Supporting Information

Electroreductive Deuteroarylation of Alkenes Enabled by an Organo-Mediator

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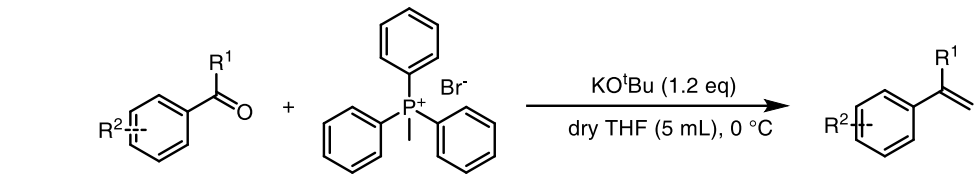
1. General Methods

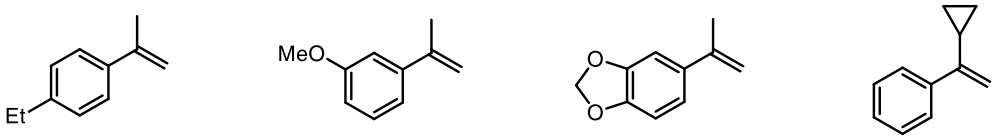
Unless otherwise stated, all the reagents were purchased from commercial sources (Energy Chemical, J&K Chemic, TCI, Fluka, Acros, SCRC), and used without further purification. Technical grade petroleum ether (40-60°C bp.) and ethyl acetate were used for the chromatography column. Proton nuclear magnetic resonance (^{1}H NMR) spectra and proton-decoupled carbon nuclear magnetic resonance (^{13}C NMR) spectra were recorded on Bruker Advance III 500 spectrometers using $CDCl_3$ as solvent with TMS as the internal standard. The chemical shifts are referenced to signals at 7.28 and 77.0 ppm, respectively. Chemical shift (δ) and coupling constants (J) are given in ppm and in Hz, respectively. The peak patterns are indicated as follows: s, singlet, d, doublet, t, triplet, q, quartet, m, multiplet. The chemical shift signals at 1.26 and 1.56 ppm in ^{1}H NMR are the signal peaks of impurities. The chemical shift signals at 29.77 ppm in ^{13}C NMR are the signal peaks of impurities. Electrolysis reactions were conducted using an ElectraSyn 2.0 Package supply purchased from IKA Instruments. Cyclic voltammetry (CV) analysis was performed on CHI660E electrochemical workstation purchased from Shanghai Chenhua Instrument Co., Ltd. Cyclic voltammogram was recorded at 0.1 V/s scan rate, using a glassy carbon electrode as working electrode, a platinum-plated electrode as counter electrode and Ag/AgCl electrode as a reference electrode. GC yield and mass spectra were recorded on an Agilent GCMS-5977B gas chromatograph-mass spectrometer, where *n*-dodecane was used as the internal standard when determining the yield by GC analysis. High-resolution mass spectra (HRMS) were recorded using electrospray ionization (ESI) and time-of-flight (TOF) mass analysis. TLC was performed by using commercially prepared 100-400 mesh silica gel plates and visualization was affected at 254 nm.

2. Preparation of Starting Materials

General Procedure for Preparation of Alkenes[1-4]: Methyltriphenylphosphonium bromide (6.5 mmol, 1.3 equiv.) was dissolved in dry THF (5 mL) under an argon atmosphere. The solution was cooled to 0 °C, and then potassium *tert*-butoxide (6

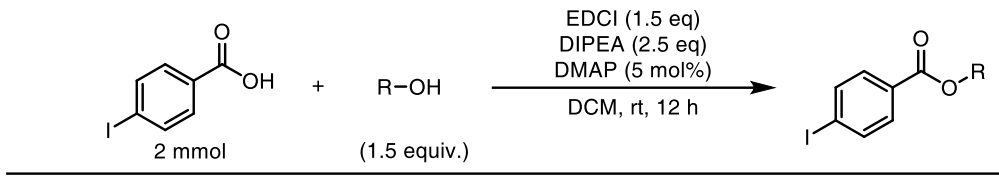
mmol, 1.2 equiv.) was added. The suspension was stirred in an ice bath for 1 min, and then acetophenone derivative (5 mmol, 1 equiv.) was added. The solution was to maintain ice bath conditions by stirring overnight. The solvent was removed under reduced pressure and the residue was subjected to column chromatography (eluted with petroleum ether) to yield the desired alkenes. The NMR spectra data of alkenes are available in the literature and are referenced accordingly.

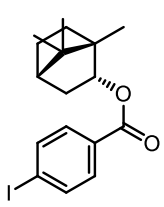




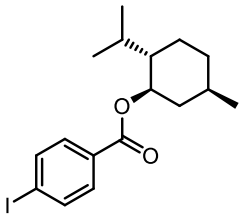
41a 44a 47a 48a

General Procedure for Preparation of Iodobenzene Derivatives[5]: EDCI (0.574 g, 3 mmol) was added to a suspension of 4-iodobenzoic acid (2 mmol), ROH (3 mmol), DIPEA (0.82 mL, 5 mmol), DMAP (0.012 g, 0.1 mmol) and DCM (10 mL) at room temperature. After addition, the resulting mixture was stirred at room temperature overnight. Water was added to the reaction followed by the addition of DCM. The combined organic layers were washed with aq. NaCl, and dried over anhydrous Na_2SO_4. Removal of the solvent under vacuum gave the crude product, which was purified by silica gel chromatography to give the product.

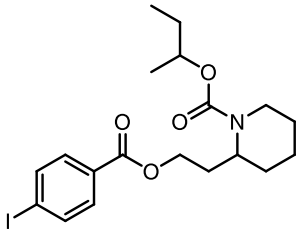




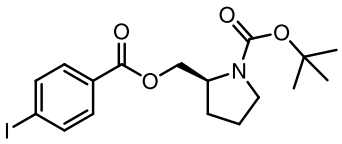
52a



53a



54a



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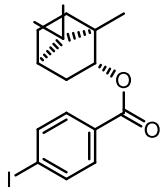

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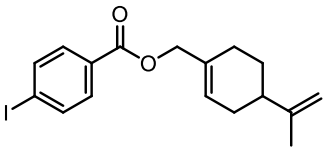
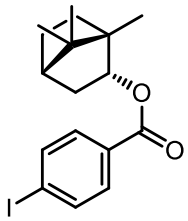


57a

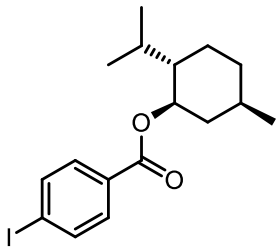
3. Characterization of Starting Materials



(1S,2R,4S)-1,7,7-Trimethylbicyclo[2.2.1]heptan-2-yl 4-iodobenzoate (52a)

The title compound was synthesized following General Procedure and purified by using silica gel chromatography to yield a white solid, 392 mg (51% yield), mp: 100-101 ºC. R_f = 0.5 (petroleum ether/ethyl acetate = 10/1, v/v). **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ 7.85 – 7.81 (m, 2H), 7.80 – 7.75 (m, 2H), 5.14 – 5.10 (m, 1H), 2.54 – 2.45 (m, 1H), 2.14 – 2.06 (m, 1H), 1.87 – 1.79 (m, 1H), 1.76 (t, *J* = 4.5 Hz, 1H), 1.47 – 1.39 (m, 1H), 1.35 – 1.29 (m, 1H), 1.15 – 1.09 (m, 1H), 0.98 (s, 3H), 0.94 (s, 3H), 0.92 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$, ppm) δ 166.3, 137.7, 131.0, 130.4, 100.5, 80.9, 49.1, 47.9, 45.0, 36.9, 28.1, 27.4, 19.7, 18.9, 13.6.

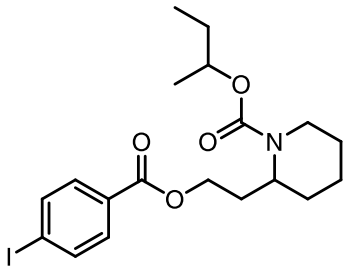
The ^{1}H and ^{13}C NMR data were in accordance with those reported in the literature[5].



(1R,2S,5R)-2-Isopropyl-5-methylcyclohexyl 4-iodobenzoate (53a)

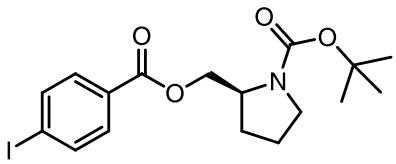
The title compound was synthesized following General Procedure and purified by using silica gel chromatography to yield the colorless liquid, 386 mg (50% yield). $\boldsymbol{R_f}$ = 0.6 (petroleum ether/ethyl acetate = 10/1, v/v). **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ 7.85 – 7.80 (m, 2H), 7.79 – 7.75 (m, 2H), 4.97 – 4.90 (m, 1H), 2.16 – 2.10 (m, 1H), 1.96 – 1.91 (m, 1H), 1.78 – 1.73 (m, 2H), 1.60 – 1.53 (m, 2H), 1.17 – 1.09 (m, 2H), 0.95 (d, *J* = 6.6 Hz, 3H), 0.93 (d, *J* = 7.0 Hz, 3H), 0.80 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$, ppm) δ 165.6, 137.7, 131.1, 130.3, 100.5, 75.2, 47.2, 40.9, 34.3, 31.5, 26.5, 23.6, 22.1, 20.8, 16.5.

The ^{1}H and ^{13}C NMR data were in accordance with those reported in the literature[5].



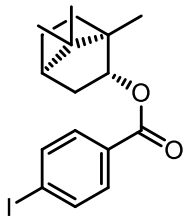
sec-Butyl 2-(2-((4-iodobenzoyl)oxy)ethyl)piperidine-1-carboxylate (54a)

The title compound was synthesized following General Procedure and purified by using silica gel chromatography to yield the colorless liquid, 459 mg (50% yield). $\boldsymbol{R_f}$ = 0.5 (petroleum ether/ethyl acetate = 10/1, v/v). **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ 7.83 – 7.79 (m, 2H), 7.78 – 7.73 (m, 2H), 4.78 – 4.70 (m, 1H), 4.57 – 4.48 (m, 1H), 4.36 – 4.30 (m, 2H), 4.15 – 4.04 (m, 1H), 2.86 (t, *J* = 13.1 Hz, 1H), 2.27 – 2.18 (m, 1H), 1.93 – 1.86 (m, 1H), 1.70 – 1.57 (m, 6H), 1.56 – 1.45 (m, 3H), 1.18 (d, *J* = 6.3 Hz, 2H), 0.88 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$, ppm) δ 166.1, 155.5, 137.7, 131.1, 129.8, 100.7, 73.0, 62.9, 48.0, 39.0, 29.1, 28.8, 28.6, 25.5, 19.8, 19.1, 9.8. **HRMS (ESI)** m/z calcd for $C_{19}H_{27}INO_4$ $[M+H]^+$: 460.0979; found: 460.0977.



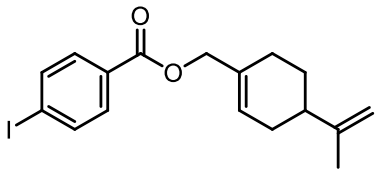
tert-Butyl (S)-2-(((4-iodobenzoyl)oxy)methyl)pyrrolidine-1-carboxylate (55a)

The title compound was synthesized following General Procedure and purified by using silica gel chromatography to yield a yellow oil, 109 mg (51% yield). $\boldsymbol{R_f}$ = 0.4 (petroleum ether/ethyl acetate = 8/1, v/v). **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ 7.81 (d, *J* = 8.2 Hz, 2H), 7.75 (d, *J* = 8.2 Hz, 2H), 4.43 – 4.23 (m, 3H), 3.54 – 3.36 (m, 2H), 1.98 – 1.84 (m, 4H), 1.47 (s, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$, ppm) δ 168.9, 157.9, 139.6, 137.2, 132.0, 130.6, 123.8, 112.4, 99.9, 71.9, 67.7, 45.5, 21.5. **HRMS (ESI)** m/z calcd for $C_{17}H_{22}INO_4Na$ $[M+Na]^+$: 454.0485; found: 454.0476.



(1R,2R,4R)-1,7,7-Trimethylbicyclo[2.2.1]heptan-2-yl 4-iodobenzoate (56a)

The title compound was synthesized following General Procedure and purified by using silica gel chromatography to yield a white solid, 65 mg (34% yield), mp: 100-101 ºC. $\boldsymbol{R_f}$ = 0.5 (petroleum ether/ethyl acetate = 10/1, v/v). **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ 7.84 – 7.80 (m, 2H), 7.75 – 7.70 (m, 2H), 4.92 (dd, *J* = 7.6, 4.0 Hz, 1H), 1.95 – 1.89 (m, 2H), 1.83 (t, *J* = 4.2 Hz, 1H), 1.79 – 1.73 (m, 1H), 1.64 (dd, *J* = 12.7, 4.2 Hz, 1H), 1.27 – 1.22 (m, 1H), 1.20 – 1.15 (m, 1H), 1.12 (s, 3H), 0.93 (s, 3H), 0.91 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$, ppm) δ 165.6, 137.8, 131.0, 130.4, 100.5, 81.9, 49.1, 47.1, 45.1, 38.9, 33.7, 27.1, 20.1, 20.1, 11.6. **HRMS (ESI)** m/z calcd for $C_{17}H_{21}IO_2Na$ $[M+Na]^+$: 407.0478; found: 407.0470.



(4-(Prop-1-en-2-yl)cyclohex-1-en-1-yl)methyl 4-iodobenzoate (57a)

The title compound was synthesized following General Procedure and purified by using silica gel chromatography to yield a yellow oil, 110 mg (58% yield). $\boldsymbol{R_f}$ = 0.6 (petroleum ether/ethyl acetate = 8/1, v/v). **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ 7.83 – 7.80 (m, 2H), 7.80 – 7.76 (m, 2H), 5.86 (td, *J* = 3.1, 1.5 Hz, 1H), 4.78 – 4.74 (m, 2H), 4.73 (s, 2H), 2.25 – 2.15 (m, 4H), 2.07 – 1.97 (m, 1H), 1.90 (dtt, *J* = 12.7, 4.2, 2.4 Hz, 1H), 1.77 (s, 3H), 1.59 – 1.50 (m, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$, ppm) δ 166.0, 149.5, 137.7, 132.5, 131.1, 129.9, 126.0, 108.9, 100.7, 69.2, 40.8, 30.5, 27.3, 26.5, 20.8. **HRMS (ESI)** m/z calcd for $C_{17}H_{19}IO_2Na$ $[M+Na]^+$: 405.0321; found: 405.0315.

4. General Procedures of Electrochemical Reaction

General Procedure A for Preparation of Deuterated Alkylarenes 3-57: A mixture of alkenes (0.75 mmol, 1.5 equiv.), aryl iodides (0.5 mmol), 2,2'-bipyridine (0.1 mmol, 20 mol%), Et_4NI (0.25 mmol, 0.5 equiv.), Cs_2CO_3 (0.25 mmol, 0.5 equiv.), D_2O (15 mmol, 30 equiv.) in 4 mL dry DMF was added to an electrolytic cell (30 mL). The electrolytic cell was equipped with high-density graphite rods (ϕ 5 mm) as anode and cathode. The solution was electrolyzed at ambient temperature under a constant current (12 mA) for 18 h. After electrolysis, the mixture was poured into water and extracted with ethyl acetate twice. The combined organic layer was washed with brine (10 mL), dried over anhydrous $MgSO_4$, filtered, and concentrated. The resulting mixture was purified by silica gel column chromatography (eluted with petroleum ether) to afford the desired products**.**

Procedure for the Scale-up Synthesis of 3 and 5: A mixture of styrene (7.5 or 15 mmol, 1.5 equiv., 0.781 g/1.561 g), iodobenzene (5 mmol, 1.020 g or 10 mmol, 2.040 g) or 1-bromo-4-iodobenzene (10 mmol, 2.818 g), 2,2'-bipyridine (1 or 2 mmol, 20 mol%, 0.156 g/0.312 g), Et_4NI (2.5 or 5 mmol, 0.5 equiv., 0.643 g/1.286 g), Cs_2CO_3

(2.5 or 5 mmol, 0.5 equiv., 0.815 g/1.629 g), D_2O (150 or 300 mmol, 30 equiv., 3.004 g/6.008 g) in 40/80 mL dry DMF was added to a three-necked flask (100 mL). The electrolytic cell was equipped with graphite rods (ϕ 15 mm) as anode and cathode. The solution was electrolyzed at ambient temperature under a constant current (60 mA) for 36 or 72 h. After electrolysis, the mixture was poured into water and extracted with ethyl acetate three times. The combined organic layer was washed with brine (30 mL), dried over $MgSO_4$, filtered, and concentrated. The resulting mixture was purified by silica gel column chromatography (eluted with petroleum ether) to afford **3** (0.824 g, 90%, 99% D-inc or 1.538 g, 84%, 99% D-inc) and **5** (1.227 g, 47%, 99% D-inc), respectively.

General Procedure B for Preparation of Alkyne Products 58-59: A mixture of 1-bromo-4-(2-phenylpropyl-2-*d*)benzene (0.5 mmol, 1 equiv.), ethisterone or ethinylestradiol (0.75 mmol, 1.5 equiv.), bis(triphenylphosphine)palladium(II) chloride (0.05 mmol, 10 mol%), CuI (0.1 mmol, 20 mol%), Et_3N (1 mL) in 1.5 mL dry MeCN was added to a reaction bottle (30 mL). The solution was stirred under nitrogen at 70 ℃ for 8 hours. After the reaction finished, the mixture was poured into water and extracted with ethyl acetate twice. The combined organic layer was washed with brine (10 mL), dried over $MgSO_4$, filtered, and concentrated. The resulting mixture was purified by silica gel column chromatography (eluted with petroleum ether/ ethyl acetate) to afford the desired products.

General Procedure C for Preparation of Alkyne Product 60: A mixture of 1-bromo-4-(2-phenylpropyl-2-*d*)benzene (0.5 mmol, 1 equiv.), 3,4,5-trimethoxybenzeneboronic acid (0.55 mmol, 1.1 equiv.), tetrakis(triphenylphosphine)palladium (0.05 mmol, 10 mol%), K_2CO_3 (0.1 mmol, 2.5 equiv.), in 2 mL dry 1,4-dioxane/H_2O (4:1) was added to a reaction bottle (30 mL). The solution was stirred overnight under nitrogen at 100 ℃. After reaction finished, the mixture was poured into water and extracted with ethyl acetate twice. The combined organic layer was washed with brine (10 mL), dried over $MgSO_4$, filtered, and concentrated. The resulting mixture was purified by silica gel column

chromatography (eluted with petroleum ether/ ethyl acetate) to afford the desired products.

General Procedure D for Preparation of Alkylarenes 63-67: A mixture of alkenes (0.75 mmol, 1.5 equiv.), aryl bromides (0.5 mmol), Et_4NI (0.25 mmol, 0.5 equiv.), Cs_2CO_3 (0.25 mmol, 0.5 equiv.), 2,2'-bipyridine (0.1 mmol, 0.2 equiv.) in 4 mL DMF was added to an electrolytic cell (30 mL). The electrolytic cell was equipped with high-density graphite rods (ϕ 5 mm) as anode and cathode. The solution was electrolyzed at ambient temperature under a constant current (12 mA) for 18 h. After electrolysis, the mixture was poured into water and extracted with ethyl acetate twice. The combined organic layer was washed with brine (10 mL), dried over $MgSO_4$, filtered, and concentrated. The resulting mixture was purified by silica gel column chromatography (eluted with petroleum ether) to afford the desired products.

5. Photographic Guide for Electrochemical Reaction

5.1. Overview of Materials Used

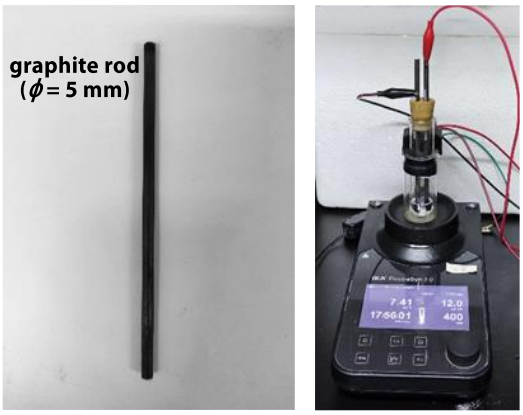
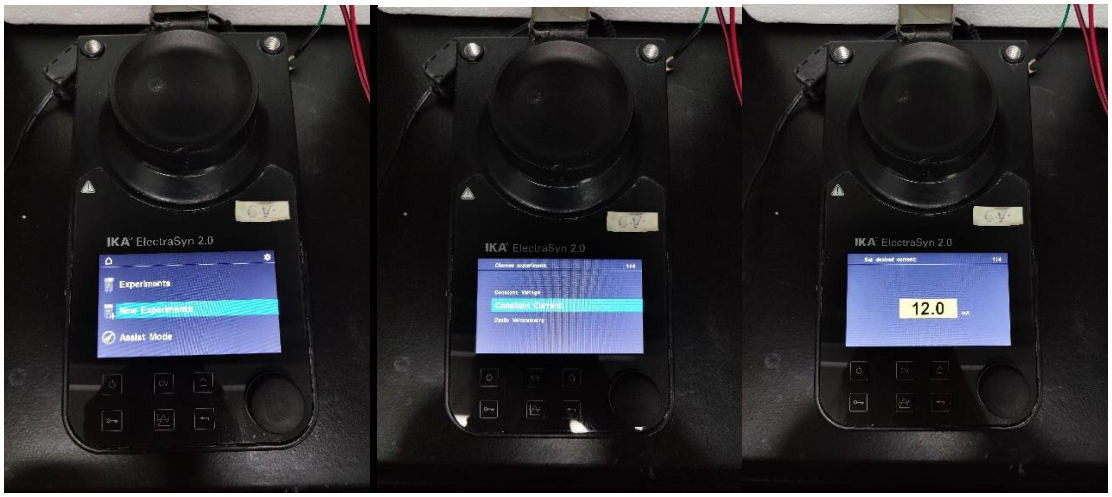
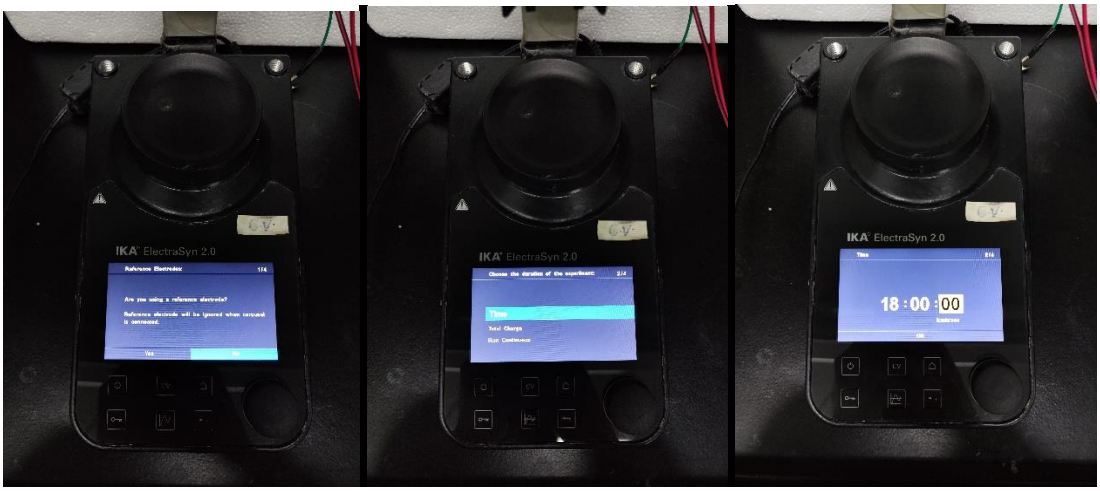


Fig. S1. (A) graphite rod (ϕ = 5 mm). (B) electrolysis device.

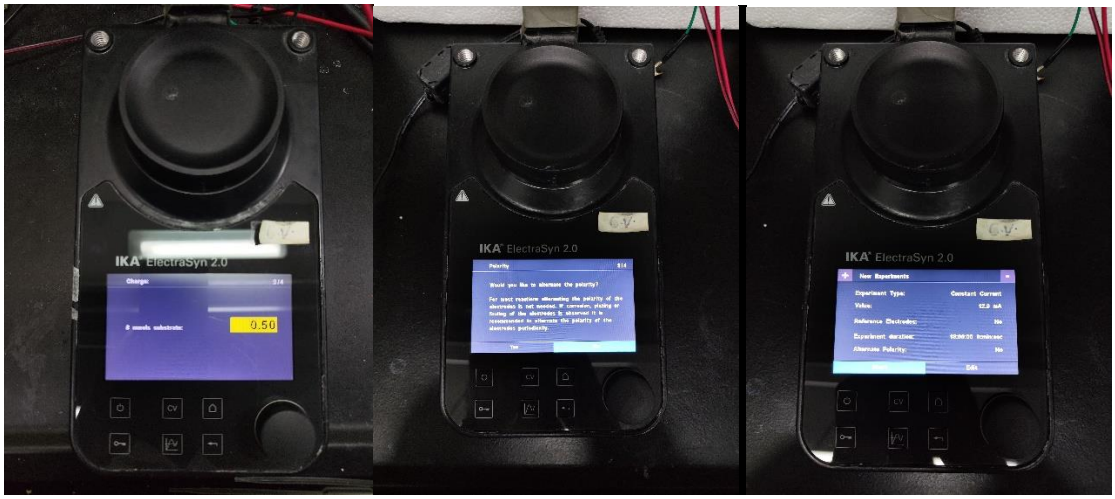
Step to step:



Left. Chose “New Experiment”. **Middle.** Chose “Constant Current”. **Right.** Select “12.0 mA”.



Left. “Reference electrodes:” chose “No”. **Middle.** Chose “Time”. **Right.** Select “18 hours”.



Left. Select “0.50 mmol”. **Middle.** “Alternate the Polarity” chose “No”. **Right.** Chose “Start”.

5.2. Iodine Release in Electrolysis

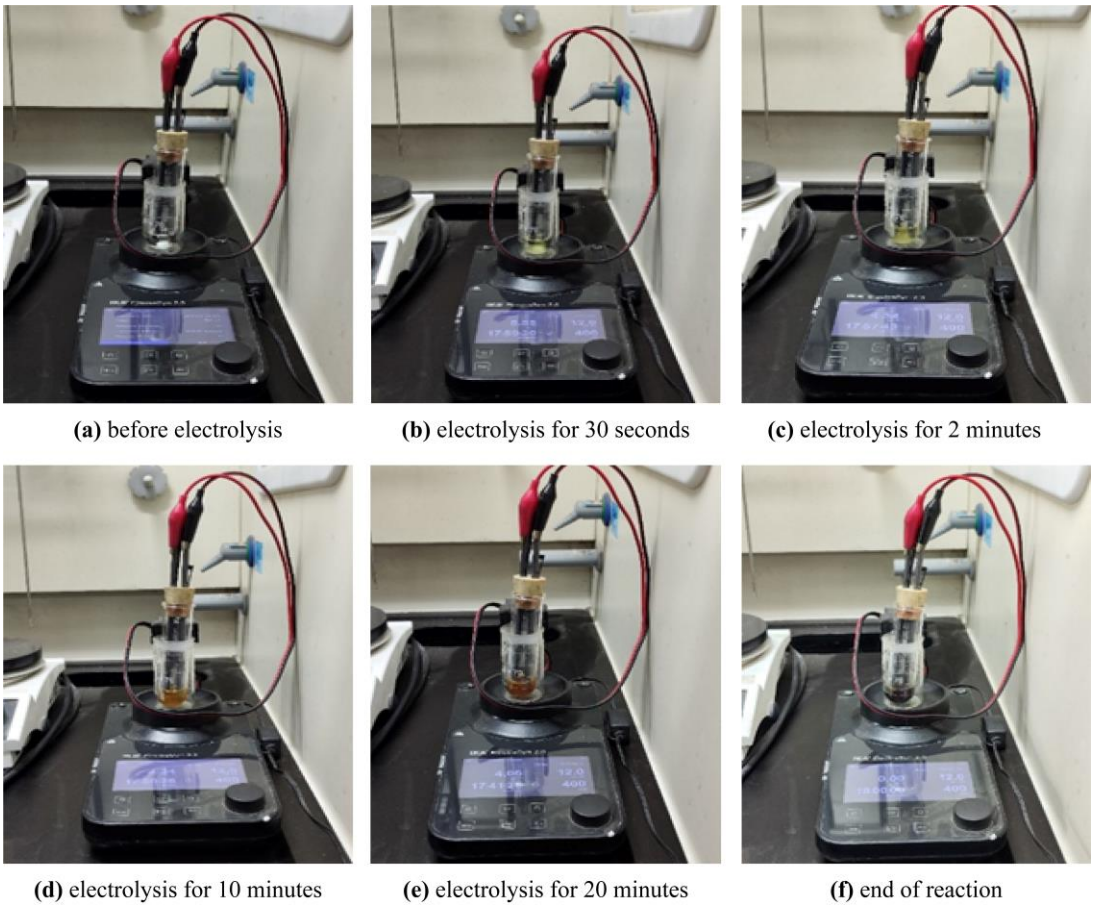


Fig. S2. Reaction phenomenon of iodine release in electrolysis.

5.3. Scale-up Experiment Device

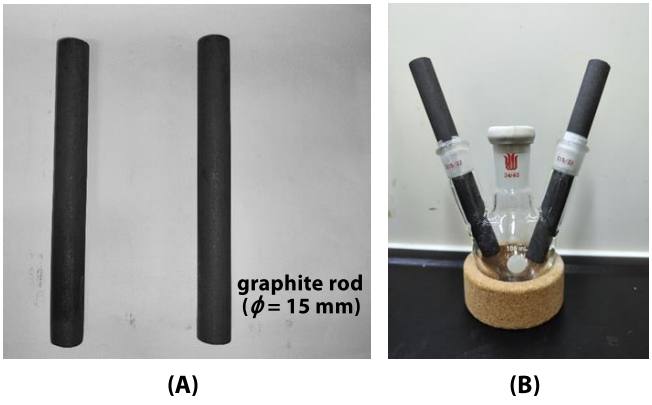


Fig. S3. (A) graphite rod (ϕ = 15 mm). (B) scale-up experiment device.

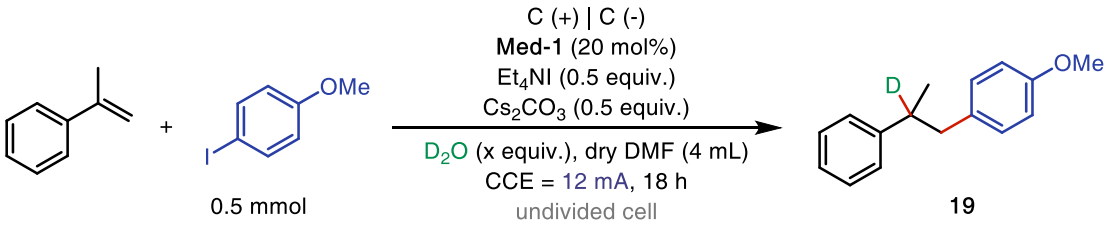
5.4. CV Analysis Device

Fig. S4. (A) Pt plate electrode (1 cm×1 cm×0.1 cm). (B) glassy carbon electrode (ϕ = 6 mm). (C) Ag/AgCl (saturated KCl) reference electrode.

6. Supplementary Control Experiments

6.1. Effect of D_2O Dosages

Table S1. Effect of D_2O dosages. Reaction conditions: undivided cell, graphite rods (ϕ 6 mm) as anode and cathode, constant current = 12 mA, α-methylstyrene (0.75 mmol), 4-iodoanisole (0.5 mmol), **Med-1** (20 mol%), Et_4NI (0.5 equiv.), Cs_2CO_3 (0.5 equiv.), D_2O, DMF (3 mL), air, 18 h. Isolated yield. Deuterium incorporation determined by ^1H NMR.



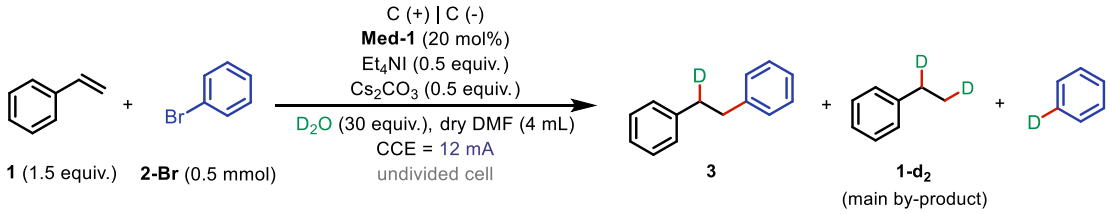
Entry	D_2O (equiv.)	Yield (%)	D-Inc (%)
1	0	<5	0
2	5	28	36
3	10	24	46
4	15	36	63
5	20	44	82
6	25	60	80
7	**30**	**61**	**90**
8	35	60	86

To obtain the optimal conditions with high efficiency and high D-incorporation, we subsequently investigated the changes in isolated yield and D-incorporation of **19** under different D_2O dosages (Table S1). Only a trace amount of product was isolated

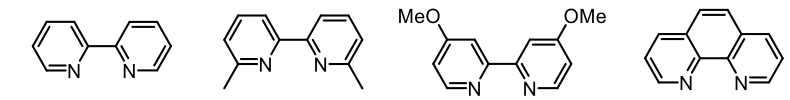
in the absence of D_2O (Entry 1). With the increase in the amount of D_2O, the yield and D-incorporation of **19** were increasing (Entries 2-7). When D_2O was increased to 30 equiv., the yield and D-incorporation reached the maximum (Entry 7). When using 35 equivalents of D_2O, the yield dropped slightly (Entry 8). Therefore, the use of 30 equivalents of D_2O was considered to be the most suitable.

6.2. Optimization of Electroreductive Deuteroarylation Involving Bromobenzene

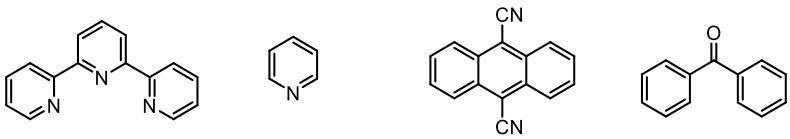
Table S2. Optimization of the reaction conditions. Reaction conditions: undivided cell, graphite rods (ϕ 5 mm) as anode and cathode, constant current = 12 mA, **1** (1.5 equiv.), **2-Br** (0.5 mmol), **Med** (20 mol%), Et_4NI (0.5 equiv.), Cs_2CO_3 (0.5 equiv.), D_2O (30 equiv.), dry DMF (4 mL), air, 18 h. Yield determined by GC analysis with hexadecane as the internal standard. **Med** = mediator.



Entry	Variation from conditions	Yield of 3 (%)
1	none	7
2	**Med-2** instead of **Med-1**	10
3	**Med-3** instead of **Med-1**	12
4	**Med-4** instead of **Med-1**	6
5	**Med-5** instead of **Med-1**	5
6	**Med-6** instead of **Med-1**	5
7	**Med-7** instead of **Med-1**	11
8	**Med-8** instead of **Med-1**	5



Med-1 (E_{red} = -2.89 V) | **Med-2** (E_{red} = -3.24 V) | **Med-3** (E_{red} = -2.48 V) | **Med-4** (E_{red} = -3.10 V)



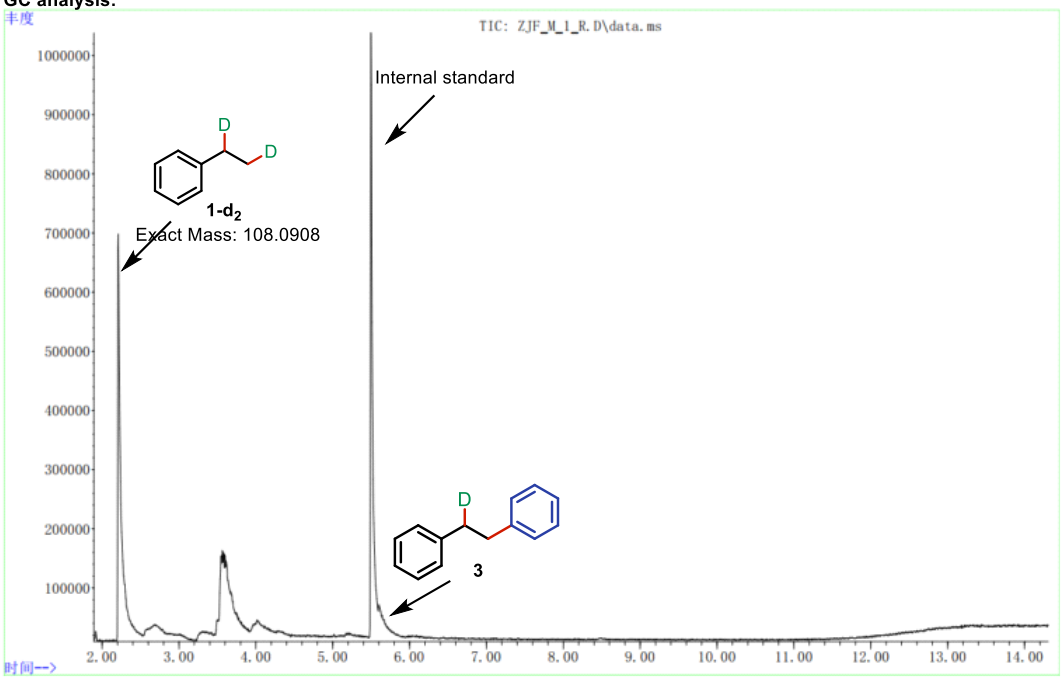
Med-5 (E_{red} = -3.09 V) | **Med-6** (E_{red} < -3.25 V) | **Med-7** (E_{red} = -1.22 V) | **Med-8** (E_{red} = -1.83 V)

We then investigated the reaction effect of styrene and bromobenzene under the action of different organo-mediators (Table S2). The results showed that no satisfactory results were obtained with different mediators, and the expected product (**3**) was detected with a yield of less than 12%. Meanwhile, styrene was detected in the system as essentially converted to deuterated product (**1-d$_2$**). In addition, due to the small molecular weight of benzene-*d*, it was difficult to demonstrate the deuteration of bromobenzene.

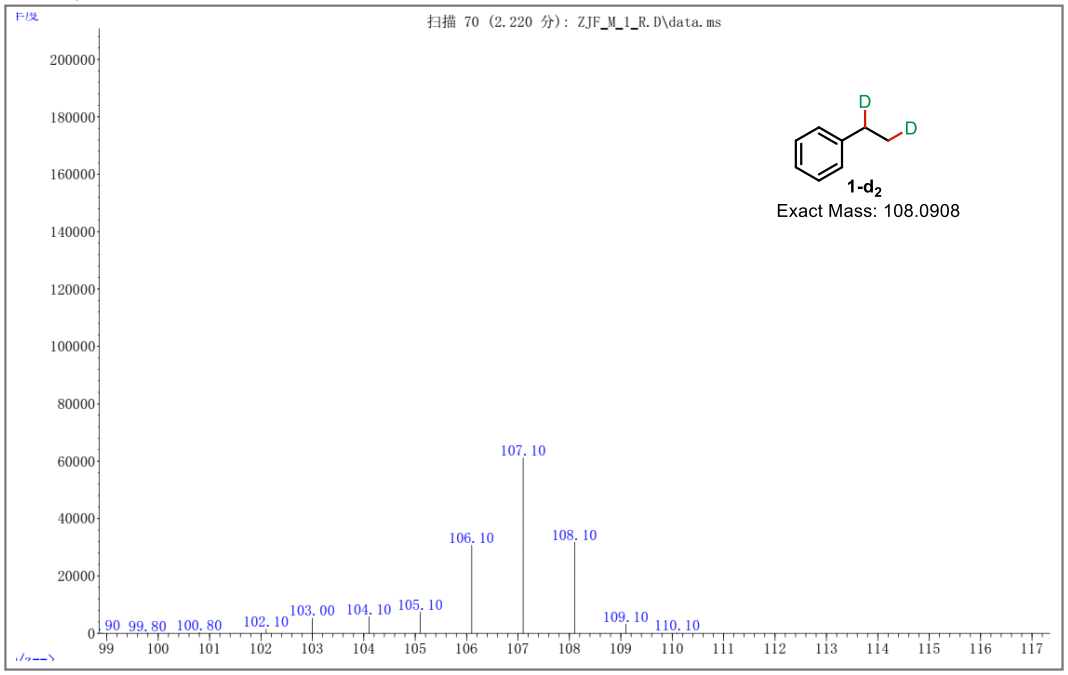
GC-MS analysis of entry 1:

(primary by-product)

GC analysis:

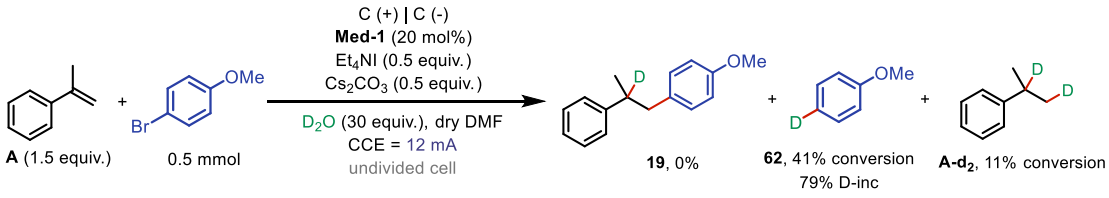


MS analysis:



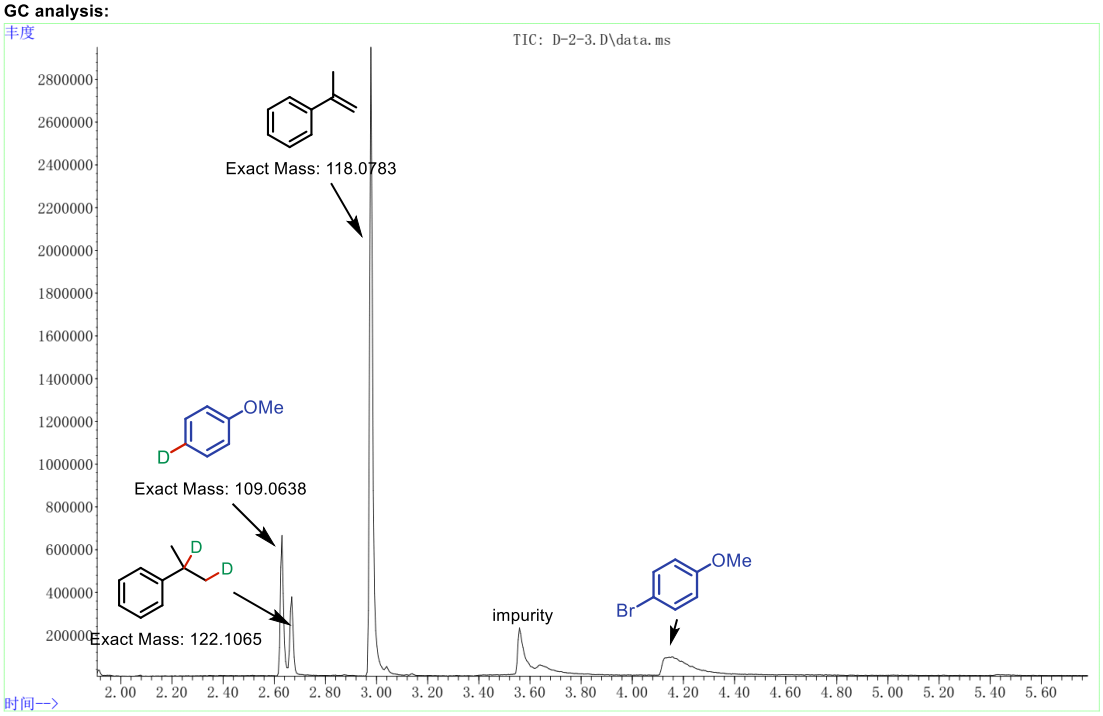
6.3. Analysis of Deuterated By-products

The cathodic conversion between *α*-methylstyrene and 1-bromo-4-methoxybenzene was investigated under standard conditions. The results showed that no expected product **19** was produced in the reaction, but the deuterated by-products **62** and **A-d$_2$** could be detected, and by-products were demonstrated by MS analysis. Meanwhile, the deuteration rate of **62** (79% D-inc) had been proved by MS and ^{1}H NMR analysis.

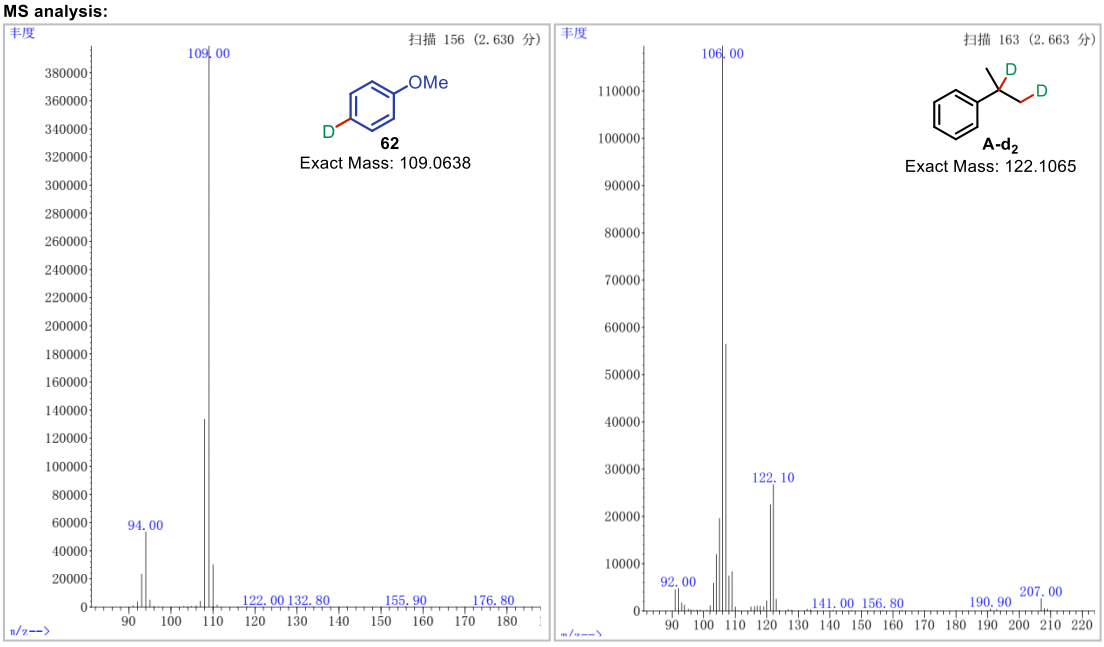


GC-MS analysis:

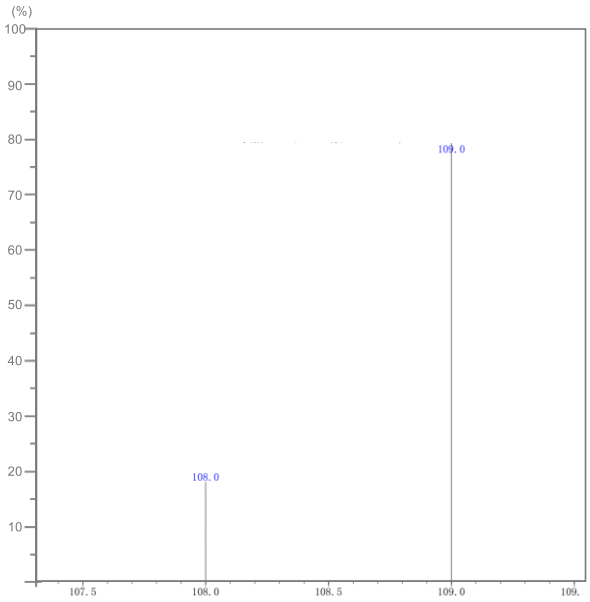
GC analysis:



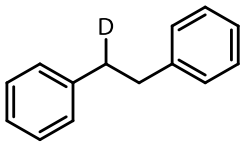
MS analysis:



D-Incorporation analysis of 62:



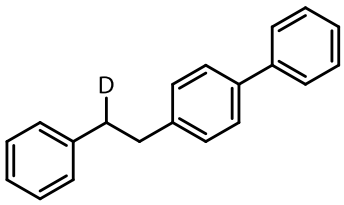
7. Characterization Data for Products



(Ethane-1,2-diyl-1-d)dibenzene (3)

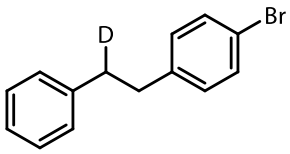
The title compound was synthesized following General Procedure A and purified by using silica gel chromatography to yield a yellow oil, 86 mg (94% yield). $\boldsymbol{R_f}$ = 0.7 (petroleum ether); 99% Deuterium incorporation was determined by ^{1}H NMR. **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ 7.35 – 7.31 (m, 4H), 7.27 – 7.21 (m, 6H), 2.99 – 2.95 (m, 3.01H). **^{13}C NMR** (126 MHz, $CDCl_3$, ppm) δ 141.8, 128.5, 128.4, 126.0, 38.0, 37.9.

The ^{1}H and ^{13}C NMR data were in accordance with those reported in the literature[6].



4-(2-Phenylethyl-2-d)-1,1'-biphenyl (4)

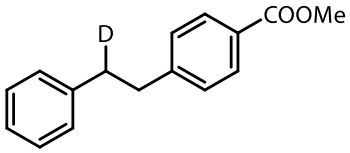
The title compound was synthesized following General Procedure A and purified by using silica gel chromatography to yield a white solid, 70 mg (54% yield). $\boldsymbol{R_f}$ = 0.5 (petroleum ether); 99% Deuterium incorporation was determined by ^{1}H NMR. **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ 7.64 – 7.60 (m, 2H), 7.55 (dt, *J* = 8.2, 2.1 Hz, 2H), 7.49 – 7.42 (m, 2H), 7.38 – 7.29 (m, 5H), 7.26 – 7.22 (m, 3H), 3.01 – 2.97 (m, 3.01H). **^{13}C NMR** (126 MHz, $CDCl_3$, ppm) δ 141.7, 141.1, 140.9, 138.9, 128.9, 128.7, 128.5, 128.4, 127.09, 127.06, 127.0, 126.0, 37.5, 29.7. **HRMS (ESI)** m/z calcd for $C_{20}H_{17}DNa$ $[M+Na]^+$: 282.1378; found: 282.1384.



1-Bromo-4-(2-phenylethyl-2-d)benzene (5)

The title compound was synthesized following General Procedure A and purified by using silica gel chromatography to yield a yellow oil, 98 mg (75% yield). $\boldsymbol{R_f}$ = 0.7 (petroleum ether); 99% Deuterium incorporation was determined by ^{1}H NMR. **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ 7.41 (dt, *J* = 8.3, 2.3 Hz, 2H), 7.33 – 7.29 (m, 2H), 7.25 – 7.21 (m, 1H), 7.20 – 7.16 (m, 2H), 7.06 (dt, *J* = 8.3, 2.5 Hz, 2H), 2.92 – 2.89 (m, 3.01H). **^{13}C NMR** (126 MHz, $CDCl_3$, ppm) δ 141.2, 140.6, 131.4, 130.3, 128.5, 128.4, 126.1, 119.7, 37.3, 37.2.

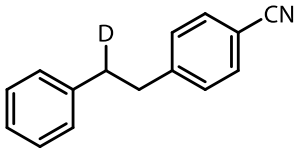
The ^{1}H and ^{13}C NMR data were in accordance with those reported in the literature[7].



Methyl 4-(2-phenylethyl-2-d)benzoate (6)

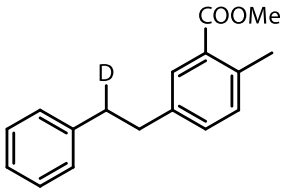
The title compound was synthesized following General Procedure A and purified by using silica gel chromatography to yield a yellow oil, 77 mg (64% yield). $\boldsymbol{R_f}$ = 0.5 (petroleum ether/ethyl acetate = 20/1, v/v); 98% Deuterium incorporation was determined by ^{1}H NMR. **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ 7.99 – 7.95 (m, 2H),

7.32 – 7.28 (m, 2H), 7.26 – 7.20 (m, 3H), 7.18 (d, *J* = 7.1 Hz, 2H), 3.93 (s, 3H), 3.01 – 2.92 (m, 3.02H). **^{13}C NMR** (126 MHz, $CDCl_3$, ppm) δ 167.2, 147.2, 141.1, 129.7, 128.6, 128.5, 128.4, 127.9, 126.1, 52.0, 37.8, 37.3. **HRMS (ESI)** m/z calcd for $C_{16}H_{16}DO_2$ $[M+H]^+$: 242.1301; found: 242.1294.



4-(2-Phenylethyl-2-d)benzonitrile (7)

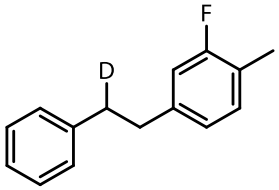
The title compound was synthesized following General Procedure A and purified by using silica gel chromatography to yield a yellow oil, 79 mg (76% yield). $\boldsymbol{R_f}$ = 0.7 (petroleum ether/ethyl acetate = 20/1, v/v); 99% Deuterium incorporation was determined by ^{1}H NMR. **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ 7.59 – 7.56 (m, 2H), 7.30 (t, *J* = 7.4 Hz, 2H), 7.27 – 7.21 (m, 3H), 7.15 (d, *J* = 7.1 Hz, 2H), 3.02 – 2.99 (m, 2.01H), 2.94 (q, *J* = 7.9, 7.4 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$, ppm) δ 147.2, 140.6, 132.2, 129.3, 128.5, 128.4, 126.3, 119.1, 109.8, 37.9, 37.3. **HRMS (ESI)** m/z calcd for $C_{15}H_{12}DNK$ $[M+K]^+$: 247.0757; found: 247.0747.



Methyl 2-methyl-5-(2-phenylethyl-2-d)benzoate (8)

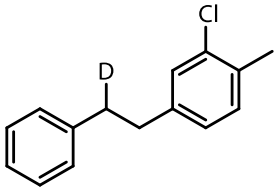
The title compound was synthesized following General Procedure A and purified by using silica gel chromatography to yield a yellow oil, 76 mg (59% yield). $\boldsymbol{R_f}$ = 0.9 (petroleum ether/ethyl acetate = 10/1, v/v); 94% Deuterium incorporation was determined by ^{1}H NMR. **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ 7.78 (d, *J* = 1.7 Hz, 1H), 7.31 (t, *J* = 7.5 Hz, 2H), 7.25 – 7.19 (m, 4H), 7.18 – 7.16 (m, 1H), 3.92 (s, 3H), 2.94 – 2.89 (m, 3.06H), 2.59 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$, ppm) δ 168.2, 141.5,

139.2, 137.7, 132.2, 131.7, 130.5, 129.5, 128.5, 128.4, 126.0, 51.8, 37.8, 37.2, 21.3. **HRMS (ESI)** m/z calcd for $C_{17}H_{18}DO_2$ $[M+H]^+$: 256.1457; found: 256.1452.



2-Fluoro-1-methyl-4-(2-phenylethyl-2-d)benzene (9)

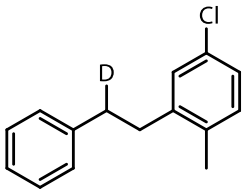
The title compound was synthesized following General Procedure A and purified by using silica gel chromatography to yield a yellow oil, 90 mg (84% yield). $\boldsymbol{R_f}$ = 0.8 (petroleum ether); 99% Deuterium incorporation was determined by ^{1}H NMR. **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ 7.36 – 7.32 (m, 2H), 7.27 – 7.21 (m, 3H), 7.12 (t, *J* = 8.0 Hz, 1H), 6.90 (t, *J* = 2.2 Hz, 1H), 6.89 – 6.87 (m, 1H), 2.96 – 2.91 (m, 3.01H), 2.29 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$, ppm) δ 161.3 (d, $^1J_{C\text{-}F}$ = 244.2 Hz), 141.5, 141.4 (d, $^3J_{C\text{-}F}$ = 6.8 Hz), 131.2 (d, $^3J_{C\text{-}F}$ = 5.5 Hz), 128.5, 128.4, 126.0, 123.8 (d, $^4J_{C\text{-}F}$ = 3.2 Hz), 122.1 (d, $^2J_{C\text{-}F}$ = 17.2 Hz), 114.9 (d, $^2J_{C\text{-}F}$ = 21.8 Hz), 37.5, 37.2, 14.2 (d, $^3J_{C\text{-}F}$ = 3.5 Hz). **HRMS (ESI)** m/z calcd for $C_{15}H_{14}DFK$ $[M+K]^+$: 254.0867; found: 254.0866.



2-Chloro-1-methyl-4-(2-phenylethyl-2-d)benzene (10)

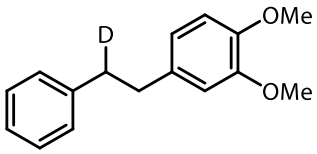
The title compound was synthesized following General Procedure A and purified by using silica gel chromatography to yield a yellow oil, 84 mg (73% yield). $\boldsymbol{R_f}$ = 0.7 (petroleum ether); 99% Deuterium incorporation was determined by ^{1}H NMR. **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ 7.33 (t, *J* = 7.5 Hz, 2H), 7.25 (d, *J* = 7.4 Hz, 1H), 7.23 – 7.19 (m, 3H), 7.16 (d, *J* = 7.7 Hz, 1H), 6.99 (d, *J* = 7.6 Hz, 1H), 2.95 – 2.88 (m, 3.01H), 2.38 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$, ppm) δ 141.4, 141.0, 134.1, 133.4,

130.8, 129.0, 128.5, 128.4, 126.8, 126.1, 37.8, 37.1, 19.6. **HRMS (ESI)** m/z calcd for $C_{15}H_{15}DCl$ $[M+H]^+$: 232.1013; found: 232.1019.



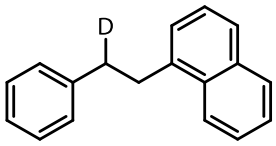
4-Chloro-1-methyl-2-(2-phenylethyl-2-d)benzene (11)

The title compound was synthesized following General Procedure A and purified by using silica gel chromatography to yield a yellow oil, 91 mg (79% yield). $\boldsymbol{R_f}$ = 0.7 (petroleum ether); 99% Deuterium incorporation was determined by ^{1}H NMR. **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ 7.34 (t, *J* = 7.5 Hz, 2H), 7.28 – 7.24 (m, 1H), 7.22 (d, *J* = 7.4 Hz, 2H), 7.17 (s, 1H), 7.14 – 7.08 (m, 2H), 2.91 – 2.86 (m, 3.01H), 2.27 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$, ppm) δ 141.8, 141.5, 134.4, 131.4, 128.7, 128.5, 128.4, 126.2, 126.0, 36.5, 35.2, 18.7. **HRMS (ESI)** m/z calcd for $C_{15}H_{15}DCl$ $[M+H]^+$: 232.1013; found: 232.1020.



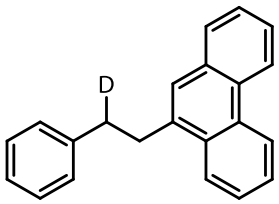
1,2-Dimethoxy-4-(2-phenylethyl-2-d)benzene (12)

The title compound was synthesized following General Procedure A and purified by using silica gel chromatography to yield a yellow oil, 104 mg (86% yield). $\boldsymbol{R_f}$ = 0.7 (petroleum ether/ethyl acetate = 20/1, v/v); 99% Deuterium incorporation was determined by ^{1}H NMR. **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ 7.31 (t, *J* = 7.5 Hz, 2H), 7.25 – 7.22 (m, 1H), 7.22 – 7.19 (m, 2H), 6.82 (d, *J* = 8.1 Hz, 1H), 6.76 (dd, *J* = 8.1, 1.8 Hz, 1H), 6.67 (d, *J* = 1.9 Hz, 1H), 3.89 (s, 3H), 3.86 (s, 3H), 2.93 – 2.88 (m, 3.01H). **^{13}C NMR** (126 MHz, $CDCl_3$, ppm) δ 148.7, 147.2, 141.7, 134.4, 128.6, 128.3, 125.9, 120.2, 111.9, 111.1, 55.9, 55.8, 38.2, 37.5. **HRMS (ESI)** m/z calcd for $C_{16}H_{17}DO_2K$ $[M+K]^+$: 282.1016; found: 282.1018.



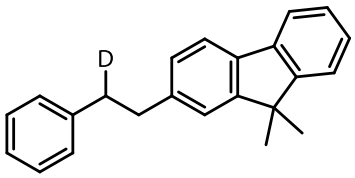
1-(2-Phenylethyl-2-d)naphthalene (13)

The title compound was synthesized following General Procedure A and purified by using silica gel chromatography to yield a yellow oil, 89 mg (76% yield). $\boldsymbol{R_f}$ = 0.6 (petroleum ether); 99% Deuterium incorporation was determined by ^{1}H NMR. **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ 8.14 (d, *J* = 8.4 Hz, 1H), 7.91 (d, *J* = 8.0 Hz, 1H), 7.77 (d, *J* = 8.2 Hz, 1H), 7.57 (t, *J* = 7.5 Hz, 1H), 7.53 (t, *J* = 7.4 Hz, 1H), 7.43 (t, *J* = 7.5 Hz, 1H), 7.38 – 7.33 (m, 3H), 7.31 – 7.25 (m, 3H), 3.41 (d, *J* = 8.3 Hz, 2H), 3.12 – 3.06 (m, 1.01H). **^{13}C NMR** (126 MHz, $CDCl_3$, ppm) δ 142.0, 137.8, 133.9, 131.8, 128.9, 128.5, 126.8, 126.0, 126.0, 125.9, 125.6, 125.5, 123.7, 36.8, 35.1. **HRMS (ESI)** m/z calcd for $C_{18}H_{15}DNa$ $[M+Na]^+$: 256.1222; found: 256.1221.



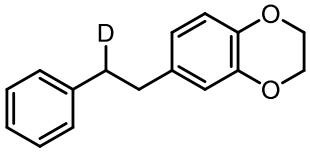
9-(2-Phenylethyl-2-d)phenanthrene (14)

The title compound was synthesized following General Procedure A and purified by using silica gel chromatography to yield a yellow solid, 83 mg (58% yield). $\boldsymbol{R_f}$ = 0.7 (petroleum ether/ethyl acetate = 20/1, v/v); 99% Deuterium incorporation was determined by ^{1}H NMR. **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ 8.81 – 8.78 (m, 1H), 8.70 (d, *J* = 8.1 Hz, 1H), 8.23 – 8.19 (m, 1H), 7.84 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.74 – 7.68 (m, 2H), 7.67 – 7.59 (m, 3H), 7.39 – 7.32 (m, 4H), 7.29 – 7.25 (m, 1H), 3.47 – 3.43 (m, 2.01H), 3.16 (q, *J* = 8.6 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$, ppm) δ 142.0, 135.9, 131.9, 131.1, 130.8, 129.7, 128.51, 128.47, 128.1, 126.7, 126.22, 126.21, 126.09, 126.07, 124.3, 123.3, 122.5, 36.6, 35.4. **HRMS (ESI)** m/z calcd for $C_{22}H_{18}D$ $[M+H]^+$: 284.1559; found: 284.1555.



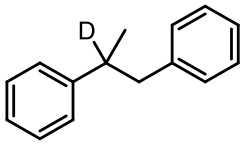
9,9-Dimethyl-2-(2-phenylethyl-2-d)-9H-fluorene (15)

The title compound was synthesized following General Procedure A and purified by using silica gel chromatography to yield a yellow oil, 102 mg (68% yield). $\boldsymbol{R_f}$ = 0.6 (petroleum ether/ethyl acetate = 20/1, v/v); 99% Deuterium incorporation was determined by ^{1}H NMR. **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ 7.73 (d, *J* = 7.2 Hz, 1H), 7.67 (d, *J* = 8.1 Hz, 1H), 7.46 (d, *J* = 7.2 Hz, 1H), 7.38 – 7.30 (m, 4H), 7.26 – 7.19 (m, 5H), 3.05 – 2.97 (m, 3.01H), 1.49 (s, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$, ppm) δ 153.8, 153.6, 141.8, 141.1, 139.3, 137.1, 128.6, 128.3, 127.3, 126.9, 126.8, 125.9, 122.9, 122.6, 119.8, 119.7, 46.7, 38.4, 38.3, 27.2. **HRMS (ESI)** m/z calcd for $C_{23}H_{22}D$ $[M+H]^+$: 300.1872; found: 300.1869.



6-(2-Phenylethyl-2-d)-2,3-dihydrobenzo[b][1,4]dioxine (16)

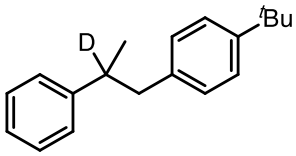
The title compound was synthesized following General Procedure A and purified by using silica gel chromatography to yield a yellow oil, 110 mg (91% yield). $\boldsymbol{R_f}$ = 0.5 (petroleum ether/ethyl acetate = 20/1, v/v); 99% Deuterium incorporation was determined by ^{1}H NMR. **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ 7.34 – 7.30 (m, 2H), 7.25 – 7.21 (m, 3H), 6.81 (d, *J* = 8.2 Hz, 1H), 6.75 (d, *J* = 2.0 Hz, 1H), 6.69 (dd, *J* = 8.2, 2.0 Hz, 1H), 4.27 (s, 4H), 2.93 – 2.87 (m, 1.01H), 2.87 – 2.83 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$, ppm) δ 143.3, 141.8, 141.7, 135.2, 128.5, 128.4, 125.9, 121.4, 117.03, 117.02, 64.5, 64.4, 38.1, 37.1. **HRMS (ESI)** m/z calcd for $C_{16}H_{16}DO_2$ $[M+H]^+$: 242.1301; found: 242.1294.



(Propane-1,2-diyl-2-d)dibenzene (17)

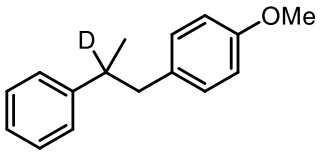
The title compound was synthesized following General Procedure A and purified by using silica gel chromatography to yield a yellow oil, 57 mg (58% yield). $\boldsymbol{R_f}$ = 0.6 (petroleum ether); 95% Deuterium incorporation was determined by ^{1}H NMR. **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ 7.32 (t, *J* = 7.6 Hz, 2H), 7.28 (t, *J* = 7.4 Hz, 2H), 7.25 – 7.19 (m, 4H), 7.12 (d, *J* = 7.2 Hz, 2H), 3.07 – 3.02 (m, 0.05H), 3.01 – 2.96 (m, 1H), 2.83 – 2.78 (m, 1H), 1.28 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$, ppm) δ 147.0, 140.8, 129.2, 128.3, 128.1, 127.1, 126.0, 125.9, 45.0, 41.9, 21.1.

The ^{1}H and ^{13}C NMR data were in accordance with those reported in the literature[9].



1-(tert-Butyl)-4-(2-phenylpropyl-2-d)benzene (18)

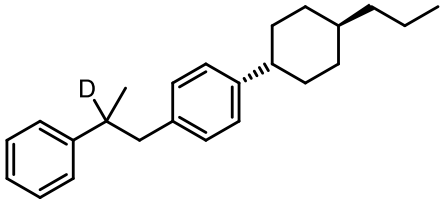
The title compound was synthesized following General Procedure A and purified by using silica gel chromatography to yield a yellow oil, 108 mg (85% yield). $\boldsymbol{R_f}$ = 0.6 (petroleum ether); 92% Deuterium incorporation was determined by ^{1}H NMR. **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ 7.37 – 7.31 (m, 4H), 7.31 – 7.22 (m, 3H), 7.11 (dd, *J* = 8.2, 2.0 Hz, 2H), 3.08 – 3.04 (m, 0.08H), 3.00 (d, *J* = 13.4 Hz, 1H), 2.77 (d, *J* = 13.5 Hz, 1H), 1.37 (d, 9H), 1.28 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$, ppm) δ 148.6, 147.4, 137.8, 128.8, 128.4, 127.1, 126.0, 125.0, 44.4, 41.8, 34.4, 31.5, 21.1. **HRMS (ESI)** m/z calcd for $C_{19}H_{23}DNa$ $[M+Na]^+$: 276.1838; found: 276.1835.



1-Methoxy-4-(2-phenylpropyl-2-d)benzene (19)

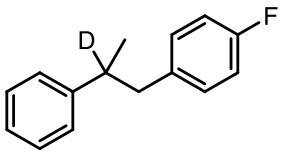
The title compound was synthesized following General Procedure A and purified by using silica gel chromatography to yield a yellow oil, 79 mg (71% yield). $\boldsymbol{R_f}$ = 0.6 (petroleum ether); 90% Deuterium incorporation was determined by ^{1}H NMR. **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ 7.32 (t, *J* = 7.7 Hz, 2H), 7.25 – 7.19 (m, 3H), 7.02 (dd, *J* = 8.5, 1.9 Hz, 2H), 6.82 (dd, *J* = 8.7, 2.1 Hz, 2H), 3.81 (s, 3H), 3.05 – 2.95 (m, 0.10H), 2.91 (d, *J* = 13.5 Hz, 1H), 2.75 (d, *J* = 13.5 Hz, 1H), 1.30 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$, ppm) δ 157.8, 147.1, 132.9, 130.1, 128.3, 127.1, 126.0, 113.5, 55.2, 44.1, 42.1, 21.0.

The ^{1}H and ^{13}C NMR data were in accordance with those reported in the literature[9].



1-(2-Phenylpropyl-2-d)-4-((1s,4r) -4-propylcyclohexyl)benzene (20)

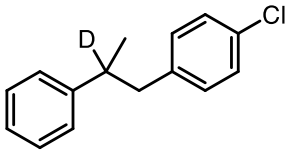
The title compound was synthesized following General Procedure A and purified by using silica gel chromatography to yield a yellow oil, 51 mg (32% yield). $\boldsymbol{R_f}$ = 0.6 (petroleum ether); 90% Deuterium incorporation was determined by ^{1}H NMR. **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ 7.32 (t, *J* = 7.6 Hz, 2H), 7.27 – 7.20 (m, 3H), 7.12 (d, *J* = 7.9 Hz, 2H), 7.05 (d, *J* = 7.9 Hz, 2H), 3.06 – 2.99 (m, 0.01H), 2.99 – 2.92 (m, 1H), 2.77 – 2.70 (m, 1H), 2.45 (tt, *J* = 12.2, 3.3 Hz, 1H), 2.05 – 1.84 (m, 4H), 1.51 – 1.42 (m, 2H), 1.42 – 1.35 (m, 2H), 1.35 – 1.28 (m, 2H), 1.25 (s, 3H), 1.24 – 1.19 (m, 1H), 1.07 (qd, *J* = 13.6, 3.8 Hz, 2H), 0.93 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$, ppm) δ 147.3, 145.4, 138.2, 129.0, 128.3, 127.0, 126.6, 126.0, 44.5, 44.2, 39.8, 37.1, 34.4, 33.6, 21.0, 20.1, 14.4. **HRMS (ESI)** m/z calcd for $C_{24}H_{31}DK$ $[M+K]^+$: 360.2204; found: 360.2204.



1-Fluoro-4-(2-phenylpropyl-2-d)benzene (21)

The title compound was synthesized following General Procedure A and purified by using silica gel chromatography to yield a Brown oil, 61 mg (56% yield). $\boldsymbol{R_f}$ = 0.6 (petroleum ether); 90% Deuterium incorporation was determined by ^{1}H NMR. **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ 7.32 (t, *J* = 7.5 Hz, 2H), 7.25 – 7.17 (m, 3H), 7.07 – 7.00 (m, 2H), 6.94 (tt, *J* = 8.7, 2.5 Hz, 2H), 3.04 – 2.96 (m, 0.10H), 2.95 – 2.90 (m, 1H), 2.83 – 2.78 (m, 1H), 1.28 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$, ppm) δ 161.3 (d, $^1J_{C\text{-}F}$ = 243.3 Hz), 146.5, 136.4 (d, $^4J_{C\text{-}F}$ = 3.2 Hz), 130.55 (d, $^3J_{C\text{-}F}$ = 7.8 Hz), 128.4, 127.1, 126.1, 114.8 (d, $^2J_{C\text{-}F}$ = 21.1 Hz), 44.1, 42.0, 21.1.

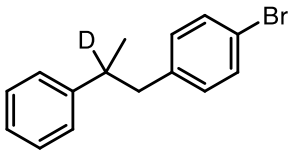
The ^{1}H and ^{13}C NMR data were in accordance with those reported in the literature[9].



1-Chloro-4-(2-phenylpropyl-2-d)benzene (22)

The title compound was synthesized following General Procedure A and purified by using silica gel chromatography to yield a yellow oil, 61 mg (53% yield). $\boldsymbol{R_f}$ = 0.6 (petroleum ether); 89% Deuterium incorporation was determined by ^{1}H NMR. **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ 7.33 (t, *J* = 7.5 Hz, 2H), 7.26 – 7.22 (m, 3H), 7.22 – 7.18 (m, 2H), 7.02 (d, *J* = 8.2 Hz, 2H), 3.07 – 2.96 (m, 0.11H), 2.96 – 2.90 (m, 1H), 2.83 – 2.78 (m, 1H), 1.29 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$, ppm) δ 146.4, 139.2, 131.6, 130.5, 128.4, 128.2, 127.0, 126.2, 44.3, 41.8, 21.1.

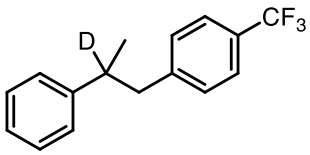
The ^{1}H and ^{13}C NMR data were in accordance with those reported in the literature[9].



1-Bromo-4-(2-phenylpropyl-2-d)benzene (23)

The title compound was synthesized following General Procedure A and purified by using silica gel chromatography to yield a yellow oil, 73 mg (53% yield). $\boldsymbol{R_f}$ = 0.6

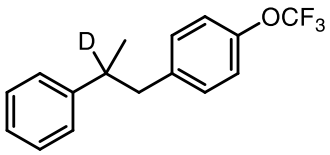
(petroleum ether); 91% Deuterium incorporation was determined by ^{1}H NMR. **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ 7.36 (dt, *J* = 8.3, 2.4 Hz, 2H), 7.31 (t, *J* = 7.7 Hz, 2H), 7.24 – 7.20 (m, 1H), 7.17 (d, *J* = 7.1 Hz, 2H), 6.95 (d, *J* = 8.2 Hz, 2H), 3.07 – 2.96 (m, 0.09H), 2.92 – 2.87 (m, 1H), 2.80 – 2.75 (m, 1H), 1.29 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$, ppm) δ 146.3, 139.7, 131.1, 130.9, 128.4, 127.0, 126.2, 119.7, 44.3, 41.8, 21.1. **HRMS (ESI)** m/z calcd for $C_{15}H_{14}DBrNa$ $[M+Na]^+$: 298.0318; found: 298.0313.



1-(2-Phenylpropyl-2-d)-4-(trifluoromethyl)benzene (24)

The title compound was synthesized following General Procedure A and purified by using silica gel chromatography to yield a Brown oil, 77 mg (58% yield). $\boldsymbol{R_f}$ = 0.6 (petroleum ether); 90% Deuterium incorporation was determined by ^{1}H NMR. **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ 7.50 (d, *J* = 7.8 Hz, 2H), 7.31 (t, *J* = 7.3 Hz, 2H), 7.22 (t, *J* = 7.5 Hz, 1H), 7.20 – 7.12 (m, 4H), 3.08 – 3.02 (m, 0.10H), 3.00 (d, *J* = 13.5 Hz, 1H), 2.87 (d, *J* = 13.3 Hz, 1H), 1.28 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$, ppm) δ 146.2, 144.9 (q, $^4J_{C\text{-}F}$ = 1.3 Hz), 129.4, 128.5, 128.2 (q, $^2J_{C\text{-}F}$ = 32.3 Hz), 127.0, 126.3, 125.0 (q, $^3J_{C\text{-}F}$ = 3.8 Hz), 124.4 (q, $^1J_{C\text{-}F}$ = 271.8 Hz), 44.7, 41.7, 21.2.

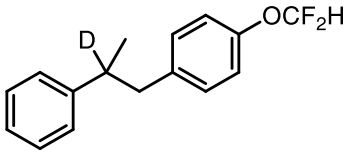
The ^{1}H and ^{13}C NMR data were in accordance with those reported in the literature[9].



1-(2-Phenylpropyl-2-d)-4-(trifluoromethoxy)benzene (25)

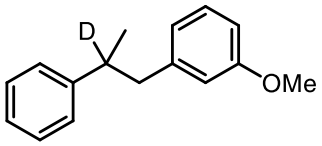
The title compound was synthesized following General Procedure A and purified by using silica gel chromatography to yield a yellow oil, 111 mg (79% yield). $\boldsymbol{R_f}$ = 0.6 (petroleum ether); 92% Deuterium incorporation was determined by ^{1}H NMR. **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ 7.36 – 7.30 (m, 2H), 7.26 – 7.23 (m, 1H), 7.23 –

7.18 (m, 2H), 7.15 – 7.08 (m, 4H), 3.04 – 3.00 (m, 0.08H), 3.00 – 2.93 (m, 1H), 2.87 – 2.80 (m, 1H), 1.30 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$, ppm) δ 147.5 (q, $^2J_{C\text{-}F}$ = 1.5 Hz), 146.4, 139.5, 130.3, 128.4, 127.0, 126.2, 120.6, 120.5 (q, $^1J_{C\text{-}F}$ = 256.4 Hz), 44.2, 41.9, 21.1. **HRMS (ESI)** m/z calcd for $C_{16}H_{14}DF_3ONa$ $[M+Na]^+$: 304.1035; found: 304.1029.



1-(Difluoromethoxy)-4-(2-phenylpropyl-2-d)benzene (26)

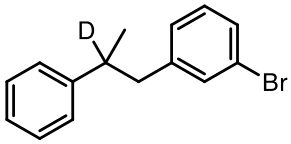
The title compound was synthesized following General Procedure A and purified by using silica gel chromatography to yield a yellow oil, 98 mg (75% yield). $\boldsymbol{R_f}$ = 0.5 (petroleum ether); 89% Deuterium incorporation was determined by ^{1}H NMR. **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ 7.33 (t, *J* = 7.4 Hz, 2H), 7.27 – 7.19 (m, 3H), 7.12 – 7.07 (m, 2H), 7.06 – 7.00 (m, 2H), 6.50 (t, *J* = 74.3 Hz, 1H), 3.06 – 2.99 (m, 0.11H), 2.96 (d, *J* = 13.5 Hz, 1H), 2.82 (d, *J* = 13.5 Hz, 1H), 1.30 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$, ppm) δ 149.5 (t, $^2J_{C\text{-}F}$ = 2.9 Hz), 146.5, 138.1, 130.4, 128.4, 127.1, 126.2, 119.2, 116.2 (t, $^1J_{C\text{-}F}$ = 258.8 Hz), 44.2, 41.9, 21.1. **HRMS (ESI)** m/z calcd for $C_{16}H_{14}DF_2ONa$ $[M+Na]^+$: 285.1051; found: 285.1059.



1-Methoxy-3-(2-phenylpropyl-2-d)benzene (27)

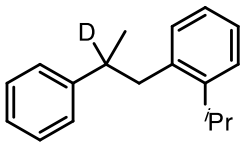
The title compound was synthesized following General Procedure A and purified by using silica gel chromatography to yield a yellow oil, 91 mg (80% yield). $\boldsymbol{R_f}$ = 0.6 (petroleum ether); 91% Deuterium incorporation was determined by ^{1}H NMR. **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ 7.40 – 7.30 (m, 2H), 7.28 – 7.22 (m, 3H), 7.22 – 7.18 (m, 1H), 6.80 – 6.71 (m, 2H), 6.66 (t, *J* = 2.1 Hz, 1H), 3.78 (s, 3H), 3.12 – 3.03 (m, 0.09H), 3.00 – 2.93 (m, 1H), 2.85 – 2.75 (m, 1H), 1.29 (s, 3H). **^{13}C NMR** (126

MHz, $CDCl_3$, ppm) δ 159.4, 147.0, 142.4, 129.0, 128.3, 127.1, 126.0, 121.6, 114.8, 111.3, 55.1, 45.0, 41.8, 21.1. **HRMS (ESI)** m/z calcd for $C_{16}H_{17}DONa$ $[M+Na]^+$: 250.1318; found: 250.1315.



1-Bromo-3-(2-phenylpropyl-2-d)benzene (28)

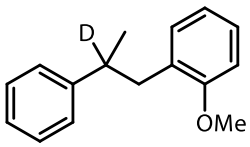
The title compound was synthesized following General Procedure A and purified by using silica gel chromatography to yield a yellow oil, 76 mg (55% yield). $\boldsymbol{R_f}$ = 0.6 (petroleum ether); 89% Deuterium incorporation was determined by ^{1}H NMR. **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ 7.35 – 7.31 (m, 3H), 7.26 – 7.19 (m, 3H), 7.13 (t, *J* = 7.8 Hz, 1H), 7.01 (d, *J* = 7.6 Hz, 1H), 3.06 – 2.98 (m, 0.11H), 2.96 – 2.91 (m, 1H), 2.80 – 2.76 (m, 1H), 1.28 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$, ppm) δ 146.4, 143.2, 132.1, 129.7, 129.0, 128.4, 127.8, 127.0, 126.2, 122.2, 44.6, 41.7, 21.0. **HRMS (ESI)** m/z calcd for $C_{15}H_{14}DBrK$ $[M+K]^+$: 314.0057; found: 314.0053.



1-Isopropyl-2-(2-phenylpropyl-2-d)benzene (29)

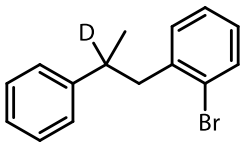
The title compound was synthesized following General Procedure A and purified by using silica gel chromatography to yield a yellow oil, 42 mg (35% yield). $\boldsymbol{R_f}$ = 0.7 (petroleum ether); 99% Deuterium incorporation was determined by ^{1}H NMR. **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ 7.37 – 7.33 (m, 2H), 7.31 (dd, *J* = 7.8, 1.1 Hz, 1H), 7.27 – 7.22 (m, 4H), 7.11 (td, *J* = 7.4, 1.3 Hz, 1H), 7.06 (dd, *J* = 7.6, 1.3 Hz, 1H), 3.36 – 3.31 (m, 0.01H), 3.25 – 3.18 (m, 1H), 3.03 (d, *J* = 13.7 Hz, 1H), 2.87 (d, *J* = 13.7 Hz, 1H), 1.33 (s, 3H), 1.28 (d, *J* = 6.9 Hz, 3H), 1.23 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$, ppm) δ 147.2, 147.0, 137.4, 130.5, 128.4, 127.0, 126.4, 126.1,

125.3, 125.2, 41.8, 28.7, 24.2, 24.1, 21.0. **HRMS (ESI)** m/z calcd for $C_{18}H_{21}DNa$ $[M+Na]^+$: 262.1682; found: 262.1675.



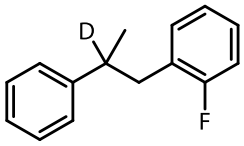
1-Methoxy-2-(2-phenylpropyl-2-d)benzene (30)

The title compound was synthesized following General Procedure A and purified by using silica gel chromatography to yield a yellow oil, 77 mg (68% yield). $\boldsymbol{R_f}$ = 0.7 (petroleum ether); 90% Deuterium incorporation was determined by ^{1}H NMR. **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ 7.34 – 7.27 (m, 3H), 7.27 – 7.21 (m, 2H), 7.20 – 7.17 (m, 1H), 7.00 (dd, *J* = 7.3, 1.4 Hz, 1H), 6.93 – 6.78 (m, 2H), 3.82 (s, 3H), 3.13 – 3.05 (m, 0.1H), 2.99 – 2.91 (m, 1H), 2.85 – 2.78 (m, 1H), 1.24 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$, ppm) δ 157.7, 147.6, 130.9, 129.3, 128.1, 127.1, 127.0, 125.8, 120.1, 110.2, 55.2, 39.9, 39.3, 20.9. **HRMS (ESI)** m/z calcd for $C_{16}H_{17}DONa$ $[M+Na]^+$: 250.1318; found: 250.1314.



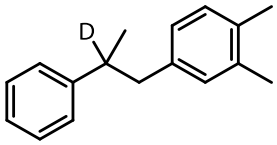
1-Bromo-2-(2-phenylpropyl-2-d)benzene (31)

The title compound was synthesized following General Procedure A and purified by using silica gel chromatography to yield a yellow oil, 79 mg (57% yield). $\boldsymbol{R_f}$ = 0.6 (petroleum ether); 88% Deuterium incorporation was determined by ^{1}H NMR. **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ 7.57 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.34 – 7.30 (m, 2H), 7.26 – 7.20 (m, 3H), 7.16 (td, *J* = 7.4, 1.3 Hz, 1H), 7.06 (td, *J* = 7.7, 1.8 Hz, 1H), 7.01 (dd, *J* = 7.5, 1.7 Hz, 1H), 3.22 – 3.14 (m, 0.12H), 3.07 – 3.02 (m, 1H), 2.99 – 2.94 (m, 1H), 1.30 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$, ppm) δ 146.6, 140.1, 132.8, 131.5, 128.3, 127.7, 127.0, 127.0, 126.1, 124.8, 45.1, 39.8, 20.7. **HRMS (ESI)** m/z calcd for $C_{15}H_{14}DBrNa$ $[M+Na]^+$: 298.0318; found: 298.0322.



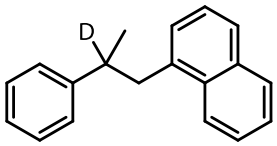
1-Fluoro-2-(2-phenylpropyl-2-d)benzene (32)

The title compound was synthesized following General Procedure A and purified by using silica gel chromatography to yield a yellow oil, 55 mg (51% yield). $\boldsymbol{R_f}$ = 0.6 (petroleum ether); 92% Deuterium incorporation was determined by ^{1}H NMR. **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ 7.33 – 7.29 (m, 2H), 7.27 – 7.13 (m, 4H), 7.08 – 6.96 (m, 3H), 3.12 – 3.05 (m, 0.08H), 2.99 – 2.92 (m, 1H), 2.91 – 2.85 (m, 1H), 1.29 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$, ppm) δ 161.3 (d, $^1J_{C\text{-}F}$ = 244.6 Hz), 146.7, 131.5 (d, $^3J_{C\text{-}F}$ = 5.1 Hz), 128.3, 127.7 (d, $^2J_{C\text{-}F}$ = 15.9 Hz), 127.6 (d, $^3J_{C\text{-}F}$ = 8.0 Hz), 127.0, 126.1, 123.6 (d, $^4J_{C\text{-}F}$ = 3.4 Hz), 115.1 (d, $^2J_{C\text{-}F}$ = 22.5 Hz), 40.6, 38.0, 20.9. **HRMS (ESI)** m/z calcd for $C_{15}H_{14}DFNa$ $[M+Na]^+$: 238.1118; found: 238.1113.



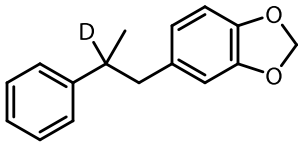
1,2-Dimethyl-4-(2-phenylpropyl-2-d)benzene (33)

The title compound was synthesized following General Procedure A and purified by using silica gel chromatography to yield a yellow oil, 45 mg (40% yield). $\boldsymbol{R_f}$ = 0.6 (petroleum ether); 95% Deuterium incorporation was determined by ^{1}H NMR. **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ 7.40 – 7.34 (m, 2H), 7.31 – 7.22 (m, 3H), 7.07 (d, *J* = 7.6 Hz, 1H), 6.96 (s, 1H), 6.93 – 6.86 (m, 1H), 3.05 (dd, *J* = 15.0, 6.7 Hz, 0.05H), 3.01 – 2.95 (m, 1H), 2.80 – 2.70 (m, 1H), 2.29 (s, 6H), 1.28 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$, ppm) δ 147.4, 138.3, 136.2, 133.9, 130.6, 129.4, 128.3, 127.1, 126.5, 126.0, 44.5, 41.9, 21.0, 19.8, 19.4. **HRMS (ESI)** m/z calcd for $C_{17}H_{19}DNa$ $[M+Na]^+$: 248.1525; found: 248.1524.



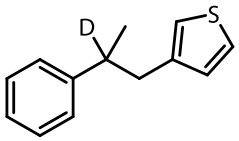
1-(2-Phenylpropyl-2-d)naphthalene (34)

The title compound was synthesized following General Procedure A and purified by using silica gel chromatography to yield a yellow oil, 64 mg (52% yield). $\boldsymbol{R_f}$ = 0.6 (petroleum ether); 99% Deuterium incorporation was determined by ^{1}H NMR. **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ 8.13 (d, *J* = 8.3 Hz, 1H), 7.92 (d, *J* = 7.7 Hz, 1H), 7.77 (d, *J* = 8.2 Hz, 1H), 7.60 – 7.56 (m, 1H), 7.56 – 7.51 (m, 1H), 7.41 – 7.34 (m, 3H), 7.31 – 7.25 (m, 3H), 7.23 (d, *J* = 6.9 Hz, 1H), 3.51 – 3.44 (m, 1.01H), 3.29 – 3.21 (m, 1H), 1.33 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$, ppm) δ 147.4, 136.9, 134.0, 132.1, 128.9, 128.5, 127.4, 127.0, 126.8, 126.2, 125.8, 125.4, 125.3, 124.0, 42.2, 40.8, 21.4. **HRMS (ESI)** m/z calcd for $C_{19}H_{17}DNa$ $[M+Na]^+$: 270.1369; found: 270.1371.



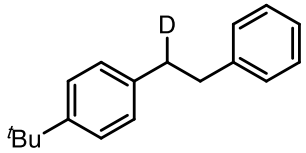
5-(2-Phenylpropyl-2-d)benzo[d][1,3]dioxole (35)

The title compound was synthesized following General Procedure A and purified by using silica gel chromatography to yield a yellow oil, 54 mg (45% yield). $\boldsymbol{R_f}$ = 0.6 (petroleum ether); 93% Deuterium incorporation was determined by ^{1}H NMR. **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ 7.34 – 7.29 (m, 2H), 7.24 – 7.19 (m, 3H), 6.71 (d, *J* = 7.9 Hz, 1H), 6.61 (d, *J* = 1.4 Hz, 1H), 6.55 (dd, *J* = 7.8, 1.4 Hz, 1H), 5.93 (s, 2H), 2.97 (dd, *J* = 14.5, 7.2 Hz, 0.07H), 2.91 – 2.85 (m, 1H), 2.77 – 2.69 (m, 1H), 1.25 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$, ppm) δ 147.3, 146.8, 145.6, 134.7, 128.3, 127.0, 126.1, 122.0, 109.5, 107.9, 100.7, 44.6, 42.1, 21.0. **HRMS (ESI)** m/z calcd for $C_{16}H_{15}DO_2Na$ $[M+Na]^+$: 264.1111; found: 264.1109.



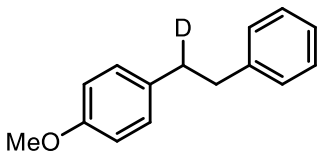
3-(2-Phenylpropyl-2-d)thiophene (36)

The title compound was synthesized following General Procedure A and purified by using silica gel chromatography to yield a yellow oil, 52 mg (51% yield). $\boldsymbol{R_f}$ = 0.6 (petroleum ether); 90% Deuterium incorporation was determined by ^{1}H NMR. **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ 7.33 – 7.29 (m, 2H), 7.27 – 7.16 (m, 4H), 7.04 – 6.67 (m, 2H), 3.06 – 3.00 (m, 0.1H), 2.99 – 2.94 (m, 1H), 2.90 – 2.84 (m, 1H), 1.28 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$, ppm) δ 146.9, 141.1, 128.6, 128.3, 127.0, 126.1, 124.9, 121.2, 39.1, 29.7, 21.4. **HRMS (ESI)** m/z calcd for $C_{13}H_{13}DSNa$ $[M+Na]^+$: 226.0777; found: 226.0785.



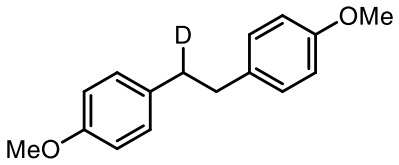
1-(tert-Butyl)-4-(2-phenylethyl-1-d)benzene (37)

The title compound was synthesized following General Procedure A and purified by using silica gel chromatography to yield a yellow oil, 112 mg (94% yield). $\boldsymbol{R_f}$ = 0.7 (petroleum ether); 97% Deuterium incorporation was determined by ^{1}H NMR. **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ 7.41 – 7.33 (m, 4H), 7.30 – 7.24 (m, 3H), 7.22 (d, *J* = 8.2 Hz, 2H), 3.02 – 2.89 (m, 3.03H), 1.38 (s, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$, ppm) δ 148.8, 142.1, 138.8, 128.5, 128.4, 128.1, 125.9, 125.3, 37.9, 37.5, 34.4, 31.5. The ^{1}H and ^{13}C NMR data were in accordance with those reported in the literature[6].



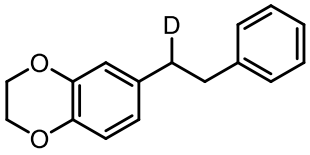
1-Methoxy-4-(2-phenylethyl-1-d)benzene (38)

The title compound was synthesized following General Procedure A and purified by using silica gel chromatography to yield a yellow oil, 88 mg (83% yield). $\boldsymbol{R_f}$ = 0.7 (petroleum ether); 99% Deuterium incorporation was determined by ^{1}H NMR. **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ 7.33 (t, *J* = 7.5 Hz, 2H), 7.26 – 7.20 (m, 3H), 7.14 (dt, *J* = 8.6, 2.8 Hz, 2H), 6.88 (dt, *J* = 8.6, 2.6 Hz, 2H), 3.84 (s, 3H), 2.95 – 2.86 (m, 3.01H). **^{13}C NMR** (126 MHz, $CDCl_3$, ppm) δ 157.9, 141.9, 133.9, 129.4, 128.5, 128.3, 125.9, 113.8, 55.3, 38.2, 37.1. The ^{1}H and ^{13}C NMR data were in accordance with those reported in the literature[8].



4,4'-(Ethane-1,2-diyl-1-d)bis(methoxybenzene) (39)

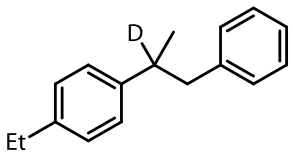
The title compound was synthesized following General Procedure A and purified by using silica gel chromatography to yield a yellow oil, 92 mg (76% yield). $\boldsymbol{R_f}$ = 0.6 (petroleum ether); 99 % Deuterium incorporation was determined by ^{1}H NMR. **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ 7.15 – 7.09 (m, 4H), 6.90 – 6.82 (m, 4H), 3.82 (s, 6H), 2.87 – 2.83 (m, 3.01H). **^{13}C NMR** (126 MHz, $CDCl_3$, ppm) δ 157.8, 134.0, 129.4, 113.7, 55.3, 37.3, 37.2. **HRMS (ESI)** m/z calcd for $C_{16}H_{18}DO_2$ $[M+H]^+$: 244.1448; found: 244.1442.



6-(2-Phenylethyl-1-d)-2,3-dihydrobenzo[b][1,4]dioxine (40)

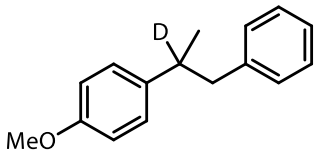
The title compound was synthesized following General Procedure A and purified by using silica gel chromatography to yield a yellow oil, 117 mg (97% yield). $\boldsymbol{R_f}$ = 0.5 (petroleum ether/ethyl acetate = 20/1, v/v); 99% Deuterium incorporation was determined by ^{1}H NMR. **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ 7.31 (t, *J* = 7.6 Hz, 2H), 7.24 – 7.19 (m, 3H), 6.80 (d, *J* = 8.2 Hz, 1H), 6.74 (s, 1H), 6.68 (d, *J* = 8.2 Hz, 1H),

4.27 (s, 4H), 2.92 – 2.88 (m, 2.01H), 2.86 – 2.80 (m, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$, ppm) δ 143.3, 141.8, 141.7, 135.2, 128.4, 128.3, 125.9, 121.4, 117.0, 64.44, 64.35, 38.0, 37.0. **HRMS (ESI)** m/z calcd for $C_{16}H_{16}DO_2$ $[M+H]^+$: 242.1301; found: 242.1292.



1-Ethyl-4-(1-phenylpropan-2-yl-2-d)benzene (41)

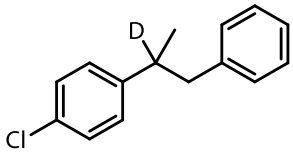
The title compound was synthesized following General Procedure A and purified by using silica gel chromatography to yield a yellow oil, 68 mg (61% yield). $\boldsymbol{R_f}$ = 0.7 (petroleum ether); 93% Deuterium incorporation was determined by ^{1}H NMR. **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ 7.29 – 7.25 (m, 3H), 7.19 (t, *J* = 7.2 Hz, 1H), 7.15 – 7.14 (m, 3H), 7.13 (d, *J* = 7.5 Hz, 2H), 3.04 – 3.00 (m, 0.07H), 3.00 – 2.95 (m, 1H), 2.78 – 2.72 (m, 1H), 2.65 (q, *J* = 7.6 Hz, 2H), 1.26 (t, *J* = 7.5 Hz, 3H), 1.23 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$, ppm) δ 144.3, 141.8, 141.0, 129.2, 128.1, 127.8, 126.9, 125.8, 45.0, 41.4, 28.4, 21.0, 15.6. **HRMS (ESI)** m/z calcd for $C_{17}H_{19}DNa$ $[M+Na]^+$: 248.1525; found: 248.1528.



1-Methoxy-4-(1-phenylpropan-2-yl-2-d)benzene (42)

The title compound was synthesized following General Procedure A and purified by using silica gel chromatography to yield a yellow oil, 68 mg (60% yield). $\boldsymbol{R_f}$ = 0.7 (petroleum ether); 89% Deuterium incorporation was determined by ^{1}H NMR. **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ 7.28 – 7.24 (m, 2H), 7.21 – 7.17 (m, 1H), 7.16 – 7.12 (m, 2H), 7.12 – 7.09 (m, 2H), 6.86 (dt, *J* = 8.7, 2.6 Hz, 2H), 3.82 (s, 3H), 3.02 – 2.97 (m, 0.11H), 2.96 – 2.90 (m, 1H), 2.80 – 2.75 (m, 1H), 1.24 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$, ppm) δ 157.8, 140.9, 139.1, 129.2, 128.1, 127.9, 125.8, 113.7,

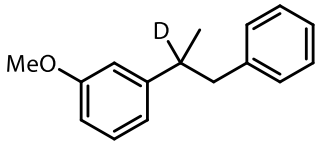
55.3, 45.2, 41.0, 21.3. **HRMS (ESI)** m/z calcd for $C_{16}H_{17}DONa$ $[M+Na]^+$: 250.1318; found: 250.1314.



1-Chloro-4-(1-phenylpropan-2-yl-2-d)benzene (43)

The title compound was synthesized following General Procedure A and purified by using silica gel chromatography to yield a yellow oil, 58 mg (51% yield). $\boldsymbol{R_f}$ = 0.7 (petroleum ether); 92% Deuterium incorporation was determined by ^{1}H NMR. **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ 7.28 – 7.24 (m, 4H), 7.21 – 7.18 (m, 1H), 7.15 – 7.10 (m, 2H), 7.07 (d, *J* = 7.2 Hz, 2H), 3.02 (q, *J* = 7.2 Hz, 0.08H), 2.95 – 2.87 (m, 1H), 2.85 – 2.73 (m, 1H), 1.26 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$, ppm) δ 145.3, 140.4, 131.6, 129.1, 128.4, 128.4, 128.2, 126.0, 44.9, 41.4, 21.2.

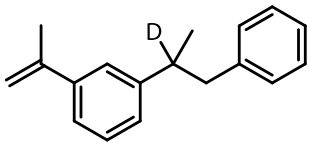
The ^{1}H and ^{13}C NMR data were in accordance with those reported in the literature[10].



1-Methoxy-3-(1-phenylpropan-2-yl-2-d)benzene (44)

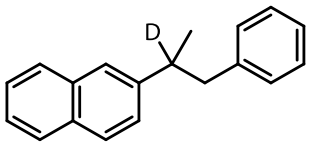
The title compound was synthesized following General Procedure A and purified by using silica gel chromatography to yield a yellow oil, 67 mg (60% yield). $\boldsymbol{R_f}$ = 0.7 (petroleum ether); 92% Deuterium incorporation was determined by ^{1}H NMR. **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ 7.28 – 7.17 (m, 4H), 7.12 (d, *J* = 7.1 Hz, 2H), 6.82 (d, *J* = 7.7 Hz, 1H), 6.78 – 6.75 (m, 2H), 3.81 (s, 3H), 3.04 – 3.00 (m, 0.08H), 2.99 – 2.95 (m, 1H), 2.81 – 2.75 (m, 1H), 1.25 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$, ppm) δ 159.6, 148.7, 140.8, 129.3, 129.2, 128.1, 125.9, 119.5, 113.0, 111.1, 55.2, 44.9, 41.9, 21.0.

The ^{1}H and ^{13}C NMR data were in accordance with those reported in the literature[10].



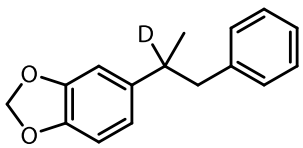
1-(1-Phenylpropan-2-yl-2-d)-3-(prop-1-en-2-yl)benzene (45)

The title compound was synthesized following General Procedure A and purified by using silica gel chromatography to yield a yellow oil, 76 mg (64% yield). $\boldsymbol{R_f}$ = 0.6 (petroleum ether); 88% Deuterium incorporation was determined by ^{1}H NMR. **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ 7.35 – 7.32 (m, 1H), 7.31 – 7.26 (m, 4H), 7.23 – 7.18 (m, 1H), 7.17 – 7.11 (m, 3H), 5.36 (s, 1H), 5.11 – 5.09 (m, 1H), 3.09 – 3.03 (m, 0.12H), 3.01 – 2.95 (m, 1H), 2.84 – 2.78 (m, 1H), 2.18 (s, 3H), 1.28 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$, ppm) δ 146.8, 143.6, 141.2, 140.8, 129.2, 128.2, 128.1, 126.1, 125.9, 124.4, 123.3, 112.3, 45.0, 42.0, 21.9, 21.0. **HRMS (ESI)** m/z calcd for $C_{18}H_{20}D$ $[M+H]^+$: 238.1706; found: 238.1704.



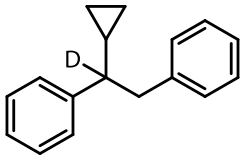
2-(1-Phenylpropan-2-yl-2-d)naphthalene (46)

The title compound was synthesized following General Procedure A and purified by using silica gel chromatography to yield a yellow oil, 74 mg (60% yield). $\boldsymbol{R_f}$ = 0.6 (petroleum ether); 90% Deuterium incorporation was determined by ^{1}H NMR. **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ 7.84 (s, 3H), 7.67 (s, 1H), 7.47 (d, *J* = 28.0 Hz, 3H), 7.34 – 7.11 (m, 5H), 3.24 (s, 0.10H), 3.11 (d, *J* = 8.9 Hz, 1H), 2.93 (d, *J* = 8.9 Hz, 1H), 1.39 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$, ppm) δ 144.5, 140.8, 133.7, 132.3, 129.2, 128.2, 127.9, 127.7, 127.6, 126.0, 125.9, 125.9, 125.2, 125.2, 44.9, 42.0, 21.2. **HRMS (ESI)** m/z calcd for $C_{19}H_{17}DNa$ $[M+Na]^+$: 270.1369; found: 270.1367.



5-(1-Phenylpropan-2-yl-2-d)benzo[d][1,3]dioxole (47)

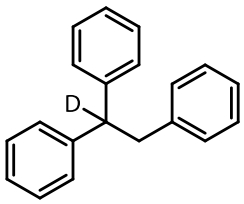
The title compound was synthesized following General Procedure A and purified by using silica gel chromatography to yield a Brown oil, 102 mg (85% yield). $\boldsymbol{R_f}$ = 0.6 (petroleum ether); 89% Deuterium incorporation was determined by ^{1}H NMR. **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ 7.28 – 7.24 (m, 2H), 7.23 – 7.16 (m, 1H), 7.10 (d, *J* = 7.1 Hz, 2H), 6.75 – 6.72 (m, 2H), 6.63 (dd, *J* = 8.0, 1.6 Hz, 1H), 5.95 (q, *J* = 1.4 Hz, 2H), 2.98 – 2.94 (m, 0.11H), 2.93 – 2.88 (m, 1H), 2.78 – 2.73 (m, 1H), 1.22 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$, ppm) δ 147.5, 145.6, 141.0, 140.7, 129.1, 128.1, 125.9, 119.9, 108.0, 107.4, 100.8, 45.1, 41.7, 21.4. **HRMS (ESI)** m/z calcd for $C_{16}H_{15}DO_2Na$ $[M+Na]^+$: 264.1111; found: 264.1114.



(1-Cyclopropylethane-1,2-diyl-1-d)dibenzene (48)

The title compound was synthesized following General Procedure A and purified by using silica gel chromatography to yield a yellow oil, 75 mg (67% yield). $\boldsymbol{R_f}$ = 0.6 (petroleum ether); 91% Deuterium incorporation was determined by ^{1}H NMR. **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ 7.34 – 7.29 (m, 2H), 7.26 – 7.22 (m, 3H), 7.21 – 7.16 (m, 3H), 7.07 (d, *J* = 7.0 Hz, 2H), 3.18 – 3.12 (m, 1H), 3.10 – 3.04 (m, 1H), 2.84 (q, *J* = 7.1 Hz, 0.09H), 1.17 – 1.06 (m, 1H), 0.65 – 0.54 (m, 1H), 0.48 – 0.41 (m, 1H), 0.16 – 0.09 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$, ppm) δ 145.1, 140.6, 129.4, 128.1, 127.9, 127.8, 126.1, 125.7, 53.1, 43.4, 16.8, 5.8, 3.8.

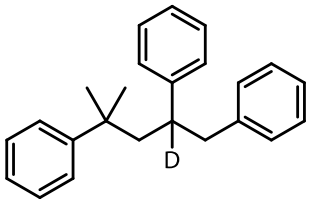
^{1}H and ^{13}C NMR data were in accordance with those reported in the literature[11].



(Ethane-1,1,2-triyl-1-d)tribenzene (49)

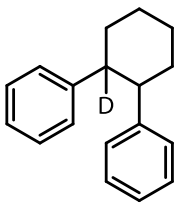
The title compound was synthesized following General Procedure A and purified by using silica gel chromatography to yield a yellow oil, 59 mg (45% yield). $\boldsymbol{R_f}$ = 0.5 (petroleum ether); 86% Deuterium incorporation was determined by ^{1}H NMR. **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ 7.38 – 7.29 (m, 8H), 7.29 – 7.23 (m, 4H), 7.21 (t, *J* = 7.2 Hz, 1H), 7.14 – 7.07 (m, 2H), 4.33 (t, *J* = 7.8 Hz, 0.14H), 3.46 (s, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$, ppm) δ 144.5, 144.5, 140.3, 129.1, 128.4, 128.1, 126.3, 126.0, 53.2, 42.1.

^{1}H and ^{13}C NMR data were in accordance with those reported in the literature[10].



(4-Methylpentane-1,2,4-triyl-2-d)tribenzene (50)

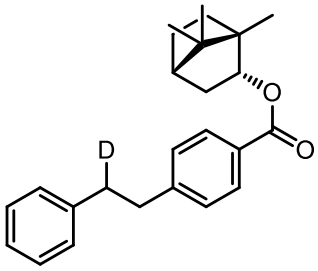
The title compound was synthesized following General Procedure A and purified by using silica gel chromatography to yield a yellow oil, 100 mg (64% yield). $\boldsymbol{R_f}$ = 0.6 (petroleum ether); 93% Deuterium incorporation was determined by ^{1}H NMR. **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ 7.28 – 7.23 (m, 2H), 7.21 – 7.10 (m, 9H), 6.98 (d, *J* = 7.1 Hz, 2H), 6.83 (d, *J* = 6.6 Hz, 2H), 2.73 – 2.61 (m, 2.07H), 2.16 – 2.07 (m, 2H), 1.21 (s, 3H), 1.09 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$, ppm) δ 149.0, 146.7, 140.5, 129.2, 128.1, 127.8, 127.9, 127.9, 126.0, 125.6, 125.7, 125.4, 49.3, 45.8, 44.9, 38.4, 31.3, 27.9. **HRMS (ESI)** m/z calcd for $C_{24}H_{25}DK$ $[M+K]^+$: 354.1734; found: 354.1730.



(Cyclohexane-1,2-diyl-1-d)dibenzene (51)

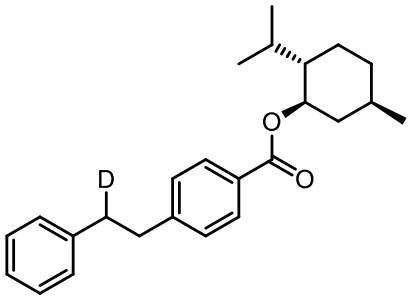
The title compound was synthesized following General Procedure A and purified by using silica gel chromatography to yield a yellow oil, 46 mg (39% yield). $\boldsymbol{R_f}$ = 0.6

(petroleum ether); 97 % Deuterium incorporation was determined by ^{1}H NMR. **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ 7.14 – 7.08 (m, 6H), 7.01 – 6.98 (m, 4H), 3.25 – 3.21 (m, 1.03H), 2.14 – 2.09 (m, 2H), 2.04 – 1.98 (m, 2H), 1.96 – 1.89 (m, 2H), 1.71 – 1.64 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$, ppm) δ 144.5, 144.5, 128.8, 128.8, 127.5, 125.5, 46.8, 46.7, 29.2, 29.1, 24.4, 24.3. **HRMS (ESI)** m/z calcd for $C_{18}H_{19}DNa$ $[M+Na]^+$: 260.1525; found: 260.1528.



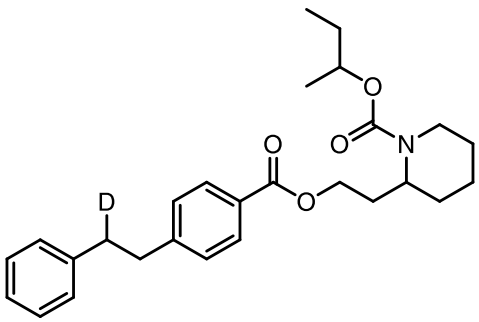
(1S,2R,4S)-1,7,7-Trimethylbicyclo[2.2.1]heptan-2-yl 4-(2-phenylethyl-2-d)benzoate (52)

The title compound was synthesized following General Procedure A and purified by using silica gel chromatography to yield a yellow oil, 111 mg (61% yield). R_f = 0.6 (petroleum ether/ethyl acetate = 10/1, v/v); 99% Deuterium incorporation was determined by ^{1}H NMR. **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ 8.01 (dt, *J* = 8.2, 2.0 Hz, 2H), 7.34 – 7.30 (m, 2H), 7.29 – 7.26 (m, 2H), 7.26 – 7.23 (m, 1H), 7.22 – 7.19 (m, 2H), 5.15 (ddd, *J* = 9.9, 3.5, 2.1 Hz, 1H), 3.05 – 3.00 (m, 2.01H), 2.96 (q, *J* = 7.2 Hz, 1H), 2.55 – 2.48 (m, 1H), 2.18 (ddd, *J* = 13.4, 9.5, 4.4 Hz, 1H), 1.84 (ddt, *J* = 11.9, 7.9, 3.8 Hz, 1H), 1.77 (t, *J* = 4.5 Hz, 1H), 1.44 (ddt, *J* = 12.0, 10.0, 2.2 Hz, 1H), 1.36 – 1.33 (m, 1H), 1.16 (dd, *J* = 13.8, 3.5 Hz, 1H), 1.01 (s, 3H), 0.96 (s, 3H), 0.95 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$, ppm) δ 166.9, 147.0, 141.2, 129.7, 128.7, 128.5, 128.5, 128.4, 126.1, 80.4, 49.1, 47.9, 45.0, 37.8, 37.0, 28.1, 27.4, 19.8, 19.0, 13.7. **HRMS (ESI)** m/z calcd for $C_{25}H_{30}DO_2$ $[M+H]^+$: 364.2396; found: 364.2388.



(1R,2S,5R)-2-Isopropyl-5-methylcyclohexyl 4-(2-phenylethyl-2-d)benzoate (53)

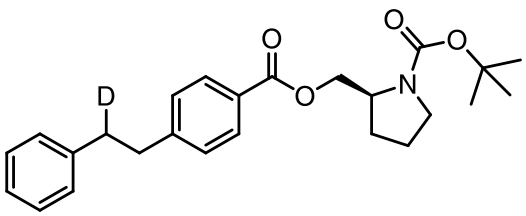
The title compound was synthesized following General Procedure A and purified by using silica gel chromatography to yield a colorless oil, 113 mg (62% yield). $\boldsymbol{R_f}$ = 0.6 (petroleum ether/ethyl acetate = 10/1, v/v); 99% Deuterium incorporation was determined by ^{1}H NMR. **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ 7.98 (dt, *J* = 8.2, 1.9 Hz, 2H), 7.33 – 7.29 (m, 2H), 7.27 – 7.22 (m, 3H), 7.22 – 7.19 (m, 2H), 4.95 (dt, *J* = 10.9, 5.4 Hz, 1H), 3.03 – 2.98 (m, 2.01H), 2.97 – 2.92 (m, 1H), 2.17 – 2.13 (m, 1H), 1.99 (ddt, *J* = 11.2, 6.9, 4.2 Hz, 1H), 1.75 (dt, *J* = 12.2, 2.8 Hz, 2H), 1.60 – 1.54 (m, 2H), 1.21 – 1.11 (m, 2H), 0.96 – 0.93 (m, 6H), 0.82 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$, ppm) δ 166.2, 147.0, 141.2, 129.7, 128.6, 128.5, 128.5, 128.4, 126.1, 74.7, 47.3, 41.0, 37.8, 34.4, 31.5, 26.5, 23.6, 22.1, 20.8, 16.5. **HRMS (ESI)** m/z calcd for $C_{25}H_{31}DO_2Na$ $[M+Na]^+$: 388.2363; found: 388.2368.



sec-Butyl 2-(2-((4-(2-phenylethyl-2-d)benzoyl)oxy)ethyl)piperidine-1-carboxylate (54)

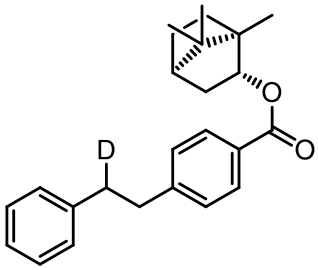
The title compound was synthesized following General Procedure A and purified by using silica gel chromatography to yield a colorless oil, 97 mg (44% yield). $\boldsymbol{R_f}$ = 0.5 (petroleum ether/ethyl acetate = 10/1, v/v); 99% Deuterium incorporation was determined by ^{1}H NMR. **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ 7.97 (d, *J* = 8.1 Hz, 2H),

7.33 – 7.28 (m, 2H), 7.27 – 7.20 (m, 3H), 7.20 – 7.13 (m, 2H), 4.77 (dtd, *J* = 12.5, 6.3, 2.2 Hz, 1H), 4.55 (s, 1H), 4.33 (q, *J* = 6.3 Hz, 2H), 4.15 – 4.05 (m, 1H), 3.04 – 2.97 (m, 2.01H), 2.97 – 2.92 (m, 1H), 2.89 (t, *J* = 12.3 Hz, 1H), 2.27 – 2.20 (m, 1H), 1.96 – 1.88 (m, 1H), 1.71 – 1.61 (m, 6H), 1.60 – 1.45 (m, 3H), 1.20 (d, *J* = 6.3 Hz, 2H), 0.90 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$, ppm) δ 166.6, 155.5, 147.2, 141.1, 129.7, 128.5, 128.5, 128.4, 128.1, 126.1, 73.0, 62.5, 48.0, 39.0, 37.8, 37.5, 29.1, 28.9, 28.6, 25.5, 19.8, 19.1, 9.8. **HRMS (ESI)** m/z calcd for $C_{27}H_{34}DNO_4Na$ $[M+Na]^+$: 461.2527; found: 461.2532.



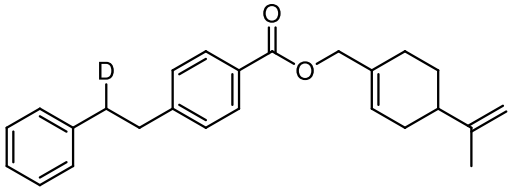
tert-Butyl (2S)-2-(((4-(2-phenylethyl-2-d)benzoyl)oxy)methyl)pyrrolidine-1-carboxylate (55)

The title compound was synthesized following General Procedure A and purified by using silica gel chromatography to yield a colorless oil, 107 mg (52% yield). R_f = 0.5 (petroleum ether/ethyl acetate = 10/1, v/v); 99% Deuterium incorporation was determined by ^{1}H NMR. **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ 8.06 (d, *J* = 7.7 Hz, 2H), 7.96 (d, *J* = 7.9 Hz, 1H), 7.65 – 7.51 (m, 1H), 7.48 – 7.46 (m, 1H), 7.35 – 7.26 (m, 2H), 7.24 (d, *J* = 8.4 Hz, 1H), 7.17 (d, *J* = 7.2 Hz, 1H), 4.45 – 4.35 (m, 2H), 4.31 – 4.26 (m, 1H), 4.18 – 4.08 (m, 1H), 3.52 – 3.37 (m, 3H), 3.08 – 2.89 (m, 1.01H), 2.00 – 1.89 (m, 4H), 1.49 (s, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$, ppm) δ 166.4, 154.5, 133.1, 129.8, 129.6, 128.6, 128.4, 128.4, 126.1, 79.8, 65.3, 55.7, 46.5, 37.8, 37.5, 28.5, 23.9, 23.1. **HRMS (ESI)** m/z calcd for $C_{25}H_{30}DNO_4Na$ $[M+Na]^+$: 433.2208; found: 433.2199.



(1R,2R,4R)-1,7,7-Trimethylbicyclo[2.2.1]heptan-2-yl 4-(2-phenylethyl-2-d)benzoate (56)

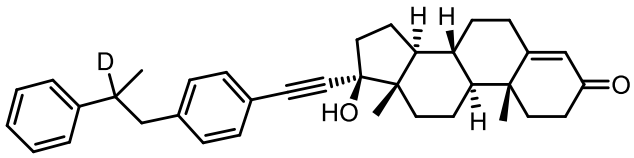
The title compound was synthesized following General Procedure A and purified by using silica gel chromatography to yield a colorless oil, 116 mg (64% yield). $\boldsymbol{R_f}$ = 0.6 (petroleum ether/ethyl acetate = 10/1, v/v); 99% Deuterium incorporation was determined by ^{1}H NMR. **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ 7.97 – 7.93 (m, 2H), 7.33 – 7.29 (m, 2H), 7.27 – 7.22 (m, 3H), 7.21 – 7.18 (m, 2H), 4.94 (dd, *J* = 7.3, 4.2 Hz, 1H), 3.04 – 2.98 (m, 2.01H), 2.97 – 2.92 (m, 1H), 1.97 – 1.90 (m, 2H), 1.83 (t, *J* = 3.9 Hz, 1H), 1.80 – 1.74 (m, 1H), 1.62 (dd, *J* = 12.0, 4.1 Hz, 1H), 1.26 (dd, *J* = 9.3, 3.7 Hz, 1H), 1.20 – 1.17 (m, 1H), 1.15 (s, 3H), 0.96 (s, 3H), 0.92 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$, ppm) δ 166.1, 147.0, 141.2, 129.6, 128.7, 128.5, 128.4, 128.4, 126.1, 81.4, 49.0, 47.1, 45.1, 39.0, 37.8, 37.5, 33.8, 27.1, 20.2, 20.1, 11.6. **HRMS (ESI)** m/z calcd for $C_{25}H_{29}DO_2Na$ $[M+Na]^+$: 386.2200; found: 386.2191.



(4-(Prop-1-en-2-yl)cyclohexyl-1,2-d2)methyl 4-(2-phenylethyl-2-d)benzoate (57)

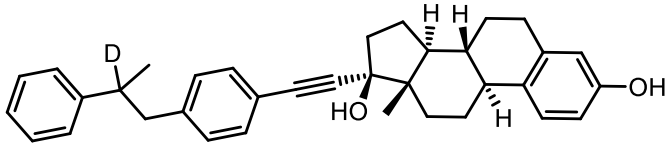
The title compound was synthesized following General Procedure A and purified by using silica gel chromatography to yield a colorless oil, 77 mg (43% yield). $\boldsymbol{R_f}$ = 0.5 (petroleum ether/ethyl acetate = 10/1, v/v); 99% Deuterium incorporation was determined by ^{1}H NMR. **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ 8.10 – 8.07 (m, 2H), 7.84 – 7.81 (m, 3H), 7.80 – 7.77 (m, 2H), 7.47 (dt, *J* = 7.5, 3.6 Hz, 2H), 5.90 – 5.83 (m, 2H), 4.79 – 4.70 (m, 5H), 4.00 – 3.91 (m, 1.01H), 2.23 – 2.16 (m, 3H), 2.07 –

1.98 (m, 2H), 1.94 – 1.86 (m, 2H), 1.77 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$, ppm) δ 166.0, 149.6, 137.7, 132.9, 132.5, 131.1, 129.6, 128.4, 128.3, 126.0, 125.7, 108.9, 100.7, 69.2, 68.9, 40.9, 40.8, 30.5, 27.3, 26.5, 20.8. **HRMS (ESI)** m/z calcd for $C_{25}H_{27}DO_2Na$ $[M+Na]^+$: 384.2044; found: 384.2052.



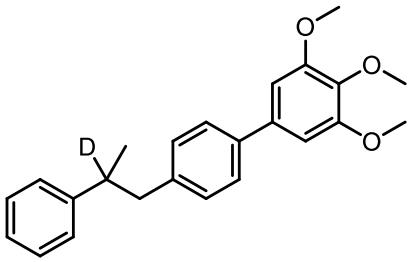
(8R,9S,13S,14S,17S)-17-Hydroxy-10,13-dimethyl-17-((4-(2-phenylpropyl-2-d)phenyl)ethynyl)-1,2,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-3H-cyclopenta[a]phenanthren-3-one (58)

The title compound was synthesized following General Procedure B and purified by using silica gel chromatography to yield a White flocculent solid, 198 mg (78% yield), mp: 187–188 °C. R_f = 0.8 (petroleum ether/ethyl acetate = 20/1, v/v); 91% Deuterium incorporation was determined by ^{1}H NMR. **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ 7.31 – 7.27 (m, 4H), 7.22 – 7.15 (m, 3H), 7.02 (d, *J* = 8.1 Hz, 2H), 5.76 (s, 1H), 3.02 – 2.98 (m, 0.09H), 2.95 – 2.91 (m, 1H), 2.82 – 2.78 (m, 1H), 2.47 – 2.35 (m, 4H), 2.33 – 2.28 (m, 1H), 2.15 – 2.00 (m, 3H), 1.90 – 1.85 (m, 1H), 1.83 – 1.64 (m, 6H), 1.63 – 1.54 (m, 2H), 1.49 – 1.39 (m, 2H), 1.25 (s, 3H), 1.23 (s, 3H), 1.12 – 1.06 (m, 1H), 0.96 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$, ppm) δ 199.6, 171.3, 146.4, 141.3, 131.4, 129.1, 128.3, 127.0, 126.1, 123.9, 120.2, 91.9, 86.2, 80.1, 53.5, 50.1, 47.1, 44.8, 41.8, 39.0, 38.7, 36.3, 35.7, 34.0, 32.8, 32.8, 31.5, 23.2, 21.2, 20.8, 17.5, 12.9. **HRMS (ESI)** m/z calcd for $C_{36}H_{41}DO_2Na$ $[M+Na]^+$: 530.3145; found: 530.3149.



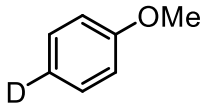
(8R,9S,13S,14S,17S)-13-Methyl-17-((4-(2-phenylpropyl-2-d)phenyl)ethynyl)-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthrene-3,17-diole (59)

The title compound was synthesized following General Procedure B and purified by using silica gel chromatography to yield a Brown flocculent solid, 204 mg (83% yield), mp: 96–97 °C. R_f = 0.5 (petroleum ether/ethyl acetate = 20/1, v/v); 91% Deuterium incorporation was determined by ^{1}H NMR. **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ 7.36 – 7.32 (m, 2H), 7.31 – 7.28 (m, 2H), 7.22 – 7.16 (m, 4H), 7.03 (d, *J* = 8.1 Hz, 2H), 6.66 (dd, *J* = 8.4, 2.8 Hz, 1H), 6.59 (d, *J* = 2.7 Hz, 1H), 4.77 (s, 1H), 3.03 – 2.98 (m, 0.09H), 2.97 – 2.91 (m, 1H), 2.88 – 2.83 (m, 2H), 2.82 – 2.78 (m, 1H), 2.47 – 2.35 (m, 2H), 2.24 (td, *J* = 11.6, 4.2 Hz, 1H), 2.16 – 2.08 (m, 1H), 2.00 (td, *J* = 13.0, 4.0 Hz, 2H), 1.93 – 1.88 (m, 1H), 1.86 – 1.76 (m, 3H), 1.54 – 1.37 (m, 4H), 1.25 (s, 3H), 0.95 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$, ppm) δ 153.3, 146.5, 141.3, 138.3, 132.7, 131.4, 129.1, 128.3, 127.0, 126.6, 126.1, 120.3, 115.3, 112.7, 92.2, 86.1, 80.4, 49.7, 47.6, 44.8, 43.6, 41.8, 39.5, 39.1, 33.1, 29.7, 27.2, 26.5, 22.9, 21.2, 12.9. **HRMS (ESI)** m/z calcd for $C_{35}H_{37}DO_2Na$ $[M+Na]^+$: 514.2832; found: 514.2831.



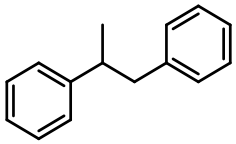
3,4,5-Trimethoxy-4'-(2-phenylpropyl-2-d)-1,1'-biphenyl (60)

The title compound was synthesized following General Procedure C and purified by using silica gel chromatography to yield a yellow oil, 114 mg (63% yield). R_f = 0.5 (petroleum ether/ethyl acetate = 20/1, v/v); 91% Deuterium incorporation was determined by ^{1}H NMR. **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ 7.46 (d, *J* = 8.0 Hz, 2H), 7.33 (t, *J* = 7.6 Hz, 2H), 7.26 – 7.22 (m, 3H), 7.17 (d, *J* = 8.0 Hz, 2H), 6.79 (s, 2H), 3.95 (s, 6H), 3.92 (s, 3H), 3.10 – 3.05 (m, 0.09H), 3.04 – 2.99 (m, 1H), 2.87 – 2.82 (m, 1H), 1.30 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$, ppm) δ 153.4, 146.9, 140.1, 138.9, 137.4, 137.1, 129.6, 128.4, 127.1, 126.8, 126.1, 104.2, 61.0, 56.2, 44.5, 41.9, 21.2. **HRMS (ESI)** m/z calcd for $C_{24}H_{25}DO_3Na$ [M+Na]: 386.1842; found: 386.1846.



Anisole-4-d (62)

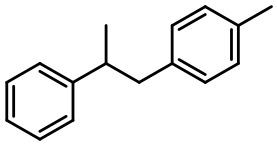
The title compound was purified by using silica gel chromatography to yield a colorless oil. $\boldsymbol{R_f}$ = 0.5 (petroleum ether); 79% Deuterium incorporation was determined by ^{1}H NMR. **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ 7.36 – 7.31 (m, 2H), 7.01 – 6.97 (m, 0.21H), 6.97 – 6.92 (m, 2H), 3.85 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$, ppm) δ 159.6, 129.4, 120.7, 113.9, 55.2. **HRMS (ESI)** m/z calcd for C_7H_7DOK $[M+K]^+$: 148.0269; found: 148.0275.



Propane-1,2-diyldibenzene (63)

The title compound was synthesized following General Procedure D and purified by using silica gel chromatography to yield a yellow oil, 79 mg (81% yield). $\boldsymbol{R_f}$ = 0.7 (petroleum ether); **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ 7.37 – 7.33 (m, 2H), 7.30 (t, *J* = 7.4 Hz, 2H), 7.27 – 7.21 (m, 4H), 7.15 (d, *J* = 7.3 Hz, 2H), 3.11 – 3.05 (m, 1H), 3.04 – 2.99 (m, 1H), 2.87 – 2.81 (m, 1H), 1.31 (d, *J* = 6.8 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$, ppm) δ 147.0, 140.8, 129.2, 128.3, 128.1, 127.1, 126.0, 125.8, 45.1, 41.9, 21.2.

The ^{1}H and ^{13}C NMR data were in accordance with those reported in the literature[6].

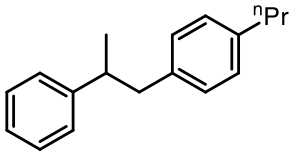


1-Methyl-4-(2-phenylpropyl)benzene (64)

The title compound was synthesized following General Procedure D and purified by using silica gel chromatography to yield a yellow oil, 101 mg (96% yield). $\boldsymbol{R_f}$ = 0.7

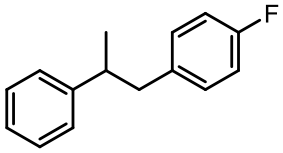
(petroleum ether); **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ 7.35 – 7.30 (m, 2H), 7.26 – 7.21 (m, 3H), 7.09 (d, *J* = 7.7 Hz, 2H), 7.02 (d, *J* = 7.8 Hz, 2H), 3.06 – 3.00 (m, 1H), 2.99 – 2.94 (m, 1H), 2.80 – 2.73 (m, 1H), 2.35 (s, 3H), 1.28 (d, *J* = 6.8 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$, ppm) δ 147.2, 137.8, 135.3, 129.1, 128.8, 128.3, 127.1, 126.0, 44.6, 41.9, 21.2, 21.1.

The ^{1}H and ^{13}C NMR data were in accordance with those reported in the literature[6].



1-(2-Phenylpropyl)-4-propylbenzene (65)

The title compound was synthesized following General Procedure D and purified by using silica gel chromatography to yield a yellow oil, 55 mg (46% yield). $\boldsymbol{R_f}$ = 0.7 (petroleum ether); **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ 7.33 – 7.29 (m, 2H), 7.25 – 7.19 (m, 3H), 7.08 (d, *J* = 8.0 Hz, 2H), 7.03 (d, *J* = 8.0 Hz, 2H), 3.04 – 2.98 (m, 1H), 2.98 – 2.93 (m, 1H), 2.78 – 2.72 (m, 1H), 2.57 (t, *J* = 7.6 Hz, 2H), 1.68 – 1.61 (m, 2H), 1.25 (d, *J* = 6.8 Hz, 3H), 0.95 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$, ppm) δ 147.3, 140.1, 138.0, 129.0, 128.3, 128.2, 127.1, 126.0, 44.6, 41.9, 37.7, 24.6, 21.1, 13.9. **HRMS (ESI)** m/z calcd for $C_{18}H_{22}Na$ $[M+Na]^+$: 261.1619; found: 261.1617.

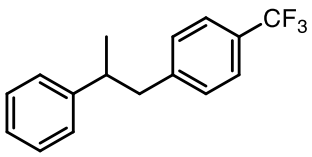


1-Fluoro-4-(2-phenylpropyl)benzene (66)

The title compound was synthesized following General Procedure D and purified by using silica gel chromatography to yield a yellow oil, 91 mg (85% yield). $\boldsymbol{R_f}$ = 0.6 (petroleum ether); **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ 7.34 –7.30 (m, 2H), 7.26 – 7.23 (m, 1H), 7.22 – 7.19 (m, 2H), 7.07 – 7.02 (m, 2H), 6.98 – 6.92 (m, 2H), 3.03 – 2.98 (m, 1H), 2.96 – 2.91 (m, 1H), 2.83 – 2.78 (m, 1H), 1.30 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$, ppm) δ 161.3 (d, $^1J_{C\text{-}F}$ = 243.4 Hz), 146.6, 136.4 (d, $^4J_{C\text{-}F}$ =

3.2 Hz), 130.4 (d, $^{3}J_{C\text{-}F}$ = 7.8 Hz), 128.3, 127.1, 126.1, 114.8 (d, $^{2}J_{C\text{-}F}$ = 21.0 Hz), 44.2, 42.0, 21.2.

The ^{1}H and ^{13}C NMR data were in accordance with those reported in the literature[6].



1-(2-Phenylpropyl)-4-(trifluoromethyl)benzene (67)

The title compound was synthesized following General Procedure D and purified by using silica gel chromatography to yield a yellow oil, 106 mg (80% yield). $\boldsymbol{R_f}$ = 0.6 (petroleum ether); **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ 7.51 (d, *J* = 8.0 Hz, 2H), 7.32 (t, *J* = 7.5 Hz, 2H), 7.25 – 7.22 (m, 1H), 7.21 – 7.18 (m, 4H), 3.08 – 2.99 (m, 2H), 2.92 – 2.87 (m, 1H), 1.31 (d, *J* = 6.7 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$, ppm) δ 146.2, 144.9 (q, $^{3}J_{C\text{-}F}$ = 1.2 Hz), 129.4, 128.4, 128.2 (q, $^{2}J_{C\text{-}F}$ = 33.1 Hz), 127.0, 126.3, 125.0 (q, $^{3}J_{C\text{-}F}$ = 3.8 Hz), 124.4 (q, $^{1}J_{C\text{-}F}$ = 272.6 Hz), 44.8, 41.7, 21.3.

The ^{1}H and ^{13}C NMR data were in accordance with those reported in the literature[6].

8. Electrochemical Testing Experiments

8.1. Cyclic Voltammetry Experiments

General Information: Cyclic voltammetry (CV) was conducted in a 30 mL glass vial fitted with a glassy carbon working electrode (6 mm in diameter, BASi), a Ag/AgCl (saturated KCl) reference electrode, and a Pt plate counter electrode at 26 °C. CV Study was started with a starting potential (-0.5 V or 0 V), the initial scan direction was negative, and the scan rate was 0.1 V/s. The graphs were plotted using the IUPAC convention.

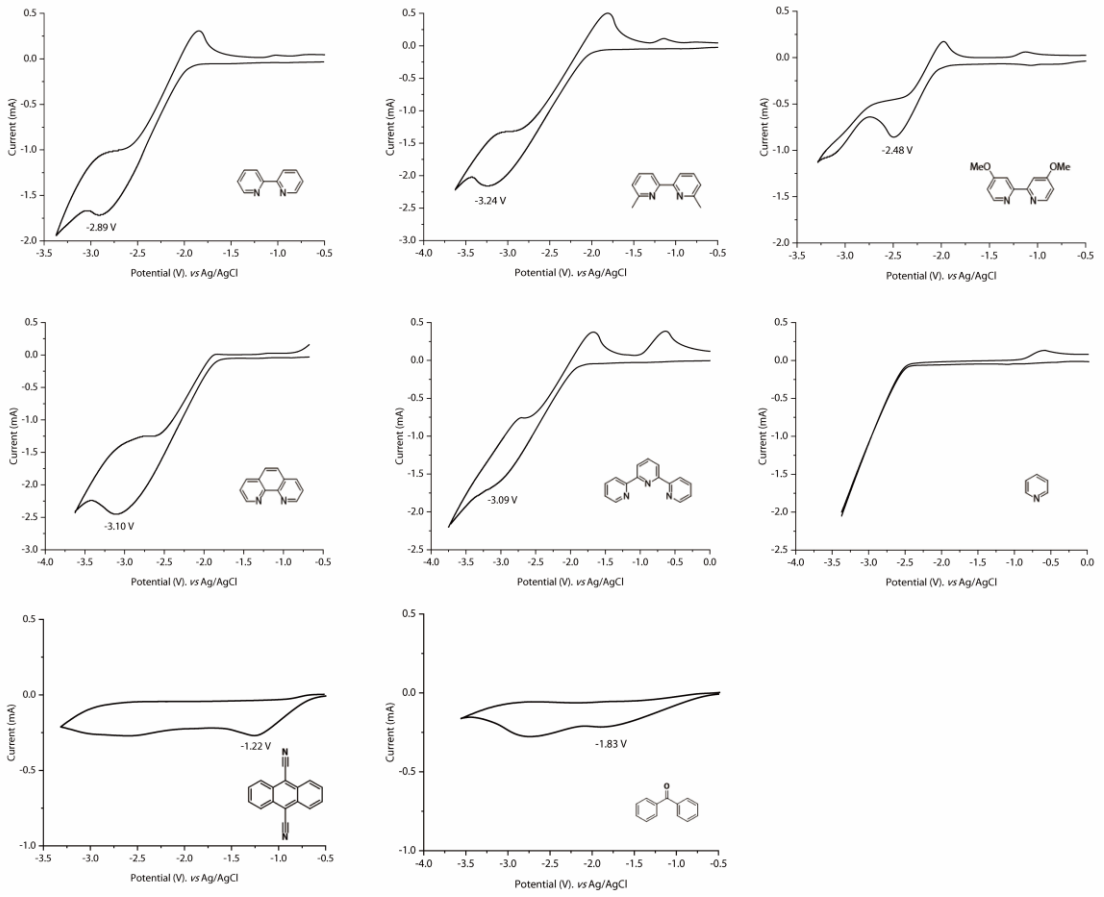


Fig. S5. Cyclic voltammograms of reactants and their mixtures in 0.1 M $^{n}Bu_4NPF_6$ solution in DMF at room temperature. Each organo-mediator was added at 0.02 M concentration. Starting potential: -0.5 V or 0 V. Initial scan direction: negative. Scan rate: 0.1 V/s. The graphs were plotted using the IUPAC convention.

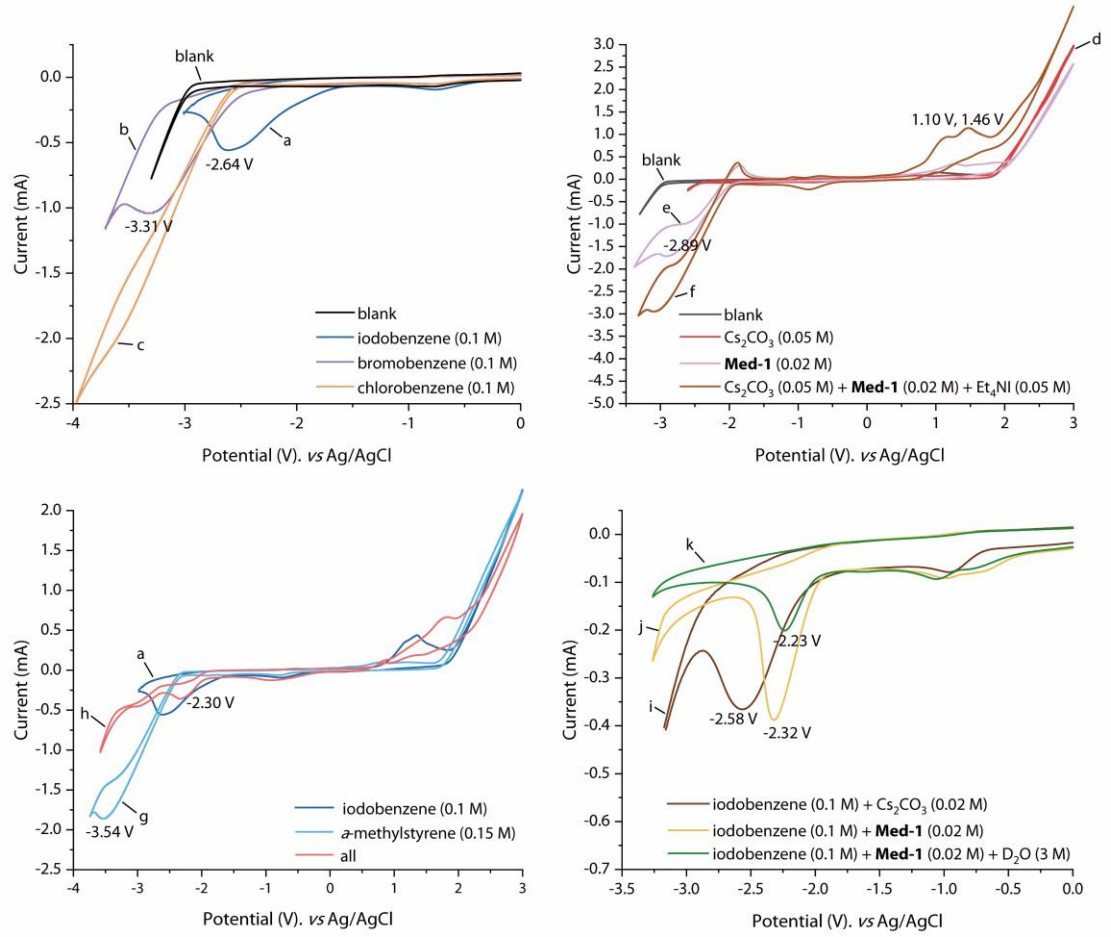


Fig. S6. Cyclic voltammograms of reactants and their mixtures in 0.1 M $^{n}Bu_4NPF_6$ solution in DMF at room temperature. a. iodobenzene (0.1 M). b. bromobenzene (0.1 M). c. chlorobenzene (0.1 M). d. Cs_2CO_3 (0.05 M). e. **Med-1** (0.02 M). f. Cs_2CO_3 (0.05 M) + **Med-1** (0.02 M) + Et_4NI (0.05 M). g. α-methylstyrene (0.15 M). h. all (Et_4NI (0.05 M) + Cs_2CO_3 (0.05 M) + **Med-1** (0.02 M) + iodobenzene (0.1 M) + α-methylstyrene (0.15 M). i. iodobenzene (0.1 M) + Cs_2CO_3 (0.05 M). J. iodobenzene (0.1 M) + **Med-1** (0.02 M). k. iodobenzene (0.1 M) + **Med-1** (0.02 M) + D_2O (3.0 M).

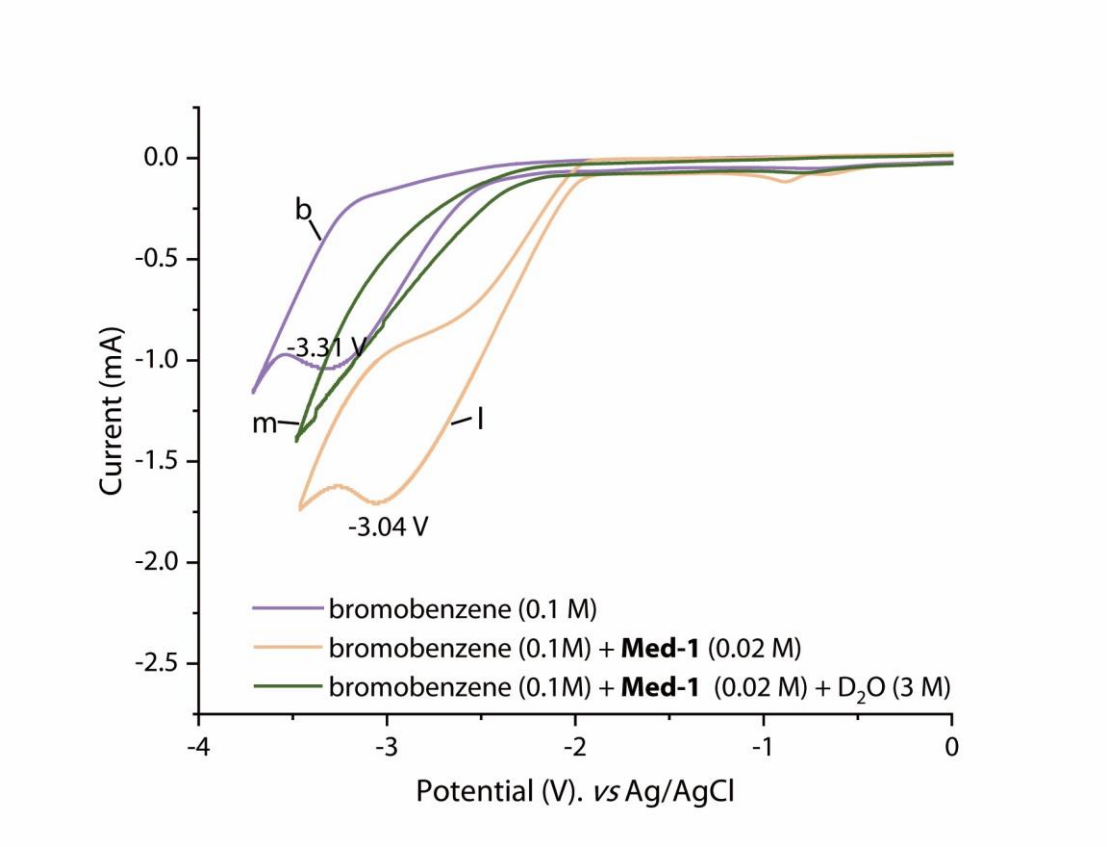
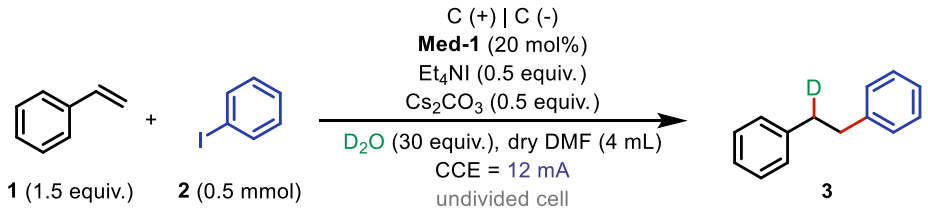


Fig. S7. Cyclic voltammograms of reactants and their mixtures in 0.1 M $^{n}Bu_4NPF_6$ solution in DMF at room temperature. b. bromobenzene (0.1 M). l. bromobenzene (0.1 M) + **Med-1** (0.02 M). m. bromobenzene (0.1 M) + **Med-1** (0.02 M) + D_2O (3 M).

8.2. Potential Test Experiments

Template reaction for potential testing:



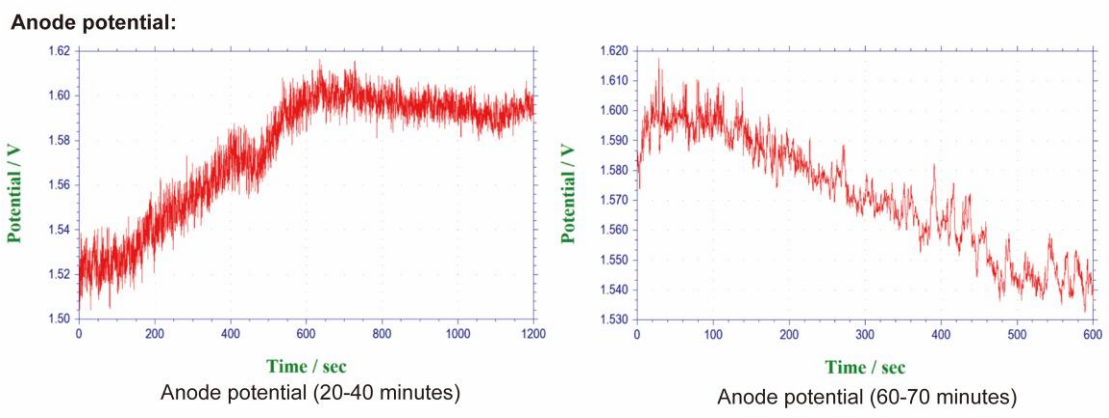


Fig. S8. Segmented testing of anode potential. The anode potential was in the range of 1.52–1.60 V (*vs* Ag/AgCl)

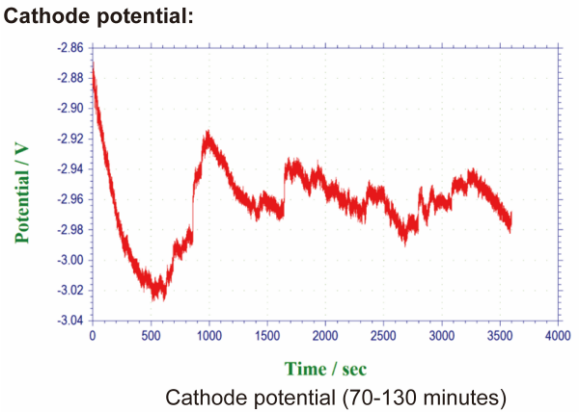


Fig. S9. Test of cathode potential. The cathode potential was in the range of -3.02–(-2.88) V (*vs* Ag/AgCl).

9. DFT Calculations

9.1. Computational Methods

The DFT calculations were performed with the Gaussian 16 program[12]. Geometries of the minimum energy structures were optimized at the SMD(*N*,*N*-dimethylformamide)/M06-2X/DGDZVP level of theory[13]. The harmonic vibrational frequency calculations were performed to confirm whether they are local minima and to derive the thermochemical corrections for the enthalpies and free energies. Solvent effects in DMF were considered implicitly using the SMD polarizable continuum model[14-15]. The single-point energies were obtained at the SMD(*N*,*N*-dimethylformamide)/M06-2X/def2-TZVPP level of theory with more accurate energy information[13]. The molecular orbital calculation were obtained at the SMD(*N*,*N*-dimethylformamide)/B3LYP/def2-TZVP level of theory[16-17], together with the

Grimme D3BJ correction term to the electronic energy[18-20]. The iodobenzene radical anion and phenyl radical were optimized and analyzed for the electron spin density distribution and the atomic charge, by the Multiwfn (Multifunctional Wavefunction Analyzer)[21] and VMD (Visual Molecular Dynamics) software[22].

The electrostatic potential (ESP) and electron spin density distribution of **TS1** showed that the negative charge was mainly distributed in the iodine part and the single electron was mainly located at the single carbon atom of phenyl.

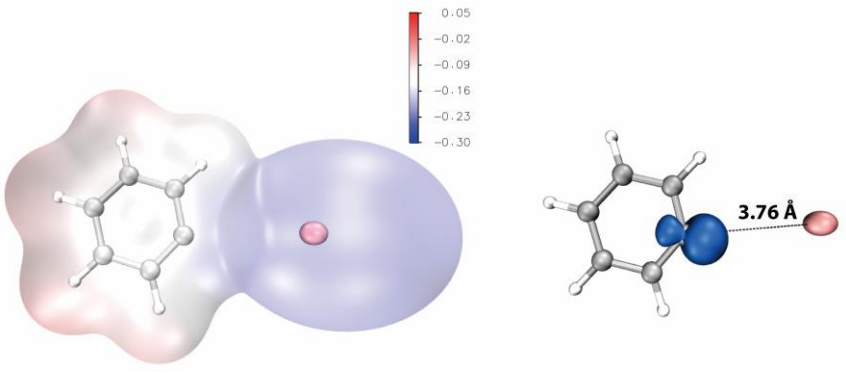


Fig. S10. Electrostatic potential and electron spin density distribution of iodobenzene radical anion (**TS1**), with an isovalue of 0.02 atomic unit.

9.2. Calculated Energies

Structure	**E [M06-2X/def2-TZVPP, SMD (DMF)] (kcal/mol)**	**ΔG[M06-2X/ DGDZVP, SMD (DMF)] (kcal/mol)**	**G = E + ΔG (kcal/mol)**	**H (kcal/mol)**
2	-332119.049	37.1109414	-332081.9381	-332057.8034
[Med-1]$^{\bullet-}$	-310897.3144	75.37524618	-310821.9391	-310793.4125
2-Med	-643021.8481	124.7113374	-642897.1368	-642855.4701
Med-1	-310849.6207	78.44565261	-310771.175	-310743.5451
TS1	-332183.64	34.13	-332149.51	-332123.02
I$^-$	-186882.78	-10.57	-186893.35	-186881.30
B	-145299.03	38.51	-145260.53	-145240.09

A	-218964.20	82.13	-218882.07	-218856.30
TS2	-364263.12	133.17	-364129.95	-364095.89
C	-364310.33	135.74	-364174.59	-364141.34

9.3. Cartesian Coordinates of Calculated Structures

2-Med

C	-4.64200105	-0.24324106	-0.80094887
C	-2.77012466	0.66267455	0.25757113
C	-3.14332242	-0.02622751	1.46061092
C	-4.25968656	-0.83006432	1.48758277
C	-5.05183594	-0.96662044	0.31966450
H	-5.23110903	-0.30559133	-1.71735895
H	-2.54531352	0.06886671	2.36063975
H	-4.52810773	-1.35366761	2.40198693
H	-5.94000134	-1.58872647	0.29057776
C	-1.56621593	1.44258918	0.16082419
C	-0.64614646	1.57339763	1.25677352
C	0.52465564	2.27923378	1.10504283
H	-0.85605754	1.10768742	2.21386671
C	-0.13300031	2.73300014	-1.15218367
C	0.82008387	2.88253249	-0.14400165
H	1.21846936	2.36336201	1.93810202
H	0.04700579	3.19497200	-2.12438390
H	1.73251043	3.44399062	-0.31492340
N	-3.56530339	0.54078351	-0.86731575
N	-1.27924852	2.06072340	-1.04369164
C	-0.59783535	-2.33260369	0.32741918
C	-1.14107783	-2.11030754	-0.94015750
C	-0.43155268	-1.35980872	-1.87824263
C	0.82461948	-0.83407085	-1.55982167

C	1.35441415	-1.07064058	-0.29219640
C	0.65438546	-1.81331591	0.66118997
H	-1.14907369	-2.90882441	1.06505728
H	-2.11960733	-2.51110999	-1.19019148
H	-0.85145258	-1.17408216	-2.86246599
H	1.37517463	-0.24909846	-2.29016284
H	1.07567860	-1.98632365	1.64643630
I	3.26248285	-0.30624841	0.19519079

TS1

C	-3.22025244	1.33639150	0.00001372
C	-4.17479114	0.31509524	0.00014529
C	-3.78179706	-1.02635668	0.00009011
C	-2.41969139	-1.36227951	-0.00009624
C	-1.51863647	-0.31632867	-0.00022613
C	-1.85290186	1.02306207	-0.00015976
H	-3.53409477	2.37654299	0.00006331
H	-5.23127853	0.56597666	0.00029116
H	-4.52997694	-1.81433135	0.00019312
H	-2.10012671	-2.40073140	-0.00015964
H	-1.09788588	1.80483984	-0.00022438
I	2.23210915	-0.00660001	0.00002329

B

C	1.21398910	-0.63253006	-0.00000017
C	-0.00000002	-1.32502584	-0.00000060
C	-1.21398906	-0.63253014	-0.00000018
C	-1.22627331	0.77065156	0.00000030
C	-0.00000003	1.40219322	0.00000050
C	1.22627333	0.77065151	0.00000031
H	2.15398649	-1.17726824	-0.00000039

H	0.00000006	-2.41083092	-0.00000102
H	-2.15398652	-1.17726819	-0.00000040
H	-2.16225143	1.32245283	0.00000043
H	2.16225133	1.32245299	0.00000045

TS2

C	2.34435944	-1.86103708	0.86976514
C	3.51394851	-1.81133693	0.10536436
C	3.80577107	-0.65715230	-0.62185867
C	2.94097867	0.43749733	-0.58308521
C	1.77085545	0.41051877	0.19554186
C	1.48375180	-0.76721033	0.91281505
C	0.85952352	1.57797784	0.22778145
C	-0.08139410	1.72131935	1.19301471
C	0.95697155	2.58236835	-0.89177300
H	2.09708623	-2.76023697	1.42678324
H	4.18325493	-2.66589292	0.07132502
H	4.70792538	-0.60727196	-1.22478176
H	3.19000226	1.32388940	-1.15877962
H	0.56858904	-0.84007567	1.49382566
H	-0.71360856	2.60538530	1.21184505
H	-0.11327673	1.08488292	2.07268229
H	1.89657979	3.14393011	-0.84378963
H	0.92451087	2.09194945	-1.87086245
H	0.13514017	3.29958024	-0.83395962
C	-3.95147056	-1.16854390	-0.70799163
C	-2.74413992	-1.04054238	-1.40150689
C	-1.72007305	-0.23267477	-0.88669113
C	-1.95892404	0.41474344	0.31078847
C	-3.13585450	0.31723244	1.02983795

C	-4.14989252	-0.49513723	0.50090798
H	-4.74084688	-1.79613386	-1.11098356
H	-2.59697469	-1.56735844	-2.34065128
H	-0.77381325	-0.12529043	-1.41460658
H	-3.28010370	0.84423352	1.97006633
H	-5.09093281	-0.59972636	1.03442430

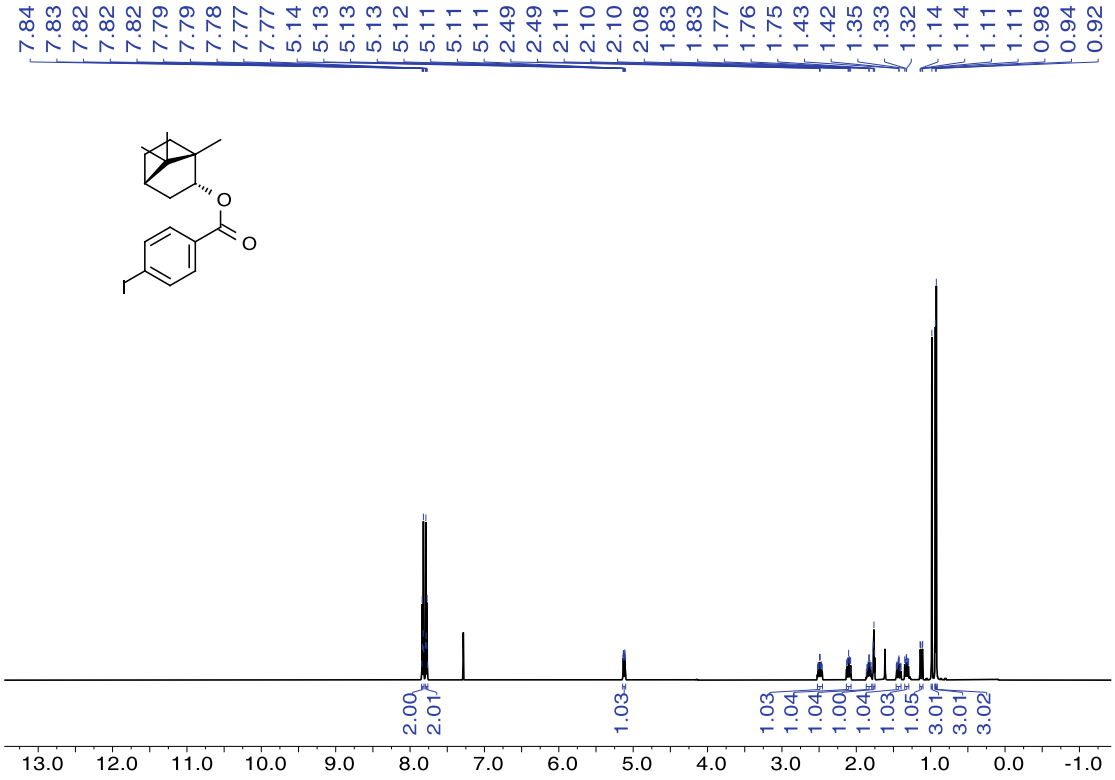
C

C	2.26030876	-2.00290363	0.36458901
C	3.41672049	-1.73597843	-0.37861003
C	3.65334529	-0.43027902	-0.82458211
C	2.75522292	0.59053777	-0.53729132
C	1.57537405	0.34525597	0.21781145
C	1.35682463	-0.98939547	0.65939550
C	0.65094254	1.40031833	0.51145343
C	-0.60083682	1.12185449	1.30157375
C	0.89203082	2.78568862	-0.01254731
H	2.06361491	-3.01231366	0.71507592
H	4.11970051	-2.53137974	-0.60656449
H	4.54682291	-0.20918701	-1.40196994
H	2.96596298	1.59295618	-0.89729692
H	0.46869257	-1.23221179	1.23517969
H	-1.02184557	2.07306027	1.64342822
H	-0.37344696	0.54144086	2.20269810
H	1.81824927	3.21668454	0.39032284
H	0.99282169	2.79598951	-1.10536986
H	0.06999185	3.45293946	0.25449856
C	-3.67470715	-0.96286778	-0.93997624
C	-3.39643412	-1.32601105	0.37868377
C	-2.40043767	-0.65779894	1.09504292

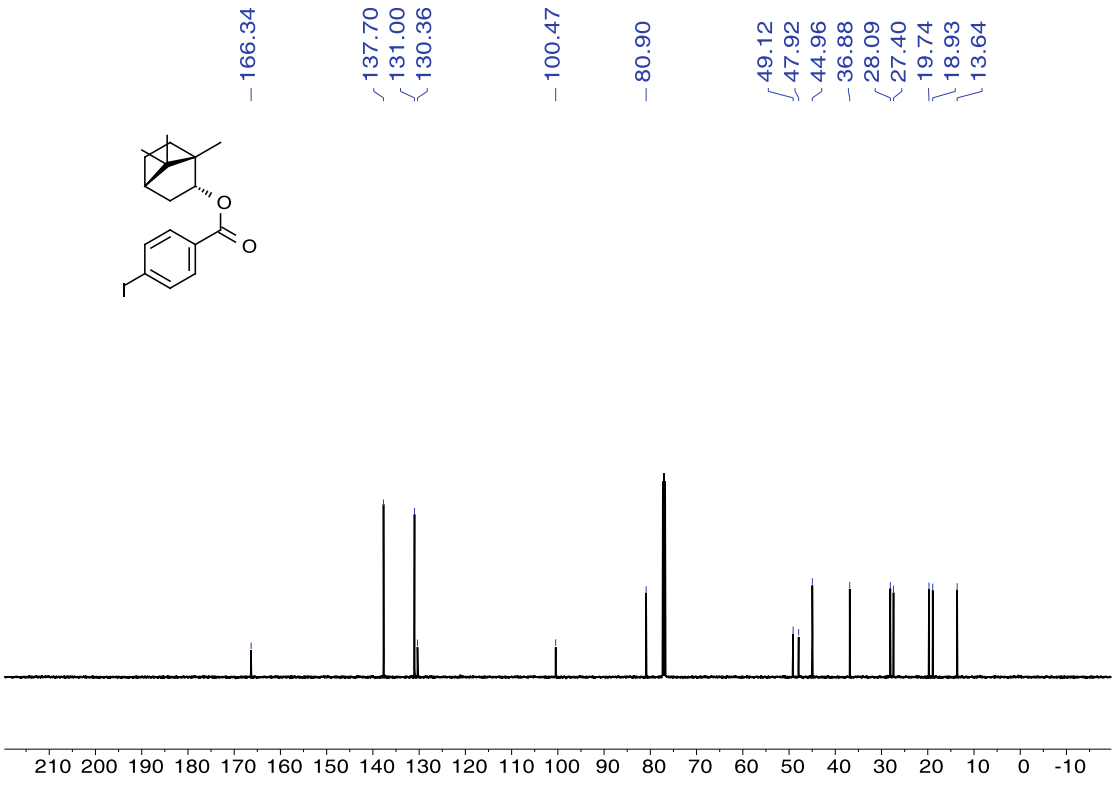
C	-1.67006858	0.38150345	0.50853215
C	-1.95511342	0.73733496	-0.81643700
C	-2.94959189	0.07242629	-1.53526747
H	-4.44627227	-1.48310425	-1.49993458
H	-3.95033560	-2.13303166	0.84991486
H	-2.18363564	-0.95068042	2.12015175
H	-1.39448423	1.53920284	-1.29270315
H	-3.15731542	0.36152146	-2.56165412

10. NMR Spectra of Products

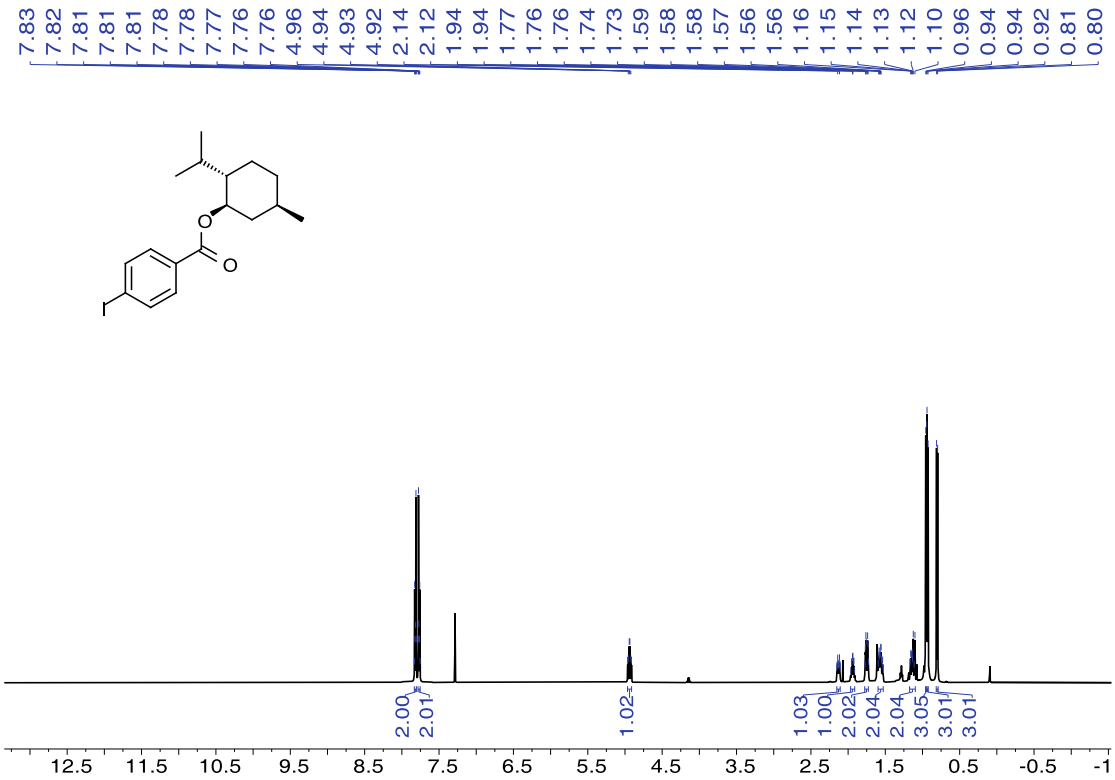
^{1}H NMR spectra of 52a (500 MHz, $CDCl_3$)



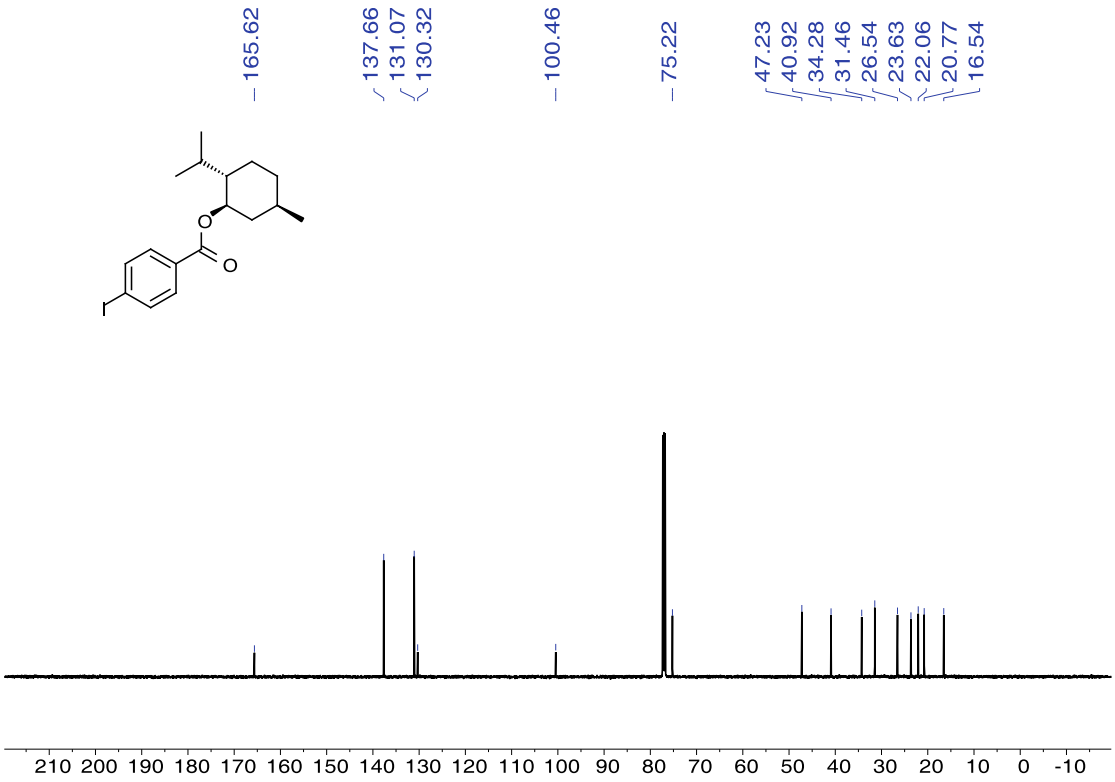
^{13}C NMR spectra of 52a (126 MHz, $CDCl_3$)



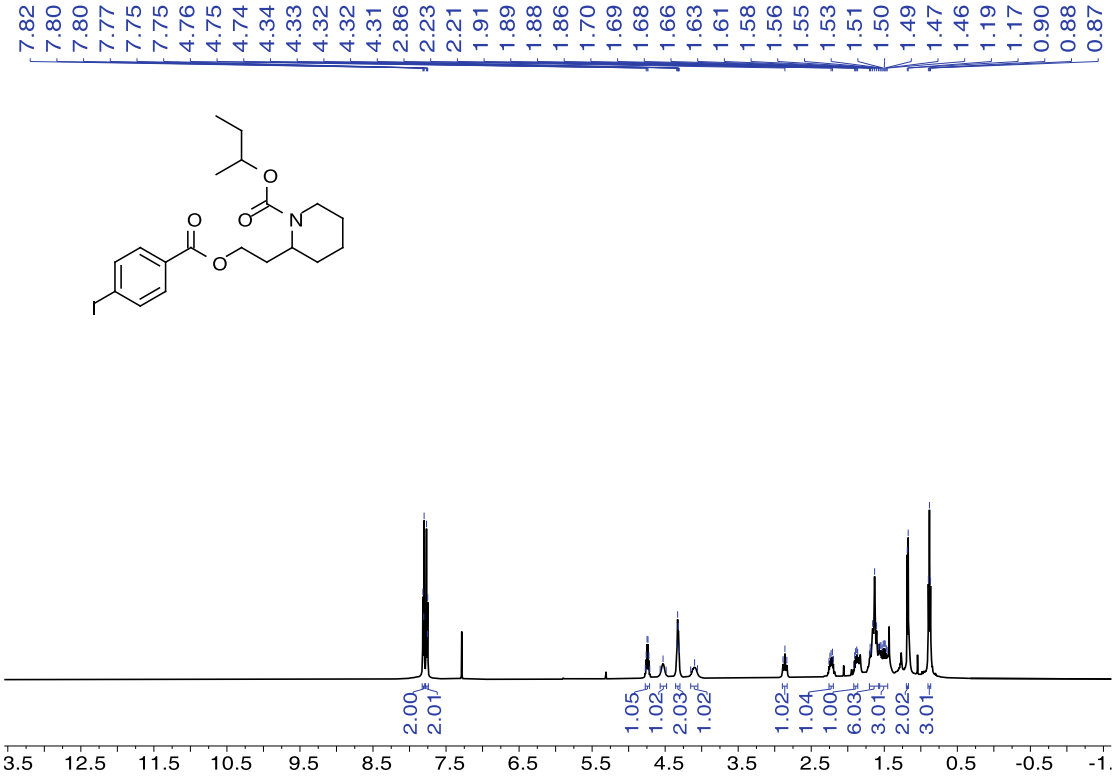
^{1}H NMR spectra of 53a (500 MHz, $CDCl_3$)



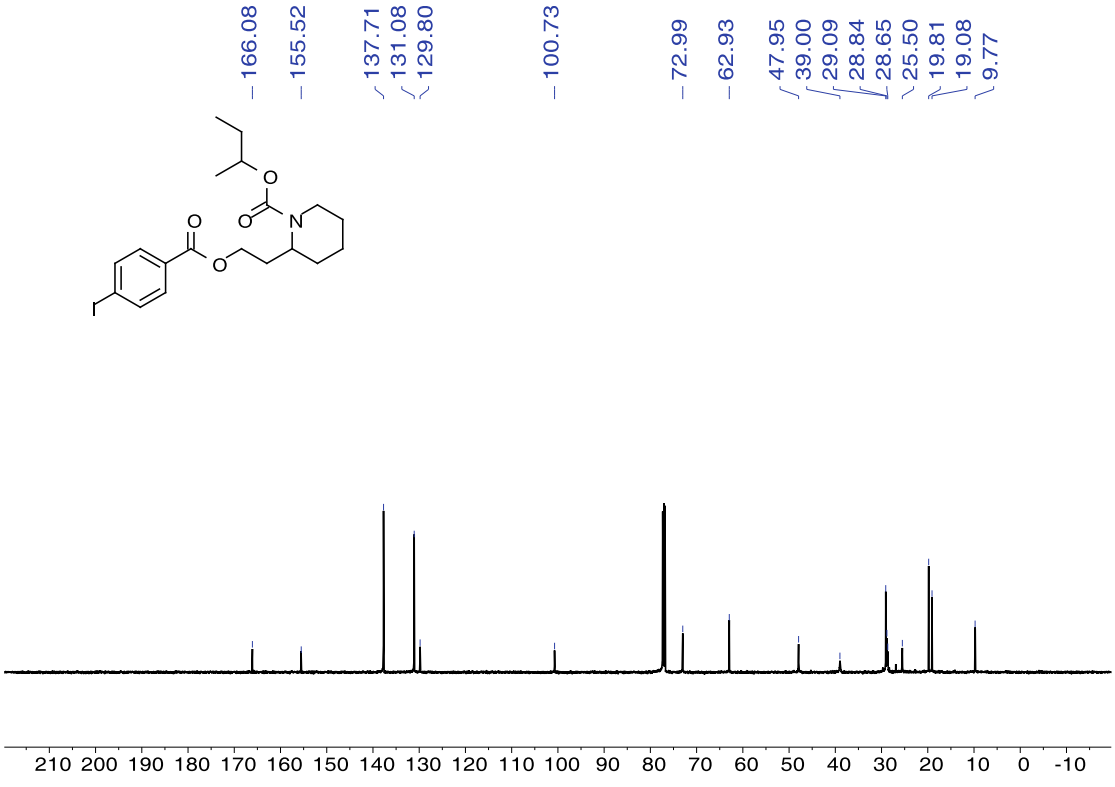
^{13}C NMR spectra of 53a (126 MHz, $CDCl_3$)



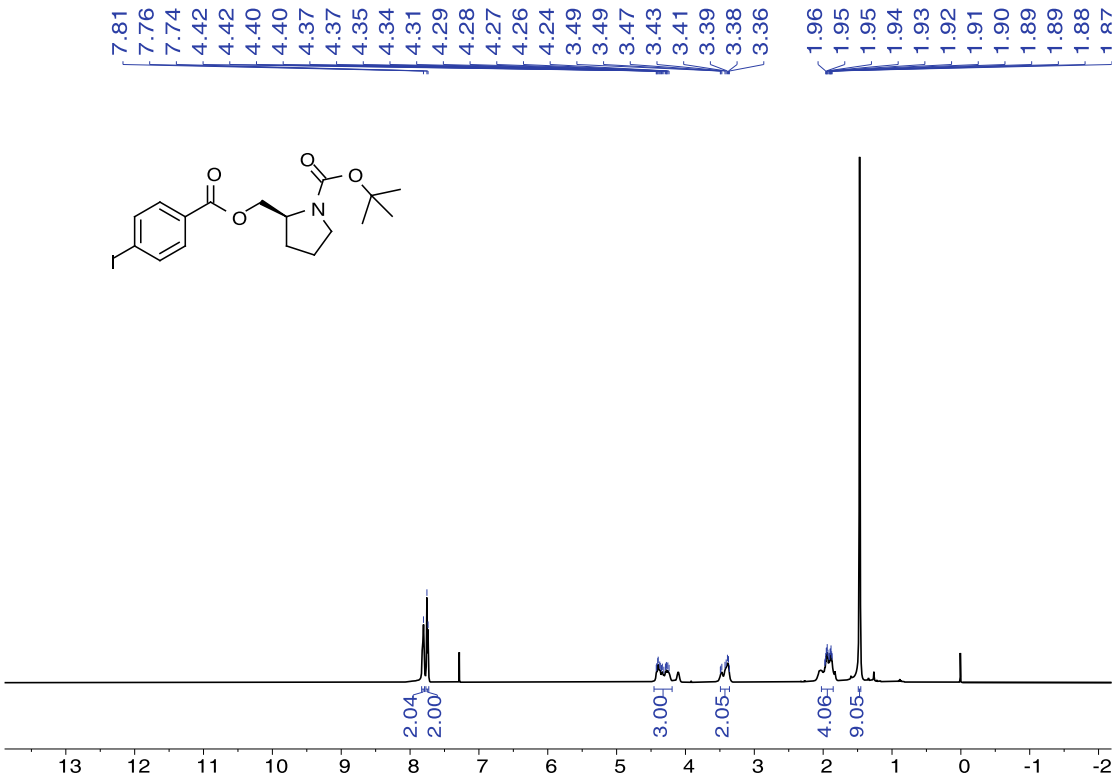
^{1}H NMR spectra of 54a (500 MHz, $CDCl_3$)



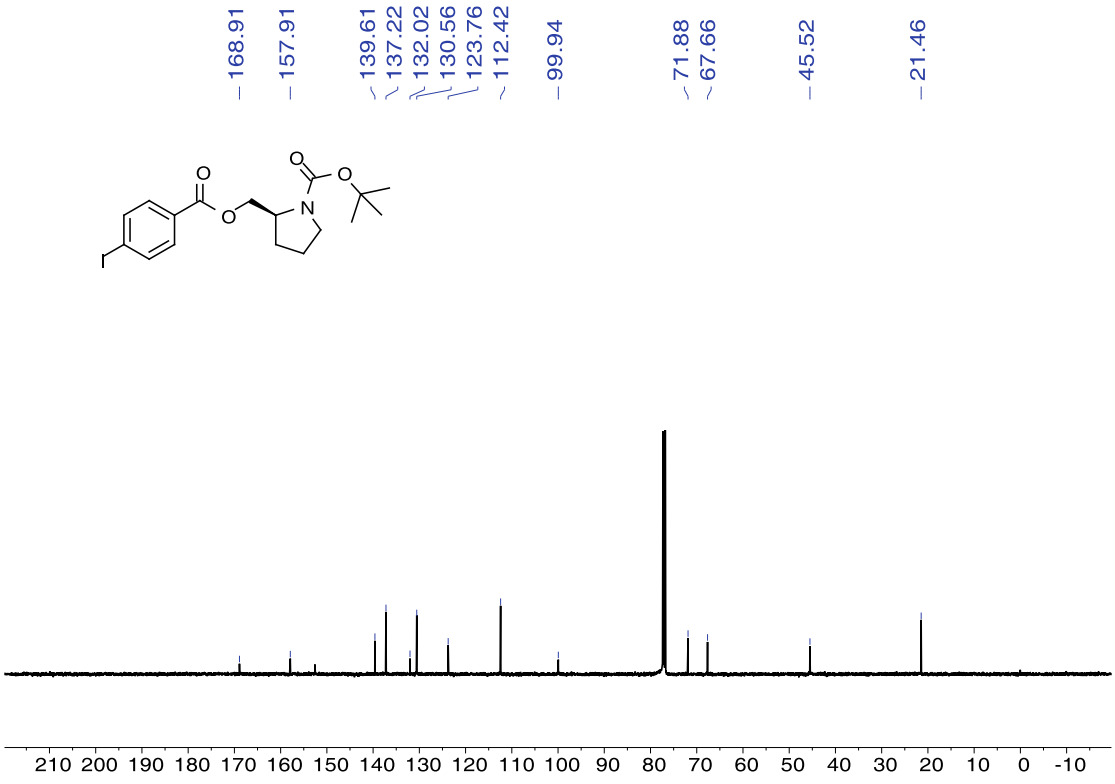
^{13}C NMR spectra of 54a (126 MHz, $CDCl_3$)



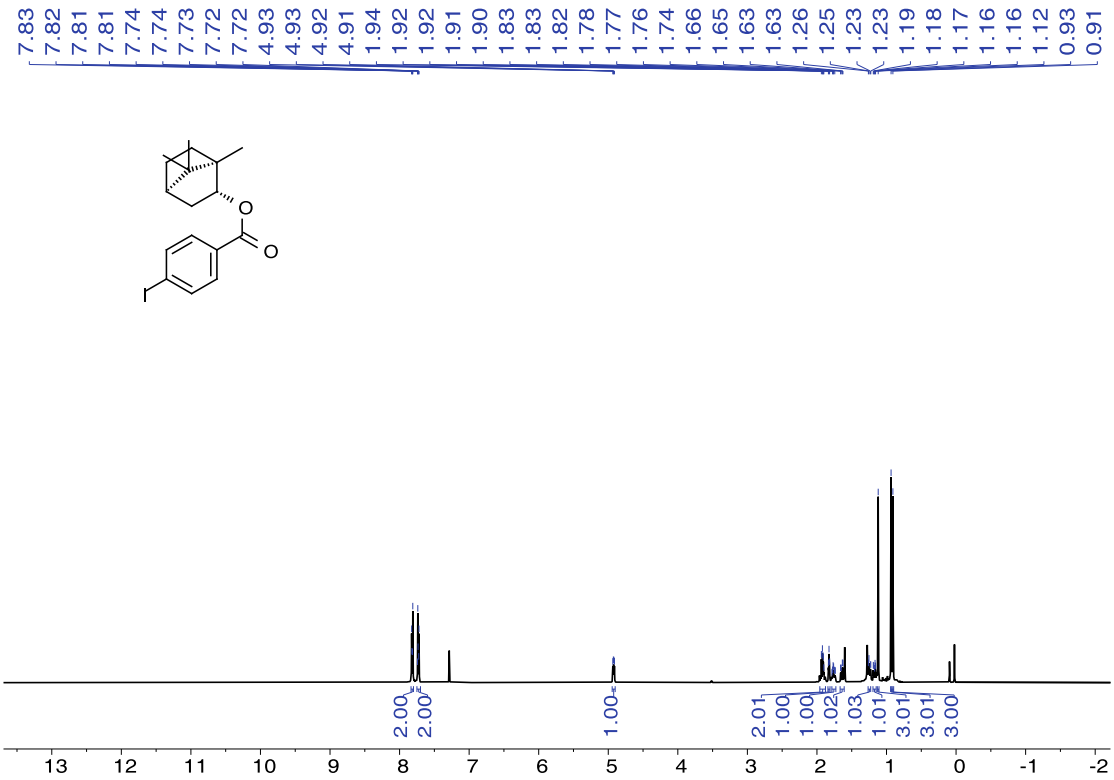
^{1}H NMR spectra of 55a (500 MHz, $CDCl_3$)



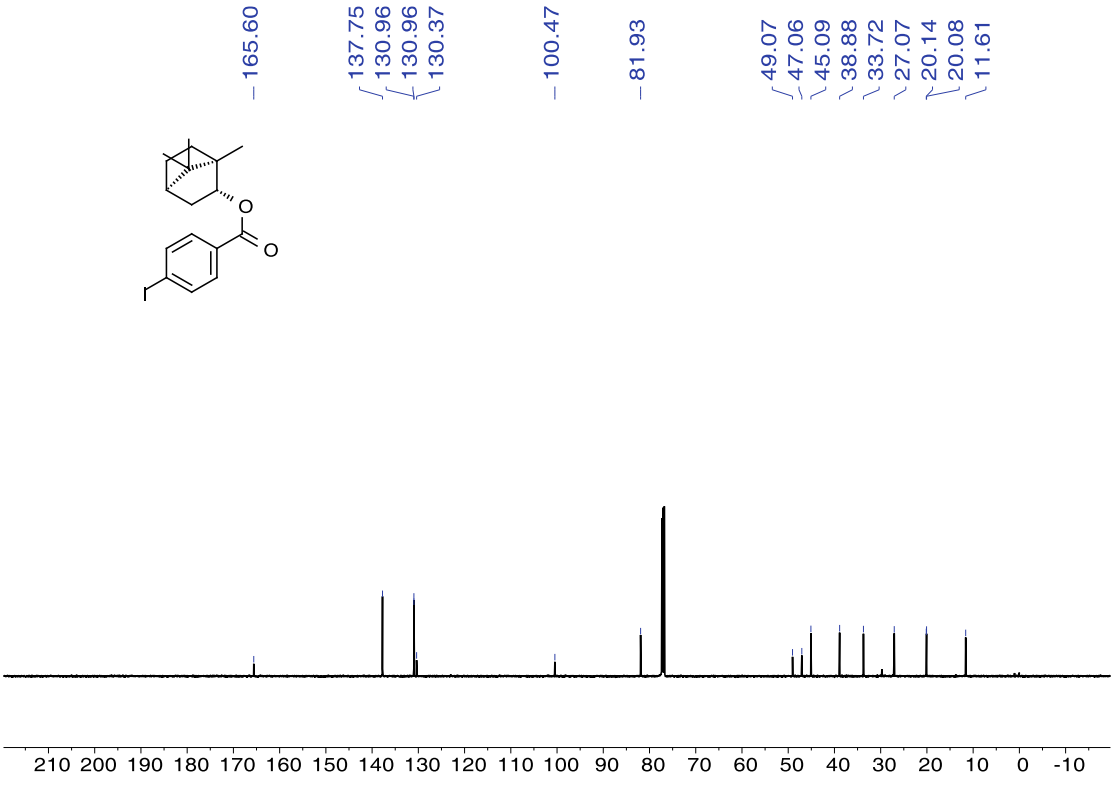
^{13}C NMR spectra of 55a (126 MHz, $CDCl_3$)



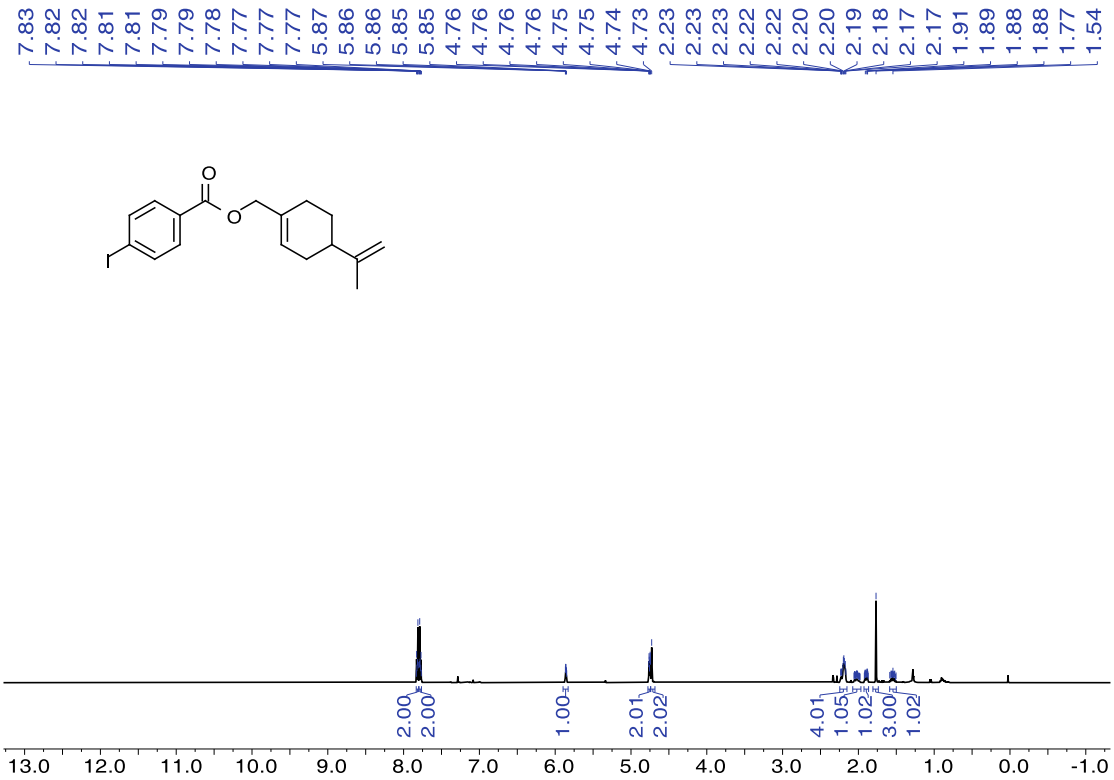
^{1}H NMR spectra of 56a (500 MHz, $CDCl_3$)



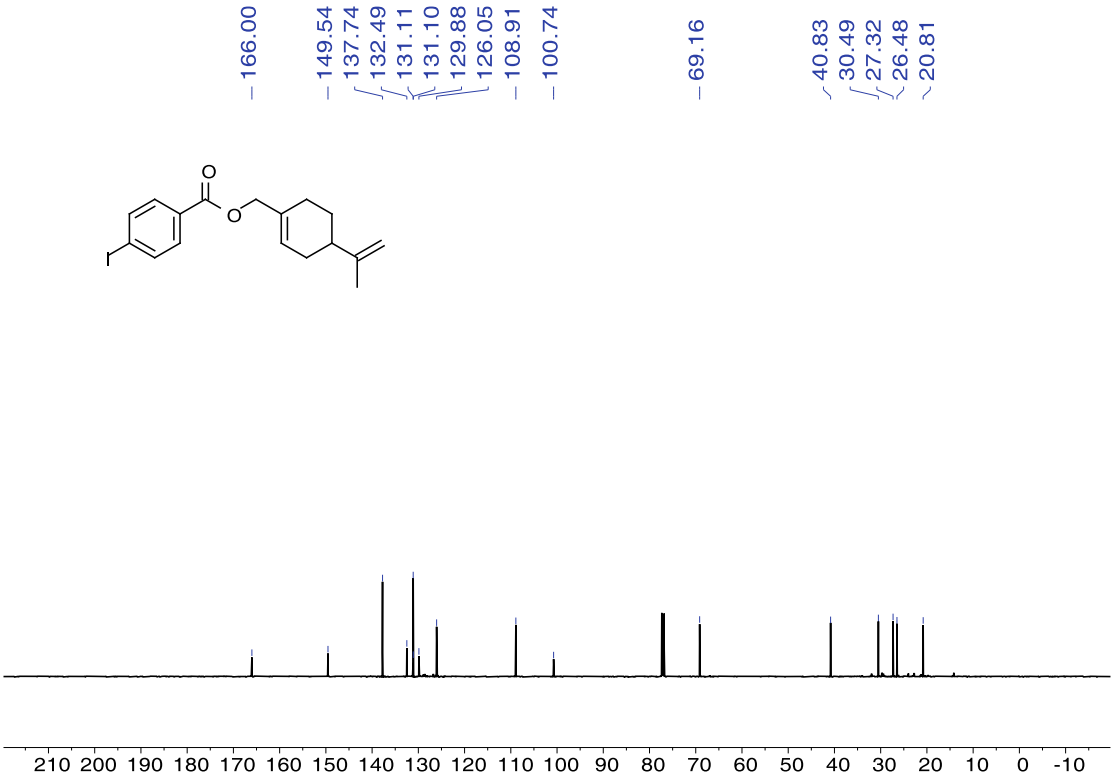
^{13}C NMR spectra of 56a (126 MHz, $CDCl_3$)



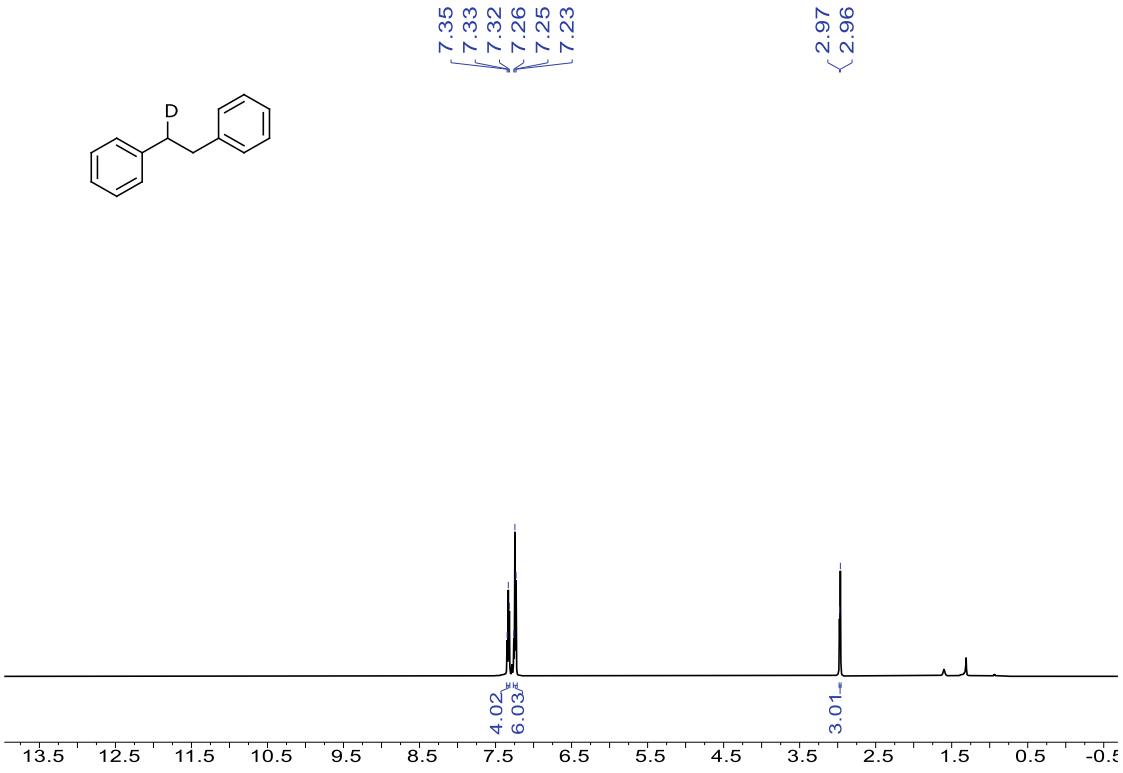
^{1}H NMR spectra of 57a (500 MHz, $CDCl_3$)



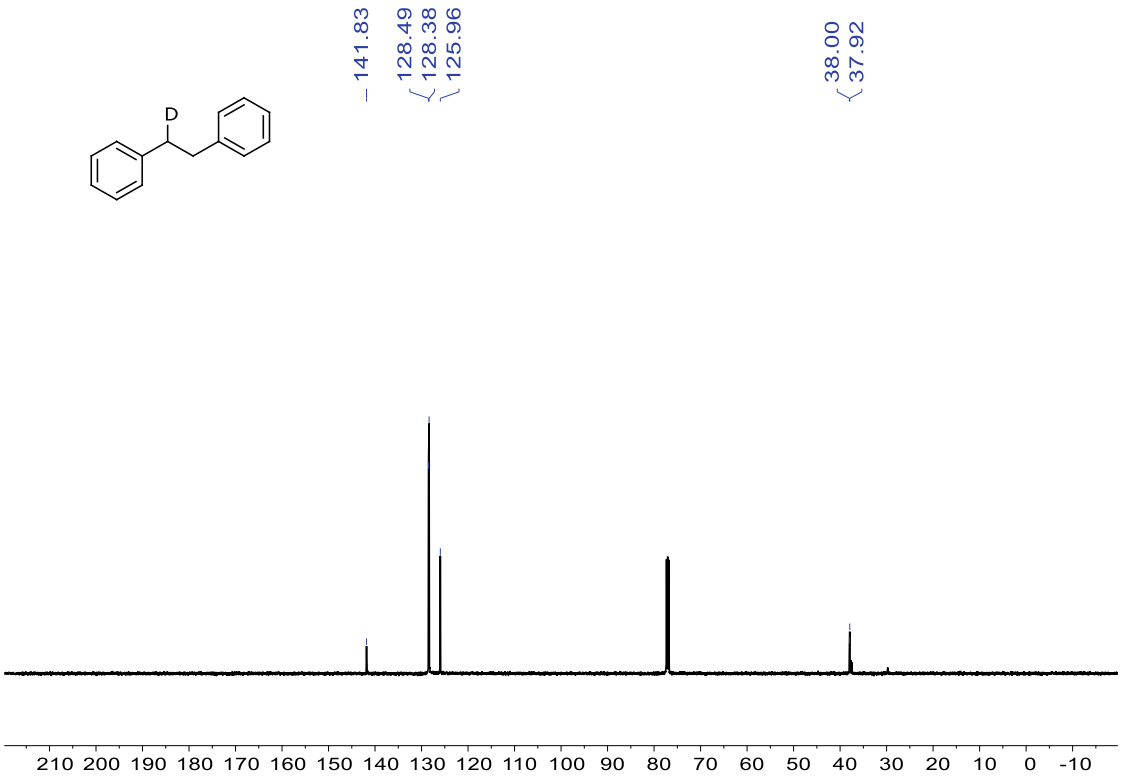
^{13}C NMR spectra of 57a (126 MHz, $CDCl_3$)



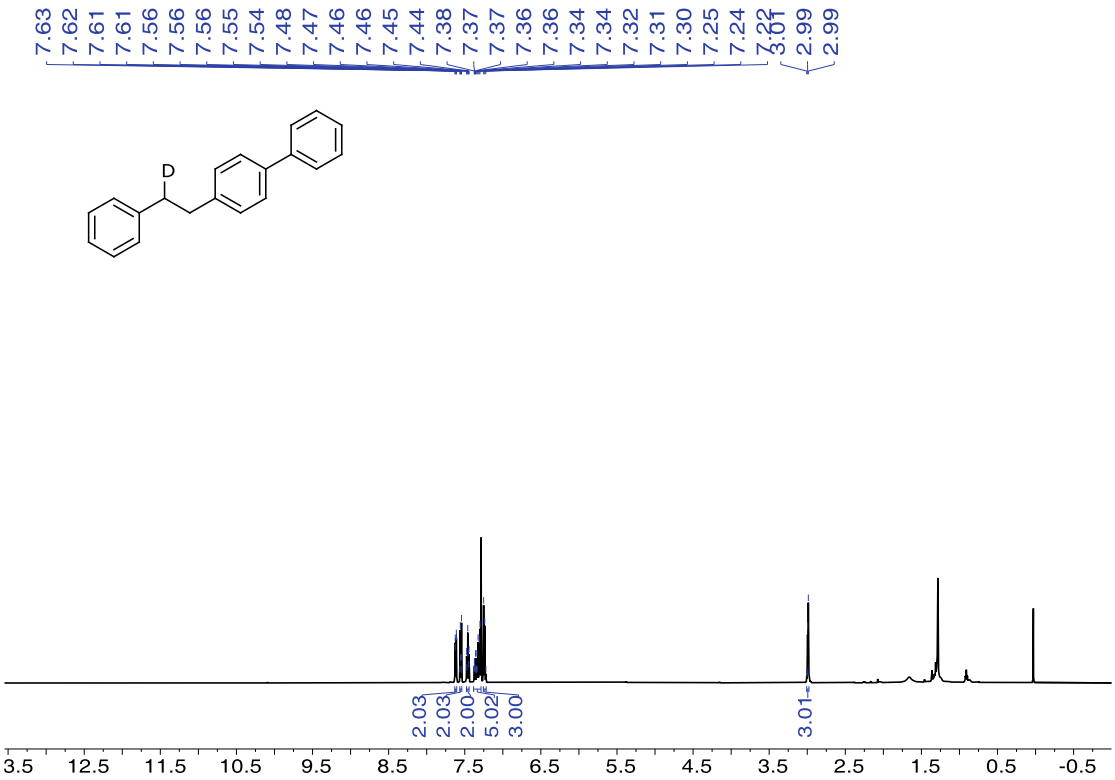
^{1}H NMR spectra of 3 (500 MHz, $CDCl_3$)



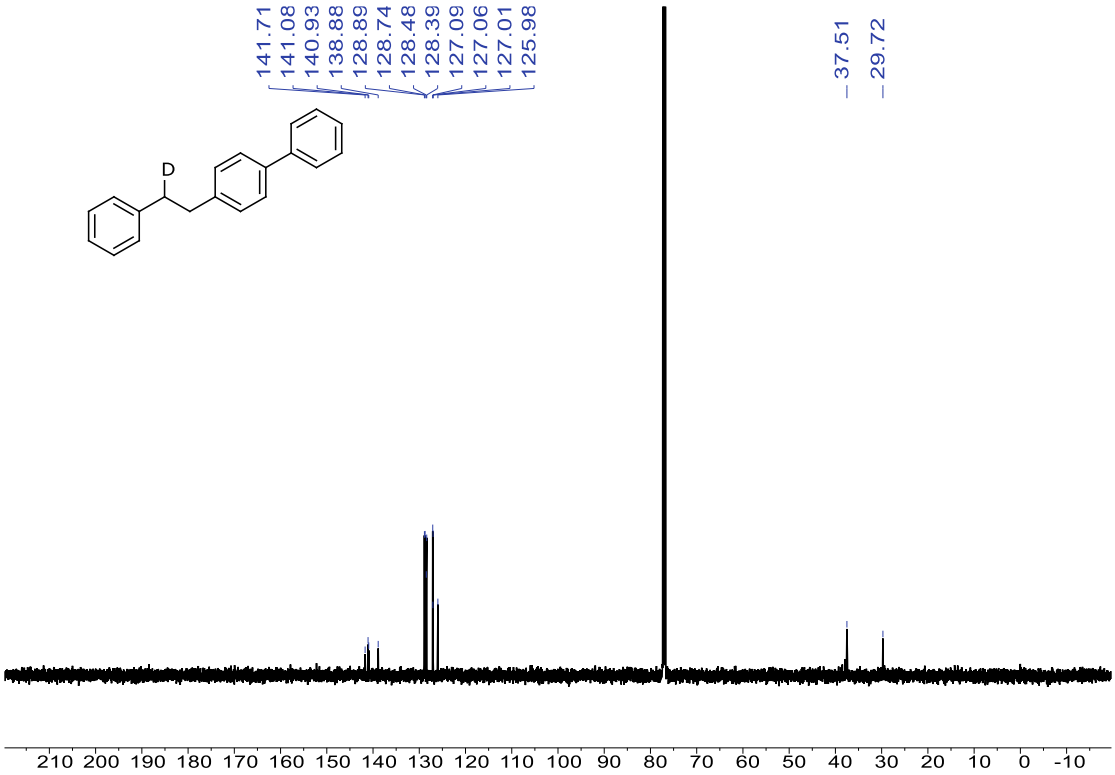
^{13}C NMR spectra of 3 (126 MHz, $CDCl_3$)



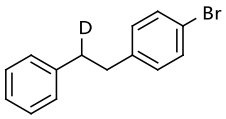
^{1}H NMR spectra of 4 (500 MHz, $CDCl_3$)

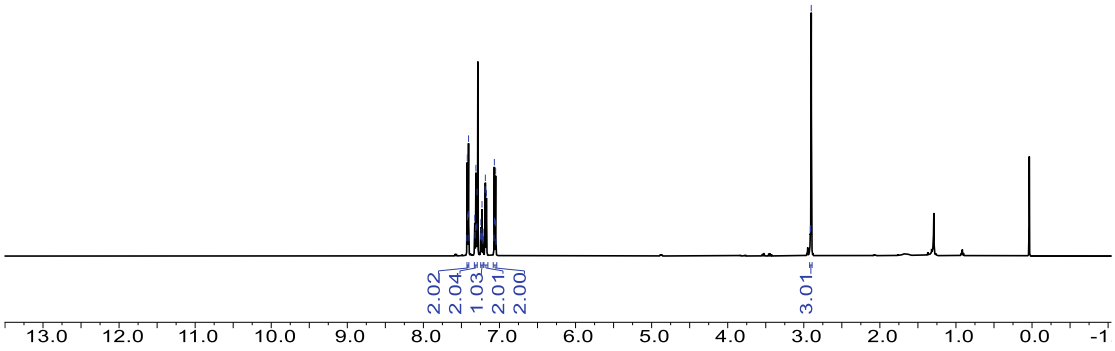


^{13}C NMR spectra of 4 (126 MHz, $CDCl_3$)

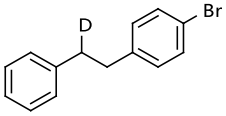


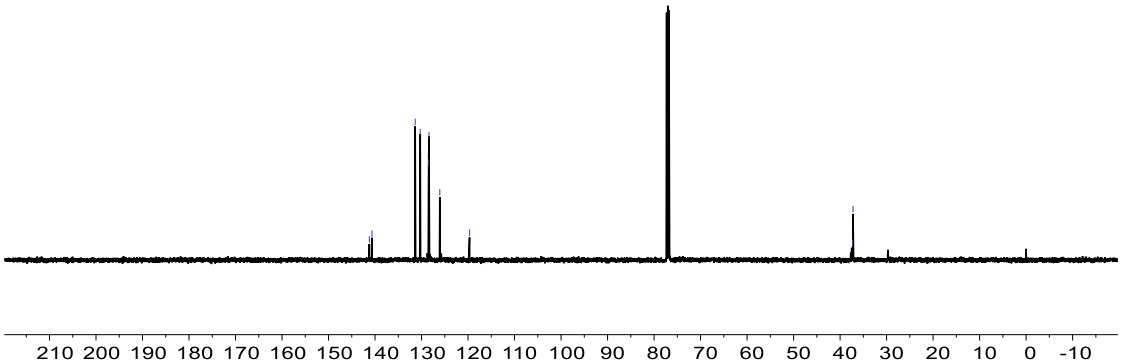
^{1}H NMR spectra of 5 (500 MHz, $CDCl_3$)



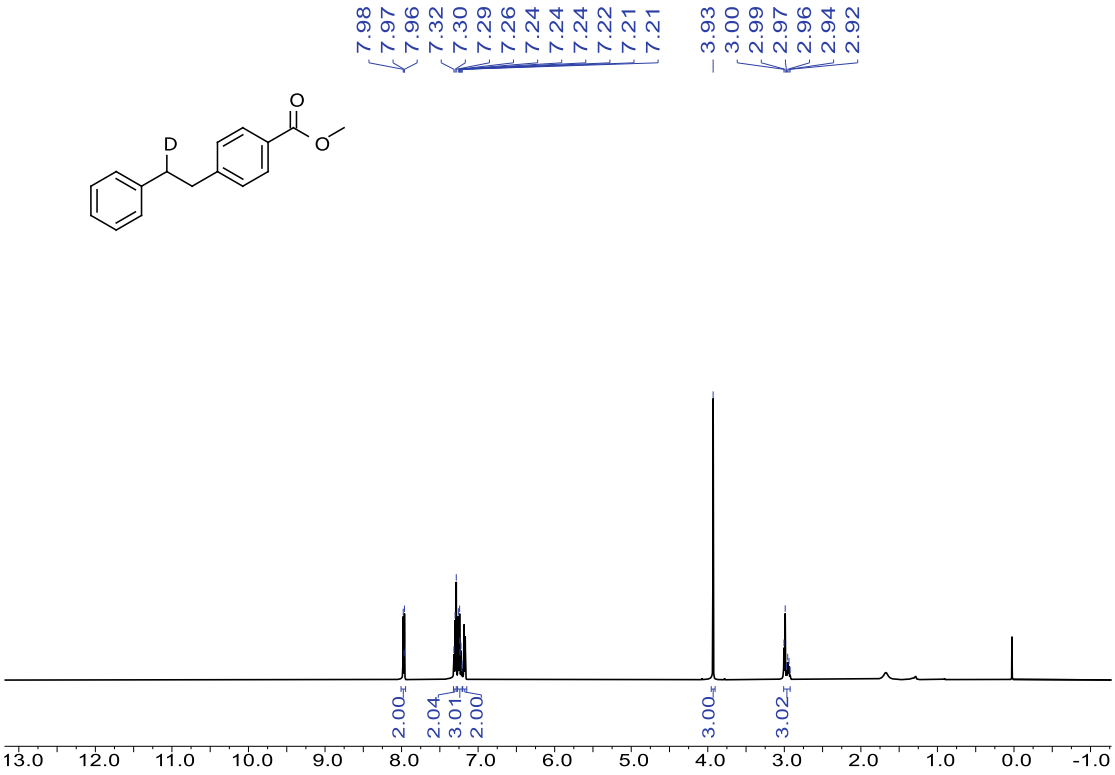


^{13}C NMR spectra of 5 (126 MHz, $CDCl_3$)

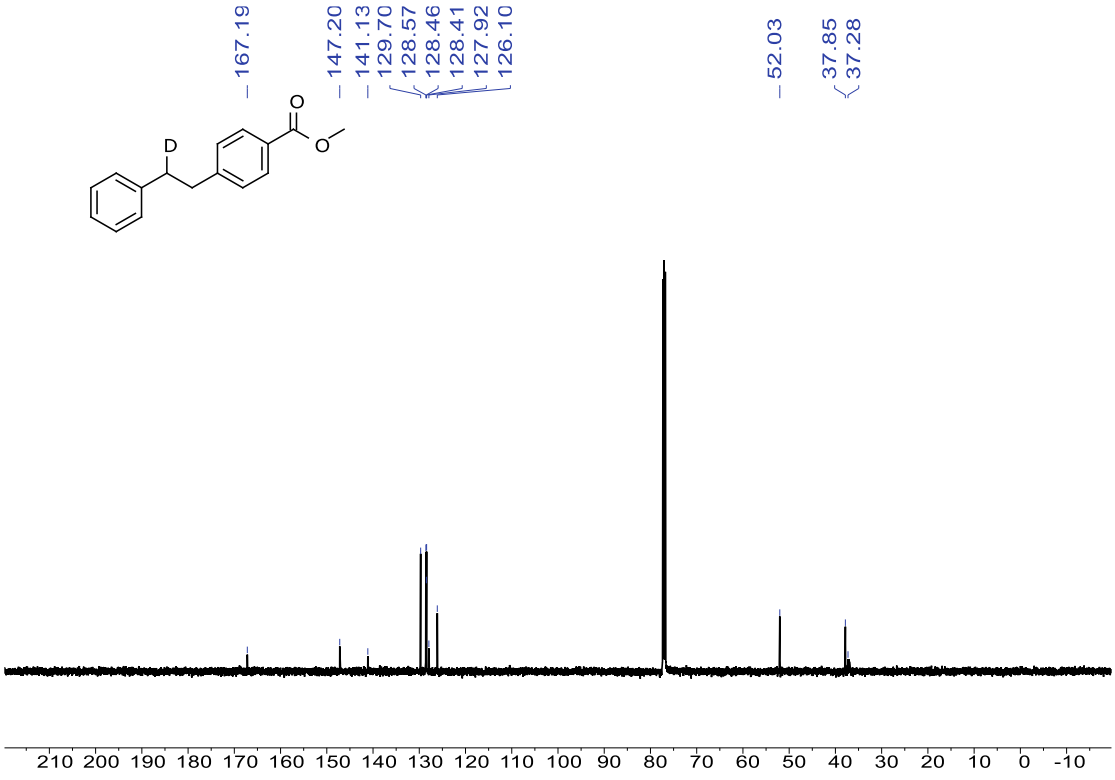




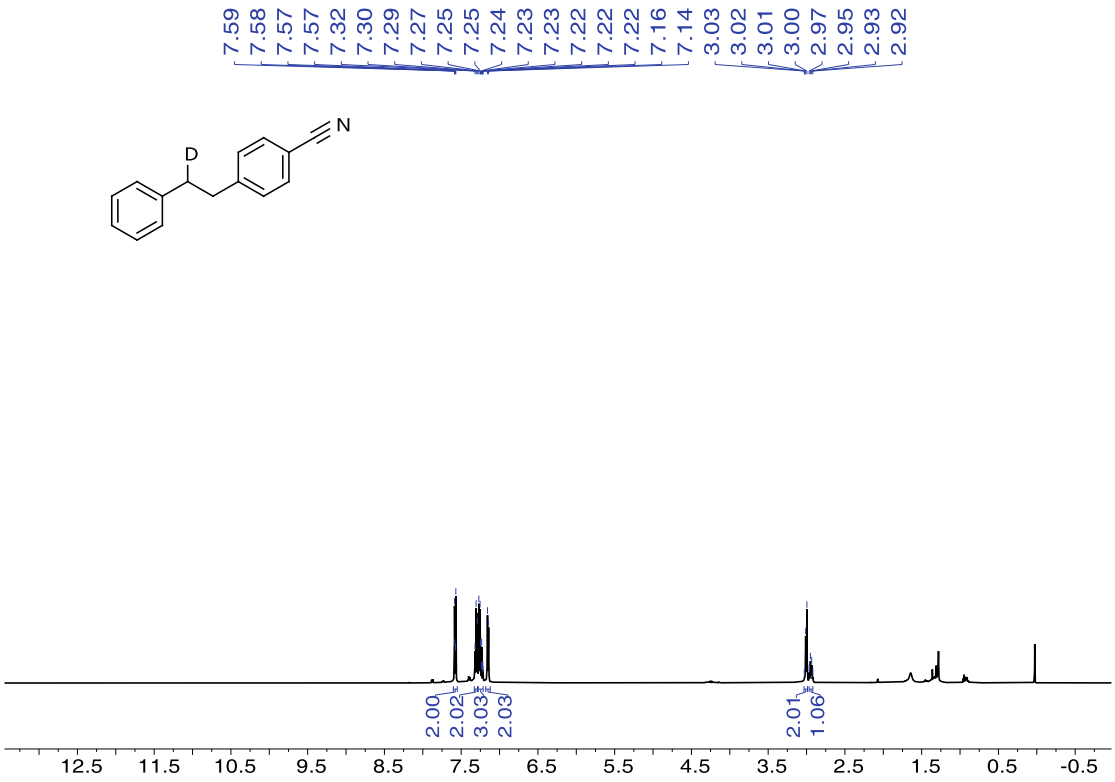
^{1}H NMR spectra of 6 (500 MHz, $CDCl_3$)



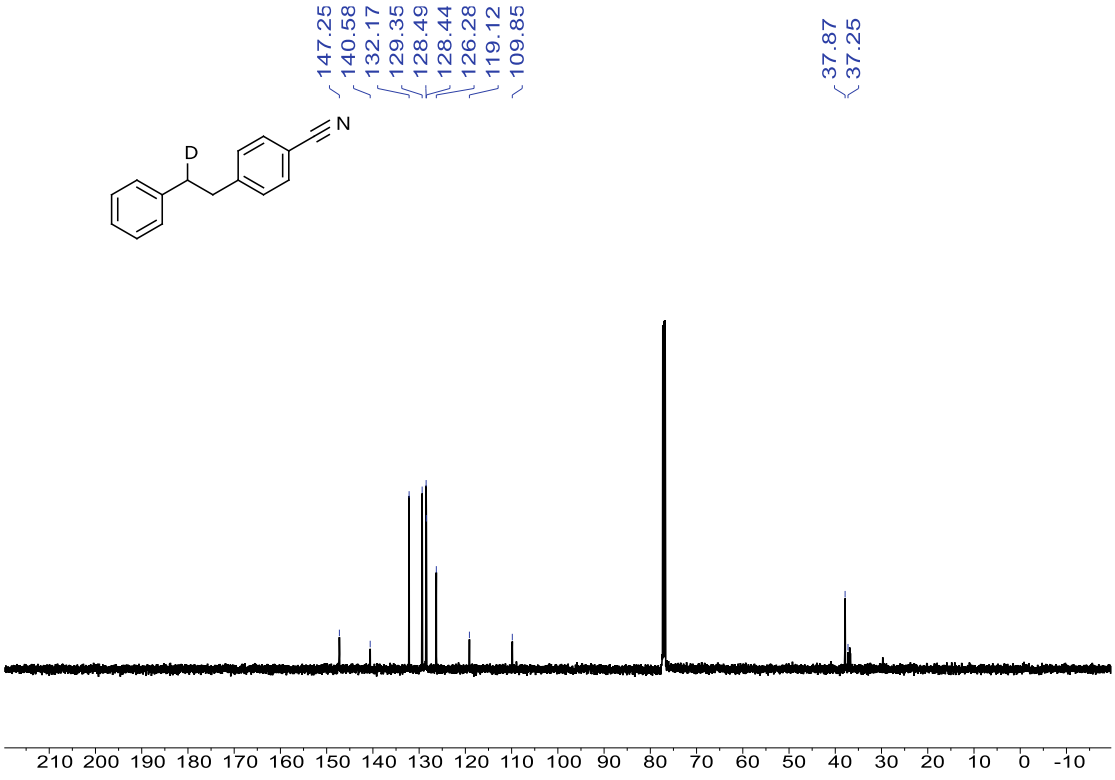
^{13}C NMR spectra of 6 (126 MHz, $CDCl_3$)



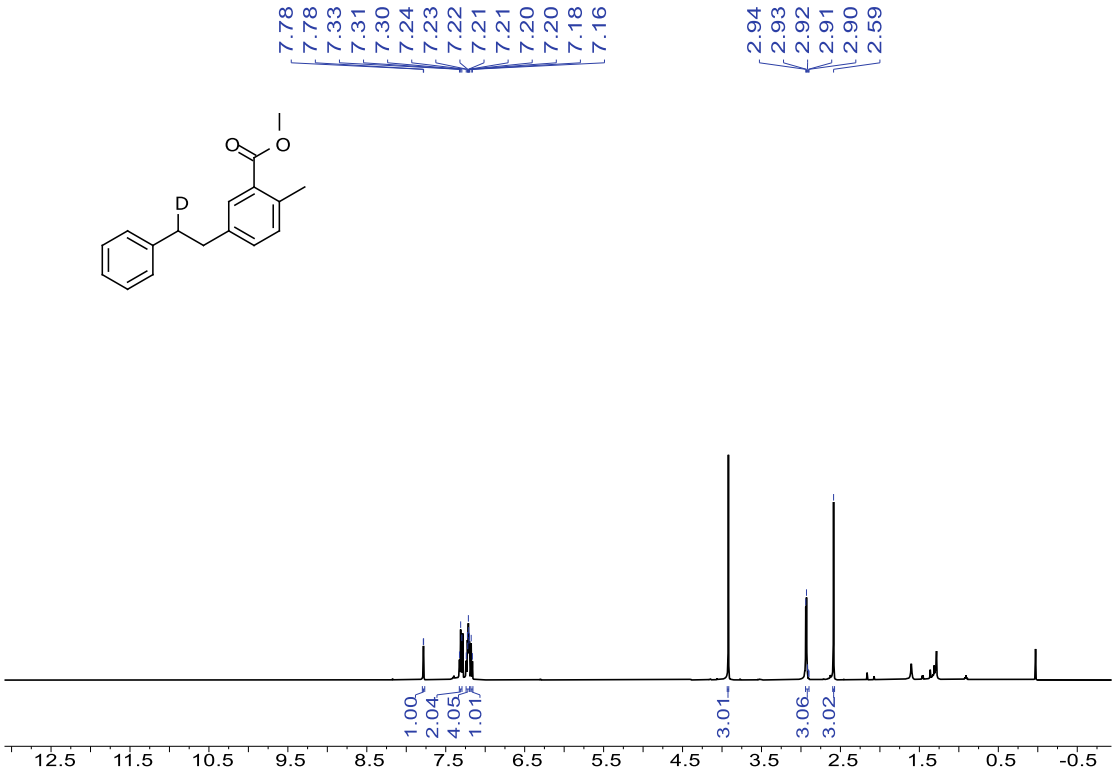
^{1}H NMR spectra of 7 (500 MHz, $CDCl_3$)



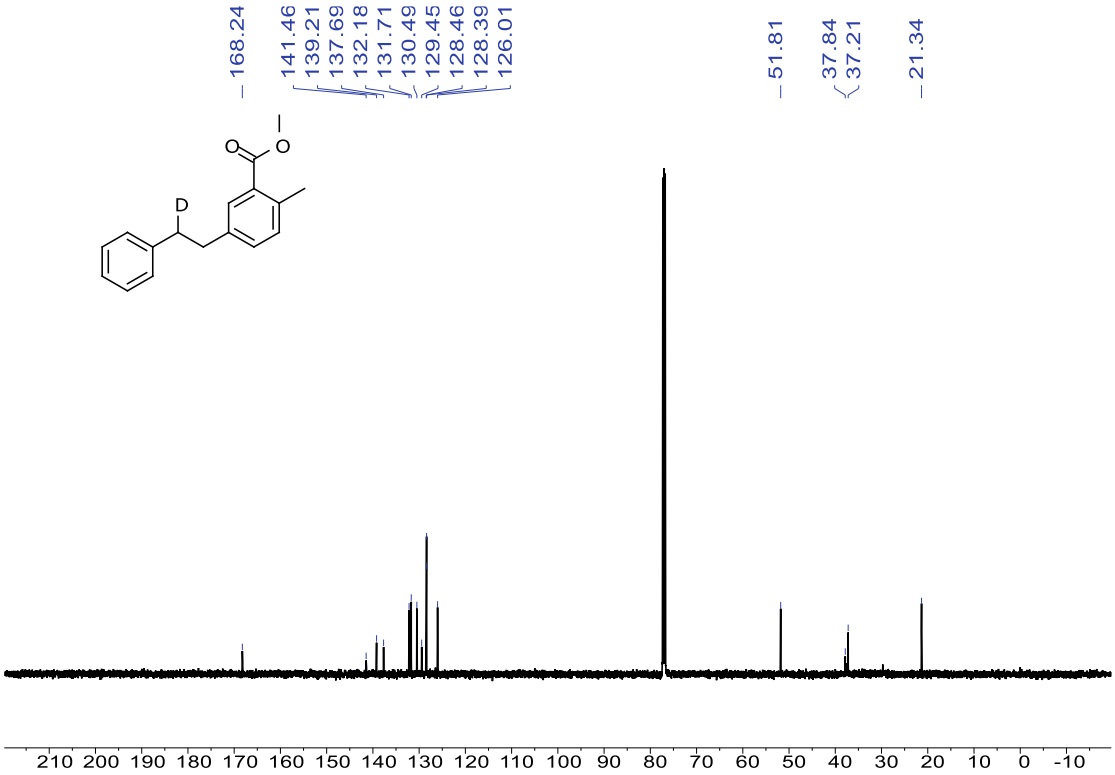
^{13}C NMR spectra of 7 (126 MHz, $CDCl_3$)



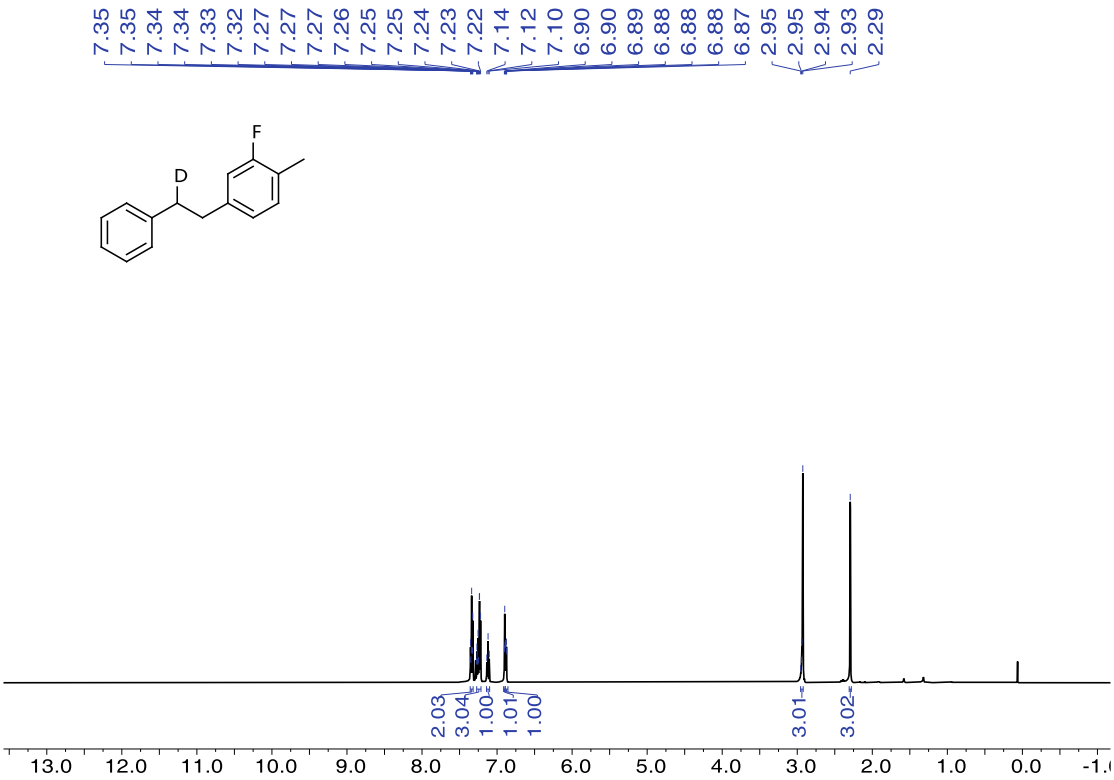
^{1}H NMR spectra of 8 (500 MHz, $CDCl_3$)



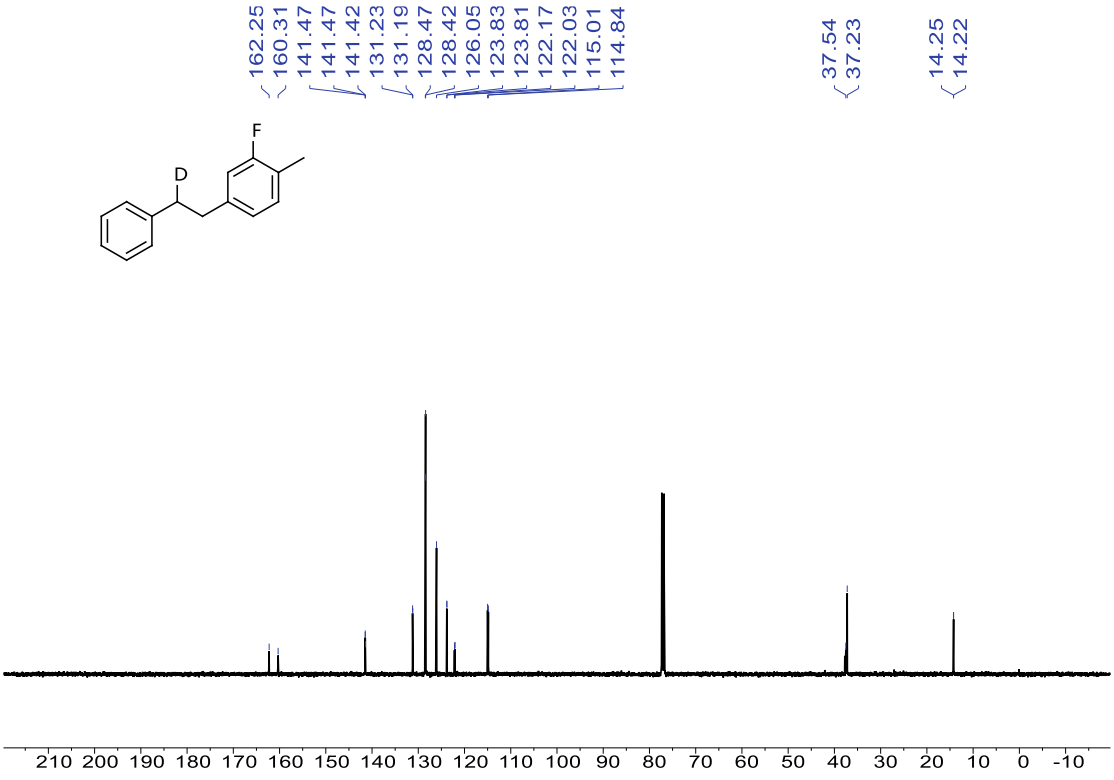
^{13}C NMR spectra of 8 (126 MHz, $CDCl_3$)



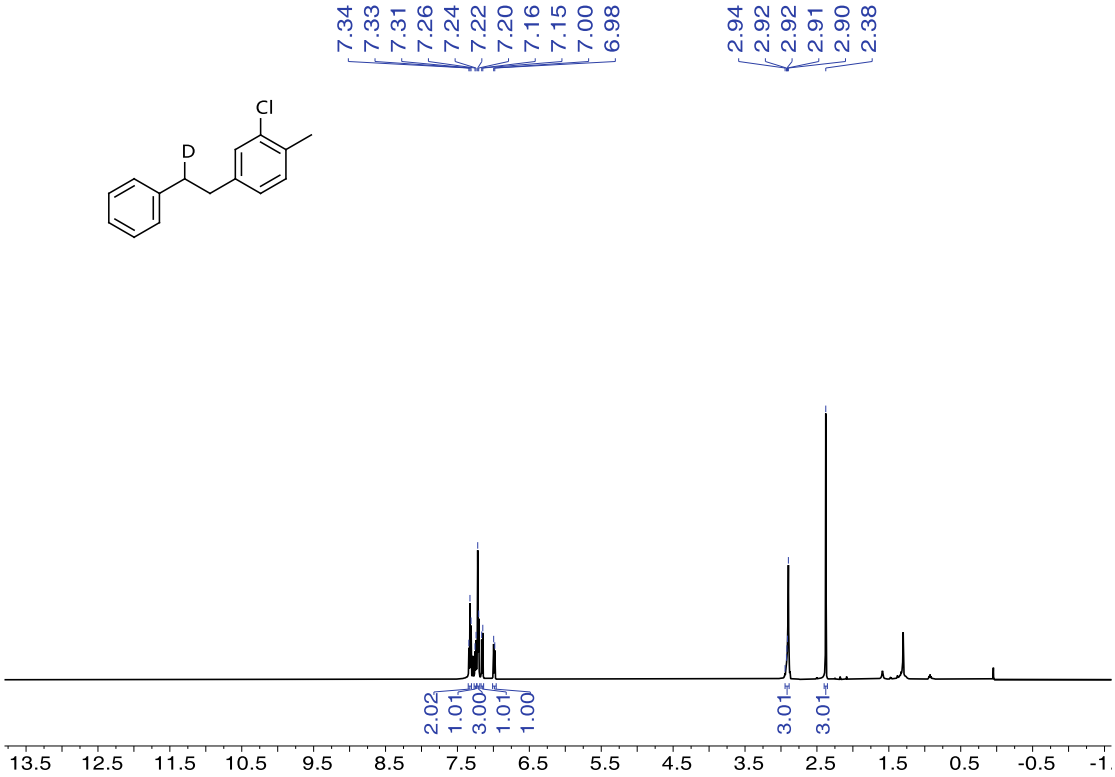
^{1}H NMR spectra of 9 (500 MHz, $CDCl_3$)



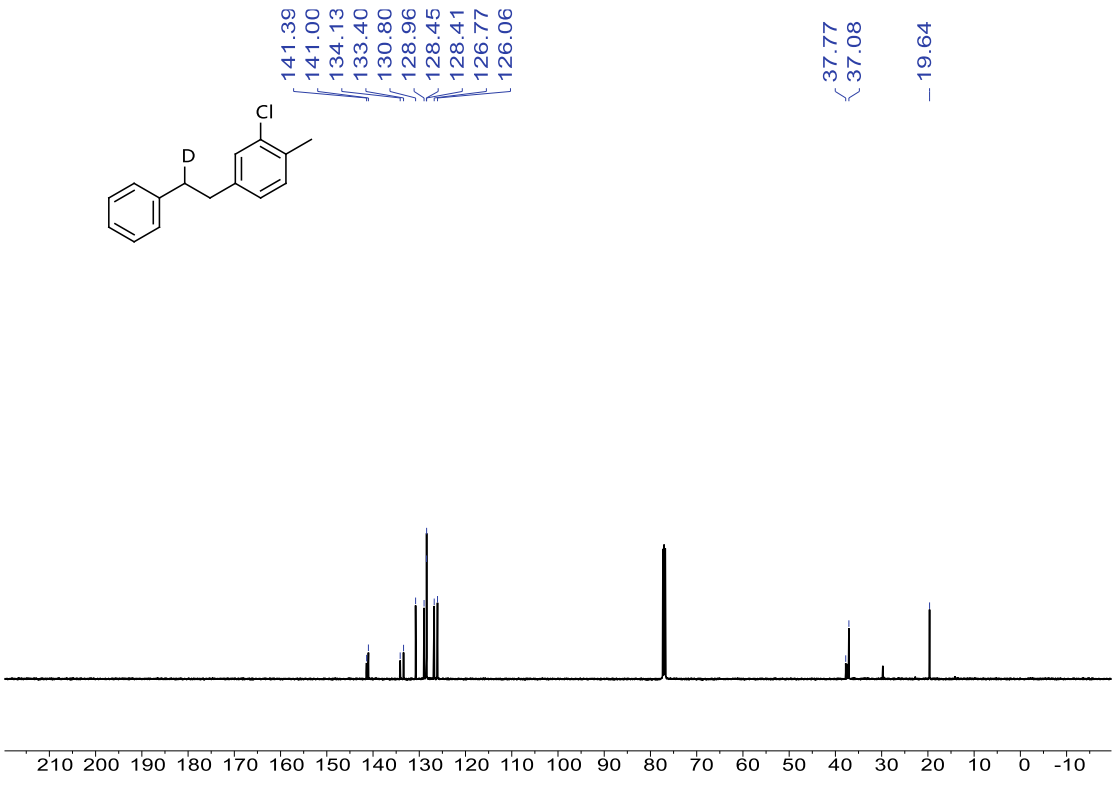
^{13}C NMR spectra of 9 (126 MHz, $CDCl_3$)



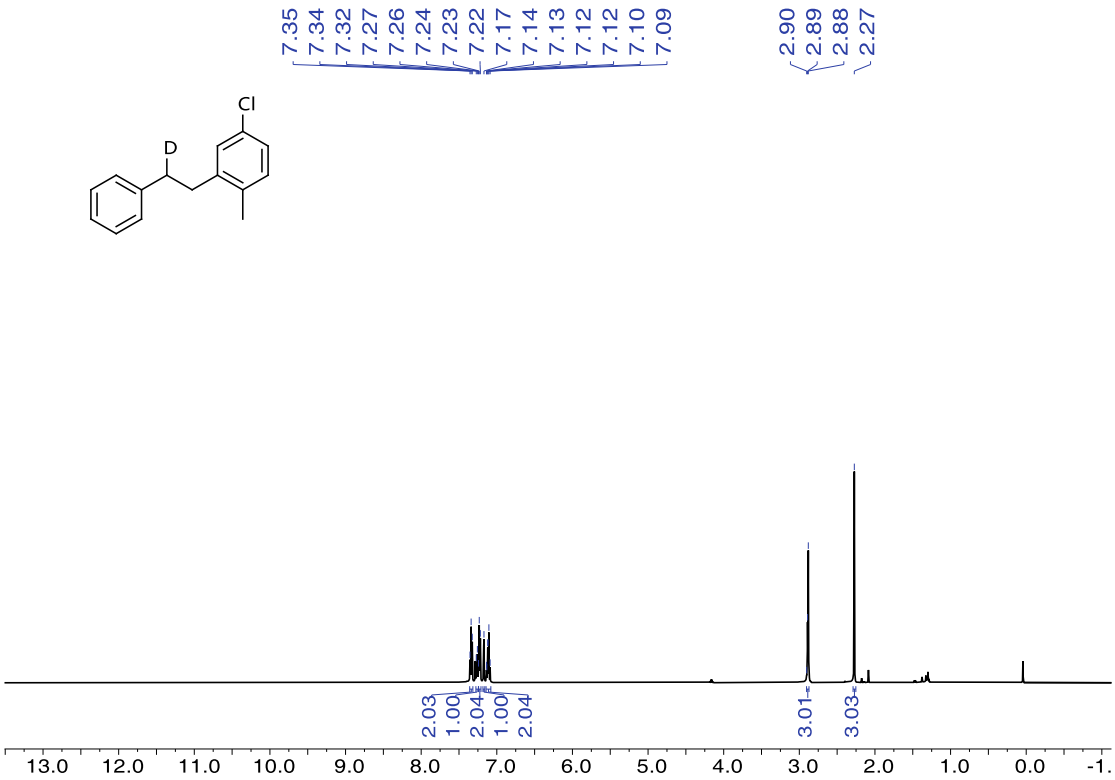
^{1}H NMR spectra of 10 (500 MHz, $CDCl_3$)



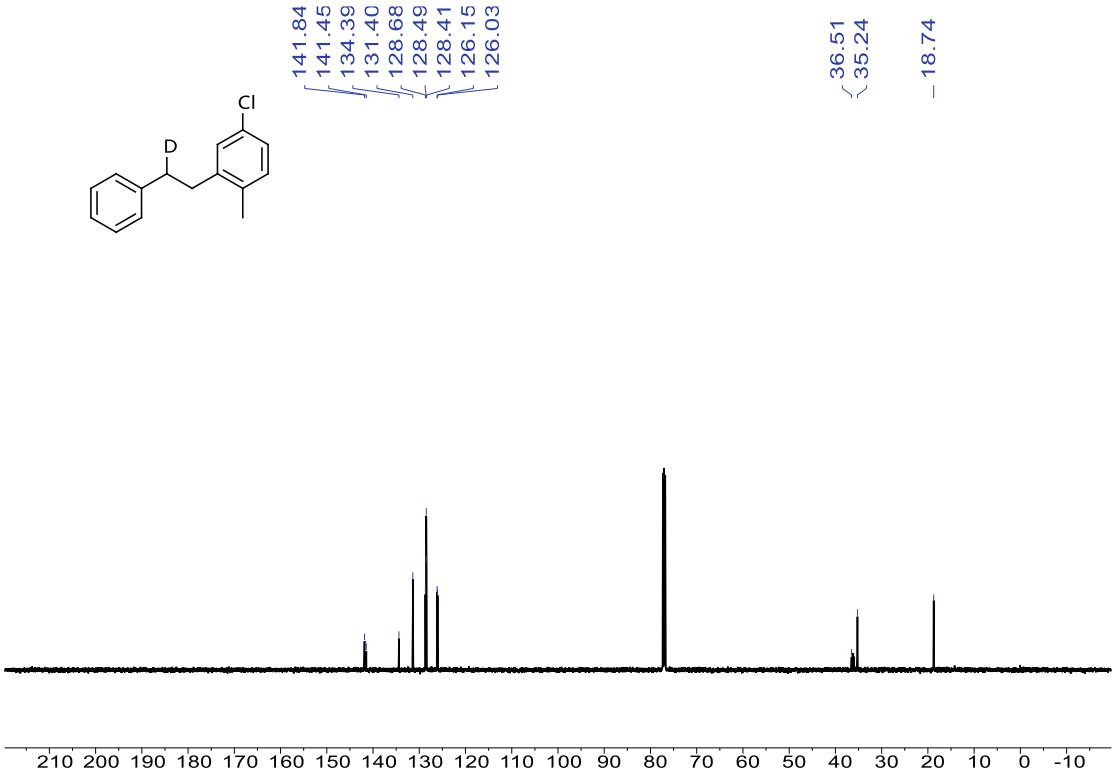
^{13}C NMR spectra of 10 (126 MHz, $CDCl_3$)



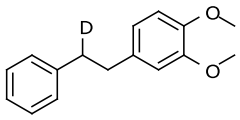
^{1}H NMR spectra of 11 (500 MHz, $CDCl_3$)

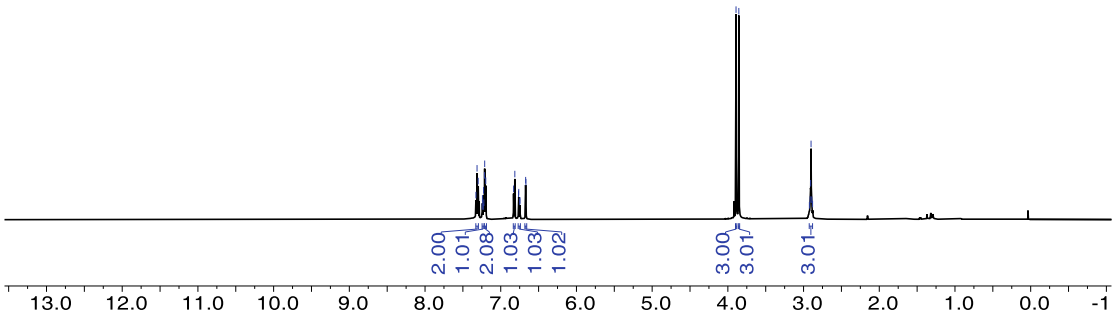


^{13}C NMR spectra of 11 (126 MHz, $CDCl_3$)

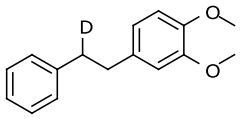


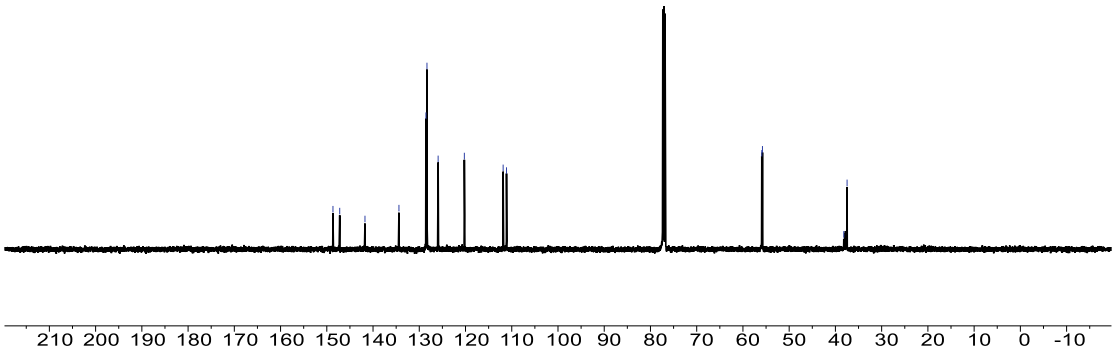
^{1}H NMR spectra of 12 (500 MHz, $CDCl_3$)



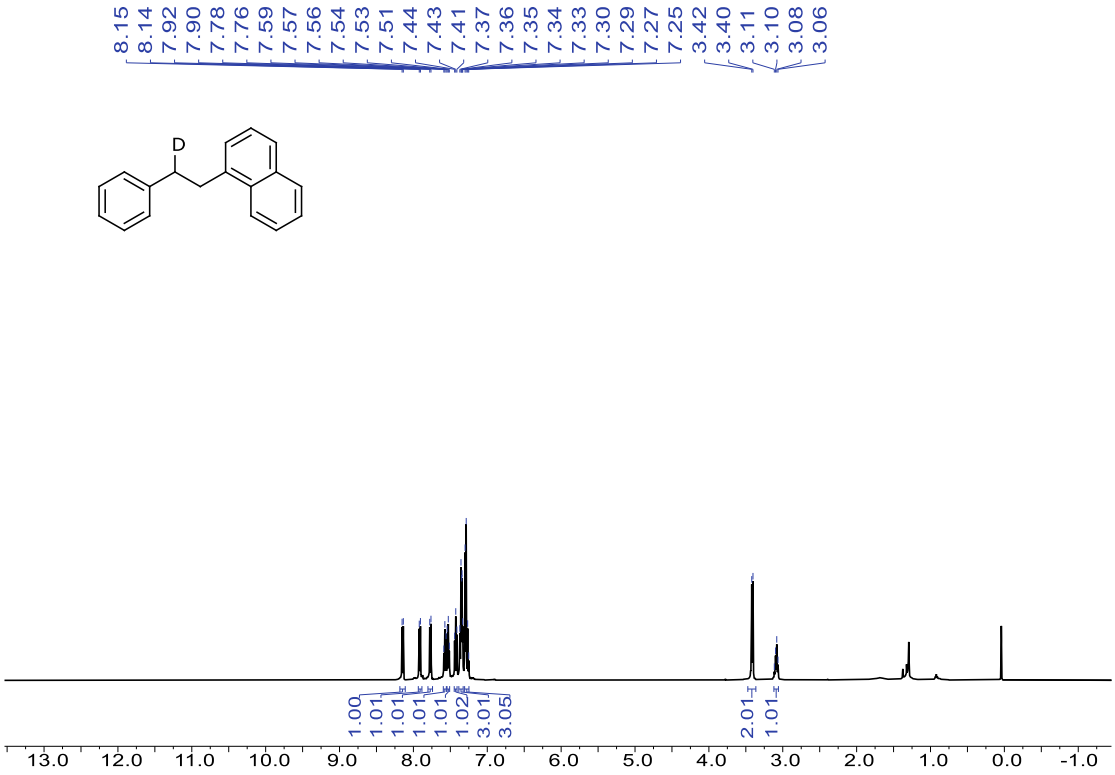


^{13}C NMR spectra of 12 (126 MHz, $CDCl_3$)

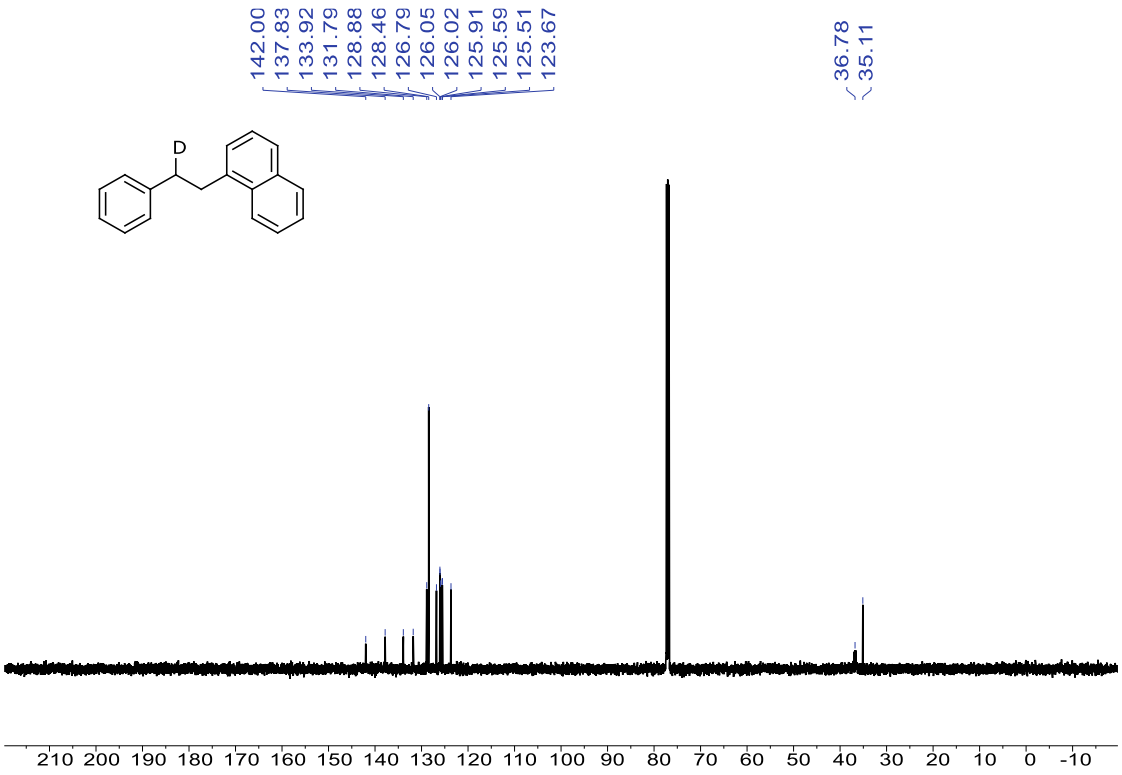




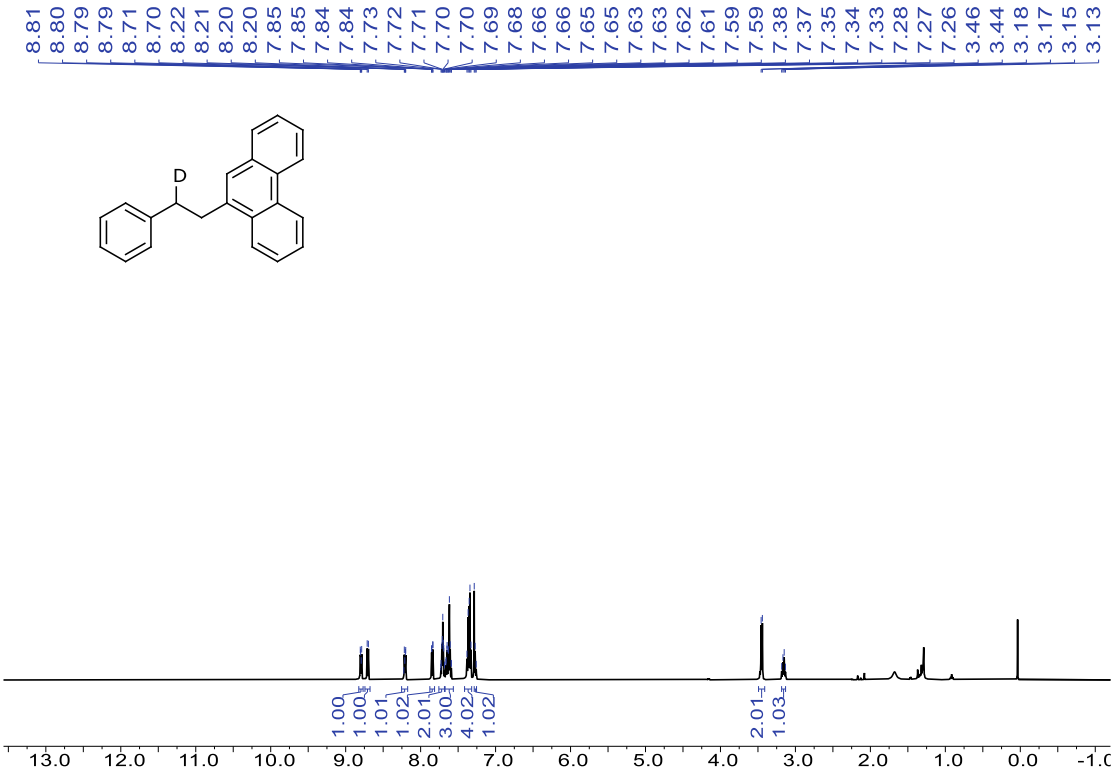
^{1}H NMR spectra of 13 (500 MHz, $CDCl_3$)



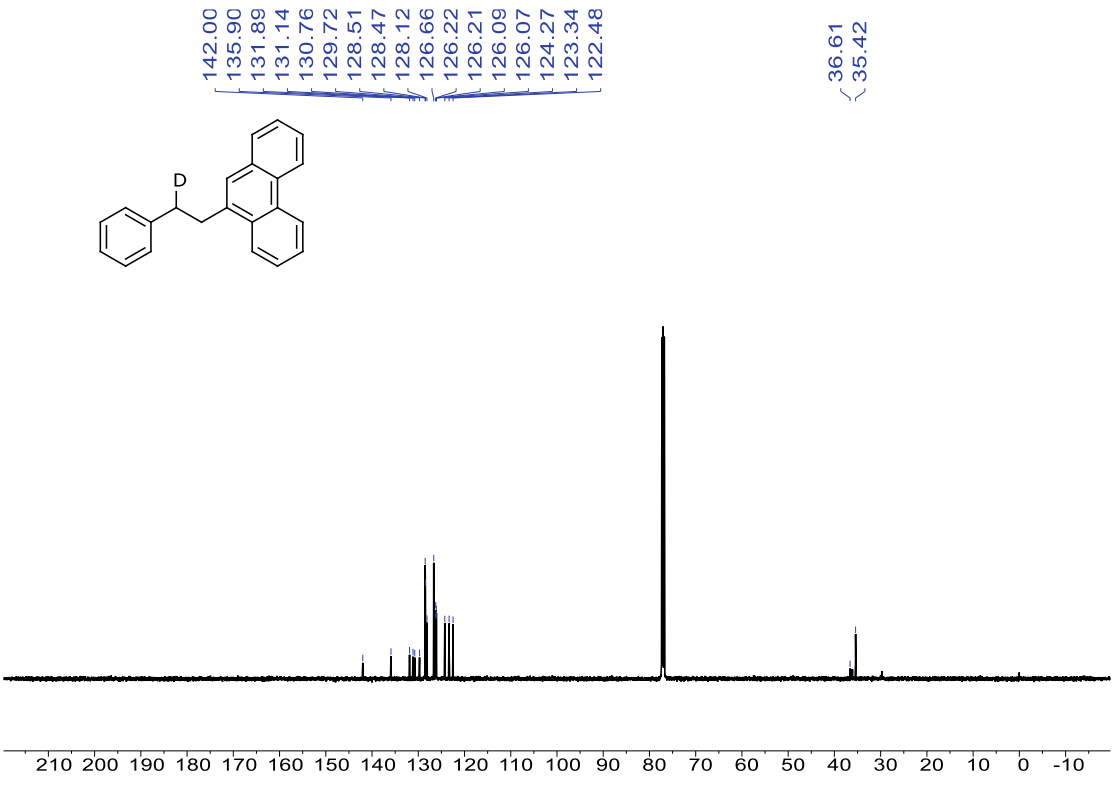
^{13}C NMR spectra of 13 (126 MHz, $CDCl_3$)



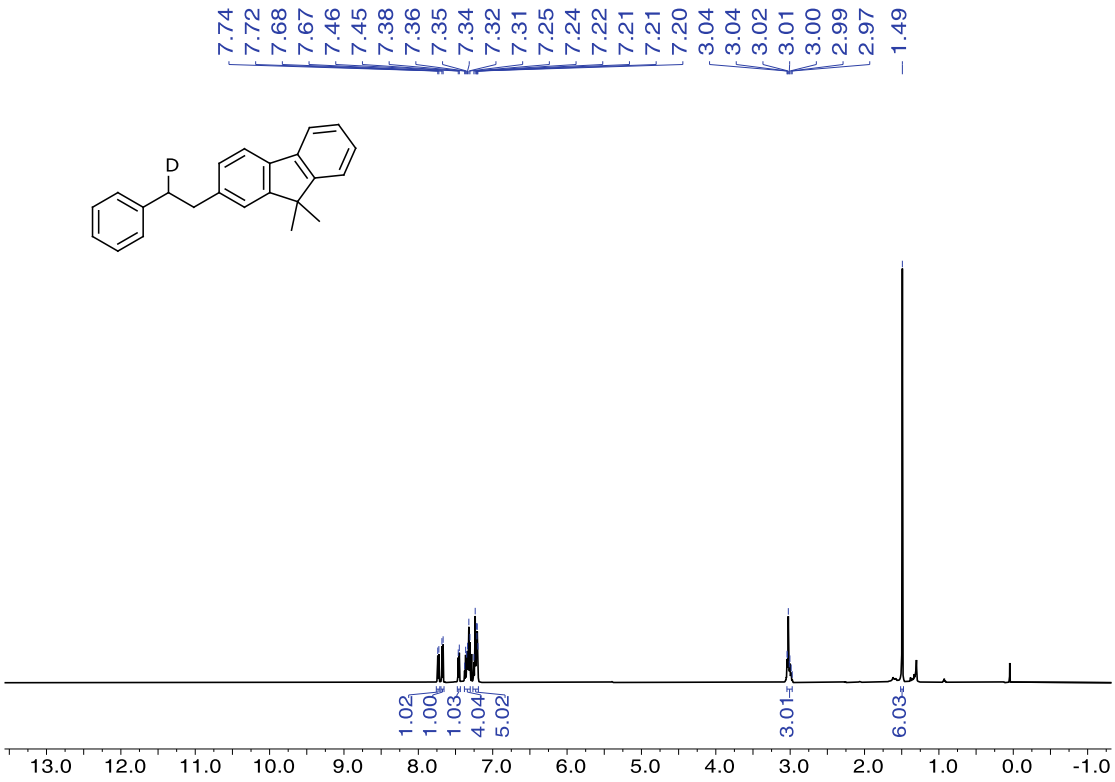
^{1}H NMR spectra of 14 (500 MHz, $CDCl_3$)



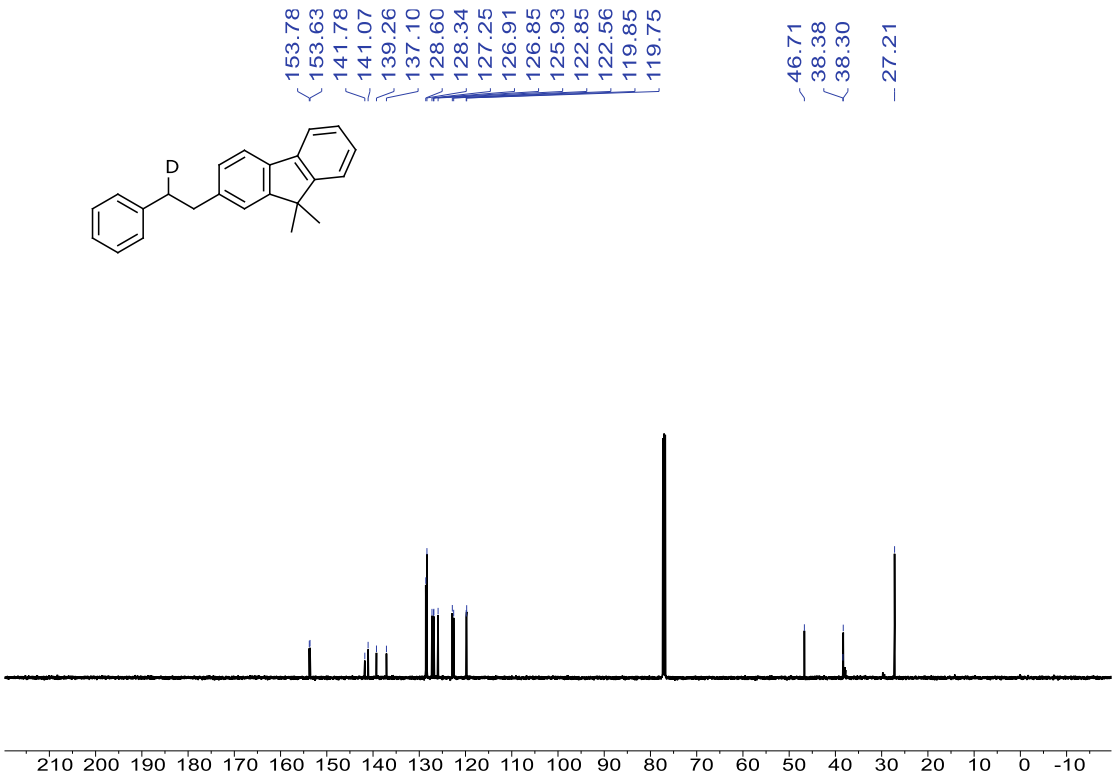
^{13}C NMR spectra of 14 (126 MHz, $CDCl_3$)



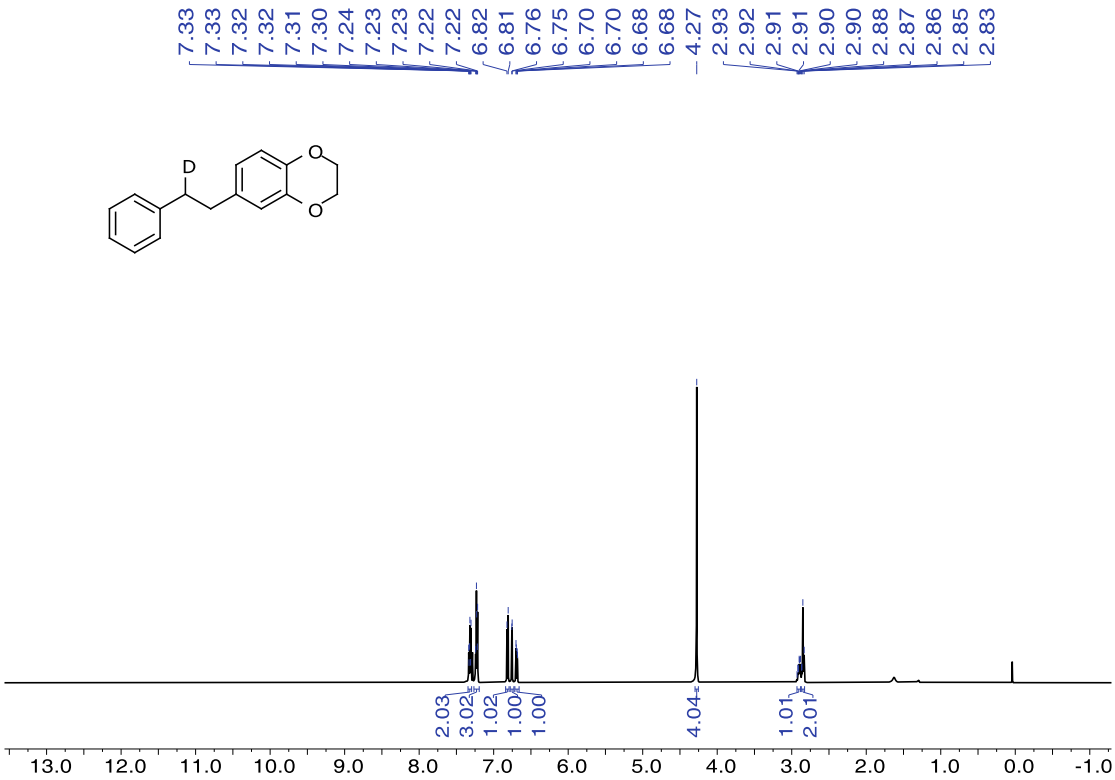
^{1}H NMR spectra of 15 (500 MHz, $CDCl_3$)



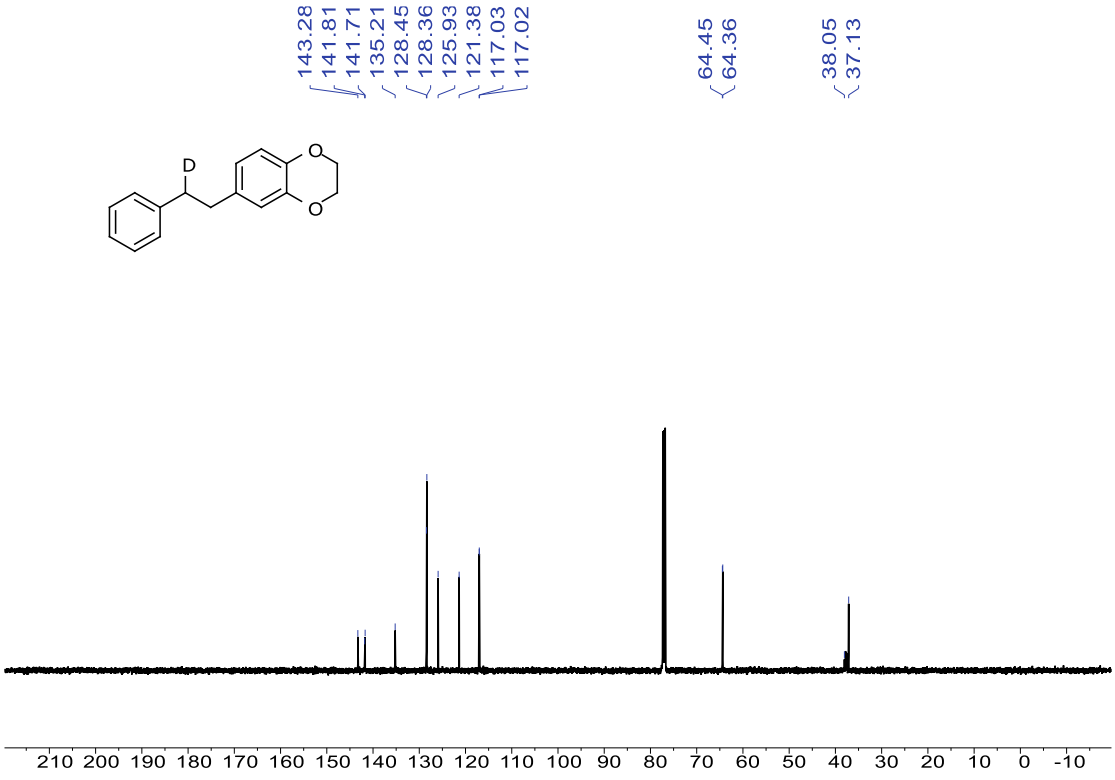
^{13}C NMR spectra of 15 (126 MHz, $CDCl_3$)



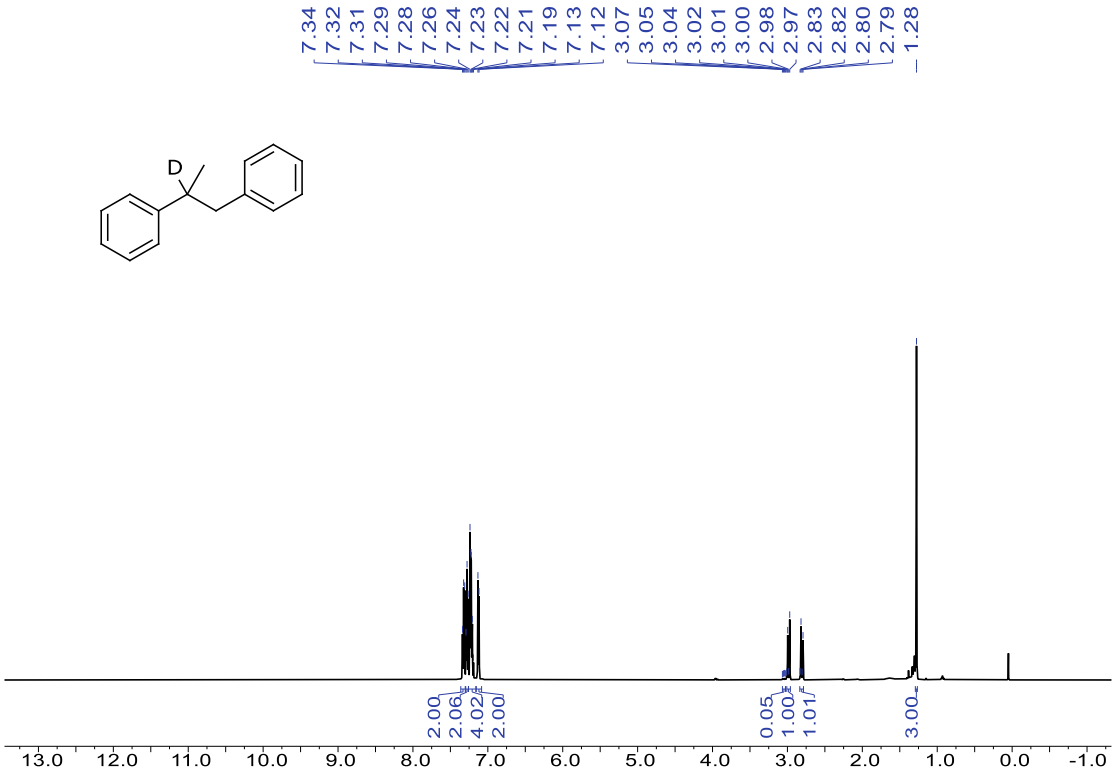
^{1}H NMR spectra of 16 (500 MHz, $CDCl_3$)



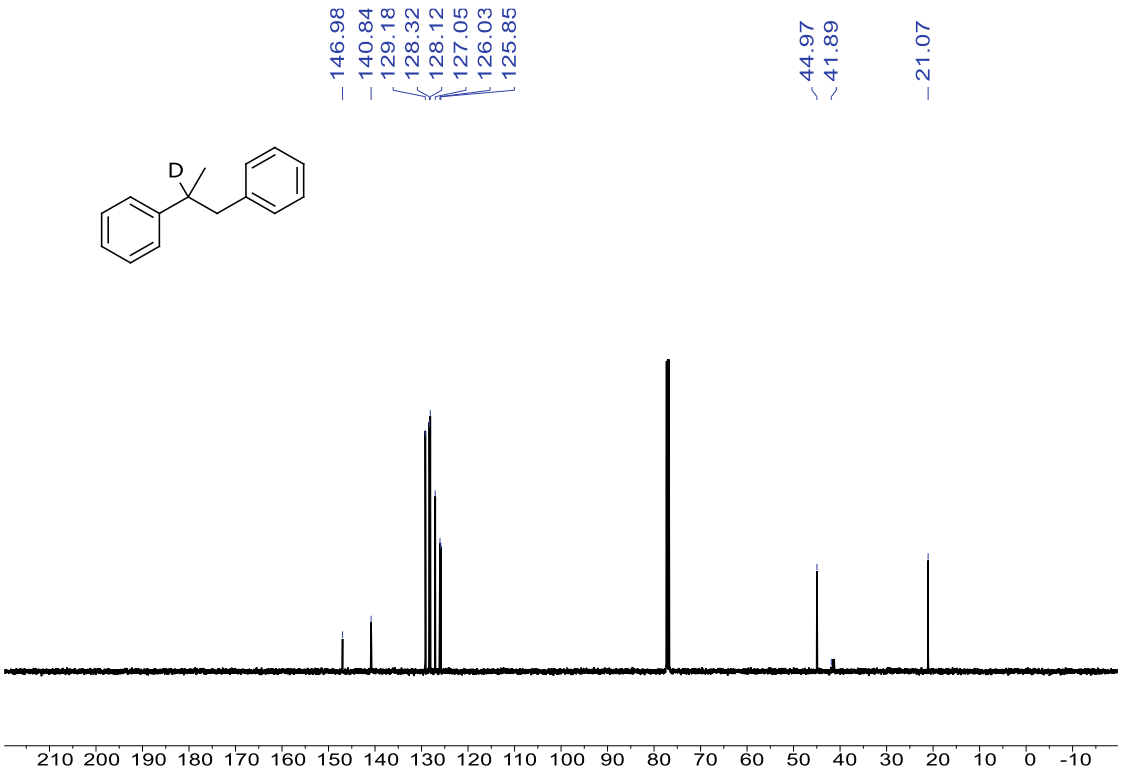
^{13}C NMR spectra of 16 (126 MHz, $CDCl_3$)



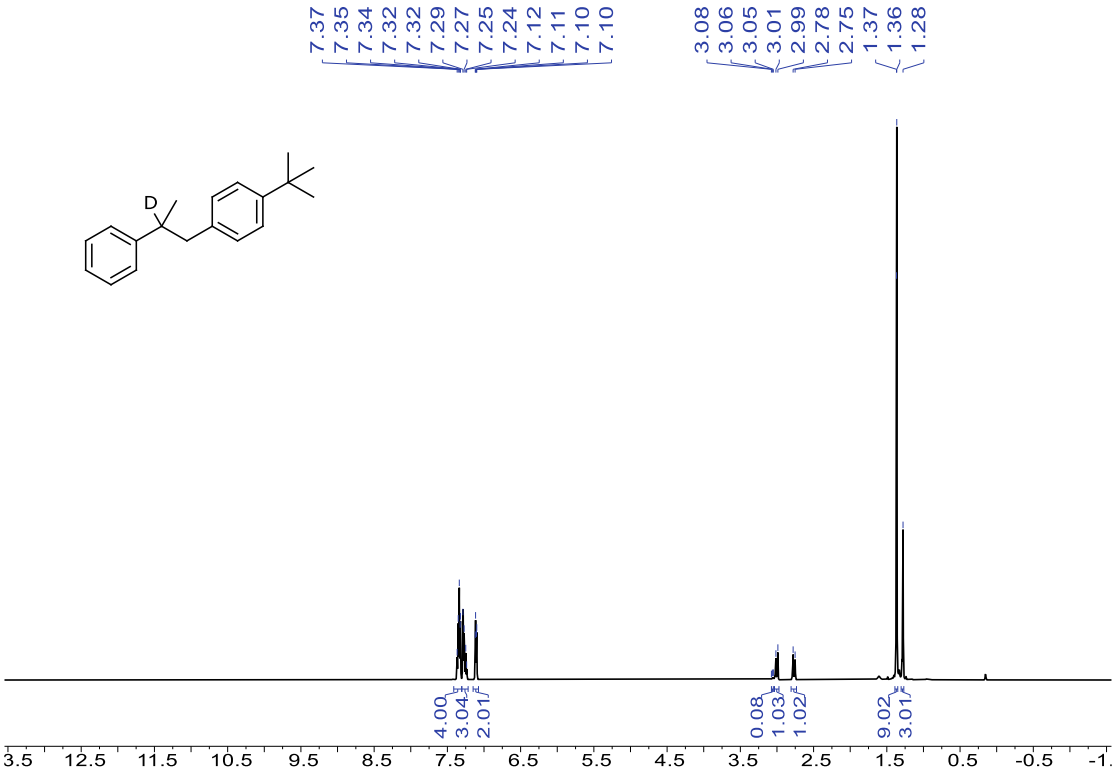
^{1}H NMR spectra of 17 (500 MHz, $CDCl_3$)



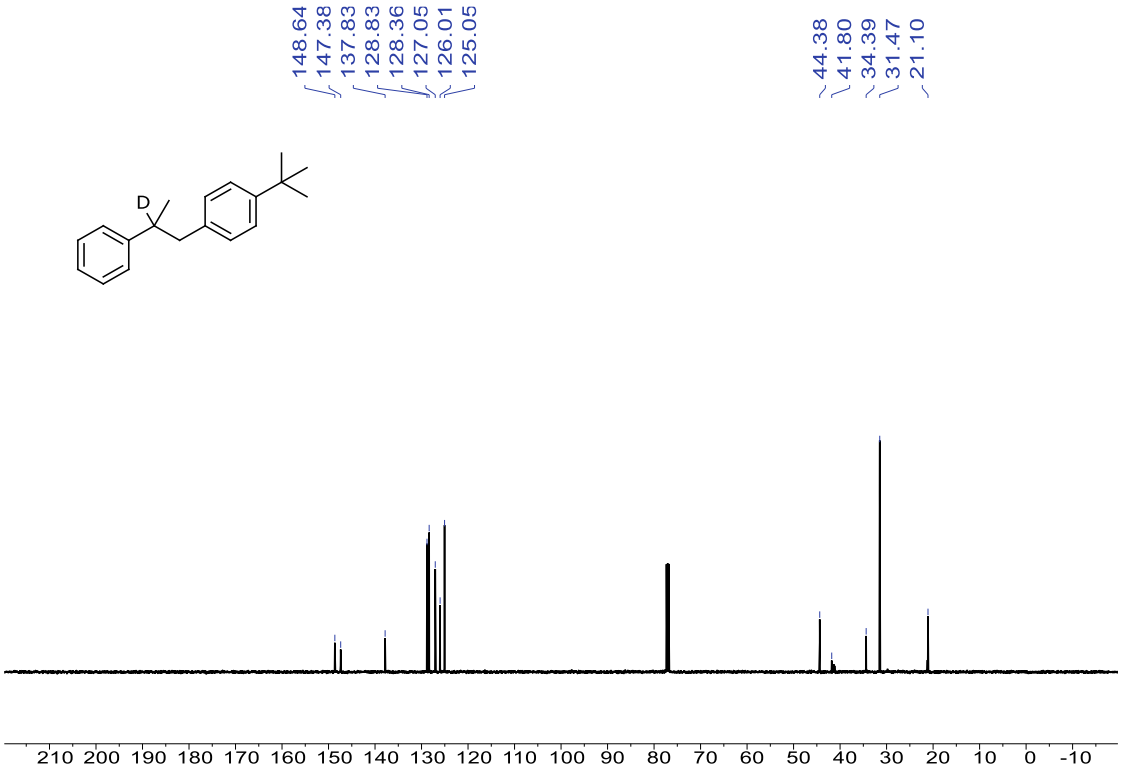
^{13}C NMR spectra of 17 (126 MHz, $CDCl_3$)



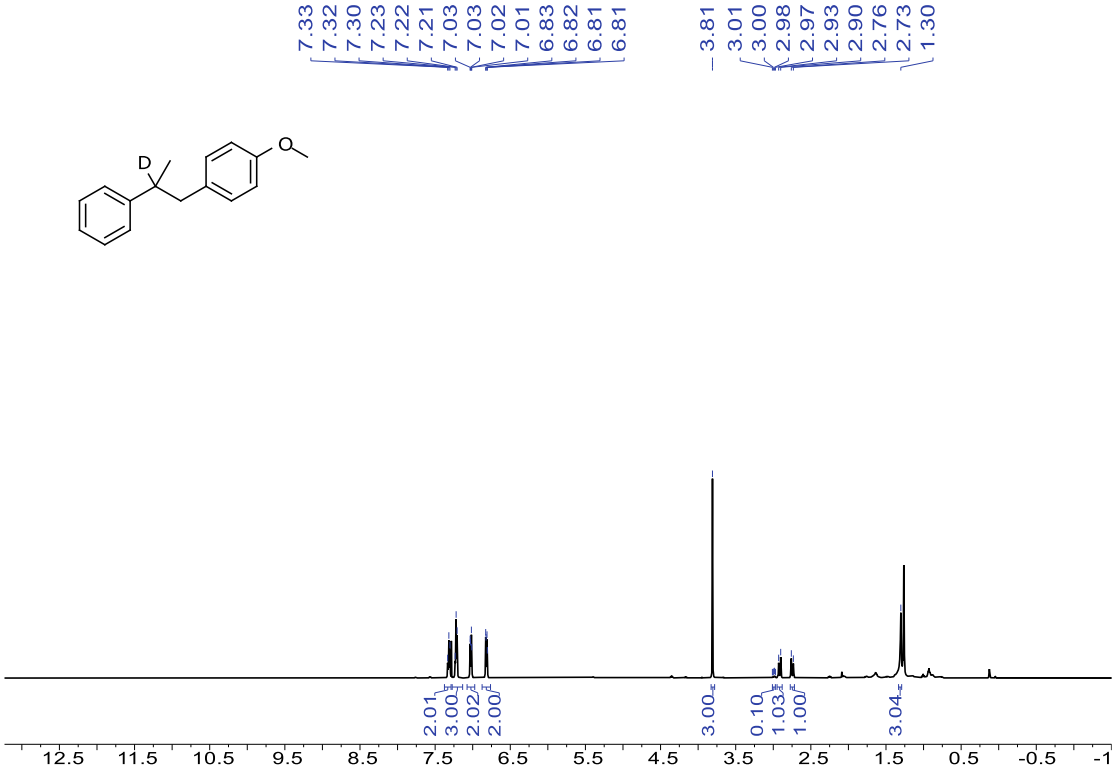
^{1}H NMR spectra of 18 (500 MHz, $CDCl_3$)



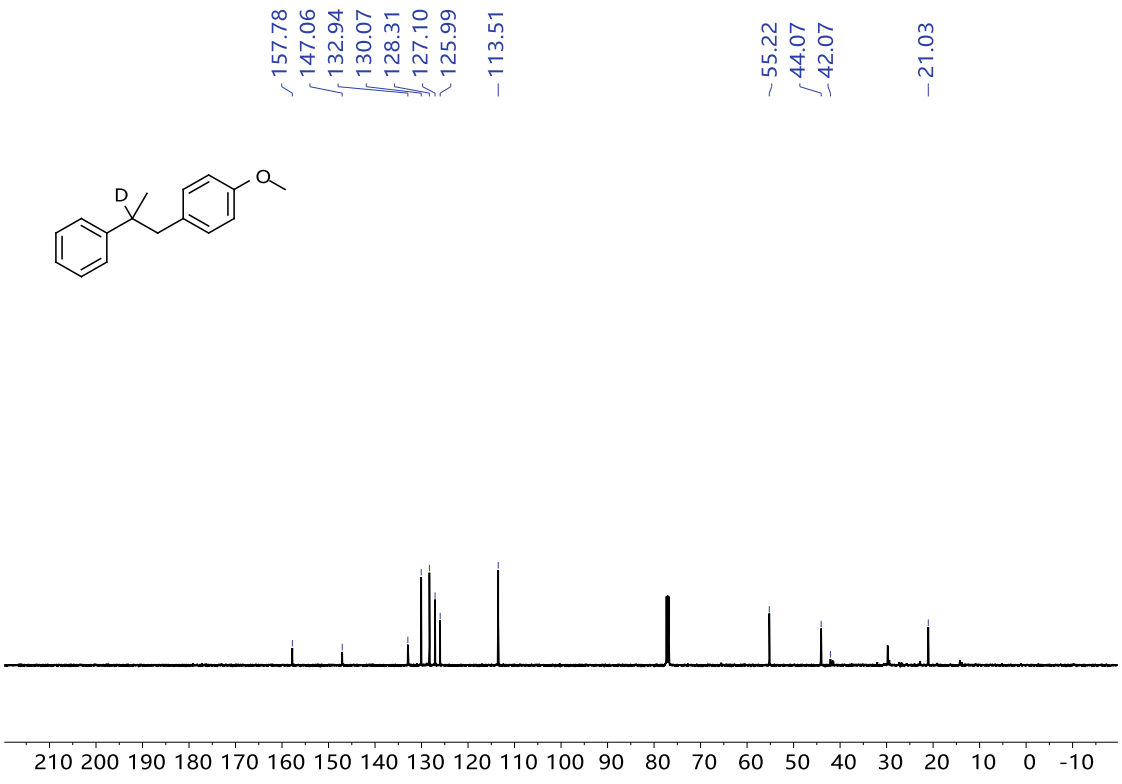
^{13}C NMR spectra of 18 (126 MHz, $CDCl_3$)



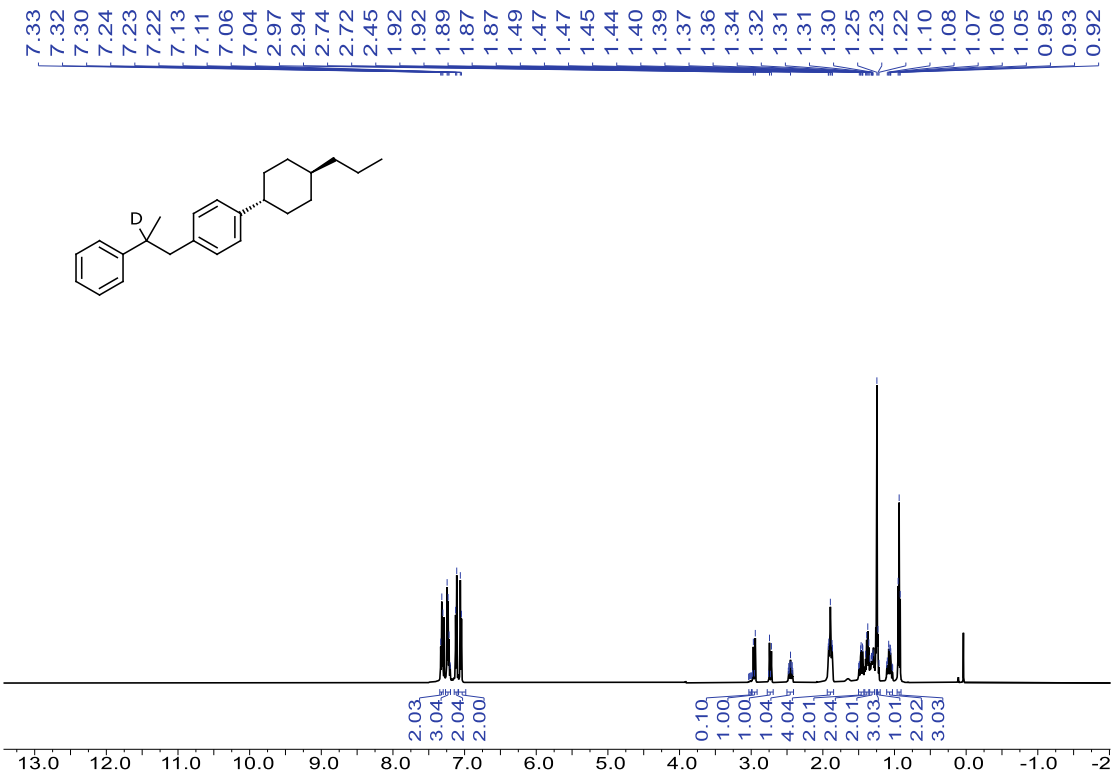
^{1}H NMR spectra of 19 (500 MHz, $CDCl_3$)



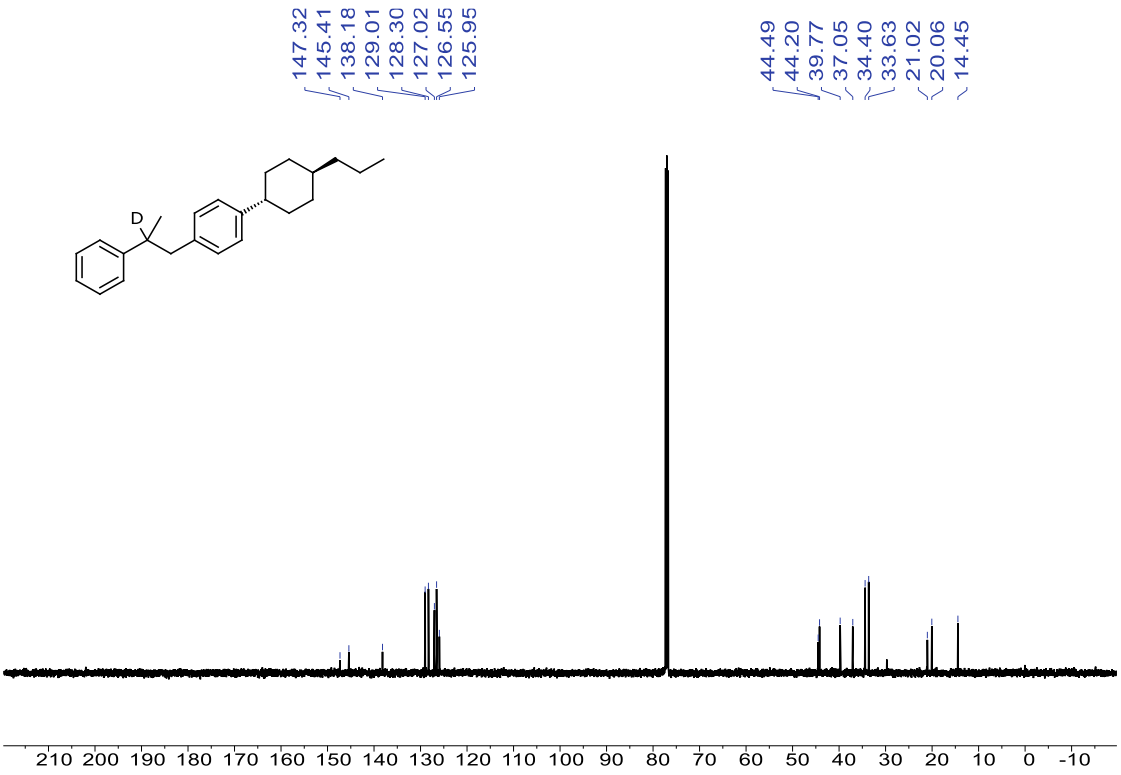
^{13}C NMR spectra of 19 (126 MHz, $CDCl_3$)



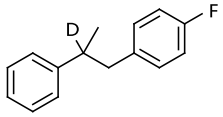
^{1}H NMR spectra of 20 (500 MHz, $CDCl_3$)

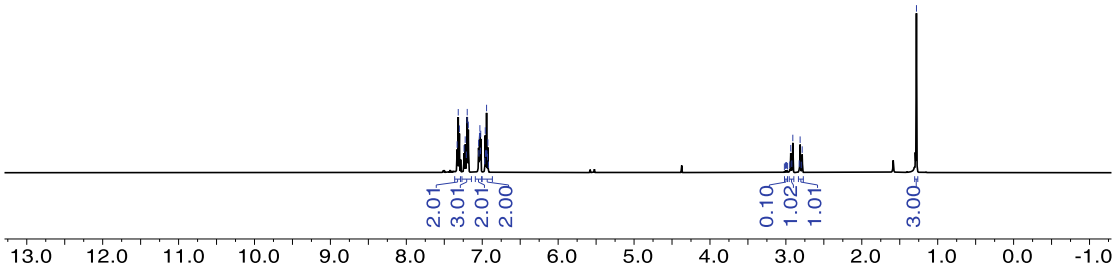


^{13}C NMR spectra of 20 (126 MHz, $CDCl_3$)

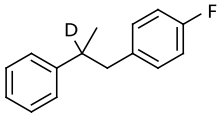


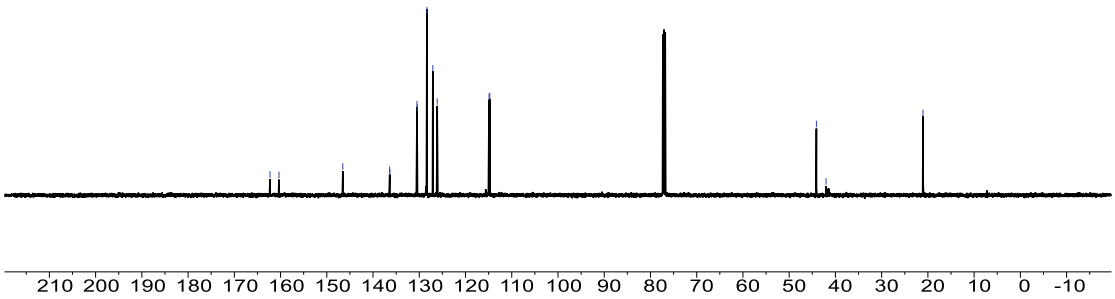
^{1}H NMR spectra of 21 (500 MHz, $CDCl_3$)



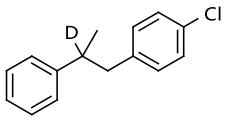


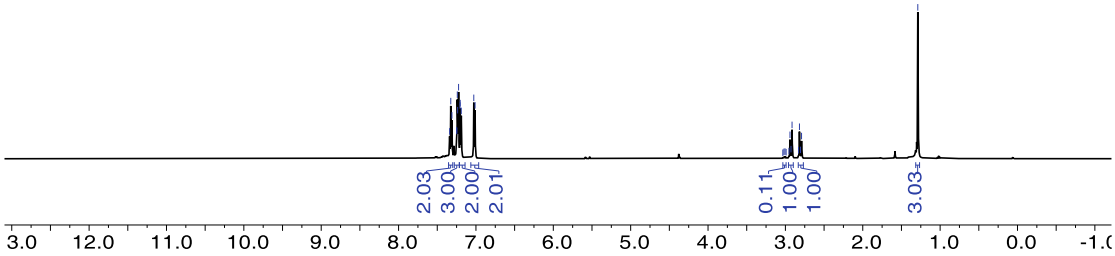
^{13}C NMR spectra of 21 (126 MHz, $CDCl_3$)



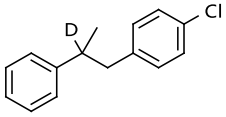


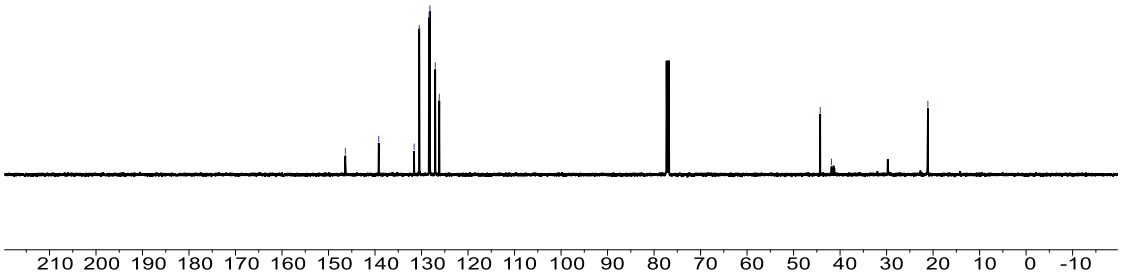
^{1}H NMR spectra of 22 (500 MHz, $CDCl_3$)



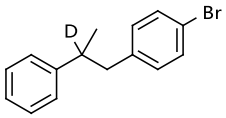


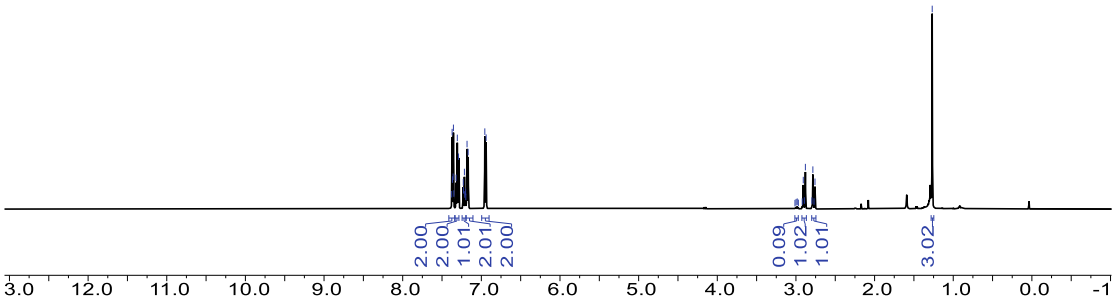
^{13}C NMR spectra of 22 (126 MHz, $CDCl_3$)



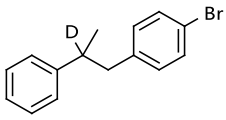


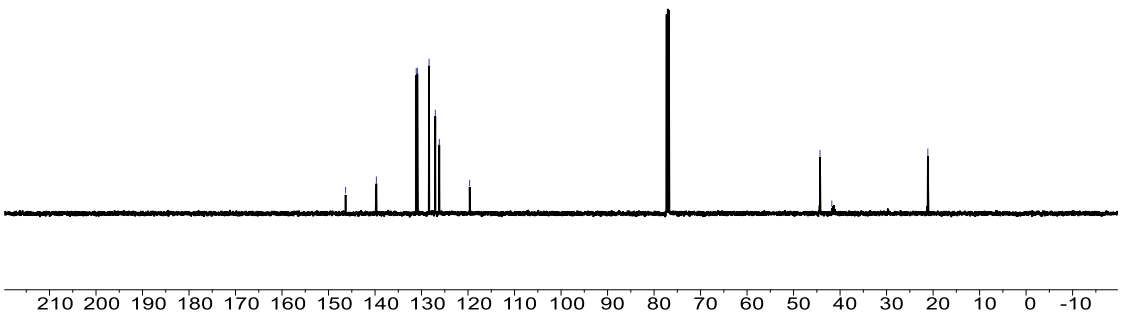
^{1}H NMR spectra of 23 (500 MHz, $CDCl_3$)



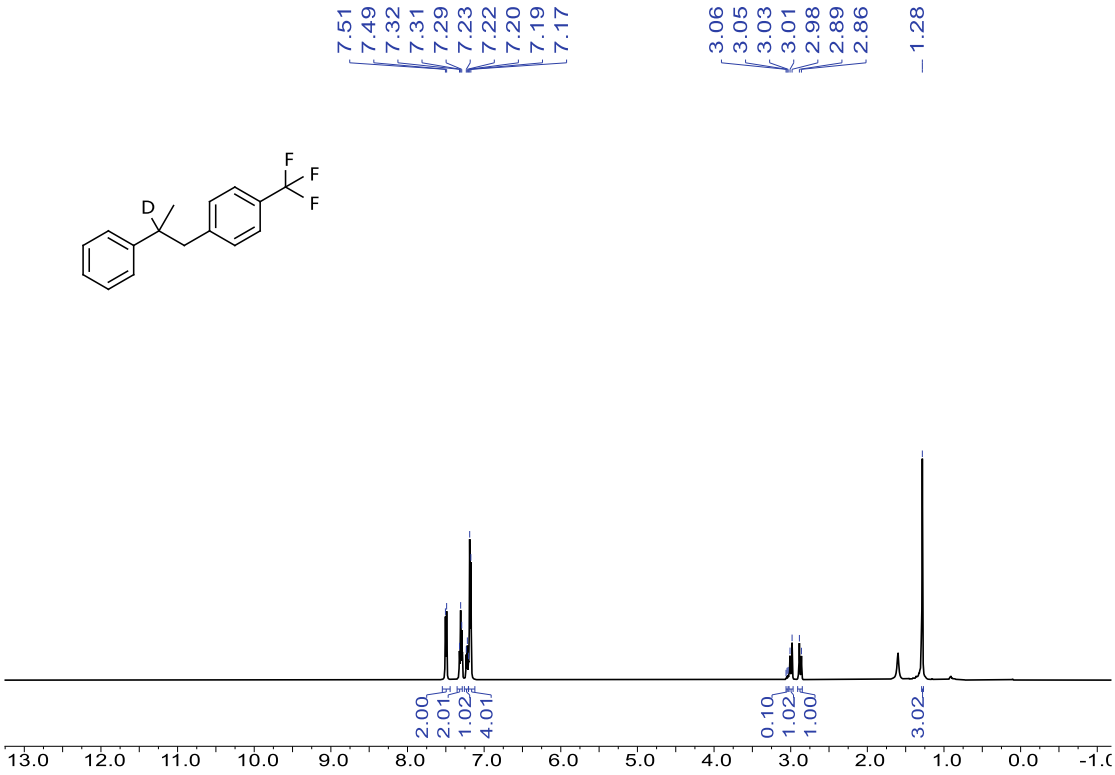


^{13}C NMR spectra of 23 (126 MHz, $CDCl_3$)

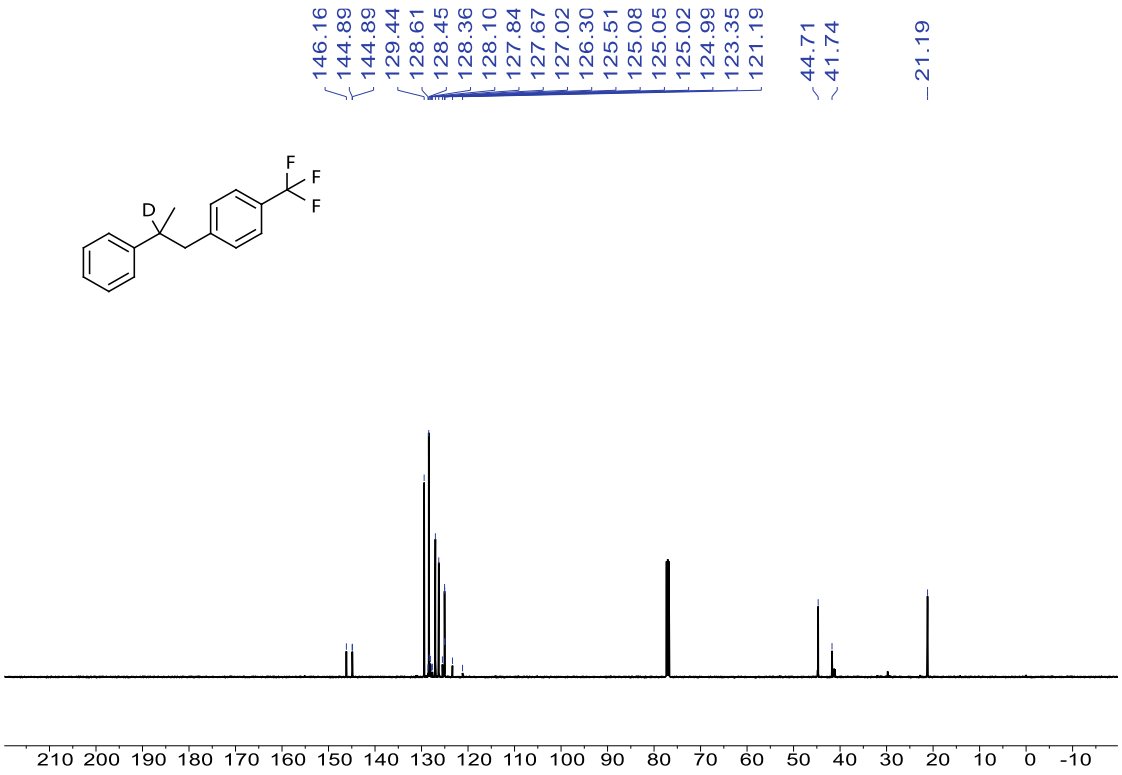




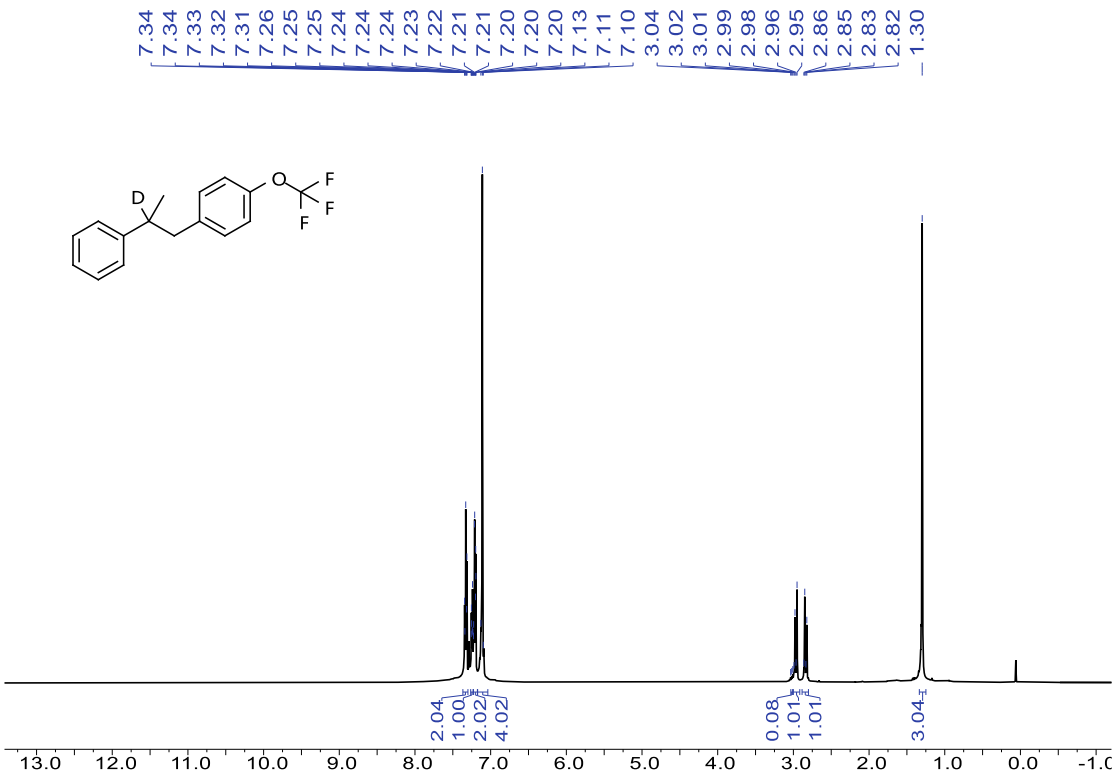
^{1}H NMR spectra of 24 (500 MHz, $CDCl_3$)



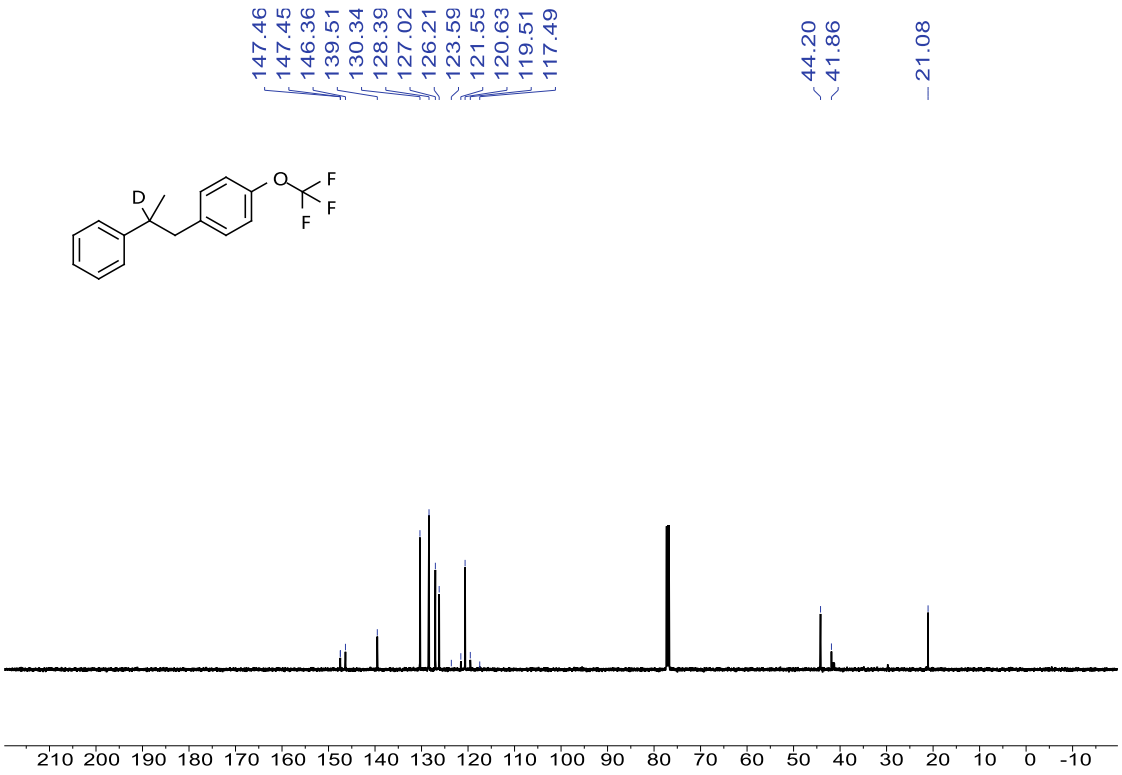
^{13}C NMR spectra of 24 (126 MHz, $CDCl_3$)



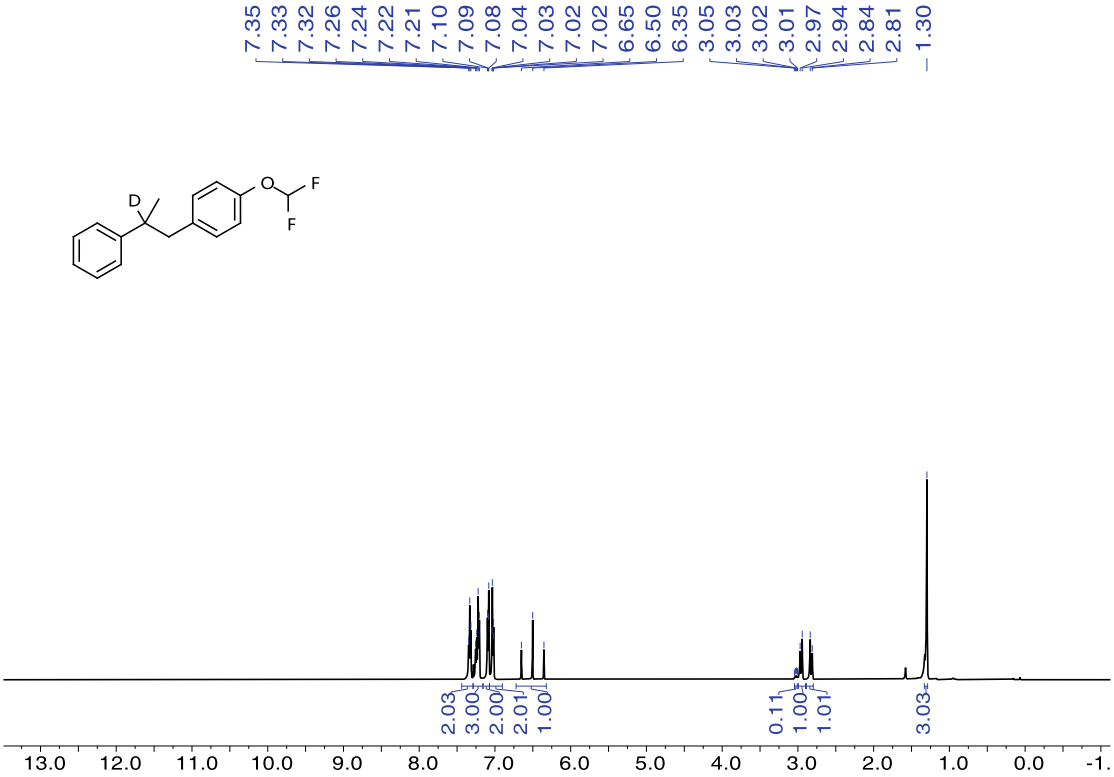
^{1}H NMR spectra of 25 (500 MHz, $CDCl_3$)



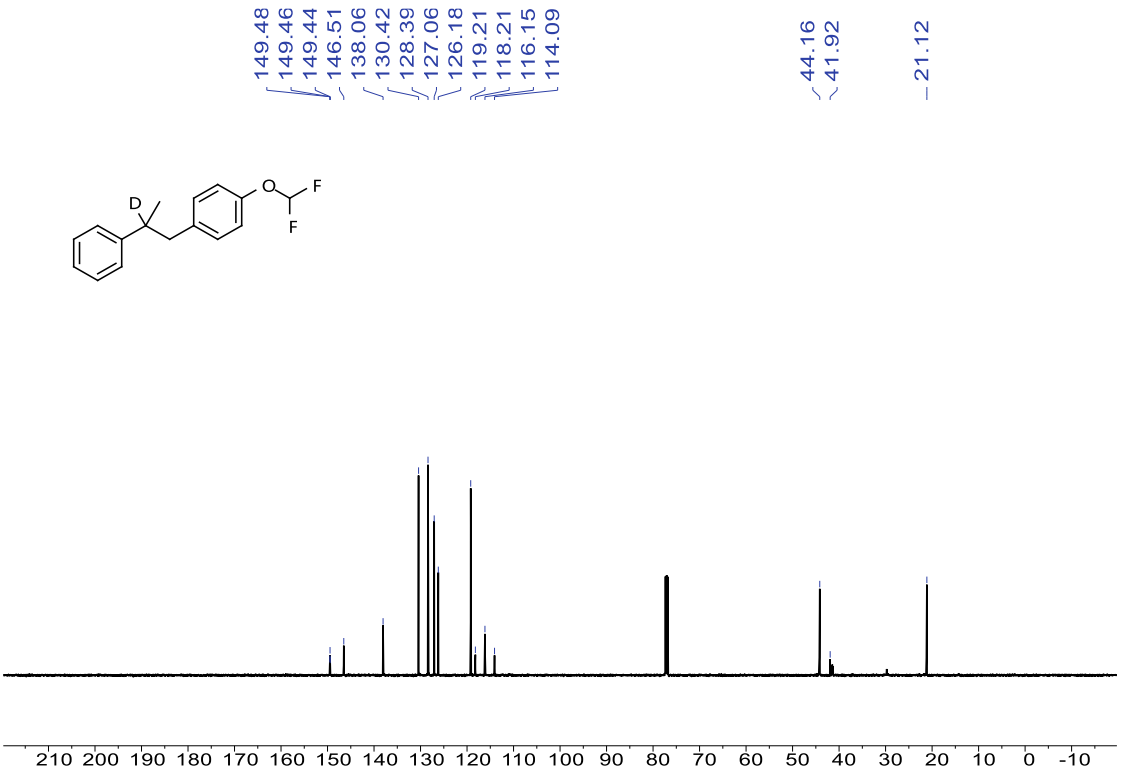
^{13}C NMR spectra of 25 (126 MHz, $CDCl_3$)



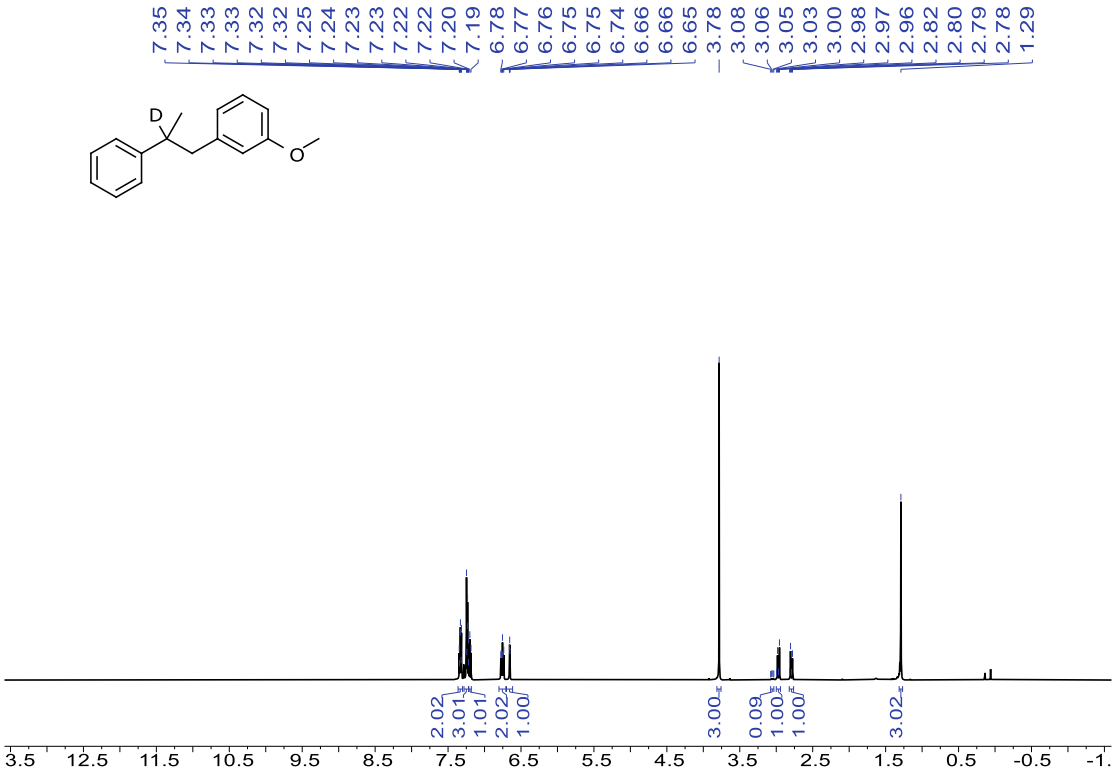
^{1}H NMR spectra of 26 (500 MHz, $CDCl_3$)



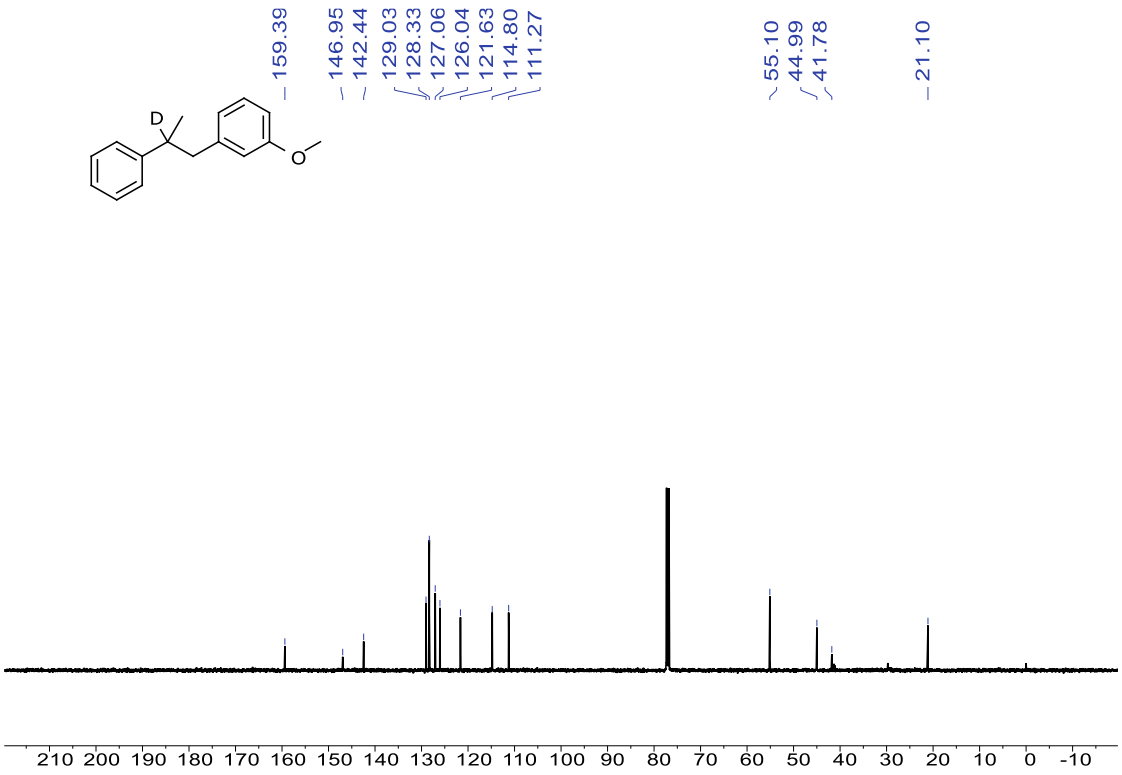
^{13}C NMR spectra of 26 (126 MHz, $CDCl_3$)



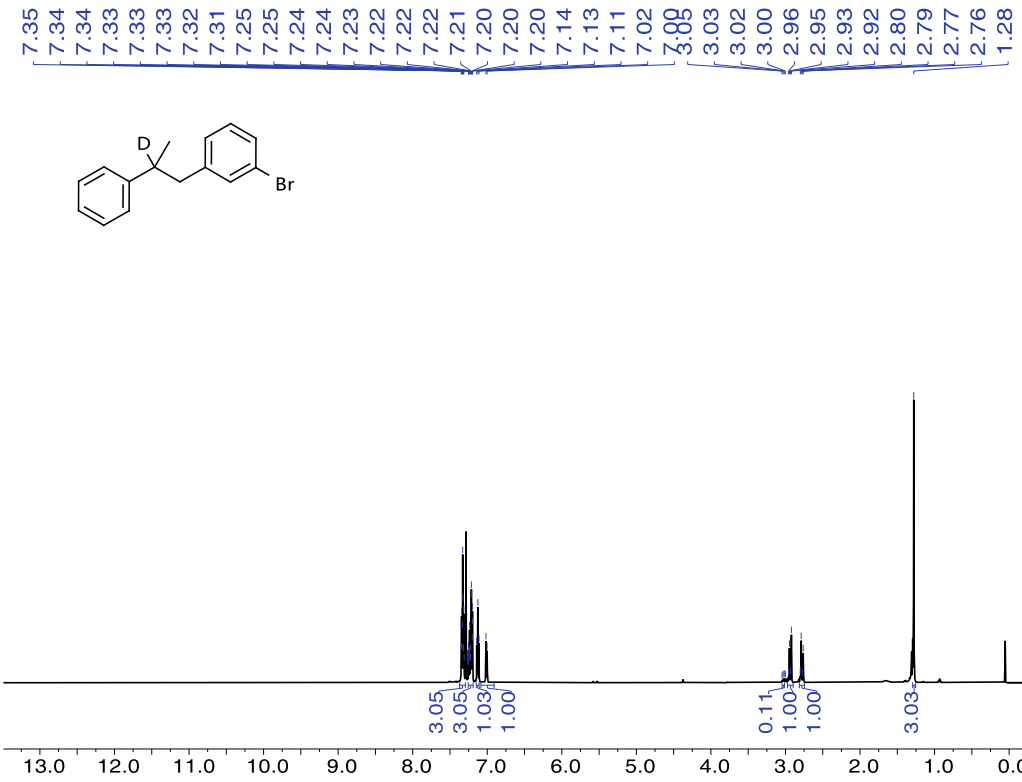
^{1}H NMR spectra of 27 (500 MHz, $CDCl_3$)



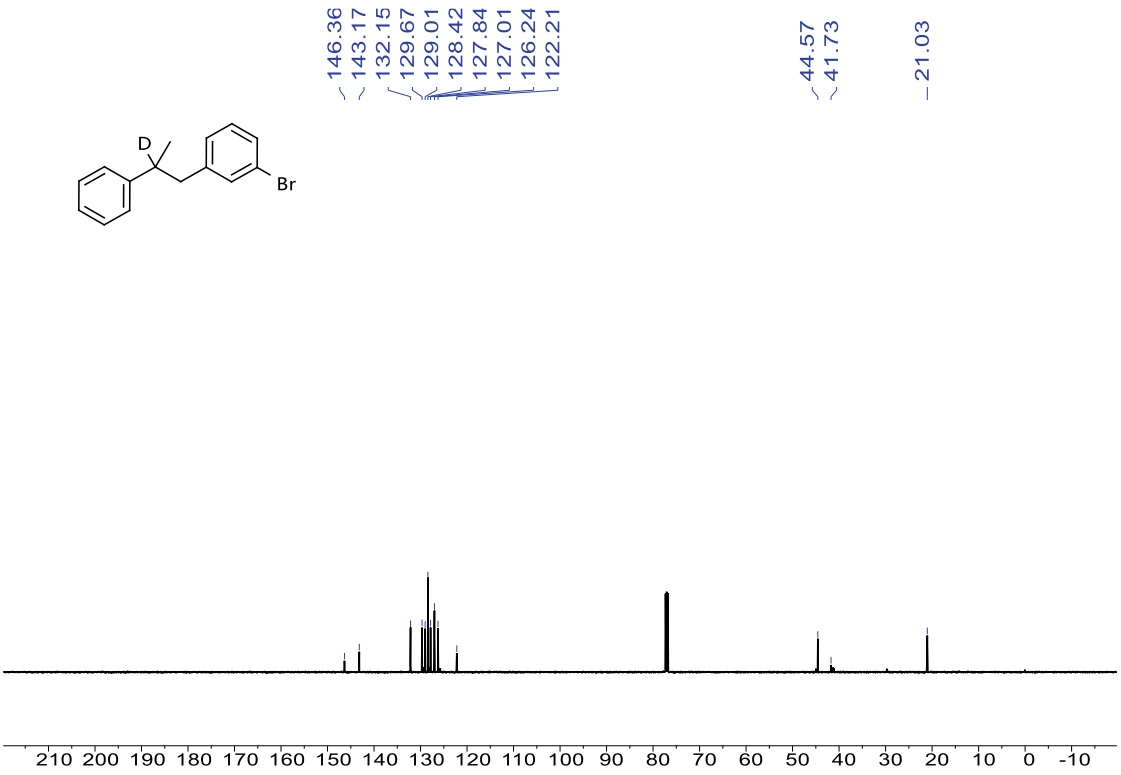
^{13}C NMR spectra of 27 (126 MHz, $CDCl_3$)



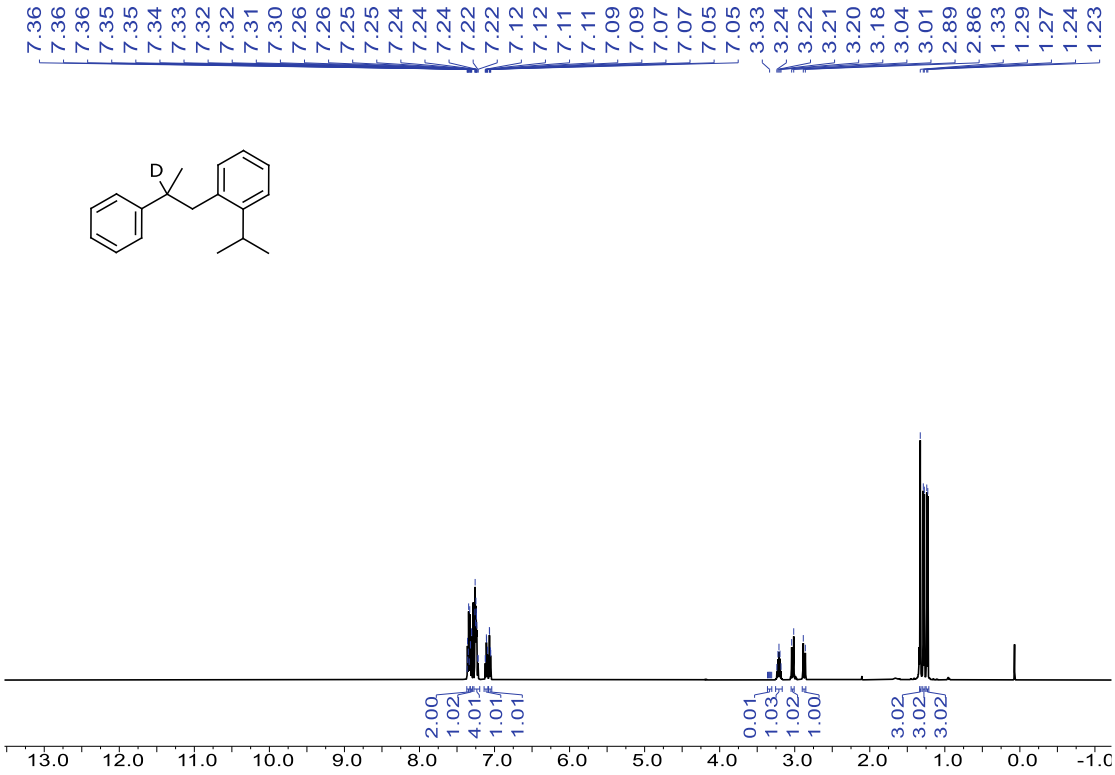
^{1}H NMR spectra of 28 (500 MHz, $CDCl_3$)



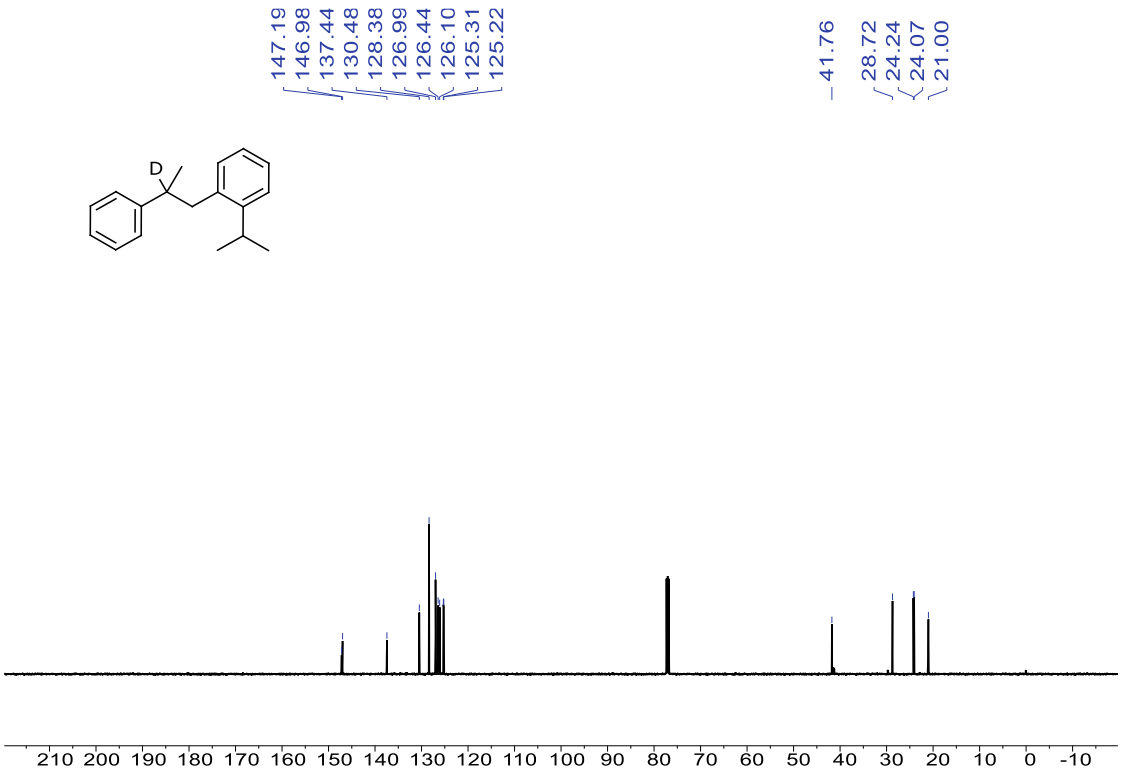
^{13}C NMR spectra of 28 (126 MHz, $CDCl_3$)



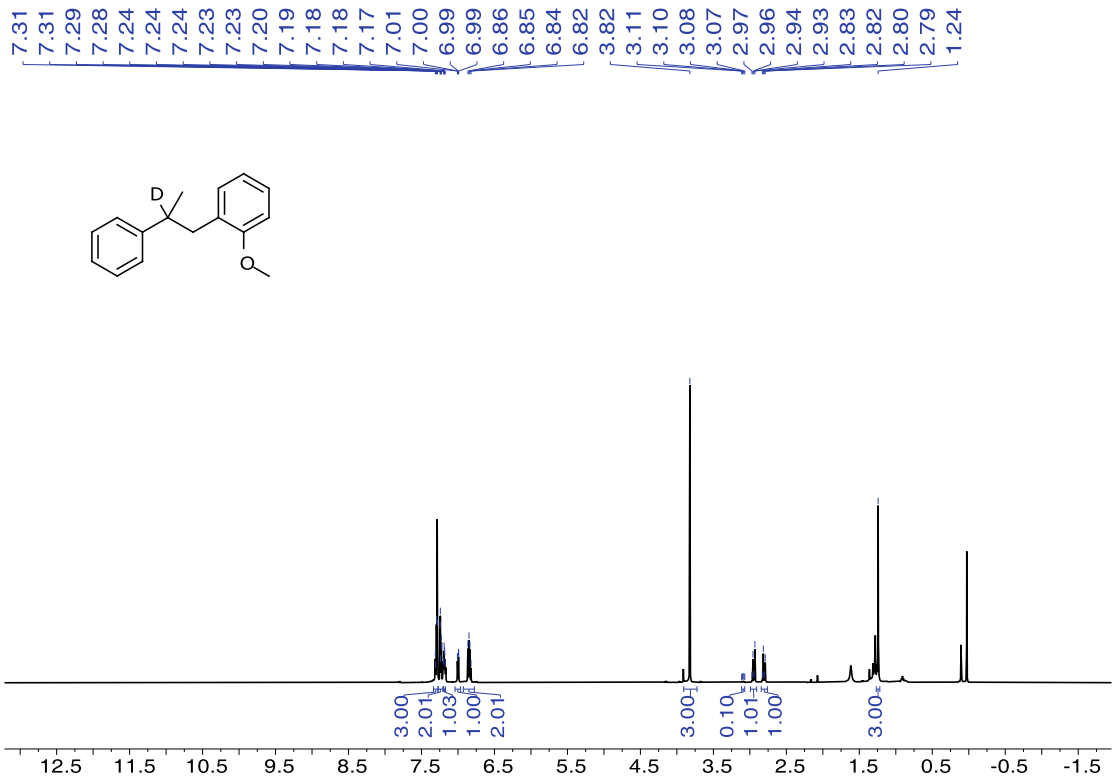
^{1}H NMR spectra of 29 (500 MHz, $CDCl_3$)



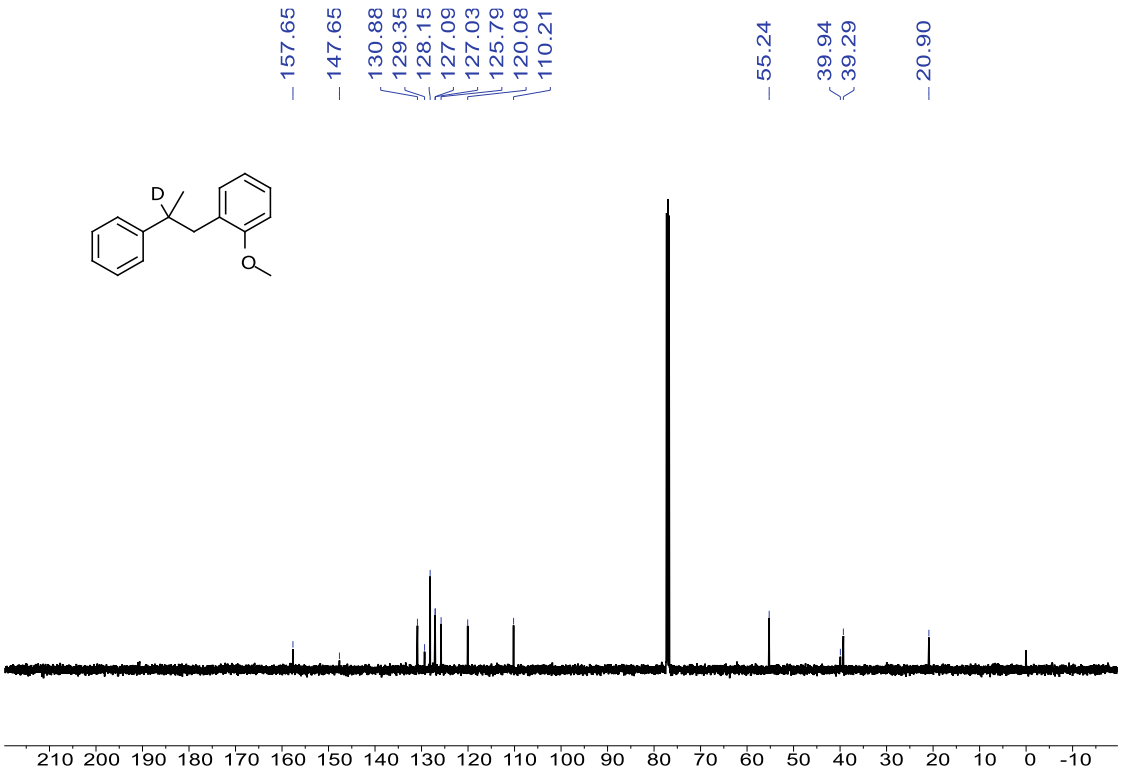
^{13}C NMR spectra of 29 (126 MHz, $CDCl_3$)



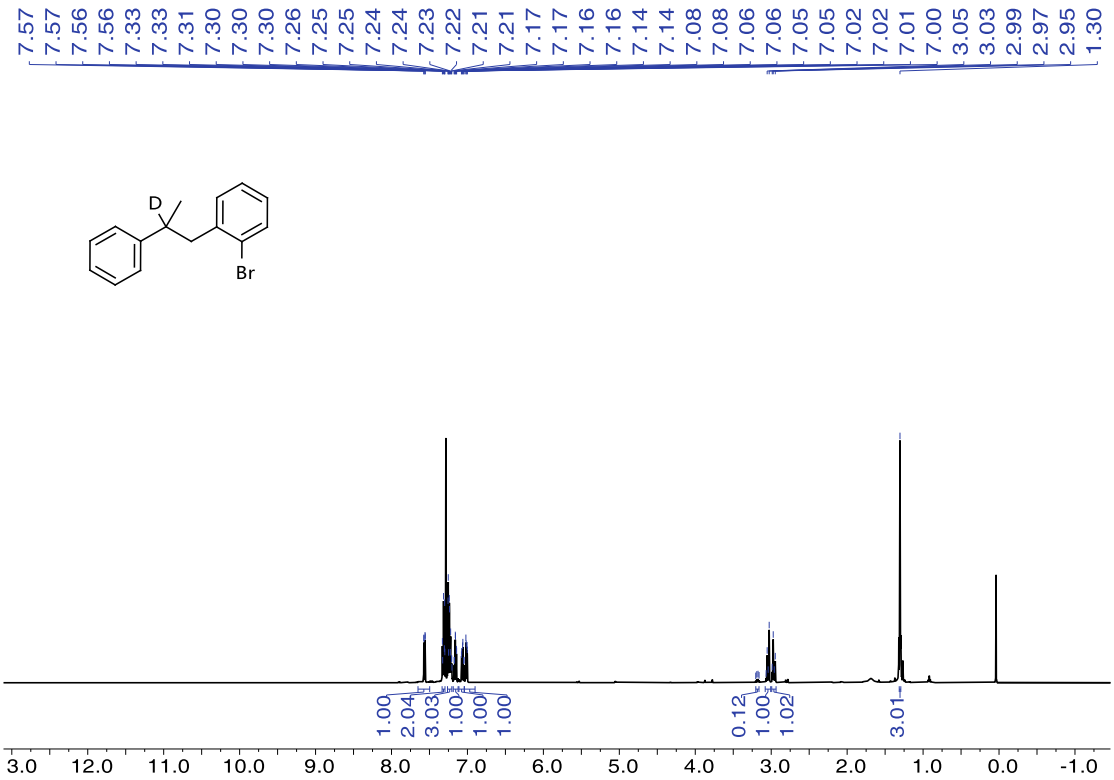
^{1}H NMR spectra of 30 (500 MHz, $CDCl_3$)



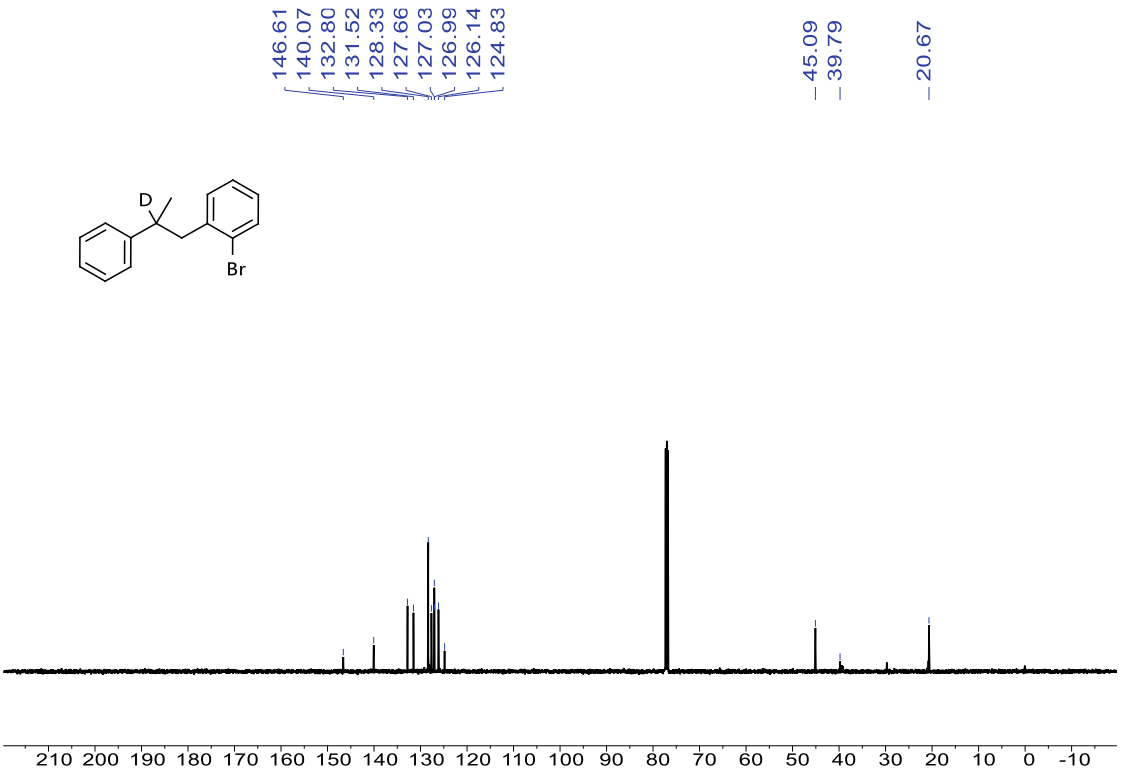
^{13}C NMR spectra of 30 (126 MHz, $CDCl_3$)



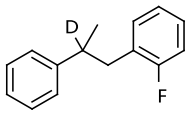
^{1}H NMR spectra of 31 (500 MHz, $CDCl_3$)

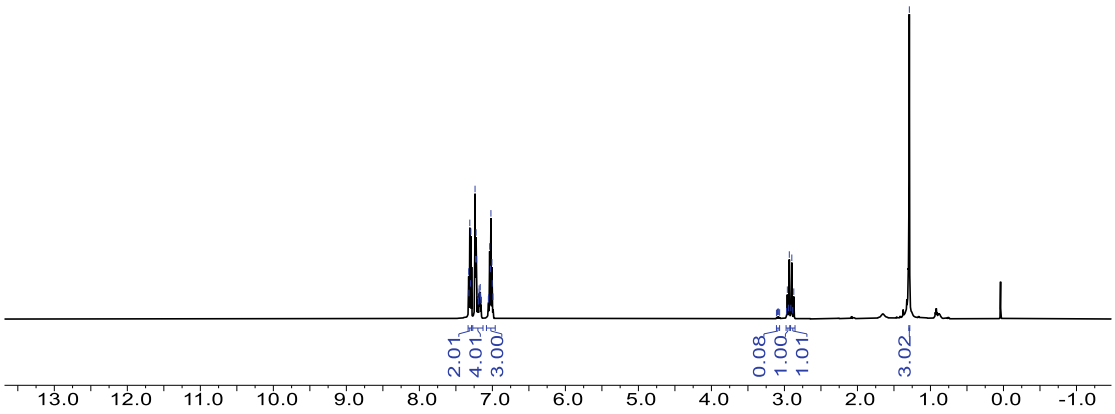


^{13}C NMR spectra of 31 (126 MHz, $CDCl_3$)

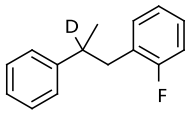


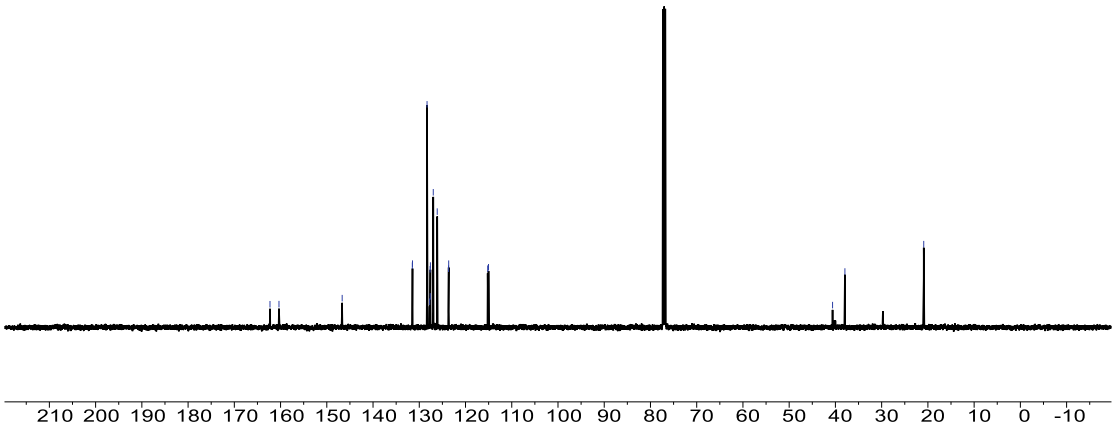
^{1}H NMR spectra of 32 (500 MHz, $CDCl_3$)



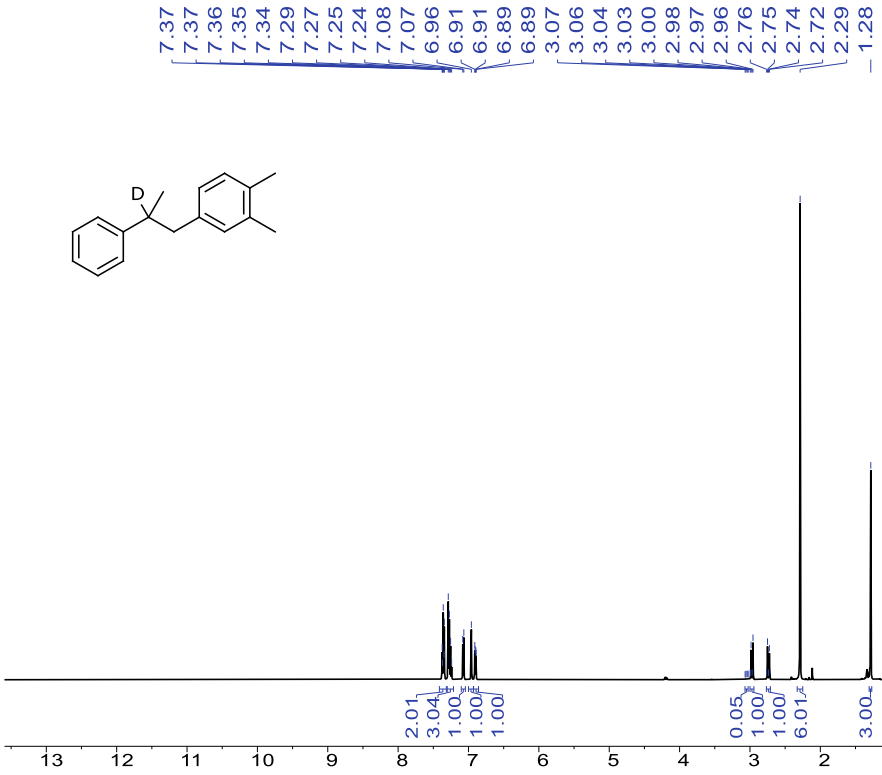


^{13}C NMR spectra of 32 (126 MHz, $CDCl_3$)

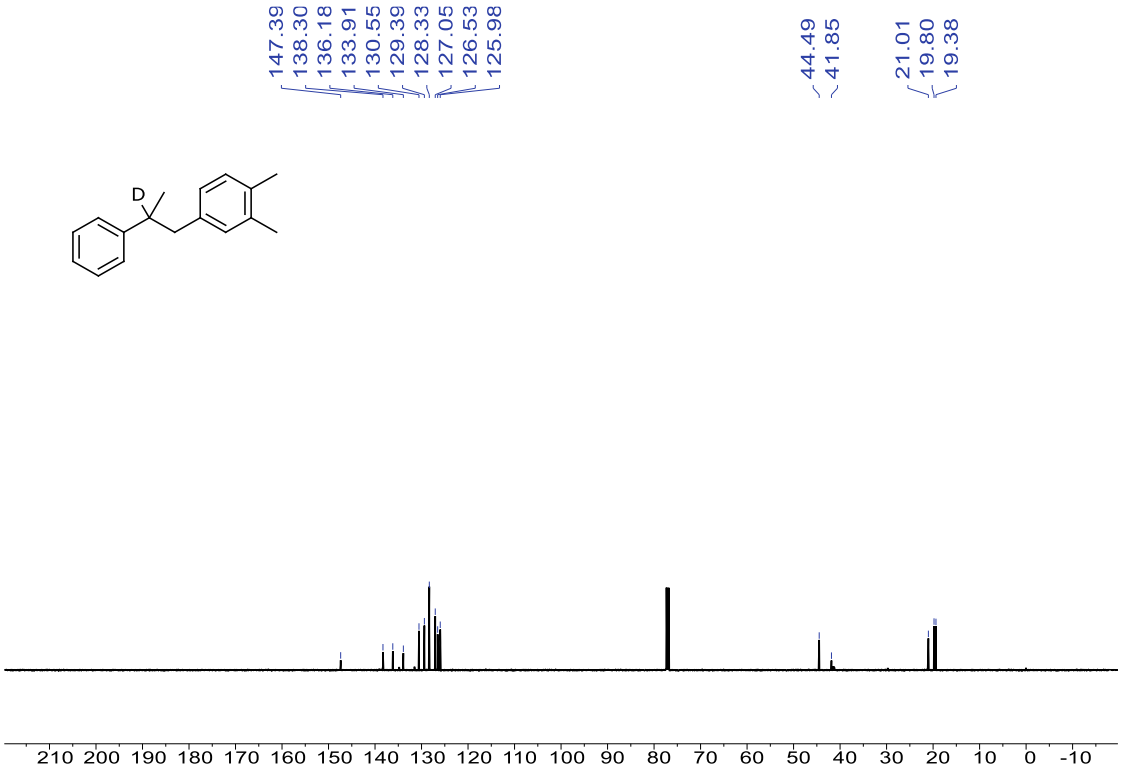




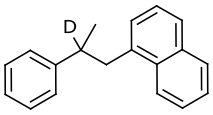
^{1}H NMR spectra of 33 (500 MHz, $CDCl_3$)

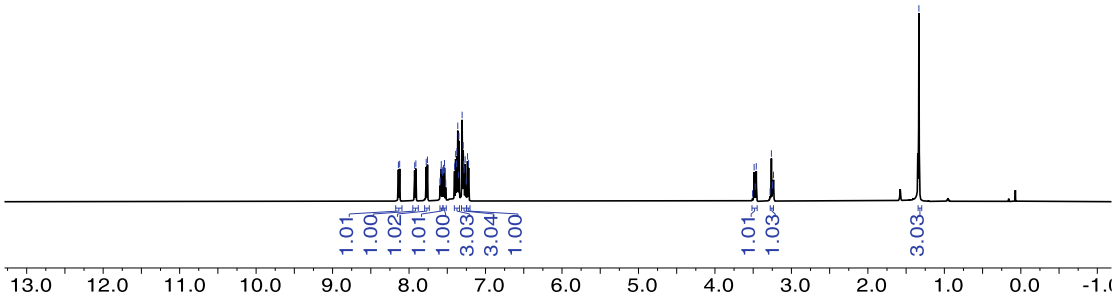


^{13}C NMR spectra of 33 (126 MHz, $CDCl_3$)

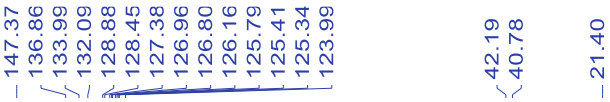


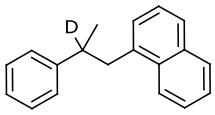
^{1}H NMR spectra of 34 (500 MHz, $CDCl_3$)

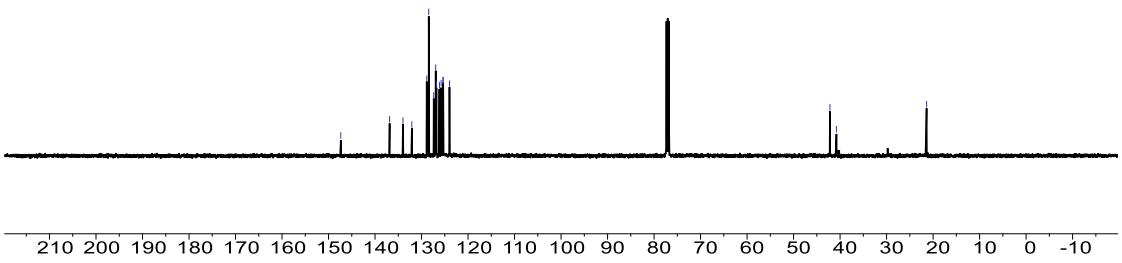




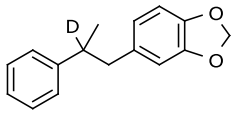
^{13}C NMR spectra of 34 (126 MHz, $CDCl_3$)

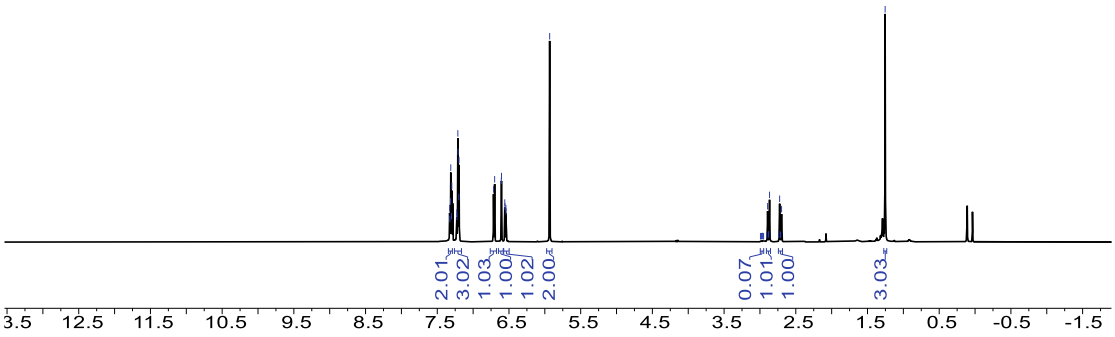




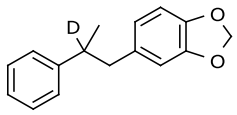


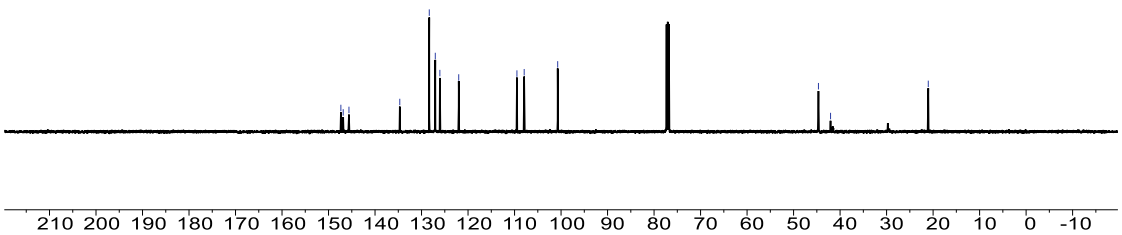
^{1}H NMR spectra of 35 (500 MHz, $CDCl_3$)



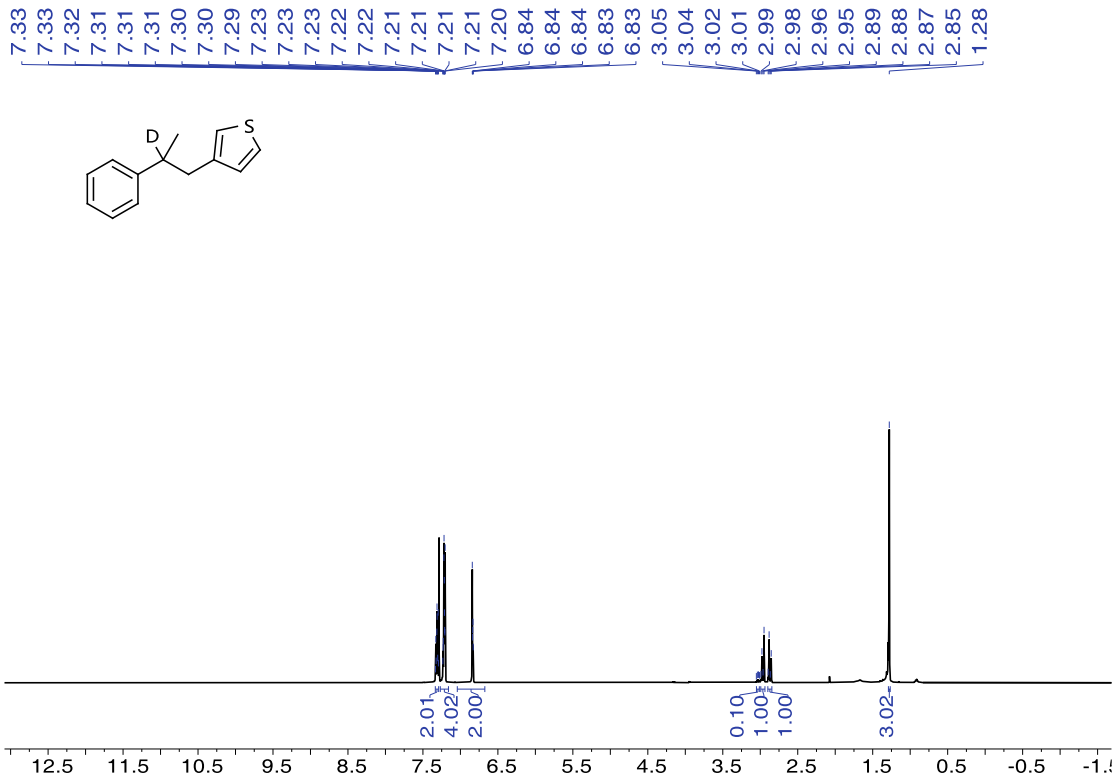


^{13}C NMR spectra of 35 (126 MHz, $CDCl_3$)

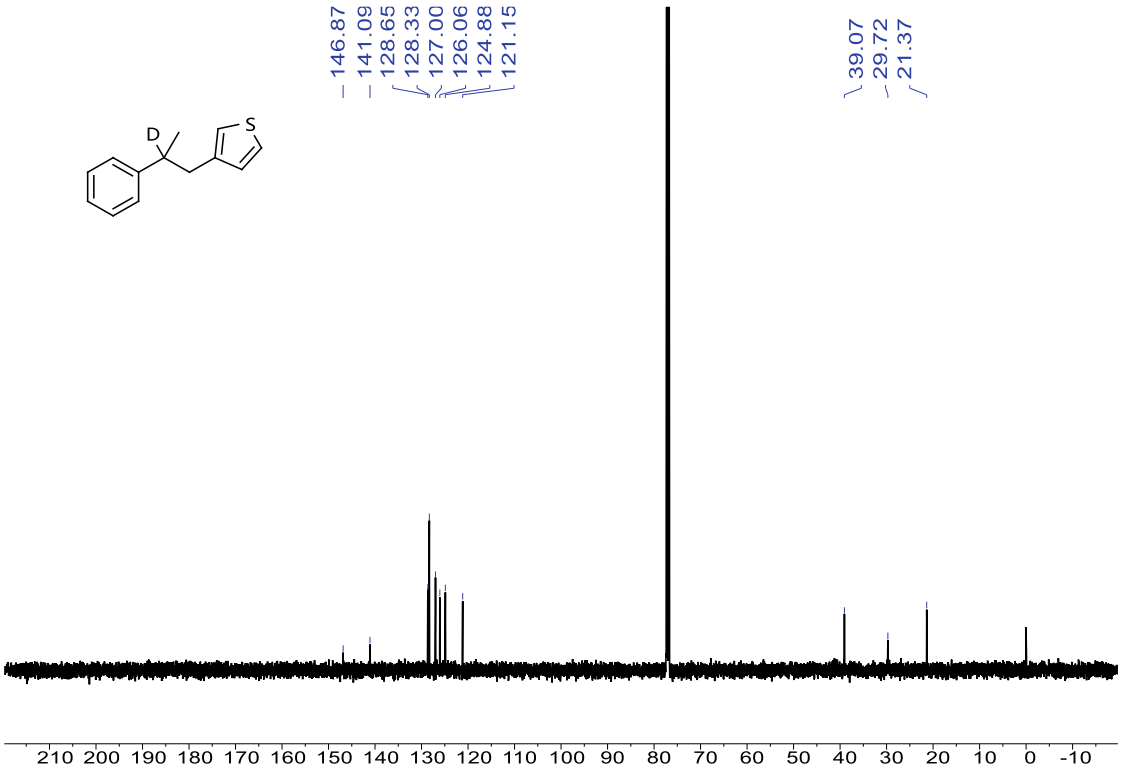




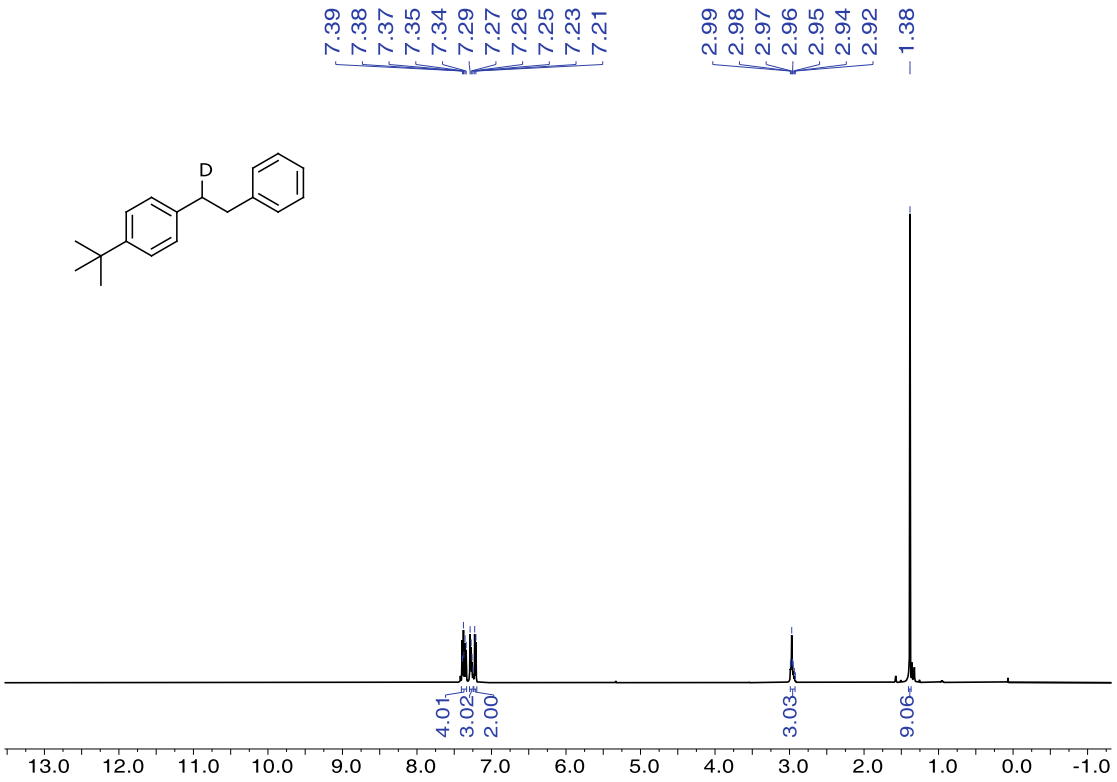
^{1}H NMR spectra of 36 (500 MHz, $CDCl_3$)



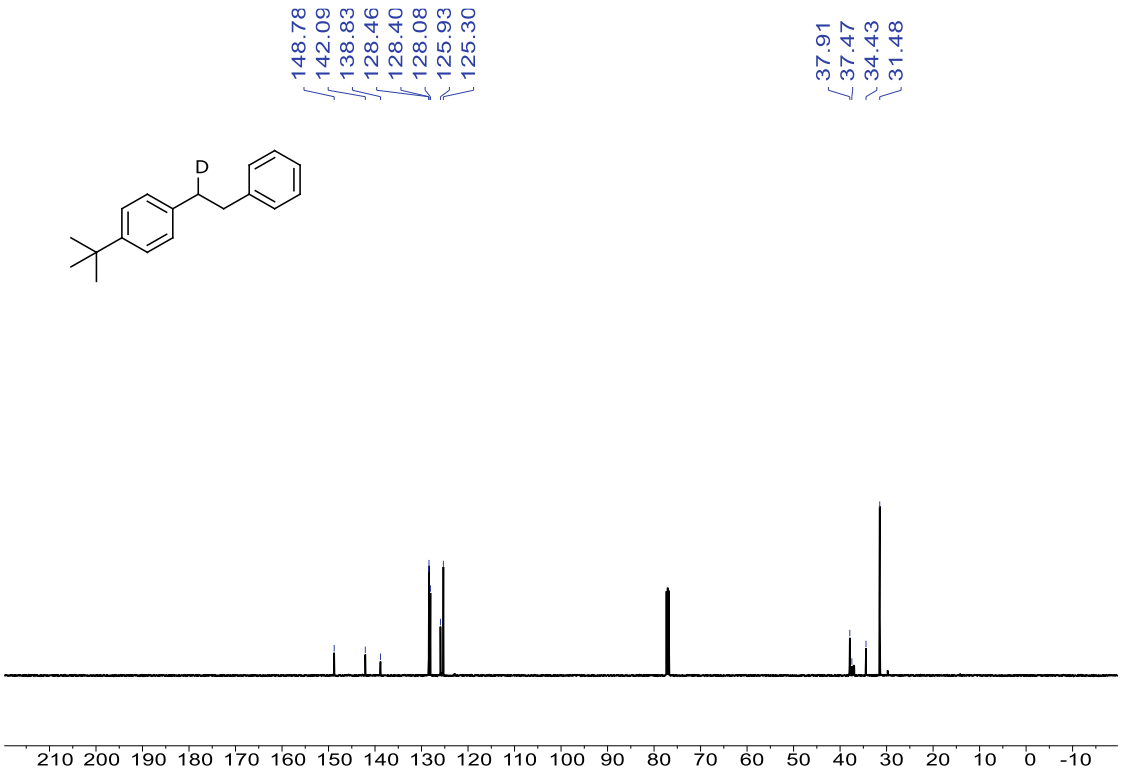
^{13}C NMR spectra of 36 (126 MHz, $CDCl_3$)



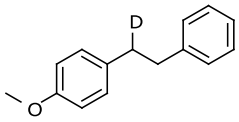
^{1}H NMR spectra of 37 (500 MHz, $CDCl_3$)

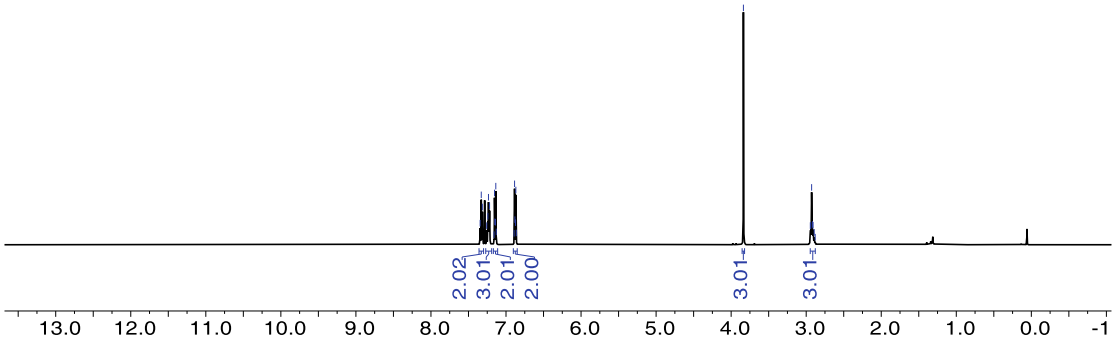


^{13}C NMR spectra of 37 (126 MHz, $CDCl_3$)

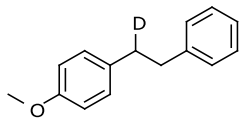


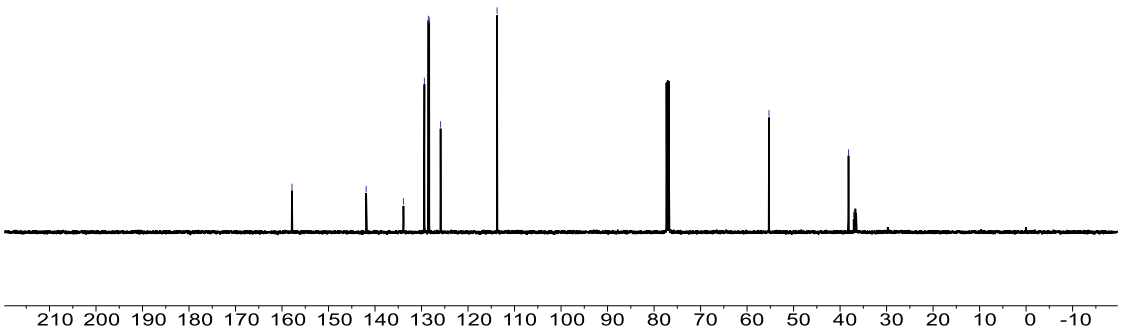
^{1}H NMR spectra of 38 (500 MHz, $CDCl_3$)



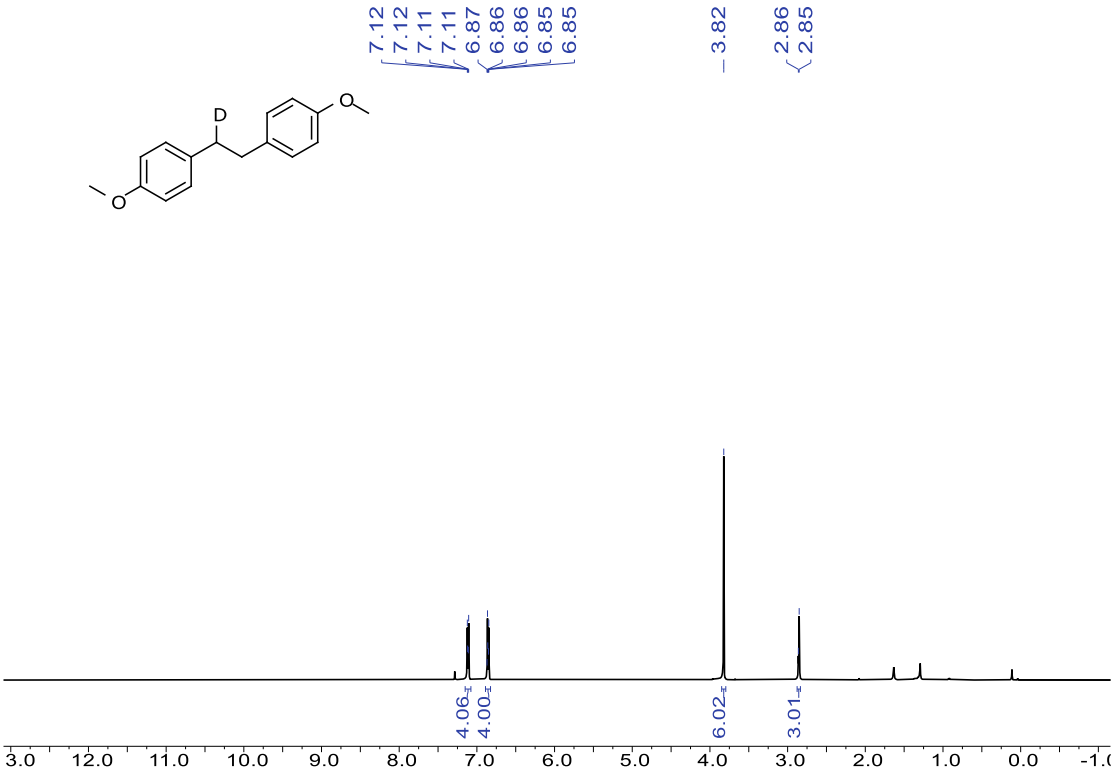


^{13}C NMR spectra of 38 (126 MHz, $CDCl_3$)

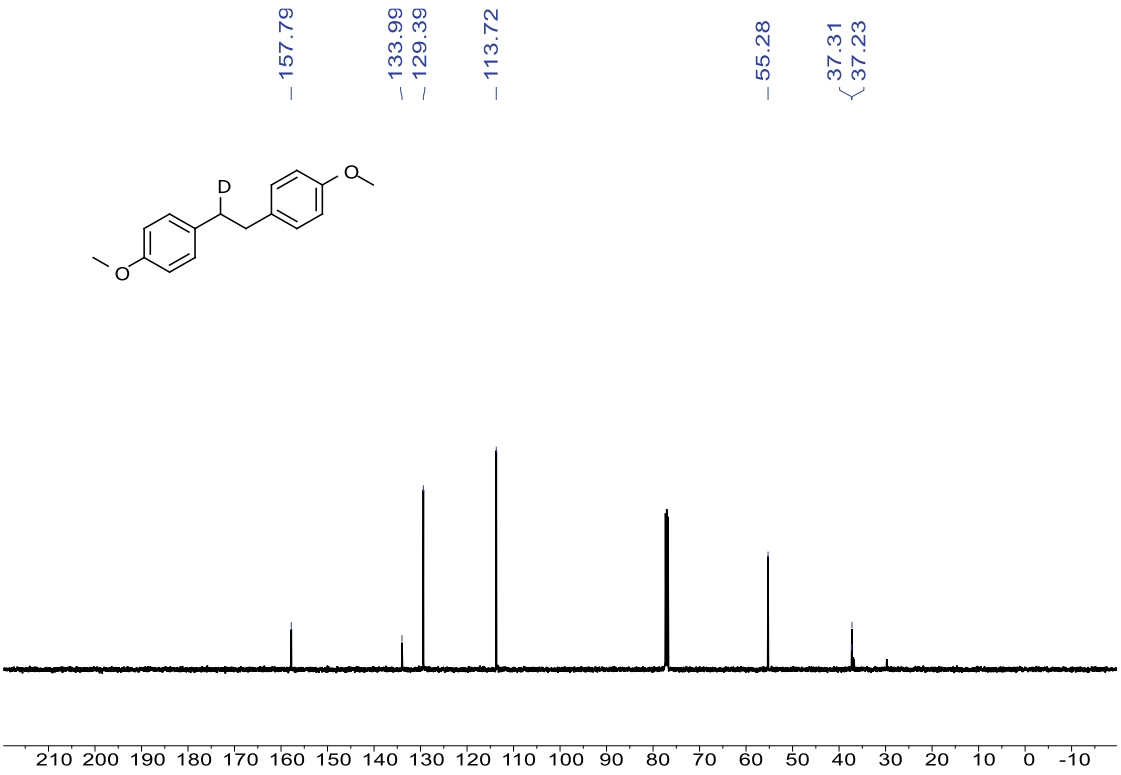




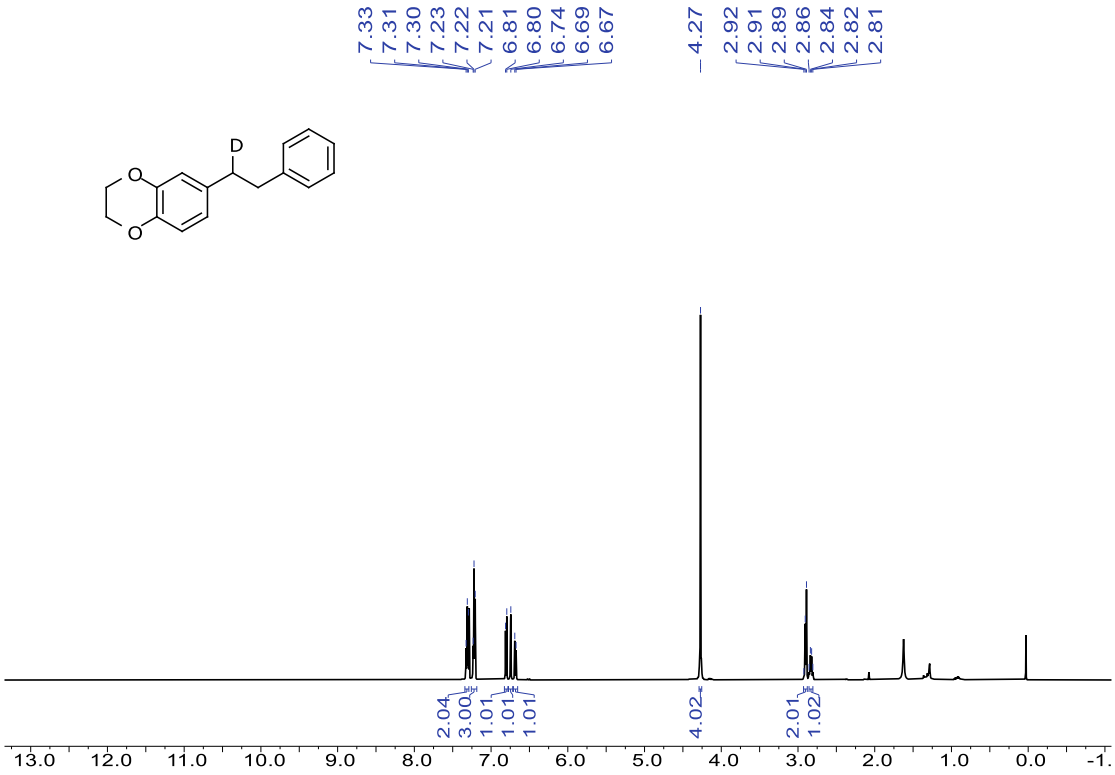
^{1}H NMR spectra of 39 (500 MHz, $CDCl_3$)



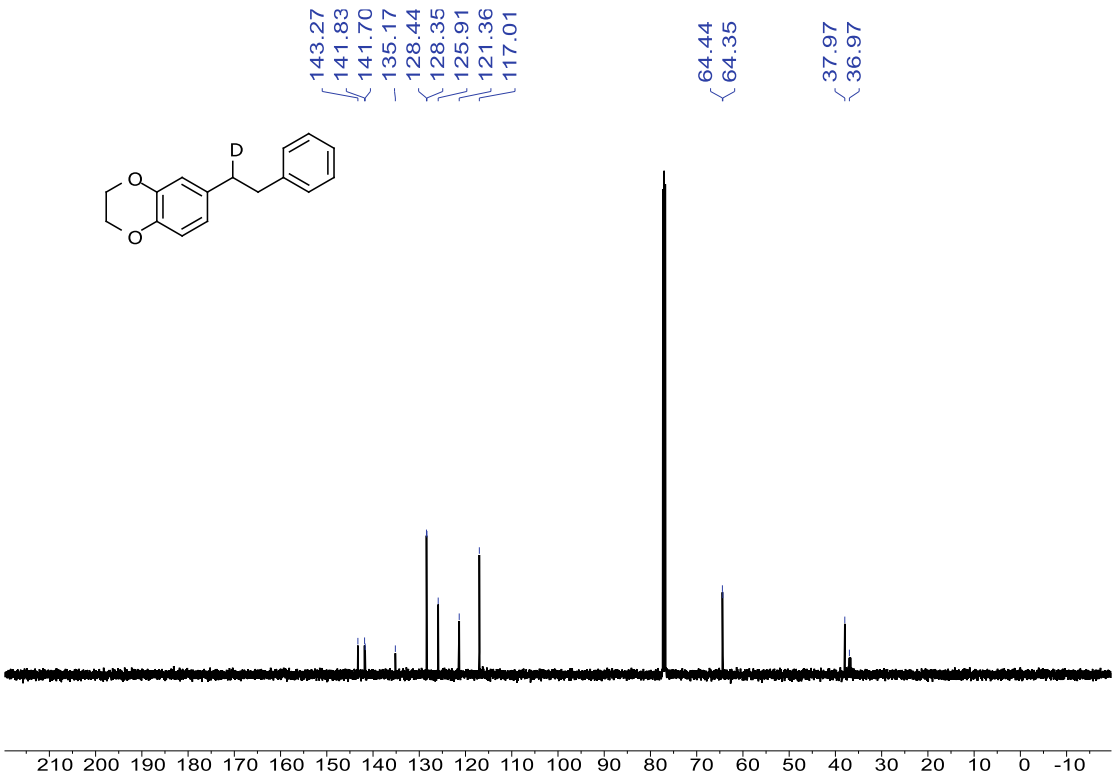
^{13}C NMR spectra of 39 (126 MHz, $CDCl_3$)



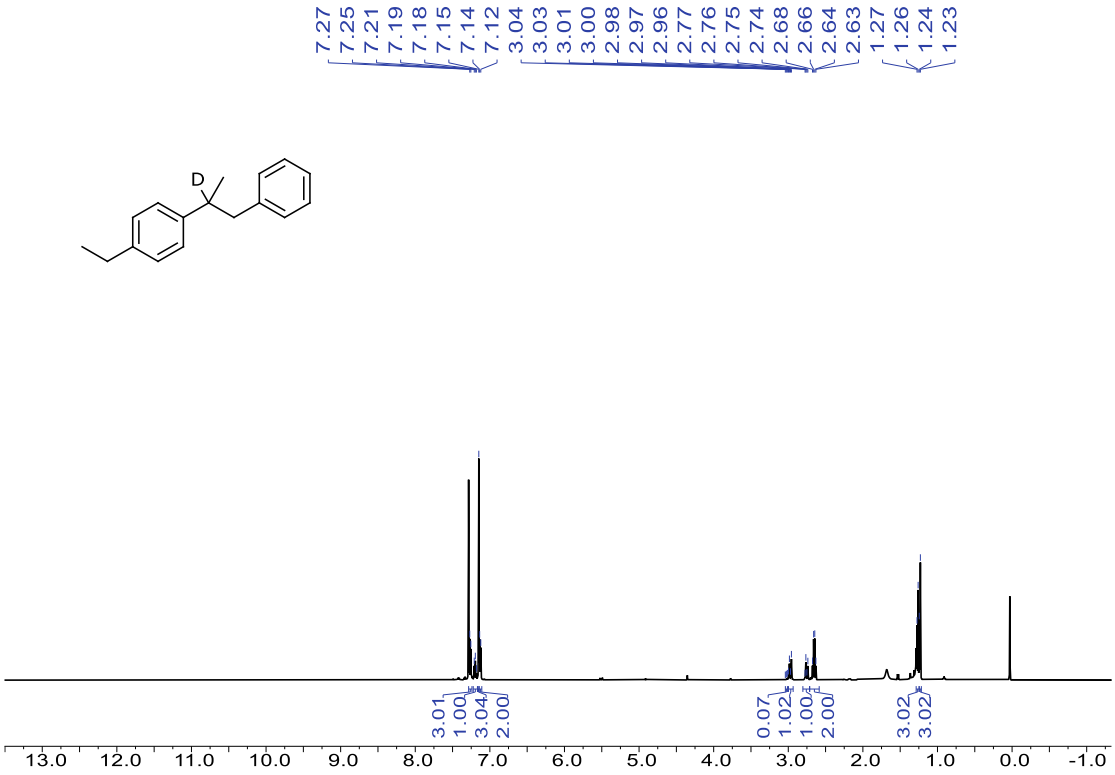
^{1}H NMR spectra of 40 (500 MHz, $CDCl_3$)



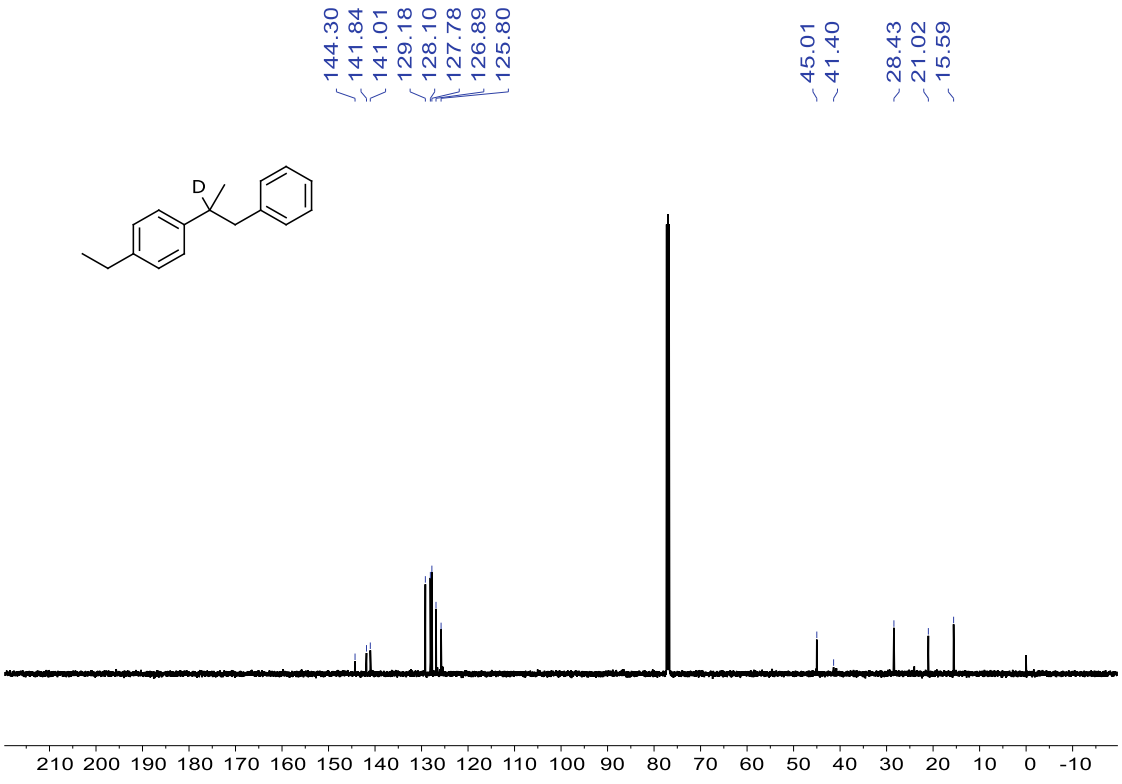
^{13}C NMR spectra of 40 (126 MHz, $CDCl_3$)



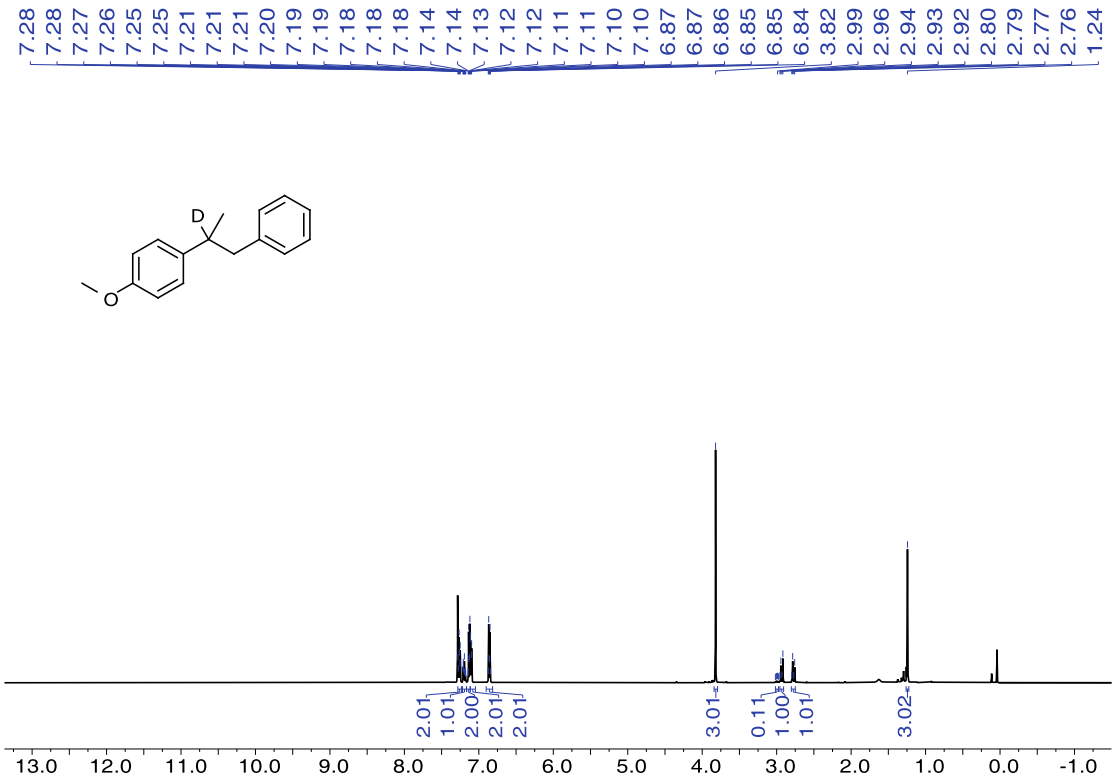
^{1}H NMR spectra of 41 (500 MHz, $CDCl_3$)



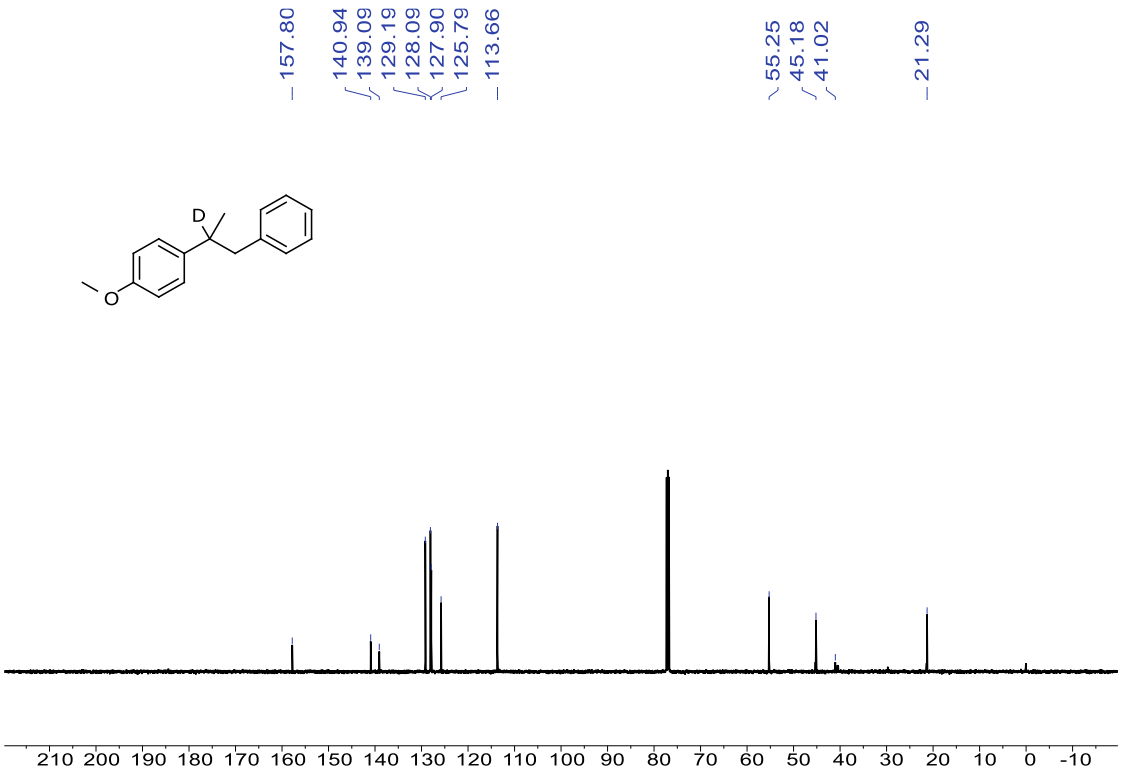
^{13}C NMR spectra of 41 (126 MHz, $CDCl_3$)



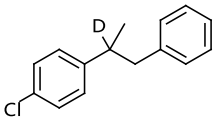
^{1}H NMR spectra of 42 (500 MHz, $CDCl_3$)

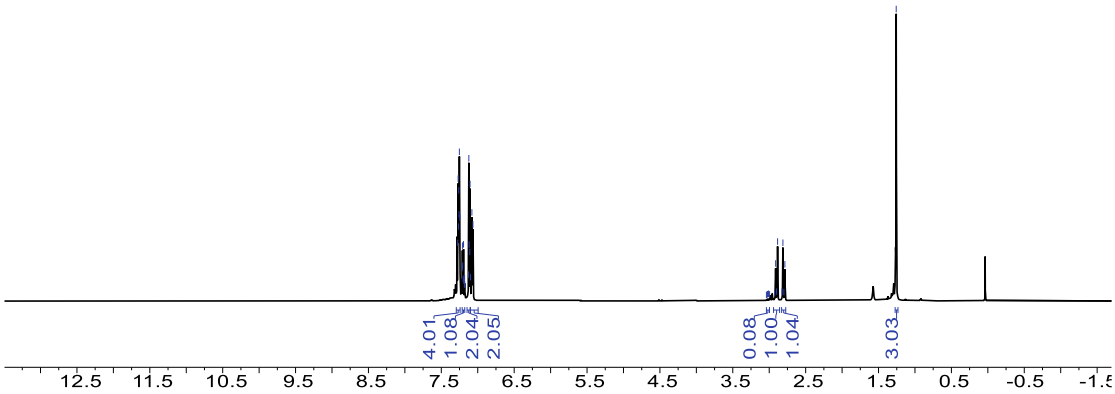


^{13}C NMR spectra of 42 (126 MHz, $CDCl_3$)

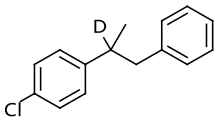


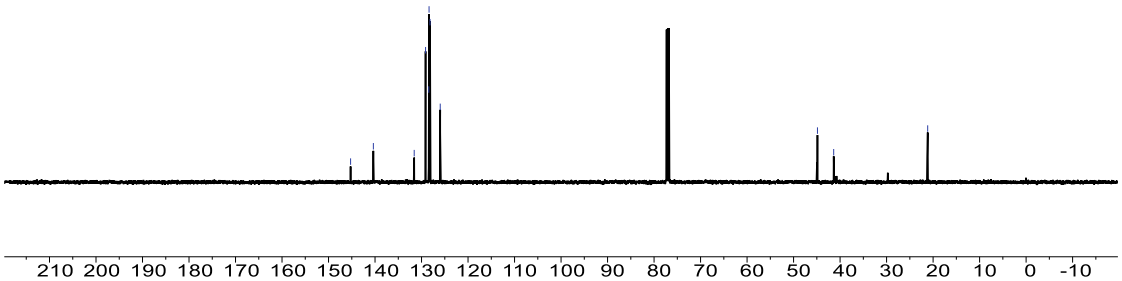
^{1}H NMR spectra of 43 (500 MHz, $CDCl_3$)



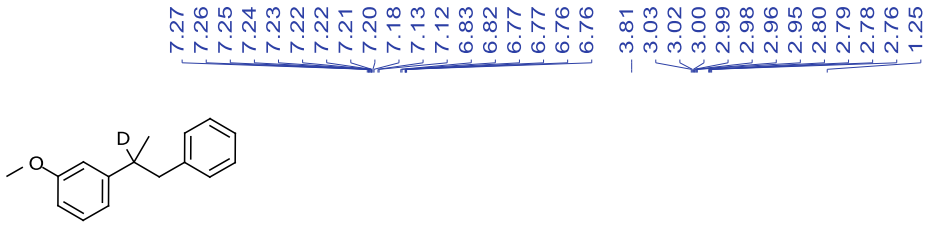


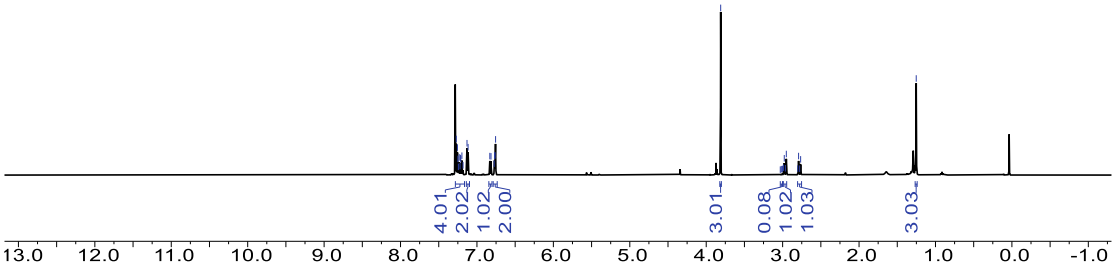
^{13}C NMR spectra of 43 (126 MHz, $CDCl_3$)



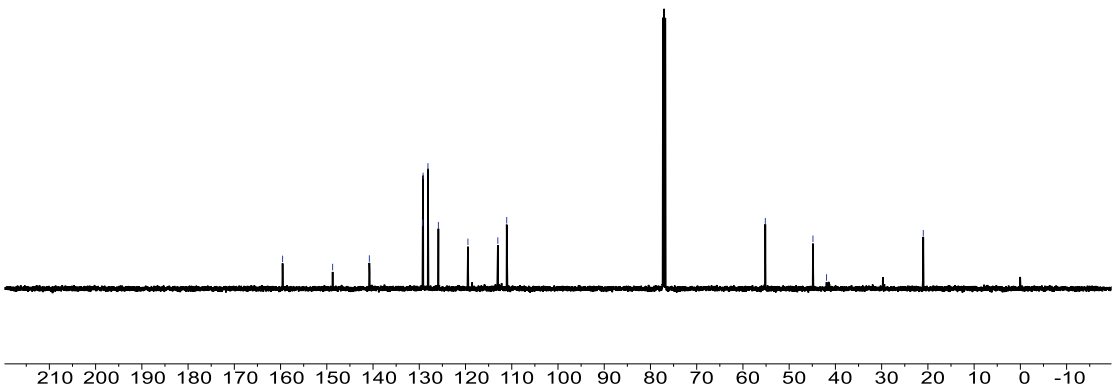


^{1}H NMR spectra of 44 (500 MHz, $CDCl_3$)

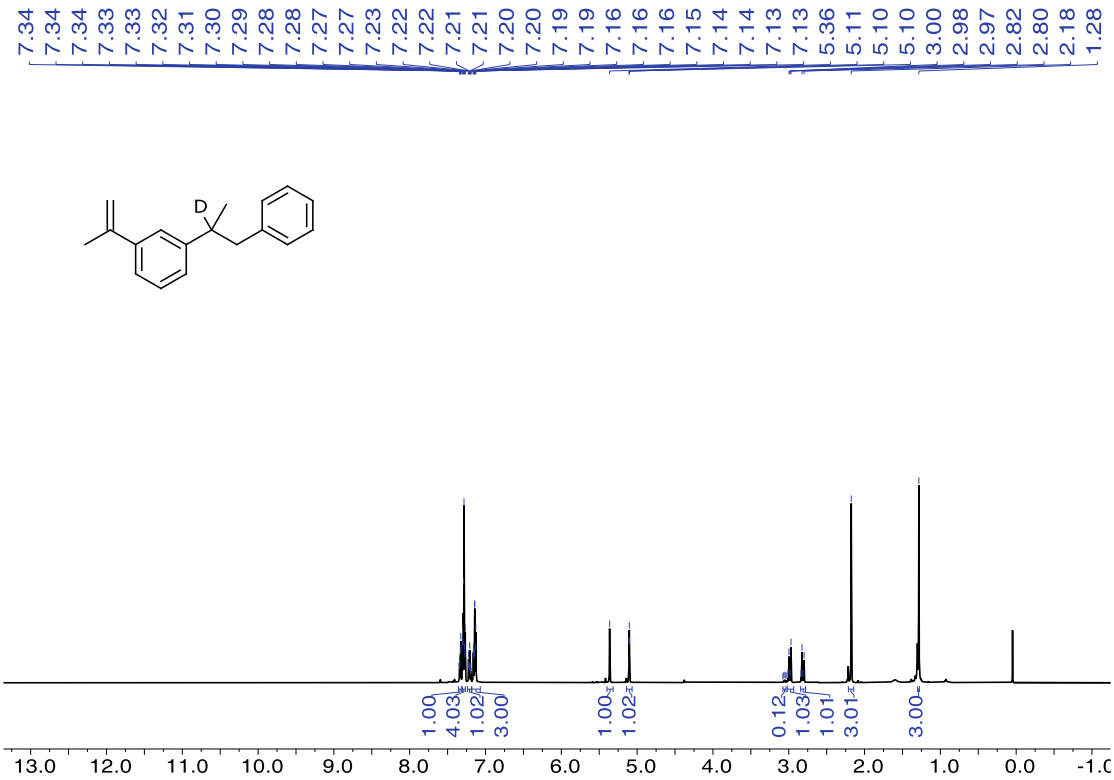




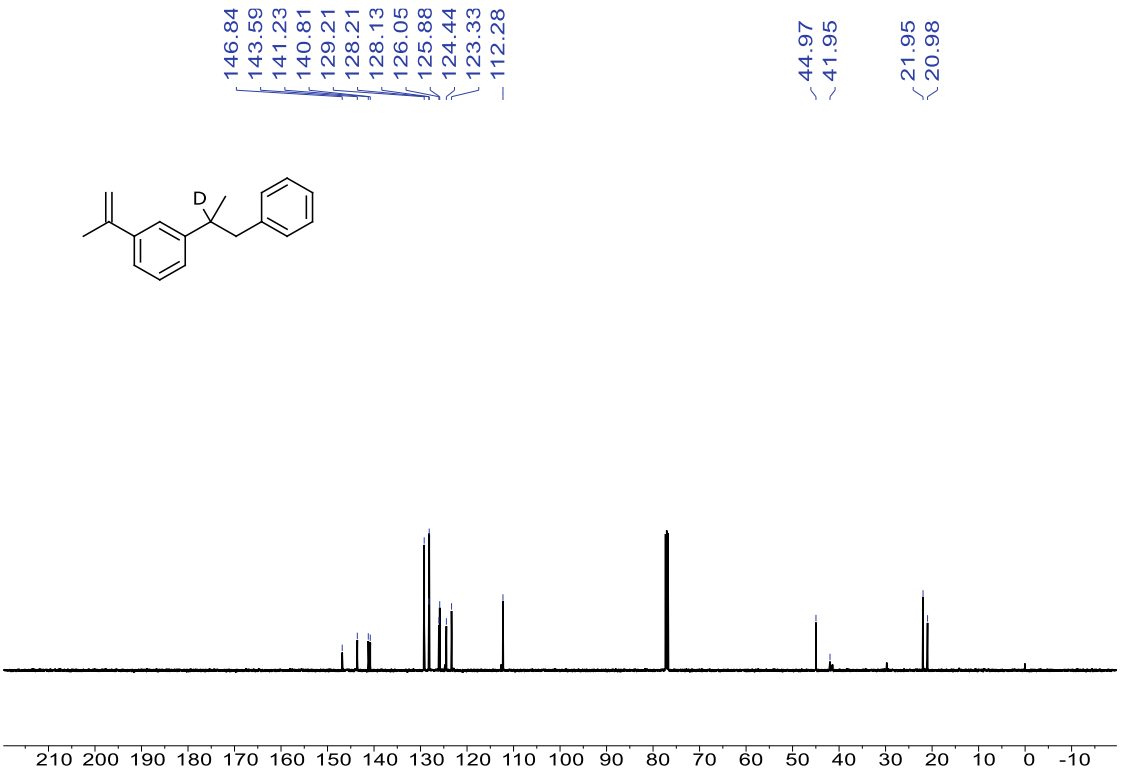
^{13}C NMR spectra of 44 (126 MHz, $CDCl_3$)



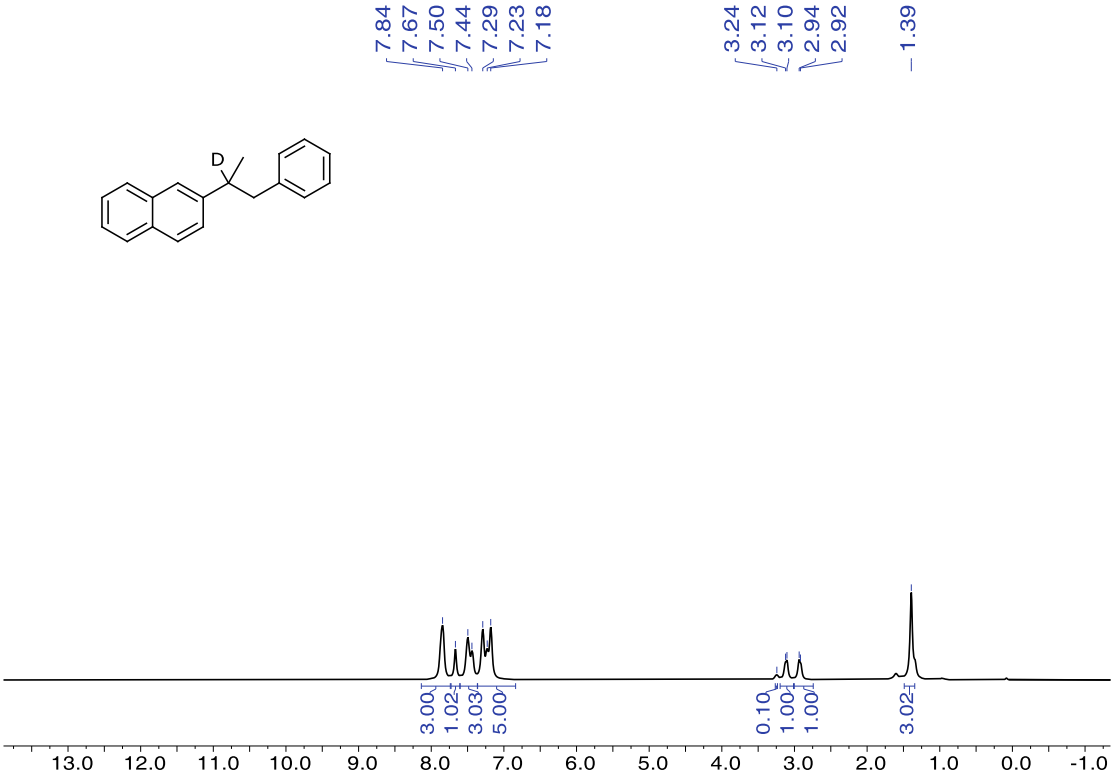
^{1}H NMR spectra of 45 (500 MHz, $CDCl_3$)



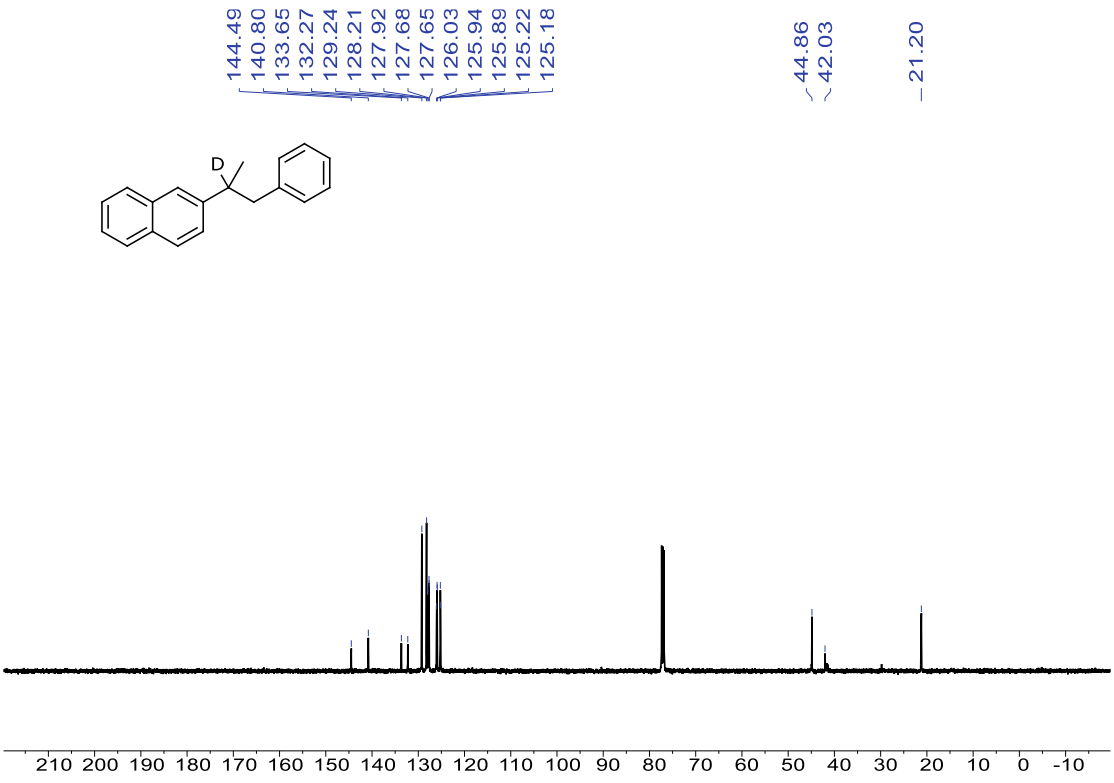
^{13}C NMR spectra of 45 (126 MHz, $CDCl_3$)



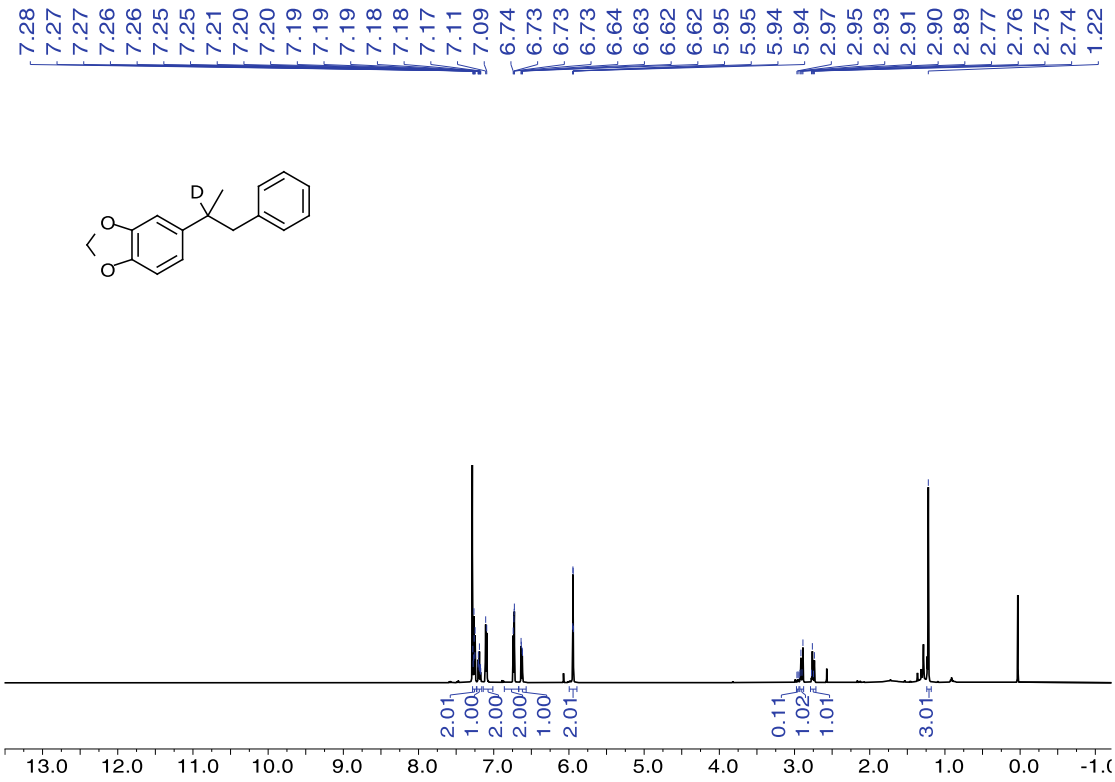
^{1}H NMR spectra of 46 (500 MHz, $CDCl_3$)



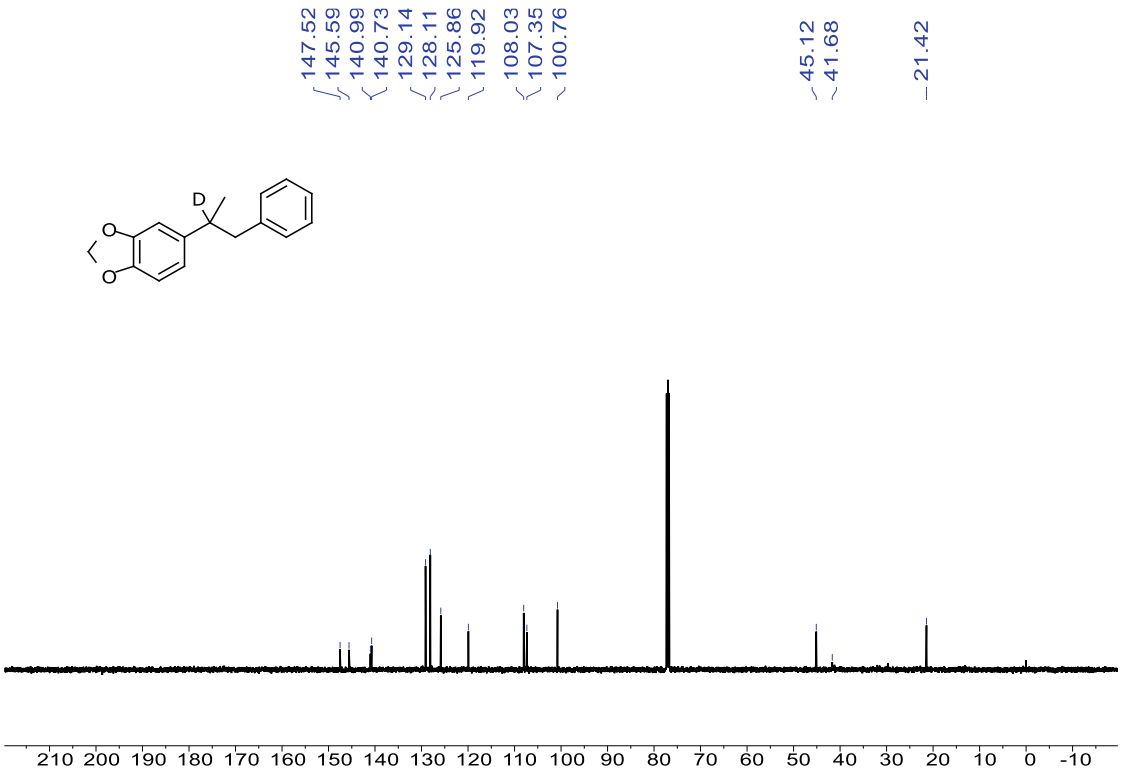
^{13}C NMR spectra of 46 (126 MHz, $CDCl_3$)



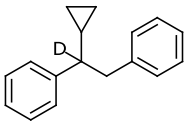
^{1}H NMR spectra of 47 (500 MHz, $CDCl_3$)

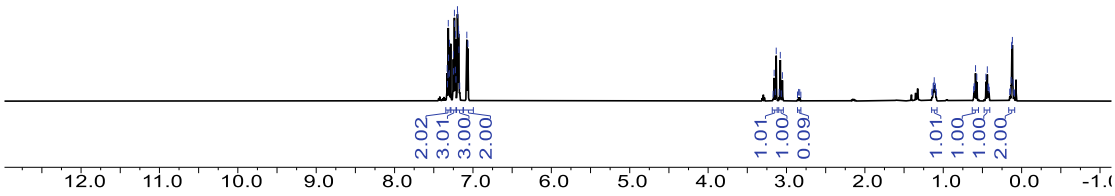


^{13}C NMR spectra of 47 (126 MHz, $CDCl_3$)

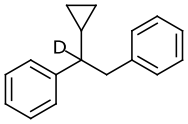


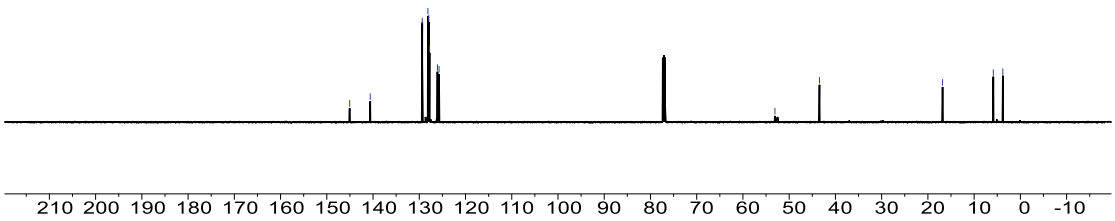
^{1}H NMR spectra of 48 (500 MHz, $CDCl_3$)



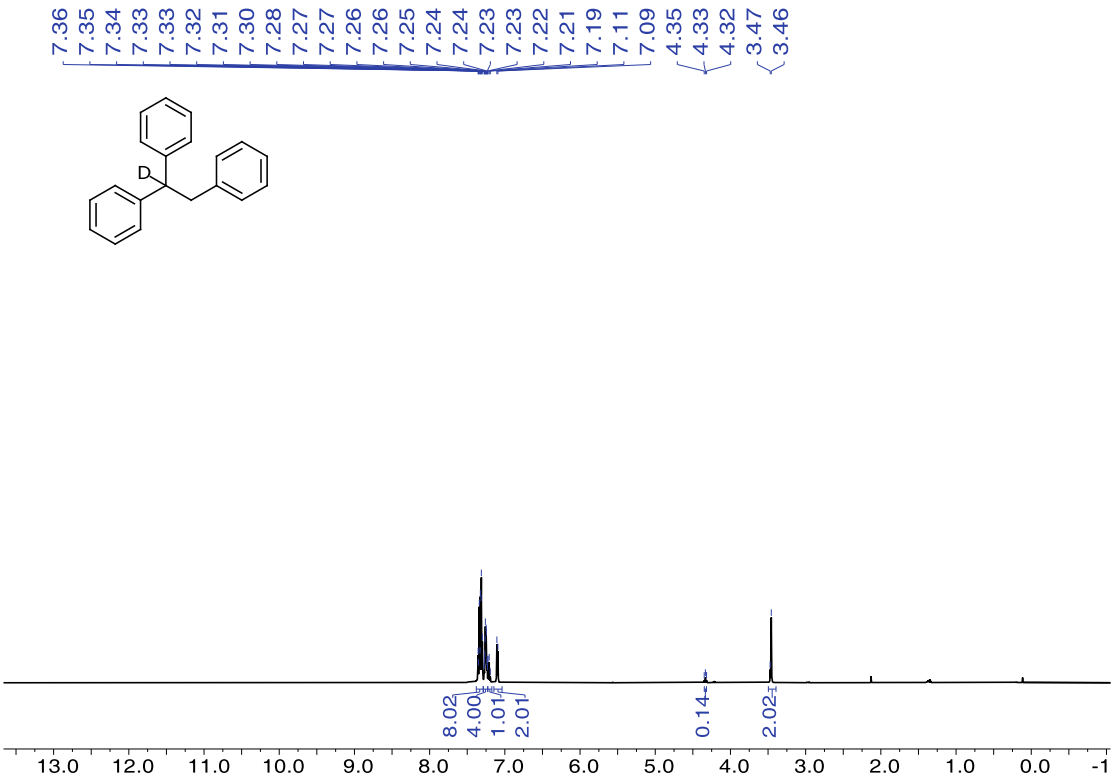


^{13}C NMR spectra of 48 (126 MHz, $CDCl_3$)

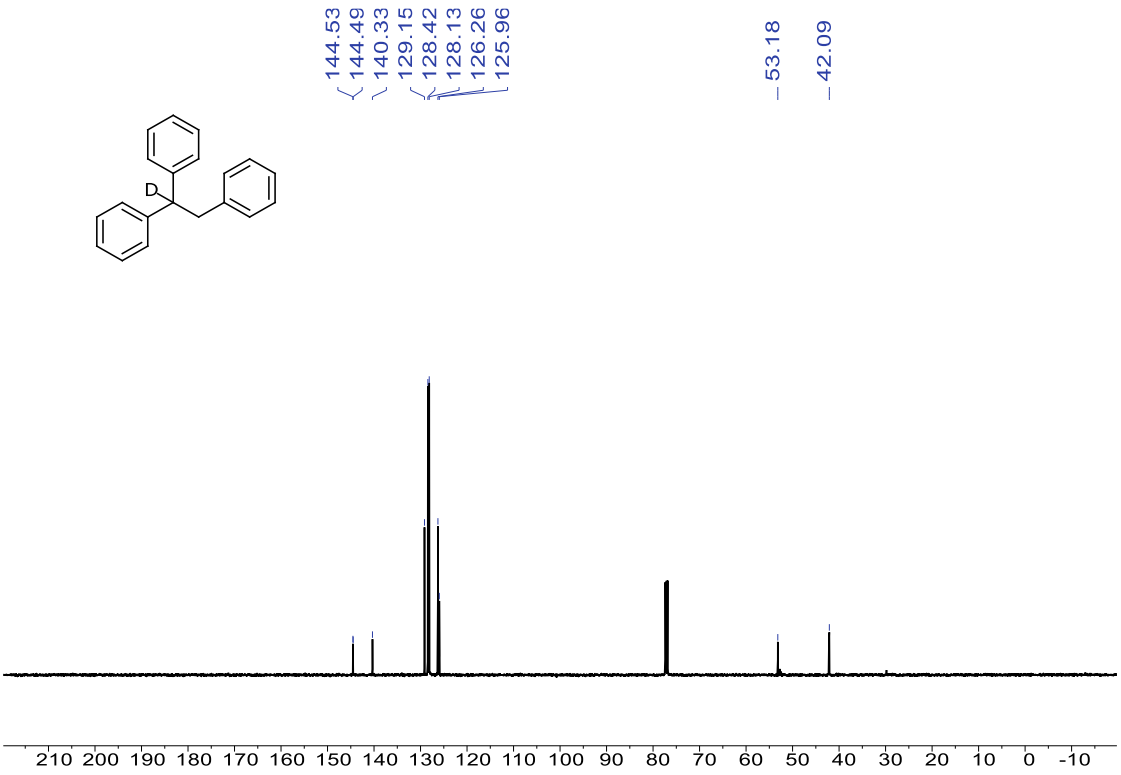




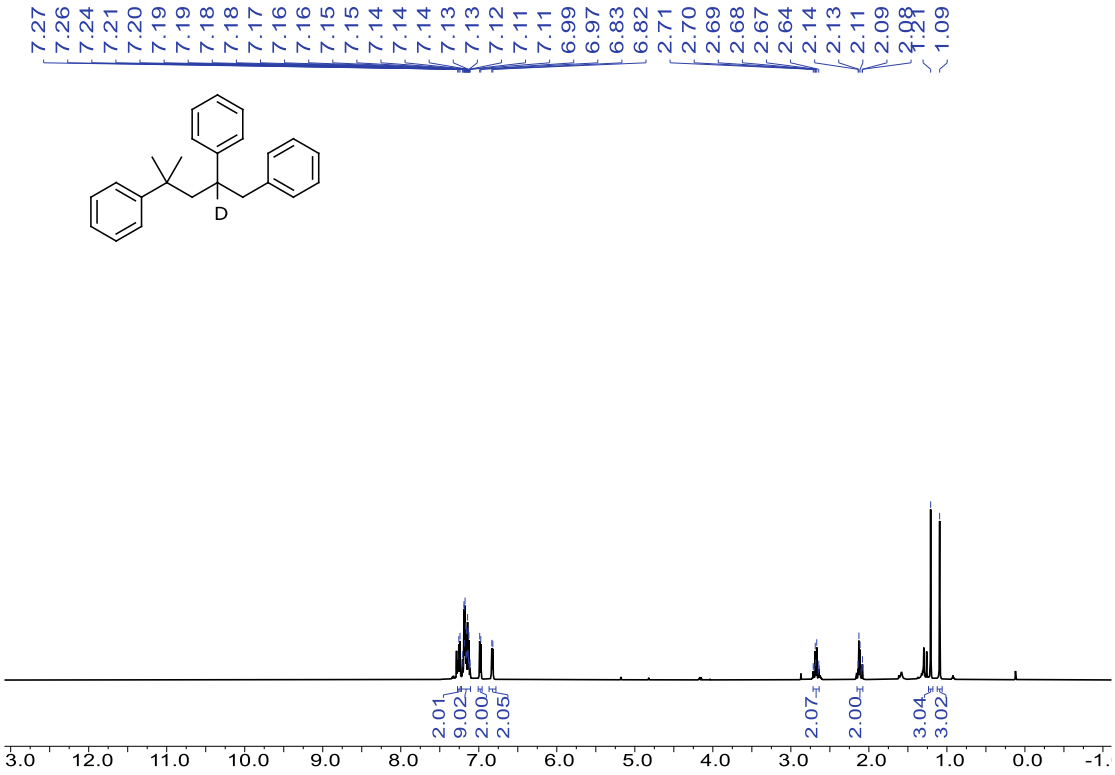
^{1}H NMR spectra of 49 (500 MHz, $CDCl_3$)



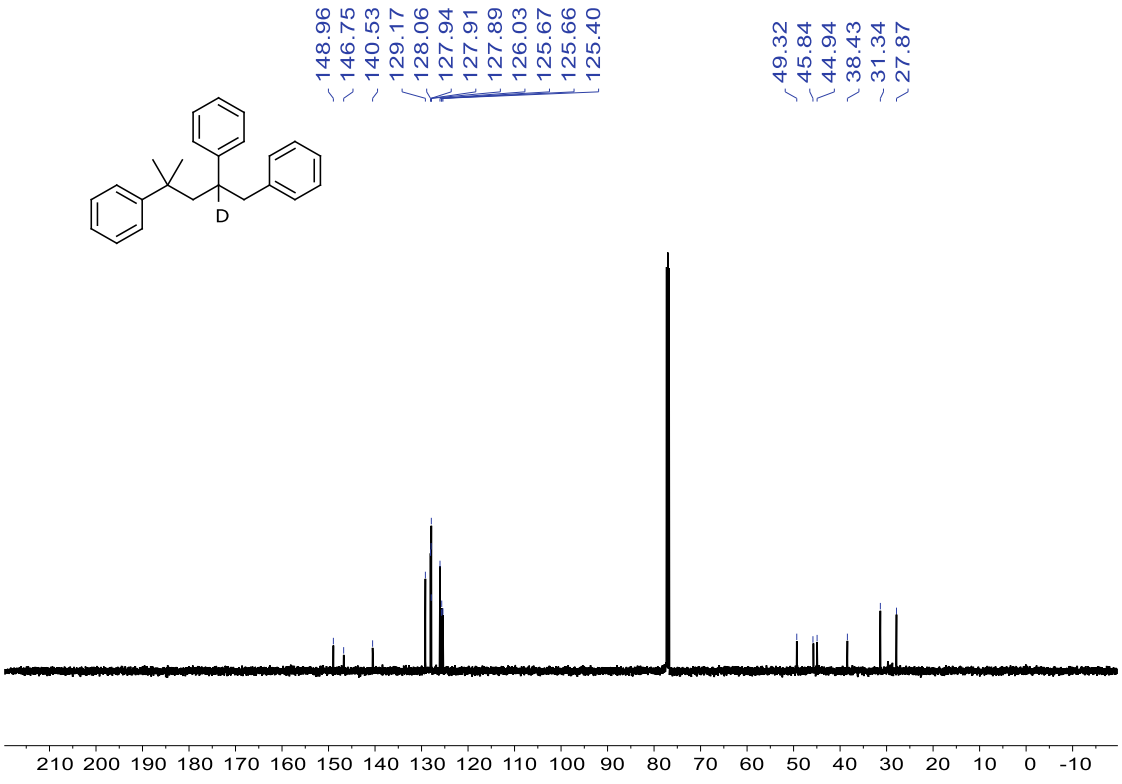
^{13}C NMR spectra of 49 (126 MHz, $CDCl_3$)



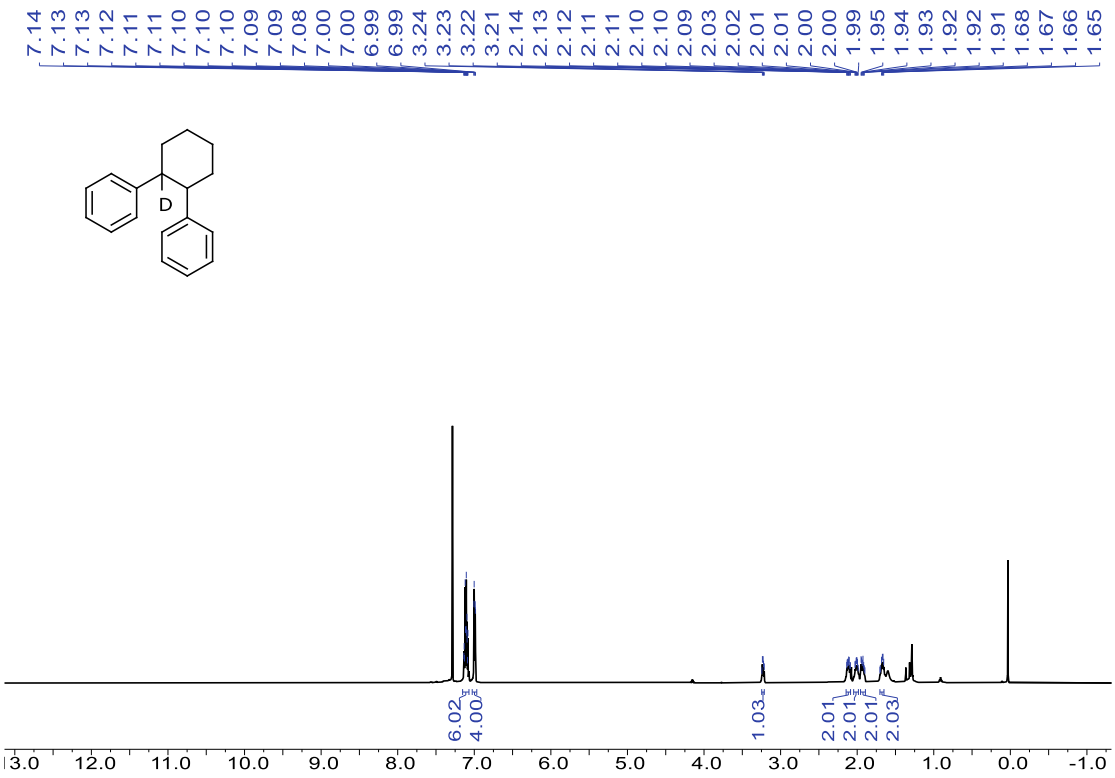
^{1}H NMR spectra of 50 (500 MHz, $CDCl_3$)



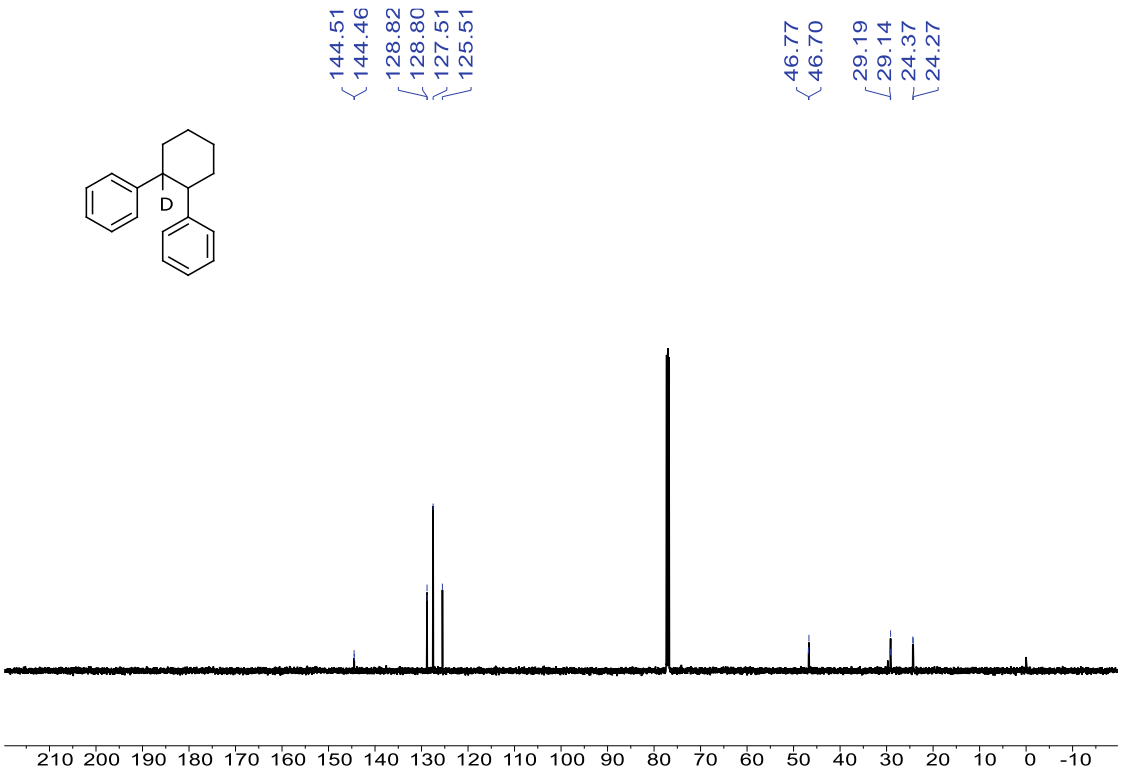
^{13}C NMR spectra of 50 (126 MHz, $CDCl_3$)



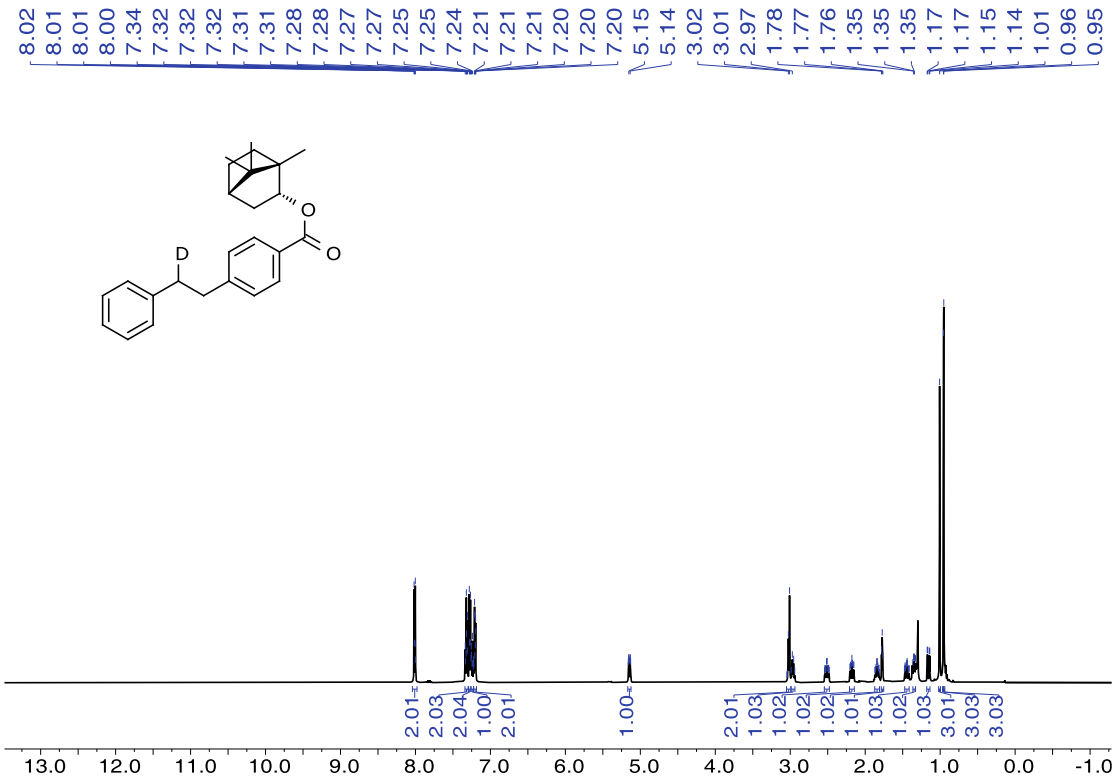
^{1}H NMR spectra of 51 (500 MHz, $CDCl_3$)



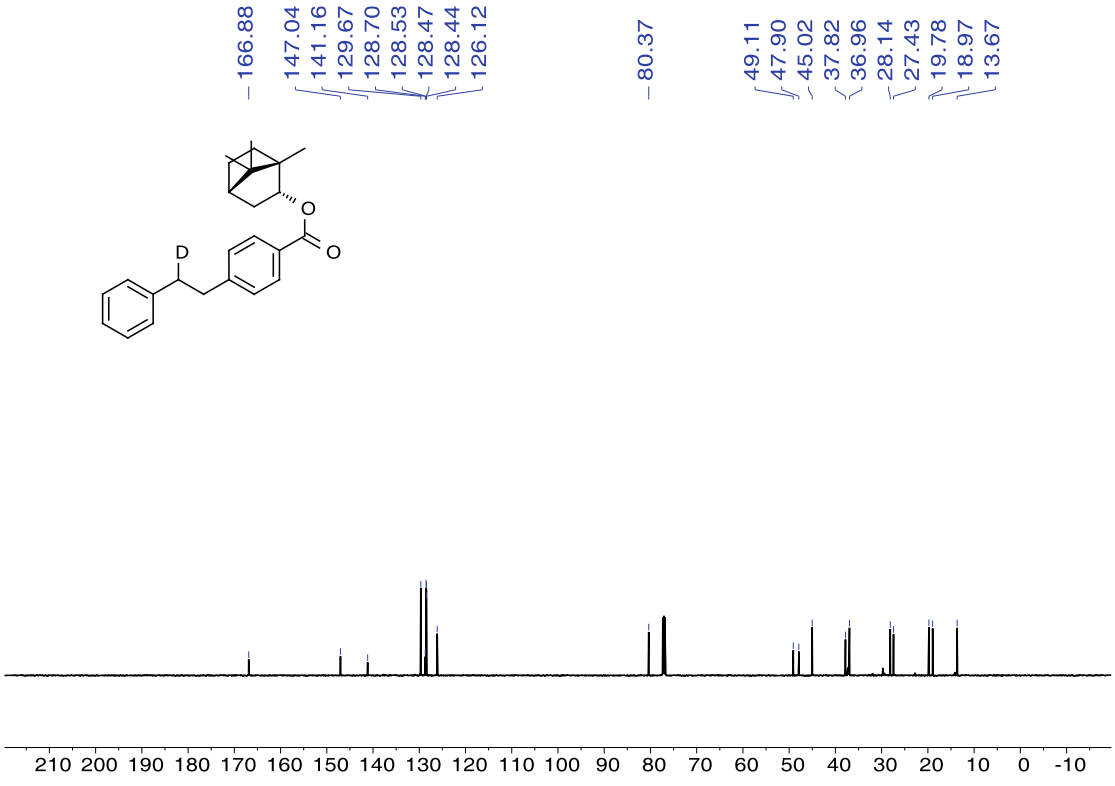
^{13}C NMR spectra of 51 (126 MHz, $CDCl_3$)



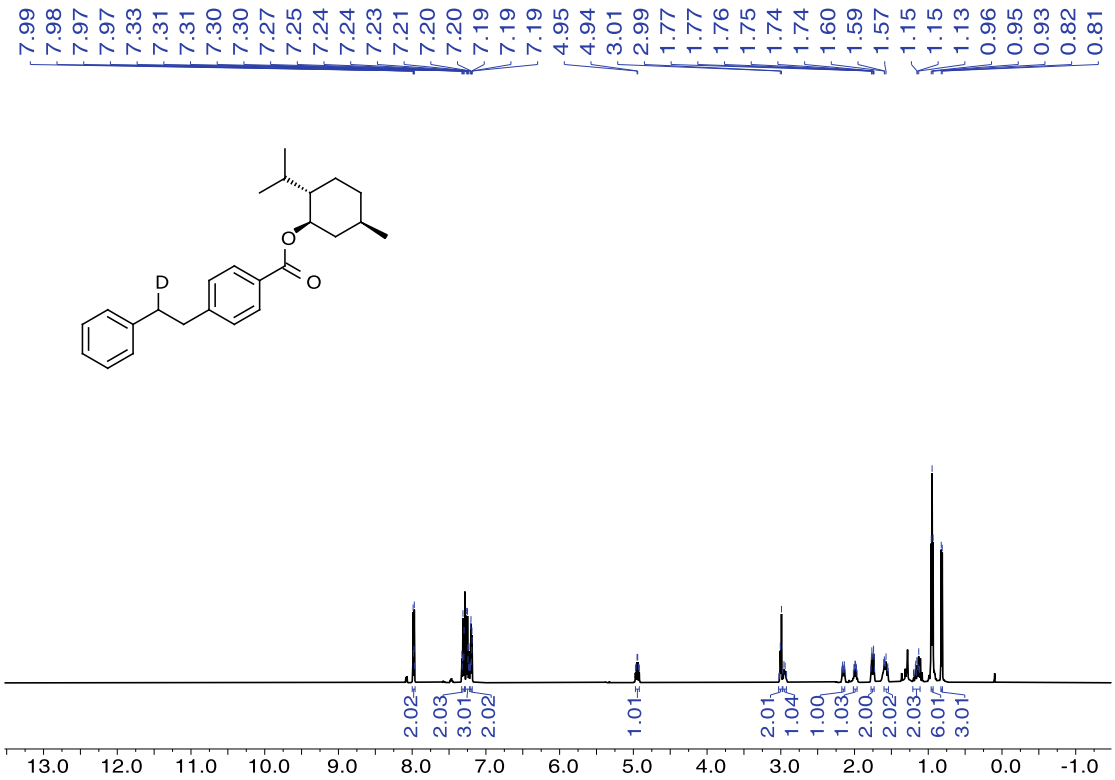
^{1}H NMR spectra of 52 (500 MHz, $CDCl_3$)



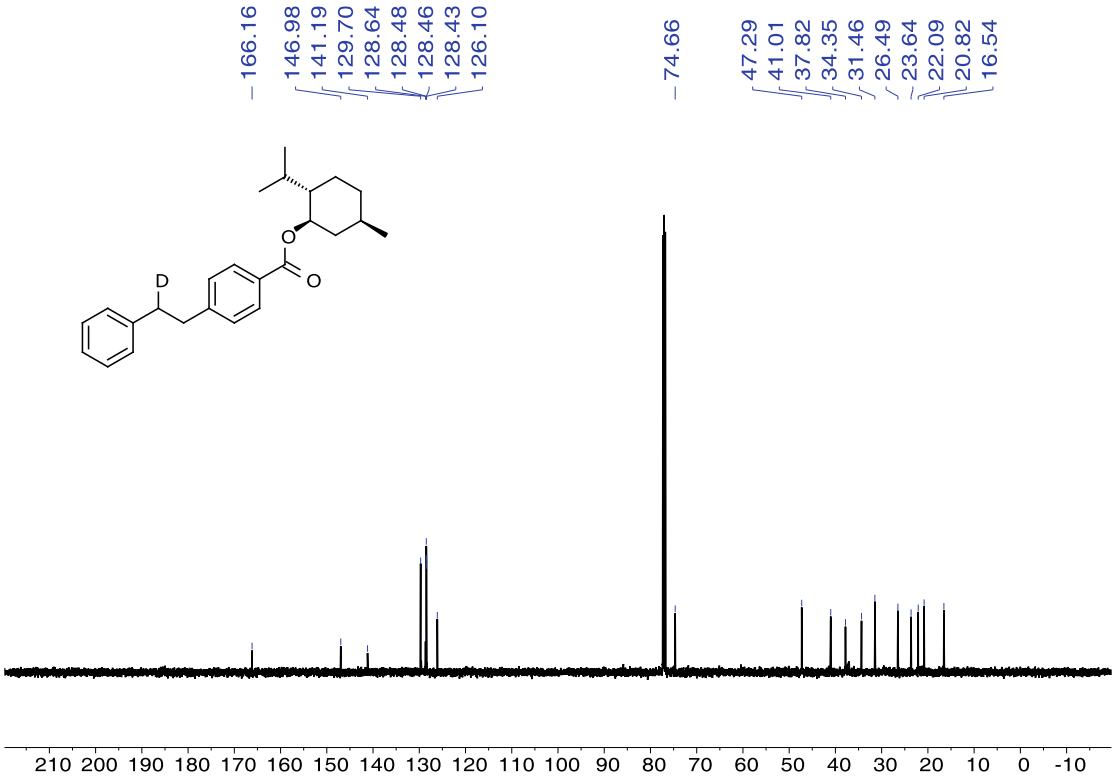
^{13}C NMR spectra of 52 (126 MHz, $CDCl_3$)



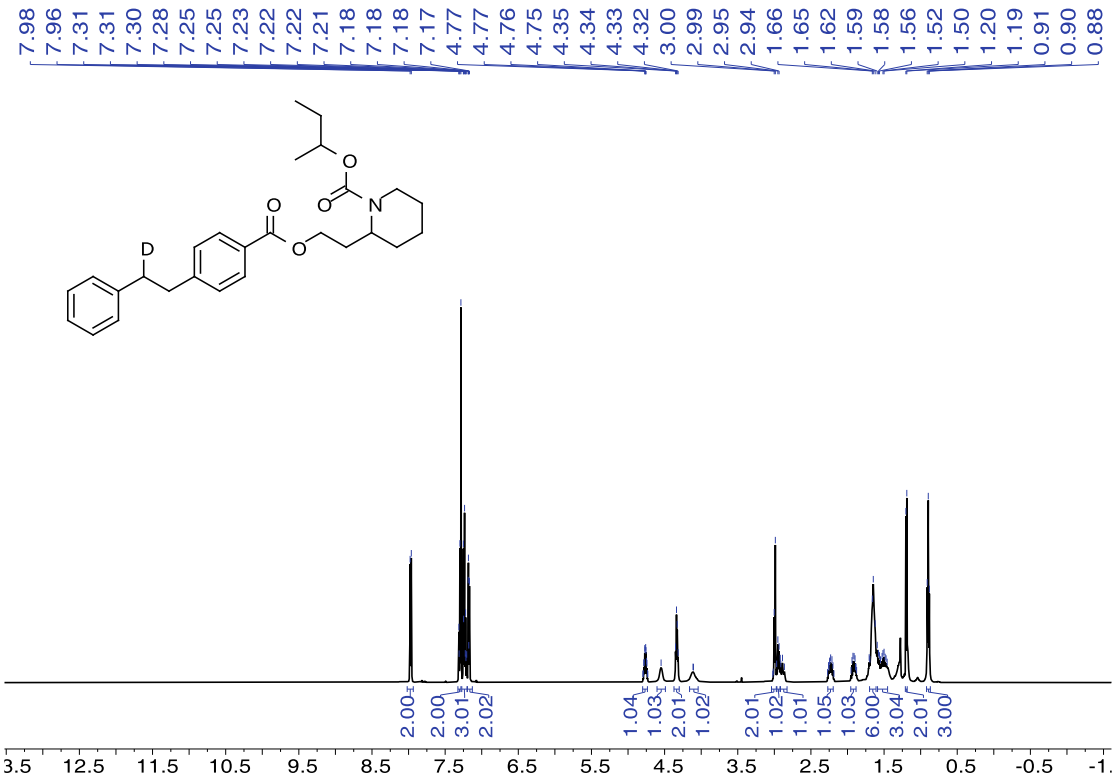
^{1}H NMR spectra of 53 (500 MHz, $CDCl_3$)



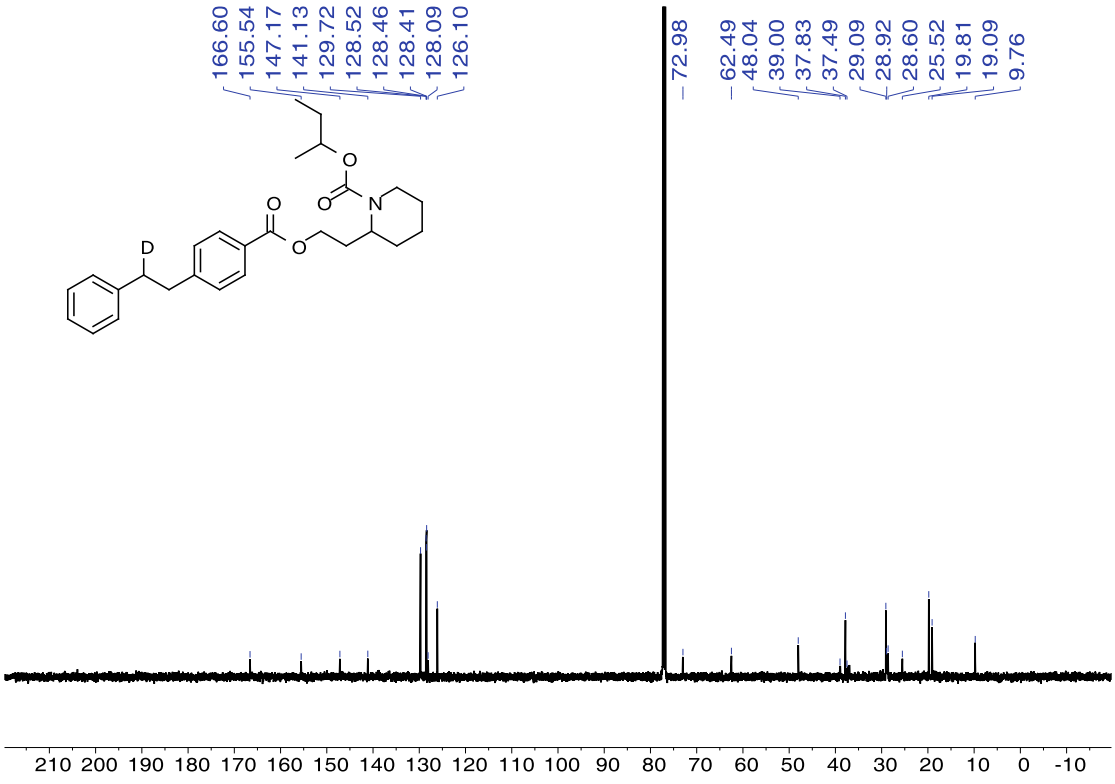
^{13}C NMR spectra of 53 (126 MHz, $CDCl_3$)



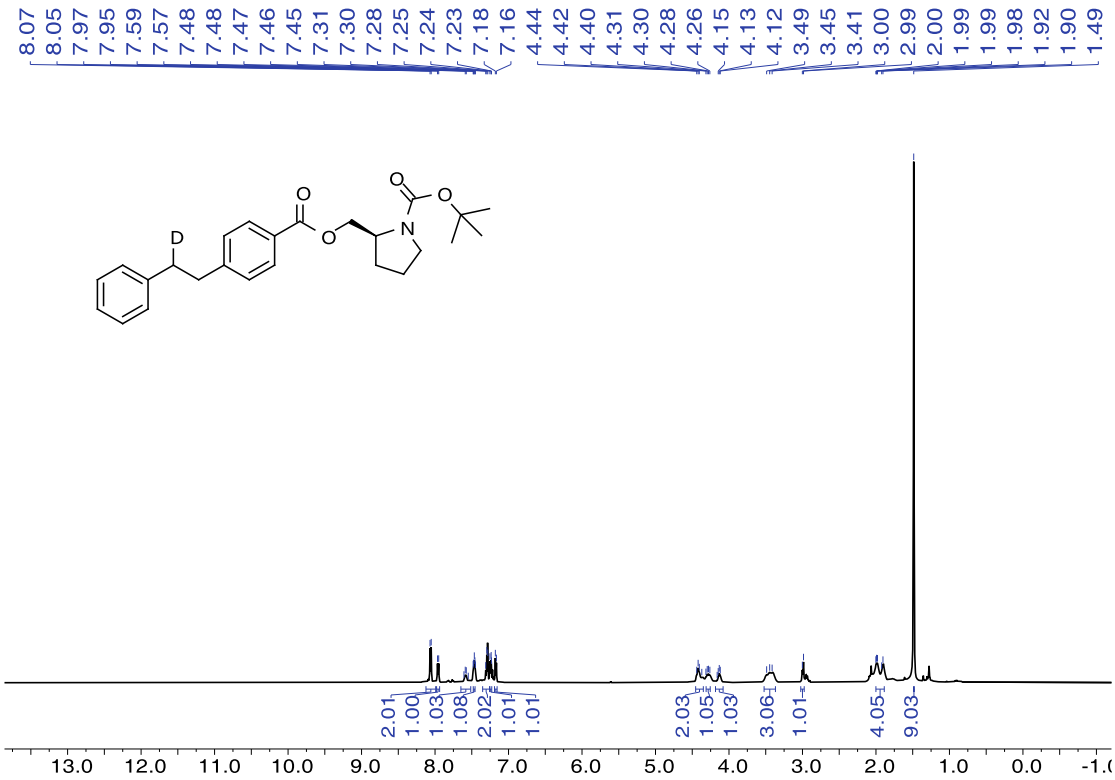
^{1}H NMR spectra of 54 (500 MHz, $CDCl_3$)



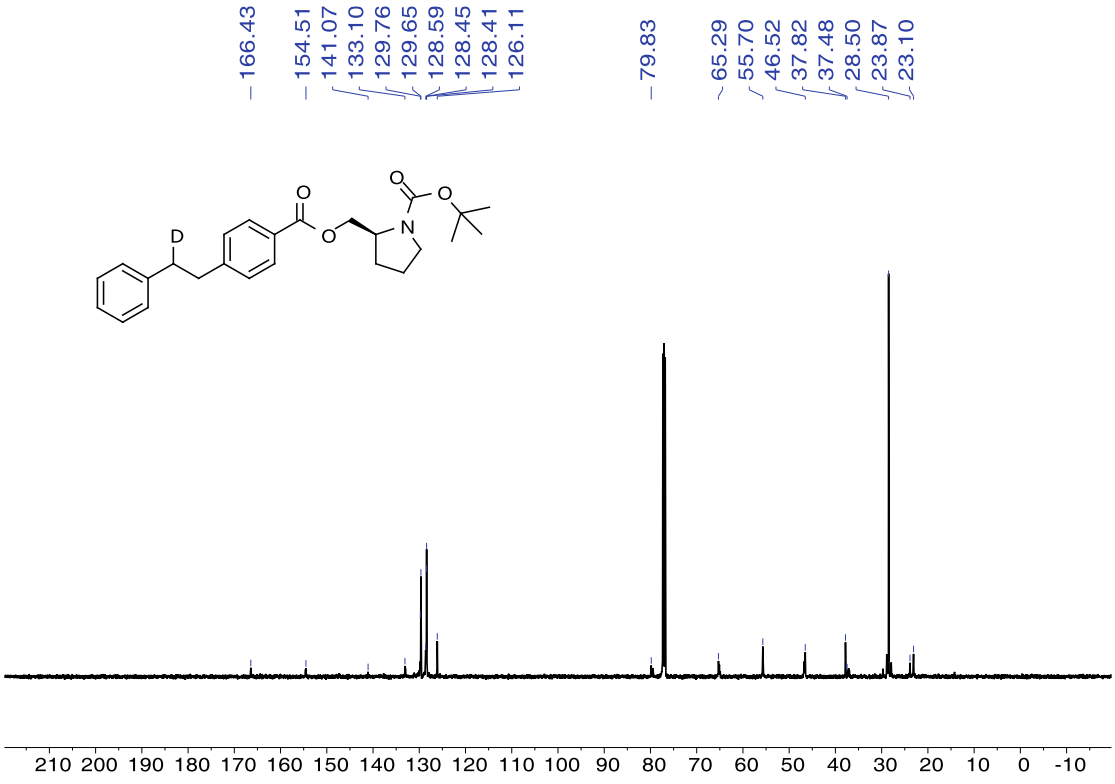
^{13}C NMR spectra of 54 (126 MHz, $CDCl_3$)



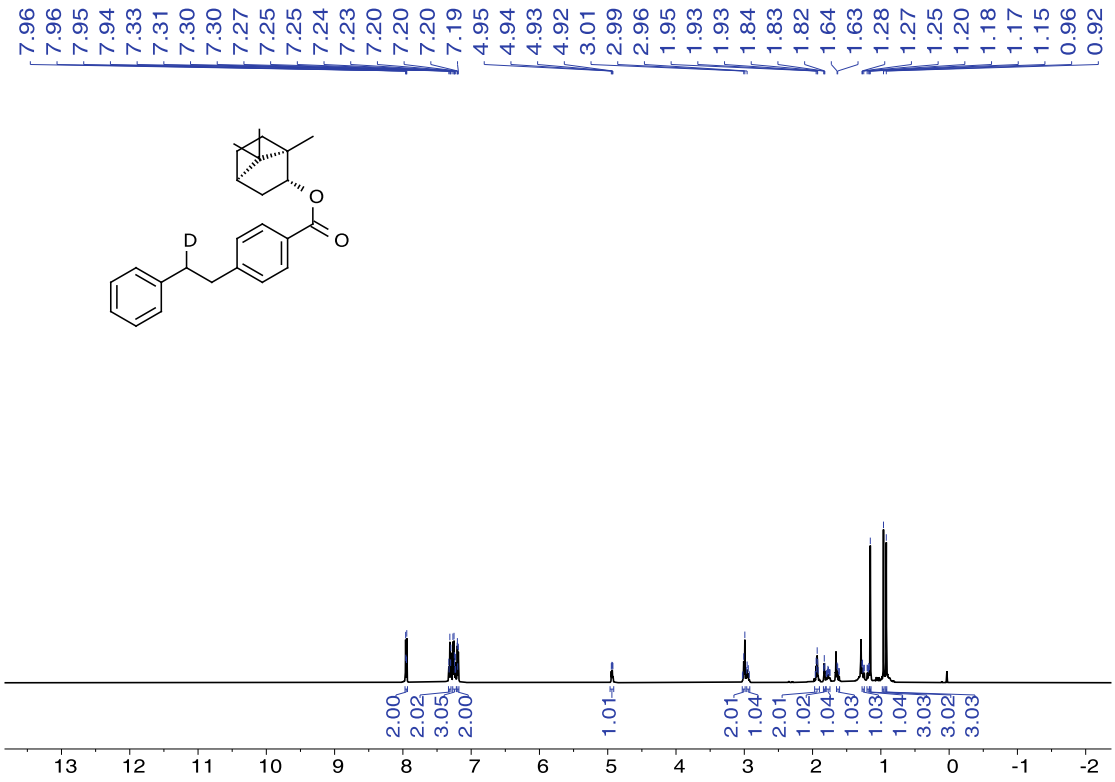
^{1}H NMR spectra of 55 (500 MHz, $CDCl_3$)



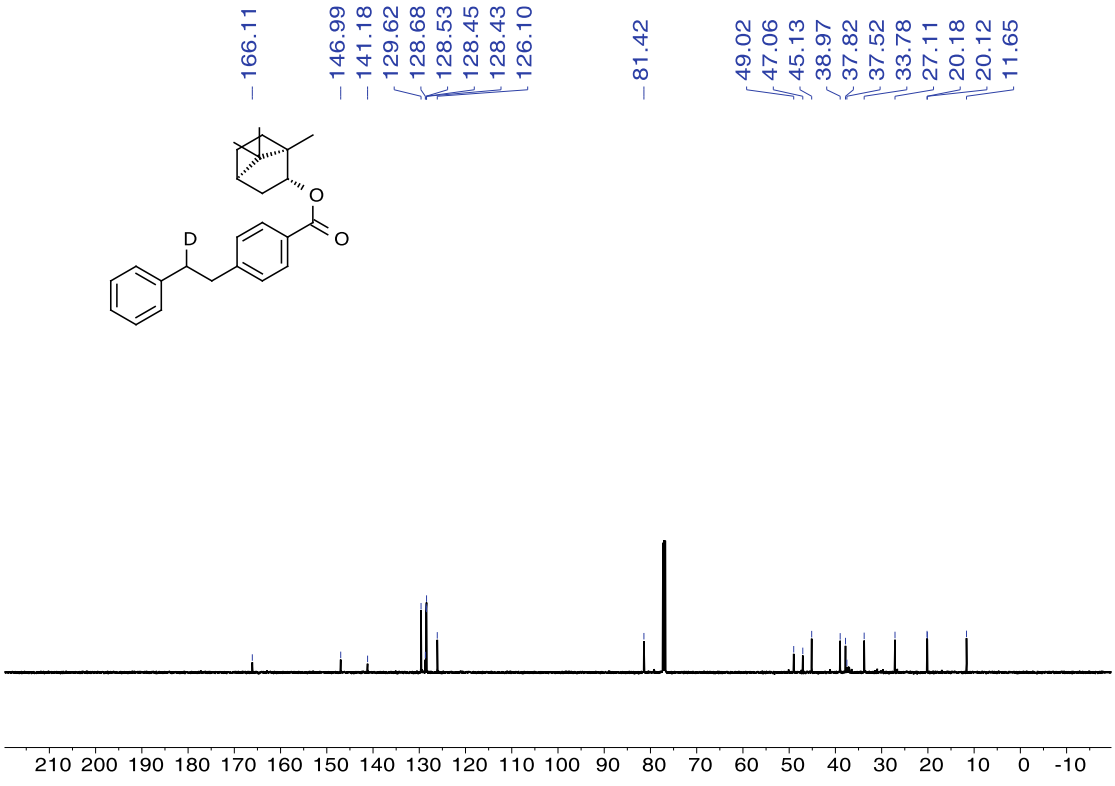
^{13}C NMR spectra of 55 (126 MHz, $CDCl_3$)



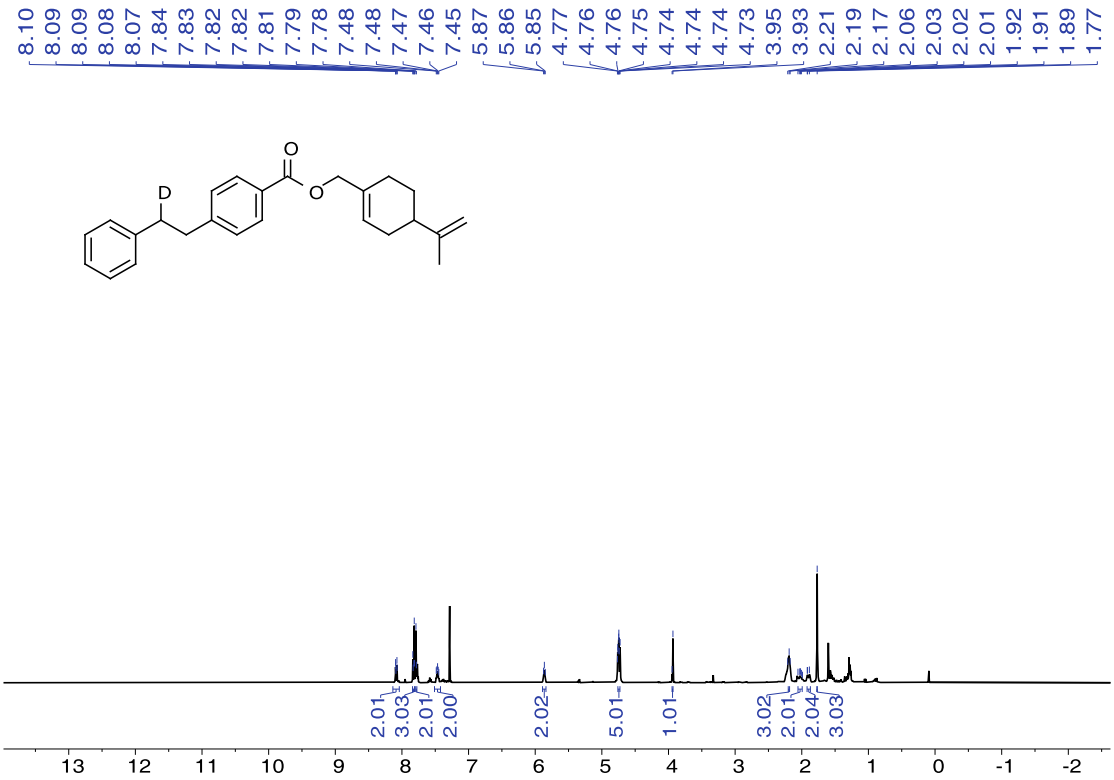
^{1}H NMR spectra of 56 (500 MHz, $CDCl_3$)



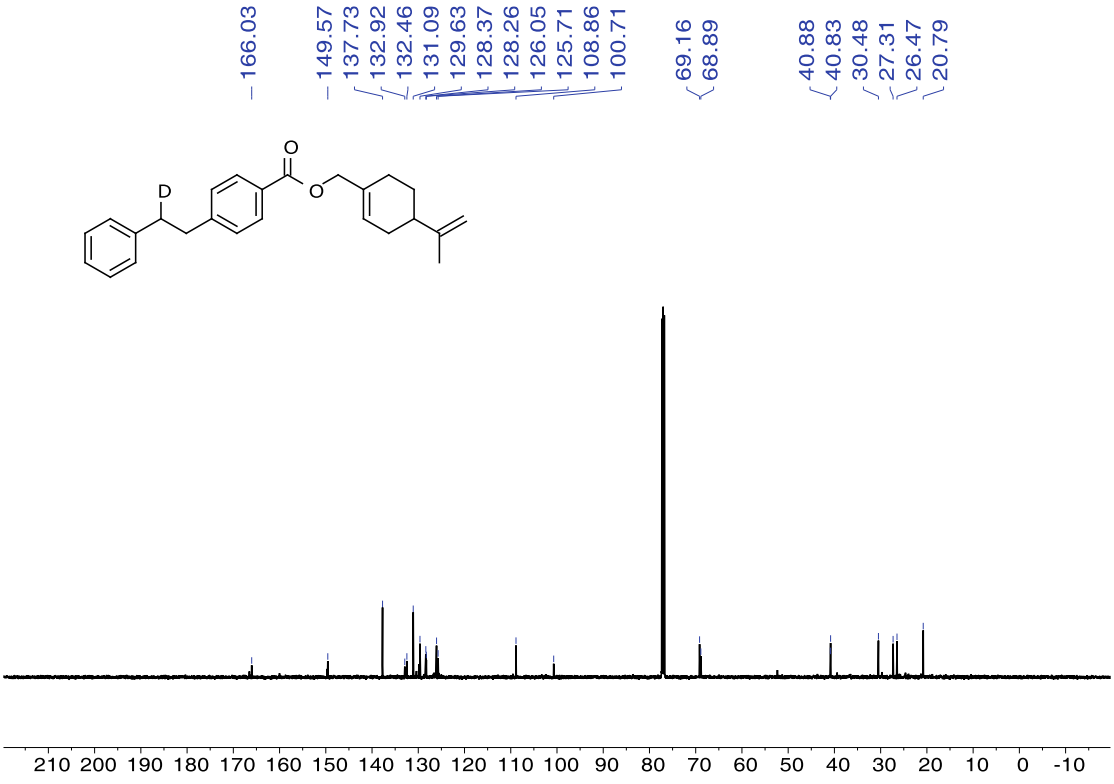
^{13}C NMR spectra of 56 (126 MHz, $CDCl_3$)



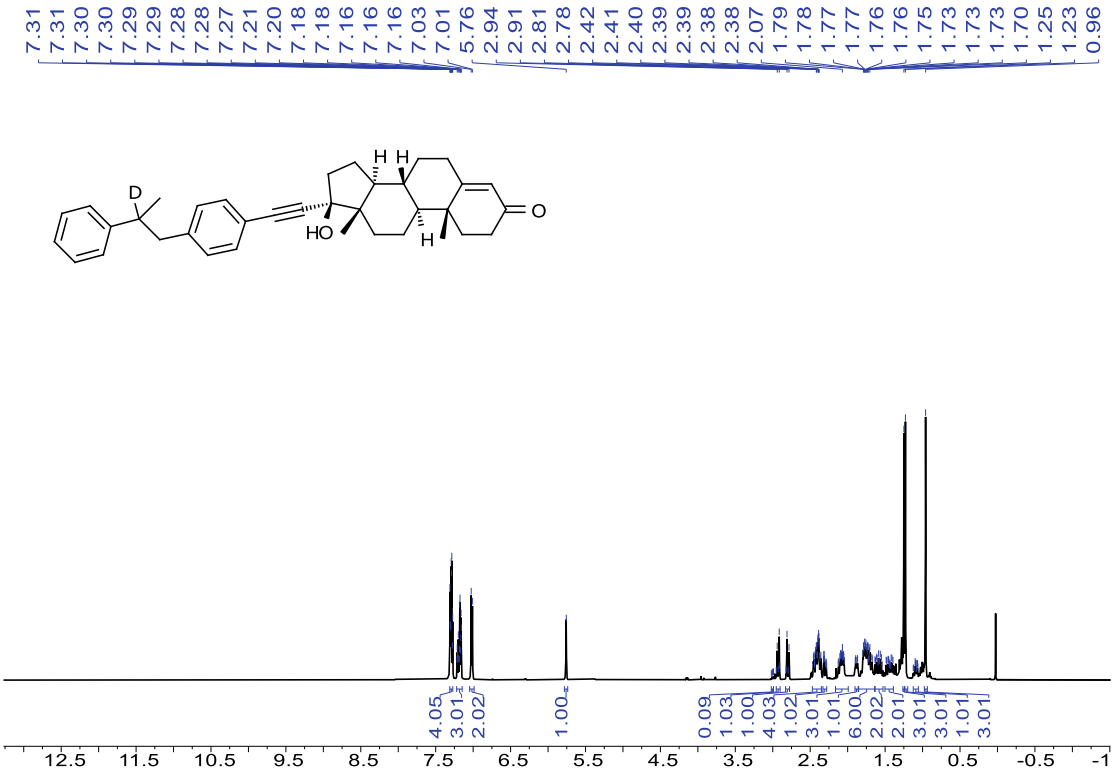
^{1}H NMR spectra of 57 (500 MHz, $CDCl_3$)



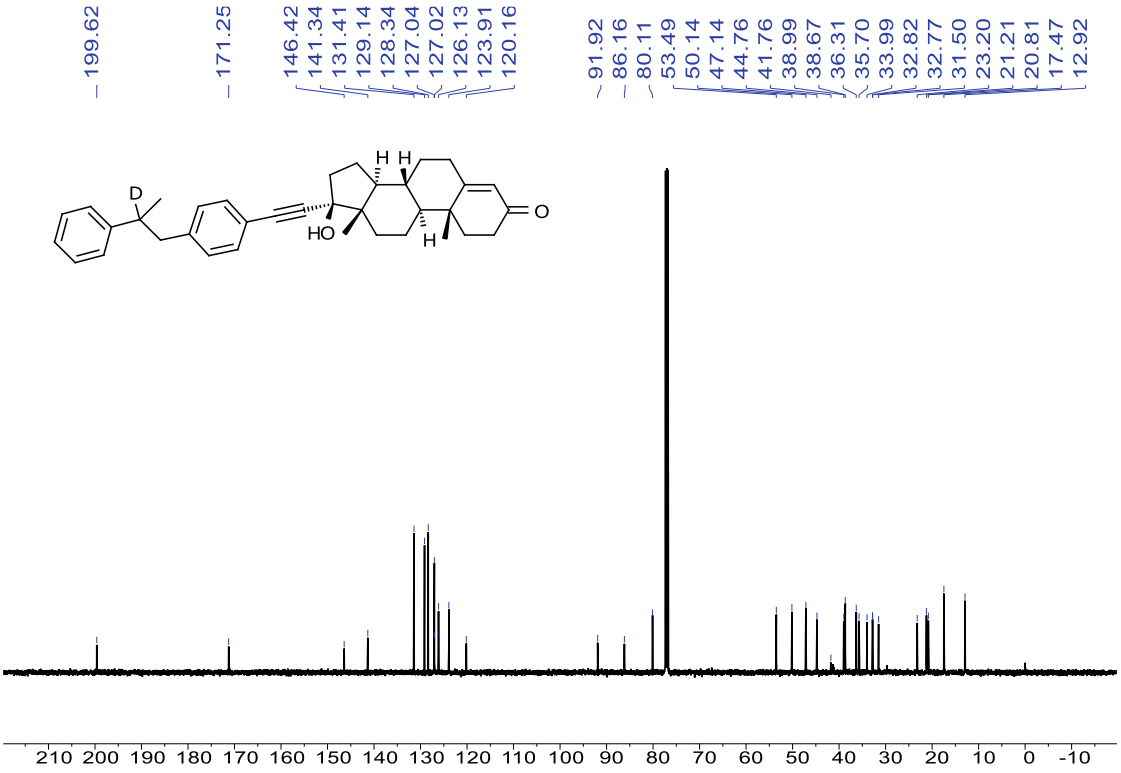
^{13}C NMR spectra of 57 (126 MHz, $CDCl_3$)



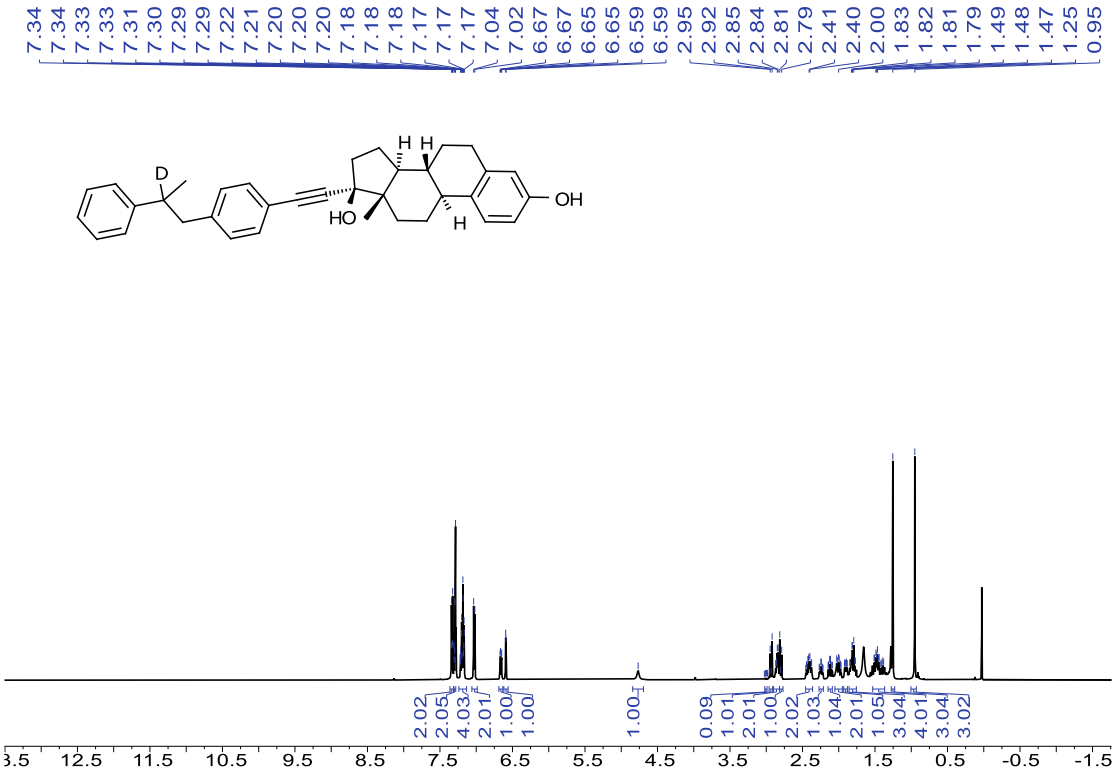
^{1}H NMR spectra of 58 (500 MHz, $CDCl_3$)



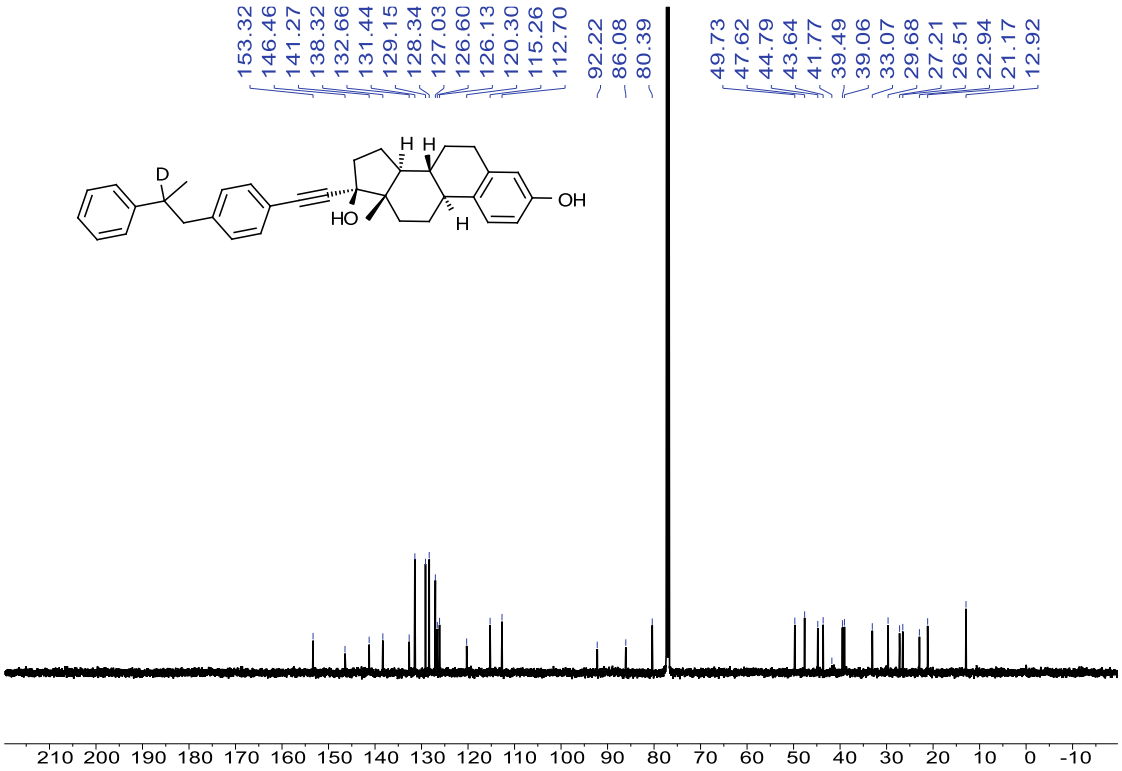
^{13}C NMR spectra of 58 (126 MHz, $CDCl_3$)



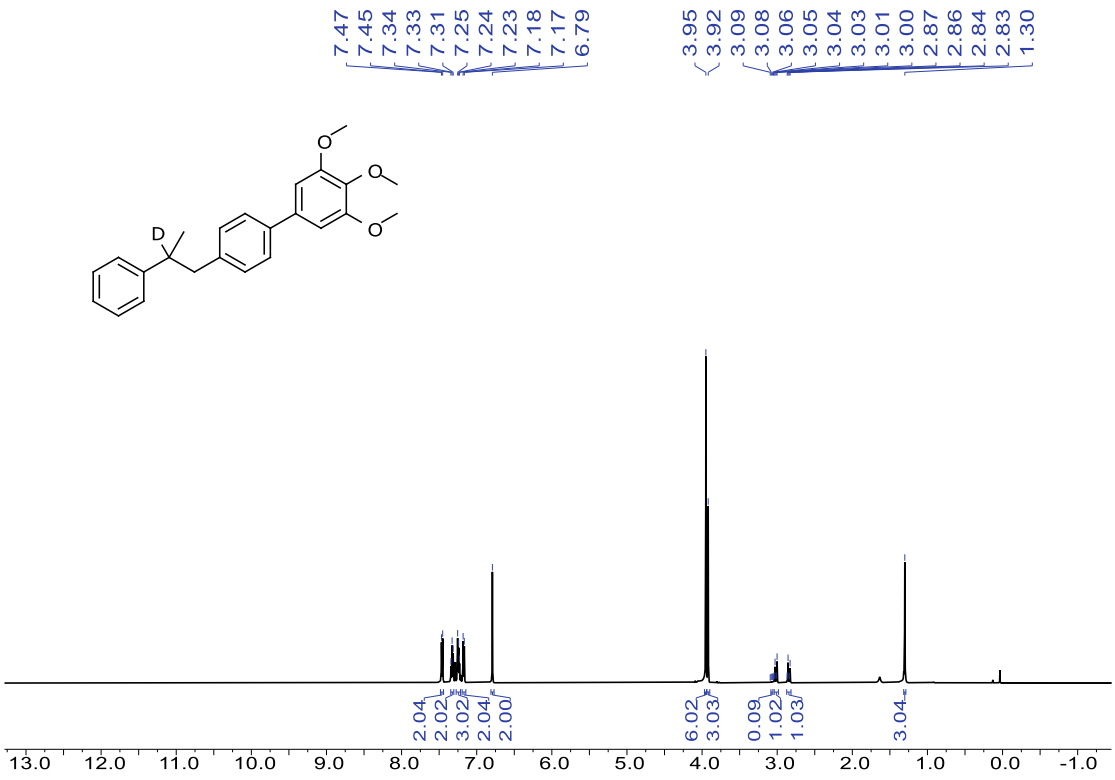
^{1}H NMR spectra of 59 (500 MHz, $CDCl_3$)



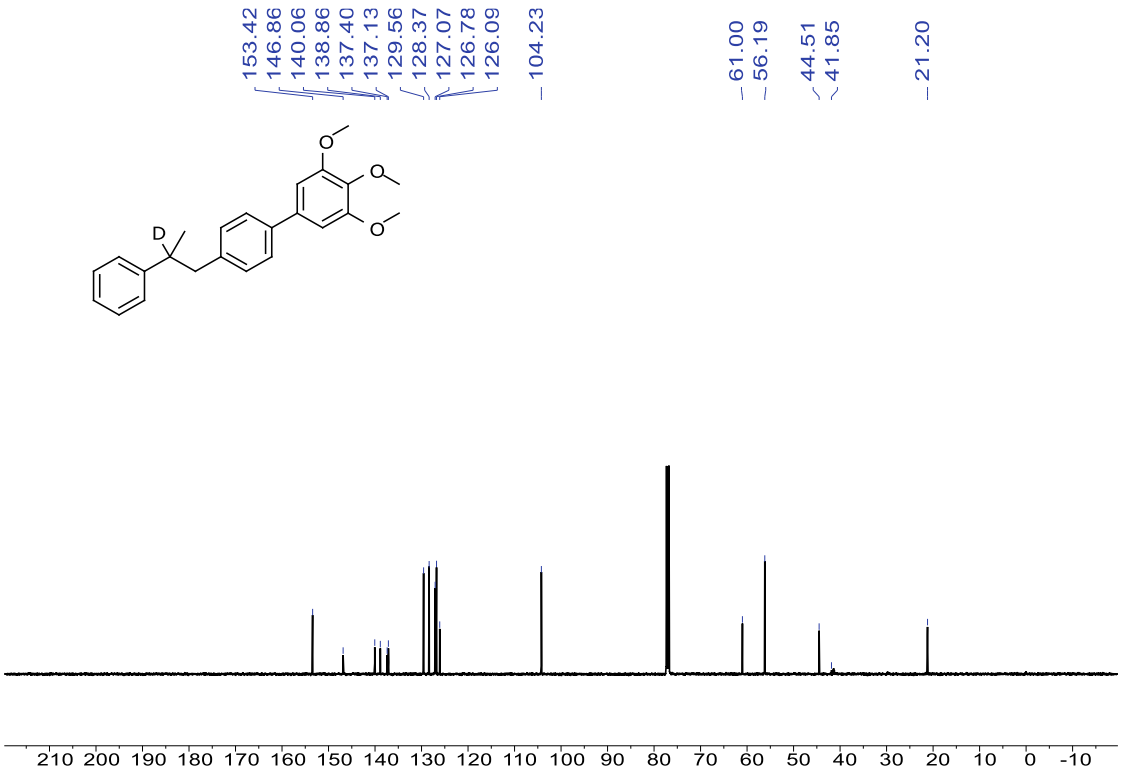
^{13}C NMR spectra of 59 (126 MHz, $CDCl_3$)



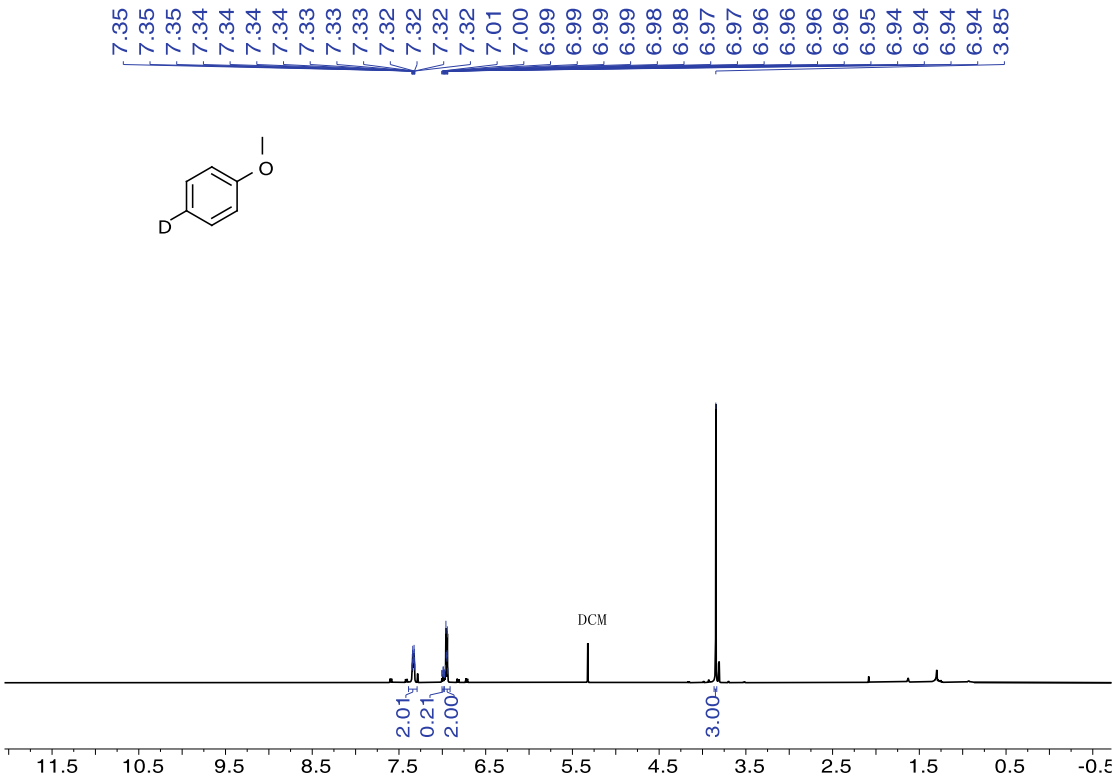
^{1}H NMR spectra of 60 (500 MHz, $CDCl_3$)



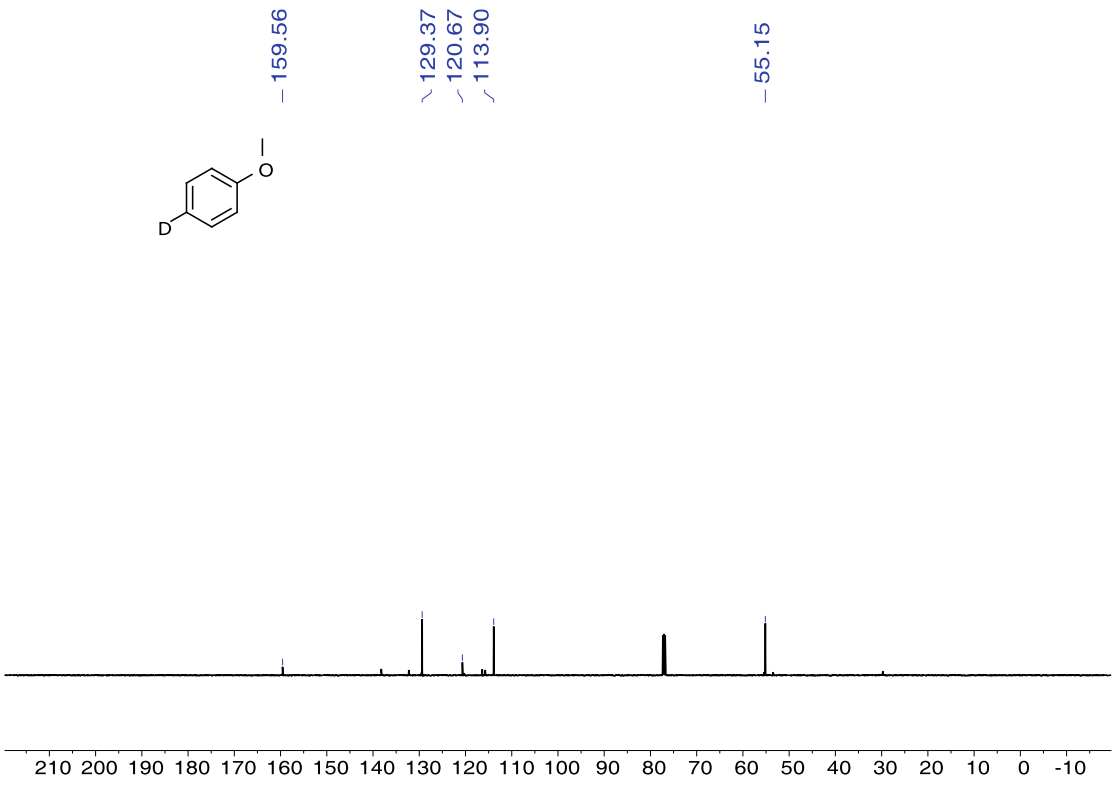
^{13}C NMR spectra of 60 (126 MHz, $CDCl_3$)



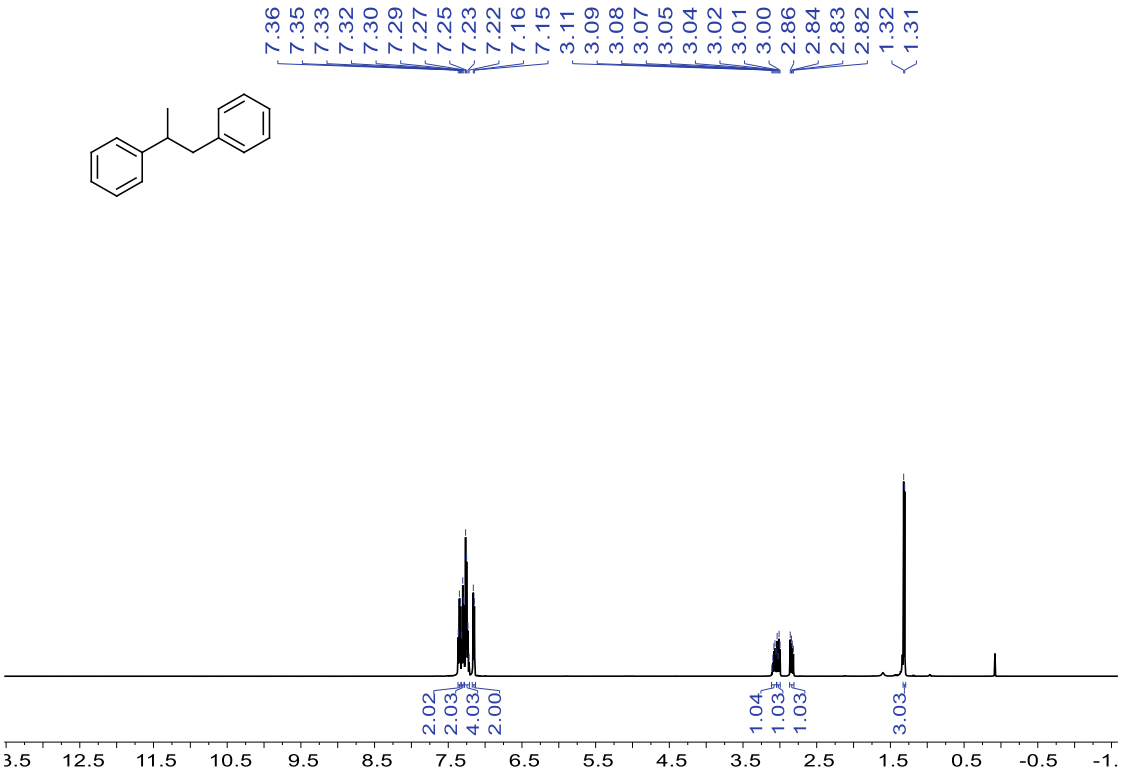
^{1}H NMR spectra of 62 (500 MHz, $CDCl_3$)



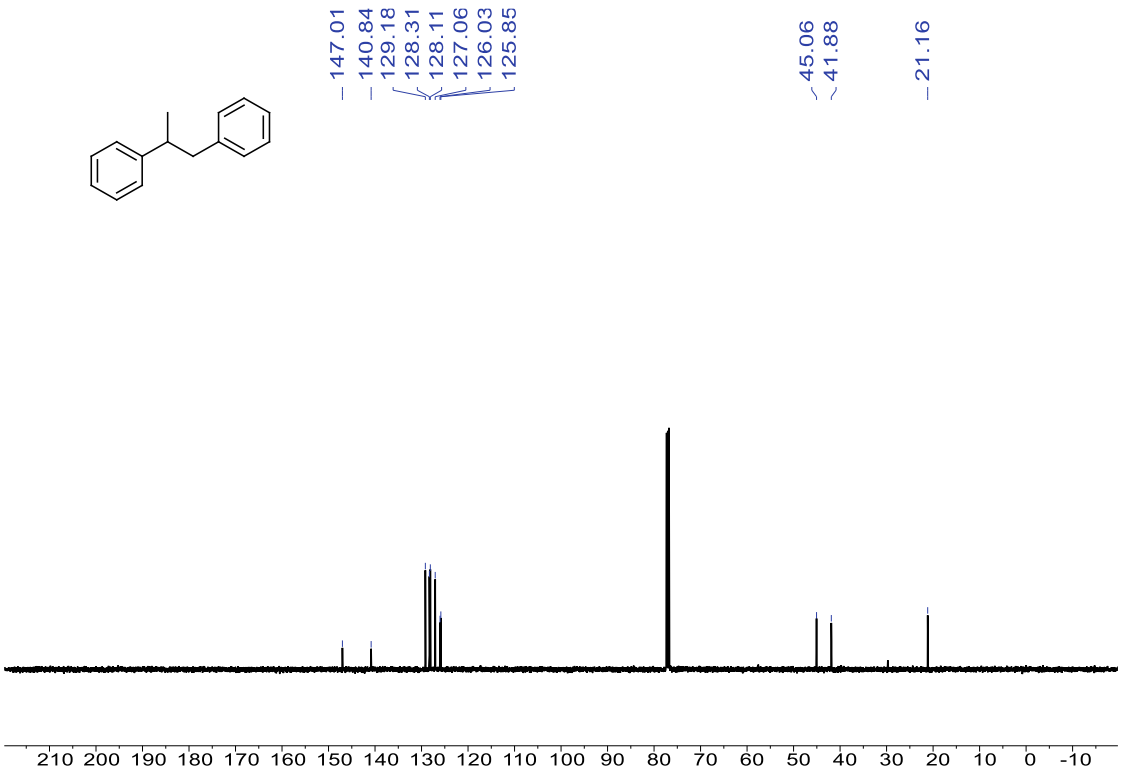
^{13}C NMR spectra of 62 (126 MHz, $CDCl_3$)



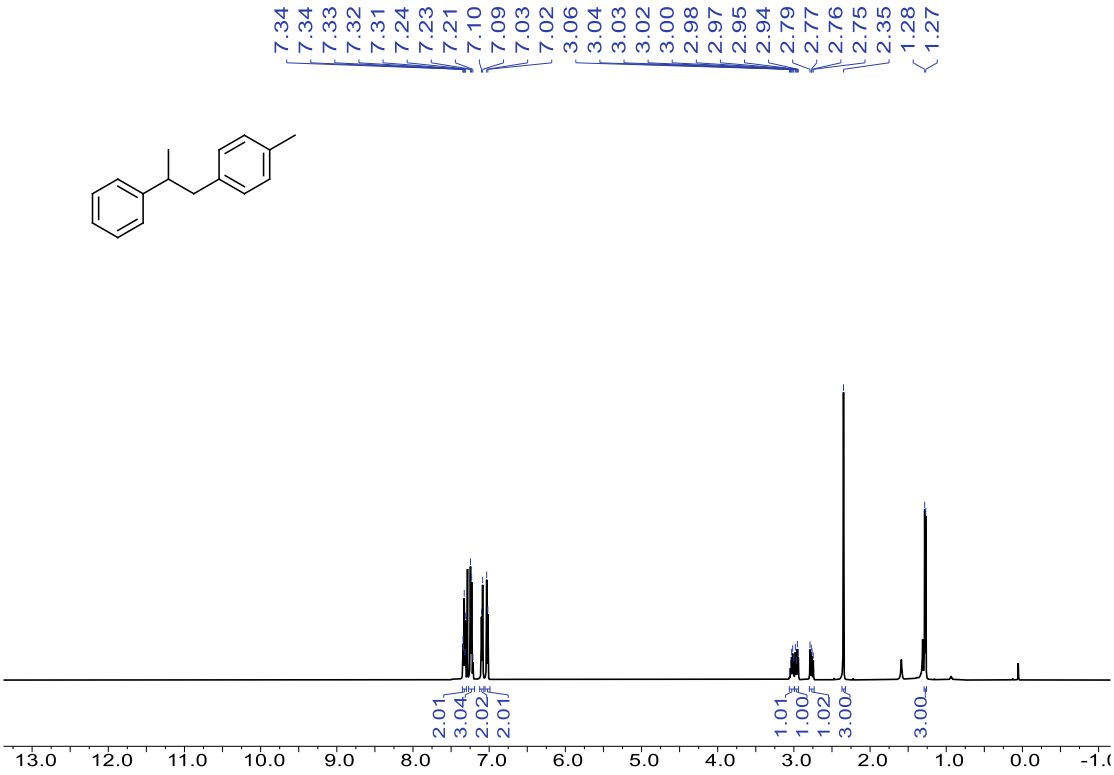
^{1}H NMR spectra of 63 (500 MHz, $CDCl_3$)



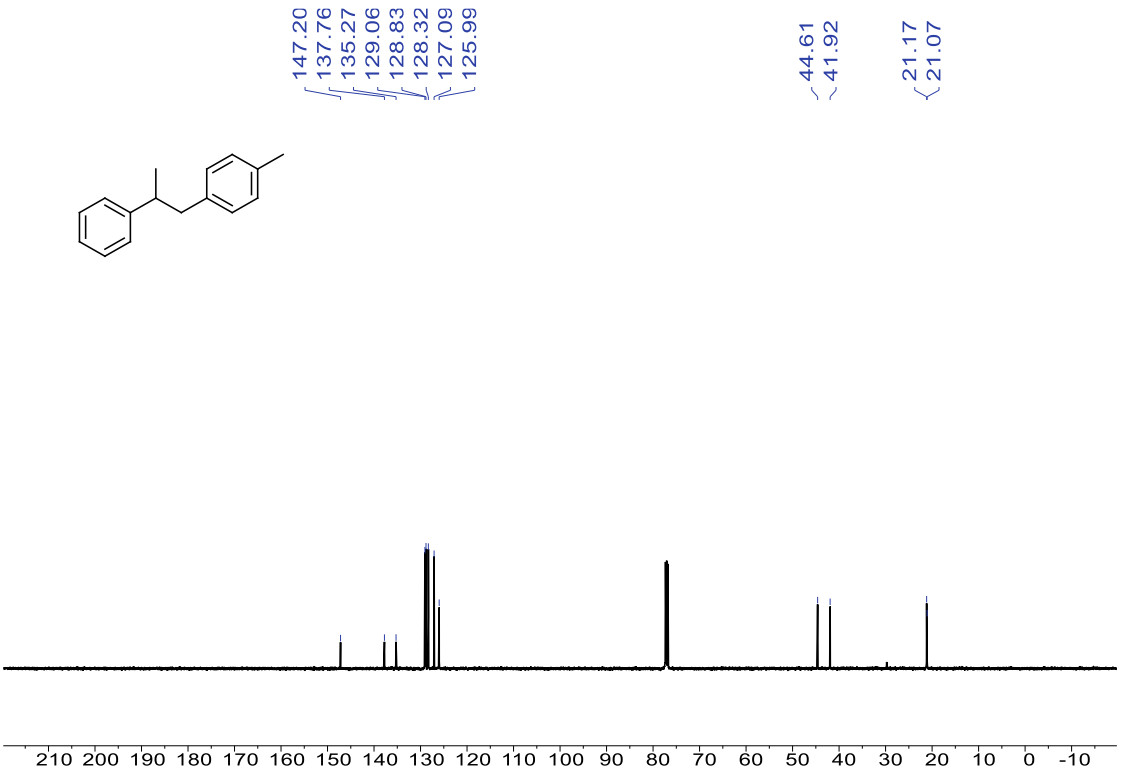
^{13}C NMR spectra of 63 (126 MHz, $CDCl_3$)



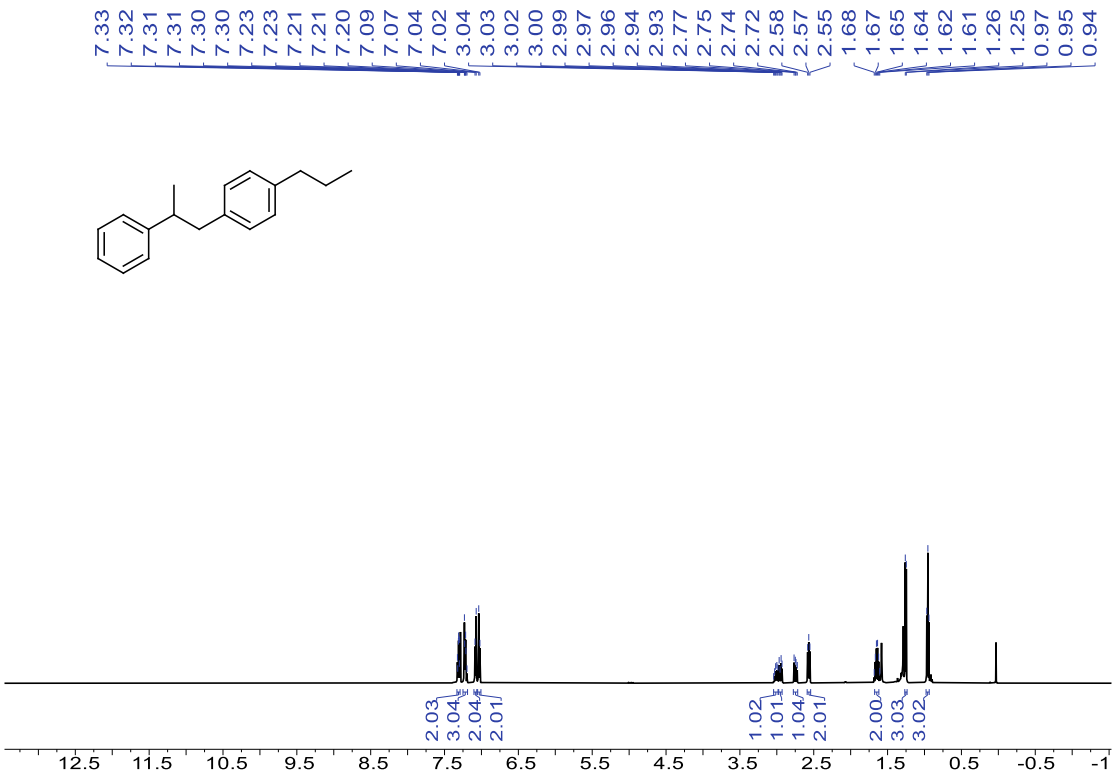
^{1}H NMR spectra of 64 (500 MHz, $CDCl_3$)



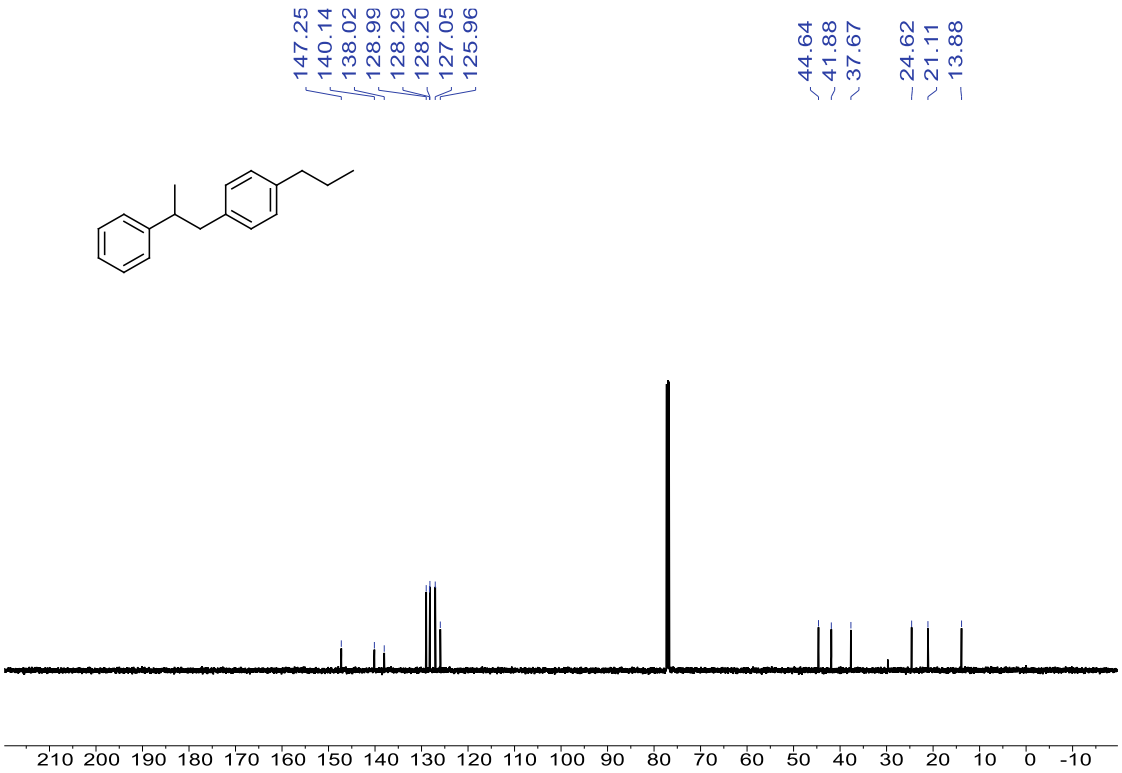
^{13}C NMR spectra of 64 (126 MHz, $CDCl_3$)



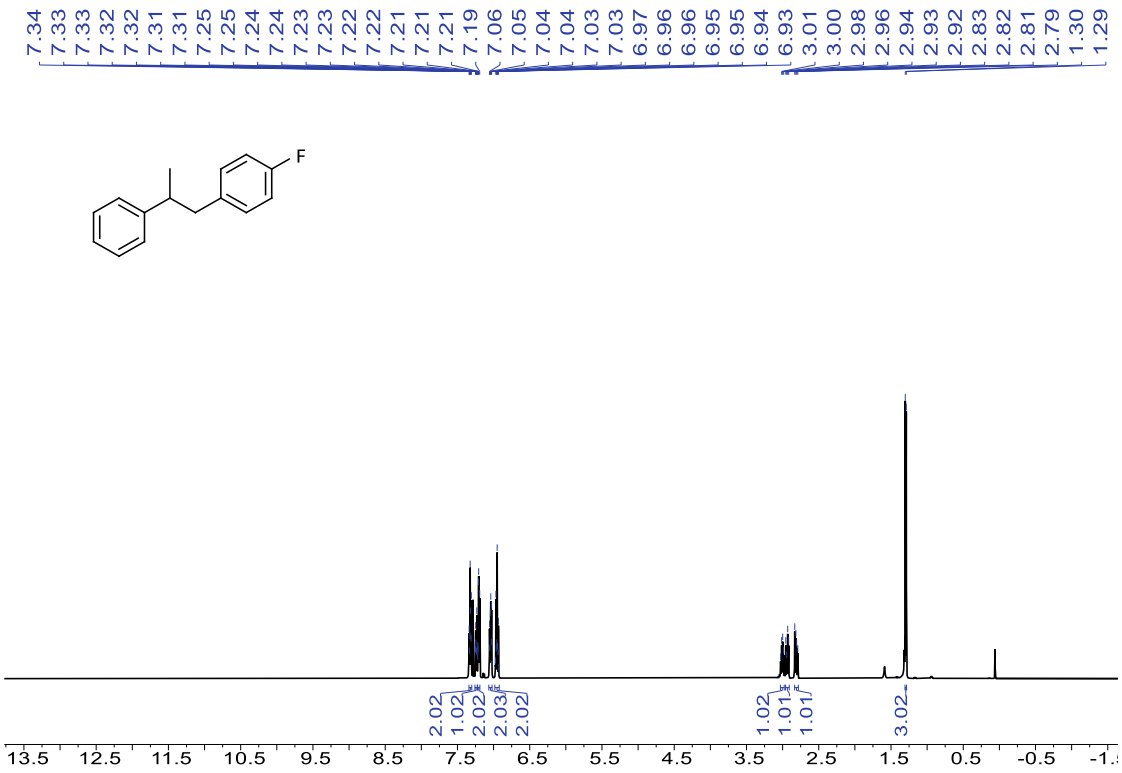
^{1}H NMR spectra of 65 (500 MHz, $CDCl_3$)



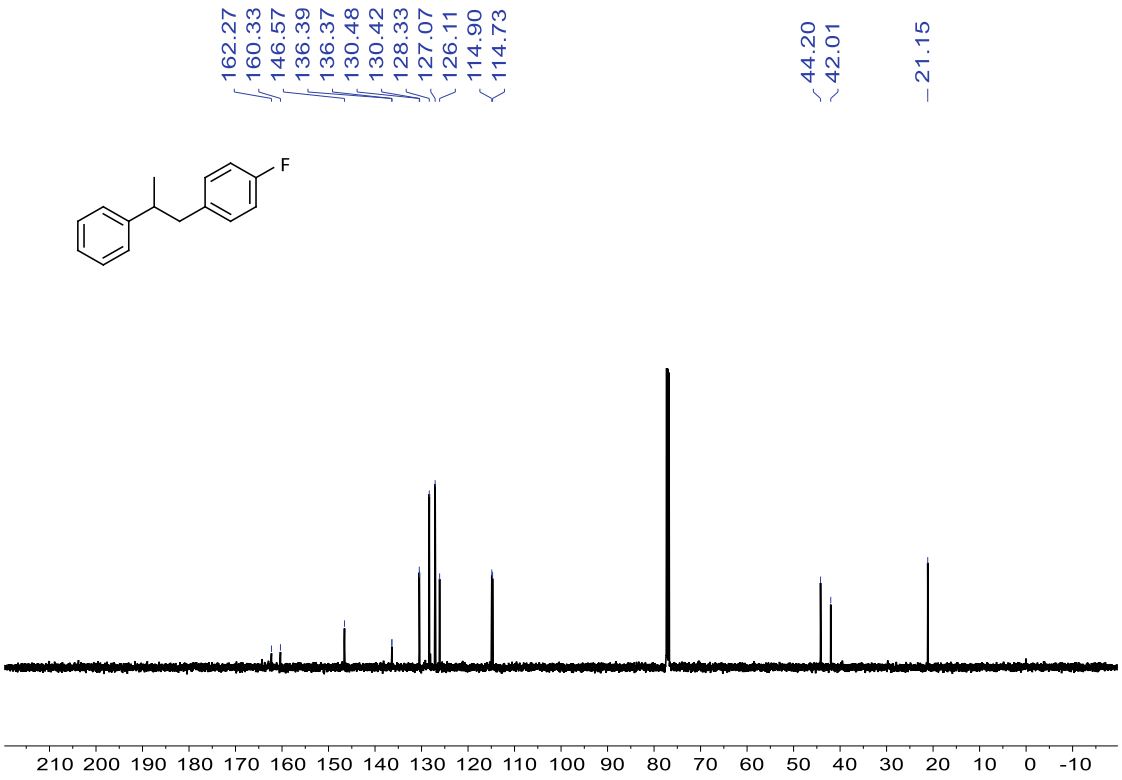
^{13}C NMR spectra of 65 (126 MHz, $CDCl_3$)



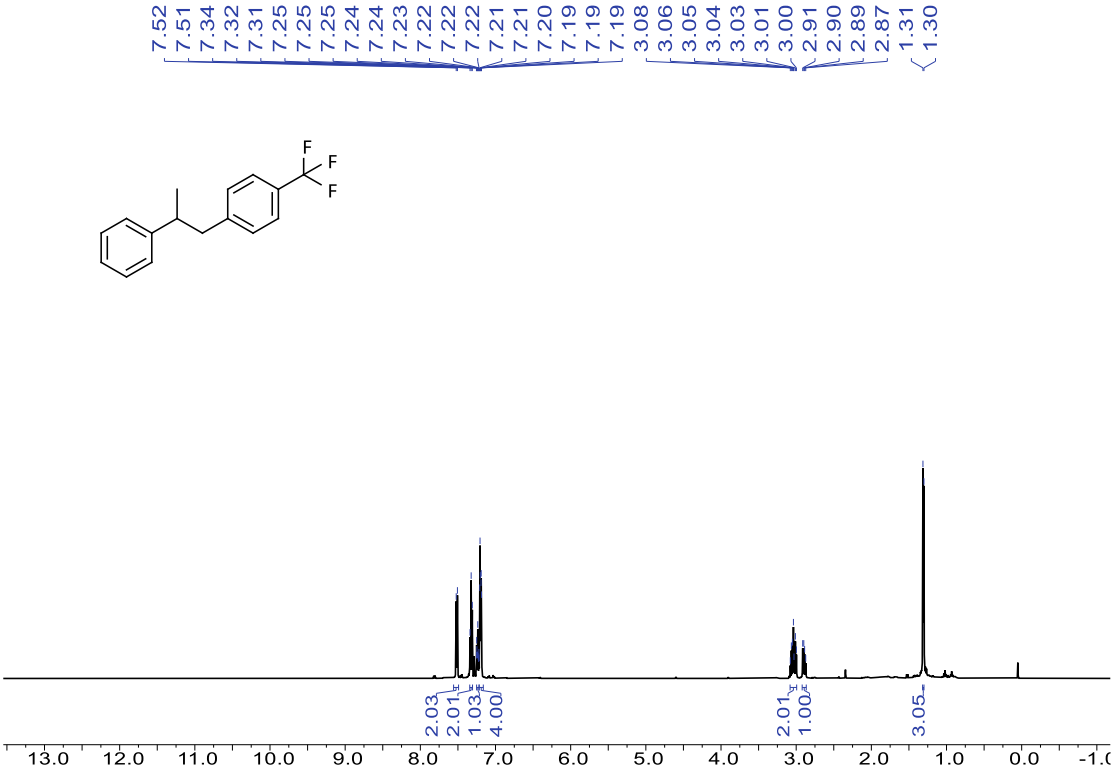
^{1}H NMR spectra of 66 (500 MHz, $CDCl_3$)



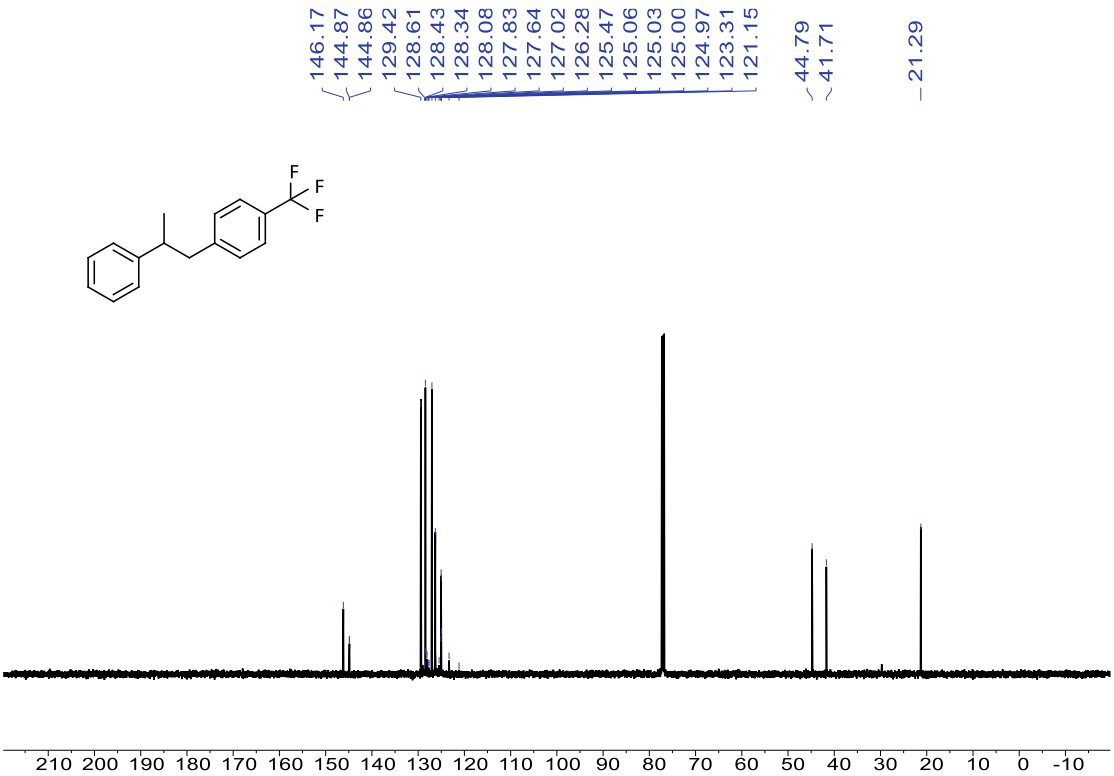
^{13}C NMR spectra of 66 (126 MHz, $CDCl_3$)



^{1}H NMR spectra of 67 (500 MHz, $CDCl_3$)



^{13}C NMR spectra of 67 (126 MHz, $CDCl_3$)



11. References

1. Lebel, H.; Guay, D.; Paquet, V.; Huard, K.; Highly efficient synthesis of terminal alkenes from ketones. *Org. Lett.* **2004**, *6*, 3047.

2. Rueping, M.; Bootwicha, T.; Kambutong, S.; Sugiono, E.; Asymmetric calcium catalysis: highly enantioselective carbonyl-ene and friedel–crafts reactions for the synthesis of quaternary α-hydroxy esters bearing a trifluoromethyl group. *Chem. Asian J.* **2012**, *7*, 1195.

3. Kristensen, S. K.; Laursen, S. L. R.; Taarning, E.; Skrydstrup, T.; Ex situ formation of methanethiol: Application in the gold(I)-promoted anti-Markovnikov hydrothiolation of olefins. *Angew. Chem. Int. Ed.* **2018**, *57*, 13887.

4. Pratsch, G.; Overman, L. E.; Synthesis of 2,5-diaryl-1,5-dienes from allylic bromides using visible-light photoredox catalysis. *J. Org. Chem.* **2015**, *80*, 11388.

5. Han, Y.-Q.; Yang, X.; Kong, K.-X.; Deng, Y.-T.; Wu, L.-S.; Ding, Y.; Shi, B.-F. Synthesis of acyclic aliphatic amides with contiguous stereogenic centers *via* palladium-catalyzed enantio-, chemo- and diastereoselective methylene C(sp^3)−H arylation. *Angew. Chem. Int. Ed.* **2020**, *59*, 20455.

6. Zhou, F.; Hu, X.; Zhang, W.; Li, C.-J. Copper-catalyzed radical reductive arylation of styrenes with aryl iodides mediated by zinc in water. *J. Org. Chem.* **2018**, *83*, 7416.

7. Gole, B.; Sanyal, U.; Banerjee, R.; Mukherjee, P. S. High loading of Pd nanoparticles by interior functionalization of MOFs for heterogeneous catalysis. *Inorg. Chem.* **2016**, *55*, 2345.

8. Xue, Y.; Chen, J.; Song, P.; He, Y.; Zhu, S. Nickel-catalyzed regiodivergent reductive hydroarylation of styrenes. *Synlett* **2021**, *32*, 1647.

9. Basnet, P.; Thapa, S.; Dickie, D. A.; Giri, R. The copper-catalysed Suzuki–Miyaura coupling of alkylboron reagents: disproportionation of anionic (alkyl)(alkoxy)borates to anionic dialkylborates prior to transmetalation. *Chem. Commun.* **2016**, *52*, 11072.

10. Li, Z.; Thiery, G.; Lichtenthaler, M. R.; Guillot, R.; Krossing, I.; Gandon, V.; Bour, C. Catalytic use of low-valent cationic gallium(I) complexes as *π*-acids. *Adv. Synth. Catal.* **2018**, *360*, 544.

11. Takeda, T.; Arai, K.; Shimokawa, H.; Tsubouchi, A. Transformation of thioacetals to cyclopropanes. *Tetrahedron Lett.* **2005**, *46*, 775.

12. Gaussian 16, Revision C.02, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Petersson, G. A.; Nakatsuji, H.; Li, X.; Caricato, M.; Marenich, A. V.; Bloino, J.; Janesko, B. G.;

Gomperts, R.; Mennucci, B.; Hratchian, H. P.; Ortiz, J. V.; Izmaylov, A. F.; Sonnenberg, J. L.; Williams-Young, D.; Ding, F.; Lipparini, F.; Egidi, F.; Goings, J.; Peng, B.; Petrone, A.; Henderson, T.; Ranasinghe, D.; Zakrzewski, V. G.; Gao, J.; Rega, N.; Zheng, G.; Liang, W.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Throssell, K.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M. J.; Heyd, J. J.; Brothers, E. N.; Kudin, K. N.; Staroverov, V. N.; Keith, T. A.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A. P.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Millam, J. M.; Klene, M.; Adamo, C.; Cammi, R.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Farkas, O.; Foresman, J. B.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2016.

13. Zhao, Y.; Truhlar, D. G.; The M06 suite of density functionals for main group thermochemistry, thermochemical kinetics, noncovalent interactions, excited states, and transition elements: two new functionals and systematic testing of four M06-class functionals and 12 other functionals. *Theor. Chem. Acc.* **2008**, *120*, 215.

14. Cossi, M.; Barone, V.; Cammi, R.; Tomasi, J.; Ab Initio study of solvated molecules: A new implementation of the polarizable continuum model. *Chem. Phys. Lett.* **1996**, *255*, 327.

15. Mennucci, B.; Cancès, E.; Tomasi, J.; Evaluation of solvent effects in isotropic and anisotropic dielectrics and in ionic solutions with a unified integral equation method: Theoretical bases, computational implementation, and numerical applications. *J. Phys. Chem. B* **1997**, *101*, 10506.

16. Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. A consistent and accurate *ab initio* parametrization of density functional dispersion correction (DFT-D) for the 94 elements H-Pu. *J. Chem. Phys.* **2010**, *132*, 154104.

17. Grimme, S.; Ehrlich, S.; Goerigk, L. Effect of the damping function in dispersion corrected density functional theory. *J. Comput. Chem.* **2011**, *32*, 1456.

18. Lee, C.; Yang, W.; Parr, R. G. Development of the colle-salvetti correlation-energy formula into a functional of the electron density. *Phys. Rev. B* **1988**, *37*, 785.

19. Becke, A. D. Density-functional thermochemistry. III. The role of exact exchange. *J. Chem. Phys*. **1993**, *98*, 5648.

20. Stephens, P. J.; Devlin, F. J.; Chabalowski, C. F.; Frisch, M. J. Ab Initio calculation of vibrational absorption and circular dichroism spectra using density functional force fields. *J. Phys. Chem.* **1994**, *98*, 11623.

21. Lu, T.; Chen, F. Multiwfn: A multifunctional wavefunction analyzer. *J. Comput. Chem.* **2012**, *33*, 580.

22. Humphrey, W.; Dalke, A.; Schulten, K. VMD: Visual molecular dynamics. *J. Molec. Graphics.* **1996**, *14*, 33−38 (). http://www.ks.uiuc.edu/Research/vmd/