Supporting Information

Recyclable and Reusable Ionic Liquid-Supported Azo Precursors in Mitsunobu Reactions

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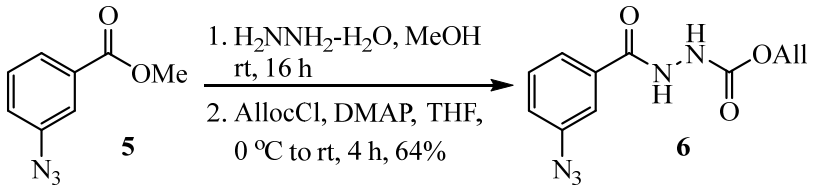
A. General Information

Unless otherwise noted, all reagents and solvents were obtained commercially and used without further purification. ^{1}H and ^{13}C NMR spectra were recorded on Varian Mercury-400 MHz, Varian Mercury-600 MHz and Jeol-400 MHz spectrometers. Chloroform-*d* (δ = 7.24) or deuterium oxide (δ = 4.60) or DMSO-*d*6 (δ = 2.49) was used as internal standard in ^{1}H NMR spectra. The center peak of deuterochloroform (δ = 77.0) or deuterated DMSO (δ = 39.5) was used as internal standard in ^{13}C NMR spectra. High-resolution mass spectrometry (HRMS) analyses were determined on a Thermo Scientific Orbitrap LTQ XL mass spectrometer. Elemental analyses were measured on an elemental analyzer. Optical rotations were measured in CH_2Cl_2 solution with a cuvette of 1 dm length on a Rudolph Autopol IV automatic polarimeter at λ =589 nm (Na). IR spectra were recorded with a Thermo Scientific Nicolet iS5 FT-IR spectrophotometer and only structurally important peaks are listed. Melting points were measured on a melting point apparatus with a capillary melting point tube. Thin-layer chromatography (TLC) plates visualized by exposure to ultraviolet light at 254 nm and/or immersion in a staining solution (phosphomolybdic acid, potassium permanganate, or *p*-anisaldehyde) followed by heating on a hot plate. Flash chromatography was carried out utilizing silica gel 60, 70-230 mesh ASTM.

B. Experimental section



Allyl 2-(3-azidobenzoyl)hydrazine-1-carboxylate (6). A solution of methyl 3-azidobenzoate[S1] (8 g, 45.2 mmol) in methanol (30 mL) was treated with hydrazine hydrate (11 mL, 5 equiv) and the mixture was stirred at room temperature for 16 h. The reaction mixture was concentrated and extracted with EtOAc. The combined organic layers were washed with brine, dried over anhydrous $MgSO_4$, filtered and concentrated to give the crude benzhydrazide [R_f: 0.25 (hexane/EtOAc = 2:1)] as a brown liquid and the crude material was used directly without further purification.

To a solution of the crude benzhydrazide (45.2 mmol) and DMAP (1.03 g, 0.2 equiv) in dry THF (50 mL) at 0 °C was added allyl chloroformate (4.8 mL, 1 equiv), and it became cloudy immediately after the addition. The mixture was allowed to warm up to room temperature and kept stirring for 4 h (the progress was monitored by TLC). The reaction mixture was concentrated. The residue was treated with brine and extracted with EtOAc. The combined organic layers were dried over anhydrous $MgSO_4$, filtered and concentrated. The crude residue was purified by column chromatography [silica gel, hexanes/ethyl acetate 5/1 (v/v)] to afford the title compound.

Yield: 7.55 g (64%); white solid.

Mp: 113–118 ℃.

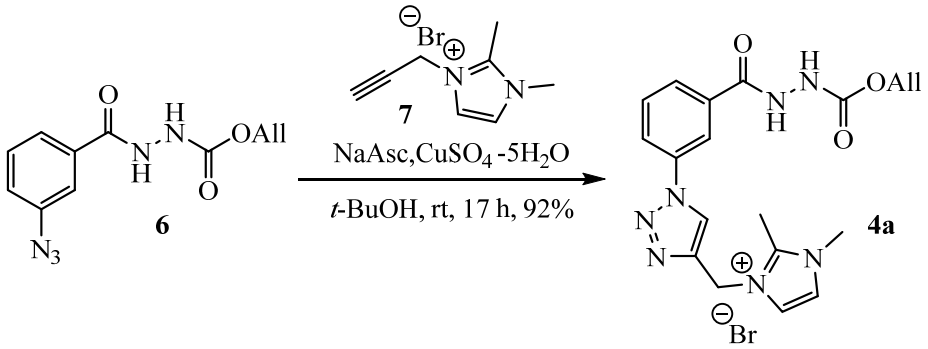
R_f: 0.64 (hexane/EtOAc = 2:1).

IR (neat, cm^{-1}): 3584, 3280, 1730, 1666, 1583, 1528, 1483.

^1H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, *J* = 7.8 Hz, 1H), 7.43 (s, 1H), 7.32 (t, *J* = 7.9 Hz, 2H), 7.14–7.04 (m, 1H), 5.92–5.82 (m, 1H), 5.31 (dd, *J* = 17.2, 1.2 Hz, 1H), 5.22 (dd, *J* = 10.5, 1.0 Hz, 1H), 4.59 (d, *J* = 5.7 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 165.8, 156.8, 140.3, 132.4, 131.3, 129.5, 123.1, 122.3, 118.0, 117.8, 66.5.

HRMS (ESI): *m/z*: $[M + H]^+$ calcd for $C_{11}H_{10}O_3N_5$ 260.0778, found 260.0788.



3-((1-(3-(2-((Allyloxy)carbonyl)hydrazine-1-carbonyl)phenyl)-1*H*-1,2,3-triazol-4-yl)methyl)-1,2-dimethyl-1*H*-imidazol-3-ium bromide (4a). To a solution of compound **7** (2.15 g, 10 mmol) and compound **6** (3 g, 1.05 equiv) in *t*-BuOH and water (1:1, 30 mL) was added 1 M $NaAsc_{(aq)}$ (2 mL, 0.2 equiv), and 1 M $CuSO_{4(aq)}$ (500 μL, 0.05 equiv). The mixture was stirred at room temperature for 15 h. After the reaction was over, the reaction mixture was extracted with EtOAc and brine. The resulting aqueous layer was extracted with *n*-BuOH (×3). The organic layers were dried over anhydrous $MgSO_4$, filtered and concentrated. H_2O was added to the residue and the mixture was washed with EtOAc (1×) and ether (1×). The aqueous layer was then concentrated to give the title compound.

Yield: 4.38 g (92%); viscous brown oil.

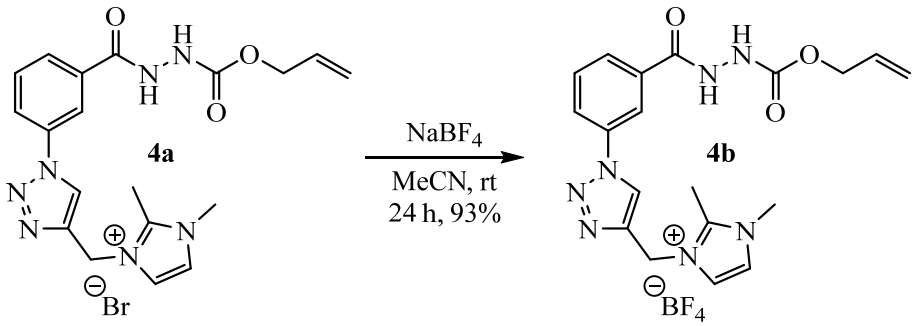
R_f: 0.25 (CH_3Cl/MeOH = 1:1).

IR (neat, cm^{-1}): 3390, 3080, 1776, 1663, 1589, 1538, 1495, 1451, 1417.

^1H NMR (400 MHz, D_2O) δ δ 8.64 (s, 1H), 8.14 (s, 1H), 7.98 (s, 1H), 7.95 (dd, *J* = 18.4, 7.6 Hz, 2H), 7.73 (t, *J* = 7.5 Hz, 1H), 7.48 (s, 1H), 7.41 (s, 1H), 6.01 (s, 1H), 5.59 (s, 2H), 5.41 (d, *J* = 16.6 Hz, 1H), 5.32 (d, *J* = 9.1 Hz, 1H), 4.72 (d, *J* = 3.2 Hz, 2H), 3.82 (s, 3H), 2.71 (s, 3H).

^{13}C NMR (100 MHz, D_2O) δ 168.6, 161.5, 144.9, 136.3, 132.8, 131.9, 130.6, 128.1, 124.7, 123.3, 122.5, 120.7, 119.9, 117.8, 66.8, 42.5, 34.7, 9.0.

HRMS (ESI): *m/z*: $[M – Br]^+$ calcd for $C_{19}H_{21}O_3N_7$ 396.1779, found 396.1770.



3-((1-(3-(2-((Allyloxy)carbonyl)hydrazine-1-carbonyl)phenyl)-1*H*-1,2,3-triazol-4-yl)methyl)-1,2-dimethyl-1*H*-imidazol-3-ium tetrafluoroborate (4b). A mixture of **4a** (2 g, 4.2 mmol) and sodium tetrafluoroborate (1.6 g, 2 equiv) in acetonitrile (15 mL). The mixture was stirred 24 h under nitrogen at room temperature. The reaction mixture was filtered and the filtrate was concentrated under reduced pressure to get the title compound **4b**.

Yield: 1.89 g (93%); brown liquid.

R_f: 0.25 (CH_3Cl/MeOH = 1:1).

IR (neat, cm^{-1}): 3285, 3078, 1774, 1649, 1589, 1538, 1488, 1450, 1425.

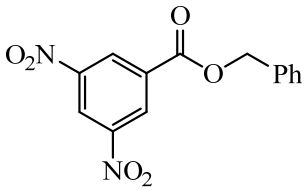
^1H NMR (400 MHz, D_2O) δ 8.43 (s, 1H), 8.00 (s, 1H), 7.82 (d, *J* = 7.9 Hz, 1H), 7.75 (d, *J* = 7.8 Hz, 1H), 7.55 (t, *J* = 8.0 Hz, 1H), 7.24 (d, *J* = 1.7 Hz, 1H), 7.17 (s, 1H), 5.79 (s, 1H), 5.38 (s, 2H), 5.19 (d, *J* = 17.7 Hz, 1H), 5.10 (d, *J* = 9.8 Hz, 1H), 4.49 (d, *J* = 5.1 Hz, 2H), 3.59 (s, 2H), 2.48 (s, 3H).

^{13}C NMR (100 MHz, DMSO-*d*6) δ 164.8, 156.2, 145.0, 142.0, 136.6, 134.8, 134.1, 133.1, 130.6, 127.9, 122.7, 121.3, 119.4, 118.2, 65.2, 59.2, 42.6, 34.88, 9.6.

HRMS (ESI): *m/z*: $[M - BF_4]^+$ calcd for $C_{19}H_{21}O_3N_7$ 396.1779, found 396.1780.

Typical procedure for the Mitsunobu reaction with ionic liquid-supported hydrazidecarboxylate

A mixture of benzyl alcohol (104 μL, 1 mmol), 3,5-dinitrobenzoic acid (255 mg, 1.2 equiv), $PhI(OAc)_2$ (387 mg, 1.2 equiv), TPP (393 mg, 1.5 equiv) and catalyst **4b** (193 mg, 0.4 equiv) in THF (5 mL) was stirred at room temperature for 15 h. The residue was rinsed with shaking with ether (5 mL), ethyl acetate (5 mL), and dichloromethane (5 mL) respectively. After the simple decantation, **4b** was recovered in the bottle and the combined organic solution was purified by the filtration through a short pad of silica gel with DCM rinsing. The solvents were removed under reduced pressure to obtain the desired product. The crude product cab be purified by column chromatography if necessary.



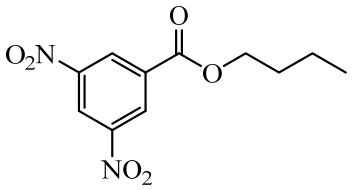
Entry 1, **Table 3**[S2]

Yield: 257 mg (85%); light yellow solid.

R_f: 0.55 (hexane/EtOAc = 4:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.20 (t, *J* = 2.1 Hz, 1H), 9.16–9.14 (m, 2H), 7.43 (dd, *J* = 18.0, 4.4 Hz, 6H), 5.46 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 162.4, 148.6, 134.5, 133.8, 129.5, 129.0, 128.9, 128.8, 122.4, 68.6.



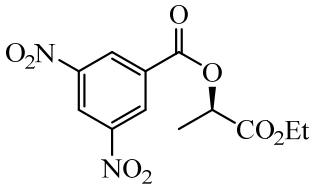
Entry 2, **Table 3**[S3]

Yield: 190 mg (71%); white solid.

R_f: 0.62 (hexane/EtOAc = 4:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.21 (d, *J* = 2.2 Hz, 1H), 9.14 (d, *J* = 2.2 Hz, 1H), 4.44 (t, *J* = 6.7 Hz, 1H), 1.81 (dt, *J* = 14.6, 6.8 Hz, 1H), 1.48 (dd, *J* = 15.1, 7.5 Hz, 1H), 0.99 (t, *J* = 7.4 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 162.9, 149.0, 134.5, 129.7, 122.6, 67.2, 30.9, 19.5, 14.0.



Entry 3, **Table 3**[S4]

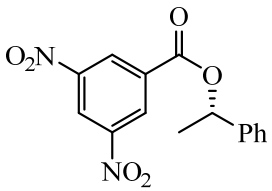
Yield: 247 mg (79%); white solid.

R_f: 0.25 (hexane/EtOAc = 4:1).

$[\alpha]_D^{26}$ –6.00 (*c* 0.01, CH_2Cl_2).

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.24 (t, *J* = 2.1 Hz, 1H), 9.18 (d, *J* = 2.1 Hz, 2H), 5.39 (d, *J* = 7.1 Hz, 1H), 4.25 (q, *J* = 7.1 Hz, 2H), 1.70 (d, *J* = 7.0 Hz, 4H), 1.29 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.7, 162.0, 148.7, 133.2, 129.6, 122.7, 77.3, 77.0, 76.7, 70.8, 61.9, 16.9, 14.1.



Entry 4, **Table 3**[S4]

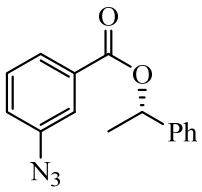
Yield: 266 mg (84%); white solid.

R_f: 0.62 (hexane/EtOAc = 4:1).

$[\alpha]_D^{26}$ +38.8 (*c* 0.01, CH_2Cl_2).

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.19 (t, *J* = 2.1 Hz, 1H), 9.14 (d, *J* = 2.1 Hz, 2H), 7.45 (d, *J* = 7.0 Hz, 2H), 7.40–7.33 (m, 3H), 6.20 (q, *J* = 6.6 Hz, 1H), 1.75 (d, *J* = 6.6 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 161.8, 148.6, 140.1, 134.2, 129.4, 128.8, 128.6, 126.3, 122.3, 77.3, 77.0, 76.7, 75.5, 21.9.



Entry 5, **Table 3**

Typical procedure for the Mitsunobu reaction with larger scale

A mixture of (*R*)-(+)-1-phenylethanol (1.22 g, 10 mmol), 3-azidobenzoic acid (1.96 g, 1.2 equiv), $PhI(OAc)_2$ (3.87 g, 1.2 equiv), TPP (3.93 g, 1.5 equiv) and catalyst **4b** (reused form, not freshly prepared, 1.93 g, 0.4 equiv) in THF (50 mL) was stirred at room temperature for 15 h. The reaction mixture was concentrated under reduced pressure. The residue was rinsed with shaking with ether (50 mL), ethyl acetate (50 mL), and dichloromethane (50 mL) respectively. After the simple decantation, **4b** was recovered in the bottle (1.66 g, 86%) and the combined organic solution was washed with aqueous $NaHCO_3$ saturated solution and purified by the filtration through a short pad of silica gel with DCM rinsing. The solvents were removed under reduced pressure to obtain the crude product which allowed to be furthermore purified by column chromatography [silica gel, hexanes/ethyl acetate 3/1 (v/v)] to get rid of the remaining TPPO to obtain the analytically pure product (2.35 g, 88%) as a yellow liquid.

R_f: 0.25 (hexane/EtOAc = 4:1).

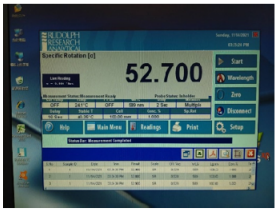
$[\alpha]_D^{20}$ +22.3 (*c* 0.01, CH_2Cl_2).

IR (neat, cm^{-1}): 3035, 2921, 2108, 1722, 1586, 1483, 1443.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85–7.83 (m, 1H), 7.72 (t, *J* = 1.8 Hz, 1H), 7.59–7.71 (1H), 7.44–7.27 (m, 6H), 7.19 (ddd, *J* = 8.1, 2.3, 0.9 Hz, 1H), 6.12 (q, *J* = 6.6 Hz, 1H), 1.67 (d, *J* = 6.6 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 165.0, 141.6, 140.6, 132.4, 129.9, 128.7, 128.1, 126.2, 126.2, 123.4, 120.2, 73.5, 22.4.

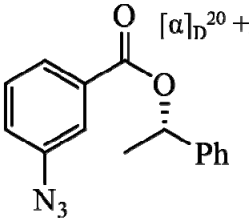
HRMS (APCI): *m/z*: $[M + H]^+$ calcd for $C_{15}H_{14}N_3O_2$ 267.1003, found 267.1008.



OH
Ph
(10 mmol)

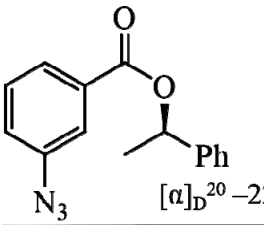
$[\alpha]_D^{24}$ +52.7 (*c* 0.01, CH_2Cl_2)

3-azidobenzoic acid (1.2 equiv)
4b (0.4 equiv)
TPP (1.5 equiv)
$PhI(OAc)_2$ (1.2 equiv)
THF, rt, 15 h, 88%

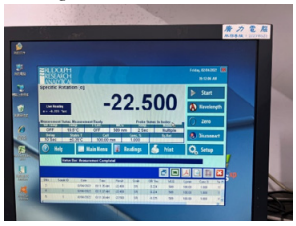


$[\alpha]_D^{20}$ +22.3 (*c* 0.01, CH_2Cl_2)

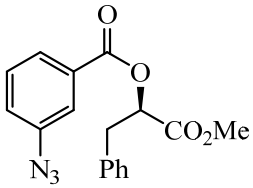
3-azidobenzoic acid (1.5 equiv)
EDCI (2 equiv)
DMAP (0.2 equiv)
THF, rt, 15 h, 90%



$[\alpha]_D^{20}$ –22.5 (*c* 0.01, CH_2Cl_2)



(*R*)-(+)-1-phenylethanol, $[\alpha]_D^{27}$ +54.9 (*c* 1.00, $CHCl_3$), 96%ee.[S5]



Entry 6, **Table 3**

Yield: 267 mg (82%); yellow liquid.

R*f*: 0.25 (hexane/EtOAc = 4:1).

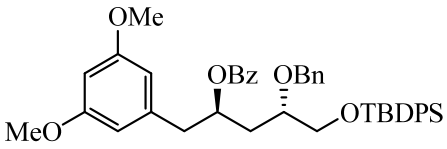
$[\alpha]_D^{26}$ +70.6 (*c* 0.01, CH_2Cl_2).

IR (neat, cm^{-1}): 2955, 2118, 1728, 1638, 1587, 1484, 1441.

^1H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 7.8 Hz, 1H), 7.66 (t, *J* = 1.8 Hz, 1H), 7.39 (t, *J* = 7.9 Hz, 1H), 7.33–7.24 (m, 5H), 7.19–7.16 (m, 1H), 5.43 (dd, *J* = 8.2, 4.7 Hz, 1H), 3.74 (s, 3H), 3.30–3.26 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.8, 164.9, 140.5, 135.7, 131.0, 129.8, 129.3, 128.6, 127.1, 126.2, 123.8, 120.0, 77.3, 77.0, 76.7, 73.6, 60.3, 52.4, 37.4, 21.0, 14.1.

HRMS (APCI): *m/z*: $[M + H]^+$ calcd for $C_{17}H_{16}N_3O_4$ 326.1135, found 326.1126.



Entry 7, **Table 3**

Yield: 475 mg (69%); colorless oil.

R_f: 0.4 (hexane/EtOAc = 6:1).

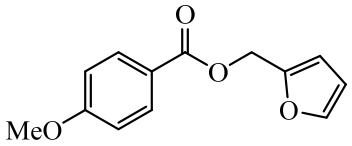
$[\alpha]_D^{26}$ –7.1 (*c* 1, CH_2Cl_2).

IR (neat, cm^{-1}): 2928, 2857, 1716, 1598, 1461, 1428.

^1H NMR (600 MHz, $CDCl_3$) δ 8.06 (d, *J* = 7.9 Hz, 2H), 7.67 (d, *J* = 6.9 Hz, 4H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.47–7.20 (m, 13H), 6.40 (d, *J* = 1.9 Hz, 2H), 6.34 (t, *J* = 2.0 Hz, 1H), 5.69–5.65 (m, 1H), 4.54 (d, *J* = 10.9 Hz, 1H), 4.36 (d, *J* = 10.9 Hz, 1H), 3.76 (dd, *J* = 10.4, 5.1 Hz, 1H), 3.69 (s, 6H), 3.66 (dd, *J* = 10.5, 5.4 Hz, 1H), 3.62–3.59 (m, 1H), 3.05 (dd, *J* = 13.7, 5.6 Hz, 1H), 2.95 (dd, *J* = 13.8, 6.5 Hz, 1H), 2.01–1.97 (m, 1H), 1.86 (ddd, *J* = 14.6, 10.2, 2.2 Hz, 1H), 1.07 (s, 9H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 165.8, 160.5, 139.3, 138.3, 135.5, 133.3, 133.3, 132.8, 130.5, 129.6, 129.5, 128.3, 128.2, 128.0, 127.6, 127.5, 107.5, 98.8, 76.2, 72.7, 71.9, 65.9, 55.1, 41.3, 36.3, 26.8, 19.1.

HRMS (APCI): *m/z*: $[M + Na]^+$ calcd for $C_{43}H_{48}O_6SiNa$ 711.3112, found 711.3129.



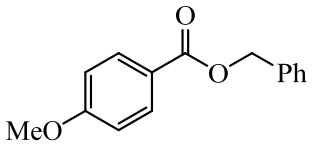
Entry 8, **Table 3**[S6]

Yield: 151 mg (65%); pale yellow liquid.

R_f: 0.49 (hexane/EtOAc = 4:1).

^1H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.5 Hz, 1H), 7.42 (s, 1H), 6.88 (d, *J* = 8.4 Hz, 1H), 6.45 (s, 1H), 6.36 (s, 1H), 5.26 (s, 1H), 3.83 (s, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 165.6, 163.1, 149.4, 142.8, 131.4, 121.9, 113.2, 110.2, 57.9, 55.0.



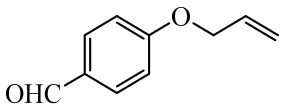
Entry 9, **Table 3**[S7]

Yield: 145 mg (60%); pale yellow liquid.

R_f: 0.53 (hexane/EtOAc = 4:1).

^1H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.3 Hz, 1H), 7.42 (d, *J* = 7.2 Hz, 1H), 7.40–7.29 (m, 1H), 6.90 (d, *J* = 8.2 Hz, 1H), 5.32 (s, 1H), 3.84 (s, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 166.0, 163.3, 136.2, 131.6, 128.4, 128.0, 127.9, 122.4, 113.5, 66.2, 55.2.



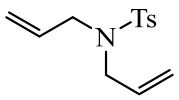
Entry 10, **Table 3**[S8]

Yield: 125 mg (77%); colorless liquid.

R_f: 0.25 (hexane/EtOAc = 4:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.87 (s, 1H), 7.83–7.80 (m, 2H), 7.00 (d, *J* = 8.8 Hz, 2H), 6.04 (dt, *J* = 17.2, 5.3 Hz, 1H), 5.44–5.30 (m, 2H), 4.61 (d, *J* = 5.2 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 190.8, 163.6, 132.3, 132.0, 130.0, 118.4, 115.0, 77.3, 77.0, 76.7, 69.0, 29.7.



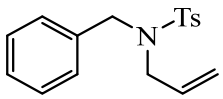
Entry 11, **Table 3**[S9]

Yield: 204 mg (81%); colorless liquid.

R_f: 0.25 (hexane/EtOAc = 4:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.2 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 5.62–5.56 (m, 2H), 5.14–5.10 (m, 4H), 3.78 (d, *J* = 6.2 Hz, 4H), 2.41 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 143.2, 137.4, 132.6, 129.7, 127.2, 118.9, 77.3, 77.0, 76.7, 49.3, 21.5.



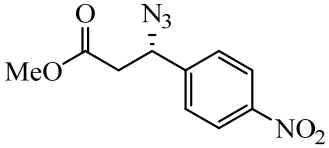
Entry 12, **Table 3**[S10]

Yield: 238 mg (79%); colorless liquid.

R_f: 0.25 (hexane/EtOAc = 4:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.2 Hz, 2H), 7.30–7.22 (m, 7H), 5.45–5.41 (m, 1H), 5.05–4.95 (m, 2H), 4.31 (s, 2H), 3.73 (d, *J* = 6.5 Hz, 2H), 2.41 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 171.1, 143.2, 137.5, 135.9, 132.1, 129.7, 128.4, 128.4, 127.6, 127.1, 119.3, 77.3, 77.0, 76.7, 60.3, 50.1, 49.4, 21.4, 21.0, 14.1.



Entry 13, **Table 3**

Yield: 170 mg (68%); pale yellow liquid.

R_f: 0.6 (hexane/EtOAc = 3:1).

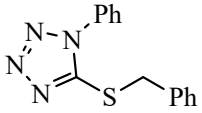
$[\alpha]_D^{26}$ –142.5 (*c* 0.01, CH_2Cl_2).

IR (neat, cm^{-1}): 3452, 2164, 2036, 1639.

^1H NMR (400 MHz, $CDCl_3$) δ 8.24 (d, *J* = 8.7 Hz, 2H), 7.52 (d, *J* = 8.7 Hz, 2H), 5.09 (dd, *J* = 8.7, 5.6 Hz, 1H), 3.70 (s, 3H), 2.82 (dd, *J* = 16.4, 8.7 Hz, 1H), 2.69 (dd, *J* = 16.2, 5.6 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.0, 147.9, 145.6, 127.7, 124.2, 61.2, 52.2, 41.1, 29.7.

HRMS (ESI): *m/z*: $[M + Na]^+$ calcd for $C_{10}H_{10}O_4N_4Na$ 273.0594, found 273.0588.



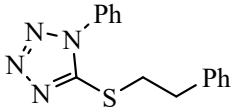
Entry 14, **Table 3**[S11]

Yield: 225 mg (84%); white solid.

R_f: 0.25 (hexane/EtOAc = 4:1).

^1H NMR (400 MHz, $CDCl_3$) δ 7.50 (s, 5H), 7.41–7.39 (m, 2H), 7.31–7.29 (m, 3H), 4.61 (s, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 153.8, 135.1, 133.5, 130.1, 129.7, 129.2, 128.8, 128.1, 123.7, 77.3, 77.0, 76.7, 37.6, 21.6.



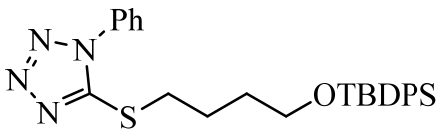
Entry 15, **Table 3**[S12]

Yield: 257 mg (91%); colorless liquid.

R_f: 0.25 (hexane/EtOAc = 4:1).

^1H NMR (400 MHz, $CDCl_3$) δ 7.56–7.54 (m, 5H), 7.32–7.30 (m, 2H), 7.26–7.24 (m, 3H), 3.64 (t, *J* = 7.6 Hz, 2H), 3.15 (t, *J* = 7.6 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 154.1, 138.9, 133.6, 130.1, 129.7, 128.6, 128.6, 126.8, 123.8, 77.3, 77.0, 76.7, 35.4, 34.4.



Entry 16, **Table 3**[S13]

Yield: 342 mg (70%); colorless liquid.

R_f: 0.25 (hexane/EtOAc = 4:1).

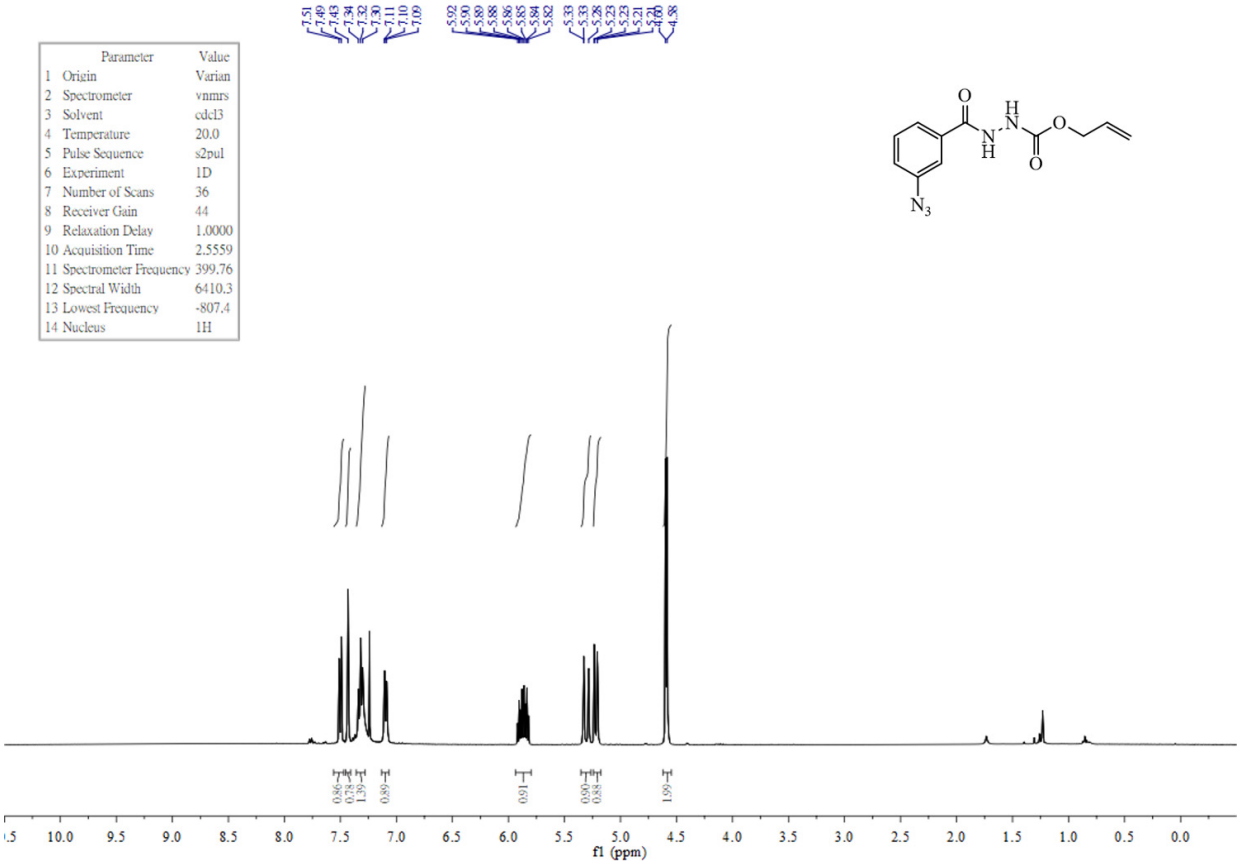
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64–7.62 (m, 4H), 7.56–7.53 (m, 4H), 7.40–7.33 (m, 5H), 3.67 (t, *J* = 6.0 Hz, 2H), 3.39 (t, *J* = 7.2 Hz, 2H), 1.92 (d, *J* = 7.4 Hz, 2H), 1.69 (d, *J* = 8.0 Hz, 2H), 1.02 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 154.3, 135.4, 133.7, 130.0, 129.7, 129.5, 127.6, 123.7, 77.3, 77.0, 76.7, 63.0, 33.1, 31.3, 26.8, 25.6, 19.1.

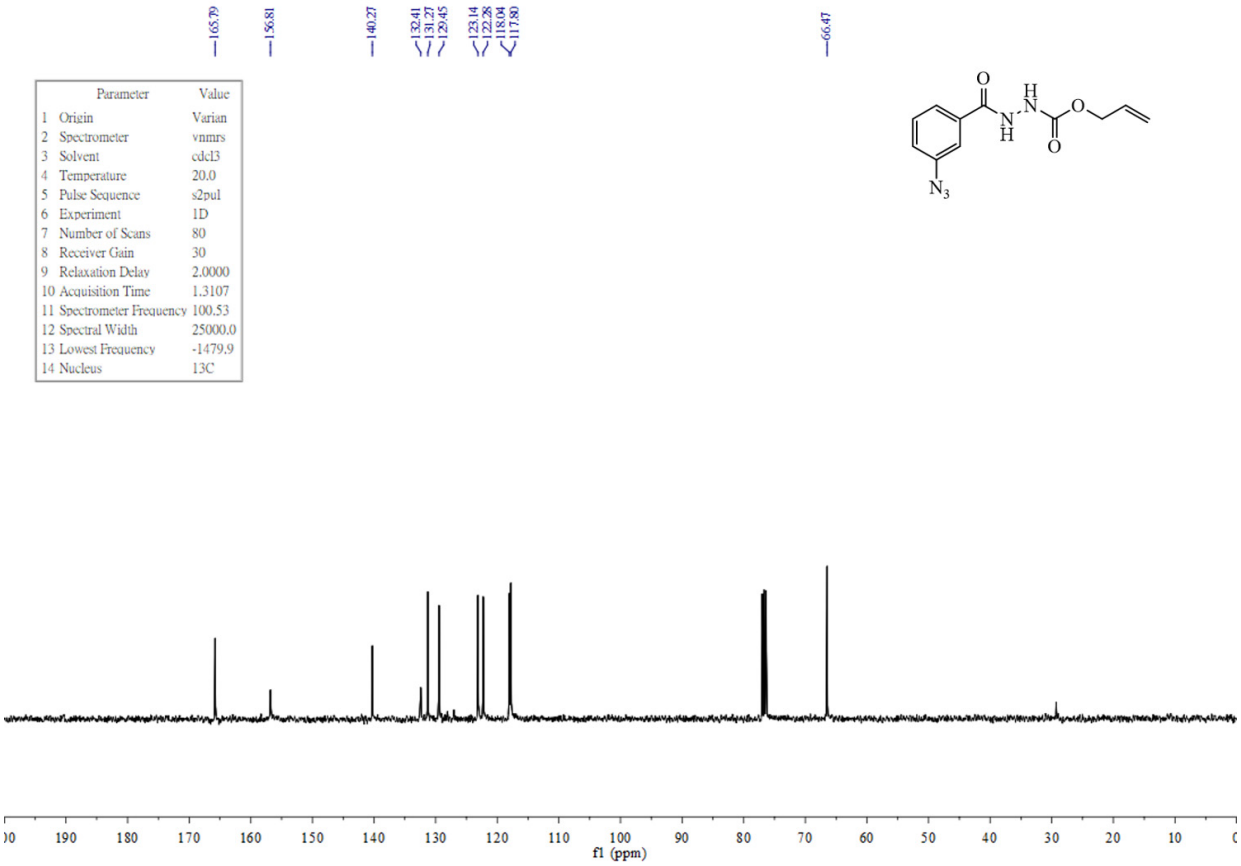
The recovery of ionic liquid-supported hydrazidecarboxylate

After the reaction was over, the ionic liquid-supported hydrazidecarboxylate would become another liquid layer below the DCM layer. We could slowly pour the reaction mixture into a flask. The ionic liquid-supported hydrazidecarboxylate which stuck on the wall of the round-bottomed flask can be obtained purely by washing with successive ether and dichloromethane.

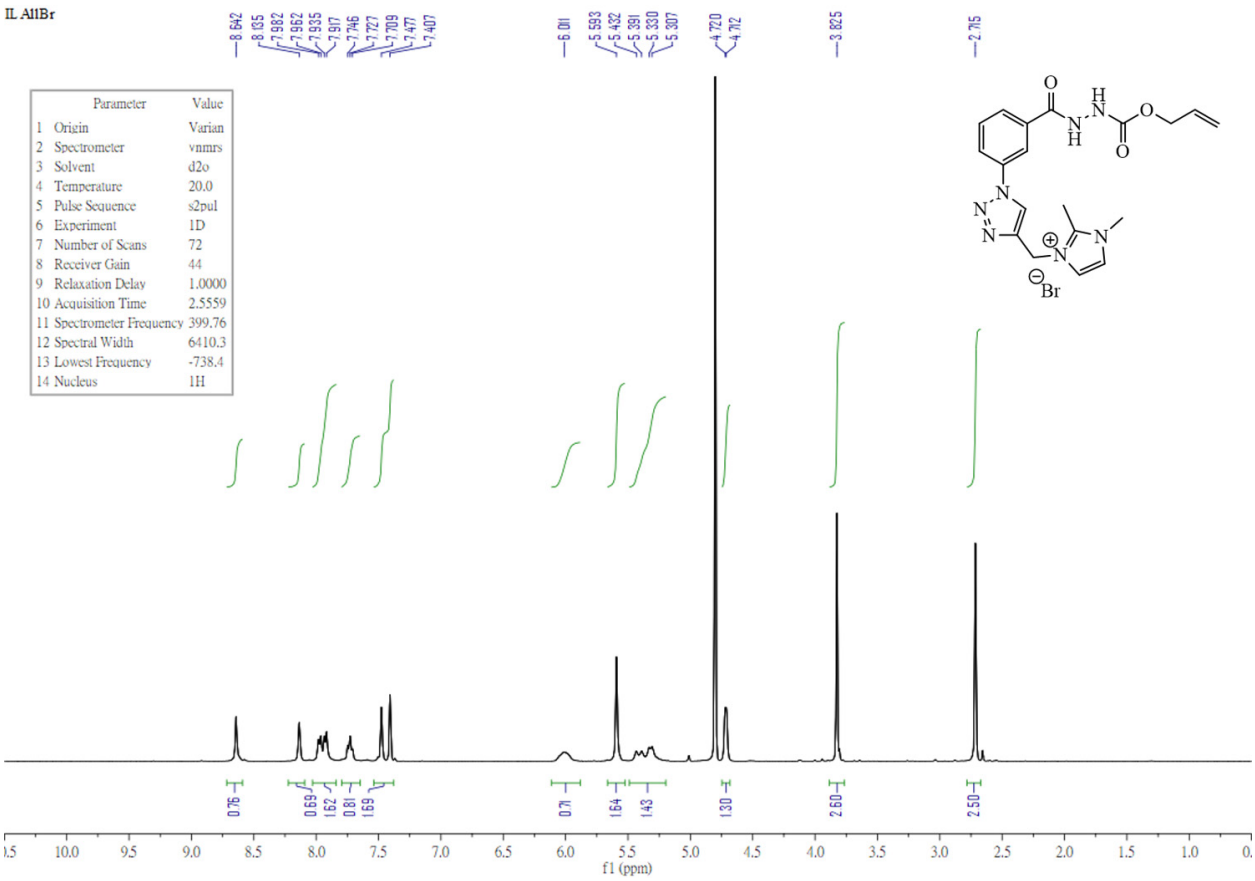
C. NMR Spectra for the synthesized compounds



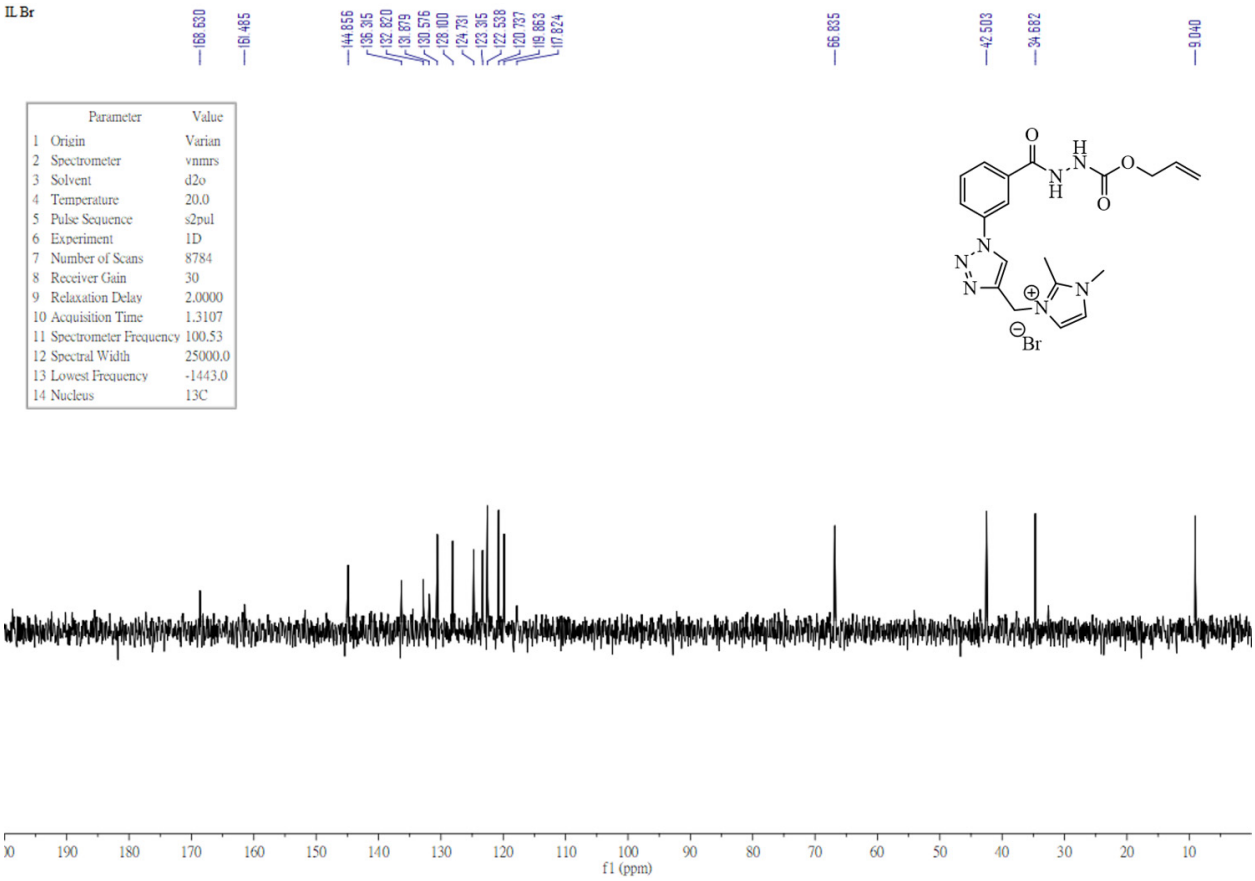
^{1}H NMR spectrum of compound **6** (400 MHz, $CDCl_3$)



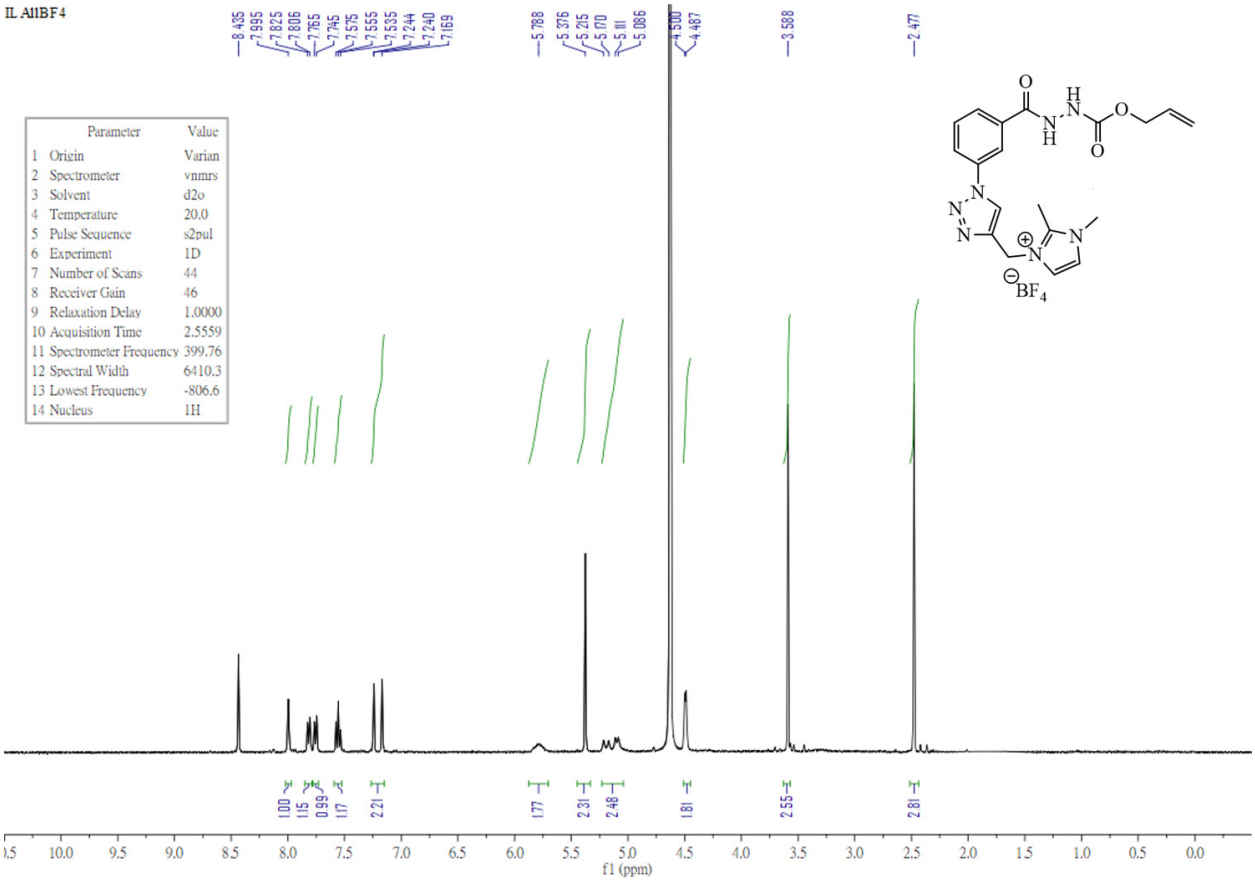
^{13}C NMR spectrum of compound **6** (100 MHz, $CDCl_3$)



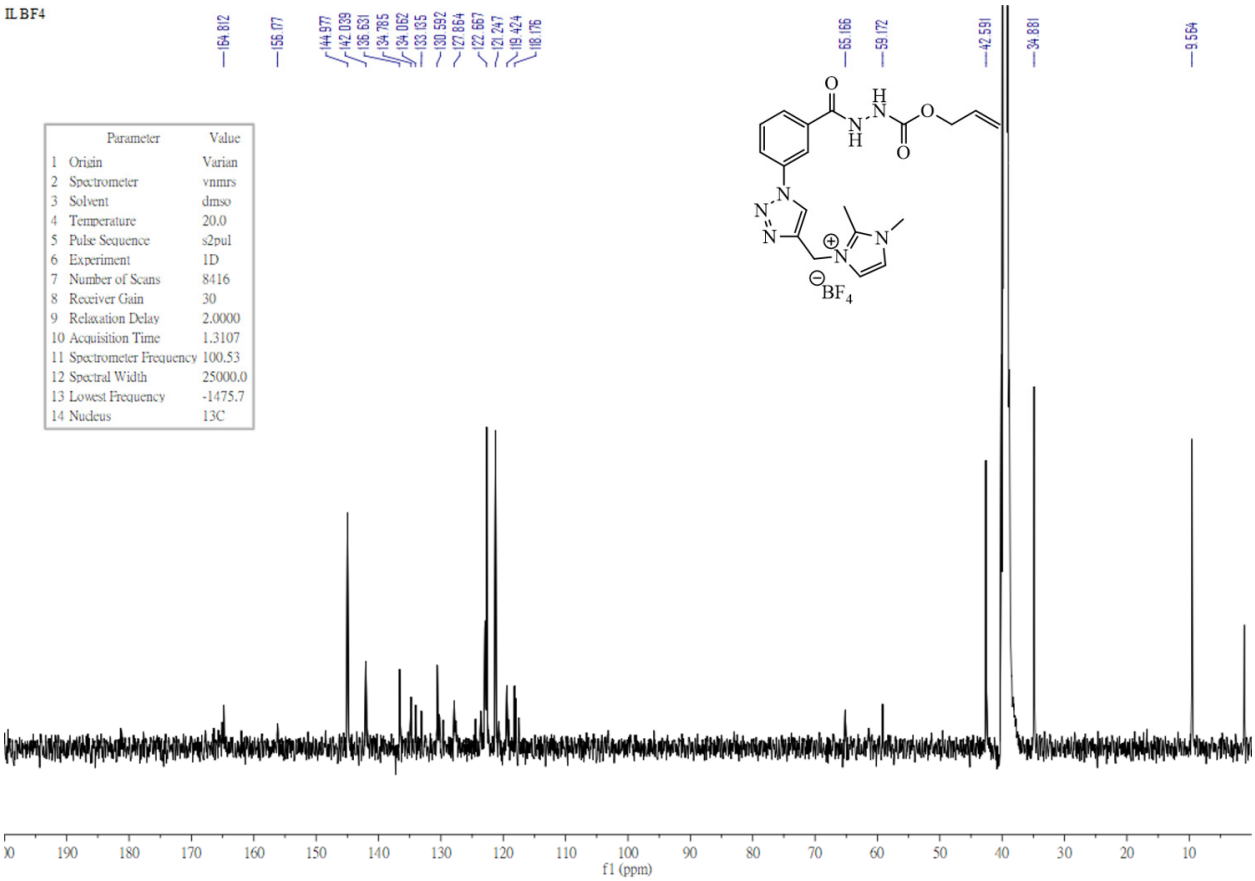
^{1}H NMR spectrum of compound **4a** (400 MHz, D_2O)



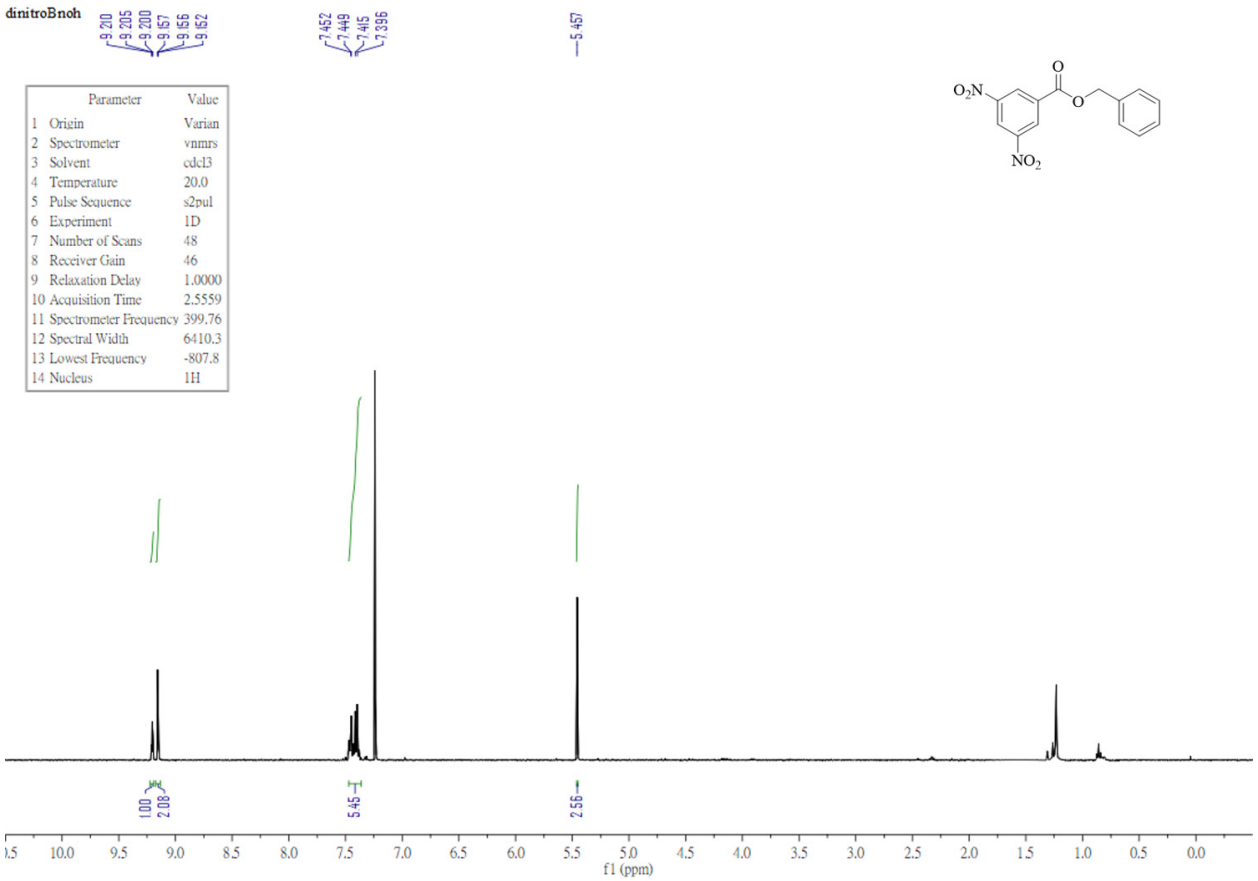
^{13}C NMR spectrum of compound **4a** (100 MHz, D_2O)



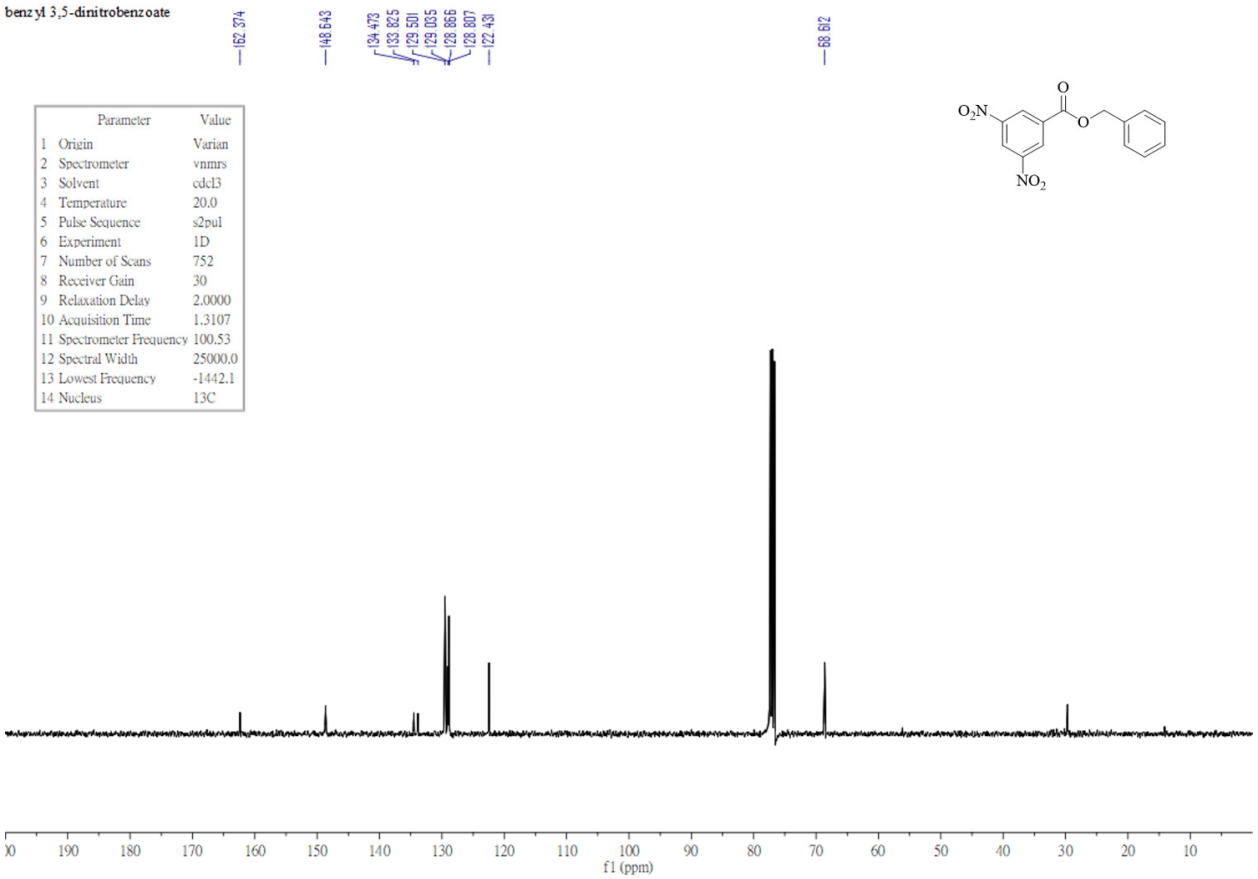
^{1}H NMR spectrum of compound **4b** (400 MHz, D_2O)



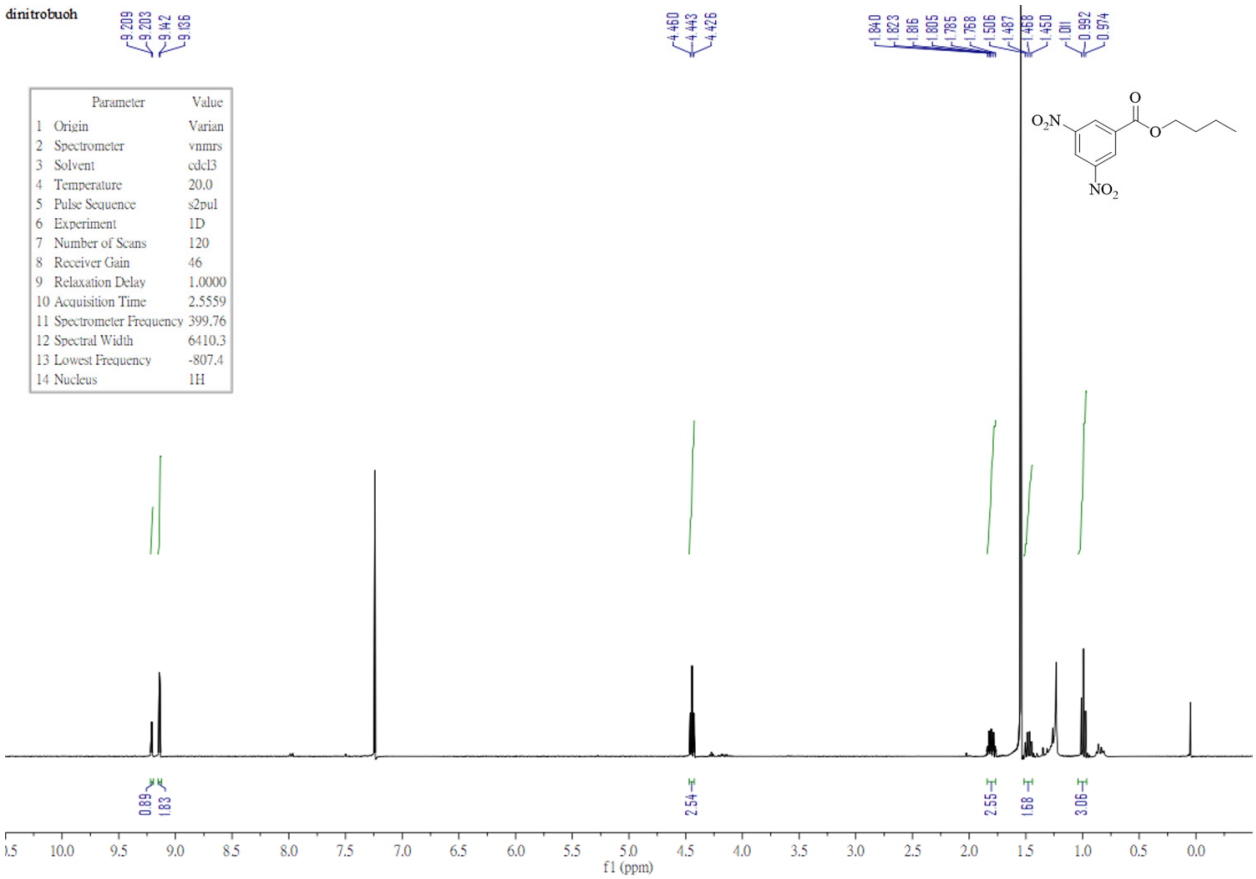
^{13}C NMR spectrum of compound **4b** (100 MHz, D_2O)



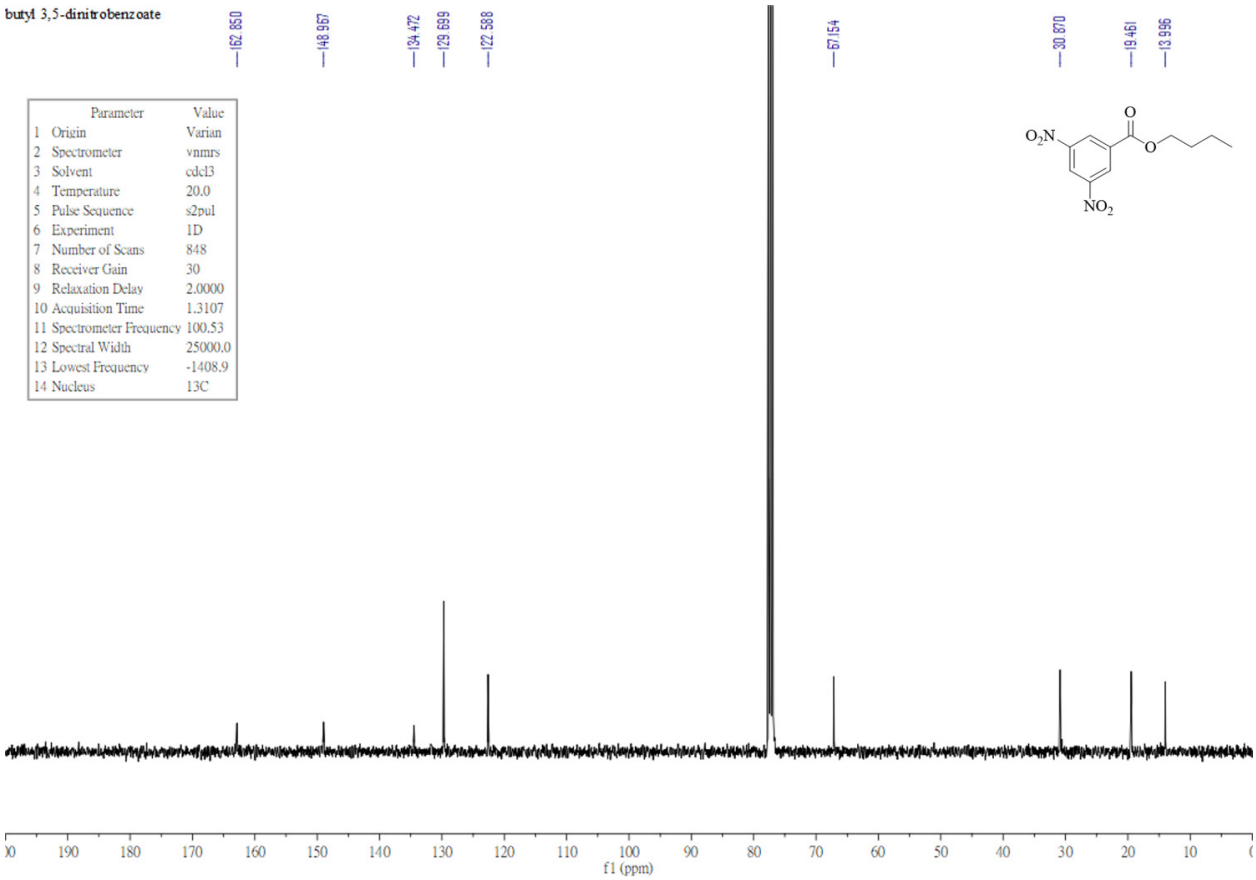
^{1}H NMR spectrum of compound **entry 1 (Table 3)** (400 MHz, $CDCl_3$)



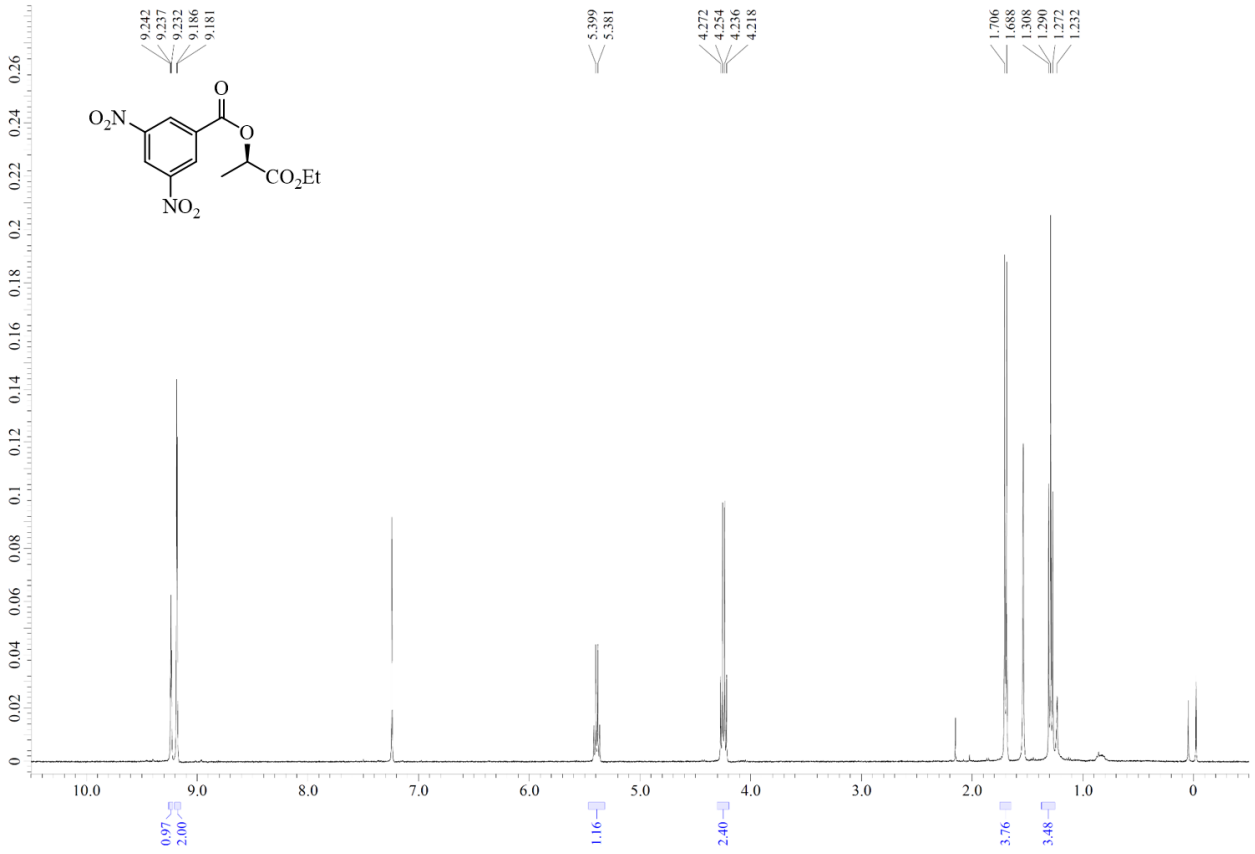
^{13}C NMR spectrum of compound **entry 1 (Table 3)** (100 MHz, $CDCl_3$)



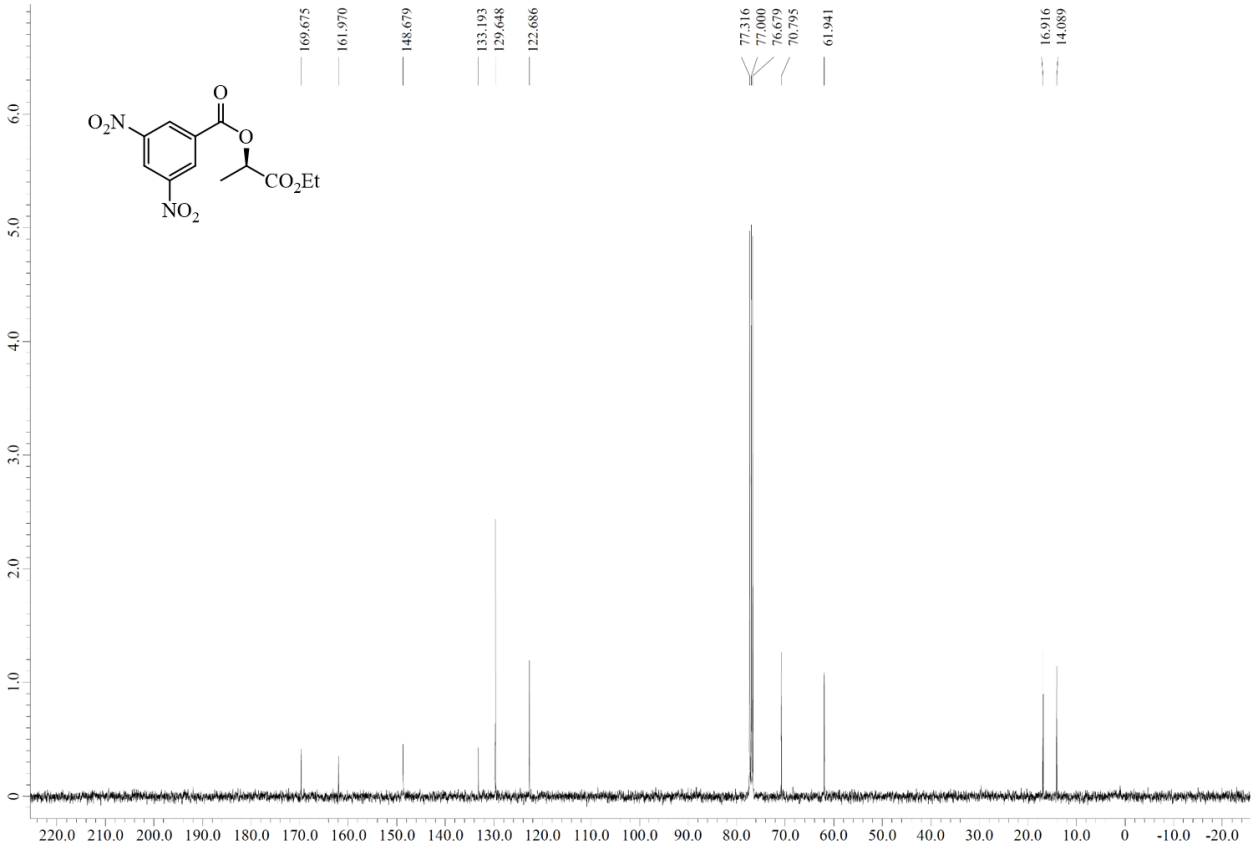
^{1}H NMR spectrum of compound **entry 2 (Table 3)** (400 MHz, $CDCl_3$)



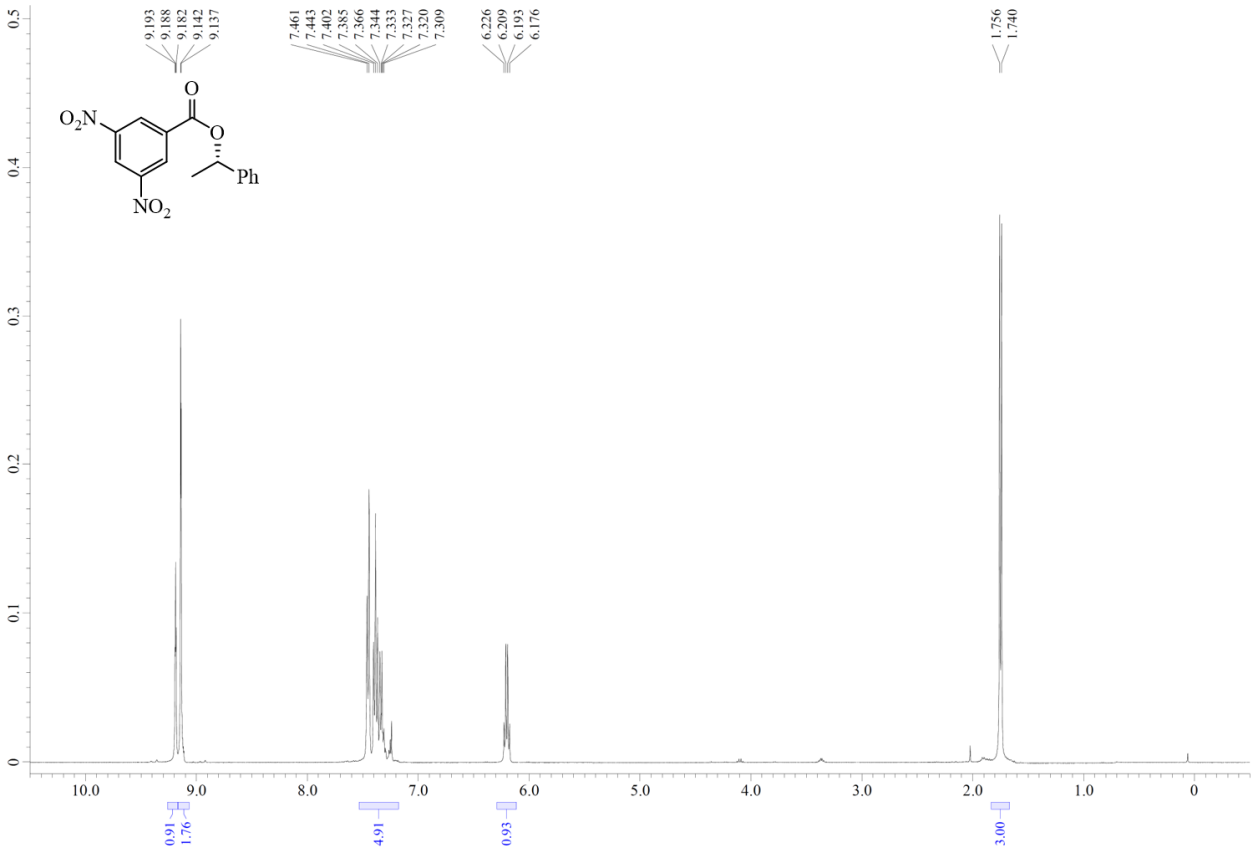
^{13}C NMR spectrum of compound **entry 2 (Table 3)** (100 MHz, $CDCl_3$)



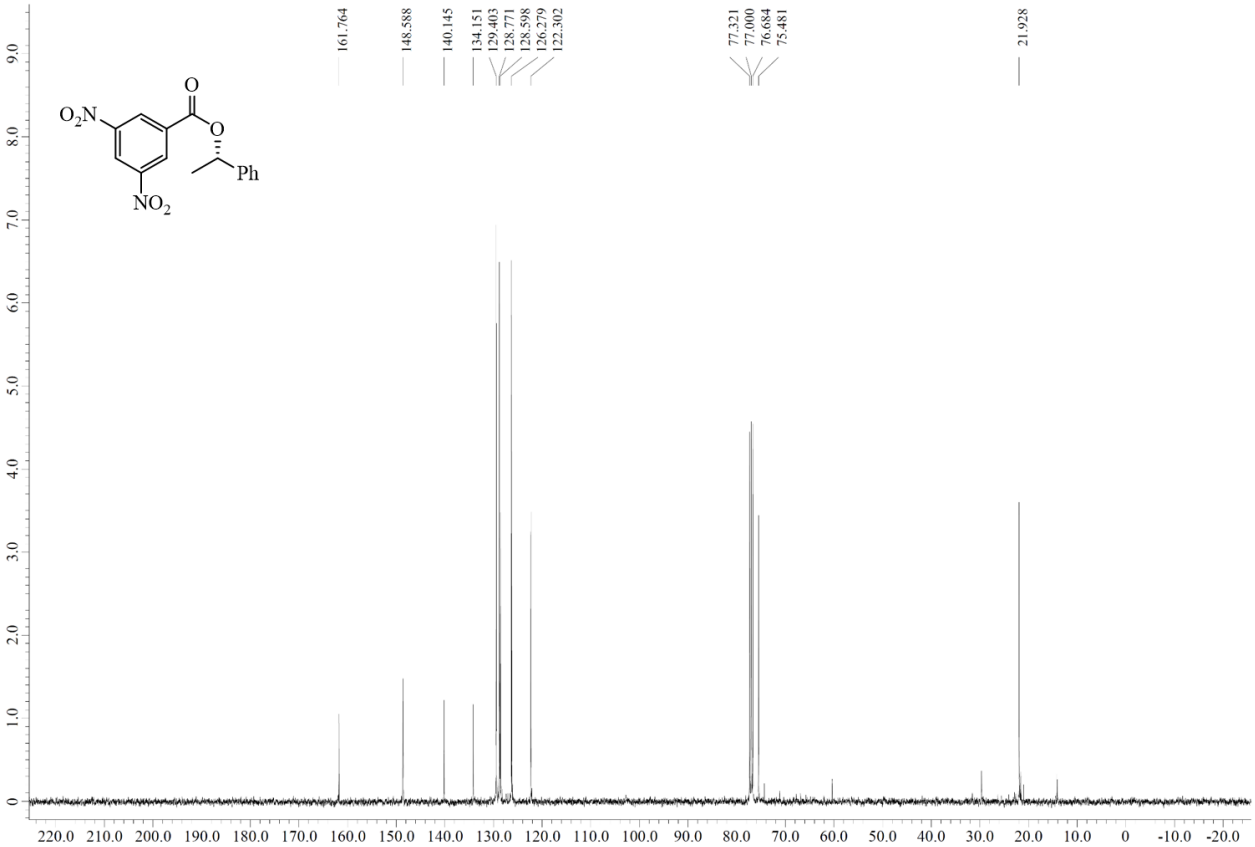
^{1}H NMR spectrum of compound **entry 3 (Table 3)** (400 MHz, $CDCl_3$)



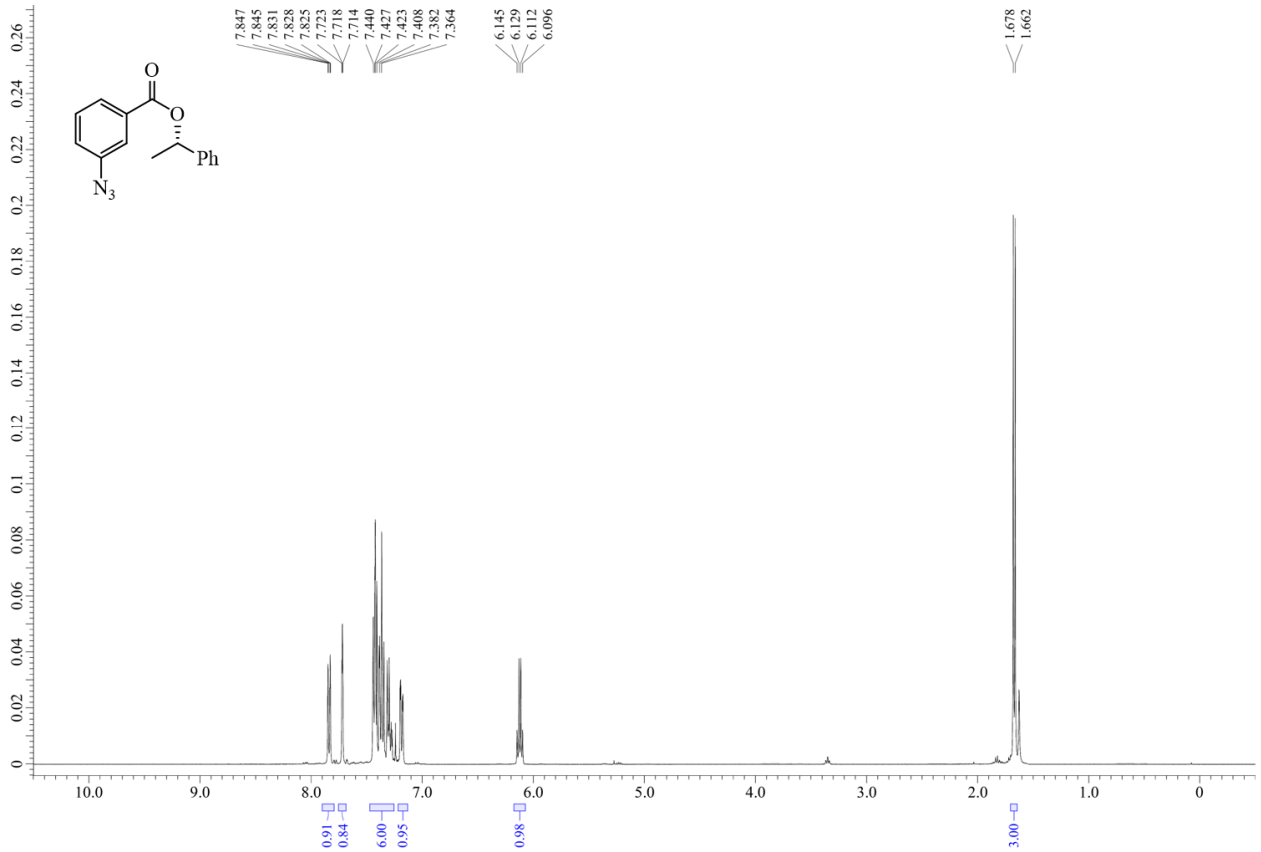
^{13}C NMR spectrum of compound **entry 3 (Table 3)** (100 MHz, $CDCl_3$)



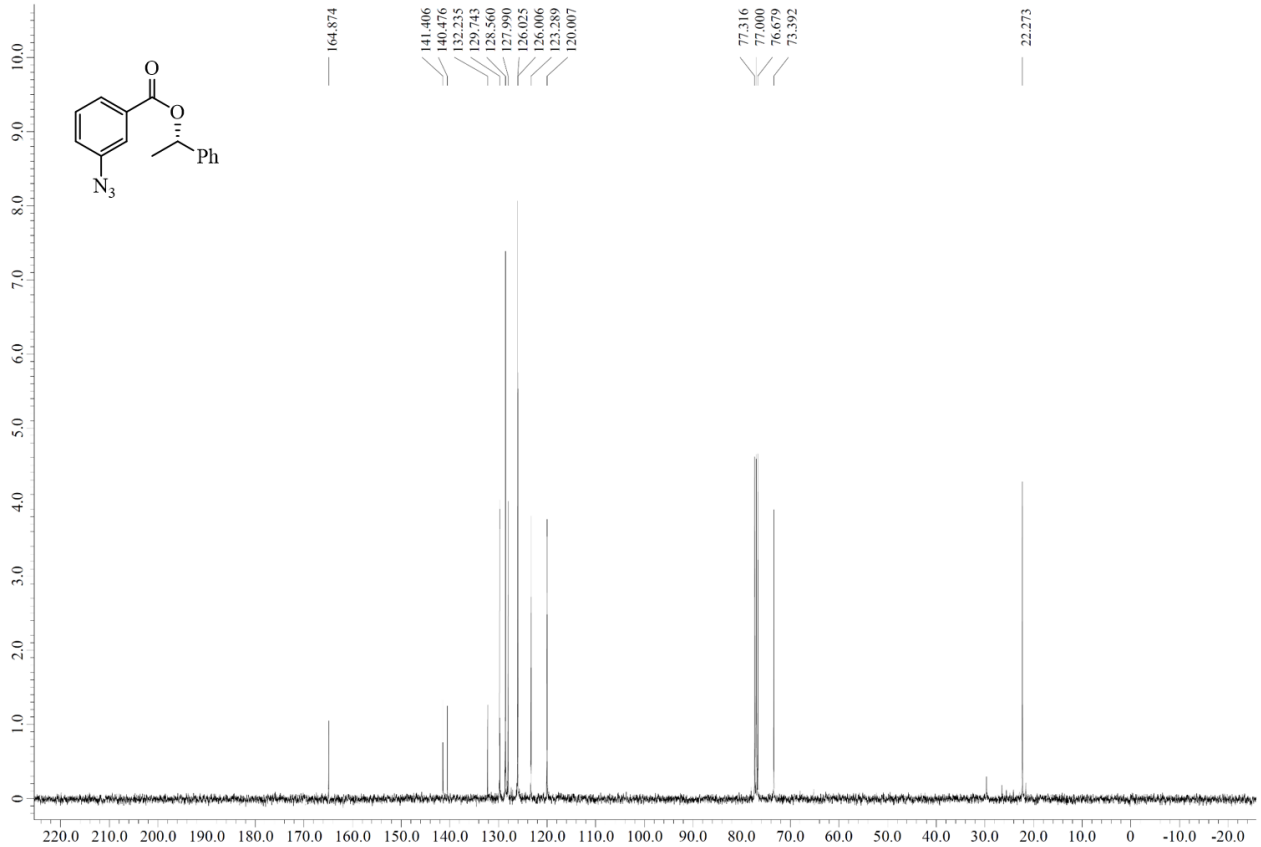
^{1}H NMR spectrum of compound **entry 4 (Table 3)** (400 MHz, $CDCl_3$)



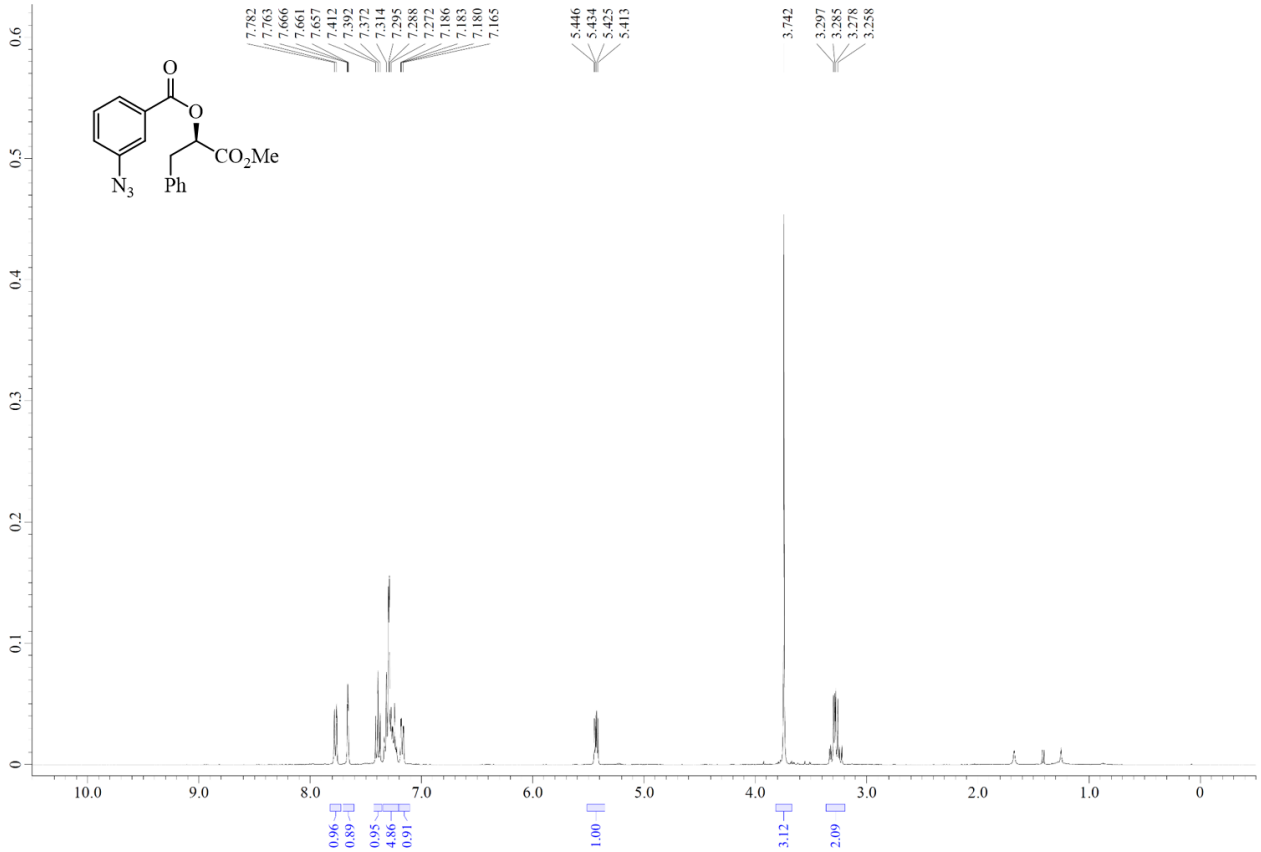
^{13}C NMR spectrum of compound **entry 4 (Table 3)** (100 MHz, $CDCl_3$)



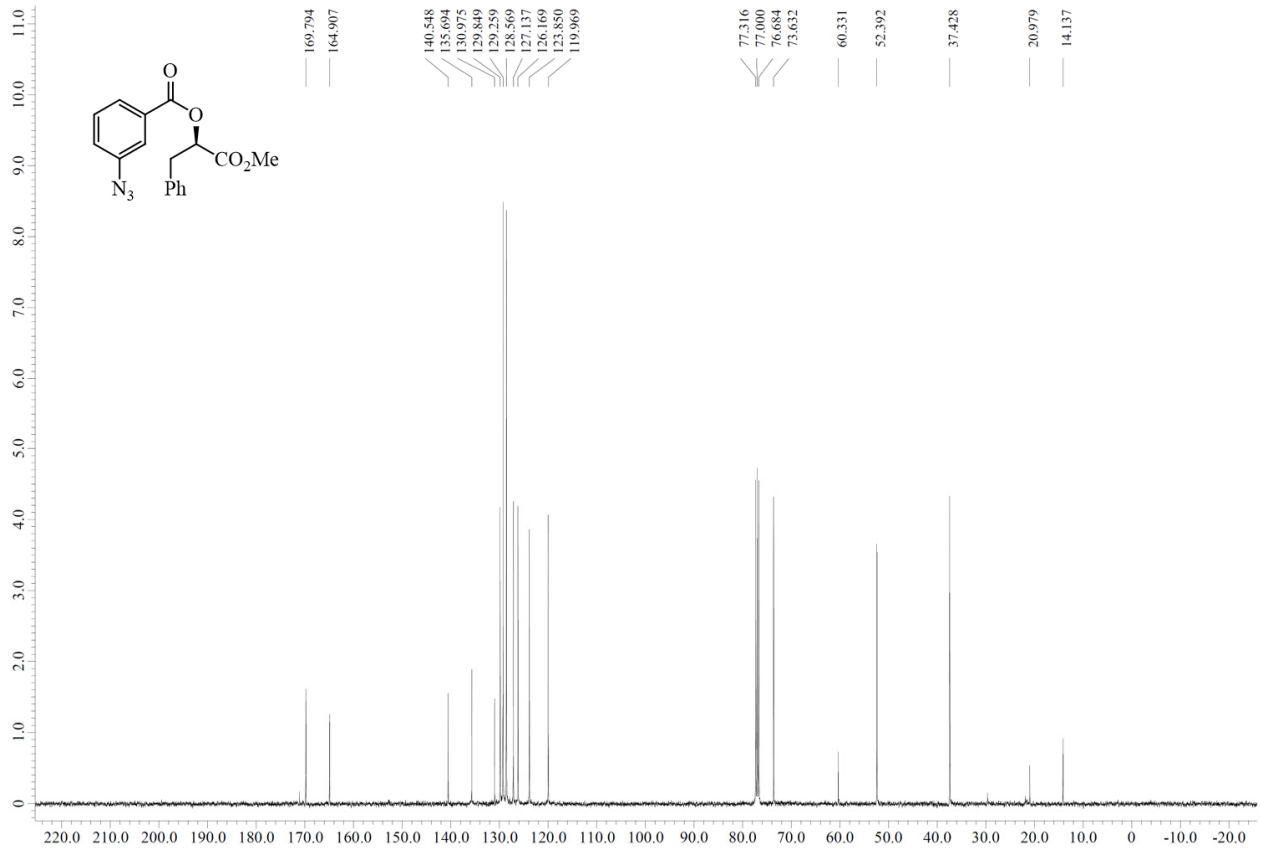
^{1}H NMR spectrum of compound **entry 5 (Table 3)** (400 MHz, $CDCl_3$)



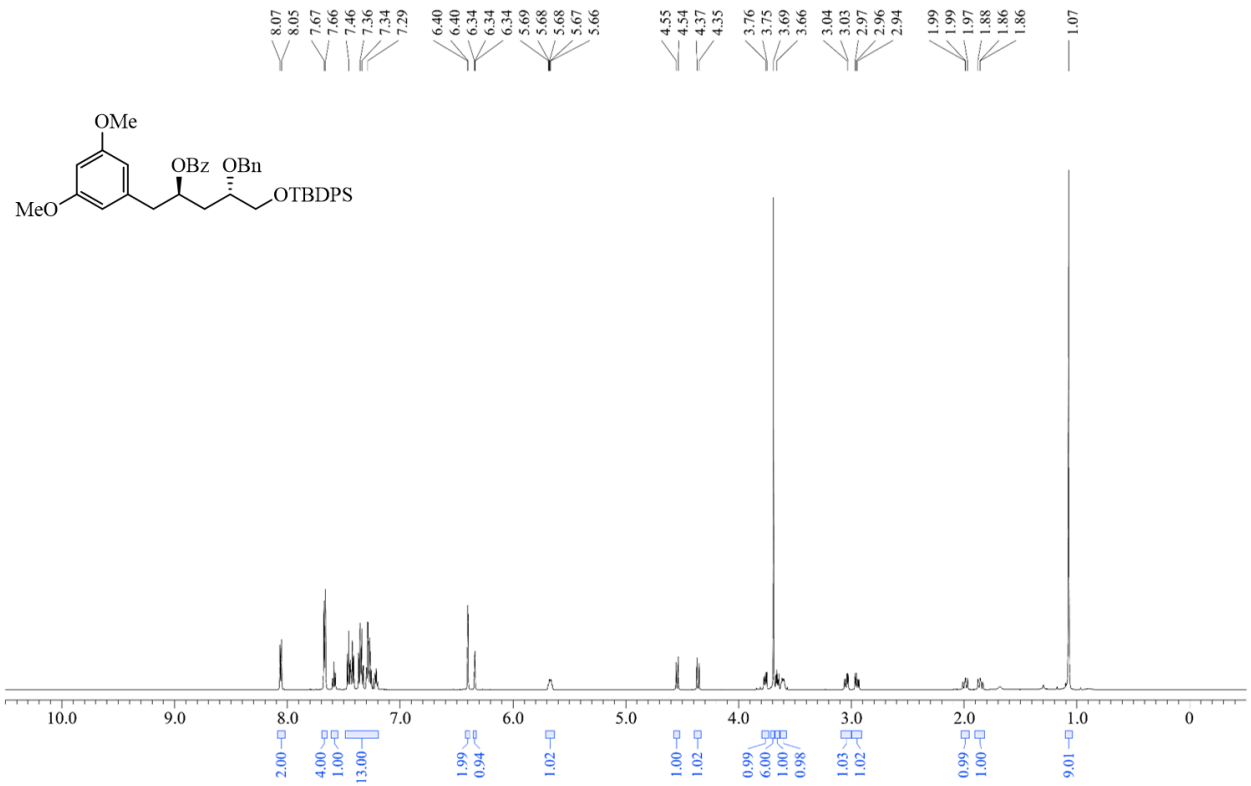
^{13}C NMR spectrum of compound **entry 5 (Table 3)** (100 MHz, $CDCl_3$)



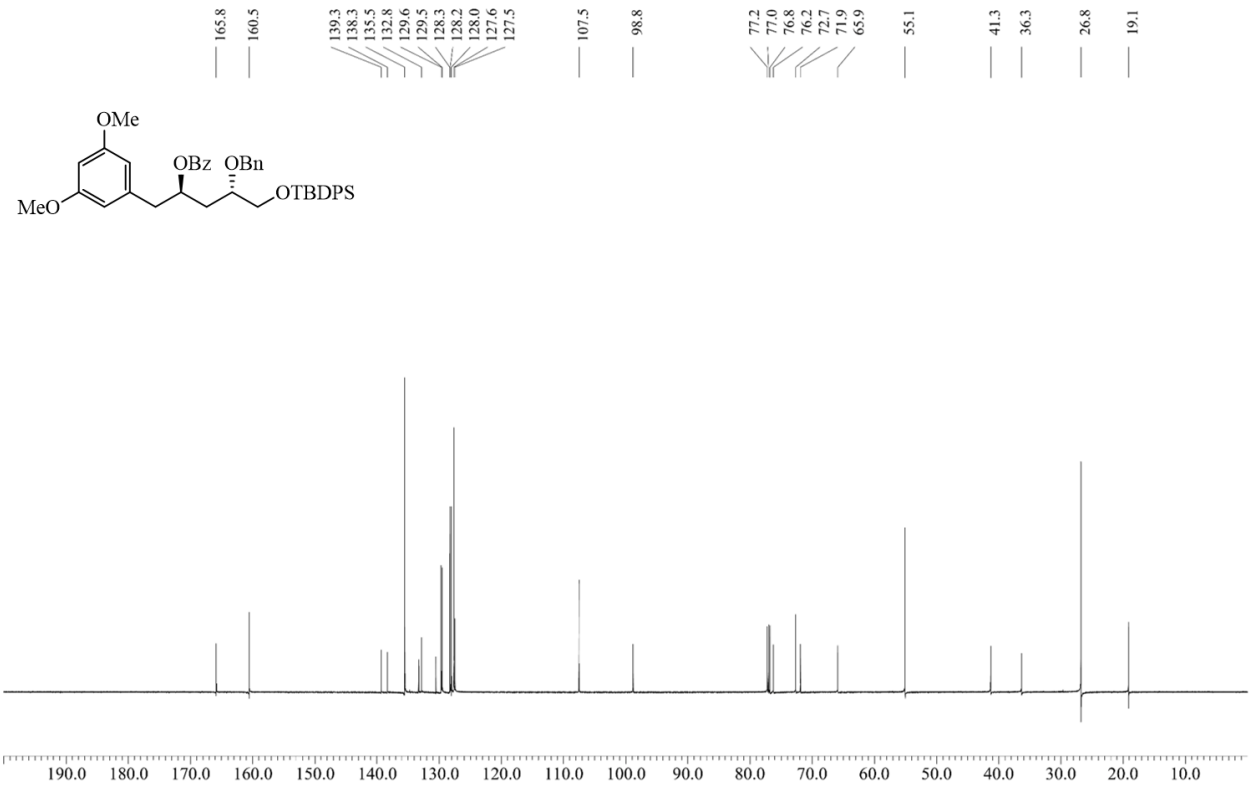
^{1}H NMR spectrum of compound **entry 6 (Table 3)** (400 MHz, $CDCl_3$)



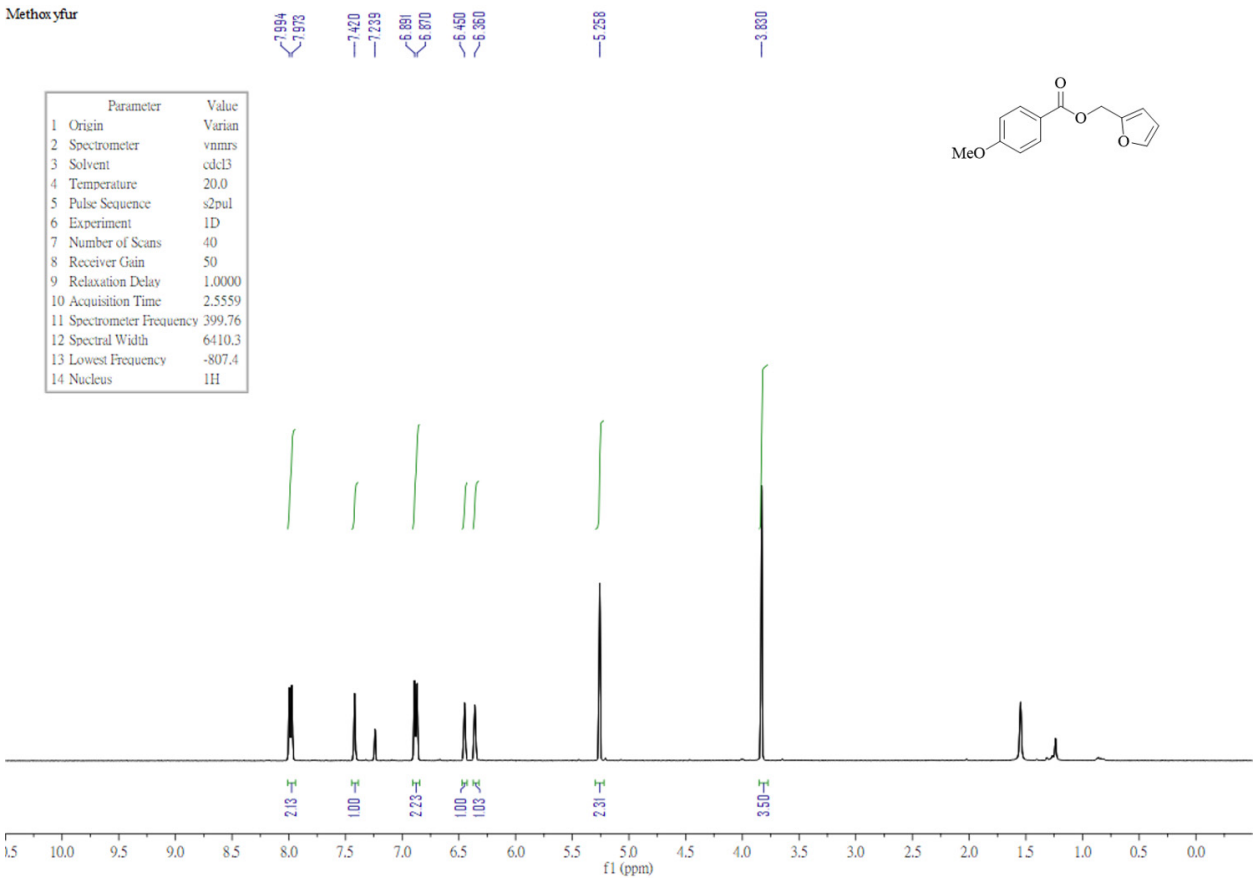
^{13}C NMR spectrum of compound **entry 6 (Table 3)** (100 MHz, $CDCl_3$)



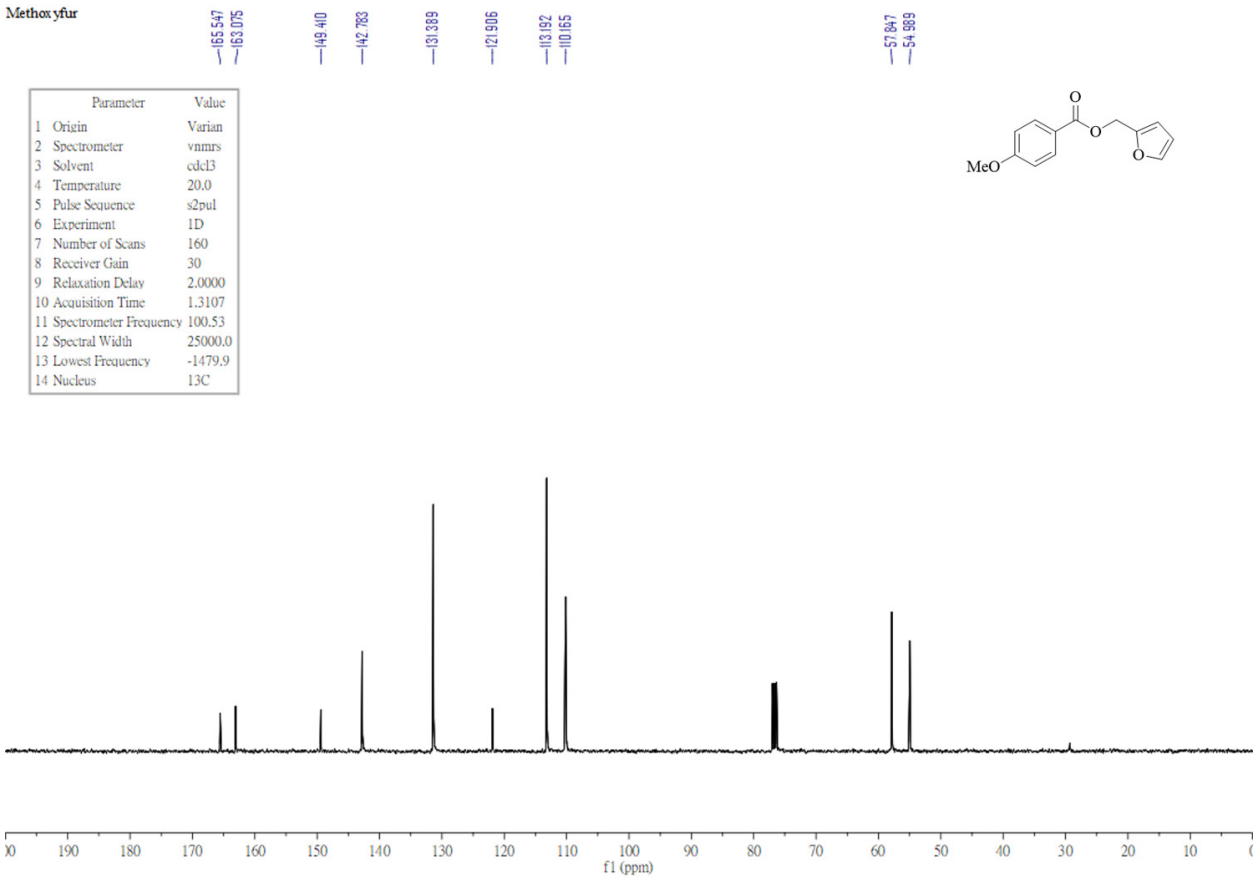
^{1}H NMR spectrum of compound **entry 7 (Table 3)** (400 MHz, $CDCl_3$)



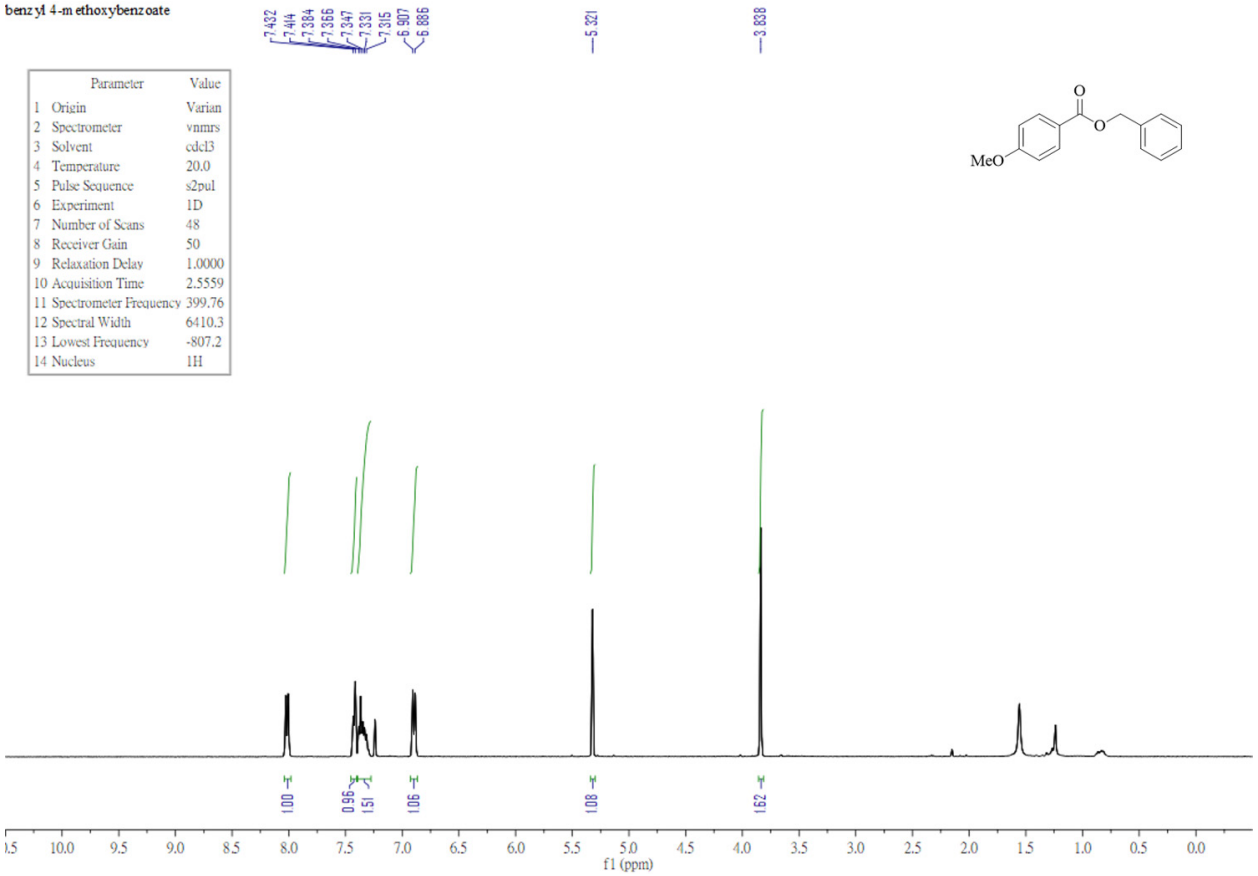
^{13}C NMR spectrum of compound **entry 7 (Table 3)** (100 MHz, $CDCl_3$)



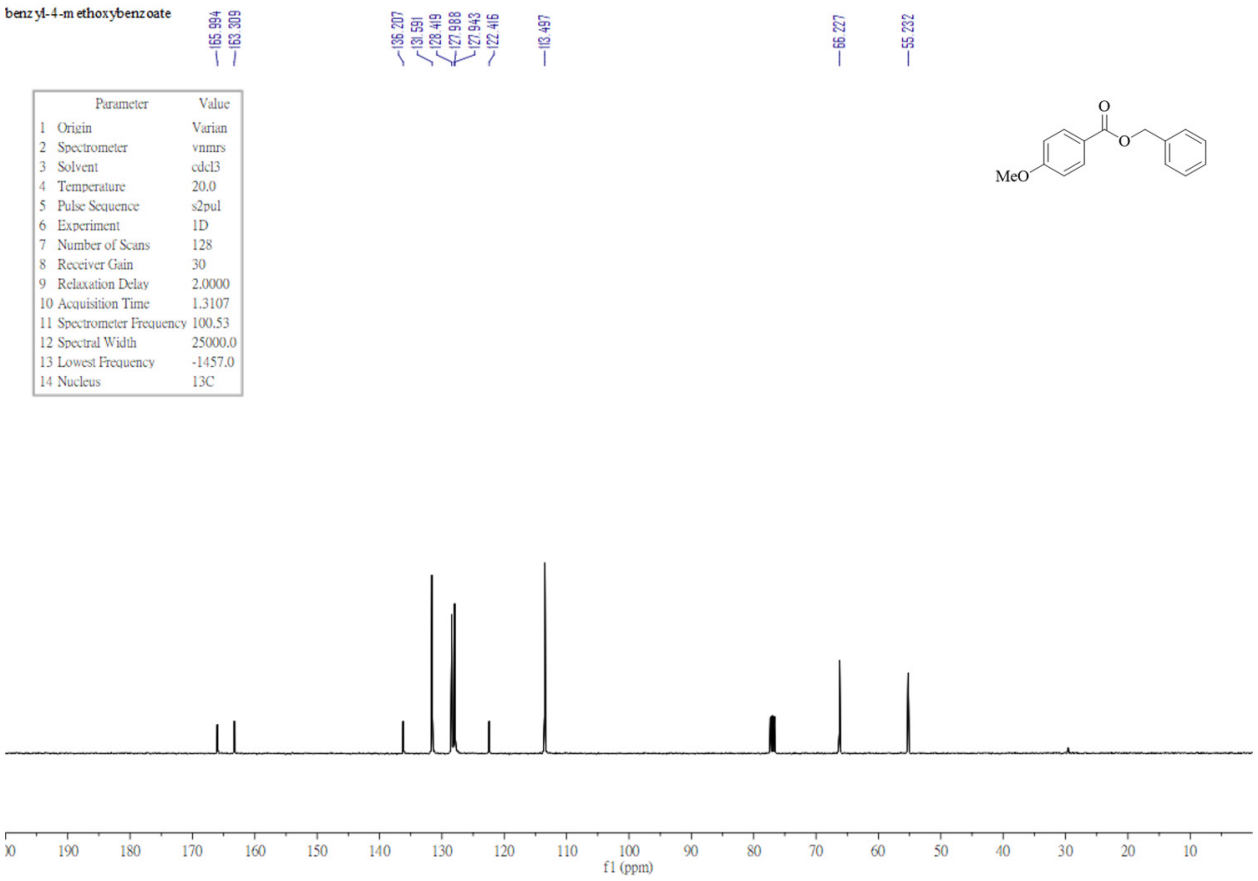
^{1}H NMR spectrum of compound **entry 8 (Table 3)** (400 MHz, $CDCl_3$)



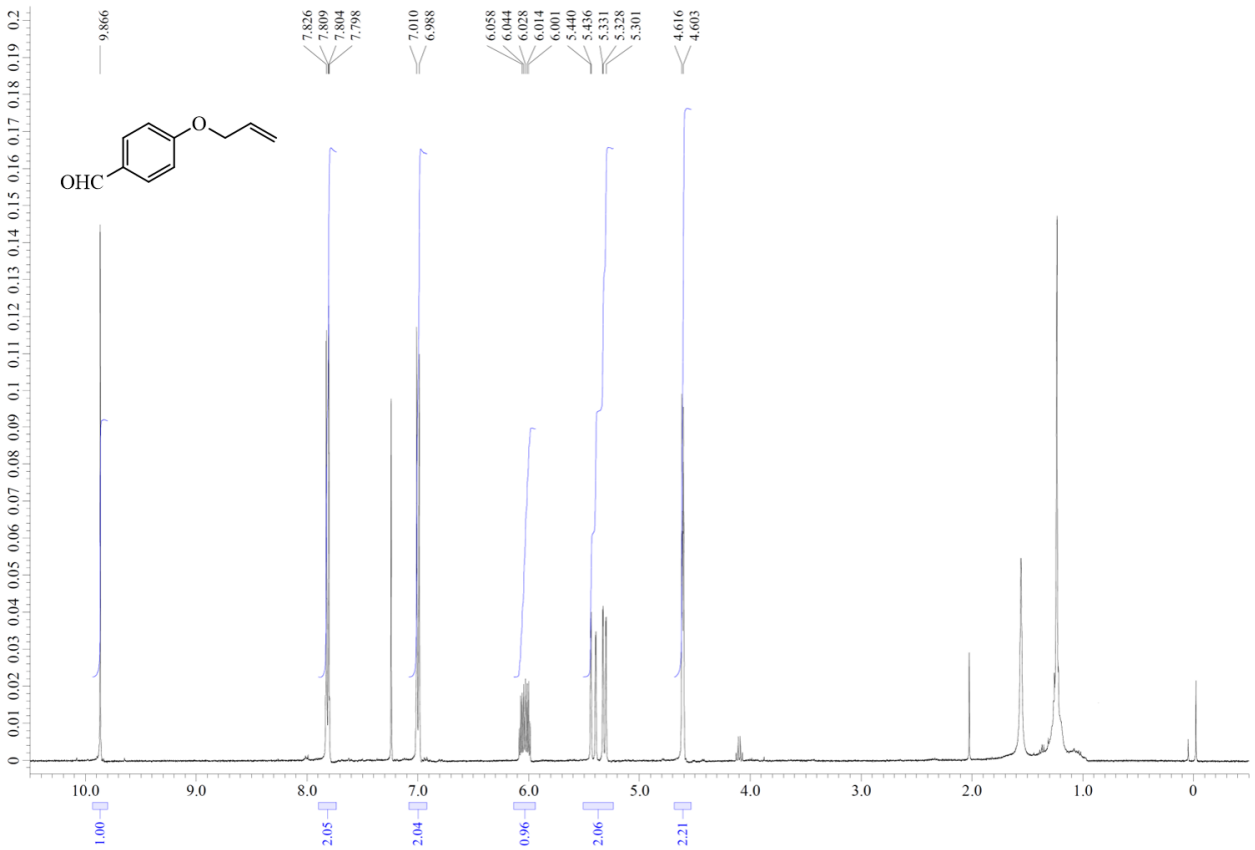
^{13}C NMR spectrum of compound **entry 8 (Table 3)** (100 MHz, $CDCl_3$)



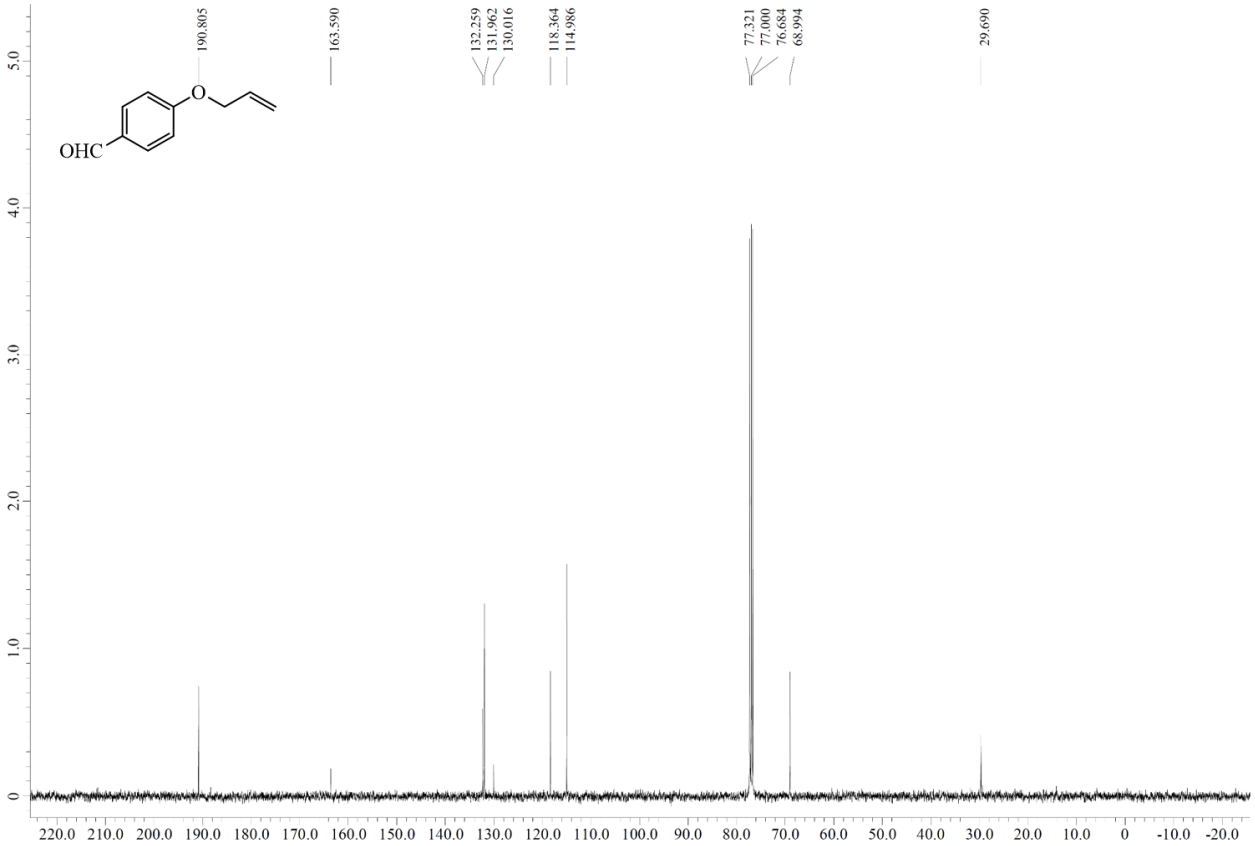
^{1}H NMR spectrum of compound **entry 9 (Table 3)** (400 MHz, $CDCl_3$)



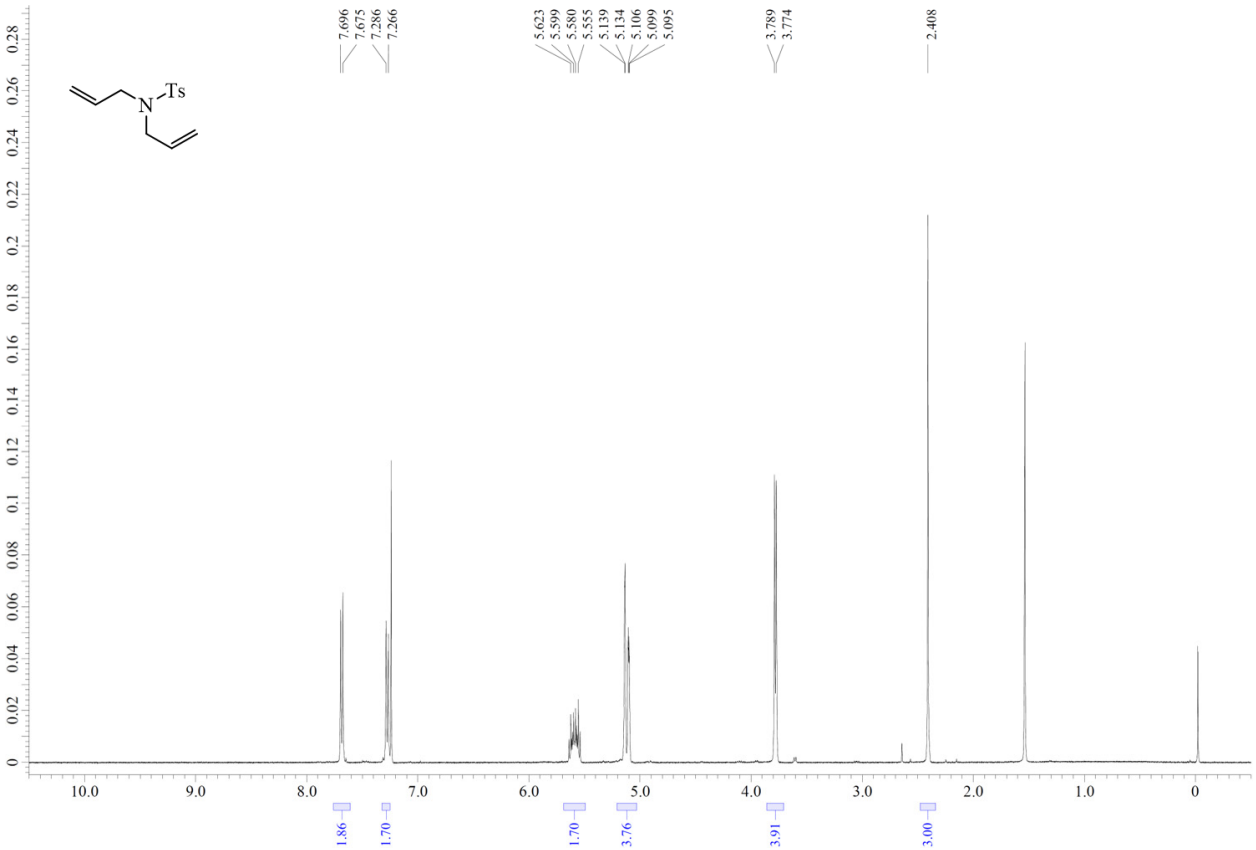
^{13}C NMR spectrum of compound **entry 9 (Table 3)** (100 MHz, $CDCl_3$)



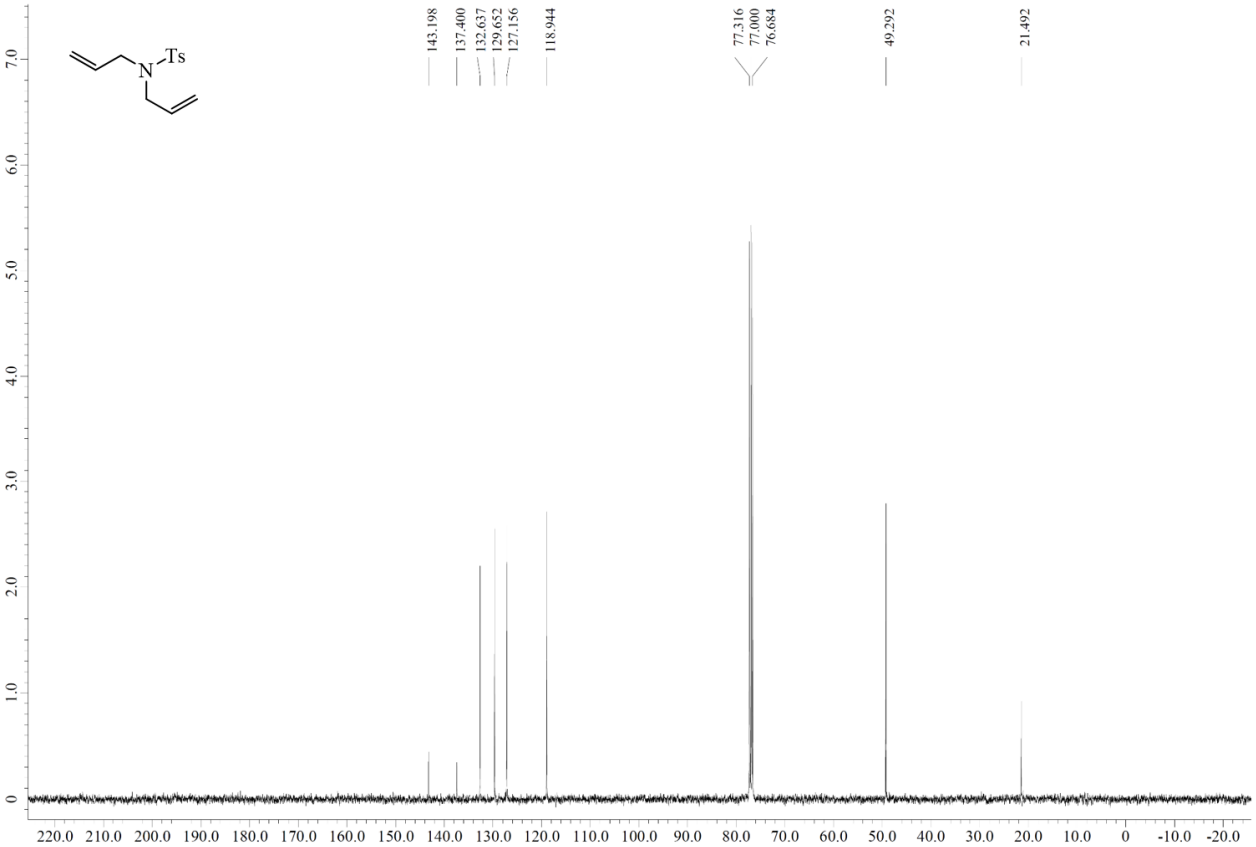
^{1}H NMR spectrum of compound **entry 10 (Table 3)** (400 MHz, $CDCl_3$)



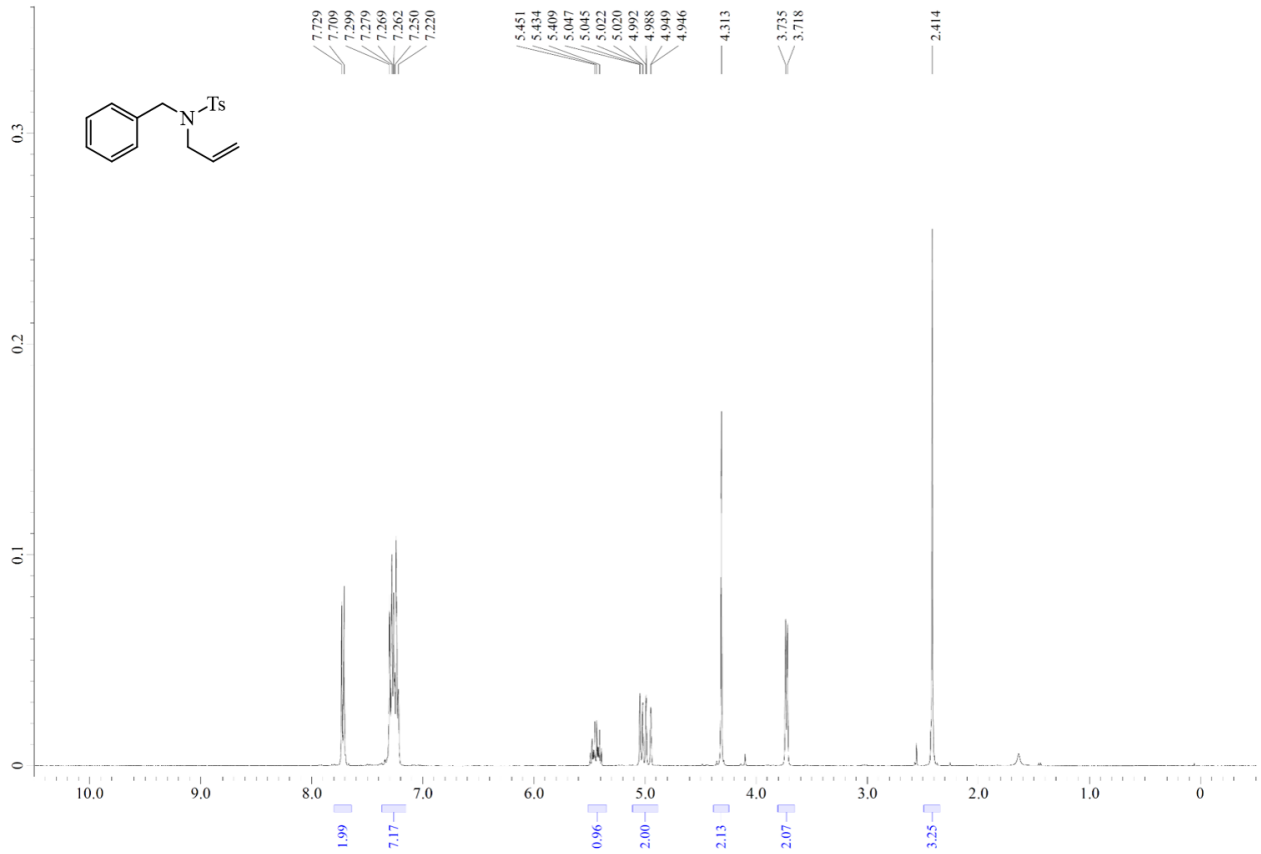
^{13}C NMR spectrum of compound **entry 10 (Table 3)** (100 MHz, $CDCl_3$)



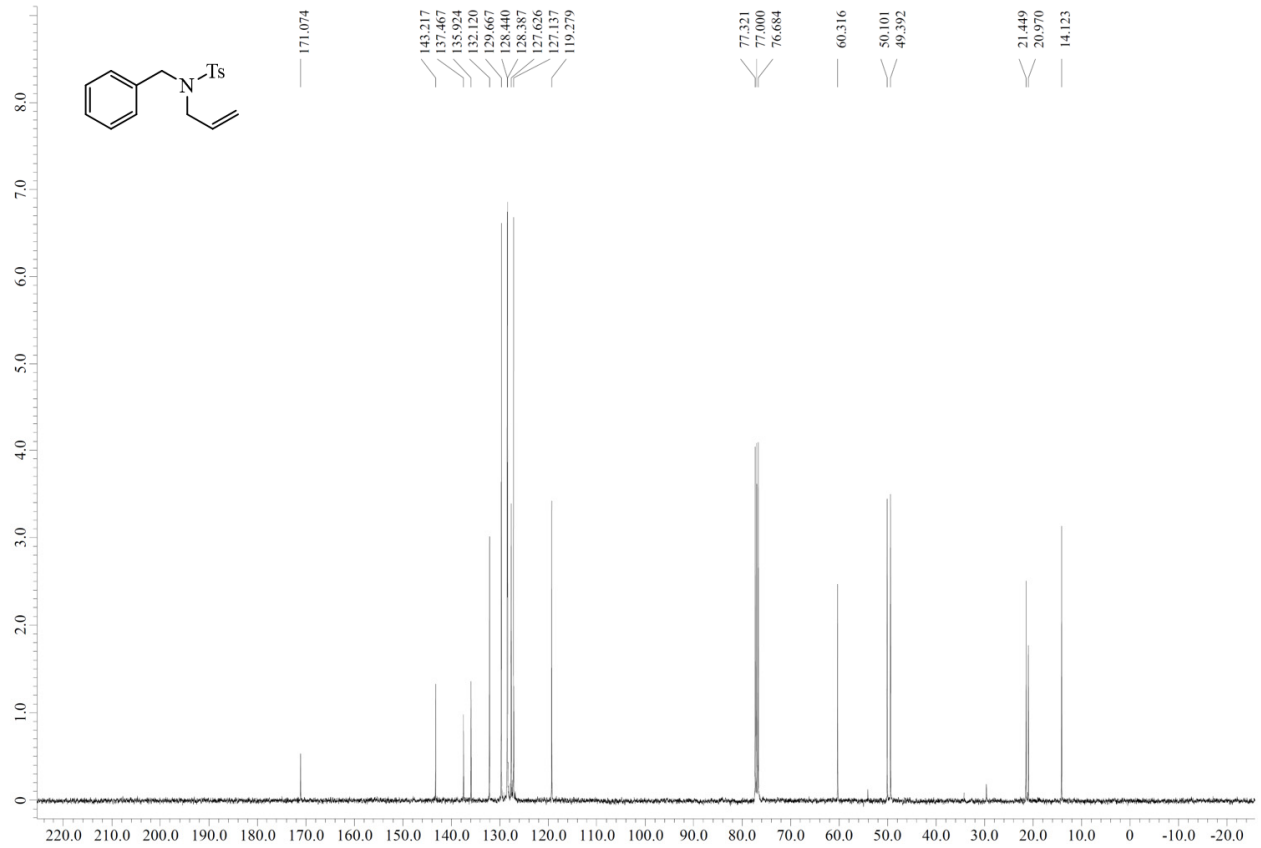
^{1}H NMR spectrum of compound **entry 11 (Table 3)** (400 MHz, $CDCl_3$)



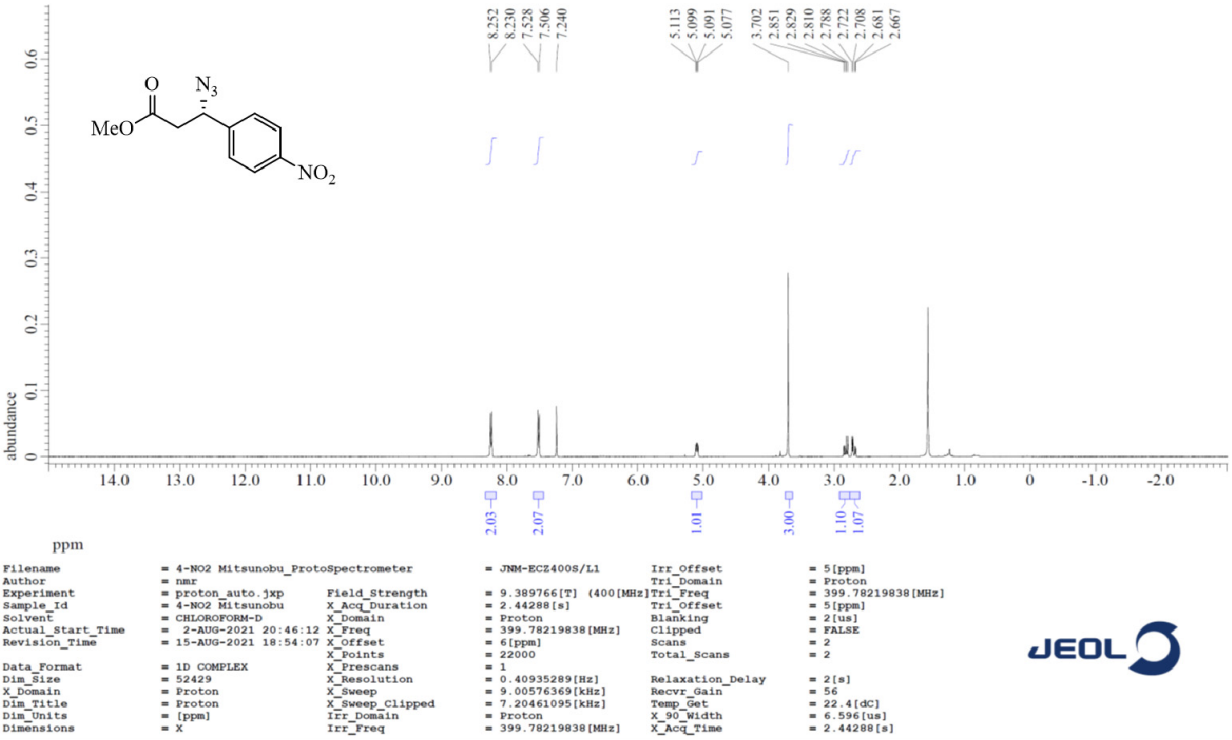
^{13}C NMR spectrum of compound **entry 11 (Table 3)** (100 MHz, $CDCl_3$)



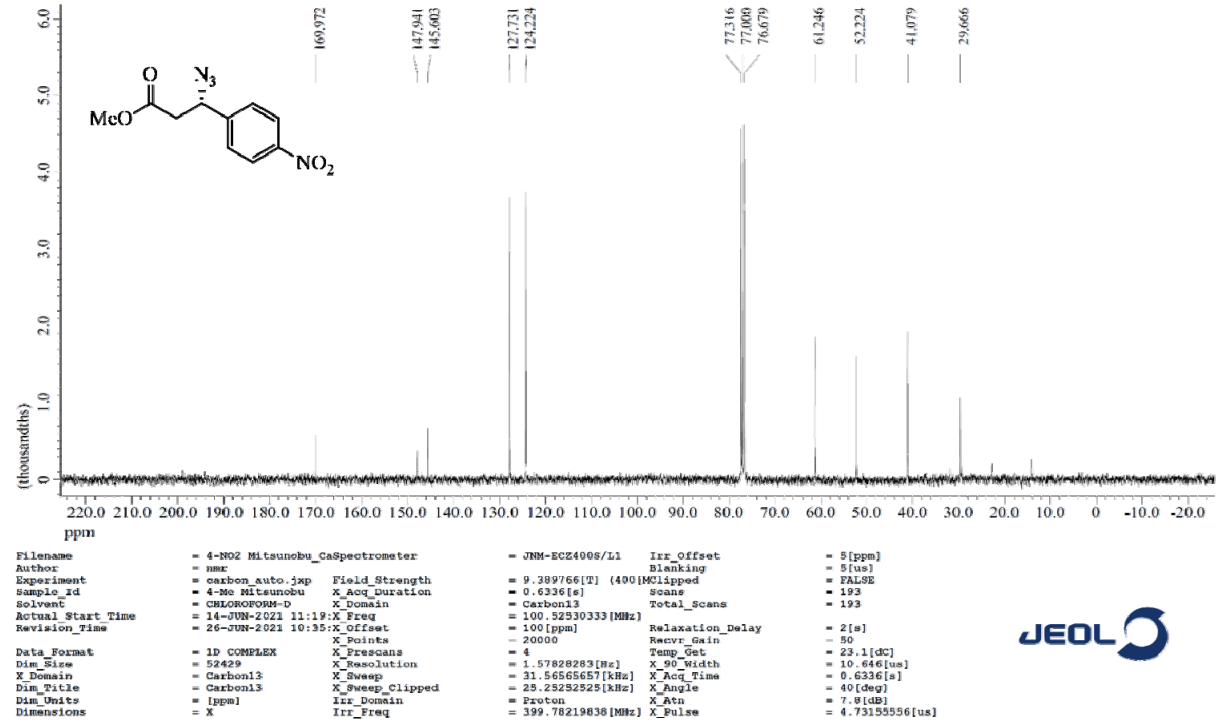
^{1}H NMR spectrum of compound **entry 12 (Table 3)** (400 MHz, $CDCl_3$)



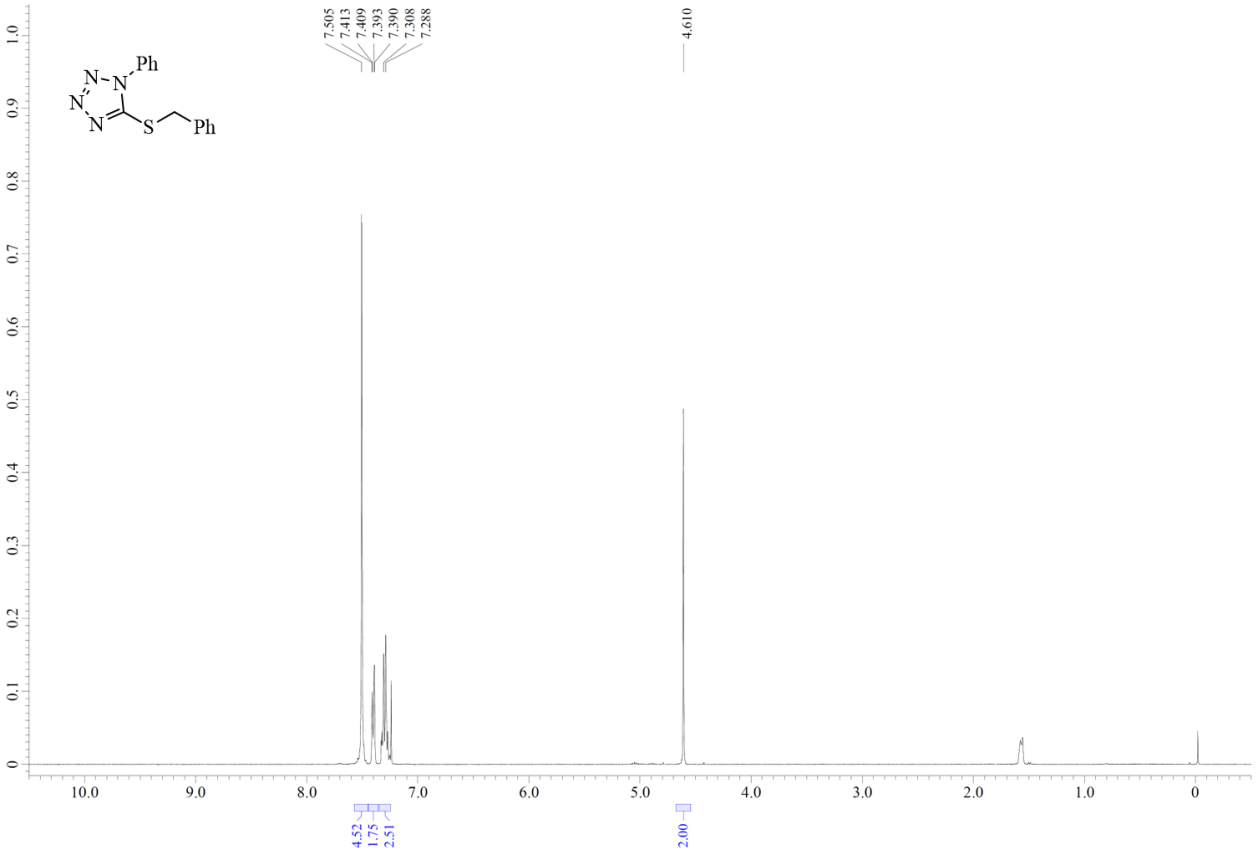
^{13}C NMR spectrum of compound **entry 12 (Table 3)** (100 MHz, $CDCl_3$)



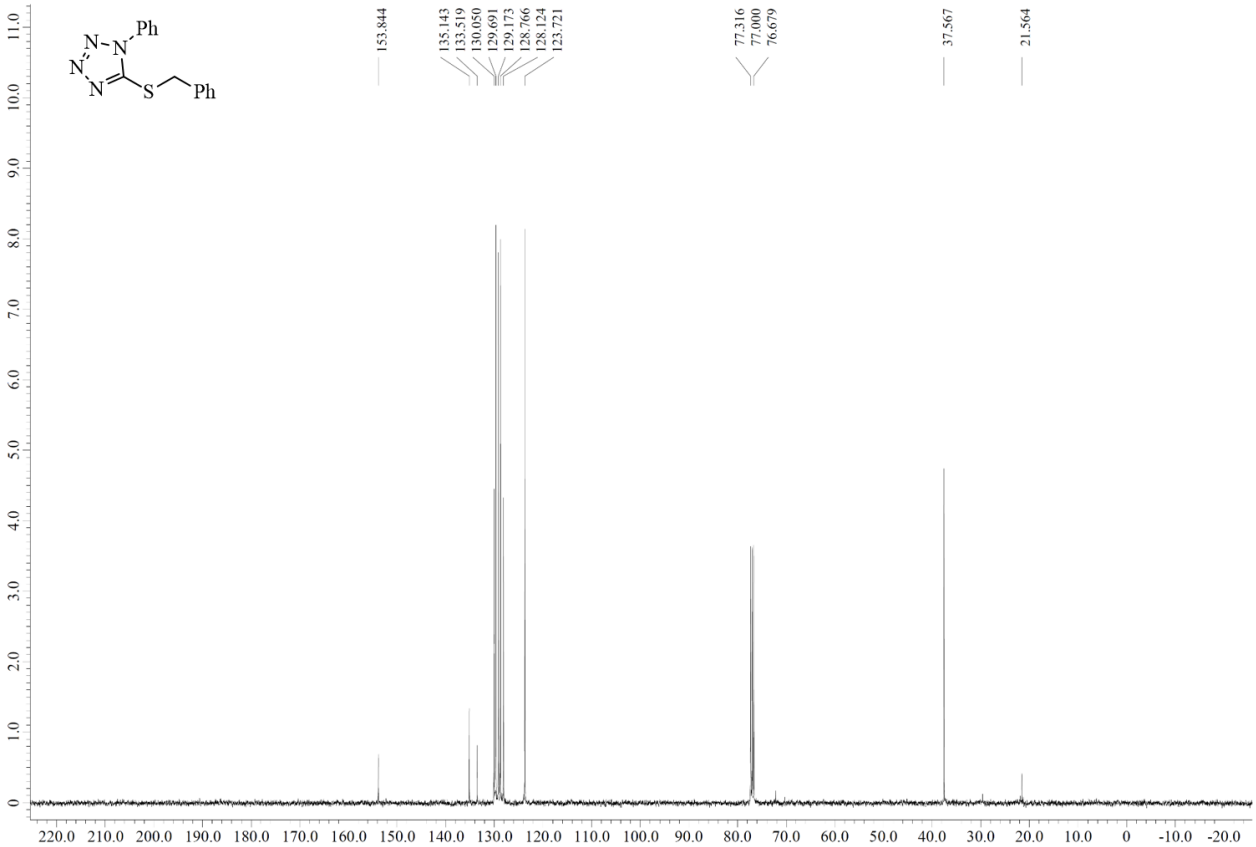
^{1}H NMR spectrum of compound **entry 13 (Table 3)** (400 MHz, $CDCl_3$)



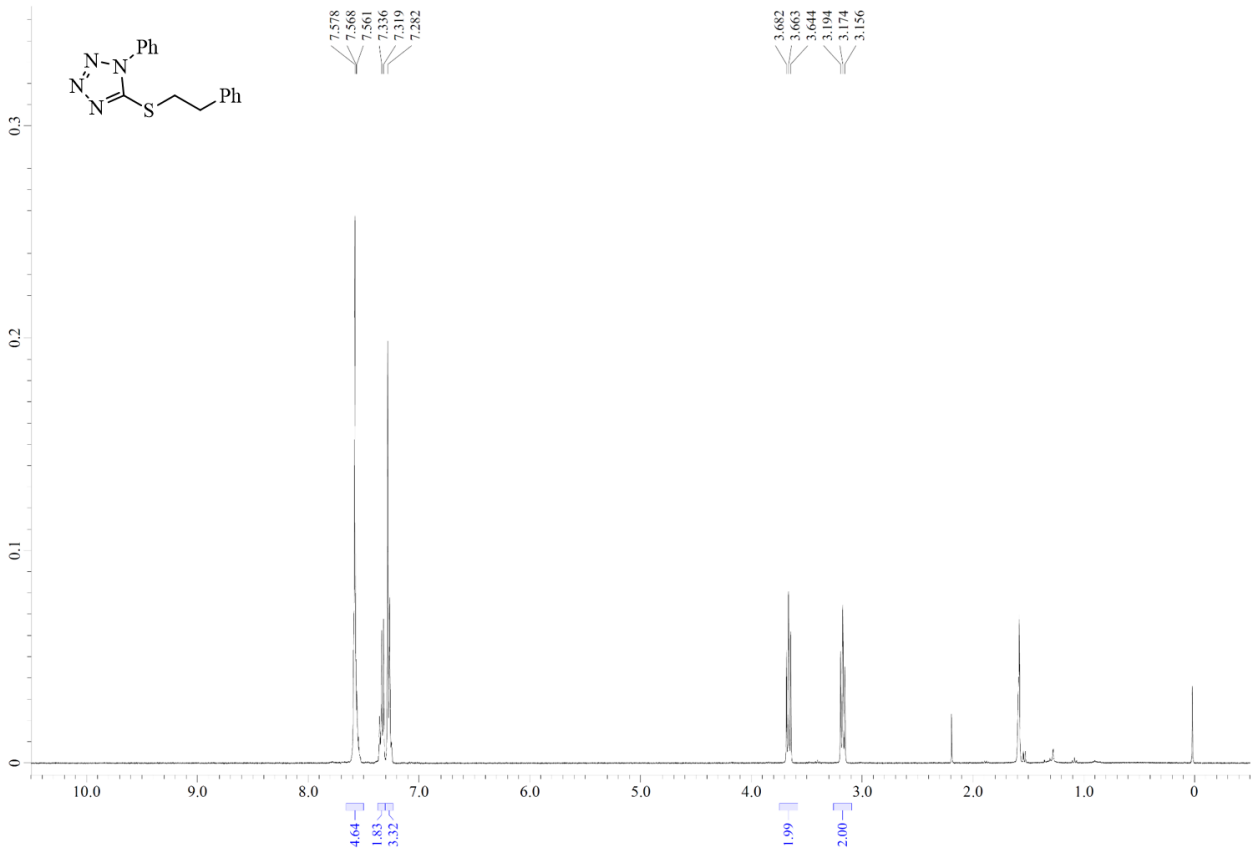
^{13}C NMR spectrum of compound **entry 13 (Table 3)** (100 MHz, $CDCl_3$)



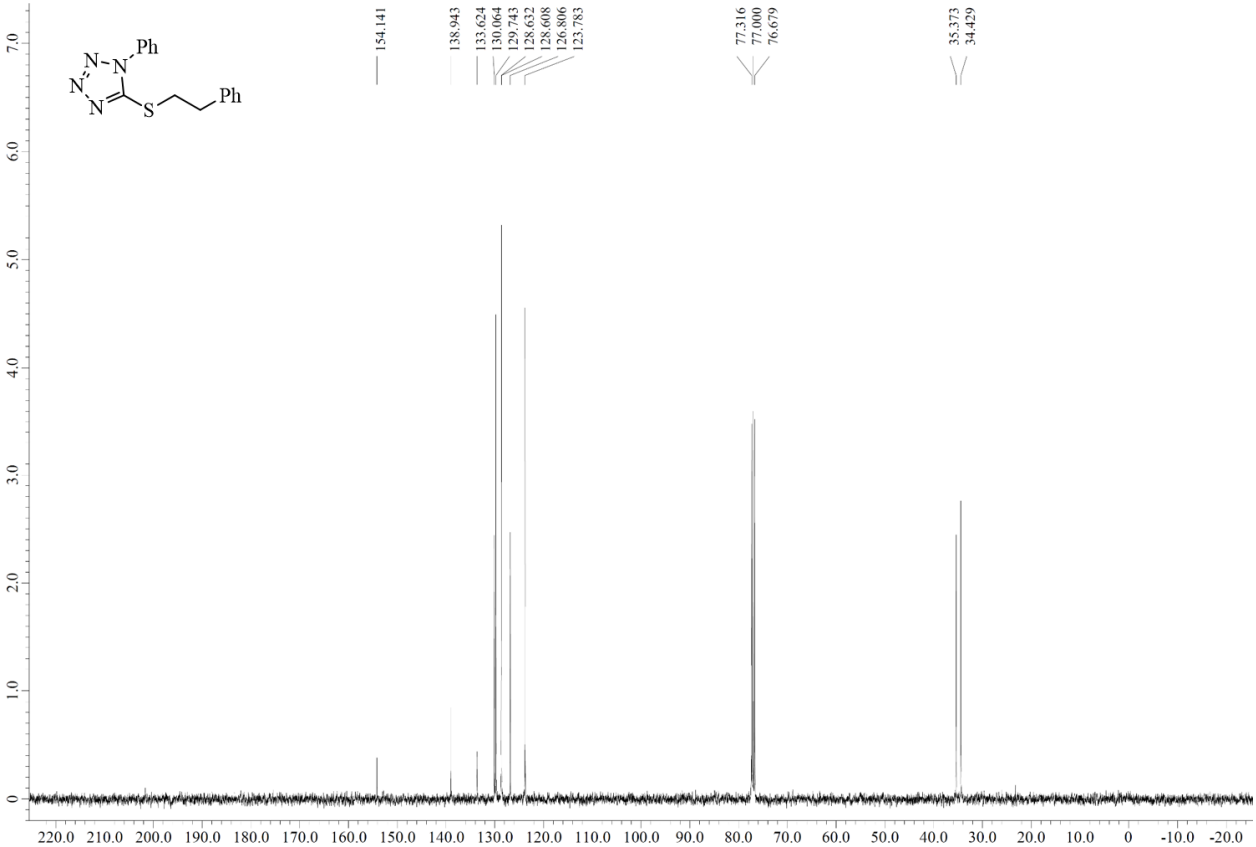
^{1}H NMR spectrum of compound **entry 14 (Table 3)** (400 MHz, $CDCl_3$)



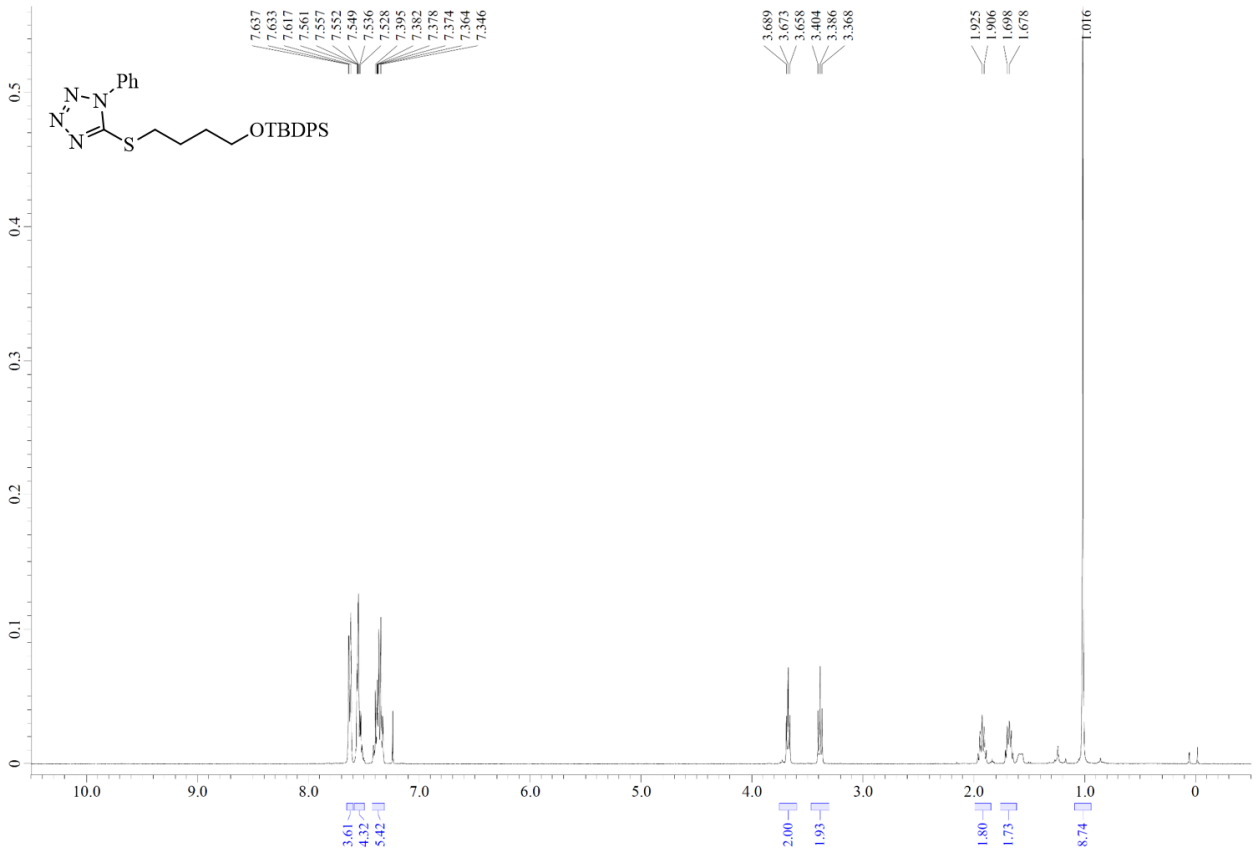
^{13}C NMR spectrum of compound **entry 14 (Table 3)** (100 MHz, $CDCl_3$)



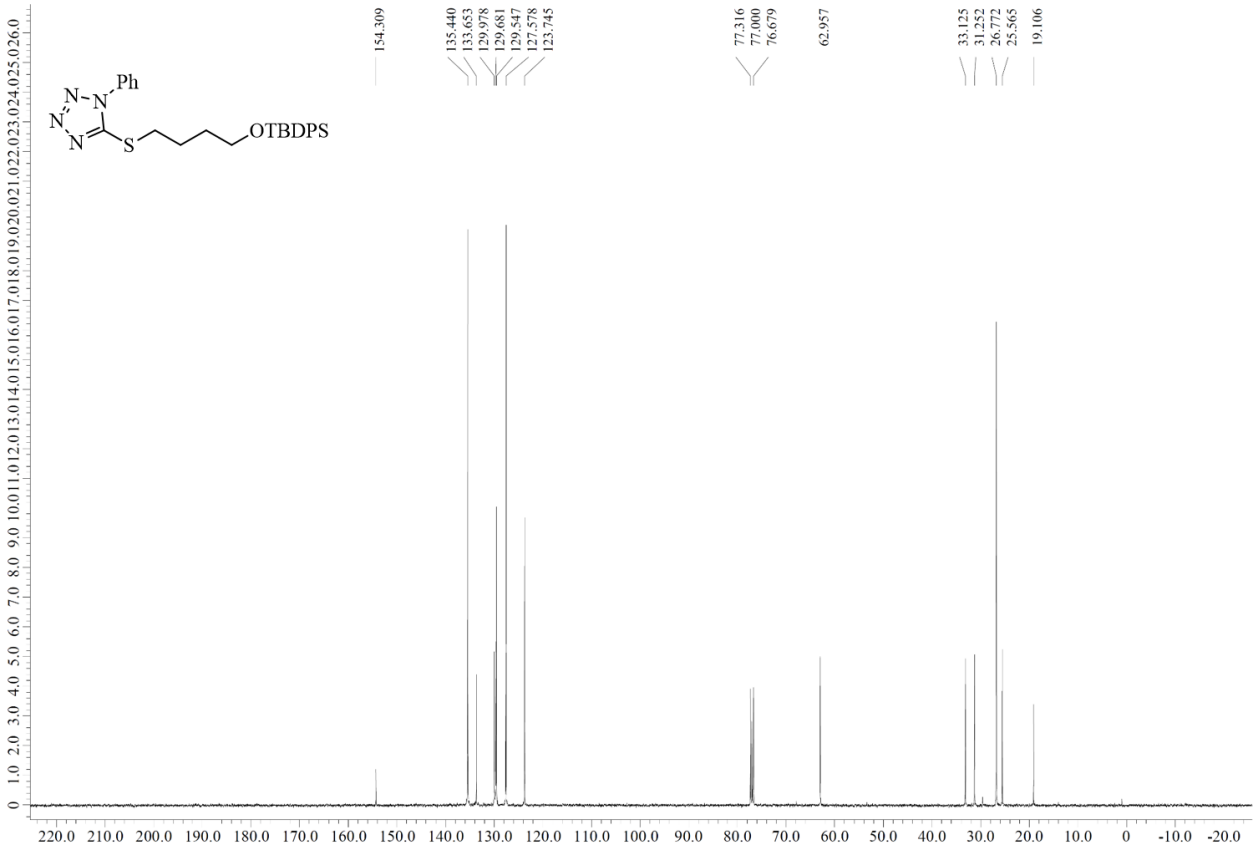
^{1}H NMR spectrum of compound **entry 15 (Table 3)** (400 MHz, $CDCl_3$)



^{13}C NMR spectrum of compound **entry 15 (Table 3)** (100 MHz, $CDCl_3$)



^{1}H NMR spectrum of compound **entry 16 (Table 3)** (400 MHz, $CDCl_3$)



^{13}C NMR spectrum of compound **entry 16 (Table 3)** (100 MHz, $CDCl_3$)

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