Supplementary Information (SI) for Organic & Biomolecular Chemistry.
This journal is © The Royal Society of Chemistry 2025

Supporting Information

Titanium-catalyzed Radical-type Deuteriodeboronation of Arylboronates

Zhihui Wang, Biao Ma, Haocong Li, Yiru Wang and Zhanyu Li*

Chemical Engineering and Resource Utilization, College of Chemistry, Northeast Forestry University, Harbin 150040, China. E-mail: Lizy567@nefu.edu.cn.

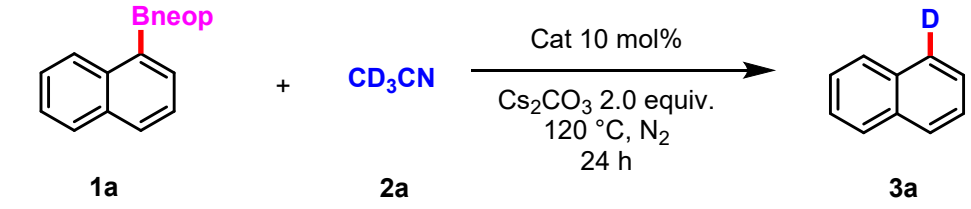
Table of contents

1. General information

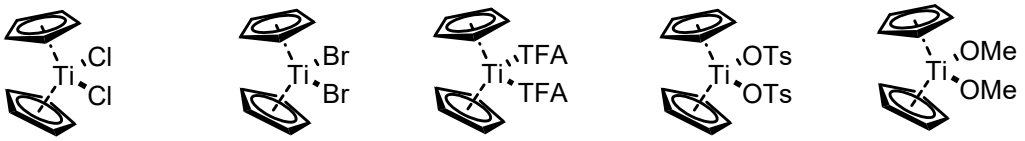
All experiments were performed under a nitrogen atmosphere unless otherwise noted. All solvents were purchased from the highest commercial grade and were not further purified. Further purification. Flash column chromatography was performed using silica gel (200-300 mesh). Thin layer chromatography (TLC) was performed using silica gel 60 F254 plates for thin layer chromatography. NMR spectra were recorded for ^{1}H NMR (500 MHz), ^{13}C NMR (126 MHz) using TMS as an internal standard and Bruker AV 500 as aninstrument and ^{1}H NMR (600 MHz), ^{13}C NMR (151 MHz) using TMS as an internal standard and Bruker AV 600 as aninstrument. Chemical shifts (ppm) were referenced to $CDCl_3$ (δ: 7.26 ppm) or DMSO-d_6 (δ: 2.50 ppm). Te ^{13}C NMR spectra were recorded by the same ^{13}C NMR spectra were obtained from the same NMR spectrometer and calibrated with $CDCl_3$ (δ: 77.00 ppm)or DMSO-d_6 (δ: 39.52 ppm). The abbreviations for NMR data were NMR data are abbreviated as s (singlet), d (doublet), t (triplet), q (quadruplet), quin (quintuplet), sxt (sextuplet). High-resolution mass spectra (HRMS) were obtained with Thermo Fisher Scientific Orbitrap Exploris 120 spectrometers. (Hetero)arylboronates **1a**-**1ak** were synthesised from the corresponding (hetero)arylboronic acids according to methods in the literature[1].

2. Optimization of the reaction condition

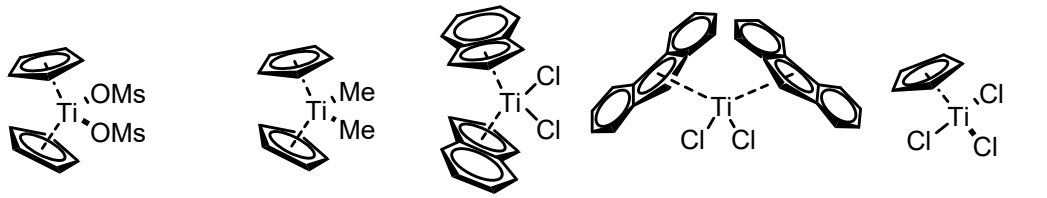
Table S1 Evaluation of catalysts.



1a **2a** **3a**



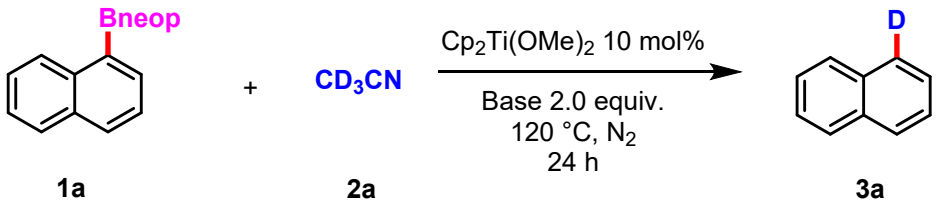
Cat 1 67% **Cat 2** 58% **Cat 3** 51% **Cat 4** 55% **Cat 5** 82%



Cat 6 55% **Cat 7** 41% **Cat 8** 43% **Cat 9** 59% **Cat 10** 62%

Reaction conditions: **1a** (0.2 mmol), **2a** (0.5 mL), Catalyst (10 mol%) and Cs_2CO_3 (2.0 equiv.) were stirred with 120 °C under N_2 for 24 h.

Table S2 Evaluation of different base.

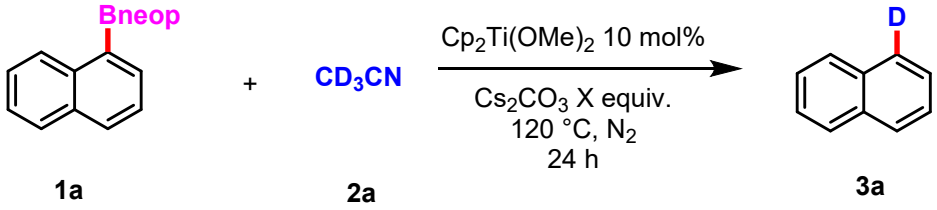


1a **2a** **3a**

Entry	Base	Yield/%
1	Cs_2CO_3	82
2	NaOH	67
3	K_2CO_3	51
4	K_3PO_4	75
5	CH_3OK	67
6	^tBuOK	63
7	CH_3ONa	59
8	DBU	trace
9	Et_3N	trace

Reaction conditions: **1a** (0.2 mmol), **2a** (0.5 mL), $Cp_2Ti(OMe)_2$ (10 mol%) and Base (2.0 equiv.) were stirred with 120 °C under N_2 for 24 h.

Table S3 Evaluation of different amount of base.

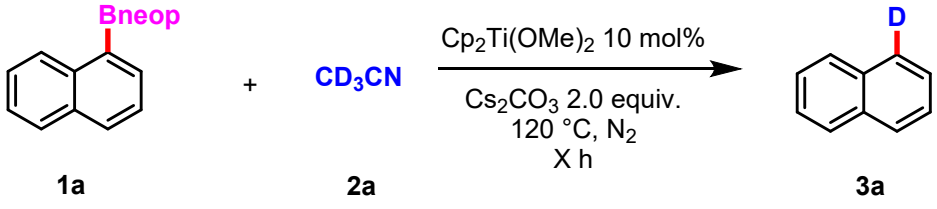


1a **2a** **3a**

Entry	X/equiv.	Yield/%
1	0.5	67
2	1	70
3	1.5	74
4	2	82
5	2.5	78

Reaction conditions: **1a** (0.2 mmol), **2a** (0.5 mL), $Cp_2Ti(OMe)_2$ (10 mol%) and Cs_2CO_3 (X equiv.) were stirred with 120 °C under N_2 for 24 h.

Table S4 Evaluation of different reaction times.

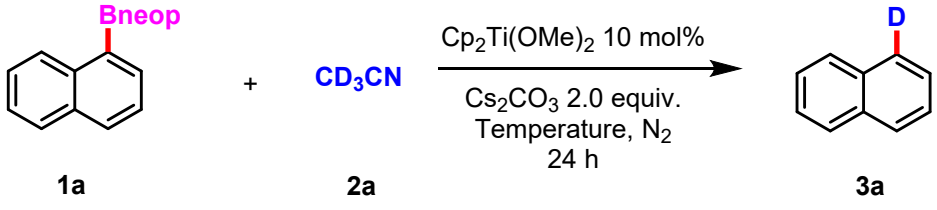


1a **2a** **3a**

Entry	X/h	Yield/%
1	4	21
2	12	48
3	16	70
4	24	82
5	36	82

Reaction conditions: **1a** (0.2 mmol), **2a** (0.5 mL), $Cp_2Ti(OMe)_2$ (10 mol%) and Cs_2CO_3 (2.0 equiv.) were stirred with 120 °C under N_2 for X h.

Table S5 Evaluate different reaction temperature.

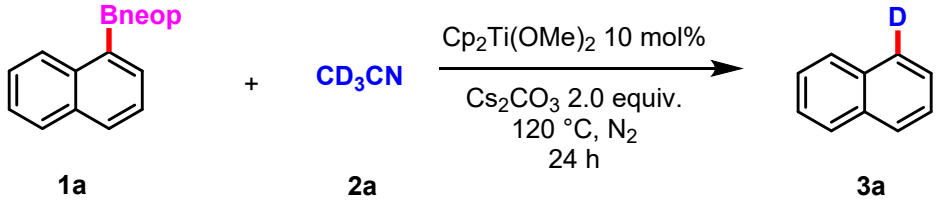


1a **2a** **3a**

Entry	Temperature/°C	Yield/%
1	120	82
2	100	70
3	80	33
4	50	N.R.

Reaction conditions: **1a** (0.2 mmol), **2a** (0.5 mL), $Cp_2Ti(OMe)_2$ (10 mol%) and Cs_2CO_3 (2.0 equiv.) were stirred under N_2 for 24 h.

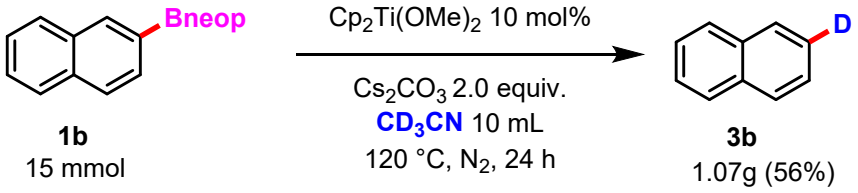
3. General steps in the titanium-catalysed arylboronate deuteriodeboronation reaction



A 10 mL Schlenk tube containing 1-naphthylboronate **1a** (0.2 mmol, 1.0 equiv.), $Cp_2Ti(OMe)_2$ (0.02 mmol, 10 mol%), Cs_2CO_3 (0.4 mmol, 2.0 equiv.), and deuterated acetonitrile **2a** (0.5 mL). The tube was then filled with N_2 and sealed. The reaction was placed on a magnetic stirrer at 120 °C for 24 h. Upon completion, the solvent was removed under reduced pressure and the product was separated by column chromatography to give product **3a** (20.9 mg, 82% yield, 99%D), which was analyzed by ^1H NMR to determine the deuterium incorporation rate.

4. Gram-scale synthesis and synthesis of deuterated methylduloxetine

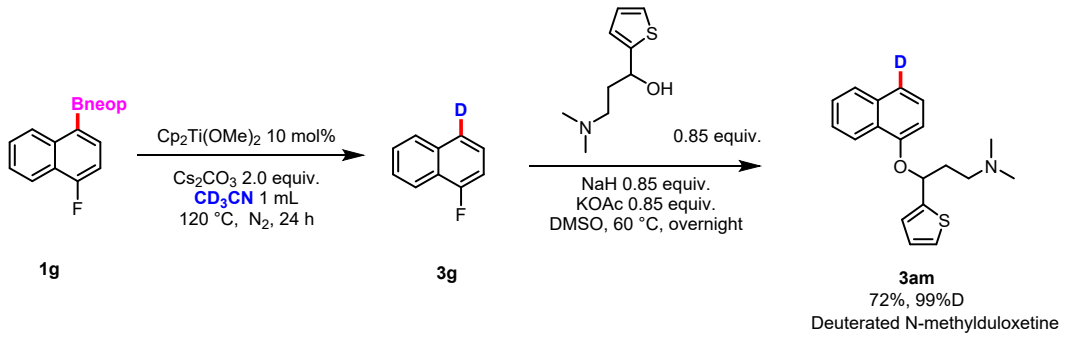
4.1 Gram-scale synthesis



A mixture of 2-naphthylboronate **1b** (3.6 g, 15 mmol, 1.0 equiv.), deuterated acetonitrile **2a** (10 mL), $Cp_2Ti(OMe)_2$ (0.36 g, 1.5 mmol, 10 mol%) and Cs_2CO_3 (9.77 g, 30 mmol, 2.0 equiv.) was prepared and stirred for 24 h at 120 °C under N_2. After completion of the reaction, the crude residue was concentrated under reduced pressure. Purification by column chromatography gave 1.07 g of crude residue, **3b** as a white

solid in 56% yield.

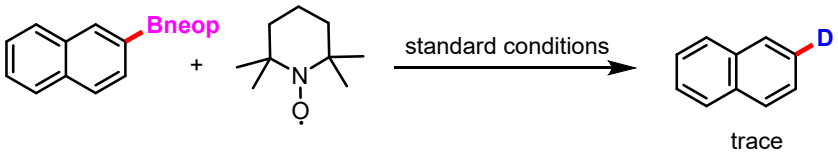
4.2 Synthesis of deuterated *N*-methylduloxetine



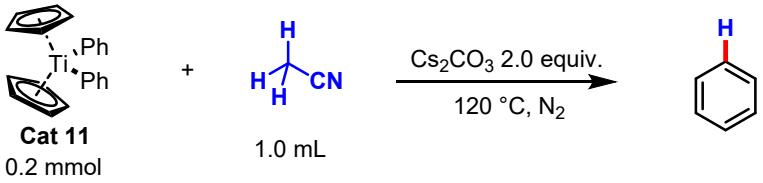
A mixture of 4-fluoro-1-naphthylboronate **1g** (129 mg, 0.5 mmol, 1.0 equiv.), CD_3CN (1 mL), $Cp_2Ti(OMe)_2$ (15 mg, 0.05 mmol, 10 mol%), and Cs_2CO_3 (326 mg, 1 mmol, 2.0 equiv.) was charged into a dried 10 mL Schlenk tube under nitrogen atmosphere. The system was evacuated and backfilled with N_2 (three cycles) before being immersed in a heating module at 120 °C for 24 h with vigorous stirring. After cooling to ambient temperature, volatiles were removed under reduced pressure. The residue was purified by flash column chromatography (petroleum ether/ethyl acetate 10:1) to afford **3g** (63 mg, 86% yield) as a colorless oil. In a dried 10 mL reaction tube, (S)-*N*,*N*-dimethyl-3-hydroxy-3-(2-thienyl)propanamine (37 mg, 0.2 mmol, 1.0 equiv.) was dissolved in anhydrous DMSO (2 mL). Sodium hydride (5 mg, 0.2 mmol, 1.0 equiv.) was added portionwise at room temperature. After stirring for 20 min, KOAc (19.6 mg, 0.2 mmol, 1.0 equiv.) was introduced, followed by an additional 15 min of stirring. Compound **3g** (29 mg, 0.24 mmol, 1.2 equiv.) was then added, and the reaction mixture was heated at 60 °C for 12 h. The cooled mixture was diluted with H_2O (10 mL) and adjusted to pH 5-6 with 1 M HCl. The aqueous layer was subsequently basified to pH 10-12 using 2 M NaOH and extracted with ethyl acetate (3 × 15 mL). The combined organic extracts were washed with brine (10 mL), dried over anhydrous $MgSO_4$, filtered, and concentrated in vacuo. Purification by column chromatography (10% methanol in dichloromethane) give the desired white solid product **3am** (52mg, 84%, 99%D). ^1H NMR (600 MHz, $CDCl_3$) δ: 8.37 (dd, J = 5.6,

4.0 Hz, 1H), 7.80–7.76 (m, 1H), 7.52–7.47 (m, 2H), 7.28 (dd, *J* = 7.8, 4.4 Hz, 1H), 7.21 (d, *J* = 4.7 Hz, 1H), 7.07 (d, *J* = 3.3 Hz, 1H), 6.94 (dd, *J* = 4.9, 3.7 Hz, 1H), 6.88 (d, *J* = 7.7 Hz, 1H), 5.79–5.76 (m, 1H), 2.54–2.49 (m, 2H), 2.49–2.42 (m, 1H), 2.26 (s, 6H), 2.20 (td, *J* = 13.2, 6.2 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ: 153.57, 145.41, 134.62, 127.54, 126.65, 126.40, 126.25, 125.75, 125.31, 124.82, 124.75, 122.30, 120.36(t, *J* = 24.16 Hz,), 107.15, 74.77, 55.88, 45.71, 37.14. Spectroscopic data in agreement with the literature[2].

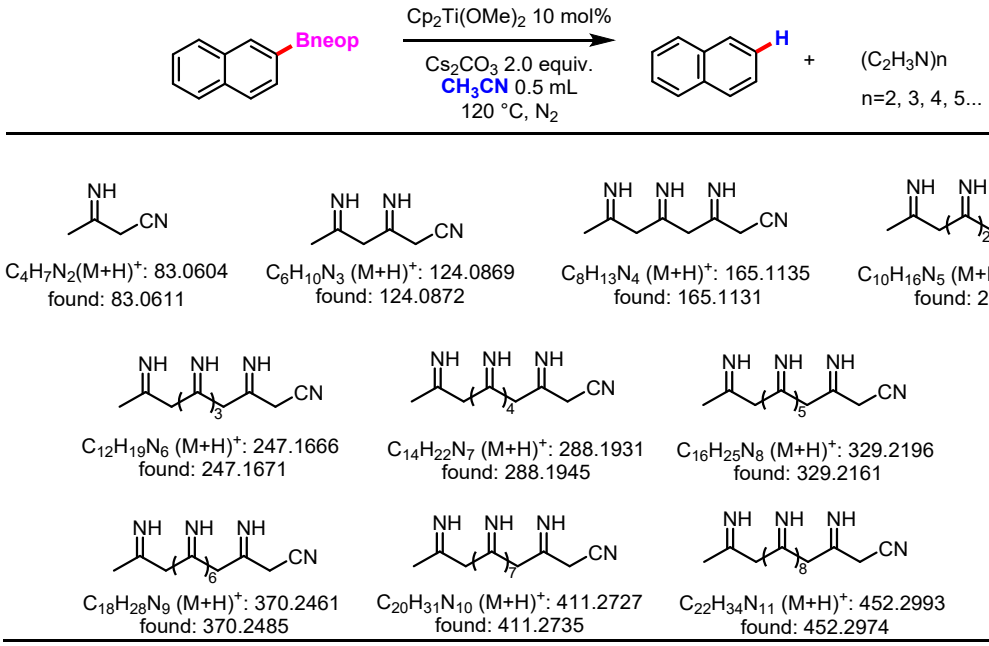
5. Mechanism Studies



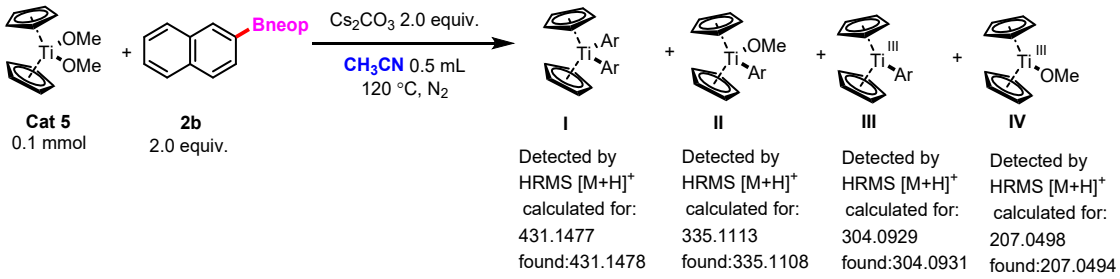
To a dried 10 mL Schlenk tube were added 2-naphthylboronate **1b** (0.048 g, 0.2 mmol, 1.0 equiv.), $Cp_2Ti(OMe)_2$ (0.005 g, 0.02 mmol, 10 mol%), Cs_2CO_3 (0.131 g, 0.4 mmol, 2.0 equiv.), TEMPO (0.0625 g, 0.4 mmol, 2.0 equiv.) and deuterated acetonitrile **2a** (0.5 mL). The reaction was placed on a magnetic stirrer at 120 °C for 24 h under N_2 atmosphere. After completion of the reaction the solvent was removed by vacuum concentration and the product was detected by TLC as trace.



To a dried 10 mL Schlenk tube was added catalyst **Cat 11** (0.066 g, 0.2 mmol, 1.0 equiv.), Cs_2CO_3 (0.131 g, 0.4 mmol, 2.0 equiv.) and CH_3CN (0.5 mL). The reaction was placed in a magnetic stirrer and stirred at 120 °C for 24 h under N_2 atmosphere. Upon completion of the reaction, the products of benzene were analyzed by HRMS in the reaction mixture. HRMS (ESI-TOF, m/z) Calcd for C_6H_7 $(M+H)^+$: 79.0542, found: 79.0549.

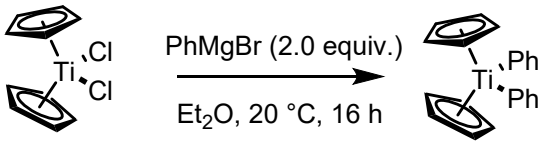


To a dried Schlenk tube, add compound **2a** (0.048 g, 0.2 mmol, 1.0 equiv.), $Cp_2Ti(OMe)_2$ (0.005 g, 0.02 mmol, 10 mol%), and Cs_2CO_3 (0.131 g, 0.4 mmol, 2.0 equiv.) followed by CH_3CN (0.5 mL). The reaction mixture was stirred under a N_2 atmosphere at 120 °C for 24 h using a magnetic stirrer. After the reaction, we performed HRMS analysis of the reaction mixture of the template reaction and detected the product of protonation of the acetonitrile radical with the acetonitrile titanium intermediate after ten consecutive additions of the imine.



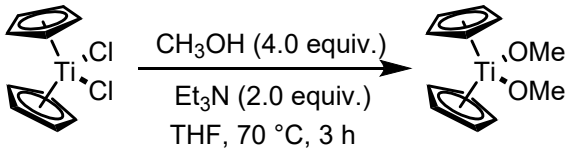
To a dried Schlenk tube, add compound **2b** (0.048 g, 0.2 mmol, 2.0 equiv.), $Cp_2Ti(OMe)_2$ (0.025 g, 0.1 mmol), and Cs_2CO_3 (0.131 g, 0.4 mmol, 2.0 equiv.) followed by CH_3CN (0.5 mL). The reaction mixture was stirred under a N_2 atmosphere at 120 °C for 24 h using a magnetic stirrer. After the reaction, we performed HRMS analysis of the reaction mixture for the template reaction and detected products of intermediates I II III IV.

6. Synthesis of catalysts and catalyst intermediate



Cat 1 **Cat 11**

Cp_2TiCl_2 (**Cat 1**) (0.248 g, 1.0 mmol, 1.0 equiv.) was placed in a dry three-necked flask, 25 mL of anhydrous Et_2O was added under N_2 atmosphere, and PhMgBr (0.71 mL, 2.8 M in 2-MeTHF, 2.0 mmol, 2.0 equiv.) was added slowly at 20 °C. The reaction lasted for 15 min. and resulted in a pale yellow solution. Then 0.5 mL of anhydrous 1,4-dioxane was added and a white solid was formed immediately and stirring was continued for 16 h. At the end of the reaction, the solid was washed with toluene. After filtration, the filtrate was concentrated and dried under vacuum to give orange crystals **Cat 11** (Yield: 88%). ^{1}H NMR (600 MHz, $CDCl_3$) δ: 6.98 (dd, J = 10.1, 4.5, 4H), 6.91–6.87 (m, 6H), 6.21 (s, 10H). ^{13}C NMR (151 MHz, $CDCl_3$) δ: 191.07, 134.81, 126.38, 123.56, 115.75.



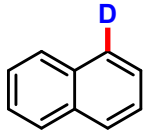
Cat 1 **Cat 5**

A dry three-necked flask was charged with Cp_2TiCl_2 (**Cat 1**) (0.497 g, 2.0 mmol, 1.0 equiv.) under N_2 atmosphere. Anhydrous THF (25 mL) was introduced via syringe, followed by sequential dropwise addition of CH_3OH (0.256 g, 8.0 mmol, 4.0 equiv.) and Et_3N (0.405 g, 4.0 mmol, 2.0 equiv.) at 25 °C, and the reaction was stirred for 3 h at 70 °C. At the end of the reaction, the solid was washed with anhydrous THF and the solvent was concentrated and dried in vacuum to give an orange solid **Cat 5** (Yield: 82%). ^{1}H NMR (600 MHz, $CDCl_3$) δ: 5.93 (s, 10H), 3.87 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ: 112.05, 65.95.

All remaining titanium-related catalysts were obtained by the general procedure described in the published article[3].

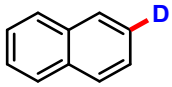
7. Experimental procedures and characterization of the products

naphthalene-1-d(**3a**)



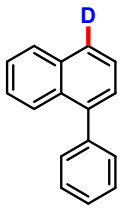
Following the general procedure described above, the reaction of **1a** (0.2 mmol, 48 mg), Cs_2CO_3 (0.4 mmol, 131 mg) was reacted with deuterated acetonitrile (0.5 mL) to give a white solid **3a** (21 mg, 82% yield, 99%D). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.86 (dd, J = 5.7, 3.7 Hz, 3H), 7.53–7.44 (m, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ: 133.50, 133.44, 127.95, 127.91, 127.63 (t, J = 25.2 Hz), 125.89, 125.78. Spectroscopic data in agreement with the literature[4].

naphthalene-2-d(**3b**)



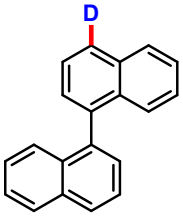
Following the general procedure described above, the reaction of **1b** (0.2 mmol, 48 mg) Cs_2CO_3 (0.4 mmol, 131 mg) was reacted with deuterated acetonitrile (0.5 mL) to give a white solid **3b** (18 mg, 71% yield, 90%D). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.86 (dd, J = 5.8, 3.2 Hz, 4H), 7.50 (dd, J = 6.3, 3.2 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ: 133.51, 127.96, 127.84, 125.89, 125.80, 125.44(t, J = 22.68 Hz). Spectroscopic data in agreement with the literature[4].

1-phenylnaphthalene-4-d(**3c**)



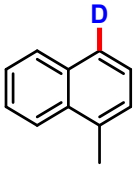
Following the general procedure described above, the reaction of **1c** (0.2 mmol, 64 mg) Cs_2CO_3 (0.4 mmol, 131 mg) was reacted with deuterated acetonitrile (0.5 mL) to give a colorless oil **3c** (35 mg, 85% yield, 69%D). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.93 (d, *J* = 8.6 Hz, 2H), 7.56–7.49 (m, 6H), 7.45 (dt, *J* = 8.1, 4.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ: 140.81, 140.29, 133.76, 131.64, 130.12, 128.30, 128.25, 127.54, 127.27 (t, *J* = 12.6 Hz), 126.96, 126.07, 126.06, 125.80, 125.30. HRMS (ESI-TOF, m/z) Calcd for $C_{16}H_{12}D$ $(M+H)^+$: 206.1074, found: 206.1049.

1,1'-binaphthalene-4-d(**3d**)



Following the general procedure described above, the reaction of **1d** (0.2 mmol, 73 mg) Cs_2CO_3 (0.4 mmol, 131 mg) was reacted with deuterated acetonitrile (0.5 mL) to give a white solid **3d** (48 mg, 94% yield, 97%D). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.97 (dd, *J* = 8.2, 4.1 Hz, 3H), 7.64–7.59 (m, 2H), 7.50 (dd, *J* = 16.6, 7.1 Hz, 4H), 7.42 (d, *J* = 8.4 Hz, 2H), 7.34–7.28 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ: 138.50, 138.49, 133.56, 133.48, 132.89, 128.18, 128.13, 127.93, 127.87, 127.60 (t, *J* = 25.2 Hz), 126.60, 126.01, 125.84, 125.42, 125.29. HRMS (ESI-TOF, m/z) Calcd for $C_{20}H_{14}D$ $(M+H)^+$: 256.1231, found: 256.1260.

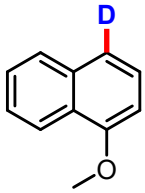
1-methylnaphthalene-4-d(**3e**)



Following the general procedure described above, the reaction of **1e** (0.2 mmol, 51 mg), Cs_2CO_3 (0.4 mmol, 131 mg) were reacted with deuterated acetonitrile (0.5 mL)

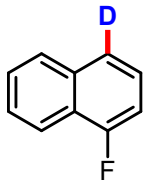
to give a white solid **3e** (22 mg, 79% yield, 94%D). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.02 (d, *J* = 8.4 Hz, 1H), 7.87 (d, *J* = 7.8 Hz, 1H), 7.57–7.48 (m, 2H), 7.39 (d, *J* = 6.9 Hz, 1H), 7.34 (d, *J* = 6.9 Hz, 1H), 2.72 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ: 134.29, 133.49, 132.61, 128.49, 126.58, 126.07 (t, *J* = 25.2 Hz), 125.73, 125.56, 125.47, 124.14, 19.43. Spectroscopic data in agreement with the literature[4].

1-methoxynaphthalene-4-d(**3f**)



Following the general procedure described above, the reaction of **1f** (0.2 mmol, 54 mg), Cs_2CO_3 (0.4 mmol, 131 mg) were reacted with deuterated acetonitrile (0.5 mL) to give a white solid **3f** (25 mg, 79% yield, 99%D). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.30–8.26 (m, 1H), 7.84–7.80 (m, 1H), 7.53–7.48 (m, 2H), 7.40 (d, *J* = 7.6 Hz, 1H), 6.83 (d, *J* = 7.6 Hz, 1H), 4.02 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ: 155.46, 134.42, 127.42, 126.41, 125.89, 125.76, 125.20, 121.99, 120.24, 119.94 (t, *J* = 25.2 Hz), 103.78, 55.53. Spectroscopic data in agreement with the literature[5].

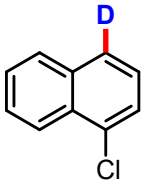
1-fluoronaphthalene-4-d(**3g**)



Following the general procedure described above, the reaction of **1g** (0.2 mmol, 52 mg), Cs_2CO_3 (0.4 mmol, 131 mg) were reacted with deuterated acetonitrile (0.5 mL) to give a colorless oil **3g** (25 mg, 86% yield, 99%D). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.13 (dd, *J* = 5.5, 3.9 Hz, 1H), 7.91–7.84 (m, 1H), 7.59–7.52 (m, 2H), 7.44–7.38 (m, 1H), 7.16 (dd, *J* = 10.6, 7.7 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ: 158.82(d, *J* = 252 Hz), 134.82 (d, *J* = 5.04 Hz), 127.49 (d, *J* = 2.52 Hz), 126.85, 126.19 (d, *J* = 1.26

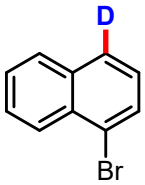
Hz), 125.52 (d, J = 2.52 Hz), 123.66, 123.37 (t, J = 25.2 Hz), 120.55 (d, J = 5.04 Hz), 109.36 (d, J = 20.16 Hz). Spectroscopic data in agreement with the literature[4].

1-chloronaphthalene-4-d(**3h**)



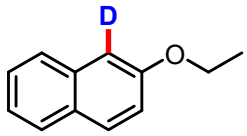
Following the general procedure described above, the reaction of **1h** (0.2 mmol, 55 mg), Cs_2CO_3 (0.4 mmol, 131 mg) were reacted with deuterated acetonitrile (0.5 mL) to give a colorless oil **3h** (30 mg, 94% yield, 89%D). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.29 (d, J = 8.4 Hz, 1H), 7.87 (d, J = 8.2 Hz, 1H), 7.64–7.53 (m, 3H), 7.40 (dd, J = 7.4, 4.5 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ: 131.94, 130.82, 128.24, 128.19, 127.18, 126.87 (t, J = 23.94 Hz), 126.18, 125.74, 125.62, 124.43. Spectroscopic data in agreement with the literature[6].

1-bromonaphthalene-4-d(**3i**)



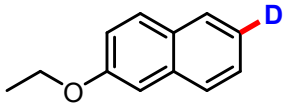
Following the general procedure described above, the reaction of **1i** (0.2 mmol, 64 mg), Cs_2CO_3 (0.4 mmol, 131 mg) were reacted with deuterated acetonitrile (0.5 mL) to give a colorless oil **3i** (39 mg, 97% yield, 98%D). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.25 (d, J = 8.5 Hz, 1H), 7.85 (d, J = 8.1 Hz, 1H), 7.79 (d, J = 7.4 Hz, 1H), 7.60 (d, J = 7.5 Hz, 1H), 7.54 (t, J = 7.5 Hz, 1H), 7.33 (d, J = 7.4 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ: 134.59, 132.02, 129.93, 128.29, 127.64 (t, J = 25.2 Hz), 127.36, 127.13, 126.73, 126.10, 122.84. Spectroscopic data in agreement with the literature[7].

2-ethoxynaphthalene-1-d(**3j**)



Following the general procedure described above, the reaction of **1j** (0.2 mmol, 57 mg), Cs_2CO_3 (0.4 mmol, 131 mg) were reacted with deuterated acetonitrile (0.5 mL) to give a colorless oil **3j** (33 mg, 97% yield, 50%D). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.79–7.72 (m, 3H), 7.47–7.42 (m, 1H), 7.34 (t, *J* = 7.5 Hz, 1H), 7.18–7.14 (m, 2H), 4.16 (q, *J* = 7.0 Hz, 2H), 1.50 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ: 156.95 (CH), 156.90 (CD), 134.65 (CH), 134.58 (CD), 129.37 (CH), 129.36 (CD), 128.93 (CH), 128.92 (CD), 127.67 (CH/CD), 126.74 (CH), 126.68 (CD), 126.32 (CH/CD), 123.52 (CH/CD), 119.04 (CH/CD), 106.57 (CH), 106.26 (t, *J* = 25.2 Hz, CD), 63.47 (CH/CD), 14.86 (CH/CD). HRMS (ESI-TOF, m/z) Calcd for $C_{12}H_{12}DO$ $(M+H)^+$: 174.1023, found: 174.0997.

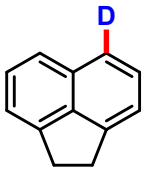
2-ethoxynaphthalene-6-d(**3k**)



Following the general procedure described above, the reaction of **1k** (0.2 mmol, 57 mg), Cs_2CO_3 (0.4 mmol, 131 mg) were reacted with deuterated acetonitrile (0.5 mL) to give a colorless oil **3k** (17 mg, 50% yield, 98%D). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.74 (dd, *J* = 16.5, 7.9 Hz, 3H), 7.43 (d, *J* = 8.2 Hz, 1H), 7.15 (dd, *J* = 11.3, 2.4 Hz, 2H), 4.16 (q, *J* = 7.0 Hz, 2H), 1.49 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ: 156.98, 134.68, 129.42, 128.96, 127.60, 126.78, 126.27, 123.28(t, *J* = 25.2 Hz), 119.07, 106.60, 63.52, 14.91.

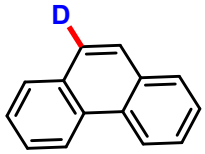
HRMS (ESI-TOF, m/z) Calcd for $C_{12}H_{12}DO$ $(M+H)^+$: 174.1023, found: 174.1037.

1,2-dihydroacenaphthylene-5-d(**3l**)



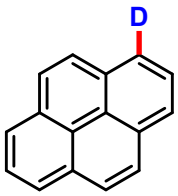
Following the general procedure described above, the reaction of **1l** (0.2 mmol, 53 mg), Cs_2CO_3 (0.4 mmol, 131 mg) were reacted with deuterated acetonitrile (0.5 mL) to give a white solid **3l** (20 mg, 56% yield, 99%D). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.62 (d, *J* = 8.2 Hz, 1H), 7.47 (dt, *J* = 8.0, 4.2 Hz, 2H), 7.31 (d, *J* = 6.8 Hz, 2H), 3.43 (s, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ: 146.04, 139.32, 131.56, 127.82, 127.71, 122.21, 121.95 (t, *J* = 25.2 Hz), 119.20, 30.39. HRMS (ESI-TOF, m/z) Calcd for $C_{12}H_9D$ $(M+H)^+$: 156.0918, found: 156.0938.

phenanthrene-9-d(**3m**)



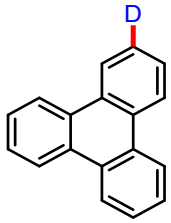
Following the general procedure described above, the reaction of **1m** (0.2 mmol, 58 mg), Cs_2CO_3 (0.4 mmol, 131 mg) were reacted with deuterated acetonitrile (0.5 mL) to give a white solid **3m** (29 mg, 80% yield, 98%D). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.72 (d, *J* = 8.2 Hz, 2H), 7.92 (d, *J* = 7.7 Hz, 2H), 7.77 (s, 1H), 7.71–7.59 (m, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ: 132.16, 132.10, 130.42, 128.69, 128.64, 127.04, 126.91 (t, *J* = 27.72 Hz), 126.68, 122.78. Spectroscopic data in agreement with the literature[4].

pyrene-1-d(**3n**)



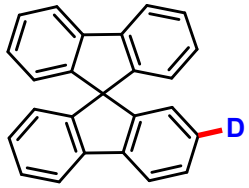
Following the general procedure described above, the reaction of **1n** (0.2 mmol, 63 mg), Cs_2CO_3 (0.4 mmol, 131 mg) were reacted with deuterated acetonitrile (0.5 mL) to give a white solid **3n** (38 mg. 95% yield, 99%D). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.21 (d, *J* = 7.6 Hz, 3H), 8.10 (s, 4H), 8.06–8.00 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ: 131.24, 131.16, 127.49, 127.45, 125.97, 125.85, 125.05, 124.77, 124.73 (t, *J* = 23.94 Hz). Spectroscopic data in agreement with the literature[8].

triphenylene-2-d(**3o**)



Following the general procedure described above, the reaction of **1o** (0.2 mmol, 68 mg), Cs_2CO_3 (0.4 mmol, 131 mg) were reacted with deuterated acetonitrile (0.5 mL) to give a white solid **3o** (33 mg, 71% yield, 94%D). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.67 (dd, *J* = 5.8, 3.4 Hz, 6H), 7.67 (dd, *J* = 6.2, 3.2 Hz, 5H). ^{13}C NMR (126 MHz, $CDCl_3$) δ: 129.81, 127.24, 126.95 (t, *J* = 23.94 Hz), 123.33, 123.21. HRMS (ESI-TOF, m/z) Calcd for $C_{18}H_{12}D$ $(M+H)^+$: 230.1074, found: 230.1081.

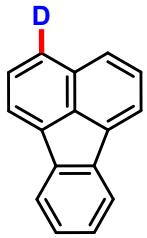
9,9'-spirobi[fluorene]-2-d(**3p**)



Following the general procedure described above, the reaction of **1p** (0.2 mmol, 85 mg), Cs_2CO_3 (0.4 mmol, 131 mg) were reacted with deuterated acetonitrile (0.5 mL) to give a white solid **3p** (35 mg, 57% yield, 90%D). ^{1}H NMR (500 MHz, $CDCl_3$ δ: 7.86 (d, *J* = 7.6 Hz, 4H), 7.38 (t, *J* = 7.5 Hz, 4H), 7.12 (t, *J* = 7.5 Hz, 3H), 6.78–6.71

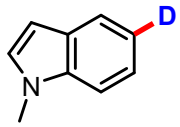
(m, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ: 148.80, 141.80, 127.73 (t, *J* = 13.86 Hz), 124.07, 123.96, 120.01. Spectroscopic data in agreement with the literature[4].

fluoranthene-3-d(**3q**)



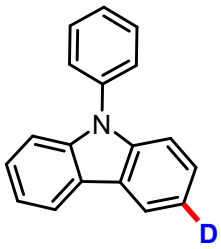
Following the general procedure described above, the reaction of **1q** (0.2 mmol, 63 mg), Cs_2CO_3 (0.4 mmol, 131 mg) were reacted with deuterated acetonitrile (0.5 mL) to give a yellow solid **3q** (20 mg, 50% yield, 96%D). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.98–7.91 (m, 4H), 7.86 (d, *J* = 8.2 Hz, 1H), 7.68–7.62 (m, 2H), 7.40 (dd, *J* = 5.5, 3.1 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ: 139.49, 137.00, 132.42, 129.94, 127.99, 127.88, 127.58, 126.64, 126.37 (t, *J* = 25.2 Hz), 121.57, 120.09. HRMS (ESI-TOF, m/z) Calcd for $C_{16}H_{10}D(M+H)^+$: 204.0918, found: 204.0910.

1-methyl-1H-indole-5-d(**3r**)



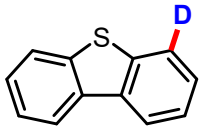
Following the general procedure described above, the reaction of **1r** (0.2 mmol, 49 mg), Cs_2CO_3 (0.4 mmol, 131 mg) were reacted with deuterated acetonitrile (0.5 mL) to give a white solid **3r** (12 mg, 46% yield, 98%D). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.65 (s, 1H), 7.35 (d, *J* = 8.2 Hz, 1H), 7.24 (d, *J* = 8.2 Hz, 1H), 7.07 (d, *J* = 2.8 Hz, 1H), 6.50 (d, *J* = 2.8 Hz, 1H), 3.81 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ: 136.69, 128.81, 128.46, 121.39, 120.77, 119.00 (t, *J* = 23.94 Hz), 109.19, 100.89, 32.85. Spectroscopic data in agreement with the literature[4].

9-phenyl-9H-carbazole-3-d(**3s**)



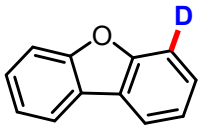
Following the general procedure described above, the reaction of **1s** (0.2 mmol, 74 mg), Cs_2CO_3 (0.4 mmol, 131 mg) were reacted with deuterated acetonitrile (0.5 mL) to give a white solid **3s** (20 mg, 42% yield, 93%D). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.19–8.13 (m, 2H), 7.64–7.56 (m, 4H), 7.45 (d, J = 28.6 Hz, 5H), 7.30 (ddd, J = 8.0, 4.7, 3.4 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ: 140.91, 137.73, 129.89, 127.47, 127.17, 126.11 (t, J = 25.2 Hz), 125.93, 125.82, 123.36, 120.31, 120.20, 119.90, 109.78. Spectroscopic data in agreement with the literature[4].

dibenzo[b,d]thiophene-4-d(**3t**)



Following the general procedure described above, the reaction of **1t** (0.2 mmol, 59 mg), Cs_2CO_3 (0.4 mmol, 131 mg) were reacted with deuterated acetonitrile (0.5 mL) to give a white solid **3t** (30 mg, 83% yield, 90%D). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.20–8.15 (m, 2H), 7.87 (dd, J = 5.9, 3.1 Hz, 1H), 7.50–7.45 (m, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ: 139.46, 139.34, 135.56, 126.73, 126.61, 124.38, 122.84, 122.56 (t, J = 25.2 Hz), 121.60. Spectroscopic data in agreement with the literature[4].

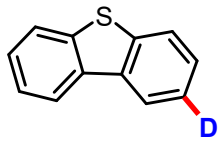
dibenzo[b,d]furan-4-d(**3u**)



Following the general procedure described above, the reaction of **1u** (0.2 mmol, 56 mg), Cs_2CO_3 (0.4 mmol, 131 mg) were reacted with deuterated acetonitrile (0.5 mL)

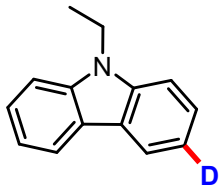
to give a white solid **3u** (29 mg, 86% yield, 53%D). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.97 (d, *J* = 7.7 Hz, 2H), 7.59 (d, *J* = 8.2 Hz, 1H), 7.50–7.45 (m, 2H), 7.36 (t, *J* = 7.5 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ: 156.30, 156.25, 127.25, 127.14, 124.34, 122.80, 120.77, 111.79, 111.55 (t, *J* = 25.2 Hz). Spectroscopic data in agreement with the literature[8].

dibenzo[b,d]thiophene-2-d(**3v**)



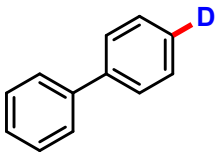
Following the general procedure described above, the reaction of **1v** (0.2 mmol, 60 mg), Cs_2CO_3 (0.4 mmol, 131 mg) were reacted with deuterated acetonitrile (0.5 mL) to give a white solid **3v** (15 mg, yield 42%, 90%D). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.17 (t, *J* = 4.5 Hz, 2H), 7.89–7.84 (m, 2H), 7.47 (dd, *J* = 6.0, 3.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ: 139.44, 135.56, 126.71, 126.61, 124.36, 124.09 (t, *J* = 25.2 Hz), 122.83, 121.59, 121.48. Spectroscopic data in agreement with the literature[9].

9-ethyl-9H-carbazole-3-d(**3w**)



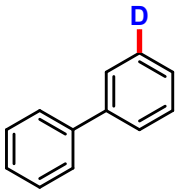
Following the general procedure described above, the reaction of **1w** (0.2 mmol, 64 mg), Cs_2CO_3 (0.4 mmol, 131 mg) were reacted with deuterated acetonitrile (0.5 mL) to give a white solid **3w** (18 mg, yield 46%, 88%D). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.19–8.13 (m, 2H), 7.51 (dt, *J* = 7.1, 3.1 Hz, 2H), 7.46 (d, *J* = 8.2 Hz, 2H), 7.28 (d, *J* = 6.2 Hz, 1H), 4.42 (q, *J* = 7.2 Hz, 2H), 1.48 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ: 139.95, 125.62, 125.51, 122.95, 120.44, 120.33, 118.75, 118.49 (t, *J* = 25.2 Hz), 108.44, 37.53, 13.83. Spectroscopic data in agreement with the literature[5].

1,1'-biphenyl-4-d(**3x**)



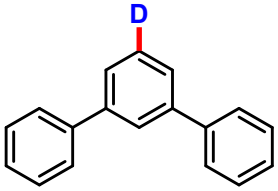
Following the general procedure described above, the reaction of **1x** (0.2 mmol, 53 mg), Cs_2CO_3 (0.4 mmol, 131 mg) were reacted with deuterated acetonitrile (0.5 mL) to give a white solid **3x** (11 mg, 36% yield, 97%D). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.61 (d, *J* = 7.9 Hz, 4H), 7.45 (dt, *J* = 7.8, 3.6 Hz, 4H), 7.36 (t, *J* = 7.4 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ: 141.26, 128.78, 128.67, 127.27, 126.99 (t, *J* = 25.2 Hz). Spectroscopic data in agreement with the literature[4].

1,1'-biphenyl-3-d(**3y**)



Following the general procedure described above, the reaction of **1y** (0.2 mmol, 53 mg), Cs_2CO_3 (0.4 mmol, 131 mg) were reacted with deuterated acetonitrile (0.5 mL) to give a white solid **3y** (9 mg, 30% yield, 80%D). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.66–7.59 (m, 4H), 7.46 (t, *J* = 7.8 Hz, 3H), 7.41–7.34 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ: 141.35, 128.88, 128.78, 128.59, 128.39, 127.29 (t, *J* = 12.6 Hz), 127.26. Spectroscopic data in agreement with the literature[5].

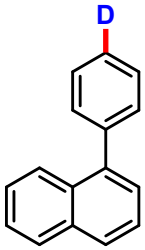
1,1':3',1''-terphenyl-5'-d(**3z**)



Following the general procedure described above, the reaction of **1z** (0.2 mmol, 69 mg), Cs_2CO_3 (0.4 mmol, 131 mg) were reacted with deuterated acetonitrile (0.5 mL)

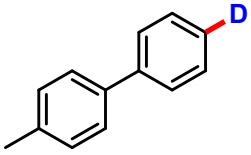
to give a white solid **3z** (12 mg, 26% yield, 98%D). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.83 (s, 1H), 7.67 (d, *J* = 7.9 Hz, 4H), 7.62–7.58 (m, 2H), 7.48 (t, *J* = 7.6 Hz, 4H), 7.39 (t, *J* = 7.4 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ: 141.82, 141.22, 128.85, 127.45, 126.21, 126.17 (t, *J* = 16.38 Hz). HRMS (ESI-TOF, m/z) Calcd for $C_{18}H_{14}D$ $(M+H)^+$: 232.1231, found: 232.1201.

1-(phenyl-4-d)naphthalene(**3aa**)



Following the general procedure described above, the reaction of **1aa** (0.2 mmol, 63 mg), Cs_2CO_3 (0.4 mmol, 131 mg) were reacted with deuterated acetonitrile (0.5 mL) to give a colorless oil **3aa** (31 mg, 76% yield, 99%D). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.91 (dd, *J* = 23.5, 8.4 Hz, 3H), 7.53 (d, *J* = 6.0 Hz, 6H), 7.48–7.43 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ: 140.87, 140.38, 133.90, 131.73, 130.19, 128.38, 128.27, 128.00, 127.75, 127.35, 127.05 (t, *J* = 25.2 Hz), 126.15, 126.14, 125.88, 125.50. HRMS (ESI-TOF, m/z) Calcd for $C_{16}H_{12}D$ $(M+H)^+$: 206.1074, found: 206.1051.

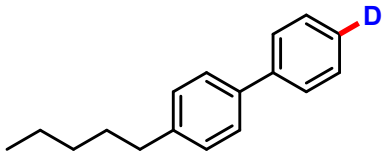
4-methyl-1,1'-biphenyl-4'-d(**3ab**)



Following the general procedure described above, the reaction of **1ab** (0.2 mmol, 56 mg), Cs_2CO_3 (0.4 mmol, 131 mg) were reacted with deuterated acetonitrile (0.5 mL) to give a white solid **3ab** (13 mg, 38% yield, 97%D). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.60 (d, *J* = 8.2 Hz, 2H), 7.51 (d, *J* = 8.1 Hz, 2H), 7.44 (d, *J* = 8.0 Hz, 2H), 7.28 (s, 2H), 2.41 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ: 141.19, 138.39, 137.05, 129.50,

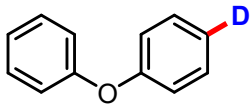
128.63, 127.02, 127.00, 126.71 (t, J = 25.2 Hz), 21.13. Spectroscopic data in agreement with the literature[9].

4-pentyl-1,1'-biphenyl-4'-d(**3ac**)



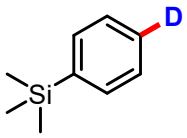
Following the general procedure described above, the reaction of **1ac** (0.2 mmol, 67 mg), Cs_2CO_3 (0.4 mmol, 131 mg) were reacted with deuterated acetonitrile (0.5 mL) to give a white solid **3ac** (18 mg, 40% yield, 95%D). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.60 (d, J = 8.1 Hz, 2H), 7.53 (d, J = 8.1 Hz, 2H), 7.44 (d, J = 8.0 Hz, 2H), 7.28 (s, 2H), 2.68–2.63 (m, 2H), 1.67 (p, J = 7.3 Hz, 2H), 1.37 (dt, J = 7.1, 3.9 Hz, 4H), 0.92 (t, J = 6.8 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ: 142.14, 141.22, 138.57, 128.85, 128.61, 127.01, 126.68 (t, J = 25.2 Hz), 35.62, 31.60, 31.24, 22.61, 14.09. HRMS (ESI-TOF, m/z) Calcd for $C_{17}H_{20}D$ $(M+H)^+$: 226.1700, found: 226.1708.

1-phenoxybenzene-4-d(**3ad**)



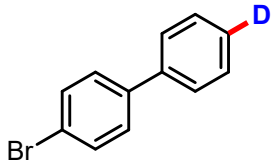
Following the general procedure described above, the reaction of **1ad** (0.2 mmol, 57 mg), Cs_2CO_3 (0.4 mmol, 131 mg) were reacted with deuterated acetonitrile (0.5 mL) to give a colorless oil **3ad** (12 mg, 35% yield, 84%D). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.34 (dt, J = 7.6, 3.7 Hz, 4H), 7.11 (t, J = 7.4 Hz, 1H), 7.02 (d, J = 8.0 Hz, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ: 157.35, 129.85, 129.75, 123.33, 123.06 (t, J = 25.2 Hz), 119.00. Spectroscopic data in agreement with the literature[4].

trimethyl(phenyl-4-d)silane(**3ae**)



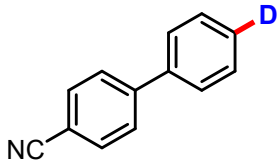
Following the general procedure described above, the reaction of **1ae** (0.2 mmol, 53 mg), Cs_2CO_3 (0.4 mmol, 131 mg) were reacted with deuterated acetonitrile (0.5 mL) to give a colorless oil **3ae** (12 mg, 40% yield, 99%D). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.62 (d, J = 2.2 Hz, 4H), 0.32 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ: 141.69, 139.44, 133.95, 126.64 (t, J = 25.2 Hz), -0.94. Spectroscopic data in agreement with the literature[10].

4-bromo-1,1'-biphenyl-4'-d(**3af**)



Following the general procedure described above, the reaction of **1af** (0.2 mmol, 69 mg), Cs_2CO_3 (0.4 mmol, 131 mg) were reacted with deuterated acetonitrile (0.5 mL) to give a white solid **3af** (17 mg, 37% yield, 99%D). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.58–7.53 (m, 4H), 7.48–7.42 (m, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ: 140.16, 140.03, 131.88, 128.81, 128.77, 127.38 (t, J = 25.2 Hz), 126.97, 121.55. Spectroscopic data in agreement with the literature[4].

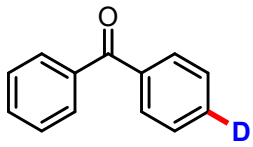
[1,1'-biphenyl]-4-carbonitrile-4'-d(**3ag**)



Following the general procedure described above, the reaction of **1ag** (0.2 mmol, 58 mg), Cs_2CO_3 (0.4 mmol, 131 mg) were reacted with deuterated acetonitrile (0.5 mL) to give a white solid **3ag** (17 mg, 47% yield, 99%D) was obtained. ^{1}H NMR (500

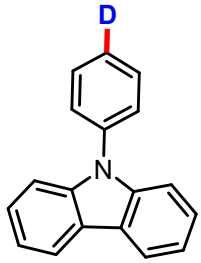
MHz, $CDCl_3$) δ: 7.73 (d, *J* = 8.3 Hz, 2H), 7.69 (d, *J* = 8.3 Hz, 2H), 7.59 (d, *J* = 8.1 Hz, 2H), 7.49 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ: 145.71, 139.21, 132.62, 129.14, 129.03, 128.42 (t, *J* = 23.94 Hz), 127.76, 127.25, 118.98, 110.93. HRMS (ESI-TOF, m/z) Calcd for $C_{13}H_9DN$ $(M+H)^+$: 181.0870, found: 181.0863.

phenyl(phenyl-4-d)methanone(**3ah**)



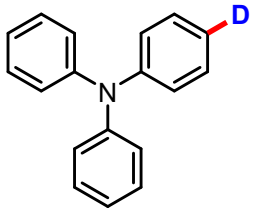
Following the general procedure described above, the reaction of **1ah** (0.2 mmol, 59 mg), Cs_2CO_3 (0.4 mmol, 131 mg) were reacted with deuterated acetonitrile (0.5 mL) to give a white solid **3ah** (17 mg, 47% yield, 94%D). ^1H NMR (500 MHz, $CDCl_3$) δ: 7.81 (d, *J* = 8.1 Hz, 4H), 7.62–7.57 (m, 1H), 7.53–7.46 (m, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ: 196.81, 137.61, 132.45, 132.15 (t, *J* = 25.2 Hz), 130.09, 128.30, 128.19. Spectroscopic data in agreement with the literature[11].

9-(phenyl-4-d)-9H-carbazole(**3ai**)



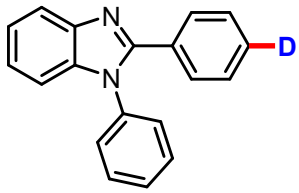
Following the general procedure described above, the reaction of **1ai** (0.2 mmol, 74 mg), Cs_2CO_3 (0.4 mmol, 131 mg) were reacted with deuterated acetonitrile (0.5 mL) to give a white solid **3ai** (13 mg, 27% yield, 95%D). ^1H NMR (500 MHz, $CDCl_3$) δ: 8.16 (d, *J* = 7.7 Hz, 2H), 7.64–7.56 (m, 4H), 7.45–7.40 (m, 4H), 7.30 (ddd, *J* = 8.0, 4.5, 3.5 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ: 140.92, 137.73, 129.78, 127.17 (t, *J* = 25.2 Hz), 125.93, 123.36, 120.31, 119.90, 109.78. Spectroscopic data in agreement with the literature[5].

N,N-diphenylaniline-4-d(**3aj**)



Following the general procedure described above, the reaction of **1aj** (0.2 mmol, 72 mg), Cs_2CO_3 (0.4 mmol, 131 mg) were reacted with deuterated acetonitrile (0.5 mL) to give a white solid **3aj** (20 mg, 41% yield, 95%D). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.31–7.26 (m, 6H), 7.12 (d, *J* = 7.9 Hz, 6H), 7.04 (t, *J* = 7.3 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ: 147.73, 129.08, 128.97, 124.04, 122.54, 122.27 (t, *J* = 25.2 Hz). Spectroscopic data in agreement with the literature[4].

1-phenyl-2-(phenyl-4-d)-1H-benzo[d]imidazole(**3ak**)



Following the general procedure described above, the reaction of **1ak** (0.2 mmol, 77 mg), Cs_2CO_3 (0.4 mmol, 131 mg) were reacted with deuterated acetonitrile (0.5 mL) to give a white solid **3ak** (16 mg, 30% yield, 86%D). ^{1}H NMR (500 MHz, DMSO-d_6) δ: 7.80 (d, *J* = 7.8 Hz, 1H), 7.60–7.51 (m, 5H), 7.43 (d, *J* = 7.0 Hz, 2H), 7.38–7.26 (m, 4H), 7.20 (d, *J* = 8.0 Hz, 1H). ^{13}C NMR (126 MHz, DMSO) δ: 152.25, 142.68, 137.45, 136.83, 130.52, 130.09, 129.62, 129.37, 128.84, 128.73, 128.00, 123.91, 123.32, 119.72, 110.99. Spectroscopic data in agreement with the literature[12].

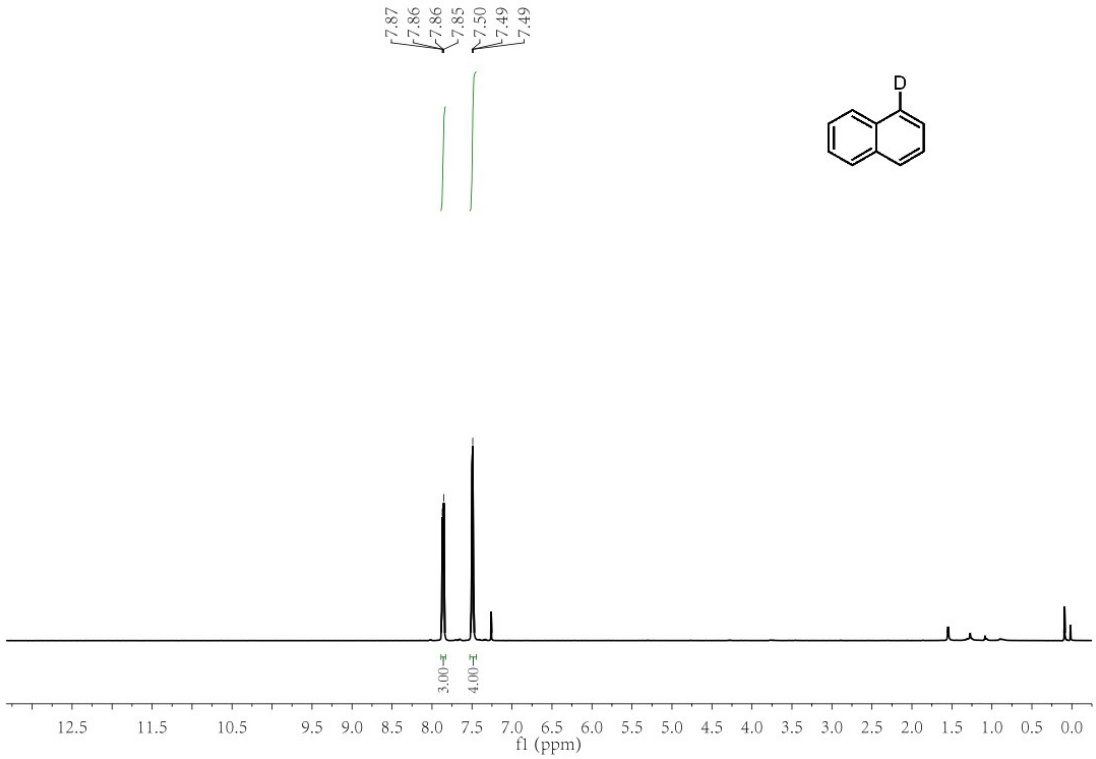
8. References

1. K. Ukai, M. Aoki, J. Takaya and N. Iwasawa, *J. Am. Chem. Soc.*, 2006, **128**, 8706-8707.
2. X. Wang, M.-H. Zhu, D. P. Schuman, D. Zhong, W.-Y. Wang, L.-Y. Wu, W. Liu, B. M. Stoltz and W.-B. Liu, *J. Am. Chem. Soc.*, 2018, **140**, 10970-10974.

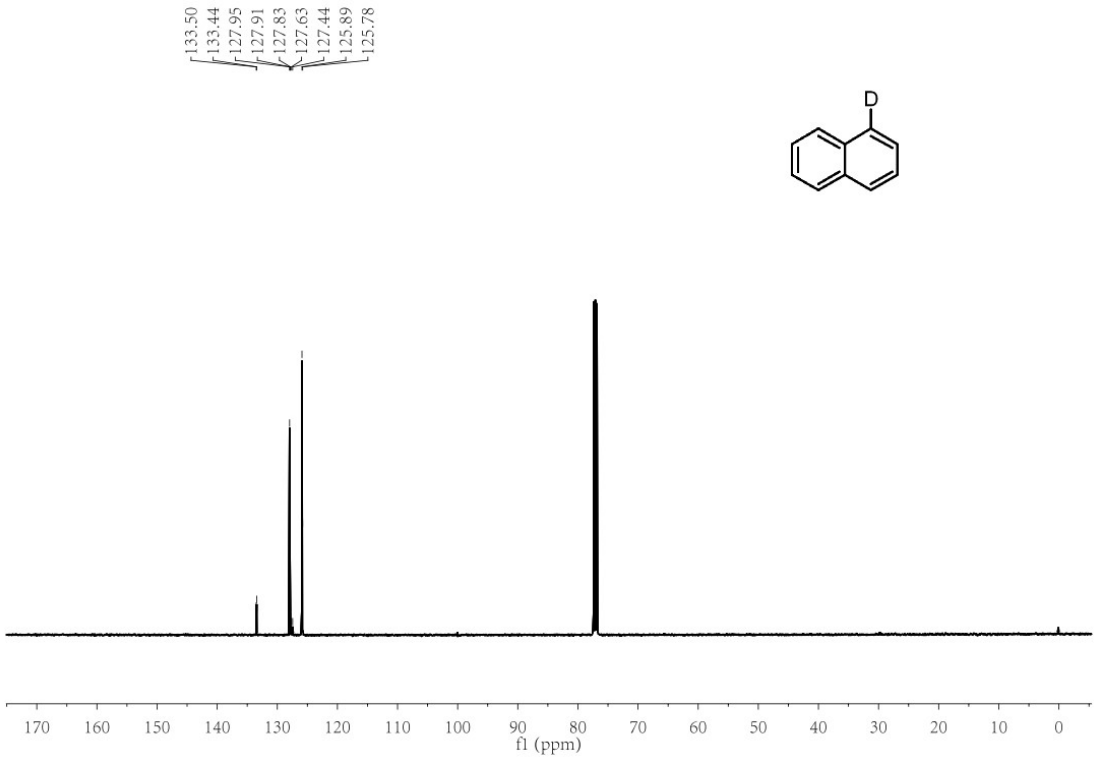
3. (a) W. Hao, J. H. Harenberg, X. Wu, S. N. MacMillan and S. Lin, *J. Am. Chem. Soc.*, 2018, **140**, 3514-3517; (b) T. Liedtke, P. Spannring, L. Riccardi and A. Gansaeuer, *Angew. Chem., Int. Ed.*, 2018, **57**, 5006-5010; (c) G. A. Luinstra, *J. Organomet. Chem.*, 1996, **517**, 209-215; (d) R. B. Richrath, T. Olyschlaeger, S. Hildebrandt, D. G. Enny, G. D. Fianu, R. A. Flowers, II and A. Gansaeuer, *Chem. Eur. J.*, 2018, **24**, 6371-6379; (e) E. i. Negishi and T. Takahashi, *Science of Synthesis*, Thieme Chemistry, 2003.
4. J. Dong, M. Yu, F. Yue, H. Song, Y. Liu, L. Wu, D. Si, C. Yang, G. Yang and Q. Wang, *Org. Lett.*, 2022, **24**, 2064-2068.
5. B.-D. Wu, J. Zhu, Q. Liu, L. Cao, H. Gu and J.-P. Lang, *Tetrahedron Lett.*, 2024, **144**, 155152.
6. M. Wang, W. H. Pang, O. Y. Yuen, S. S. Ng and C. M. So, *Org. Lett.*, 2023, **25**, 8429-8433.
7. S. Vanderheiden, B. Bulat, T. Zevaco, N. Jung and S. Braese, *Chem. Commun.*, 2011, **47**, 9063-9065.
8. R. Qu, S. Wan, X. Zhang, X. Wang, L. Xue, Q. Wang, G.-J. Cheng, L. Dai and Z. Lian, *Angew. Chem., Int. Ed.*, 2024, **136**, e202400645.
9. Z.-Y. Wang, X. Zhang, W.-Q. Chen, G.-D. Sun, X. Wang, L. Tan, H. Xu and H.-X. Dai, *Angew. Chem., Int. Ed.*, 2024, **63**, e202319773.
10. C. Liu, Z. Chen, C. Su, X. Zhao, Q. Gao, G.-H. Ning, H. Zhu, W. Tang, K. Leng, W. Fu, B. Tian, X. Peng, J. Li, Q.-H. Xu, W. Zhou and K. P. Loh, *Nat. Commun.*, 2018, **9**, 80-88.
11. Y. Yang, X. Gao, X. Zeng, J. Han and B. Xu, *Chem. Eur. J*, 2021, **27**, 1297-1300.
12. B. Zhang, C. Qiu, S. Wang, H. Gao, K. Yu, Z. Zhang, X. Ling, W. Ou and C. Su, *Sci. Bull.*, 2021, **66**, 562-569.

9. Spectroscopic Data

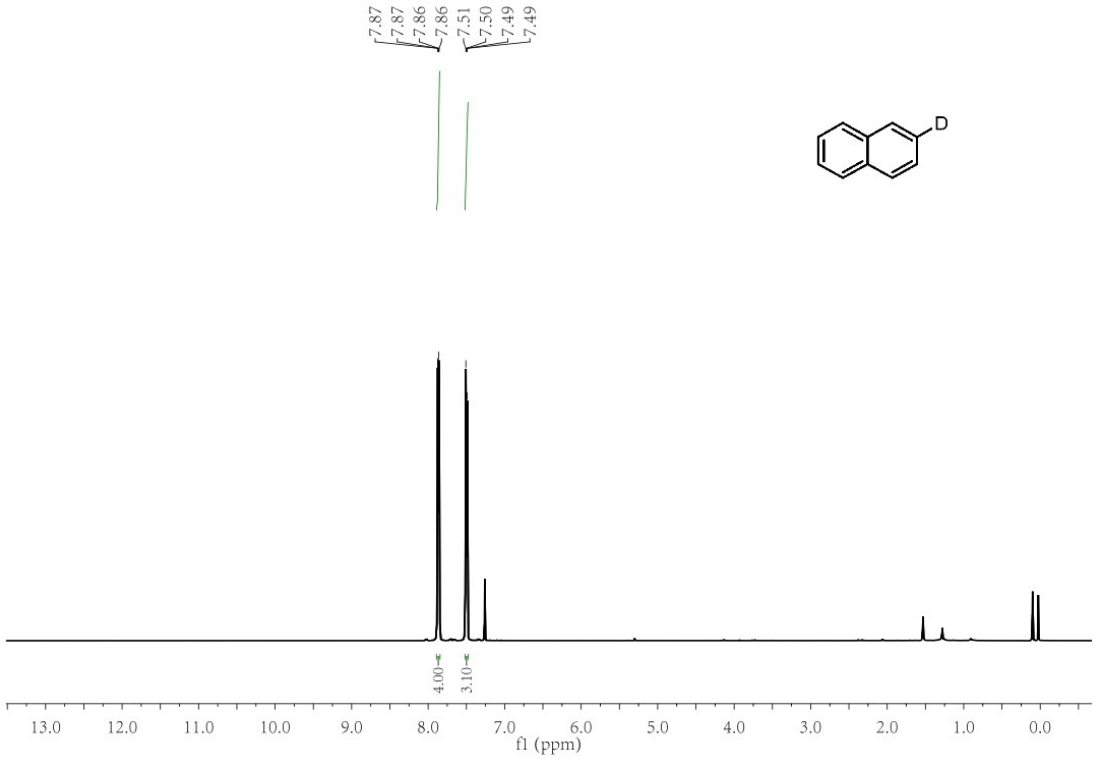
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3a**.



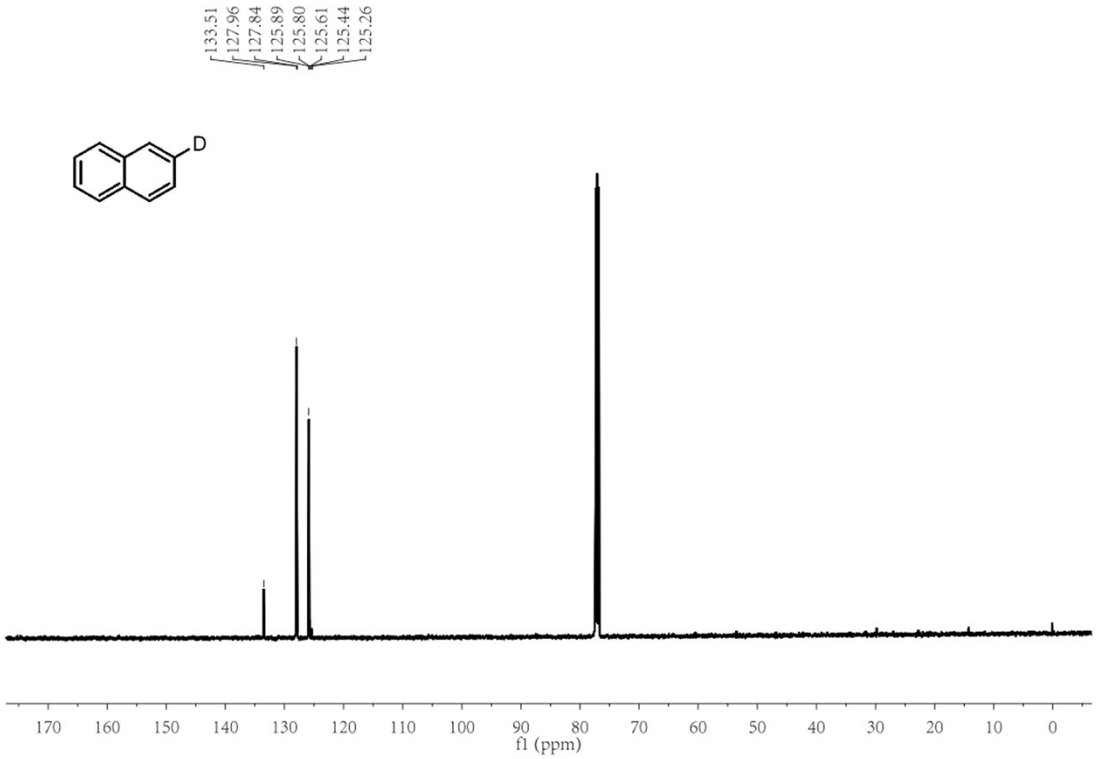
^{13}C NMR (126 MHz, $CDCl_3$) of compound **3a**.



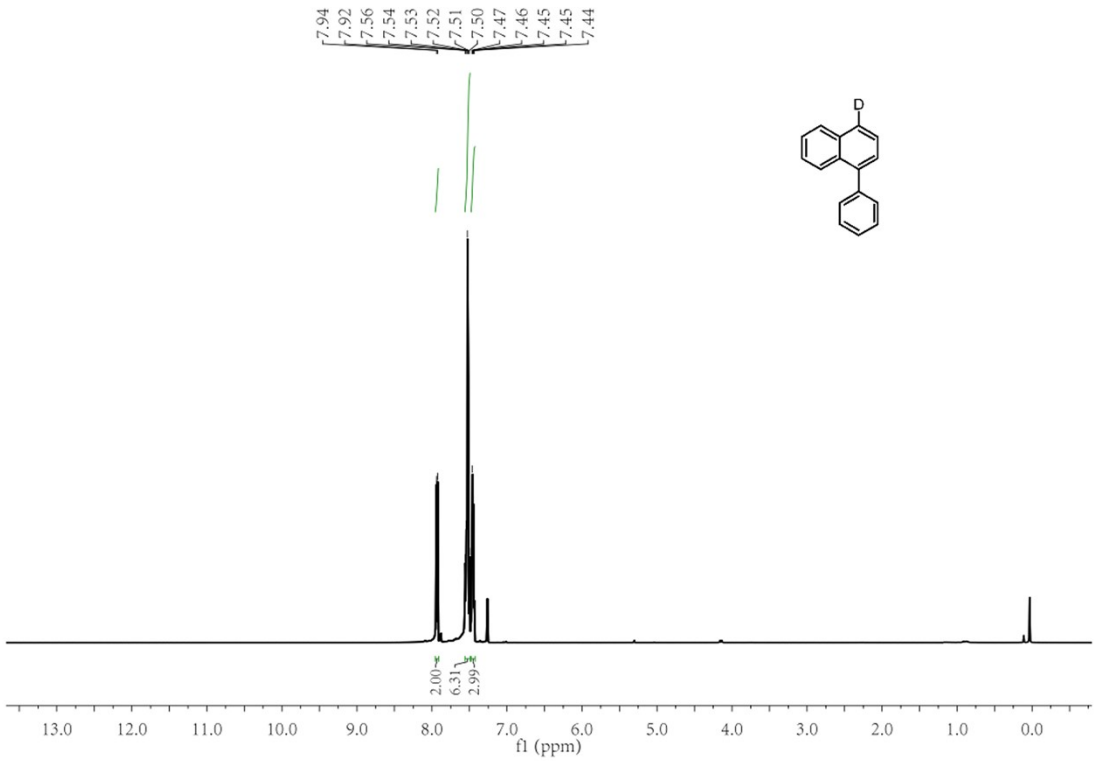
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3b**.



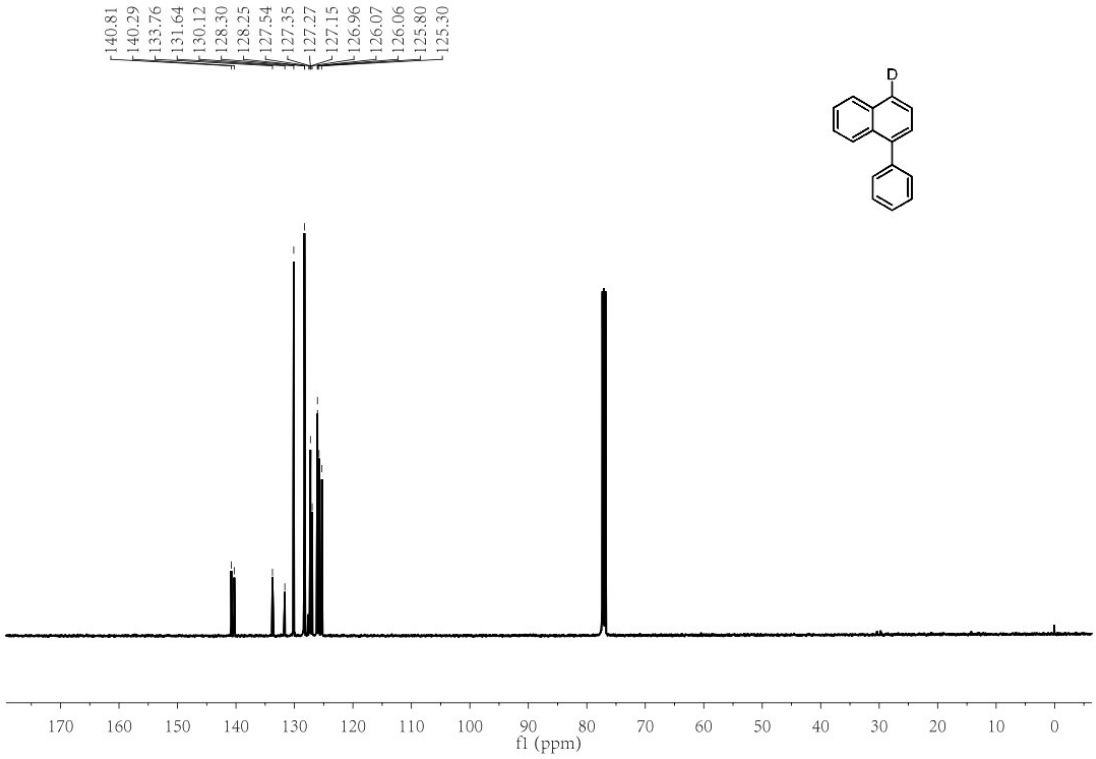
^{13}C NMR (126 MHz, $CDCl_3$) of compound **3b**.



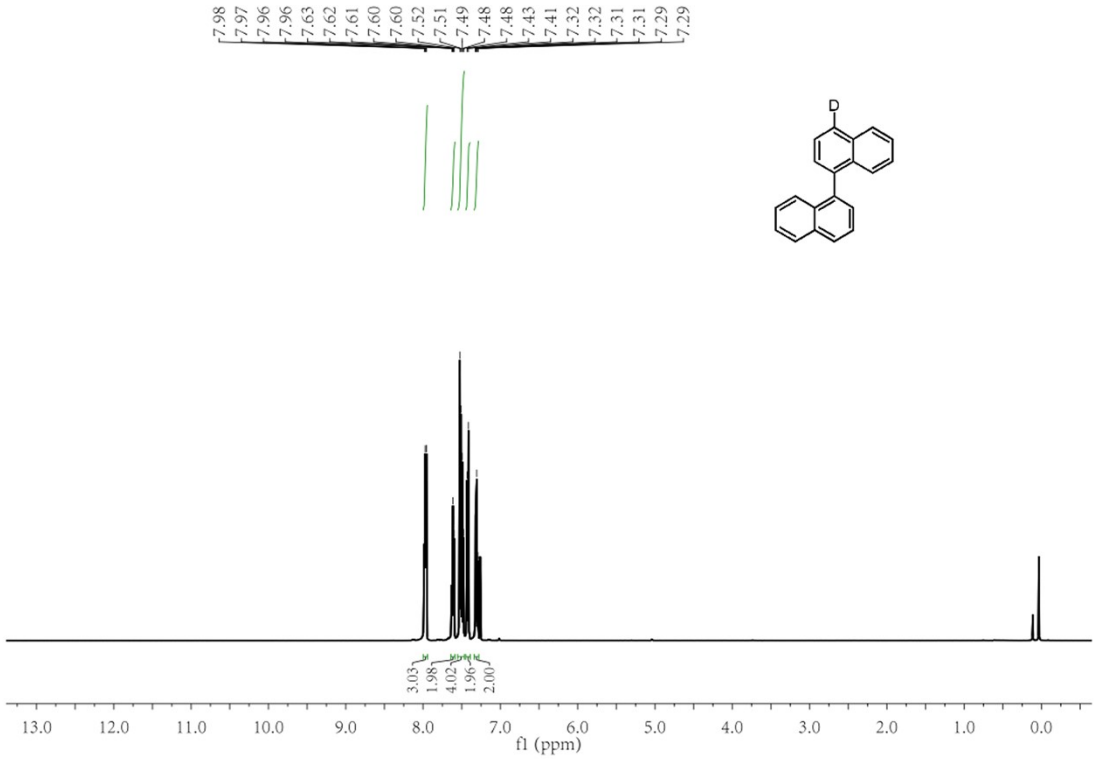
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3c**.



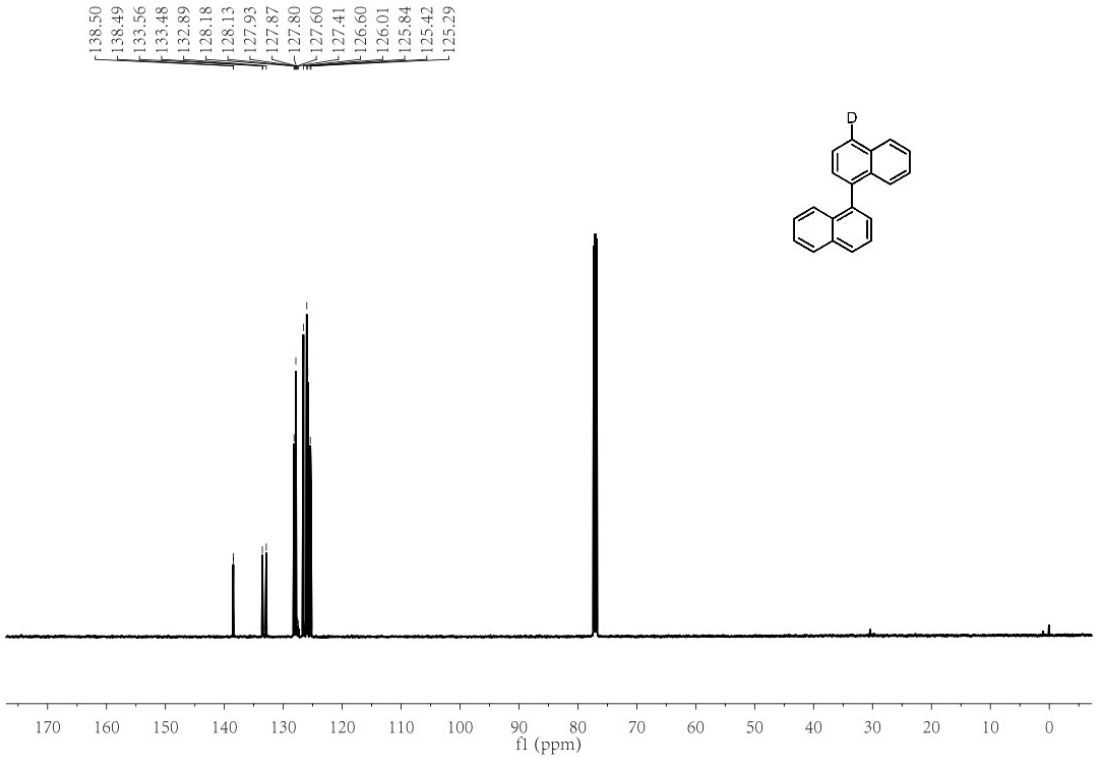
^{13}C NMR (126 MHz, $CDCl_3$) of compound **3c**.



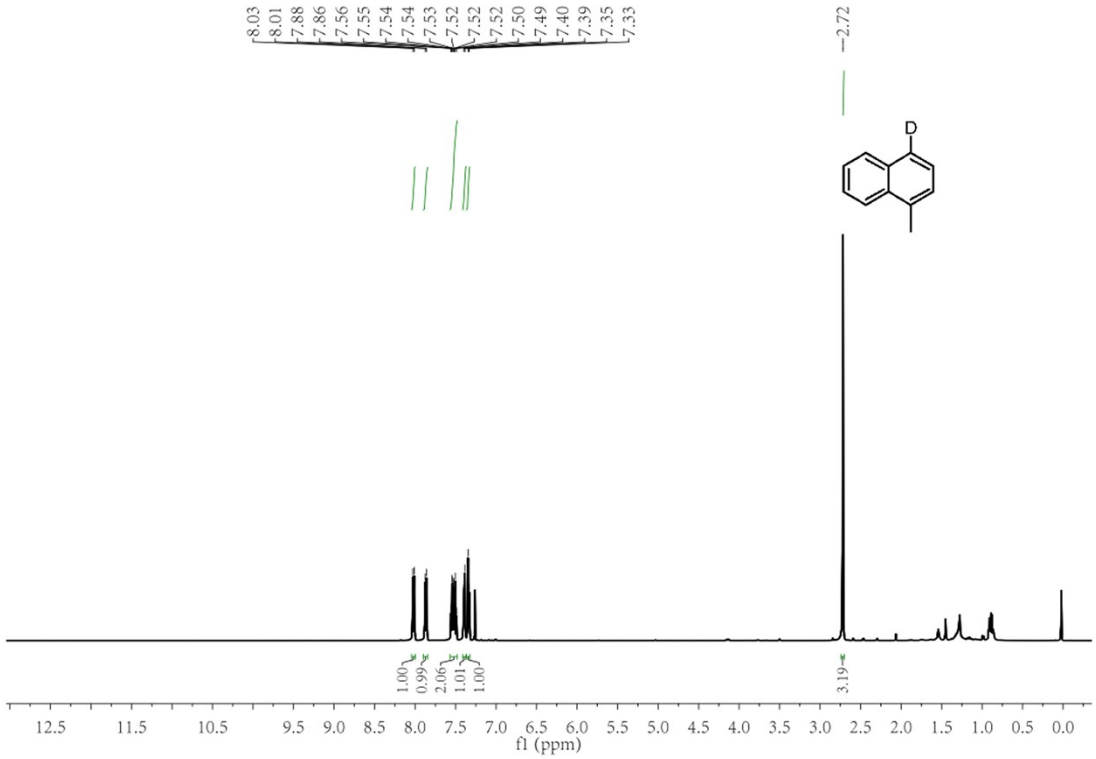
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3d**.



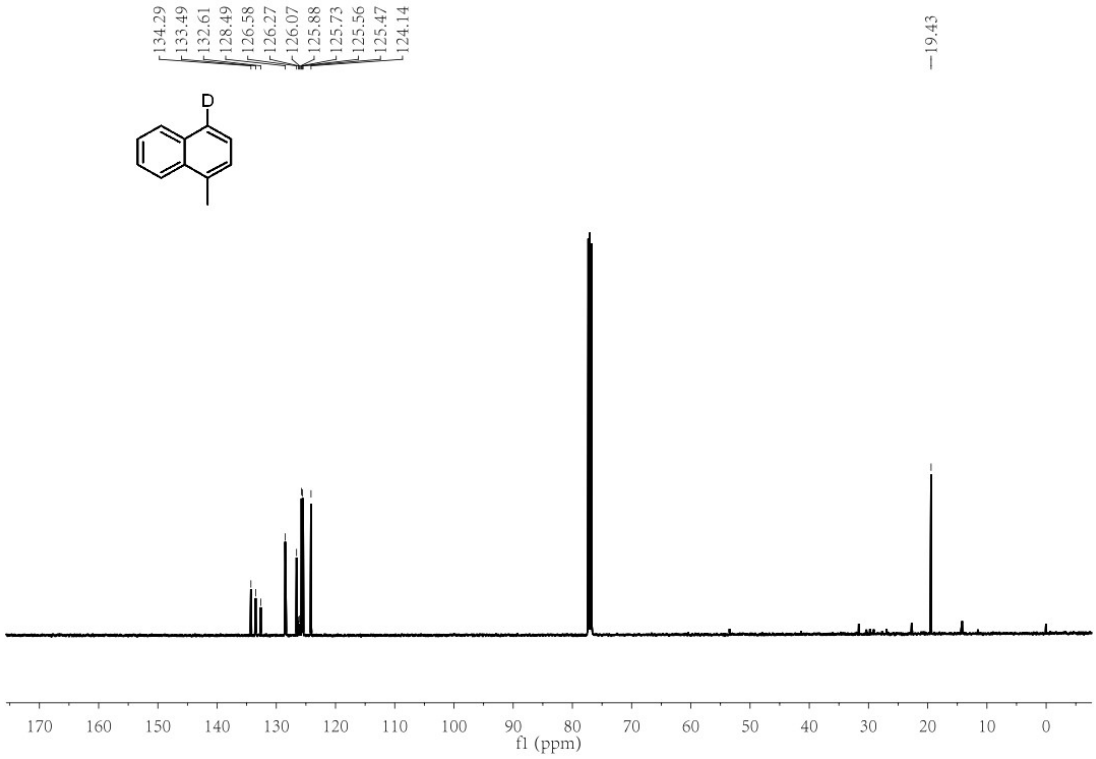
^{13}C NMR (126 MHz, $CDCl_3$) of compound **3d**.



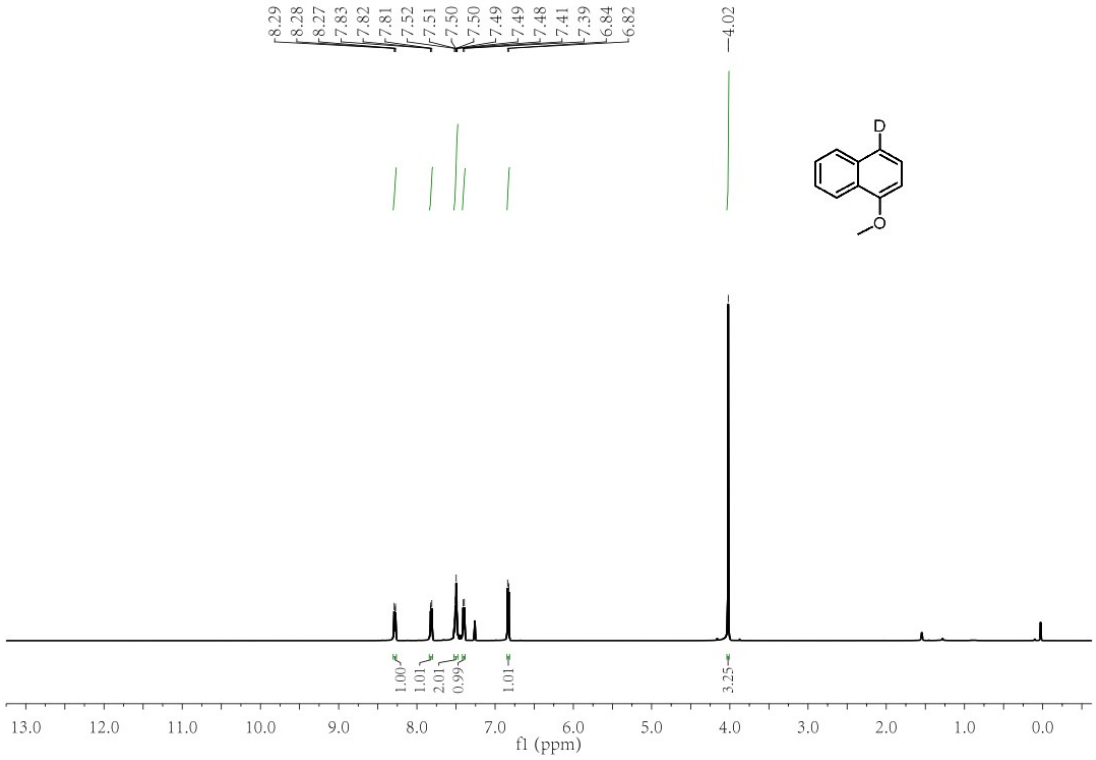
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3e**.



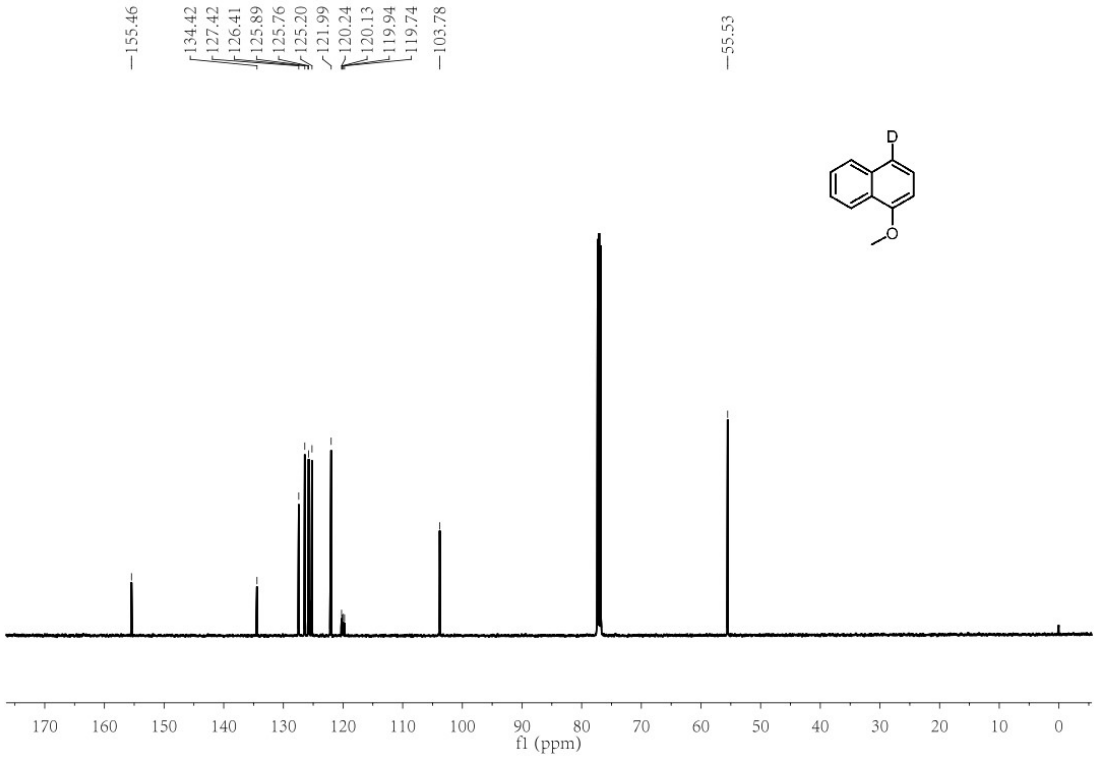
^{13}C NMR (126 MHz, $CDCl_3$) of compound **3e**.



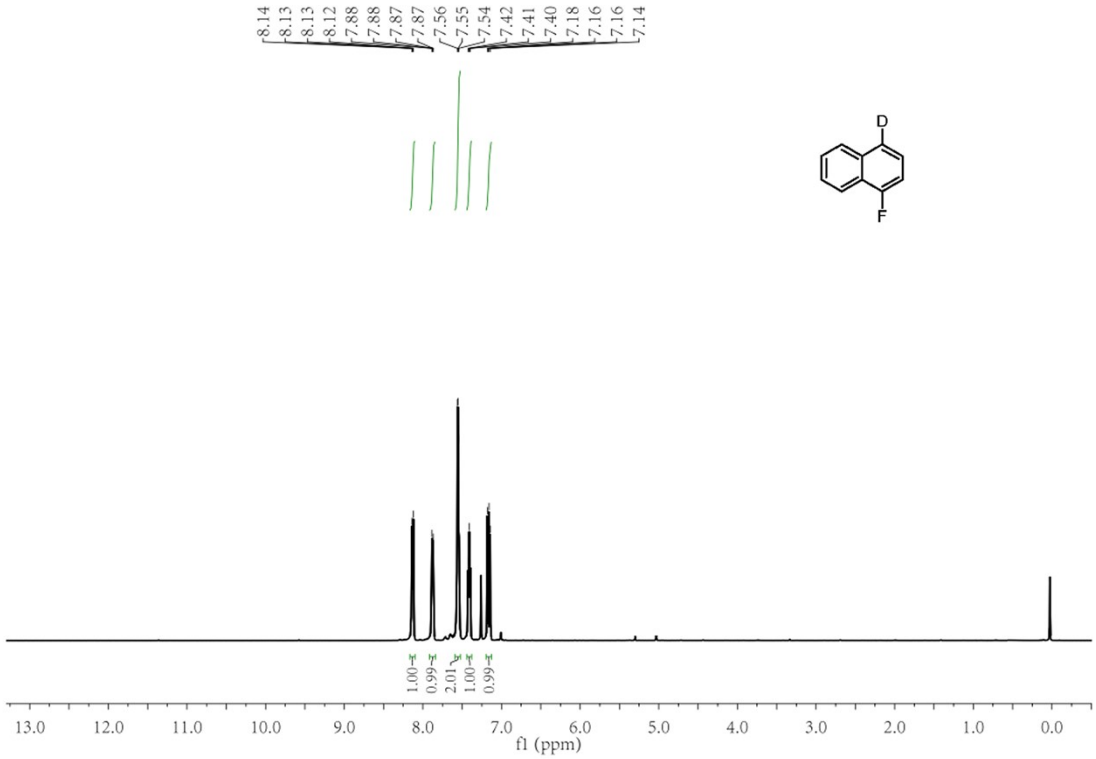
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3f**.



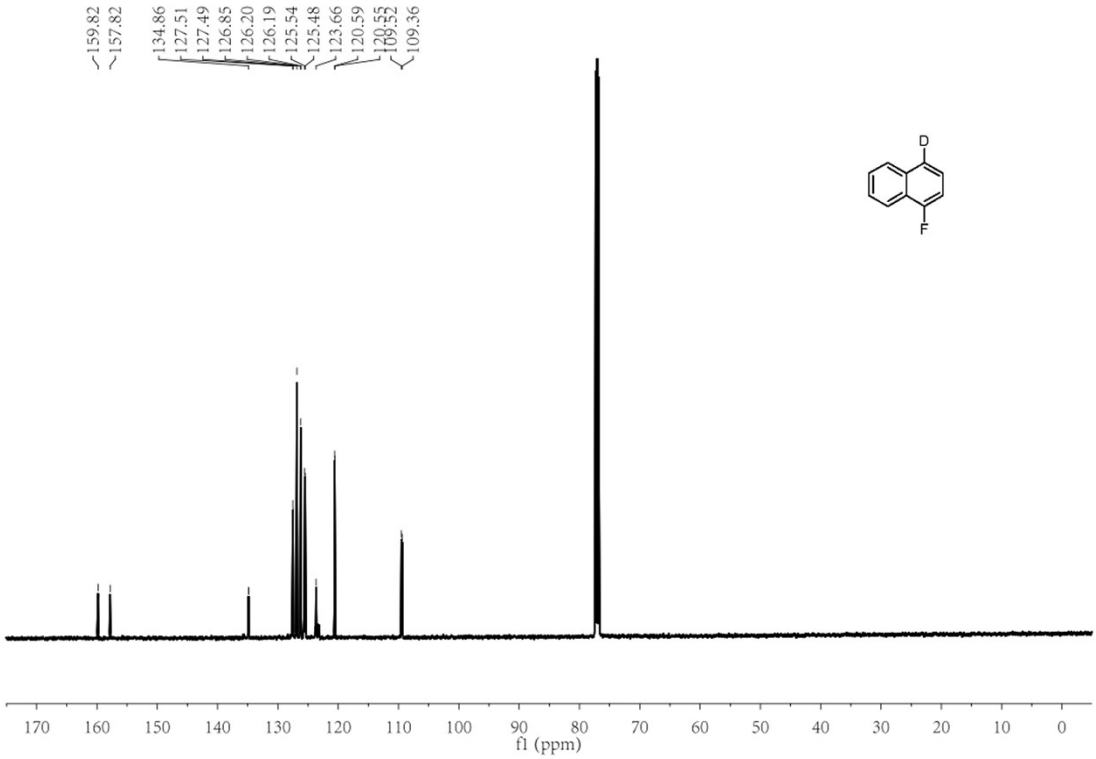
^{13}C NMR (126 MHz, $CDCl_3$) of compound **3f**.



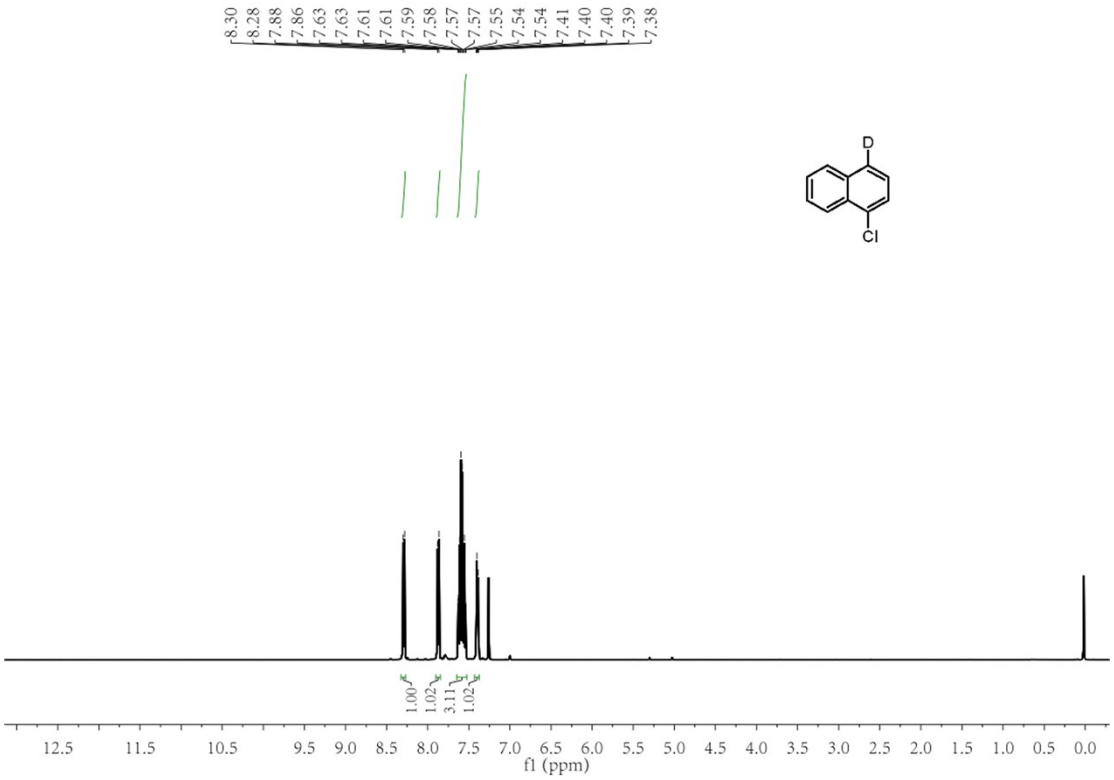
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3g**.



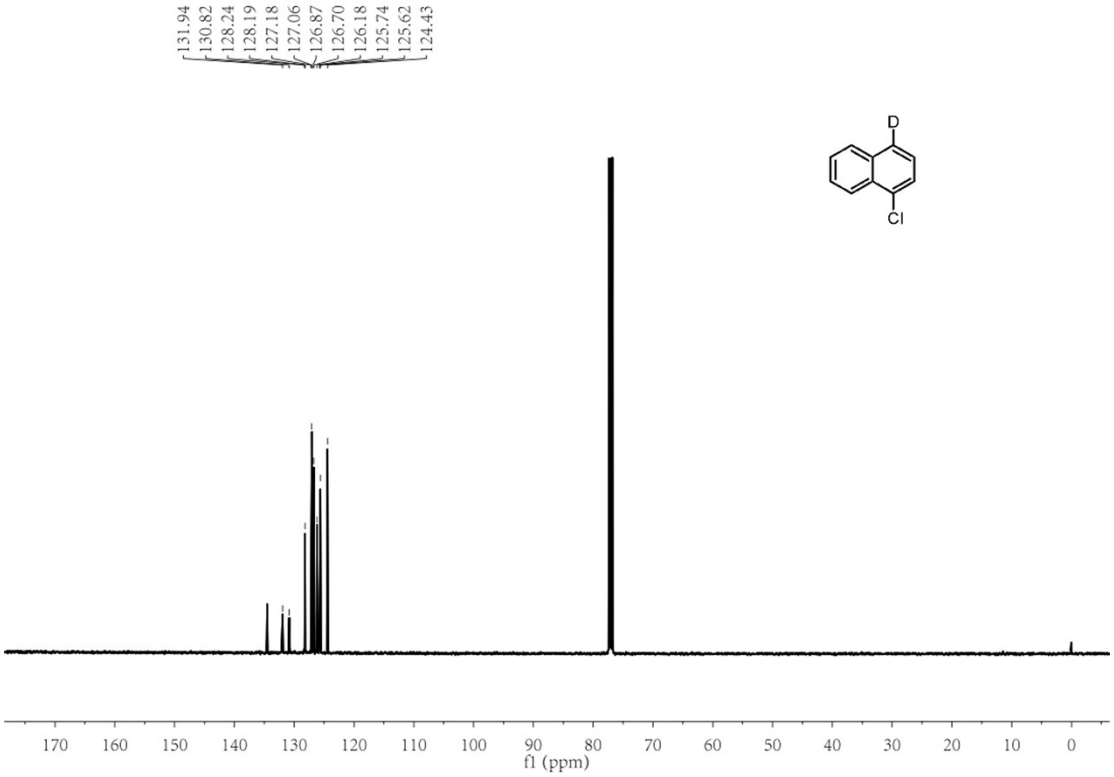
^{13}C NMR (126 MHz, $CDCl_3$) of compound **3g**.



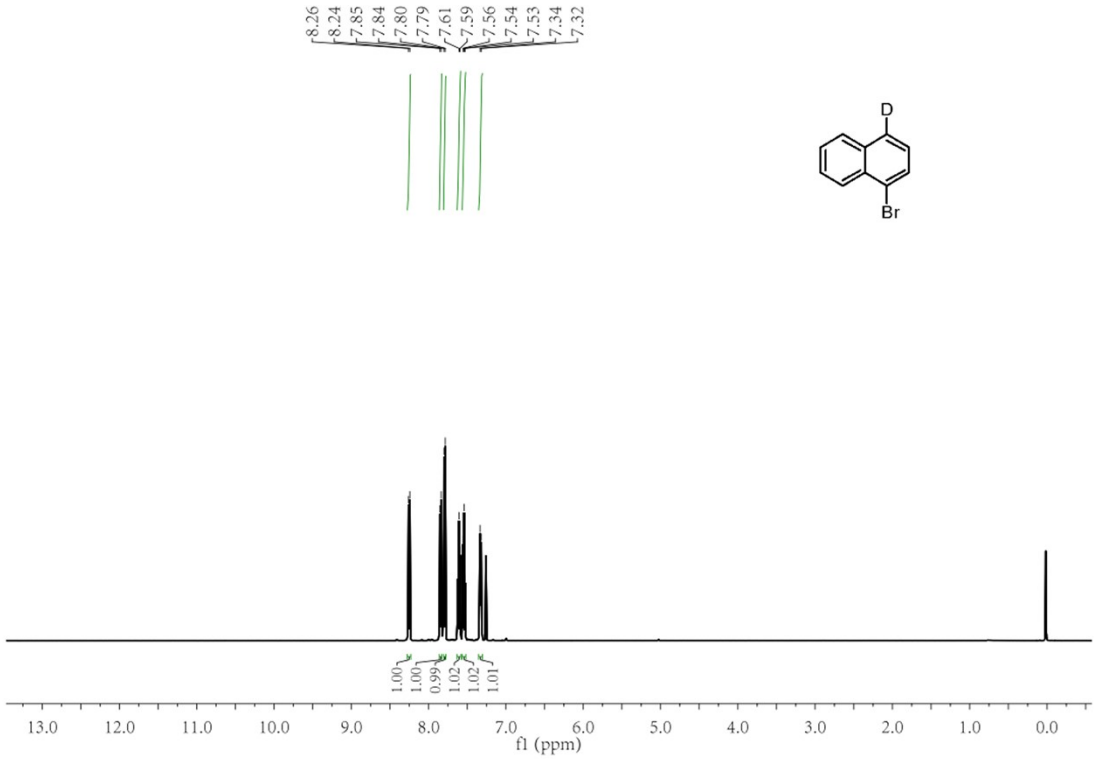
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3h**.



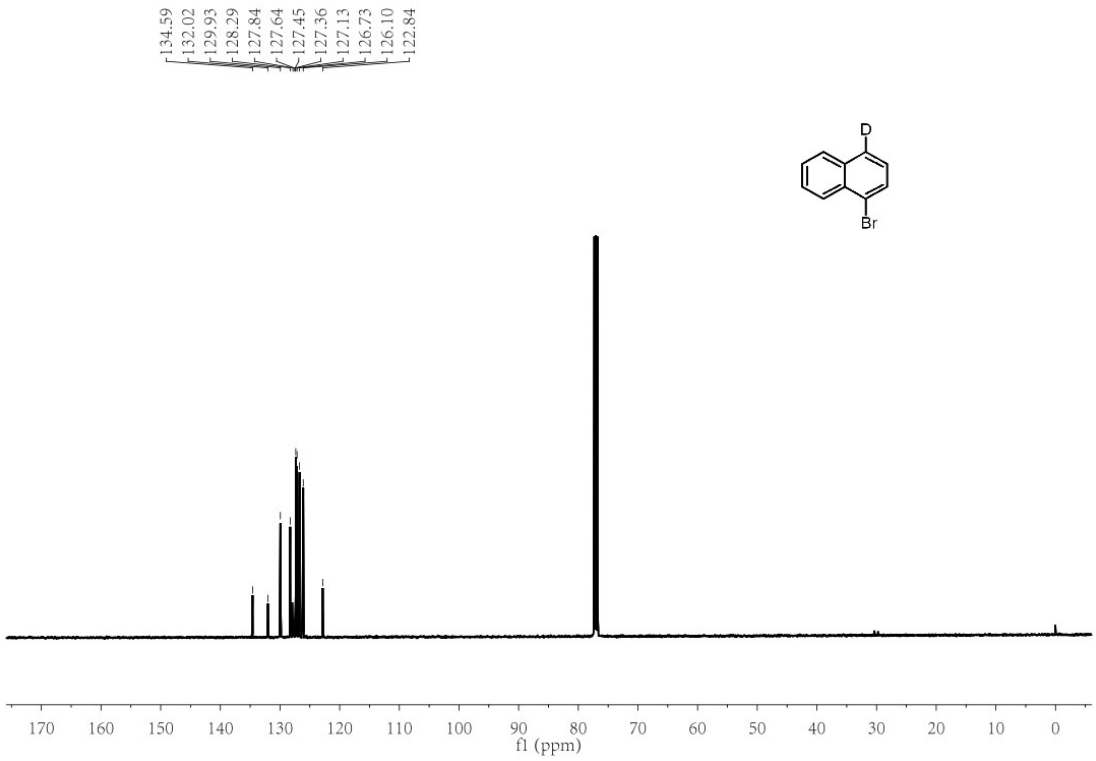
^{13}C NMR (126 MHz, $CDCl_3$) of compound **3h**.



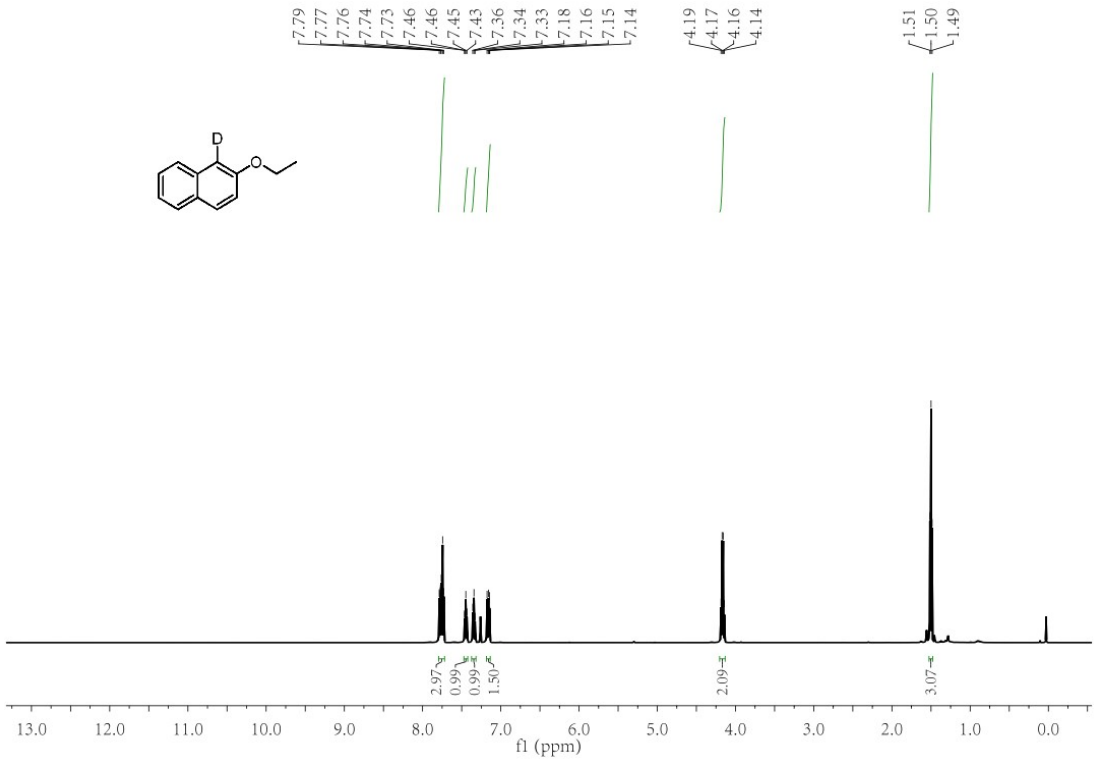
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3i**.



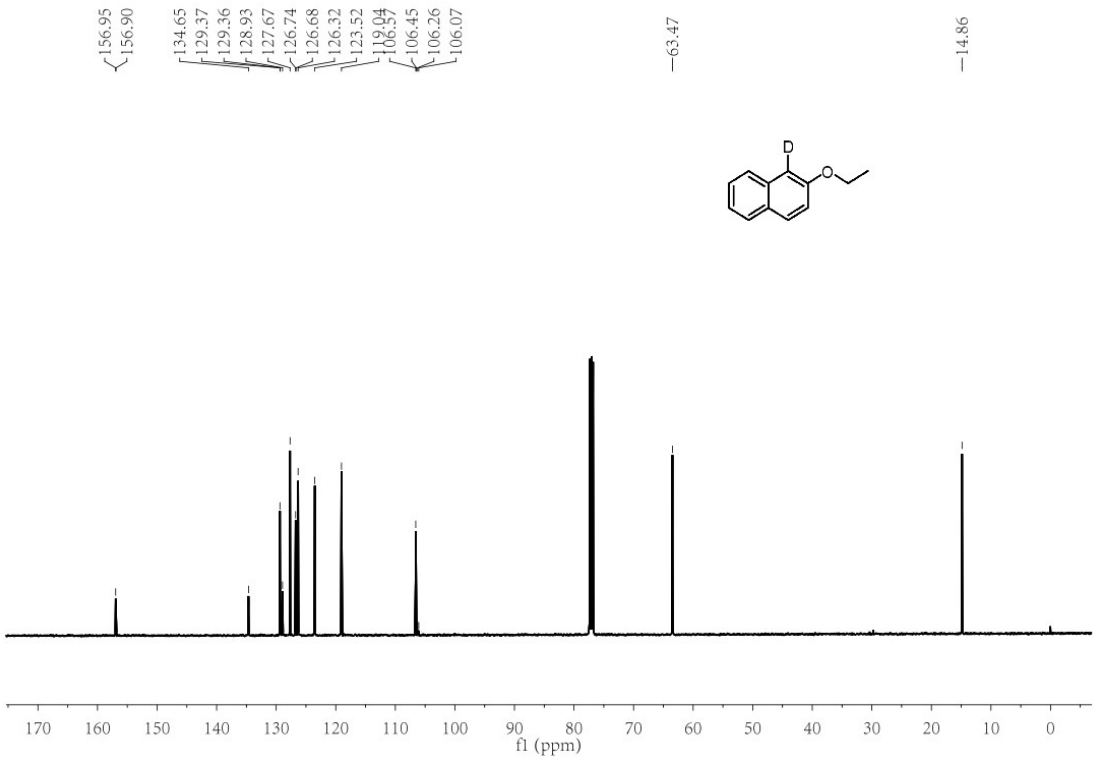
^{13}C NMR (126 MHz, $CDCl_3$) of compound **3i**.



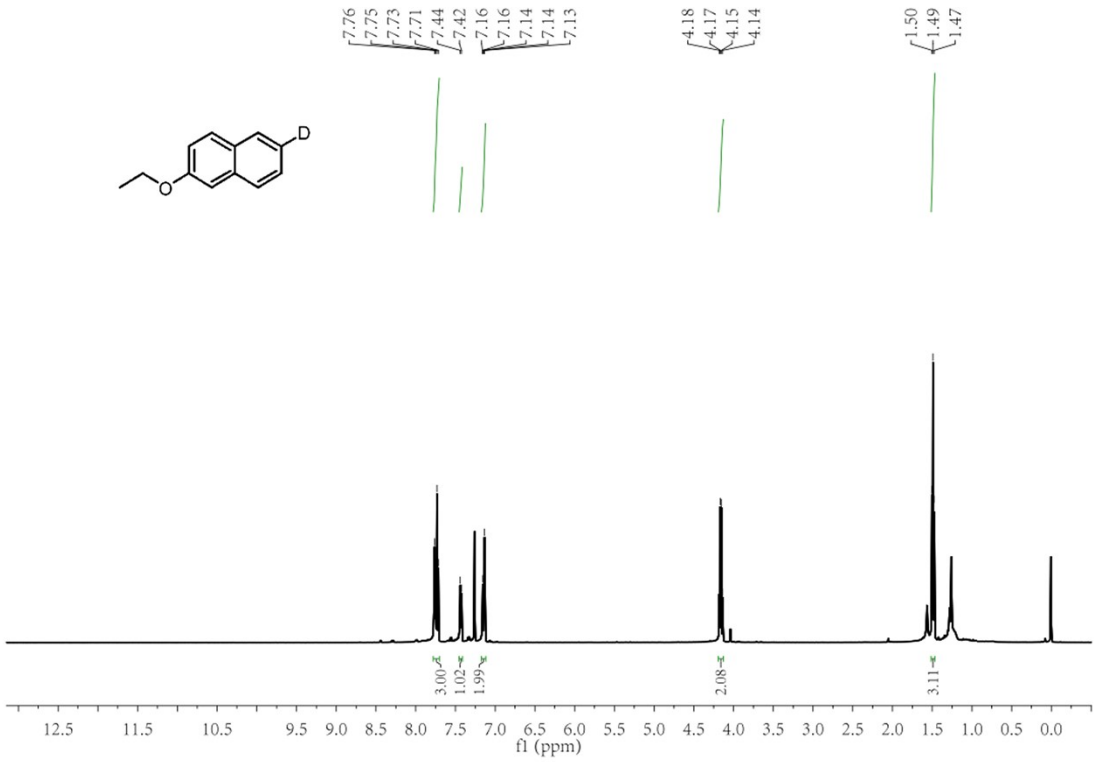
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3j**.



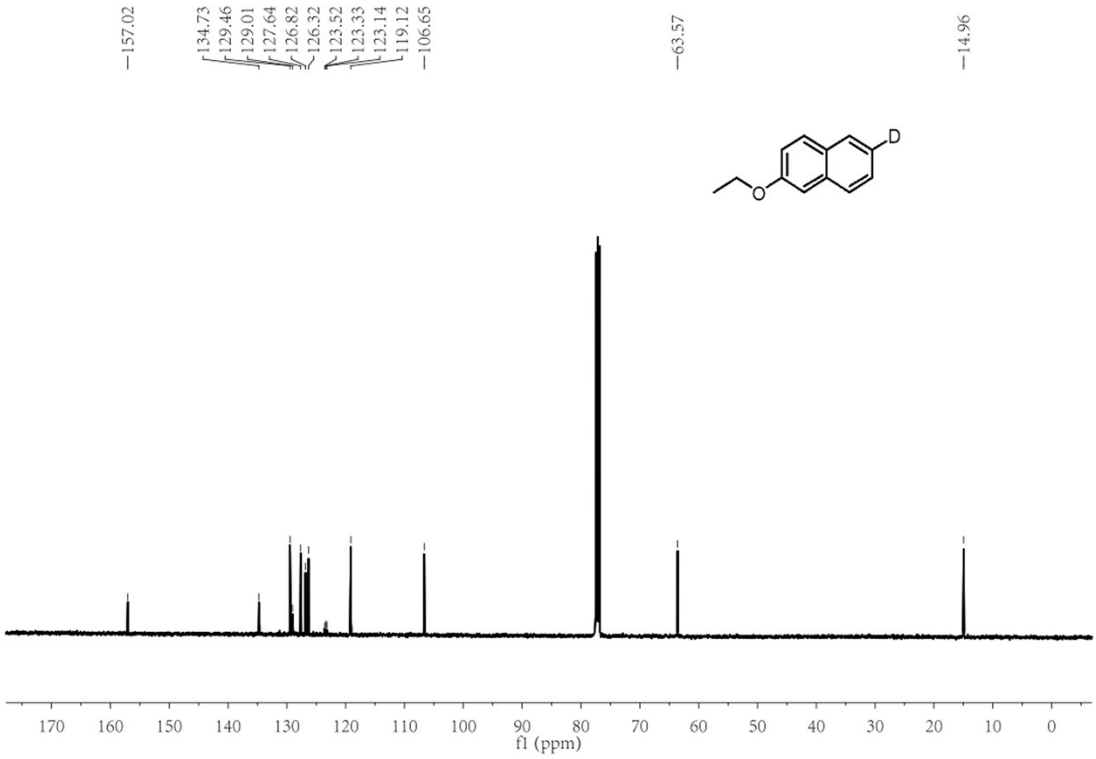
^{13}C NMR (126 MHz, $CDCl_3$) of compound **3j**.



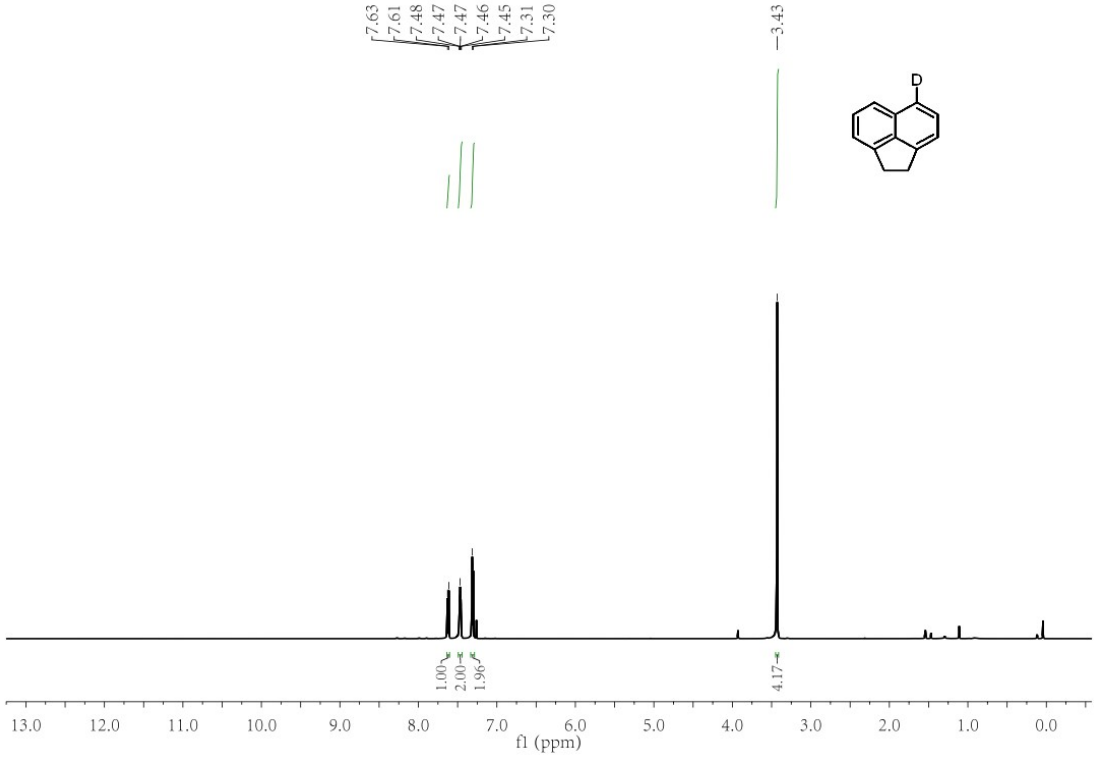
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3k**.



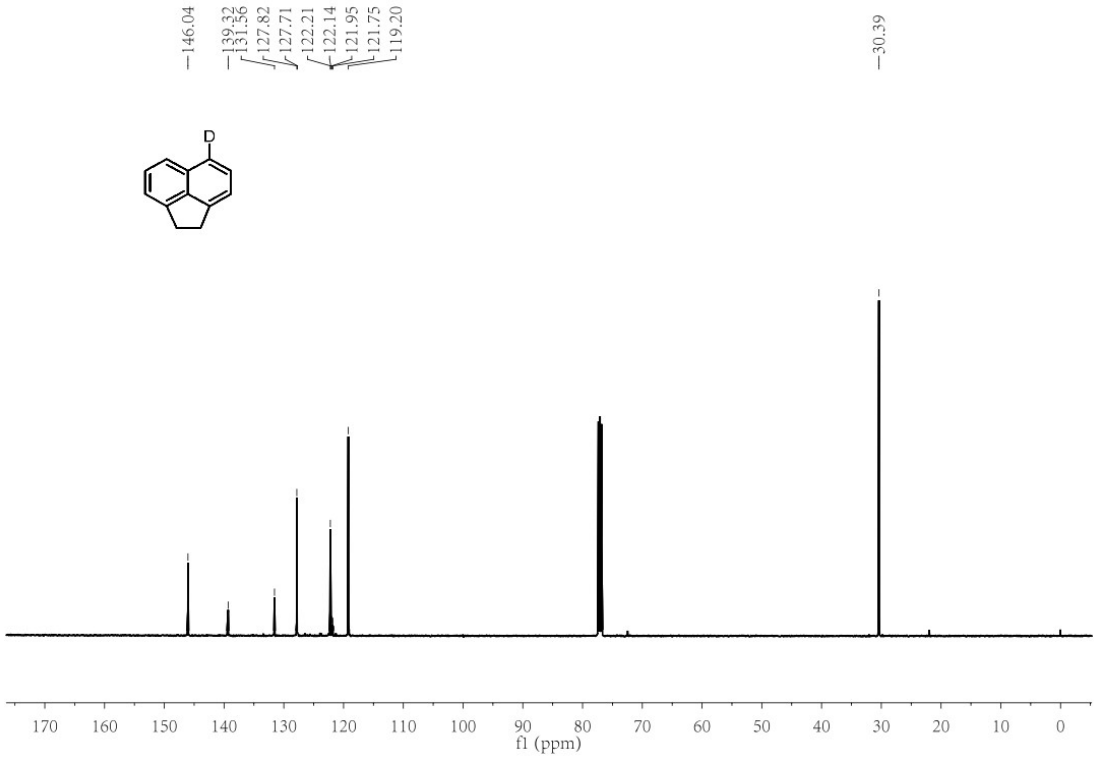
^{13}C NMR (126 MHz, $CDCl_3$) of compound **3k**.



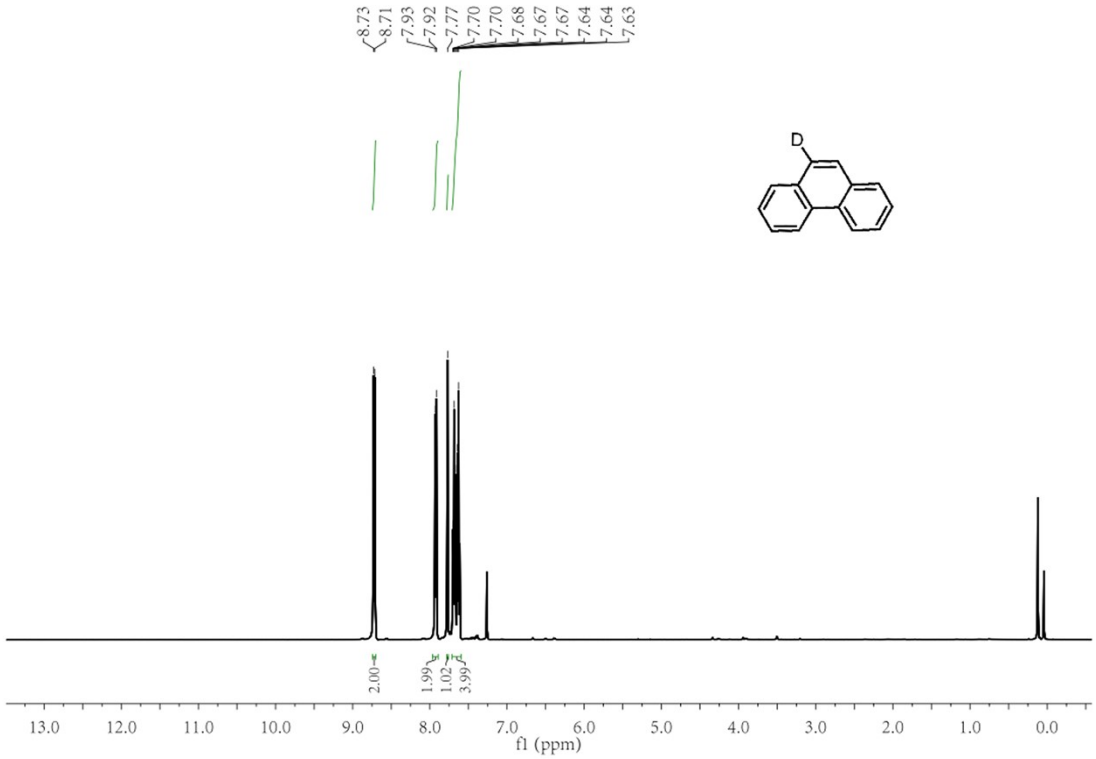
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3l**.



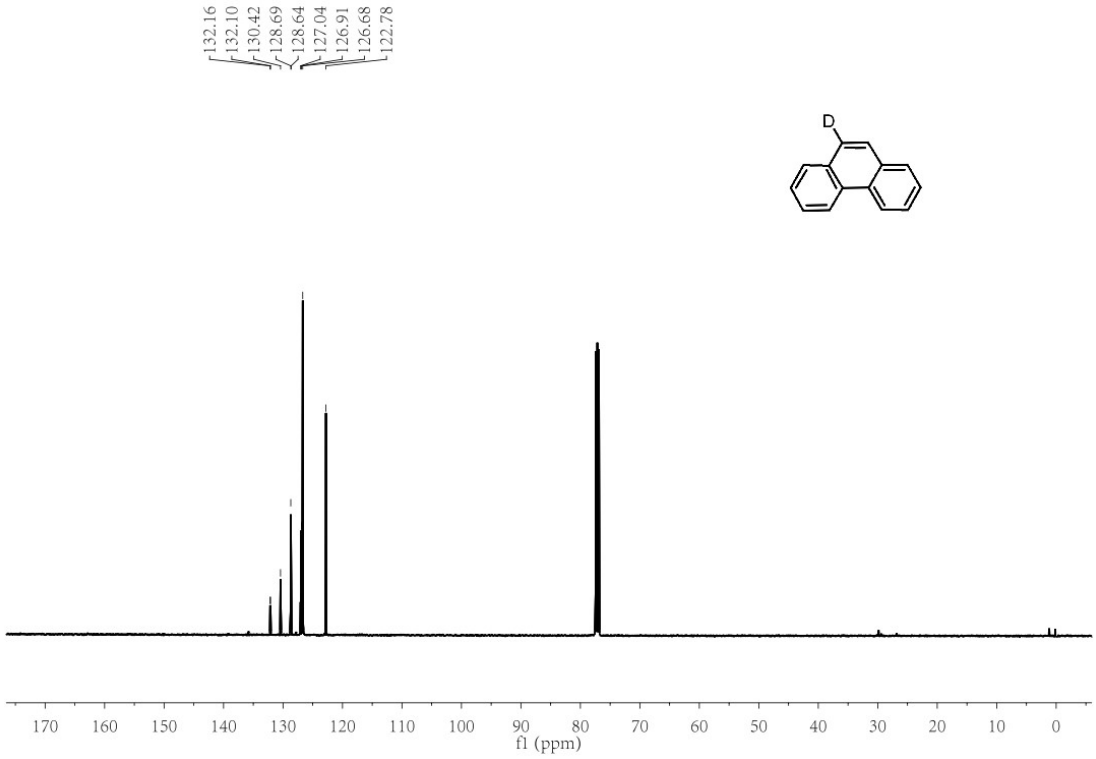
^{13}C NMR (126 MHz, $CDCl_3$) of compound **3l**.



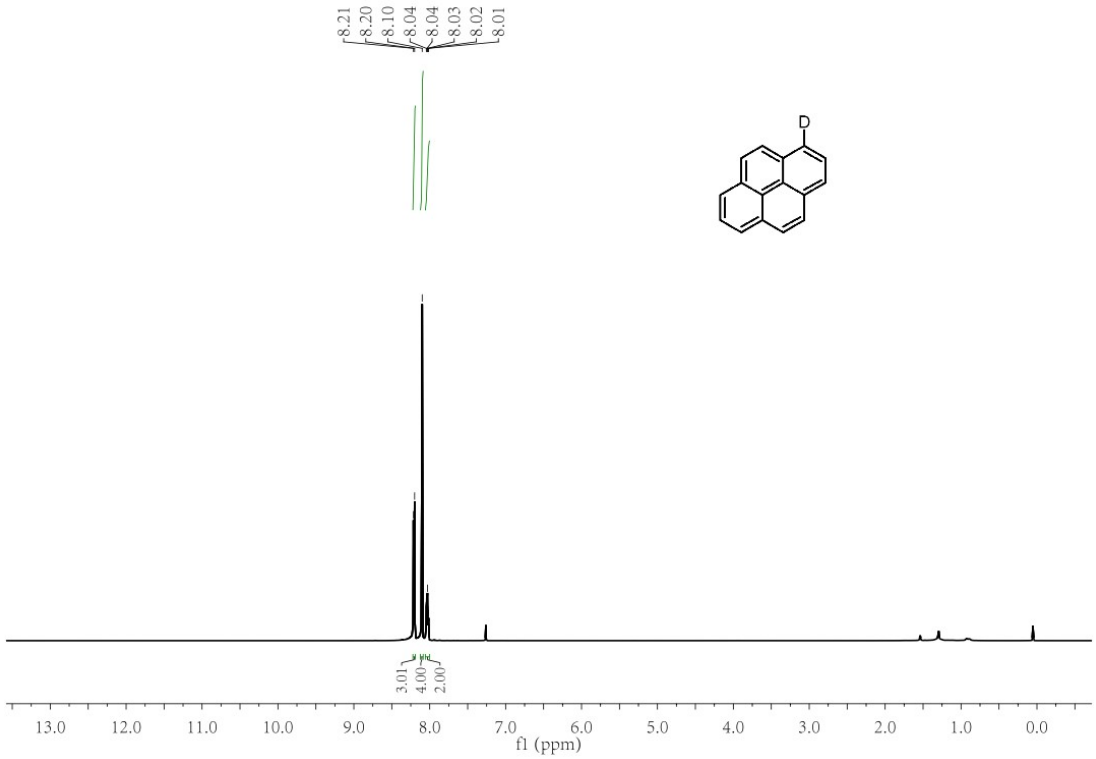
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3m**.



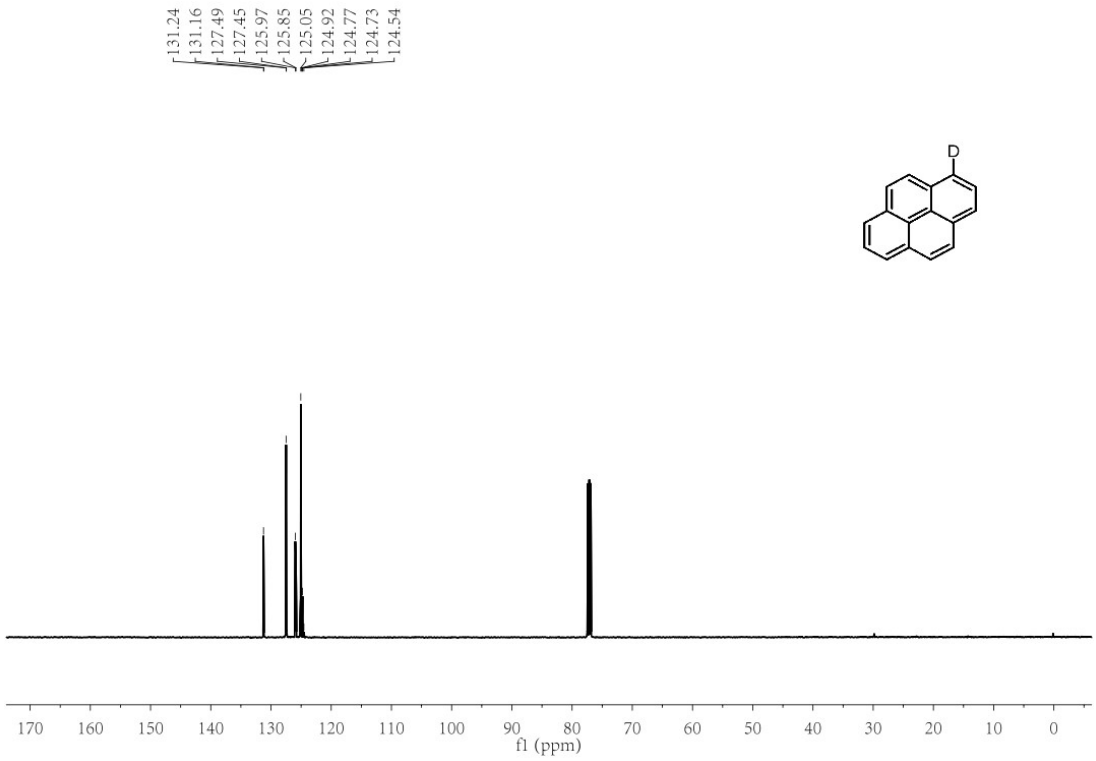
^{13}C NMR (126 MHz, $CDCl_3$) of compound **3m**.



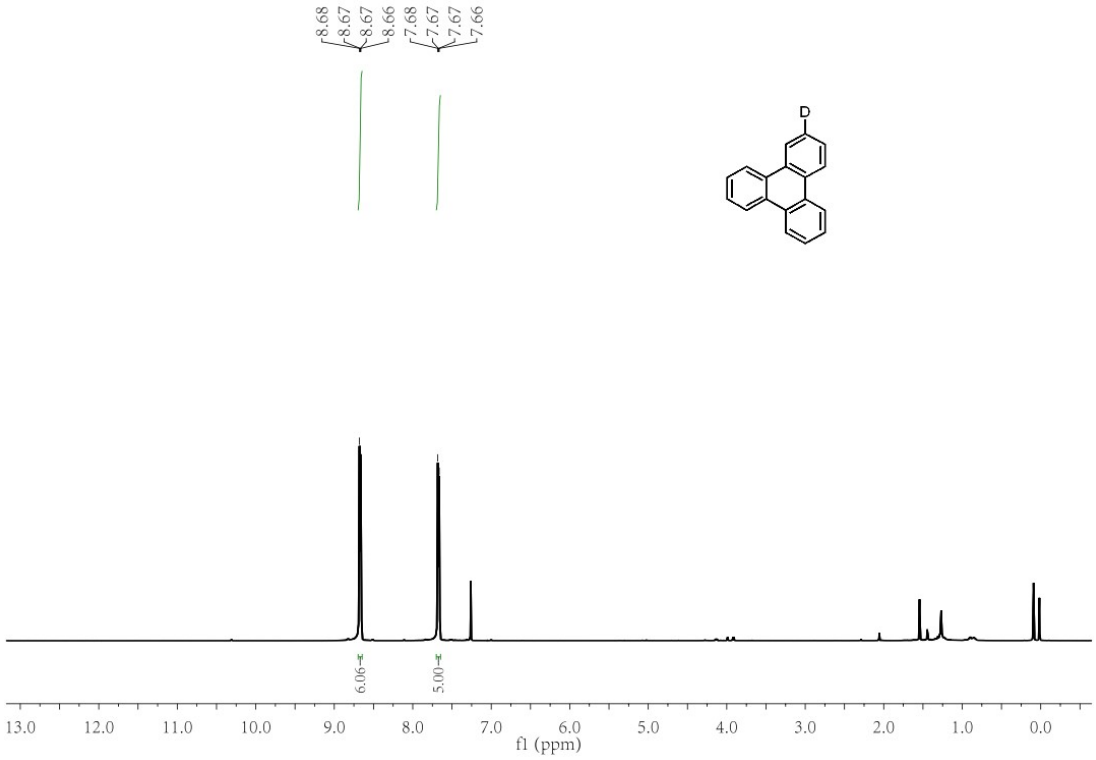
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3n**.



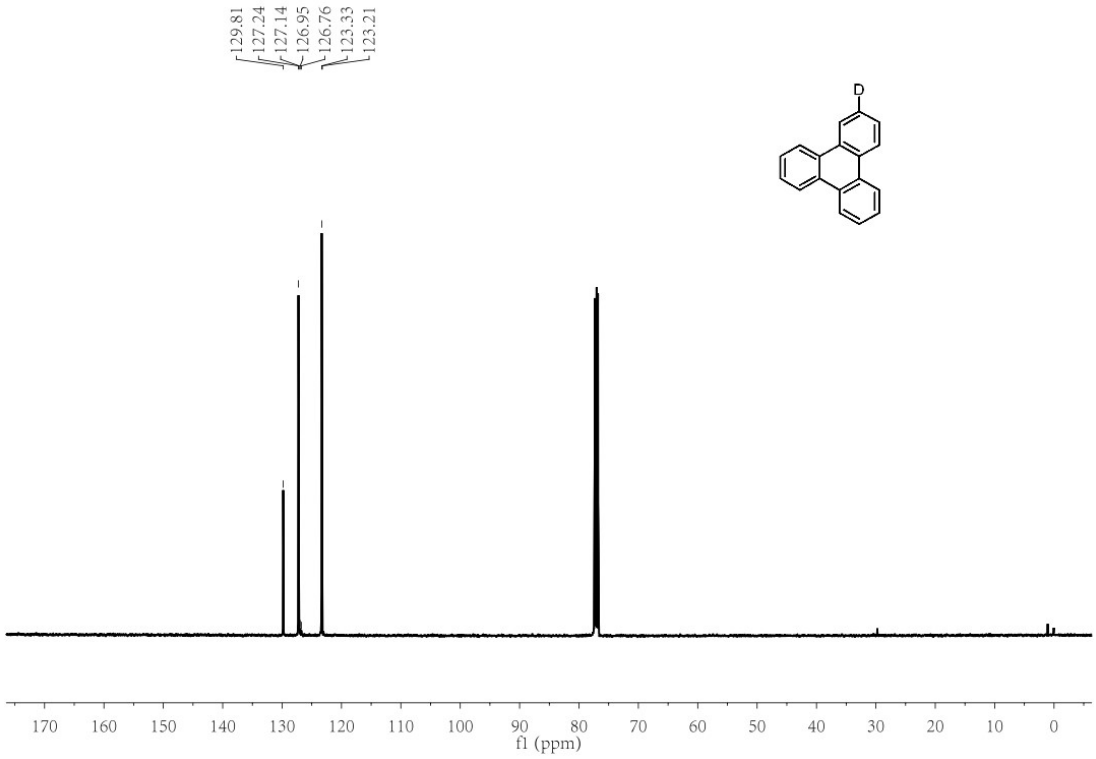
^{13}C NMR (126 MHz, $CDCl_3$) of compound **3n**.



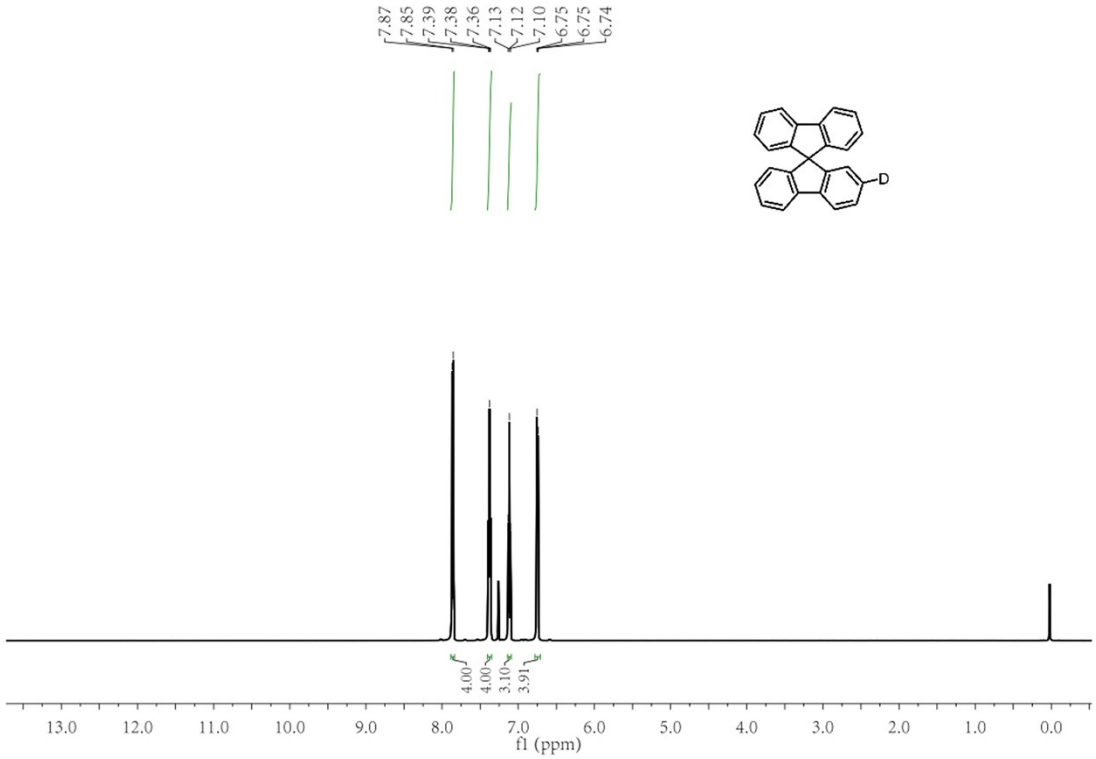
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3o**.



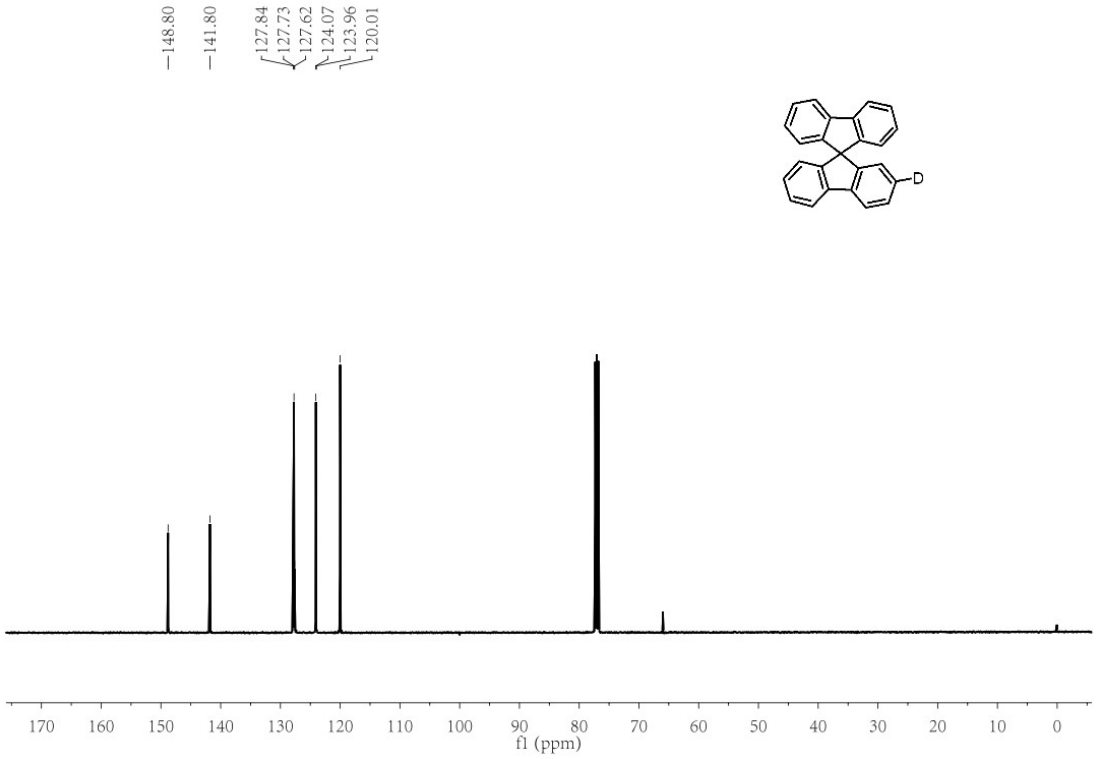
^{13}C NMR (126 MHz, $CDCl_3$) of compound **3o**.



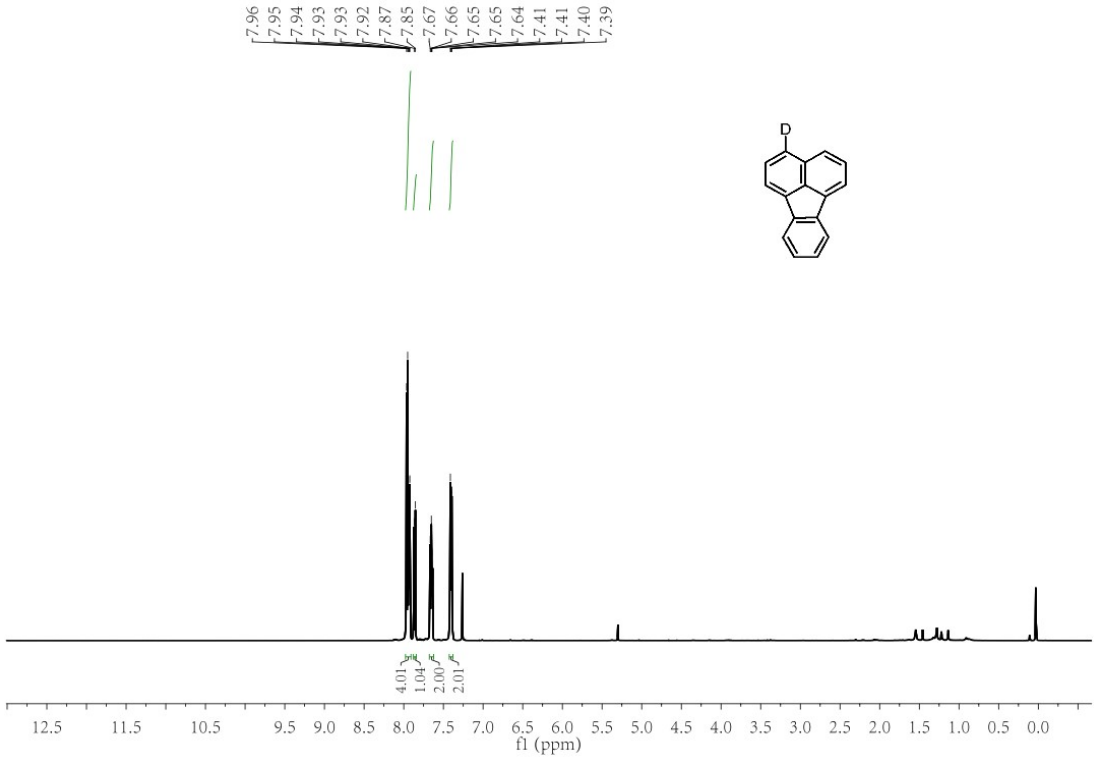
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3p**.



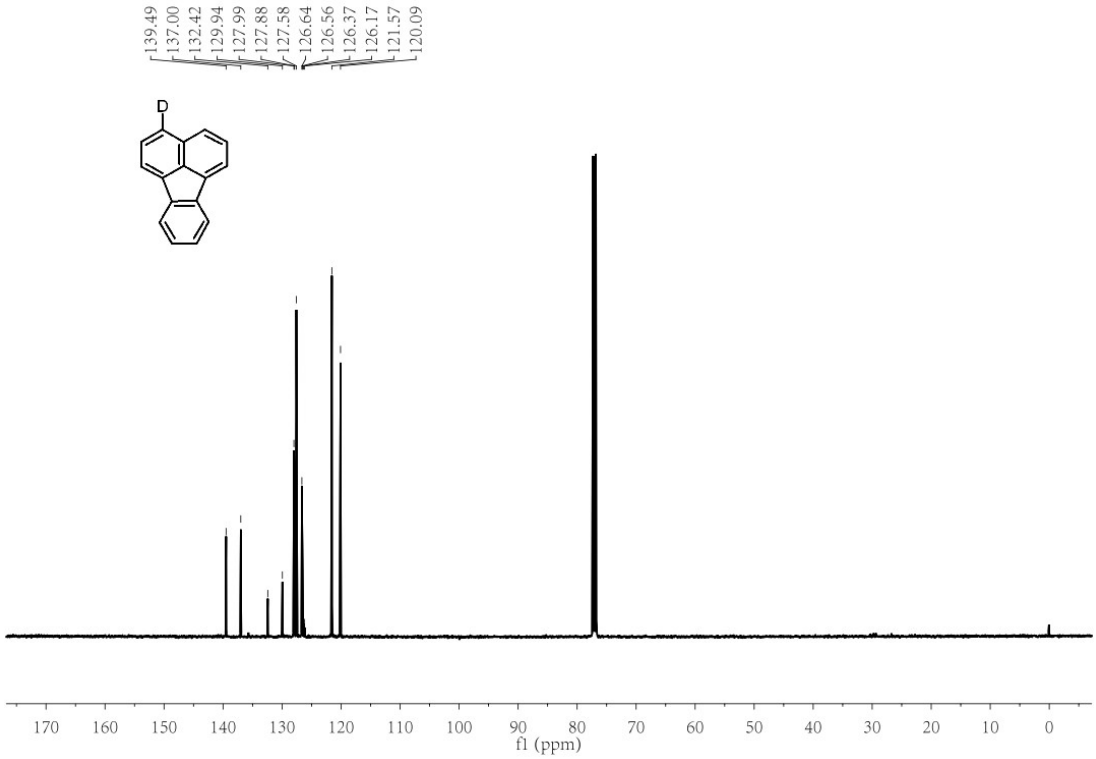
^{13}C NMR (126 MHz, $CDCl_3$) of compound **3p**.



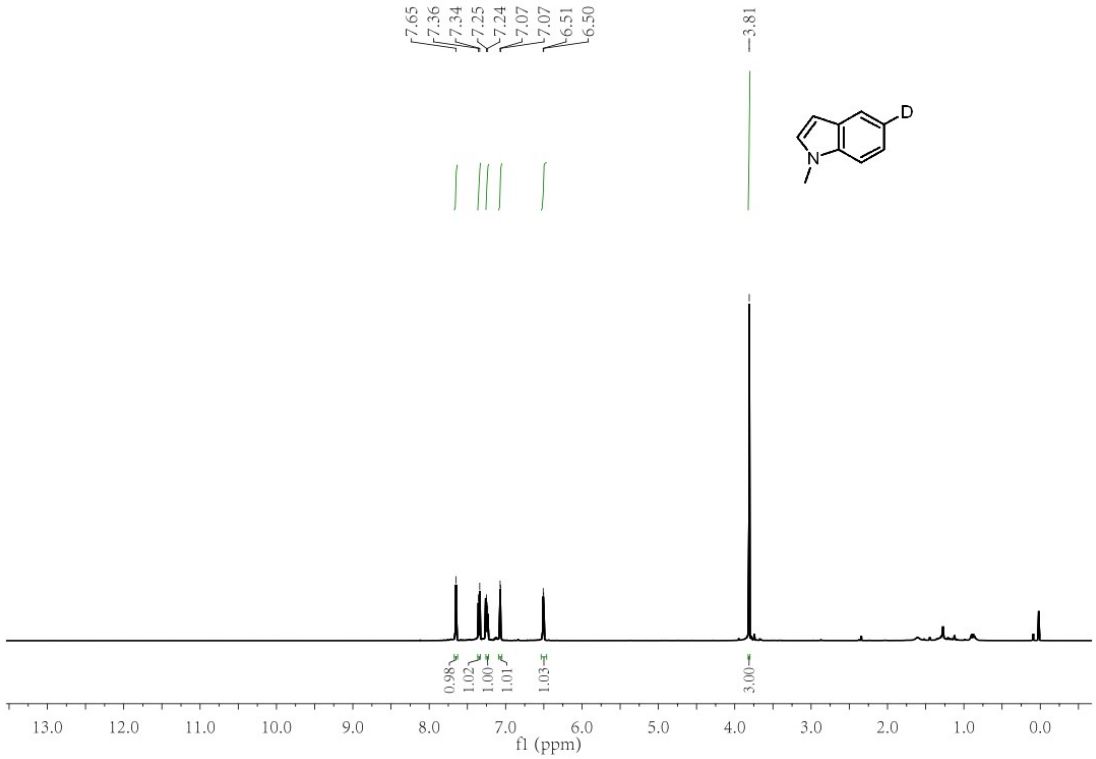
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3q**.



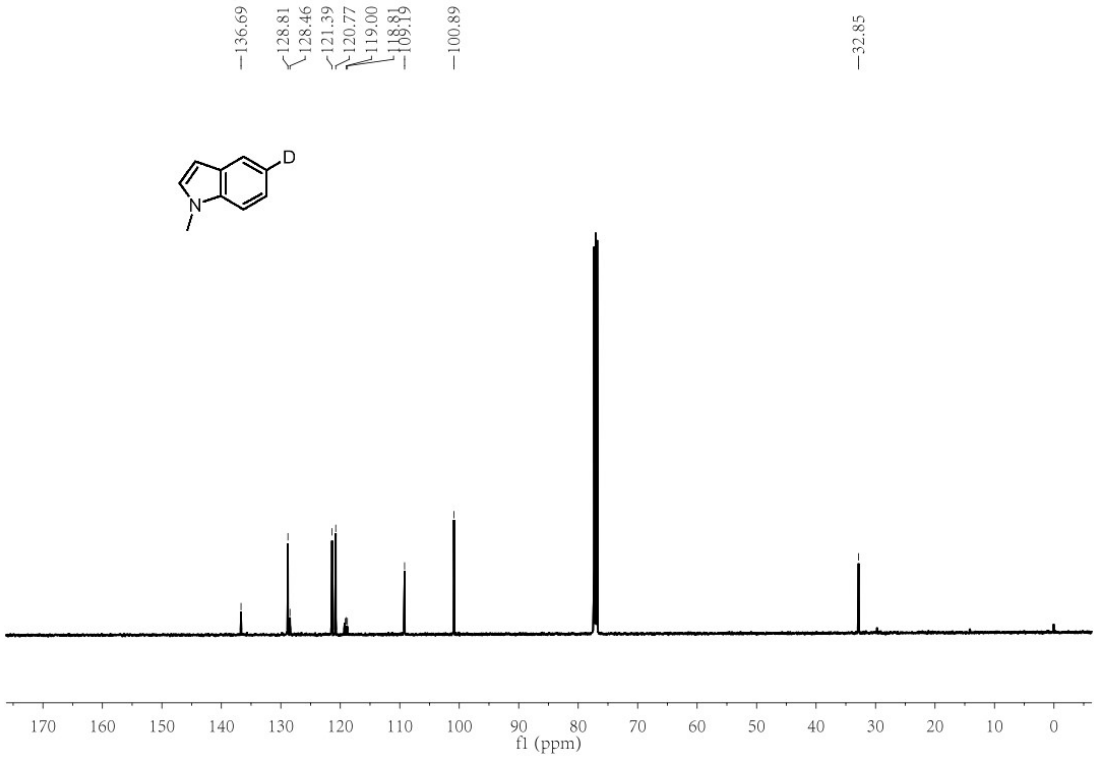
^{13}C NMR (126 MHz, $CDCl_3$) of compound **3q**.



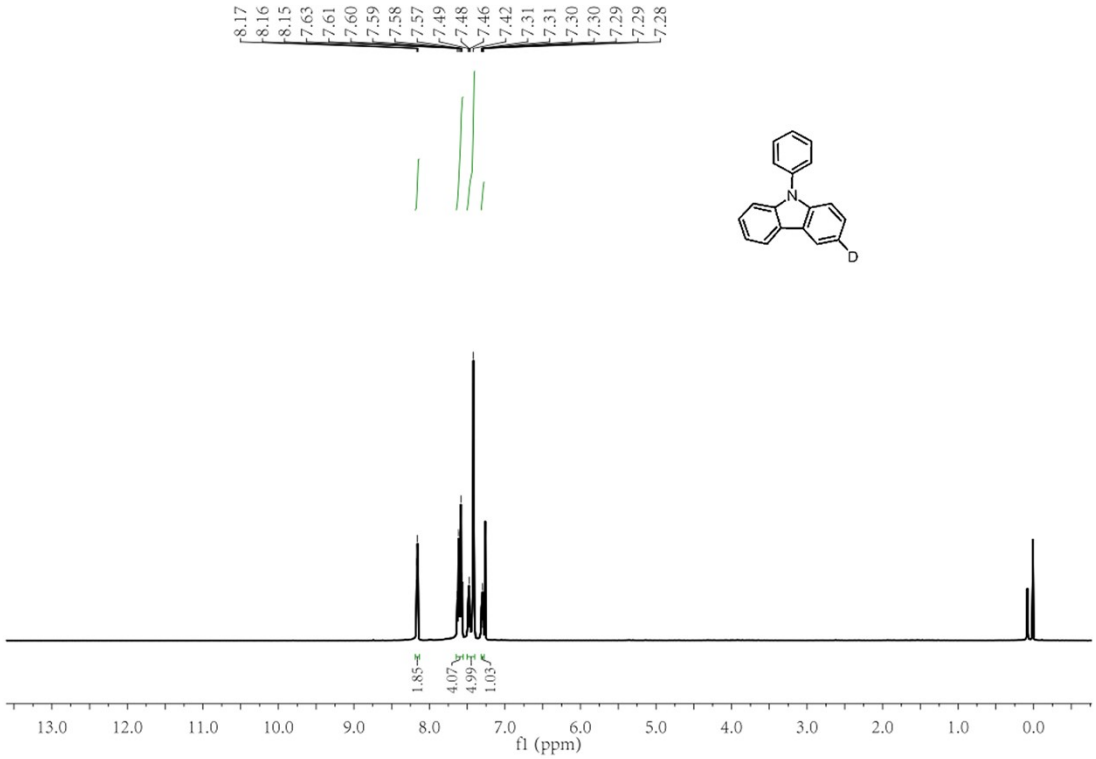
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3r**.



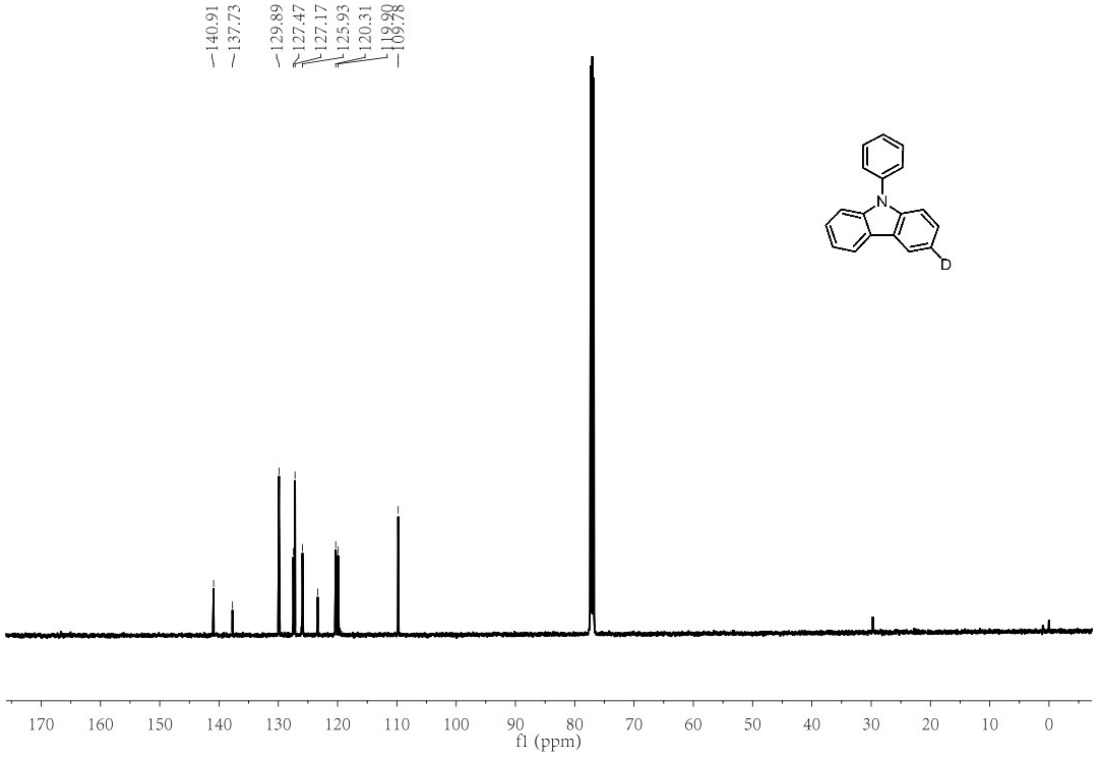
^{13}C NMR (126 MHz, $CDCl_3$) of compound **3r**.



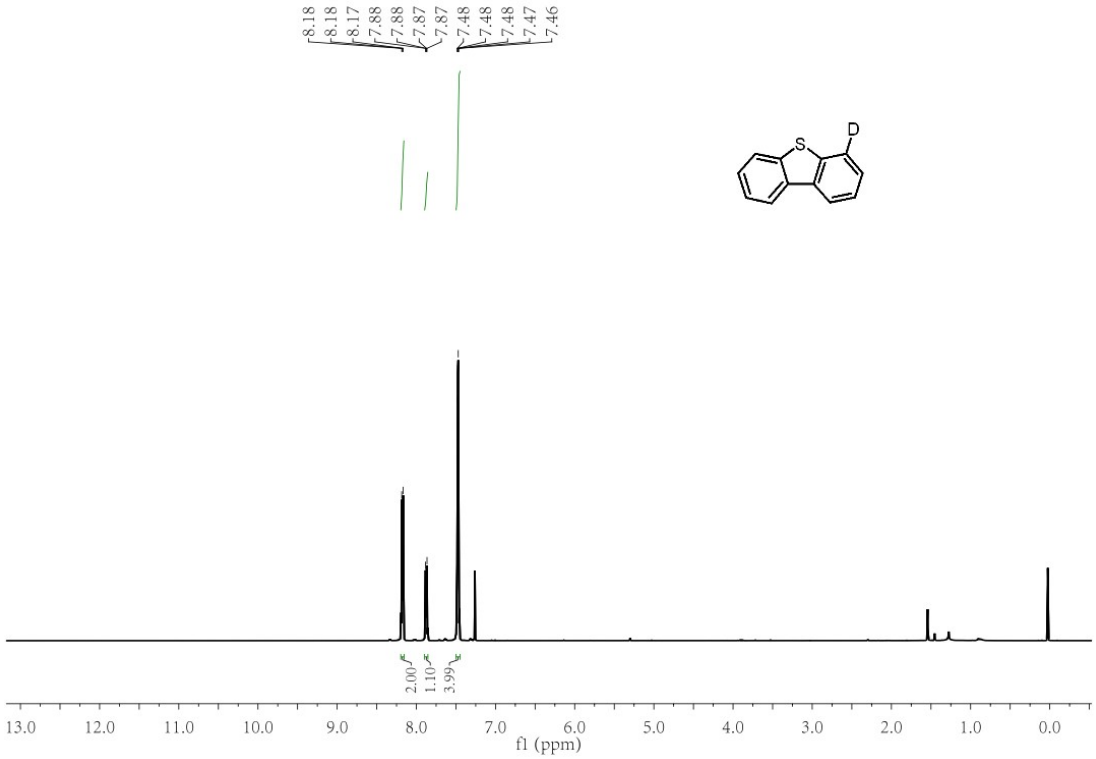
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3s**.



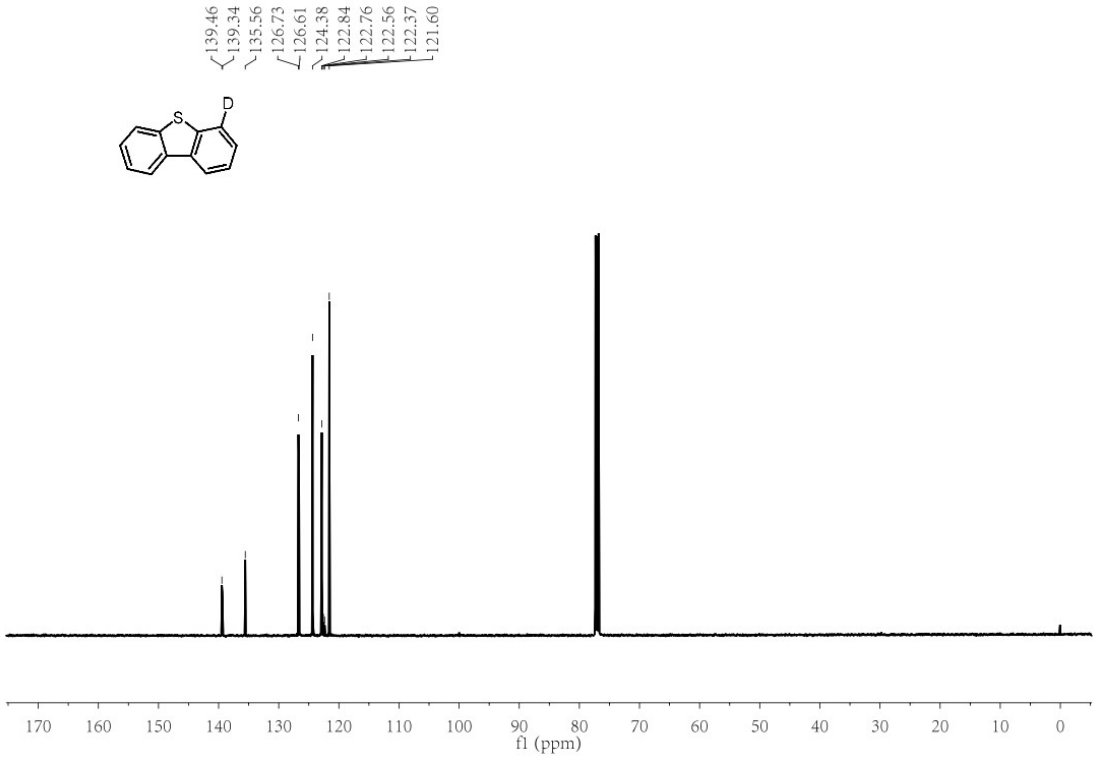
^{13}C NMR (126 MHz, $CDCl_3$) of compound **3s**.



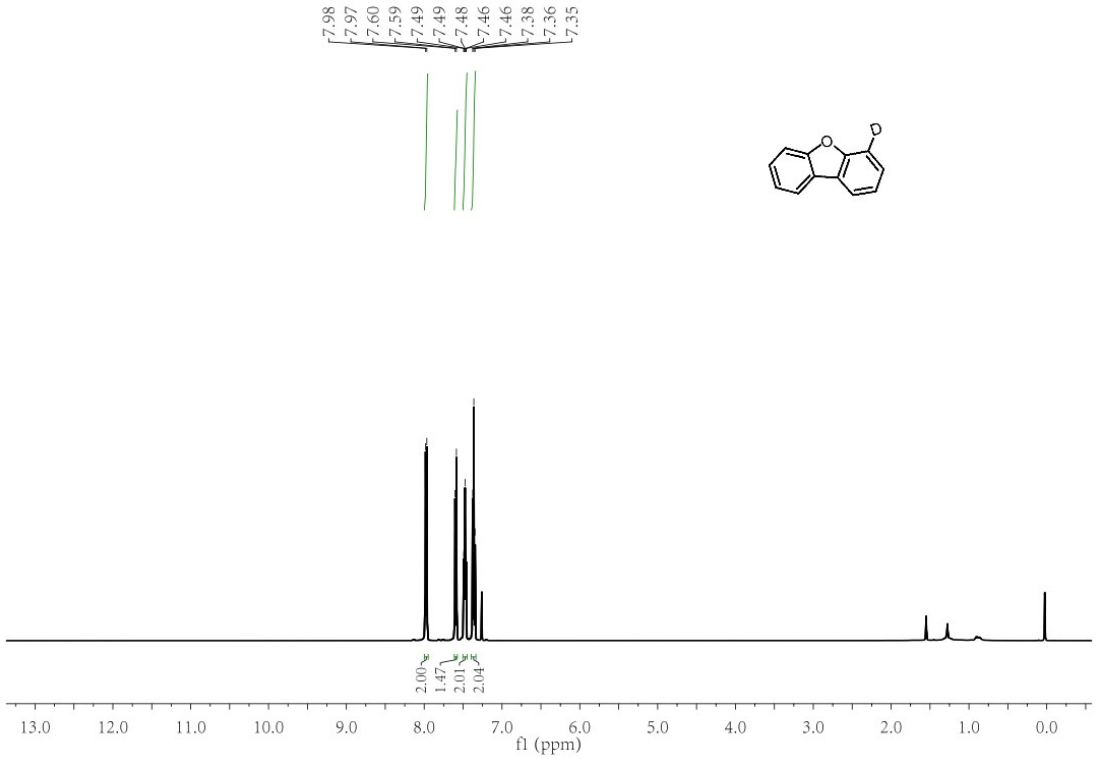
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3t**.



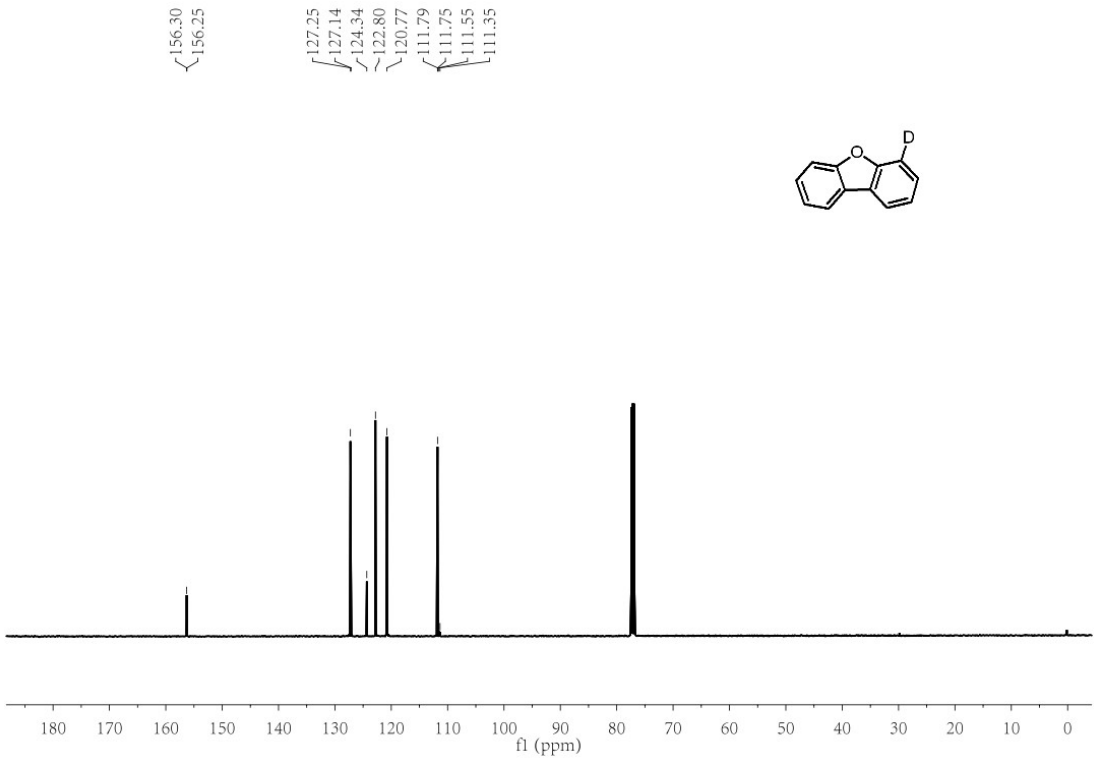
^{13}C NMR (126 MHz, $CDCl_3$) of compound **3t**.



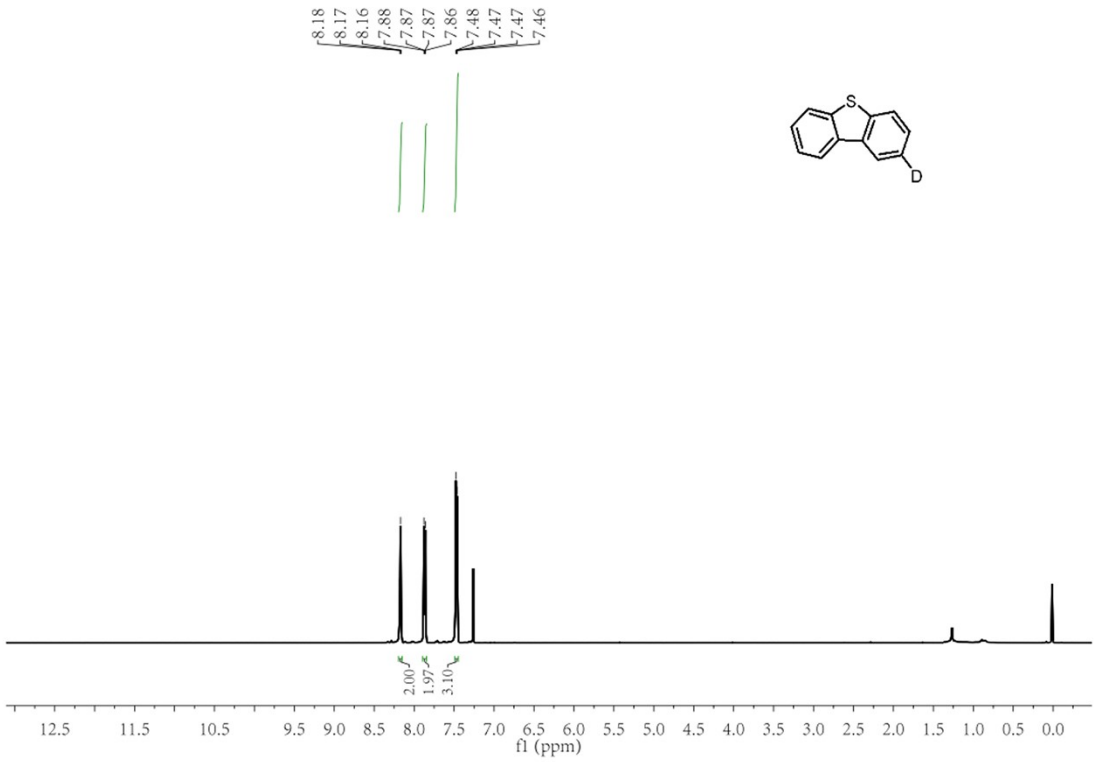
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3u**.



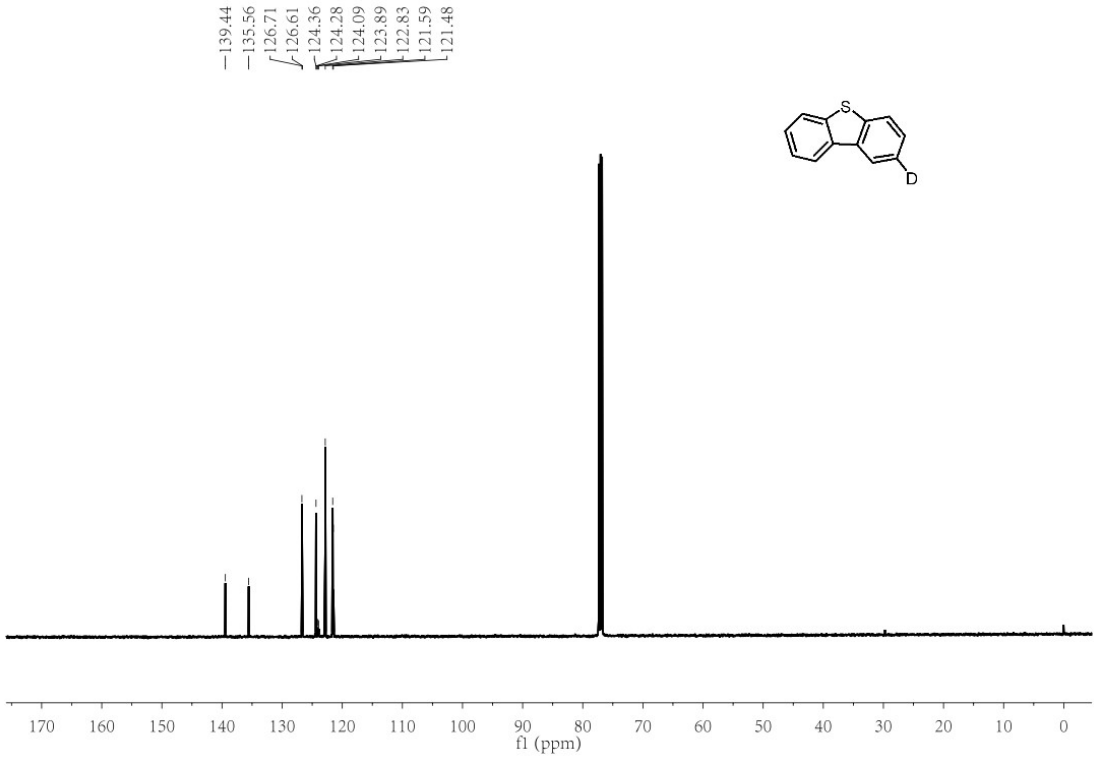
^{13}C NMR (126 MHz, $CDCl_3$) of compound **3u**.



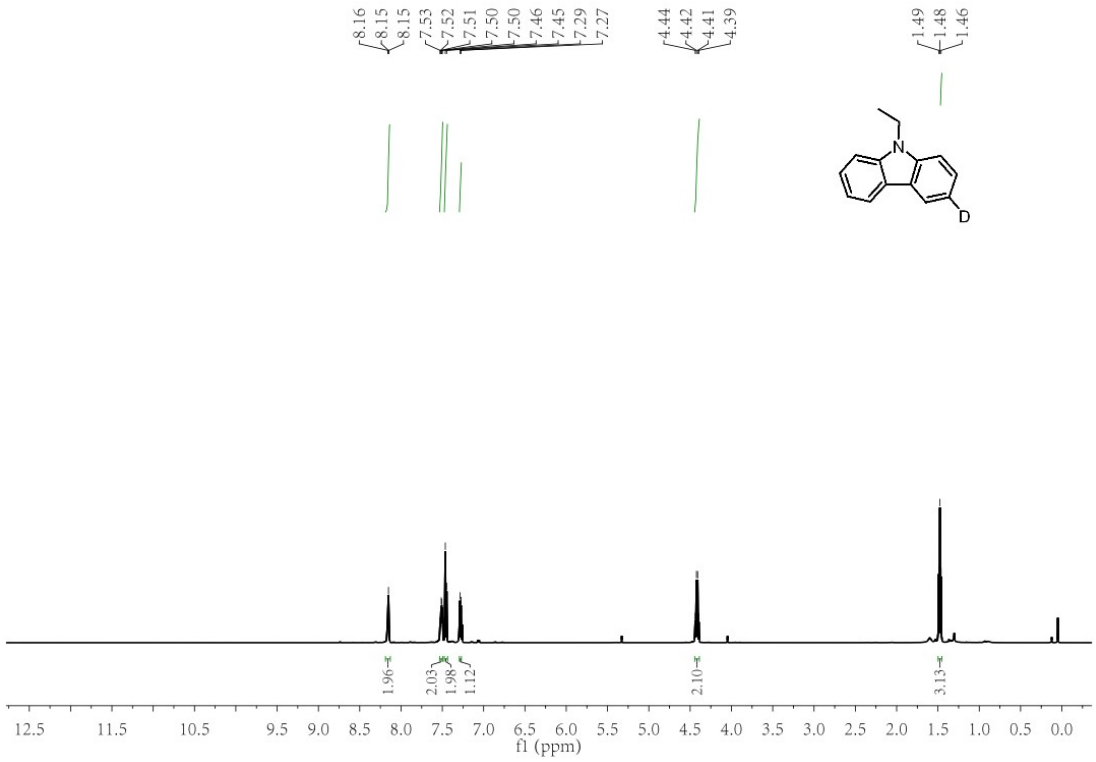
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3v**.



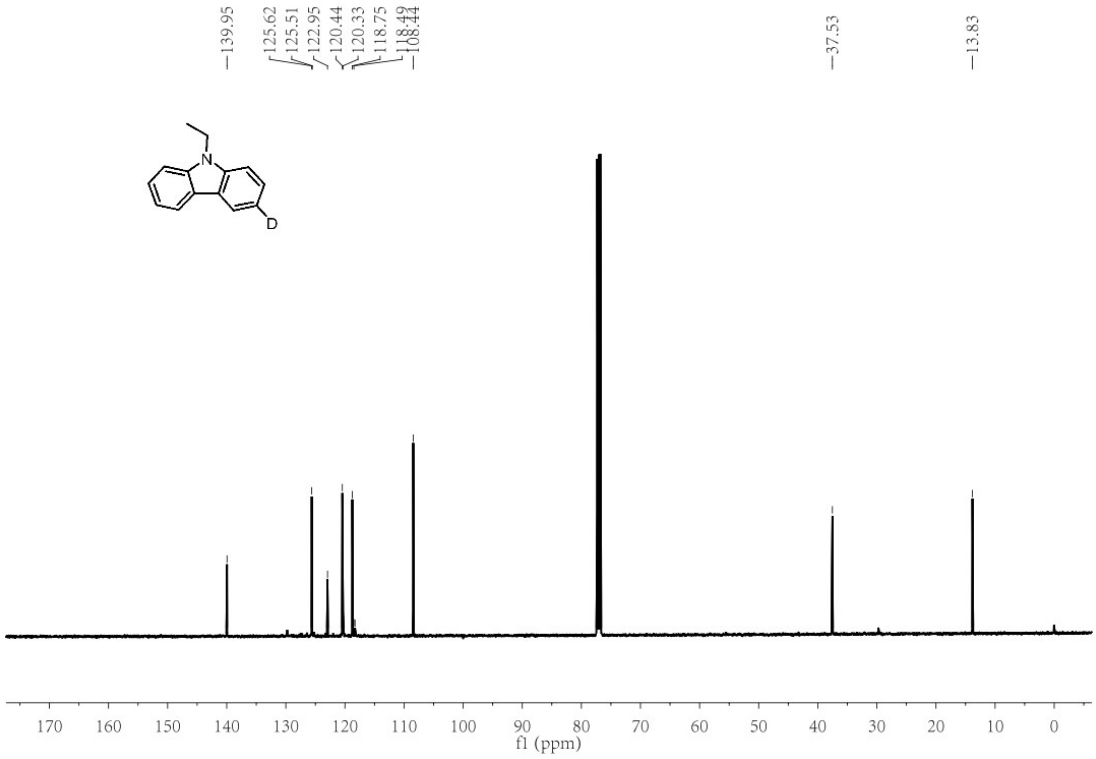
^{13}C NMR (126 MHz, $CDCl_3$) of compound **3v**.



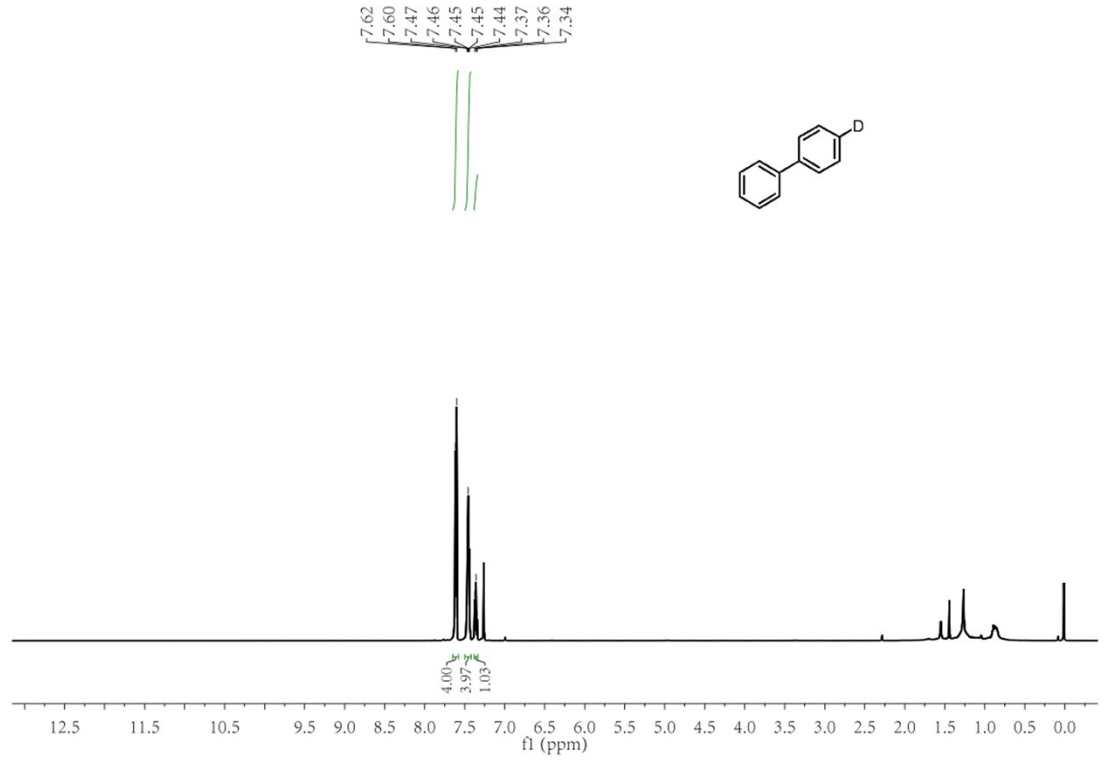
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3w**.



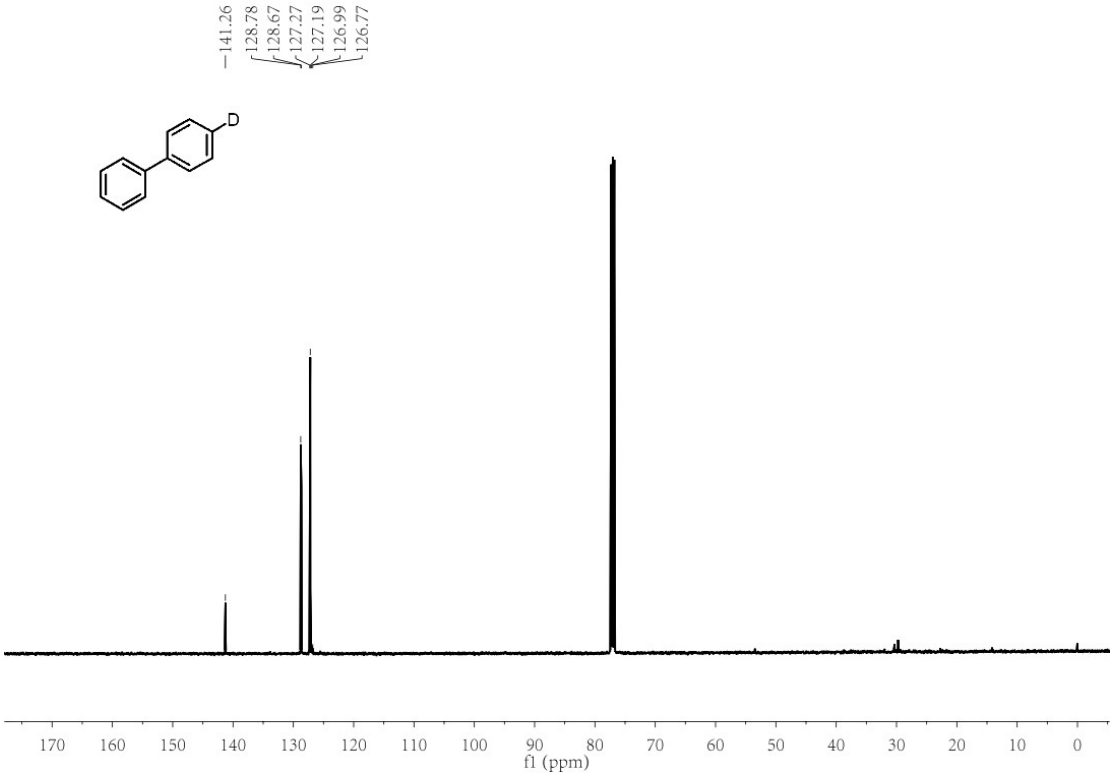
^{13}C NMR (126 MHz, $CDCl_3$) of compound **3w**.



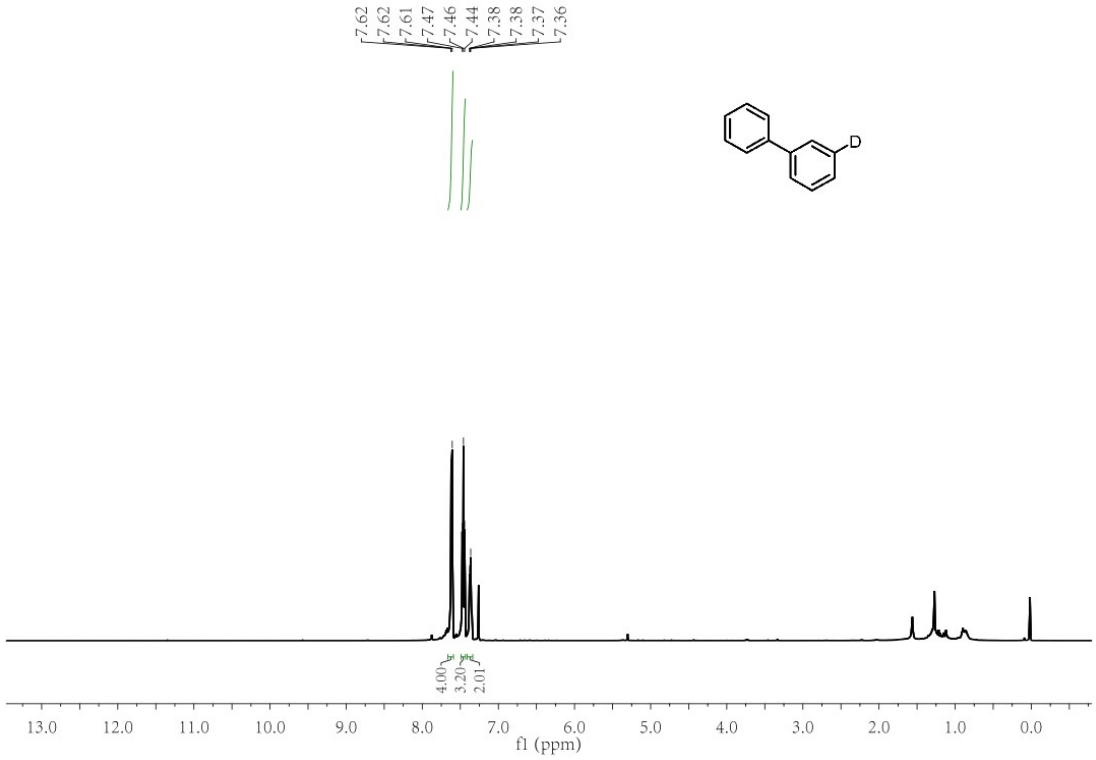
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3x**.



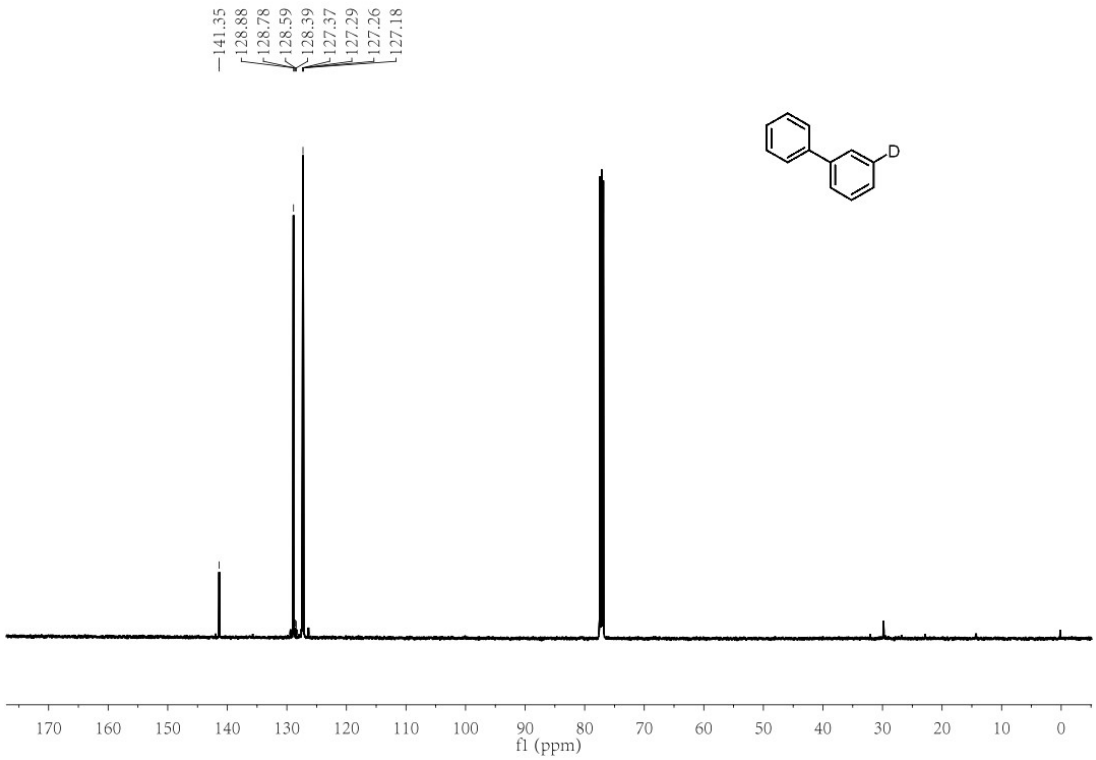
^{13}C NMR (126 MHz, $CDCl_3$) of compound **3x**.



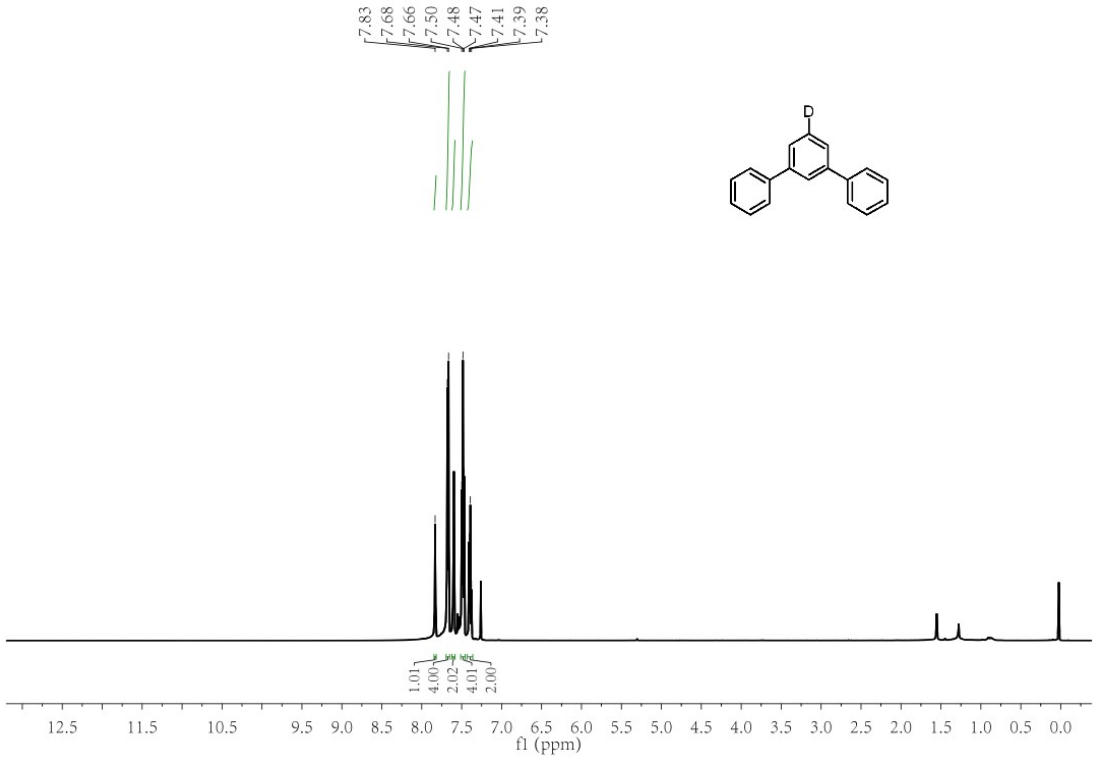
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3y**.



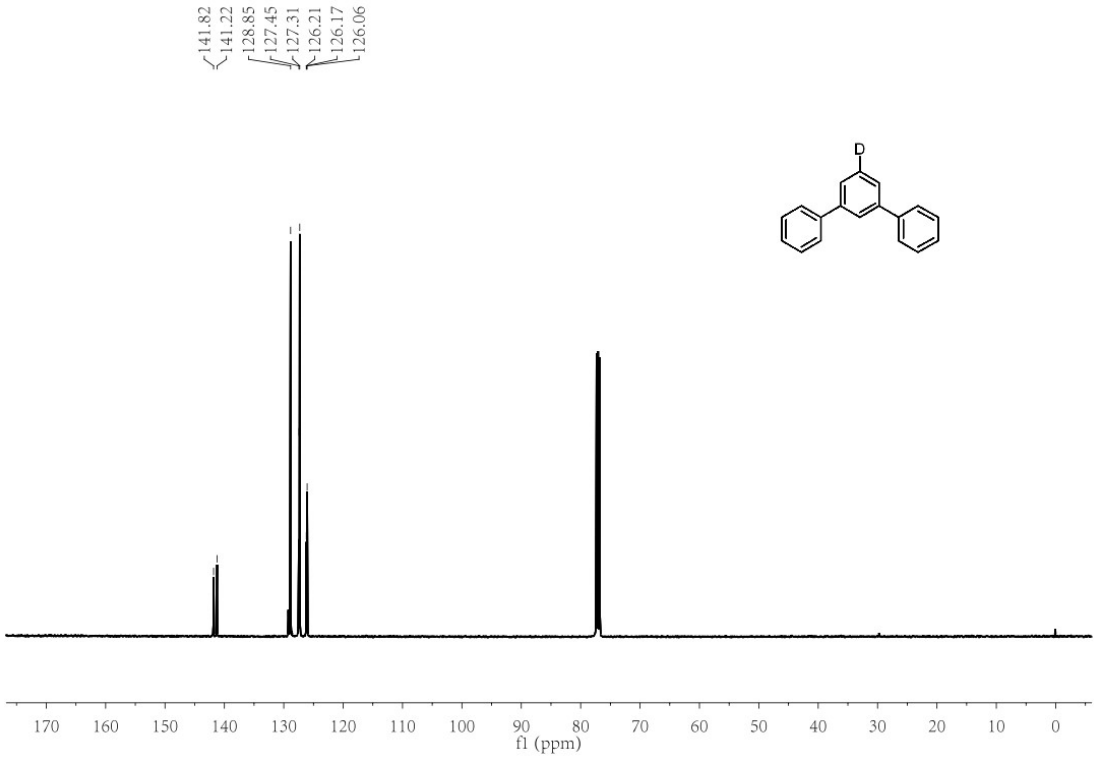
^{13}C NMR (126 MHz, $CDCl_3$) of compound **3y**.



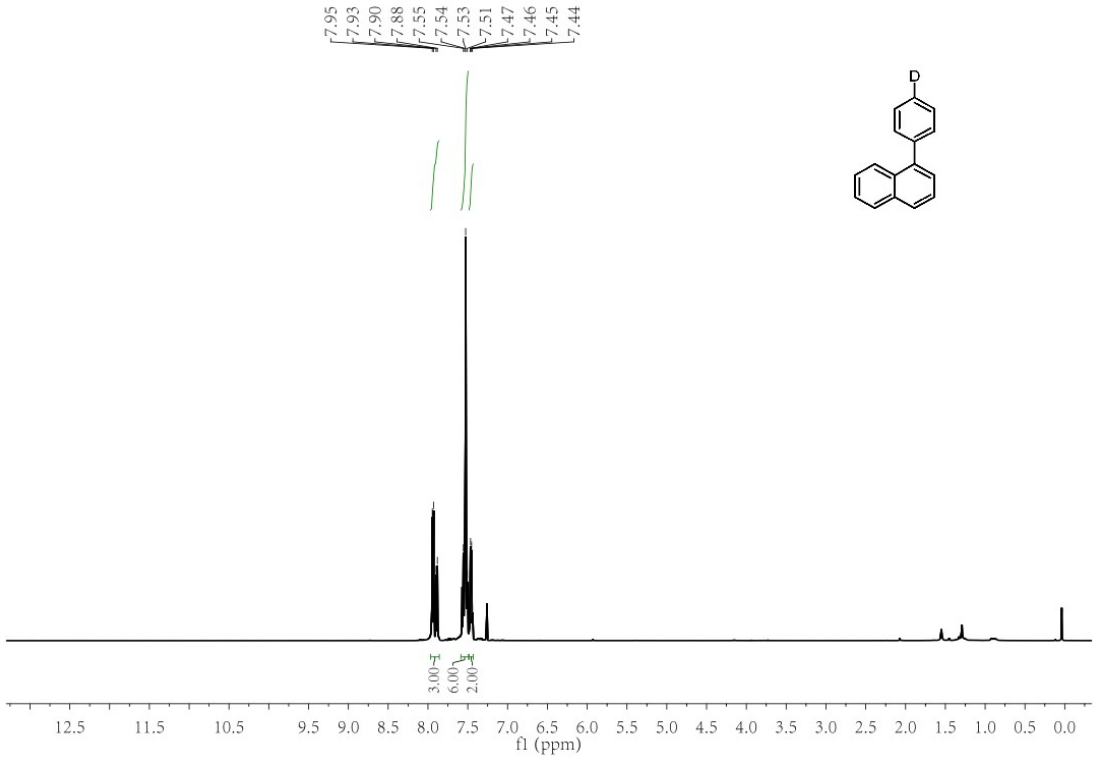
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3z**.



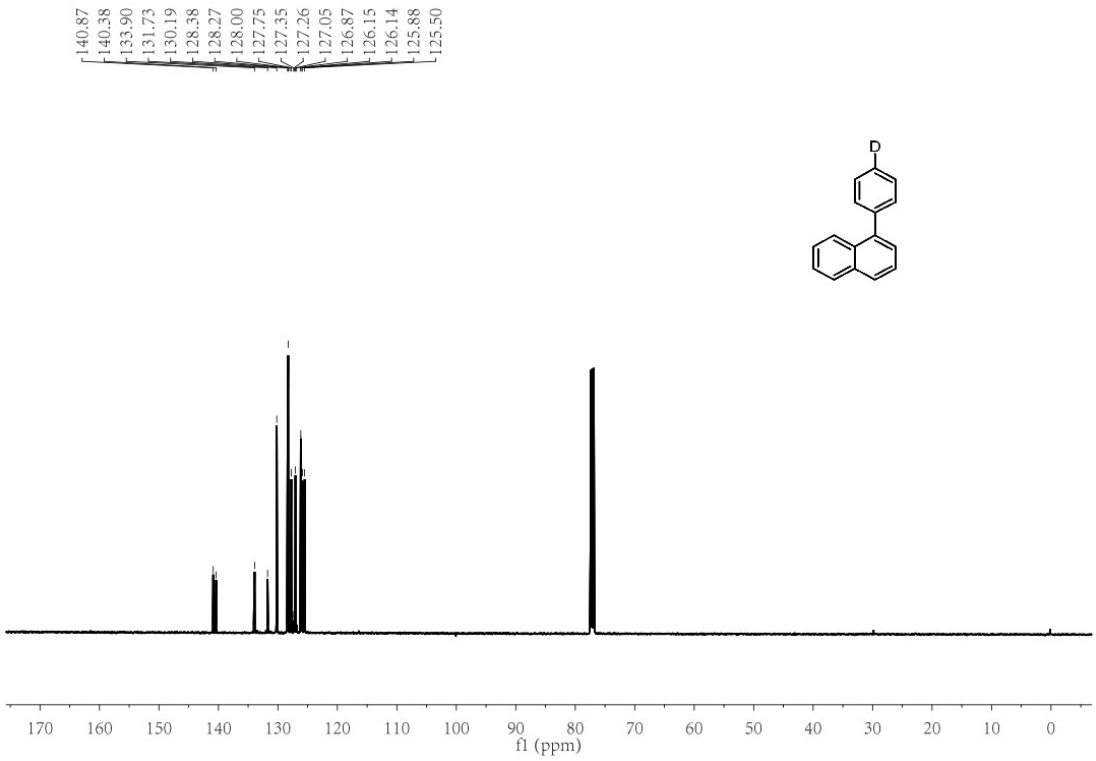
^{13}C NMR (126 MHz, $CDCl_3$) of compound **3z**.



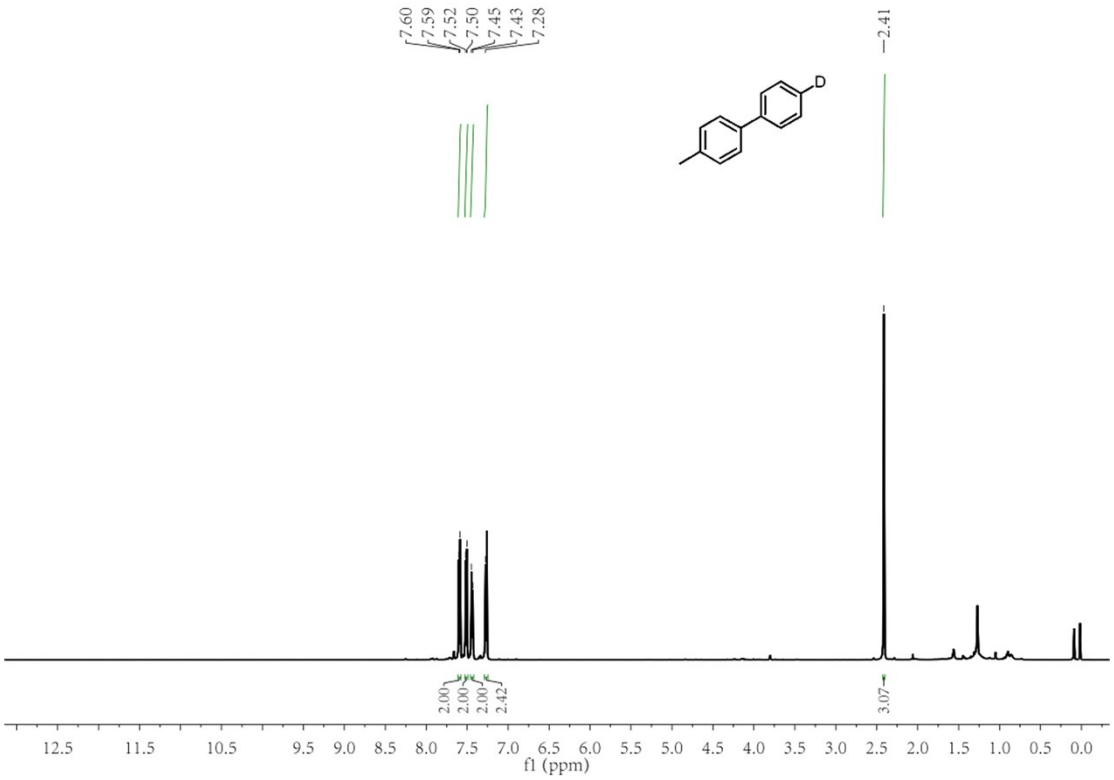
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3aa**.



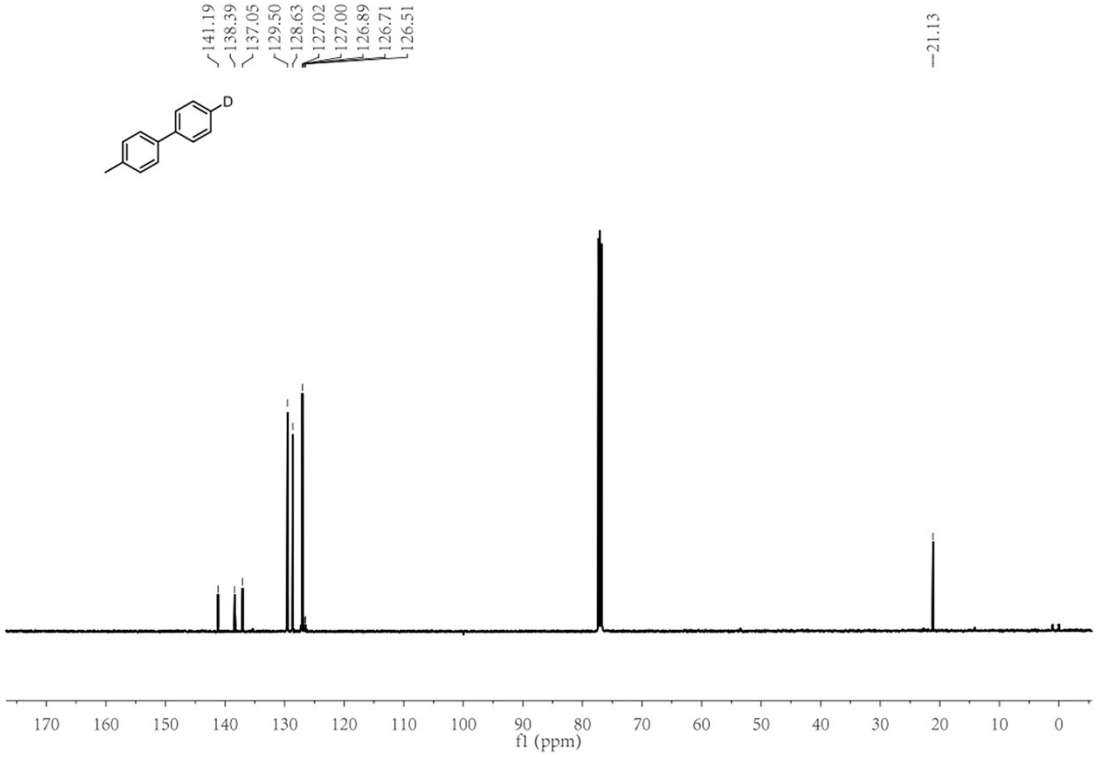
^{13}C NMR (126 MHz, $CDCl_3$) of compound **3aa**.



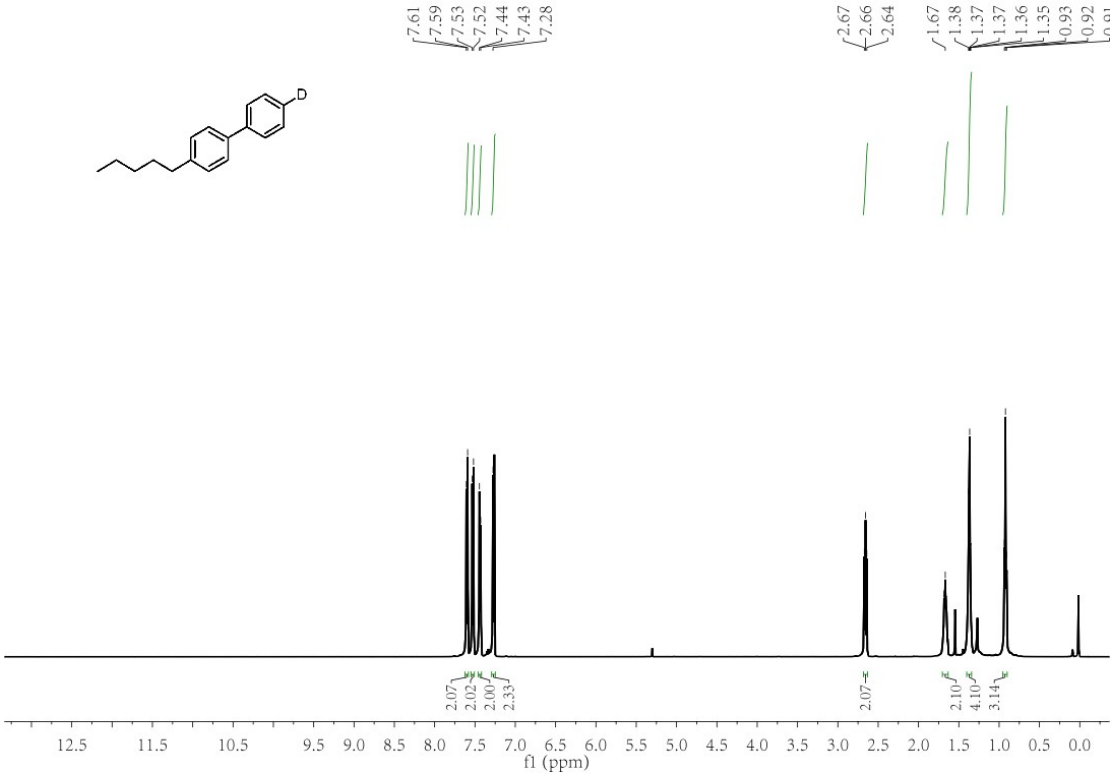
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3ab**.



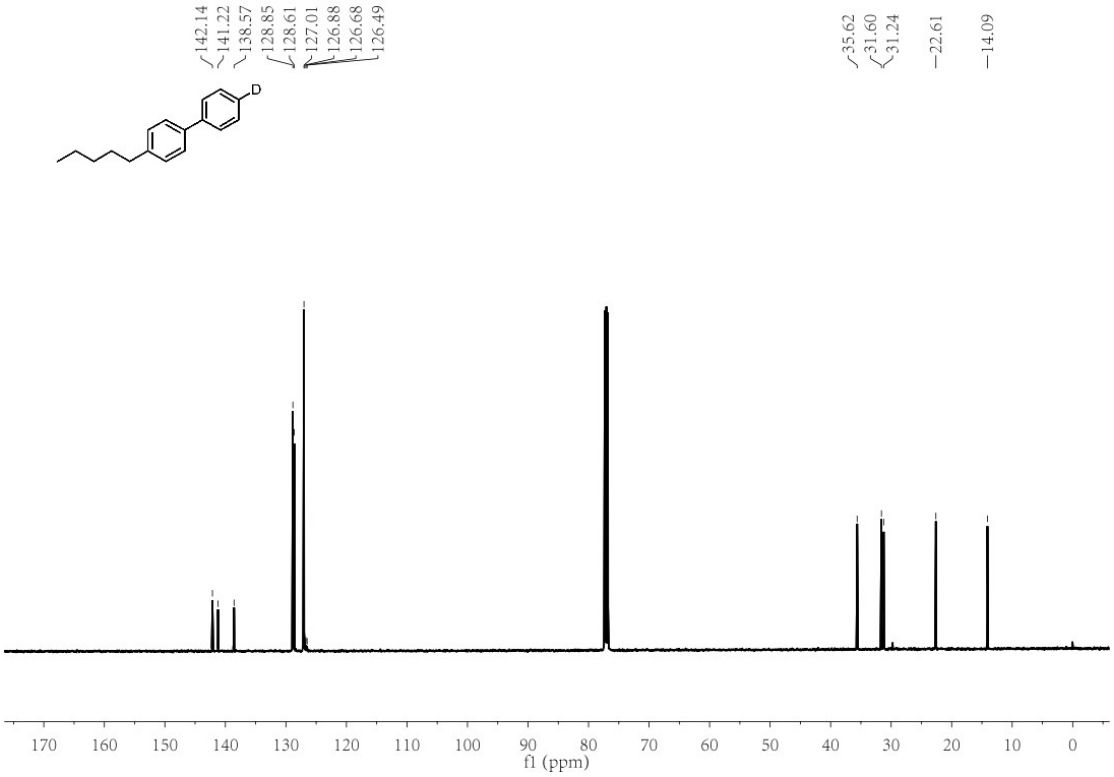
^{13}C NMR (126 MHz, $CDCl_3$) of compound **3ab**.



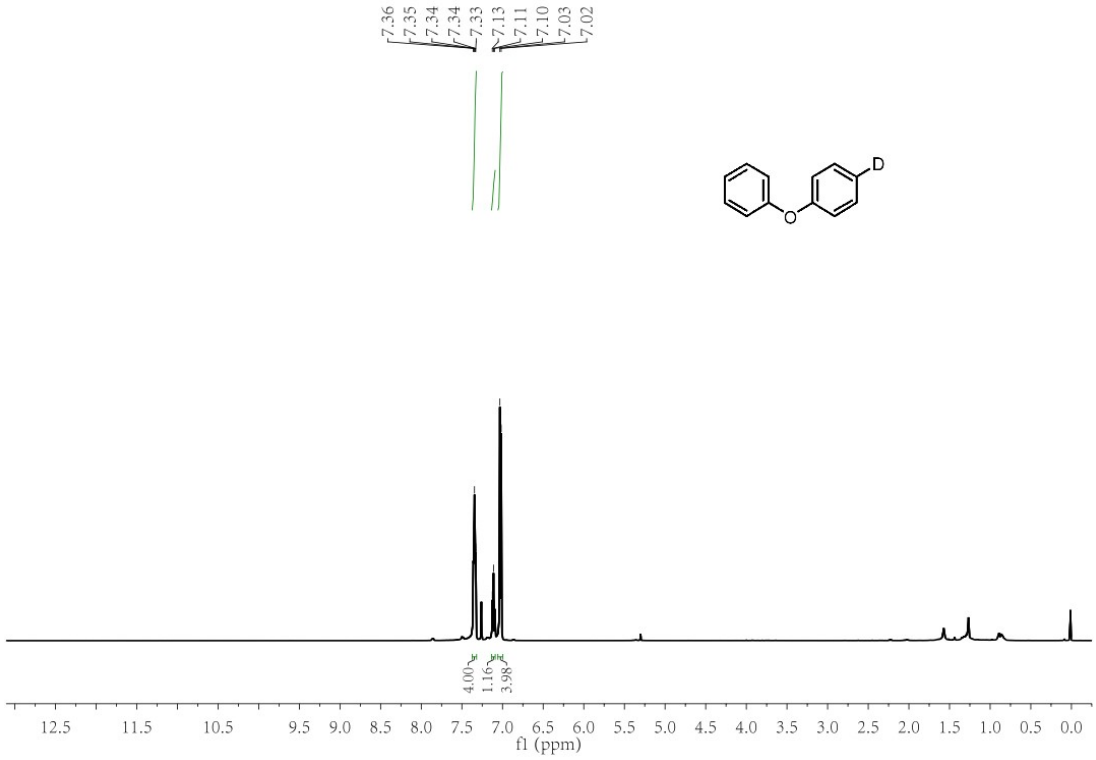
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3ac**.



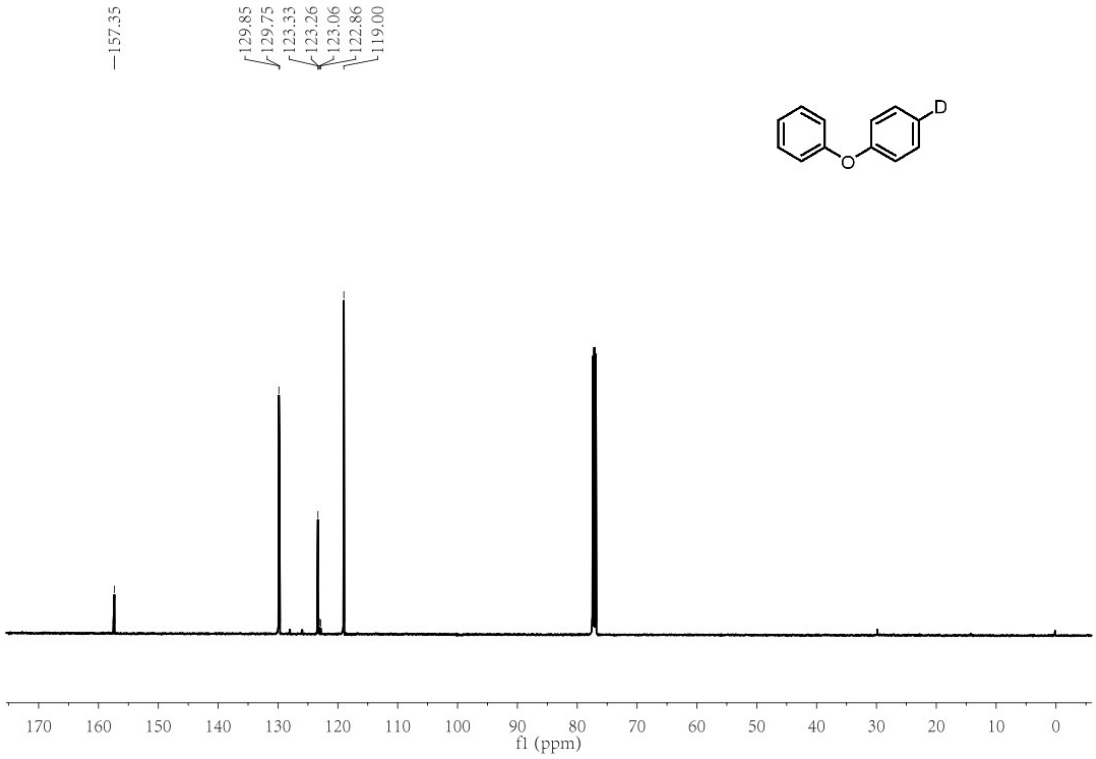
^{13}C NMR (126 MHz, $CDCl_3$) of compound **3ac**.



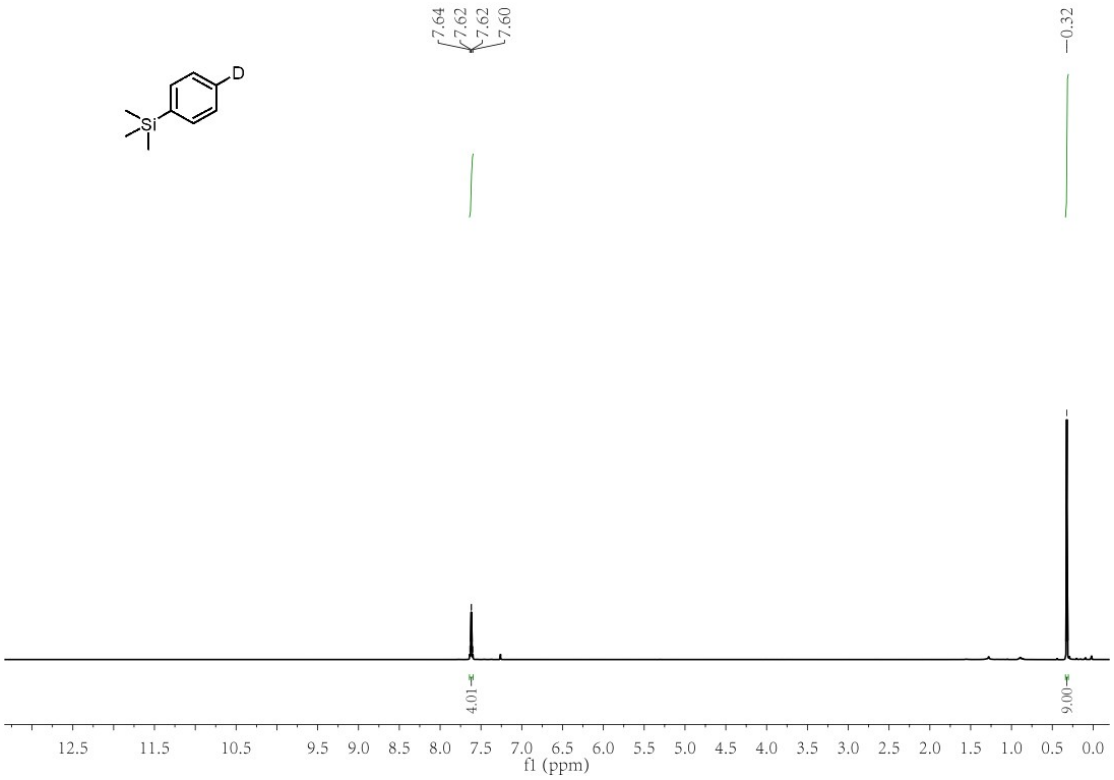
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3ad**.



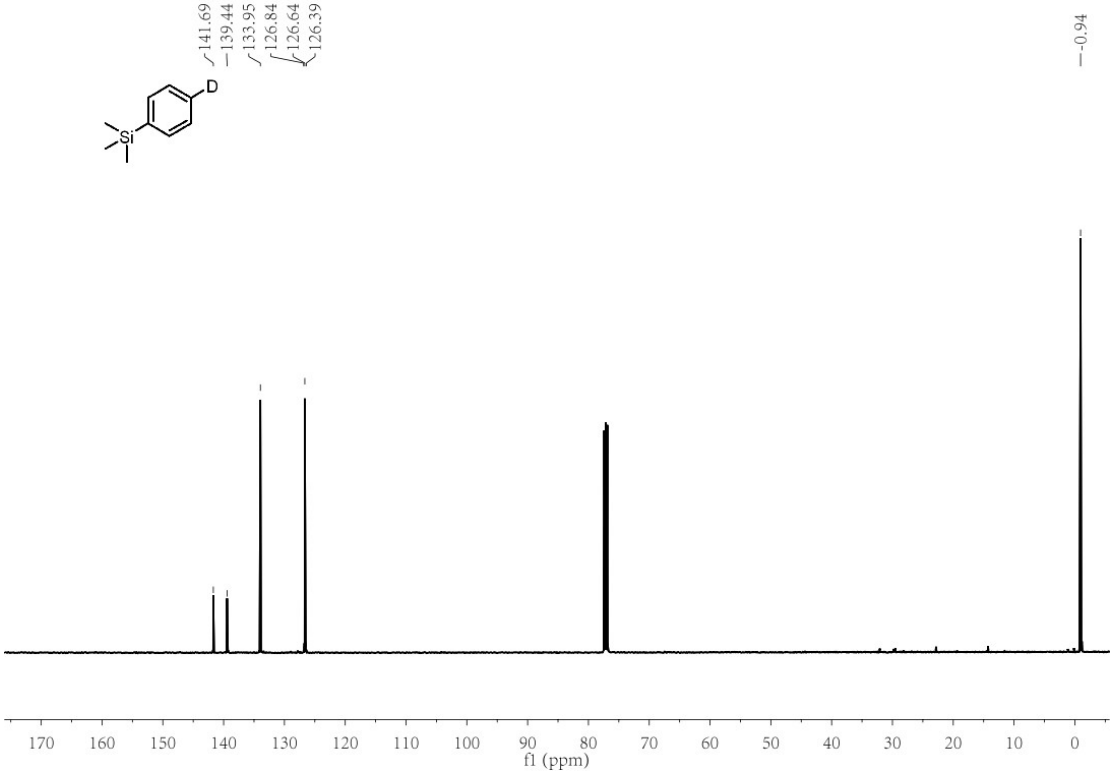
^{13}C NMR (126 MHz, $CDCl_3$) of compound **3ad**.



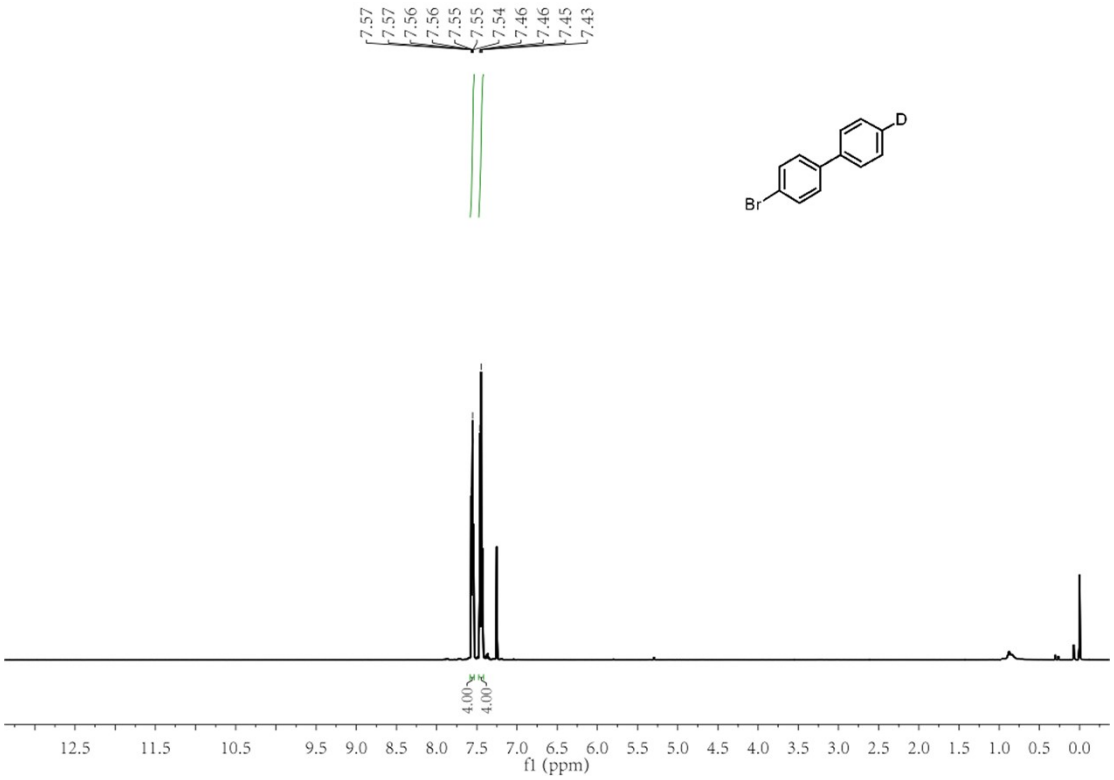
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3ae**.



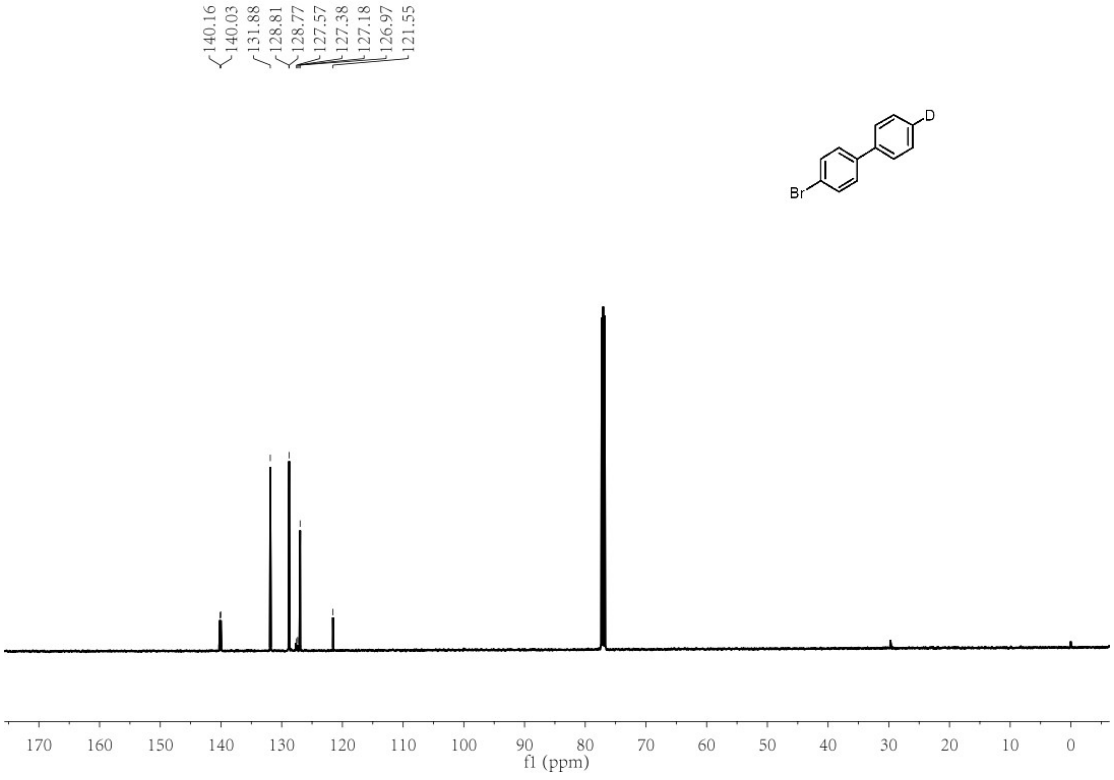
^{13}C NMR (126 MHz, $CDCl_3$) of compound **3ae**.



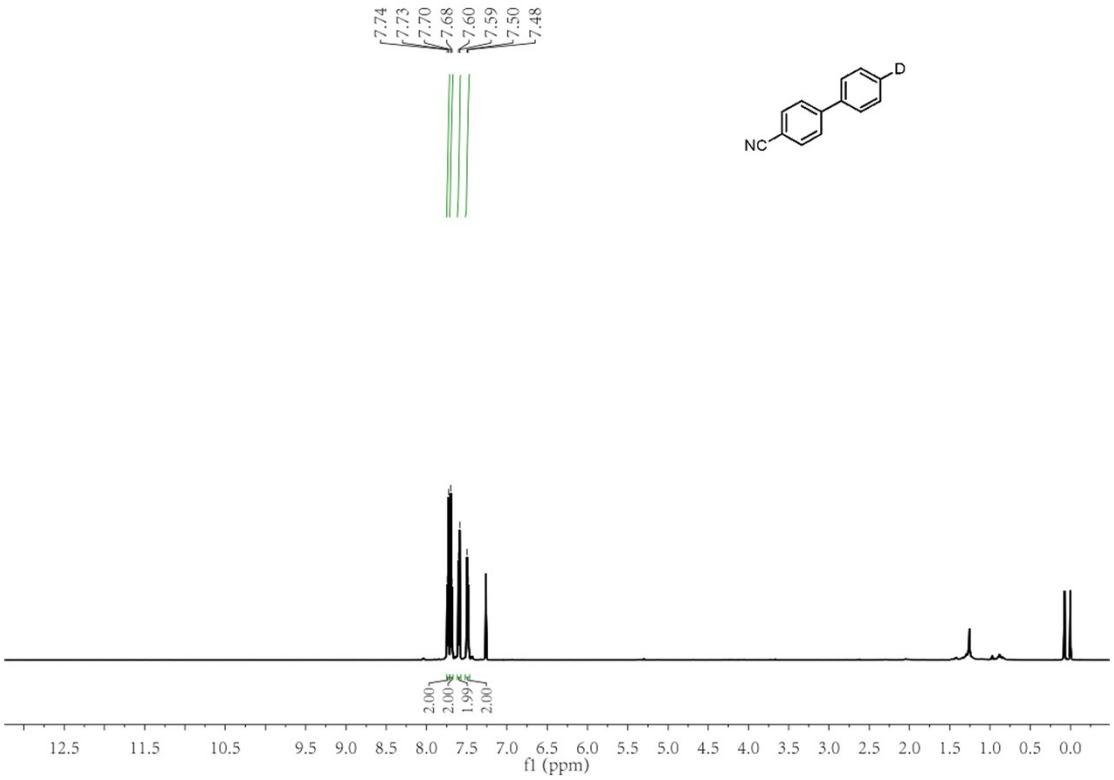
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3af**.



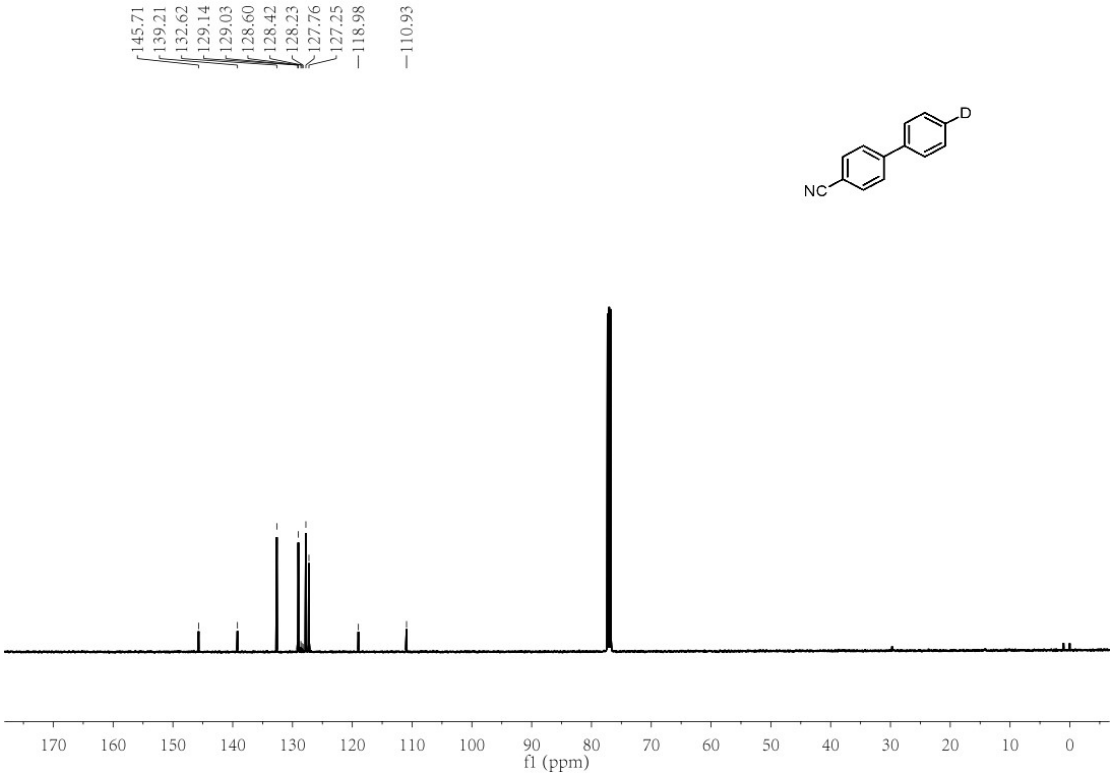
^{13}C NMR (126 MHz, $CDCl_3$) of compound **3af**.



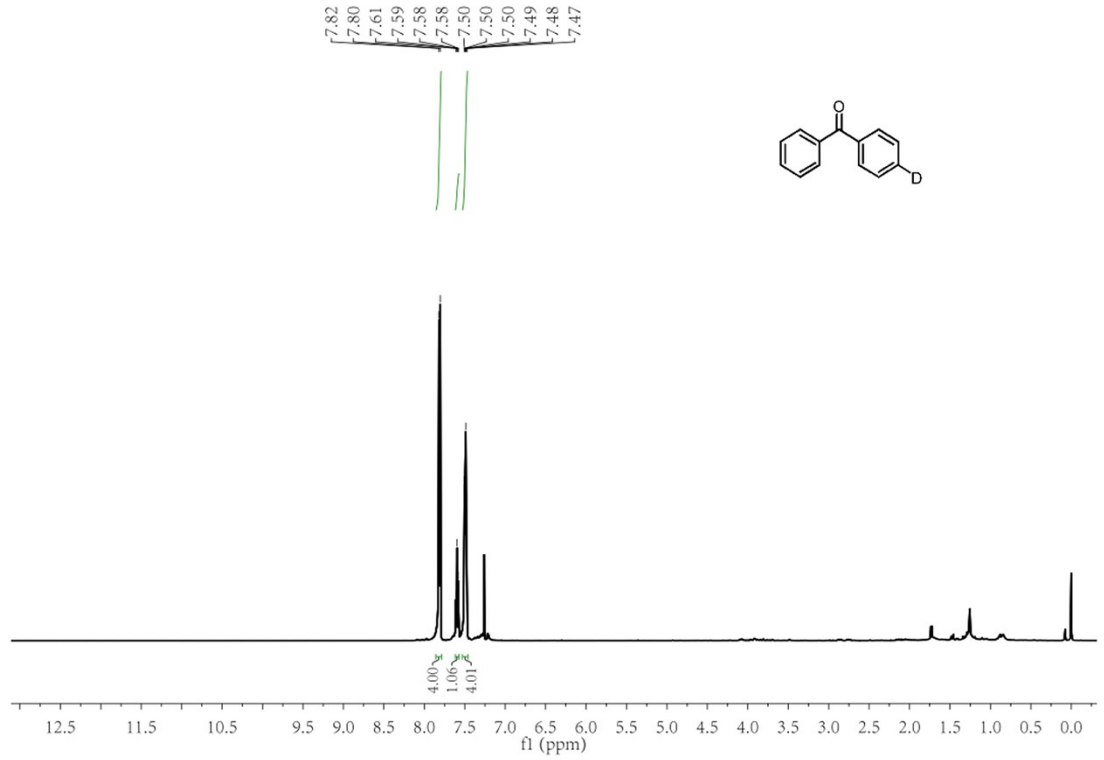
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3ag**.



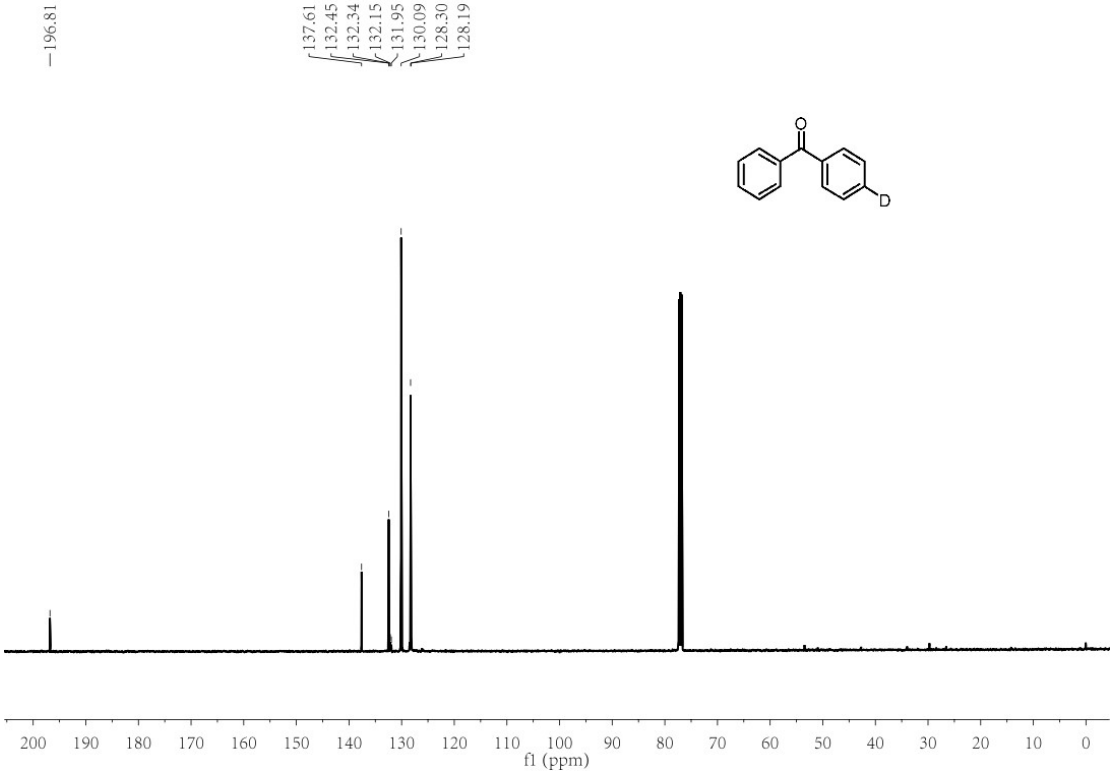
^{13}C NMR (126 MHz, $CDCl_3$) of compound **3ag**.



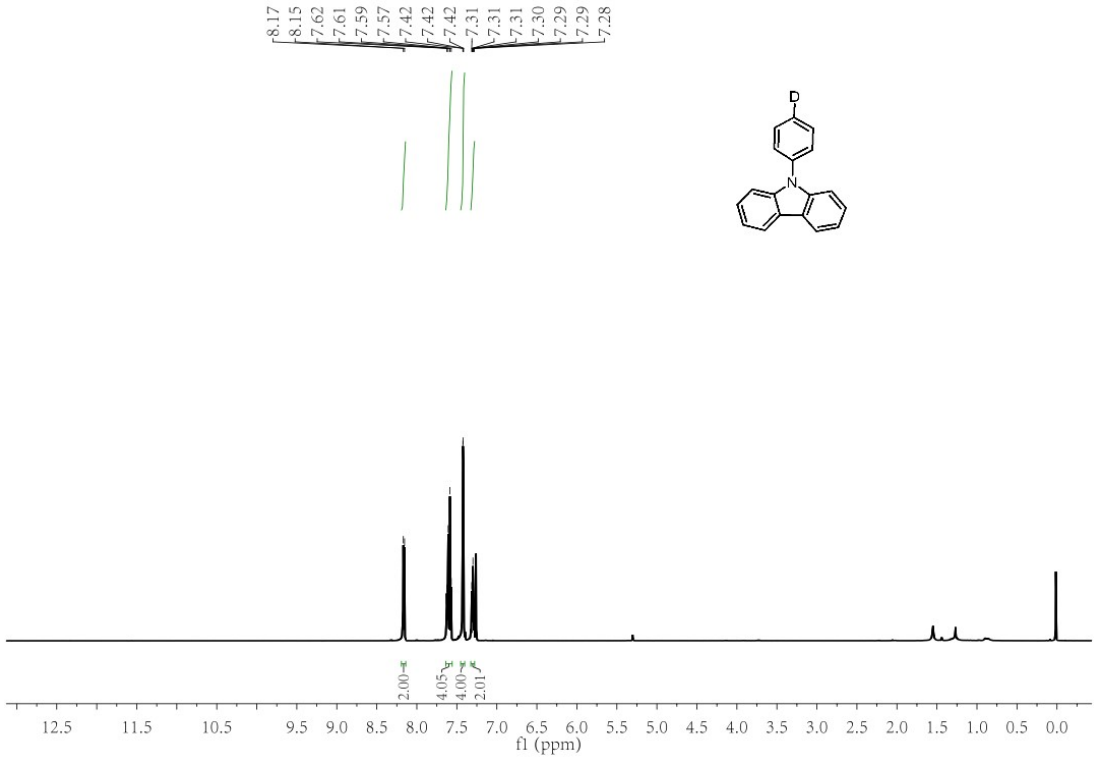
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3ah**.



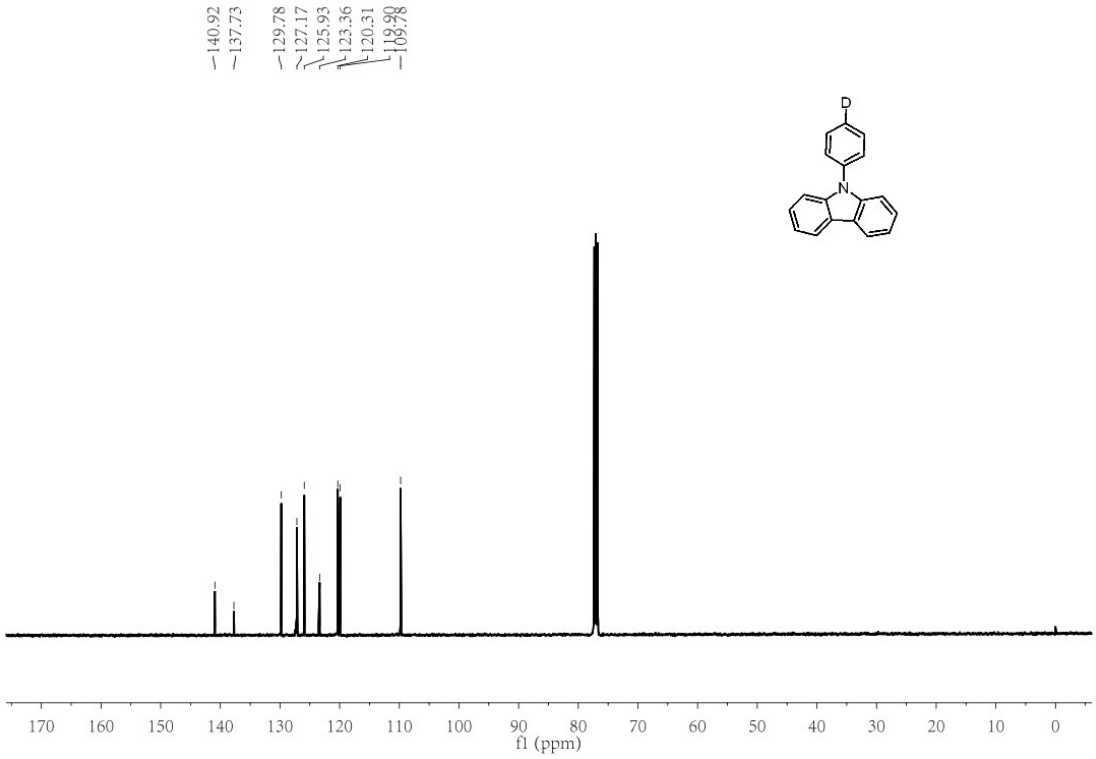
^{13}C NMR (126 MHz, $CDCl_3$) of compound **3ah**.



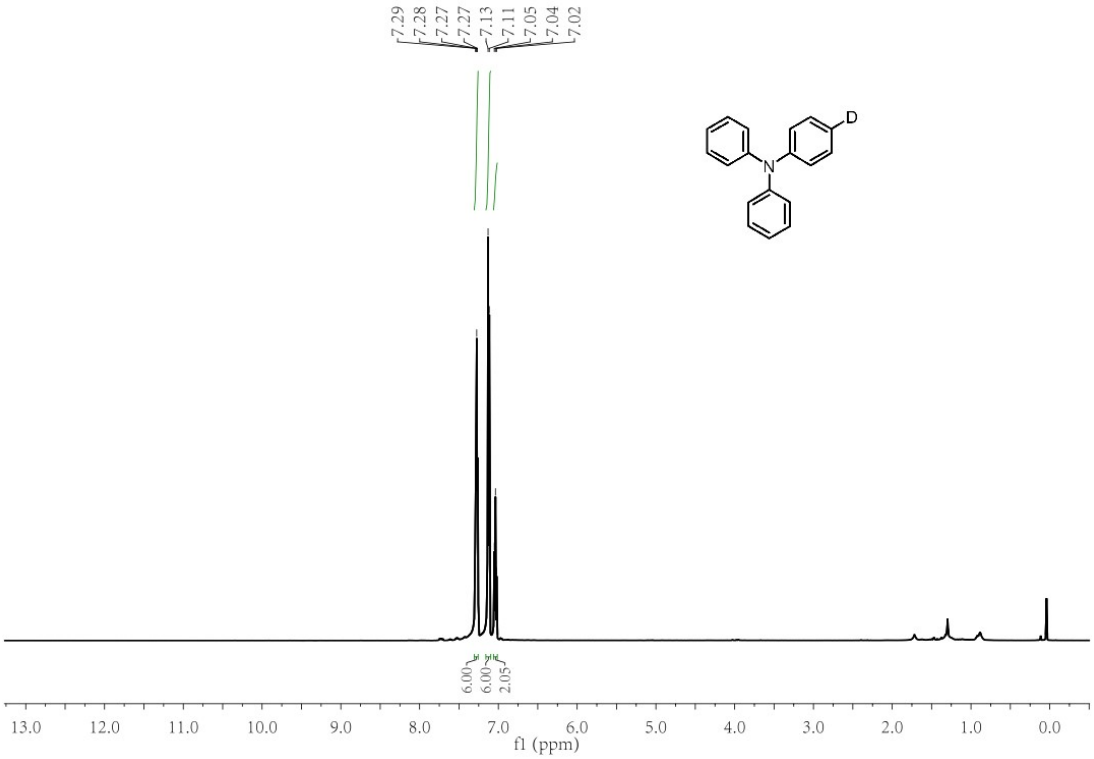
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3ai**.



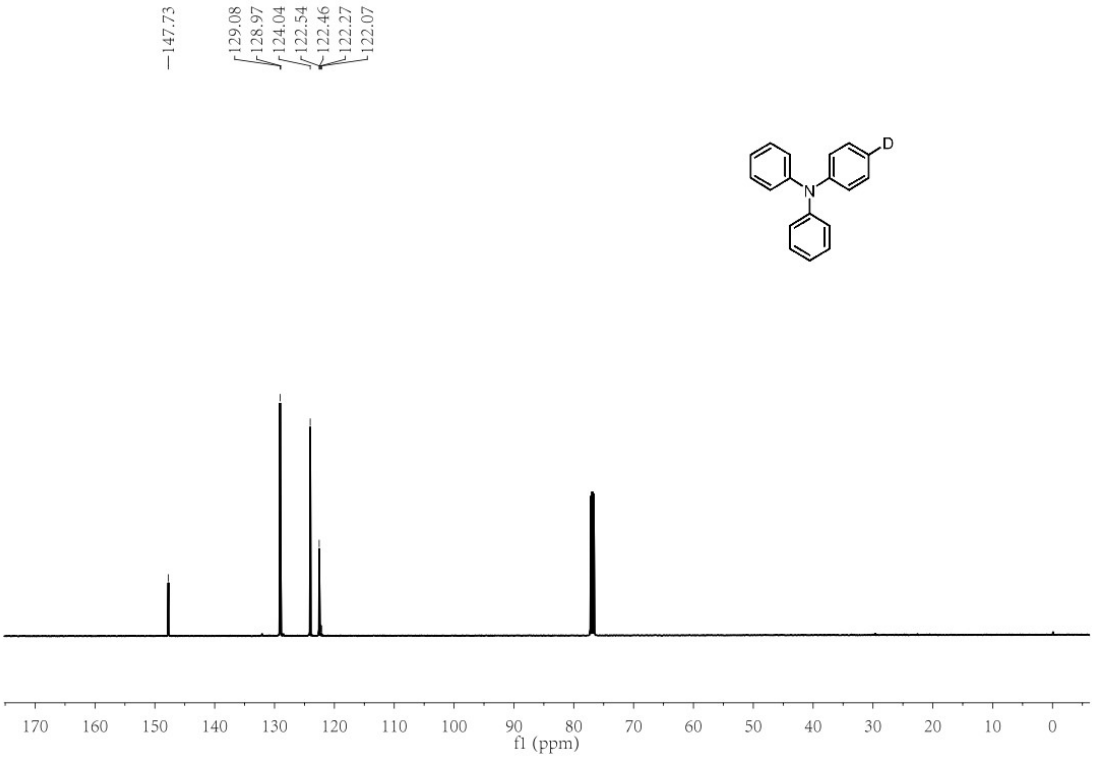
^{13}C NMR (126 MHz, $CDCl_3$) of compound **3ai**.



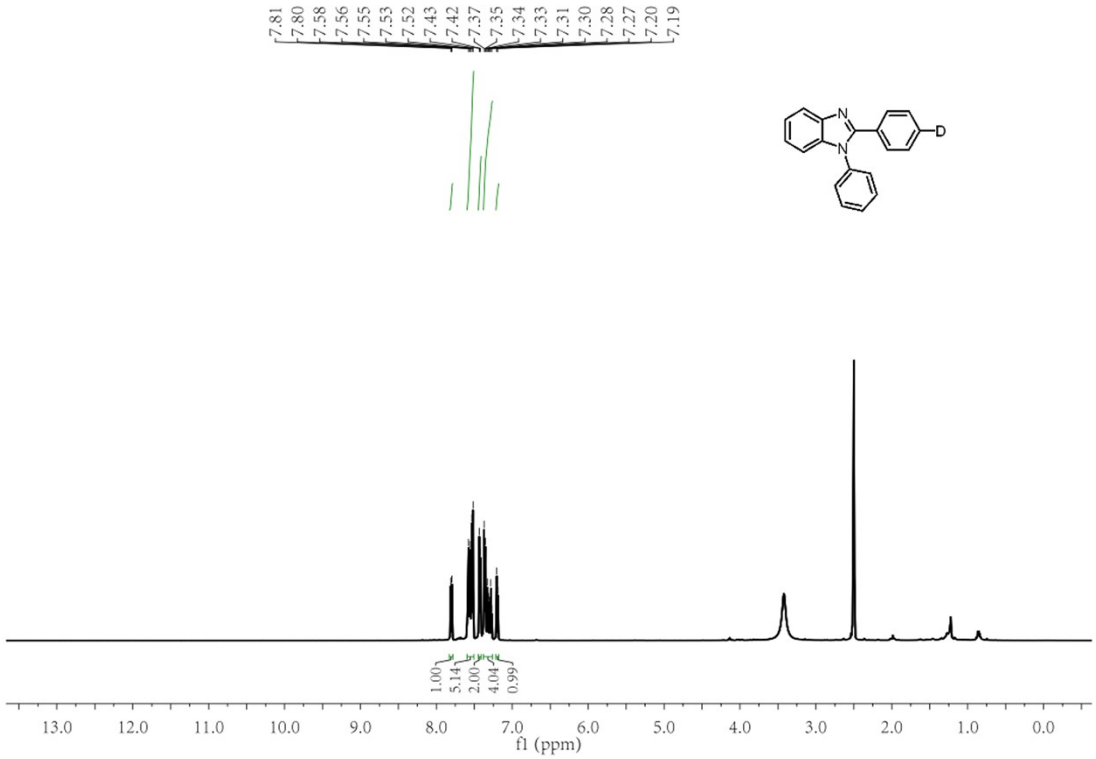
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3aj**.



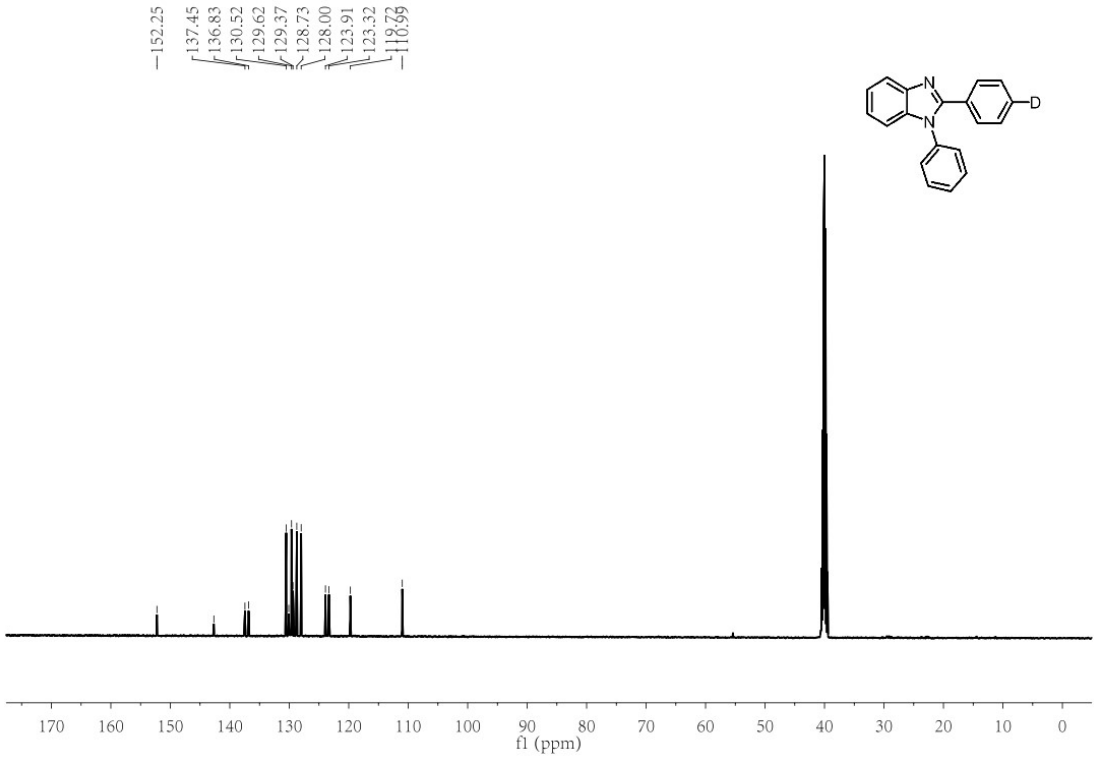
^{13}C NMR (126 MHz, $CDCl_3$) of compound **3aj**.



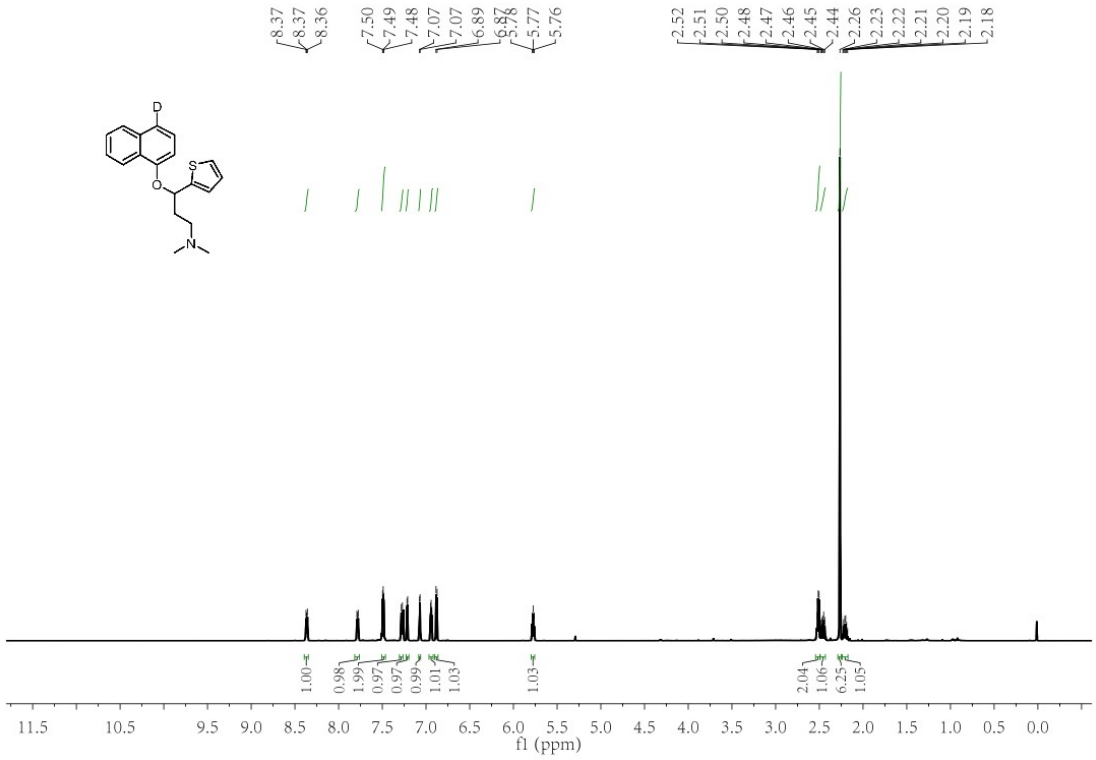
^{1}H NMR (500 MHz, DMSO-d_6) of compound **3ak**.



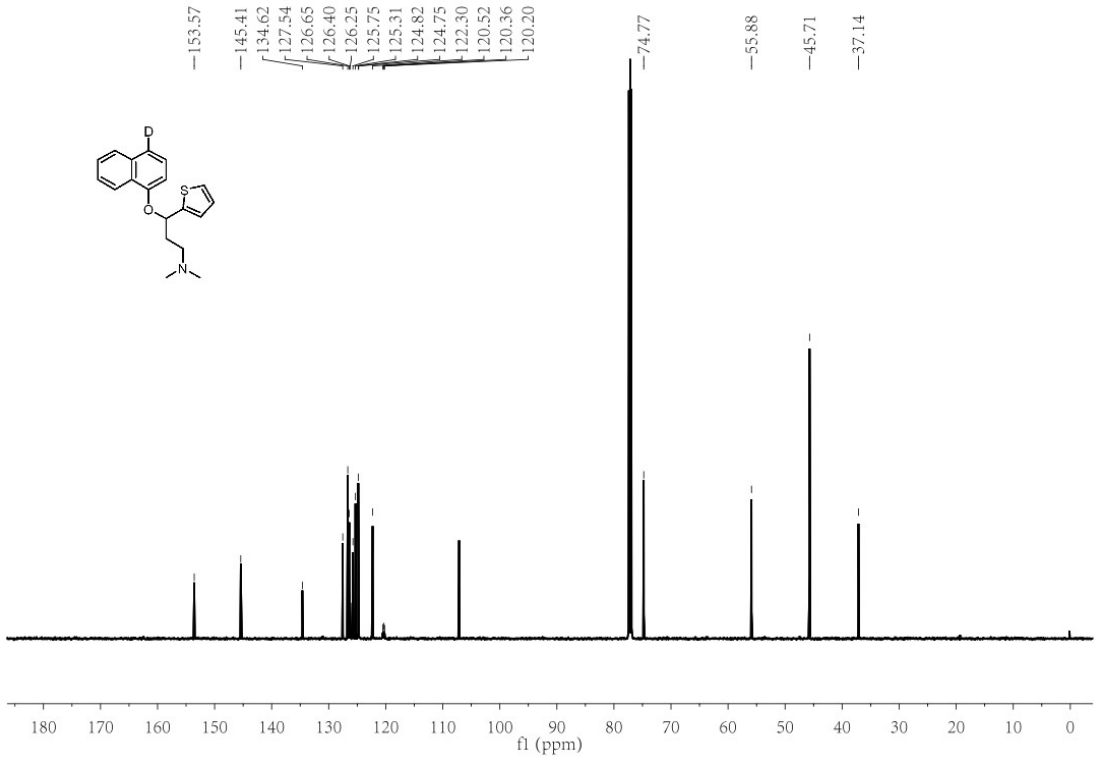
^{13}C NMR (126 MHz, DMSO-d_6) of compound **3ak**.



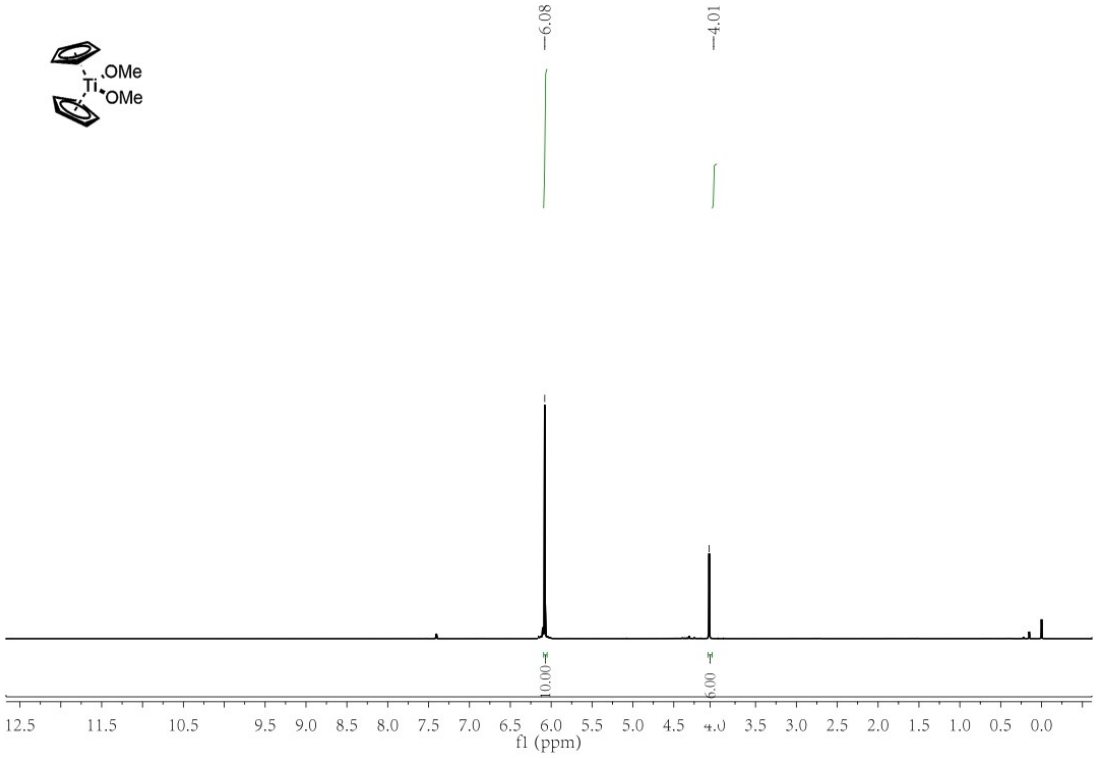
^{1}H NMR (600 MHz, $CDCl_3$) of compound **3am**.



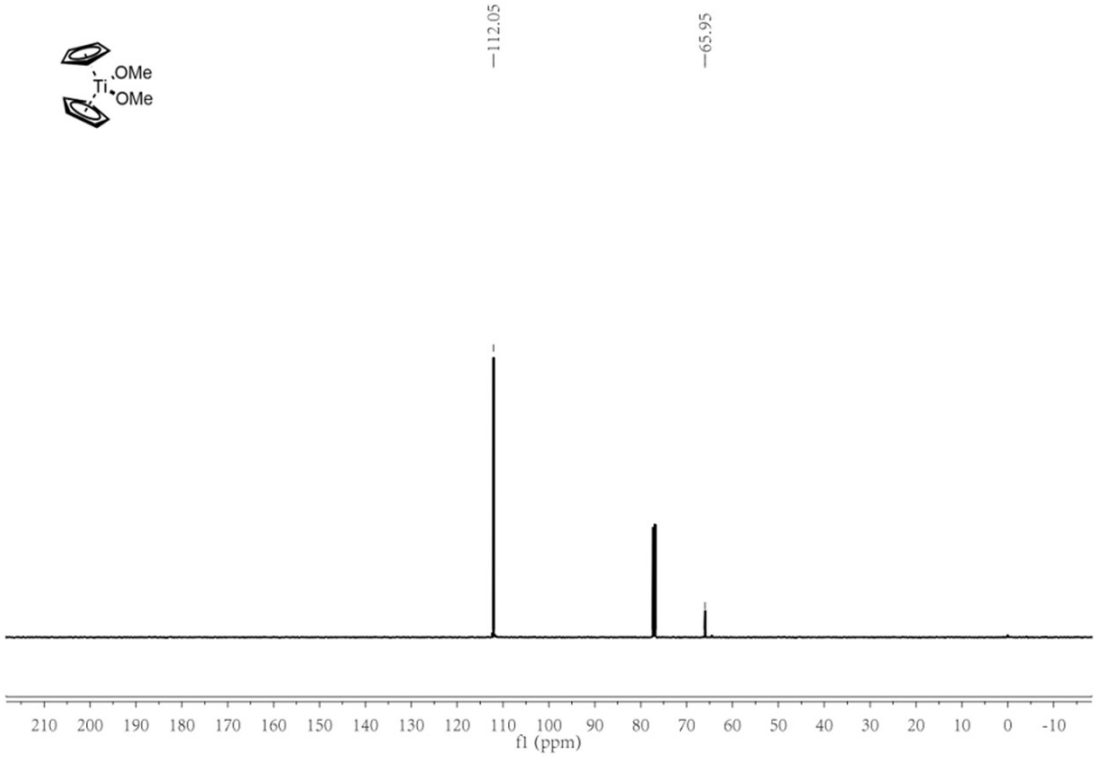
^{13}C NMR (151 MHz, $CDCl_3$) of compound **3am**.



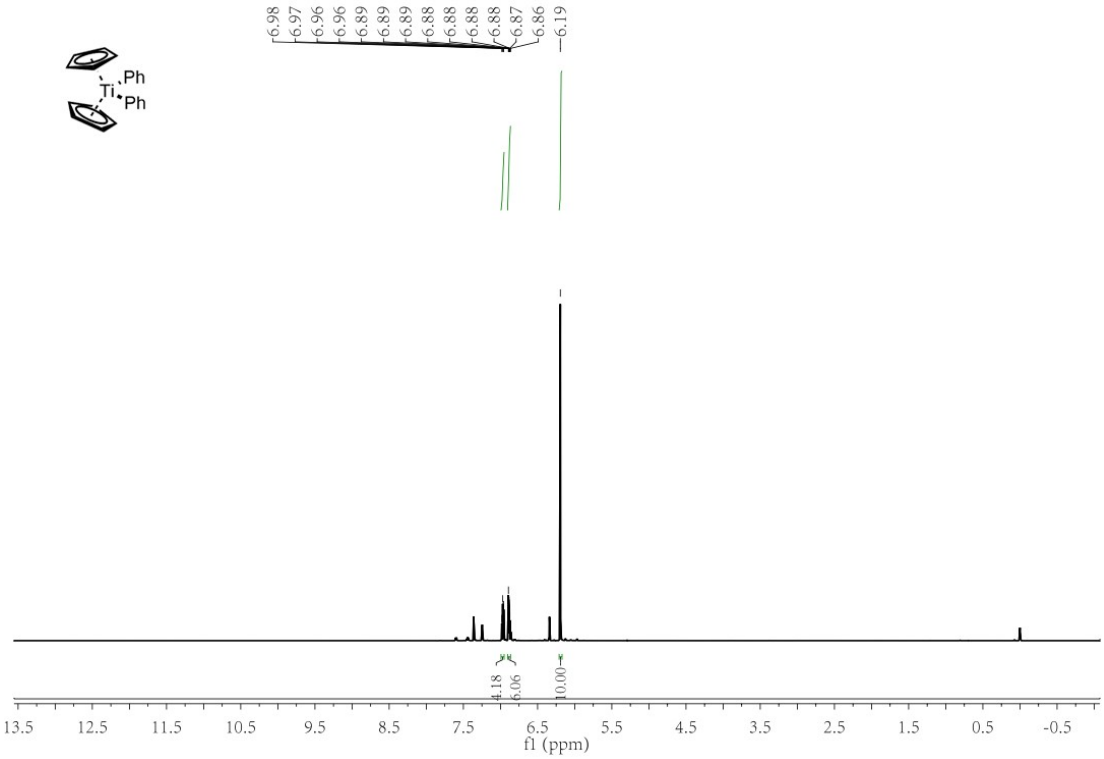
^{1}H NMR (600 MHz, $CDCl_3$) of compound **Cat 5**.



^{13}C NMR (151 MHz, $CDCl_3$) of compound **Cat 5**.



^{1}H NMR (600 MHz, $CDCl_3$) of compound **Cat 11**.



^{13}C NMR (151 MHz, $CDCl_3$) of compound **Cat 11**.