Supporting Information

Mechanochemical base-catalyzed isomerization and deuteration of allylbenzenes

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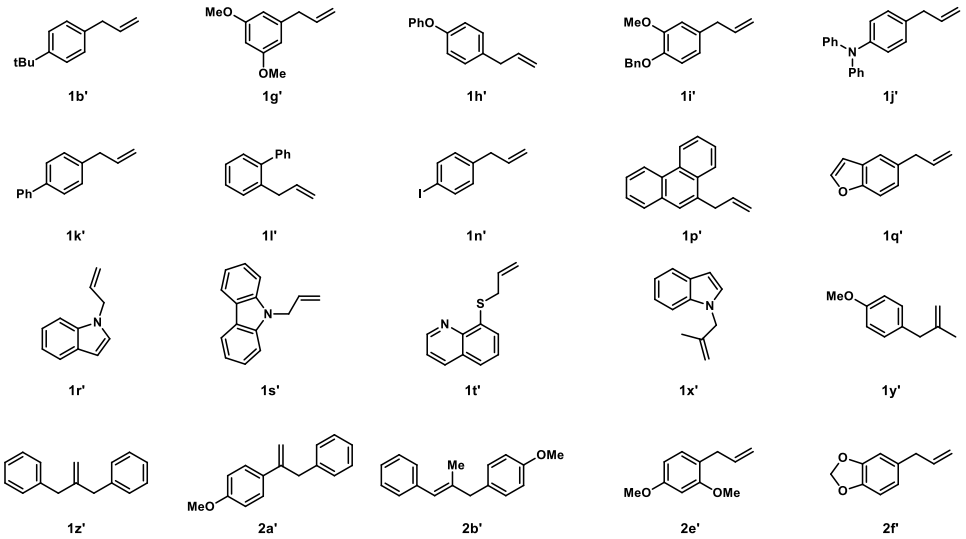
1. General information

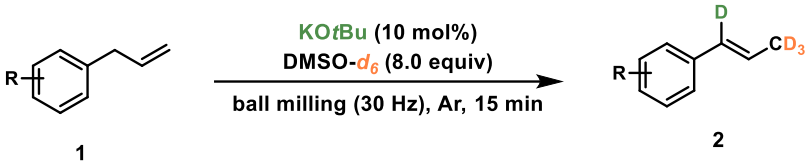
Materials were obtained from commercial suppliers and purified by standard procedures unless otherwise noted. Dimethyl Sulfoxide-d_6 (Energy chemical, D, 99.9%), Potassium tert-butoxide (Energy chemical, 98%) were purchased from 3A Materials®. Terminal alkenes were purchased from Adamas-beta®, Energy chemical or Bidepharm without further purification. All reactions were performed using grinding vessels in Beijing Gladman vibration ball mill GT300. Both jars and balls were made of stainless steel. Solvents for reactions were purchased from commercial suppliers. ^{1}H NMR, ^{19}F NMR, ^{13}C NMR spectra were recorded in $CDCl_3$ on 400 MHz and 101 MHz spectrometers. Multiplicity was recorded as follows: s = singlet, brs = broad singlet, d = doublet, t = triplet, q = quartet, m = multiplet. Chemical shifts (δ) were reported with respect to the corresponding solvent residual peak at 7.26 ppm for $CDCl_3$ for ^{1}H NMR. ^{13}C NMR spectra (1H-broadband decoupled) were reported in ppm using the central peak of $CDCl_3$ (77.16 ppm).
GC yields were recorded with a Shimadzu GC-2030 equipped with a Rtx-5 column (30 m × 0.25 mm) and dodecane was added as an internal standard. GC-MS analysis was conducted on Agilent 5977B GC/MSD instrument equipped with a HP-5MS UI column (30 m × 0.25 mm).
High-resolution mass data were recorded on a high-resolution mass spectrometer in the EI mode or ESI mode. The molecular ion $[M]^+$ $[M+H]^+$, $[M+Na]^+$ are given in m/z units. Column chromatography was generally performed on silica gel (300-400 mesh) and reactions were monitored by thin layer chromatography (TLC) using UV light to visualize the course of the reactions.

2. Preparation of starting materials



Unless otherwise noted, commercial reagents were purchased from Sigma-Aldrich, TCI, Energy, Alfa Aesar and Bide used as received. **1b', 1h', 1l', 1n', 1q'** were prepared according to the literature procedure.[1] **1g'** were prepared according to the literature procedure.[2] **1i', 1k', 2a', 2e', 2f'** were prepared according to the literature procedure.[3] **1j'** were prepared according to the literature procedure.[4] **1p'** were prepared according to the literature procedure.[5] **1r', 1x'** were prepared according to the literature procedure.[6] **1s'** were prepared according to the literature procedure.[7] **1t'** were prepared according to the literature procedure.[8] **1y', 1z'**were prepared according to the literature procedure.[9] **2b'** were prepared according to the literature procedure.[10]

3. General procedure for isomerization and deuteration of allylbenzenes

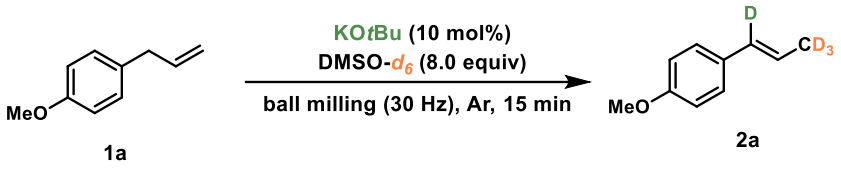


1 2

A dried 5 mL stainless-steel milling jar was charged with corresponding terminal alkenes (0.40 mmol) under air, then add KO*t*Bu (10 mol%), DMSO-d_6 (8.0 equiv) and two stainless-steel balls (7 mm, diameter) in an argon fulfilled glovebox were added. After the jar was closed in argon, the jar was placed in Gladman vibration ball mill GT300 (30 Hz). After grinding for 15 min, the reaction mixture was washed with ethyl acetate. The solvent was evaporated and the crude residue was purified through by flash chromatography on silica gel to afford product **2**.

4. Optimization of reaction conditions

Table S1. Optimization of base

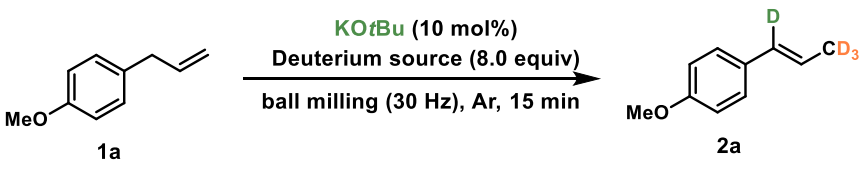


1a 2a

Entry	Base	Yield	D_1-inc	CD_3-inc
1	KO*t*Bu	99%	90%	92%
2	NaO*t*Bu	94%	---	44%
3	KOMe	98%	---	68%
4	KOH	97%	20%	86%
5	NaOH	90%	---	15%
6	K_2CO_3	ND	---	---

Reaction conditions: A dried 5 mL stainless-steel milling jar was charged with corresponding terminal alkenes (0.40 mmol) under air, then add base (10 mol%), DMSO-d_6 (8.0 equiv) and two stainless-steel balls (7 mm, diameter) in an argon fulfilled glovebox were added. After the jar was closed in argon, the jar was placed in Gladman vibration ball mill GT300 (30 Hz, 15 min); the yields were determined by GC analysis using decane as an internal standard. Deuterium incorporation was determined by ^{1}H NMR spectrum.

Table S2. Optimization of deuterium source



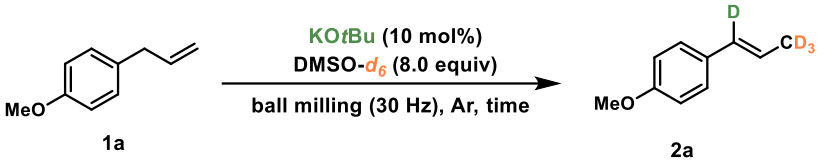
1a 2a

Entry	Deuterium source	Yield	D_1-inc	CD_3-inc
1	D_2O	ND	---	---
2	CD_3OD	ND	---	---
3	CD_3COCD_3	5%	---	---
4	CD_3CN	62%	---	23%

Reaction conditions: A dried 5 mL stainless-steel milling jar was charged with corresponding terminal alkenes (0.40

mmol) under air, then add KO*t*Bu (10 mol%), Deuterium source (8.0 equiv) and two stainless-steel balls (7 mm, diameter) in an argon fulfilled glovebox were added. After the jar was closed in argon, the jar was placed in Gladman vibration ball mill GT300 (30 Hz, 15 min); the yields were determined by GC analysis using decane as an internal standard. Deuterium incorporation was determined by ^{1}H NMR spectrum.

Table S3. Optimization of reaction time

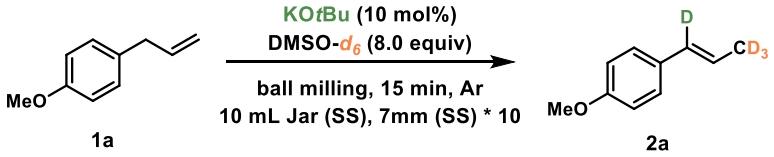


1a 2a

Entry	Time	Yield	D_1-inc	CD_3-inc
1	60 min	99%	89%	92%
2	15 min	99%	90%	92%
3	10 min	98%	75%	92%

Reaction conditions: A dried 5 mL stainless-steel milling jar was charged with corresponding terminal alkenes (0.40 mmol) under air, then add KO*t*Bu (10 mol%), DMSO-d_6 (8.0 equiv) and two stainless-steel balls (7 mm, diameter) in an argon fulfilled glovebox were added. After the jar was closed in argon, the jar was placed in Gladman vibration ball mill GT300 (30 Hz, X h); the yields were determined by GC analysis using decane as an internal standard. Deuterium incorporation was determined by ^{1}H NMR spectrum.

5. The procedure for the scale-up reaction



1a 2a

8.0 mmol — D: 91% D, CD_3: 91% D, 95% yield, 1.16g

6.0 mmol — D: 90% D, CD_3: 91% D, 96% yield, 876 mg

A dried 10 mL stainless-steel milling jar was charged with estragole (**1a**, 8.0 mmol/6.0 mmol) under air, then add KO*t*Bu (10 mol%), DMSO-d_6 (8.0 equiv) and ten stainless-steel balls (7 mm, diameter) in an argon fulfilled glovebox were added. After the jar was closed in argon, the jar was placed in Gladman vibration ball mill GT300 (30 Hz). After grinding for 15 min, the reaction mixture was washed with ethyl acetate. The solvent was evaporated and the crude residue was purified through by flash chromatography on silica gel (eluted with PE/EA = 100:1) to afford product **2a** (1.16g, 95% yield, D: 91% D, CD_3: 91% D/876 mg, 96% yield, D: 90% D, CD_3: 91% D) as a colorless oil.

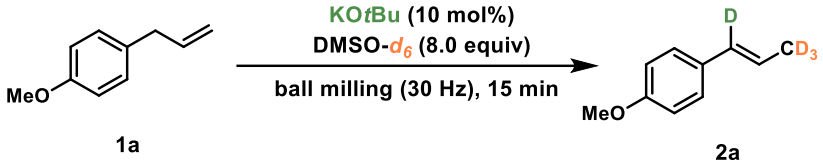
6. Control experiments with other vessel materials

4-allylanisole of alkene double-bond migration (**1a**) were conducted using a ZrO_2/PTFE ball-milling jar and ZrO_2/PTFE balls instead of stainless-steel milling jar and balls to investigate whether the metals in the ball mill are involved in the reaction.

A dried 5 mL stainless-steel milling jar was charged with corresponding terminal alkenes (0.40 mmol) under air, then add KO*t*Bu (10 mol%), DMSO-d_6 (8.0 equiv) and two stainless-steel balls (7 mm, diameter) in an argon fulfilled glovebox were added. After the jar was closed in argon, the jar

was placed in Gladman vibration ball mill GT300 (30 Hz). After grinding for 15 min, the reaction mixture was washed with ethyl acetate. the yields were determined by GC analysis using decane as an internal standard. Deuterium incorporation was determined by ^{1}H NMR spectrum.

Table S4.

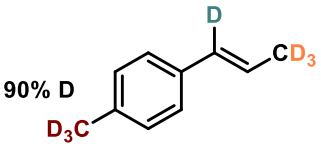


1a 2a

Entry	Jar type	2 (GC yield)	D_1-inc	CD_3-inc
1	stainless-steel jar	99%	90%	92%
2	ZrO_2 jar	96%	90%	92%
3	PTFE jar	98%	85%	91%

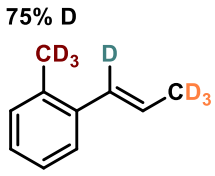
7. Characterization data of products

(*E*)-1-(methyl-d_3)-4-(prop-1-en-1-yl-1,3,3,3-d_4)benzene (2b)



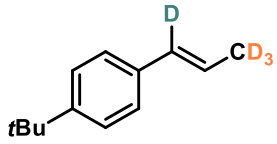
A dried 5 mL stainless-steel milling jar was charged with corresponding terminal alkenes (0.40 mmol) under air, then add KO*t*Bu (10 mol%), DMSO-d_6 (10.0 equiv) and two stainless-steel balls (7 mm, diameter) in an argon fulfilled glovebox were added. After the jar was closed in argon, the jar was placed in Gladman vibration ball mill GT300 (30 Hz). After grinding for 15 min, the reaction mixture was washed with ethyl acetate. The solvent was evaporated and the crude residue was purified through by flash chromatography on silica gel (eluted with PE) to afford product 2b (55.0 mg, 99% yield, *E:Z* >99:1, D: 88% D, CD_3: 90% D) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (d, J = 6.7 Hz, 2H), 7.12 (d, J = 6.5 Hz, 2H), 6.40 (d, J = 16.0 Hz, 0.12H), 6.27-6.13 (m, 1H), 2.35-2.30 (m, 0.30H), 1.90-1.83 (m, 0.31H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.3, 135.0, 130.8, 130.5-130.0 (m, C-D), 129.1, 125.6, 124.4. HR-MS (EI): m/z calcd for $[M]^+$ $C_{10}H_5D_7^+$, 139.1373; found 139.1375.

(*E*)-1-(methyl-d_3)-2-(prop-1-en-1-yl-1,3,3,3-d_4)benzene (2c)



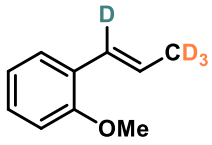
A dried 5 mL stainless-steel milling jar was charged with corresponding terminal alkenes (0.40 mmol) under air, then add KO*t*Bu (10 mol%), DMSO-d_6 (8.0 equiv) and two stainless-steel balls (7 mm, diameter) in an argon fulfilled glovebox were added. After the jar was closed in argon, the jar was placed in Gladman vibration ball mill GT300 (30 Hz). After grinding for 15 min, the reaction mixture was washed with ethyl acetate. The solvent was evaporated and the crude residue was purified through by flash chromatography on silica gel (eluted with PE) to afford product 2c (33.9 mg, 61% yield, *E:Z* 98:2, D: 89% D, CD_3: 90% D) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, J = 6.8 Hz, 1H), 7.24-7.02 (m, 3H), 6.61 (d, J = 14.1 Hz, 0.11H), 6.11 (m, 1H), 2.37-2.29 (m, 0.75H), 1.89 (m, 0.31H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.9, 130.1, 128.8, 126.7, 126.0, 125.3. HR-MS (EI): m/z calcd for $[M]^+$ $C_{10}H_5D_7^+$, 139.1372; found 139.1373.

(*E*)-1-(tert-butyl)-4-(prop-1-en-1-yl-1,3,3,3-d_4)benzene (2d)



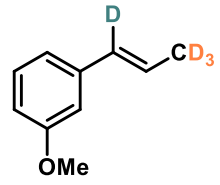
A dried 5 mL stainless-steel milling jar was charged with corresponding terminal alkenes (0.40 mmol) under air, then add KO*t*Bu (10 mol%), DMSO-d_6 (8.0 equiv) and two stainless-steel balls (7 mm, diameter) in an argon fulfilled glovebox were added. After the jar was closed in argon, the jar was placed in Gladman vibration ball mill GT300 (30 Hz). After grinding for 15 min, the reaction mixture was washed with ethyl acetate. The solvent was evaporated and the crude residue was purified through by flash chromatography on silica gel (eluted with PE) to afford product 2d (66.2 mg, 93% yield, *E:Z* 99:1, D: 91% D, CD_3: 92% D) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 8.8 Hz, 2H), 7.33 (d, *J* = 8.6 Hz, 2H), 6.45 (d, *J* = 15.8 Hz, 0.09H), 6.31-6.17 (m, 1H), 1.90 (m, 0.24H), 1.38 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.6, 135.1, 130.91-129.90 (m), 125.5, 125.4, 124.6, 34.4, 31.3, 18.1-17.3 (m). HR-MS (EI): m/z calcd for $[M]^+$ $C_{13}H_{14}D_4^+$, 178.1654; found 178.1650.

(*E*)-1-methoxy-2-(prop-1-en-1-yl-1,3,3,3-*d*$_4$)benzene (2e)



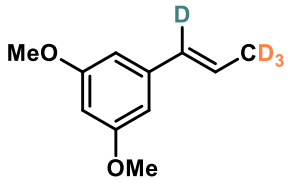
A dried 5 mL stainless-steel milling jar was charged with corresponding terminal alkenes (0.40 mmol) under air, then add KO*t*Bu (10 mol%), DMSO-d_6 (8.0 equiv) and two stainless-steel balls (7 mm, diameter) in an argon fulfilled glovebox were added. After the jar was closed in argon, the jar was placed in Gladman vibration ball mill GT300 (30 Hz). After grinding for 15 min, the reaction mixture was washed with ethyl acetate. The solvent was evaporated and the crude residue was purified through by flash chromatography on silica gel (eluted with PE/EA=100:1) to afford product 2e (52.9 mg, 87% yield, *E:Z* 98:2, D: 91% D, CD_3: 93% D) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 7.6 Hz, 1H), 7.21 (t, *J* = 7.0 Hz, 1H), 6.93 (t, *J* = 7.4 Hz, 1H), 6.87 (d, *J* = 8.4 Hz, 1H), 6.75 (d, *J* = 16.0 Hz, 0.09H), 6.21-6.28 (m, 1H), 3.86 (s, 3H), 1.93-1.87 (m, 0.22H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.0, 127.7, 126.9, 126.4, 126.3, 125.7-124.9 (m, C-D), 120.6, 110.6, 55.3, 18.5-17.7 (m, CD_3). HR-MS (ESI): m/z calcd for $[M+H]^+$ $C_{10}H_9D_4O^+$, 153.1212; found 153.1212.

(*E*)-1-methoxy-3-(prop-1-en-1-yl-1,3,3,3-*d*$_4$)benzene (2f)



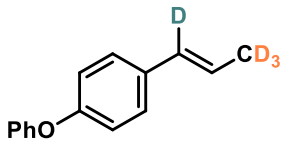
A dried 5 mL stainless-steel milling jar was charged with corresponding terminal alkenes (0.40 mmol) under air, then add KO*t*Bu (10 mol%), DMSO-d_6 (8.0 equiv) and two stainless-steel balls (7 mm, diameter) in an argon fulfilled glovebox were added. After the jar was closed in argon, the jar was placed in Gladman vibration ball mill GT300 (30 Hz). After grinding for 15 min, the reaction mixture was washed with ethyl acetate. The solvent was evaporated and the crude residue was purified through by flash chromatography on silica gel (eluted with PE/EA=100:1) to afford product 2f (48.6 mg, 80% yield, *E:Z* >99:1, D: 90% D, CD_3: 92% D) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (t, *J* = 7.9 Hz, 1H), 6.95 (d, *J* = 7.7 Hz, 1H), 6.89 (s, 1H), 6.77 (dd, *J* = 8.4, 2.3 Hz, 1H), 6.39 (d, *J* = 15.7 Hz, 0.09H), 6.23 (d, *J* = 2.8 Hz, 1H), 3.82 (s, 3H), 1.89-1.83 (m, 0.23H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.7, 139.3, 131.0-130.2 (m, C-D), 129.4, 125.8, 118.4, 112.2, 111.1, 55.1. HR-MS (ESI): m/z calcd for $[M+H]^+$ $C_{10}H_9D_4O^+$, 153.1212; found 153.1216.

(*E*)-1,3-dimethoxy-5-(prop-1-en-1-yl-1,3,3,3-*d*$_4$)benzene (2g)



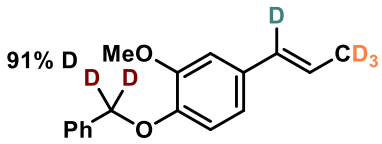
A dried 5 mL stainless-steel milling jar was charged with corresponding terminal alkenes (0.40 mmol) under air, then add KO*t*Bu (10 mol%), DMSO-d_6 (8.0 equiv) and two stainless-steel balls (7 mm, diameter) in an argon fulfilled glovebox were added. After the jar was closed in argon, the jar was placed in Gladman vibration ball mill GT300 (30 Hz). After grinding for 15 min, the reaction mixture was washed with ethyl acetate. The solvent was evaporated and the crude residue was purified through by flash chromatography on silica gel (eluted with PE/EA=100:1) to afford product 2g (63.3 mg, 87% yield, *E:Z* >99:1, D: 97% D, CD_3: 94% D) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.57-6.45 (m, 2H), 6.41-6.30 (m, 1.03H), 6.27-6.19 (m, 1H), 3.80 (s, 6H), 1.90-1.81 (m, 0.18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.8, 139.9, 131.1-129.7 (m), 126.1, 103.8, 99.0, 55.2. HR-MS (EI): m/z calcd for $[M]^+$ $C_{11}H_{10}D_4O_2^+$, 182.1239; found 182,1243.

(*E*)-1-phenoxy-4-(prop-1-en-1-yl-1,3,3,3-*d*$_4$)benzene (2h)



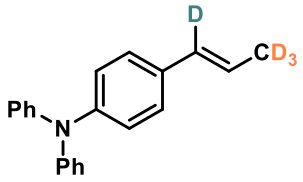
A dried 5 mL stainless-steel milling jar was charged with corresponding terminal alkenes (0.40 mmol) under air, then add KO*t*Bu (10 mol%), DMSO-d_6 (8.0 equiv) and two stainless-steel balls (7 mm, diameter) in an argon fulfilled glovebox were added. After the jar was closed in argon, the jar was placed in Gladman vibration ball mill GT300 (30 Hz). After grinding for 15 min, the reaction mixture was washed with ethyl acetate. The solvent was evaporated and the crude residue was purified through by flash chromatography on silica gel (eluted with PE) to afford product 2h (60.8 mg, 71% yield, *E:Z* >99:1, D: 91% D, CD_3: 92% D) as a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.29 (m, 4H), 7.14-7.08 (m, 1H), 7.06-6.99 (m, 2H), 6.98-6.93 (m, 2H), 6.40 (d, *J* = 15.8 Hz, 0.09H), 6.19-6.12 (m, 1H), 1.90-1.83 (m, 0.23H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.4, 156.0, 133.3, 129.7, 127.0, 124.6, 123.1, 119.0, 118.9, 118.7. HR-MS (EI): m/z calcd for $[M]^+$ $C_{15}H_{10}D_4O^+$, 214.1290; found 214.1293.

(*E*)-2-methoxy-1-(phenylmethoxy-*d*$_2$)-4-(prop-1-en-1-yl-1,3,3,3-*d*$_4$)benzene (2i)



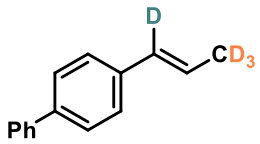
A dried 5 mL stainless-steel milling jar was charged with corresponding terminal alkenes (0.40 mmol) under air, then add KO*t*Bu (10 mol%), DMSO-d_6 (8.0 equiv) and two stainless-steel balls (7 mm, diameter) in an argon fulfilled glovebox were added. After the jar was closed in argon, the jar was placed in Gladman vibration ball mill GT300 (30 Hz). After grinding for 15 min, the reaction mixture was washed with ethyl acetate. The solvent was evaporated and the crude residue was purified through by flash chromatography on silica gel (eluted with PE/EA=20:1) to afford product 2i (99.8 mg, 96% yield, *E:Z* 99:1, D: 85% D, CD_3: 90% D) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50-7.44 (m, 2H), 7.42-7.36 (m, 2H), 7.36-7.29 (m, 1H), 6.95 (s, 1H), 6.83 (s, 2H), 6.37 (d, *J* = 15.8 Hz, 0.15H), 6.12 (d, *J* = 3.2 Hz, 1H), 5.15 (s, 0.18H), 3.92 (s, 3H), 1.90-1.83 (m, 0.30H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.5, 147.1, 137.0, 131.5, 130.6-129.8 (m, C-D), 128.4, 127.7, 127.2, 123.6, 118.4, 114.0, 108.9, 71.0-69.9 (m, C-D), 55.8, 18.3-17.0 (m, CD_3). HR-MS (ESI): m/z calcd for $[M+H]^+$ $C_{17}H_{13}D_6O_2^+$, 261.1756; found 261.1749.

(*E*)-N,N-diphenyl-4-(prop-1-en-1-yl-1,3,3,3-*d*$_4$)aniline (2j)



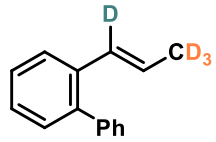
A dried 5 mL stainless-steel milling jar was charged with corresponding terminal alkenes (0.40 mmol) under air, then add KO*t*Bu (10 mol%), DMSO-d_6 (8.0 equiv) and two stainless-steel balls (7 mm, diameter) in an argon fulfilled glovebox were added. After the jar was closed in argon, the jar was placed in Gladman vibration ball mill GT300 (30 Hz). After grinding for 15 min, the reaction mixture was washed with ethyl acetate. The solvent was evaporated and the crude residue was purified through by flash chromatography on silica gel (eluted with PE/EA=50:1) to afford product 2j (83.2 mg, 72% yield, *E:Z* 98:2, D: 86% D, CD_3: 93% D) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50-7.44 (m, 2H), 7.42-7.36 (m, 2H), 7.36-7.29 (m, 1H), 6.95 (s, 1H), 6.83 (s, 2H), 6.37 (d, *J* = 15.8 Hz, 0.15H), 6.12 (d, *J* = 3.2 Hz, 1H), 5.15 (s, 0.18H), 3.92 (s, 3H), 1.90-1.83 (m, 0.30H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.7, 146.4, 132.5, 130.6-129.5 (m, C-D), 129.1, 126.5, 124.1, 124.1, 124.0, 122.6. HR-MS (ESI): m/z calcd for $[M+H]^+$ $C_{21}H_{16}D_4N^+$, 290.1842; found 290.1838.

(*E*)-4-(prop-1-en-1-yl-1,3,3,3-d_4)-1,1'-biphenyl (2k)



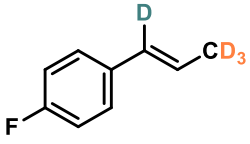
A dried 5 mL stainless-steel milling jar was charged with corresponding terminal alkenes (0.40 mmol) under air, then add KO*t*Bu (10 mol%), DMSO-d_6 (8.0 equiv) and two stainless-steel balls (7 mm, diameter) in an argon fulfilled glovebox were added. After the jar was closed in argon, the jar was placed in Gladman vibration ball mill GT300 (30 Hz). After grinding for 15 min, the reaction mixture was washed with ethyl acetate. The solvent was evaporated and the crude residue was purified through by flash chromatography on silica gel (eluted with PE) to afford product 2k (57.8 mg, 73% yield, *E:Z* >99:1, D: 68% D, CD_3: 93% D) as a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8.2 Hz, 2H), 7.57 (d, *J* = 7.6 Hz, 2H), 7.49-7.40 (m, 4H), 7.36 (t, *J* = 7.4 Hz, 1H), 6.47 (d, *J* = 15.8 Hz, 0.32H), 6.31 (d, *J* = 9.7 Hz, 1H), 1.96-1.86 (m, 0.22H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.0, 139.6, 137.1, 130.7, 128.9, 127.32, 127.27, 127.0, 126.3, 125.8. HR-MS (EI): m/z calcd for $[M]^+$ $C_{15}H_{10}D_4^+$, 198.1341; found 198.1341.

(*E*)-2-(prop-1-en-1-yl-1,3,3,3-d_4)-1,1'-biphenyl (2l)



A dried 5 mL stainless-steel milling jar was charged with corresponding terminal alkenes (0.40 mmol) under air, then add KO*t*Bu (10 mol%), DMSO-d_6 (8.0 equiv) and two stainless-steel balls (7 mm, diameter) in an argon fulfilled glovebox were added. After the jar was closed in argon, the jar was placed in Gladman vibration ball mill GT300 (30 Hz). After grinding for 15 min, the reaction mixture was washed with ethyl acetate. The solvent was evaporated and the crude residue was purified through by flash chromatography on silica gel (eluted with PE) to afford product 2l (64.2 mg, 81% yield, *E:Z* 97:3, D: 91% D, CD_3: 91% D) as a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 7.2 Hz, 1H), 7.49-7.43 (m, 2H), 7.43-7.38 (m, 3H), 7.38-7.34 (m, 1H), 7.33-7.28 (m, 2H), 6.44 (d, *J* = 15.8 Hz, 0.09H), 6.20 (d, *J* = 3.7 Hz, 1H), 1.84-1.77 (m, 0.27H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.2, 140.1, 135.8, 130.1, 129.8, 129.6-128.6 (m, C-D), 128.0, 127.4, 126.8, 126.7, 126.2, 125.7. HR-MS (EI): m/z calcd for $[M]^+$ $C_{15}H_{10}D_4^+$, 198.1341; found 198.1344.

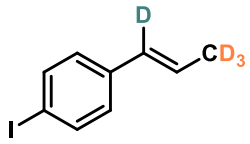
(*E*)-1-fluoro-4-(prop-1-en-1-yl-1,3,3,3-d_4)benzene (2m)



A dried 5 mL stainless-steel milling jar was charged with corresponding terminal alkenes (0.40 mmol) under air, then add KO*t*Bu (10 mol%), DMSO-d_6 (8.0 equiv) and two stainless-steel balls (7 mm, diameter) in an argon fulfilled glovebox were added. After the jar was closed in argon, the jar was placed in Gladman vibration ball mill GT300 (30 Hz). After grinding for 15 min, the reaction mixture was washed with ethyl acetate. The solvent was evaporated

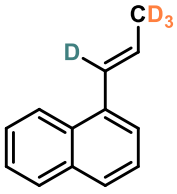
and the crude residue was purified through by flash chromatography on silica gel (eluted with PE) to afford product 2m (41.7 mg, 75% yield, *E:Z* >99:1, D: 91% D, CD_3: 94% D) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40-7.21 (m, 2H), 7.00 (t, *J* = 7.7 Hz, 2H), 6.39 (d, *J* = 15.2 Hz, 0.09H), 6.22-6.11 (m, 1H), 1.91-1.83 (m, 0.18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.2, 160.7, 134.1, 129.7, 127.3, 127.2, 125.3, 115.5, 115.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ -116.01 (s, 1F). HR-MS (EI): m/z calcd for $[M]^+$ $C_9H_6D_4F^+$, 140.0934; found 140.0932.

(*E*)-1-iodo-4-(prop-1-en-1-yl-3,3,3-*d*$_3$)benzene (2n)



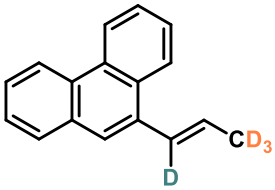
A dried 5 mL stainless-steel milling jar was charged with corresponding terminal alkenes (0.40 mmol) under air, then add KO*t*Bu (10 mol%), DMSO-*d*$_6$ (10.0 equiv) and two stainless-steel balls (7 mm, diameter) in an argon fulfilled glovebox were added. After the jar was closed in argon, the jar was placed in Gladman vibration ball mill GT300 (30 Hz). After grinding for 1 h, the reaction mixture was washed with ethyl acetate. The solvent was evaporated and the crude residue was purified through by flash chromatography on silica gel (eluted with PE) to afford product 2n (79.4 mg, 80% yield, *E:Z* 99:1, D: 80% D, CD_3: 97% D) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.0Hz, 2H), 7.07 (d, *J* = 8.0 Hz, 2H), 6.32 (d, *J* = 16.0 Hz, 0.20H), 6.27-6.20 (m, 1H), 1.88-1.80 (m, 0.10H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.4, 137.3, 130.0, 127.61, 127.58 126.5, 91.7. HR-MS (EI): m/z calcd for $[M]^+$ $C_9H_5D_5I^+$, 247.9995; found 247.9995.

(*E*)-1-(prop-1-en-1-yl-1,3,3,3-*d*$_4$)naphthalene (2o)



A dried 5 mL stainless-steel milling jar was charged with corresponding terminal alkenes (0.40 mmol) under air, then add KO*t*Bu (10 mol%), DMSO-*d*$_6$ (8.0 equiv) and two stainless-steel balls (7 mm, diameter) in an argon fulfilled glovebox were added. After the jar was closed in argon, the jar was placed in Gladman vibration ball mill GT300 (30 Hz). After grinding for 15 min, the reaction mixture was washed with ethyl acetate. The solvent was evaporated and the crude residue was purified through by flash chromatography on silica gel (eluted with PE) to afford product 2o (26.1 mg, 38% yield, *E:Z* 96:4, D: 85% D, CD_3: 91% D) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 7.3 Hz, 1H), 7.88-7.81 (m, 1H), 7.74 (d, *J* = 8.0 Hz, 1H), 7.60-7.41 (m, 4H), 7.23-7.15 (m, 0.15H), 6.26 (d, *J* = 6.5 Hz, 1H), 2.00-1.95 (m, 0.27H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.7, 133.6, 131.0, 128.7, 128.4, 127.2, 125.74, 125.66, 125.6, 123.9, 123.4. HR-MS (EI): m/z calcd for $[M]^+$ $C_{10}H_8D_4O^+$, 172.1185; found 172.1189.

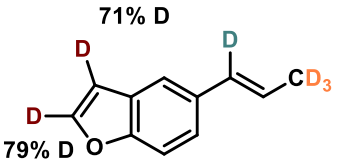
(*E*)-9-(prop-1-en-1-yl-1,3,3,3-*d*$_4$)phenanthrene (2p)



A dried 5 mL stainless-steel milling jar was charged with corresponding terminal alkenes (0.40 mmol) under air, then add KO*t*Bu (10 mol%), DMSO-*d*$_6$ (8.0 equiv) and two stainless-steel balls (7 mm, diameter) in an argon fulfilled glovebox were added. After the jar was closed in argon, the jar was placed in Gladman vibration ball mill GT300 (30 Hz). After grinding for 15 min, the reaction mixture was washed with ethyl acetate. The solvent was evaporated and the crude residue was purified through by flash chromatography on silica gel (eluted with PE/EA=50:1) to afford product 2p (61.2 mg, 69% yield, *E:Z* 91:9, D: 80% D, CD_3: 92% D) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.74 (d, *J* = 7.6 Hz, 1H), 8.67 (d, *J* = 7.3 Hz, 1H), 8.20 (d, *J* = 8.0 Hz, 1H), 7.89 (d, *J* = 7.0 Hz, 1H), 7.79 (s, 1H), 7.72-7.56 (m, 4H), 7.15 (d, *J* = 17.5 Hz, 0.20H), 6.33 (d, *J* = 4.1 Hz, 1H), 2.06-1.99 (m, 0.23H). ^{13}C NMR (101 MHz, $CDCl_3$)

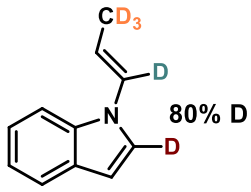
δ 134.7, 132.1, 130.9, 130.4, 130.0, 129.2, 128.6, 126.8, 126.6, 126.4, 126.3, 124.9, 124.4, 123.1, 122.6. HR-MS (EI): m/z calcd for $[M]^+$ $C_{17}H_{10}D_4^+$, 222.1341; found 222.1341.

(*E*)-5-(prop-1-en-1-yl-1,3,3,3-*d*$_4$)benzofuran-2,3-*d*$_2$ (2q)



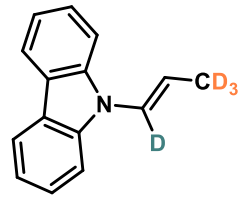
A dried 5 mL stainless-steel milling jar was charged with corresponding terminal alkenes (0.40 mmol) under air, then add KO*t*Bu (10 mol%), DMSO-*d*$_6$ (8.0 equiv) and two stainless-steel balls (7 mm, diameter) in an argon fulfilled glovebox were added. After the jar was closed in argon, the jar was placed in Gladman vibration ball mill GT300 (30 Hz). After grinding for 15 min, the reaction mixture was washed with ethyl acetate. The solvent was evaporated and the crude residue was purified through by flash chromatography on silica gel (eluted with PE/EA=50:1) to afford product 2q (56.4 mg, 86% yield, *E:Z* 98:2, D: 90% D, CD_3: 89% D) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65-7.60 (m, 0.12H), 7.60-7.51 (m, 1H), 7.50-7.42 (m, 1H), 7.40-7.30 (m, 1H), 6.75 (s, 0.25H), 6.55 (d, *J* = 15.8 Hz, 0.11H), 6.23 (s, 1H), 1.95-1.87 (m, 0.31H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.1, 145.5-144.2 (m, C-D), 133.0, 131.3-130.3 (m, C-D), 127.6, 124.2, 122.3, 118.2, 111.2, 106.8-105.6 (m, C-D). HR-MS (EI): m/z calcd for $[M]^+$ $C_{11}H_4D_6O^+$, 164.1102; found 164.1103.

(*E*)-1-(prop-1-en-1-yl-1,3,3,3-*d*$_4$)-1*H*-indole-2-*d* (2r)



A dried 5 mL stainless-steel milling jar was charged with corresponding terminal alkenes (0.40 mmol) under air, then add KO*t*Bu (10 mol%), DMSO-*d*$_6$ (8.0 equiv) and two stainless-steel balls (7 mm, diameter) in an argon fulfilled glovebox were added. After the jar was closed in argon, the jar was placed in Gladman vibration ball mill GT300 (30 Hz). After grinding for 15 min, the reaction mixture was washed with ethyl acetate. The solvent was evaporated and the crude residue was purified through by flash chromatography on silica gel (eluted with PE/EA=20:1) to afford product 2r (58.3 mg, 90% yield, *E:Z* 93:7, D: 90% D, CD_3: 90% D) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 7.8 Hz, 1H), 7.34 (d, *J* = 8.4 Hz, 1H), 7.24-7.19 (m, 0.20H), 7.19-7.09 (m, 1H), 7.03 (t, *J* = 7.4 Hz, 1H), 6.87 (d, *J* = 13.9 Hz, 0.10H), 6.54-6.42 (m, 1H), 5.67-6.58 (m, 1H), 1.78-1.70 (m, 0.30H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.2, 128.7, 124.9-123.5 (m, C-D), 122.2, 121.0, 120.2, 110.3, 109.5, 103.5. HR-MS (ESI): m/z calcd for $[M+H]^+$ $C_{11}H_7D_5N^+$, 163.1278; found 163.1277.

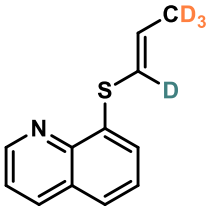
(*E*)-9-(prop-1-en-1-yl-1,3,3,3-*d*$_4$)-9*H*-carbazole (2s)



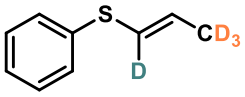
A dried 5 mL stainless-steel milling jar was charged with corresponding terminal alkenes (0.40 mmol) under air, then add KO*t*Bu (10 mol%), DMSO-*d*$_6$ (8.0 equiv) and two stainless-steel balls (7 mm, diameter) in an argon fulfilled glovebox were added. After the jar was closed in argon, the jar was placed in Gladman vibration ball mill GT300 (30 Hz). After grinding for 15 min, the reaction mixture was washed with ethyl acetate. The solvent was evaporated and the crude residue was purified through by flash chromatography on silica gel (eluted with PE/EA=20:1) to afford product 2s (79.3 mg, 94% yield, *E:Z* 75:25, D: 92% D, CD_3: 94% D) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26-8.06 (m, 2H), 7.65 (d, *J* = 7.8 Hz, 2H), 7.53 (t, *J* = 7.5 Hz, 2H), 7.41-7.30 (m, 2H), 7.00 (d, *J* = 13.8 Hz, 0.08H), 6.09 (d, *J* = 62.1 Hz, 1H), 2.06-2.00 (m, 0.17H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.7, 125.9, 125.8, 123.3, 120.1, 119.9, 118.2, 110.0. HR-MS (ESI): m/z calcd for $[M+H]^+$ $C_{15}H_{10}D_4N^+$, 212.1372; found 212.1366.

(*E*)-8-((prop-1-en-1-yl-1,3,3,3-*d*$_4$)thio)quinoline (2t)

A dried 5 mL stainless-steel milling jar was charged with corresponding terminal alkenes (0.40 mmol) under air, then add KO*t*Bu (10 mol%), DMSO-d_6 (8.0 equiv) and two stainless-steel balls (7 mm, diameter) in an argon fulfilled glovebox were added. After the jar was closed in argon, the jar was placed in Gladman vibration ball mill GT300 (30 Hz). After grinding for 15 min, the reaction mixture was washed with ethyl acetate. The solvent was evaporated and the crude residue was purified through by flash chromatography on silica gel (eluted with PE/EA=10:1) to afford product 2t (73.8 mg, 90% yield, *E:Z* 74:26, D: 96% D, CD_3: 91% D) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.94-8.87 (m, 1H), 8.10-8.04 (m 1H), 7.59-7.46 (m, 2H), 7.46-7.34 (m, 2H), 6.40 (d, J = 9.2 Hz, 0.04H), 6.32-6.12 (m, 1H), 1.92-1.84 (m, 0.27H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.2, 145.1, 138.7, 136.2, 131.8, 128.2, 126.5, 124.7, 124.3, 121.5, 120.8-118.7 (m, C-D). HR-MS (ESI): m/z calcd for $[M+H]^+$ $C_{12}H_8D_4NS^+$, 206.0936; found 206.0931.

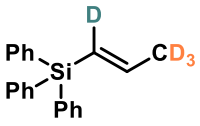


(*E*)-phenyl(prop-1-en-1-yl-1,3,3,3-d_4)sulfane (2u)



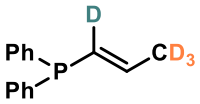
A dried 5 mL stainless-steel milling jar was charged with corresponding terminal alkenes (0.40 mmol) under air, then add KO*t*Bu (10 mol%), DMSO-d_6 (8.0 equiv) and two stainless-steel balls (7 mm, diameter) in an argon fulfilled glovebox were added. After the jar was closed in argon, the jar was placed in Gladman vibration ball mill GT300 (30 Hz). After grinding for 15 min, the reaction mixture was washed with ethyl acetate. The solvent was evaporated and the crude residue was purified through by flash chromatography on silica gel (eluted with PE) to afford product 2u (58.5 mg, 95% yield, *E:Z* >99:1, D: 90% D, CD_3: 92% D) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26-7.15 (m, 4H), 7.12-7.01 (m, 1H), 6.15-6.02 (m, 0.10H), 5.92-5.72 (m, 1H), 1.74-1.65 (m, 0.25H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.0, 129.1, 128.8, 127.5, 127.1. HR-MS (EI): m/z calcd for $[M]^+$ $C_9H_6D_4S^+$, 154.0749; found 154.0755.

(*E*)-triphenyl(prop-1-en-1-yl-1,3,3,3-d_4)silane (2v)



A dried 5 mL stainless-steel milling jar was charged with corresponding terminal alkenes (0.40 mmol) under air, then add KO*t*Bu (10 mol%), DMSO-d_6 (8.0 equiv) and two stainless-steel balls (7 mm, diameter) in an argon fulfilled glovebox were added. After the jar was closed in argon, the jar was placed in Gladman vibration ball mill GT300 (30 Hz). After grinding for 2 h, the reaction mixture was washed with ethyl acetate. The solvent was evaporated and the crude residue was purified through by flash chromatography on silica gel (eluted with PE) to afford product 2v (58.5 mg, 68% yield, *E:Z* 97:3, D: 97% D, CD_3: 71% D) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, J = 7.8 Hz, 6H), 7.49-7.36 (m, 9H), 6.32-6.17 (m, 1.03H), 2.00-1.92 (m, 0.87H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.2, 135.9, 135.0, 129.4, 127.8. HR-MS (EI): m/z calcd for $[M]^+$ $C_{21}H_{16}D_4Si^+$, 304.1579; found 304.1583.

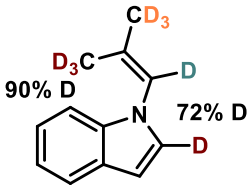
(*E*)-diphenyl(prop-1-en-1-yl-1,3,3,3-d_4)phosphane (2w)



A dried 5 mL stainless-steel milling jar was charged with corresponding terminal alkenes (0.40 mmol) under air, then add KO*t*Bu (10 mol%), DMSO-d_6 (8.0 equiv) and two stainless-steel balls (7 mm, diameter) in an argon fulfilled glovebox were added. After the jar was closed in argon, the jar was placed in Gladman vibration ball mill GT300 (30 Hz). After grinding for 15 min, the reaction mixture was washed with ethyl acetate. The solvent was evaporated and the crude residue was purified through by flash chromatography on silica gel (eluted with PE) to afford product 2w (76.4

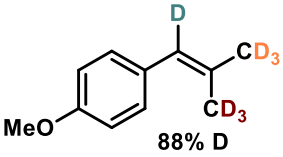
mg, 83% yield, *E:Z* >99:1, D: 86% D, CD_3: 93% D) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33-7.27 (m, 4H), 7.25-7.18 (m, 6H), 6.40 (d, *J* = 23.6 Hz, 0.14H), 6.22-6.11 (d, *J* = 14.9 Hz, 1H), 1.81-1.75 (m, 0.21H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.0, 139.3, 132.8, 128.6, 128.5. HR-MS (EI): m/z calcd for $[M]^+$ $C_{15}H_{11}D_4P^+$, 230.1156; found 230.1159.

1-(2-(methyl-*d*$_3$)prop-1-en-1-yl-1,3,3,3-*d*$_4$)-1H-indole-2-*d* (2x)



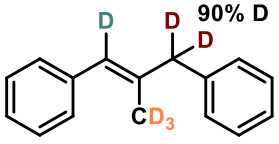
A dried 5 mL stainless-steel milling jar was charged with corresponding terminal alkenes (0.40 mmol) under air, then add KO*t*Bu (10 mol%), DMSO-*d*$_6$ (8.0 equiv) and two stainless-steel balls (7 mm, diameter) in an argon fulfilled glovebox were added. After the jar was closed in argon, the jar was placed in Gladman vibration ball mill GT300 (30 Hz). After grinding for 15 min, the reaction mixture was washed with ethyl acetate. The solvent was evaporated and the crude residue was purified through by flash chromatography on silica gel (eluted with PE/EA=20:1) to afford product 2x (61.6 mg, 86% yield, D: 90% D, CD_3: 90% D) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 7.8 Hz, 1H), 7.17 (d, *J* = 8.3 Hz, 1H), 7.14-7.09 (m, 1H), 7.06-7.00 (m, 1H), 6.99 (d, *J* = 3.4 Hz, 0.28H), 6.48 (s, 0.10H), 6.46-6.43 (m, 1H), 1.81-1.76 (m, 0.29H), 1.60-1.54 (m, 0.29H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.4, 128.2, 128.0, 121.7, 120.7, 119.7, 110.2, 101.9, 101.7. HR-MS (ESI): m/z calcd for $[M+H]^+$ $C_{12}H_6D_8N^+$, 180.1623; found 180.1618.

1-methoxy-4-(2-(methyl-*d*$_3$)prop-1-en-1-yl-1,3,3,3-*d*$_4$)benzene (2y)



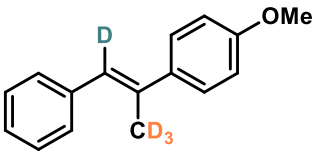
A dried 5 mL stainless-steel milling jar was charged with corresponding terminal alkenes (0.40 mmol) under air, then add KO*t*Bu (10 mol%), DMSO-*d*$_6$ (8.0 equiv) and two stainless-steel balls (7 mm, diameter) in an argon fulfilled glovebox were added. After the jar was closed in argon, the jar was placed in Gladman vibration ball mill GT300 (30 Hz). After grinding for 15 min, the reaction mixture was washed with ethyl acetate. The solvent was evaporated and the crude residue was purified through by flash chromatography on silica gel (eluted with PE) to afford product 2y (57.5 mg, 85% yield, D: 88% D, CD_3: 88% D) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 (d, *J* = 6.6 Hz, 2H), 6.89 (d, *J* = 6.5 Hz, 2H), 6.24 (s, 0.12H), 3.82 (s, 3H), 1.93-1.80 (m, 0.73H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.8, 133.8, 131.4, 129.9, 124.9-123.7 (m, C-D), 113.6. HR-MS (EI): m/z calcd for $[M]^+$ $C_{11}H_7D_7O^+$, 169.1478; found 169.1481.

(*E*)-(2-(methyl-*d*$_3$)prop-1-ene-1,3-diyl-1,3,3-*d*$_3$)dibenzene (2z)



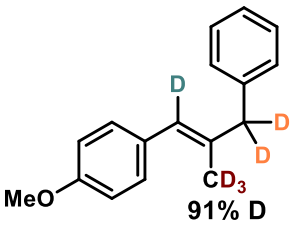
A dried 5 mL stainless-steel milling jar was charged with corresponding terminal alkenes (0.40 mmol) under air, then add KO*t*Bu (10 mol%), DMSO-*d*$_6$ (8.0 equiv) and two stainless-steel balls (7 mm, diameter) in an argon fulfilled glovebox were added. After the jar was closed in argon, the jar was placed in Gladman vibration ball mill GT300 (30 Hz). After grinding for 15 min, the reaction mixture was washed with ethyl acetate. The solvent was evaporated and the crude residue was purified through by flash chromatography on silica gel (eluted with PE) to afford product 2z (83.0 mg, 97% yield, *E:Z* 75:25, D: 90% D, CD_3: 90% D) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27-7.05 (m, 10H), 6.29 (s, 0.10H), 3.37 (d, *J* = 8.6 Hz, 0.21H), 1.71-1.63 (m, 0.32H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.9, 138.4, 129.1, 129.0, 128.6, 128.5, 128.2, 126.3, 126.2. HR-MS (EI): m/z calcd for $[M]^+$ $C_{16}H_{10}D_6^+$, 214.1623; found 214.1623.

(*E*)-1-methoxy-4-(1-phenylprop-1-en-2-yl-1,3,3,3-*d*$_4$)benzene (3a)



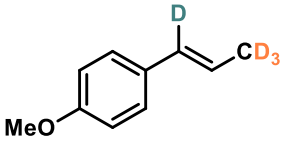
A dried 5 mL stainless-steel milling jar was charged with corresponding terminal alkenes (0.40 mmol) under air, then add KO*t*Bu (10 mol%), DMSO-d_6 (8.0 equiv) and two stainless-steel balls (7 mm, diameter) in an argon fulfilled glovebox were added. After the jar was closed in argon, the jar was placed in Gladman vibration ball mill GT300 (30 Hz). After grinding for 15 min, the reaction mixture was washed with ethyl acetate. The solvent was evaporated and the crude residue was purified through by flash chromatography on silica gel (eluted with PE) to afford product 3a (81.2 mg, 89% yield, *E:Z* >99:1, D: 90% D, CD_3: 90% D) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 7.1 Hz, 2H), 7.51-7.40 (m, 4H), 7.36-7.26 (m, 1H), 7.06-6.95 (m, 2H), 6.88 (s, 0.10H), 3.90 (d, *J* = 1.7 Hz, 3H), 2.35-2.28 (m, 0.22H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.9, 138.4, 136.5, 136.3, 129.1, 128.1, 127.0, 126.2, 113.6, 55.3. HR-MS (EI): m/z calcd for $[M]^+$ $C_{16}H_{12}D_4O^+$, 228.1446; found 228.1450.

(*E*)-1-methoxy-4-(2-(methyl-d_3)-3-phenylprop-1-en-1-yl-1,3,3-d_3)benzene (3b)



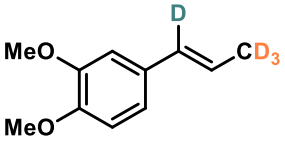
A dried 5 mL stainless-steel milling jar was charged with corresponding terminal alkenes (0.40 mmol) under air, then add KO*t*Bu (10 mol%), DMSO-d_6 (8.0 equiv) and two stainless-steel balls (7 mm, diameter) in an argon fulfilled glovebox were added. After the jar was closed in argon, the jar was placed in Gladman vibration ball mill GT300 (30 Hz). After grinding for 30 min, the reaction mixture was washed with ethyl acetate. The solvent was evaporated and the crude residue was purified through by flash chromatography on silica gel (eluted with PE/EA=50:1) to afford product 3b (94.7 mg, 97% yield, *E:Z* 82:18, D: 90% D, D_2: 93% D) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27-6.88 (m, 7H), 6.78-6.66 (m, 2H), 6.43-6.17 (m, 0.10H), 3.67 (s, 3H), δ 3.30 (d, *J* = 17.7 Hz, 0.14H), 1.69-1.62 (m, 0.28H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.5, 139.6, 138.0, 129.6, 129.1, 128.6, 128.0, 127.7, 125.7, 113.1, 54.9. HR-MS (EI): m/z calcd for $[M]^+$ $C_{17}H_{12}D_6N^+$, 224.1728; found 224.1731.

(*E*)-1-methoxy-4-(prop-1-en-1-yl-1,3,3,3-d_4)benzene (2a)



A dried 5 mL stainless-steel milling jar was charged with corresponding terminal alkenes (0.40 mmol) under air, then add KO*t*Bu (10 mol%), DMSO-d_6 (8.0 equiv) and two stainless-steel balls (7 mm, diameter) in an argon fulfilled glovebox were added. After the jar was closed in argon, the jar was placed in Gladman vibration ball mill GT300 (30 Hz). After grinding for 15 min, the reaction mixture was washed with ethyl acetate. The solvent was evaporated and the crude residue was purified through by flash chromatography on silica gel (eluted with PE/EA=100:1) to afford product 2a (60.2 mg, 99% yield, *E:Z* >99:1, D: 90% D, CD_3: 92% D) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 (d, *J* = 8.7 Hz, 2H), 6.75 (d, *J* = 8.9 Hz, 2H), 6.26 (d, *J* = 15.7 Hz, 0.10H), 6.12 -5.86 (m, 1H), 3.71 (s, 3H), 1.74 (m, J = 6.5, 2.3 Hz, 0.23H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.5, 130.7, 130.5-129.6 (m, C-D), 126.8, 123.2, 113.9, 55.2. HR-MS (ESI): m/z calcd for $[M+H]^+$ $C_{10}H_9D_4O^+$, 153.1212; found 153.1212.

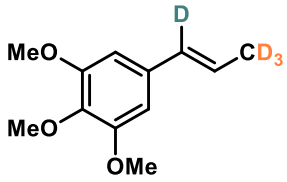
(*E*)-1,2-dimethoxy-4-(prop-1-en-1-yl-1,3,3,3-d_4)benzene (3c)



A dried 5 mL stainless-steel milling jar was charged with corresponding terminal alkenes (0.40 mmol) under air, then add KO*t*Bu (10 mol%), DMSO-d_6 (8.0 equiv) and two stainless-steel balls (7 mm, diameter) in an argon fulfilled glovebox were added. After the jar was closed in argon, the jar was placed in Gladman vibration ball mill GT300 (30 Hz). After grinding for 15 min,

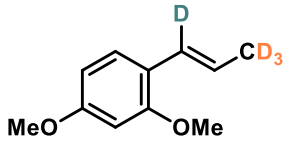
the reaction mixture was washed with ethyl acetate. The solvent was evaporated and the crude residue was purified through by flash chromatography on silica gel (eluted with PE/EA=100:1) to afford product 3c (72.1 mg, 99% yield, *E:Z* 99:1, D: 89% D, CD_3: 92% D) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.89 (d, *J* = 2.2 Hz, 1H), 6.85 (dd, *J* = 8.2, 2.1 Hz, 1H), 6.78 (d, *J* = 8.2 Hz, 1H), 6.33 (d, *J* = 15.8 Hz, 0.12H), 6.13-6.04 (m, 1H), 3.88 (s, 3H), 3.85 (s, 3H), 1.83 (m, 0.16H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.8, 148.0, 131.0, 130.7-129.8 (m, C-D), 123.4, 118.5, 111.0, 108.3, 55.8, 55.6, 17.9-17.0 (m, CD_3). HR-MS (ESI): m/z calcd for $[M+H]^+$ $C_{11}H_{11}D_4O_2^+$, 183.1318; found 183.1312.

(*E*)-1,2,3-trimethoxy-5-(prop-1-en-1-yl-1,3,3,3-*d*$_4$)benzene (3d)



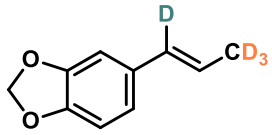
A dried 5 mL stainless-steel milling jar was charged with corresponding terminal alkenes (0.40 mmol) under air, then add KO*t*Bu (10 mol%), DMSO-*d*$_6$ (8.0 equiv) and two stainless-steel balls (7 mm, diameter) in an argon fulfilled glovebox were added. After the jar was closed in argon, the jar was placed in Gladman vibration ball mill GT300 (30 Hz). After grinding for 15 min, the reaction mixture was washed with ethyl acetate. The solvent was evaporated and the crude residue was purified through by flash chromatography on silica gel (eluted with PE/EA=50:1) to afford product 3d (80.5 mg, 95% yield, *E:Z* >99:1, D: 90% D, CD_3: 92% D) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.55 (s, 2H), 6.32 (d, *J* = 15.5 Hz, 0.10H), 6.21-6.07 (m, 1H), 3.85 (s, 6H), 3.83 (s, 3H), 1.83 (m, 0.23H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.1, 136.8, 133.6, 130.9-130.0 (m, C-D), 125.0, 102.5, 60.8, 55.8. HR-MS (ESI): m/z calcd for $[M+H]^+$ $C_{12}H_{13}D_4O_3^+$, 213.1423; found 213.1423.

(*E*)-2,4-dimethoxy-1-(prop-1-en-1-yl-1,3,3,3-*d*$_4$)benzene (3e)



A dried 5 mL stainless-steel milling jar was charged with corresponding terminal alkenes (0.40 mmol) under air, then add KO*t*Bu (10 mol%), DMSO-*d*$_6$ (8.0 equiv) and two stainless-steel balls (7 mm, diameter) in an argon fulfilled glovebox were added. After the jar was closed in argon, the jar was placed in Gladman vibration ball mill GT300 (30 Hz). After grinding for 15 min, the reaction mixture was washed with ethyl acetate. The solvent was evaporated and the crude residue was purified through by flash chromatography on silica gel (eluted with PE/EA=100:1) to afford product 3e (59.7 mg, 82% yield, *E:Z* >99:1, D: 87% D, CD_3: 93% D) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (d, *J* = 8.2 Hz, 1H), 6.64 (d, *J* = 15.8 Hz, 0.13H), 6.54-6.36 (m, 2H), 6.21-6.03 (m, 1H), 3.83 (s, 3H), 3.81 (s, 3H), 1.89-1.83 (m, 0.22H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.7, 157.1, 126.9, 125.4-124.5 (m, C-D), 124.1, 120.0, 104.6, 98.3, 55.3, 55.3. HR-MS (EI): m/z calcd for $[M]^+$ $C_{11}H_{10}D_4O_2^+$, 182.1239; found 192.1241.

1-(methyl-D)-4-phenoxybenzene (3f)



A dried 5 mL stainless-steel milling jar was charged with corresponding terminal alkenes (0.40 mmol) under air, then add KO*t*Bu (10 mol%), DMSO-*d*$_6$ (8.0 equiv) and two stainless-steel balls (7 mm, diameter) in an argon fulfilled glovebox were added. After the jar was closed in argon, the jar was placed in Gladman vibration ball mill GT300 (30 Hz). After grinding for 15 min, the reaction mixture was washed with ethyl acetate. The solvent was evaporated and the crude residue was purified through by flash chromatography on silica gel (eluted with PE/EA=100:1) to afford product 3f (61.1 mg, 92% yield, D: *E:Z* 93:7, 91% D, CD_3: 91% D) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.92 (s, 1H), 6.78 (s, 2H), 6.35 (d, *J* = 13.7 Hz, 0.09H), 6.08 (s, 1H), 5.99-5.95 (m, 2H), 1.85 (m, 0.27H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.9, 146.5, 132.9-129.8 (m, C-D), 123.6, 120.0, 108.2, 105.3, 100.8, 31.3. HR-MS (EI): m/z calcd for $[M]^+$ $C_{10}H_6D_4O_2^+$, 166.0926; found

166.0925.

8. References

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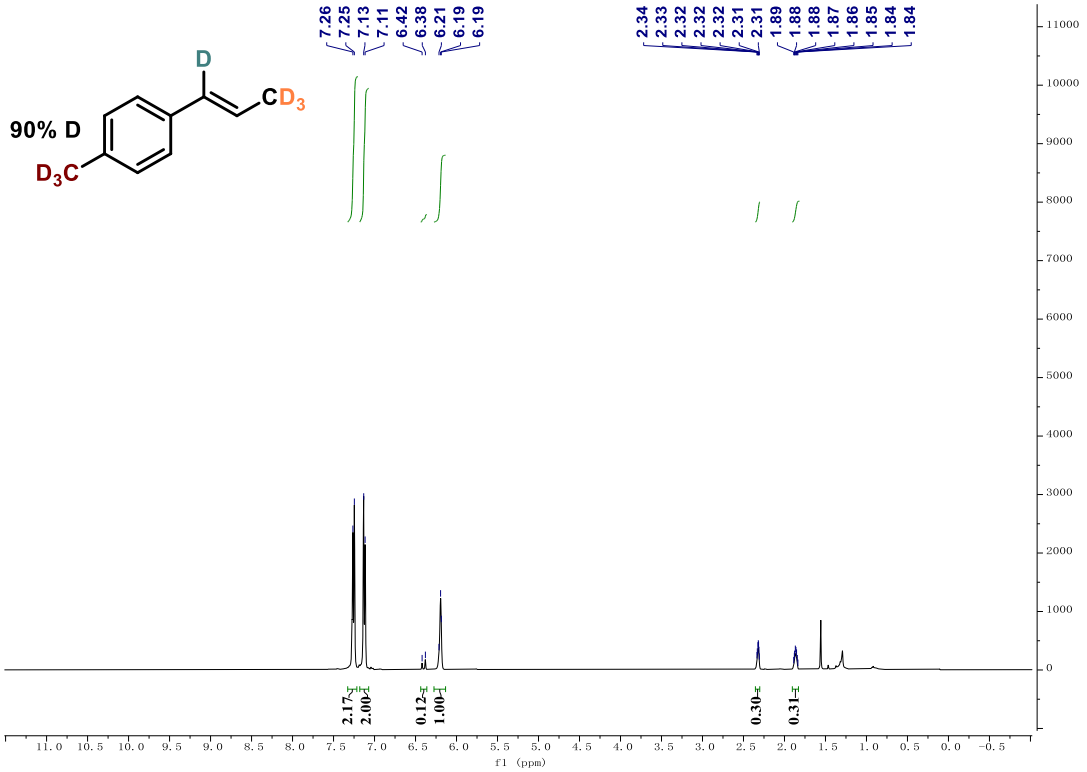
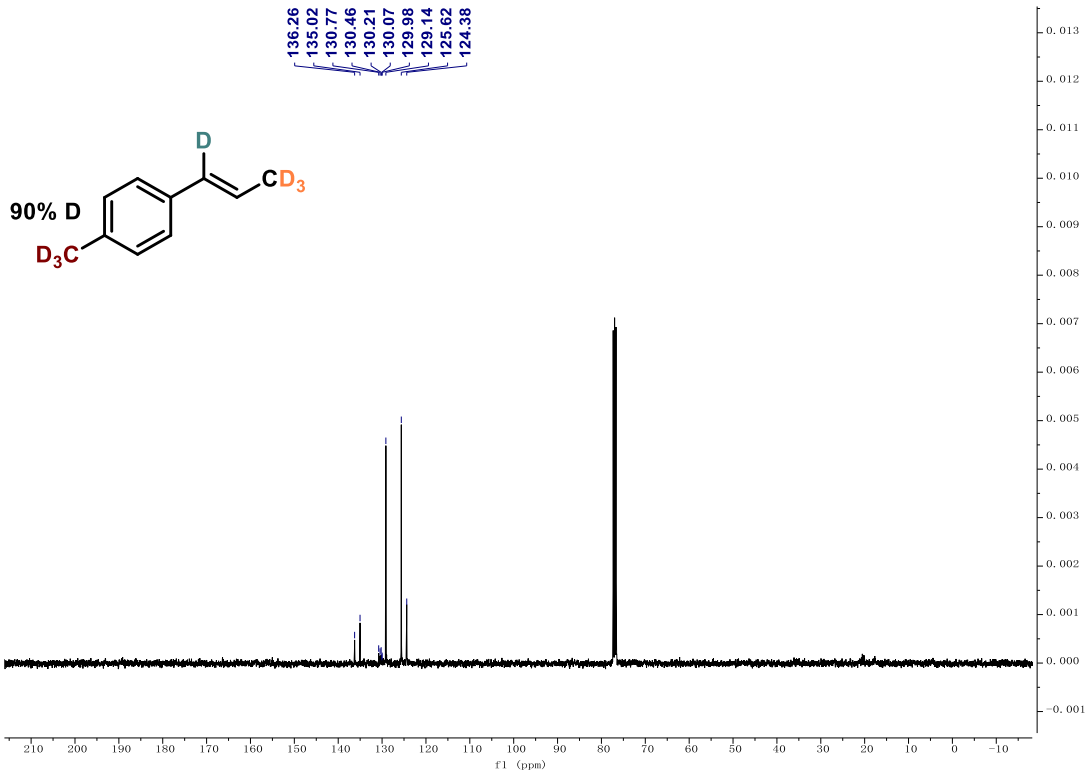
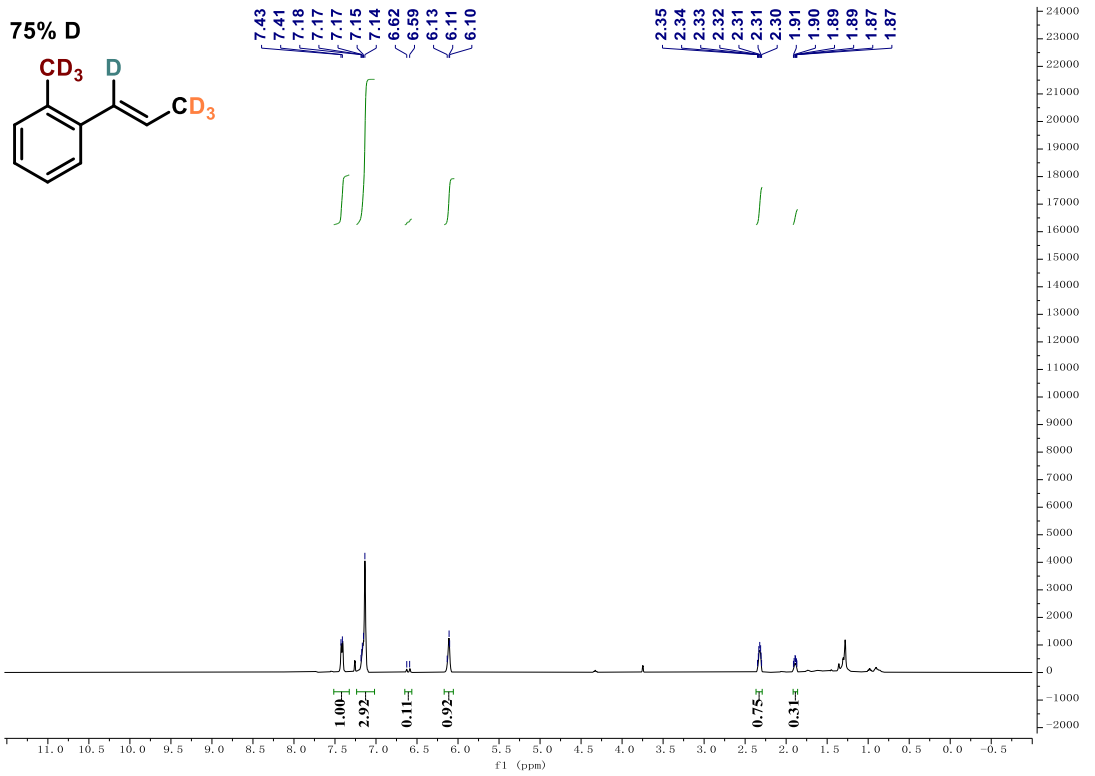
9. NMR spectra of products 2



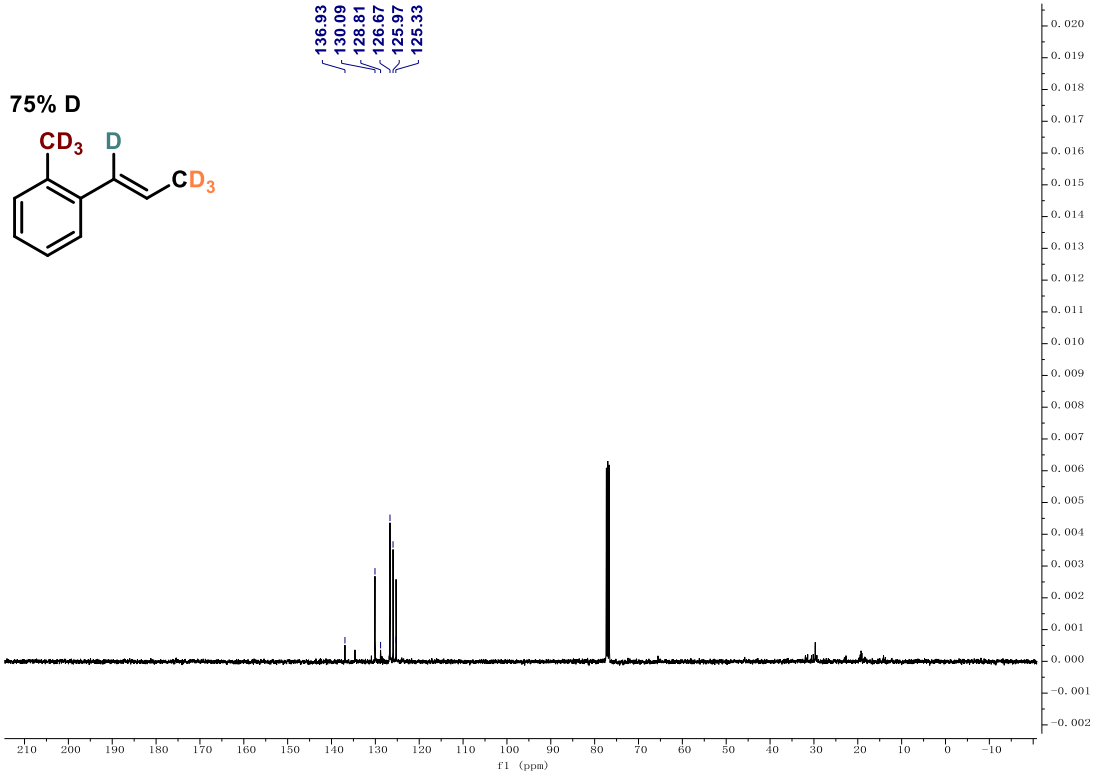
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of compound **2b**



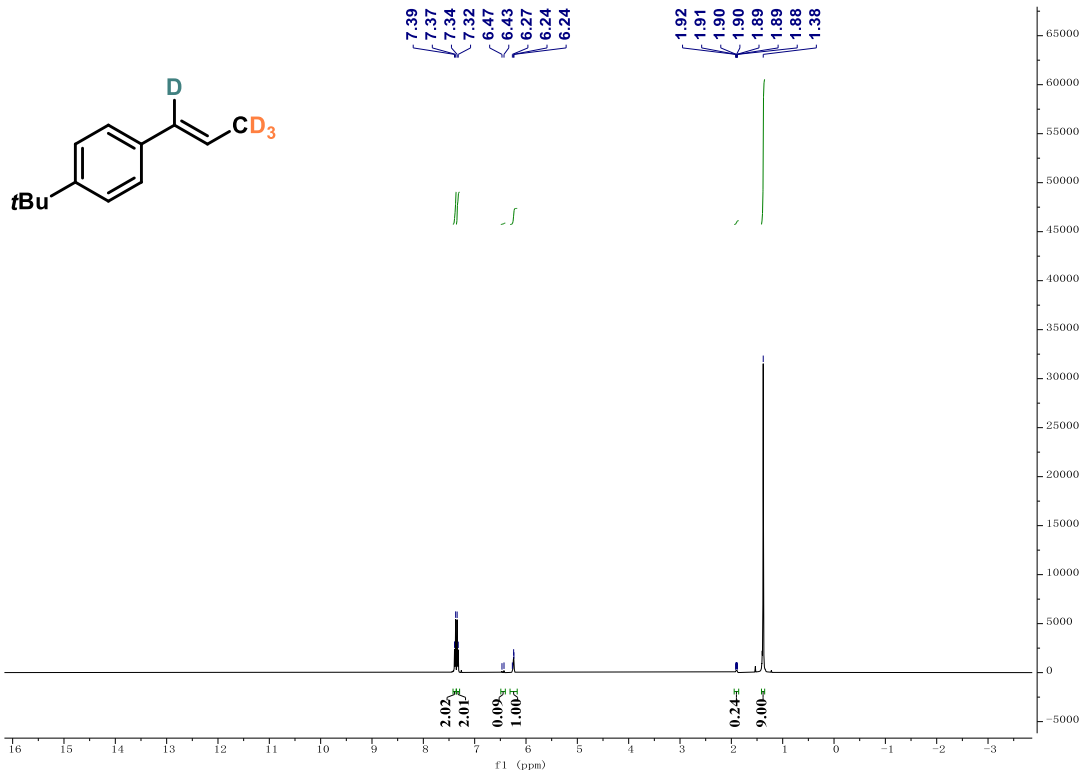
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of compound **2b**



^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of compound **2c**



^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of compound **2c**



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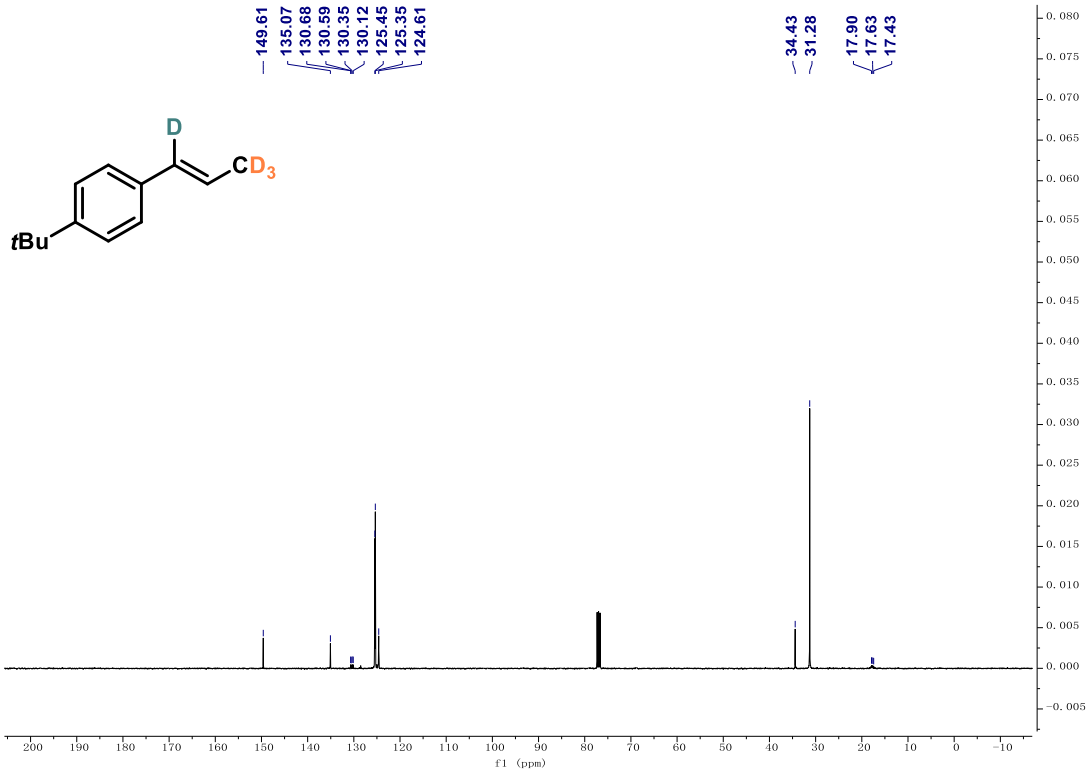
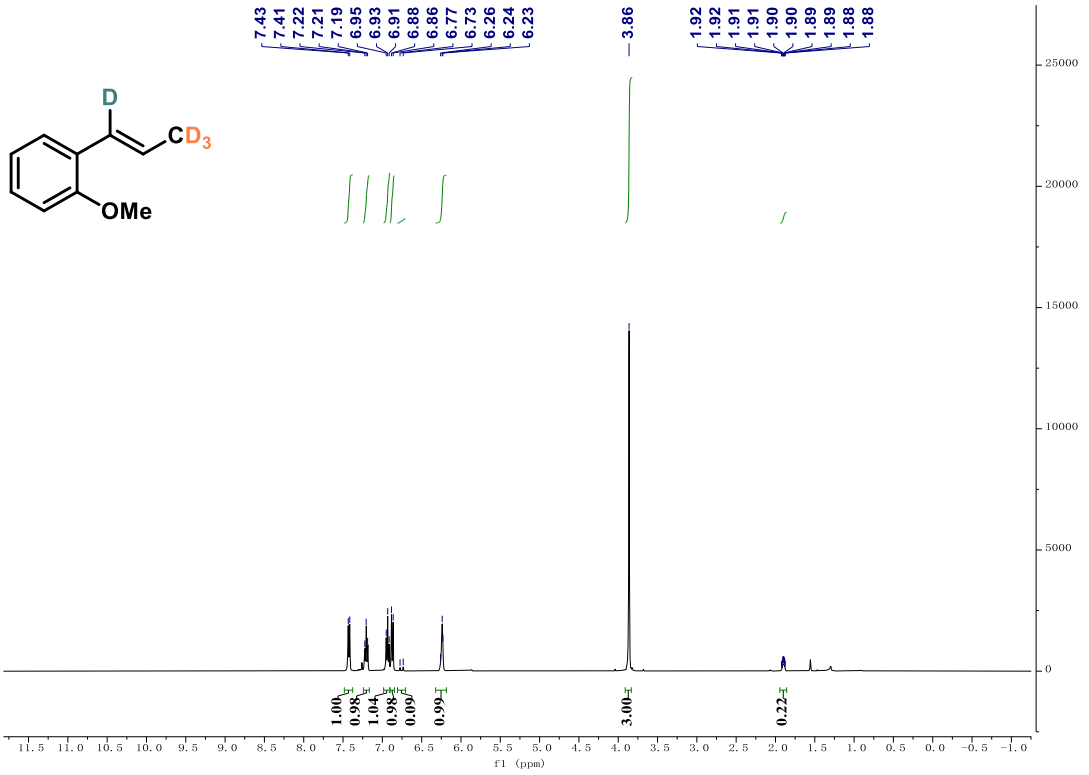
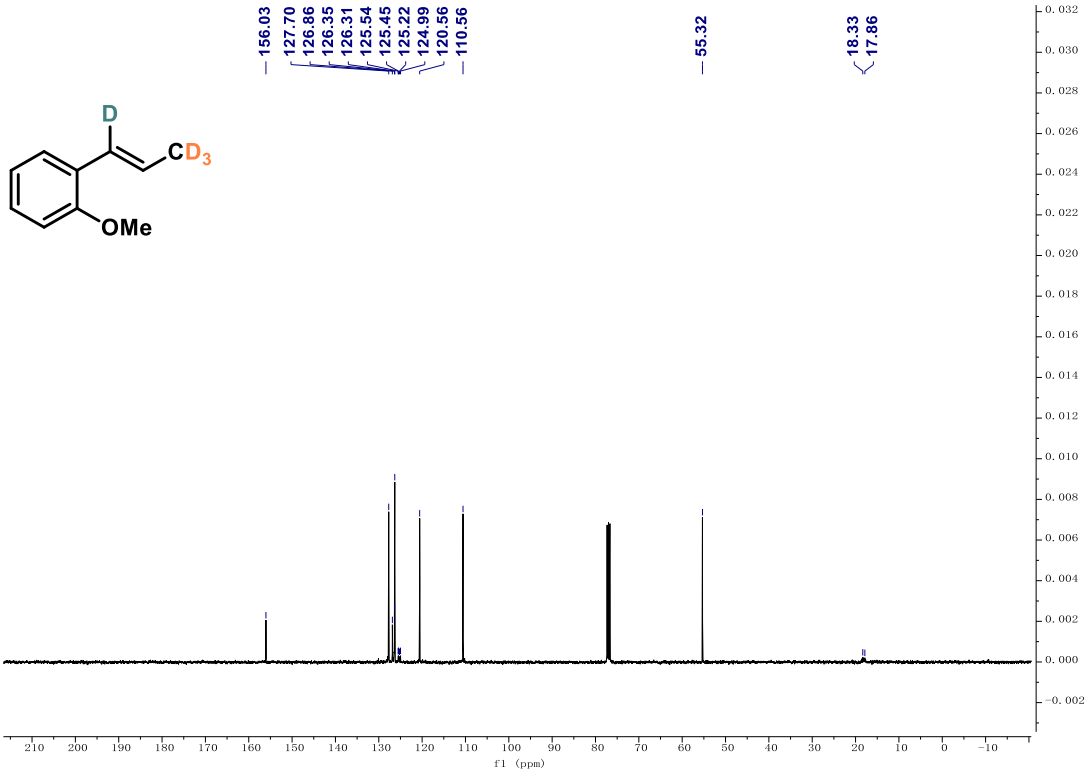


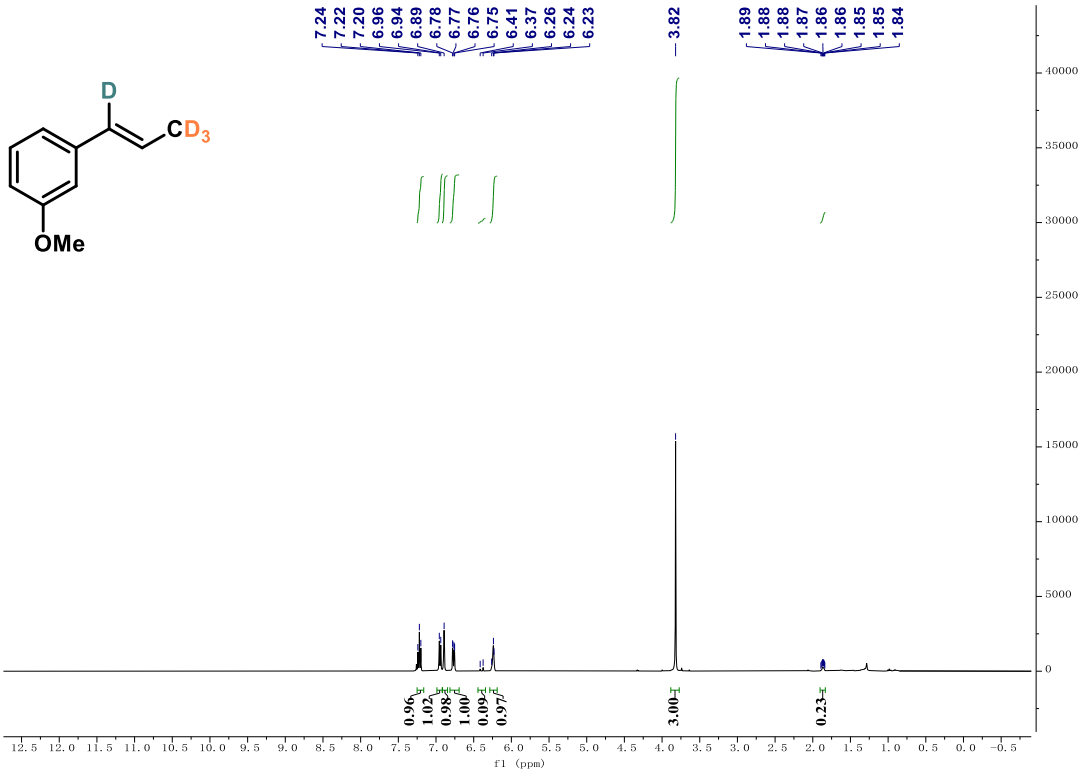
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of compound **2d**



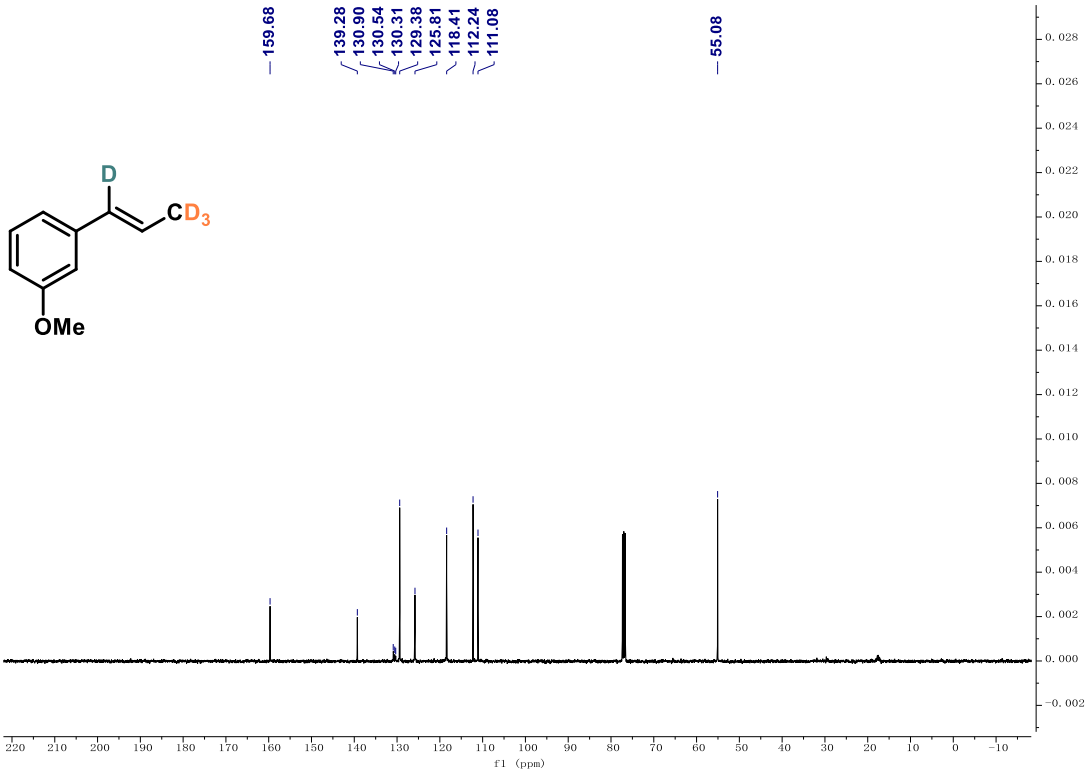
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of compound **2e**



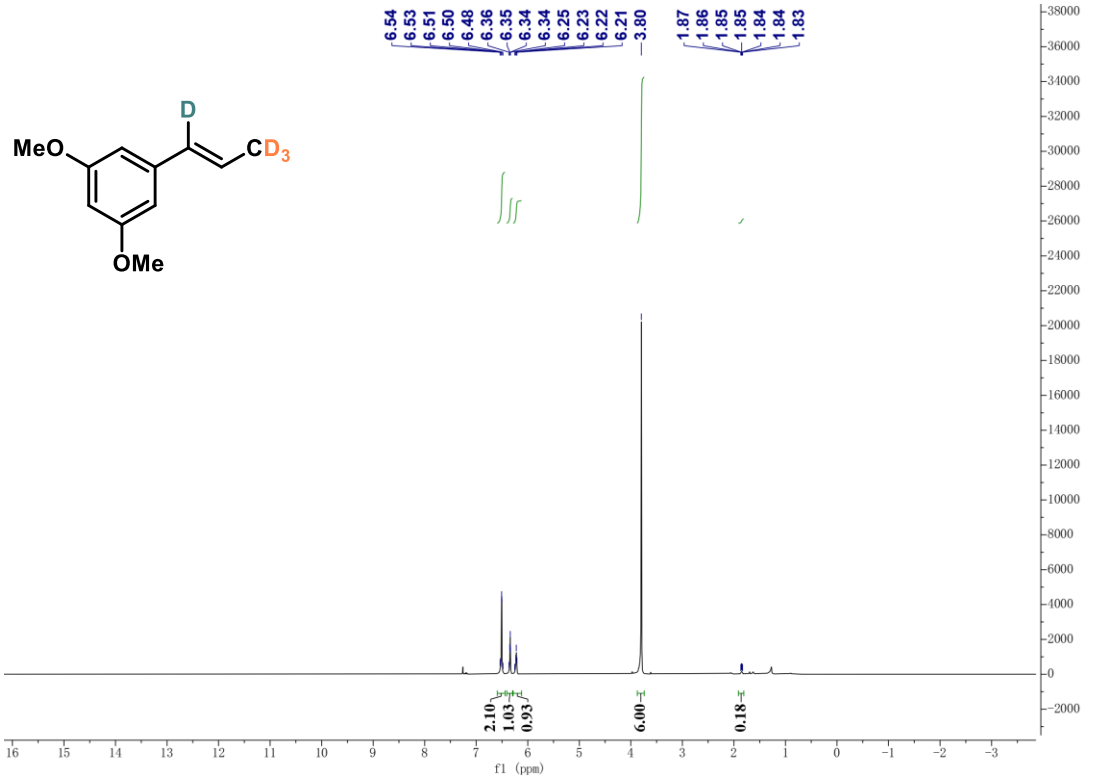
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of compound **2e**



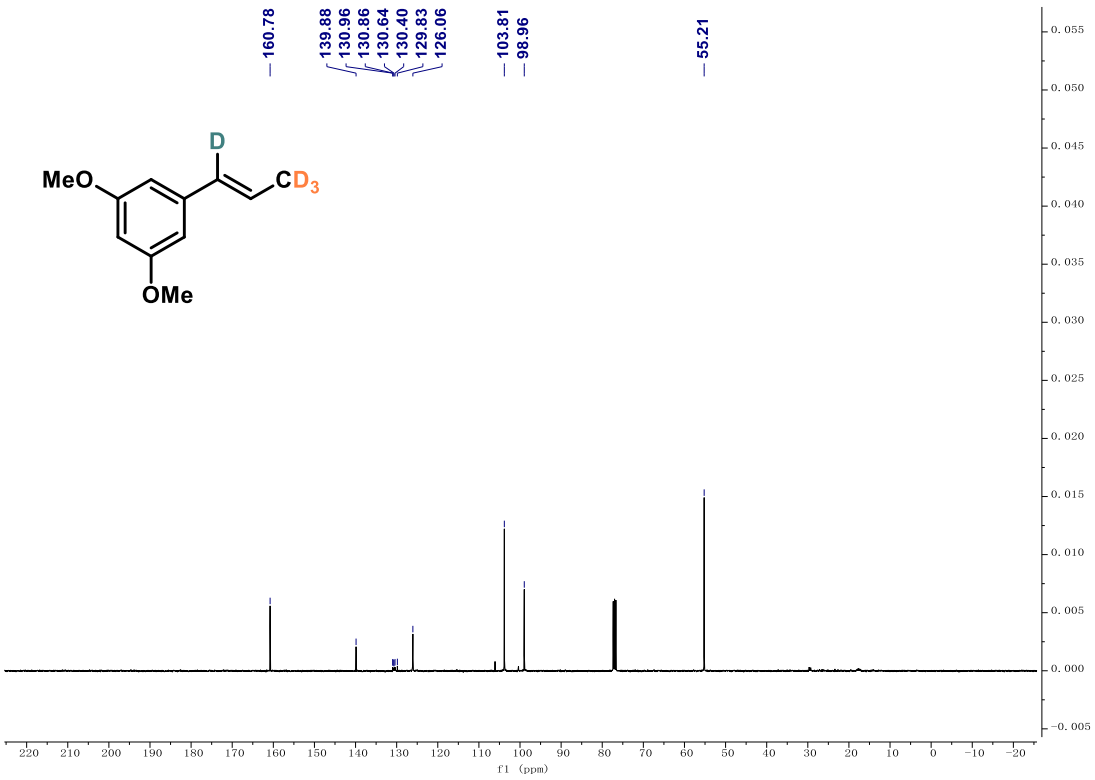
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of compound **2f**



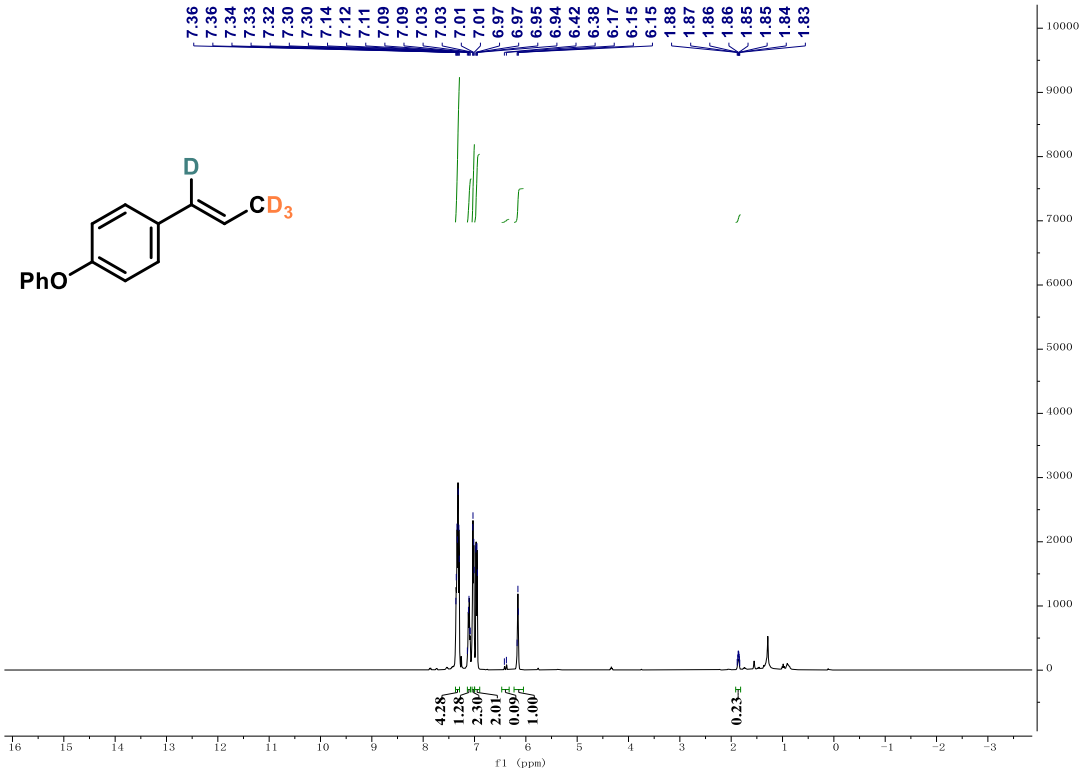
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of compound **2f**



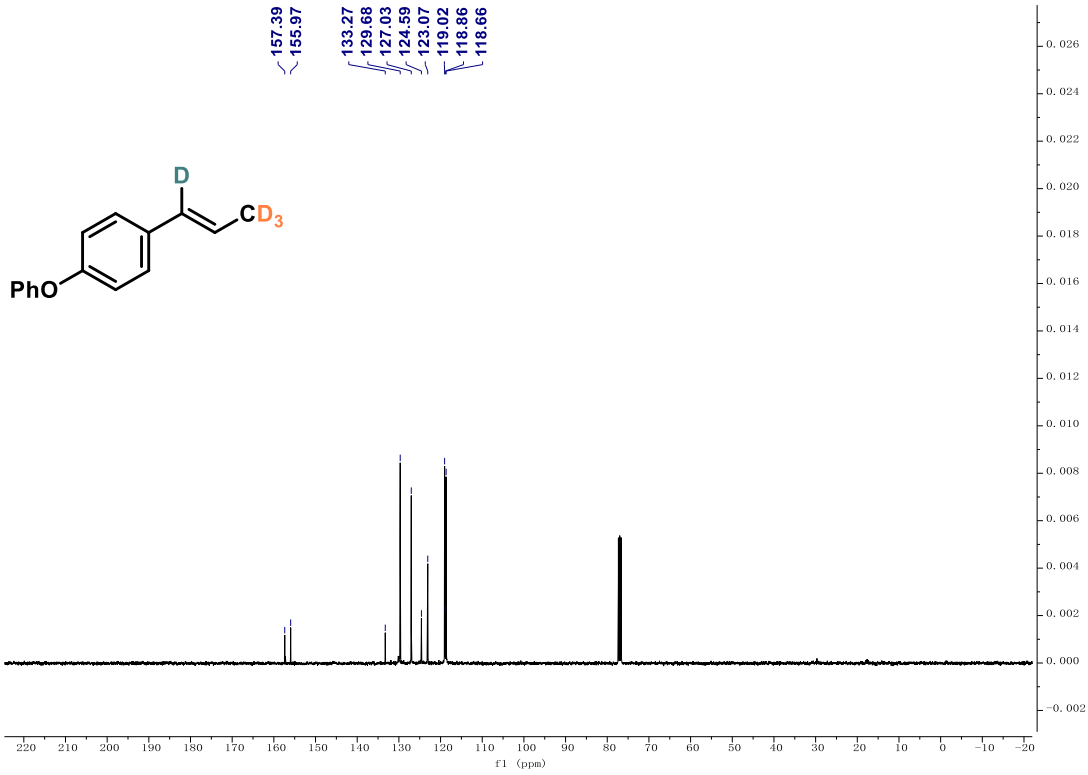
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of compound **2g**



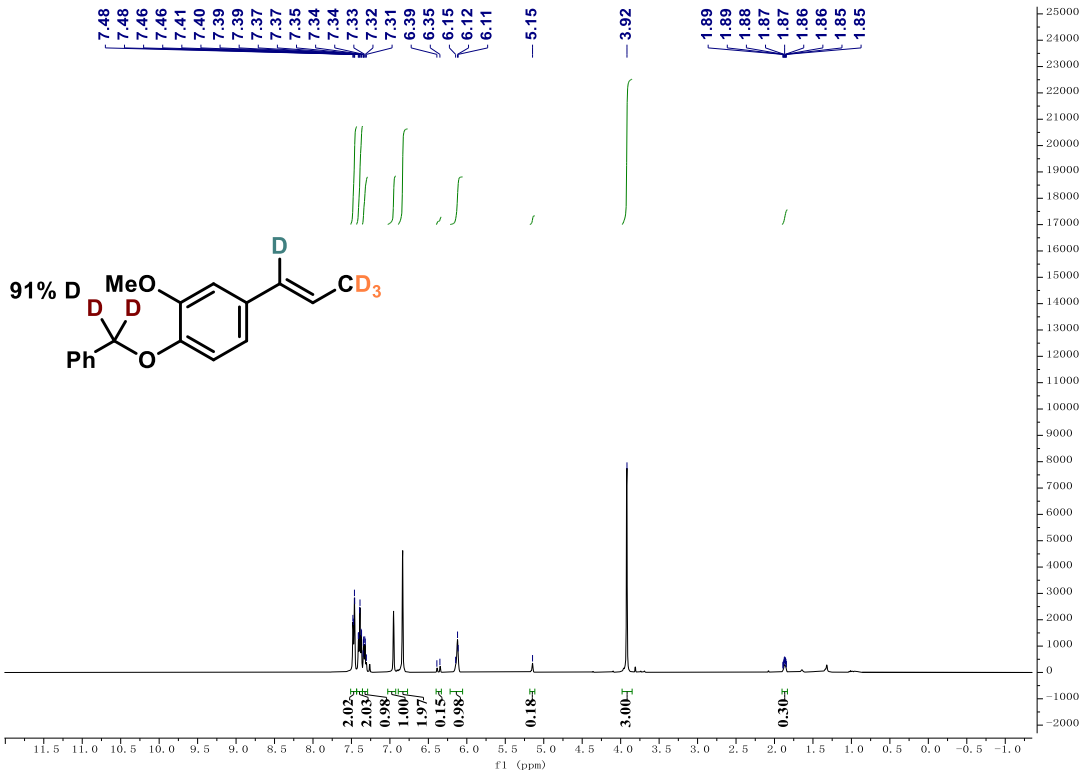
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of compound **2g**



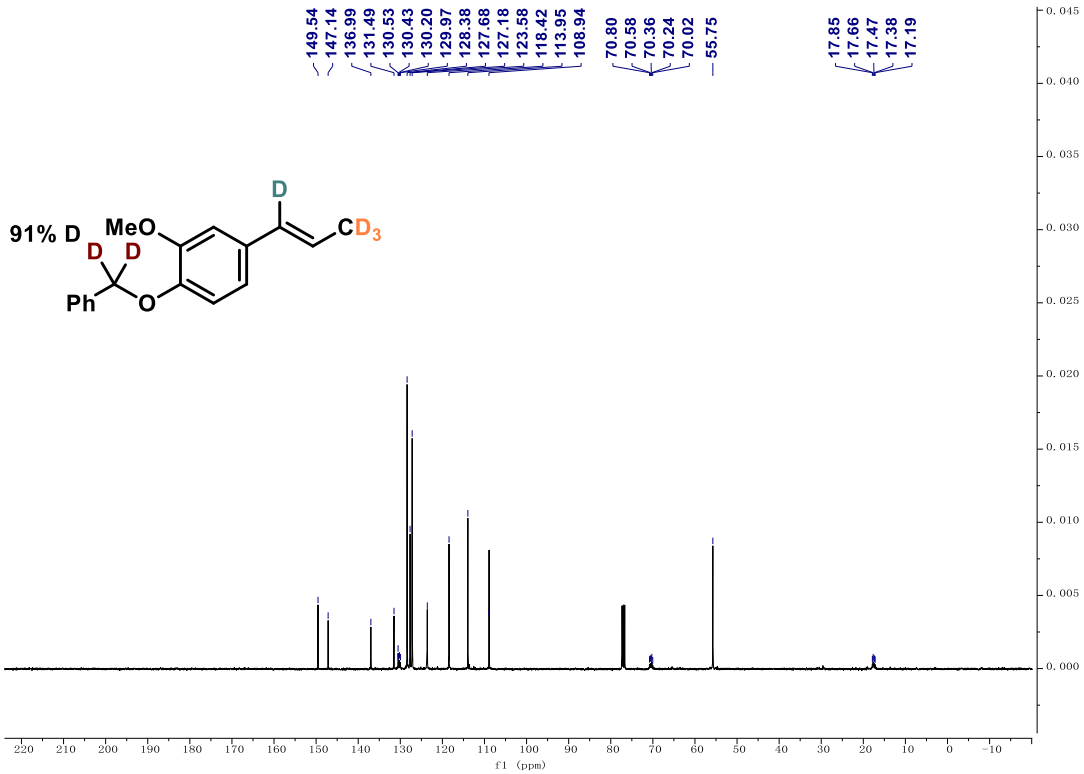
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of compound **2h**



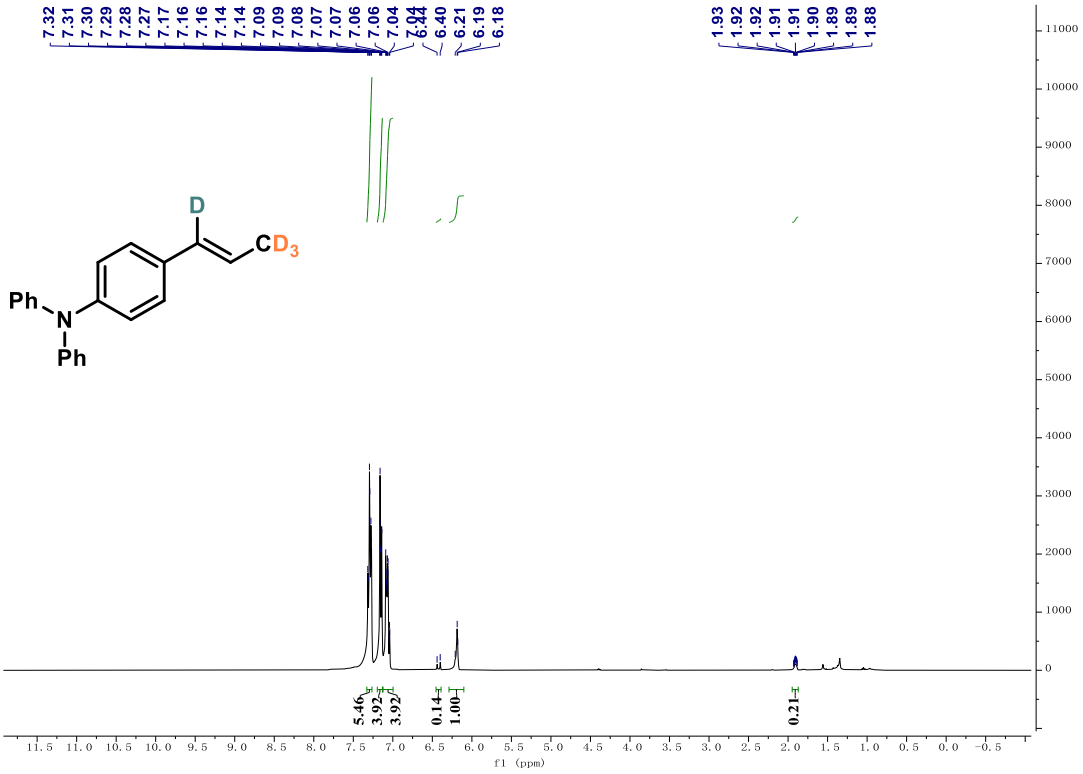
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of compound **2h**



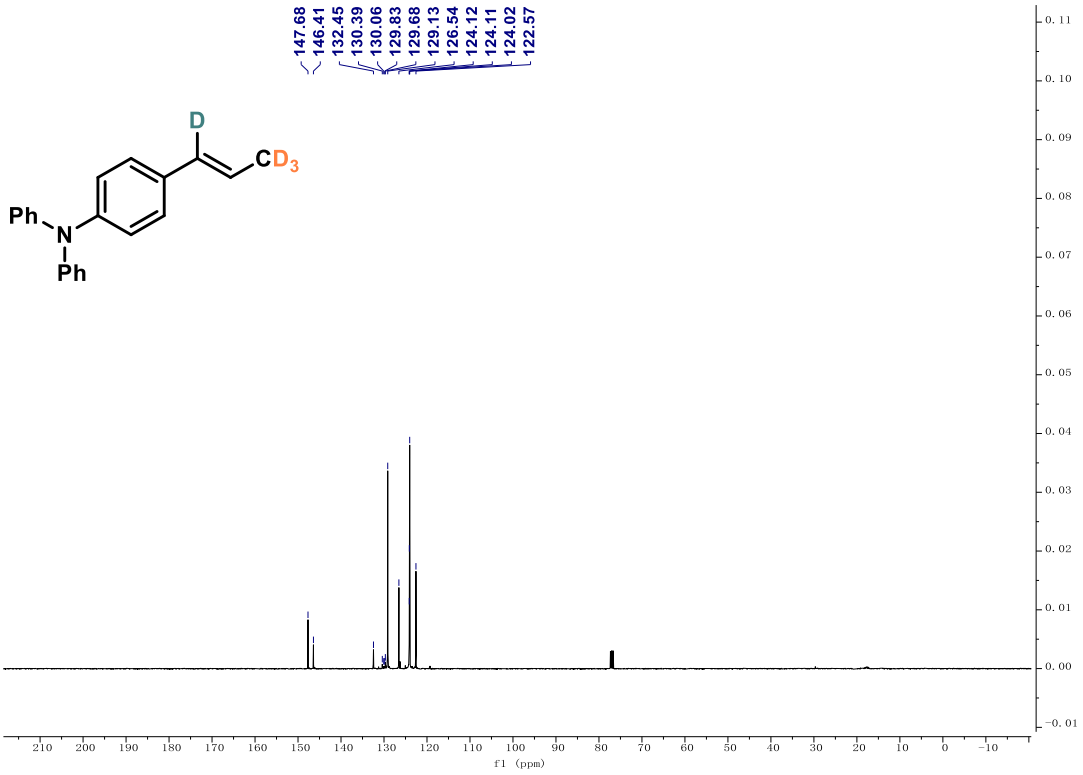
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of compound **2i**



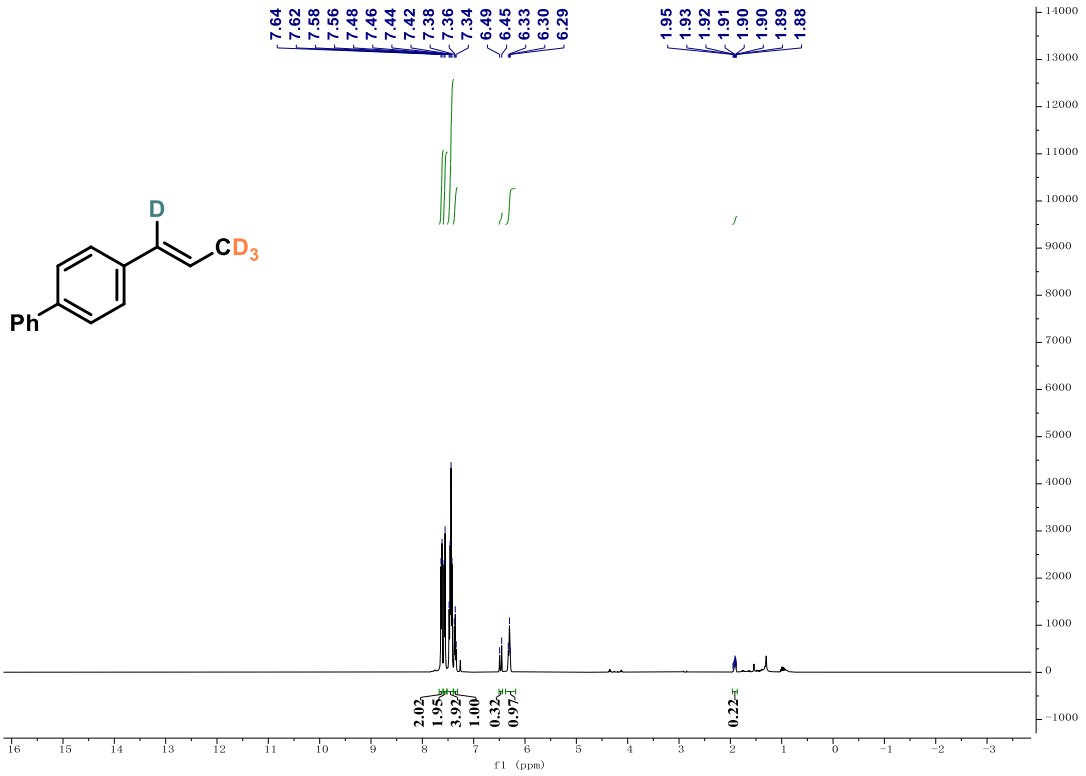
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of compound **2i**



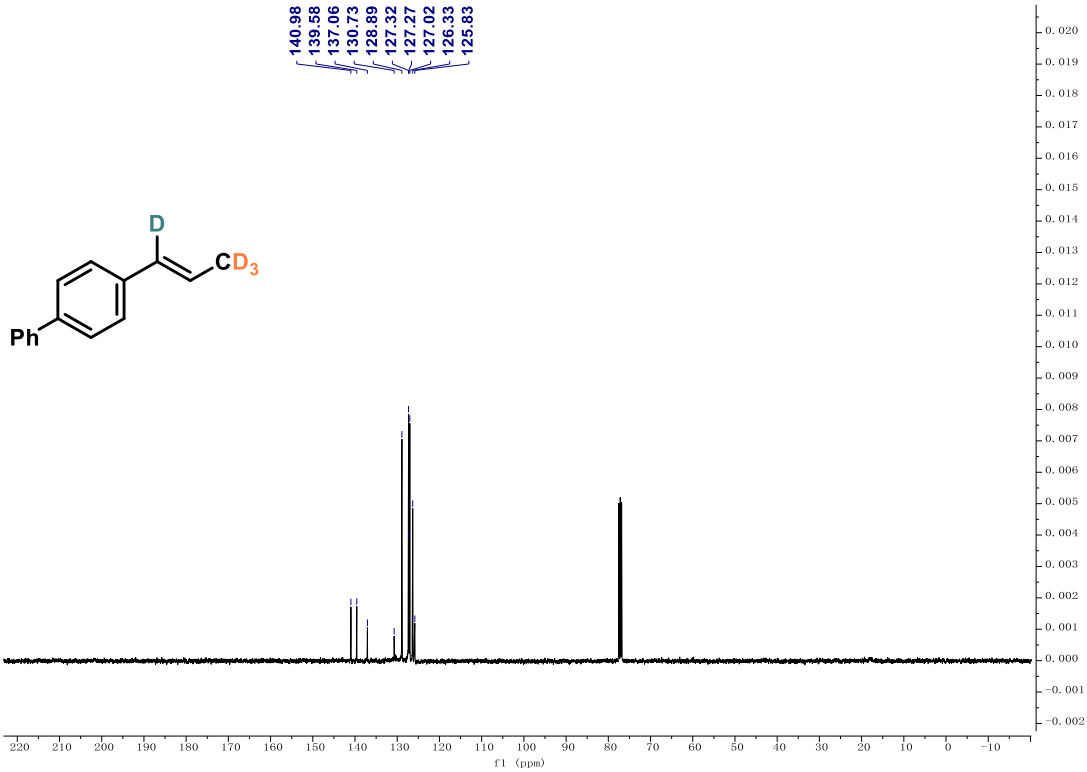
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of compound **2j**



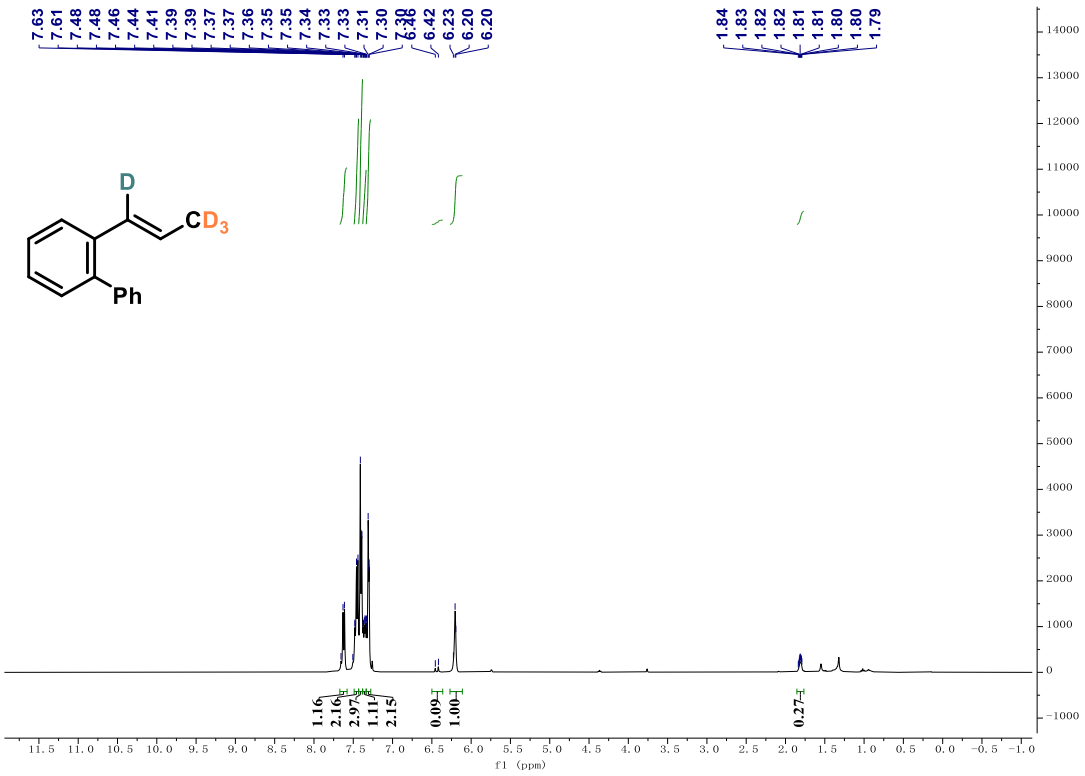
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of compound **2j**



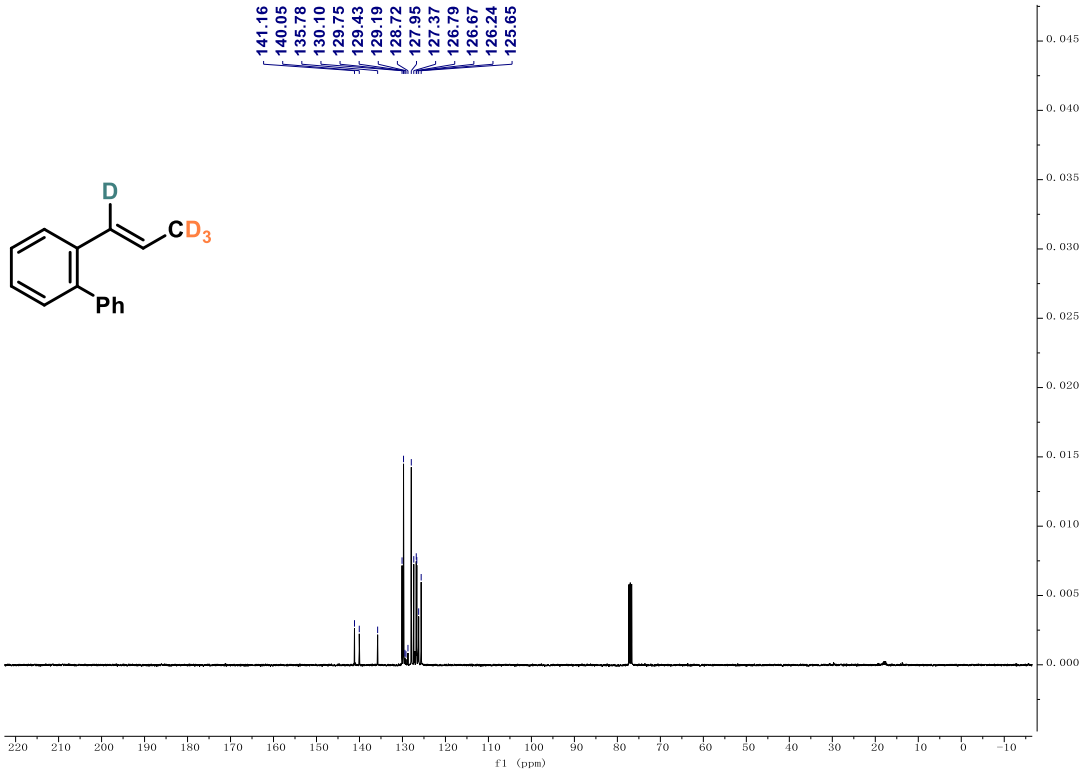
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of compound **2k**



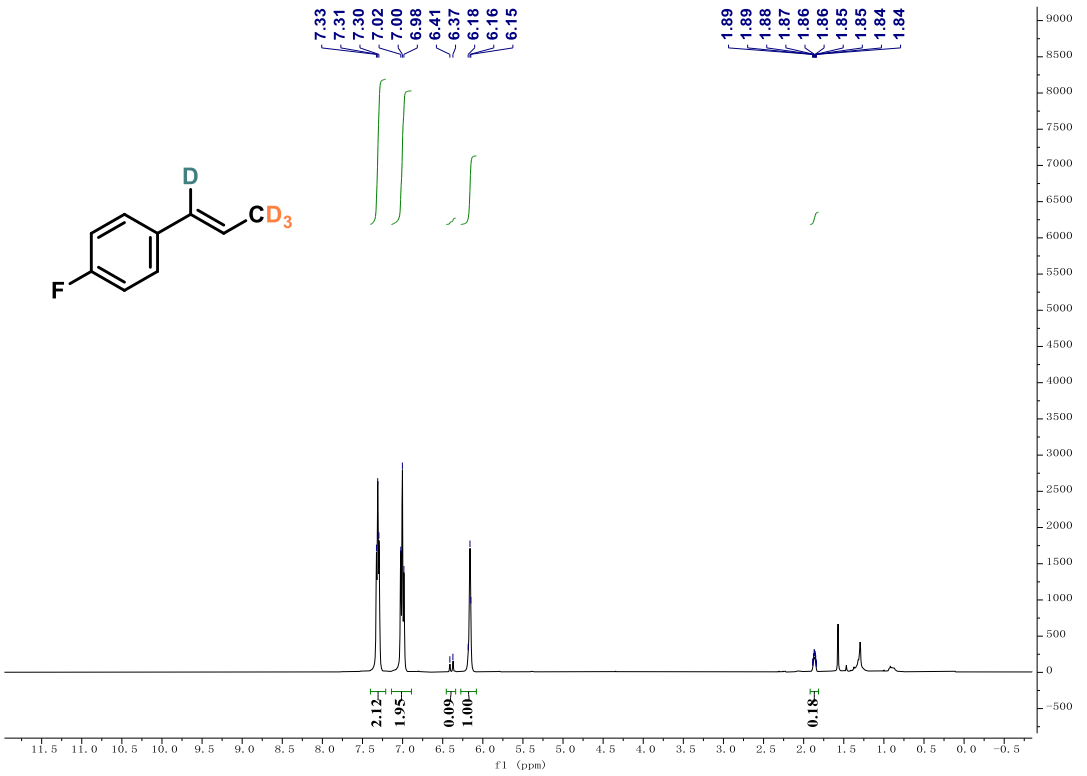
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of compound **2k**



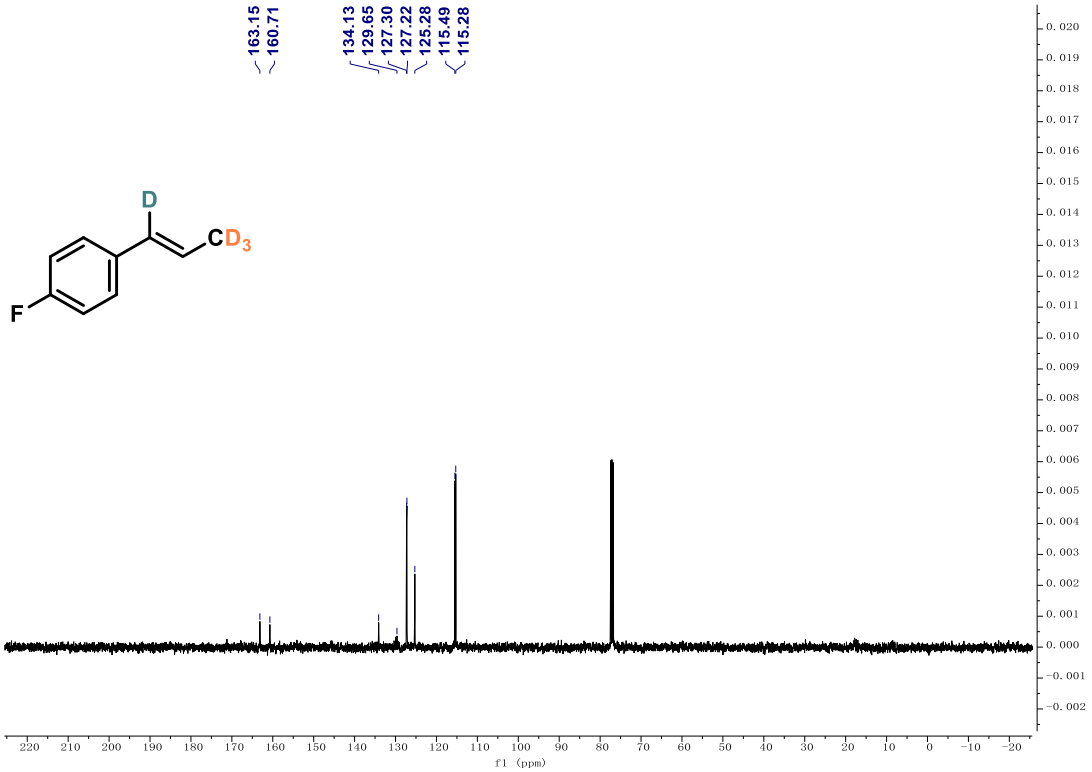
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of compound **2l**



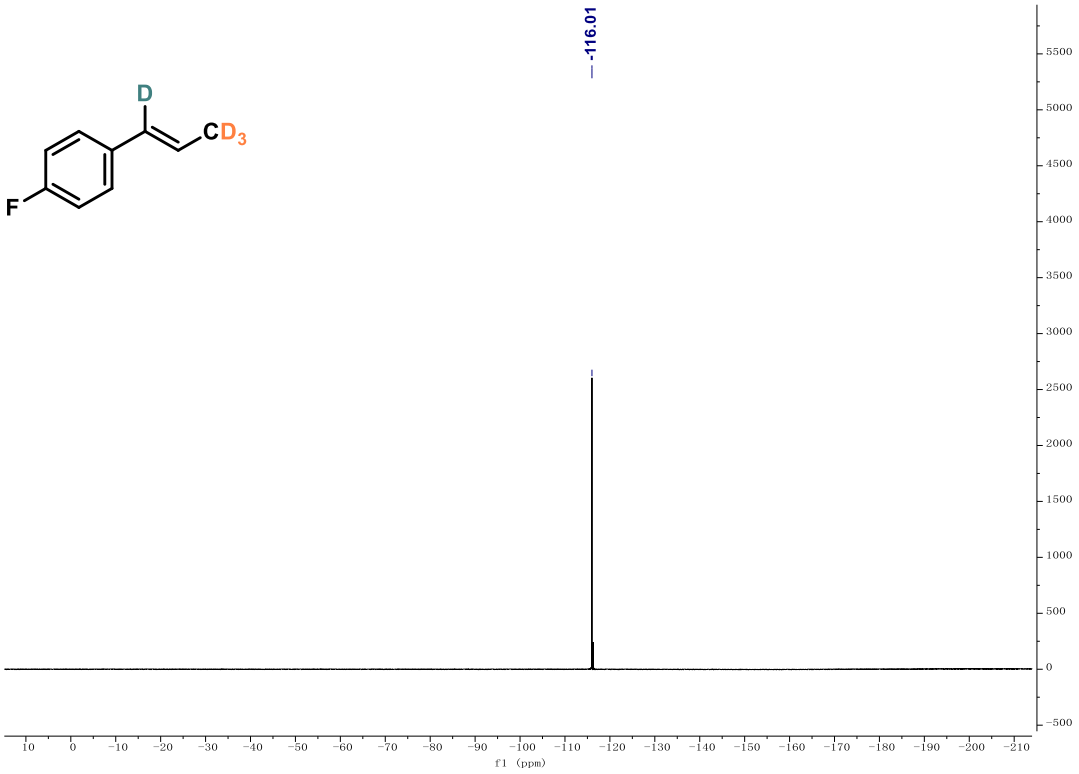
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of compound **2l**



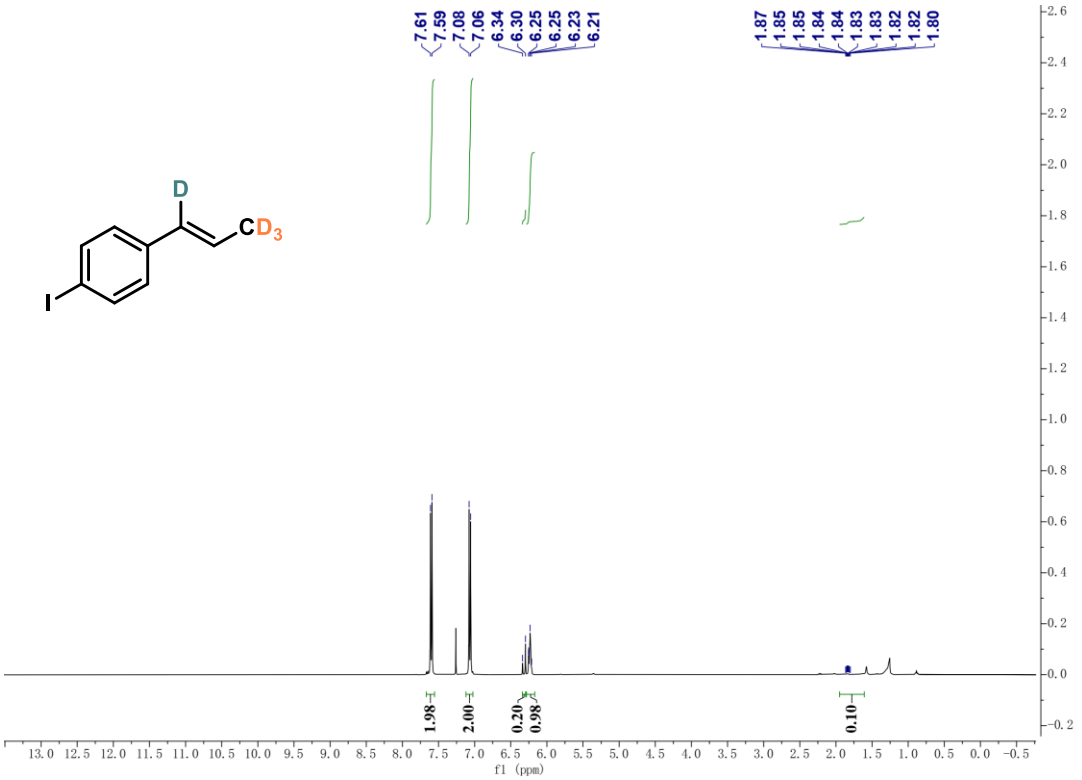
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of compound **2m**



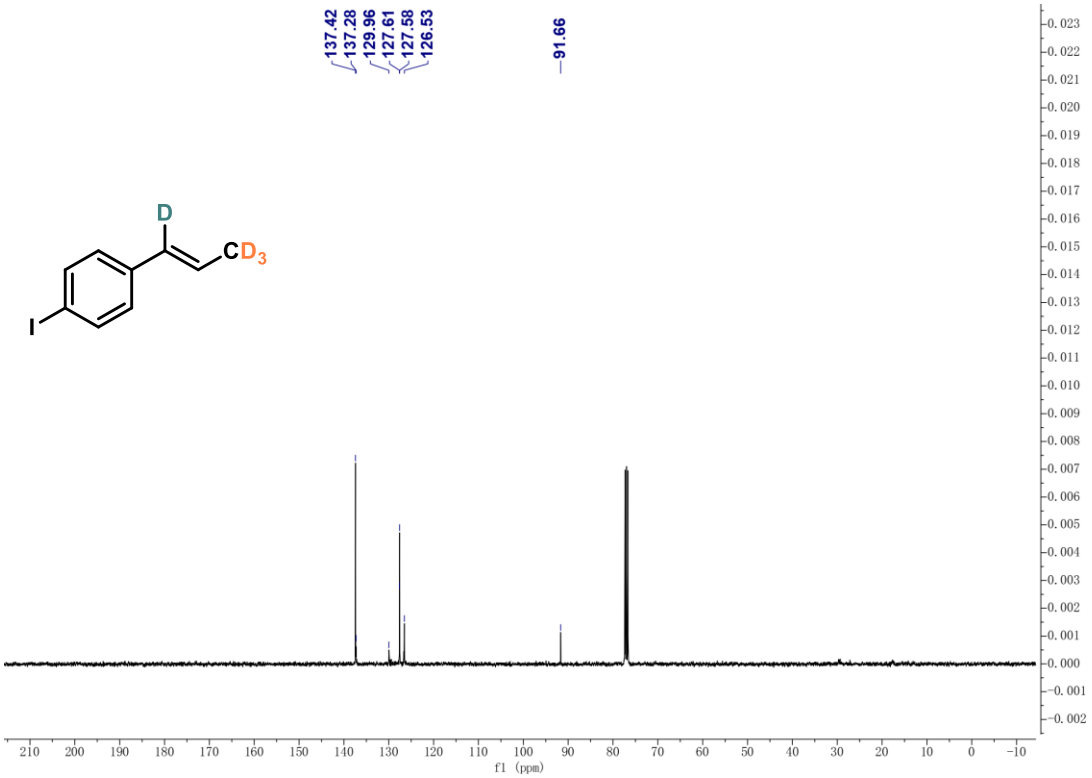
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of compound **2m**



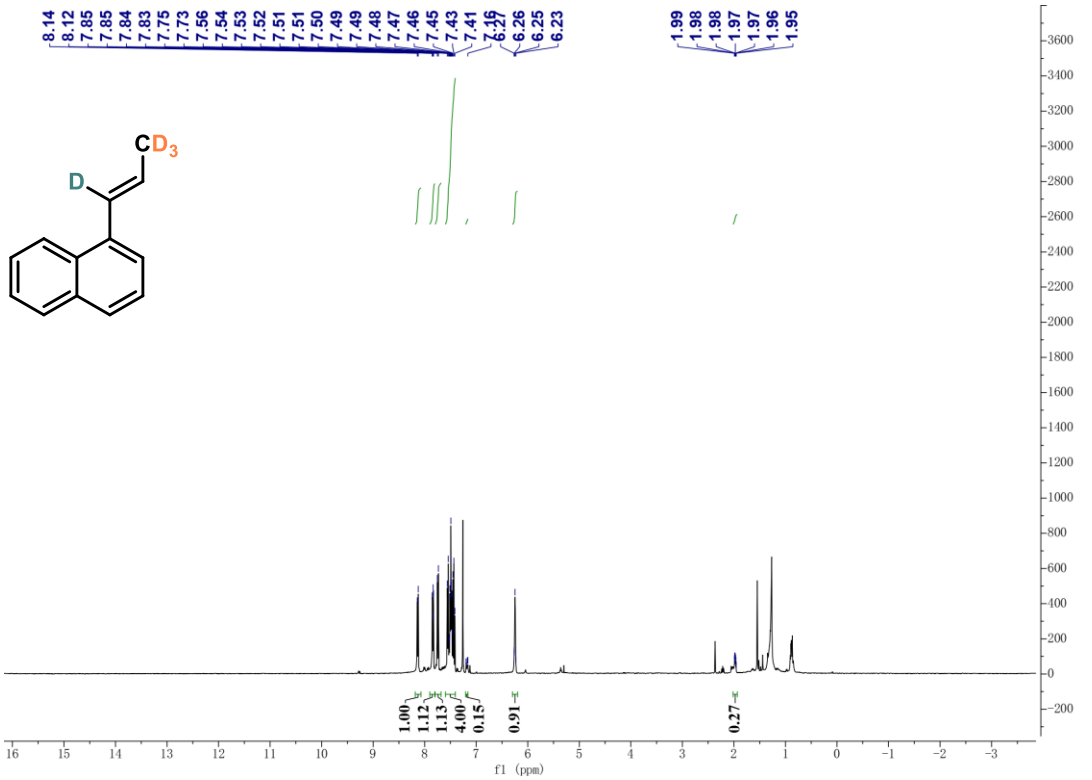
^{19}F NMR (376 MHz, $CDCl_3$) Spectrum of compound **2m**



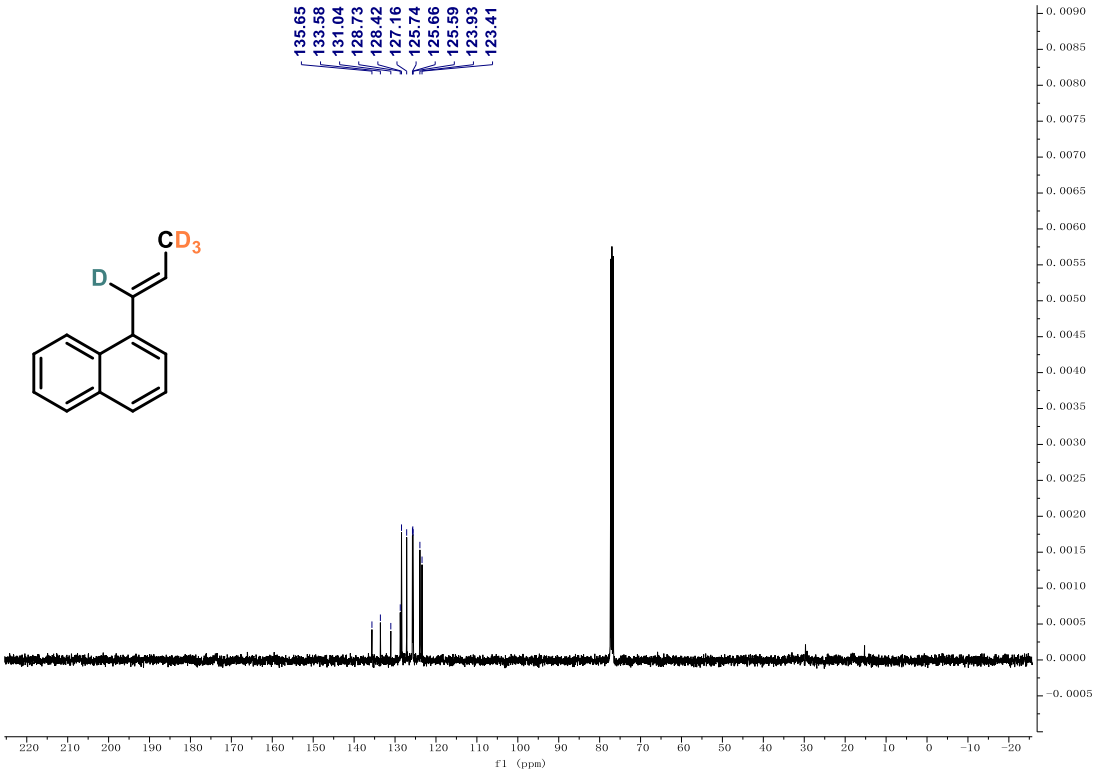
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of compound **2n**



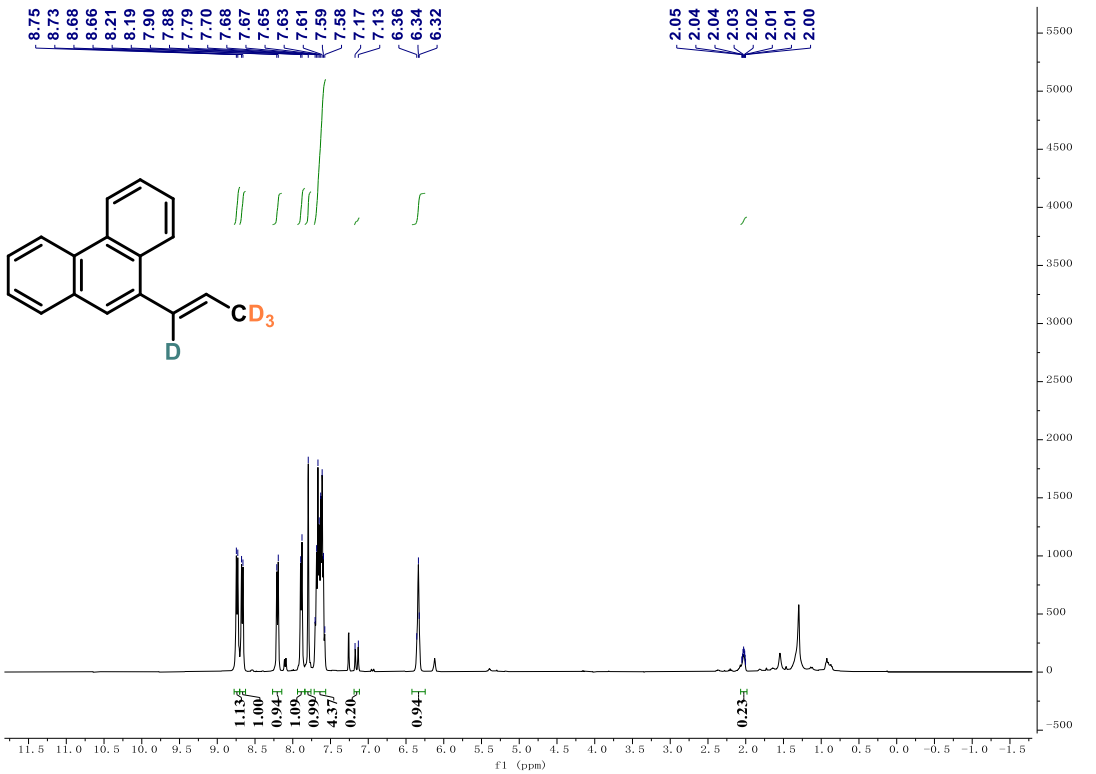
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of compound **2n**



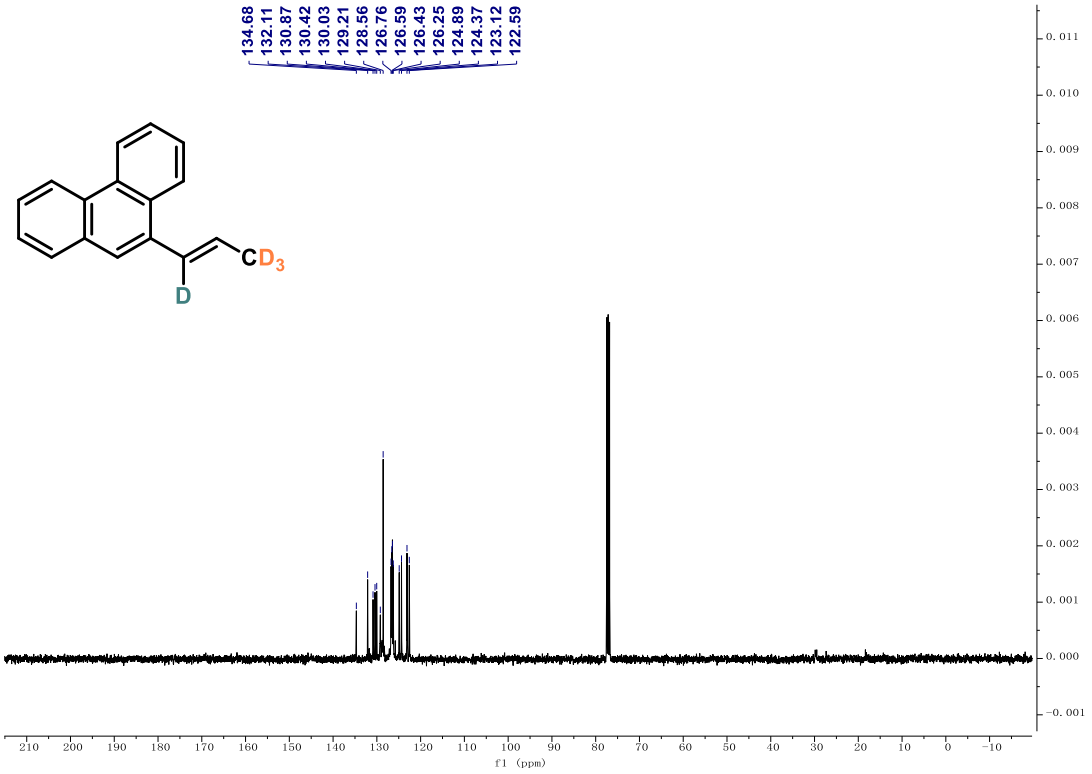
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of compound **2o**



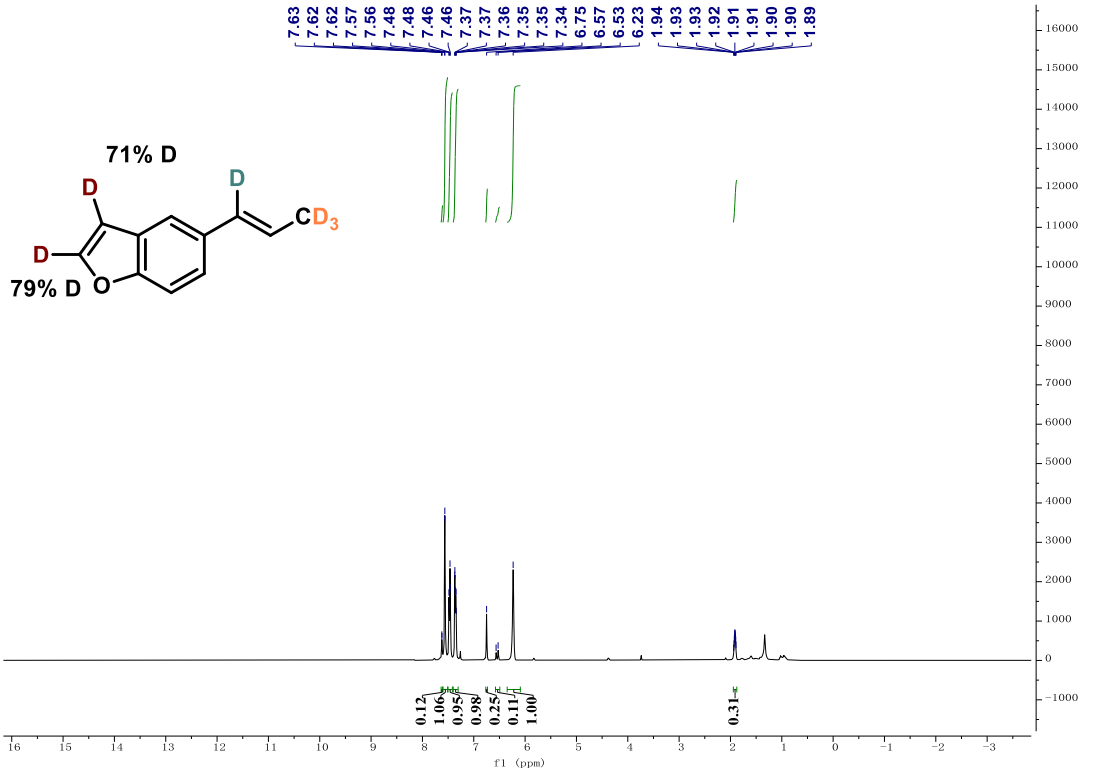
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of compound **2o**



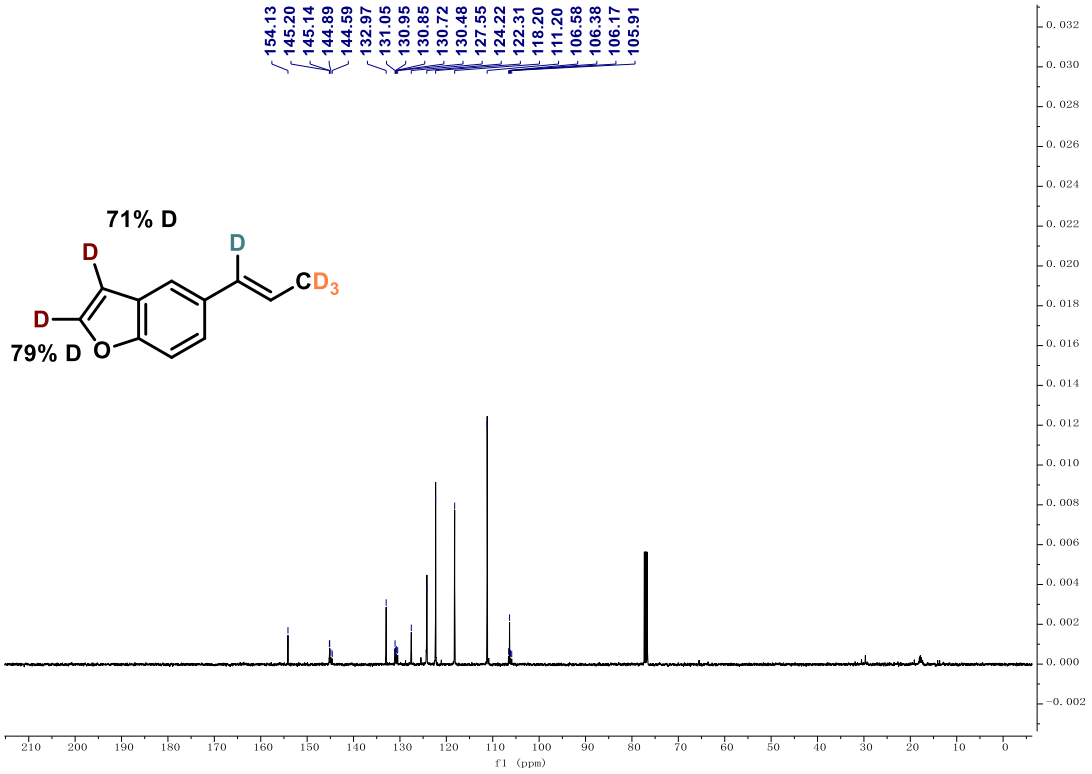
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of compound **2p**



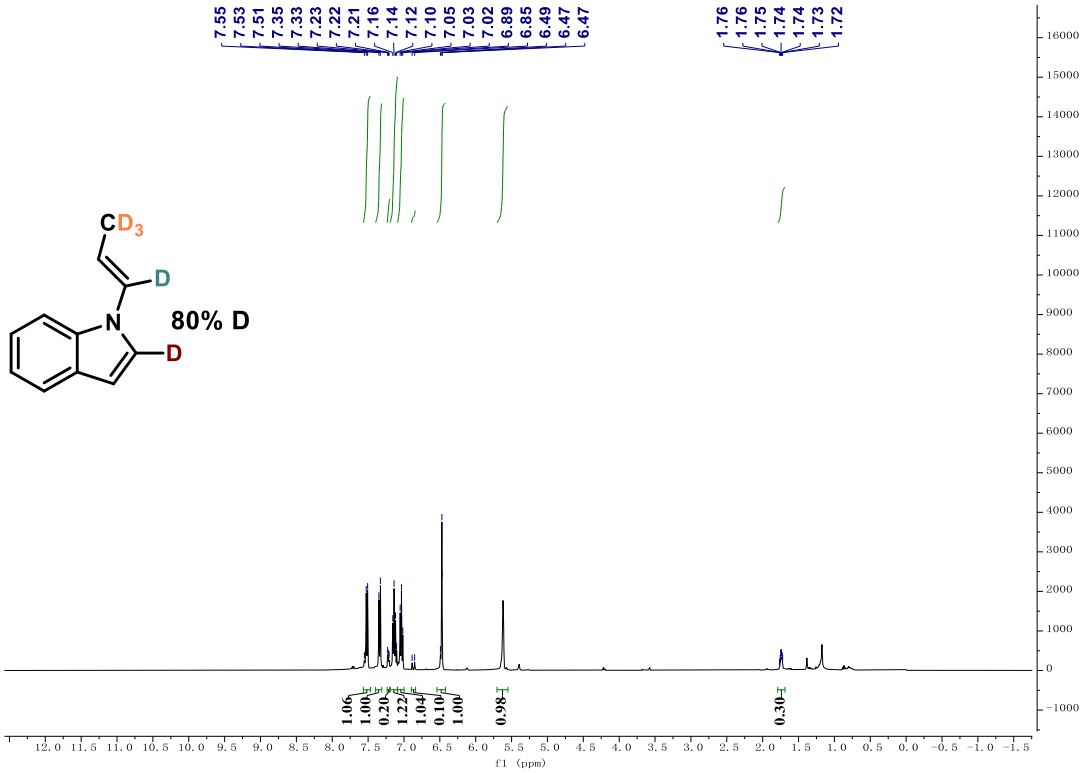
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of compound **2p**



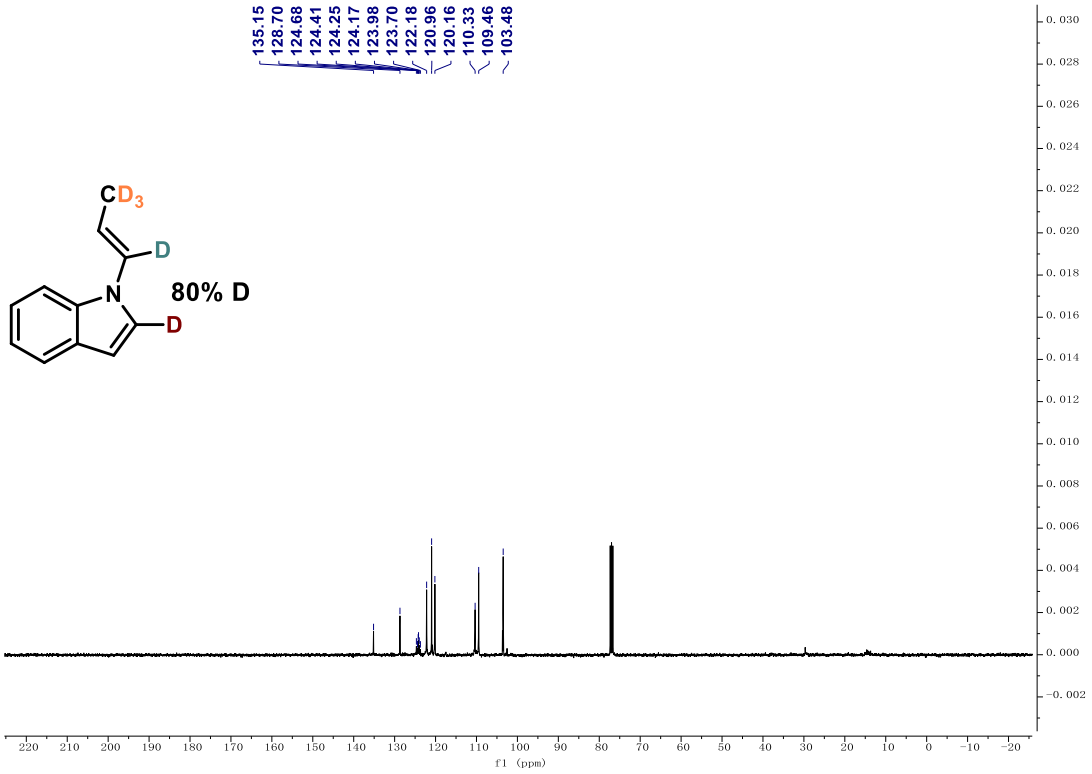
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of compound **2q**



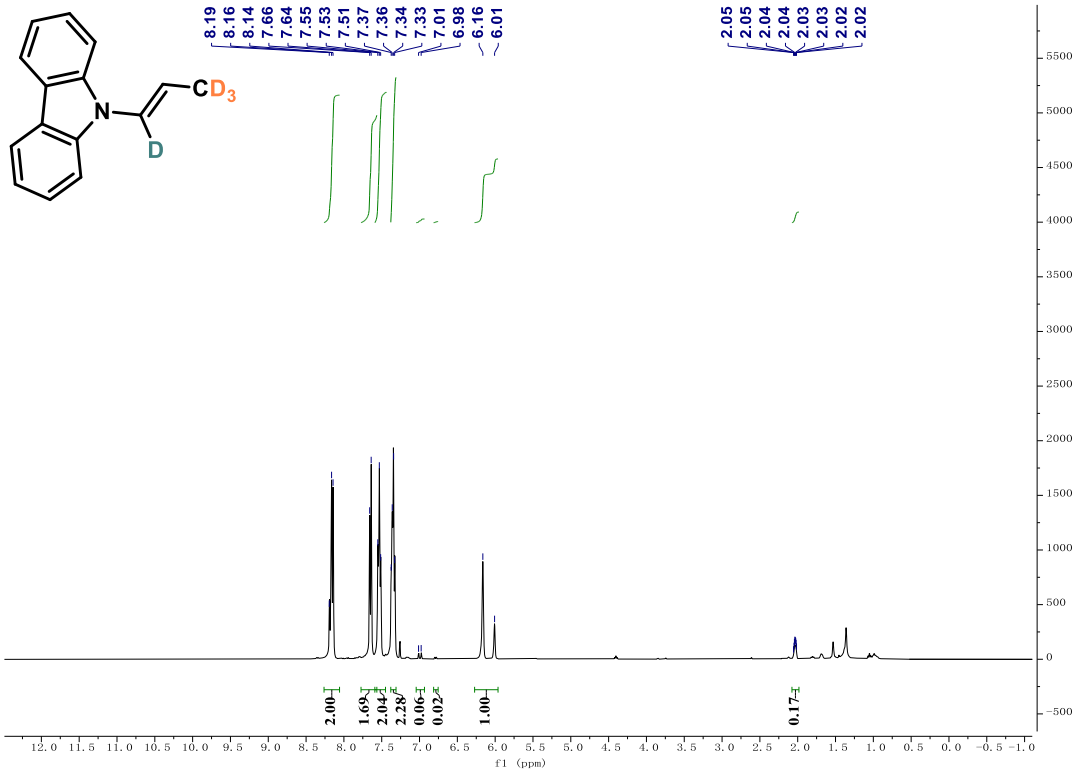
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of compound **2q**



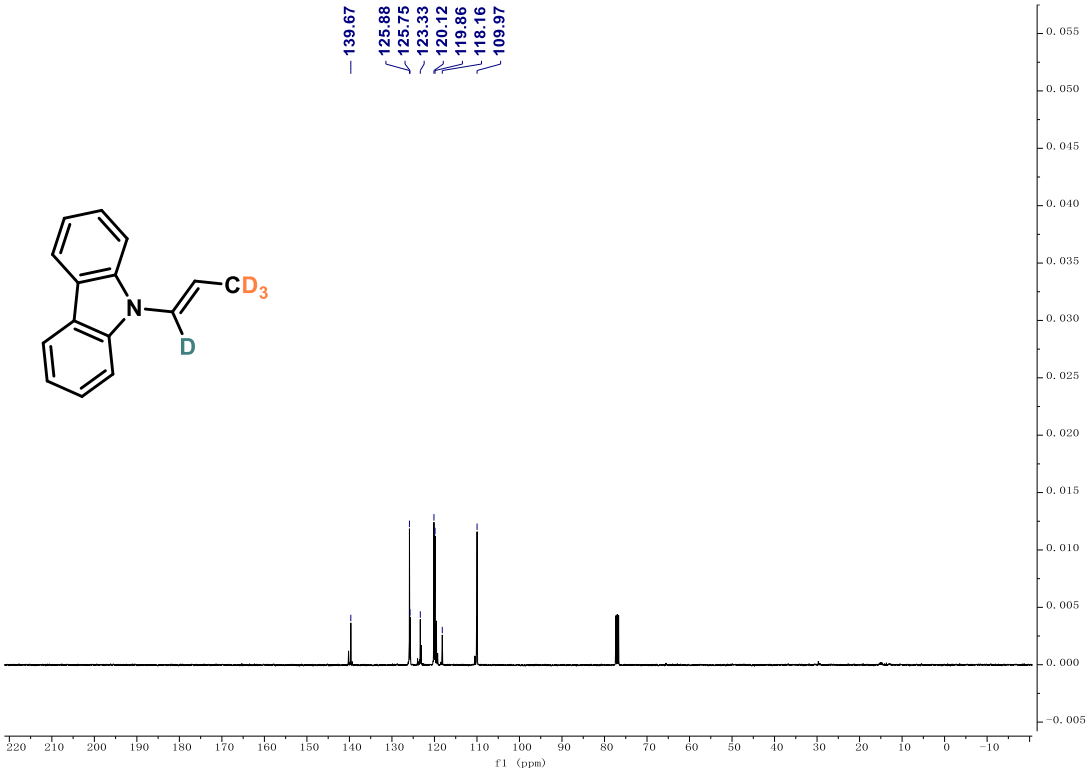
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of compound **2r**



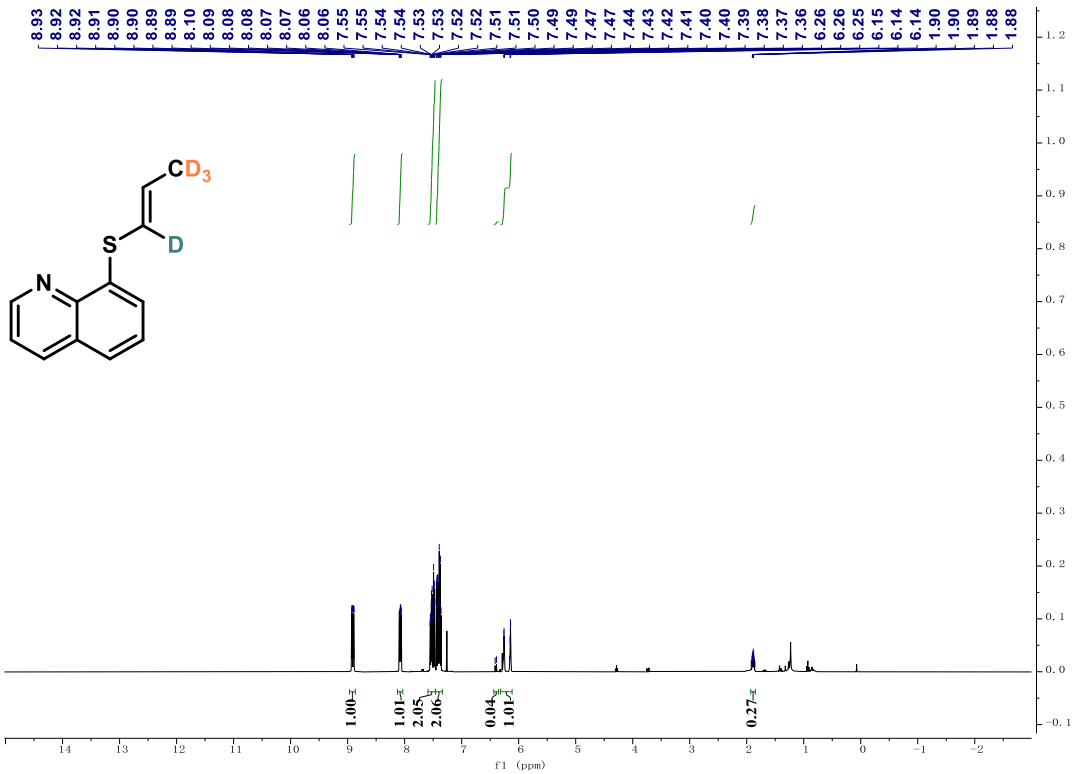
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of compound **2r**



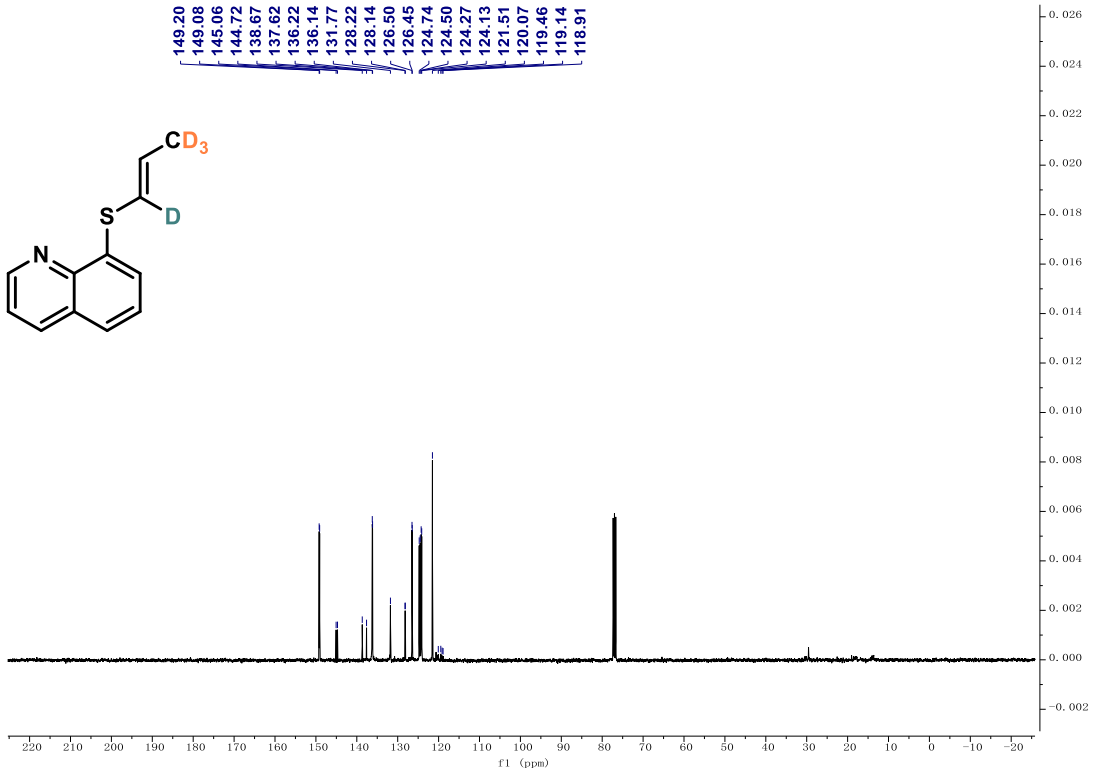
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of compound **2s**



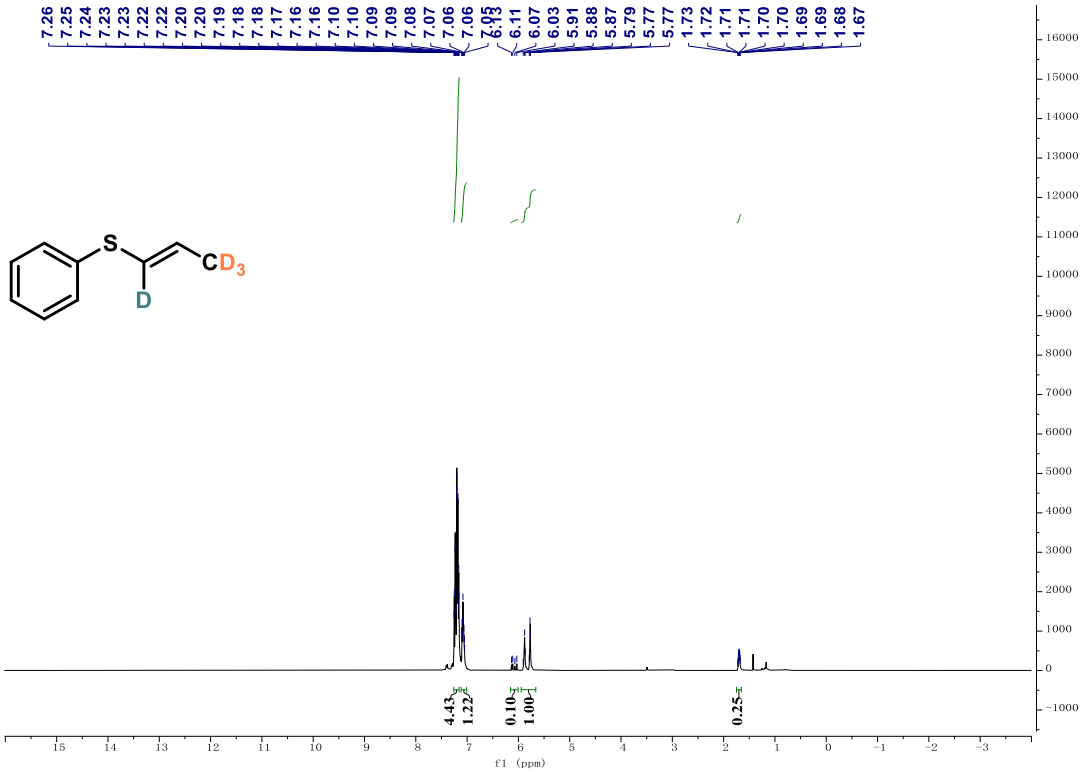
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of compound **2s**



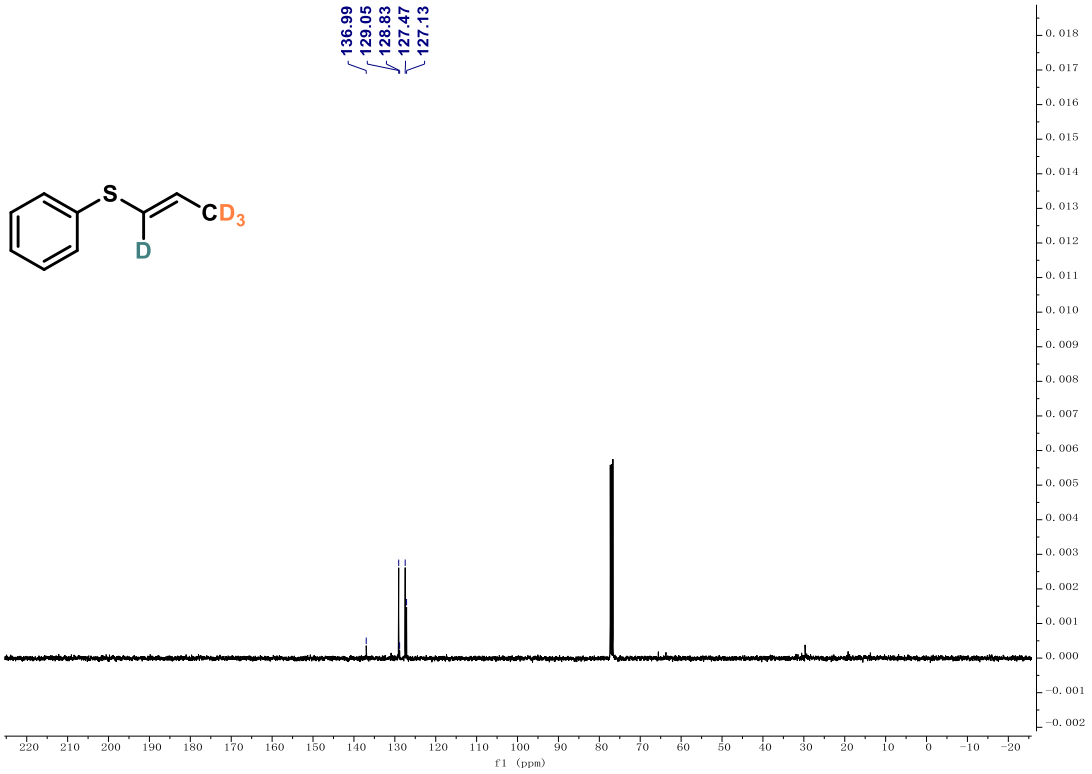
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of compound **2t**



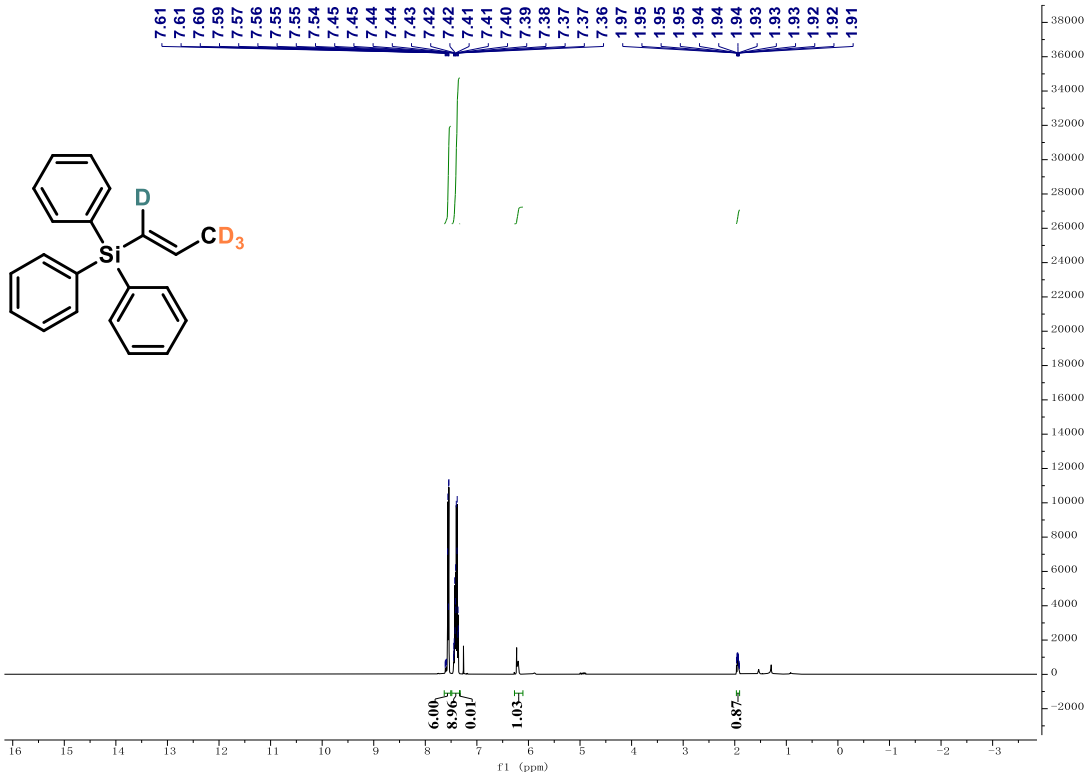
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of compound **2t**



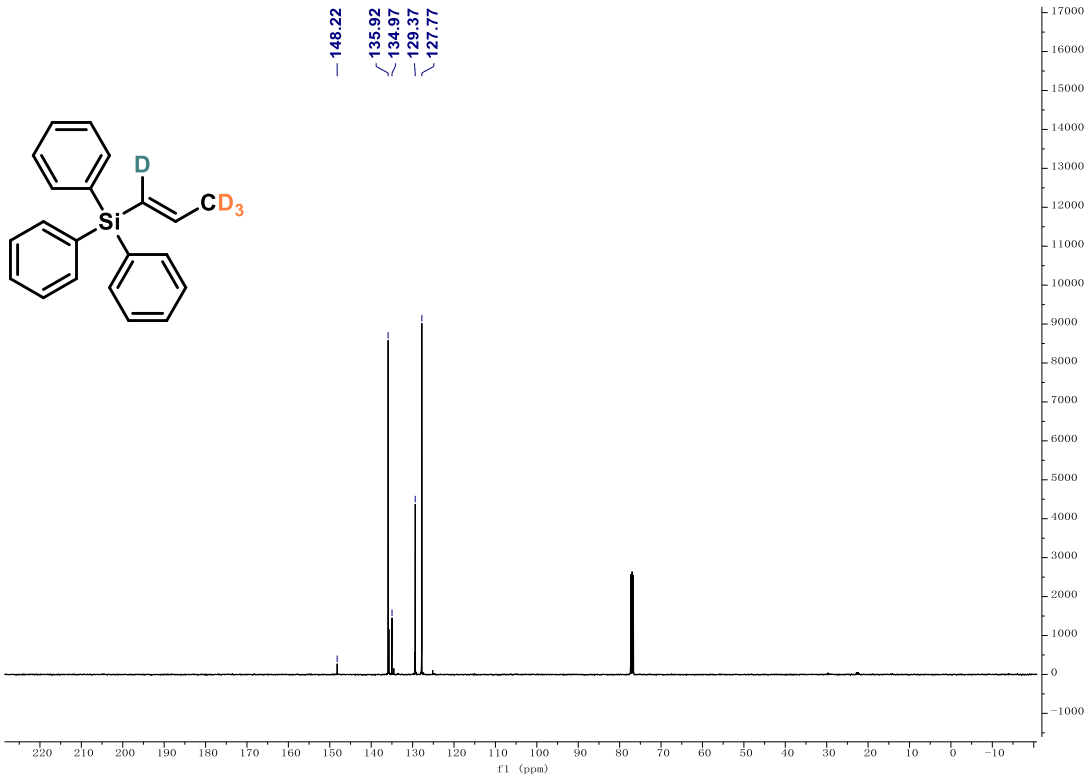
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of compound **2u**



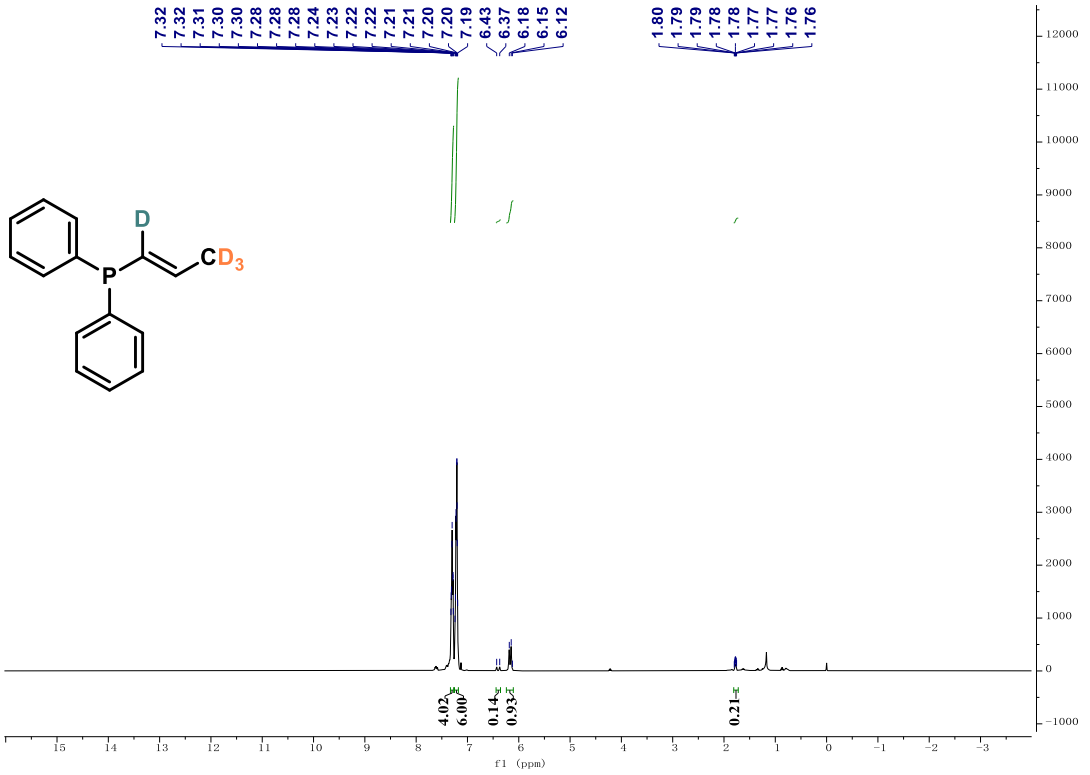
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of compound **2u**



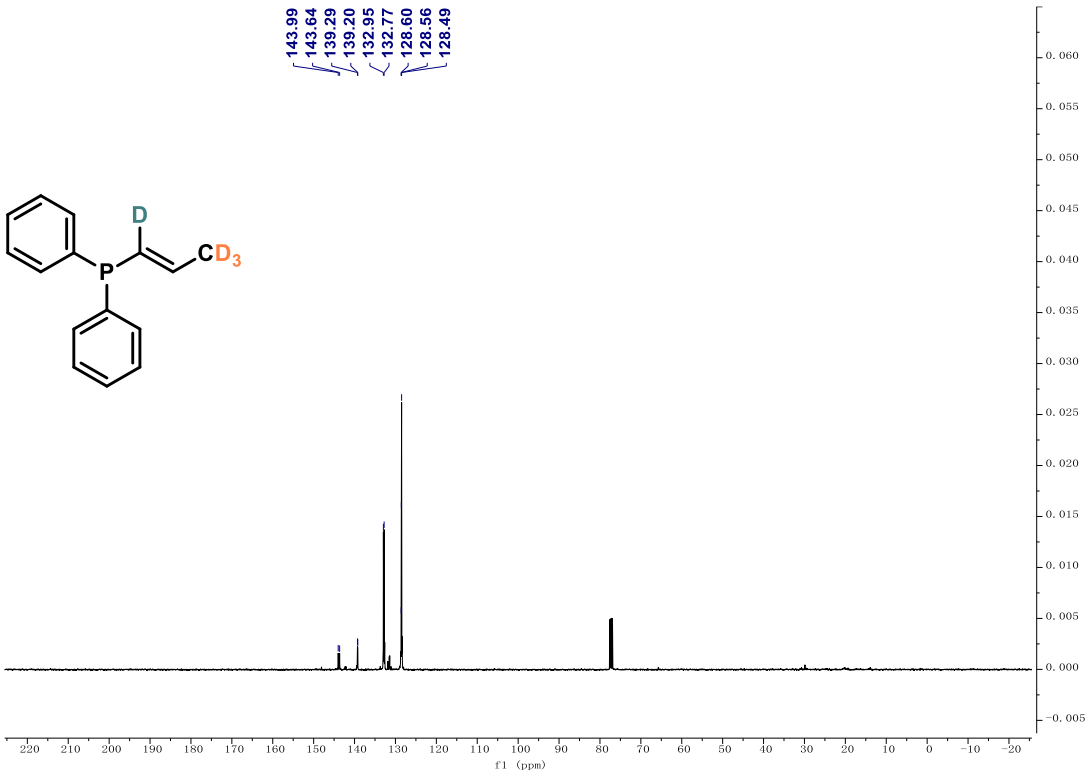
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of compound **2v**



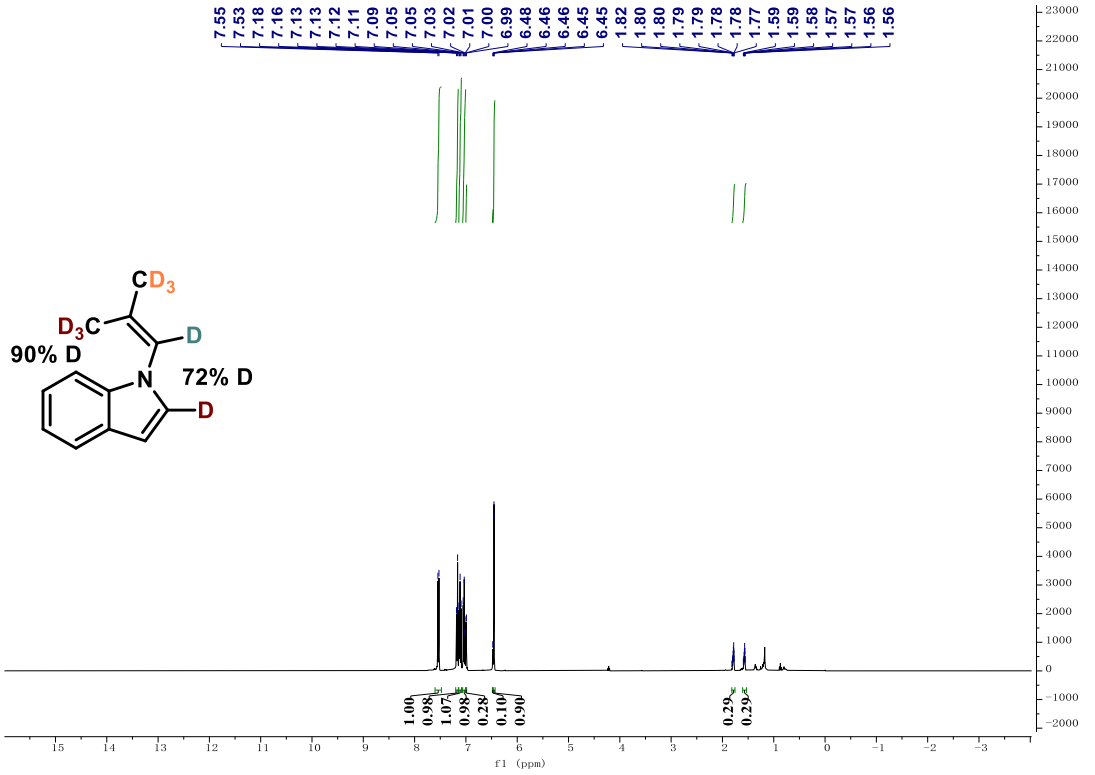
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of compound **2v**



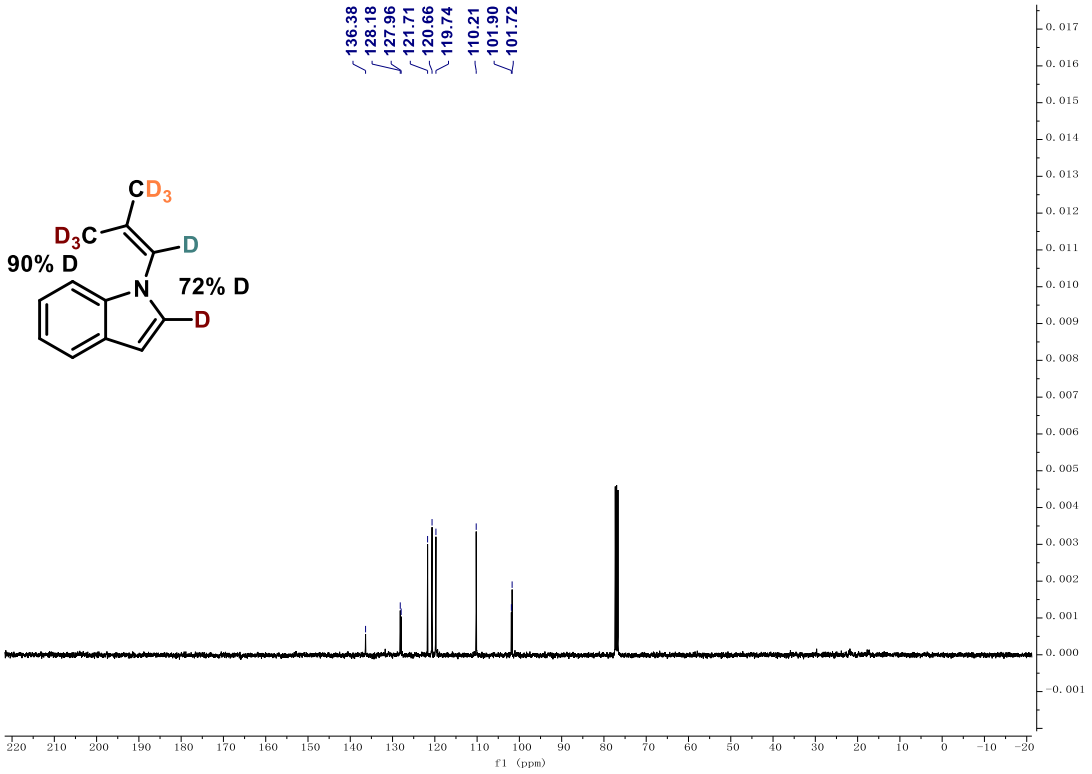
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of compound **2w**



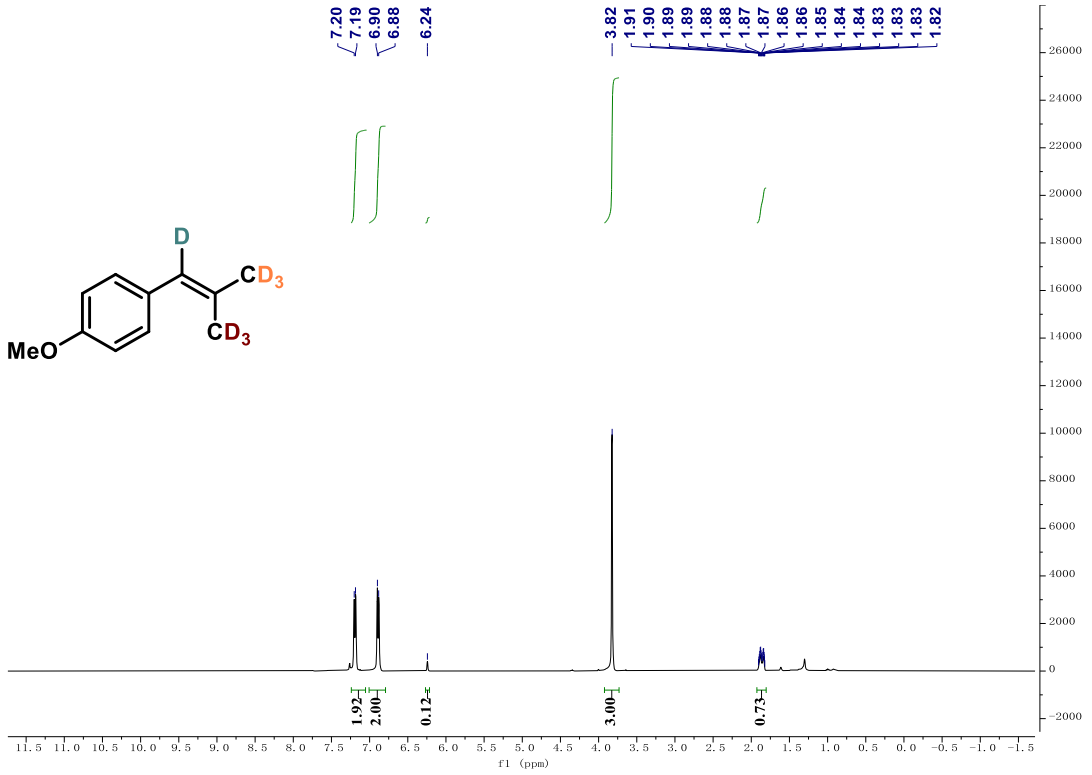
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of compound **2w**



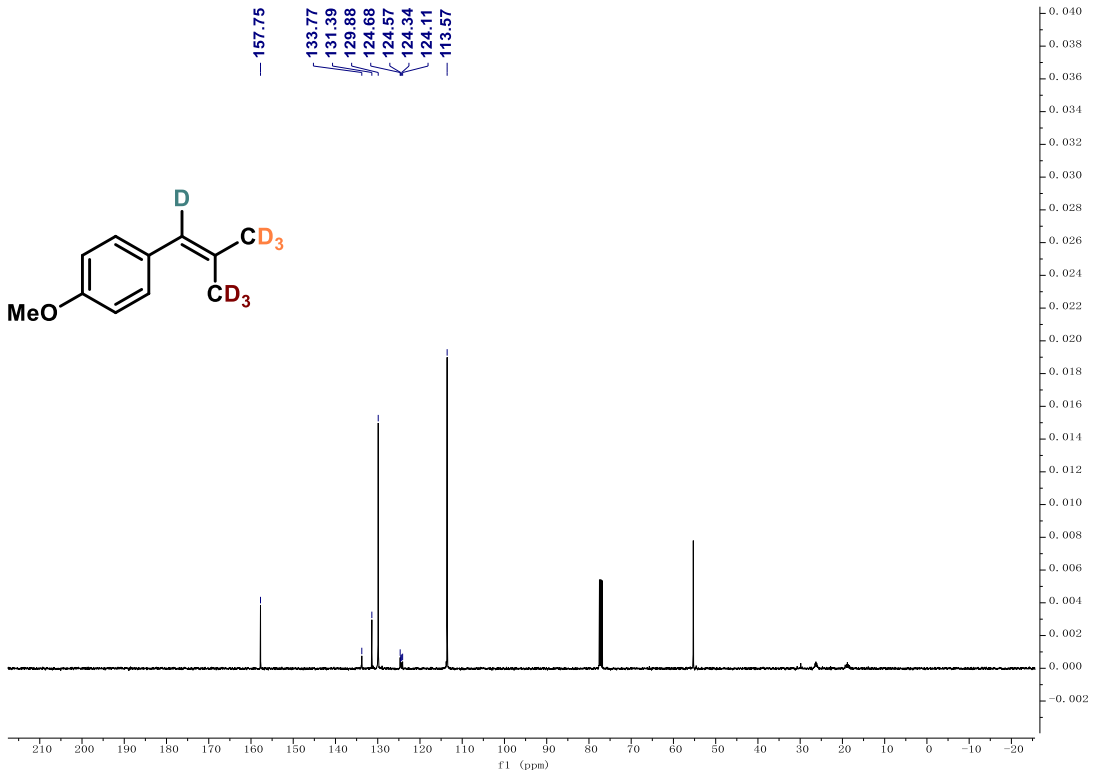
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of compound **2x**



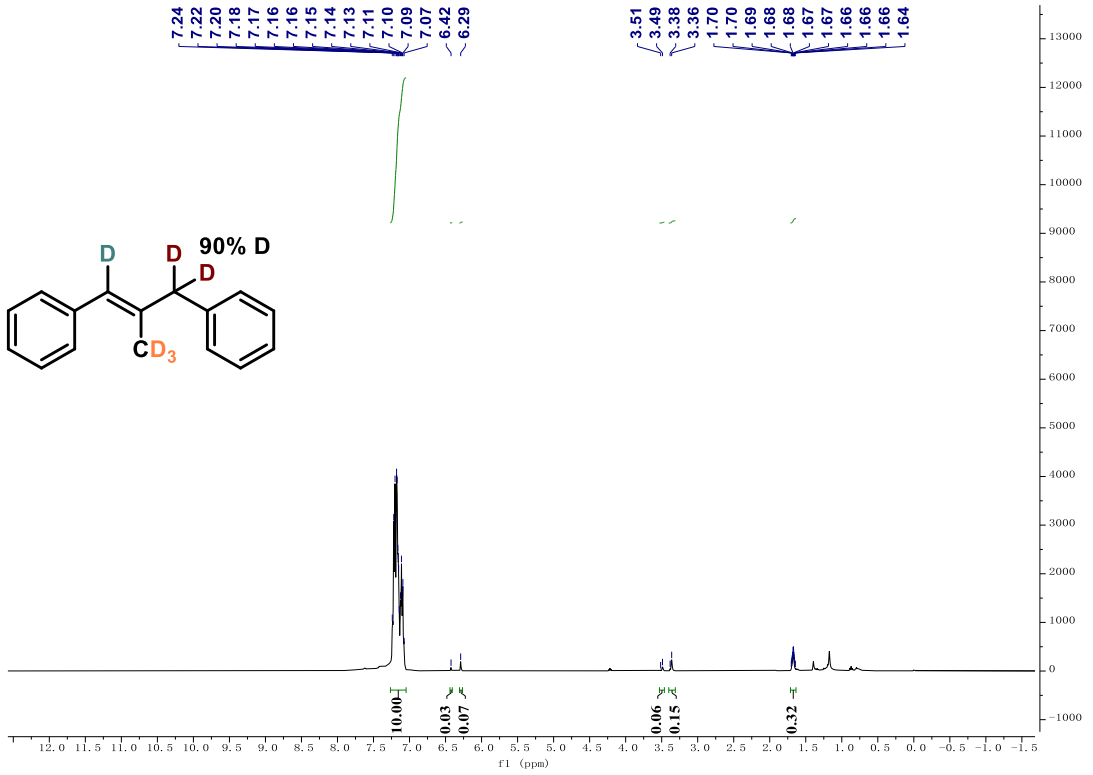
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of compound **2x**



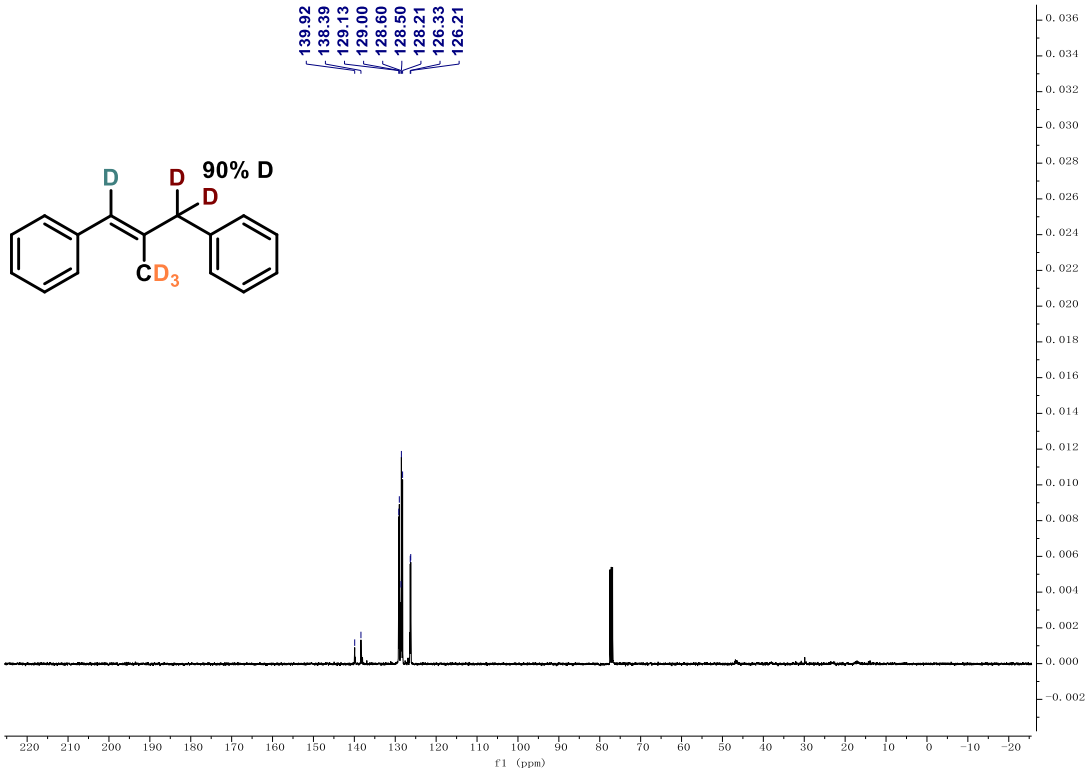
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of compound **2y**



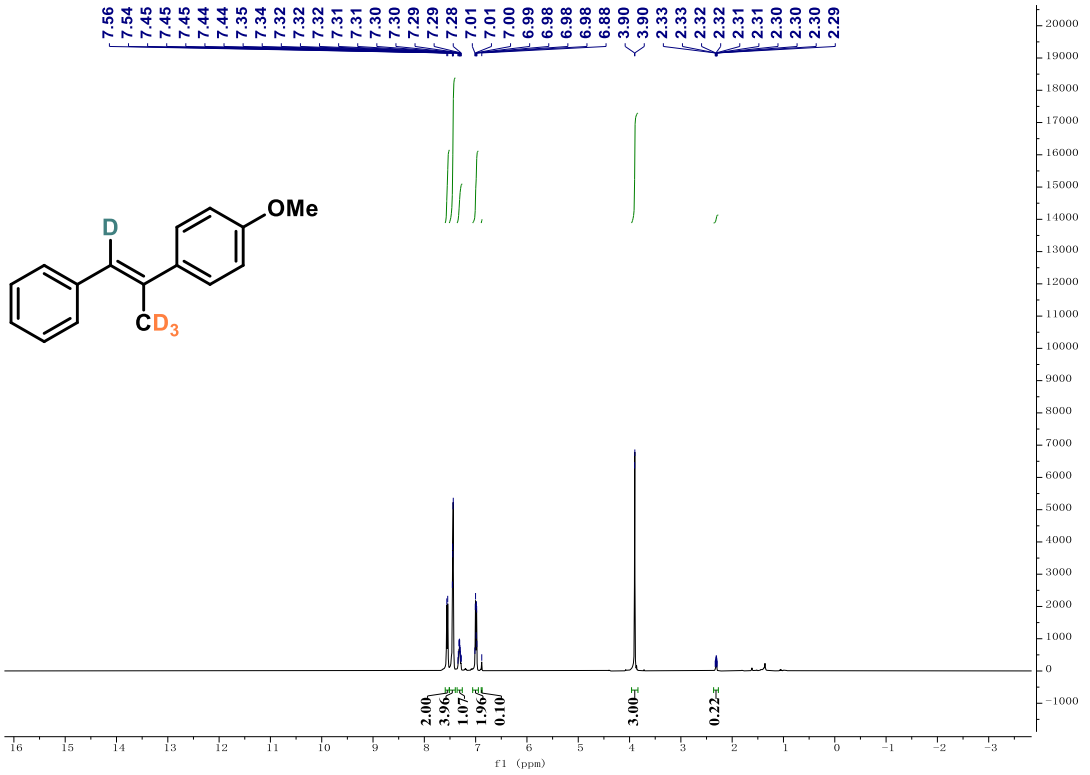
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of compound **2y**



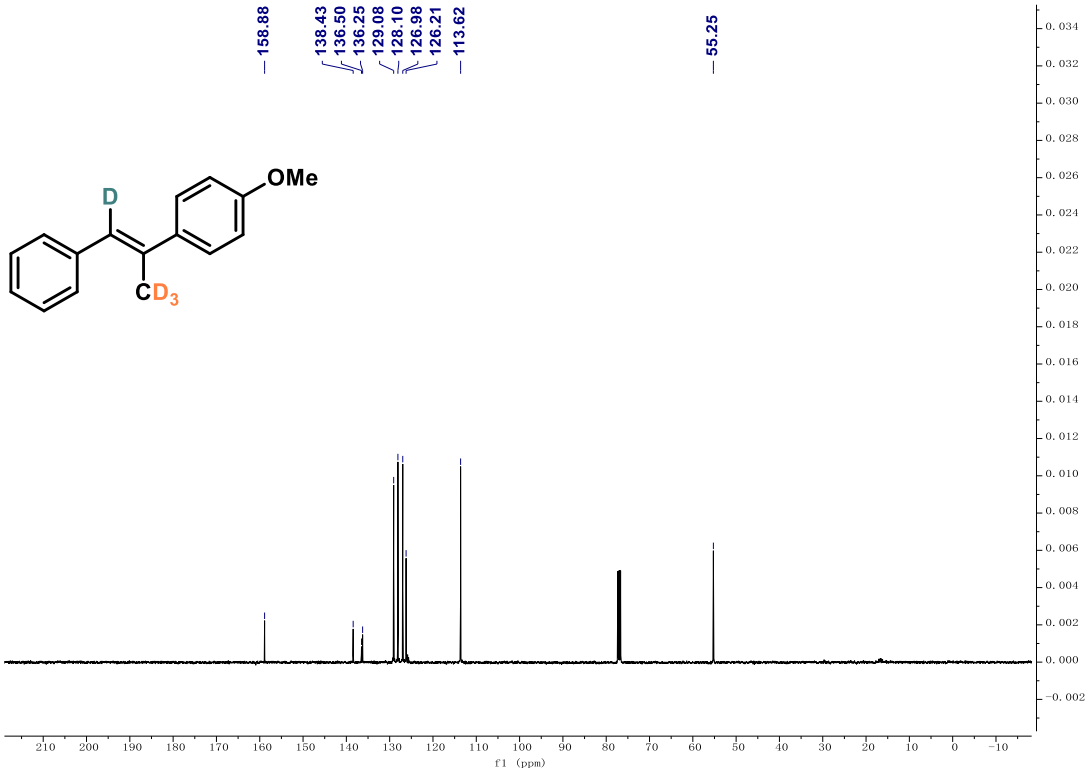
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of compound **2z**



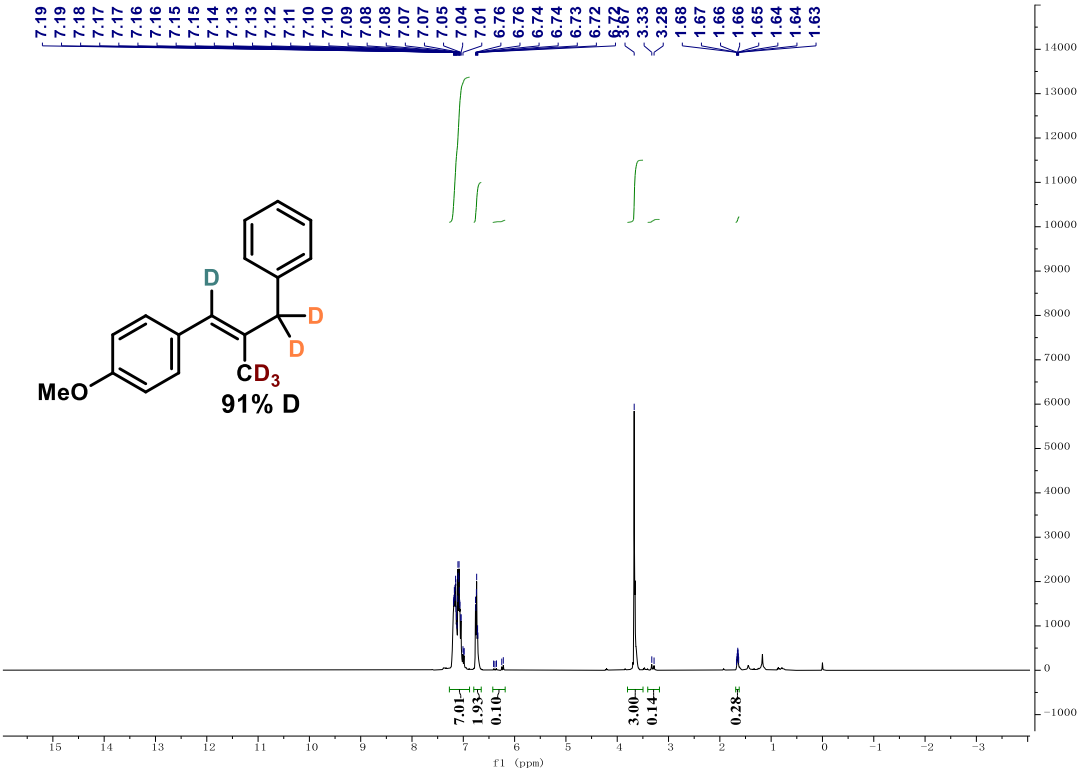
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of compound **2z**



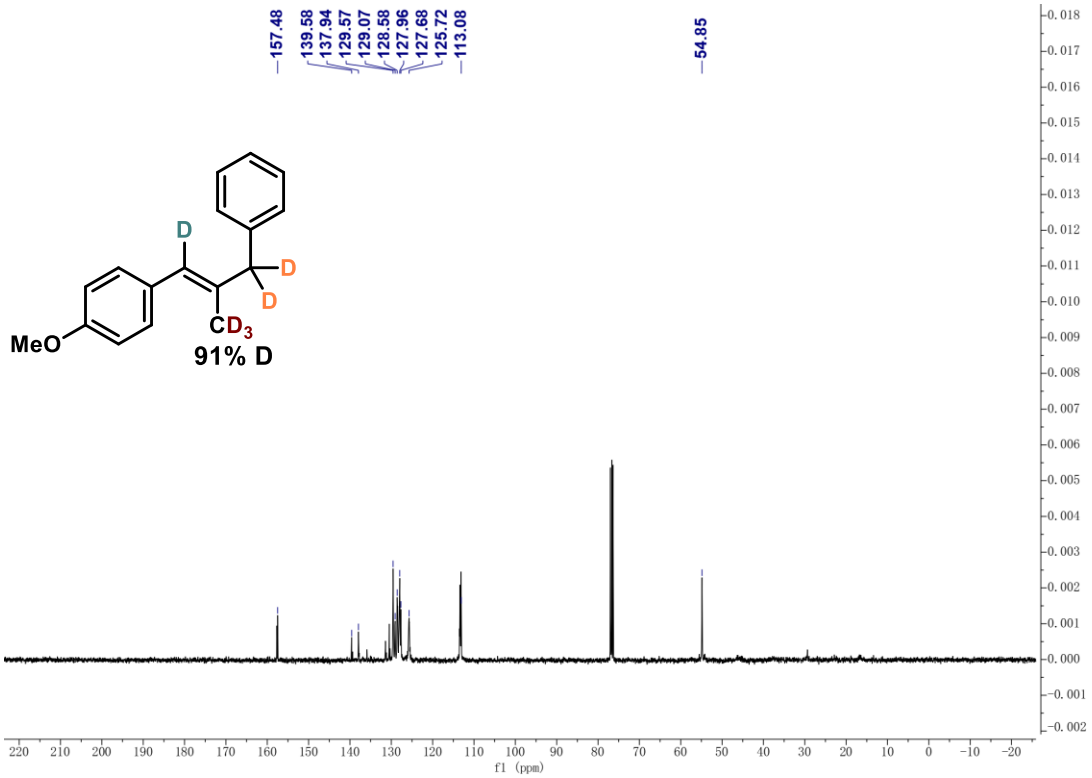
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of compound **3a**



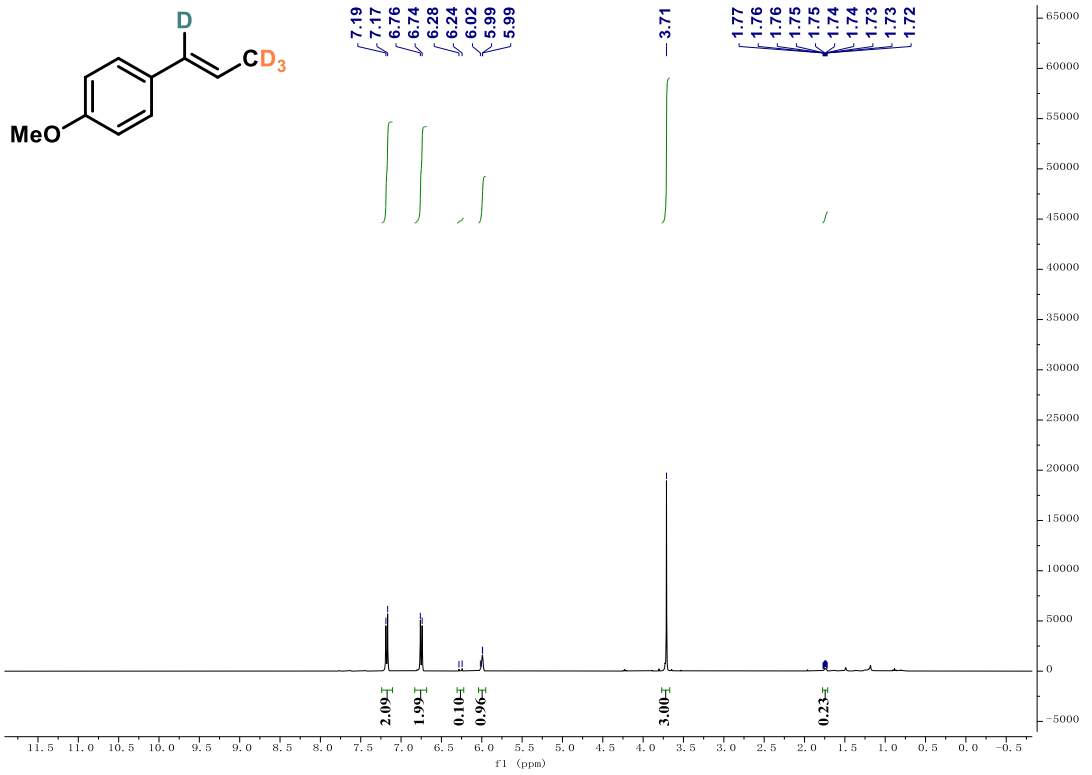
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of compound **3a**



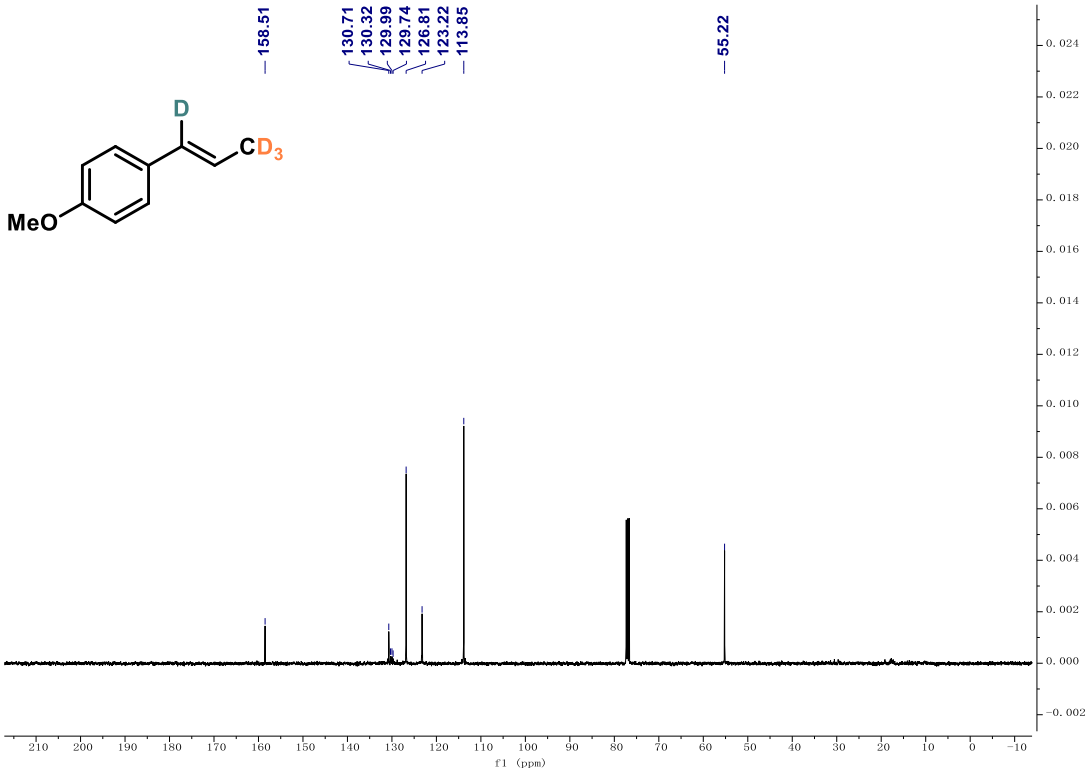
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of compound **3b**



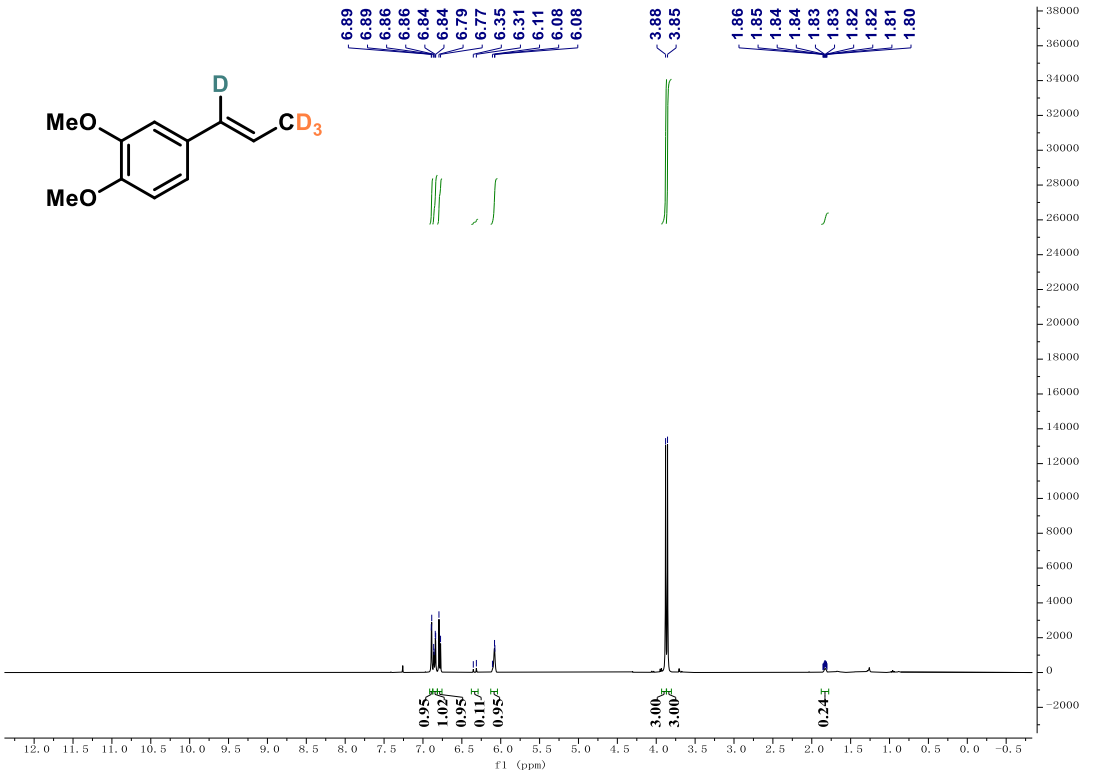
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of compound **3b**



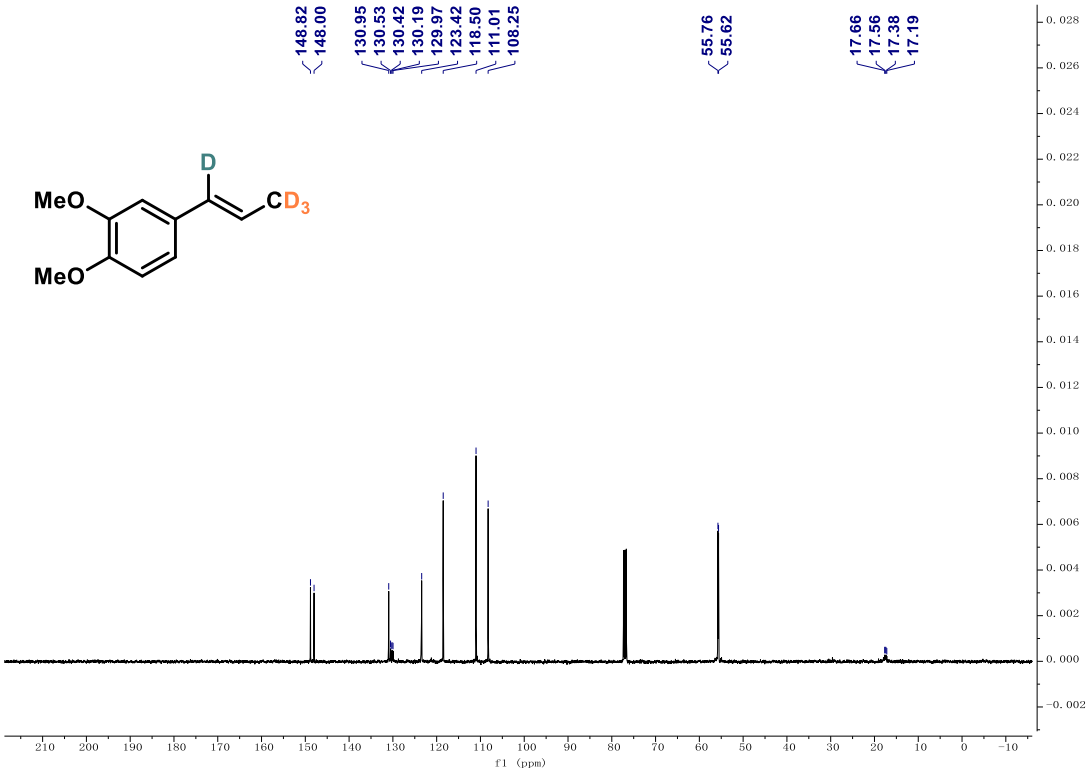
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of compound **2a**



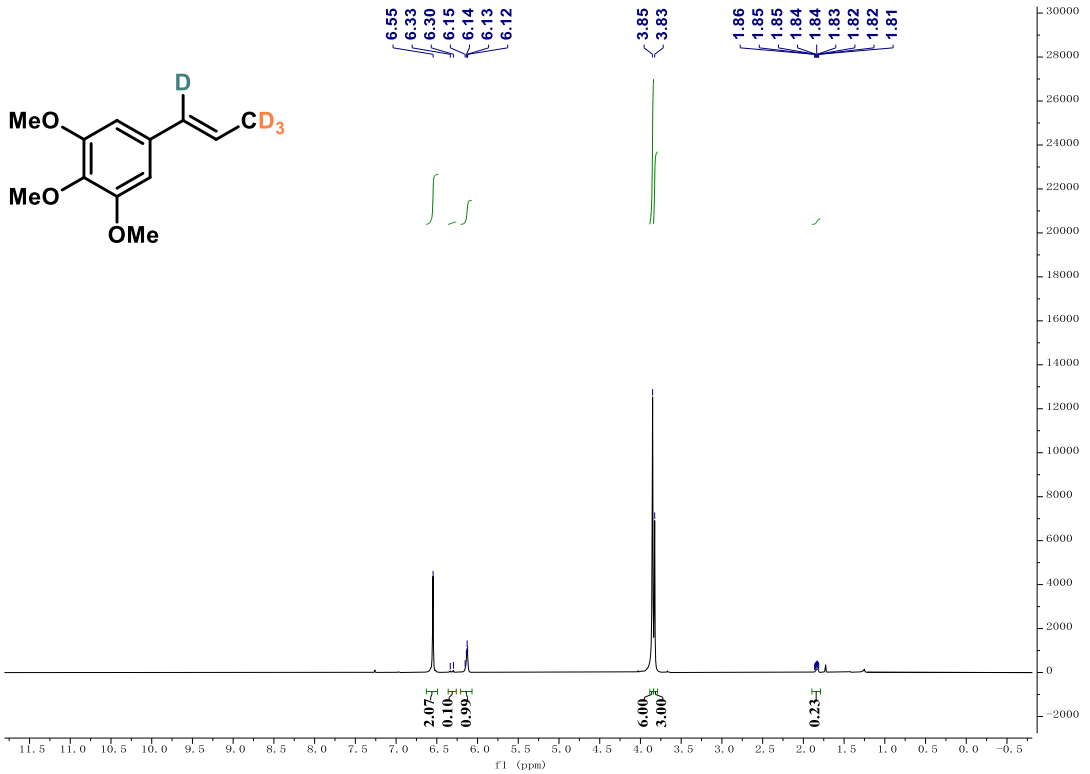
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of compound **2a**



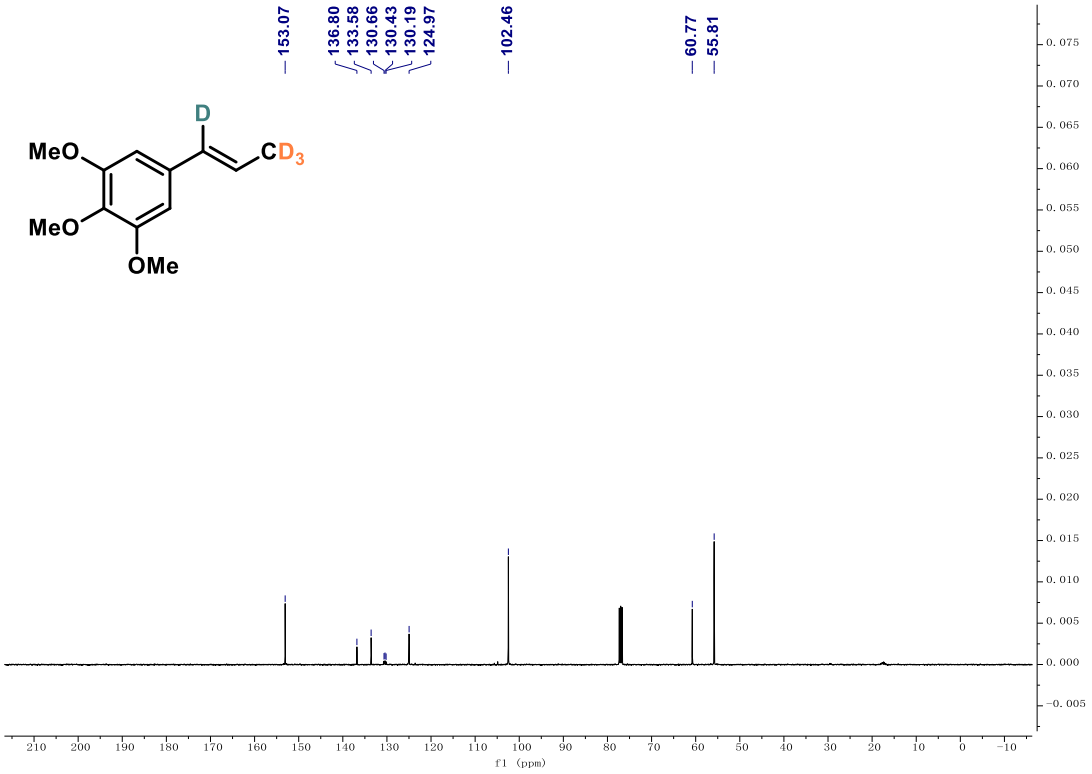
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of compound **3c**



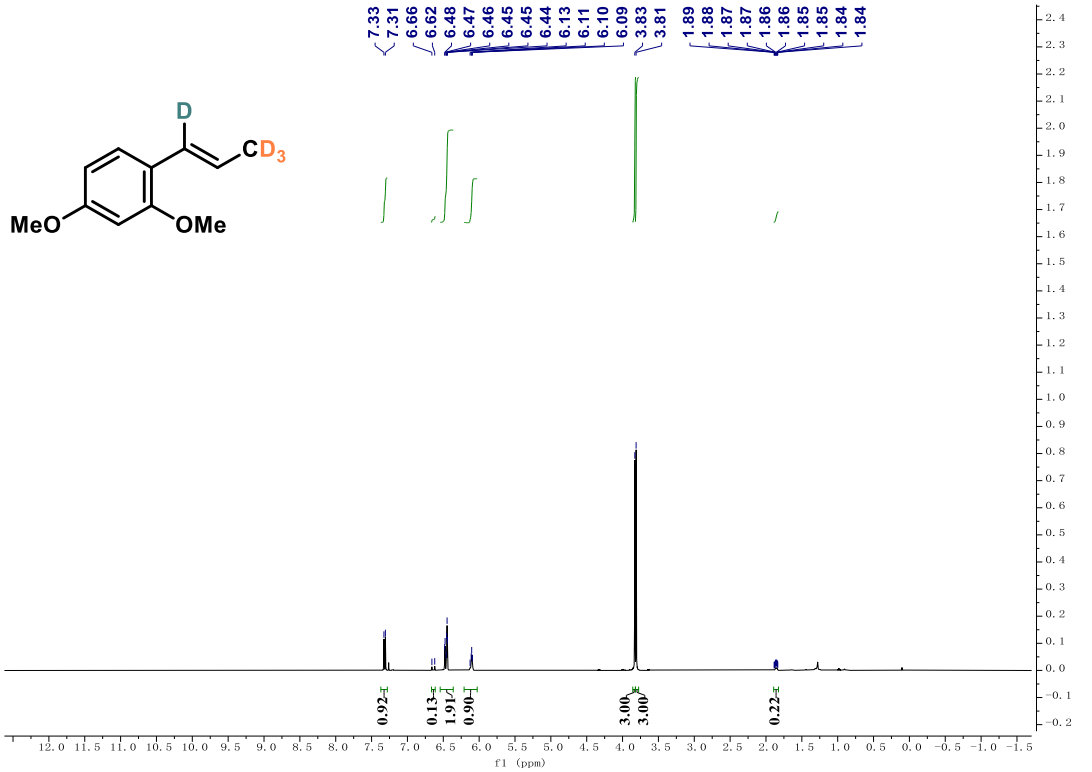
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of compound **3c**



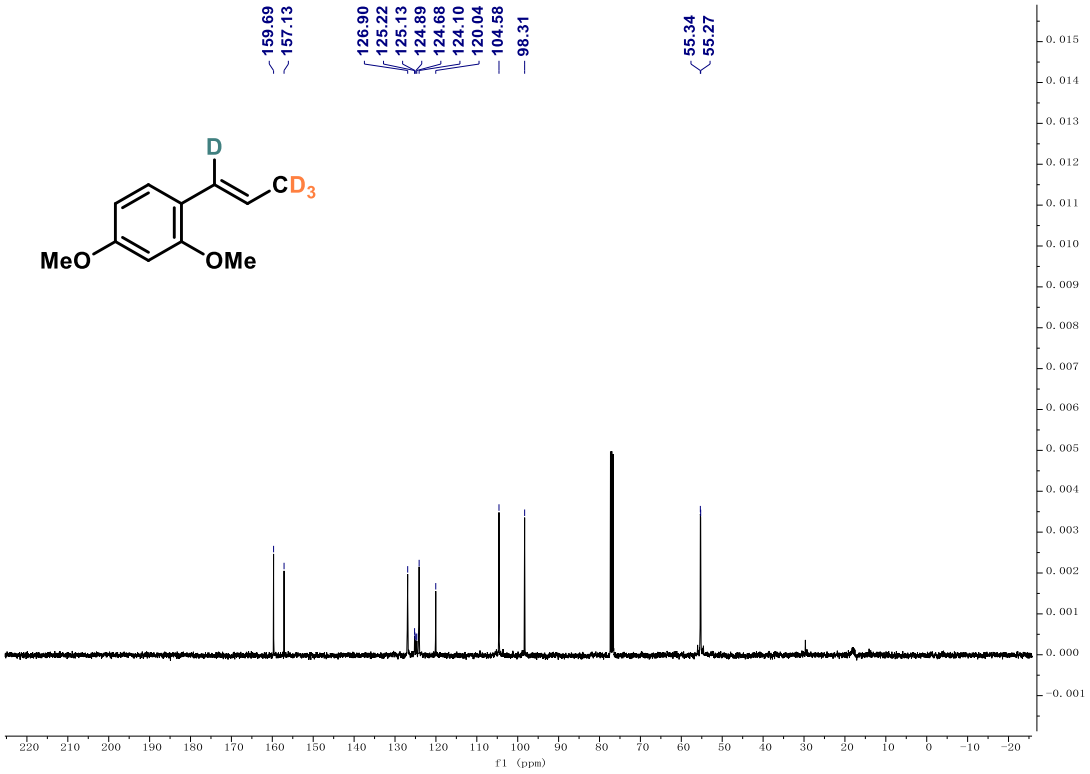
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of compound **3d**



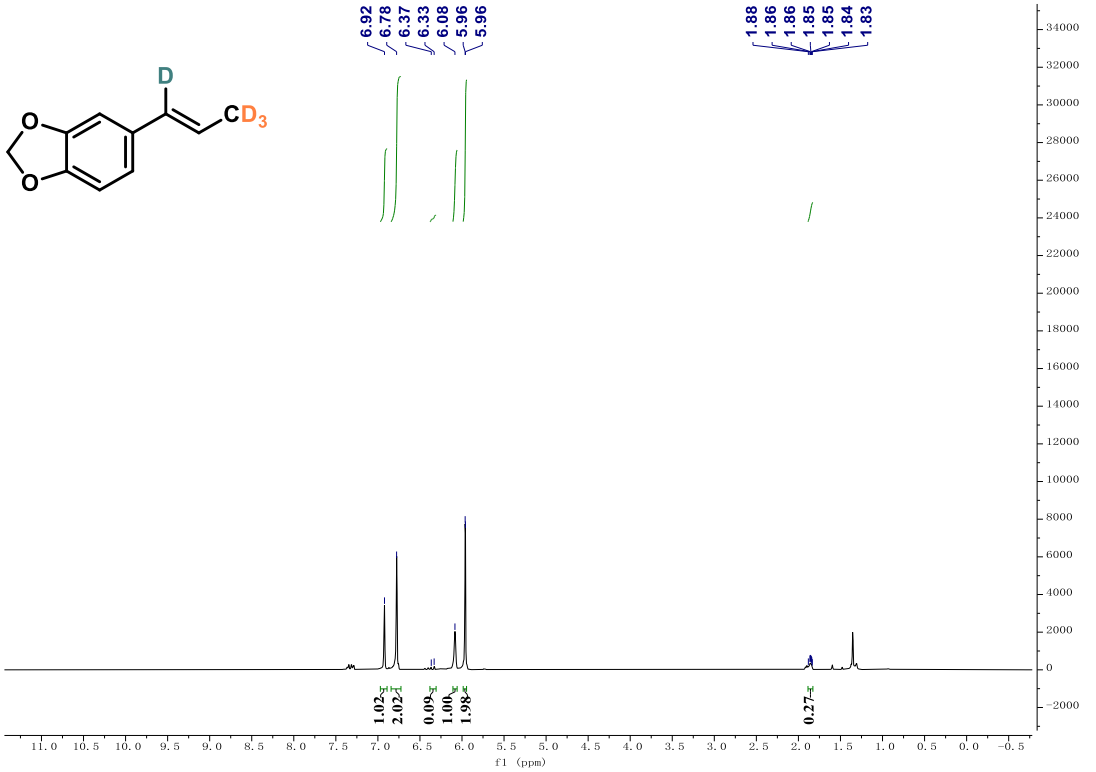
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of compound **3d**



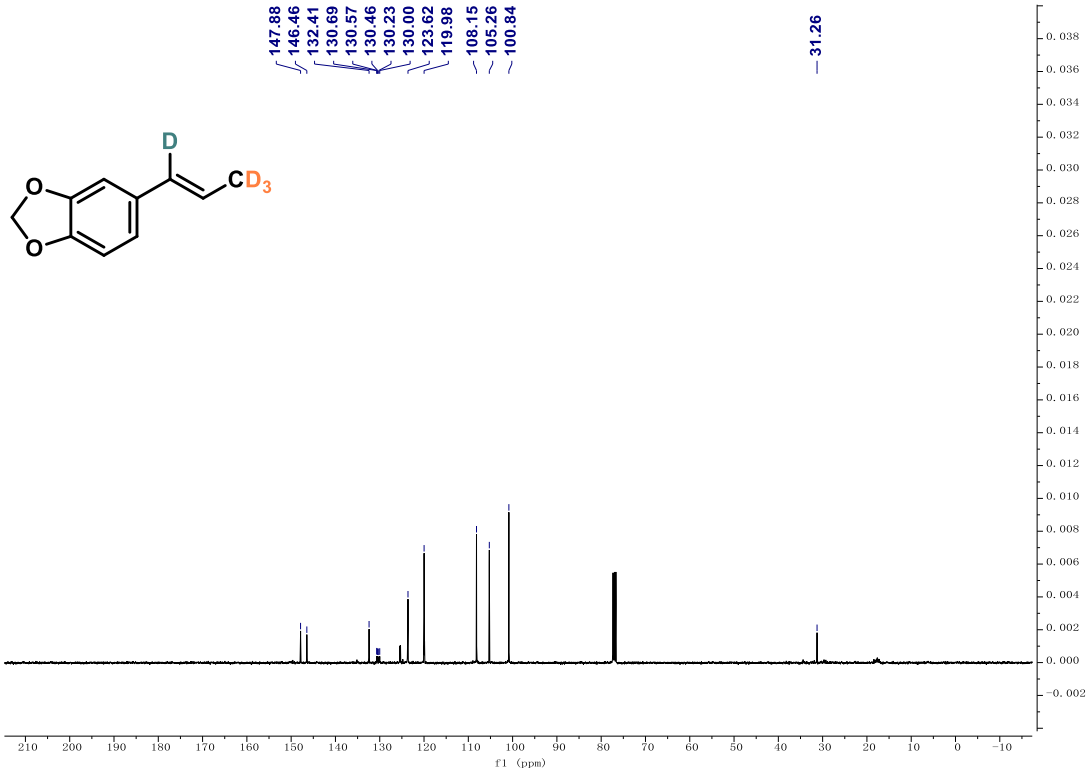
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of compound **3e**



^{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**