Supporting Information
for
Acridinium Amidate as a Hydrogen-Bonding Photocatalyst for Direct Decarboxylative Alkylation of Native Carboxylic Acids

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Contents

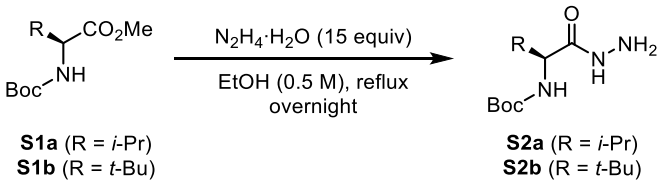
General Information

^{1}H, $^{13}C\{^{1}H\}$, and ^{19}F NMR spectra were recorded on a JEOL JNM-ECS-400, ECZ400S, JNM-ECX-500, JNM-ECZ-500, or JEOL JNM-ECA600II spectrometer. Chemical shifts are reported in ppm relative to the tetramethylsilane resonance (0.0 ppm for ^{1}H NMR) or the solvent resonance ($CDCl_3$; 77.0 ppm for ^{13}C NMR) as the internal references, while ^{19}F NMR chemical shifts are referenced to benzotrifluoride (–64.0 ppm) as an external standard. Data are reported as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, and br = broad) and coupling constants (Hz). Chemical shifts were assigned by using ^{1}H-^{1}H COSY, ^{1}H-^{13}C HMQC, and ^{1}H-^{13}C HMBC spectra. The high-resolution mass spectra were measured on Thermo Fisher Scientific Exactive Plus (ESI-orbitrap). Analytical thin layer chromatography (TLC) was performed on Merck precoated TLC plates (silica gel 60 GF254, 0.25 mm). Preparative thin-layer chromatography (PTLC) was performed using Merck silica gel 60 F254 pre-coated plates (0.5 mm). Flash column chromatography was performed on Silica gel 60 N (spherical, neutral, 40–50 μm; Kanto Chemical Co., Inc.).

Photocatalytic reactions were carried out using Kessil H150 Blue lamps (34 W, λ_{max} = 456 nm), Kessil PR160L Blue lamps (40 W, λ_{max} = 456 nm), or EvoluChem LED 450PF Blue lamps (18 W, λ_{max} = 450 nm). The reaction system using the blue LED was externally cooled with a circulator to maintain an internal temperature below 40 °C. All air- and moisture-sensitive reactions were performed under an atmosphere of argon (Ar) in dried glassware. Dichloroethane (DCE), acetonitrile (MeCN), tetrahydrofuran (THF), toluene, diethyl ether (Et_2O), dichloromethane (DCM), and *N*,*N*-dimethylformamide (DMF) were supplied from Kanto Chemical Co., Inc. as "Dehydrated" and further purified by both A2 alumina and Q5 reactant using a GlassContour solvent dispensing system (Nikko Hansen & Co., Ltd.). Acridinium amidates **1a** and **1b** were synthesized according to the literature procedures.[1] Other simple chemicals were purchased and used as such.

Preparation and Characterization of Acridinium Amidates 1c and 1d

Preparation of hydrazide **S2**:

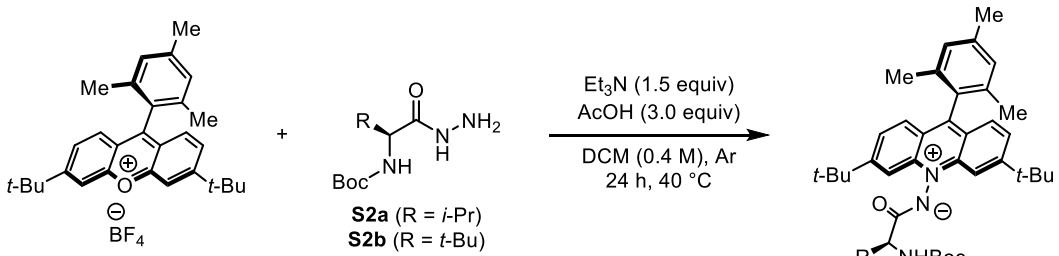


S1a (R = *i*-Pr)
S1b (R = *t*-Bu)

S2a (R = *i*-Pr)
S2b (R = *t*-Bu)

A 100 mL round-bottom flask equipped with a magnetic stirring bar was charged with the corresponding *N*-Boc protected amino acid methyl ester **S1** (6.0 mmol) and EtOH (12.0 mL, 0.5 M). To this solution was added $N_2H_4 \cdot H_2O$ (4.4 mL, 90 mmol, 15 equiv), and the resulting mixture was heated at reflux overnight. After cooling to room temperature, the reaction mixture was diluted with EtOAc and transferred to a separatory funnel. The organic solution was washed with distilled water (twice) and brine, dried over Na_2SO_4, filtered, and concentrated in vacuo. The crude residue was used directly in the subsequent step without purification.

Preparation of acridinium amidates **1c** *and* **1d**:

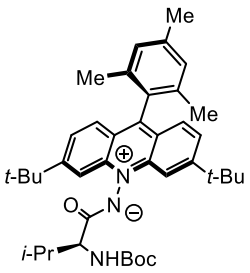


S3
(0.3 mmol)

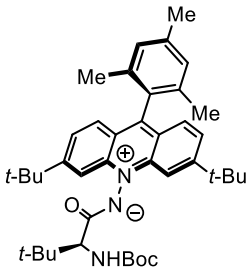
S2a (R = *i*-Pr)
S2b (R = *t*-Bu)
(1.5 equiv)

1c (R = *i*-Pr)
1d (R = *t*-Bu)

Acridinium amidates **1c** and **1d** were prepared according to the literature procedure with slight modification.[1] An oven-dried test tube equipped with a magnetic stirring bar was charged with xanthylium salt **S3**[2] (0.15 g, 0.30 mmol) and the corresponding hydrazide **S2** (0.45 mmol, 1.5 equiv) under an Ar atmosphere. Dry DCM (0.75 mL, 0.4 M), AcOH (51 μL, 0.90 mmol, 3.0 equiv), and Et_3N (62 μL, 0.45 mmol, 1.5 equiv) were successively introduced, and the tube was sealed and wrapped with aluminum foil to exclude light. The reaction mixture was stirred at 40 °C for 24 h, then diluted with DCM and transferred to a separatory funnel. The organic solution was washed with distilled water and saturated aqueous solution of $NaHCO_3$, and then dried over Na_2SO_4, filtered, and concentrated in vacuo. The resulting crude residue was purified by column chromatography on silica gel (hexane/ethyl acetate (EtOAc) = 1:2 to 0:1 as eluent) to afford the corresponding acridinium amidate (**1c** or **1d**) as a yellow solid.

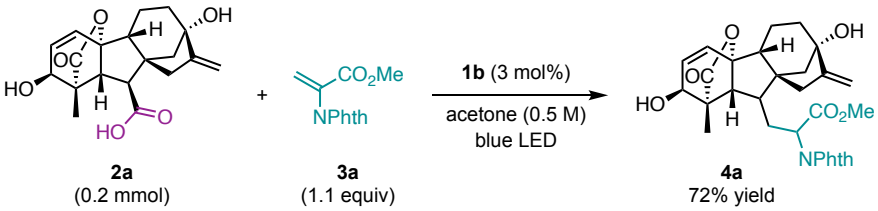


1c: prepared according to the procedure described above using hydrazide **S2a** (0.10 g, 0.45 mmol, 1.5 equiv), obtained as a yellow solid (0.15 g, 0.24 mmol, 80% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.68 (1H, s), 8.56 (1H, s), 7.63-7.51 (4H, m), 7.10 (2H, s), 5.64 (1H, d, J = 9.2 Hz), 4.67 (1H, dd, J = 9.2, 6.4 Hz), 2.46 (3H, s), 1.77 (3H, s), 1.68 (3H, s), 1.49 (9H, s), 1.44 (18H, s), 1.27 (3H, d, J = 6.8 Hz), 1.21 (3H, d, J = 6.8 Hz); Detectable signals of ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 175.3, 159.7, 159.6, 156.1, 151.4, 141.0, 139.2, 136.8, 136.4, 130.6, 128.8, 128.6, 126.9, 126.7, 124.3, 124.2, 115.7, 115.4, 78.5, 59.9, 36.4(4), 36.3(5), 32.9, 30.7, 28.6, 21.4, 20.5, 20.3, 20.1, 18.6; HRMS (ESI) Calcd for $C_{40}H_{54}N_3O_3^+$ ([M+H]$^+$) 624.4160, Found 624.4156.



1d: prepared according to the procedure above using hydrazide **S2b** (0.11 g, 0.45 mmol, 1.5 equiv), obtained as a yellow solid (0.14 g, 0.22 mmol, 73% yield); ^{1}H NMR (400 MHz, $CDCl_3$) (mixture of rotamers) δ 8.76-8.70 (1H, m), 8.58-8.52 (1H, m), 7.64-7.50 (4H, m), 7.12-7.07 (2H, m), 5.77 (1H x38/48, d, J = 9.2 Hz), 5.52 (1H x10/48, d, J = 10.8 Hz), 4.66 (1H x38/48, d, J = 9.6 Hz), 4.54 (1H x10/48, d, J = 10.0 Hz), 2.46 (3H, s), 1.78 (3H, s), 1.66 (3H, s), 1.48 (9H, s), 1.44 (18H, s), 1.30 (9H, s); Detectable signals of ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 174.8, 159.8, 159.6, 155.8, 151.5, 141.1, 140.9, 139.2, 136.7, 136.4, 130.6, 128.8, 128.7, 126.9, 126.7(8), 126.7(6), 124.3, 124.2, 115.9, 115.7, 78.5, 62.4, 36.6, 36.4, 35.6, 30.9, 30.8, 28.6, 27.6, 21.4, 20.3, 20.0; HRMS (ESI) Calcd for $C_{41}H_{56}N_3O_3^+$ ([M+H]$^+$) 638.4317, Found 638.4319.

Procedure for Direct Decarboxylative Alkylation of Gibberellin A$_3$



To an oven-dried test tube equipped with a magnetic stirring bar were added **2a** (69.3 mg, 0.2 mmol), **3a** (50.9 mg, 0.22 mmol, 1.1 equiv), and **1b** (3.1 mg, 0.006 mmol, 3 mol%) under an N_2 atmosphere. Acetone (0.4 mL) was then added, and the resulting mixture was stirred under irradiation with two EvoluChem LED 450PF Blue lamps with fans (fans are employed to maintain the temperature below 40 °C). After stirring for 6 h, the reaction mixture was concentrated in vacuo and purified by column chromatography on silica gel (chloroform/EtOAc = 3:2 as eluent) to afford **4a** as a white solid as a mixture of diastereomers (78.7 mg, 0.148 mmol, 72%, d.r. = 7:3.5:1:1, determined by ^{1}H NMR analysis of the crude reaction mixture).

Major diastereomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90-7.86 (2H, m), 7.80-7.75 (2H, m), 6.34-6.20 (1H, m), 5.87-5.79 (1H, m), 5.34-5.22 (1H, m), 5.07-4.96 (1H, m), 4.95-4.78 (1H, m), 4.18-4.06 (1H,

m), 3.78-3.70 (2H, m), 3.49 (2H, d, J = 5.2 Hz), 2.75-1.59 (13H, m), 1.55-1.48 (1H, m), 1.45-1.10 (3H, m). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 179.1, 169.4, 167.9, 156.8, 134.7, 133.5, 132.2, 131.6, 123.8, 107.6, 90.6, 78.1, 70.4, 55.5, 54.1, 53.1, 51.0, 50.1, 46.5, 41.6, 38.1, 32.1, 30.7, 17.2, 14.7. HRMS (ESI): m/z calcd. for $C_{30}H_{32}NO_8^+$ ($[M+H]^+$) 534.2122; found: 534.2126.

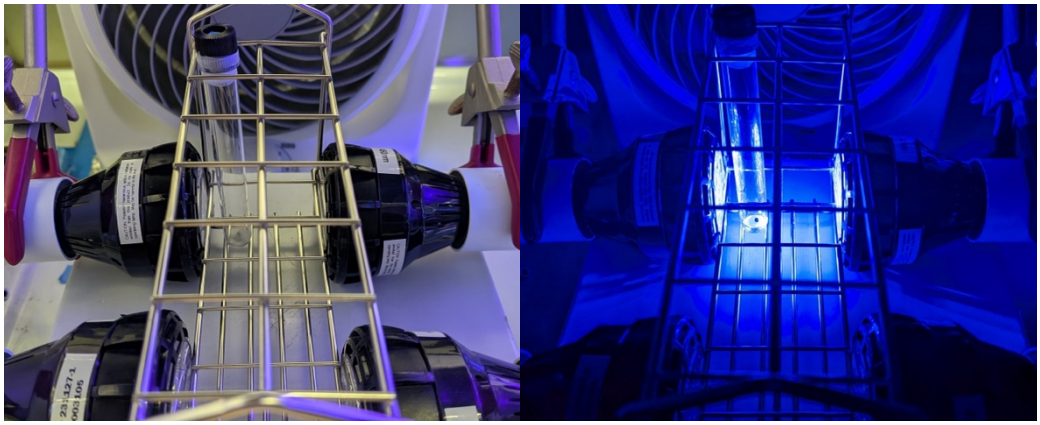
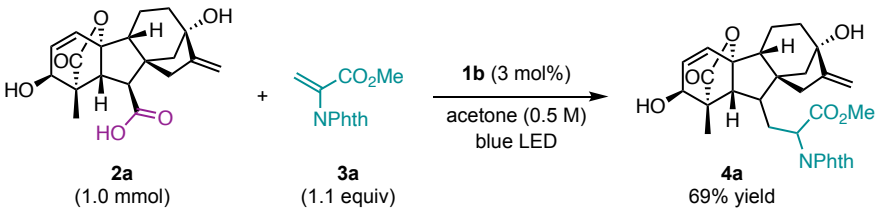


Fig. S1. Reaction set-up for photocatalytic reactions with EvoluChem LED 450PF Blue lamps. **Left**: LEDs are turned off. **Right**: turned on.

Scale-up Experiment

Direct decarboxylative alkylation of **2a** could be readily performed on a 1 mmol scale under the above-described standard conditions without modification of the reaction setup, providing **4a** in comparable yield.

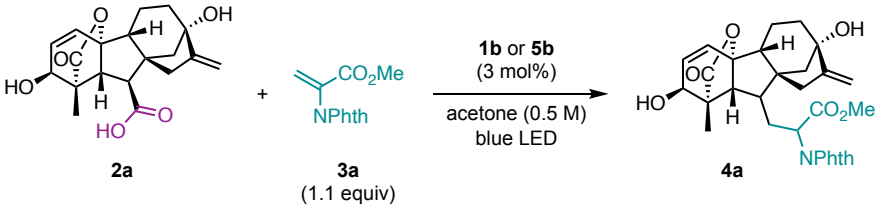


2a (1.0 mmol) **3a** (1.1 equiv) **4a** 69% yield

To an oven-dried test tube equipped with a magnetic stirring bar were added **2a** (347.1 mg, 1.0 mmol), **3a** (254.0 mg, 1.09 mmol, 1.1 equiv), and **1b** (15.4 mg, 0.03 mmol, 3 mol%) under an N_2 atmosphere. Acetone (2.0 mL) was then added, and the resulting mixture was stirred under irradiation with two EvoluChem LED 450PF Blue lamps with fans (fans are employed to maintain the temperature below 40 °C). After stirring for 15 h, the reaction mixture was concentrated in vacuo and purified by column chromatography on silica gel (chloroform/MeOH = 32:1 as eluent) to afford **4a** as a white solid as a mixture of diastereomers (367.3 mg, 0.688 mmol, 69%).

Additional Control Experiments

Although **1b** was largely recovered after the reaction, crude mass spectrometric analysis revealed partial cleavage of the N–N bond, generating acridine **5b**. To assess whether **5b** formed in situ could serve as the true catalytically active species, we compared the catalytic performance of **1b** and **5b** under blue-light irradiation. To ensure rigorous and reproducible control of photon flux and reaction temperature, the experiments were conducted using a calibrated LED light source (Asahi Spectra Co., Ltd., MPOT-LED-H-470) equipped with a temperature-controlled apparatus (Techno Sigma UCR-150).



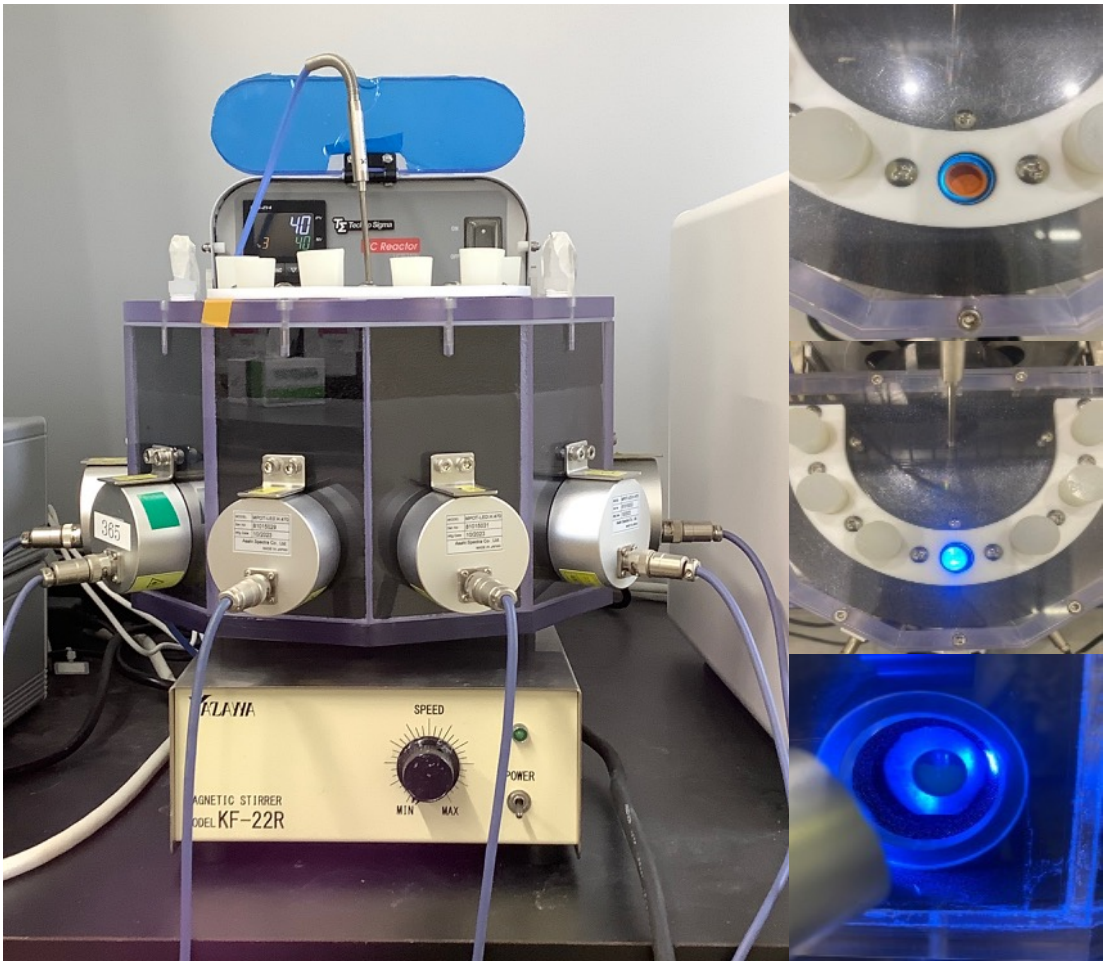


Fig. S2. Reaction set-up for control experiments with rigorous temperature control.

Under these controlled irradiation conditions, the reaction catalyzed by **1b** proceeded in a time-dependent manner, affording **4a** in 4%, 8%, and 36% yield after 30 min, 60 min, and 6 h, respectively (Fig. S3). In contrast, when **5b** was employed as the catalyst, the formation of **4a** was not detected even after 6 h of irradiation.

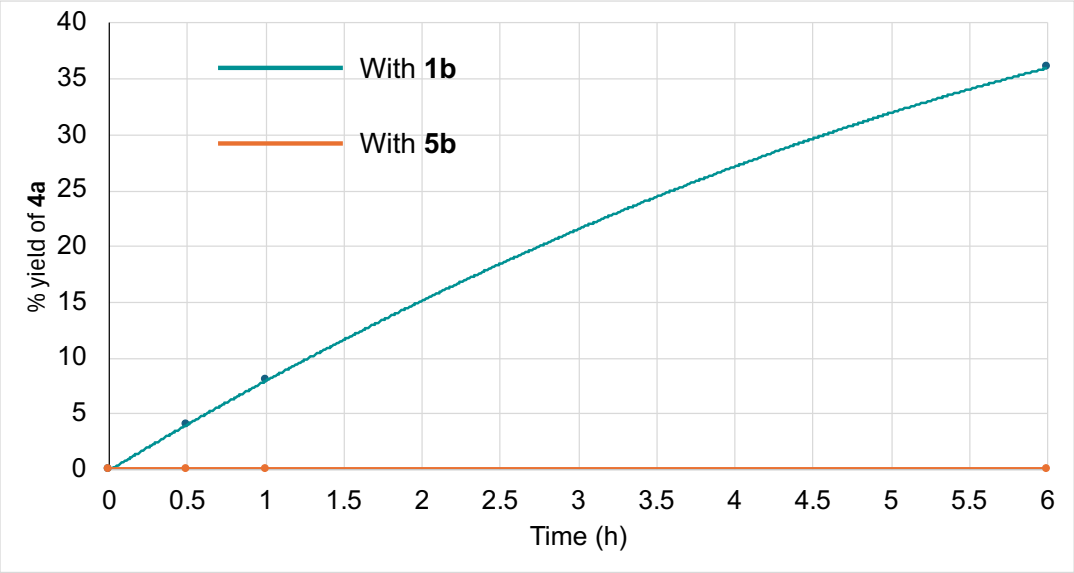
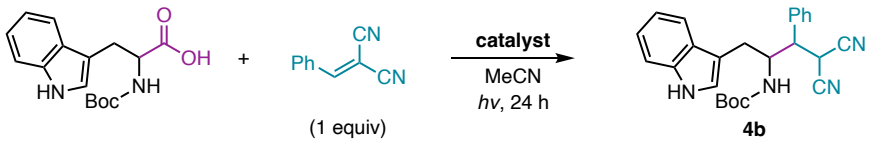


Fig. S3. A time-course experiment under rigorously controlled irradiation conditions.

The difference in reactivity is consistent with the distinct absorption profiles of **1b** and **5b** in the visible-light region.

To further evaluate the catalytic performance of acridinium amidate in comparison with acridine **5b**, we examined the reaction between *N*-Boc-tryptophan and benzalmalononitrile under representative photochemical conditions (Table S1). Under blue-light irradiation (450 nm LED), amidate **1a** (1 mol%) efficiently promoted the reaction to afford the product in 95% yield. Notably, the reaction still proceeded when the catalyst loading was reduced to 0.1 mol%, giving the product in 59% yield. In contrast, when acridine **5b** (1 mol%) was employed under violet-light irradiation (390 nm LED), the reaction efficiency decreased significantly, providing the product in 49% yield. These results highlight the higher catalytic efficiency of acridinium amidate **1a** under blue-light irradiation and further illustrate the distinct photophysical behavior of this catalyst system compared with conventional acridine photocatalysts.

Table S1. Comparison of catalytic performance between acridinium amidate **1a** and acridine **5b**.



entry	catalyst (x mol%)	*hv*	yield of **4b** (%)
1	**1a** (1 mol%)	450 nm LED	95
2	**1a** (0.1 mol%)	450 nm LED	59
3	**5b** (1 mol%)	390 nm LED	49

UV-vis Absorption Spectra

A solution of **1b** or **5b** in MeCN (0.01 mM) was transferred to a 1 cm square quartz cuvette and sparged with N_2 for 5 min. UV-vis spectra were recorded on a SHIMADZU UV3600 spectrophotometer and the obtained spectra are summarized in Fig. S4.

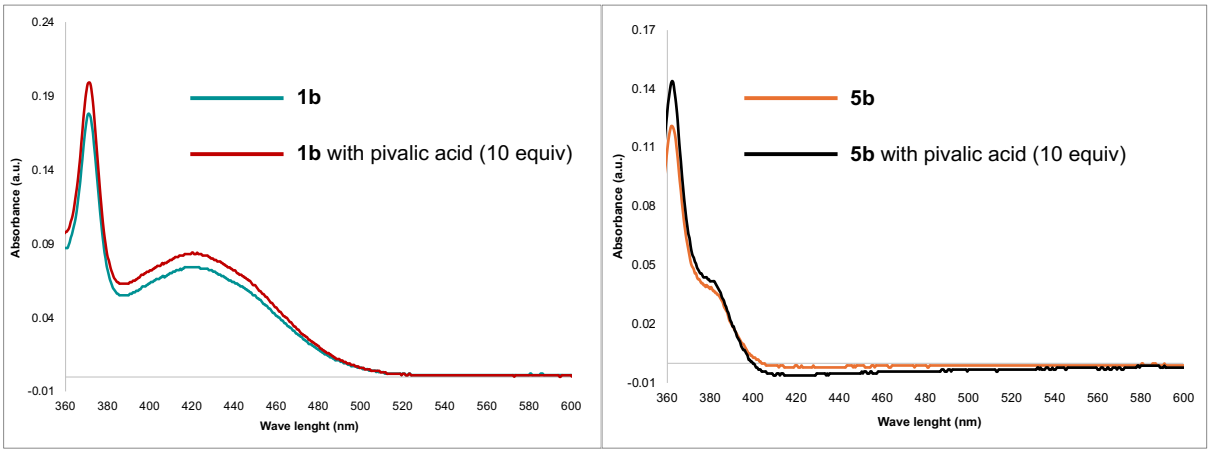
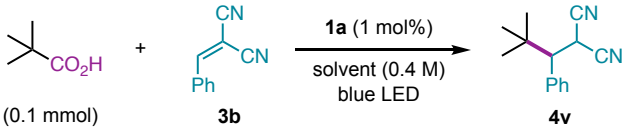


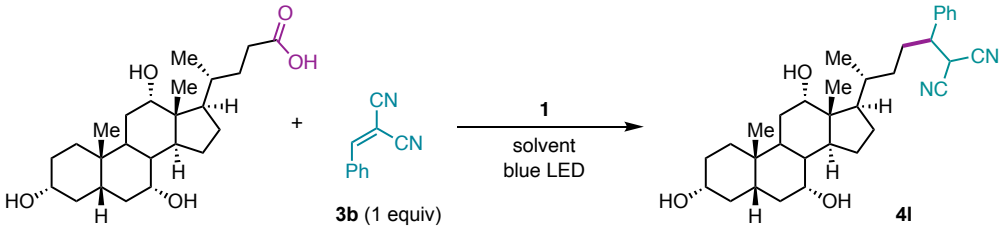
Fig. S4. Left: Absorption spectra of acridinium amidate **1b** in MeCN at 0.01 mM with or without pivalic acid (10 equiv). **Right**: Absorption spectra of acridine **5b** in MeCN at 0.01 mM with or without pivalic acid (10 equiv).

Optimization Data for Direct Decarboxylative Alkylation of Simple Carboxylic Acid



entry	**3b** (equiv)	solvent	time (h)	yield of **4v** (%)
1	2.0	MeCN	18	99
2	1.5	MeCN	18	95
3	1.25	MeCN	18	91
4	1.0	MeCN	18	91
5	1.0	MeCN	21	88
6	1.0	HFIP	21	32
7	1.0	DCE	21	67
8	1.0	DMSO	21	23
9	1.0	MeOH	21	29
10	1.0	EtOAc	21	32
11	1.0	Acetone	21	77
12	1.0	$CHCl_3$	21	11
13	1.0	DCM	21	83
14	1.0	DMF	21	68
15	1.0	MeCN	24	**98 (isolated)**

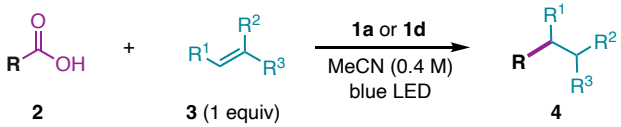
Optimization Data for Direct Decarboxylative Alkylation of Cholic Acid



entry	catalyst **1**	solvent	yield of **4l** (%)
1	**1a** (1 mol%)	MeCN (0.4 M)	0
2	**1a** (3 mol%)	MeCN (0.4 M)	16
3	**1a** (3 mol%)	MeCN/MeOH (v/v = 9:1, 0.1 M)	30
4	**1a** (3 mol%)	MeCN/DMF (v/v = 1:1, 0.1 M)	27
5	**1d** (3 mol%)	MeCN/DMF (v/v = 1:1, 0.1 M)	**54**

General Procedure for Direct Decarboxylative Alkylation of Native Carboxylic Acids

General Procedure 1 (GP1)



To an oven-dried test tube equipped with a magnetic stirring bar were added carboxylic acid **2** (0.1 mmol), olefin **3** (0.1 mmol, 1.0 equiv; for solid substrates), and acridinium amidate (**1a** or **1d**, see the characterization of the corresponding products for details) under an Ar atmosphere. MeCN (0.25 mL, 0.4 M) and olefin **3** (0.1 mmol, 1.0 equiv; for liquid substrates) were successively added, and the resulting mixture was stirred under irradiation with two Kessil H150 Blue lamps with fans to maintain the internal temperature below 40 °C. After stirring for 24 h, the reaction mixture was concentrated in vacuo and purified by column chromatography on silica gel (hexane/EtOAc as eluent, see the characterization of the corresponding products for details) to afford the corresponding product.

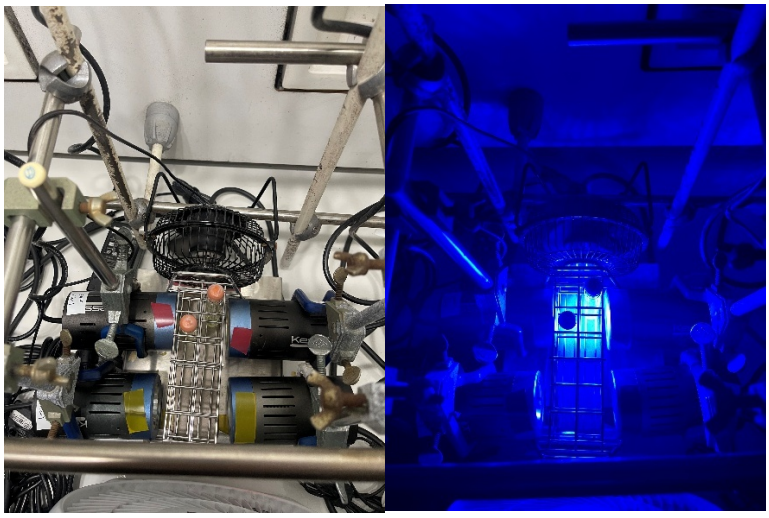
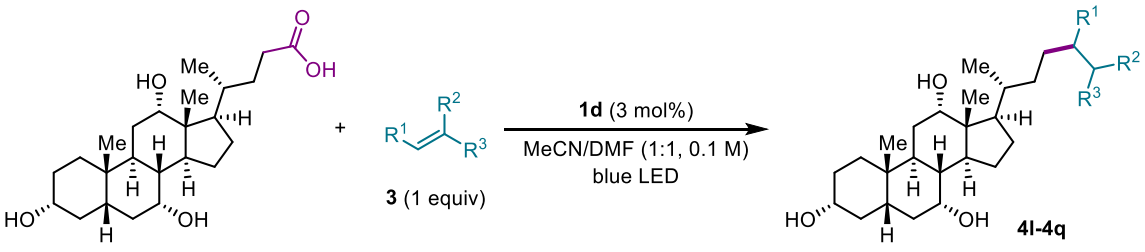


Fig. S5. Reaction set-up for photocatalytic reactions with Kessil Blue LED lamps. **Left**: LEDs are turned off. **Right**: turned on.

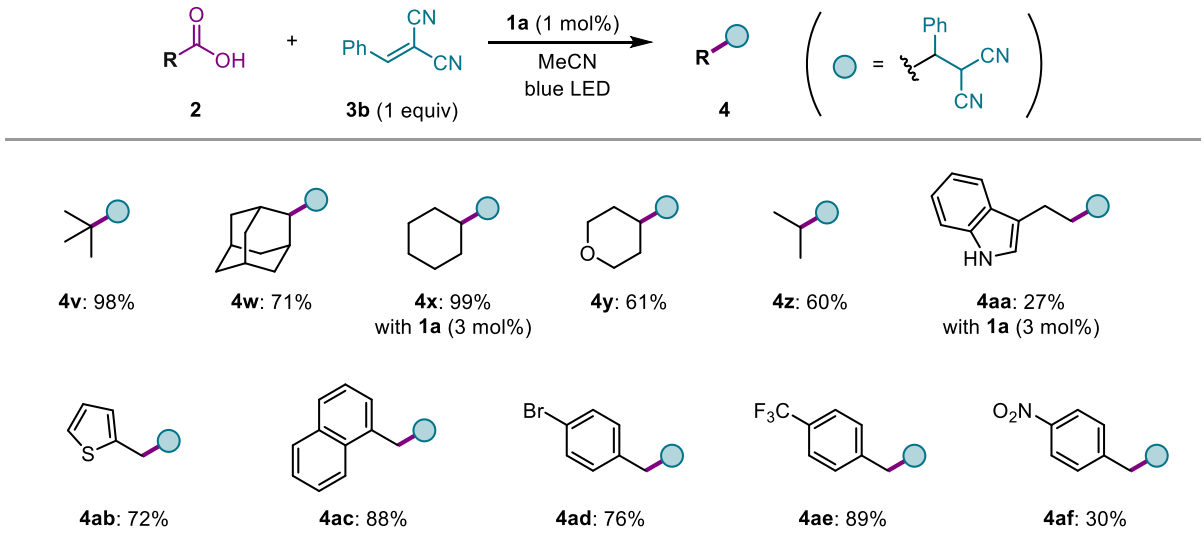
General Procedure 2 (GP2) (for cholic acid with olefins)



To an oven-dried test tube equipped with a magnetic stirring bar were added cholic acid (41.0 mg, 0.1 mmol), olefin **3** (0.1 mmol, 1.0 equiv; for solid substrates), and **1d** (1.9 mg, 0.003 mmol, 3 mol%) under an Ar atmosphere. MeCN (0.5 mL), DMF (0.5 mL), and olefin **3** (0.1 mmol, 1.0 equiv; for liquid substrates) were successively added, and the resulting mixture was stirred under irradiation with two

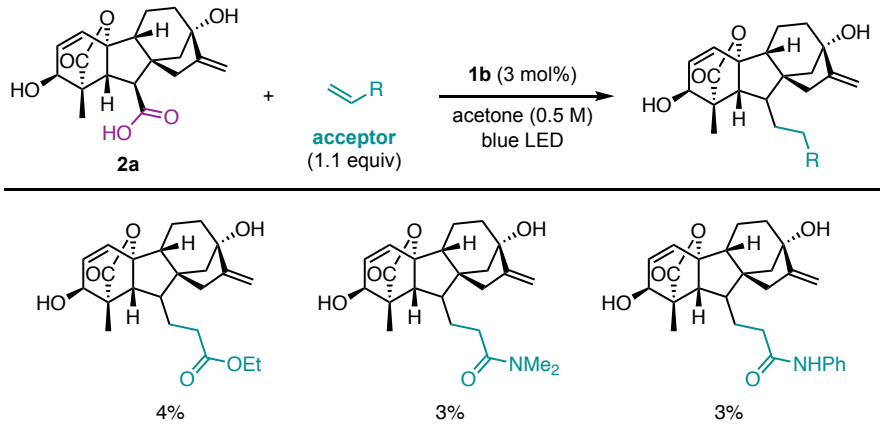
Kessil H150 Blue lamps with fans to maintain the internal temperature below 40 °C. After stirring for 24 h, the reaction mixture was diluted with EtOAc and transferred to a separatory funnel. The organic layer was washed with a saturated aqueous solution of $NaHCO_3$ (twice), distilled water (twice), and brine. The organic phase was then dried over Na_2SO_4, and the solvent was removed under reduced pressure. The resulting crude residue was purified by column chromatography on silica gel (hexane/acetone as eluent, see the characterization of the corresponding products for details) to afford the corresponding product.

Additional Substrate Scope of Simple Carboxylic Acids

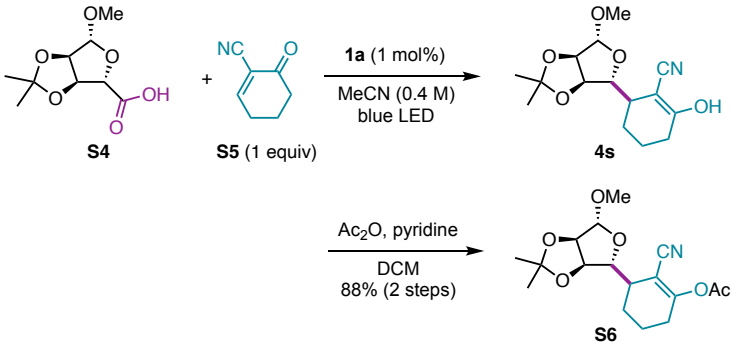


Unsuccessful Examples of Radical Acceptors

The reaction of **2a** with less activated radical acceptors, such as simple acrylates and acrylamides, afforded only trace amounts of the desired products under the optimized reaction conditions, thereby delineating the current limitations of the catalytic system.



Procedure for Direct Decarboxylative Alkylation with Base-, Acid-, or Photo-Labile Enones

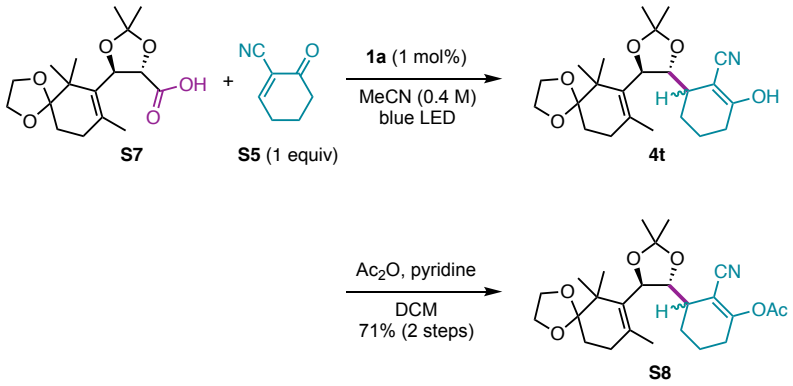


To an oven-dried test tube equipped with a magnetic stirring bar were added **S4**[3] (21.8 mg, 99.9 μmol), **S5** (12.1 mg, 99.9 μmol),[4] and **1a** (0.5 mg, 0.9 μmol). MeCN (250 μL) was added, and the resulting mixture was stirred under irradiation with one Kessil PR160L Blue lamp with fans to maintain the internal temperature below 40 °C. After the reaction mixture was stirred for 2 h, the resultant mixture was concentrated to afford the crude adduct **4s** (36.1 mg), which was used in the next reaction without further purification.

The above crude adduct **4s** (36.1 mg) was dissolved in Ac_2O (62.4 μL), pyridine (125 μL), and DCM (312 μL). After the reaction mixture was stirred at 21 °C for 9 h, H_2O (1 mL) was added to the mixture. After the resultant mixture was extracted with DCM (1 mL x3), the combined organic layers were washed with brine (3 mL), dried over Na_2SO_4, filtered, and concentrated. The residue was purified by column chromatography on silica gel (hexane/EtOAc = 10:1 to 5:1; toluene/EtOAc = 25:1 to 15:1) to afford the major isomer (18.8 mg, 55.7 μmol) and the minor isomer (10.9 mg, 32.3 μmol) of **S6** in 56% and 32% yields over 2 steps, respectively. The analytical data of the major and minor isomers of **S6** were identical to those reported previously.[5]

Major diastereomer: colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.07 (1H, d, J = 5.9 Hz), 4.95 (1H, s), 4.60 (1H, d, J = 5.9 Hz), 4.20 (1H, d, J = 9.6 Hz), 3.37 (3H, s), 2.59 (1H, m), 2.38-2.34 (2H, m), 2.23 (3H, s), 2.02 (1H, m), 1.87 (1H, m), 1.75 (1H, m), 1.64 (1H, m), 1.48 (3H, s), 1.32 (3H, s). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 167.5, 165.4, 116.1, 112.6, 109.8, 101.6, 87.8, 85.3, 81.7, 55.7, 38.8, 28.1, 26.5, 25.0, 22.7, 20.8, 17.5.

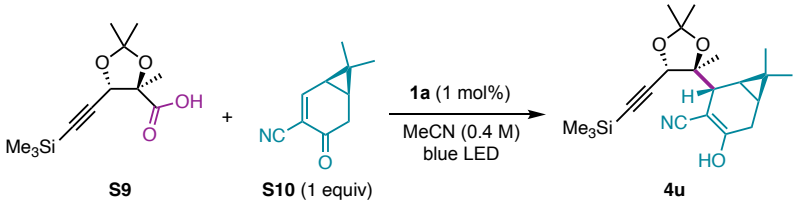
Minor diastereomer: colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.04 (1H, s), 4.69 (1H, dd, J = 6.0, 2.3 Hz), 4.56 (1H, d, J = 6.0 Hz), 4.13 (1H, dd, J = 9.6, 2.3 Hz), 3.49 (3H, s), 2.59 (1H, m), 2.39-2.32 (2H, m), 2.25 (3H, s), 1.89-1.82 (2H, m), 1.73 (1H, m), 1.61 (1H, m), 1.49 (3H, s), 1.32 (3H, s). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 167.7, 164.3, 116.0, 113.1, 109.3, 103.2, 90.2, 85.1, 82.1, 56.5, 39.8, 28.3, 26.8, 25.3, 24.0, 20.8, 18.8.



S7 **S5** (1 equiv) **4t** **S8**

To an oven-dried test tube equipped with a magnetic stirring bar were added **S7**[6] (30.8 mg, 94.4 μmol), **S5** (11.4 mg, 94.1 μmol), and **1a** (0.5 mg, 0.9 μmol). MeCN (236 μL) was added, and the resulting mixture was stirred under irradiation with one Kessil PR160L Blue lamp with fans to maintain the internal temperature below 40 °C. After the reaction mixture was stirred for 2 h, the resultant mixture was concentrated to afford the crude adduct **4t** (49.5 mg), which was used in the next reaction without further purification.

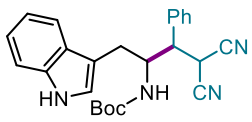
The above crude adduct **4t** (49.5 mg) was dissolved in Ac_2O (59.0 μL), pyridine (118 μL), and DCM (295 μL). After the reaction mixture was stirred at 21 °C for 9 h, H_2O (1 mL) was added to the mixture. After the resultant mixture was extracted with DCM (1 mL x3), the combined organic layers were washed with brine (3 mL), dried over Na_2SO_4, filtered, and concentrated. The residue was purified by column chromatography on silica gel (hexane/EtOAc = 6:1 to 3:1) and PTLC (20 cm x 10 cm, 2 plates, hexane/EtOAc = 3:2) to afford acetate **S8** (d.r. = 1.7:1, 29.7 mg, 66.7 μmol) in 71% yield over 2 steps. The analytical data of **S8** were identical to those reported previously.[6] **S8** (d.r. = 1.7:1): colorless amorphous. ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.67 (1H x10/27, m), 4.67 (1H x17/27, *J* = 8.7 Hz), 4.48 (1H x 10/27, d, *J* = 9.6 Hz), 4.22 (1H x17/27, dd, *J* = 8.7, 6.4 Hz), 3.98-3.94 (4H, m), 2.68 (1H x17/27, m), 2.53 (1H x10/27, m), 2.36-2.30 (2H, m), 2.24 (3H, s), 2.21-2.17 (2H, m), 1.92 (3H x17/27, s), 1.87 (3H x10/27, s), 1.83-1.81 (1H x10/27 + 1H, m), 1.77-1.73 (3H, m), 1.66-1.58 (1H x 17/27 + 1H, m), 1.51(1) (3H x10/27, s), 1.50(6) (3H x17/27, s), 1.46 (3H x17/27, s), 1.37 (3H x10/27, s), 1.18 (3H x17/27, s), 1.17 (3H x10/27, s), 1.15 (3H x17/27, s), 1.05 (3H x10/27, s). Detectable signals of ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 167.7, 167.6, 164.0, 163.5, 136.1, 135.4, 131.0, 129.6, 116.6, 114.9, 111.9, 111.8, 108.0, 107.8, 104.3, 102.1, 80.8, 78.5, 75.5, 65.0, 64.9(3), 64.8(8), 64.8(5), 43.4, 43.2, 35.0, 32.3, 32.2, 28.0, 27.8, 27.5, 27.4, 26.6, 26.5, 26.4, 23.7, 22.5, 22.4, 20.8, 20.7(2), 20.6(6), 20.6, 20.2, 18.5.



S9 **S10** (1 equiv) **4u**

To an oven-dried test tube equipped with a magnetic stirring bar were added **S9**[7] (25.7 mg, 100 μmol), **S10** (16.1 mg, 99.9 μmol),[7] and **1a** (0.5 mg, 0.9 μmol). MeCN (250 μL) was added, and the resulting mixture was stirred under irradiation with one Kessil PR160L Blue lamp with fans to maintain the internal temperature below 40 °C. After the reaction mixture was stirred for 3 h, the resultant mixture was concentrated. The residue was purified by column chromatography on silica gel (hexane/EtOAc = 10:1 to 5:1) to afford **4u** (28.1 mg, 75.2 μmol) in 75% yield. The analytical data of **4u** were identical to those reported previously.[7] **4u** (1:4.7:1.4 mixture of the enol and diastereomeric keto nitriles): colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 4.87 (1H x47/71, s), 4.78 (1H x14/71, s), 4.58 (1H x10/71, s), 3.44 (1H x47/71, d, *J* = 2.9 Hz), 3.34 (1H x14/71, d, *J* = 12.0 Hz), 2.92 (1H x47/71, dd, *J* = 19.5, 8.6 Hz), 2.81 (1H x10/71, s, OH), 2.71 (1H x14/71, dd, *J* = 17.2, 8.0 Hz), 2.65 (1H x10/71, ddd, *J* = 20.1, 6.9, 2.3 Hz), 2.37 (1H x10/71, dd, *J* = 20.1, 2.3 Hz), 2.24 (1H x14/71, dd, *J* = 17.2, 5.2 Hz), 2.19 (1H x47/71, dd, *J* = 19.5, 4.6 Hz), 2.15 (1H x14/71, dd, *J* = 12.0, 7.5 Hz), 1.69 (1H x57/71, m), 1.59 (3H x14/71, s), 1.55 (3H x14/71, s), 1.52 (3H x57/71, s), 1.45 (3H x10/71, s), 1.40 (3H x47/71, s), 1.39 (3H x47/71, s), 1.36 (3H x24/71, s), 1.33 (1H x10/71, m), 1.32 (1H x61/71, m), 1.18 (3H x47/71, s), 1.14 (3H x14/71, s), 1.12 (1H x14/71, m), 1.06 (3H x10/71, s), 1.03 (3H x14/71, s), 0.97 (3H x47/71, s), 0.94 (1H x47/71, m), 0.92 (3H x10/71, s), 0.90 (1H x10/71, m), 0.18 (9H x14/71, s), 0.17 (9H x47/71, s), 0.16 (9H x10/71, s). Detectable signals of ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 203.4, 201.8, 168.0, 118.4, 117.1, 115.7, 110.0, 109.7, 109.4, 100.8, 99.9, 99.1, 94.4, 94.3, 93.1, 86.3, 84.0, 83.08, 83.05, 71.6, 71.0, 70.6, 53.9, 42.8, 42.0, 41.6, 41.4, 40.3, 35.2, 34.3, 29.3, 29.2, 28.4(3), 28.3(6), 28.3, 27.4, 27.2, 26.5(9), 26.5(7), 24.8, 22.3, 22.2, 22.0(0), 21.9(7), 21.4, 20.9, 20.5(1), 20.4(9), 20.0, 19.9, 17.7, 14.9(4), 14.9(0), 14.8, 13.4, −0.37, −0.38, −0.57.

Characterization of Products

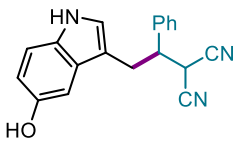


4b: obtained according to GP1 using **1a** (0.5 mg, 0.001 mmol), purified by column chromatography on silica gel (hexane/EtOAc = 5:1 to 1:1 as eluent) to give a pale brown solid, 39.4 mg, 95% yield, d.r. = 1.3:1.

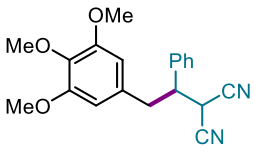
Major diastereomer: pale brown solid, 22.3 mg, 54% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (1H, brs), 7.58-7.45 (5H, m), 7.41-7.32 (2H, m), 7.21 (1H, t, *J* = 7.4 Hz), 7.11 (1H, t, *J* = 7.4 Hz), 6.90 (1H, s), 4.77-4.63 (1H, brm), 4.53-4.26 (2H, brm), 3.62-3.48 (1H, brm), 3.02-2.85 (2H, brm), 1.45 (9H, brs), rotational conformers were observed; ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 155.9, 136.3, 135.3, 129.8, 129.6, 128.8, 127.5, 123.2, 122.5, 119.9, 118.7, 112.6, 111.8, 111.4, 110.5, 80.7, 53.6, 50.2, 28.4, 27.8, 27.1; HRMS (ESI) Calcd for $C_{25}H_{25}N_4O_2^-$ ([M–H]$^-$) 413.1983, Found 413.1978.

Minor diastereomer: pale brown solid, 17.1 mg, 41% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (1H, brs), 7.63-7.36 (5H, m), 7.26-7.07 (5H, m), 4.76-4.67 (1H, brm), 4.56-4.48 (1H, brm), 4.37-4.26 (1H, brm), 3.59-3.47 (1H, brm), 2.87-2.75 (2H, brm), 1.43 (9H, brs), rotational conformers were observed; ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 156.3, 136.4, 133.1, 129.3, 127.2, 122.7, 120.0, 118.7, 112.9, 112.3,

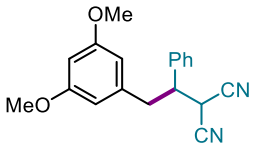
111.5, 110.7, 80.7, 51.8, 49.6, 29.9, 28.4, 27.2; HRMS (ESI) Calcd for $C_{25}H_{25}N_4O_2^-$ ([M–H]$^-$) 413.1983, Found 413.1979.



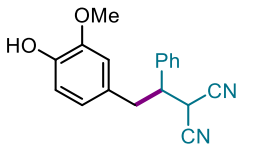
4c: obtained according to GP1 using **1a** (0.5 mg, 0.001 mmol), purified by column chromatography on silica gel (hexane/EtOAc = 2:1 as eluent) to give a purple oil, 20.0 mg, 66% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (1H, s), 7.48-7.38 (5H, m), 7.27 (1H, d, J = 8.8 Hz), 7.06 (1H, s), 6.96 (1H, s), 6.83 (1H, d, J = 8.8 Hz), 4.64 (1H, s), 3.96 (1H, d, J = 4.8 Hz), 3.59 (1H, ddd, J = 9.6, 5.6, 4.8 Hz), 3.41 (1H, dd, J = 15.2, 9.6 Hz), 3.33 (1H, dd, J = 15.2 Hz, 5.6 Hz); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 150.0, 137.1, 131.8, 129.3, 129.2, 128.2, 127.5, 124.4, 112.8, 112.5, 112.4, 111.8, 110.4, 103.0, 46.8, 28.8, 28.6; HRMS (ESI) Calcd for $C_{19}H_{14}N_3O^-$ ([M–H]$^-$) 300.1142, Found 300.1138.



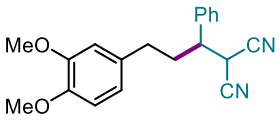
4d: obtained according to GP1 using **1a** (0.5 mg, 0.001 mmol), purified by column chromatography on silica gel (hexane/EtOAc = 10:1 to 4:1 as eluent) to give a white solid, 32.0 mg, 95% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47-7.37 (5H, m), 6.36 (2H, s), 3.90 (1H, d, J = 5.2 Hz), 3.83 (3H, s), 3.82 (6H, s), 3.45 (1H, dt, J = 7.6 Hz, 4.4 Hz), 3.20 (2H, d, J = 7.6 Hz); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 153.7, 137.4, 136.5, 132.2, 129.4, 129.3, 128.2, 112.2, 111.6, 105.9, 61.0, 56.3, 48.5, 39.1, 28.6; HRMS (ESI) Calcd for $C_{20}H_{19}N_2O_3^-$ ([M–H]$^-$) 335.1401, Found 335.1396.



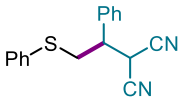
4e: obtained according to GP1 using **1a** (0.5 mg, 0.001 mmol), purified by column chromatography on silica gel (hexane/EtOAc = 10:1 to 5:1 as eluent) to give a colorless oil, 19.9 mg, 65% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46-7.37 (5H, m), 6.37 (1H, s), 6.34 (2H, s), 3.89 (1H, d, J = 4.4 Hz), 3.77 (6H, s), 3.42 (1H, dt, J = 7.6 Hz, 5.2 Hz), 3.19 (2H, d, J = 8.4 Hz); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 161.4, 139.0, 136.5, 129.3, 129.2, 128.2, 112.2, 111.6, 107.0, 99.3, 55.5, 48.2, 38.8, 28.5; HRMS (ESI) Calcd for $C_{16}H_{17}N_2O_2^-$ ([M–H]$^-$) 305.1295, Found 305.1290.



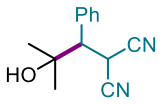
4f: obtained according to GP1 using **1a** (0.5 mg, 0.001 mmol), purified by column chromatography on silica gel (hexane/EtOAc = 10:1 to 4:1 as eluent) to give a colorless oil, 28.3 mg, 97% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46-7.36 (5H, m), 6.87 (1H, d, J = 8.0 Hz), 6.71 (1H, d, J = 8.0 Hz), 6.61 (1H, s), 5.56 (1H, s), 3.88 (1H, d, J = 5.6 Hz), 3.84 (3H, s), 3.41 (1H, dt, J = 8.0 Hz, 5.6 Hz), 3.19 (2H, d, J = 8.0 Hz); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 146.9, 145.1, 136.6, 129.3, 129.2, 128.4, 128.2, 121.8, 115.0, 112.3, 111.7, 111.4, 56.1, 48.6, 38.4, 28.4; HRMS (ESI) Calcd for $C_{18}H_{15}N_2O_2^-$ ([M–H]$^-$) 291.1139, Found 291.1136.



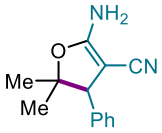
4g: obtained according to GP1 using **1a** (1.6 mg, 0.003 mmol), purified by column chromatography on silica gel (hexane/EtOAc = 5:1 to 2:1 as eluent) to give a pale yellow oil, 24.3 mg, 76% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48-7.38 (3H, m), 7.35-7.30 (2H, m), 6.80 (1H, d, *J* = 8.4 Hz), 6.62 (1H, d, *J* = 8.4 Hz), 6.57 (1H, s), 3.87 (3H, s), 3.85 (3H, s), 3.84 (1H, d, *J* = 5.6 Hz), 3.17 (1H, ddd, *J* = 10.0, 5.6, 5.2 Hz), 2.68-2.58 (1H, m), 2.45-2.28 (3H, m); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 149.1, 147.8, 136.3, 132.4, 129.5, 129.2, 128.2, 120.4, 112.0, 111.9, 111.6, 111.4, 56.0, 55.9, 45.5, 33.5, 32.3, 30.5; HRMS (ESI) Calcd for $C_{20}H_{19}N_2O_2^-$ ([M–H]$^-$) 319.1452, Found 319.1451.



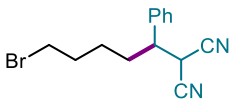
4h: obtained according to GP1 using **1a** (0.5 mg, 0.001 mmol), purified by column chromatography on silica gel (hexane/EtOAc = 10:1 as eluent) to give a colorless oil, 23.0 mg, 83% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46-7.28 (10H, m), 4.60 (1H, d, *J* = 4.8 Hz), 3.50 (1H, dd, *J* = 14.0, 5.6 Hz), 3.41 (1H, dd, *J* = 14.0, 9.6 Hz), 3.30 (ddd, *J* = 9.6, 5.6, 4.8 Hz); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 135.6, 133.1, 130.9, 129.8, 129.6, 129.5, 128.1, 127.9, 112.0, 111.2, 45.7, 36.6, 28.0; HRMS (ESI) Calcd for $C_{17}H_{13}N_2S^-$ ([M–H]$^-$) 277.0804, Found 277.0799.



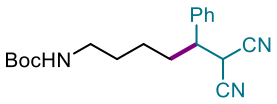
4i: obtained according to GP1 using **1a** (0.5 mg, 0.001 mmol), 93% NMR yield with 1,3,5-trimethoxybenzene as the internal standard, isolated as the cyclized product **4i´** after column chromatography on silica gel (hexane/EtOAc = 5:1 to 2:1 as eluent).



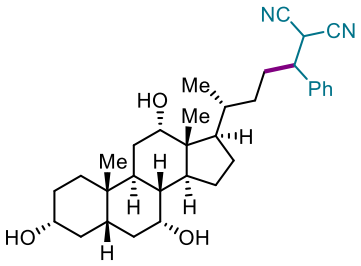
4i´: white solid, 20.7 mg, 96 % yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.31 (2H, m), 7.30-7.25 (1H, m), 7.21-7.16 (2H, m), 4.66 (2H, br), 4.04 (1H, s), 1.56 (3H, s), 0.88 (3H, s), one aromatic proton signal partially overlaps with the residual $CHCl_3$ peak (7.26 ppm), the integration value was determined including the overlapping region, which corresponds to the expected number of protons; ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 166.8, 138.7, 128.6, 128.4, 127.7, 119.6, 91.7, 57.5, 56.2, 29.2, 24.4; HRMS (ESI) Calcd for $C_{13}H_{14}N_2ONa^+$ ([M+Na]$^+$) 237.0999, Found 237.0999.



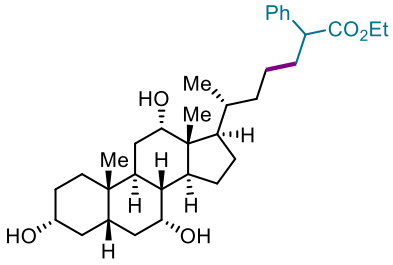
4j: obtained according to GP1 using **1a** (1.6 mg, 0.003 mmol), purified by column chromatography on silica gel (hexane/EtOAc = 5:1 as eluent) to give a white solid, 16.6 mg, 57% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46-7.36 (3H, m), 7.32 (2H, d, *J* = 6.8 Hz), 3.89 (1H, d, *J* = 6.0 Hz), 3.37 (1H, td, *J* = 11.8, 6.0 Hz), 3.34 (1H, td, *J* = 11.8, 6.0 Hz), 3.22 (1H, td, *J* = 7.8, 6.0 Hz), 2.04 (2H, dt, *J* = 7.8, 7.6 Hz), 1.95-1.81 (2H, m), 1.48-1.32 (2H, m); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 136.4, 129.6, 129.2, 127.9, 112.0, 111.9, 46.6, 33.0, 32.1, 31.3, 30.4, 25.7; HRMS (ESI) Calcd for $C_{14}H_{15}BrN_2Na^+$ ([M+Na]$^+$) 313.0311, Found 313.0316.



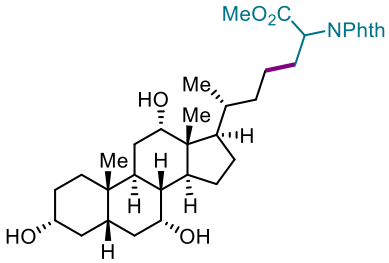
4k: obtained according to GP1 using **1a** (1.6 mg, 0.003 mmol), purified by column chromatography on silica gel (hexane/EtOAc = 5:1 to 2:1 as eluent) to give a white solid, 26.3 mg, 80% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45-7.35 (3H, m), 7.30 (2H, d, *J* = 7.2 Hz), 4.46 (1H, br), 3.89 (1H, d, *J* = 6.4 Hz), 3.20 (1H, dt, *J* = 7.6, 6.4 Hz), 3.06 (2H, m), 2.02 (2H, dt, J = 7.8, 7.6 Hz), 1.56-1.43 (2H, m), 1.42 (9H, s), 1.30-1.19 (2H, m); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 156.0, 136.6, 129.4, 129.1, 128.0, 112.0, 79.3, 46.7, 40.2, 31.9, 30.4, 29.9, 28.5, 24.3; HRMS (ESI) Calcd for $C_{19}H_{24}N_3O_2^-$ ([M–H]$^-$) 326.1874, Found 326.1874.



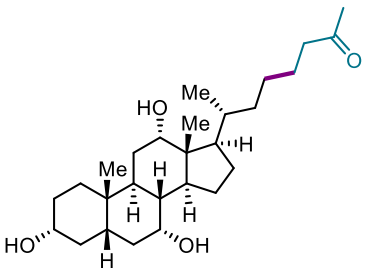
4l: obtained according to GP2, purified by column chromatography on silica gel (hexane/acetone = 2:1 to 1:1 as eluent) to give a white solid, 27.8 mg, 54% yield, d.r. = 1:1. ^{1}H NMR (400 MHz, $CDCl_3$) (mixture of diastereomers) δ 7.44-7.34 (3H, m), 7.33-7.28 (2H, m), 3.95 (1H, s), 3.93 (1H x1/2, d, *J* = 6.0 Hz), 3.89 (1H x1/2, d, *J* = 6.4 Hz), 3.83 (1H, s), 3.50-3.39 (1H, m), 3.20-3.09 (1H, m), 2.27-2.00 (3H, m), 1.99-1.45 (20H, m), 1.44-1.21 (4H, m), 1.19-0.92 (6H, m), 0.89 (3H, s), 0.66 (3H x1/2, s), 0.64 (3H x1/2, s); Detectable signals of ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) (mixture of diastereomers) δ 137.2, 136.9, 129.3(8), 129.3(5), 128.9(9), 128.9(5), 128.0, 112.2, 112.1, 73.1, 72.0, 68.6, 47.3, 47.0, 46.8, 46.6, 46.5, 41.7, 41.5, 39.7, 39.5, 35.6, 35.4, 35.3, 34.9, 34.8, 33.4, 33.1, 30.5, 30.2, 28.7, 28.6, 28.2, 27.6, 27.5, 26.4, 23.3, 22.5, 17.9, 17.6, 12.5(3), 12.4(9); HRMS (ESI) Calcd for $C_{33}H_{45}N_2O_3^-$ ([M–H]$^-$) 517.3435, Found 517.3424.



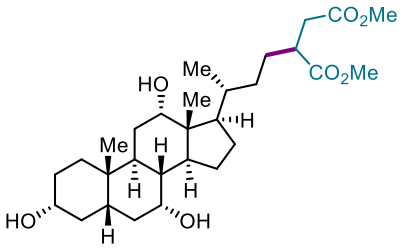
4m: obtained according to GP2, purified by column chromatography on silica gel (hexane/acetone = 2:1 to 1:1 as eluent) to give a white solid, 13.5 mg, 25% yield, d.r. = 1:1. ^{1}H NMR (400 MHz, $CDCl_3$) (mixture of diastereomers) δ 7.34-7.29 (4H, m), 7.28-7.22 (1H, m), 4.20-4.03 (2H, m), 3.98 (1H, s), 3.85 (1H, s), 3.56-3.40 (2H, m), 2.29-1.92 (4H, m), 1.91-1.47 (13H, m), 1.46-0.97 (15H, m), 0.96-0.87 (6H, m), 0.68 (3H x1/2, s), 0.67 (3H x1/2, s), one aromatic proton signal partially overlaps with the residual $CHCl_3$ peak (7.26 ppm), the integration value was determined including the overlapping region, which corresponds to the expected number of protons; Detectable signals of ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) (mixture of diastereomers) δ 174.4, 174.3, 139.6, 139.5, 128.7, 128.1, 128.0, 127.2, 73.2, 72.1, 68.6, 60.8, 51.9, 47.7, 46.6, 41.9, 41.6, 39.8, 39.7, 35.6, 35.5, 35.4, 34.8, 34.7, 34.2, 34.0, 30.6, 28.3, 27.7, 26.7, 24.4, 24.3, 23.3, 22.6, 17.7, 14.3, 12.7; HRMS (ESI) Calcd for $C_{34}H_{52}O_5Na^+$ ([M+Na]$^+$) 563.3707, Found 563.3704.



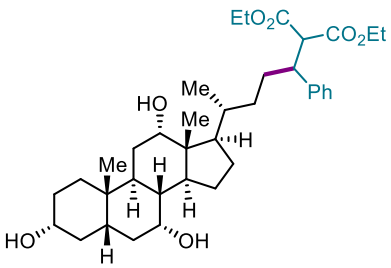
4n: obtained according to GP2, purified by column chromatography on silica gel (hexane/acetone = 2:1 to 1:1 as eluent) to give a white solid, 29.7 mg, 50% yield, d.r. = 1.1:1. ^{1}H NMR (400 MHz, $CDCl_3$) (mixture of diastereomers) δ 7.88 (2H, d, *J* = 3.2 Hz), 7.76 (2H, d, *J* = 3.2 Hz), 4.89-4.81 (1H, m), 3.95 (1H, s), 3.84 (1H, s), 3.73 (3H, s), 3.49-3.39 (1H, m), 2.37-2.09 (4H, m), 1.99-1.90 (1H, m), 1.89-1.45 (17H, m), 1.44-1.03 (9H, m), 1.02-0.85 (6H, m), 0.66 (3H x11/21, s), 0.65 (3H x10/21, s); Detectable signals of ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) (mixture of diastereomers) δ 170.2, 167.9, 134.4, 131.9, 123.7, 73.2, 72.1, 68.6, 52.9, 52.3, 52.2, 47.6, 47.5, 46.5, 41.8, 41.6, 39.7, 39.6, 35.6, 35.5, 35.4, 35.2, 35.1, 34.8, 34.7, 30.5, 29.2, 29.0, 28.2, 27.7, 26.5, 23.3, 23.2, 23.1, 22.6, 17.7, 17.6, 12.6; HRMS (ESI) Calcd for $C_{35}H_{49}NO_7Na^+$ ([M+Na]$^+$) 618.3402, Found 618.3412.



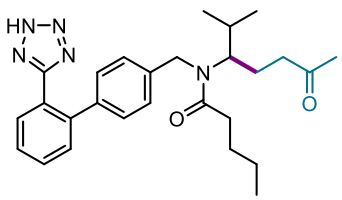
4o: obtained according to GP2, purified by column chromatography on silica gel (hexane/acetone = 2:1 to 1:1 as eluent) to give a white solid, 15.4 mg, 35% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.99 (1H, s), 3.86 (1H, s), 3.51-3.41 (1H, m), 2.42 (2H, t, *J* = 7.2 Hz), 2.29-2.15 (2H, m), 2.14 (3H, s), 2.01-1.46 (18H, m), 1.45-1.00 (9H, m), 0.96 (3H, d, *J* = 6.4 Hz), 0.90 (3H, s), 0.69 (3H, s); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 209.6, 73.2, 72.1, 68.6, 47.6, 46.6, 44.0, 42.0, 41.6, 39.8, 39.7, 35.7, 35.5, 35.4, 34.8, 34.7, 30.6, 30.1, 28.3, 27.7, 26.7, 25.8, 24.4, 23.3 22.7, 17.8, 12.7; HRMS (ESI) Calcd for $C_{27}H_{46}O_4Na^+$ ([M+Na]$^+$) 457.3289, Found 457.3286.



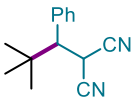
4p: obtained according to GP2 using dimethyl fumarate (14.4 mg, 0.1 mmol, 1.0 equiv.) as olefin **3**, purified by column chromatography on silica gel (hexane/acetone = 2:1 to 1:1 as eluent) to give a white solid, 21.5 mg, 42% yield, d.r. = 1.3:1. ^{1}H NMR (400 MHz, $CDCl_3$) (mixture of diastereomers) δ 3.98 (1H, s), 3.85 (1H, s), 3.70 (3H, s), 3.68 (3H, s), 3.52-3.39 (1H, m), 2.85-2.66 (2H, m), 2.46 (1H x13/23, t, *J* = 5.6 Hz), 2.42 (1H x10/23, t, *J* = 5.6 Hz), 2.29-2.14 (2H, m), 2.01-1.31 (22H, m), 1.30-1.01 (3H, m), 1.00-0.94 (3H, m), 0.89 (3H, s), 0.68 (3H, s); Detectable signals of ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) (mixture of diastereomers) δ 175.7(2), 175.6(5), 172.7, 172.6, 73.2, 72.0, 68.6, 52.0, 51.9, 47.1(3), 47.0(8), 46.5, 41.8, 41.6, 41.5(2), 41.5(0), 39.7, 39.6, 36.2, 35.6(2), 35.5(8), 35.4(0), 35.3(7), 34.9, 34.8, 32.9, 30.6, 28.7, 28.5, 28.3, 27.6, 27.5, 26.5, 23.3, 22.6, 17.7, 17.6, 12.6; HRMS (ESI) Calcd for $C_{29}H_{48}O_7Na^+$ ([M+Na]$^+$) 531.3293, Found 531.3296.



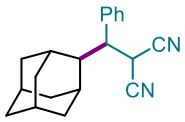
4q: obtained according to GP2, purified by column chromatography on silica gel (hexane/acetone = 2:1 to 1:1 as eluent) to give a colorless oil, 13.9 mg, 23% yield, d.r. = 1.1:1. ^{1}H NMR (400 MHz, $CDCl_3$) (mixture of diastereomers) δ 7.30-7.23 (2H, m), 7.22-7.15 (3H, m), 4.25 (2H, q, J = 7.2 Hz), 3.97-3.79 (4H, m), 3.66-3.58 (1H, m), 3.51-3.39 (1H, m), 3.35-3.21 (1H, m), 2.28-2.10 (2H, m), 1.99-1.90 (1H, m), 1.85-0.84 (33H, m), 0.65 (3H x11/21, s), 0.60 (3H x10/21, s), two aromatic proton signals partially overlap with the residual $CHCl_3$ peak (7.26 ppm), the integration value was determined including the overlapping region, which corresponds to the expected number of protons; Detectable signals of ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) (mixture of diastereomers) δ 168.7(2), 168.7(0), 168.1, 141.2, 140.8, 128.5(2), 128.4(6), 128.3(7), 127.0, 126.9, 73.1(4), 73.0(6), 72.1, 68.5, 61.7, 61.2, 59.2, 59.0, 47.4, 47.1, 46.6, 46.5, 46.4, 45.7, 41.9, 41.6, 39.8, 39.7, 35.5, 35.3, 34.8, 34.7, 33.4, 33.0, 30.6, 30.4, 30.3, 28.3, 27.3, 26.7, 23.2, 22.6, 18.0, 17.5, 14.3, 13.8, 12.6(4), 12.5(7); HRMS (ESI) Calcd for $C_{37}H_{56}O_7Na^+$ ([M+Na]$^+$) 635.3919, Found 635.3918.



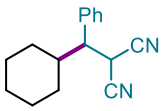
4r: obtained according to GP1 using **1d** (1.9 mg, 0.003 mmol), purified by column chromatography on silica gel (hexane/EtOAc = 1:1 to 0:1, then EtOAc/MeOH = 10:1 to 4:1 as eluent) to give a colorless oil, 31.7 mg, 69% yield. ^{1}H NMR (400 MHz, $CDCl_3$) (mixture of rotamers) δ 8.12-8.04 (1H, m), 7.65-7.50 (2H, m), 7.49-7.42 (1H, m), 7.29 (1H, d, J = 7.6 Hz), 7.19 (1H, d, J = 8.0 Hz), 7.13 (1H, d, J = 8.0 Hz), 7.09 (1H, d, J = 7.6 Hz), 5.39 (1H x13/23, d, J = 14.8 Hz), 4.90-4.65 (1H x10/23, brm), 4.43-4.02 (2H x10/23, brm), 3.72 (1H x13/23, d, J = 15.6 Hz), 3.39 (1H x13/23, t, J = 10.4 Hz), 2.67-2.31 (3H, m), 2.28-2.11 (1H, m), 2.04 (3H x13/23, s), 2.01 (3H x10/23, s), 2.00-1.68 (4H, m), 1.57-1.34 (3H, m), 1.06 (3H x13/23, d, J = 6.4 Hz), 1.03-0.93 (3H x10/23 + 3H, m), 0.91 (3H x13/23, d, J = 6.4 Hz), 0.87 (3H x10/23, d, J = 6.8 Hz); Detectable signals of ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) (mixture of rotamers) δ 211.8, 210.2, 175.1, 140.8, 140.4, 139.6, 137.8, 131.5, 131.4, 131.3, 131.0, 130.9, 130.7, 129.7, 129.3, 128.6, 128.4, 128.2, 127.2, 64.0, 44.4, 41.4, 40.5, 34.4, 33.6, 31.2, 30.4, 30.2(0), 30.1(6), 28.1, 27.6, 24.5, 22.8, 22.7, 20.8, 20.6, 20.1, 19.9, 14.1, 14.0; HRMS (ESI) Calcd for $C_{27}H_{35}N_5O_2Na^+$ ([M+Na]$^+$) 484.2683, Found 484.2686.



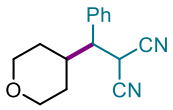
4v: obtained according to GP1 using **1a** (0.5 mg, 0.001 mmol), purified by column chromatography on silica gel (hexane/EtOAc = 10:1 as eluent) to give a pale yellow solid, 20.9 mg, 98% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43-7.35 (5H, m), 4.22 (1H, d, J = 5.6 Hz), 3.01 (1H, d, J = 5.6 Hz), 1.11 (9H, s); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 136.4, 129.4, 128.9, 128.8, 113.3, 113.2, 56.9, 35.1, 28.6, 25.2; HRMS (ESI) Calcd for $C_{14}H_{15}N_2^-$ ([M–H]$^-$) 211.1240, Found 211.1233.



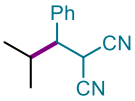
4w: obtained according to GP1 using **1a** (0.5 mg, 0.001 mmol), purified by column chromatography on silica gel (hexane/EtOAc = 10:1 as eluent) to give a white solid, 20.8 mg, 71% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43-7.33 (5H, m), 4.25 (1H, d, *J* = 5.6 Hz), 2.81 (1H, d, *J* = 5.6 Hz), 2.03 (3H, brs), 1.74-1.56 (12H, m); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 135.2, 129.6, 128.6, 128.5, 113.4, 113.3, 58.0, 40.4, 36.5, 36.3, 28.3, 23.7; HRMS (ESI) Calcd for $C_{20}H_{21}N_2^-$ ([M–H]$^-$) 289.1710, Found 289.1710.



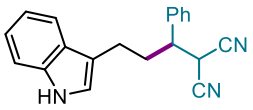
4x: obtained according to GP1 using **1a** (1.6 mg, 0.003 mmol), purified by column chromatography on silica gel (hexane/EtOAc = 10:1 as eluent) to give a pale yellow oil, 24.8 mg, 99% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44-7.34 (3H, m), 7.33-7.29 (2H, m), 4.19 (1H, d, *J* = 5.6 Hz), 2.88 (1H, dd, *J* = 9.6, 5.6 Hz), 2.08-1.97 (1H, m), 1.96-1.89 (1H, m), 1.88-1.80 (1H, m), 1.73-1.62 (2H, m), 1.52-1.32 (2H, m), 1.27-1.00 (3H, m), 0.90-0.76 (1H, m); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 136.8, 129.3, 128.9, 128.4, 112.3, 112.1, 52.5, 39.3, 31.3, 30.7, 27.2, 26.0, 25.9(4), 25.8(6); HRMS (ESI) Calcd for $C_{16}H_{17}N_2^-$ ([M–H]$^-$) 237.1397, Found 237.1390.



4y: obtained according to GP1 using **1a** (0.5 mg, 0.001 mmol), purified by column chromatography on silica gel (hexane/EtOAc = 5:1 to 3:1 as eluent) to give a pale yellow oil, 14.7 mg, 61% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46-7.39 (3H, m), 7.37-7.31 (2H, m), 4.17 (1H, d, *J* = 5.2 Hz), 4.08 (1H, dd, *J* = 11.6, 4.4 Hz), 3.90 (1H, dd, *J* = 11.2, 4.4 Hz), 3.48 (1H, td, *J* = 12.0, 2.0 Hz), 3.34 (1H, td, *J* = 12.0, 2.0 Hz), 2.91 (1H, dd, *J* = 10.0 Hz, 5.2 Hz), 2.27 (1H, qt, *J* =10.8, 4.0 Hz), 1.85-1.78 (1H, m), 1.48 (1H, qd, *J* = 11.6, 4.4 Hz), 1.36-1.15 (2H, m); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 135.8, 129.5, 129.2, 128.4, 111.9, 111.8, 67.7, 67.2, 52.1, 37.1, 31.2, 30.8, 27.0; HRMS (ESI) Calcd for $C_{15}H_{15}N_2O^-$ ([M–H]$^-$) 239.1189, Found 239.1185.

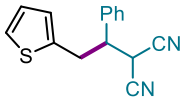


4z: obtained according to GP1 using **1a** (0.5 mg, 0.001 mmol), purified by column chromatography on silica gel (hexane/EtOAc = 10:1 as eluent) to give a colorless oil, 11.8 mg, 60% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44-7.35 (3H, m), 7.34-7.30 (2H, m), 4.17 (1H, d, *J* = 6.0 Hz), 2.84 (1H, dd, *J* = 10.0, 6.0 Hz), 2.45-2.34 (1H, m), 1.15 (3H, d, *J* = 6.8 Hz), 0.84 (1H, d, *J* = 7.2 Hz); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 136.7, 129.3, 129.0, 128.4, 112.3, 112.0, 53.6, 30.4, 27.9, 21.1, 20.5; HRMS (ESI) Calcd for $C_{13}H_{13}N_2^-$ ([M–H]$^-$) 197.1084, Found 197.1074.

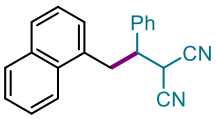


4aa: obtained according to GP1 using **1a** (1.6 mg, 0.003 mmol), purified by column chromatography on silica gel (hexane/EtOAc = 5:1 to 2:1 as eluent) to give a brown oil, 8.0 mg, 27% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (1H, brs), 7.49-7.33 (7H, m), 7.21 (1H, t, *J* = 7.2 Hz), 7.11 (1H, t, *J* = 7.2 Hz), 6.93 (1H, s), 3.87 (1H, d, *J* = 6.0 Hz), 3.27 (1H, td, *J* = 7.8, 6.0 Hz), 2.86-2.76 (1H, m), 2.70-2.60 (1H, m), 2.48-2.40 (2H, m); Detectable signals of ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 136.4(8), 136.4(6), 129.5, 129.2, 128.3, 127.1,

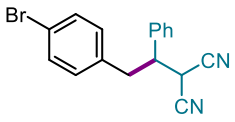
122.4, 121.7, 119.7, 118.8, 114.3, 112.0, 111.4, 45.8, 32.4, 30.5, 22.5; HRMS (ESI) Calcd for $C_{20}H_{16}N_3^-$ ([M–H]$^-$) 298.1349, Found 298.1344.



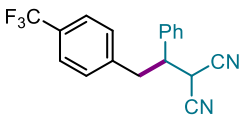
4ab: obtained according to GP1 using **1a** (0.5 mg, 0.001 mmol), purified by column chromatography on silica gel (hexane/EtOAc = 20:1 as eluent) to give a yellow oil, 18.2 mg, 72% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48-7.38 (5H, m), 7.22 (1H, d, *J* = 4.8 Hz), 6.96 (1H, t, *J* = 4.0 Hz), 6.91 (1H, s), 3.97 (1H, d, *J* = 3.6 Hz), 3.62-3.40 (3H, m); Detectable signals of ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 138.6, 136.0, 129.4, 128.1, 127.5, 127.2, 125.5, 112.0, 111.3, 48.6, 32.8, 28.7; HRMS (ESI) Calcd for $C_{15}H_{11}N_2S^-$ ([M–H]$^-$) 251.0648, Found 251.0642.



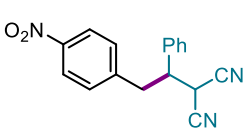
4ac: obtained according to GP1 using **1a** (0.5 mg, 0.001 mmol), purified by column chromatography on silica gel (hexane/EtOAc = 10:1 to 5:1 as eluent) to give a colorless oil, 26.0 mg, 88% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (1H, d, *J* = 8.4 Hz), 7.92 (1H, d, *J* = 8.4 Hz), 7.83 (1H, d, *J* = 8.4 Hz), 7.62-7.52 (2H, m), 7.49-7.33 (7H, m), 3.85 (1H, d, *J* = 4.0 Hz), 3.79-3.63 (3H, m); Detectable signals of ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 136.8, 134.4, 132.7, 131.4, 129.5, 129.4, 129.3, 128.7, 128.1, 127.7, 127.0, 126.3, 125.6, 123.0, 112.2, 111.7, 47.0, 36.1, 28.8; HRMS (ESI) Calcd for $C_{21}H_{15}N_2^-$ ([M–H]$^-$) 295.1240, Found 295.1238.



4ad: obtained according to GP1 using **1a** (0.5 mg, 0.001 mmol), purified by column chromatography on silica gel (hexane/EtOAc = 10:1 to 5:1 as eluent) to give a colorless oil, 24.8 mg, 76% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45-7.37 (5H, m), 7.36-7.31 (2H, m), 7.03 (2H, d, *J* = 8.4 Hz), 3.86 (1H, d, *J* = 5.2 Hz), 3.43 (1H, td, *J* = 7.8, 5.6 Hz), 3.27 (1H, dd, *J* = 14.0, 7.6 Hz), 3.20 (1H, dd, *J* = 14.0 Hz, 7.6 Hz); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 136.0, 135.6, 132.3, 130.8, 129.4, 129.3, 128.1, 121.6, 111.9, 111.5, 48.2, 38.0, 28.9; HRMS (ESI) Calcd for $C_{17}H_{12}BrN_2^-$ ([M–H]$^-$) 323.0189, Found 323.0188.



4ae: obtained according to GP1 using **1a** (0.5 mg, 0.001 mmol), purified by column chromatography on silica gel (hexane/EtOAc = 10:1 to 4:1 as eluent) to give a colorless oil, 27.9 mg, 89% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (2H, d, *J* = 8.0 Hz), 7.44-7.38 (3H, m), 7.36-7.32 (2H, m), 7.26 (2H, d, *J* = 8.0 Hz), 3.87 (1H, d, *J* = 5.6 Hz), 3.49 (1H, td, *J* = 7.8, 5.6 Hz), 3.39 (1H, dd, *J* = 14.0, 7.2 Hz), 3.32 (1H, dd, *J* = 13.6 Hz, 8.4 Hz); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 140.8, 135.8, 129.9 (q, *J* = 33.2 Hz), 129.4(58) (q, *J* = 8.6 Hz), 129.4(57), 128.04, 126.1 (q, *J* = 4.2 Hz), 124.0 (q, *J* = 271.8 Hz), 111.8, 111.5, 48.1, 38.4, 29.1; ^{19}F NMR (373 MHz, $CDCl_3$) δ –62.5; HRMS (ESI) Calcd for $C_{18}H_{12}F_3N_2^-$ ([M–H]$^-$) 313.0958, Found 313.0956.



4af: obtained according to GP1 using **1a** (0.5 mg, 0.001 mmol), purified by column chromatography on silica gel (hexane/EtOAc = 10:1 to 4:1 as eluent) to give a pale yellow solid, 8.9 mg, 30% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (2H, d, J = 8.4 Hz), 7.43-7.37 (3H, m), 7.33-7.25 (4H, m), 3.93 (1H, d, J = 5.6 Hz), 3.57-3.43 (2H, m), 3.36 (1H, dd, J = 13.6, 8.8 Hz); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 147.4, 144.2, 135.4, 130.0, 129.6(3), 129.6(1), 127.9, 124.2, 111.6, 111.5, 48.0, 38.4, 29.5; HRMS (ESI) Calcd for $C_{17}H_{12}N_3O_2^-$ ([M–H]$^-$) 290.0935, Found 290.0934.

Cyclic Voltammetry (CV) Measurements

CV measurements were performed on ALS/CH Instruments Electrochemical Analyzer using glassy carbon working electrode, Pt wire counter electrode, and $Ag/AgNO_3$ reference electrode. The glassy carbon electrode was polished with Al_2O_3 powder on a polishing pad wetted with distilled water and then washed with distilled water. Voltammograms were recorded at room temperature in MeCN containing 100 mM tetrabutylammonium perchlorate ($Bu_4N{\cdot}ClO_4$) and one of the following components (1 mM each): **1a**; preformed **1a**·HBF_4;[1] or a mixture of **1a** and *n*-$PrCO_2H$. The solution was deoxygenated by flowing Ar for 10 min before measurements. The initial potential was 0 V vs Ag/Ag^+, and the direction was negative. The obtained value was referenced to Ag/Ag^+ and converted to the SCE scale.[8]

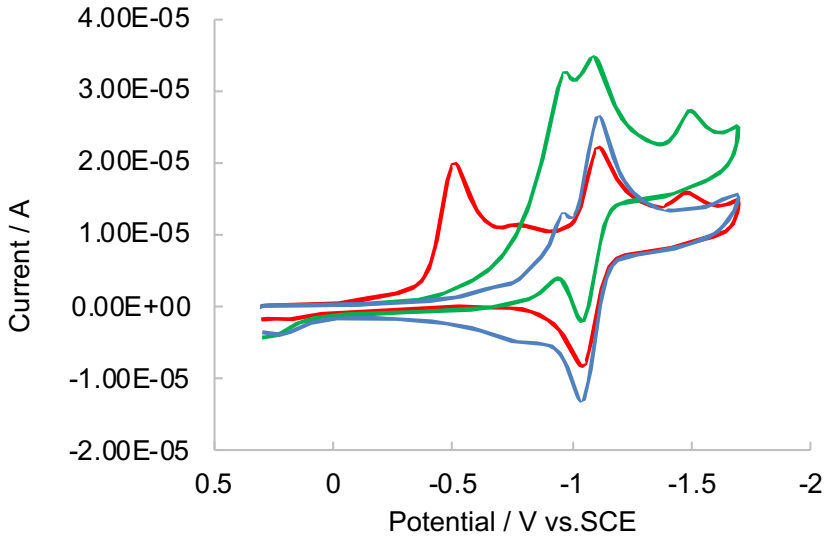
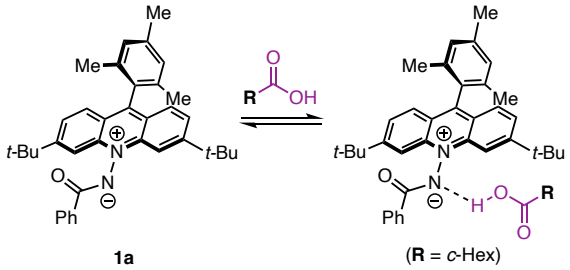


Fig. S6. CV measurements of **1a** (blue line), **1a**·HBF_4 (red line), and a mixture of **1a** and *n*-$PrCO_2H$ (green line); conditions: the designated substance (1 mM) and $Bu_4N{\cdot}ClO_4$ (100 mM) in MeCN, glassy carbon working electrode, Pt wire counter electrode, $Ag/AgNO_3$ reference electrode; the initial potential: 0 V vs Ag/Ag^+; direction of the initial scan: negative.

Titration of Carboxylic Acid with Acridinium Amidate

The NMR titration of **1a** with cyclohexanecarboxylic acid was performed in CD_3CN as described in the following. Two different stock solutions containing either **1a** (5 mM, stock solution **A**) or cyclohexanecarboxylic acid (5 mM, stock solution **B**) were prepared.

Different NMR samples were prepared according to Table S2 with a final volume of 600 µL, c (*c*-$HexCO_2H$) = 1.67 mM, and varying equivalents of **1a**.



Assuming a 1:1 complex, the association constant K_a was calculated to be $(4.8 \pm 1.0) \times 10^2$ M^{-1} based on the chemical shift changes of the α-C–H of cyclohexanecarboxylic acid.

Table S2. Preparation of a mixture of **1a** and cyclohexanecarboxylic acid for NMR titration.

Entry	Equiv of **1a**	Volume of **A**	Volume of **B**	Volume of added solvent
1	0	0 µL	200 µL	400 µL
2	0.1	20 µL	200 µL	380 µL
3	0.2	40 µL	200 µL	360 µL
4	0.3	60 µL	200 µL	340 µL
5	0.5	100 µL	200 µL	300 µL
6	0.7	140 µL	200 µL	260 µL
7	1.0	200 µL	200 µL	200 µL
8	2.0	400 µL	200 µL	0 µL

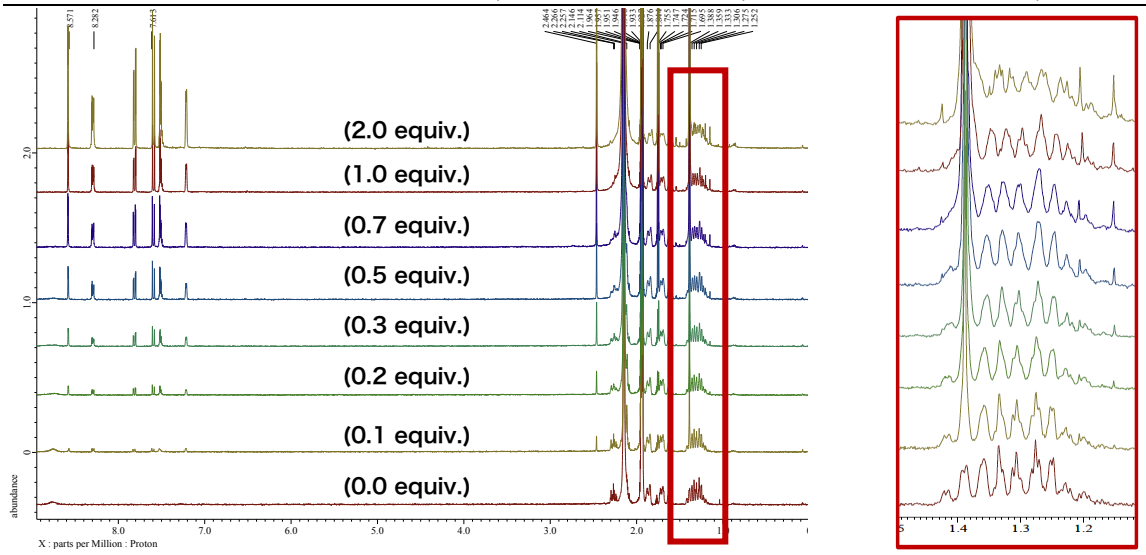


Fig. S7. NMR titration of cyclohexanecarboxylic acid (1.67 mM) with **1a** (0 – 1.0 equiv) in CD_3CN at 298 K. Spectra from bottom to top correspond to entries 1–8, respectively. The right panel shows an expanded view of the selected signals.

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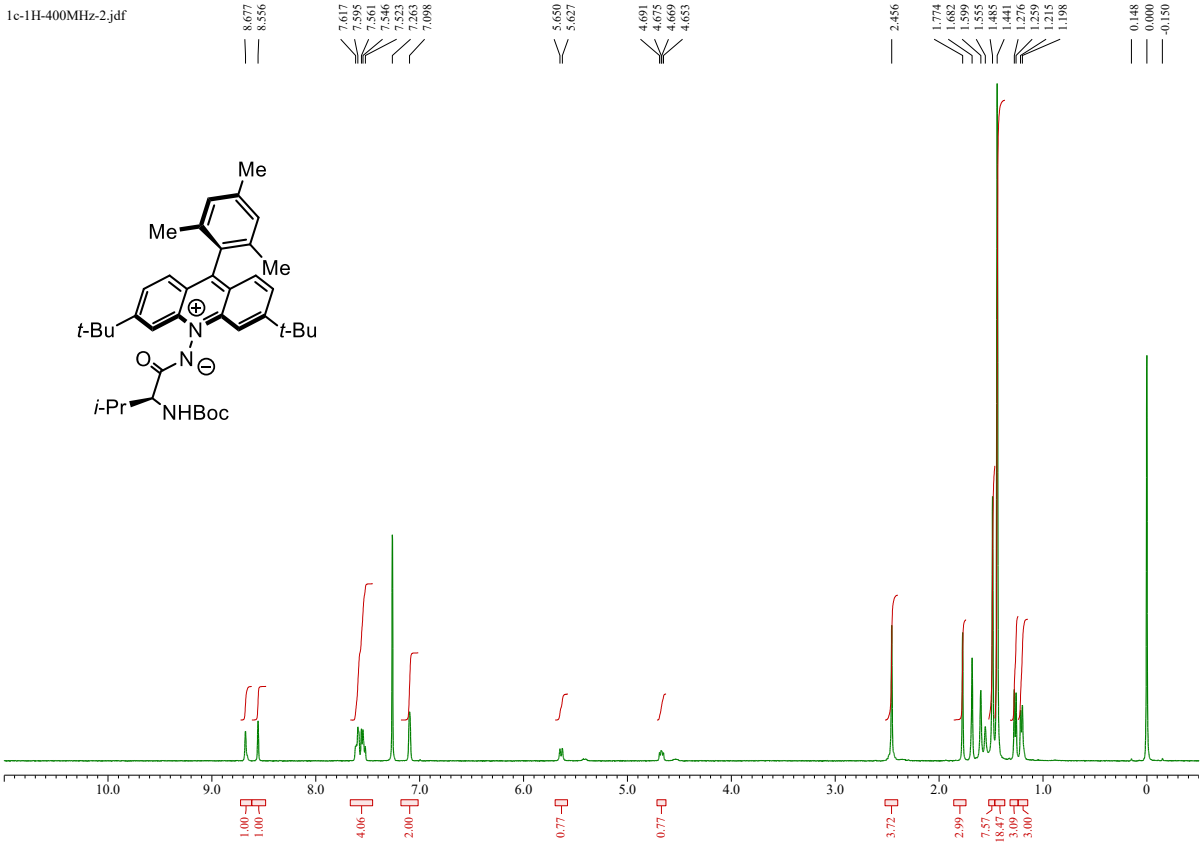
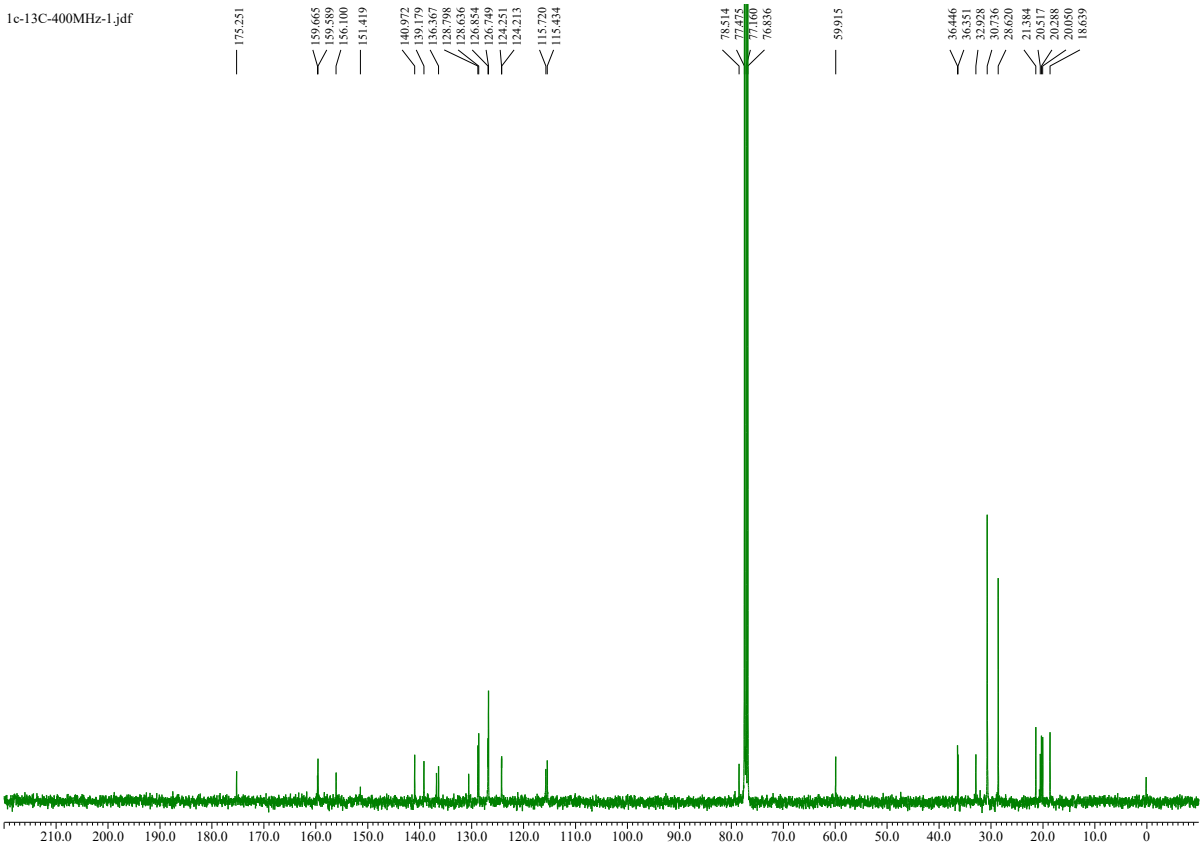
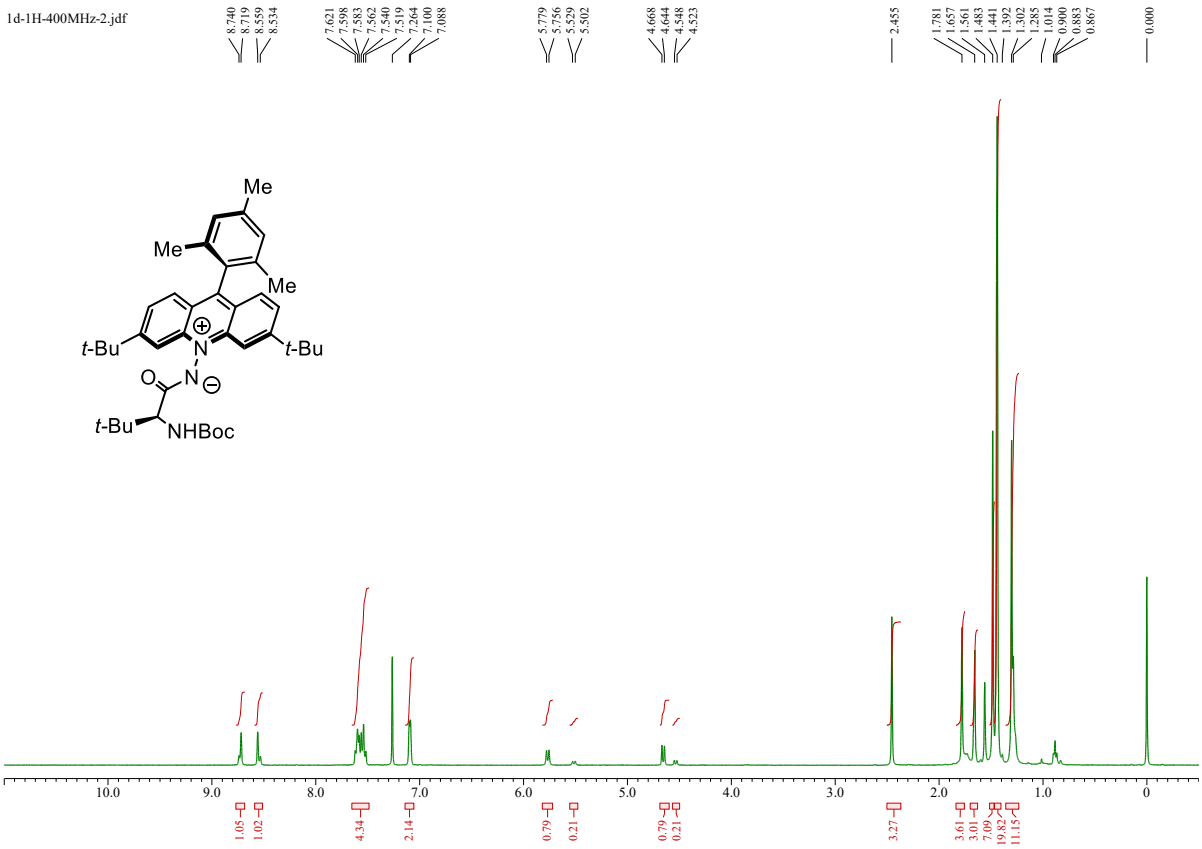
^{1}H and ^{13}C NMR Spectra



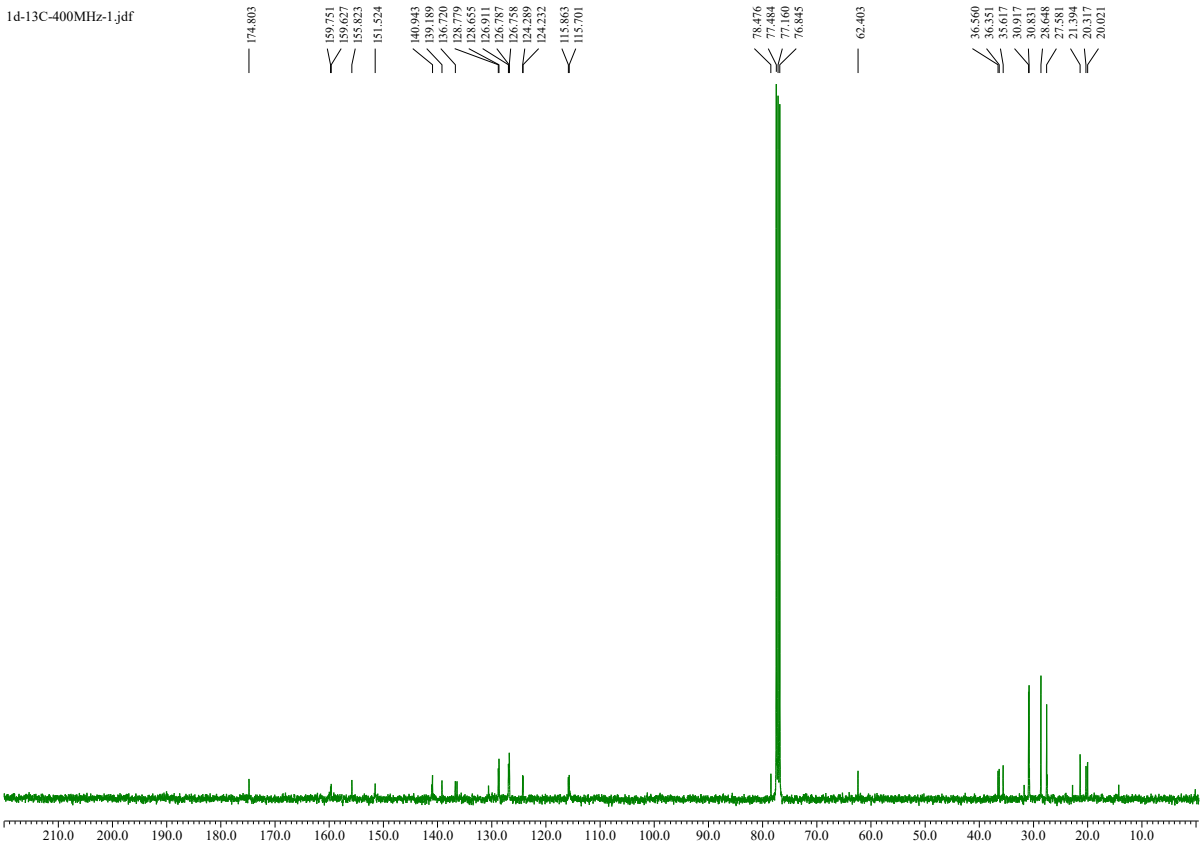
^{1}H NMR spectra (400 MHz) of **1c** in $CDCl_3$



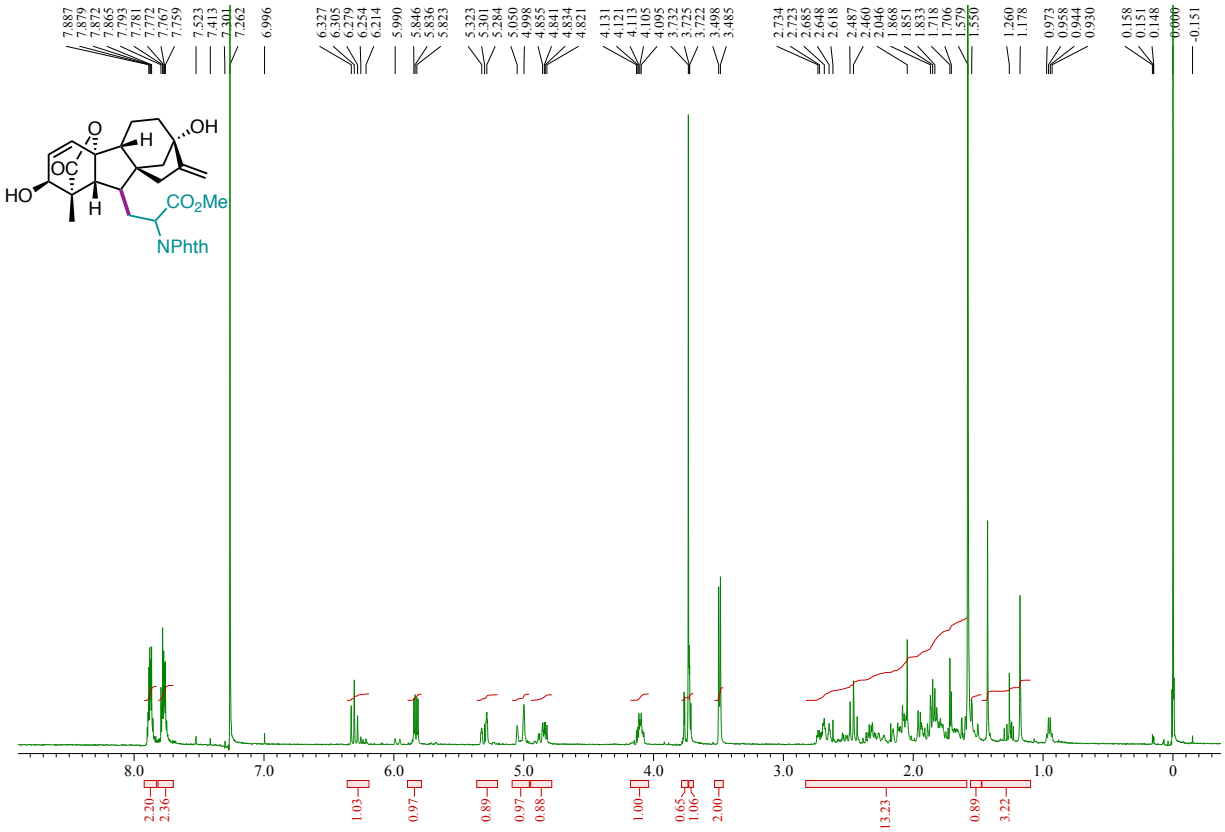
^{13}C NMR spectra (101 MHz) of **1c** in $CDCl_3$



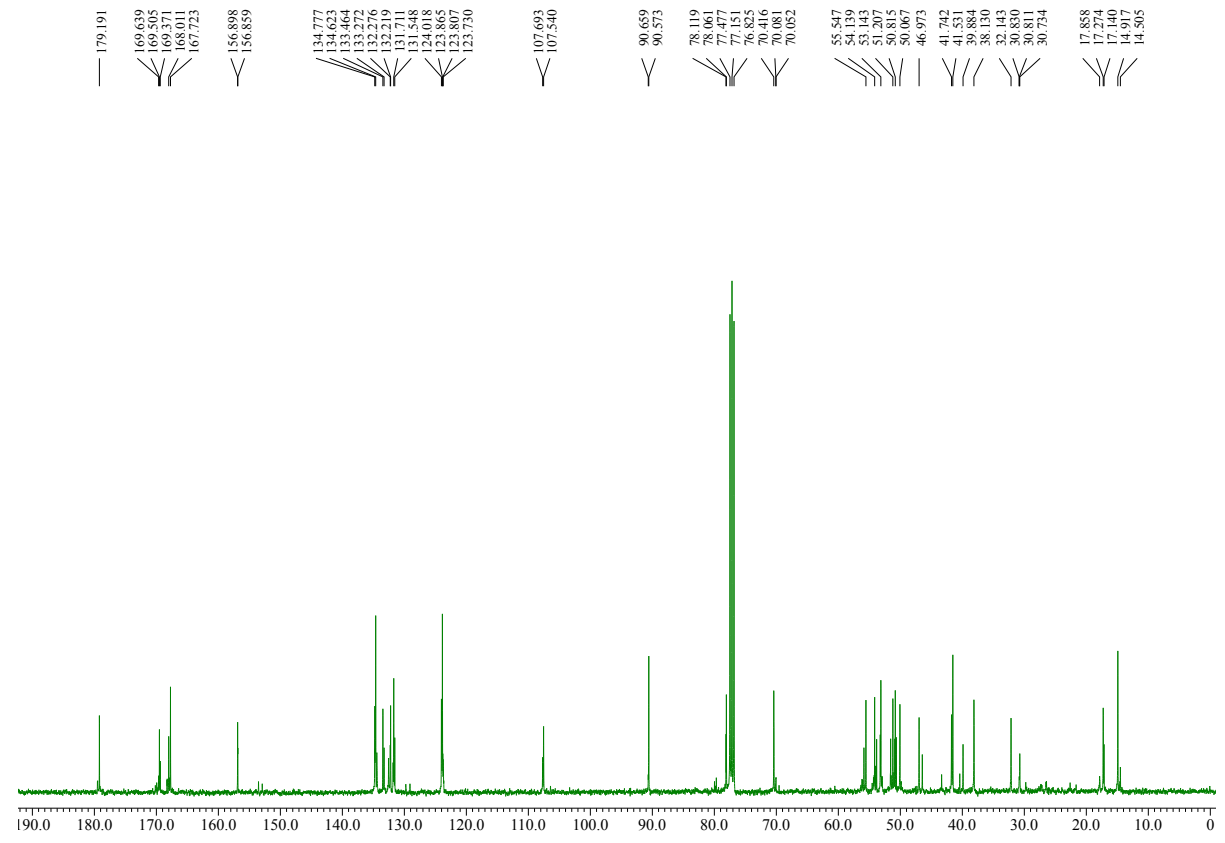
^{1}H NMR spectra (400 MHz) of **1d** in $CDCl_3$



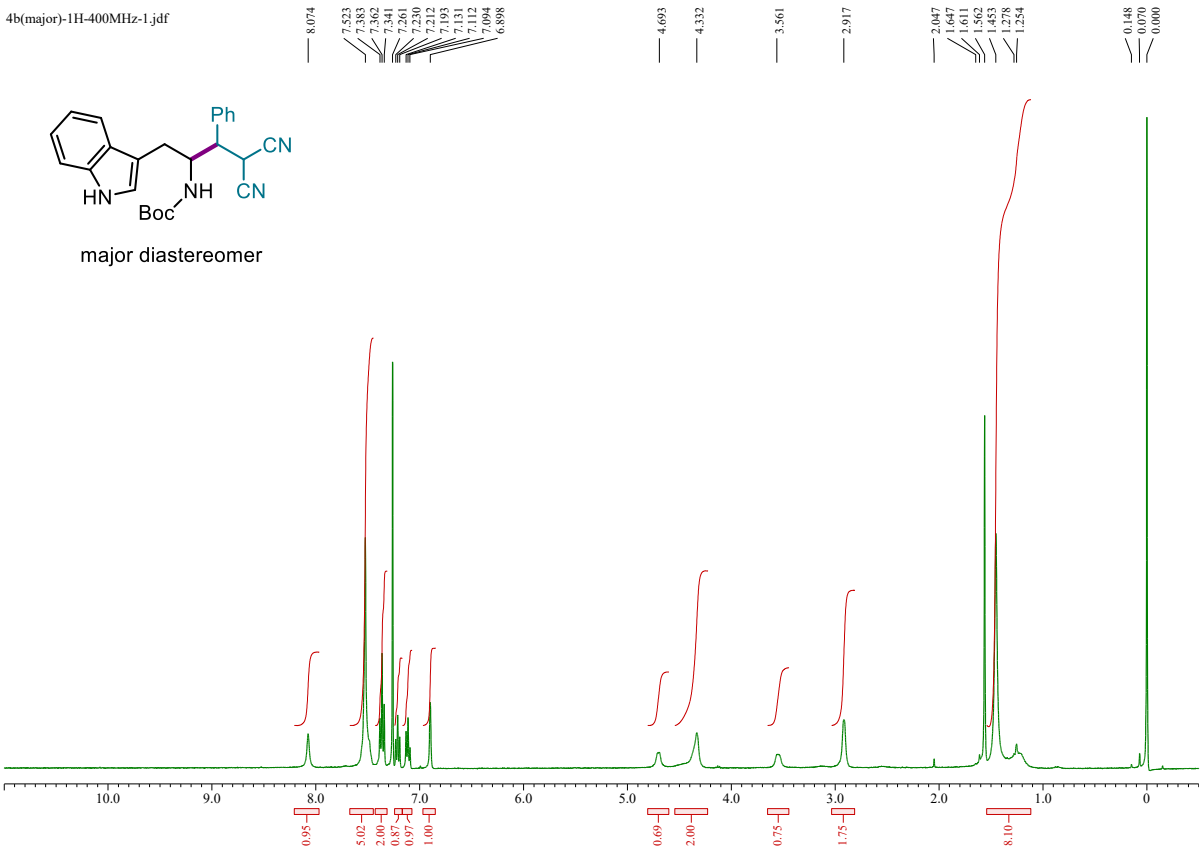
^{13}C NMR spectra (101 MHz) of **1d** in $CDCl_3$



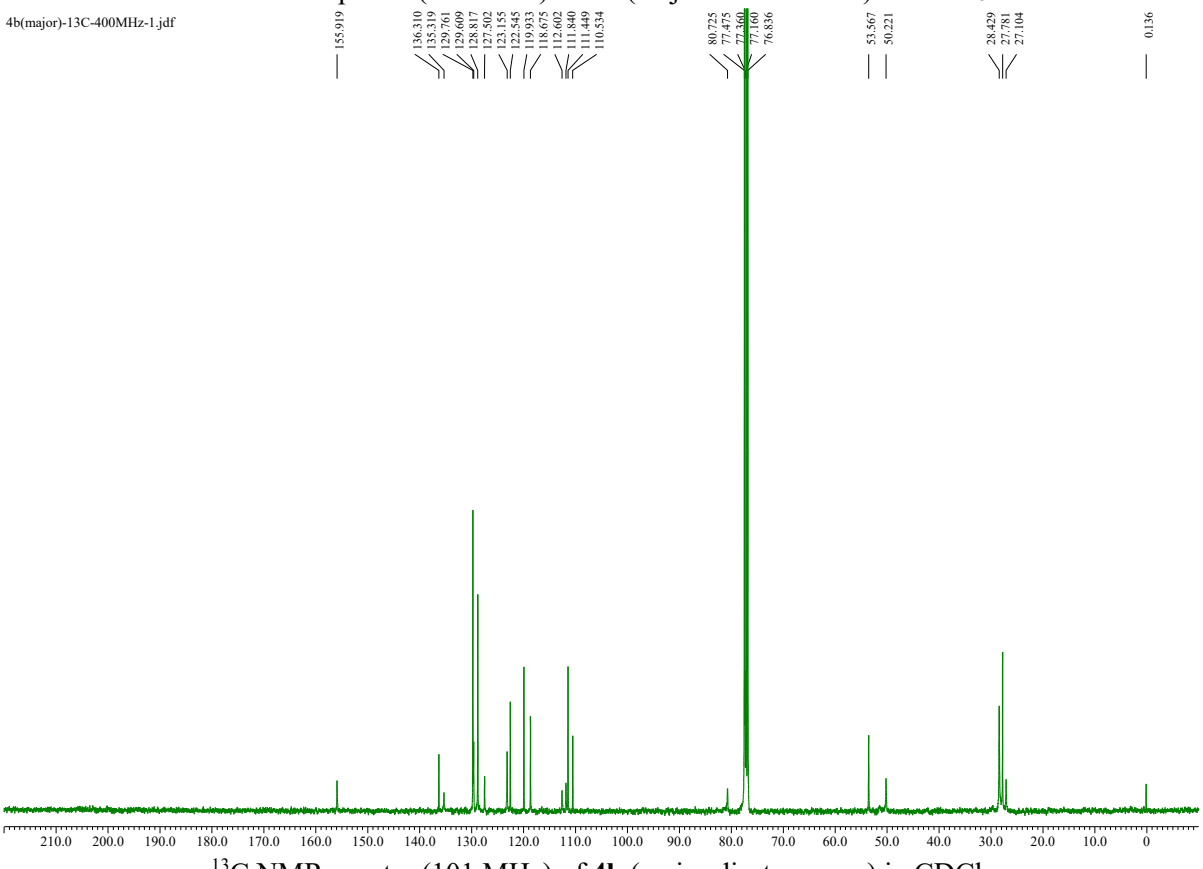
^{1}H NMR spectra (400 MHz) of **4a** (major diastereomer) in $CDCl_3$



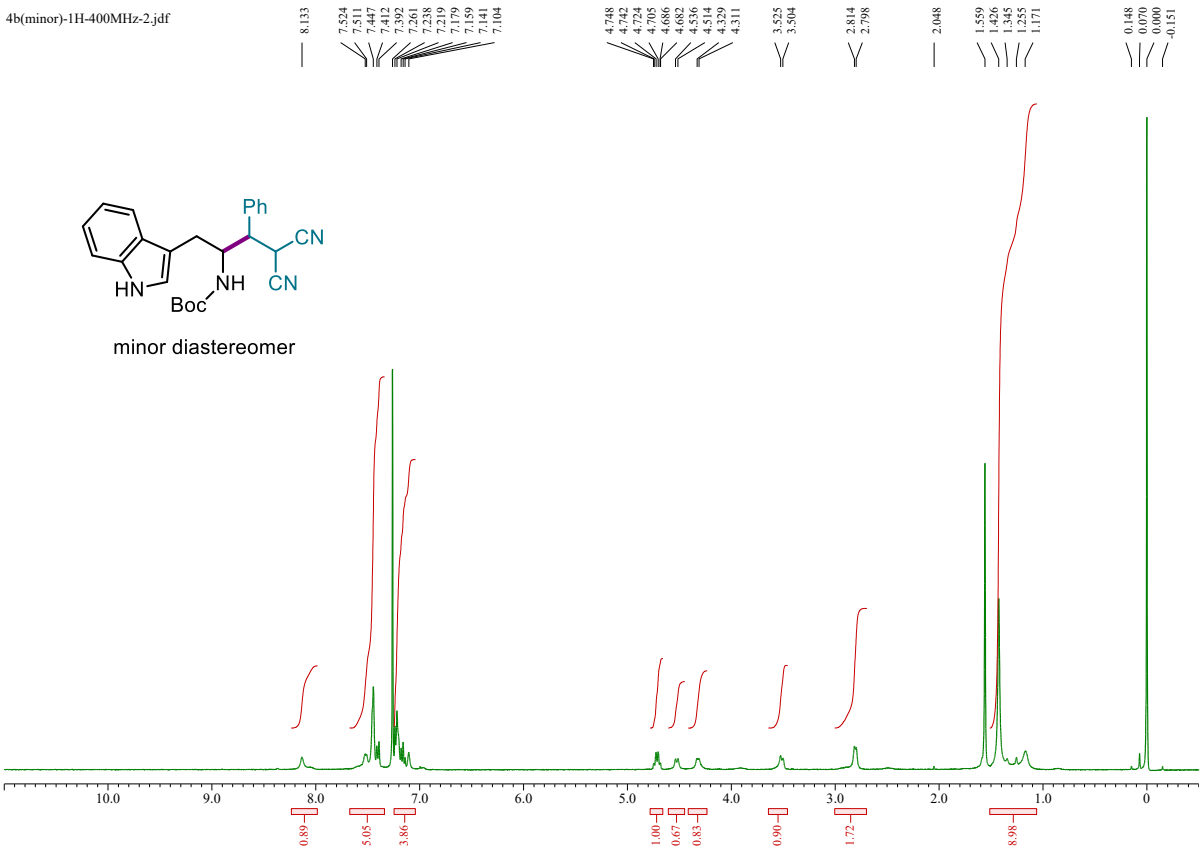
^{13}C NMR spectra (101 MHz) of **4a** (major diastereomer) in $CDCl_3$



^{1}H NMR spectra (400 MHz) of **4b** (major diastereomer) in $CDCl_3$



^{13}C NMR spectra (101 MHz) of **4b** (major diastereomer) in $CDCl_3$



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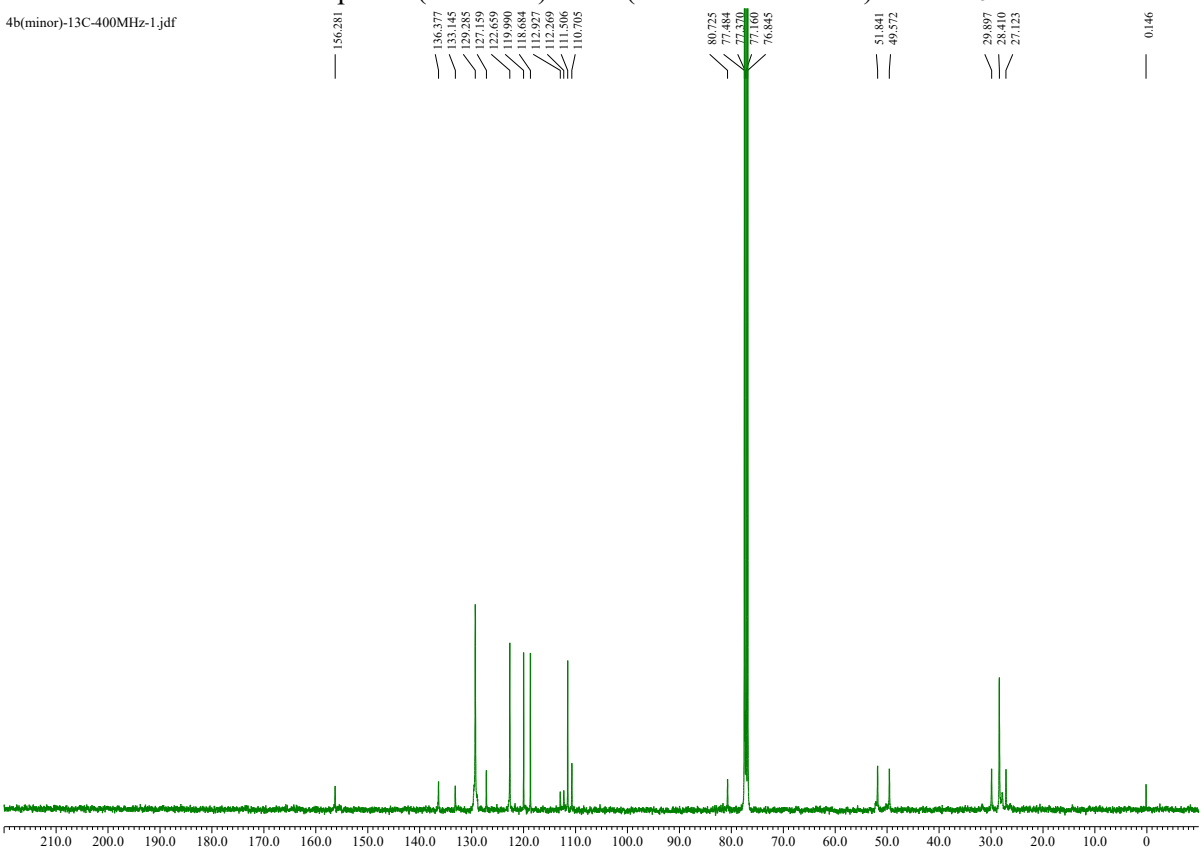
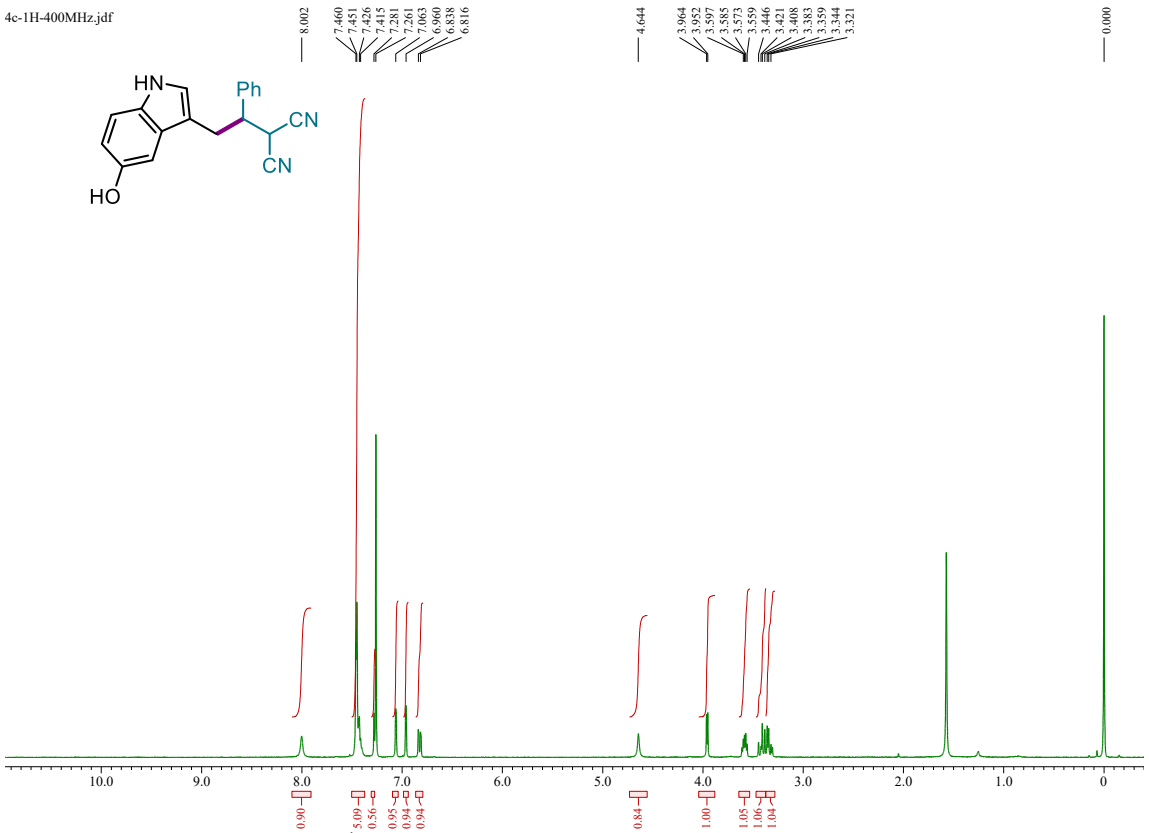
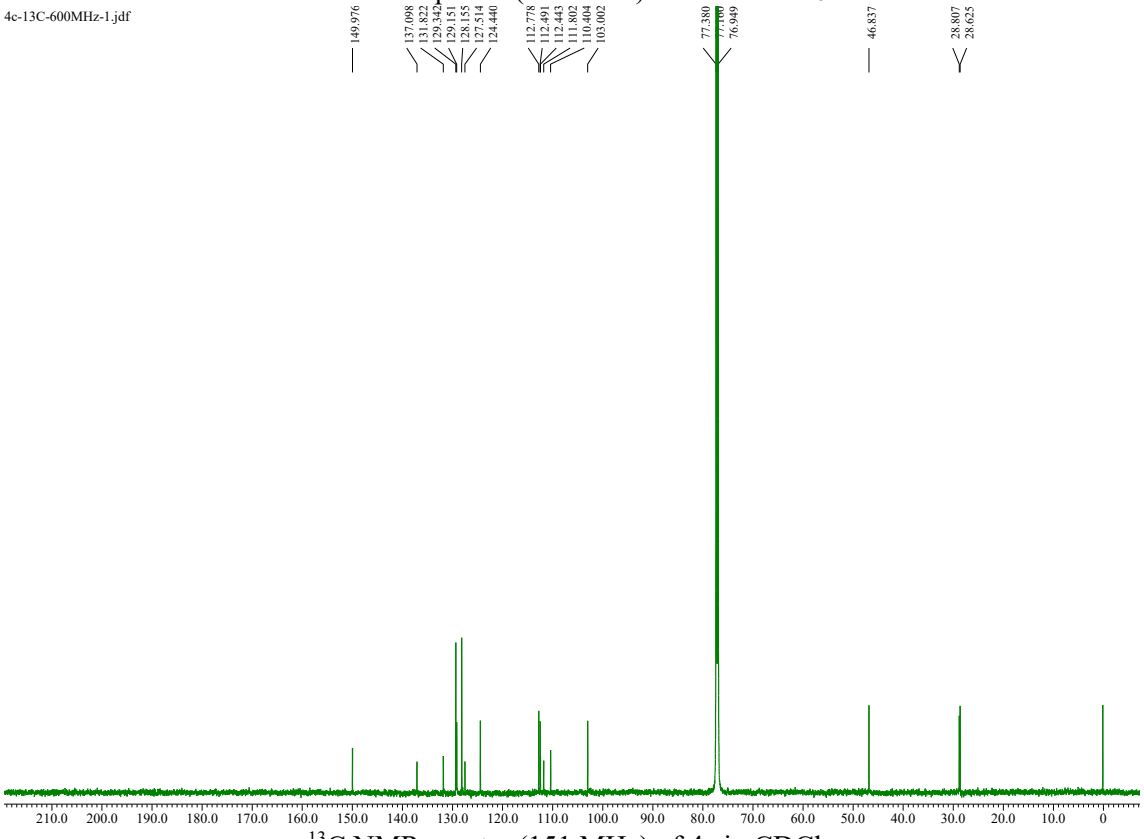


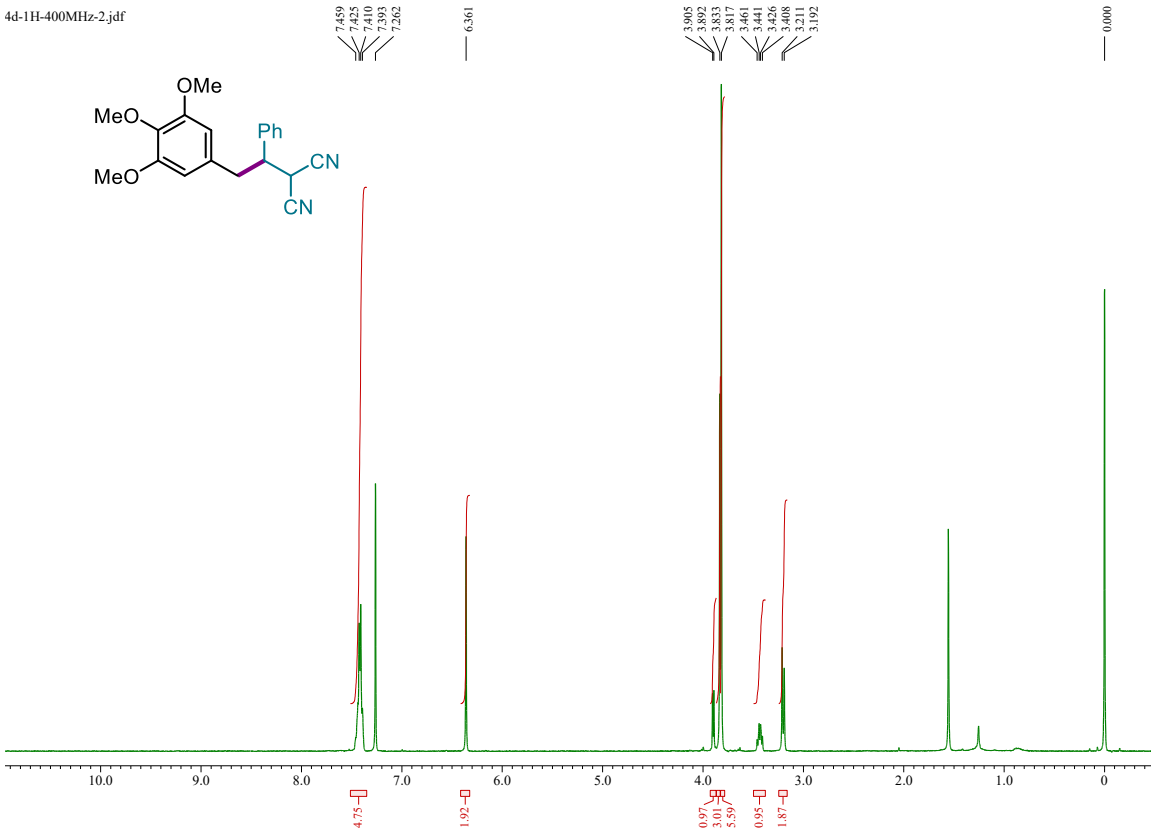
^{13}C NMR spectra (101 MHz) of **4b** (minor diastereomer) in $CDCl_3$



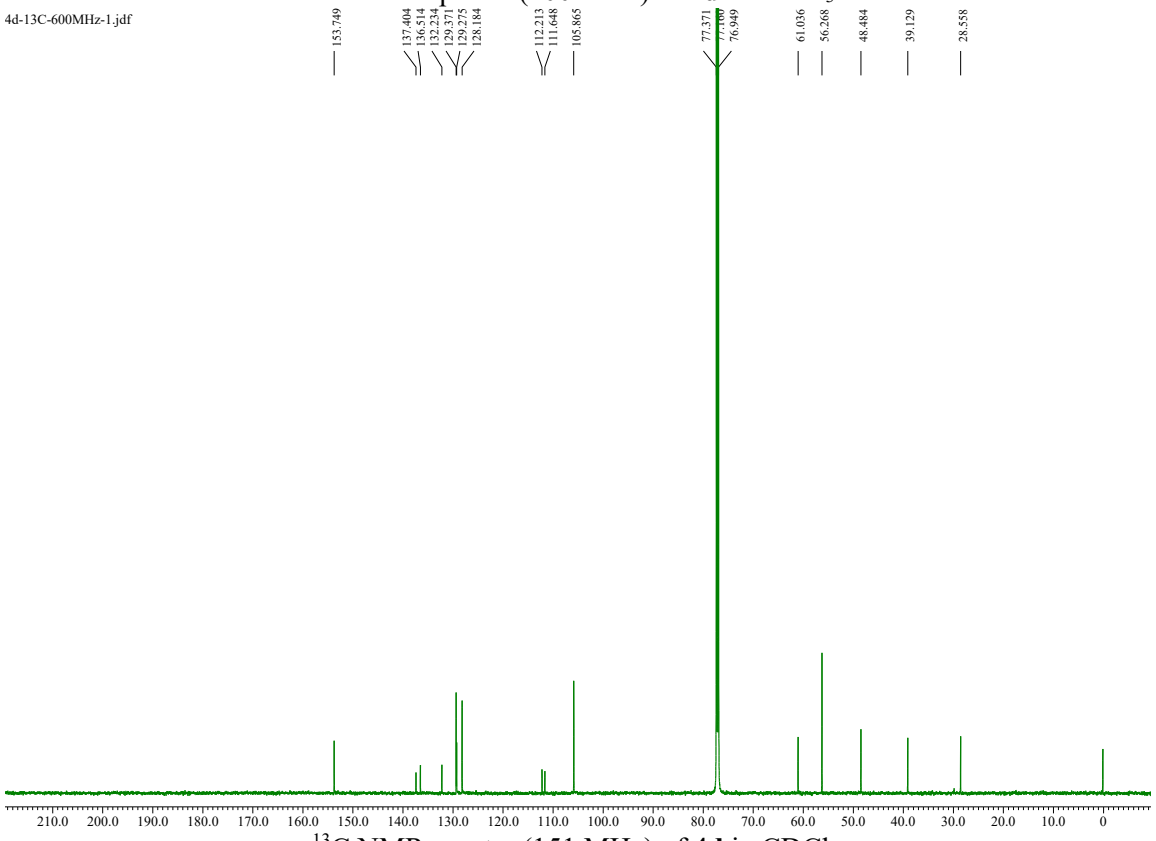
^{1}H NMR spectra (400 MHz) of **4c** in $CDCl_3$



^{13}C NMR spectra (151 MHz) of **4c** in $CDCl_3$



^{1}H NMR spectra (400 MHz) of **4d** in $CDCl_3$



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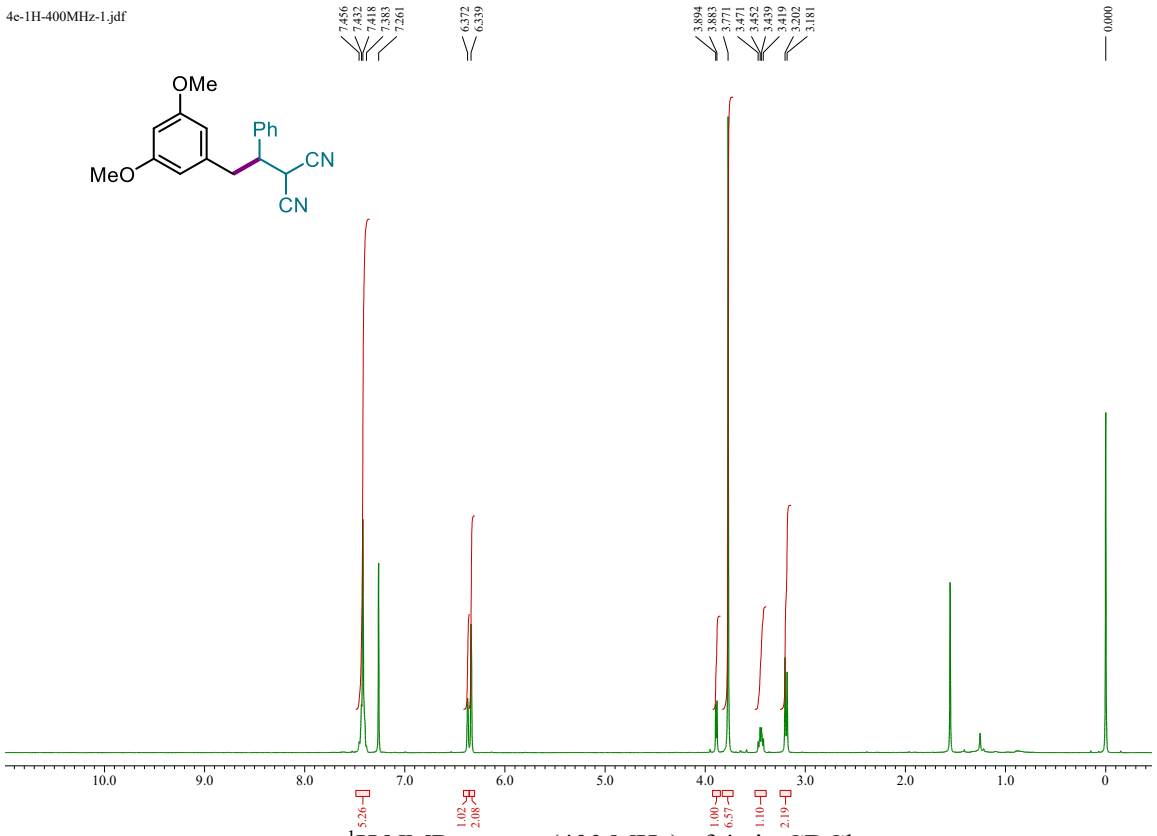
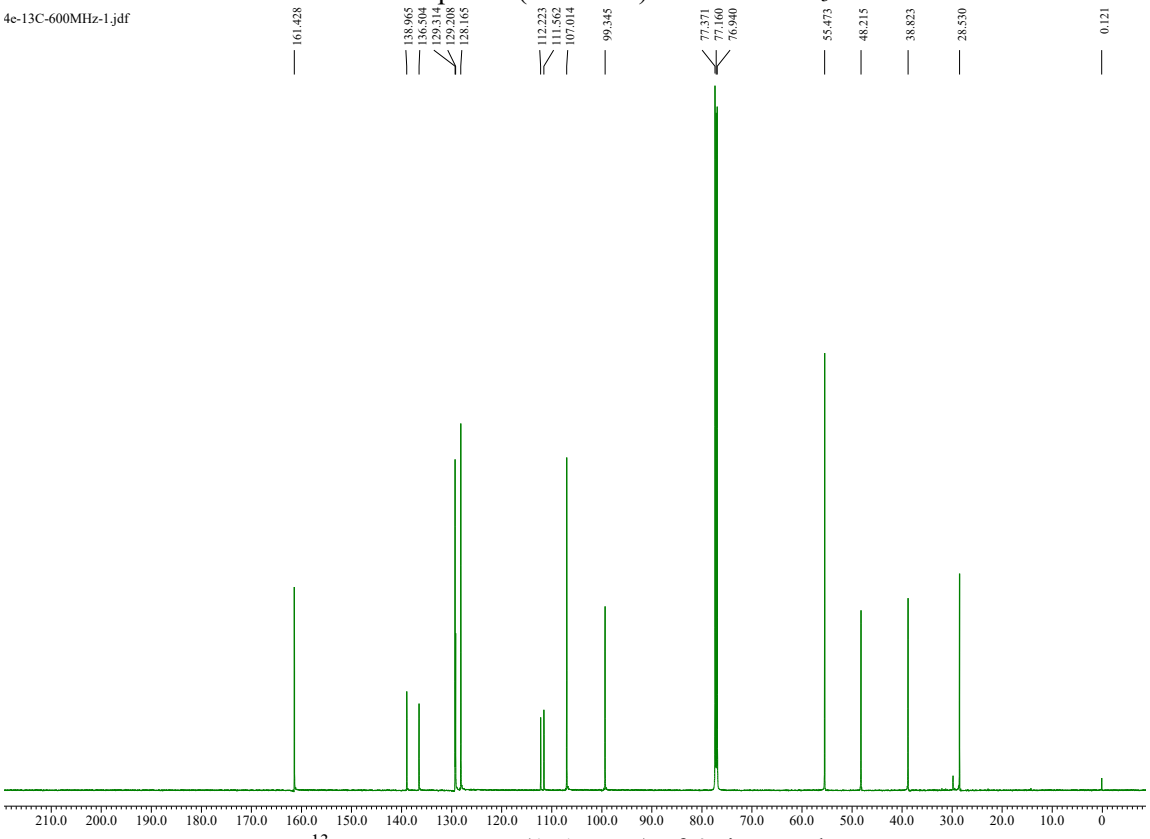
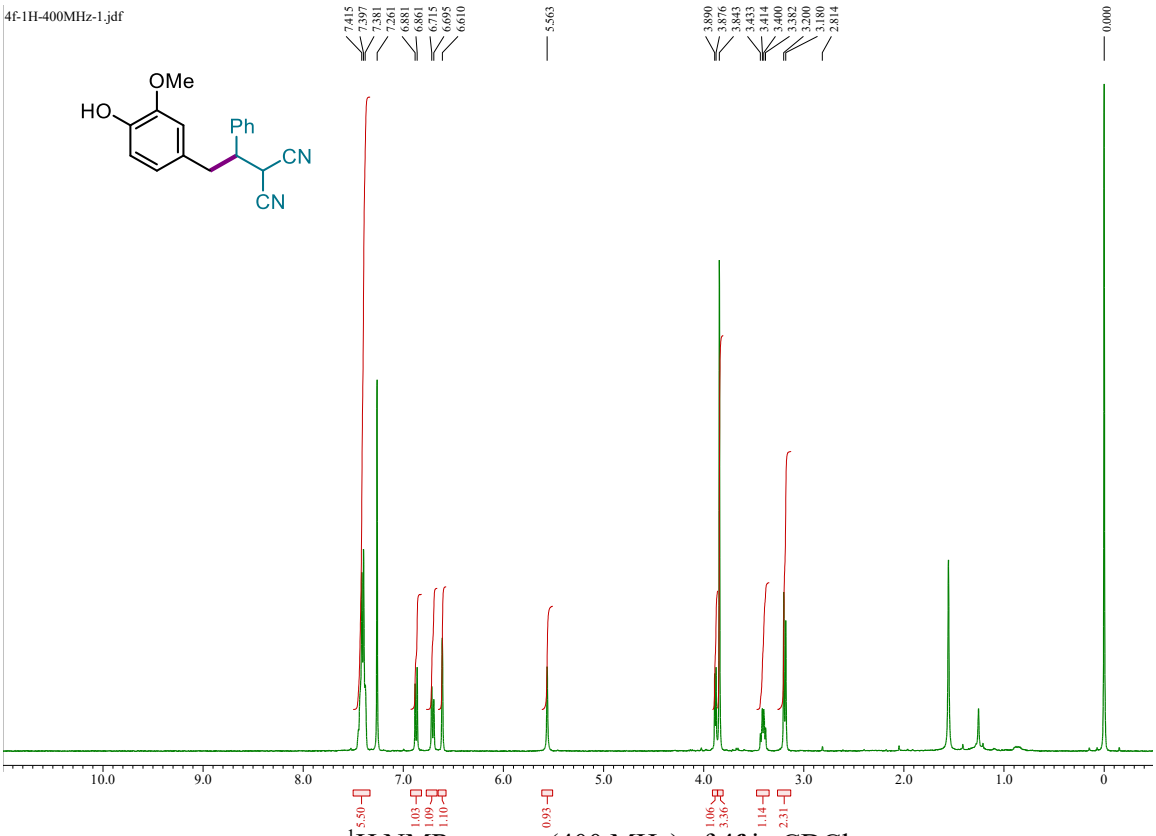


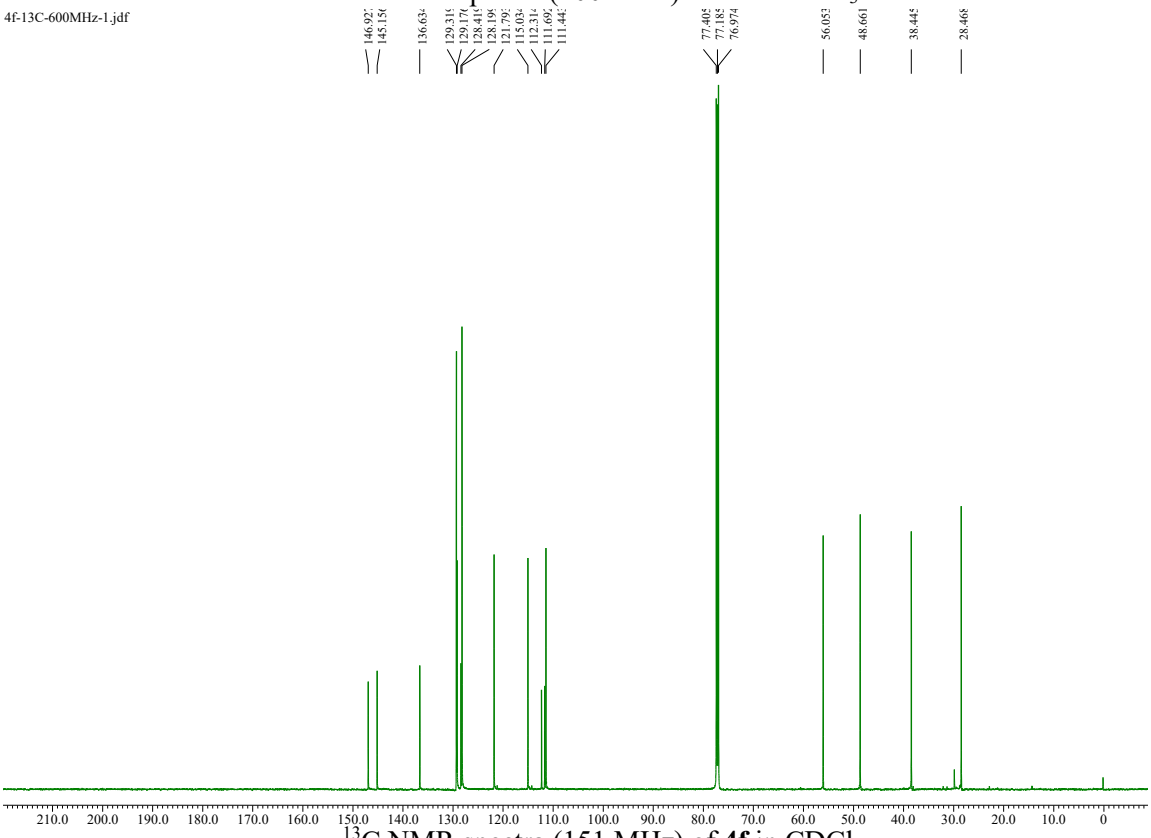
^{1}H NMR spectra (400 MHz) of **4e** in $CDCl_3$



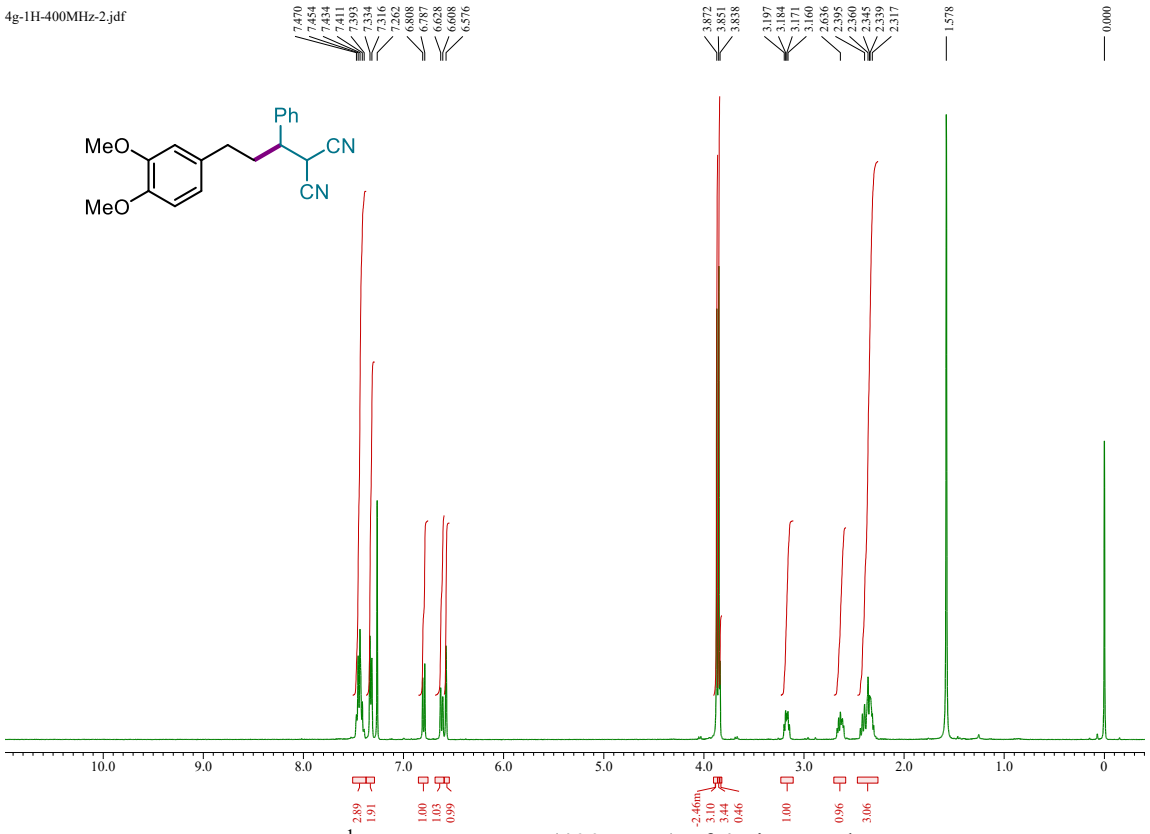
^{13}C NMR spectra (151 MHz) of **4e** in $CDCl_3$



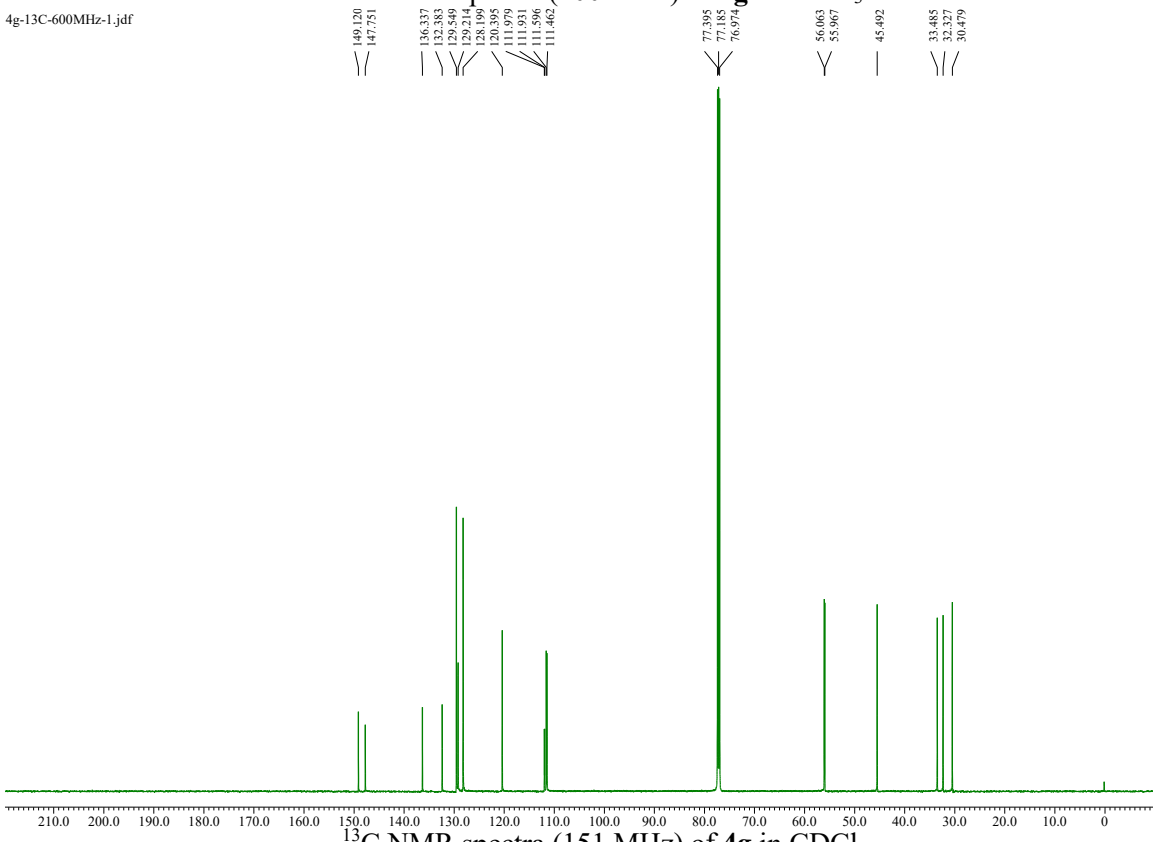
^{1}H NMR spectra (400 MHz) of **4f** in $CDCl_3$



^{13}C NMR spectra (151 MHz) of **4f** in $CDCl_3$



^{1}H NMR spectra (400 MHz) of **4g** in $CDCl_3$



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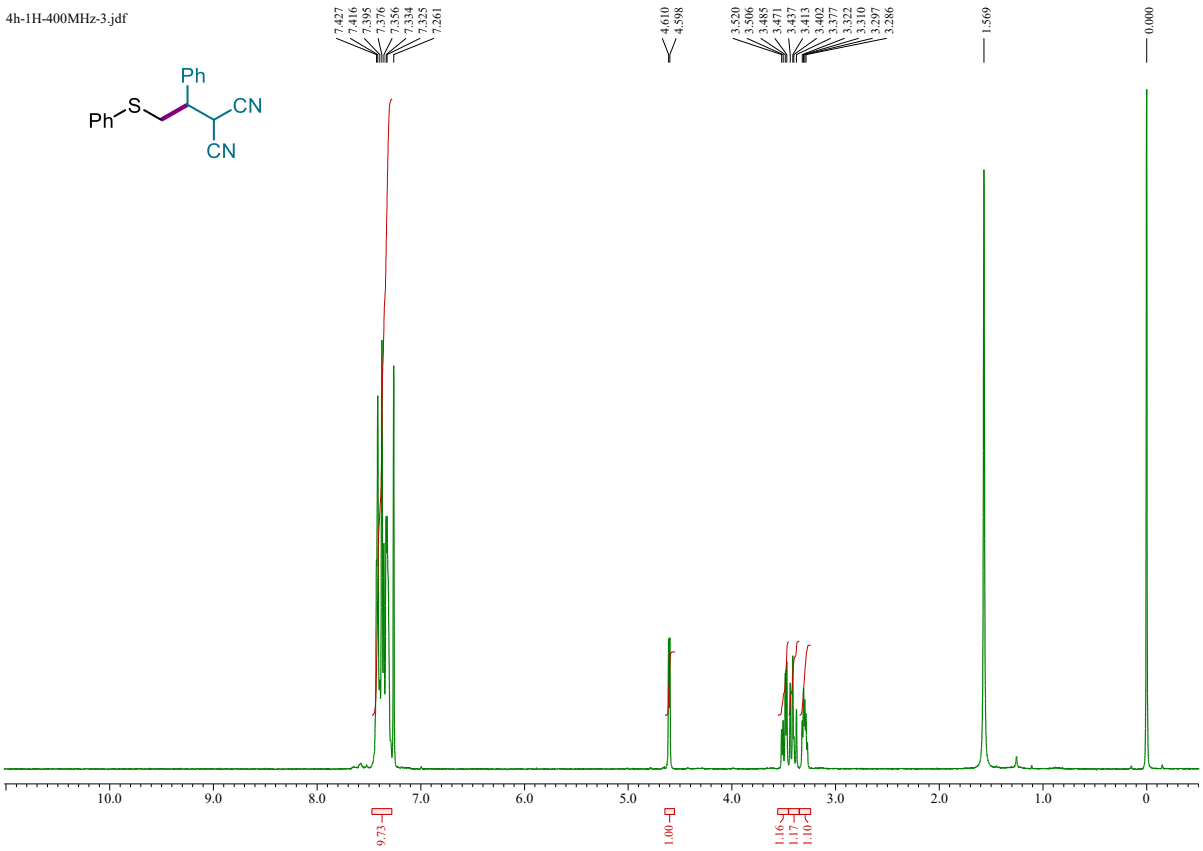
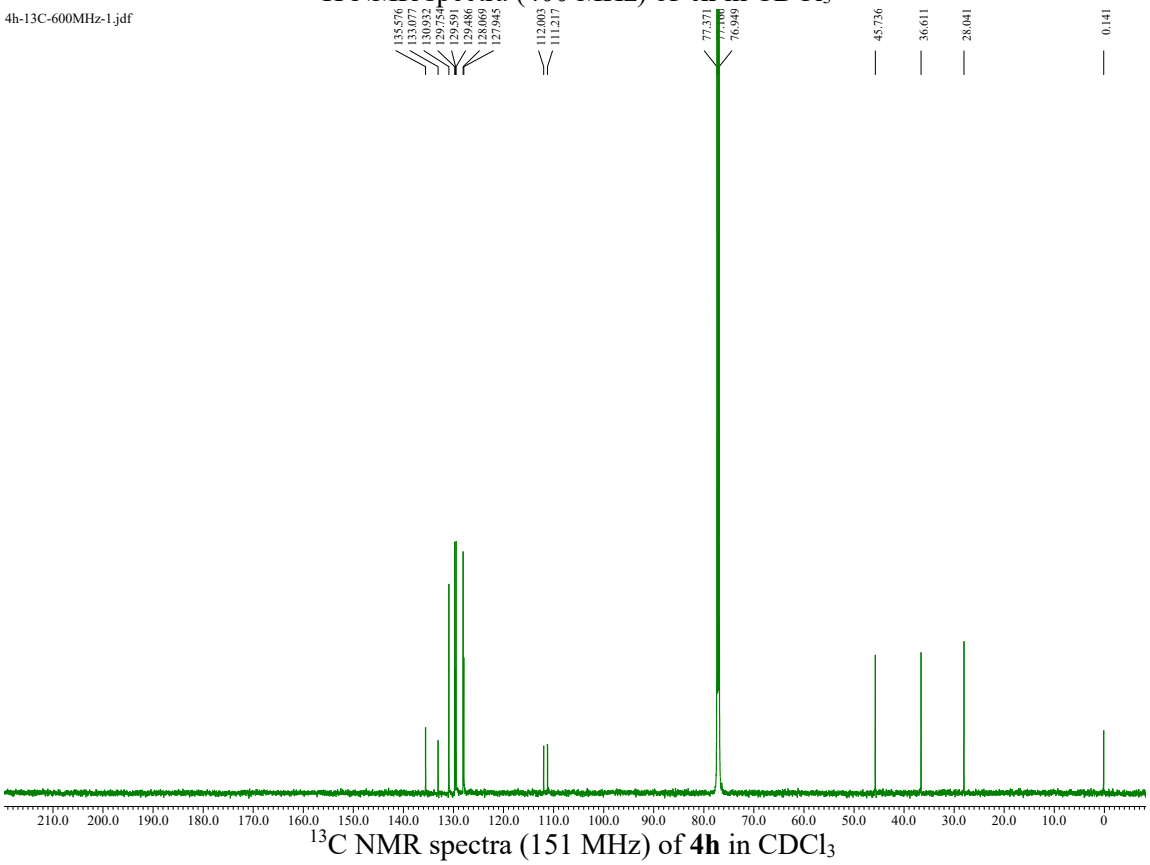
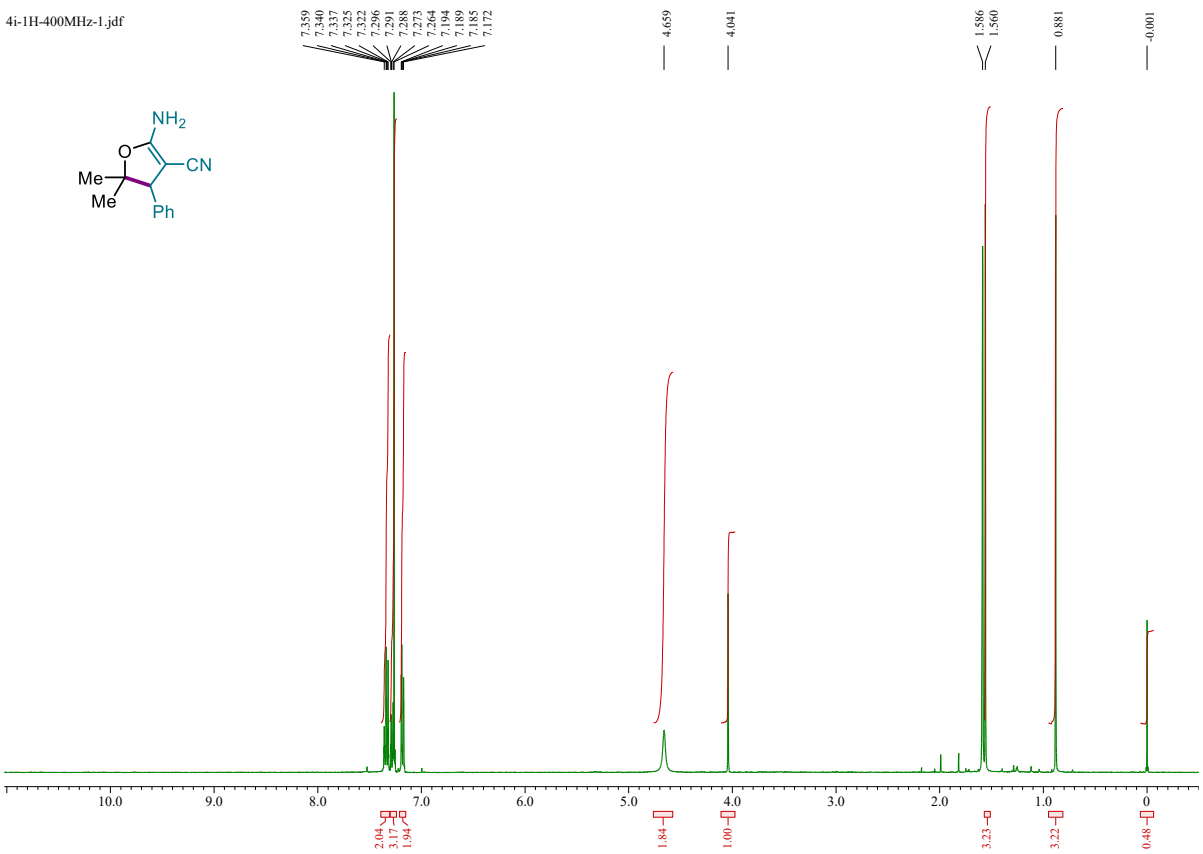


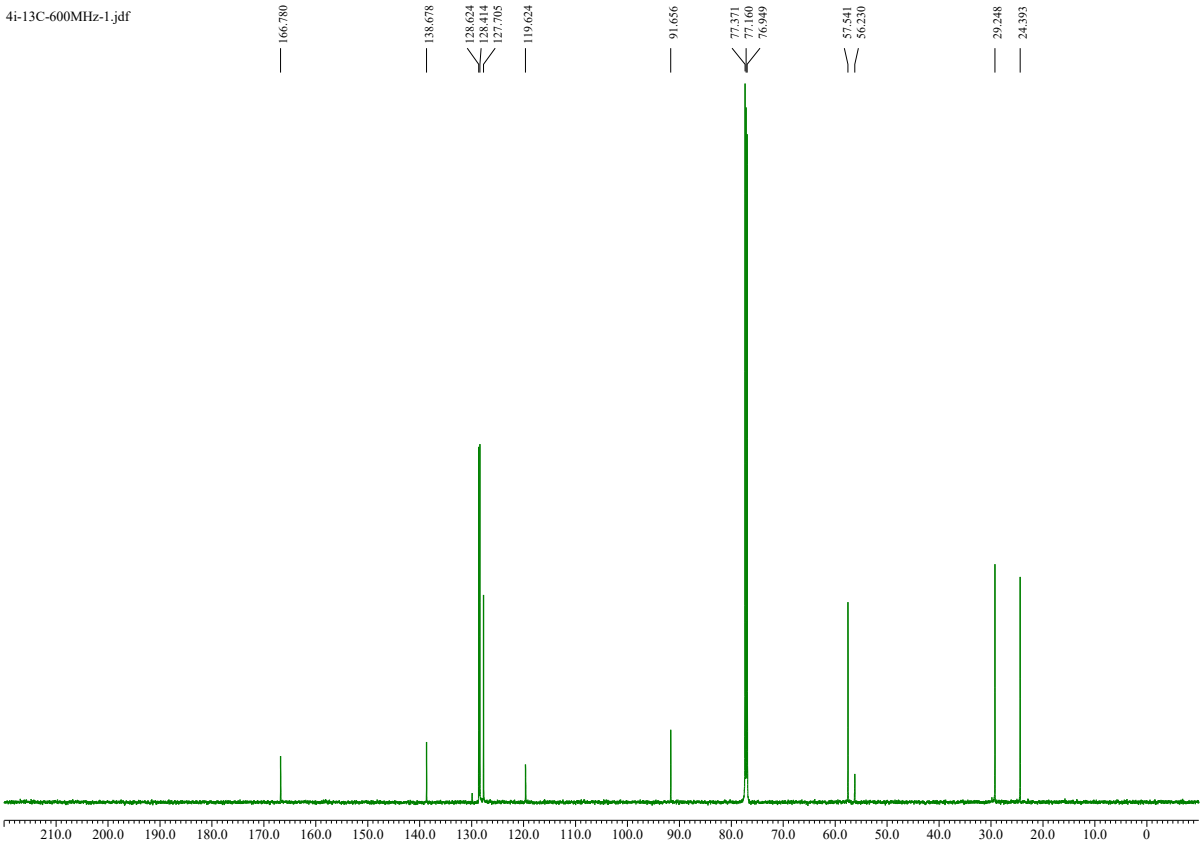
^{1}H NMR spectra (400 MHz) of **4h** in $CDCl_3$



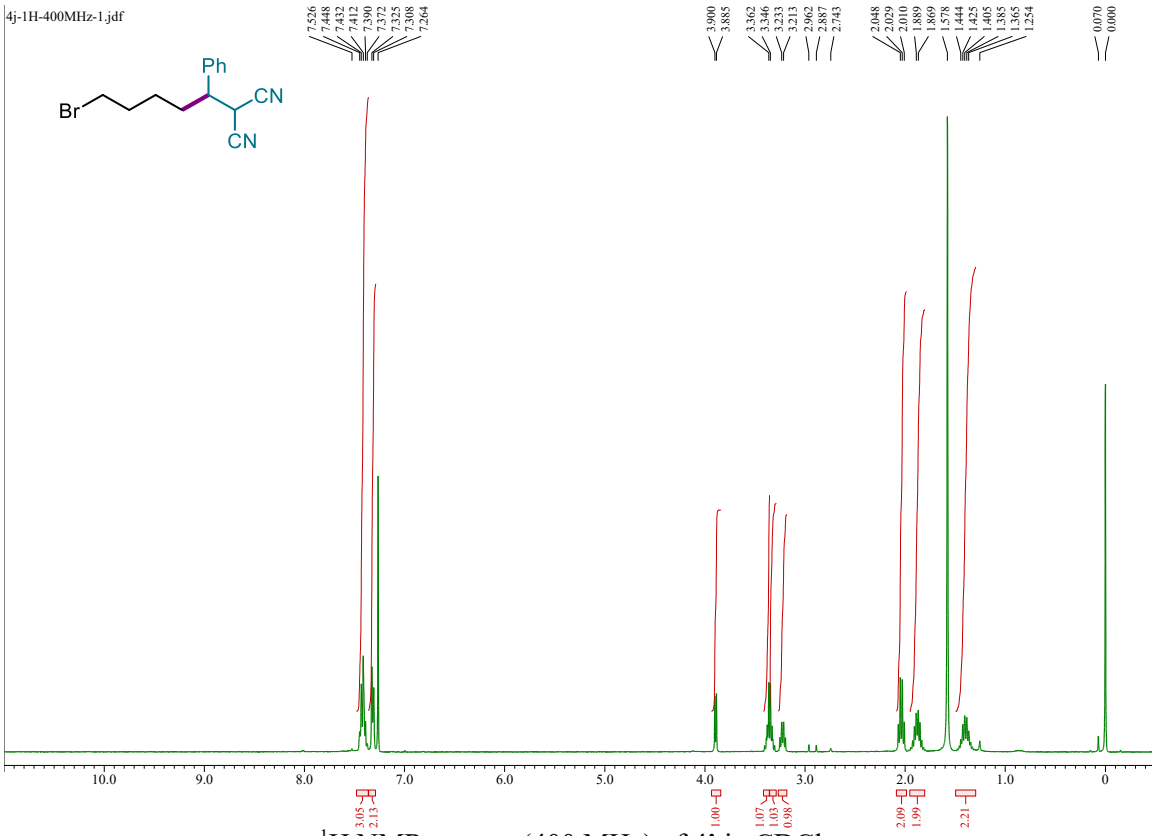
^{13}C NMR spectra (151 MHz) of **4h** in $CDCl_3$



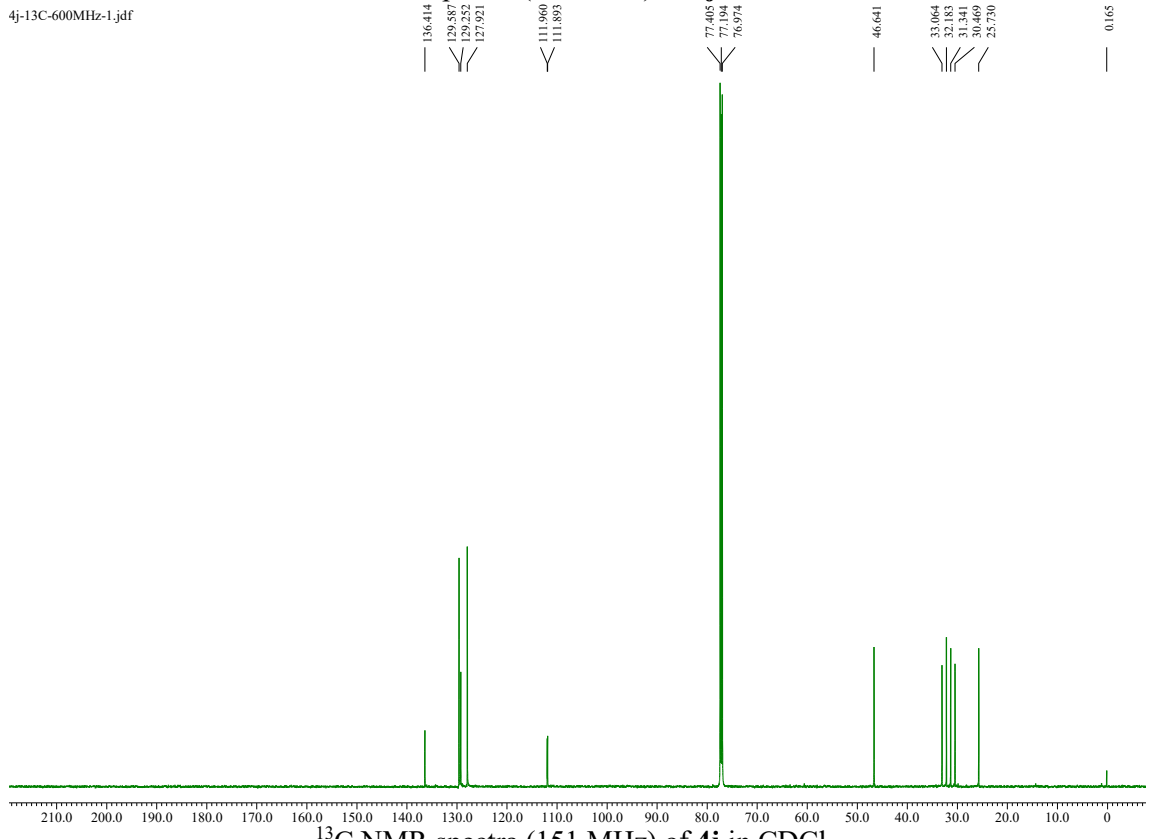
^{1}H NMR spectra (400 MHz) of **4i'** in $CDCl_3$



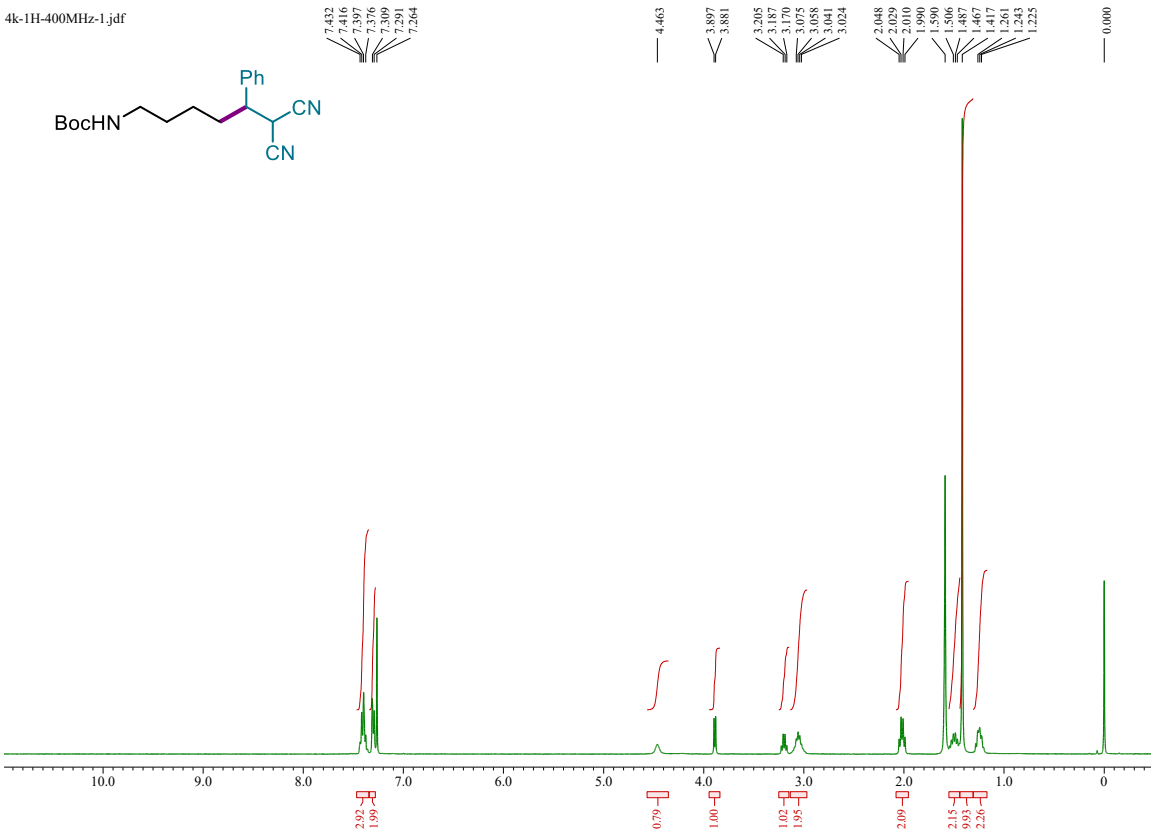
^{13}C NMR spectra (151 MHz) of **4i'** in $CDCl_3$



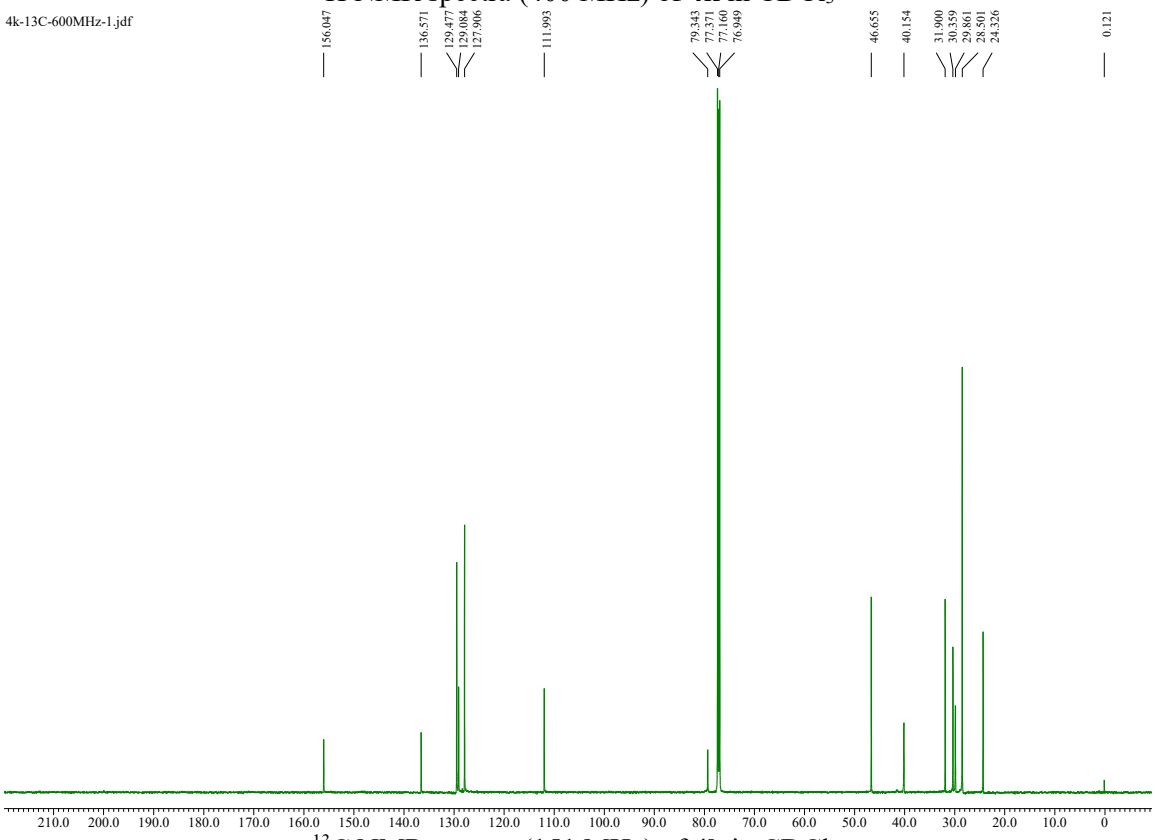
^{1}H NMR spectra (400 MHz) of **4j** in $CDCl_3$



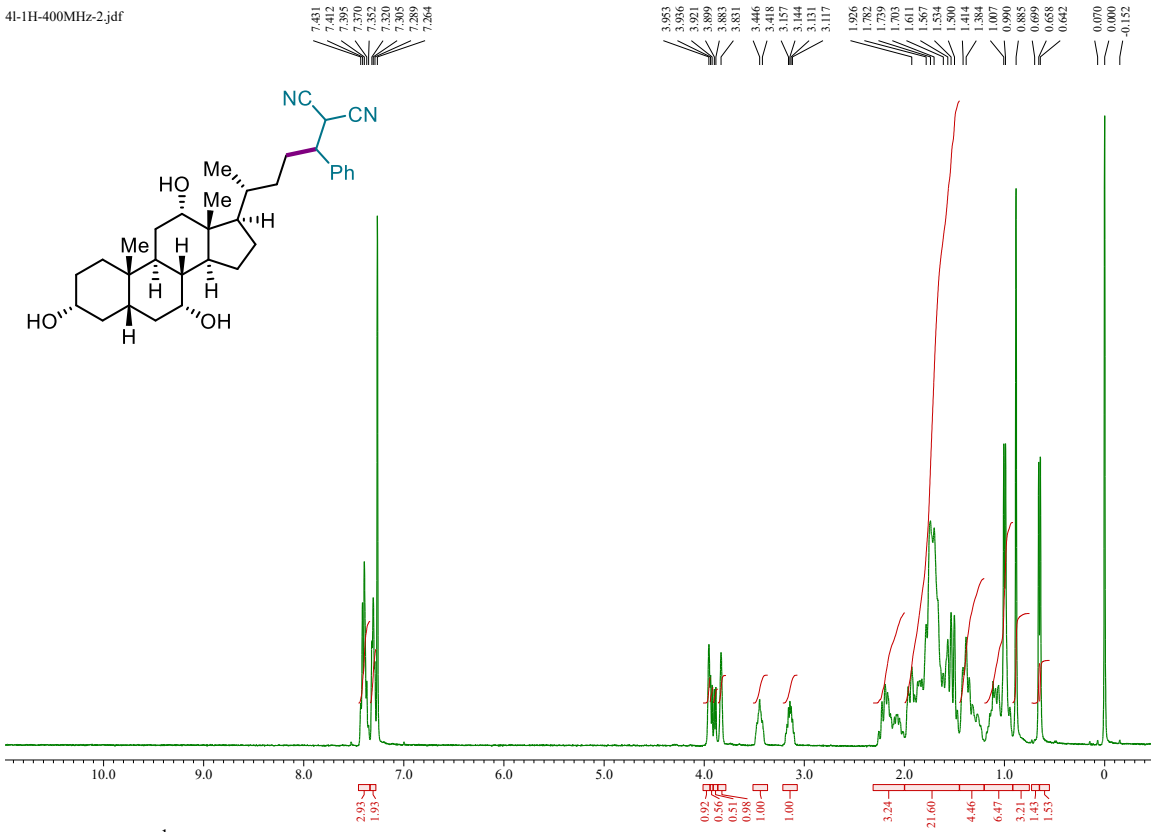
^{13}C NMR spectra (151 MHz) of **4j** in $CDCl_3$



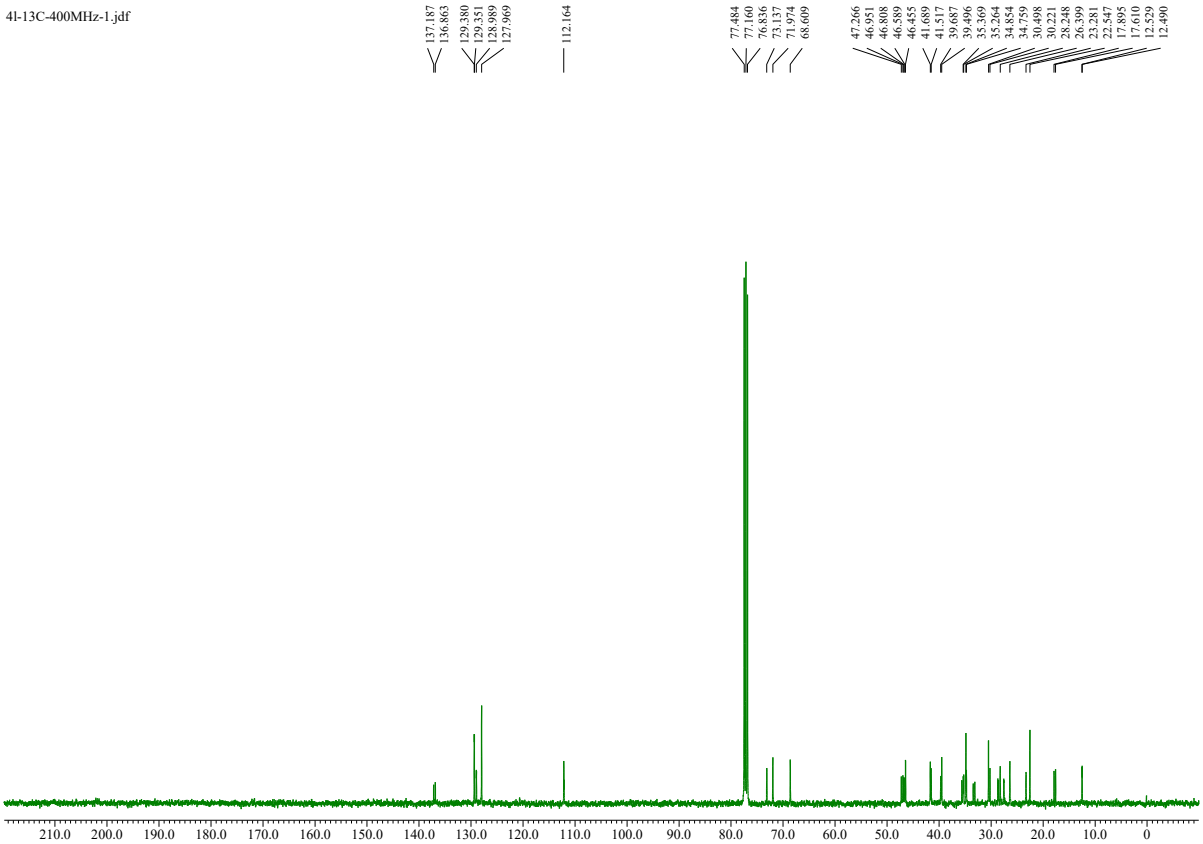
^{1}H NMR spectra (400 MHz) of **4k** in $CDCl_3$



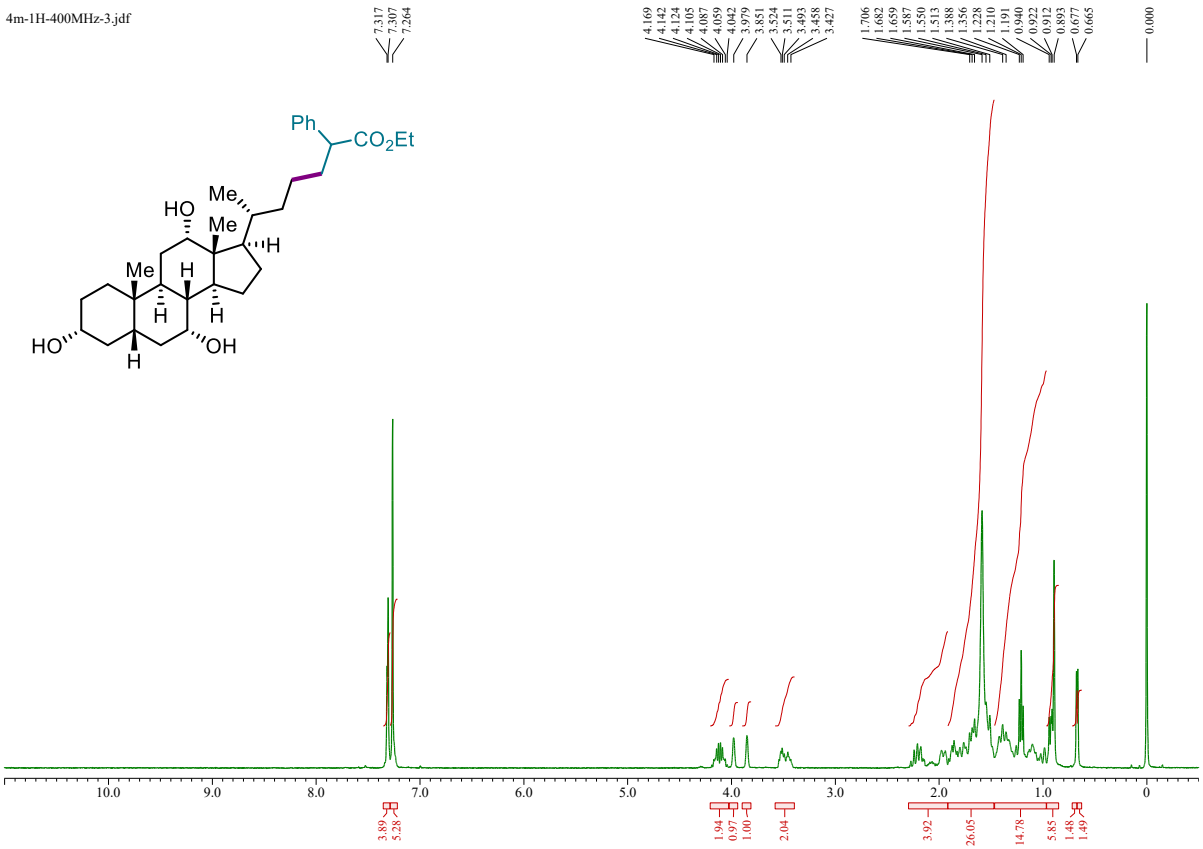
^{13}C NMR spectra (151 MHz) of **4k** in $CDCl_3$



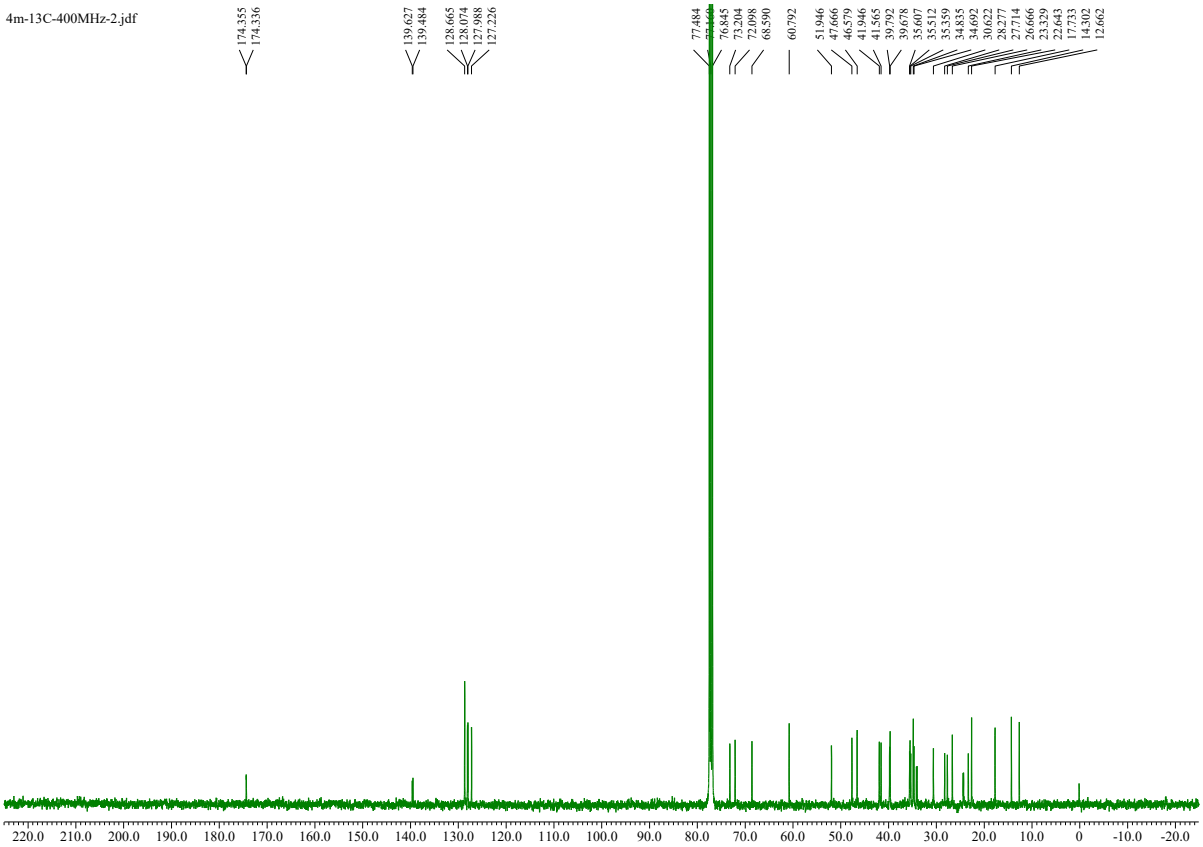
^{1}H NMR spectra (400 MHz) of **4l** (mixture of diastereomers) in $CDCl_3$



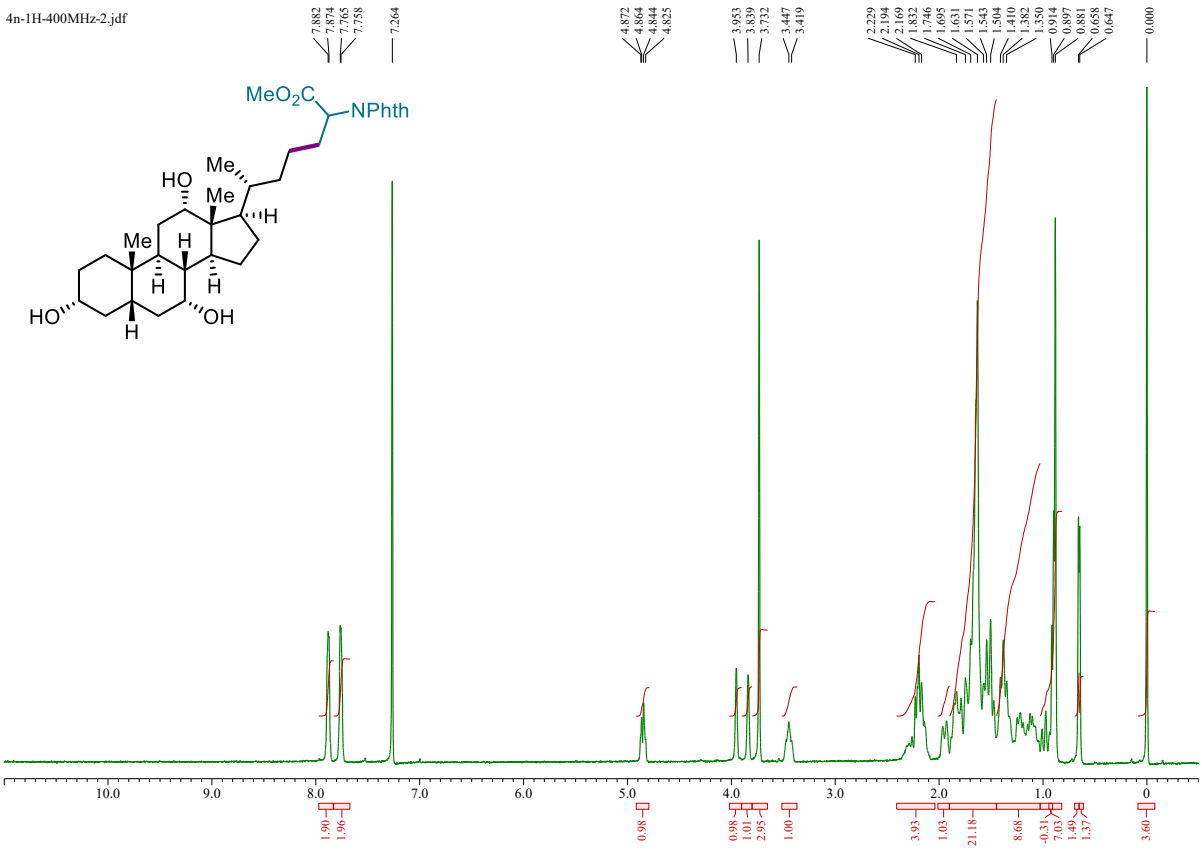
^{13}C NMR spectra (101 MHz) of **4l** (mixture of diastereomers) in $CDCl_3$



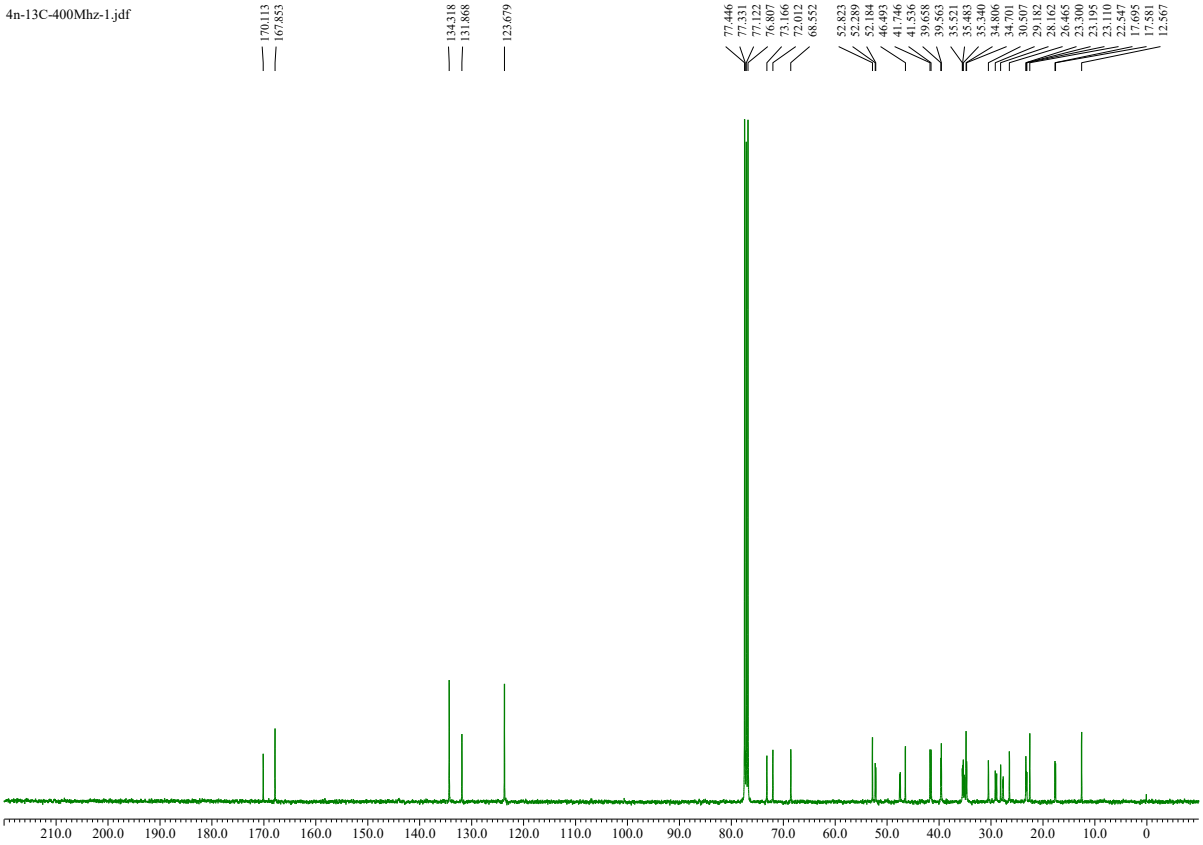
^{1}H NMR spectra (400 MHz) of **4m** (mixture of diastereomers) in $CDCl_3$.



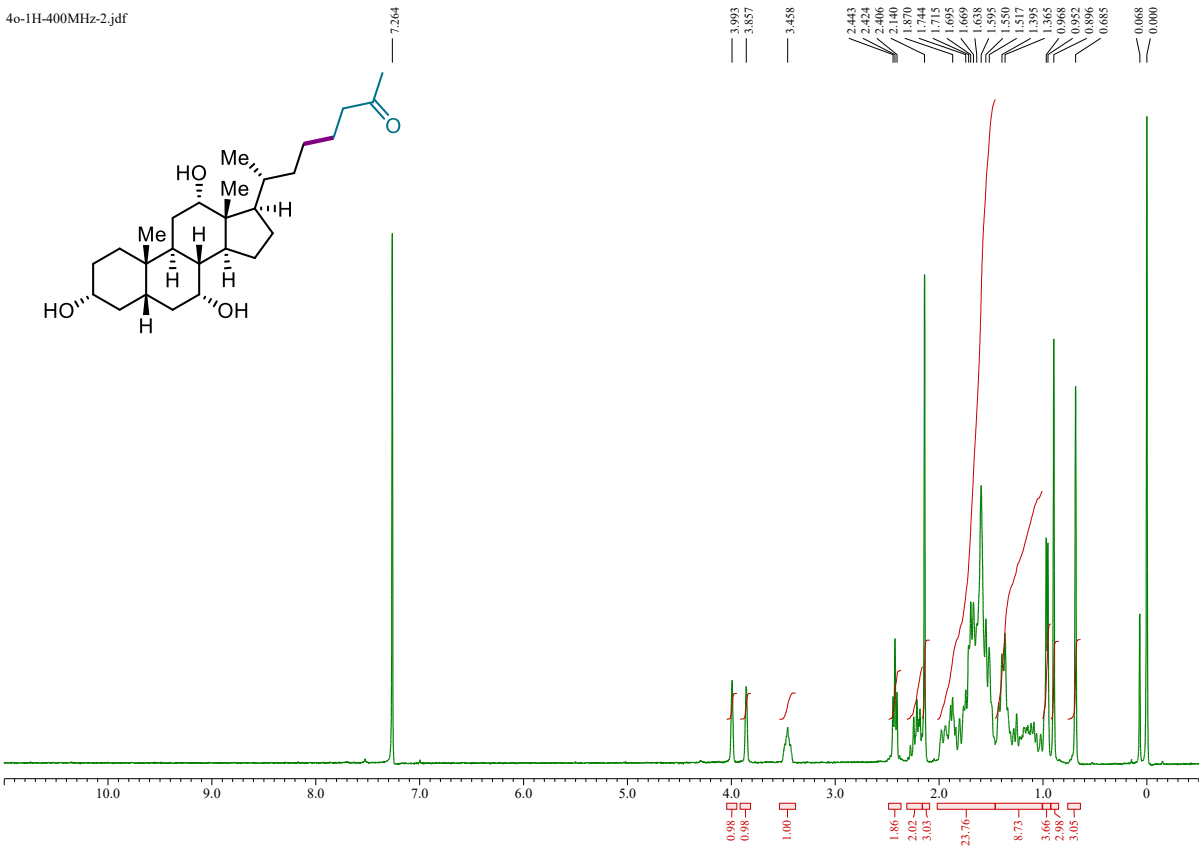
^{13}C NMR spectra (101 MHz) of **4m** (mixture of diastereomers) in $CDCl_3$



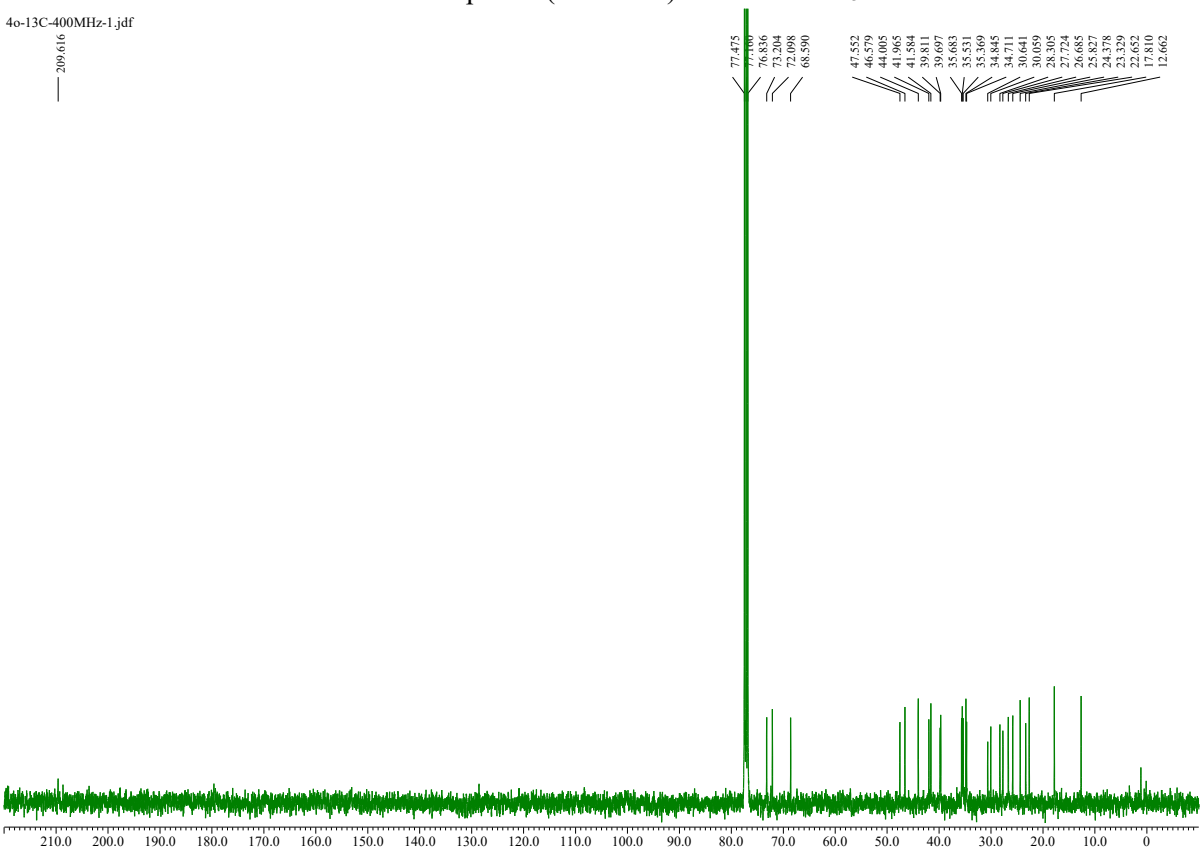
^{1}H NMR spectra (400 MHz) of **4n** (mixture of diastereomers) in $CDCl_3$



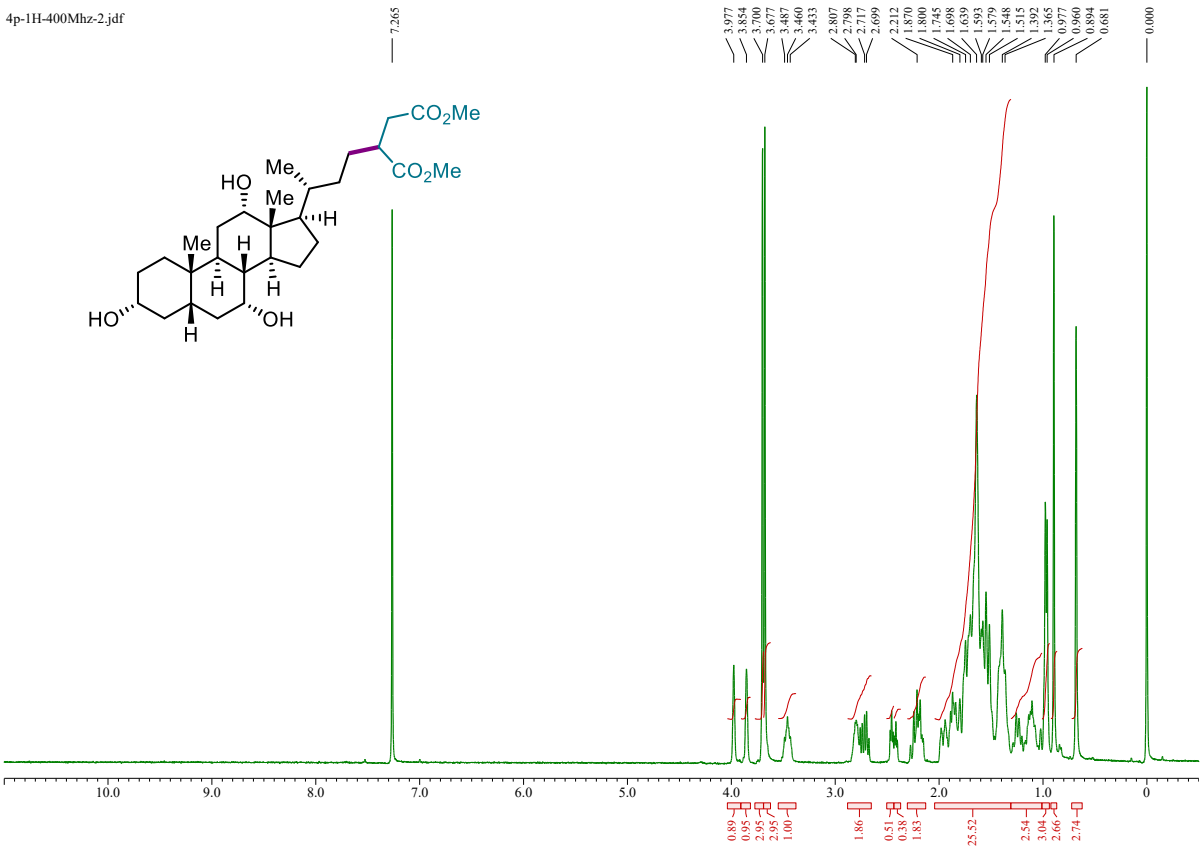
^{13}C NMR spectra (101 MHz) of **4n** (mixture of diastereomers) in $CDCl_3$



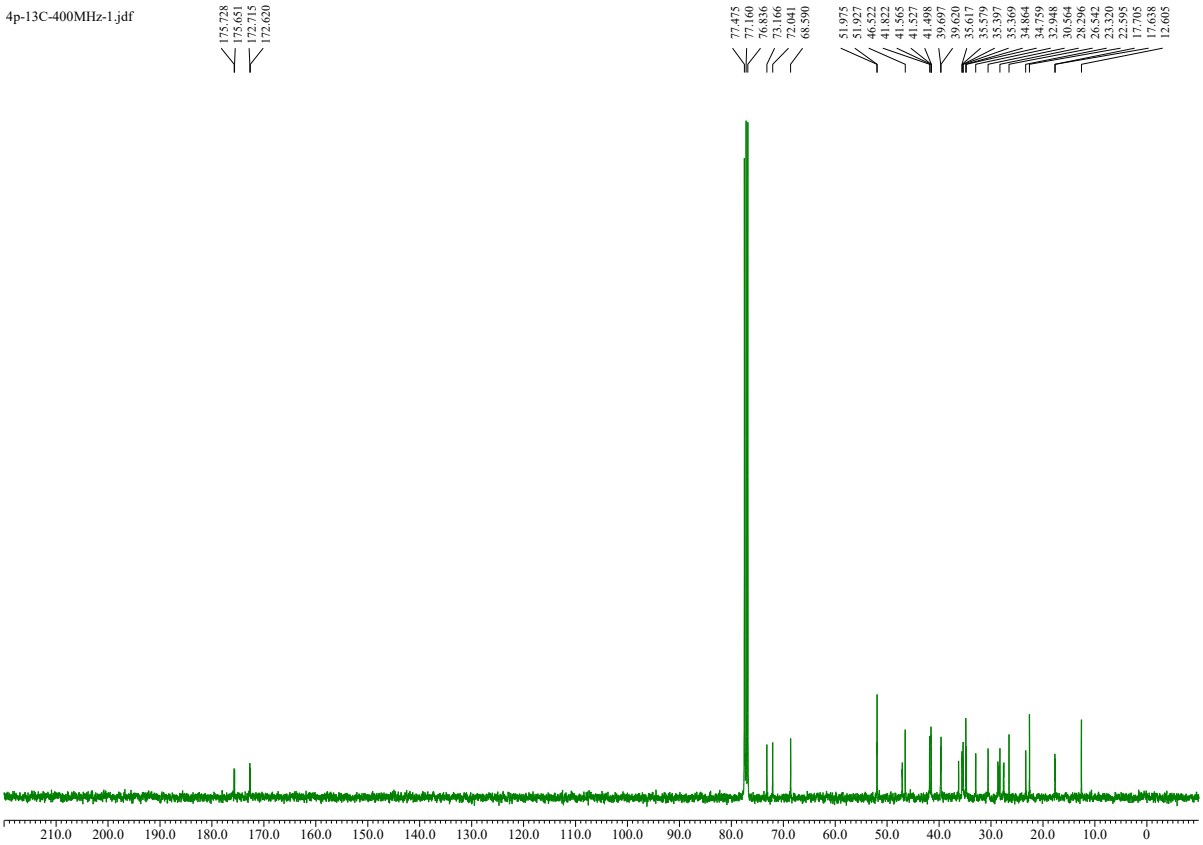
^{1}H NMR spectra (400 MHz) of **4o** in $CDCl_3$



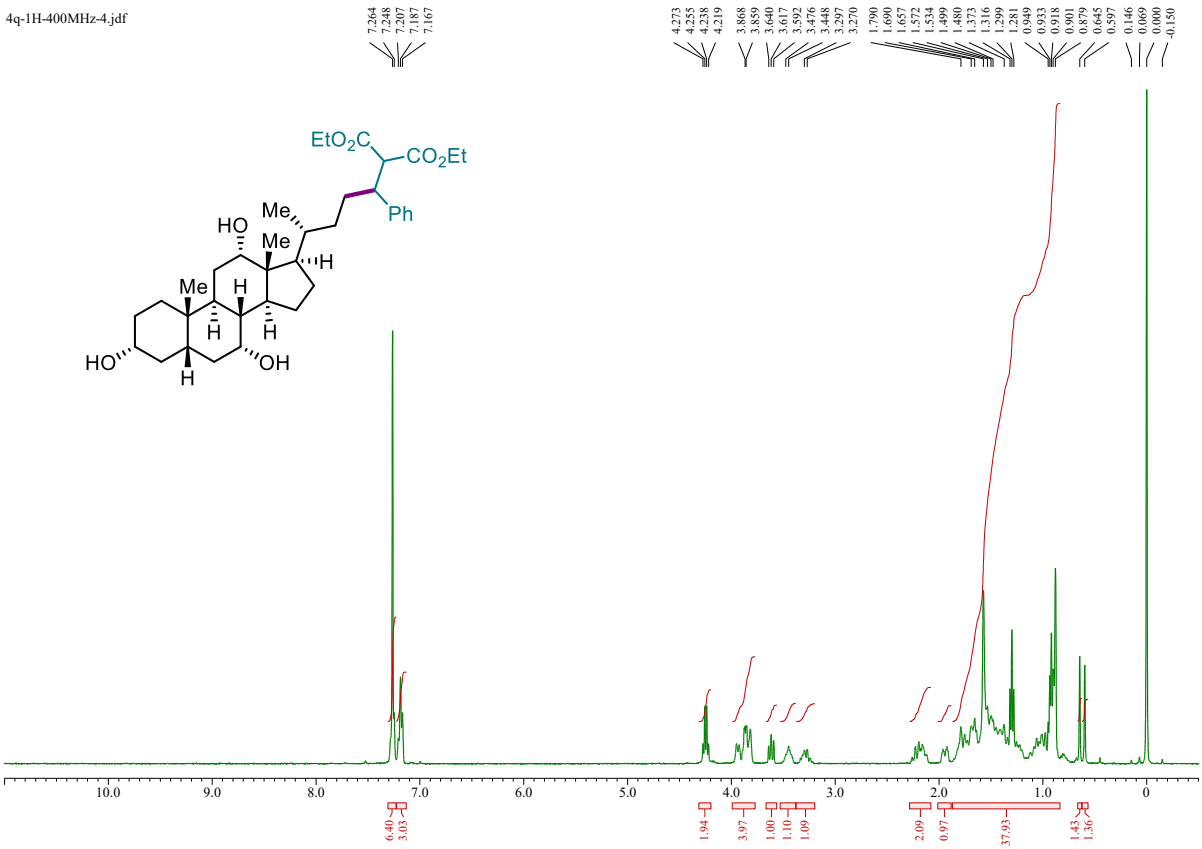
^{13}C NMR spectra (101 MHz) of **4o** in $CDCl_3$



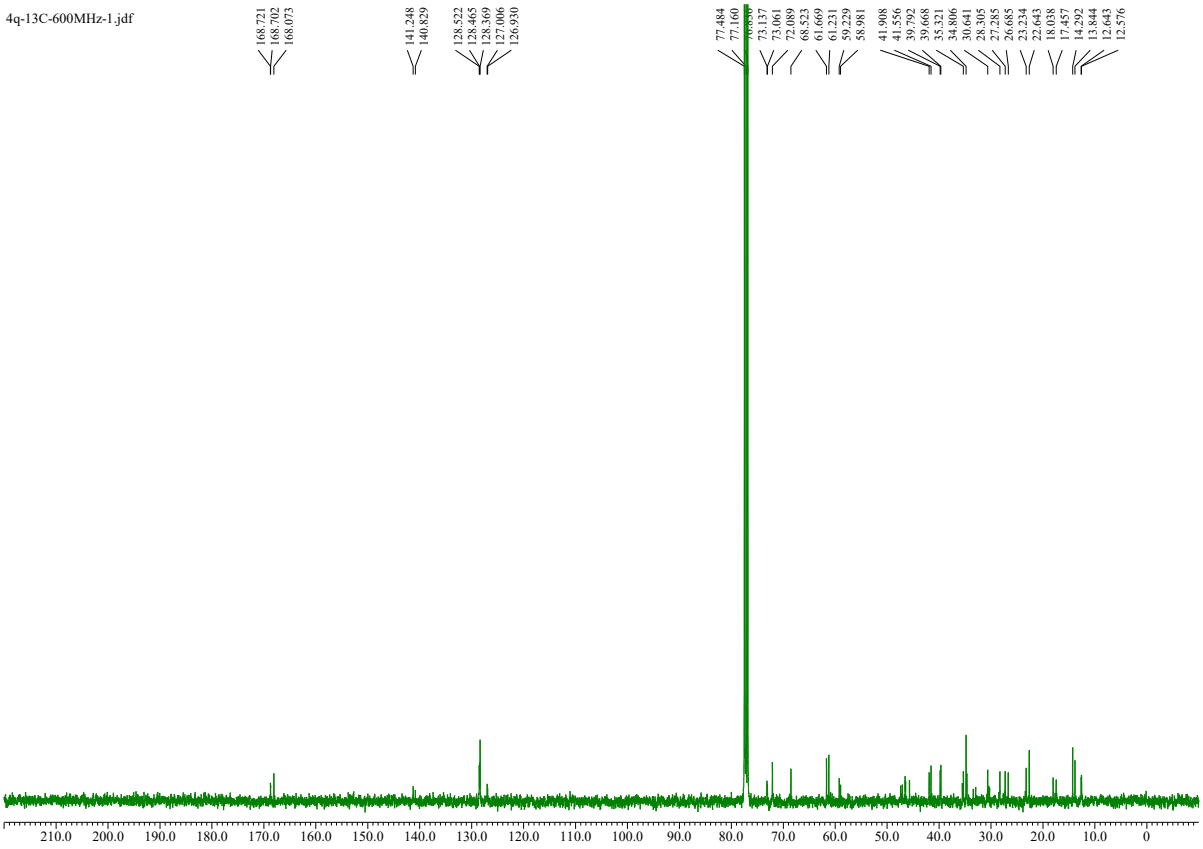
^{1}H NMR spectra (400 MHz) of **4p** (mixture of diastereomers) in $CDCl_3$



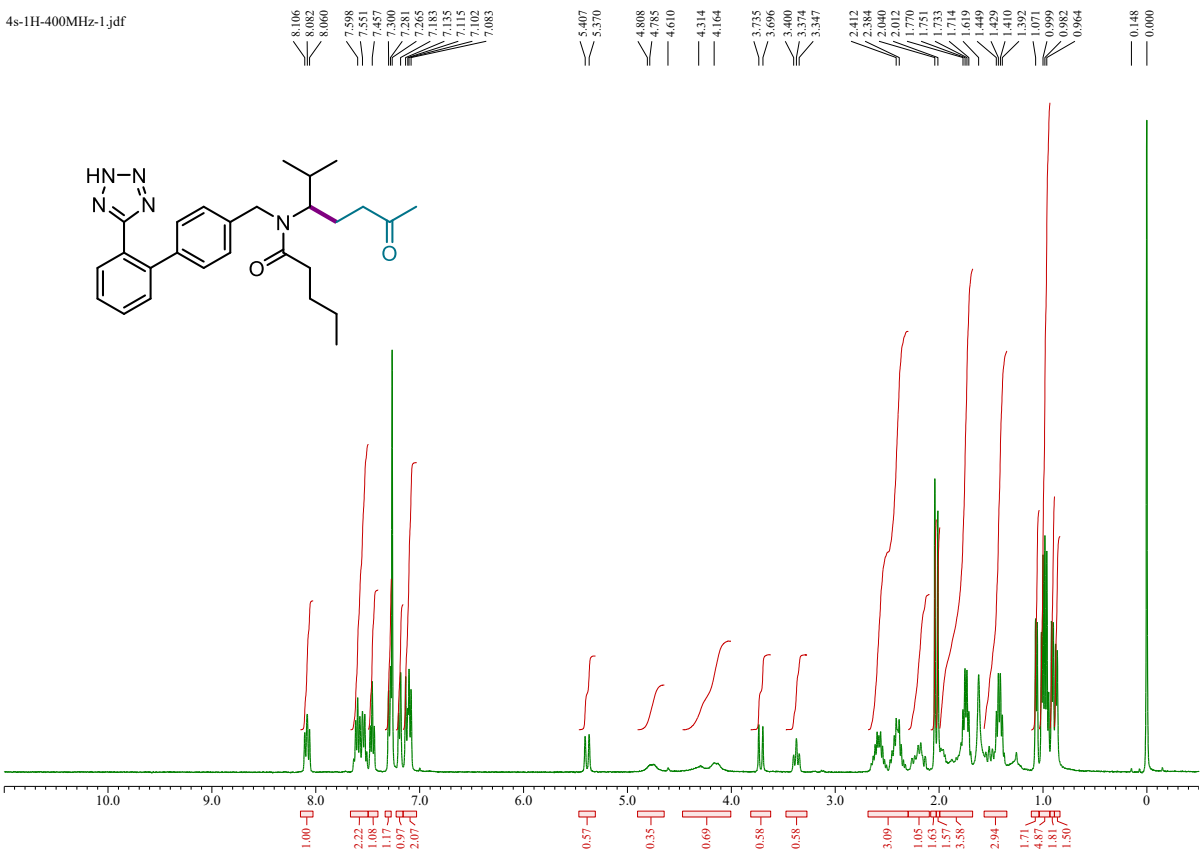
^{13}C NMR spectra (101 MHz) of **4p** (mixture of diastereomers) in $CDCl_3$



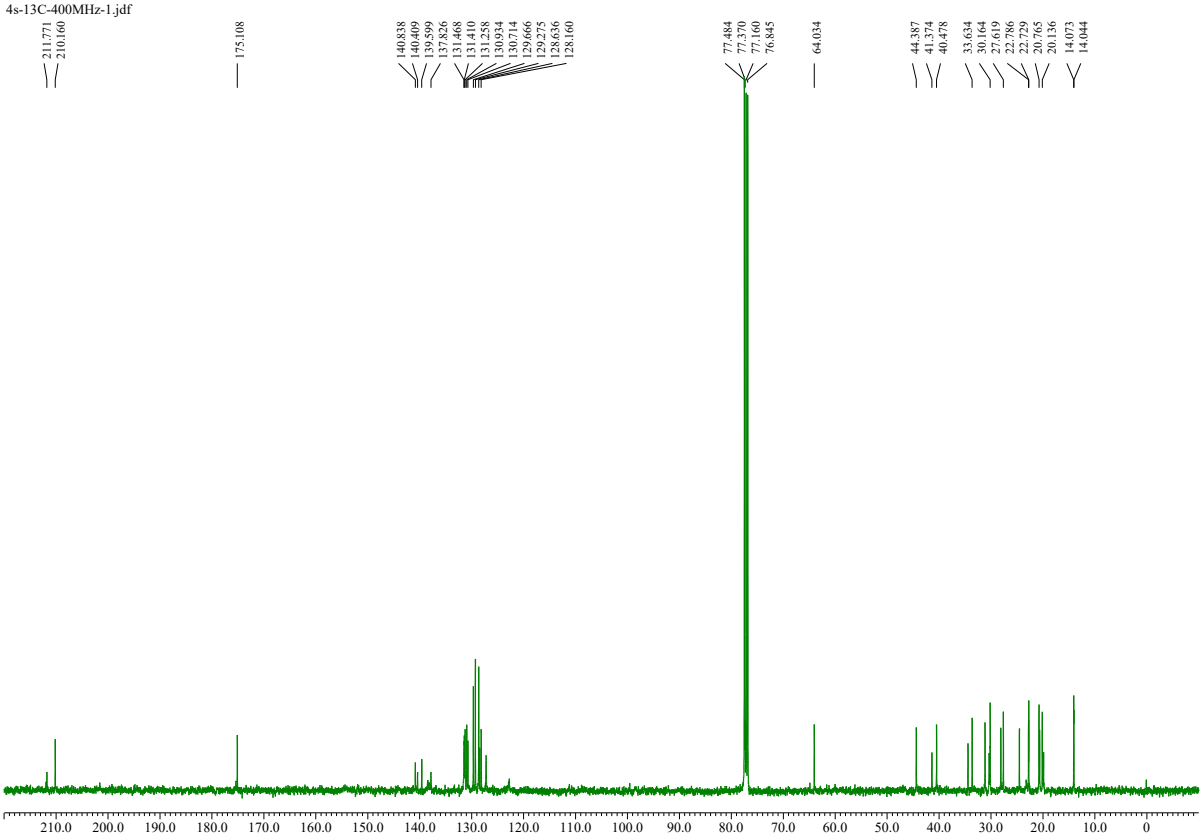
^{1}H NMR spectra (400 MHz) of **4q** (mixture of diastereomers) in $CDCl_3$



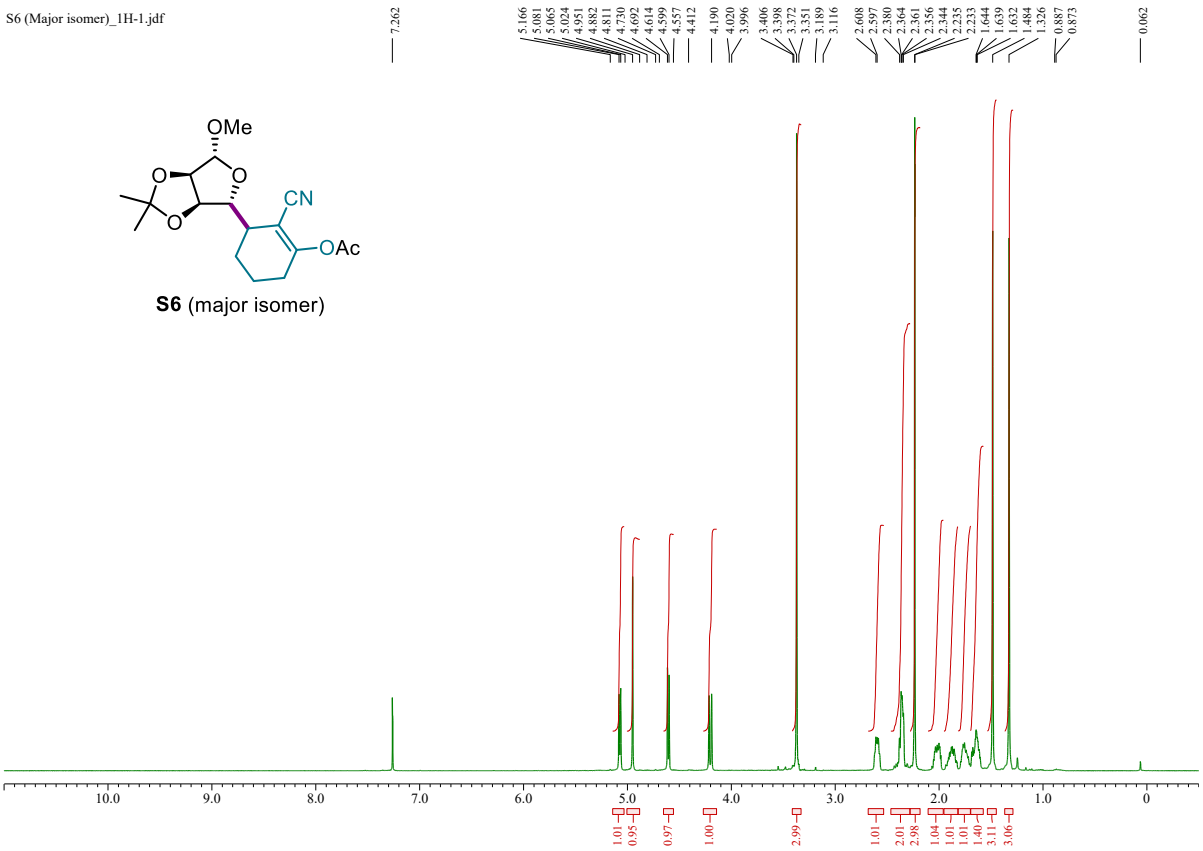
^{13}C NMR spectra (101 MHz) of **4q** (mixture of diastereomers) in $CDCl_3$



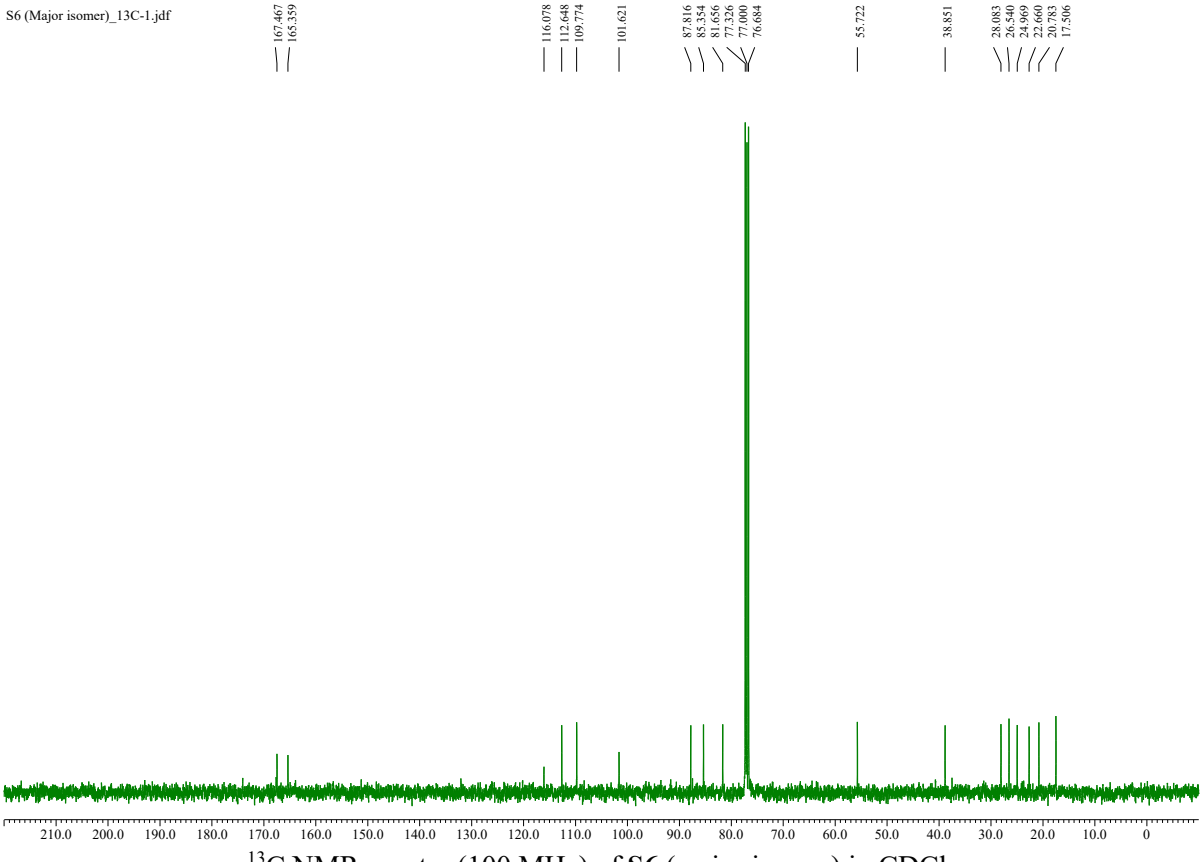
^{1}H NMR spectra (400 MHz) of **4r** (mixture of rotamers) in $CDCl_3$



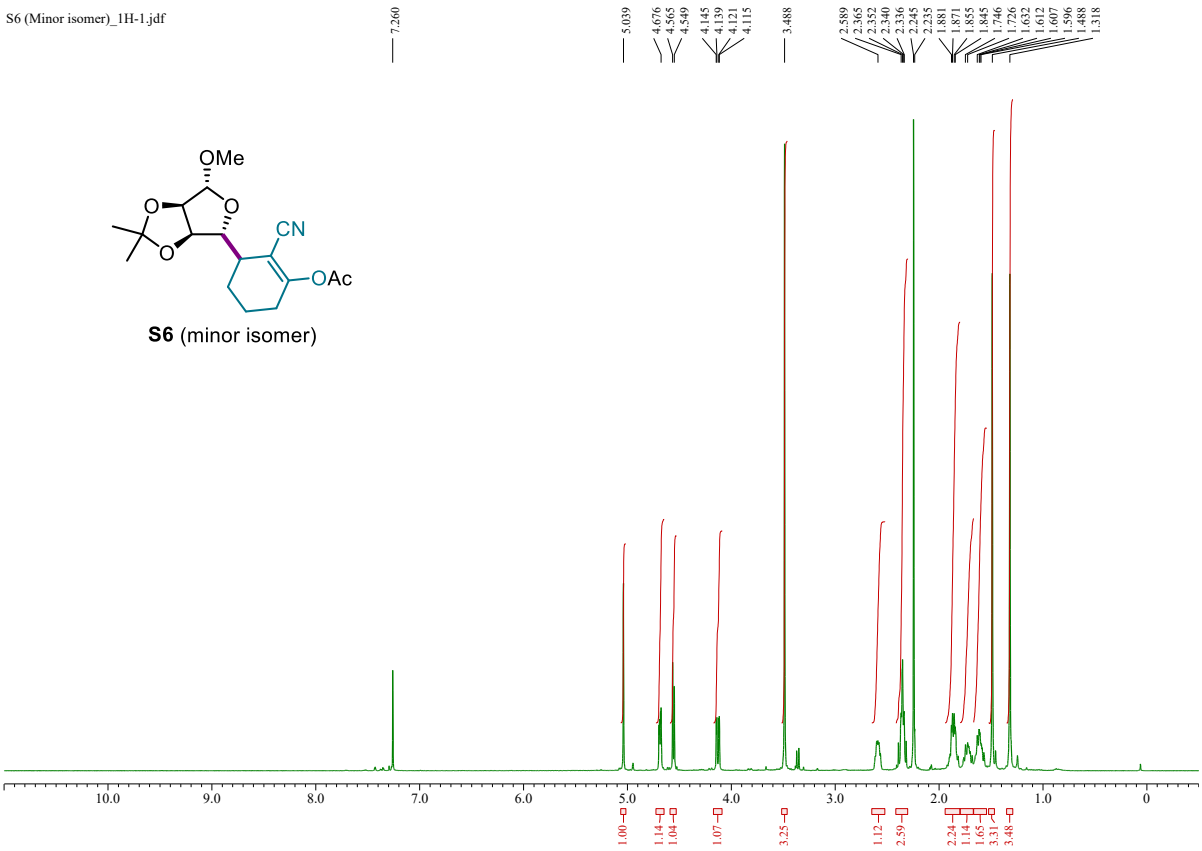
^{13}C NMR spectra (101 MHz) of **4r** (mixture of rotamers) in $CDCl_3$



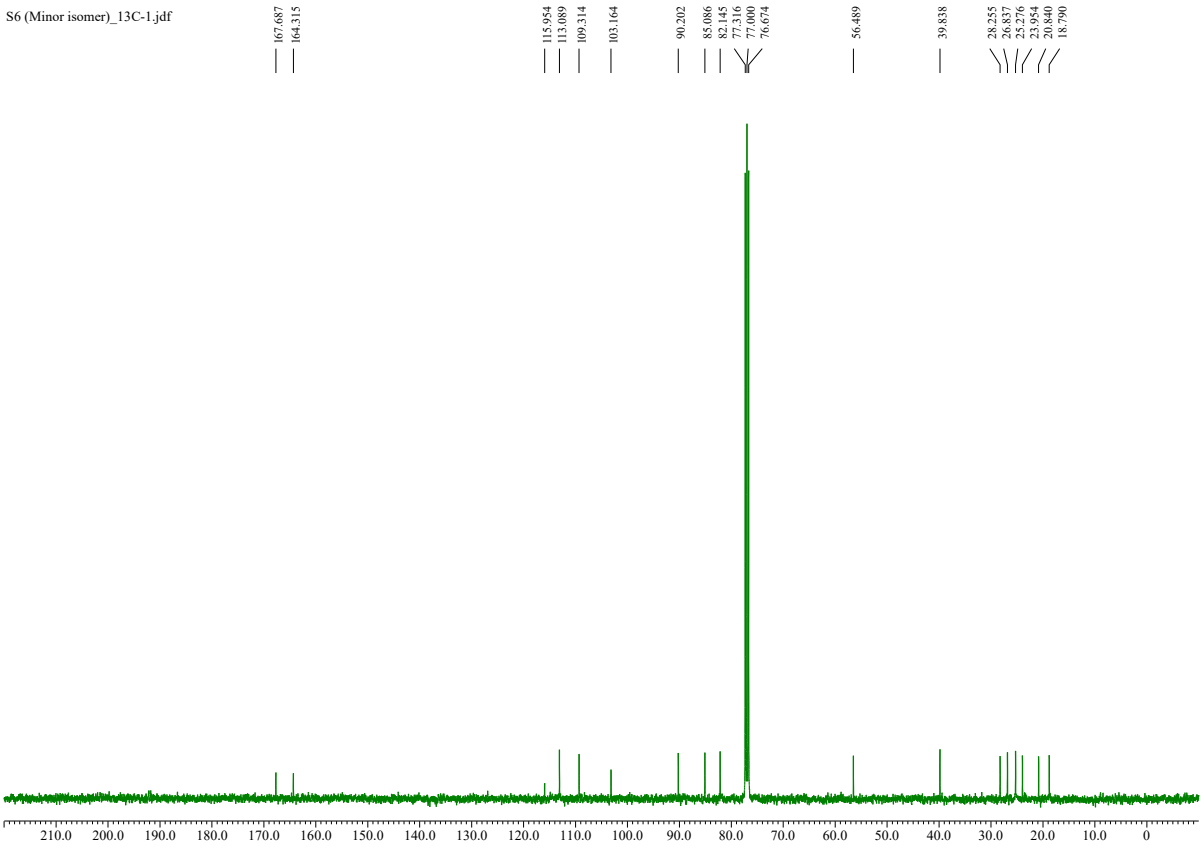
^{1}H NMR spectra (400 MHz) of **S6** (major isomer) in $CDCl_3$



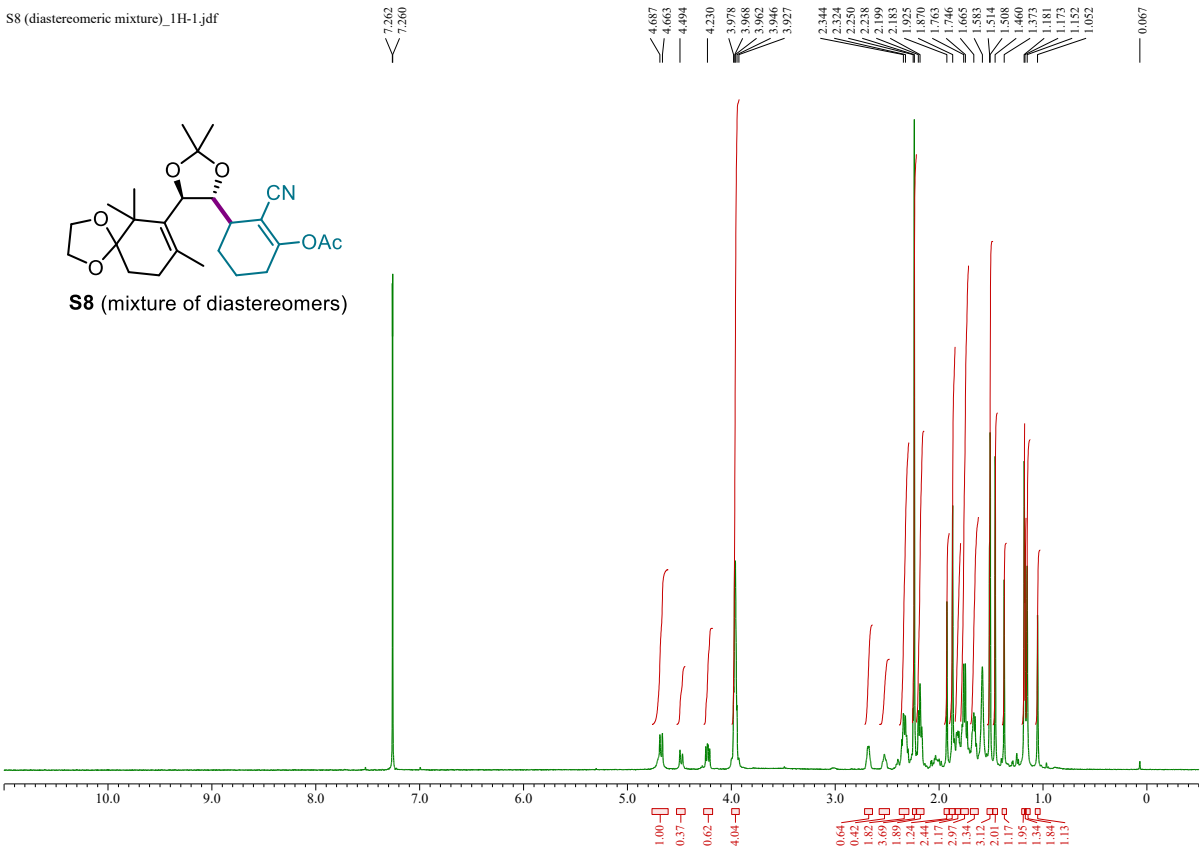
^{13}C NMR spectra (100 MHz) of **S6** (major isomer) in $CDCl_3$



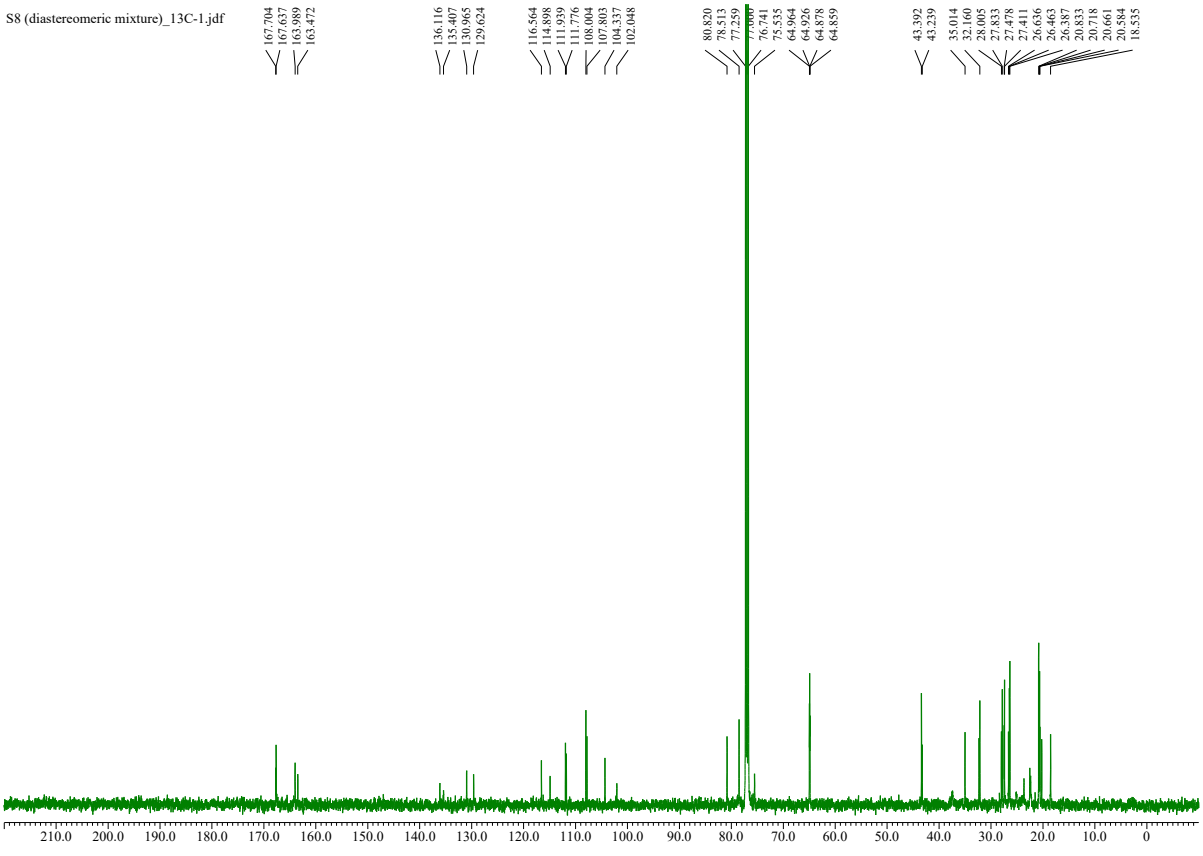
^{1}H NMR spectra (400 MHz) of **S6** (minor isomer) in $CDCl_3$



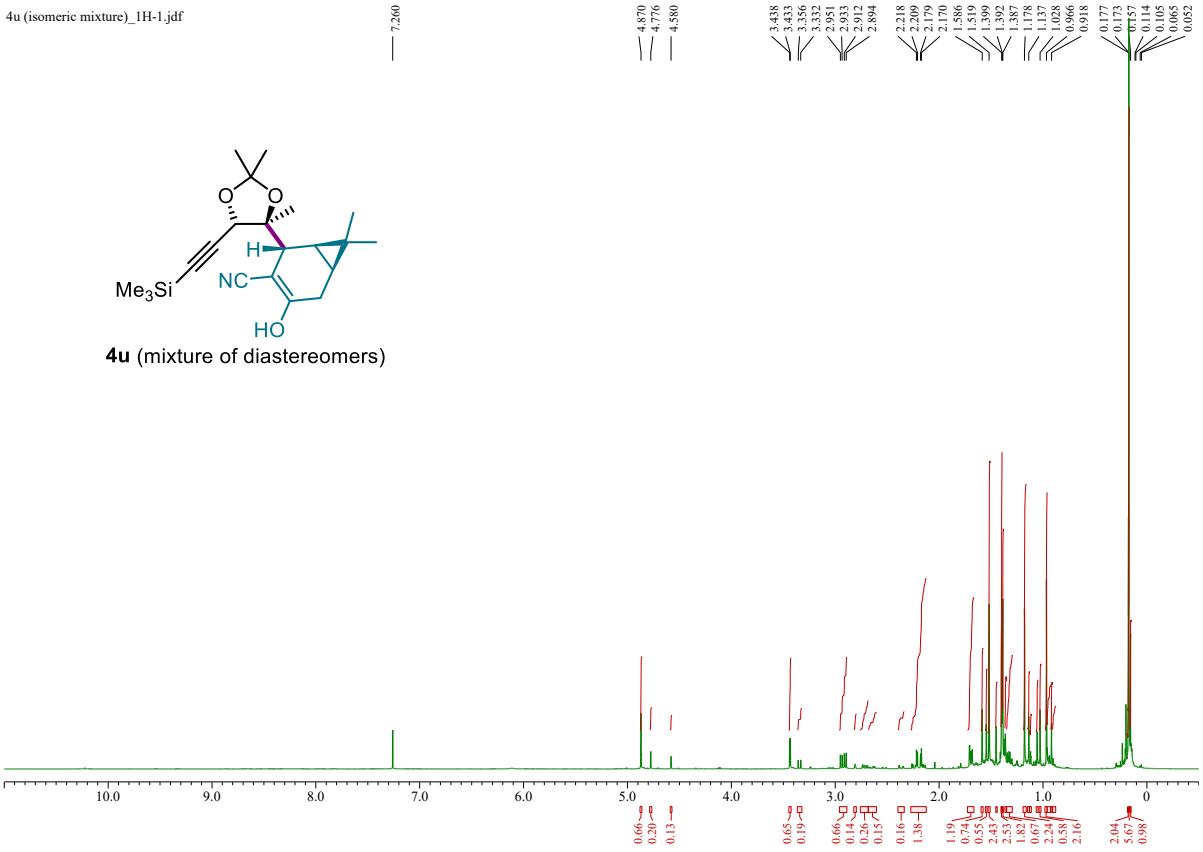
^{13}C NMR spectra (100 MHz) of **S6** (minor isomer) in $CDCl_3$



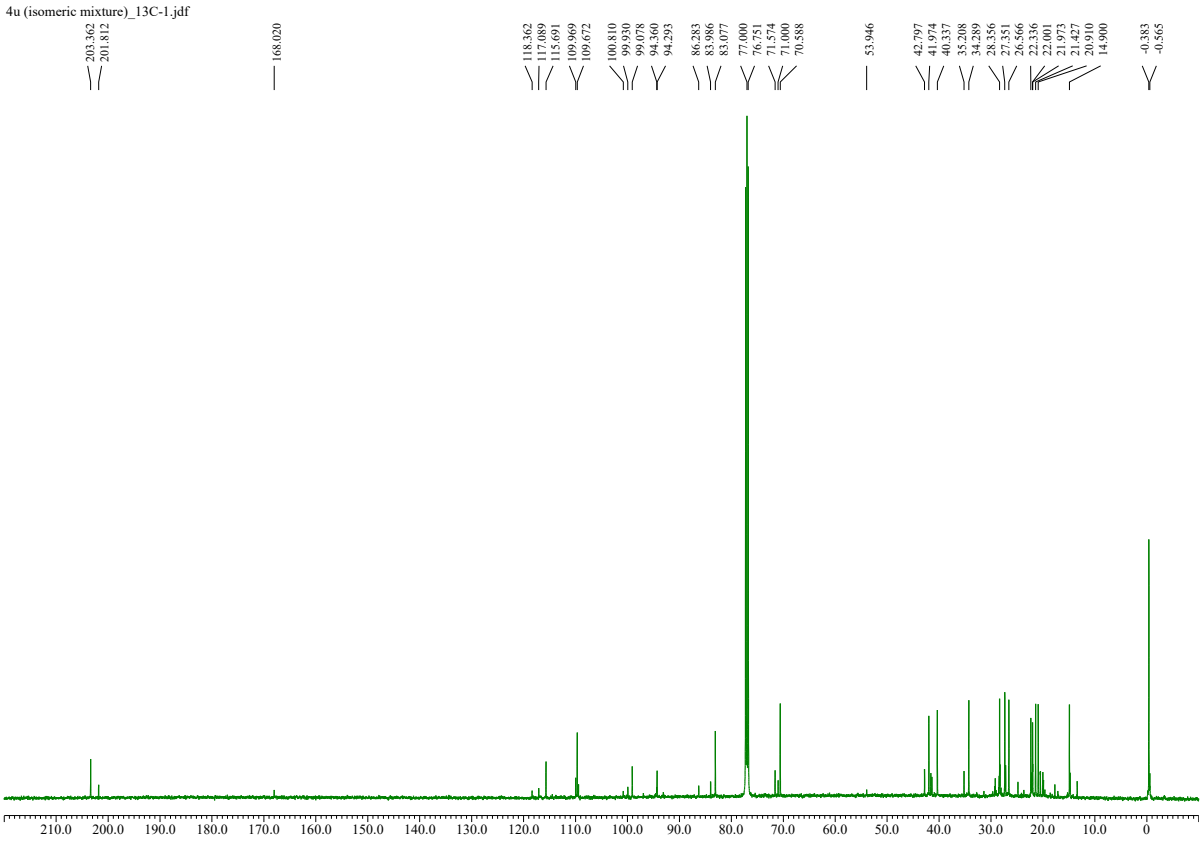
^{1}H NMR spectra (400 MHz) of **S8** (mixture of diastereomers) in $CDCl_3$



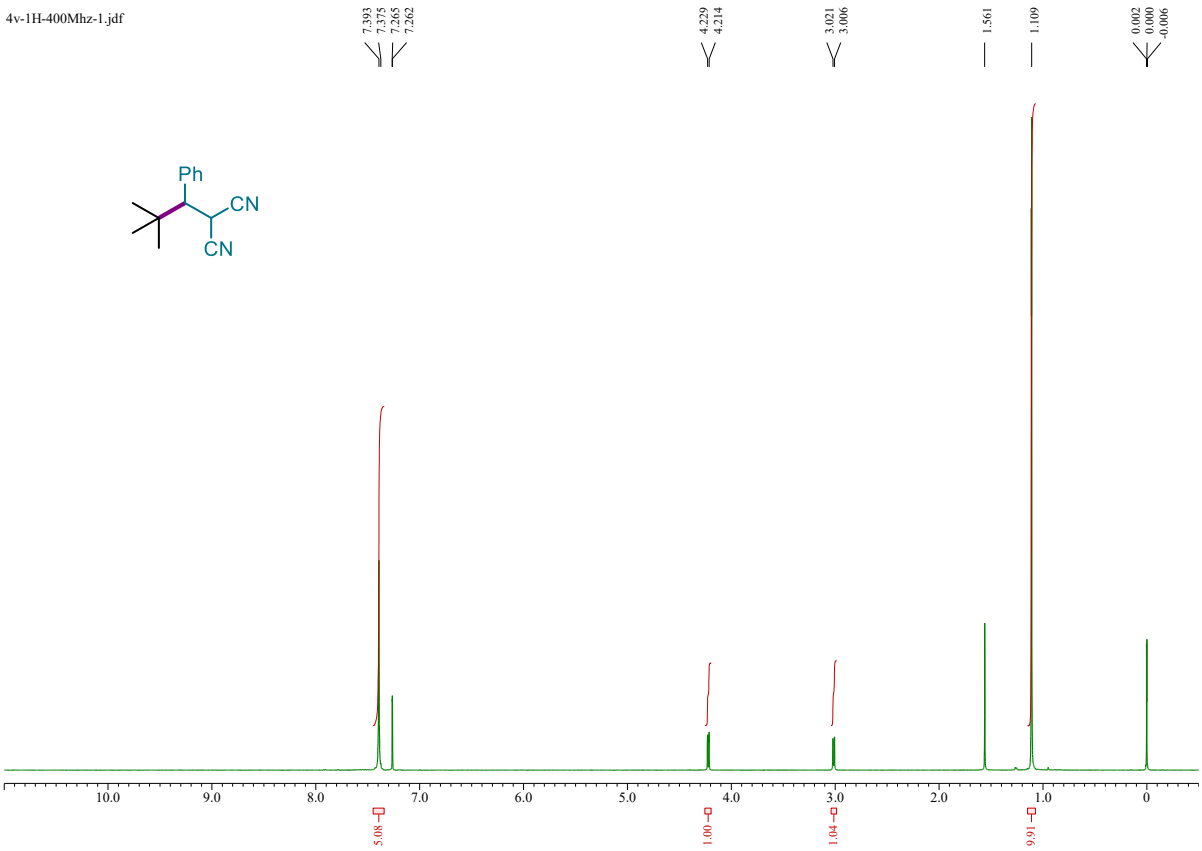
^{13}C NMR spectra (125 MHz) of **S8** (mixture of diastereomers) in $CDCl_3$



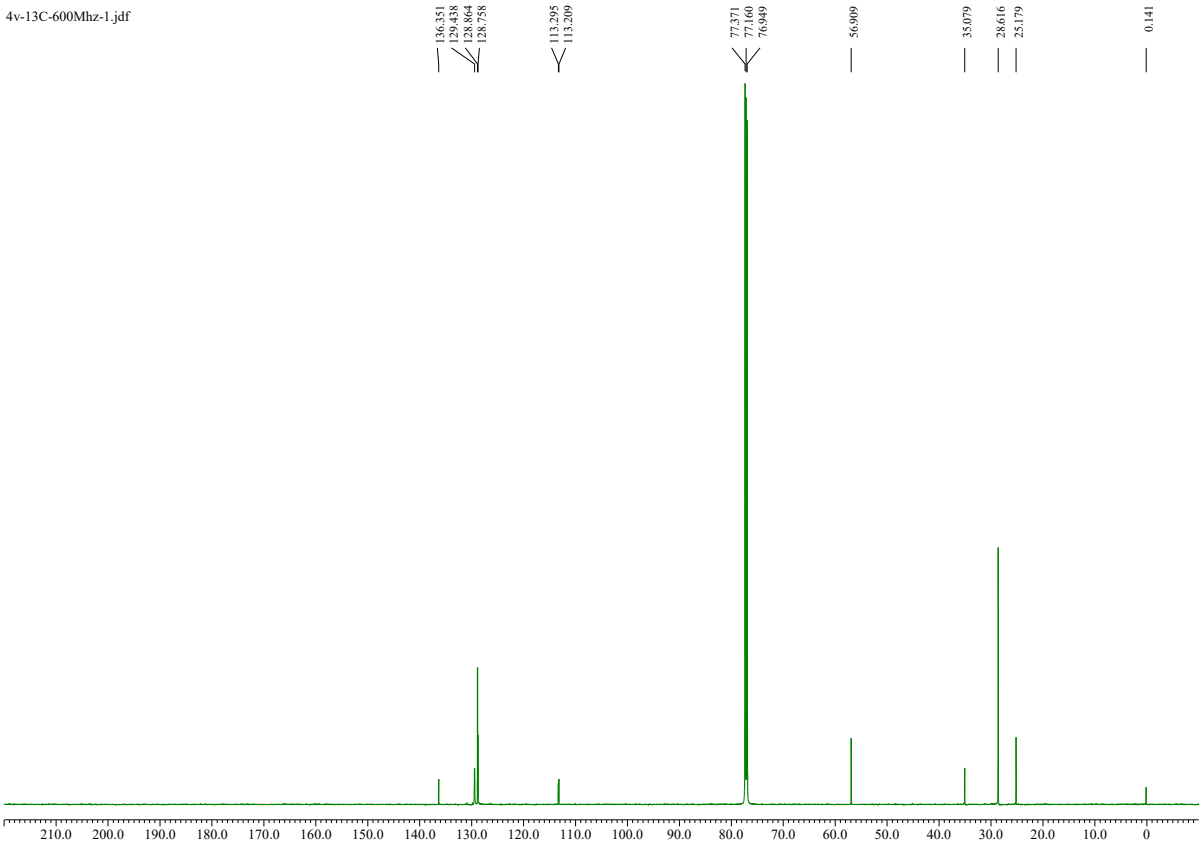
^{1}H NMR spectra (400 MHz) of **4u** (mixture of tautomers and diastereomers) in $CDCl_3$



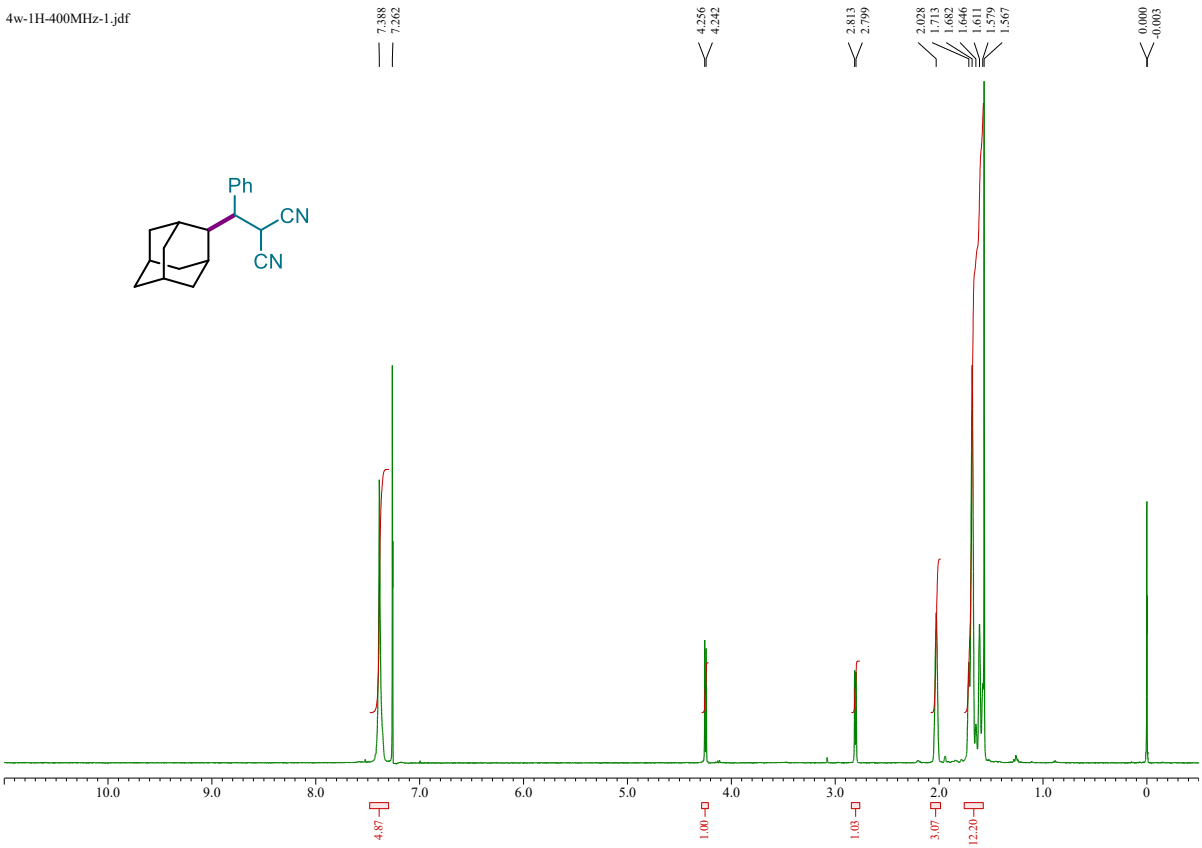
^{13}C NMR spectra (125 MHz) of **4u** (mixture of tautomers and diastereomers) in $CDCl_3$



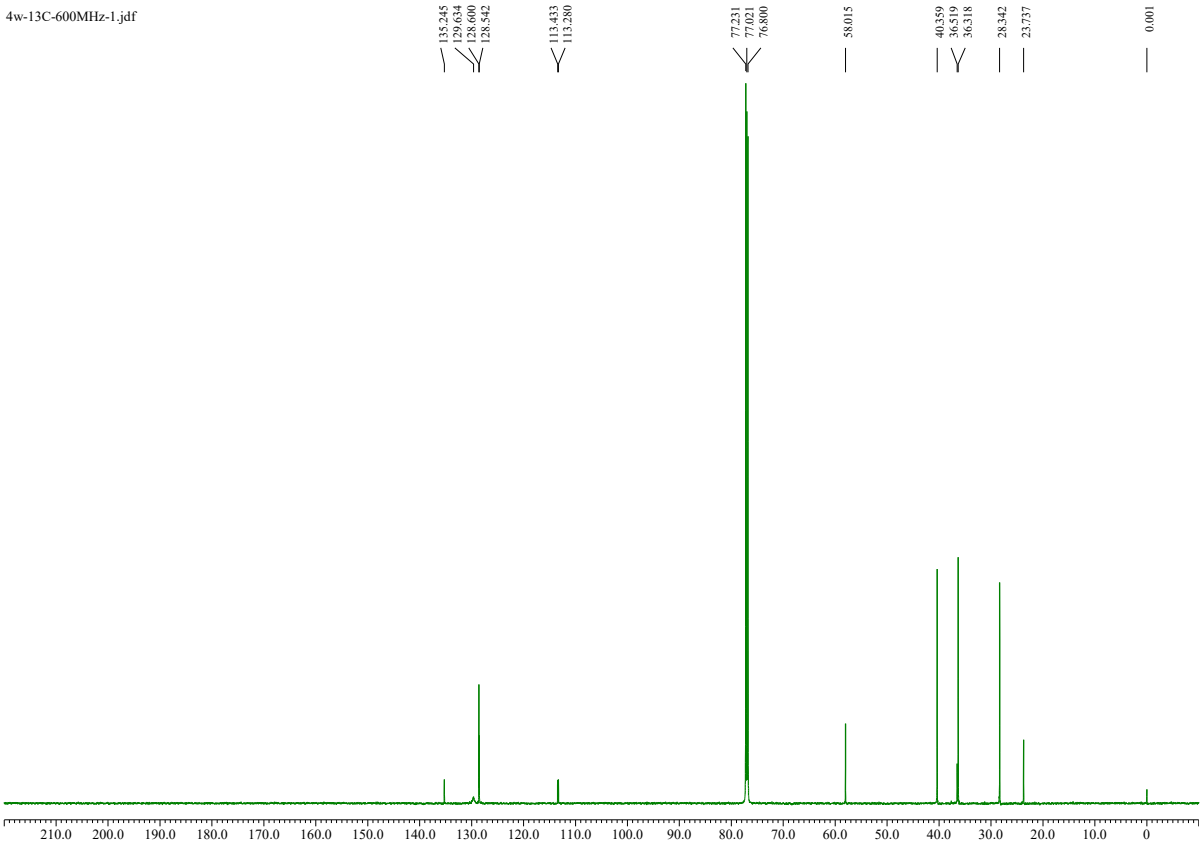
^{1}H NMR spectra (400 MHz) of **4v** in $CDCl_3$



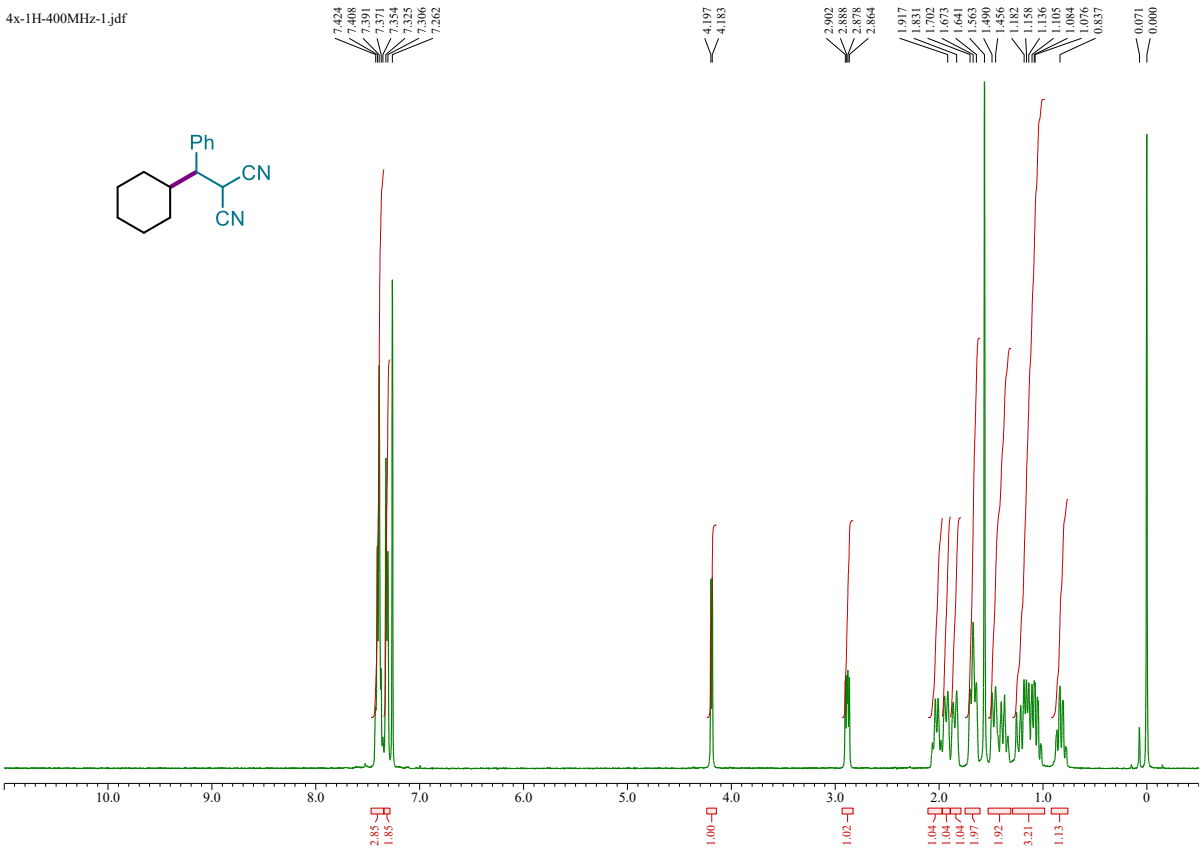
^{13}C NMR spectra (151 MHz) of **4v** in $CDCl_3$



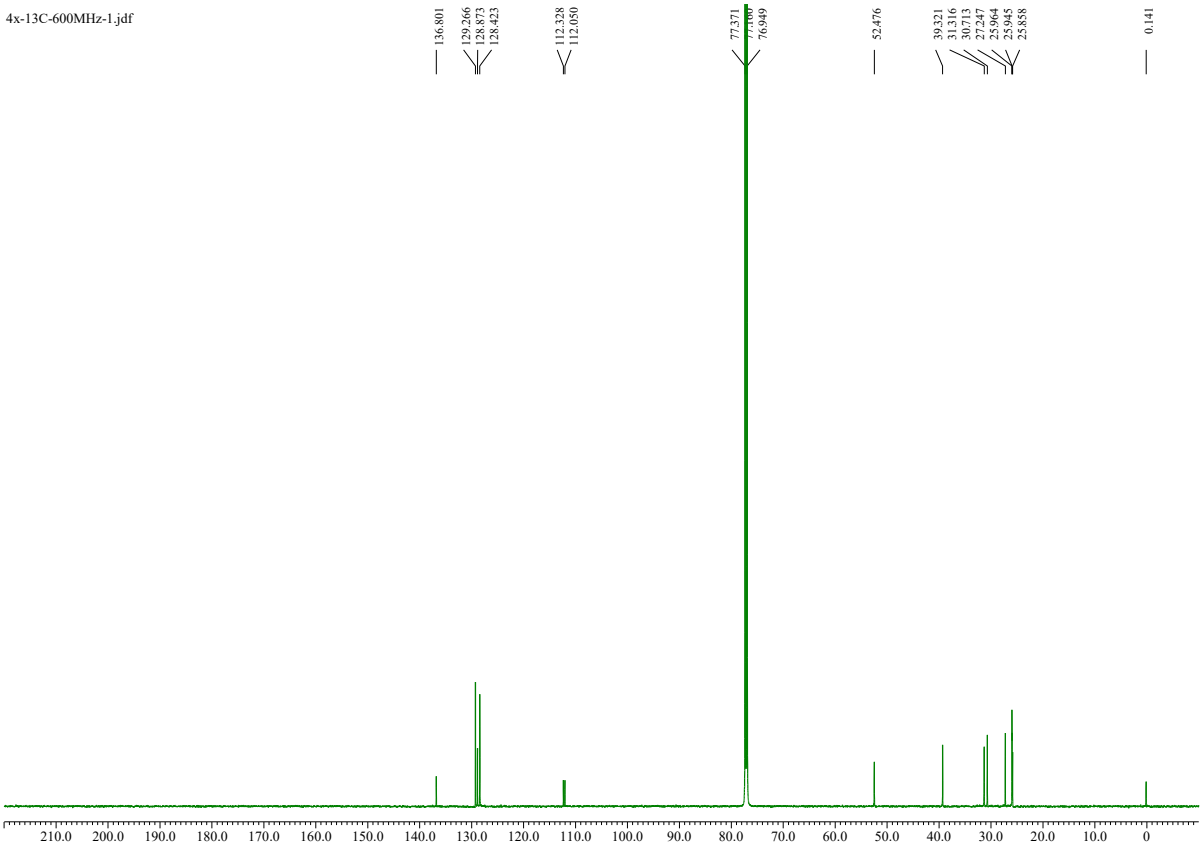
^{1}H NMR spectra (400 MHz) of **4w** in $CDCl_3$



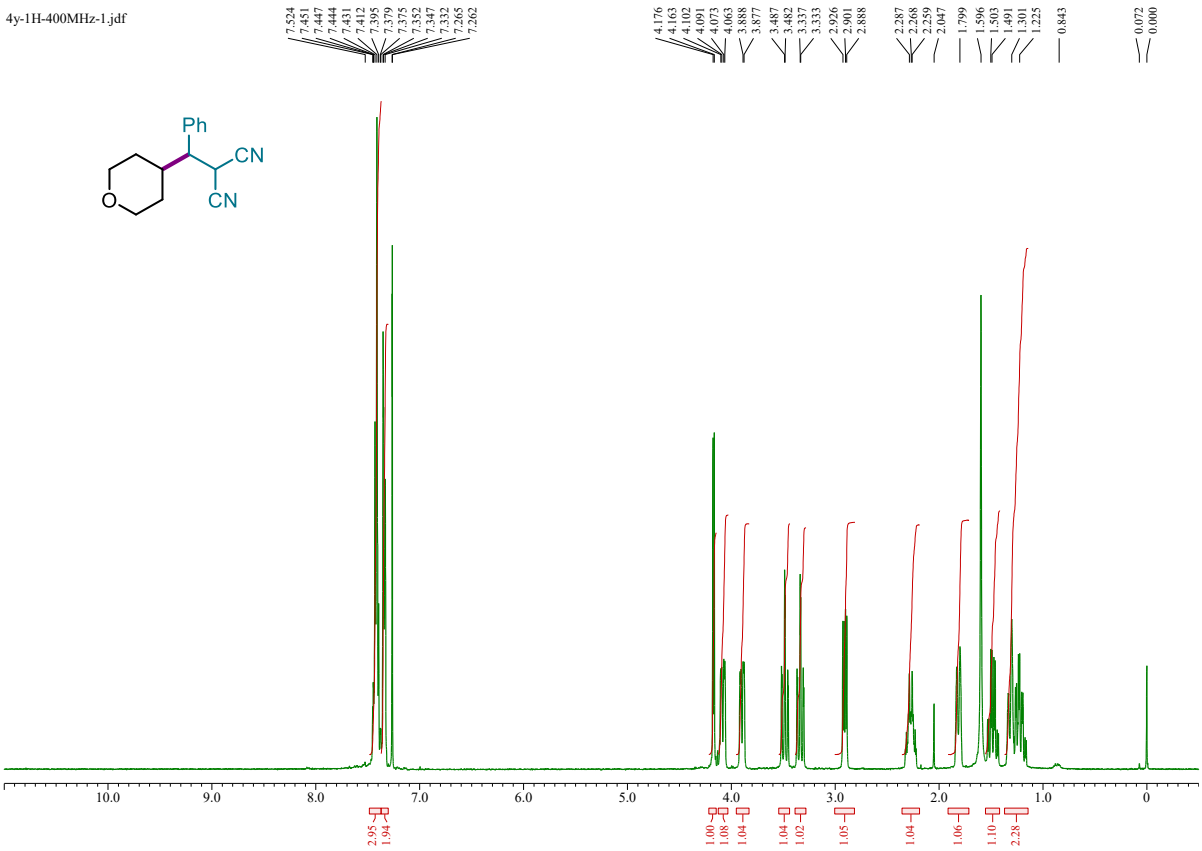
^{13}C NMR spectra (151 MHz) of **4w** in $CDCl_3$



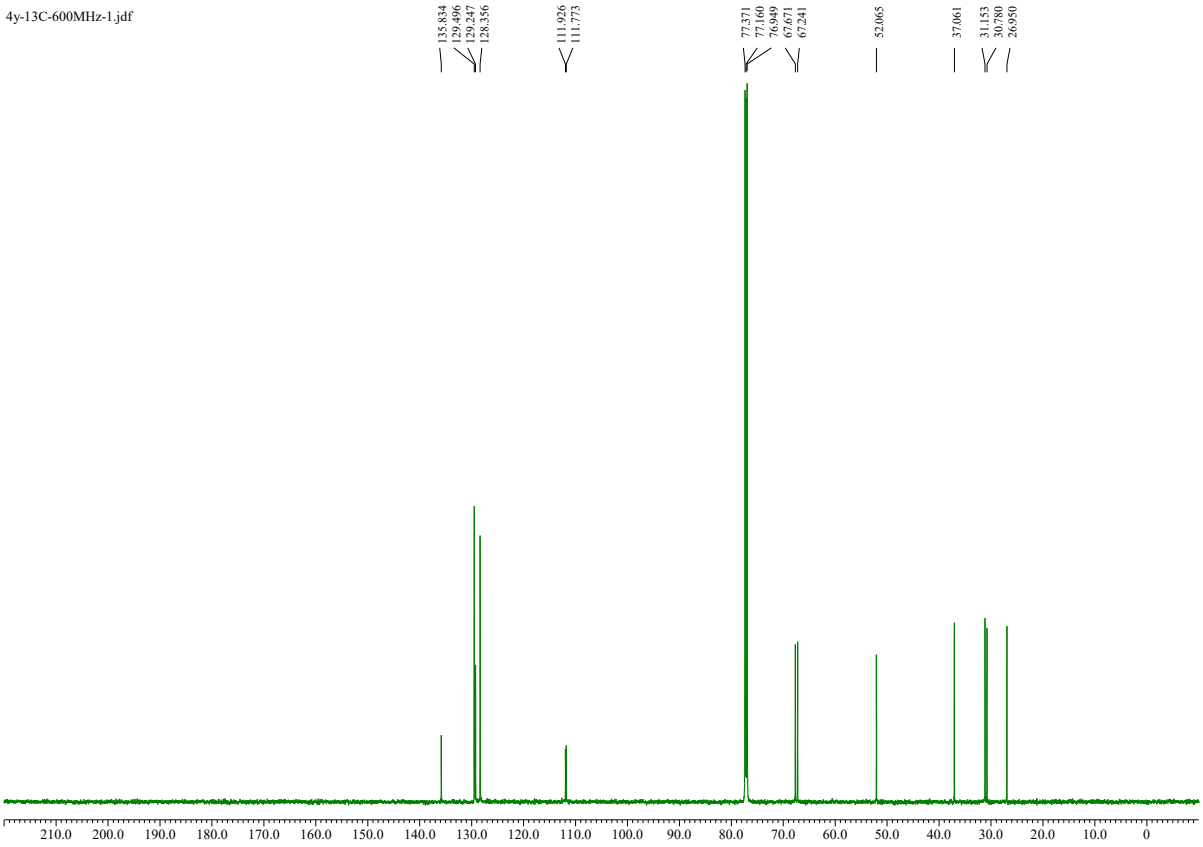
^{1}H NMR spectra (400 MHz) of **4x** in $CDCl_3$



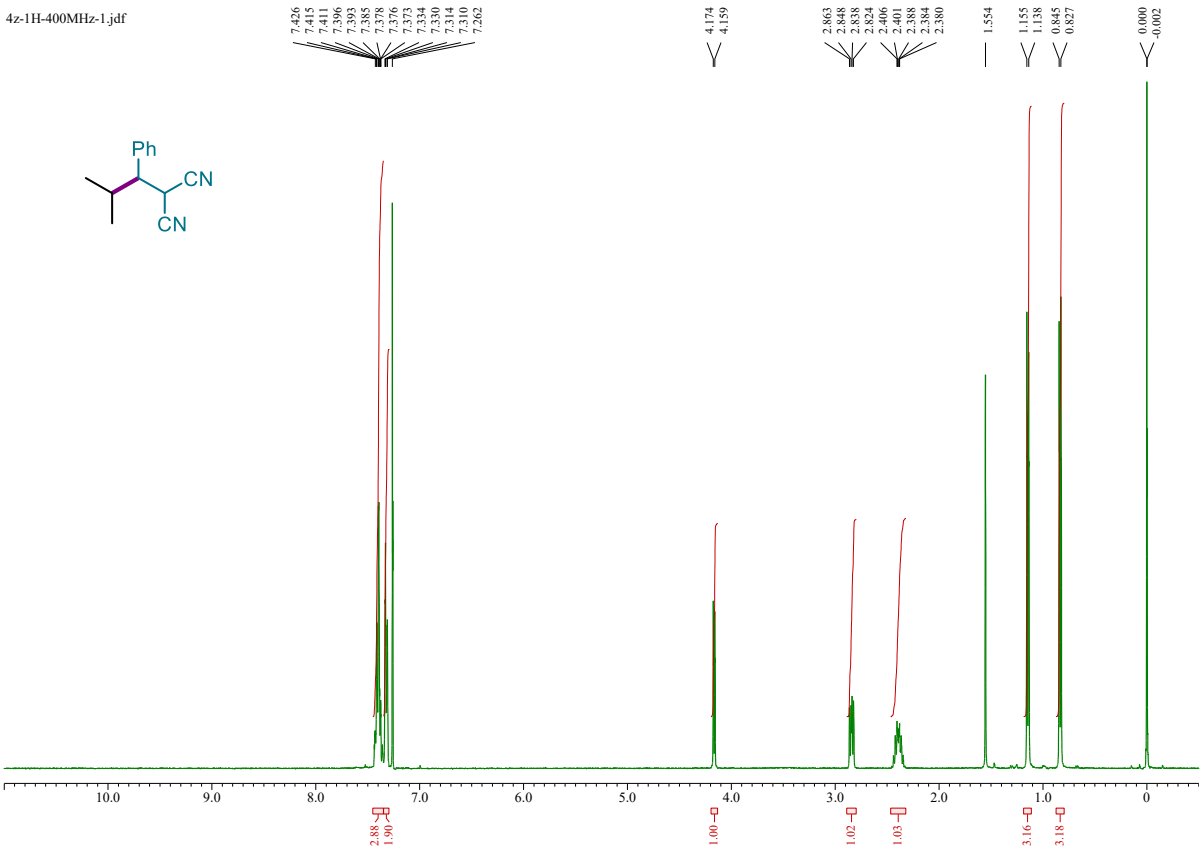
^{13}C NMR spectra (151 MHz) of **4x** in $CDCl_3$



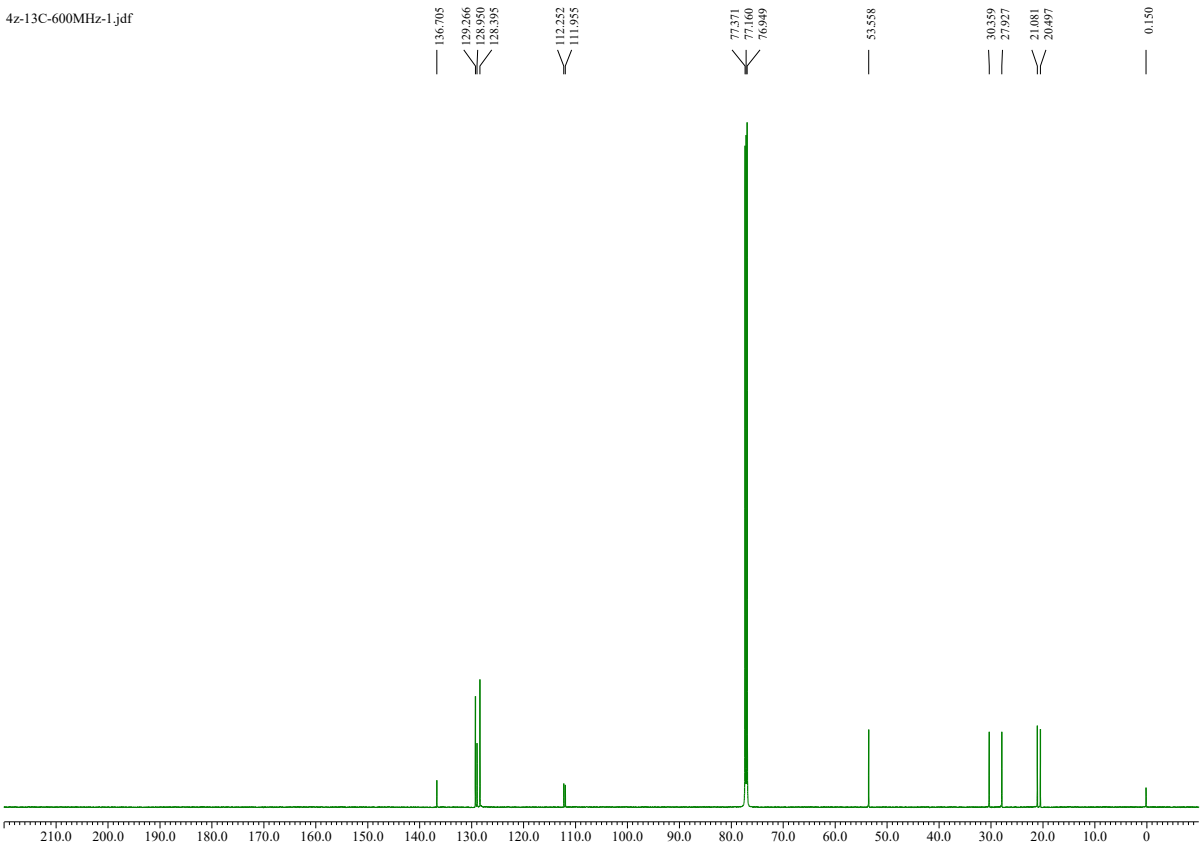
^{1}H NMR spectra (400 MHz) of **4y** in $CDCl_3$



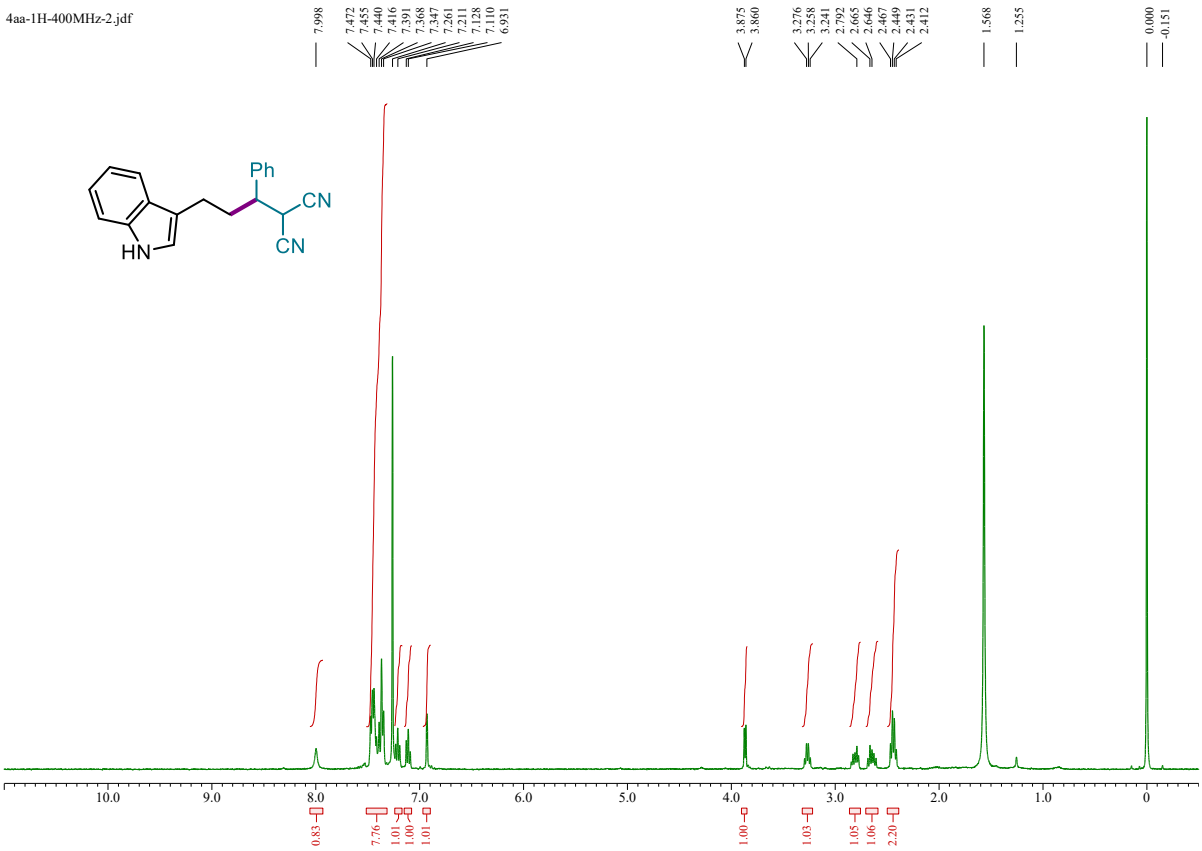
^{13}C NMR spectra (151 MHz) of **4y** in $CDCl_3$



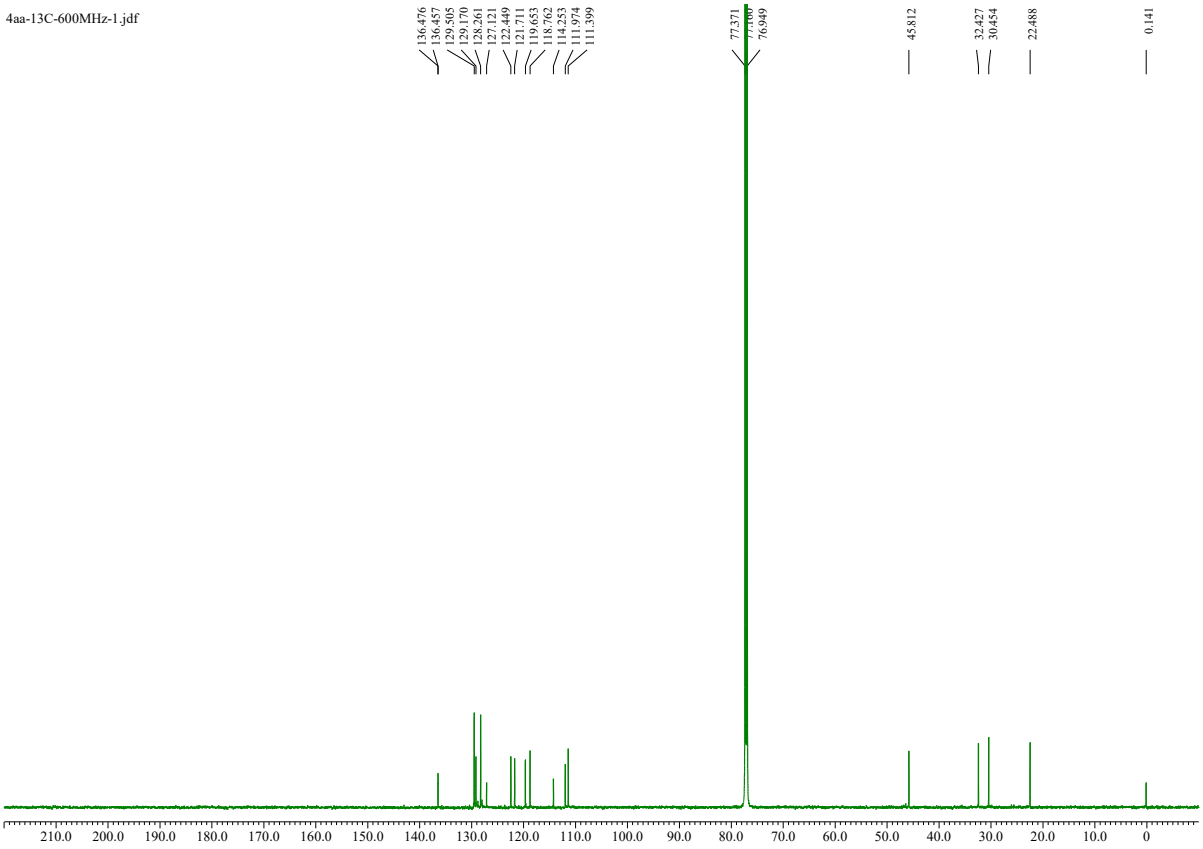
^{1}H NMR spectra (400 MHz) of **4z** in $CDCl_3$



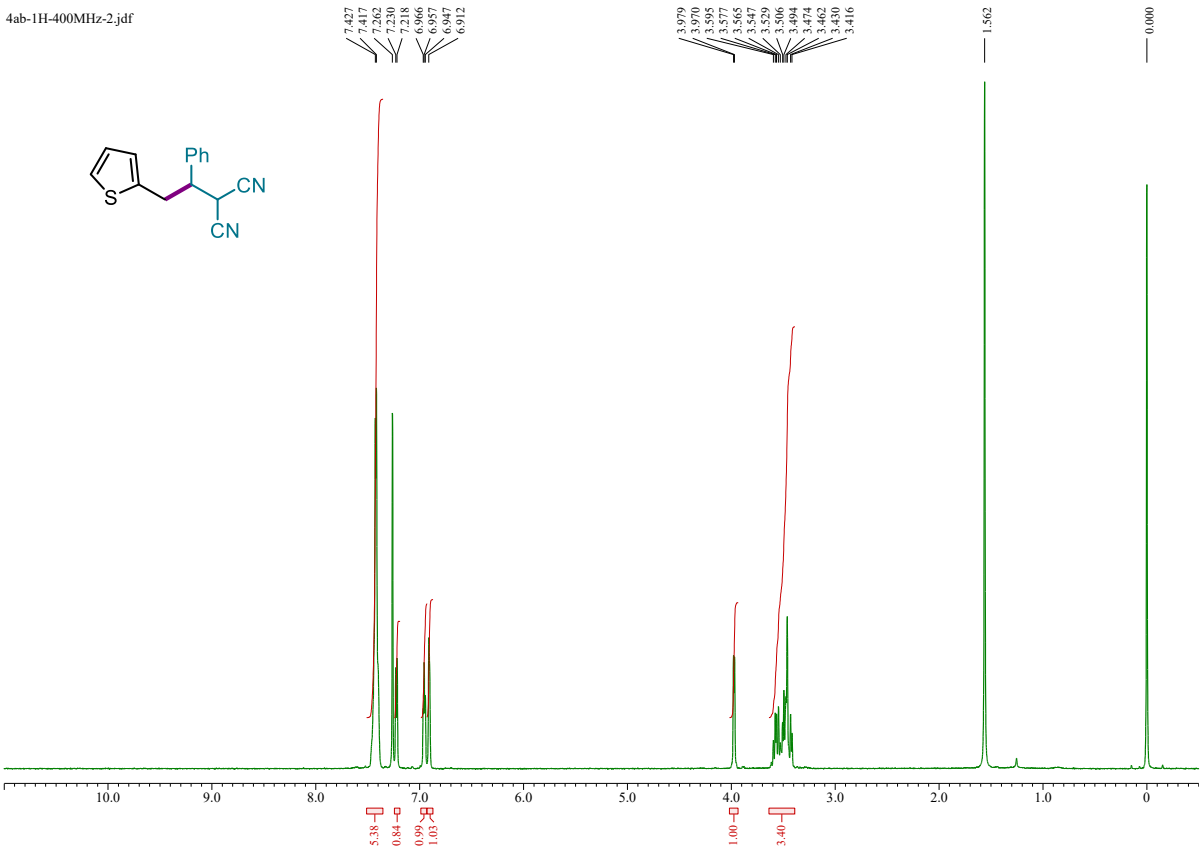
^{13}C NMR spectra (151 MHz) of **4z** in $CDCl_3$



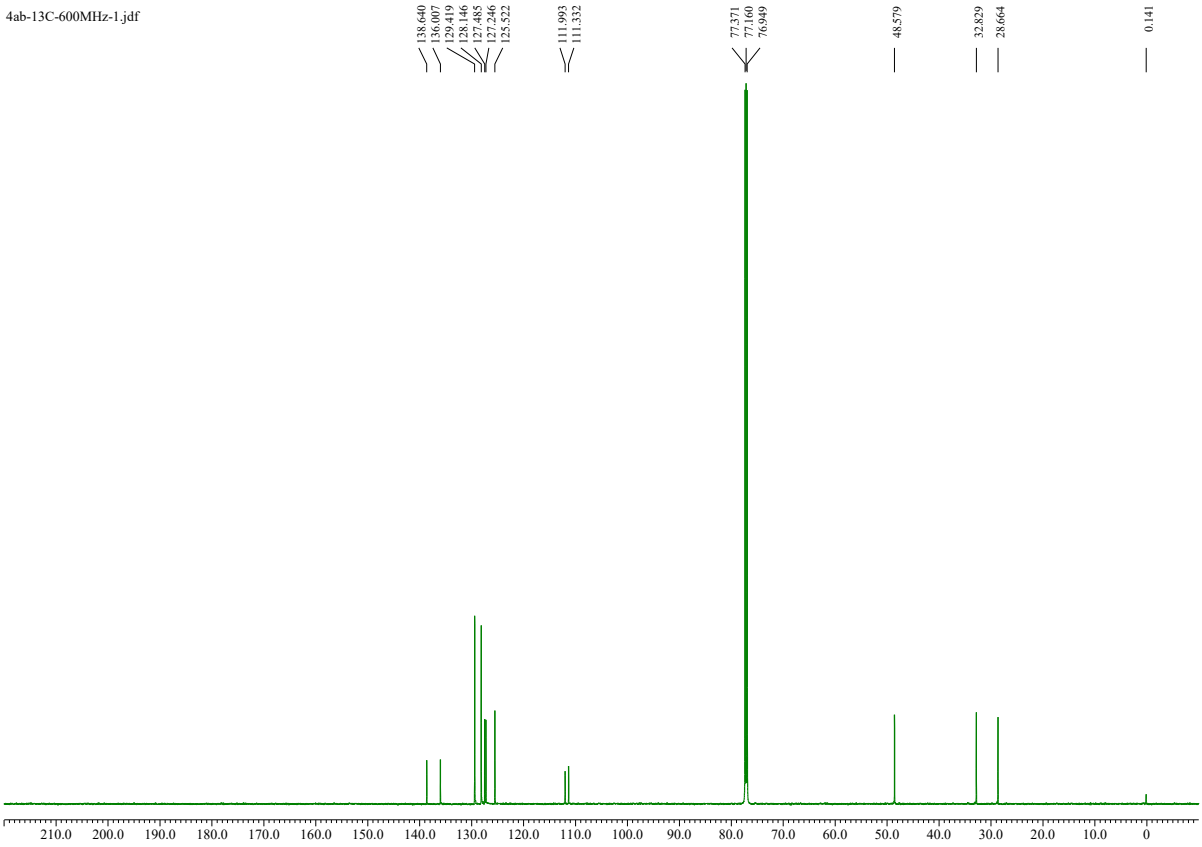
^{1}H NMR spectra (400 MHz) of **4aa** in $CDCl_3$



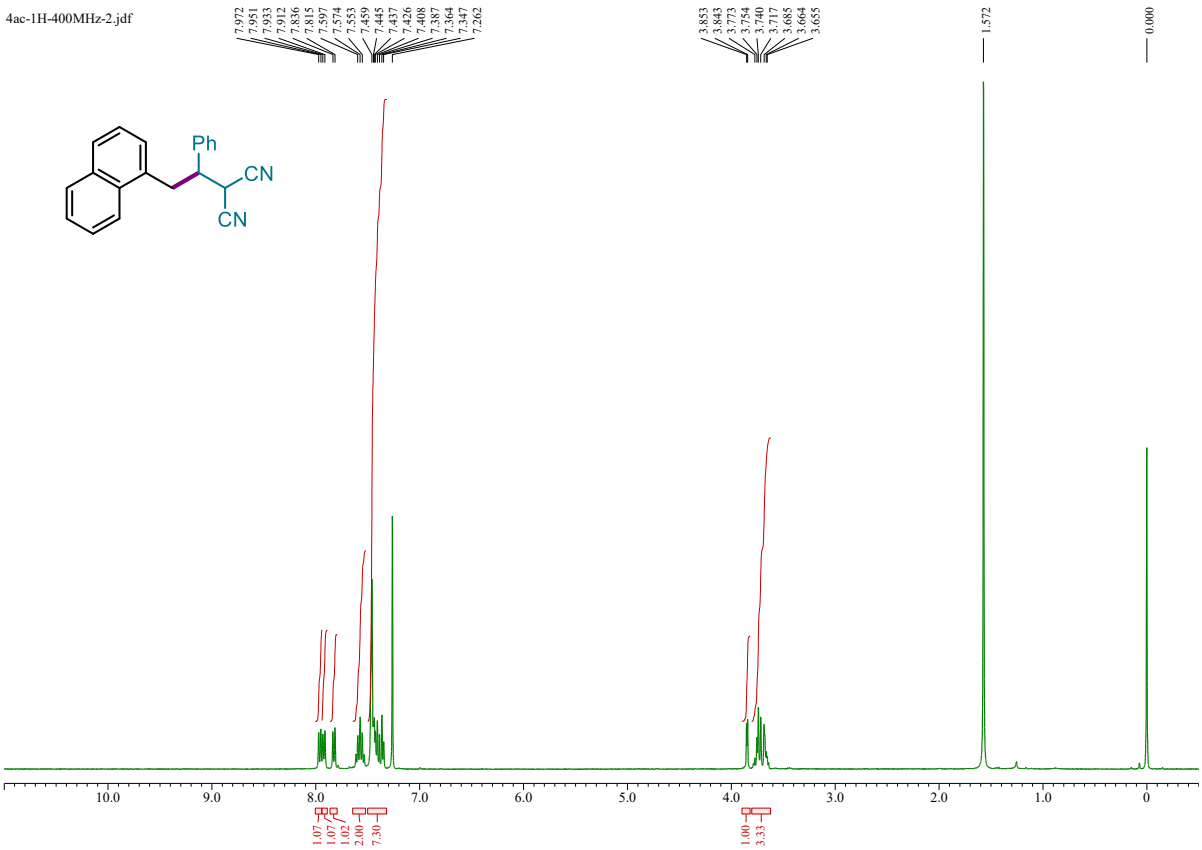
^{13}C NMR spectra (151 MHz) of **4aa** in $CDCl_3$



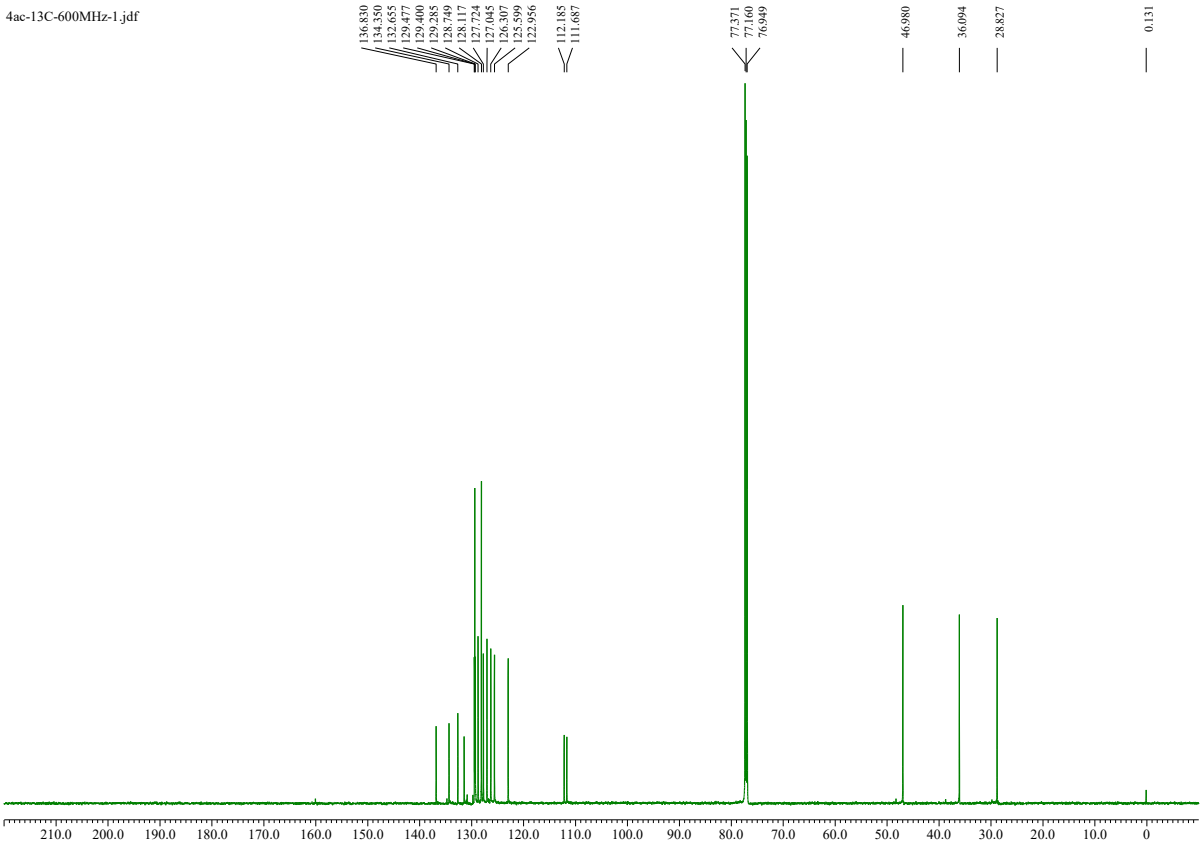
^{1}H NMR spectra (400 MHz) of **4ab** in $CDCl_3$



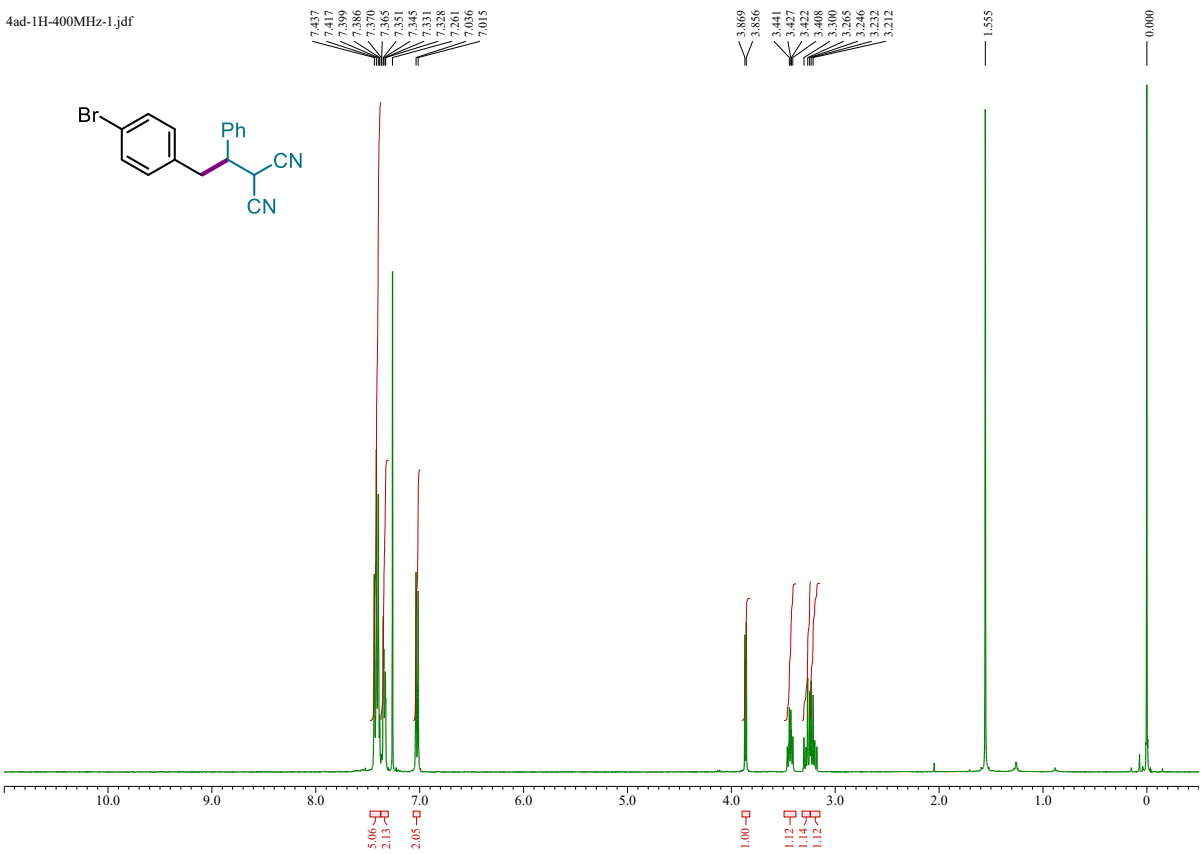
^{13}C NMR spectra (151 MHz) of **4ab** in $CDCl_3$



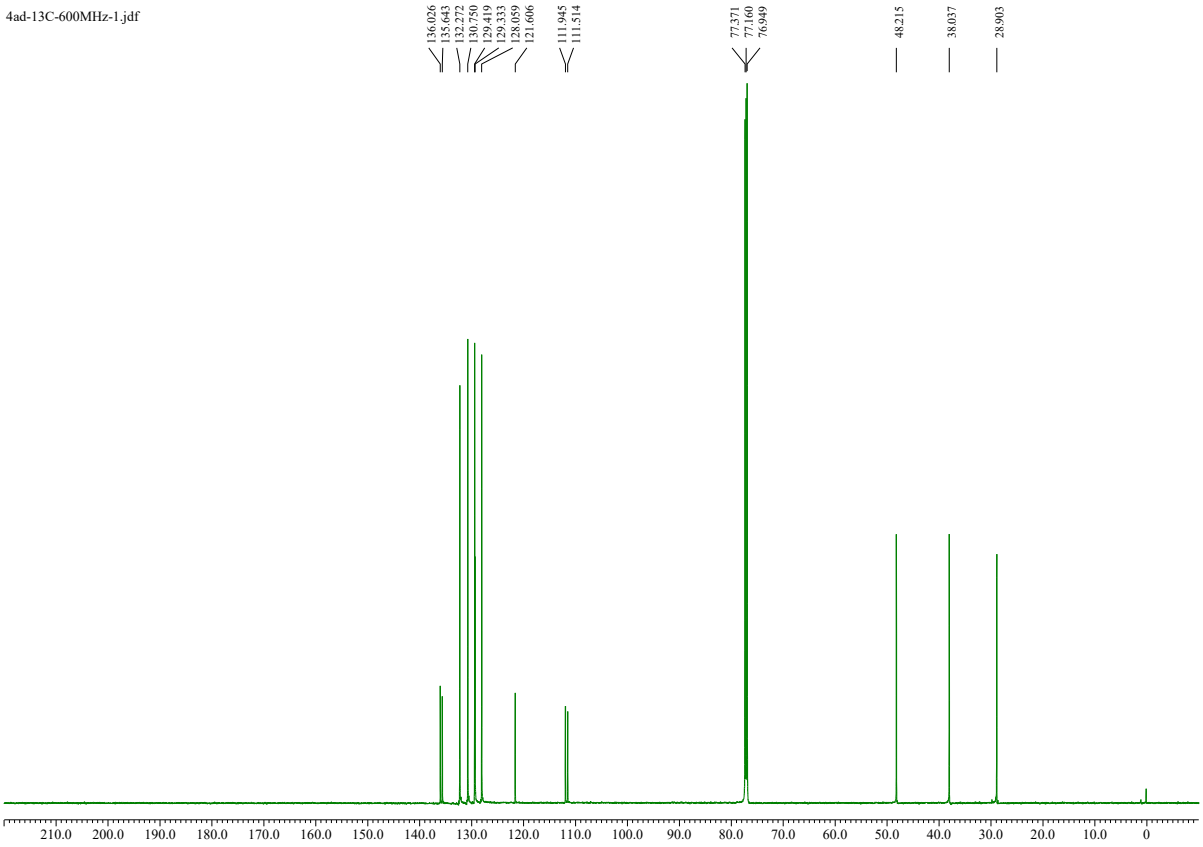
^{1}H NMR spectra (400 MHz) of **4ac** in $CDCl_3$



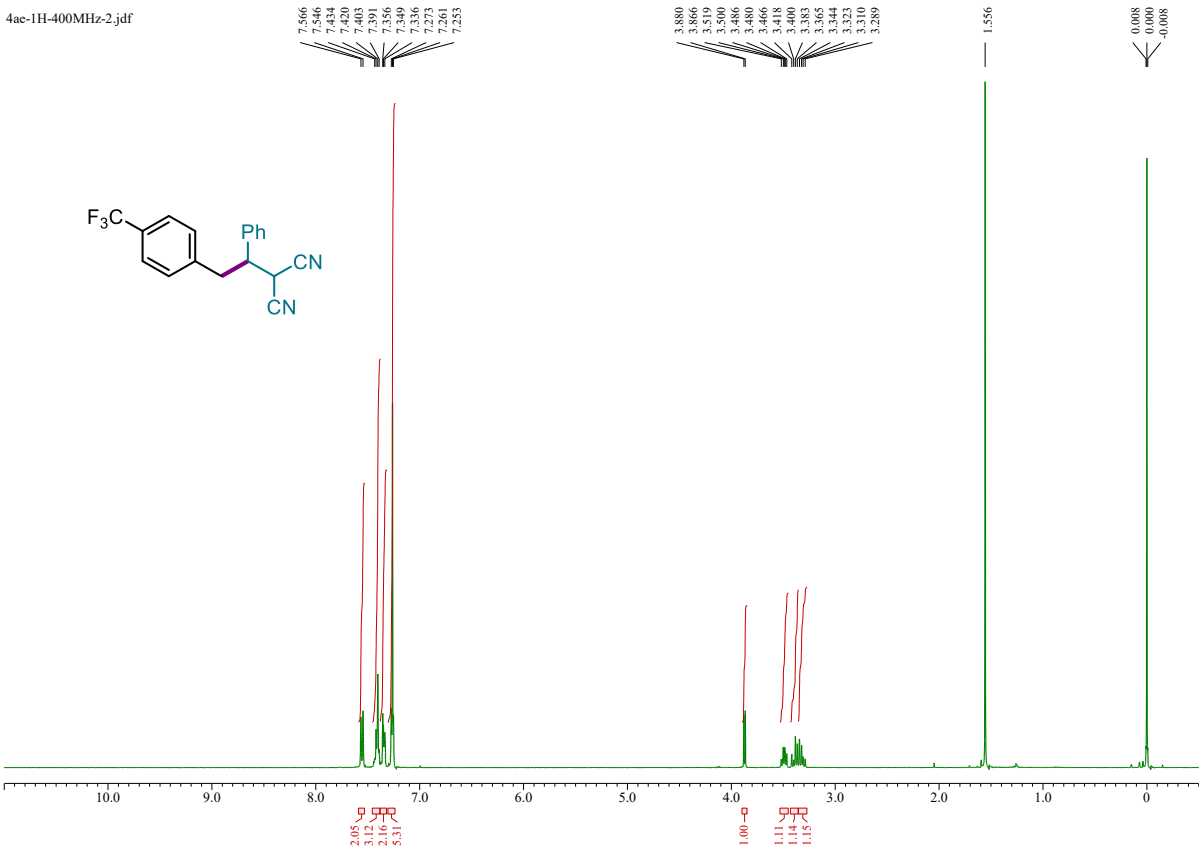
^{13}C NMR spectra (151 MHz) of **4ac** in $CDCl_3$



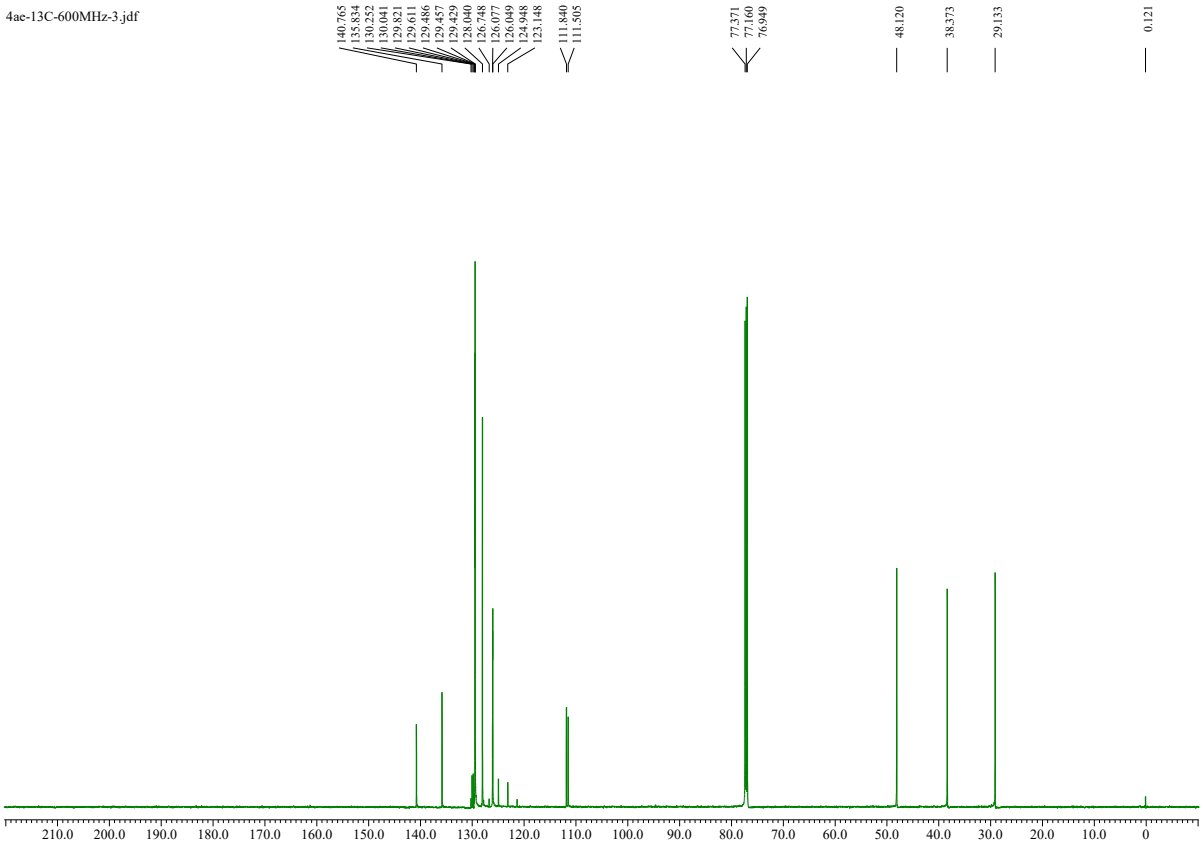
^{1}H NMR spectra (400 MHz) of **4ad** in $CDCl_3$



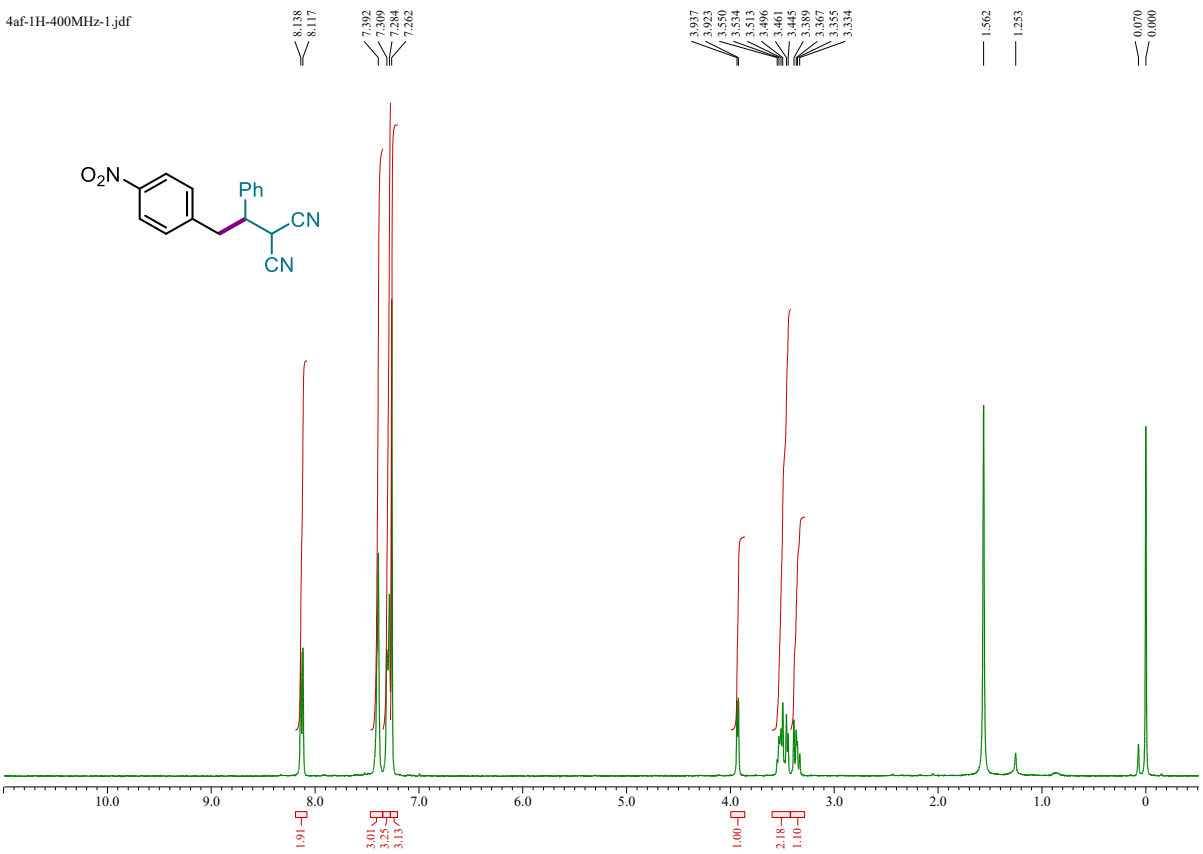
^{13}C NMR spectra (151 MHz) of **4ad** in $CDCl_3$



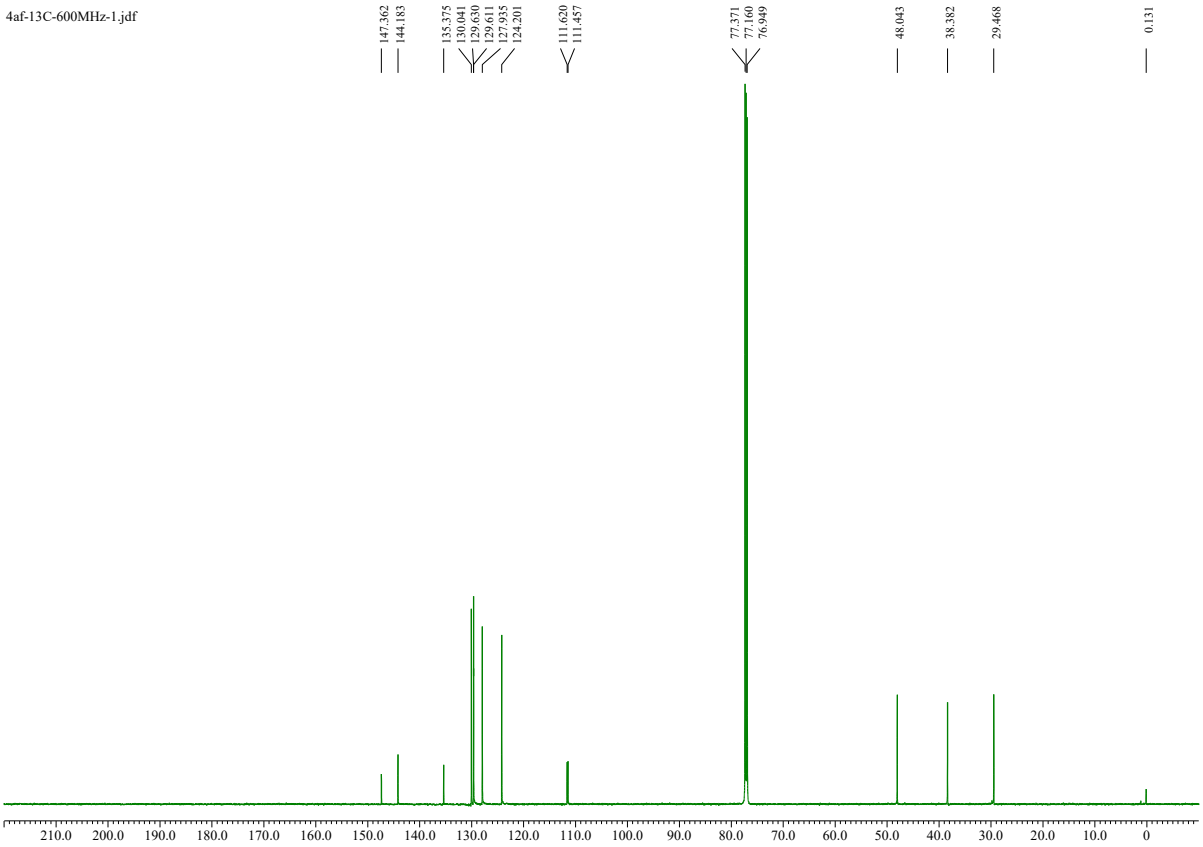
^{1}H NMR spectra (400 MHz) of **4ae** in $CDCl_3$



^{13}C NMR spectra (151 MHz) of **4ae** in $CDCl_3$



^{1}H NMR spectra (400 MHz) of **4af** in $CDCl_3$



^{13}C NMR spectra (151 MHz) of **4af** in $CDCl_3$