Supplementary information for

Novel *N*-Transfer Reagent for Converting α-Amino Acid Derivatives to α-Diazo Compounds

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Table of Contents

1 General Information

Chemical reagents were obtained from chemical suppliers and used without further purification. Acetonitrile, dichloromethane, and tetrahydrofuran were distilled over calcium hydride. Hexane and ethyl acetate were purified by reduced pressure and stored with 4Å molecular sieve. Other anhydrous solvents were purchased from the suppliers. Chromatography was performed with columns of 60 μm silica gel (FUJI). Thin-layer chromatography (TLC) were performed on the plates of Silicagel 60 F_{254} (Merck). Products were visualized by using UV radiation at 254 nm or staining with aqueous solution of potassium permanganate. The phrase "concentrated under reduced pressure" refers to the removal of solvents and other volatile materials using a rotary evaporator. Residual solvents was removed from samples at high vacuum.

^{1}H NMR spectra were recorded by Brucker spectrometer 400 and 500 MHz. $^{13}C\{^{1}H\}$ NMR spectra were recorded by Brucker spectrometer 100 and 125 MHz. $^{31}P\{^{1}H\}$ NMR spectra were recorded by Brucker spectrometer 161.6 and 202 MHz. Standard abbreviations of spin multiplicity such as s, d, t, q, p, sext, sept, m, br, dd, td, ABq were respectively referring to singlet, doublet, triplet, quartet, pentet, sextet, septet, multiplet, broad, doublet of doublet, triplet of doublet, AB quartet. Chemical shift are reported in ppm with a solvent resonance as an internal standard (^{1}H NMR; TMS, DMSO-d_6, CD_3OD, D_2O, $CDCl_3$, as internal standard, indicating 0, 2.50, 3.31, 4.79, 7.26 ppm, respectively, $^{13}C\{^{1}H\}$ NMR; DMSO-d_6, CD_3OD, $CDCl_3$, as internal standard, indicating 39.52, 49.00, 77.16 ppm, respectively.) As for $^{31}P\{^{1}H\}$ NMR spectra, PPh_3 (-6.0 ppm) was used as an external reference standard and the recorded s.r. value (s.r. = 70.02) served as manual calibration to every $^{31}P\{^{1}H\}$ NMR spectra. As for $^{15}N\{^{1}H\}$ NMR spectra, formamide (112.5 ppm) was used as an external reference standard and the recorded s.r. value (s.r. = 12.91) served as manual calibration to every $^{15}N\{^{1}H\}$ NMR spectra.

Infrared spectra were obtained from Perkin-Elmer Spectrum RX FTIR spectrometer. All the absorption maxima value are expressed in wavenumber (cm^{-1}). For mass spectra, Electron Ionization (EI) were collected on a High Resolution Gas Chromatography Time of Flight Mass Spectrometer (brand: JEOL; model: AccuTOF GCx-plus), Electrospray Ionization (ESI) were collected on a High Resolution Orbitrap Mass Spectrometer Tandem Liquid Chromatography and Electrophoresis Analysis System (brand: Thermo Fisher Scientific Inc.; model: Q-Extractive Plus). Electrospray Ionization (ESI) were also collected on High Performance Liquid Chromatography Tandem Mass Spectrometer (brand: Varian; Model: VARIAN 901-MS). Td (5%) was measured on Thermogravimetric Analyzer (Brand: TA Instrument；Model: TA-Q50) and melting point was measured on BUCHI Melting Point B-450.

2 Tracing Isotope ^{15}N of the *N*-Transfer Reaction on NMR

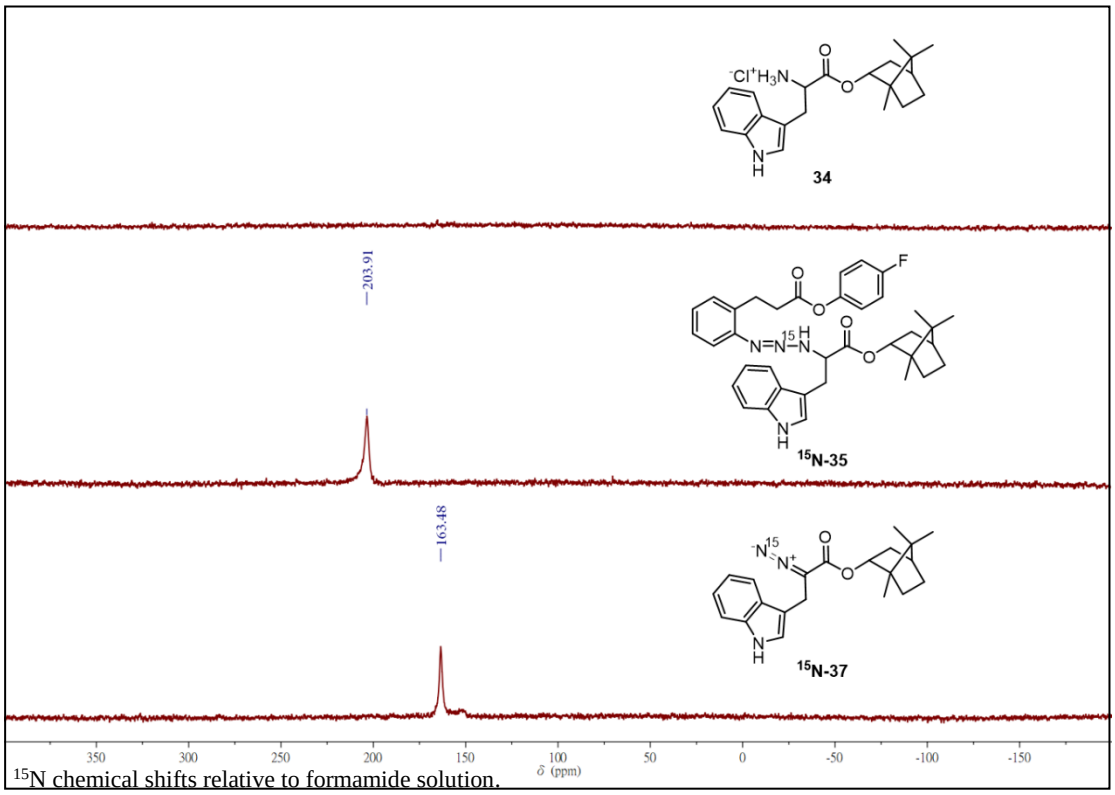


Figure S1. Tracing Isotope ^{15}N of the *N*-Transfer Reaction

3 NMR Experiments for Monitoring the Thermal Decomposition of Triazene 35

The synthesized triazene **35** from construction of diazonium salt **D7** and tryptophan bornyl ester hydrochloride **34** was purified by column chromatography. The isolated triazene **35** which was sealed in the NMR tube with 1,3,5-trimethoxybenzene as an internal standard (IS) in chloroform-d solution (mole ratio of **35**: IS = 3:1) was put in the water bath at 40 ℃ for the thermal decomposition (Figure S2). The integration of internal standard at δ 6.09 ppm was set as 1.13 for normalizing the two proton signals (-C**H**$_2$-CO_2R) as 2 at δ 2.84 ppm of the triazene structure **35**. The decreased integral value of triazene was approximately equal to the increased integral value of 3,4-dihydro-2-quinolone **(36)** (at δ 2.64 ppm for two proton signals, -C**H**$_2$-CO_2R). However, at 40 ℃, the diazo product showed slow and disproportionate growth of integration for two protons at δ 3.81 ppm (-C**H**$_2$-CN_2-CO_2R) due to its thermally unstable property (Figure S3). The decomposition of triazene, formation of 3,4-dihydro-2-quinolone **(36)**, and generation of diazo compound **37** were recorded by ^{1}H-NMR with the time passing by for 17 days and the integral values of those important signals were summarized in the following Table S1.

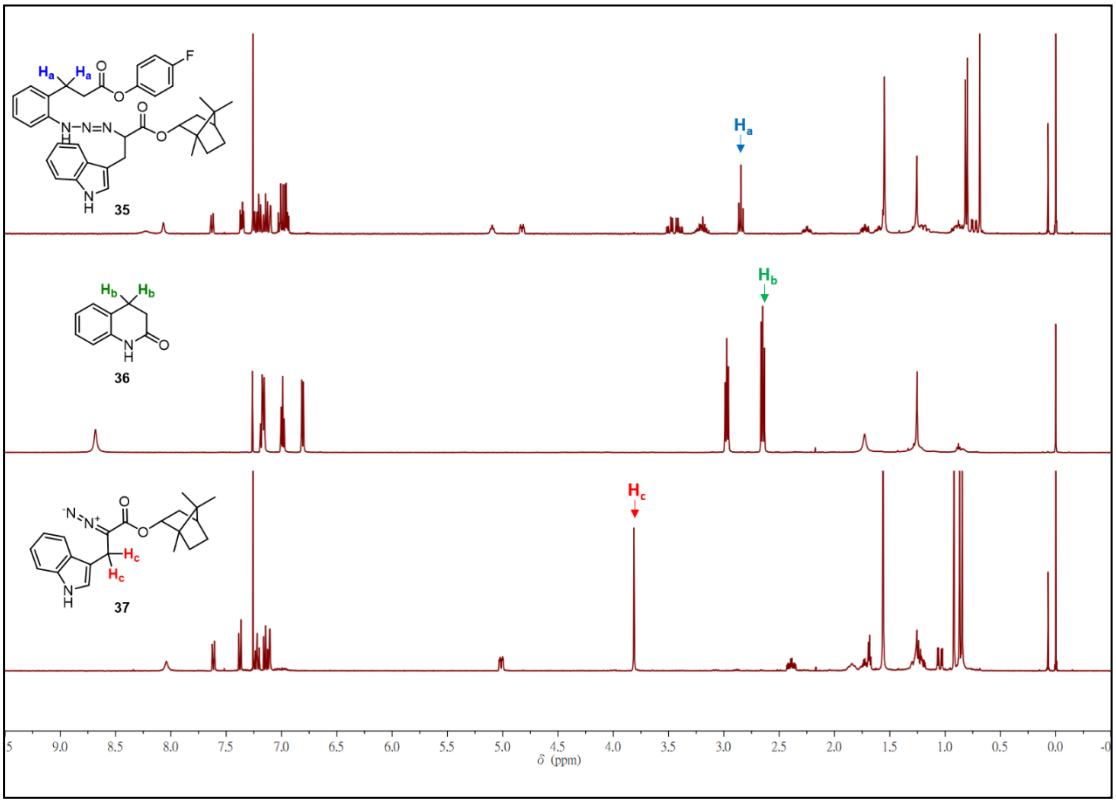


Figure S2. The Standard ^{1}H NMR Spectra of Compound **35, 36, and 37**

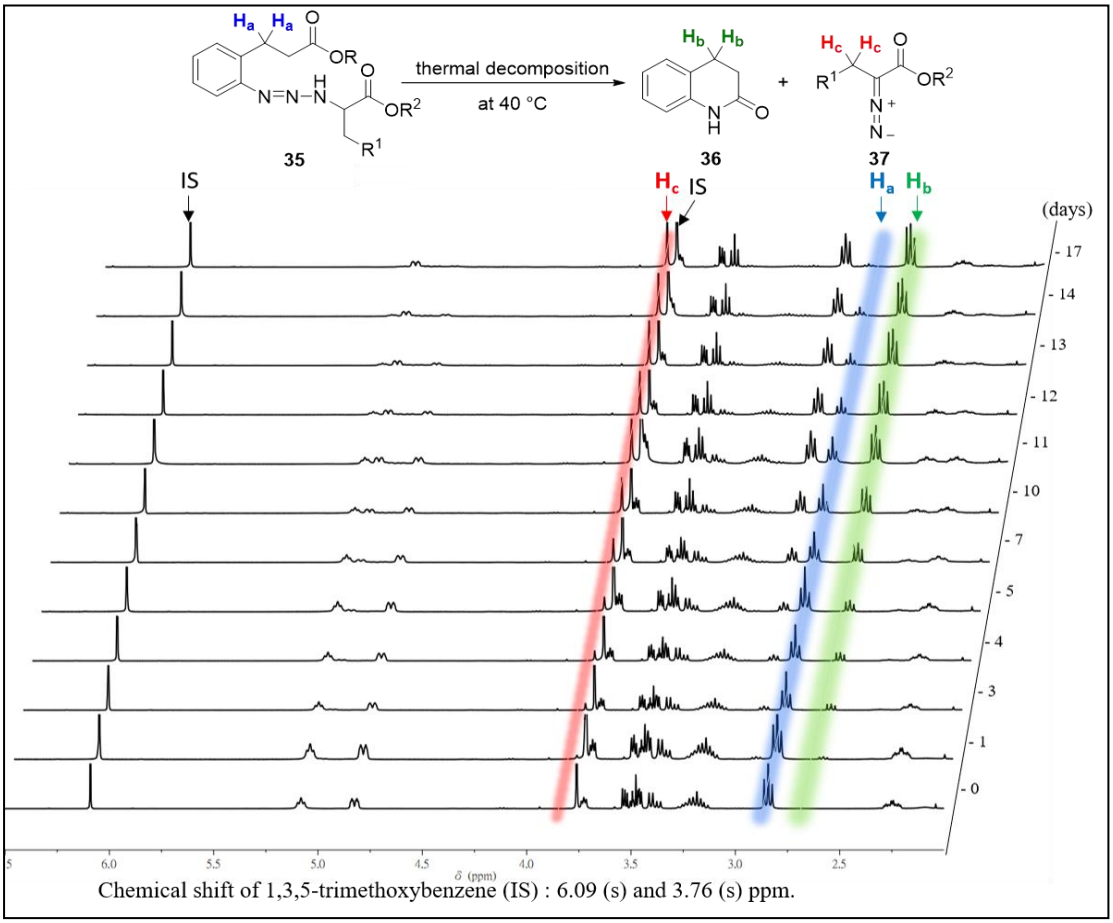


Figure S3. The Overlay ^{1}H NMR Spectra of the Decomposition of Triazene **35**.

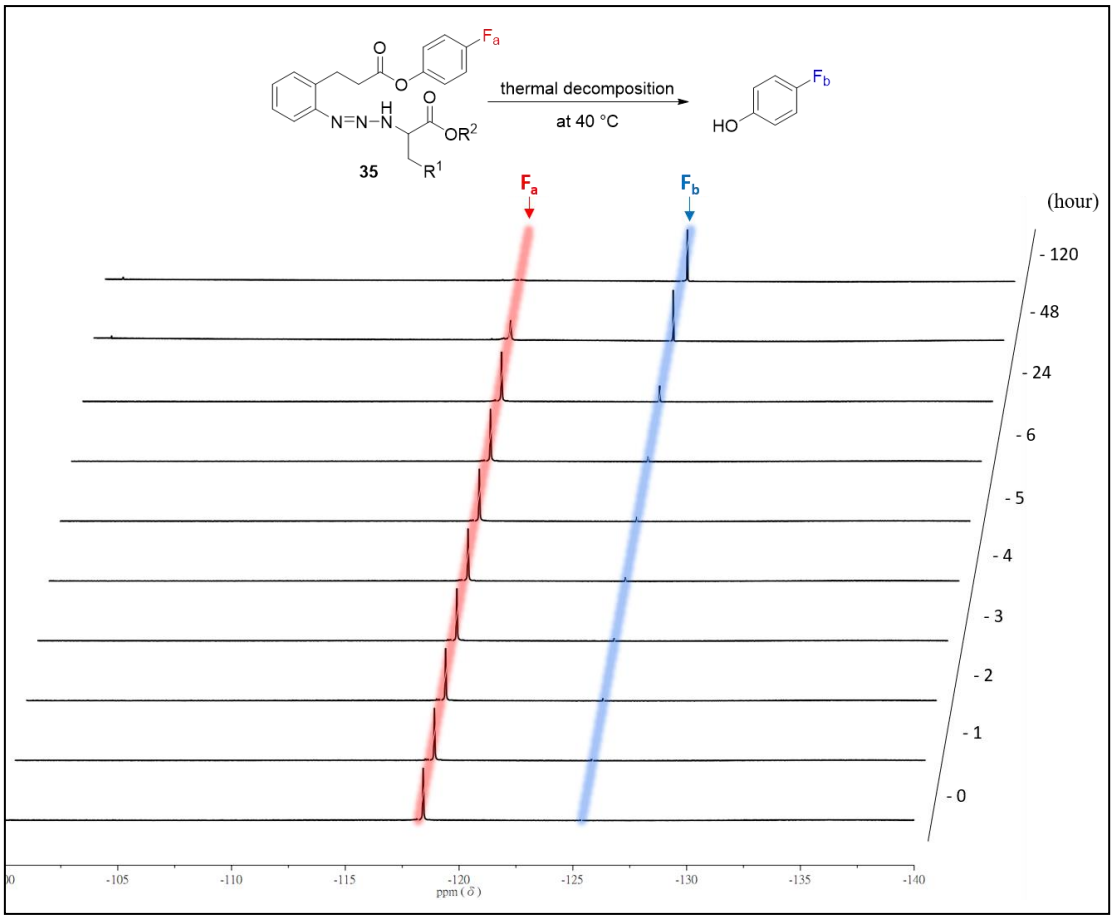
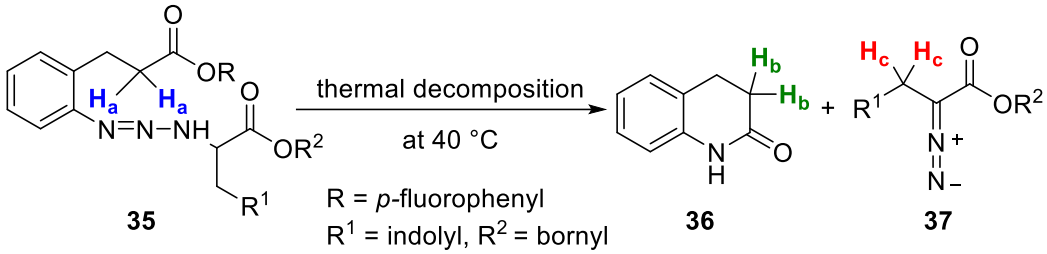


Figure S4. The Overlay ^{19}F NMR Spectra of the Decomposition of Triazene **35**.

Table S1. Percentage of Each Compound in Thermal Triazene Decomposition



time (days)	integration of IS	(2 x H_a)	(2 x H_b)	(2 x H_c)	remaining ratio of **35**	produced ratio of **36**	produced ratio of **37**
0	1.13	2.00	0.00	0.00	100.0%	0.0%	0.0%
1	1.13	1.92	0.10	0.12	96.0%	5.0%	6.0%
3	1.13	1.74	0.27	0.15	87.0%	13.5%	7.5%
4	1.13	1.67	0.37	0.29	83.5%	18.5%	14.5%
5	1.13	1.55	0.45	0.36	77.5%	22.5%	18.0%
7	1.13	1.25	0.73	0.46	62.5%	36.5%	23.0%
10	1.13	0.96	1.04	0.73	48.0%	52.0%	36.5%
11	1.13	0.81	1.21	0.74	40.5%	60.5%	37.0%
12	1.13	0.63	1.33	0.79	31.5%	66.5%	39.5%
13	1.13	0.50	1.45	0.88	25.0%	72.5%	44.0%
14	1.13	0.43	1.60	0.95	21.5%	80.0%	47.5%
17	1.13	0.23	1.77	1.07	11.5%	88.5%	53.5%

$$\text{Remaining ratio of } \mathbf{35} = \frac{\text{Integration of } 2 \text{ x } H_a \text{ of triazene } \mathbf{35}}{2}$$

$$\text{Produced ratio of } \mathbf{36} = \frac{\text{Integration of } 2 \text{ x } H_b \text{ of quinolone } \mathbf{36}}{2}$$

$$\text{Produced ratio of } \mathbf{37} = \frac{\text{Integration of } 2 \text{ x } H_c \text{ of diazo } \mathbf{37}}{2}$$

4 NMR Experiments for Monitoring the Decomposition of Triazene with K_3PO_4(aq) in THF-D_8/D_2O solution

The isolated triazene sealed in the NMR tube with 1,3,5-trimethoxybenzene as an internal standard (IS) was decomposed by basic K_3PO_4(*aq*) in THF-D_8:D_2O (v/v) = 20:1 solution (mole ratio of triazene: IS = 1:1.2). The solid base K_2CO_3(*s*) used in the general *N*-transfer reaction was replaced with homogeneous K_3PO_4(*aq*) in D_2O for better NMR resolution. The decomposition of triazene, formation of 3,4-dihydro-2-quinolone, and generation of diazo compound were recorded by ^{1}H-NMR with the time pass by for 7 hours and the integral values of those important signals were summarized in the following table. The integration of internal standard at δ 3.70 ppm was set as 10.33 for normalizing the two proton signals (PhC**H$_2$**) of the triazene structure (at δ 2.81 ppm). The decreased integral value of triazene was approximately equal to the increased integral value of 3,4-dihydro-2-quinolone (at δ 2.47 ppm for two proton signals, PhC**H$_2$**). Although we could observed the increased signal of α-H_d (at δ 5.11 ppm) of diazo compound, the integration of this acidic α-proton was not proportional to the other proton signals due to the proton exchange with D_2O solution. To acquire the correct ratio of diazo compound, we used the benzylic proton (H_e) to do the integration for the ratio calculation.

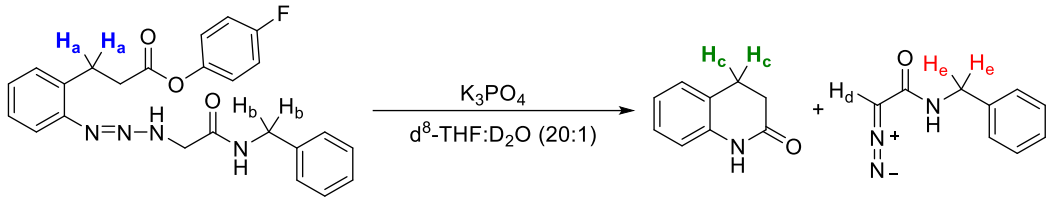


Table S2. Percentage of each compound in the thermal triazene decomposition

time	integration of				remaining	produced	produced
(hr)	IS	(2 x H_a)	(2 x H_c)	(2 x H_e)	ratio of H_a	ratio of H_c	ratio of H_e
0	10.33	1.86	0.13	0.14	93%	6.5%	7%
1	10.33	1.77	0.24	0.28	88.5%	12%	14%
2	10.33	1.33	0.70	0.69	66.5%	35%	34.5%
3	10.33	0.66	1.34	1.27	33%	67%	63.5%
4	10.33	0.28	1.75	1.62	14%	87.5%	81%
5	10.33	0.16	1.87	1.75	8%	93.5%	87.5%
6	10.33	0.12	1.93	1.80	6%	96.5%	90%
7	10.33	0.10	1.94	1.81	5%	97%	90.5%

$$\text{Remaining ratio of triazene} = \frac{\text{Integration of } 2 \text{ x } H_a \text{ of triazene}}{2}$$

$$\text{Produced ratio of quinolone} = \frac{\text{Integration of } 2 \text{ x } H_c \text{ of quinolone}}{2}$$

$$\text{Produced ratio of diazo} = \frac{\text{Integration of } 2 \text{ x } [(H_b + H_e) - H_a]}{2}$$

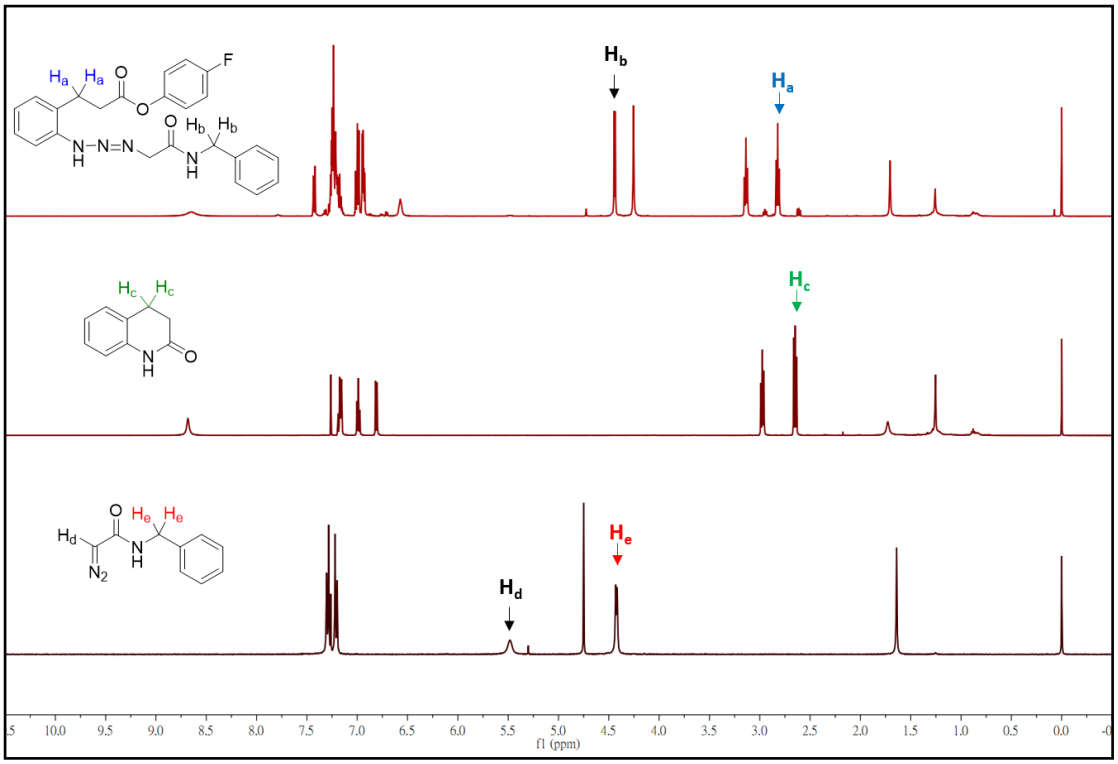


Figure S5. The Standard NMR Spectra of Major Compounds

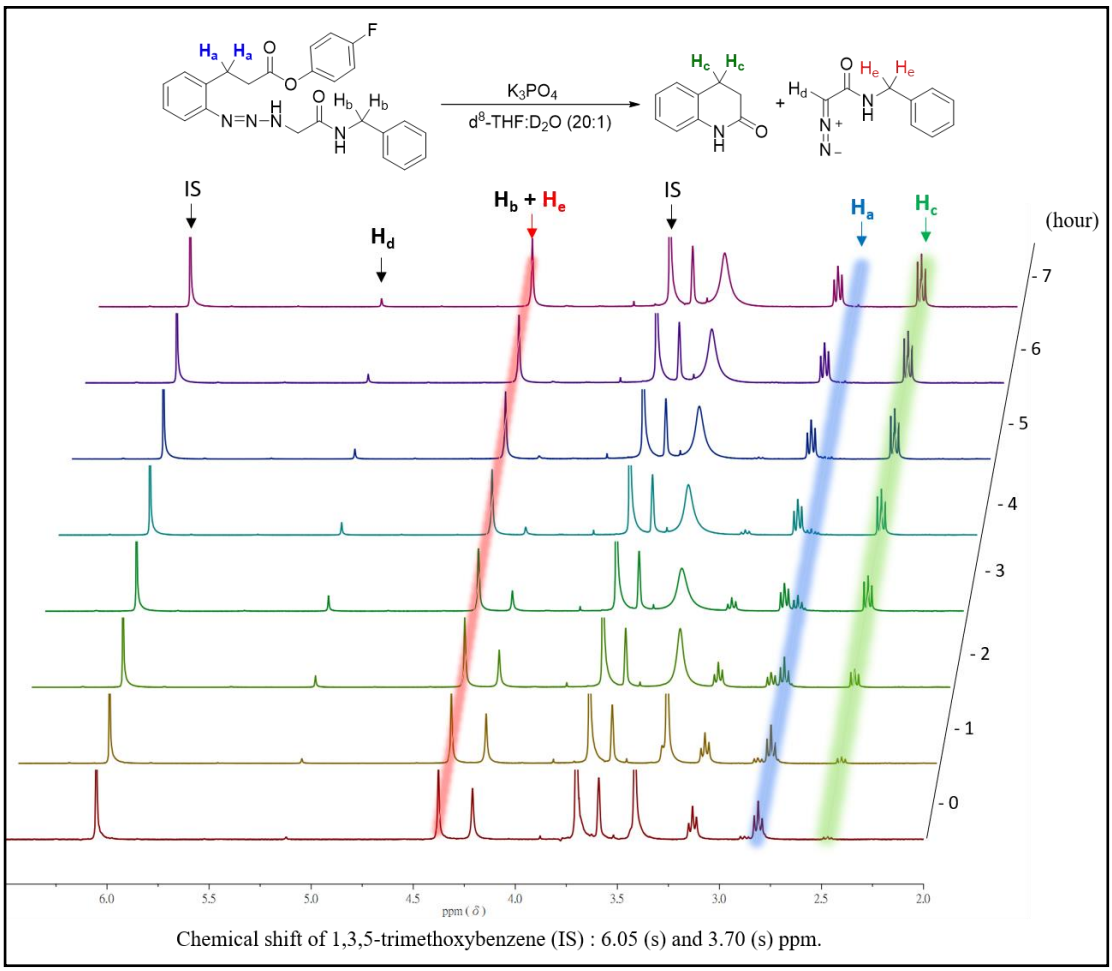


Figure S6. The Overlay ^{1}H NMR Spectra of the Decomposition of Triazene

5 Thermogravimetric Analysis Curve of the *N*-Transfer Reagent D7

The thermogravimetric analyzer (TGA; Model: TGA-Q50 from TA Instruments) was used to measure the stability of *N*-transfer reagent **D7**. The diazonium salt (14.375 mg) on the platinum sample plain was heated from room temperature to 250 °C at the constant rate of 5 °C/min and purged by N_2 gas at the flow rate of 60 mL/min in the furnace. The weight change of sample was continuously recorded, and plotted as a TGA curve with percentage of original mass on the y axis versus temperature on the x-axis (Figure S4). The thermal decomposition temperature Td (5%) = 75.2 °C was reported at which the mass of the sample is 5.0% less than its mass measured at the initial temperature. Other two independent experiments (12.210 mg and 11.495 mg) were repeated according to the same protocol for determining the reproducibility (Table S2).

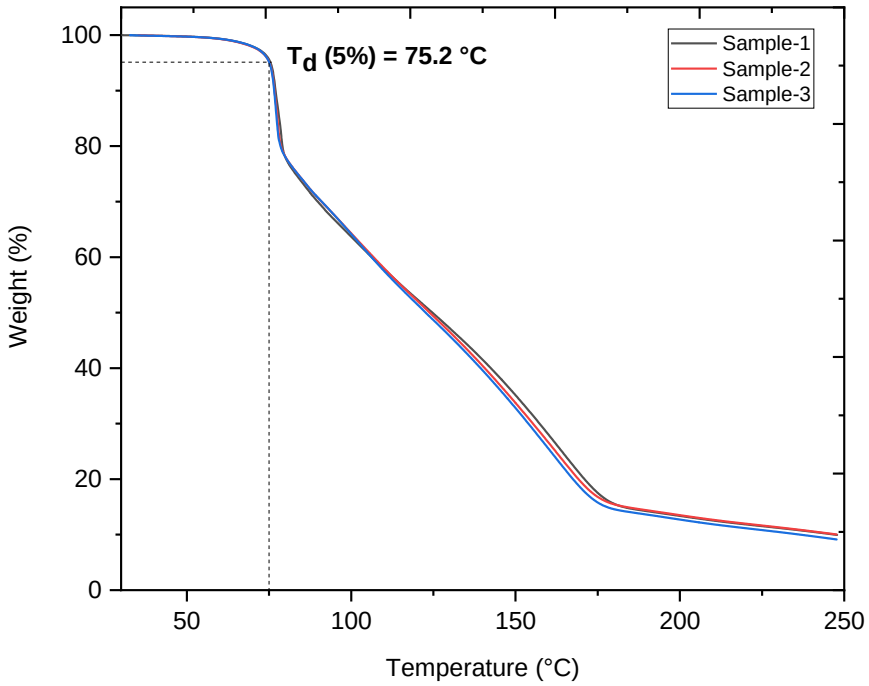


Figure S7. The TGA curve of *N*-transfer reagent **D7.**

Table S3. The thermal decomposition temperature Td (5%) of *N*-transfer reagent **D7.**

sample	weight	T_d (5%)
1	14.375 mg	75.4 °C
2	12.210 mg	75.2 °C
3	11.495 mg	75.1 °C
	average	75.2 °C

6 Acquisition of NMR Spectrum for the Stability Test of *N*-Transfer Reagent D7

After acquiring the standard ^{1}H-NMR spectrum of diazonium salt **D7**, the synthesized one-batch reagent was divided into two portions. One of them was stored in a refrigerator at 4 ℃, while the other was kept at an ambient room temperature, separately. After a period of time, certain amount of compound was taken out from each capped vail for acquiring a ^{1}H-NMR spectrum and returned to the previous applied environment again until the next data collection. The combination of all data showed that the diazonium salt **D7** could be stored at 4 ℃ for at least 45 days without obvious decomposition (Figure S5). In contrast, the reagent was not stable at the room temperature even for a few days (Figure S6).

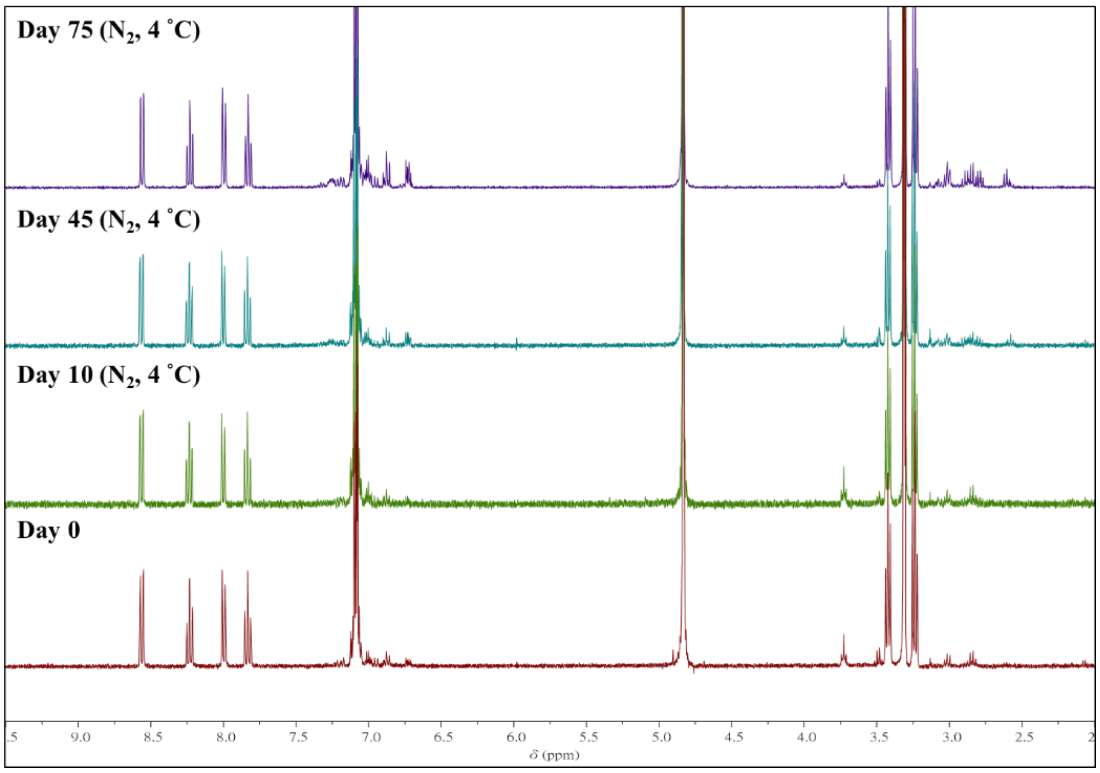


Figure S8. Diazonium Salt **D7** was Stored at 4 ℃

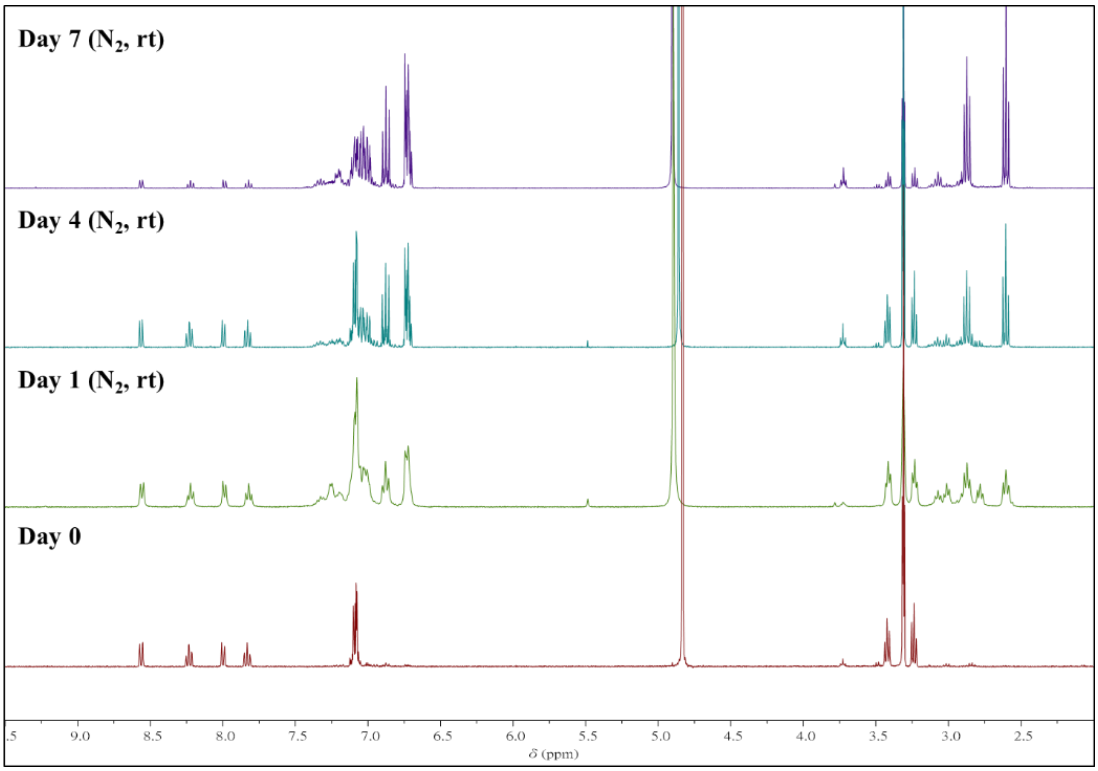
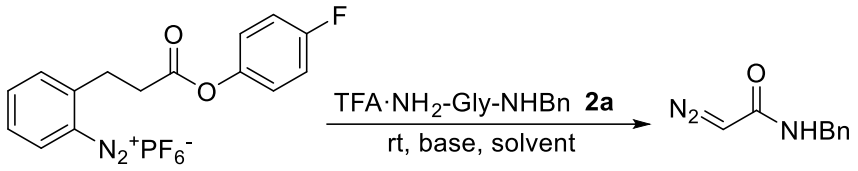


Figure S9. Diazonium Salt **D7** was Stored at Room Temperature

7 Optimization of Reaction Conditions

Table S4. Evaluation of Reaction Conditions for Diazo Generation with **D7** and **2a**[a]



D7 **11a**

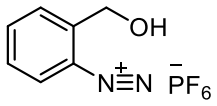
entry	base (eq)	solvent (v/v %)	time (h)	yield of **11a** (%)[a]
1	K_2CO_3 (1.2)	THF: H_2O (20:1)	37	67
2	K_2CO_3 (3.0)	THF: H_2O (20:1)	5	62
3	K_2CO_3 (4.0)	THF: H_2O (20:1)	3	80
4	K_2CO_3 (4.0)	THF: H_2O (20:5)	> 48	62
5	$NaHCO_3$ (4.0)	THF: H_2O (20:1)	> 48	23
6	pyridine (4.0)	THF: H_2O (20:1)	3	-
7	TEA (4.0)	THF: H_2O (20:1)	3	-
8	DBU (4.0)	THF: H_2O (20:1)	3	-
9	K_2CO_3 (4.0)	MeOH	3	-
10	K_2CO_3 (4.0)	acetone	3	-
11	K_2CO_3 (4.0)	THF	3	trace
12	K_2CO_3 (4.0)	CH_3CN	3	trace
13	K_2CO_3 (4.0)	DMF	3	-
14	K_2CO_3 (4.0)	DMSO	3	-
15	K_2CO_3 (4.0)	CH_3CN: H_2O (20:1)	3	66

[a]Isolated yield.

8 Experimental Procedures and Characterization Data

8.1 Synthetic Procedure for Scheme 2

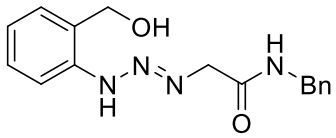
2-(Hydroxymethyl)benzenediazonium hexafluorophosphate(V) (1)



$NaNO_2$ (67.2 mg, 0.974 mmol) in 0.4 ml H_2O and 60% HPF_6 (0.96 ml, 0.812 mmol) were subsequently added into a solution of 2-amino-benzylalcohol (100 mg, 0.812 mmol) in 2.0 ml THF at -5 °C to obtain a mixture. After 15 minutes, the mixture was concentrated under reduced pressure, and the residual concentrate was recrystallized from the addition of diethyl ether (Et_2O) to obtain diazonium salt. The diazonium salt was collected by filtration, washed with Et_2O, and dried under high vacuum to get diazonium salt **1** as a white solid (126 mg, 0.450 mmol, 55%).

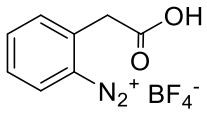
^{1}H NMR (400 MHz, CD_3CN, ppm) δ = 8.76 (d, *J* = 8.4 Hz, 1H), 8.21 (dd, *J* = 7.6, 7.6 Hz, 1H), 7.90-7.86 (m, 2H), 5.19 (s, 2H). (The compound was not stable for the long time ^{13}C-NMR acquisition.)

(*E*)-*N*-Benzyl-2-(3-(2-(hydroxymethyl)phenyl)triaz-1-en-1-yl)acetamide (3)



Compound **2a** (48 mg, 0.173 mmol) with K_2CO_3 (80 mg, 0.579 mmol) in 0.7 ml THF: H_2O (v/v) = 20:1 (0.2 M) solution was added by diazonium salt **1** (40 mg, 0.143 mmol) at 0 °C. The mixture was warm up to the room temperature after 15 minutes. Until the reaction completed according to the TLC observation, the solution was quenched with H_2O and diluted with EtOAc. The mixture was extracted with EtOAc for three times. The organic layers were combined, dehydrated with NaCl (sat.), dried over $MgSO_4$ (s), filtered, and concentrated under reduced pressure to give the crude residue. The residue was purified by column chromatography on silica gel, eluting with 30% v/v EtOAc in Hexane (R_f = 0.25) to give **3** as a yellow solid (8.8 mg, 0.023 mmol, 16 % yield).
^{1}H NMR (500 MHz, MeOD, ppm) δ = 7.45-7.16 (m, 9H), 4.77 (s, 2H), 4.60 (br, 1H), 4.42 (s, 2H), 4.22 (s, 2H) ;^{13}C{^{1}H} NMR (125 MHz, MeOD,ppm) δ = 171.3, 148.3, 139.7, 136.9, 129.4, 128.7, 128.4, 128.1, 127.3, 117.6, 61.7, 44.0; IR (KBr, cm^{-1}): 3312, 2962, 2925, 1652, 1537, 1427, 1261, 1094, 1018, 800, 753, 699; HRMS (EI$^+$) *m/z* calc. for $C_{16}H_{18}O_2N_4^+$: 298.1424; found: 298.1421.

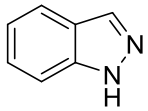
2-(Carboxymethyl)benzenediazonium tetrafluoridoborate (4)



$NaNO_2$ (41.4 mg, 0.594 mmol) in 0.25 ml H_2O and 50% HBF_4 (0.17 ml, 1.364 mmol) were subsequently added into commercially available 2-(carboxymethyl)-benzenammonium chloride (93 mg, 0.496 mmol) in 0.6 ml THF at -5 °C to obtain a mixture. After 15 minutes, the mixture was concentrated under reduced pressure, and the residual concentrate was recrystallized from the addition of diethyl ether (Et_2O) to obtain diazonium salt. The diazonium salt was collected by filtration, washed with Et_2O, and dried under high vacuum to get diazonium salt **4** as a white solid (75 mg, 0.300 mmol, 60% yield).

^{1}H NMR (400 MHz, MeOD, ppm) δ = 8.66 (d, *J* = 8.4 Hz, 1H), 8.23 (dd, *J* = 8.0, 8.0 Hz, 1H), 7.92-7.88 (m, 2H), 4.28 (s, 2H). (The compound was not stable for the long time ^{13}C-NMR acquisition.)

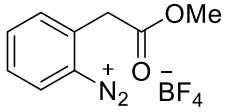
Benzofuran-2-ol (5)



Compound **2a** (48.5 mg, 0.174 mmol) with K_2CO_3 (77.8 mg, 0.563 mmol) in 0.7 ml THF: H_2O (v/v) = 20:1 (0.2 M) solution was added by diazonium salt **4** (35.3 mg, 0.141 mmol) at 0 °C. The solution was warm up to room temperature after 15 minutes. Until the reaction completed according to the TLC observation, the solution was quenched with H_2O and diluted with EtOAc. The mixture was extracted with EtOAc for three times. The organic layers were combined, dehydrated with NaCl (sat.), dried over $MgSO_4$ (s), filtered, and concentrated under reduced pressure to give the crude residue. The residue was purified by column chromatography on silica gel, eluting with 25% v/v EtOAc in Hexane (R_f = 0.40) to give **5** as white solid (8.5 mg, 0.072 mmol, 51 % yield).

^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ = 10.55 (br, 1H), 8.11 (d, *J* = 1.0 Hz, 1H), 7.78 (ddd, *J* = 6.4, 6.4, 1.0 Hz, 1H), 7.51 (dd, *J* = 8.5, 1.0 Hz, 1H), 7.42-7.39 (m, 1H), 7.20-7.17 (m, 1H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, ppm) δ = 140.2, 135.0, 127.0, 123.3, 121.1, 121.0, 109.8; IR (KBr, cm^{-1}): 3177.3, 1381.6, 1355.8, 1075.7, 951.2, 845.5, 741.6; HRMS (EI$^+$) *m/z* calc. for $C_7H_6N_2^+$: 118.0526; found: 118.0523. All spectroscopic data were in agreement with the literature values.[1]

2-(2-Methoxy-2-oxoethyl)benzenediazonium tetrafluoridoborate (6)

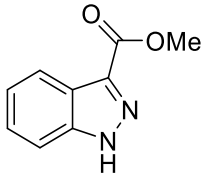


Hydrogenation: A flask was charged with 17.5 mg of palladium on carbon (10% Pd/C, 20 wt% of the nitrobenzene starting material) and filled with nitrogen gas. MeOH was added into the reaction flask at r.t. to form a mixture, to which a solution of methyl 2-(2-nitrophenyl)acetate (84.9 mg, 0.435 mmol) in MeOH was added. Subsequently, the flask was purged with hydrogen gas to replace the nitrogen gas. The reaction was stirred at r.t. and monitored by TLC. Upon completion, the mixture was filtered through a celite-cotton pad, and the pad was washed with MeOH. The filtrate containing an aniline compound was concentrated for diazotization.

Diazotization: $NaNO_2$ (36.0 mg, 0.522 mmol) in 0.22 ml H_2O and 50% HBF_4 (0.15 ml, 1.178 mmol) were subsequently added into previous aniline in 2.5 ml THF at -5 °C to obtain a mixture. After 15 minutes, the mixture was concentrated under reduced pressure, and the residual concentrate was recrystallized from the addition of diethyl ether (Et_2O) to obtain diazonium salt. The diazonium salt was collected by filtration, washed with Et_2O, and dried under high vacuum to get diazonium salt **6** as a white solid (74.7 mg, 0.283 mmol, 65% yield).

^{1}H NMR (400 MHz, CD_3CN, ppm) δ = 8.53 (d, *J* = 7.6 Hz, 1H), 8.19 (ddd, *J* = 8.0, 8.0, 1.0 Hz, 1H), 7.88-7.82 (m, 2H), 4.18 (s, 2H), 3.75 (s, 3H). (The compound was not stable for the long time ^{13}C-NMR acquisition.)

Methyl 1*H*-indazole-3-carboxylate (7)

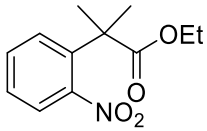


Compound **2a** (100 mg, 0.359 mmol) with K_2CO_3 (164 mg, 1.187 mmol) in 1.5 ml THF: H_2O (v/v) = 20:1 (0.2 M) solution was added by diazonium salt **6** (78.4 mg, 0.297 mmol) at 0 °C. The solution was warm up to room temperature after 15 minutes. Until the reaction completed according to the TLC observation, the solution was quenched with H_2O and diluted with EtOAc. The mixture was extracted with EtOAc for three times. The organic layers were combined, dehydrated with NaCl (sat.), dried over $MgSO_4$ (s), filtered, and concentrated under reduced pressure to give the crude residue. The residue

was purified by column chromatography on silica gel, eluting with 50% v/v EtOAc in Hexane (R_f = 0.50) to give **7** as white solid (39.3 mg, 0.223 mmol, 75 % yield).

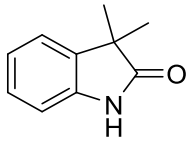
^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ = 13.38 (br, 1H), 8.20 (d, *J* = 8.3 Hz, 1H), 7.83 (d, *J* = 8.5 Hz, 1H), 7.46 (ddd, *J* = 8.3, 7.0, 1.2 Hz, 1H), 7.35 (ddd, *J* = 8.0, 6.8, 0.9 Hz, 1H), 4.07 (s, 3H); 13C{^{1}H} NMR (125 MHz, $CDCl_3$, ppm) δ = 163.8, 141.6, 136.2, 127.4, 123.4, 122.5, 121.7, 111.7, 52.2. All spectroscopic data were in agreement with the literature values.[2]

Ethyl 2-methyl-2-(2-nitrophenyl)propanoate (8)



The solution of ethyl 2-(2-nitrophenyl)acetate (50 mg, 0.239 mmol) in DMF (0.48 ml) was carefully added by 60% NaH (29 mg, 0.710 mmol) at 0 °C for deprotonation. After 30 min, the solution was added by MeI (33 µl, 0.53 mmol) at 0 °C and stirred for 15 minutes before removing the reaction to r.t. for another 1 hour. The mixture was quenched with H_2O (10 mL) and extracted with ether (10 mL × 3). The organic layers were combined, dried over $MgSO_4$, filtered, and concentrated under reduced pressure to give the curde residue. The crude was purified by column chromatography on silica gel, eluting with 15% v/v EtOAc in hexane (R_f = 0.70) to give **8** as yellow oil (38.6 mg, 0.163 mmol, 68% yield).
^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ = 7.92 (d, *J* = 7.8 Hz, 1H), 7.61-7.56 (m, 2H), 7.44-7.38 (m, 1H), 4.12 (q, *J* = 7.1 Hz, 2H), 1.67 (s, 6H), 1.20 (t, 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$, ppm) δ = 175.3, 148.9, 139.6, 133.2, 128.2, 127.8, 125.7, 61.3, 46.6, 27.7, 14.1. All spectroscopic data were in agreement with the literature values.[3]

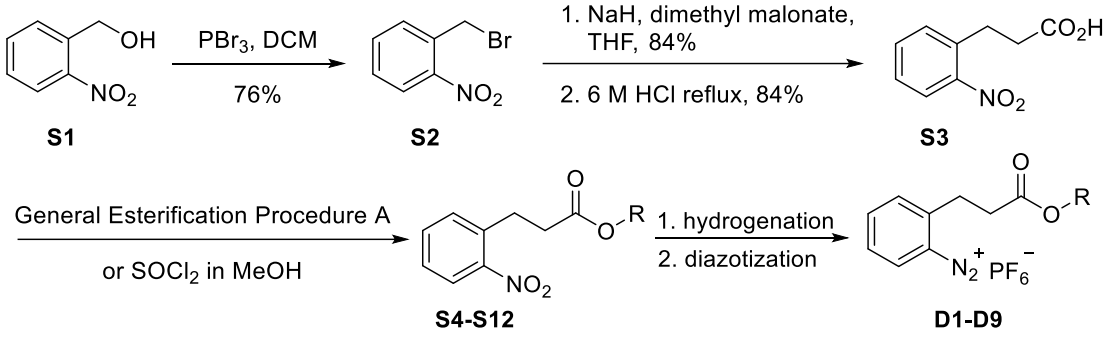
3,3-Dimethylindolin-2-one (9)



A flask was charged with 7.7 mg of palladium on carbon (10% Pd/C, 20 wt% of compound **8**) and filled with nitrogen gas. MeOH was added into the reaction flask at r.t. to form a mixture, to which a solution of compound **8** (38.6 mg, 0.163 mmol) in MeOH was added. Subsequently, the flask was purged with hydrogen gas to replace the nitrogen gas. The reaction was stirred at r.t. and monitored by TLC. Upon completion, the mixture was filtered through a celite-cotton pad, and the pad was washed with EtOAc. The filtrate was concentrated to afford compound **9** as white solid (14.3 mg,

0.089 mmole, 54% yield).
^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ = 8.46 (br, 1H), 7.21-7.18 (m, 2H), 7.03 (ddd, *J* = 7.5, 7.5, 1.0 Hz, 1H), 6.92 (d, *J* = 7.5 Hz, 1H), 1.41 (s, 6H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, ppm) δ = 184.1, 139.9, 136.5, 127.9, 122.9, 122.7, 111.0, 44.9, 24.6. All spectroscopic data were in agreement with the literature values[4].

8.2 Synthetic Procedure for Various *N*-Transfer reagents D1-D9



Scheme S1. Synthetic Procedure for Various *N*-Transfer reagents **D1-D9**

General Esterification Procedure

3-(2-Nitrophenyl)propanoic acid (**S3**, 1.0 eq.) was dissolved in DCM (0.5 M), followed by adding an alcohol compound (1.1 eq.), EDC·HCl (1.1 eq.), *N*,*N*-diisopropylethylamine (DIPEA, until the solid salt completely dissolved), and DMAP (catalytic amount) in order. The reaction was stirred at room temperature until the reaction completed according to the thin layer chromatography (TLC) observation. The mixture was quenched with H_2O, extracted with DCM three times. The combined organics were dried over $MgSO_4$, filtered, and concentrated to give the residue. The crude product was purified by silica gel column chromatography to obtain a nitrobenzene precursor.

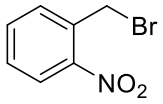
General Hydrogenation and Diazotization Procedure

Hydrogenation: A flask was charged with an appropriate amount of palladium on carbon (10% Pd/C, the amount in use was 10-20 wt% of the nitrobenzene precursor) and filled with nitrogen gas. THF was added into the reaction flask at 0 °C to form a mixture, to which a solution of certain moles of **S4-S12** in THF was added. Subsequently, the flask was purged with hydrogen gas to replace the nitrogen gas. The reaction was stirred at 0-4 °C and monitored by TLC. Upon completion, the mixture was filtered through a celite-cotton pad, and the pad was washed with chilly THF. The filtrate containing an aniline compound was kept at -5 °C for diazotization. Herein, the moles of the aniline compound were approximately the same as the moles of the nitrobenzene precursor, *i.e.* the yield of the hydrogenation was almost 100%.

Diazotization: Sodium nitrite ($NaNO_2$ (*s*), 1.2 eq.) in H_2O (2.0 M) and hexafluorophosphoric acid (HPF_6, 1.4 M) were subsequently added into a solution of the *in situ* synthesized aniline compound in THF at -5 °C to obtain a mixture. After 15 minutes, the mixture was concentrated under reduced pressure, and the residual concentrate was recrystallized from the addition of diethyl ether (Et_2O) to obtain

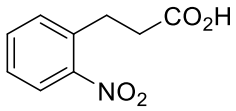
diazonium salt. The diazonium salt was collected by filtration, washed with Et_2O, and dried under high vacuum so as to obtain an *N*-transfer reagent, which was stored under N_2 at 0 °C for the future usage.

1-(Bromomethyl)-2-nitrobenzene (S2)



PBr_3 (0.31 mL, 3.26 mmol) was carefully added into 2-nitrobenzylalcohol (**S1**, 500 mg, 3.27 mmol) in DCM (6.5 mL, 0.5 M) under N_2 at 0 °C. The mixture was stirred at room temperature for 1 hour, then quenched with H_2O (10 mL) and extracted with DCM (30 mL × 3). The organic layers were combined, dried over $MgSO_4$, filtered, and concentrated under reduced pressure to give the residue. The crude product was purified by column chromatography on silica gel, eluting with 25% v/v EtOAc in hexane (R_f = 0.7) to give **S2** as white solid (534.1 mg, 2.47 mmol, 76% yield).
^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ = 8.04 (dd, *J* = 8.5, 1.5 Hz, 1H), 7.63-7.57 (m, 2H), 7.49 (ddd, *J* = 7.5, 7.5, 2.0 Hz, 1H), 4.84 (s, 2H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$, ppm) δ = 147.7, 136.8, 134.1, 130.0, 128.5, 125.0, 62.6; IR (KBr, cm^{-1}): 1525, 1437, 1344, 1306, 1260, 1225, 1093, 1019, 856, 805, 748, 699, 613; HRMS (EI^+) calc'd m/z for $C_7H_6BrO_2N^+$: 214.9582, found: 214.9584.

3-(2-Nitrophenyl)propanoic acid (S3)



Dimethyl malonate (0.21 mL, 1.85 mmol) was added dropwise into the suspension solution of NaH (60%, 56 mg, 1.40 mmol) in THF (1.9 mL, 1.0 M) under N_2 at 0 °C. After 5 minutes, a solution of compound **S2** (200 mg, 0.93 mmol) in THF (1.2 mL, 0.8 M) was slowly added into the mixture. The solution was stirred at room temperature for 30 minutes, then quenched with H_2O (10 mL) and extracted with EtOAc (30 mL × 3). The organic layers were combined, dried over $MgSO_4$, filtered, and concentrated under reduced pressure to give the residue. The crude product was purified by column chromatography on silica gel, eluting with 20% v/v EtOAc in hexane (R_f = 0.60) to give **dimethyl 2-(2-nitrobenzyl)malonate** as colorless oil (207.9 mg, 0.78 mmol, 84% yield).

The synthesized dimethyl 2-(2-nitrobenzyl)malonate (2 g, 9.3 mmol) was refluxed in aqueous 6 M HCl (aq.) solution (18 mL, 0.5 M) at 165 °C for 16 hours. The solution was then cooled to room temperature, diluted with H_2O (20 mL), extracted with EtOAc (60 mL × 3). The organic layers were combined, dried over $MgSO_4$, filtered, and concentrated under reduced pressure to give the residue. The crude product was purified by column chromatography on silica gel, eluting with 50% v/v EtOAc in hexane (R_f = 0.33) to give **S3** as white solid (1.52 g, 7.78 mmol, 84% yield).

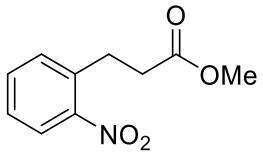
Dimethyl 2-(2-nitrobenzyl)malonate

^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ = 8.00 (dd, J = 8.0, 1.5 Hz, 1H), 7.53 (ddd, *J* = 7.5, 7.5, 1.5 Hz, 1H), 7.43-7.38 (m, 2H), 3.92 (t, *J* = 7.5 Hz, 1H), 3.70 (s, 6H), 3.51 (d, *J* = 7.5 Hz, 2H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, ppm) δ = 168.9, 149.1, 133.3, 133.0, 132.9, 128.3, 125.2, 52.7, 52.1, 32.2; HRMS (EI^+) calc'd m/z for $C_{12}H_{13}NO_6^+$: 267.0742, found: 267.0746. All spectroscopic data were in agreement with the literature values[5].

3-(2-Nitrophenyl)propanoic acid (S3)

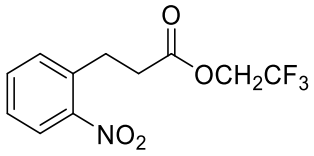
^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ = 7.96 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.55 (ddd, *J* = 7.5, 7.5, 1.5 Hz, 1H), 7.43-7.38 (m, 2H), 3.24 (t, *J* = 7.5 Hz, 2H), 2.80 (t, *J* = 7.5 Hz, 2H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, ppm) δ = 177.4, 149.3, 135.0, 133.3, 132.1, 127.8, 125.0, 34.4, 28.1; HRMS (EI^+) calc'd m/z for $C_9H_9NO_4^+$: 195.0532, found: 195.0532. All spectroscopic data were in agreement with the literature values[6].

Methyl 3-(2-nitrophenyl)propanoate (S4)



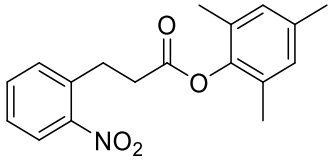
After dropwise adding $SOCl_2$ (28 µl, 0.386 mmol) into methanol solution (0.51 mL, 0.5 M) of **S3** (50 mg, 0.256 mmol) at 0 °C, the mixture was warmed up to room temperature and stirred for 16 hours. The mixture was concentrated under reduced pressure to remove methanol solvent, the residue was diluted with H_2O (5 mL) then extracted with DCM (15 mL × 3). The organic layers were combined, dried over $MgSO_4$, filtered, and concentrated under reduced pressure to give the residue. The residue was purified by column chromatography on silica gel, eluting with 5% v/v EtOAc in hexane (EA/Hex 25%, R_f = 0.70) to give **S4** as colorless oil (51.1 mg, 0.244 mmol, 95% yield).
^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ = 7.94 (dd, *J* = 8.5, 1.5 Hz, 1H), 7.53 (ddd, *J* = 7.5, 7.5, 1.5 Hz, 1H), 7.42-7.36 (m, 2H), 3.67 (s, 3H), 3.23 (t, *J* = 7.5 Hz, 2H), 2.73 (t, *J* = 7.5 Hz, 2H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, ppm) δ = 172.8, 149.3, 135.6, 133.2, 132.1, 127.6, 124.9, 51.7, 34.6, 28.4; IR (KBr, cm^{-1}): 2952, 2360, 1735, 1609, 1525, 1437, 1347, 1289, 1261, 1197, 1169, 1080, 1053, 984, 858, 787, 746, 709. HRMS (EI$^+$) calcd. *m/z* for $C_{10}H_{11}O_4N^+$: 209.0688, found: 209.0685.

2,2,2-Trifluoroethyl 3-(2-nitrophenyl)propanoate (S5)



According to the General Esterification Procedure, **S3** (300 mg, 1.537 mmol), 2,2,2-trifluoroethan-1-ol (178.5 mg, 1.84 mmol), EDC·HCl (352.7 mg, 1.84 mmol), DIPEA (until the solid salt completely dissolved), and DMAP (cat.) was dissolved in DCM. The residue was purified by column chromatography on silica gel, eluting with 5% v/v EtOAc in hexane (EA/Hex 10%, R_f = 0.70) to give **S5** as yellow oil (332 mg, 1.20 mmol, 78% yield).
^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ = 7.97 (dd, *J* = 8.5, 1.5 Hz, 1H), 7.55 (ddd, *J* = 7.5, 7.5, 1.0 Hz, 1H), 7.42-7.39 (m, 2H), 4.46 (q, $^2J_{H\text{-}F}$ = 8.5 Hz, 2H), 3.26 (t, *J* = 7.5 Hz, 2H), 2.86 (t, *J* = 7.5 Hz, 2H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, ppm) δ = 170.9, 149.3, 135.3, 135.1, 132.3, 128.1, 125.2, 122.8 (q, $^1J_{C\text{-}F}$ = 275.0 Hz), 60.4 (q, $^2J_{C\text{-}F}$ = 36.3 Hz), 24.4, 28.4; IR (KBr, cm^{-1}): 2974, 1759, 1612, 1531, 1415, 1348, 1278, 1155, 1065, 977, 857, 788, 747, 703, 665; HRMS (EI$^+$) calcd. *m/z* for $C_{11}H_{10}F_3O_4N^+$: 277.0562, found: 277.0560.

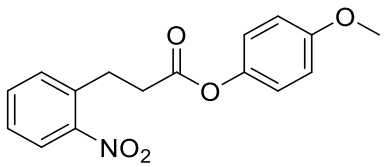
Mesityl 3-(2-nitrophenyl)propanoate (S6)



According to the General Esterification Procedure, **S3** (500 mg, 2.563 mmol), 2,4,6-trimethylphenol (384 mg, 2.82 mmol), EDC·HCl (540 mg, 2.82 mmol), DIPEA (until the solid salt completely dissolved), and DMAP (cat.) was dissolved in DCM. The residue was purified by column chromatography on silica gel, eluting with 5% v/v EtOAc in hexane (EA/Hex 15%, R_f = 0.63) to give **S6** as white solid (240.4 mg, 0.767 mmol, 30% yield)**.**

^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ = 8.00 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.57 (ddd, *J* = 7.5, 7.5, 1.5 Hz, 1H), 7.49 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.41 (ddd, *J* = 7.5, 7.5, 1.5 Hz, 1H), 6.85 (s, 2H), 3.37 (t, *J* = 7.5 Hz, 2H), 3.03 (t, *J* = 7.5 Hz, 2H), 2.25 (s, 3H), 2.02 (s, 6H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, ppm) δ = 170.7, 149.5, 146.0, 135.6, 133.5, 132.7, 129.8, 129.4, 128.0, 125.3, 34.6, 28.7, 20.9, 16.4; IR (KBr, cm^{-1}): 2921, 1755, 1519, 1346, 1312, 1286, 1195, 1138, 1037, 856, 789, 754, 703, 703, 665; HRMS (EI^+) calcd. *m/z* for $C_{18}H_{19}O_4N^+$:313.1309; found: 313.1308.

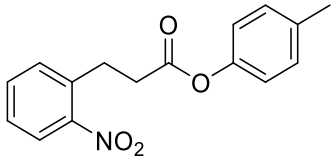
4-Methoxyphenyl 3-(2-nitrophenyl)propanoate (S7)



According to the General Esterification Procedure, **S3** (500 mg, 2.563 mmol), 4-methoxyphenol (476 mg, 3.834 mmol), EDC·HCl (590 mg, 3.08 mmol), DIPEA (until the solid salt completely dissolved), and DMAP (cat.) was dissolved in DCM. The residue was purified by column chromatography on silica gel, eluting with 20% v/v EtOAc in hexane (R_f = 0.4) to give **S7** as yellow solid (753.4 mg, 2.501 mmol, 98% yield)**.**

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ = 7.99 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.56 (ddd, *J* = 8.9, 7.5, 1.4 Hz, 1H), 7.48 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.41 (ddd, *J* = 8.4, 7.3, 1.6 Hz, 1H), 6.97-6.93 (m, 2H), 6.89-6.85 (m, 2H), 3.79 (s, 3H), 3.34 (t, *J* = 7.4 Hz, 2H), 2.98 (t, *J* = 7.4 Hz, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, ppm) δ = 171.4, 157.4, 149.3, 144.1, 135.4, 133.4, 132.5, 127.9, 125.1, 122.3, 114.5, 55.7, 34.9, 28.6; IR (KBr, cm^{-1}): 2952, 2360, 1735, 1610, 1526, 1437, 1347, 1289, 1197, 1169, 858, 787, 746, 709; HRMS (ESI^+) Calc. for $(C_{16}H_{15}O_5N+H)^+$: 302.1023, found: 302.1021.

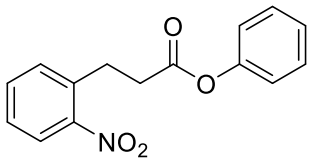
***p*-Tolyl 3-(2-nitrophenyl)propanoate (S8)**



According to the General Esterification Procedure, **S3** (300 mg, 1.537 mmol), *p*-cresol (166 mg, 1.54 mmol), EDC·HCl (324 mg, 1.69 mmol), DIPEA (until the solid salt completely dissolved), and DMAP (cat.) was dissolved in DCM. The residue was purified by column chromatography on silica gel, eluting with 10% v/v EtOAc in hexane (EA/Hex 15%, R_f = 0.45) to give **S8** as yellow oil (315.7 mg, 1.106 mmol, 72% yield)**.**

^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ = 7.99 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.58-7.55 (m, 1H), 7.47 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.42-7.4 (m, 1H), 7.17-6.90 (m, 4H), 3.34 (t, *J* = 7.0 Hz, 2H), 2.99 (t, *J* = 7.0 Hz, 2H), 2.35 (s, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, ppm) δ = 171.4, 149.5, 148.5, 135.8, 135.6, 133.5, 132.6, 130.1, 128.0, 125.3, 121.3, 35.1, 28.7, 21.1; IR (KBr, cm^{-1}): 2963.3, 2358.4, 1749.7, 1522.25, 1505, 1343.9, 1260.7, 1196.9, 1127.3, 1096.7, 1018.3, 800.83, 739.9, 700.7; HRMS (EI$^+$) calc'd *m/z* for $C_{16}H_{15}O_4N^+$: 285.0996, found: 285.0997.

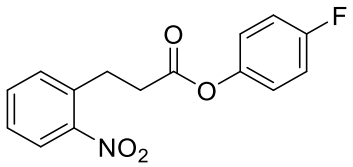
Phenyl 3-(2-nitrophenyl)propanoate (S9)



According to the General Esterification Procedure, **S3** (300 mg, 1.537 mmol), phenol (173.2 mg, 1.840 mmol), EDC·HCl (352.7 mg, 1.839 mmol), DIPEA (until the solid salt completely dissolved), and DMAP (cat.) was dissolved in DCM. The residue was purified by column chromatography on silica gel, eluting with 10% v/v EtOAc in hexane (EA/Hex 15%, R_f = 0.50) to give **S9** as a white solid (360.6 mg, 1.329 mmol, 86% yield).

^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ = 7.99 (dd, *J* = 8.5, 1.5 Hz, 1H), 7.57 (ddd, *J* = 7.5, 7.5, 1.5 Hz, 1H), 7.48 (dd, *J* = 7.5, 1.0 Hz, 1H), 7.44-7.40 (m, 1H), 7.39-7.35 (m, 2H), 7.24-7.21 (m, 1H), 7.05-7.02 (m, 2H), 3.35 (t, *J* = 7.5 Hz, 2H), 3.01 (t, *J* = 7.5 Hz, 2H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, ppm) δ = 171.1, 150.7, 149.4, 135.5, 133.5, 132.6, 129.6, 128.0, 126.0, 125.2, 121.6, 35.0, 28.6; IR (KBr, cm^{-1}): 2963, 2926, 2365, 1750, 1513, 1340, 1261, 1191, 1096, 1023, 861, 799, 689, 496; HRMS (EI$^+$) calcd. *m/z* for $C_{15}H_{13}O_4N^+$: 271.0845, found: 271.0845.

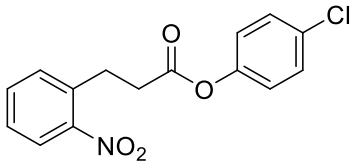
4-Fluorophenyl 3-(2-nitrophenyl)propanoate (S10)



According to the General Esterification Procedure, **S3** (400 mg, 2.049 mmol), 4-fluorophenol (230 mg, 2.052 mmol), EDC·HCl (430 mg, 2.24 mmol), DIPEA (until the solid salt completely dissolved), and DMAP (cat.) was dissolved in DCM. The residue was purified by column chromatography on silica gel, eluting with 10% v/v EtOAc in hexane (EA/Hex 15%, R_f = 0.45) to give **S10** as yellow oil (544 mg, 1.881 mmol, 92% yield)**.**

^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ = 8.00 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.57 (ddd, *J* = 7.5, 7.5, 1.5 Hz, 1H), 4.47 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.42 (ddd, *J* = 7.0, 7.0 1.5 Hz, 1H), 7.06-6.99 (m, 4H), 3.34 (t, *J* = 7.5 Hz, 2H), 2.99 (t, *J* = 7.5 Hz, 2H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, ppm) δ = 171.2, 160.5 (d, $^1J_{C\text{-}F}$ = 242.5 Hz), 149.5, 146.6, 135.4, 133.6, 132.6, 128.1, 125.3, 123.1 (d, $^3J_{C\text{-}F}$ = 8.8 Hz), 116.3 (d, $^2J_{C\text{-}F}$ = 22.5 Hz), 35.0, 28.7; IR (KBr, cm^{-1}):2963.5, 2918.8, 2358.5, 2330.5, 1751.0, 1499.3, 1342.6, 1260.4, 1183.2, 1093.7, 1019.4, 798.8; HRMS (EI$^+$) calc'd *m/z* for $C_{15}H_{12}O_4NF^+$: 289.0745, found: 289.0744.

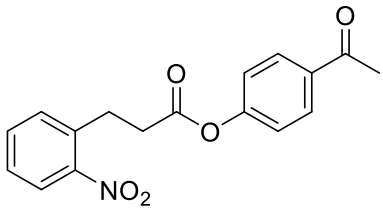
4-Chlorophenyl 3-(2-nitrophenyl)propanoate (S11)



According to the General Esterification Procedure, **S3** (500 mg, 2.562 mmol), 4-chlorophenol (363.8 mg, 2.830 mmol), EDC·HCl (542.5 mg, 2.830 mmol), DIPEA (until the solid salt completely dissolved), and DMAP (cat.) was dissolved in DCM. The residue was purified by column chromatography on silica gel, eluting with 10% v/v EtOAc in hexane (EA/Hex 25%, R_f = 0.55) to give **S11** yellow oil (274 mg, 0.896 mmol, 35% yield)**.**

^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ = 8.02 (dd, *J* = 8.5, 1.5 Hz, 1H), 7.57 (ddd, *J* = 7.5, 7.5, 1.5 Hz, 1H), 7.47 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.42 (ddd, *J* = 7.0, 7.0, 1.5 Hz, 1H), 7.34-7.31 (m, 2H), 7.00-7.97 (m, 2H), 3.33 (t, *J* = 7.5 Hz, 2H), 2.99 (t, *J* = 7.5 Hz, 2H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, ppm) δ = 170.9, 149.5, 149.2, 135.4, 133.6, 132.6, 131.5, 129.7, 128.1, 125.3, 123.1, 35.1, 28.7; IR (KBr, cm^{-1}): 2920, 1754, 1487, 1345, 1261, 1199, 1085, 1014, 801, 728, 503; HRMS (EI$^+$) calc'd *m/z* for $C_{15}H_{12}NO_4Cl^+$: 305.0449, found: 305.0446.

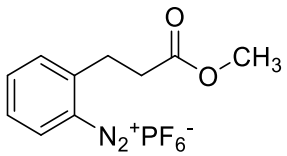
4-Acetylphenyl 3-(2-nitrophenyl)propanoate (S12)



According to the General Esterification Procedure, **S3** (500 mg, 2.562 mmol), 1-(4-hydroxyphenyl)ethan-1-one (384 mg, 2.820 mmol), EDC·HCl (540 mg, 2.820 mmol), DIPEA (until the solid salt completely dissolved), and DMAP (cat.) was dissolved in DCM. The residue was purified by column chromatography on silica gel, eluting with 25% v/v EtOAc in hexane (R_f = 0.38) to give **S12** as yellow oil (789 mg, 2.51 mmol, 98% yield).

^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ = 8.02-7.97 (m, 3H), 7.58 (ddd, *J* = 7.5, 7.5, 1.5 Hz, 1H), 7.47 (dd, *J* = 7.5, 1.5 Hz, 2H), 7.43 (ddd, *J* = 7.5, 7.5, 1.5 Hz, 2H), 3.35 (t, *J* = 7.5 Hz, 2H), 3.03 (t, *J* = 7.5 Hz, 2H), 2.60 (s, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, ppm) δ = 197.0, 170.6, 154.4, 149.5, 135.3, 135.0, 133.6, 132.6, 130.2, 128.2, 125.4, 121.9, 33.2, 28.7, 26.8; IR (KBr, cm^{-1}): 3064, 2964, 1754, 1681, 1521, 1429, 1348, 1261, 1200, 1094, 1017, 799, 741, 591; HRMS (EI^+) calc'd *m/z* for $C_{17}H_{15}O_5N^+$: 313.0945; found: 313.0943.

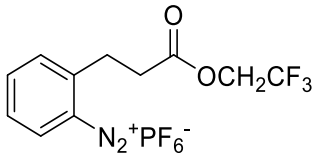
2-(3-Methoxy-3-oxopropyl)benzenediazonium hexafluorophosphate (V) (D1)



According to the General Hydrogenation and Diazotization Procedure, nitrobenzene **S4** (304 mg, 1.453 mmol) was used to afford the diazonium salt **D1** as white solid (366.0 mg, 1.089 mmol, 75% yield).

^{1}H NMR (400 MHz, CD_3CN, ppm) δ = 8.38 (d, *J* = 8.0 Hz, 1H), 8.17 (dd, *J* = 8.0, 7.6 Hz, 1H), 7.82(d, *J* = 8.0 Hz, 1H), 7.76 (dd, *J* = 8.0, 7.6 Hz, 1H), 3.61 (s, 3H), 3.23 (t, *J* = 6.4 Hz, 2H), 2.86(t, *J* = 6.4 Hz, 2H); ^{31}P{^{1}H} NMR (202.5 MHz, CD_3CN, ppm) δ = -145.0 (sept, $J_{P\text{-}F}$ = 704.7 Hz); HRMS (ESI^+) *m/z* calc'd for $C_{10}H_{11}N_2O_2$ $[M\text{-}PF_6]^+$ = 191.0815, found: 191.0815. (The compound was not stable for the long time ^{13}C-NMR acquisition.)

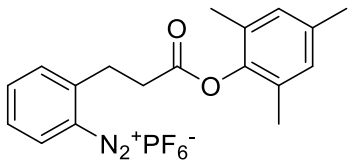
2-(3-Oxo-3-(2,2,2-trifluoroethoxy)propyl)benzenediazonium hexafluorophosphate (V) (D2)



According to the General Hydrogenation and Diazotization Procedure, nitrobenzene **S5** (100 mg, 0.361 mmol) was used to afford the diazonium salt **D2** as white solid (105.6 mg, 0.261mmol, 72% yield).

^{1}H NMR (400 MHz, CD_3OD, ppm) δ = 8.60 (dd, *J* = 8.0, 1.2 Hz, 1H), 8.23 (ddd, *J* = 8.0, 8.0, 1.6 Hz, 1H), 7.96 (d, *J* = 8.0 Hz, 1H), 7.85 (dd, *J* = 8.0, 1.2 Hz, 1H), 4.63 (q, $J_{H\text{-}F}$ = 8.4 Hz, 2H) , 3.40 (t, *J* = 6.8 Hz, 2H), 3.11 (t, *J* = 6.8 H, 2H); ^{31}P{^{1}H} NMR (202.5 MHz, CD_3OD, ppm) δ = -145.0 (sept, $J_{P\text{-}F}$ = 708.8 Hz) HRMS (ESI^+) *m/z* calc'd for $C_{11}H_{10}F_3N_2O_2$ $[M\text{-}PF_6]^+$ = 259.0689, found: 259.0690. (The compound was not stable for the long time ^{13}C-NMR acquisition.)

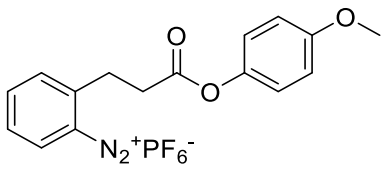
2-(3-(Mesityloxy)-3-oxopropyl)benzenediazonium hexafluorophosphate (V) (D3)



According to the General Hydrogenation and Diazotization Procedure, nitrobenzene **S6** (200 mg, 0.638 mmol) was used to afford the diazonium salt **D3** as white solid (216.0 mg, 0.491 mmol, 77% yield).

^{1}H NMR (400 MHz, CD_3OD, ppm) δ = 8.56 (dd, *J* = 8.4, 1.3 Hz, 1H), 8.25 (ddd, *J* = 7.9, 7.9, 1.4 Hz, 1H), 8.04 (dd, *J* = 7.9, 0.5 Hz, 1H), 7.84 (ddd, *J* = 8.4, 8.4, 0.9 Hz, 1H), 6.84 (s, 2H), 3.44 (t, *J* = 6.4 Hz, 2H), 3.31 (t, *J* = 6.4 Hz, 2H), 2.23 (s, 3H), 1.90 (s, 6H); ^{31}P NMR{^{1}H} (162 MHz, CD_3OD, ppm) δ = -144.6 (sept, $^{1}J_{P\text{-}F}$ = 712.8 Hz); HRMS (ESI^+) *m/z* calc'd for $C_{18}H_{19}N_2O_2$ $[M\text{-}PF_6]^+$ = 295.1441, found: 295.1442. (The compound was not stable for the long time ^{13}C-NMR acquisition.)

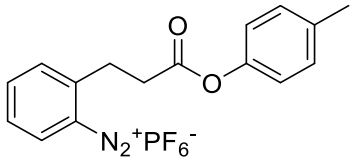
2-(3-(4-Methoxyphenoxy)-3-oxopropyl)benzenediazonium hexafluorophosphate (V) (D4)



According to the General Hydrogenation and Diazotization Procedure, nitrobenzene **S7** (200 mg, 0.664 mmol) was used to afford the diazonium salt **D4** as white solid (250 mg, 0.584 mmol, 88% yield).

^{1}H NMR (400 MHz, CD_3OD, ppm) δ = 8.57 (d, *J* = 8.3 Hz, 1H), 8.24 (dd, *J* = 8.3, 8.3 Hz, 1H), 8.00 (d, *J* = 8.0 Hz, 1H), 7.83 (dd, *J* = 8.0, 8.0 Hz, 1H), 6.98-6.95 (m, 2H), 6.91-6.89 (m, 2H), 3.78 (s, 3H), 3.42 (t, *J* = 6.6 Hz, 2H), 3.22 (t, *J* = 6.6 Hz, 2H); ^{31}P{^{1}H} NMR (162 MHz, CD_3OD, ppm) δ = -144.6 (sept, $^1J_{P\text{-}F}$ = 712.8 Hz); HRMS (ESI^+) *m/z* calc'd for $C_{16}H_{15}N_2O_2$ $[M\text{-}PF_6]^+$ = 283.1077, found: 283.1076. (The compound was not stable for the long time ^{13}C-NMR acquisition.)

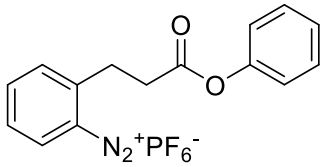
2-(3-Oxo-3-(*p*-tolyloxy)propyl)benzenediazonium hexafluorophosphate (V) (D5)



According to the General Hydrogenation and Diazotization Procedure, nitrobenzene **S8** (234 mg, 0.820 mmol) was used to afford the diazonium salt **D5** as white solid (135.0 mg, 0.328 mmol, 40% yield).

^{1}H NMR (400 MHz, CD_3OD, ppm) δ = 8.56 (dd, *J* = 8.3, 1.0 Hz, 1H), 8.24 (ddd, *J* = 7.8, 7.8, 1.3 Hz, 1H), 8.00 (dd, *J* = 7.8, 1.1 Hz, 1H), 7.83 (ddd, *J* = 8.6, 8.6, 1.2 Hz, 1H), 7.16 (d, *J* = 8.4 Hz, 2H), 6.91 (d, *J* = 8.4 Hz, 2H), 3.41 (t, *J* = 6.0 Hz, 2H), 3.22 (t, *J* = 6.0 Hz, 2H), 2.22 (s, 3H); ^{31}P{^{1}H} NMR (162 MHz, CD_3OD, ppm) δ = -144.6 (sept, $^1J_{P\text{-}F}$ = 712.8 Hz); HRMS (ESI^+) *m/z* calc'd for $C_{16}H_{15}N_2O_2$ $[M\text{-}PF_6]^+$ = 267.1128, found: 267.1130. (The compound was not stable for the long time ^{13}C-NMR acquisition.)

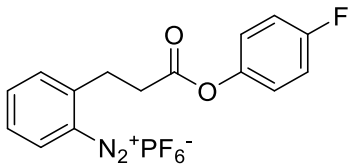
2-(3-Oxo-3-phenoxypropyl)benzenediazonium hexafluorophosphate (V) (D6)



According to the General Hydrogenation and Diazotization Procedure, nitrobenzene **S9** (465.3 mg, 1.715 mmol) was used to afford the diazonium salt **D6** as white solid (627 mg, 1.574 mmol, 92% yield).

^{1}H NMR (400 MHz, CD_3OD, ppm) δ = 8.60 (dd, *J* = 8.4, 1.2 Hz, 1H), 8.28 (ddd, *J* = 7.9, 7.9, 1.3 Hz, 1H), 8.04 (dd, *J* = 8.0, 0.6 Hz, 1H), 7.87 (ddd, *J* = 8.5, 8.5, 1.2 Hz, 1H), 7.43-7.38 (m, 2H), 7.27 (tt, *J* = 7.6, 1.2 Hz, 1H), 7.10-7.06 (m, 2H), 3.46 (t, *J* = 6.0 Hz, 2H), 3.28 (t, *J* = 6.0 Hz, 2H); ^{31}P{^{1}H} NMR (162 MHz, CD_3OD, ppm) δ = -144.6 (sept, $^{1}J_{P\text{-}F}$ = 712.8 Hz); HRMS (ESI+) m/z calc'd for $C_{15}H_{13}N_2O_2$ $[M\text{-}PF_6]^+$ = 253.0972, found 253.0972. (The compound was not stable for the long time ^{13}C-NMR acquisition.)

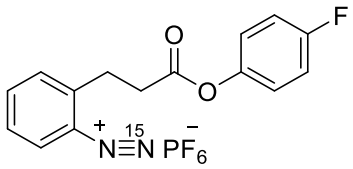
2-(3-(4-Fluorophenoxy)-3-oxopropyl)benzenediazonium hexafluorophosphate (V) (D7)



According to the General Hydrogenation and Diazotization Procedure, nitrobenzene **S10** (300 mg, 1.037 mmol) was used to afford the diazonium salt **D7** as white solid (370 mg, 0.889 mmol, 86% yield).

^{1}H NMR (400 MHz, CD_3OD, ppm) δ = 8.57 (dd, *J* = 8.5, 1.2 Hz, 1H), 8.23 (ddd, *J* = 8.6, 7.6, 1.2 Hz, 1H), 8.00 (dd, *J* = 8.1, 0.7 Hz, 1H), 7.84 (ddd, *J* = 7.9, 7.9, 1.3 Hz, 1H), 7.12-7.07 (m, 4H), 3.42 (t, *J* = 6.0 Hz, 2H), 3.24 (t, *J* = 6.0 Hz, 2H); ^{31}P{^{1}H} NMR (162 MHz, CD_3OD, ppm) δ = -144.6 (sept, $^{1}J_{P\text{-}F}$ = 712.8 Hz); IR (KBr, cm^{-1}): 2944, 2861, **2268**, 1748, 1503, 1293, 1186, 1143, 1062, 840, 760, 558, 482; HRMS (ESI+) m/z calc'd for $C_{15}H_{12}FN_2O_2$ $[M\text{-}PF_6]^+$ = 271.0877, found: 271.0879. (The compound was not stable for the long time ^{13}C-NMR acquisition.)

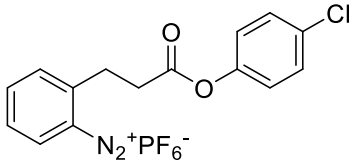
2-(3-(4-Fluorophenoxy)-3-oxopropyl)benzenediazonium hexafluorophosphate (V) (^{15}N-D7)



According to the General Hydrogenation and Diazotization Procedure, nitrobenzene **S10** (200 mg, 0.691 mmol) and **$Na^{15}NO_2$** was used to afford the diazonium salt **^{15}N-D7** as white solid (244 mg, 0.585 mmol, 85% yield).

^{1}H NMR (400 MHz, CD_3OD, ppm) δ = 8.57 (dd, *J* = 8.5, 1.2 Hz, 1H), 8.23 (ddd, *J* = 8.6, 7.6, 1.2 Hz, 1H), 8.00 (dd, *J* = 8.1, 0.7 Hz, 1H), 7.84 (ddd, *J* = 7.9, 7.9, 1.3 Hz, 1H), 7.12-7.07 (m, 4H), 3.42 (t, *J* = 6.0 Hz, 2H), 3.24 (t, *J* = 6.0 Hz, 2H); ^{31}P{^{1}H} NMR (162 MHz, CD_3OD, ppm) δ = -144.6 (sept, $^1J_{P\text{-}F}$ = 712.8 Hz); IR (KBr, cm^{-1}): 2944, 2861, **2236**, 1748, 1503, 1293, 1186, 1143, 1062, 834, 768, 558, 482; HRMS (ESI+) m/z calc'd for $C_{15}H_{12}FN^{15}NO_2$ $[M\text{-}PF_6]^+$ = 272.0848 found: 272.0842. (The compound was not stable for the long time ^{13}C-NMR acquisition.)

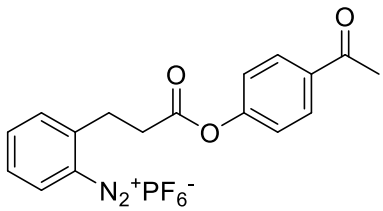
2-(3-(4-Chlorophenoxy)-3-oxopropyl)benzenediazonium hexafluorophosphate (V) (D8)



According to the General Hydrogenation and Diazotization Procedure, nitrobenzene **S11** (200 mg, 0.654 mmol) was used to afford the diazonium salt **D8** as white solid (218.0 mg, 0.504 mmol, 77% yield).

^{1}H NMR (400 MHz, CD_3OD, ppm) δ = 8.57 (dd, *J* = 8.4, 1.3 Hz, 1H), 8.23 (ddd, *J* = 7.8, 7.8, 1.3 Hz, 1H), 8.00 (dd, *J* = 8.0, 0.7 Hz, 1H), 7.83 (ddd, *J* = 8.6, 8.6, 1.1 Hz, 1H), 7.38-7.35 (m, 2H), 7.08-7.06 (m, 2H), 3.43 (d, *J* = 6.4 Hz, 2H), 3.25 (d, *J* = 6.4 Hz, 2H); ^{31}P{^{1}H} NMR (162 MHz, CD_3OD, ppm) δ = -144.6 (sept, $^1J_{P\text{-}F}$ = 712.8 Hz); HRMS (ESI^+) *m/z* calc'd for $C_{15}H_{12}ClN_2O_2$ $[M\text{-}PF_6]^+$ = 287.0582, found: 287.0581. (The compound was not stable for the long time ^{13}C-NMR acquisition.)

2-(3-(4-Acetylphenoxy)-3-oxopropyl)benzenediazonium hexafluorophosphate (V) (D9)

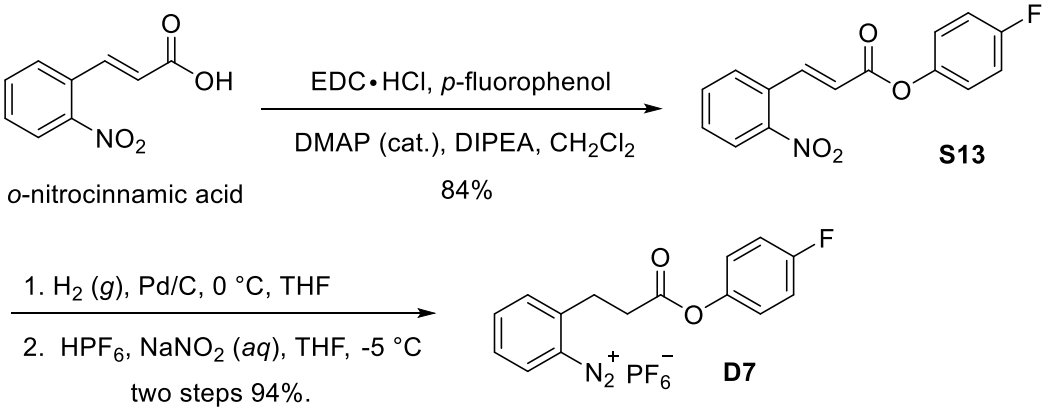


According to the General Hydrogenation and Diazotization Procedure, nitrobenzene **S12** (400 mg, 1.278 mmol) was used to afford the diazonium salt **D9** as white solid (269.0 mg, 0.611 mmol, 48% yield).

^{1}H NMR (400 MHz, CD_3OD, ppm) δ = 8.57 (dd, *J* = 8.4, 0.9 Hz, 1H), 8.24 (ddd, *J* = 7.8, 7.8, 1.2 Hz, 1H), 8.04-8.00 (m, 3H), 7.84 (ddd, *J* = 8.8, 8.8, 0.8 Hz, 1H), 7.23 (d, *J* = 8.8 Hz, 2H), 3.44 (t, *J* = 6.4 Hz, 2H), 3.28 (t, *J* = 6.4 Hz, 2H), 2.59 (s, 3H); ^{31}P{^{1}H} NMR (162 MHz, CD_3OD, ppm) δ = -144.6 (sept, $^1J_{P\text{-}F}$ = 712.8 Hz); HRMS (ESI+) m/z calc'd for $C_{17}H_{15}N_2O_3$ $[M\text{-}PF_6]^+$ = 295.1077, found: 295.1078. (The compound was not stable for the long time ^{13}C-NMR acquisition.)

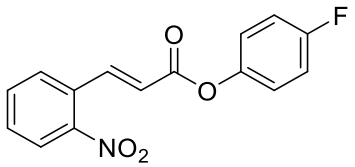
8.3 Concise Synthesis of the *N*-Transfer Reagent D7

Commercially available *o*-nitrocinnamic acid was used to synthesize the target *N*-transfer reagent **D7**. After the esterification with *p*-fluorophenol, continuous hydrogenation, and diazotization at low temperature, the white solid *N*-transfer reagent **D7** could be synthesized over a half gram in three steps with an overall 79% yield (Scheme S2).



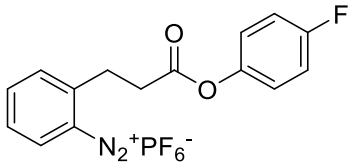
Scheme S2 Concise Synthesis of the *N*-Transfer Reagent **D7**.

4-Fluorophenyl (*E*)-3-(2-nitrophenyl)acrylate (S13)



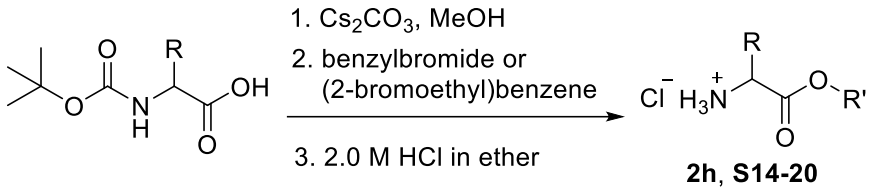
To the solution of *o*-nitrocinnamic acid (1.007 g, 5.213 mmol) in DCM (0.5 M, 10.4 mL) were added *p*-fluorophenol (570.1 mg, 5.086 mmol), EDC·HCl (1.491 g, 7.778 mmol), *N*,*N*-diisopropylethylamine (DIPEA, 5.224 mmol, 0.91 mL), and DMAP (83.2 mg, 0.681 mmol). The mixture was kept stirring at room temperature. Upon completion, the reaction was quenched with water. The organic and aqueous layers were separated, and the aqueous layer was extracted with DCM (30 mL x 3). The combined organic layers were extracted with 1 N NaOH (aq.) (20 mL x 3), dried over anhydrous $MgSO_4$, filtered, and then concentrated under reduced pressure to obtain a crude product. The residue was purified by column chromatography on silica gel, eluting with 50% DCM in hexane (R_f = 0.75) to give **S13** as white solid (1.234 g, 4.296 mmol, 84% yield).
^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ = 8.32 (d, *J* = 16.0 Hz, 1H), 8.09 (d, *J* = 8.0 Hz, 1H), 7.71-7.69 (m, 2H), 7.61-7.58 (m, 1H), 7.17-7.14 (m, 2H), 7.12-7.08 (m, 2H), 6.54 (d, *J* = 16.0 Hz, 1H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, ppm) δ = 164.4, 160.5 (d, $^1J_{C\text{-}F}$ = 242.5 Hz), 148.6, 146.6, 142.4, 133.9, 130.9, 130.5, 129.5, 125.3, 123.1 (d, $^3J_{C\text{-}F}$ = 28.0 Hz), 122.3, 116.3 (d, $^2J_{C\text{-}F}$ = 76.0 Hz); IR (KBr, cm^{-1}): 1733.0, 1731.9, 1633.6, 1515.9, 1345.5, 1293.0, 1186.2, 1139.9, 1090.9, 975.1, 859.6, 788.1, 751.8, 515.7; HRMS (EI^+) calc'd *m/z* for $C_{15}H_{10}NO_4F^+$:287.0588 found: 287.0591.

2-(3-(4-Fluorophenoxy)-3-oxopropyl)benzenediazonium hexafluorophosphate(V) (D7)



According to the General Hydrogenation and Diazotization Procedure, nitrobenzene **S13** (500 mg, 1742 mmol) was used to afford the diazonium salt **D7** as white solid (576 mg, 1.384 mmol, 79% yield).
^{1}H NMR (400 MHz, CD_3OD, ppm) δ = 8.57 (dd, *J* = 8.5, 1.2 Hz, 1H), 8.23 (ddd, *J* = 8.6, 7.6, 1.2 Hz, 1H), 8.00 (dd, *J* = 8.1, 0.7 Hz, 1H), 7.84 (ddd, *J* = 7.9, 7.9, 1.3 Hz, 1H), 7.12-7.07 (m, 4H), 3.42 (t, *J* = 6.0 Hz, 2H), 3.24 (t, *J* = 6.0 Hz, 2H); ^{31}P{^{1}H} NMR (162 MHz, CD_3OD, ppm) δ = -144.6 (sept, $^1J_{P\text{-}F}$ = 712.8 Hz); IR (KBr, cm^{-1}): 2944, 2861, 2268, 1748, 1503, 1293, 1186, 1143, 1062, 840, 760, 558, 482; HRMS (ESI+) m/z calc'd for $C_{15}H_{12}FN_2O_2$ $[M\text{-}PF_6]^+$ = 271.0877, found: 271.0879. (The compound was not stable for the long time ^{13}C-NMR acquisition.)

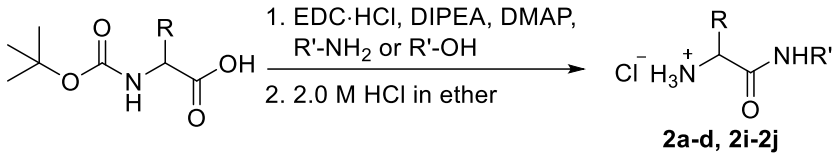
8.4 Synthetic Procedure for Various Ammonium Salts 2h, S14-S20[7]



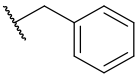
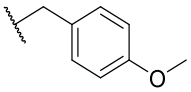
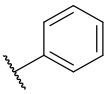
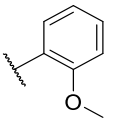
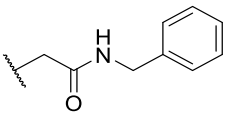
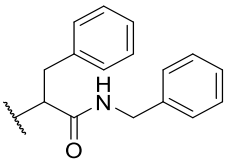
entry	Boc-amino acid	R-group	R'-group	product	yield
1 [a]	Boc-Gly (Glycine)	H–	-Bn	**2h**	78%
2 [a]	Boc-Gly (Glycine)	H–	-CH_2Bn	**S14**	78%
3 [a]	Boc-Ala (Alanine)	Me–	-CH_2Bn	**S15**	87%
4 [a]	Boc-Val (Valine)		-CH_2Bn	**S16**	84%
5 [a]	Boc-Leu (Leucine)		-CH_2Bn	**S17**	76%
6 [a]	Boc-Ile (Isoleucine)		-CH_2Bn	**S18**	65%
7 [a]	Boc-Met (Methionine)	S	-CH_2Bn	**S19**	73%
8 [a]	Boc-Phe (Phenylalanine)		-CH_2Bn	**S20**	81%

[a] Hydrochloride salt. [b] 2,2,2-trifluoroacetate salt; TFA in CH_2Cl_2 was used.

8.5 Synthetic Procedure for Various Ammonium Salts 2a-d, 2i-2j[8]

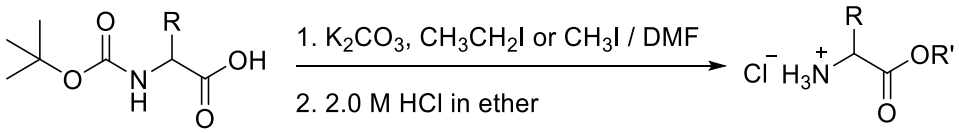


2a-d, 2i-2j

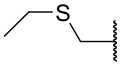
entry	Boc-amino acid	R-group	R'-group	product	yield
9 [b]	Boc-Gly (Glycine)	H		**2a**	55%
10 [b]	Boc-Gly (Glycine)	H		**2b**	37%
11 [a]	Boc-Gly (Glycine)	H		**2c**	54%
12 [c]	Boc-Gly (Glycine)	H		**2d**	75%
13 [a]	Boc-Gly (Glycine)	H		**2i**	30%
14 [a]	Boc-Gly (Glycine)	H		**2j**	44%

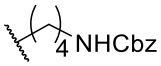
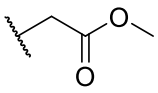
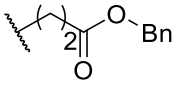
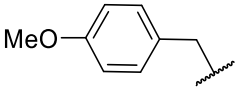
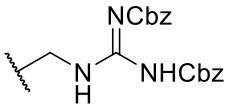
[a] Hydrochloride salt. [b] 2,2,2-trifluoroacetate salt; TFA in CH_2Cl_2 was used. [c] Use CDI as a coupling reagent rather than EDC·HCl.

8.6 Synthetic Procedure for Various Ammonium Salts S21, S24-S26, S28, S33, S34[9]



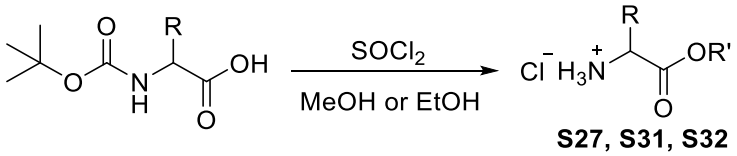
S21, S24-26, S28, S33, S34

entry	Boc-amino acid	R-group	R'-group	product	yield
15 [a]	Boc-Cys (Cysteine)		-Et	**S21**	21%

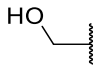
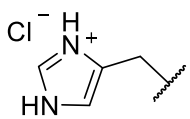
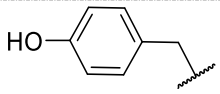
16[b]	Boc-Lys(cbz) (Lysine)		-Et	**S24**	99%
17[b]	Boc-Asp(OMe) (Aspartic acid)		-Et	**S25**	76%
18[b]	Boc-Glu(OBn) (Glutamic acid)		-Et	**S26**	30%
19[a]	Boc-Thr (Threonine)		-Et	**S28**	64%
20[a]	Boc-Tyr(OMe) (Tyrosine)		-Me	**S33**	63%
21[b]	Boc-Arg(Cbz)$_2$ (Arginine)		-Et	**S34**	99%

[a] Hydrochloride salt. [b] 2,2,2-trifluoroacetate salt; TFA in CH_2Cl_2 was used. [c] Without column chromatography.

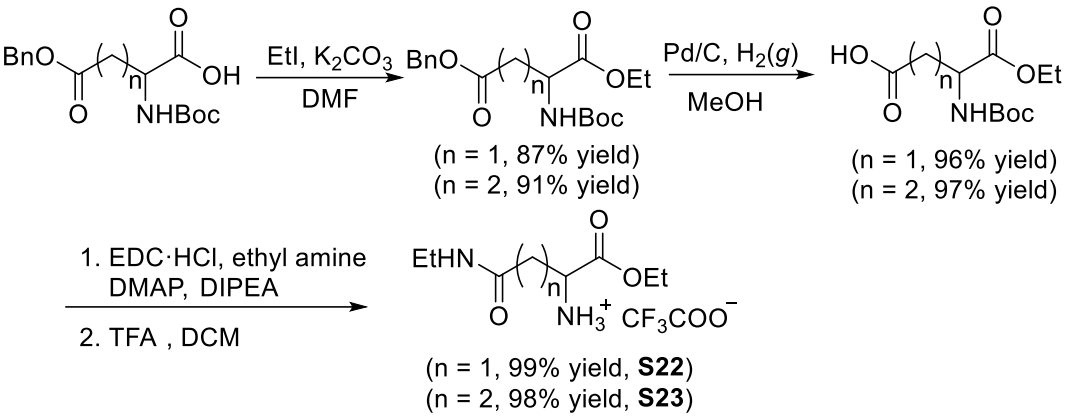
8.7 Synthetic Procedure for Various Ammonium Salts S27, S31-S32[10]



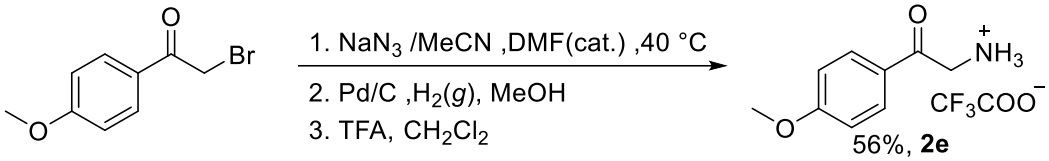
S27, S31, S32

entry	Boc-amino acid	R-group	R'-group	product	yield
23	Boc-Ser (Serine)		-Et	**S27**	95%
24	L-Histidine		-Me	**S31**	98%
22	Boc-Tyr (Tyrosine)		-Me	**S32**	94%

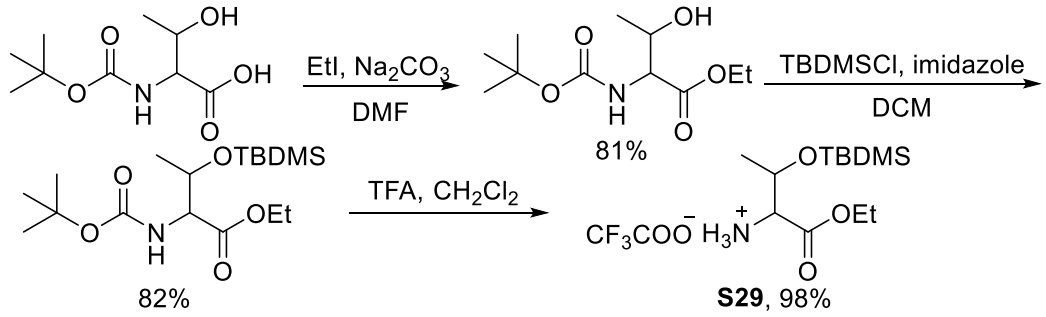
8.8 Synthetic Procedure for Various Ammonium Salts S22-S23 [8-9, 11]



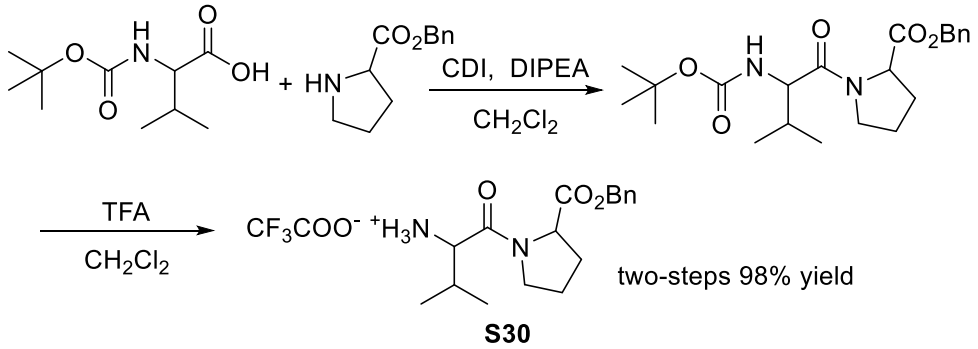
8.9 Synthetic Procedure for Compound 2e [12]



8.10 Synthetic Procedure for Compound S29 [9, 13]



8.11 Synthetic Procedure for Ammonium Trifluoroacetate Salt of Dipeptide NH_2-Val-Pro-OBn S30 [8]



8.12 **Synthetic Procedure for α-Diazo Compounds**

General Procedure A for Diazo Synthesis

Ammonium chloride salt (**1.0 or 1.2 eq.**) in mixture of THF and H_2O solution (v/v % = 20:1, 0.2 M) was added by K_2CO_3 (4.0 eq.) and diazonium salt **D7** (1.0 eq) at 0 °C. **After stirring for 15 minutes**, the solution was then warmed up to the room temperature. Until the reaction finished according to the thin layer chromatography (TLC) observation, the solution was quenched with H_2O and diluted with EtOAc. The mixture was extracted with EtOAc for three times. The organic layers were combined, dehydrated with NaCl (sat.), dried over $MgSO_4$, filtered, and concentrated under reduced pressure to give the crude residue. The residue was purified by column chromatography on silica gel, eluting with EtOAc in hexane or with DCM in hexane to obtain the desired diazo compound.

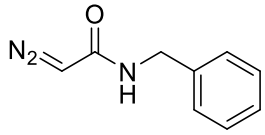
General Procedure B for Diazo Synthesis

Ammonium chloride salt (**1.2 eq.**) in mixture of THF and H_2O solution (v/v % = 20:1, 0.2 M) was added by K_2CO_3 (4.0 eq.) and diazonium salt **D7** (1.0 eq) at 0 °C. After stirring for **one hour**, the solution was then warmed up to the room temperature. Until the reaction finished according to the thin layer chromatography (TLC) observation, the solution was quenched with H_2O and diluted with EtOAc. The mixture was extracted with EtOAc for three times. The organic layers were combined, dehydrated with NaCl (sat.), dried over $MgSO_4$, filtered, and concentrated under reduced pressure to give the crude residue. The residue was purified by column chromatography on silica gel, eluting with EtOAc in hexane or with DCM in hexane to obtain the desired diazo compound.

General Procedure C for Diazo Synthesis

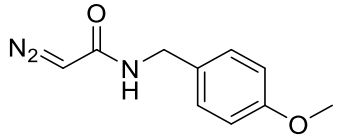
Ammonium chloride salt (**2.0 eq.**) in mixture of THF and H_2O solution (v/v % = 20:1, 0.2 M) was added by K_2CO_3 (4.0 eq.) and diazonium salt **D7** (1.0 eq) at 0 °C. **After stirring for 15 minutes**, the solution was then warmed up to the room temperature and **an extra amount of K_2CO_3 (1.0 eq.) was applied**. Until the reaction finished according to the thin layer chromatography (TLC) observation, the solution was quenched with H_2O and diluted with EtOAc. The mixture was extracted with EtOAc for three times. The organic layers were combined, dehydrated with NaCl (sat.), dried over $MgSO_4$, filtered, and concentrated under reduced pressure to give the crude residue. The residue was purified by column chromatography on silica gel, eluting with EtOAc in hexane or with DCM in hexane to obtain the desired diazo compound.

_N_-Benzyl-2-diazoacetamide (11a)



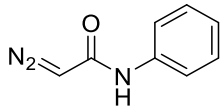
According to the General Procedure A for Diazo Synthesis, using diazonium salt **D7** (70 mg, 0.168 mmol), ammonium trifluoroacetate salt **2a** (70.4 mg, 0.252 mmol), K_2CO_3 (93 mg, 0.673 mmol), the reaction was completed in 4 hours. The residue was purified by column chromatography on silica gel, eluting with 25% v/v EtOAc in hexane (R_f = 0.50) to give **11a** as yellow solid (23.5 mg, 0.134 mmol, 80% yield).
^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ = 7.36-7.28 (m, 5H), 5.29 (br, 1H), 4.72 (s, 1H), 4.48 (d, *J* = 5.6 Hz, 2H). All spectroscopic data were in agreement with the literature values[14].

2-Diazo-_N_-(4-methoxybenzyl)acetamide (11b)



According to the General Procedure A for Diazo Synthesis, using diazonium salt **D7** (70 mg, 0.168 mmol), ammonium trifluoroacetate salt **2b** (63.9 mg, 0.207 mmol), K_2CO_3 (93.3 mg, 0.673 mmol), the reaction was completed in 3.5 hours. The residue was purified by column chromatography on silica gel, eluting with 25% v/v EtOAc in hexane (R_f = 0.50) to give **11b** as yellow oil (31.2 mg, 0.152 mmol, 91% yield).
^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ = 7.21 (ddd, *J* = 8.6, 2.9, 2.0 Hz, 2H), 6.86 (ddd, *J* = 8.6, 3.0, 2.2 Hz, 2H), 5.33 (br, 1H), 4.71(s, 1H), 4.39 (d, *J* = 5.5 Hz, 2H), 3.79 (s, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, ppm) δ = 165.4, 159.2, 130.5, 129.3, 114.3, 55.5, 47.3, 43.7; IR (KBr, cm^{-1}): 3244, 3070, 2104, 1600, 1373, 1345, 1243, 1227, 1028, 816, 707, 565; HRMS (EI^+) calc'd *m/z* for $C_{10}H_{11}O_2N_3^+$: 205.0849, found: 205.0846.

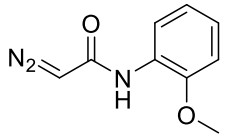
2-Diazo-_N_-phenylacetamide (11c)



According to the General Procedure A for Diazo Synthesis, using diazonium salt **D7** (70 mg, 0.168 mmol), ammonium chloride salt **2c** (37.7 mg, 0.202 mmol), K_2CO_3 (93 mg, 0.673 mmol), the reaction was completed in 2 hours. The residue was purified by column chromatography on silica gel, eluting with 35% v/v EtOAc in hexane (R_f = 0.48) to give **11c** as yellow solid (21.3 mg, 0.132 mmol, 79% yield).

^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ = 7.41 (d, *J* = 7.5 Hz, 2H), 7.32 (dd, *J* = 8.0, 8.0 Hz, 2H), 7.12 (dd, *J* = 8.0, 8.0 Hz, 1H), 6.78 (br, 1H), 4.89 (s, 1H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, ppm) δ = 138.0, 129.3, 124.7, 48.6; IR (KBr, cm^{-1}): 3087, 1353, 2095, 1603, 1443, 1372, 1316, 1258, 1189, 1014, 797, 750, 723, 692, 512; HRMS (EI^+) calc'd *m/z* for $C_8H_7N_3O^+$: 161.0586, found: 161.0584.

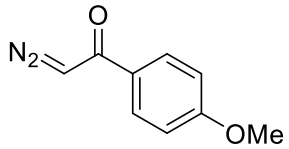
2-Diazo-*N*-(2-methoxyphenyl)acetamide (11d)



According to the General Procedure A for Diazo Synthesis, using diazonium salt **D7** (70 mg, 0.168 mmol), amine **2d** (36.4 mg, 0.202 mmol), K_2CO_3 (93 mg, 0.673 mmol), the reaction was completed in 3 hours. The residue was purified by column chromatography on silica gel, eluting with 35% v/v EtOAc in hexane (R_f = 0.48) to give **11d** as yellow solid (22.6 mg, 0.118 mmol, 70% yield).

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ = 8.28 (d, br, *J* = 7.6 Hz, 1H), 7.34 (br, 1H), 7.02 (ddd, *J* = 7.6, 7.6, 1.6 Hz, 1H), 6.95 (ddd, *J* = 7.6, 7.6, 1.6 Hz, 1H), 6.86 (dd, *J* =8.0, 1.2 Hz, 1H), 4.96 (s, 1H), 3.86, (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, ppm) δ = 163.5, 148.0, 128.1, 123.6, 121.3, 120.1, 110.1, 55.8, 48.9; IR (KBr, cm^{-1}): 3290, 3091, 2102, 1599, 1538, 1487, 1462, 1435, 1372, 1256, 1224, 1177, 1028, 802, 748; HRMS (EI^+) calc'd *m/z* for $C_9H_9N_3O_2^+$: 191.0690, found: 191.0689.

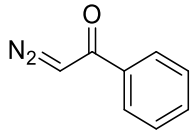
2-Diazo-1-(4-methoxyphenyl)ethan-1-one (11e)



According to the General Procedure A for Diazo Synthesis, using diazonium salt **D7** (70 mg, 0.168 mmol), ammonium trifluoroacetate salt **2e** (56.7 mg, 0.203 mmol), K_2CO_3 (93.3 mg, 0.675 mmol), the reaction was completed in 5 hours. The residue was purified by column chromatography on silica gel, eluting with 25% v/v EtOAc in hexane (R_f = 0.50) to give **11e** as yellow solid (24.7 mg, 0.140 mmol, 83% yield).

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ = 7.74-7.72 (m, 2H), 6.92-6.91 (m, 2H), 5.84 (s, 1H), 3.85 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, ppm) δ = 185.3, 163.4, 129.7, 128.9, 113.9, 55.6, 53.6; IR (KBr, cm^{-1}): 3100, 2964, 2115, 1613, 1372, 1262, 1184, 1021, 844, 792, 7556, 685; HRMS (EI^+) calc'd *m/z* for $C_9H_8N_2O_2^+$: 176.0578, found: 176.0580.

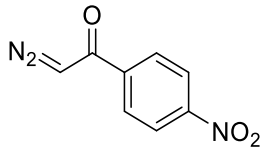
2-Diazo-1-phenylethan-1-one (11f)



According to the General Procedure A for Diazo Synthesis, using diazonium salt **D7** (70 mg, 0.168 mmol), commercially available 2-aminoacetophenone hydrochloride (34.6 mg, 0.202 mmol), K_2CO_3 (93 mg, 0.673 mmol), the reaction was completed in 4.5 hours. The residue was purified by column chromatography on silica gel, eluting with 15% v/v EtOAc in hexane (R_f = 0.45) to give **11f** as yellow oil (16.1 mg, 0.110 mmol, 66% yield).

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ = 7.78-7.75 (m, 2H), 7.58-7.53 (m, 1H), 7.48-7.43(m, 2H), 5.91 (s, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, ppm) δ = 186.3, 136.7, 132.7, 128.6, 126.7, 54.1; IR (KBr, cm^{-1}): 3068, 2963, 2924, 2105, 1609, 1574, 1364, 1261, 1092, 1068, 1017, 800, 698; HRMS (EI^+) *m/z* calc'd for $C_8H_6ON_2^+$: 146.0480, found: 146.0477.

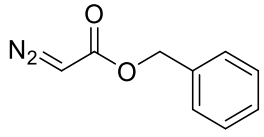
2-diazo-1-(4-nitrophenyl)ethan-1-one(11g)



According to the General Procedure A for Diazo Synthesis, using diazonium salt **D7** (70 mg, 0.168 mmol), (4-nitrophenyl)-2-oxoethan-1-aminium 4-methylbenzene sulfonate (71.1 mg, 0.202 mmol), K_2CO_3 (93 mg, 0.673 mmol), the reaction was completed in 14 hours. The residue was purified by column chromatography on silica gel, eluting with 20% v/v EtOAc in hexane (R_f = 0.25) to give **11g** as yellow solid (11.9 mg, 0.062 mmol, 37% yield).

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ = 8.31 (ddd, *J* =9.0, 4.1, 2.2 Hz, 2H), 7.92 (ddd, *J* =9.3, 4.4, 2.4 Hz, 2H), 5.95 (br, 1H). All spectroscopic data were in agreement with the literature values[15].

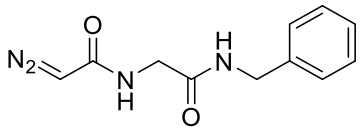
Benzyl 2-diazoacetate (11h)



According to the General Procedure A for Diazo Synthesis, using diazonium salt **D7** (70 mg, 0.168 mmol), ammonium chloride salt **2h** (41 mg, 0.202 mmol), K_2CO_3 (93.0 mg, 0.673 mmol), the reaction was completed in 4 hours. The residue was purified by

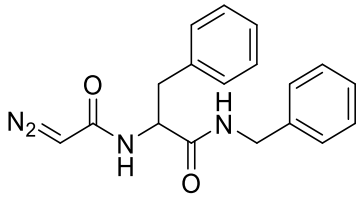
column chromatography on silica gel, eluting with 15% v/v EtOAc in hexane (R_f = 0.70) to give **11h** as yellow solid (21.1 mg, 0.120 mmol, 71% yield).
^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ = 7.38-7.33 (m, 5H), 5.20 (s, 2H), 4.79 (br, 1H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$, ppm) δ = 136.1, 128.8, 128.5, 128.4, 66.7, 46.6; HRMS (EI^+) calc'd *m/z* for $C_9H_8N_2O_2^+$: 176.0580, found: 176.0584. All spectroscopic data were in agreement with the literature values[16]

***N*-Benzyl-2-(2-diazoacetamido)acetamide (11i)**



According to the General Procedure A for Diazo Synthesis, using diazonium salt **D7** (70 mg, 0.168 mmol), ammonium chloride salt **2i** (48 mg, 0.186 mmol), K_2CO_3 (93 mg, 0.673 mmol), the reaction was completed in 3 hours. The residue was purified by column chromatography on silica gel, eluting with 5% v/v MeOH in DCM (R_f = 0.35) to give **11i** (31.6 mg, 0.136 mmol, 81% yield).
^{1}H NMR (500 MHz, CD_3OD, ppm) δ = 7.32-7.23 (m, 4H), 7.23-7.21 (m, 1H), 5.23 (s, 1H), 4.39 (s, 2H), 3.92 (s, 2H); $^{13}C\{^1H\}$ NMR (125 MHz, CD_3OD, ppm) δ = 171.8, 169.2, 139.8, 129.5, 128.5, 128.2, 47.9, 44.0, 43.8; IR (KBr, cm^{-1}): 3272, 3092, 2927, 2100, 1670, 1621, 1564, 1424, 1378, 1248, 736, 697, 668, 614, 573; HRMS (EI^+) calc'd *m/z* for $C_{11}H_{12}N_4O_2^+$: 232.0955, found: 232.0958.

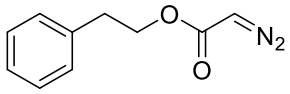
***N*-Benzyl-2-(2-diazoacetamido)-3-phenylpropanamide (11j)**



According to the General Procedure A for Diazo Synthesis, using diazonium salt **D7** (70 mg, 0.168 mmol), ammonium chloride salt **2j** (70.3 mg, 0.202 mmol), K_2CO_3 (93 mg, 0.673 mmol), the reaction was completed in 3.5 hours. The residue was purified by column chromatography on silica gel, eluting with 35% v/v EtOAc in hexane (R_f = 0.18) to give **11j** (45.6 mg, 0.141 mmol, 84% yield).
^{1}H NMR (500 MHz, CD_3OD, ppm) δ = 7.27-7.21 (m, 8H), 7.11 (d, *J* = 6.5 Hz, 2H), 5.19 (s, 1H), 4.67 (dd, *J* = 7.5, 7.5 Hz, 1H), 4.35, 4.26 (ABq, *J* = 15.0 Hz, 2H), 3.08, 2.92 (ABqd, *J* = 13.8, 7.2 Hz, 2H) ; $^{13}C\{^1H\}$ NMR (125 MHz, CD_3OD, ppm) δ = 173.5, 168.4, 139.5, 138.3, 130.3, 129.5, 129.4, 128.5, 128.1, 127.8, 56.6, 47.8, 44.0, 39.5; IR

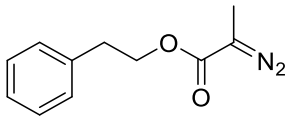
(KBr, cm^{-1}): 3281, 3104, 2103, 1655, 1611, 1543, 1390, 1375, 1235, 700; HRMS (EI^+) calc'd *m/z* for $C_{18}H_{18}N_4O_2^+$: 322.1425, found: 322.1424.

Phenethyl 2-diazoacetate (12)



According to the General Procedure A for Diazo Synthesis, using diazonium salt **D7** (70 mg, 0.168 mmol), ammonium chloride salt **S14** (43.4 mg, 0.202 mmol), K_2CO_3 (93 mg, 0.673 mmol), the reaction was completed in 6 hours. The residue was purified by column chromatography on silica gel, eluting with 60% v/v DCM in hexane (R_f = 0.65) to give **12** as yellow oil (25 mg, 0.131 mmol, 78% yield).
According to the General Procedure B for Diazo Synthesis, using diazonium salt **D7** (70 mg, 0.168 mmol), ammonium chloride salt **S14** (43.4 mg, 0.202 mmol), K_2CO_3 (93 mg, 0.673 mmol), the reaction was completed in 6 hours. The residue was purified by column chromatography on silica gel, eluting with 60% v/v DCM in hexane (R_f = 0.65) to give **12** as yellow oil (26.3 mg, 0.138 mmol, 84% yield).
^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ = 7.33-7.29 (m, 2H), 7.25-7.19 (m, 3H), 4.72 (br, 1H), 4.37 (t, *J* = 7.2 Hz, 2H), 2.96 (t, *J* = 7.2 Hz, 2H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$, ppm) δ = 137.8, 129.0, 128.6, 126.7, 65.4, 46.3, 35.4; HRMS (EI^+) calc'd *m/z* for $C_{10}H_{10}N_2O_2^+$: 190.0737; found: 190.0736. All spectroscopic data were in agreement with the literature values[17].

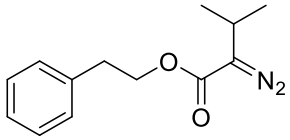
Phenethyl 2-diazopropanoate (13)



According to the General Procedure A for Diazo Synthesis, using diazonium salt **D7** (70 mg, 0.168 mmol), ammonium chloride salt **S15** (46.2 mg, 0.202 mmol), K_2CO_3 (93 mg, 0.673 mmol), the reaction was completed in 15 hours. The residue was purified by column chromatography on silica gel, eluting with 50% v/v DCM in hexane (R_f = 0.68) to give **13** as yellow oil (23.3 mg, 0.114 mmol, 68% yield).
According to the General Procedure B for Diazo Synthesis, using diazonium salt **D7** (70 mg, 0.168 mmol), ammonium chloride salt **S15** (46.2 mg, 0.202 mmol), K_2CO_3 (93 mg, 0.673 mmol), the reaction was completed in 14 hours. The residue was purified by column chromatography on silica gel, eluting with 50% v/v DCM in hexane (R_f = 0.68) to give **13** as yellow oil (24.6 mg, 0.121 mmol, 72% yield).

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ = 7.33- 7.29 (m, 2H), 7.25-7.19 (m, 3H), 4.36 (t, *J* = 6.8 Hz, 2H), 2.95 (t, *J* = 6.8 Hz, 2H), 1.94 (s, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$, ppm) δ = 138.0, 129.1, 128.6, 126.7, 65.5, 35.6, 8.5; IR (KBr, cm^{-1}): 3064, 3030, 2957, 2928, 2084, 1694, 1455, 1390, 1325, 1309, 1136, 1087, 1001, 848, 750, 735, 700, 633, 576, 527, 495; HRMS (EI^+) calc'd *m/z* for $C_{11}H_{12}N_2O_2^+$: 204.0893, found: 204.0892.

Phenethyl 2-diazo-3-methylbutanoate (14)

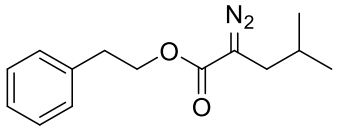


According to the General Procedure A for Diazo Synthesis, using diazonium salt **D7** (70 mg, 0.168 mmol), ammonium chloride salt **S16** (52 mg, 0.202 mmol), K_2CO_3 (93 mg, 0.673 mmol), the reaction was completed in 17 hours. The residue was purified by column chromatography on silica gel, eluting with 45% v/v DCM in hexane (R_f = 0.65) to give **14** as yellow oil (20.6 mg, 0.089 mmol, 53% yield).

According to the General Procedure B for Diazo Synthesis, using diazonium salt **D7** (70 mg, 0.168 mmol), ammonium chloride salt **S16** (52 mg, 0.202 mmol), K_2CO_3 (93 mg, 0.673 mmol), the reaction was completed in 18 hours. The residue was purified by column chromatography on silica gel, eluting with 45% v/v DCM in hexane (R_f = 0.65) to give **14** as yellow oil (30.2 mg, 0.130 mmol, 77% yield).

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ = 7.33- 7.28 (m, 2H), 7.25-7.20 (m, 3H), 4.36 (t, *J* = 6.8 Hz, 2H), 2.95 (t, *J* = 6.8 Hz, 2H), 2.72 (sept, *J* = 6.9 Hz, 1H), 1.12 (d, *J* = 6.8 Hz, 6H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$, ppm) δ = 138.0, 129.1 , 128.6, 126.7, 65.2, 35.6, 23.3, 20.6; IR (KBr, cm^{-1}): 3029, 2964, 2927, 2081, 1692, 1459, 1388, 1348, 1266, 1170, 1115, 1082, 741, 700; HRMS (EI^+) calc'd *m/z* for $C_{13}H_{16}N_2O_2^+$: 232.1206, found: 232.1204.

Phenethyl 2-diazo-4-methylpentanoate (15)



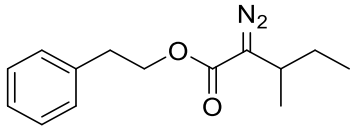
According to the General Procedure A for Diazo Synthesis, using diazonium salt **D7** (70 mg, 0.168 mmol), ammonium chloride salt **S17** (54.7 mg, 0.202 mmol), K_2CO_3 (93. mg, 0.673 mmol), the reaction was completed in 13 hours. The residue was purified by column chromatography on silica gel, eluting with 5% v/v EtOAc in hexane (R_f = 0.80) to give **15** as yellow oil (19.5 mg, 0.079 mmol, 47% yield).

According to the General Procedure B for Diazo Synthesis, using diazonium salt **D7** (70 mg, 0.168 mmol), ammonium chloride salt **S17** (54.7 mg, 0.202 mmol), K_2CO_3 (93.

mg, 0.673 mmol), the reaction was completed in 15 hours. The residue was purified by column chromatography on silica gel, eluting with 5% v/v EtOAc in hexane (R_f = 0.80) to give **15** as yellow oil (29.8 mg, 0.121 mmol, 72% yield).

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ = 7.32-7.27 (m, 2H), 7.25-7.20 (m, 3H), 4.36 (t, *J* = 7.0 Hz, 2H), 2.95 (t, *J* = 7.0 Hz, 2H), 2.13 (d, *J* = 7.1 Hz, 2H), 1.83 (nonet, *J* = 6.8 Hz, 1H), 0.93 (d, *J* = 6.7 Hz, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, ppm) δ = 138.0, 129.1, 128.6, 126.7, 65.3, 35.6, 32.3, 28.1, 22.0; IR (KBr, cm^{-1}): 3030, 2959, 2927, 2871, 2083, 1695, 1498, 1456, 1387, 1350, 1322, 1274, 1218, 1137, 1074, 974, 806, 740, 699; HRMS (EI^+) calc'd *m/z* for $C_{14}H_{18}N_2O_2^+$: 246.1363, found: 246.1360.

Phenethyl 2-diazo-3-methylpentanoate (16)

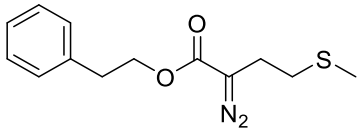


According to the General Procedure A for Diazo Synthesis, using diazonium salt **D7** (70 mg, 0.168 mmol), ammonium chloride salt **S18** (54.8 mg, 0.202 mmol), K_2CO_3 (93 mg, 0.673 mmol), the reaction was completed in 8 hours. The residue was purified by column chromatography on silica gel, eluting with 5% v/v EtOAc in hexane (R_f = 0.81) to give **16** as yellow oil (21.5 mg, 0.088 mmol, 52% yield).

According to the General Procedure B for Diazo Synthesis, using diazonium salt **D7** (70 mg, 0.168 mmol), ammonium chloride salt **S18** (54.8 mg, 0.202 mmol), K_2CO_3 (93 mg, 0.673 mmol), the reaction was completed in 15.5 hours. The residue was purified by column chromatography on silica gel, eluting with 5% v/v EtOAc in hexane (R_f = 0.81) to give **16** as yellow oil (30.2 mg, 0.123 mmol, 73% NMR yield).

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ = 7.32- 7.28 (m, 2H), 7.25-7.20 (m, 3H), 4.36 (t, *J* = 7.0 Hz, 2H), 2.95 (t, *J* = 7.0 Hz, 2H), 2.47 (sext. *J* = 7.0 Hz, 1H), 1.49-1.38 (m, 2H), 1.11 (d, *J* = 7.0 Hz, 3H), 0.91 (t, *J* = 7.4 Hz, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, ppm) δ = 138.0, 129.1, 128.6, 126.7, 65.2, 35.6, 30.0, 27.9, 18.2, 11.7; IR (KBr, cm^{-1}): 3029, 2963, 2927, 2854, 2079, 1692, 1498, 1459, 1384, 1354, 1284, 1164, 1092, 802, 741, 699, 494; HRMS (EI^+) calc'd *m/z* for $C_{14}H_{18}N_2O_2^+$: 246.1363, found: 246.1360.

Phenethyl 2-diazo-4-(methylthio)butanoate (17)



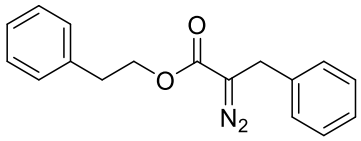
According to the General Procedure A for Diazo Synthesis, using diazonium salt **D7** (70 mg, 0.168 mmol), ammonium chloride salt **S19** (58.5 mg, 0.202 mmol), K_2CO_3 (93 mg, 0.673 mmol), the reaction was completed in 4 hours. The residue was purified by

column chromatography on silica gel, eluting with 15% v/v EtOAc in hexane (R_f = 0.75) to give **17** as yellow oil (22.7 mg, 0.086 mmol, 51% yield).

According to the General Procedure C for Diazo Synthesis, using diazonium salt **D7** (73.3 mg, 0.176 mmol), ammonium chloride salt **S19** (102.1 mg, 0.352 mmol), K_2CO_3 (121.6 mg, 0.880 mmol), the reaction was completed in 8 hours. The residue was purified by column chromatography on silica gel, eluting with 15% v/v EtOAc in hexane (R_f = 0.75) to give **17** as yellow oil (36 mg, 0.136 mmol, 77% yield).

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ = 7.33-7.28 (m, 2H), 7.25-7.19 (m, 3H), 4.37 (t, *J* = 6.9 Hz, 2H), 2.96 (t, *J* = 6.9 Hz, 2H), 2.70-2.60 (m, 2H), 2.60-2.54 (m, 2H), 2.11 (s, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, ppm) δ = 167.2, 137.9, 129.1, 128.6, 126.7, 65.5, 35.5, 33.0, 24.0, 15.5; IR (KBr, cm^{-1}): 2920, 2086, 1688, 1387, 1334, 1160, 1103, 739, 700; HRMS (EI$^+$) calc'd *m/z* for $C_{13}H_{16}N_2O_2S^+$: 264.0927, found: 264.0927.

Phenethyl 2-diazo-3-phenylpropanoate (18)

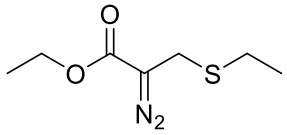


According to the General Procedure A for Diazo Synthesis, using diazonium salt **D7** (70 mg, 0.168 mmol), ammonium chloride salt **S20** (61.6 mg, 0.202 mmol), K_2CO_3 (93 mg, 0.673 mmol), the reaction was completed in 12 hours. The residue was purified by column chromatography on silica gel, eluting with 12.5% v/v EtOAc in hexane (R_f = 0.75) to give **18** as yellow oil (31.9 mg, 0.114 mmol, 67% yield).

According to the General Procedure C for Diazo Synthesis, using diazonium salt **D7** (70 mg, 0.168 mmol), ammonium chloride salt **S20** (103 mg, 0.336 mmol), K_2CO_3 (116 mg, 0.839 mmol), the reaction was completed in 12 hours. The residue was purified by column chromatography on silica gel, eluting with 15% v/v EtOAc in hexane (R_f = 0.75) to give **18** as yellow oil (37.9 mg, 0.135 mmol, 81% yield).

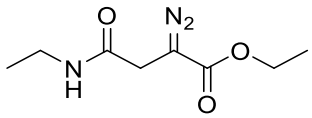
^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ = 7.33- 7.27 (m, 3H), 7.25-7.20 (m, 7H), 4.39 (t, *J* = 6.9 Hz, 2H), 3.60 (s, 2H), 2.95 (t, *J* = 6.9 Hz, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, ppm) δ = 137.9, 137.3, 129.1, 128.9, 128.6, 128.4, 127.2, 126.7, 65.5, 35.3, 29.4; IR (KBr, cm^{-1}): 3032, 2920, 2851, 2373, 2346, 2082, 1686, 1313, 1173, 1103, 735, 698, 572, 494; HRMS (EI$^+$) calc'd *m/z* for $C_{17}H_{16}N_2O_2^+$: 280.1206, found: 280.1203.

Ethyl 2-diazo-3-(ethylthio)propanoate (19)



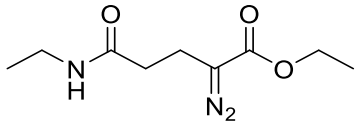
According to the General Procedure A for Diazo Synthesis, using diazonium salt **D7** (190.3 mg, 0.457 mmol), ammonium chloride salt **S21** (47.5 mg, 0.223 mmol), K_2CO_3 (8.1 eq., 251.4 mg, 1.819 mmol), the reaction was completed in 8 hours. The residue was purified by column chromatography on silica gel, eluting with 50% v/v DCM in hexane (R_f = 0.63) to give **19** as yellow oil (26.8 mg, 0.143 mmol, 64 % yield).
^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ = 4.24 (q, *J* = 7.1 Hz, 2H), 3.53 (s, 2H), 2.60 (q, *J* = 7.4 Hz, 2H), 1.26 (t, *J* = 7.2 Hz, 6H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, ppm) δ = 166.6, 61.2, 26.1, 25.8, 14.7, 14.6; IR (KBr, cm^{-1}): 2979, 2928, 2360, 2088, 1695, 1505, 1371, 1325, 1250, 1184, 1131, 1102, 1020, 745; HRMS (EI$^+$) calc'd for $C_7H_{12}N_2O_2S^+$: 188.0614, found: 188.0610.

Ethyl 2-diazo-4-(ethylamino)-4-oxobutanoate (20)



According to the General Procedure A for Diazo Synthesis, using diazonium salt **D7** (141.6 mg, 0.340 mmol), ammonium trifluoroacetate salt **S22** (123.3mg, 0.408 mmol), K_2CO_3 (188.1 mg, 1.363 mmol), the reaction was completed in 2.5 hours. The residue was purified by column chromatography on silica gel, eluting with 40% v/v EtOAc in hexane (R_f = 0.23) to give **20** as yellow oil (39.4 mg, 0.198 mmol, 58%).
According to the General Procedure B for Diazo Synthesis, using diazonium salt **D7** (70 mg, 0.168 mmol), ammonium trifluoroacetate salt **S22** (45.3mg, 0.202 mmol), K_2CO_3 (93 mg, 0.672 mmol), the reaction was completed in 3 hours. The residue was purified by column chromatography on silica gel, eluting with 40% v/v EtOAc in hexane (R_f = 0.23) to give **20** as yellow oil (24.8 mg, 0.124 mmol, 74%).
^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ = 5.95 (br, 1H), 4.25 (q, *J* = 7.1 Hz, 2H), 3.29 (qd, *J* = 7.3, 5.6 Hz, 2H), 3.10 (s, 2H), 1.29 (t, *J* = 7.1 Hz, 3H), 1.14 (t, *J* = 7.3 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, ppm) δ = 169.0, 167.6, 61.4, 34.8, 30.9, 14.8, 14.6; IR (KBr, cm^{-1}): 3083, 2980, 2932, 2094, 1686, 15460, 1460, 1396, 1373, 1320, 1191, 1112, 1020, 929, 867, 746, 653, 567; HRMS (ESI$^+$) calc'd for $C_8H_{13}N_3O_3$ (M+Na)$^+$: 222.0849, found: 222.0846.

Ethyl 2-diazo-5-(ethylamino)-5-oxopentanoate (21)

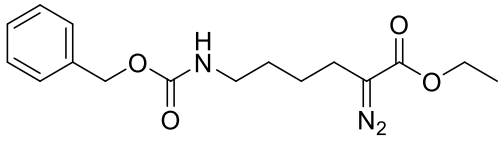


According to the General Procedure A for Diazo Synthesis, using diazonium salt **D7** (33.9 mg, 0.082 mmol), ammonium chloride salt **S23** (23.3 mg, 0.098 mmol), K_2CO_3 (45.1 mg, 0.326 mmol), the reaction was completed in 4.5 hours. The residue was purified by column chromatography on silica gel, eluting with 30% v/v EtOAc in hexane (R_f = 0.23) to give **21** as yellow oil (9.3 mg, 0.044 mmol, 54% yield).

According to the General Procedure B for Diazo Synthesis, using diazonium salt **D7** (60.7 mg, 0.146 mmol), ammonium chloride salt **S23** (41.8 mg, 0.175 mmol), K_2CO_3 (80.7 mg, 0.584 mmol), the reaction was completed in 4 hours. The residue was purified by column chromatography on silica gel, eluting with 30% v/v EtOAc in hexane (R_f = 0.23) to give **21** as yellow oil (23.0 mg, 0.108 mmol, 74% yield).

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ = 5.52 (br, 1H), 4.21 (q, *J* = 7.1 Hz, 2H), 3.29 (qd, *J* = 7.3, 5.6 Hz, 2H), 2.63 (t, *J* = 6.6 Hz, 2H), 2.44 (t, *J* = 6.8 Hz, 2H), 1.27 (t, *J* = 7.1 Hz, 3H), 1.13 (t, *J* = 7.2 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, ppm) δ =171.1, 167.6, 60.7, 34.4, 34.2, 19.9, 14.7, 14.5; IR (KBr, cm^{-1}): 3085, 2978, 2929, 2855, 2089.0 1686, 1656, 1560, 1546, 1460, 1448, 1373, 1327, 1306, 1178, 1112, 1024, 742, 576, 537; HRMS (ESI$^+$) calc'd for $C_9H_{15}N_3O_3$ $(M+Na)^+$: 236.1006, found: 236.1004.

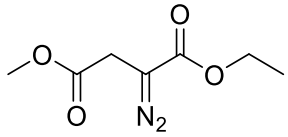
Ethyl 6-(((benzyloxy)carbonyl)amino)-2-diazohexanoate (22)



According to the General Procedure A for Diazo Synthesis, using diazonium salt **D7** (136.9 mg, 0.329 mmol), ammonium trifluoroacetate salt **S24** (166.6 mg, 0.395 mmol), K_2CO_3 (181.8 mg, 1.315 mmol), the reaction was completed in 8 hours. The residue was purified by column chromatography on silica gel, eluting with 20% v/v EtOAc in hexane (R_f = 0.48) to give **22** as yellow oil (76 mg, 0.238 mmol, 72 % yield).

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ = 7.39-7.30 (m, 5H), 5.09 (s, 2H), 4.77 (br, 1H), 4.21 (q, *J* = 7.1 Hz, 2H), 3.25-3.20 (m, 2H), 2.34-2.31 (m, 2H), 1.61-1.48 (m, 4H), 1.26 (t, *J* = 7.1 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, ppm) δ = 167.6, 156.5, 136.6, 128.5, 128.1, 66.7, 60.8, 40.7, 29.2, 25.0, 22.9, 14.6; IR (KBr, cm^{-1}): 3349, 3034, 2934, 2866, 2364, 2083, 1694, 1529, 1456, 1396, 1372, 1306, 1247, 1179, 1132, 1020, 776, 738, 698; HRMS (ESI$^+$) calc'd for $C_{16}H_{21}N_3O_4$ $(M+Na)^+$: 342.1424, found: 342.1418.

1-Ethyl 4-methyl 2-diazosuccinate (23)

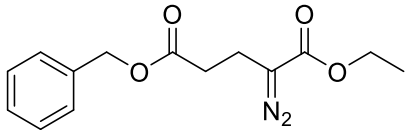


According to the General Procedure A for Diazo Synthesis, using diazonium salt **D7** (159.4 mg, 0.383 mmol), ammonium trifluoroacetate salt **S25** (132.8 mg, 0.460 mmol), K_2CO_3 (211.6 mg, 1.531 mmol), the reaction was completed in 5 hours. The residue was purified by column chromatography on silica gel, eluting with 15% v/v EtOAc in hexane (R_f = 0.55) to give **23** as yellow oil (44.6 mg, 0.240 mmol, 63 % yield).

According to the General Procedure C for Diazo Synthesis, using diazonium salt **D7** (75.1 mg, 0.180 mmol), ammonium trifluoroacetate salt **S25** (104.3 mg, 0.361 mmol), K_2CO_3 (124.7 mg, 0.902 mmol), the reaction was completed in 5 hours. The residue was purified by column chromatography on silica gel, eluting with 15% v/v EtOAc in hexane (R_f = 0.55) to give **23** as yellow oil (24.7 mg, 0.133 mmol, 73 % yield).

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ = 4.23 (q, *J* = 7.1 Hz, 2H), 3.74 (s, 3H), 3.32 (s, 2H), 1.27 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ = 170.2, 166.8, 61.3, 52.6, 28.8, 14.6; IR (KBr, cm^{-1}): 3363, 2984, 2957, 2851, 2097, 1744, 1691, 1438, 1398, 1373, 1312, 1257, 1195, 1112, 1019, 921, 868, 749, 667, 569; HRMS (ESI$^+$) calc'd for $C_7H_{10}N_2O_4$ $(M+Na)^+$: 209.0533, found: 209.0532.

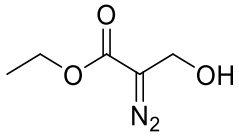
5-Benzyl 1-ethyl 2-diazopentanedioate (24)



According to the General Procedure A for Diazo Synthesis, using diazonium salt **D7** (46.8 mg, 0.113 mmol), ammonium trifluoroacetate salt **S26** (51.2 mg, 0.135 mmol), K_2CO_3 (74.7 mg, 0.540 mmol), the reaction was completed in 8 hours. The residue was purified by column chromatography on silica gel, eluting with 10% v/v EtOAc in hexane (R_f = 0.50) to give **24** as yellow oil (26.7 mg, 0.097 mmol, 86 % yield).

^{1}H NMR (400 MHz, CD_3OD, ppm) δ = 7.36-7.29 (m, 5H), 5.13 (s, 2H), 4.19 (q, *J* = 7.1 Hz, 2H), 2.65-2.58 (m, 4H), 1.25 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ = 172.4, 135.8, 128.7, 128.5, 66.7, 60.9, 32.6, 19.7, 14.6; IR (KBr, cm^{-1}): 3352, 3067, 3035, 2958, 2926, 2855, 2360, 2091, 1733, 1684, 1498, 1456, 1418, 1372, 1324, 1259, 1164.8, 1111, 1025, 740, 69, 578, 457; HRMS (EI$^+$) calc'd for $C_{14}H_{16}N_2O_4^+$: 276.1105, found: 276.1106.

Ethyl 2-diazo-3-hydroxypropanoate (25)

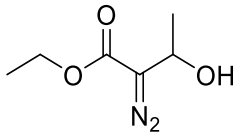


According to the General Procedure A for Diazo Synthesis, using diazonium salt **D7** (70 mg, 0.168 mmol), ammonium chloride salt **S27** (34.3 mg, 0.202 mmol), K_2CO_3 (93 mg, 0.672 mmol), the reaction was completed in 1 hours. The residue was purified by column chromatography on silica gel, eluting with 30% v/v EtOAc in hexane (R_f = 0.35) to give **25** as yellow oil (15.8 mg, 0.110 mmol, 65%).

According to the General Procedure B for Diazo Synthesis, using diazonium salt **D7** (70 mg, 0.168 mmol), ammonium chloride salt **S27** (34.3 mg, 0.202 mmol), K_2CO_3 (46.4 mg, 0.336 mmole + 46.4 mg 0.336 mmole), the reaction was completed in 1 hours. The residue was purified by column chromatography on silica gel, eluting with 30% v/v EtOAc in hexane (R_f = 0.35) to give **25** as yellow oil (18.4 mg, 0.128 mmol, 75%).

^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ = 4.50 (s, 2H), 4.25 (q, *J* = 7.0 Hz, 2H), 1.29 (t, *J* = 7.0 Hz, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$, ppm) δ = 166.7, 61.3, 57.9, 14.6; HRMS (EI^+) calc'd *m/z* for $C_5H_8N_2O_3^+$: 144.0529, found: 144.0530. All spectroscopic data were in agreement with the literature value[18].

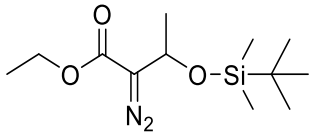
Ethyl 2-diazo-3-hydroxybutanoate (26)



According to the General Procedure A for Diazo Synthesis, using diazonium salt **D7** (75.2 mg, 0.181 mmol), ammonium chloride salt **S28** (56.6 mg, 0.217 mmol), K_2CO_3 (119.8 mg, 0.867 mmol), the reaction was completed in 3 hours. The residue was purified by column chromatography on silica gel, eluting with 15% v/v EtOAc in hexane (R_f = 0.78) to give **26** as yellow oil (4.9 mg, 0.031 mmol, 17% yield).

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ = 4.93 (q, *J* = 6.6 Hz, 1H), 4.25 (q, *J* = 7.1 Hz, 2H), 2.46 (br, 1H), 1.41 (d, *J* = 6.6 Hz, 3H), 1.29 (t, *J* = 7.1 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, ppm) δ = 166.7, 62.7, 61.2, 19.7, 14.6; HRMS (ESI^+) calc'd for $C_6H_{10}N_2O_3$ $(M+Na)^+$: 181.0584, found: 181.0581. All spectroscopic data were in agreement with the literature values[19].

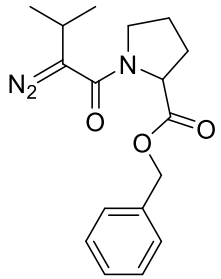
Ethyl 3-((tert-butyldimethylsilyl)oxy)-2-diazobutanoate (27)



According to the General Procedure A for Diazo Synthesis, using diazonium salt **D7** (69.8 mg, 0.168 mmol), ammonium trifluoroacetate salt **S29** (75.5 mg, 0.201 mmol), K_2CO_3 (92.6 mg, 0.670 mmol), the reaction was completed in 7 hours. The residue was purified by column chromatography on silica gel, eluting with 10% v/v EtOAc in hexane (R_f = 0.88) to give **27** as yellow oil (29.0 mg, 0.107 mmol, 63% yield).

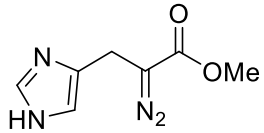
^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ = 4.81 (q, *J* = 6.3 Hz, 1H), 4.22 (q, *J* = 7.1 Hz, 2H), 1.36 (d, *J* = 6.3 Hz, 3H), 1.28 (t, *J* = 7.1 Hz, 3H), 0.87 (s, 9H), 0.09 (s, 3H), 0.06 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, ppm) δ = 62.9, 60.8, 25.8, 22.9, 18.1, 14.6, -4.9, -5.1; IR (KBr, cm^{-1}): 2957, 2930, 2857, 2360., 2341, 2093, 1694, 1463, 1373, 1287, 1259, 1090, 958, 837, 779; HRMS (ESI$^+$) calc'd for $C_{12}H_{24}N_2O_3Si$ $(M+Na)^+$: 295.1448, found: 295.1447.

Benzyl (2-diazo-3-methylbutanoyl)prolinate (28)



According to the General Procedure B for Diazo Synthesis, using diazonium salt **D7** (70.0 mg, 0.168 mmol), ammonium trifluoroacetate salt **S30** (102.0 mg, 0.299 mmol), K_2CO_3 (93.7 mg, 0.678 mmol), the reaction was completed in 18 hours. The residue was purified by column chromatography on silica gel, eluting with 30% v/v EtOAc in hexane (R_f = 0.75) to give **28** as yellow oil (36.1 mg, 0.114 mmol, 68% yield).
^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ = 7.38-7.29 (m, 5H), 5.22, 5.12 (ABq, *J* = 12.4 Hz, 2H), 4.60 (dd, *J* = 8.2, 4.9 Hz, 1H), 3.60-3.53 (m, 1H), 3.50-3.44 (m, 1H), 2.90 (sept, *J* = 6.8 Hz, 1H), 2.24-2.15 (m, 1H), 2.12-2.03 (m, 1H), 2.01-1.86 (m, 2H), 1.13 (d, *J* = 6.8 Hz, 3H), 1.13 (d, *J* = 6.8 Hz, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, ppm) δ = 172.4, 165.4, 135.9, 128.7, 128.3, 128.2, 66.9, 60.3, 48.2, 29.1, 25.2, 24.2, 20.6, 20.3; IR (KBr, cm^{-1}): 2961, 2926, 2360, 2344, 2055, 1742, 1615, 1386.1, 1167, 731, 698; HRMS (ESI$^+$) calc'd *m/z* for $(C_{17}H_{21}N_3O_3+H)^+$: 316.1656, found: 316.1657.

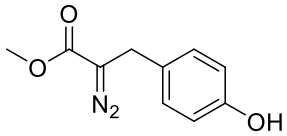
Methyl 2-diazo-3-(1H-imidazol-4-yl)propanoate (29)



According to the General Procedure A for Diazo Synthesis, using diazonium salt **D7** (70 mg, 0.168 mmol), ammonium chloride salt **S31** (44.6 mg, 0.185 mmol), K_2CO_3 (116 mg, 0.839 mmol), the reaction was completed in 13 hours. The residue was purified by column chromatography on silica gel, eluting with 5% v/v MeOH in DCM (R_f = 0.73) to give **29** as yellow oil (17.1 mg, 0.095 mmol, 57% yield).
According to the General Procedure C for Diazo Synthesis, using diazonium salt **D7** (70 mg, 0.168 mmol), ammonium chloride salt **S31** (81.0 mg, 0.337 mmol), K_2CO_3 (139 mg, 1.005 mmol), the reaction was completed in 16 hours. The residue was purified by column chromatography on silica gel, eluting with 5% v/v MeOH in DCM (R_f = 0.73) to give **29** as yellow oil (19.3 mg, 0.107 mmol, 64% yield).
^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ = 7.59 (s, 1H), 6.89 (s, 1H), 6.54 (br, 1H), 3.76 (s, 3H), 3.62 (s, 2H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, ppm) δ = 168.2, 135.4, 133.7, 117.2, 52.2, 21.7; IR (KBr, cm^{-1}): 2952, 3644, 2095, 1674, 1438, 1354, 1194, 1172,

1109, 811, 754, 688, 627; HRMS (EI^+) calc'd *m/z* for $C_7H_8N_4O_2^+$: 180.0642, found: 180.0642.

Methyl 2-diazo-3-(4-hydroxyphenyl)propanoate (30)

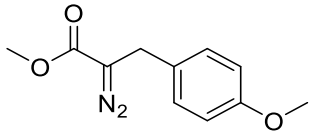


According to the General Procedure A for Diazo Synthesis, using diazonium salt **D7** (70 mg, 0.168 mmol), ammonium chloride salt **S32** (47 mg, 0.202 mmol), K_2CO_3 (93 mg, 0.673 mmol), the reaction was completed in 13 hours. The residue was purified by column chromatography on silica gel, eluting with 25% v/v EtOAc in hexane (R_f = 0.50) to give **30** as yellow oil (13.2 mg, 0.064 mmol, 38% yield).

According to the General Procedure C for Diazo Synthesis, using diazonium salt **D7** (70 mg, 0.168 mmol),ammonium chloride salt **S32** (77.7 mg, 0.336 mmol), K_2CO_3 (93 mg, 0.673 mmol), the reaction was completed in 13 hours. The residue was purified by column chromatography on silica gel, eluting with 25% v/v EtOAc in hexane (R_f = 0.50) to give **30** as yellow oil (16.1 mg, 0.078 mmol, 46% yield).

^1H NMR (500 MHz, $CDCl_3$, ppm) δ = 7.10 (d, *J* = 8.5 Hz, 2H), 6.78 (d, *J* = 8.5 Hz, 2H), 5.29 (br, 1H), 3.79 (s, 3H), 3.56 (s, 2H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$, ppm) δ = 155.0, 129.8, 129.2, 115.8, 52.2, 28.7; IR (KBr, cm^{-1}): 3243.6, 3070.0, 2104.1, 1600.4, 1373.4, 1345.2, 1243.2, 1227.4, 1027.7, 816.1, 706.6, 564.6; HRMS (EI^+) calc'd *m/z* for $C_{10}H_{10}O_3N_2^+$: 206.0687, found: 206.0686.

Methyl 2-diazo-3-(4-methoxyphenyl)propanoate (31)

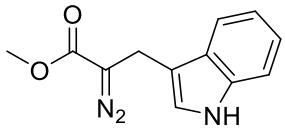


According to the General Procedure A for Diazo Synthesis, using diazonium salt **D7** (70 mg, 0.168 mmol), ammonium chloride salt **S33** (49.5 mg, 0.202 mmol), K_2CO_3 (93 mg, 0.673 mmol), the reaction was completed in 13.5 hours. The residue was purified by column chromatography on silica gel, eluting with 40% v/v DCM in hexane (R_f = 0.38) to give **31** as yellow oil (13.8 mg, 0.063 mmol, 45% yield).

According to the General Procedure C for Diazo Synthesis, using diazonium salt **D7** (60 mg, 0.144 mmol), ammonium chloride salt **S33** (70.7 mg, 0.288 mmol), K_2CO_3 (99.7 mg, 0.721 mmol), the reaction was completed in 15.5 hours. The residue was purified by column chromatography on silica gel, eluting with 40% v/v DCM in hexane (R_f = 0.38) to give **31** as yellow oil (21.6 mg, 0.098 mmol, 68% yield).

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ = 7.18-7.14 (m, 2H), 6.87-6.84 (m, 2H), 3.79 (s, 3H), 3.78 (s, 3H), 3.58 (s, 2H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$, ppm) δ = 167.8, 158.9, 129.6, 129.2, 114.3, 55.4, 52.1, 28.7. All spectroscopic data were in agreement with the literature values[20].

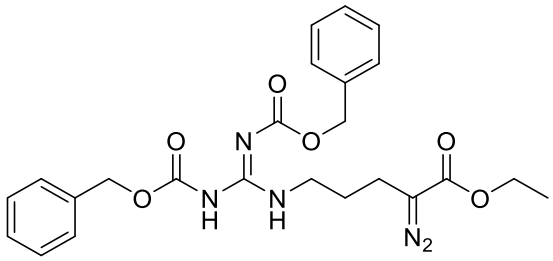
Methyl 2-diazo-3-(1H-indol-3-yl)propanoate (32)



According to the General Procedure A for Diazo Synthesis, using diazonium salt **D7** (45 mg, 0.108 mmol), ammonium chloride salt (33.1 mg, 0.130 mmol), K_2CO_3 (60 mg, 0.434 mmol), the reaction was completed in 5 hours. The residue was purified by column chromatography on silica gel, eluting with 20% v/v EtOAc in hexane (R_f = 0.55) to give **32** as yellow oil (18.3 mg, 0.080 mmol, 74%).

^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ = 8.07 (br, 1H), 7.60 (d, *J* = 7.9 Hz, 1H), 7.37 (ddd, *J* = 8.1, 0.8, 0.8 Hz, 1H), 7.22 (ddd, *J* = 8.1, 7.1, 1.1 Hz, 1H), 7.14 (ddd, *J* = 8.0, 7.1, 1.1 Hz, 1H), 7.09 (d, *J* = 2.4 Hz, 1H), 3.81 (d, *J* = 0.9 Hz, 2H), 3.80 (s, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$, ppm) δ = 136.6, 127.0, 122.7, 122.6, 120.0, 119.0, 111.42, 111.37, 52.1, 19.7; IR (KBr, cm^{-1}): 3402, 2954, 2087.7, 1679, 1436, 1338, 1312, 1193, 1110, 744; HRMS (EI^+) calc'd *m/z* for $C_{12}H_{11}O_2N_3^+$: 229.0848, found: 229.0846.

Ethyl (E)-5-(2,3-bis((benzyloxy)carbonyl)guanidino)-2-diazopentanoate (33)

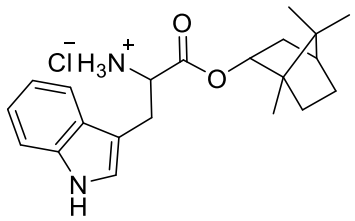


According to the General Procedure A for Diazo Synthesis, using diazonium salt **D7** (96.8 mg, 0.233 mmol), ammonium trifluoroacetate salt **S34** (163 mg, 0.279 mmol), K_2CO_3 (128.5 mg, 0.930 mmol), the reaction was completed in 16 hours. The residue was purified by column chromatography on silica gel, eluting with 30% v/v EtOAc in hexane (R_f = 0.85) to give **33** as yellow oil (75.6 mg, 0.157 mmol, 68% yield).

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ = 9.44 (br, 1H), 9.25 (br, 1H), 7.41-7.28 (m, 10H), 5.25 (s, 2H), 5.14 (s, 2H), 4.17 (q, *J* = 7.1 Hz, 2H), 4.04 (dd, *J* = 7.4, 7.4 Hz, 2H), 2.30 (t, *J* = 7.5 Hz, 2H), 1.81 (m, 2H), 1.23 (t, *J* = 7.1 Hz, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$, ppm) δ = 167.4, 164.0, 160.5, 155.9, 137.0, 134.7, 128.91, 128.88, 128.5, 128.4, 128.0, 127.9, 69.1, 67.1, 60.8, 43.9, 26.8, 20.6, 14.6; IR (KBr, cm^{-1}): 3389, 3278, 3066,

3034, 2980, 2959, 2932, 2084, 1720, 1690, 1648, 1610, 1510, 1455, 1403, 1375, 1309, 1256, 1188, 1108, 1009, 909, 808, 776, 738, 698, 586, 534, 497; HRMS (ESI^+) calc'd for $C_{24}H_{27}N_5O_6$ $(M+Na)^+$: 504.1859, found: 504.1852.

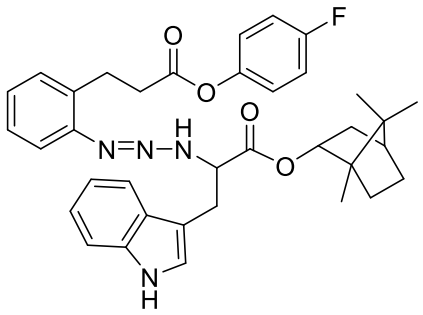
3-(1H-Indol-3-yl)-1-oxo-1-(((1R,2R,4S)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl)oxy)propan-2-aminium chloride (34)



Boc-Try-OH (200 mg, 0.657 mmol) in DCM (8 mL, 0.08 M) was slowly added by (-)-borneol (111.7 mg, 0.724 mmol), DMAP (catalytic amount), and DCC (173 mg, 0.838 mmol in DCM 8 mL, 0.11 M) at 0 °C. The mixture was warmed up to room temperature and stirred until the reaction completed according to TLC observation. The suspension of byproduct DCU was filtered off, and the filtrate was concentrated to give the residue. The crude product was purified by silica gel column chromatography, eluting with 20% v/v EtOAc in hexane (R_f = 0.43) to give Boc-product which was directly deprotected by 2.0 M HCl in diethyl ether. The reaction mixture was stirred for overnight and concentrated under the reduced pressure to afford the ammonium chloride salt **34** as yellow solid (195.9 mg, 0.520 mmol, 79% yield).

^1H NMR (400 MHz, CD_3OD) : δ = 7.60 (d, *J* = 7.6 Hz, 1H), 7.42 (d, *J* = 8.0 Hz, 1H), 7.22 (s, 1H), 7.18 (dd, *J* = 8.0, 7.2 Hz, 1H), 7.10 (dd, *J* = 8.0, 6.8 Hz, 1H), 4.91-4.87 (m, 1H), 4.39 (t, *J* = 7.6 Hz, 1H), 3.41 (d, *J* = 7.6 Hz, 2H), 2.24-2.17 (m, 1H), 1.66-1.49 (m, 3H), 0.91-0.87 (m, 8H), 0.79 (s, 3H), 0.63 (dd, *J* = 14.0, 3.6 Hz, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, CD_3OD) : δ = 170.8, 138.1, 128.1, 125.4, 122.8, 120.1, 118.9, 112.6, 107.7, 83.5, 54.6, 45.8, 36.8, 28.3, 28.2, 27.7, 19.9, 19.0, 13.7; IR (KBr, cm^{-1}) : 3411, 2923, 1733, 1598, 1455, 1362, 1286, 1259, 1113, 1012, 992, 962, 886, 821, 740, 704, 556; HRMS (ESI+) : Calc. for $C_{21}H_{29}N_2O_2^+$ $(M-Cl^-)^+$: 341.2224, found: 341.2223.

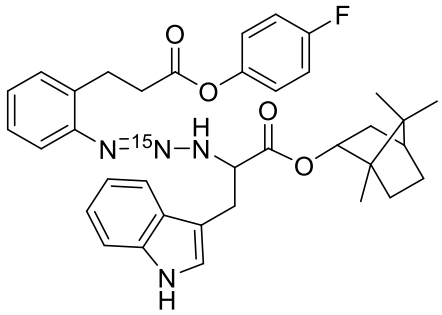
(1R,2R,4S)-1,7,7-Trimethylbicyclo[2.2.1]heptan-2-yl ((2-(3-(4-fluorophenoxy)-3-oxopropyl)phenyl)diazenyl)tryptophanate (35)



Ammonium chloride salt **34** (42.7 mg, 0.113 mmol) in mixture of THF/H_2O (v/v % = 20:1, 0.05 M) solution was added by K_2CO_3 (31.5 mg, 0.304 mmol) and diazonium salt **D7** (31.4 mg, 0.076 mmol) under 0 °C. After stirring for one hour, the solution was then warmed up to the room temperature and diluted with H_2O (5 mL) and EtOAc (5 mL). The mixture was extracted with EtOAc (15 mL x 3). The organic layers were combined, dehydrated with NaCl (sat.), dried over $MgSO_4$, filtered, and concentrated under reduced pressure to give the crude residue. The residue was purified by column chromatography on silica gel, eluting with 20% v/v EtOAc in hexane (R_f = 0.50) to give **35** as yellow solid (27.7 mg, 0.045 mmol, 60% yield).

^{1}H NMR (400 MHz, $CDCl_3$) : δ = 8.23 (br, 1H), 8.07 (br, 1H), 7.63 (dd, *J* = 8.0, 0.8 Hz, 1H), 7.38-7.34 (m, 2H), 7.26-7.10 (m, 6H), 7.03-6.93 (m, 4H), 5.10 (t, *J* = 6.4 Hz, 1H), 4.83 (ddd, *J* = 10, 3.2, 2.4 Hz, 1H), 3.49, 3.41 (ABqdd, *J* = 14.8, 6.0, 0.8 Hz, 2H), 3.19 (m, 2H), 2.85 (t, *J* = 7.6 Hz, 2H), 2.28-2.21 (m, 1H), 1.76-1.69 (m, 1H), 1.61-1.58 (m, 1H), 1.29-1.18 (m, 2H), 0.94-0.85 (m, 1H), 0.82 (s, 3H), 0.80 (s, 3H), 0.74 (dd, *J* = 13.6, 3.2 Hz, 1H), 0.69 (s, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) : δ = 171.9, 171.7, 160.3 (d, $^1J_{C\text{-}F}$ = 242.4 Hz), 146.7, 136.4, 130.2, 127.6, 127.5, 126.7, 123.2 (d, $^3J_{C\text{-}F}$ = 8.5 Hz), 123.0, 122.6, 120.0, 118.8, 117.3, 116.1 (d, $^2J_{C\text{-}F}$ = 23.4 Hz), 111.4, 110.4, 81.3, 48.9, 47.9, 44.9, 36.5, 35.6, 27.9, 27.3, 27.2, 19.7, 18.9, 13.4; IR (KBr, cm^{-1}) : 3406, 3059, 2955, 2085, 1732, 1504, 1484, 1456, **1408**, 1287, 1187, 1134, 1014, 941, 885, 823, 762, 742, 599, 516, 425; HRMS (ESI+) : Calc. for $C_{36}H_{39}FN_4NaO_4^+$ $(M+Na)^+$: 633.2848, found:633.2846.

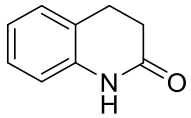
(1R,2R,4S)-1,7,7-Trimethylbicyclo[2.2.1]heptan-2-yl ((2-(3-(4-fluorophenoxy)-3-oxopropyl)phenyl)diazenyl-1-15N)tryptophanate (^{15}N-35)



Ammonium chloride salt **34** (68 mg, 0.180 mmol) in mixture of THF/H_2O (v/v % = 20:1, 0.05 M) solution was added by K_2CO_3 (49.7 mg, 0.360 mmol) and diazonium salt **^{15}N-D7** (50 mg, 0.120 mmol) under 0 °C. After stirring for one hour, the solution was then warmed up to the room temperature and diluted with H_2O (5 mL) and EtOAc (5 mL). The mixture was extracted with EtOAc (15 mL x 3). The organic layers were combined, dehydrated with NaCl (sat.), dried over $MgSO_4$, filtered, and concentrated under reduced pressure to give the crude residue. The residue was purified by column chromatography on silica gel, eluting with 20% v/v EtOAc in hexane (R_f = 0.50) to give **^{15}N-35** as yellow solid (43.3 mg, 0.045 mmol, 59% yield).

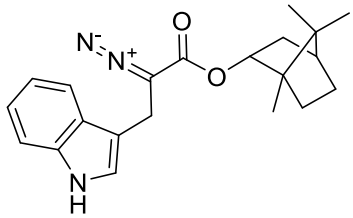
^{1}H NMR (400 MHz, $CDCl_3$) : δ = 8.23 (br, 1H), 8.07 (br, 1H), 7.63 (dd, *J* = 8.0, 0.8 Hz, 1H), 7.38-7.34 (m, 2H), 7.26-7.10 (m, 6H), 7.03-6.93 (m, 4H), 5.10 (t, *J* = 6.4 Hz, 1H), 4.83 (ddd, *J* = 10, 3.2, 2.4 Hz, 1H), 3.49, 3.41 (ABqdd, *J* = 14.8, 6.0, 0.8 Hz, 2H), 3.19 (m, 2H), 2.85 (t, *J* = 7.6 Hz, 2H), 2.28-2.21 (m, 1H), 1.76-1.69 (m, 1H), 1.61-1.58 (m, 1H), 1.29-1.18 (m, 2H), 0.94-0.85 (m, 1H), 0.82 (s, 3H), 0.80 (s, 3H), 0.74 (dd, *J* = 13.6, 3.2 Hz, 1H), 0.69 (s, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) : δ = 171.9, 171.7, 160.3 (d, $^1J_{C\text{-}F}$ = 242.4 Hz), 146.7, 136.4, 130.2, 127.6, 127.5, 126.7, 123.2 (d, $^3J_{C\text{-}F}$ = 8.5 Hz), 123.0, 122.6, 120.0, 118.8, 117.3, 116.1 (d, $^2J_{C\text{-}F}$ = 23.4 Hz), 111.4, 110.4, 81.3, 48.9, 47.9, 44.9, 36.5, 35.6, 27.9, 27.3, 27.2, 19.7, 18.9, 13.4; ^{15}N{^{1}H} NMR (50 MHz, $CDCl_3$) : δ = 583.9; IR (KBr, cm^{-1}) : 3406, 3059, 2955, 2085, 1732, 1504, 1484, 1456, **1388**, 1287, 1187, 1134, 1014, 941, 885, 823, 762, 742, 599, 516, 425; HRMS (ESI+) : Calc. for $C_{36}H_{39}FN_3{}^{15}NNaO_4^+$ $(M+Na)^+$: 634.2818, found:634.2815.

3,4-Dihydroquinolin-2(1H)-one (36)



^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ = 8.67 (br, 1H), 7.19-7.15 (m, 2H), 6.99 (ddd, *J* = 7.5, 7.5, 1.5 Hz, 1H), 6.81 (d, *J* = 9.5, 1H), 2.97(t, *J* = 7.2 Hz, 2H), 2.65 (t, *J* = 7.2 Hz, 2H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, ppm) δ = 171.9, 137.3, 127.9, 127.5, 123.6, 123.1, 115.4, 30.7, 25.3. The spectroscopic data were in agreement with the literature[21].

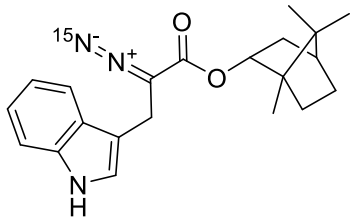
(1R,2R,4S)-1,7,7-Trimethylbicyclo[2.2.1]heptan-2-yl 2-diazo-3-(1H-indol-3-yl) propanoate (37)



Ammonium chloride salt **34** (136.5 mg, 0.362 mmol) in mixture of THF/H_2O (v/v % = 20:1, 0.2 M) solution was added by K_2CO_3 (133 mg, 0.964 mmol) and diazonium salt **D7** (100 mg, 0.240 mmol) under 0 °C. After stirring for 15 minutes, the solution was then warmed up to 50 °C, the reaction was completed in 7 hours. Until the reaction finished, the solution was diluted with H_2O (5 mL) and EA (5 mL). The mixture was extracted with EtOAc (15 mL x 3). The organic layers were combined, dehydrated with NaCl (sat.), dried over $MgSO_4$, filtered, and concentrated under reduced pressure to give the crude residue. The residue was purified by column chromatography on silica gel, eluting with 20% v/v EtOAc in hexane (R_f = 0.30) to give **37** as yellow oil (54.4 mg, 0.155 mmol, 65% yield).

^{1}H NMR (500 MHz, $CDCl_3$) : δ = 8.04 (br, 1H), 7.62 (ddd, *J* = 10.0, 2.5, 1.0 Hz, 1H), 7.38 (ddd, *J* = 10.0, 1.5, 1.0 Hz, 1H), 7.22 (ddd, *J* = 10.0, 9.0, 1.5 Hz, 1H), 7.14 (ddd, *J* = 10.0, 9.0, 1.5 Hz, 1H), 7.11 (d, *J* = 3.5 Hz, 1H), 5.01 (ddd, *J* = 12.5, 4.5, 2.5 Hz, 1H), 3.81 (s, 2H), 2.42-2.35 (m, 1H), 1.84 (br, 1H), 1.76-1.67 (m, 2H), 1.30-1.18 (m, 2H), 1.05 (dd, *J* = 17.5, 4.5 Hz, 1H), 0.92 (s, 3H), 0.87 (s, 3H), 0.85 (s, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) : δ = 136.6, 127.1, 122.7, 122.6, 120.0, 119.0, 111.7, 111.4, 80.6, 77.4, 49.1, 48.0, 45.1, 37.1, 28.2, 27.2, 19.9, 19.7, 19.0, 13.7; IR (KBr, cm^{-1}) : 3358, 3058, 2955, **2084**, 1669, 1456, 1383, 1338, 1310, 1185, 1115, 1013, 978, 771, 741, 424; HRMS (EI^+): calc. *m/z* for $C_{21}H_{25}N_3O_2^+$: 351.1941; found:351.1941.

(1R,2R,4S)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl 2-(diazo)-3-(1H-indol-3-yl)propanoate (^{15}N-37)



Ammonium chloride salt **34** (80.0 mg, 0.212 mmol) in mixture of THF/H_2O (v/v % = 20:1, 0.2 M) solution was added by K_2CO_3 (97.6 mg, 0.707 mmol) and diazonium salt **^{15}N-D7** (73.8 mg, 0.177 mmol) under 0 °C. After stirring for 15 minutes, the solution was then warmed up to 50 °C, the reaction was completed in 7 hours. Until the reaction finished, the solution was diluted with H_2O (5 mL) and EA (5 mL). The mixture was extracted with EtOAc (15 mL x 3). The organic layers were combined, dehydrated with NaCl (sat.), dried over $MgSO_4$, filtered, and concentrated under reduced pressure to give the crude residue. The residue was purified by column chromatography on silica gel, eluting with 20% v/v EtOAc in hexane (R_f = 0.30) to give **^{15}N-37** as yellow oil (38.2 mg, 0.108 mmol, 61% yield).

^{1}H NMR (500 MHz, $CDCl_3$) : δ = 8.04 (br, 1H), 7.62 (ddd, *J* = 10.0, 2.5, 1.0 Hz, 1H), 7.38 (ddd, *J* = 10.0, 1.5, 1.0 Hz, 1H), 7.22 (ddd, *J* = 10.0, 9.0, 1.5 Hz, 1H), 7.14 (ddd, *J* = 10.0, 9.0, 1.5 Hz, 1H), 7.11 (d, *J* = 3.5 Hz, 1H), 5.01 (ddd, *J* = 12.5, 4.5, 2.5 Hz, 1H), 3.81 (s, 2H), 2.42-2.35 (m, 1H), 1.84 (br, 1H), 1.76-1.67 (m, 2H), 1.30-1.18 (m, 2H), 1.05 (dd, *J* = 17.5, 4.5 Hz, 1H), 0.92 (s, 3H), 0.87 (s, 3H), 0.85 (s, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) : δ = 136.6, 127.1, 122.7, 122.6, 120.0, 119.0, 111.7, 111.4, 80.6, 77.4, 49.1, 48.0, 45.1, 37.1, 28.2, 27.2, 19.9, 19.7, 19.0, 13.7; ^{15}N{^{1}H} NMR (50 MHz, $CDCl_3$) : δ = 543.5; IR (KBr, cm^{-1}) : 3358, 3058, 2955, **2057**, 1669, 1456, 1383, 1338, 1310, 1185, 1115, 1013, 978, 771, 741, 424; HRMS (EI^+): calc. *m/z* for $C_{21}H_{25}N_2{}^{15}NO_2^+$: 352.1912; found:352.1914.

9 Reference

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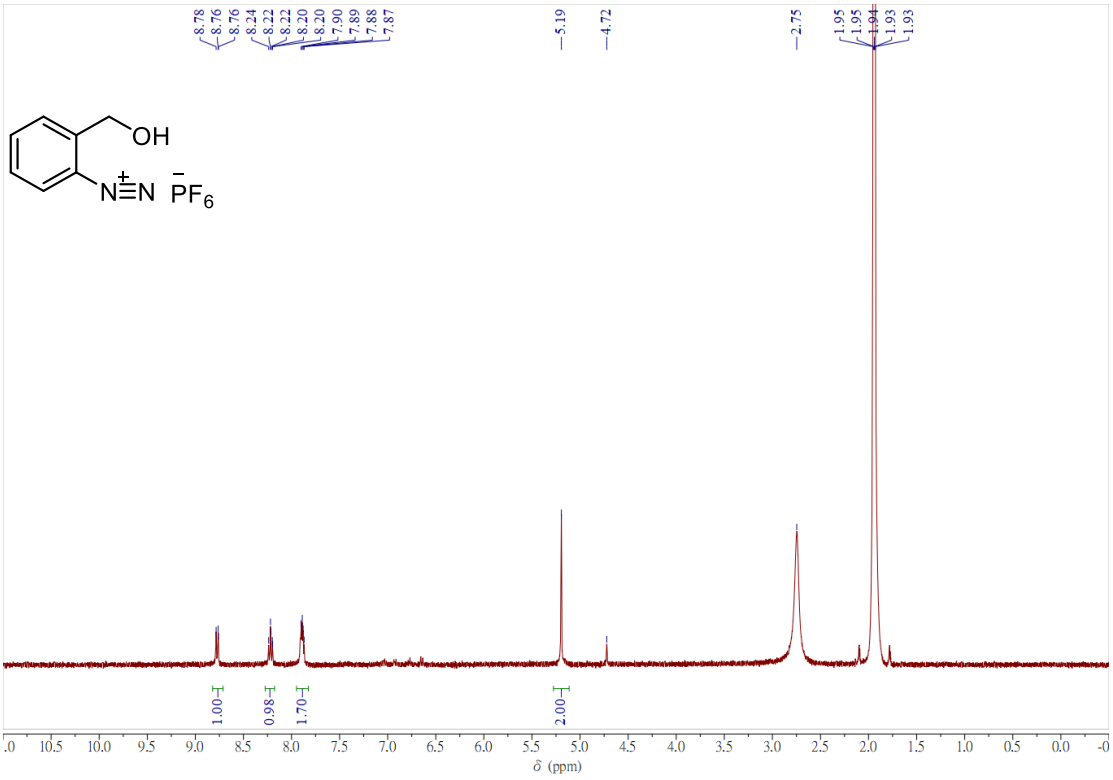
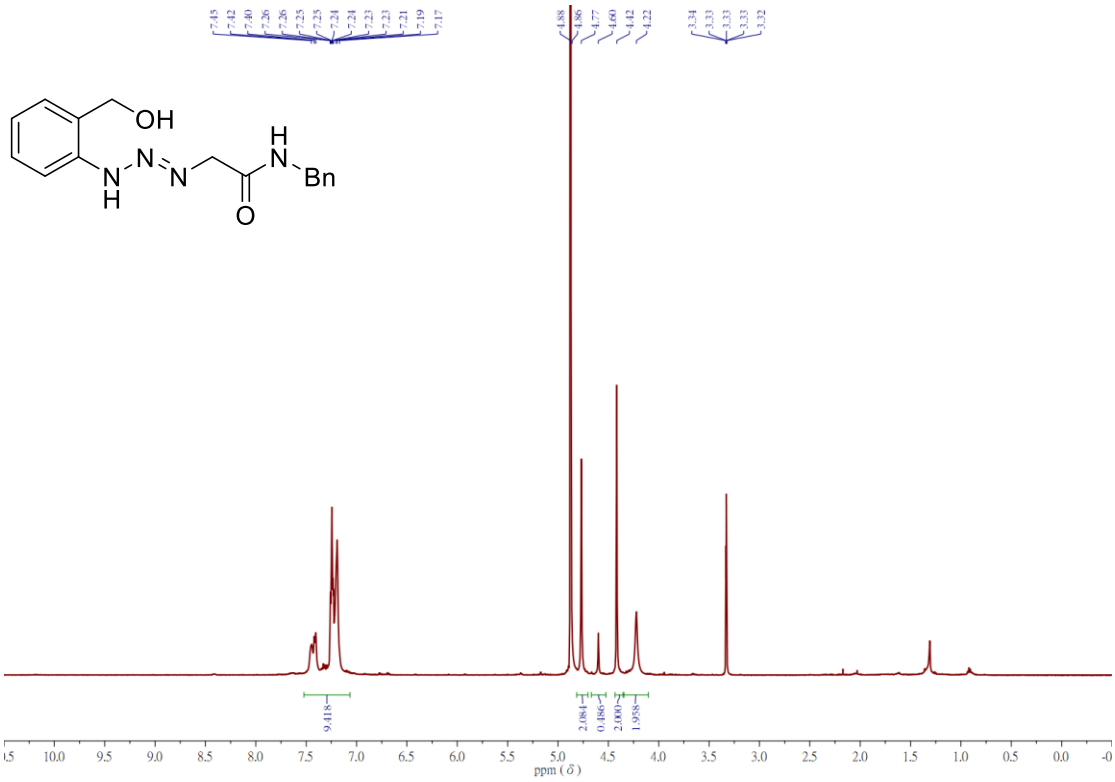
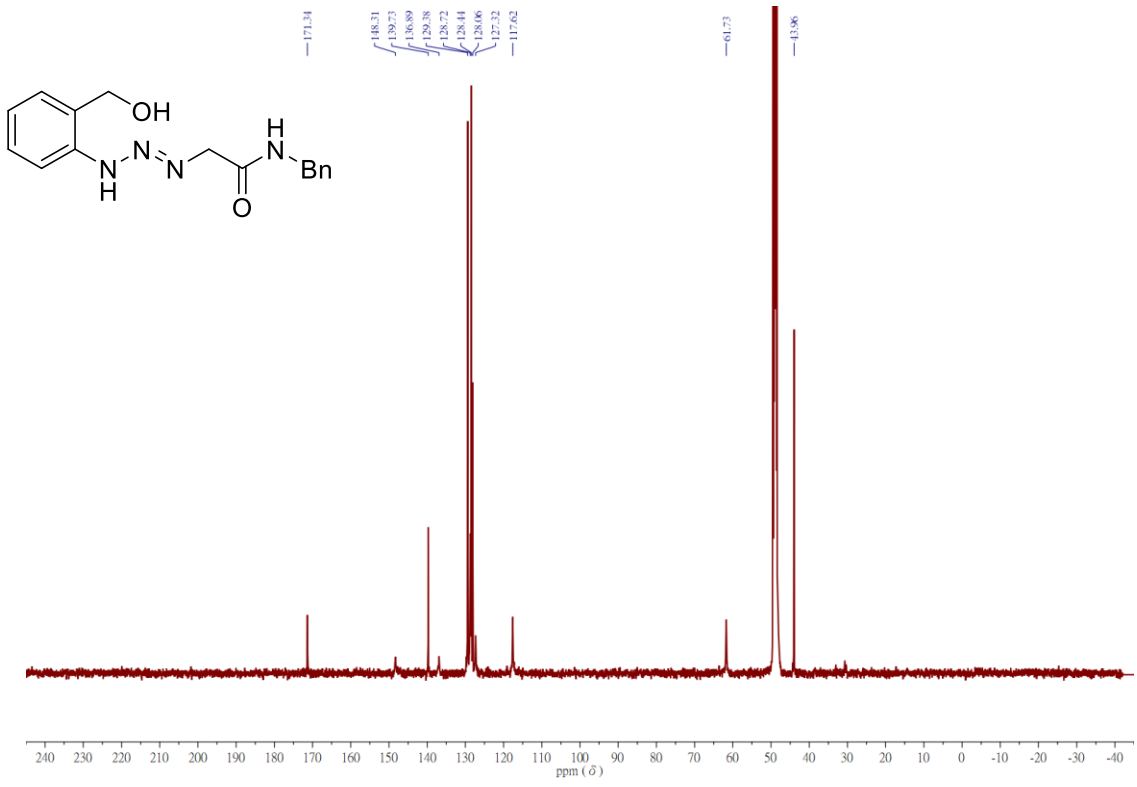
10 NMR Spectra



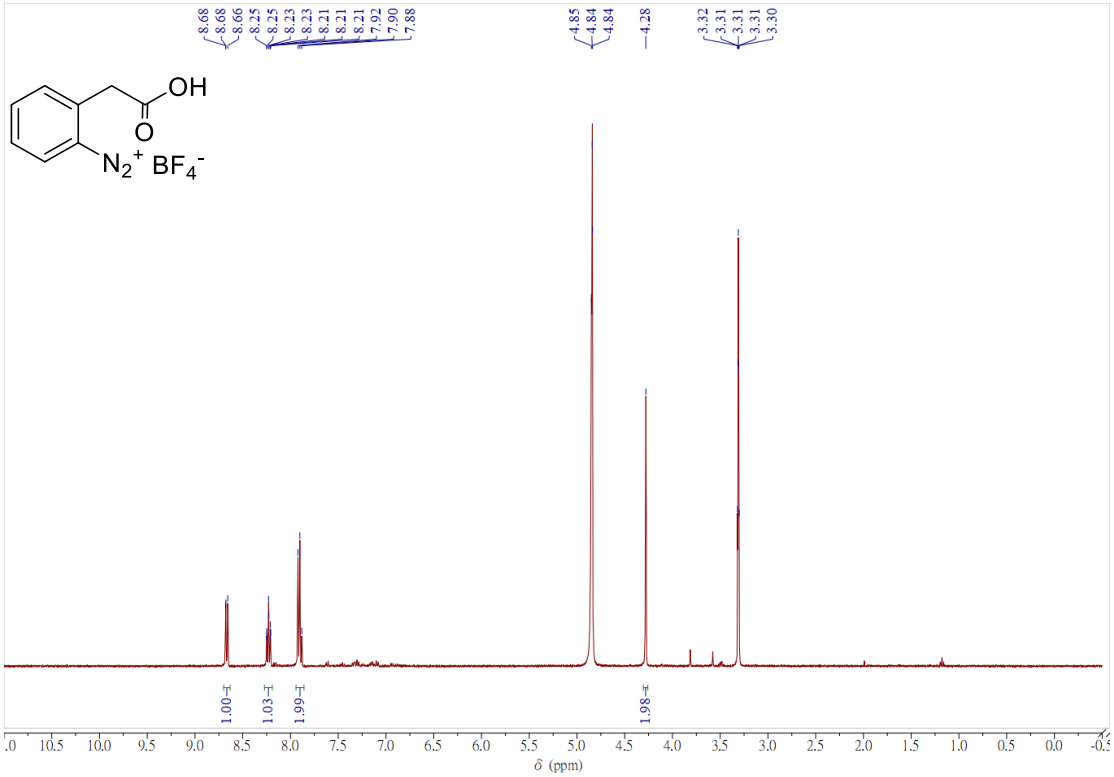
^{1}H NMR Spectrum of **1** in CD_3CN (400 MHz)



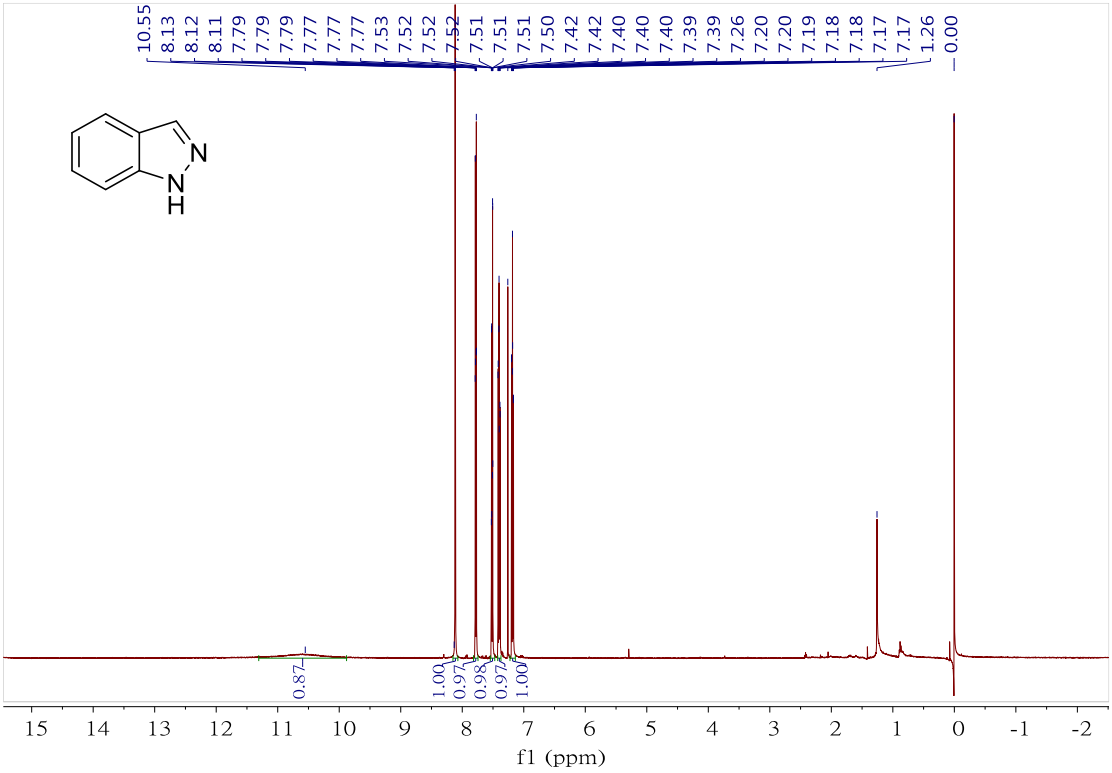
^{1}H NMR Spectrum of **3** in CD_3OD (500 MHz)



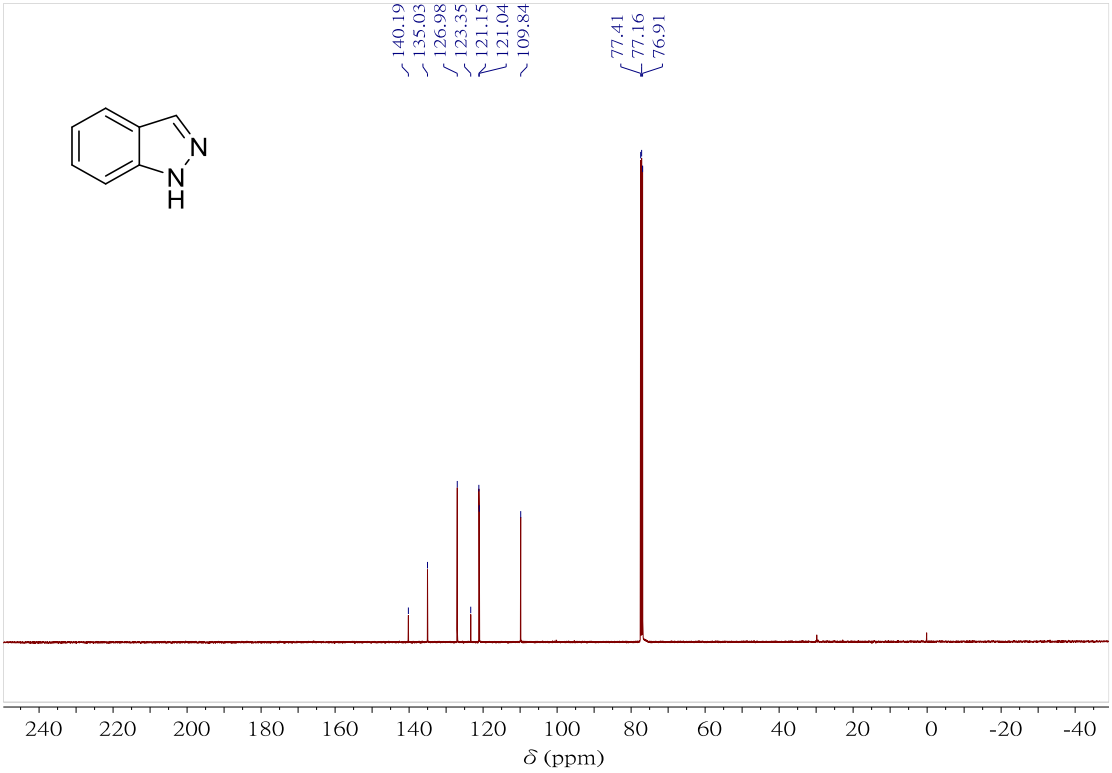
^{13}C NMR Spectrum of **3** in CD_3OD (125 MHz)



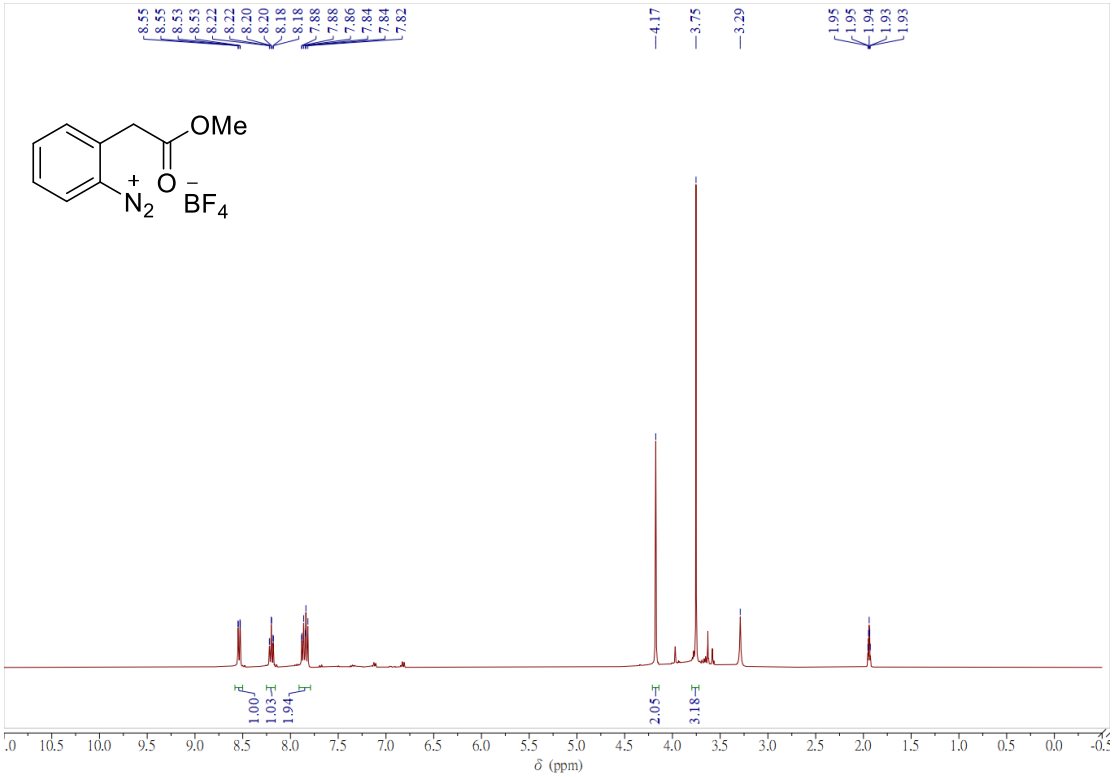
^{1}H NMR Spectrum of **4** in CD_3OD (400 MHz)



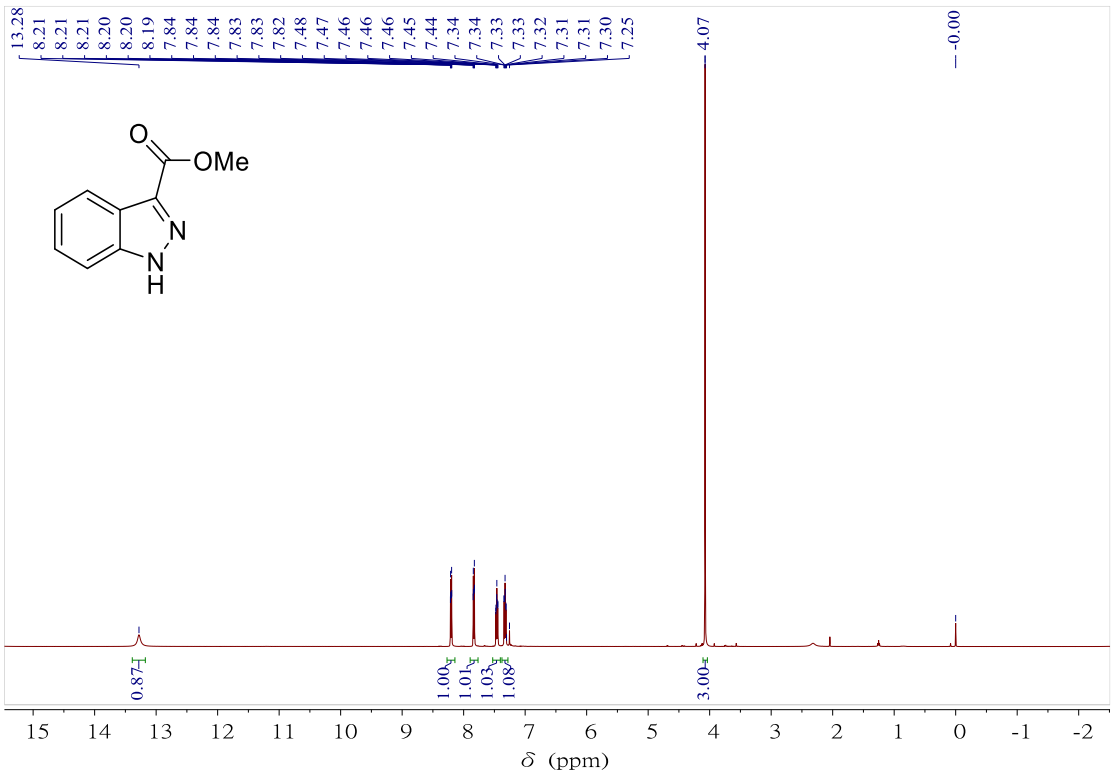
^{1}H NMR Spectrum of **5** in $CDCl_3$ (400 MHz)



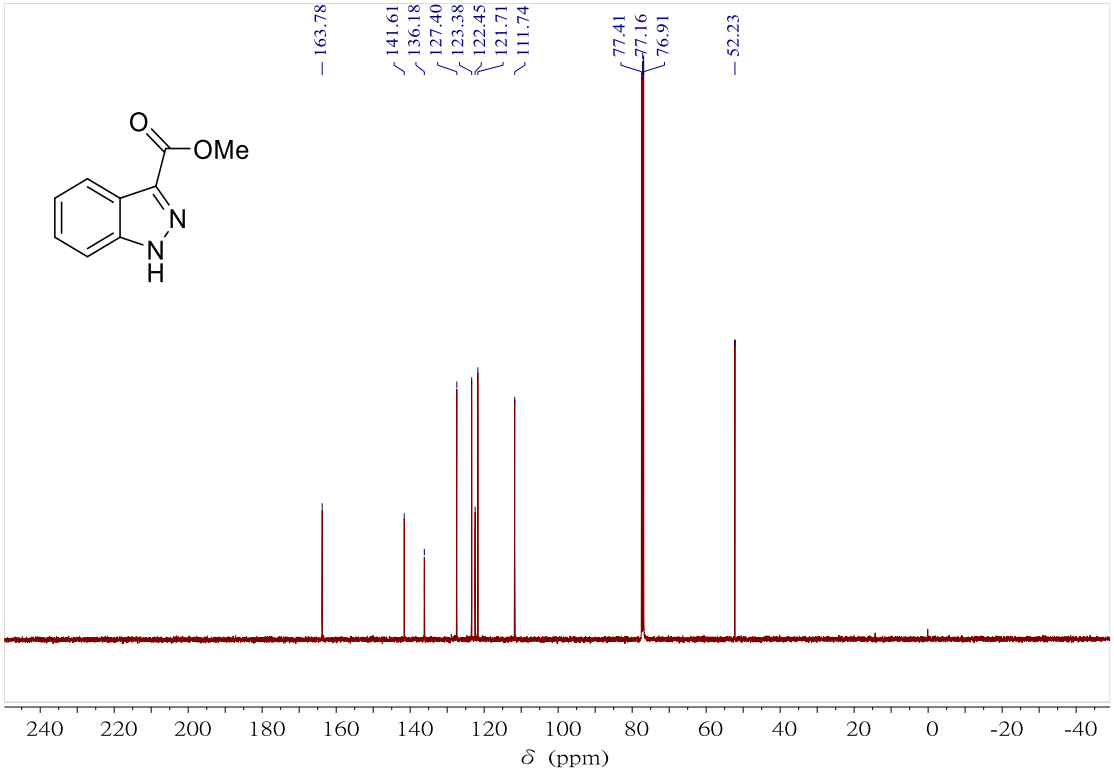
^{13}C NMR Spectrum of **5** in $CDCl_3$ (125 MHz)



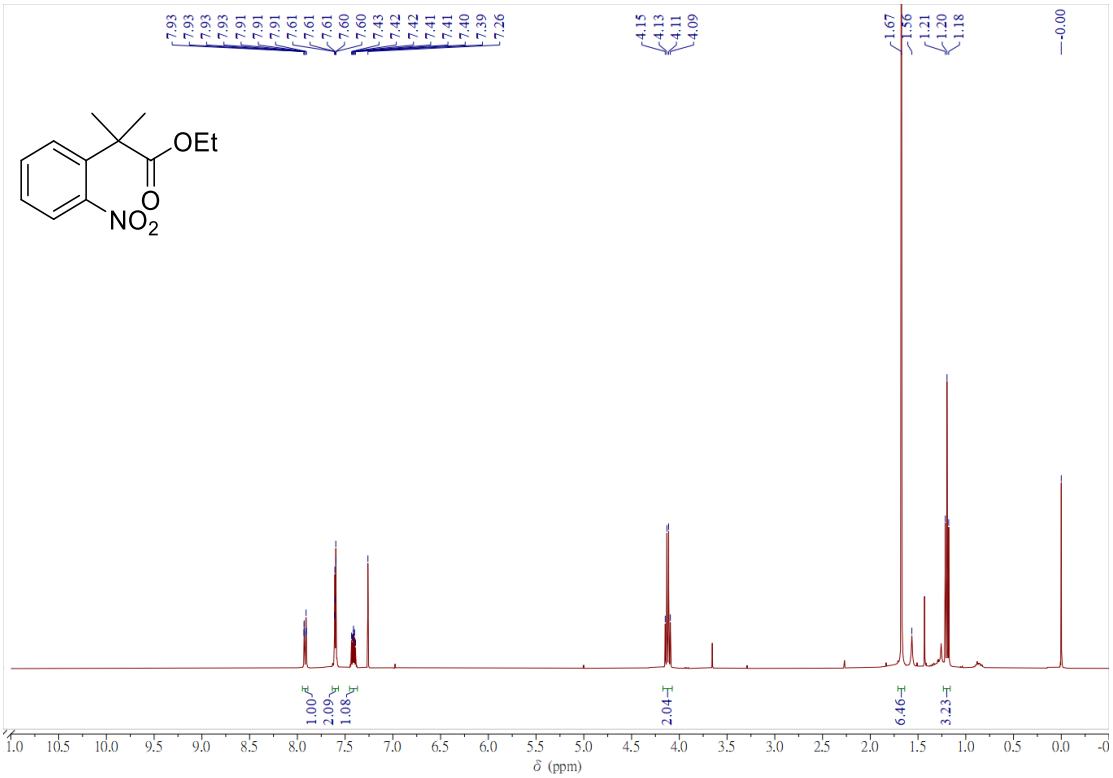
^{1}H NMR Spectrum of **6** in $CDCl_3$ (400 MHz)



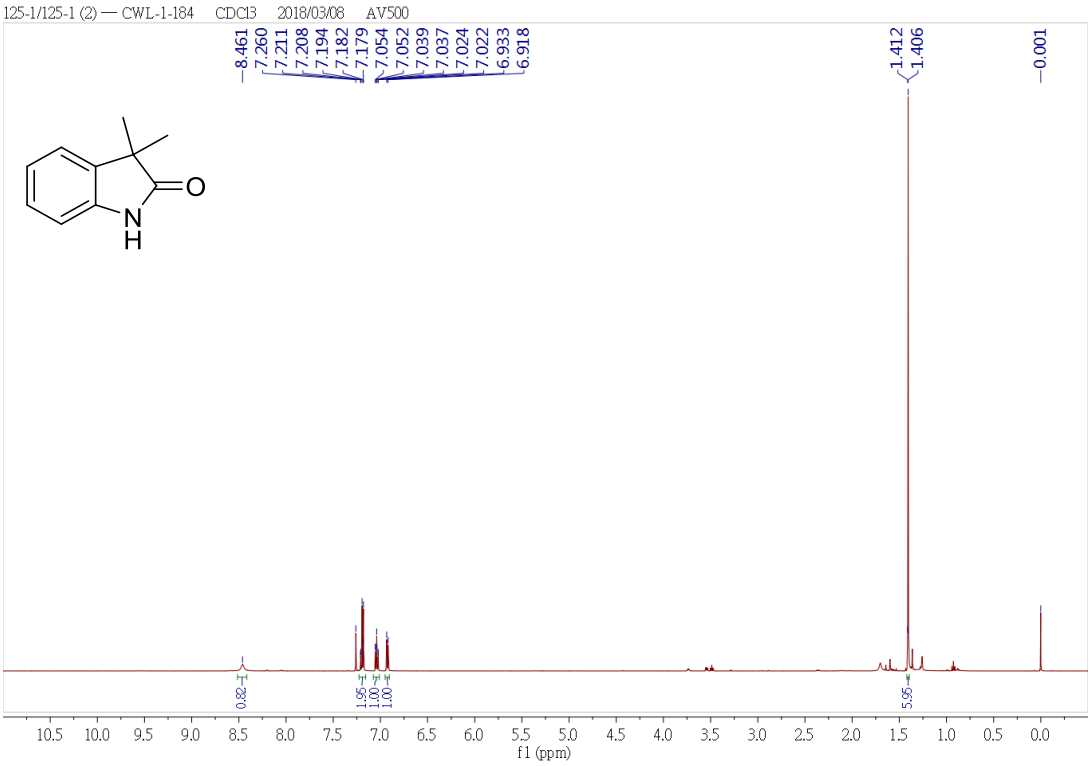
^{1}H NMR Spectrum of **7** in $CDCl_3$ (500 MHz)



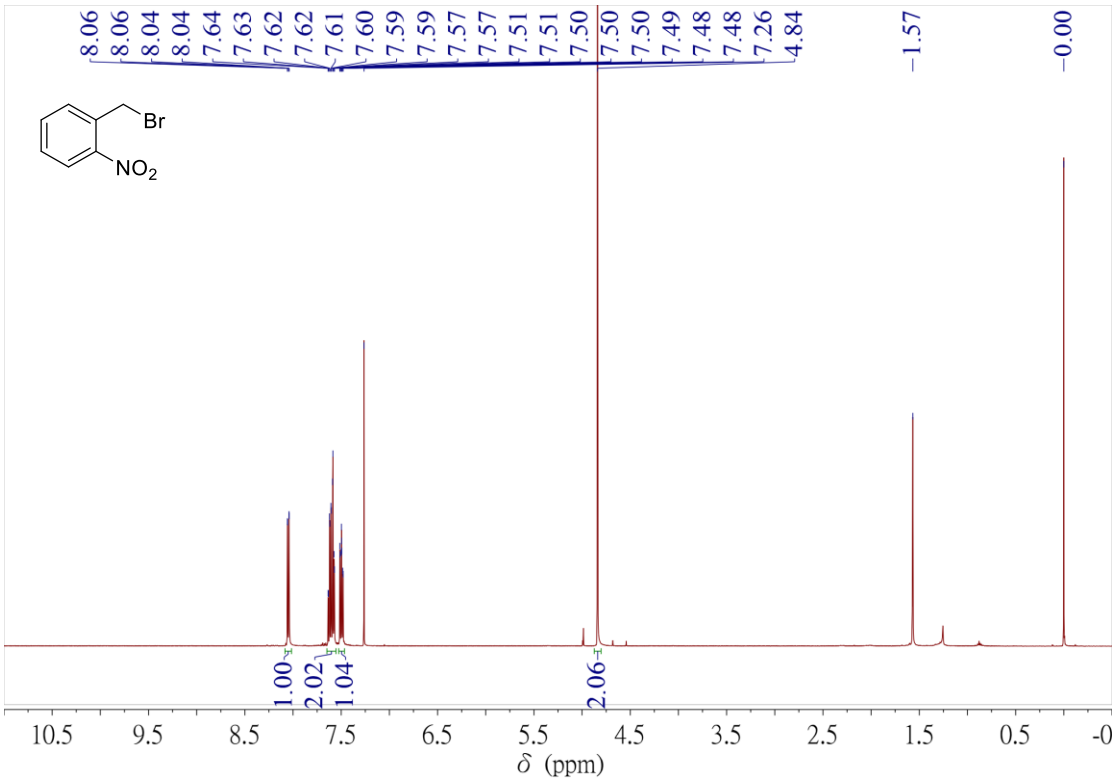
^{13}C NMR Spectrum of **7** in $CDCl_3$ (125 MHz)



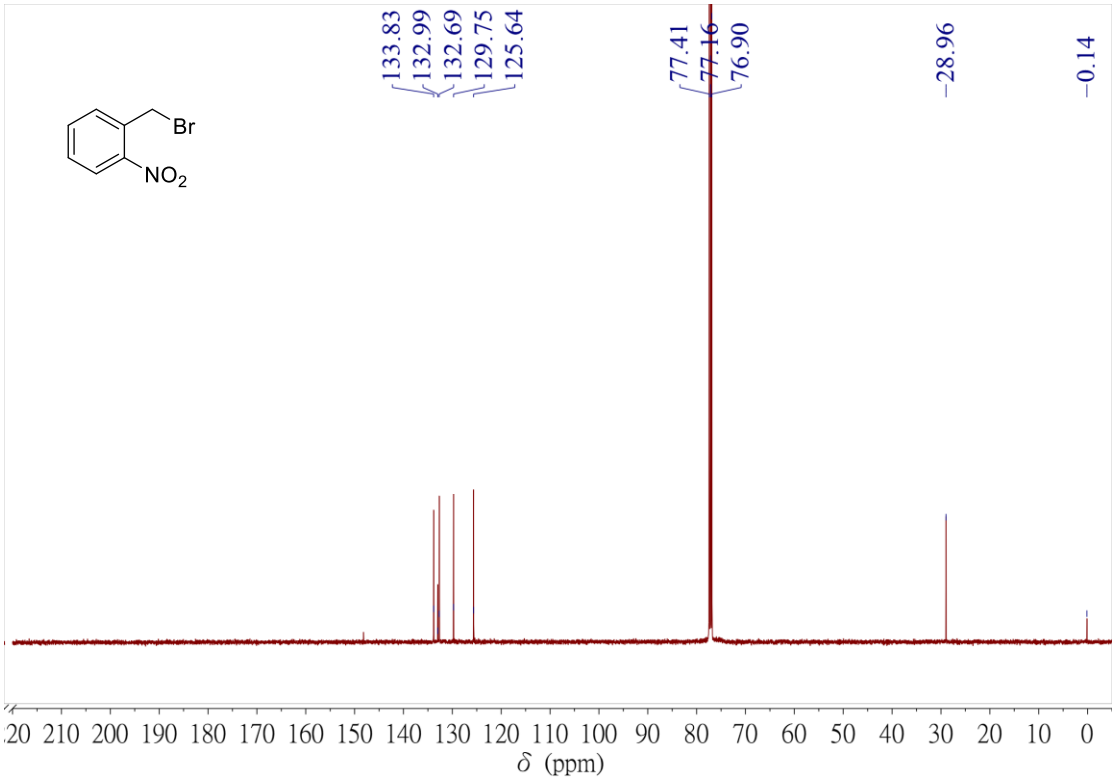
^{1}H NMR Spectrum of **8** in $CDCl_3$ (400 MHz)



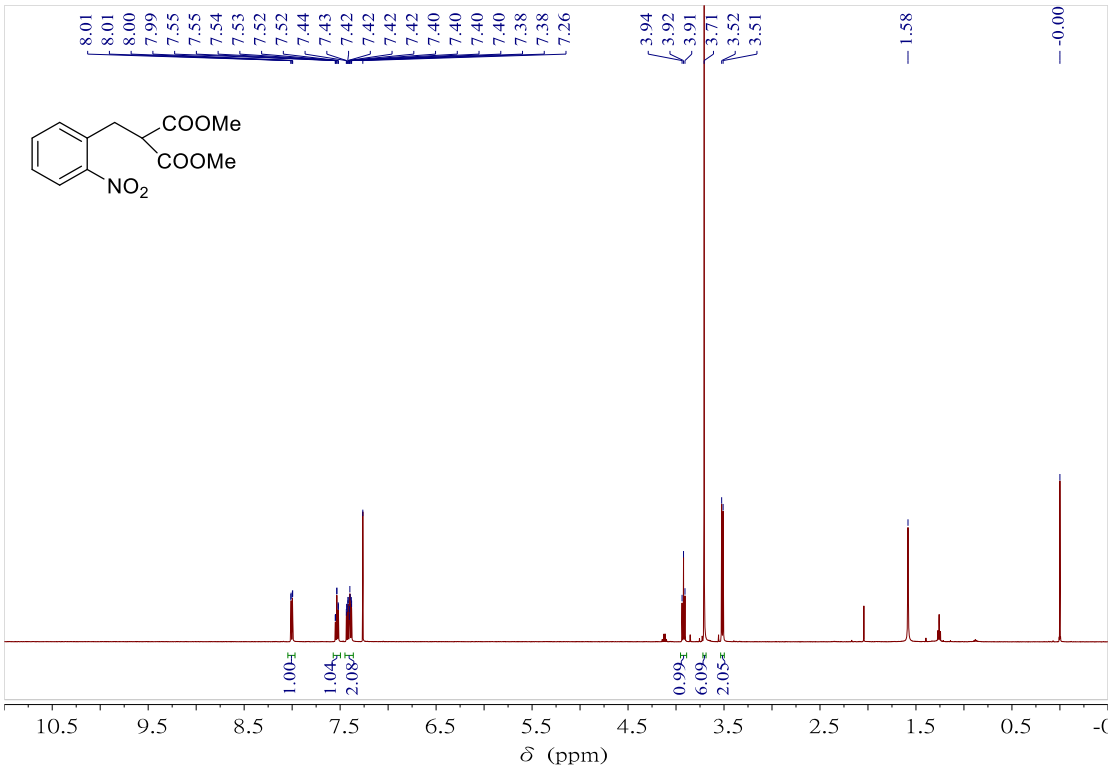
^{1}H NMR Spectrum of **9** in $CDCl_3$ (500 MHz)



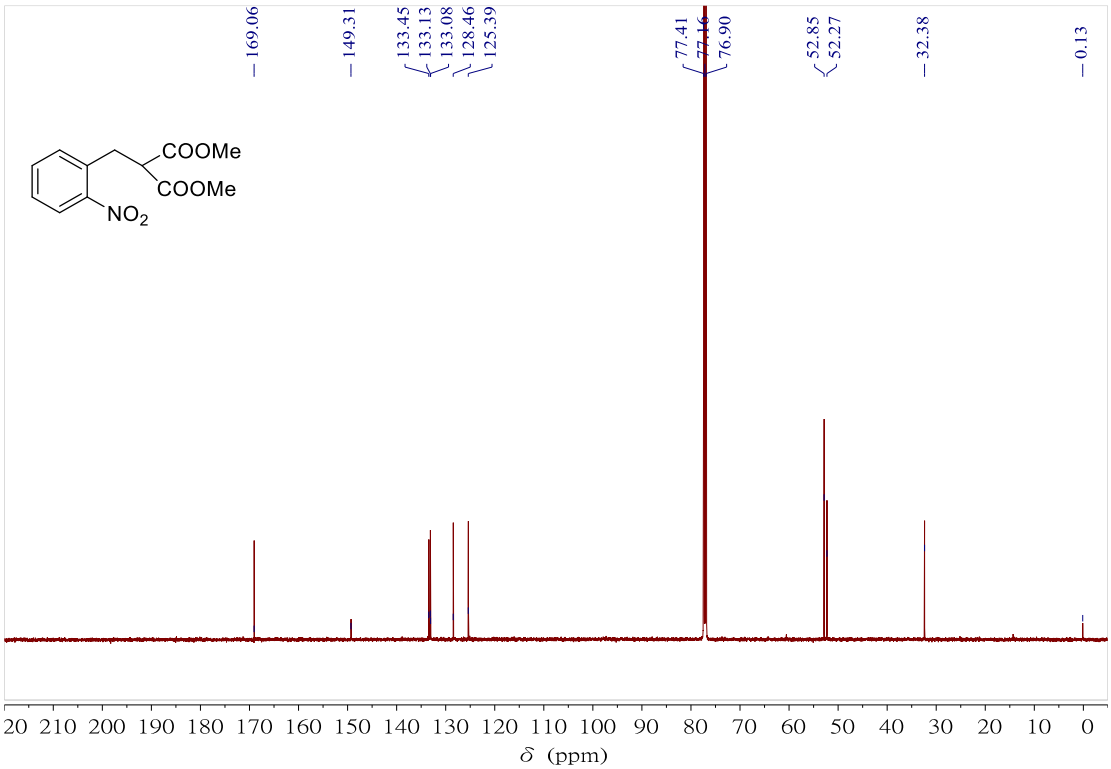
^{1}H NMR Spectrum of **S2** in $CDCl_3$ (500 MHz)



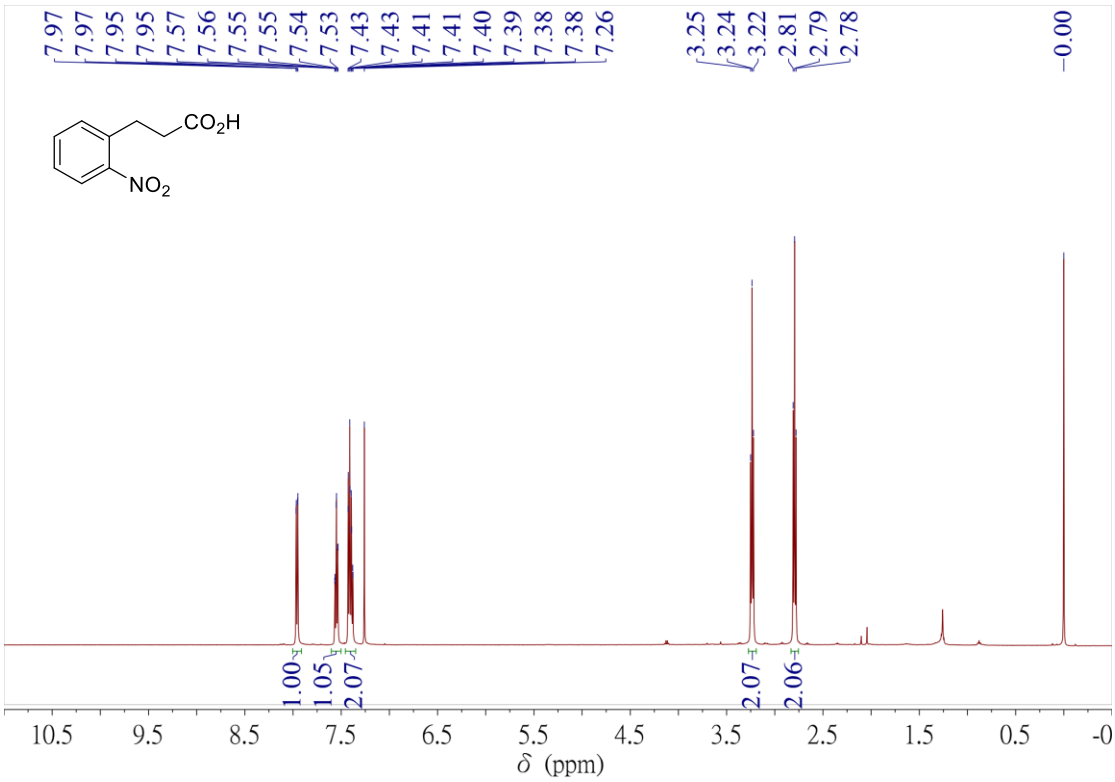
^{13}C NMR Spectrum of **S2** in $CDCl_3$ (125 MHz)



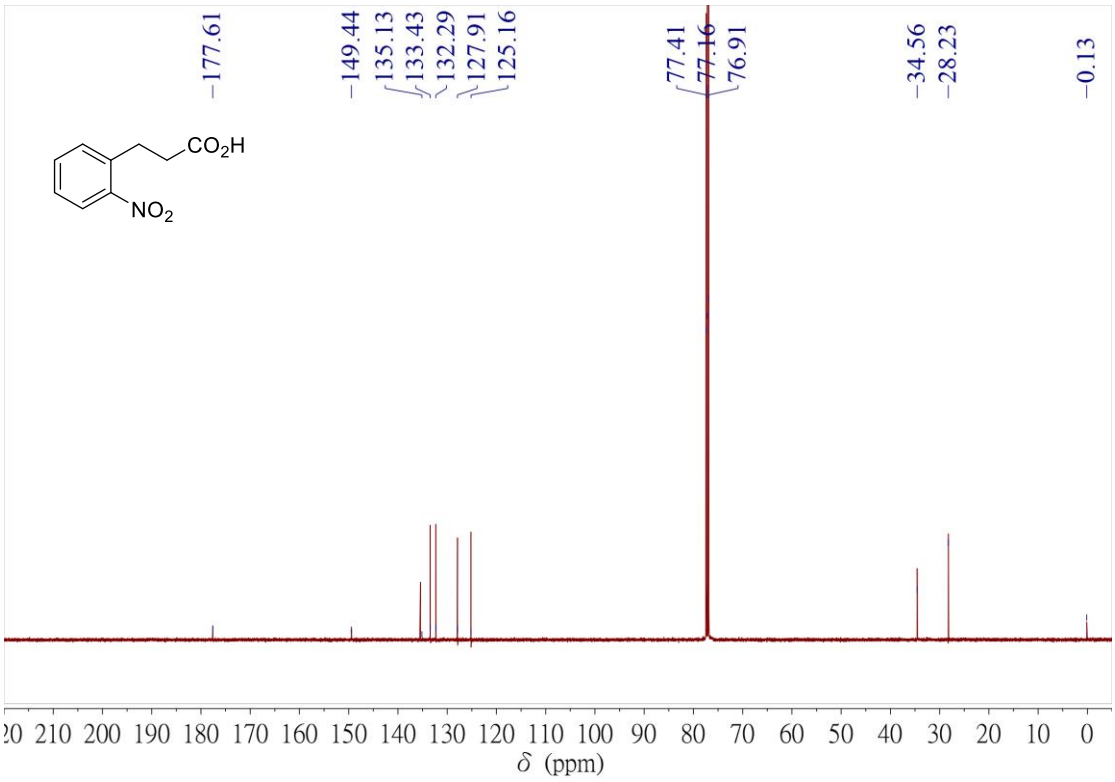
^{1}H NMR Spectrum of **dimethyl 2-(2-nitrobenzyl)malonate** in $CDCl_3$ (500 MHz)



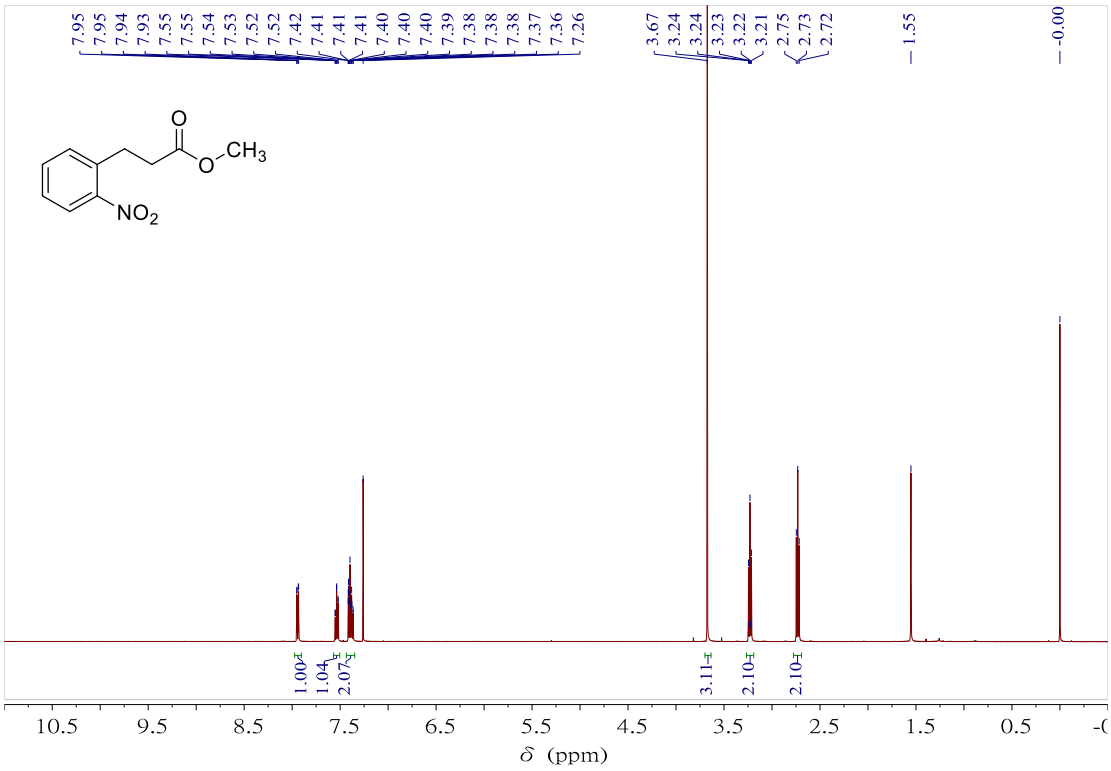
^{13}C NMR Spectrum of **dimethyl 2-(2-nitrobenzyl)malonate** in $CDCl_3$ (125 MHz)



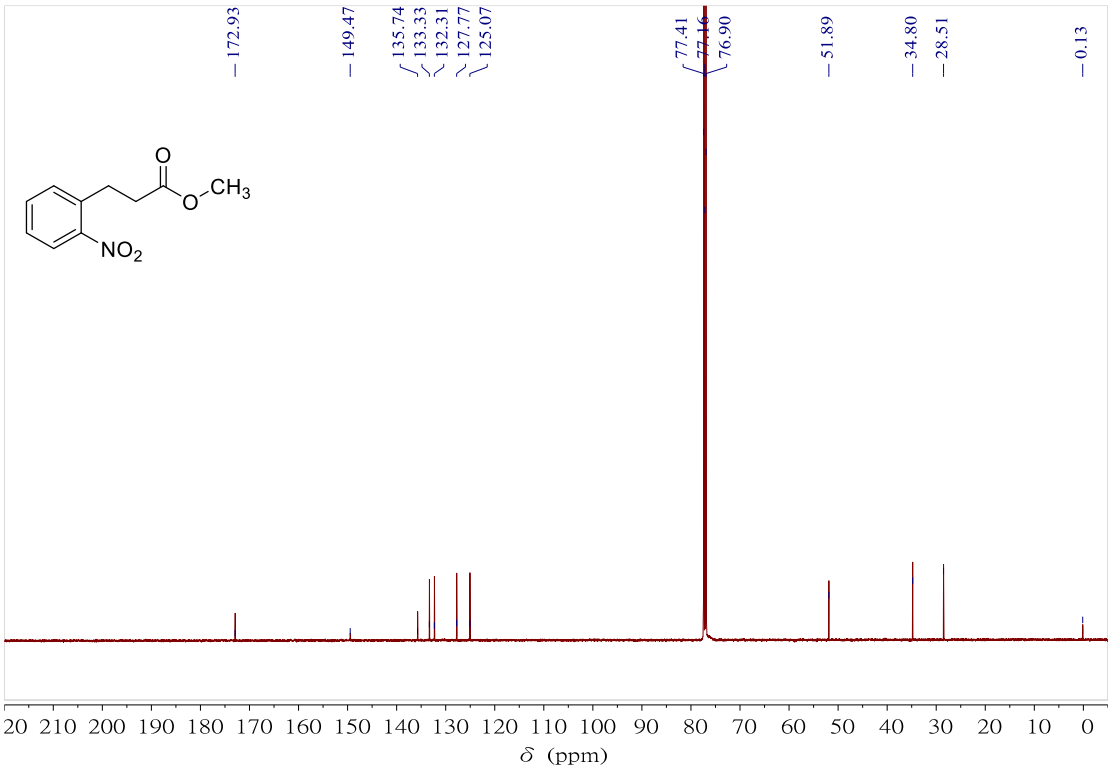
^{1}H NMR Spectrum of **S3** in $CDCl_3$ (500 MHz)



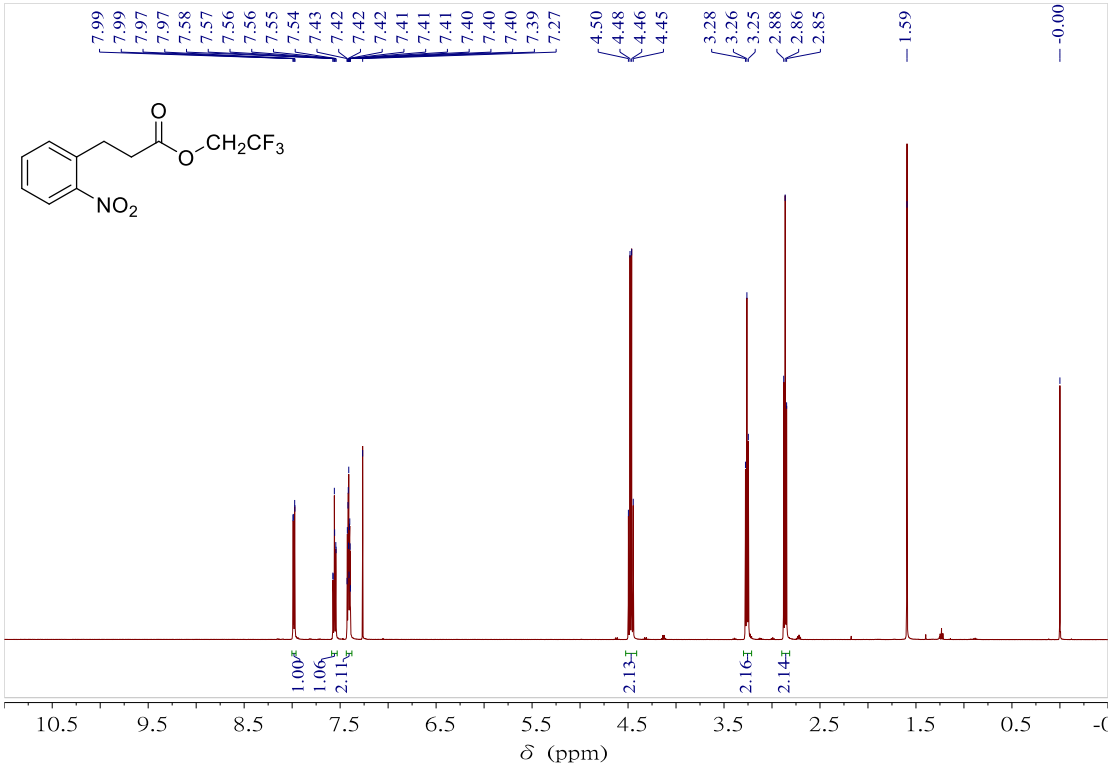
^{13}C NMR Spectrum of **S3** in $CDCl_3$ (125 MHz)



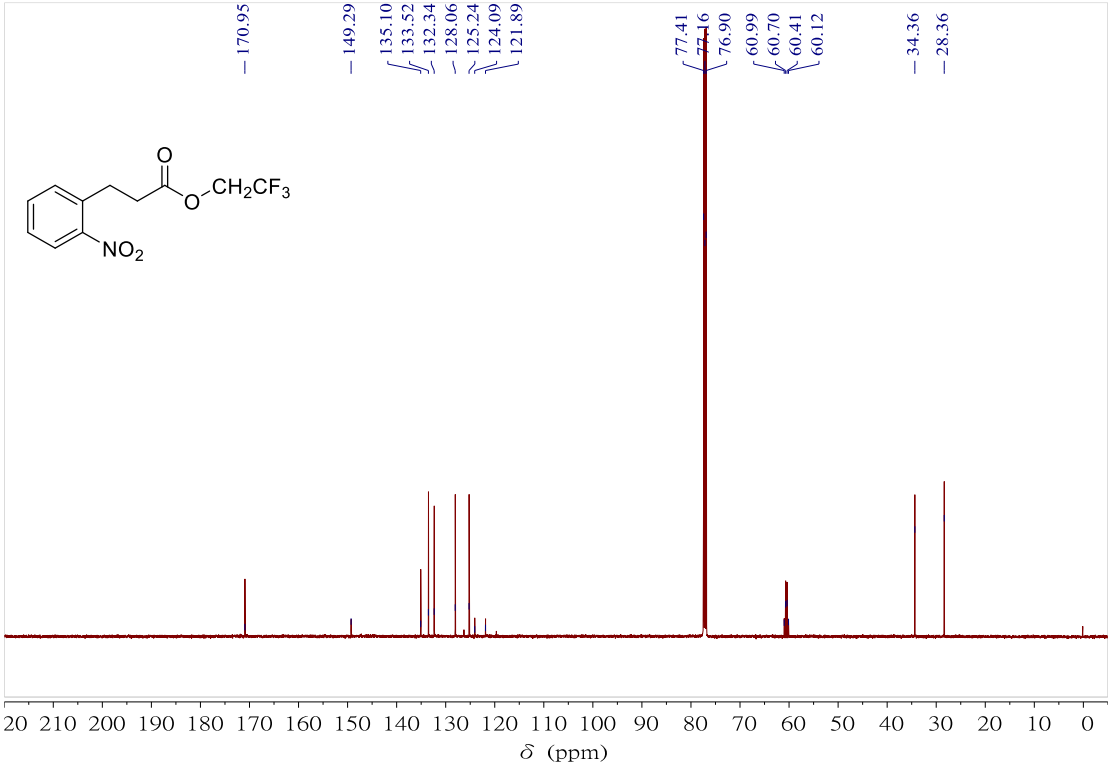
^{1}H NMR Spectrum of **S4** in $CDCl_3$ (500 MHz)



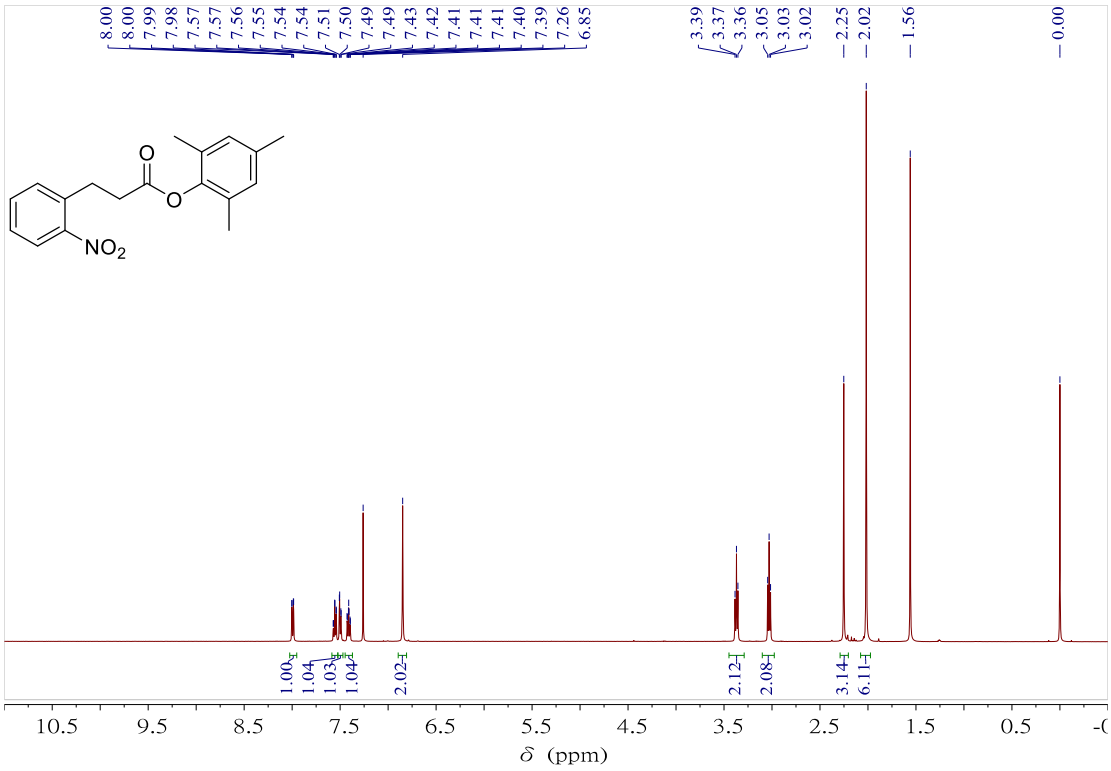
^{13}C NMR Spectrum of **S4** in $CDCl_3$ (125 MHz)



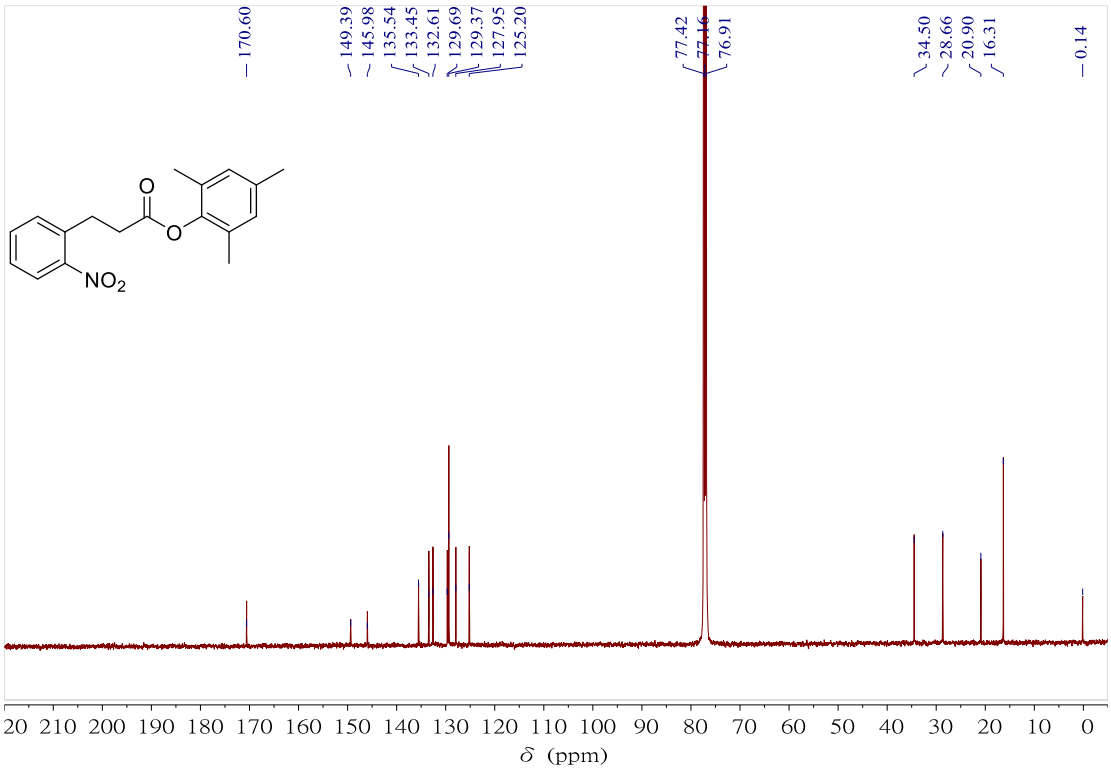
^{1}H NMR Spectrum of **S5** in $CDCl_3$ (500 MHz)



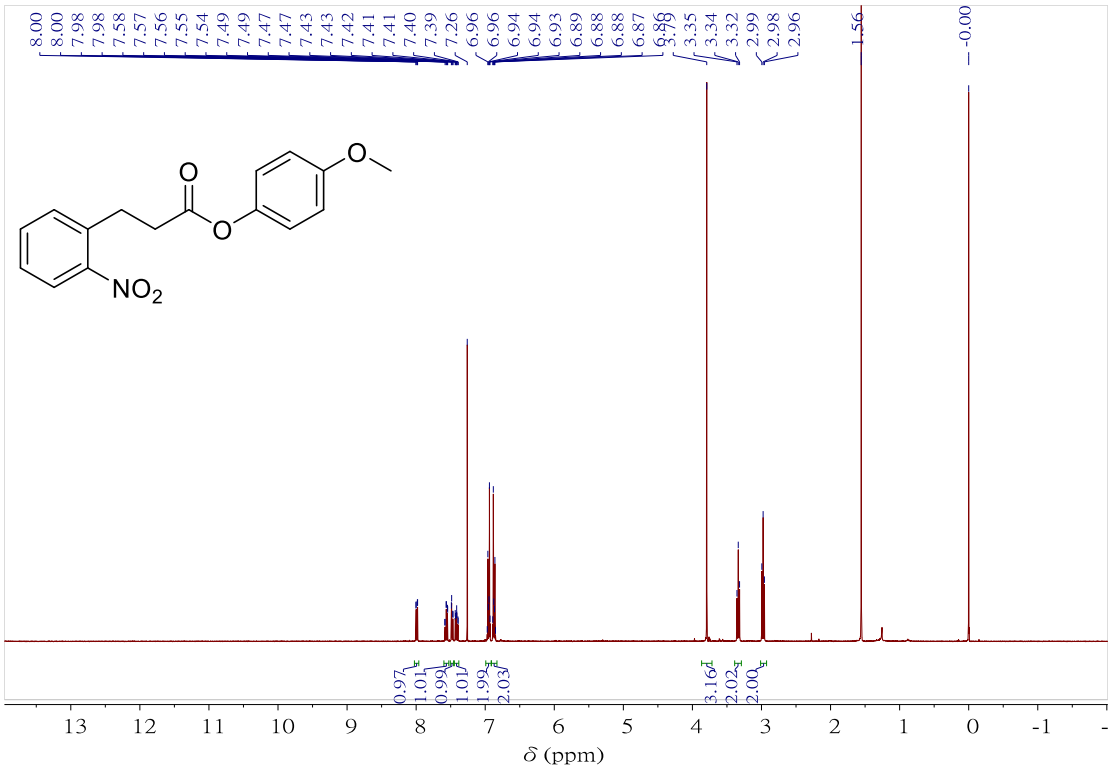
^{13}C NMR Spectrum of **S5** in $CDCl_3$ (125 MHz)



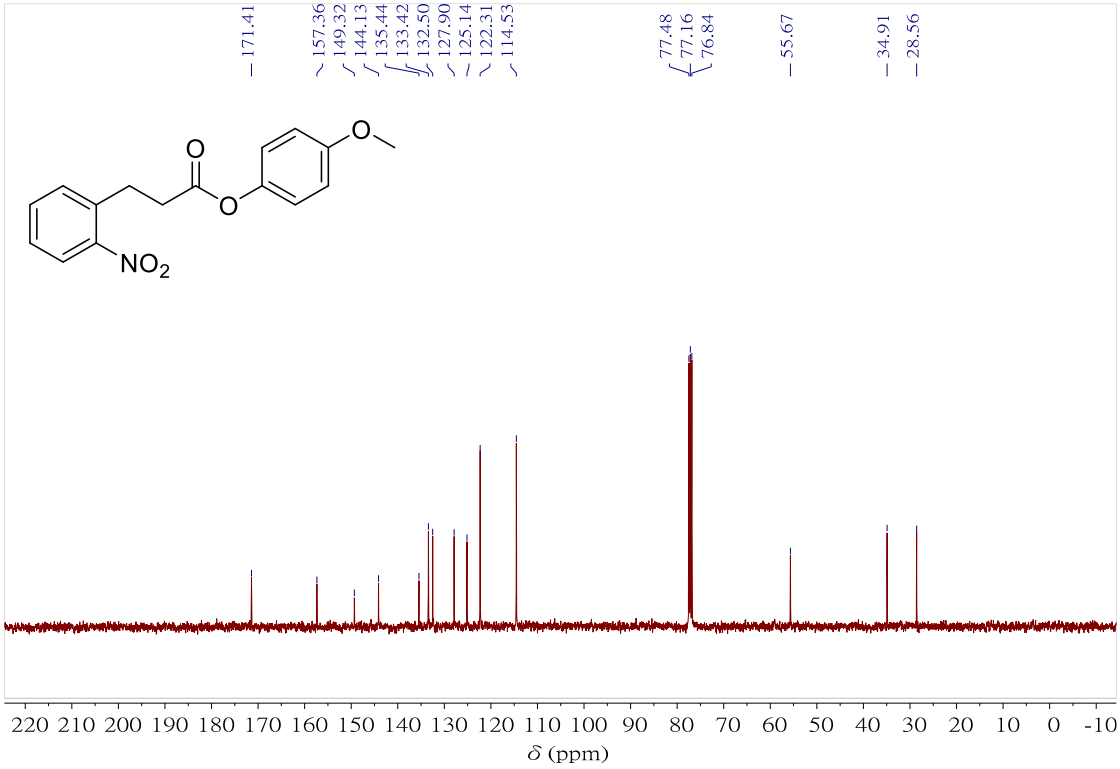
^{1}H NMR Spectrum of **S6** in $CDCl_3$ (500 MHz)



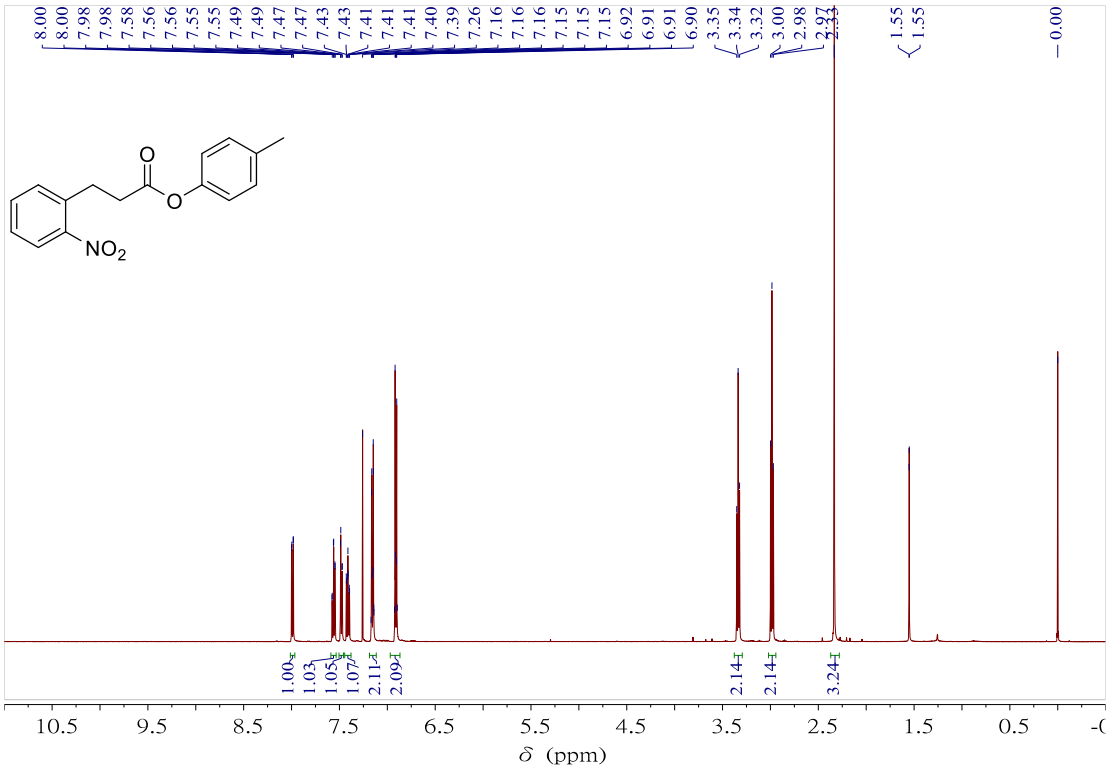
^{13}C NMR Spectrum of **S6** in $CDCl_3$ (125 MHz)



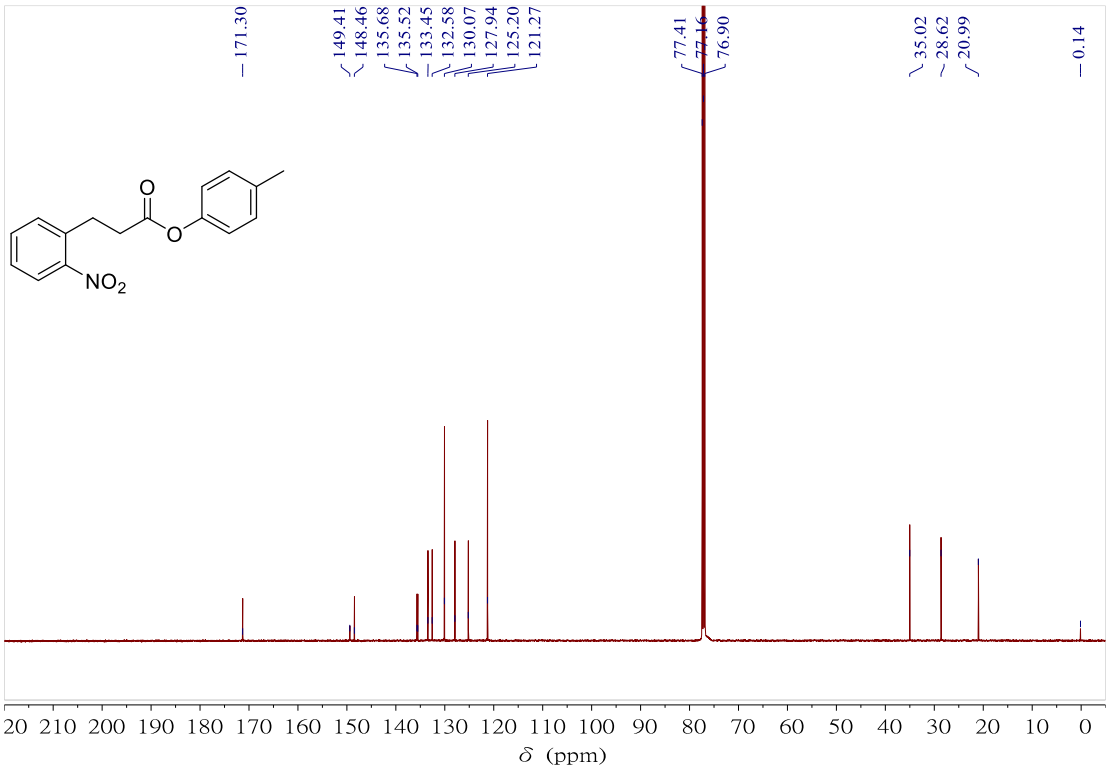
^{1}H NMR Spectrum of **S7** in $CDCl_3$ (400 MHz)



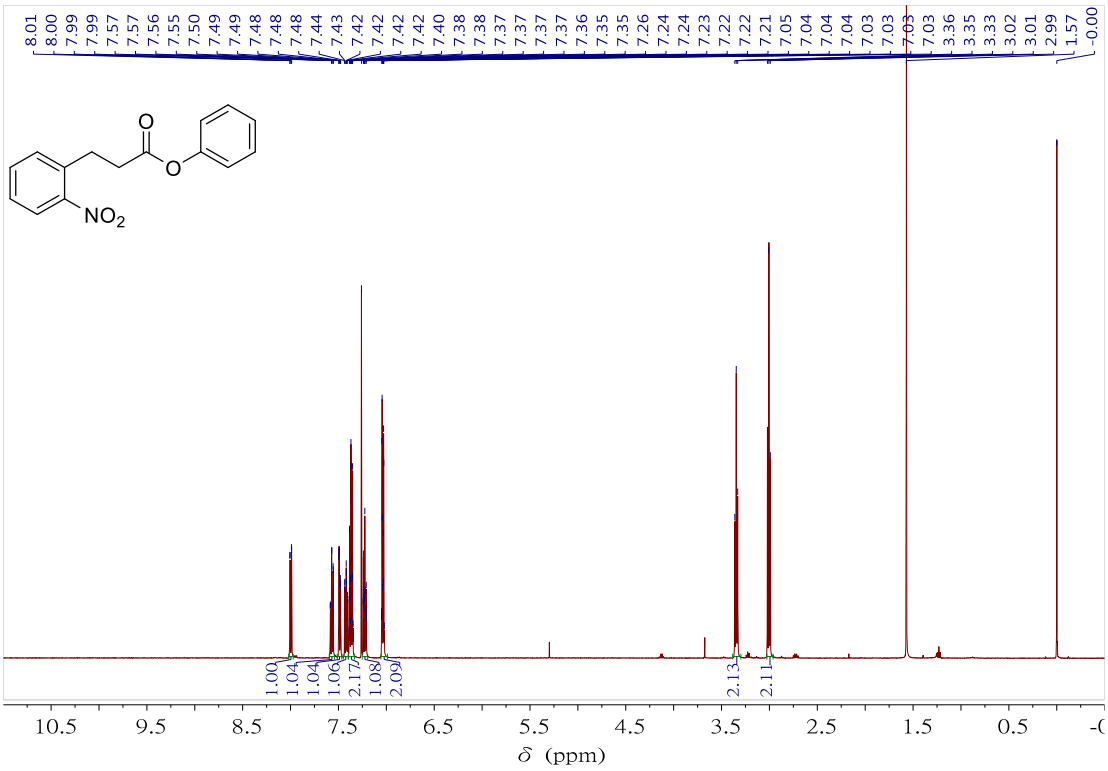
^{13}C NMR Spectrum of **S7** in $CDCl_3$ (100 MHz)



^{1}H NMR Spectrum of **S8** in $CDCl_3$ (500 MHz)



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



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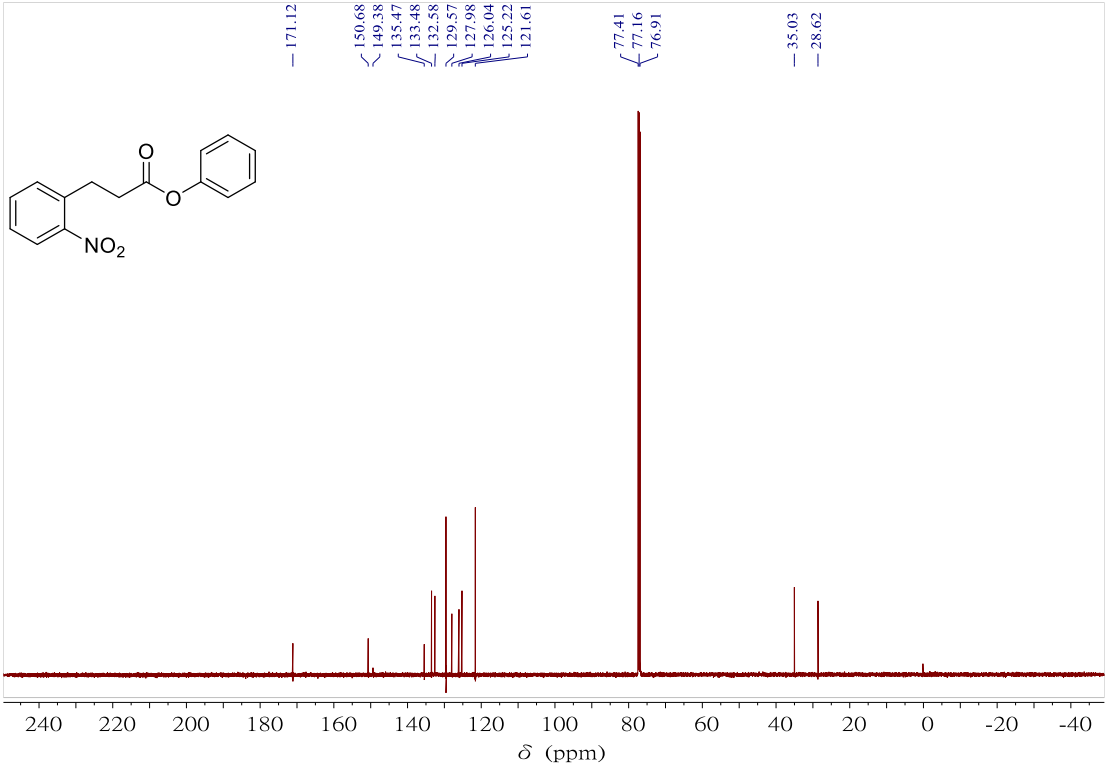
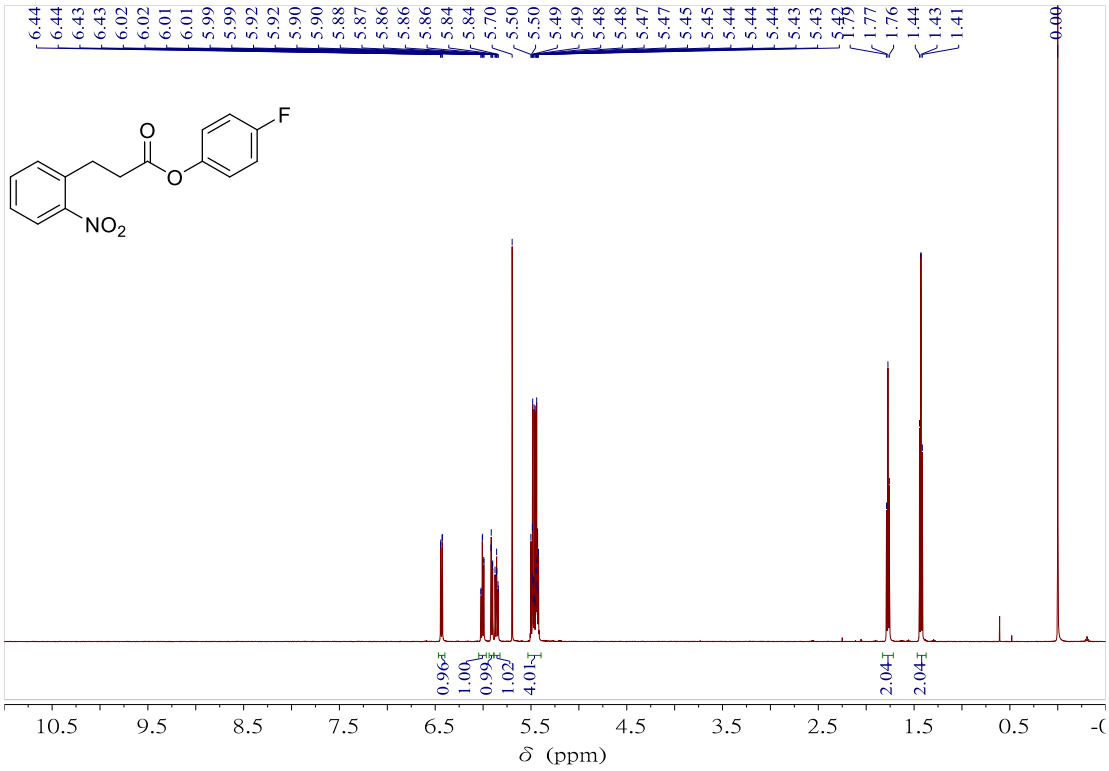
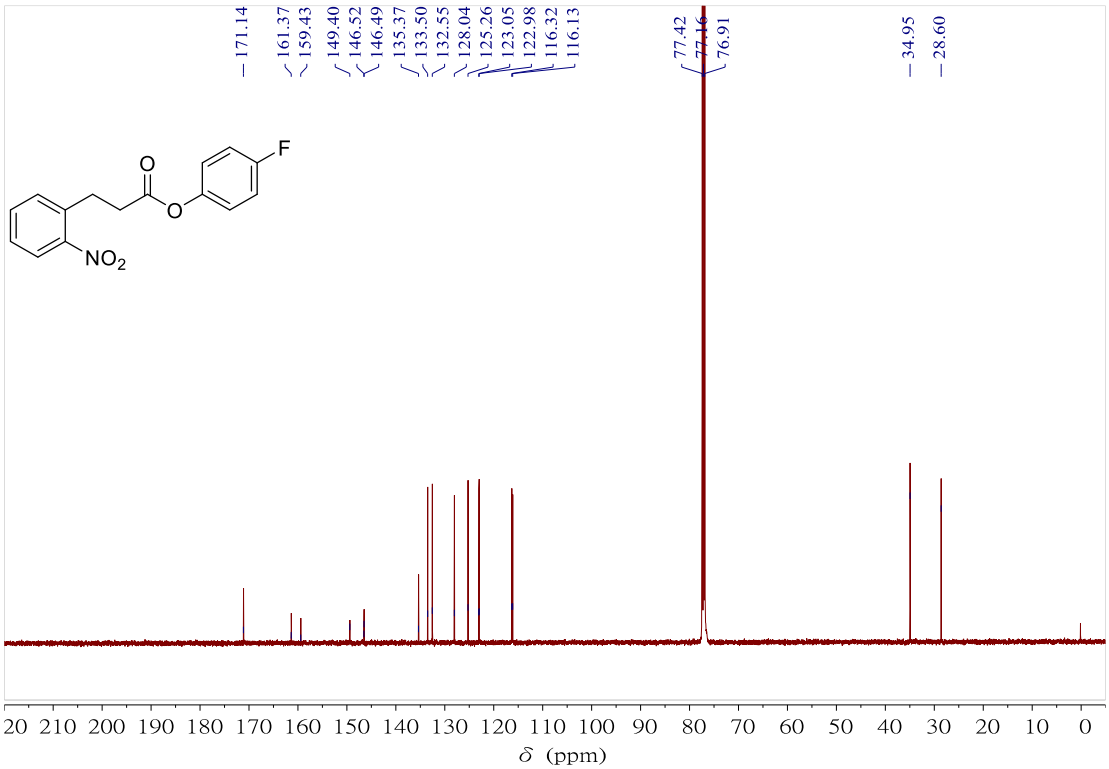


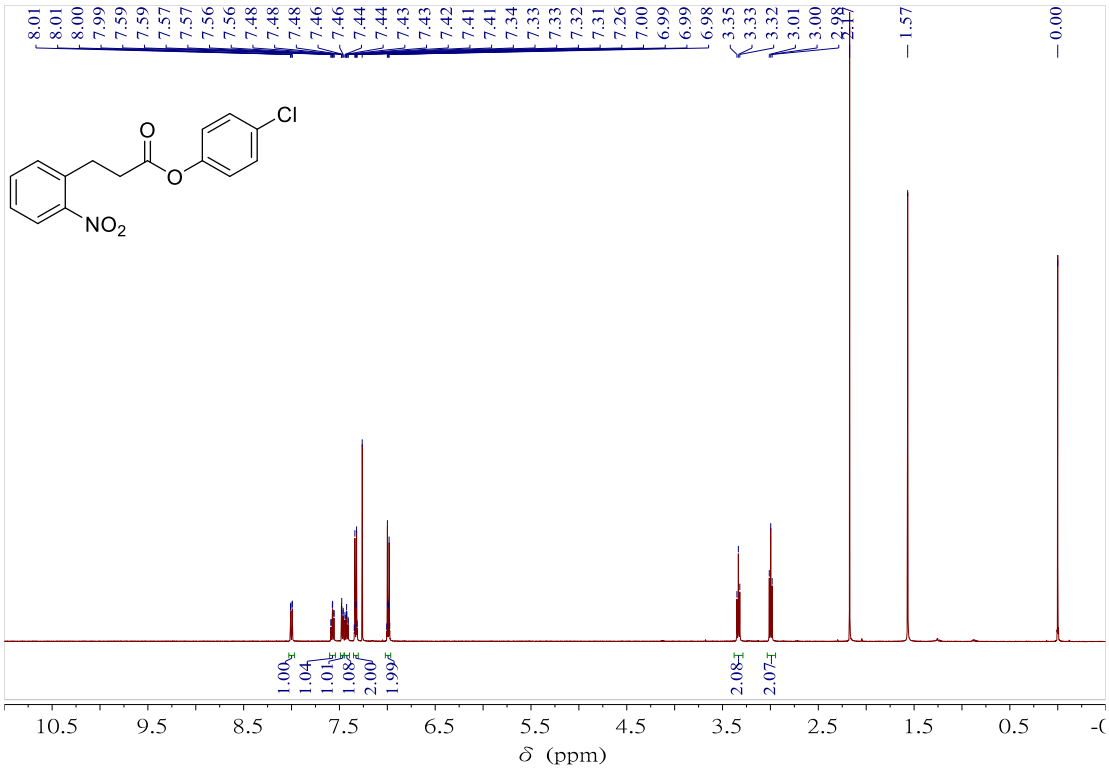
^{13}C NMR Spectrum of **S9** in $CDCl_3$ (125 MHz)



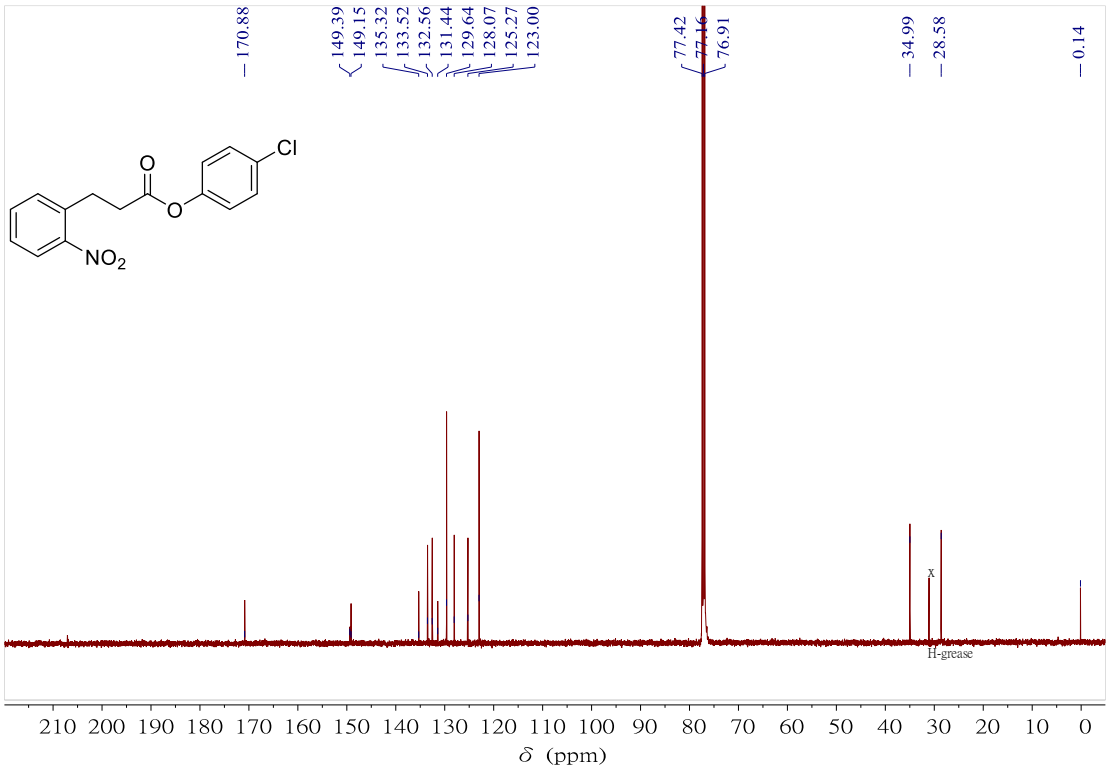
^{1}H NMR Spectrum of **S10** in $CDCl_3$ (500 MHz)



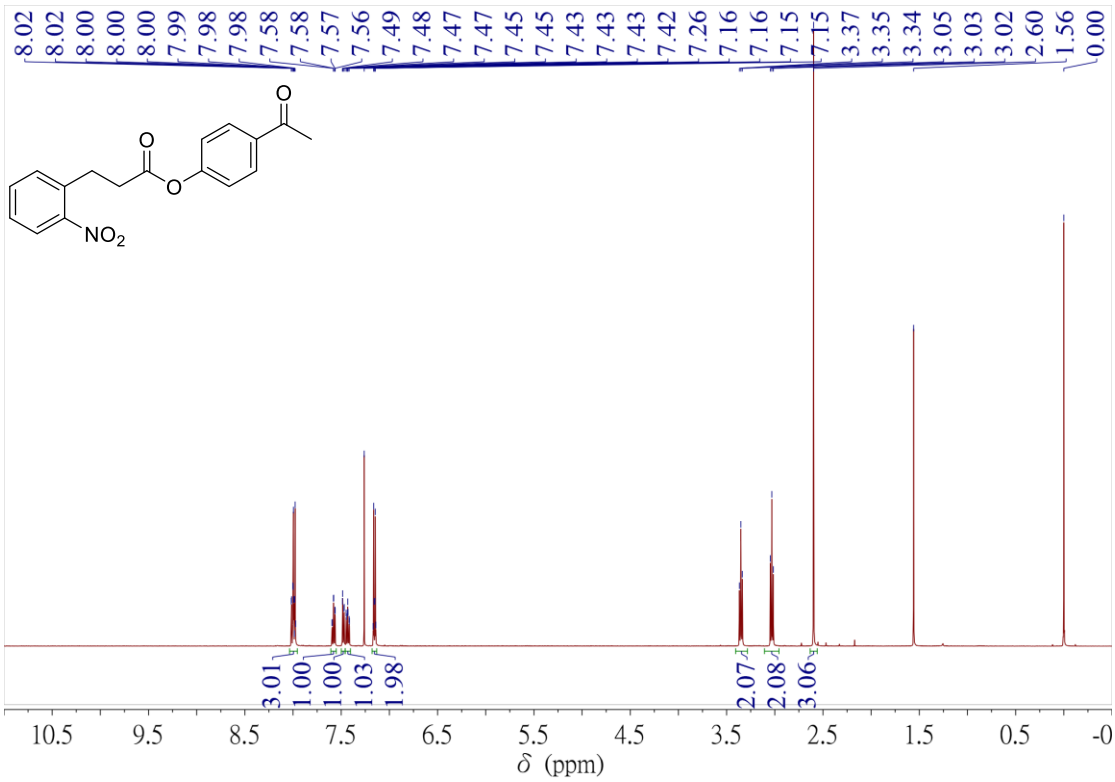
^{13}C NMR Spectrum of **S10** in $CDCl_3$ (125 MHz)



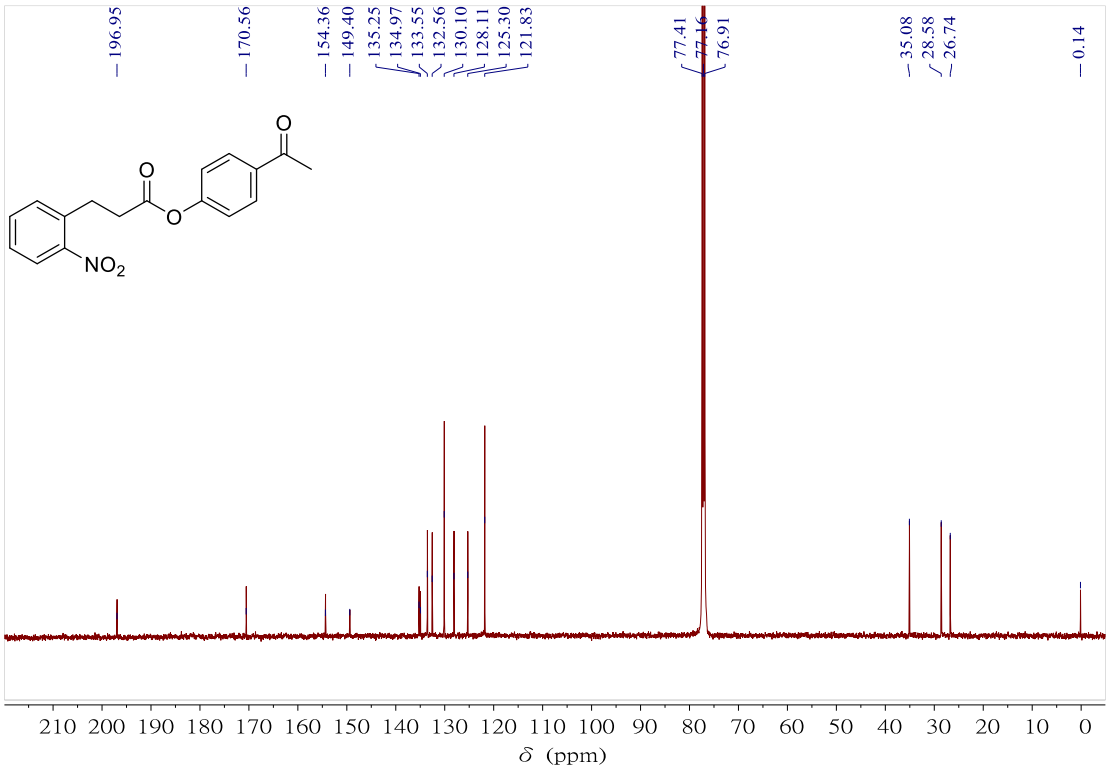
^{1}H NMR Spectrum of **S11** in $CDCl_3$ (500 MHz)



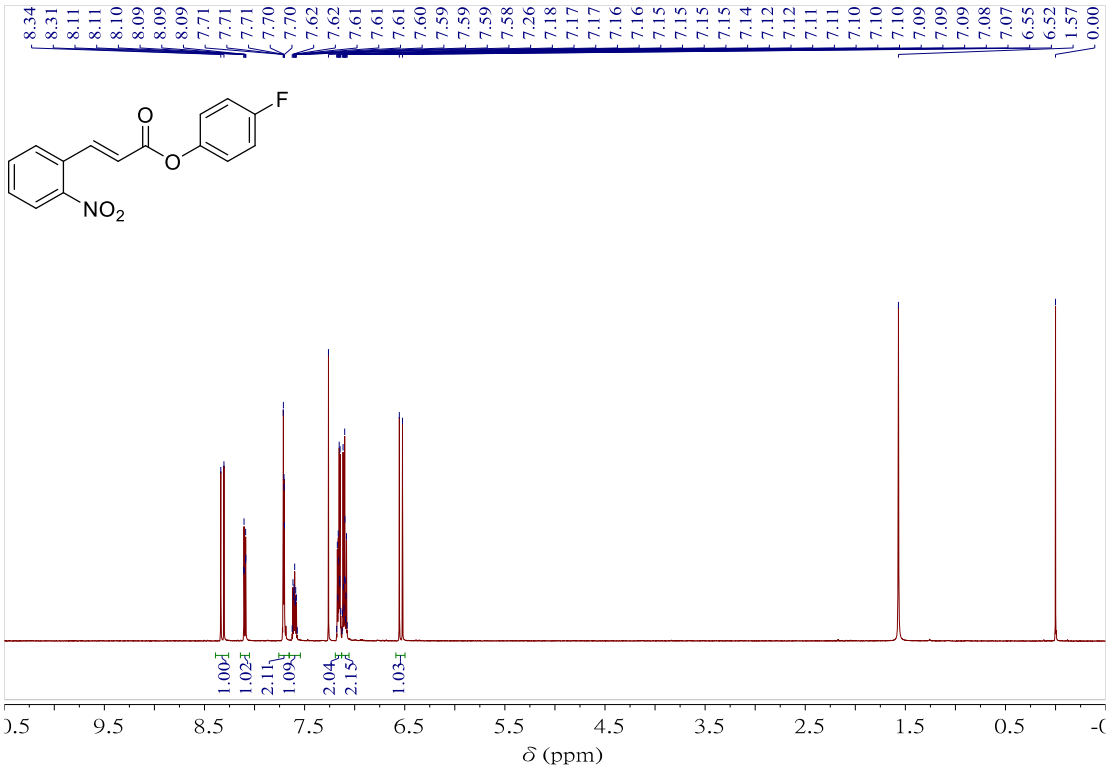
^{13}C NMR Spectrum of **S11** in $CDCl_3$ (125 MHz)



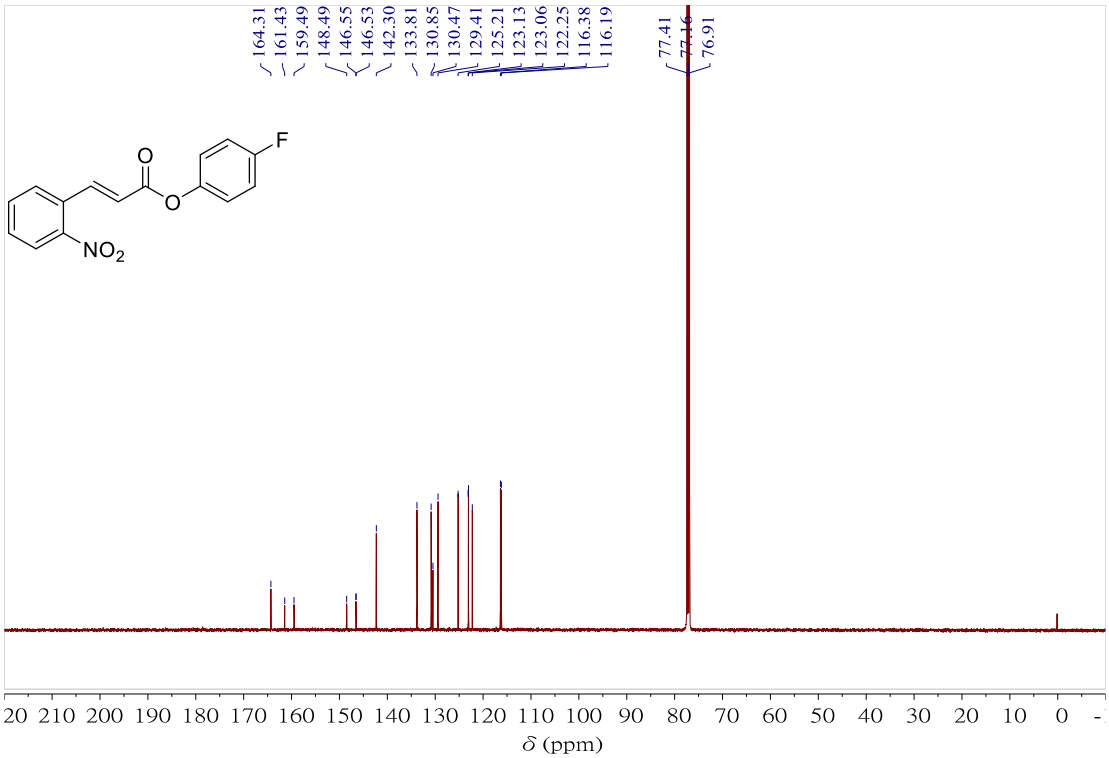
^{1}H NMR Spectrum of **S12** in $CDCl_3$ (500 MHz)



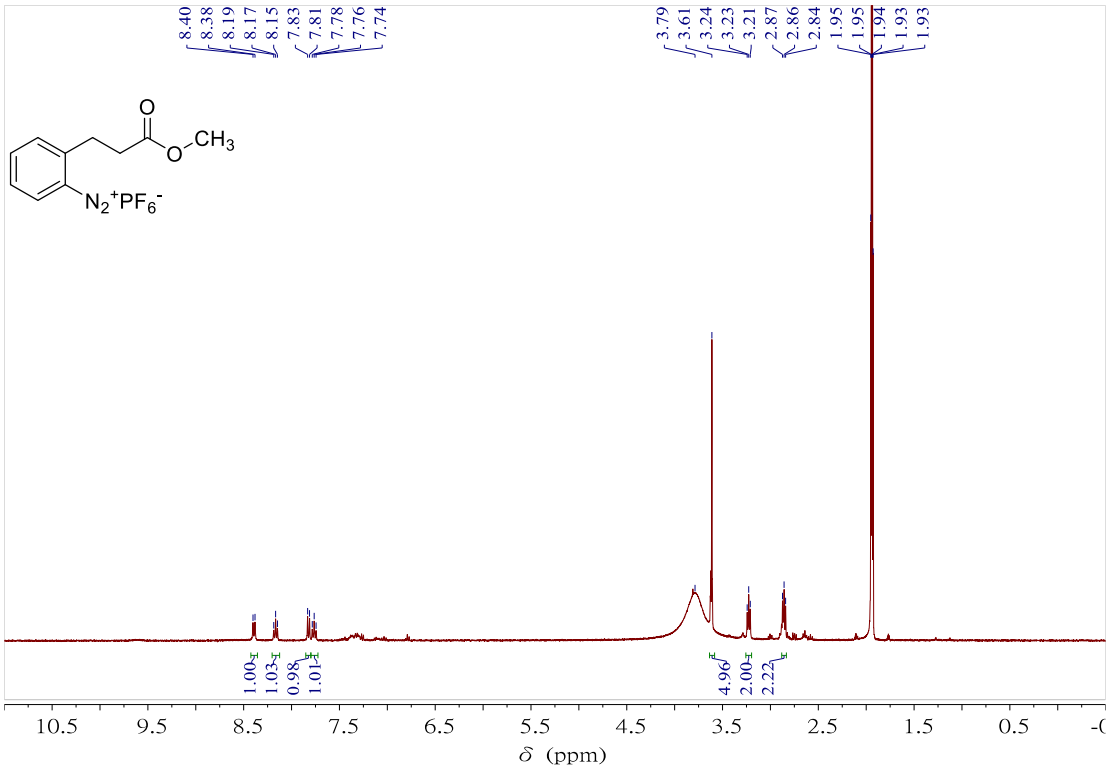
^{13}C NMR Spectrum of **S12** in $CDCl_3$ (125 MHz)



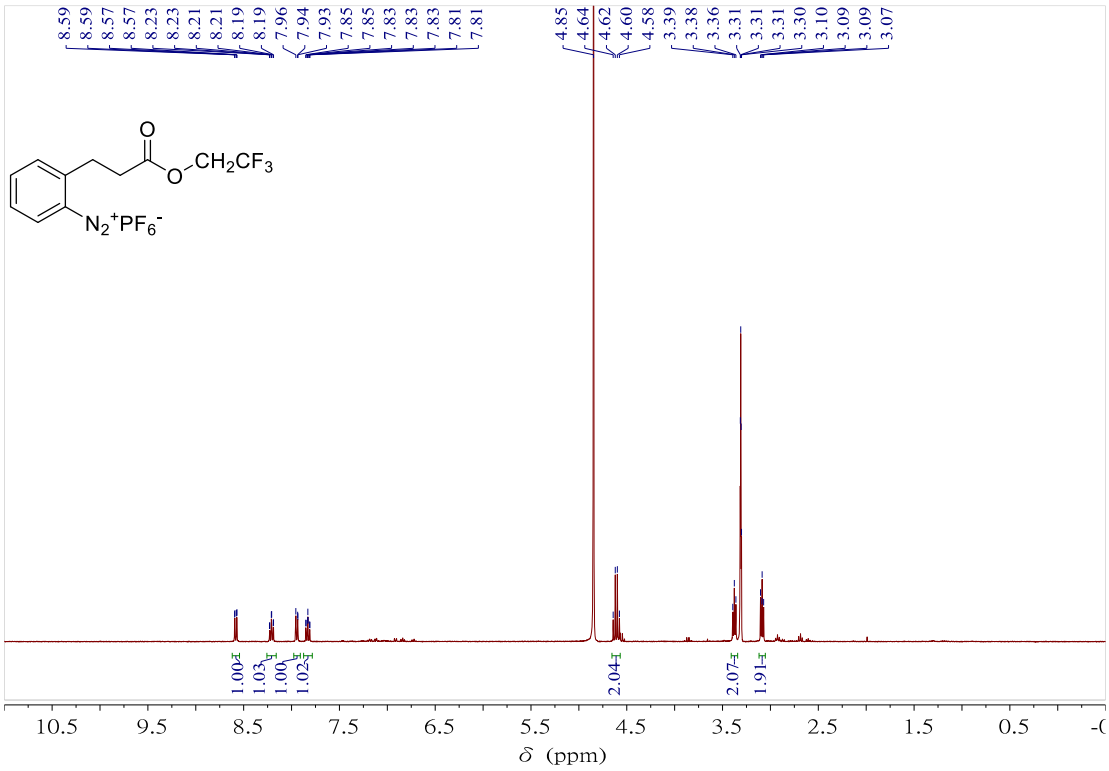
^{1}H NMR Spectrum of **S13** in $CDCl_3$ (500 MHz)



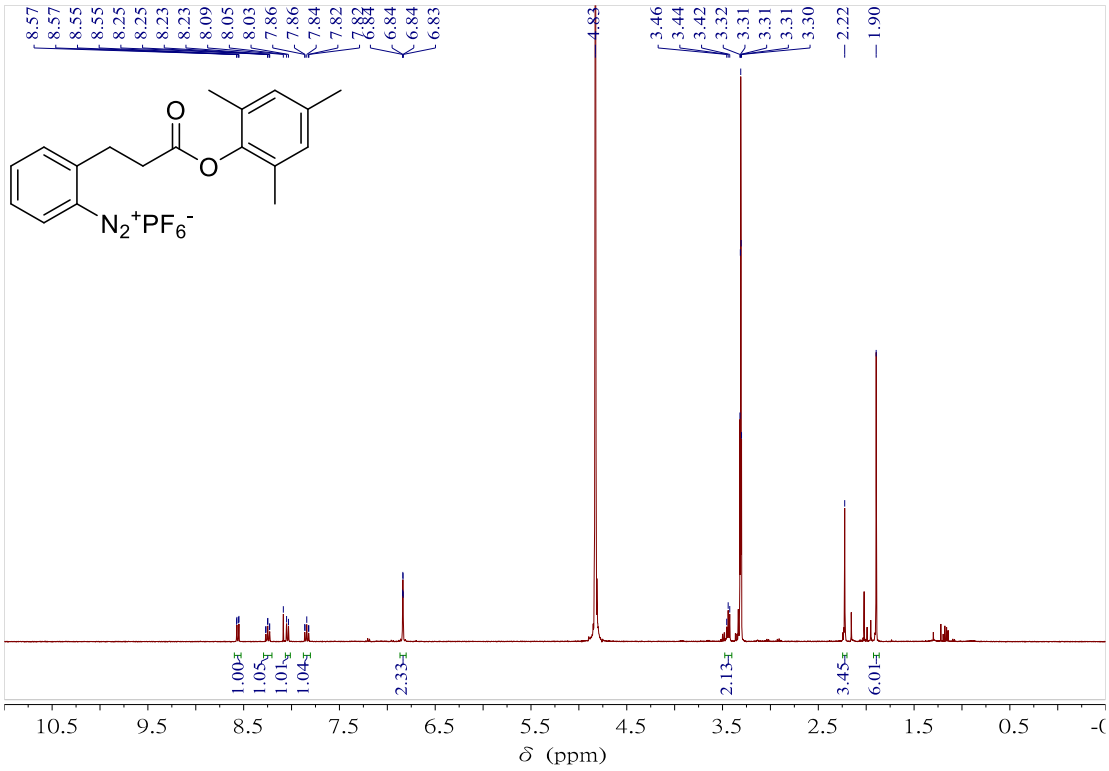
^{13}C NMR Spectrum of **S13** in $CDCl_3$ (125 MHz)



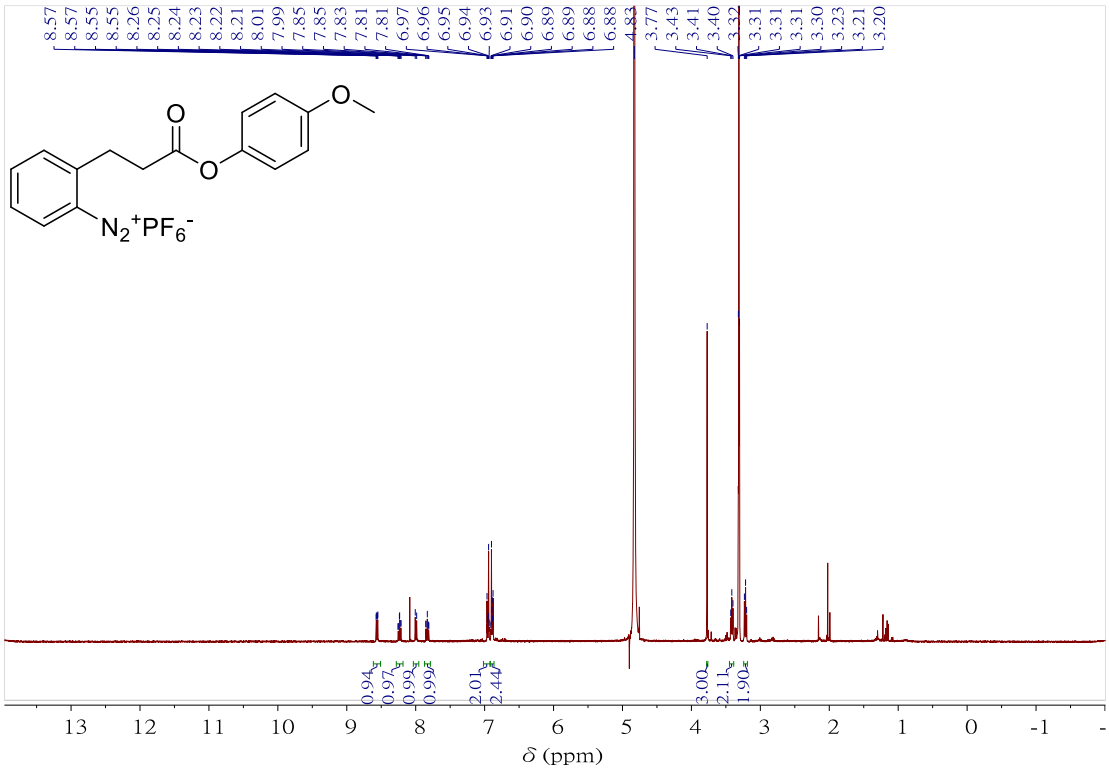
^{1}H NMR Spectrum of **D1** in CD_3CN (400 MHz)



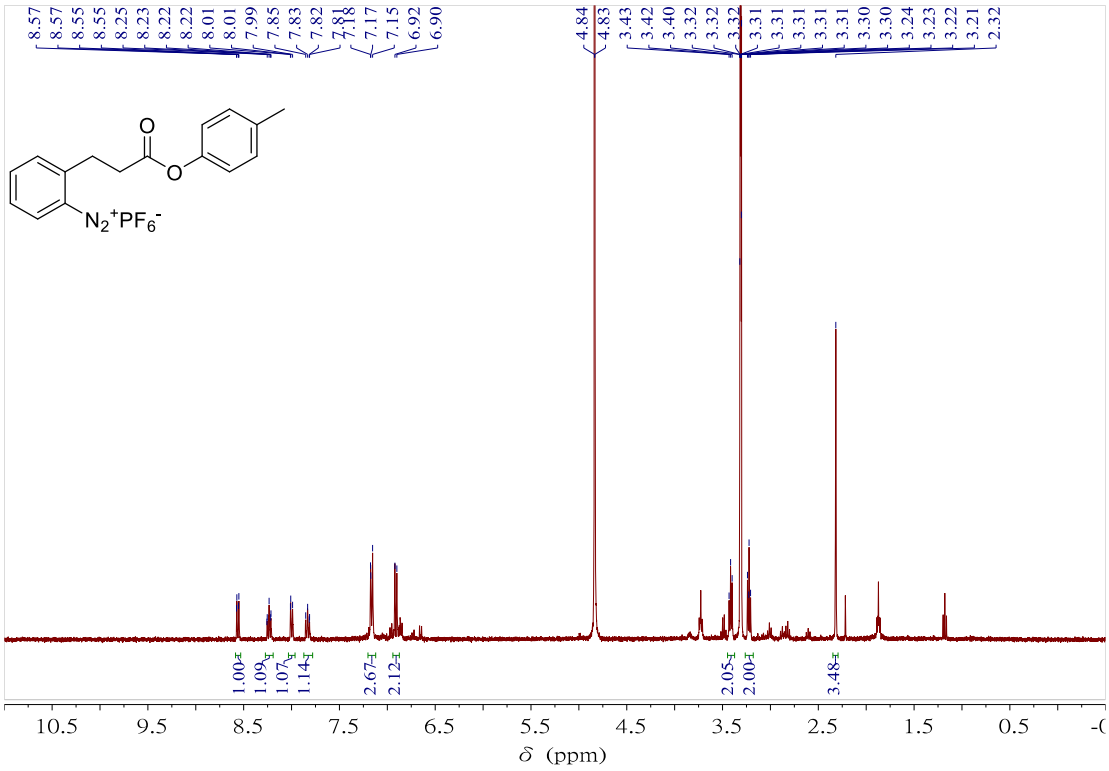
^{1}H NMR Spectrum of **D2** in CD_3OD (400 MHz)



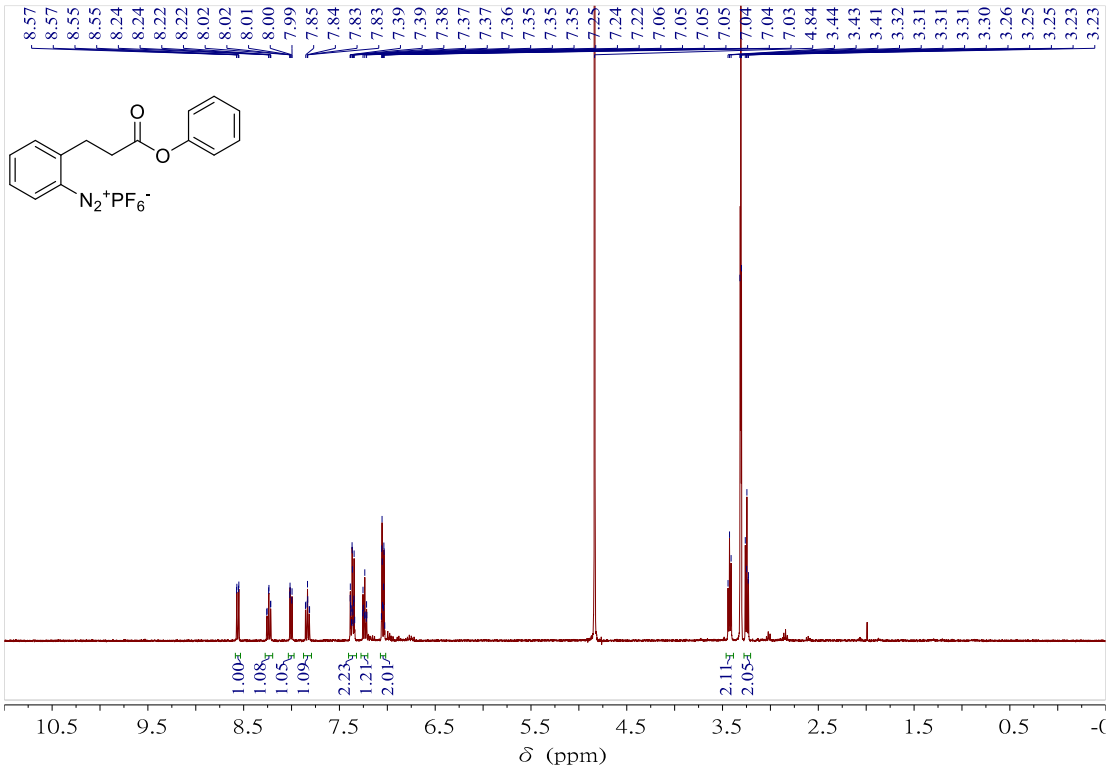
^{1}H NMR Spectrum of **D3** in CD_3OD (400 MHz)



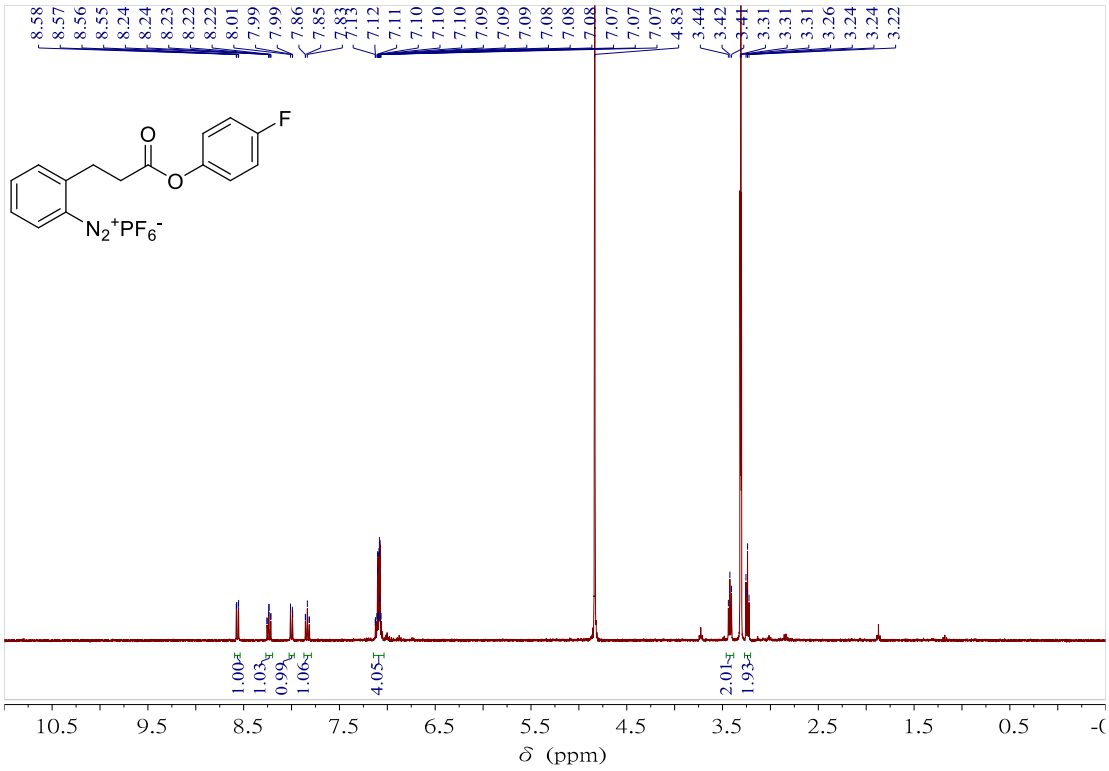
^{1}H NMR Spectrum of **D4** in CD_3OD (400 MHz)



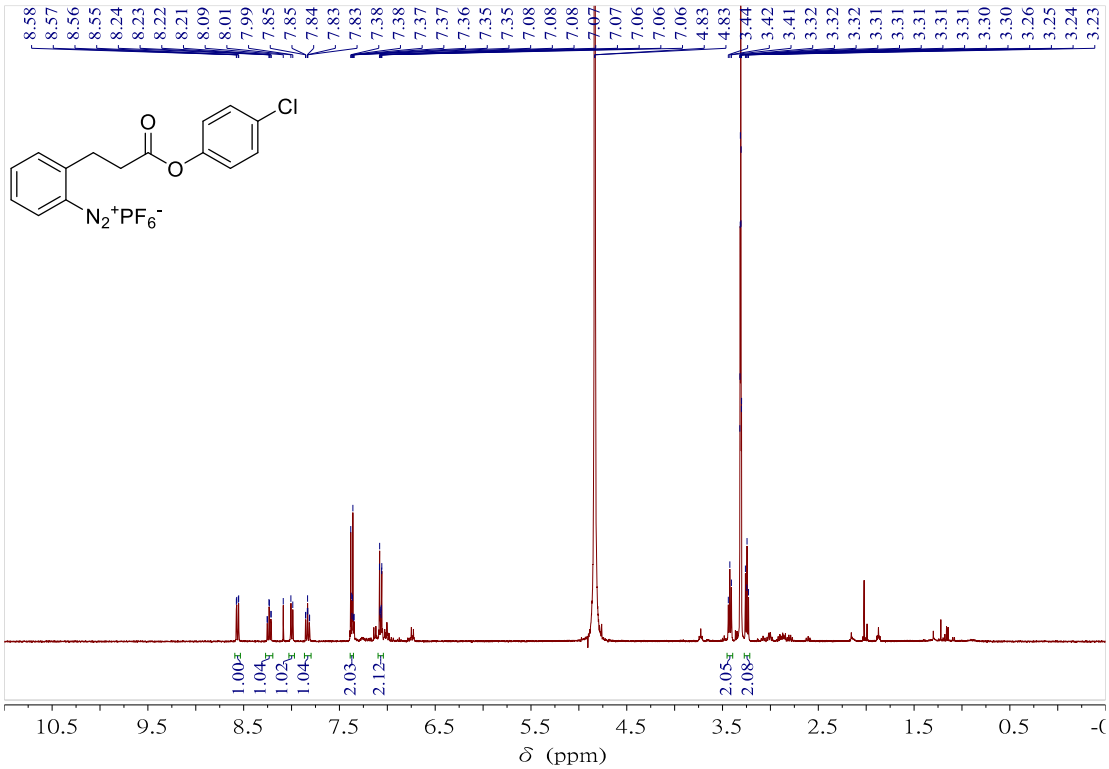
^{1}H NMR Spectrum of **D5** in CD_3OD (400 MHz)



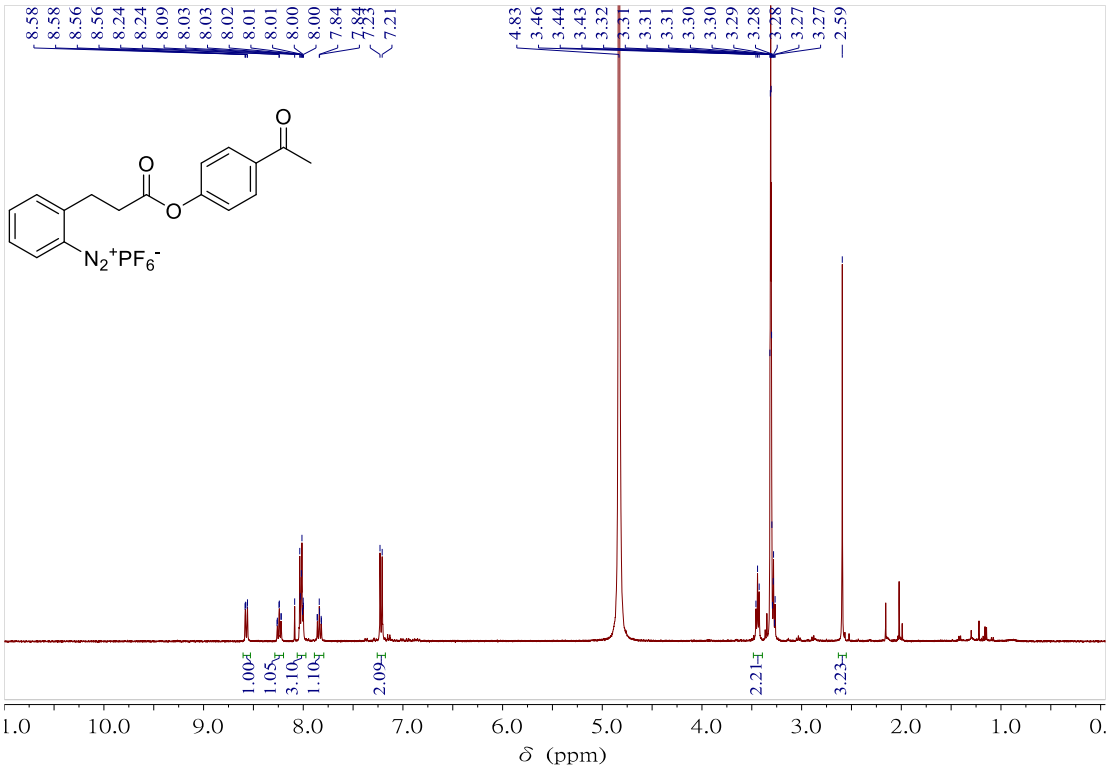
^{1}H NMR Spectrum of **D6** in CD_3OD (400 MHz)



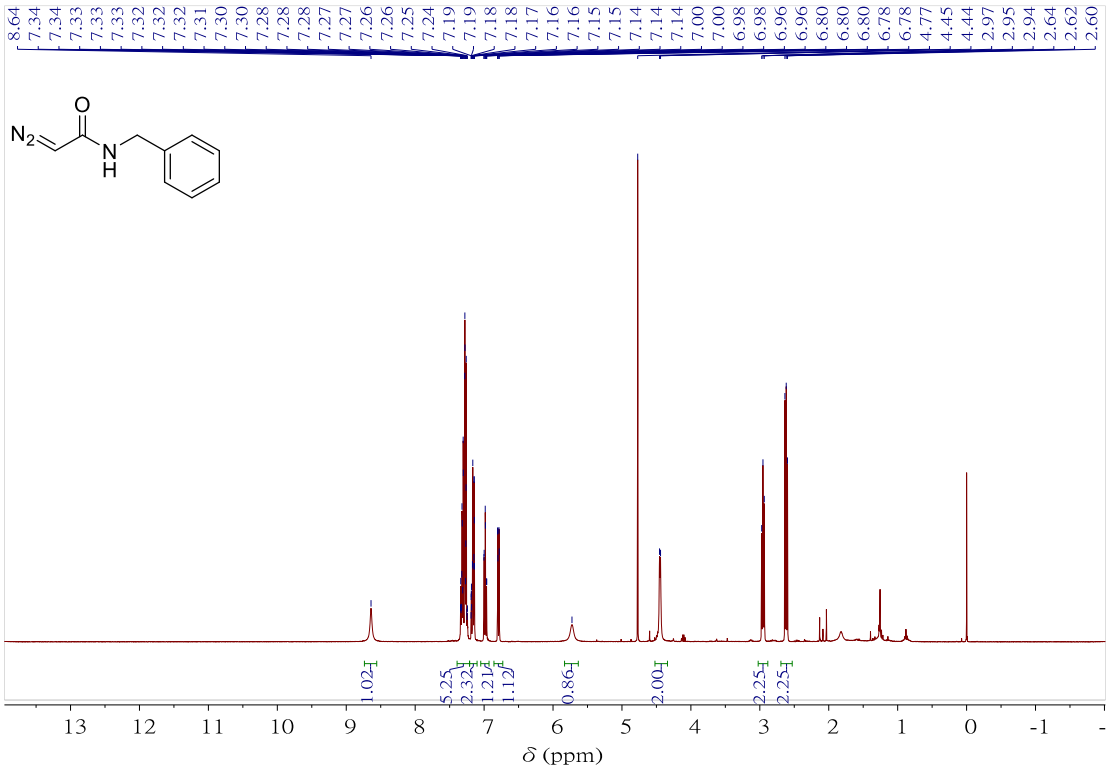
^{1}H NMR Spectrum of **D7** in CD_3OD (400 MHz)



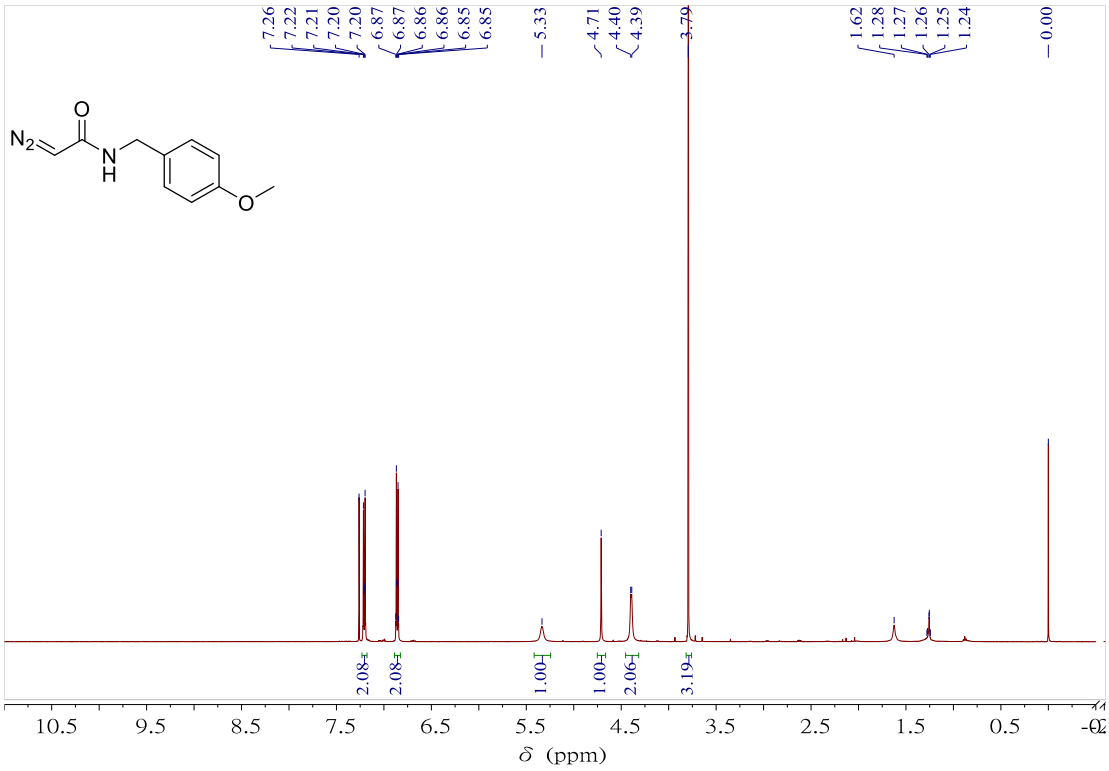
^{1}H NMR Spectrum of **D8** in CD_3OD (400 MHz)



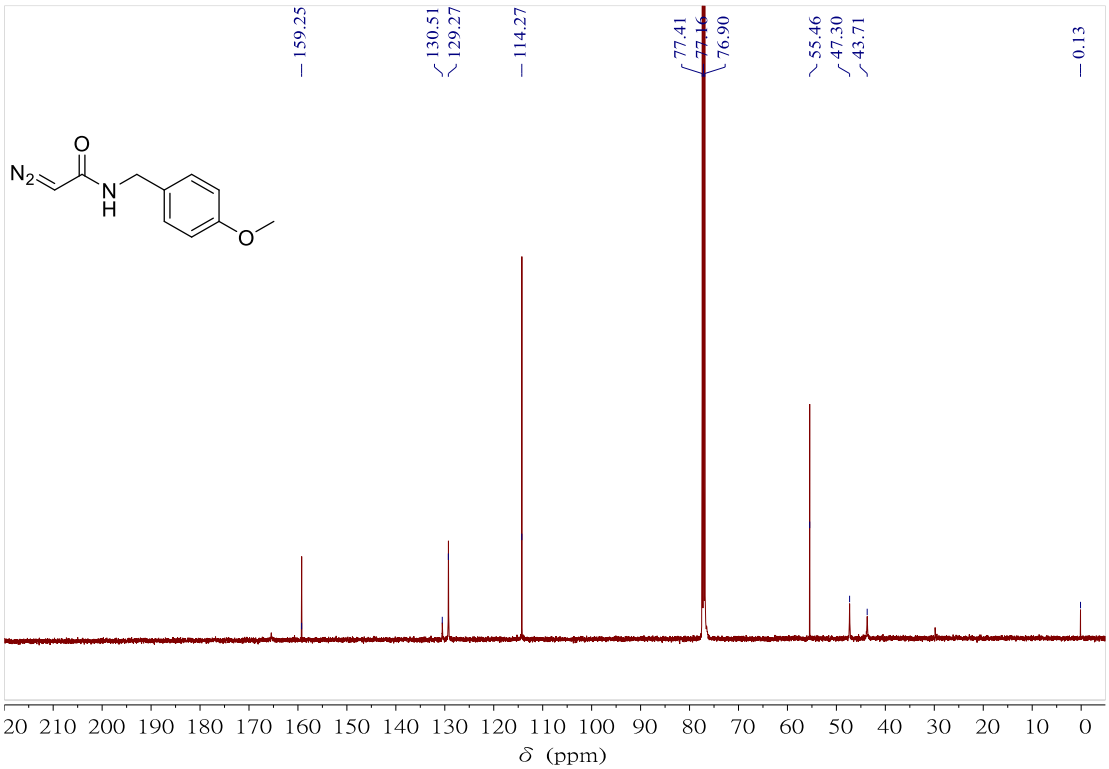
^{1}H NMR Spectrum of **D9** in CD_3OD (400 MHz)



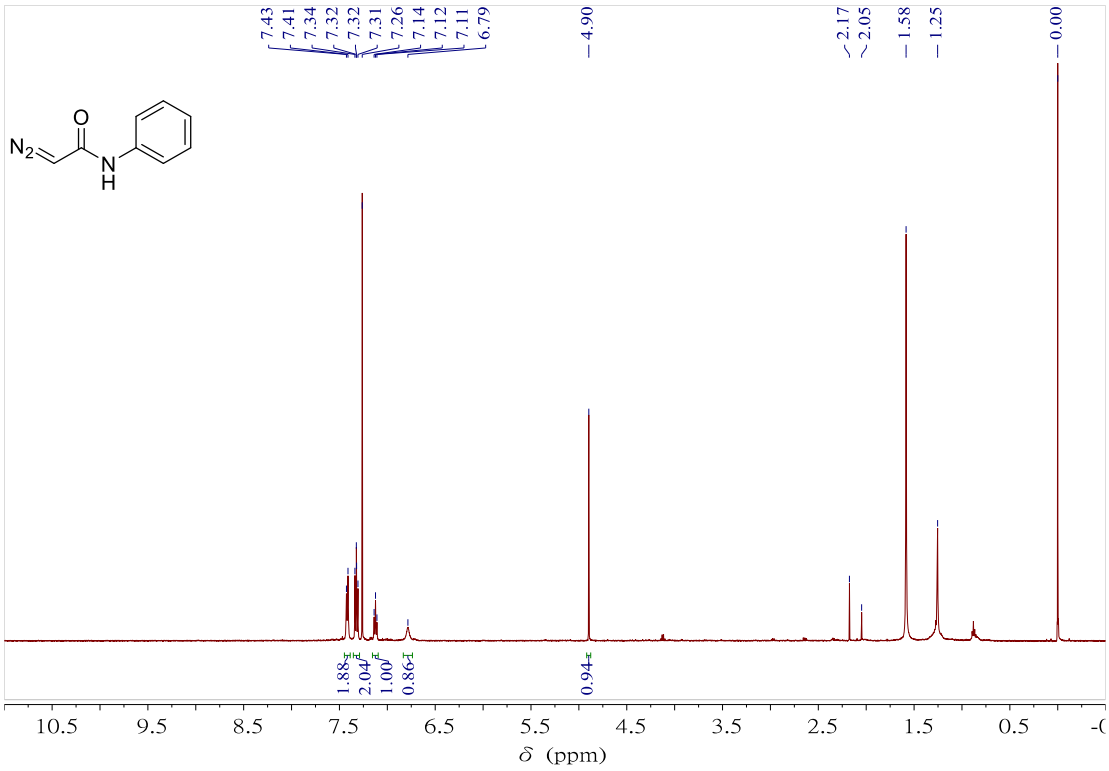
^{1}H NMR Spectrum of **11a** in $CDCl_3$ (400 MHz)



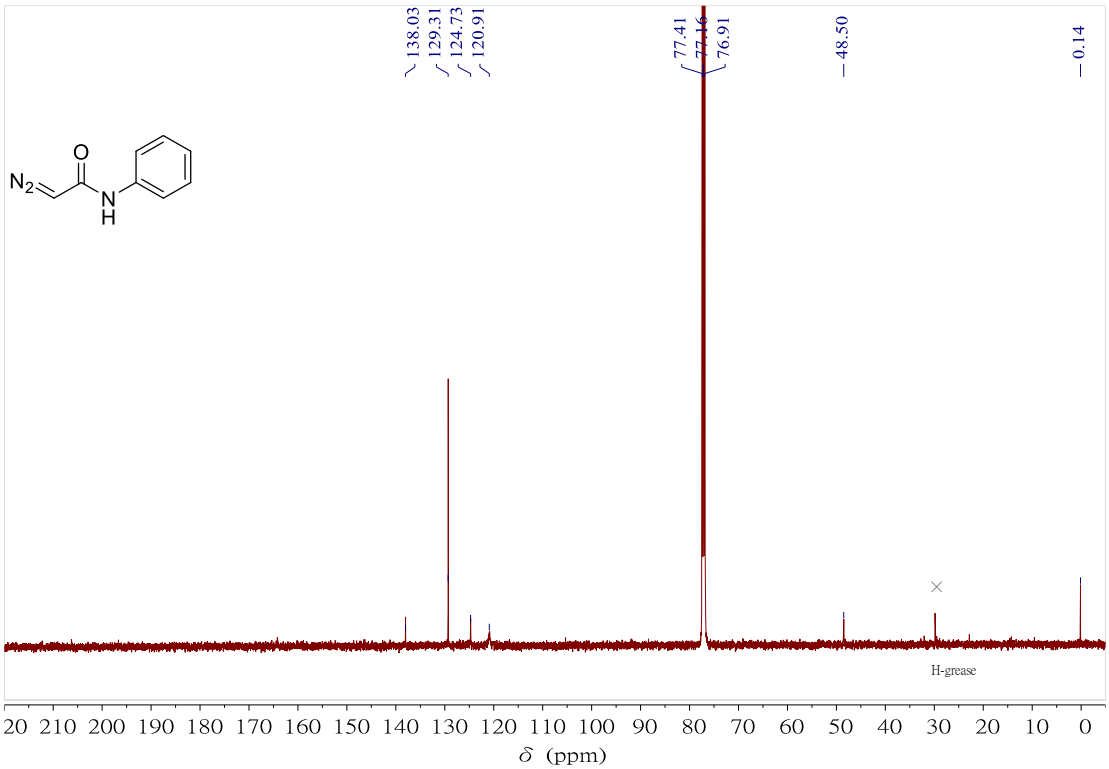
^{1}H NMR Spectrum of **11b** in $CDCl_3$ (500 MHz)



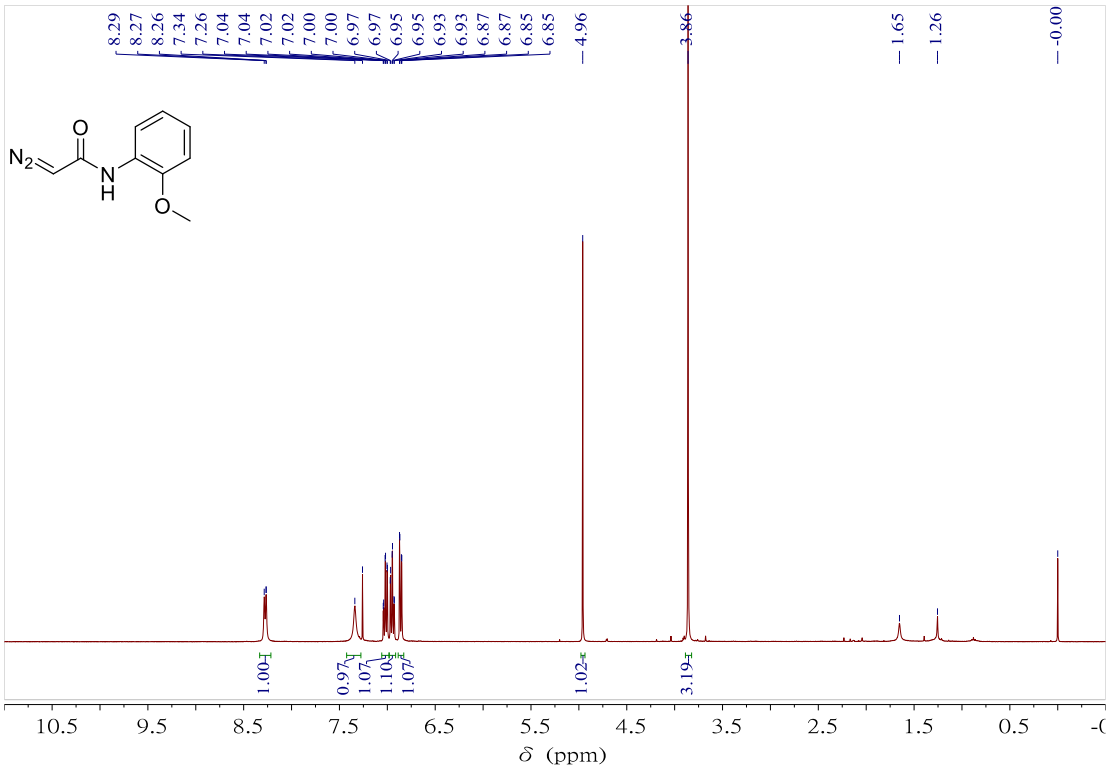
^{13}C NMR Spectrum of **11b** in $CDCl_3$ (125 MHz)



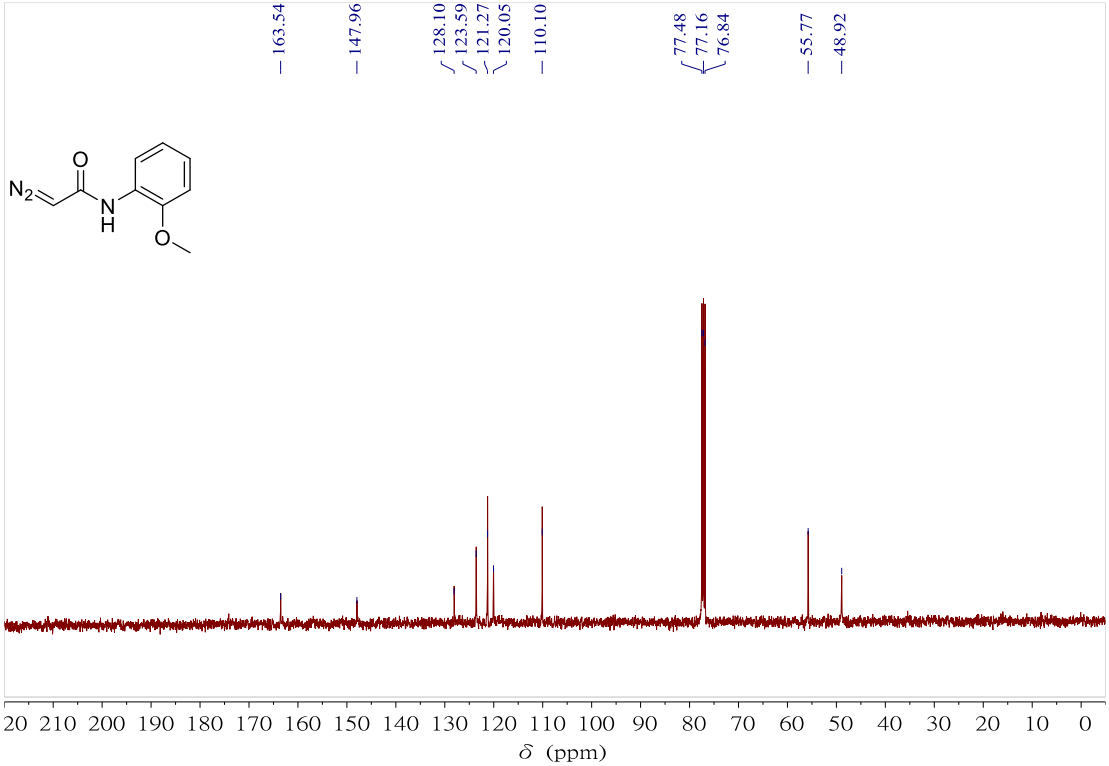
^{1}H NMR Spectrum of **11c** in $CDCl_3$ (500 MHz)



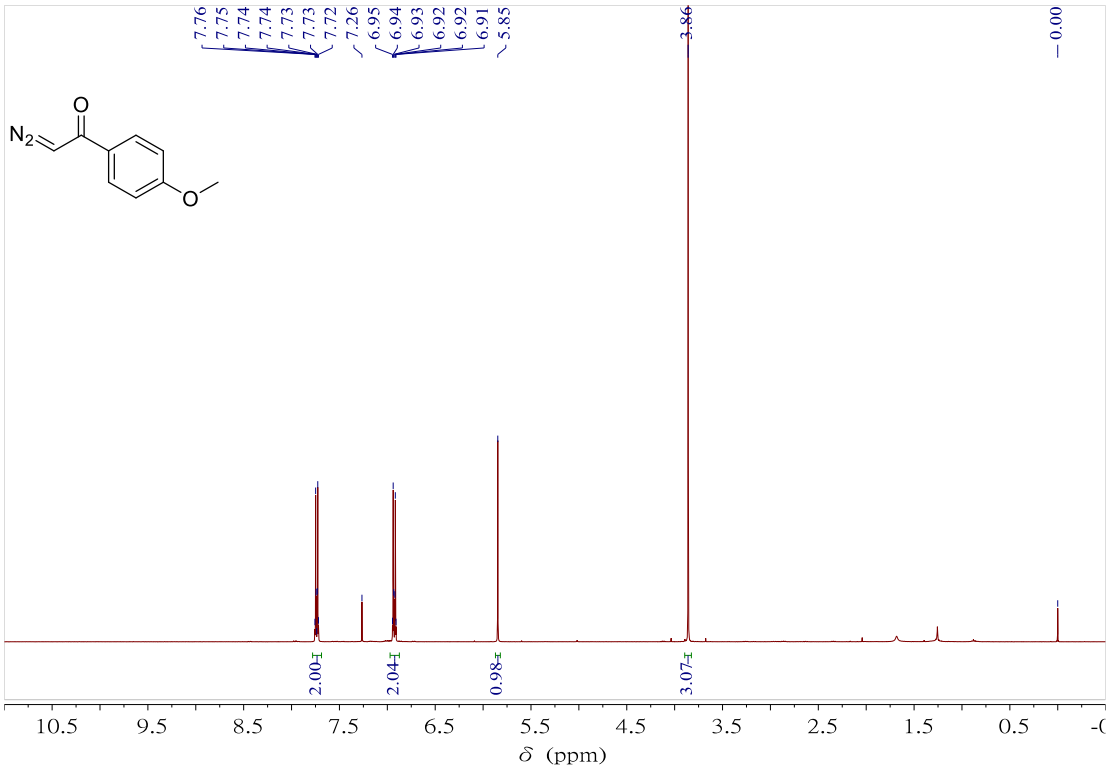
^{13}C NMR Spectrum of **11c** in $CDCl_3$ (125 MHz)



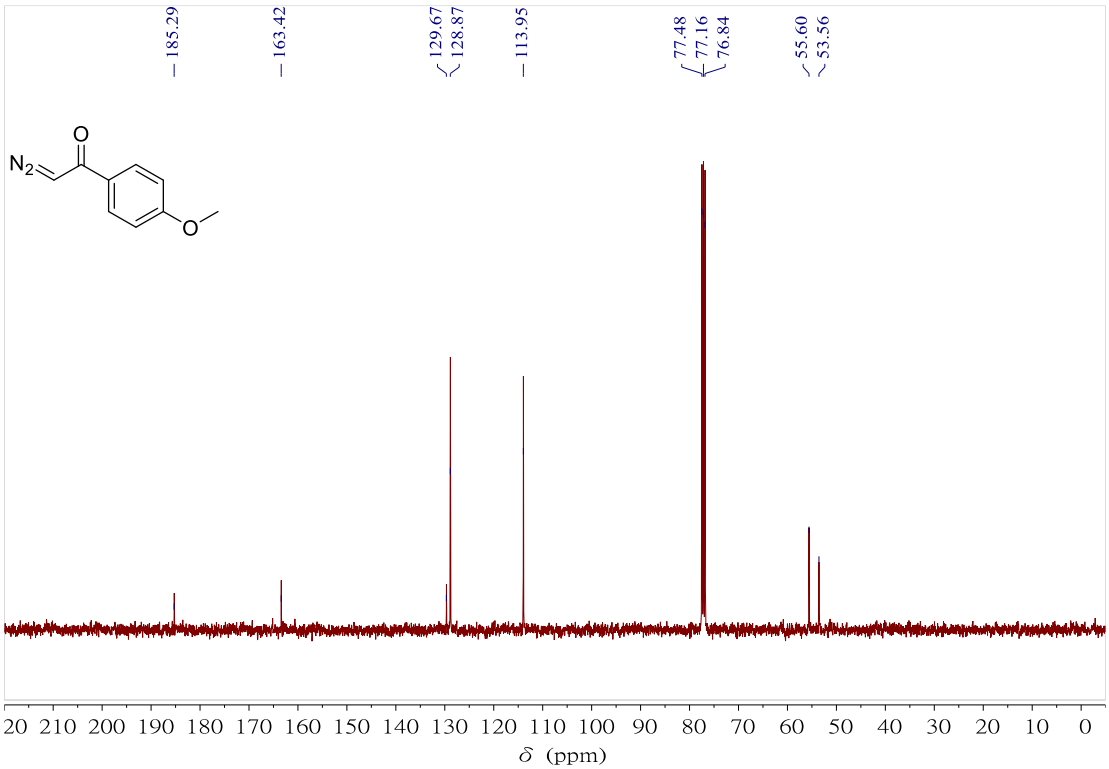
^{1}H NMR Spectrum of **11d** in $CDCl_3$ (400 MHz)



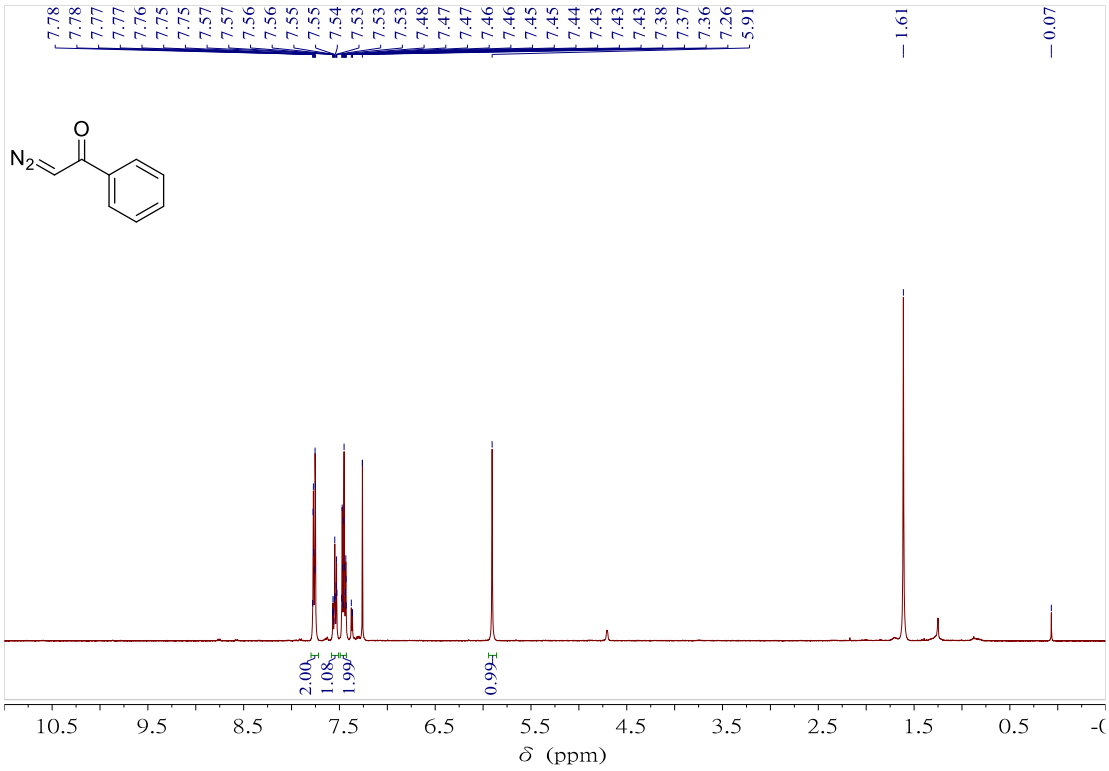
^{13}C NMR Spectrum of **11d** in $CDCl_3$ (100 MHz)



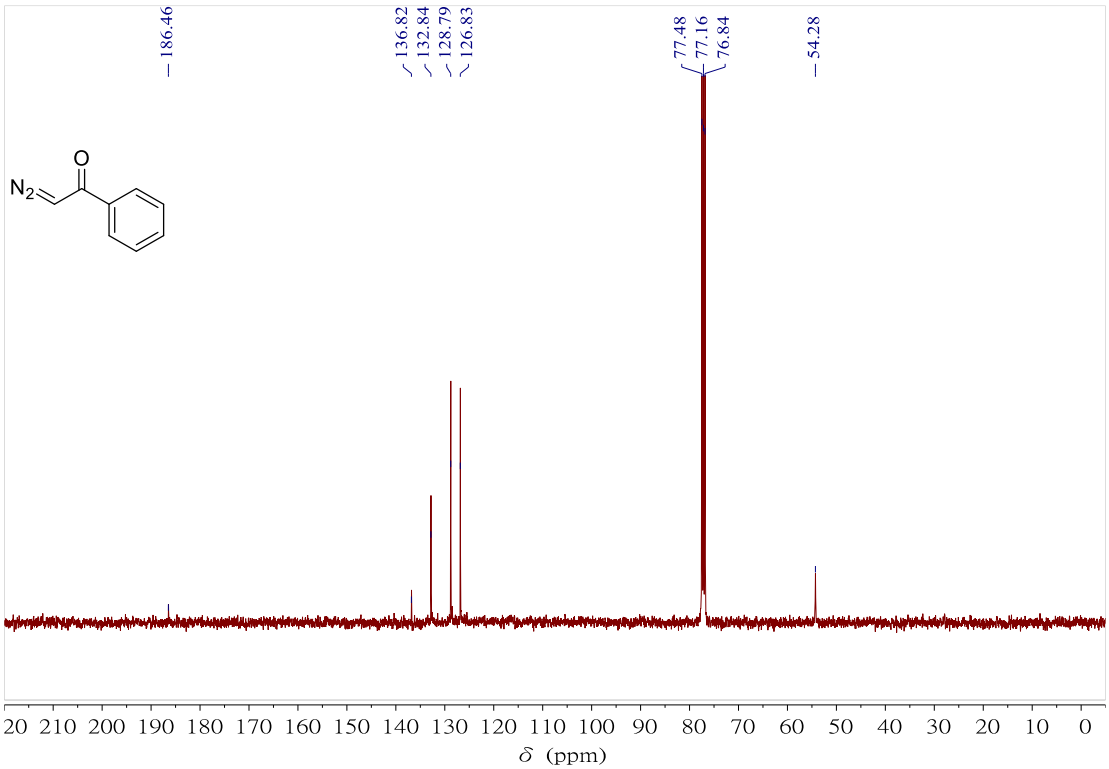
^{1}H NMR Spectrum of **11e** in $CDCl_3$ (400 MHz)



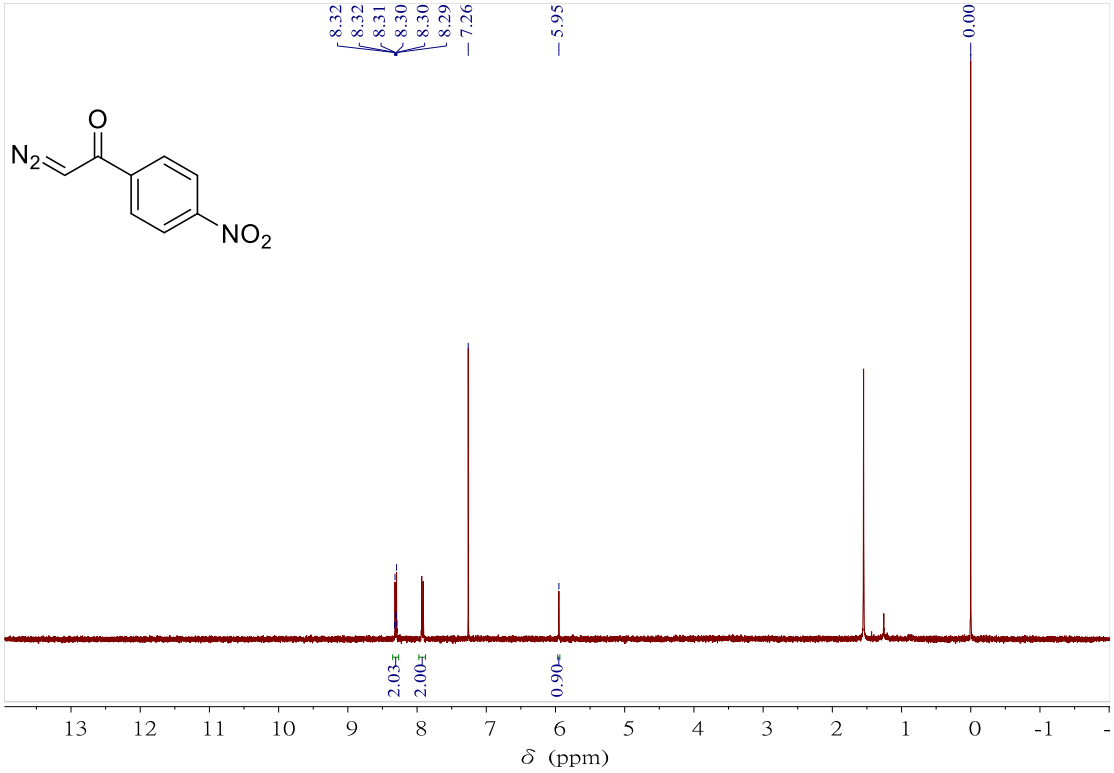
^{13}C NMR Spectrum of **11e** in $CDCl_3$ (100 MHz)



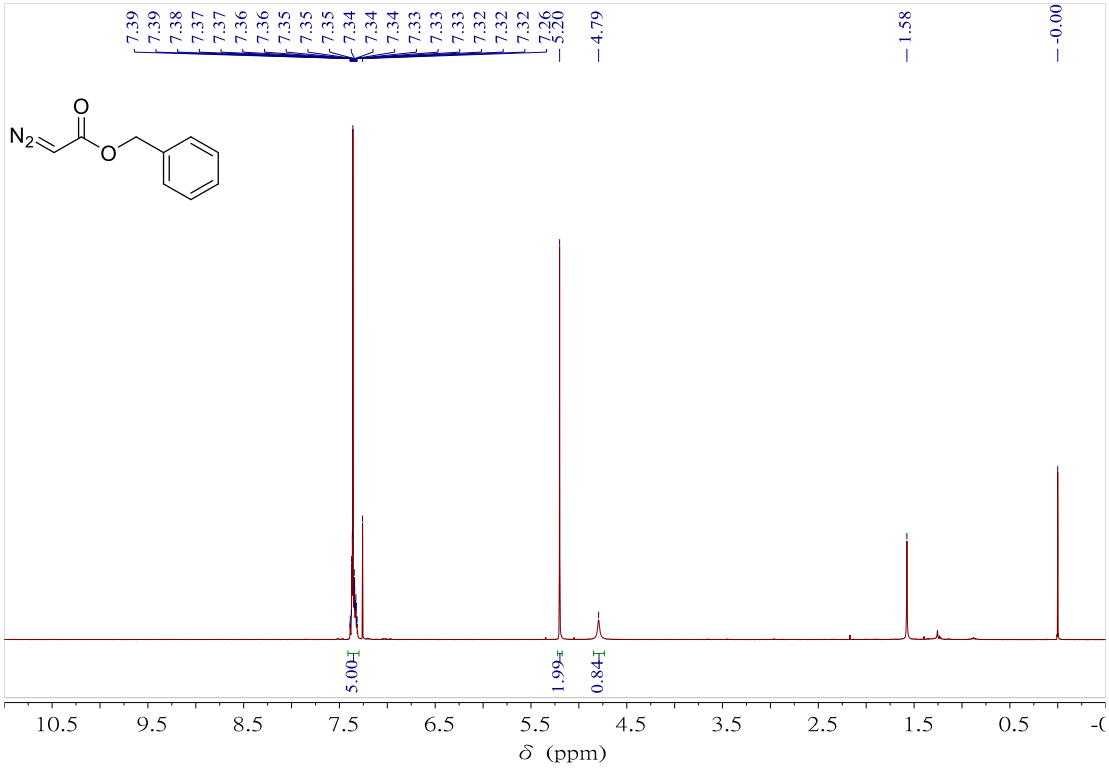
^{1}H NMR Spectrum of **11f** in $CDCl_3$ (400 MHz)



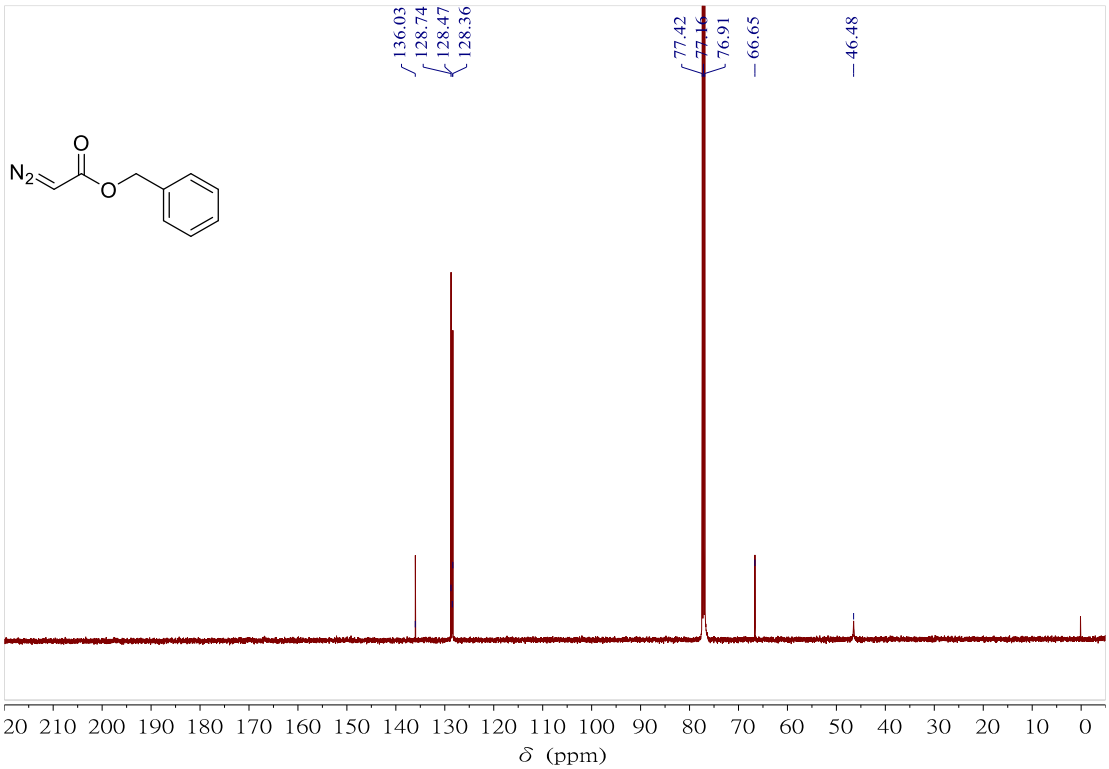
^{13}C NMR Spectrum of **11f** in $CDCl_3$ (100 MHz)



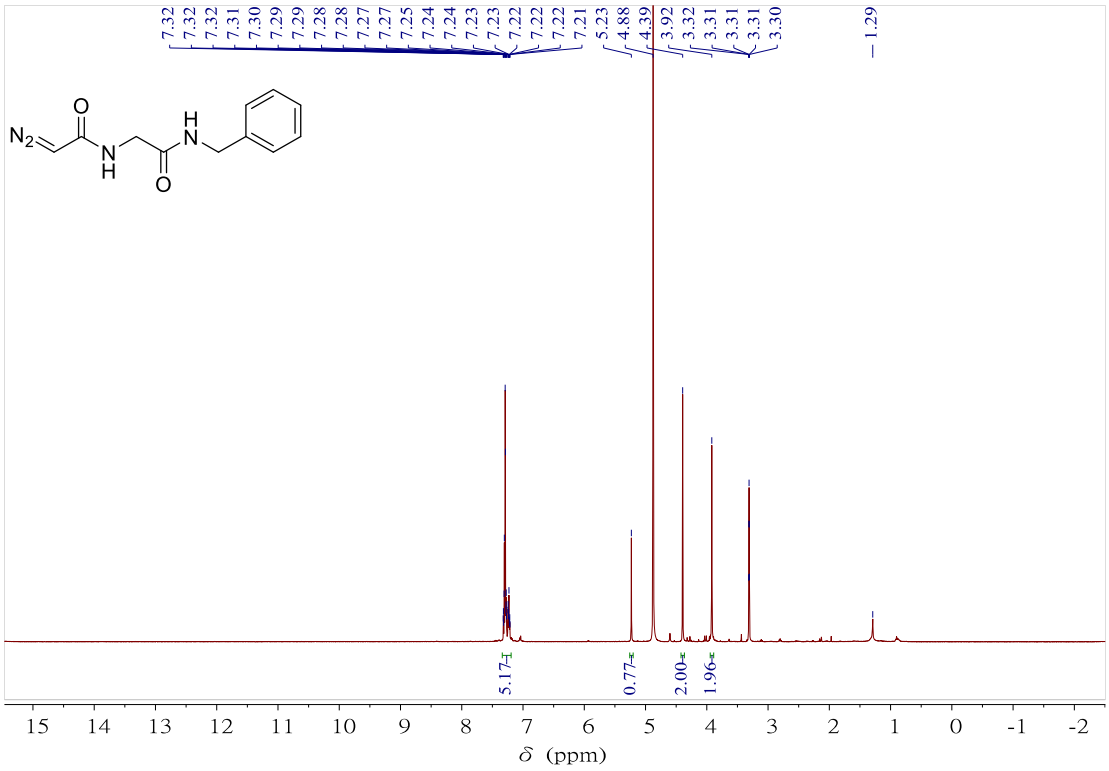
^{1}H NMR Spectrum of **11g** in $CDCl_3$ (400 MHz)



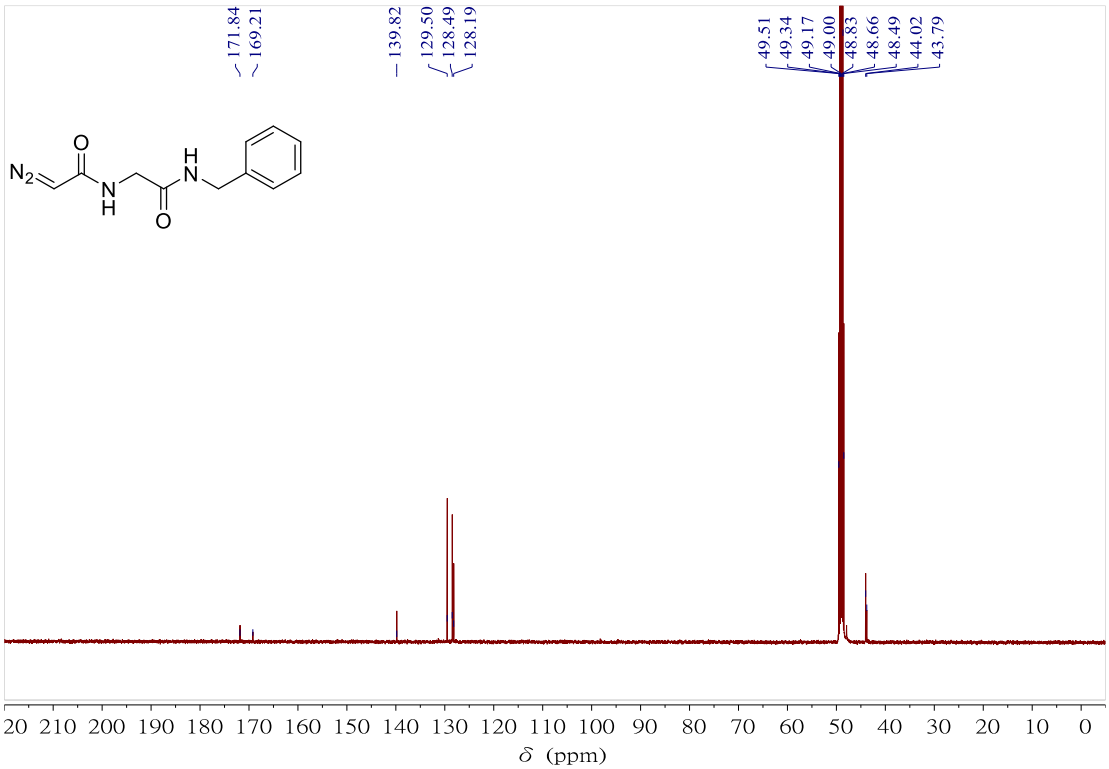
^{1}H NMR Spectrum of **11h** in $CDCl_3$ (500 MHz)



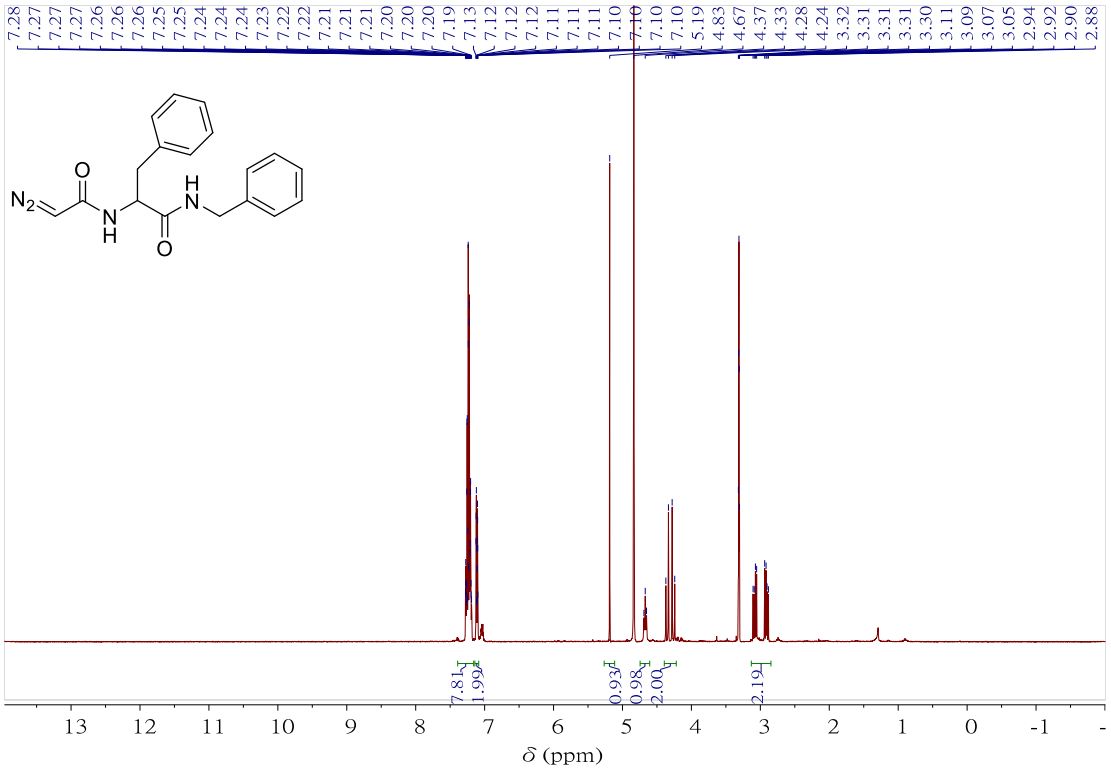
^{13}C NMR Spectrum of **11h** in $CDCl_3$ (125 MHz)



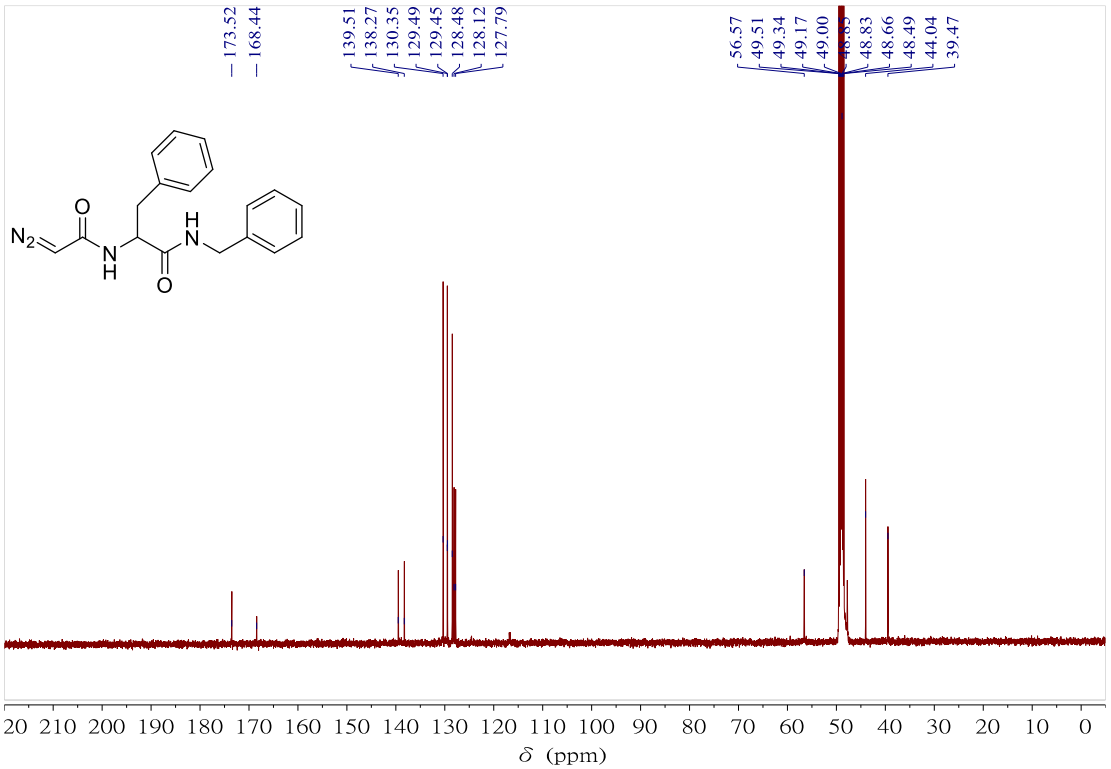
^{1}H NMR Spectrum of **11i** in CD_3OD (500 MHz)



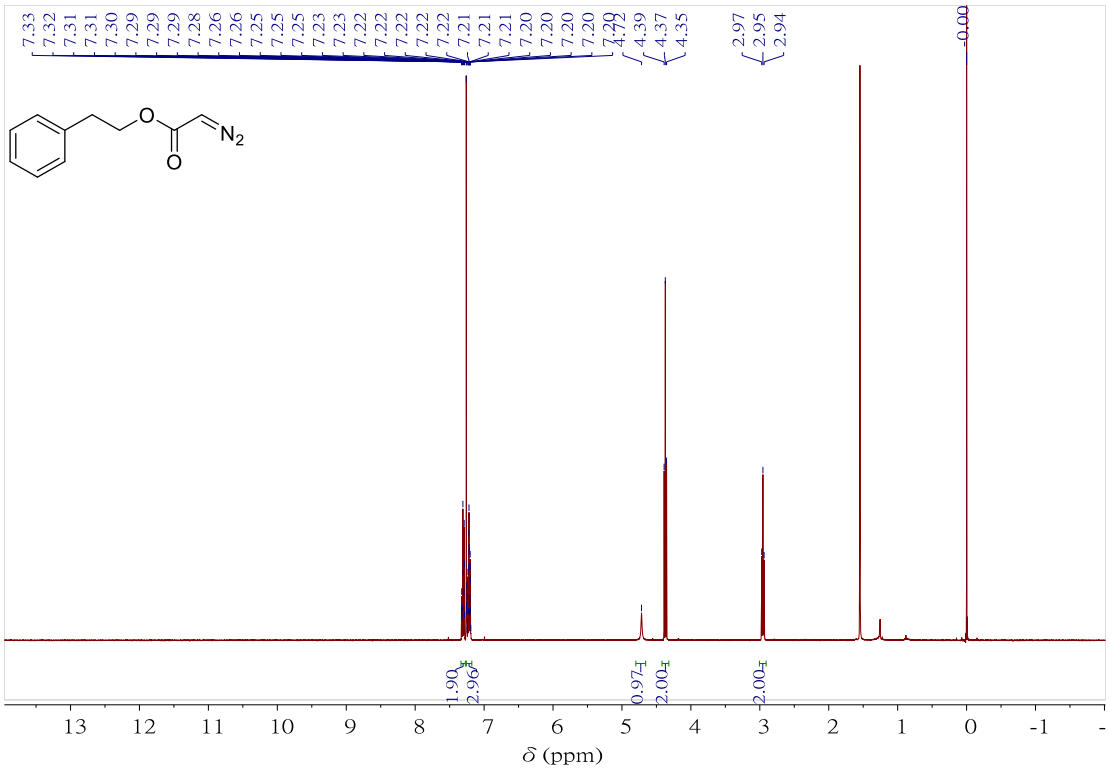
^{13}C NMR Spectrum of **11i** in CD_3OD (125 MHz)



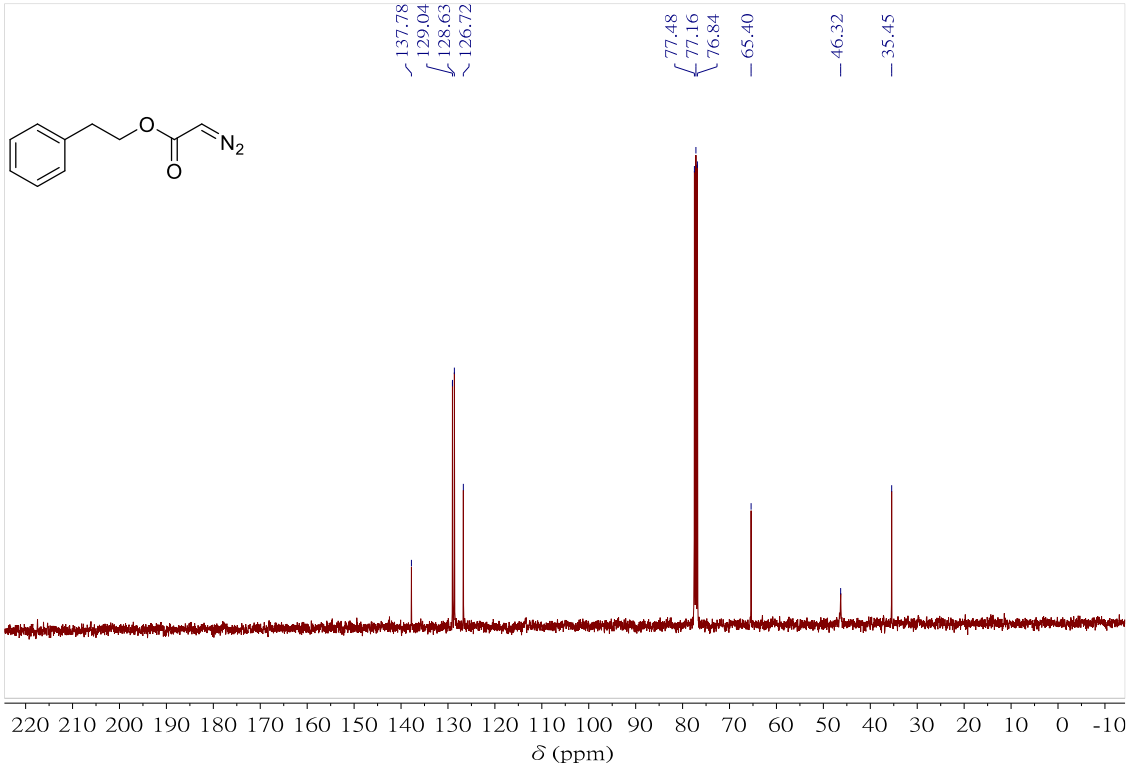
^{1}H NMR Spectrum of **11j** in CD_3OD (400 MHz)



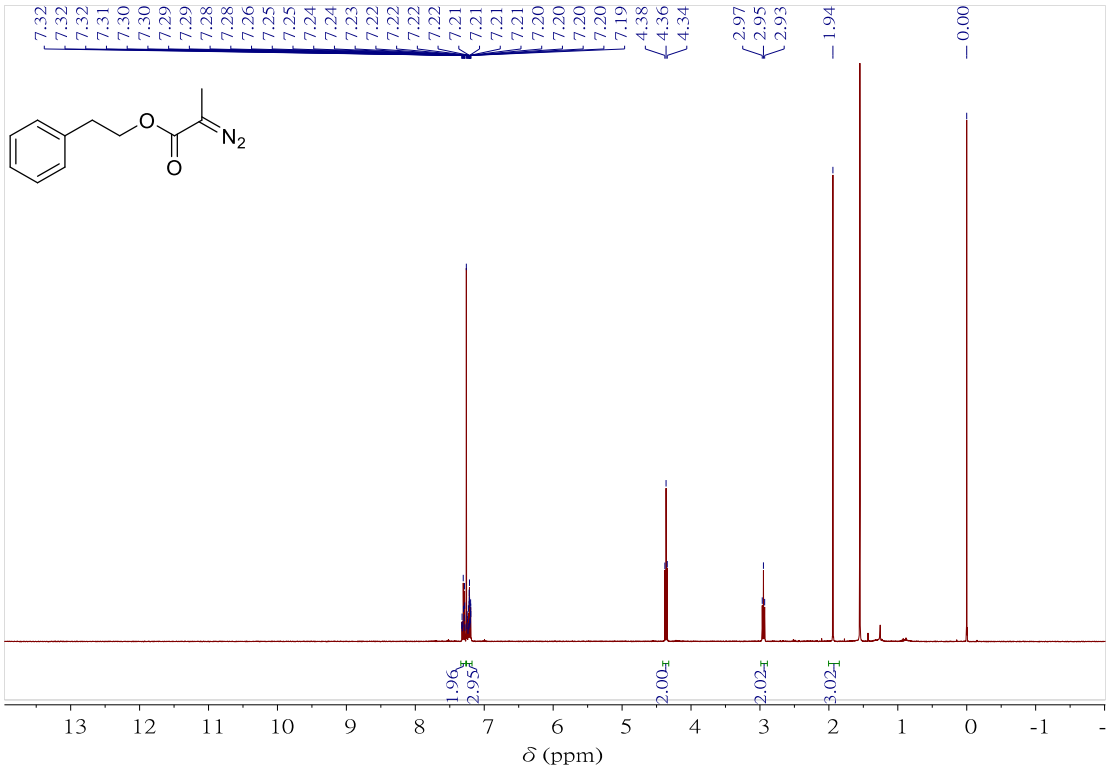
^{13}C NMR Spectrum of **11j** in CD_3OD (125 MHz)



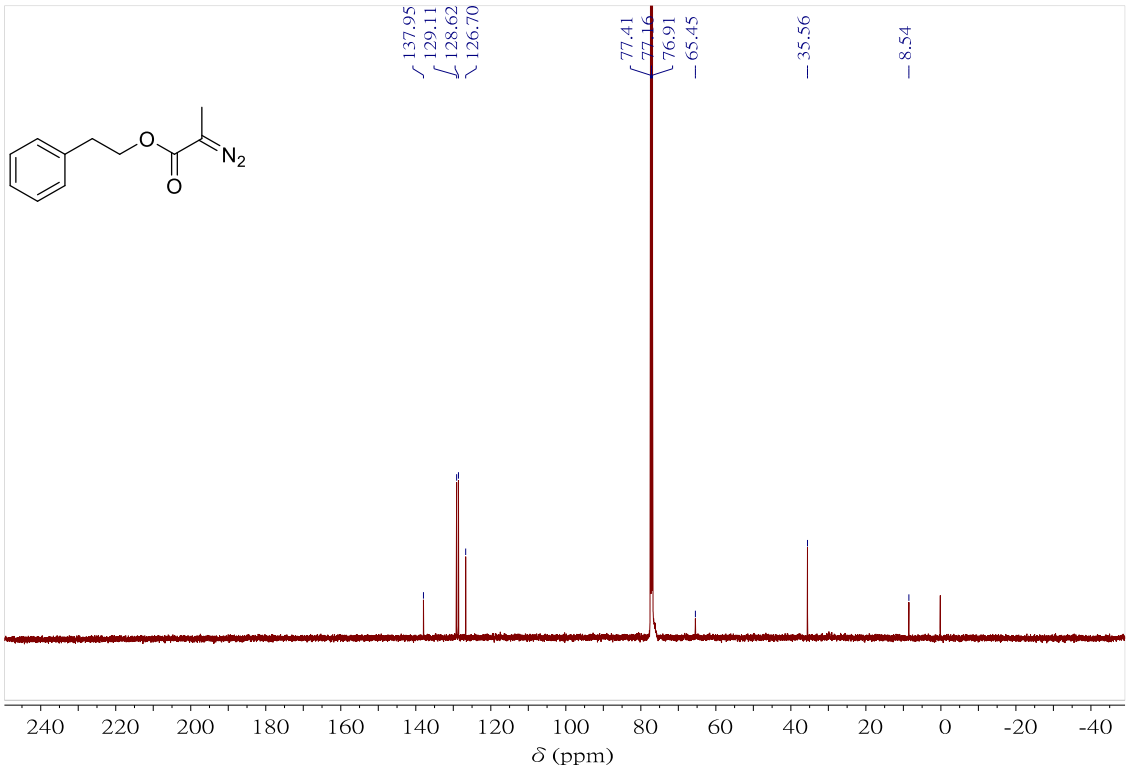
^{1}H NMR Spectrum of **12** in $CDCl_3$ (400 MHz)



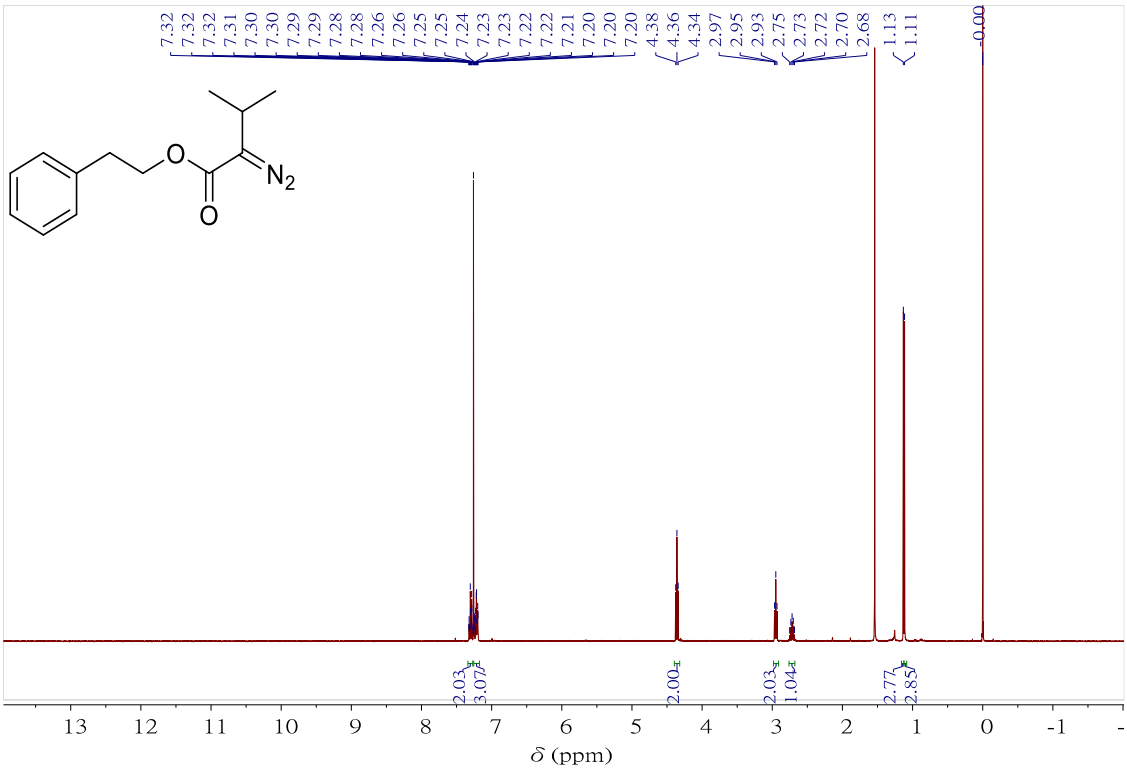
^{13}C NMR Spectrum of **12** in $CDCl_3$ (100 MHz)



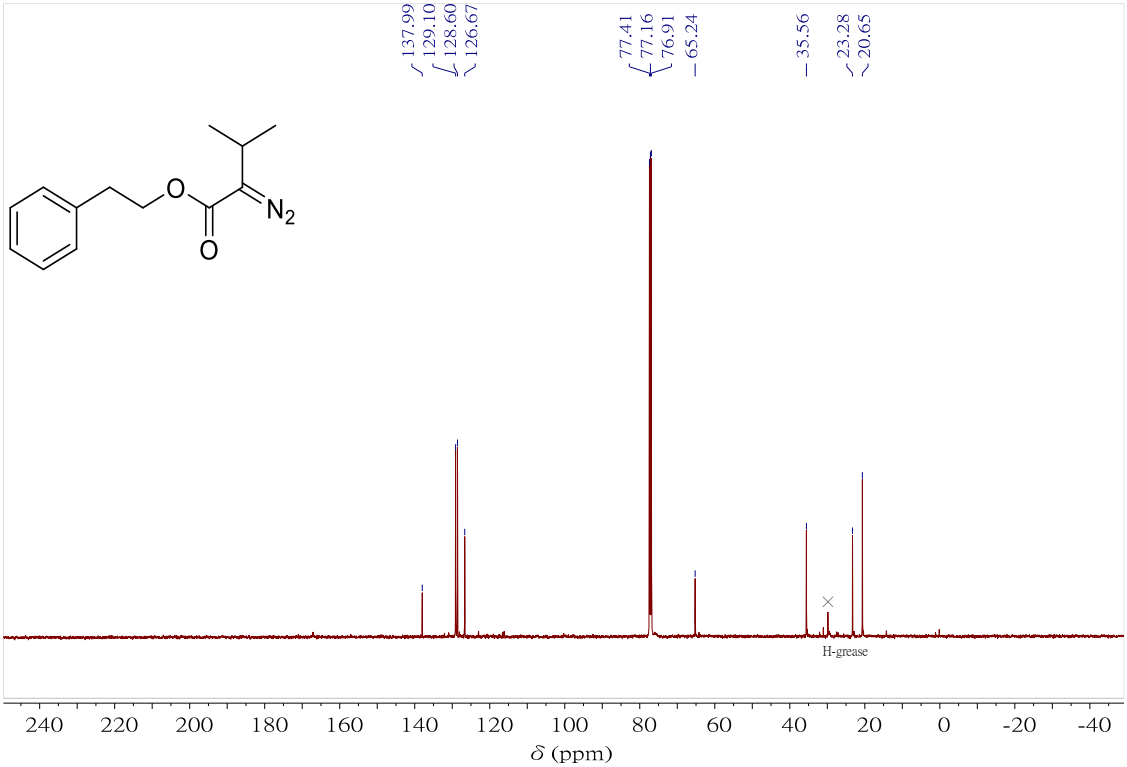
^{1}H NMR Spectrum of **13** in $CDCl_3$ (400 MHz)



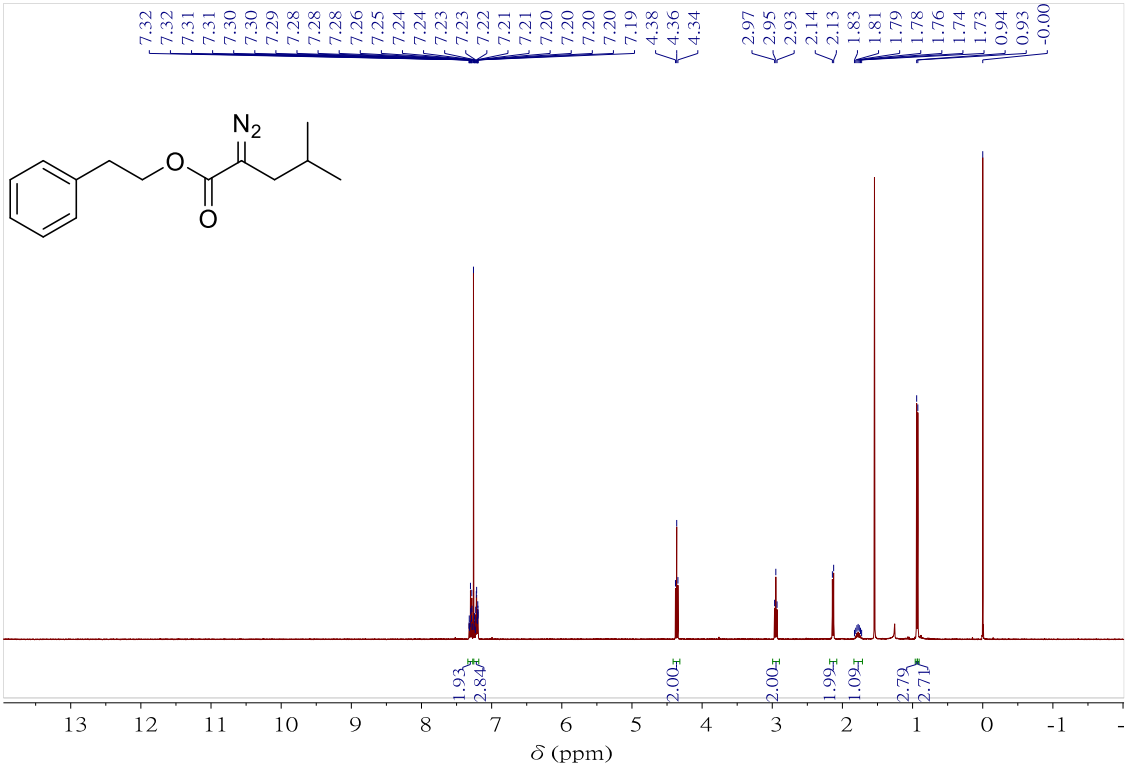
^{13}C NMR Spectrum of **13** in $CDCl_3$ (125 MHz)



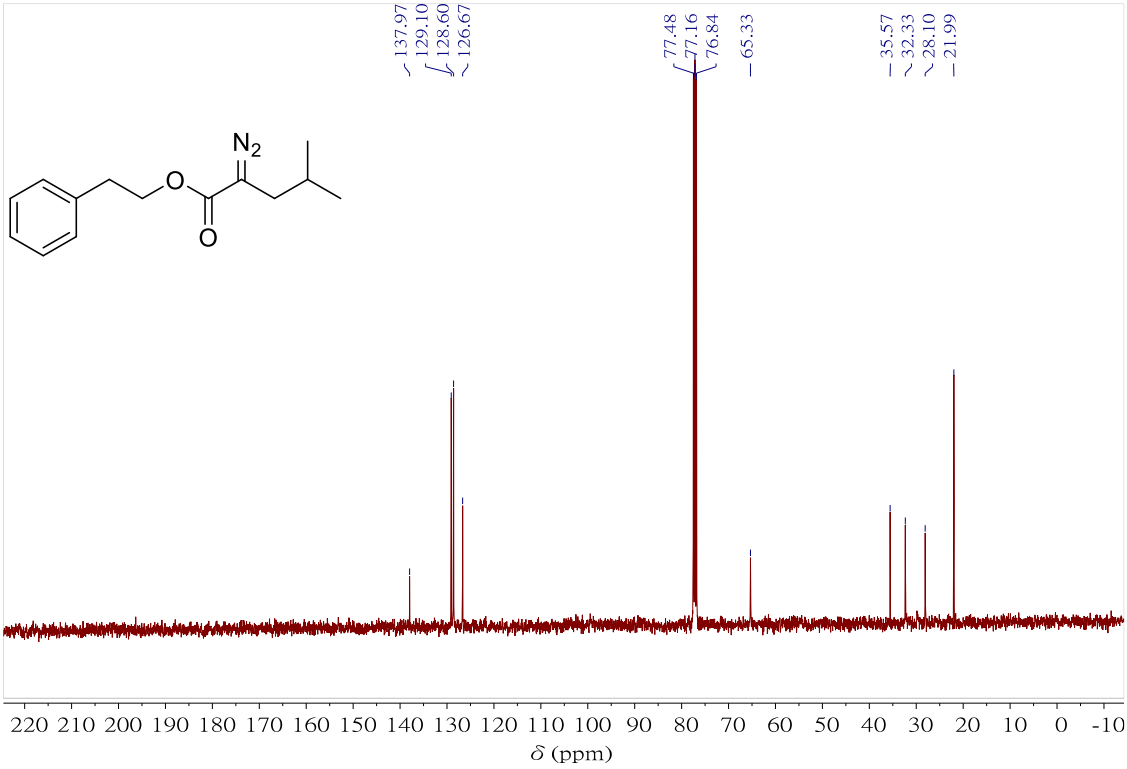
^{1}H NMR Spectrum of **14** in $CDCl_3$ (400 MHz)



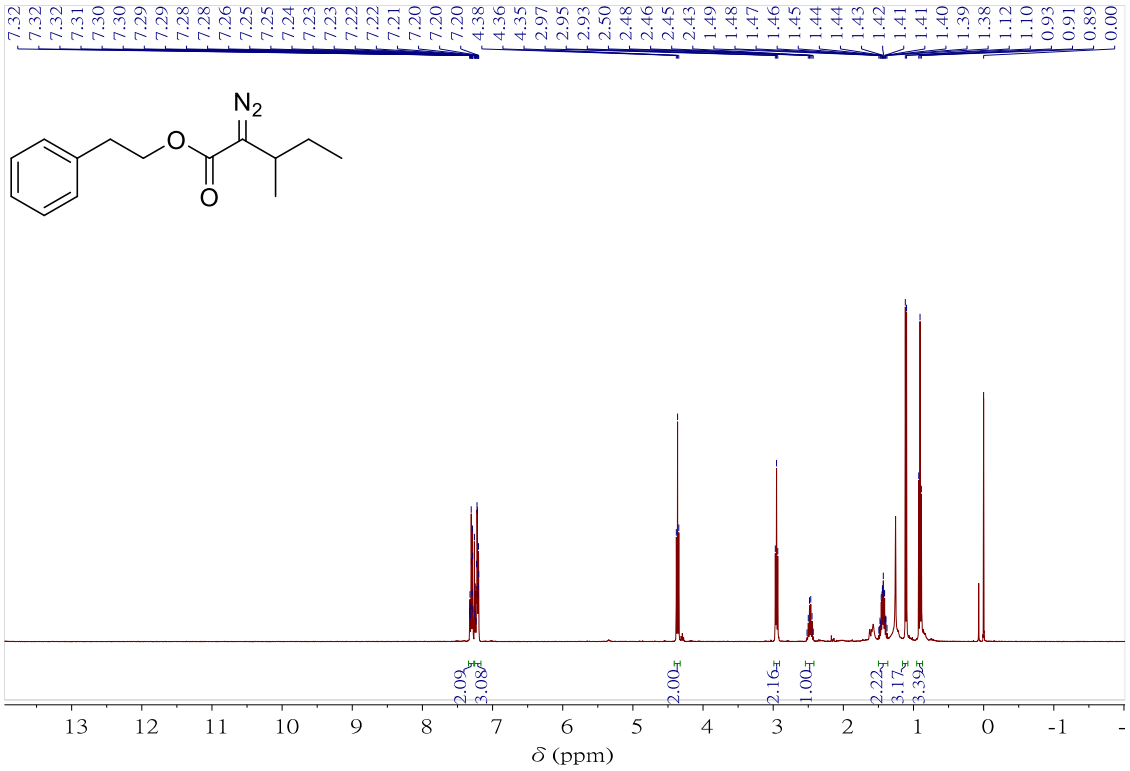
^{13}C NMR Spectrum of **14** in $CDCl_3$ (125 MHz)



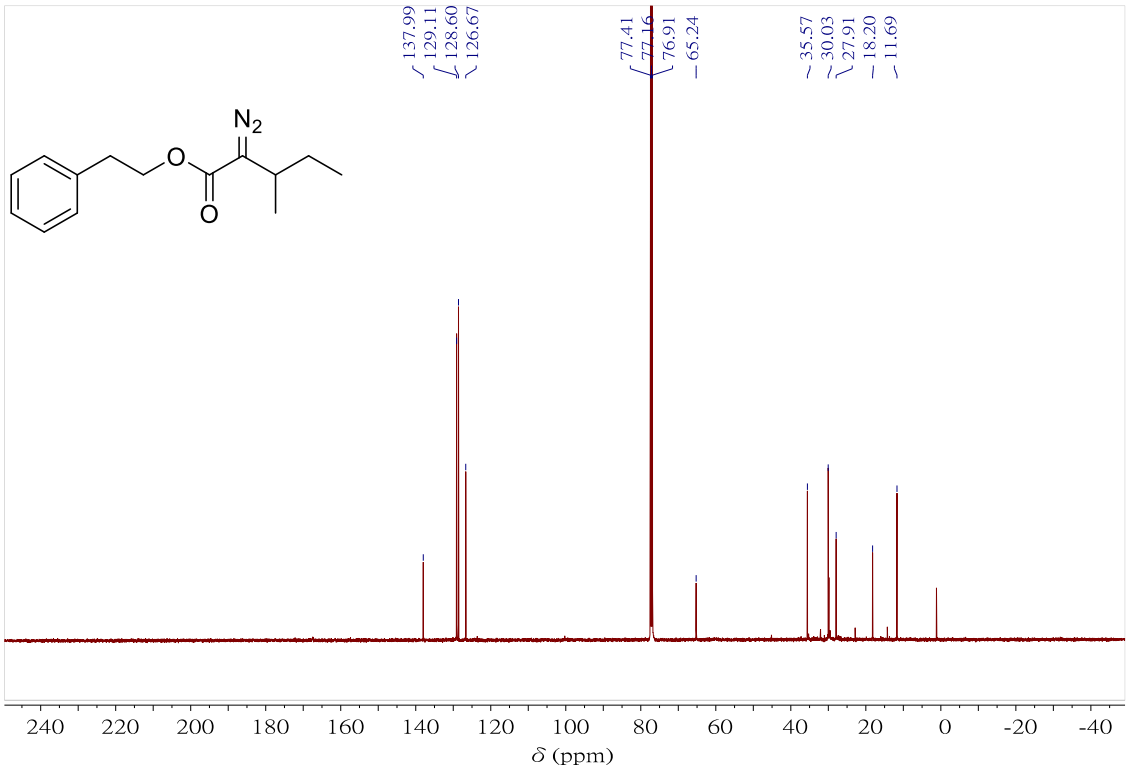
^{1}H NMR Spectrum of **15** in $CDCl_3$ (400 MHz)



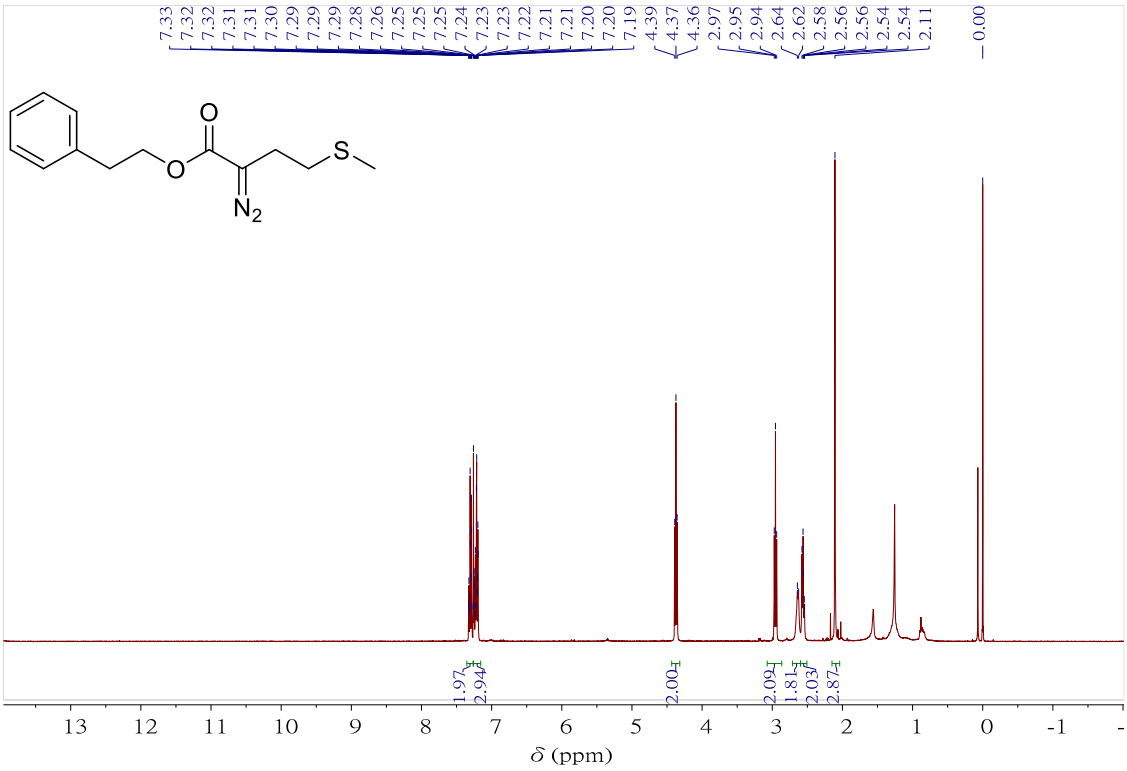
^{13}C NMR Spectrum of **15** in $CDCl_3$ (100 MHz)



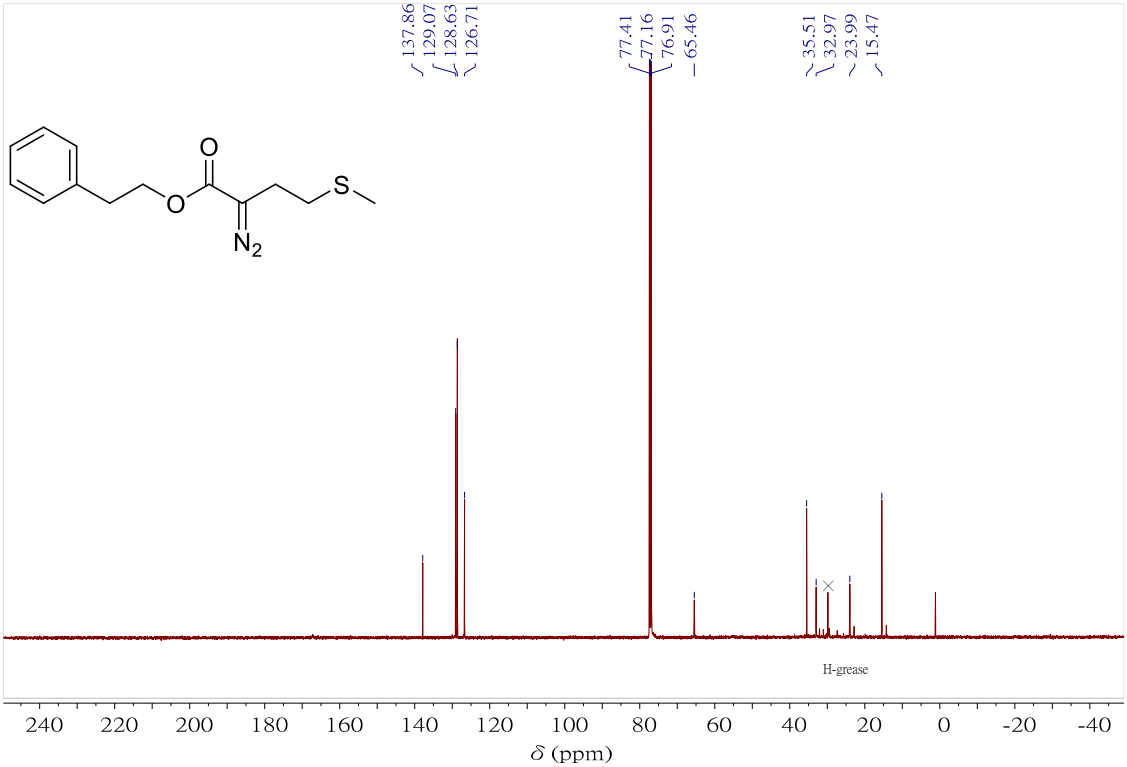
^{1}H NMR Spectrum of **16** in $CDCl_3$ (400 MHz)



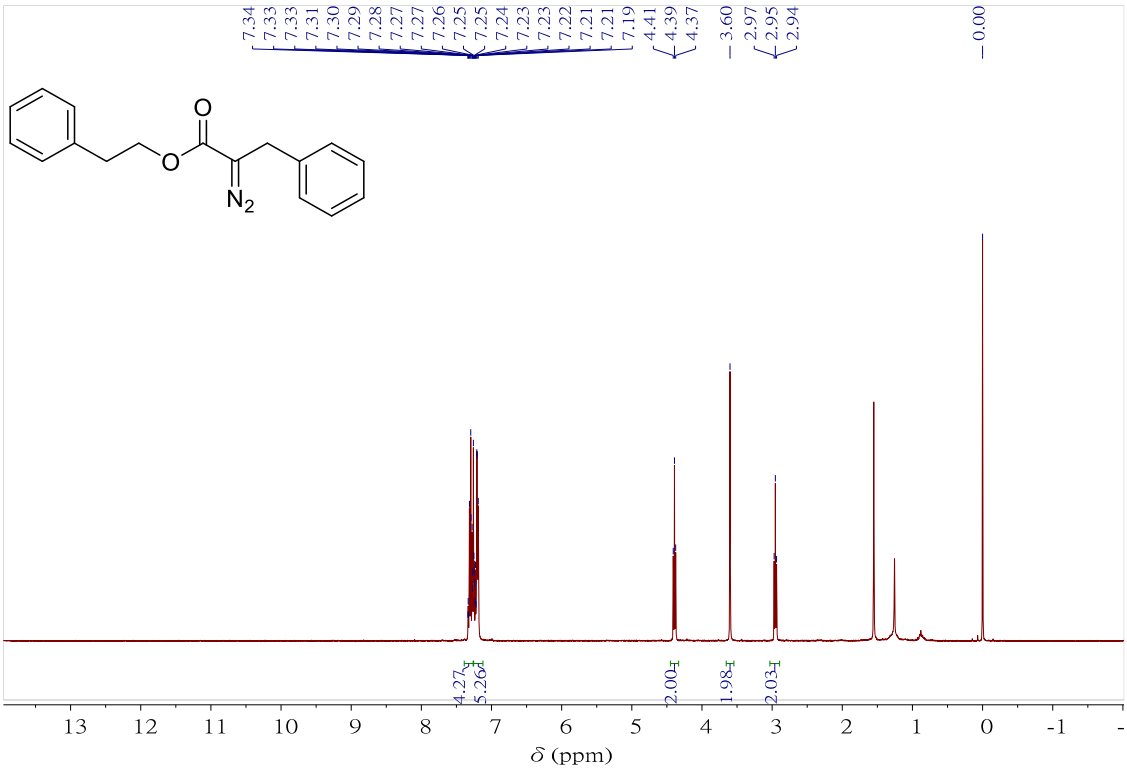
^{13}C NMR Spectrum of **16** in $CDCl_3$ (125 MHz)



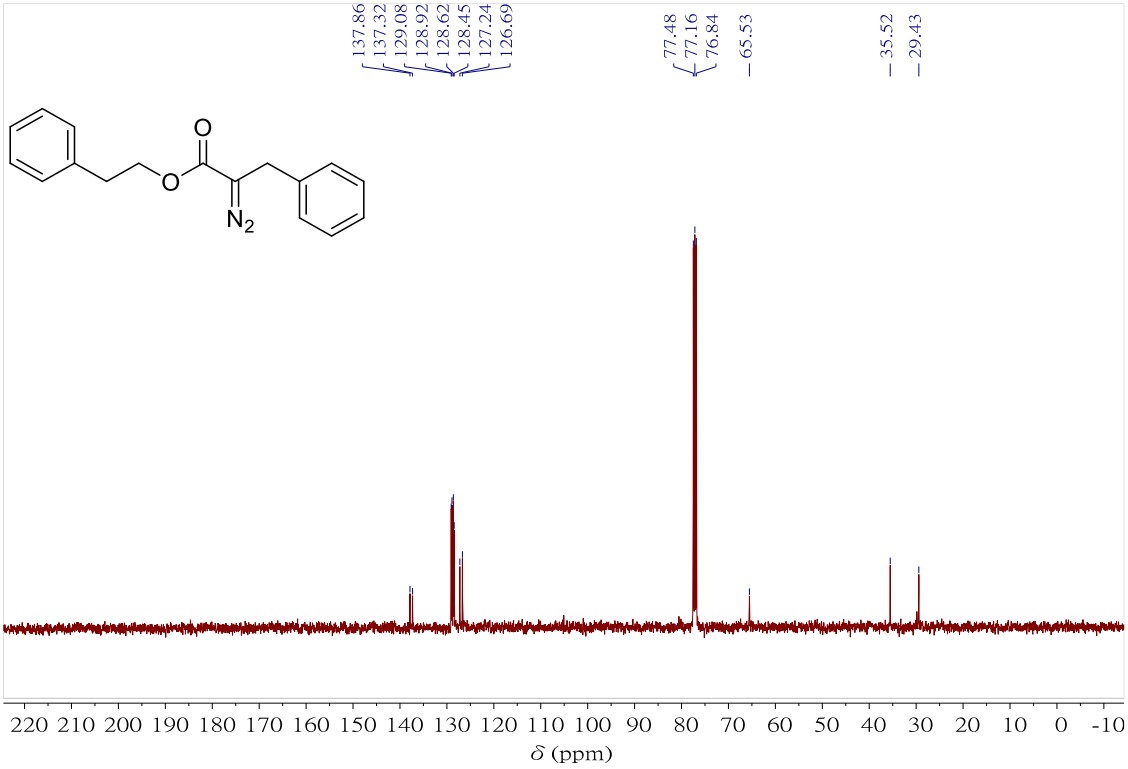
^{1}H NMR Spectrum of **17** in $CDCl_3$ (400 MHz)



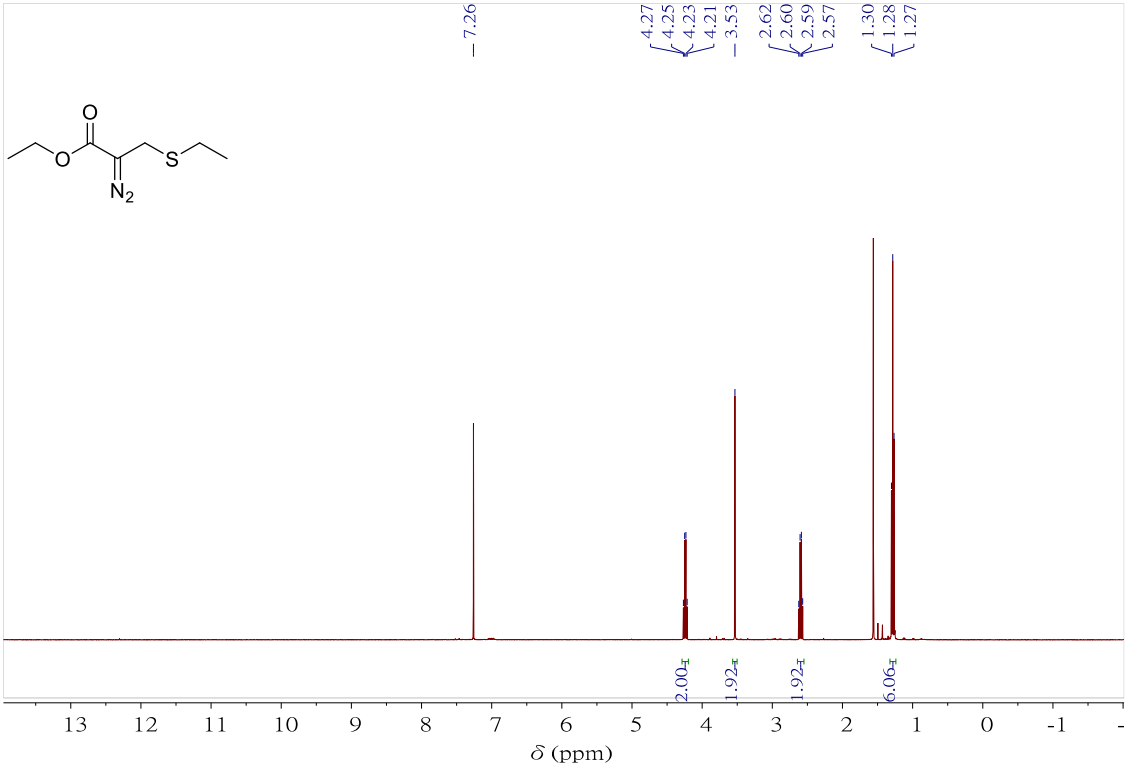
^{13}C NMR Spectrum of **17** in $CDCl_3$ (125 MHz)



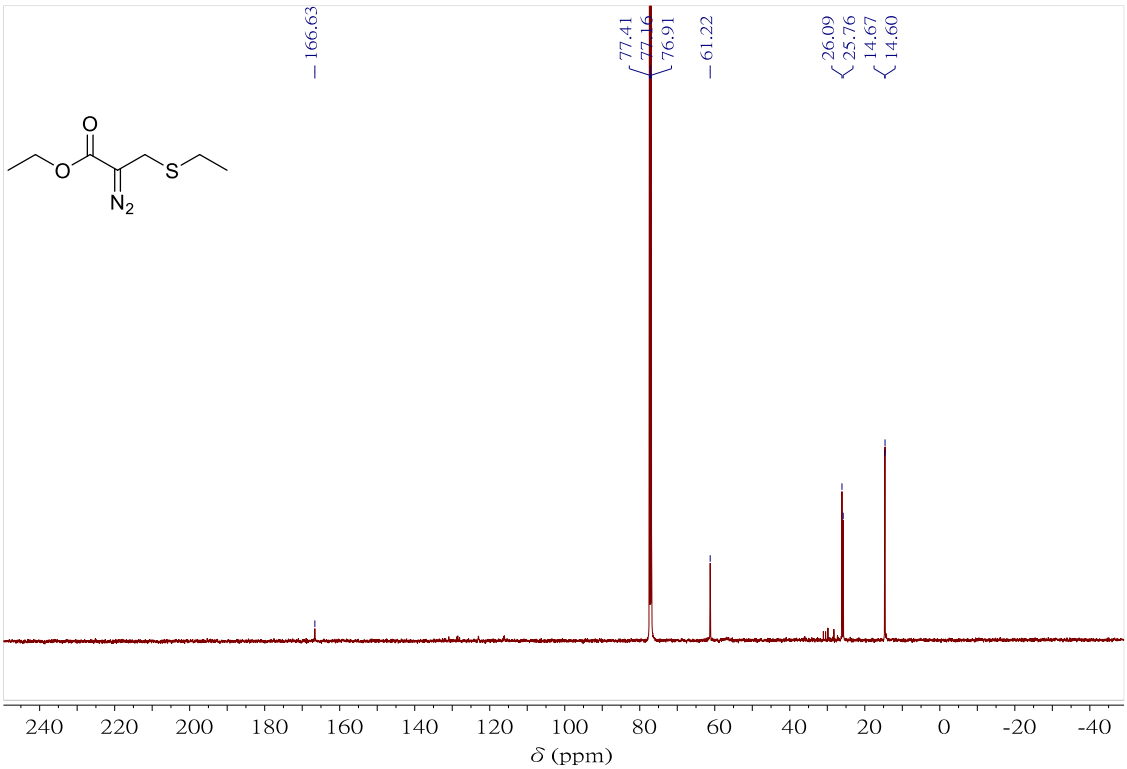
^{1}H NMR Spectrum of **18** in $CDCl_3$ (400 MHz)



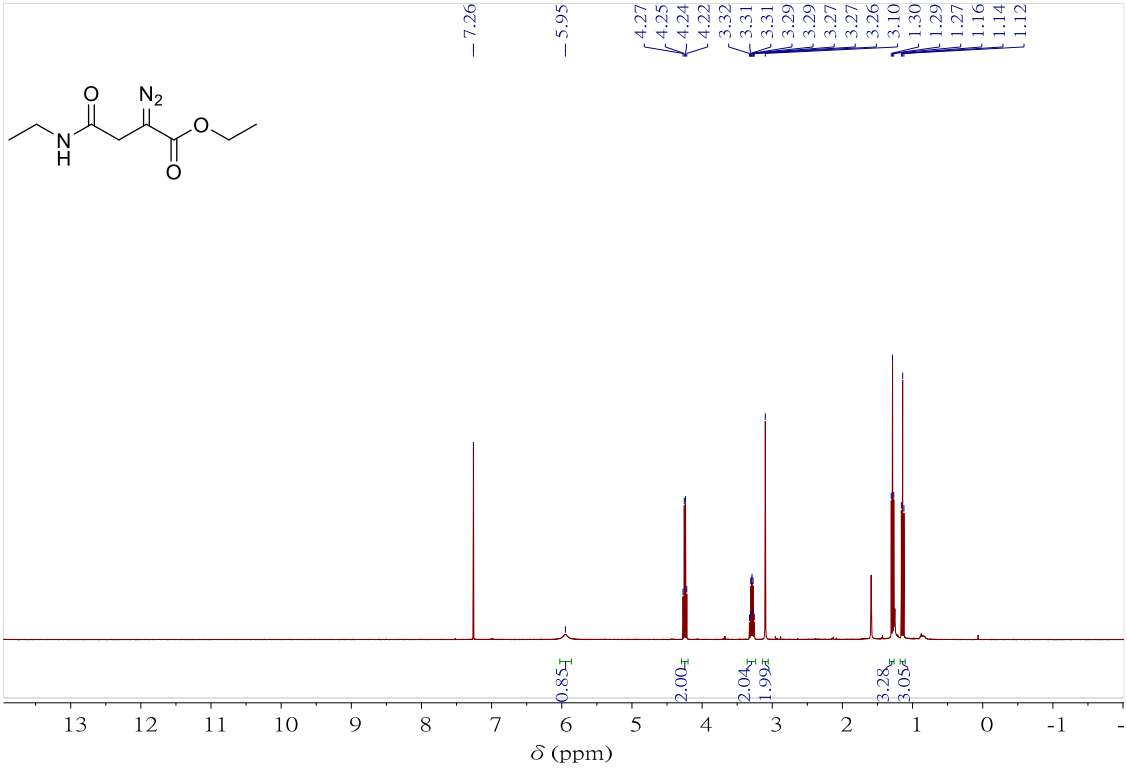
^{13}C NMR Spectrum of **18** in $CDCl_3$ (100 MHz)



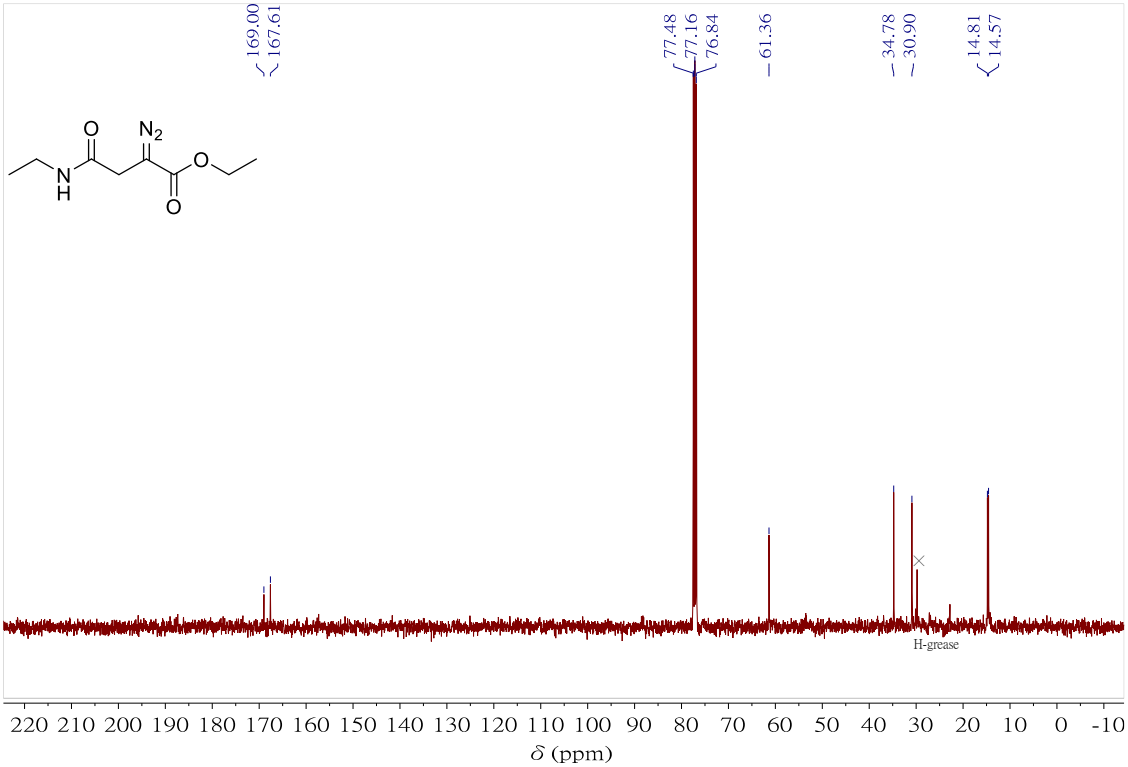
^{1}H NMR Spectrum of **19** in $CDCl_3$ (400 MHz)



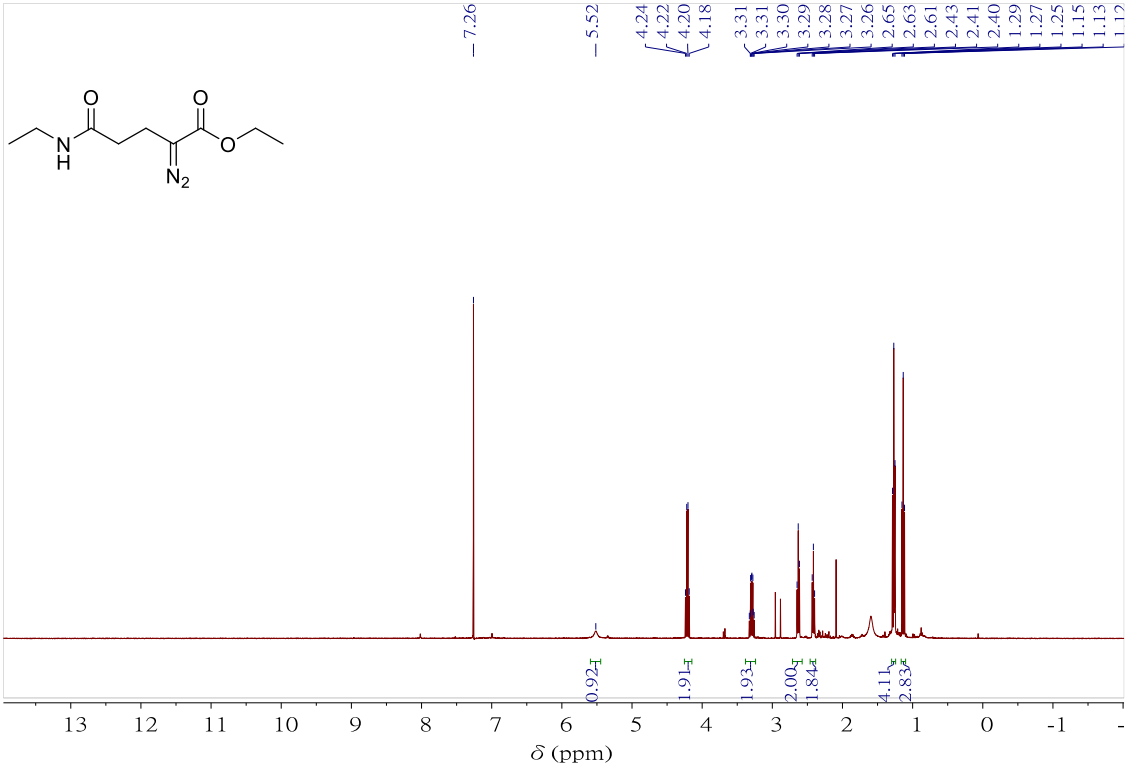
^{13}C NMR Spectrum of **19** in $CDCl_3$ (125 MHz)



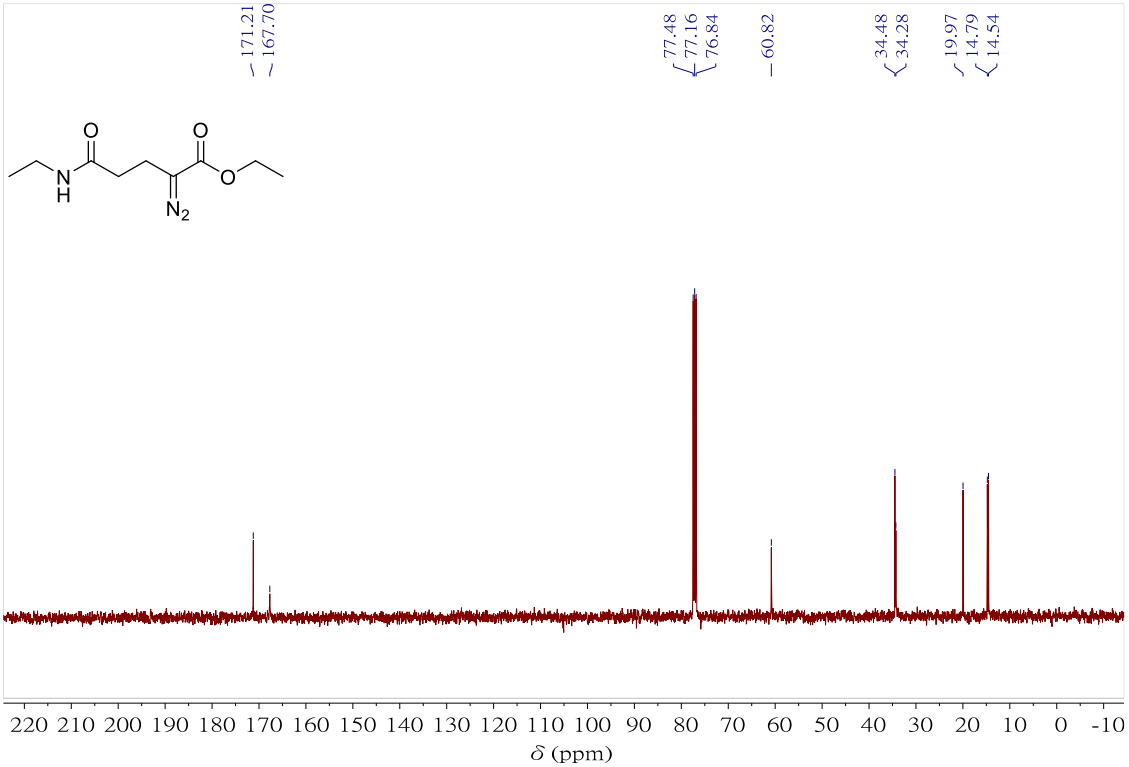
^{1}H NMR Spectrum of **20** in $CDCl_3$ (400 MHz)



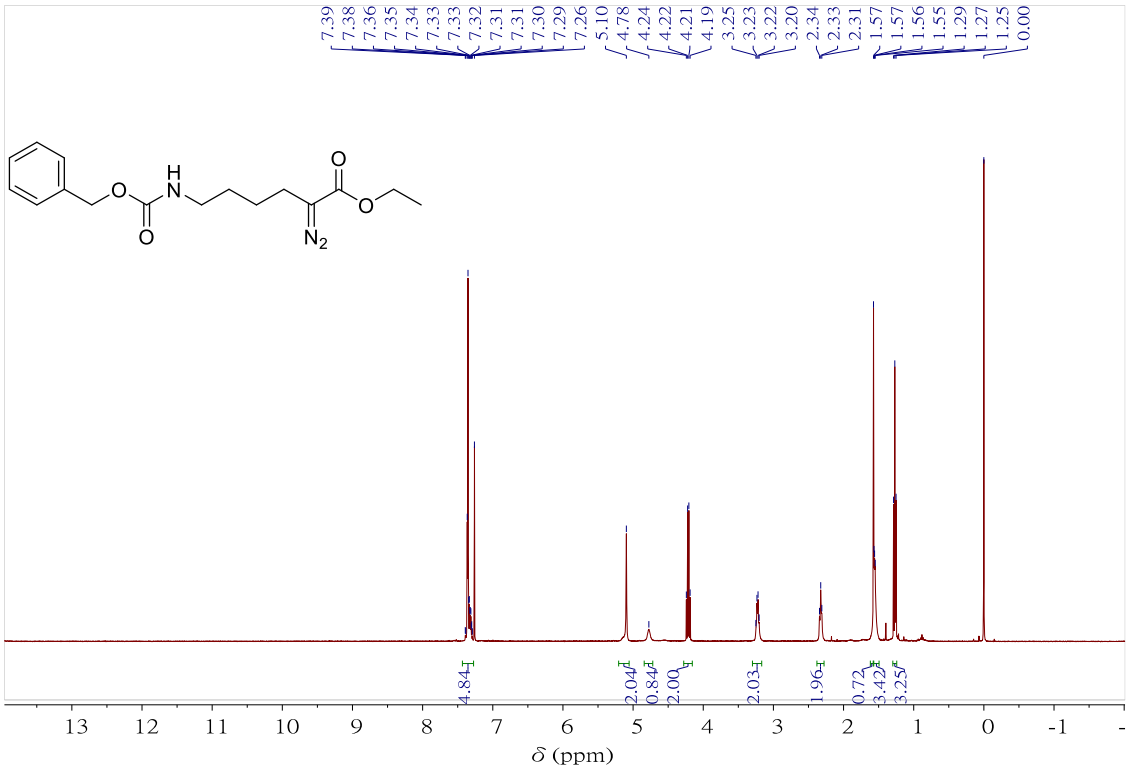
^{13}C NMR Spectrum of **20** in $CDCl_3$ (100 MHz)



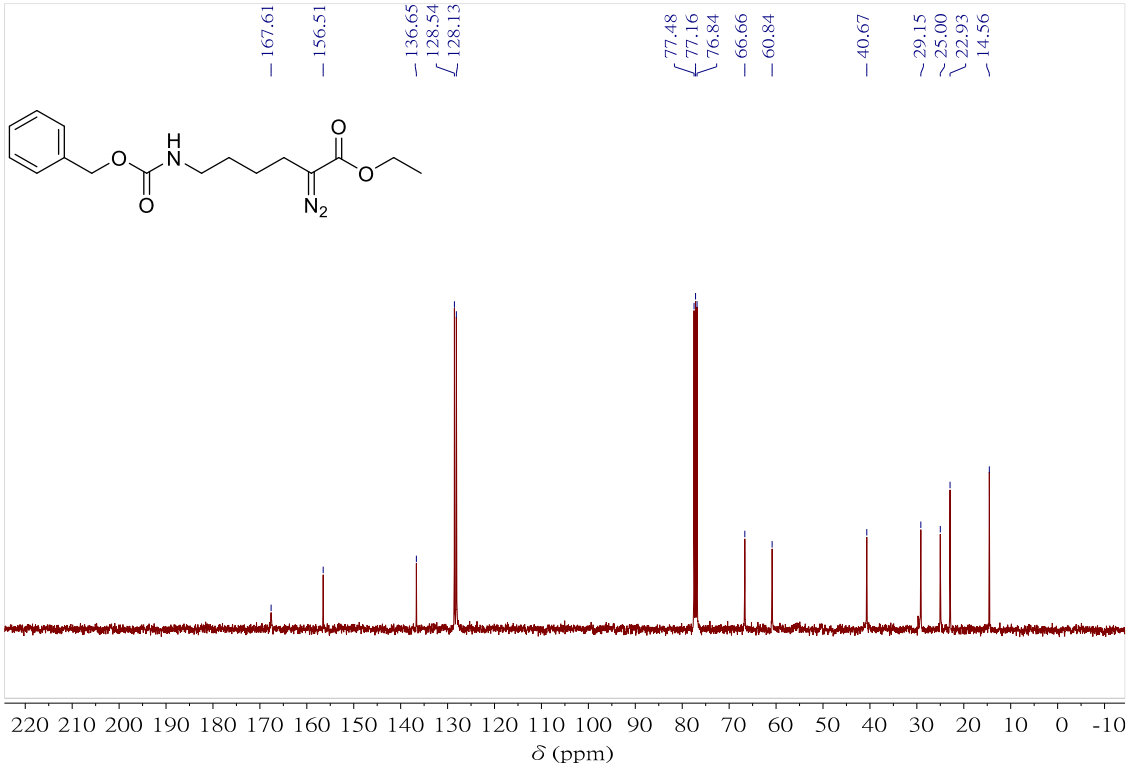
^{1}H NMR Spectrum of **21** in $CDCl_3$ (400 MHz)



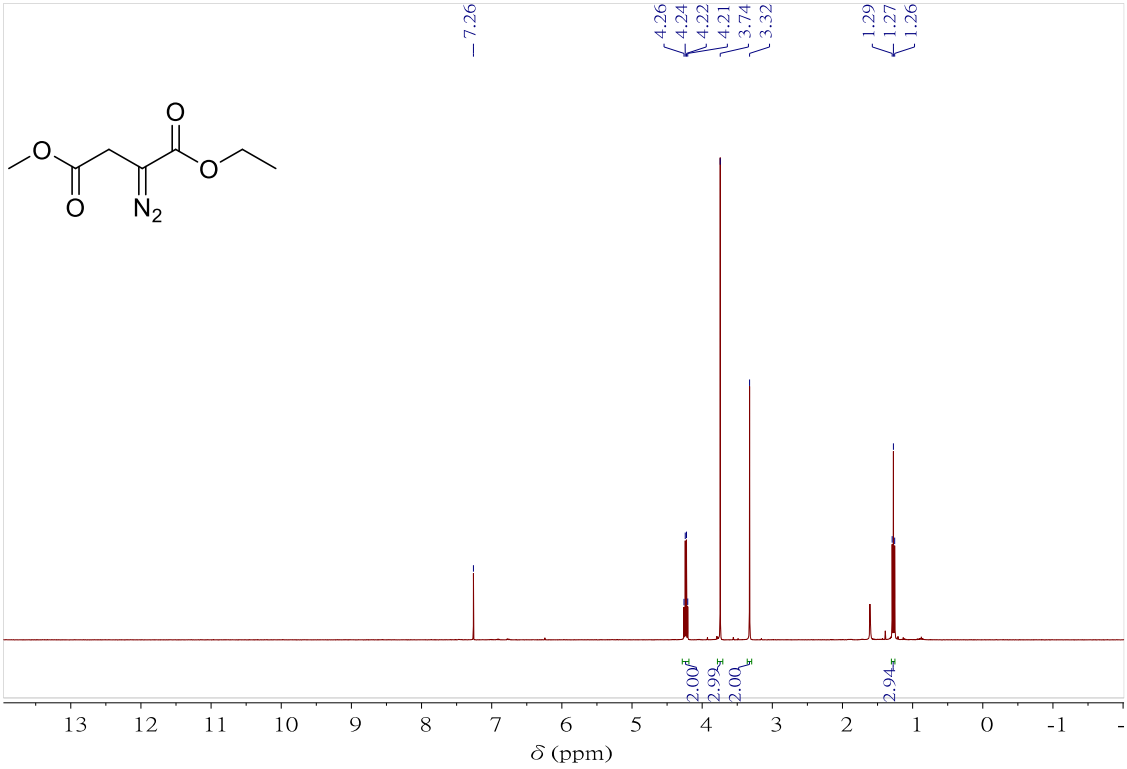
^{13}C NMR Spectrum of **21** in $CDCl_3$ (100 MHz)



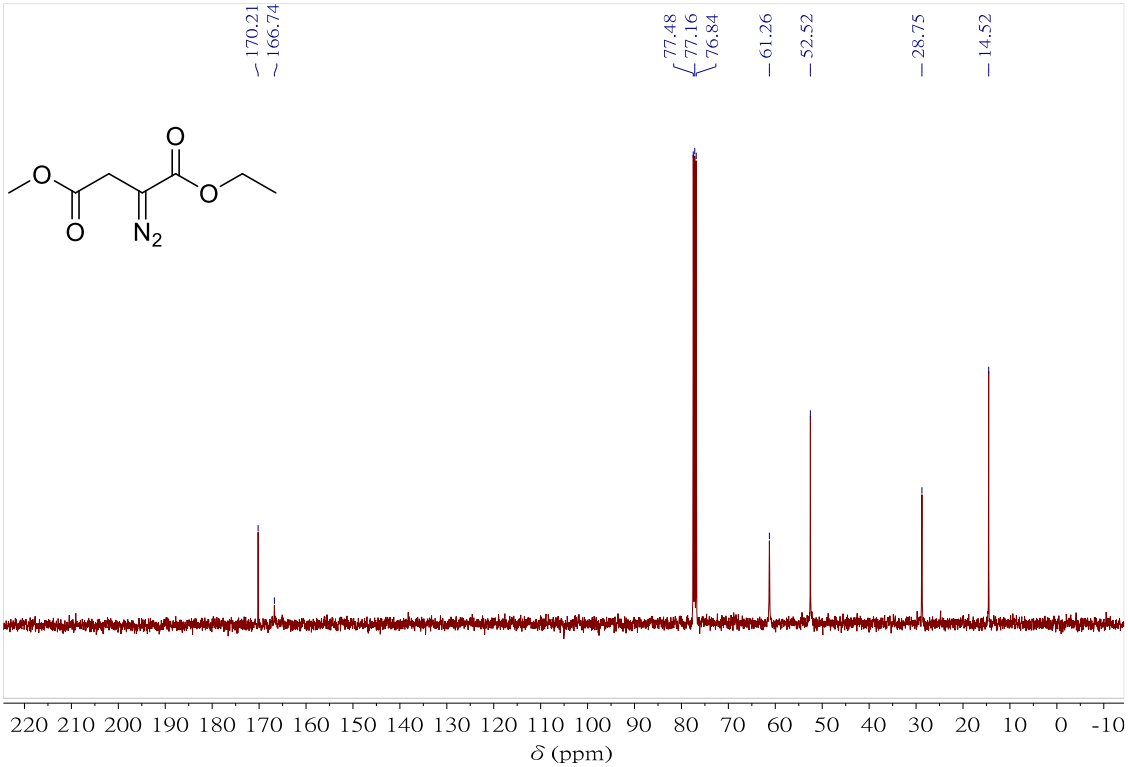
^{1}H NMR Spectrum of **22** in $CDCl_3$ (400 MHz)



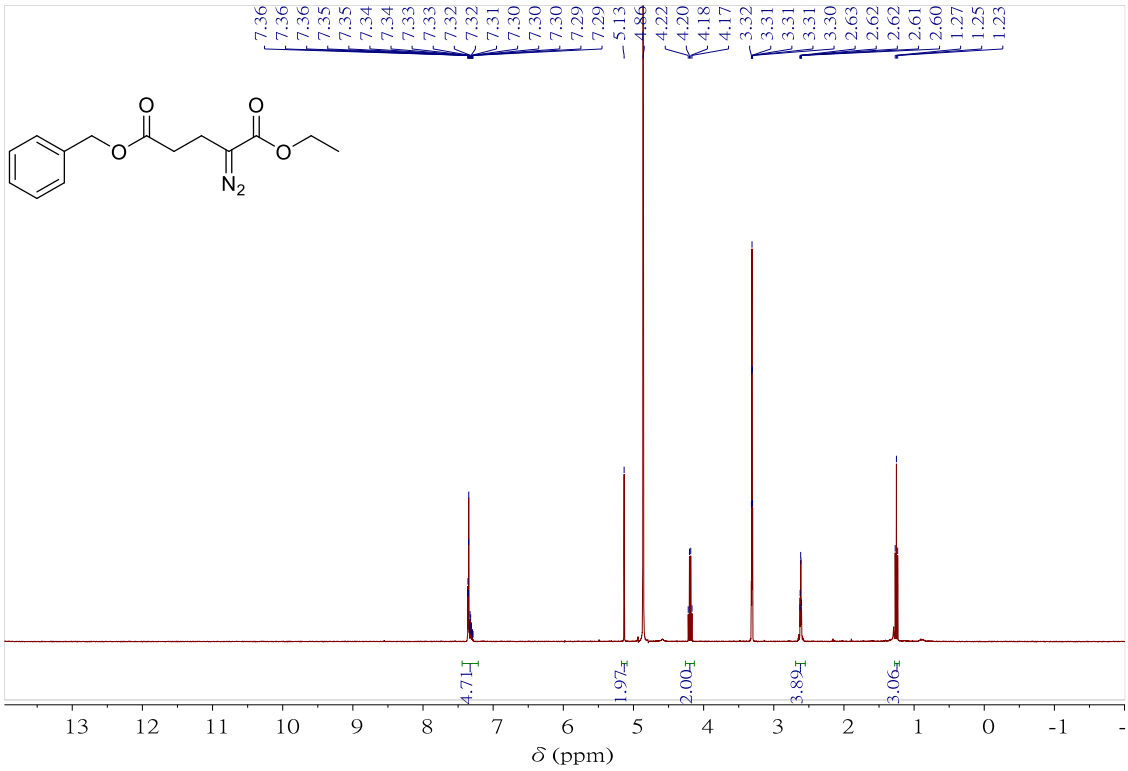
^{13}C NMR Spectrum of **22** in $CDCl_3$ (100 MHz)



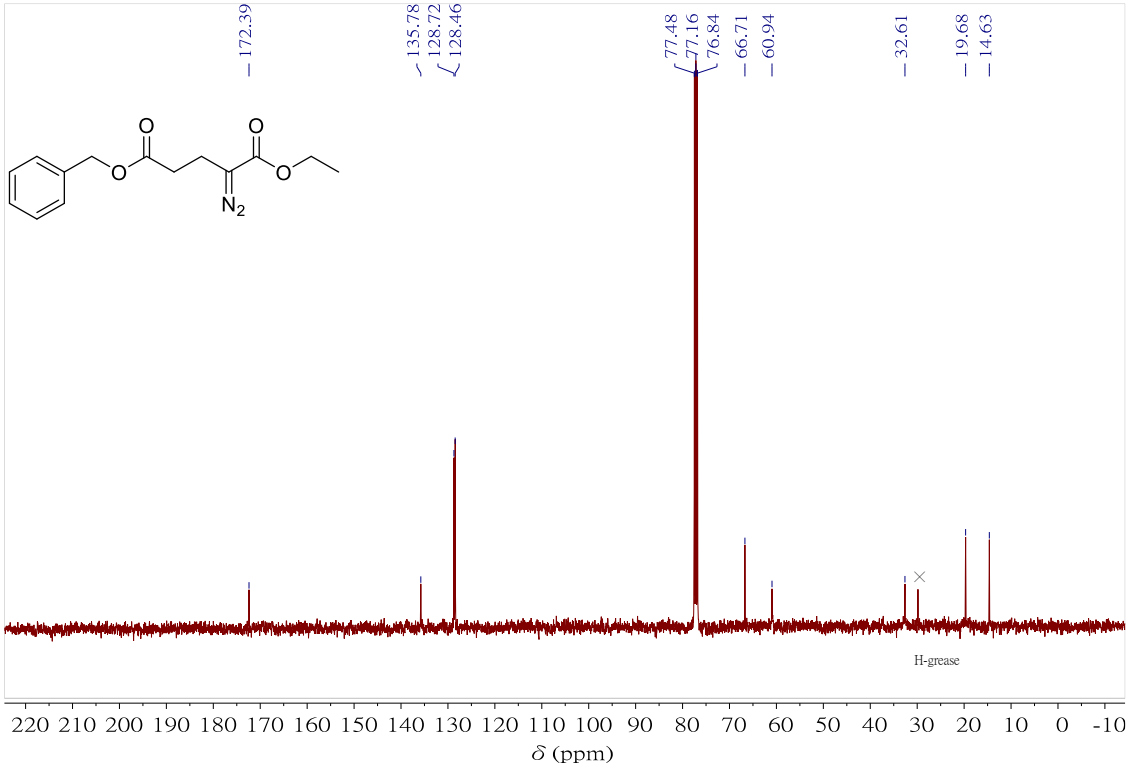
^{1}H NMR Spectrum of **23** in $CDCl_3$ (400 MHz)



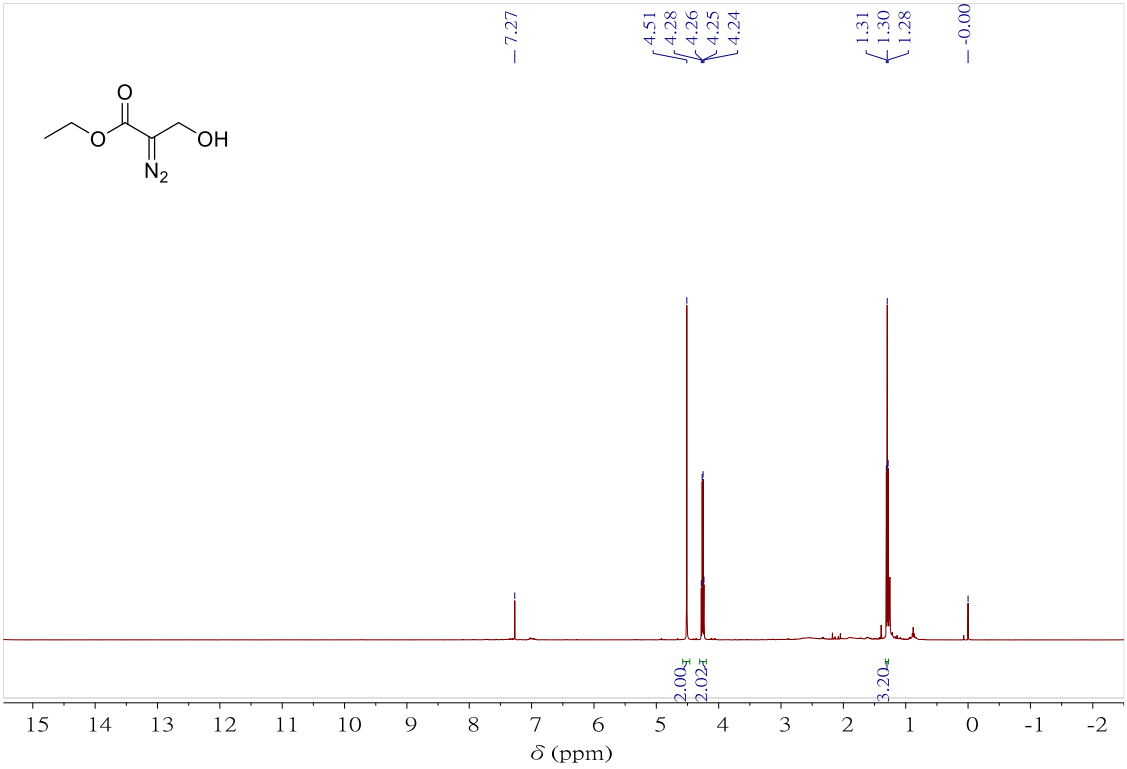
^{13}C NMR Spectrum of **23** in $CDCl_3$ (100 MHz)



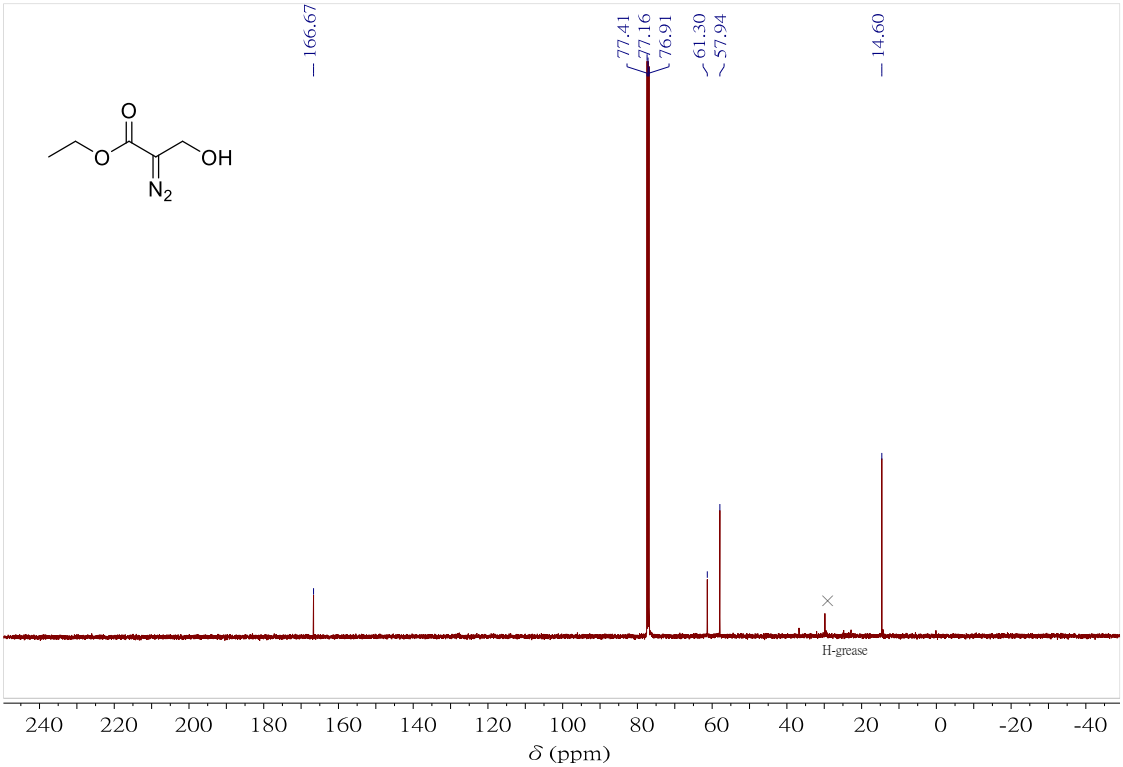
^{1}H NMR Spectrum of **24** in CD_3OD (400 MHz)



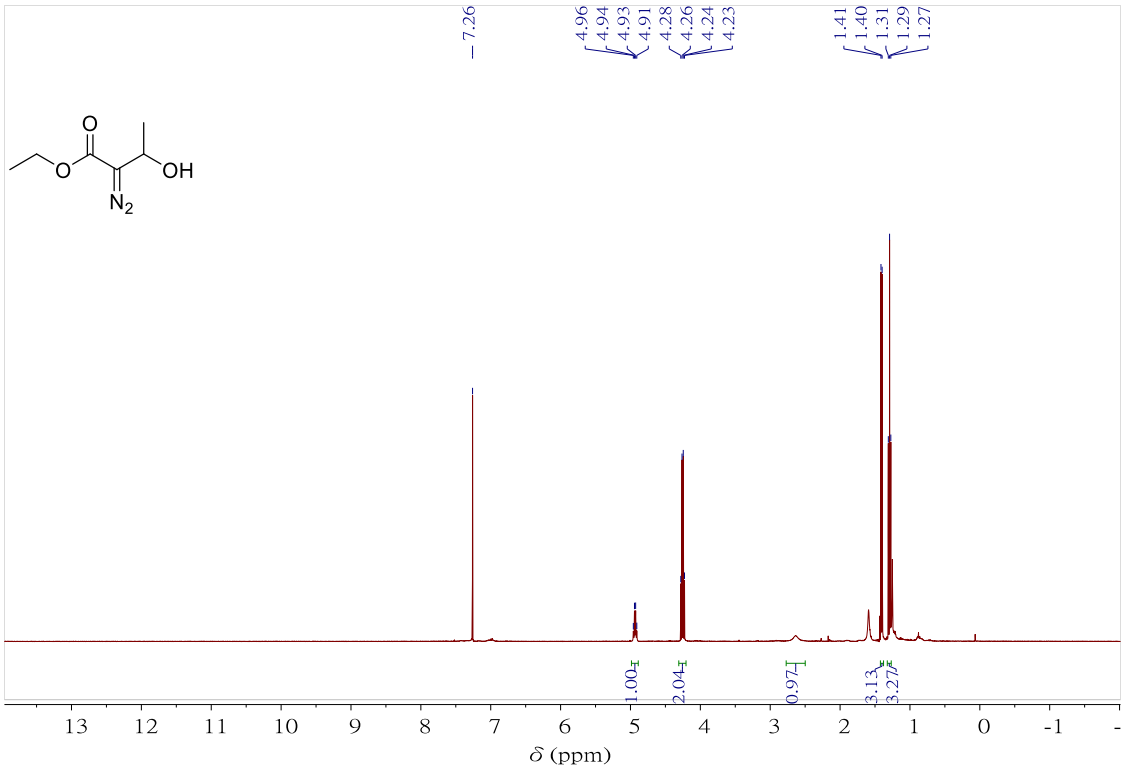
^{13}C NMR Spectrum of **24** in $CDCl_3$ (100 MHz)



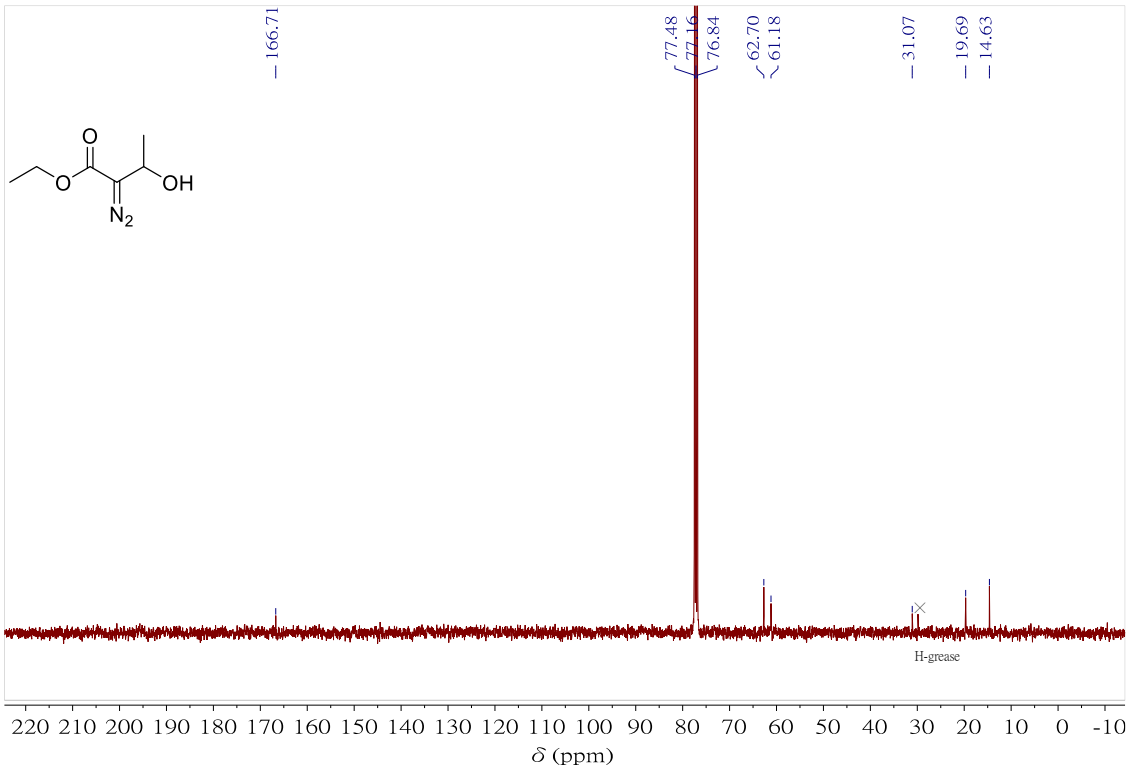
^{1}H NMR Spectrum of **25** in $CDCl_3$ (500 MHz)



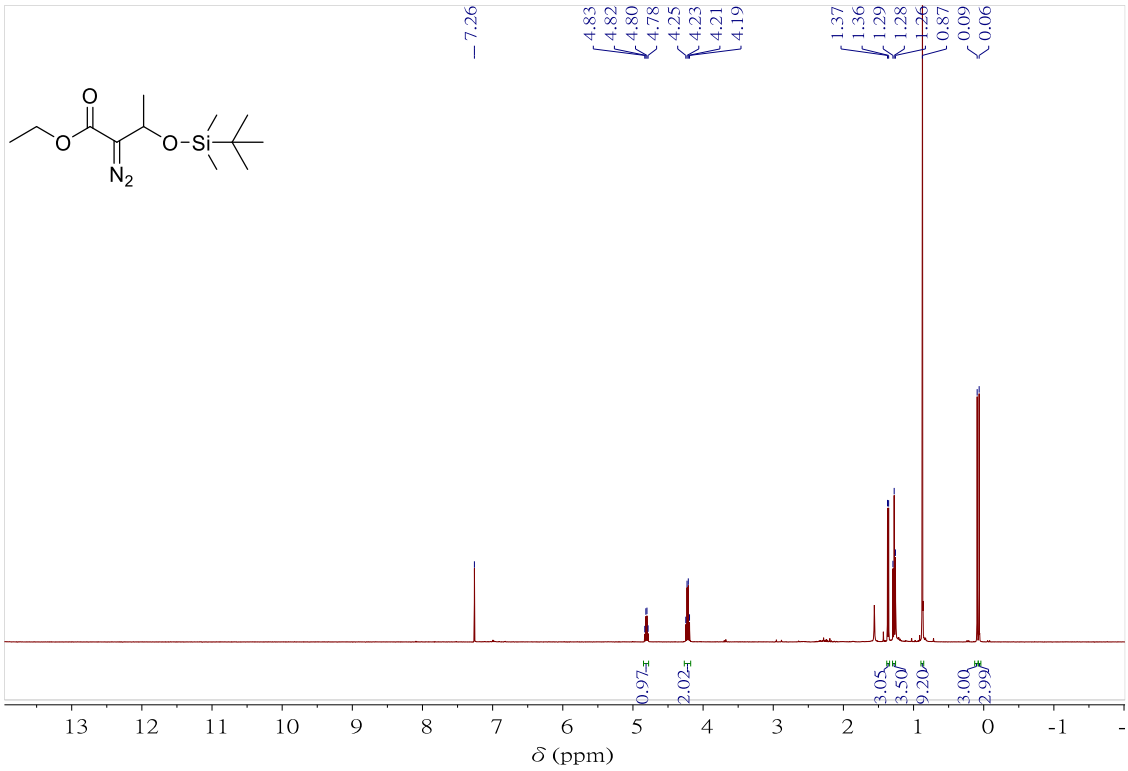
^{13}C NMR Spectrum of **25** in $CDCl_3$ (125 MHz)



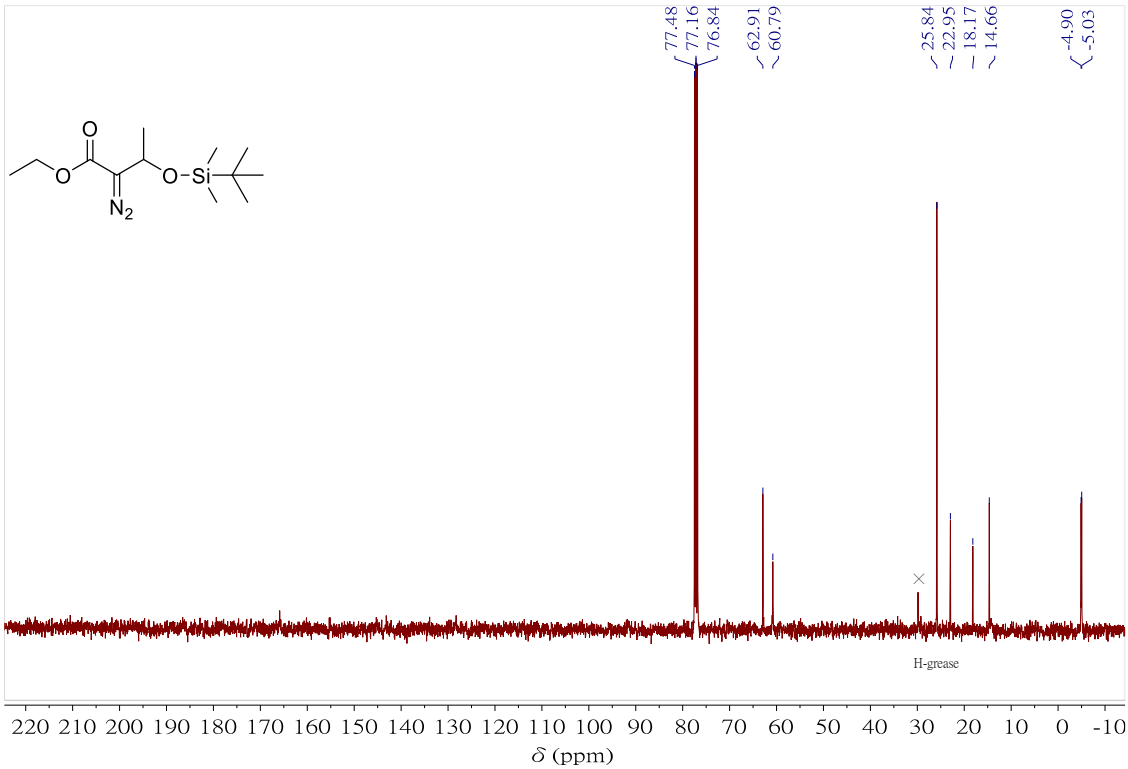
^{1}H NMR Spectrum of **26** in $CDCl_3$ (400 MHz)



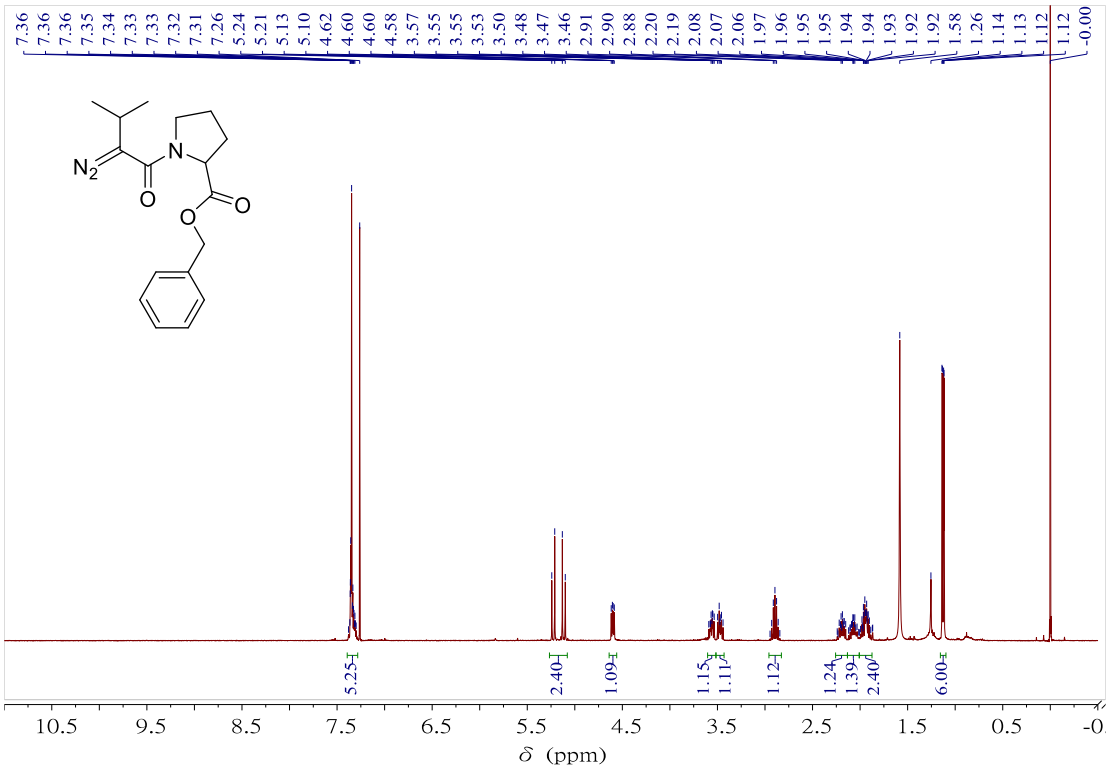
^{13}C NMR Spectrum of **26** in $CDCl_3$ (100 MHz)



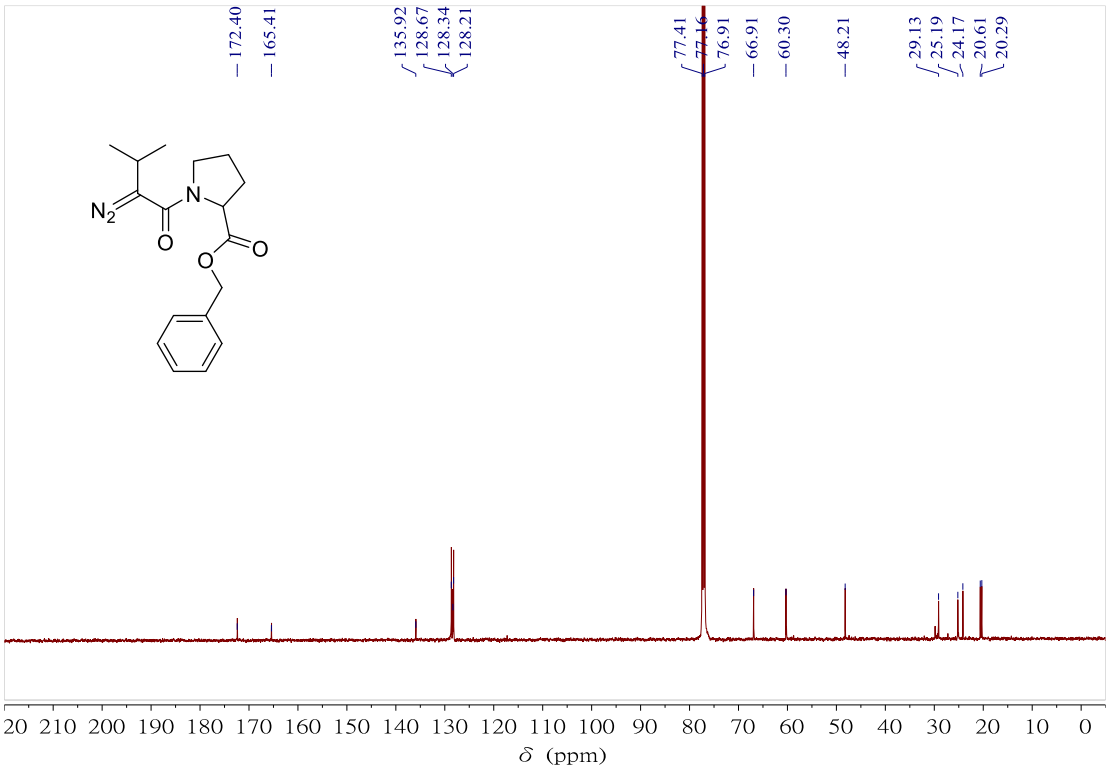
^{1}H NMR Spectrum of **27** in $CDCl_3$ (400 MHz)



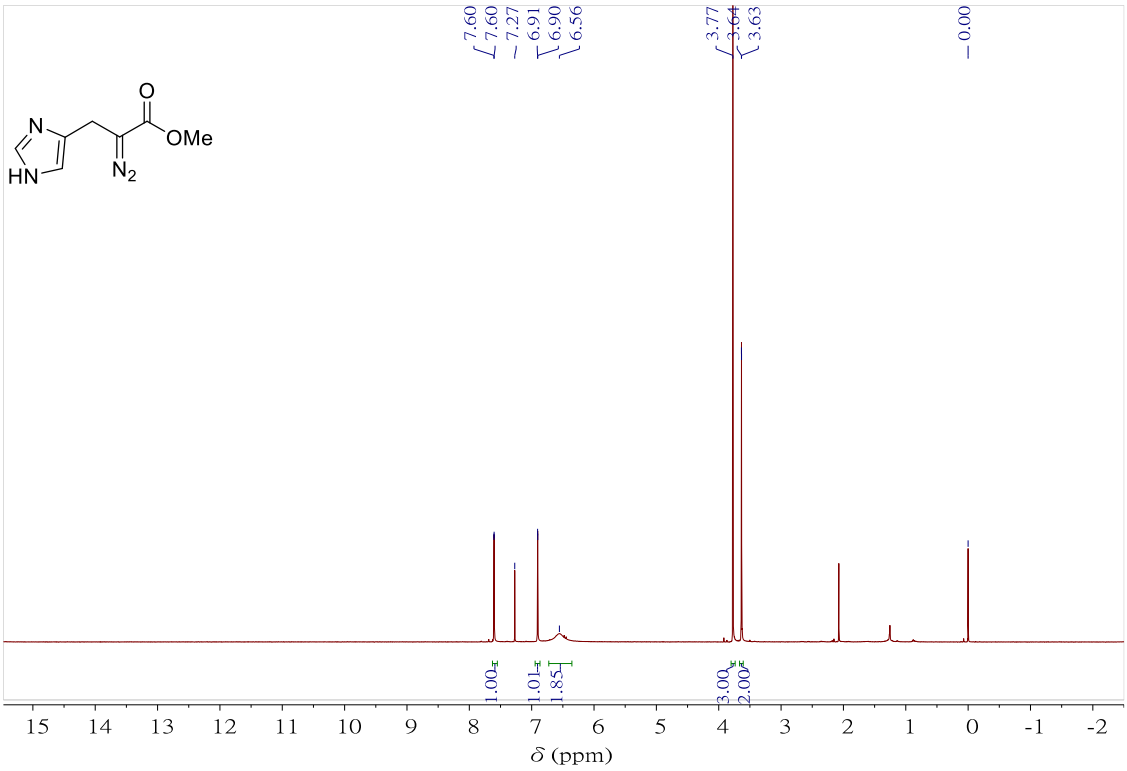
^{13}C NMR Spectrum of **27** in $CDCl_3$ (100 MHz)



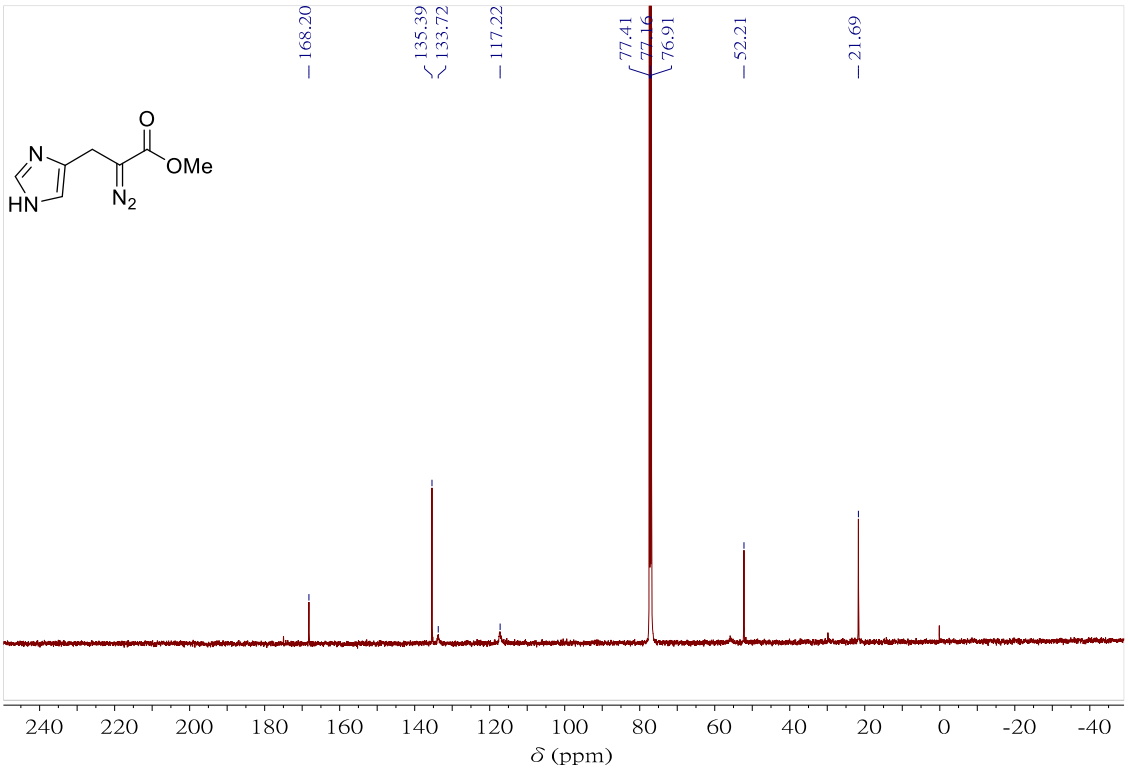
^{1}H NMR Spectrum of **28** in $CDCl_3$ (400 MHz)



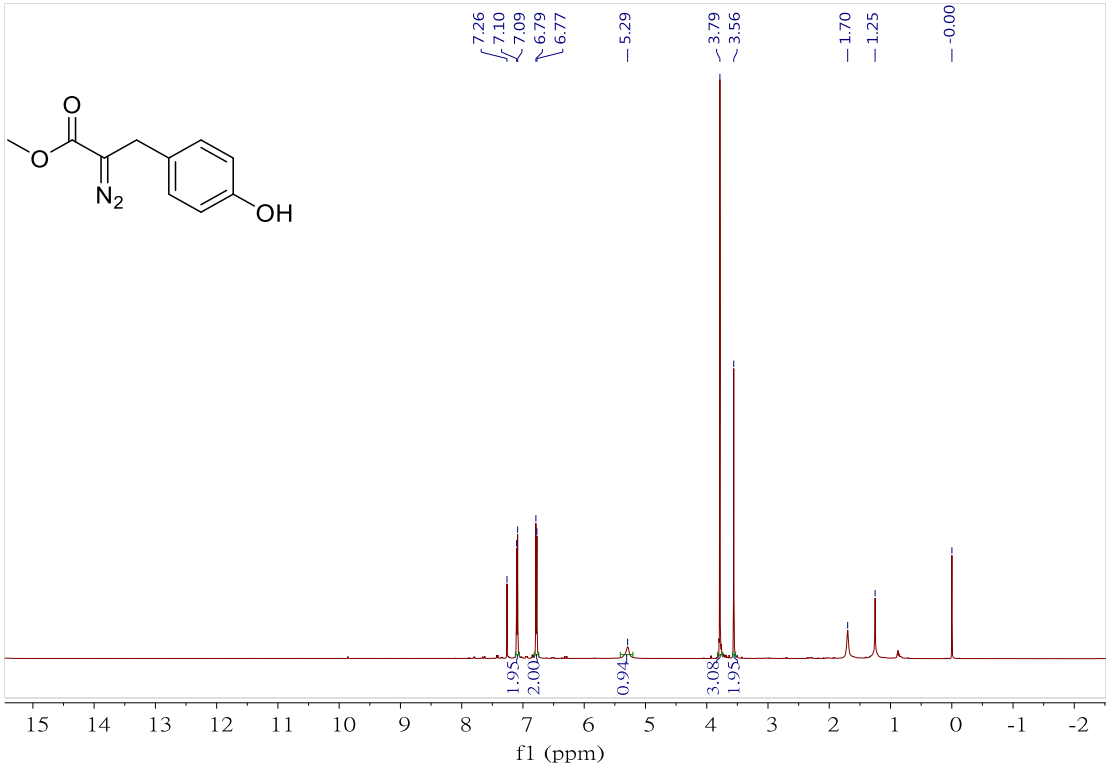
^{13}C NMR Spectrum of **28** in $CDCl_3$ (125 MHz)



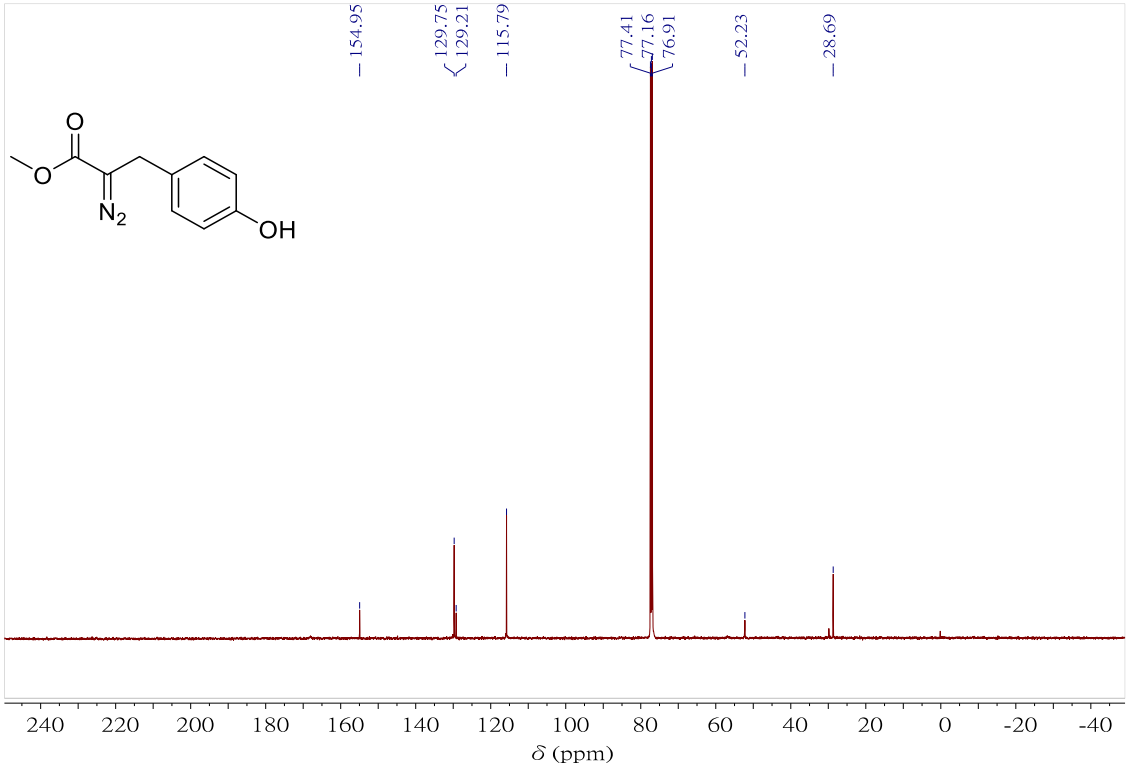
^{1}H NMR Spectrum of **29** in $CDCl_3$ (500 MHz)



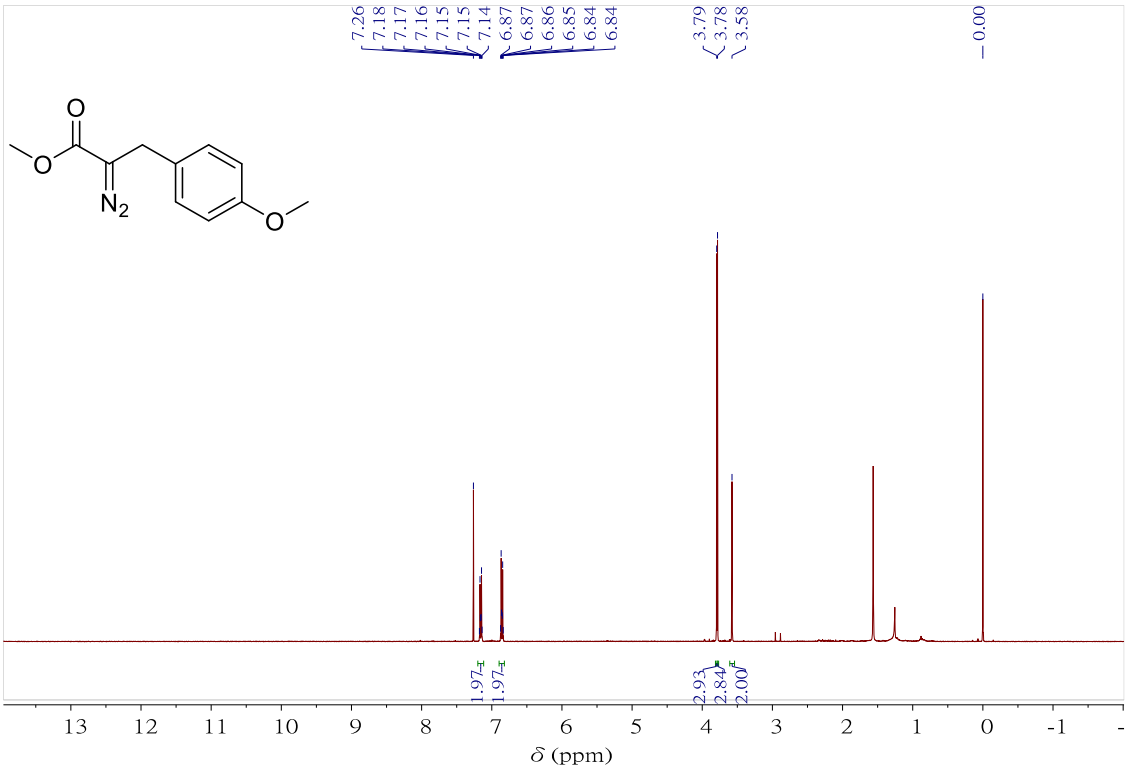
^{13}C NMR Spectrum of **29** in $CDCl_3$ (125 MHz)



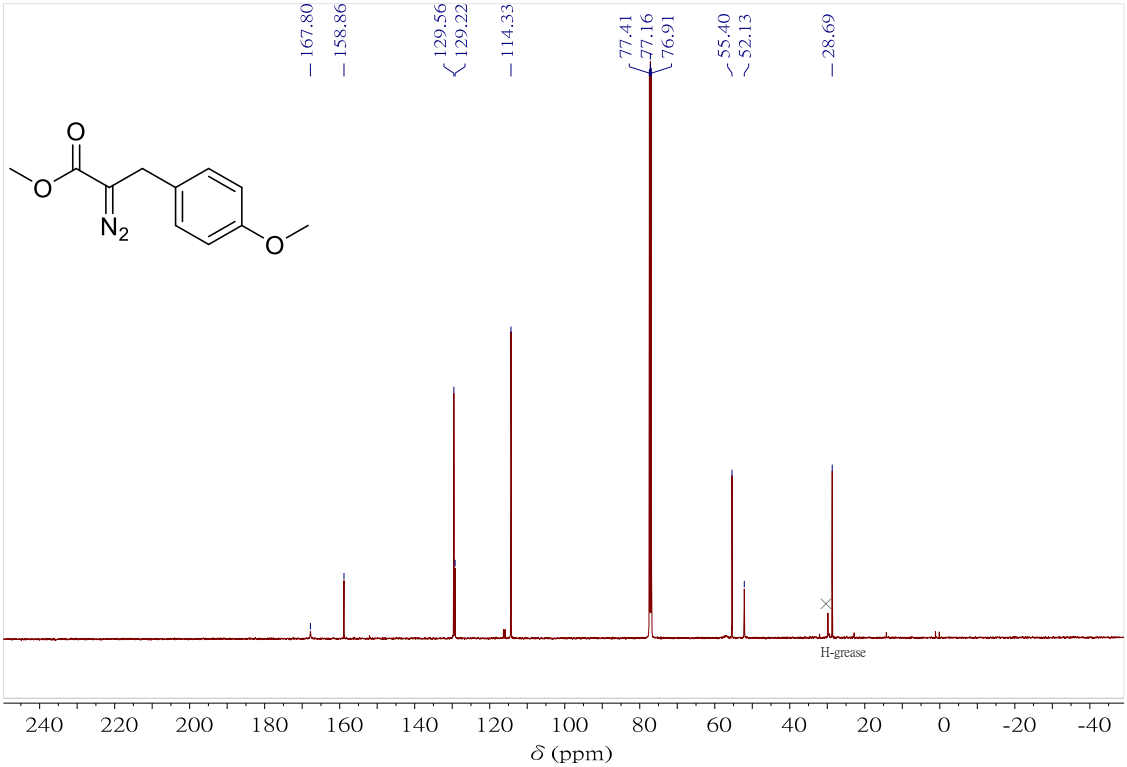
^{1}H NMR Spectrum of **30** in $CDCl_3$ (500 MHz)



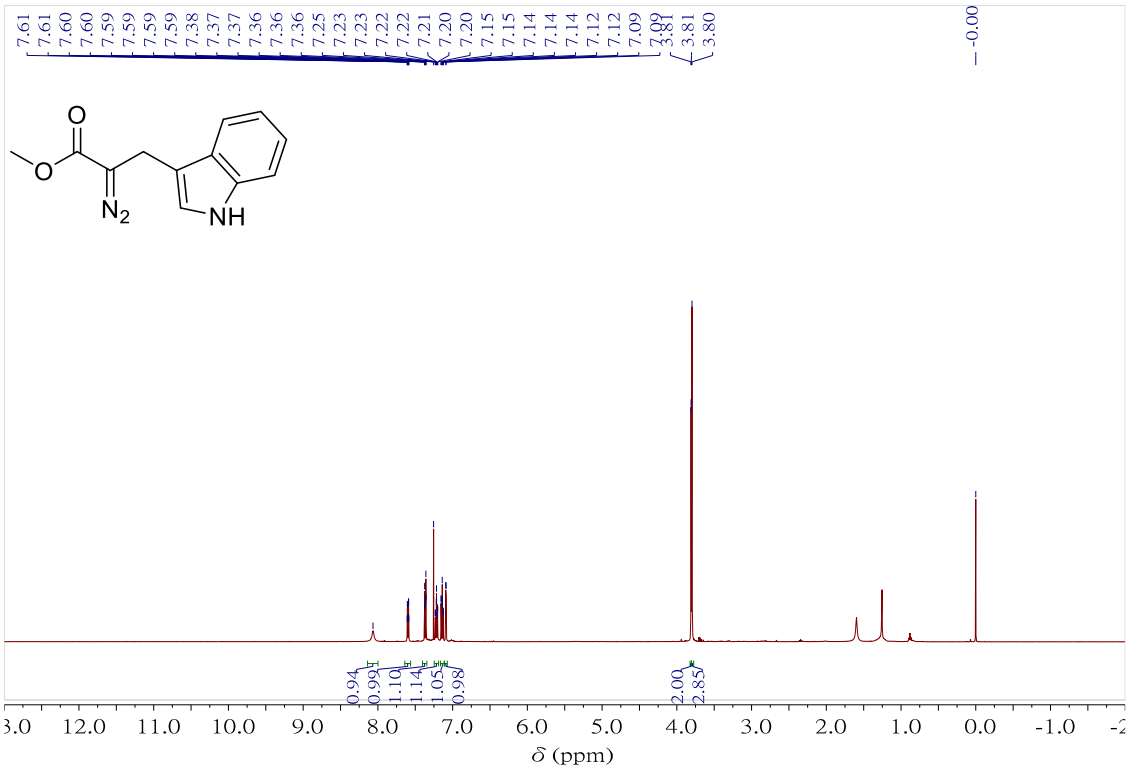
^{13}C NMR Spectrum of **30** in $CDCl_3$ (125 MHz)



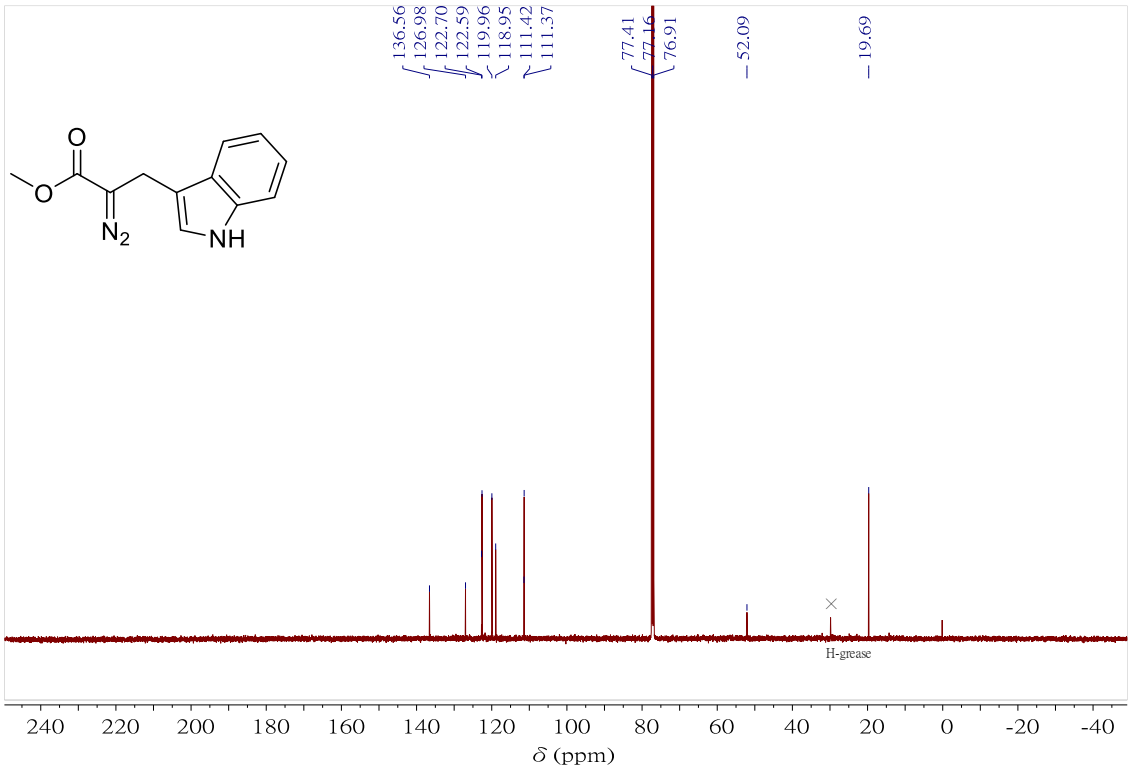
^{1}H NMR Spectrum of **31** in $CDCl_3$ (400 MHz)



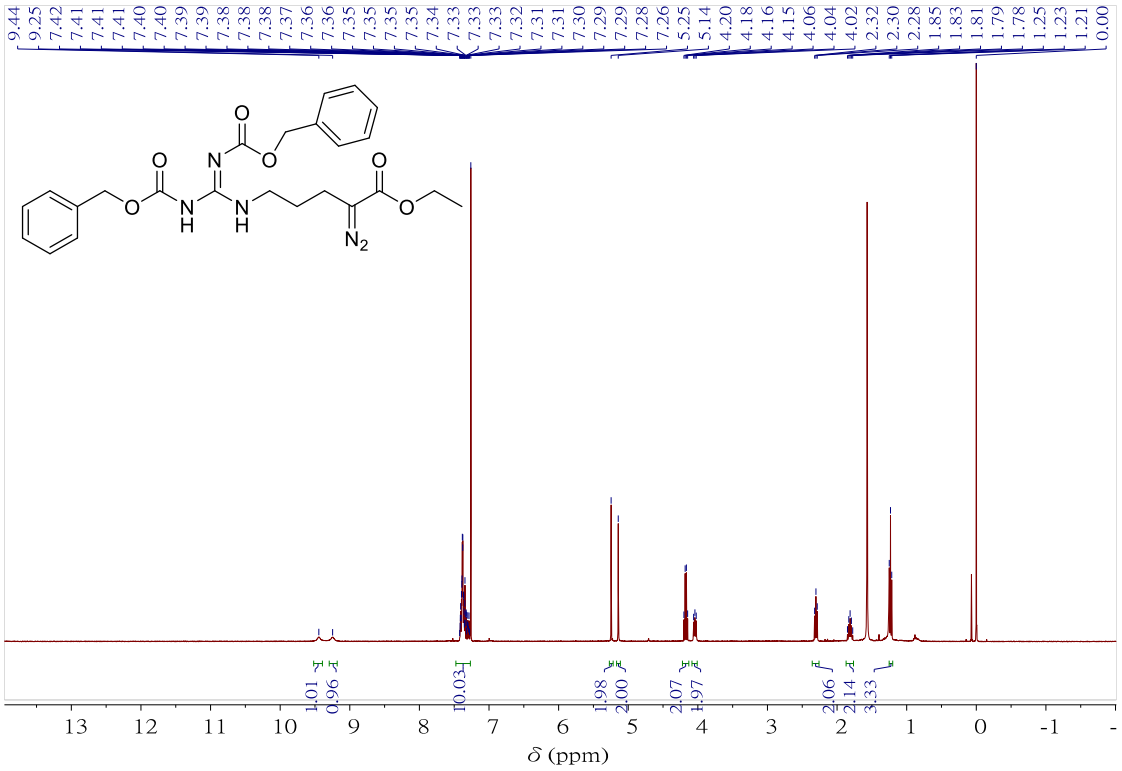
^{13}C NMR Spectrum of **31** in $CDCl_3$ (125 MHz)



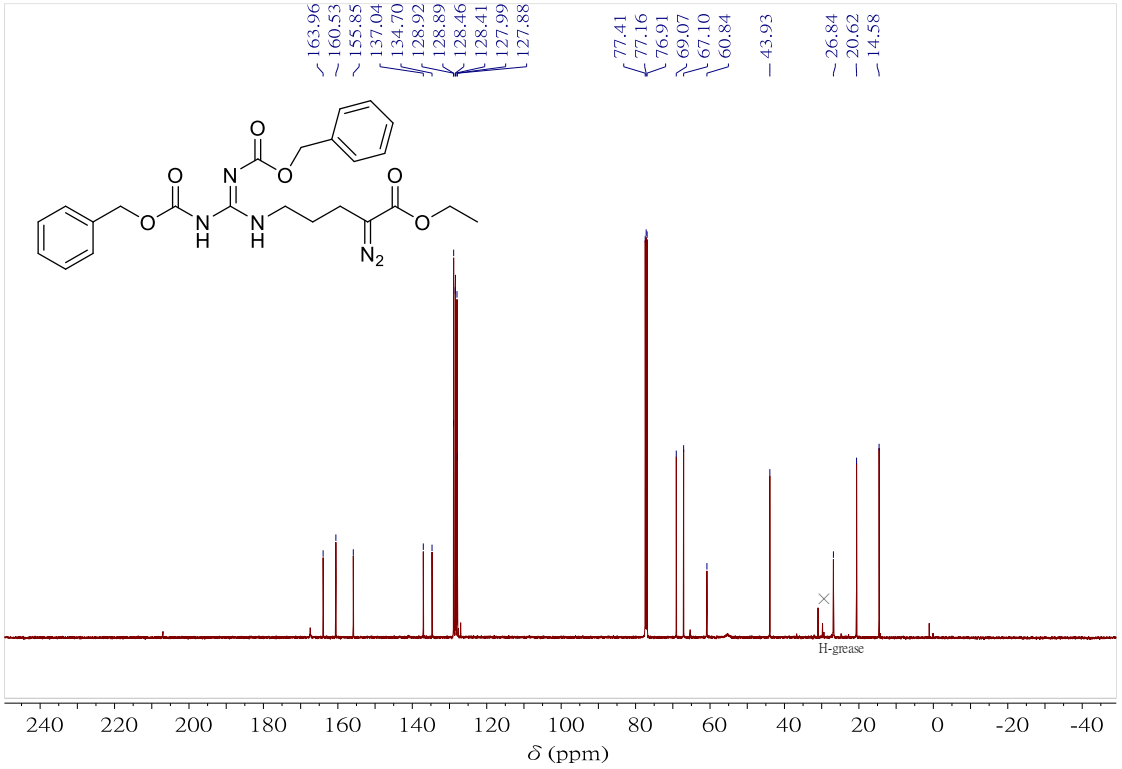
^{1}H NMR Spectrum of **32** in $CDCl_3$ (500 MHz)



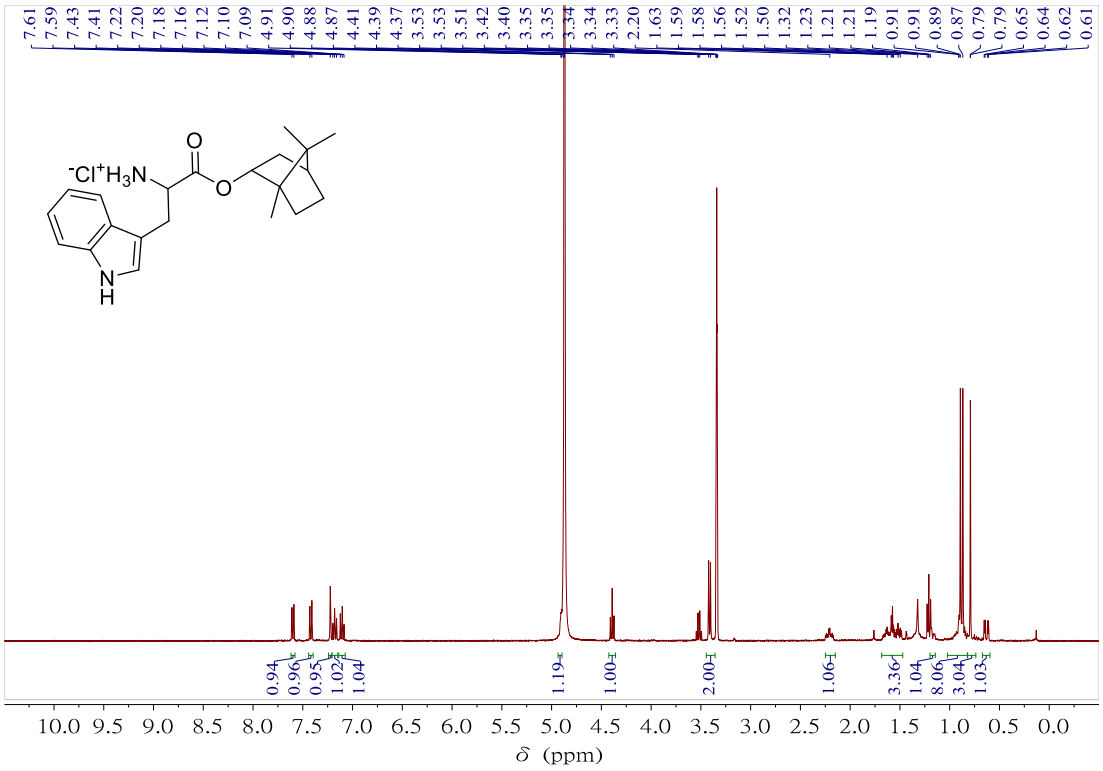
^{13}C NMR Spectrum of **32** in $CDCl_3$ (125 MHz)



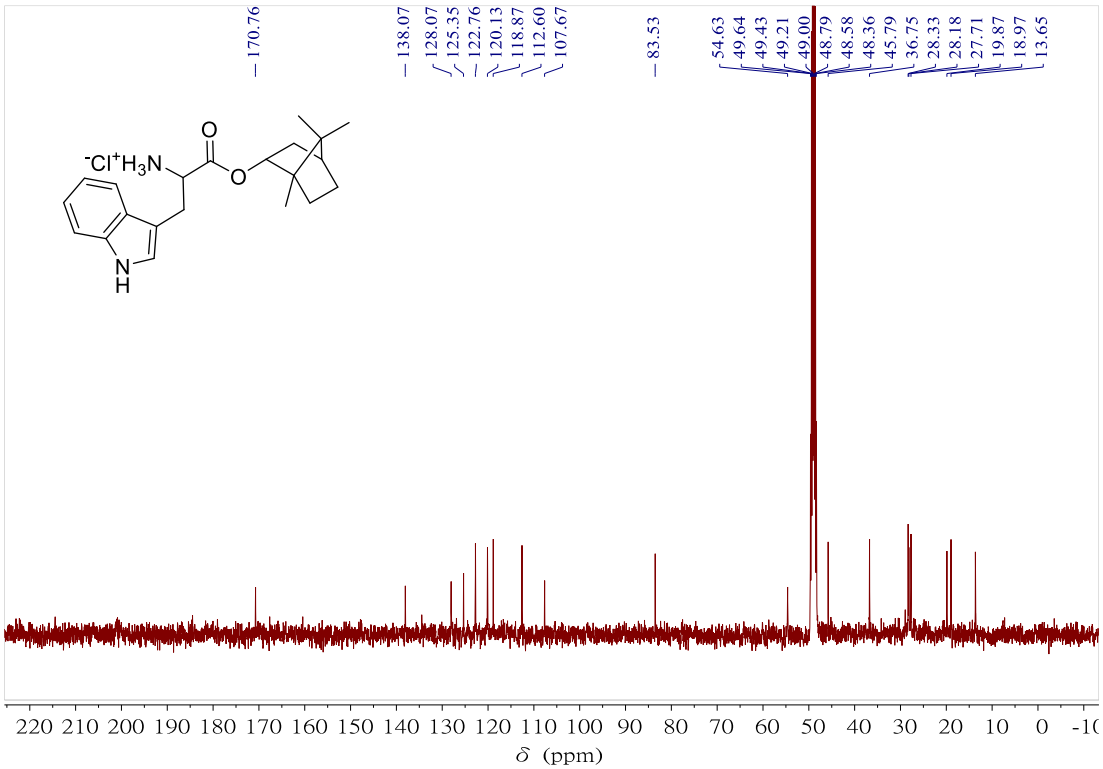
^{1}H NMR Spectrum of **33** in $CDCl_3$ (400 MHz)



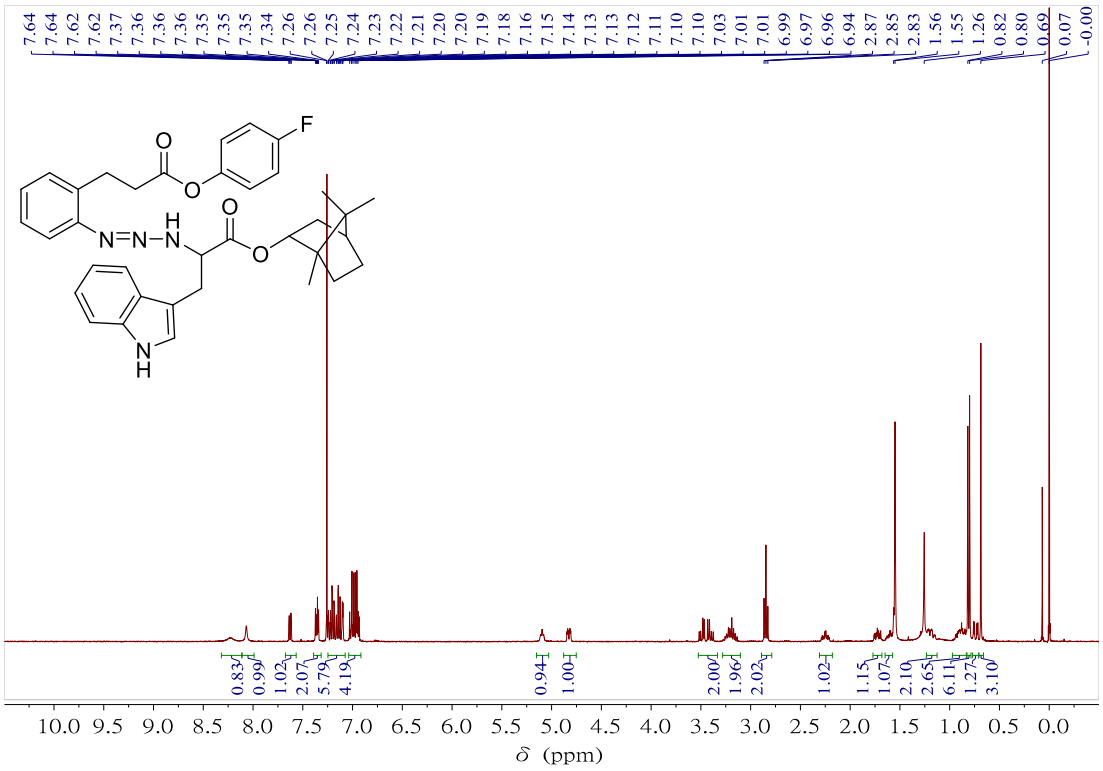
^{13}C NMR Spectrum of **33** in $CDCl_3$ (125 MHz)



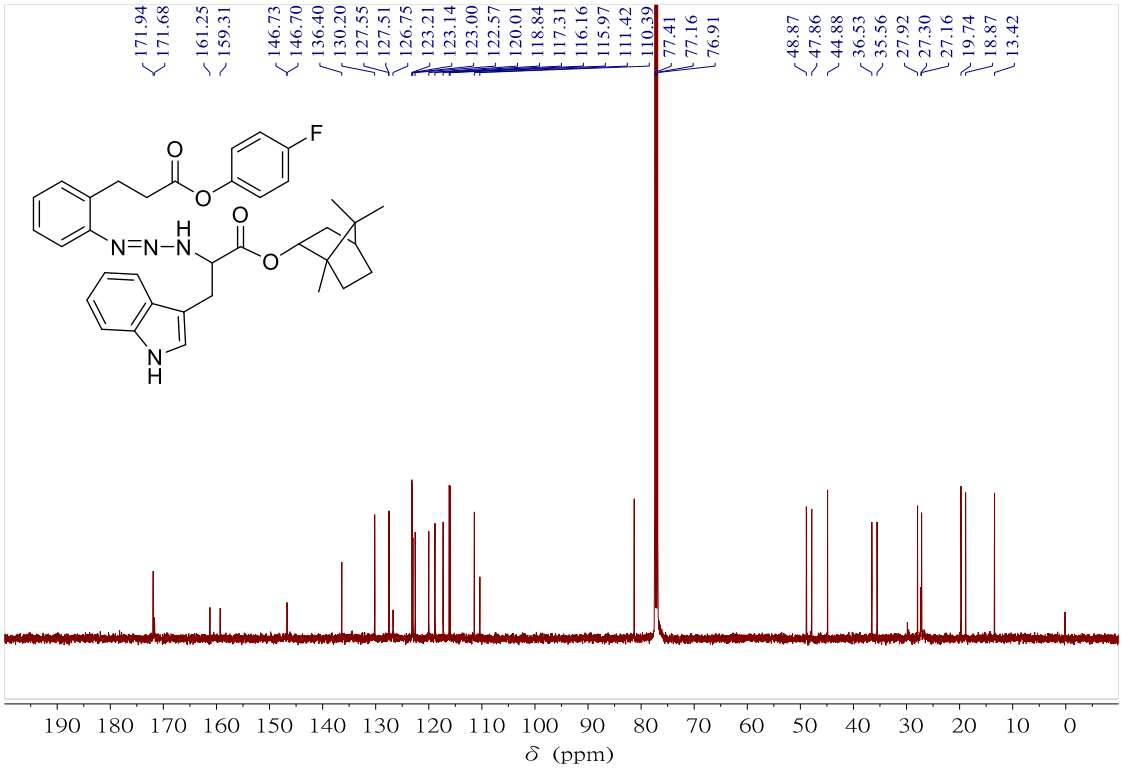
^{1}H NMR Spectrum of **34** in CD_3OD (400 MHz)



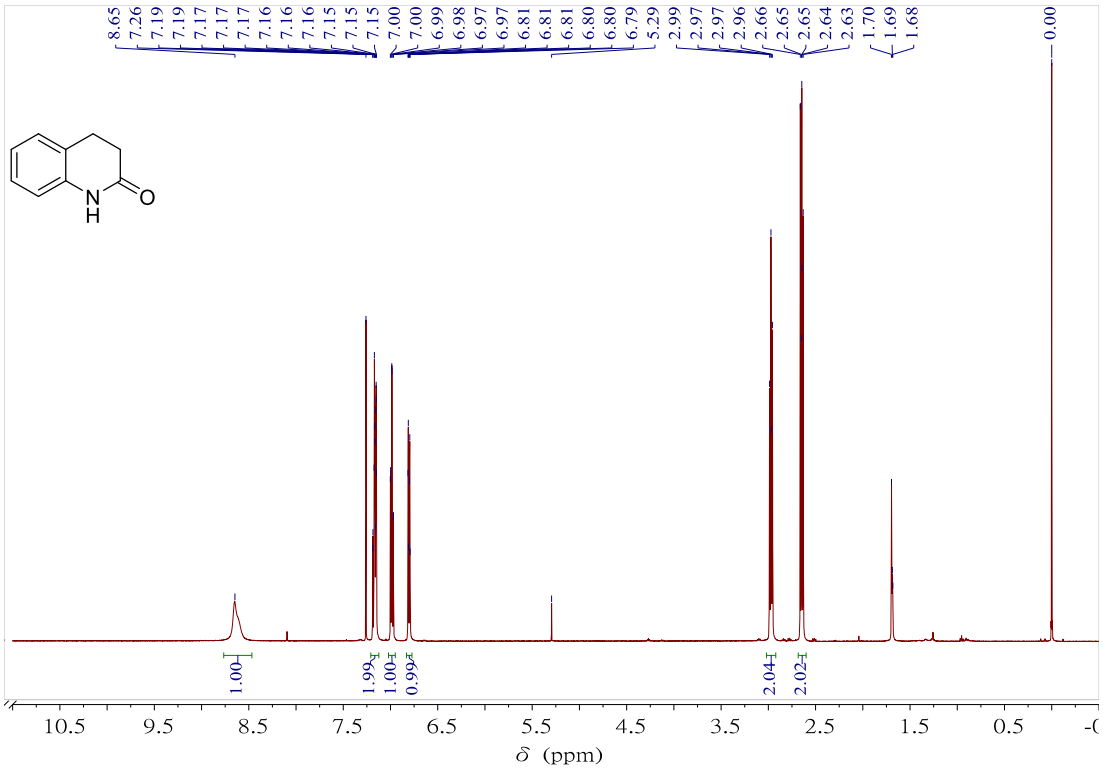
^{13}C NMR Spectrum of **34** in CD_3OD (100 MHz)



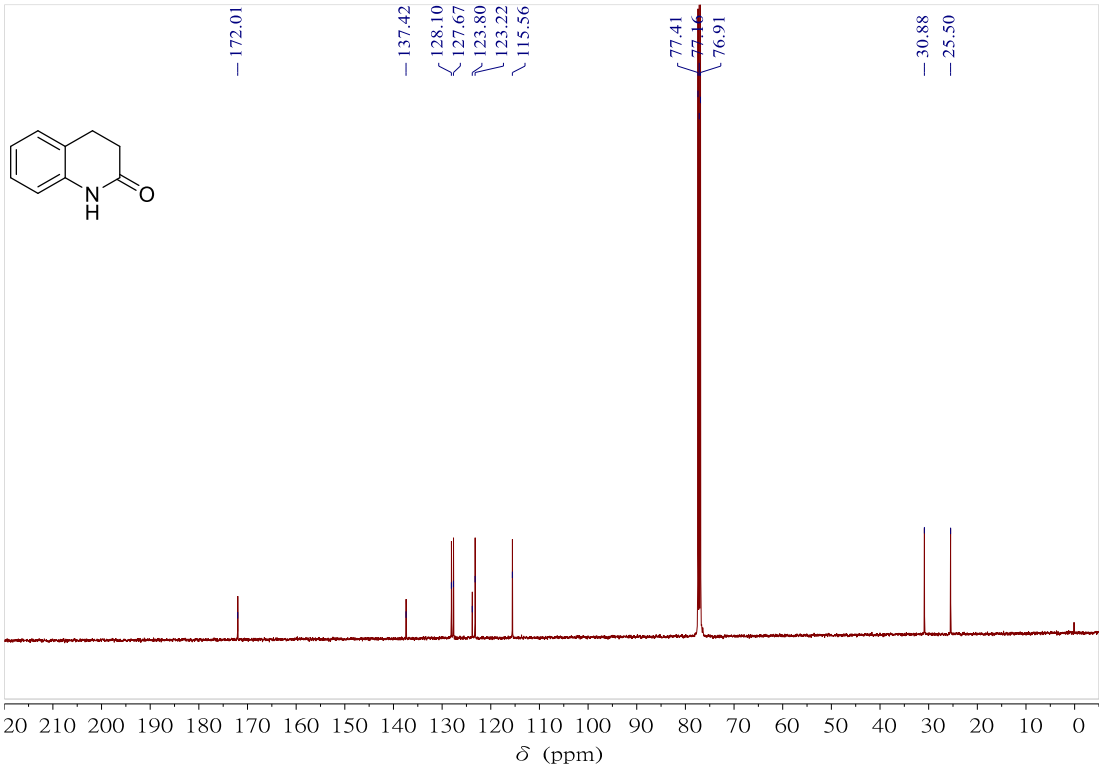
^{1}H NMR Spectrum of **35** in $CDCl_3$ (400 MHz)



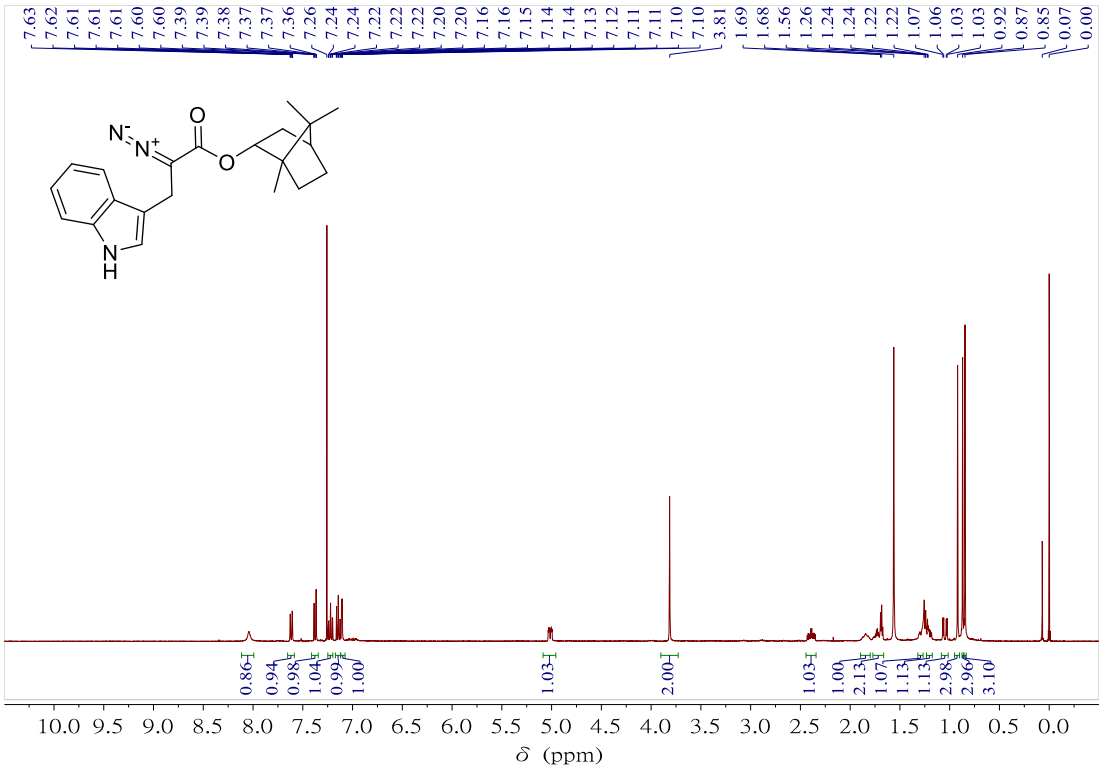
^{13}C NMR Spectrum of **35** in $CDCl_3$ (125 MHz)



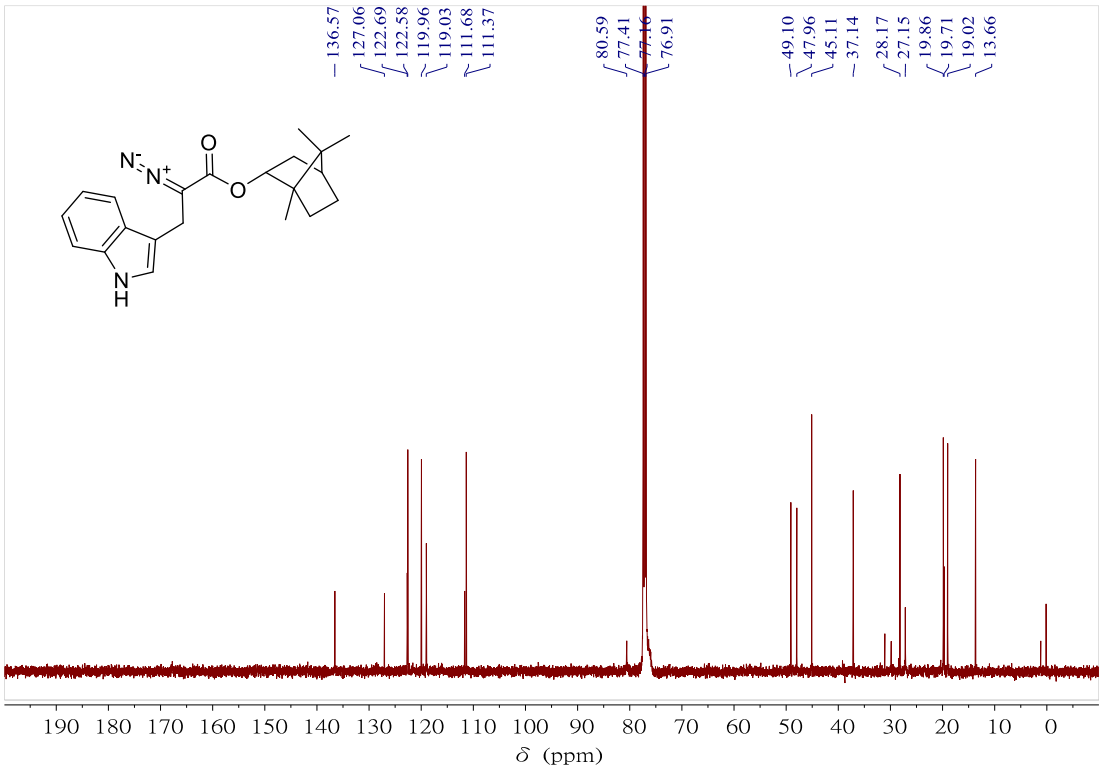
^{1}H NMR Spectrum of **36** in $CDCl_3$ (500 MHz)



^{13}C NMR Spectrum of **36** in $CDCl_3$ (125 MHz)



^{1}H NMR Spectrum of **37** in $CDCl_3$ (500 MHz)



^{13}C NMR Spectrum of **37** in $CDCl_3$ (125 MHz)