl, 0.3 mmol, 1.5 equiv). Pyrazoline **35d** was obtained after column chromatography (hexane: EtOAc, 3:1) as a colourless oil (50.3 mg, 0.162 mmol, 81%).

^{1}H NMR (500 MHz, CD_3OD) δ 8.06–7.92 (m, 1H), 7.87 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.77 (d, *J* = 8.2 Hz, 1H), 7.68 (dd, *J* = 7.4, 1.2 Hz, 1H), 7.54–7.37 (m, 3H), 4.20 (t, *J* = 6.8 Hz, 2H), 3.48 (d, *J* = 17.1 Hz, 1H), 3.18 (d, *J* = 17.1 Hz, 1H), 1.72 (s, 3H), 1.71–1.61 (m, 2H), 1.49–1.35 (m, 2H), 0.94 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (126 MHz, CD_3OD) δ 161.4, 139.3, 136.2, 133.0, 127.8, 127.1, 126.2, 123.4, 123.0, 122.9, 122.7, 121.3, 68.0, 62.3, 42.6, 28.5, 25.3, 16.8, 10.7.

HRMS (ESI+), *m/z*: calculated for $C_{19}H_{22}N_2O_2$ $[M + H]^+$: 311.1754, found: 311.1753.

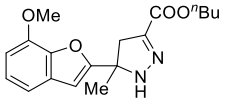


Butyl 5-(benzofuran-2-yl)-5-methyl-4,5-dihydro-1*H*-pyrazole-3-carboxylate (36d): Prepared according to the general procedure A, the title compound was prepared from *N*-tosylhydrazone (**36b**) (65.7 mg, 0.2 mmol, 1.0 equiv) and butyl acrylate (**1c**) (44.0 µl, 0.3 mmol, 1.5 equiv). Pyrazoline **36d** was obtained after column chromatography (hexane: EtOAc, 3:1) as a colourless oil (21.0 mg, 0.07 mmol, 35%).

^{1}H NMR (500 MHz, CD_3OD) δ 7.60–7.49 (m, 1H), 7.43 (dd, *J* = 8.1, 1.0 Hz, 1H), 7.21 (ddd, *J* = 21.9, 7.9, 1.2 Hz, 2H), 6.70 (d, *J* = 0.9 Hz, 1H), 4.21 (t, *J* = 6.6 Hz, 2H), 3.34 (d, *J* = 17.2 Hz, 1H), 3.01 (d, *J* = 17.1 Hz, 1H), 1.73–1.63 (m, 5H), 1.49–1.36 (m, 2H), 0.95 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (126 MHz, CD_3OD) δ 162.5, 159.0, 154.6, 138.5, 127.6, 123.5, 122.1, 120.3, 110.1, 101.2, 65.0, 63.9, 42.1, 30.0, 23.1, 18.3, 12.2.

HRMS (ESI+), *m/z*: calculated for $C_{17}H_{20}N_2O_3$ $[M + H]^+$: 301.1547, found: 301.1565.

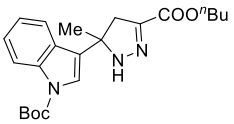


Butyl 5-(7-methoxybenzofuran-2-yl)-5-methyl-4,5-dihydro-1*H*-pyrazole-3-carboxylate (37d): Prepared according to the general procedure A, the title compound was prepared from *N*-tosylhydrazone (**37b**) (71.6 mg, 0.2 mmol, 1.0 equiv) and butyl acrylate (**1c**) (44.0 µl, 0.3 mmol, 1.5 equiv). Pyrazoline **37d** was obtained after column chromatography (hexane: EtOAc, 3:1) as a colourless oil (48.2 mg, 0.146 mmol, 73%).

^{1}H NMR (500 MHz, CD_3OD) δ 7.23–7.06 (m, 2H), 6.94–6.79 (m, 1H), 6.71 (d, *J* = 2.7 Hz, 1H), 4.27–4.20 (m, 2H), 3.98 (s, 3H), 3.38 (d, *J* = 17.1 Hz, 1H), 3.04 (d, *J* = 17.1 Hz, 1H), 1.70 (s, 5H), 1.53–1.38 (m, 2H), 0.98 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (126 MHz, CD_3OD) δ 164.4, 160.8, 146.7, 145.7, 140.4, 131.2, 124.7, 114.4, 108.0, 103.4, 67.0, 65.8, 56.5, 44.0, 31.9, 25.0, 20.2, 14.1.

HRMS (ESI+), *m/z*: calculated for $C_{18}H_{23}N_2O_4$ $[M + H]^+$: 331.1652, found: 331.1689.

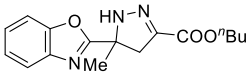


Tert-butyl 3-(3-(butoxycarbonyl)-5-methyl-4,5-dihydro-1*H*-pyrazol-5-yl)-1*H*-indole-1-carboxylate (38d): Prepared according to the general procedure A, the title compound was prepared from *N*-tosylhydrazone (**38b**) (80.6 mg, 0.2 mmol, 1.0 equiv) and butyl acrylate (**1c**) (44.0 µl, 0.3 mmol, 1.5 equiv). Pyrazoline **38d** was obtained after column chromatography (hexane: EtOAc, 3:1) as a colourless oil (62.3 mg, 0.156 mmol, 78%).

^{1}H NMR (500 MHz, CD_3OD) δ 8.16 (d, *J* = 8.3 Hz, 1H), 7.61–7.48 (m, 2H), 7.40–7.27 (m, 1H), 7.27–7.17 (m, 1H), 4.24 (t, *J* = 6.7 Hz, 2H), 3.15 (q, *J* = 17.1 Hz, 2H), 1.68 (d, *J* = 5.9 Hz, 14H), 1.45 (dq, *J* = 14.8, 7.4 Hz, 2H), 0.98 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (126 MHz, CD_3OD) δ 164.7, 151.0, 139.9, 137.7, 129.2, 126.4, 125.5, 123.7, 123.0, 121.4, 116.4, 85.1, 66.6, 65.8, 45.0, 31.9, 28.4, 26.6, 20.2, 14.1.

HRMS (ESI+), *m/z*: calculated for $C_{22}H_{29}N_3O_4$ $[M + K]^+$: 438.1790, found: 438.1836.

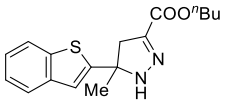


Butyl 5-(benzo[d]oxazol-2-yl)-5-methyl-4,5-dihydro-1*H*-pyrazole-3-carboxylate (39d): Prepared according to the general procedure A, the title compound was prepared from *N*-tosylhydrazone (**39b**) (66.0 mg, 0.2 mmol, 1.0 equiv) and butyl acrylate (**1c**) (44.0 µl, 0.3 mmol, 1.5 equiv). Pyrazoline **39d** was obtained after column chromatography (hexane: EtOAc, 3:1) as a colourless oil (30.1 mg, 0.1 mmol, 50%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78–7.65 (m, 1H), 7.58–7.46 (m, 1H), 7.43–7.31 (m, 2H), 6.72 (s, 1H), 4.25 (t, *J* = 6.8 Hz, 2H), 3.79 (d, *J* = 17.4 Hz, 1H), 3.12 (d, *J* = 17.4 Hz, 1H), 1.82 (s, 3H), 1.76–1.65 (m, 2H), 1.48–1.37 (m, 2H), 0.94 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 168.3, 163.6, 152.5, 144.0, 142.0, 127.0, 126.1, 121.7, 112.2, 67.6, 66.7, 44.4, 32.1, 26.7, 20.6, 15.1.

HRMS (ESI+), *m/z*: calculated for $C_{16}H_{19}N_3O_3$ $[M + H]^+$: 302.1499, found: 302.1535.

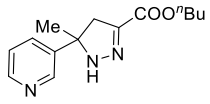


Butyl 5-(benzo[b]thiophen-2-yl)-5-methyl-4,5-dihydro-1*H*-pyrazole-3-carboxylate (40d): Prepared according to the general procedure A, the title compound was prepared from *N*-tosylhydrazone (**40b**) (68.8 mg, 0.2 mmol, 1.0 equiv) and butyl acrylate (**1c**) (44.0 µl, 0.3 mmol, 1.5 equiv). Pyrazoline **40d** was obtained after column chromatography (hexane: EtOAc, 3:1) as a colourless oil (37.9 mg, 0.12 mmol, 60%).

^{1}H NMR (500 MHz, CD_3OD) δ 7.78 (d, *J* = 8.0 Hz, 1H), 7.75–7.64 (m, 1H), 7.33–7.23 (m, 3H), 4.20 (t, *J* = 6.6 Hz, 2H), 3.21–3.08 (m, 2H), 1.77–1.63 (m, 5H), 1.47–1.36 (m, 2H), 0.95 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (126 MHz, CD_3OD) δ 162.5, 150.2, 139.4, 138.9, 138.5, 123.6, 123.5, 122.7, 121.3, 119.2, 67.3, 64.0, 45.9, 30.0, 24.8, 18.3, 12.2.

HRMS (ESI+), *m/z*: calculated for $C_{17}H_{20}N_2O_2S$ $[M + Na]^+$: 339.1138, found: 339.1114.

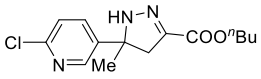


Butyl 5-methyl-5-(pyridin-3-yl)-4,5-dihydro-1*H*-pyrazole-3-carboxylate (41d): Prepared according to the general procedure A, the title compound was prepared from *N*-tosylhydrazone (**41b**) (58.0 mg, 0.2 mmol, 1.0 equiv) and butyl acrylate (**1c**) (44.0 µl, 0.3 mmol, 1.5 equiv). Pyrazoline **41d** was obtained after column chromatography (hexane: EtOAc, 3:1) as a colourless oil (30.8 mg, 0.118 mmol, 59%).

^{1}H NMR (500 MHz, CD_3OD) δ 8.63 (d, *J* = 2.4 Hz, 1H), 8.45 (d, *J* = 6.4 Hz, 1H), 8.00–7.85 (m, 1H), 7.51–7.36 (m, 1H), 4.21 (t, *J* = 6.6 Hz, 2H), 3.20 (d, *J* = 17.0 Hz, 1H), 2.99 (d, *J* = 17.0 Hz, 1H), 1.75–1.64 (m, 2H), 1.59 (s, 3H), 1.43 (dq, *J* = 14.8, 7.4 Hz, 2H), 0.96 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (126 MHz, CD_3OD) δ 164.4, 148.7, 147.5, 143.8, 140.5, 135.6, 125.2, 69.7, 65.8, 46.5, 31.9, 27.4, 20.2, 14.0.

HRMS (ESI+), *m/z*: calculated for $C_{14}H_{19}N_3O_2$ $[M + Na]^+$: 284.1369, found: 284.1338.

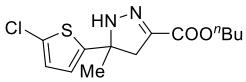


Butyl 5-(6-chloropyridin-3-yl)-5-methyl-4,5-dihydro-1*H*-pyrazole-3-carboxylate (42d): Prepared according to the general procedure A, the title compound was prepared from *N*-tosylhydrazone (**42b**) (65.0 mg, 0.2 mmol, 1.0 equiv) and butyl acrylate (**1c**) (44.0 µl, 0.3 mmol, 1.5 equiv). Pyrazoline **42d** was obtained after column chromatography (hexane: EtOAc, 3:1) as a colourless oil (37.2 mg, 0.126 mmol, 63%).

^{1}H NMR (500 MHz, CD_3OD) δ 8.43 (dd, *J* = 2.6, 0.7 Hz, 1H), 7.87 (dd, *J* = 8.4, 2.6 Hz, 1H), 7.44 (dd, *J* = 8.4, 0.7 Hz, 1H), 4.21 (t, *J* = 6.6 Hz, 2H), 3.18 (d, *J* = 17.0 Hz, 1H), 2.98 (d, *J* = 17.1 Hz, 1H), 1.75–1.62 (m, 2H), 1.58 (s, 3H), 1.51–1.38 (m, 2H), 0.95 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (126 MHz, CD_3OD) δ 164.3, 151.0, 148.1, 142.6, 140.7, 138.6, 125.4, 69.3, 65.9, 46.5, 31.9, 27.3, 20.2, 14.1.

HRMS (ESI+), *m/z*: calculated for $C_{14}H_{18}N_3O_2$ $[M + H]^+$: 296.1160, found: 296.1189.

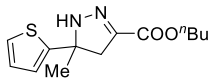


Butyl 5-(5-chlorothiophen-2-yl)-5-methyl-4,5-dihydro-1*H*-pyrazole-3-carboxylate (43d): Prepared according to the general procedure A, the title compound was prepared from *N*-tosylhydrazone (**43b**) (65.6 mg, 0.2 mmol, 1.0 equiv) and butyl acrylate (**1c**) (44.0 µl, 0.3 mmol, 1.5 equiv). Pyrazoline **43d** was obtained after column chromatography (hexane: EtOAc, 3:1) as a colourless oil (53.5 mg, 0.178 mmol, 89%).

^{1}H NMR (500 MHz, CD_3OD) δ 6.82 (d, *J* = 2.0 Hz, 2H), 4.20 (td, *J* = 6.6, 2.0 Hz, 2H), 3.12–2.95 (m, 2H), 1.73–1.61 (m, 2H), 1.60 (s, 3H), 1.42 (qd, *J* = 7.5, 1.9 Hz, 2H), 0.95 (td, *J* = 7.4, 1.8 Hz, 3H).

^{13}C NMR (126 MHz, CD_3OD) δ 162.3, 148.9, 138.9, 127.9, 125.5, 122.1, 67.0, 64.0, 46.1, 30.0, 24.5, 18.3, 12.2.

HRMS (ESI+), *m/z*: calculated for $C_{13}H_{17}N_2ClO_2S$ $[M + Na]^+$: 323.0591, found: 323.0628.

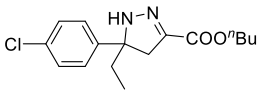


Butyl 5-methyl-5-(thiophen-2-yl)-4,5-dihydro-1*H*-pyrazole-3-carboxylate (44d): Prepared according to the general procedure A, the title compound was prepared from *N*-tosylhydrazone (**44b**) (29,4 mg, 0.1 mmol, 1.0 equiv) and butyl acrylate (**1c**) (22.0 µl, 0.15 mmol, 1.5 equiv). Pyrazoline **44d** was obtained after column chromatography (hexane: EtOAc, 3:1) as a colourless oil (41.0 mg, 0.154 mmol, 77%).

^{1}H NMR (500 MHz, CD_3OD) δ 7.28 (dd, *J* = 5.1, 1.2 Hz, 1H), 7.05 – 6.91 (m, 2H), 4.21 (t, *J* = 6.6 Hz, 2H), 3.06 (d, *J* = 1.3 Hz, 2H), 1.73–1.60 (m, 5H), 1.48–1.34 (m, 2H), 0.96 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (126 MHz, CD_3OD) δ 164.4, 151.5, 140.2, 128.0, 125.6, 124.4, 68.9, 65.8, 48.0, 31.9, 27.3, 20.2, 14.1.

HRMS (ESI+), *m/z*: calculated for $C_{13}H_{18}N_2O_2S$ $[M + K]^+$: 305.0721, found: 305.0754.

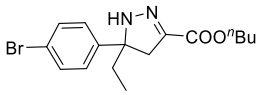


Butyl 5-(4-chlorophenyl)-5-ethyl-4,5-dihydro-1*H*-pyrazole-3-carboxylate (45d): Prepared according to the general procedure A, the title compound was prepared from *N*-tosylhydrazone (**45b**) (67.2 mg, 0.2 mmol, 1.0 equiv) and butyl acrylate (**1c**) (44.0 µl, 0.3 mmol, 1.5 equiv). Pyrazoline **45d** was obtained after column chromatography (hexane: EtOAc, 3:1) as a colourless oil (59.3 mg, 0.192 mmol, 96%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 (d, *J* = 8.6 Hz, 2H), 7.25 (t, *J* = 8.0 Hz, 2H), 6.49 (s, 1H), 4.22 (t, *J* = 6.8 Hz, 2H), 3.15 (d, *J* = 17.1 Hz, 1H), 3.02 (d, *J* = 17.2 Hz, 1H), 1.91 (ddd, *J* = 50.8, 14.2, 7.2 Hz, 2H), 1.75–1.64 (m, 2H), 1.47–1.31 (m, 2H), 0.93 (t, *J* = 7.4 Hz, 3H), 0.78 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 162.2, 142.4, 140.8, 132.5, 128.3, 126.5, 72.5, 64.6, 44.0, 32.8, 30.2, 18.7, 13.3, 7.8.

HRMS (ESI+), *m/z*: calculated for $C_{16}H_{21}N_2O_2Cl$ $[M + H]^+$: 309.1363, found: 309.1405.

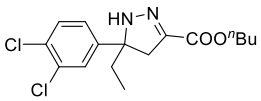


Butyl 5-(4-bromophenyl)-5-ethyl-4,5-dihydro-1*H*-pyrazole-3-carboxylate (46d): Prepared according to the general procedure A, the title compound was prepared from *N*-tosylhydrazone (**46b**) (76.0 mg, 0.2 mmol, 1.0 equiv) and butyl acrylate (**1c**) (44.0 µl, 0.3 mmol, 1.5 equiv). Pyrazoline **46d** was obtained after column chromatography (hexane: EtOAc, 3:1) as a colourless oil (64.9 mg, 0.184 mmol, 92%).

^{1}H NMR (500 MHz, CD_3OD) δ 7.49 (d, *J* = 8.5 Hz, 2H), 7.27 (d, *J* = 8.6 Hz, 2H), 4.18 (t, *J* = 6.6 Hz, 2H), 3.17 (d, *J* = 17.2 Hz, 1H), 2.97 (d, *J* = 17.2 Hz, 1H), 2.00–1.79 (m, 2H), 1.75–1.61 (m, 2H), 1.49–1.32 (m, 2H), 0.95 (t, *J* = 7.4 Hz, 3H), 0.79 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (126 MHz, CD_3OD) δ 164.5, 146.0, 139.6, 132.6, 128.8, 121.7, 74.7, 65.7, 44.3, 35.0, 31.9, 20.2, 14.1, 8.7.

HRMS (ESI+), *m/z*: calculated for $C_{16}H_{21}N_2O_2Br$ $[M + H]^+$: 353.0859, found: 353.0867.

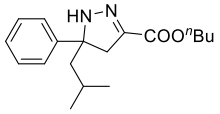


Butyl 5-(3,4-dichlorophenyl)-5-ethyl-4,5-dihydro-1*H*-pyrazole-3-carboxylate (47d): Prepared according to the general procedure A, the title compound was prepared from *N*-tosylhydrazone (**47b**) (74.2 mg, 0.2 mmol, 1.0 equiv) and butyl acrylate (**1c**) (44.0 µl, 0.3 mmol, 1.5 equiv). Pyrazoline **47d** was obtained after column chromatography (hexane: EtOAc, 3:1) as a colourless oil (66.5 mg, 0.194 mmol, 97%).

^{1}H NMR (500 MHz, CD_3OD) δ 7.56–7.43 (m, 2H), 7.35–7.22 (m, 1H), 4.27–4.12 (m, 2H), 3.26–3.12 (m, 1H), 2.97 (d, *J* = 17.2 Hz, 1H), 1.96–1.78 (m, 2H), 1.70–1.61 (m, 2H), 1.40 (q, *J* = 7.7 Hz, 2H), 0.97–0.90 (m, 3H), 0.85–0.72 (m, 3H).

^{13}C NMR (126 MHz, CD_3OD) δ 164.4, 147.6, 139.8, 133.5, 131.8, 131.7, 129.0, 126.8, 74.3, 65.8, 44.4, 35.0, 31.9, 20.2, 14.1, 8.7.

HRMS (ESI+), *m/z*: calculated for $C_{16}H_{20}N_2O_2Cl_2$ $[M + H]^+$: 343.0975, found: 343.1001.

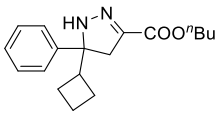


Butyl 5-isobutyl-5-phenyl-4,5-dihydro-1*H*-pyrazole-3-carboxylate (48d): Prepared according to the general procedure A, the title compound was prepared from *N*-tosylhydrazone (**48b**) (66.1 mg, 0.2 mmol, 1.0 equiv) and butyl acrylate (**1c**) (44.0 µl, 0.3 mmol, 1.5 equiv). Pyrazoline **48d** was obtained after column chromatography (hexane: EtOAc, 3:1) as a colourless oil (50.2 mg, 0.166 mmol, 83%).

^{1}H NMR (500 MHz, CD_3OD) δ 7.39–7.29 (m, 4H), 7.28–7.16 (m, 1H), 4.18 (t, *J* = 6.6 Hz, 2H), 3.13 (d, *J* = 17.0 Hz, 1H), 3.04 (d, *J* = 16.9 Hz, 1H), 1.88 (dd, *J* = 5.9, 1.4 Hz, 2H), 1.69–1.62 (m, 2H), 1.60–1.51 (m, 1H), 1.45–1.37 (m, 2H), 0.94 (t, *J* = 7.4 Hz, 3H), 0.82 (d, *J* = 6.7 Hz, 3H), 0.70 (d, *J* = 6.6 Hz, 3H).

^{13}C NMR (126 MHz, CD_3OD) δ 162.8, 144.6, 137.7, 127.7, 126.1, 124.7, 73.2, 63.8, 49.1, 43.8, 30.0, 23.9, 22.9, 22.5, 18.3, 12.2.

HRMS (ESI+), *m/z*: calculated for $C_{18}H_{26}N_2O_2$ $[M + Na]^+$: 325.1886, found: 325.1906.

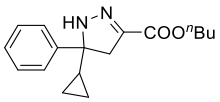


Butyl 5-cyclobutyl-5-phenyl-4,5-dihydro-1*H*-pyrazole-3-carboxylate (49d): Prepared according to the general procedure A, the title compound was prepared from *N*-tosylhydrazone (**49b**) (65.6 mg, 0.2 mmol, 1.0 equiv) and butyl acrylate (**1c**) (44.0 µl, 0.3 mmol, 1.5 equiv). Pyrazoline **49d** was obtained after column chromatography (hexane: EtOAc, 3:1) as a colourless oil (46.8 mg, 0.156 mmol, 78%).

^{1}H NMR (500 MHz, CD_3OD) δ 7.36–7.26 (m, 4H), 7.25–7.19 (m, 1H), 4.18 (t, *J* = 6.6 Hz, 2H), 3.11 (d, *J* = 17.2 Hz, 1H), 2.93 (m, 2H), 1.93–1.74 (m, 4H), 1.72–1.58 (m, 4H), 1.46–1.36 (m, 2H), 0.95 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (126 MHz, CD_3OD) δ 164.7, 146.0, 138.4, 129.5, 128.0, 126.6, 76.0, 65.6, 46.1, 42.8, 31.9, 24.3, 24.0, 20.2, 17.6, 14.1.

HRMS (ESI+), *m/z*: calculated for $C_{18}H_{24}N_2O_2$ [M + Na]$^+$: 323.1730, found: 323.1772.

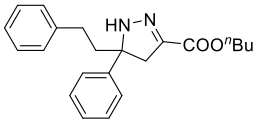


Butyl 5-cyclopropyl-5-phenyl-4,5-dihydro-1*H*-pyrazole-3-carboxylate (50d): Prepared according to the general procedure A, the title compound was prepared from *N*-tosylhydrazone (**50b**) (62.8 mg, 0.2 mmol, 1.0 equiv) and butyl acrylate (**1c**) (44.0 µl, 0.3 mmol, 1.5 equiv). Pyrazoline **50d** was obtained after column chromatography (hexane: EtOAc, 3:1) as a colourless oil (43.5 mg, 0.152 mmol, 76%).

^{1}H NMR (500 MHz, CD_3OD) δ 7.40 (tt, *J* = 6.8, 1.2 Hz, 3H), 7.35 – 7.31 (m, 2H), 4.19 (t, *J* = 6.7 Hz, 2H), 3.22 (d, *J* = 17.2 Hz, 1H), 3.08 (d, *J* = 17.2 Hz, 1H), 1.74–1.59 (m, 2H), 1.51–1.32 (m, 3H), 0.96 (t, *J* = 7.4 Hz, 3H), 0.60–0.36 (m, 2H), 0.39–0.25 (m, 2H).

^{13}C NMR (126 MHz, CD_3OD) δ 164.6, 146.7, 139.3, 129.4, 129.2, 128.2, 127.3, 127.0, 79.3, 73.9, 65.7, 45.3, 31.9, 20.2, 14.1, 2.1, 1.7.

HRMS (ESI+), *m/z*: calculated for $C_{17}H_{22}N_2O_2$ [M + Na]$^+$: 309.1573, found: 309.1542.

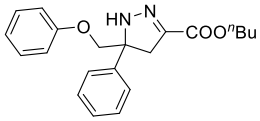


Butyl 5-phenethyl-5-phenyl-4,5-dihydro-1*H*-pyrazole-3-carboxylate (51d): Prepared according to the general procedure A, the title compound was prepared from *N*-tosylhydrazone (**51b**) (75.6 mg, 0.2 mmol, 1.0 equiv) and butyl acrylate (**1c**) (44.0 µl, 0.3 mmol, 1.5 equiv). Pyrazoline **51d** was obtained after column chromatography (hexane: EtOAc, 3:1) as a colourless oil (39.2 mg, 0.112 mmol, 56%).

^{1}H NMR (500 MHz, CD_3OD) δ 7.42–7.35 (m, 4H), 7.26 (ddd, *J* = 8.6, 5.4, 2.1 Hz, 1H), 7.21 (t, *J* = 7.6 Hz, 2H), 7.14–7.06 (m, 3H), 4.18 (t, *J* = 6.7 Hz, 2H), 3.22 (d, *J* = 17.1 Hz, 1H), 3.03 (d, *J* = 17.1 Hz, 1H), 2.59–2.49 (m, 1H), 2.36 (ddd, *J* = 13.2, 11.1, 5.4 Hz, 1H), 2.22–2.10 (m, 2H), 1.73–1.57 (m, 2H), 1.48–1.36 (m, 2H), 0.94 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (126 MHz, CD_3OD) δ 164.6, 146.4, 143.0, 139.6, 129.8, 129.5, 129.3, 128.1, 126.9, 126.5, 74.6, 65.7, 44.9, 44.8, 31.9, 31.8, 20.2, 14.1.

HRMS (ESI+), *m/z*: calculated for $C_{22}H_{26}N_2O_2$ $[M + H]^+$: 351.2067, found: 351.2101.

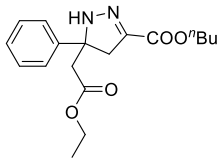


Butyl 5-(phenoxymethyl)-5-phenyl-4,5-dihydro-1*H*-pyrazole-3-carboxylate (52d): Prepared according to the general procedure A, the title compound was prepared from *N*-tosylhydrazone (**52b**) (76.1 mg, 0.2 mmol, 1.0 equiv) and butyl acrylate (**1c**) (44.0 µl, 0.3 mmol, 1.5 equiv). Pyrazoline **52d** was obtained after column chromatography (hexane: EtOAc, 3:1) as a colourless oil (39.4 mg, 0.112 mmol, 56%).

^{1}H NMR (500 MHz, CD_3OD) δ 7.52–7.41 (m, 2H), 7.37 (dd, *J* = 8.5, 7.0 Hz, 2H), 7.33–7.17 (m, 3H), 6.98–6.80 (m, 3H), 4.22 (t, *J* = 6.6 Hz, 2H), 4.17 (d, *J* = 2.4 Hz, 2H), 3.45 (d, *J* = 17.2 Hz, 1H), 3.06 (d, *J* = 17.3 Hz, 1H), 1.76–1.60 (m, 2H), 1.50–1.37 (m, 2H), 0.96 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (126 MHz, CD_3OD) δ 162.5, 158.3, 142.3, 138.5, 128.6, 127.8, 126.6, 125.2, 120.3, 113.9, 72.5, 71.9, 63.9, 40.7, 30.0, 18.3, 12.2.

HRMS (ESI+), *m/z*: calculated for $C_{21}H_{24}N_2O_3$ $[M + H]^+$: 353.1860, found: 353.1895.

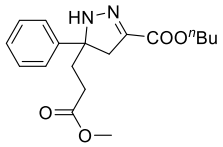


Butyl 5-(2-methoxy-2-oxoethyl)-5-phenyl-4,5-dihydro-1*H*-pyrazole-3-carboxylate (53d): Prepared according to the general procedure A, the title compound was prepared from *N*-tosylhydrazone (**53b**) (72.0 mg, 0.2 mmol, 1.0 equiv) and butyl acrylate (**1c**) (44.0 µl, 0.3 mmol, 1.5 equiv). Pyrazoline **53d** was obtained after column chromatography (hexane: EtOAc, 3:1) as a colourless oil (36.5 mg, 0.11 mmol, 55%).

^{1}H NMR (500 MHz, CD_3OD) δ 7.40–7.31 (m, 4H), 7.29–7.23 (m, 1H), 4.20 (t, *J* = 6.6 Hz, 2H), 3.96 (q, *J* = 7.1 Hz, 2H), 3.41 (d, *J* = 17.1 Hz, 1H), 3.00 (d, *J* = 17.1 Hz, 1H), 2.95 (d, *J* = 2.0 Hz, 2H), 1.71–1.62 (m, 2H), 1.48–1.38 (m, 2H), 1.06 (t, *J* = 7.1 Hz, 3H), 0.95 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (126 MHz, CD_3OD) δ 172.0, 164.3, 145.1, 141.0, 129.7, 128.4, 126.6, 72.5, 65.8, 61.7, 45.4, 45.3, 31.9, 20.2, 14.3, 14.1.

HRMS (ESI+), *m/z*: calculated for $C_{17}H_{22}N_2O_4$ $[M + H]^+$: 333.1809, found: 333.1848.

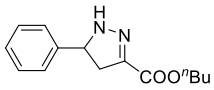


Butyl 5-(3-methoxy-3-oxopropyl)-5-phenyl-4,5-dihydro-1*H*-pyrazole-3-carboxylate (54d): Prepared according to the general procedure A, the title compound was prepared from *N*-tosylhydrazone (**54b**) (72.1 mg, 0.2 mmol, 1.0 equiv) and butyl acrylate (**1c**) (44.0 µl, 0.3 mmol, 1.5 equiv). Pyrazoline **54d** was obtained after column chromatography (hexane: EtOAc, 3:1) as a colourless oil (39.8 mg, 0.12 mmol, 60%).

^{1}H NMR (500 MHz, CD_3OD) δ 7.41–7.22 (m, 5H), 4.18 (t, *J* = 6.6 Hz, 2H), 3.58 (s, 3H), 3.19 (d, *J* = 17.2 Hz, 1H), 3.02 (d, *J* = 17.2 Hz, 1H), 2.34–2.09 (m, 4H), 1.74–1.61 (m, 2H), 1.47–1.37 (m, 2H), 0.95 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (126 MHz, CD_3OD) δ 175.2, 164.5, 145.7, 139.8, 129.8, 128.3, 126.5, 74.0, 65.7, 52.2, 44.7, 37.1, 31.9, 30.2, 20.2, 14.1.

HRMS (ESI+), *m/z*: calculated for $C_{18}H_{24}N_2O_2$ $[M + H]^+$: 333.1809, found: 333.1817.

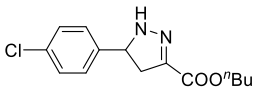


Butyl 5-methyl-5-phenyl-4,5-dihydro-1*H*-pyrazole-3-carboxylate (55d): Prepared according to the general procedure A, the title compound was prepared from *N*-tosylhydrazone (**55b**) (54.8 mg, 0.2 mmol, 1.0 equiv) and butyl acrylate (**1c**) (44.0 µl, 0.3 mmol, 1.5 equiv). Pyrazoline **55d** was obtained after column chromatography (hexane: EtOAc, 3:1) as a colourless oil (32.5 mg, 0.132 mmol, 66%).

^{1}H NMR (500 MHz, CD_3OD) δ 7.73–7.61 (m, 2H), 7.46–7.30 (m, 3H), 4.43 (t, *J* = 8.8 Hz, 1H), 4.17 (t, *J* = 6.6 Hz, 2H), 3.41–3.34 (m, 2H), 1.69–1.60 (m, 2H), 1.40 (dq, *J* = 14.8, 7.4 Hz, 2H), 0.93 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (126 MHz, CD_3OD) δ 174.2, 153.6, 133.4, 130.3, 129.7, 127.2, 66.5, 61.8, 37.3, 31.8, 20.1, 14.0.

HRMS (ESI+), *m/z*: calculated for $C_{14}H_{18}N_2O_2$ $[M + H]^+$: 247.1441, found: 247.1471.

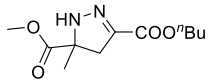


Butyl 5-(4-chlorophenyl)-5-methyl-4,5-dihydro-1*H*-pyrazole-3-carboxylate (56d): Prepared according to the general procedure A, the title compound was prepared from *N*-tosylhydrazone (**56b**) (61.6 mg, 0.2 mmol, 1.0 equiv) and butyl acrylate (**1c**) (44.0 µl, 0.3 mmol, 1.5 equiv). Pyrazoline **56d** was obtained after column chromatography (hexane: EtOAc, 3:1) as a colourless oil (34.8 mg, 0.124 mmol, 62%).

^{1}H NMR (500 MHz, CD_3OD) δ 7.63 (d, *J* = 8.6 Hz, 2H), 7.38 (d, *J* = 8.6 Hz, 2H), 4.44 (t, *J* = 8.9 Hz, 1H), 4.16 (t, *J* = 6.6 Hz, 2H), 3.34 (d, *J* = 8.8 Hz, 2H), 1.71–1.56 (m, 2H), 1.40 (dq, *J* = 14.8, 7.4 Hz, 2H), 0.93 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (126 MHz, CD_3OD) δ 174.1, 152.2, 136.0, 132.2, 129.8, 128.6, 66.5, 62.0, 37.0, 31.7, 20.1, 14.0.

HRMS (ESI+), *m/z*: calculated for $C_{14}H_{17}N_2O_2$ $[M + H]^+$: 281.1051, found: 281.1101.

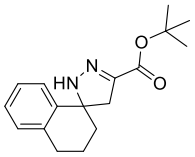


3-Butyl 5-methyl 5-methyl-4,5-dihydro-1*H*-pyrazole-3,5-dicarboxylate (57d): Prepared according to the general procedure A, the title compound was prepared from *N*-tosylhydrazone (**57b**) (54.0 mg, 0.2 mmol, 1.0 equiv) and butyl acrylate (**1c**) (44.0 µl, 0.3 mmol, 1.5 equiv). Pyrazoline **57d** was obtained after column chromatography (hexane: EtOAc, 3:1) as a colourless oil (31.4 mg, 0.13 mmol, 65%).

^{1}H NMR (500 MHz, CD_3OD) δ 4.20 (t, *J* = 6.6 Hz, 2H), 3.75 (s, 3H), 3.38 (d, *J* = 17.4 Hz, 1H), 2.81 (d, *J* = 17.4 Hz, 1H), 1.72–1.63 (m, 2H), 1.48 (s, 3H), 1.46–1.38 (m, 2H), 0.96 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (126 MHz, CD_3OD) δ 175.3, 164.0, 71.0, 65.9, 53.3, 42.2, 31.8, 23.9, 20.2, 14.0.

HRMS (ESI+), *m/z*: calculated for $C_{11}H_{18}N_2O_4$ $[M + H]^+$: 243.1339, found: 243.1305.

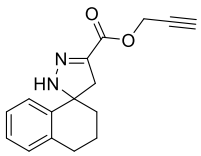


Tert-butyl 2',3,4,4'-tetrahydro-2*H*-spiro[naphthalene-1,3'-pyrazole]-5'-carboxylate (58d): Prepared according to the general procedure A, the title compound was prepared from *N*-tosylhydrazone (**1b**) (62.8 mg, 0.2 mmol, 1.0 equiv) and butyl acrylate (**58c**) (44.0 µl, 0.3 mmol, 1.5 equiv). Spiropyrazoline **58d** was obtained after column chromatography (hexane: EtOAc, 3:1) as a colourless oil (54.9 mg, 0.192 mmol, 96%).

^{1}H NMR (500 MHz, CD_3OD) δ 7.32 (dd, *J* = 7.5, 1.8 Hz, 1H), 7.18–7.10 (m, 2H), 7.09–7.03 (m, 1H), 3.07 (d, *J* = 17.5 Hz, 1H), 2.96 (d, *J* = 17.5 Hz, 1H), 2.79 (t, *J* = 5.2 Hz, 2H), 2.04–1.81 (m, 4H), 1.52 (s, 9H).

^{13}C NMR (126 MHz, CD_3OD) δ 162.3, 140.2, 137.2, 135.8, 128.0, 126.4, 126.0, 125.7, 80.6, 67.9, 46.3, 35.1, 28.4, 26.6, 19.1.

HRMS (ESI+), *m/z*: calculated for $C_{17}H_{22}N_2O_2$ $[M + H]^+$: 287.1754, found: 287.1774.

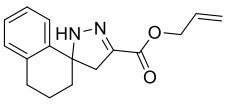


Prop-2-yn-1-yl 2',3,4,4'-tetrahydro-2*H*-spiro[naphthalene-1,3'-pyrazole]-5'-carboxylate (59d): Prepared according to the general procedure A, the title compound was prepared from *N*-tosylhydrazone (**1b**) (62.8 mg, 0.2 mmol, 1.0 equiv) and butyl acrylate (**59c**) (33.0 µl, 0.3 mmol, 1.5 equiv). Spiropyrazoline **59d** was obtained after column chromatography (hexane: EtOAc, 3:1) as a colourless oil (27.9 mg, 0.11 mmol, 55%).

^{1}H NMR (500 MHz, CD_3OD) δ 7.31 (dd, *J* = 7.4, 1.9 Hz, 1H), 7.15 (ddd, *J* = 6.7, 4.5, 1.8 Hz, 2H), 7.11–7.03 (m, 1H), 4.82 (d, *J* = 2.5 Hz, 2H), 3.14 (d, *J* = 17.4 Hz, 1H), 3.03 (d, *J* = 17.4 Hz, 1H), 2.93 (t, *J* = 2.5 Hz, 1H), 2.84–2.76 (m, 2H), 2.04 – 1.83 (m, 4H).

^{13}C NMR (126 MHz, CD_3OD) δ 163.8, 141.8, 137.7, 135.9, 130.0, 128.4, 127.9, 127.7, 78.9, 76.3, 70.2, 52.8, 47.7, 37.0, 30.2, 20.9.

HRMS (ESI+), *m/z*: calculated for $C_{16}H_{16}N_2O_2$ $[M + H]^+$: 269.1285, found: 269.1300.

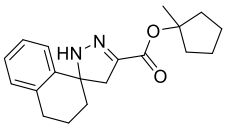


Allyl 2',3,4,4'-tetrahydro-2*H*-spiro[naphthalene-1,3'-pyrazole]-5'-carboxylate (60d): Prepared according to the general procedure A, the title compound was prepared from *N*-tosylhydrazone (**1b**) (62.8 mg, 0.2 mmol, 1.0 equiv) and butyl acrylate (**60c**) (36.0 µl, 0.3 mmol, 1.5 equiv). Spiropyrazoline **60d** was obtained after column chromatography (hexane: EtOAc, 3:1) as a colourless oil (42.1 mg, 0.156 mmol, 78%).

^{1}H NMR (500 MHz, CD_3OD) δ 7.31 (dd, *J* = 7.3, 1.9 Hz, 1H), 7.21–7.03 (m, 3H), 6.00 (ddt, *J* = 17.2, 10.4, 5.7 Hz, 1H), 5.36 (dd, *J* = 17.2, 1.6 Hz, 1H), 5.24 (dd, *J* = 10.5, 1.4 Hz, 1H), 4.71 (dd, *J* = 5.6, 1.5 Hz, 2H), 3.13 (d, *J* = 17.4 Hz, 1H), 3.03 (d, *J* = 17.4 Hz, 1H), 2.80 (t, *J* = 5.1 Hz, 2H), 2.07–1.78 (m, 4H).

^{13}C NMR (126 MHz, CD_3OD) δ 164.4, 141.9, 137.7, 136.9, 133.7, 130.0, 128.4, 127.9, 127.6, 118.5, 70.0, 66.3, 47.8, 37.0, 30.3, 21.0.

HRMS (ESI+), *m/z*: calculated for $C_{16}H_{18}N_2O_2$ $[M + H]^+$: 271.1441, found: 271.1450.

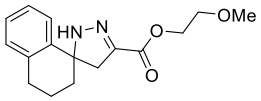


1-methylcyclopentyl 2',3,4,4'-tetrahydro-2*H*-spiro[naphthalene-1,3'-pyrazole]-5'-carboxylate (61d): Prepared according to the general procedure A, the title compound was prepared from *N*-tosylhydrazone (**1b**) (62.8 mg, 0.2 mmol, 1.0 equiv) and butyl acrylate (**61c**) (51.0 µl, 0.3 mmol, 1.5 equiv). Spiropyrazoline **61d** was obtained after column chromatography (hexane: EtOAc, 3:1) as a colourless oil (51.2 mg, 0.164 mmol, 82%).

^{1}H NMR (500 MHz, CD_3OD) δ 7.32 (dd, *J* = 7.4, 1.8 Hz, 1H), 7.22–7.01 (m, 3H), 3.07 (d, *J* = 17.5 Hz, 1H), 2.96 (d, *J* = 17.4 Hz, 1H), 2.79 (s, 2H), 2.30–2.13 (m, 2H), 2.04–1.83 (m, 4H), 1.79–1.71 (m, 4H), 1.61 (s, 5H).

^{13}C NMR (126 MHz, CD_3OD) δ 164.3, 142.0, 138.9, 137.6, 129.9, 128.3, 127.9, 127.6, 92.0, 69.9, 48.1, 40.2, 40.1, 36.9, 30.3, 24.8, 24.8, 21.0.

HRMS (ESI+), *m/z*: calculated for $C_{19}H_{24}N_2O_2$ $[M + H]^+$: 313.1911, found: 313.1921.

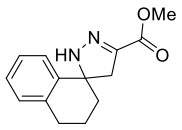


2-methoxyethyl 2',3,4,4'-tetrahydro-2*H*-spiro[naphthalene-1,3'-pyrazole]-5'-carboxylate (62d): Prepared according to the general procedure A, the title compound was prepared from *N*-tosylhydrazone (**1b**) (62.8 mg, 0.2 mmol, 1.0 equiv) and butyl acrylate (**62c**) (39.0 µl, 0.3 mmol, 1.5 equiv). Spiropyrazoline **62d** was obtained after column chromatography (hexane: EtOAc, 3:1) as a colourless oil (46.1 mg, 0.16 mmol, 80%).

^{1}H NMR (500 MHz, CD_3OD) δ 7.32 (dd, *J* = 7.3, 2.0 Hz, 1H), 7.21–7.01 (m, 3H), 4.38–4.29 (m, 2H), 3.70–3.62 (m, 2H), 3.31 (s, 3H), 3.14 (d, *J* = 17.4 Hz, 1H), 3.03 (d, *J* = 17.4 Hz, 1H), 2.89–2.76 (m, 2H), 2.06–1.80 (m, 4H).

^{13}C NMR (126 MHz, CD_3OD) δ 164.7, 141.9, 137.7, 136.8, 129.9, 128.4, 127.9, 127.6, 71.5, 70.0, 64.7, 59.1, 47.8, 37.0, 30.2, 21.0.

HRMS (ESI+), *m/z*: calculated for $C_{16}H_{20}N_2O_3$ $[M + H]^+$: 289.1547, found: 289.1560.

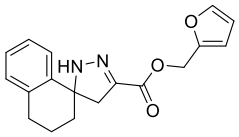


Methyl 2',3,4,4'-tetrahydro-2*H*-spiro[naphthalene-1,3'-pyrazole]-5'-carboxylate (63d): Prepared according to the general procedure A, the title compound was prepared from *N*-tosylhydrazone (**1b**) (62.8 mg, 0.2 mmol, 1.0 equiv) and butyl acrylate (**63c**) (27.0 µl, 0.3 mmol, 1.5 equiv). Spiropyrazoline **63d** was obtained after column chromatography (hexane: EtOAc, 3:1) as a colourless oil (41.5 mg, 0.17 mmol, 85%).

^{1}H NMR (500 MHz, CD_3OD) δ 7.31 (dd, *J* = 7.1, 2.2 Hz, 1H), 7.21–7.01 (m, 3H), 3.78 (s, 3H), 3.12 (d, *J* = 17.4 Hz, 1H), 3.01 (d, *J* = 17.5 Hz, 1H), 2.80 (t, *J* = 7.0 Hz, 2H), 2.06–1.77 (m, 4H).

^{13}C NMR (126 MHz, CD_3OD) δ 165.2, 141.9, 137.7, 137.0, 130.0, 128.4, 127.9, 127.6, 70.0, 52.2, 36.9, 30.3, 21.0.

HRMS (ESI+), *m/z*: calculated for $C_{14}H_{16}N_2O_2$ $[M + K]^+$: 283.0843, found: 283.1832.

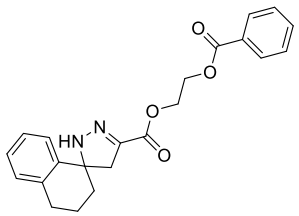


Furan-2-ylmethyl 2',3,4,4'-tetrahydro-2*H*-spiro[naphthalene-1,3'-pyrazole]-5'-carboxylate (64d): Prepared according to the general procedure A, the title compound was prepared from *N*-tosylhydrazone (**1b**) (62.8 mg, 0.2 mmol, 1.0 equiv) and butyl acrylate (**64c**) (40.0 µl, 0.3 mmol, 1.5 equiv). Spiropyrazoline **64d** was obtained after column chromatography (hexane: EtOAc, 3:1) as a colourless oil (34.1 mg, 0.11 mmol, 55%).

^{1}H NMR (500 MHz, CD_3OD) δ 7.49 (dd, *J* = 1.9, 0.8 Hz, 1H), 7.35–7.24 (m, 1H), 7.22–7.00 (m, 3H), 6.48 (dd, *J* = 3.3, 0.7 Hz, 1H), 6.44–6.36 (m, 1H), 5.19 (s, 2H), 3.10 (d, *J* = 17.4 Hz, 1H), 2.99 (d, *J* = 17.4 Hz, 1H), 2.85–2.71 (m, 2H), 2.05–1.75 (m, 4H).

^{13}C NMR (126 MHz, CD_3OD) δ 164.3, 151.1, 144.6, 141.8, 137.7, 136.5, 129.9, 128.4, 128.0, 127.6, 111.9, 111.7, 70.1, 59.1, 47.8, 36.9, 30.2, 20.9.

HRMS (ESI+), *m/z*: calculated for $C_{18}H_{18}N_2O_3$ $[M + H]^+$: 311.1390, found: 311.1403.

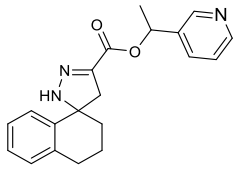


2-(benzoyloxy)ethyl 2',3,4,4'-tetrahydro-2*H*-spiro[naphthalene-1,3'-pyrazole]-5'-carboxylate (65d): Prepared according to the general procedure A, the title compound was prepared from *N*-tosylhydrazone (**1b**) (62.8 mg, 0.2 mmol, 1.0 equiv) and butyl acrylate (**65c**) (66.0 µl, 0.3 mmol, 1.5 equiv). Spiropyrazoline **65d** was obtained after column chromatography (hexane: EtOAc, 3:1) as a colourless oil (53.7 mg, 0.142 mmol, 71%).

^{1}H NMR (500 MHz, CD_3OD) δ 8.08–8.04 (m, 1H), 8.02–7.98 (m, 2H), 7.60–7.54 (m, 1H), 7.45 (dt, *J* = 13.4, 7.8 Hz, 3H), 7.14–7.07 (m, 2H), 4.63–4.50 (m, 4H), 4.42–4.34 (m, 1H), 3.86 (dd, *J* = 5.8, 4.0 Hz, 1H), 3.07 (d, *J* = 17.4 Hz, 1H), 2.97 (d, *J* = 17.4 Hz, 1H), 2.76 (td, *J* = 6.8, 5.2, 3.1 Hz, 2H), 2.01–1.70 (m, 4H).

^{13}C NMR (126 MHz, CD_3OD) δ 167.8, 164.5, 141.8, 137.6, 136.7, 134.4, 134.3, 131.2, 130.7, 130.0, 129.6, 129.6, 128.4, 127.9, 127.6, 70.1, 67.6, 64.1, 63.5, 61.2, 47.8, 36.9, 30.2, 21.0.

HRMS (ESI+), *m/z*: calculated for $C_{22}H_{22}N_2O_4$ $[M + H]^+$: 379.1652, found: 379.1669.

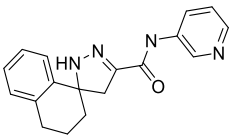


1-(pyridin-3-yl)ethyl (1R)-2',3,4,4'-tetrahydro-2*H*-spiro[naphthalene-1,3'-pyrazole]-5'-carboxylate (66d): Prepared according to the general procedure A, the title compound was prepared from *N*-tosylhydrazone (**1b**) (62.8 mg, 0.2 mmol, 1.0 equiv) and butyl acrylate (**66c**) (53.0 µl, 0.3 mmol, 1.5 equiv). Spiropyrazoline **66d** was obtained after column chromatography (hexane: EtOAc, 3:1) as a colourless oil (37.5 mg, 0.112 mmol, 56%).

^{1}H NMR (500 MHz, CD_3OD) δ 8.62 (dd, *J* = 7.9, 2.3 Hz, 1H), 8.48 (td, *J* = 5.0, 1.6 Hz, 1H), 8.01–7.89 (m, 1H), 7.45 (td, *J* = 7.2, 4.9 Hz, 1H), 7.38–7.26 (m, 1H), 7.23–7.11 (m, 2H), 7.12–7.00 (m, 1H), 6.05 (q, *J* = 6.6 Hz, 1H), 3.14 (d, *J* = 17.4 Hz, 1H), 3.03 (d, *J* = 17.4 Hz, 1H), 2.81 (q, *J* = 4.4 Hz, 2H), 2.04–1.81 (m, 4H), 1.64 (dd, *J* = 6.7, 5.1 Hz, 3H).

^{13}C NMR (126 MHz, CD_3OD) δ 163.8, 149.5, 148.3, 141.9, 139.7, 137.7, 136.5, 136.1, 129.9, 128.4, 127.9, 127.6, 125.3, 71.7, 70.1, 47.7, 37.0, 30.2, 22.4, 21.0.

HRMS (ESI+), *m/z*: calculated for $C_{20}H_{21}N_3O_2$ $[M + H]^+$: 336.1707, found: 336.1726.

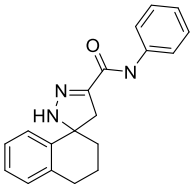


(Pyridin-3-yl-l2-azanyl)(2',3,4,4'-tetrahydro-2*H*-spiro[naphthalene-1,3'-pyrazol]-5'-yl)methanone (67d): Prepared according to the general procedure A, the title compound was prepared from *N*-tosylhydrazone (**1b**) (62.8 mg, 0.2 mmol, 1.0 equiv) and butyl acrylate (**68c**) (44.0 µl, 0.3 mmol, 1.5 equiv). Spiropyrazoline **67d** was obtained after column chromatography (hexane: EtOAc, 3:1) as a colourless oil (52.0 mg, 0.17 mmol, 85%).

^{1}H NMR (500 MHz, CD_3OD) δ 8.86 (d, *J* = 2.5 Hz, 1H), 8.32–8.11 (m, 2H), 7.47–7.32 (m, 2H), 7.22–7.00 (m, 3H), 3.19 (d, *J* = 17.4 Hz, 1H), 3.08 (d, *J* = 17.3 Hz, 1H), 2.81 (d, *J* = 5.4 Hz, 2H), 2.11–1.81 (m, 4H).

^{13}C NMR (126 MHz, CD_3OD) δ 164.0, 144.8, 142.2, 142.1, 140.9, 137.7, 137.4, 130.0, 129.1, 128.4, 127.9, 127.6, 125.2, 70.1, 47.4, 37.0, 30.3, 21.1.

HRMS (ESI+), *m/z*: calculated for $C_{18}H_{17}N_4O_2$ $[M + H]^+$: 306.1475, found: 306.1454.

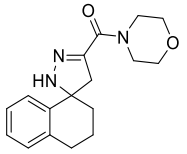


(Phenyl-l2-azanyl)(2',3,4,4'-tetrahydro-2*H*-spiro[naphthalene-1,3'-pyrazol]-5'-yl)methanone (68d): Prepared according to the general procedure A, the title compound was prepared from *N*-tosylhydrazone (**1b**) (62.8 mg, 0.2 mmol, 1.0 equiv) and butyl acrylate (**69c**) (44.0 mg, 0.3 mmol, 1.5 equiv). Spiropyrazoline **68d** was obtained after column chromatography (hexane: EtOAc, 3:1) as a colourless oil (31.7 mg, 0.104 mmol, 52%).

^{1}H NMR (500 MHz, CD_3OD) δ 7.68–7.59 (m, 2H), 7.40 (dd, *J* = 7.5, 1.8 Hz, 1H), 7.31 (dd, *J* = 8.6, 7.4 Hz, 2H), 7.17–7.05 (m, 4H), 3.18 (d, *J* = 17.4 Hz, 1H), 3.07 (d, *J* = 17.4 Hz, 1H), 2.88–2.78 (m, 2H), 2.07–1.84 (m, 4H).

^{13}C NMR (126 MHz, CD_3OD) δ 161.6, 140.3, 140.0, 137.7, 135.8, 128.0, 127.9, 126.4, 126.0, 125.7, 123.2, 119.5, 68.0, 45.7, 35.1, 28.4, 19.2.

HRMS (ESI+), *m/z*: calculated for $C_{19}H_{18}N_3O_2$ $[M + H]^+$: 305.1523, found: 305.1550.

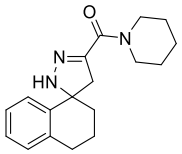


Morpholino(2',3,4,4'-tetrahydro-2*H*-spiro[naphthalene-1,3'-pyrazol]-5'-yl)methanone (69d): Prepared according to the general procedure A, the title compound was prepared from *N*-tosylhydrazone (**1b**) (62.8 mg, 0.2 mmol, 1.0 equiv) and butyl acrylate (**70c**) (39.0 µl, 0.3 mmol, 1.5 equiv). Spiropyrazoline **69d** was obtained after column chromatography (hexane: EtOAc, 3:1) as a colourless oil (49.0 mg, 0.164 mmol, 82%).

^{1}H NMR (500 MHz, CD_3OD) δ 7.39 (dd, *J* = 7.4, 2.0 Hz, 1H), 7.20–7.09 (m, 2H), 7.10–7.01 (m, 1H), 4.28–3.92 (m, 2H), 3.71 (t, *J* = 4.6 Hz, 6H), 3.15 (d, *J* = 17.4 Hz, 1H), 3.09 (d, *J* = 17.3 Hz, 1H), 2.86-2.75 (m, 2H), 2.03–1.83 (m, 4H).

^{13}C NMR (126 MHz, CD_3OD) δ 164.6, 142.6, 142.2, 137.9, 129.9, 128.2, 127.8, 127.5, 68.1, 67.9, 50.2, 36.8, 30.8, 30.4, 21.2.

HRMS (ESI+), *m/z*: calculated for $C_{17}H_{21}N_3O_2$ $[M + H]^+$: 300.1707, found: 300.1739.

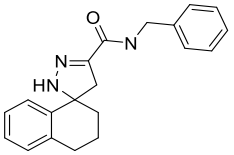


Piperidin-1-yl(2',3,4,4'-tetrahydro-2*H*-spiro[naphthalene-1,3'-pyrazol]-5'-yl)methanone (70d): Prepared according to the general procedure A, the title compound was prepared from *N*-tosylhydrazone (**1b**) (62.8 mg, 0.2 mmol, 1.0 equiv) and butyl acrylate (**71c**) (42.0 mg, 0.3 mmol, 1.5 equiv). Spiropyrazoline **70d** was obtained after column chromatography (hexane: EtOAc, 3:1) as a colourless oil (45.2 mg, 0.152 mmol, 76%).

^{1}H NMR (500 MHz, CD_3OD) δ 7.42 (dd, *J* = 7.4, 1.8 Hz, 1H), 7.19–7.02 (m, 3H), 3.93 (s, 2H), 3.63 (s, 2H), 3.17–3.03 (m, 2H), 2.80 (dd, *J* = 5.8, 3.2 Hz, 2H), 2.04–1.80 (m, 4H), 1.74–1.58 (m, 6H).

^{13}C NMR (126 MHz, CD_3OD) δ 162.8, 141.7, 140.4, 136.0, 128.0, 126.3, 125.9, 125.6, 66.0, 48.6, 46.1, 34.9, 28.5, 23.8, 19.4, 7.4.

HRMS (ESI+), *m/z*: calculated for $C_{18}H_{23}N_3O$ $[M + H]^+$: 298.1914, found: 298.1926.

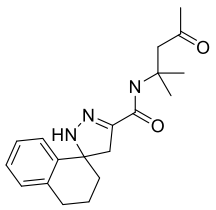


(Benzyl-l2-azanyl)(2',3,4,4'-tetrahydro-2*H*-spiro[naphthalene-1,3'-pyrazol]-5'-yl)methanone (71d): Prepared according to the general procedure A, the title compound was prepared from *N*-tosylhydrazone (**1b**) (62.8 mg, 0.2 mmol, 1.0 equiv) and butyl acrylate (**72c**) (48.3 mg, 0.3 mmol, 1.5 equiv). Spiropyrazoline **71d** was obtained after column chromatography (hexane: EtOAc, 3:1) as a colourless oil (39.6 mg, 0.124 mmol, 62%).

^{1}H NMR (500 MHz, CD_3OD) δ 7.37 (dd, *J* = 7.3, 2.0 Hz, 1H), 7.32 (d, *J* = 5.2 Hz, 4H), 7.24 (dt, *J* = 5.1, 2.8 Hz, 1H), 7.18–7.10 (m, 2H), 7.10–7.03 (m, 1H), 4.47 (d, *J* = 1.0 Hz, 2H), 3.13 (d, *J* = 17.5 Hz, 1H), 3.02 (d, *J* = 17.5 Hz, 1H), 2.80 (t, *J* = 4.7 Hz, 2H), 2.03–1.82 (m, 4H).

^{13}C NMR (126 MHz, CD_3OD) δ 165.4, 142.2, 142.1, 140.3, 137.7, 129.9, 129.5, 128.5, 128.2, 128.2, 127.9, 127.5, 69.6, 47.9, 43.8, 37.0, 30.3, 21.1.

HRMS (ESI+), *m/z*: calculated for $C_{20}H_{20}N_3O$ $[M + H]^+$: 319.1679, found: 319.1690.

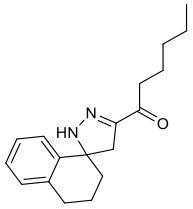


4-methyl-4-((2',3,4,4'-tetrahydro-2*H*-spiro[naphthalene-1,3'-pyrazole]-5'-carbonyl)-l2-azanyl)pentan-2-one (72d): Prepared according to the general procedure A, the title compound was prepared from *N*-tosylhydrazone (**1b**) (62.8 mg, 0.2 mmol, 1.0 equiv) and butyl acrylate (**73c**) (50.8 mg, 0.3 mmol, 1.5 equiv). Spiropyrazoline **72d** was obtained after column chromatography (hexane: EtOAc, 3:1) as a colourless oil (29.4 mg, 0.09 mmol, 45%).

^{1}H NMR (500 MHz, CD_3OD) δ 7.42–7.29 (m, 1H), 7.21–7.00 (m, 3H), 3.06 (d, *J* = 17.5 Hz, 1H), 3.03 (s, 2H), 2.95 (d, *J* = 17.5 Hz, 1H), 2.79 (t, *J* = 4.8 Hz, 2H), 2.13 (s, 3H), 2.00–1.79 (m, 4H), 1.44 (s, 6H).

^{13}C NMR (126 MHz, CD_3OD) δ 210.1, 164.8, 142.9, 142.2, 137.7, 129.9, 128.2, 127.9, 127.5, 69.7, 53.3, 52.2, 47.6, 36.9, 31.7, 30.3, 27.6, 21.1.

HRMS (ESI+), *m/z*: calculated for $C_{19}H_{24}N_3O_2$ $[M + H]^+$: 327.1941, found: 327.1968.

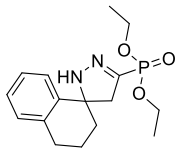


1-(2',3,4,4'-tetrahydro-2*H*-spiro[naphthalene-1,3'-pyrazol]-5'-yl)hexan-1-one (73d): Prepared according to the general procedure A, the title compound was prepared from *N*-tosylhydrazone (**1b**) (62.8 mg, 0.2 mmol, 1.0 equiv) and butyl acrylate (**74c**) (46.0 µl, 0.3 mmol, 1.5 equiv). Spiropyrazoline **73d** was obtained after column chromatography (hexane: EtOAc, 3:1) as a colourless oil (30.1 mg, 0.106 mmol, 53%).

^{1}H NMR (500 MHz, CD_3OD) δ 7.26–7.18 (m, 1H), 7.18–7.11 (m, 2H), 7.11–7.02 (m, 1H), 3.04 (d, *J* = 17.2 Hz, 1H), 2.93 (d, *J* = 17.1 Hz, 1H), 2.81 (dd, *J* = 7.6, 3.3 Hz, 4H), 2.01–1.83 (m, 4H), 1.65 (p, *J* = 7.4 Hz, 2H), 1.35 (ddd, *J* = 9.0, 7.2, 4.9 Hz, 4H), 0.92 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (126 MHz, CD_3OD) δ 199.3, 145.0, 141.9, 137.6, 130.0, 128.4, 127.8, 127.7, 70.4, 46.2, 38.2, 37.2, 32.8, 30.2, 26.3, 23.6, 21.0, 14.4.

HRMS (ESI+), *m/z*: calculated for $C_{18}H_{24}N_2O_2$ $[M + H]^+$: 285.1968, found: 285.1961.

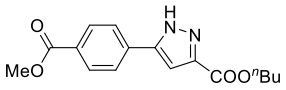


Diethyl (2',3,4,4'-tetrahydro-2*H*-spiro[naphthalene-1,3'-pyrazol]-5'-yl)phosphonate (74d): Prepared according to the general procedure A , the title compound was prepared from *N*-tosylhydrazone (**1b**) (62.8 mg, 0.2 mmol, 1.0 equiv) and butyl acrylate (**75c**) (48.0 µl, 0.3 mmol, 1.5 equiv). Spiropyrazoline **74d** was obtained after column chromatography (hexane: EtOAc, 3:1) as a colourless oil (49.6 mg, 0.154 mmol, 77%).

^{1}H NMR (500 MHz, CD_3OD) δ 7.35–7.31 (m, 1H), 7.23–7.01 (m, 3H), 4.17 (ddd, *J* = 8.1, 7.0, 2.3 Hz, 4H), 3.07 (dd, *J* = 17.1, 1.3 Hz, 1H), 2.97 (dd, *J* = 17.2, 1.4 Hz, 1H), 2.80 (p, *J* = 4.3 Hz, 2H), 2.04–1.79 (m, 4H), 1.35 (td, *J* = 7.1, 3.1 Hz, 6H).

^{13}C NMR (126 MHz, CD_3OD) δ 141.9, 137.8, 131.3, 130.0, 129.4, 128.4, 127.7, 127.5, 69.0, 64.2, 50.6, 36.6, 30.3, 21.2, 16.7.

HRMS (ESI+), *m/z*: calculated for $C_{16}H_{23}N_2O_3P$ $[M + H]^+$: 323.1519, found: 323.1565.

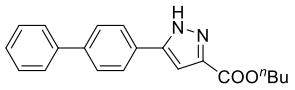


Butyl 5-(4-(methoxycarbonyl)phenyl)-1*H*-pyrazole-3-carboxylate (77d): Prepared according to the general procedure B, the title compound was prepared from *N*-tosylhydrazone (**77b**) (66.4 mg, 0.2 mmol, 1.0 equiv) and butyl acrylate (**1c**) (44.0 µl, 0.3 mmol, 1.5 equiv). Pyrazole **77d** was obtained after column chromatography (hexane: EtOAc, 3:1) as a colourless oil (39.3 mg, 0.13 mmol, 65%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.13–8.09 (m, 2H), 7.88 (d, *J* = 8.5 Hz, 2H), 7.19 (s, 1H), 4.37 (t, *J* = 6.7 Hz, 2H), 3.94 (s, 4H), 1.77 (dt, *J* = 14.5, 6.7 Hz, 2H), 1.48 (dq, *J* = 14.8, 7.4 Hz, 2H), 0.99 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 168.2, 161.2, 137.4, 131.6, 131.6, 131.3, 127.0, 121.4, 107.7, 66.9, 53.6, 32.1, 20.6, 15.1.

HRMS (ESI+), *m/z*: calculated for $C_{16}H_{18}N_2O_4$ $[M + H]^+$: 303.1339, found: 303.1355.

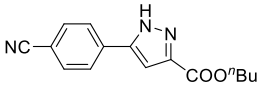


Butyl 5-([1,1'-biphenyl]-4-yl)-1*H*-pyrazole-3-carboxylate (78d): Prepared according to the general procedure B, the title compound was prepared from *N*-tosylhydrazone (**78b**) (64.0 mg, 0.2 mmol, 1.0 equiv) and butyl acrylate (**1c**) (44.0 µl, 0.3 mmol, 1.5 equiv). Pyrazole **78d** was obtained after column chromatography (hexane: EtOAc, 3:1) as a white solid (25.6 mg, 0.08 mmol, 40%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.1 Hz, 2H), 7.69–7.61 (m, 4H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.40–7.35 (m, 1H), 7.14 (s, 1H), 4.35 (t, *J* = 6.7 Hz, 2H), 1.75 (p, *J* = 6.9 Hz, 2H), 1.55–1.38 (m, 2H), 0.97 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 161.9, 142.8, 141.9, 130.3, 130.2, 129.0, 128.9, 128.8, 128.4, 127.5, 107.0, 66.7, 32.1, 20.6, 15.2.

HRMS (ESI+), *m/z*: calculated for $C_{20}H_{20}N_2O_2$ [M + H]$^+$: 321.1598, found: 321.1615.

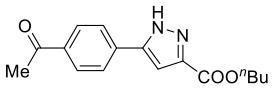


Butyl 5-(4-cyanophenyl)-1*H*-pyrazole-3-carboxylate (79d): Prepared according to the general procedure B, the title compound was prepared from *N*-tosylhydrazone (**79b**) (60.0 mg, 0.2 mmol, 1.0 equiv) and butyl acrylate (**1c**) (44.0 µl, 0.3 mmol, 1.5 equiv). Pyrazole **79d** was obtained after column chromatography (hexane: EtOAc, 3:1) as a white solid (28.0 mg, 0.104 mmol, 52%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99–7.91 (m, 2H), 7.76–7.67 (m, 2H), 7.19 (s, 1H), 4.38 (t, *J* = 6.6 Hz, 2H), 1.77 (dt, *J* = 14.6, 6.8 Hz, 2H), 1.48 (h, *J* = 7.4 Hz, 2H), 0.99 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 161.0, 137.8, 134.1, 127.6, 120.2, 113.2, 107.8, 67.1, 32.0, 20.6, 15.1.

HRMS (ESI+), *m/z*: calculated for $C_{15}H_{15}N_3O_2$ [M + H]$^+$: 270.1237, found: 270.1254.

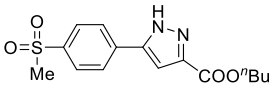


Butyl 5-(4-acetylphenyl)-1*H*-pyrazole-3-carboxylate (80d): Prepared according to the general procedure B, the title compound was prepared from *N*-tosylhydrazone (**80b**) (57.2 mg, 0.2 mmol, 1.0 equiv) and butyl acrylate (**1c**) (44.0 µl, 0.3 mmol, 1.5 equiv). Pyrazole **80d** was obtained after column chromatography (hexane: EtOAc, 3:1) as a colourless oil (21.7 mg, 0.76 mmol, 38%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05–8.00 (m, 2H), 7.95–7.89 (m, 2H), 7.19 (s, 1H), 4.37 (t, *J* = 6.7 Hz, 2H), 2.64 (d, *J* = 1.0 Hz, 3H), 1.77 (p, *J* = 6.8 Hz, 2H), 1.48 (h, *J* = 7.4 Hz, 2H), 0.99 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 199.0, 174.1, 161.3, 138.2, 137.4, 130.4, 127.2, 121.4, 107.7, 66.9, 32.1, 28.1, 20.6, 15.1.

HRMS (ESI+), *m/z*: calculated for $C_{16}H_{18}N_2O_3$ $[M + H]^+$: 287.1390, found: 287.1437.

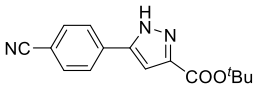


Butyl 5-(4-(methylsulfonyl)phenyl)-1*H*-pyrazole-3-carboxylate (81d): Prepared according to the general procedure B, the title compound was prepared from *N*-tosylhydrazone (**81b**) (70.4 mg, 0.2 mmol, 1.0 equiv) and butyl acrylate (**1c**) (44.0 µl, 0.3 mmol, 1.5 equiv). Pyrazole **81d** was obtained after column chromatography (hexane: EtOAc, 3:1) as a white solid (30.2 mg, 0.094 mmol, 47%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01 (q, *J* = 8.6 Hz, 4H), 7.20 (s, 1H), 4.37 (t, *J* = 6.7 Hz, 2H), 3.09 (s, 3H), 1.84–1.71 (m, 3H), 1.49 (dt, *J* = 15.1, 7.4 Hz, 3H), 0.99 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 160.4, 141.3, 141.0, 129.4, 127.8, 121.4, 118.6, 107.8, 66.9, 46.0, 32.1, 20.6, 15.1.

HRMS (ESI+), *m/z*: calculated for $C_{15}H_{18}N_2O_4S$ $[M + Na]^+$: 345.0879, found: 345.0870.

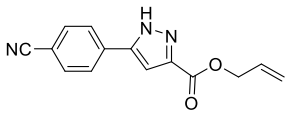


Tert-butyl 5-(4-cyanophenyl)-1*H*-pyrazole-3-carboxylate (82d): Prepared according to the general procedure B, the title compound was prepared from *N*-tosylhydrazone (**79b**) (60.0 mg, 0.2 mmol, 1.0 equiv) and butyl acrylate (**58c**) (44.0 µl, 0.3 mmol, 1.5 equiv). Pyrazole **82d** was obtained after column chromatography (hexane: EtOAc, 3:1) as a colourless oil (27.5 mg, 0.102 mmol, 51%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.5 Hz, 2H), 7.72 (d, *J* = 8.4 Hz, 2H), 7.12 (s, 1H), 1.63 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 160.1, 134.1, 134.1, 130.7, 127.6, 121.4, 120.3, 113.0, 107.6, 84.7, 29.6.

HRMS (ESI+), *m/z*: calculated for $C_{15}H_{15}N_3O_2$ $[M + H]^+$: 270.1237, found: 270.1254.

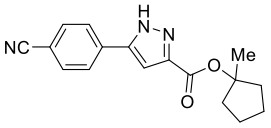


Allyl 5-(4-cyanophenyl)-1*H*-pyrazole-3-carboxylate (83d): Prepared according to the general procedure B, the title compound was prepared from *N*-tosylhydrazone (**79b**) (60.0 mg, 0.2 mmol, 1.0 equiv) and butyl acrylate (**60c**) (44.0 µl, 0.3 mmol, 1.5 equiv). Pyrazole **83d** was obtained after column chromatography (hexane: EtOAc, 3:1) as a colourless oil (16.7 mg, 0.66 mmol, 33%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.4 Hz, 2H), 7.73 (d, *J* = 8.4 Hz, 2H), 7.22 (s, 1H), 6.10–5.99 (m, 1H), 5.49–5.32 (m, 2H), 4.87 (d, *J* = 5.9 Hz, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 160.4, 137.7, 134.1, 133.7, 132.7, 131.2, 127.6, 121.0, 120.2, 113.3, 108.0, 67.6.

HRMS (ESI+), *m/z*: calculated for $C_{14}H_{11}N_3O_2$ $[M + H]^+$: 254.092 4, found: 254.0950.

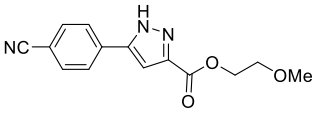


1-methylcyclopentyl 5-(4-cyanophenyl)-1*H*-pyrazole-3-carboxylate (84d): Prepared according to the general procedure B, the title compound was prepared from *N*-tosylhydrazone (**79b**) (60.0 mg, 0.2 mmol, 1.0 equiv) and butyl acrylate (**61c**) (44.0 µl, 0.3 mmol, 1.5 equiv). Pyrazole **84d** was obtained after column chromatography (hexane: EtOAc, 3:1) as a colourless oil (36.0 mg, 0.102 mmol, 61%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.5 Hz, 2H), 7.72 (d, *J* = 8.6 Hz, 2H), 7.12 (s, 1H), 2.35–2.22 (m, 2H), 1.82 (dddd, *J* = 13.5, 11.5, 4.7, 2.7 Hz, 4H), 1.71 (s, 5H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 160.1, 138.1, 134.1, 133.8, 130.7, 127.6, 120.3, 113.1, 107.5, 94.2, 40.7, 25.8, 25.2.

HRMS (ESI+), *m/z*: calculated for $C_{17}H_{17}N_3O_2$ $[M + H]^+$: 296.1394, found: 296.1380.

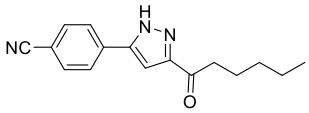


2-methoxyethyl 5-(4-cyanophenyl)-1*H*-pyrazole-3-carboxylate (85d): Prepared according to the general procedure B, the title compound was prepared from *N*-tosylhydrazone (**79b**) (60.0 mg, 0.2 mmol, 1.0 equiv) and butyl acrylate (**62c**) (39.0 µl, 0.3 mmol, 1.5 equiv). Pyrazole **83d** was obtained after column chromatography (hexane: EtOAc, 3:1) as a white solid (24.4 mg, 0.09 mmol, 45%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.4 Hz, 2H), 7.72 (d, *J* = 8.4 Hz, 2H), 7.24 (s, 1H), 4.55–4.50 (m, 2H), 3.77–3.71 (m, 2H), 3.45 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 160.4, 142.7, 137.9, 134.1, 127.6, 121.4, 120.2, 113.2, 108.2, 71.7, 65.7, 60.5.

HRMS (ESI+), *m/z*: calculated for $C_{14}H_{13}N_3O_2$ $[M + H]^+$: 272.1030, found: 272.1055.

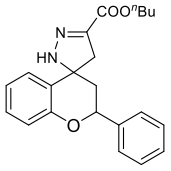


4-(3-hexanoyl-1*H*-pyrazol-5-yl)benzonitrile (86d): Prepared according to the general procedure B, the title compound was prepared from *N*-tosylhydrazone (**79b**) (60.0 mg, 0.2 mmol, 1.0 equiv) and butyl acrylate (**74c**) (46.0 µl, 0.3 mmol, 1.5 equiv). Pyrazole **83d** was obtained after column chromatography (hexane: EtOAc, 3:1) as a white solid (20.8 mg, 0.078 mmol, 39%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.4 Hz, 2H), 7.73 (d, *J* = 8.5 Hz, 2H), 7.14 (s, 1H), 2.92 (t, *J* = 7.5 Hz, 2H), 1.78 (dt, *J* = 11.9, 6.0 Hz, 2H), 1.38 (dd, *J* = 10.4, 4.1 Hz, 4H), 0.98–0.89 (m, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 193.2, 152.0, 137.8, 134.1, 128.7, 127.5, 120.2, 113.3, 106.9, 41.0, 32.8, 25.2, 23.9, 15.4.

HRMS (ESI+), *m/z*: calculated for $C_{16}H_{17}N_3O$ $[M + H]^+$: 268.1444, found: 268.1465.

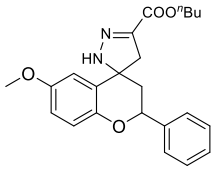


Butyl 2-phenyl-2',4'-dihydrospiro[chromane-4,3'-pyrazole]-5'-carboxylate (87d): Prepared according to the general procedure A, the title compound was prepared from *N*-tosylhydrazone (**88b**) (78.4 mg, 0.2 mmol, 1.0 equiv) and butyl acrylate (**1c**) (44.0 µl, 0.3 mmol, 1.5 equiv). Spiropyrazoline **87d** was obtained after column chromatography (hexane: EtOAc, 3:1) as a yellow oil (51.0 mg, 0.14 mmol, 70%, dr = 1:1).

^{1}H NMR (500 MHz, CD_3OD) δ 7.54–7.29 (m, 6H), 7.20 (m, 1H), 7.04–6.79 (m, 2H), 5.19 (t, *J* = 9.8 Hz, 1H), 4.22 (q, *J* = 6.8 Hz, 2H), 3.45–3.31 (m, 1H), 3.13 (dd, *J* = 56.1, 17.7 Hz, 1H), 2.37–2.09 (m, 2H), 1.69 (m, 2H), 1.44 (qd, *J* = 7.5, 1.9 Hz, 2H), 0.96 (td, *J* = 7.4, 1.7 Hz, 3H).

^{13}C NMR (126 MHz, CD_3OD) δ 164.6, 164.4, 155.5, 155.5, 142.2, 142.1, 139.8, 137.9, 130.6, 130.2, 129.6, 129.6, 129.2, 129.1, 128.2, 128.1, 127.6, 127.2, 127.1, 122.7, 122.3, 118.4, 118.0, 77.0, 76.3, 67.6, 65.8, 65.8, 65.6, 45.6, 45.6, 42.6, 31.9, 20.2, 14.1.

HRMS (ESI+), *m/z*: calculated for $C_{22}H_{24}N_2O_3$ $[M + H]^+$: 365.1860, found: 365.1889.

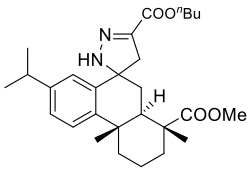


Butyl 6-methoxy-2-phenyl-2',4'-dihydrospiro[chromane-4,3'-pyrazole]-5'-carboxylate (88d): Prepared according to the general procedure A, the title compound was prepared from *N*-tosylhydrazone (**89b**) (78.4mg, 0.2 mmol, 1.0 equiv) and butyl acrylate (**1c**) (44.0 µl, 0.3 mmol, 1.5 equiv). Spiropyrazoline **88d** was obtained after column chromatography (hexane: EtOAc, 3:1) as a yellow oil (56.8 mg, 0.144 mmol, 72%, dr =1:1).

^{1}H NMR (500 MHz, CD_3OD) δ 7.53 – 7.21 (m, 5H), 6.95 – 6.71 (m, 3H), 5.18 – 5.06 (m, 1H), 4.22 (q, *J* = 6.7 Hz, 2H), 3.71 (s, 3H), 3.38-3.28 (m, 1H), 3.19-3.05 (m, 1H), 2.48 – 1.97 (m, 2H), 1.74 – 1.63 (m, 2H), 1.48 – 1.38 (m, 2H), 0.96 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (126 MHz, CD_3OD) δ 164.6, 164.4, 155.7, 155.5, 149.7, 149.6, 142.3, 142.2, 139.8, 138.1, 131.2, 129.6, 129.6, 129.1, 129.0, 127.9, 127.3, 127.2, 127.1, 119.2, 118.8, 117.3, 116.9, 112.1, 112.0, 76.9, 76.3, 67.9, 65.9, 65.8, 56.2, 56.2, 45.8, 45.7, 42.6, 31.9, 20.2, 14.1.

HRMS (ESI+), *m/z*: calculated for $C_{22}H_{26}N_2O_4$ $[M + H]^+$: 395.1965, found: 395.1955.

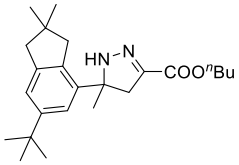


5'-butyl 1-methyl (1R,4aS,10aR)-7-isopropyl-1,4a-dimethyl-2,2',3,4,4a,4',10,10a-octahydro-1*H*-spiro[phenanthrene-9,3'-pyrazole]-1,5'-dicarboxylate (89d): Prepared according to the general procedure A, the title compound was prepared from *N*-tosylhydrazone (**90b**) (99.2mg, 0.2 mmol, 1.0 equiv) and butyl acrylate (**1c**) (44.0 µl, 0.3 mmol, 1.5 equiv). Spiropyrazoline **89d** was obtained after column chromatography (hexane: EtOAc, 3:1) as a colourless oil (30.9 mg, 0.066 mmol, 33%, dr > 20:1).

^{1}H NMR (500 MHz, CD_3OD) δ 7.28–7.15 (m, 2H), 7.14–7.06 (m, 1H), 4.25–4.19 (m, 2H), 3.67 (s, 3H), 3.32 (d, *J* = 1.2 Hz, 1H), 2.85–2.79 (m, 2H), 2.32 (dd, *J* = 41.7, 12.8 Hz, 2H), 2.01–1.79 (m, 4H), 1.70–1.66 (m, 3H), 1.51–1.42 (m, 4H), 1.27 (s, 6H), 1.20–1.17 (m, 6H), 0.97 (dd, *J* = 7.3, 1.4 Hz, 3H).

^{13}C NMR (126 MHz, CD_3OD) δ 179.9, 164.9, 148.1, 147.7, 140.1, 136.9, 127.1, 126.4, 125.5, 121.4, 72.3, 65.6, 52.6, 43.8, 39.2, 38.8, 37.6, 35.1, 34.5, 32.0, 25.7, 24.5, 24.4, 20.2, 19.5, 17.0, 14.1.

HRMS (ESI+), *m/z*: calculated for $C_{28}H_{40}N_2O_4$ $[M + H]^+$: 469.3061, found: 469.3060.

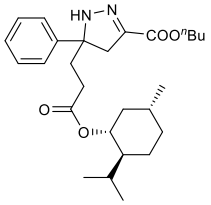


Butyl 5-(6-(tert-butyl)-2,2-dimethyl-2,3-dihydro-1H-inden-4-yl)-5-methyl-4,5-dihydro-1*H*-pyrazole-3-carboxylate (90d): Prepared according to the general procedure A, the title compound was prepared from *N*-tosylhydrazone (**91b**) (82.4 mg, 0.2 mmol, 1.0 equiv) and butyl acrylate (**1c**) (44.0 µl, 0.3 mmol, 1.5 equiv). Pyrazoline **90d** was obtained after column chromatography (hexane: EtOAc, 3:1) as a colourless oil (42.3 mg, 0.11 mmol, 55%).

^{1}H NMR (500 MHz, CD_3OD) δ 7.27 (d, *J* = 1.7 Hz, 1H), 7.12–7.05 (m, 1H), 4.21 (t, *J* = 6.7 Hz, 2H), 3.15 (d, *J* = 16.8 Hz, 1H), 2.97 (d, *J* = 16.7 Hz, 1H), 2.92–2.80 (m, 2H), 1.90 (t, *J* = 7.1 Hz, 3H), 1.72–1.66 (m, 2H), 1.50 (s, 3H), 1.46–1.40 (m, 2H), 1.32 (s, 9H), 1.23 (d, *J* = 2.2 Hz, 6H), 0.96 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (126 MHz, CD_3OD) δ 163.0, 153.1, 149.2, 140.4, 137.9, 135.4, 119.7, 116.8, 69.7, 63.8, 43.3, 42.5, 40.8, 33.8, 30.2, 30.0, 28.8, 27.1, 25.4, 18.3, 12.2.

HRMS (ESI+), *m/z*: calculated for $C_{24}H_{26}N_2O_2$ $[M + H]^+$: 385.2850, found: 385.2810.

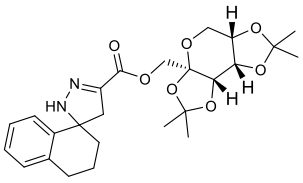


Butyl 5-(3-(((1R,2S,5R)-2-isopropyl-5-methylcyclohexyl)oxy)-3-oxopropyl)-5-phenyl-4,5-dihydro-1*H*-pyrazole-3-carboxylate (91d): Prepared according to the general procedure A, the title compound was prepared from *N*-tosylhydrazone (**92b**) (96.8 mg, 0.2 mmol, 1.0 equiv) and butyl acrylate (**1c**) (44.0 µl, 0.3 mmol, 1.5 equiv). Pyrazoline **91d** was obtained after column chromatography (hexane: EtOAc, 3:1) as a colourless oil (75.8 mg, 0.166 mmol, 83%, dr > 20:1).

^{1}H NMR (500 MHz, CD_3OD) δ 7.43–7.32 (m, 4H), 7.31–7.21 (m, 1H), 4.63 (tdd, *J* = 10.9, 3.4, 1.2 Hz, 1H), 4.18 (t, *J* = 6.6 Hz, 2H), 3.20 (dd, *J* = 17.2, 1.3 Hz, 1H), 3.02 (d, *J* = 17.2 Hz, 1H), 2.33–2.07 (m, 4H), 1.92–1.76 (m, 2H), 1.66 (dq, *J* = 9.3, 6.4 Hz, 4H), 1.47–1.32 (m, 4H), 1.06 (qd, *J* = 13.4, 12.8, 3.7 Hz, 1H), 0.97–0.87 (m, 11H), 0.72 (dd, *J* = 6.9, 3.6 Hz, 3H).

^{13}C NMR (126 MHz, CD_3OD) δ 174.4, 174.4, 164.5, 145.8, 145.8, 139.8, 139.8, 129.8, 128.3, 126.5, 75.6, 75.6, 74.0, 74.0, 65.7, 44.8, 44.6, 42.0, 37.2, 37.2, 35.4, 32.7, 31.9, 30.8, 27.5, 27.5, 24.6, 22.5, 21.1, 20.2, 16.8, 14.1.

HRMS (ESI+), *m/z*: calculated for $C_{27}H_{40}N_2O_4$ $[M + H]^+$: 457.3061, found: 457.3086.

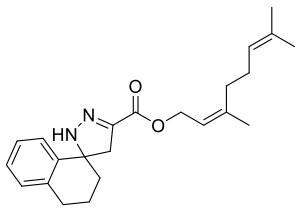


(2,2,7,7-tetramethyltetrahydro-3aH-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran-3a-yl)methyl 2',3,4,4'-tetrahydro-2*H*-spiro[naphthalene-1,3'-pyrazole]-5'-carboxylate (92d): Prepared according to the general procedure A, the title compound was prepared from *N*-tosylhydrazone (**1b**) (62.8 mg, 0.2 mmol, 1.0 equiv) and butyl acrylate (**93c**) (94.0 µl, 0.3 mmol, 1.5 equiv). Spiropyrazoline **92d** was obtained after column chromatography (hexane: EtOAc, 3:1) as a colourless oil (58.6 mg, 0.124 mmol, 62%, dr =3:1).

^{1}H NMR (500 MHz, CD_3OD) δ 7.88 (d, *J* = 8.4 Hz, 1H), 7.37–7.21 (m, 1H), 7.16–7.11 (m, 2H), 4.65 (dd, *J* = 7.9, 2.7 Hz, 1H), 4.57 (dd, *J* = 11.7, 4.3 Hz, 1H), 4.46–4.34 (m, 1H), 4.27–4.04 (m, 1H), 3.96–3.89 (m, 1H), 3.73–3.50 (m, 2H), 3.14 (dd, *J* = 17.3, 1.2 Hz, 1H), 3.03 (dd, *J* = 17.2, 3.8 Hz, 1H), 2.80–2.53 (m, 2H), 1.99–1.78 (m, 4H), 1.50 (d, *J* = 4.2 Hz, 3H), 1.43 (d, *J* = 4.7 Hz, 3H), 1.42–1.36 (m, 3H), 1.33 (d, *J* = 3.5 Hz, 3H).

^{13}C NMR (126 MHz, CD_3OD) δ 173.0, 164.1, 164.0, 154.6, 145.2, 141.8, 141.3, 137.7, 137.7, 137.6, 136.2, 136.1, 133.1, 130.5, 130.5, 130.0, 130.0, 129.5, 129.2, 128.4, 127.9, 127.9, 127.6, 127.6, 127.3, 125.8, 110.2, 110.2, 110.1, 109.7, 104.6, 102.9, 102.9, 72.5, 72.3, 71.7, 71.6, 71.4, 71.3, 70.1, 65.4, 64.8, 62.4, 62.2, 61.6, 47.9, 47.9, 37.0, 37.0, 30.4, 30.2, 30.2, 27.1, 26.9, 26.8, 26.8, 26.3, 26.2, 25.9, 25.9, 24.3, 24.3, 22.9, 21.6, 21.0, 20.9, 14.5.

HRMS (ESI+), *m/z*: calculated for $C_{25}H_{32}N_2O_7$ $[M + H]^+$: 473.2282, found: 473.2312.

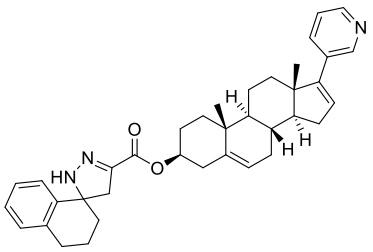


(Z)-3,7-dimethylocta-2,6-dien-1-yl 2',3,4,4'-tetrahydro-2*H*-spiro[naphthalene-1,3'-pyrazole]-5'-carboxylate (93d): Prepared according to the general procedure A, the title compound was prepared from *N*-tosylhydrazone (**1b**) (62.8 mg, 0.2 mmol, 1.0 equiv) and butyl acrylate (**94c**) (65.0 µl, 0.3 mmol, 1.5 equiv). Spiropyrazoline **93d** was obtained after column chromatography (hexane: EtOAc, 3:1) as a colourless oil (57.1 mg, 0.156 mmol, 78%).

^{1}H NMR (500 MHz, CD_3OD) δ 7.36–7.26 (m, 1H), 7.19–7.01 (m, 3H), 5.42 (td, *J* = 7.3, 1.6 Hz, 1H), 5.12 (ddt, *J* = 6.9, 5.4, 1.5 Hz, 1H), 4.69 (dd, *J* = 7.3, 1.1 Hz, 2H), 3.10 (d, *J* = 17.5 Hz, 1H), 2.99 (d, *J* = 17.4 Hz, 1H), 2.79 (p, *J* = 4.0, 3.3 Hz, 2H), 2.23–2.08 (m, 4H), 2.02–1.81 (m, 4H), 1.77 (d, *J* = 1.3 Hz, 3H), 1.63 (dd, *J* = 30.3, 1.3 Hz, 6H).

^{13}C NMR (126 MHz, CD_3OD) δ 164.7, 143.9, 141.9, 137.6, 137.2, 133.0, 130.0, 128.4, 127.9, 127.6, 124.9, 120.5, 70.0, 62.3, 48.0, 37.0, 33.1, 30.3, 27.7, 26.0, 23.8, 21.0, 17.9.

HRMS (ESI+), *m/z*: calculated for $C_{23}H_{30}N_2O_2$ $[M + H]^+$: 367.2380, found: 367.2373.

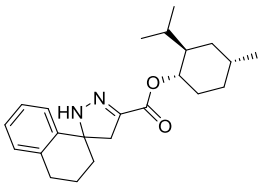


(3S,8R,9S,10R,13S,14S)-10,13-dimethyl-17-(pyridin-3-yl)-2,3,4,7,8,9,10,11,12,13,14,15-dodecahydro-1*H*-cyclopenta[a]phenanthren-3-yl 2',3,4,4'-tetrahydro-2*H*-spiro[naphthalene-1,3'-pyrazole]-5'-carboxylate (94d): Prepared according to the general procedure A, the title compound was prepared from *N*-tosylhydrazone (**1b**) (62.8 mg, 0.2 mmol, 1.0 equiv) and butyl acrylate (**95c**) (120.9 mg, 0.3 mmol, 1.5 equiv). Spiropyrazoline **94d** was obtained after column chromatography (hexane: EtOAc, 3:1) as a white solid (50.5 mg, 0.09 mmol, 45%, dr > 20:1).

^{1}H NMR (500 MHz, CD_3OD) δ 8.53 (s, 1H), 8.38 (s, 1H), 7.84 (dd, *J* = 7.9, 2.0 Hz, 1H), 7.46–7.28 (m, 2H), 7.22–7.01 (m, 3H), 6.09 (q, *J* = 1.8 Hz, 1H), 5.46 (s, 1H), 4.76–4.64 (m, 1H), 3.12 (dd, *J* = 17.5, 2.0 Hz, 1H), 3.01 (d, *J* = 17.4 Hz, 1H), 2.80 (d, *J* = 4.5 Hz, 2H), 2.42 (t, *J* = 6.6 Hz, 2H), 2.15–1.64 (m, 16H), 1.62 – 1.46 (m, 2H), 1.11 (dd, *J* = 20.5, 2.6 Hz, 7H).

^{13}C NMR (126 MHz, CD_3OD) δ 164.2, 152.7, 148.1, 148.0, 142.0, 141.4, 137.7, 137.4, 136.0, 135.0, 131.0, 130.0, 128.4, 127.9, 127.6, 125.0, 123.5, 75.8, 70.0, 59.0, 51.9, 47.9, 39.3, 38.2, 38.0, 37.0, 36.5, 32.8, 32.7, 31.8, 30.3, 28.9, 22.0, 21.0, 19.8, 17.0.

HRMS (ESI+), *m/z*: calculated for $C_{37}H_{43}N_3O_2$ $[M + H]^+$: 562.3428, found: 562.3416.

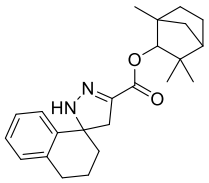


(1S,2R,4R)-2-isopropyl-4-methylcyclohexyl 2',3,4,4'-tetrahydro-2*H*-spiro[naphthalene-1,3'-pyrazole]-5'-carboxylate (95d): Prepared according to the general procedure A, the title compound was prepared from *N*-tosylhydrazone (**1b**) (62.8 mg, 0.2 mmol, 1.0 equiv) and butyl acrylate (**96c**) (65.0 µl,, 0.3 mmol, 1.5 equiv). Spiropyrazoline **95d** was obtained after column chromatography (hexane: EtOAc, 3:1) as a white solid (61.1 mg, 0.166 mmol, 83%, dr = 2:1).

^{1}H NMR (500 MHz, CD_3OD) δ 7.36–7.25 (m, 1H), 7.22–7.02 (m, 3H), 4.84–4.78 (m, 1H), 3.10 (dd, *J* = 17.4, 12.0 Hz, 1H), 3.00 (dd, *J* = 17.4, 9.3 Hz, 1H), 2.80 (q, *J* = 5.3, 4.7 Hz, 2H), 2.04–1.83 (m, 6H), 1.72 (dt, *J* = 12.7, 2.9 Hz, 2H), 1.53–1.45 (m, 2H), 1.16–1.05 (m, 2H), 0.95–0.89 (m, 7H), 0.80 (dd, *J* = 9.8, 6.9 Hz, 3H).

^{13}C NMR (126 MHz, CD_3OD) δ 162.6, 162.6, 140.0, 135.8, 135.5, 128.1, 126.5, 126.0, 125.8, 74.0, 68.1, 46.1, 40.3, 35.1, 33.5, 30.9, 28.4, 25.8, 22.9, 20.6, 19.2, 19.1, 15.1.

HRMS (ESI+), *m/z*: calculated for $C_{23}H_{32}N_2O_2$ $[M + Na]^+$: 391.2356, found: 391.2380.

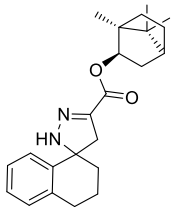


1,3,3-trimethylbicyclo[2.2.1]heptan-2-yl 2',3,4,4'-tetrahydro-2*H*-spiro[naphthalene-1,3'-pyrazole]-5'-carboxylate (96d): Prepared according to the general procedure A, the title compound was prepared from *N*-tosylhydrazone (**1b**) (62.8 mg, 0.2 mmol, 1.0 equiv) and butyl acrylate (**97c**) (65.0 µl,, 0.3 mmol, 1.5 equiv). Spiropyrazoline **96d** was obtained after column chromatography (hexane: EtOAc, 3:1) as a white solid (60.8 mg, 0.166 mmol, 83%, dr = 1:1).

^{1}H NMR (500 MHz, CD_3OD) δ 7.32 (dt, *J* = 6.9, 1.8 Hz, 1H), 7.21–7.00 (m, 3H), 4.48 (dd, *J* = 4.1, 1.9 Hz, 1H), 3.14 (dd, *J* = 17.4, 2.2 Hz, 1H), 3.04 (dd, *J* = 17.4, 2.9 Hz, 1H), 2.81 (d, *J* = 5.2 Hz, 2H), 2.10–1.59 (m, 8H), 1.49 (dddd, *J* = 16.8, 9.7, 7.6, 4.4 Hz, 1H), 1.42–1.17 (m, 2H), 1.15–1.05 (m, 6H), 0.82 (d, *J* = 18.1 Hz, 3H).

^{13}C NMR (126 MHz, CD_3OD) δ 165.3, 142.0, 137.6, 137.2, 123.0, 128.4, 127.8, 127.7, 87.9, 70.0, 49.8, 48.1, 42.3, 40.8, 37.1, 37.0, 30.3, 30.2, 27.6, 26.8, 21.0, 20.7, 19.8.

HRMS (ESI+), *m/z*: calculated for $C_{23}H_{30}N_2O_2$ $[M + H]^+$: 367.2380, found: 367.2368.

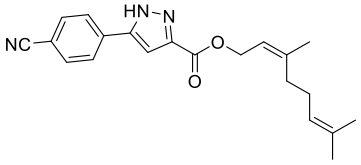


(1S,2R,4R)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl 2',3,4,4'-tetrahydro-2*H*-spiro[naphthalene-1,3'-pyrazole]-5'-carboxylate (97d): Prepared according to the general procedure A, the title compound was prepared from *N*-tosylhydrazone (**1b**) (62.8 mg, 0.2 mmol, 1.0 equiv) and butyl acrylate (**98c**) (65.0 µl,, 0.3 mmol, 1.5 equiv). Spiropyrazoline **97d** was obtained after column chromatography (hexane: EtOAc, 3:1) as a white solid (49.1 mg, 0.134 mmol, 67%, dr = 2:1).

^{1}H NMR (500 MHz, CD_3OD) δ 7.31 (dt, *J* = 6.9, 1.7 Hz, 1H), 7.23–7.01 (m, 3H), 4.84–4.75 (m, 1H), 3.09 (d, *J* = 17.4 Hz, 1H), 2.98 (d, *J* = 17.4 Hz, 1H), 2.80 (s, 2H), 2.05–1.79 (m, 6H), 1.79–1.71 (m, 2H), 1.69–1.54 (m, 1H), 1.24–1.08 (m, 2H), 1.02 (d, *J* = 3.5 Hz, 3H), 0.93–0.84 (m, 6H).

^{13}C NMR (126 MHz, CD_3OD) δ 164.4, 142.0, 137.6, 137.4, 130.0, 128.4, 127.8, 127.6, 82.6, 70.0, 50.0, 48.1, 48.0, 46.5, 39.8, 37.0, 34.7, 30.3, 28.0, 21.0, 20.6, 20.5, 11.9.

HRMS (ESI+), *m/z*: calculated for $C_{23}H_{30}N_2O_2$ $[M + H]^+$: 367.2380, found: 367.2390.

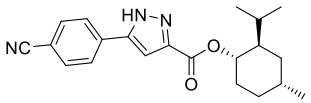


(Z)-3,7-dimethylocta-2,6-dien-1-yl 5-(4-cyanophenyl)-1*H*-pyrazole-3-carboxylate (98d): Prepared according to the general procedure B, the title compound was prepared from *N*-tosylhydrazone (**79b**) (60.0 mg, 0.2 mmol, 1.0 equiv) and butyl acrylate (**94c**) (65.0 µl, 0.3 mmol, 1.5 equiv). Pyrazole **98d** was obtained after column chromatography (hexane: EtOAc, 3:1) as a colourless oil (46.8 mg, 0.134 mmol, 67%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.5 Hz, 2H), 7.72 (d, *J* = 8.4 Hz, 2H), 7.19 (s, 1H), 5.53–5.42 (m, 1H), 5.19–5.06 (m, 1H), 4.86 (dd, *J* = 7.4, 1.0 Hz, 2H), 2.24–2.09 (m, 4H), 1.81 (d, *J* = 1.3 Hz, 3H), 1.68 (d, *J* = 1.5 Hz, 4H), 1.61 (d, *J* = 1.3 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 160.8, 151.9, 145.5, 137.9, 134.1, 133.9, 130.7, 127.6, 124.8, 120.2, 119.7, 113.2, 107.9, 63.7, 33.7, 28.1, 27.1, 25.0, 19.1.

HRMS (ESI+), *m/z*: calculated for $C_{21}H_{23}N_3O_2$ $[M + H]^+$: 350.1863, found: 350.1901.

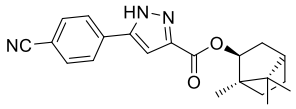


(1S,2R,4R)-2-isopropyl-4-methylcyclohexyl 5-(4-cyanophenyl)-1*H*-pyrazole-3-carboxylate (99d): Prepared according to the general procedure B, the title compound was prepared from *N*-tosylhydrazone (**79b**) (60.0 mg, 0.2 mmol, 1.0 equiv) and butyl acrylate (**96c**) (65.0 µl, 0.3 mmol, 1.5 equiv). Pyrazole **99d** was obtained after column chromatography (hexane: EtOAc, 3:1) as a colourless oil (49.2 mg, 0.14 mmol, 70%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.4 Hz, 2H), 7.73 (d, *J* = 8.5 Hz, 2H), 7.19 (s, 1H), 4.99 (td, *J* = 10.9, 4.5 Hz, 1H), 2.19–2.10 (m, 1H), 1.92 (dd, *J* = 7.0, 2.8 Hz, 1H), 1.80–1.69 (m, 2H), 1.66–1.48 (m, 2H), 1.21–1.08 (m, 2H), 0.94 (dd, *J* = 11.0, 6.8 Hz, 6H), 0.81 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 160.5, 137.9, 134.1, 133.8, 130.7, 127.6, 120.2, 113.1, 107.8, 77.5, 48.6, 42.3, 35.6, 32.9, 28.0, 25.0, 23.4, 22.1, 17.9.

HRMS (ESI+), *m/z*: calculated for $C_{21}H_{25}N_3O_2$ $[M + H]^+$: 352.2020, found: 352.2043.



(1R,2S,4S)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl 5-(4-cyanophenyl)-1*H*-pyrazole-3-carboxylate (100d): Prepared according to the general procedure B, the title compound was prepared from *N*-tosylhydrazone (**79b**) (60.0 mg, 0.2 mmol, 1.0 equiv) and butyl acrylate (**98c**) (65.0 µl, 0.3 mmol, 1.5 equiv). Pyrazole **100d** was obtained after column chromatography (hexane: EtO Ac, 3:1) as a colourless oil (31.4 mg, 0.09 mmol, 45%).

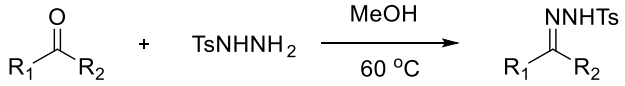
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.5 Hz, 2H), 7.73 (d, *J* = 8.5 Hz, 2H), 7.11 (s, 1H), 4.97 (t, *J* = 5.8 Hz, 1H), 1.99–1.91 (m, 2H), 1.85 (dd, *J* = 4.3, 2.3 Hz, 1H), 1.81–1.63 (m, 2H), 1.12 (s, 5H), 0.93 (d, *J* = 24.6 Hz, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 160.4, 138.0, 134.1, 133.8, 130.7, 127.6, 120.2, 113.2, 107.5, 84.2, 50.6, 48.5, 46.5, 40.1, 35.0, 28.4, 21.5, 21.5, 13.0.

HRMS (ESI+), *m/z*: calculated for $C_{21}H_{23}N_3O_2$ $[M + H]^+$: 350.1863, found: 350.1901.

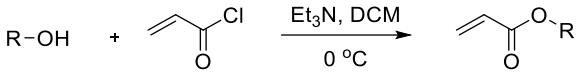
5. Procedures of synthesizing starting material and characterization data

Synthesis of *N*-tosylhydrazones

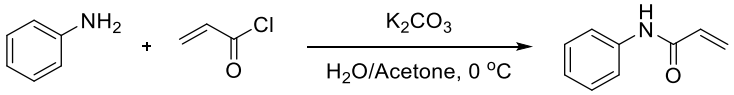


N-tosylhydrazones were prepared according a reported procedure.[2] To a stirred solution of tosylhydrazide (10.0 mmol) in MeOH (10.0 mL) at 60 ℃, ketone (1.0 equiv) was added dropwise (or portionwise if solid). The reaction was completed within 0.5-3 h. After that, the solvent was removed directly under reduced pressure, and the crude mixture was further purified by recrystallization or silica gel chromatography.

Synthesis of alkenes

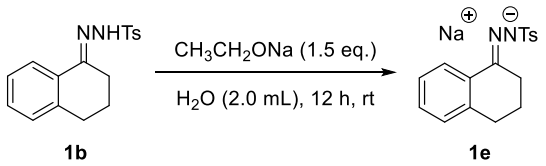


To a stirred suspension of alcohol (6.5 mmol, 1.0 equiv) in dry CH_2Cl_2 (25.0 mL) was added Et_3N (9.8 mmol, 1.5 equiv). Acryloyl chloride (7.8 mmol, 1.2 equiv) was added dropwise to the mixture at 0 ℃ and the mixture was stirred for 12 h at room temperature (the progress can be monitored *via* TLC). After the reaction, the resulting reaction mixture was poured into water and subsequently extracted with dichloromethane for three times. The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo*. Afterwards, products were obtained *via* silica gel chromatography[3-5](hexane: EtOAc, 30:1).



To a stirred suspension of potassium carbonate (2.8 g, 20.0 mmol, 2.0 equiv) in distilled water (5.0 mL) and acetone (20.0 mL) was added acryloyl chloride (1.8 g, 20.0 mmol, 2.0 equiv) at 0 ℃ under the atmosphere of argon. Aniline (0.9 mL, 10.0 mmol, 1.0 equiv) was then added dropwise to the mixture and stirred for 1 h at 0 °C. After filtration, the mixture was concentrated under reduced pressure and extracted three times with dichloromethane[3]. The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo*. The residue was purified by flash chromatography with EtOAc/n–Hexane to give the corresponding product as a white solid in 98% yield.

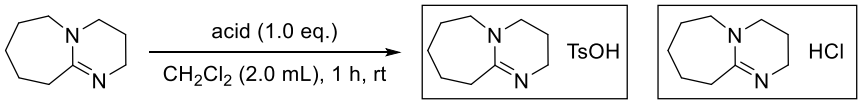
Synthesis of *N*-tosylhydrazone sodium salt



1b **1e**

To a stirred suspension of *N*-tosylhydrazone (1.0 mmol, 1.0 equiv) in H_2O (2.0 mL) was added CH_3CH_2ONa (1.5 mmol, 1.5 equiv). The mixture was stirred for 12 h at room temperature. After the reaction, yield hydrazone salt in quantitative yield. Solid hydrazone salt was then ground using a pestle and mortar to give a free flowing powder[6-7].

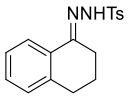
Synthesis of ammonium salts of DBU



101e **101f**

To a stirred suspension of DBU (2.0 mmol, 1.0 equiv) in CH_2Cl_2 (2.0 mL) was added TsOH or HCl (2.0 mmol, 1.0 equiv). The mixture was stirred for 2 h at room temperature. After the reaction, yield DBU salt in quantitative yield.

Characterization data for the *N*-tosylhydrazones

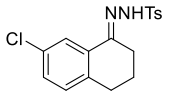


***N'*-(3,4-Dihydronaphthalen-1(2*H*)-ylidene)-4-methylbenzenesulfonohydrazide (1b) :** Prepared according to the synthesis of *N*-tosylhydrazones, the title compound was prepared from tosylhydrazide (10.0 mmol) in MeOH (10.0 mL) , ketone (1.0 equiv), *N*-tosylhydrazones **1b** was obtained as a white solid by recrystallization (isolated yield: 90%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 (d, *J* = 6.6 Hz, 1H), 7.93 (d, *J* = 8.3 Hz, 2H), 7.76 (s, 1H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.26 – 7.17 (m, 2H), 7.09 (d, *J* = 8.0 Hz, 1H), 2.77 – 2.69 (m, 2H), 2.47 (t, *J* = 6.6 Hz, 2H), 2.41 (s, 3H), 1.89 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 143.7, 139.3, 135.0, 131.0, 129.1, 129.1, 127.9, 127.7, 126.0, 124.6, 28.8, 24.9, 21.2, 20.9.

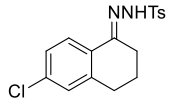
HRMS (ESI+), *m/z*: calculated for $C_{17}H_{18}N_2O_2S$ $[M + H]^+$: 315.1163, found: 315.1188.



***N'*-(7-Chloro-3,4-dihydronaphthalen-1(2*H*)-ylidene)-4-methylbenzenesulfonohydrazide (2b):** Prepared according to the synthesis of *N*-tosylhydrazones, the title compound was prepared from tosylhydrazide (10.0 mmol) in MeOH (10.0 mL) , ketone (1.0 equiv), *N*-tosylhydrazones **2b** was obtained as a white solid by recrystallization (isolated yield: 76%).

^{1}H NMR (500 MHz, DMSO-*d*$_6$) δ 10.58 (s, 1H), 7.79 (d, *J* = 8.3 Hz, 2H), 7.65 (d, *J* = 2.3 Hz, 1H), 7.41 (d, *J* = 8.1 Hz, 2H), 7.29 (dd, *J* = 8.2, 2.3 Hz, 1H), 7.19 (d, *J* = 8.2 Hz, 1H), 2.66 (t, *J* = 6.0 Hz, 2H), 2.57 – 2.45 (m, 5H), 1.80 – 1.64 (m, 2H).

HRMS (ESI+), *m/z*: calculated for $C_{17}H_{17}ClN_2O_2S$ $[M + H]^+$: 349.0772, found: 349.0802.

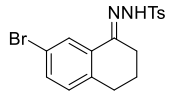


***N'*-(6-Chloro-3,4-dihydronaphthalen-1(2*H*)-ylidene)-4-methylbenzenesulfonohydrazide (3b):** Prepared according to the synthesis of *N*-tosylhydrazones, the title compound was prepared from tosylhydrazide (10.0 mmol) in MeOH (10.0 mL) , ketone (1.0 equiv), *N*-tosylhydrazones **3b** was obtained as a white solid by recrystallization (isolated yield: 85%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 – 7.87 (m, 3H), 7.80 (s, 1H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.15 (dd, *J* = 8.5, 2.2 Hz, 1H), 7.08 (d, *J* = 2.0 Hz, 1H), 2.70 – 2.65 (m, 2H), 2.45 (t, *J* = 6.6 Hz, 2H), 2.42 (s, 3H), 1.87 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 150.9, 143.8, 140.7, 134.9, 129.7, 129.5, 129.2, 127.8, 127.7, 126.4, 126.1, 28.6, 24.7, 21.2, 20.7.

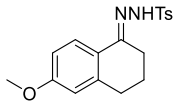
HRMS (ESI+), *m/z*: calculated for $C_{17}H_{17}ClN_2O_2S$ $[M + H]^+$: 349.0772, found: 349.0768.



***N'*-(7-Bromo-3,4-dihydronaphthalen-1(2*H*)-ylidene)-4-methylbenzenesulfonohydrazide (4b):** Prepared according to the synthesis of *N*-tosylhydrazones, the title compound was prepared from tosylhydrazide (10.0 mmol) in MeOH (10.0 mL) , ketone (1.0 equiv), *N*-tosylhydrazones **4b** was obtained as a white solid by recrystallization (isolated yield: 85%).

^{1}H NMR (500 MHz, DMSO-d_6) δ 10.59 (s, 1H), 7.87 – 7.73 (m, 3H), 7.49 – 7.36 (m, 3H), 7.13 (d, *J* = 8.2 Hz, 1H), 2.70 – 2.62 (m, 2H), 2.51 (d, *J* = 6.5 Hz, 2H), 2.36 (s, 3H), 1.73 (m, 2H).

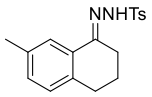
HRMS (ESI+), *m/z*: calculated for $C_{17}H_{17}BrN_2O_2S$ $[M + H]^+$: 393.0267, found: 393.0298.



***N*'-(6-Methoxy-3,4-dihydronaphthalen-1(2*H*)-ylidene)-4-methylbenzenesulfonohydrazide (5b):** Prepared according to the synthesis of *N*-tosylhydrazones, the title compound was prepared from tosylhydrazide (10.0 mmol) in MeOH (10.0 mL) , ketone (1.0 equiv), *N*-tosylhydrazones **5b** was obtained as a white solid by recrystallization (isolated yield: 81%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 (dd, *J* = 8.5, 1.6 Hz, 3H), 7.60 (s, 1H), 7.31 (d, *J* = 8.1 Hz, 2H), 6.75 (dd, *J* = 8.8, 2.7 Hz, 1H), 6.58 (d, *J* = 2.6 Hz, 1H), 3.79 (s, 3H), 2.72 – 2.62 (m, 2H), 2.44 (t, *J* = 6.6 Hz, 2H), 2.41 (s, 3H), 1.93 – 1.79 (m, 2H).

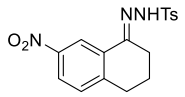
HRMS (ESI+), *m/z*: calculated for $C_{18}H_{20}N_2O_3S$ $[M + H]^+$: 345.1267, found: 345.1288.



4-Methyl-*N*′-(7-methyl-3,4-dihydronaphthalen-1(2*H*)-ylidene)benzenesulfonohydrazide (6b): Prepared according to the synthesis of *N*-tosylhydrazones, the title compound was prepared from tosylhydrazide (10.0 mmol) in MeOH (10.0 mL) , ketone (1.0 equiv), *N*-tosylhydrazones **6b** was obtained as a white solid by recrystallization (isolated yield: 89%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.4 Hz, 2H), 7.79 (d, *J* = 1.8 Hz, 1H), 7.57 (s, 1H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.09 – 6.95 (m, 2H), 2.66 (m, 2H), 2.49 – 2.42 (m, 2H), 2.41 (s, 3H), 2.33 (s, 3H), 1.90 – 1.82 (m, 2H).

HRMS (ESI+), *m/z*: calculated for $C_{18}H_{20}N_2O_2S$ $[M + H]^+$: 329.1318, found: 329.1344.

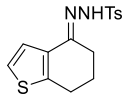


4-Methyl-*N′*-(7-nitro-3,4-dihydronaphthalen-1(2*H*)-ylidene)benzenesulfonohydrazide (7b): Prepared according to the synthesis of *N*-tosylhydrazones, the title compound was prepared from tosylhydrazide (10.0 mmol) in MeOH (10.0 mL) , ketone (1.0 equiv), *N*-tosylhydrazones **7b** was obtained as a white solid by recrystallization (isolated yield: 92%).

^{1}H NMR (500 MHz, DMSO-*d*$_6$) δ 10.75 (s, 1H), 8.49 (d, *J* = 2.5 Hz, 1H), 8.06 (dd, *J* = 8.4, 2.5 Hz, 1H), 7.81 (d, *J* = 8.3 Hz, 2H), 7.43 (dd, *J* = 13.9, 8.3 Hz, 3H), 2.81 (t, *J* = 5.9 Hz, 2H), 2.57 (t, *J* = 6.5 Hz, 2H), 2.36 (s, 3H), 1.78 (m, 2H).

^{13}C NMR (126 MHz, DMSO-*d*$_6$) δ 150.7, 147.2, 146.2, 143.6, 136.0, 132.9, 130.4, 129.5, 127.5, 123.2, 118.7, 28.7, 25.5, 21.0, 20.4.

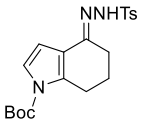
HRMS (ESI+), *m/z*: calculated for $C_{17}H_{17}N_3O_4S$ $[M + H]^+$: 360.1013, found: 321.1043.



***N′*-(6,7-dihydrobenzo[b]thiophen-4(5*H*)-ylidene)-4-methylbenzenesulfonohydrazide (8b):** Prepared according to the synthesis of *N*-tosylhydrazones, the title compound was prepared from tosylhydrazide (10.0 mmol) in MeOH (10.0 mL) , ketone (1.0 equiv), *N*-tosylhydrazones **8b** was obtained as a white solid by recrystallization (isolated yield: 77%).

^{1}H NMR (500 MHz, CDCl$_3$) δ 7.90 (d, *J* = 8.3 Hz, 2H), 7.51 (s, 1H), 7.32 (dd, *J* = 8.3, 6.7 Hz, 3H), 7.01 (d, *J* = 5.3 Hz, 1H), 2.81 (t, *J* = 6.1 Hz, 2H), 2.43 (s, 2H), 2.41 (s, 3H), 2.05 – 1.93 (m, 2H).

HRMS (ESI+), *m/z*: calculated for $C_{15}H_{16}N_2O_2S_2$ $[M + H]^+$: 321.0726, found: 321.0776.

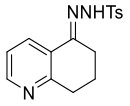


Tert-butyl-4-(2-tosylhydrazono)-4,5,6,7-tetrahydro-1*H*-indole-1-carboxylate (9b): Prepared according to the synthesis of *N*-tosylhydrazones, the title compound was prepared from tosylhydrazide (10.0 mmol) in MeOH (10.0 mL) , ketone (1.0 equiv), *N*-tosylhydrazones **9b** was obtained as a white solid by recrystallization (isolated yield: 80%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.3 Hz, 2H), 7.29 (d, *J* = 8.1 Hz, 2H), 7.10 (d, *J* = 3.5 Hz, 1H), 6.45 (d, *J* = 3.5 Hz, 1H), 2.95 (t, *J* = 6.2 Hz, 2H), 2.40 (s, 3H), 2.37 (t, *J* = 6.5 Hz, 2H), 1.98 – 1.92 (m, 2H), 1.57 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 148.5, 143.5, 134.9, 129.5, 129.0, 127.8, 127.7, 120.7, 120.6, 106.6, 83.8, 27.5, 23.3, 23.2, 21.7, 21.1.

HRMS (ESI+), *m/z*: calculated for $C_{20}H_{25}N_3O_4S$ $[M + H]^+$: 404.1639, found: 404.1598.

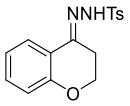


***N'*-(7,8-dihydroquinolin-5(6*H*)-ylidene)-4-methylbenzenesulfonohydrazide (10b):** Prepared according to the synthesis of *N*-tosylhydrazones, the title compound was prepared from tosylhydrazide (10.0 mmol) in MeOH (10.0 mL) , ketone (1.0 equiv), *N*-tosylhydrazones **10b** was obtained as a white solid by recrystallization (isolated yield: 90%).

^{1}H NMR (500 MHz, DMSO-d_6) δ 10.60 (s, 1H), 8.42 (dd, *J* = 4.7, 1.8 Hz, 1H), 8.05 (dd, *J* = 8.0, 1.8 Hz, 1H), 7.81 (d, *J* = 8.3 Hz, 2H), 7.39 (d, *J* = 8.0 Hz, 2H), 7.23 (dd, *J* = 8.0, 4.7 Hz, 1H), 2.82 (t, *J* = 6.1 Hz, 2H), 2.55 (t, *J* = 6.5 Hz, 2H), 2.35 (s, 3H), 1.92 – 1.77 (m, 2H).

^{13}C NMR (126 MHz, DMSO-d_6) δ 158.6, 151.6, 149.7, 143.4, 136.1, 131.7, 129.5, 127.6, 127.3, 122.1, 31.6, 25.4, 21.0, 20.4.

HRMS (ESI+), *m/z*: calculated for $C_{16}H_{17}N_3O_2S$ $[M + H]^+$: 316.1114, found: 316.1136.

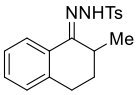


***N′*-(chroman-4-ylidene)-4-methylbenzenesulfonohydrazide (11b):** Prepared according to the synthesis of *N*-tosylhydrazones, the title compound was prepared from tosylhydrazide (10.0 mmol) in MeOH (10.0 mL) , ketone (1.0 equiv), *N*-tosylhydrazones **11b** was obtained as a white solid by recrystallization (isolated yield: 95%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 – 7.84 (m, 3H), 7.33 (d, *J* = 8.1 Hz, 2H), 7.26 – 7.21 (m, 1H), 6.93 (ddd, *J* = 8.2, 7.2, 1.2 Hz, 1H), 6.84 (dd, *J* = 8.2, 1.2 Hz, 1H), 4.21 (t, *J* = 6.2 Hz, 2H), 2.68 (t, *J* = 6.2 Hz, 2H), 2.42 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 156.7, 147.5, 143.9, 134.7, 131.1, 129.2, 127.7, 124.5, 121.1, 119.2, 117.1, 64.0, 24.6, 21.2.

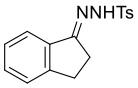
HRMS (ESI+), *m/z*: calculated for $C_{16}H_{16}N_2O_3S$ $[M + H]^+$: 317.0954, found: 317.0988.



4-Methyl-*N*'-(2-methyl-3,4-dihydronaphthalen-1(2*H*)-ylidene)benzenesulfonohydrazide (12b): Prepared according to the synthesis of *N*-tosylhydrazones, the title compound was prepared from tosylhydrazide (10.0 mmol) in MeOH (10.0 mL) , ketone (1.0 equiv), *N*-tosylhydrazones **12b** was obtained as a white solid by recrystallization (isolated yield: 85%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.92 (d, *J* = 8.4 Hz, 2H), 7.86 (s, 1H), 7.37 – 7.28 (m, 2H), 7.26 – 7.06 (m, 3H), 3.09 – 2.86 (m, 2H), 2.73 – 2.60 (m, 1H), 2.41 (s, 3H), 2.01 – 1.88 (m, 1H), 1.84 – 1.74 (m, 1H), 1.08 (d, *J* = 7.2 Hz, 3H).

HRMS (ESI+), *m/z*: calculated for $C_{18}H_{20}N_2O_2S$ $[M + H]^+$: 329.1318, found: 329.1356.

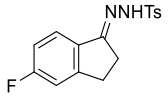


***N'*-(2,3-dihydro-1*H*-inden-1-ylidene)-4-methylbenzenesulfonohydrazide (13b):** Prepared according to the synthesis of *N*-tosylhydrazones, the title compound was prepared from tosylhydrazide (10.0 mmol) in MeOH (10.0 mL) , ketone (1.0 equiv), *N*-tosylhydrazones **13b** was obtained as a white solid by recrystallization (isolated yield: 78%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 (s, 2H), 7.70 (d, *J* = 7.7 Hz, 1H), 7.34 – 7.29 (m, 3H), 7.28 – 7.20 (m, 2H), 3.08 – 2.99 (m, 2H), 2.73 – 2.63 (m, 2H), 2.40 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 161.9, 147.9, 143.6, 136.6, 135.0, 130.4, 129.1, 127.6, 126.5, 124.9, 121.7, 27.9, 26.2, 21.1.

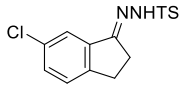
HRMS (ESI+), *m/z*: calculated for $C_{16}H_{16}N_2O_2S$ $[M + H]^+$: 301,1005, found: 301.1045.



***N'*-(5-fluoro-2,3-dihydro-1*H*-inden-1-ylidene)-4-methylbenzenesulfonohydrazide (14b):** Prepared according to the synthesis of *N*-tosylhydrazones, the title compound was prepared from tosylhydrazide (10.0 mmol) in MeOH (10.0 mL) , ketone (1.0 equiv), *N*-tosylhydrazones **14b** was obtained as a white solid by recrystallization (isolated yield: 68%).

^{1}H NMR (500 MHz, DMSO-d_6) δ 10.35 (s, 1H), 7.81 (d, *J* = 8.4 Hz, 2H), 7.50 (dd, *J* = 8.5, 5.4 Hz, 1H), 7.45 – 7.36 (m, 2H), 7.21 (dd, *J* = 9.1, 2.4 Hz, 1H), 7.10 (td, *J* = 8.9, 2.5 Hz, 1H), 3.01 (t, *J* = 6.4 Hz, 2H), 2.81 – 2.69 (m, 2H), 2.37 (s, 3H).

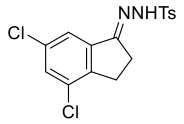
HRMS (ESI+), *m/z*: calculated for $C_{16}H_{15}FN_2O_2S$ $[M + H]^+$: 319.0911, found: 319.0954.



***N'*-(6-chloro-2,3-dihydro-1*H*-inden-1-ylidene)-4-methylbenzenesulfonohydrazide (15b):** Prepared according to the synthesis of *N*-tosylhydrazones, the title compound was prepared from tosylhydrazide (10.0 mmol) in MeOH (10.0 mL) , ketone (1.0 equiv), *N*-tosylhydrazones **15b** was obtained as a white solid by recrystallization (isolated yield: 80%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.3 Hz, 2H), 7.66 (d, *J* = 2.0 Hz, 1H), 7.39 – 7.32 (m, 3H), 7.29 (dd, *J* = 8.1, 2.1 Hz, 1H), 7.20 (d, *J* = 8.2 Hz, 1H), 3.07 – 3.00 (m, 2H), 2.69 – 2.62 (m, 2H), 2.43 (s, 3H).

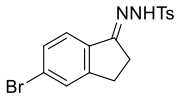
HRMS (ESI+), *m/z*: calculated for $C_{16}H_{15}ClN_2O_2S$ $[M + H]^+$: 335.0616, found: 335.0636.



***N'*-(4,6-dichloro-2,3-dihydro-1*H*-inden-1-ylidene)-4-methylbenzenesulfonohydrazide (16b):** Prepared according to the synthesis of *N*-tosylhydrazones, the title compound was prepared from tosylhydrazide (10.0 mmol) in MeOH (10.0 mL) , ketone (1.0 equiv), *N*-tosylhydrazones **16b** was obtained after column chromatography (hexane: EtO Ac, 2:1) as a white solid (isolated yield: 68%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.1 Hz, 2H), 7.57 (d, *J* = 1.7 Hz, 1H), 7.40 – 7.31 (m, 4H), 3.09 – 2.98 (m, 2H), 2.72 – 2.61 (m, 2H), 2.43 (s, 3H).

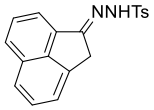
HRMS (ESI+), *m/z*: calculated for $C_{16}H_{14}Cl_2N_2O_2S$ $[M + H]^+$: 369.0226, found: 369.0220.



***N'*-(5-bromo-2,3-dihydro-1*H*-inden-1-ylidene)-4-methylbenzenesulfonohydrazide (17b):** Prepared according to the synthesis of *N*-tosylhydrazones, the title compound was prepared from tosylhydrazide (10.0 mmol) in MeOH (10.0 mL) , ketone (1.0 equiv), *N*-tosylhydrazones **17b** was obtained as a white solid by recrystallization (isolated yield: 92%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.4 Hz, 2H), 7.56 (d, *J* = 8.2 Hz, 1H), 7.44 (d, *J* = 1.5 Hz, 1H), 7.37 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.32 (d, *J* = 8.1 Hz, 3H), 3.14 – 2.92 (m, 2H), 2.70 – 2.57 (m, 2H), 2.42 (s, 3H).

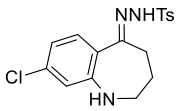
HRMS (ESI+), *m/z*: calculated for $C_{16}H_{15}BrN_2O_2S$ $[M + H]^+$: 379.0110, found: 379.0134.



***N'*-(acenaphthylen-1(2*H*)-ylidene)-4-methylbenzenesulfonohydrazide (18b):** Prepared according to the synthesis of *N*-tosylhydrazones, the title compound was prepared from tosylhydrazide (10.0 mmol) in MeOH (10.0 mL) , ketone (1.0 equiv), *N*-tosylhydrazones **18b** was obtained after column chromatography (hexane: EtO Ac, 2:1) as a white solid (isolated yield: 85%).

^{1}H NMR (500 MHz, DMSO-d_6) δ 10.76 (s, 1H), 7.91 – 7.81 (m, 3H), 7.74 (dd, *J* = 8.3, 0.8 Hz, 1H), 7.64 (dd, *J* = 7.1, 0.8 Hz, 1H), 7.61 – 7.56 (m, 1H), 7.54 (dd, *J* = 8.3, 6.9 Hz, 1H), 7.43 – 7.37 (m, 3H), 4.01 (s, 2H), 2.35 (s, 3H).

HRMS (ESI+), *m/z*: calculated for $C_{19}H_{16}N_2O_2S$ $[M + H]^+$: 337.1005, found: 337.1034.

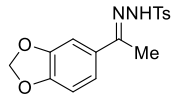


***N*'-(7-Chloro-3,4-dihydro-1*H*-benzo[b]azepin-5(2*H*)-ylidene)-4-methylbenzenesulfonohydrazide (19b):** Prepared according to the synthesis of *N*-tosylhydrazones, the title compound was prepared from tosylhydrazide (10.0 mmol) in MeOH (10.0 mL) , ketone (1.0 equiv), *N*-tosylhydrazones **19b** was obtained after column chromatography (hexane: EtO Ac, 2:1) as a white solid (isolated yield: 60%).

^{1}H NMR (500 MHz, DMSO-*d*$_6$) δ 10.54 (s, 1H), 7.75 (d, *J* = 8.3 Hz, 2H), 7.40 (d, *J* = 8.0 Hz, 2H), 7.03 (dd, *J* = 8.7, 2.6 Hz, 1H), 6.96 (dd, *J* = 2.7, 1.3 Hz, 1H), 6.69 (d, *J* = 8.7 Hz, 1H), 6.29 (s, 1H), 2.89 (s, 2H), 2.59 (t, *J* = 6.9 Hz, 2H), 2.37 (s, 3H), 1.88 (m, 2H).

^{13}C NMR (126 MHz, DMSO-*d*$_6$) δ 157.1, 149.8, 143.3, 136.3, 129.5, 128.6, 127.4, 127.3, 124.4, 120.4, 118.7, 44.9, 29.3, 27.2, 21.0.

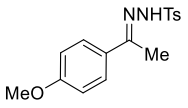
HRMS (ESI+), *m/z*: calculated for $C_{17}H_{18}ClN_3O_2S$ $[M + H]^+$: 364.0881, found: 364.0923.



***N'*-(1-(benzo[d][1,3]dioxol-5-yl)ethylidene)-4-methylbenzenesulfonohydrazide (21b):** Prepared according to the synthesis of *N*-tosylhydrazones, the title compound was prepared from tosylhydrazide (10.0 mmol) in MeOH (10.0 mL) , ketone (1.0 equiv), *N*-tosylhydrazones **21b** was obtained as a white solid by recrystallization (isolated yield: 78%).

^{1}H NMR (500 MHz, CDCl$_3$) δ 8.00 (s, 1H), 7.91 (d, *J* = 8.3 Hz, 2H), 7.31 (d, *J* = 8.1 Hz, 2H), 7.07 (dd, *J* = 8.2, 1.8 Hz, 1H), 6.74 (d, *J* = 8.2 Hz, 1H), 5.96 (s, 2H), 2.41 (s, 3H), 2.11 (s, 3H).

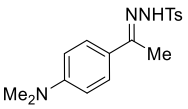
HRMS (ESI+), *m/z*: calculated for $C_{16}H_{16}N_2O_4S$ $[M + H]^+$: 333.0904, found: 333.0924.



***N′*-(1-(4-methoxyphenyl)ethylidene)-4-methylbenzenesulfonohydrazide (22b):** Prepared according to the synthesis of *N*-tosylhydrazones, the title compound was prepared from tosylhydrazide (10.0 mmol) in MeOH (10.0 mL) , ketone (1.0 equiv), *N*-tosylhydrazones **22b** was obtained as a white solid by recrystallization (isolated yield: 88%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.4 Hz, 2H), 7.83 – 7.73 (m, 1H), 7.60 (d, *J* = 8.9 Hz, 2H), 7.35 – 7.28 (m, 2H), 6.85 (d, *J* = 8.8 Hz, 2H), 3.81 (s, 3H), 2.41 (s, 3H), 2.13 (s, 3H).

HRMS (ESI+), *m/z*: calculated for $C_{16}H_{18}N_2O_3S$ $[M + H]^+$: 319.1111, found: 319.1134.

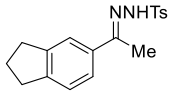


***N′*-(1-(4-(dimethylamino)phenyl)ethylidene)-4-methylbenzenesulfonohydrazide (24b):** Prepared according to the synthesis of *N*-tosylhydrazones, the title compound was prepared from tosylhydrazide (10.0 mmol) in MeOH (10.0 mL) , ketone (1.0 equiv), *N*-tosylhydrazones **24b** was obtained as a white solid by recrystallization (isolated yield: 76%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.3 Hz, 2H), 7.57 (d, *J* = 9.0 Hz, 2H), 7.30 (d, *J* = 7.8 Hz, 2H), 6.64 (d, *J* = 9.0 Hz, 2H), 2.98 (s, 6H), 2.40 (s, 3H), 2.10 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 153.2, 150.8, 143.4, 135.1, 129.0, 127.7, 127.0, 124.4, 111.0, 39.8, 21.1, 12.6.

HRMS (ESI+), *m/z*: calculated for $C_{17}H_{21}N_3O_2S$ $[M + H]^+$: 332.1427, found: 332.1454.

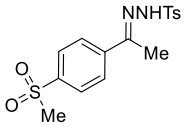


***N'*-(1-(2,3-Dihydro-1*H*-inden-5-yl)ethylidene)-4-methylbenzenesulfonohydrazide (25b)**: Prepared according to the synthesis of *N*-tosylhydrazones, the title compound was prepared from tosylhydrazide (10.0 mmol) in MeOH (10.0 mL) , ketone (1.0 equiv), *N*-tosylhydrazones **25b** was obtained as a white solid by recrystallization (isolated yield: 84%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 – 7.90 (m, 2H), 7.51 (d, *J* = 1.7 Hz, 1H), 7.42 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.34 – 7.27 (m, 2H), 7.18 (d, *J* = 7.9 Hz, 1H), 2.89 (td, *J* = 7.5, 3.2 Hz, 4H), 2.40 (s, 3H), 2.15 (s, 3H), 2.07 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 152.9, 145.7, 144.0, 143.6, 135.1, 135.1, 129.1, 127.7, 124.1, 123.6, 121.8, 32.3, 32.3, 25.0, 21.1, 13.3.

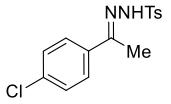
HRMS (ESI+), *m/z*: calculated for $C_{18}H_{20}N_2O_2S$ $[M+Na]^+$: 351.1143, found: 351.1124.



4-methyl-*N*'-(1-(4-(methylsulfonyl)phenyl)ethylidene)benzenesulfonohydrazide (26b): Prepared according to the synthesis of *N*-tosylhydrazones, the title compound was prepared from tosylhydrazide (10.0 mmol) in MeOH (10.0 mL) , ketone (1.0 equiv), *N*-tosylhydrazones **26b** was obtained as a white solid by recrystallization (isolated yield: 82%).

^{1}H NMR (500 MHz, DMSO-d_6) δ 10.80 (s, 1H), 7.94 – 7.71 (m, 6H), 7.39 (d, *J* = 8.1 Hz, 2H), 3.20 (s, 3H), 2.34 (s, 3H), 2.20 (s, 3H).

HRMS (ESI+), *m/z*: calculated for $C_{16}H_{18}N_2O_4S_2$[M+Na]$^+$: 389.0606, found: 389.0648.

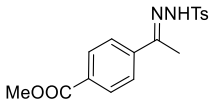


***N′*-(1-(4-Chlorophenyl)ethylidene)-4-methylbenzenesulfonohydrazide (27b)**: Prepared according to the synthesis of *N*-tosylhydrazones, the title compound was prepared from tosylhydrazide (10.0 mmol) in MeOH (10.0 mL) , ketone (1.0 equiv), *N*-tosylhydrazones **27b** was obtained as a white solid by recrystallization (isolated yield: 95%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.08 (d, *J* = 3.4 Hz, 1H), 7.91 (d, *J* = 8.4 Hz, 2H), 7.57 (d, *J* = 8.6 Hz, 2H), 7.37 – 7.28 (m, 4H), 2.41 (s, 3H), 2.14 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 150.9, 143.8, 135.2, 135.1, 134.8, 129.2, 128.1, 127.6, 127.1, 21.2, 12.9.

HRMS (ESI+), *m/z*: calculated for $C_{15}H_{15}ClN_2O_2S$ $[M+Na]^+$: 345.0440, found: 345.0404.

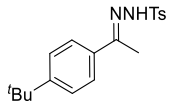


Methyl 4-(1-(2-tosylhydrazono)ethyl)benzoate (28b): Prepared according to the synthesis of *N*-tosylhydrazones, the title compound was prepared from tosylhydrazide (10.0 mmol) in MeOH (10.0 mL) , ketone (1.0 equiv), *N*-tosylhydrazones **28b** was obtained as a white solid by recrystallization (isolated yield: 99%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05 (s, 1H), 7.99 (d, *J* = 8.6 Hz, 2H), 7.92 (d, *J* = 8.4 Hz, 2H), 7.70 (d, *J* = 8.5 Hz, 2H), 7.35 – 7.30 (m, 2H), 3.91 (s, 3H), 2.41 (s, 3H), 2.17 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 166.2, 150.6, 143.9, 140.8, 134.8, 130.3, 129.2, 129.1, 127.7, 125.7, 51.8, 21.2, 12.9.

HRMS (ESI+), *m/z*: calculated for $C_{17}H_{18}N_2O_4S$ $[M+Na]^+$: 369.0885, found: 369.0897.

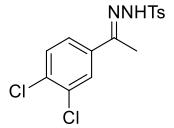


***N'*-(1-(4-(*tert*-Butyl)phenyl)ethylidene)-4-methylbenzenesulfonohydrazide (29b)**: Prepared according to the synthesis of *N*-tosylhydrazones, the title compound was prepared from tosylhydrazide (10.0 mmol) in MeOH (10.0 mL) , ketone (1.0 equiv), *N*-tosylhydrazones **29b** was obtained as a white solid by recrystallization (isolated yield: 97%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 – 7.89 (m, 2H), 7.86 – 7.73 (m, 1H), 7.64 – 7.54 (m, 2H), 7.34 (dd, *J* = 22.2, 8.3 Hz, 4H), 2.41 (s, 3H), 2.14 (s, 3H), 1.31 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 152.4, 152.2, 143.6, 135.0, 134.0, 129.1, 127.7, 125.6, 124.8, 34.2, 30.7, 30.7, 21.2, 12.9.

HRMS (ESI+), *m/z*: calculated for $C_{19}H_{25}N_2O_2S$ $[M+H]^+$: 345.1637, found: 345.1624.

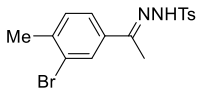


***N'*-(1-(3,4-dichlorophenyl)ethylidene)-4-methylbenzenesulfonohydrazide (30b)**: Prepared according to the synthesis of *N*-tosylhydrazones, the title compound was prepared from tosylhydrazide (10.0 mmol) in MeOH (10.0 mL) , ketone (1.0 equiv), *N*-tosylhydrazones **30b** was obtained as a white solid by recrystallization (isolated yield: 86%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 – 7.85 (m, 3H), 7.70 (d, *J* = 2.1 Hz, 1H), 7.47 (dd, *J* = 8.5, 2.1 Hz, 1H), 7.40 (d, *J* = 8.5 Hz, 1H), 7.36 – 7.30 (m, 2H), 2.43 (s, 3H), 2.12 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 149.3, 144.0, 136.7, 134.7, 133.2, 132.2, 129.8, 129.2, 127.7, 127.7, 124.9, 21.2, 12.7.

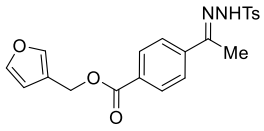
HRMS (ESI+), *m/z*: calculated for $C_{15}H_{14}Cl_2N_2O_2S$ $[M+Na]^+$: 379.0051, found: 379.0028.



***N*'-(1-(3-bromo-4-methylphenyl) ethylidene)-4-methylbenzenesulfonohydrazide (31b):** Prepared according to the synthesis of *N*-tosylhydrazones, the title compound was prepared from tosylhydrazide (10.0 mmol) in MeOH (10.0 mL) , ketone (1.0 equiv), *N*-tosylhydrazones **31b** was obtained as a white solid by recrystallization (isolated yield: 81%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.4 Hz, 2H), 7.78 (d, *J* = 1.9 Hz, 1H), 7.69 (s, 1H), 7.48 (dd, *J* = 8.0, 1.9 Hz, 1H), 7.37 – 7.30 (m, 2H), 7.19 (dd, *J* = 8.0, 0.8 Hz, 1H), 2.42 (s, 3H), 2.38 (s, 3H), 2.10 (s, 3H).

HRMS (ESI+), *m/z*: calculated for $C_{16}H_{17}BrN_2O_2S$ $[M+Na]^+$: 403.0092, found: 403.0085.

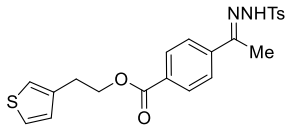


furan-2-ylmethyl 4-(1-(2-tosylhydrazono)ethyl)benzoate (34b): Prepared according to the synthesis of *N*-tosylhydrazones, the title compound was prepared from tosylhydrazide (10.0 mmol) in MeOH (10.0 mL) , ketone (1.0 equiv), *N*-tosylhydrazones **34b** was obtained after column chromatography (hexane: EtO Ac, 2:1) as a white solid (isolated yield: 59%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.6 Hz, 3H), 7.91 (d, *J* = 8.3 Hz, 2H), 7.68 (d, *J* = 8.5 Hz, 2H), 7.45 (dd, *J* = 1.9, 0.9 Hz, 1H), 7.34 – 7.29 (m, 2H), 6.49 (d, *J* = 3.2 Hz, 1H), 6.39 (dd, *J* = 3.2, 1.9 Hz, 1H), 5.30 (s, 2H), 2.41 (s, 3H), 2.16 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 165.3, 150.5, 148.9, 143.9, 142.9, 141.0, 134.7, 130.1, 129.3, 129.2, 127.7, 125.7, 110.5, 110.2, 58.2, 21.2, 12.9.

HRMS (ESI+), *m/z*: calculated for $C_{21}H_{20}N_2O_5S$ $[M+Na]^+$: 435.0991, found: 435.0970.

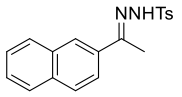


2-(thiophen-2-yl)ethyl 4-(1-(2-tosylhydrazono)ethyl)benzoate (35b): Prepared according to the synthesis of *N*-tosylhydrazones, the title compound was prepared from tosylhydrazide (10.0 mmol) in MeOH (10.0 mL) , ketone (1.0 equiv), *N*-tosylhydrazones **35b** was obtained after column chromatography (hexane: EtO Ac, 2:1) as a white solid (isolated yield: 89%).

^{1}H NMR (500 MHz, DMSO-d_6) δ 10.71 (s, 1H), 7.93 (d, *J* = 8.6 Hz, 2H), 7.85 – 7.71 (m, 4H), 7.47 – 7.30 (m, 3H), 7.06 – 6.86 (m, 2H), 4.45 (t, *J* = 6.3 Hz, 2H), 3.25 (t, *J* = 6.3 Hz, 2H), 2.35 (s, 3H), 2.18 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 167.2, 152.5, 150.8, 145.8, 144.8, 142.9, 136.6, 131.9, 131.2, 131.1, 129.7, 129.6, 127.6, 112.4, 112.1, 60.1, 23.1, 14.8.

HRMS (ESI+), *m/z*: calculated for $C_{22}H_{22}N_2O_4S$ $[M+H]^+$: 443.1099, found: 443.1070.

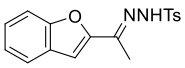


4-methyl-*N′*-(1-(naphthalen-2-yl)ethylidene)benzenesulfonohydrazide (33b): Prepared according to the synthesis of *N*-tosylhydrazones, the title compound was prepared from tosylhydrazide (10.0 mmol) in MeOH (10.0 mL) , ketone (1.0 equiv), *N*-tosylhydrazones **33b** was obtained as a white solid by recrystallization (isolated yield: 95%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.4 Hz, 3H), 7.86 – 7.77 (m, 3H), 7.49 – 7.39 (m, 2H), 7.38 – 7.30 (m, 4H), 2.46 (s, 3H), 2.31 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 154.1, 143.7, 136.0, 135.0, 133.4, 129.8, 129.2, 129.0, 128.0, 127.8, 126.0, 125.7, 125.5, 125.0, 124.5, 21.2, 17.7.

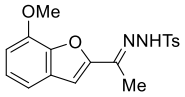
HRMS (ESI+), *m/z*: calculated for $C_{19}H_{18}N_2O_2S$ $[M+H]^+$: 339.1167, found: 339.1154.



***N*'-(1-(benzofuran-2-yl)ethylidene)-4-methylbenzenesulfonohydrazide (36b):** Prepared according to the synthesis of *N*-tosylhydrazones, the title compound was prepared from tosylhydrazide (10.0 mmol) in MeOH (10.0 mL) , ketone (1.0 equiv), *N*-tosylhydrazones **36b** was obtained as a white solid by recrystallization (isolated yield: 80%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.4 Hz, 2H), 7.73 (s, 1H), 7.62 – 7.43 (m, 2H), 7.38 – 7.30 (m, 3H), 7.23 (ddd, *J* = 8.1, 7.3, 1.0 Hz, 1H), 7.05 (d, *J* = 1.0 Hz, 1H), 2.41 (s, 3H), 2.18 (s, 3H).

HRMS (ESI+), *m/z*: calculated for $C_{17}H_{16}N_2O_3S$ $[M+Na]^+$: 351.0779, found: 351.0759.

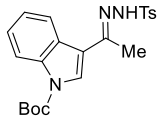


***N*′-(1-(7-methoxybenzofuran-2-yl)ethylidene)-4-methylbenzenesulfonohydrazide (37b)**: Prepared according to the synthesis of *N*-tosylhydrazones, the title compound was prepared from tosylhydrazide (10.0 mmol) in MeOH (10.0 mL) , ketone (1.0 equiv), *N*-tosylhydrazones **37b** was obtained as a white solid by recrystallization (isolated yield: 99%).

^{1}H NMR (500 MHz, DMSO-d_6) δ 10.79 (s, 1H), 7.81 (d, *J* = 8.0 Hz, 2H), 7.40 (d, *J* = 8.3 Hz, 2H), 7.24 (s, 1H), 7.21 – 7.12 (m, 2H), 6.95 (dd, *J* = 7.7, 1.2 Hz, 1H), 3.93 (s, 3H), 2.35 (s, 3H), 2.19 (s, 3H).

^{13}C NMR (126 MHz, DMSO-d_6) *δ* 152.9, 144.9, 144.6, 143.6, 143.5, 136.2, 129.6, 129.4, 127.4, 124.1, 113.7, 108.2, 107.4, 55.8, 21.0, 13.9.

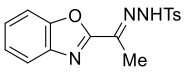
HRMS (ESI+), *m/z*: calculated for $C_{18}H_{18}N_2O_4S$ $[M+Na]^+$: 381.0885, found: 381.0816.



tert-butyl 3-(1-(2-tosylhydrazono)ethyl)-1*H*-indole-1-carboxylate (38b): Prepared according to the synthesis of *N*-tosylhydrazones, the title compound was prepared from tosylhydrazide (10.0 mmol) in MeOH (10.0 mL) , ketone (1.0 equiv), *N*-tosylhydrazones **38b** was obtained as a white solid by recrystallization (isolated yield: 78%).

^{1}H NMR (500 MHz, DMSO-*d*$_6$) δ 10.56 (s, 1H), 8.10 – 8.02 (m, 2H), 8.01 (s, 1H), 7.87 (d, *J* = 8.2 Hz, 2H), 7.42 (d, *J* = 8.1 Hz, 2H), 7.35 (m, 1H), 7.25 (td, *J* = 7.6, 7.2, 1.0 Hz, 1H), 2.36 (s, 3H), 2.23 (s, 3H), 1.63 (s, 9H).

HRMS (ESI+), *m/z*: calculated for $C_{22}H_{25}N_3O_4S$ $[M+H]^+$: 428.1639, found: 428.1666.

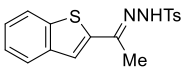


***N′*-(1-(benzo[d]oxazol-2-yl)ethylidene)-4-methylbenzenesulfonohydrazide (39b)**: Prepared according to the synthesis of *N*-tosylhydrazones, the title compound was prepared from tosylhydrazide (10.0 mmol) in MeOH (10.0 mL) , ketone (1.0 equiv), *N*-tosylhydrazones **39b** was obtained as a white solid by recrystallization (isolated yield: 95%).

^{1}H NMR (500 MHz, DMSO-*d*$_6$) δ 11.42 (s, 1H), 7.89 – 7.73 (m, 4H), 7.47 – 7.31 (m, 4H), 2.35 (s, 3H), 2.32 (s, 3H).

^{13}C NMR (126 MHz, DMSO-*d*$_6$) δ 160.2, 150.2, 143.8, 141.5, 140.7, 136.0, 129.7, 127.3, 126.5, 125.0, 120.3, 111.2, 21.0, 14.0.

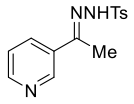
HRMS (ESI+), *m/z*: calculated for $C_{16}H_{15}N_3O_3S$ $[M+Na]^+$: 352.0732, found: 352.0748.



***N′*-(1-(benzo[b]thiophen-2-yl)ethylidene)-4-methylbenzenesulfonohydrazide (40b):** Prepared according to the synthesis of *N*-tosylhydrazones, the title compound was prepared from tosylhydrazide (10.0 mmol) in MeOH (10.0 mL) , ketone (1.0 equiv), *N*-tosylhydrazones **40b** was obtained after column chromatography (hexane: EtO Ac, 2:1) as a white solid (isolated yield: 75%).

^{1}H NMR (500 MHz, DMSO-*d*$_6$) δ 10.73 (s, 1H), 7.96 – 7.89 (m, 1H), 7.82 (td, *J* = 8.1, 1.8 Hz, 3H), 7.75 (d, *J* = 0.8 Hz, 1H), 7.44 (d, *J* = 7.9 Hz, 2H), 7.40 – 7.28 (m, 2H), 2.38 (s, 3H), 2.26 (s, 3H).

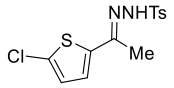
HRMS (ESI+), *m/z*: calculated for $C_{17}H_{16}N_2O_2S_2$ $[M + H]^+$: 345.0726, found: 345.0764.



4-Methyl-*N*'-(1-(pyridin-4-yl)ethylidene)benzenesulfonohydrazide (41b): Prepared according to the synthesis of *N*-tosylhydrazones, the title compound was prepared from tosylhydrazide (10.0 mmol) in MeOH (10.0 mL) , ketone (1.0 equiv), *N*-tosylhydrazones **41b** was obtained after column chromatography (hexane: EtO Ac, 2:1) as a white solid (isolated yield: 60%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.84 (d, *J* = 2.4 Hz, 1H), 8.71 – 8.53 (m, 1H), 8.19 – 8.06 (m, 1H), 7.96 (ddd, *J* = 8.1, 2.4, 1.6 Hz, 1H), 7.91 (d, *J* = 8.4 Hz, 2H), 7.38 – 7.31 (m, 2H), 7.29 (ddd, *J* = 8.1, 4.8, 0.8 Hz, 1H), 2.42 (s, 3H), 2.18 (s, 3H).

HRMS (ESI+), *m/z*: calculated for $C_{14}H_{15}N_3O_2S$ $[M+Na]^+$: 312.0783, found: 312.0759.

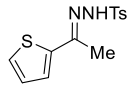


***N'*-(1-(5-chlorothiophen-2-yl)ethylidene)-4-methylbenzenesulfonohydrazide (43b):** Prepared according to the synthesis of *N*-tosylhydrazones, the title compound was prepared from tosylhydrazide (10.0 mmol) in MeOH (10.0 mL) , ketone (1.0 equiv), *N*-tosylhydrazones **43b** was obtained after column chromatography (hexane: EtO Ac, 2:1) as a white solid (isolated yield: 78%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 – 7.82 (m, 3H), 7.39 – 7.30 (m, 2H), 6.94 (d, *J* = 4.0 Hz, 1H), 6.77 (d, *J* = 4.0 Hz, 1H), 2.43 (s, 3H), 2.10 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 147.9, 143.9, 140.7, 134.5, 132.8, 129.2, 127.8, 125.8, 125.6, 21.2, 12.5.

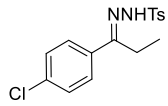
HRMS (ESI+), *m/z*: calculated for $C_{13}H_{13}ClN_2O_2S_2$ $[M + H]^+$: 329.0180, found: 329.0210.



4-methyl-*N′*-(1-(thiophen-2-yl)ethylidene)benzenesulfonohydrazide (44b): Prepared according to the synthesis of *N*-tosylhydrazones, the title compound was prepared from tosylhydrazide (10.0 mmol) in MeOH (10.0 mL) , ketone (1.0 equiv), *N*-tosylhydrazones **44b** was obtained as a white solid by recrystallization (isolated yield: 80%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.4 Hz, 2H), 7.37 (s, 1H), 7.34 – 7.29 (m, 3H), 7.21 (dd, *J* = 3.7, 1.1 Hz, 1H), 6.97 (dd, *J* = 5.1, 3.7 Hz, 1H), 2.42 (s, 3H), 2.15 (s, 3H).

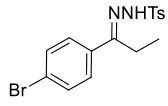
HRMS (ESI+), *m/z*: calculated for $C_{13}H_{14}N_2O_2S_2$ $[M + H]^+$: 295.0569, found: 295.0583.



***N*'-(1-(4-Chlorophenyl)propylidene)-4-methylbenzenesulfonohydrazide (45b):** Prepared according to the synthesis of *N*-tosylhydrazones, the title compound was prepared from tosylhydrazide (10.0 mmol) in MeOH (10.0 mL) , ketone (1.0 equiv), *N*-tosylhydrazones **45b** was obtained after column chromatography (hexane: EtOAc, 2:1) as a white solid (isolated yield: 77%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 (s, 1H), 7.90 (d, *J* = 8.4 Hz, 2H), 7.57 (d, *J* = 8.6 Hz, 2H), 7.33 – 7.29 (m, 4H), 2.56 (q, *J* = 7.8 Hz, 2H), 2.42 (s, 3H), 1.08 (t, *J* = 7.7 Hz, 3H).

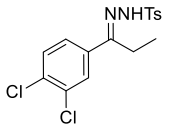
HRMS (ESI+), *m/z*: calculated for $C_{16}H_{17}ClN_2O_2S$ $[M + H]^+$: 337.0772, found: 337.0782.



***N*'-(1-(4-Bromophenyl)propylidene)-4-methylbenzenesulfonohydrazide (46b):** Prepared according to the synthesis of *N*-tosylhydrazones, the title compound was prepared from tosylhydrazide (10.0 mmol) in MeOH (10.0 mL) , ketone (1.0 equiv), *N*-tosylhydrazones **46b** was obtained after column chromatography (hexane: EtOAc, 2:1) as a white solid (isolated yield: 79%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 – 7.90 (m, 3H), 7.61 (s, 1H), 7.36 – 7.27 (m, 3H), 7.23 – 7.14 (m, 2H), 2.87 (td, *J* = 7.0, 4.1 Hz, 1H), 2.53 (s, 1H), 2.41 (s, 3H), 1.24 (d, *J* = 7.0 Hz, 3H).

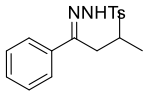
HRMS (ESI+), *m/z*: calculated for $C_{16}H_{18}BrN_2O_2S$ $[M + H]^+$: 381.0267, found: 381.0288.



***N*'-(1-(3,4-Dichlorophenyl)propylidene)-4-methylbenzenesulfonohydrazide (47b):** Prepared according to the synthesis of *N*-tosylhydrazones, the title compound was prepared from tosylhydrazide (10.0 mmol) in MeOH (10.0 mL) , ketone (1.0 equiv), *N*-tosylhydrazones **47b** was obtained after column chromatography (hexane: EtO Ac, 2:1) as a white solid (isolated yield: 86%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 – 7.86 (m, 3H), 7.69 (d, *J* = 2.2 Hz, 1H), 7.47 (dd, *J* = 8.5, 2.1 Hz, 1H), 7.41 (d, *J* = 8.5 Hz, 1H), 7.37 – 7.31 (m, 2H), 2.53 (q, *J* = 7.7 Hz, 2H), 2.43 (s, 3H), 1.08 (t, *J* = 7.7 Hz, 3H).

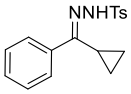
HRMS (ESI+), *m/z*: calculated for $C_{16}H_{16}Cl_2N_2O_2S$ $[M + H]^+$: 371.0382, found: 371.0366.



4-Methyl-*N*'-(3-methyl-1-phenylbutylidene)benzenesulfonohydrazide (48b): Prepared according to the synthesis of *N*-tosylhydrazones, the title compound was prepared from tosylhydrazide (10.0 mmol) in MeOH (10.0 mL) , ketone (1.0 equiv), *N*-tosylhydrazones **48b** was obtained as a white solid by recrystallization (isolated yield: 87%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.3 Hz, 2H), 7.73 (s, 1H), 7.66 – 7.54 (m, 2H), 7.37 – 7.29 (m, 5H), 2.47 (d, *J* = 7.6 Hz, 2H), 2.41 (s, 3H), 1.88 (dt, *J* = 13.7, 6.9 Hz, 1H), 0.86 (d, *J* = 6.6 Hz, 6H).

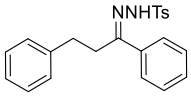
HRMS (ESI+), *m/z*: calculated for $C_{18}H_{22}N_2O_2S$ $[M + H]^+$: 331.1475, found: 331.1482.



***N′*-(cyclopropyl(phenyl)methylene)-4-methylbenzenesulfonohydrazide (50b):** Prepared according to the synthesis of *N*-tosylhydrazones, the title compound was prepared from tosylhydrazide (10.0 mmol) in MeOH (10.0 mL) , ketone (1.0 equiv), *N*-tosylhydrazones **50b** was obtained after column chromatography (hexane: EtOAc, 2:1) as a white solid (isolated yield: 56%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.3 Hz, 1H), 7.76 (d, *J* = 8.3 Hz, 1H), 7.70 – 7.59 (m, 1H), 7.48 – 7.42 (m, 1H), 7.38 – 7.30 (m, 3H), 7.09 (dd, *J* = 7.5, 2.0 Hz, 1H), 2.43 (d, *J* = 16.8 Hz, 3H), 1.78 – 1.70 (m, 1H), 1.10 (dd, *J* = 8.5, 1.9 Hz, 1H), 0.76 (dd, *J* = 8.1, 2.6 Hz, 1H), 0.67 (dd, *J* = 4.9, 2.4 Hz, 1H), 0.49 (dd, *J* = 5.9, 1.7 Hz, 1H).

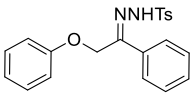
HRMS (ESI+), *m/z*: calculated for $C_{17}H_{18}N_2O_2S$ $[M + H]^+$: 315.1162, found: 315.1176.



***N*'-(1,3-Diphenylpropylidene)-4-methylbenzenesulfonohydrazide (51b):** Prepared according to the synthesis of *N*-tosylhydrazones, the title compound was prepared from tosylhydrazide (10.0 mmol) in MeOH (10.0 mL) , ketone (1.0 equiv), *N*-tosylhydrazones **51b** was obtained after column chromatography (hexane: EtO Ac, 2:1) as a white solid (isolated yield: 77%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 – 7.58 (m, 4H), 7.43 – 7.34 (m, 3H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.18 (dd, *J* = 7.4, 2.0 Hz, 3H), 7.14 – 7.03 (m, 2H), 6.84 (s, 1H), 2.95 (t, *J* = 7.2 Hz, 2H), 2.80 (t, *J* = 7.2 Hz, 2H), 2.44 (s, 3H).

HRMS (ESI+), *m/z*: calculated for $C_{22}H_{23}N_2O_2S$ $[M + H]^+$: 379.1475, found: 379.1466.

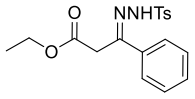


4-Methyl-*N′*-(2-phenoxy-1-phenylethylidene)benzenesulfonohydrazide (52b): Prepared according to the synthesis of *N*-tosylhydrazones, the title compound was prepared from tosylhydrazide (10.0 mmol) in MeOH (10.0 mL) , ketone (1.0 equiv), *N*-tosylhydrazones **52b** was obtained after column chromatography (hexane: EtO Ac, 2:1) as a white solid (isolated yield: 86%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.23 (s, 1H), 7.80 (dd, *J* = 8.2, 5.6 Hz, 4H), 7.70 (s, 1H), 7.61 (dd, *J* = 8.0, 1.7 Hz, 2H), 7.47 – 7.41 (m, 3H), 7.41 – 7.34 (m, 3H), 7.34 – 7.30 (m, 2H), 7.29 – 7.26 (m, 2H), 7.26 – 7.23 (m, 2H), 7.20 – 7.12 (m, 4H), 7.07 – 6.89 (m, 2H), 6.87 – 6.82 (m, 2H), 6.78 (dd, *J* = 8.8, 1.1 Hz, 2H), 5.08 (s, 2H), 4.83 (s, 2H), 2.43 (d, *J* = 33.0 Hz, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 157.6, 156.3, 152.0, 147.9, 143.8, 143.5, 135.0, 134.9, 134.8, 129.9, 129.8, 129.4, 129.4, 129.3, 129.2, 129.1, 128.9, 128.2, 127.4, 126.9, 125.8, 122.3, 120.7, 114.6, 114.4, 70.4, 64.4, 21.2, 21.1.

HRMS (ESI+), *m/z*: calculated for $C_{21}H_{20}N_2O_3S$ $[M + H]^+$: 381.1627 found: 381.1646.

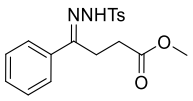


Ethyl 3-phenyl-3-(2-tosylhydrazono)propanoate (53b): Prepared according to the synthesis of *N*-tosylhydrazones, the title compound was prepared from tosylhydrazide (10.0 mmol) in MeOH (10.0 mL) , ketone (1.0 equiv), *N*-tosylhydrazones **53b** was obtained after column chromatography (hexane: EtO Ac, 2:1) as a white solid (isolated yield: 79%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.23 (s, 1H), 7.92 (d, *J* = 8.3 Hz, 2H), 7.76 – 7.65 (m, 2H), 7.38 – 7.34 (m, 3H), 7.33 – 7.28 (m, 2H), 4.15 (q, *J* = 7.2 Hz, 2H), 3.78 (s, 2H), 2.40 (s, 3H), 1.23 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 168.6, 148.3, 143.6, 135.5, 135.1, 129.6, 129.1, 128.1, 127.7, 125.9, 62.0, 34.8, 21.1, 13.5.

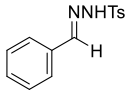
HRMS (ESI+), *m/z*: calculated for $C_{18}H_{20}N_2O_4S$ $[M + H]^+$: 361.1217, found: 361,1214.



Methyl 4-phenyl-4-(2-tosylhydrazono)butanoate (54b): Prepared according to the synthesis of *N*-tosylhydrazones, the title compound was prepared from tosylhydrazide (10.0 mmol) in MeOH (10.0 mL) , ketone (1.0 equiv), *N*-tosylhydrazones **54b** was obtained after column chromatography (hexane: EtO Ac, 2:1) as a white solid (isolated yield: 71%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.72 (s, 1H), 7.94 (d, *J* = 8.3 Hz, 2H), 7.54 (dd, *J* = 8.1, 1.7 Hz, 2H), 7.36 – 7.29 (m, 5H), 3.60 (s, 3H), 3.00 – 2.90 (m, 2H), 2.65 – 2.58 (m, 2H), 2.41 (s, 3H).

HRMS (ESI+), *m/z*: calculated for $C_{18}H_{20}N_2O_4S$ $[M + H]^+$: 361.1217, found: 361,1234.

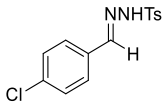


***N*'-benzylidene-4-methylbenzenesulfonohydrazide (55b)** Prepared according to the synthesis of *N*-tosylhydrazones, the title compound was prepared from tosylhydrazide (10.0 mmol) in MeOH (10.0 mL) , ketone (1.0 equiv), *N*-tosylhydrazones **55b** was obtained as a white solid by recrystallization (isolated yield: 86%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.61 (s, 1H), 7.90 (d, *J* = 8.3 Hz, 2H), 7.81 (s, 1H), 7.55 (dd, *J* = 7.7, 1.9 Hz, 2H), 7.37 – 7.27 (m, 5H), 2.38 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 147.6, 143.8, 134.8, 132.8, 129.9, 129.3, 128.1, 127.5, 126.9, 21.1.

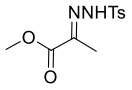
HRMS (ESI+), *m/z*: calculated for $C_{14}H_{14}N_2O_2S$ $[M+H]^+$: 275.0854, found: 275.0873.



***N*′-(4-chlorobenzylidene)-4-methylbenzenesulfonohydrazide (56b):** Prepared according to the synthesis of *N*-tosylhydrazones, the title compound was prepared from tosylhydrazide (10.0 mmol) in MeOH (10.0 mL) , ketone (1.0 equiv), *N*-tosylhydrazones **56b** was obtained as a white solid by recrystallization (isolated yield: 88%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.4 Hz, 2H), 7.82 (s, 1H), 7.70 (s, 1H), 7.51 (d, *J* = 8.6 Hz, 2H), 7.33 (dd, *J* = 8.3, 5.1 Hz, 4H), 2.42 (s, 3H).

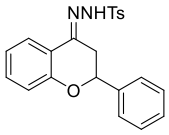
HRMS (ESI+), *m/z*: calculated for $C_{14}H_{13}ClN_2O_2S$ $[M + H]^+$: 309.0459, found: 309.0456.



Methyl -2-(2-tosylhydrazono)propanoate (57b): Prepared according to the synthesis of *N*-tosylhydrazones, the title compound was prepared from tosylhydrazide (10.0 mmol) in MeOH (10.0 mL) , ketone (1.0 equiv), *N*-tosylhydrazones **57b** was obtained after column chromatography (hexane: EtOAc, 3:1) as a white solid (isolated yield: 65%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 (s, 1H), 7.88 (d, *J* = 8.4 Hz, 2H), 7.38 – 7.30 (m, 2H), 3.80 (s, 3H), 2.44 (s, 3H), 1.98 (s, 3H).

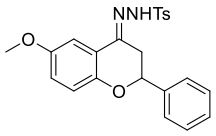
HRMS (ESI+), *m/z*: calculated for $C_{11}H_{14}N_2O_4S$ $[M + H]^+$: 271.0747, found: 271.0764.



4-Methyl-*N*'-(2-phenylchroman-4-ylidene)benzenesulfonohydrazide (88b): Prepared according to the synthesis of *N*-tosylhydrazones, the title compound was prepared from tosylhydrazide (10.0 mmol) in MeOH (10.0 mL) , ketone (1.0 equiv), *N*-tosylhydrazones **88b** was obtained after column chromatography (hexane: EtOAc, 2:1) as a yellow solid (isolated yield: 55%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 – 7.71 (m, 3H), 7.49 (s, 1H), 7.45 – 7.34 (m, 5H), 7.32 (d, *J* = 8.1 Hz, 3H), 7.03 – 6.88 (m, 2H), 5.11 – 4.99 (m, 1H), 3.02 (dd, *J* = 16.5, 3.1 Hz, 1H), 2.59 (dd, *J* = 16.5, 12.4 Hz, 1H), 2.42 (s, 3H).

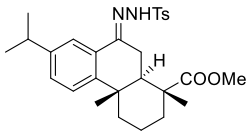
HRMS (ESI+), *m/z*: calculated for $C_{22}H_{20}N_2O_3S$ $[M + H]^+$: 393.1267, found: 393,1286.



***N′*-(6-methoxy-2-phenylchroman-4-ylidene)-4-methylbenzenesulfonohydrazide (89b):** Prepared according to the synthesis of *N*-tosylhydrazones, the title compound was prepared from tosylhydrazide (10.0 mmol) in MeOH (10.0 mL) , ketone (1.0 equiv), *N*-tosylhydrazones **89b** was obtained after column chromatography (hexane: EtO Ac, 2:1) as a yellow solid (isolated yield: 45%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.4 Hz, 2H), 7.44 – 7.35 (m, 6H), 7.32 (d, *J* = 8.2 Hz, 3H), 6.92 – 6.84 (m, 2H), 5.06 – 4.97 (m, 1H), 3.82 (s, 3H), 2.96 (dd, *J* = 16.5, 3.1 Hz, 1H), 2.56 (dd, *J* = 16.5, 12.4 Hz, 1H), 2.43 (s, 3H).

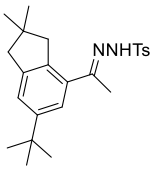
HRMS (ESI+), *m/z*: calculated for $C_{23}H_{22}N_2O_4S$ $[M + H]^+$: 423.1373, found: 423.1393.



(1*R*,4a*S*,10a*R*)-Methyl 7-isopropyl-1,4a-dimethyl-9-(2-tosylhydrazono)-1,2,3,4,4a,9,10,10a-octahydrophenanthrene-1-carboxylate (90b): Prepared according to the synthesis of *N*-tosylhydrazones, the title compound was prepared from tosylhydrazide (10.0 mmol) in MeOH (10.0 mL) , ketone (1.0 equiv), *N*-tosylhydrazones **90b** was obtained after column chromatography (hexane: EtOAc, 2:1) as a white solid (isolated yield: 65%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01 – 7.90 (m, 2H), 7.86 (d, *J* = 7.8 Hz, 1H), 7.71 (d, *J* = 2.0 Hz, 1H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.19 – 7.11 (m, 2H), 3.63 (s, 3H), 2.92 – 2.84 (m, 1H), 2.42 (s, 3H), 2.36 – 2.24 (m, 3H), 1.72 (dt, *J* = 8.6, 2.6 Hz, 4H), 1.33 (s, 3H), 1.24 (s, 6H), 1.03 (s, 3H), 0.93 – 0.90 (m, 2H).

HRMS (ESI+), *m/z*: calculated for $C_{28}H_{36}N_2O_4S$ $[M + H]^+$: 497.2469, found: 497.2489.

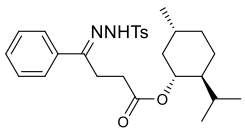


***N*'-(1-(6-(tert-butyl)-2,2-dimethyl-2,3-dihydro-1*H*-inden-4-yl)ethylidene)-4-methylbenzenesulfonohydrazide (91b):** Prepared according to the synthesis of *N*-tosylhydrazones, the title compound was prepared from tosylhydrazide (10.0 mmol) in MeOH (10.0 mL) , ketone (1.0 equiv), *N*-tosylhydrazones **91b** was obtained after column chromatography (hexane: EtOAc, 3:1) as a white solid (isolated yield: 55%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.3 Hz, 2H), 7.37 – 7.28 (m, 2H), 7.13 (d, *J* = 1.4 Hz, 2H), 2.80 (t, *J* = 7.2 Hz, 2H), 2.43 (s, 3H), 2.18 (s, 3H), 1.82 (t, *J* = 7.2 Hz, 2H), 1.26 (d, *J* = 32.4 Hz, 15H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 154.3, 153.1, 149.1, 143.6, 138.0, 135.1, 133.3, 129.1, 127.9, 122.2, 119.3, 43.2, 41.0, 34.2, 31.0, 30.0, 28.2, 21.1, 15.1.

HRMS (ESI+), *m/z*: calculated for $C_{24}H_{32}N_2O_2S$ $[M + H]^+$: 413.2257, found: 413.2286.

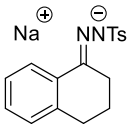


(1*R*,2*S*,5*R*)-2-Isopropyl-5-methylcyclohexyl 4-phenyl-4-(2-tosylhydrazono)butanoate (92b): Prepared according to the synthesis of *N*-tosylhydrazones, the title compound was prepared from tosylhydrazide (10.0 mmol) in MeOH (10.0 mL) , ketone (1.0 equiv), *N*-tosylhydrazones **92b** was obtained after column chromatography (hexane: EtOAc, 3:1) as a white solid (isolated yield: 88%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.93 (s, 1H), 7.93 (d, *J* = 8.1 Hz, 2H), 7.55 – 7.50 (m, 2H), 7.33 (dd, *J* = 9.6, 7.1 Hz, 3H), 7.29 – 7.26 (m, 2H), 4.57 (td, *J* = 10.9, 4.4 Hz, 1H), 2.93 (dt, *J* = 8.1, 5.8 Hz, 2H), 2.57 (t, *J* = 6.1 Hz, 2H), 2.40 (s, 3H), 1.81 (s, 1H), 1.66 (ddd, *J* = 13.3, 6.7, 3.1 Hz, 2H), 1.52 – 1.46 (m, 1H), 1.28 – 1.24 (m, 1H), 1.00 (dd, *J* = 12.8, 3.5 Hz, 1H), 0.91 (d, *J* = 6.4 Hz, 3H), 0.89 – 0.84 (m, 2H), 0.76 (d, *J* = 7.0 Hz, 3H), 0.54 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 173.5, 154.4, 143.0, 135.3, 134.9, 132.7, 129.6, 129.5, 129.3, 128.8, 128.1, 128.0, 127.9, 127.8, 127.6, 127.5, 126.3, 125.9, 75.5, 74.1, 46.5, 46.3, 40.4, 40.2, 33.8, 33.6, 33.0, 31.0, 30.9, 28.2, 25.8, 23.0, 21.5, 21.1, 20.8, 20.3, 20.1, 15.9, 15.7.

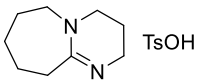
HRMS (ESI+), *m/z*: calculated for $C_{27}H_{36}N_2O_4S$ $[M + H]^+$: 485.2469, found: 485.2472.



***N'*-(3,4-Dihydronaphthalen-1(2*H*)-ylidene)-4-methylbenzenesulfonohydrazide sodium (1e) :** Prepared according to the synthesis of *N*-tosylhydrazone sodium salt. Following the workup, the product was purified ,give the title compound as a white solid (99% yield).

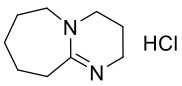
^{1}H NMR (500 MHz, DMSO-d_6) δ 7.82 (d, *J* = 8.3 Hz, 2H), 7.77 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.41 (d, *J* = 8.1 Hz, 2H), 7.25 (td, *J* = 7.5, 1.5 Hz, 1H), 7.21 – 7.13 (m, 2H), 2.68 (t, *J* = 6.0 Hz, 2H), 2.54 (t, *J* = 6.6 Hz, 2H), 2.37 (s, 3H), 1.76 (p, *J* = 6.3 Hz, 2H).

HRMS (ESI+), *m/z*: calculated for [$C_{17}H_{18}N_2O_2SNa^{++}$]: 337.0981, found: 337.0993.



2,3,4,6,7,8,9,10-octahydropyrimido[1,2-a]azepine 4-methylbenzenesulfonate (101e): Prepared according to the synthesis of ammonium salts of DBU. Following the workup, the product was purified ,give the title compound as a white solid (99% yield).

^{1}H NMR (500 MHz, DMSO-d_6) δ 9.53 (s, 1H), 7.52 – 7.47 (m, 2H), 7.13 (d, *J* = 7.6 Hz, 2H), 3.55 – 3.50 (m, 4H), 3.23 (d, *J* = 2.7 Hz, 2H), 2.64 (d, *J* = 10.8 Hz, 2H), 2.30 (s, 3H), 1.90 (s, 2H), 1.73 – 1.42 (m, 6H).

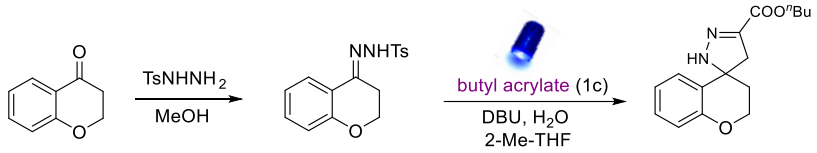


2,3,4,6,7,8,9,10-octahydropyrimido[1,2-a]azepine hydrochloride (101f): Prepared according to the synthesis of ammonium salts of DBU. Following the workup, the product was purified ,give the title compound as a white solid (99% yield).

^{1}H NMR (500 MHz, DMSO-d_6) δ 10.31 (s, 1H), 3.55 (d, *J* = 9.5 Hz, 2H), 3.47 (t, *J* = 5.9 Hz, 2H), 3.26 – 3.19 (m, 2H), 2.75 (d, *J* = 10.5 Hz, 2H), 1.90 (p, *J* = 5.8 Hz, 2H), 1.73 – 1.50 (m, 6H).

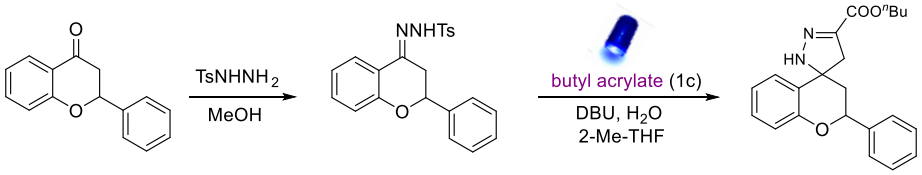
6. The applications of the visible-light-induced [3+2] cycloadditions

Synthesis of 11d in gram scale:



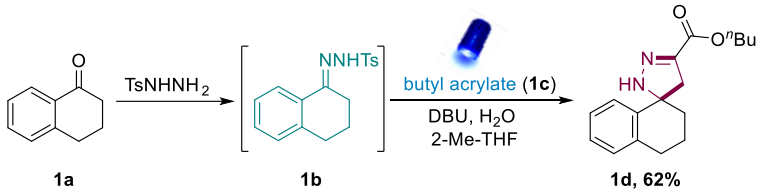
Following the general procedure A, the reaction with **11b** (1.6 g, 5.0 mmol), butyl acrylate (1.1 mL, 7.5 mmol, 1.5 equiv), DBU (2.2 mL, 15.0 mmol, 3 equiv), H_2O (275 μL, 15.0 mmol, 3.0 equiv) and 2-MeTHF (15 mL) under Ar for 40 h at room temperature afforded **11d** as yellow oil (1.2 g, 79% yield).

Synthesis of 87d in gram scale:



Following the general procedure A, the reaction with **87b** (1.57 g, 4.0 mmol), butyl acrylate (880 μL, 6 mmol, 1.5 equiv), DBU (1.8 mL, 12.0 mmol, 3 equiv), H_2O (220 μL, 12.0 mmol, 3 equiv) and 2-MeTHF (15 mL) under Ar for 40 h at room temperature afforded **87d** as yellow oil (680 mg, 47% yield).

One-pot approach



A dry 5 mL Schlenk tube containing a stirring bar was charged with 0.2 mmol of ketone **1a** (1.0 equiv), 0.2 mmol of $TsNHNH_2$ (1.0 equiv). After purging the flask for three times under vacuum and three times under argon, it was charged with anhydrous 2-MeTHF (1.0 mL). The reaction was kept for 1.5 h under 60 °C. Afterwards, 0.3 mmol butyl acrylate **1c** (1.5 equiv), 0.6 mmol DBU (3.0 equiv) and 0.6 mmol H_2O (3 equiv) were added and the reaction was kept for 16 h under 40 W Kessil lamp reaction setup (the progress can be monitored *via* TLC). Then, the resulting mixture underwent an aqueous workup (using distilled water; or brine in case of slurry phase separation) and was extracted three times with dichloromethane. The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo*. Products were purified *via* flash column chromatography with ethyl acetate and hexane as solvents.

7. Mechanistic investigations

Ultraviolet-Visible absorption experiments

Ultraviolet-visible absorption experiments were measured in a 1 cm quartz cuvette using a gilent Cary 100 spectrophotometer. Absorption spectra of individual reaction components and mixtures thereof were recorded. A bathochromic shift was observed for a mixture of **1b** and DBU in THF (0.2 M), which was a visibly intense yellow in color. This indicates the formation of a non-covalent complex (Figure S2). The concentration of each component was 2×10^{-4} M.

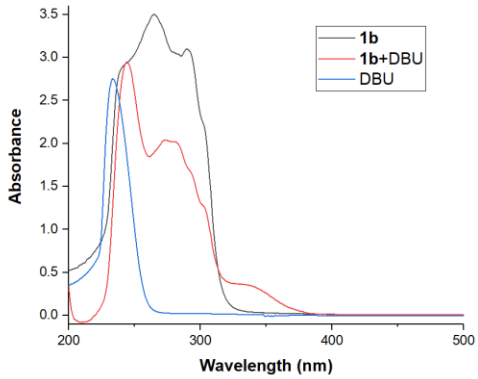


Figure S2. UV/vis absorption spectra of individual reaction components and a combination thereof. All spectra were measured in THF and with a concentration of 200 μM **1b**, 200 μM DBU.

Evaluated the reactivity of hydrazone anion (**1e**) and ammonium salts of DBU under the standard conditions. To further prove whether the non-covalent complex was formed from the hydrazone anion and different ammonium salts. We performed the UV-Vis spectra measurement and no red shift was observed in the mixture of two species.

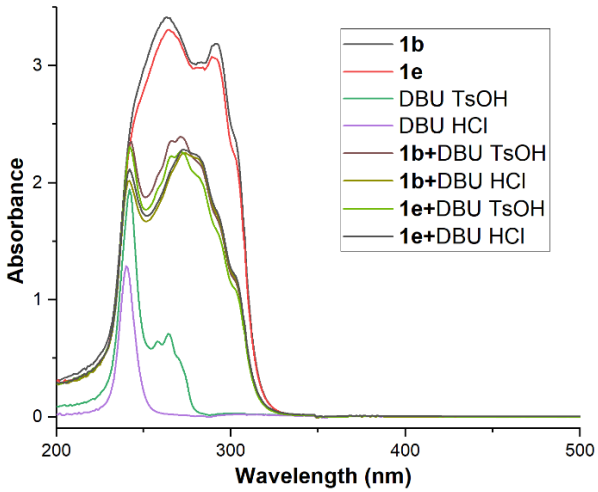


Figure S3. UV/vis absorption spectra of individual reaction components and a combination thereof.

Job's plot experiments

The total concentration of *N*-tosylhydrazone anion (**1e**) and DBU was kept constant, and DBU/**1e** was prepared as 10/0, 9/1, 8/2, 7/3, 6/4, 5/5, 4/6, 3/7, 2/8, 1/9, 0/10. and the UV-absorption spectra were carried out sequentially. The Job's curve is made, and the intersection of the two curves after fitting is the complexation ratio between **1e** and DBU.

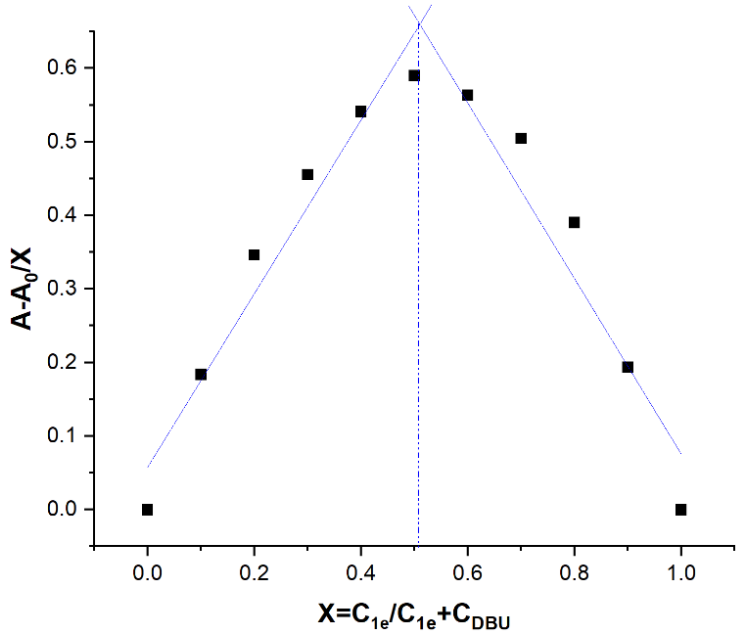


Figure S4. Job's curve UV/vis absorption spectra of different DBU/**1e** ratios.

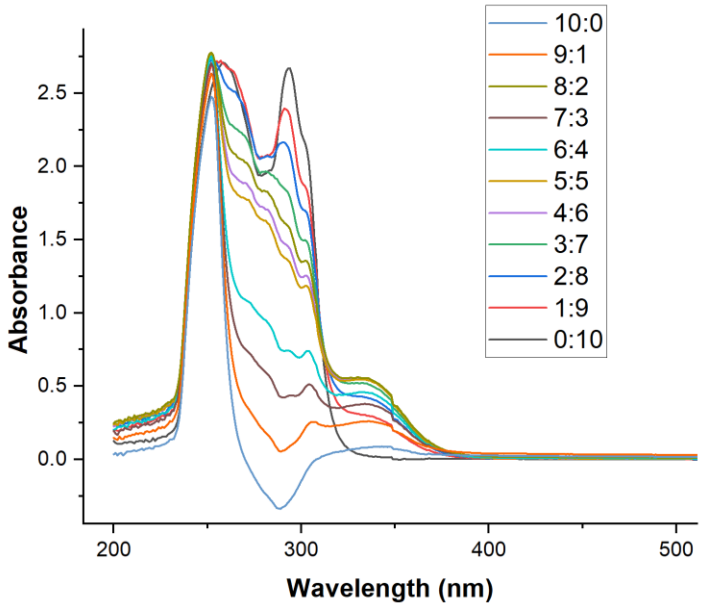


Figure S5. Job's curve UV/vis absorption spectra of different **DBU**/1e ratios.

^{1}H NMR titration experiments

N-tosylhydrazone **1b** (1 equiv, 2 mmol) and sodium ethoxide (1.5 equiv, 3 mmol) were added to the round bottom flask, 4 ml water was added, stirred overnight, and the corresponding *N*-tosylhydrazone anion **1e** were obtained by filtration. And then, solutions containing equal molar concentrations of **1e** (0.50 M in DMSO-d_6) and DBU (0.50 M in DMSO-d_6) were prepared and then mixed to cover acceptor/donor ratio from 0%, 10%, 20% to 100% donor (from 1 to 11 in Figure S6).

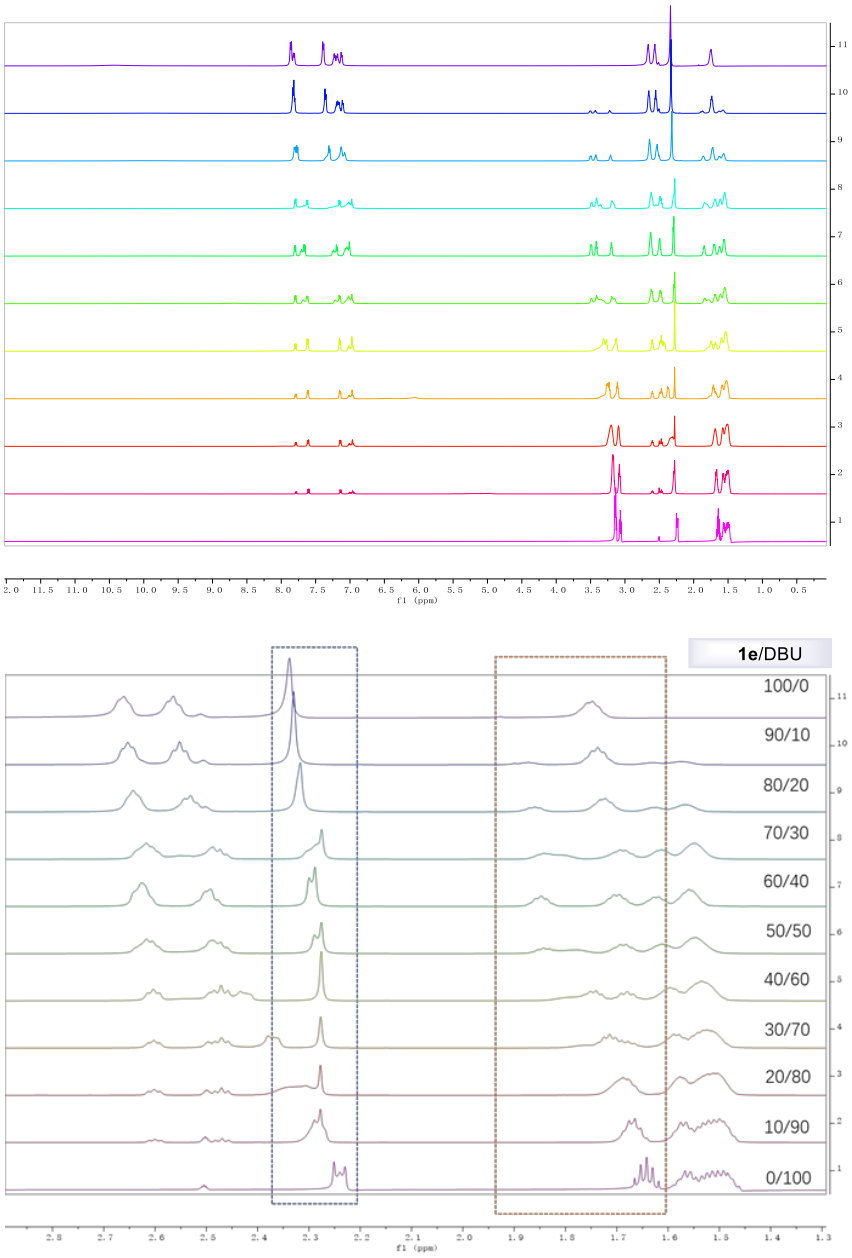


Figure S6. Titration of DBU into **1e**.

On-off experiments

An NMR toube was charged with 0.2 mmol of *N*-tosylhydrazone (1.0 equiv), 0.3 mmol of alkene (1.5 equiv), 0.6 mmol of DBU (3.0 equiv), 0.6 mmol (3.0 equiv) of H_2O. After purging the tube three times under vacuum and three times under argon, it was charged with tetrahydrofuran-*d*8 (0.5 mL) and wrapped with parafilm carefully. Then the mixture was irradiated by 40 W 456 nm Kessil lamps reaction setup at room temperature. After 1 h, the Kessil lamps were turned off, and the NMR yield was measured immediately. Then the tube was reacted in the darkness for an additional 1 h and subsequently measure the NMR yield. Then the NMR tube was put e back to the Kessil lamps setup and irradiate 1 h and further measure the NMR yield once again. So repeatedly, we got the results underneath.

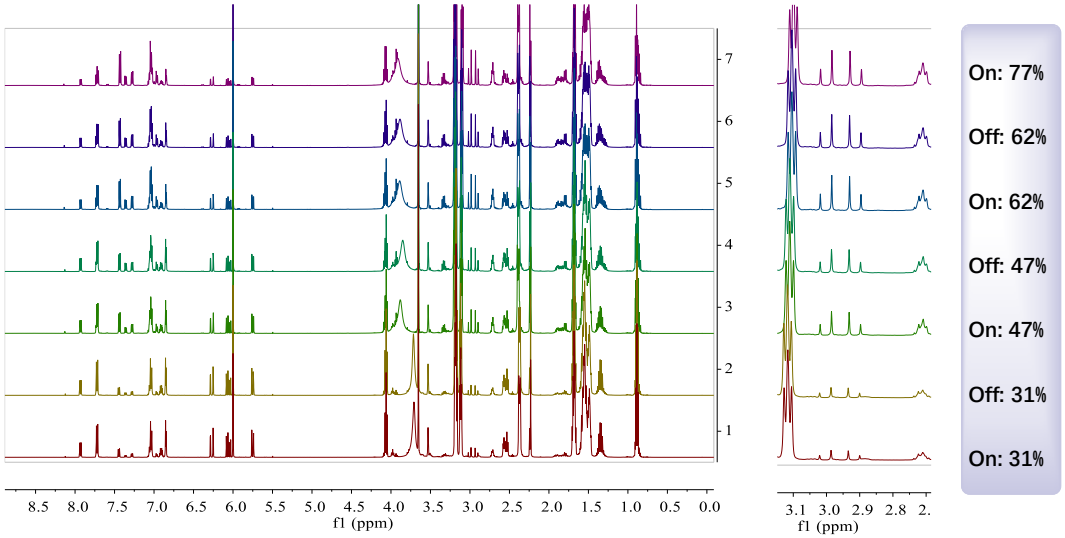
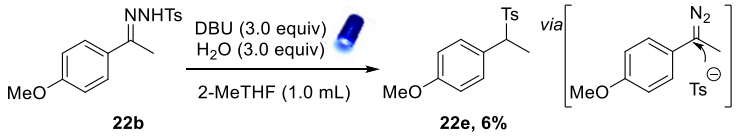
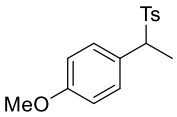


Figure S7. The comparison of On-off experiment yields determined by hydrogen spectrometry.

Determination of sulfonyl anion



A dry 5 mL Schlenk tube containing a stirring bar was charged with 0.2 mmol of *N*-tosylhydrazone (1.0 equiv), 0.6 mmol of DBU (3.0 equiv), 0.6 mmol (3.0 equiv) of H_2O. After purging the flask three times under vacuum and three times under argon, it was charged with 2-Methyltetrahydrofuran (1.0 mL). The reaction was kept for 5 h and 16 h under 40 W Kessil lamp reaction setup. Then, the resulting mixture underwent an aqueous workup (using distilled water) and was extracted three times with dichloromethane.[8] The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo*. Then the product was purified by column chromatography and determined by NMR and HR-MS.

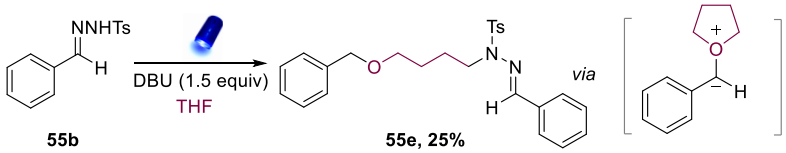


1-methoxy-4-(1-tosylethyl)benzene (22e): Prepared according to the general procedure . Following the workup, the product was purified by column chromatography (hexane: EtOAc, 10:1) to give the title compound as a colorless oil (6% yield).

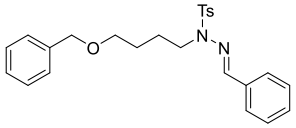
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 (d, *J* = 8.3 Hz, 2H), 7.22 (dt, *J* = 7.9, 0.7 Hz, 2H), 7.11 – 7.06 (m, 2H), 6.83 – 6.78 (m, 2H), 4.19 (q, *J* = 7.2 Hz, 1H), 3.81 (s, 3H), 2.42 (s, 3H), 1.73 (d, *J* = 7.2 Hz, 3H).

HRMS (ESI+), *m/z*: calculated for [$C_{16}H_{18}O_3SNa^+$]: 313.0869, found: 313.0874.

Carbene trapping experiment



A dry 5 mL Schlenk tube containing a stirring bar was charged with 0.2 mmol of *N*-tosylhydrazone (1.0 equiv), 0.3 mmol of DBU (1.5 equiv). After purging the flask three times under vacuum and three times under argon, it was charged with Tetrahydrofuran (1.0 mL). The reaction was kept for 16 h under 40 W Kessil lamp reaction setup (the progress can be monitored *via* TLC). Then, the resulting mixture underwent an aqueous workup (using distilled water) and was extracted three times with dichloromethane. The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo*. Then the product was purified by column chromatography and determined by NMR and HR-MS.



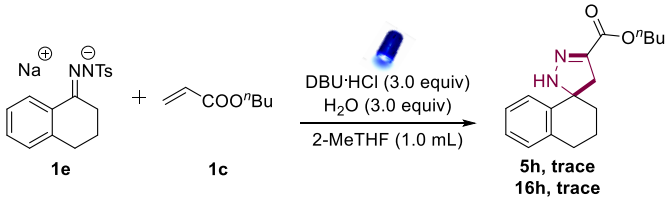
***N*'-(5-(Benzyloxy)-1-phenylpentylidene)-4-methylbenzenesulfonohydrazide (55e):** Prepared according to the general procedure . Following the workup, the product was purified by column chromatography (hexane: EtOAc, 3:1) to give the title compound as a colorless oil (25% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 (s, 1 H), 7.74 (m, 2 H), 7.61 (dt, *J*=8.6, 3.9 Hz, 2 H), 7.39–7.36 (m, 3 H), 7.32 (d, *J*=4.0 Hz, 4 H), 7.28 (d, *J*=8.0 Hz, 3 H), 4.49 (s, 2 H), 3.59 (t, *J*=6.7 Hz, 2 H), 3.52 (t, *J*=5.6 Hz, 2 H), 2.40 (s, 3 H), 1.74–1.70 (m, 4 H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 151.6, 145.3, 139.9, 135.8, 135.4, 131.8, 130.9, 130.1, 129.8, 129.6, 129.1, 129.1, 129.0, 74.4, 71.0, 49.8, 28.3, 26.0, 23.0.

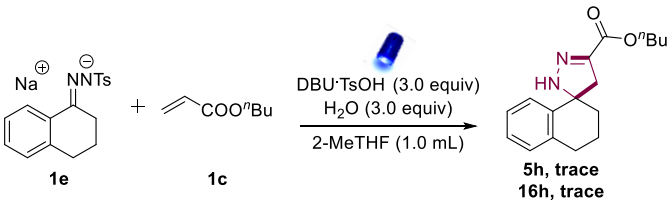
HRMS (ESI+), *m/z*: calculated for [$C_{25}H_{28}N_2O_3S$]: 436.1821, found: 436.1819.

Control experiments



1e **1c** **5h, trace** **16h, trace**

A dry 5 mL Schlenk tube containing a stirring bar was charged with 0.2 mmol of *N*-tosylhydrazone anion (1.0 equiv), 0.3 mmol of alkene (1.5 equiv), 0.6 mmol of DBU·HCl (3.0 equiv), 0.6 mmol (3.0 equiv) of H_2O. After purging the flask three times under vacuum and three times under argon, it was charged with 2-Methyltetrahydrofuran (1.0 mL). The reaction was kept for 5 h and 16 h under 40 W Kessil lamp reaction setup. Then, the resulting mixture underwent an aqueous workup (using distilled water; or brine in case of slurry phase separation) and was extracted three times with dichloromethane. The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo*. The crude sample was further analysed *via* ^{1}H NMR and trace amount of product was detected.

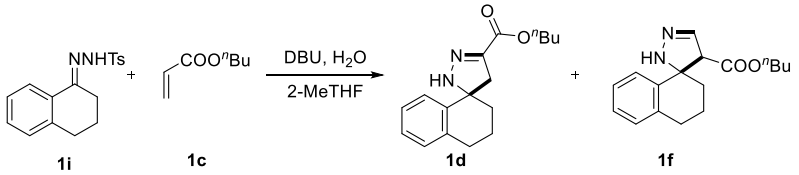


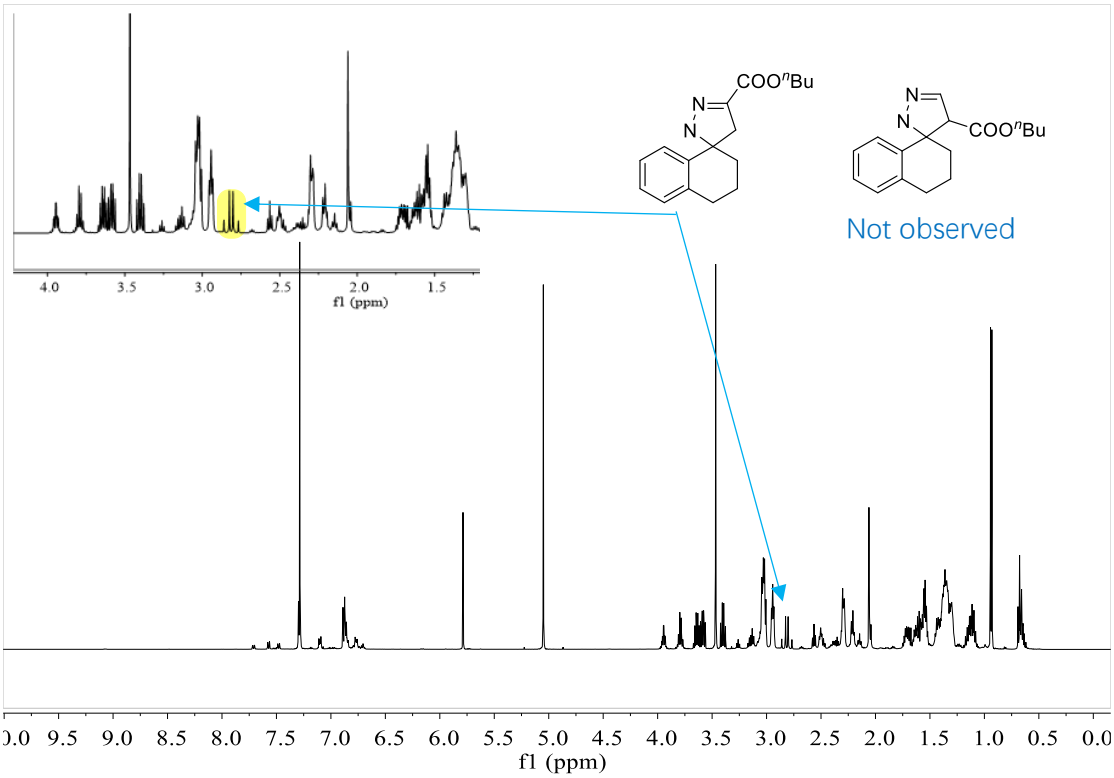
1e **1c** **5h, trace** **16h, trace**

A dry 5 mL Schlenk tube containing a stirring bar was charged with 0.2 mmol of *N*-tosylhydrazone anion (1.0 equiv), 0.3 mmol of alkene (1.5 equiv), 0.6 mmol of DBU·TsOH (3.0 equiv), 0.6 mmol (3.0 equiv) of H_2O. After purging the flask three times under vacuum and three times under argon, it was charged with 2-Methyltetrahydrofuran (1.0 mL). The reaction was kept for 5h and 16 h under 40 W Kessil lamp reaction setup, respectively. Then, the resulting mixture underwent an aqueous workup (using distilled water; or brine in case of slurry phase separation) and was extracted three times with dichloromethane. The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo*. The crude sample was further analysed *via* ^{1}H NMR and trace amount of product was detected.

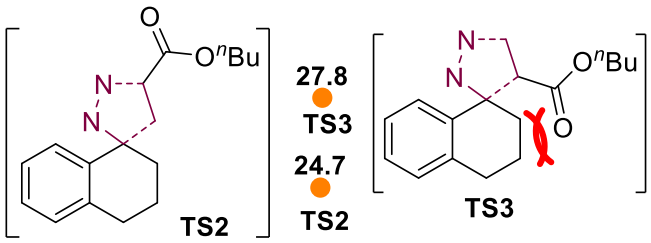
The regioselectivity of the [3+2]-cycloaddition

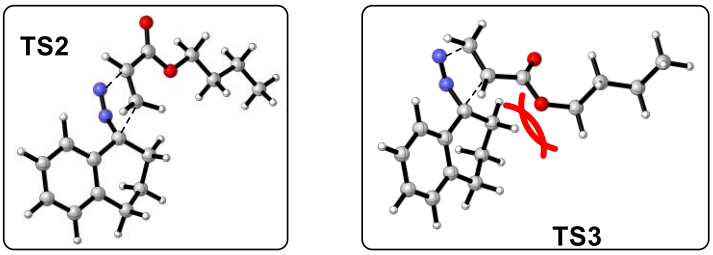
To determine the regioselectivity, we analyzed the crude simple under the standard conditions *via* NMR. From the ^{1}H NMR, assignment **1f** is not observed and 90% **1d** was identified.

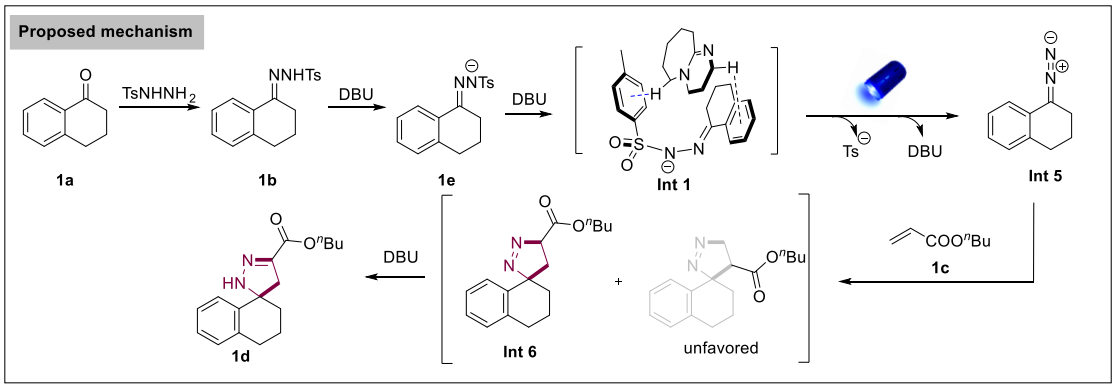




The regioselectivity for the [3+2]-cycloaddition has been reported in the literature reports.[9-10] The donor/donor diazo compounds serve as 1,3-dipoles and alkenes serves as dipolarophiles. Since the alkenes in our systems have electron-deficient groups, the electron-deficient dipolarophiles generally facilitate the [3+2]-cycloaddition to form the **1d** selectively according to calculating frontier molecular orbitals of 1, 3 dipoles and dipolarophiles.[5,11] We also give the proposed mechanism for the [3+2] cycloaddition as shown in below:


27.8
TS3
24.7
TS2
TS2
TS3


TS2
TS3


Proposed mechanism
TsNHNH2
DBU
DBU
DBU
Ts
DBU
1a
1b
1e
Int 1
Int 5
1c
DBU
1d
Int 6
unfavored

Determination of light intensity

Determination of the light intensity at 456 nm:

Standard ferrioxalate actinometry was used to determine the photon flux of the 40 W 456 nm Kesseil lamp.[12-13] A 0.15 M solution of ferrioxalate was prepared by dissolving potassium ferrioxalate trihydrate (646.5 mg, 1.5 mmol) in 0.20 M aqueous H_2SO_4 (10.0 mL). A buffered solution of 1,10-phenanthroline (0.15 M) was prepared by dissolving NaOAc (1.23 g, 15.0 mmol) and 1,10-phenanthroline (540.6 mg, 3.0 mmol) in 0.2 M aqueous H_2SO_4 (20 mL). To a 10 mL Schlenk tube was added the ferrioxalate solution (1.0 mL) and the tube was sealed and irradiated with a Kessil Lamp (40 W 456 nm) for 300 s while maintaining the temperature at room temperature through cooling with a fan. The aqueous sulfuric acid (3.0 mL) and buffered solution (4.0 mL) were added immediately. The resulting mixture was then placed in the dark for 1 h to allow the formed ferrous ions to react completely with the 1,10-phenanthroline. An aliquot (25 μL) of the resulting solution was diluted with 0.20 M aqueous sulfuric acid (3.0 mL), the solution was transferred to a cuvette (l = 1.0 cm) and the absorbance at a wavelength of 510 nm was measured by UV-Vis spectrometry. The above procedure was repeated three times, and the average absorption was used for the calculation of the photon flux. A nonirradiated sample was also prepared and the absorbance at 510 nm was measured. The photon flux was calculated as follows:

$$\text{mol Fe}^{2+} = \frac{V \times \Delta A\ (510\ \text{nm})}{l \times \varepsilon} \quad (1)$$

where V is the total volume (0.00325 L) of the solution that was analyzed, ΔA (0.48201) is the difference between the average absorption of irradiated and non-irradiated solutions at 510 nm, l is the path length (1.00 cm), and ε is the molar absorptivity of the ferrioxalate actinometer at 510 nm (11,100 $L \cdot mol^{-1} \cdot cm^{-1}$)[14].

The photon flux was calculated as follows:

$$\text{photon flux} = \frac{\text{mol Fe}^{2+}}{\phi \times t \times f} \quad (2)$$

where Φ is the quantum yield for the ferrioxalate actinometer (approximated as 0.965, which was the average value from the reported at λ = 436 nm and λ = 468 nm[3]), t is the irradiation time (300 s), and f is the fraction of light absorbed at λ = 456 nm by the ferrioxalate actinometer. This value was calculated using the following equation where A (456 nm) is the absorption of the ferrioxalate solution at 456 nm.

$$f = 1\text{-}10^{-A(456\text{nm})} = 0.62284 \quad (3)$$

The average photon flux was thus calculated to be 7.8×10^{-8} einstein s^{-1}.

Sample calculation:

$$\text{mol Fe}^{2+} = \frac{V \times \Delta A\ (510\ \text{nm})}{l \times \varepsilon} = \frac{0.00325\ \text{L} \times 0.48201}{1.0\ \text{cm} \times 11100\ \text{L mol}^{-1}\text{cm}^{-1}} = 1.4 \times 10^{-7}$$

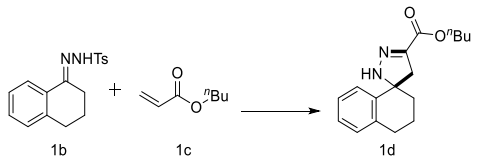
$$\text{photon flux} = \frac{\text{mol Fe}^{2+}}{\phi \times t \times f} = \frac{1.4 \times 10^{-7}}{0.965 \times 300\ \text{s} \times 0.62284} = 7.8 \times 10^{-10}\ \text{einstein s}^{-1}$$

Determination of quantum yield:

A dry 5 mL Schlenk tube containing a stirring bar was charged with 0.2 mmol of *N*-tosylhydrazone (1.0 equiv), 0.3 mmol of alkene (1.5 equiv), 0.6 mmol of DBU (3.0 equiv) and 0.6 mmol (3.0 equiv) of H_2O. After purging the flask for three times under vacuum and three times under argon, it was charged with 2-Methyltetrahydrofuran (1.0 mL). The sample was stirred and irradiated (λ = 456 nm, slit width = 10.0 nm) for 3600 s (60 min). Then, the resulting mixture underwent an aqueous workup (using distilled water; or brine in case of slurry phase separation) and was extracted three times with dichloromethane. The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo*. Products were purified *via* flash column chromatography with ethyl acetate and hexane as solvents. The yield of product formed was determined by ^{1}H NMR based on a 1,3,5-trimethoxybenzene standard.

The quantum yield was determined using eq 4.

$$\phi = \frac{\text{mol product}}{\text{flux} \times t \times f} \quad (4)$$



1b 1c 1d

Experiment 1: 62.8 mg (0.2 mmol) *N*-tosylhydrazone, 44 μL (0.3 mmol) alkene, 90 μL (0.6 mmol) DBU, 11 μL (0.6 mmol) H_2O, 1.0 mL 2-MeTHF after 3600 s yielded 31% of **1d**. Φ(31%) = 53.6.

Sample quantum yield calculation:

$$\phi = \frac{0.2 \times 10^{-3}\text{mol} \times 0.31}{7.8 \times 10^{-10}\ \text{einstein s}^{-1} \times 3600\ \text{s} \times 0.41156} = 53.6$$

8. DFT calculation

Computational studies computational details:

All calculations were performed using Gaussian 16, Revision A.03 package.[15] All of the reactants, intermediates, transition states, products were optimized by the DFT with the M06-2X functional.[16] For geometry optimizations and frequency calculations, BS-I basis set system was employed. In BS-I, we employed def2-SVP basis sets[17] for all atoms. All the stationary structures were characterized with no imaginary frequency and the transition state structures (TSs) were characterized with a single imaginary frequency. Intrinsic reaction coordinate (IRC) calculations were performed on the TSs. The solvent effect of Tetrahydrofuran was evaluated through the SMD method[18], in which a better basis system BS-II was used. In BSII, we employed def2-TZVP basis sets[19] for all atoms. All reported energies are free energies at a concentration of 1 M and a temperature of 298.15 K.

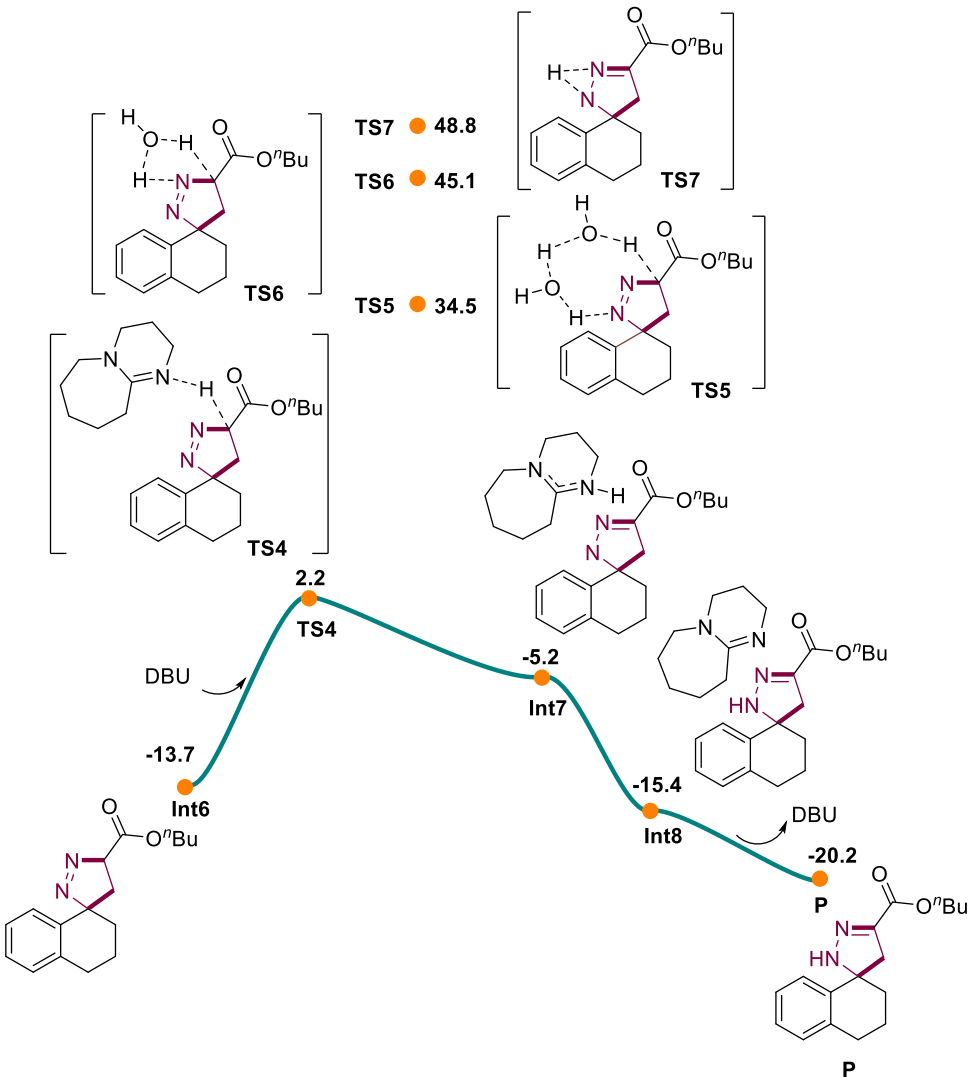


Figure S8. DFT calculated other transition states for the H-transfer process.

Cartesian coordinates of the optimized structures:

Int1

E = -1776.508374 a.u.

-1 1

C	-12.96598000	10.37372900	7.94251200
C	-11.63214400	10.45047000	7.55860200
C	-11.12774900	11.59906400	6.92040800
C	-12.00246100	12.68079000	6.67817400
C	-13.33672300	12.59385700	7.08371300
C	-13.82983100	11.44806500	7.70778000
H	-13.33639600	9.47268600	8.43625200
H	-10.93897700	9.62766800	7.73912400
C	-9.72798100	11.67826300	6.47683500
C	-11.45651200	13.89835700	5.97426900
H	-14.00097500	13.44271100	6.89799100
H	-14.87582900	11.39673000	8.01574800
C	-10.03179100	14.19043800	6.45163800
C	-9.10686300	13.01344100	6.14491800
H	-11.44499900	13.71146900	4.88355100
H	-9.64698300	15.10955800	5.98410600
H	-8.15015300	13.09132800	6.68671200
H	-8.81735000	13.01092900	5.07971600
H	-10.06165700	14.37016500	7.53942100
H	-12.12273900	14.75894000	6.13983000
N	-9.07286200	10.56734300	6.34772700
N	-7.83353000	10.64309400	5.87234600
S	-7.17514400	9.14555000	5.78986000
O	-7.23538000	8.40985300	7.05497300
O	-5.88679500	9.28498100	5.11434700
C	-8.23331500	8.20644200	4.66747600
C	-9.35167500	7.53864300	5.16375000
C	-7.93047800	8.16708000	3.30953000
C	-10.17708600	6.84054400	4.28508800
H	-9.54494400	7.56965600	6.23670800
C	-8.75968700	7.45723200	2.44097100
H	-7.03504600	8.68513300	2.95972500
C	-9.89713600	6.79214600	2.91321700
H	-11.05756500	6.31892500	4.66973800
H	-8.52054500	7.41784700	1.37464600
C	-10.82715900	6.08253300	1.96313500
H	-10.29624500	5.73933600	1.06439000
H	-11.29977200	5.21251300	2.44012000
H	-11.63444600	6.75711300	1.63387800
C	-12.64544100	11.86860200	2.39693000

N	-12.25861100	10.89688300	3.29035400
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C	-14.65999900	10.67440100	3.81700300
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H	-15.67022900	12.53226000	3.29371000
H	-13.01523900	10.52729300	5.21202900
H	-15.33109800	10.41446300	4.64919500
H	-14.32933100	12.70186900	4.44351600
C	-11.71971100	12.27706800	1.25726400
H	-11.15563700	13.17172500	1.57131800
H	-12.40858800	12.61794900	0.47488900
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H	-10.51541800	11.41989400	-0.31998900
H	-11.25715500	10.23311900	0.74999900
C	-9.46879100	11.15327300	1.56074100
H	-8.92229300	10.22307400	1.33620500
H	-8.80382100	11.98592900	1.27790500
C	-10.92192700	10.32925300	3.47262100
H	-10.84528300	9.35043900	2.95899700
H	-10.82421700	10.11522000	4.54823700
C	-9.76395500	11.22335700	3.05731400
H	-8.87693400	10.94400600	3.64721600
H	-10.00753400	12.25603700	3.35563800

TS1

E = -1776.471348 a.u.

-1 1

C	-12.51897100	10.36830700	8.06958700
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C	-12.08369300	12.78563000	6.71945200
C	-13.28307500	12.54682500	7.39451800
C	-13.52057900	11.34526800	8.06239000
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H	-10.51125300	9.83759800	7.44788200
C	-9.81129800	12.04067900	6.04119700
C	-11.84599400	14.08098000	5.97589000
H	-14.04988400	13.32791400	7.39118700
H	-14.46694800	11.17875800	8.58000500
C	-10.37164500	14.48099300	6.01527600
C	-9.52119000	13.37587800	5.39227100

H	-12.14957100	13.96736800	4.91787500
H	-10.21782500	15.43118900	5.48133300
H	-8.44610500	13.59631000	5.49704600
H	-9.72743200	13.35006800	4.30304500
H	-10.06257400	14.63409600	7.06252000
H	-12.48356800	14.87281800	6.40044700
N	-8.90017100	11.09424800	6.01907900
N	-7.81561900	10.80746300	5.63124000
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C	-9.50994500	7.40907500	4.88528800
C	-7.37440300	7.68175700	3.78018900
C	-10.03758200	6.86587900	3.71548600
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N	-12.41082000	10.94393700	3.50787400
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C	-14.79809400	11.23739200	4.04738400
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H	-15.21949400	10.85097400	3.10455800
H	-15.40671500	13.27591600	3.60254000
H	-13.22515200	10.68197600	5.43064100
H	-15.53156400	11.05750500	4.84713900
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H	-11.95245100	10.45777800	0.77795200
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H	-9.82644000	9.40783200	1.09124300
H	-8.96270600	10.94550100	1.15339100
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H	-11.61032900	9.05112400	3.06076300
H	-11.14992300	9.75219600	4.61934100
C	-9.95835400	10.43400900	2.98867600
H	-9.19443400	9.75224500	3.38862500
H	-9.70726100	11.42077500	3.40283500

^{3}Int1

E = -1776.434043 a.u.

-1 3

C	-13.06703700	9.90365900	7.13595800
C	-11.71137600	10.14838000	6.99752400
C	-11.18947500	11.47178400	7.09621300
C	-12.11383100	12.53927300	7.34868900
C	-13.46594900	12.26146800	7.48336600
C	-13.96381200	10.95327200	7.37768600
H	-13.43915600	8.87956600	7.05234000
H	-11.00850700	9.33726400	6.80862400
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C	-11.57940000	13.94827100	7.38912200
H	-14.15650200	13.09073300	7.66359600
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C	-10.19041400	13.98829400	8.02607100
C	-9.22837900	13.09113800	7.25334200
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H	-9.81033900	15.02070800	8.06089700
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H	-10.26640700	13.63266400	9.06703400
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H	-9.08432400	8.07379100	6.43720200
C	-9.13154000	7.17422100	2.66166400
H	-7.53979900	8.65648100	2.49035700

C	-10.03601800	6.53791100	3.51739700
H	-10.70268800	6.36591500	5.56449500
H	-9.12706700	6.91749700	1.59890200
C	-11.03191300	5.53577000	2.99265300
H	-10.76049000	5.19474100	1.98443600
H	-11.09610000	4.65595200	3.64913900
H	-12.03892100	5.97797200	2.93674700
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N	-12.05150300	11.24919100	2.82310100
C	-12.97263700	10.99086400	3.92553600
C	-14.41183300	11.27278600	3.54121900
C	-14.44124500	12.59533700	2.78438400
N	-13.61153300	12.53695400	1.60327900
H	-12.84723000	9.94013800	4.23784400
H	-14.79734700	10.48024200	2.87913100
H	-15.46857700	12.86148600	2.48907600
H	-12.68652600	11.60089500	4.80034300
H	-15.03056300	11.29204000	4.45037500
H	-14.09170700	13.39835900	3.46401500
C	-11.64252200	11.90709900	0.43707700
H	-10.98540100	12.79302000	0.44563300
H	-12.37144400	12.07803100	-0.36388200
C	-10.81331400	10.64814900	0.19109600
H	-10.67561600	10.49834400	-0.89112100
H	-11.37665400	9.77227000	0.55395600
C	-9.45358700	10.71373700	0.88612600
H	-9.00793100	9.70704600	0.92162000
H	-8.76363800	11.33977000	0.29633500
C	-10.71794000	10.70945600	3.10476200
H	-10.73420200	9.60419600	3.01056200
H	-10.51441900	10.91762400	4.16886000
C	-9.55944000	11.27894700	2.30153100
H	-8.63653300	11.08099400	2.86702700
H	-9.66101000	12.37607800	2.27728800

^{3}Int2

E = -1776.433431 a.u

-1 3

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N	-1.43942300	-1.27864800	2.36248100
S	-2.66260900	-0.78052300	1.20868100
O	-3.06947700	-1.95446300	0.43937300
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C	-1.81258300	0.32993200	0.11096400

C	-1.83956300	1.69947300	0.36170000
C	-0.94277900	-0.21582800	-0.83370500
C	-0.95370600	2.52699500	-0.32303200
H	-2.53844600	2.08753600	1.10524500
C	-0.04534900	0.62002200	-1.48756500
H	-0.95720200	-1.29214400	-1.01029900
C	-0.01637700	1.99380400	-1.21844100
H	-0.95753400	3.60272000	-0.12971300
H	0.68278900	0.19362900	-2.18113900
C	1.05522800	2.85971200	-1.82386200
H	0.78558500	3.92416100	-1.78476500
H	1.99547900	2.72264400	-1.26424400
H	1.25284800	2.58518000	-2.86968000
C	0.64389300	-0.20298300	2.02250700
C	1.86271900	-0.23853500	1.29099200
C	0.31249200	0.95420900	2.93801100
C	2.12453200	-1.25742200	0.32276700
C	2.86811500	0.76502700	1.48487500
C	1.15878800	2.18531100	2.62967000
H	-0.76427100	1.17560400	2.85685100
H	0.47256900	0.65865600	3.99436700
C	3.29834400	-1.25987100	-0.41634700
H	1.36939800	-2.03189700	0.17592600
C	4.02364400	0.74237800	0.71886400
C	2.63675700	1.80347700	2.55421700
H	0.99723400	2.95679200	3.39837400
H	0.84338500	2.60739000	1.66169800
C	4.26639500	-0.26358700	-0.23709000
H	3.46702100	-2.05415600	-1.14874800
H	4.77049000	1.52674400	0.88056000
H	2.94464000	1.39806500	3.53767700
H	3.26903200	2.68558900	2.36450700
H	5.18725900	-0.26320000	-0.82184300
C	3.42662700	-0.97276400	5.14195000
N	3.27029600	-1.88671900	4.12632400
C	4.32612000	-2.05582800	3.13180500
C	5.63705600	-1.44951300	3.59698000
C	5.34892300	-0.06062700	4.15321200
N	4.37824500	-0.10827700	5.22293900
H	4.44609700	-3.13873700	2.95124900
H	6.08547900	-2.06853200	4.39196200
H	6.27096000	0.40836600	4.53257800
H	4.01419500	-1.60398300	2.17612700
H	6.34163600	-1.41286000	2.75313000

H	4.98346600	0.57946200	3.32887800
C	2.46626200	-0.98810100	6.32215000
H	1.57833600	-0.37751600	6.08959000
H	3.01297600	-0.45247400	7.10625300
C	2.04396700	-2.38417900	6.78394000
H	1.84877100	-2.37621200	7.86736100
H	2.88986200	-3.07450400	6.62956000
C	0.80972100	-2.89301400	6.03479500
H	0.74824300	-3.99096000	6.11691400
H	-0.10312500	-2.49465400	6.50644900
C	2.12691500	-2.75379900	3.84255600
H	2.42843100	-3.80797400	4.01730100
H	1.92881700	-2.65559000	2.76172600
C	0.82056600	-2.47617200	4.56765300
H	0.01978100	-2.98803500	4.01537300
H	0.57931600	-1.41032800	4.46172000

^{3}TS1

E = -1776.432198 a.u

-1 3

N	-0.24916000	-1.20191700	1.89907000
N	-1.40188200	-1.34318400	2.38966500
S	-2.80070600	-0.54521800	1.29066400
O	-3.51307500	-1.63649300	0.61499700
O	-3.55690900	0.39203400	2.13485800
C	-1.88788700	0.38716200	0.08611100
C	-1.66382800	1.74899900	0.28843900
C	-1.14881000	-0.32987000	-0.85779200
C	-0.66359500	2.38481800	-0.44091300
H	-2.25921500	2.27544600	1.03733700
C	-0.14388300	0.31759900	-1.56546400
H	-1.35261900	-1.39356300	-0.99446200
C	0.14215300	1.66957500	-1.33740000
H	-0.47164600	3.44959000	-0.28402900
H	0.47162500	-0.24508100	-2.27111900
C	1.34871100	2.30355500	-1.97374400
H	1.26957300	3.39959300	-1.99011100
H	2.24731000	2.03228000	-1.39340700
H	1.49830100	1.94605100	-3.00260700
C	0.59058100	-0.16041600	2.06012700
C	1.81267400	-0.11304200	1.32416200
C	0.21099700	0.93425500	3.02966900
C	2.11736000	-1.06697100	0.30955200
C	2.77810300	0.91101300	1.58339100

C	1.01969200	2.20758000	2.80252000
H	-0.87263700	1.12217200	2.94374200
H	0.36332400	0.58674200	4.07140200
C	3.29450300	-0.98883600	-0.42059100
H	1.38797100	-1.85488700	0.11419700
C	3.94286700	0.96912900	0.82877700
C	2.50919300	1.87958600	2.70827900
H	0.83255800	2.92488700	3.61610400
H	0.69463100	2.67929800	1.86170900
C	4.22597600	0.02850700	-0.17615400
H	3.49519200	-1.73463100	-1.19433600
H	4.66107800	1.76782300	1.04050400
H	2.83318700	1.42982200	3.66685200
H	3.11196100	2.79116200	2.56929700
H	5.15062500	0.09236000	-0.75155400
C	3.42513000	-0.97085600	5.14566200
N	3.29455500	-1.84508200	4.09144900
C	4.35116900	-1.93616500	3.08779300
C	5.64368000	-1.30743400	3.57432800
C	5.31330300	0.04515600	4.19279300
N	4.34866500	-0.08051200	5.26114700
H	4.50629900	-3.00555500	2.85992600
H	6.11581900	-1.94591600	4.33949400
H	6.22143100	0.52599700	4.59024800
H	4.01979000	-1.45410300	2.15351200
H	6.34302200	-1.21084800	2.73081600
H	4.92422300	0.71035400	3.39975700
C	2.46797100	-1.06467800	6.32433800
H	1.55931000	-0.47668700	6.11456200
H	2.99677600	-0.54065100	7.12823100
C	2.09481900	-2.49115600	6.73224400
H	1.90178100	-2.53150000	7.81524900
H	2.96348500	-3.14579200	6.55097800
C	0.87700700	-3.01261700	5.96540600
H	0.85273500	-4.11429500	6.00598200
H	-0.04775400	-2.66337900	6.45232100
C	2.18325200	-2.74299000	3.77813600
H	2.52390300	-3.79116900	3.91205900
H	1.97842700	-2.61176800	2.70189600
C	0.86977800	-2.54087700	4.51494600
H	0.08689700	-3.06160700	3.94573700
H	0.58870900	-1.48140600	4.44916100

^{3}Int3

E = -1776.455621 a.u

-1 3

N	-0.51372000	-1.37791300	2.33299000
N	-1.42993300	-1.89277400	2.90803100
S	-1.71038400	1.33697700	1.25122200
O	-3.01406800	0.62987200	1.06626600
O	-1.76360100	2.82011900	1.49650200
C	-0.90323200	1.20956300	-0.37845400
C	0.02141900	2.17688100	-0.76572700
C	-1.11501700	0.07673300	-1.15638800
C	0.74910800	1.99620900	-1.93780700
H	0.14857100	3.05720400	-0.13206700
C	-0.37929800	-0.09443800	-2.33004500
H	-1.85791500	-0.65164000	-0.82289100
C	0.56799900	0.85422000	-2.73029100
H	1.48350500	2.74763300	-2.24243700
H	-0.54001100	-0.98233100	-2.94811500
C	1.39972300	0.65084800	-3.97144500
H	1.01836500	-0.18392500	-4.57555500
H	1.40797800	1.55340700	-4.60053300
H	2.44656300	0.42618200	-3.71073000
C	0.10964400	-0.19261500	2.67344900
C	1.28069400	0.19000400	1.91508600
C	-0.25825900	0.49730900	3.95710400
C	1.63459300	-0.46966900	0.71583300
C	2.07268100	1.28289700	2.35130200
C	0.26728700	1.93099300	3.98703700
H	-1.35400400	0.46576600	4.06241400
H	0.15532700	-0.06811400	4.81802200
C	2.71914500	-0.04973100	-0.04099100
H	1.01552900	-1.30379100	0.38401900
C	3.14983400	1.69561100	1.56417600
C	1.76207700	1.95138900	3.67076700
H	0.08888400	2.37292100	4.97879400
H	-0.28651400	2.53152600	3.24918500
C	3.48382700	1.04455800	0.37533700
H	2.95818100	-0.56718700	-0.97265100
H	3.74281900	2.55185300	1.89862200
H	2.30848100	1.42191600	4.47525500
H	2.14810600	2.98253700	3.65785900
H	4.32708500	1.39308700	-0.22367700
C	3.41129800	-1.15661900	5.34469900
N	3.33272000	-1.80861900	4.13360300
C	4.27994000	-1.48213200	3.07166400

C	5.48598800	-0.73224600	3.60537500
C	4.99197600	0.37523500	4.52675100
N	4.17002200	-0.14750300	5.59397000
H	4.59532100	-2.42913300	2.59947700
H	6.13554800	-1.41373800	4.17923200
H	5.83902400	0.92308900	4.96899100
H	3.77412200	-0.88854700	2.29283800
H	6.07065300	-0.33266200	2.76374800
H	4.42139000	1.10879900	3.92786400
C	2.61107000	-1.67406800	6.52963800
H	1.58853400	-1.26318900	6.50133700
H	3.10438200	-1.21604700	7.39390600
C	2.56987300	-3.19879300	6.64833400
H	2.49872100	-3.48940800	7.70747100
H	3.52760900	-3.60491400	6.28290000
C	1.40733300	-3.81024200	5.86263800
H	1.60890200	-4.87571100	5.66332500
H	0.48856800	-3.77620900	6.46996600
C	2.38436100	-2.83296200	3.70187600
H	2.92938900	-3.79078300	3.56892700
H	2.04047500	-2.52736300	2.69801600
C	1.14809900	-3.07386500	4.55207900
H	0.43309700	-3.63885200	3.93719300
H	0.65019300	-2.11221200	4.73622800

Int4

E = -957.511537 a.u

0 1

C	-12.54543000	9.36592700	7.44276200
C	-11.33108200	9.80135700	6.92426800
C	-11.11645300	11.16075000	6.63694800
C	-12.14387600	12.09514300	6.89150200
C	-13.35286600	11.63422800	7.41814100
C	-13.56737200	10.28348200	7.68863100
H	-12.69222600	8.30659900	7.65809900
H	-10.53370100	9.07712500	6.74188800
C	-9.85072800	11.65041400	6.08579200
C	-11.92897000	13.56196300	6.59345000
H	-14.14397600	12.36013200	7.62284800
H	-14.52146500	9.95136800	8.09935000
C	-10.46242700	13.96166900	6.73901900
C	-9.60657900	13.11418100	5.80075100
H	-12.25061100	13.77837800	5.55793000
H	-10.33303000	15.02552600	6.49730800

H	-8.53756300	13.34715800	5.91125700
H	-9.89074400	13.35308600	4.75986200
H	-10.13150100	13.81215400	7.77904000
H	-12.56750900	14.16531400	7.25508600
N	-8.91858000	10.78769700	5.82203200
N	-8.11922200	10.01608500	5.58565400
C	-12.24116100	12.52456600	2.88869300
N	-12.12274700	11.19143800	3.23071100
C	-13.26009000	10.49613300	3.82922100
C	-14.55464800	11.25929800	3.62072700
C	-14.31795600	12.71952400	3.97998500
N	-13.22426700	13.28330900	3.22071600
H	-13.32708200	9.49746400	3.36506300
H	-14.86388100	11.19522300	2.56524900
H	-15.22037100	13.32035800	3.79137300
H	-13.07694500	10.33786500	4.90603200
H	-15.35050600	10.81197300	4.23313100
H	-14.11573100	12.79540800	5.06413900
C	-11.19624200	13.16916700	1.98877400
H	-10.33596200	13.52247900	2.58128500
H	-11.69832900	14.06756900	1.61449000
C	-10.71779400	12.27719800	0.84123500
H	-10.44817300	12.89753700	-0.02560300
H	-11.55824800	11.64411000	0.51342800
C	-9.52716400	11.40329900	1.24142100
H	-9.43985300	10.54765700	0.55323400
H	-8.59229300	11.97767100	1.14240400
C	-10.99246400	10.29274100	3.02601400
H	-11.25703600	9.54198000	2.25379700
H	-10.87954900	9.72747800	3.96965800
C	-9.64273900	10.90381900	2.67863300
H	-8.87700200	10.13762200	2.87115500
H	-9.43153900	11.72075300	3.38395200

Int5

E = -495.9655119 a.u

0 1

C	-12.45233200	9.37210800	7.41618500
C	-11.22808300	9.82688200	6.94233300
C	-11.02067600	11.19093500	6.67489200
C	-12.07323000	12.10484200	6.89670800
C	-13.29261200	11.62616800	7.37998800
C	-13.49470500	10.27264300	7.63818300
H	-12.59184600	8.30866000	7.61593700

H	-10.41751000	9.11423500	6.77533300
C	-9.73927900	11.70338100	6.18105400
C	-11.87938000	13.57699500	6.60782000
H	-14.10129700	12.33933200	7.55778300
H	-14.45680000	9.92304700	8.01424100
C	-10.42397100	14.01070200	6.76836300
C	-9.51906400	13.16630200	5.87317400
H	-12.20444800	13.79059600	5.57417100
H	-10.31253200	15.07414500	6.51420100
H	-8.46161200	13.42691400	6.02478100
H	-9.75635000	13.37890000	4.81577300
H	-10.11670400	13.88685300	7.81890800
H	-12.53416200	14.16687100	7.26556400
N	-8.76191000	10.86872500	5.99584000
N	-7.91347500	10.13155000	5.83944100

TS2

E = -919.8466849 a.u

0 1

C	-10.59155500	9.51527700	7.88726400
C	-9.47973900	9.99584600	7.20942600
C	-9.59358100	11.06957200	6.31349300
C	-10.84137400	11.68119600	6.10631300
C	-11.95419800	11.17626400	6.79097600
C	-11.83917800	10.10589000	7.67032200
H	-10.48951500	8.68034400	8.58144200
H	-8.50040900	9.53579700	7.36587800
C	-8.38709700	11.54199900	5.56624000
C	-10.99432700	12.86939600	5.18061100
H	-12.92667700	11.64933100	6.63550800
H	-12.72036300	9.73496100	8.19563000
C	-9.67828000	13.60779100	4.95391600
C	-8.61147700	12.60926200	4.51323100
H	-11.38221500	12.51836400	4.20820100
H	-9.80742700	14.39075000	4.19331800
H	-7.64975500	13.07850100	4.26513700
H	-8.95830000	12.09634900	3.60124200
H	-9.35831100	14.10253600	5.88495100
H	-11.75871100	13.54605200	5.58949800
N	-7.30453100	11.75056000	6.35899300
N	-6.26577700	11.39396600	6.66344500
O	-5.36401200	11.36501000	3.77200800
C	-5.07139900	10.25816800	4.50531400
C	-6.27768900	9.65026500	5.08044900

O	-3.93971300	9.87716800	4.65754300
C	-7.53733700	9.89459600	4.56059100
H	-8.34826200	9.20003300	4.78891200
H	-7.59976000	10.40262700	3.59712300
H	-6.08469700	8.84575400	5.78988700
C	-4.25539000	12.00747800	3.15869600
C	-4.76082800	13.22687500	2.41698300
H	-3.75393200	11.30205700	2.47642400
H	-3.51738700	12.27995600	3.92971100
C	-3.64446300	13.96591400	1.68552700
H	-5.53730400	12.91221000	1.70002000
H	-5.24962600	13.90677700	3.13501700
C	-4.14300900	15.20132500	0.94508500
H	-2.86520300	14.25544400	2.40974700
H	-3.15880100	13.27717600	0.97474000
H	-3.32525200	15.71765500	0.42394100
H	-4.90215500	14.93107000	0.19587900
H	-4.60393900	15.91808600	1.64115900

TS3

E = -919.8470561 a.u

0 1

C	-10.58236200	9.25255300	7.72274400
C	-9.53940300	9.94697000	7.12691400
C	-9.73624000	11.23725300	6.60987600
C	-10.99811200	11.84832100	6.71725400
C	-12.04085100	11.12922400	7.31448300
C	-11.84477400	9.84542800	7.81000800
H	-10.41541800	8.24983400	8.11784500
H	-8.55058400	9.48813800	7.05039800
C	-8.61664100	11.95223500	5.93733900
C	-11.23469200	13.25900800	6.22266200
H	-13.02227500	11.60125400	7.40183200
H	-12.67246000	9.30800900	8.27493400
C	-9.94286300	14.06444400	6.11759500
C	-8.93244400	13.27779000	5.28401100
H	-11.71172100	13.21371300	5.22788900
H	-10.13975200	15.04140800	5.65426300
H	-8.00234600	13.82797100	5.09289900
H	-9.38914900	13.05767200	4.30608700
H	-9.52993400	14.25112300	7.12176600
H	-11.95557700	13.75566000	6.88832600
N	-7.43164600	11.85942800	6.56501000
N	-6.41060400	11.31948500	6.55575100

O	-9.04074200	11.38565400	2.58890300
C	-7.86019800	11.43374000	3.24066700
C	-7.80372000	10.46509400	4.34649400
O	-6.98733400	12.21513700	2.94665800
C	-6.55993100	10.15252400	4.87237500
H	-6.40672400	9.21350100	5.40700400
H	-5.67570400	10.60123800	4.41611400
H	-8.66455400	9.80646700	4.46006300
C	-9.19485300	12.27101300	1.48367500
C	-8.51788100	11.73953800	0.23202500
H	-8.78587000	13.25835400	1.74753100
H	-10.27962800	12.35952400	1.33218600
C	-8.74754700	12.64523000	-0.97389900
H	-7.43880800	11.64742400	0.43038300
H	-8.90207600	10.72728800	0.02471000
C	-8.07597100	12.12003900	-2.23752200
H	-9.83117400	12.75643000	-1.14830900
H	-8.36842300	13.65520800	-0.74578200
H	-8.24735500	12.78668400	-3.09388500
H	-6.98942300	12.02757900	-2.09323000
H	-8.46148400	11.12421200	-2.50235700

Int6

E = -919.9134361 a.u

0 1

C	-10.58217900	9.27016800	7.78645800
C	-9.54226300	9.75943000	7.00574600
C	-9.70623900	10.89256200	6.19777900
C	-10.93720000	11.56740600	6.20435100
C	-11.98066300	11.06039800	6.99049300
C	-11.81542500	9.92307400	7.77172400
H	-10.43110700	8.38642600	8.40754500
H	-8.57425600	9.25187400	7.02951200
C	-8.51646400	11.39598800	5.38601900
C	-11.16108000	12.81867800	5.38374100
H	-12.93960300	11.58419300	6.99041700
H	-12.64250300	9.55138900	8.37842000
C	-9.85305200	13.50711900	5.01375100
C	-8.90772000	12.49100700	4.38930700
H	-11.70411800	12.54656100	4.46129200
H	-10.04129000	14.33713400	4.31806600
H	-7.97999700	12.95721100	4.02319600
H	-9.39622100	12.00923400	3.52546600
H	-9.38103800	13.92741200	5.91476400

H	-11.82223900	13.49939800	5.93987000
N	-7.57698900	12.02105600	6.37382600
N	-6.48683400	11.47247600	6.44095900
O	-5.27906500	11.69284300	3.93468000
C	-5.13365800	10.57025400	4.64459900
C	-6.36037900	10.31920700	5.50395800
O	-4.16388700	9.86900200	4.59739200
C	-7.67949400	10.27787200	4.72427700
H	-8.16865600	9.29992800	4.78635100
H	-7.51293800	10.51278800	3.66564800
H	-6.14768700	9.42330900	6.10225600
C	-4.17871300	12.06611700	3.10471500
C	-4.52813200	13.36399300	2.41066100
H	-3.98212600	11.25633400	2.38454000
H	-3.27917700	12.16734400	3.73145200
C	-3.40415200	13.85183200	1.50141000
H	-5.45083500	13.21952000	1.82486300
H	-4.75409800	14.12513500	3.17485200
C	-3.74687900	15.15955600	0.79753800
H	-2.48490800	13.97992500	2.09641100
H	-3.17750000	13.07479000	0.75265300
H	-2.92644500	15.49495900	0.14870800
H	-4.64571900	15.04657100	0.17331100
H	-3.94742800	15.95777600	1.52741500

TS4

E = -1381.438895 a.u

0 1

C	-9.17079100	8.54888100	7.87958200
C	-8.86947100	9.27995800	6.73545800
C	-9.80482400	10.12550600	6.12701900
C	-11.08982900	10.22189200	6.68917200
C	-11.38816500	9.47446100	7.83697600
C	-10.44558100	8.64737200	8.43829900
H	-8.41283500	7.90319100	8.33168300
H	-7.87898700	9.20985600	6.28915800
C	-9.37980500	10.97366900	4.93361400
C	-12.16636400	11.07933200	6.06071900
H	-12.39003400	9.55342000	8.26654600
H	-10.70420700	8.08155400	9.33463100
C	-11.60357200	12.14033700	5.12260000
C	-10.59304900	11.51074300	4.17184600
H	-12.84495500	10.41538000	5.49582600
H	-12.41977000	12.62076800	4.56390500

H	-10.23282400	12.24460400	3.43540000
H	-11.05785800	10.68116500	3.61056000
H	-11.08905800	12.91967700	5.70354700
H	-12.77651100	11.53579100	6.85470700
N	-8.65580900	12.17519900	5.50877600
N	-7.46696300	12.19684900	5.15243000
O	-5.10717700	12.17973000	3.72973100
C	-5.99443900	11.20662400	3.42438200
C	-7.07303700	11.07777400	4.39094400
O	-5.81957900	10.44740300	2.49265900
C	-8.33109500	10.30831300	4.01568000
H	-8.26922500	9.22119700	4.17074100
H	-8.57895500	10.46084200	2.95292200
H	-6.11493300	10.50305000	5.41257000
C	-3.97510200	12.27084400	2.88160900
C	-3.09958200	13.39871900	3.38634200
H	-4.30130500	12.44964100	1.84419000
H	-3.43385200	11.31019600	2.87906200
C	-1.85133000	13.59449800	2.53233300
H	-3.69484500	14.32583200	3.40742600
H	-2.81471700	13.18751300	4.43043200
C	-0.96335300	14.72599400	3.03710300
H	-1.27573700	12.65401400	2.50617200
H	-2.15174900	13.79549700	1.49058800
H	-0.07101100	14.85291700	2.40855800
H	-1.51011200	15.68068700	3.04331600
H	-0.62609800	14.53171300	4.06635000
C	-5.50952900	8.95126200	6.73979700
N	-5.53259600	8.57253000	8.03418800
C	-5.76900700	9.55772800	9.10076700
C	-6.22731800	10.90572700	8.57030200
C	-5.37206300	11.27040300	7.36689200
N	-5.46226500	10.20525700	6.38519200
H	-6.52941100	9.12990600	9.77392500
H	-7.28029300	10.86371300	8.25367400
H	-5.71801700	12.18971800	6.87538900
H	-4.83793500	9.66409400	9.68430900
H	-6.14760200	11.65613100	9.36782900
H	-4.31719200	11.40737700	7.65971400
C	-5.59437700	7.97153900	5.58774900
H	-4.56732600	7.75052200	5.25274000
H	-6.03995900	8.54185900	4.75709900
C	-6.36418000	6.68250500	5.86063800
H	-6.74949800	6.28746500	4.91066300

H	-7.25273800	6.91262000	6.47028300
C	-5.50038300	5.62822200	6.55191100
H	-6.14455200	4.84317900	6.97698500
H	-4.85123500	5.13255600	5.81359400
C	-5.36462600	7.21280800	8.55379600
H	-6.35211600	6.80328800	8.83825200
H	-4.79664900	7.32736900	9.48993900
C	-4.62724800	6.23285200	7.65118200
H	-4.22476000	5.43065900	8.28626300
H	-3.75204300	6.74541100	7.22193200

TS5

E = -1072.557686 a.u

0 1

C	-1.02947000	-1.30192400	3.54130600
C	-1.03440000	-1.17583300	2.15576800
C	-2.11438600	-0.59136700	1.47551700
C	-3.22324900	-0.14721200	2.21936700
C	-3.20805500	-0.28762300	3.61279100
C	-2.12380100	-0.85002100	4.27715700
H	-0.17575300	-1.75927300	4.04338500
H	-0.18506800	-1.56153500	1.58878800
C	-2.02850800	-0.35123200	-0.02954700
C	-4.45704800	0.42070900	1.55054400
H	-4.07429500	0.05666500	4.18335500
H	-2.13482400	-0.94232100	5.36421900
C	-4.19906900	0.91263900	0.13189700
C	-3.40820200	-0.13015600	-0.64770000
H	-5.22262000	-0.37500900	1.52418800
H	-5.15214600	1.13340300	-0.36989900
H	-3.26748700	0.18174700	-1.69335400
H	-3.94853600	-1.09272000	-0.65994900
H	-3.61466000	1.84434500	0.15639800
H	-4.87437700	1.22342000	2.17685500
N	-1.23951800	0.93218200	-0.18050900
N	-0.12217100	0.70430500	-0.70151700
O	2.23317800	-0.12120600	-1.81304200
C	3.27955100	-0.33896900	-2.75493400
C	1.17992500	-1.00619900	-1.85893600
C	4.17396100	0.88410100	-2.73949200
H	2.83593800	-0.50104600	-3.74894000
H	3.82749300	-1.25633600	-2.49008900
C	0.12804100	-0.63747500	-0.92680500
O	1.22237800	-1.99478200	-2.54609000

C	3.44305900	2.16202300	-3.14358900
H	5.02288400	0.70158800	-3.41826400
H	4.60784200	1.00313700	-1.73067000
C	-1.17525900	-1.39269500	-0.79090100
C	4.33373000	3.39680100	-3.08201300
H	3.04679300	2.03633700	-4.16487100
H	2.56408100	2.28807100	-2.49211600
H	-1.09281100	-2.34643600	-0.25355500
H	-1.60956600	-1.60945800	-1.78101800
H	5.20305500	3.29278100	-3.74870300
H	3.78878600	4.30278600	-3.38085000
H	4.71784000	3.55727600	-2.06298200
H	1.17529100	-0.43988900	0.35309200
O	1.92529500	0.10518800	0.92300700
H	2.41209000	0.45090600	0.14632800
H	-0.37596400	1.75846200	1.28822600
O	0.45999400	1.94342300	1.78599300
H	1.36124100	0.90895800	1.32559500
H	0.71694000	2.82694200	1.49237100

TS6

E = -996.1850212 a.u

0 1

C	-1.29141300	-1.52182500	3.68689700
C	-1.14533200	-1.27497100	2.32603800
C	-2.13993800	-0.61023600	1.59198400
C	-3.30788900	-0.19053700	2.25028400
C	-3.44543700	-0.45280300	3.61981500
C	-2.45250300	-1.10698900	4.33966400
H	-0.50808700	-2.04705400	4.23577200
H	-0.24508400	-1.61859600	1.81036900
C	-1.89615900	-0.29525700	0.11667900
C	-4.43395200	0.49896700	1.51093900
H	-4.35798100	-0.12882100	4.12629100
H	-2.58408400	-1.29698100	5.40593500
C	-3.98722800	1.10781300	0.18756500
C	-3.18581200	0.08560600	-0.60822600
H	-5.22653300	-0.24614500	1.32005900
H	-4.86079100	1.44782800	-0.38665100
H	-2.91821700	0.47212300	-1.60310900
H	-3.78051100	-0.83085400	-0.76298500
H	-3.35048300	1.98546900	0.37452500
H	-4.88282600	1.26175500	2.16439500
N	-0.99628700	0.91255100	0.14702500

N	0.12399100	0.60494500	-0.28903300
O	2.17769400	-0.09064300	-1.89792300
C	3.12324800	-0.30327700	-2.94024200
C	1.19073300	-1.01453500	-1.78370500
C	4.07073600	0.87828300	-2.95243300
H	2.58808800	-0.40377400	-3.89764200
H	3.65182200	-1.25270800	-2.76380400
C	0.30552600	-0.74799100	-0.65139300
O	1.11075700	-1.97013600	-2.51630400
C	3.37693900	2.20174600	-3.26247200
H	4.85852300	0.68193600	-3.69811600
H	4.57158400	0.94090100	-1.97172100
C	-1.06883600	-1.38058900	-0.61481400
C	4.33302200	3.38801900	-3.23917300
H	2.89302400	2.12940000	-4.25091700
H	2.56510900	2.35289200	-2.53439000
H	-1.11018400	-2.34657200	-0.09492500
H	-1.44311900	-1.54497500	-1.63830700
H	5.13935500	3.26213000	-3.97763600
H	3.81455800	4.32984800	-3.46600700
H	4.80433800	3.49416400	-2.25036600
H	1.61272300	-0.58887300	0.45775600
O	2.16974500	0.25537500	0.87107500
H	1.45936700	0.88193200	0.31426800
H	1.89721500	0.31852800	1.80110500

TS7

E = -919.8218672 a.u

0 1

C	-0.72766400	-1.31404200	3.19528600
C	-0.86104200	-1.00160400	1.84690900
C	-2.04343800	-0.43820200	1.34238500
C	-3.11138600	-0.18777000	2.22135100
C	-2.96496500	-0.51559600	3.57536000
C	-1.78919500	-1.07072200	4.06669900
H	0.20099800	-1.75187300	3.56376900
H	-0.02654300	-1.20469400	1.17198400
C	-2.11970000	-0.04223800	-0.13172000
C	-4.42534100	0.38873600	1.73969200
H	-3.79963400	-0.32378900	4.25414400
H	-1.69987200	-1.31419500	5.12644000
C	-4.31046200	1.07464400	0.38443300
C	-3.56290100	0.17309000	-0.58789700
H	-5.15686200	-0.43558100	1.66885500

H	-5.30947800	1.31983500	-0.00293800
H	-3.54144700	0.60552800	-1.59883000
H	-4.05959000	-0.81019100	-0.65645600
H	-3.75394100	2.01937600	0.48338200
H	-4.81766400	1.08052800	2.49980700
N	-1.38882100	1.26505700	-0.26580900
N	-0.22307400	1.00146000	-0.88503100
O	2.13556200	0.17858100	-1.99751300
C	3.34232000	-0.24372000	-2.63001300
C	1.15784400	-0.73480300	-1.93009200
C	4.28495800	0.94017100	-2.66774500
H	3.10668400	-0.60840000	-3.64251400
H	3.76478000	-1.09148900	-2.06967000
C	-0.05349700	-0.23065800	-1.28765500
O	1.26492600	-1.86339000	-2.34255600
C	3.74456400	2.11466900	-3.47852800
H	5.24480200	0.59948300	-3.08926200
H	4.49108300	1.26406200	-1.63411800
C	-1.33005700	-0.99706800	-1.06805700
C	4.69476900	3.30578900	-3.49228800
H	3.54929000	1.77832400	-4.51068100
H	2.77018600	2.41076100	-3.06083700
H	-1.15424700	-1.98717200	-0.62473400
H	-1.86206000	-1.15560100	-2.02076600
H	5.66844900	3.03183300	-3.92606100
H	4.28806600	4.13982400	-4.08056600
H	4.87865800	3.67368800	-2.47165400
H	-0.13297800	1.65099300	0.06882800

Int7

E = -1381.458926 a.u

0 1

C	-8.79308000	7.80415400	6.57857500
C	-8.77072600	8.88366100	5.69929700
C	-9.73559100	9.90279600	5.76703900
C	-10.75344400	9.80771300	6.73400100
C	-10.76484500	8.71480100	7.61196100
C	-9.79454800	7.71909800	7.54844300
H	-8.04587700	7.01076300	6.49072600
H	-7.98639600	8.95330000	4.94134300
C	-9.55962300	11.15304500	4.90836800
C	-11.84411400	10.85254000	6.82913200
H	-11.55935900	8.65058300	8.36005300
H	-9.83032000	6.87278100	8.23728900

C	-11.42863400	12.19265200	6.23241500
C	-10.83959400	11.98264700	4.84305800
H	-12.72968900	10.47500700	6.28723200
H	-12.29260700	12.87228500	6.19562300
H	-10.59178100	12.94447000	4.37069300
H	-11.57245000	11.47257200	4.19291700
H	-10.65918900	12.66306100	6.86375400
H	-12.15345400	10.96264300	7.87983500
N	-8.49564600	11.92748600	5.63982700
N	-7.40916500	11.85929300	4.96960100
O	-5.21121600	11.49112700	3.34221700
C	-6.42776000	11.06779400	2.86165700
C	-7.50248700	11.22865100	3.79045200
O	-6.51850600	10.57951200	1.75201200
C	-8.93914800	10.86232400	3.52175400
H	-9.07881800	9.81986400	3.19852200
H	-9.38642800	11.50201200	2.74067100
H	-6.28582900	11.78518500	6.34018800
C	-4.13070800	11.36919800	2.43816100
C	-2.87438100	11.85582600	3.13189500
H	-4.33579200	11.95815100	1.52906500
H	-4.02737400	10.32132800	2.10930800
C	-1.64694600	11.79614500	2.22855800
H	-3.03902300	12.88834100	3.48061500
H	-2.70247500	11.24548300	4.03542200
C	-0.37699300	12.27219700	2.92426600
H	-1.50915300	10.76278600	1.86876900
H	-1.82958100	12.40798200	1.32988900
H	0.49408600	12.22477700	2.25616000
H	-0.48314000	13.31257000	3.26621300
H	-0.15690200	11.65440800	3.80816100
C	-5.73203900	10.09854500	7.26660200
N	-5.98677300	9.26121600	8.27551200
C	-7.00015200	9.58519300	9.29222200
C	-7.88330100	10.74233200	8.87243800
C	-7.01441000	11.86970900	8.34650900
N	-6.17261200	11.33814300	7.28508700
H	-7.60842800	8.67899500	9.43421000
H	-8.55919100	10.43170100	8.06259400
H	-7.62559800	12.65813800	7.89512800
H	-6.48019000	9.79707900	10.24251500
H	-8.49166800	11.06822400	9.72618200
H	-6.38009000	12.29606900	9.14158300
C	-4.92722300	9.72343600	6.04775300

H	-3.87540400	9.99252100	6.24415500
H	-5.25684200	10.40109200	5.24707200
C	-5.04211200	8.26893600	5.60221800
H	-4.85522000	8.21555700	4.52049400
H	-6.08181200	7.93701900	5.74475200
C	-4.08454400	7.34877200	6.35671800
H	-4.38655800	6.30004000	6.21212300
H	-3.06849000	7.43992200	5.94256600
C	-5.41557900	7.92184100	8.46336400
H	-6.14609300	7.17307900	8.10795900
H	-5.34274500	7.79561500	9.55374600
C	-4.04376800	7.67580500	7.84944800
H	-3.57732400	6.84572200	8.39920600
H	-3.41254400	8.55718900	8.04337200

Int8

E = -1381.48068 a.u

0 1

C	-8.91964600	8.62658600	7.59334100
C	-8.73884100	9.57771900	6.59700400
C	-9.79619500	10.39423200	6.16643600
C	-11.04785900	10.27555100	6.78970300
C	-11.22772400	9.28824300	7.77131400
C	-10.18268600	8.46505500	8.17107400
H	-8.08427500	7.99820500	7.90924900
H	-7.75580000	9.69893500	6.13242400
C	-9.52631400	11.39499900	5.04120900
C	-12.18091400	11.22115700	6.45916500
H	-12.20772200	9.19166900	8.24518600
H	-10.34454500	7.70900200	8.94116400
C	-11.66235700	12.51145900	5.83511400
C	-10.79373700	12.15976000	4.63707800
H	-12.87687800	10.73328600	5.75419400
H	-12.49894200	13.15782000	5.53434500
H	-10.47911200	13.05086900	4.07616700
H	-11.38034500	11.52644300	3.94975300
H	-11.06580400	13.07384900	6.57351600
H	-12.75783000	11.42181400	7.37446600
N	-8.45141200	12.33129200	5.46087900
N	-7.29853600	12.09435500	4.84346400
O	-5.16484200	11.26623800	3.35915500
C	-6.36141900	10.76207200	3.03564600
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C	-2.81835400	11.50848500	3.06624200
H	-4.27574900	11.12499400	1.49752400
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C	-1.58509300	11.12972400	2.25242800
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H	-0.39974500	12.88489500	2.74726500
H	-0.11795600	11.49650300	3.81604000
C	-7.02052700	11.77088800	8.68588800
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H	-10.35019600	11.88656800	10.52550900
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C	-5.28200400	10.14505400	7.66650900
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P

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0 1

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H	-0.90274100	1.66795200	0.76297300

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Peng, B.; Petrone, A.; Henderson, T.; Ranasinghe, D.; Zakrzewski, V. G.; Gao, J.; Rega, N.; Zheng, G.; Liang, W.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Throssell, K.; Montgomery, J. A.; Jr., Peralta, J. E.; Ogliaro, F.; Bearpark, M. J.; Heyd, J. J.; Brothers, E. N.; Kudin, K. N.; Staroverov, V. N.; T. A. Keith, T. A.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A. P.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Millam, J. M., Klene, M.; Adamo, C.; Cammi, R.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Farkas, O.; J. B. Foresman, J. B.; Fox, D. J.; Gaussian, Inc., Wallingford CT, **2016**.

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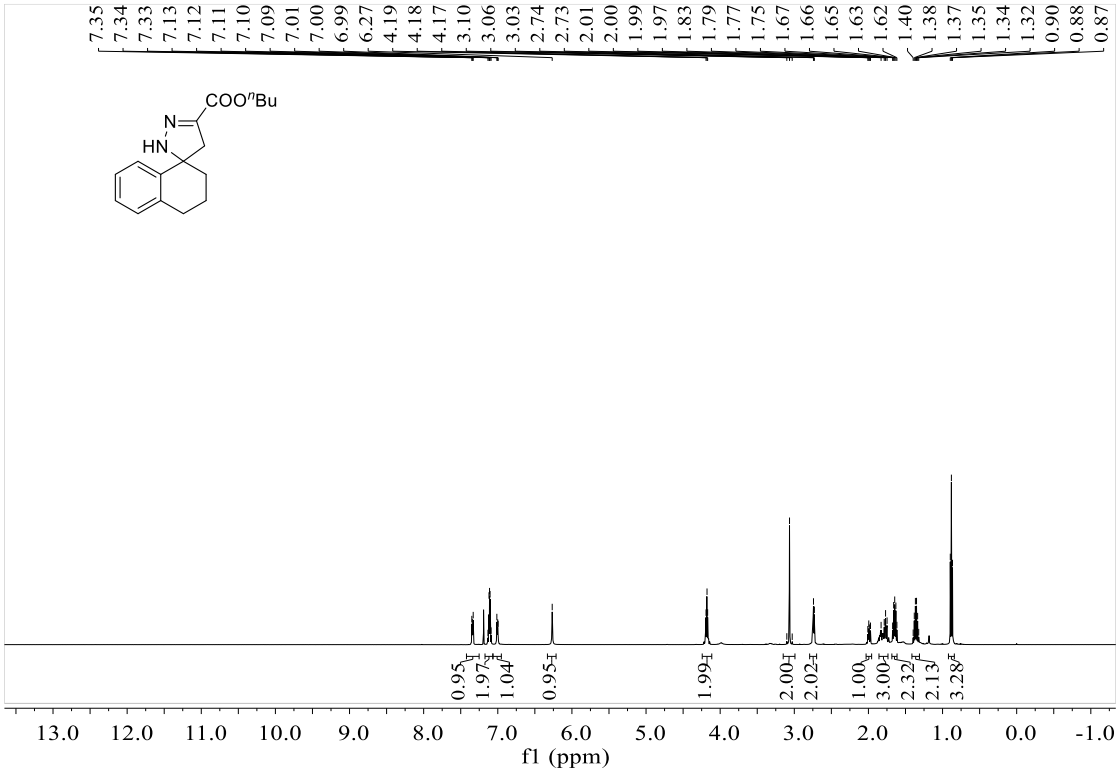
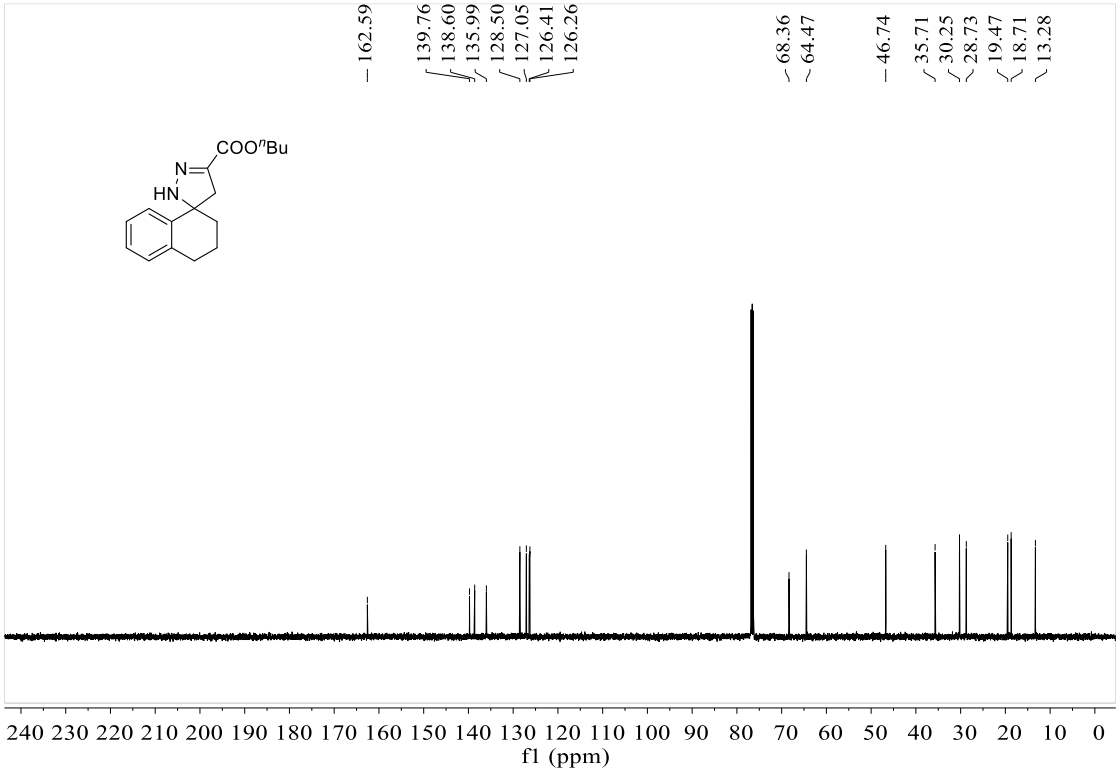
10. NMR spectra of products and synthesized substrates

^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (126 MHz, $CDCl_3$) spectra for 1d:





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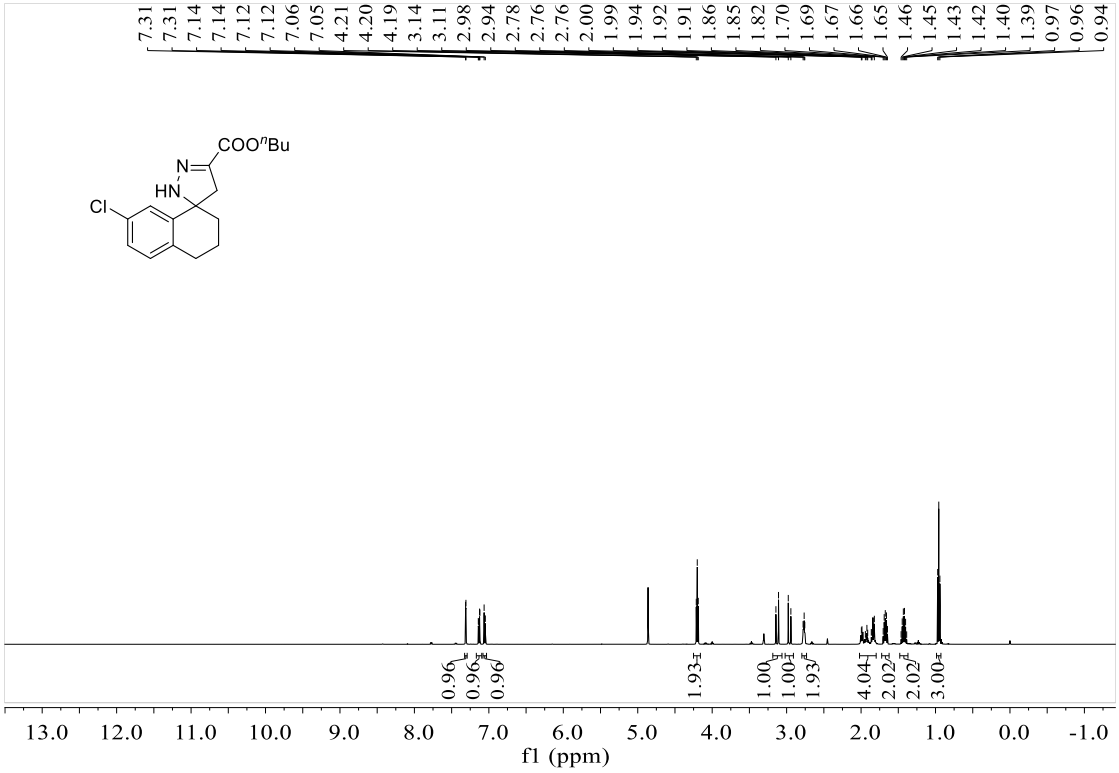

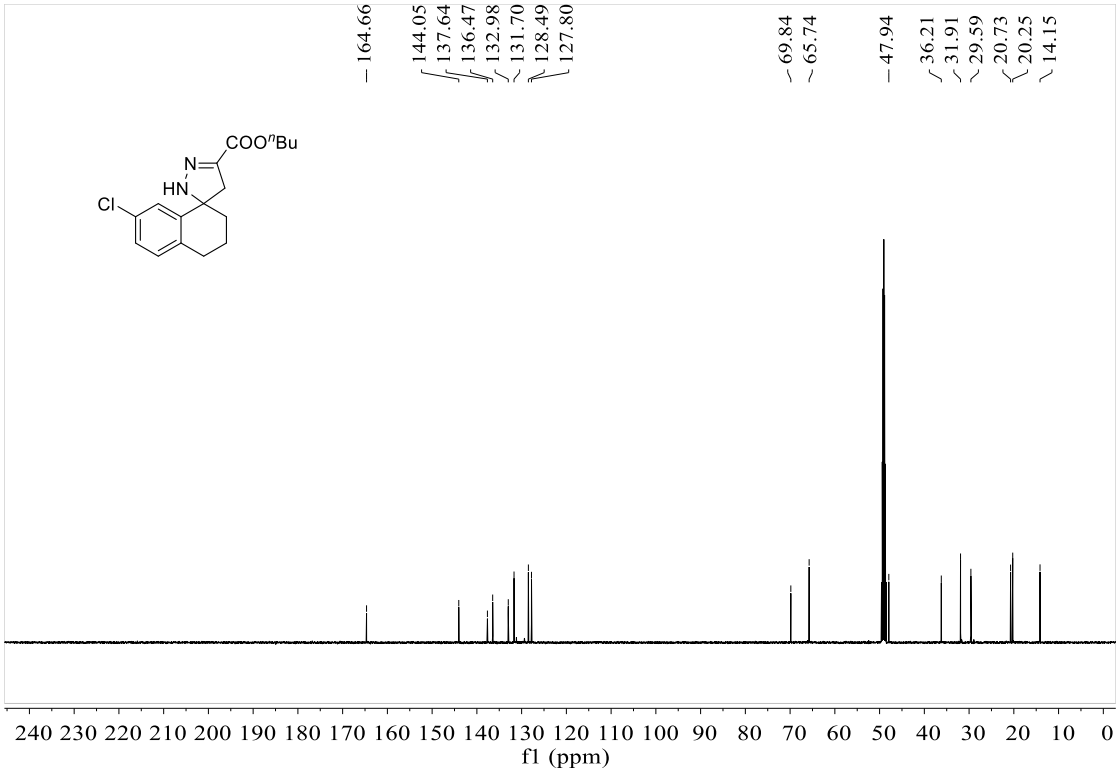

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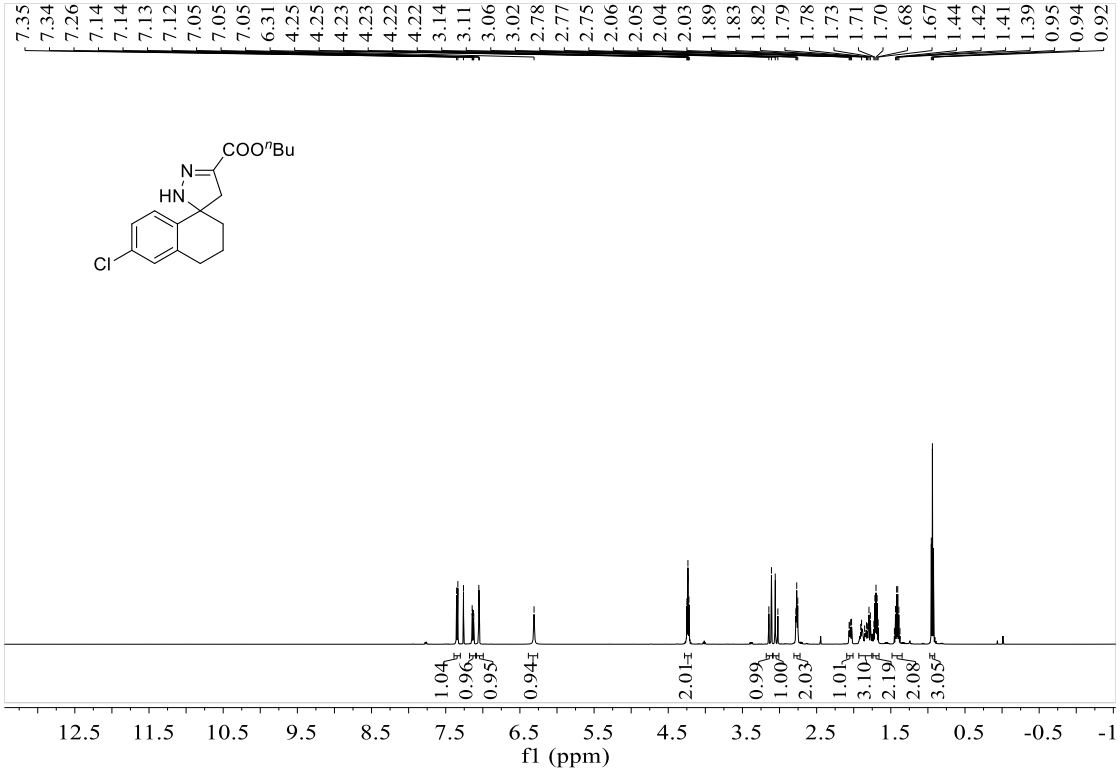
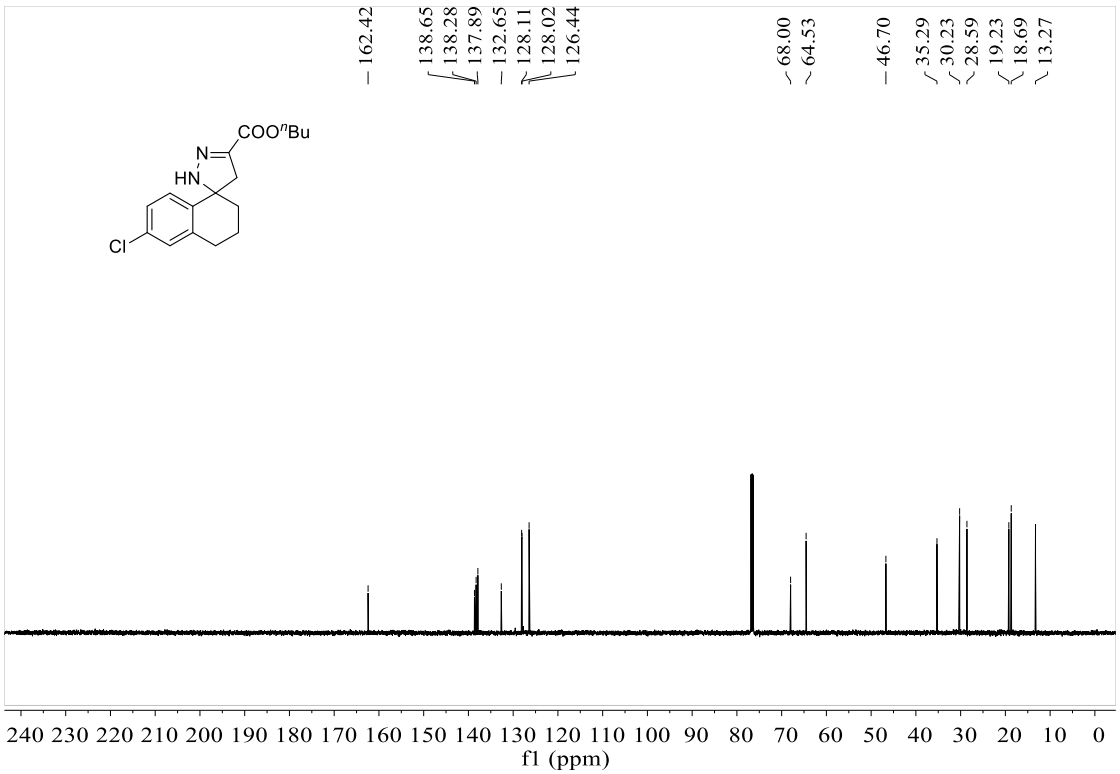
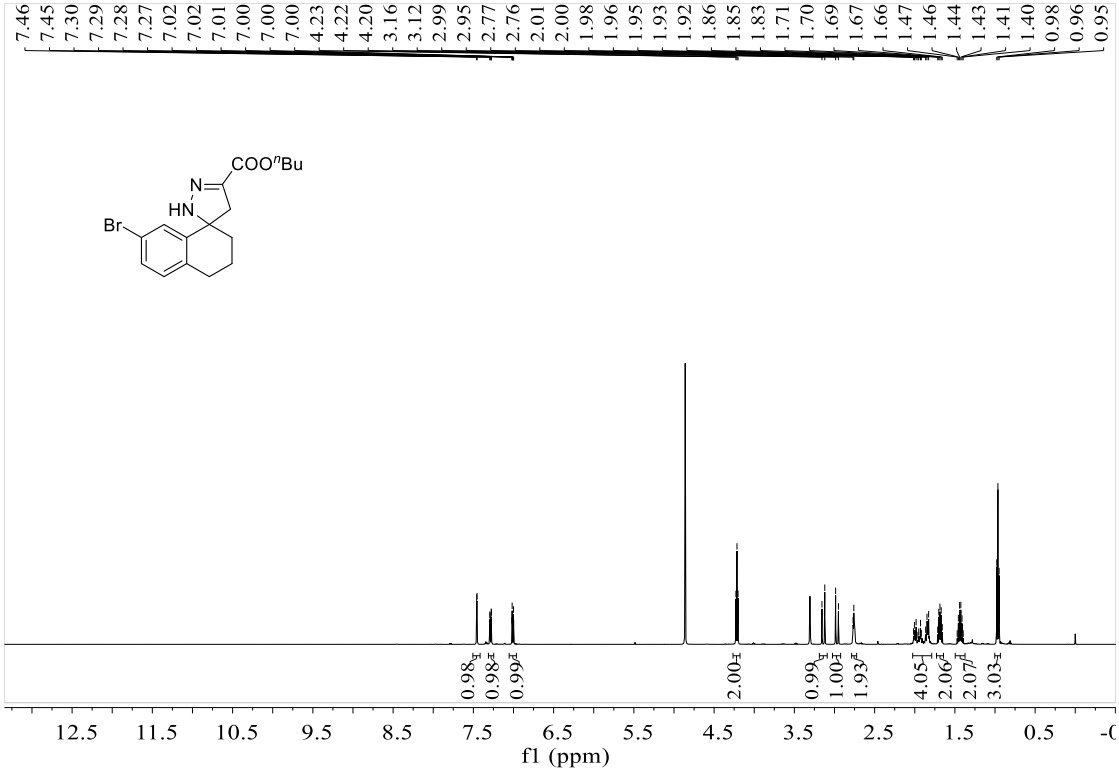
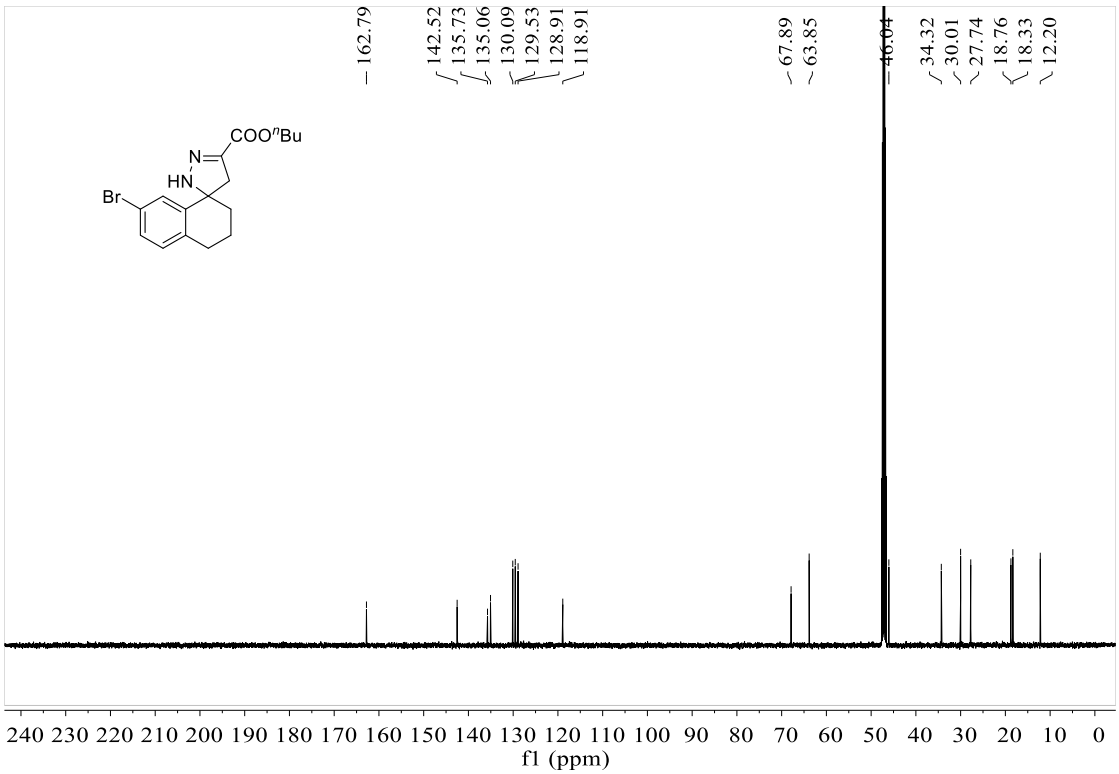




^{1}H NMR (500 MHz, CD_3OD) and ^{13}C NMR (126 MHz, CD_3OD) spectra for 4d:





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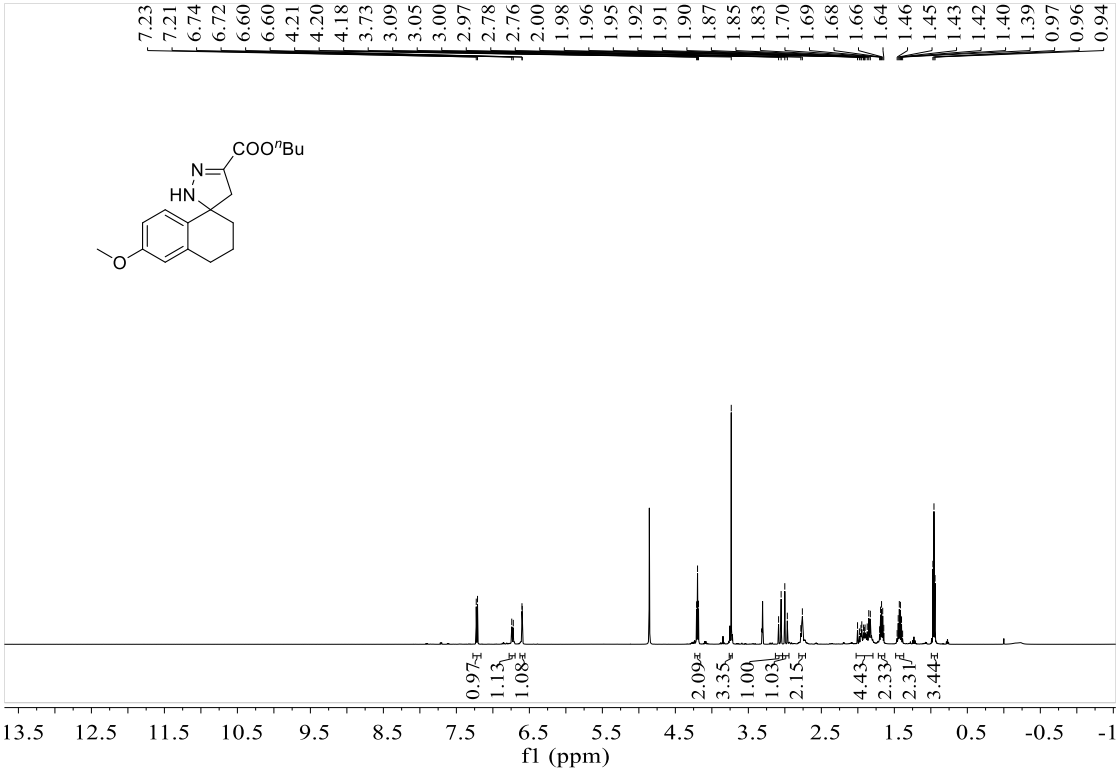

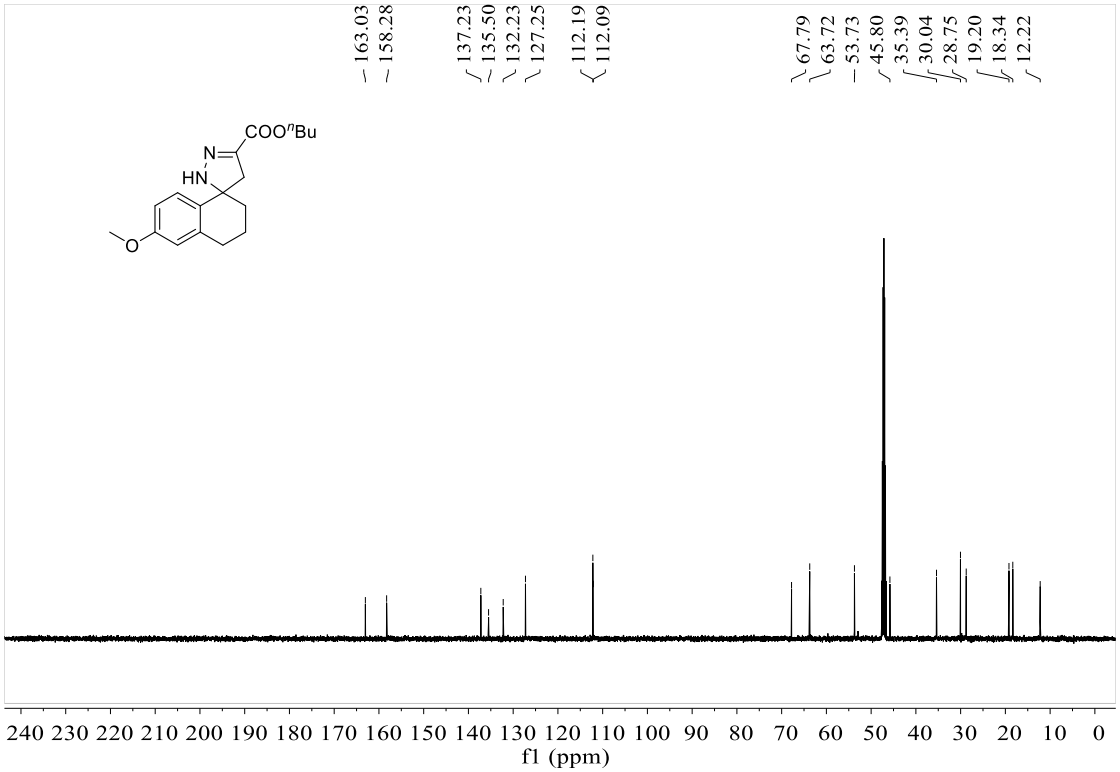

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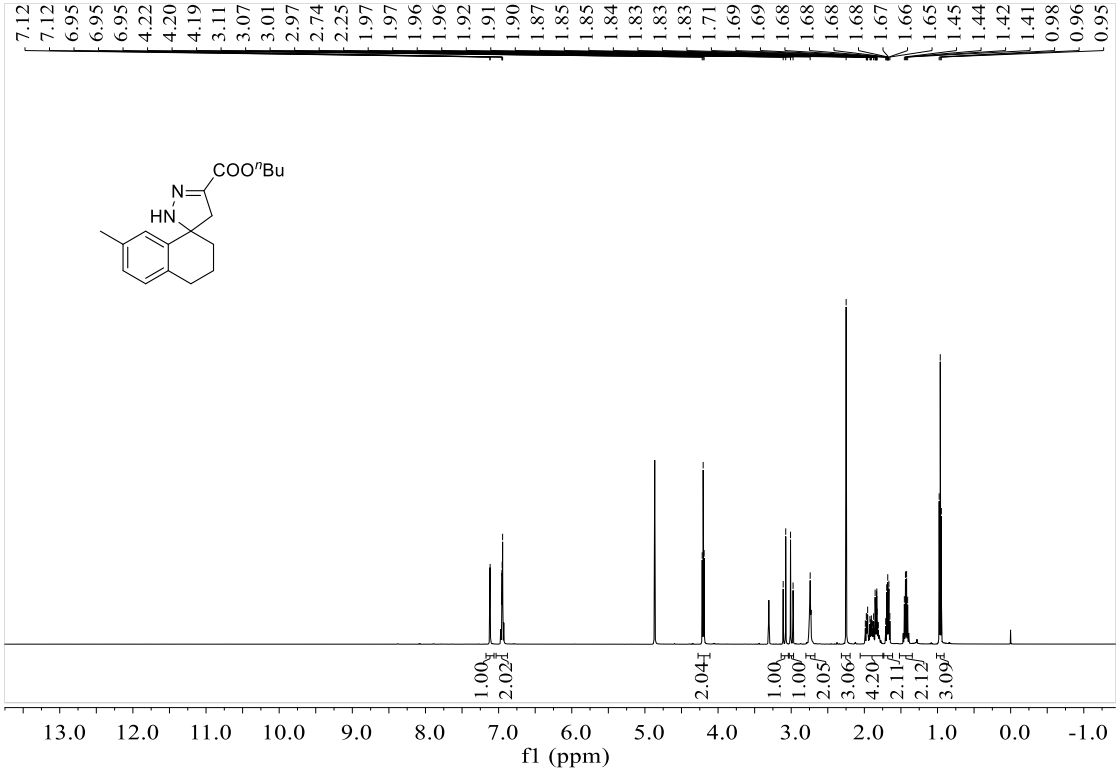

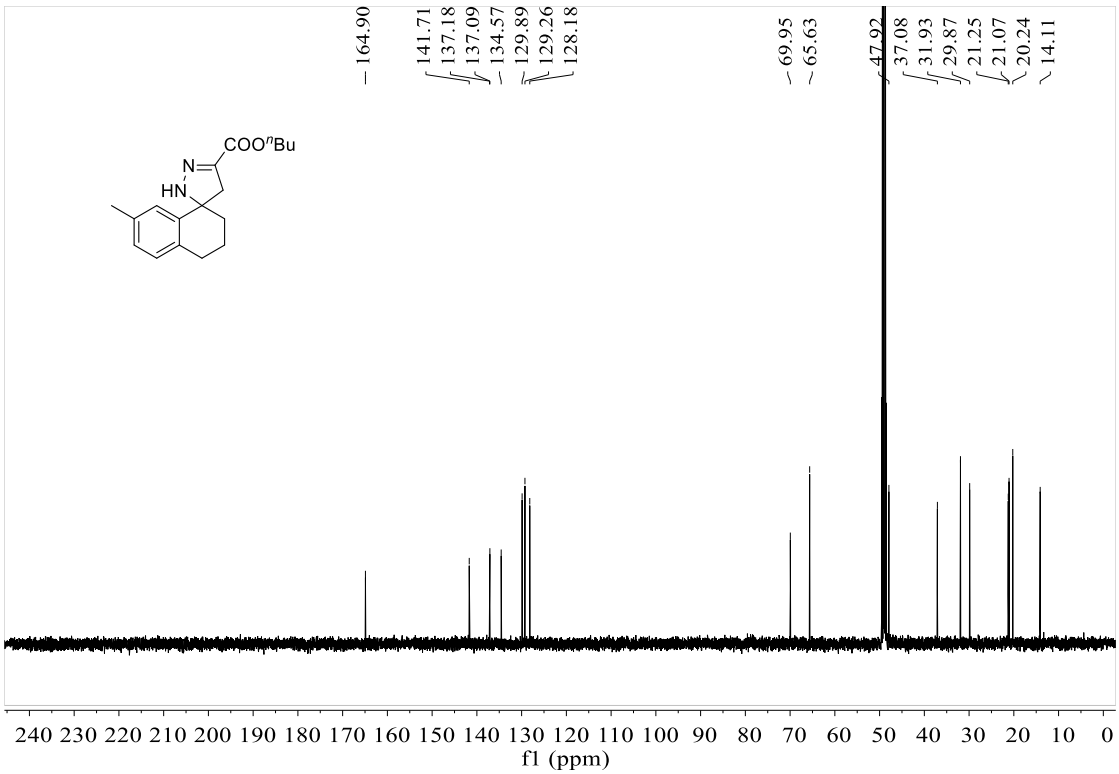

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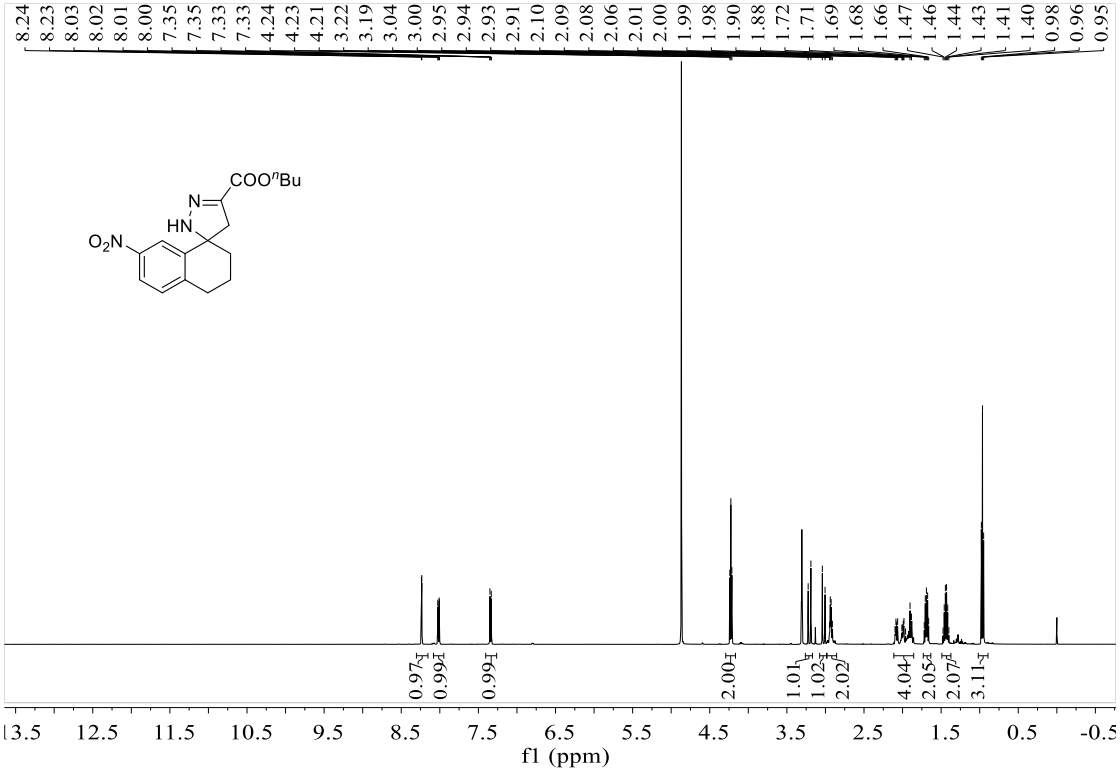

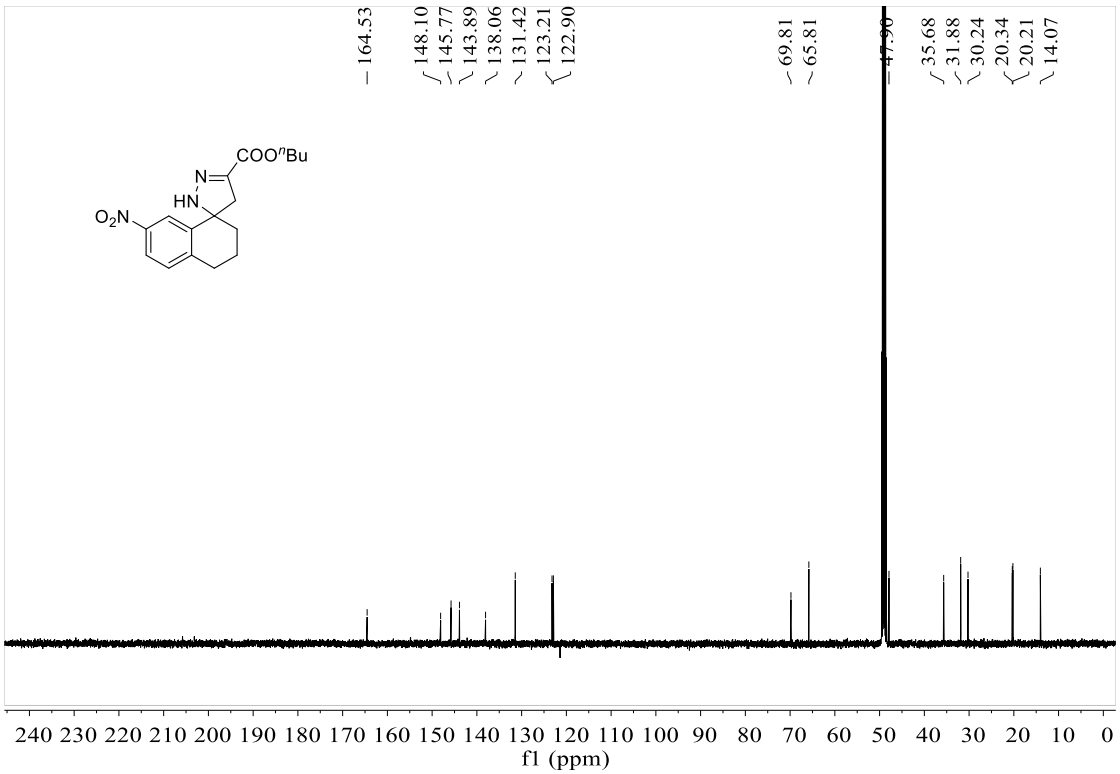

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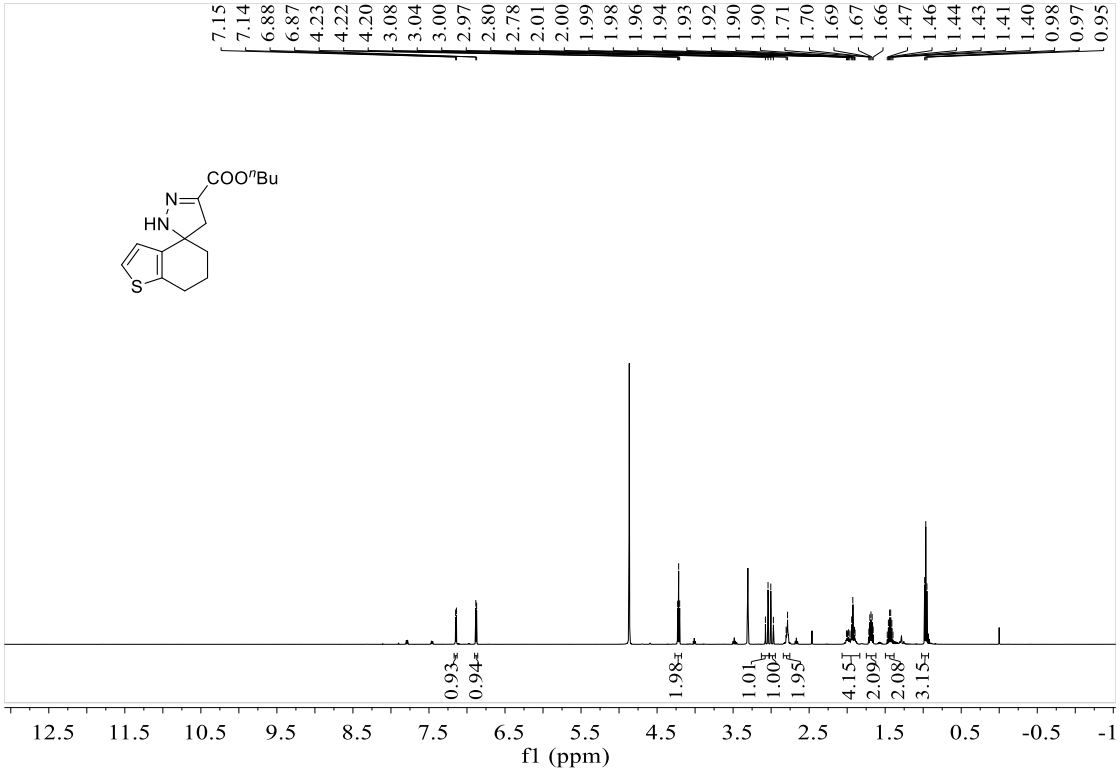

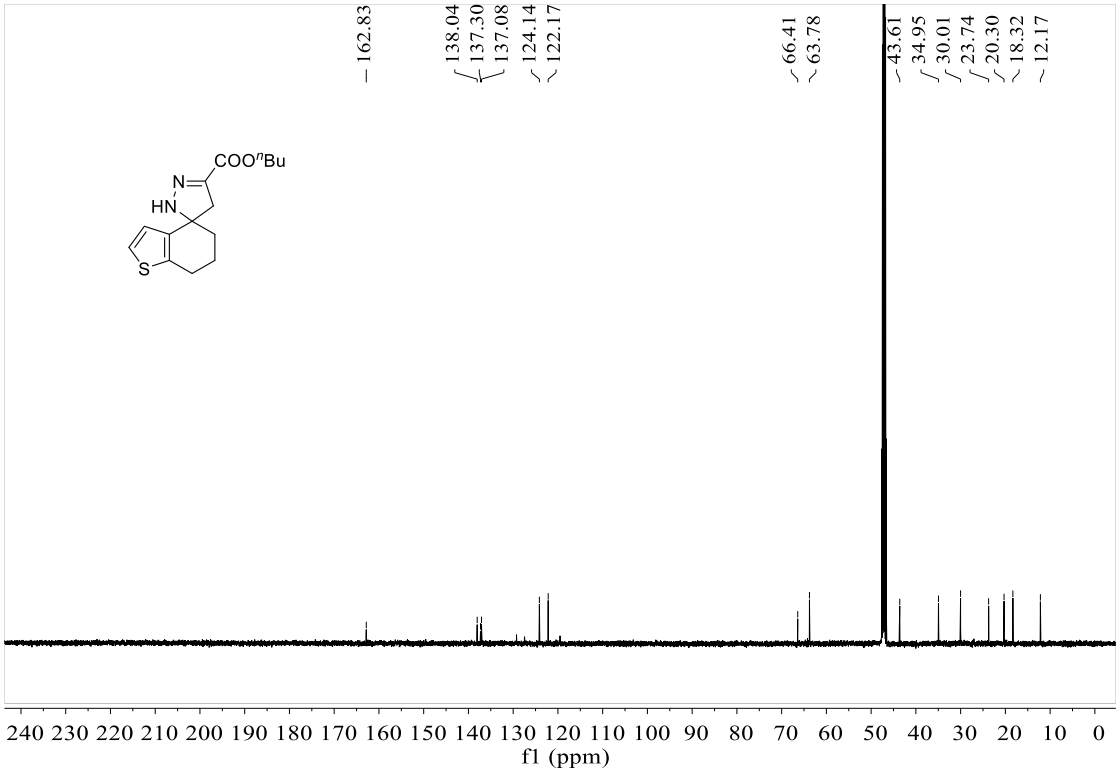

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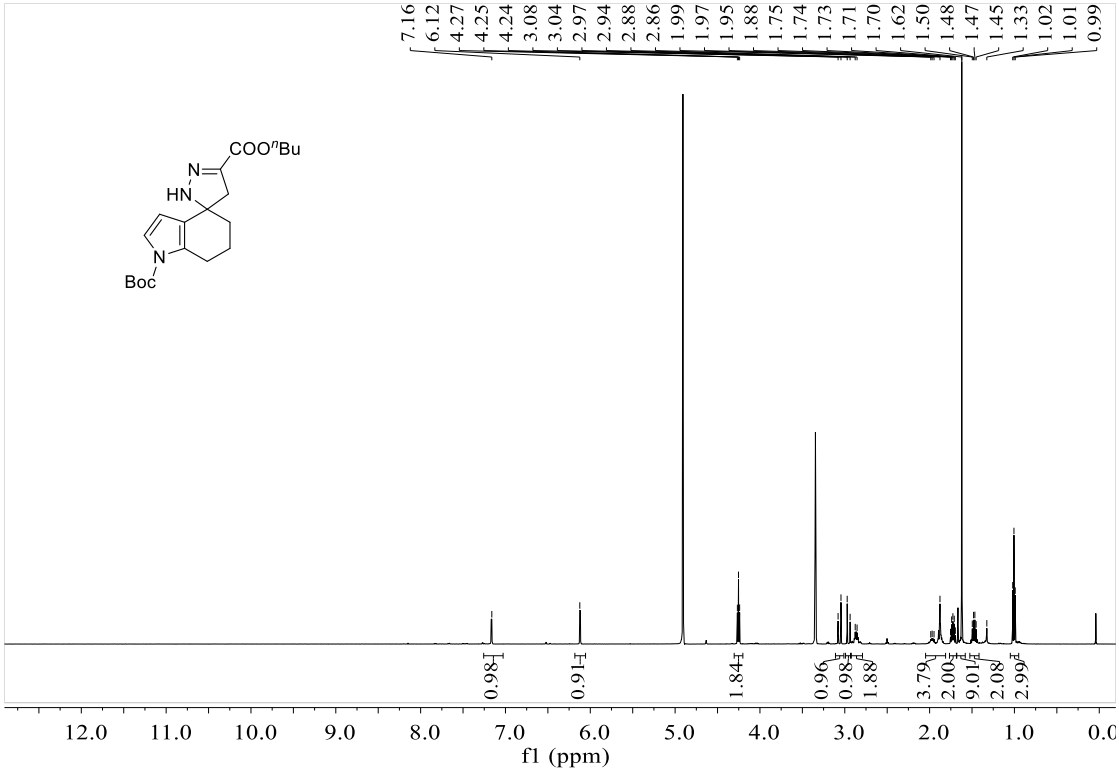

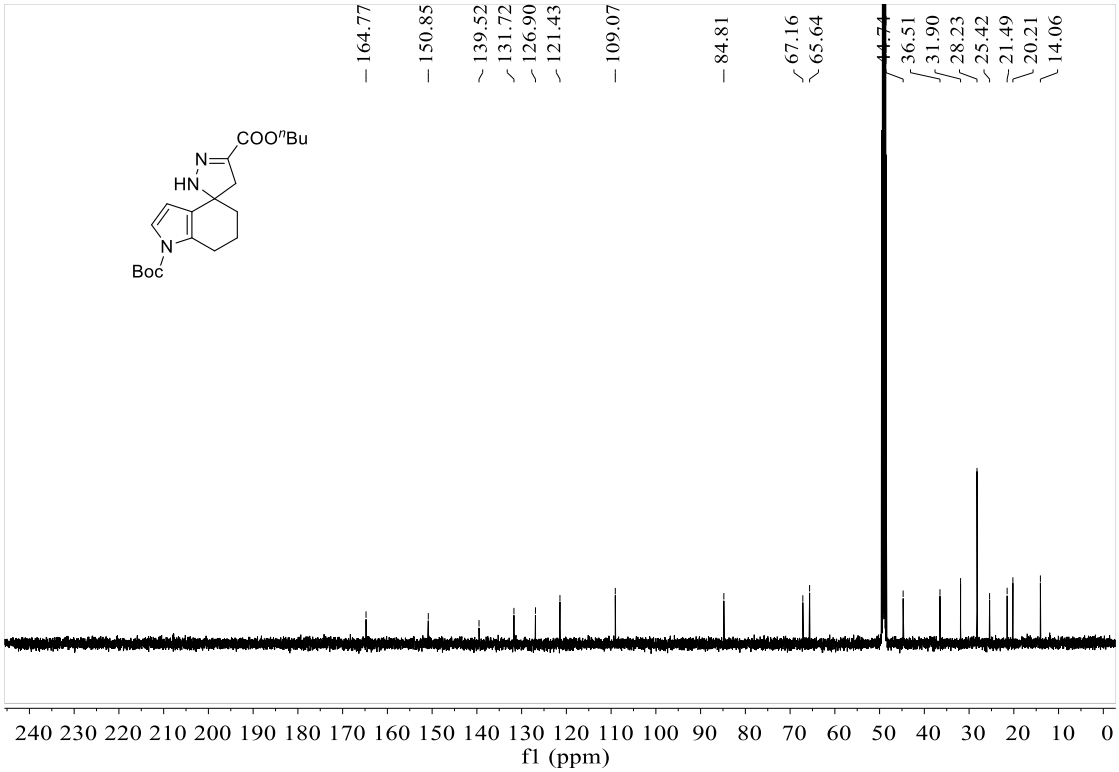

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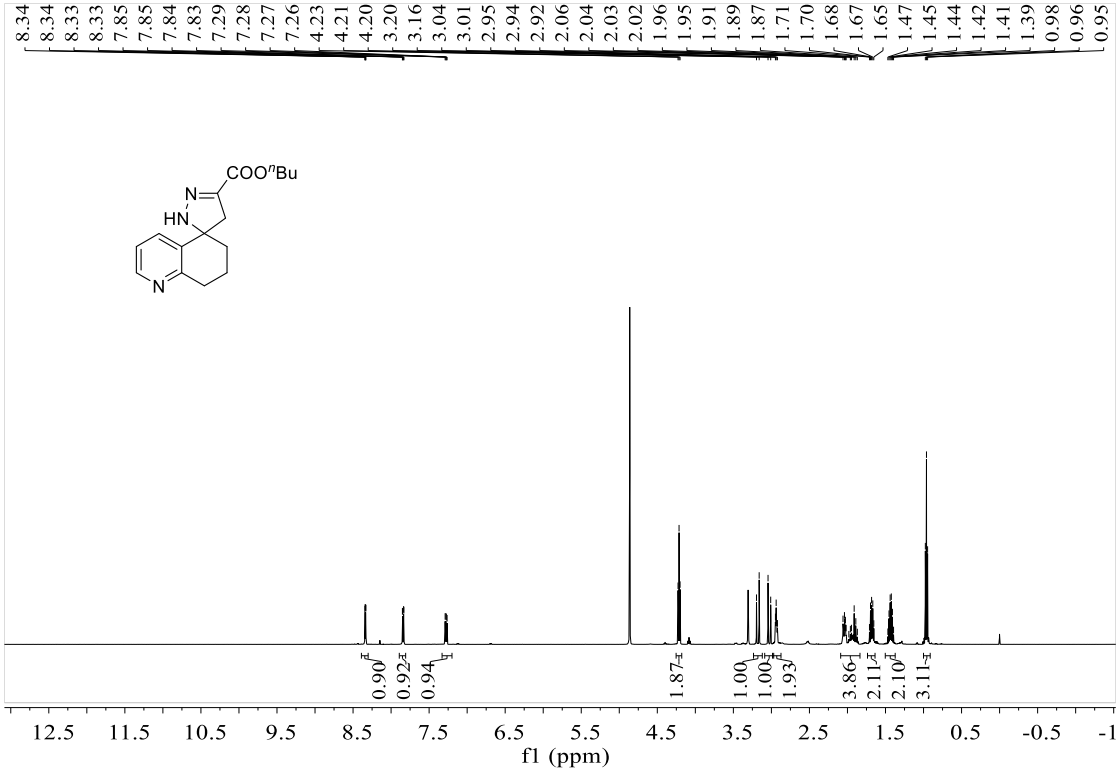

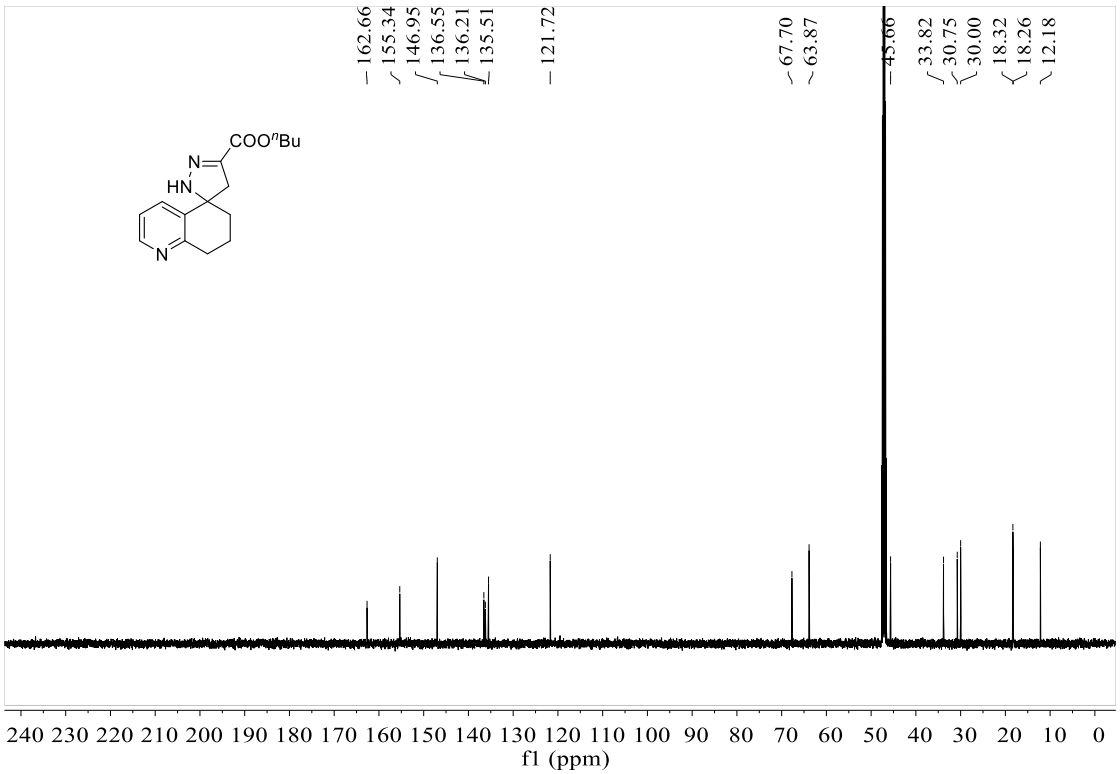

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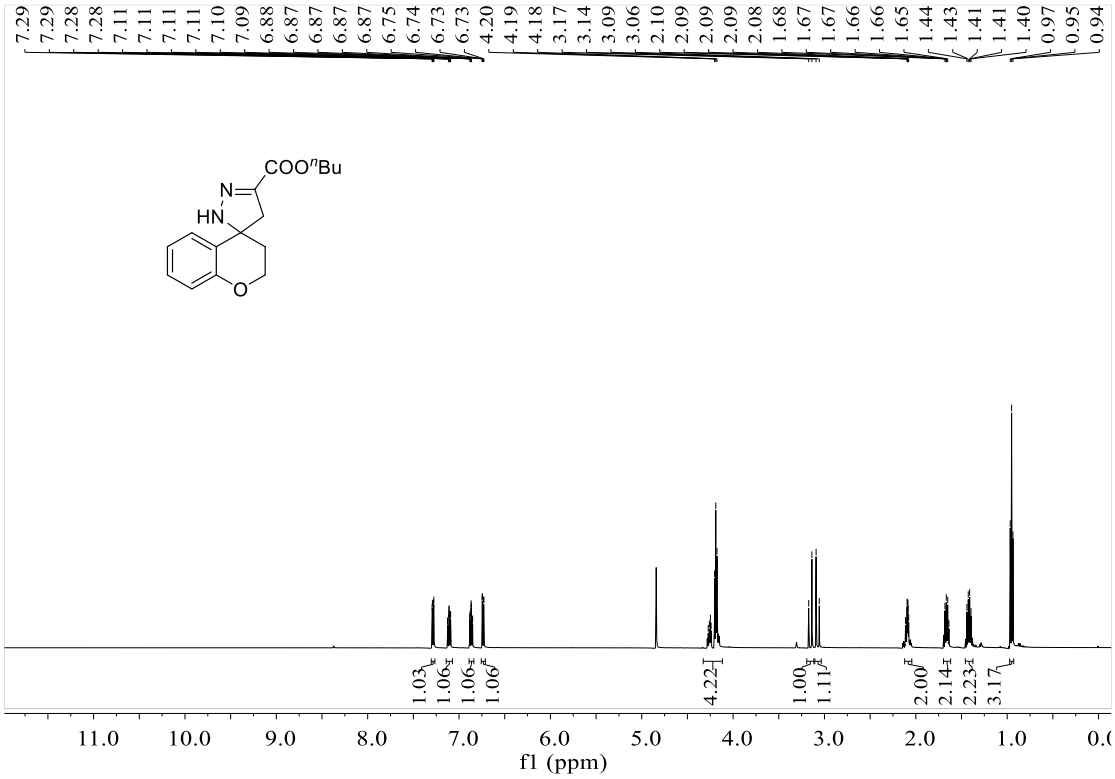

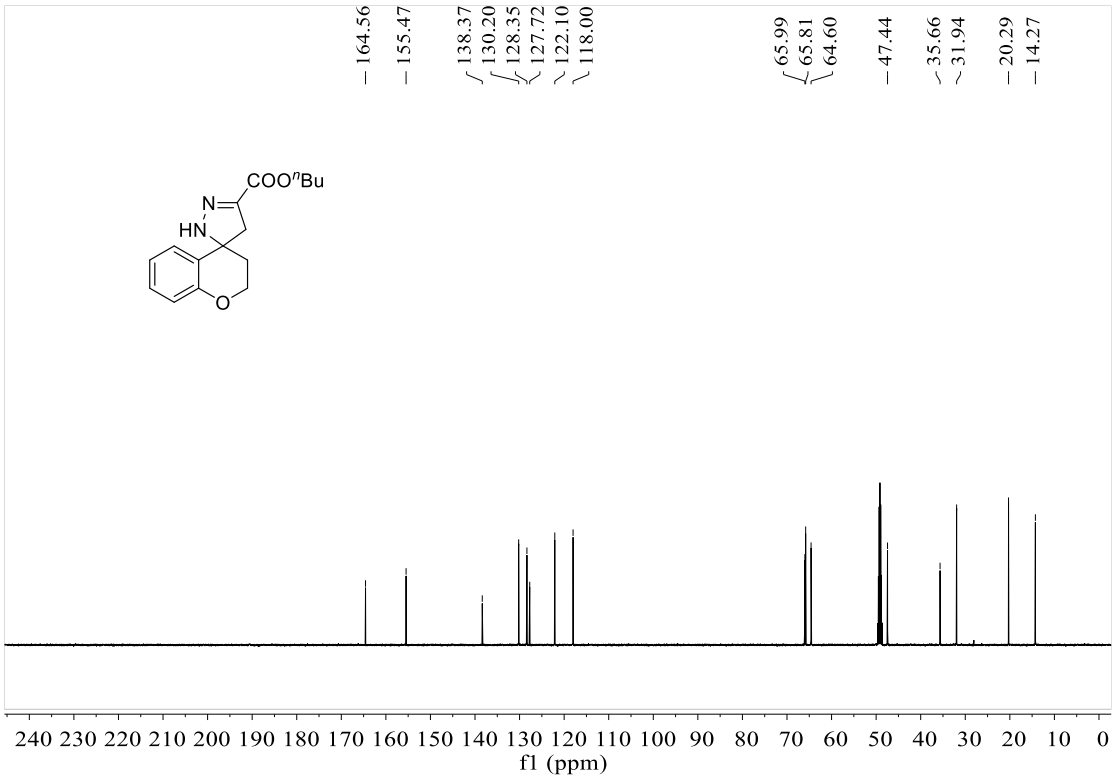

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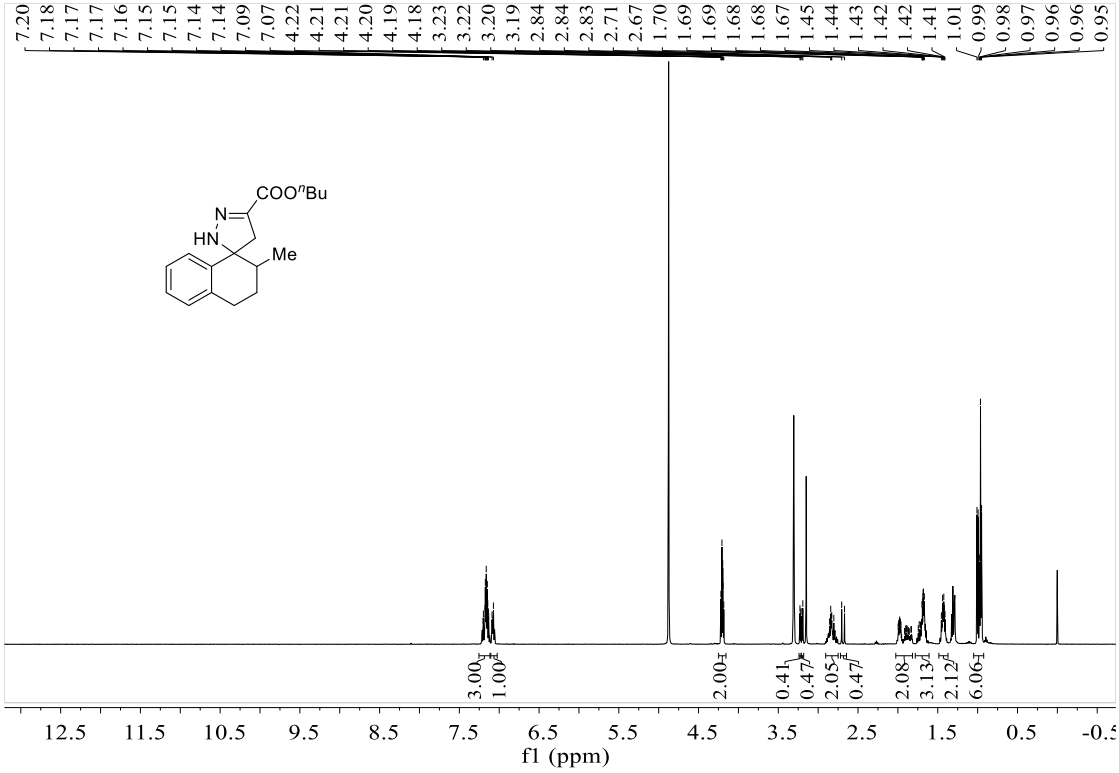

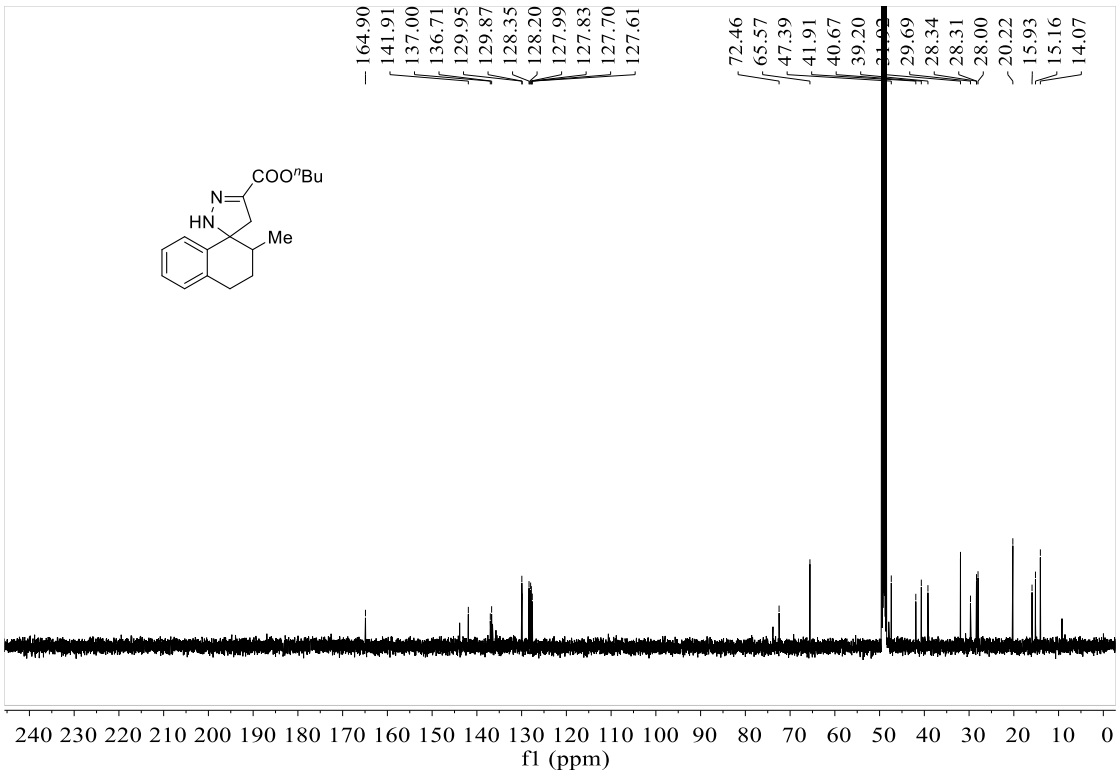

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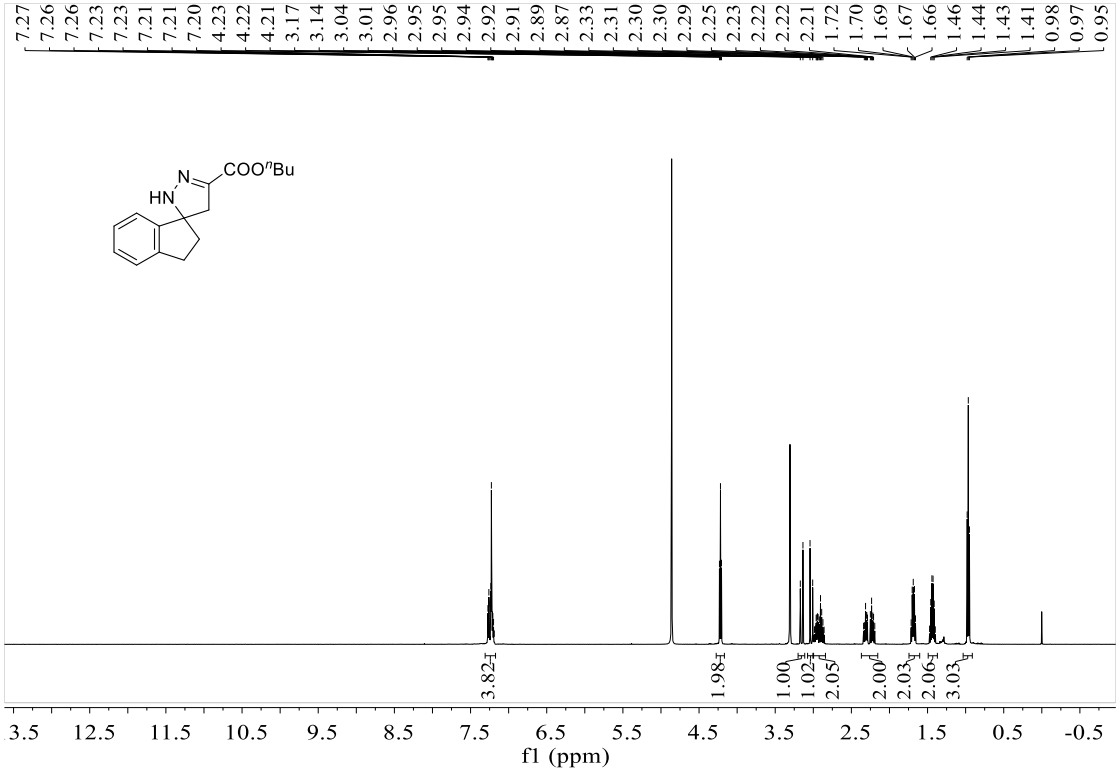

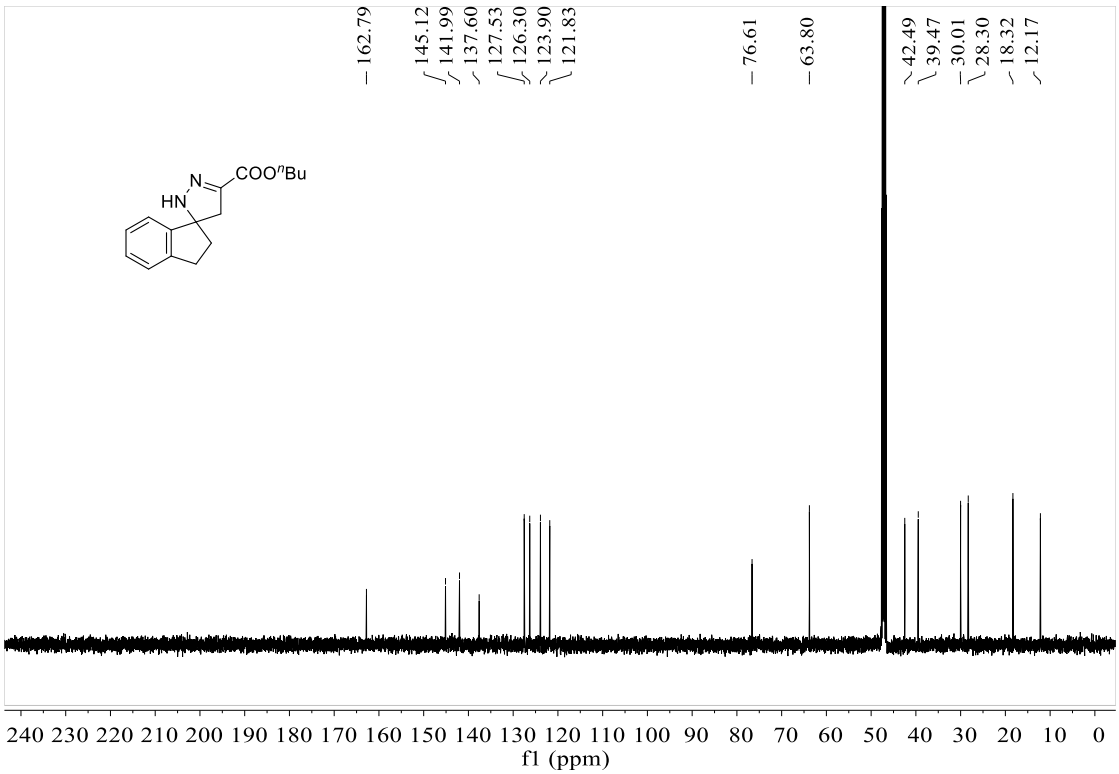

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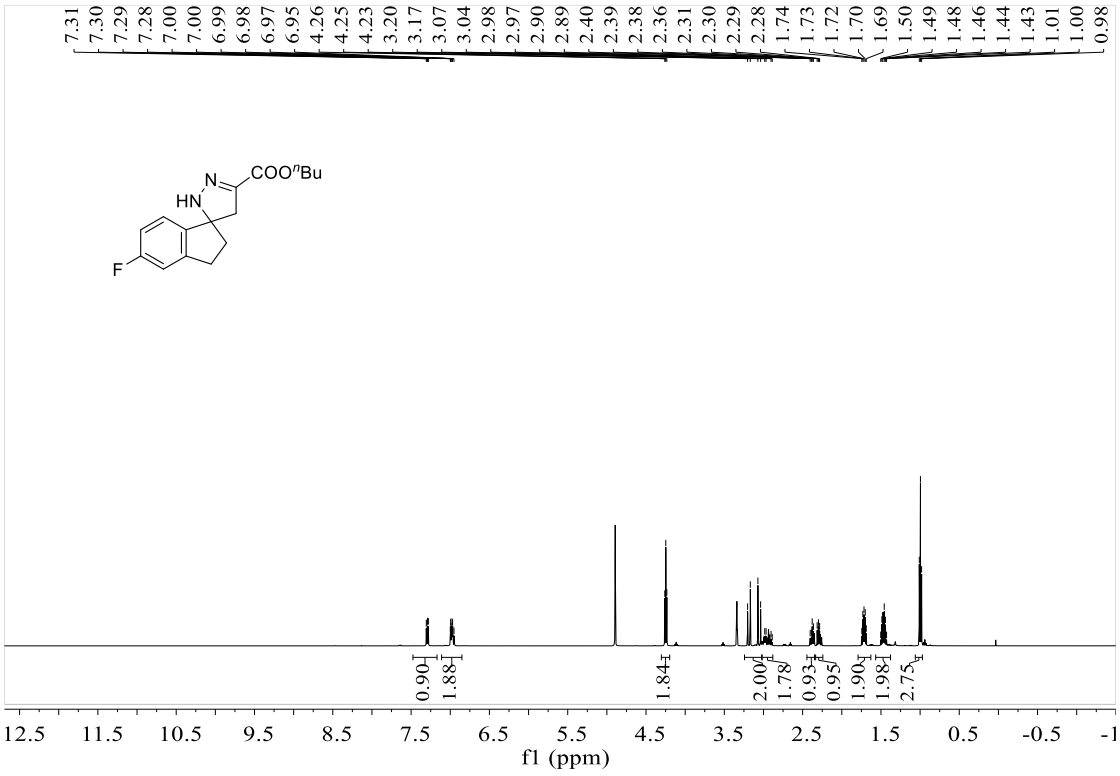

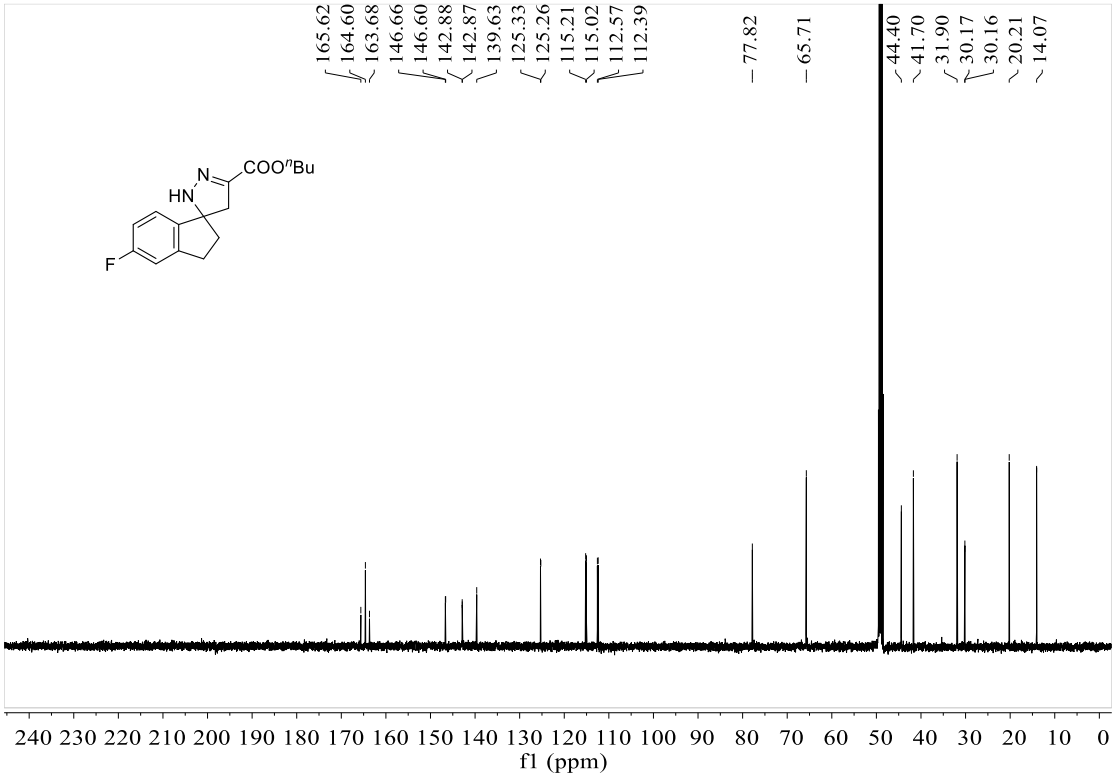

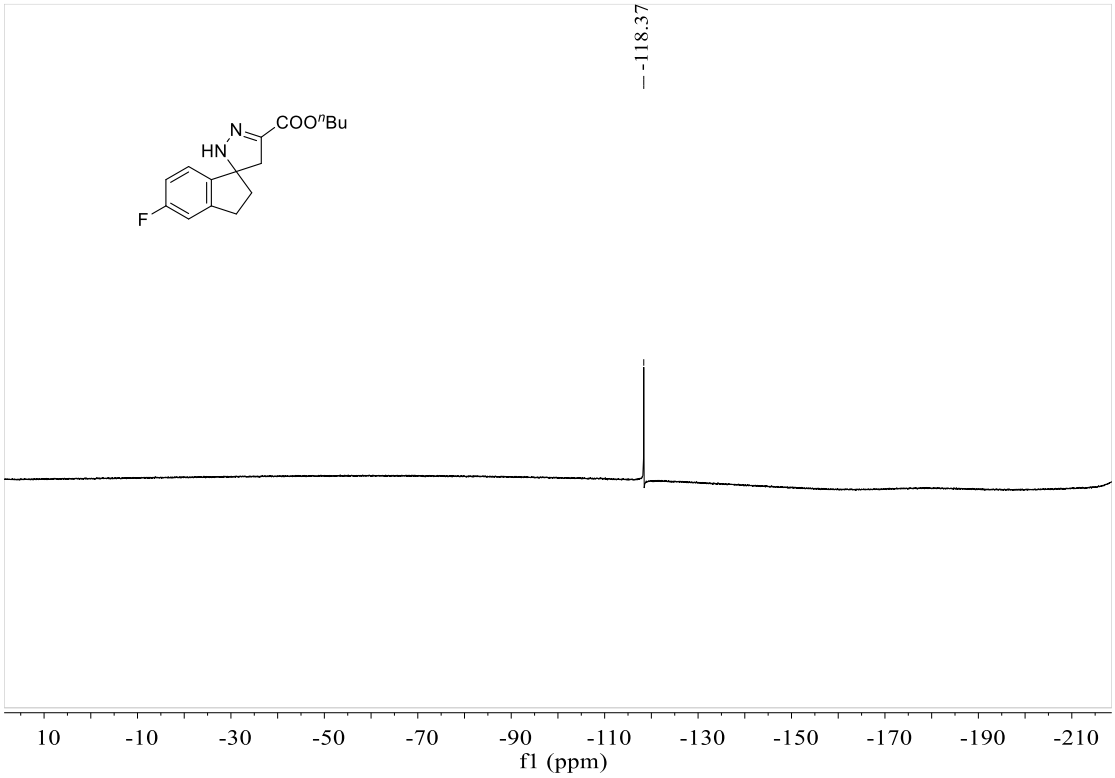
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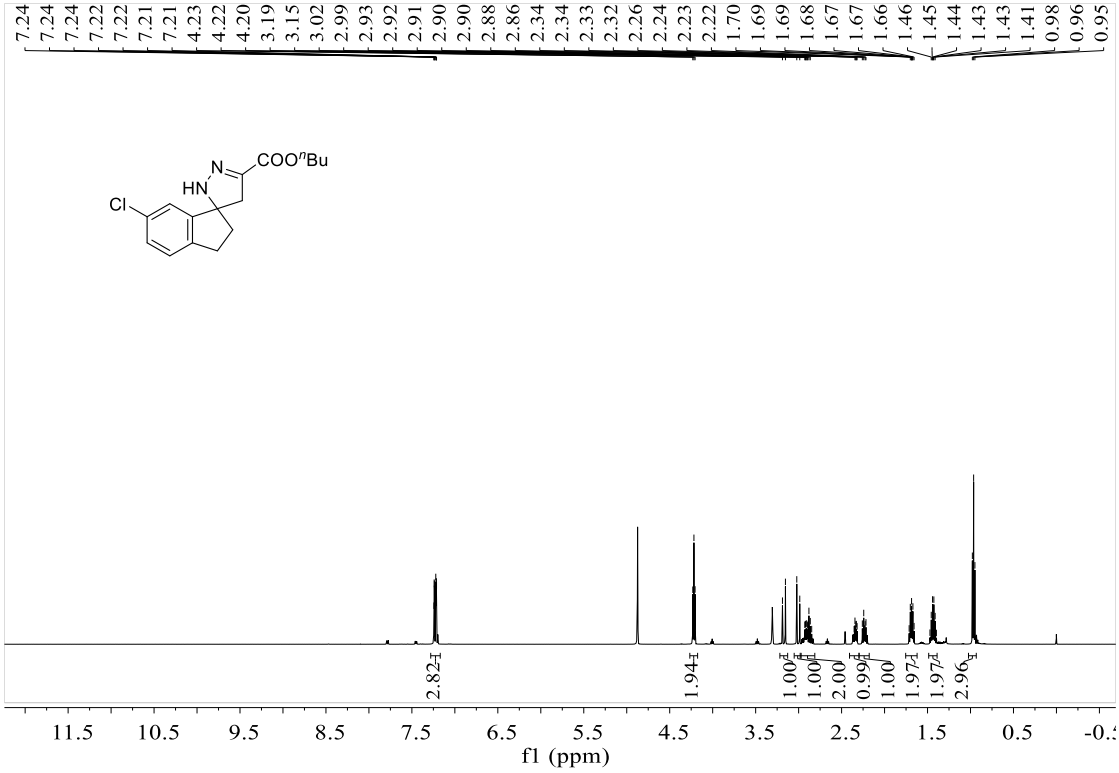
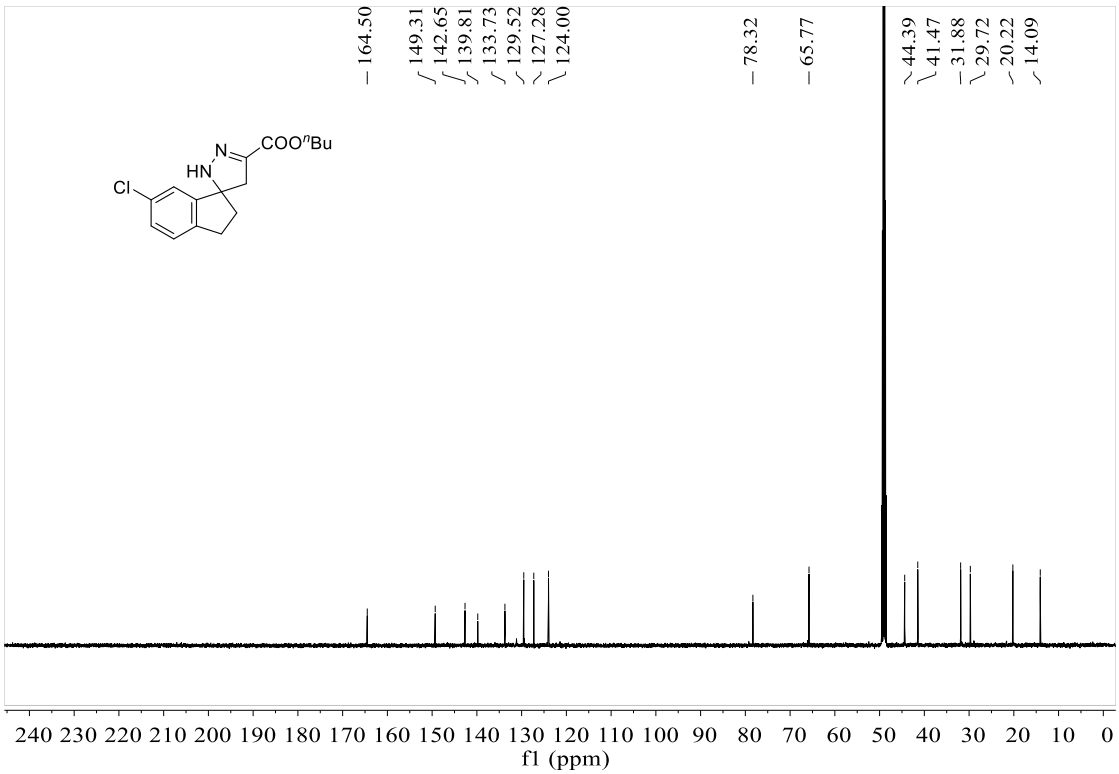
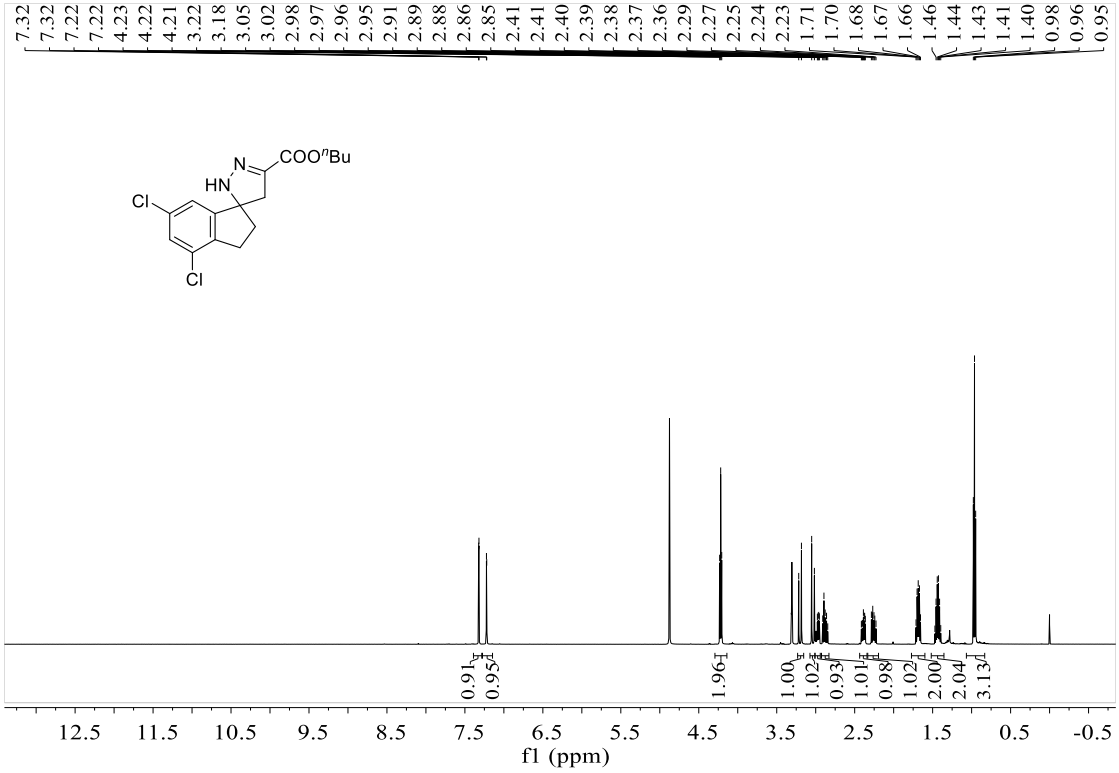
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
f1 (ppm)

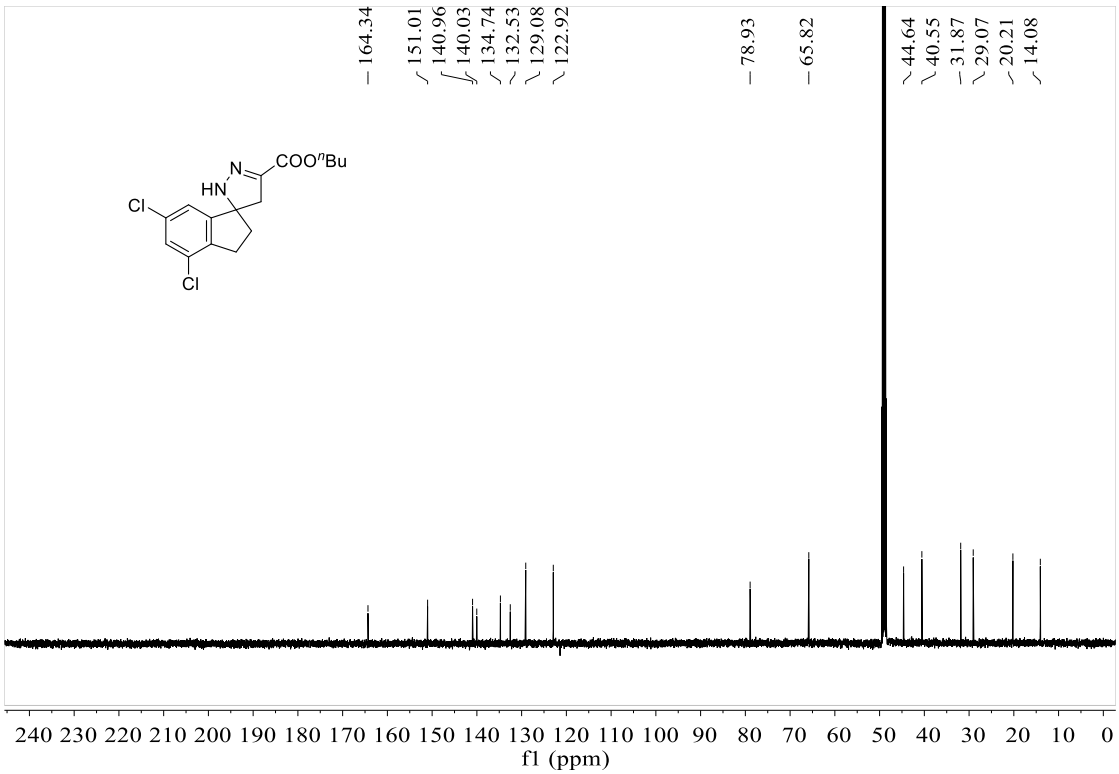
^{1}H NMR (500 MHz, CD_3OD) and ^{13}C NMR (126 MHz, CD_3OD) spectra for 15d:



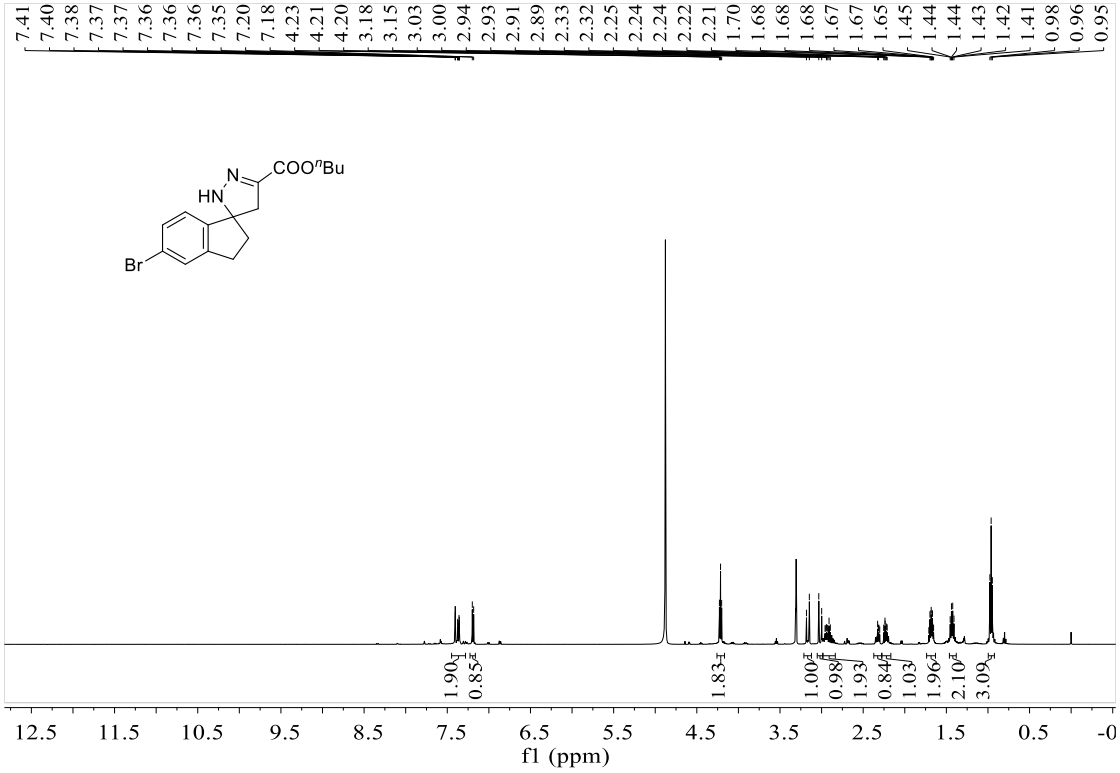


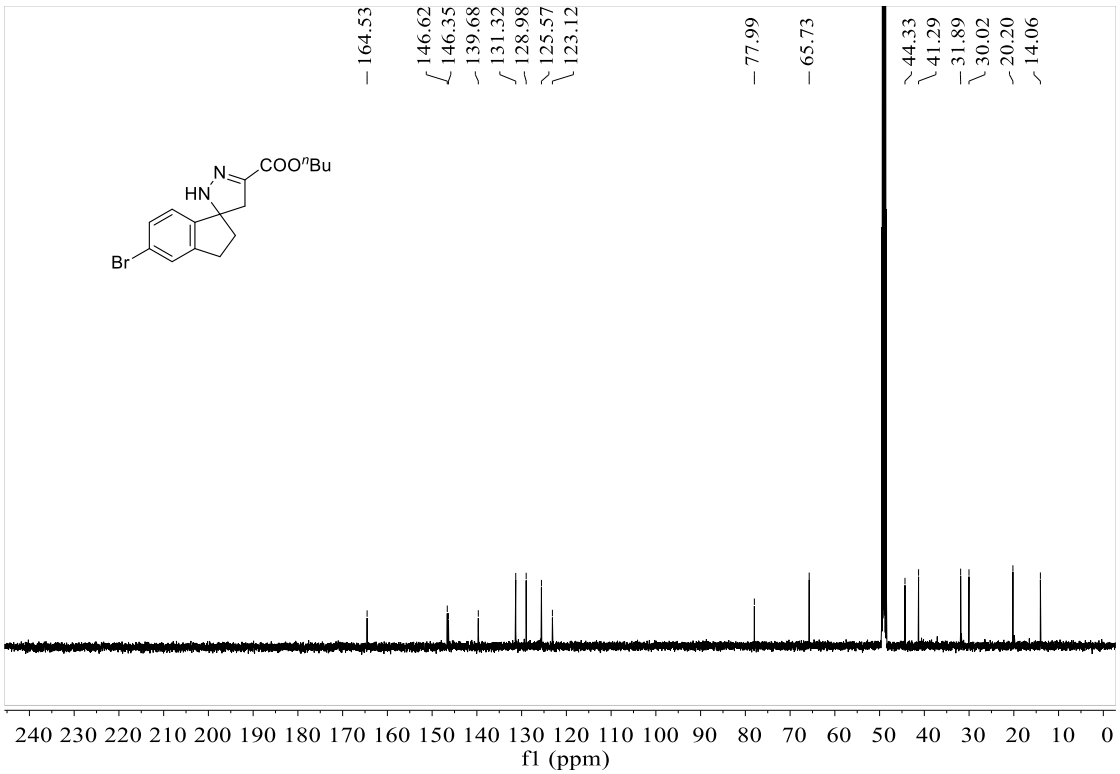
^{1}H NMR (500 MHz, CD_3OD) and ^{13}C NMR (126 MHz, CD_3OD) spectra for 16d:



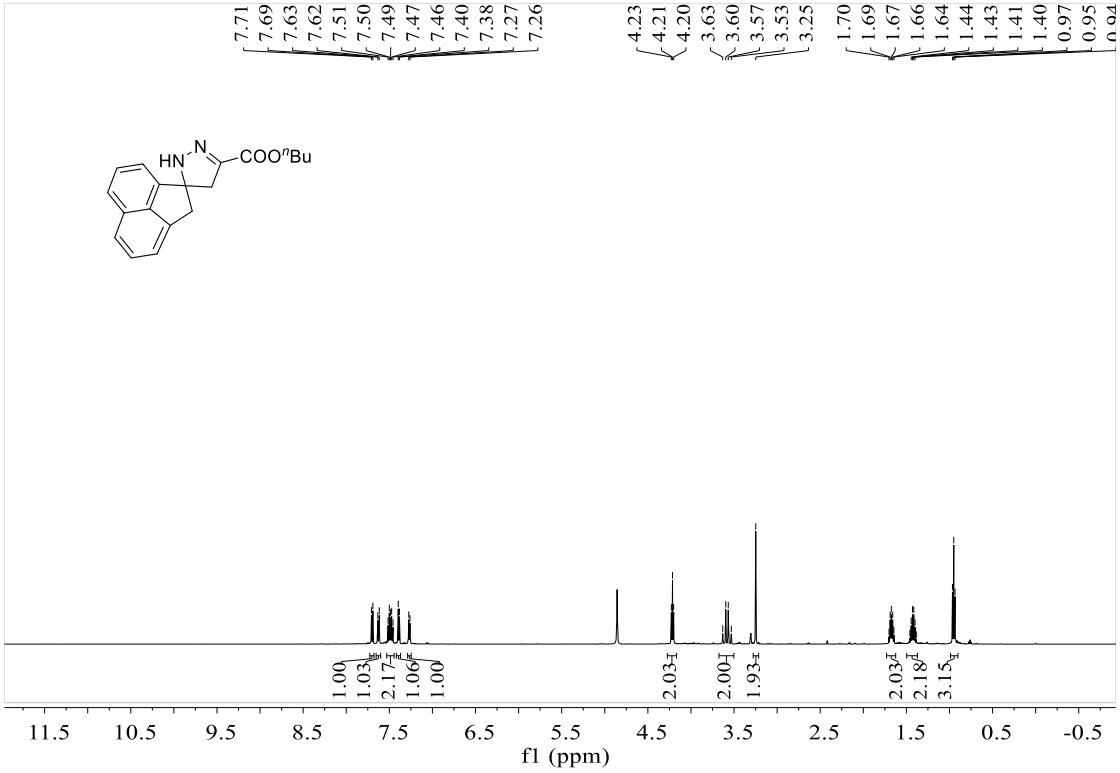


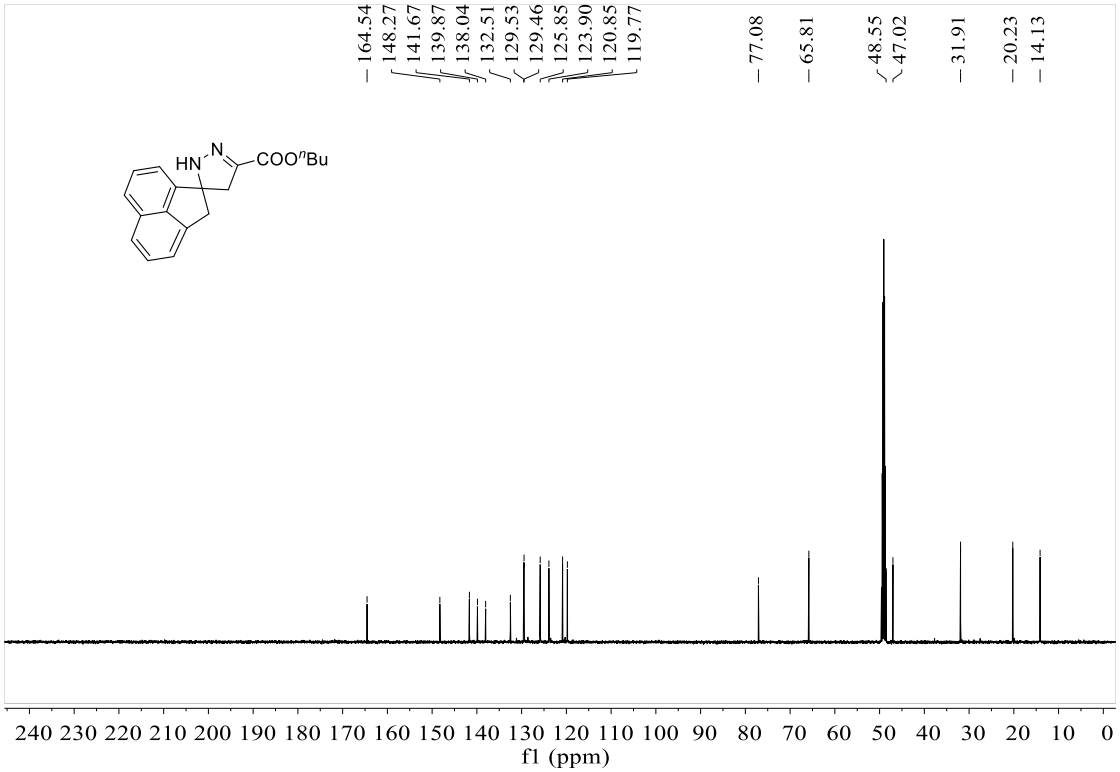
^{1}H NMR (500 MHz, CD_3OD) and ^{13}C NMR (126 MHz, CD_3OD) spectra for 17d:



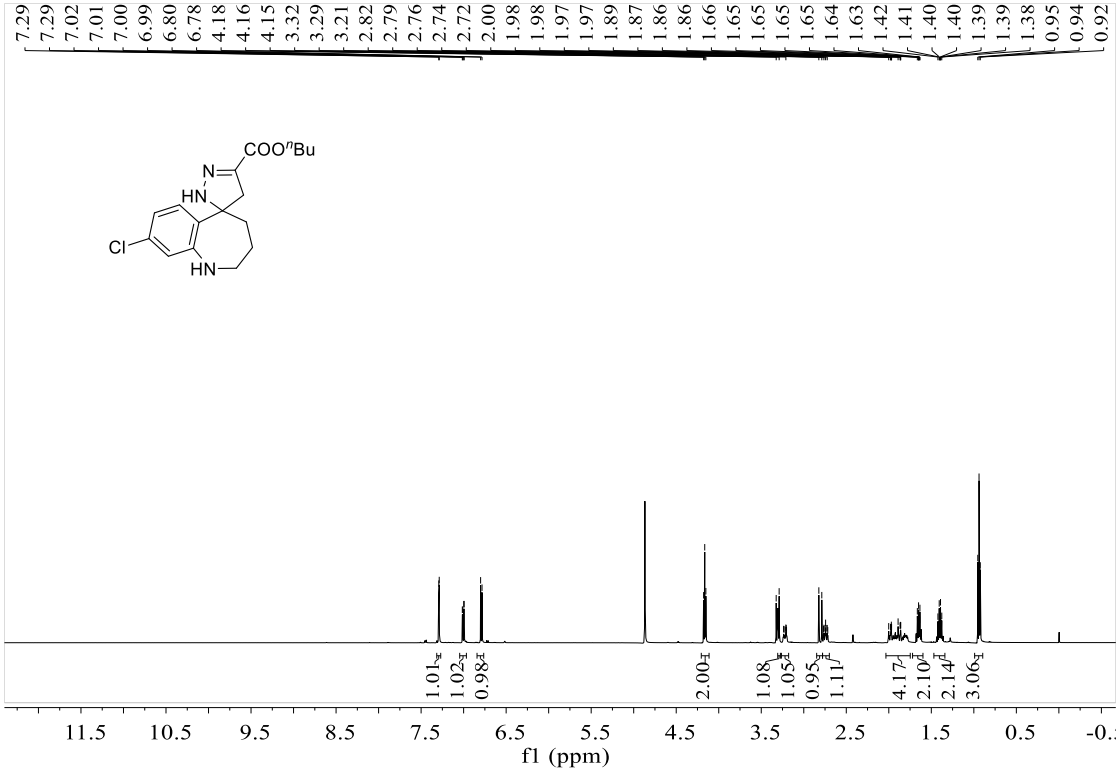


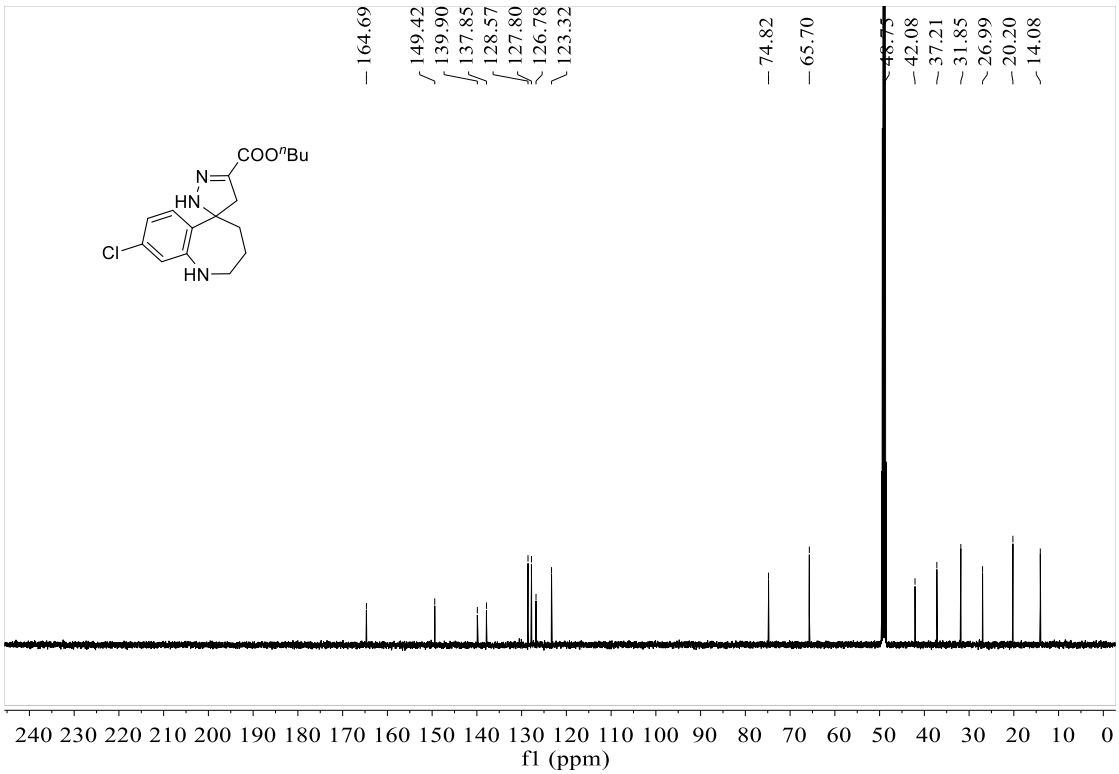
^{1}H NMR (500 MHz, CD_3OD) and ^{13}C NMR (126 MHz, CD_3OD) spectra for 18d:



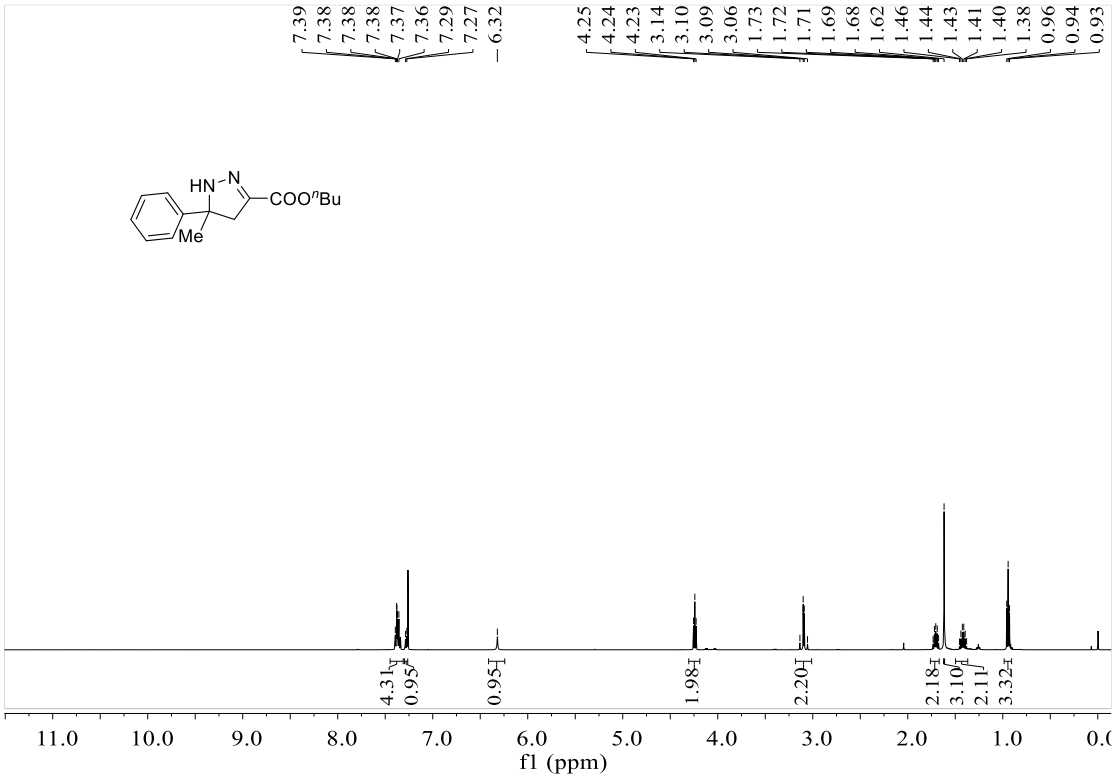


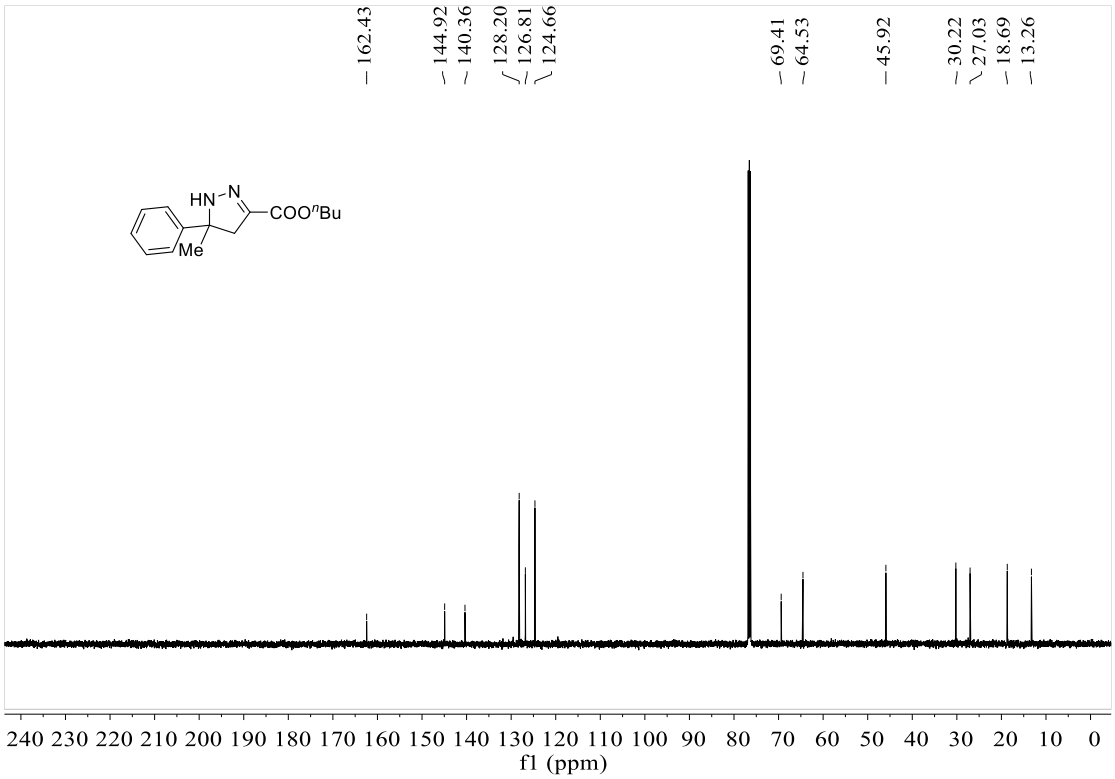
^{1}H NMR (500 MHz, CD_3OD) and ^{13}C NMR (126 MHz, CD_3OD) spectra for 19d:



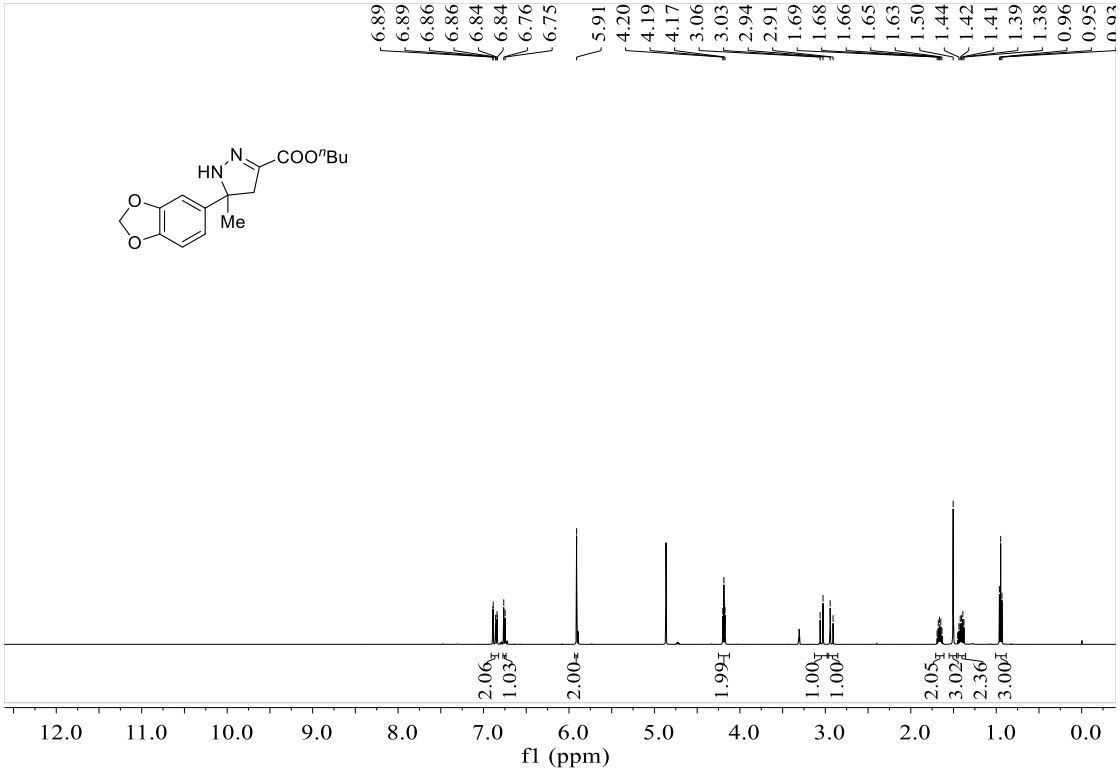


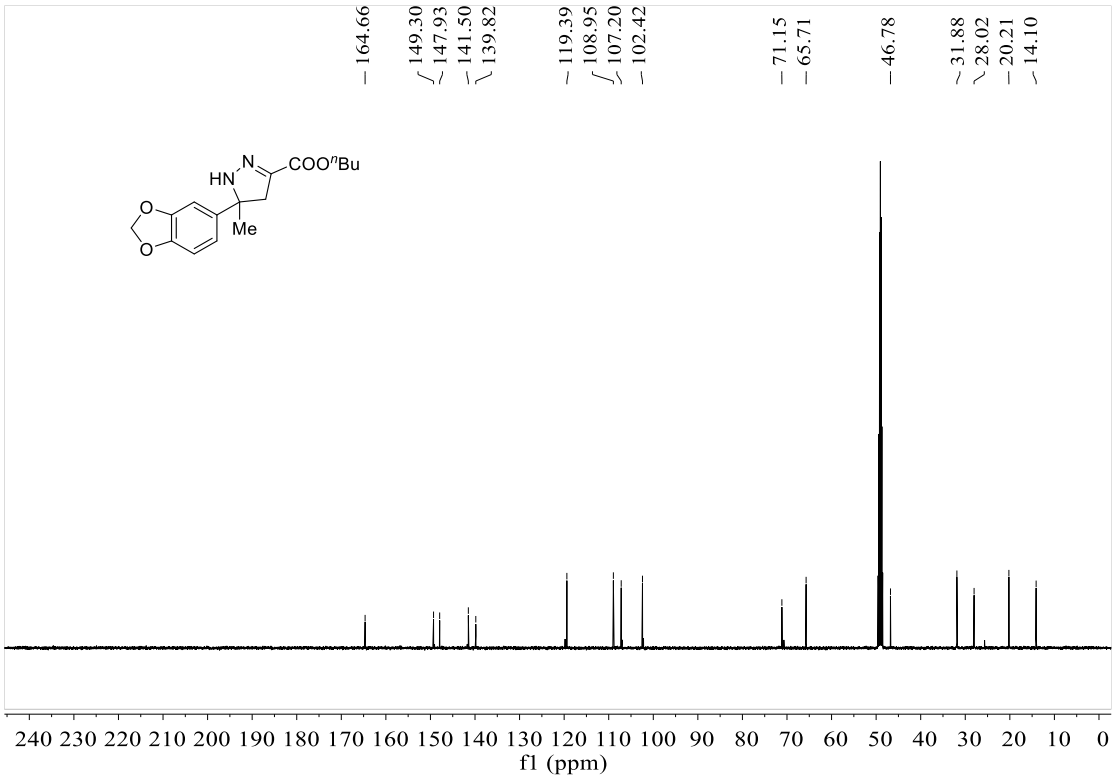
^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (126 MHz, $CDCl_3$) spectra for 20d:



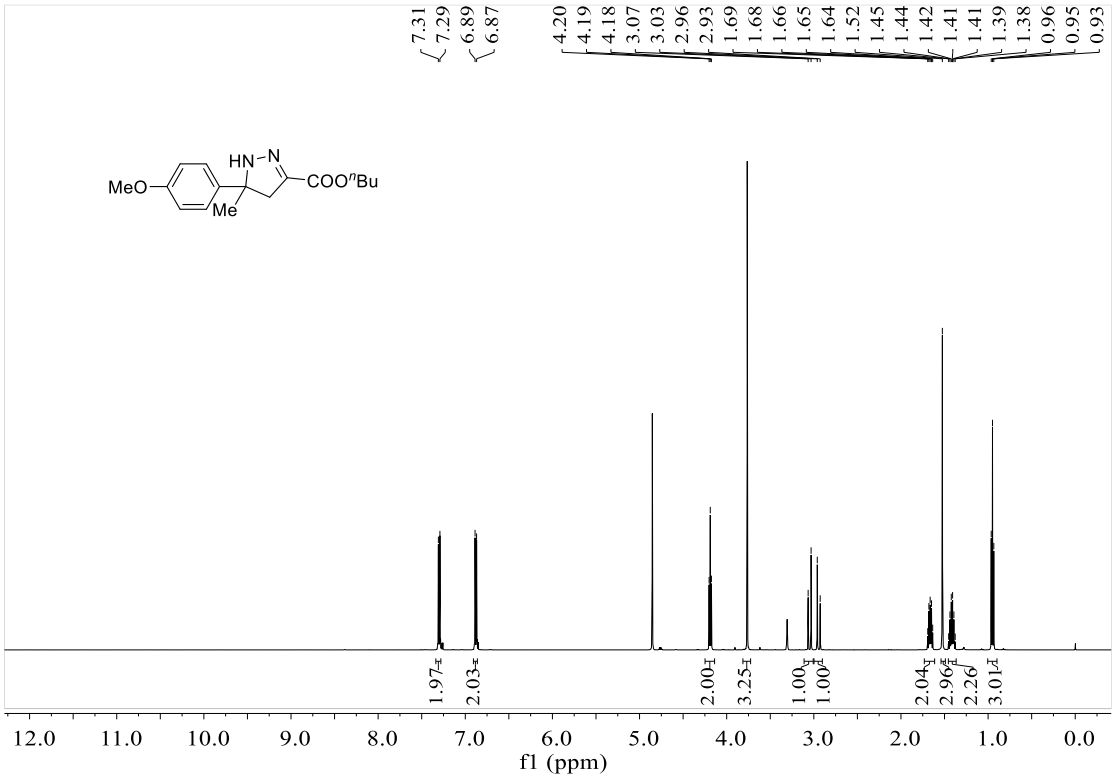


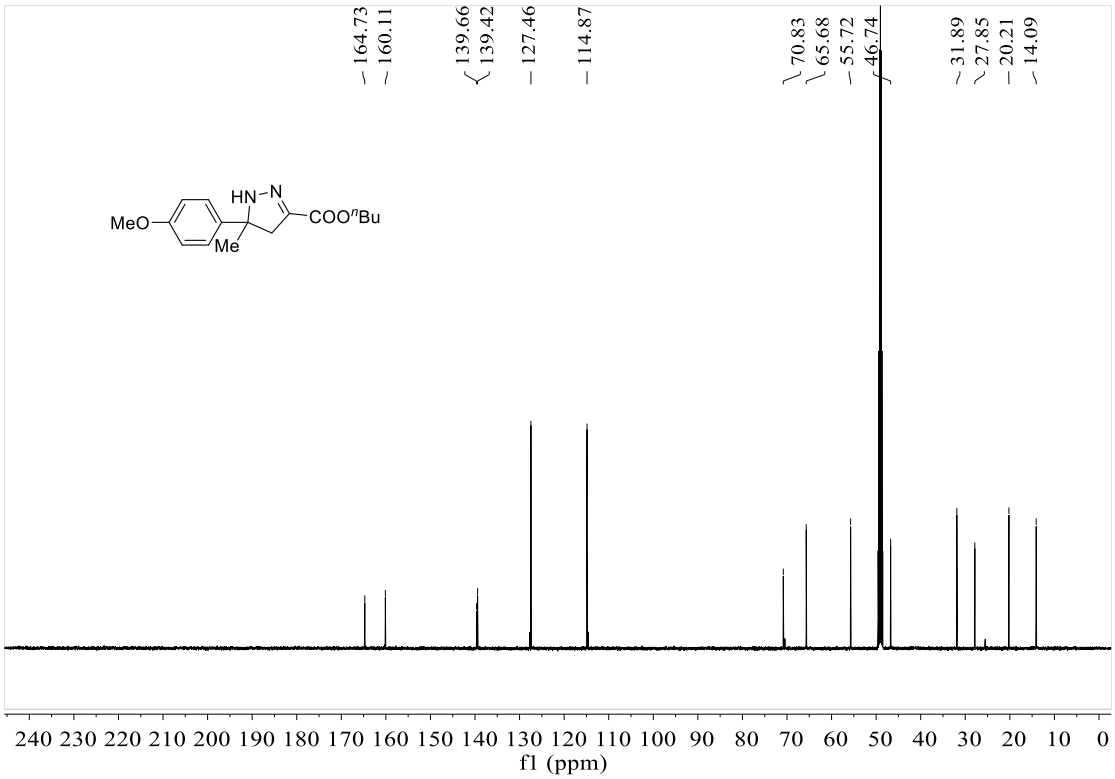
^{1}H NMR (500 MHz, CD_3OD) and ^{13}C NMR (126 MHz, CD_3OD) spectra for 21d:



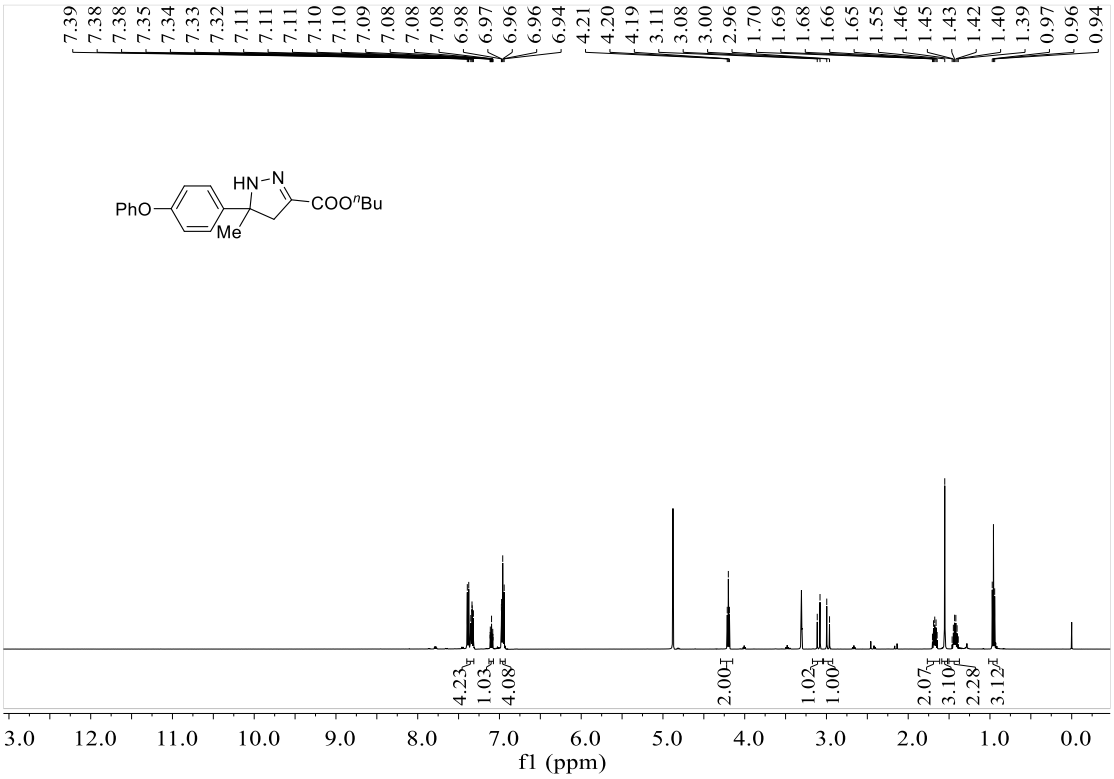


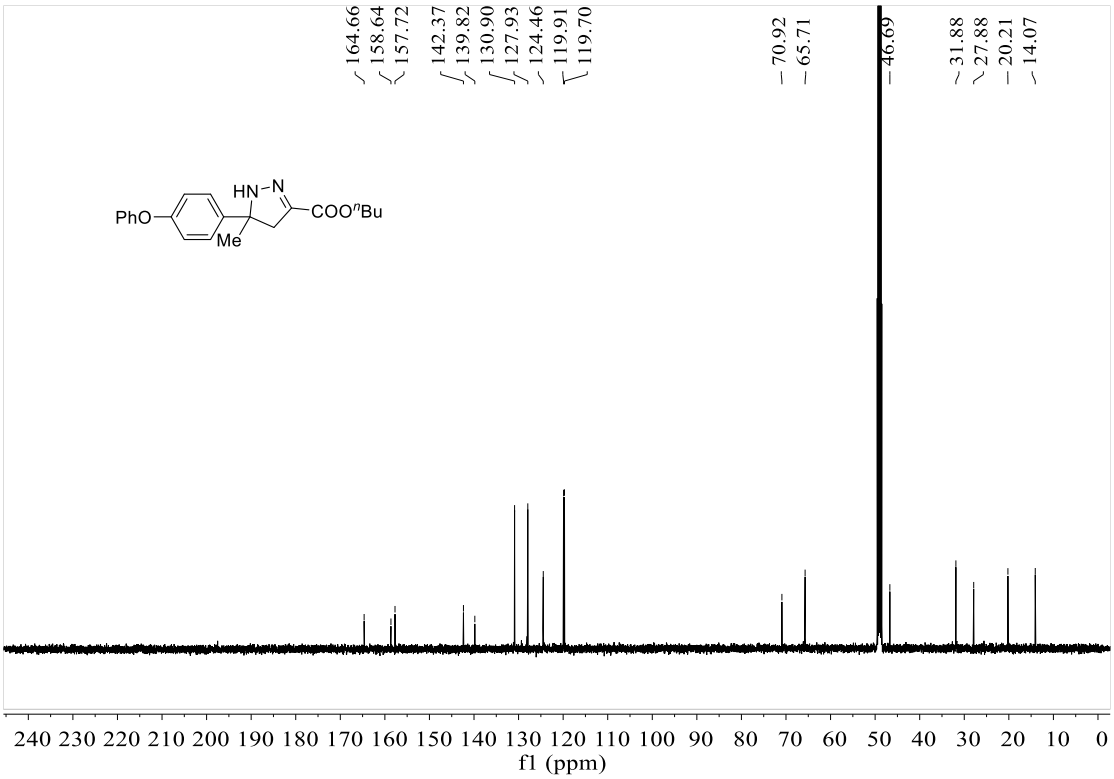
^{1}H NMR (500 MHz, CD_3OD) and ^{13}C NMR (126 MHz, CD_3OD) spectra for 22d:



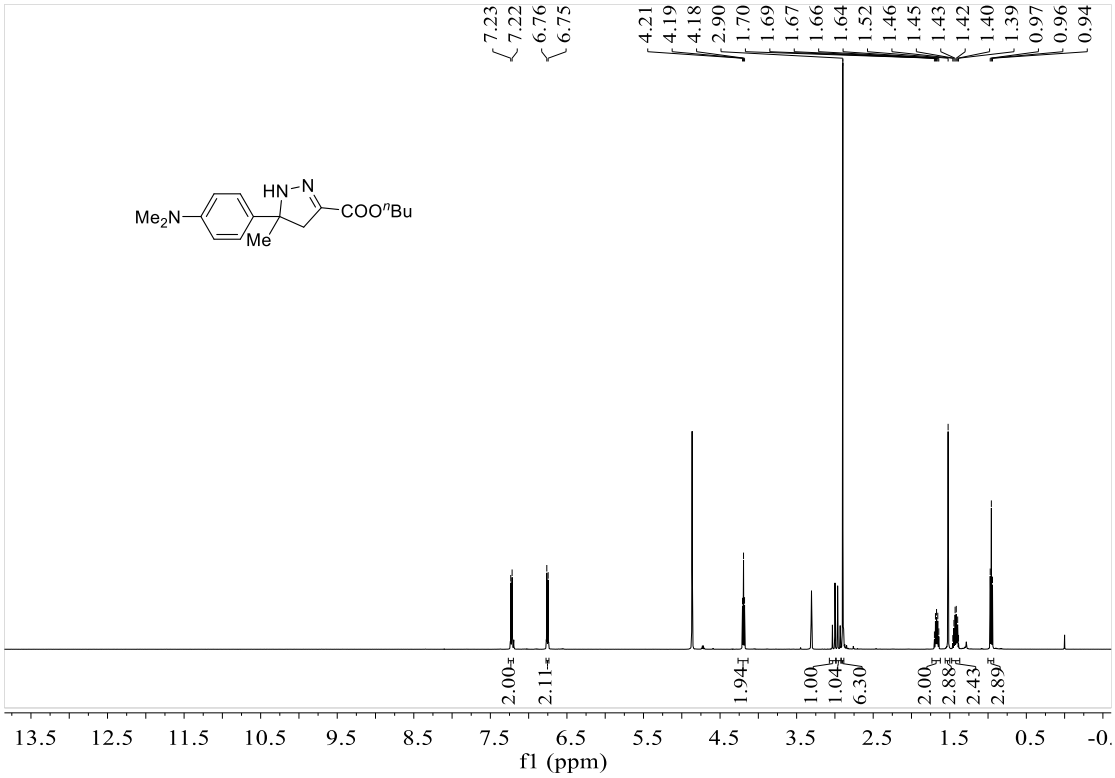


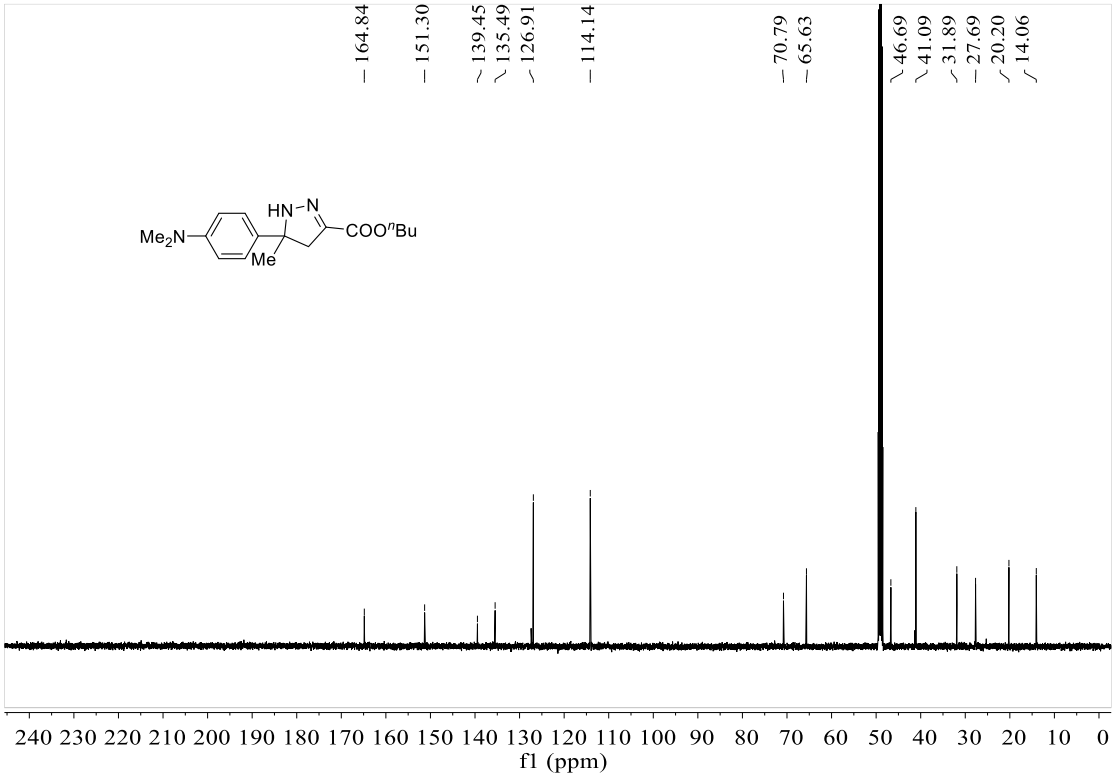
^{1}H NMR (500 MHz, CD_3OD) and ^{13}C NMR (126 MHz, CD_3OD) spectra for 23d:



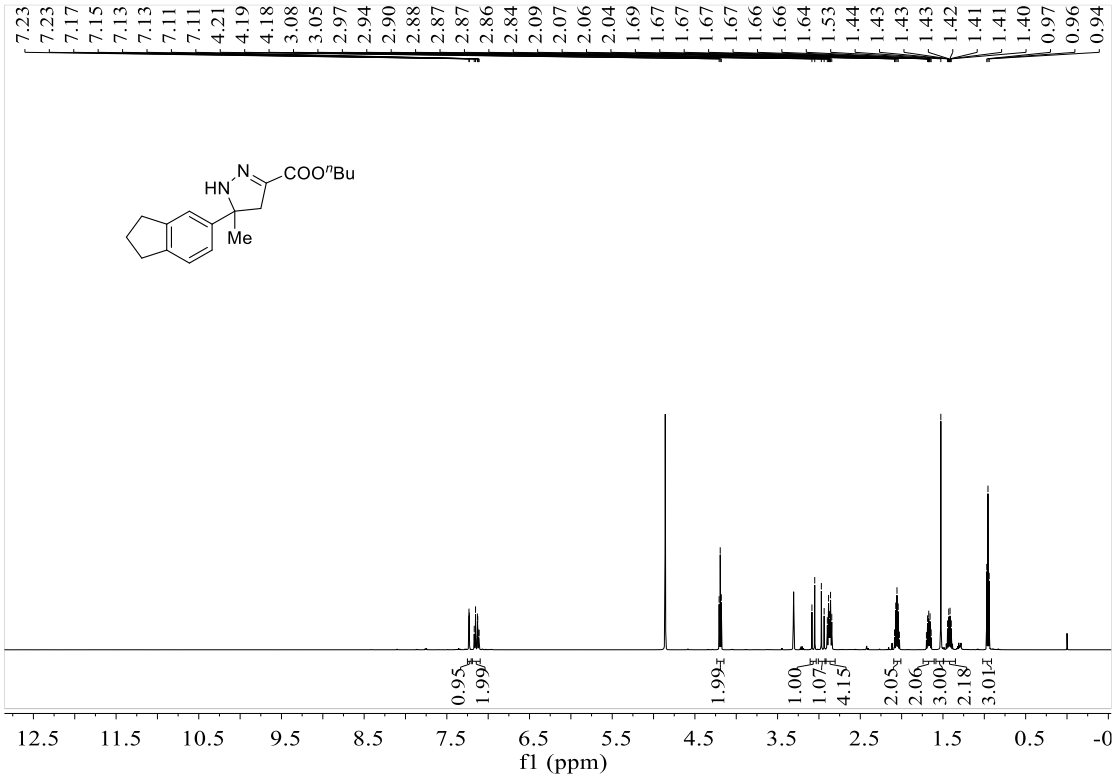


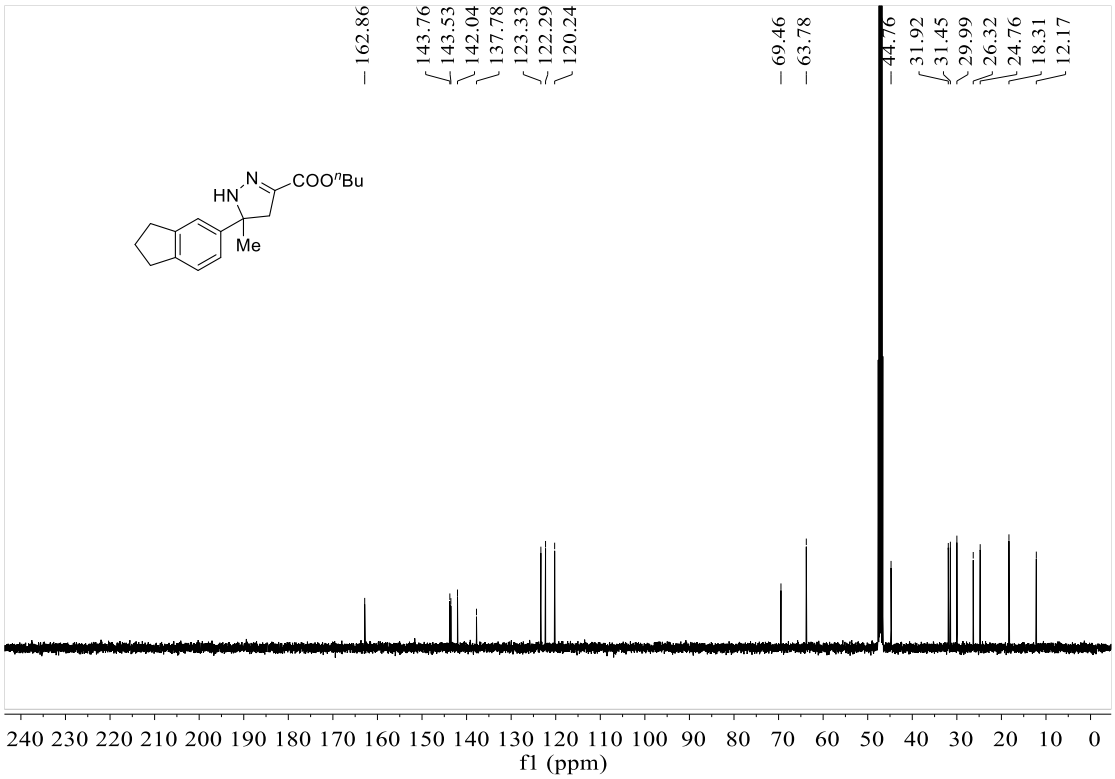
^{1}H NMR (500 MHz, CD_3OD) and ^{13}C NMR (126 MHz, CD_3OD) spectra for 24d:


7.23
7.22
6.76
6.75
4.21
4.19
4.18
2.90
1.70
1.69
1.67
1.66
1.64
1.52
1.46
1.45
1.43
1.42
1.40
1.39
0.97
0.96
0.94
HN
N
Me2N
COO^{n}Bu
Me
2.00
2.11
1.94
1.00
1.04
6.30
2.00
2.88
2.43
2.89
13.5 12.5 11.5 10.5 9.5 8.5 7.5 6.5 5.5 4.5 3.5 2.5 1.5 0.5 -0.
f1 (ppm)

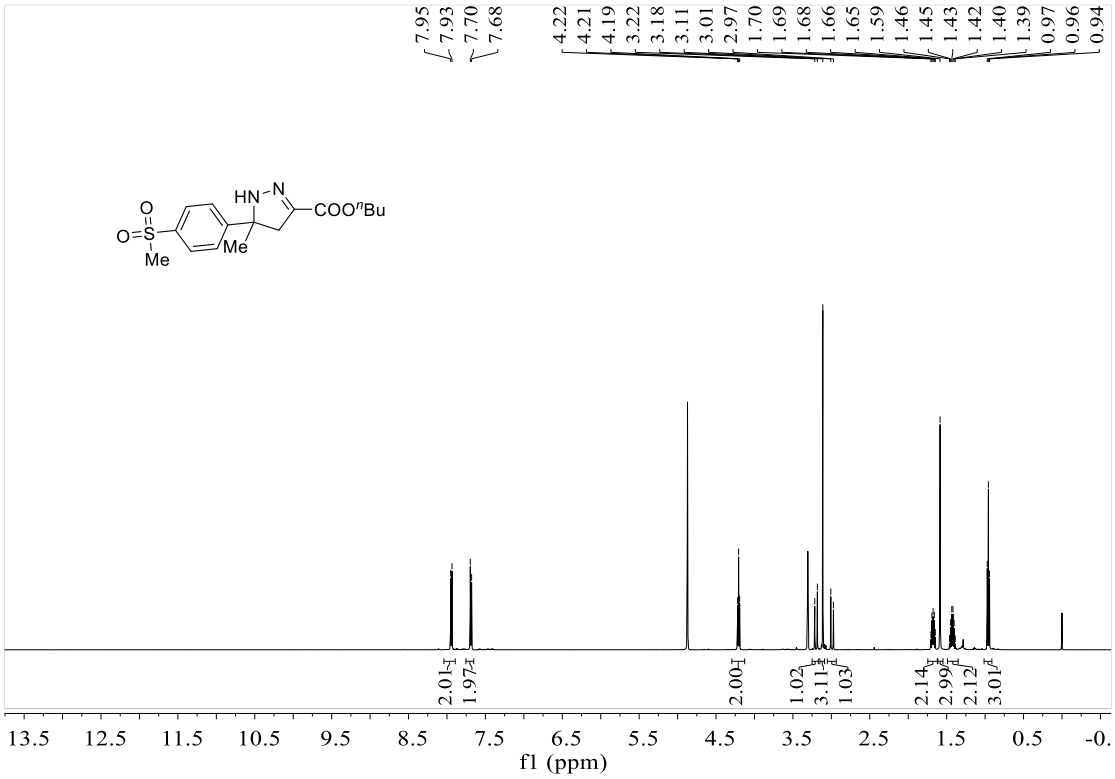

164.84
151.30
139.45
135.49
126.91
114.14
70.79
65.63
46.69
41.09
31.89
27.69
20.20
14.06
HN
N
Me2N
COO^{n}Bu
Me
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

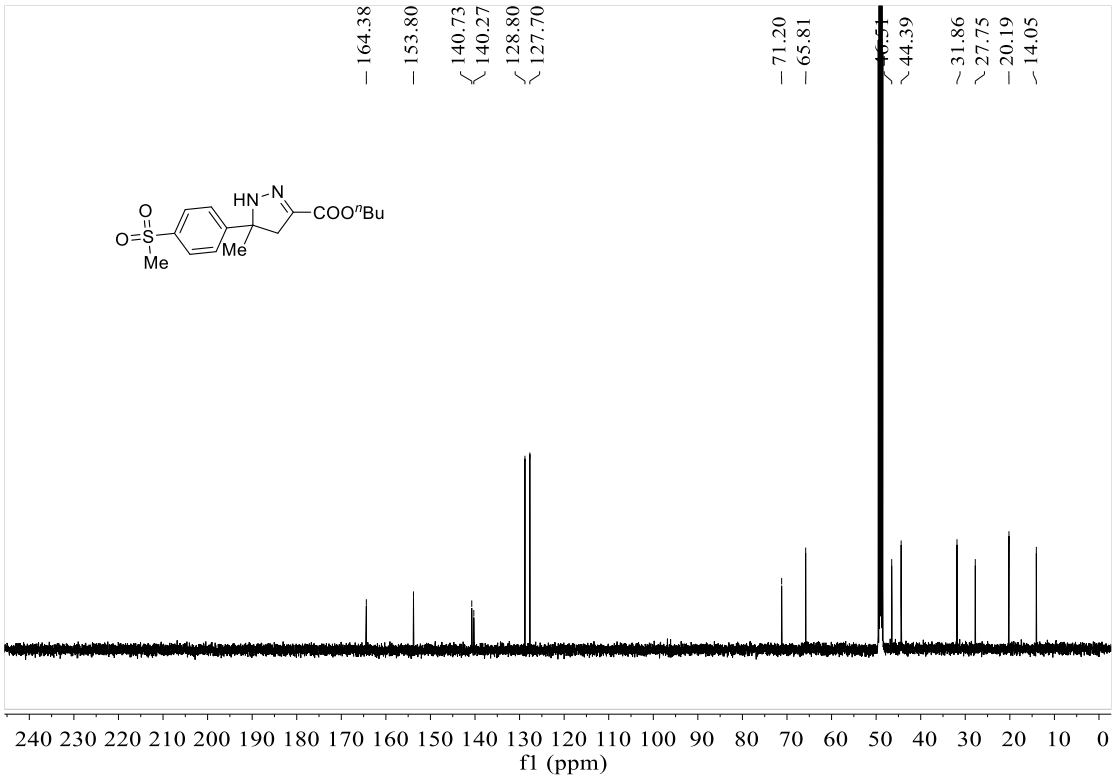
^{1}H NMR (500 MHz, CD_3OD) and ^{13}C NMR (126 MHz, CD_3OD) spectra for 25d:



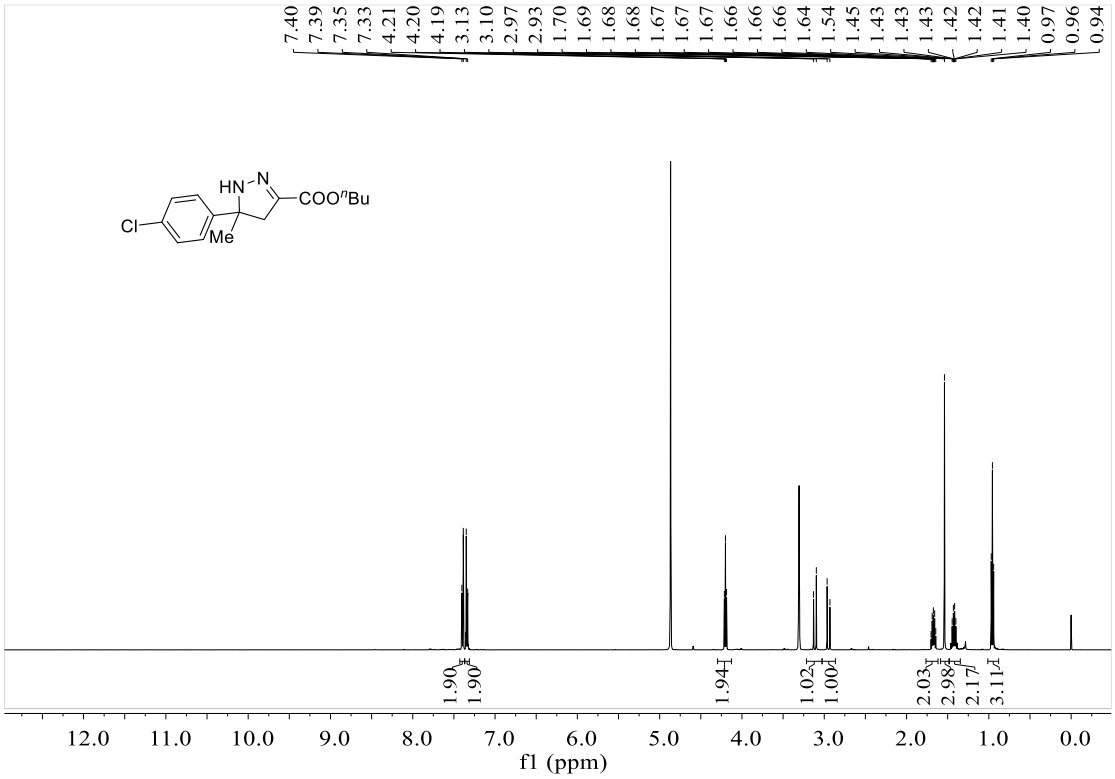


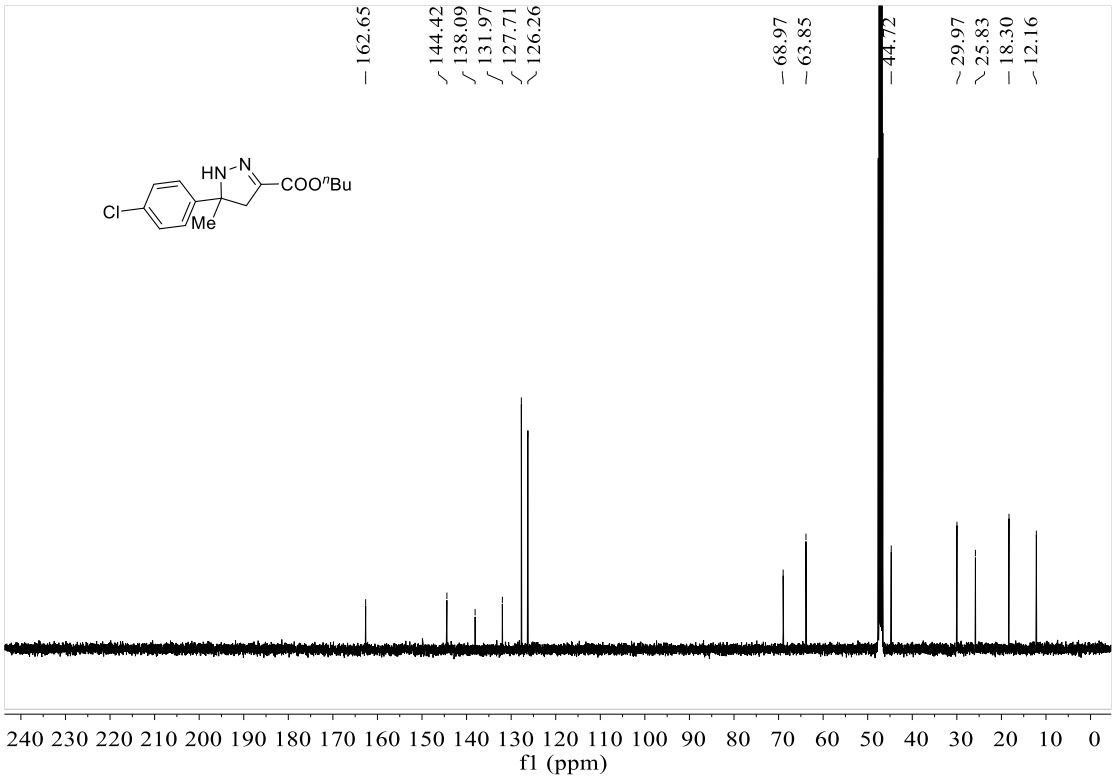
^{1}H NMR (500 MHz, CD_3OD) and ^{13}C NMR (126 MHz, CD_3OD) spectra for 26d:



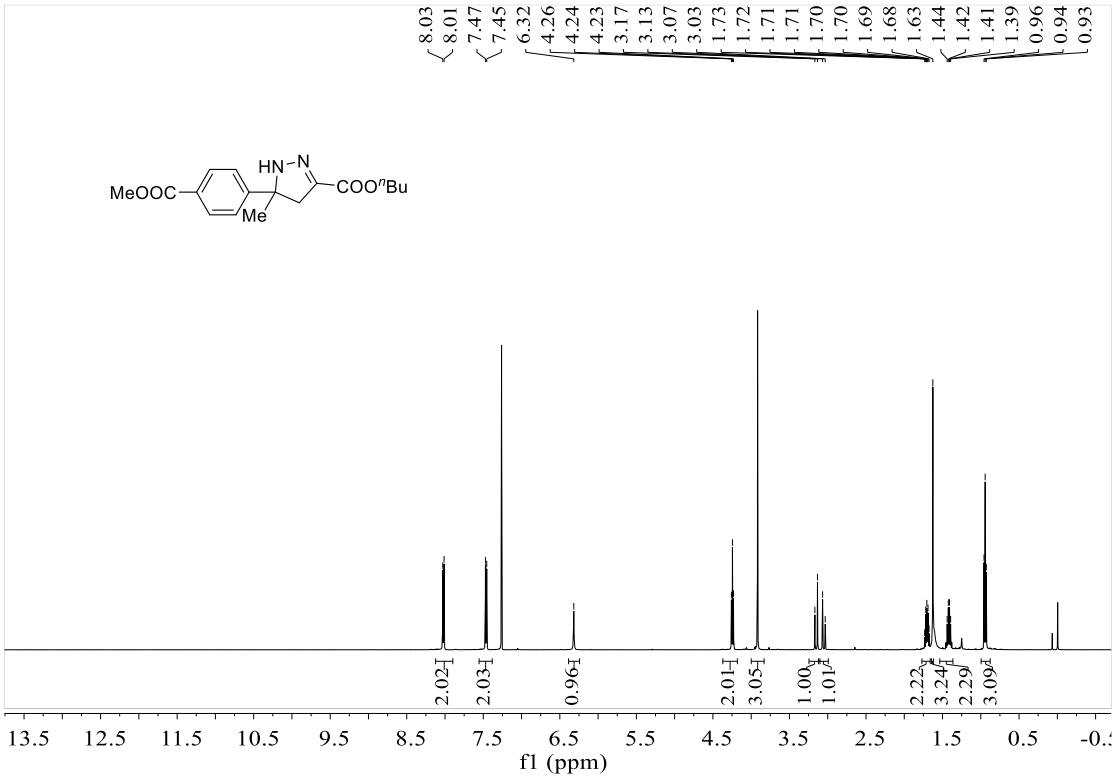


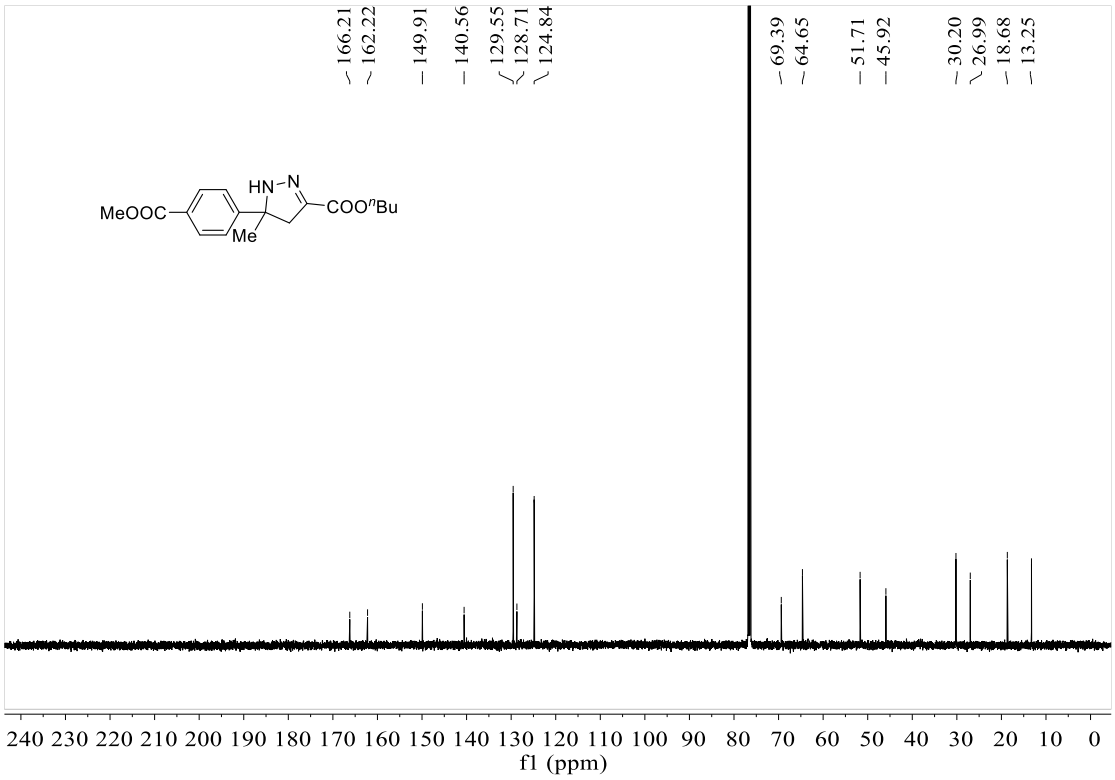
^{1}H NMR (500 MHz, CD_3OD) and ^{13}C NMR (126 MHz, CD_3OD) spectra for 27d:



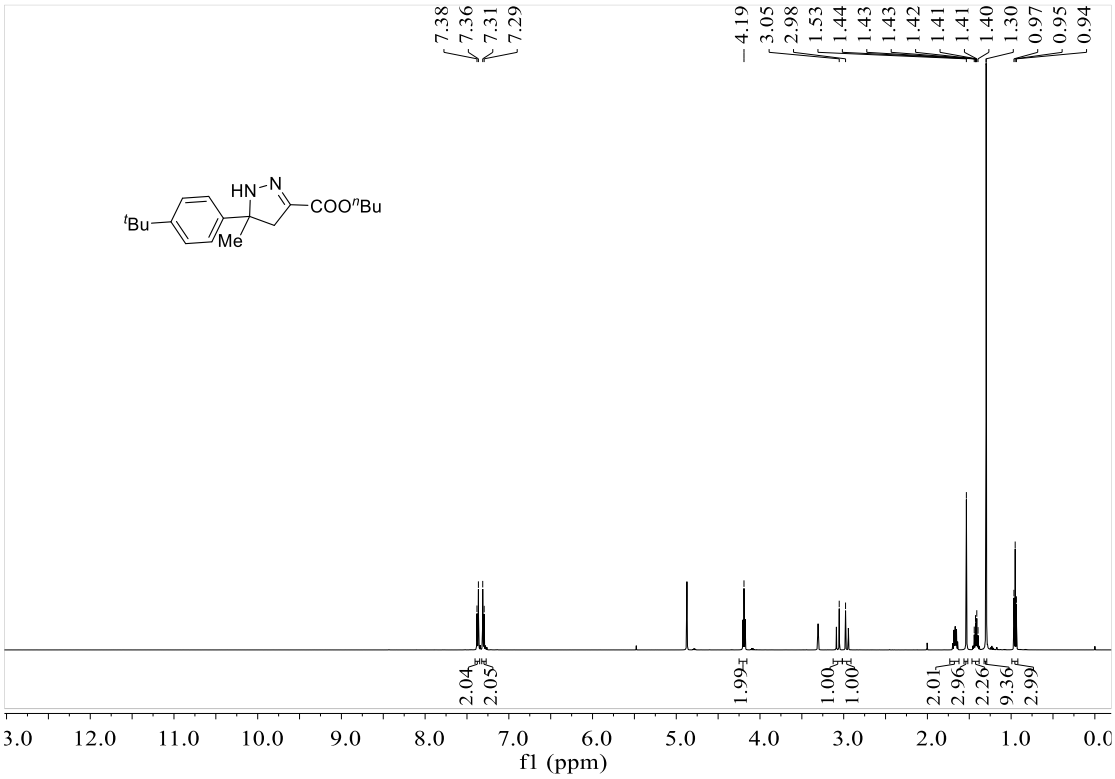


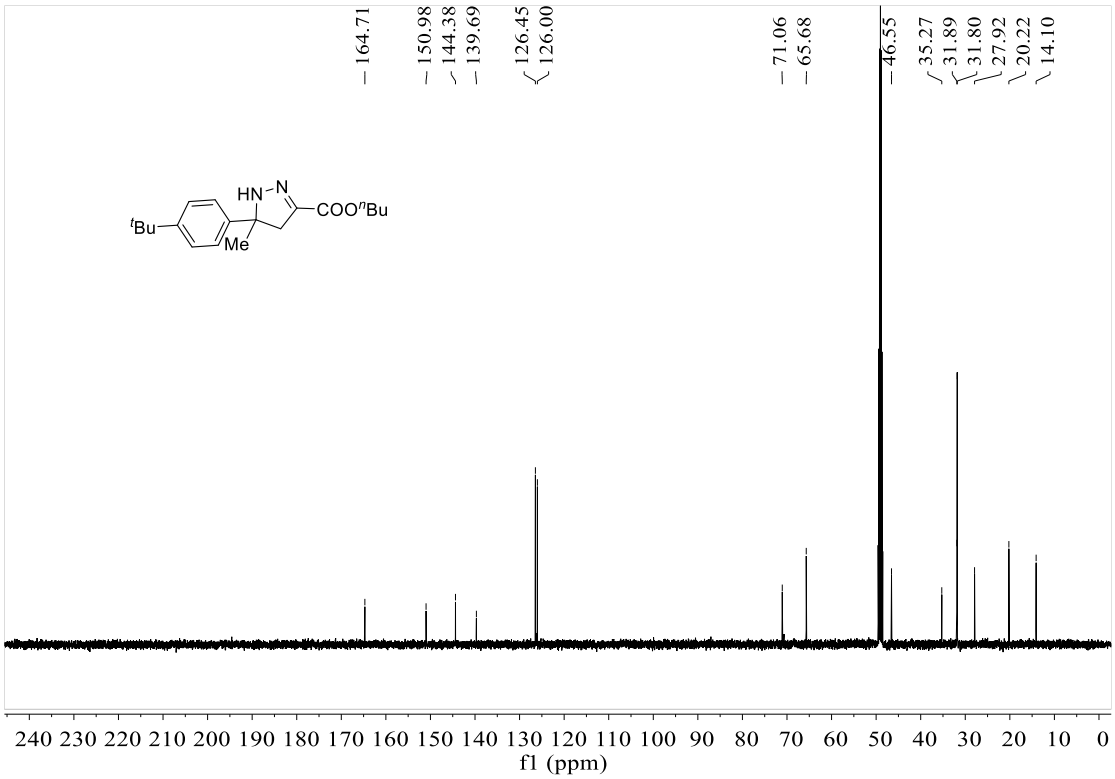
^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (126 MHz, $CDCl_3$) spectra for 28d:



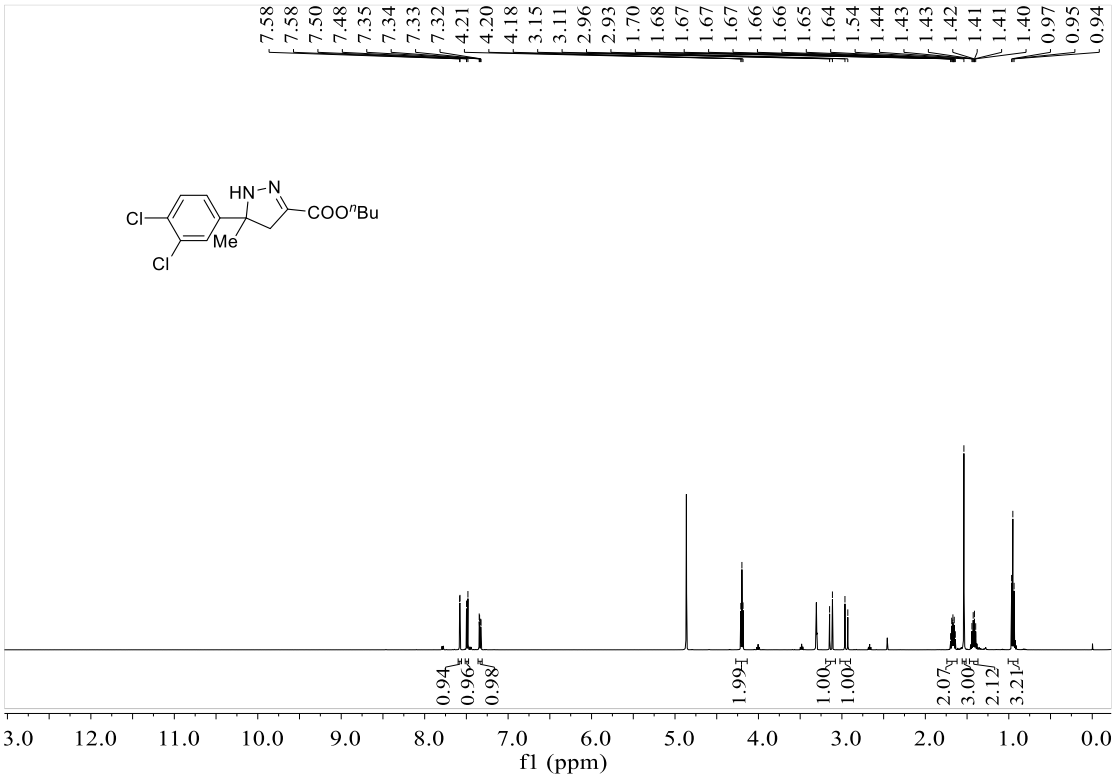


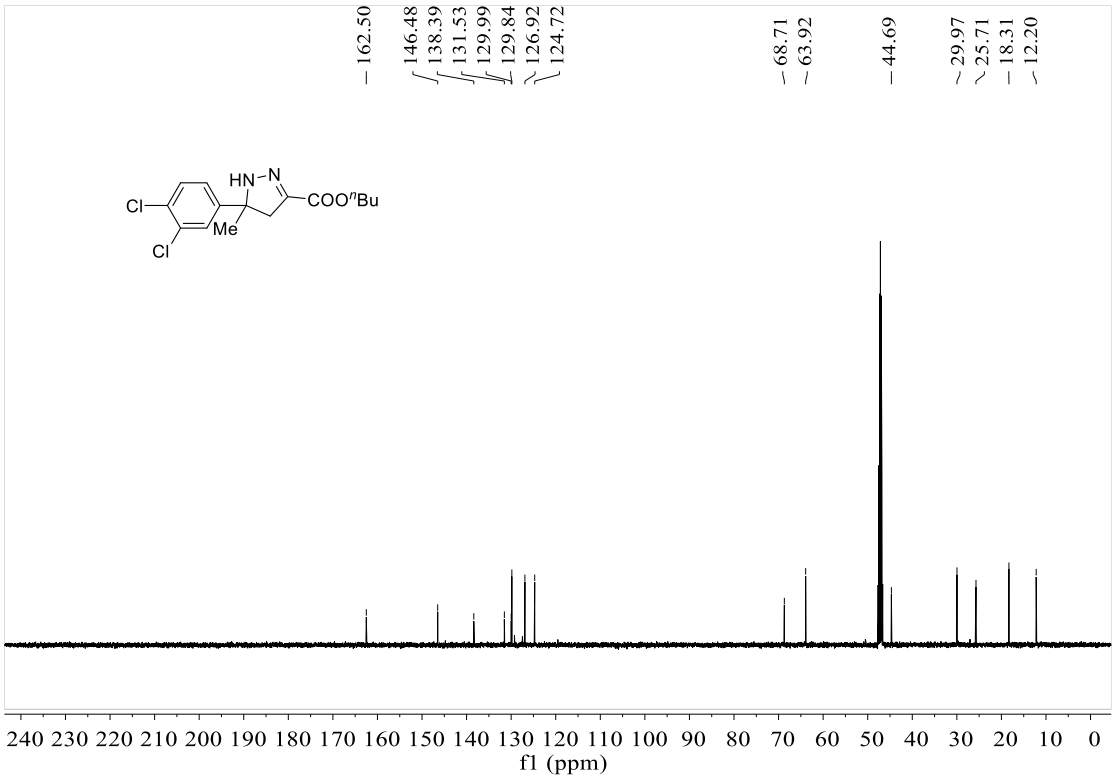
^{1}H NMR (500 MHz, CD_3OD) and ^{13}C NMR (126 MHz, CD_3OD) spectra for 29d:



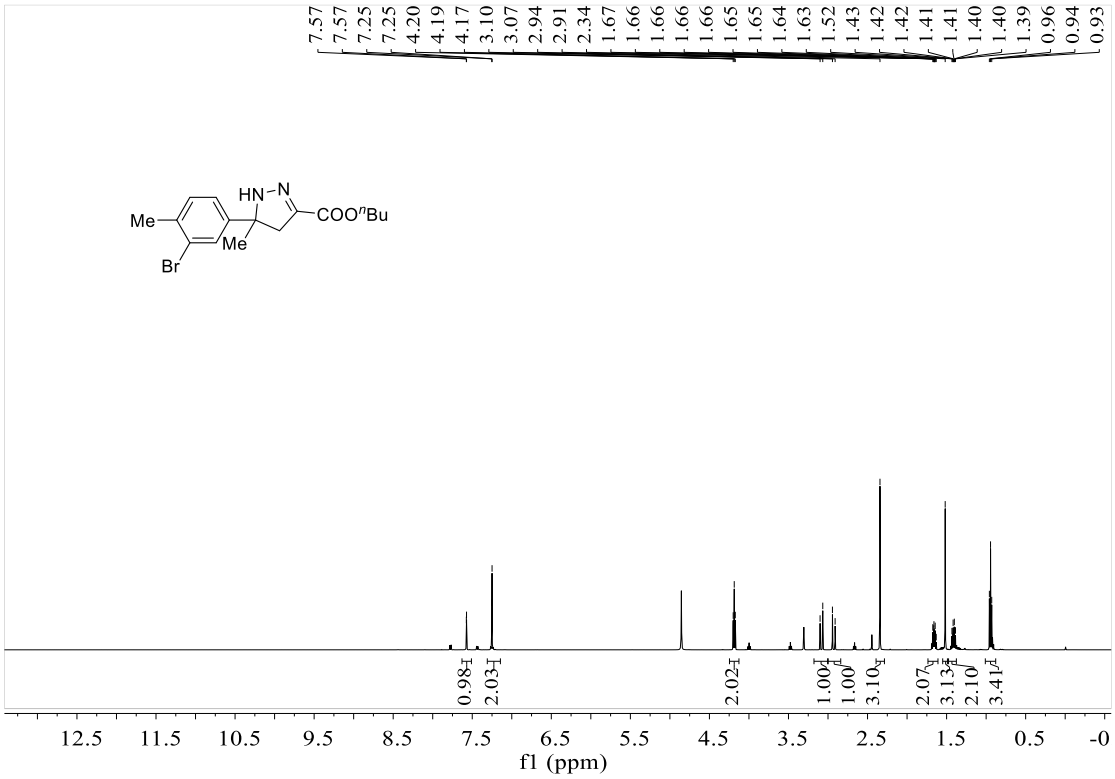


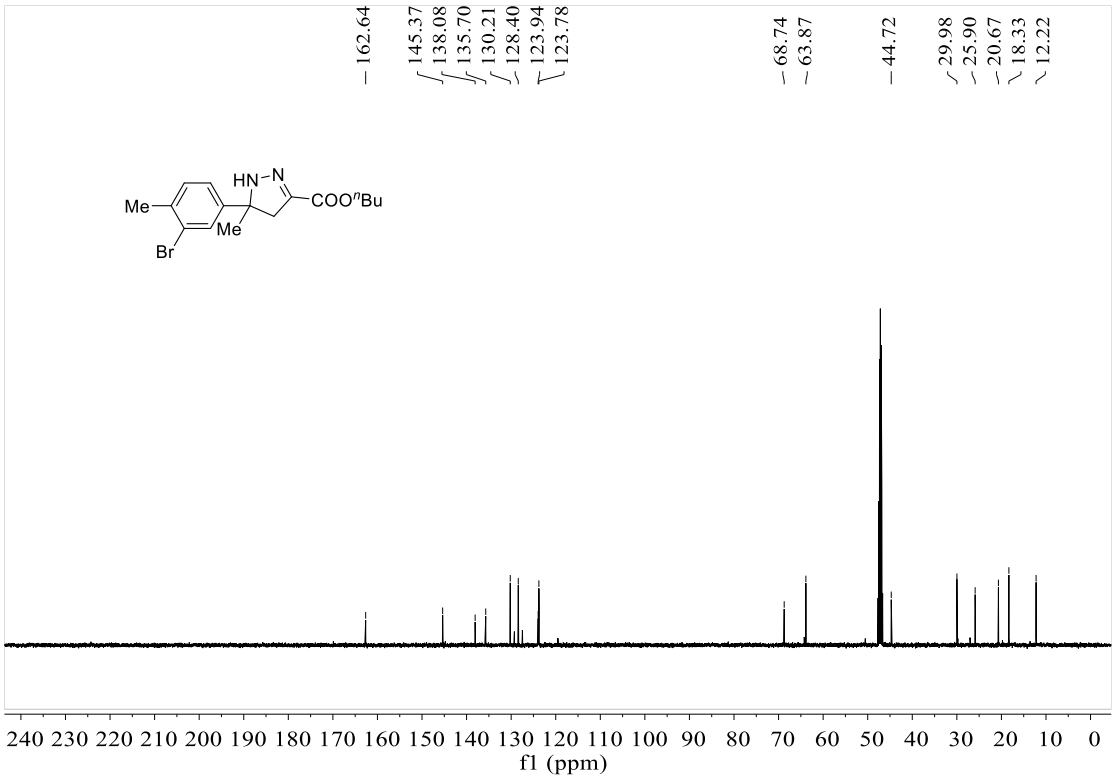
^{1}H NMR (500 MHz, CD_3OD) and ^{13}C NMR (126 MHz, CD_3OD) spectra for 30d:



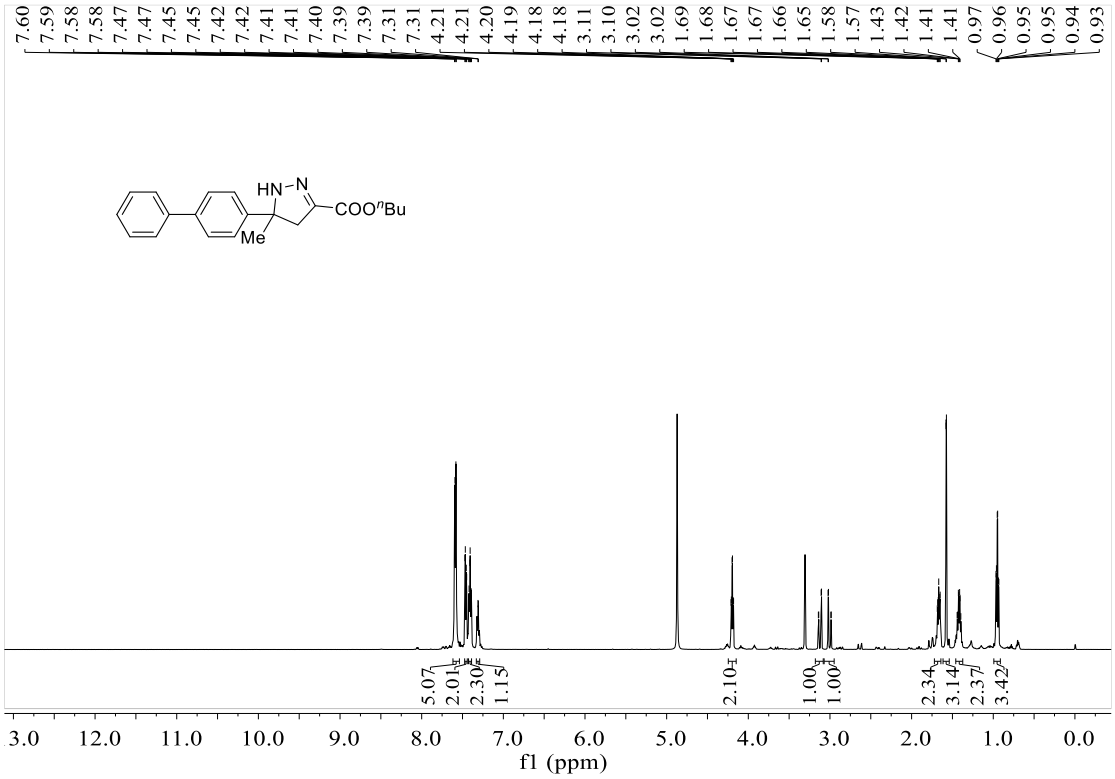


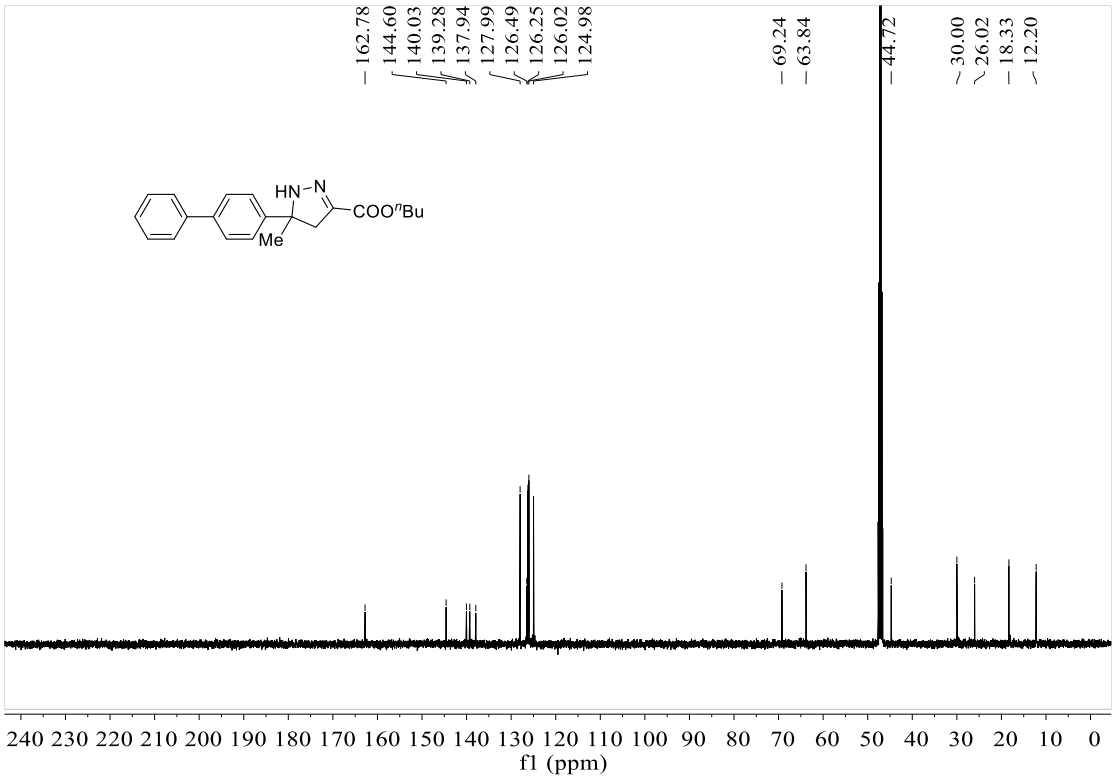
^{1}H NMR (500 MHz, CD_3OD) and ^{13}C NMR (126 MHz, CD_3OD) spectra for 31d:



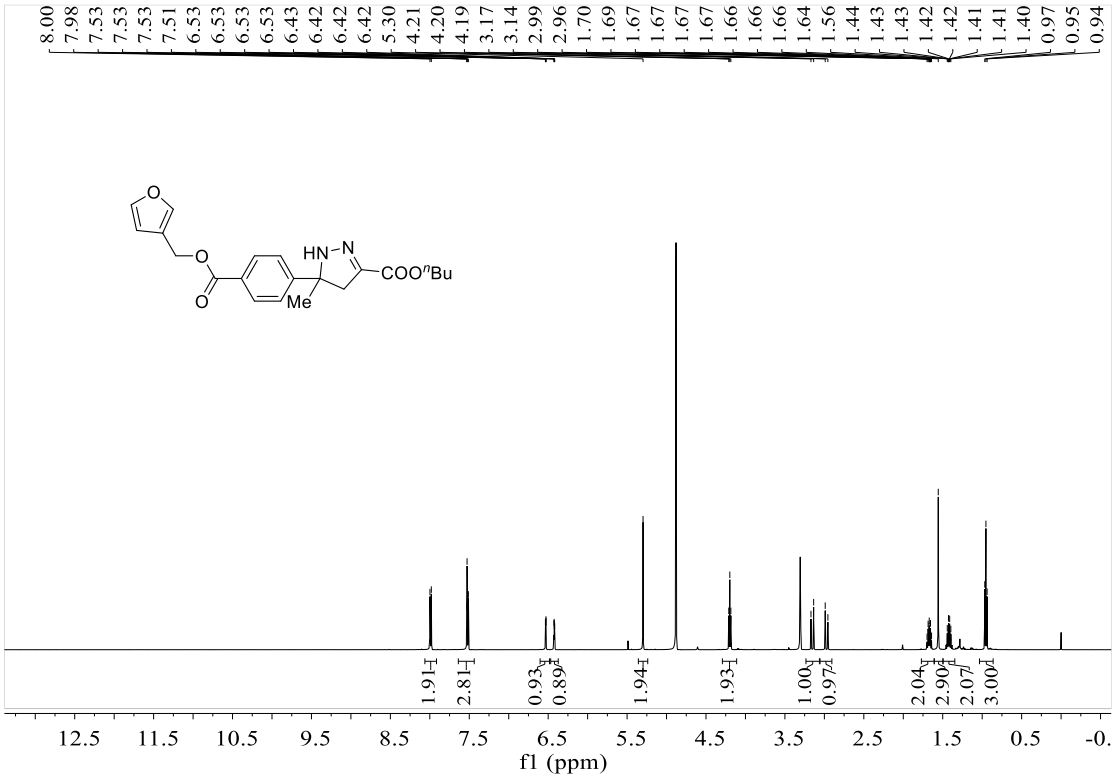


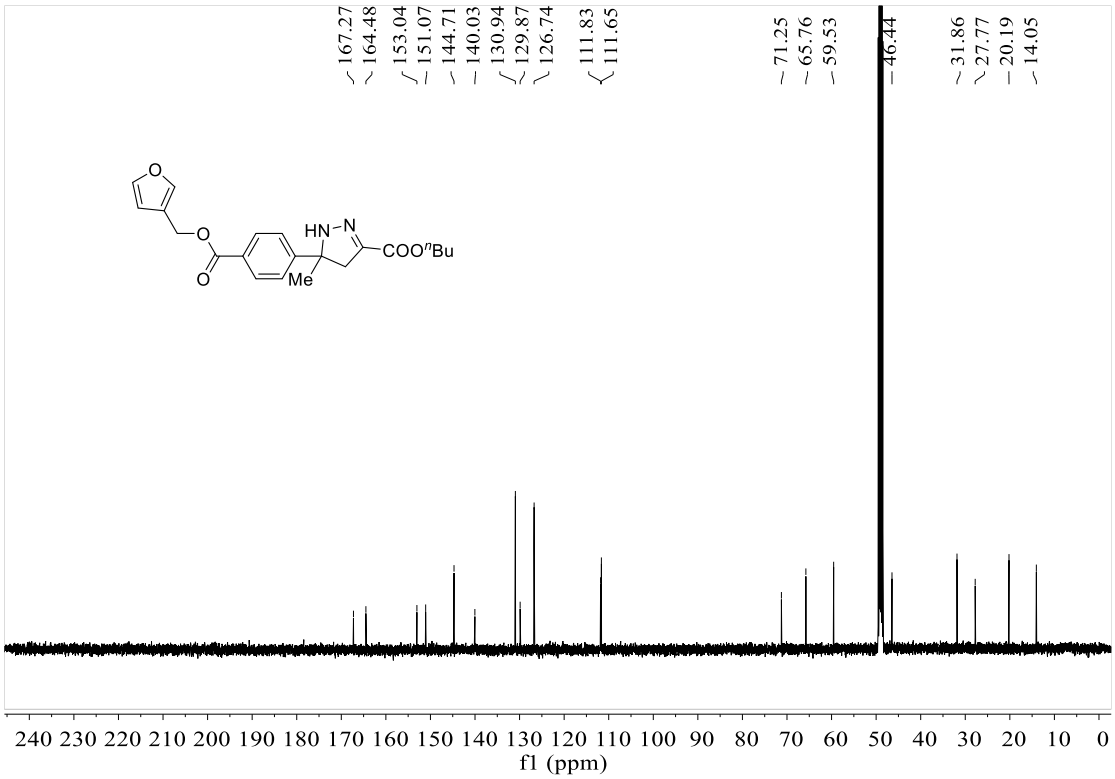
^{1}H NMR (500 MHz, CD_3OD) and ^{13}C NMR (126 MHz, CD_3OD) spectra for 32d:



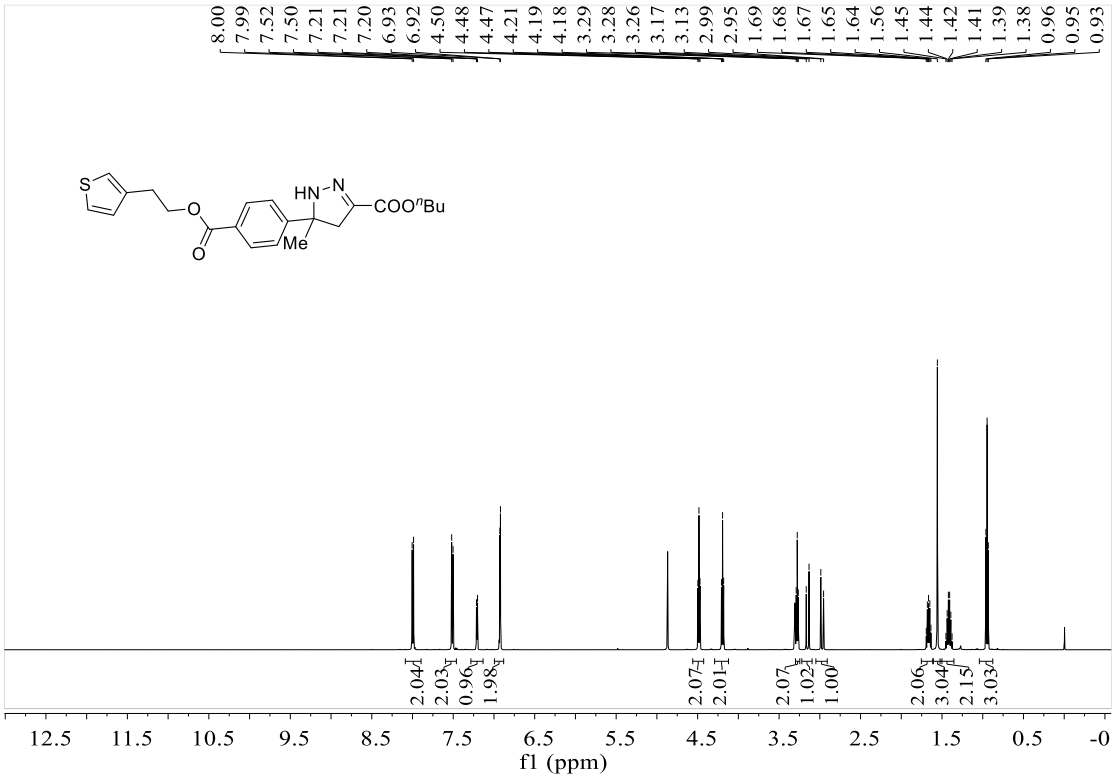


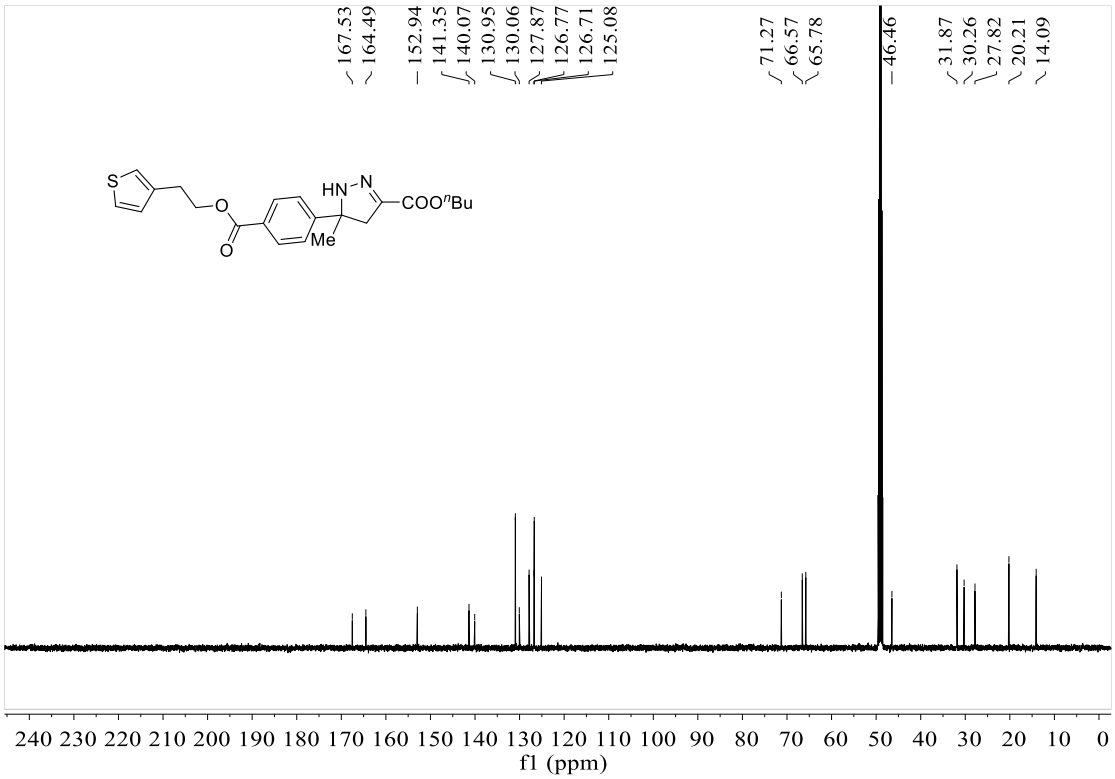
^{1}H NMR (500 MHz, CD_3OD) and ^{13}C NMR (126 MHz, CD_3OD) spectra for 33d:



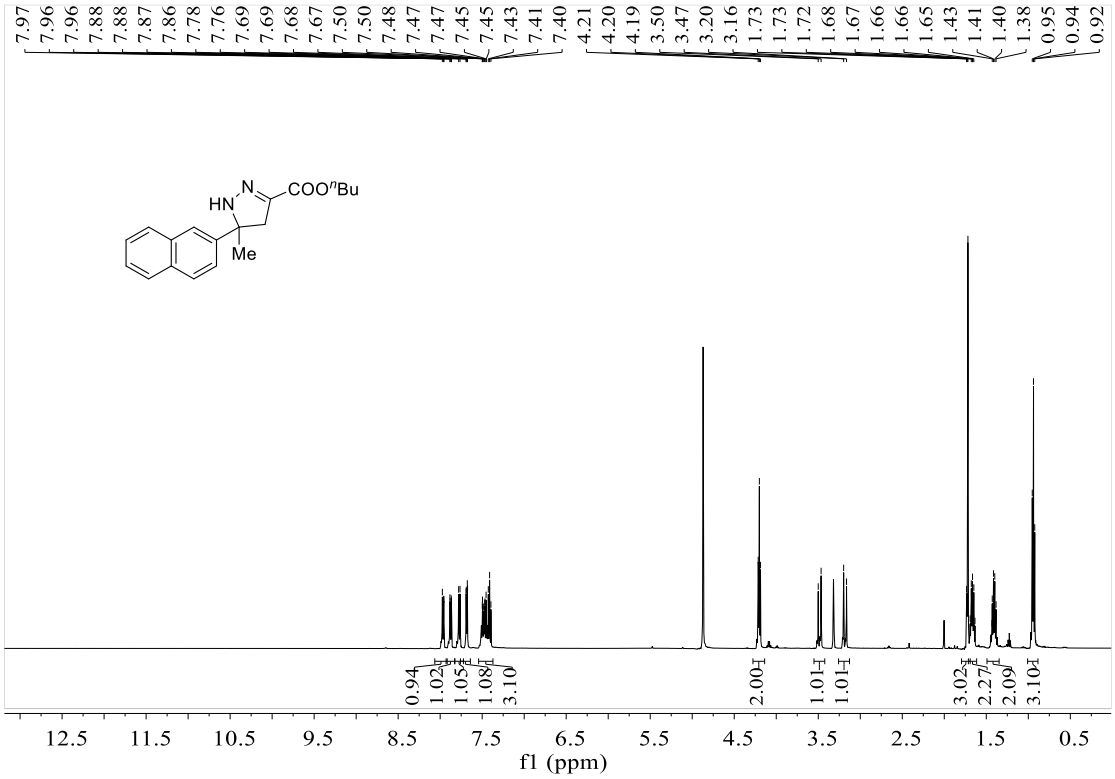


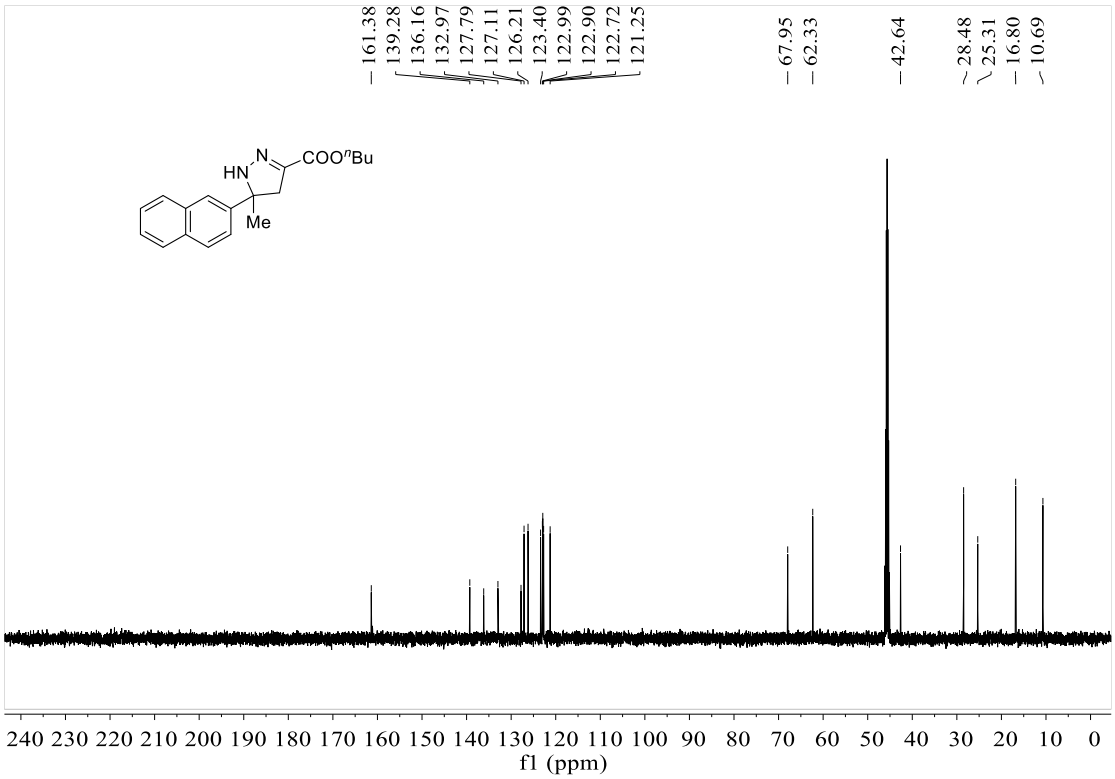
^{1}H NMR (500 MHz, CD_3OD) and ^{13}C NMR (126 MHz, CD_3OD) spectra for 34d:



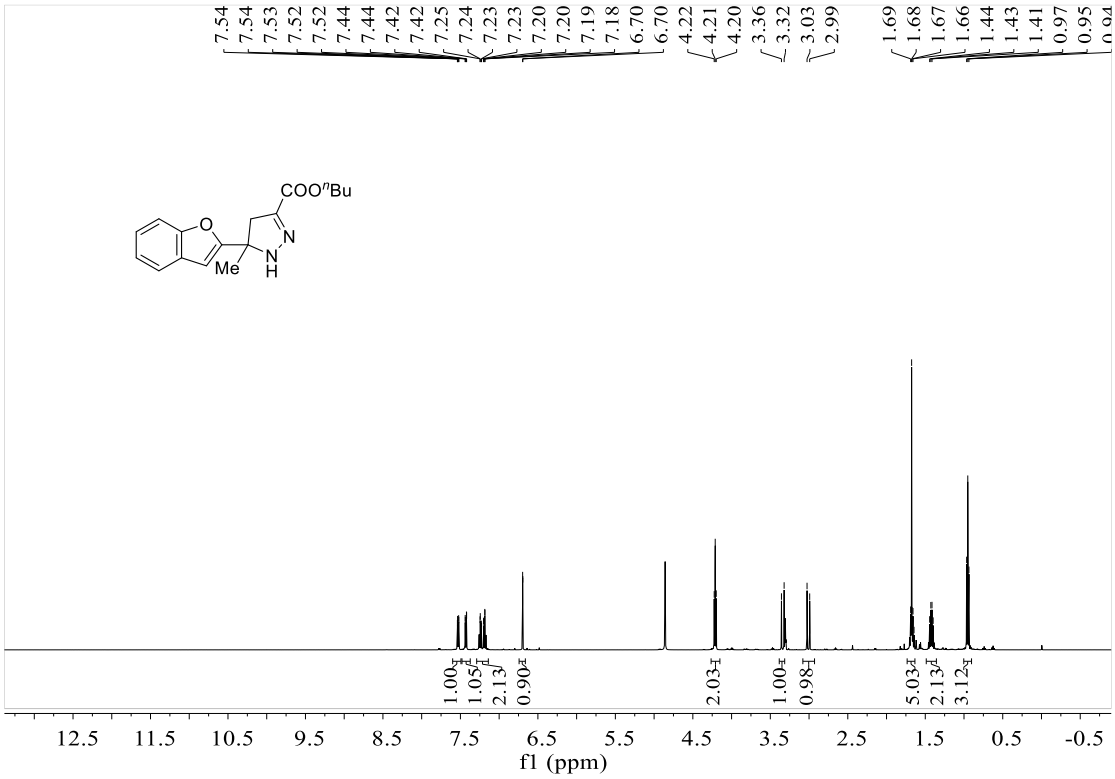


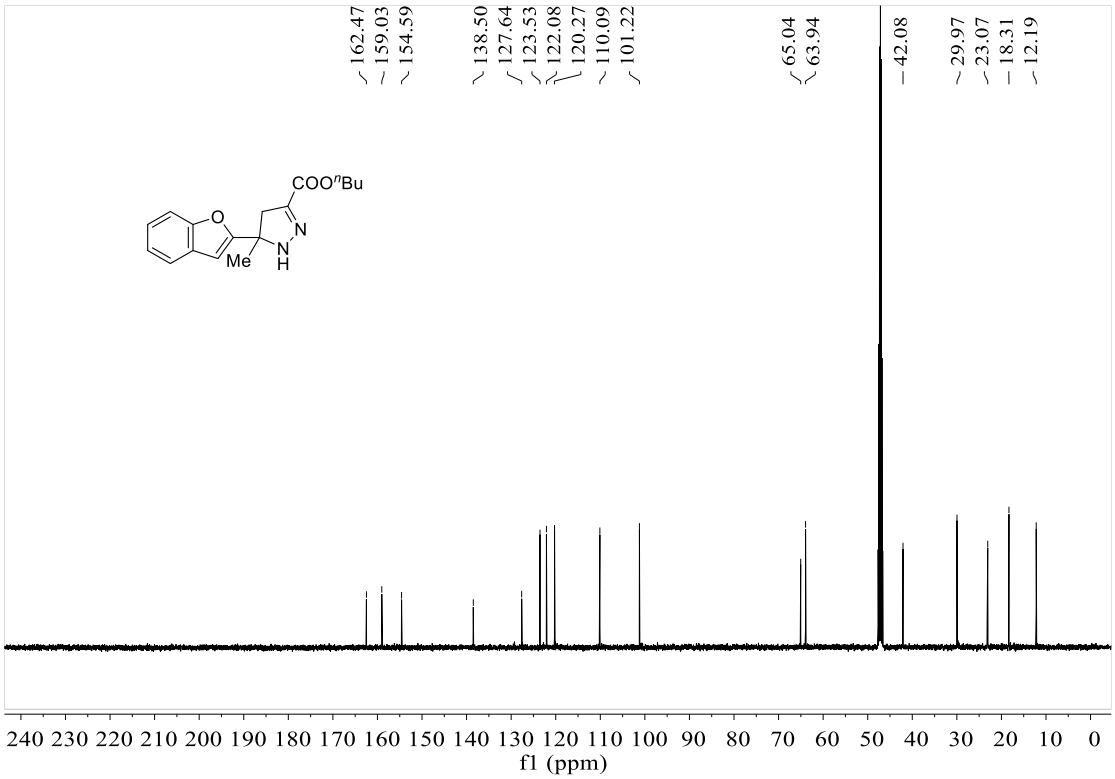
^{1}H NMR (500 MHz, CD_3OD) and ^{13}C NMR (126 MHz, CD_3OD) spectra for 35d:



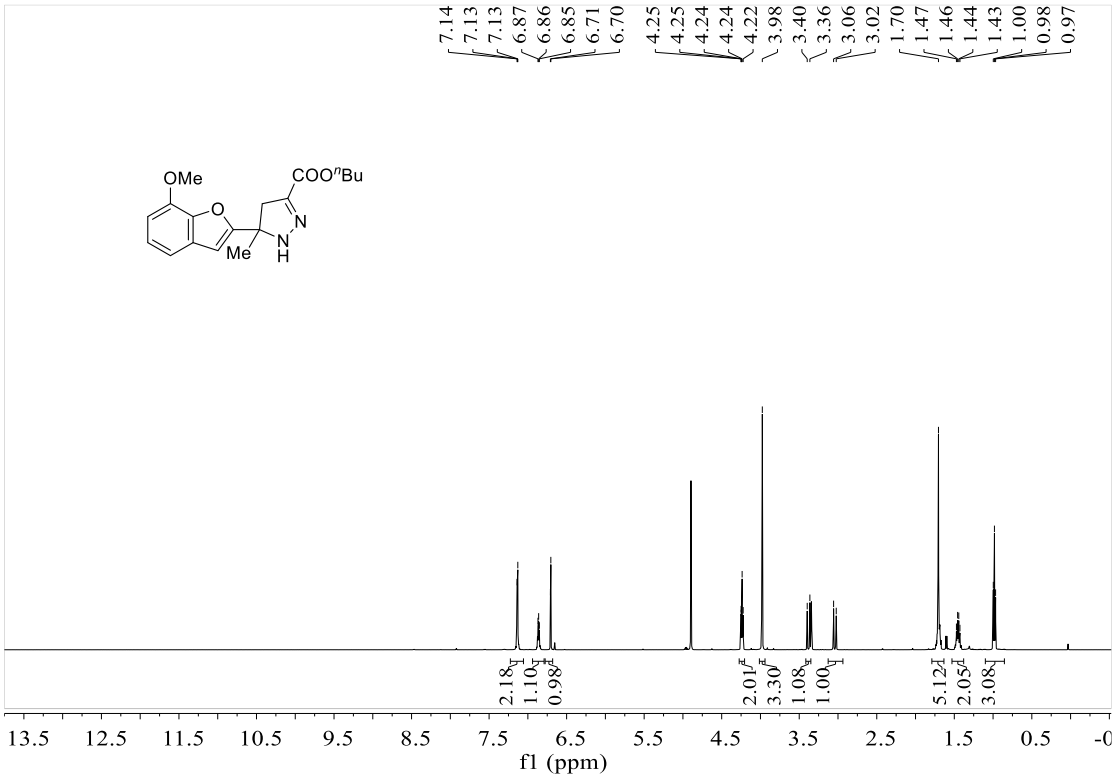


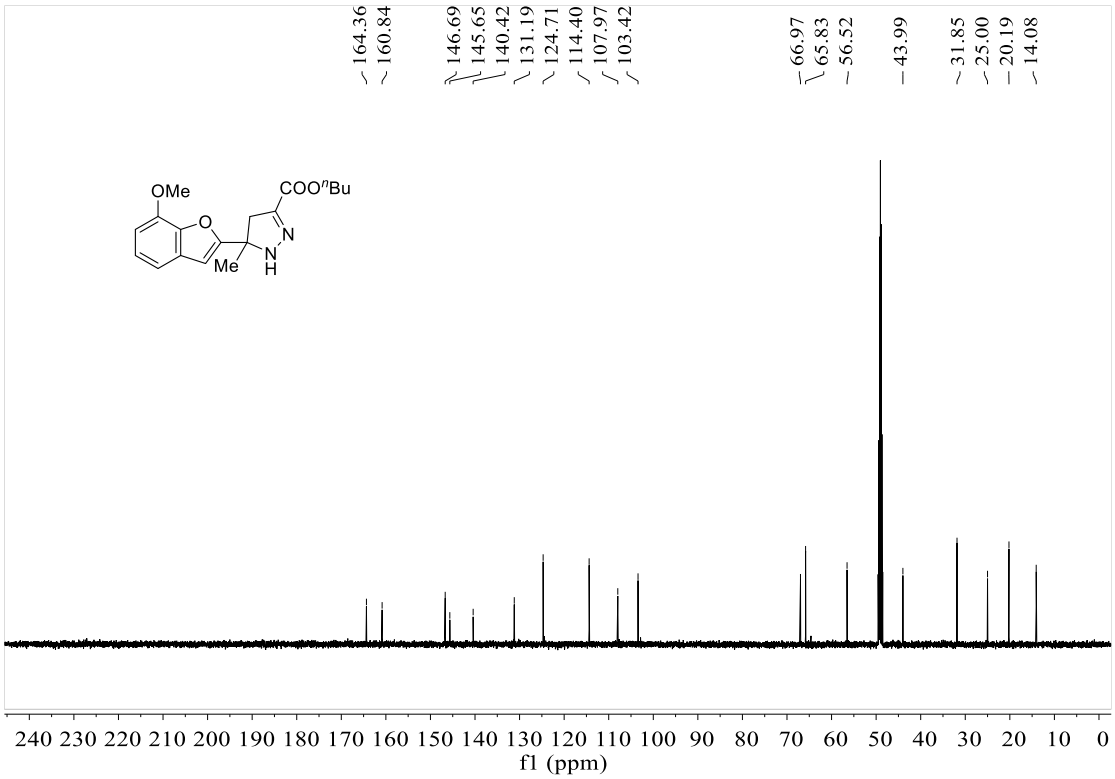
^{1}H NMR (500 MHz, CD_3OD) and ^{13}C NMR (126 MHz, CD_3OD) spectra for 36d:



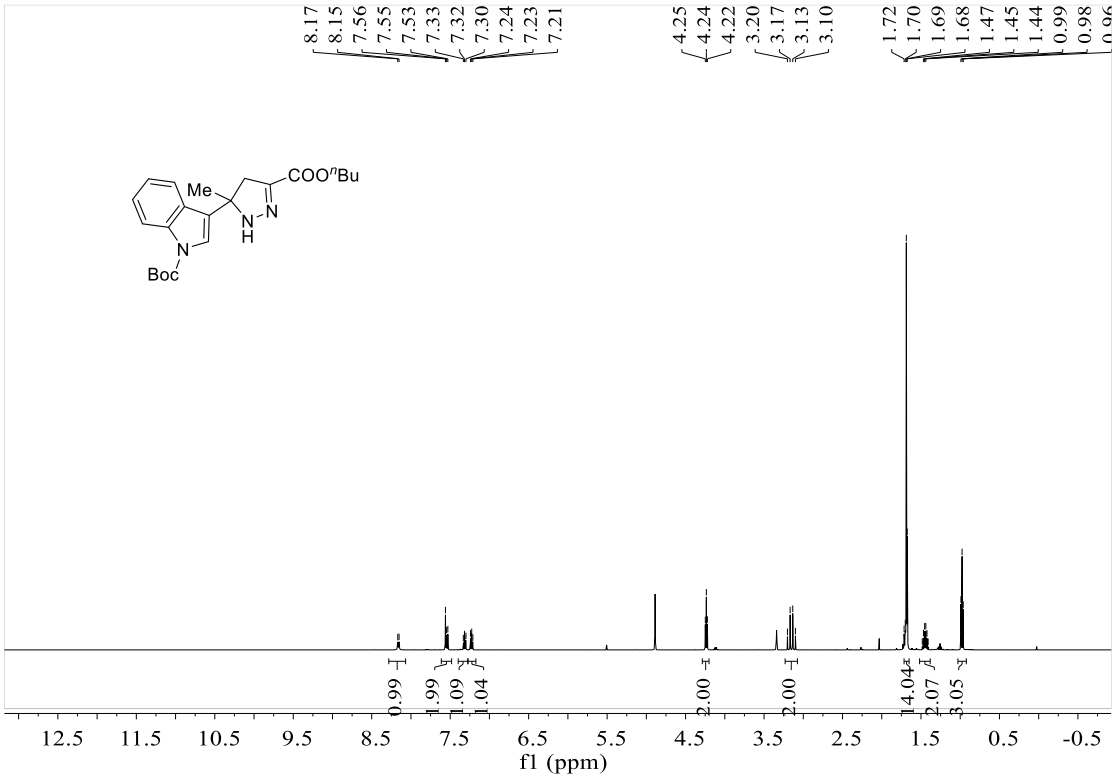


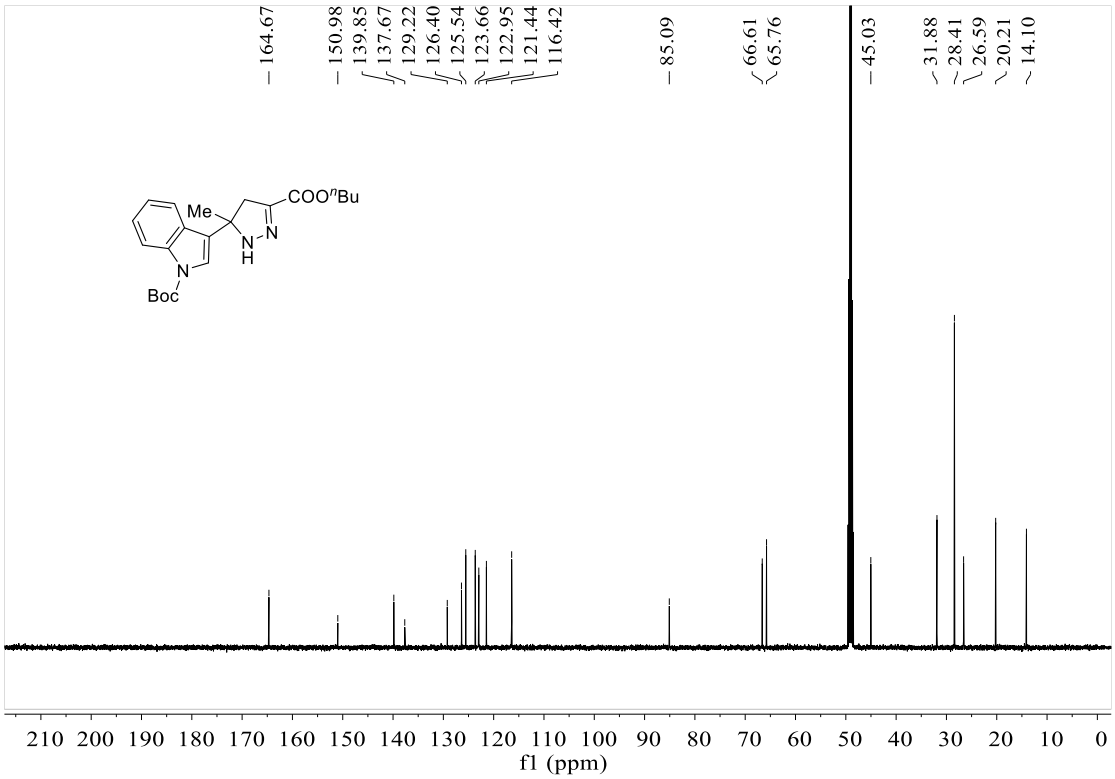
^{1}H NMR (500 MHz, CD_3OD) and ^{13}C NMR (126 MHz, CD_3OD) spectra for 37d:



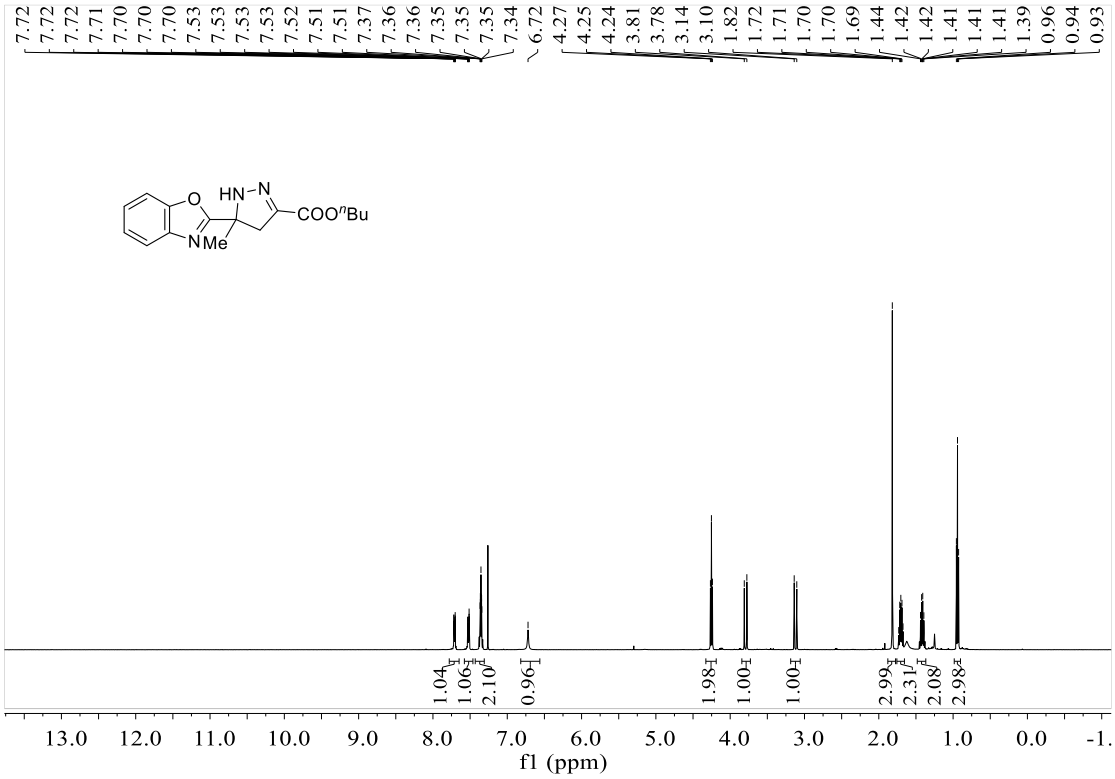


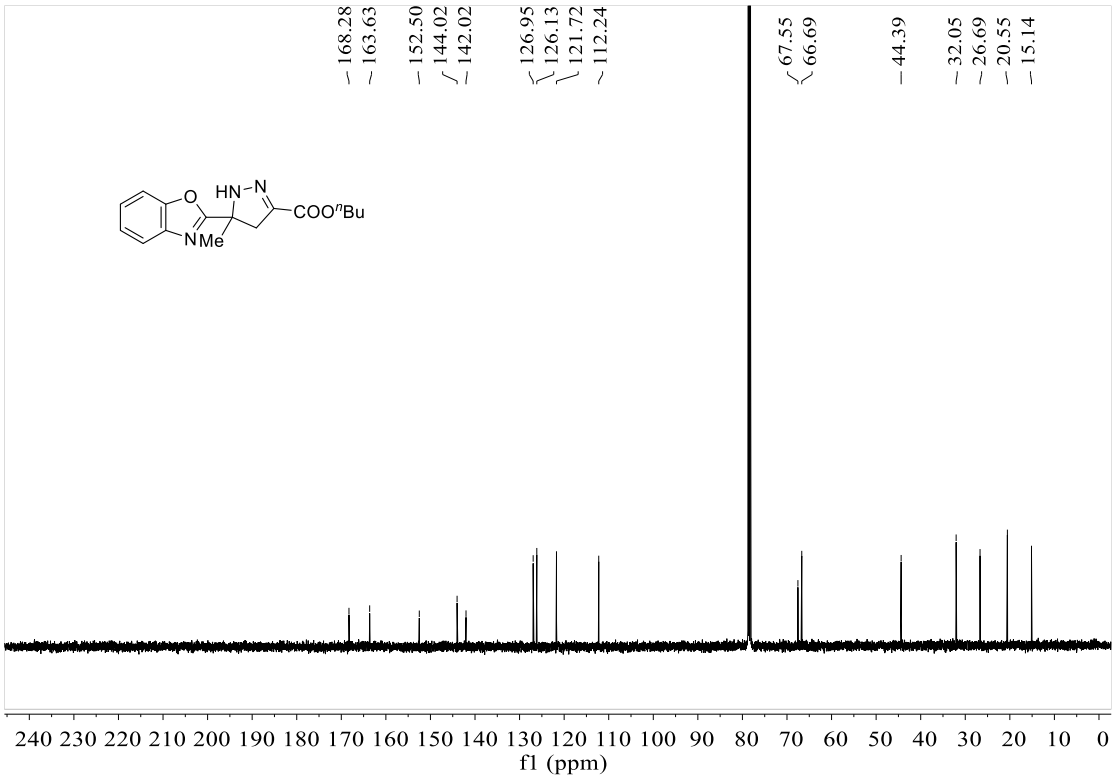
^{1}H NMR (500 MHz, CD_3OD) and ^{13}C NMR (126 MHz, CD_3OD) spectra for 38d:



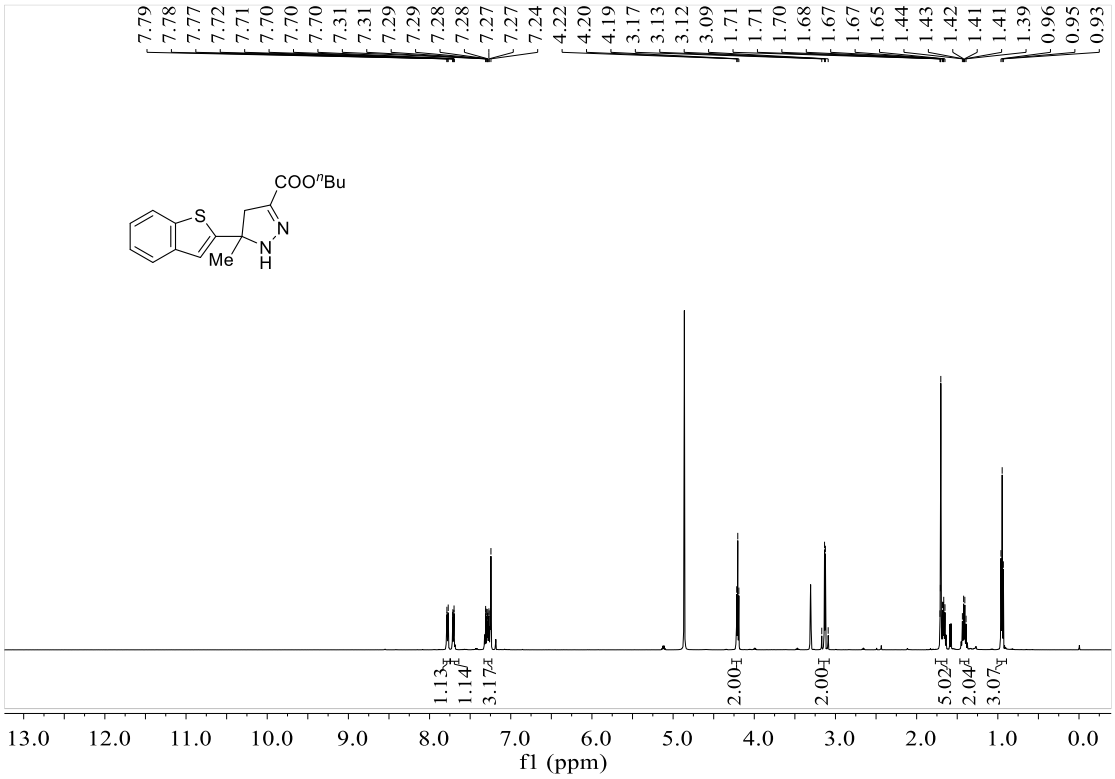


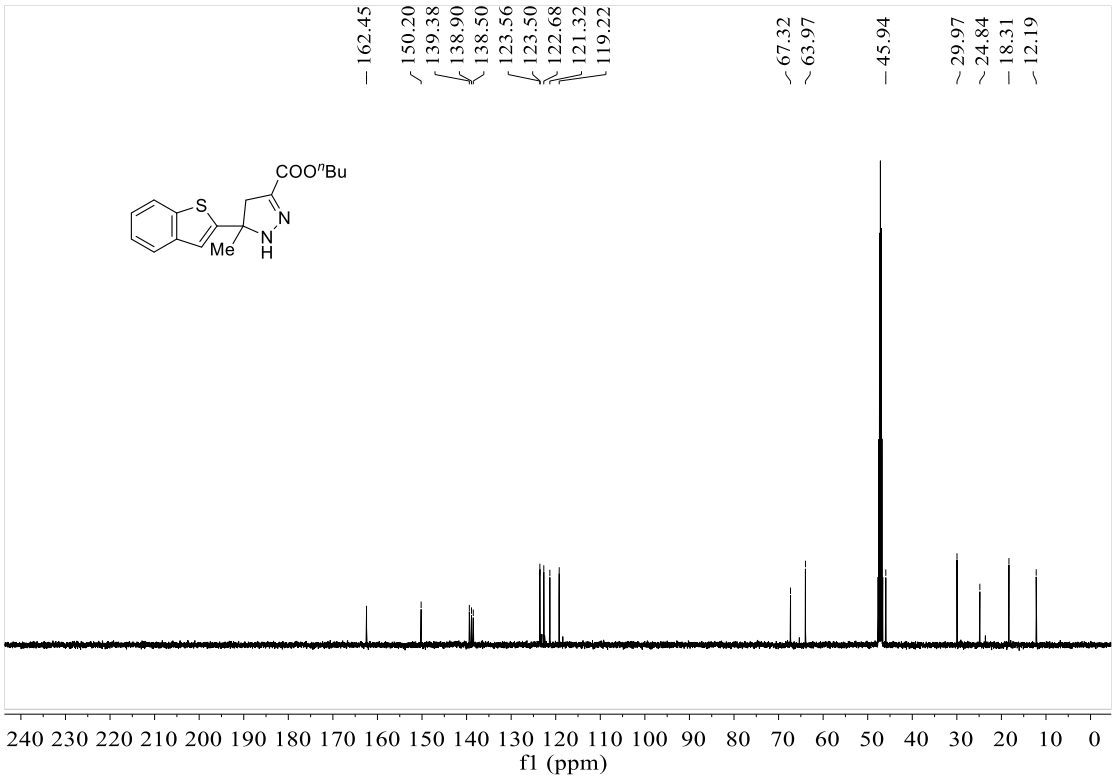
^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (126 MHz, $CDCl_3$) spectra for 39d:



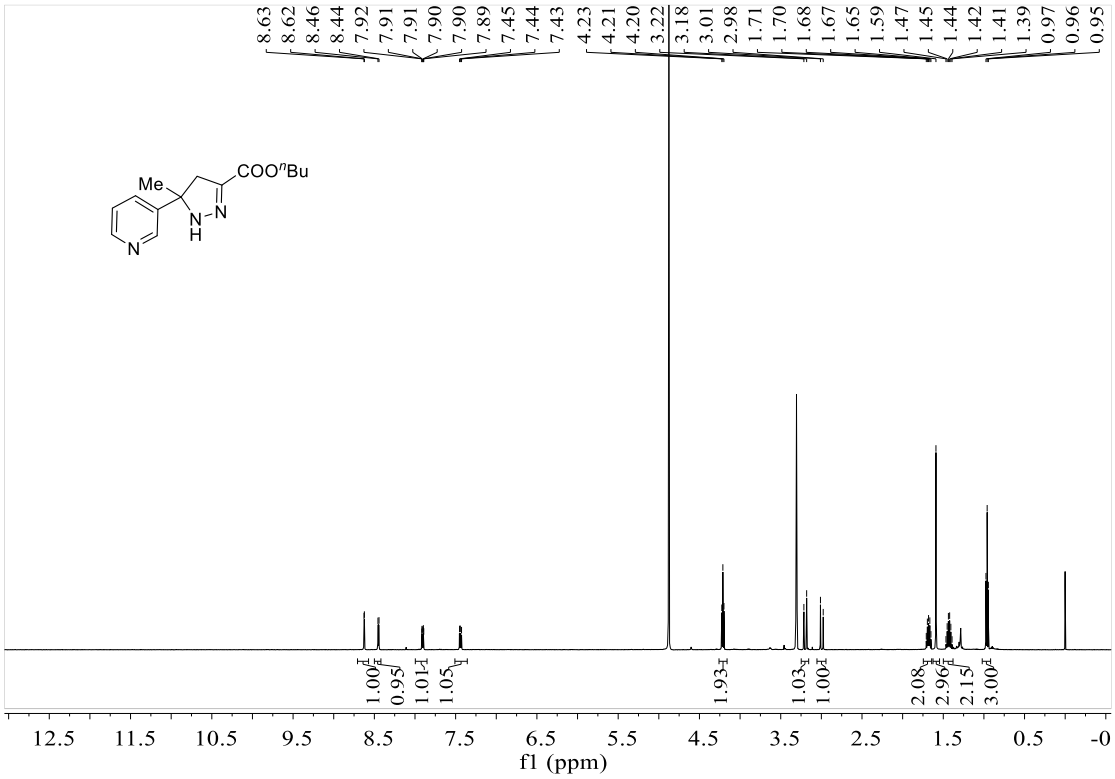


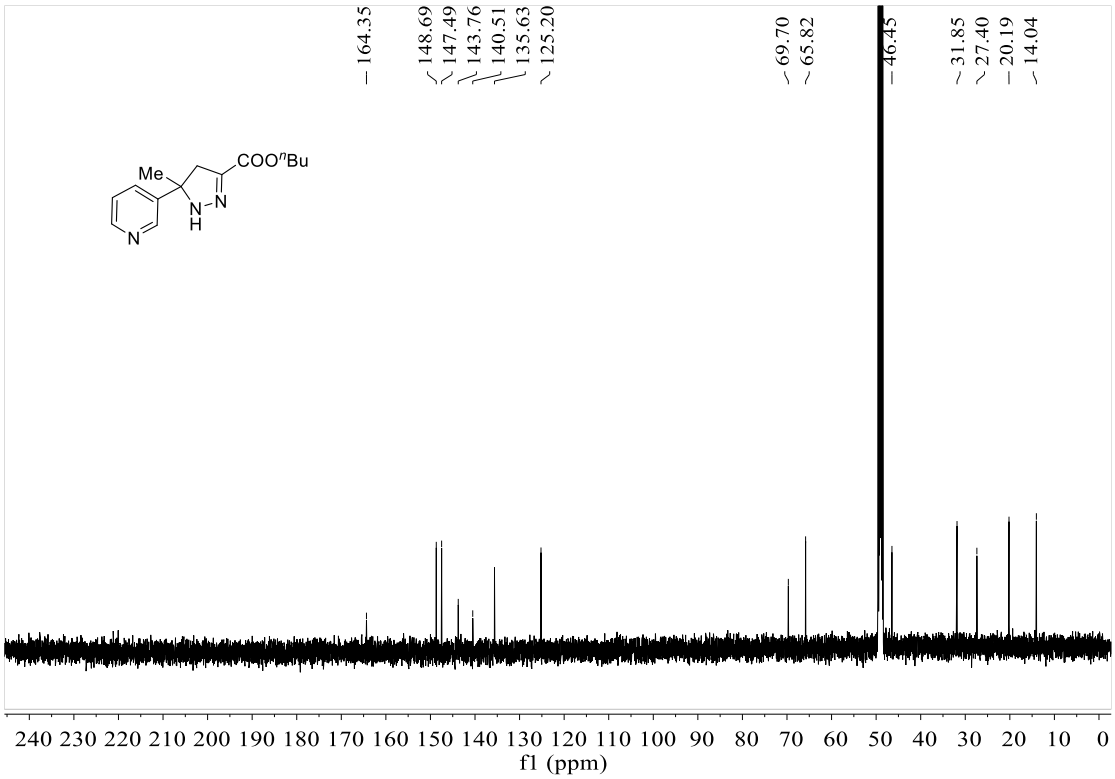
^{1}H NMR (500 MHz, CD_3OD) and ^{13}C NMR (126 MHz, CD_3OD) spectra for 40d:



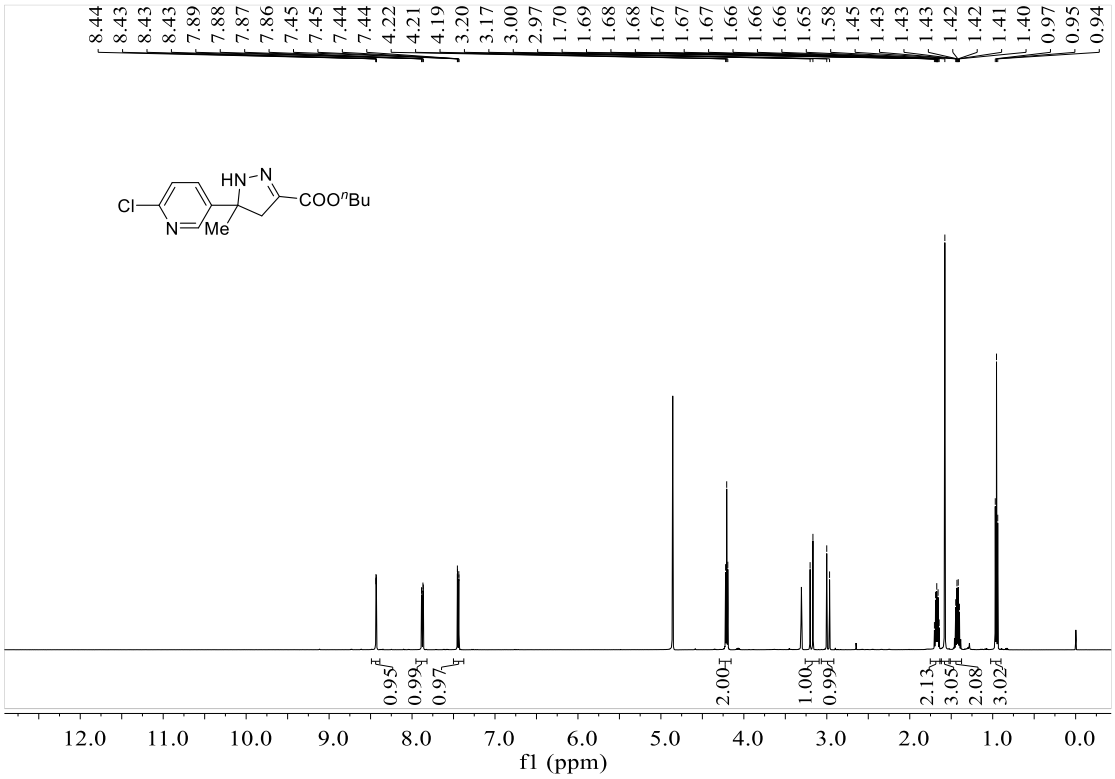


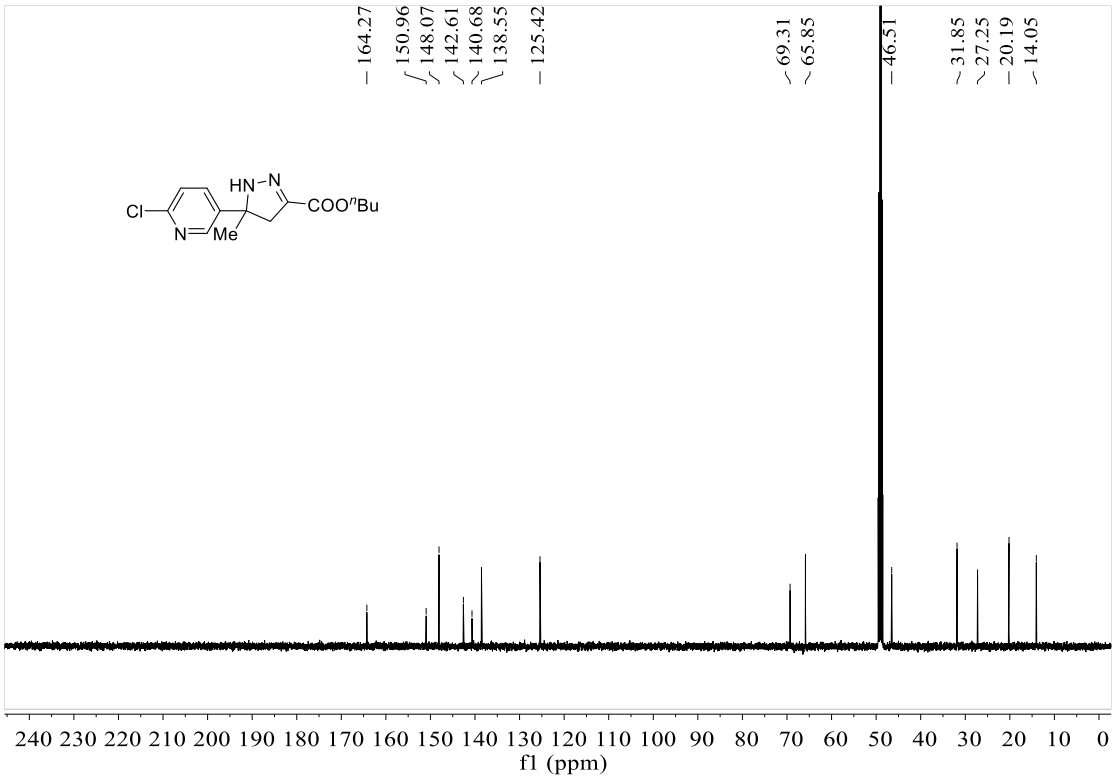
^{1}H NMR (500 MHz, CD_3OD) and ^{13}C NMR (126 MHz, CD_3OD) spectra for 41d:



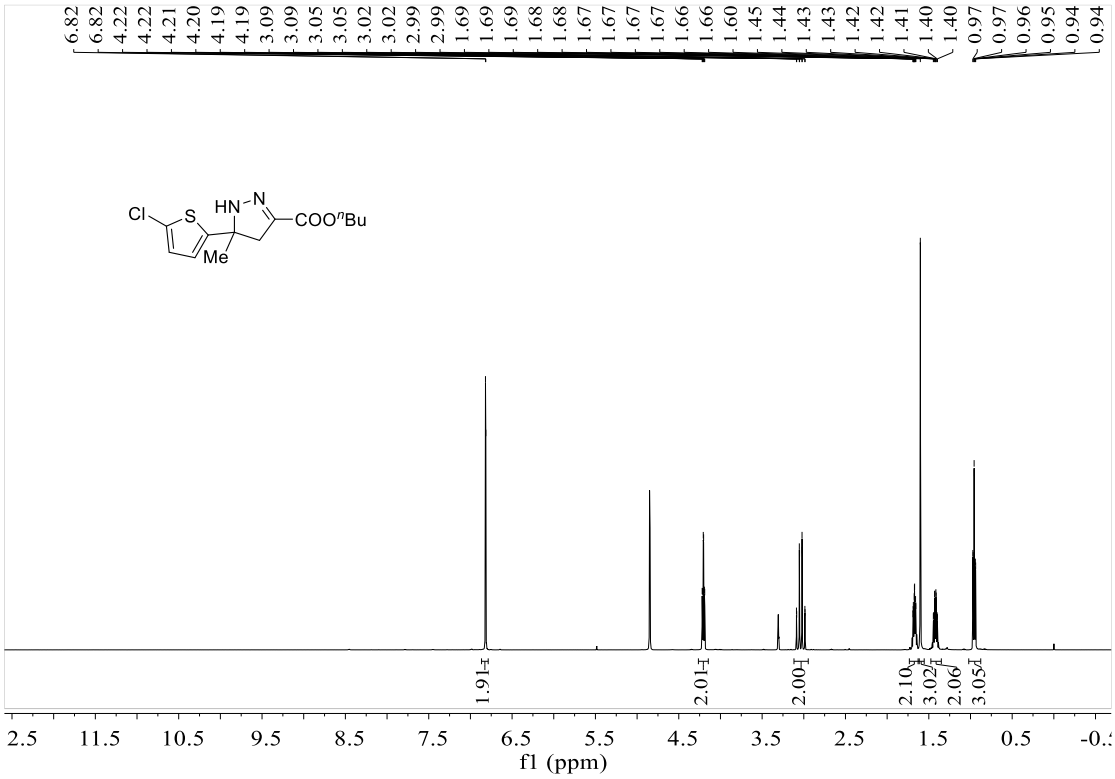


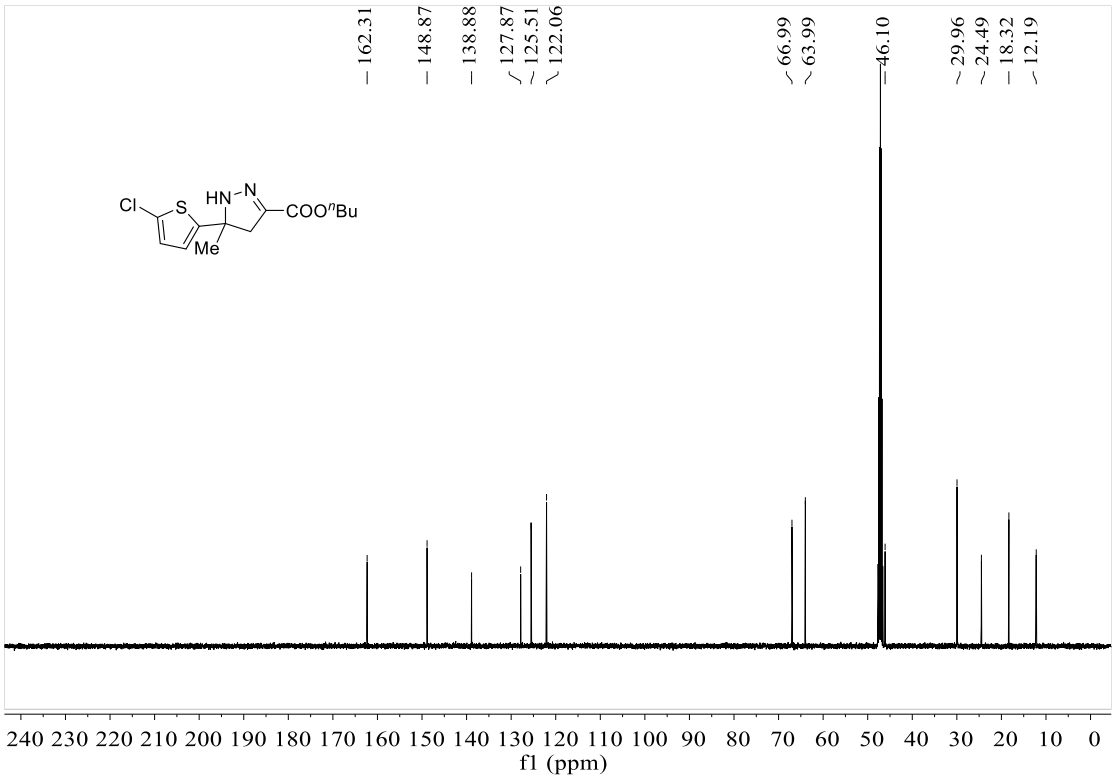
^{1}H NMR (500 MHz, CD_3OD) and ^{13}C NMR (126 MHz, CD_3OD) spectra for 42d:



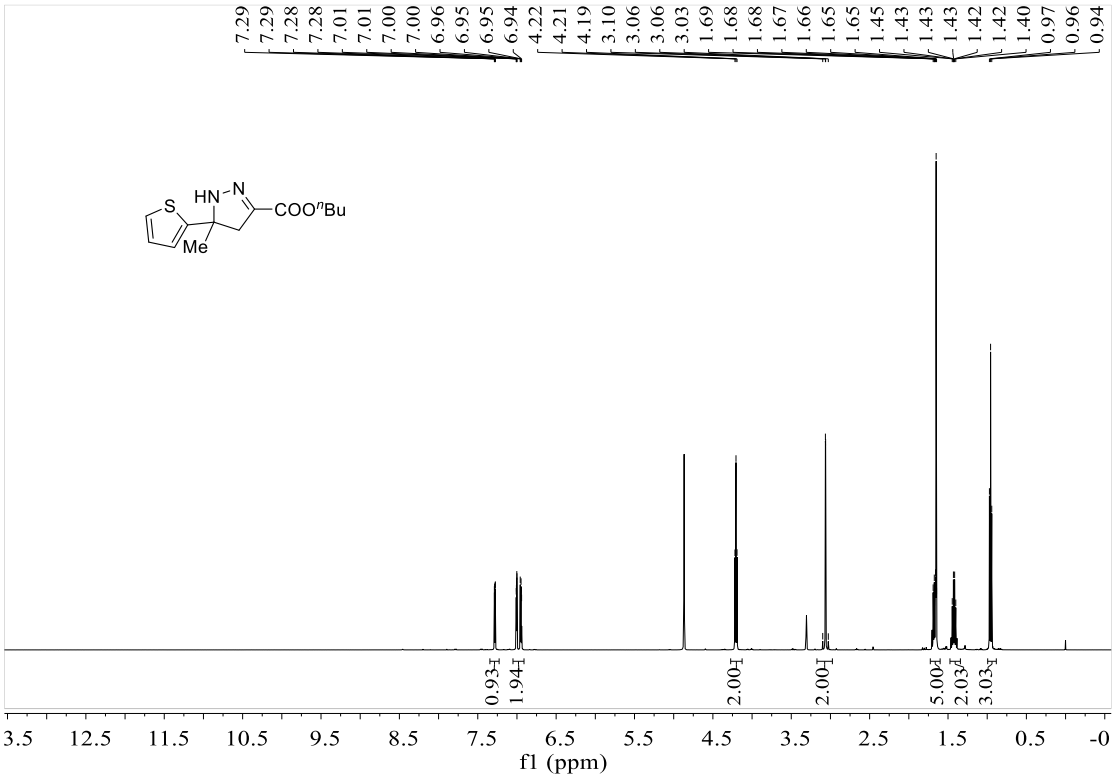


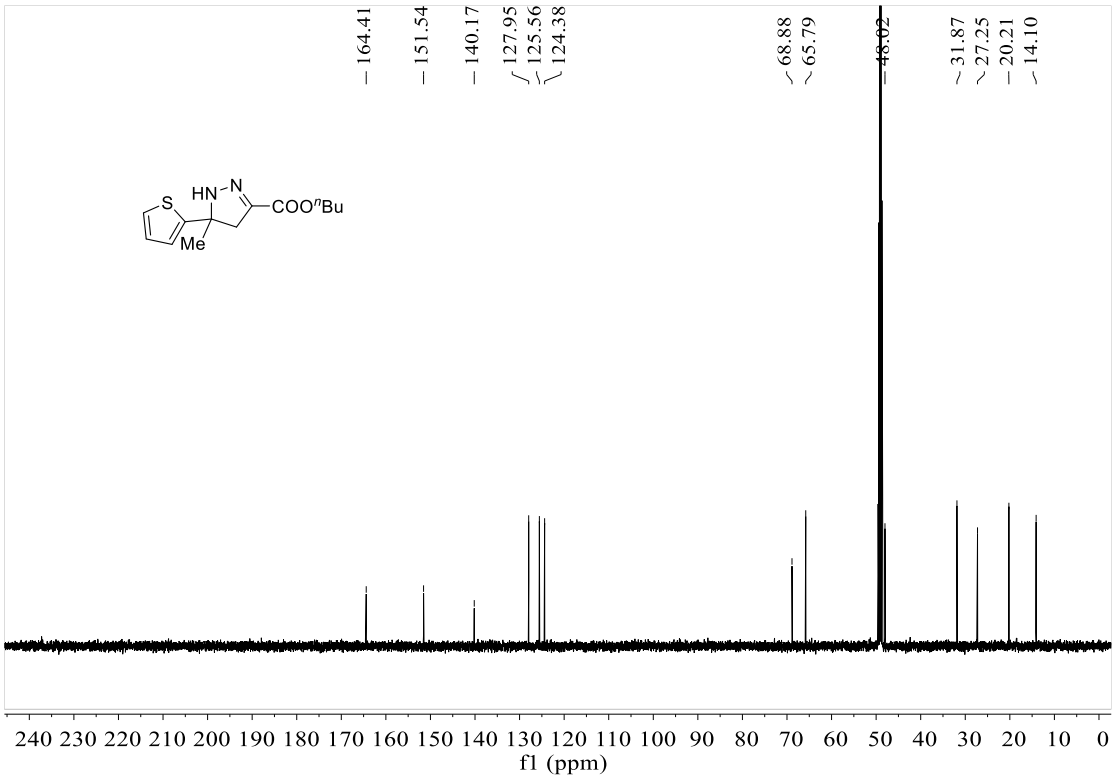
^{1}H NMR (500 MHz, CD_3OD) and ^{13}C NMR (126 MHz, CD_3OD) spectra for 43d:



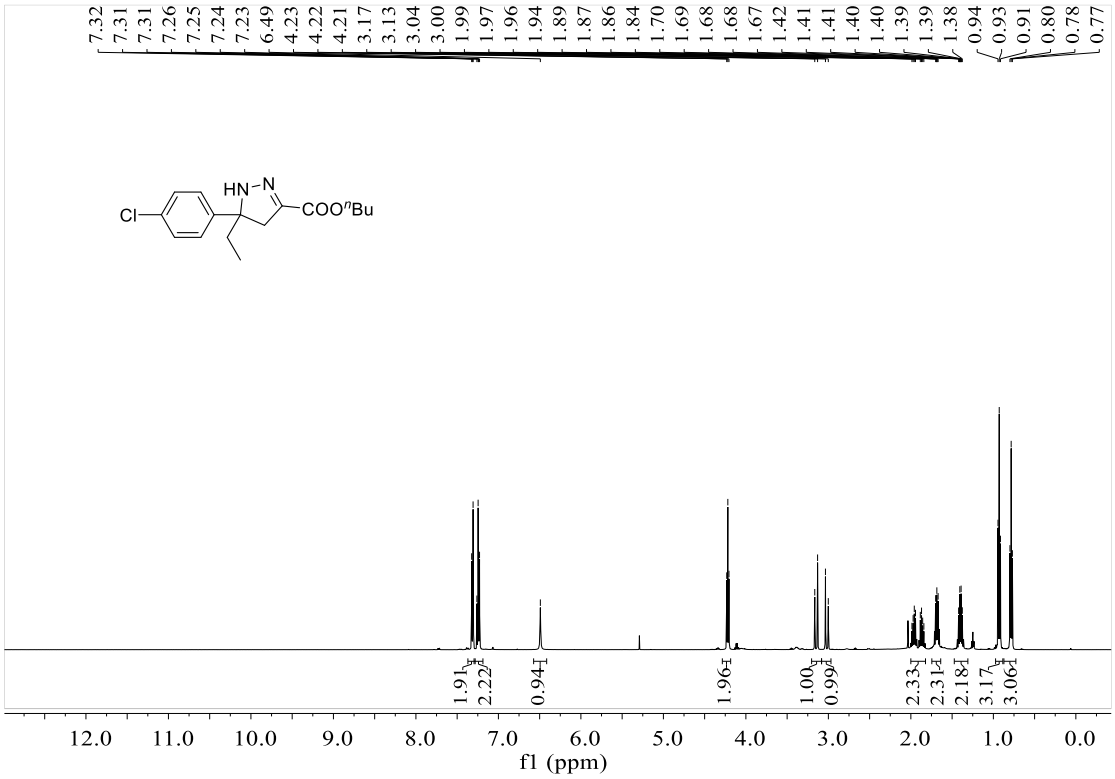


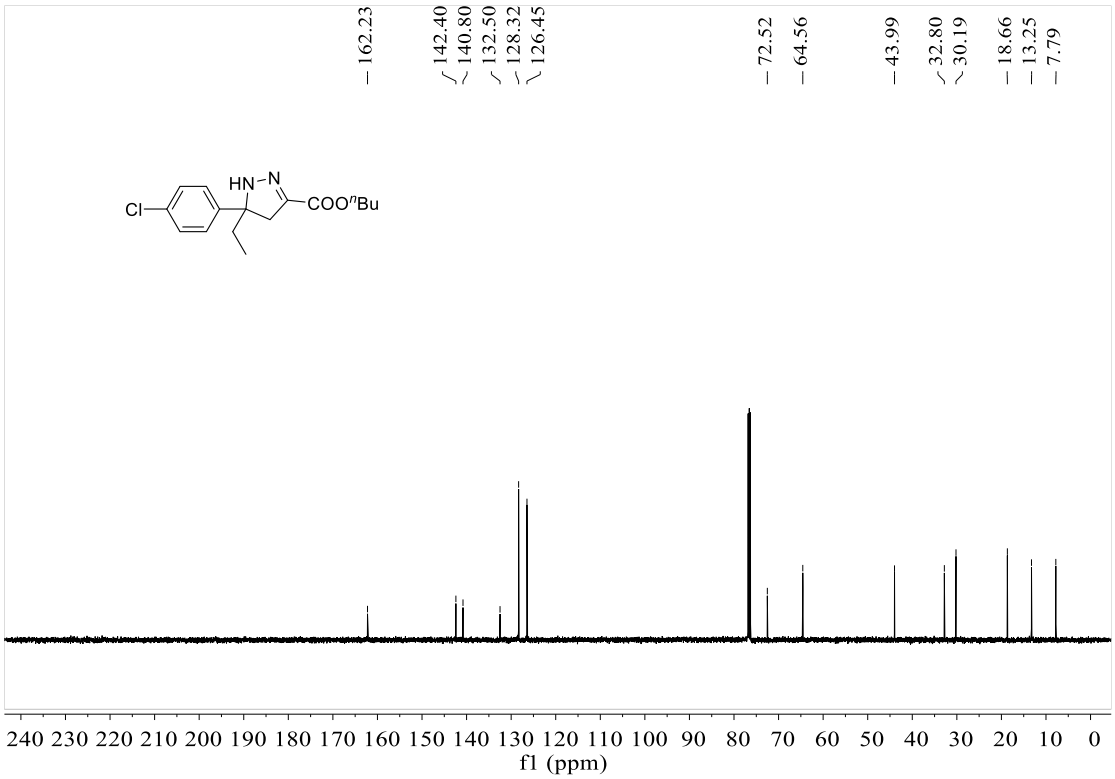
^{1}H NMR (500 MHz, CD_3OD) and ^{13}C NMR (126 MHz, CD_3OD) spectra for 44d:



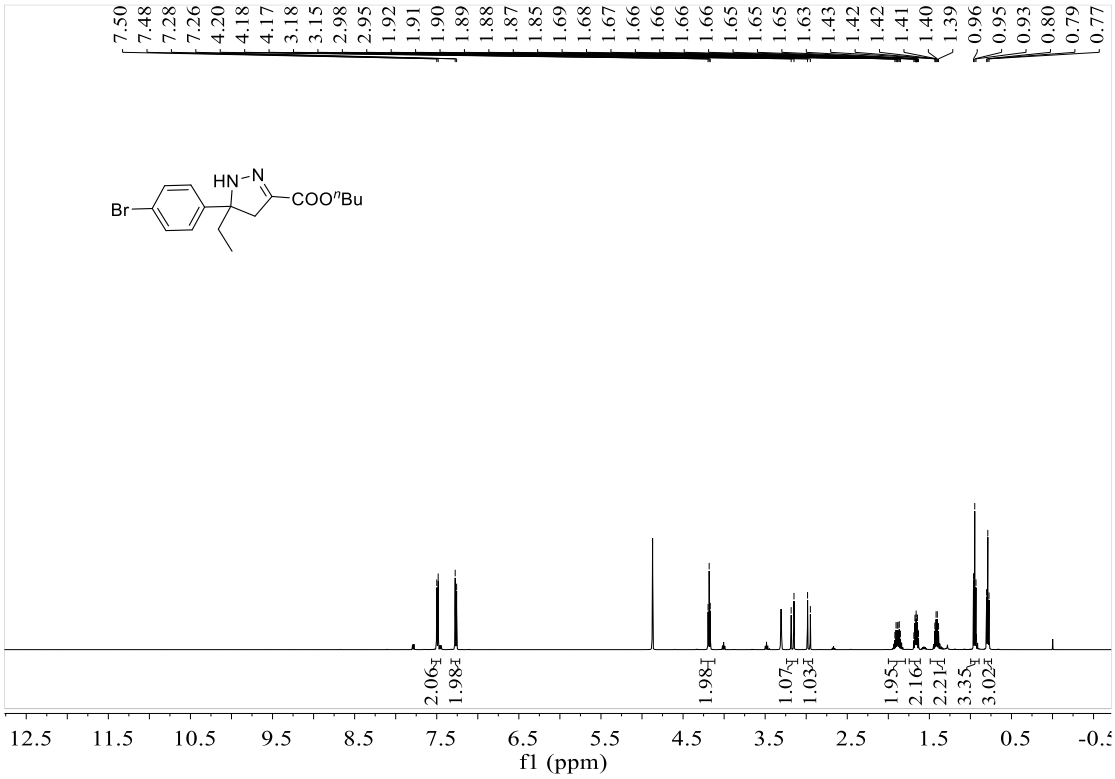


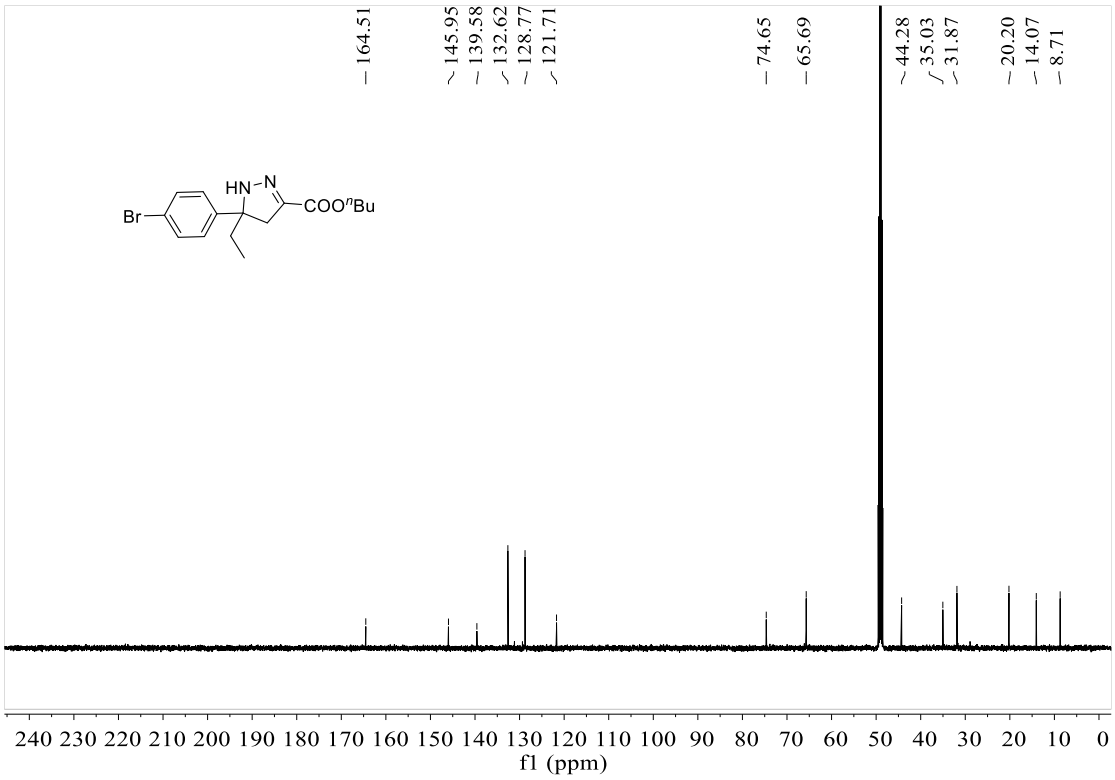
^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (126 MHz, $CDCl_3$) spectra for 45d:



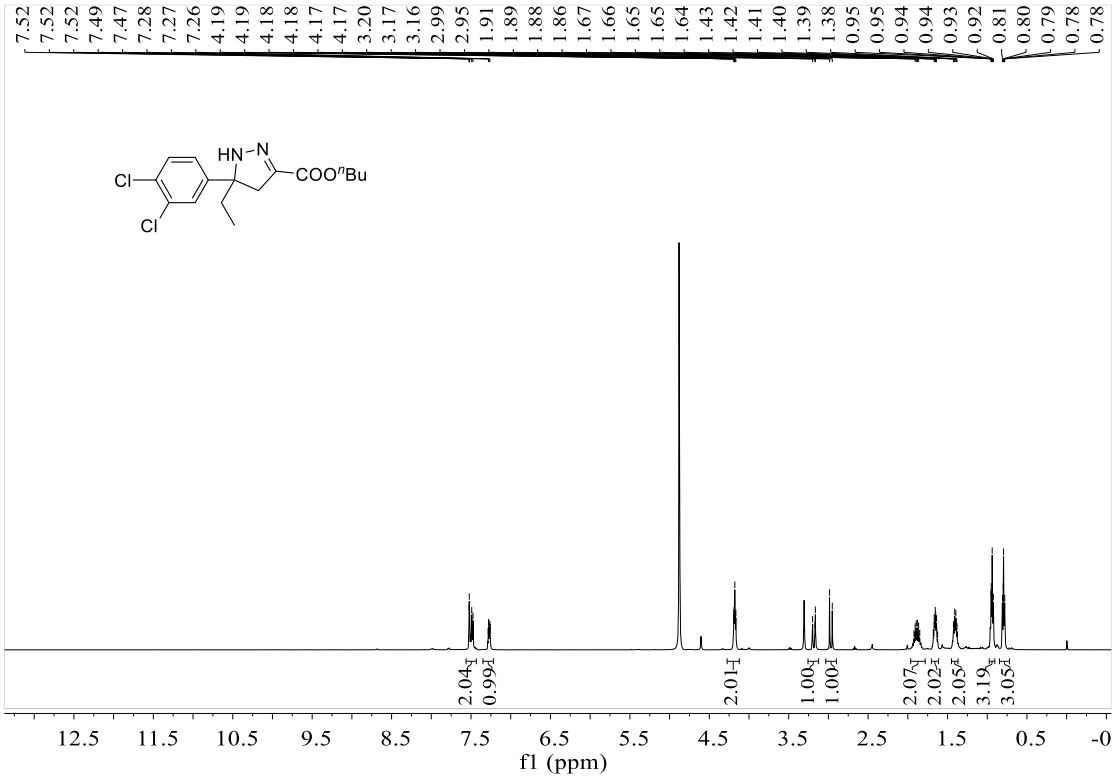


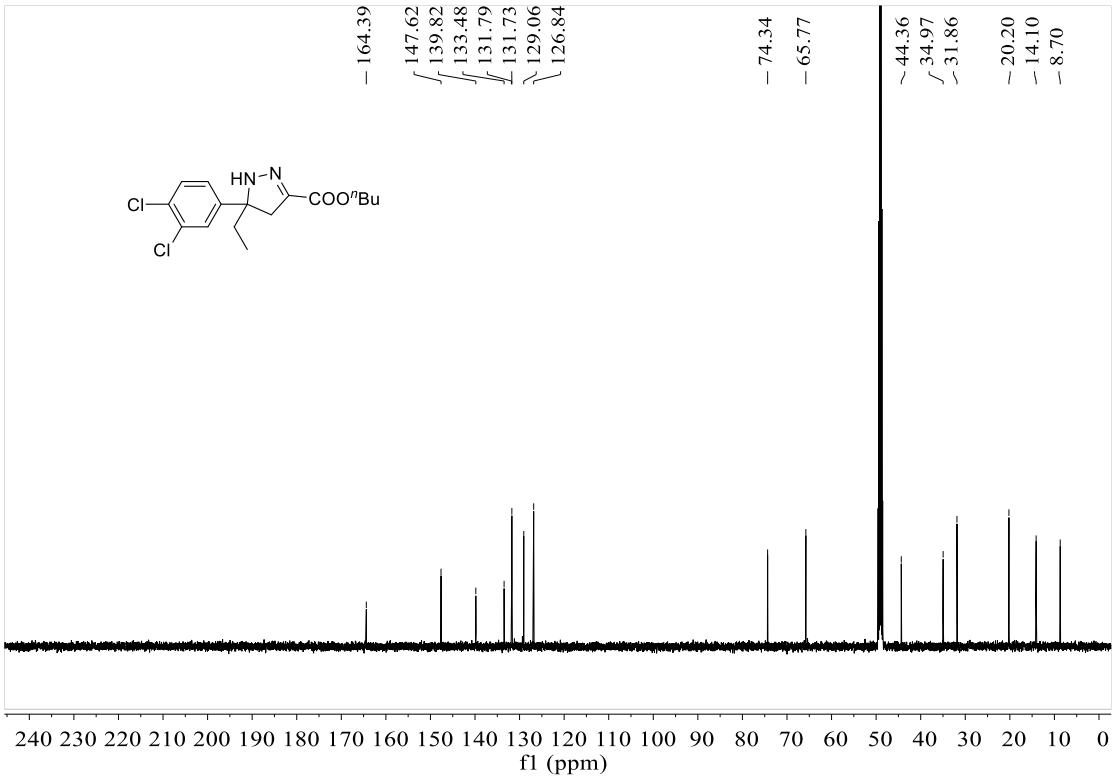
^{1}H NMR (500 MHz, CD_3OD) and ^{13}C NMR (126 MHz, CD_3OD) spectra for 46d:



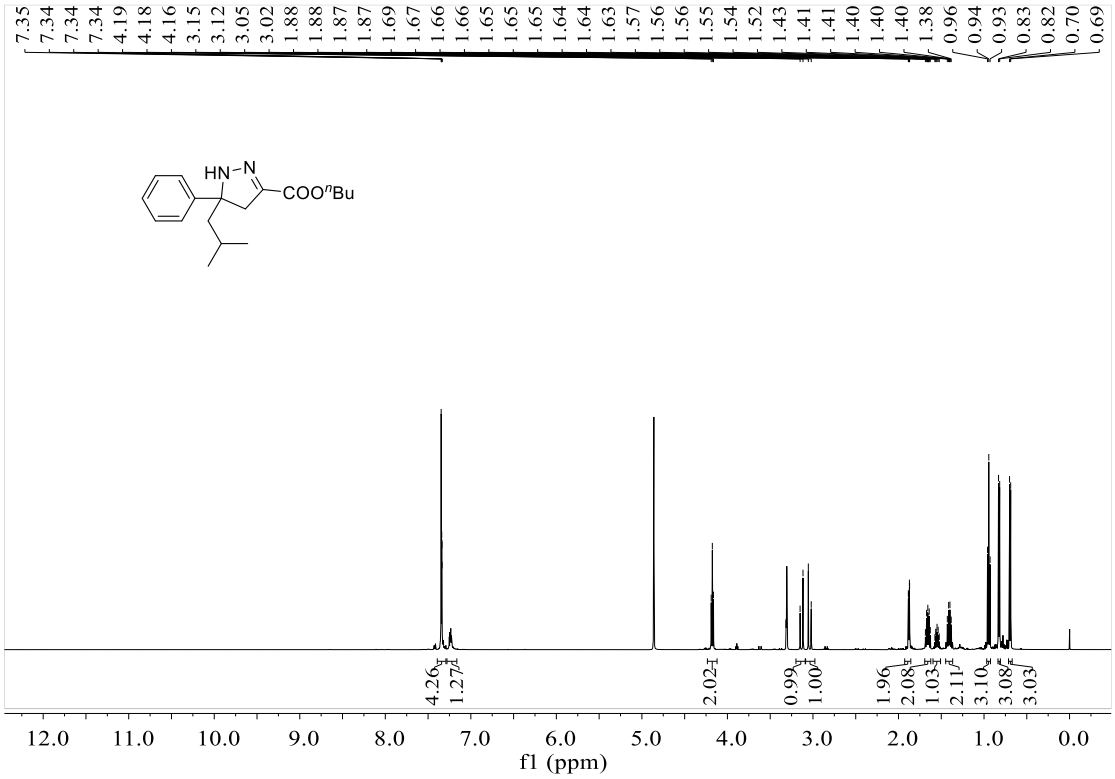


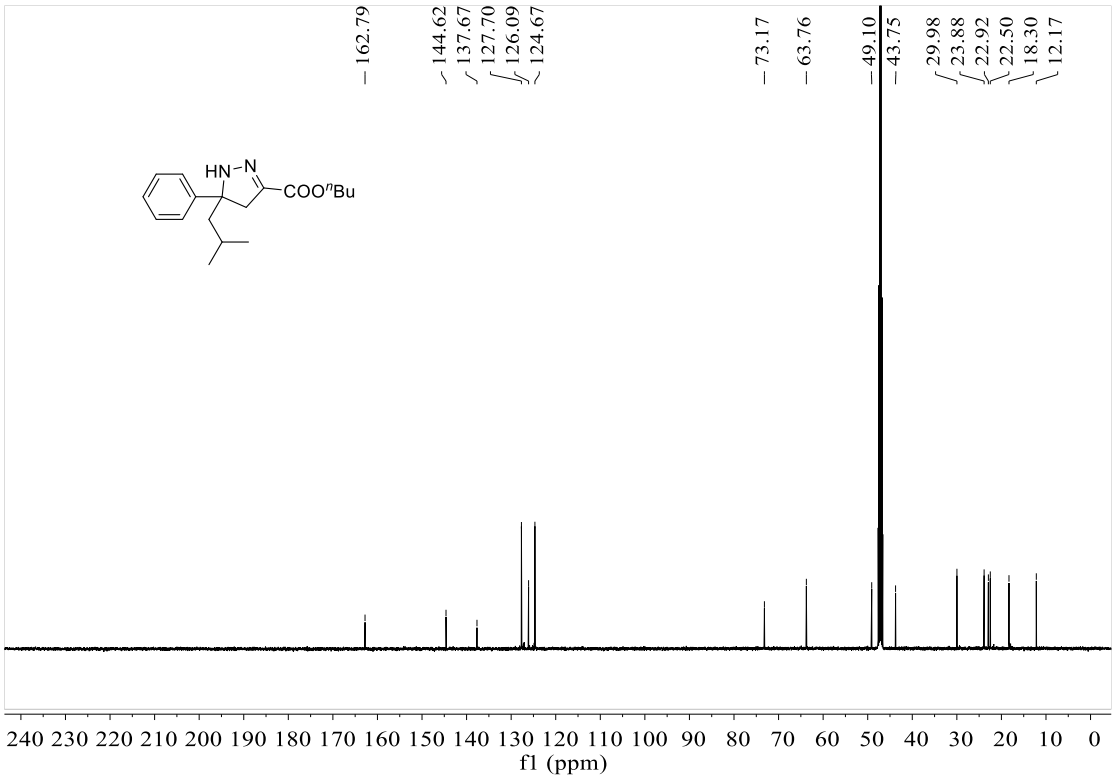
^{1}H NMR (500 MHz, CD_3OD) and ^{13}C NMR (126 MHz, CD_3OD) spectra for 47d:



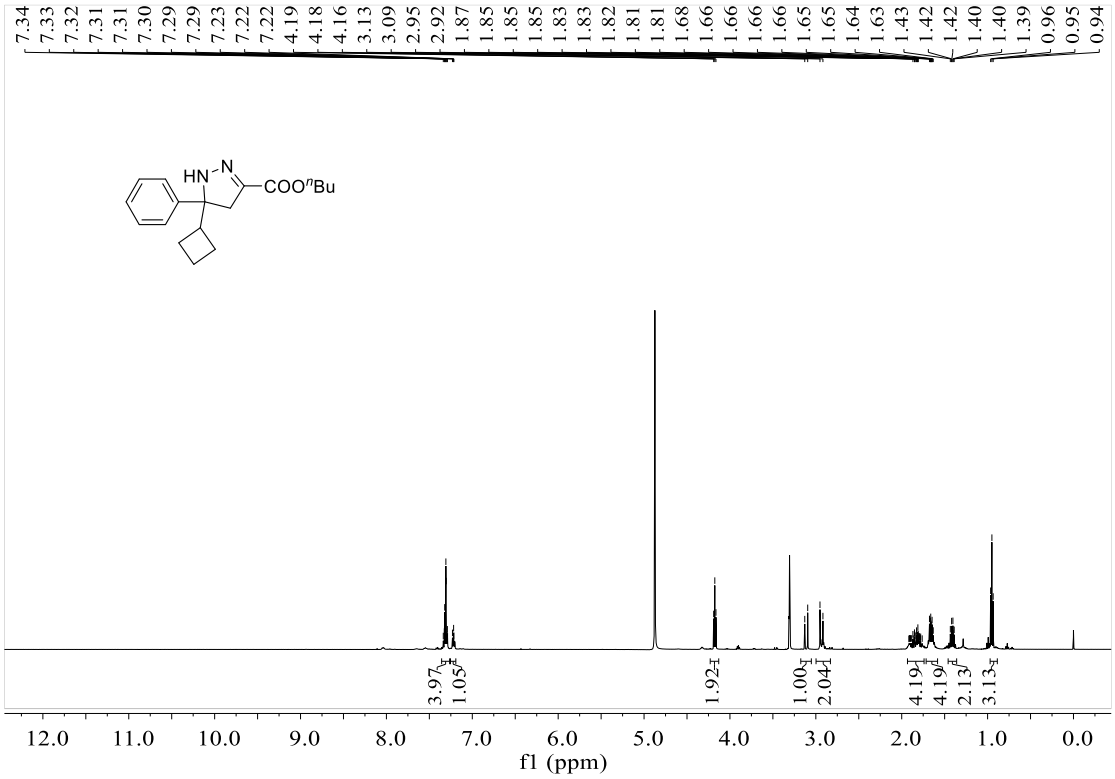


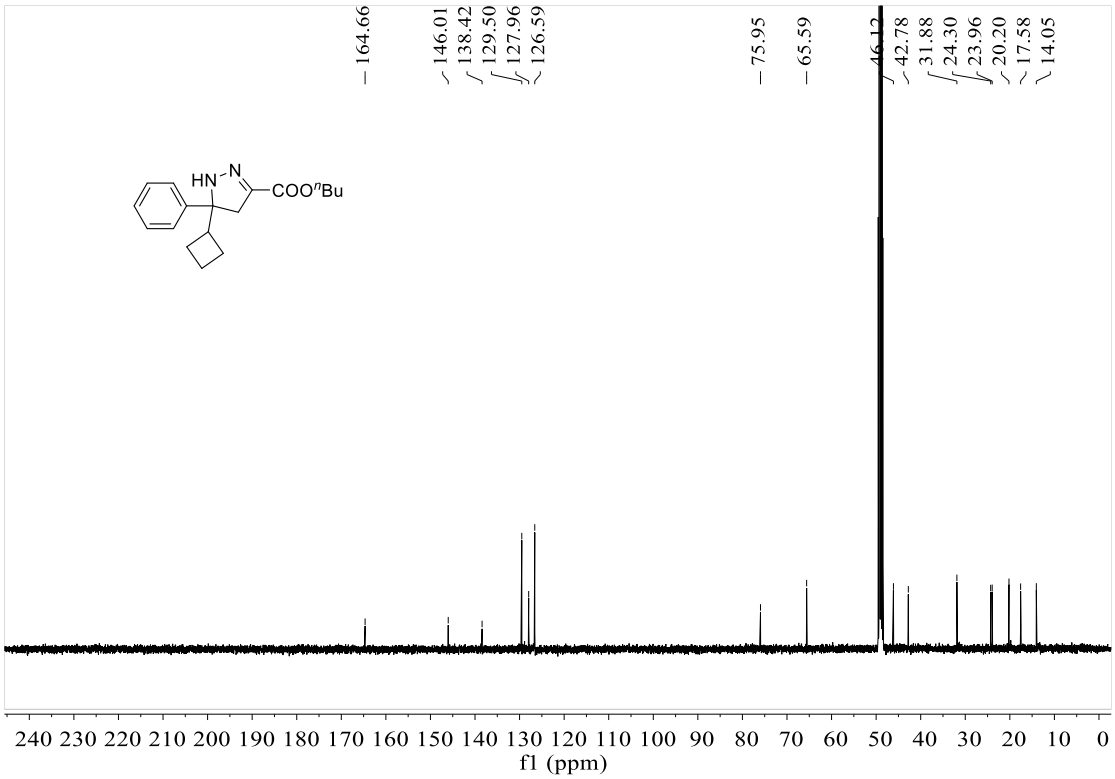
^{1}H NMR (500 MHz, CD_3OD) and ^{13}C NMR (126 MHz, CD_3OD) spectra for 48d:



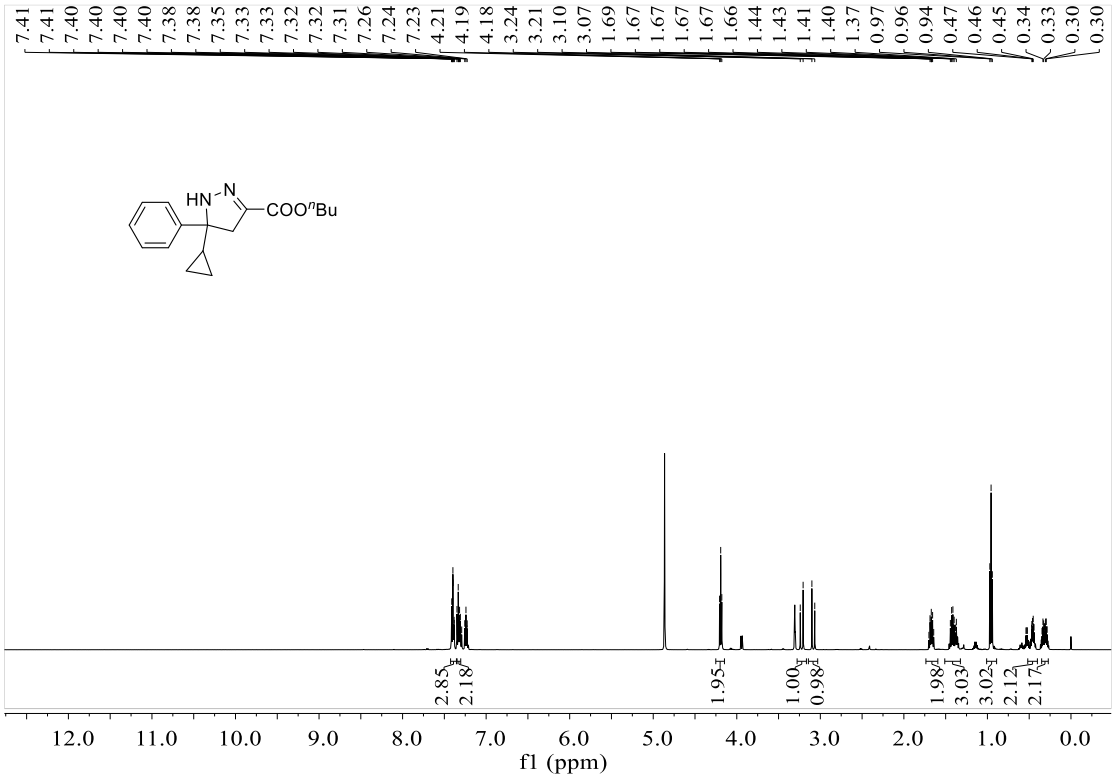


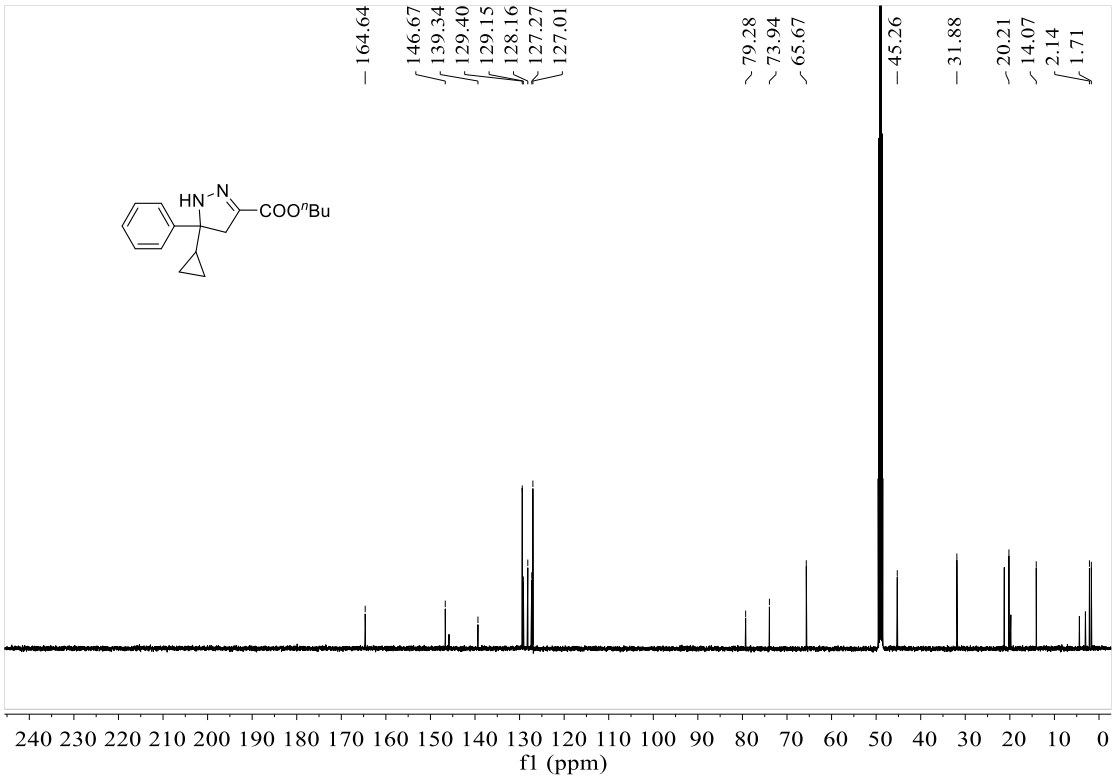
^{1}H NMR (500 MHz, CD_3OD) and ^{13}C NMR (126 MHz, CD_3OD) spectra for 49d:



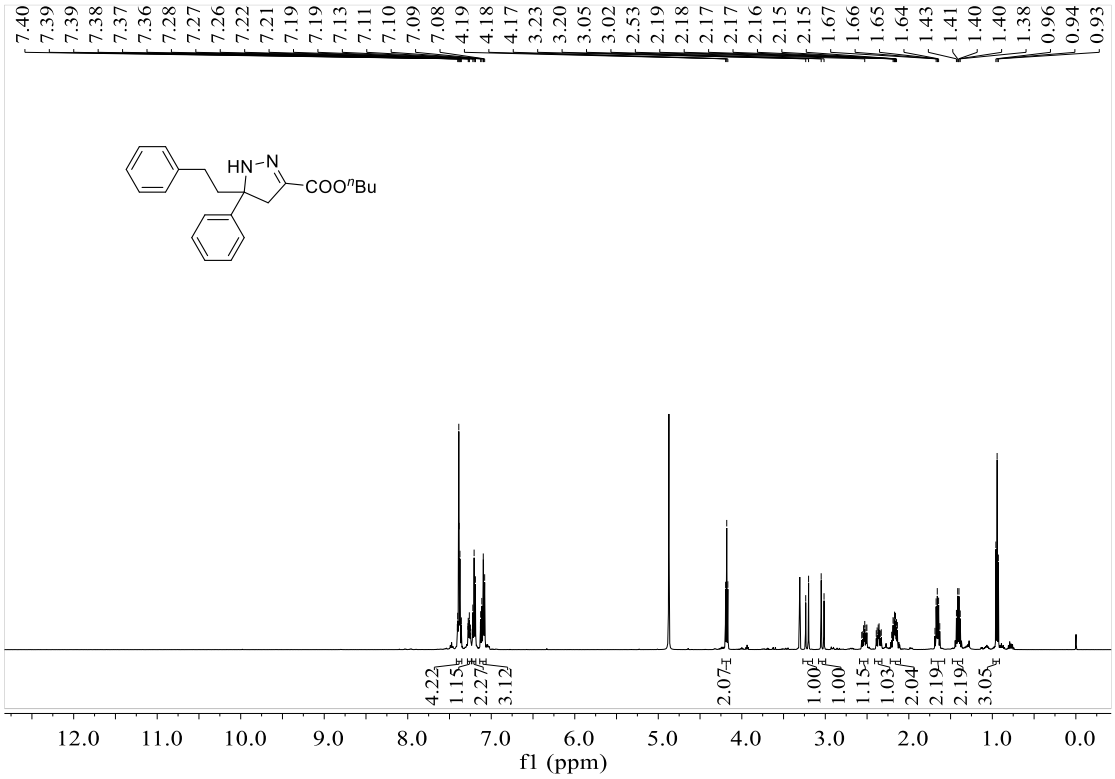


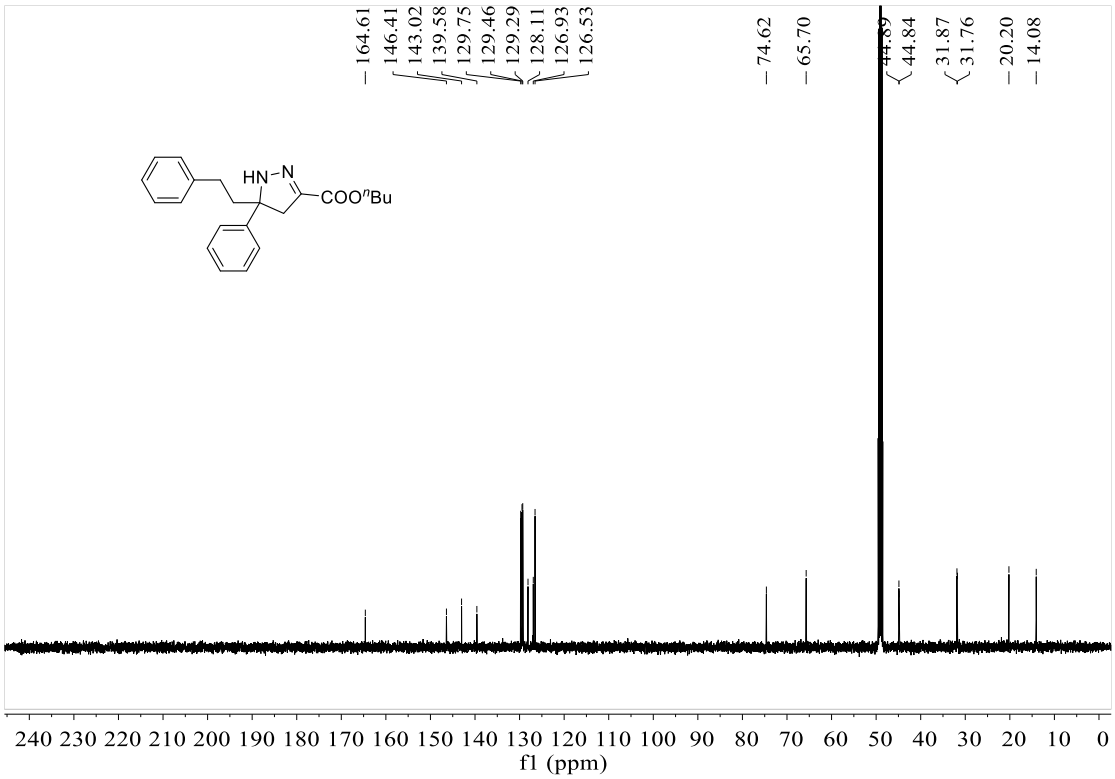
^{1}H NMR (500 MHz, CD_3OD) and ^{13}C NMR (126 MHz, CD_3OD) spectra for 50d:



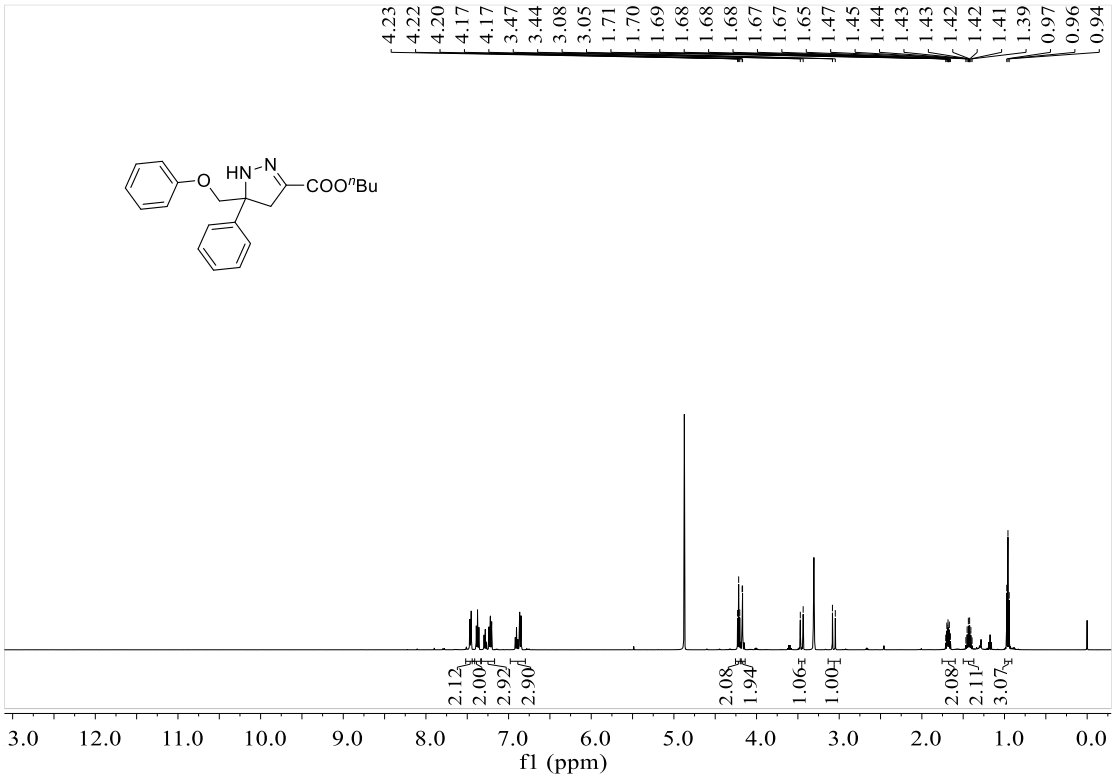


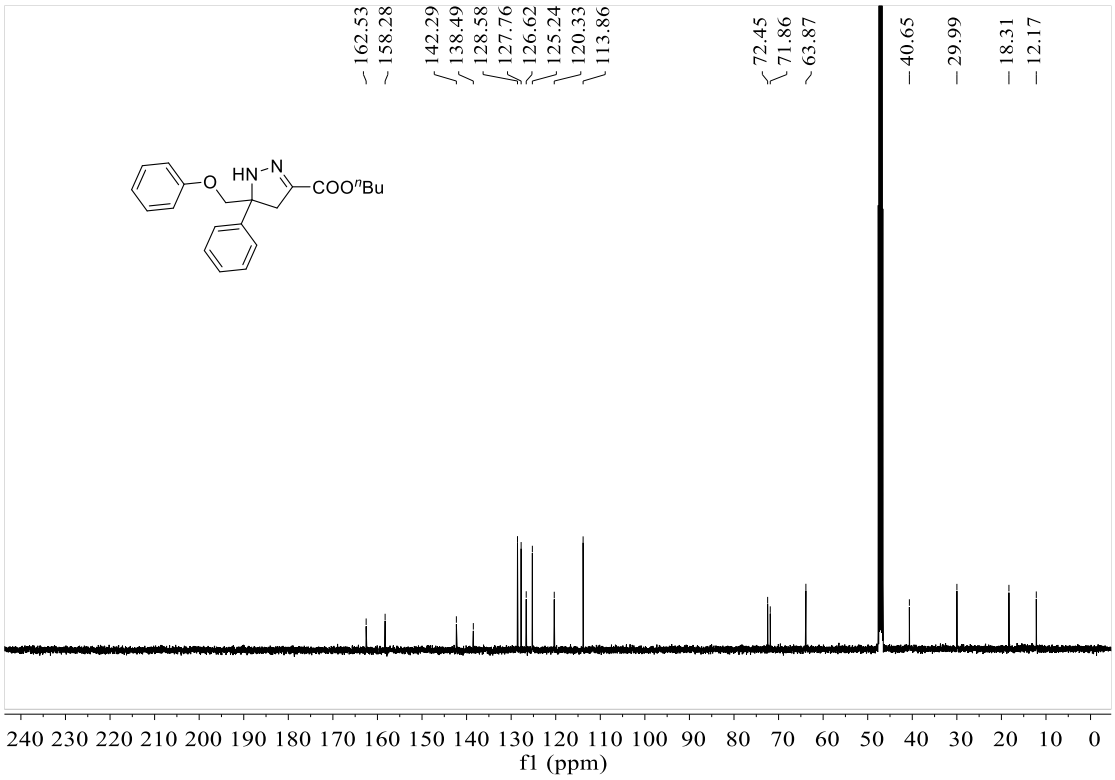
^{1}H NMR (500 MHz, CD_3OD) and ^{13}C NMR (126 MHz, CD_3OD) spectra for 51d:



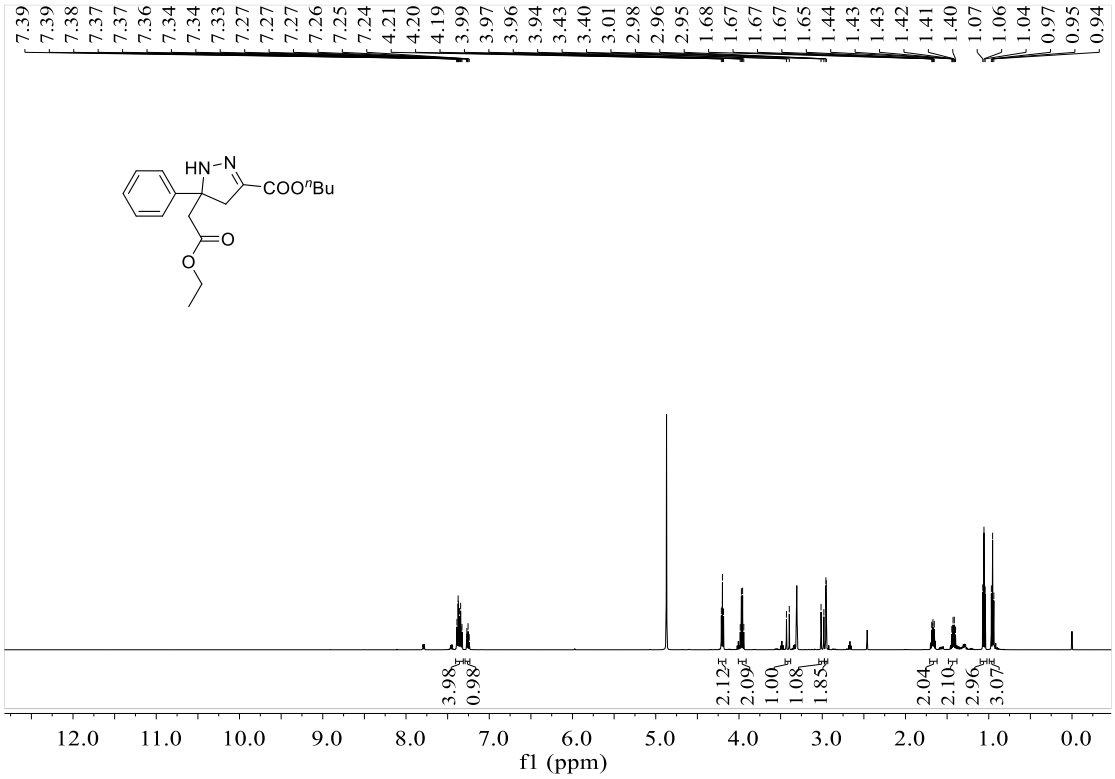


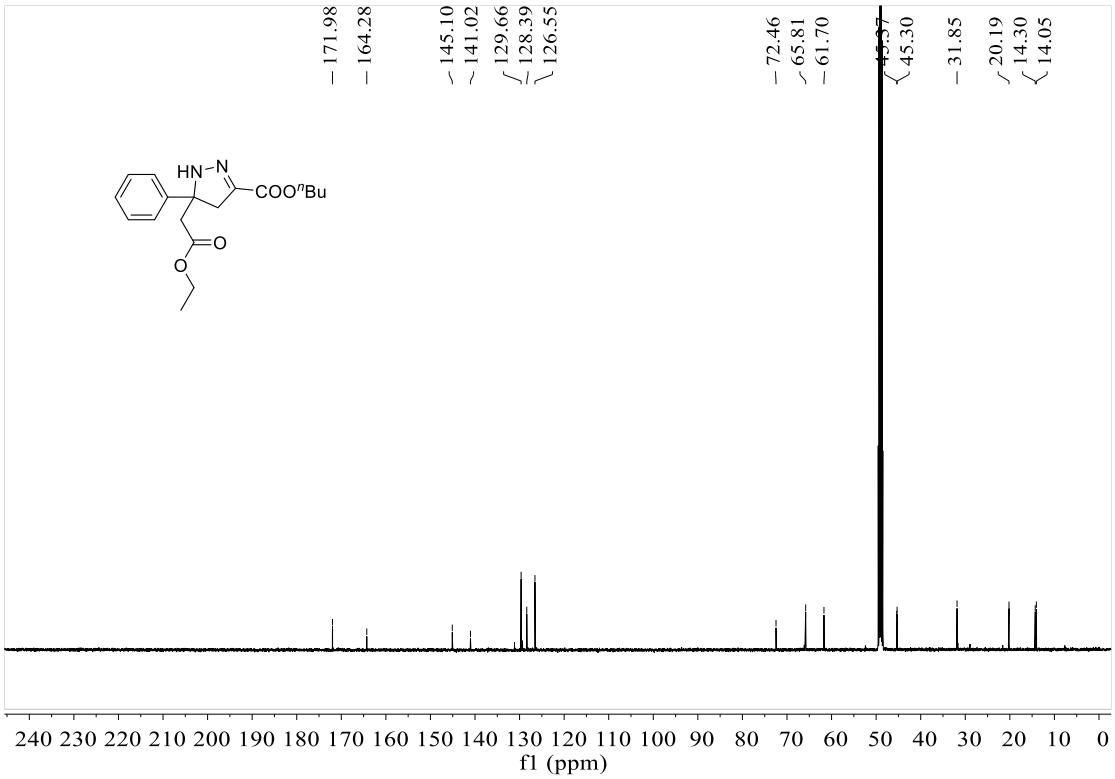
^{1}H NMR (500 MHz, CD_3OD) and ^{13}C NMR (126 MHz, CD_3OD) spectra for 52d:



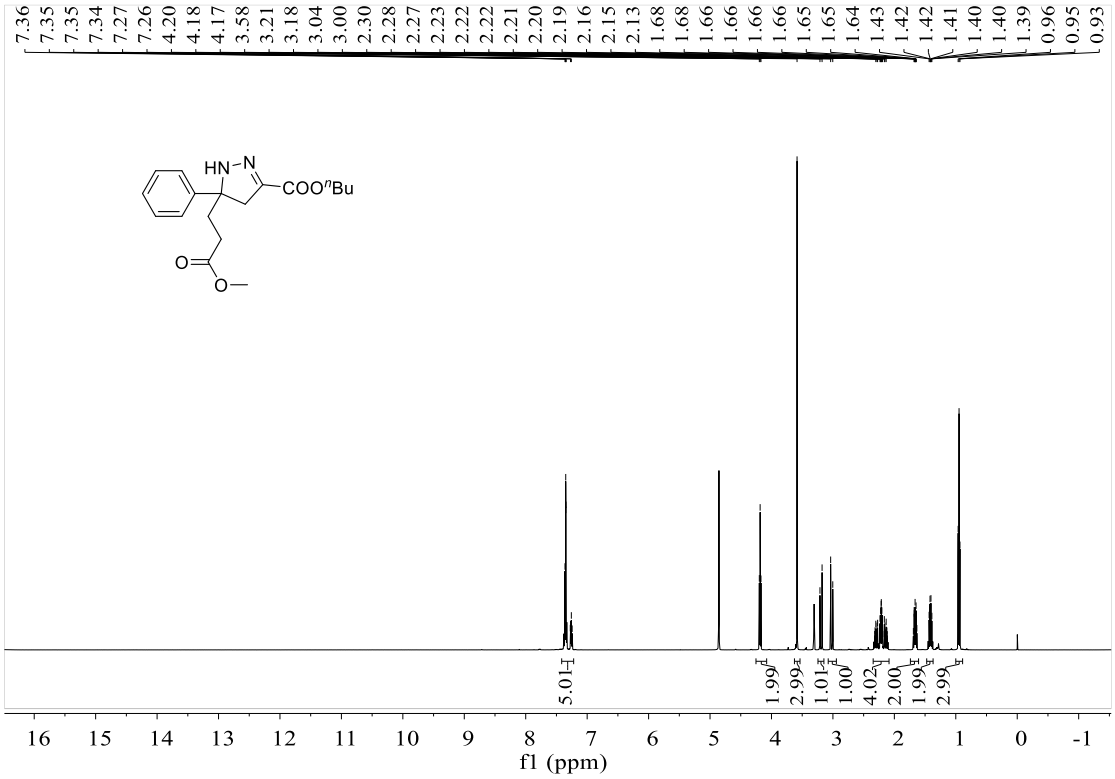


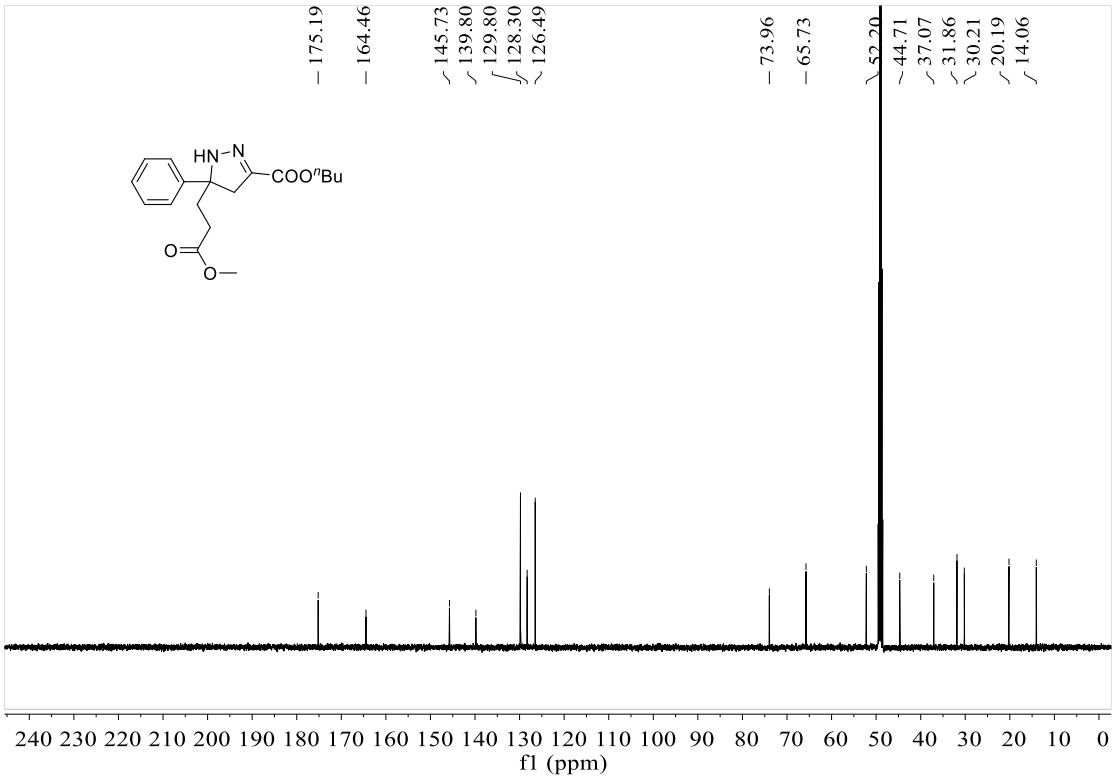
^{1}H NMR (500 MHz, CD_3OD) and ^{13}C NMR (126 MHz, CD_3OD) spectra for 53d:



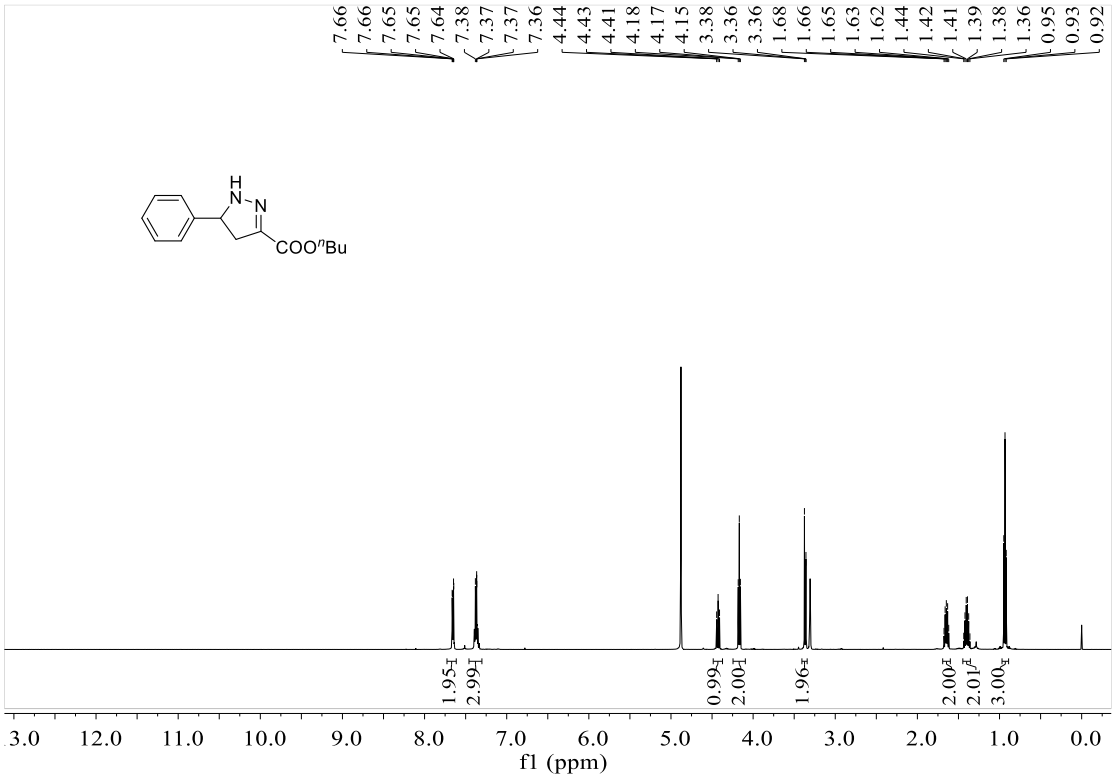


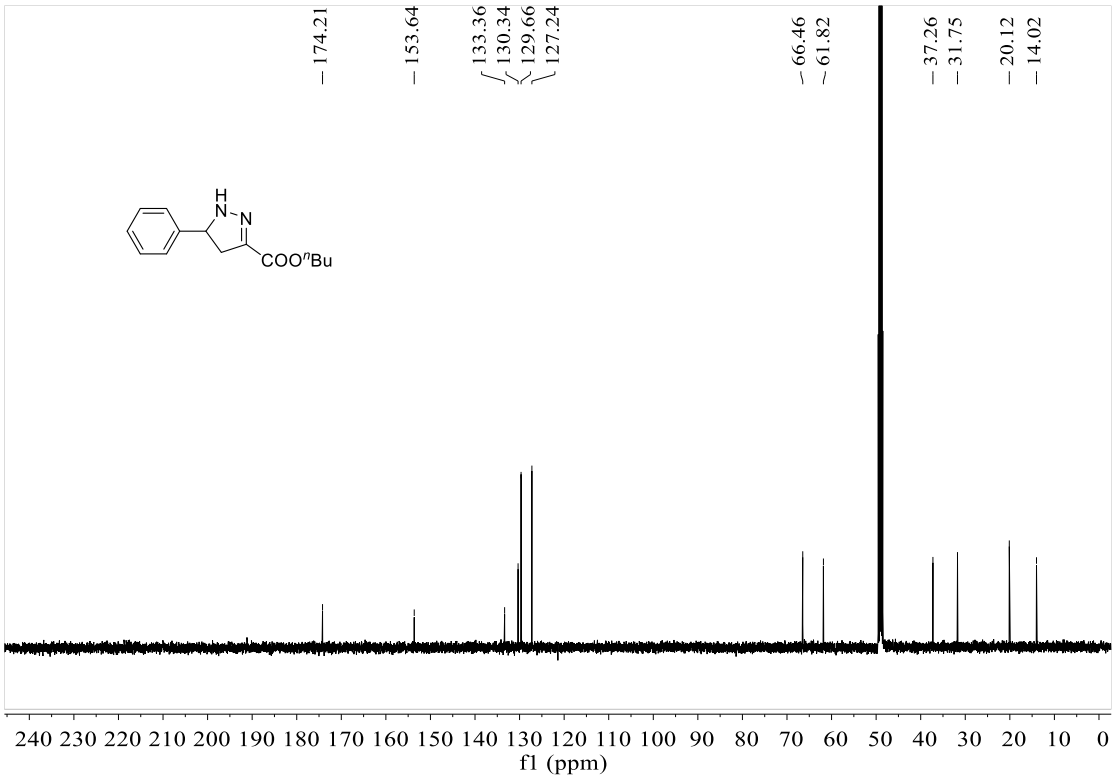
^{1}H NMR (500 MHz, CD_3OD) and ^{13}C NMR (126 MHz, CD_3OD) spectra for 54d:



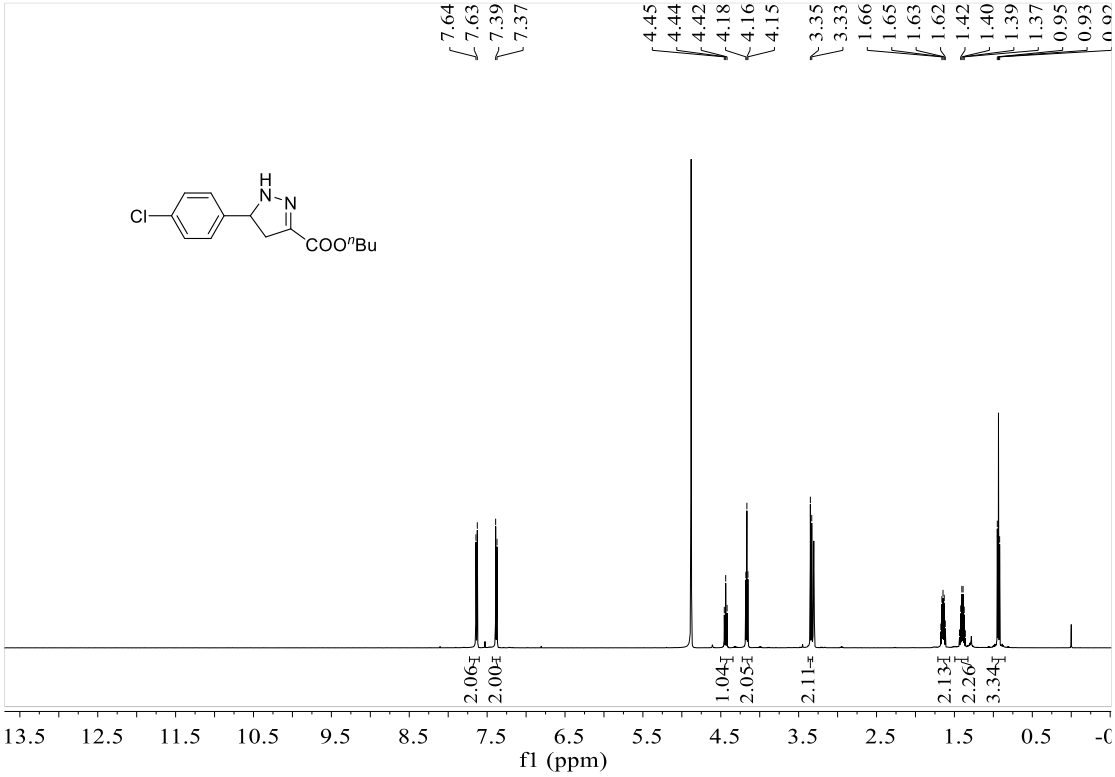


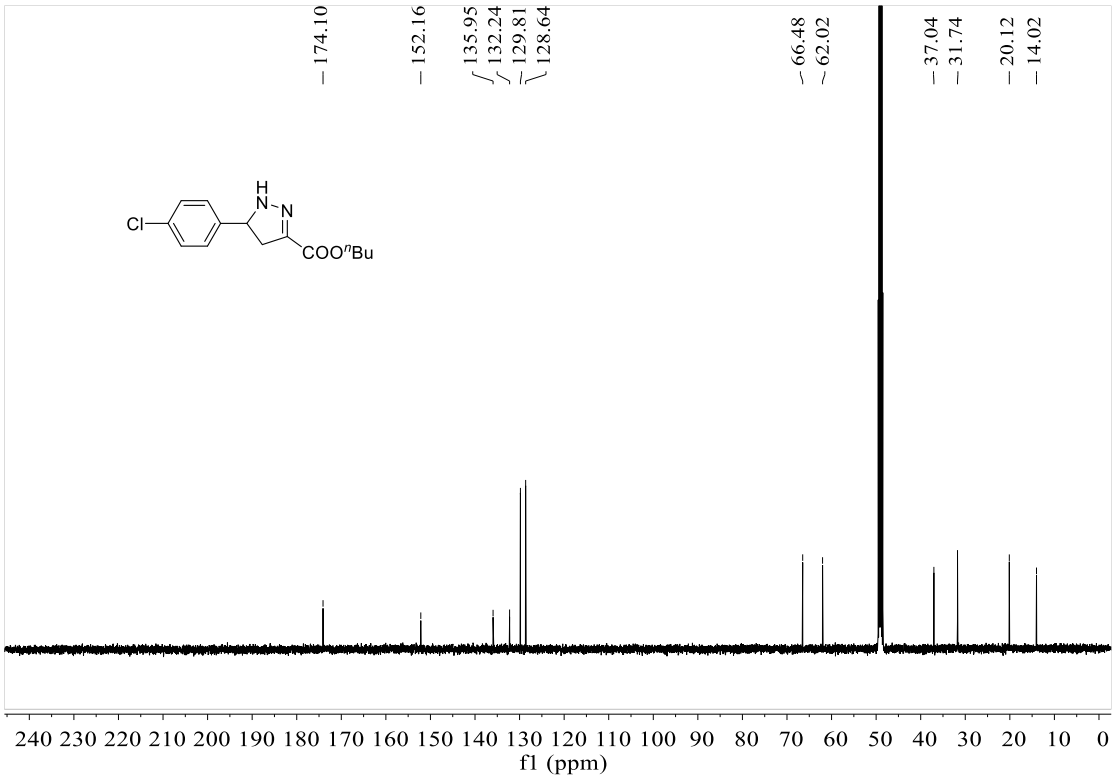
^{1}H NMR (500 MHz, CD_3OD) and ^{13}C NMR (126 MHz, CD_3OD) spectra for 55d:



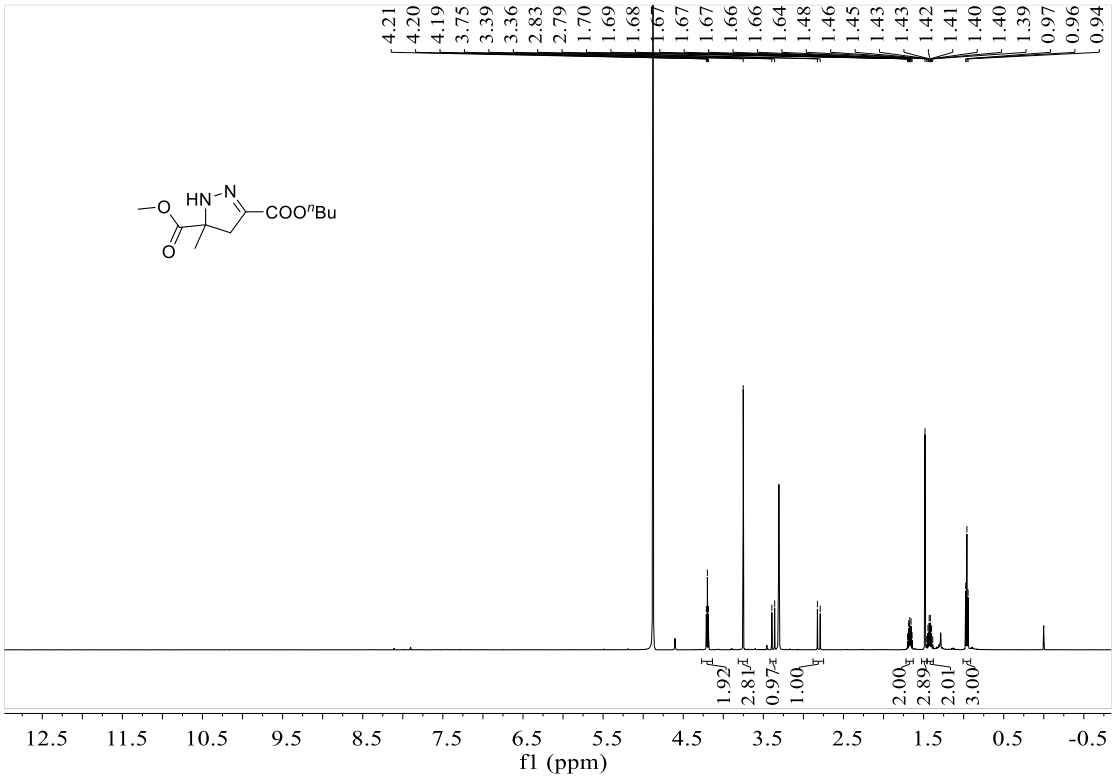


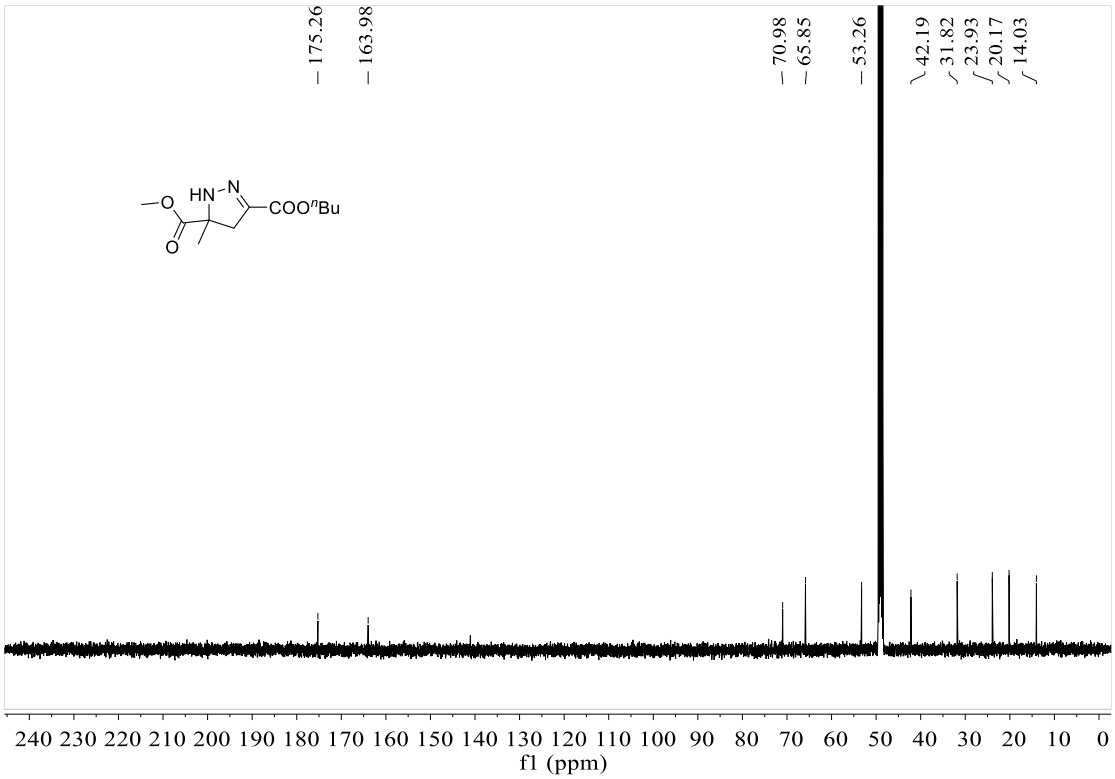
^{1}H NMR (500 MHz, CD_3OD) and ^{13}C NMR (126 MHz, CD_3OD) spectra for 56d:



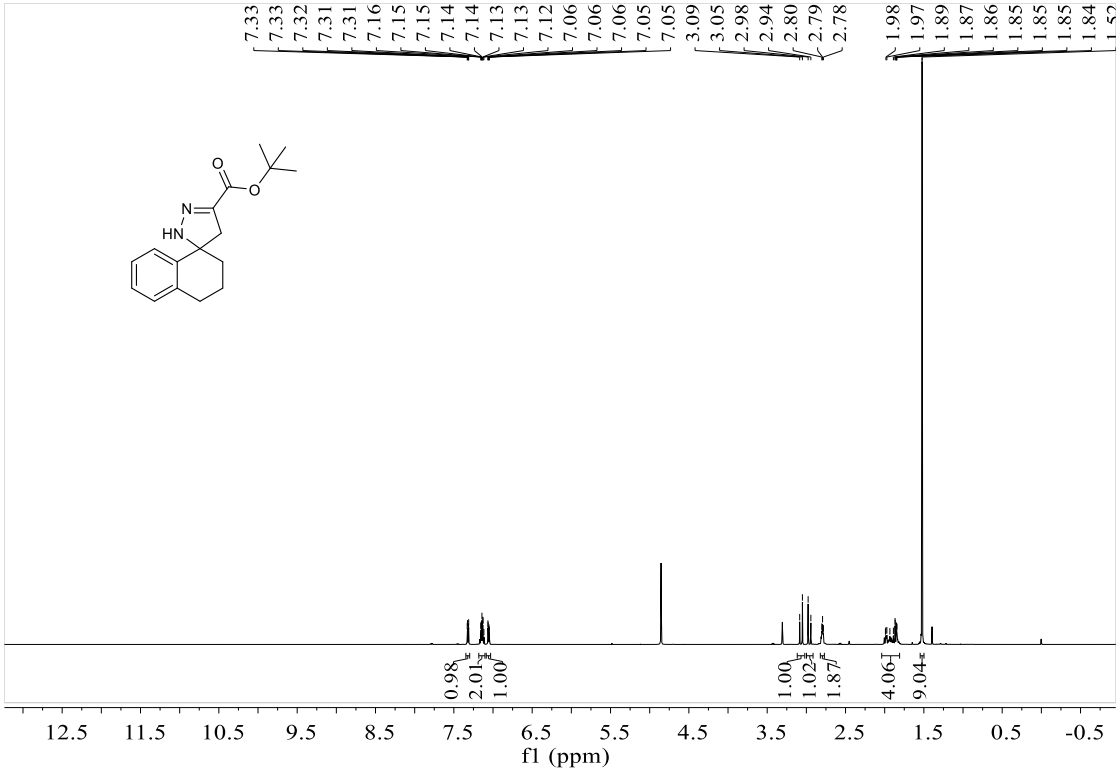


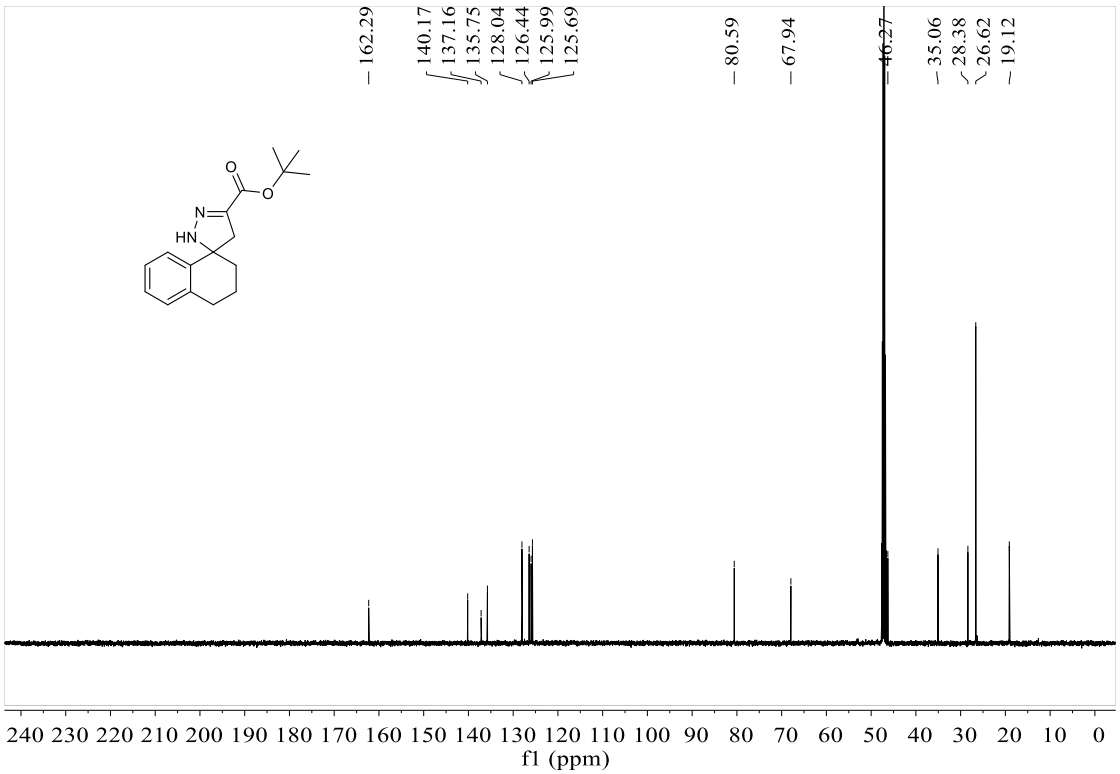
^{1}H NMR (500 MHz, CD_3OD) and ^{13}C NMR (126 MHz, CD_3OD) spectra for 57d:



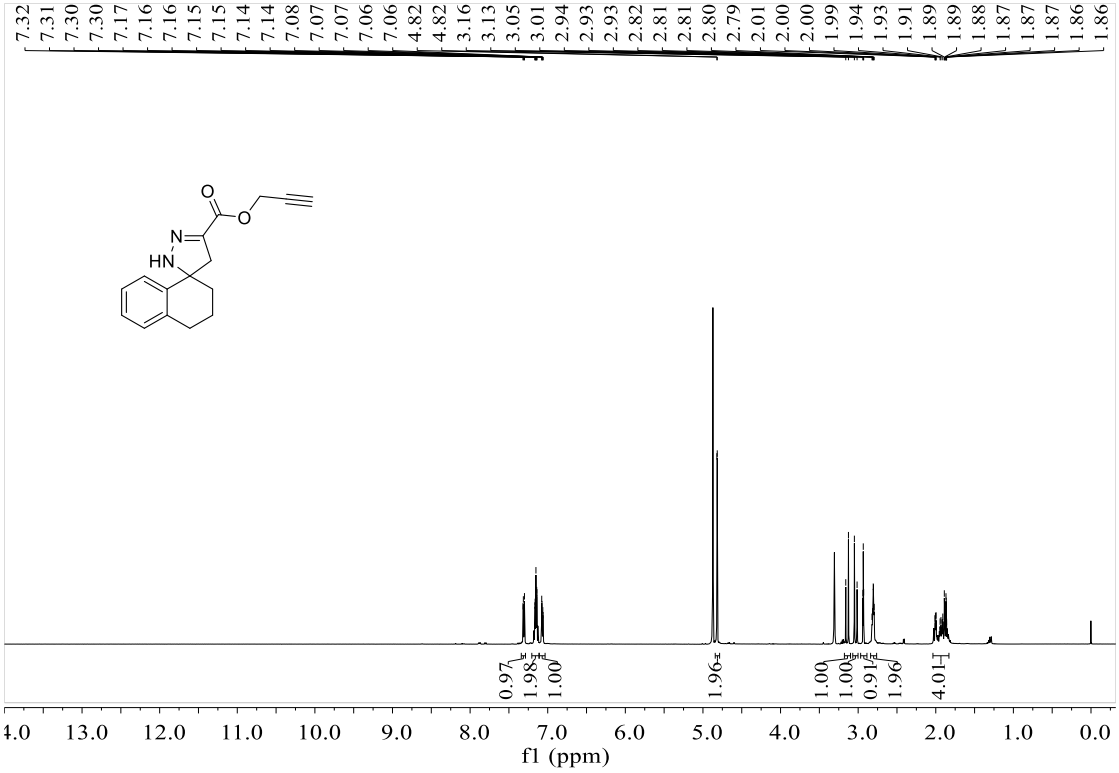


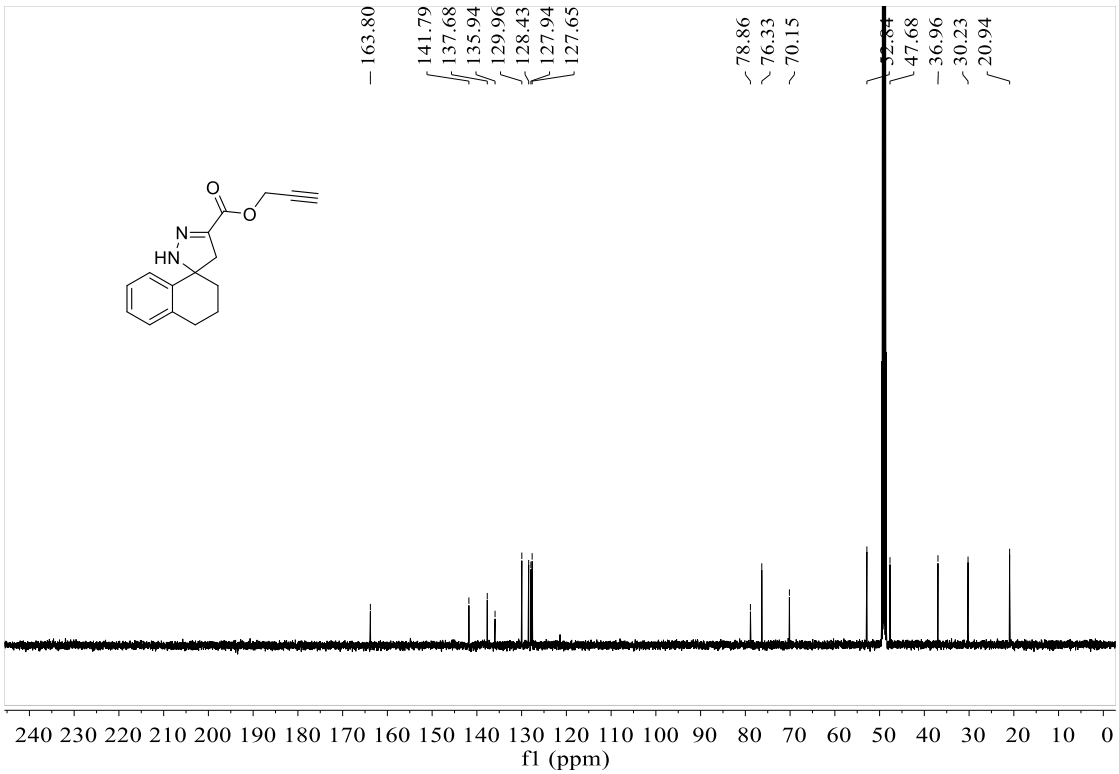
^{1}H NMR (500 MHz, CD_3OD) and ^{13}C NMR (126 MHz, CD_3OD) spectra for 58d:



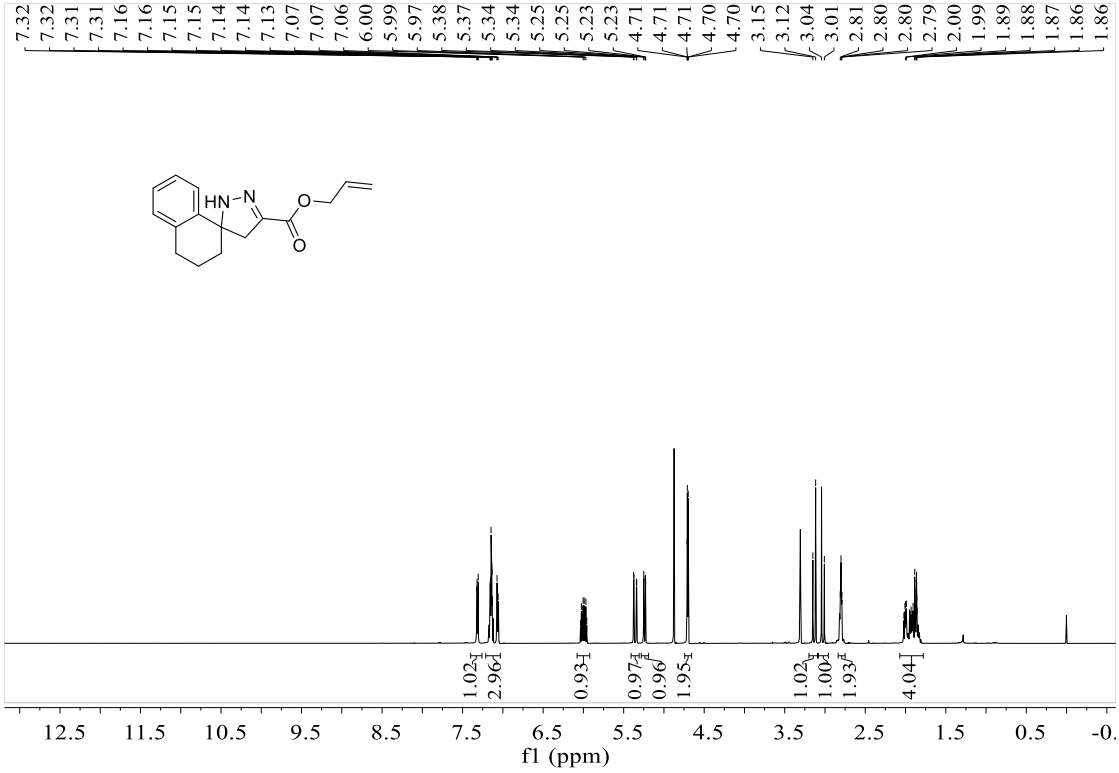


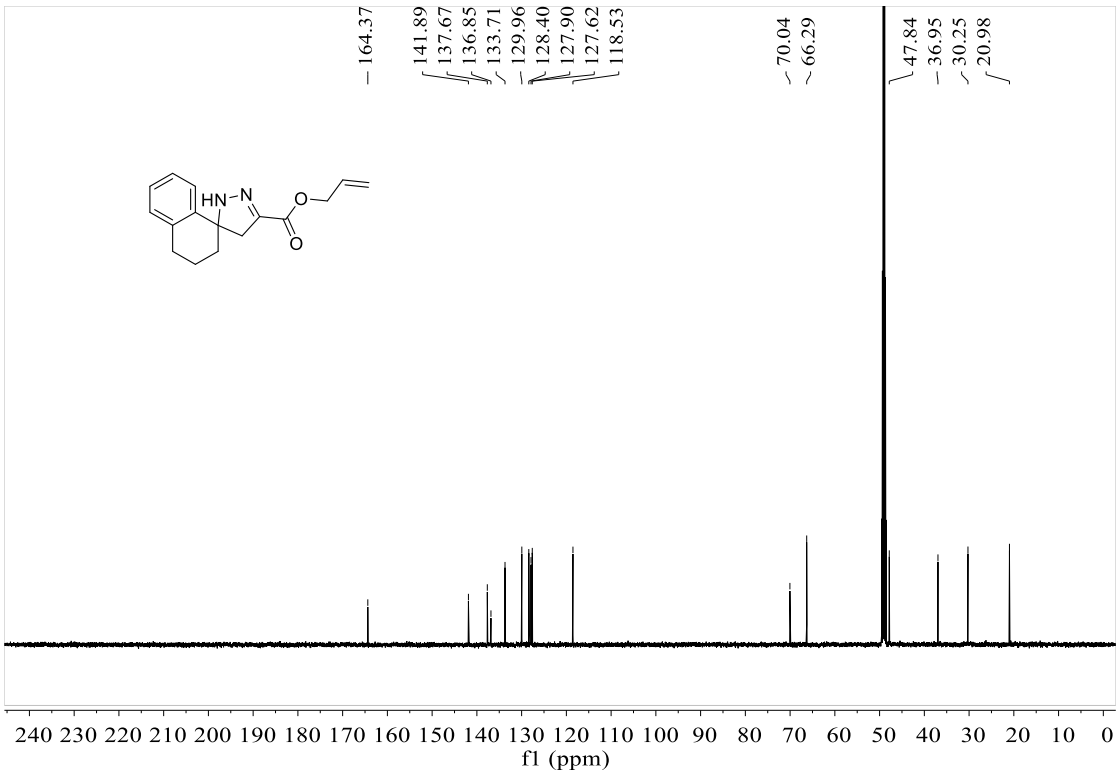
^{1}H NMR (500 MHz, CD_3OD) and ^{13}C NMR (126 MHz, CD_3OD) spectra for 59d:



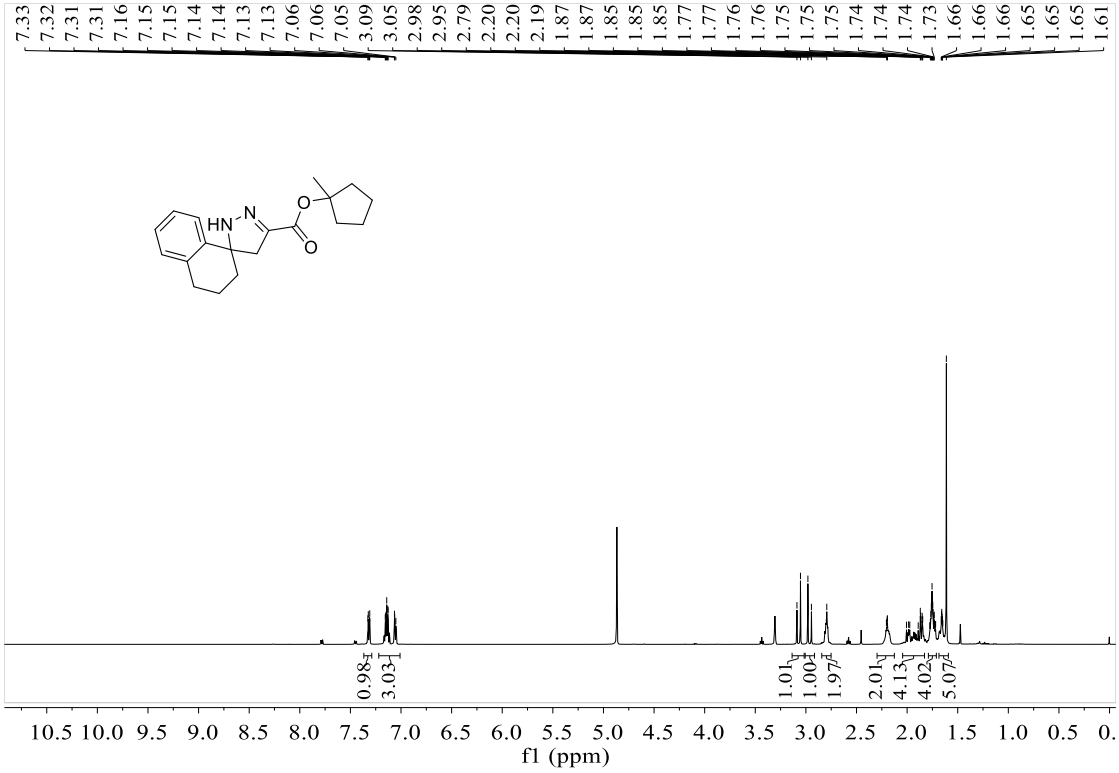


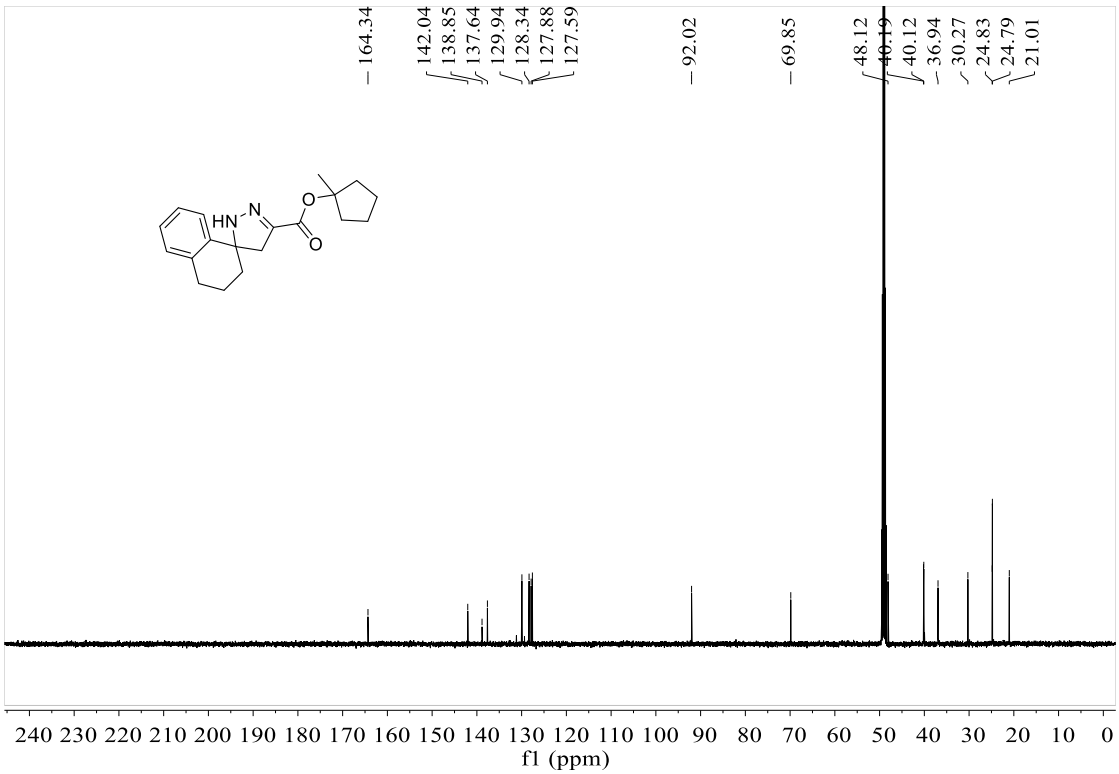
^{1}H NMR (500 MHz, CD_3OD) and ^{13}C NMR (126 MHz, CD_3OD) spectra for 60d:



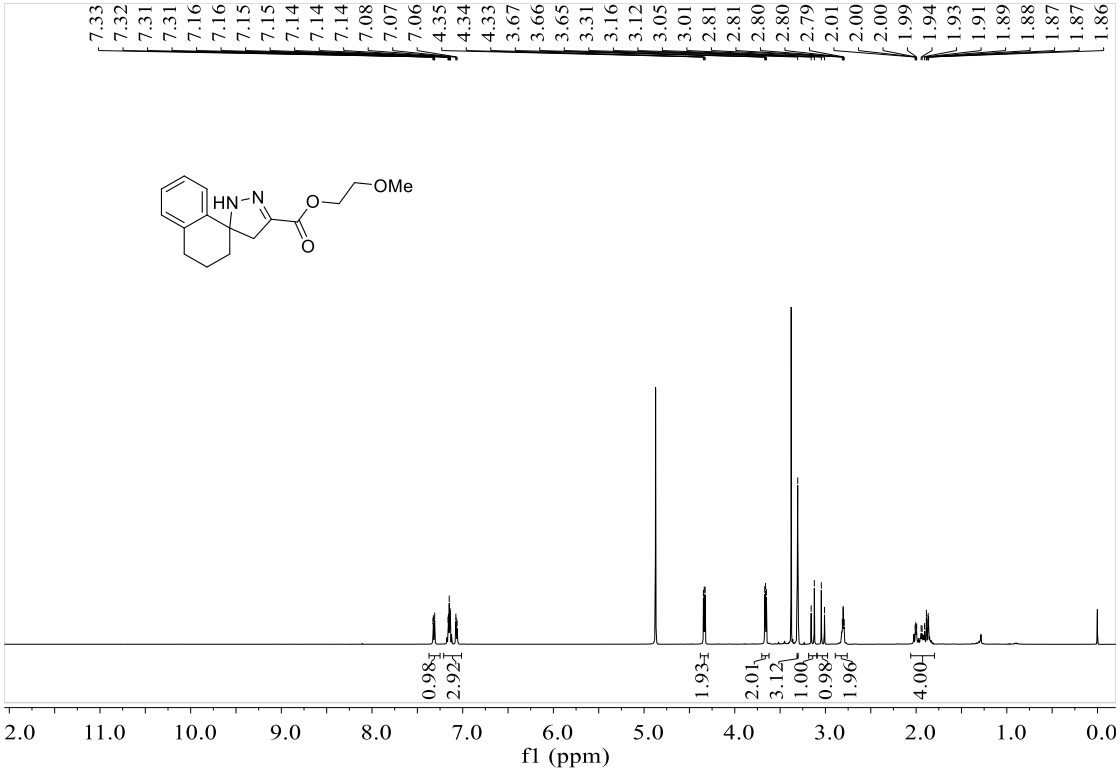


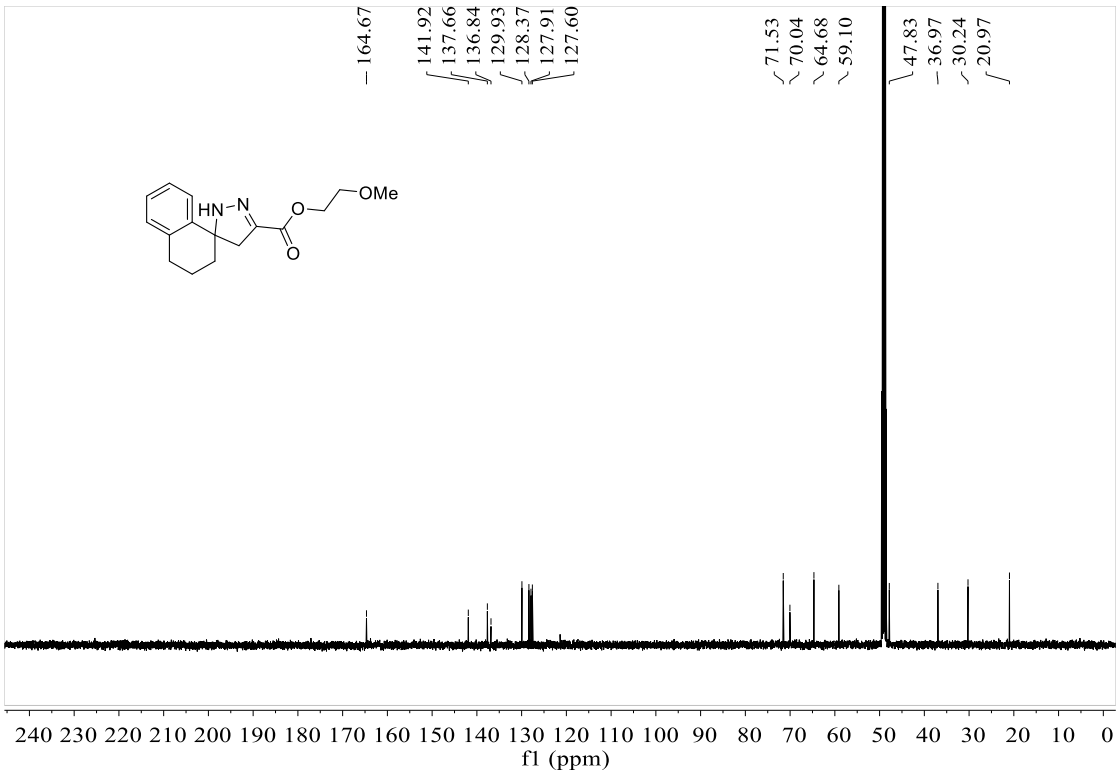
^{1}H NMR (500 MHz, CD_3OD) and ^{13}C NMR (126 MHz, CD_3OD) spectra for 61d:



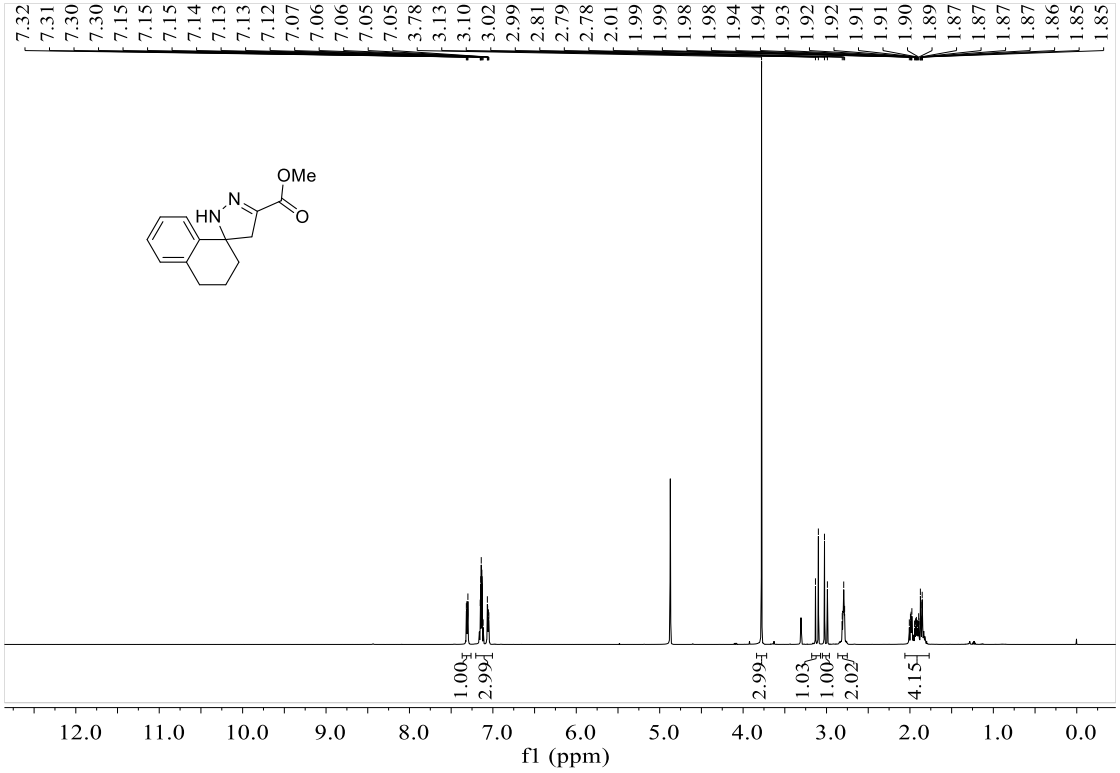


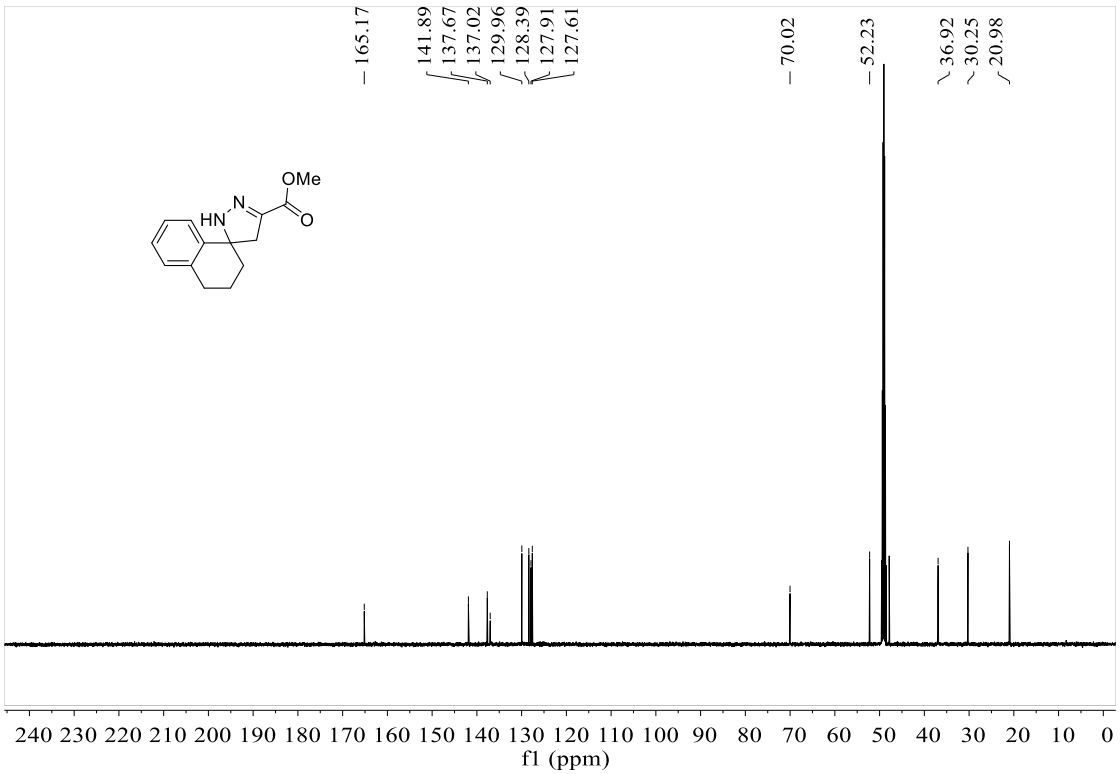
^{1}H NMR (500 MHz, CD_3OD) and ^{13}C NMR (126 MHz, CD_3OD) spectra for 62d:



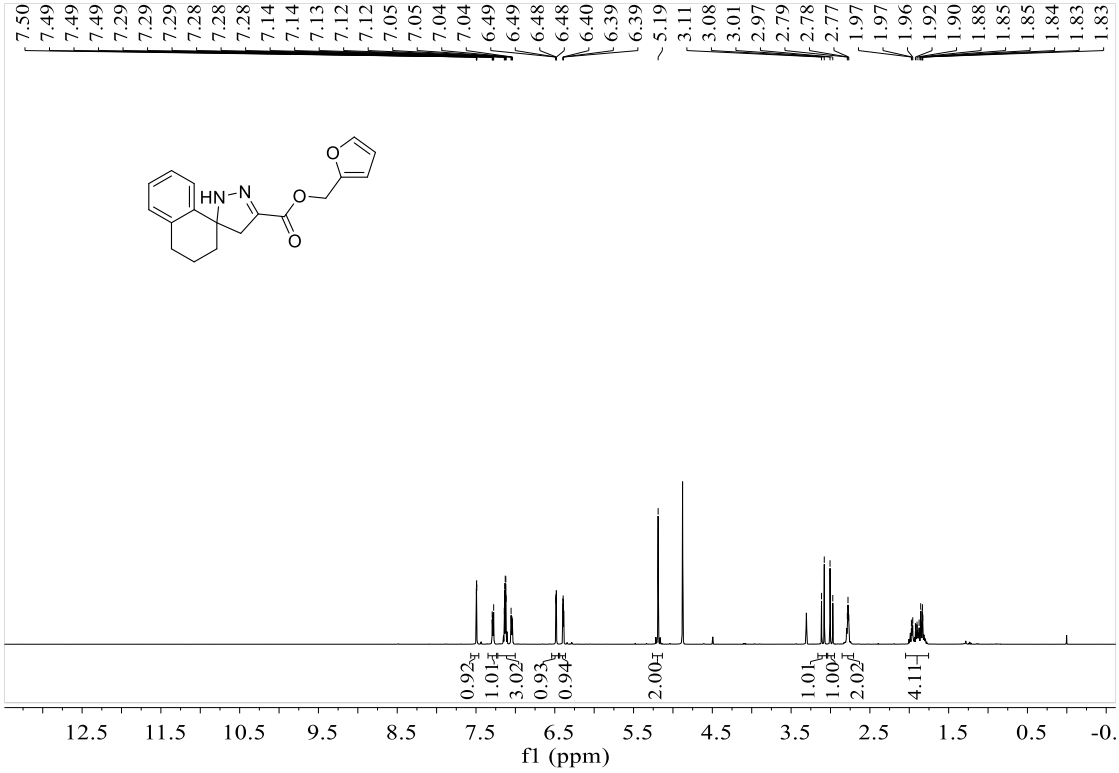


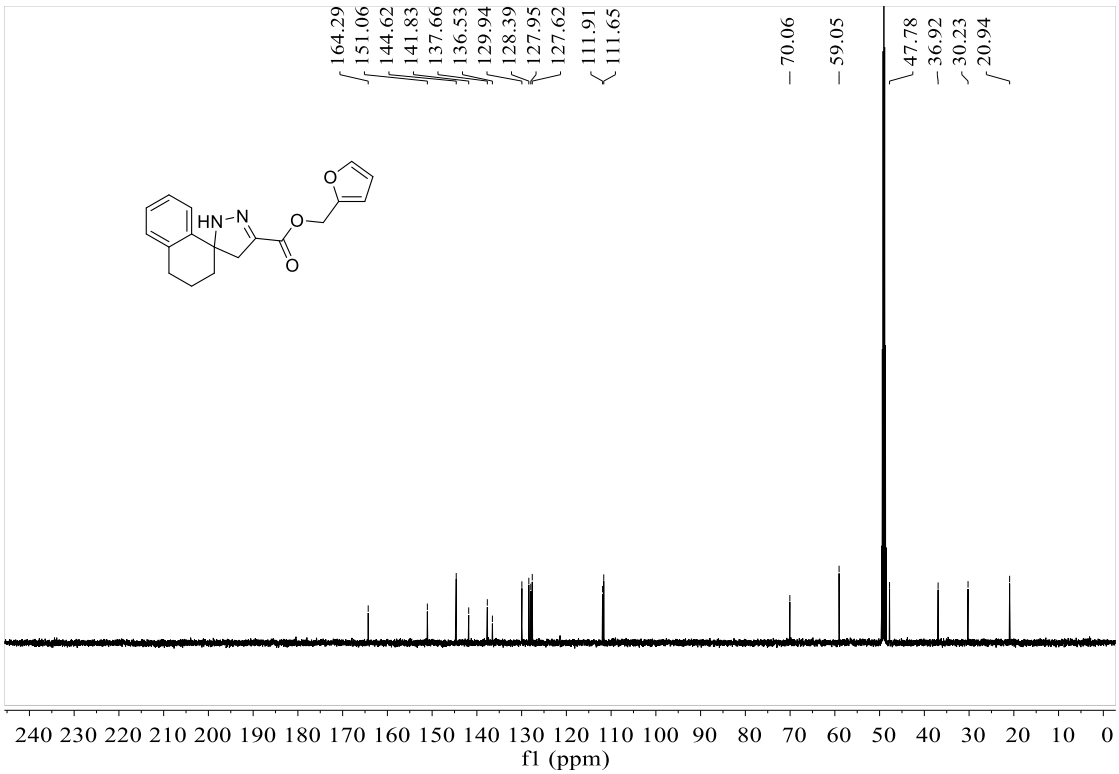
^{1}H NMR (500 MHz, CD_3OD) and ^{13}C NMR (126 MHz, CD_3OD) spectra for 63d:



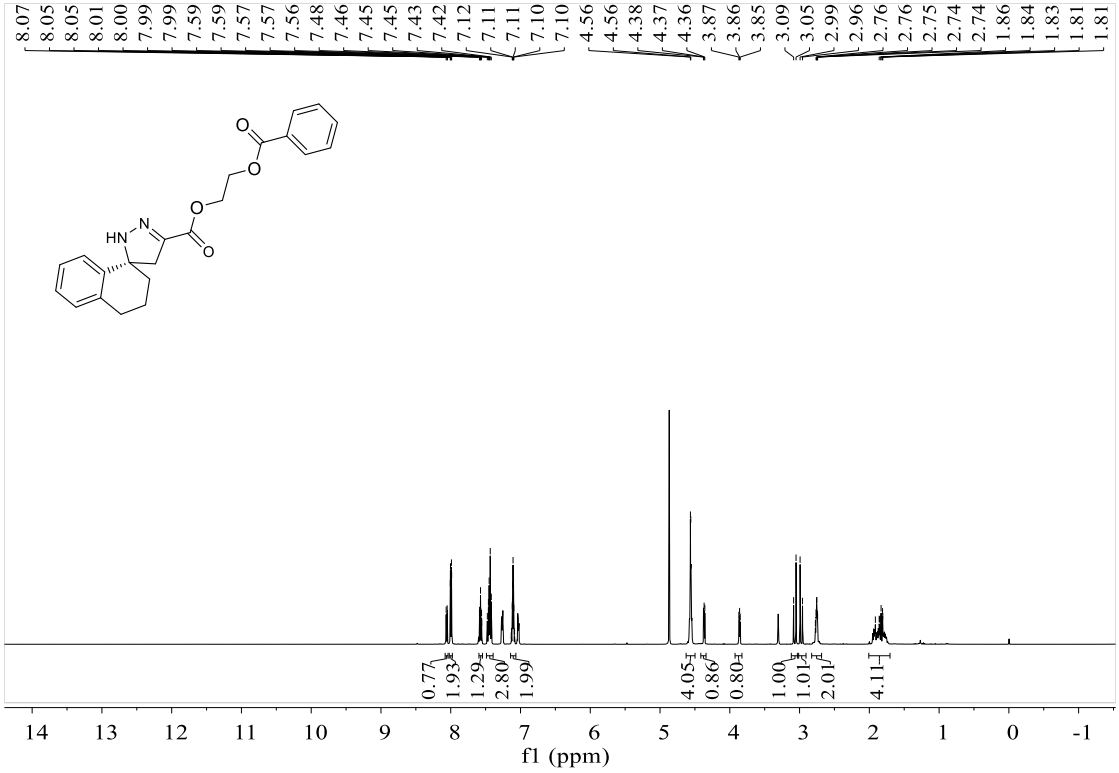


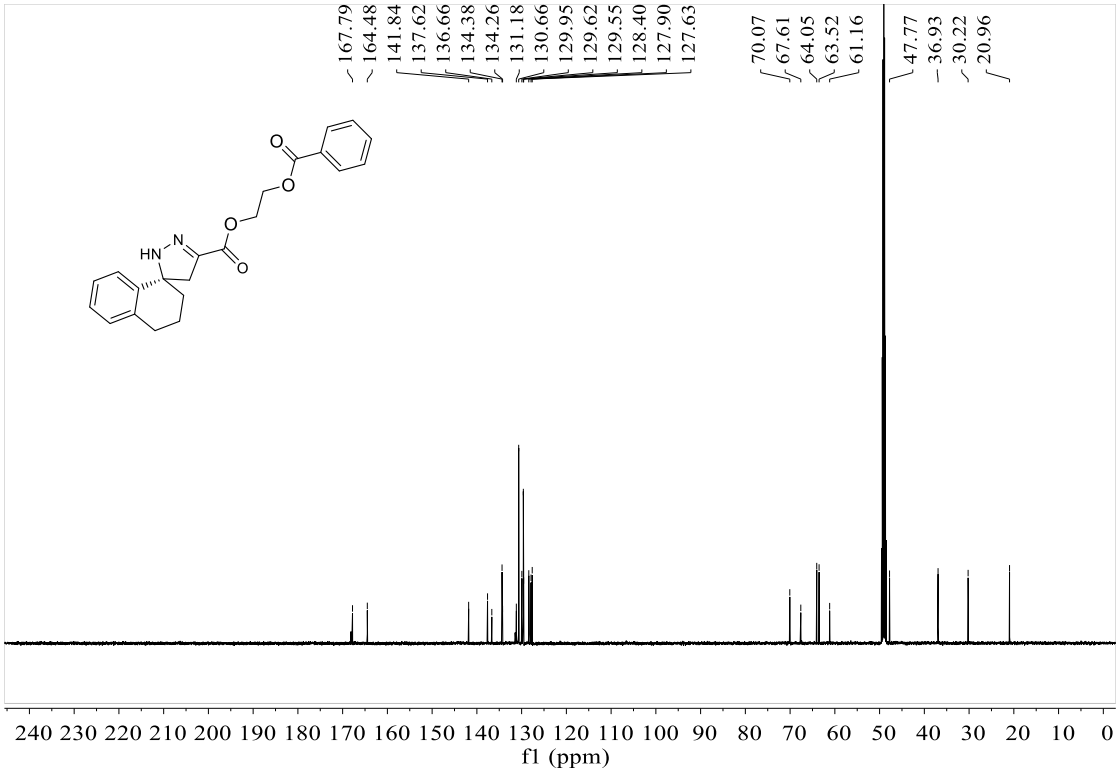
^{1}H NMR (500 MHz, CD_3OD) and ^{13}C NMR (126 MHz, CD_3OD) spectra for 64d:



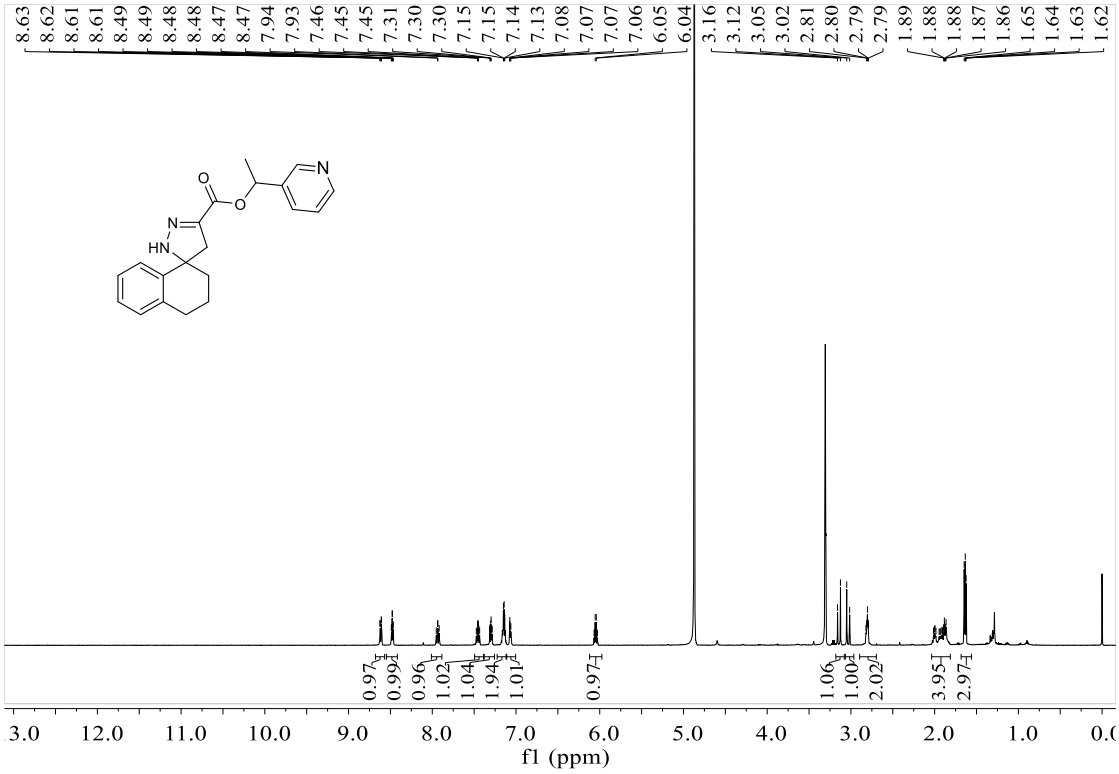


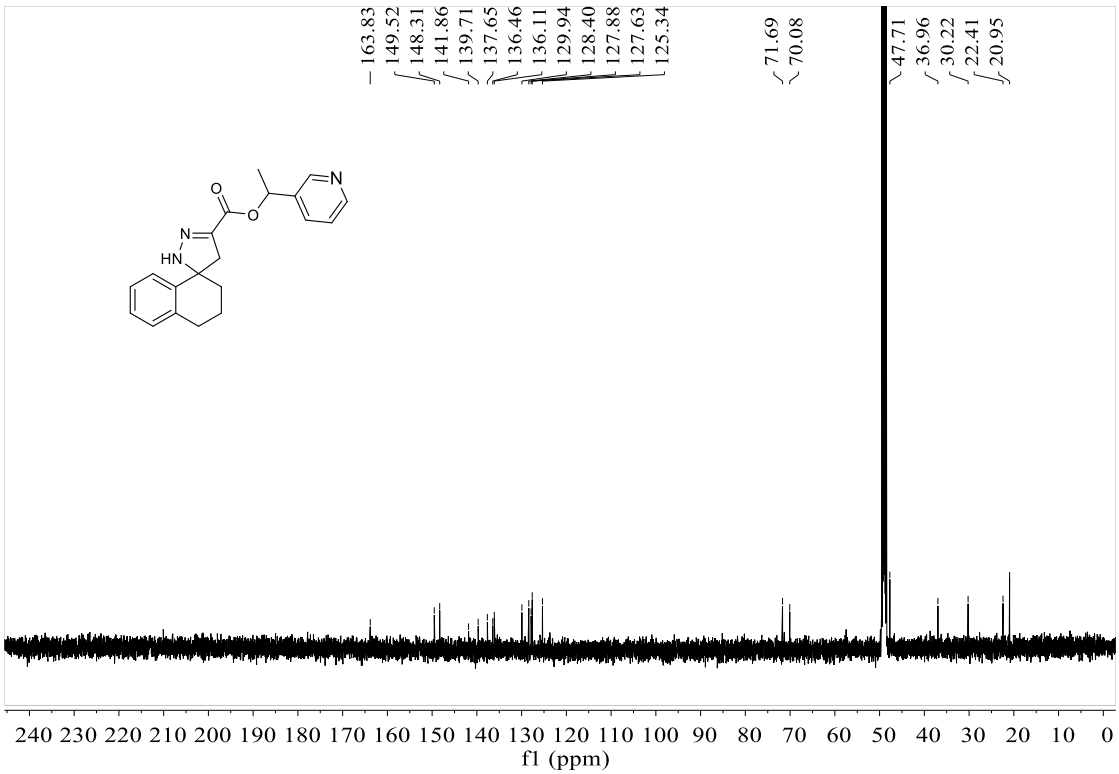
^{1}H NMR (500 MHz, CD_3OD) and ^{13}C NMR (126 MHz, CD_3OD) spectra for 65d:



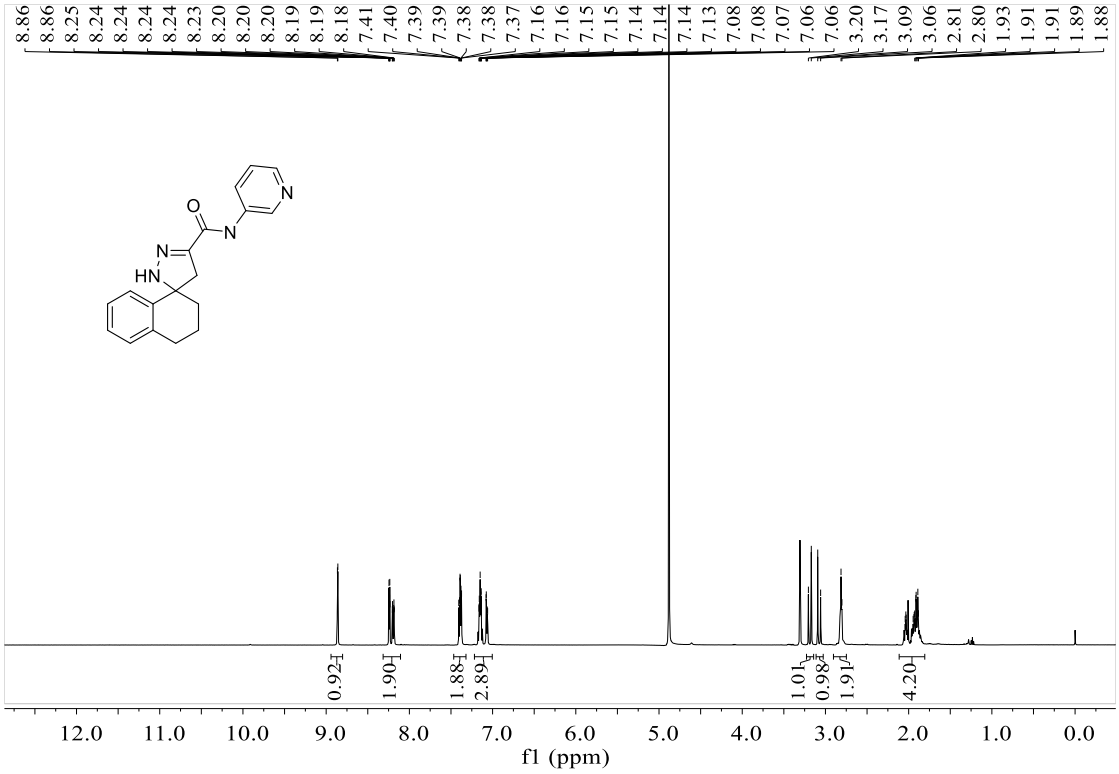


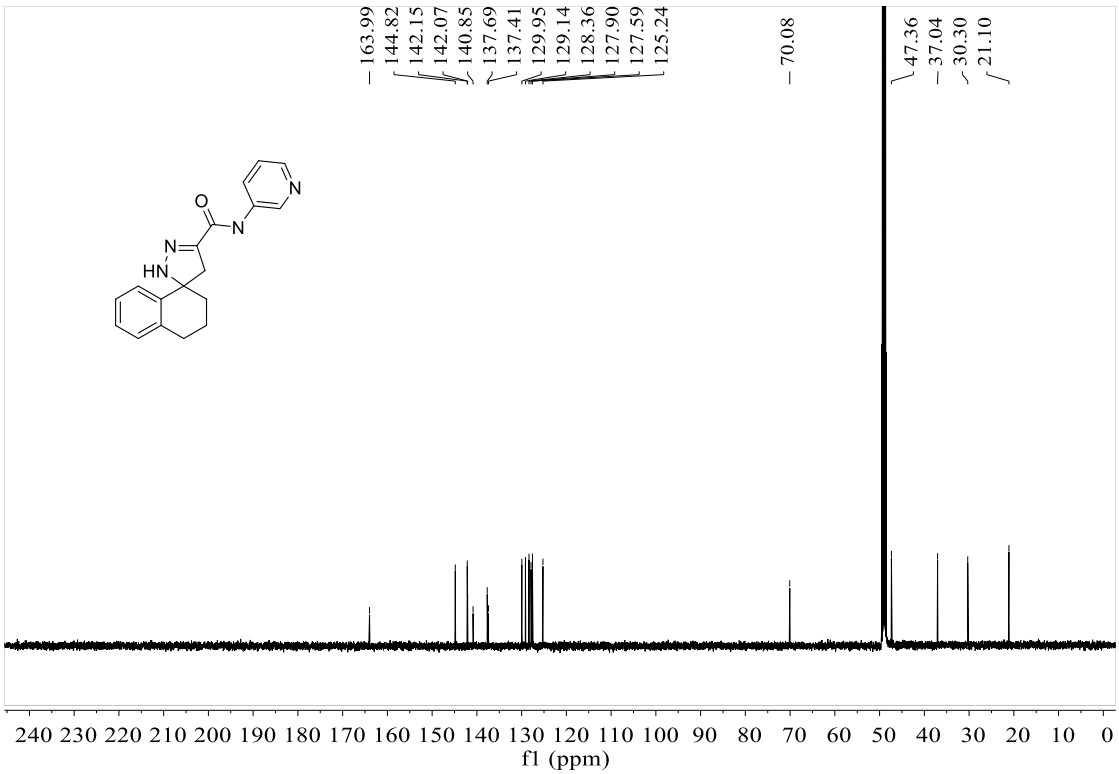
^{1}H NMR (500 MHz, CD_3OD) and ^{13}C NMR (126 MHz, CD_3OD) spectra for 66d:



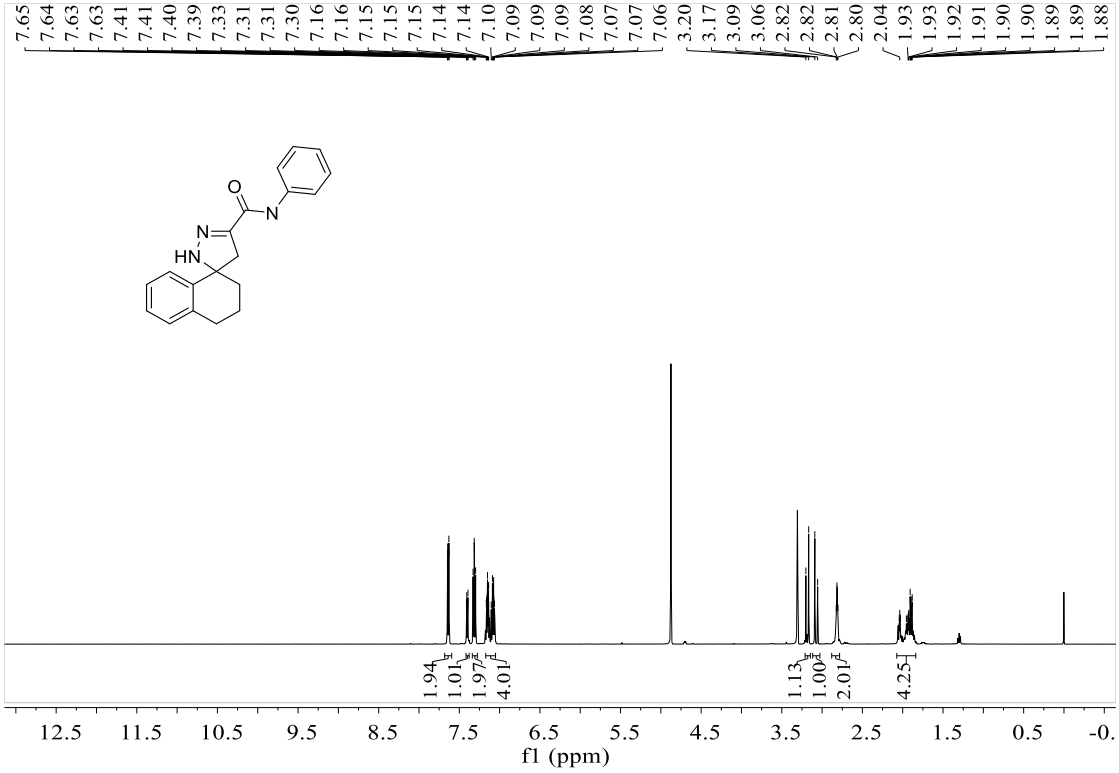


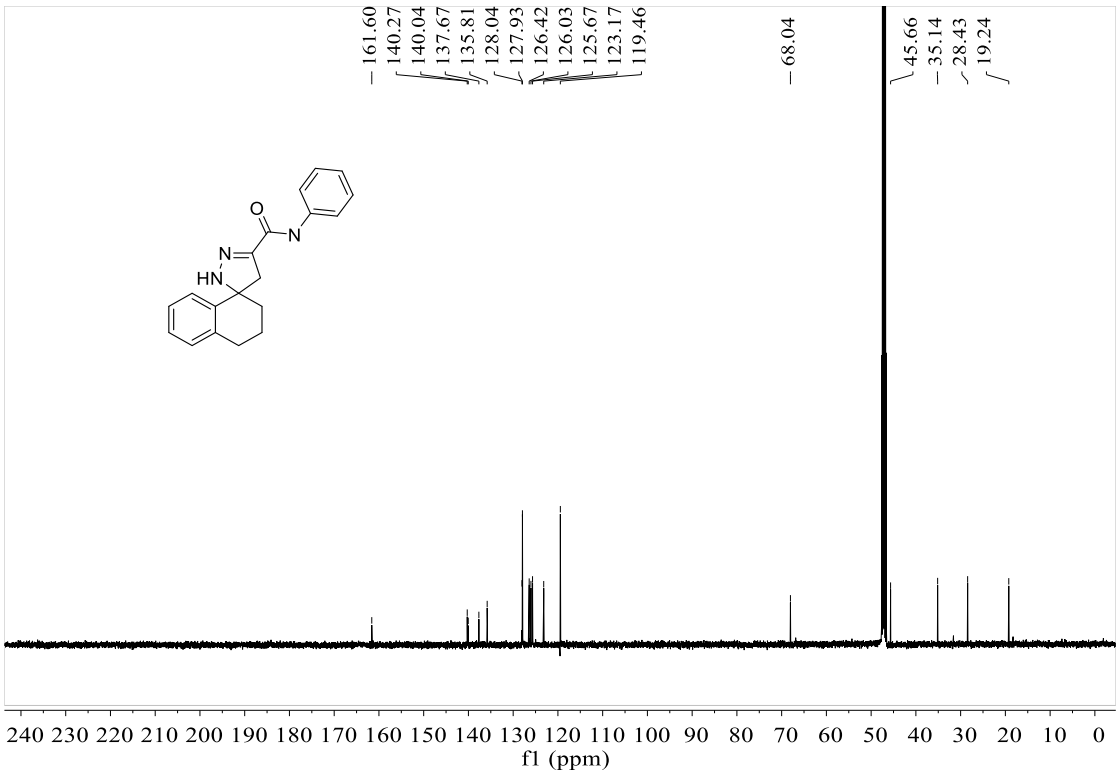
^{1}H NMR (500 MHz, CD_3OD) and ^{13}C NMR (126 MHz, CD_3OD) spectra for 67d:



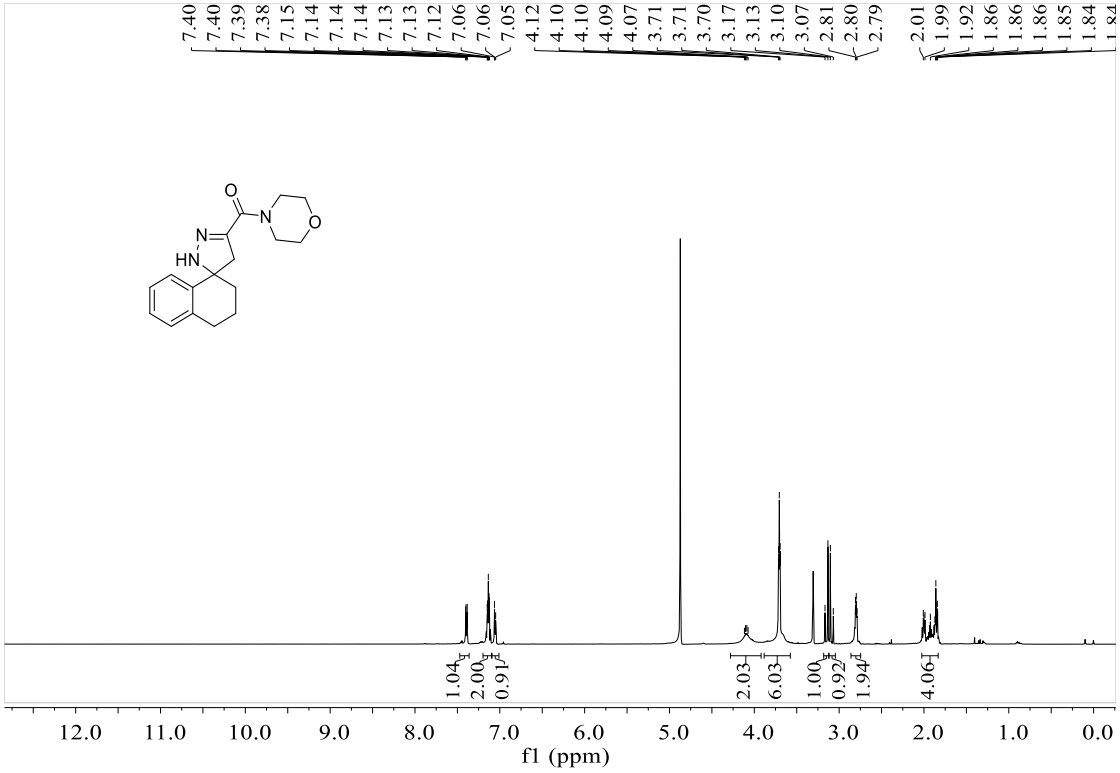


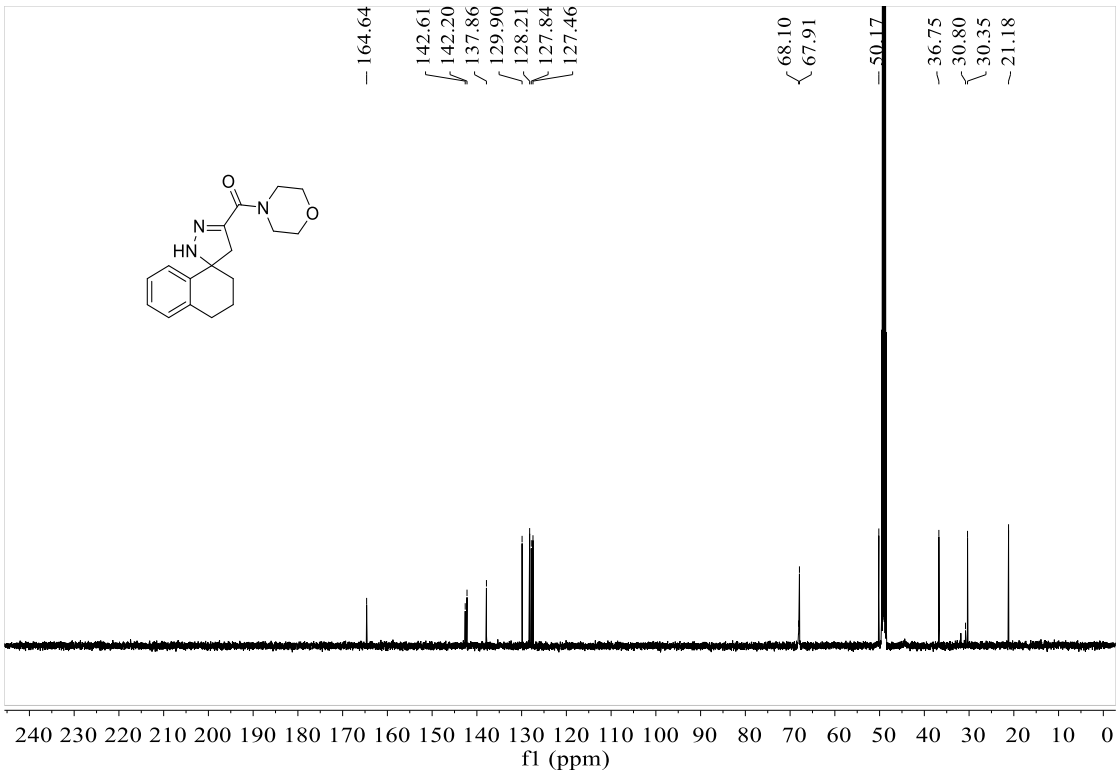
^{1}H NMR (500 MHz, CD_3OD) and ^{13}C NMR (126 MHz, CD_3OD) spectra for 68d:



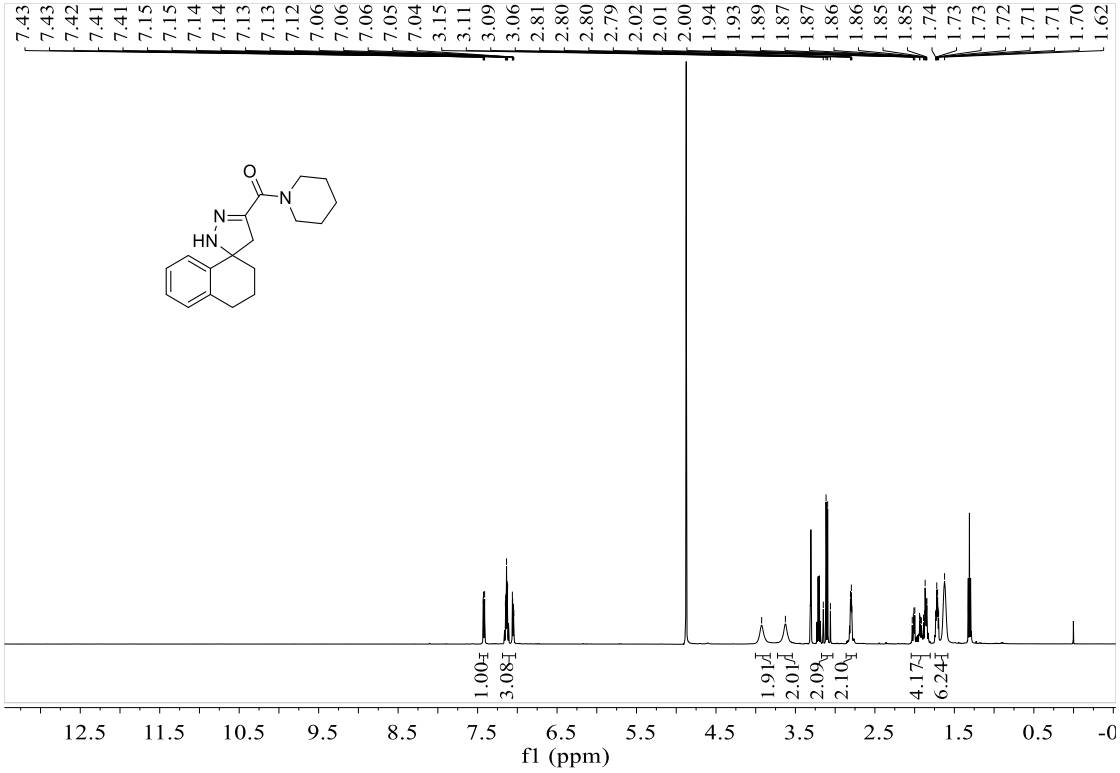


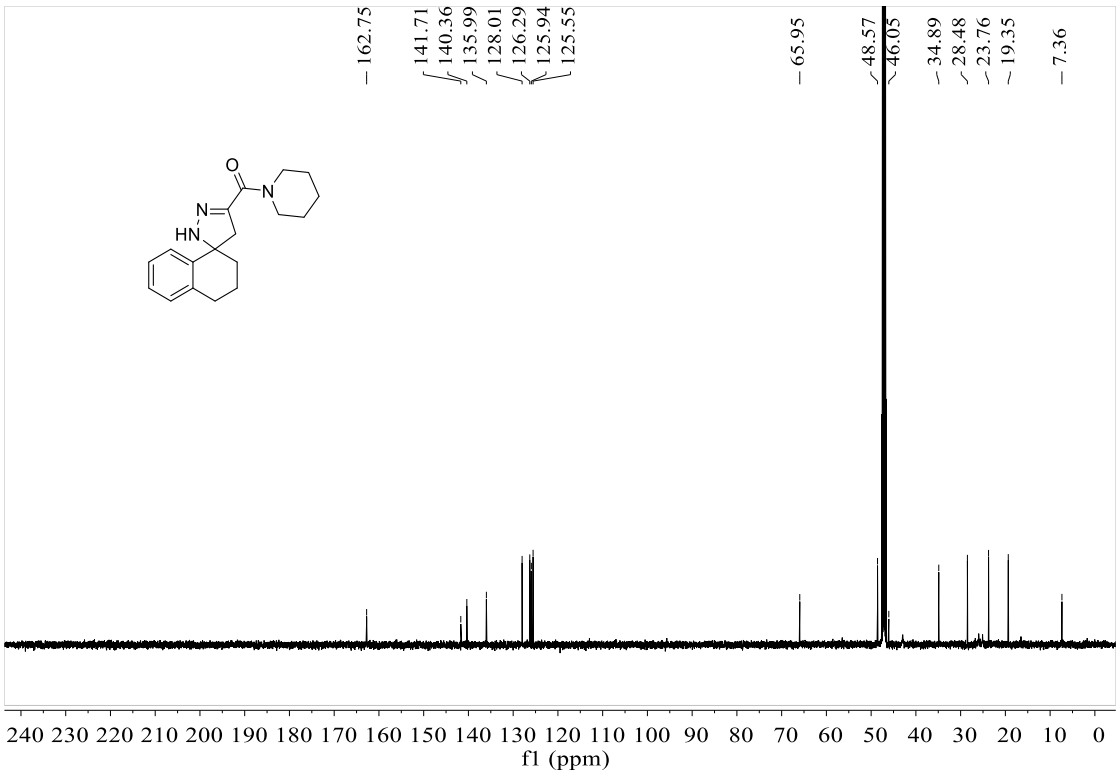
^{1}H NMR (500 MHz, CD_3OD) and ^{13}C NMR (126 MHz, CD_3OD) spectra for 69d:



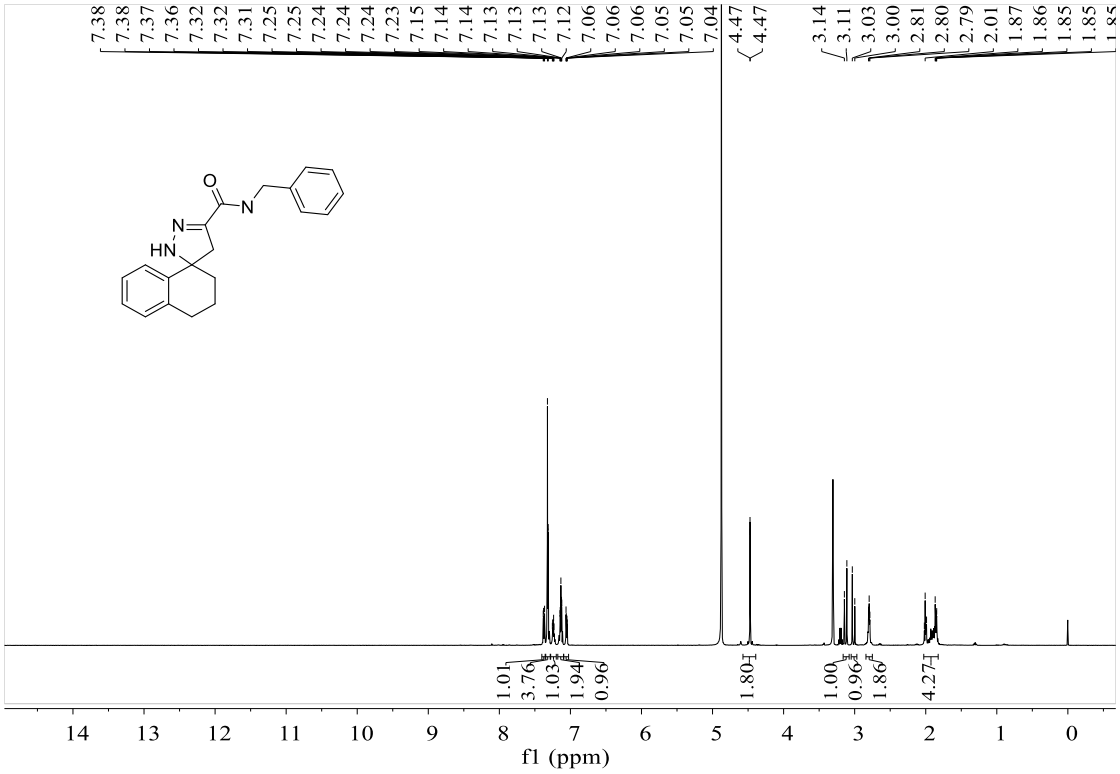


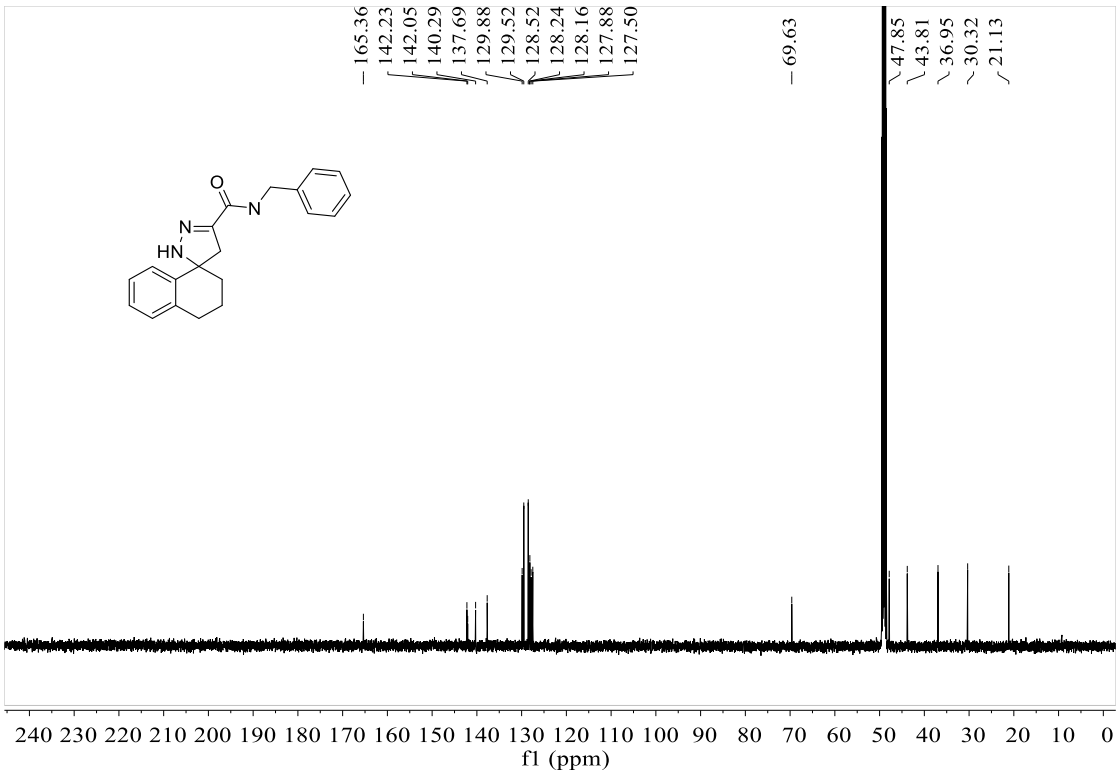
^{1}H NMR (500 MHz, CD_3OD) and ^{13}C NMR (126 MHz, CD_3OD) spectra for 70d:



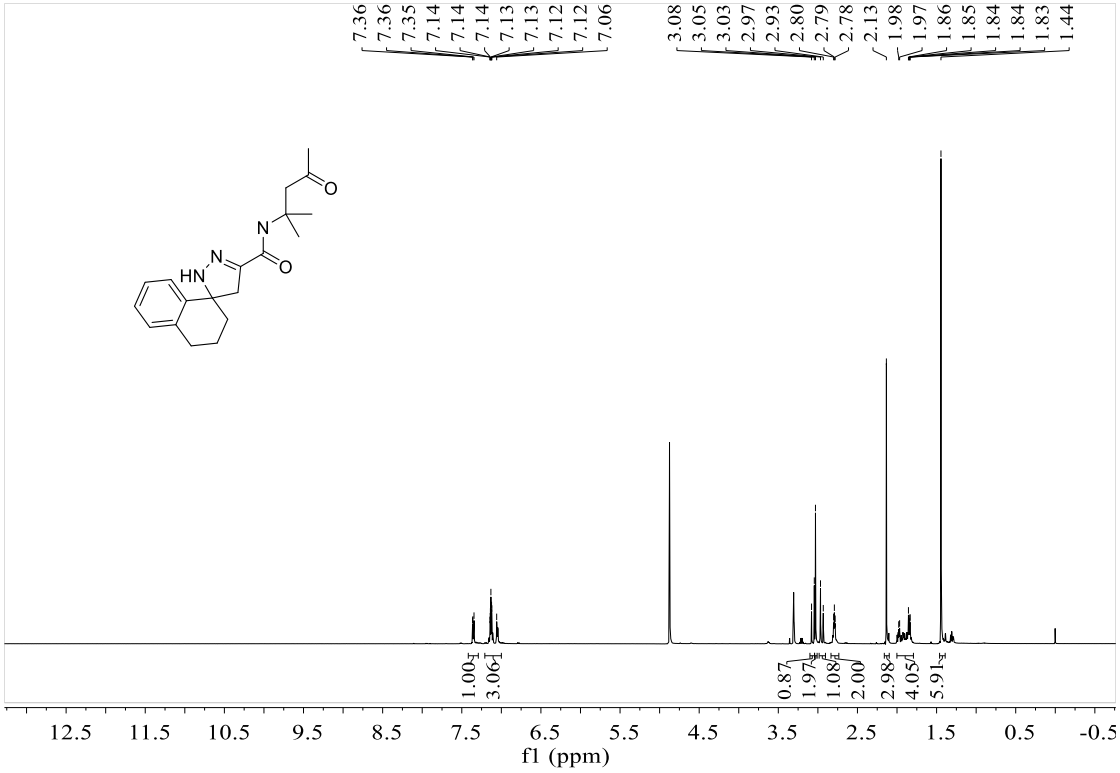


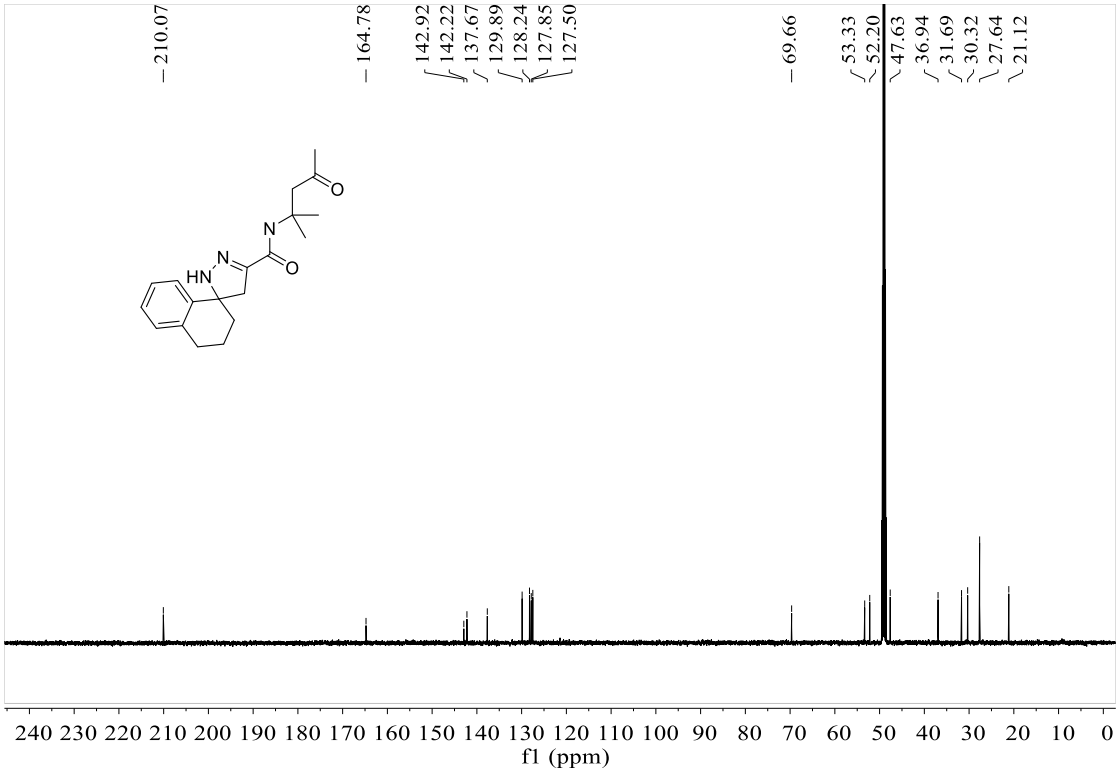
^{1}H NMR (500 MHz, CD_3OD) and ^{13}C NMR (126 MHz, CD_3OD) spectra for 71d:



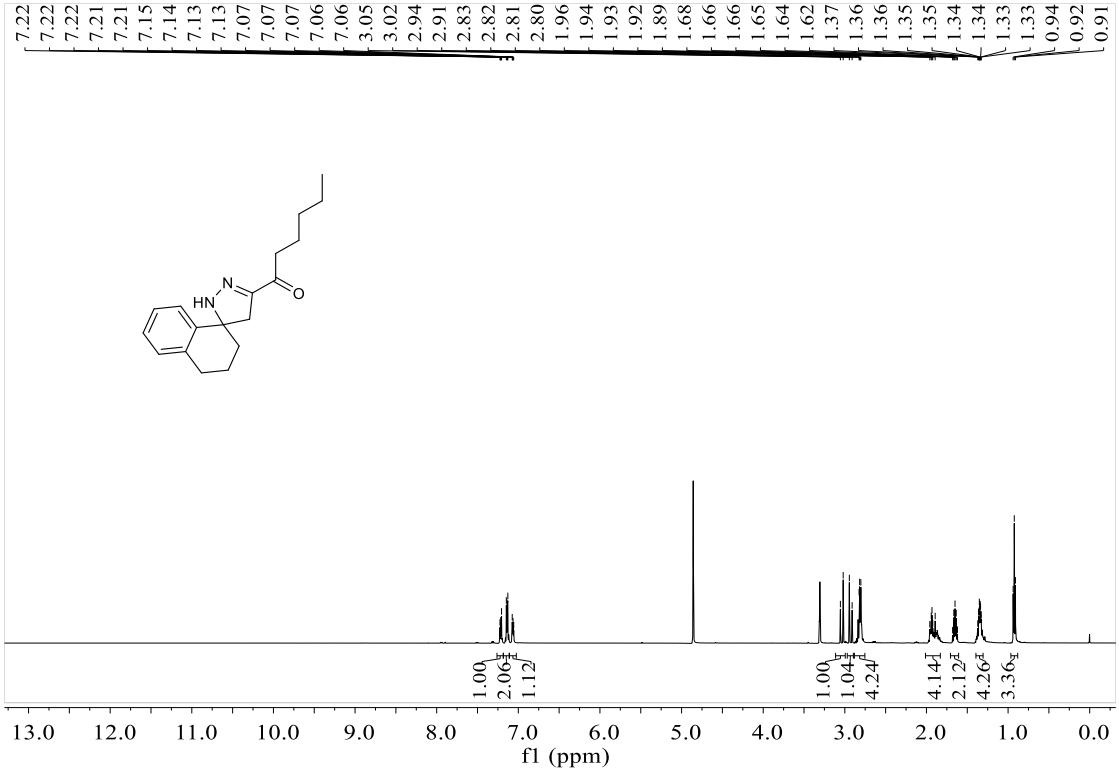


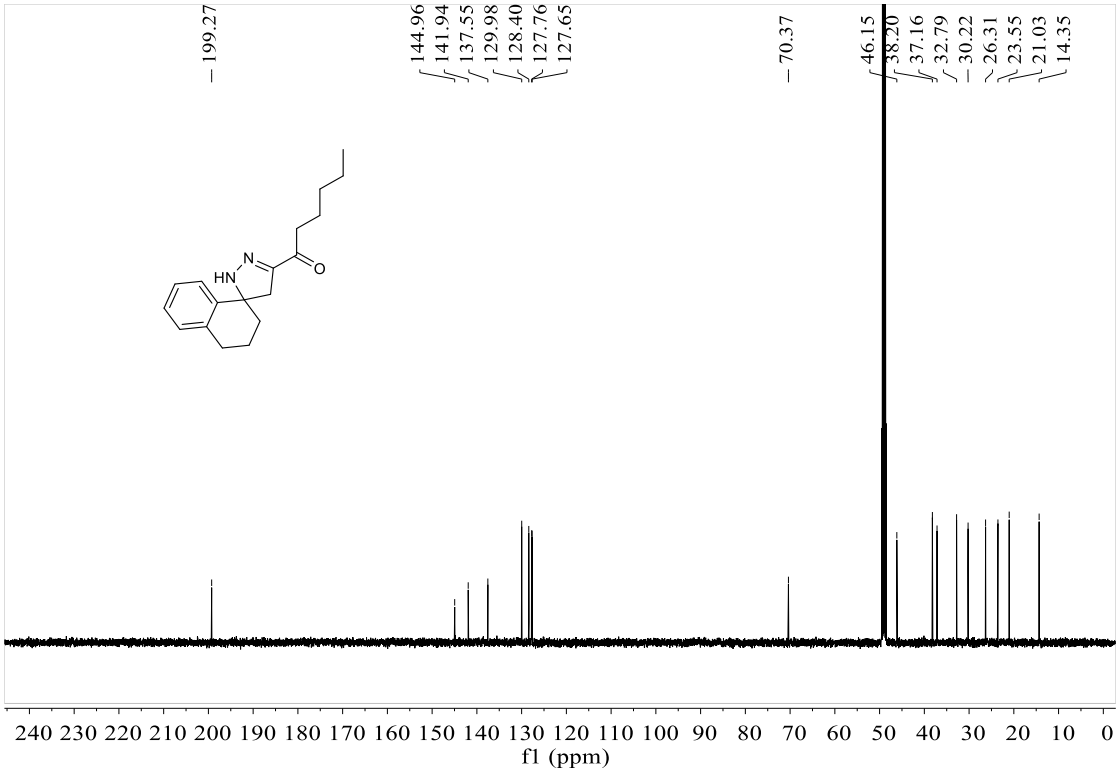
^{1}H NMR (500 MHz, CD_3OD) and ^{13}C NMR (126 MHz, CD_3OD) spectra for 72d:



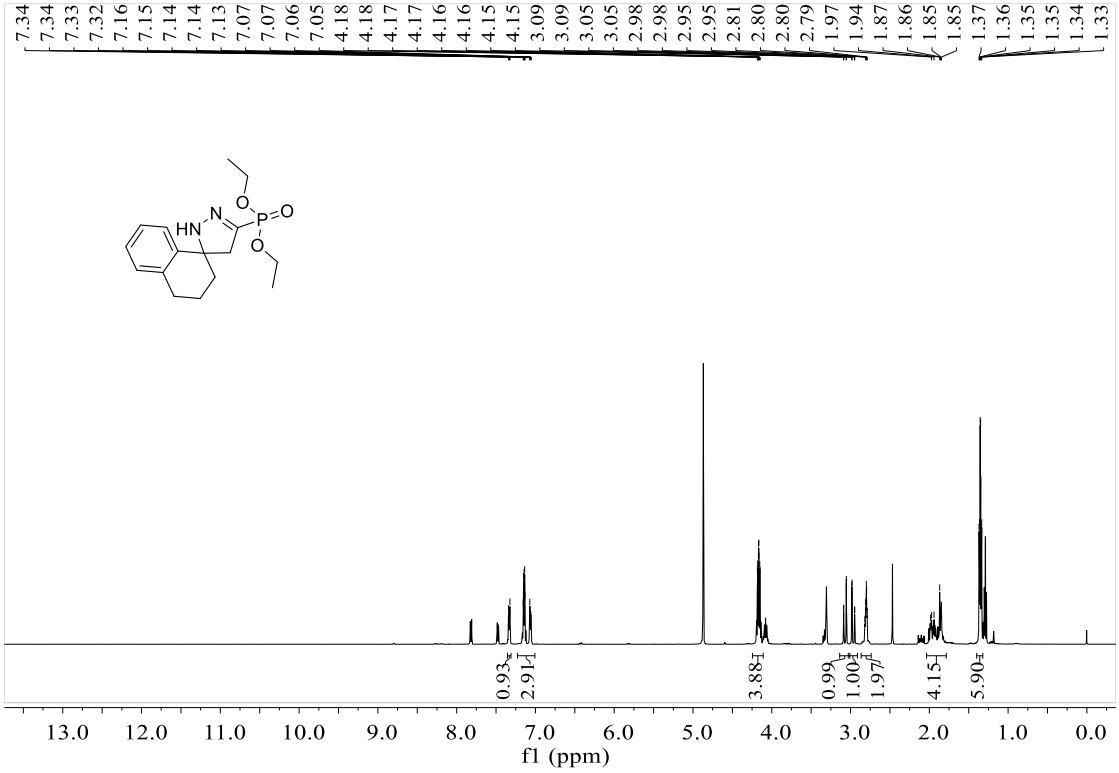


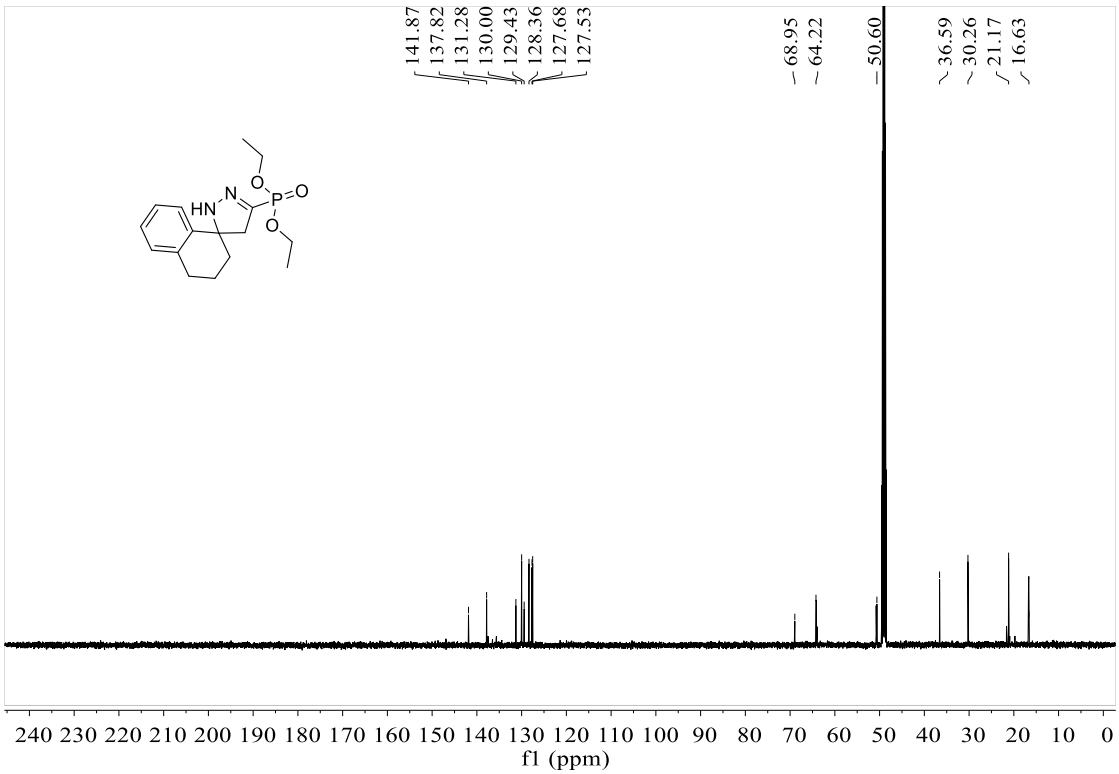
^{1}H NMR (500 MHz, CD_3OD) and ^{13}C NMR (126 MHz, CD_3OD) spectra for 73d:



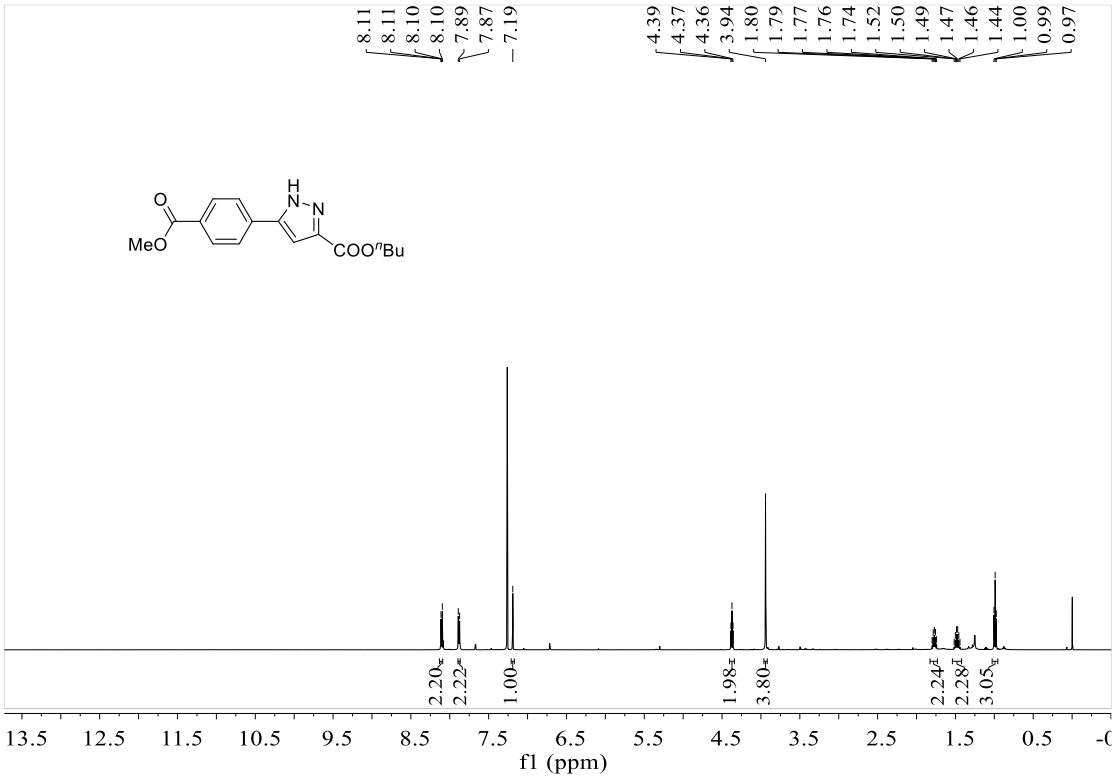


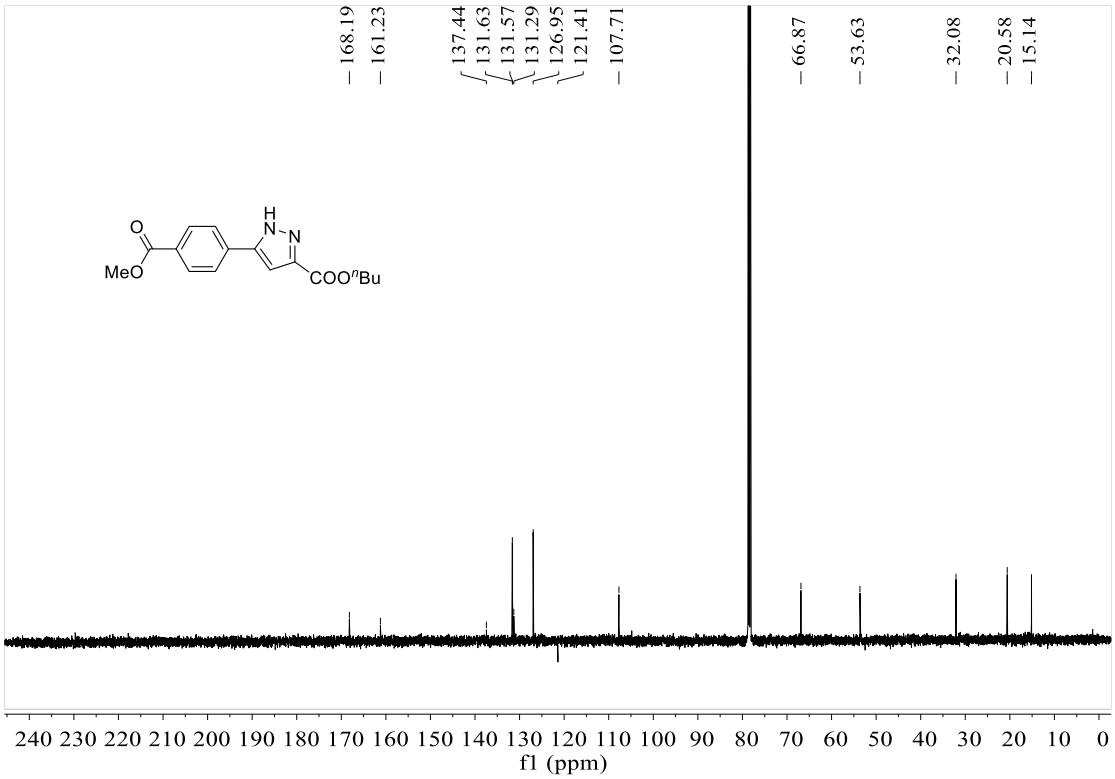
^{1}H NMR (500 MHz, CD_3OD) and ^{13}C NMR (126 MHz, CD_3OD) spectra for 74d:



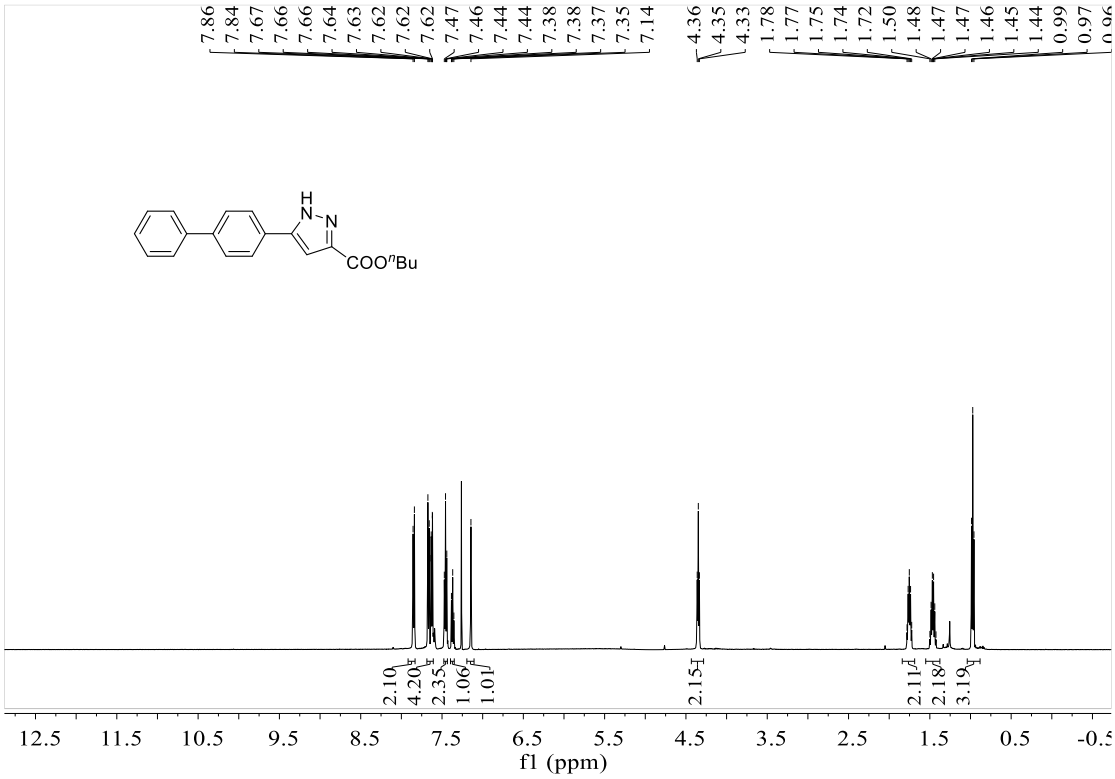


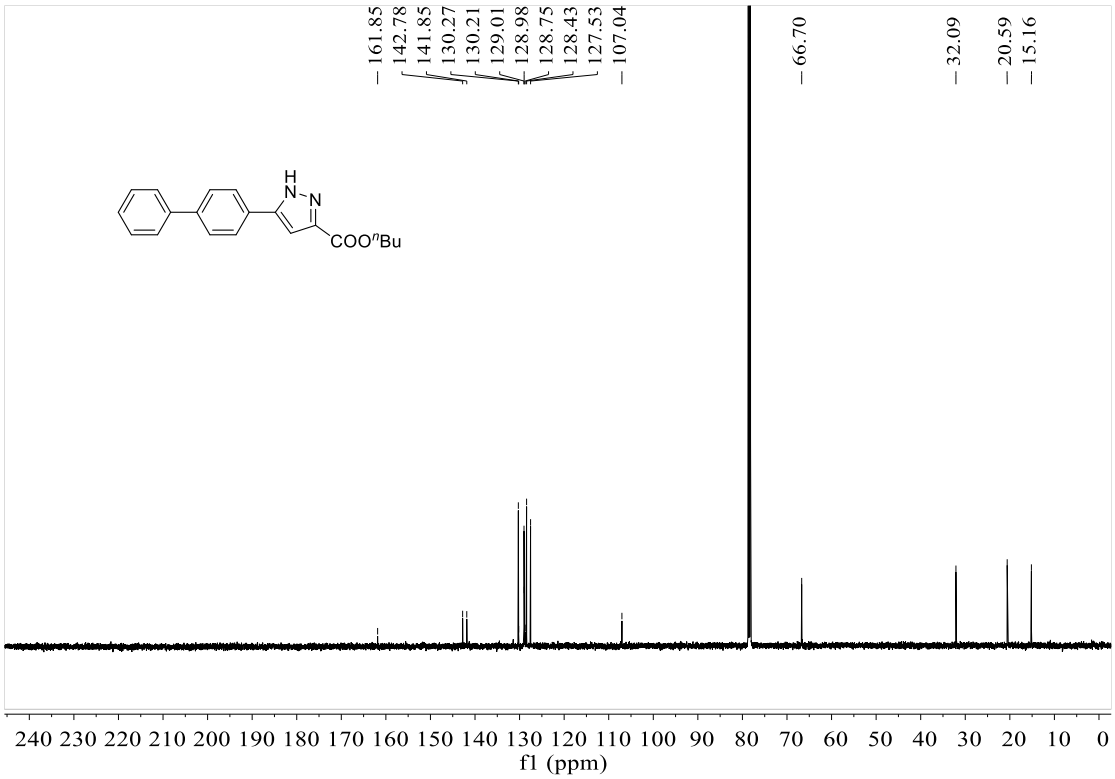
^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (126 MHz, $CDCl_3$) spectra for 77d:



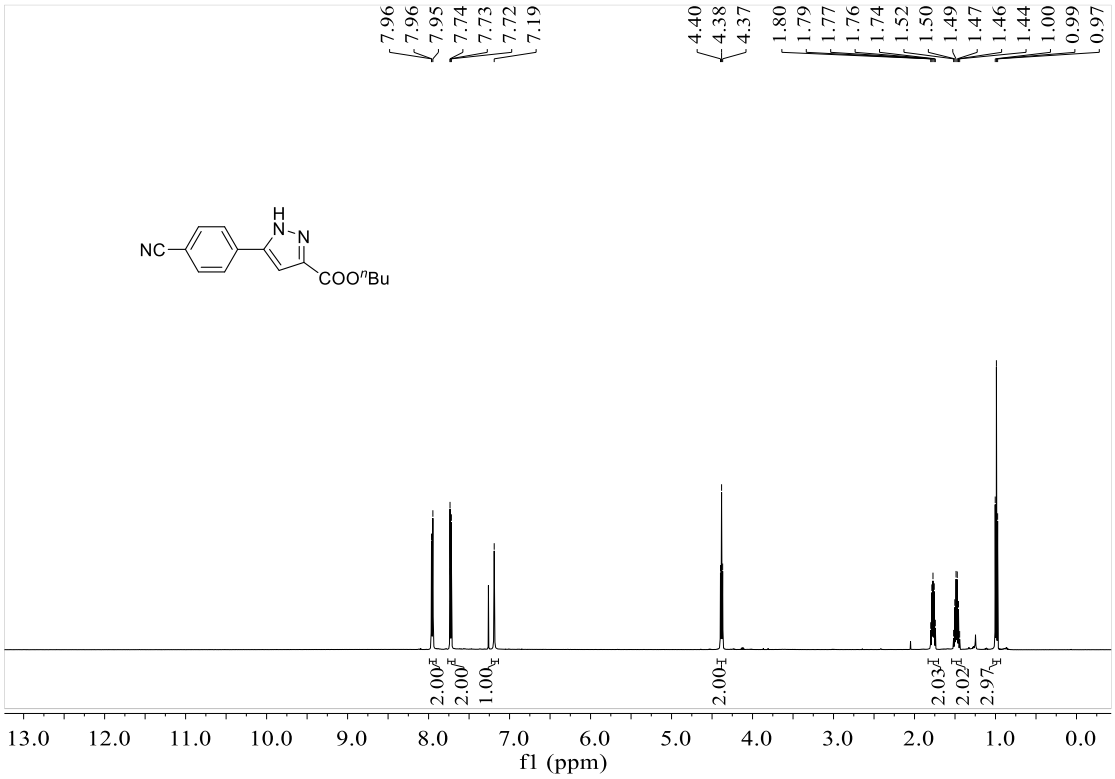


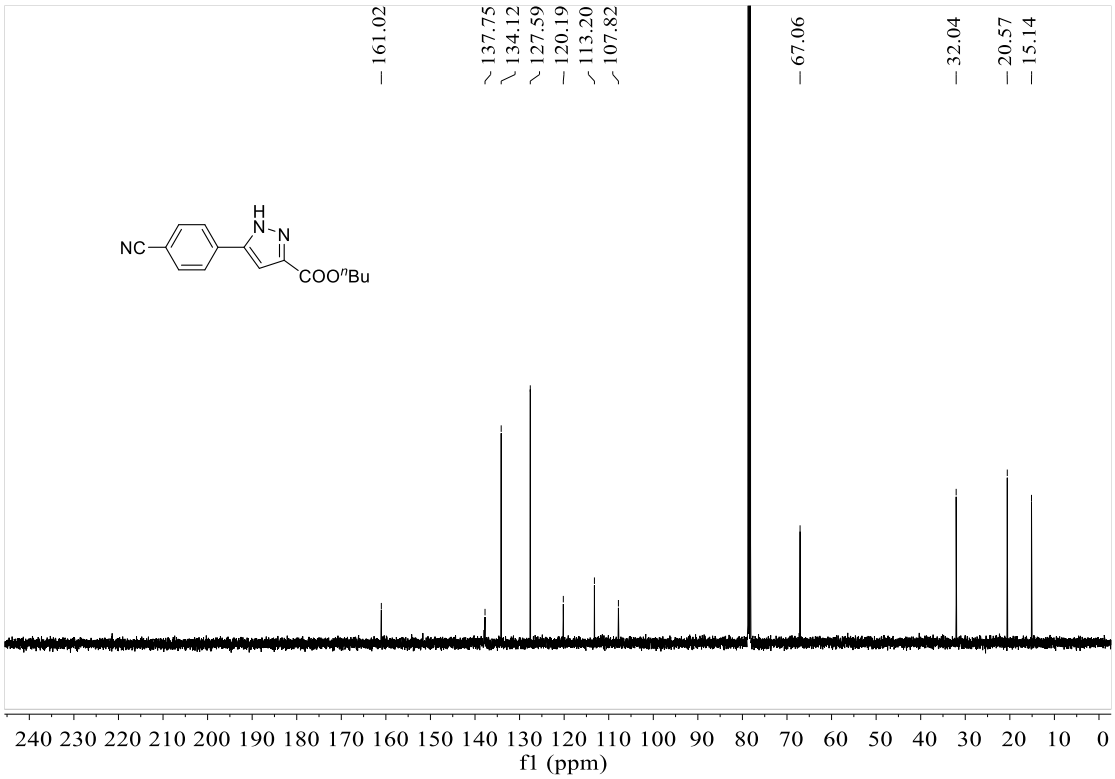
^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (126 MHz, $CDCl_3$) spectra for 78d:



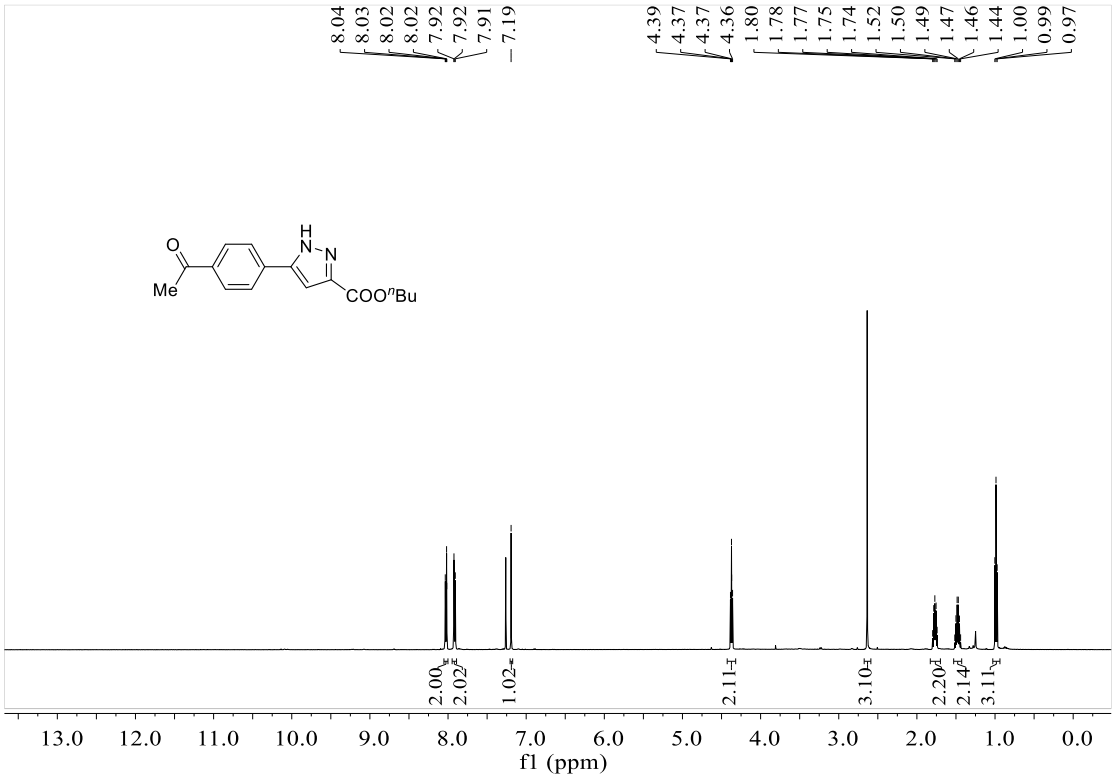


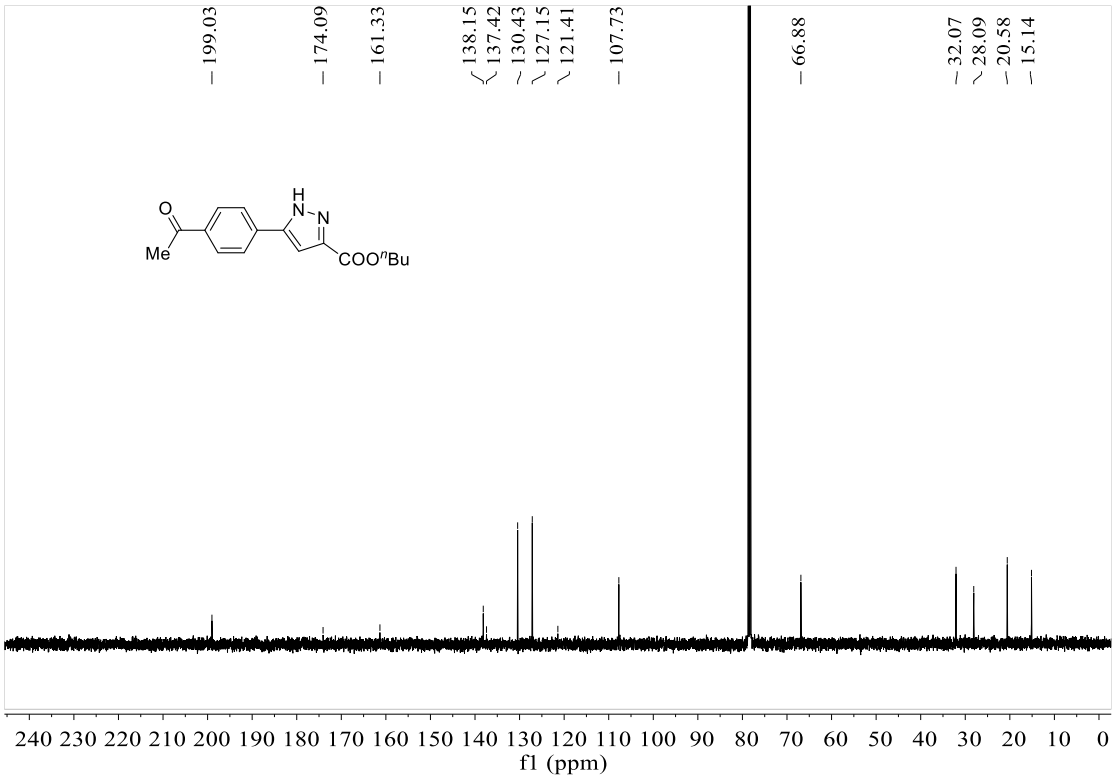
^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (126 MHz, $CDCl_3$) spectra for 79d:





^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (126 MHz, $CDCl_3$) spectra for 80d:





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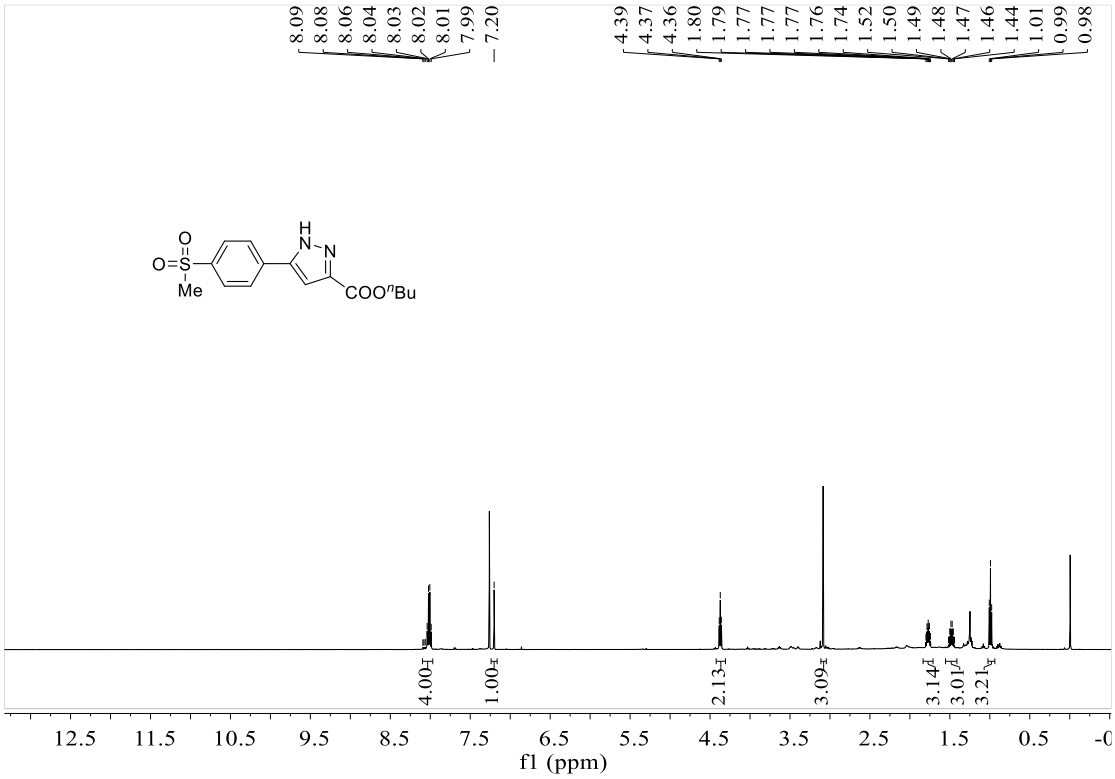
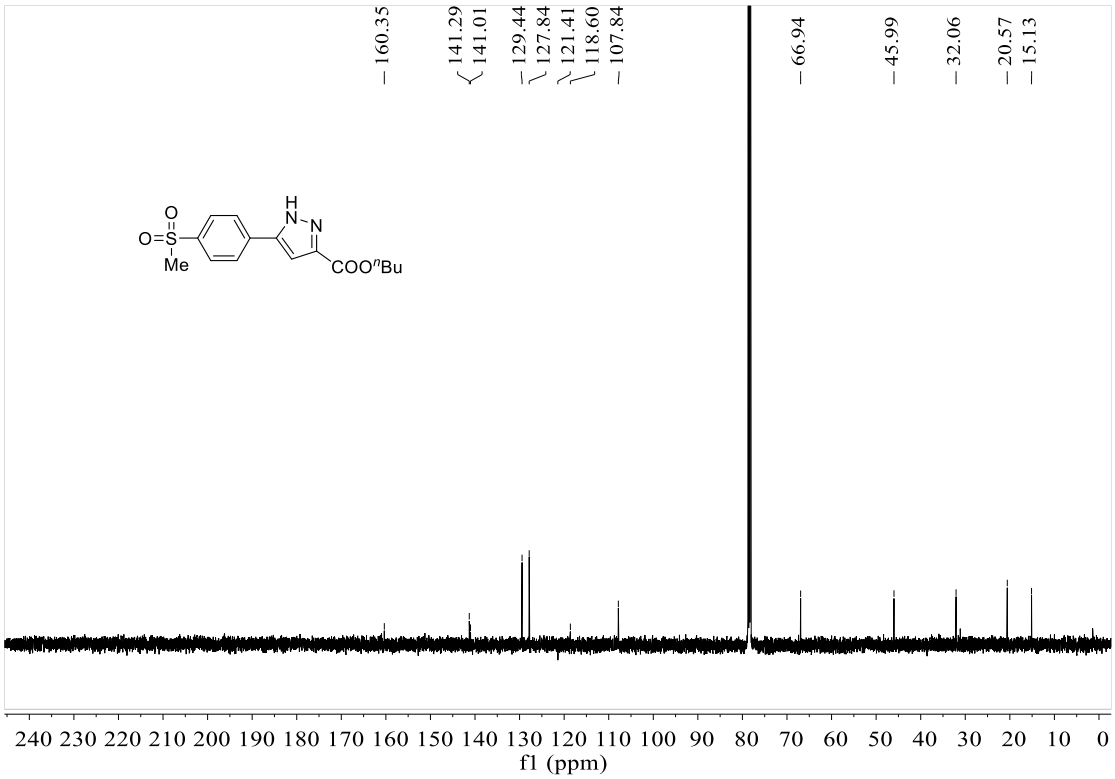
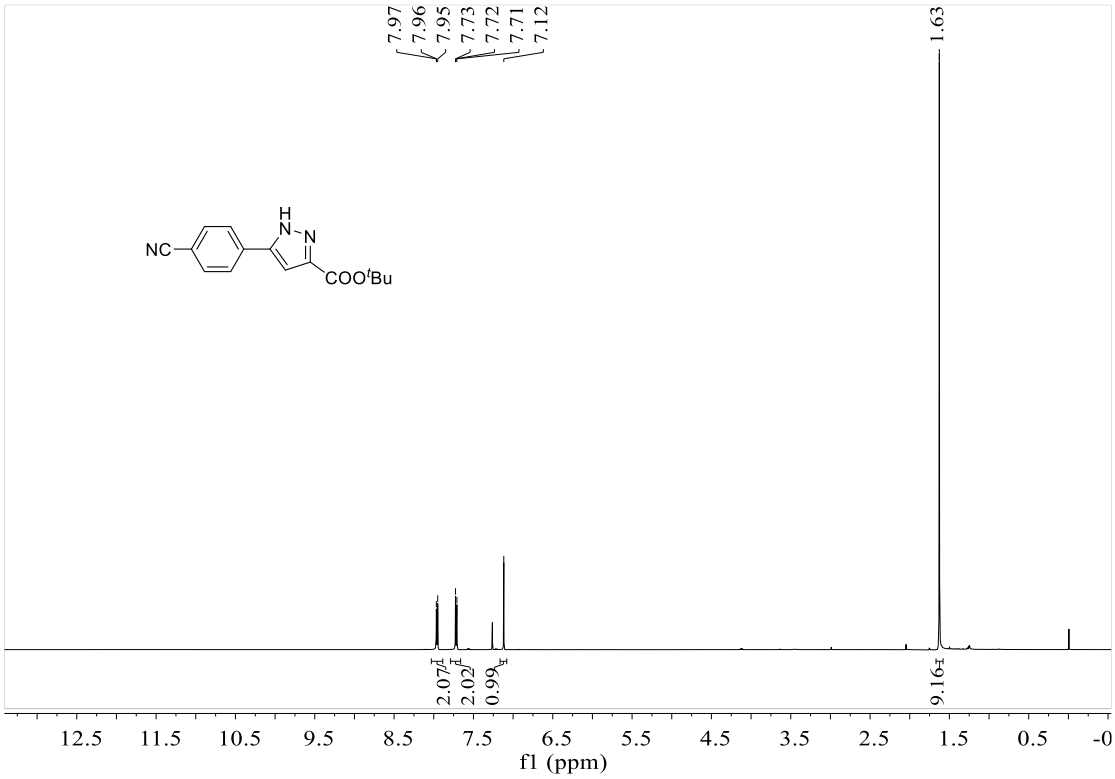
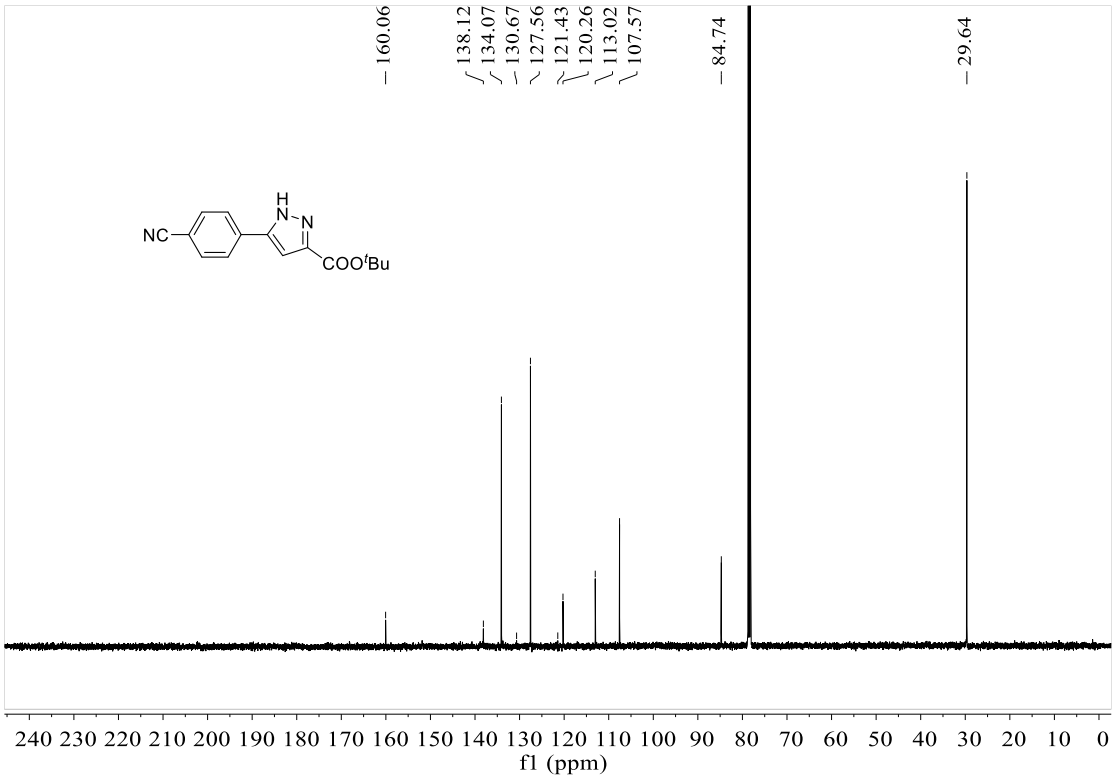


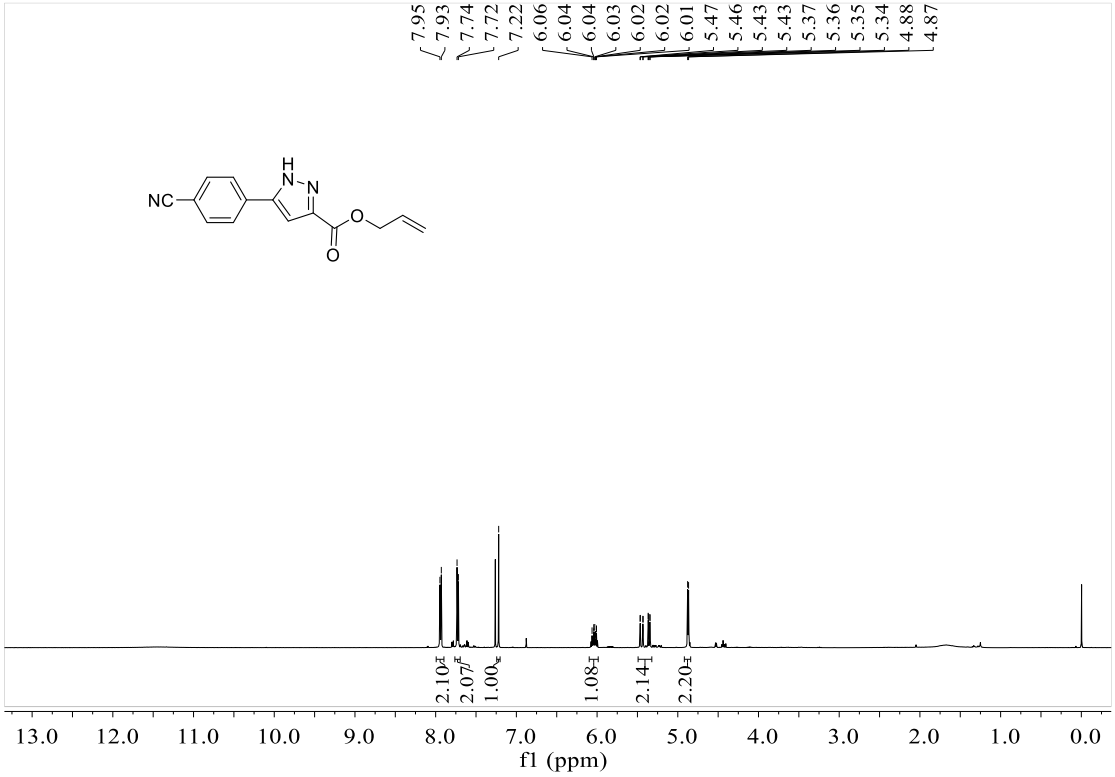


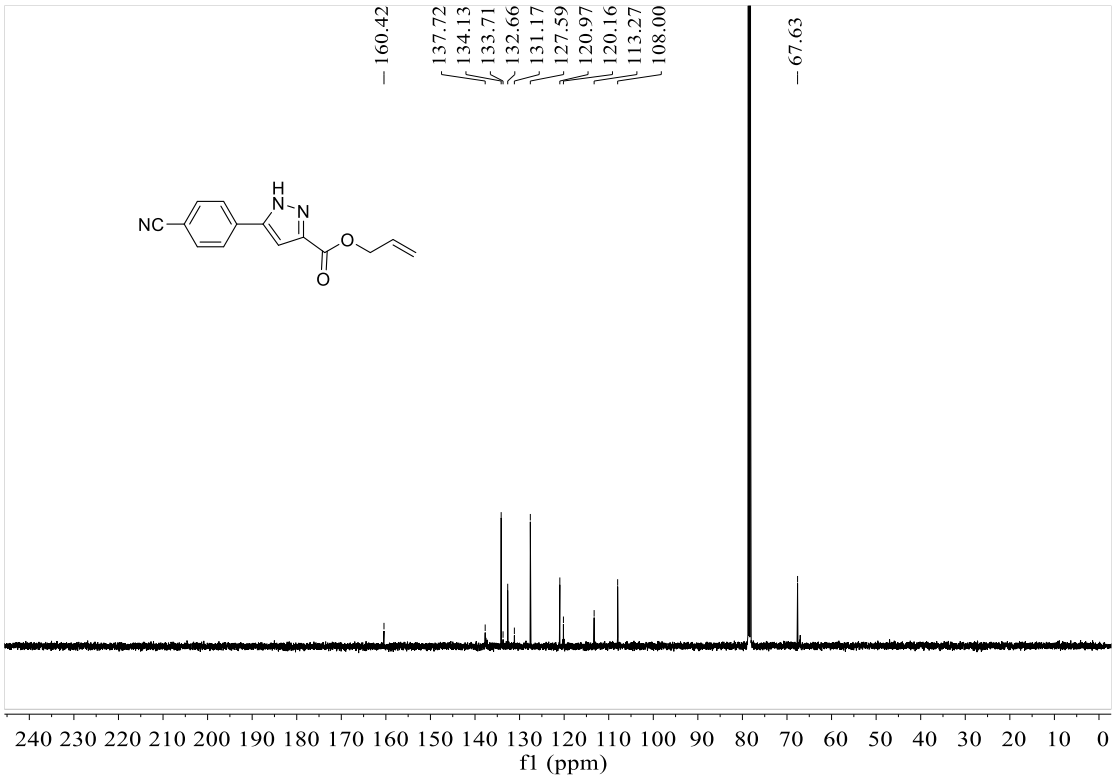
^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (126 MHz, $CDCl_3$) spectra for 82d:





^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (126 MHz, $CDCl_3$) spectra for 83d:





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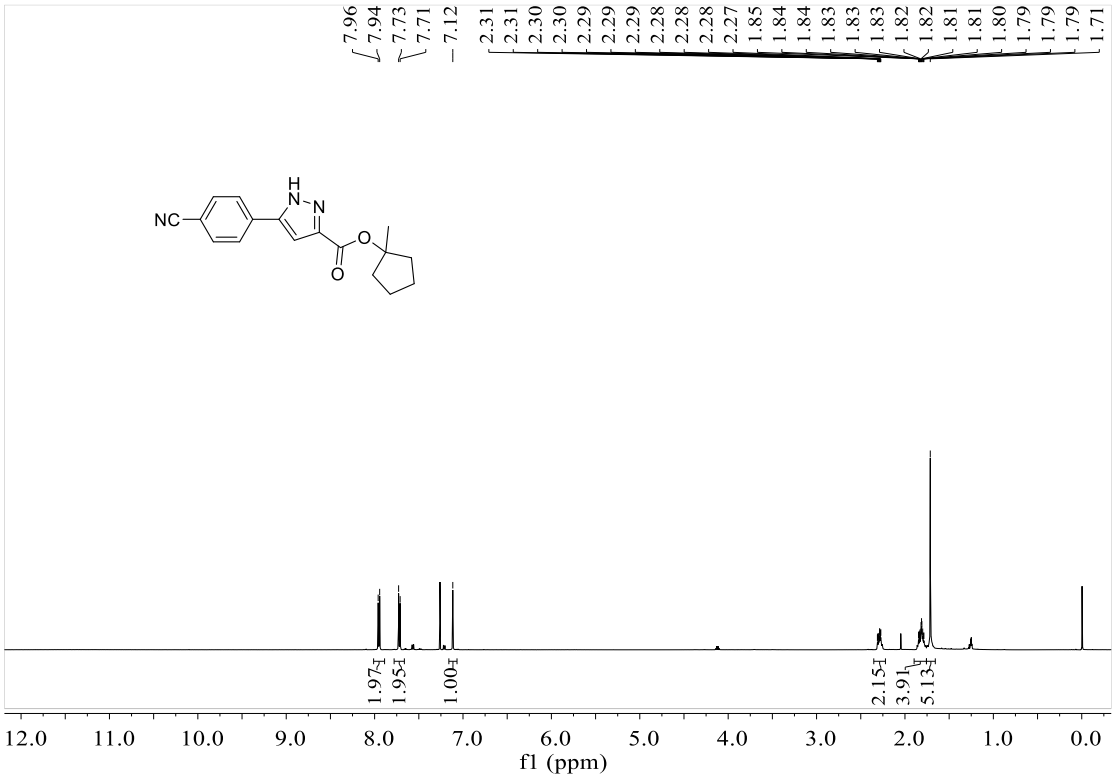

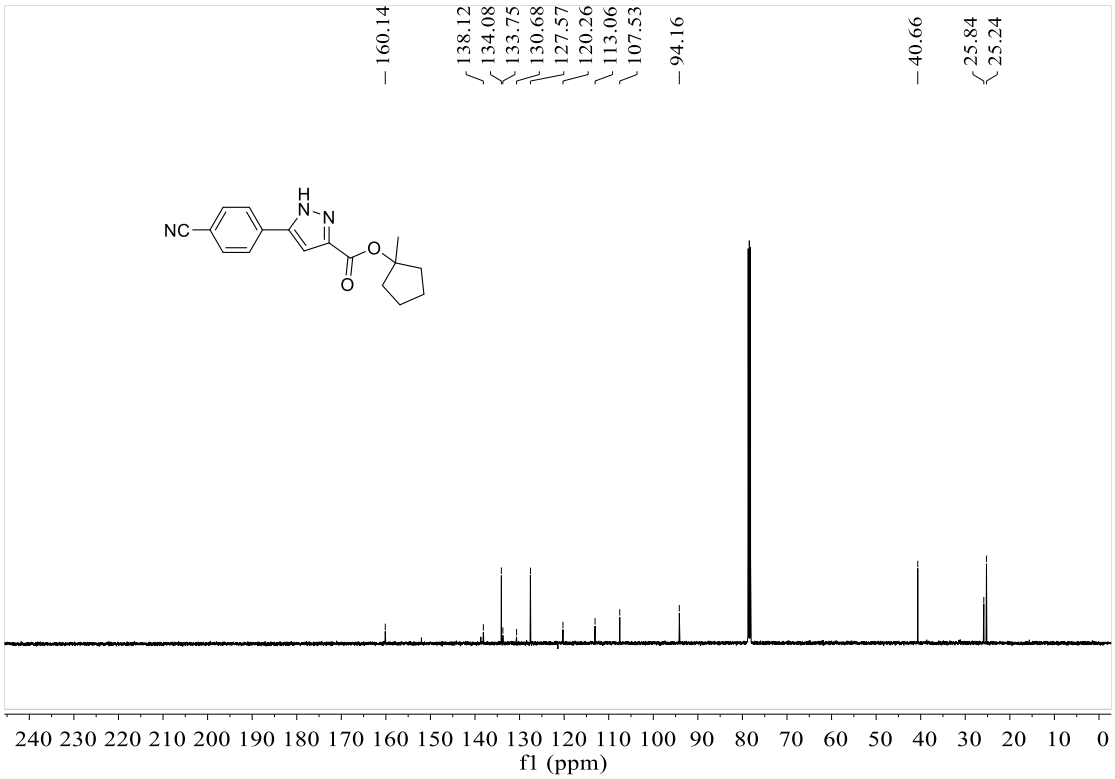

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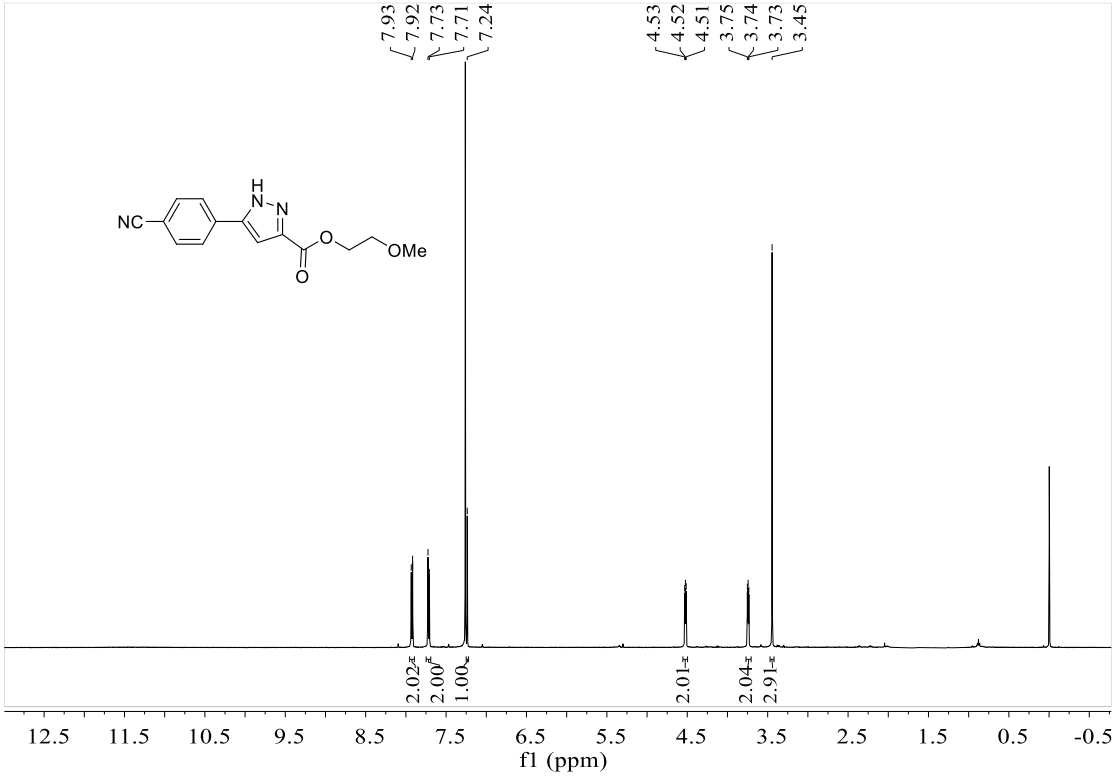
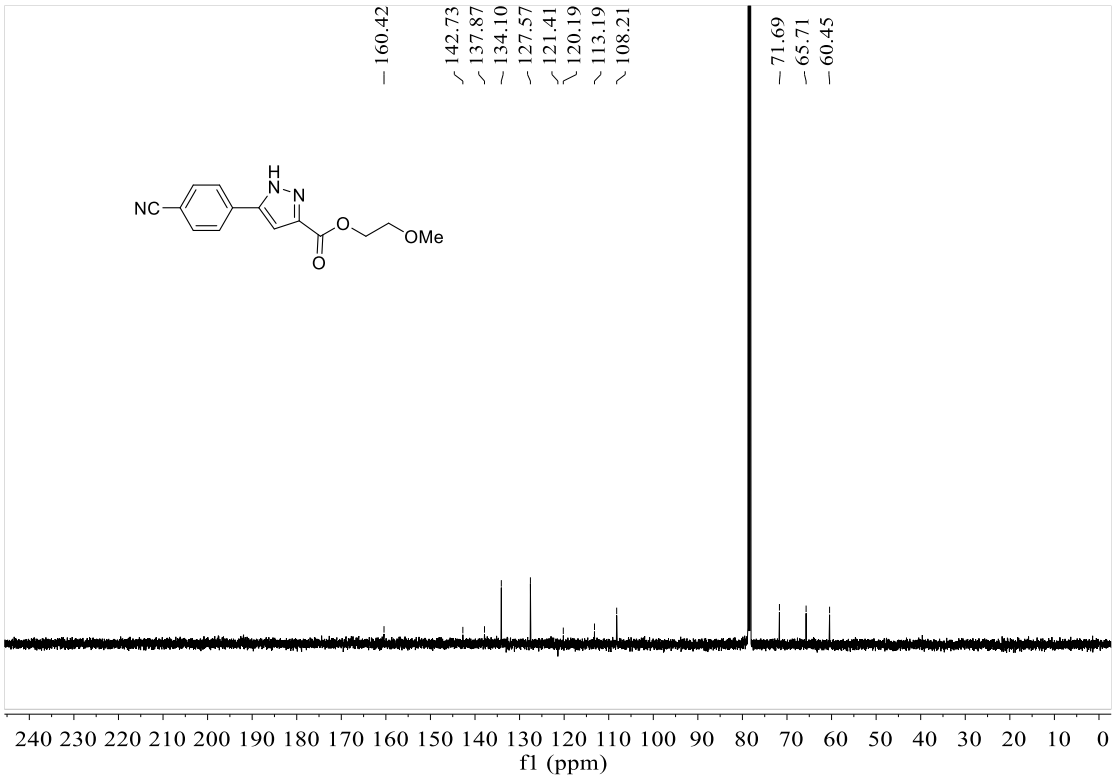
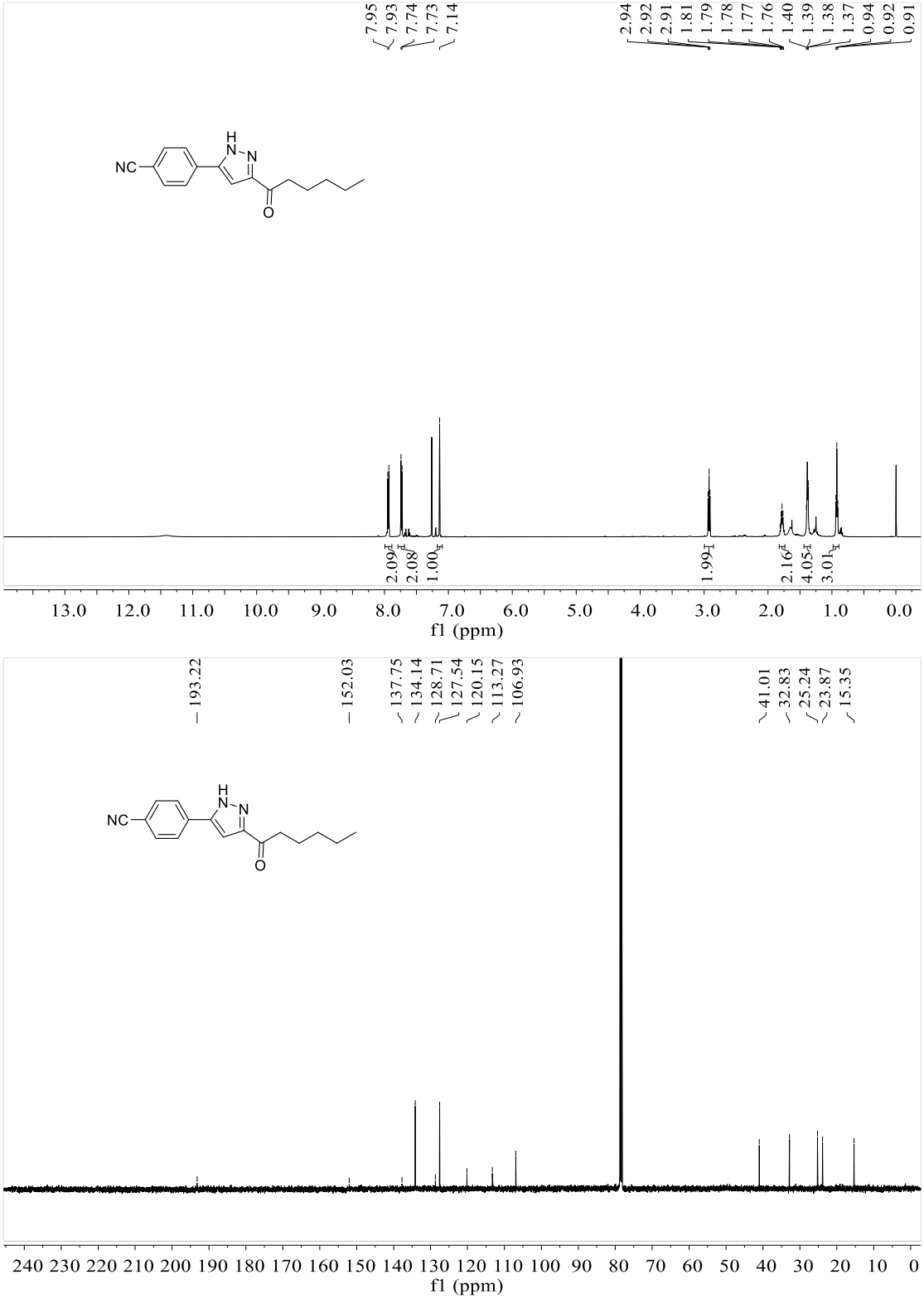
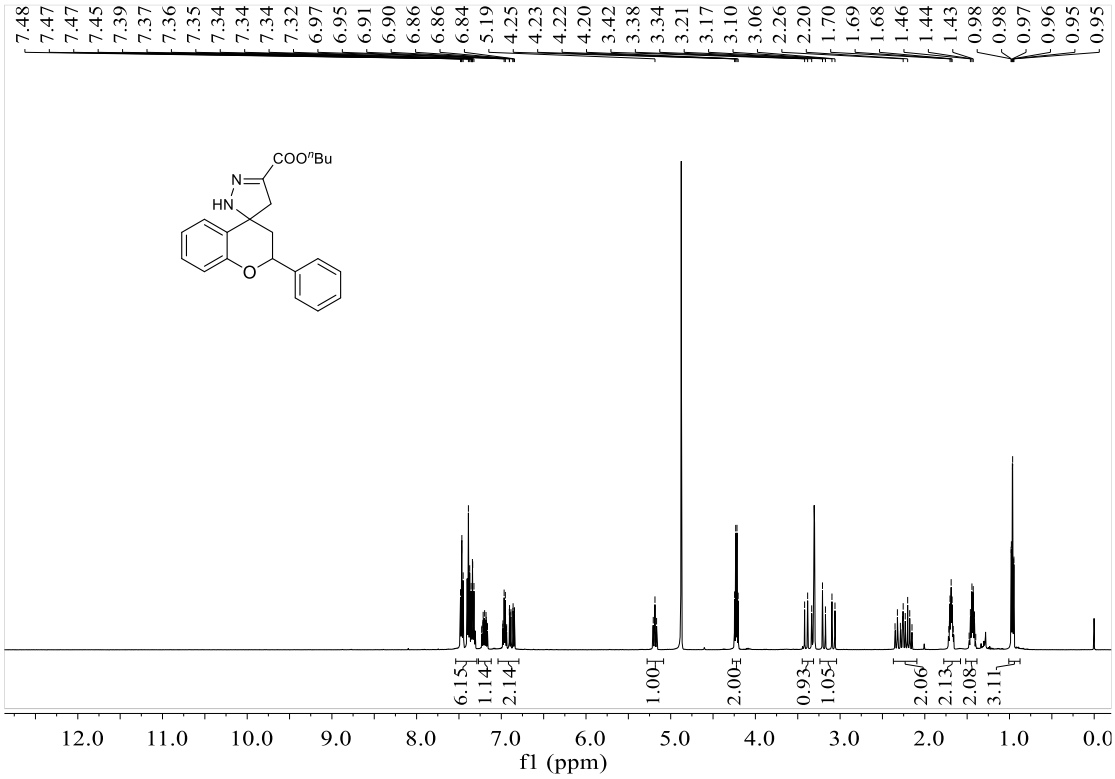


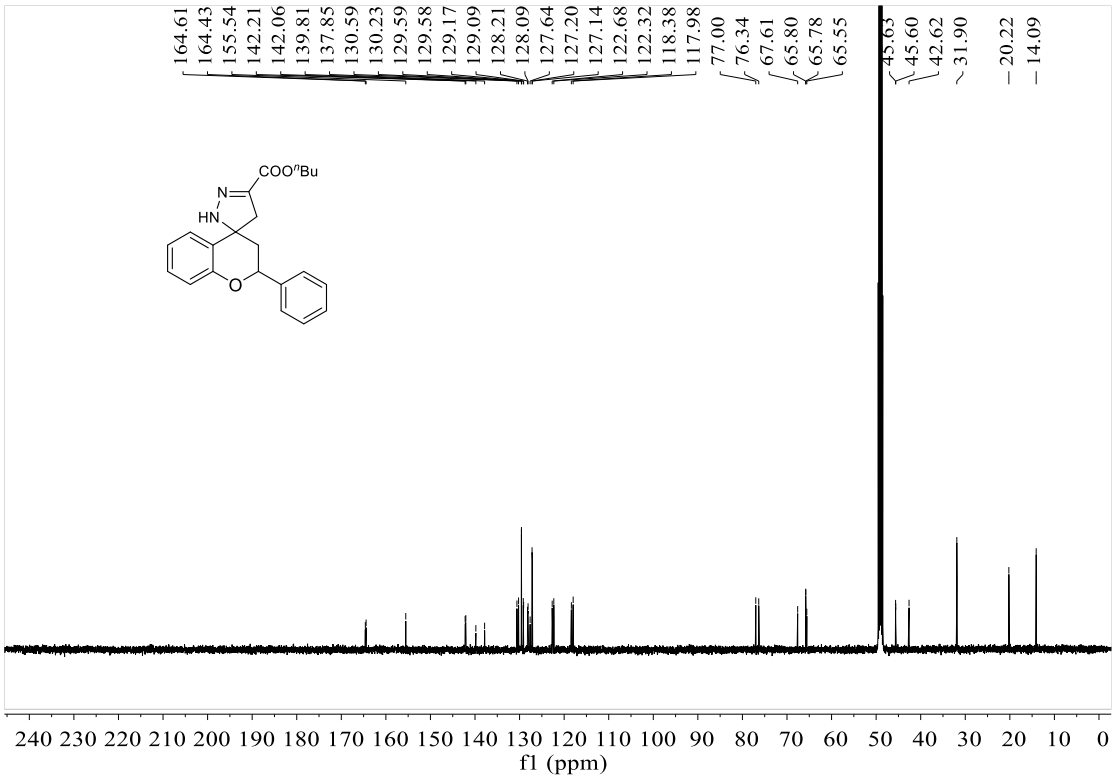


^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (126 MHz, $CDCl_3$) spectra for 86d:

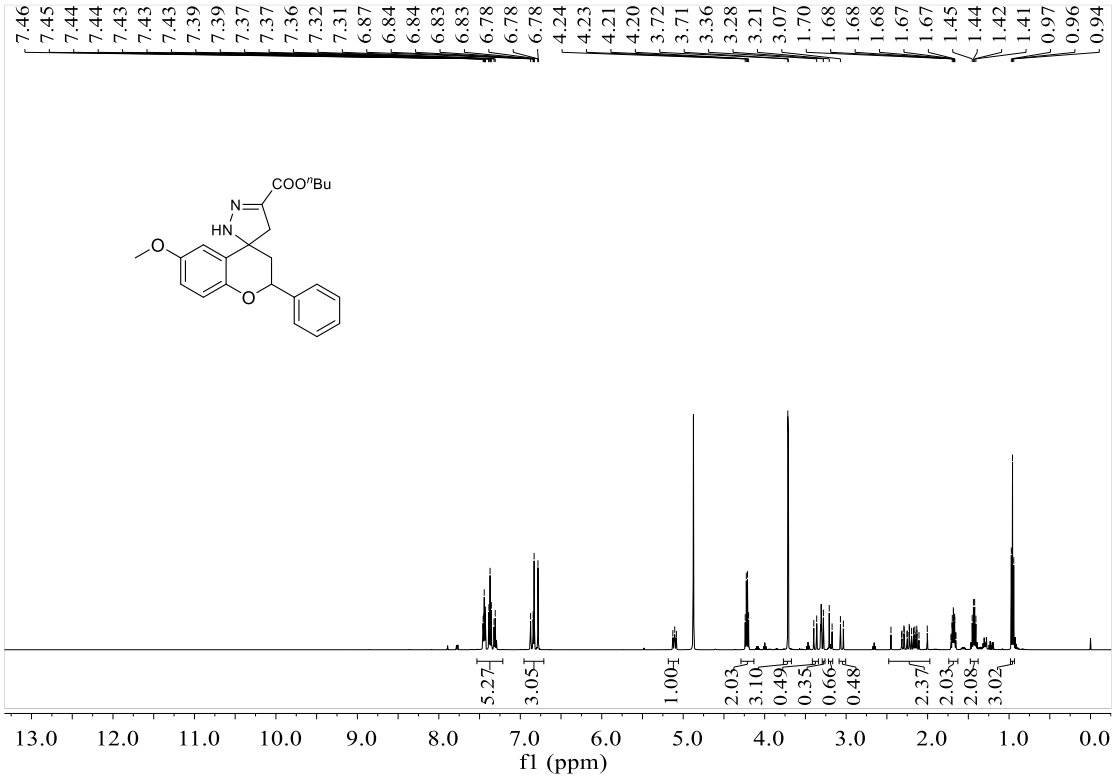


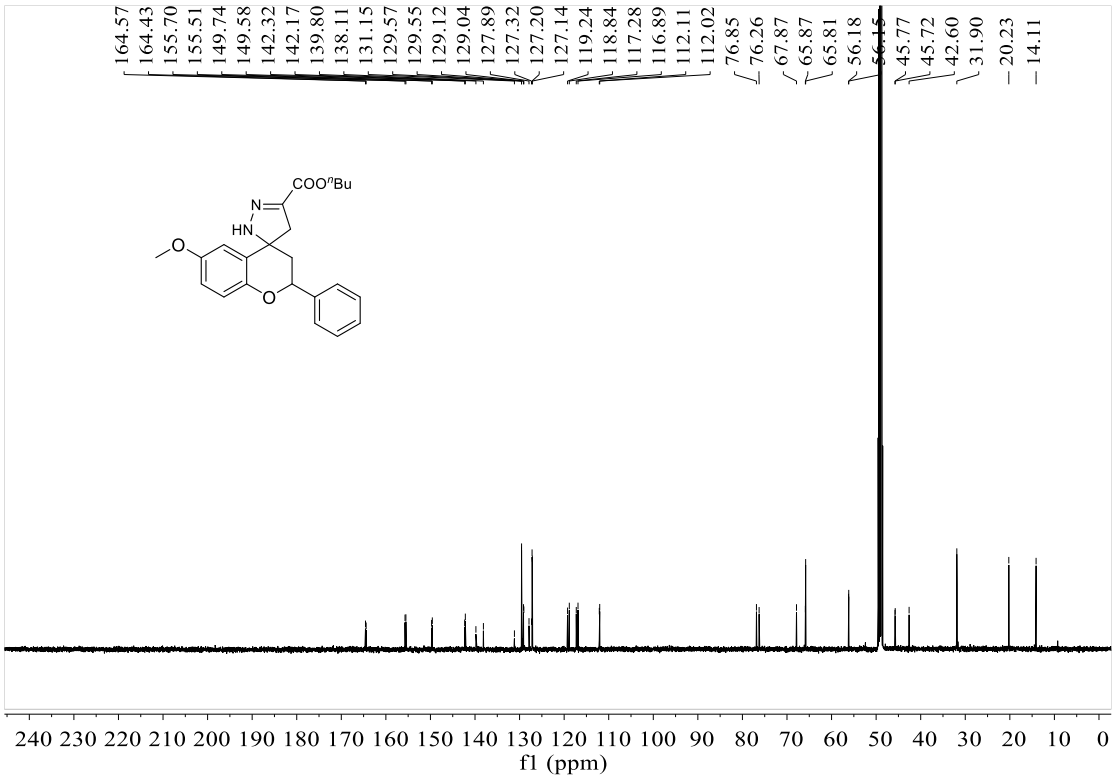
^{1}H NMR (500 MHz, CD_3OD) and ^{13}C NMR (126 MHz, CD_3OD) spectra for 87d:



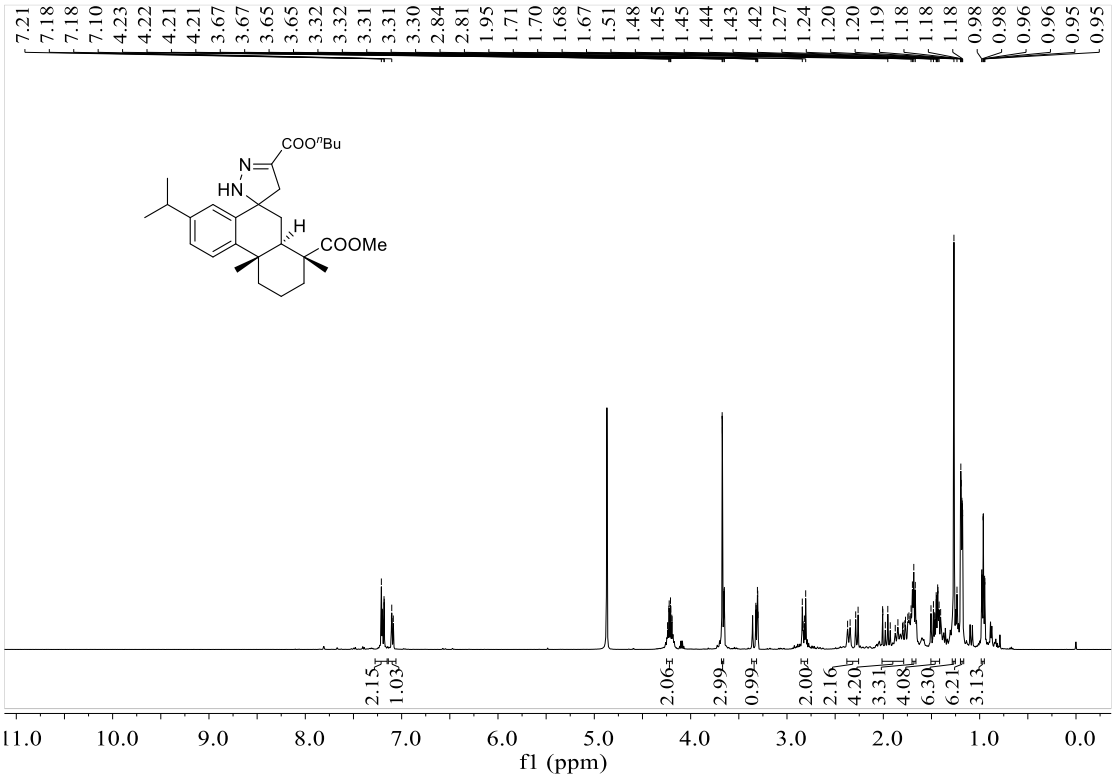


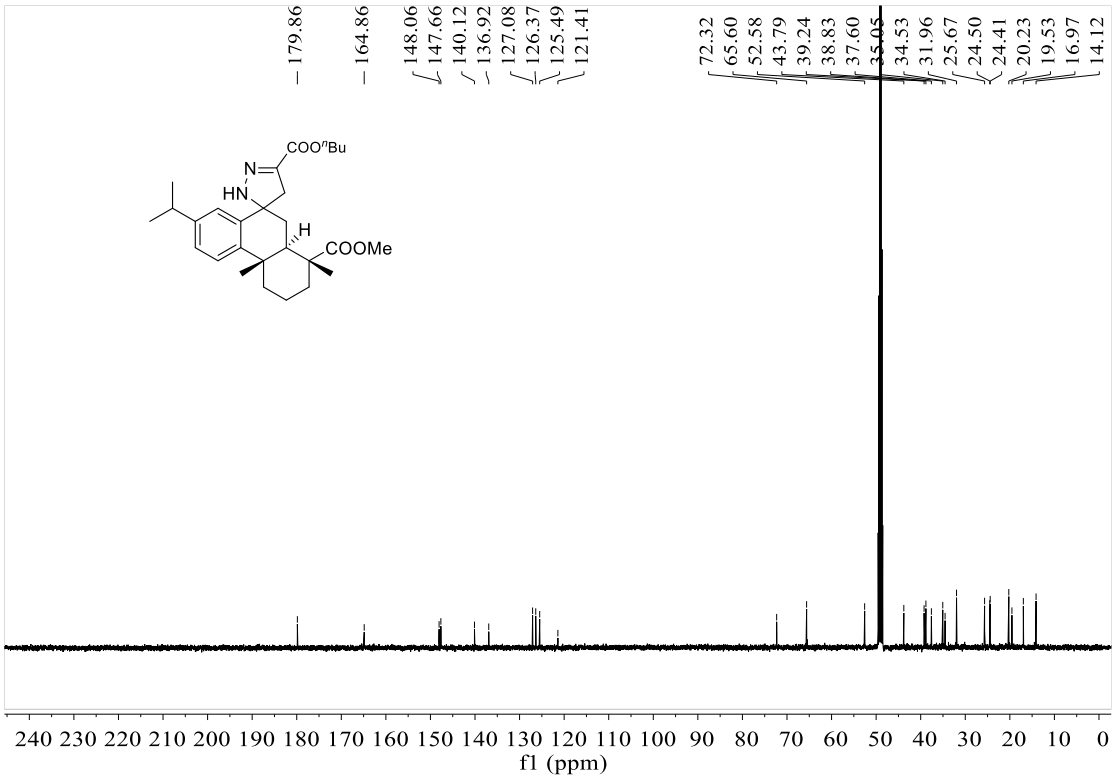
^{1}H NMR (500 MHz, CD_3OD) and ^{13}C NMR (126 MHz, CD_3OD) spectra for 88d:



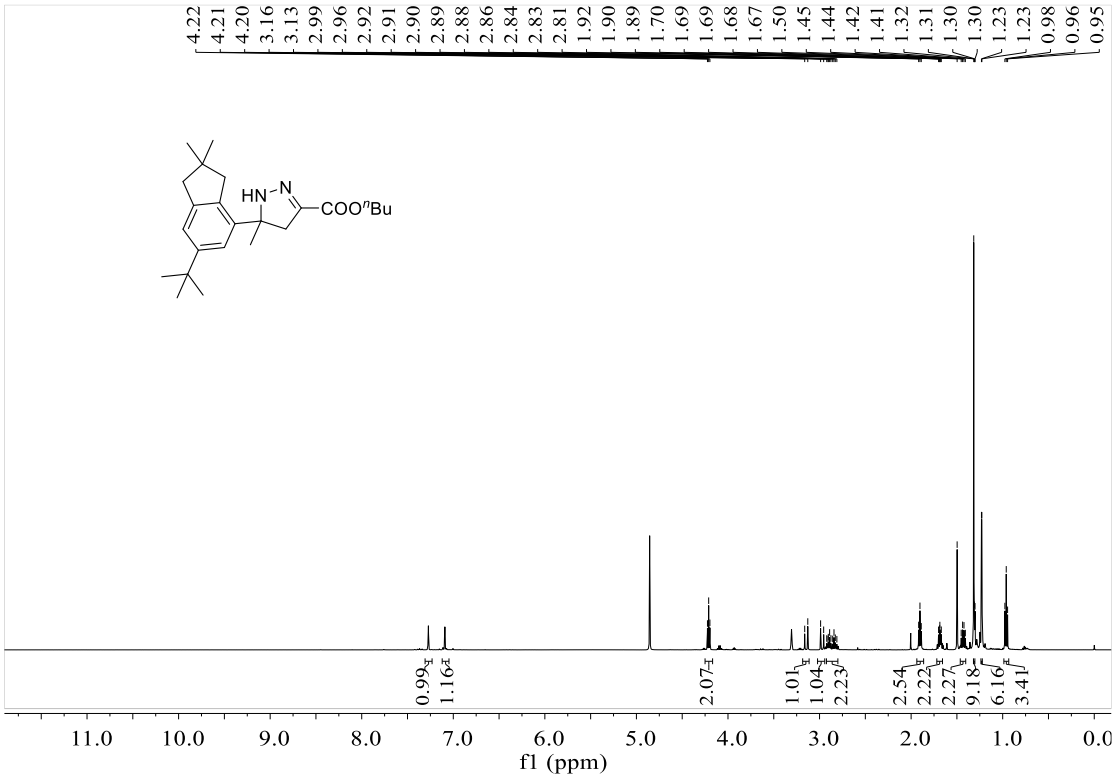


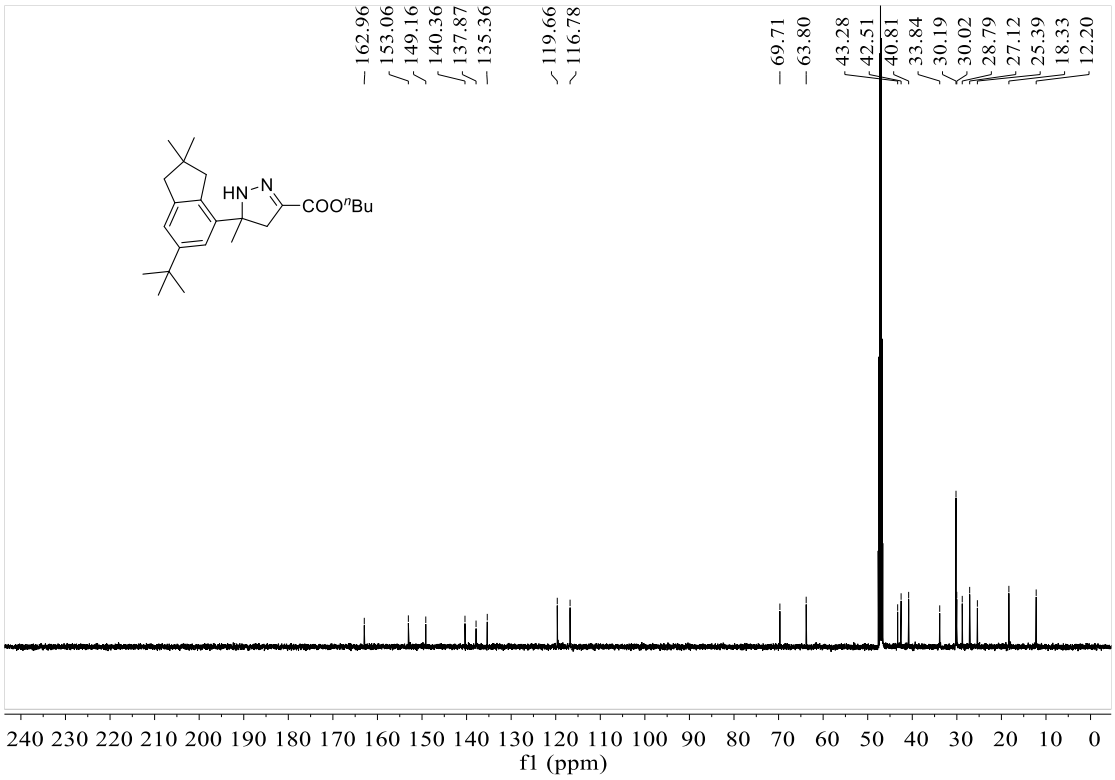
^{1}H NMR (500 MHz, CD_3OD) and ^{13}C NMR (126 MHz, CD_3OD) spectra for 89d:



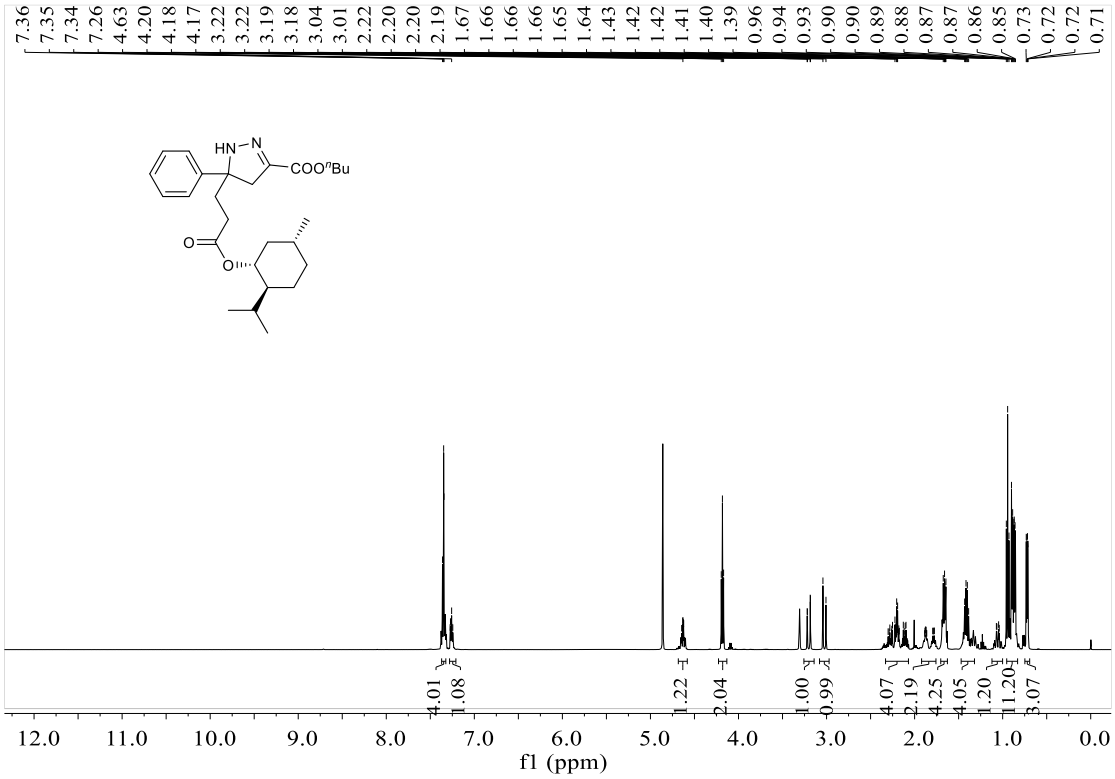


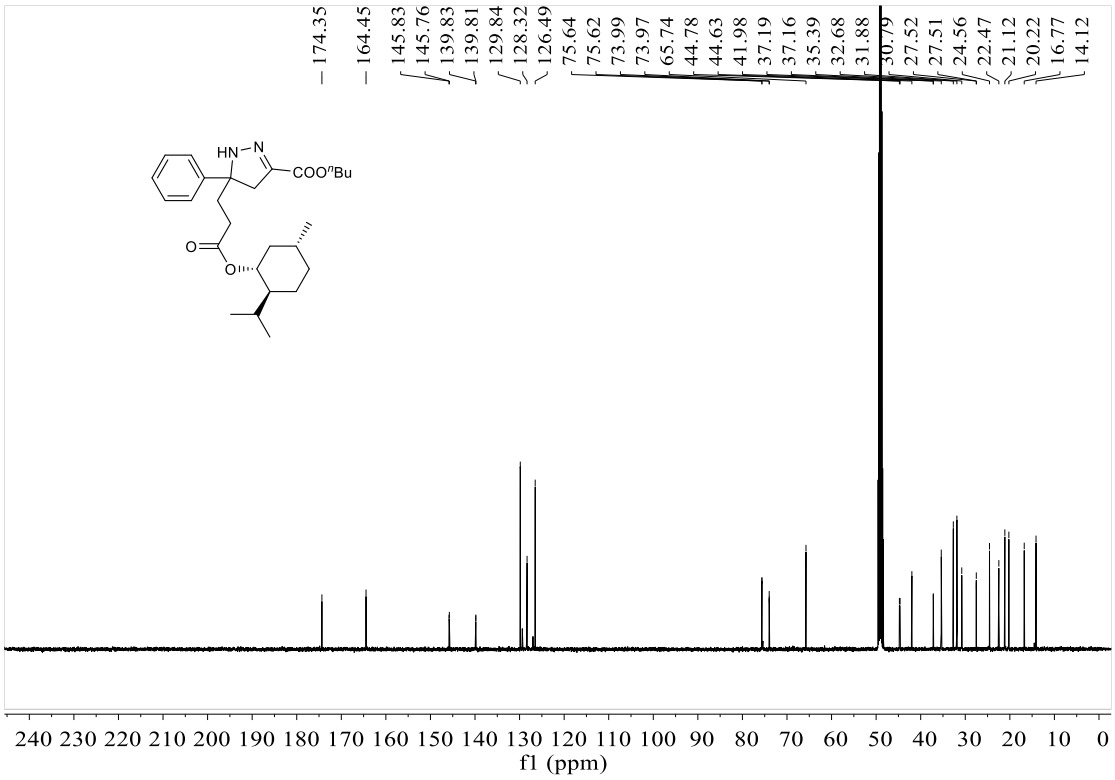
^{1}H NMR (500 MHz, CD_3OD) and ^{13}C NMR (126 MHz, CD_3OD) spectra for 90d:



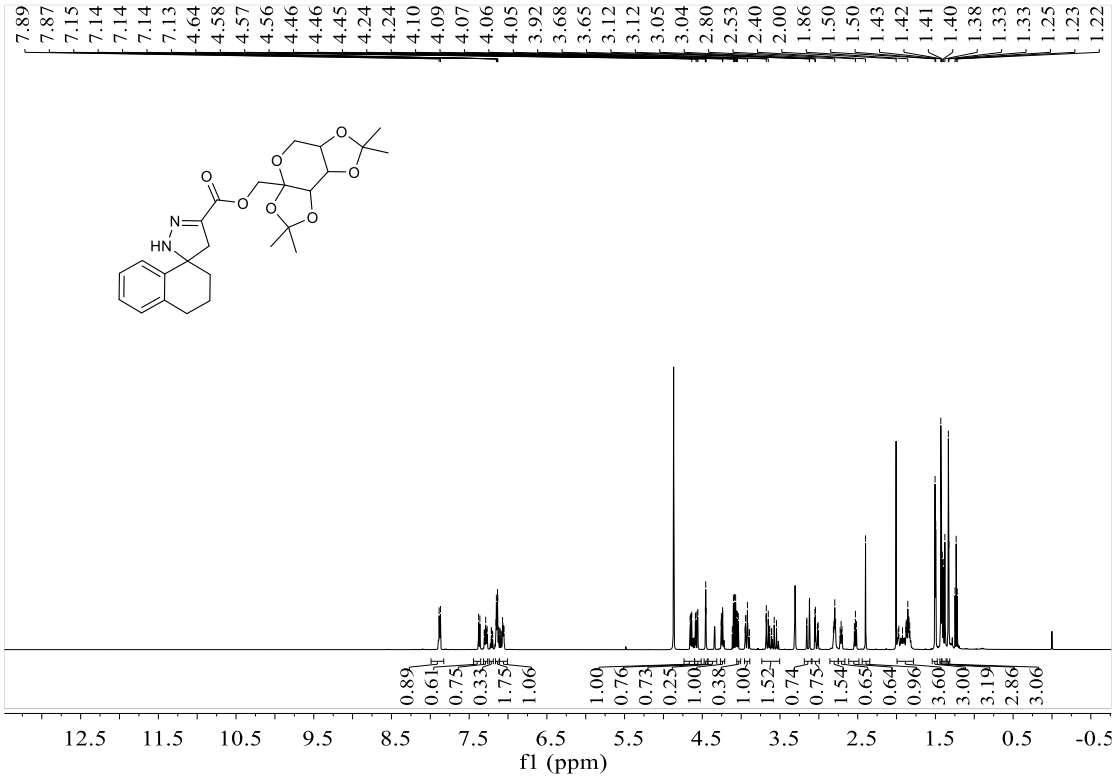


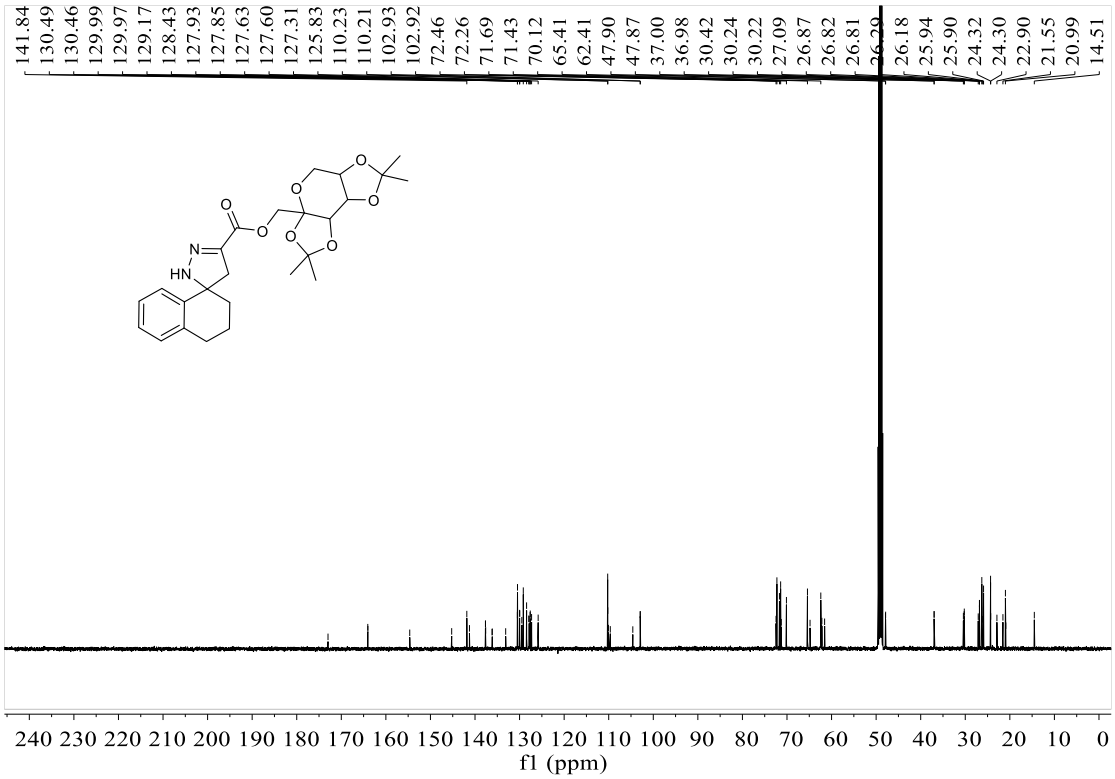
^{1}H NMR (500 MHz, CD_3OD) and ^{13}C NMR (126 MHz, CD_3OD) spectra for 91d:



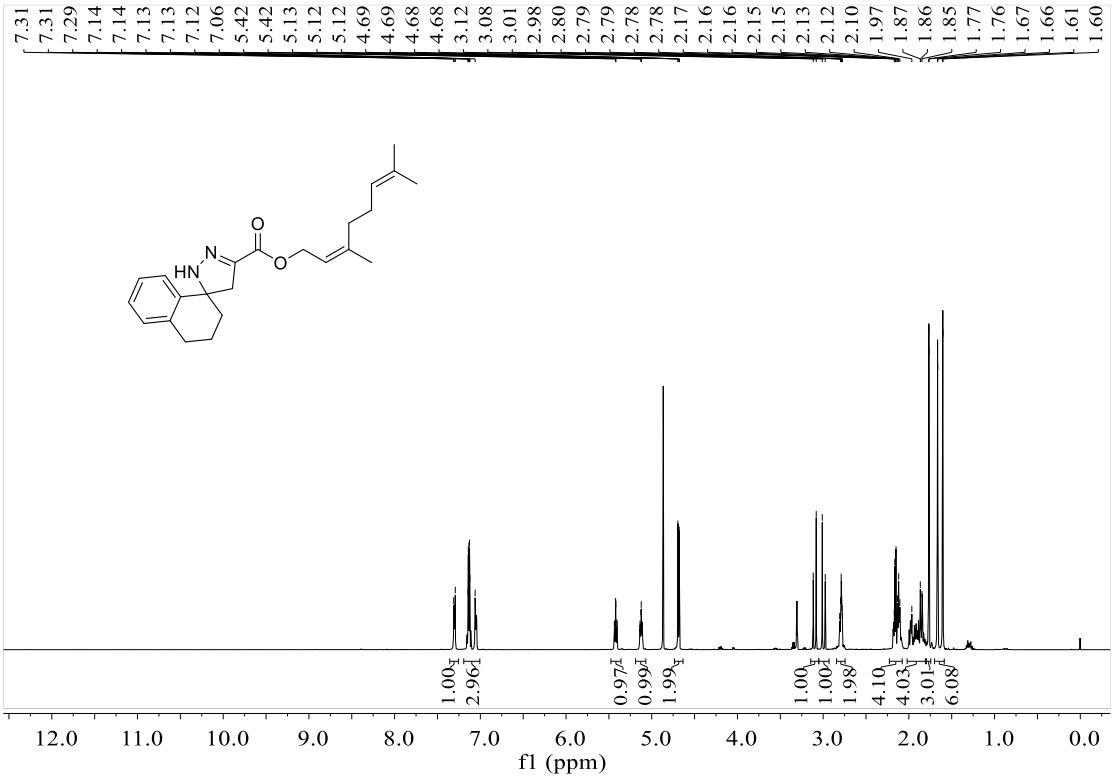


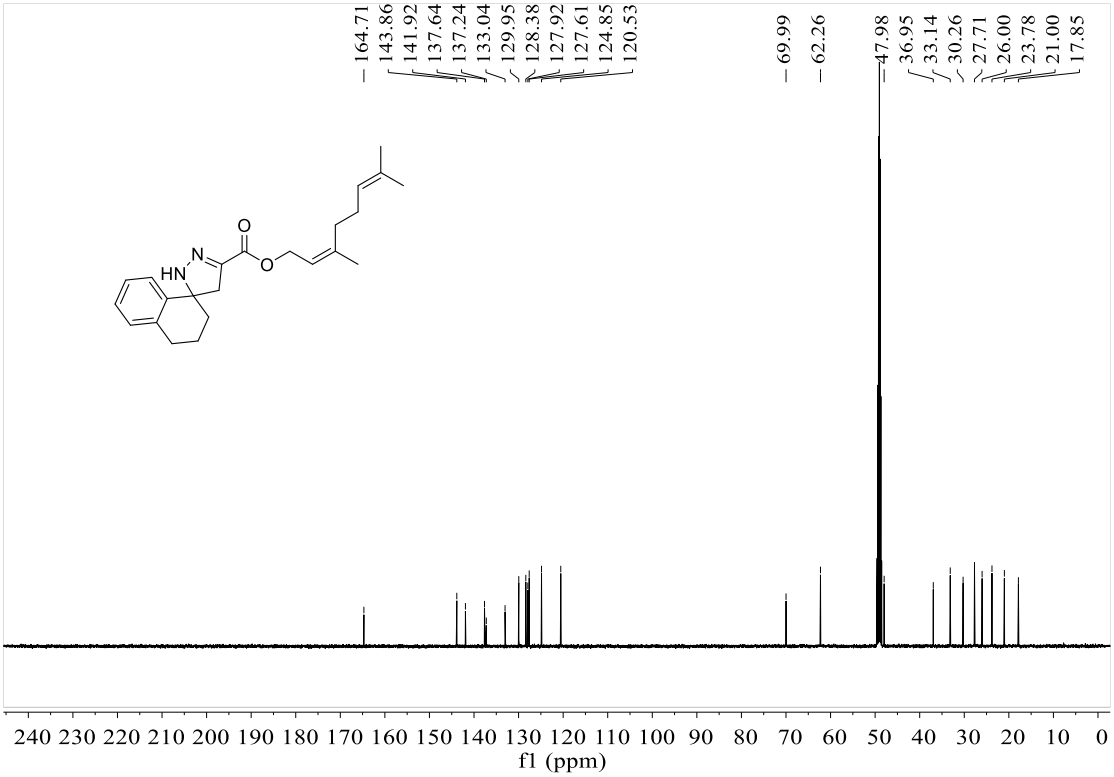
^{1}H NMR (500 MHz, CD_3OD) and ^{13}C NMR (126 MHz, CD_3OD) spectra for 92d:





^{1}H NMR (500 MHz, CD_3OD) and ^{13}C NMR (126 MHz, CD_3OD) spectra for 93d:





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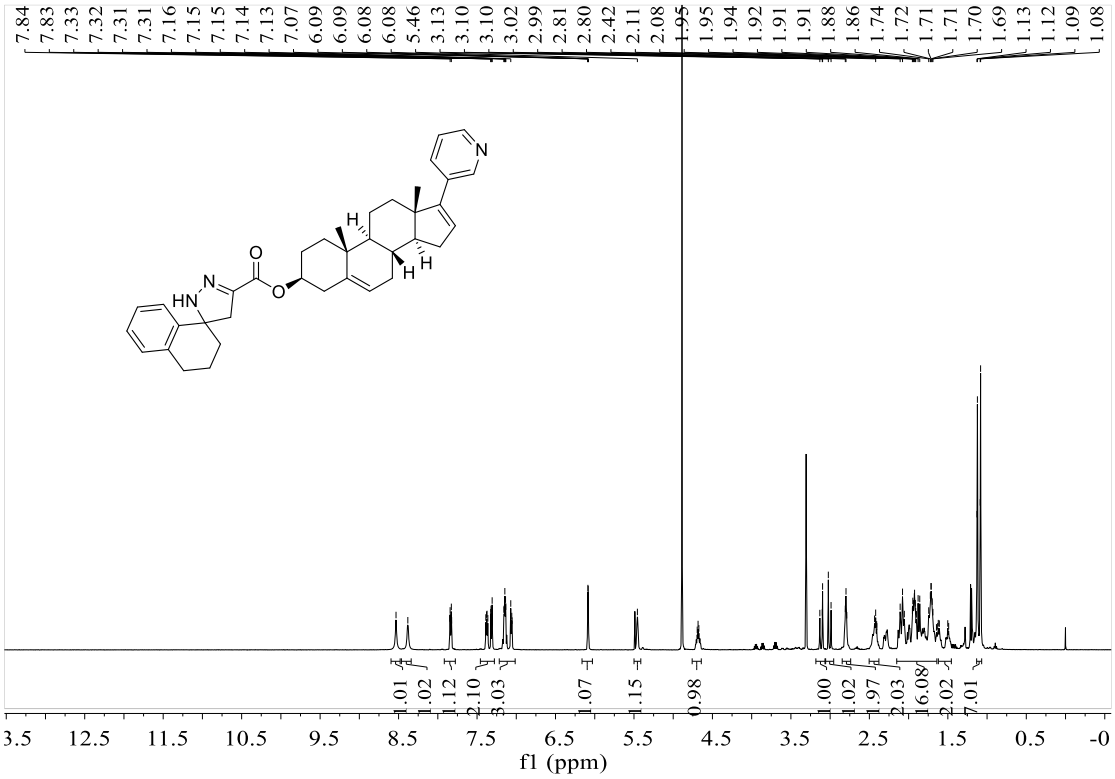
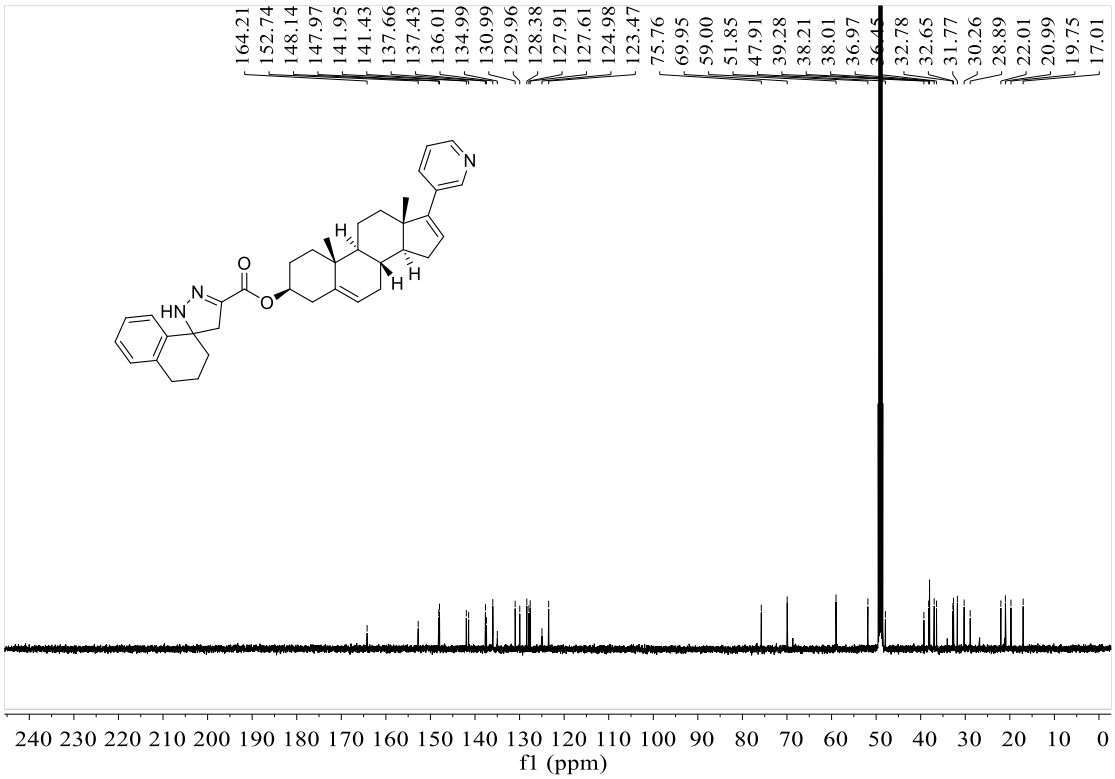
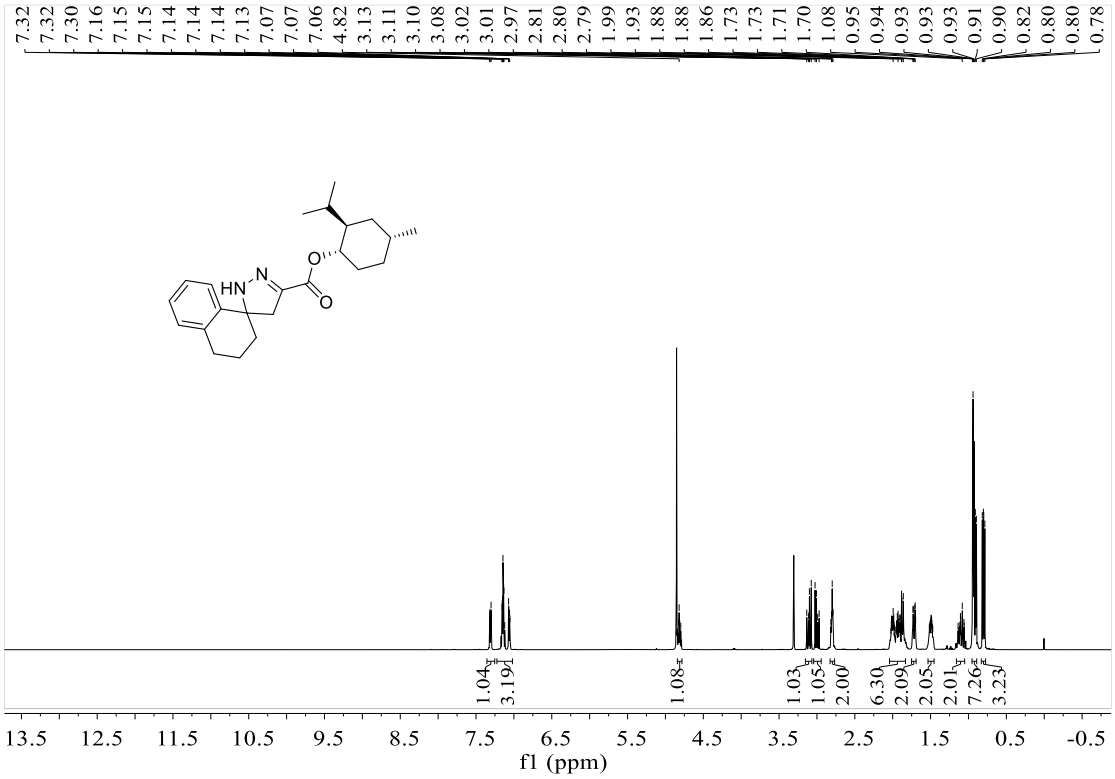
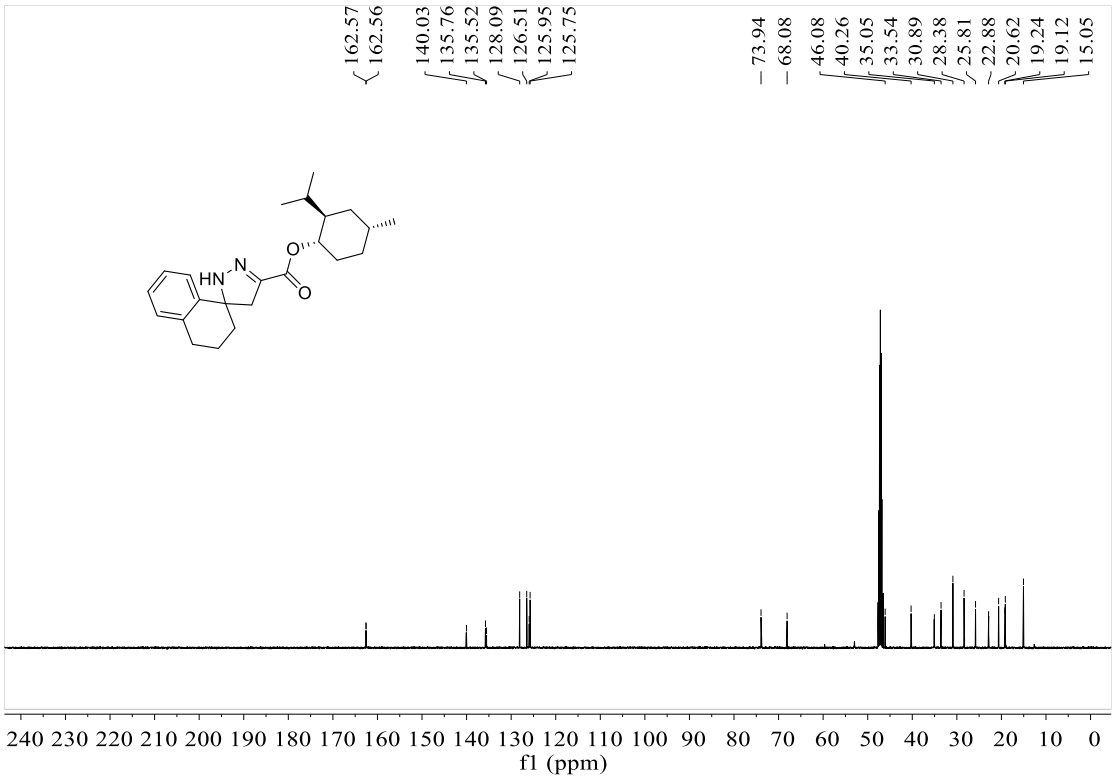


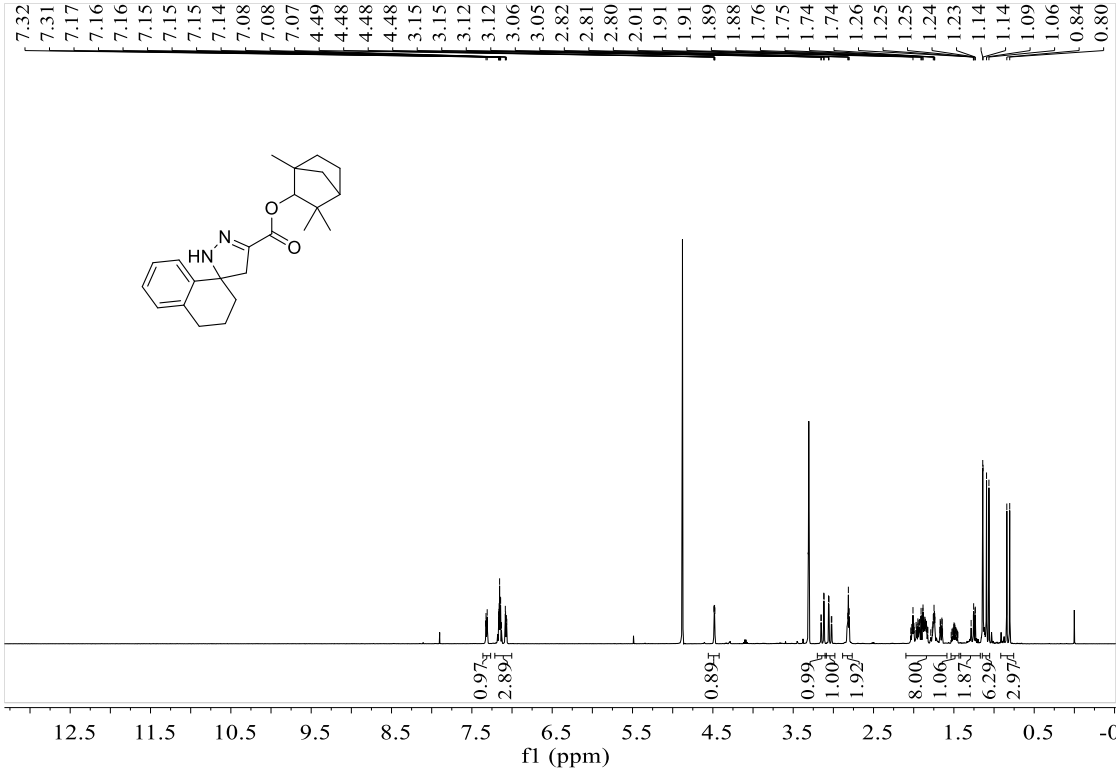


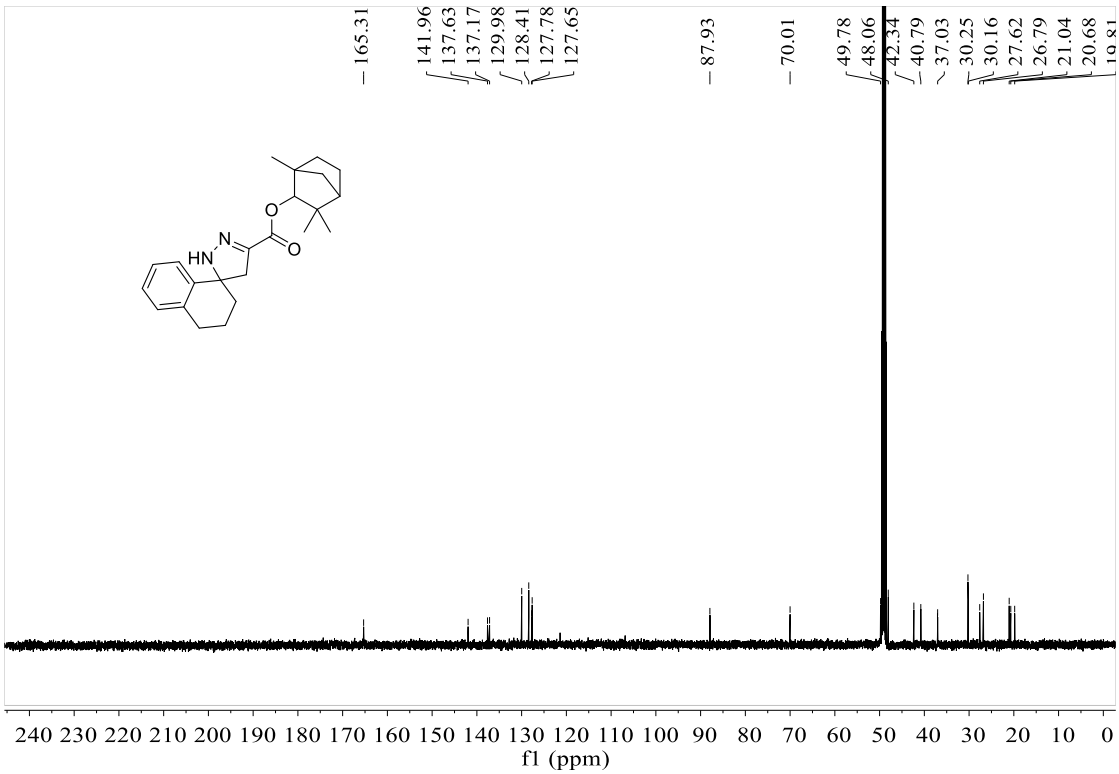
^{1}H NMR (500 MHz, CD_3OD) and ^{13}C NMR (126 MHz, CD_3OD) spectra for 95d:



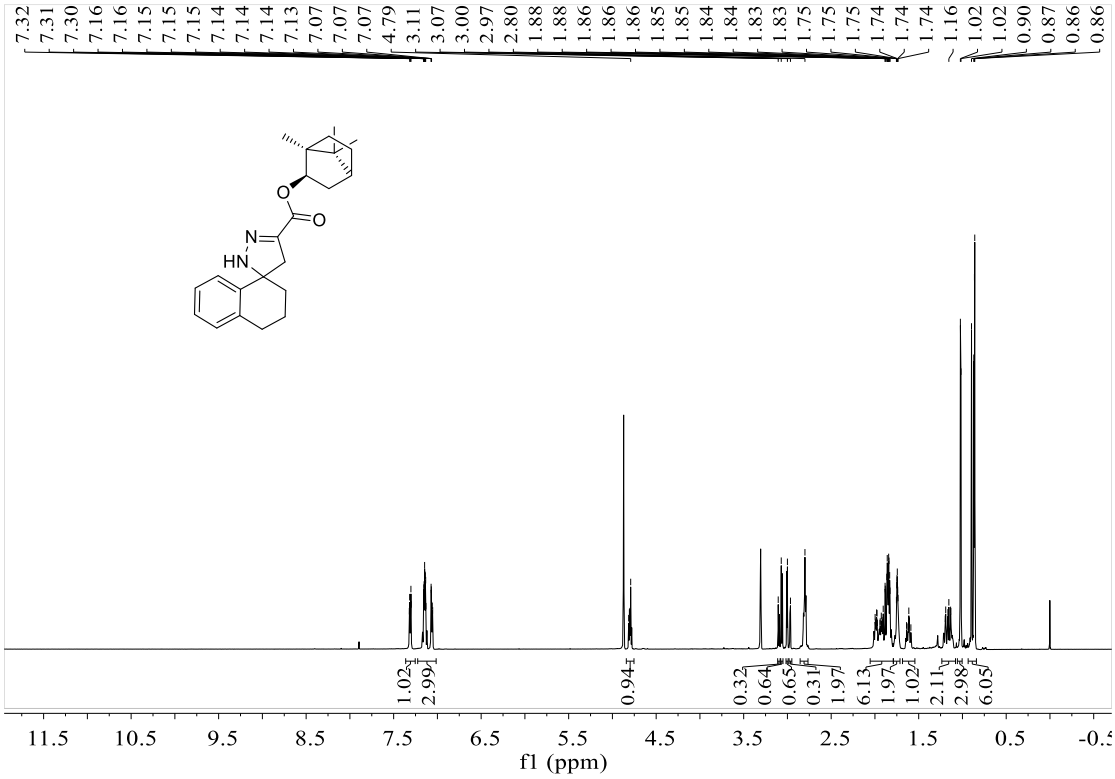


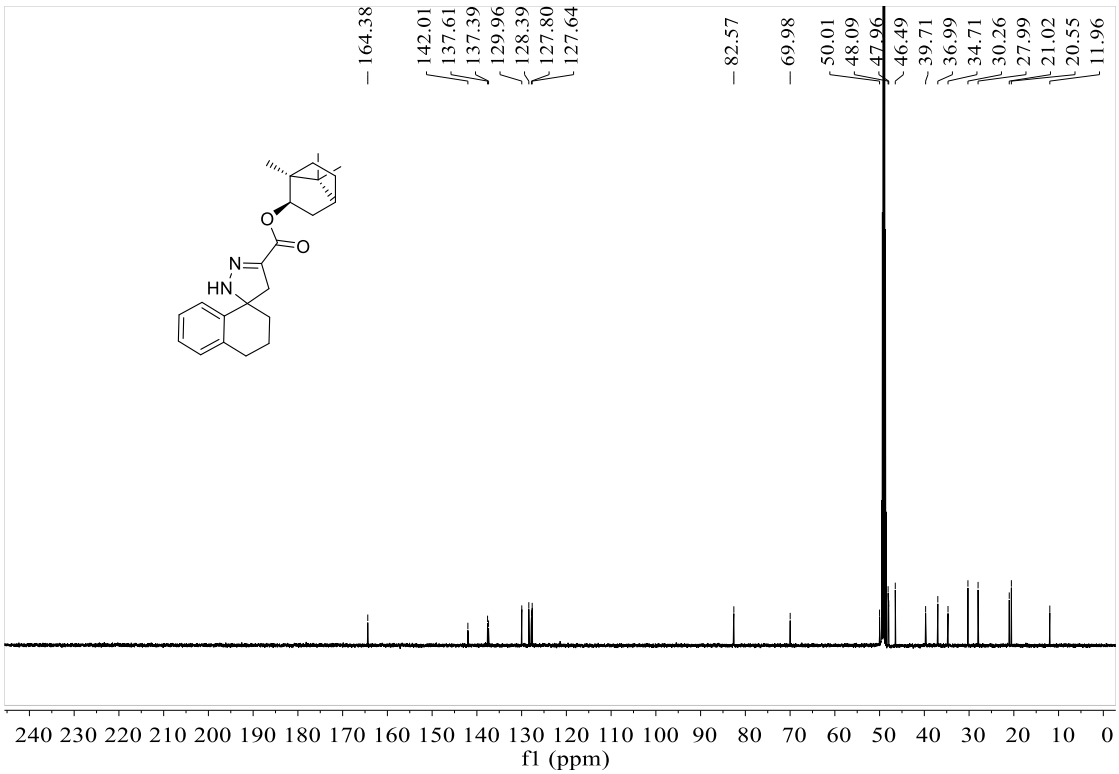
^{1}H NMR (500 MHz, CD_3OD) and ^{13}C NMR (126 MHz, CD_3OD) spectra for 96d:



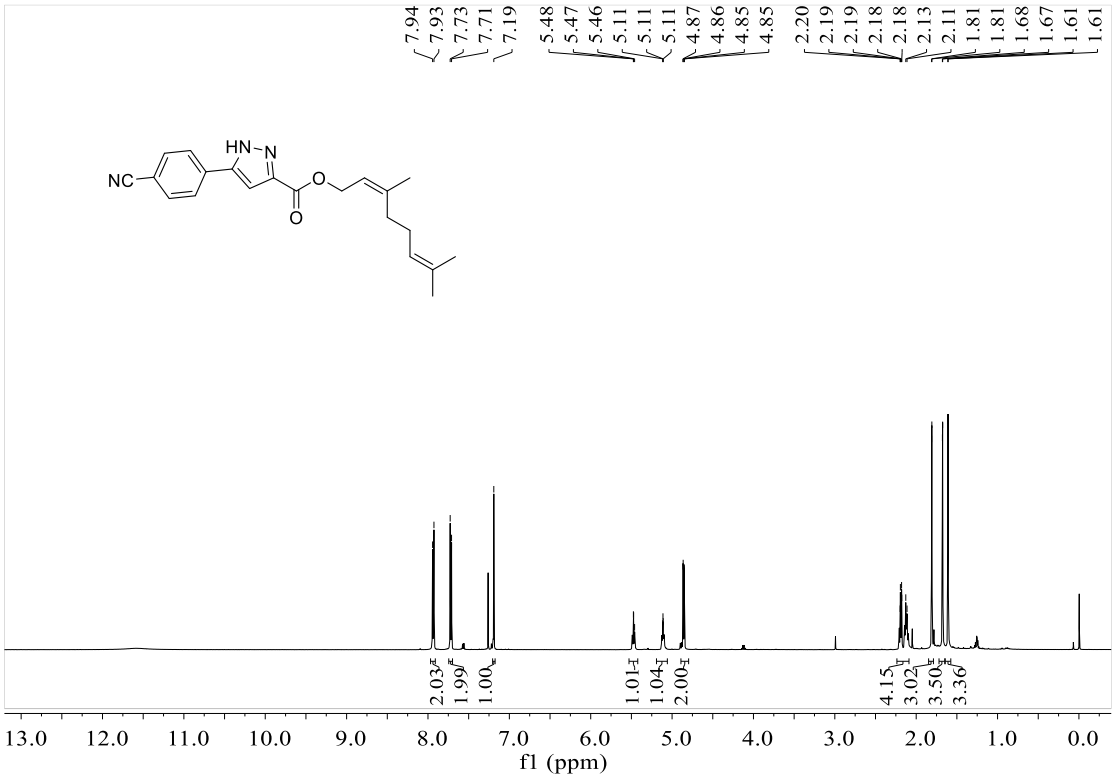


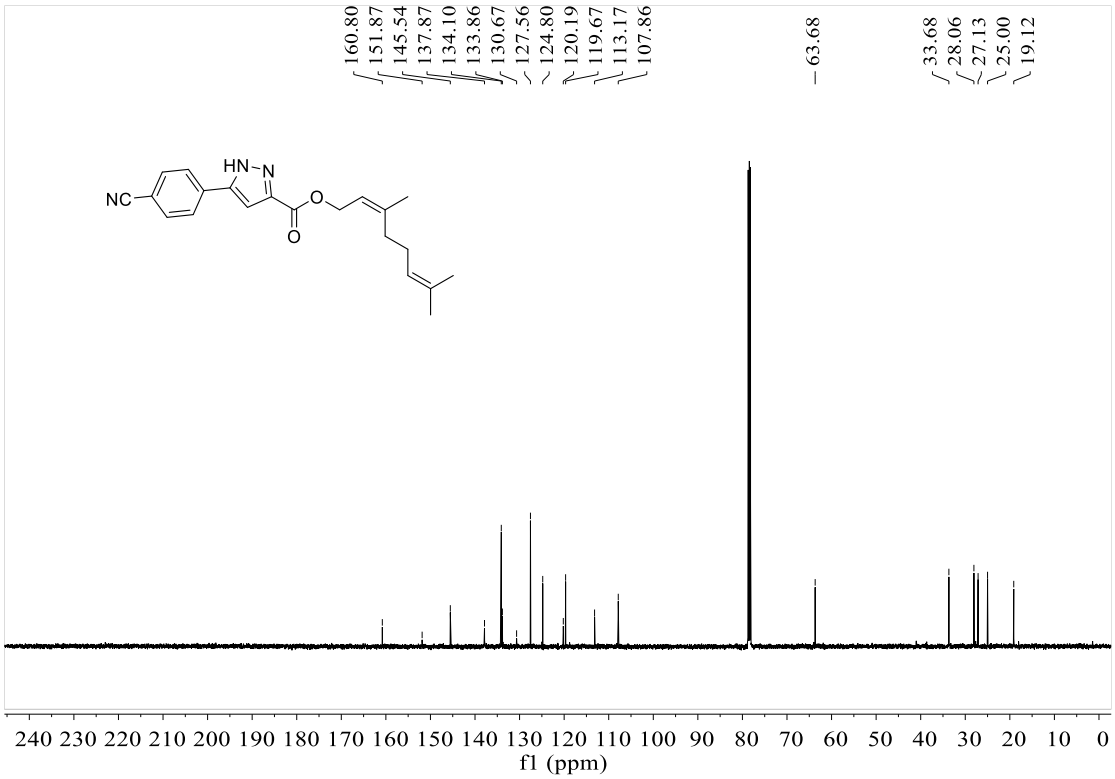
^{1}H NMR (500 MHz, CD_3OD) and ^{13}C NMR (126 MHz, CD_3OD) spectra for 97d:



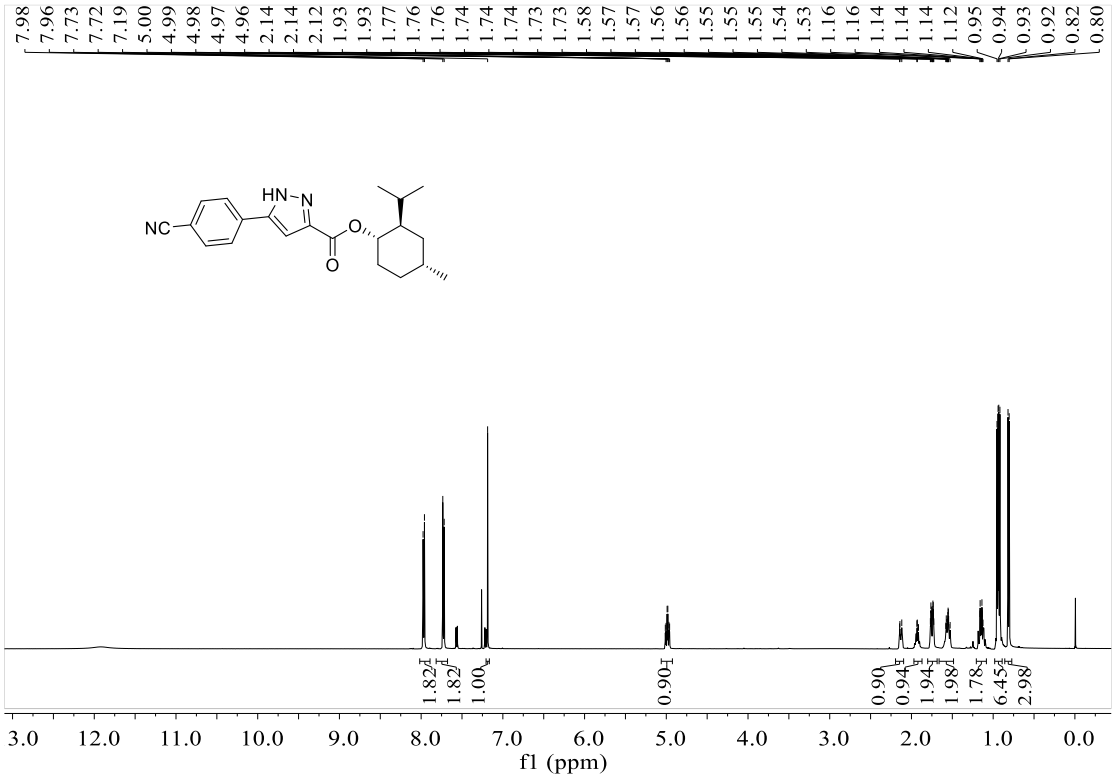


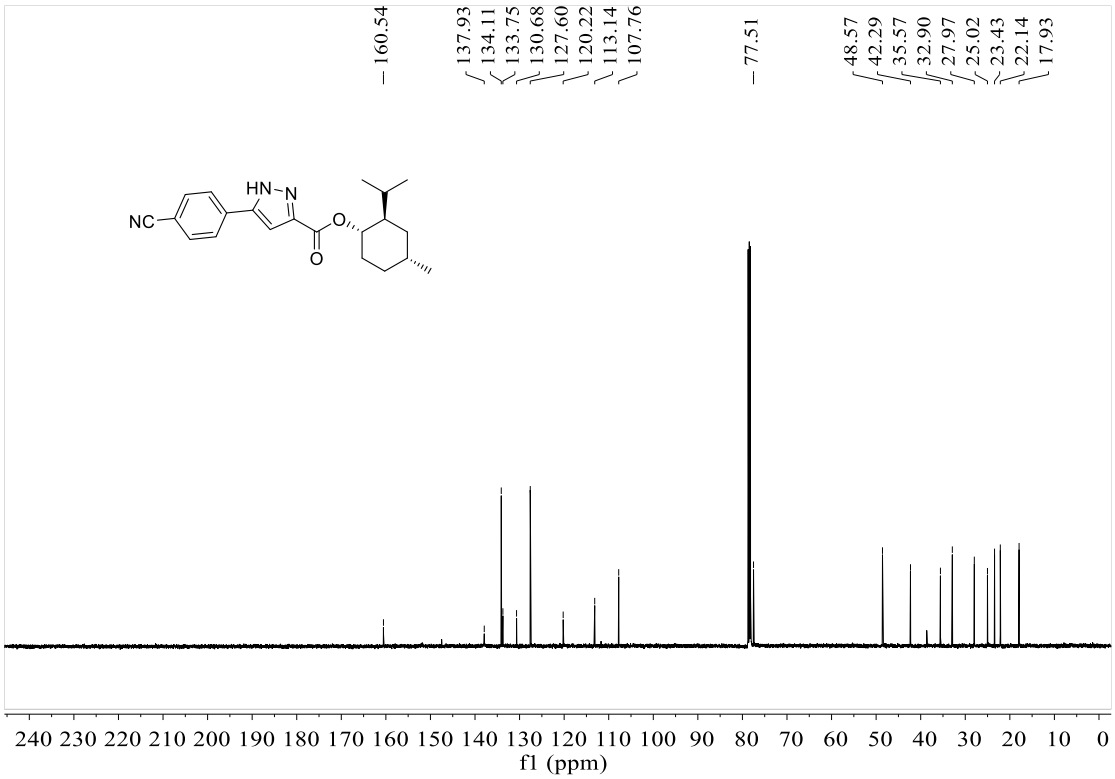
^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (126 MHz, $CDCl_3$) spectra for 98d:



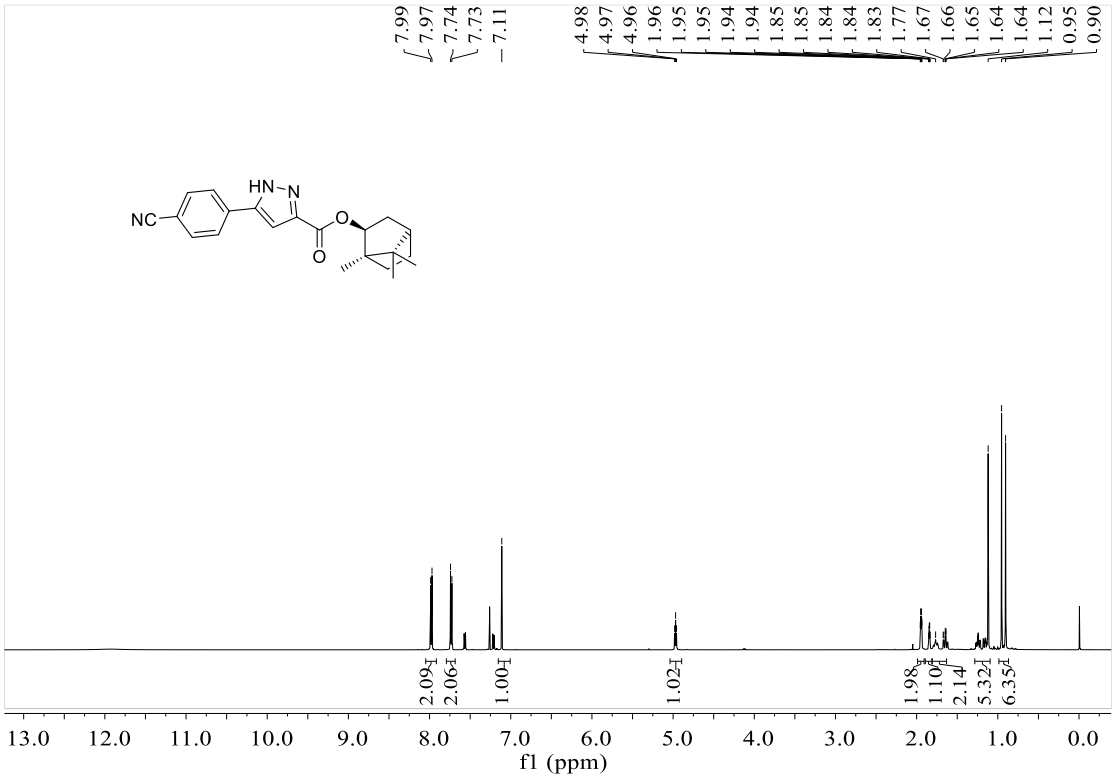


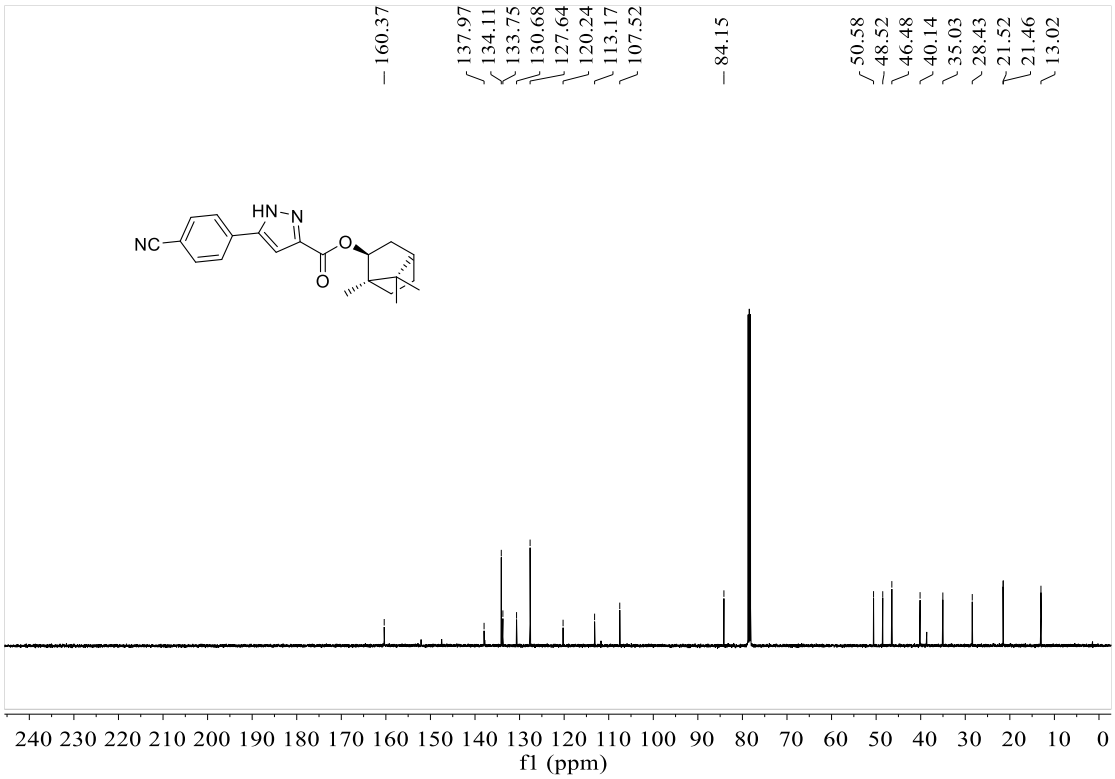
^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (126 MHz, $CDCl_3$) spectra for 99d:





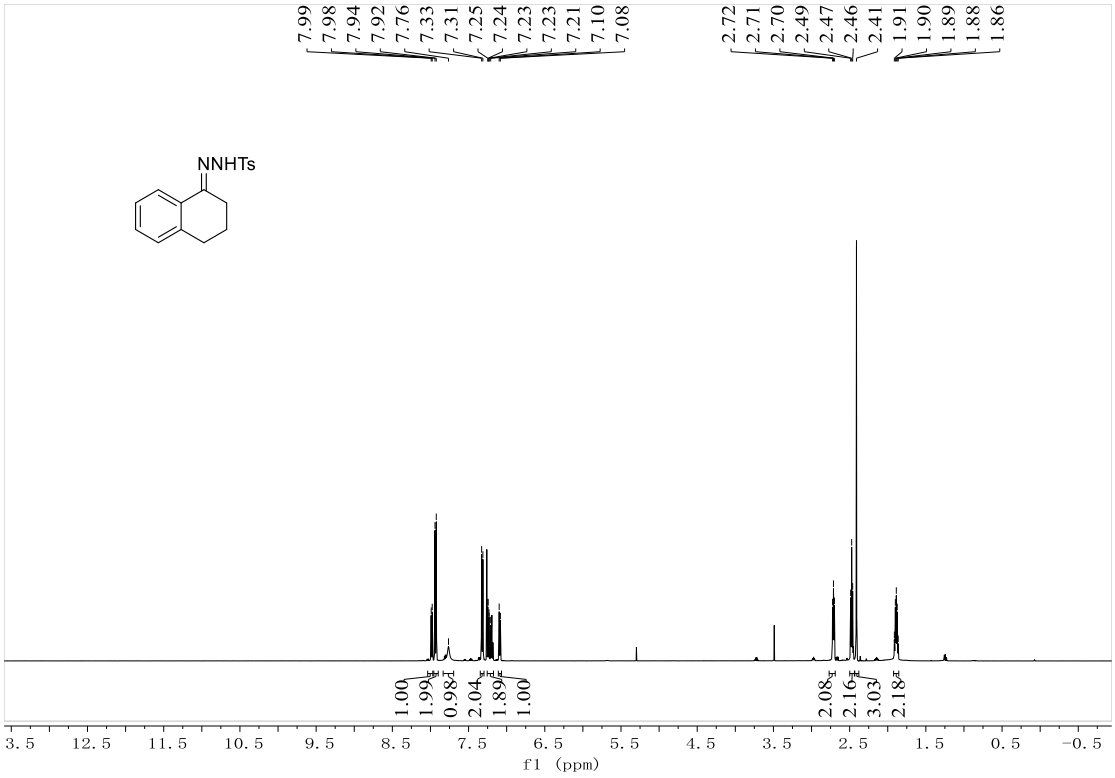
^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (126 MHz, $CDCl_3$) spectra for 100d:

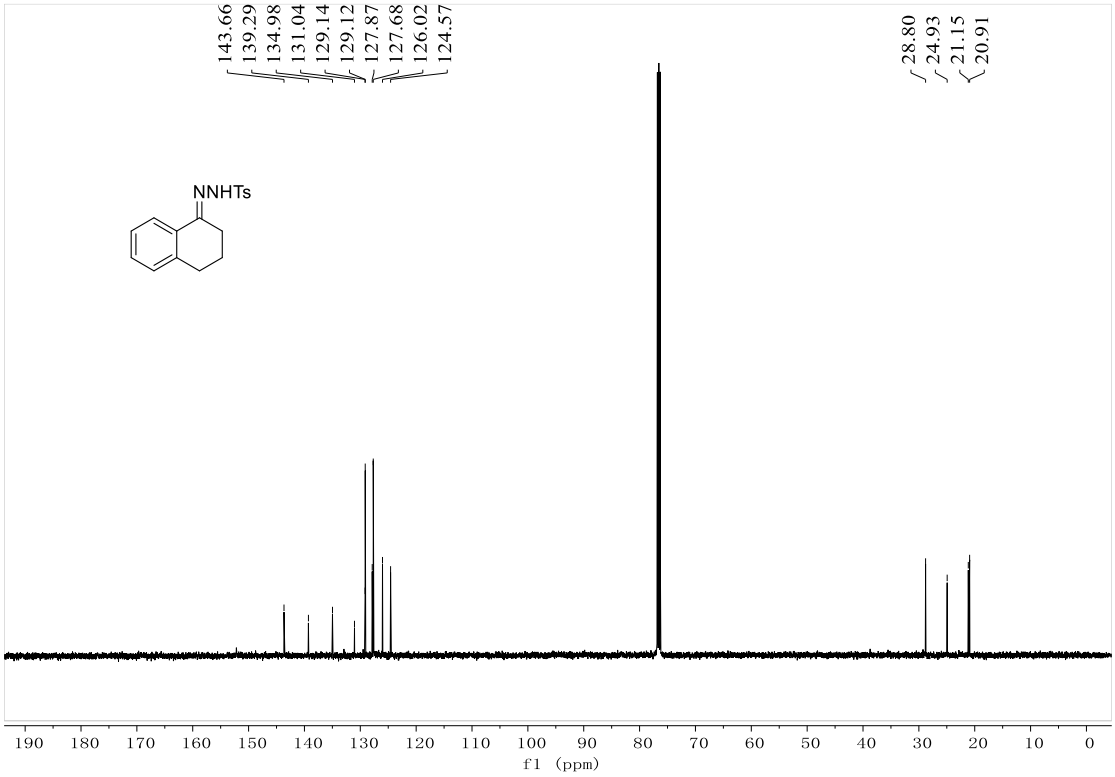




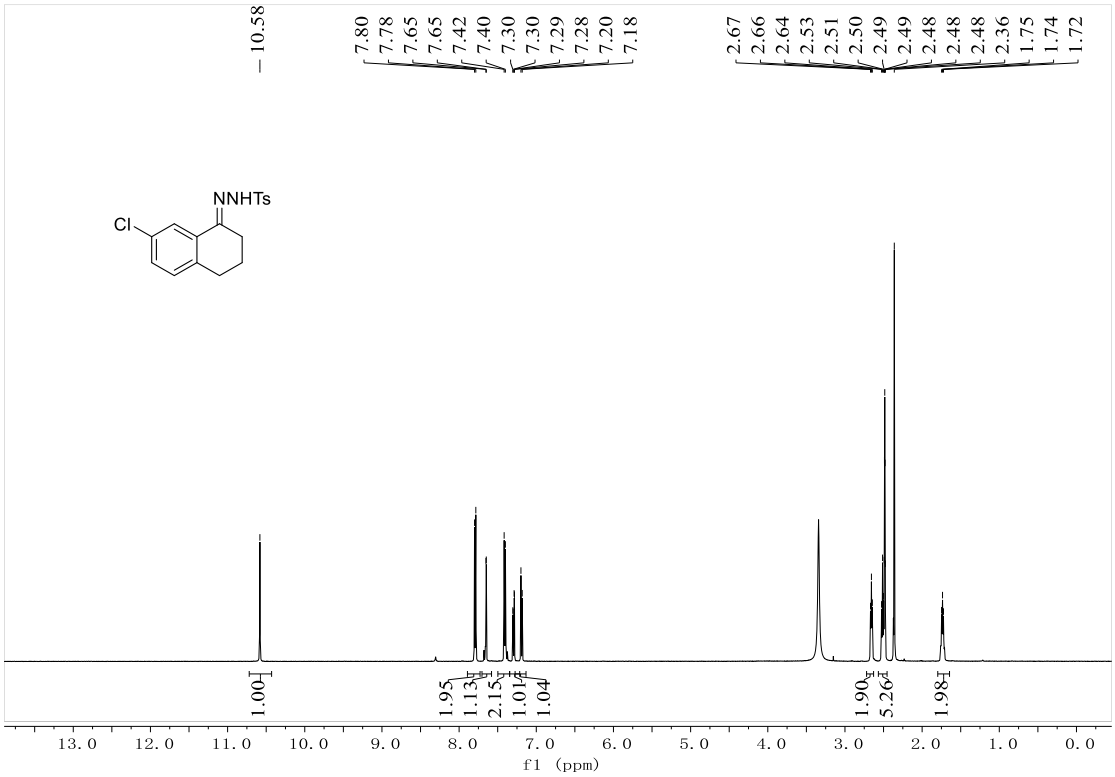
Characterization data for the *N*-tosylhydrazones

^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (126 MHz, $CDCl_3$) spectra for 1b:

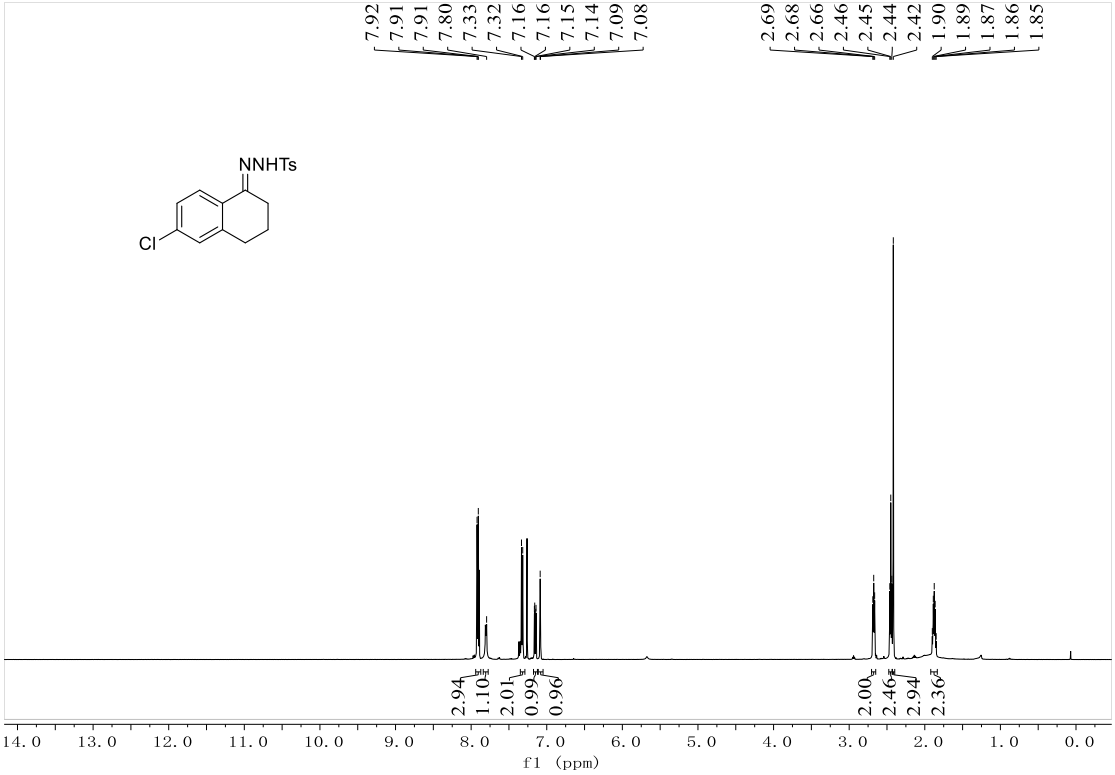


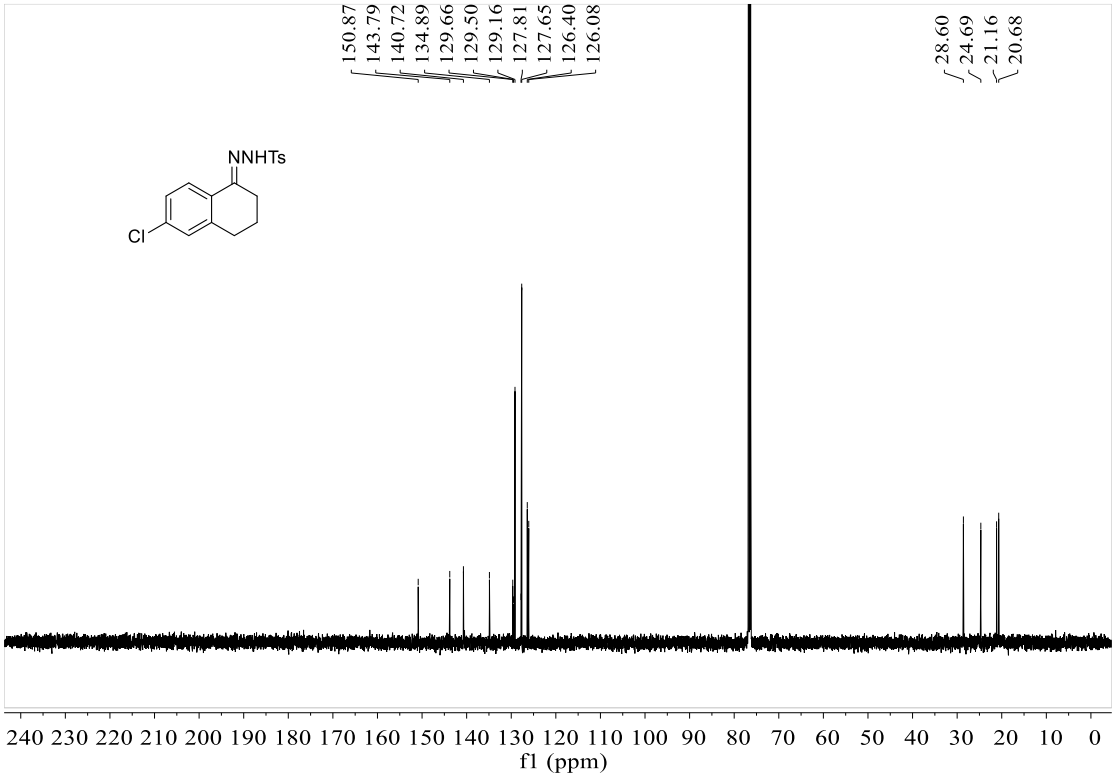


^{1}H NMR (500 MHz, DMSO-d_6) spectra for 2b:

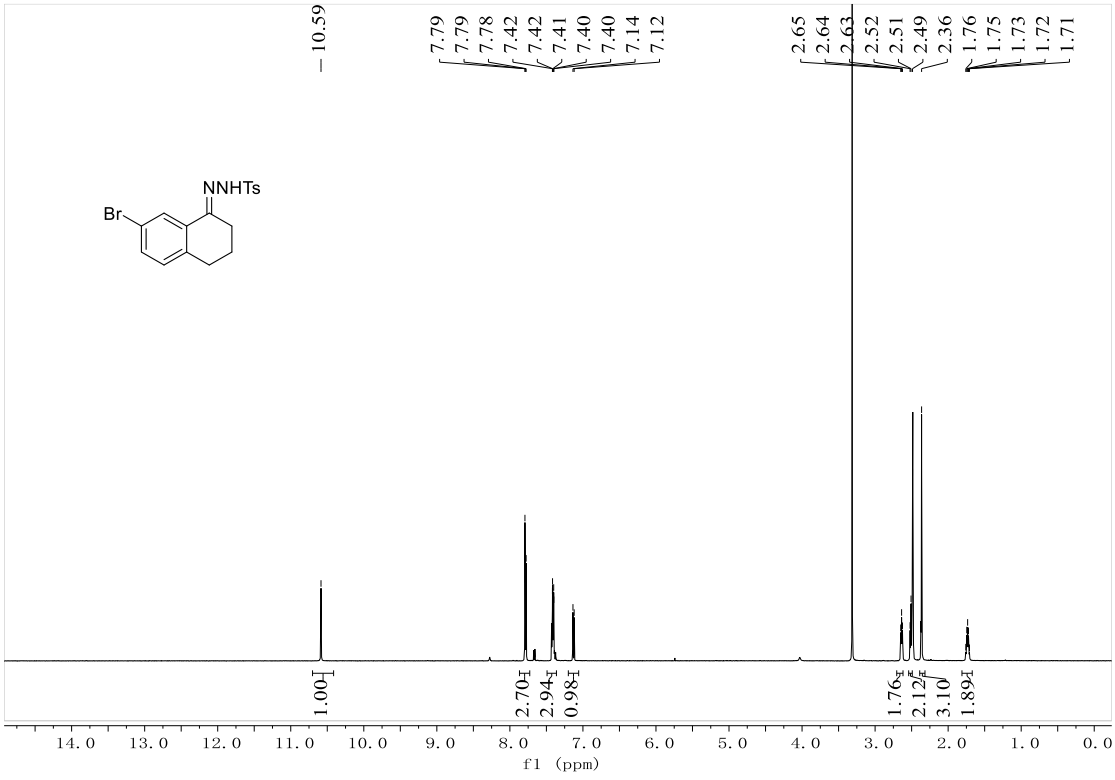


^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (126 MHz, $CDCl_3$) spectra for 3b:

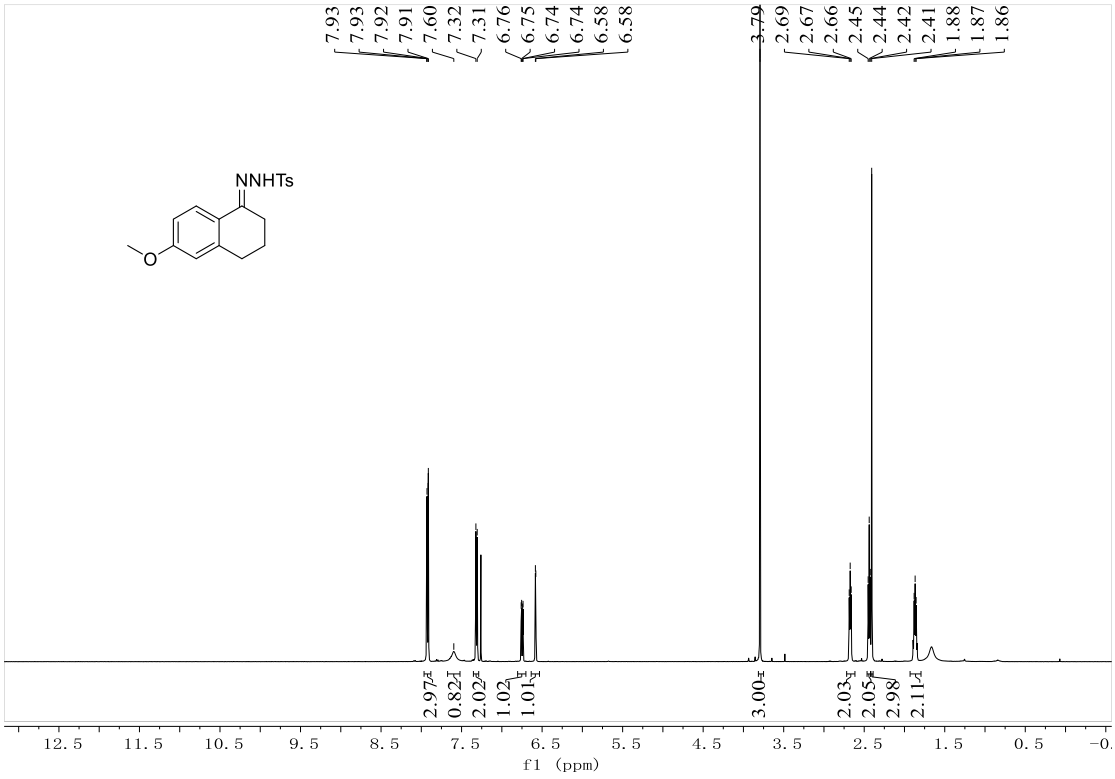




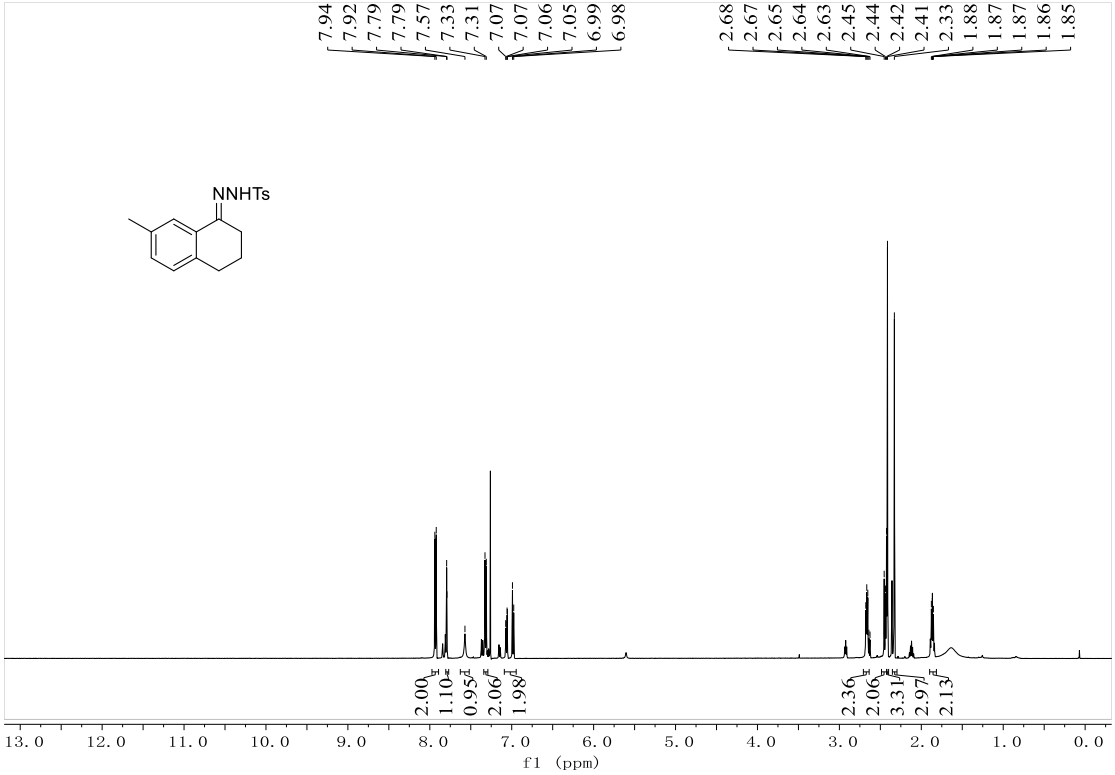
^{1}H NMR (500 MHz, DMSO-d_6) spectra for 4b:



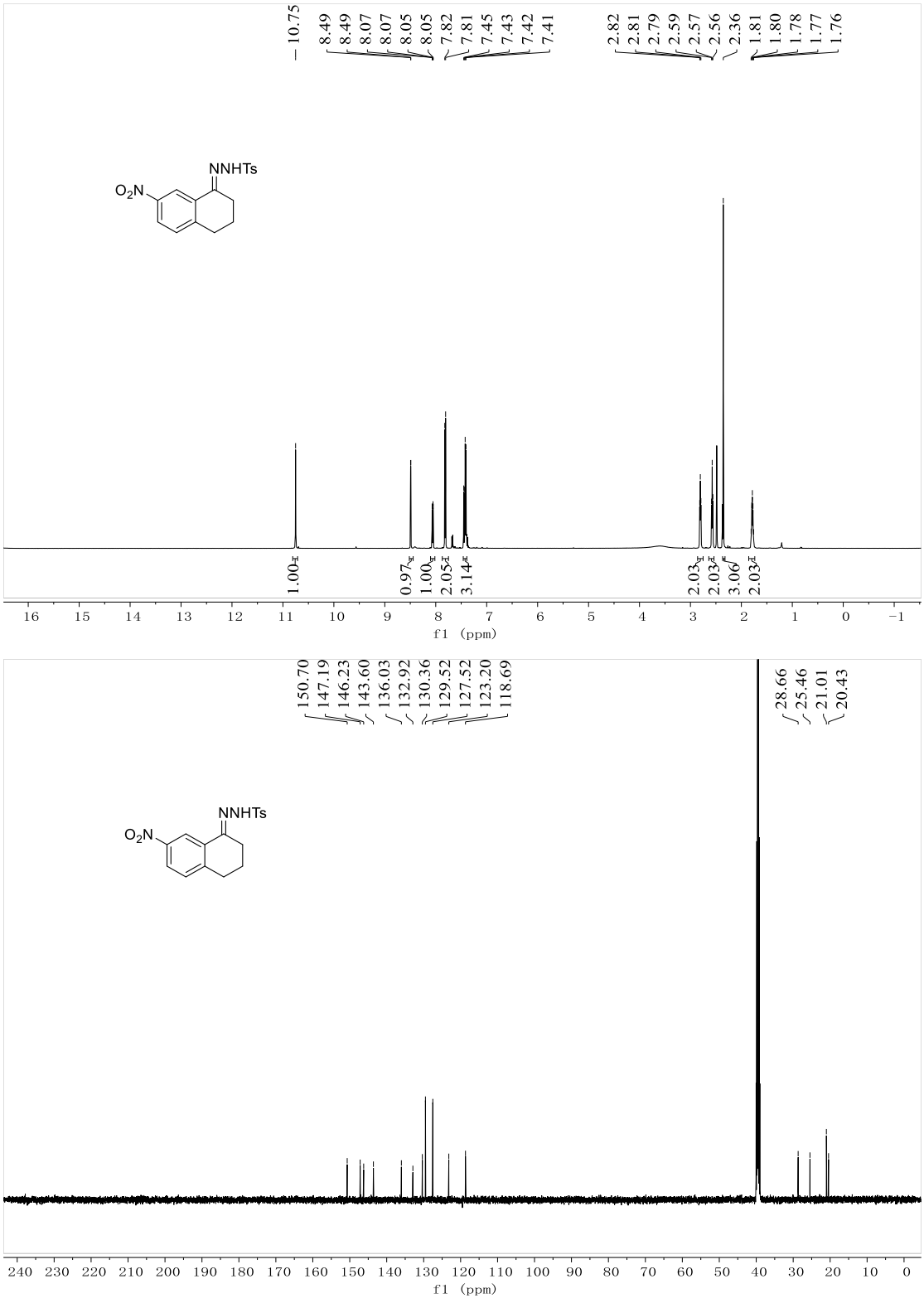
^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (126 MHz, $CDCl_3$) spectra for 5b:



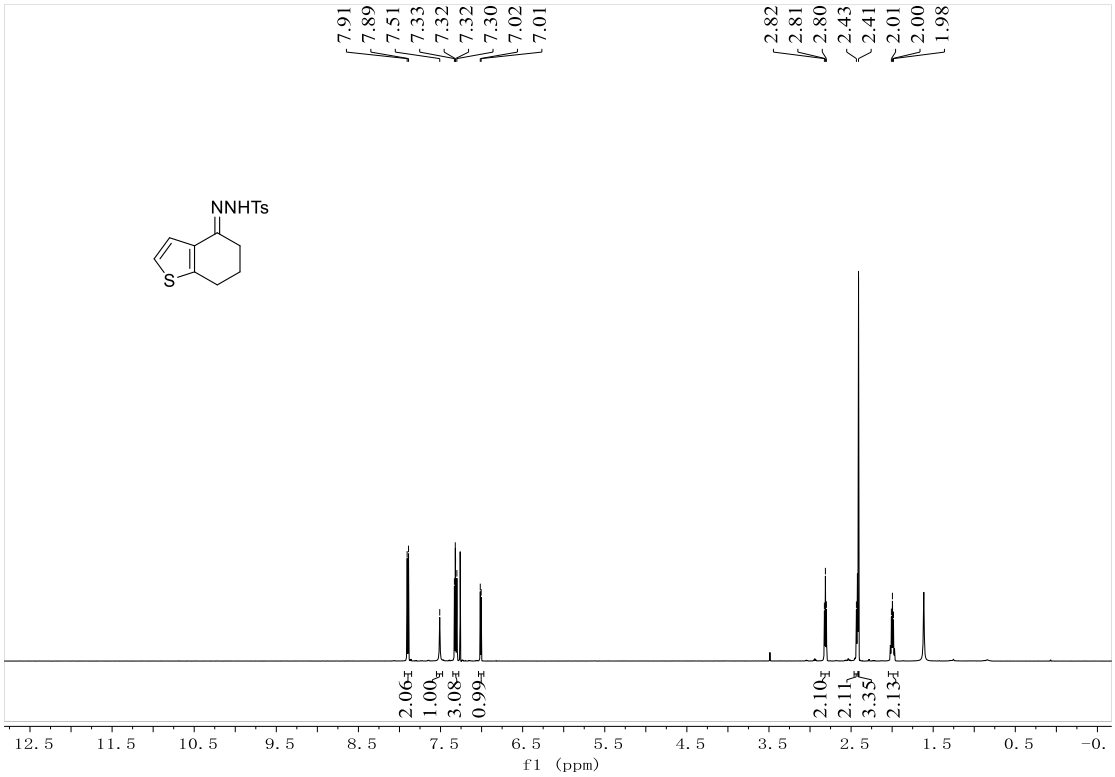
^{1}H NMR (500 MHz, $CDCl_3$) spectra for 6b:



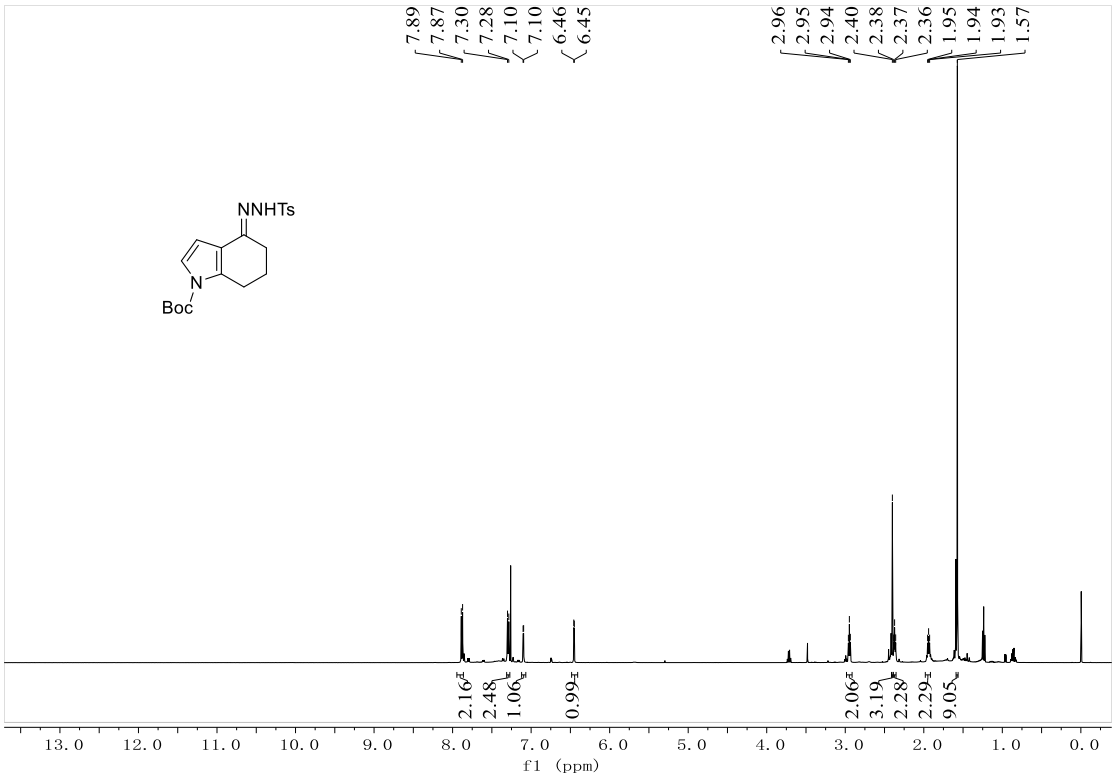
^{1}H NMR (500 MHz, DMSO-d_6) and ^{13}C NMR (126 MHz, DMSO-d_6) spectra for 7b:

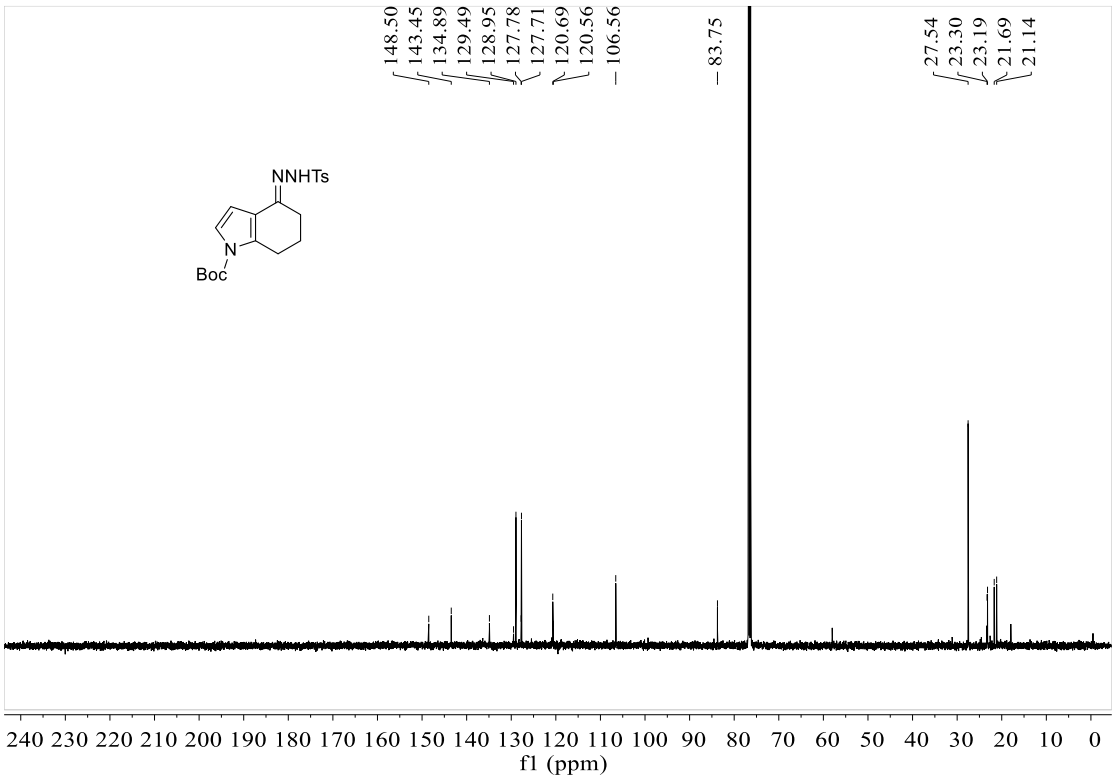


^{1}H NMR (500 MHz, $CDCl_3$) spectra for 8b:

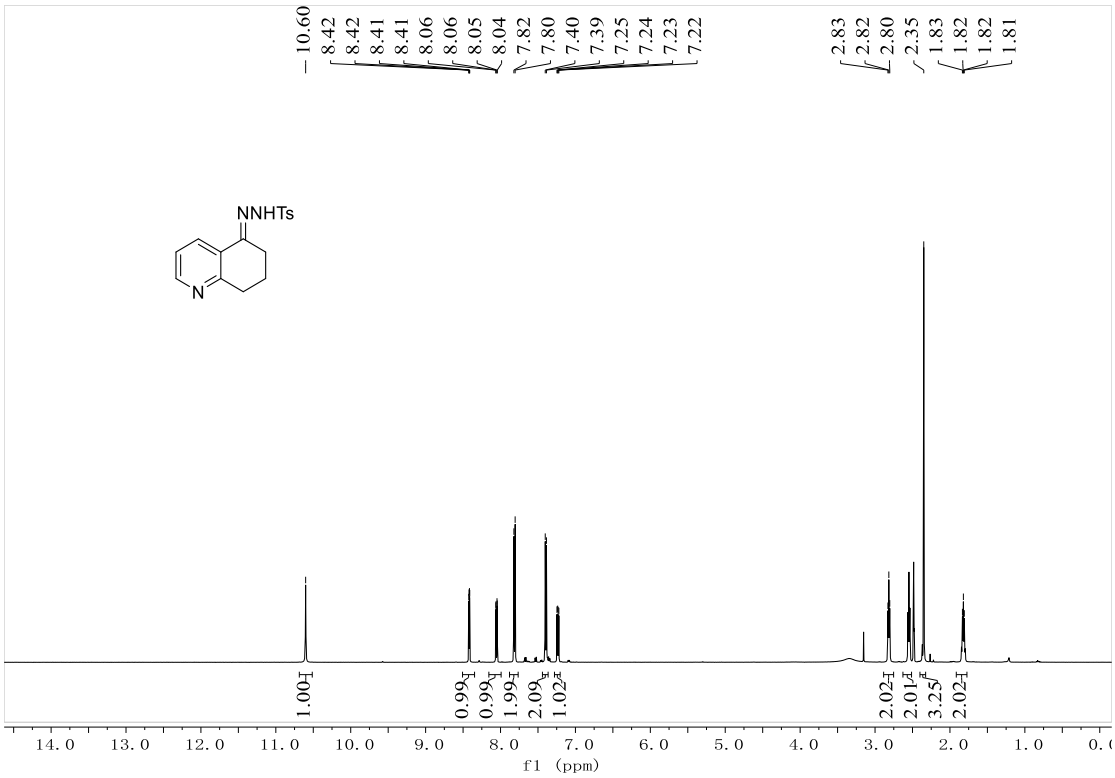


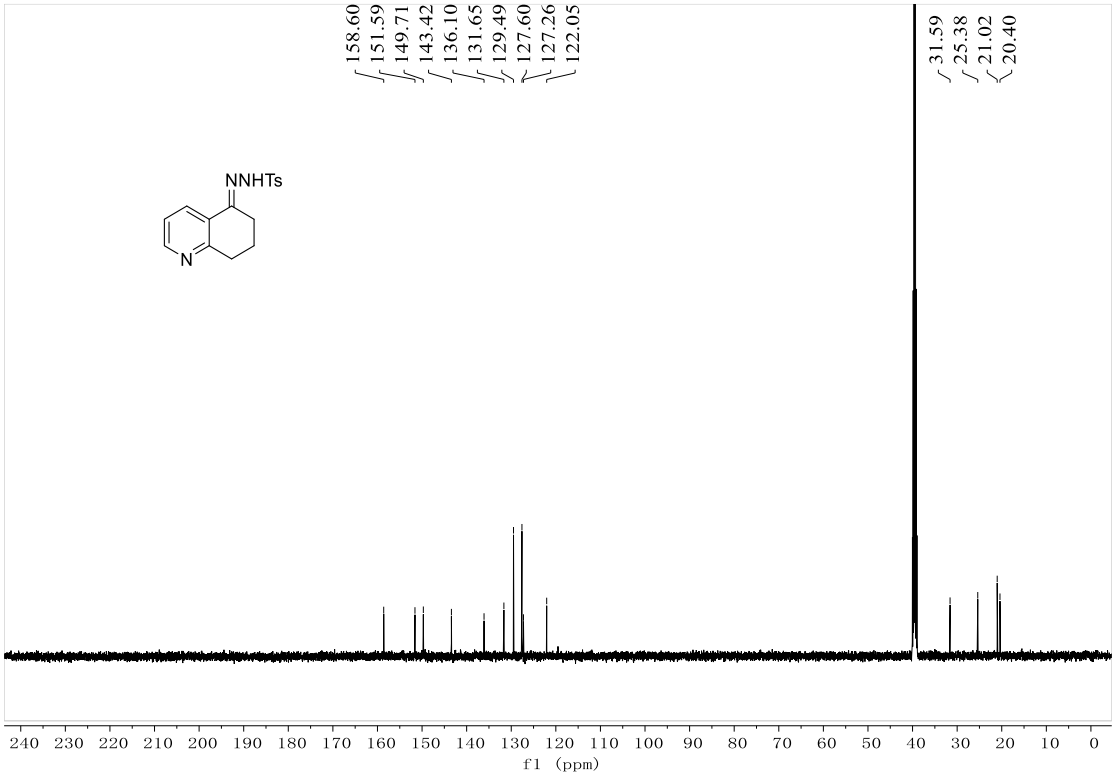
^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (126 MHz, $CDCl_3$) spectra for 9b:



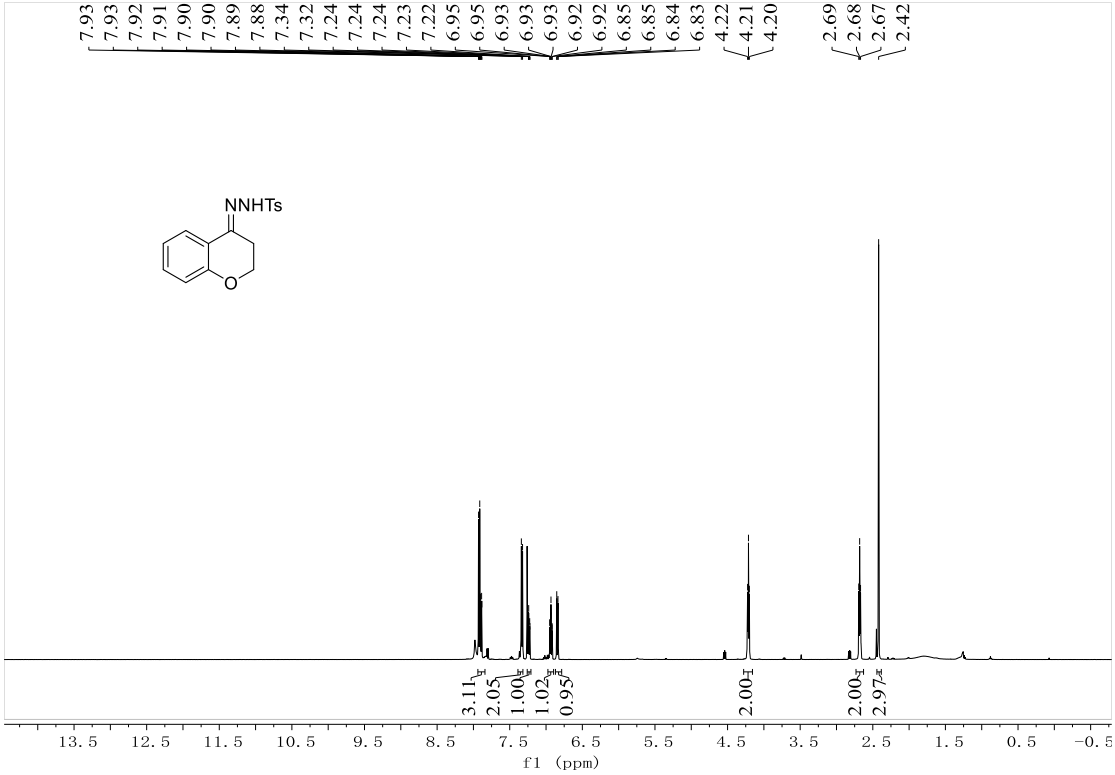


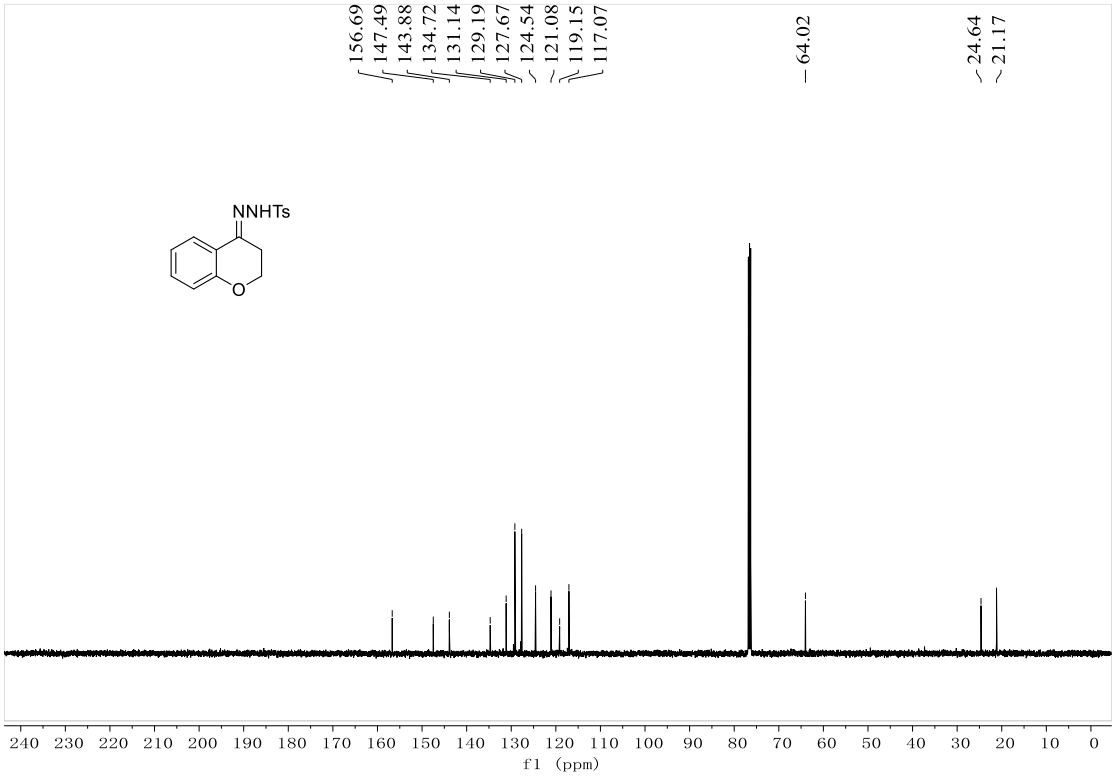
^{1}H NMR (500 MHz, DMSO-d_6) and ^{13}C NMR (126 MHz, DMSO-d_6) spectra for 10b:



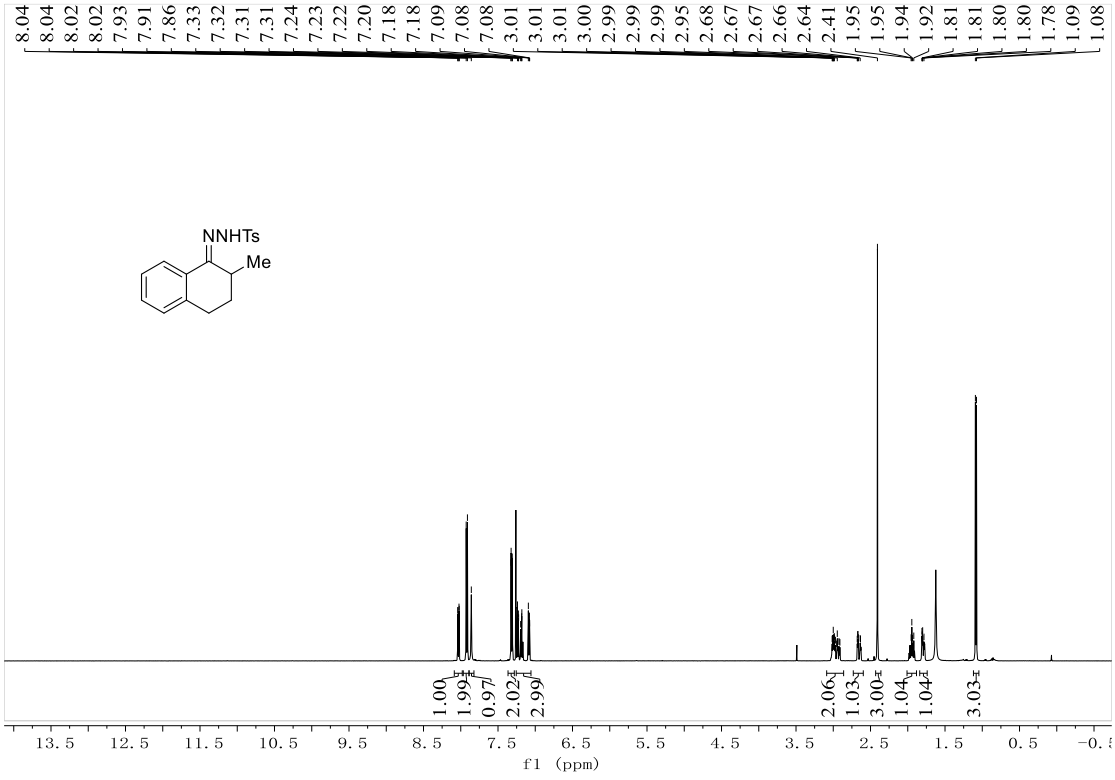


^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (126 MHz, $CDCl_3$) spectra for 11b:

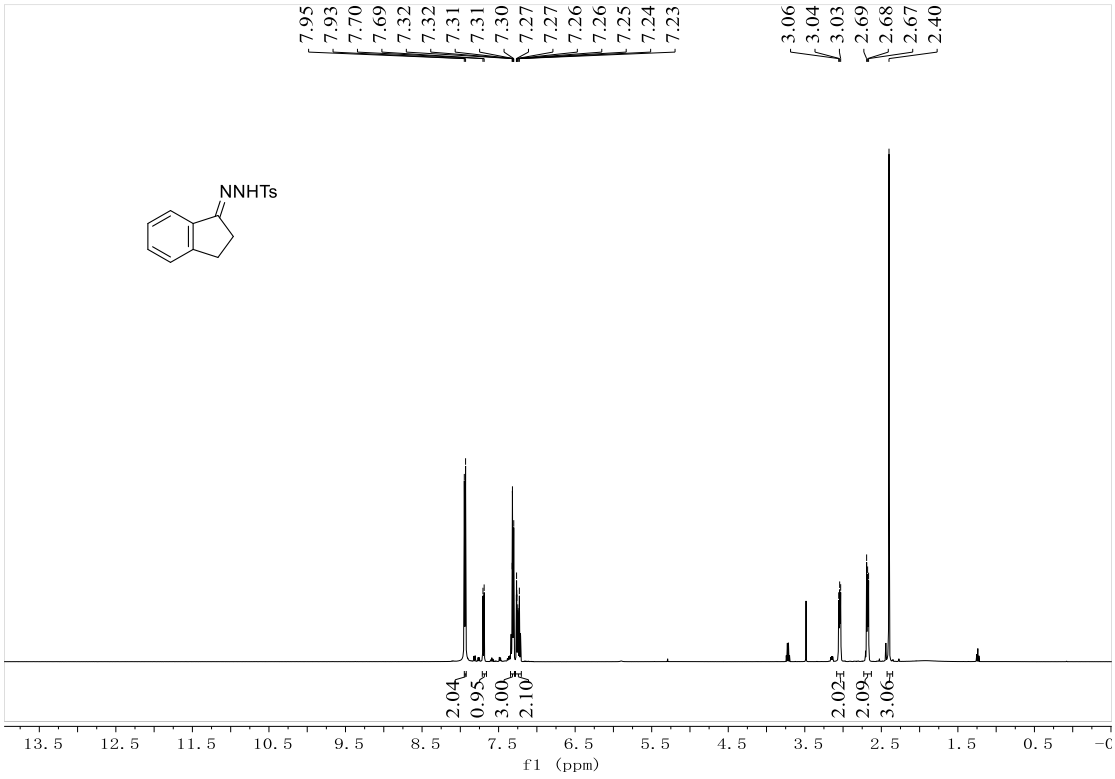


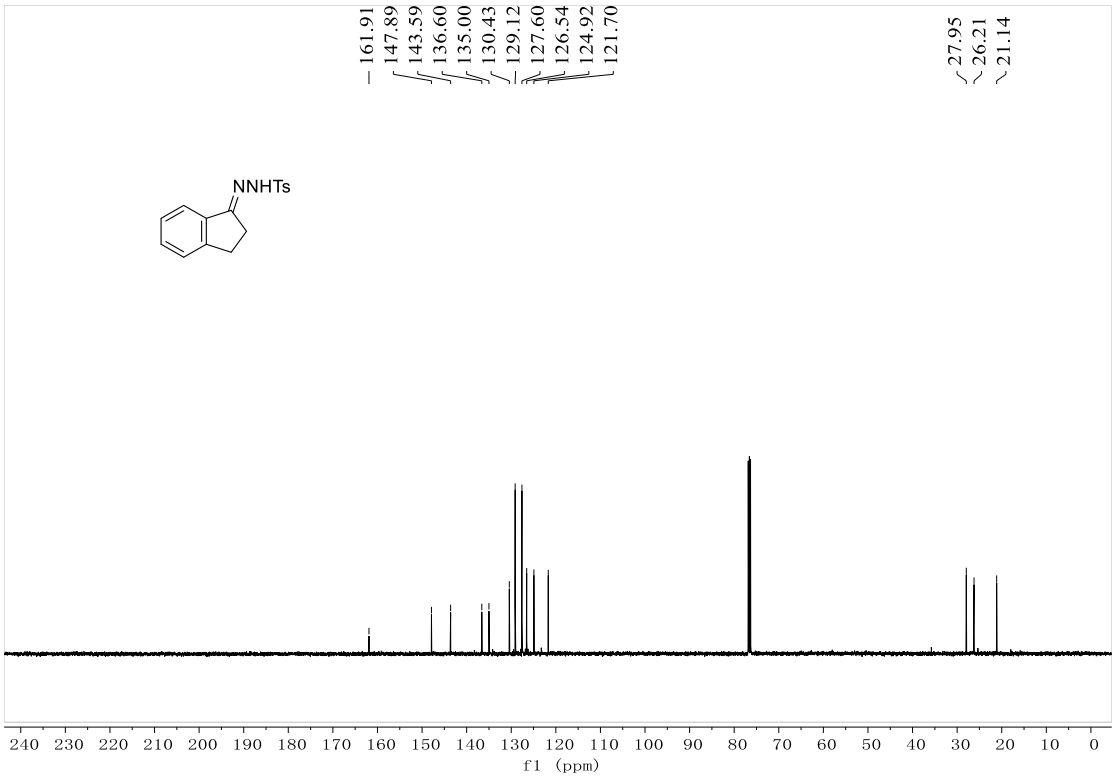


^{1}H NMR (500 MHz, $CDCl_3$) spectra for 12b:

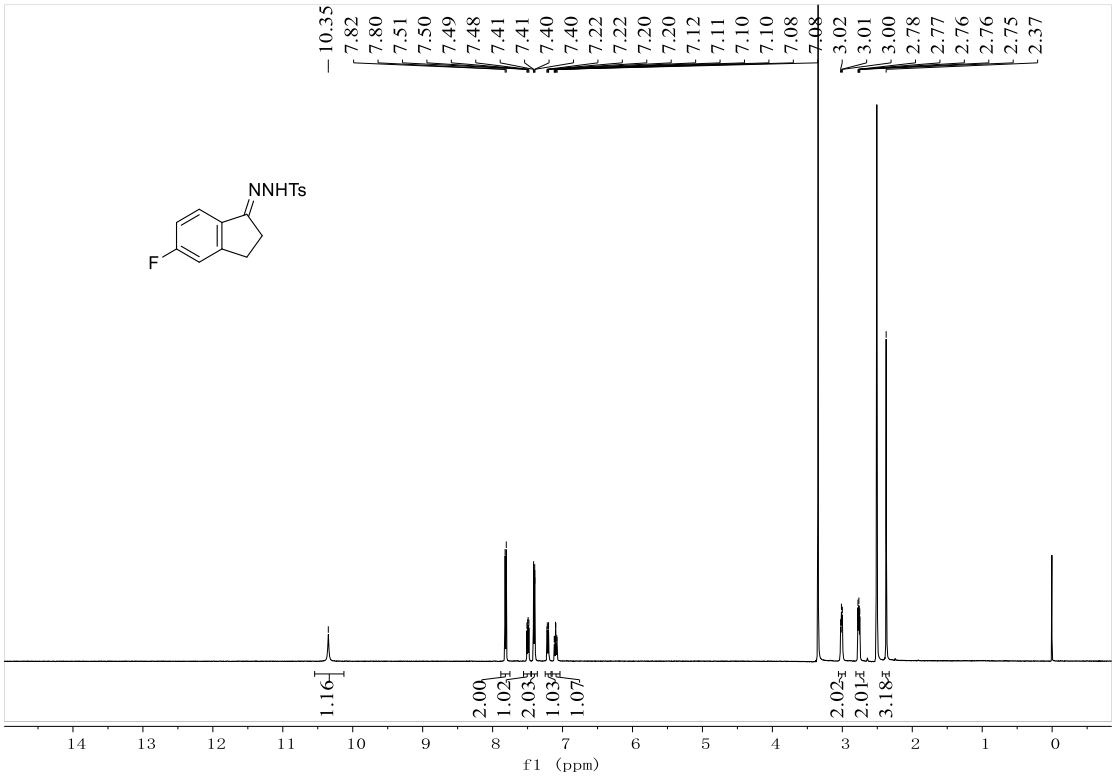


^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (126 MHz, $CDCl_3$) spectra for 13b:

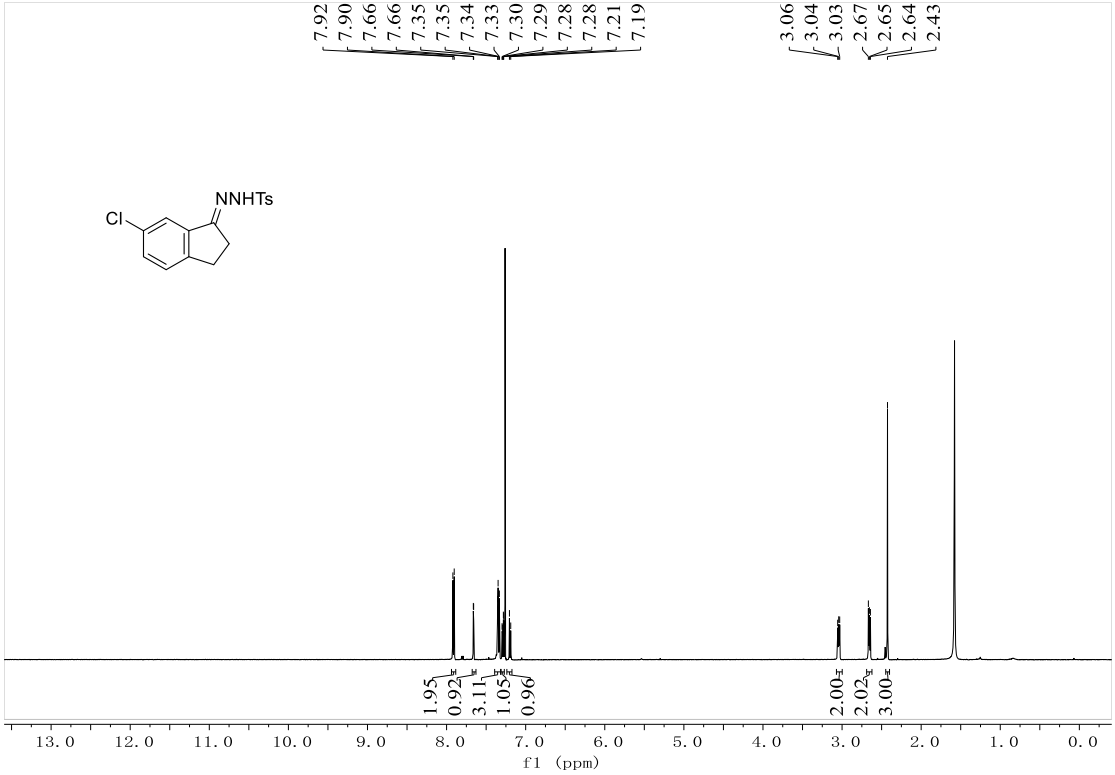




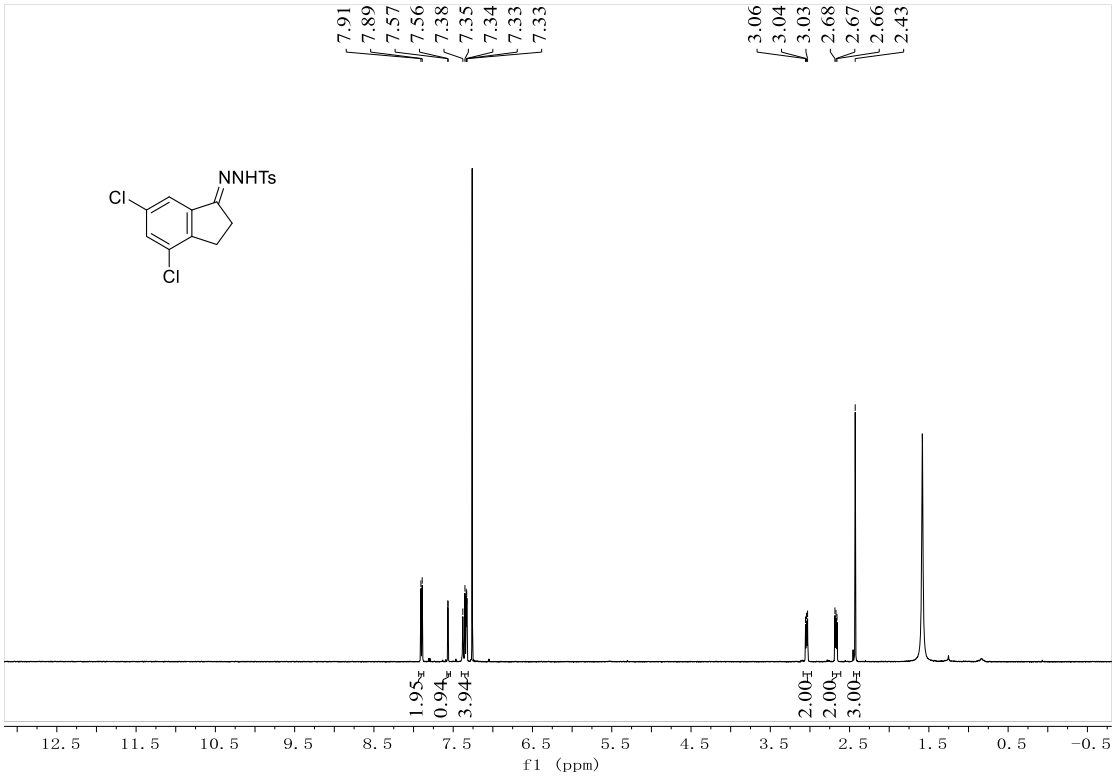
^{1}H NMR (500 MHz, DMSO-d_6) spectra for 14b:



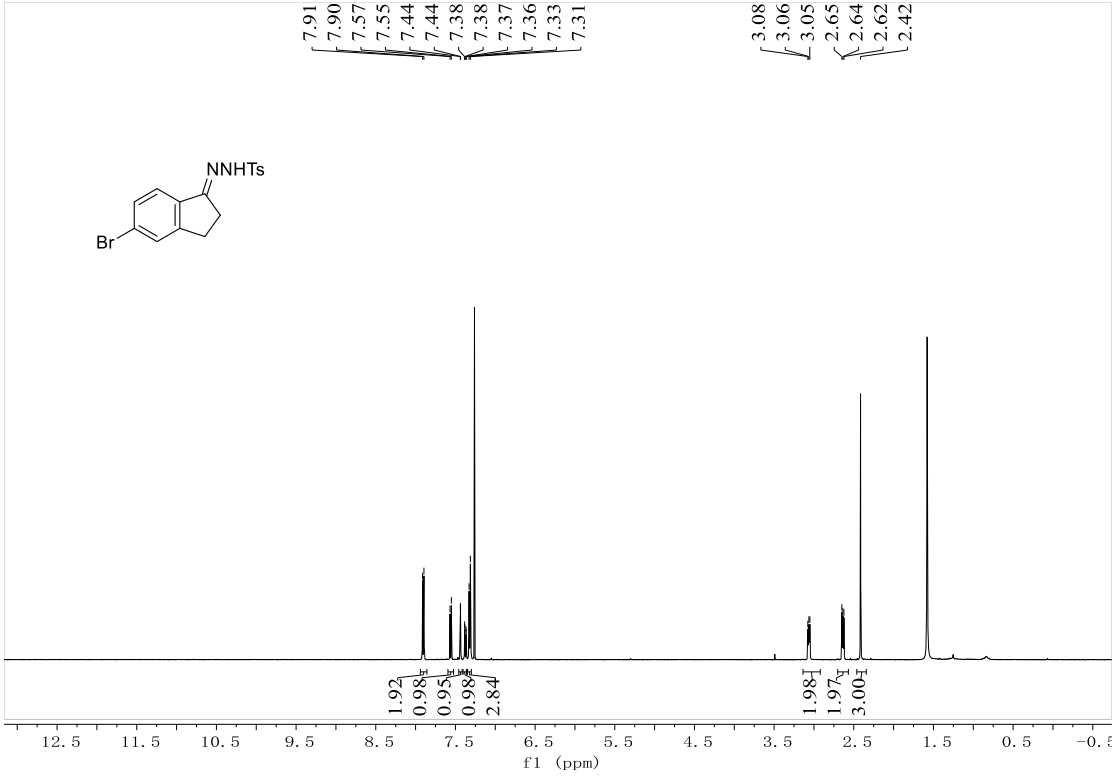
^{1}H NMR (500 MHz, $CDCl_3$) spectra for 15b:



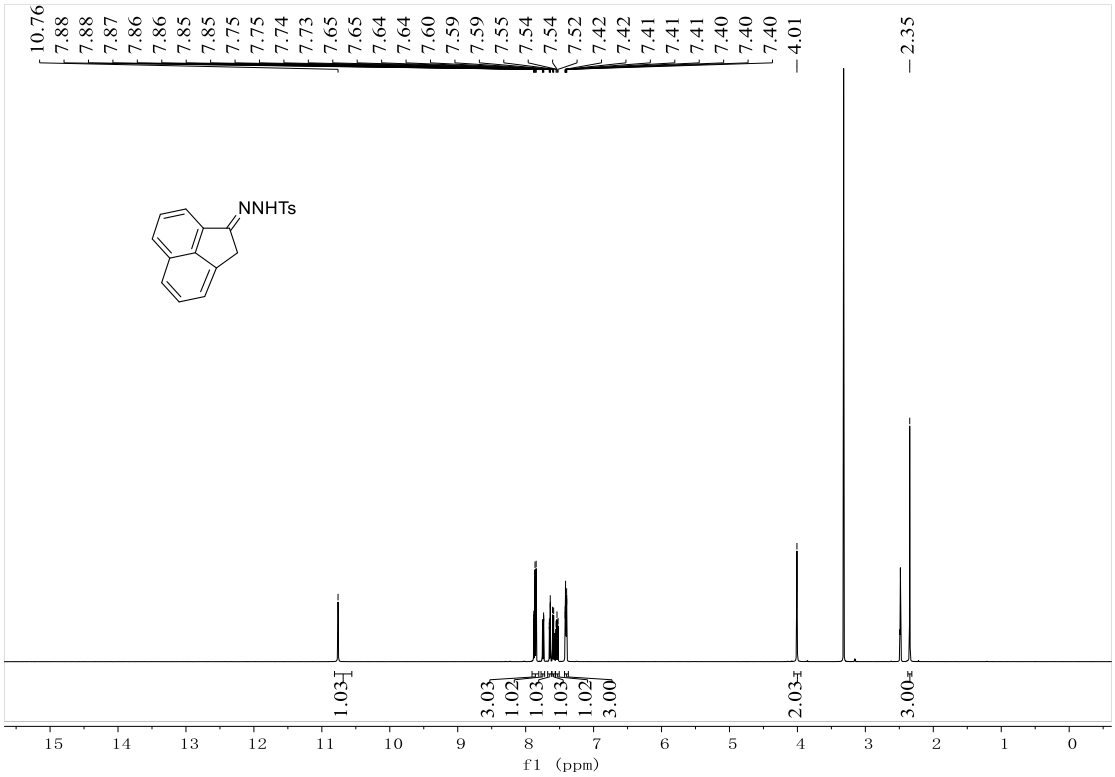
^{1}H NMR (500 MHz, $CDCl_3$) spectra for 16b:



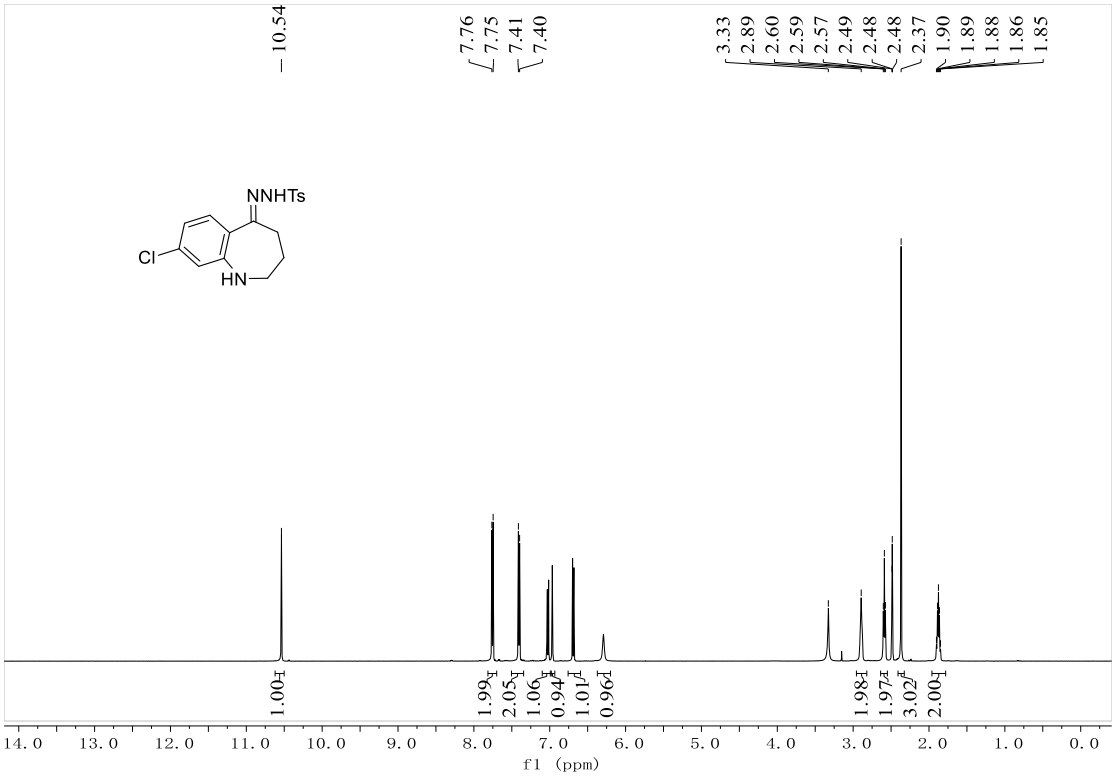
^{1}H NMR (500 MHz, $CDCl_3$) spectra for 17b:

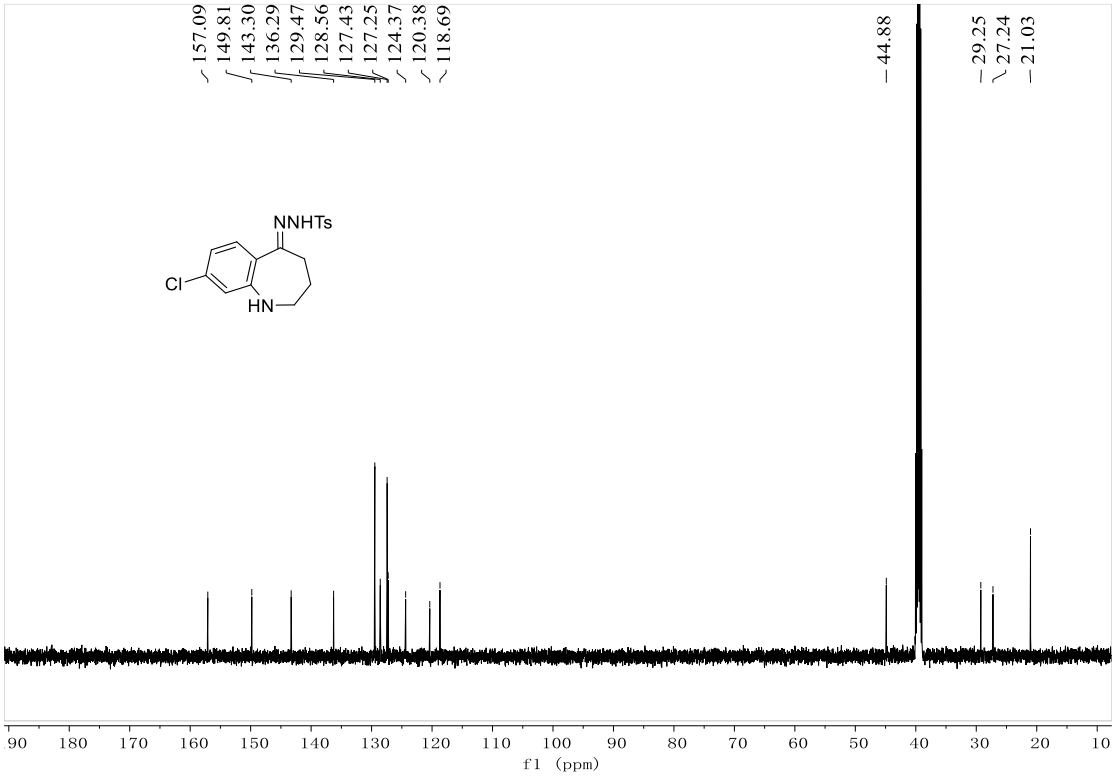


^{1}H NMR (500 MHz, DMSO-d_6) spectra for 18b:

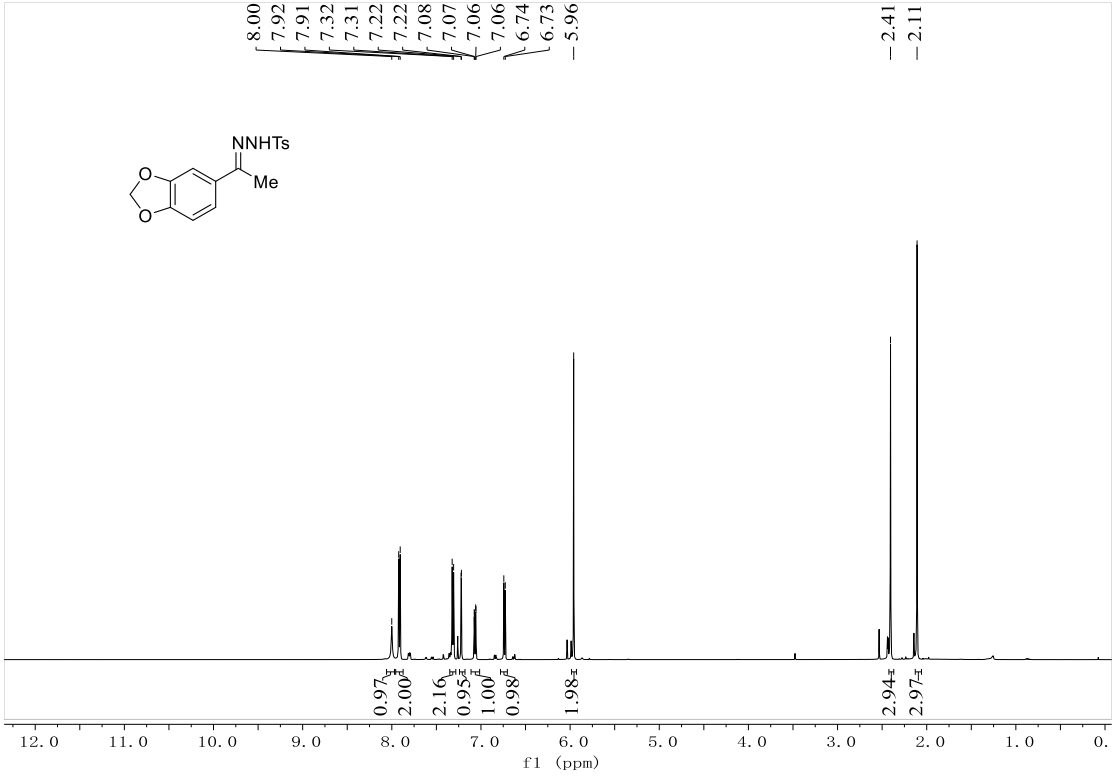


^{1}H NMR (500 MHz, DMSO-d_6) and ^{13}C NMR (126 MHz, DMSO-d_6) spectra for 19b:

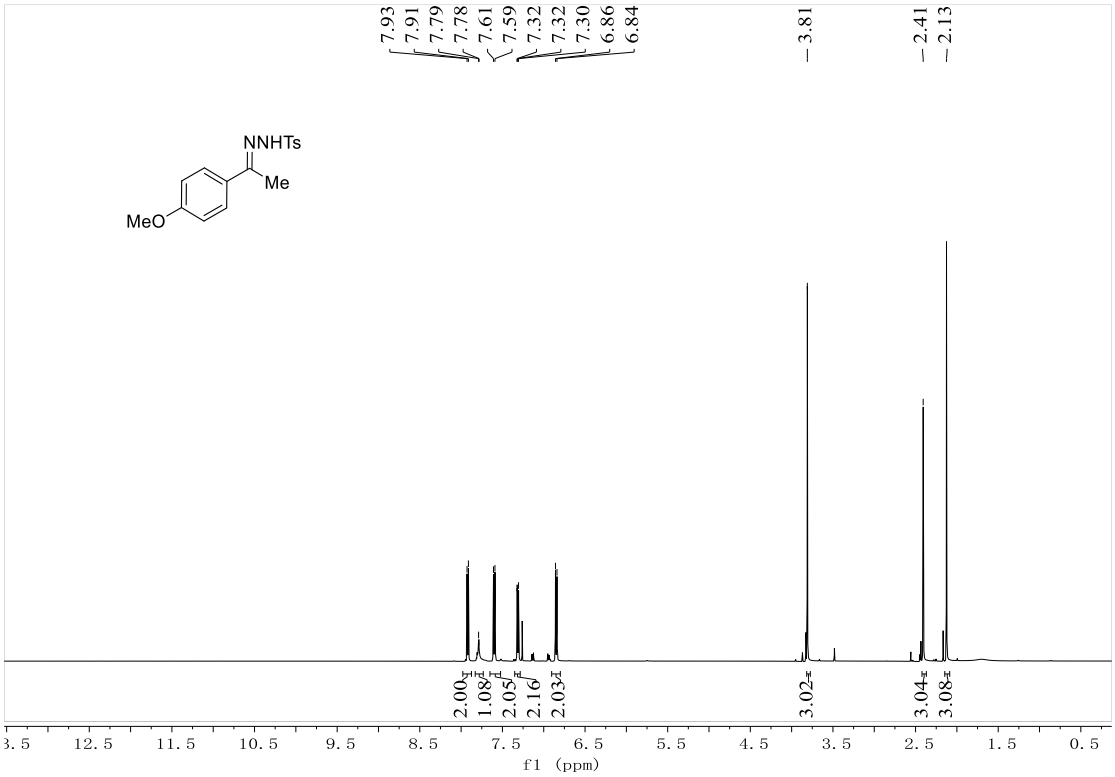




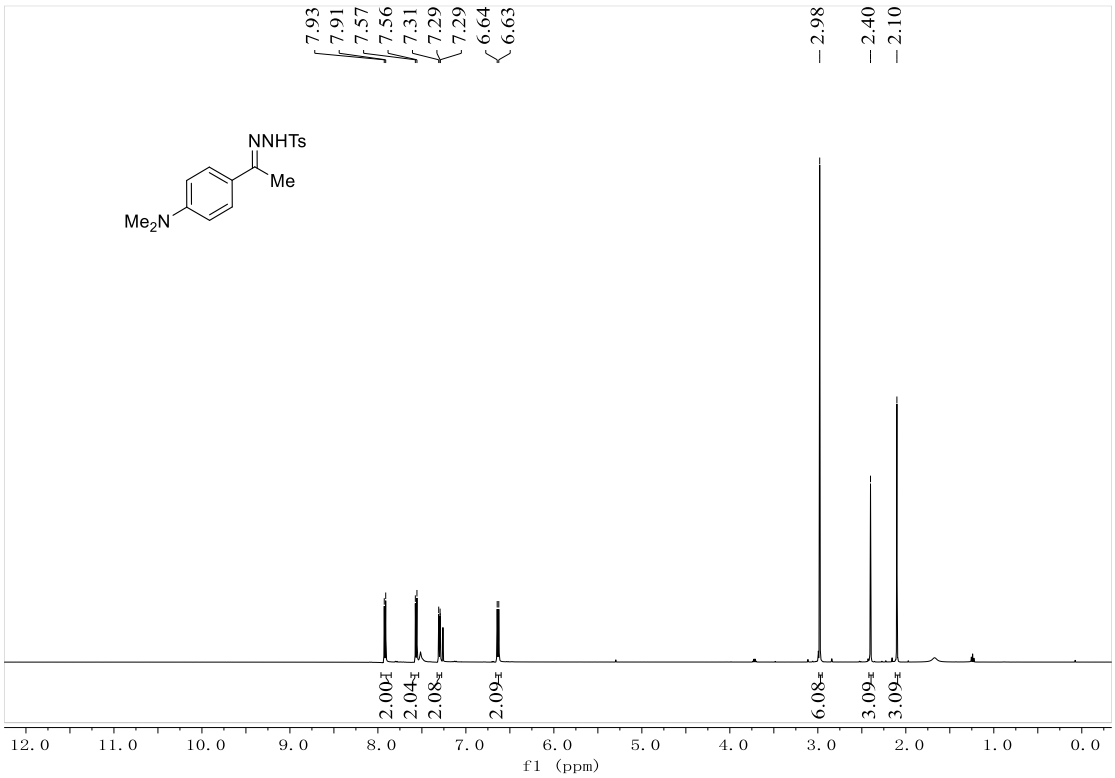
^{1}H NMR (500 MHz, $CDCl_3$) spectra for 21b:

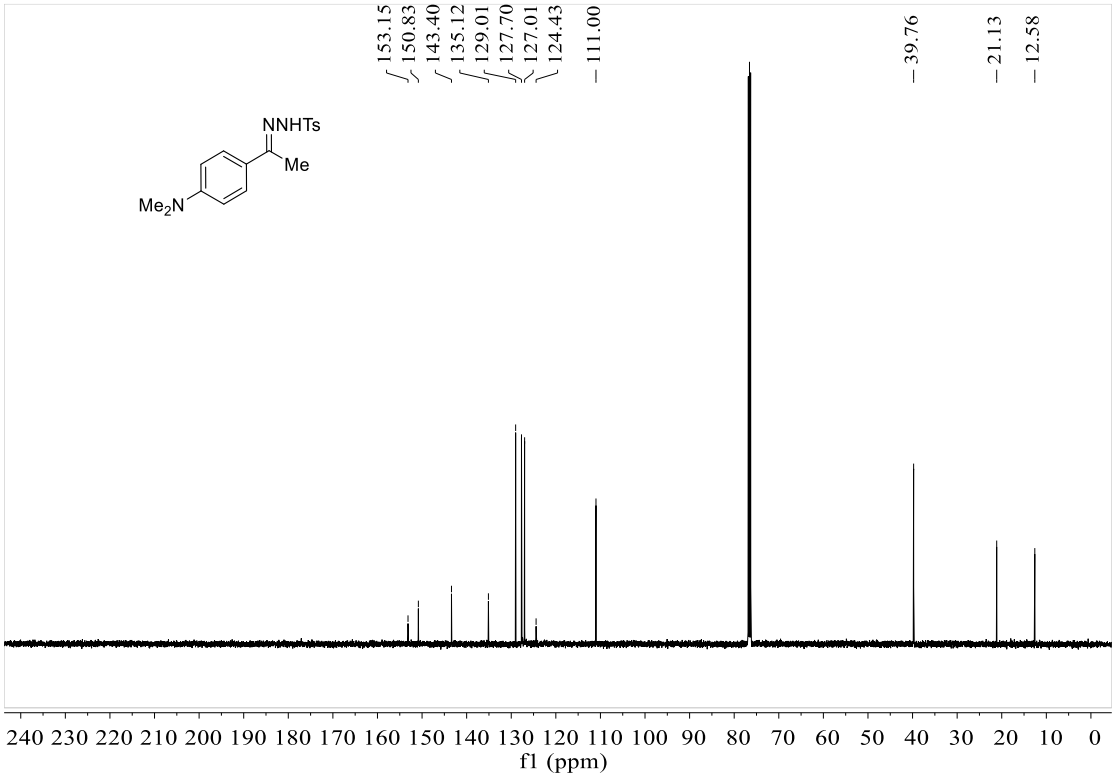


^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (126 MHz, $CDCl_3$) spectra for 22b:

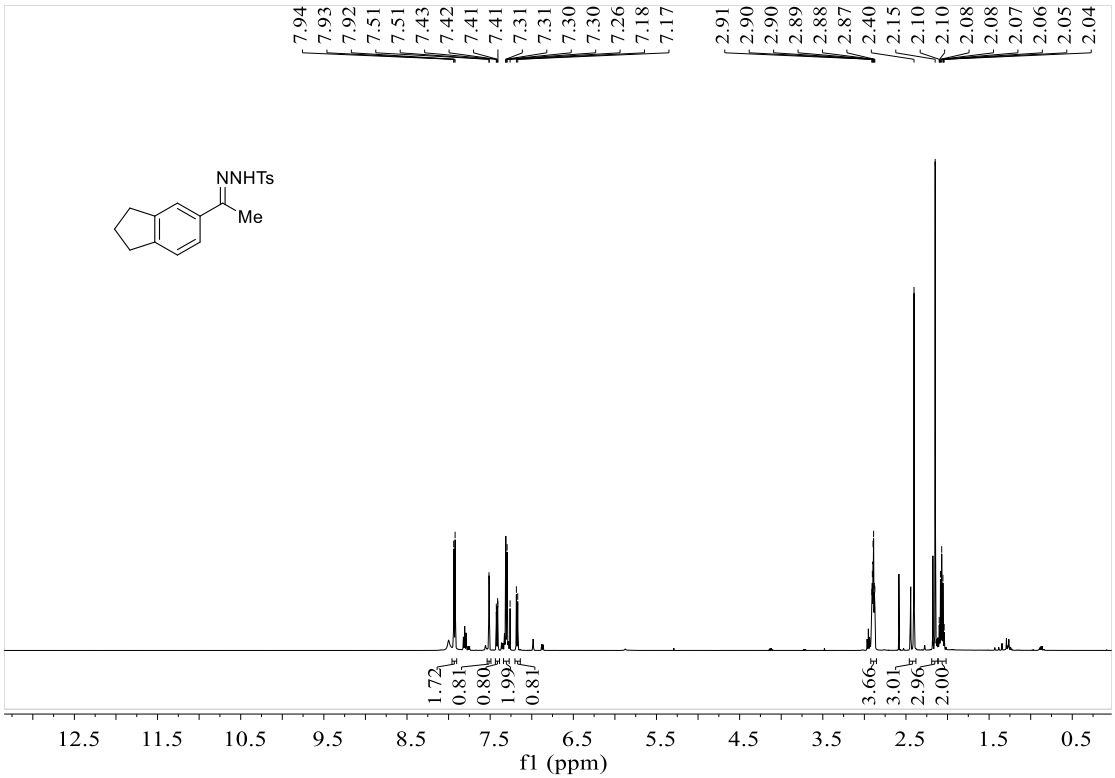


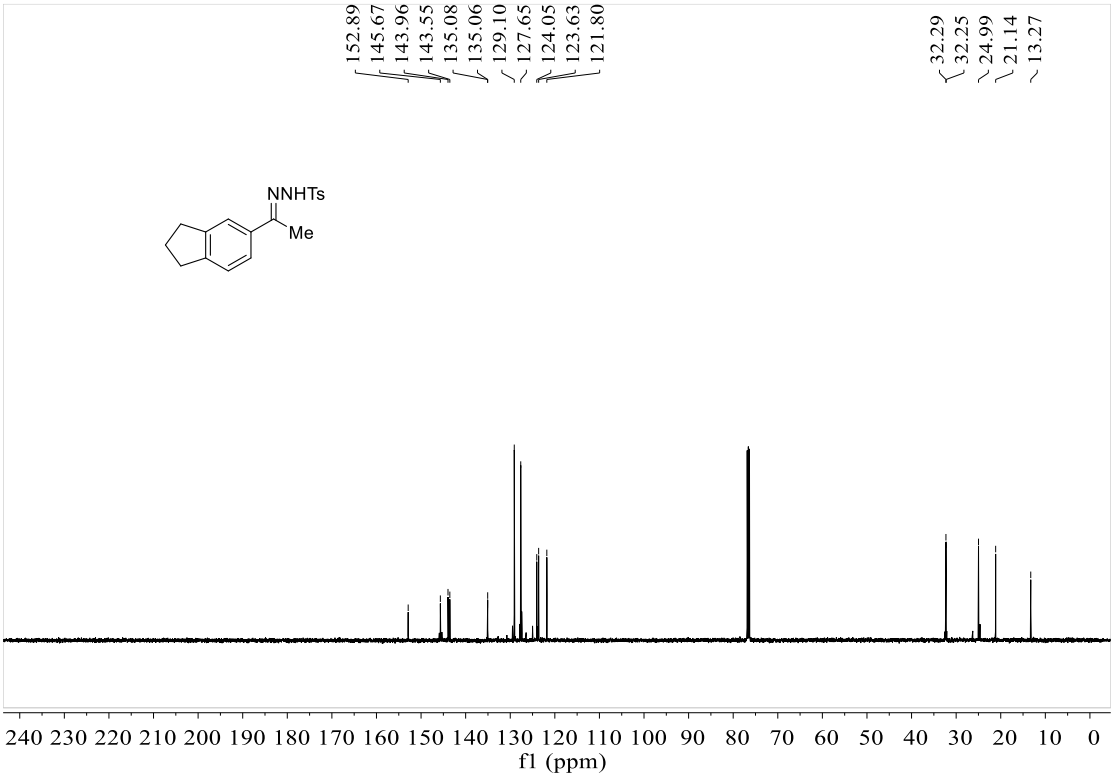
^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (126 MHz, $CDCl_3$) spectra for 24b:



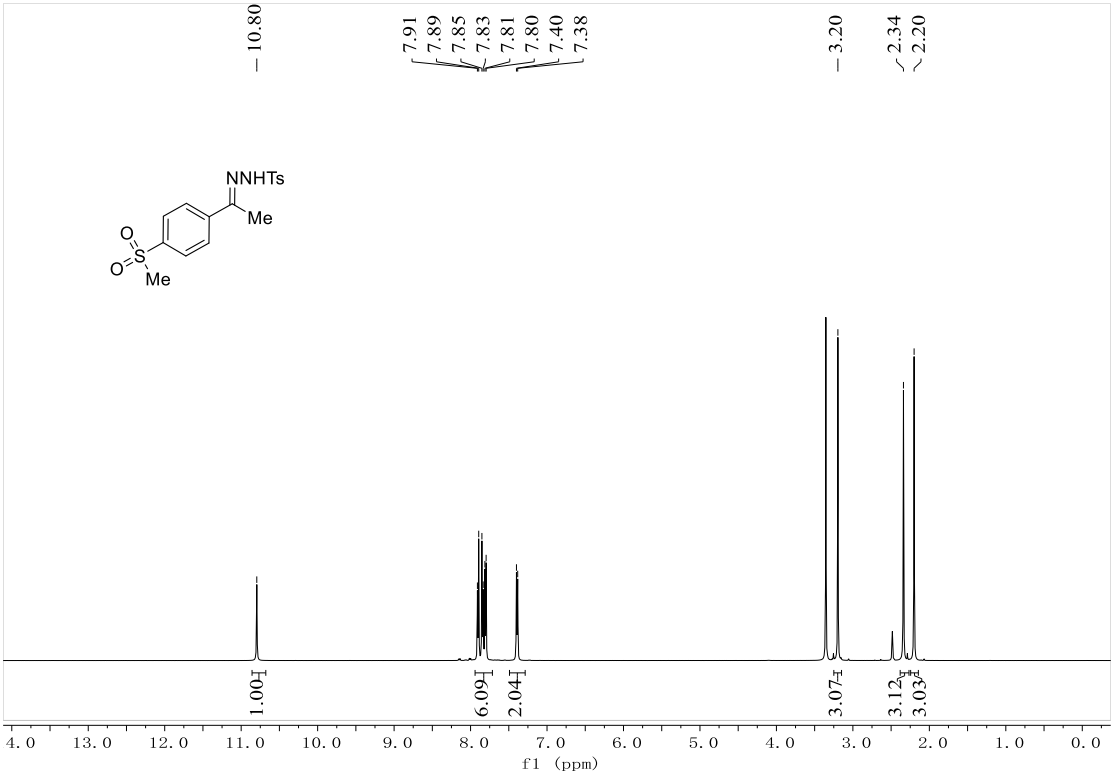


^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (126 MHz, $CDCl_3$) spectra for 25b:

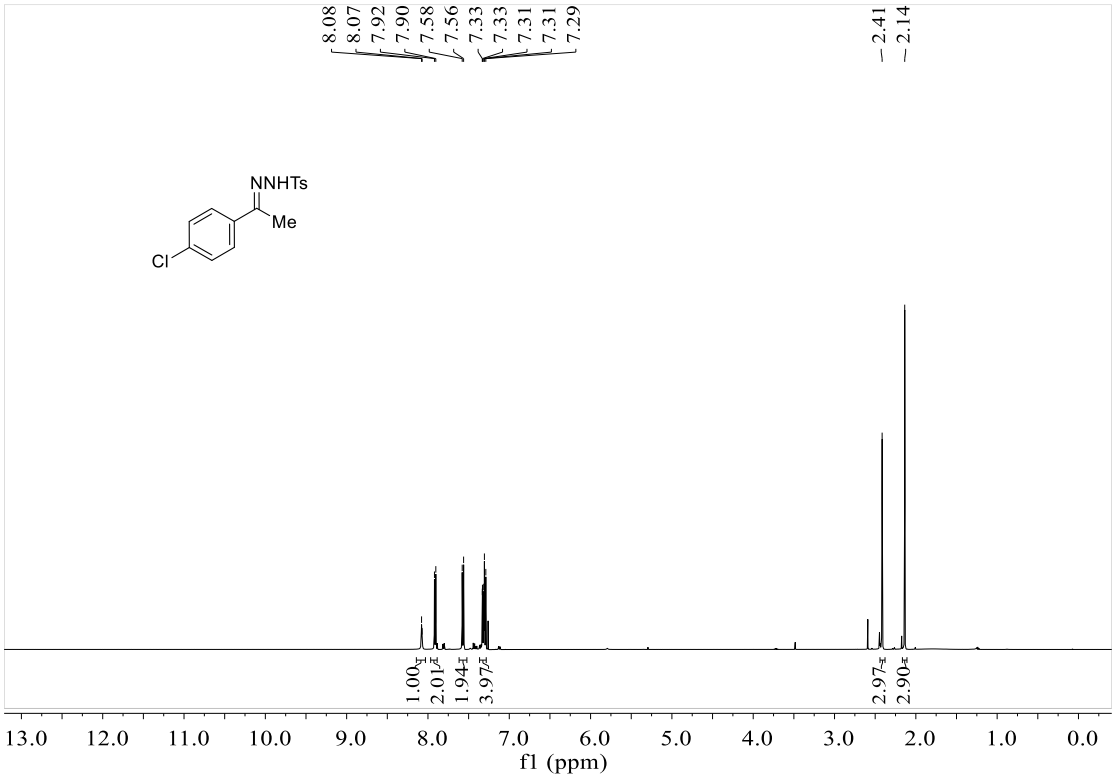


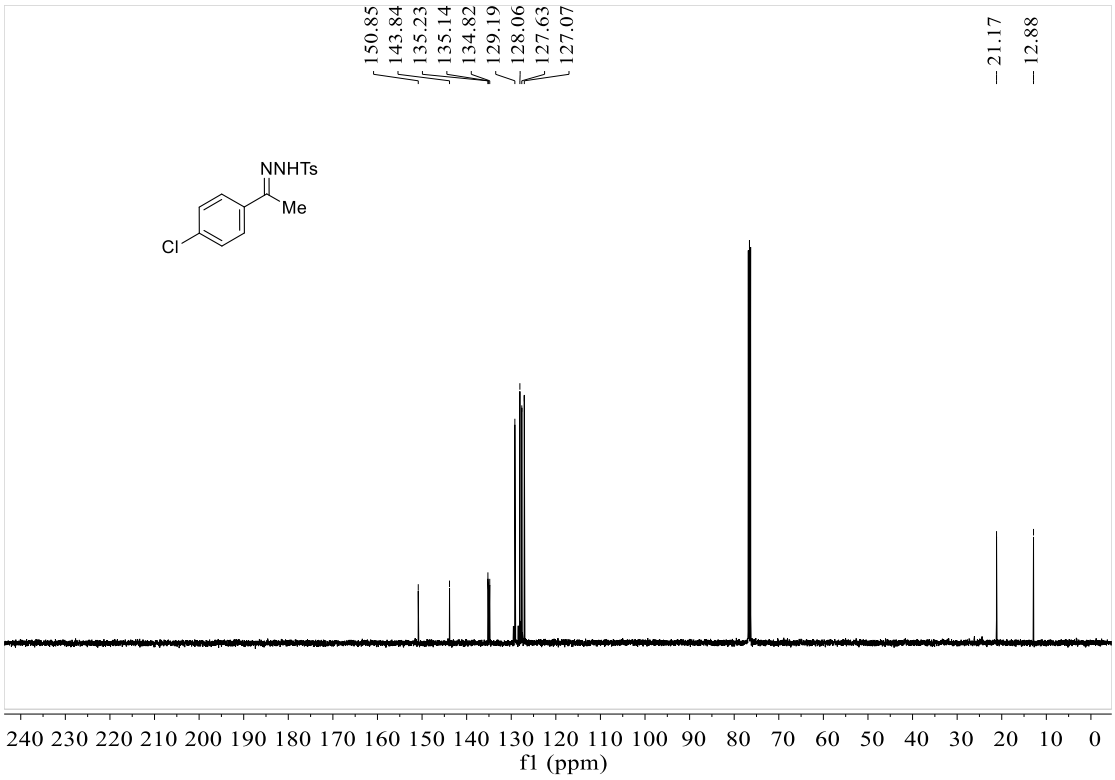


^{1}H NMR (500 MHz, DMSO-*d*$_6$) spectra for 26b:

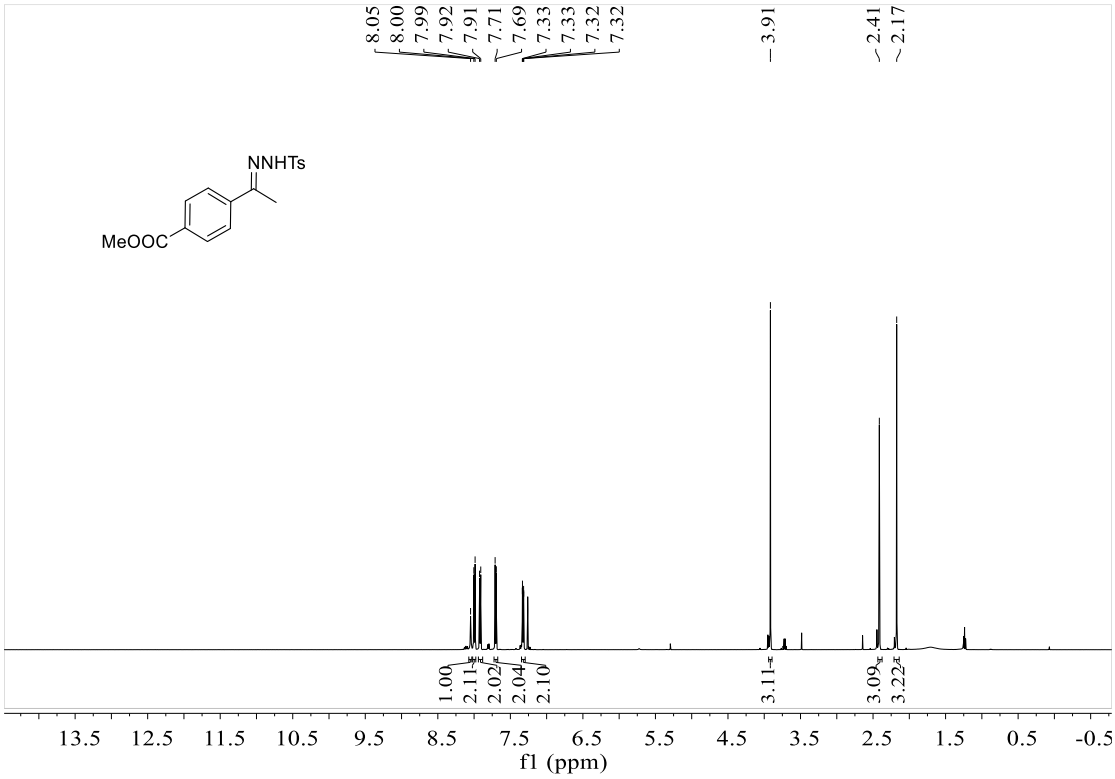


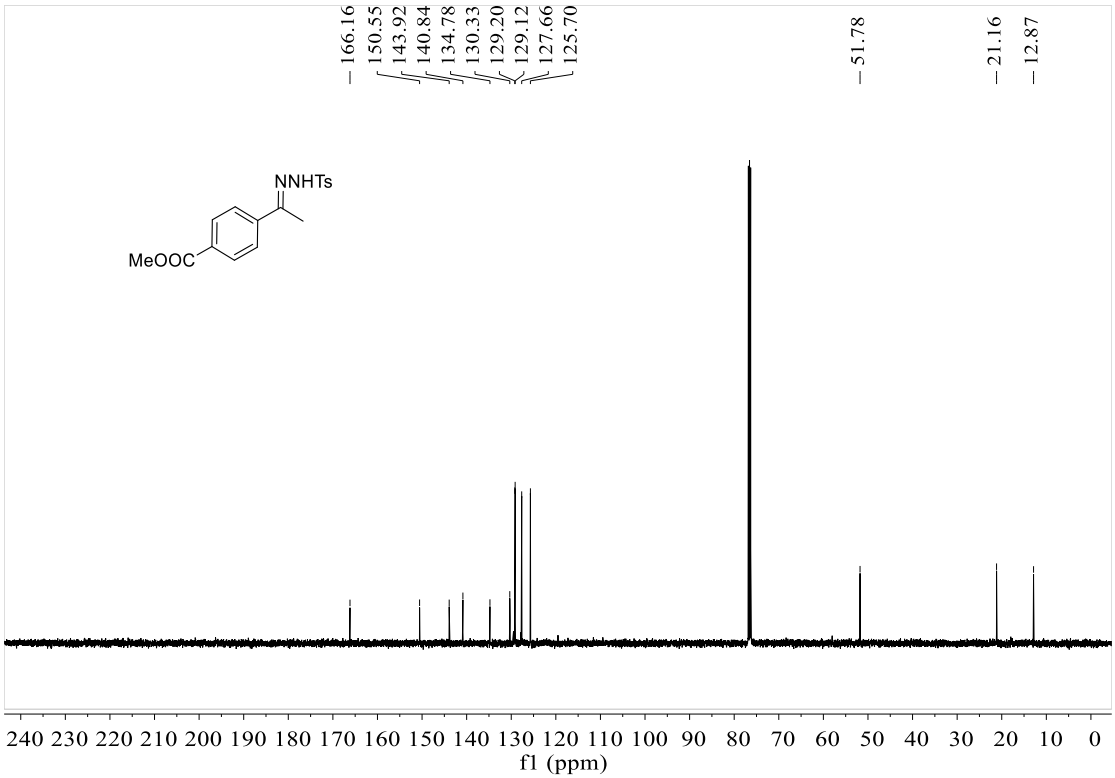
^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (126 MHz, $CDCl_3$) spectra for 27b:



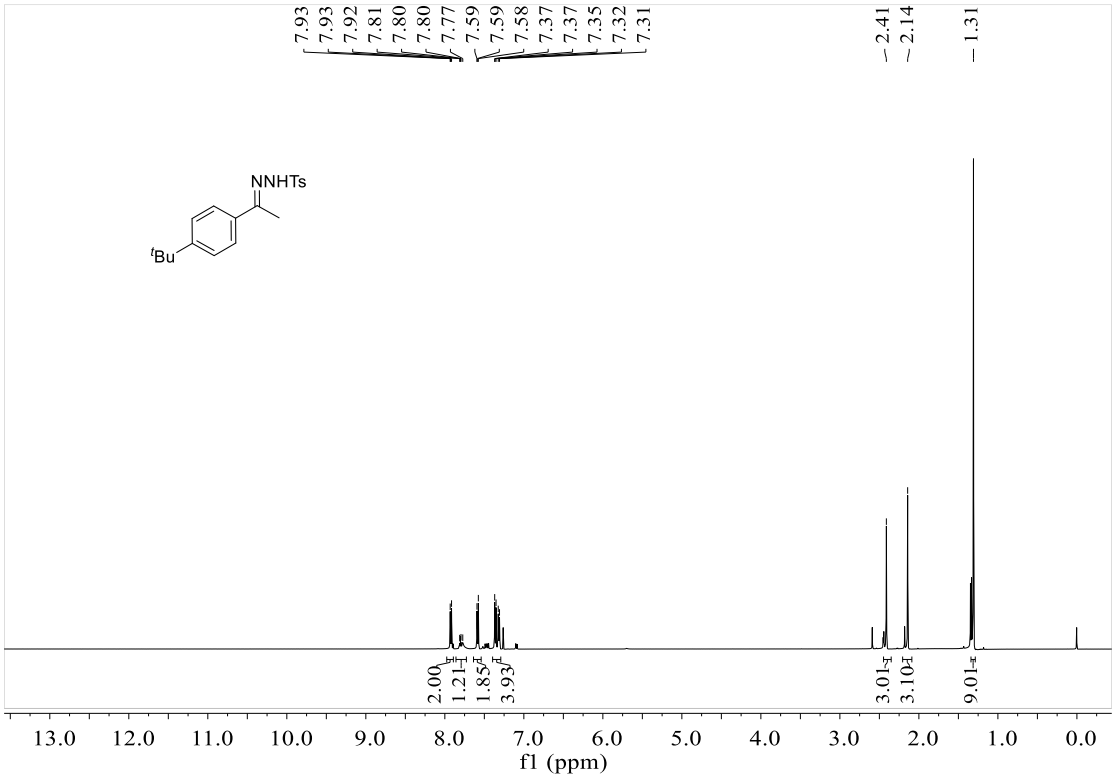


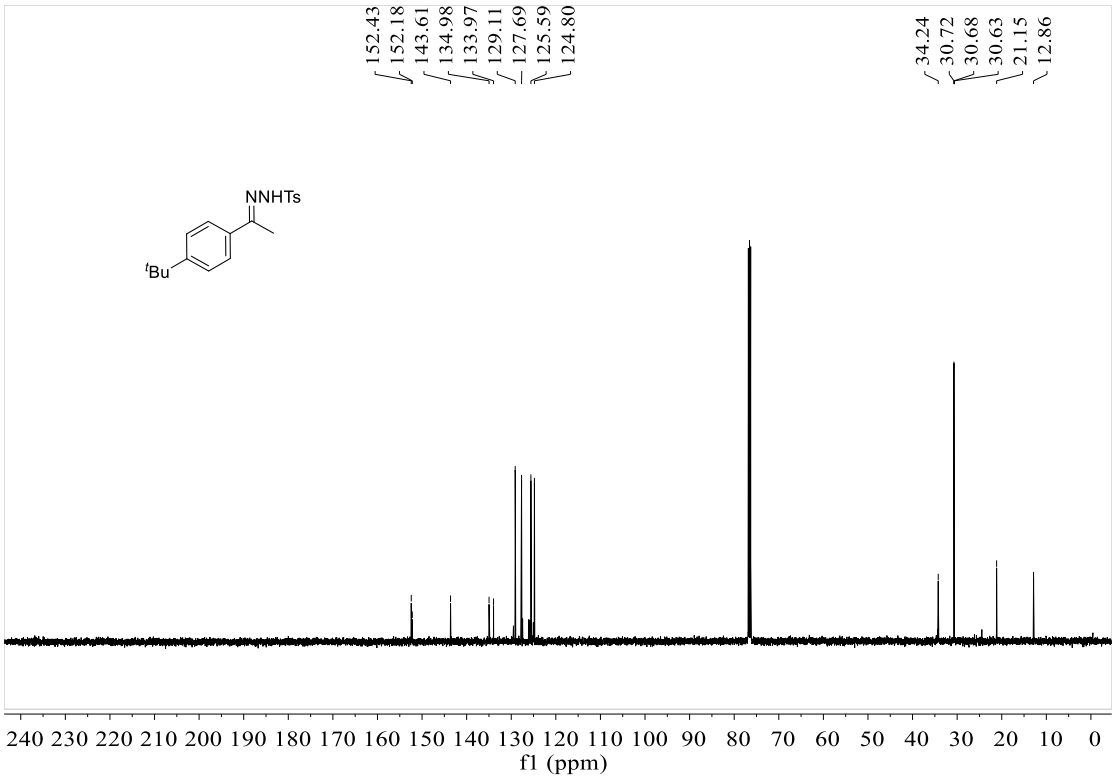
^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (126 MHz, $CDCl_3$) spectra for 28b:



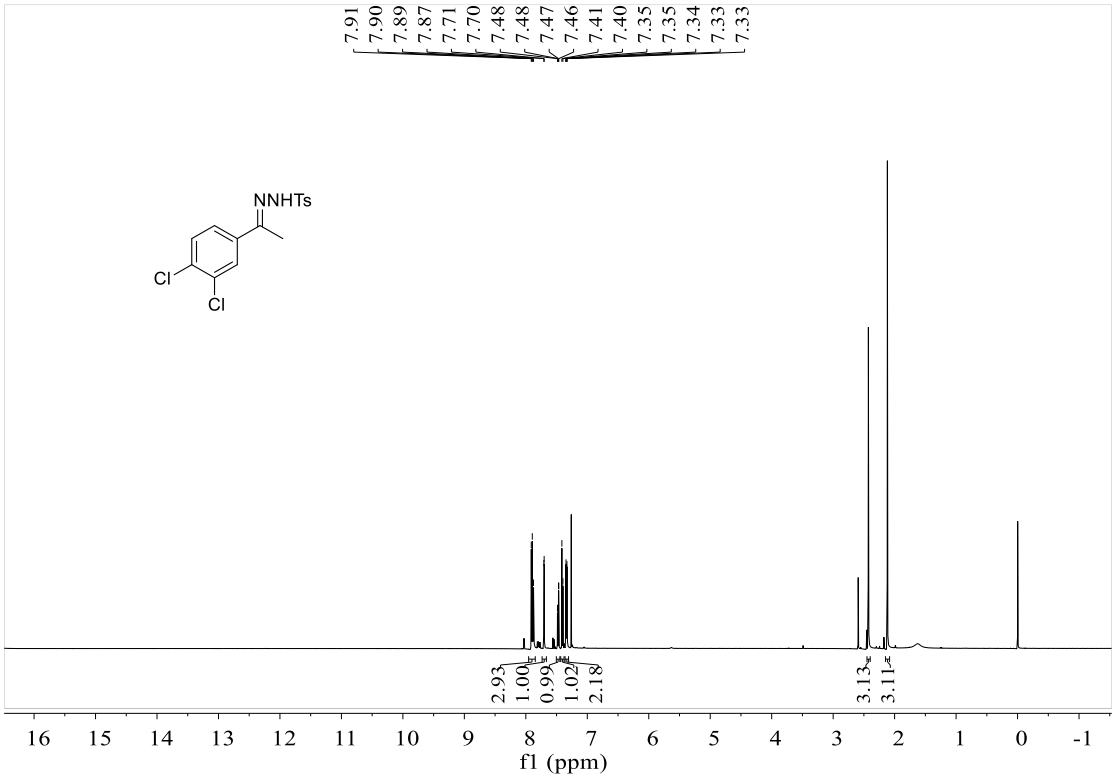


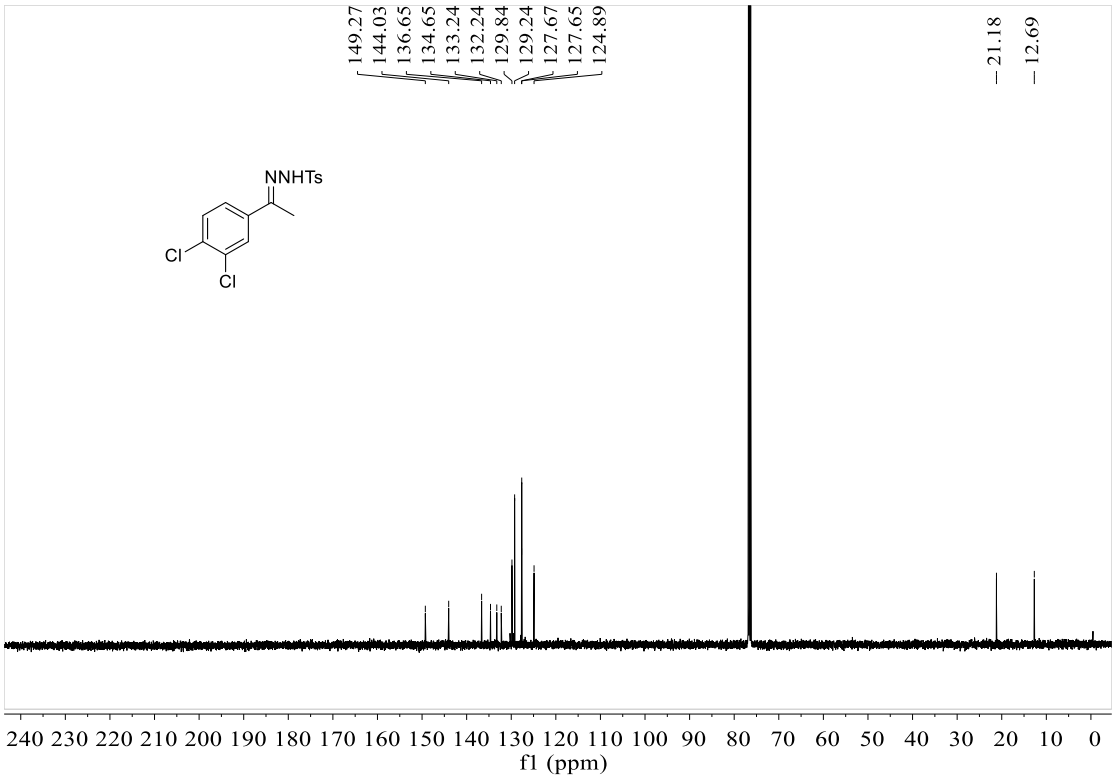
^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (126 MHz, $CDCl_3$) spectra for 29b:



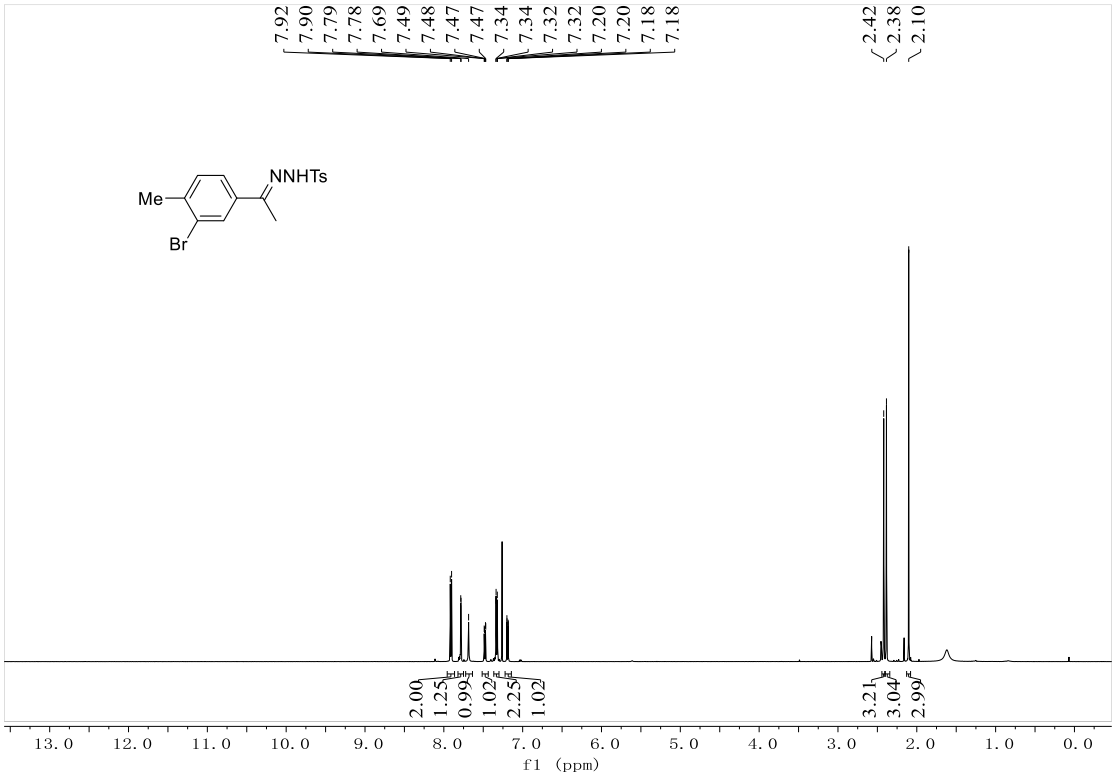


^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (126 MHz, $CDCl_3$) spectra for 30b:

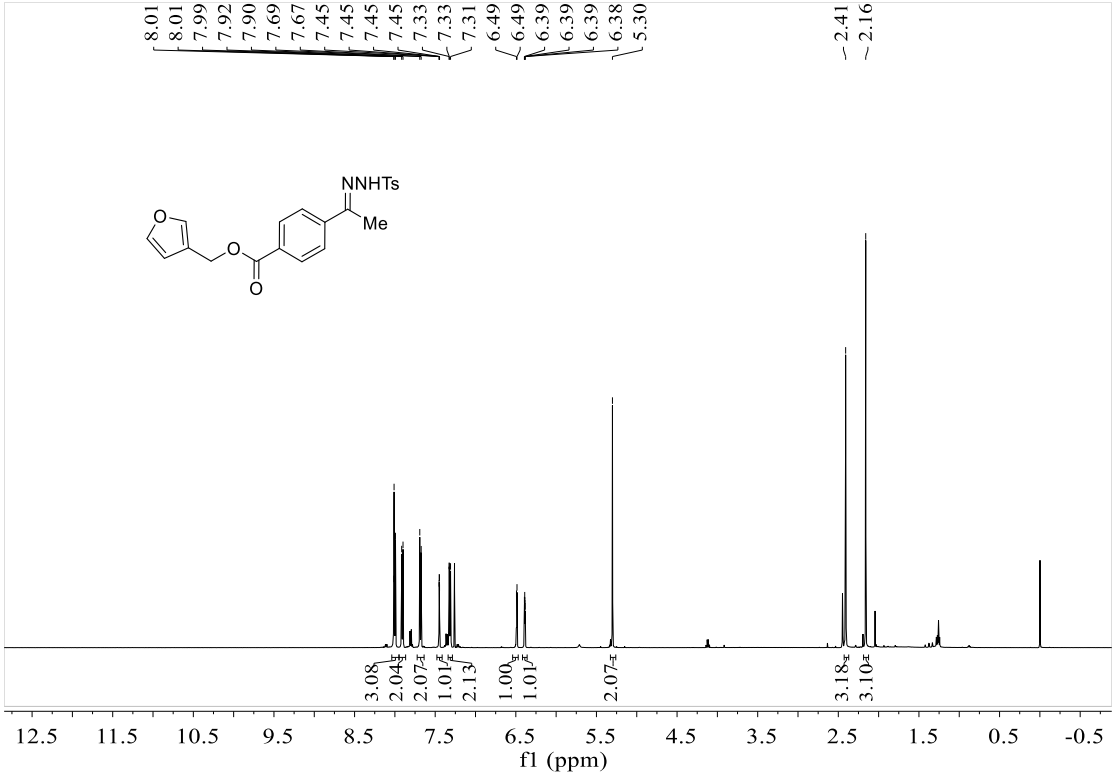


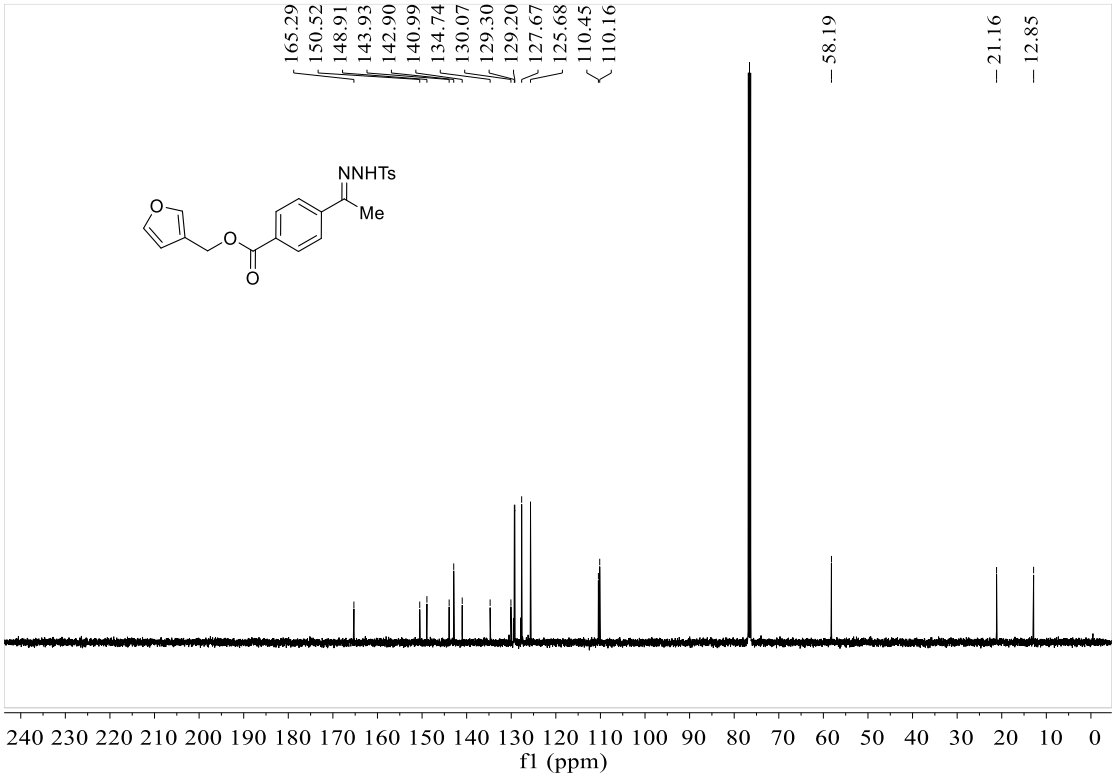


^{1}H NMR (500 MHz, $CDCl_3$) spectra for 31b:

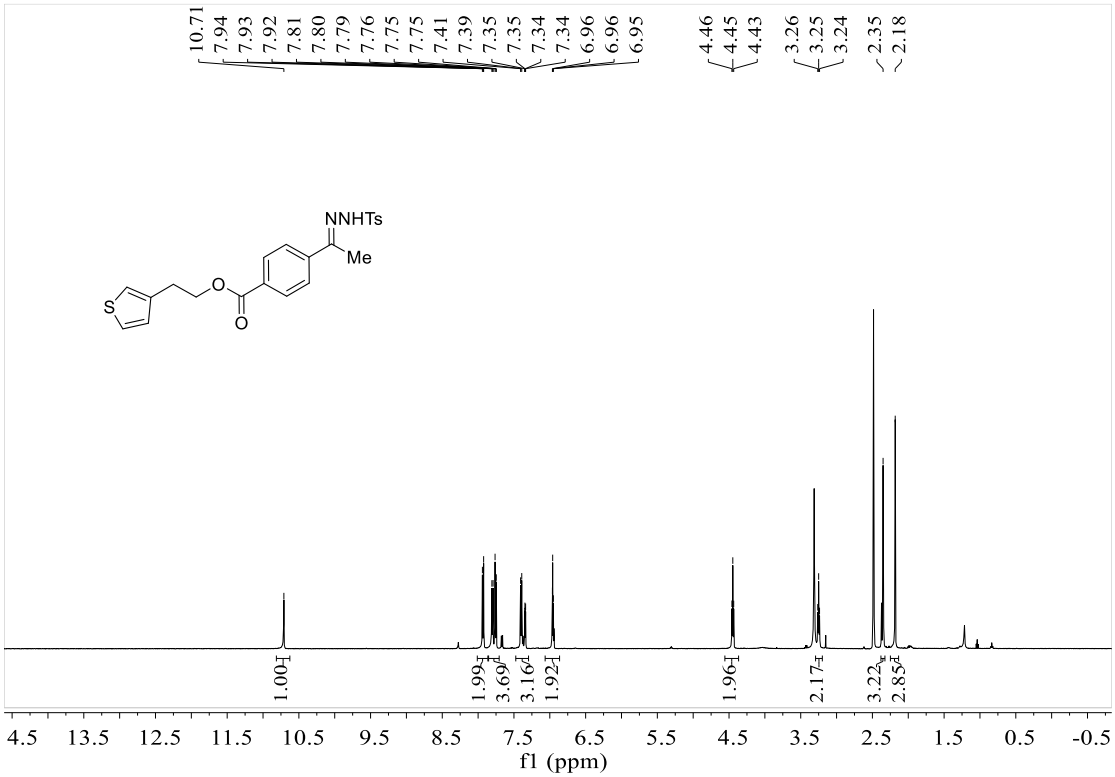


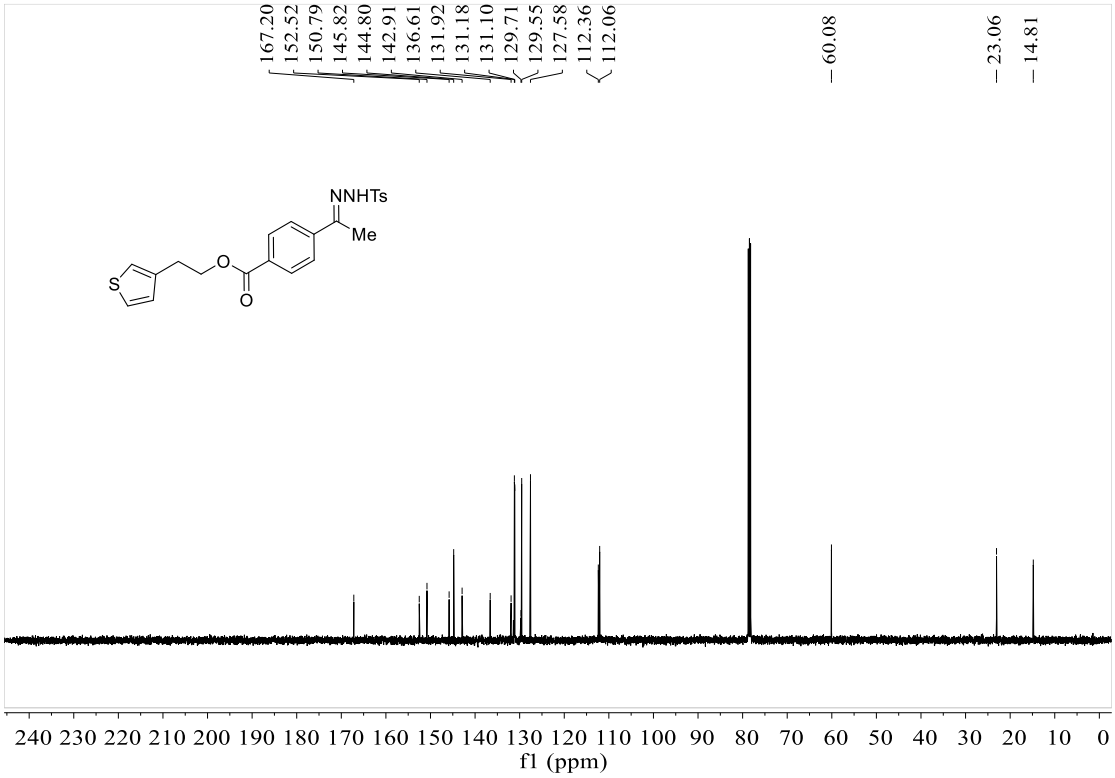
^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (126 MHz, $CDCl_3$) spectra for 34b:



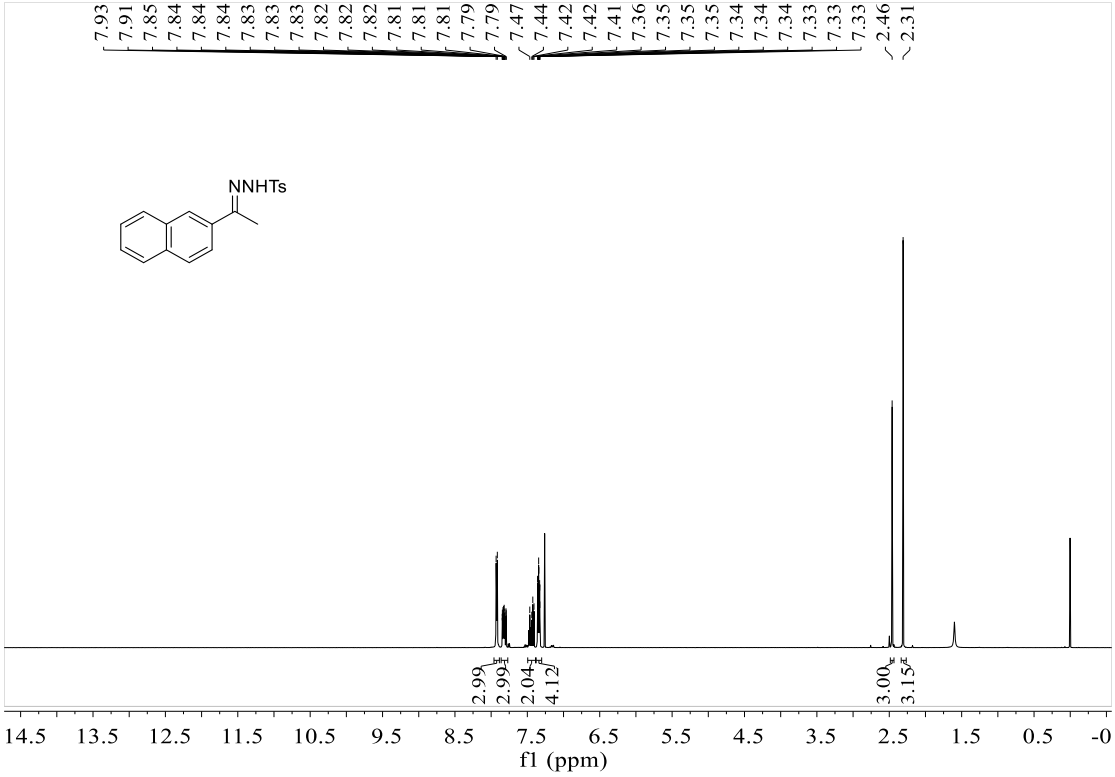


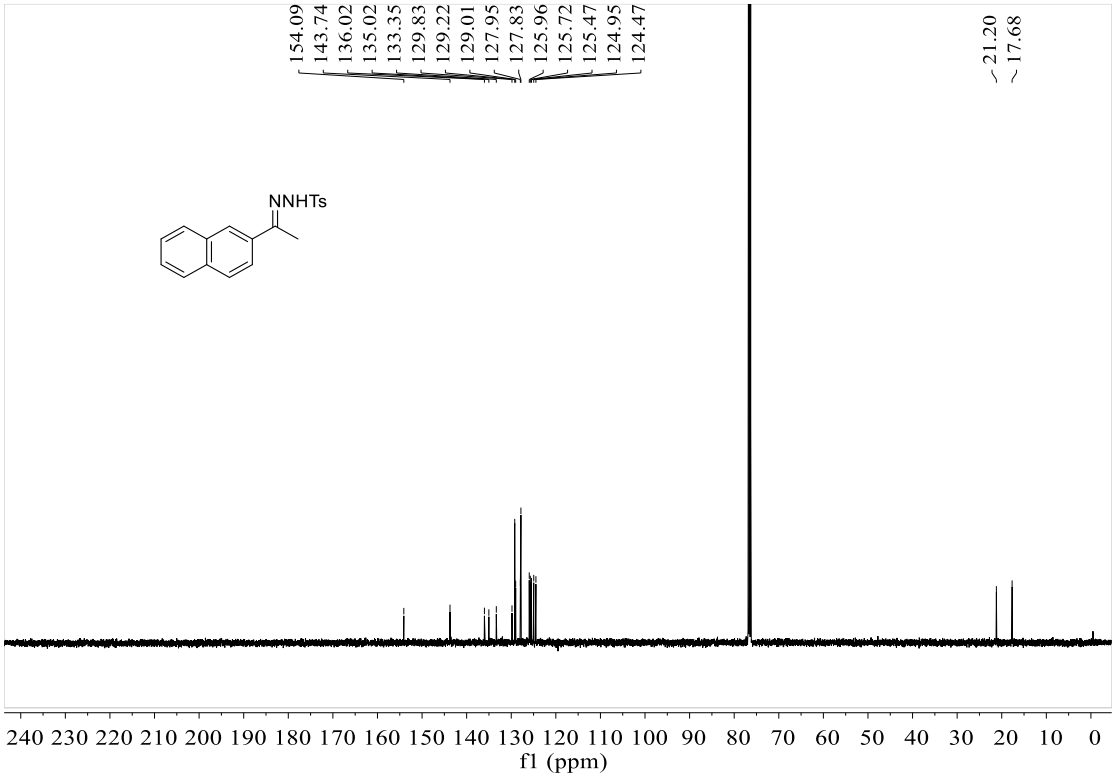
^{1}H NMR (500 MHz, DMSO-*d*$_6$) and ^{13}C NMR (126 MHz, CDCl$_3$) spectra for 35b:



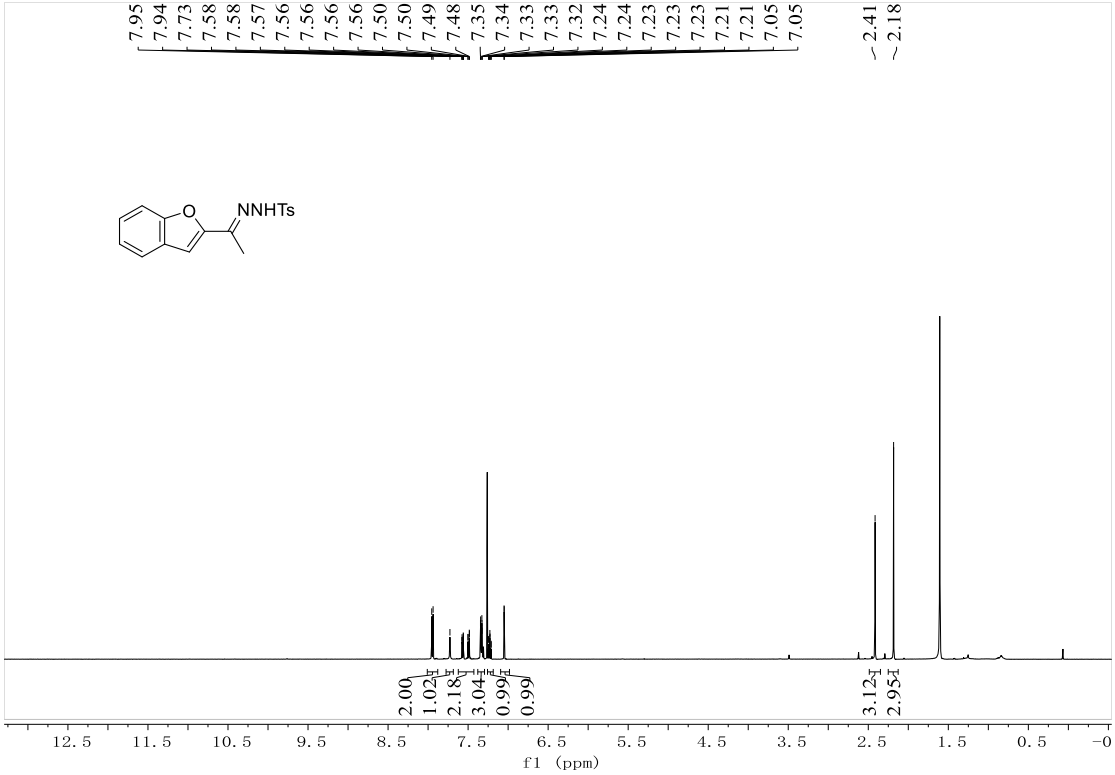


^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (126 MHz, $CDCl_3$) spectra for 33b:

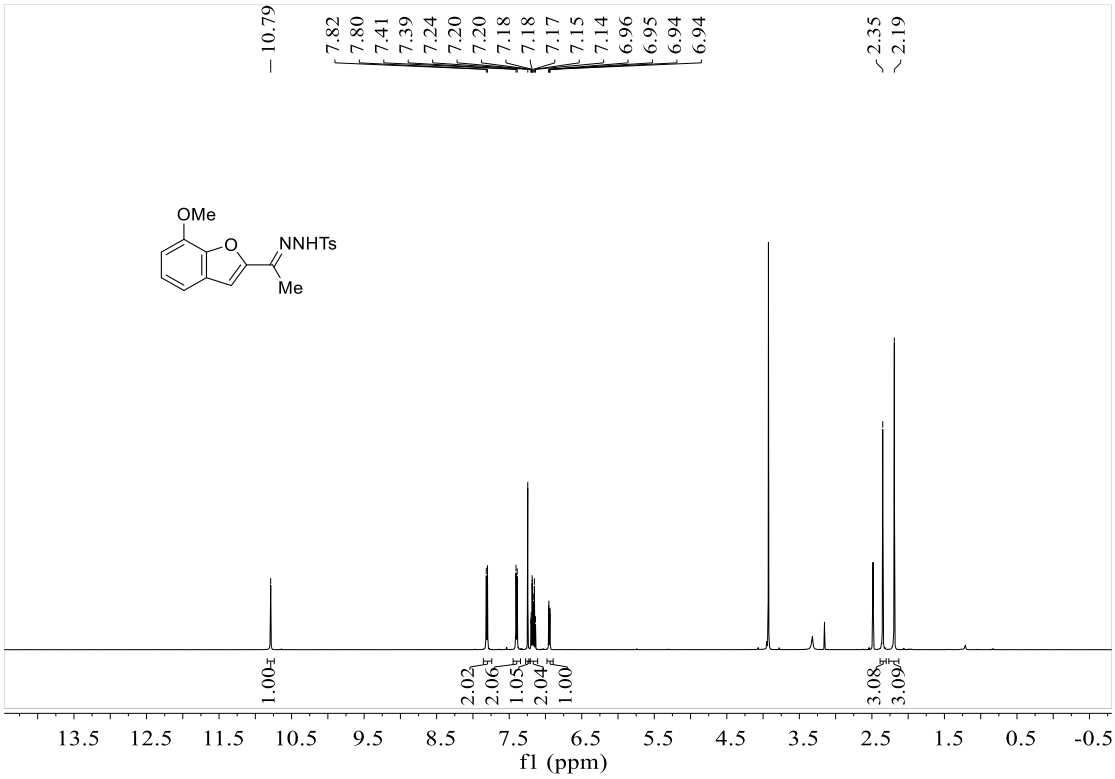


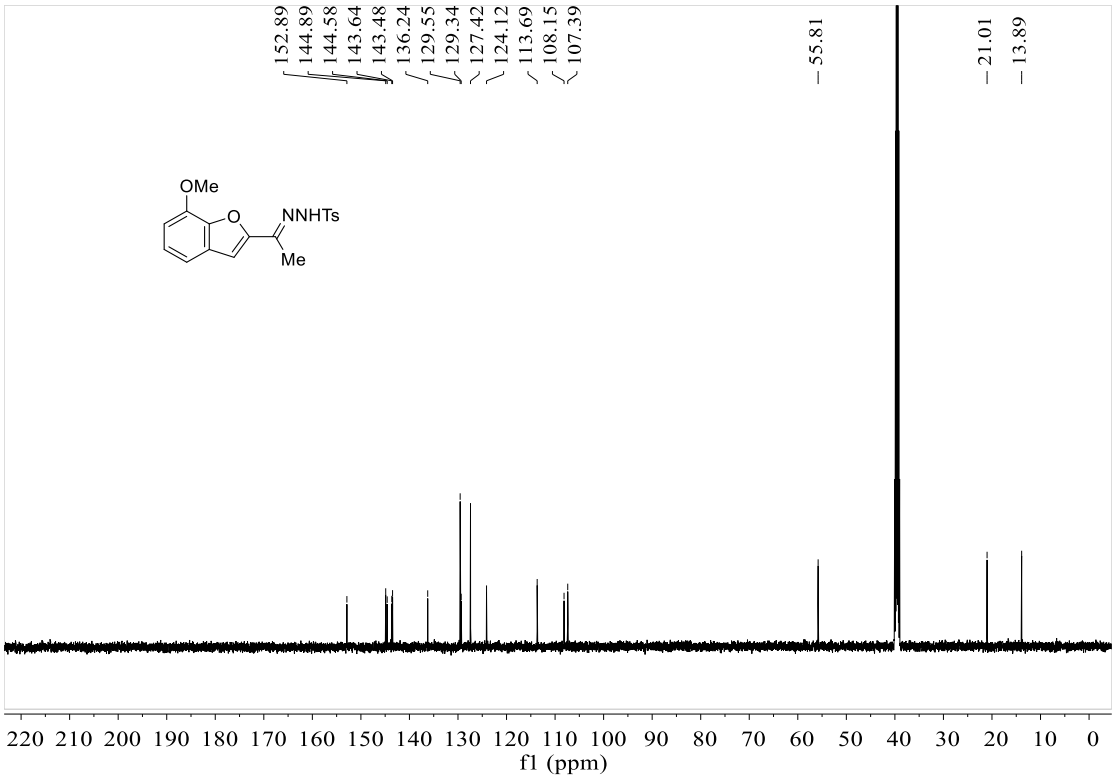


^{1}H NMR (500 MHz, $CDCl_3$) spectra for 36b:

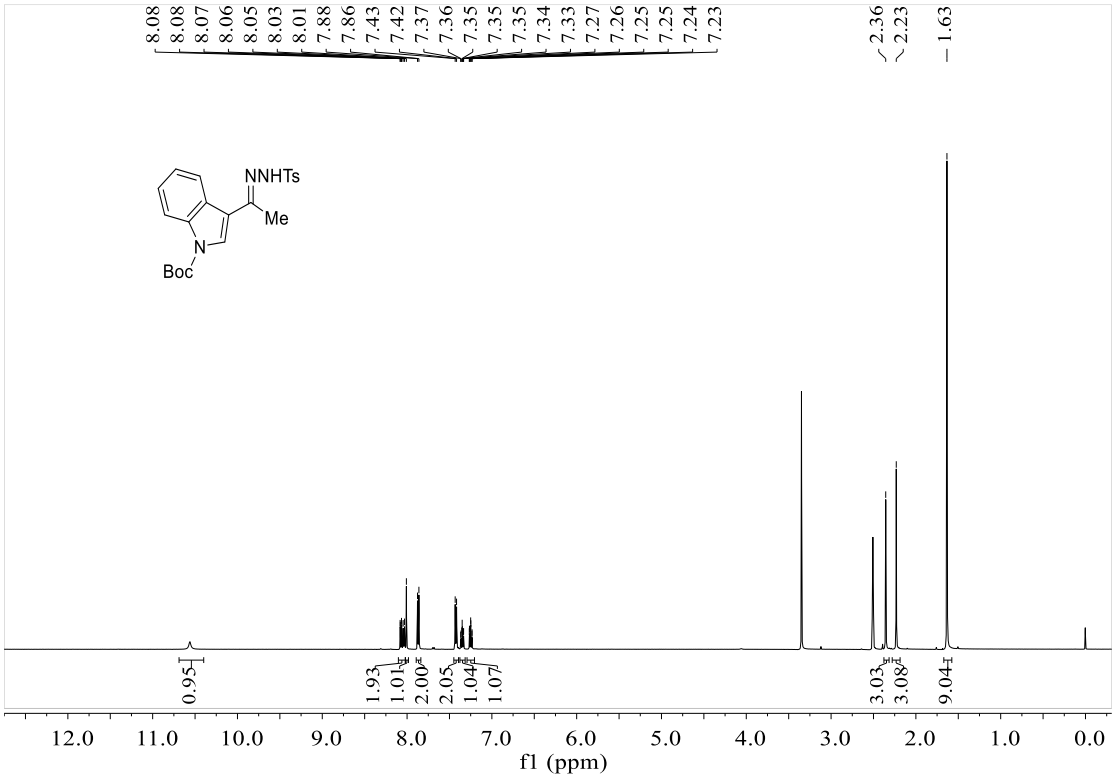


^{1}H NMR (500 MHz, DMSO-d_6) and ^{13}C NMR (126 MHz, DMSO-d_6) spectra for 37b:

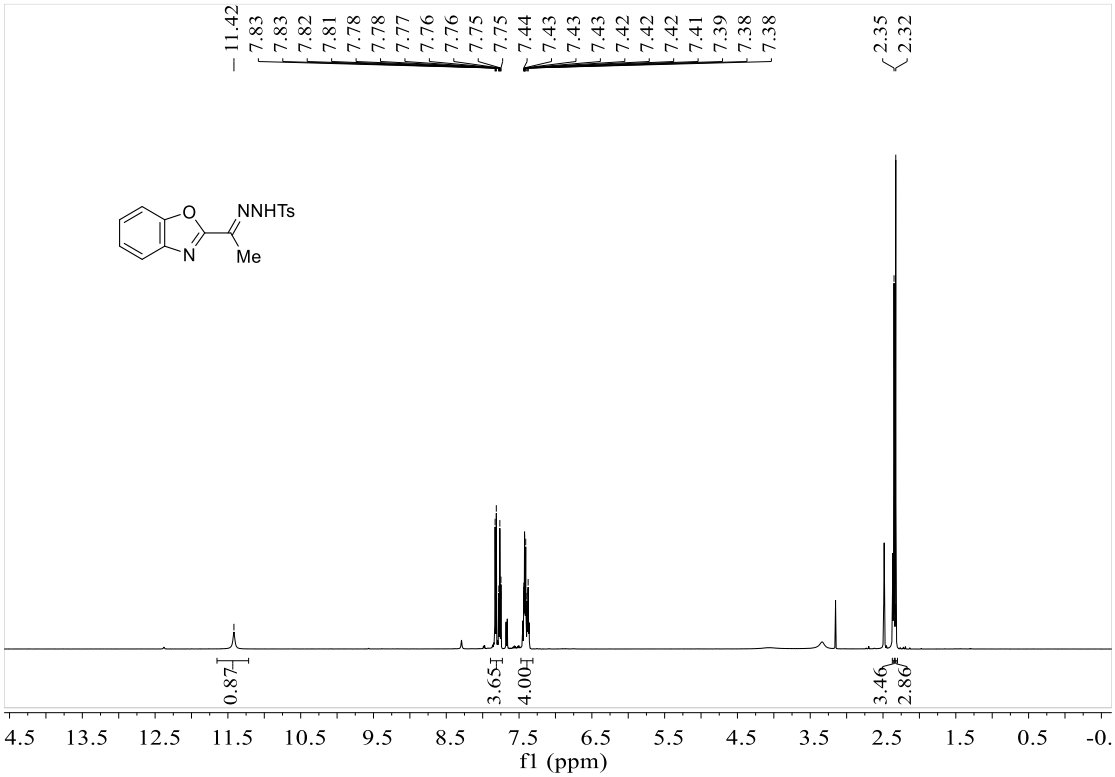


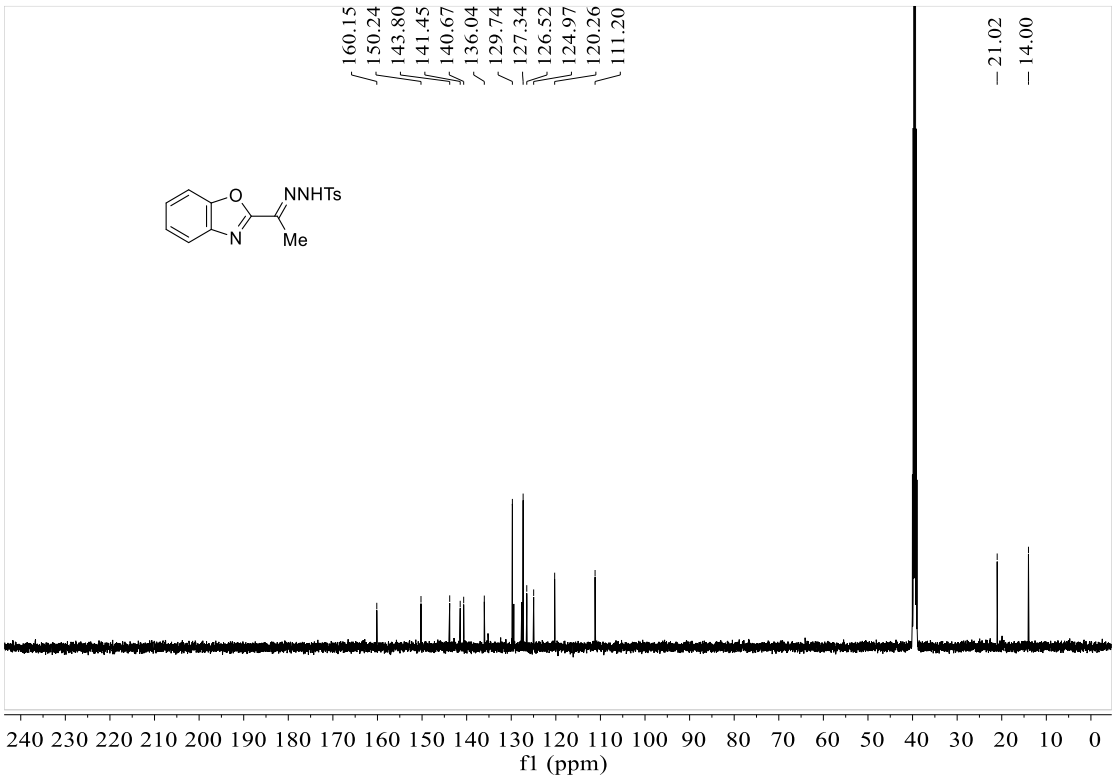


^{1}H NMR (500 MHz, DMSO-d_6) and ^{13}C NMR (126 MHz, DMSO-d_6) spectra for 38b:

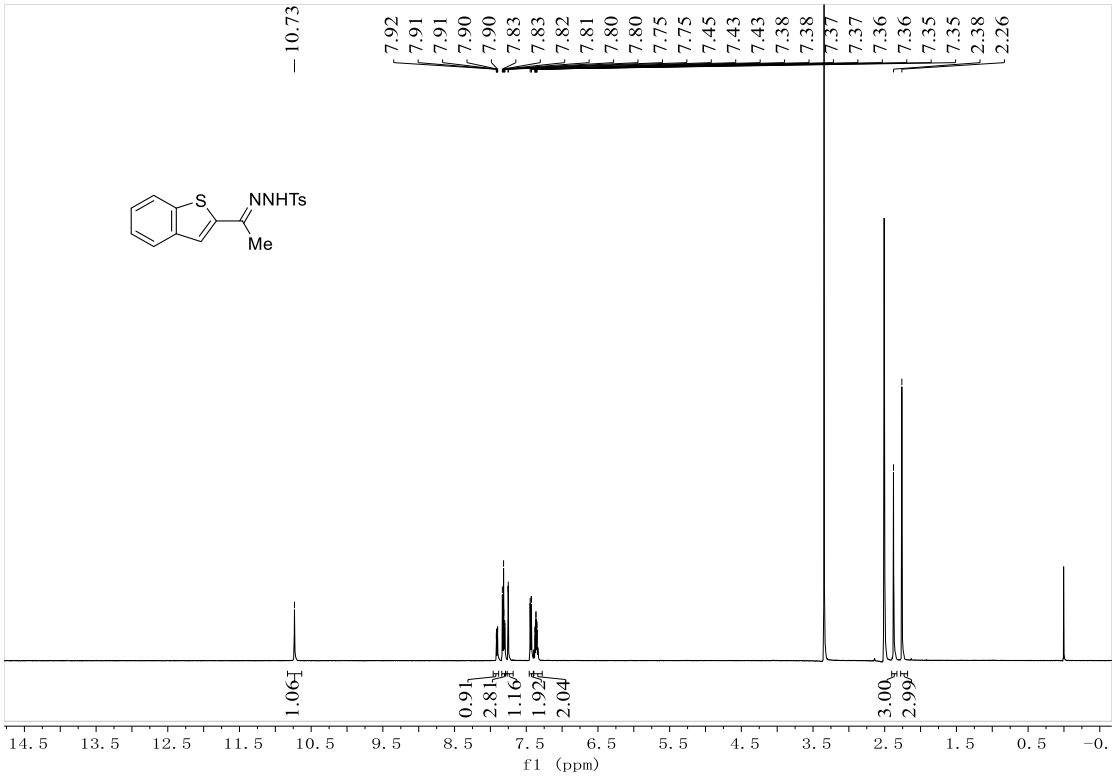


^{1}H NMR (500 MHz, DMSO-d_6) and ^{13}C NMR (126 MHz, DMSO-d_6) spectra for 39b:

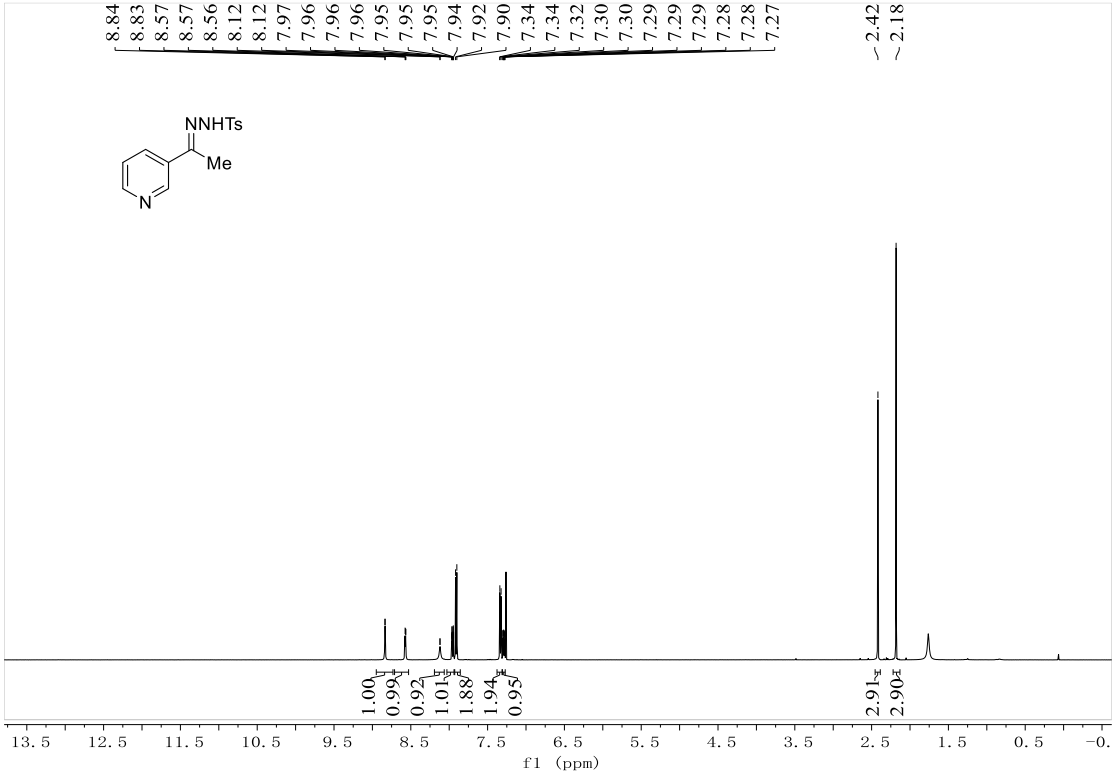




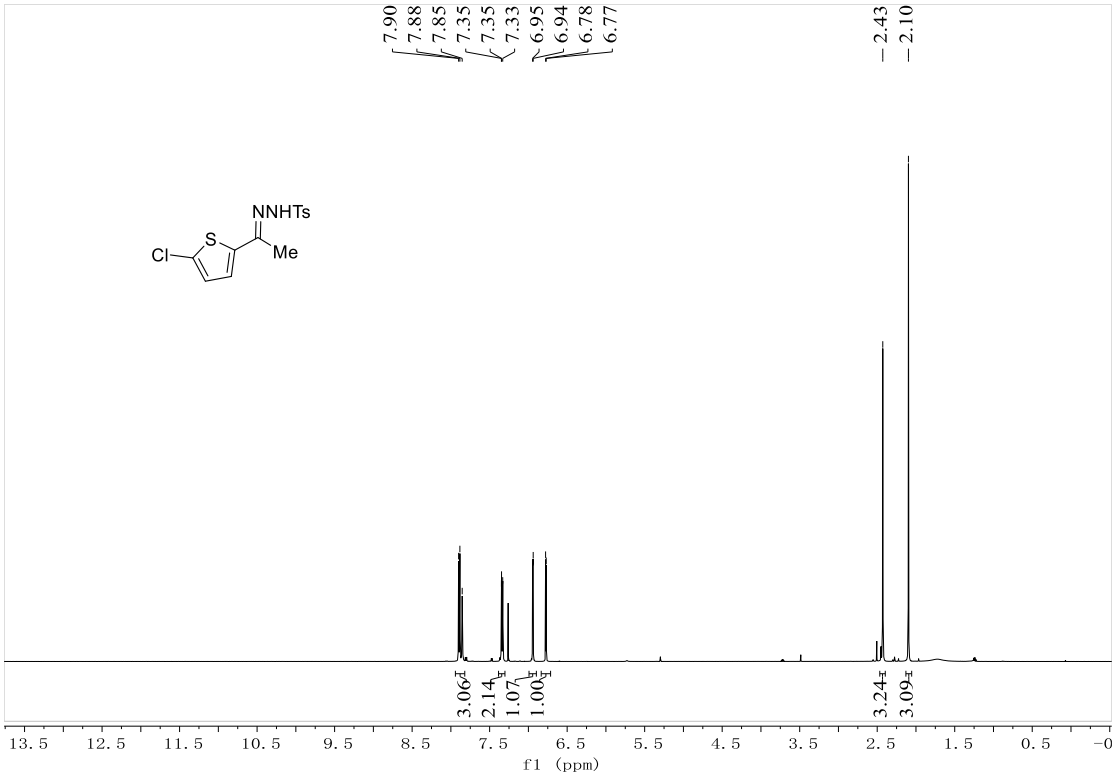
^{1}H NMR (500 MHz, DMSO-d_6) and ^{13}C NMR (126 MHz, DMSO-d_6) spectra for 40b:

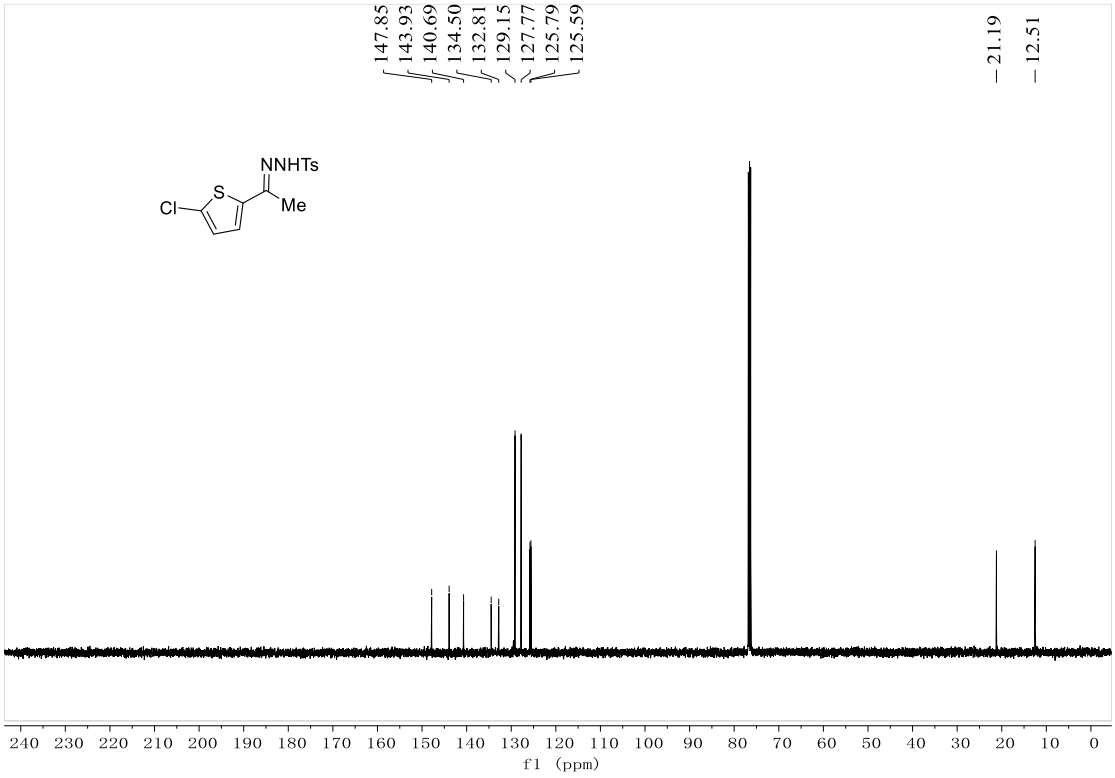


^{1}H NMR (500 MHz, $CDCl_3$) spectra for 41b:

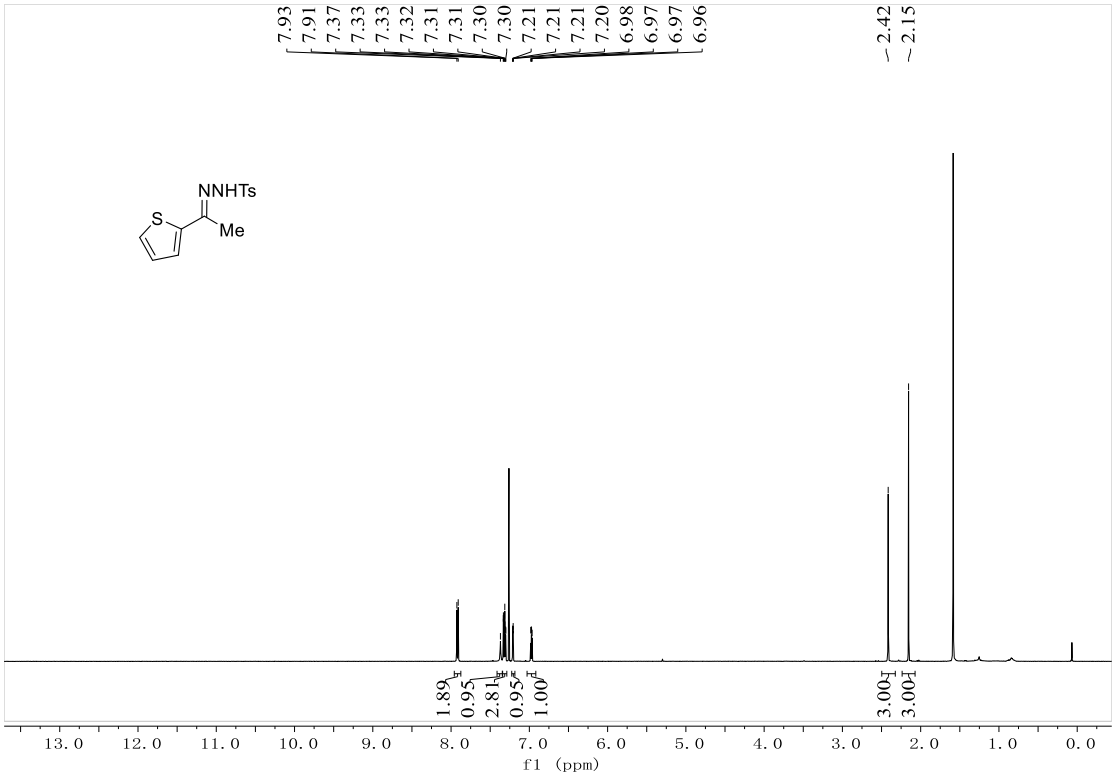


^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (126 MHz, $CDCl_3$) spectra for 43b:

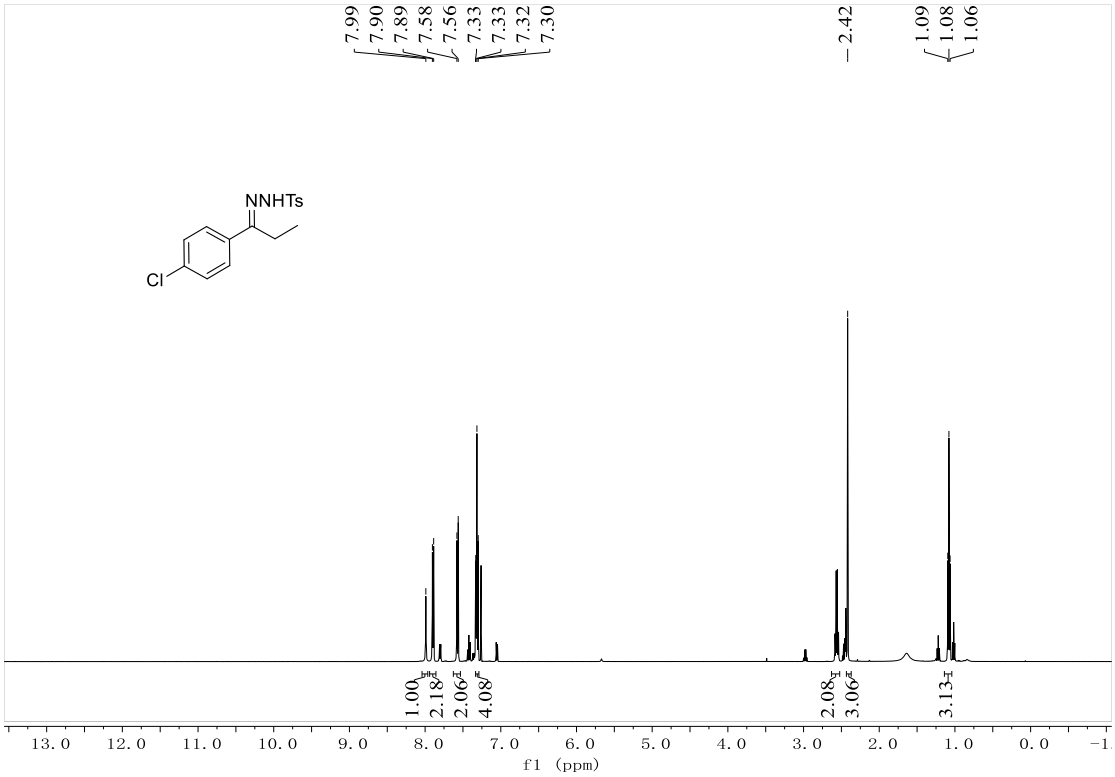




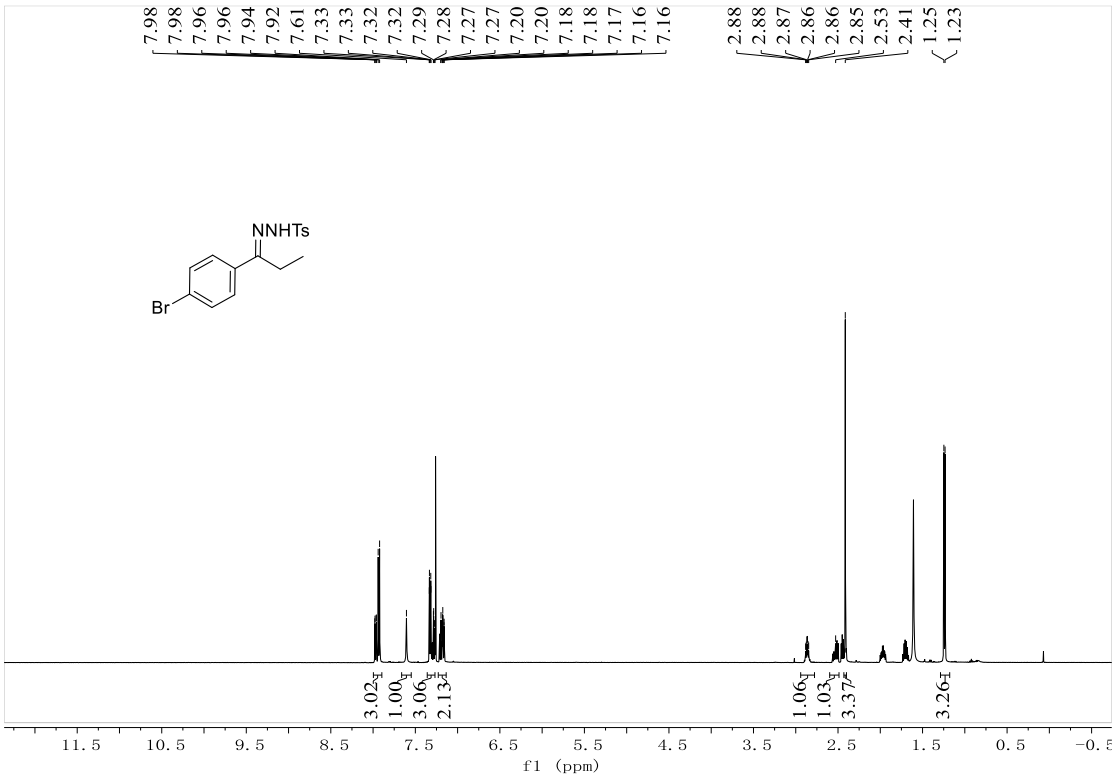
^{1}H NMR (500 MHz, $CDCl_3$) spectra for 44b:



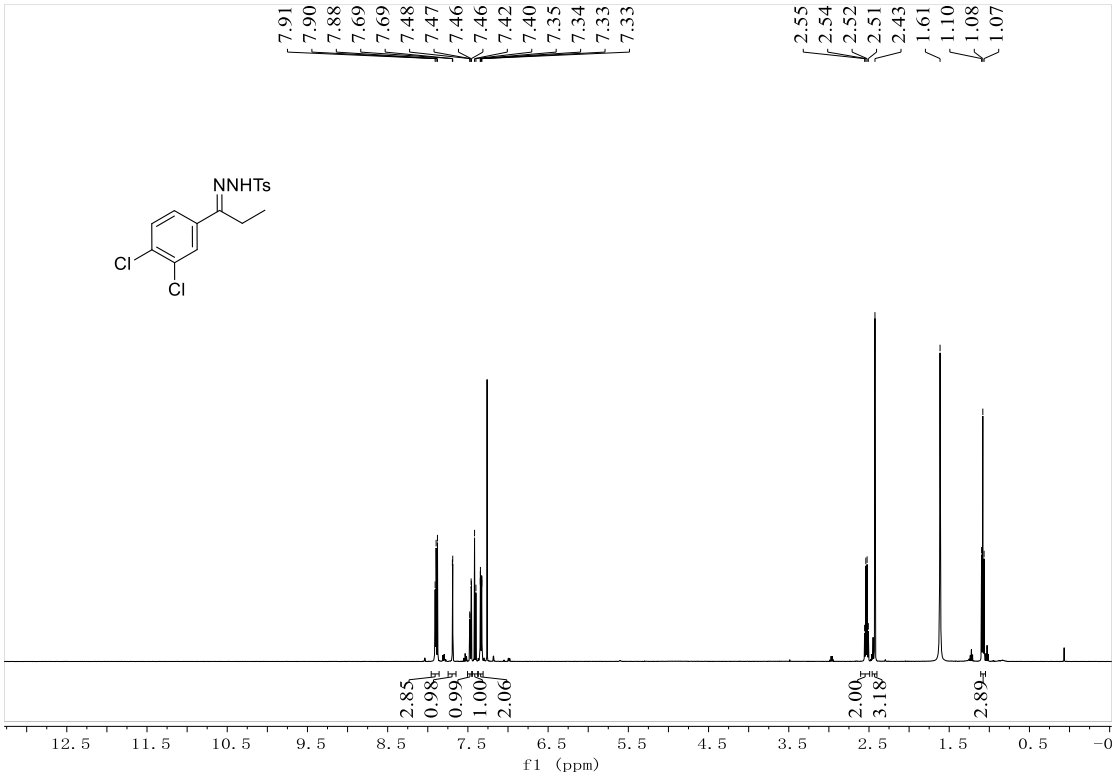
^{1}H NMR (500 MHz, $CDCl_3$) spectra for 45b:



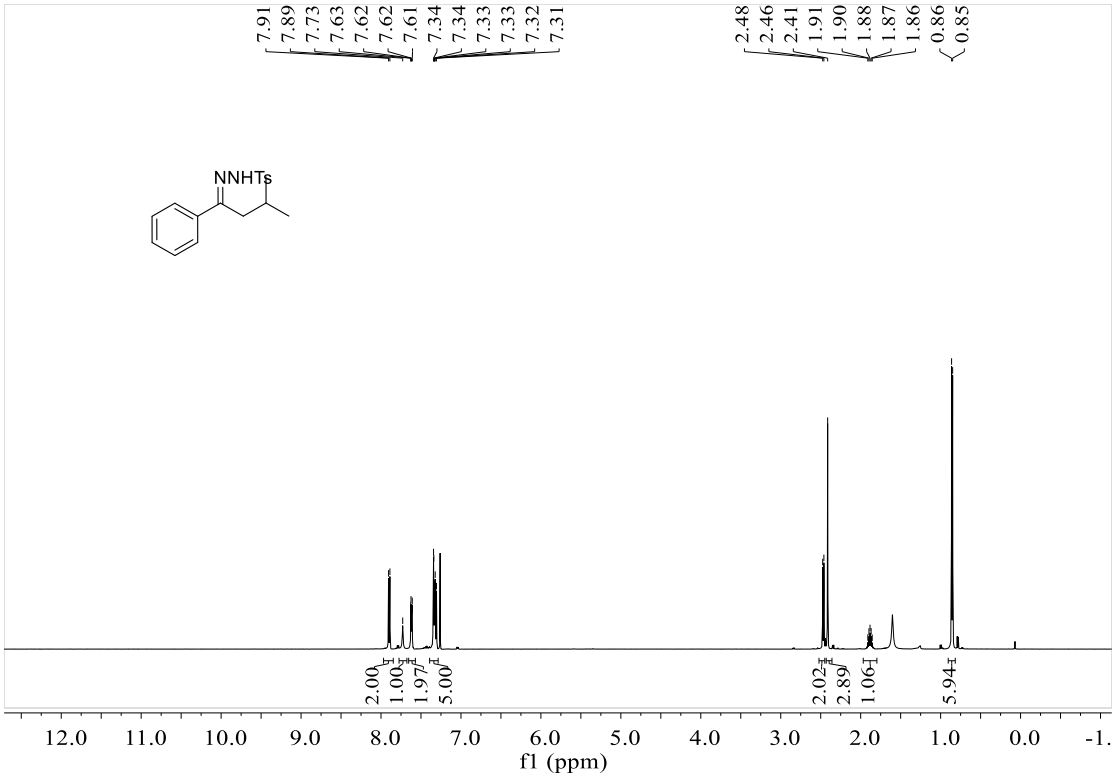
^{1}H NMR (500 MHz, $CDCl_3$) spectra for 46b:



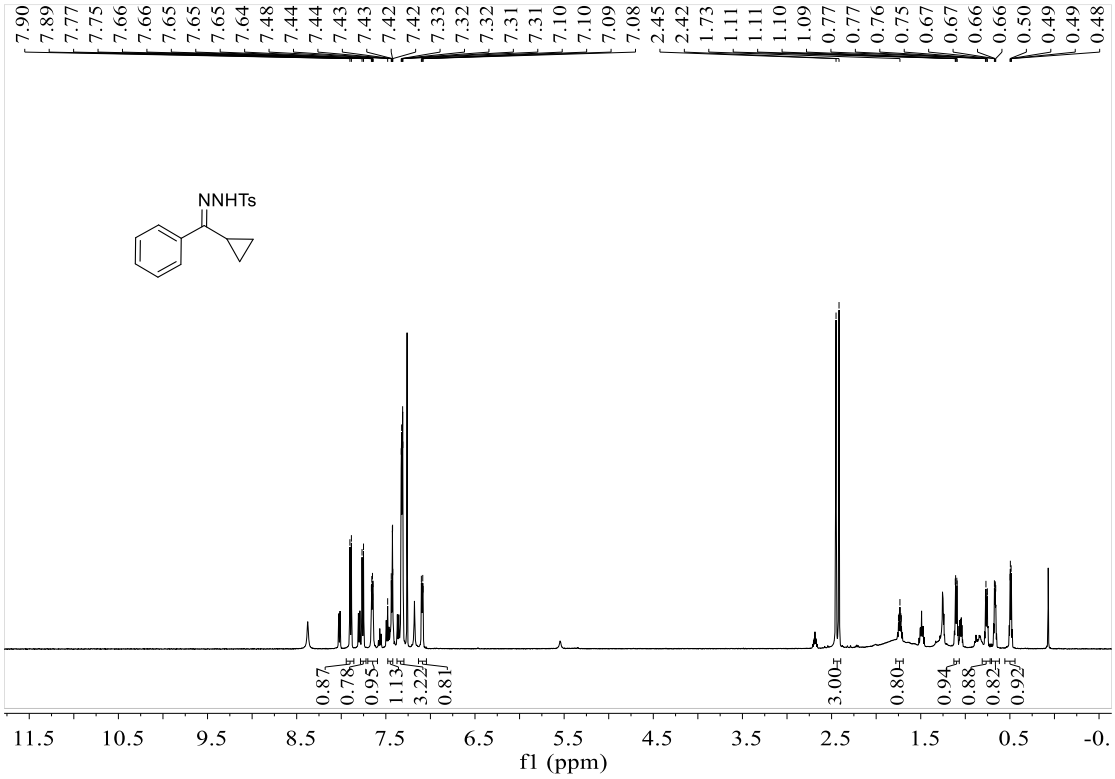
^{1}H NMR (500 MHz, $CDCl_3$) spectra for 47b:



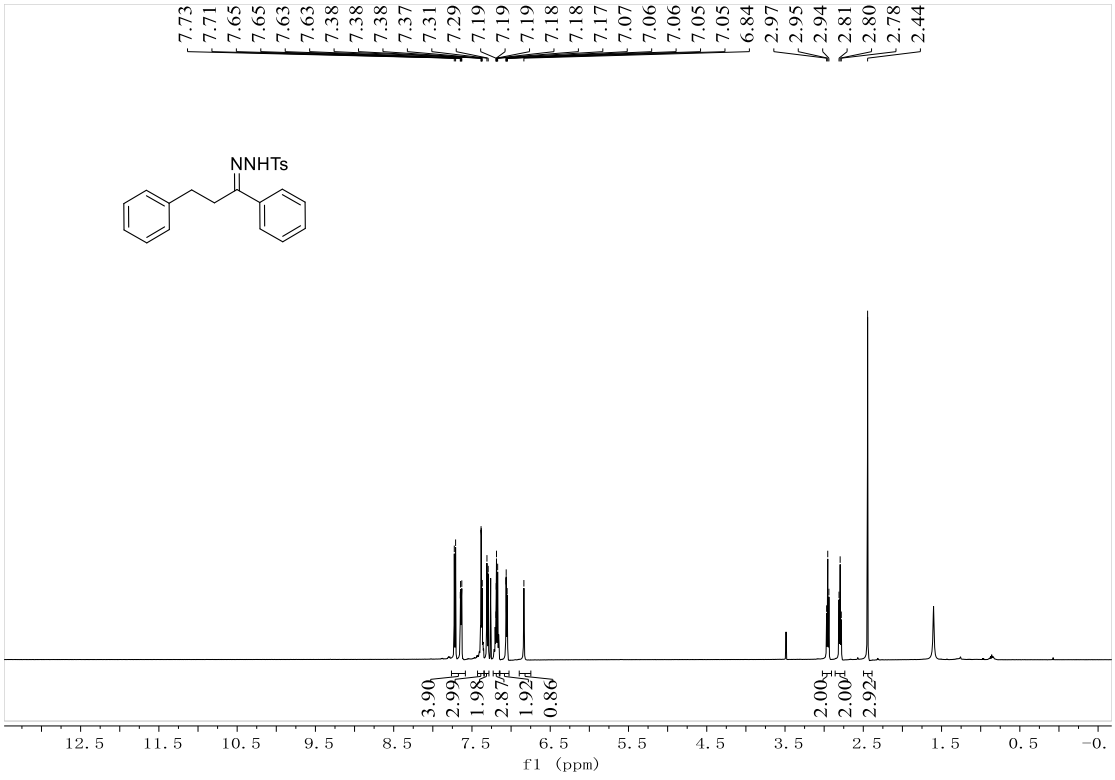
^{1}H NMR (500 MHz, $CDCl_3$) spectra for 48b:



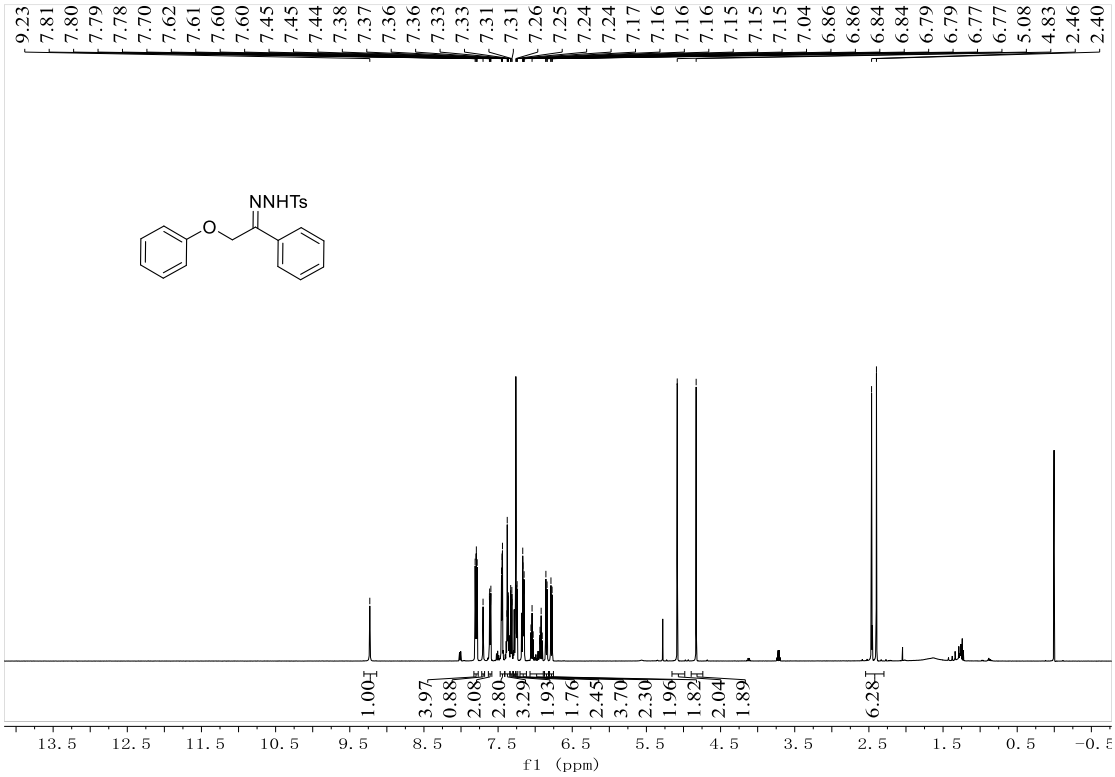
^{1}H NMR (500 MHz, $CDCl_3$) spectra for 50b:

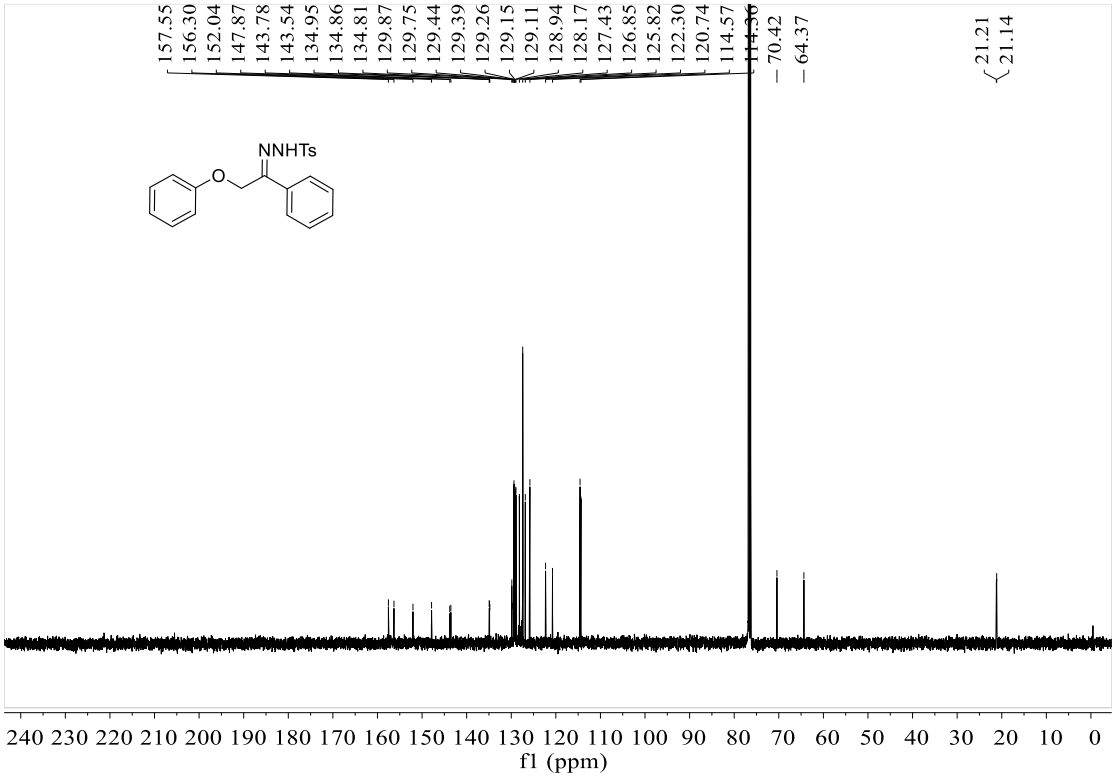


^{1}H NMR (500 MHz, $CDCl_3$) spectra for 51b:

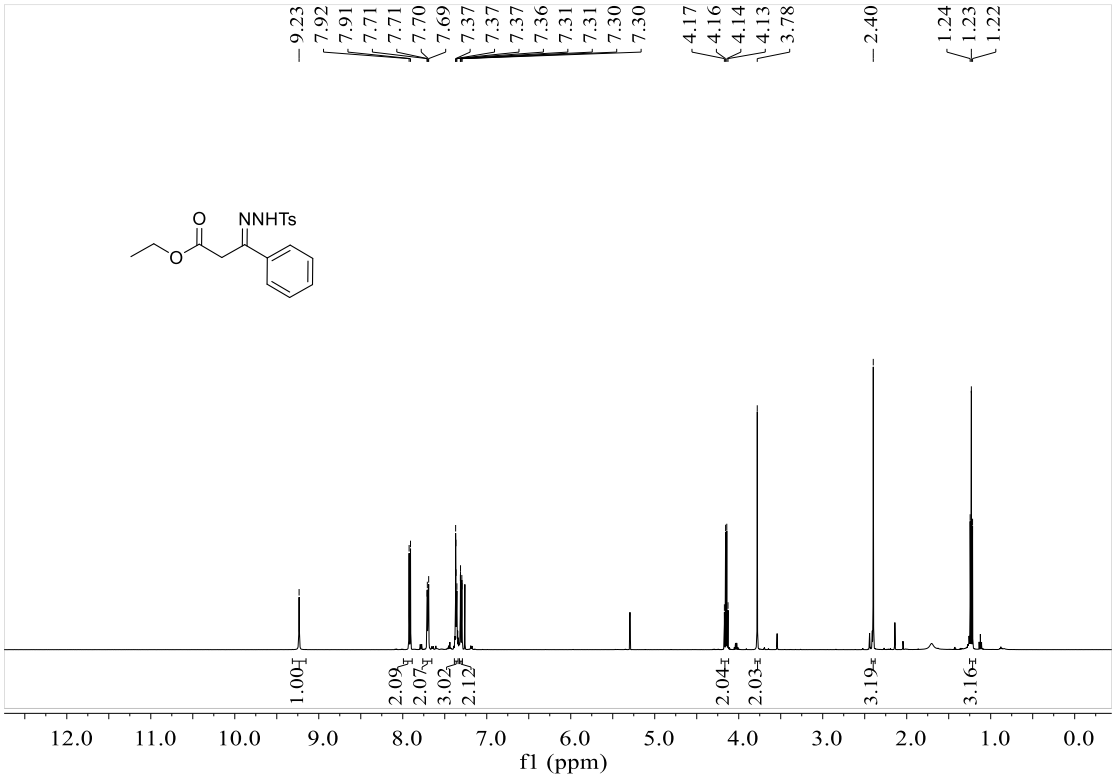


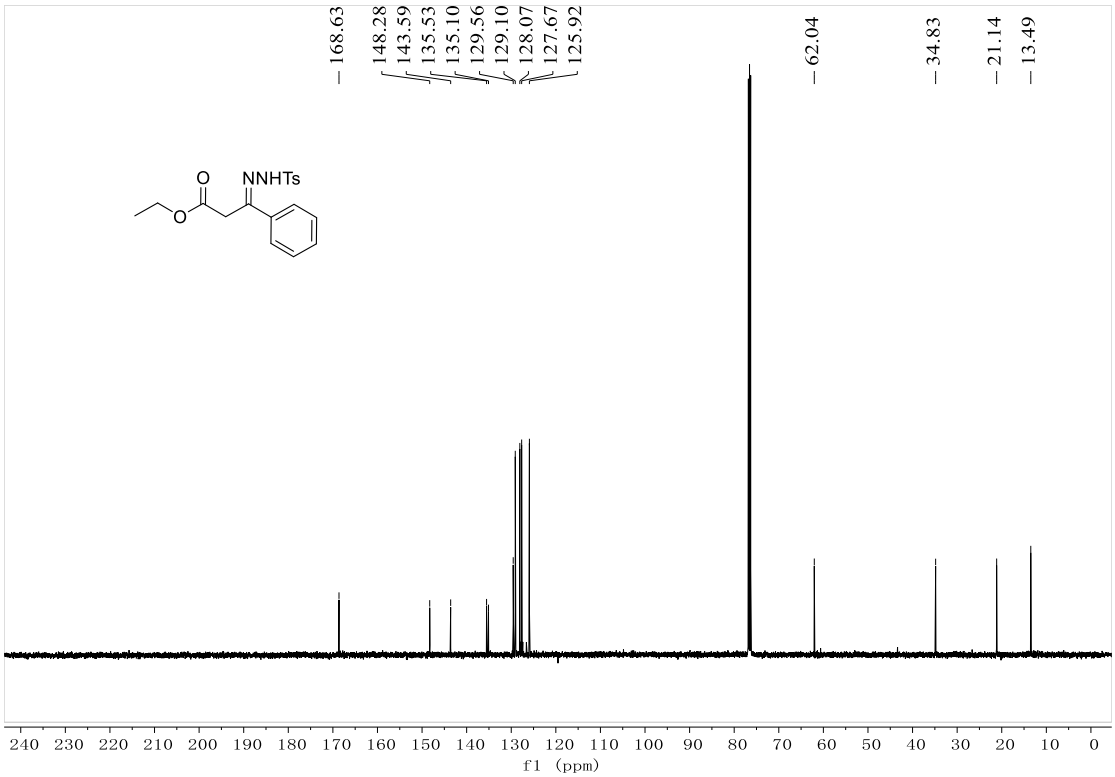
^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (126 MHz, $CDCl_3$) spectra for 52b:



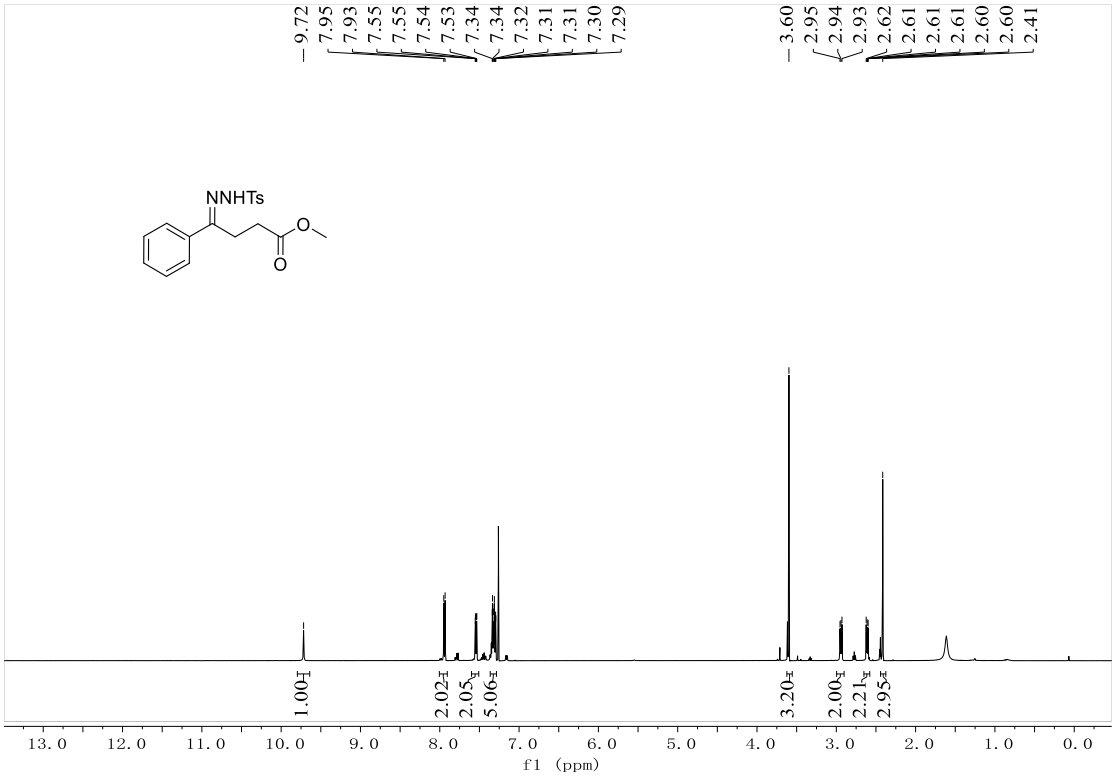


^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (126 MHz, $CDCl_3$) spectra for 53b:

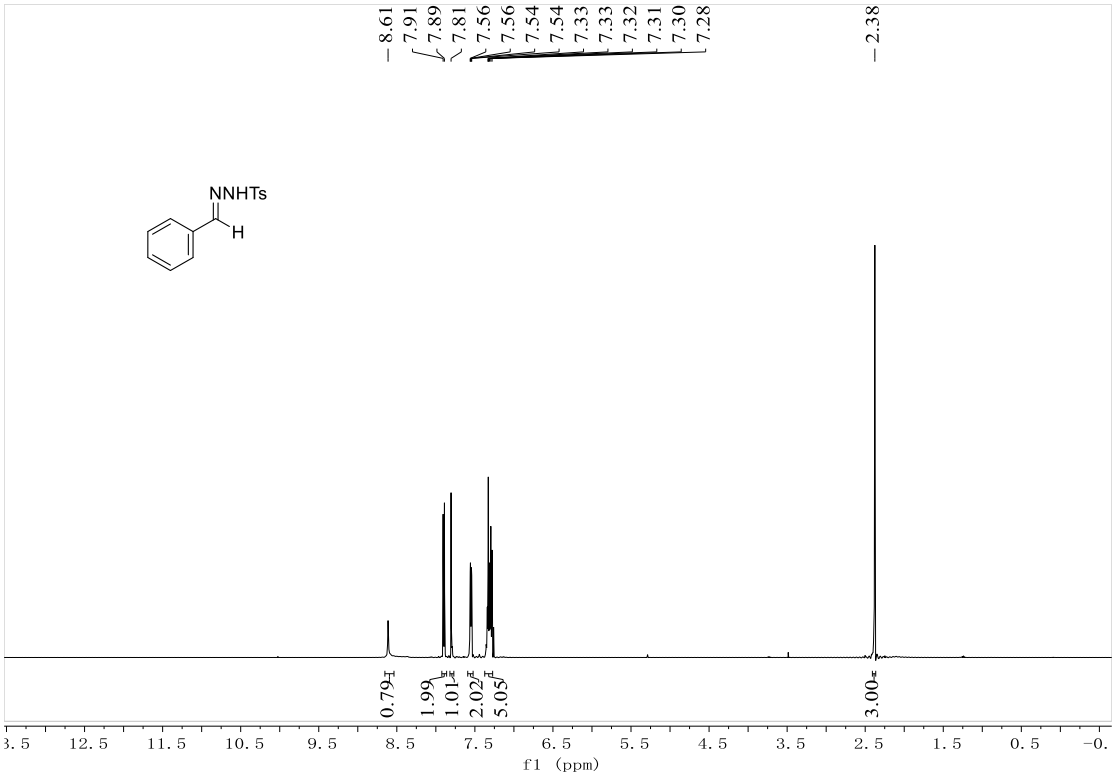


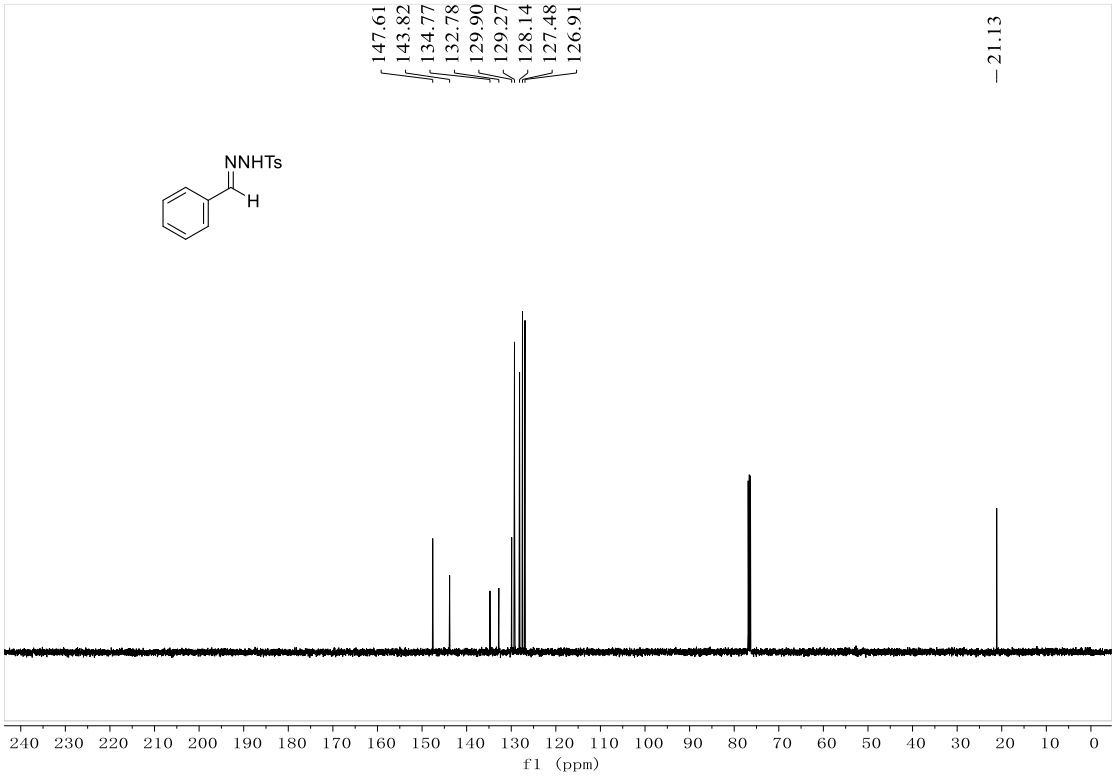


^{1}H NMR (500 MHz, $CDCl_3$) spectra for 54b:

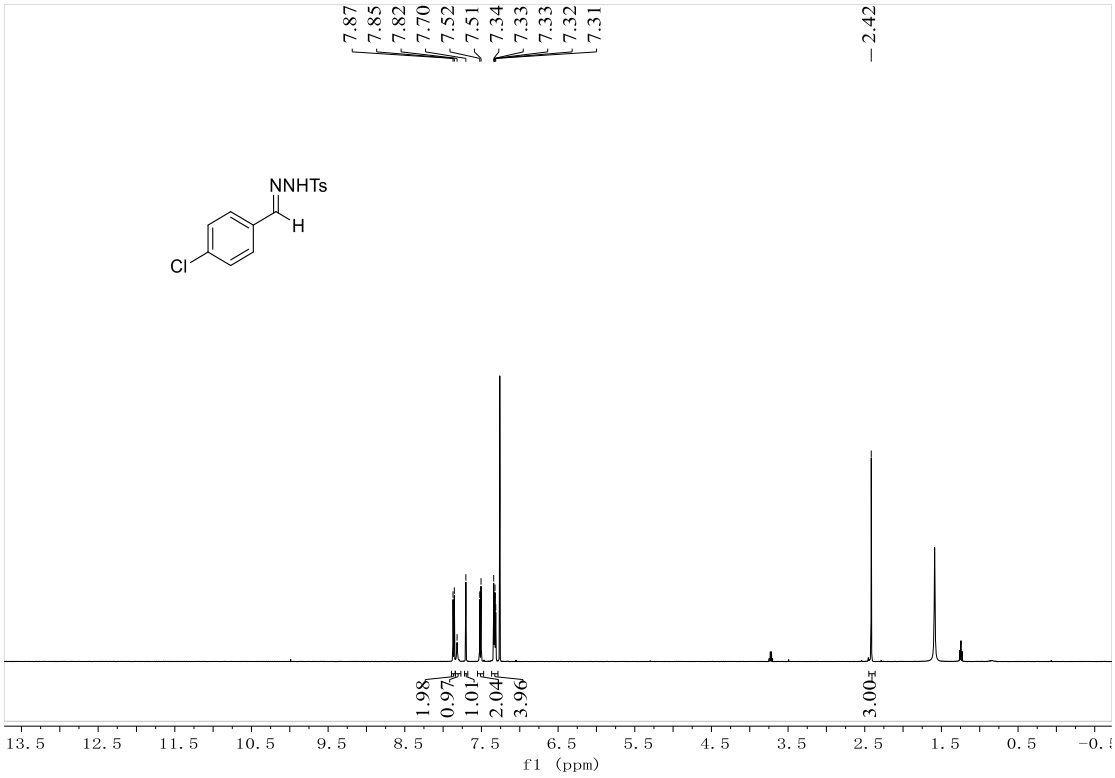


^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (126 MHz, $CDCl_3$) spectra for 55b:

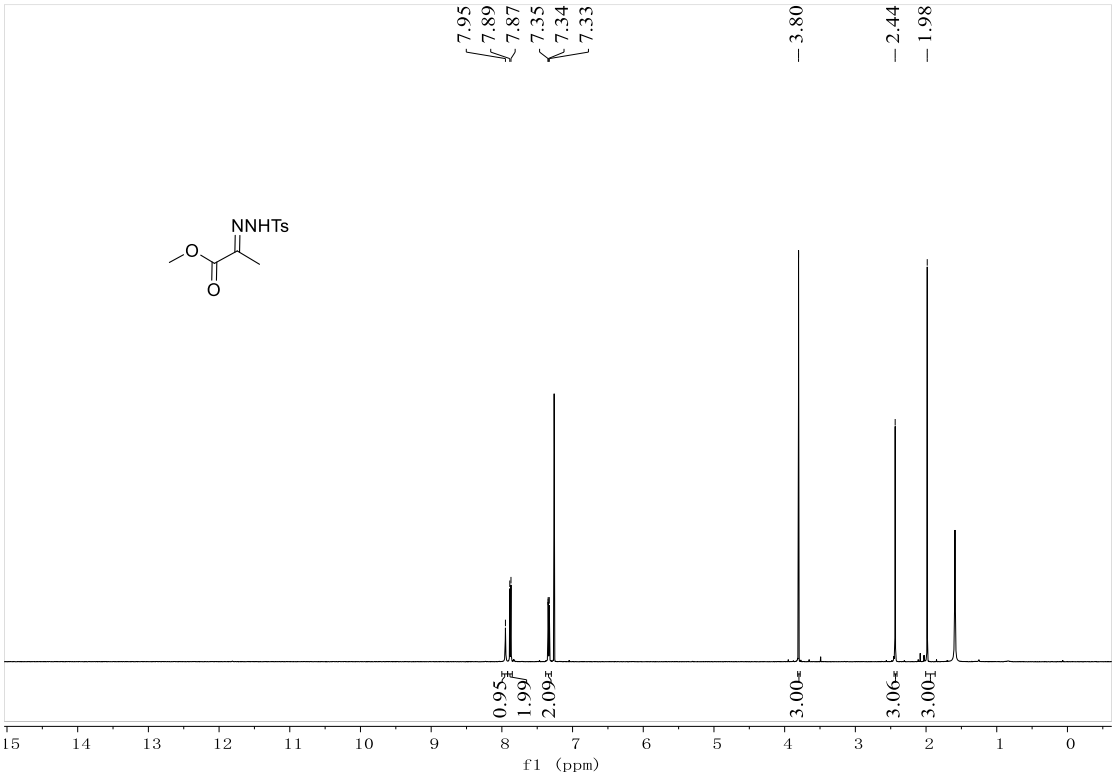




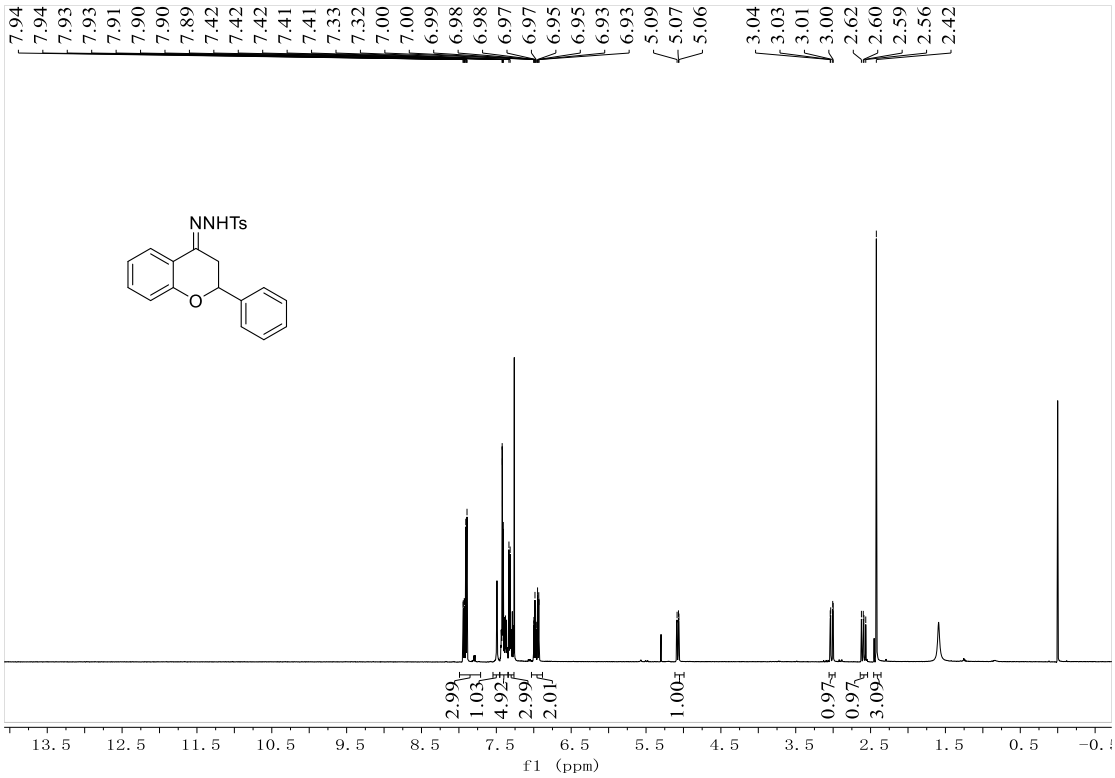
^{1}H NMR (500 MHz, $CDCl_3$) spectra for 56b:



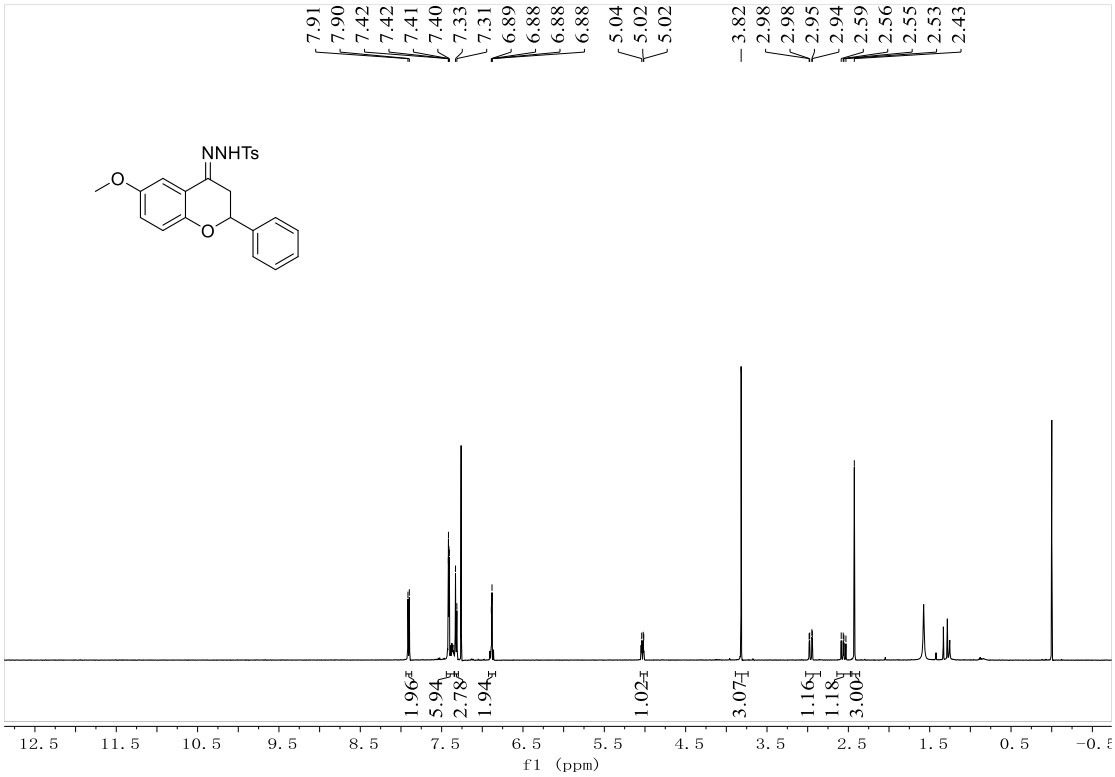
^{1}H NMR (500 MHz, $CDCl_3$) spectra for 57b:



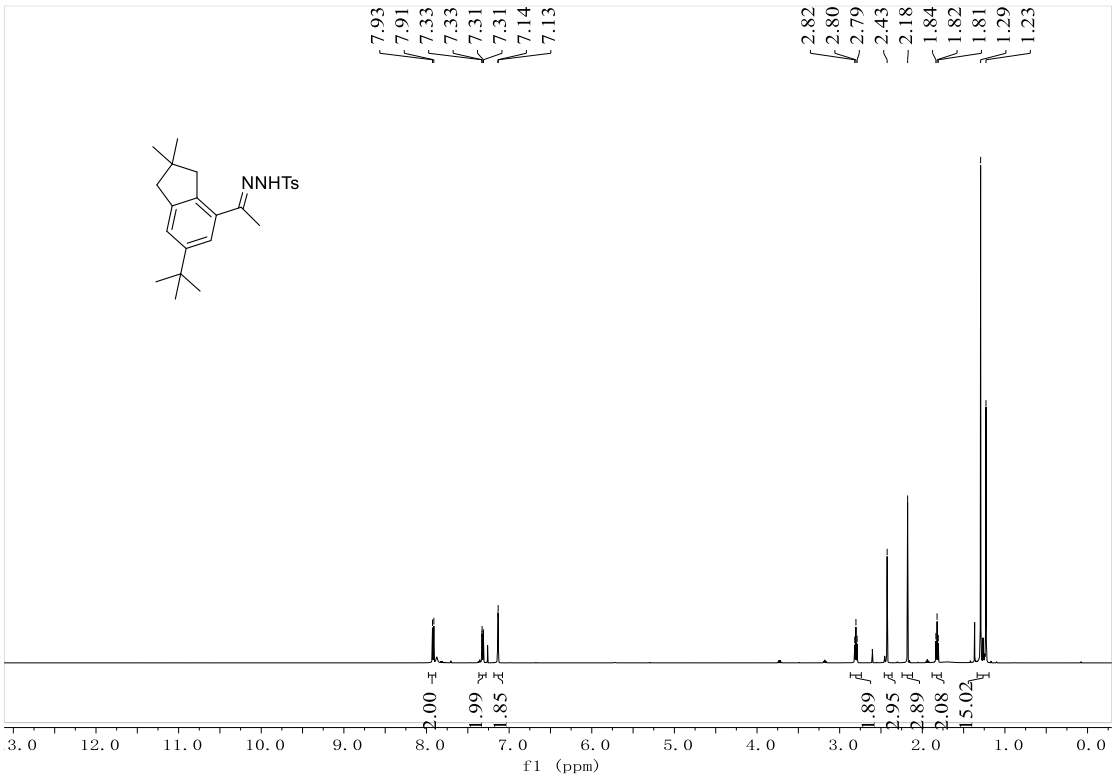
^{1}H NMR (500 MHz, $CDCl_3$) spectra for 88b:

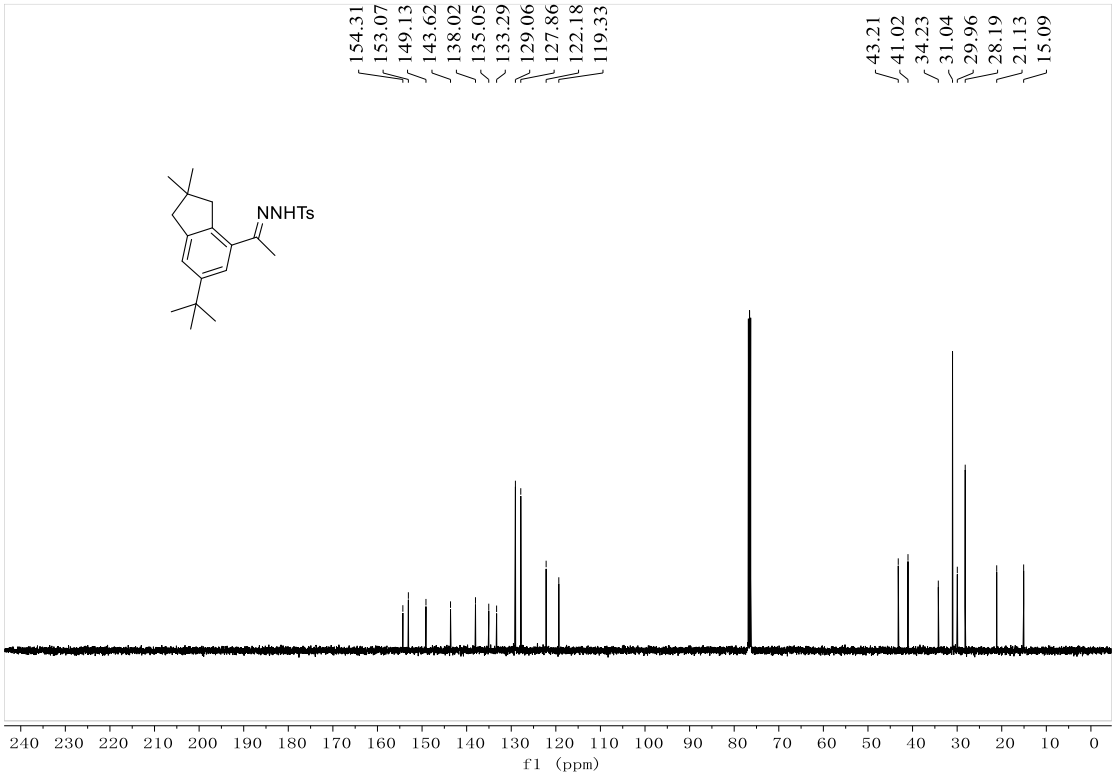


^{1}H NMR (500 MHz, $CDCl_3$) spectra for 89b:

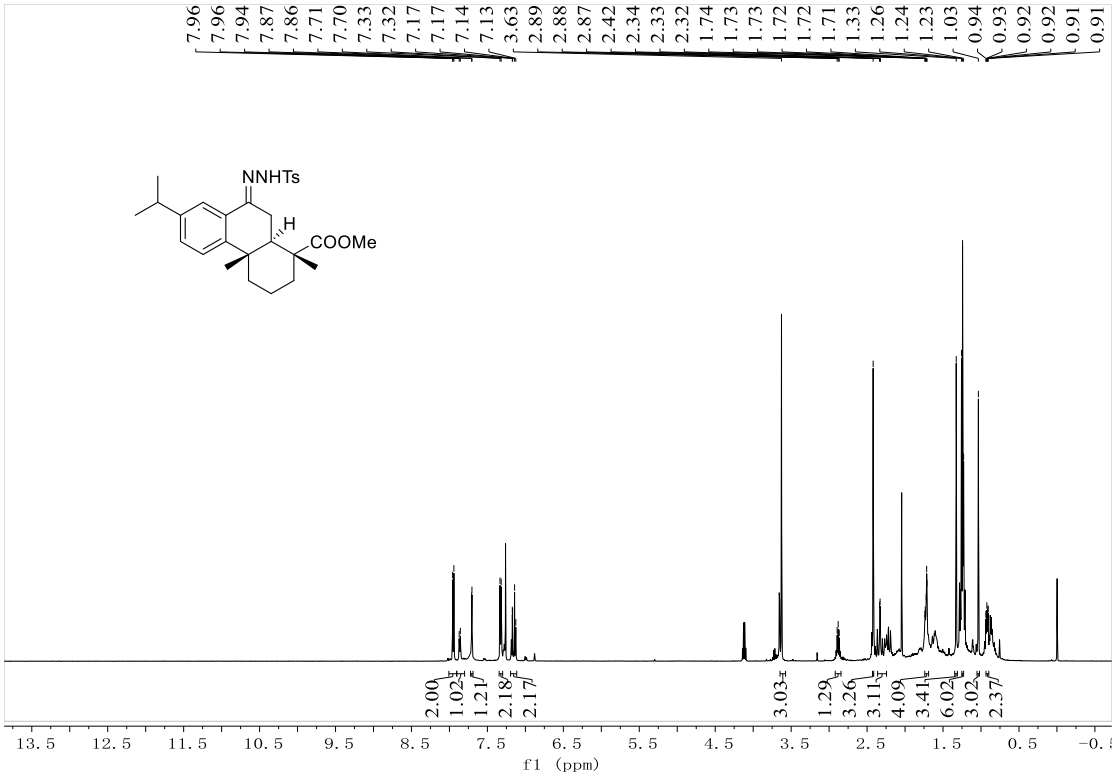


^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (126 MHz, $CDCl_3$) spectra for 90b:

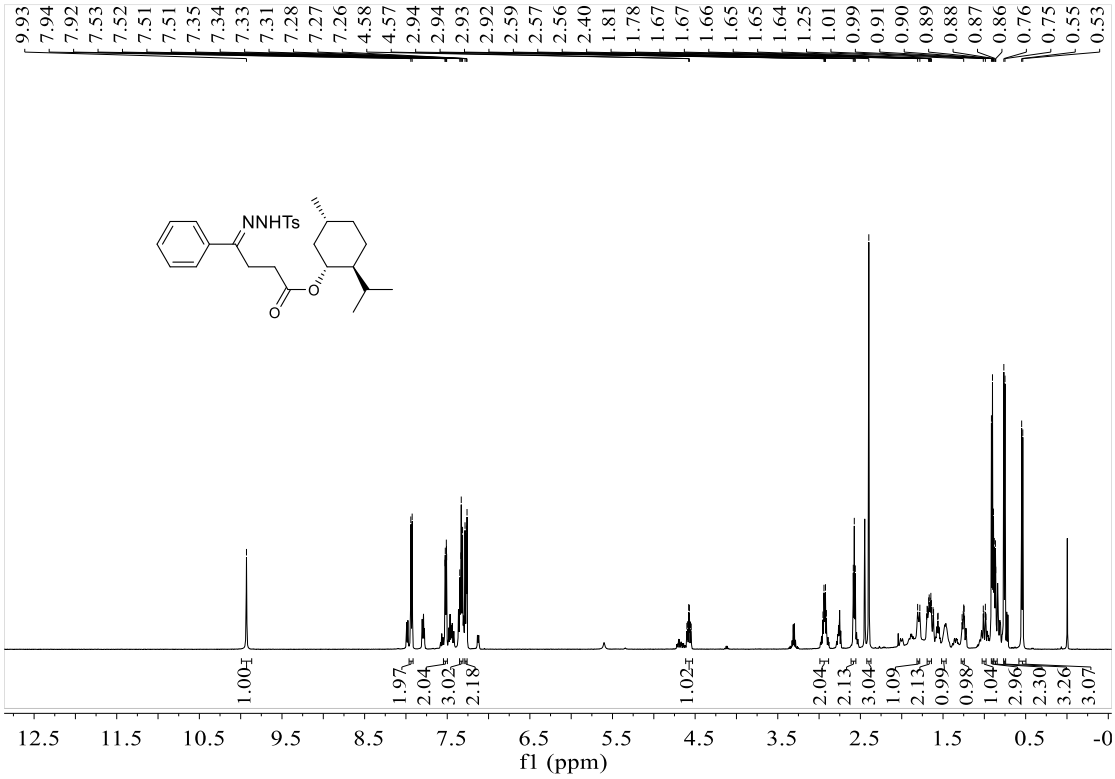


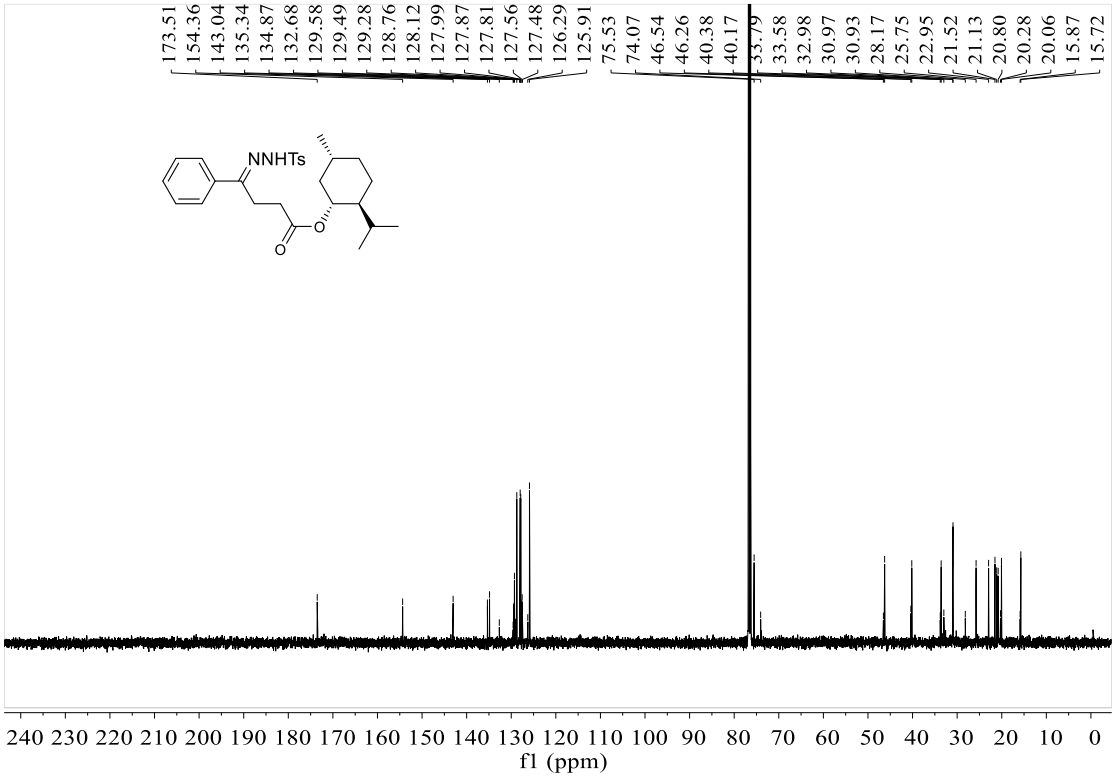


^{1}H NMR (500 MHz, $CDCl_3$) spectra for 91b:

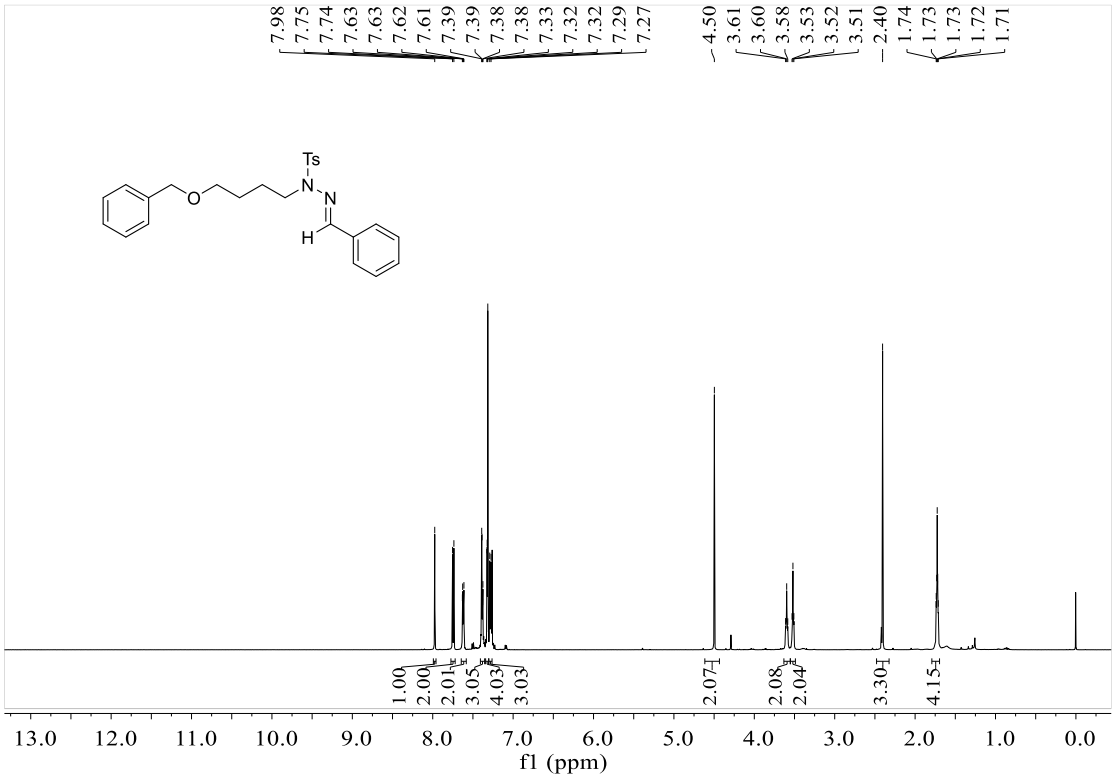


^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (126 MHz, $CDCl_3$) spectra for 92b:

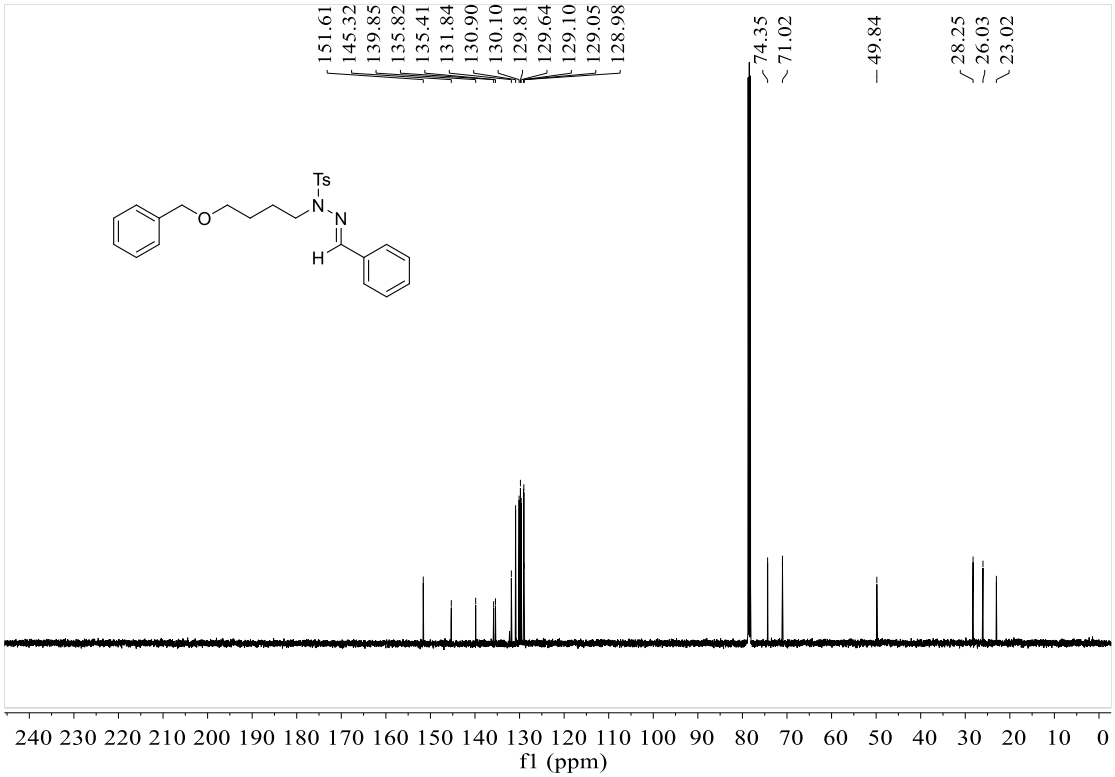




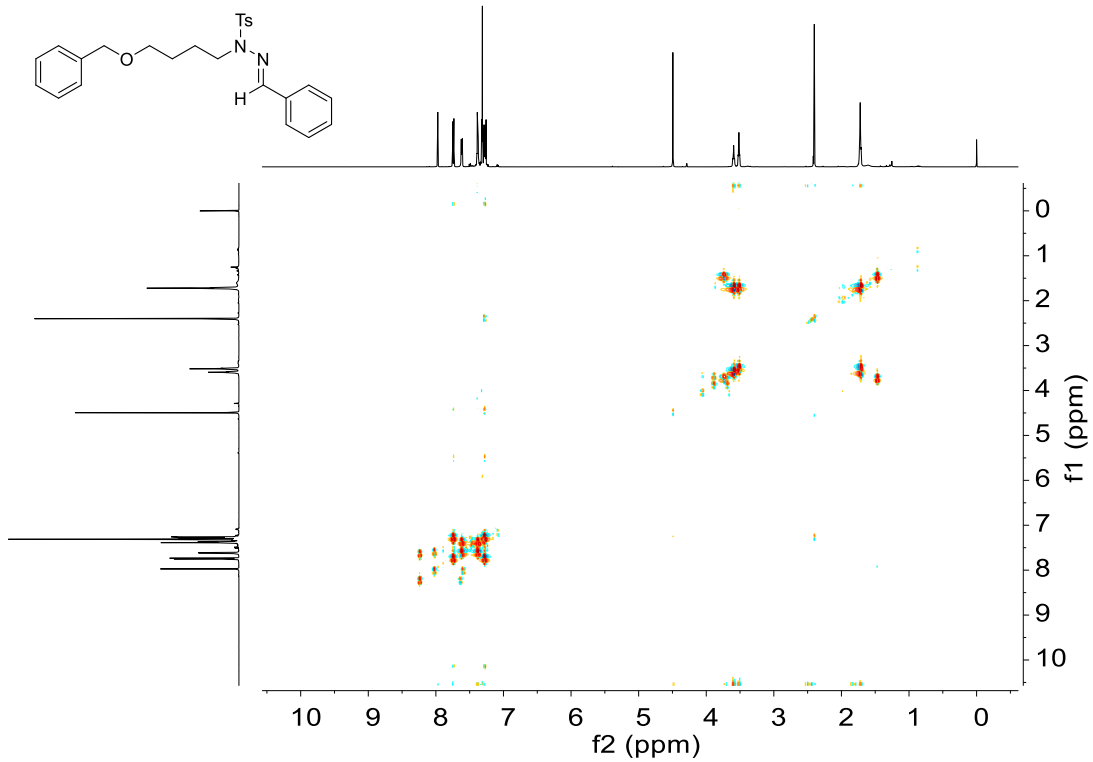
^{1}H NMR (500 MHz, $CDCl_3$) spectra for 55e:



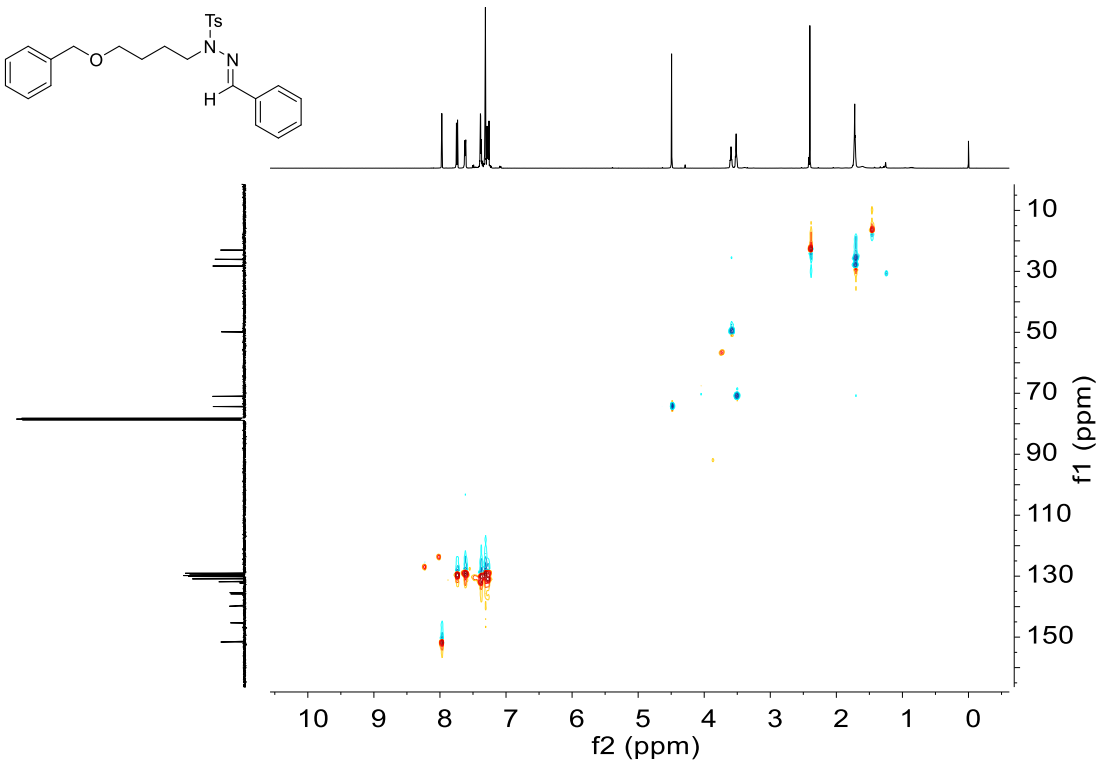
^{13}C NMR (126 MHz, $CDCl_3$) spectra for 55e:



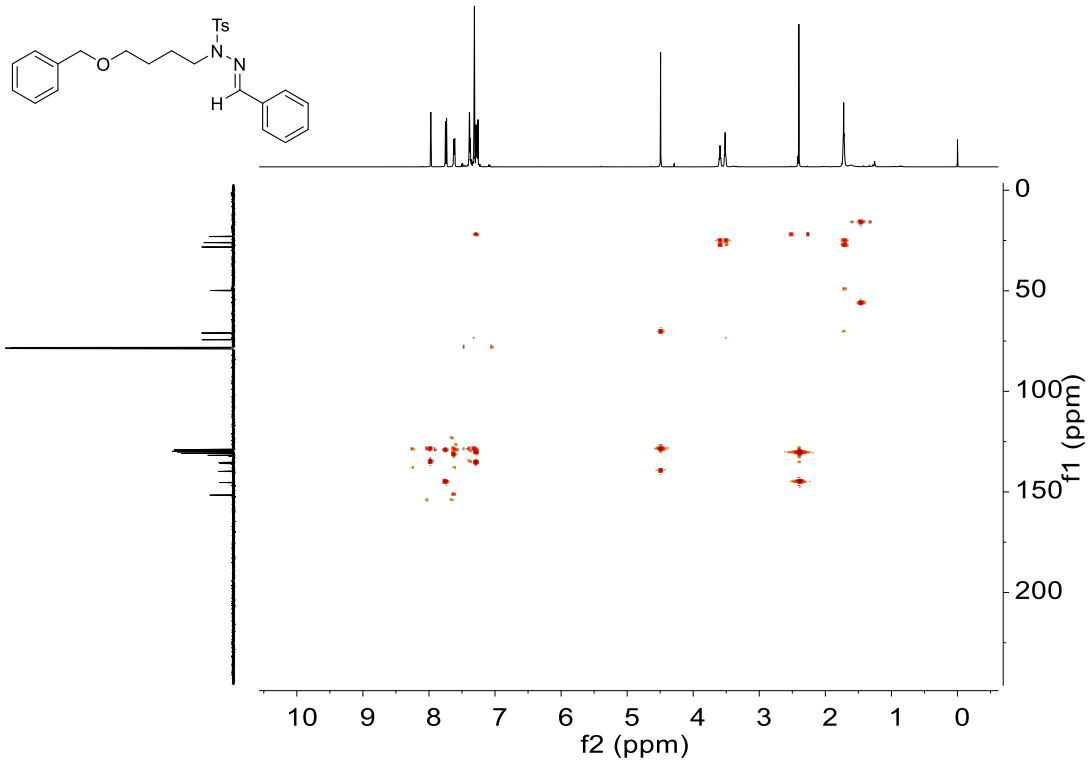
^{1}H ^{1}H COSY ($CDCl_3$) spectra for 55e:



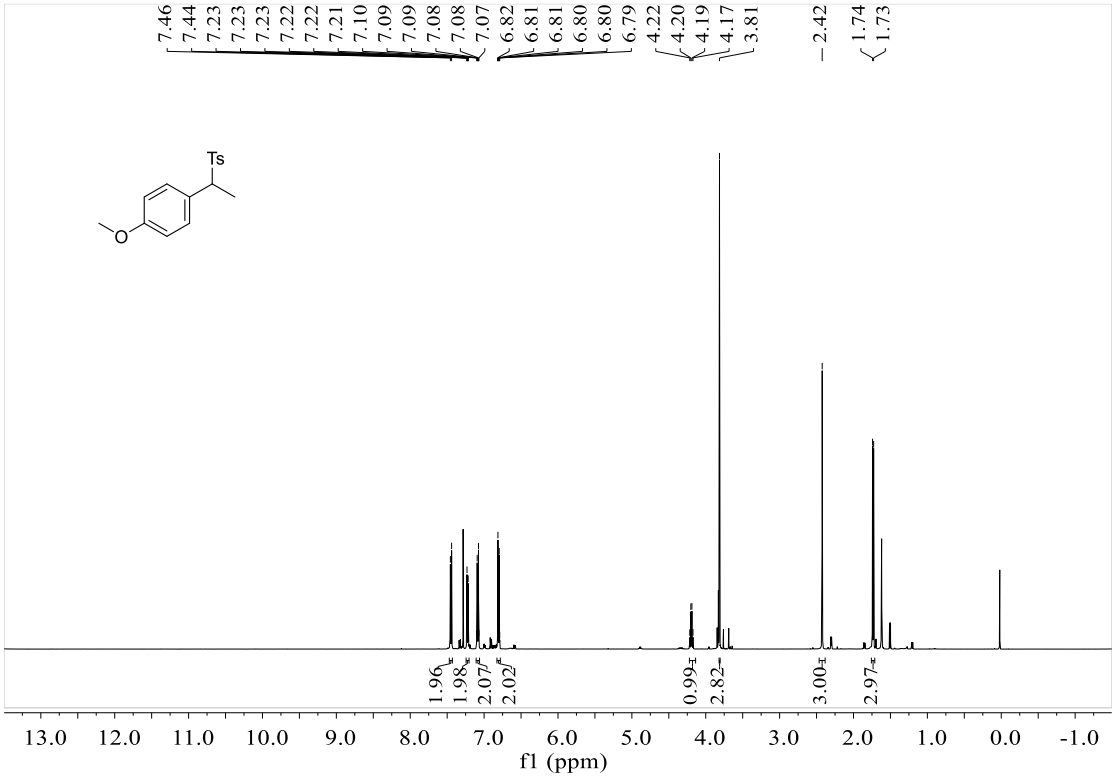
HSQC ($CDCl_3$) spectra for 55e:



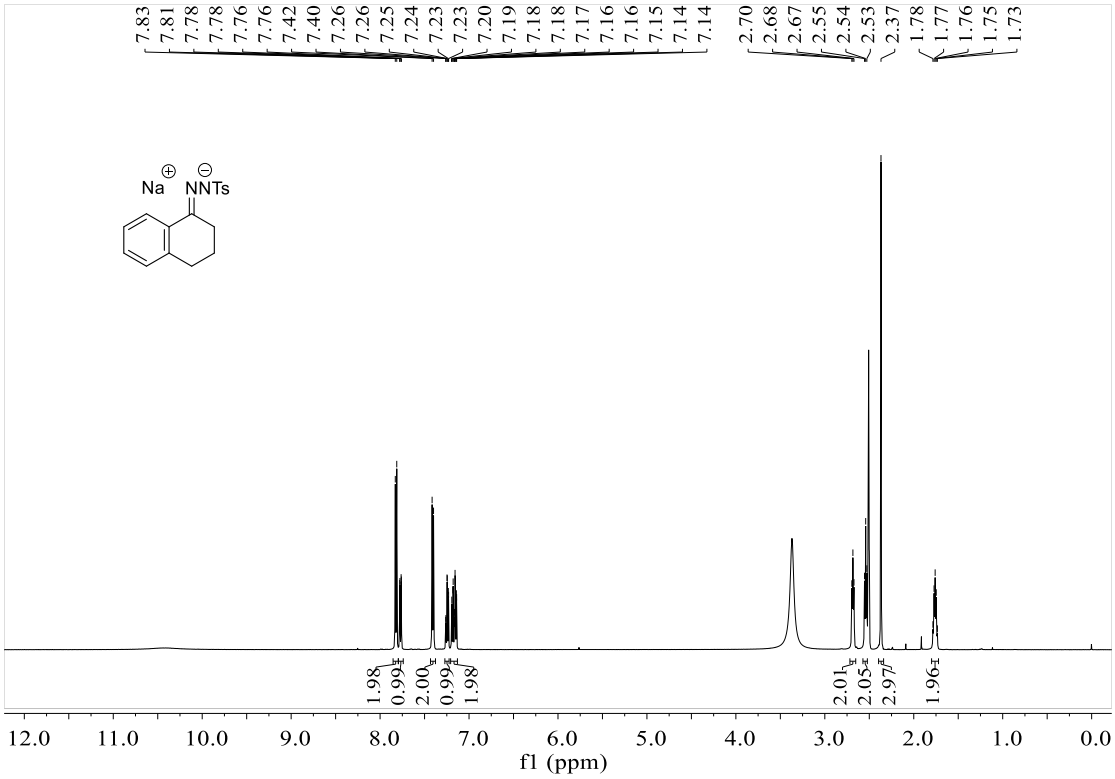
HMBC ($CDCl_3$) spectra for 55e:



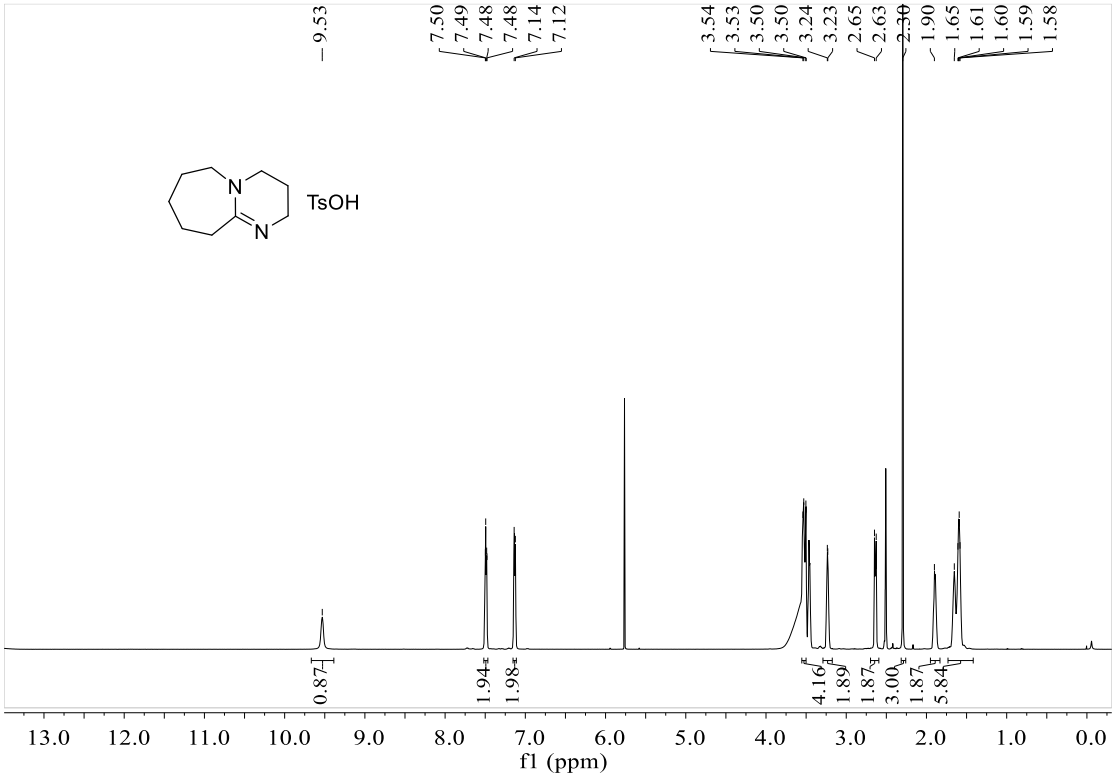
^{1}H NMR (500 MHz, DMSO-*d*6) spectra for 22e:



^{1}H NMR (500 MHz, DMSO-*d*6) spectra for 1e:



^{1}H NMR (500 MHz, DMSO-*d*6) spectra for 101e:



^{1}H NMR (500 MHz, DMSO-*d*6) spectra for 101f: