Supporting Information

Controllably, C≡C Triple Bond as One-Carbon Synthon to Assembly of Benzothiazole Framework

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A. General Methods

Melting points were determined with a Buchi Melting Point B-545 instrument. ^{1}H and ^{13}C NMR spectra were recorded using a Bruker DRX-400 spectrometer with $CDCl_3$ as solvent. The chemical shifts are referenced to signals at 7.26 and 77.0 ppm, respectively, and chloroform is solvent with TMS as the internal standard. IR spectra were obtained either as potassium bromide pellets or as liquid films between two potassium bromide pellets with a Bruker TENSOR 27 spectrometer. Mass spectra were recorded on a Thermo Scientific ISQ gas chromatograph-mass spectrometer. The data of HRMS was carried out on a high-resolution mass spectrometer (LCMS-IT-TOF). TLC was performed by using commercially prepared 100-400 mesh silica gel plates and visualization was effected at 254 nm. Unless otherwise noted, all reagents and solvents were obtained from commercial suppliers and used without further purification.

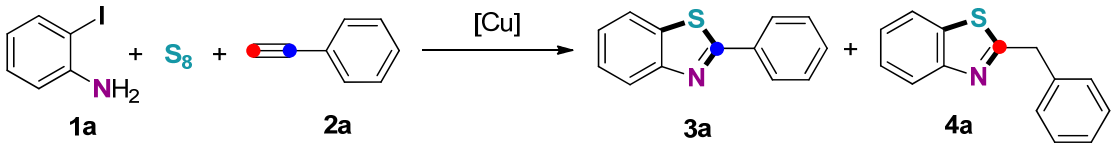
B. General Procedures

General procedure A: the synthesis of benzo[*d*]thiazole products 3a-3u: In a test tube, a mixture of 2-iodoaniline **1** (0.2 mmol), $\mathbf{S_8}$ (0.24 mmol), phenylacetylene **2** (0.3 mmol), CuI (0.02 mmol), K_3PO_4 (0.4 mmol) and 1,10-phen (0.04 mmol) was stirred in DMSO (2.0 mL). The reaction was allowed to stir at 110 °C under 1 atm O_2 for 10 h. After that, water was added and extracted with ethyl acetate twice. The combined organic phase was dried over Na_2SO_4 and concentrated. The residue was purified by flash column chromatography on silica gel with petroleum ether/ethyl acetate (PE/EA = 10:1–30:1) as the eluent to afford the desired product.

General procedure B: the synthesis of benzo[*d*]thiazole products 4a-4p: In air, a 25 mL Schlenk tube was charged with 2-iodoaniline **1** (0.2 mmol), $\mathbf{S_8}$ (0.24 mmol), phenylacetylene **2** (0.3 mmol), CuTC (0.01 mmol), DBU (0.2 mmol) and 2.5 mL $MeCN/H_2O$ (10:1). The flask was evacuated and filled with nitrogen for three cycles. The reaction was allowed to stir at 130 °C for 10 h. After that, water was added and extracted with ethyl acetate twice. The combined organic phase was dried over Na_2SO_4 and concentrated. The residue was purified by flash column chromatography on silica gel with petroleum ether/ethyl acetate (PE/EA = 20:1–30:1) as the eluent to afford the desired product.

C. Optimization of the Reaction Conditions

Table S1. Optimization of the Reaction Conditions [a,b]



1a 2a 3a 4a

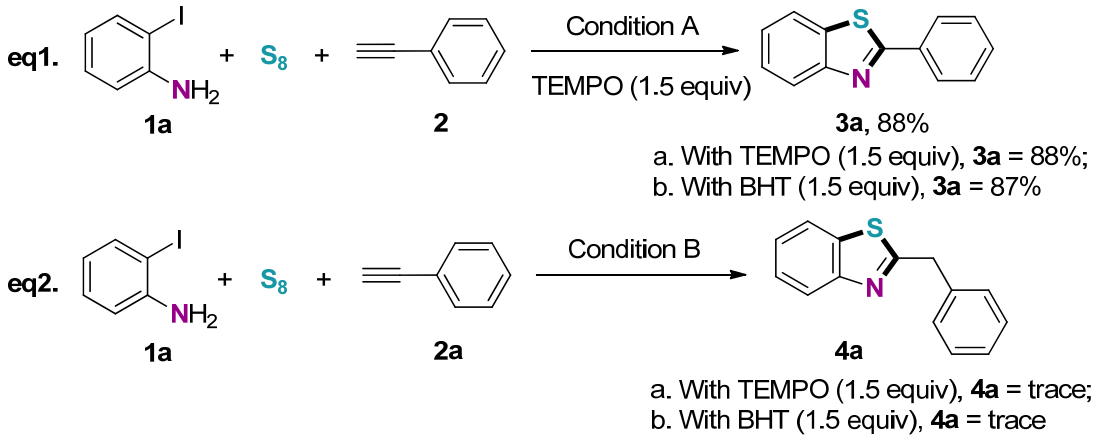
entry	[Cu]	base	additive (equiv)	solvent	Yield [d] (%)	
					3a	4a
1	CuI	K_2CO_3	-	DMSO	54	n.d
2	CuI	K_2CO_3	-	dioxane	trace	n.d
3	CuI	K_2CO_3	-	IPA	n.d	n.d
4	CuI	K_3PO_4	-	DMSO	74	n.d
5	CuI	KOAc	-	DMSO	42	n.d

6	CuI	K_3PO_4	TBAI (1)	DMSO	60	n.d
7	**CuI**	**K_3PO_4**	**1,10-phen (0.2)**	**DMSO**	**87 (84) [e]**	**n.d**
8	CuTC	DBU		MeCN	10	83
9	CuTC	DBU		MeCN [c]	trace	37
10	**CuTC**	**DBU**		**MeCN/H_2O (10:1)**	**n.d**	**95 (90) [e]**
11	CuTC	DBU		MeCN/H_2O (5:1)	n.d	89
12	CuTC	DBU		MeCN/H_2O (3:1)	n.d	86
13	CuTC	DBU		H_2O	n.d	8
14	CuTC	DBU	1,10-phen (0.2)	MeCN/H_2O (10:1)	n.d	71

[a] Reaction conditions (entries 1-7): **1a** (0.1 mmol), **S_8** (0.12 mmol), **2a** (0.15 mmol), CuI (10 mol %), base (2 equiv), additive in 1.0 mL solvent at 110 °C under 1 atm of O_2 for 10 h unless otherwise noted. [b] Reaction conditions (entries 8-13): **1a** (0.1 mmol), **S_8** (0.12 mmol), **2a** (0.15 mmol), CuTc (5 mol %), DBU (1 equiv) in 1.5 mL solvent at 130 °C under N_2 for 10 h unless otherwise noted. [c] Super dry acetonitrile. [d] GC-MS yield using *n*-dodecane as an internal standard. [e] Isolated yield.

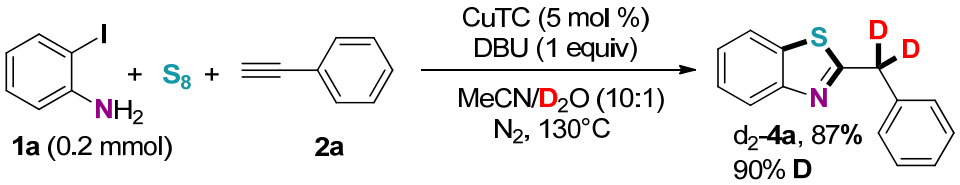
As indicated in Table S1, 2-Iodoaniline (0.1 mmol), **S_8** (0.12 mmol) and phenylacetylene (0.15 mmol) were chosen as initially investigated substrates. Through series of copper salts and alkali screening, we believed that the use of CuI and potassium is more conducive to the formation of 2-phenylbenzo[*d*]thiazole (**3a**). When the reaction was performed in the presence of CuI (10 mol %) and K_2CO_3 (2 equiv) using DMSO as solvent at 110 °C under 1 atm of O_2, 2-phenylbenzo[*d*]thiazole (**3a**) was obtained in 54% yield (entry 1). Other solvents including dioxane, IPA and MeCN did not effect on improving the yield of **3a** (entries 2-3). When K_2CO_3 was replaced by K_3PO_4 or KOAc, 74% and 42% yields were obtain, respectively (entries 4-5). In order to further improve the yield, different additives were tested in the system (entries 6-7). The result showed that the addition of phase transfer reagent (TBAI) did not work in the reaction system, while the yield increased to 87% when using 1,10-phenanthroline as a ligand (entry 7). Next, when the reaction was performed in the presence of CuTC (5 mol %) and DBU (1 equiv) using 1.5 mL of MeCN as solvent at 130 °C under N_2, 2-benzylbenzo[*d*]thiazole (**4a**) was delivered in 83% yield and 10% yield of product **3a** was detected (entry 8). The use of super dry acetonitrile was not conducive to the conversion, making the yield of **4a** drop to 37% (entry 9). Subsequently, we replaced MeCN with a mixed solvent MeCN/H_2O (10:1), and the desired product **4a** was delivered in 95% yield (entry 10) with no product **3a** detected. When increasing the proportion of water in the mixed solvent, the yield was decreased slightly (entries 11-12). However, the reaction could not proceed well when water was used as a solvent (entry 13). Besides, when adding a ligand in the system, the yield was reduced to 71% (entry 14).

D. Free Radical Verification Experiments

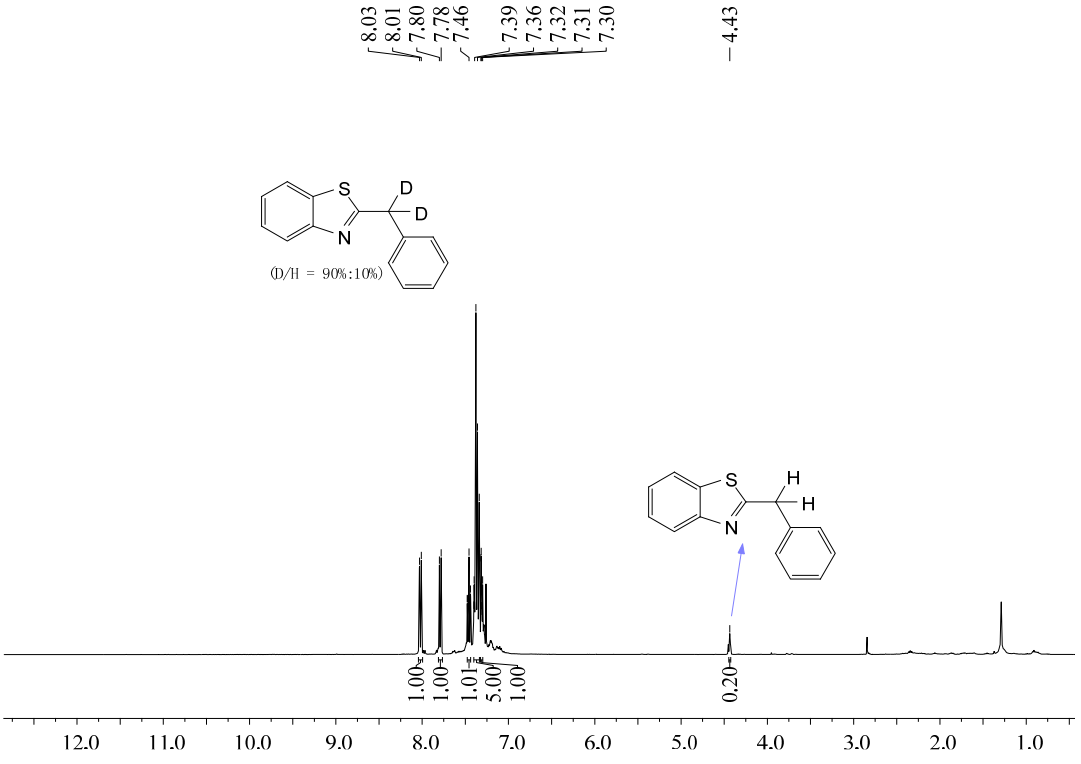


Scheme S1. Free radical verification experiments. Condition A: CuI (10 mol %), K_3PO_4 (2 equiv), 1,10-phen (20 mol %), DMSO, O_2, 110 °C, 10 h. Condition B: CuTC (5 mol %), DBU (1 equiv), MeCN/H_2O (10:1), N_2, 130 °C, 10 h.

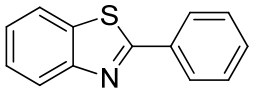
E. Deuterium-labeling Experiments



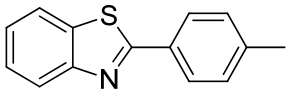
Scheme S2. Deuterium-labeling experiments. Reaction conditions: **1a** (0.2 mmol), **S_8** (0.24 mmol), **2a** (0.3 mmol), CuTC (5 mol %), DBU (1 equiv) in 2.5 mL MeCN/D_2O (10:1) at 130 °C under N_2 for 10 h unless otherwise noted. Isolated yield. The product d_2-**4a** was determined by ^{1}H NMR.



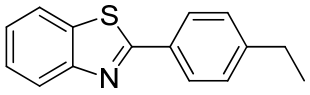
F. Characterization Data for Products



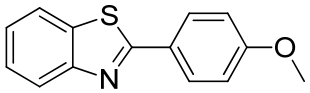
2-Phenylbenzo[*d*]thiazole (3a). White solid, yield 35 mg (84%), mp 113-114 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.11-8.05 (m, 3H), 7.88 (d, J = 7.9 Hz, 1H), 7.50-7.46 (m, 4H), 7.39-7.35 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 168.1, 154.2, 135.1, 133.6, 131.0, 129.0, 127.6, 126.4, 125.2, 123.3, 121.6. IR (KBr, cm^{-1}): 3892, 3743, 3489, 1638, 1473, 958, 759. HRMS (ESI) (m/z): calcd for $C_{13}H_{10}NS$ $[M+H]^+$: 212.0528, found: 212.0531.



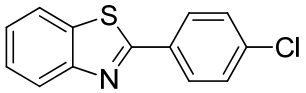
2-(*p*-Tolyl)benzo[*d*]thiazole (3b). White solid, yield 36 mg (80%), mp 86-87 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96 (tt, J = 39.3, 7.7 Hz, 4H), 7.47-7.25 (m, 4H), 2.42 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 168.3, 154.2, 141.4, 134.9, 131.0, 129.7, 127.5, 126.3, 125.0, 123.0, 121.6, 21.5. IR (KBr, cm^{-1}): 3691, 3501, 3041, 2925, 1477, 1232, 1022, 817, 751. HRMS (ESI) (m/z): calcd for $C_{14}H_{12}NS$ $[M+H]^+$: 226.0685, found: 226.0681.



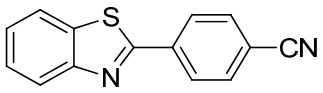
2-(4-Ethylphenyl)benzo[*d*]thiazole (3c). Yellow solid, yield 40 mg (83%), mp 61-62 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.04 (dd, J = 20.9, 7.9 Hz, 3H), 7.89 (d, J = 7.6 Hz, 1H), 7.49 (t, J = 7.2 Hz, 1H), 7.39-7.31 (m, 3H), 2.72 (dd, J = 14.6, 7.1 Hz, 2H), 1.29 (t, J = 7.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 168.3, 154.2, 147.7, 135.0, 131.2, 128.6, 127.6, 126.2, 125.0, 123.1, 121.6, 28.9, 15.3. IR (KBr, cm^{-1}): 3893, 3744, 3490, 3382, 2925, 1638, 1430, 1237, 964, 754. HRMS (ESI) (m/z): calcd for $C_{15}H_{14}NS$ $[M+H]^+$: 240.0841, found: 240.0845.



2-(4-Methoxyphenyl)benzo[*d*]thiazole (3d). White solid, yield 41 mg (86%), mp 121-122 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, J = 8.6 Hz, 3H), 7.87 (d, J = 7.9 Hz, 1H), 7.47 (t, J = 7.7 Hz, 1H), 7.35 (t, J = 7.6 Hz, 1H), 7.00 (d, J = 8.6 Hz, 2H), 3.88 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.9, 162.0, 154.1, 134.8, 129.2, 126.4, 126.2, 124.8, 122.8, 121.5, 114.4, 55.5. IR (KBr, cm^{-1}): 3893, 3745, 3305, 3049, 1724, 1559, 1306, 963, 828, 752. HRMS (ESI) (m/z): calcd for $C_{14}H_{12}NOS$ $[M+H]^+$: 242.0634, found: 242.0638.

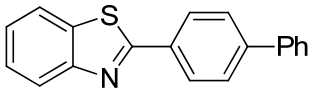


2-(4-Chlorophenyl)benzo[*d*]thiazole (3e). White solid, yield 39 mg (80%), mp 115-116 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, J = 8.2 Hz, 1H), 8.01 (d, J = 8.4 Hz, 2H), 7.88 (d, J = 8.0 Hz, 1H), 7.52-7.43 (m, 3H), 7.39 (t, J = 7.6 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.6, 154.1, 137.0, 135.1, 132.1, 129.3, 128.7, 126.5, 125.4, 123.3, 121.7. IR (KBr, cm^{-1}): 3894, 3746, 3483, 2923, 1603, 1467, 1252, 965, 831, 754. HRMS (ESI) (m/z): calcd for $C_{13}H_9ClNS$ $[M+H]^+$: 246.0139, found: 246.0141.

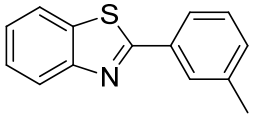


4-(Benzo[*d*]thiazol-2-yl)benzonitrile (3f). White solid, yield 33 mg (69%), mp 171-172 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, J = 8.2 Hz, 2H), 8.10 (d, J = 8.2 Hz, 1H), 7.93 (d, J = 8.0 Hz, 1H), 7.76 (d, J = 8.2 Hz, 2H), 7.54 (t, J = 7.7 Hz, 1H), 7.44 (t, J =

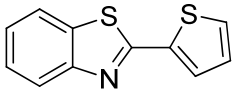
7.6 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.3, 154.0, 137.5, 135.3, 132.8, 127.93, 126.9, 126.1, 123.8, 121.8, 118.3, 114.1. IR (KBr, cm^{-1}): 3924, 3698, 3346, 2923, 1740, 1471, 1244, 962, 833, 760. HRMS (ESI) (m/z): calcd for $C_{14}H_9N_2S$ $[M+H]^+$: 237.0481, found: 237.0482.



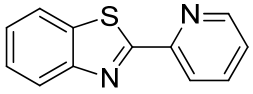
2-([1,1'-Biphenyl]-4-yl)benzo[*d*]thiazole (3g). Yellow solid, yield 26 mg (37%), mp 191-192 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, J = 8.0 Hz, 2H), 8.10 (d, J = 8.2 Hz, 1H), 7.92 (d, J = 8.0 Hz, 1H), 7.73 (d, J = 8.1 Hz, 2H), 7.67 (d, J = 7.9 Hz, 2H), 7.49 (dd, J = 13.1, 5.5 Hz, 3H), 7.40 (t, J = 7.5 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.8, 154.1, 143.8, 140.1, 135.0, 132.4, 129.0, 128.0, 128.0, 127.7, 127.1, 126.4, 125.2, 123.2, 121.6. IR (KBr, cm^{-1}): 3907, 3702, 3336, 2921, 1736, 1590, 1462, 1249, 839, 752. HRMS (ESI) (m/z): calcd for $C_{19}H_{14}NS$ $[M+H]^+$: 288.0841, found: 288.0844.



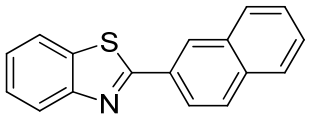
2-(*m*-Tolyl)benzo[*d*]thiazole (3h). Yellow oil, yield 38 mg (85%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, J = 8.2 Hz, 1H), 7.95 (s, 1H), 7.91-7.86 (m, 2H), 7.49 (t, J = 7.7 Hz, 1H), 7.38 (t, J = 7.6 Hz, 2H), 7.30 (d, J = 7.5 Hz, 1H), 2.45 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.4, 154.2, 138.9, 135.1, 133.5, 131.9, 129.0, 128.0, 126.3, 125.2, 124.9, 123.2, 121.6, 21.4. IR (KBr, cm^{-1}): 3893, 3744, 3481, 3050, 2100, 1738, 1505, 1246, 758. HRMS (ESI) (m/z): calcd for $C_{14}H_{12}NS$ $[M+H]^+$: 226.0685, found: 226.0689.



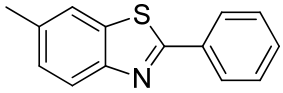
2-(Thiophen-2-yl)benzo[*d*]thiazole (3i). White solid, yield 33 mg (76%), mp 99-100 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, J = 8.2 Hz, 1H), 7.82 (d, J = 8.0 Hz, 1H), 7.64 (d, J = 3.5 Hz, 1H), 7.46 (dd, J = 13.6, 6.2 Hz, 2H), 7.35 (t, J = 7.6 Hz, 1H), 7.13-7.09 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.4, 153.7, 137.3, 134.7, 129.3, 128.7, 128.1, 126.5, 125.3, 123.0, 121.5. IR (KBr, cm^{-1}): 3893, 3741, 3071, 1743, 1608, 1417, 1227, 828, 704. HRMS (ESI) (m/z): calcd for $C_{11}H_8NS_2$ $[M+H]^+$: 218.0093, found: 218.0097.



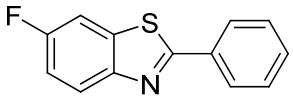
2-(Pyridin-2-yl)benzo[*d*]thiazole (3j). White solid, yield 19 mg (45%), mp 133-134 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.68 (s, 1H), 8.37 (d, J = 7.9 Hz, 1H), 8.09 (d, J = 8.2 Hz, 1H), 7.95 (d, J = 8.0 Hz, 1H), 7.83 (t, J = 7.7 Hz, 1H), 7.50 (t, J = 7.6 Hz, 1H), 7.44-7.34 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ 169.4, 154.3, 151.4, 149.7, 137.0, 136.2, 126.3, 125.7, 125.3, 123.6, 122.0, 120.8. IR (KBr, cm^{-1}): 3899, 3743, 3388, 3055, 1570, 1433, 1305, 979, 746. HRMS (ESI) (m/z): calcd for $C_{12}H_9N_2S$ $[M+H]^+$: 213.0481, found: 213.0484.



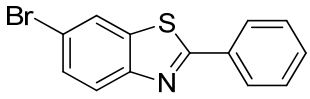
2-(Naphthalen-1-yl)benzo[*d*]thiazole (3k). White solid, yield 36 mg (70%), mp 129-130 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 (s, 1H), 8.25 (d, J = 8.6 Hz, 1H), 8.15 (d, J = 8.1 Hz, 1H), 7.98 (dd, J = 16.1, 8.1 Hz, 3H), 7.93-7.89 (m, 1H), 7.61-7.53 (m, 3H), 7.44 (t, J = 7.5 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.2, 154.2, 135.1, 134.6, 133.2, 130.9, 128.8, 127.9, 127.6, 127.5, 126.9, 126.4, 125.3, 124.5, 123.2, 121.7. IR (KBr, cm^{-1}): 3901, 3748, 3572, 3377, 2921, 1730, 1454, 1364, 840, 744. HRMS (ESI) (m/z): calcd for $C_{17}H_{12}NS$ $[M+H]^+$: 262.0685, found: 262.0686.



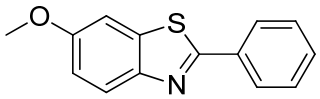
6-Methyl-2-phenylbenzo[*d*]thiazole (3l). Yellow solid, yield 36 mg (81%), mp 126-127 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10-8.06 (m, 2H), 7.96 (d, J = 8.3 Hz, 1H), 7.68 (s, 1H), 7.48 (d, J = 4.9 Hz, 3H), 7.30 (d, J = 8.4 Hz, 1H), 2.50 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.0, 152.2, 135.4, 135.21, 133.7, 130.8, 129.0, 128.0, 127.5, 122.7, 121.4, 21.6. IR (KBr, cm^{-1}): 3893, 3746, 3376, 3037, 2920, 1643, 1447, 1230, 811, 685. HRMS (ESI) (m/z): calcd for $C_{14}H_{12}NS$ $[M+H]^+$: 226.0685, found: 226.0689.



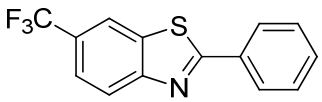
6-Fluoro-2-phenylbenzo[*d*]thiazole (3m). Yellow solid, yield 33 mg (72%), mp 134-135 ºC. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.04 (ddd, J = 13.9, 7.3, 3.7 Hz, 3H), 7.58 (dd, J = 8.1, 2.1 Hz, 1H), 7.52-7.48 (m, 3H), 7.25-7.20 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.8 (d, J = 3.5 Hz), 160.5 (d, J = 245.8 Hz), 150.8, 136.0 (d, J = 11.1 Hz), 133.4, 131.1, 129.1, 127.5, 124.2 (d, J = 9.4 Hz), 115.0 (d, J = 24.7 Hz), 107.9 (d, J = 26.8 Hz). IR (KBr, cm^{-1}): 3891, 3745, 3041, 1748, 1569, 959, 843. HRMS (ESI) (m/z): calcd for $C_{13}H_9FNS$ $[M+H]^+$: 230.0434, found: 230.0429.



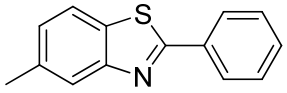
6-Bromo-2-phenylbenzo[*d*]thiazole (3n). White solid, yield 44 mg (77%), mp 156-157 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10-8.01 (m, 3H), 7.91 (d, J = 8.7 Hz, 1H), 7.58 (d, J = 8.7 Hz, 1H), 7.50 (d, J = 5.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.6, 153.0, 136.7, 133.2, 131.3, 129.9, 129.1, 127.6, 124.3, 124.2, 118.8. IR (KBr, cm^{-1}): 3895, 3740, 3057, 1727, 1478, 1301, 1077, 964, 819, 682. HRMS (ESI) (m/z): calcd for $C_{13}H_9BrNS$ $[M+H]^+$: 289.9634, found: 289.9631.



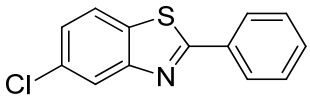
6-Methoxy-2-phenylbenzo[*d*]thiazole (3o). White solid, yield 39 mg (80%), mp 116-117 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04-7.98 (m, 2H), 7.93 (d, J = 8.9 Hz, 1H), 7.44 (d, J = 5.2 Hz, 3H), 7.29 (s, 1H), 7.06 (dd, J = 8.9, 2.0 Hz, 1H), 3.83 (d, J = 1.9 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.5, 157.8, 148.7, 136.5, 133.8, 130.6, 129.0, 127.2, 123.7, 115.7, 104.2, 55.8. IR (KBr, cm^{-1}): 3893, 3744, 3056, 1747, 1590, 1471, 1263, 1222, 821, 682. HRMS (ESI) (m/z): calcd for $C_{14}H_{12}NOS$ $[M+H]^+$: 242.0634, found: 242.0631.



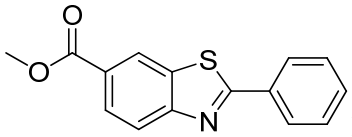
2-Phenyl-6-(trifluoromethyl)benzo[*d*]thiazole (3p). Yellow solid, yield 41 mg (74%), mp 152-153 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (s, 1H), 8.11 (dd, J = 17.6, 7.8 Hz, 3H), 7.71 (d, J = 8.5 Hz, 1H), 7.53-7.45 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.1, 156.1 (d, J = 1.1 Hz), 135.1, 133.0, 131.7, 129.2, 127.8, 127.3 (q, J = 31.3 Hz), 124.2 (q, J = 272.2 Hz), 123.5, 123.3 (q, J = 3.4 Hz), 119.3 (q, J = 4.2 Hz). IR (KBr, cm^{-1}): 3954, 3805, 3525, 3445, 1640, 1321, 1114, 759. HRMS (ESI) (m/z): calcd for $C_{14}H_9F_3NS$ $[M+H]^+$: 280.0402, found: 280.0397.



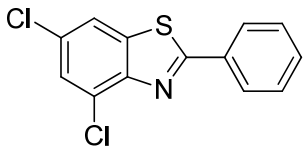
5-Methyl-2-phenylbenzo[*d*]thiazole (3q). White solid, yield 37 mg (83%), mp 147-148 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10-8.05 (m, 2H), 7.88 (s, 1H), 7.76 (d, J = 8.2 Hz, 1H), 7.50-7.46 (m, 3H), 7.21 (d, J = 8.1 Hz, 1H), 2.51 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.2, 154.5, 136.4, 133.7, 132.0, 130.9, 129.0, 127.5, 126.9, 123.3, 121.1, 21.6. IR (KBr, cm^{-1}): 3911, 3685, 3504, 3363, 3040, 2921, 1450, 1245, 765. HRMS (ESI) (m/z): calcd for $C_{14}H_{12}NS$ $[M+H]^+$: 226.0685, found: 226.0682.



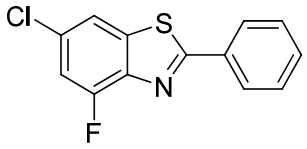
5-Chloro-2-phenylbenzo[*d*]thiazole (3r). White solid, yield 36 mg (73%), mp 139-140 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, J = 7.7 Hz, 3H), 7.76 (d, J = 8.5 Hz, 1H), 7.47 (d, J = 5.1 Hz, 3H), 7.32 (d, J = 8.5 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.9, 155.0, 133.3, 133.2, 132.3, 131.4, 129.1, 127.6, 125.7, 123.0, 122.3. IR (KBr, cm^{-1}): 3892, 3745, 3074, 2922, 1756, 1539, 1245, 1066, 886, 760, 686. HRMS (ESI) (m/z): calcd for $C_{13}H_9ClNS$ $[M+H]^+$: 246.0139, found: 246.0141.



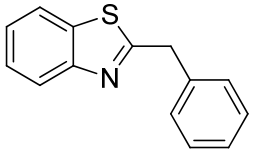
Methyl 2-phenylbenzo[*d*]thiazole-6-carboxylate (3s). White solid, yield 36 mg (66%), mp 171-172 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.73 (s, 1H), 8.10-8.03 (m, 3H), 7.93 (d, J = 8.4 Hz, 1H), 7.53-7.48 (m, 3H), 3.97 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.3, 166.9, 154.0, 139.8, 133.2, 131.4, 129.1, 128.6, 127.7, 125.8, 124.7, 121.5, 52.4. IR (KBr, cm^{-1}): 3893, 3744, 3485, 2915, 1710, 1298, 1084, 964, 756. HRMS (ESI) (m/z): calcd for $C_{15}H_{12}NO_2S$ $[M+H]^+$: 270.0583, found: 270.0580.



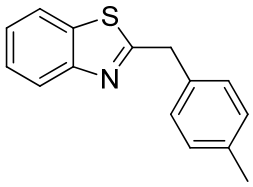
4,6-Dichloro-2-phenylbenzo[*d*]thiazole (3t). White solid, yield 39 mg (70%), mp 150-151 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12-8.08 (m, 2H), 7.77 (s, 1H), 7.53-7.47 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.3, 149.9, 137.1, 132.9, 131.6, 130.9, 129.1, 128.5, 127.8, 127.1, 119.9. IR (KBr, cm^{-1}): 3844, 3742, 3612, 2926, 1648, 1532, 679. HRMS (ESI) (m/z): calcd for $C_{13}H_8Cl_2NS$ $[M+H]^+$: 279.9749, found: 279.9745.



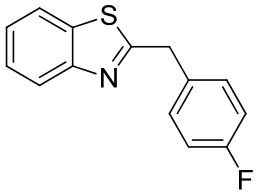
6-Chloro-4-fluoro-2-phenylbenzo[*d*]thiazole (3u). White solid, yield 35 mg (67%), mp 156-157 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, J = 7.4 Hz, 2H), 7.64 (s, 1H), 7.49 (d, J = 6.5 Hz, 3H), 7.21 (d, J = 9.9 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.0, 155.2 (d, J = 260.4 Hz), 141.8 (d, J = 13.4 Hz), 138.3 (d, J = 4.4 Hz), 132.8, 131.6, 131.1 (d, J = 8.9 Hz), 129.1, 127.8, 117.2 (d, J = 4.4 Hz), 113.6 (d, J = 21.5 Hz). IR (KBr, cm^{-1}): 3894, 3745, 3383, 3046, 1741, 1559, 1233, 984, 840, 754. HRMS (ESI) (m/z): calcd for $C_{13}H_8ClFNS$ $[M+H]^+$: 264.0045, found: 264.0039.



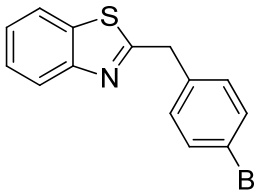
2-Benzylbenzo[*d*]thiazole (4a). Brown oil, yield 41 mg (90%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, J = 8.2 Hz, 1H), 7.81 (d, J = 8.0 Hz, 1H), 7.49 (t, J = 7.7 Hz, 1H), 7.37 (m, 6H), 4.48 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.2, 153.3, 137.2, 135.7, 129.2, 128.9, 127.4, 126.0, 124.9, 122.8, 121.6, 40.7. IR (KBr, cm^{-1}): 3876, 3742, 2924, 1685, 1510, 757, 702. HRMS (ESI) (m/z): calcd for $C_{14}H_{12}NS$ $[M+H]^+$: 226.0685, found: 226.0683.



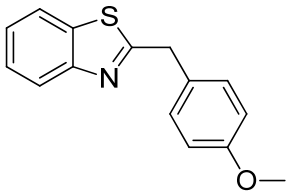
2-(4-Methylbenzyl)benzo[*d*]thiazole (4b). Brown oil, yield 42 mg (88%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, J = 8.1 Hz, 1H), 7.80 (d, J = 8.0 Hz, 1H), 7.47 (t, J = 7.7 Hz, 1H), 7.35 (t, J = 7.6 Hz, 1H), 7.29 (d, J = 7.8 Hz, 2H), 7.19 (d, J = 7.9 Hz, 2H), 4.43 (s, 2H), 2.37 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.8, 153.3, 137.0, 135.7, 134.2, 129.6, 129.07, 126.0, 124.8, 122.8, 121.5, 40.2, 21.1. IR (KBr, cm^{-1}): 3877, 3736, 2922, 1646, 1489, 1287, 1119, 889, 757. HRMS (ESI) (m/z): calcd for $C_{15}H_{14}NS$ $[M+H]^+$: 240.0841, found: 240.0844.



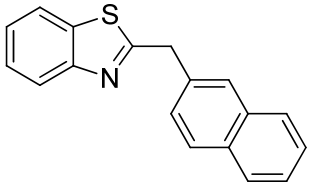
2-(4-Fluorobenzyl)benzo[*d*]thiazole (4c). Brown oil, yield 41 mg (85%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, J = 8.1 Hz, 1H), 7.81 (d, J = 8.0 Hz, 1H), 7.48 (dd, J = 11.3, 4.1 Hz, 1H), 7.35 (ddd, J = 9.1, 6.3, 2.8 Hz, 3H), 7.06 (m, 2H), 4.43 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.9, 162.2 (d, J = 246.0 Hz), 153.2, 135.6, 132.9 (d, J = 3.3 Hz), 130.7 (d, J = 8.1 Hz), 126.1, 125.0, 122.8, 121.6, 115.8 (d, J = 21.5 Hz), 39.7. IR (KBr, cm^{-1}): 3877, 3733, 2920, 1508, 1226, 830, 760. HRMS (ESI) (m/z): calcd for $C_{14}H_{11}FNS$ $[M+H]^+$: 244.0591, found: 244.0589.



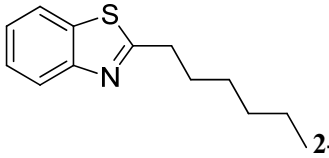
2-(4-Bromobenzyl)benzo[*d*]thiazole (4d). Yellow solid, yield 51 mg (84%), mp 84-85 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, J = 8.2 Hz, 1H), 7.82 (d, J = 8.0 Hz, 1H), 7.48 (t, J = 7.7 Hz, 3H), 7.36 (t, J = 7.6 Hz, 1H), 7.27 (t, J = 6.5 Hz, 2H), 4.40 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.1, 153.3, 136.1, 135.6, 132.0, 130.8, 126.1, 125.0, 122.9, 121.6, 121.4, 39.9. IR (KBr, cm^{-1}): 3918, 3660, 2916, 1701, 1487, 1240, 756. HRMS (ESI) (m/z): calcd for $C_{14}H_{11}BrNS$ $[M+H]^+$: 303.9790, found: 303.9798.



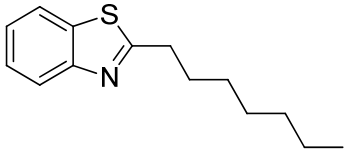
2-(4-Methoxybenzyl)benzo[*d*]thiazole (4e). Brown oil, yield 41 mg (81%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, J = 8.1 Hz, 1H), 7.77 (d, J = 7.8 Hz, 1H), 7.43 (t, J = 7.4 Hz, 1H), 7.30 (m, 3H), 6.88 (m, 2H), 4.37 (s, 2H), 3.79 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.1, 158.9, 153.3, 135.6, 130.3, 129.3, 126.0, 124.8, 122.7, 121.5, 114.3, 55.3, 39.8. IR (KBr, cm^{-1}): 3876, 3731, 2921, 1595, 1507, 1253, 760. HRMS (ESI) (m/z): calcd for $C_{13}H_{14}NOS$ $[M+H]^+$: 256.0791, found: 256.0788.



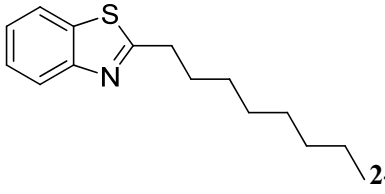
2-(Naphthalen-2-ylmethyl)benzo[*d*]thiazole (4f). Brown oil, yield 43 mg (79%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, J = 8.2 Hz, 1H), 7.81 (m, 4H), 7.76 (d, J = 8.0 Hz, 1H), 7.46 (m, 4H), 7.32 (t, J = 7.6 Hz, 1H), 4.60 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.2, 153.2, 135.7, 134.6, 133.6, 132.6, 128.7, 127.9, 127.8, 127.8, 127.2, 126.3, 126.0, 126.0, 124.9, 122.8, 121.6, 40.8. IR (KBr, cm^{-1}): 3877, 3734, 2920, 1511, 1278, 1097, 754. HRMS (ESI) (m/z): calcd for $C_{18}H_{14}NS$ $[M+H]^+$: 276.0841, found: 276.0838.



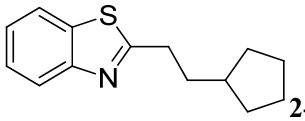
2-Hexylbenzo[*d*]thiazole (4g). Yellow oil, Yield 31 mg (70%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.04 (d, J = 7.9 Hz, 1H), 7.93 (d, J = 8.0 Hz, 1H), 7.48 (m, 1H), 7.39 (m, 1H), 3.09 (t, J = 7.5 Hz, 2H), 1.79 (dd, J = 15.0, 7.5 Hz, 2H), 1.38 (m, 2H), 1.29 (dd, J = 8.9, 5.4 Hz, 4H), 0.85 (d, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 172.2, 153.3, 135.1, 126.4, 125.2, 122.6, 122.5, 33.9, 31.4, 29.4, 28.6, 22.4, 14.3. IR (KBr, cm^{-1}): 3879, 3732, 2926, 2857, 1520, 1443, 758. HRMS (ESI) (m/z): calcd for $C_{13}H_{18}NS$ $[M+H]^+$: 220.1154, found: 220.1159.



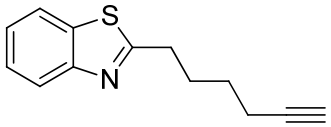
2-Heptylbenzo[*d*]thiazole (4h). Yellow oil, yield 32 mg (68%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.04 (d, J = 7.9 Hz, 1H), 7.93 (d, J = 8.0 Hz, 1H), 7.48 (m, 1H), 7.40 (dd, J = 11.2, 4.0 Hz, 1H), 3.09 (t, J = 7.5 Hz, 2H), 1.79 (dd, J = 14.8, 7.4 Hz, 2H), 1.29 (m, 8H), 0.85 (t, J = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 172.2, 168.5, 153.3, 135.1, 126.4, 125.2, 122.6, 122.5, 33.9, 31.56, 29.4, 28.9, 28.8, 22.5, 14.4. IR (KBr, cm^{-1}): 3877, 3735, 2925, 2856, 1520, 1438, 758. HRMS (ESI) (m/z): calcd for $C_{14}H_{20}NS$ $[M+H]^+$: 234.1311, found: 234.1312.



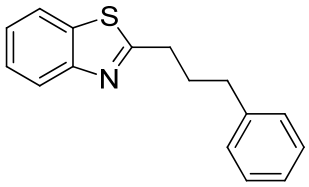
2-Octylbenzo[*d*]thiazole (4i). Yellow oil, yield 35 mg (71%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.03 (dd, J = 7.9, 0.6 Hz, 1H), 7.93 (d, J = 7.7 Hz, 1H), 7.48 (m, 1H), 7.39 (m, 1H), 3.08 (t, J = 7.5 Hz, 2H), 1.79 (m, 2H), 1.30 (m, 10H), 0.84 (t, J = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 172.2, 153.3, 135.1, 126.4, 125.2, 122.6, 122.4, 33.9, 31.7, 29.4, 29.1, 29.0, 28.9, 22.5, 14.4. IR (KBr, cm^{-1}): 3877, 3732, 2924, 2854, 1521, 1449, 759. HRMS (ESI) (m/z): calcd for $C_{15}H_{22}NS$ $[M+H]^+$: 248.1467, found: 248.1472.



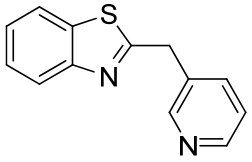
2-(2-Cyclopentylethyl)benzo[*d*]thiazole (4j). Yellow oil, yield 29 mg (63%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.03 (d, J = 7.5 Hz, 1H), 7.93 (d, J = 8.0 Hz, 1H), 7.47 (dd, J = 11.2, 4.1 Hz, 1H), 7.41-7.37 (m, 1H), 3.13-3.08 (m, 2H), 1.76-1.65 (m, 6H), 1.34-1.29 (m, 1H), 1.18-1.14 (m, 2H), 0.93 (dd, J = 21.8, 10.1 Hz, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 172.5, 153.3, 135.1, 126.4, 125.2, 122.6, 122.5, 37.0, 33.0, 31.4, 26.5, 26.2. IR (KBr, cm^{-1}): 3880, 3732, 2921, 2849, 1519, 1443, 758. HRMS (ESI) (m/z): calcd for $C_{14}H_{18}NS$ $[M+H]^+$: 232.1154, found: 232.1150.



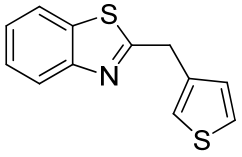
2-(Hex-5-yn-1-yl)benzo[*d*]thiazole (4k). Yellow oil, Yield 27 mg (62%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.04 (d, J = 7.6 Hz, 1H), 7.94 (d, J = 8.0 Hz, 1H), 7.48 (m, 1H), 7.40 (m, 1H), 3.13 (t, J = 7.6 Hz, 2H), 2.76 (t, J = 2.6 Hz, 1H), 2.24 (td, J = 7.1, 2.6 Hz, 2H), 1.91 (dt, J = 20.8, 7.6 Hz, 2H), 1.58 (dt, J = 14.5, 7.1 Hz, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 171.9, 153.3, 135.1, 126.4, 125.2, 122.6, 122.5, 84.6, 71.8, 33.3, 28.4, 27.8, 17.9. IR (KBr, cm^{-1}): 3877, 3734, 3296, 2926, 1519, 1436, 759, 634. HRMS (ESI) (m/z): calcd for $C_{13}H_{14}NS$ $[M+H]^+$: 216.0841, found: 216.0846.



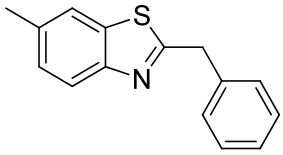
2-(3-Phenylpropyl)benzo[*d*]thiazole (4l). Brown oil, yield 38 mg (76%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.05 (d, J = 7.9 Hz, 1H), 7.94 (d, J = 8.0 Hz, 1H), 7.48 (d, J = 7.0 Hz, 1H), 7.40 (t, J = 7.1 Hz, 1H), 7.29 (d, J = 7.4 Hz, 2H), 7.21 (m, 3H), 3.11 (t, J = 7.6 Hz, 2H), 2.71 (m, 2H), 2.11 (dd, J = 12.6, 4.9 Hz, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 171.8, 153.3, 141.8, 135.1, 128.8, 128.8, 126.5, 126.4, 125.3, 122.6, 122.5, 34.8, 33.3, 31.1. IR (KBr, cm^{-1}): 3878, 3732, 2919, 1702, 1517, 1434, 752, 696. HRMS (ESI) (m/z): calcd for $C_{16}H_{16}NS$ $[M+H]^+$: 254.0998, found: 254.1002.



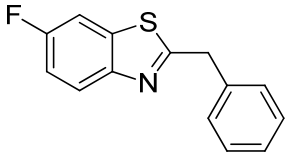
2-(Pyridin-3-ylmethyl)benzo[*d*]thiazole (4m). Yellow oil, yield 30 mg (67%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.65 (d, J = 1.7 Hz, 1H), 8.54 (dd, J = 4.7, 1.1 Hz, 1H), 7.99 (d, J = 8.1 Hz, 1H), 7.80 (d, J = 8.0 Hz, 1H), 7.69 (d, J = 7.9 Hz, 1H), 7.46 (m, 1H), 7.35 (m, 1H), 7.26 (m, 1H), 4.43 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.2, 153.3, 150.1, 148.7, 136.6, 135.5, 132.8, 126.2, 125.1, 123.7, 122.9, 121.6, 37.6. IR (KBr, cm^{-1}): 3054, 2920, 2852, 1423, 1101, 714. HRMS (ESI) (m/z): calcd for $C_{13}H_{11}N_2S$ $[M+H]^+$: 227.0637, found: 227.0639.



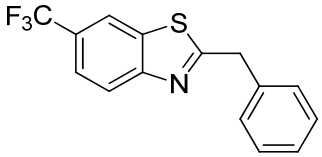
2-(Thiophen-3-ylmethyl)benzo[*d*]thiazole (4n). Brown oil, yield 30 mg (64%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, J = 8.2 Hz, 1H), 7.78 (d, J = 7.9 Hz, 1H), 7.43 (m, 1H), 7.31 (m, 2H), 7.21 (d, J = 2.0 Hz, 1H), 7.07 (d, J = 4.9 Hz, 1H), 4.45 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.7, 153.3, 137.0, 135.6, 128.4, 126.4, 126.0, 124.9, 123.1, 122.8, 121.6, 35.1. IR (KBr, cm^{-1}): 3069, 2915, 1511, 1427, 1096, 755. HRMS (ESI) (m/z): calcd for $C_{12}H_{10}NS_2$ $[M+H]^+$: 232.0249, found: 232.0251.



2-Benzyl-6-methylbenzo[*d*]thiazole (4o). Brown oil, yield 41 mg (86%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, J = 8.3 Hz, 1H), 7.56 (s, 1H), 7.34 (d, J = 6.5 Hz, 4H), 7.29 (dd, J = 5.8, 2.8 Hz, 1H), 7.24 (d, J = 2.8 Hz, 1H), 4.41 (s, 2H), 2.44 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.1, 151.2, 137.3, 135.8, 135.0, 129.2, 128.9, 127.6, 127.3, 122.2, 121.3, 40.5, 21.5. IR (KBr, cm^{-1}): 3875, 3731, 2918, 1594, 1511, 1450, 812, 697. HRMS (ESI) (m/z): calcd for $C_{15}H_{14}NS$ $[M+H]^+$: 240.0841, found: 240.0847.

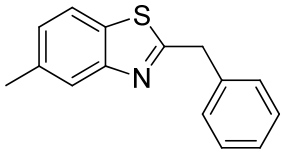


2-Benzyl-6-fluorobenzo[*d*]thiazole (4p). Brown solid, yield 40 mg (82%), mp 57-58 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (dd, J = 8.9, 4.8 Hz, 1H), 7.41 (dd, J = 8.1, 2.6 Hz, 1H), 7.33 (d, J = 4.5 Hz, 4H), 7.27 (m, 1H), 7.14 (dt, J = 8.9, 4.5 Hz, 1H), 4.38 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.9 (d, J = 3.2 Hz), 160.3 (d, J = 245.1 Hz), 149.9, 137.0, 136.6 (d, J = 11.1 Hz), 129.2, 129.0, 127.5, 123.7 (d, J = 9.4 Hz), 114.6 (d, J = 24.7 Hz), 107.8 (d, J = 26.6 Hz), 40.6. IR (KBr, cm^{-1}): 3880, 3731, 2919, 1602, 1520, 1454, 1250, 817, 701. HRMS (ESI) (m/z): calcd for $C_{14}H_{11}FNS$ $[M+H]^+$: 244.0591, found: 244.0596.

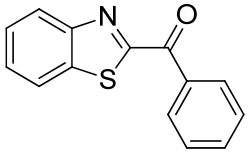


2-Benzyl-6-(trifluoromethyl)benzo[*d*]thiazole (4q). Brown oil, yield 46 mg (78%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, J = 7.7 Hz, 2H), 7.68 (dd, J = 8.7, 1.2

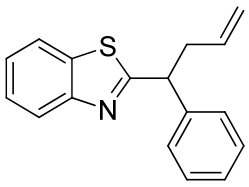
Hz, 1H), 7.33 (m, 5H), 4.45 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.7, 155.3, 136.6, 135.8, 129.2, 129.0, 127.6, 127.1 (q, J = 33.0 Hz), 124.2 (q, J = 273.0 Hz), 123.2, 123.0 (q, J = 3.5 Hz), 119.2 (q, J = 4.3 Hz), 40.8. IR (KBr, cm^{-1}): 3031, 2923, 1511, 1320, 1123, 649. HRMS (ESI) (m/z): calcd for $C_{15}H_{11}F_3NS$ $[M+H]^+$: 294.0559, found: 294.0562.



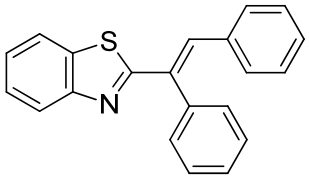
2-Benzyl-5-methylbenzo[*d*]thiazole (4r). Yellow solid, yield 41 mg (86%), mp 80-81 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (s, 1H), 7.61 (s, 1H), 7.31 (m, 5H), 7.14 (d, J = 7.7 Hz, 1H), 4.40 (s, 2H), 2.47 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.3, 153.7, 137.3, 136.1, 132.7, 129.2, 128.9, 127.3, 126.4, 122.9, 121.0, 40.7, 21.5. IR (KBr, cm^{-1}): 3880, 3736, 2919, 2856, 1506, 1451, 802, 700. HRMS (ESI) (m/z): calcd for $C_{15}H_{14}NS$ $[M+H]^+$: 240.0841, found: 240.0845.



Benzo[*d*]thiazol-2-yl(phenyl)methanone (5).[1] White solid, yield 47 mg (99%), mp 73-74 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 (d, J = 8.0 Hz, 2H), 8.24 (d, J = 8.0 Hz, 1H), 7.99 (d, J = 7.9 Hz, 1H), 7.67 (t, J = 7.3 Hz, 1H), 7.54 (dt, J = 16.1, 7.3 Hz, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 185.2, 167.2, 153.9, 137.0, 135.0, 133.9, 131.3, 128.5, 127.6, 126.9, 125.7, 122.2. IR (KBr, cm^{-1}): 3061, 2922, 1633, 1481, 1282, 1118, 884, 708. HRMS (ESI) (m/z): calcd for $C_{14}H_9NNaOS$ $[M+Na]^+$: 262.0297, found: 262.0293.

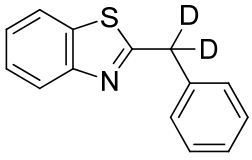


2-(1-Phenylbut-3-en-1-yl)benzo[*d*]thiazole (6). Yellow oil, yield 50 mg (95%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, J = 8.2 Hz, 1H), 7.75 (d, J = 8.0 Hz, 1H), 7.41 (m, 3H), 7.28 (m, 4H), 5.78 (ddt, J = 17.0, 10.2, 6.8 Hz, 1H), 5.10 (d, J = 17.1 Hz, 1H), 4.98 (d, J = 10.2 Hz, 1H), 4.47 (t, J = 7.8 Hz, 1H), 3.19 (dt, J = 14.3, 7.1 Hz, 1H), 2.94 (dt, J = 14.6, 7.5 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.5, 153.2, 141.2, 135.4, 135.3, 128.8, 128.2, 127.4, 125.9, 124.8, 123.0, 121.5, 117.4, 50.8, 39.8. IR (KBr, cm^{-1}): 3067, 2921, 1504, 1439, 916, 756, 705. HRMS (ESI) (m/z): calcd for $C_{17}H_{16}NS$ $[M+H]^+$: 266.0998, found: 266.0999.



(*E*)-2-(1,2-Diphenylvinyl)benzo[*d*]thiazole (7).[2] Yellow solid, yield 53 mg (84%), mp 54-55 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, J = 8.2 Hz, 1H), 7.97 (s, 1H), 7.76 (d, J = 8.0 Hz, 1H), 7.47-7.43 (m, 4H), 7.40 (dt, J = 5.0, 2.9 Hz, 2H), 7.31 (t, J = 7.6 Hz, 1H), 7.18-7.14 (m, 3H), 7.11 (dt, J = 7.9, 3.9 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.5, 154.0, 138.2, 135.8, 135.4, 134.9, 132.9, 130.4, 130.2, 129.2, 128.7, 128.4, 128.2, 126.3, 124.8, 123.1,

121.4. IR (KBr, cm^{-1}): 3058, 2922, 1604, 1488, 1437, 1114, 757, 700. HRMS (ESI) (m/z): calcd for $C_{21}H_{16}NS$ $[M+H]^+$: 314.0998, found: 314.1004.



[D_2]-2-benzylbenzo[*d*]thiazole (d_2-4a). Brown oil, yield 39 mg (87%). ^1H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, J = 8.2 Hz, 1H), 7.79 (d, J = 8.0 Hz, 1H), 7.46 (dd, J = 11.3, 4.0 Hz, 1H), 7.38 (m, 5H), 7.31 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.1, 153.3, 137.2, 135.7, 129.2, 128.9, 127.4, 126.0, 124.8, 122.8, 121.6, 29.8. IR (KBr, cm^{-1}): 3843, 3749, 2924, 1504, 1437, 697. HRMS (ESI) (m/z): calcd for $C_{14}H_{10}D_2NS$ $[M+H]^+$: 228.0811, found: 228.0812.

G. References

1. H. Sterckx, J. De Houwer, C. Mensch, I. Caretti, K. A. Tehrani, W. A. Herrebout, S. Van Doorslaer, B. U. W. Maes, *Chem. Sci.*, 2016, **7**, 346.
2. (a) G. Kaupp , D. Lübben, O. Sauerland, *Phosphorus, Sulfur, and Silicon*, 1990, **53**, 109-120. (b) G. Kaupp, *Chem. Ber.*, 1984, **117**, 1643.

H. X-ray Diffraction Parameters and Data for 4d

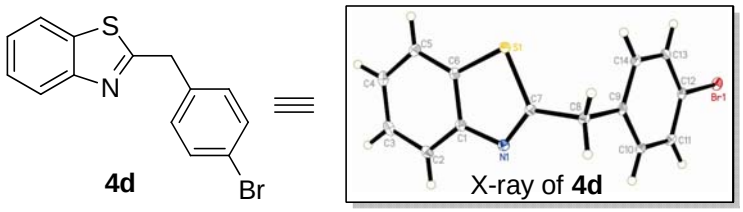


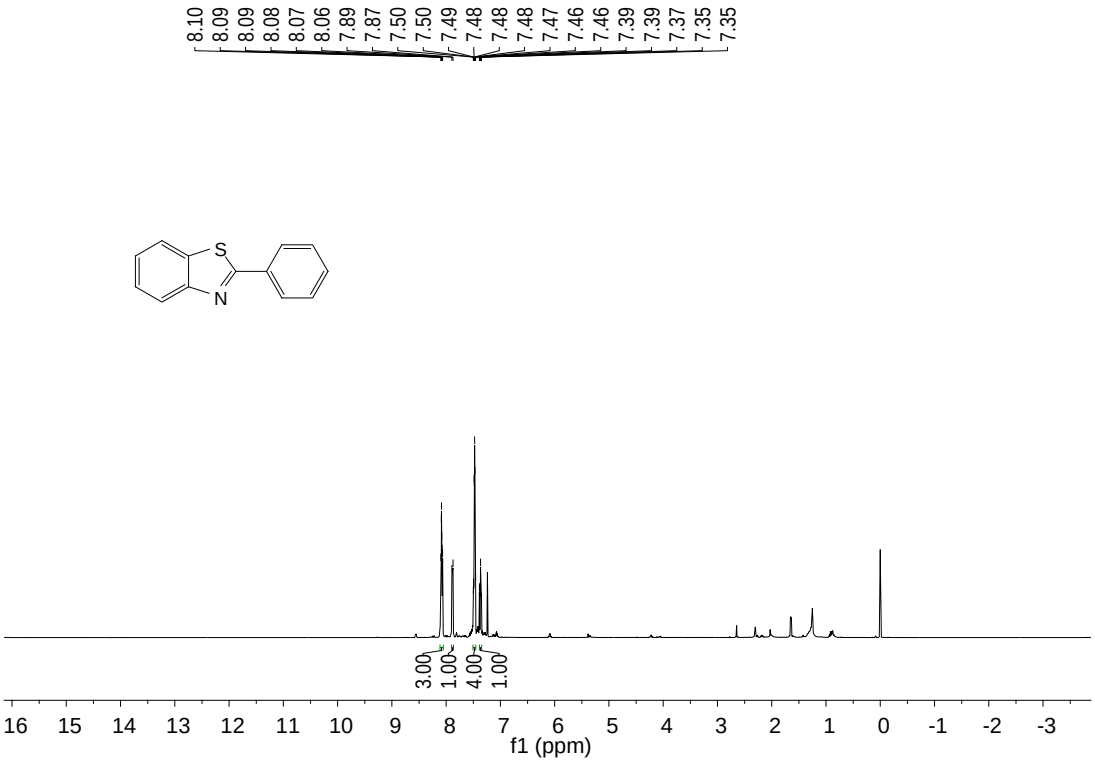
Table S2 Crystal data and structure refinement for 4d.

Identification code	4d
Empirical formula	$C_{14}H_{10}BrNS$
Formula weight	304.20
Temperature/K	100.00(10)
Crystal system	triclinic
Space group	P-1
a/Å	6.6340(3)
b/Å	9.3287(3)
c/Å	9.7895(2)
α/°	82.039(2)

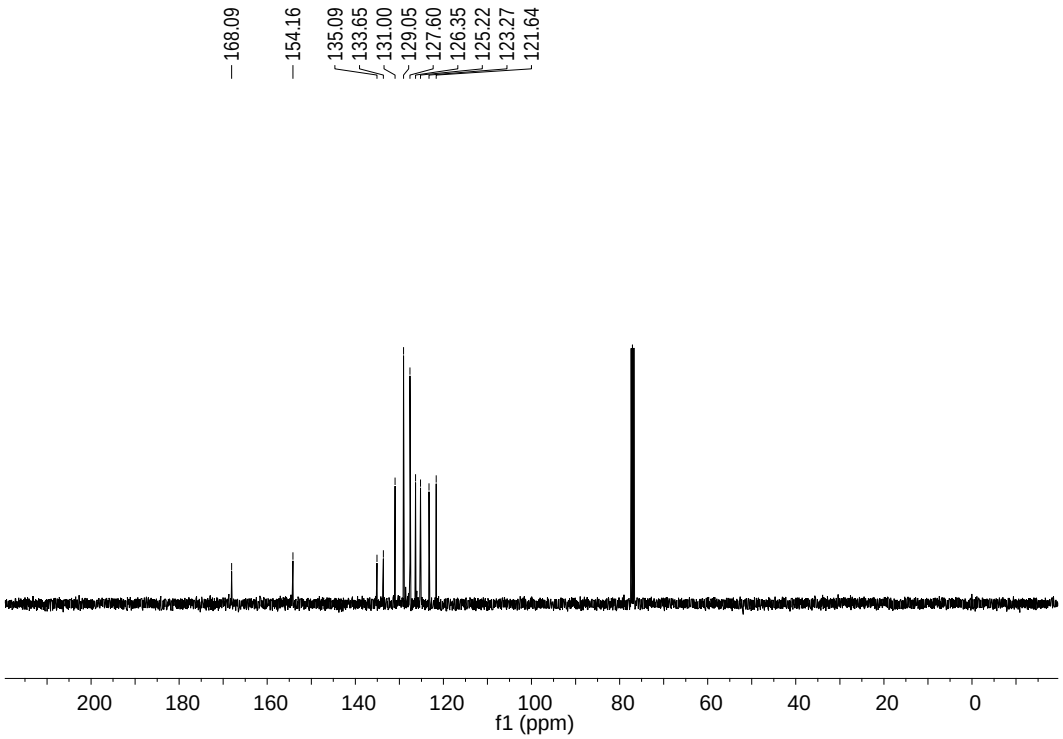
β/°	85.191(3)
γ/°	89.175(3)
Volume/Å^3	597.89(4)
Z	2
ρ_{calc}g/cm^3	1.690
μ/mm^{-1}	6.091
F(000)	304.0
Crystal size/mm^3	0.14 × 0.12 × 0.1
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	9.152 to 146.952
Index ranges	$-7 \leq h \leq 8$, $-11 \leq k \leq 11$, $-12 \leq l \leq 11$
Reflections collected	9253
Independent reflections	2350 [R_{int} = 0.0315, R_{sigma} = 0.0222]
Data/restraints/parameters	2350/0/154
Goodness-of-fit on F^2	1.053
Final R indexes [I>=2σ (I)]	R_1 = 0.0271, wR_2 = 0.0778
Final R indexes [all data]	R_1 = 0.0274, wR_2 = 0.0780
Largest diff. peak/hole / e Å^{-3}	0.61/-0.54

I. NMR Spectra

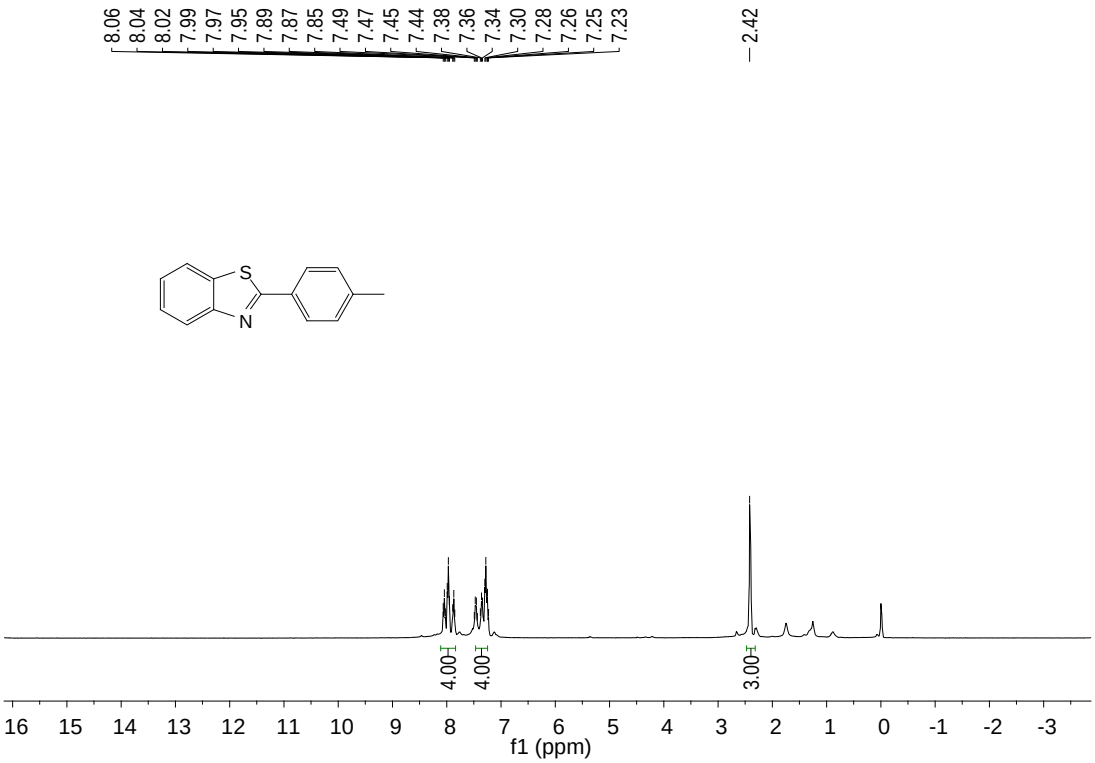
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 3a



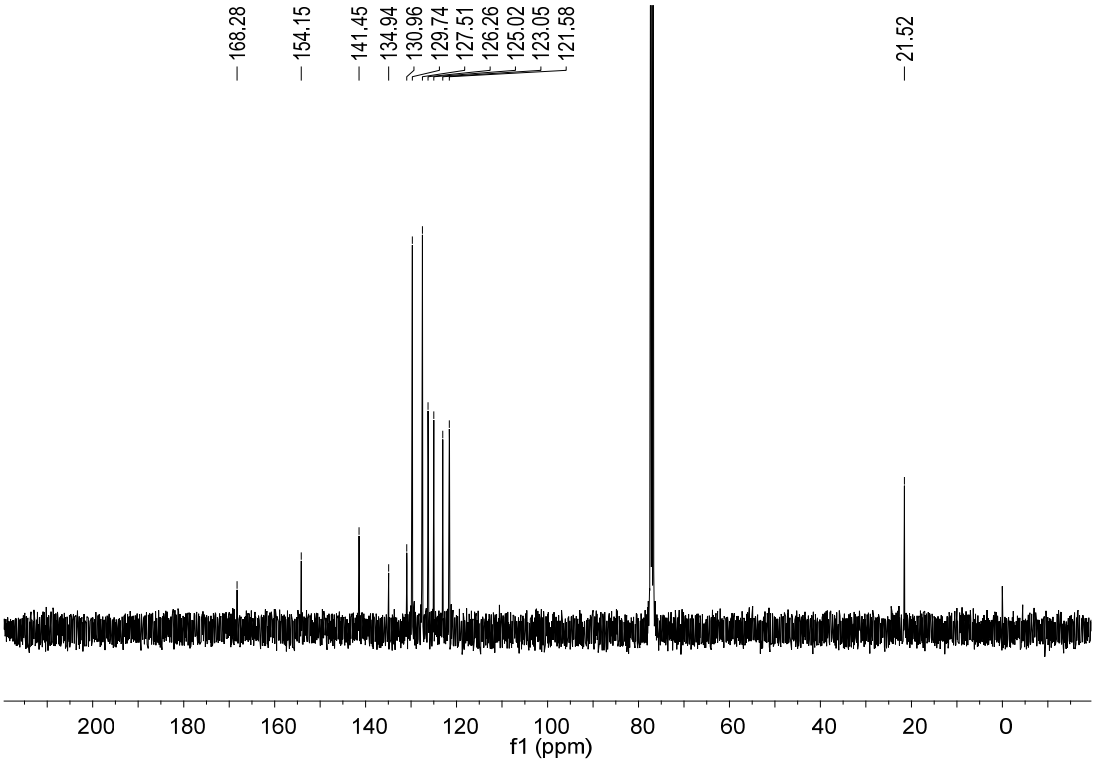
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound 3a



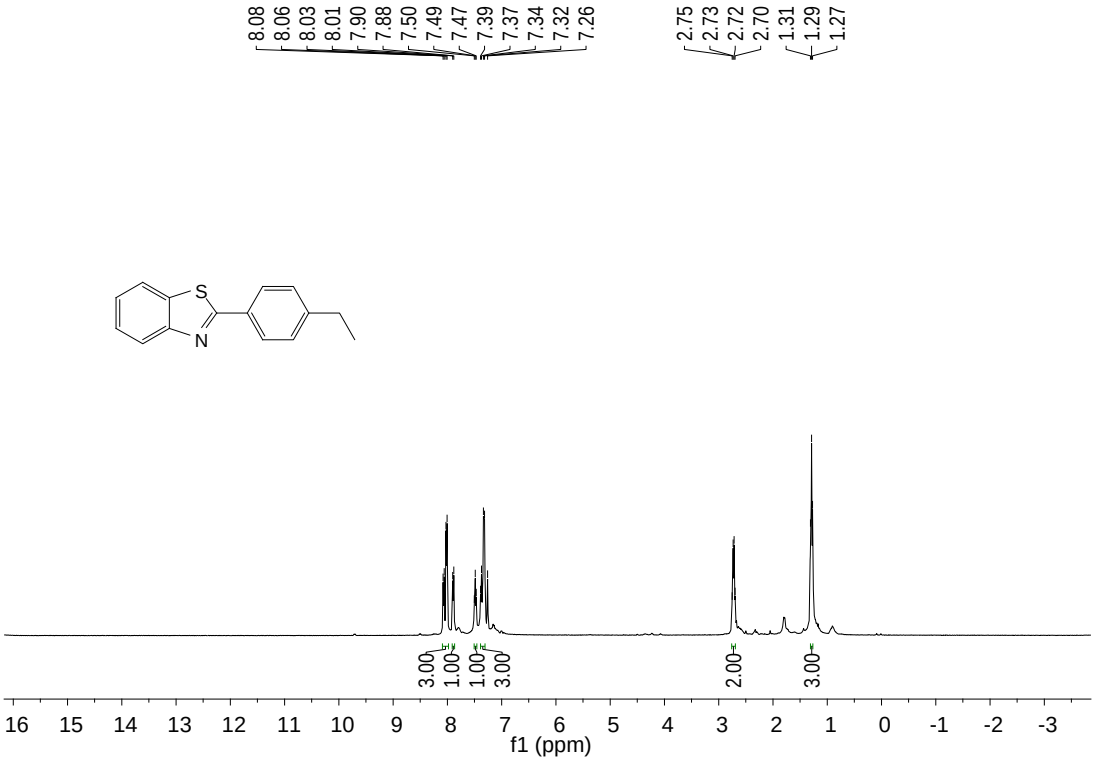
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 3b



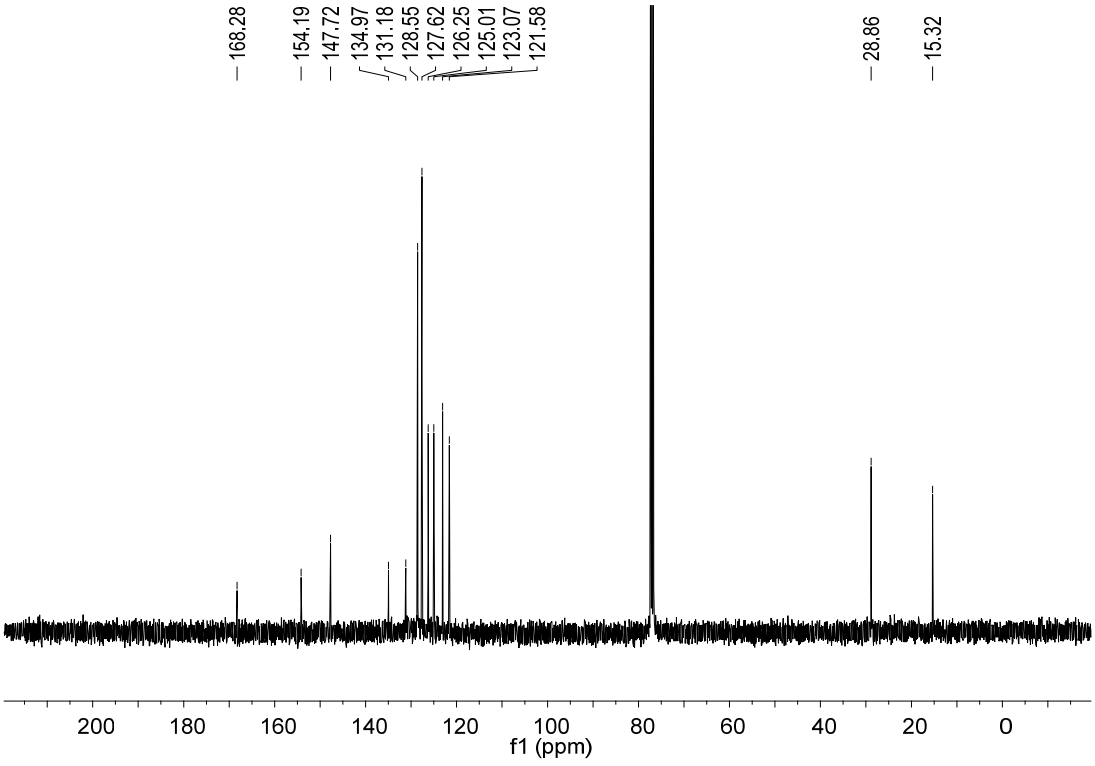
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound 3b



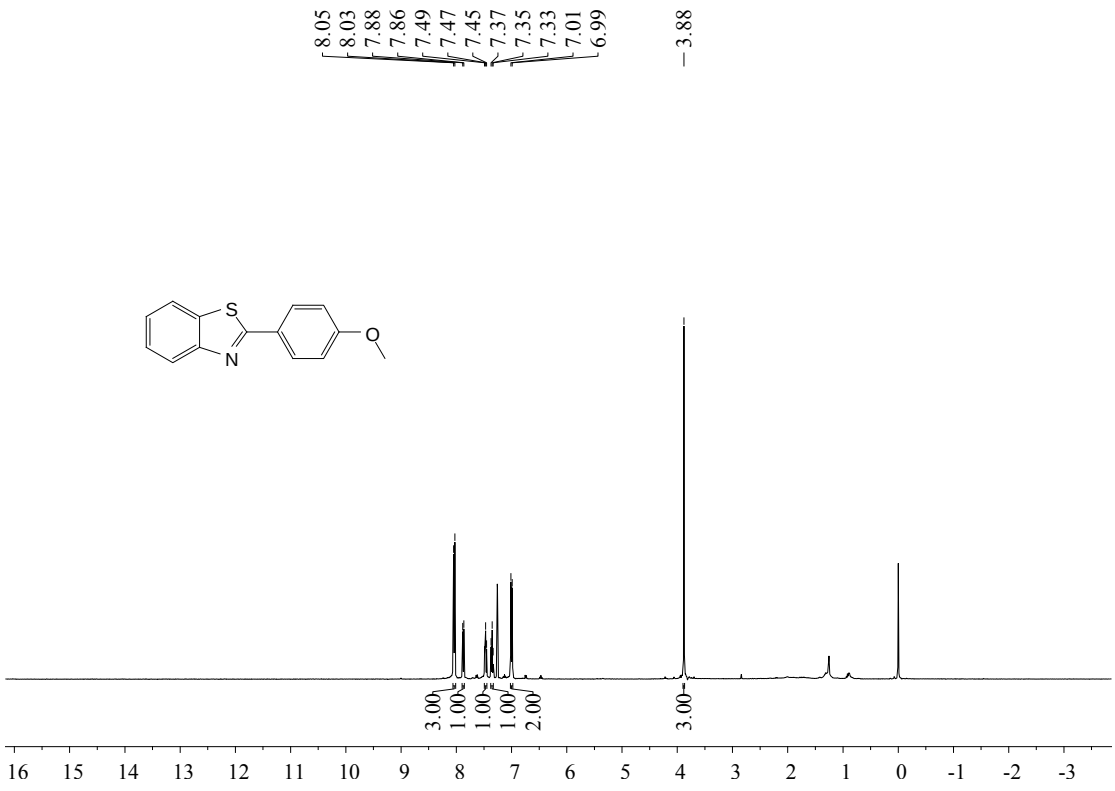
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 3c



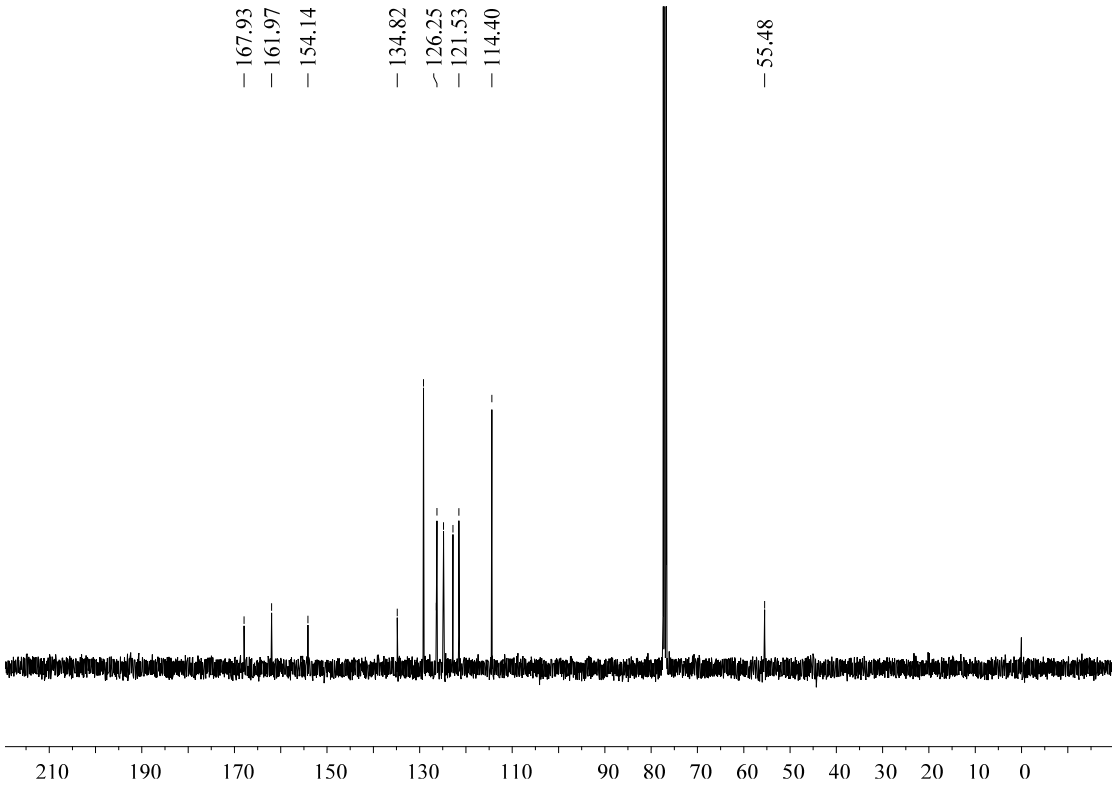
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound 3c



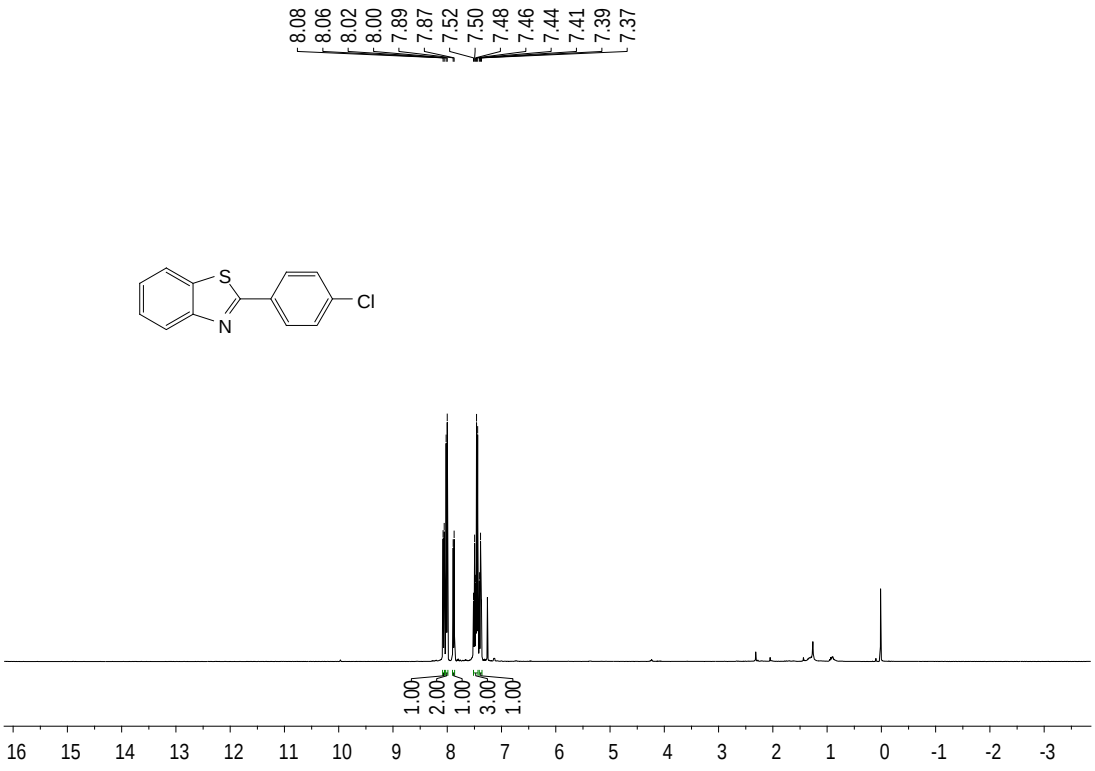
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 3d



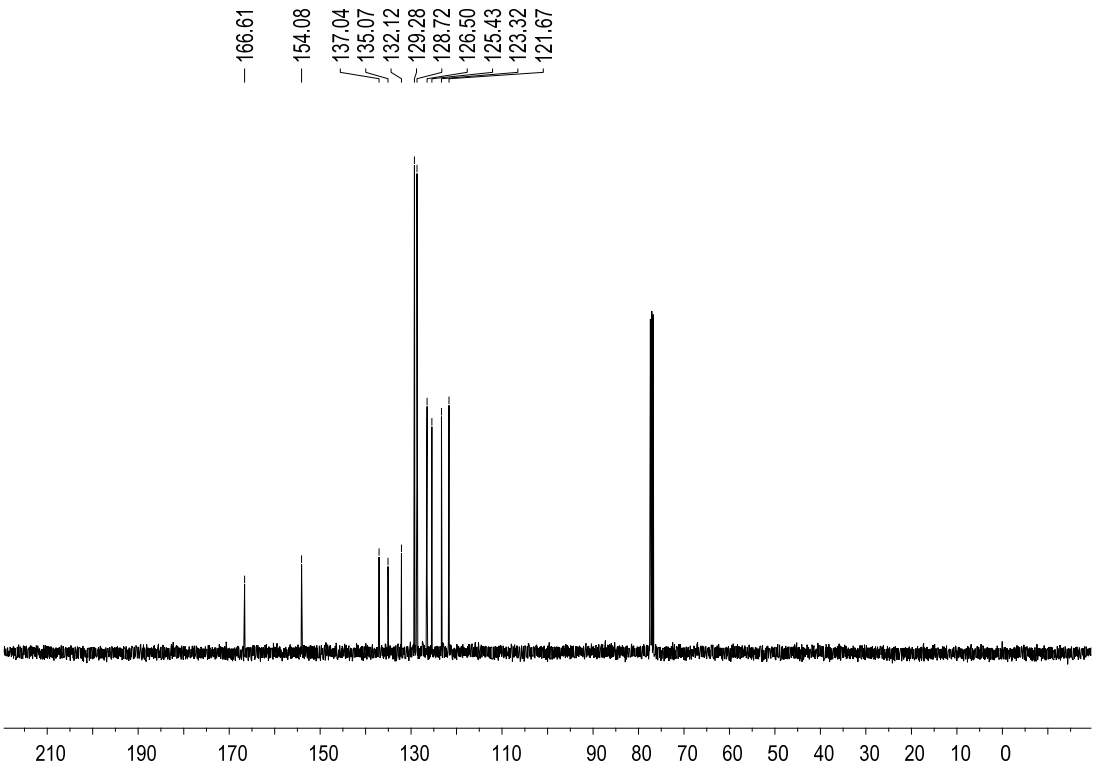
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound 3d



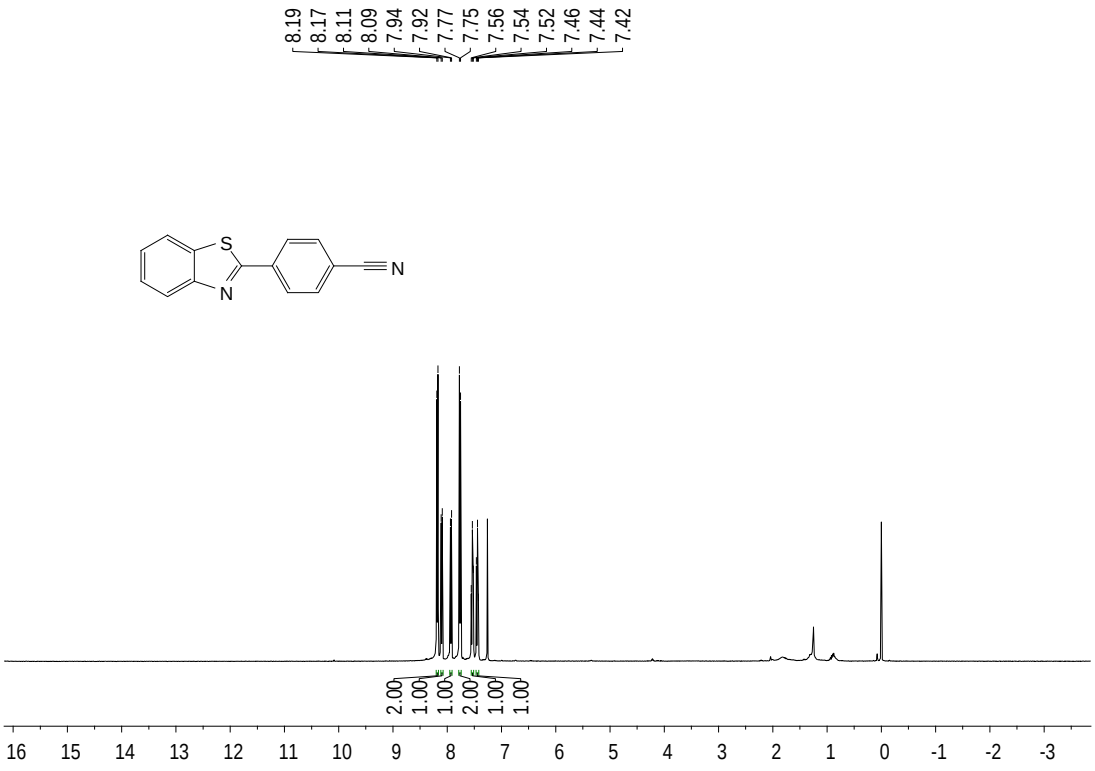
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 3e



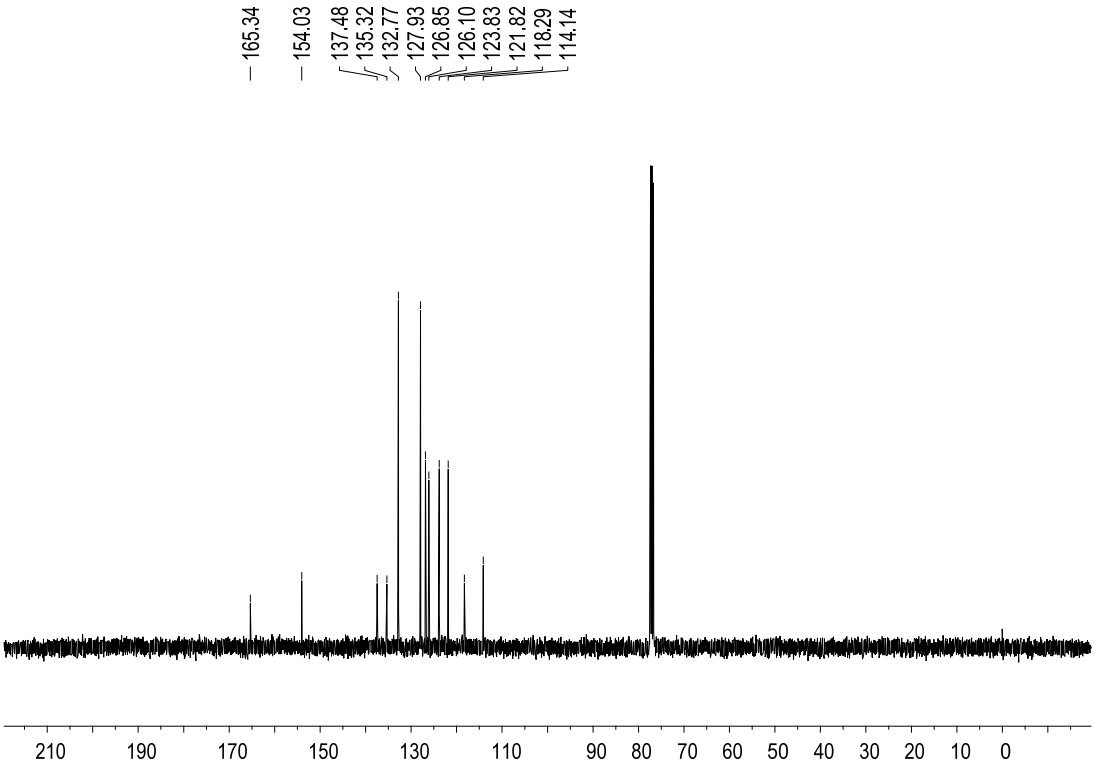
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound 3e



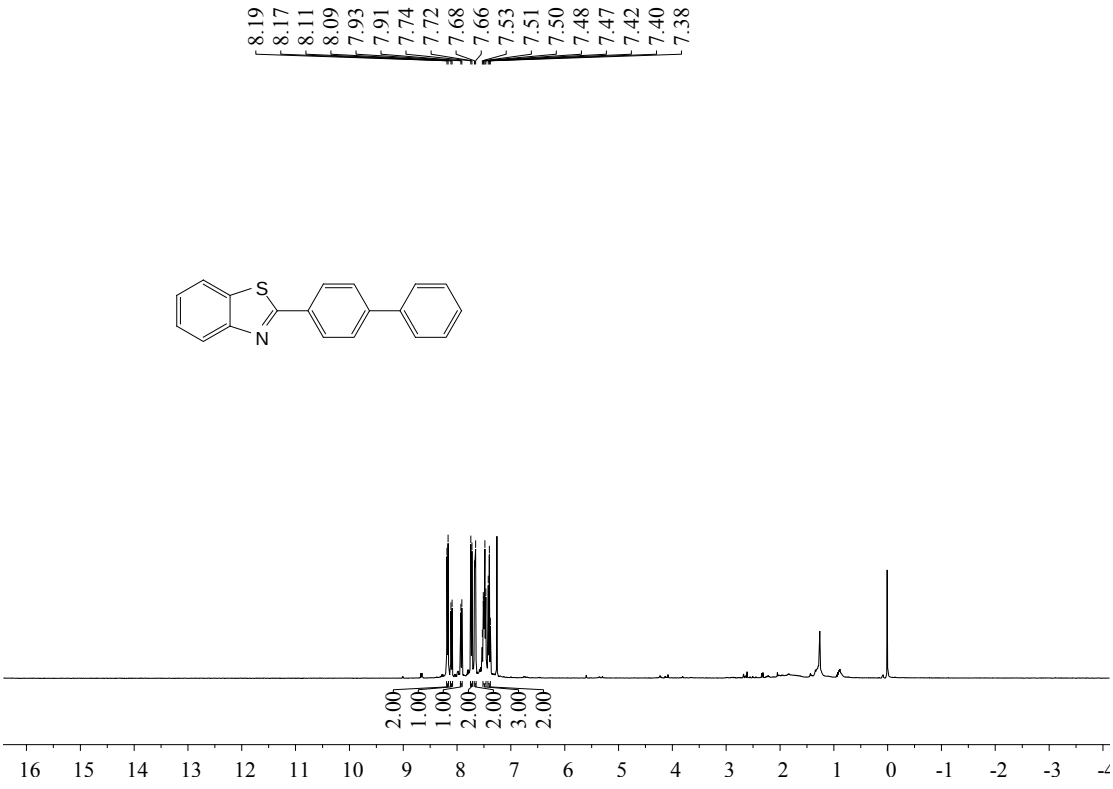
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 3f



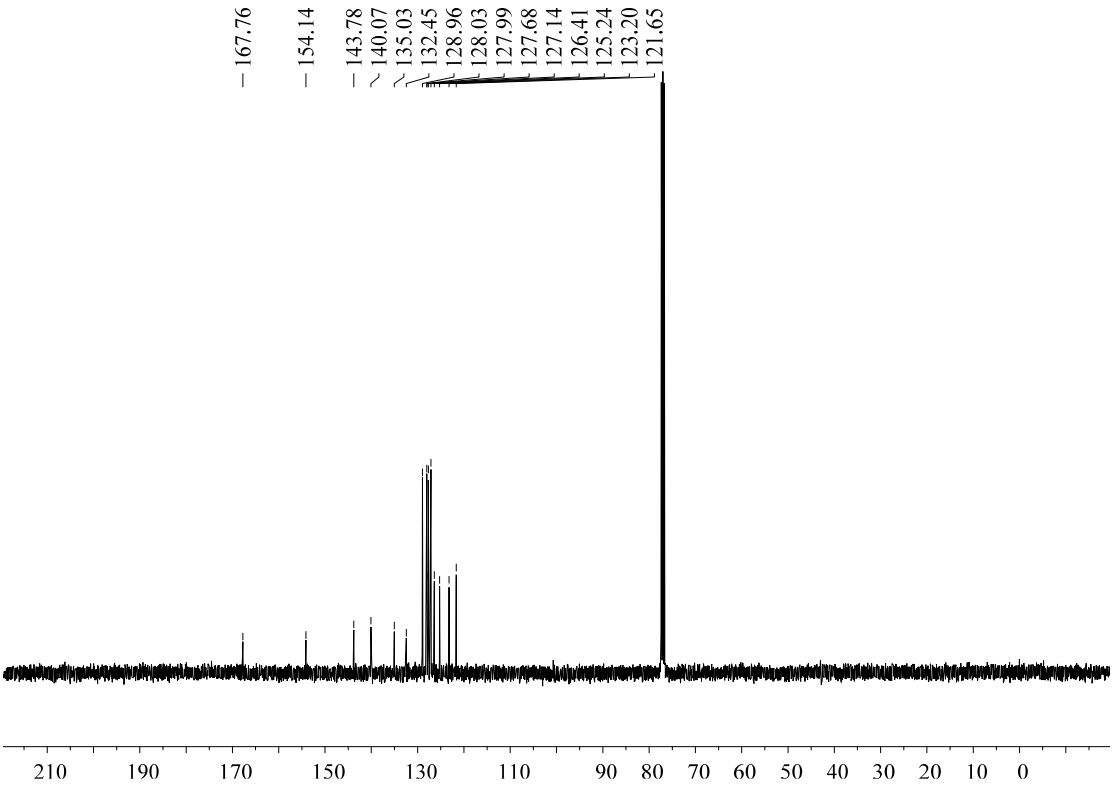
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound 3f



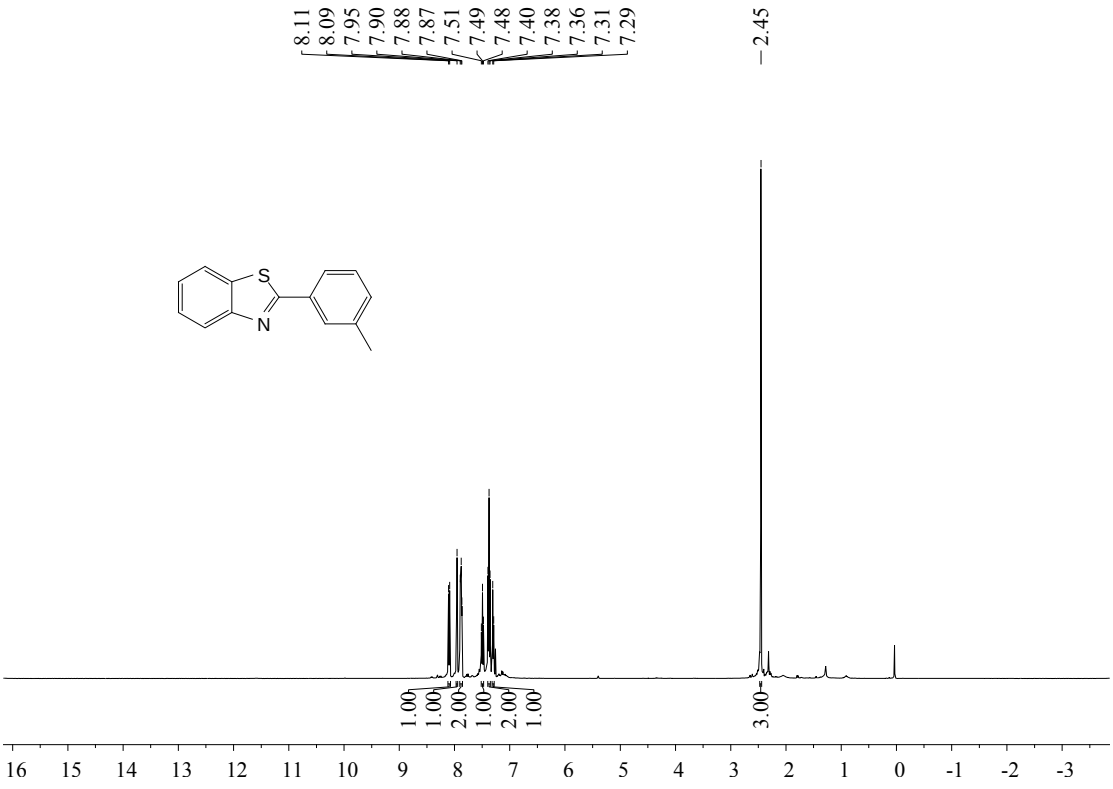
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 3g



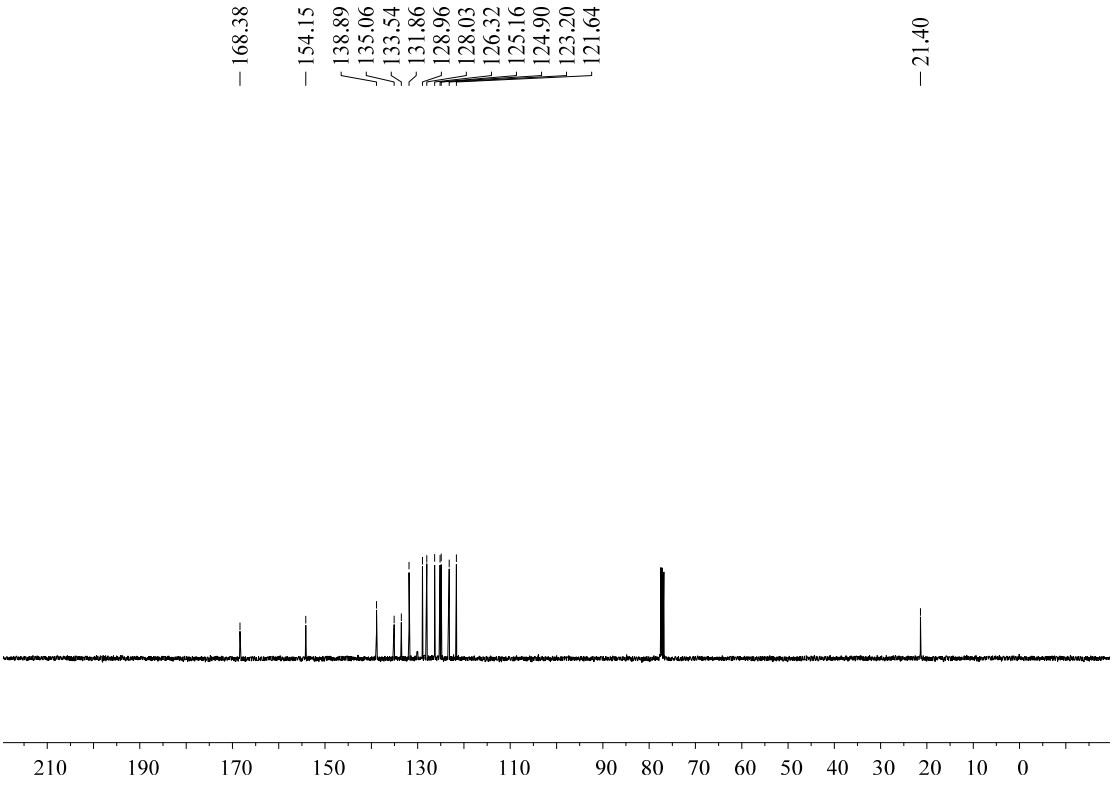
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound 3g



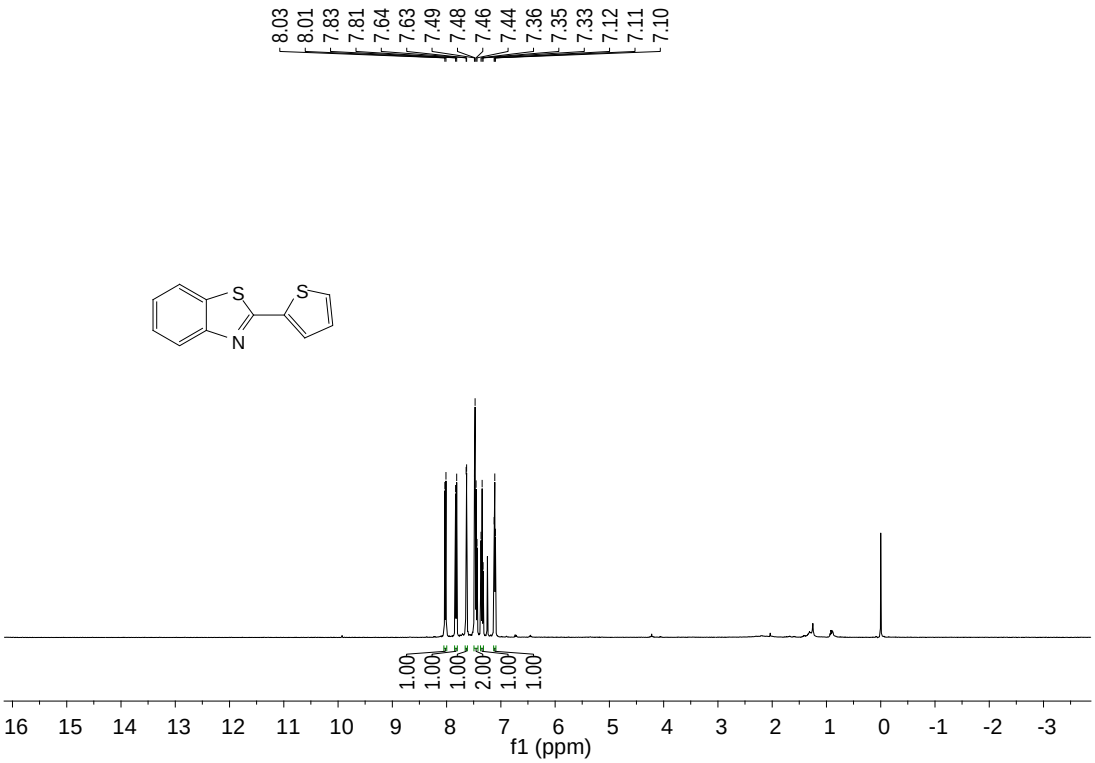
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 3h



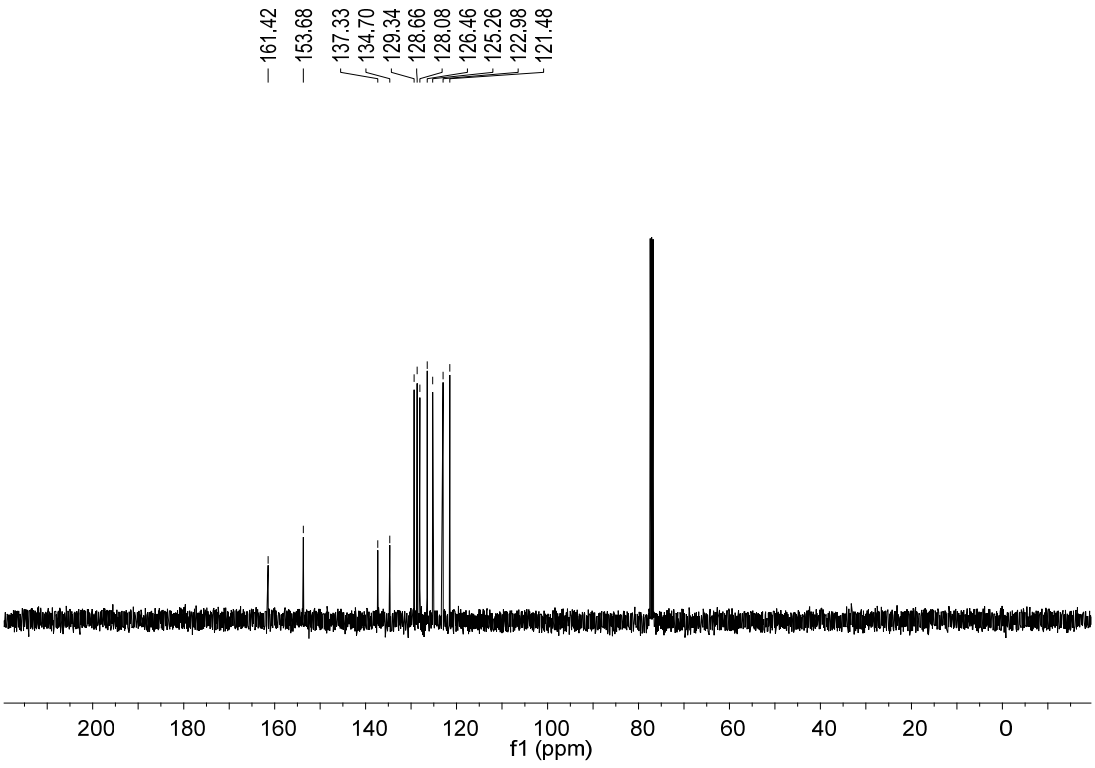
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound 3h



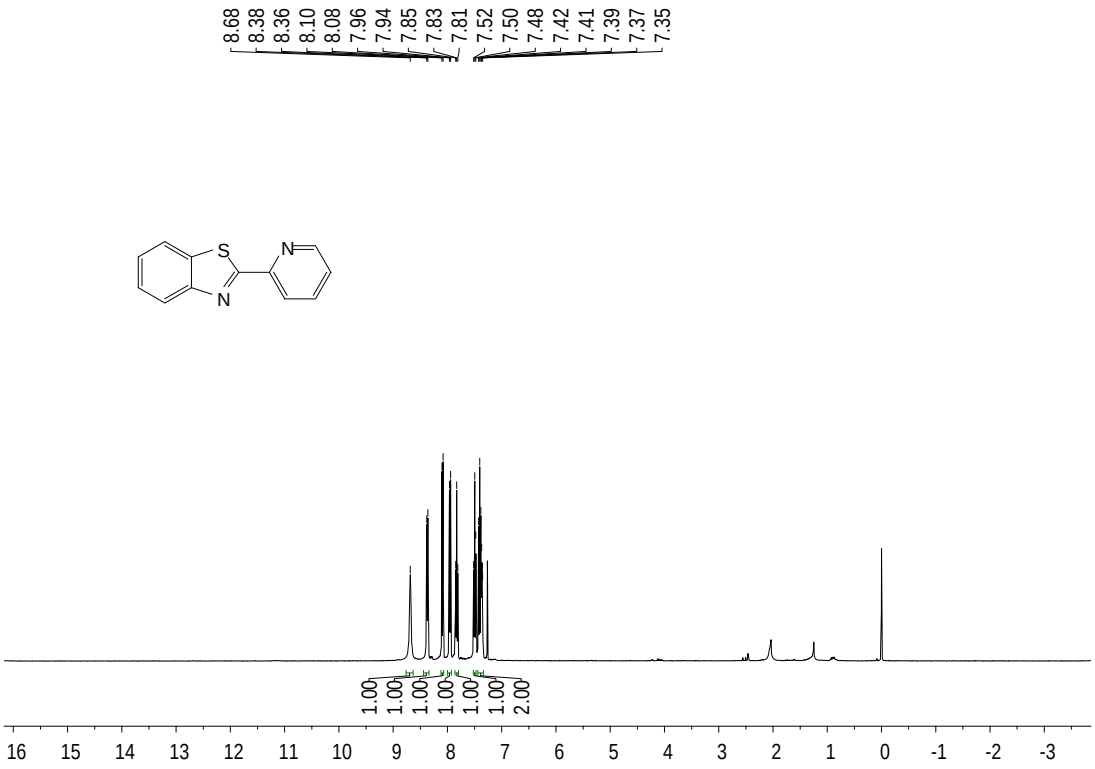
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 3i



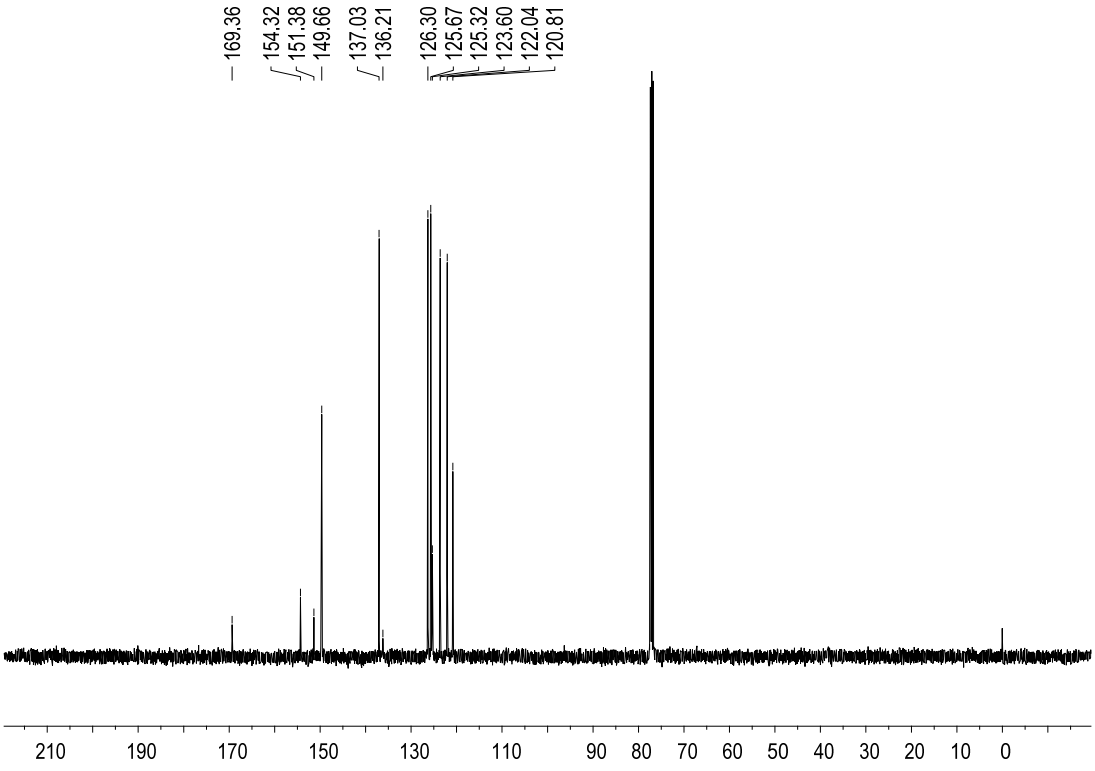
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound 3i



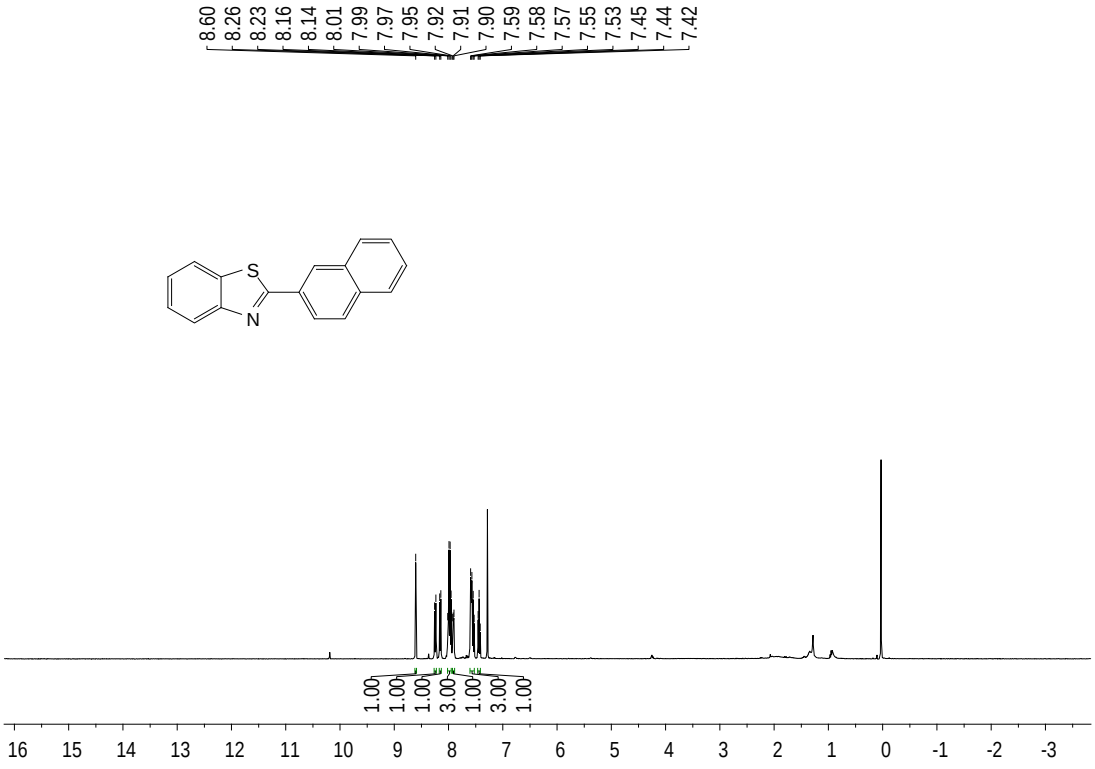
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 3j



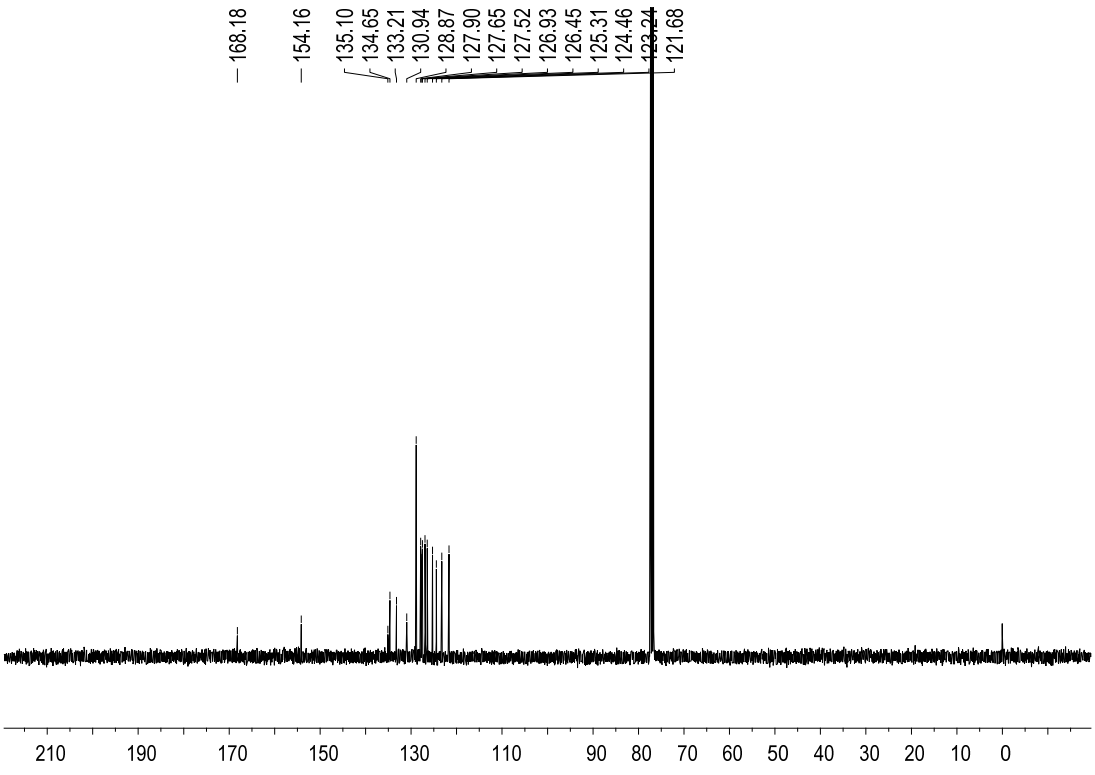
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound 3j



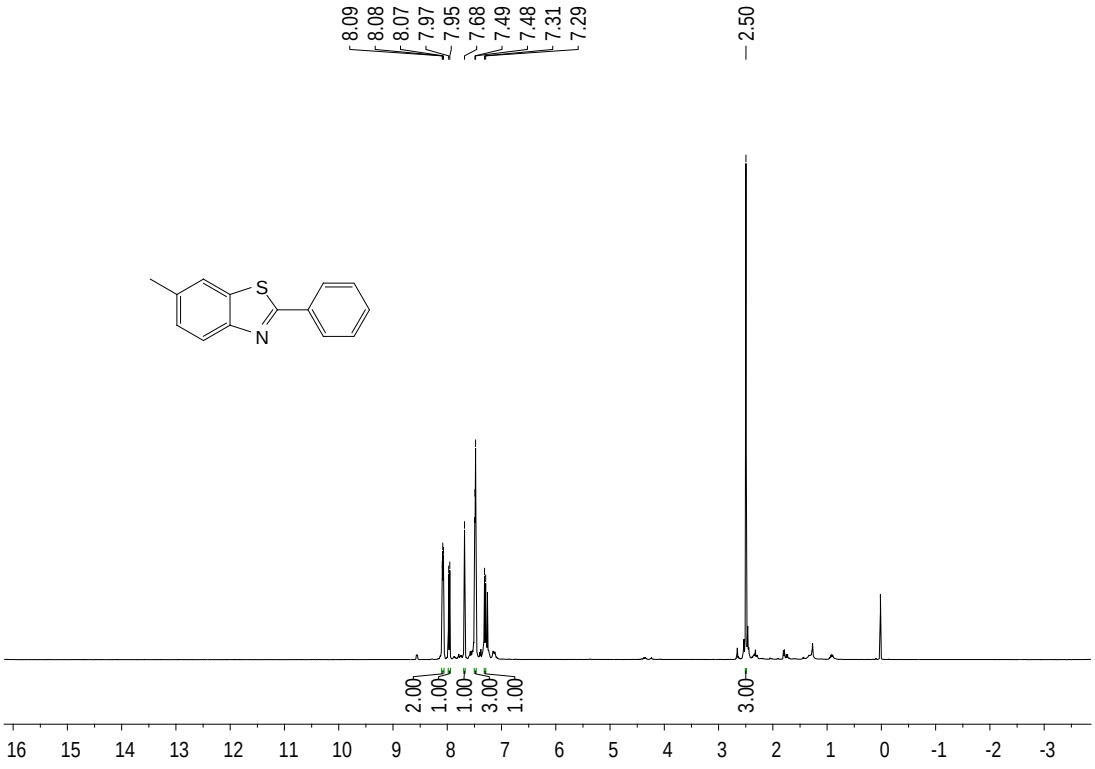
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 3k



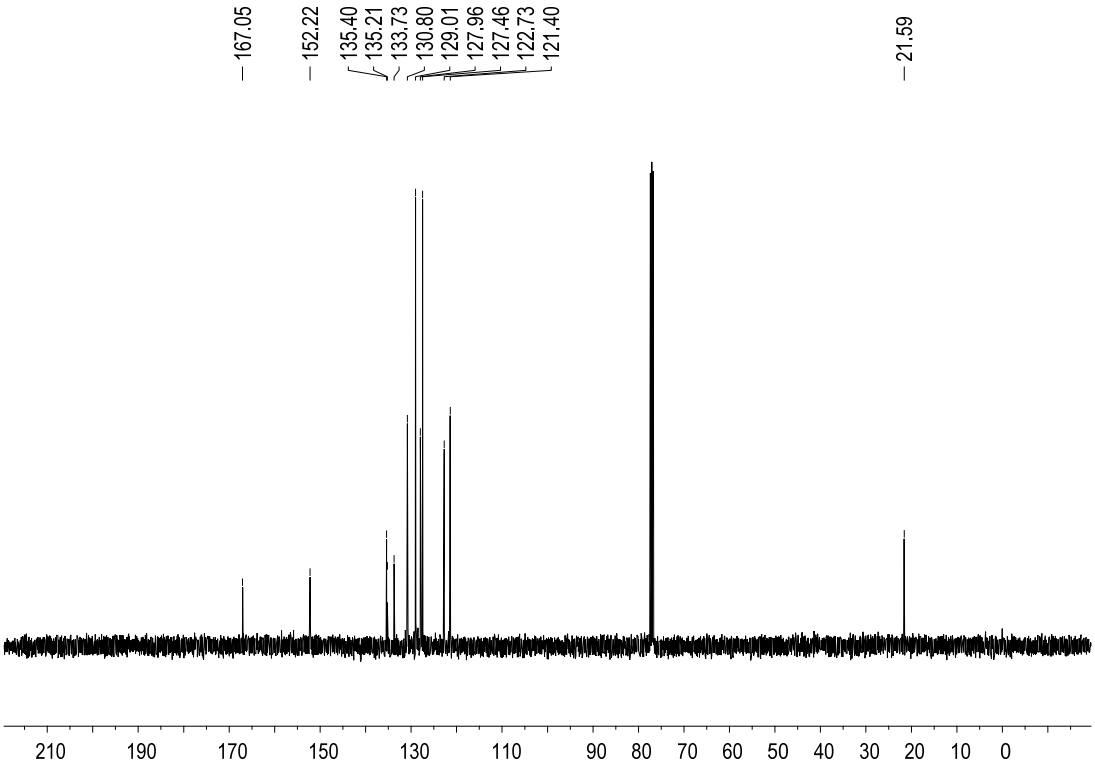
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound 3k



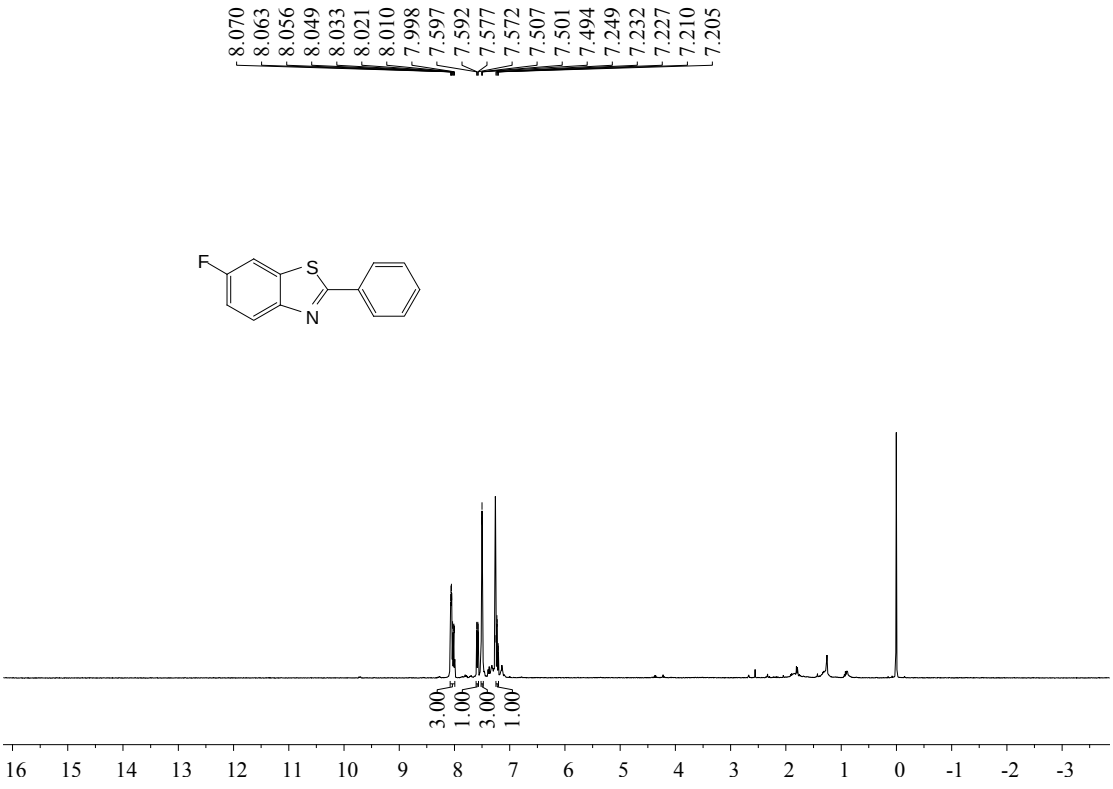
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 3l



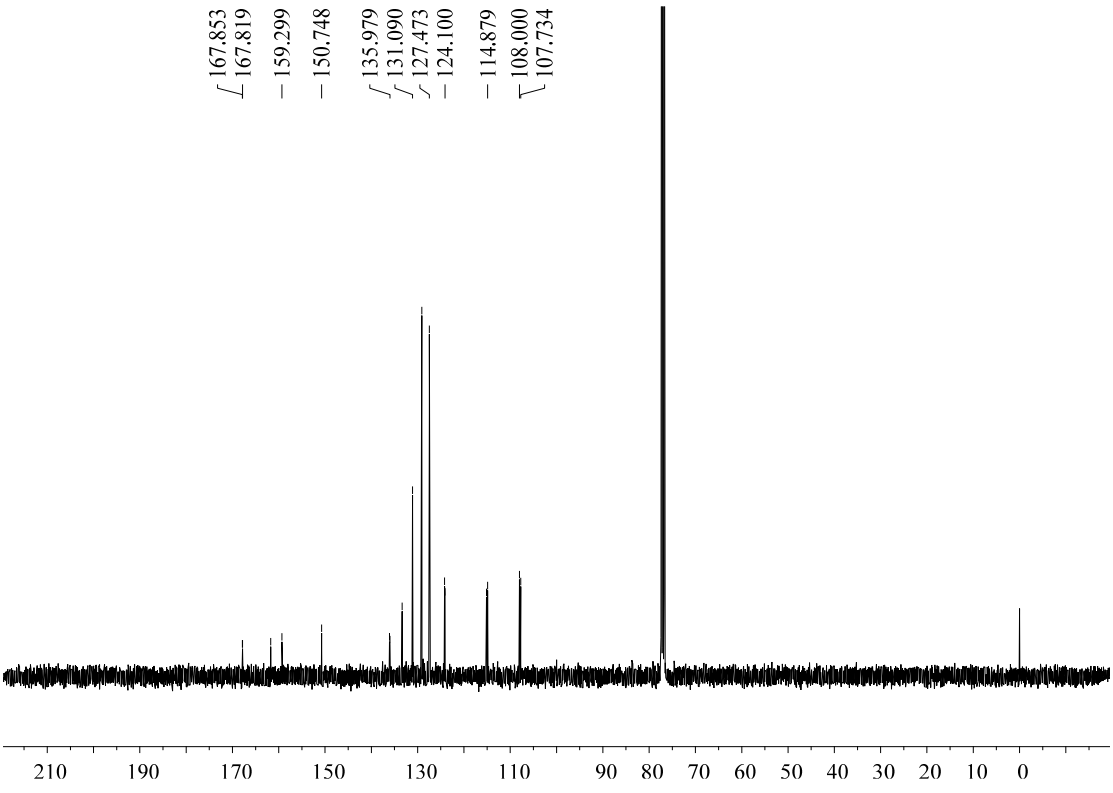
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound 3l



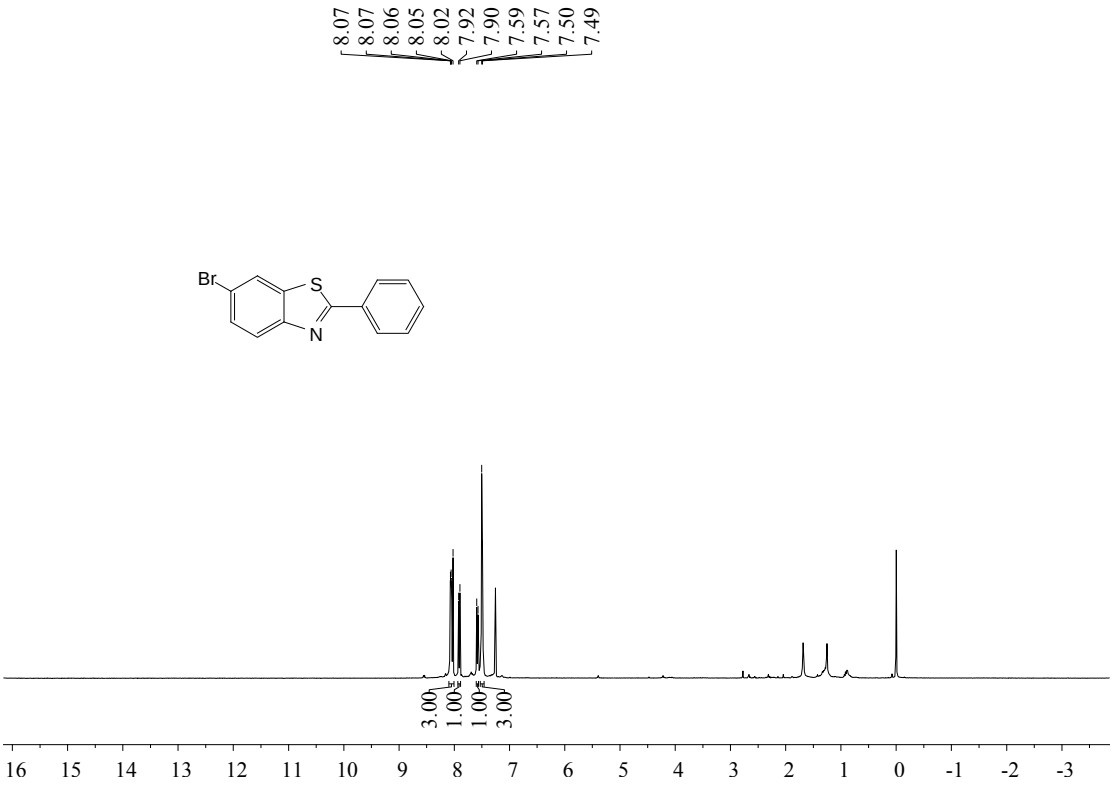
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 3m



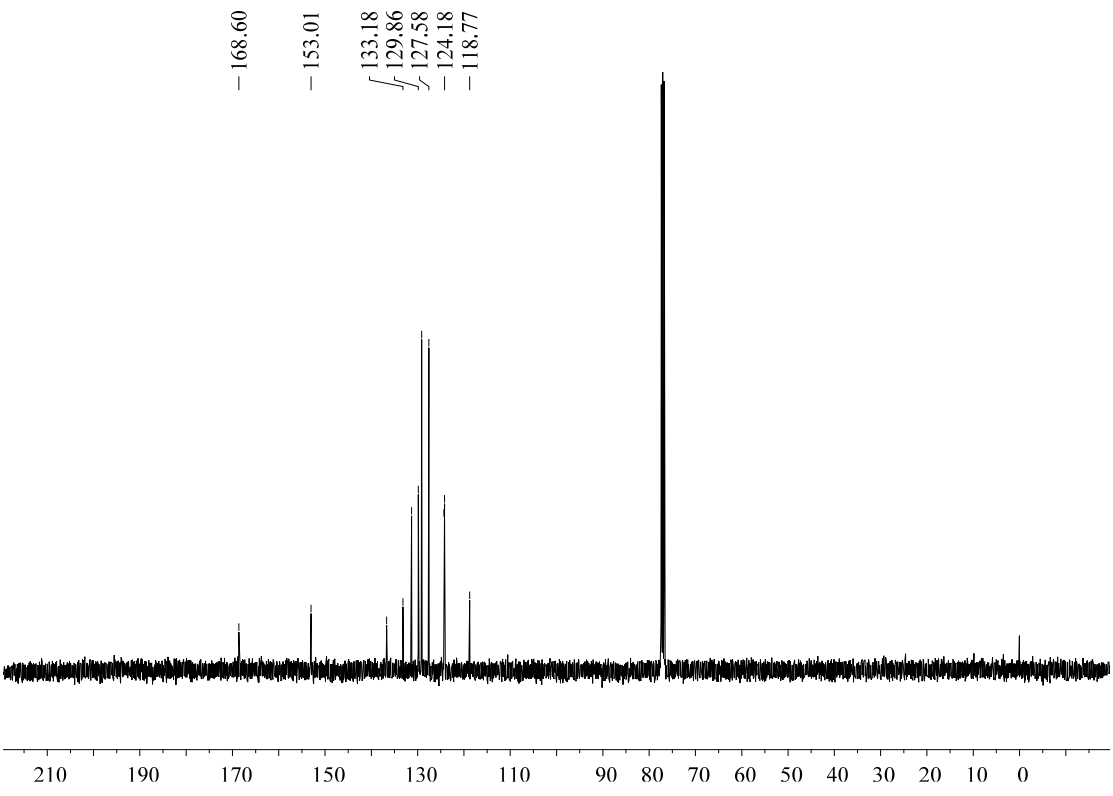
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound 3m



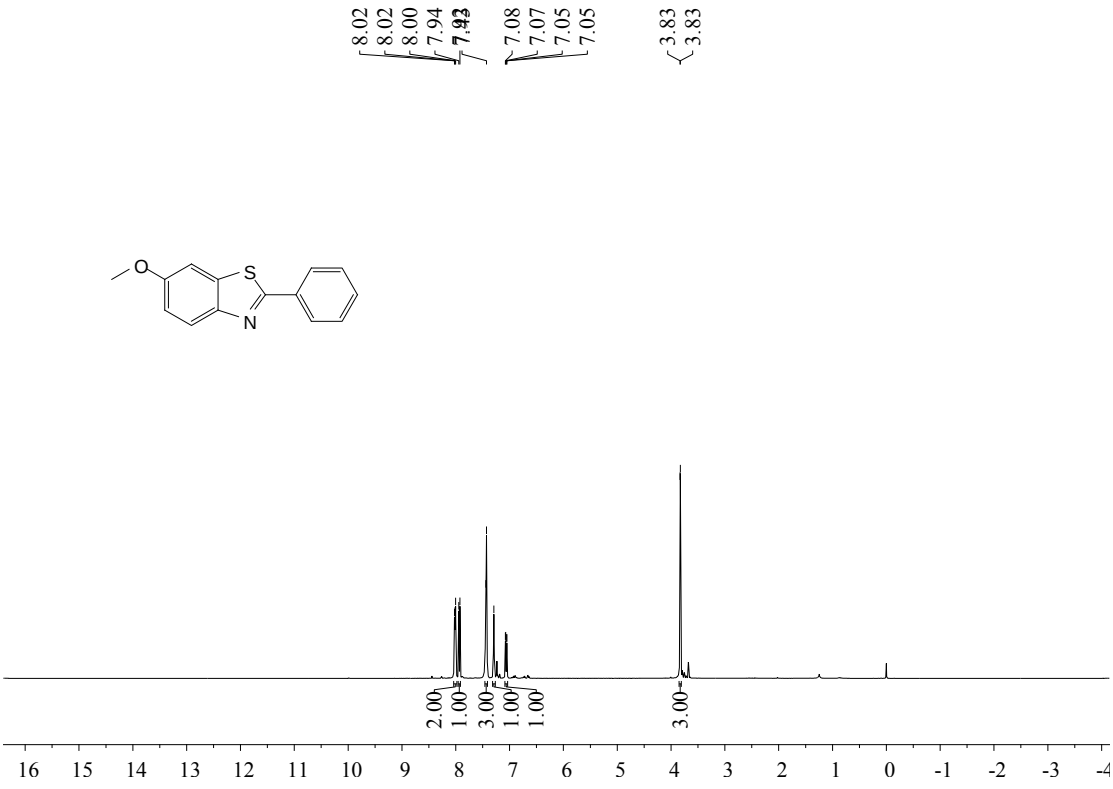
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 3n



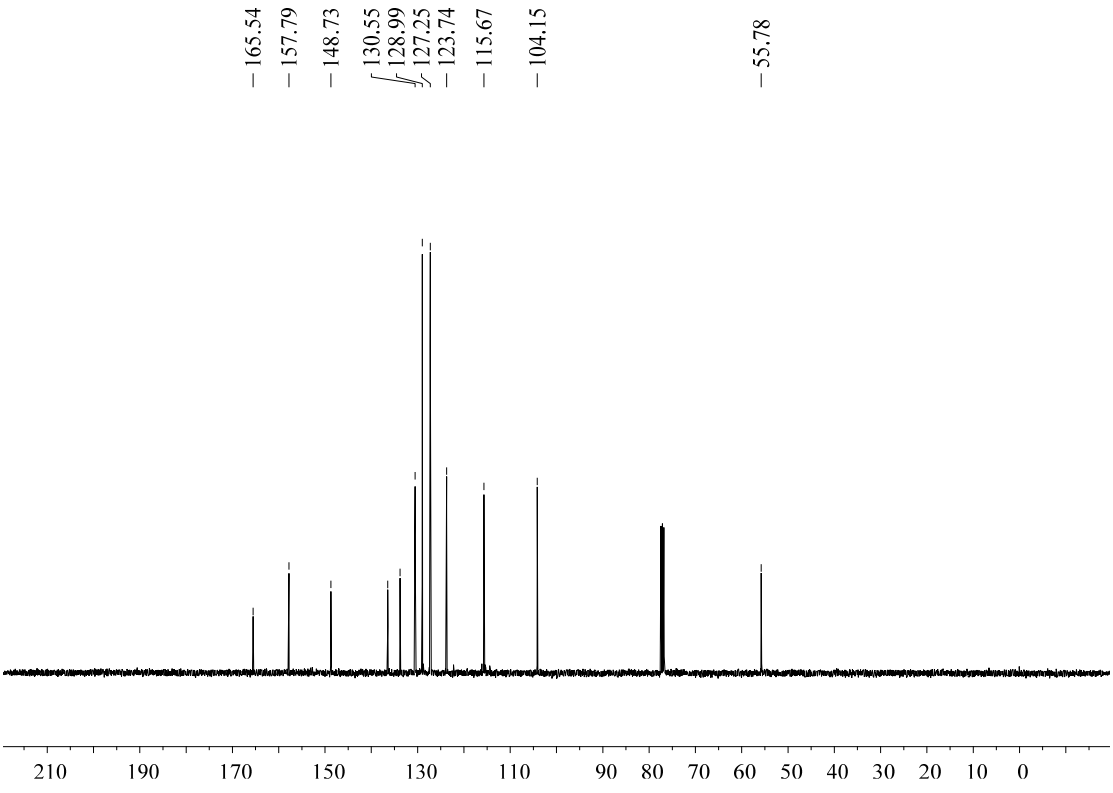
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound 3n



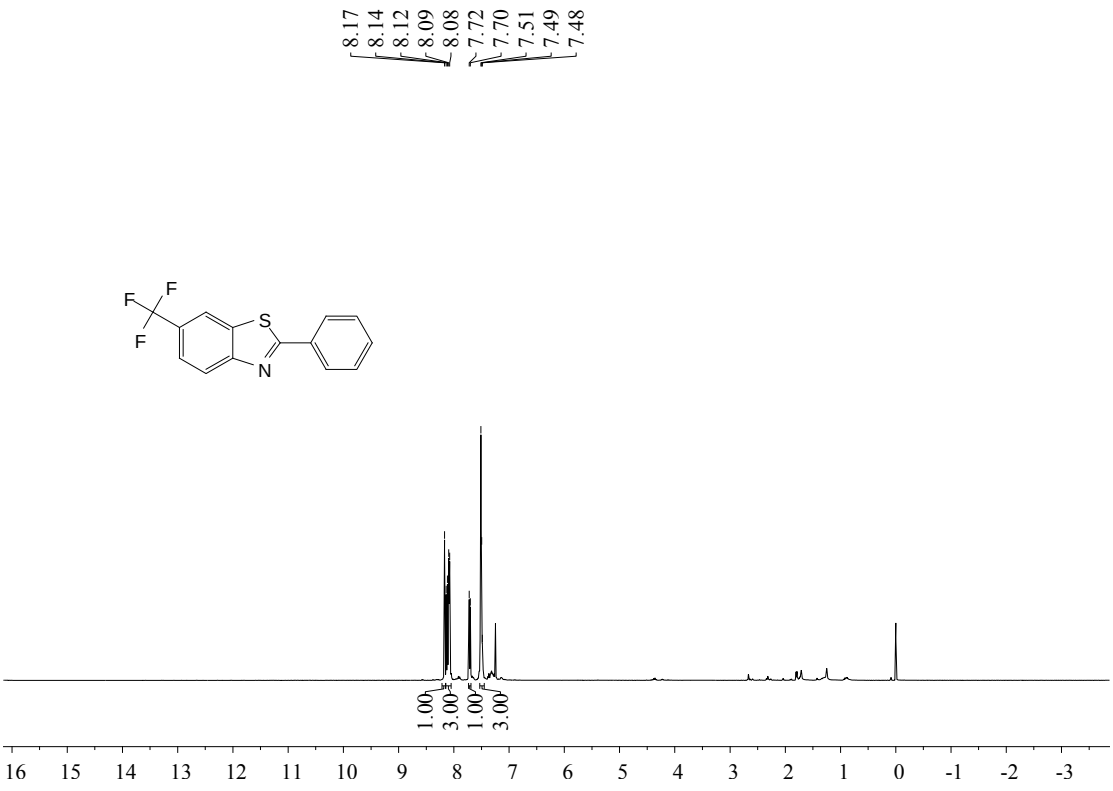
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 3o



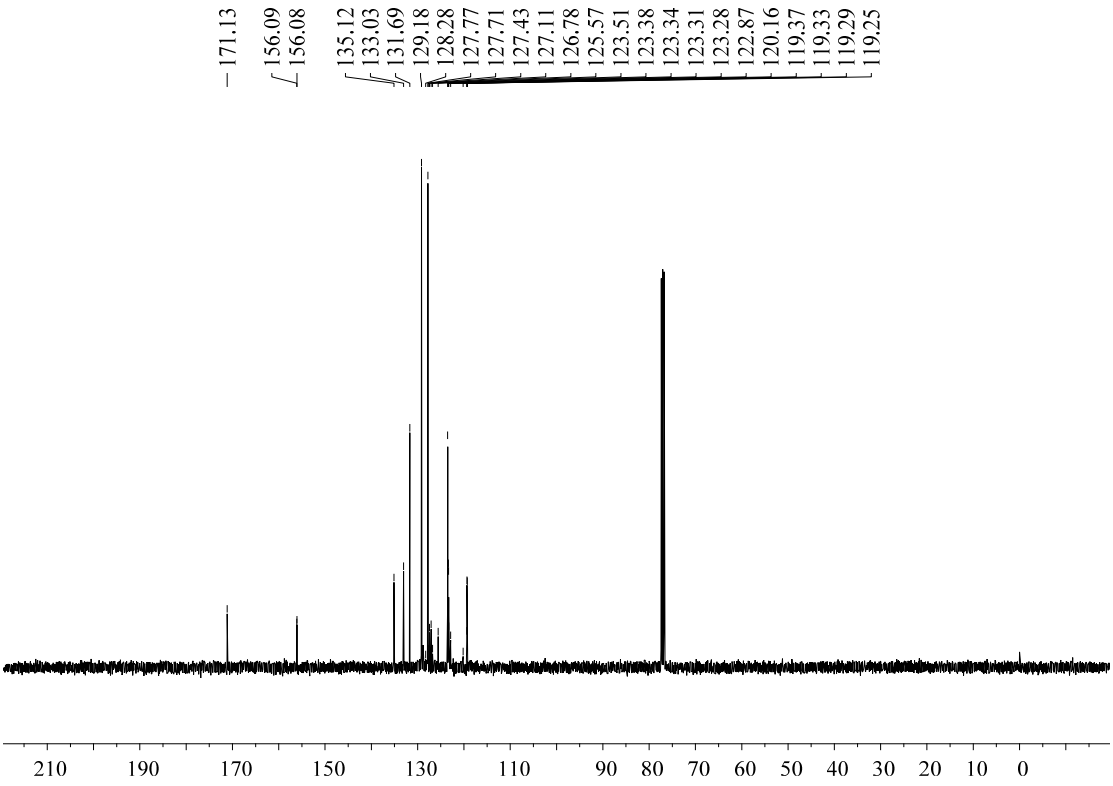
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound 3o



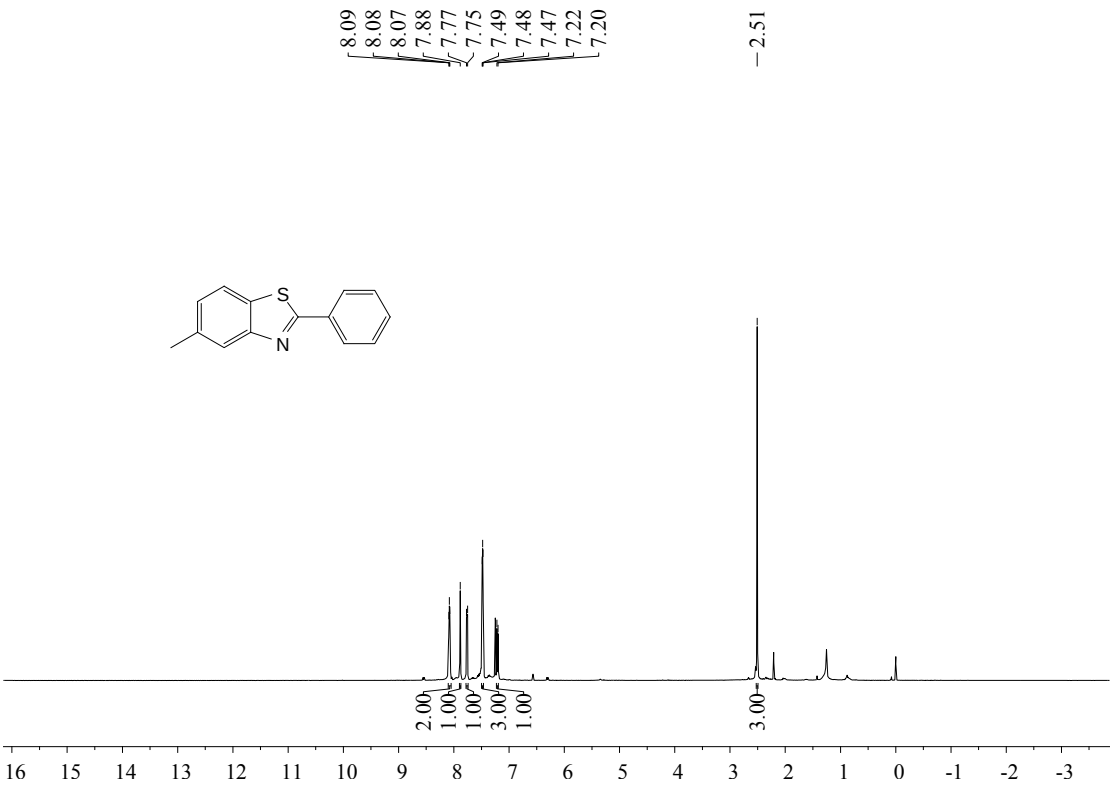
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 3p



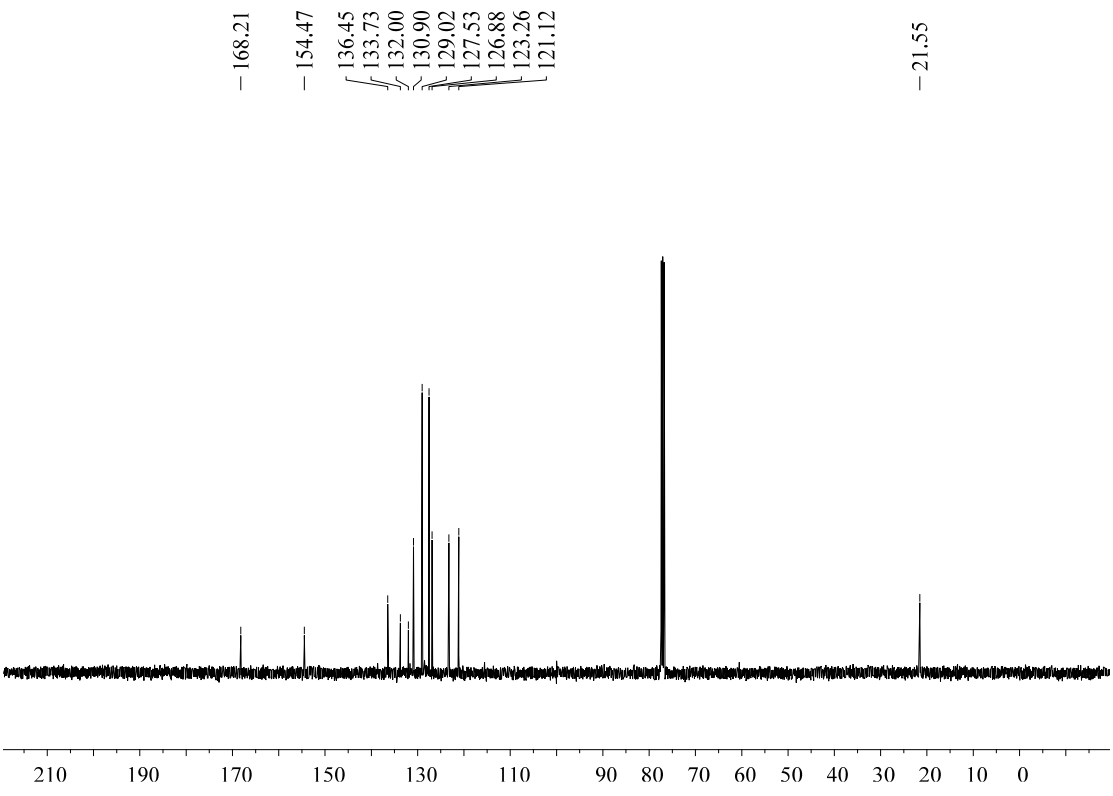
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound 3p



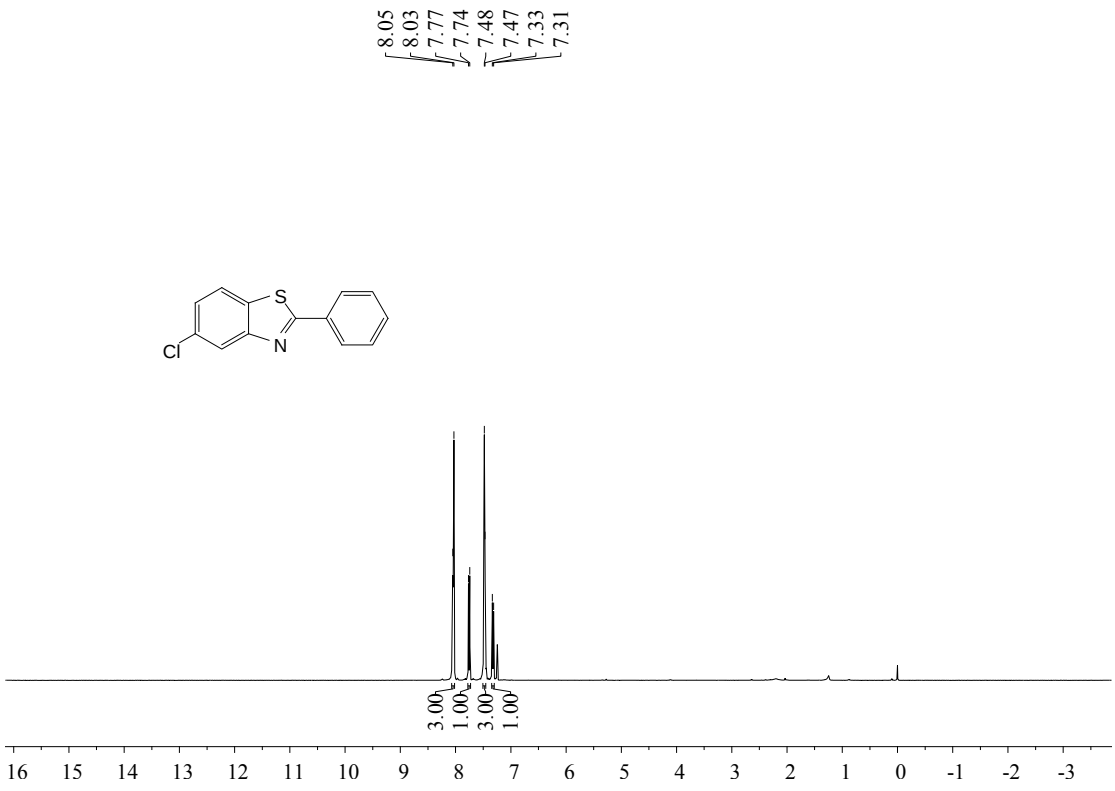
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 3q



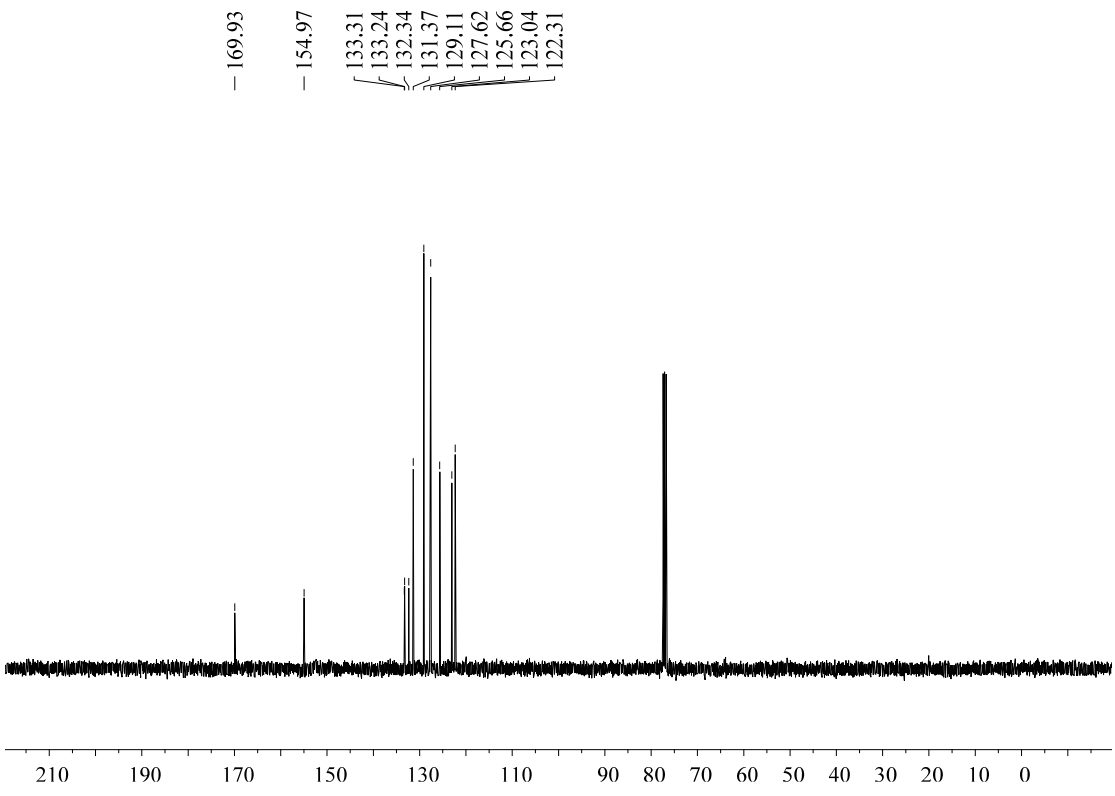
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound 3q



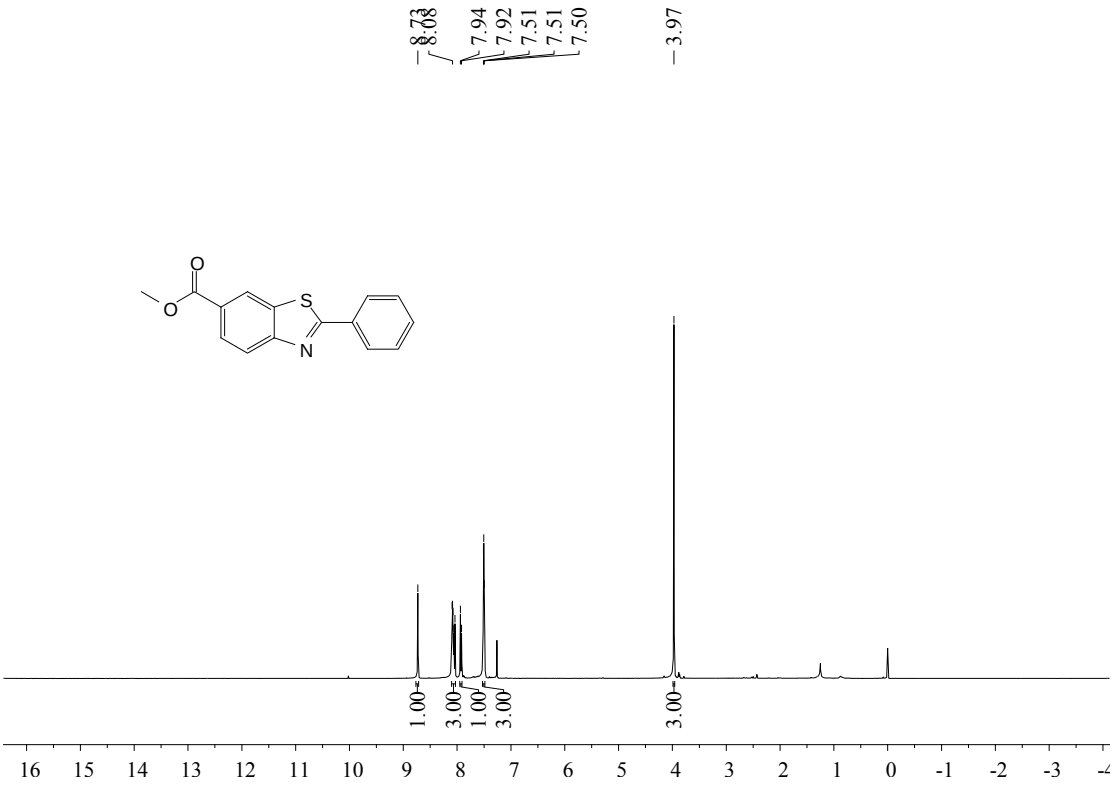
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 3r



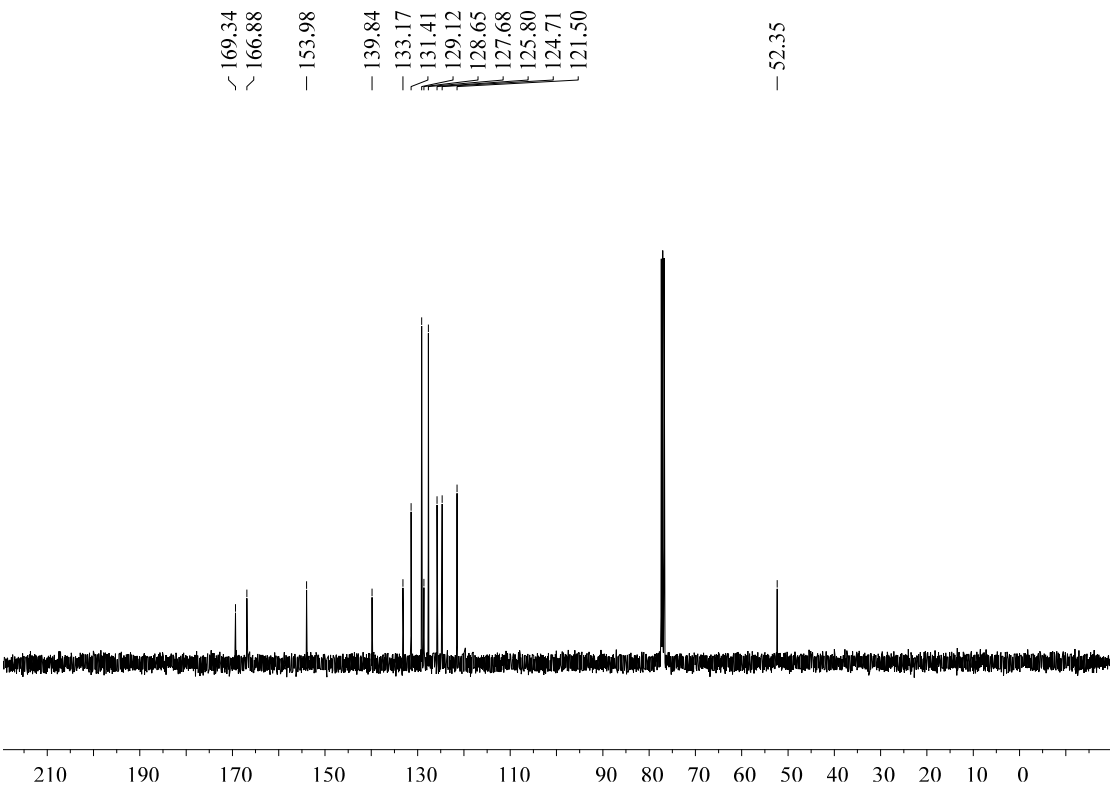
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound 3r



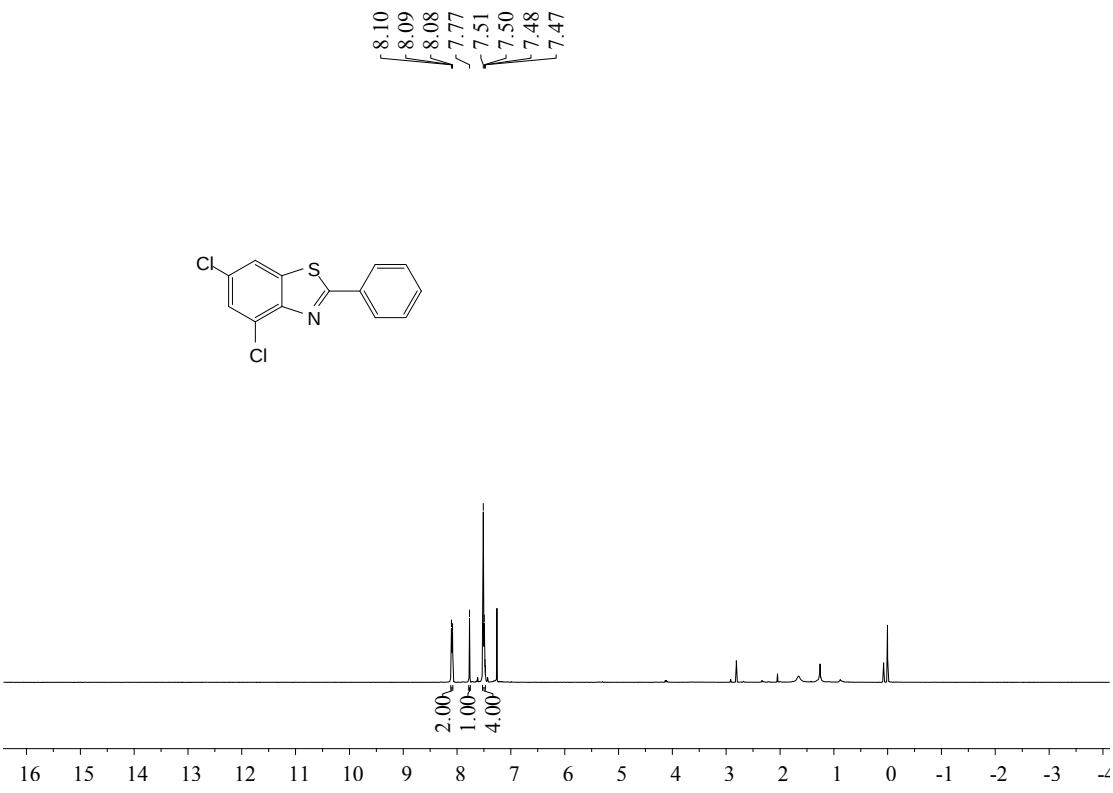
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 3s



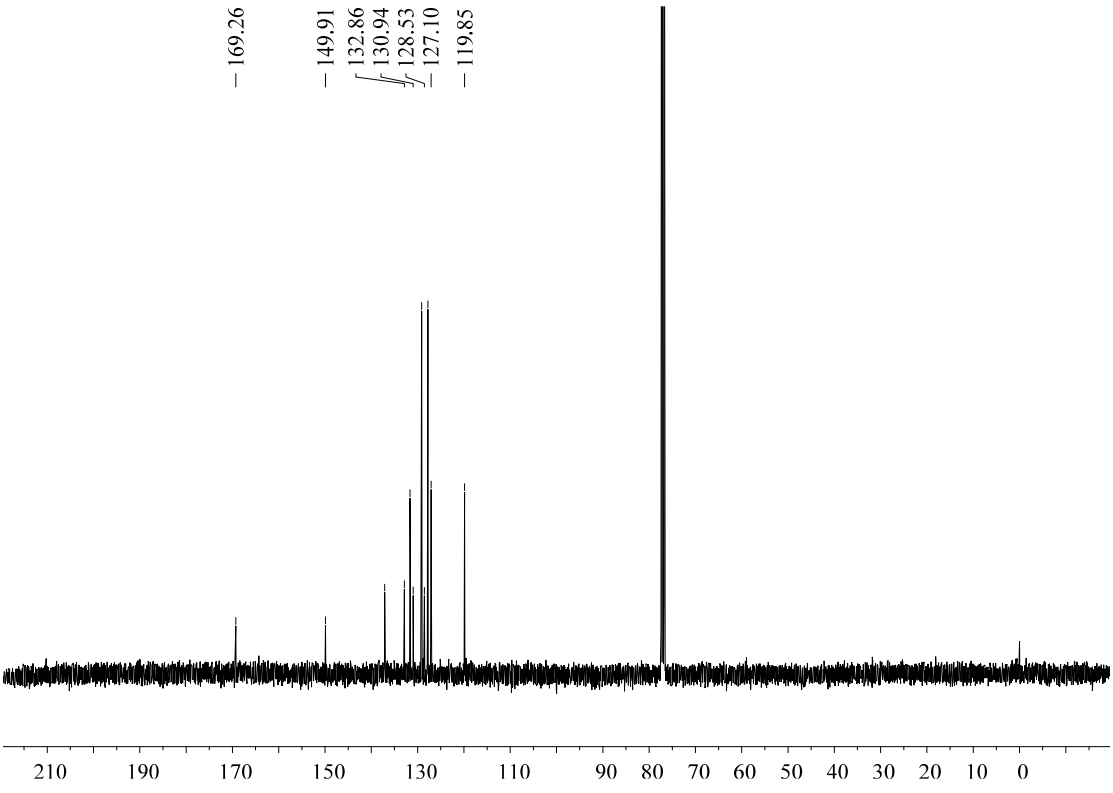
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound 3s



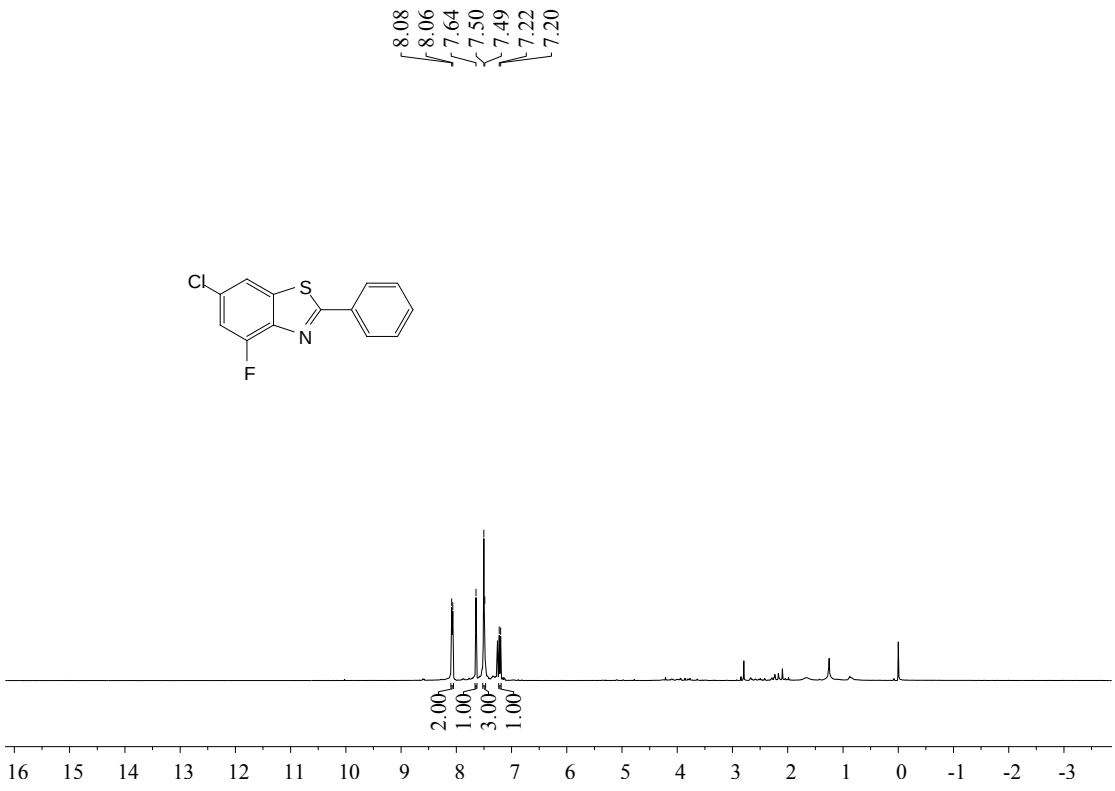
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 3t



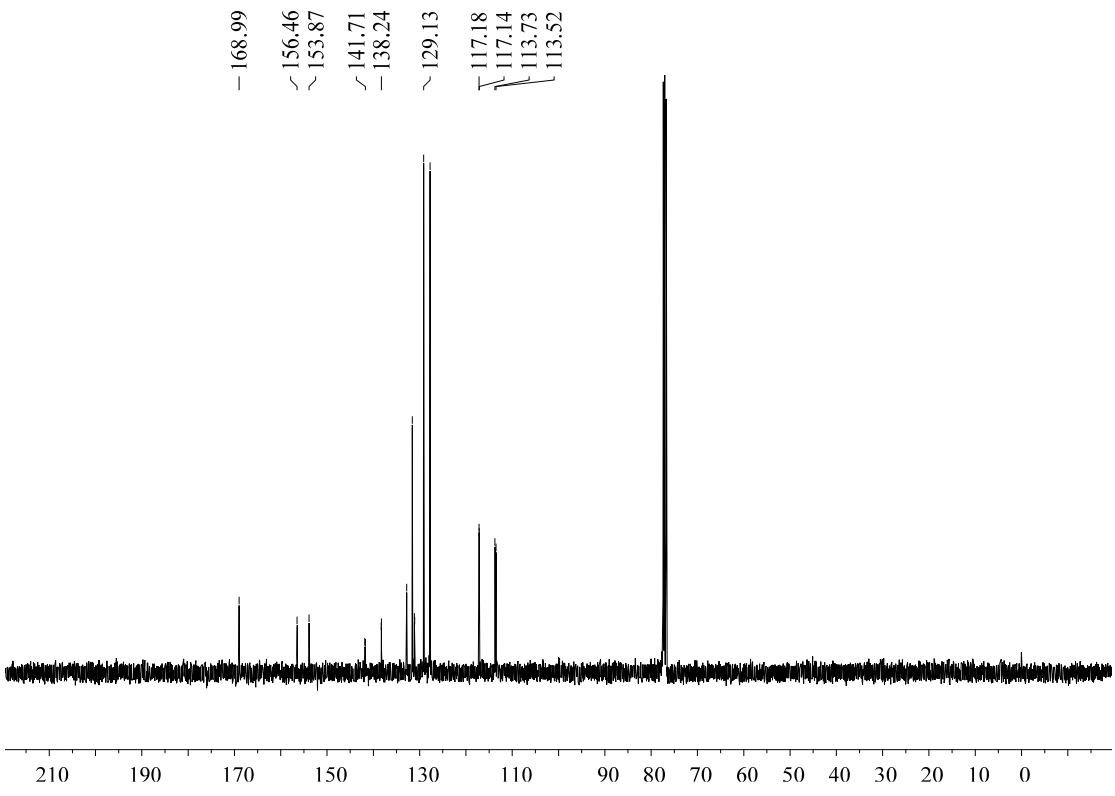
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound 3t



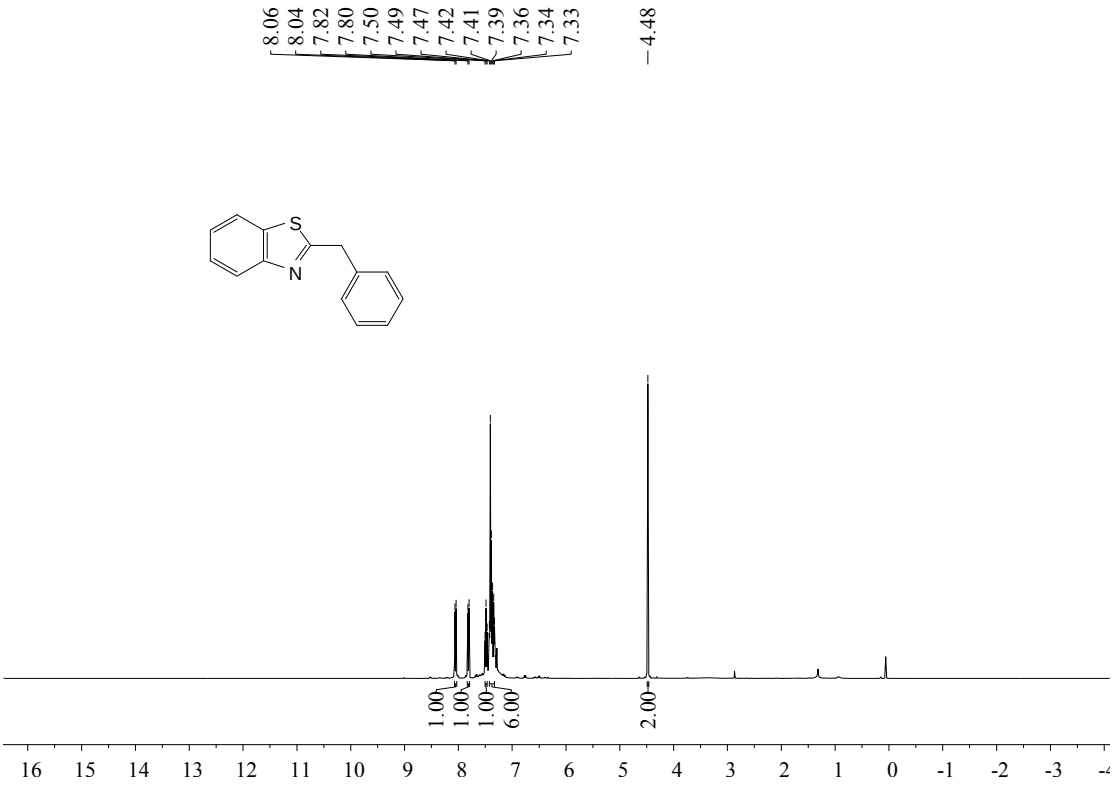
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 3u



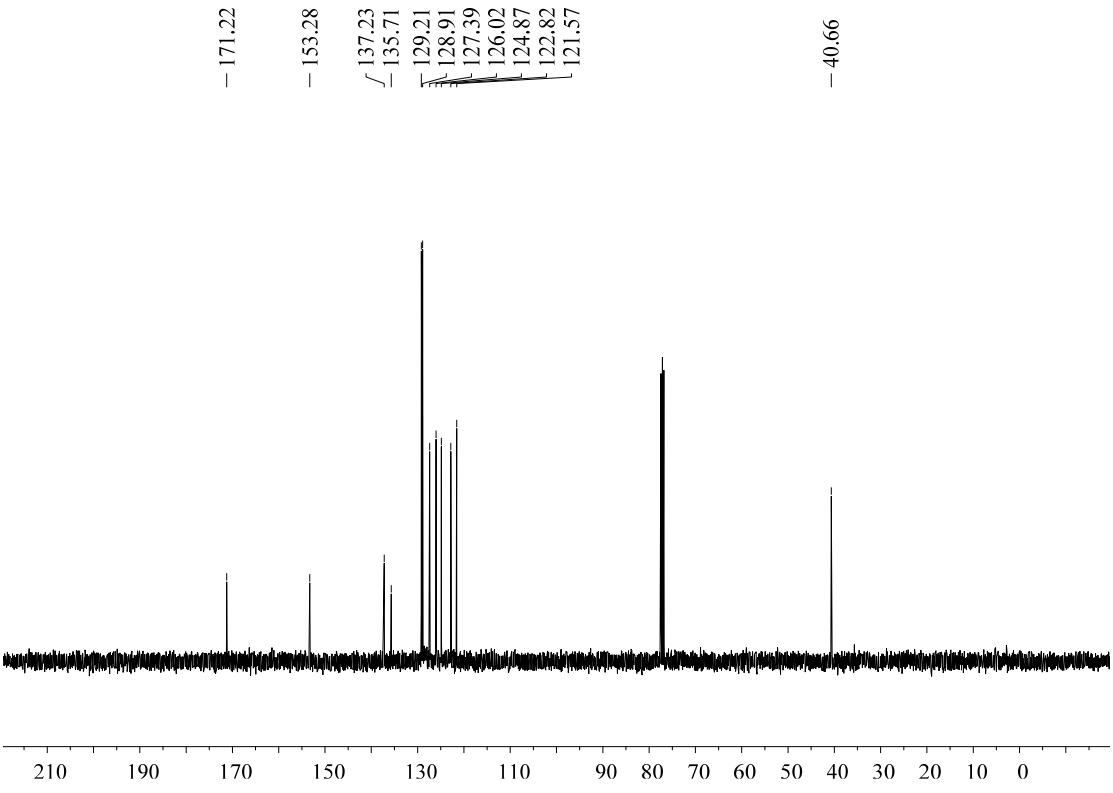
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound 3u



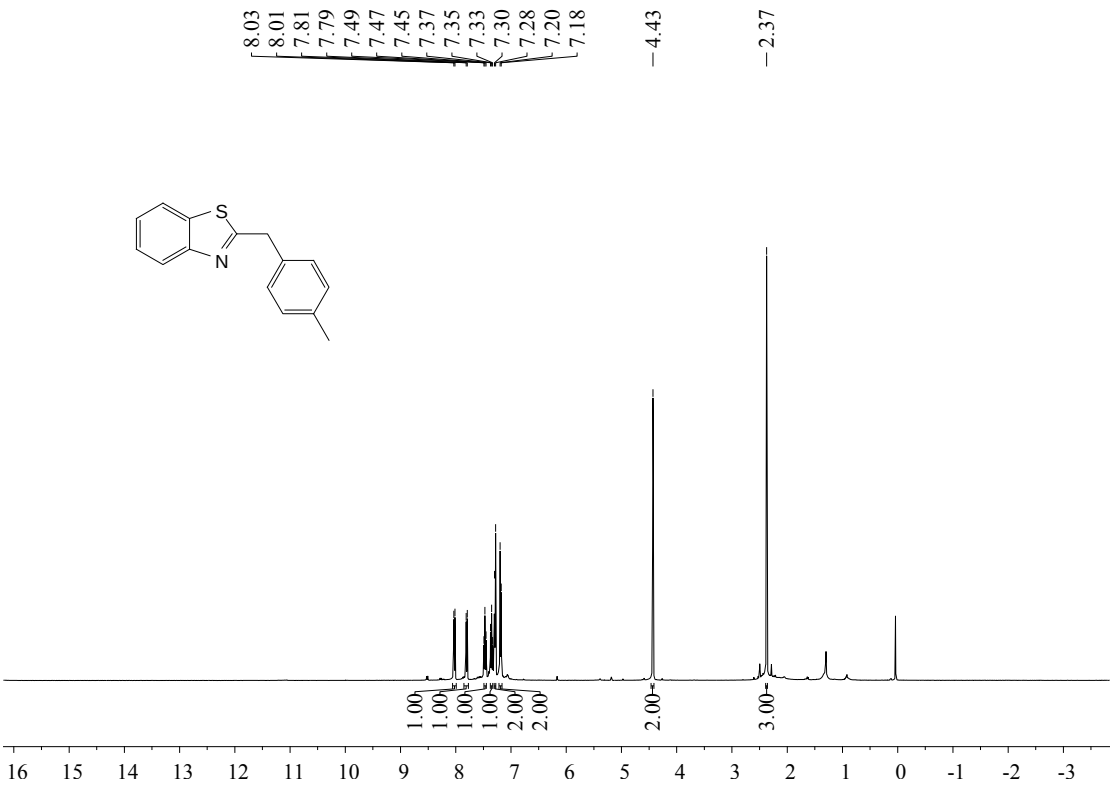
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 4a



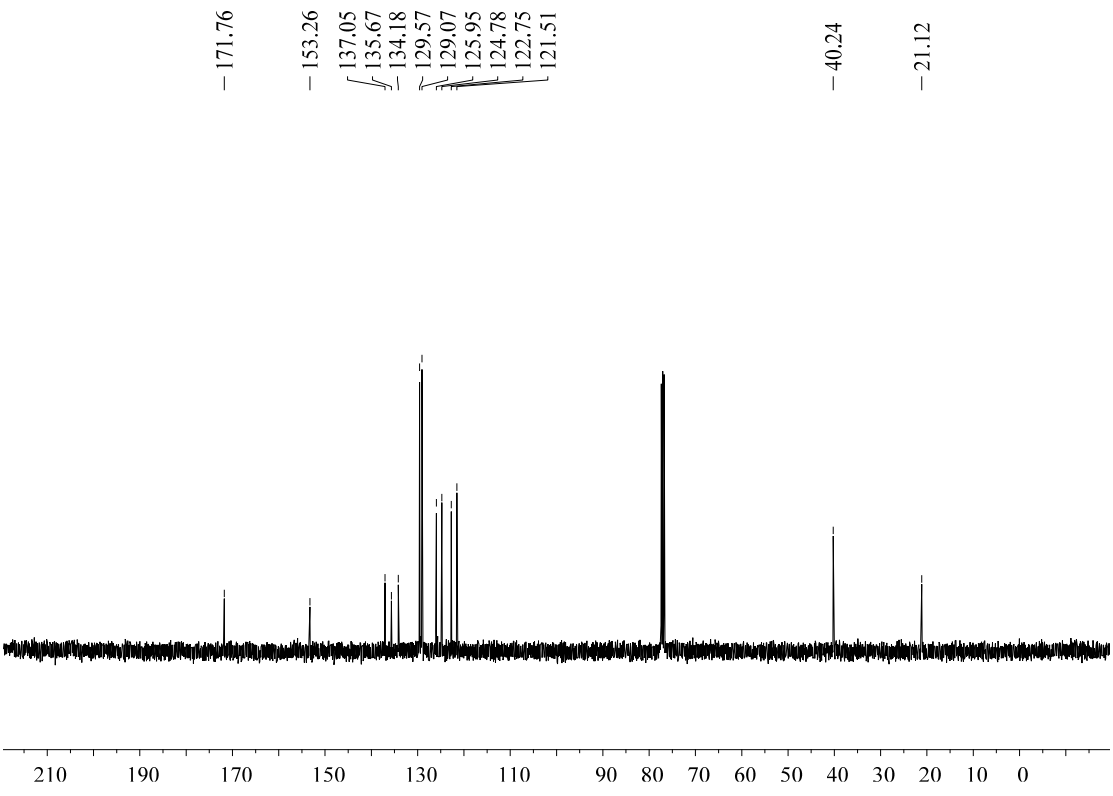
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound 4a



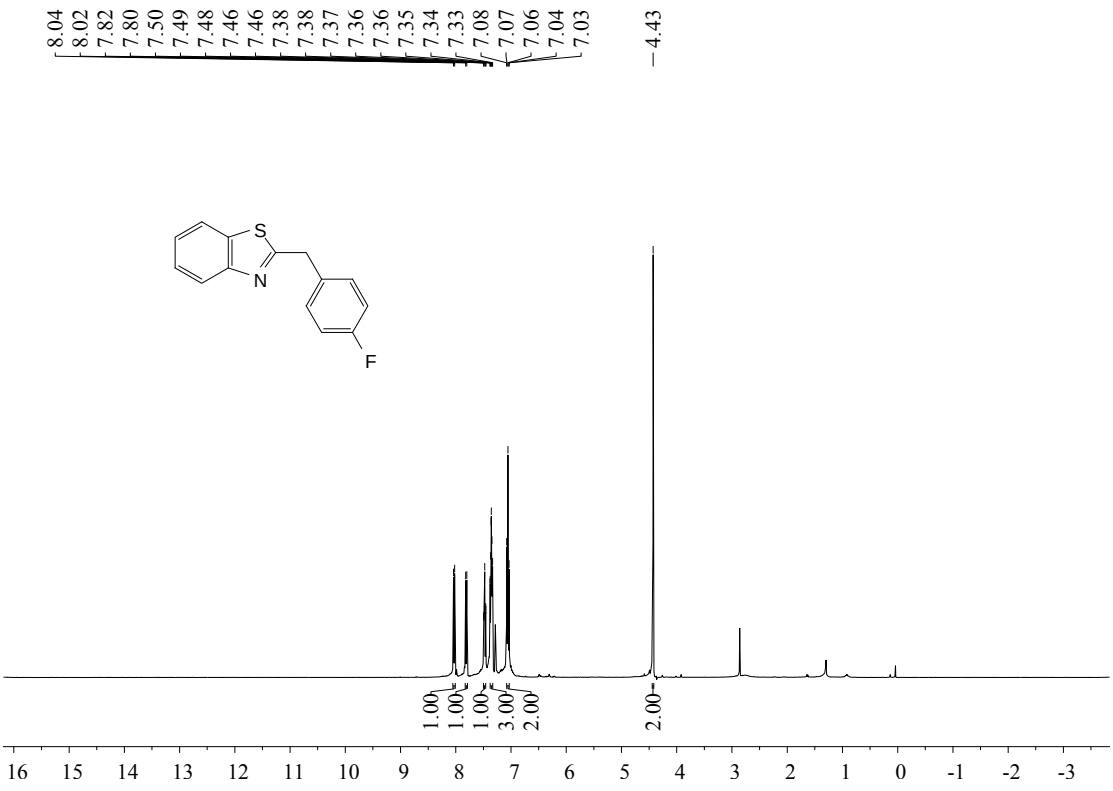
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 4b



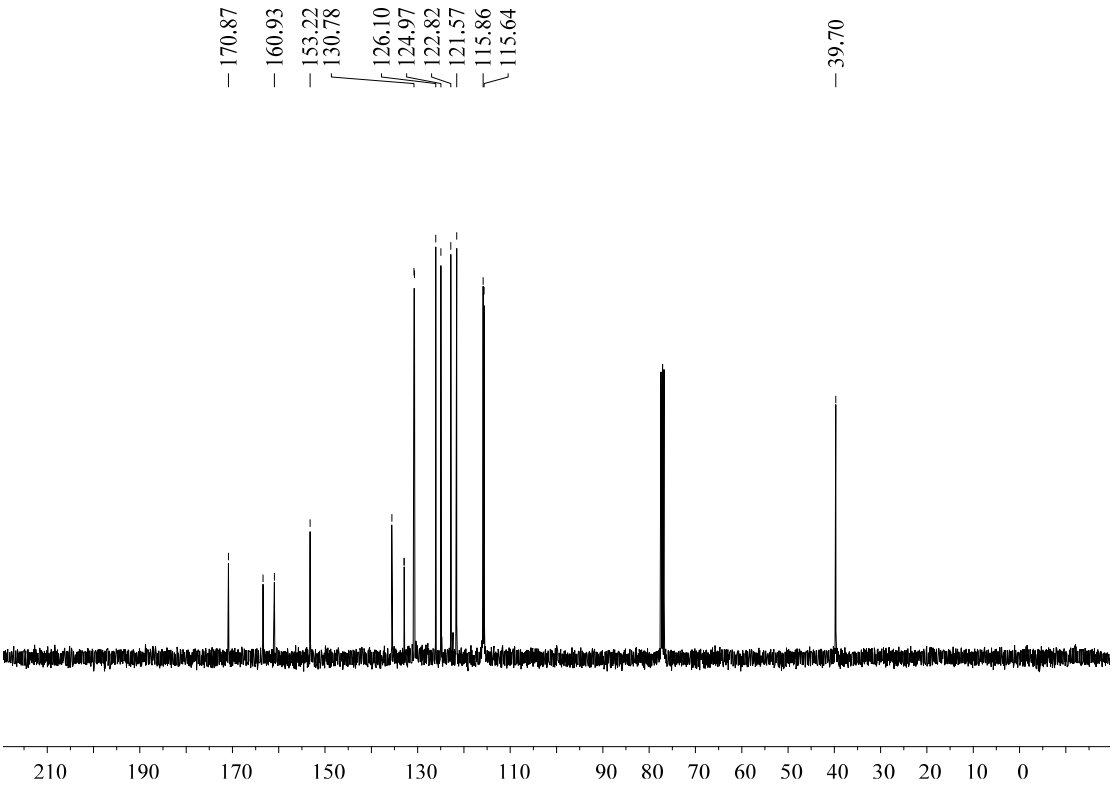
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound 4b



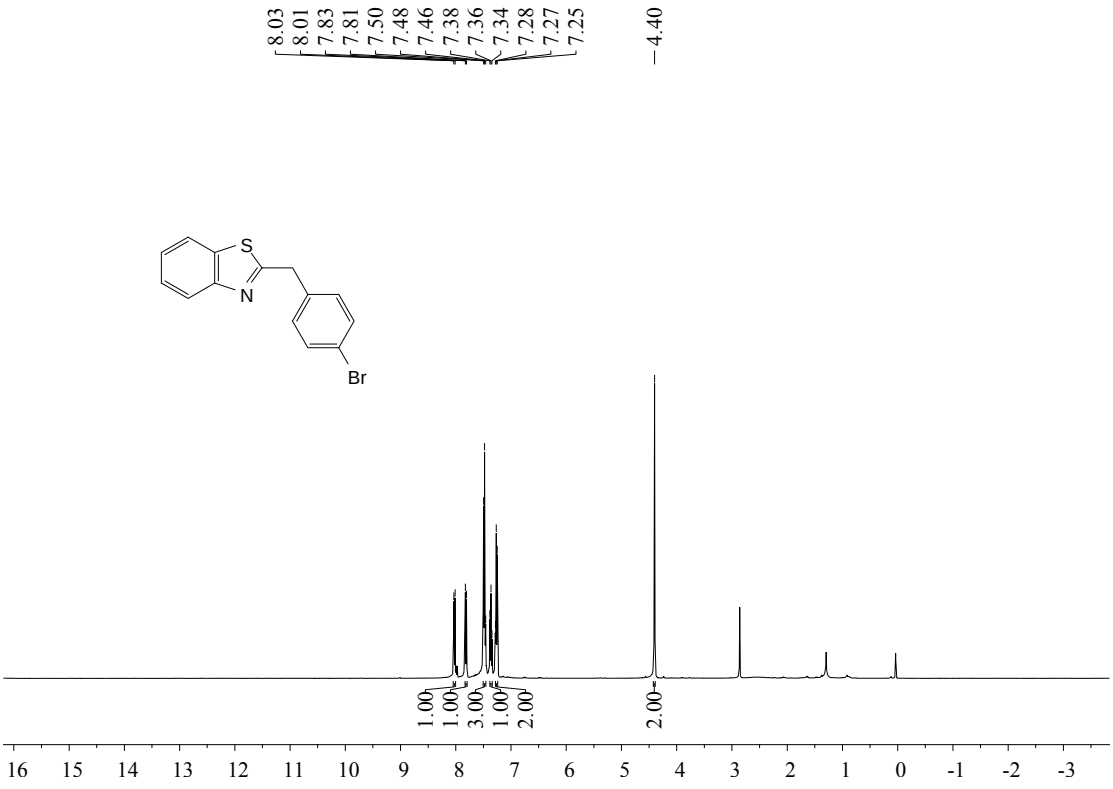
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 4c



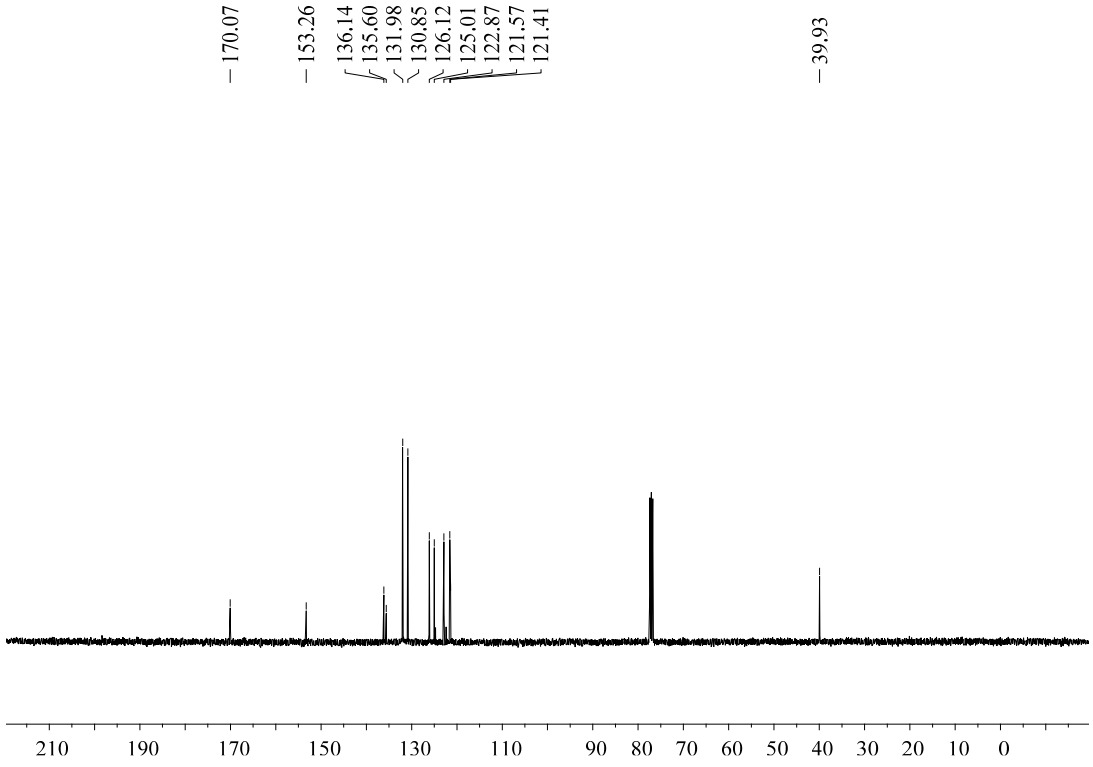
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound 4c



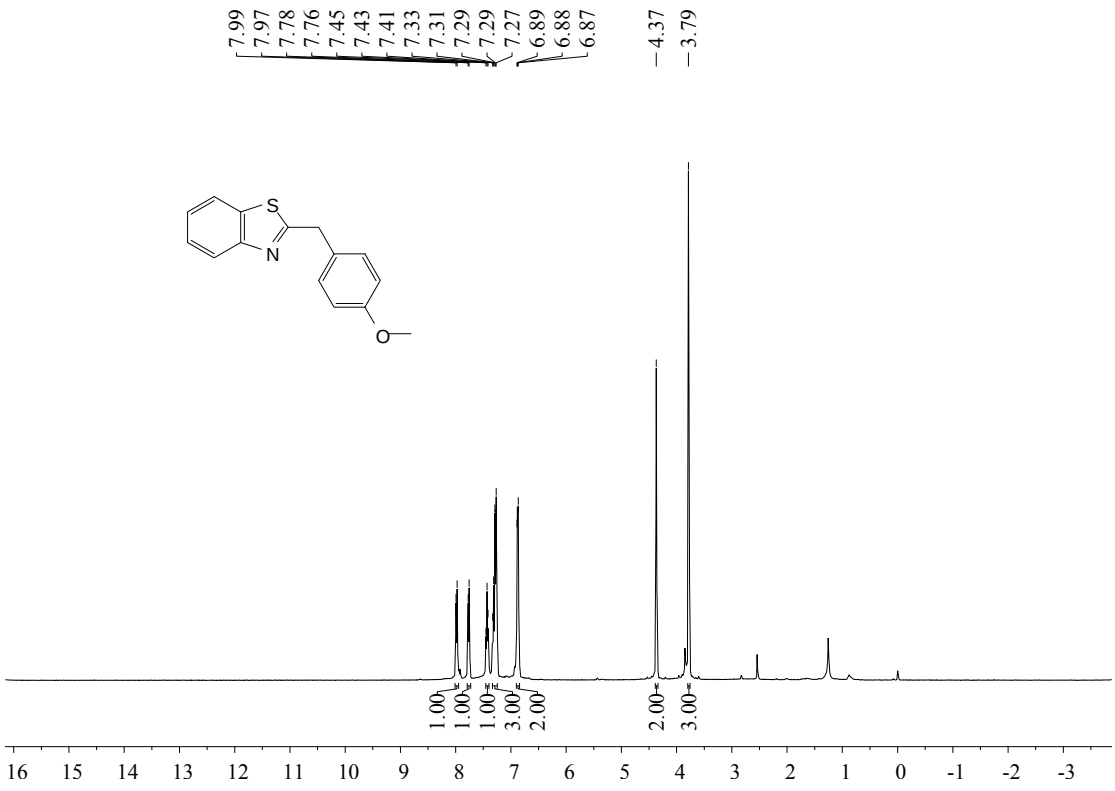
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 4d



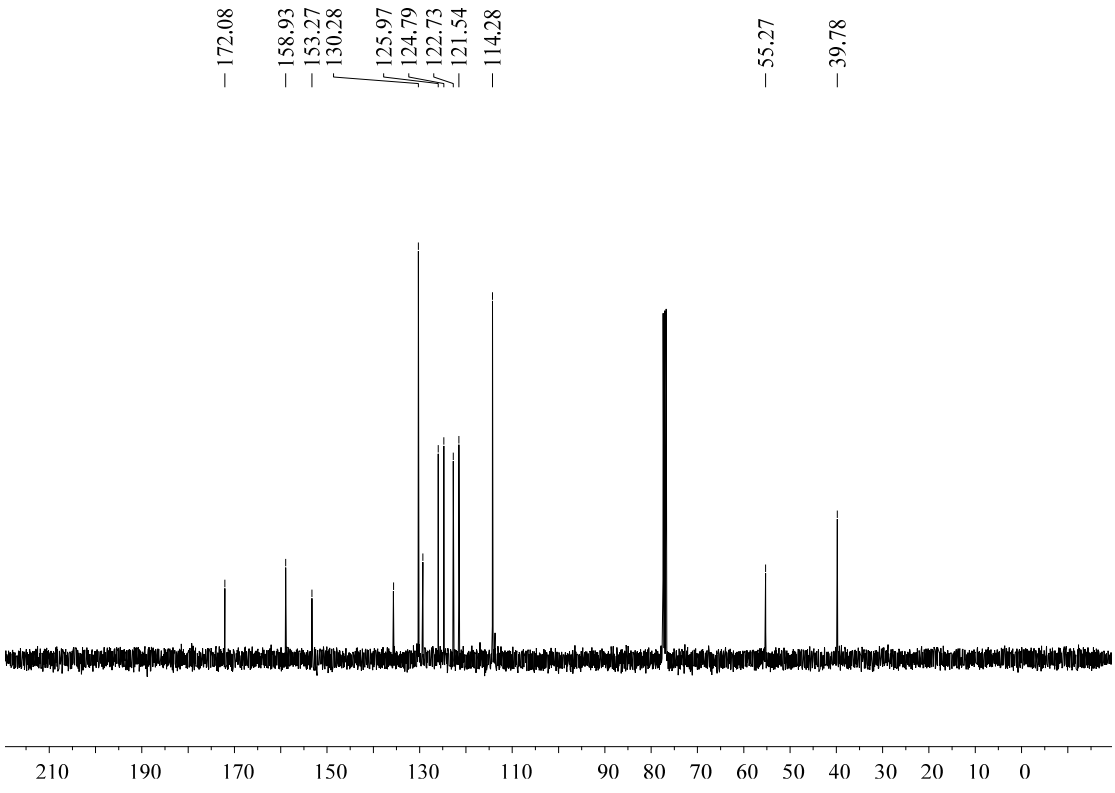
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound 4d



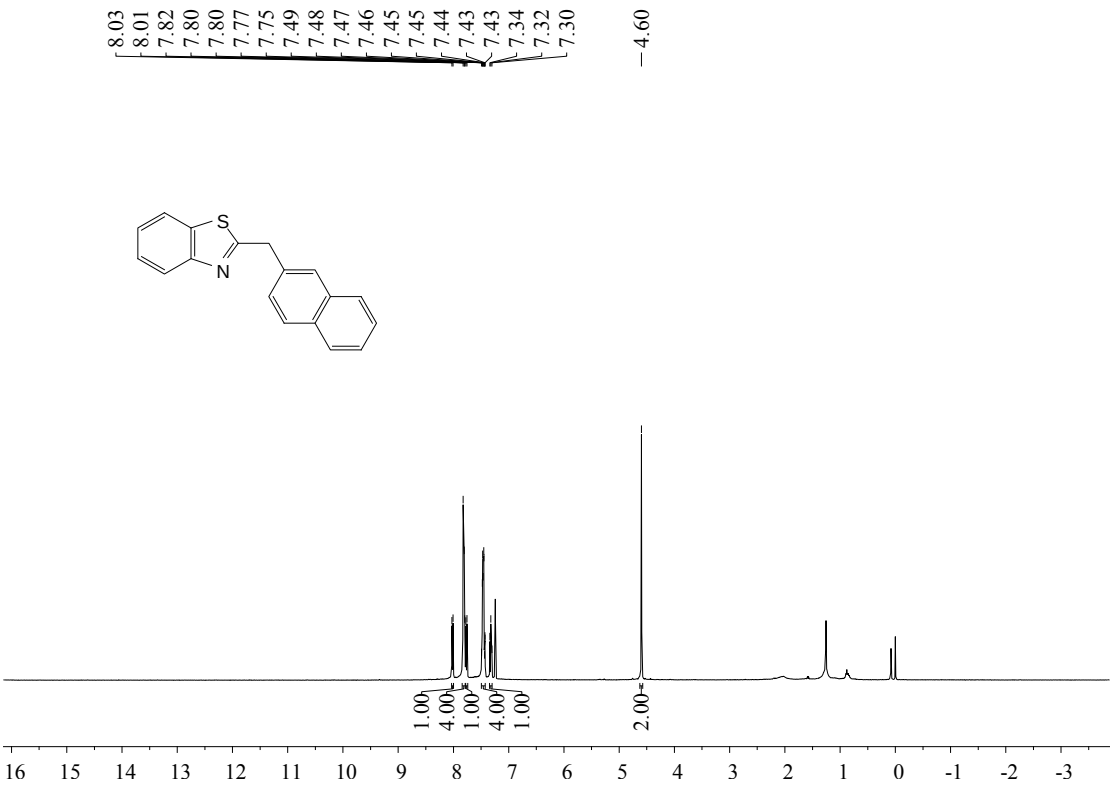
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 4e



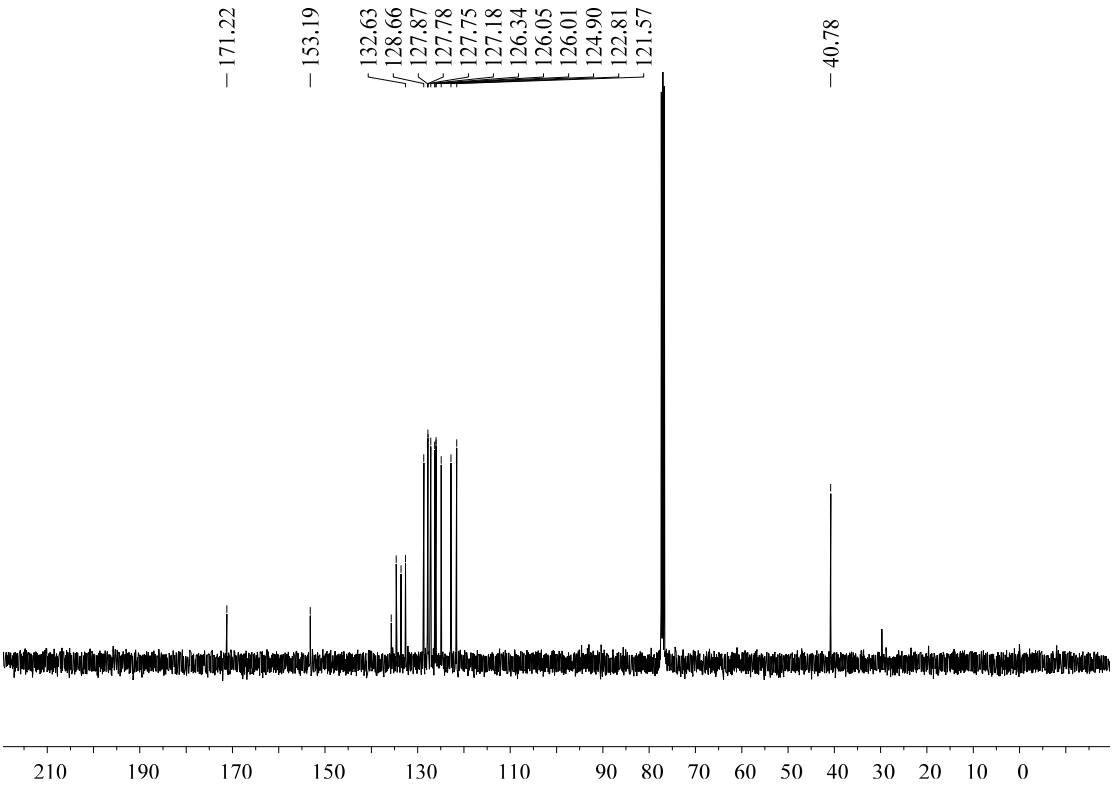
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound 4e



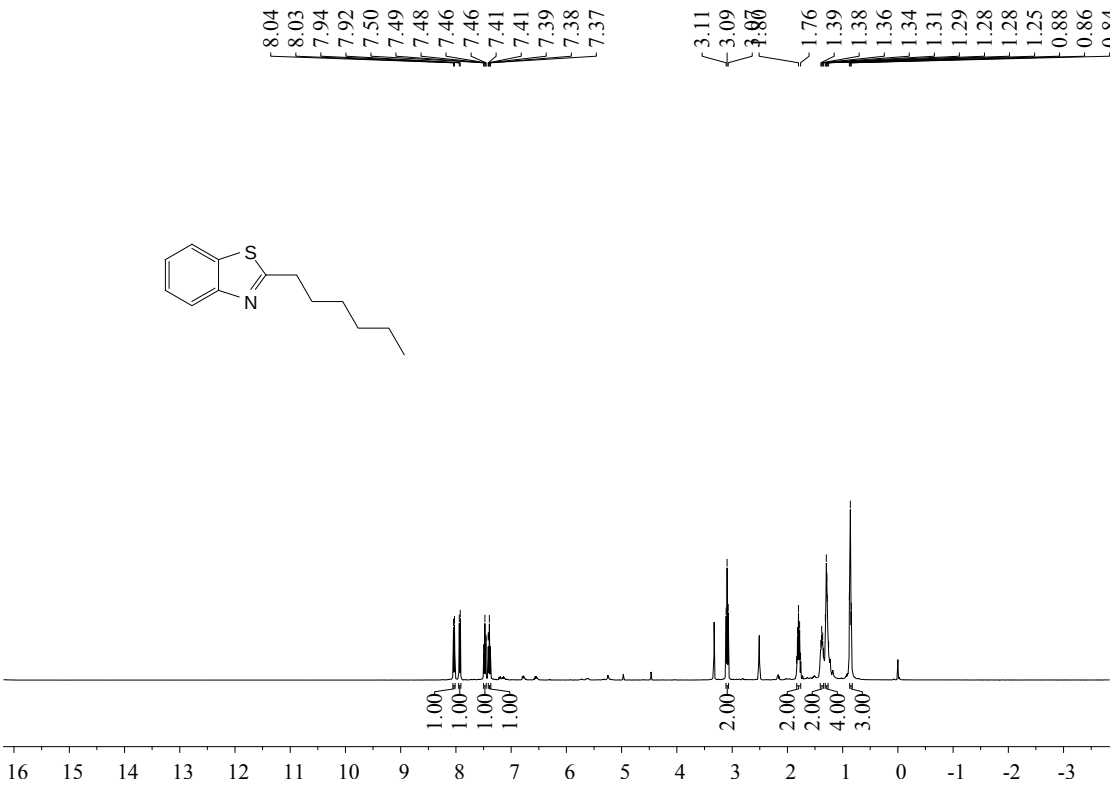
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 4f



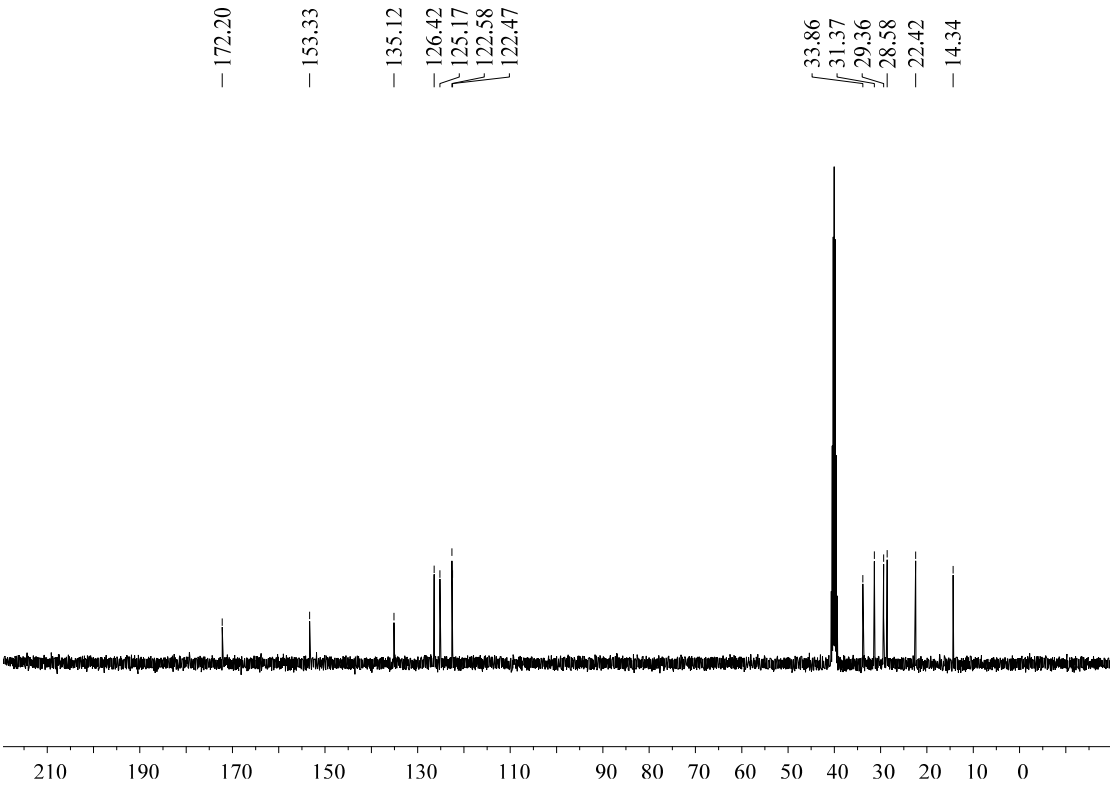
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound 4f



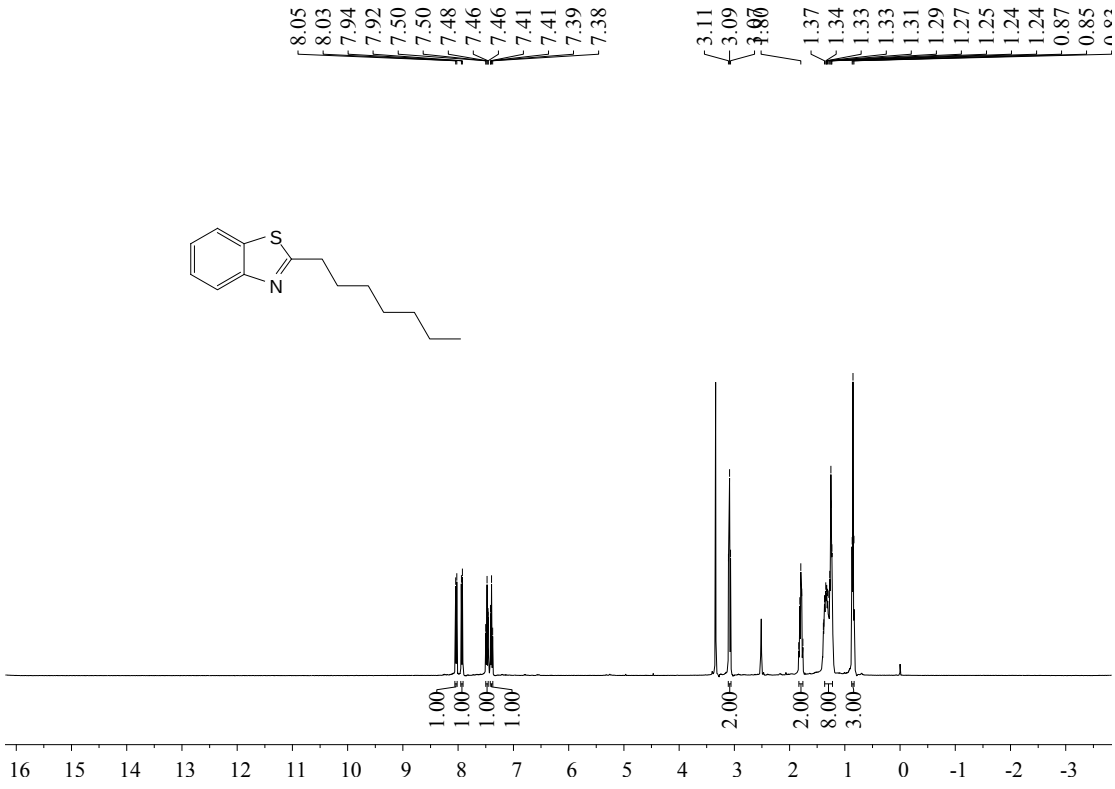
^{1}H NMR (400 MHz, DMSO-d_6) spectrum of compound 4g



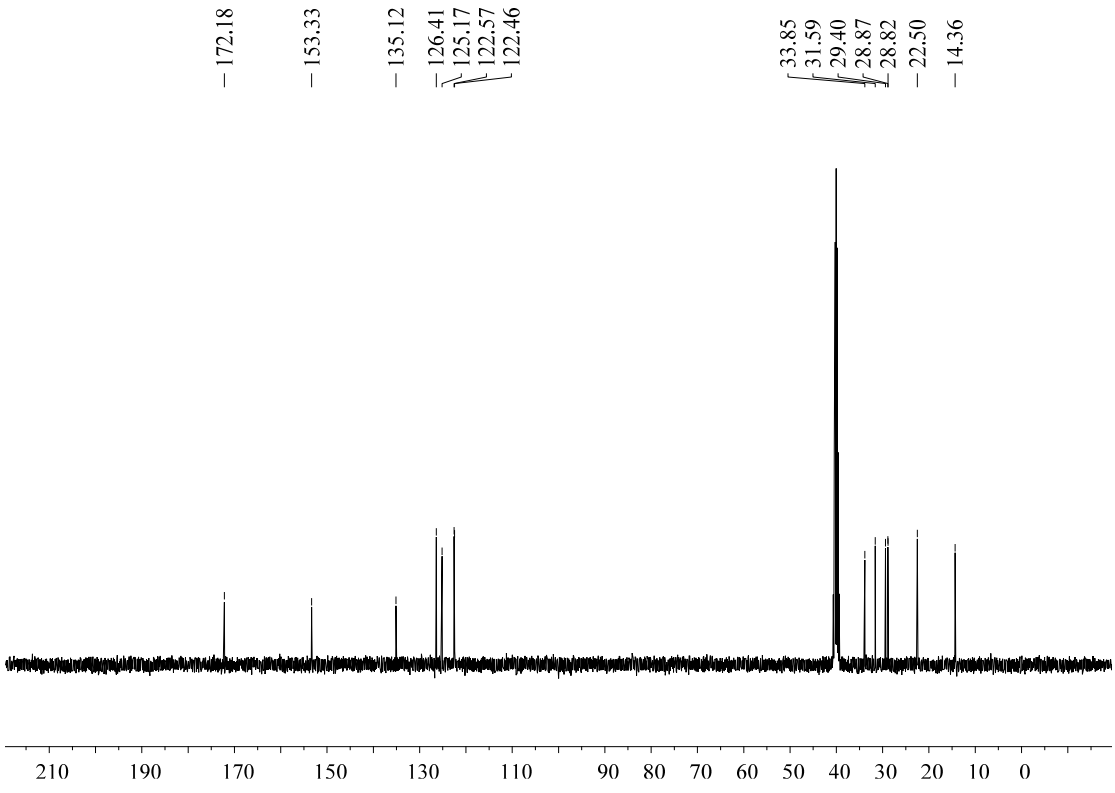
^{13}C NMR (101 MHz, DMSO-d_6) spectrum of compound 4g



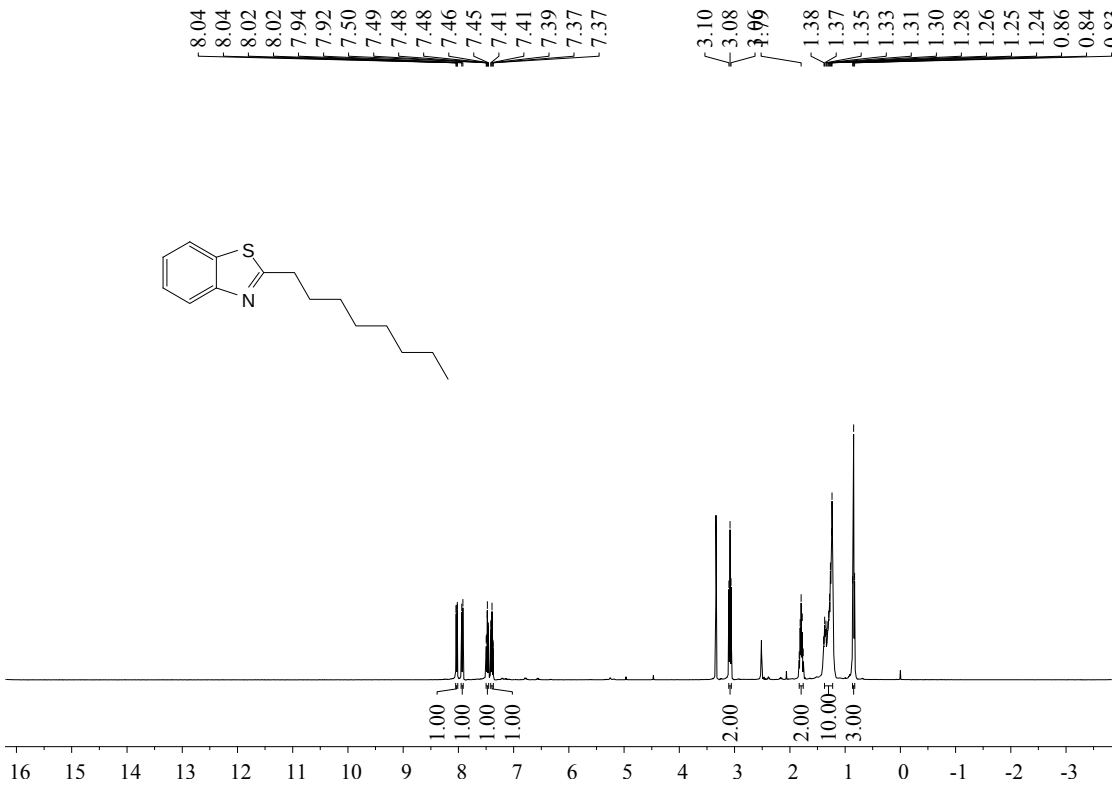
^{1}H NMR (400 MHz, DMSO-d_6) spectrum of compound 4h



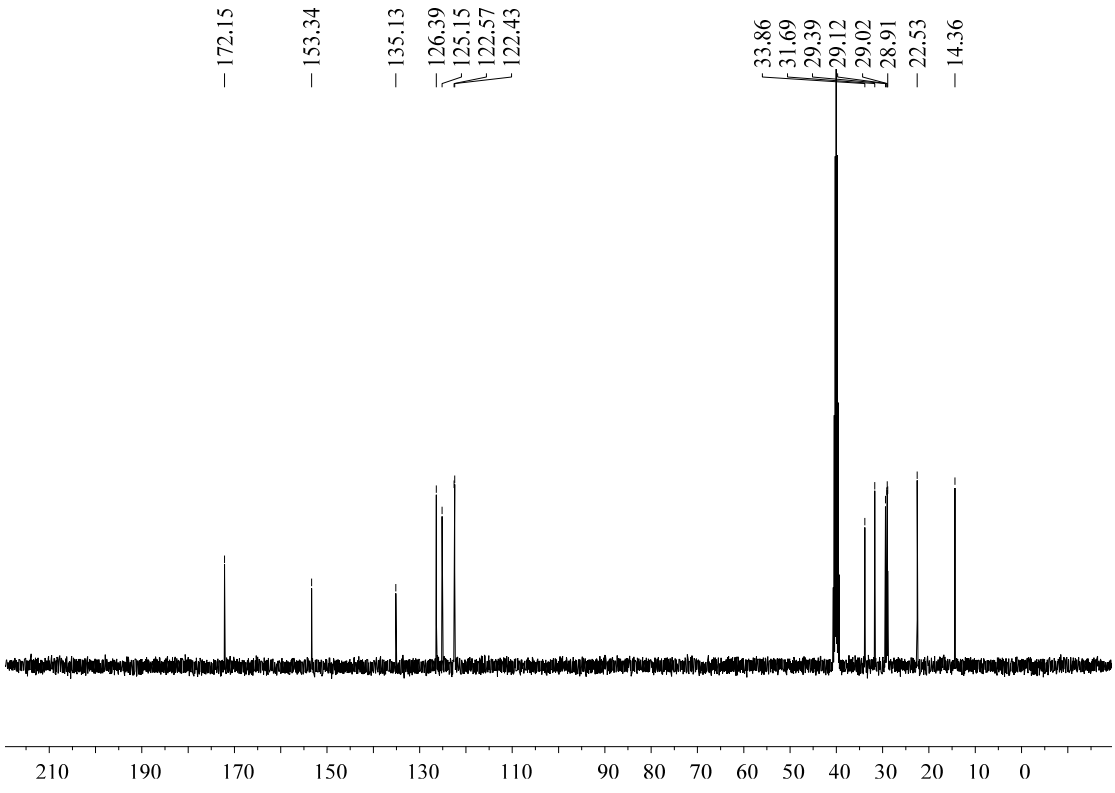
^{13}C NMR (101 MHz, DMSO-d_6) spectrum of compound 4h



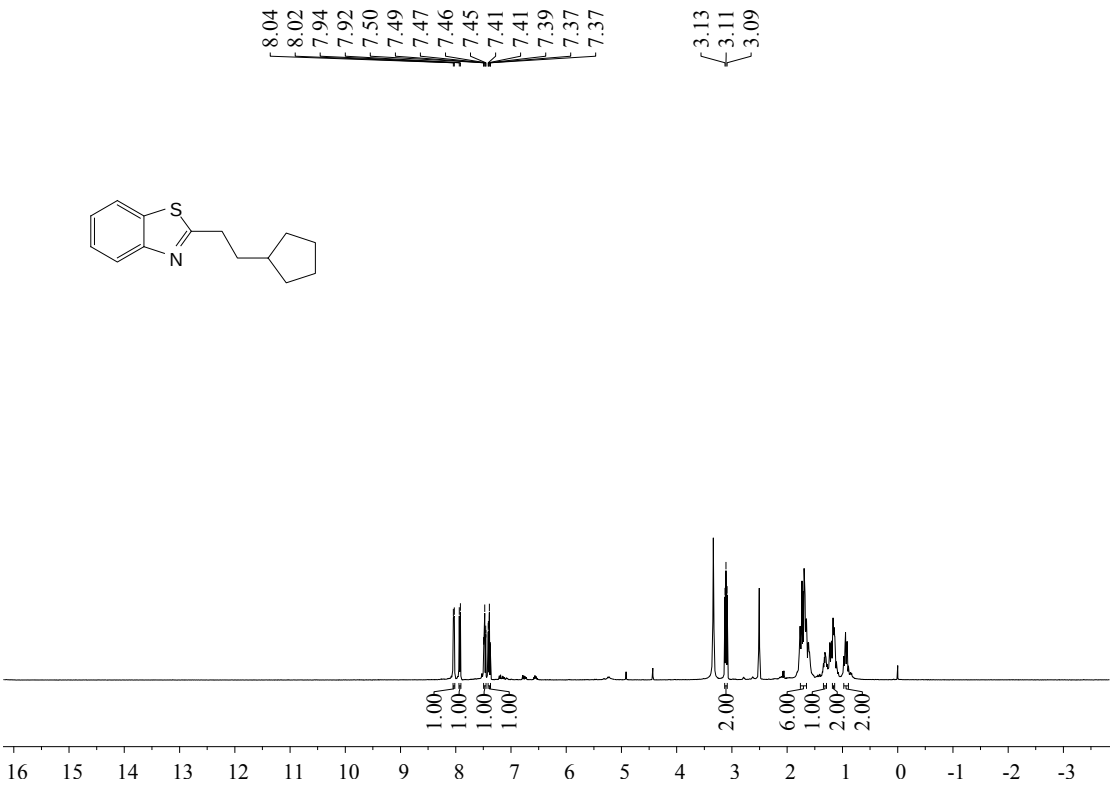
^{1}H NMR (400 MHz, DMSO-d_6) spectrum of compound 4i



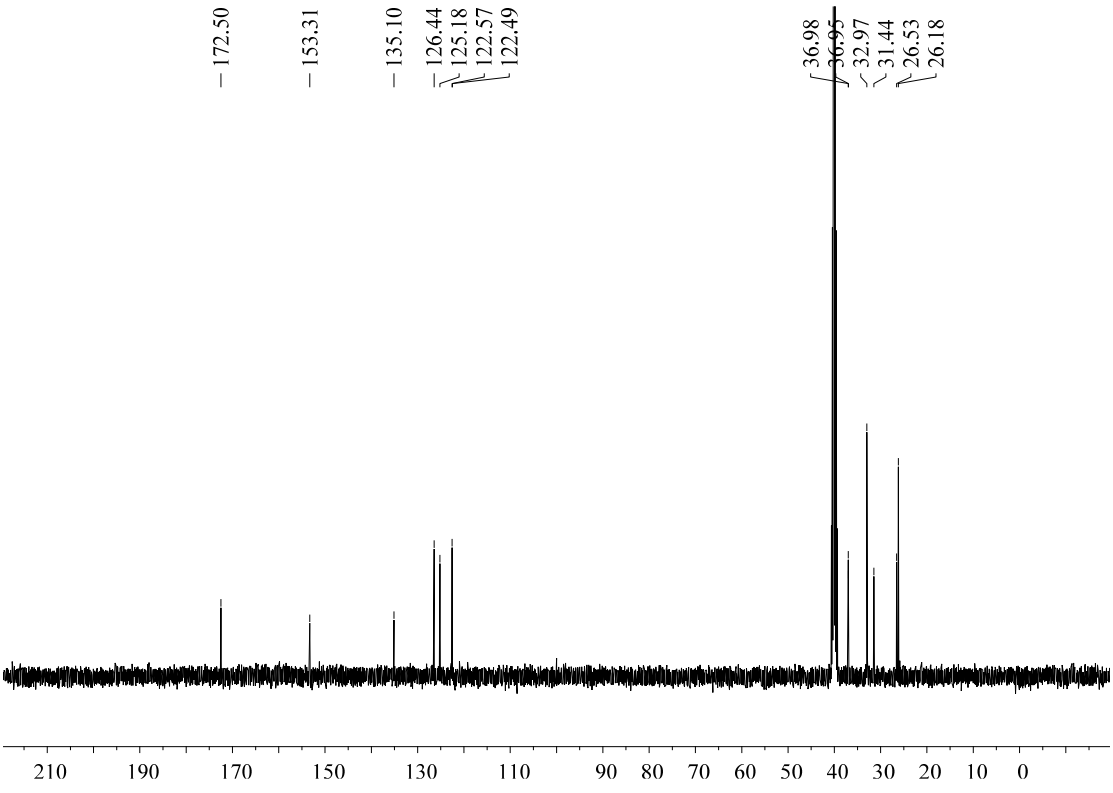
^{13}C NMR (101 MHz, DMSO-d_6) spectrum of compound 4i



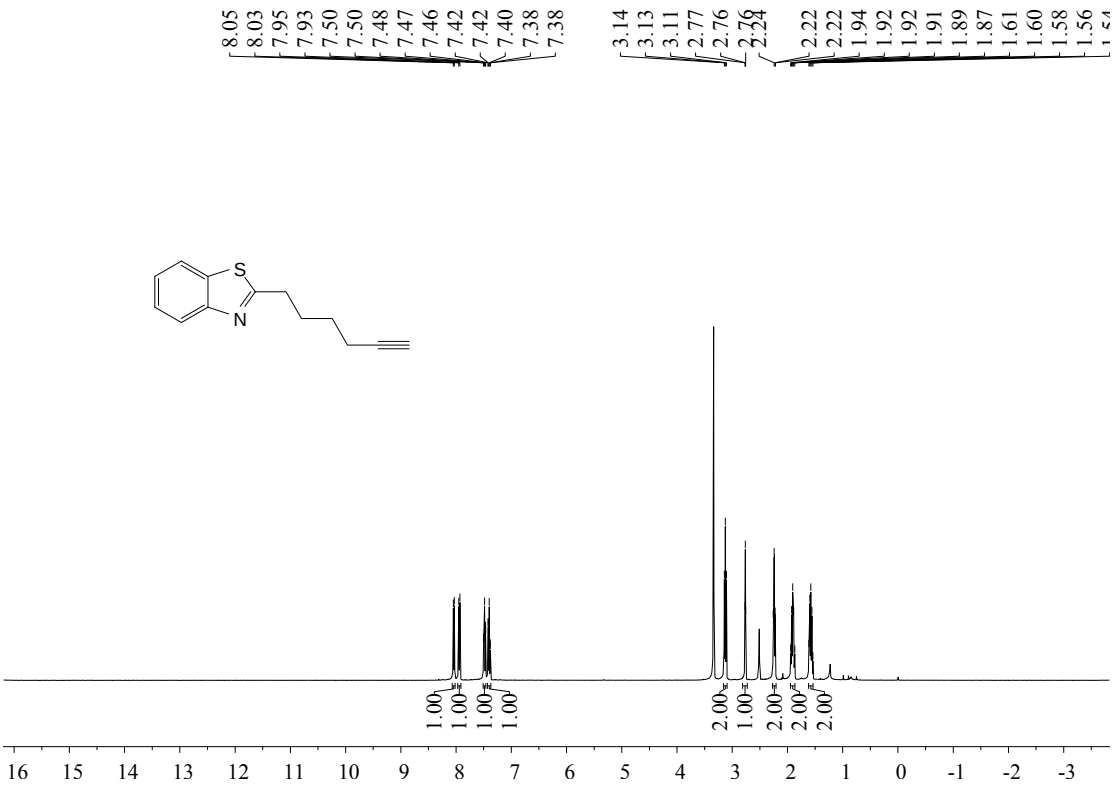
^{1}H NMR (400 MHz, DMSO-d_6) spectrum of compound 4j



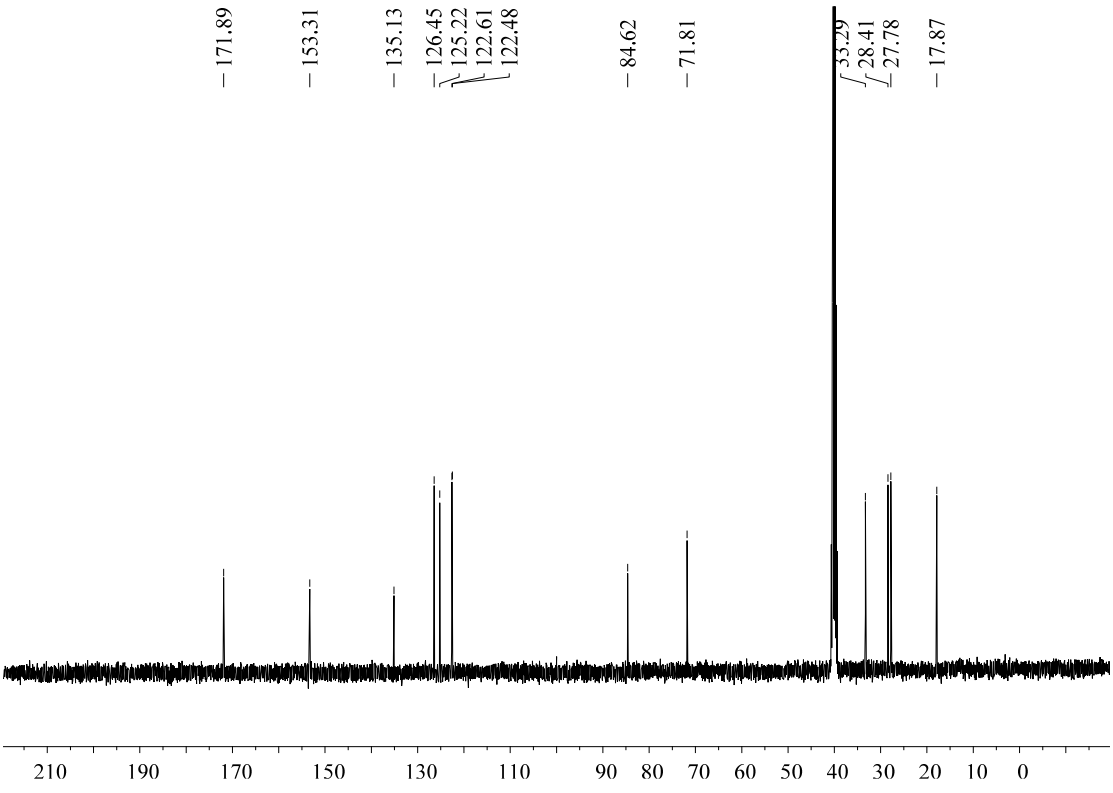
^{13}C NMR (101 MHz, DMSO-d_6) spectrum of compound 4j



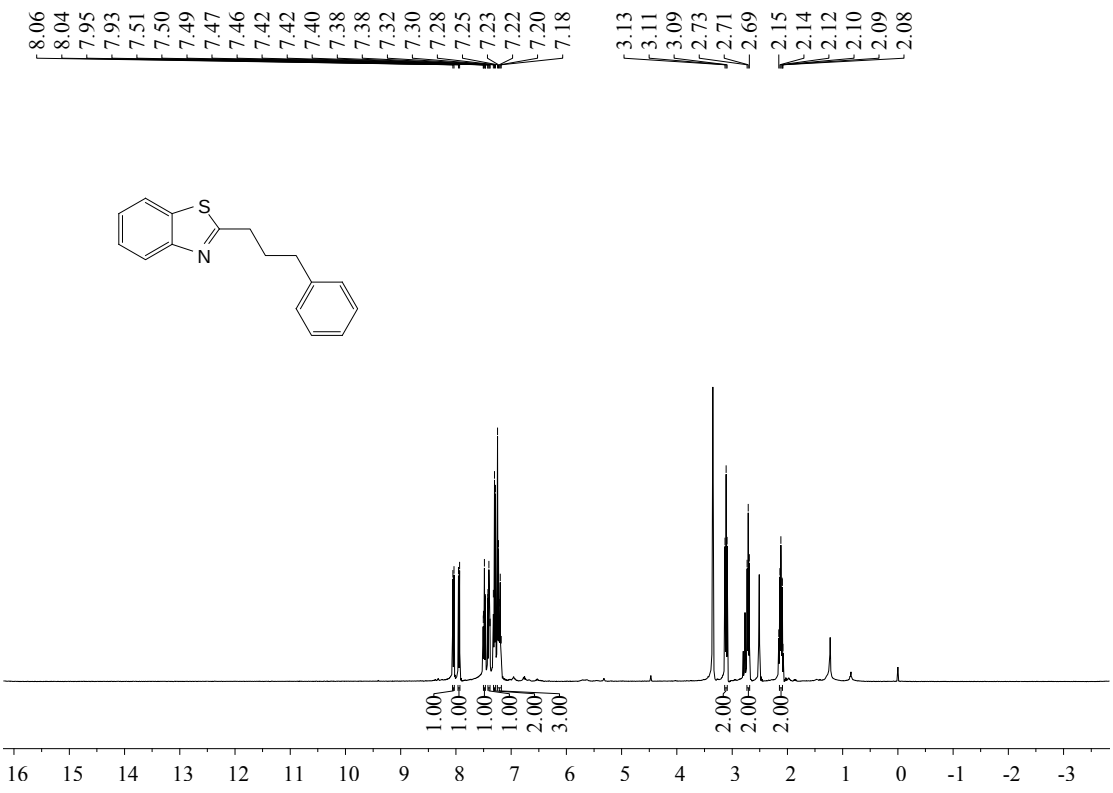
^{1}H NMR (400 MHz, DMSO-d_6) spectrum of compound 4k



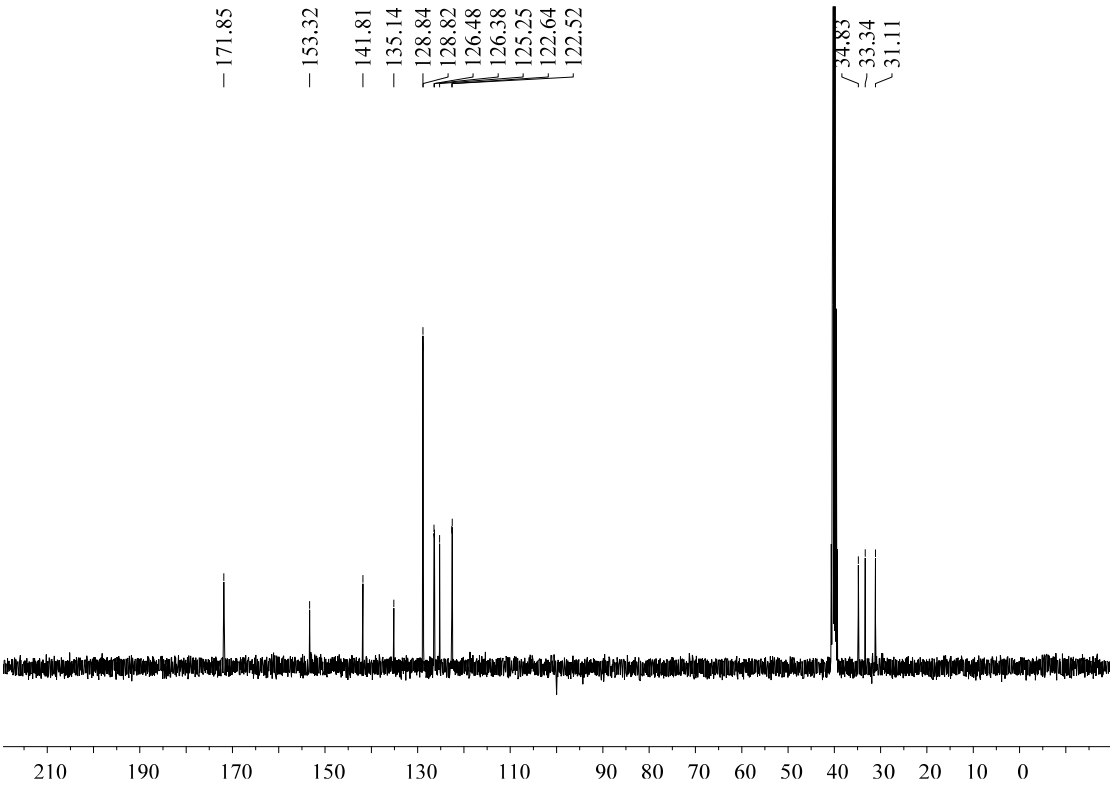
^{13}C NMR (101 MHz, DMSO-d_6) spectrum of compound 4k



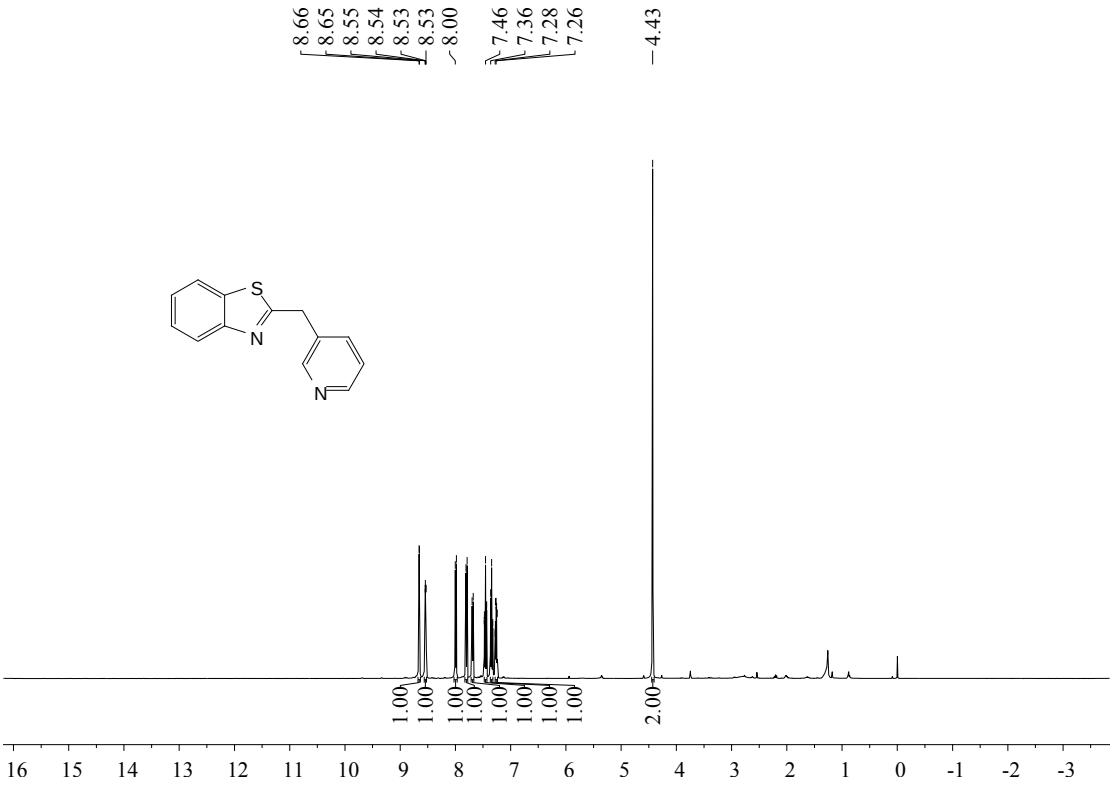
^{1}H NMR (400 MHz, DMSO-d_6) spectrum of compound 4l



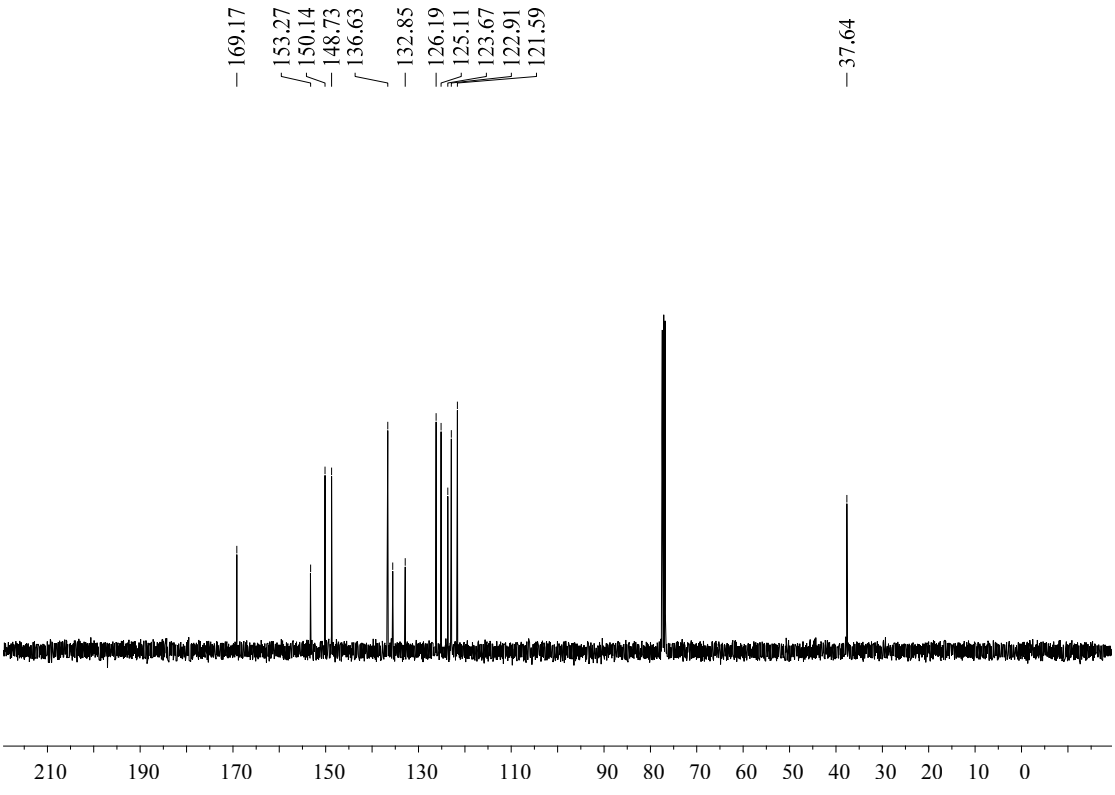
^{13}C NMR (101 MHz, DMSO-d_6) spectrum of compound 4l



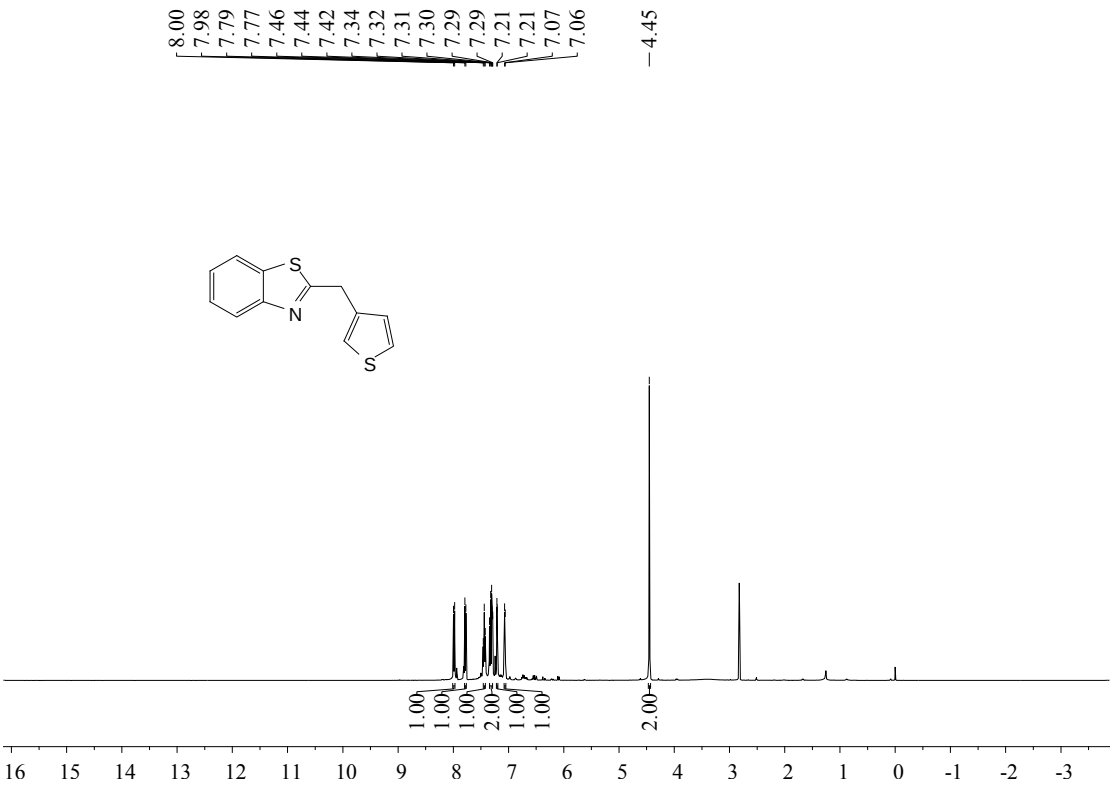
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 4m



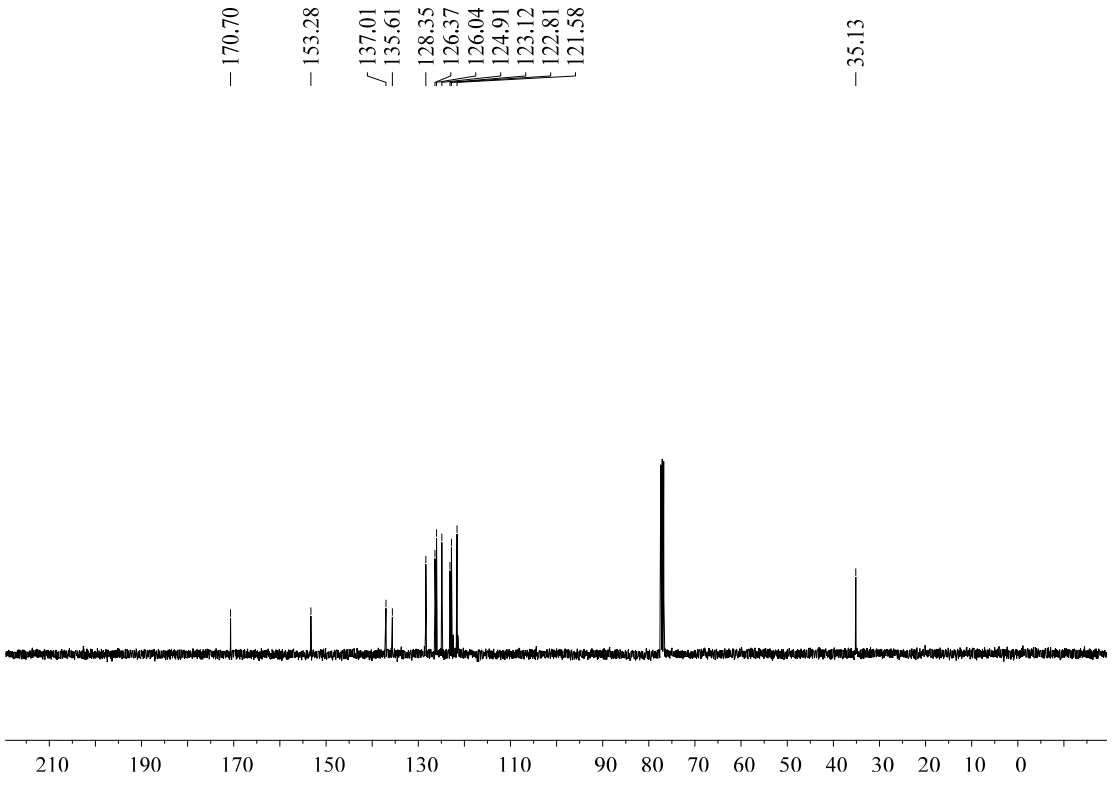
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound 4m



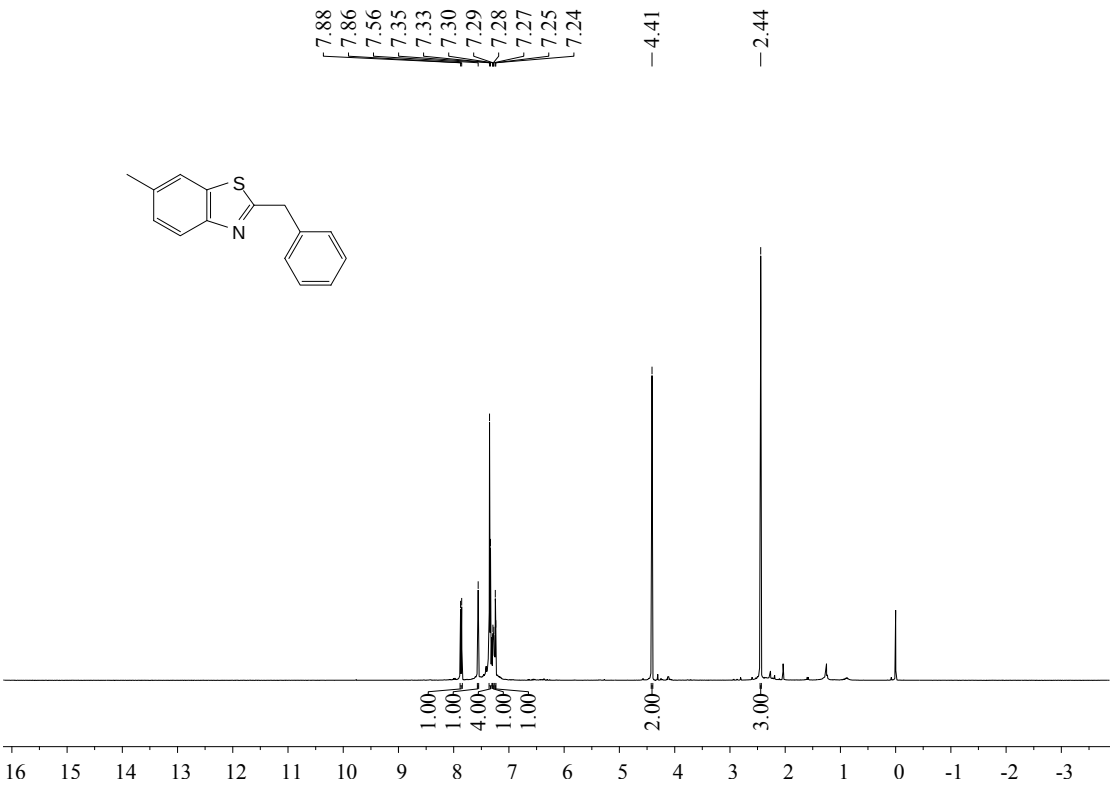
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 4n



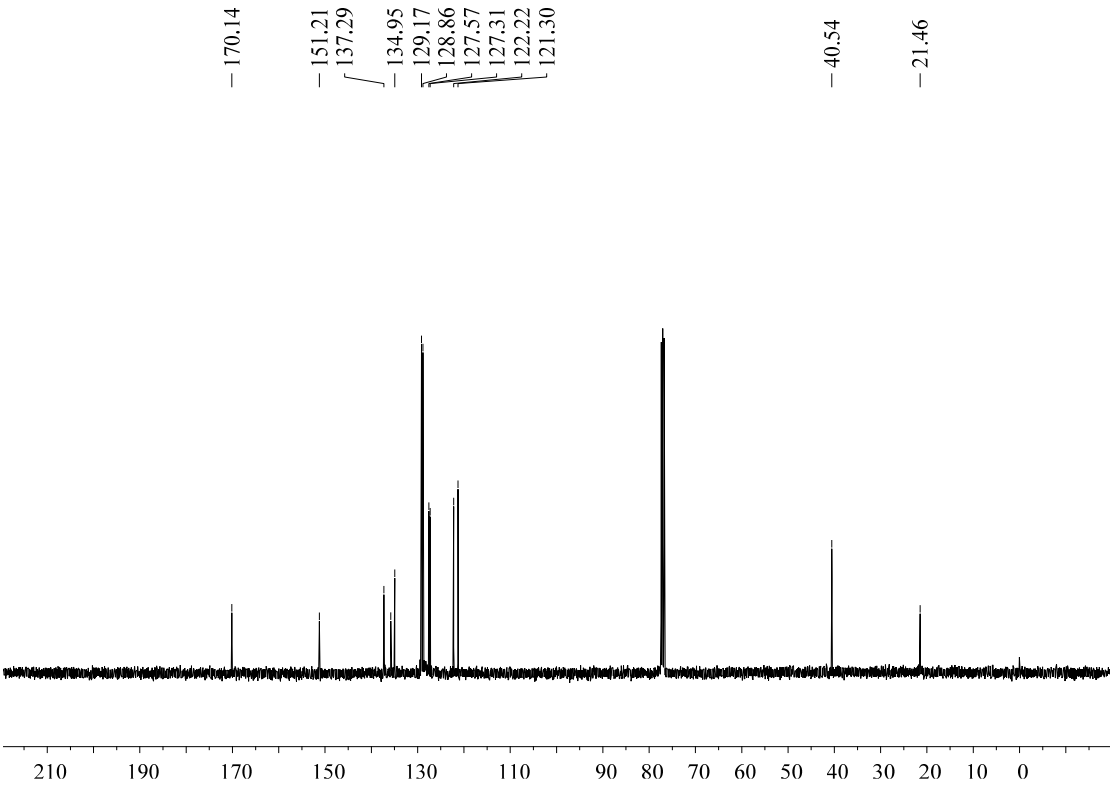
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound 4n



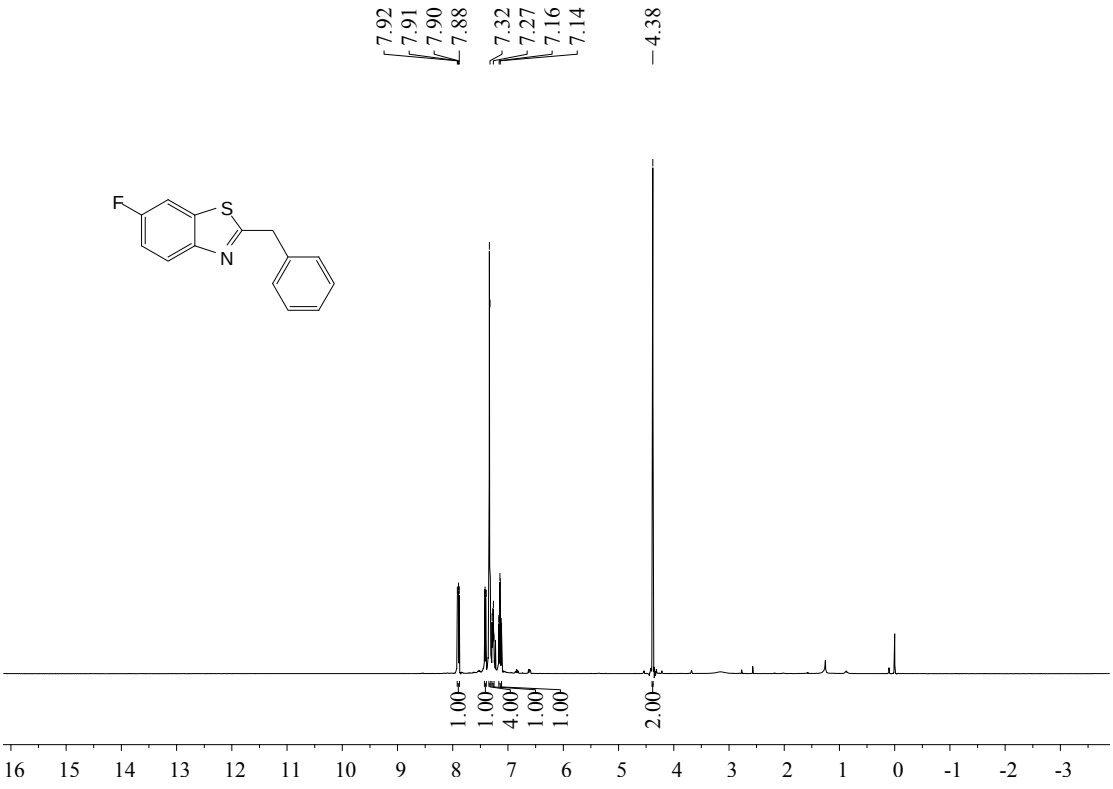
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 4o



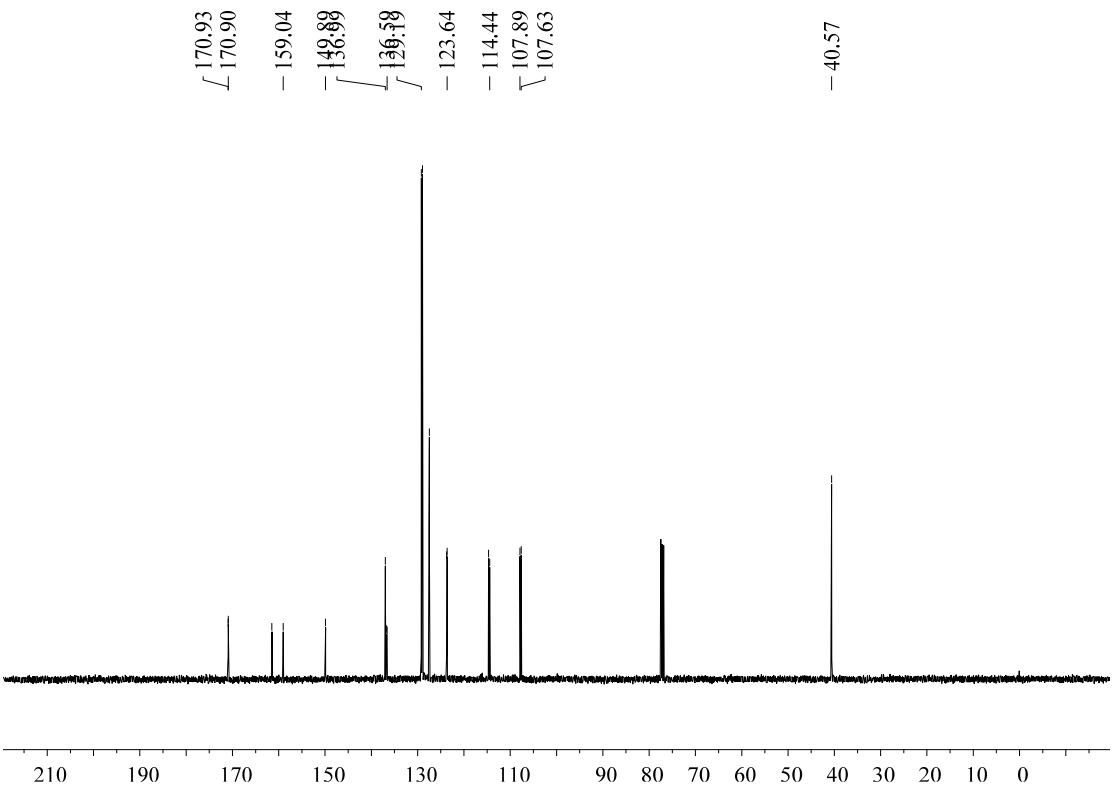
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound 4o



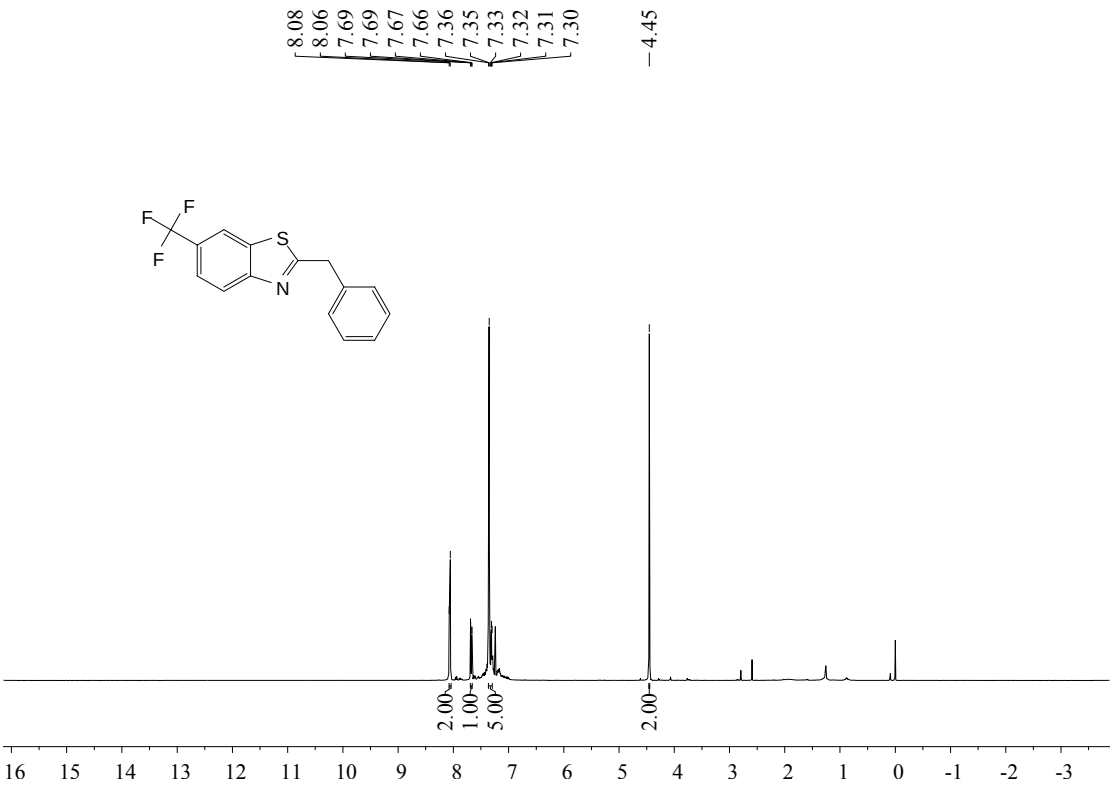
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 4p



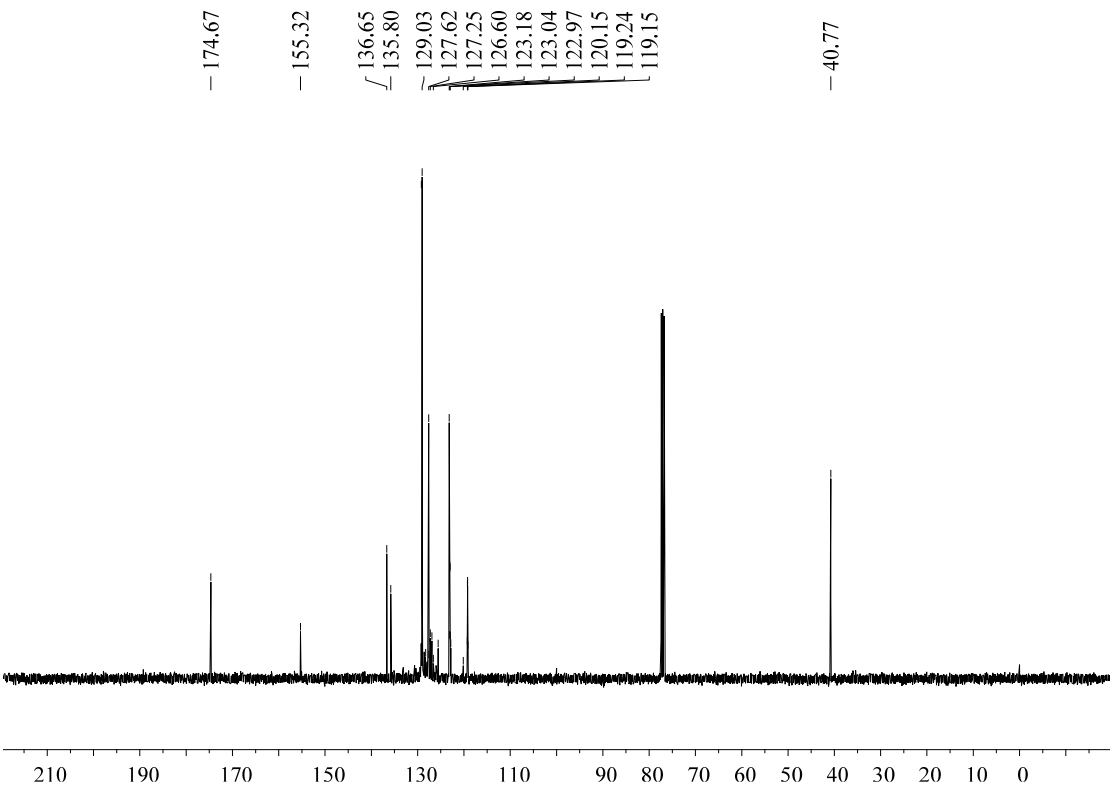
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound 4p



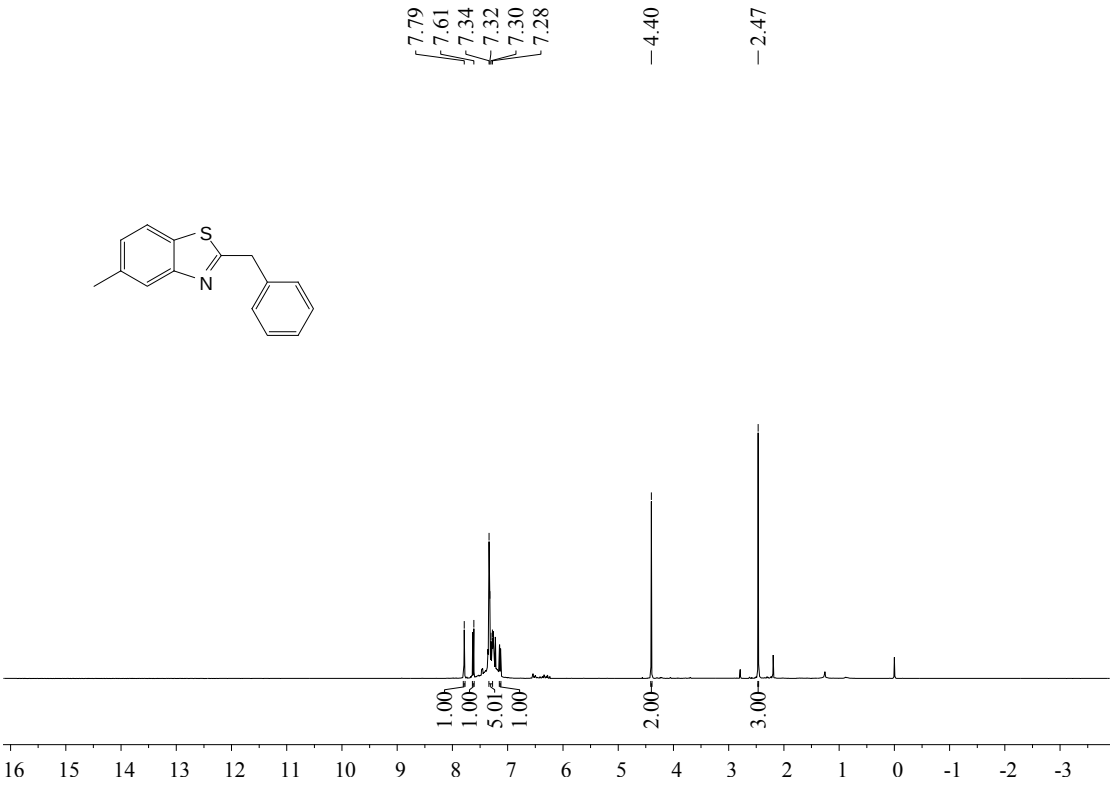
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 4q



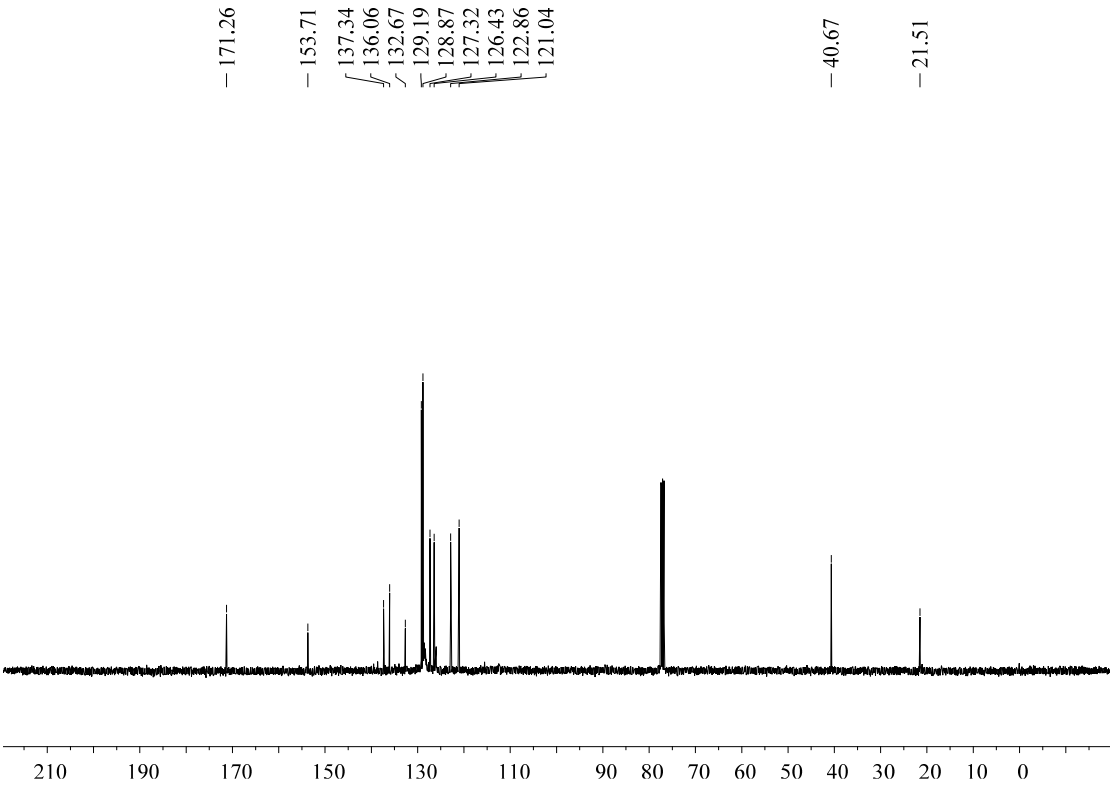
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound 4q



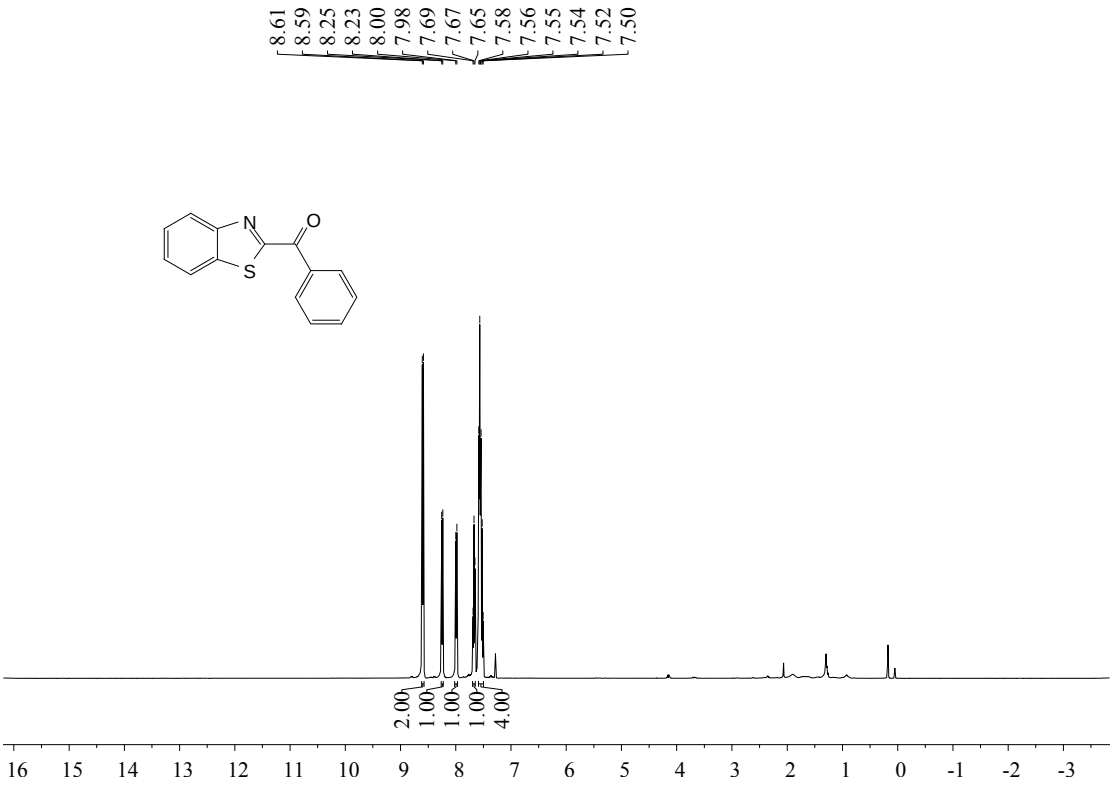
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 4r



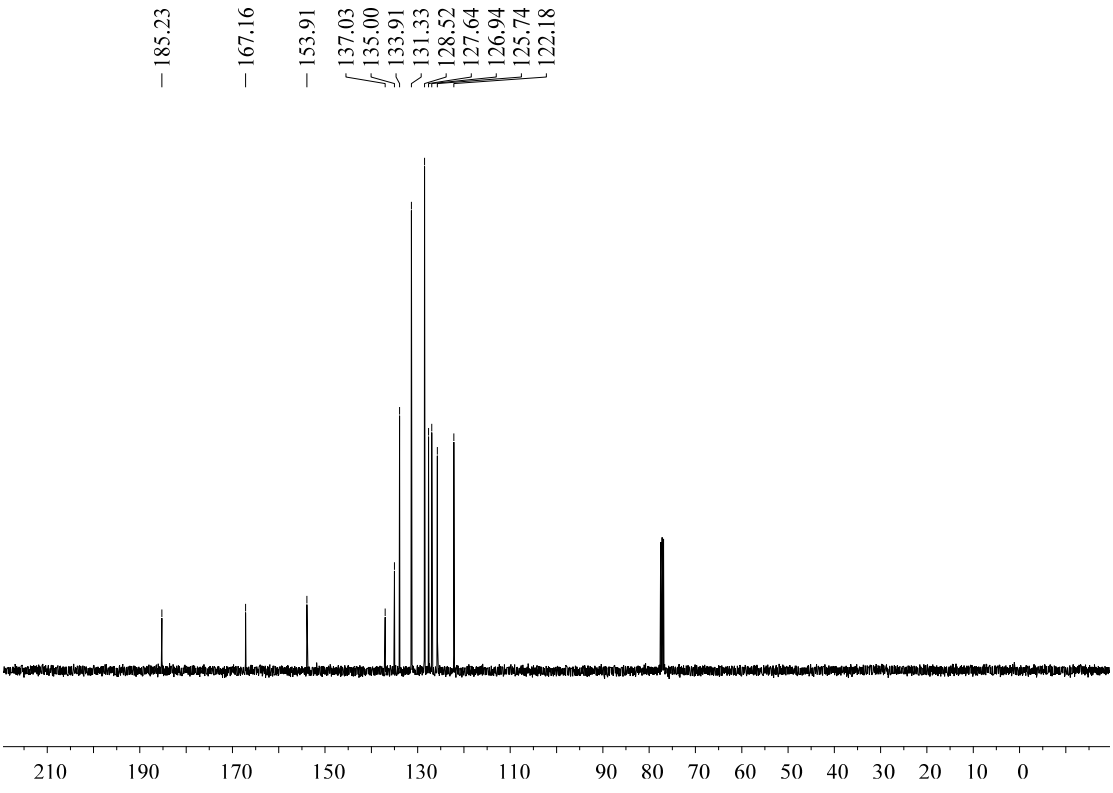
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound 4r



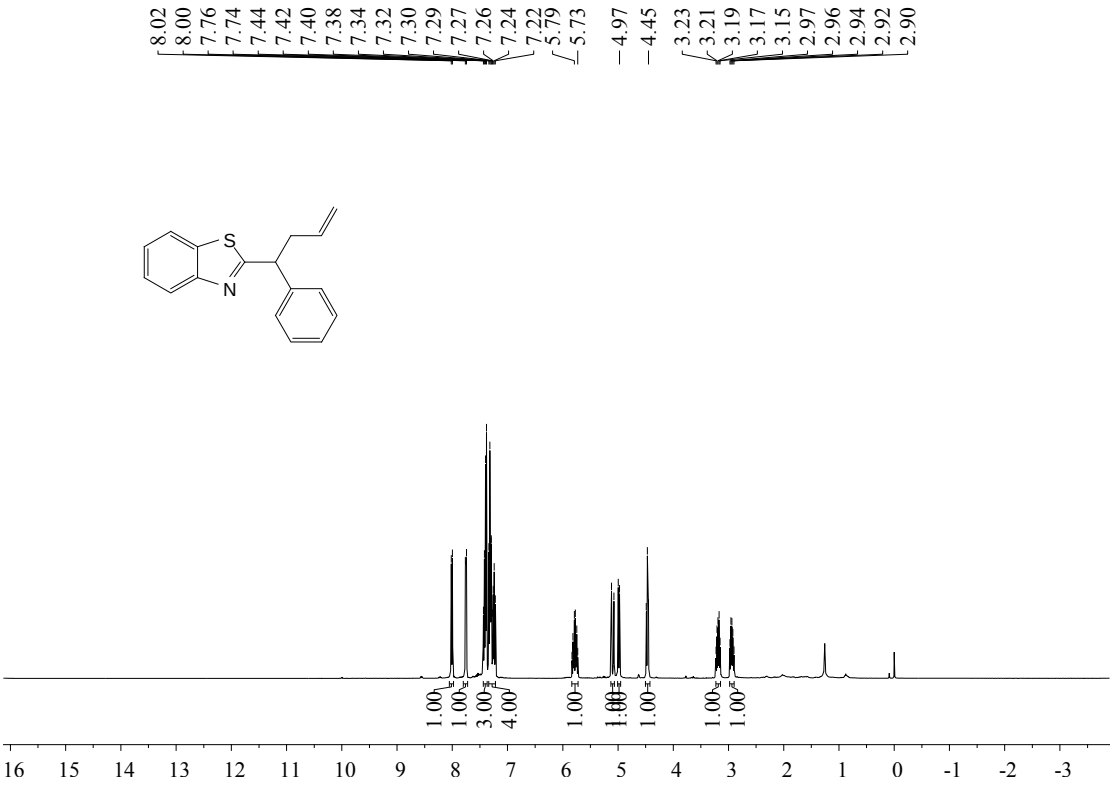
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 5



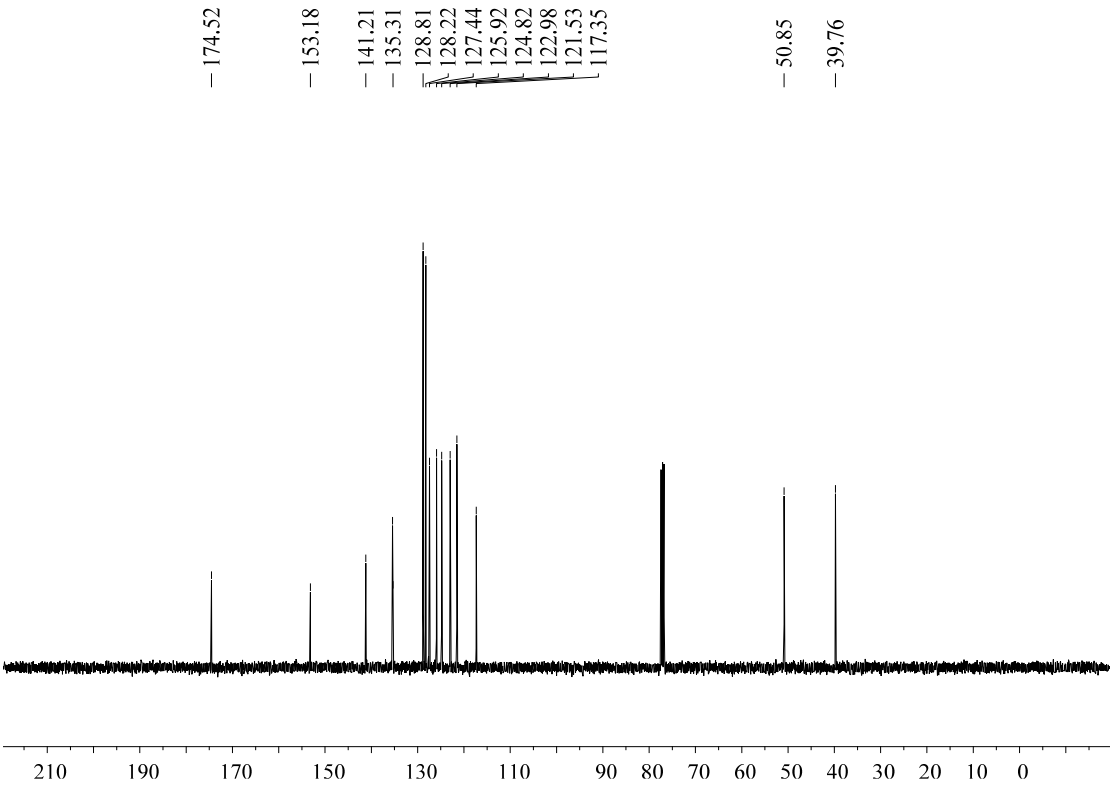
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound 5



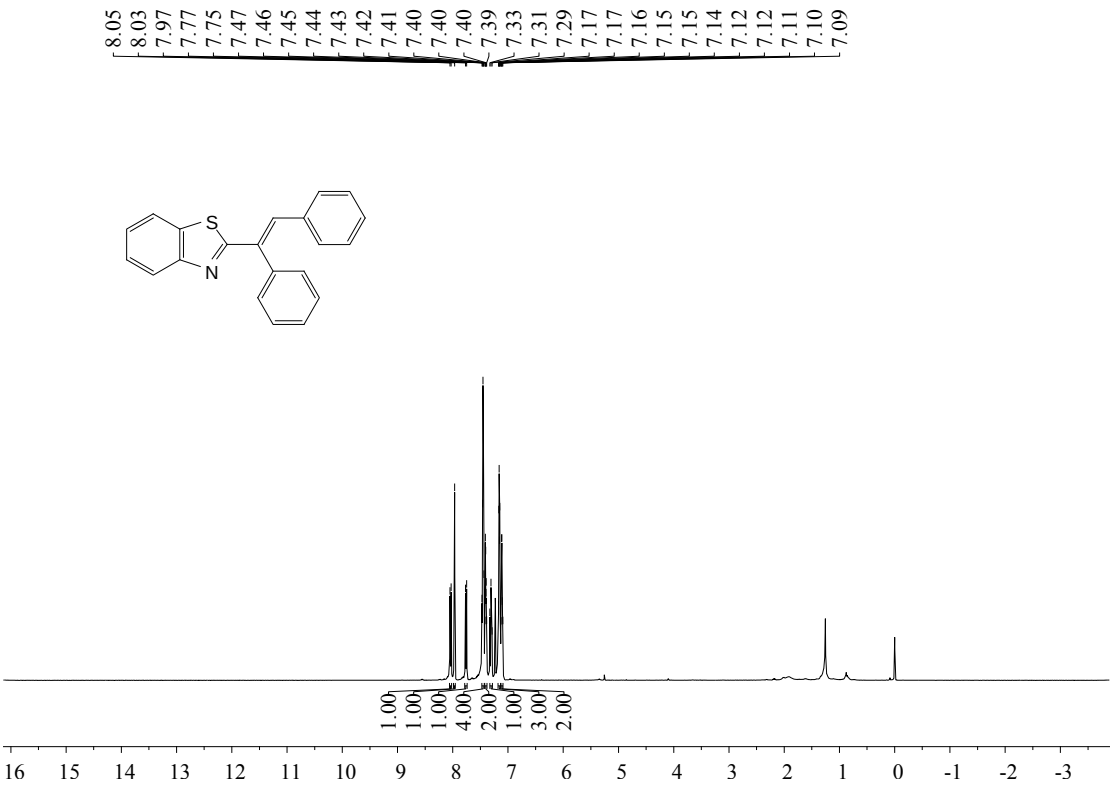
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 6



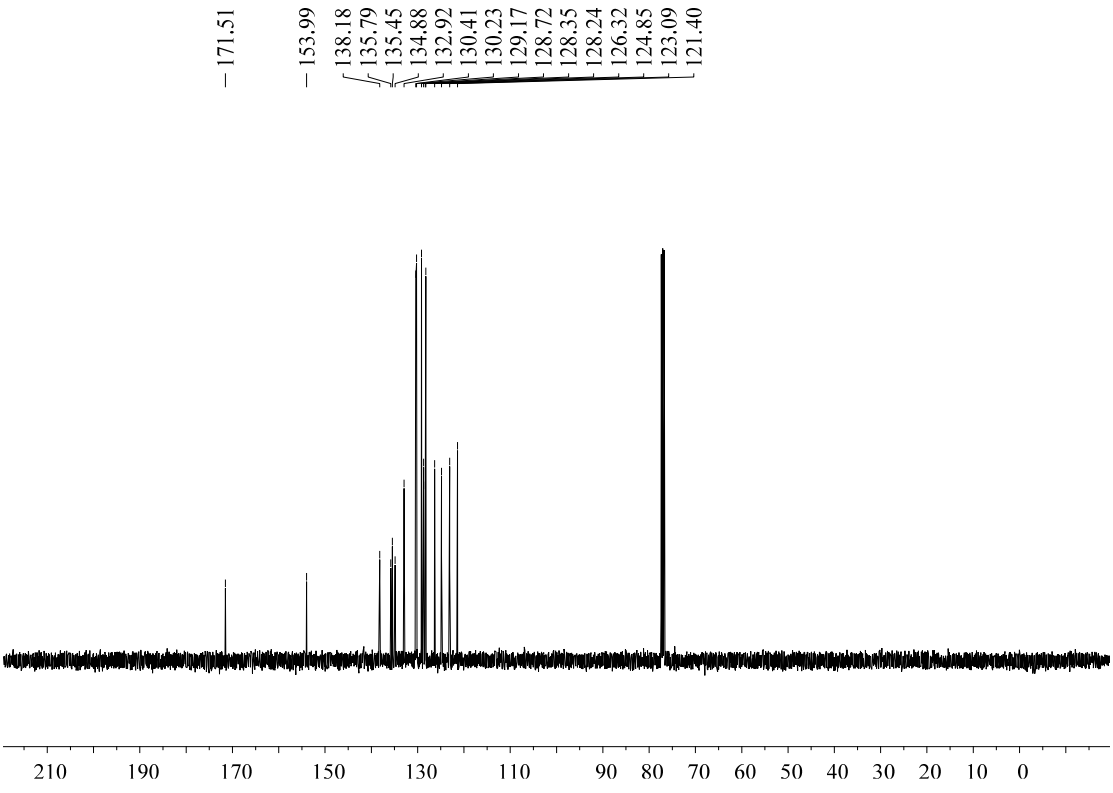
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound 6



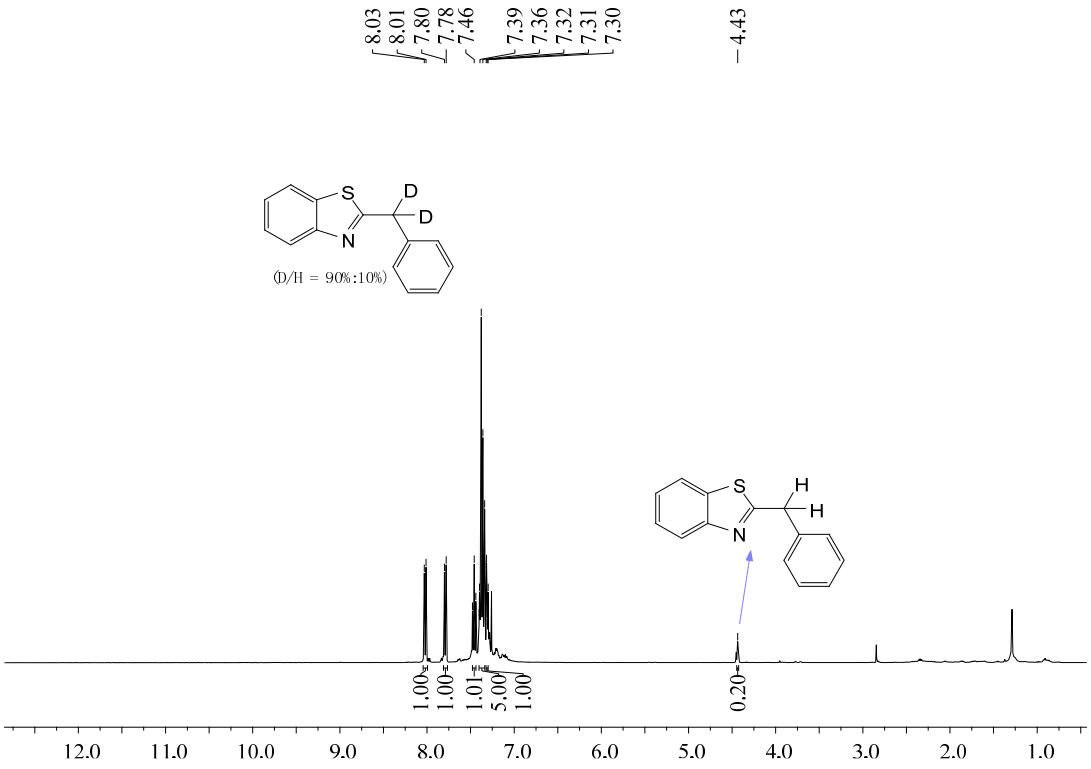
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 7



^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound 7



^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound d_2-4a



^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound d_2-4a