Supplementary Information for

Iron-Catalysed Hydroalumination of Internal Alkynes

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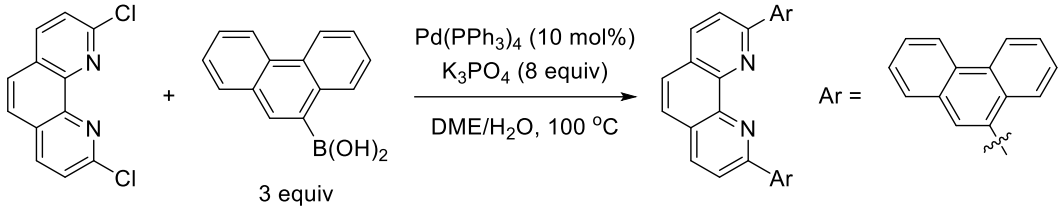
1. General Information

Unless otherwise noted, all manipulations were carried out using standard Schlenk, high-vacuum and glovebox techniques. Iron(II) chloride (99.99%) was purchased from Sigma-Aldrich and used as received. Anhydrous solvents were purified and dried following standard procedures.[1] The 2,9-di(anthracen-9-yl)-1,10-phenanthroline was prepared according to reported literature.[2] The known complexes of 2,9-diaryl-1,10-phenanthrolines with $FeCl_2$ were prepared according to the literature procedures.[3] $HAlEt_2$,[4] $DAlEt_2$, and $DAl(^iBu)_2$[5] were prepared according to reported literature. All commercially available reagents were used as received unless otherwise noted. Liquid internal alkynes were dried over CaH_2 and distilled prior to use; viscous internal alkynes and solid internal alkynes were dried under vacuum. TLC analysis was performed on pre-coated, glass-backed silica gel plates and visualized with UV light. Flash column chromatography was performed on silica gel (200-300 mesh) or Al_2O_3 (100 mesh).

Melting points were measured on a RY-I apparatus and uncorrected. Infrared spectra were recorded on a Bruker Fourier transform spectrometric (FT-IR) and reported in wave number. High resolution mass spectrometric (HRMS) analyses spectra were determined on an IonSpec FT-ICR mass spectrometer and Waters GCT Premier mass spectrometer. Trace metal contamination analyses of iron precatalysts by ICP-OES (spectro-blue) were performed using a X7 (Thermo Electron Corporation) instruments. Magnetic moment was measured on SQUID VSM (Quantum Design). ^{1}H NMR, ^{13}C NMR, ^{19}F NMR, ^{11}B NMR spectra were recorded on a Bruker 400 AV spectrometer at 400 MHz (^{1}H NMR), 101 MHz (^{13}C NMR), 376 MHz (^{19}F NMR), and 128 MHz (^{11}B NMR)in $CDCl_3$. Chemical shifts for protons were quoted in parts per million downfield from tetramethylsilane and are referenced to the solvent peak (for $CDCl_3$, ^{1}H NMR: 7.26 ppm, ^{13}C NMR: 77.16 ppm. for C_6D_6, ^{1}H NMR: 7.16 ppm, ^{13}C NMR: 128.06 ppm). Abbreviations are used in the description of NMR data as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constant (*J*, Hz).

2. Synthesis of Ligands and Catalysts

Synthesis of 2,9-di(phenanthren-9-yl)-1,10-phenanthroline (L1h)



A suspension of 2,9-dichloro-1,10-phenanthroline (2 g, 8 mmol), $Pd(PPh_3)_4$ (1 g, 0.8 mmol, 10 mol%), K_3PO_4 (13.6 g, 64 mmol, 8 equiv) and $ArB(OH)_2$ (5.3 g, 24 mmol, 3 equiv) in a mixture of DME (20 mL) and H_2O (5 mL) was purged with argon to degas. The mixture was heated up to reflux under argon atmosphere until the reaction was finished. After cooling to room temperature, the mixture was filtered and washed with H_2O (100 mL × 3). The residue was successively washed with $CHCl_3$ and toluene to give 2,9-di(phenanthren-9-yl)-1,10-phenanthroline.

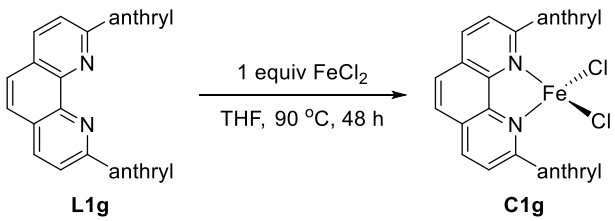
Serial number: Lwt-3-178. 3.85 g, 90 % yield, white solid, melting point: 310-314 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.76 (d, *J* = 8.3 Hz, 2H, Ar-H), 8.71 (d, *J* = 8.3 Hz, 2H, Ar-H), 8.58 (d, *J* = 8.2 Hz, 2H, Ar-H), 8.44 (d, *J* = 8.3 Hz, 2H, Ar-H), 8.18 (s, 2H, Ar-H), 8.07 (d, *J* = 8.3 Hz, 2H, Ar-H), 7.98 – 7.93 (m, 4H, Ar-H), 7.67 (t, *J* = 7.7 Hz, 4H, Ar-H), 7.59 (dt, *J* = 13.6, 7.3 Hz, 4H, Ar-H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.28, 146.34, 137.35, 136.17, 131.44, 130.85, 130.60, 129.78, 129.17, 127.76, 127.03, 126.86, 126.70, 126.62, 126.40, 125.03, 122.87, 122.53, 109.98.

HRMS (ESI) calcd for $[M+H, C_{40}H_{25}N_2]^+$: 533.2012; found 533.2016.

Synthesis of iron complex C1g



In an argon-filled glovebox, a Schlenk flask (50 mL) was charged with **L1g** (1 mmol), $FeCl_2$ (1 mmol) and dry THF (20 mL). The reaction mixture was stirred at 90 °C for 48

h, during which a yellow solid precipitated, then washed with 20 mL hexanes, and dried under vacuum to get the desired complex **C1g**.

Serial number: Lwt-2-196. 600 mg, 91% yield, yellow solid, decomposition temperature >320 ºC.

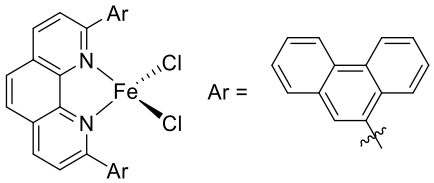
^{1}H NMR (400 MHz, $CDCl_3$) δ 1.26, 0.84.

IR (neat) 3075w, 3054w, 3021w, 1623w, 1586m, 1555m, 1509m, 1496m, 1484m, 1444m, 1353m, 1203w, 1169w, 1150w, 1012w, 945w, 893m, 871s, 848m, 790m, 734s, 630m, 558w, 549w, 502w, 437w, 416w cm^{-1}.

Anal. calcd. for $C_{44}H_{32}N_2Cl_2FeO$: C, 72.25; H, 4.41; N, 3.83. found: C, 72.45; H, 4.19; N, 3.88.

Magnetic moment χ_M = 2.08 $cm^3mol^{-1}K$.

Synthesis of iron complex C1h



C1h

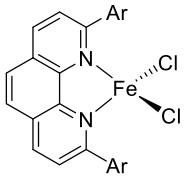
Complex **C1h** was prepared from **L1h** and $FeCl_2$ through a similar procedure as that for **C1g**.

Serial number: Lwt-4-56. 625 mg, 95% yield, yellow solid, decomposition temperature >320 ºC.

^{1}H NMR (400 MHz, $CDCl_3$) δ 1.20, 0.78.

IR (neat) 3064m, 3031w, 2975w, 2930w, 2859w, 2361w, 2341w, 1626m, 1588s, 1556m, 1528m, 1493s, 1450m, 1422w, 1389w, 1250w, 1210w, 1158m, 1142m, 1043m, 954m, 910m, 876m, 865m, 847w, 767s, 728m, 663w, 638w, 623w, 554w, 504w, 430w cm^{-1}.

Table S1. ICP-OES analysis of iron precatalysts (wt%)



C1g Ar = anthryl

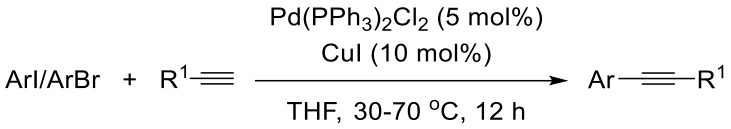
C1h Ar = phenanthryl

Element	**C1g**	**C1h**
Mg	-	-
Al	-	-
Ti	-	-
V	-	-
Cr	-	-
Mn	-	-
Fe	8.22	7.35
Co	-	-
Ni	0.168	0.114
Cu	0.071	0.055
Zn	-	-
Ru	-	-
Pd	0.005	0.025
Cd	-	-
Pt	-	-
Au	0.020	0.020
Pb	-	-

‘-’ means < 1 ppm

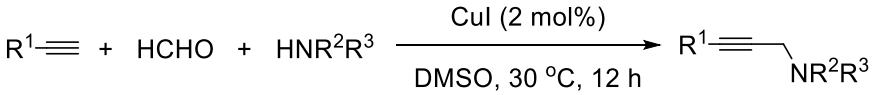
3. Preparation of Internal Alkynes

Procedure A: preparation of internal aryl alkynes (**1aa-1ap**, **1ba-1bd**, **1cc-1ch**, **1ee, 1fc**) and enynes via Sonogashira coupling.[6]



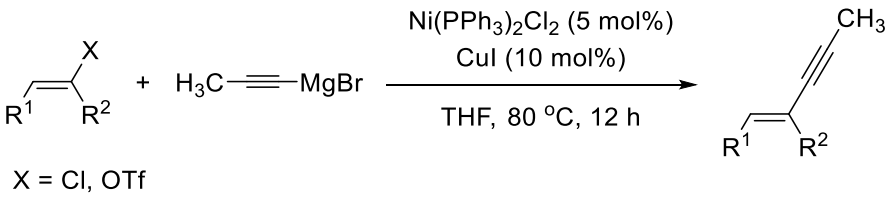
A typical operation: a dry schlenk flask was charged with aryl halide or vinyl halide (10.0 mmol), $Pd(PPh_3)_2Cl_2$ (5 mol%), CuI (10 mol%). The mixture was degassed under argon for three times. Et_3N (20 mL) and the terminal alkyne (1.2 equiv) was then added. The mixture was stirred at 30 °C until all the aryl halide or vinyl halide was consumed. The reaction mixture was diluted with diethyl ether, washed with water and brine, dried over anhydrous $MgSO_4$, and filtered. The filtrate was concentrated under vacuum. The residue was purified through silica gel flash chromatography.

Procedure B: preparation of propargylamines (**1cj**, **1ck**, **1ea-1ed**) via copper-catalyzed Mannich reaction.[7]



A typical operation: a dry schlenk flask was charged with alkyne (10 mmol), amine (1.2 equiv), aqueous formaldehyde (35% in H_2O, 4 mL) and CuI (2 mol%). The mixture was dissolved in 20 mL of DMSO, purged with argon to degas and stirred at 30 °C till the end of the reaction. After basic aqueous workup and extraction with chloroform or ether, the product was purified through silica gel flash chromatography.

Procedure C: preparation of **1de**, **1df** and **1dg** through nickel-catalyzed Kumada cross coupling.[8]

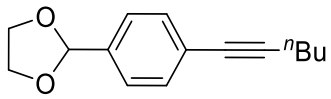


X = Cl, OTf

A typical operation: a dry schlenk flask was charged with vinyl halides or vinyl trifluoromethanesulfonate (1 mmol), $Ni(PPh_3)_2Cl_2$ (5 mol%), CuI (10 mol%) in dry THF (4.0 mL) was stirred at 30 ^oC under argon for 5 minutes, and then treated with 1-propynylmagnesium bromide (3.0 mL, 0.5 M in THF, 1.50 mmol). The resulting suspension was stirred at 80 °C for 12 hours till the end of the reaction. At ambient temperature, aqueous HCl (2.0 mL, 3M), Et_2O (10 mL), and H_2O (3 mL) were added to the reaction mixture. The separated aqueous phase was extracted with Et_2O (10 mL × 2). The combined organic layer was dried over anhydrous $MgSO_4$ and concentrated under vacuum. The remaining residue was purified through silica gel flash chromatography.

The analytical data of new alkynes were listed as following.

2-(4-(hex-1-yn-1-yl)phenyl)-1,3-dioxolane (1ai)



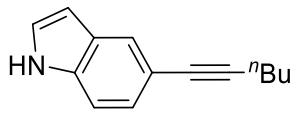
Procedure A, Serial number: Lwt-3-176. 91% yield (1.04 g, 5 mmol starting material, SM), colorless oil, R_f = 0.25 (PE/EA = 20:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.36 (m, 4H, Ar-H), 5.79 (s, 1H, OCH), 4.15 – 3.98 (m, 4H, OCH_2CH_2), 2.41 (t, J = 7.1 Hz, 2H, CH_2), 1.64 – 1.55 (m, 2H, CH_2), 1.50 – 1.43 (m, 2H, CH_2), 0.95 (t, J = 7.3 Hz, 3H, CH_3).

^{13}C NMR (101 MHz, $CDCl_3$) δ 136.97 (1C, Ar-C), 131.48 (2C, Ar-C), 126.27 (2C, Ar-C), 124.95 (1C, Ar-C), 103.36 (2C, OCH), 91.01 (1C, ≡C), 80.25 (1C, ≡C), 65.25 (2C, OCH_2), 30.76 (1C, CH_2), 21.99 (1C, CH_2), 19.09 (1C, CH_2), 13.62 (1C, CH_3).

HRMS (EI) calcd for [M-H, $C_{15}H_{17}O_2]^+$: 229.1223; found 229.1222.

5-(hex-1-yn-1-yl)-1H-indole (1bd)



Procedure A, Serial number: Lwt-3-110-1. 54% yield (532 mg, 5 mmol SM), brown oil,

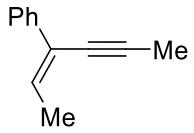
R_f = 0.57 (PE/EA = 1:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (br, 1H, N-H), 7.72 (dd, *J* = 1.5, 0.8 Hz, 1H, Ar-H), 7.30 (dt, *J* = 8.4, 0.9 Hz, 1H, Ar-H), 7.24 (dd, *J* = 8.4, 1.5 Hz, 1H, Ar-H), 7.20 (dd, *J* = 3.2, 2.4 Hz, 1H, Ar-H), 6.51 (ddd, *J* = 3.1, 2.0, 0.9 Hz, 1H, Ar-H), 2.43 (t, *J* = 7.0 Hz, 2H, CH_2), 1.65 – 1.56 (m, 2H, CH_2), 1.54 – 1.45 (m, 2H, CH_2), 0.96 (t, *J* = 7.3 Hz, 3H, CH_3).

^{13}C NMR (101 MHz, $CDCl_3$) δ 134.98 (1C, Ar-C), 127.68 (1C, Ar-C), 125.66 (1C, Ar-C), 124.78 (1C, Ar-C), 124.25 (1C, Ar-C), 115.21 (1C, Ar-C), 110.87 (1C, Ar-C), 102.67 (1C, Ar-C), 87.51 (1C, ≡C), 81.63 (1C, ≡C), 31.07 (1C, CH_2), 22.04 (1C, CH_2), 19.16 (1C, CH_2), 13.69 (1C, CH_3).

HRMS (EI) calcd for [M, $C_{14}H_{15}N$]$^+$: 197.1204; found 197.1197.

(Z)-hex-2-en-4-yn-3-ylbenzene (1df)



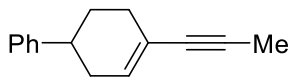
Pecedure C, Serial number: Lwt-4-149. 70% yield (437 mg, 4 mmol SM), colorless oil, R_f = 0.8 (PE).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.53 (m, 2H, Ar-H), 7.36 – 7.27 (m, 2H, Ar-H), 7.23 (dd, *J* = 6.4, 2.3 Hz, 1H, Ar-H), 6.38 (q, *J* = 7.0 Hz, 1H, =CH), 2.10 (s, 3H, CH_3), 2.03 (d, *J* = 6.9 Hz, 3H, CH_3).

^{13}C NMR (101 MHz, $CDCl_3$) δ 138.88 (1C, Ar-C), 131.66 (1C, =CH), 128.18 (2C, Ar-C), 127.12 (1C, Ar-C), 125.83 (2C, Ar-C), 124.67 (1C, =C), 91.92 (1C, ≡C), 76.86 (1C, ≡C), 16.71 (1C, CH_3), 4.45 (1C, CH_3).

HRMS (EI) calcd for [M, $C_{12}H_{12}$]$^+$: 156.0939; found 156.0909.

4-(prop-1-yn-1-yl)-1,2,3,6-tetrahydro-1,1'-biphenyl (1dg)



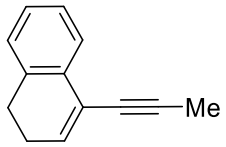
Procedure C, Serial number: Lwt-3-151-1. 92% yield (905 mg, SM = 5 mmol), white solid, R_f = 0.23 (PE).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (dd, *J* = 8.3, 6.9 Hz, 2H, Ar-H), 7.21 (d, *J* = 7.5 Hz, 3H, Ar-H), 6.08 (q, *J* = 2.8 Hz, 1H, =CH), 2.76 (ddq, *J* = 11.4, 7.9, 2.9 Hz, 1H, CH), 2.43 – 2.15 (m, 4H, CH_2CH_2), 1.95 (s, 3H, CH_3), 1.98 – 1.90 (m, 1H, CH), 1.84 – 1.69 (m, 1H, CH).

^{13}C NMR (101 MHz, $CDCl_3$) δ 146.51 (1C, Ar-C), 132.51 (1C, =C), 128.39 (2C, Ar-C), 126.81 (2C, Ar-C), 126.11 (1C, Ar-C), 120.96 (1C, =C), 83.40 (1C, ≡C), 81.02 (1C, ≡C), 39.21 (1C, CH), 33.66 (1C, CH_2), 30.15 (1C, CH_2), 29.58 (1C, CH_2), 4.19 (1C, CH_3).

HRMS (EI) calcd for [M, $C_{15}H_{16}$]$^{+}$: 196.1252; found 196.1245.

4-(prop-1-yn-1-yl)-1,2-dihydronaphthalene (1dh)



Procedure C, Serial number: Lwt-3-165-2. 80% yield (2.27 g, 5 mmol SM), colorless oil, R_f = 0.42 (PE).

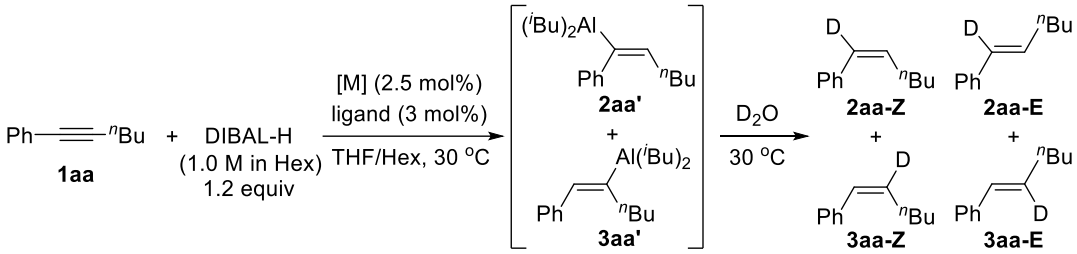
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (dd, *J* = 7.5, 1.4 Hz, 1H, Ar-H), 7.24 – 7.16 (m, 1H, Ar-H), 7.16 (td, *J* = 7.4, 1.5 Hz, 1H, Ar-H), 7.11 – 7.07 (m, 1H, Ar-H), 6.36 (t, *J* = 4.8 Hz, 1H, =CH), 2.77 (t, *J* = 8.1 Hz, 2H, CH_2), 2.35 (td, *J* = 8.1, 4.9 Hz, 2H, =$CHCH_2$), 2.06 (s, 3H, CH_3).

^{13}C NMR (101 MHz, $CDCl_3$) δ 135.10 (1C, Ar-C), 133.94 (1C, Ar-C), 133.11 (1C, Ar-C), 127.40 (1C, Ar-C), 127.21 (1C, Ar-C), 126.45 (1C, Ar-C), 124.99 (1C, =C), 121.98 (1C, =C), 86.44 (1C, ≡C), 77.43 (1C, ≡C), 27.23 (1C, CH_2), 23.48 (1C, CH_2), 4.28 (1C, CH_3).

HRMS (EI) calcd for [M, $C_{13}H_{12}$]$^{+}$: 168.0939; found 168.0926.

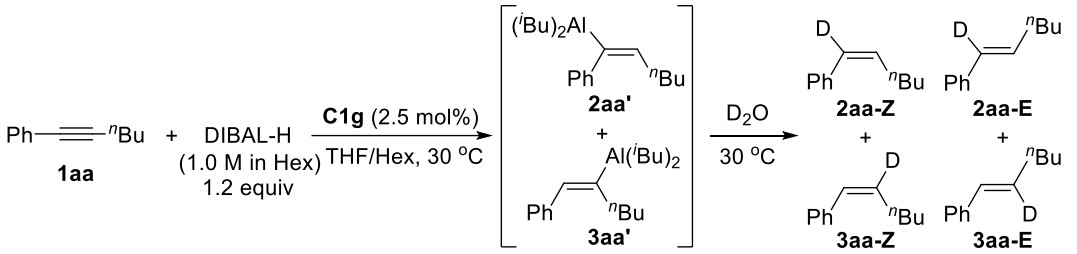
4. Additional Data of Reaction Condition Optimization

Method A (using in situ generated metal complexes):



In an argon-filled glovebox, a vial (10 mL) was charged with ligand (0.006 mmol), metal salt (0.005 mmol), anhydrous THF (1 mL). The reaction mixture was stirred at 70 °C for 6 h, then cooled to room temperature. Internal alkynes (0.2 mmol), DIBAL-H (1.0 M in hexanes, 240 μL, 0.24 mmol, 1.2 equiv) was added sequentially. After stirring at 30 °C for 10 hours, the vial was removed from the glovebox and the reaction mixture was quenched with D_2O (30 °C, 30 minutes) and filtered over silica gel with hexanes. The combined organic phases were concentrated by rotary evaporation, and determined the product yield, conversion, regioisomeric ratio (r.r., **2aa**/**3aa**), and *Z*/*E* (**2aa-*Z***/**2aa-*E***) by NMR analysis.

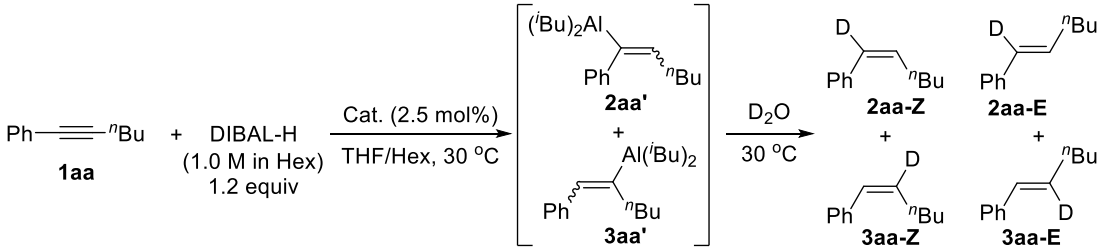
Method B (using pre-formed iron complexes):



In an argon-filled glovebox, a vial (10 mL) was charged with complex **C1g** (0.005 mmol), anhydrous solvent (1 mL) and internal alkynes (0.2 mmol), aluminium reagent (0.24 mmol, 1.2 equiv) was added sequentially. The reaction mixture was stirred at room temperature for 1 minute, then additive (0.03 mmol, 6 mol%) was added when noted. After stirring at 30 °C for 10 hours, the vial was removed from the glovebox and the reaction mixture was quenched with D_2O (30 °C, 30 minutes) and filtered over silica

gel with hexanes. The combined organic phases were concentrated by rotary evaporation, and determined the product yield, conversion, r.r. (**2aa**/**3aa**), and *Z*/*E* (**2aa-*Z***/**2aa-*E***) by NMR analysis.

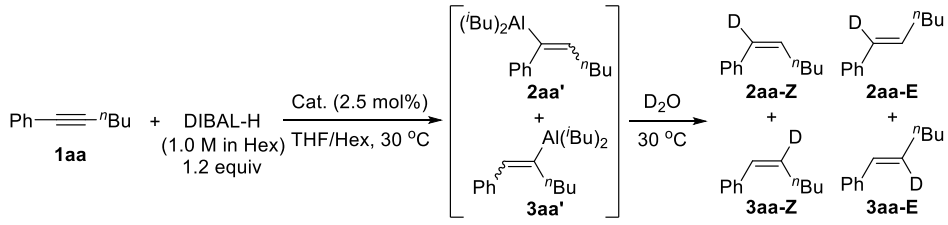
Table S2. Control experiments

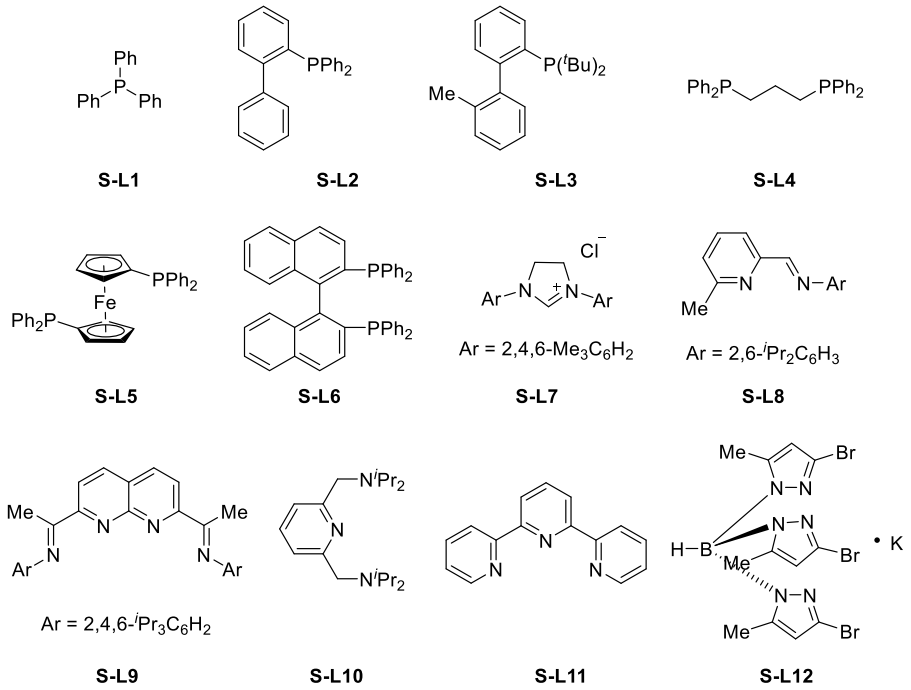


Entry[a]	Condition	Conv. (%)	**2aa** (yield %)[b]	r.r. (**2aa**/**3aa**)[c]	Z/E (**2aa**)[c]
1	**C1g**, 30 °C	100	81	91:9	97:3
2	Without **C1g**, 30 °C, 12 h	trace	NA[d]	NA	NA
3	Without **C1g**, 80 °C, 12 h	trace	NA	NA	NA
4	Without $FeCl_2$, 30 °C, 12 h	trace	NA	NA	NA
5	Without $FeCl_2$, 80 °C, 12 h	trace	NA	NA	NA
6	Without **L1g**, 30 °C, 12 h	trace	NA	NA	NA
7	Without **L1g**, 80 °C, 12 h	trace	NA	NA	NA

[a] Method A. [b] NMR yields with 1,3,5-trimethoxybenzene as internal standard. [c] Determined by ^{1}H NMR. [d] NA = not analyzed.

Table S3. Evaluation of other ligands

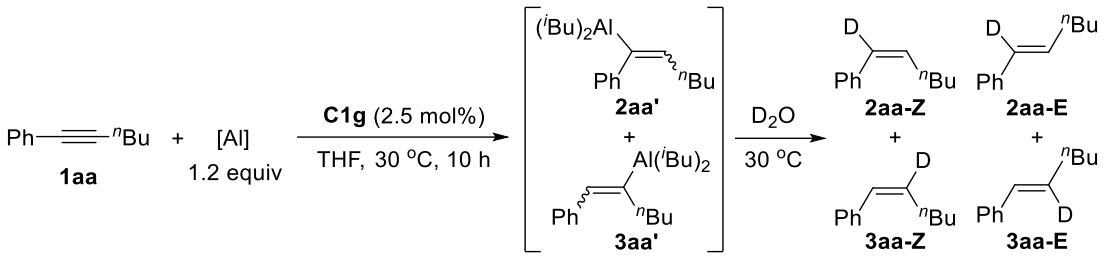




Entry	Ligand	Conv. (%)	Yield (%)[b]	r.r.[d]	*Z*/*E*[d]
1[c]	**S-L1**	9	8	NA[e]	NA
2[c]	**S-L2**	8	7	NA	NA
3[c]	**S-L3**	<2	NA	NA	NA
4[c]	**S-L4**	3	2	NA	NA
5[c]	**S-L5**	<5	NA	NA	NA
6[c]	**S-L6**	0	NA	NA	NA
7	**S-L7**	<2	NA	NA	NA
8	**S-L8**	85	61	63:37	96:4
9	**S-L9**	16	12	58:42	85:15
10	**S-L10**	6	4	NA	NA
11	**S-L11**	99	98	57:43	95:5
12	**S-L12**	0	NA	NA	NA

[a] Method A. [b] NMR yield with 1,3,5-trimethoxybenzene as internal standard. [c] $FeCl_2$/ligand = 1:1.2 [d] Determined by ^1H NMR. [e] Not analyzed.

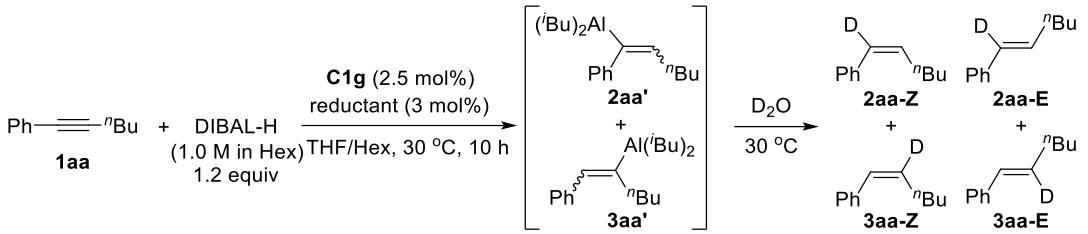
Table S4. Evaluation of Al reagents



Entry	[Al]	conv. (%)	yield (%)[b]	r.r.[c]	*Z*/*E*[c]
1	DIBAL-H	100	81	91:9	97:3
2	Red-Al	<1	NA[d]	NA	NA
3	$LiAlH_4$	20	15	49:51	90:10
4	$LiAlH(O^tBu)_3$	0	NA	NA	NA
5	$HAlCl_2{\cdot}2THF$	100	50	65:35	98:2
6	$Al(^iBu)_3$	11	8	82:18	98:2
7	$Al(^iBu)_2Cl$	<5	NA	NA	NA
8	$AlEt_2Cl$	0	NA	NA	NA

[a] Method B. [b] NMR yield with 1,3,5-trimethoxybenzene as internal standard. [c] Determined by ^1H NMR. [d] Not analyzed.

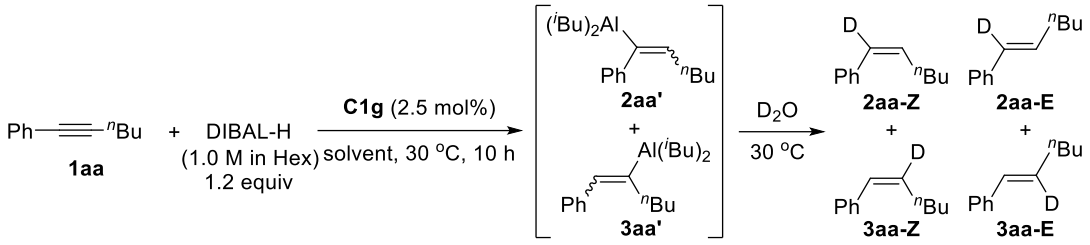
Table S5. Evaluation of reductants



Entry	Reductant	Conv. (%)	Yield (%)[b]	r.r.[c]	*Z*/*E*[c]
1	None	100	81	91:9	97:3
2	EtMgBr	99	87	89:11	95:5
3	MeMgCl	90	83	88:12	97:3
4	^{n}BuLi	37	32	81:19	95:5
5	$TMSCH_2Li$	29	25	80:20	93:7
6	$NaHBEt_3$	76	59	74:26	93:7
7	$Mg(C_4H_6)(THF)_2$	6	NA[d]	NA	NA
8	^{t}BuOK	18	17	79:21	95:5

[a] Method B. [b] NMR yield with 1,3,5-trimethoxybenzene as internal standard. [c] Determined by ^{1}H NMR. [d] Not analyzed.

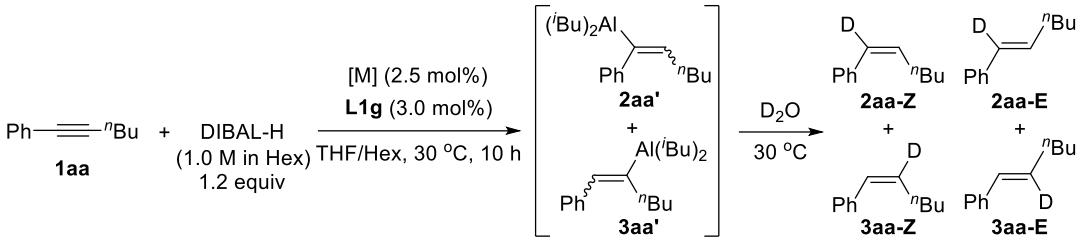
Table S6. Evaluation of solvents



Entry	Solvent	Conv. (%)	Yield (%)[b]	r.r.[c]	*Z*/*E*[c]
1	THF	100	81	91:9	97:3
2	2-MeTHF	100	87	82:18	96:4
3	dioxane	69	58	78:22	>98:2
4	Et_2O	24	22	66:34	98:2
5	MTBE[d]	39	28	39:61	93:7
6	CPME[e]	24	22	54:46	96:4
7	PhOMe	62	44	73:27	98:2
8	hexanes	26	21	87:13	>98:2
9	benzene	60	38	82:18	98:2
10	toluene	76	61	81:19	98:2

[a] Method B. [b] NMR yield with 1,3,5-trimethoxybenzene as internal standard. [c] Determined by ^{1}H NMR. [d] MTBE = methyl tertbutyl ether. [e] CPME = cyclopentyl methyl ether.

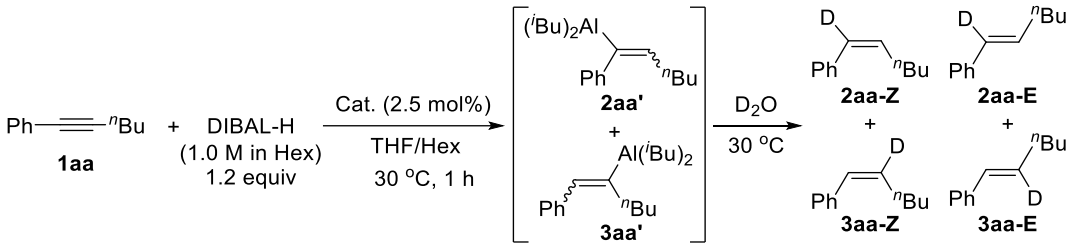
Table S7. Evaluation of metal salts



Entry	[M]	Conv. (%)	Yield (%)[b]	r.r. (**2aa**/**3aa**)[c]	*Z*/*E* (**2aa**)[c]
1	FeF_2	0	NA[d]	NA	NA
2	$FeCl_2$	100	81	91:9	97:3
3[c]	$FeBr_2$	100	88	89:11	97:3
4	$Fe(acac)_2$	<5	NA	NA	NA
5	$Fe(SO_3CF_3)_2$	87	82	83:17	96:4
6	$Fe(OAc)_2$	8	8	72:28	94:6
7	$CoCl_2$	65	57	54:46	85:15
8	$CuCl_2$	<3	NA	NA	NA
9	$NiCl_2$	99	87	76:24	93:7
10	$MnCl_2$	12	11	79:21	85:15
11	$PdCl_2$	50	48	50:50	89:11
12	$AuCl_3$	0	NA	NA	NA

[a] Method A. [b] NMR yield with 1,3,5-trimethoxybenzene as internal standard. [c] Determined by ^{1}H NMR. [d] Not analyzed.

5. Typical Procedure of Iron-Catalyzed Hydroalumination



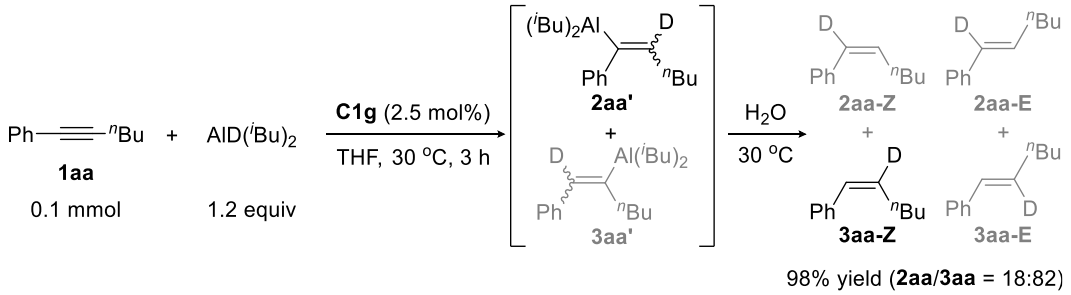
General procedure: In an argon-filled glovebox, a vial (10 mL) was charged with **C1g** (0.005 mmol) and THF (1 mL). The reaction mixture was stirred at 30 °C for 1 minute. Alkynes (0.2 mmol), DIBAL-H (1 M in hexanes, 240 μL, 0.24 mmol, 1.2 equiv) was added sequentially. After stirring at 30 °C for 1 hour, the vial was removed from the glovebox and the reaction mixture was quenched with D_2O (30 °C, 30 minutes) and filtered over silica gel with PE as eluant. The combined organic phases were concentrated by rotary evaporation to give the product. The regioselectivity was determined by NMR analysis.

In an argon-filled glovebox, a vial (10 mL) was charged with **C1g** (0.005 mmol) and THF (1 mL). The reaction mixture was stirred at 30 °C for 1 minute. **1aa** (0.2 mmol), DIBAL-H (1 M in hexanes, 240 μL, 0.24 mmol, 1.2 equiv) was added sequentially. After stirring for 1 h at 30 °C, THF was removed under vacumm. The reaction mixture was filtered through a pad of Celite and washed with hexanes. Then the filtrate was concentrated under vacumm to afford dark purple oil **2aa'-THF**. The structure was determined by NMR analysis with C_6D_6.

In an argon-filled glovebox, a vial (10 mL) was charged with **C1g** (0.005 mmol) and THF (1 mL). The reaction mixture was stirred at 30 °C for 1 minute. **1aa** (0.2 mmol), DIBAL-H (1 M in hexanes, 240 μL, 0.24 mmol, 1.2 equiv) was added sequentially. After stirring for 1 h at 30 °C, the reaction mixture was added into DMAP. After stirring for 6 h at 30 °C, THF was removed under vacumm. The residue was stired in hexanes with Celite, filtered through a pad of Celite and washed with hexanes. Then the filtrate was concentrated under vacumm to afford yellow solid **2aa'-DMAP**. The structure was determined by NMR analysis with C_6D_6.

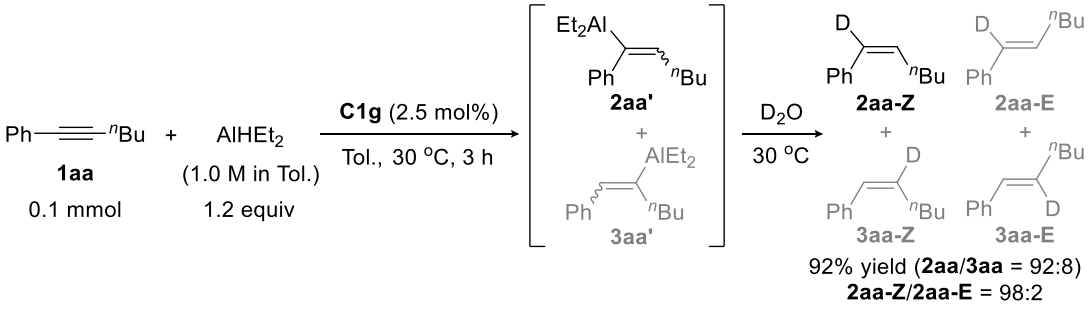
6. Mechanistic Studies

(a) Deuterium labelling experiment of DIBAL-D



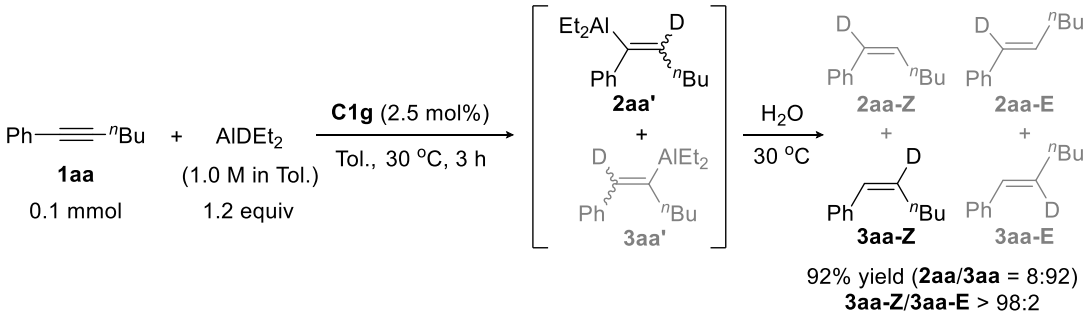
In an argon-filled glovebox, a vial (10 mL) was charged with **C1g** (1.6 mg, 0.0025 mmol), THF (1 mL), **1aa** (15.8 mg, 0.1 mmol). The reaction mixture was stirred at 30 °C for 1 minute, Al(^{i}Bu)$_2$D (0.12 mmol) was added. After stirring at 30 °C for 3 hours, the vial was removed from the glovebox. The reaction mixture was quench with water (30 °C, 30 minutes) and filtered over silica gel with PE. The combined organic phases were concentrated by rotary evaporation, and isolated yield was given. The r.r. (**2aa**/**3aa**), and *Z*/*E* (**2aa-*Z***/**2aa-*E***) were determined by NMR analysis.

(b) Hydroalumination of 1aa and AlHEt$_2$



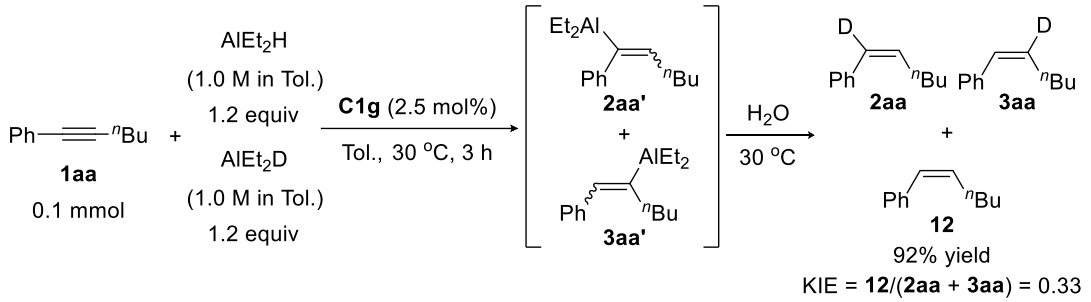
In an argon-filled glovebox, a vial (10 mL) was charged with **C1g** (1.6 mg, 0.0025 mmol), toluene (1 mL), **1aa** (15.8 mg, 0.1 mmol). The reaction mixture was stirred at 30 °C for 1 minute, then AlEt$_2$H (1M in toluene, 0.12 mmol) was added. After stirring at 30 °C for 3 hours, the vial was removed from the glovebox. The reaction mixture was quench with D$_2$O (30 °C, 30 minutes) and filtered over silica gel with PE. The combined organic phases were concentrated by rotary evaporation, and isolated yield was given. The r.r. (**2aa**/**3aa**), and *Z*/*E* (**2aa-*Z***/**2aa-*E***) were determined by NMR analysis.

(c) Deuterium labelling experiment of $AlDEt_2$



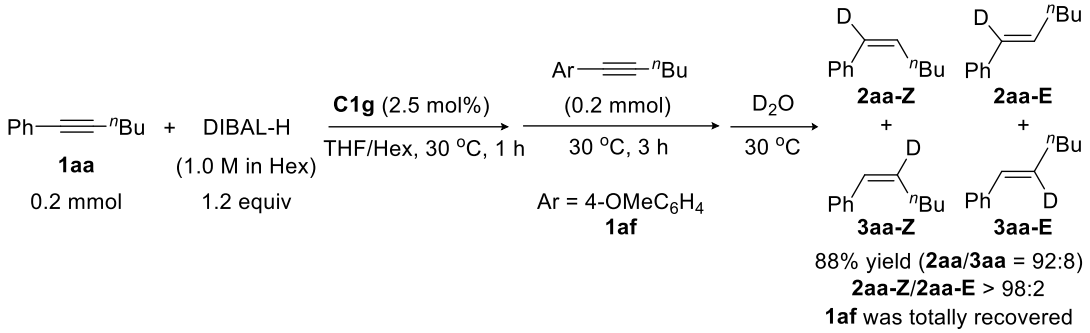
In an argon-filled glovebox, a vial (10 mL) was charged with **C1g** (1.6 mg, 0.0025 mmol), THF (1 mL), **1aa** (15.8 mg, 0.1 mmol). The reaction mixture was stirred at 30 ^{o}C for 1 minute, then $AlEt_2D$ (1M in toluene, 0.12 mmol) was added. After stirring at 30 ^{o}C for 3 hours, the vial was removed from the glovebox. The reaction mixture was quench with water (30 ^{o}C, 30 minutes) and filtered over silica gel with PE. The combined organic phases were concentrated by rotary evaporation, and isolated yield was given. The r.r. (**2aa**/**3aa**), and *Z*/*E* (**2aa-*Z***/**2aa-*E***) were determined by NMR analysis.

(d) Kinetic isotopic effect experiment



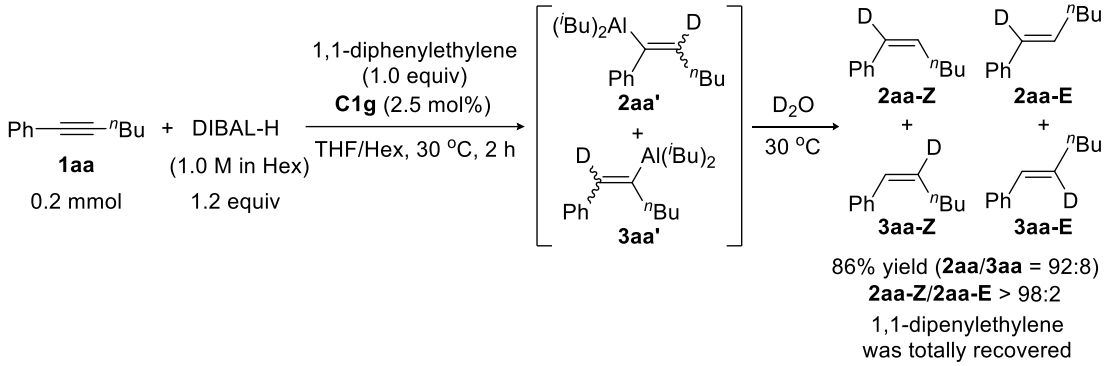
In an argon-filled glovebox, a vial (10 mL) was charged with **C1g** (1.6 mg, 0.0025 mmol), toluene (1 mL), **1aa** (15.8 mg, 0.1 mmol). The reaction mixture was stirred at 30 ^{o}C for 1 minute, then $AlEt_2H$ (1 M in toluene, 120 μL, 0.12 mmol) and $AlEt_2D$ (1 M in toluene, 120 μL, 0.12 mmol) was added. After stirring at 30 ^{o}C for 3 hours, the vial was removed from the glovebox. The reaction mixture was quench with water (30 ^{o}C, 30 minutes) and filtered over silica gel with PE. The combined organic phases were concentrated by rotary evaporation, and isolated yield was given. The r.r. (**2aa**/**3aa**/**12**) was determined by NMR analysis.(LWT-6-74). The ratio of **2aa**, **3aa**, **12** is 0.14: 0.61: 0.25. The inverse KIE is 0.33, (KIE = k_H/k_D = **12**/(**2aa**+**3aa**) = 0.33).

(e) Alkyne crossover experiment



In an argon-filled glovebox, a vial (10 mL) was charged with **C1g** (3.3 mg, 0.005 mmol), THF (1 mL), **1aa** (31.6 mg, 0.2 mmol). The reaction mixture was stirred at 30 ^{o}C for 1 minute, then DIBAL-H (1.0 M in hexanes, 240 μL, 0.24 mmol, 1.2 equiv) was added. After stirring at 30 ^{o}C for 1 hour, the vial was removed from the glovebox. The alkyne **1af** (37.7 mg, 0.2 mmol) was added and stirring at 30 ^{o}C for 1 hour. The reaction mixture was quench with D_2O (30^{o}C, 30 minutes) and filtered over silica gel with PE. The combined organic phases were concentrated by rotary evaporation, and isolated yield was given. The r.r. (**2aa**/**3aa**), and *Z*/*E* (**2aa-*Z***/**2aa-*E***) were determined by NMR analysis.

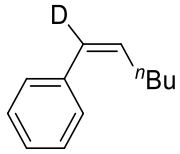
(f) Radical trap experiment



In an argon-filled glovebox, a vial (10 mL) was charged with **C1g** (3.3 mg, 0.005 mmol), THF (1 mL), **1aa** (31.6 mg, 0.2 mmol), 1,1-diphenylethylene (36.1 mg, 0.2 mmol), DIBAL-H (1.0 M in hexanes, 240 μL, 0.24 mmol, 1.2 equiv) was added sequentially. After stirring at 30 ^{o}C for 2 hours, the vial was removed from the glovebox and the reaction mixture was quench with D_2O (30 ^{o}C, 30 minutes) and filtered over silica gel with PE. The combined organic phases were concentrated by rotary evaporation, and isolated yield was given. The r.r. (**2aa**/**3aa**), and *Z*/*E* (**2aa-*Z***/**2aa-*E***) were determined by NMR analysis.[9]

7. Analytical Data of Products

(*Z*)-(hex-1-en-1-yl-1-D)benzene (2aa)



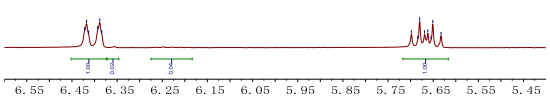
Serial number: Lwt-3-142G. colorless oil, TLC R_f = 0.8 (PE), 81% yield (26.1 mg), r.r. = 91:9, *Z*/*E* = 97:3.

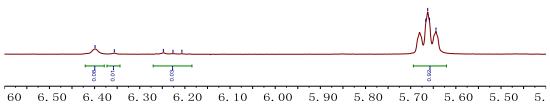
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.27 (m, 4H, Ar-H), 7.23 – 7.19 (m, 1H, Ar-H), 5.66 (tt, *J* = 7.3, 1.7 Hz, 1H, =CH), 2.33 (q, *J* = 7.3 Hz, 2H, CH_2), 1.46-1.32 (m, 4H, CH_2CH_2), 0.90 (t, *J* = 7.2 Hz, 3H, CH_3).

^{13}C NMR (101 MHz, $CDCl_3$) δ 137.74 (1C, Ar-C), 133.08 (1C, =C), 128.72 (2C, Ar-C), 128.41(t, *J* = 22.2 Hz, 1C, =CD), 128.07 (2C, Ar-C), 126.38 (1C, Ar-C), 32.16 (1C, CH_2), 28.32 (1C, CH_2), 22.42 (1C, CH_2), 13.97 (1C, CH_3).

HRMS (EI) calcd for [M, $C_{12}H_{15}D$]$^+$: 161.1315; found 161.1308.

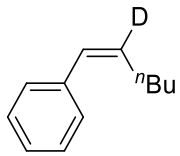
The r.r. (**2aa**/**3aa**) and *Z*/*E* (**2aa-*Z***/**2aa-*E***) was determined by analysis of 400 MHz ^{1}H NMR spectra of the protonated sample (below left) with deuterated product (below right). The corresponding data of **2ab**-**2ap** were obtained similarly.





Peak	Chem shift (ppm)	Area	Area (%)	Product	Chem shift (ppm)	Area	Area (%)
1	6.40	1.00	48.5	**3aa-*Z***	6.40	0.08	8
2	6.36	0.02	1	**3aa-*E***	6.36	0.01	1
3	6.23	0.04	2	**2aa-*E***	6.23	0.03	3
4	5.66	1.00	48.5	**2aa-*Z***	5.66	0.92	88

(*Z*)-(hex-1-en-1-yl-2-D)benzene (3aa)



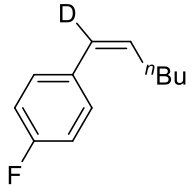
Serial number: Lwt-6-72. colorless oil, TLC R_f = 0.8 (PE), 92% yield (15.0 mg, 0.1 mmol SM), r.r. = 92:8, *Z*/*E* = 98:2.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.31 (m, 2H, Ar-H), 7.29 – 7.26 (m, 2H, Ar-H), 7.23 – 7.18 (m, 1H, Ar-H), 6.40 s, 1H, =CH), 2.33 (t, *J* = 7.3 Hz, 2H, CH_2), 1.47 – 1.30 (m, 4H, CH_2CH_2), 0.89 (t, *J* = 7.2 Hz, 3H, CH_3).

^{13}C NMR (101 MHz, $CDCl_3$) δ 137.82 (1C, Ar-C), 132.84 (1C, t, *J* = 23.2 Hz, 1C, =CD), 128.73 (2C, Ar-C), 128.54(1C, =C), 128.07 (2C, Ar-C), 126.37 (1C, Ar-C), 32.13 (1C, CH_2), 28.24 (1C, CH_2), 22.42 (1C, CH_2), 13.96 (1C, CH_3).

HRMS (EI) calcd for [M, $C_{12}H_{15}D]^+$: 161.1315; found 161.1308.

(*Z*)-1-fluoro-4-(hex-1-en-1-yl-1-D)benzene (2ab)



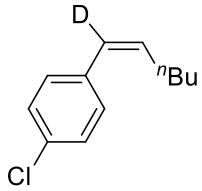
Serial number: Lwt-3-80. **C1h** was used instead. colorless oil, TLC R_f = 0.75 (PE), 98% yield (35.1 mg), r.r. = 88:12, *Z*/*E* = 98:2.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 – 7.21 (m, 2H, Ar-H), 7.03 – 6.98 (m, 2H, Ar-H), 5.64 (tt, *J* = 7.4 Hz, 1.7 Hz, 1H, =CH), 2.29 (q, *J* = 7.3 Hz, 2H, CH_2), 1.45 – 1.31 (m, 4H, CH_2CH_2), 0.89 (t, *J* = 7.1 Hz, 3H, CH_3).

^{13}C NMR (101 MHz, $CDCl_3$) δ 161.39 (d, *J* = 245.5 Hz, 1C, Ar-C), 133.73 (d, *J* = 2.9 Hz, 1C, Ar-C), 132.90 (1C, =C), 130.22 (d, *J* = 7.8 Hz, 2C, Ar-C), 127.23 (t, *J* = 23.2 Hz, 1C, =CD), 114.93 (d, *J* = 21.7 Hz, 2C, Ar-C), 32.07 (1C, CH_2), 28.18 (1C, CH_2), 22.39 (1C, CH_2), 13.94 (1C, CH_3).

HRMS (EI) calcd for [M, $C_{12}H_{14}DF]^+$: 179.1221; found 179.1212.

(*Z*)-1-chloro-4-(hex-1-en-1-yl-1-D)benzene (2ac)



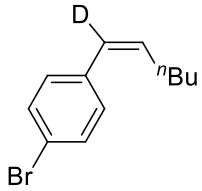
Serial number: Lwt-3-81. colorless oil, TLC R_f = 0.70 (PE), 98% yield (38.3 mg), r.r. = 90:10, *Z*/*E* = 96:4.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (d, *J* = 8.3 Hz, 2H, Ar-H), 7.19 (d, *J* = 8.3 Hz, 2H, Ar-H), 5.67 (tt, *J* = 7.4, 1.6 Hz, 1H, =CH), 2.29 (q, *J* = 7.3 Hz, 2H, CH_2), 1.45-1.31 (m, 4H, CH_2CH_2), 0.89 (t, *J* = 7.1 Hz, 3H, CH_3).

^{13}C NMR (101 MHz, $CDCl_3$) δ 136.16 (1C, Ar-C), 133.74 (1C, =C), 132.08 (1C, Ar-C), 129.98 (2C, Ar-C), 128.23 (2C, Ar-C), 127.18 (t, *J* = 23.2 Hz, 1C, =CD), 32.02 (1C, CH_2), 28.26 (1C, CH_2), 22.38 (1C, CH_2), 13.92 (1C, CH_3).

HRMS (EI) calcd for [M, $C_{12}H_{14}DCl]^+$: 195.0925; found 195.0915.

(*Z*)-1-bromo-4-(hex-1-en-1-yl-1-D)benzene (2ad)



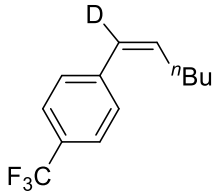
Serial number: Lwt-3-87. **C1h** was used instead. colorless oil, TLC R_f = 0.80 (PE), 94% yield (45.0 mg), r.r. = 90:10, *Z*/*E* = 98:2.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.40 (m, 2H, Ar-H), 7.18 – 7.11 (m, 2H, Ar-H), 5.68 (tt, *J* = 7.3 Hz, 1.6 Hz, 1H, =CH), 2.28 (q, *J* = 7.3 Hz, 2H, CH_2), 1.46 – 1.31 (m, 4H, CH_2CH_2), 0.90 (t, *J* = 7.2 Hz, 3H, CH_3).

^{13}C NMR (101 MHz, $CDCl_3$) δ 136.57 (1C, Ar-C), 133.87 (1C, =C), 131.17 (2C, Ar-C), 130.32 (2C, Ar-C), 127.20 (t, *J* = 23.2 Hz, 1C, =CD), 120.20 (1C, Ar-C), 32.00 (1C, CH_2), 28.27 (1C, CH_2), 22.38 (1C, CH_2), 13.94 (1C, CH_3).

HRMS (EI) calcd for [M, $C_{12}H_{14}DBr]^+$: 239.0420; found 239.0413.

(*Z*)-1-(hex-1-en-1-yl-1-D)-4-(trifluoromethyl)benzene (2ae)



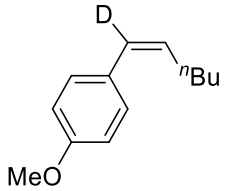
Serial number: Lwt-3-84. colorless oil, TLC R_f = 0.90 (PE), 83% yield (38.1 mg), r.r. = 88:12, *Z*/*E* = 97:3.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 8.0 Hz, 2H, Ar-H), 7.37 (d, *J* = 8.0 Hz, 2H, Ar-H), 5.78 (dd, *J* = 7.4 Hz, 1H, =CH), 2.31 (q, *J* = 7.4 Hz, 2H, CH_2), 1.46 – 1.41 (m, 2H, CH_2), 1.38 – 1.31 (m, 2H, CH_2), 0.89 (t, *J* = 7.2 Hz, 3H, CH_3).

^{13}C NMR (101 MHz, $CDCl_3$) δ 141.28 (1C, Ar-C), 135.26 (1C, =C), 128.88 (2C, Ar-C), 127.18 (t, *J* = 23.2 Hz, 1C, =CD), 126.46 (q, *J* = 255.5 Hz, 1C, CF_3), 125.01 (q, *J* = 3.7 Hz, 2C, Ar-C), 122.93 (1C, Ar-C), 31.97 (1C, CH_2), 28.33 (1C, CH_2), 22.38 (1C, CH_2), 13.91 (1C, CH_3).

HRMS (EI) calcd for [M, $C_{13}H_{14}DF_3$]$^+$: 229.1189; found 229.1182.

(*Z*)-1-(hex-1-en-1-yl-1-D)-4-methoxybenzene (2af)



Serial number: Lwt-3-54. colorless oil, TLC R_f = 0.40 (PE/EA = 50:1), 95% yield (36.3 mg), r.r. = 94:6, *Z*/*E* = 98:2.

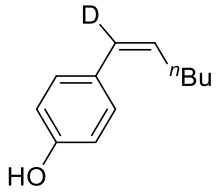
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 – 7.20 (m, 2H, Ar-H), 6.90 – 6.84 (m, 2H, Ar-H), 5.56 (t, *J* = 7.2 Hz, 1H, =CH), 3.80 (s, 3H, OCH_3), 2.32 (q, *J* = 7.3 Hz, 2H, CH_2), 1.45 – 1.39 (m, 2H, CH_2), 1.35 (q, *J* = 7.3 Hz, 2H, CH_2), 0.90 (t, *J* = 7.1 Hz, 3H, CH_3).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.11 (1C, Ar-C), 131.48 (1C, =C), 130.46 (1C, Ar-C), 129.89 (2C, Ar-C), 127.72 (t, *J* = 23.2 Hz, 1C, =CD), 113.51 (2C, Ar-C), 55.21 (1C, OCH_3), 32.22 (1C, CH_2), 28.32 (1C, CH_2), 22.44 (1C, CH_2), 13.97

(1C, CH_3).

HRMS (EI) calcd for [M, $C_{13}H_{17}DO]^+$: 191.1420; found 191.1414.

(*Z*)-4-(hex-1-en-1-yl-1-D)phenol (2ag)



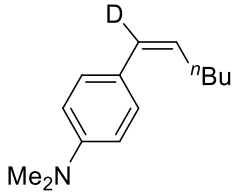
Serial number: Lwt-3-184A. pink oil, TLC *Rf* = 0.55 (PE/EA = 3:1), 79% yield (28.0 mg), r.r. = 90:10, *Z*/*E* =98:2.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 – 7.16 (m, 2H, Ar-H), 6.81 – 6.78 (m, 2H, Ar-H), 5.56 (t, *J* = 7.2 Hz, 1H, =CH), 5.09 (s, 1H, OH), 2.31 (q, *J* = 7.3 Hz, 2H, CH_2), 1.45 – 1.32 (m, 4H, CH_2CH_2), 0.89 (t, *J* = 7.1 Hz, 3H, CH_3).

^{13}C NMR (101 MHz, $CDCl_3$) δ 153.94 (1C, Ar-C), 131.56 (1C, =C), 130.60 (1C, Ar-C), 130.08 (2C, Ar-C), 127.60 (t, *J* = 23.2 Hz, 1C, =CD), 114.96 (2C, Ar-C), 32.17 (1C, CH_2), 28.29 (1C, CH_2), 22.42 (1C, CH_2), 13.97 (1C, CH_3).

HRMS (EI) calcd for [M, $C_{12}H_{15}DO]^+$: 177.1264; found 177.1257.

(*Z*)-4-(hex-1-en-1-yl-1-D)-*N*,*N*-dimethylaniline (2ah)



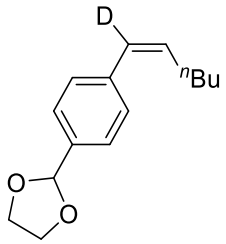
Serial number: Lwt-3-196A. colorless oil, TLC *Rf* = 0.38 (PE/EA = 50:1), 96% yield (39.2 mg), r.r. = 90:10, *Z*/*E* = 95:5.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (d, *J* = 8.8 Hz, 2H, Ar-H), 6.70 (d, *J* = 8.8 Hz, 2H, Ar-H), 5.48 (t, *J* = 7.1 Hz, 1H, =CH), 2.94 (s, 6H, $N(CH_3)_2$), 2.35 (q, *J* = 7.2 Hz, 2H, CH_2), 1.46 – 1.32 (m, 4H, CH_2CH_2), 0.90 (t, *J* = 7.1 Hz, 3H, CH_3).

^{13}C NMR (101 MHz, $CDCl_3$) δ 149.07 (1C, Ar-C), 129.85 (1C, =C), 129.66 (2C, Ar-C), 128.01 (t, *J* = 23.2 Hz, 1C, =CD), 126.36 (1C, Ar-C), 112.13 (2C, Ar-C), 40.54 (2C, $N(CH_3)_2$), 32.35 (1C, CH_2), 28.50 (1C, CH_2), 22.49 (1C, CH_2), 14.03 (1C, CH_3).

HRMS (EI) calcd for [M, $C_{14}H_{20}DN]^+$: 204.1737; found 204.1720.

(*Z*)-2-(4-(hex-1-en-1-yl-1-D)phenyl)-1,3-dioxolane (2ai)



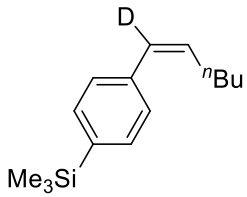
Serial number: Lwt-3-177B. **C1h** was used instead, colorless oil, TLC R_f = 0.25 (PE/EA = 20:1), 87% yield (40.6 mg), r.r. = 87:13, *Z*/*E* > 98:2.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 8.1 Hz, 2H, Ar-H), 7.29 (d, *J* = 8.1 Hz, 2H, Ar-H), 5.80 (s, 1H, OCH), 5.68 (t, *J* = 7.3 Hz, 1H, =CH), 4.15 – 4.01 (m, 4H, CH_2CH_2), 2.32 (q, *J* = 7.3 Hz, 2H, CH_2), 1.44 – 1.31 (m, 4H, CH_2CH_2), 0.89 (t, *J* = 7.2 Hz, 3H, CH_3).

^{13}C NMR (101 MHz, $CDCl_3$) δ 138.70 (1C, Ar-C), 135.81 (1C, Ar-C), 133.61 (1C, =C), 128.70 (2C, Ar-C), 128.00 (t, *J* = 22.2 Hz, 1C, =CD), 126.17 (2C, Ar-C), 103.64 (1C, OCH), 65.28 (2C, OCH_2), 32.08 (1C, CH_2), 28.28 (1C, CH_2), 22.38 (1C, CH_2), 13.94 (1C, CH_3).

HRMS (EI) calcd for [M-H, $C_{15}H_{18}DO_2]^+$: 232.1442; found 232.1440.

(*Z*)-(4-(hex-1-en-1-yl-1-D)phenyl)trimethylsilane (2aj)



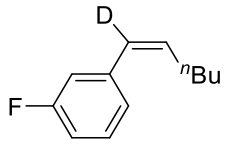
Serial number: Lwt-4-27B. **C1h** was used instead, colorless oil, TLC R_f = 0.9 (PE), 96% yield (39.2 mg), r.r. = 91:9, *Z*/*E* = 97:3.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.47 (m, 2H, Ar-H), 7.31 – 7.22 (m, 2H, Ar-H), 5.67 (t, *J* = 7.3 Hz, 1H, =CH), 2.35 (q, *J* = 7.3 Hz, 2H, CH_2), 1.46 – 1.39 (m, 2H, CH_2), 1.38 – 1.32 (m, 2H, CH_2), 0.90 (t, *J* = 7.2 Hz, 3H, CH_3). 0.27 (s, 9H, $Si(CH_3)_3$).

^{13}C NMR (101 MHz, $CDCl_3$) δ 138.37 (1C, Ar-C), 138.17 (1C, Ar-C), 133.38 (1C, =C), 133.14 (2C, Ar-C), 128.28 (t, *J* = 23.2 Hz, 1C, =CD), 128.05 (2C, Ar-C), 32.20 (1C, CH_2), 28.48 (1C, CH_2), 22.46 (1C, CH_2), 14.01 (1C, CH_3), -1.11 (3C, $Si(CH_3)_3$).

HRMS (EI) calcd for [M, $C_{15}H_{23}DSi]^+$: 233.1710; found 233.1704.

(*Z*)-1-fluoro-3-(hex-1-en-1-yl-1-D)benzene (2ak)



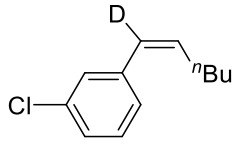
Serial number: Lwt-3-162B. **C1h** was used instead, colorless oil, TLC R_f = 0.75 (PE), 93% yield (33.3 mg), r.r. = 88:12, *Z*/*E* = 97:3.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.25 (m, 1H, Ar-H), 7.04 (dt, *J* = 7.7, 1.3 Hz, 1H, Ar-H), 6.98 (ddd, *J* = 10.3, 2.6, 1.5 Hz, 1H, Ar-H), 6.91 (tdd, *J* = 8.5, 2.6, 1.0 Hz, 1H, Ar-H), 5.70 (tt, *J* = 7.4, 1.6 Hz, 1H, =CH), 2.32 (q, *J* = 7.3 Hz, 2H, CH_2), 1.46 – 1.30 (m, 4H, CH_2CH_2), 0.90 (t, *J* = 7.2 Hz, 3H, CH_3).

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.65 (d, *J* = 244.5 Hz, 1C, Ar-C), 139.92 (d, *J* = 8.0 Hz, 1C, Ar-C), 134.28 (1C, =C), 129.45 (d, *J* = 8.3 Hz, 1C, Ar-C), 127.30 (t, *J* = 22.7 Hz, 1C, =CD), 124.48 (d, *J* = 2.6 Hz, 1C, Ar-C), 115.35 (d, *J* = 21.5 Hz, 1C, Ar-C), 113.21 (d, *J* = 21.1 Hz, 1C, Ar-C), 32.01 (1C, CH_2), 28.30 (1C, CH_2), 22.38 (1C, CH_2), 13.94 (1C, CH_3).

HRMS (EI) calcd for [M, $C_{12}H_{14}DF]^+$: 179.1221; found 179.1216.

(*Z*)-1-chloro-3-(hex-1-en-1-yl-1-D)benzene (2al)



Serial number: Lwt-3-159C. **C1h** was used instead, colorless oil, TLC R_f = 0.70 (PE), 95% yield (37.1 mg), r.r. = 89:11, Z/E = 98:2.

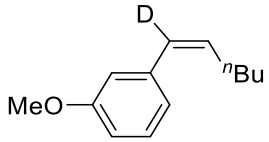
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 – 7.23 (m, 2H, Ar-H), 7.18 (dt, *J* = 8.0, 1.5 Hz, 1H, Ar-H), 7.14 (dt, *J* = 7.4, 1.5 Hz, 1H, Ar-H), 5.70 (tt, *J* = 7.3, 1.7 Hz, 1H,

=CH), 2.30 (q, J = 7.3 Hz, 2H, CH_2), 1.45 – 1.32 (m, 4H, CH_2CH_2), 0.89 (t, J = 7.2 Hz, 3H, CH_3).

^{13}C NMR (101 MHz, $CDCl_3$) δ 139.53 (1C, Ar-C), 134.43 (1C, Ar-C), 133.95 (1C, =C), 129.30 (1C, Ar-C), 128.67 (1C, Ar-C), 127.35 (t, J = 23.2 Hz, 1C, =CD), 126.85 (1C, Ar-C), 126.44 (1C, Ar-C), 31.98 (1C, CH_2), 28.24 (1C, CH_2), 22.35 (1C, CH_2), 13.92 (1C, CH_3).

HRMS (EI) calcd for [M, $C_{12}H_{14}DCl]^+$: 195.0925; found 195.0919.

(*Z*)-1-(hex-1-en-1-yl-1-D)-3-methoxybenzene (2am)



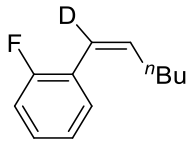
Serial number: Lwt-3-175C. colorless oil, TLC R_f = 0.5 (PE/EA = 10:1), 87% yield (33.3 mg), r.r. = 96:4, Z/E > 98:2.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (t, J = 7.9 Hz, 1H, Ar-H), 6.88 (dt, J = 7.5, 1.3 Hz, 1H, Ar-H), 6.83 (t, J = 2.1 Hz, 1H, Ar-H), 6.77 (ddd, J = 8.2, 2.6, 1.0 Hz, 1H, Ar-H), 5.66 (tt, J = 7.5, 1.7 Hz, 1H, =CH), 3.80 (s, 3H, OCH_3), 2.34 (q, J = 7.3 Hz, 2H, CH_2), 1.45 – 1.32 (m, 4H, CH_2CH_2), 0.89 (t, J = 7.2 Hz, 3H, CH_3).

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.33 (1C, Ar-C), 139.11 (1C, Ar-C), 133.36 (1C, =C), 129.02 (1C, Ar-C), 128.21 (t, J = 22.7 Hz, 1C, =CD), 121.30 (1C, Ar-C), 114.27 (1C, Ar-C), 111.90 (1C, Ar-C), 55.13(1C, OCH_3), 32.13 (1C, CH_2), 28.39 (1C, CH_2), 22.42 (1C, CH_2), 13.98 (1C, CH_3).

HRMS (EI) calcd for [M, $C_{13}H_{17}DO]^+$: 191.1420; found 191.1414.

(*Z*)-1-fluoro-2-(hex-1-en-1-yl-1-D)benzene (2an)



Serial number: Lwt-3-106B. **C1h** was used instead, colorless oil, TLC R_f = 0.70 (PE), 72% yield (25.8 mg), r.r. = 95:5, Z/E = 98:2.

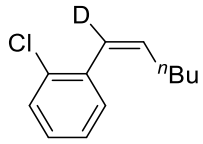
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.25 (m, 1H, Ar-H), 7.23 (tdd, J = 7.4, 5.2, 1.8

Hz, 1H, Ar-H), 7.12 (td, *J* = 7.5, 1.3 Hz, 1H, Ar-H), 7.06 (ddd, *J* = 9.7, 8.2, 1.3 Hz, 1H, Ar-H), 5.82 (tt, *J* = 7.4, 1.7 Hz, 1H, =CH), 2.26 (q, *J* = 7.4 Hz, 2H, CH_2), 1.46 – 1.30 (m, 4H, CH_2CH_2), 0.88 (t, *J* = 7.2 Hz, 3H, CH_3).

^{13}C NMR (101 MHz, $CDCl_3$) δ 161.12 (d, *J* = 246.4 Hz, 1C, Ar-C), 135.07 (1C, =C), 130.48 (d, *J* = 3.5 Hz, 1C, Ar-C), 128.22 (d, *J* = 8.6 Hz, 1C, Ar-C), 125.30 (d, *J* = 14.8 Hz, 1C, Ar-C), 123.45 (d, *J* = 3.6 Hz, 1C, Ar-C), 120.89 (t, *J* = 23.7 Hz, 1C, =CD), 115.28 (d, *J* = 22.2 Hz, 1C, Ar-C), 31.84 (1C, CH_2), 28.47 (1C, CH_2), 22.36 (1C, CH_2), 13.91 (1C, CH_3).

HRMS (EI) calcd for [M, $C_{12}H_{14}DF]^+$: 179.1221; found 179.1215.

(*Z*)-1-chloro-2-(hex-1-en-1-yl-1-D)benzene (2ao)



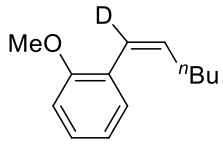
Serial number: Lwt-3-92B. **C1h** was used instead, colorless oil, TLC R_f = 0.70 (PE), 95% yield (37.1 mg), r.r. = 95:5, *Z*/*E* > 98:2.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (dd, *J* = 7.4, 1.6 Hz, 1H, Ar-H), 7.29 (dd, *J* = 7.5, 2.0 Hz, 1H, Ar-H), 7.19 (dtd, *J* = 18.5, 7.4, 1.7 Hz, 2H, Ar-H), 5.79 (tt, *J* = 7.4, 1.6 Hz, 1H, =CH), 2.20 (q, *J* = 7.4 Hz, 2H, CH_2), 1.45 – 1.29 (m, 4H, CH_2CH_2), 0.88 (t, *J* = 7.2 Hz, 3H, CH_3).

^{13}C NMR (101 MHz, $CDCl_3$) δ 135.83 (1C, Ar-C), 134.26 (1C, =C), 133.59 (1C, Ar-C), 130.50 (1C, Ar-C), 129.28 (1C, Ar-C), 127.87 (1C, Ar-C), 126.09 (1C, Ar-C), 125.64 (t, *J* = 24.2 Hz, 1C, =CD), 31.84 (1C, CH_2), 28.13 (1C, CH_2), 22.31 (1C, CH_2), 13.89 (1C, CH_3).

HRMS (EI) calcd for [M, $C_{12}H_{14}DCl]^+$: 195.0925; found 195.0919.

(*Z*)-1-(hex-1-en-1-yl-1-D)-2-methoxybenzene (2ap)



Serial number: Lwt-3-58. colorless oil, TLC R_f = 0.38 (PE/EA = 50:1), 80% yield (30.6

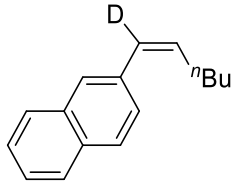
mg), r.r. = 95:5, *Z*/*E* > 98:2.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.13 (m, 2H, Ar-H), 6.92 (t, *J* = 7.4 Hz, 1H, Ar-H), 6.87 (t, *J* = 8.2 Hz, 1H, Ar-H), 5.72 (t, *J* = 7.4 Hz, 1H, =CH), 3.83 (s, 3H, OCH_3), 2.25 (q, *J* = 7.4 Hz, 2H, CH_2), 1.45 – 1.31 (m, 4H, CH_2CH_2), 0.88 (t, *J* = 7.1 Hz, 3H, CH_3).

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.97 (1C, OAr-C), 132.91 (1C, =C), 129.98 (1C, Ar-C), 127.89 (1C, Ar-C), 126.50 (1C, Ar-C), 123.63 (t, *J* = 23.7 Hz, 1C, =CD), 119.95 (1C, Ar-C), 110.32 (1C, Ar-C), 55.39 (1C, OCH_3), 32.14 (1C, CH_2), 28.38 (1C, CH_2), 22.45 (1C, CH_2), 13.97 (1C, CH_3).

HRMS (EI) calcd for [M, $C_{13}H_{17}DO]^+$: 191.1420; found 191.1413.

(*Z*)-2-(hex-1-en-1-yl-1-D)naphthalene (2ba)



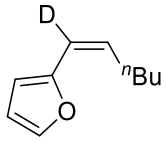
Serial number: Lwt-4-107a. colorless oil, TLC R_f = 0.60 (PE), 98% yield (41.4 mg), r.r. = 91:9, *Z*/*E* = 98:2.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (t, *J* = 7.6 Hz, 3H, Ar-H), 7.71 (s, 1H, Ar-H), 7.47 – 7.39 (m, 3H, Ar-H), 5.74 (t, *J* = 7.3 Hz, 1H, =CH), 2.42 (q, *J* = 7.3 Hz, 2H, CH_2), 1.46 (q, *J* = 7.6 Hz, 2H, CH_2), 1.36 (q, *J* = 7.4 Hz, 2H, CH_2), 0.90 (t, *J* = 7.2 Hz, 3H, CH_3).

^{13}C NMR (101 MHz, $CDCl_3$) δ 135.29 (1C, Ar-C), 133.57 (1C, =C), 133.32 (1C, Ar-C), 132.09 (1C, Ar-C), 128.36 (t, *J* = 22.7 Hz, 1C, =CD), 127.89 (1C, Ar-C), 127.54 (1C, Ar-C), 127.50 (1C, Ar-C), 127.32 (1C, Ar-C), 127.25 (1C, Ar-C), 125.96 (1C, Ar-C), 125.58 (1C, Ar-C), 32.16 (1C, CH_2), 28.42 (1C, CH_2), 22.42 (1C, CH_2), 13.99 (1C, CH_3).

HRMS (EI) calcd for [M, $C_{16}H_{17}D]^+$: 211.1471; found 211.1466.

(*Z*)-2-(hex-1-en-1-yl-1-D)furan (2bb)



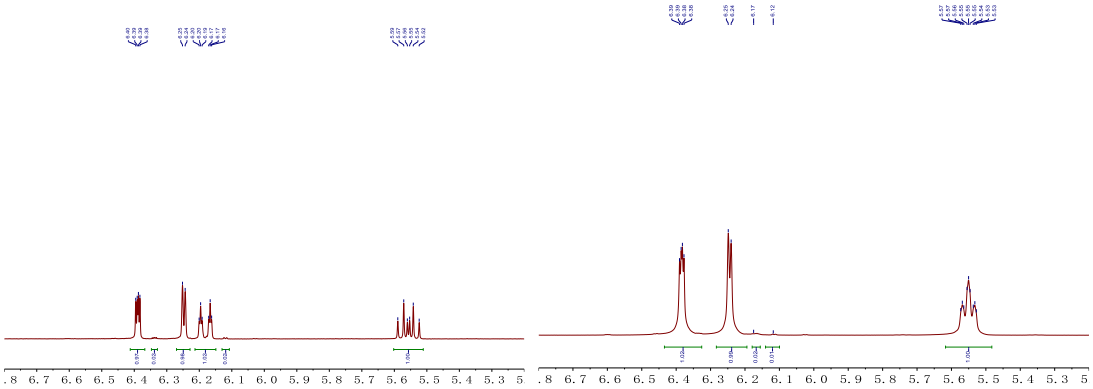
Serial number: Lwt-3-115A. colorless oil, TLC R_f = 0.60 (PE), 77% yield (23.3 mg), r.r. = 98:2, *Z*/*E* = 98:2.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, *J* = 1.8 Hz, 1H, Ar-H), 6.38 (dd, *J* = 3.3, 1.9 Hz, 1H, Ar-H), 6.24 (d, *J* = 3.4 Hz, 1H, Ar-H), 5.55 (tt, *J* = 7.3, 1.8 Hz, 1H, =CH), 2.44 (q, *J* = 7.3 Hz, 2H, CH_2), 1.50 – 1.35 (m, 4H, CH_2CH_2), 0.92 (t, *J* = 7.1 Hz, 3H, CH_3).

^{13}C NMR (101 MHz, $CDCl_3$) δ 153.35 (1C, Ar-C), 141.10 (1C, Ar-C), 131.28 (1C, =C), 116.90 (t, *J* = 24.2 Hz, 1C, =CD), 111.00 (1C, Ar-C), 108.62 (1C, Ar-C), 31.68 (1C, CH_2), 28.93 (1C, CH_2), 22.46 (1C, CH_2), 13.98 (1C, CH_3).

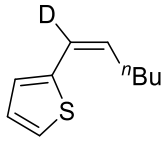
HRMS (EI) calcd for [M, $C_{10}H_{13}DO$]$^+$: 151.1107; found 151.1103.

The r.r. (**2bb**/**3bb**) and *Z*/*E* (**2bb-*Z***/**2bb-*E***) was determined by analysis of 400 MHz ^{1}H NMR spectra of the protonated sample (below left) with deuterated product (below right). The corresponding data of **2ba** and **2bc**-**2be** were obtained similarly.



Peak	Chem shift (ppm)	Area	Area (%)	Product	Chem shift (ppm)	Area	Area (%)
1	6.18	1.02	50.0	**3bb-*Z***	6.17	0.02	2
2	6.12	0.02	1	**2bb-*E***	6.12	0.01	1
3	5.56	1.00	49.0	**2bb-*Z***	5.56	1.00	97

(*Z*)-2-(hex-1-en-1-yl-1-D)thiophene (2bc)



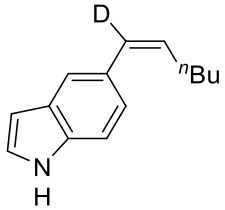
Serial number: Lwt-3-101. **C1h** was used instead, colorless oil, TLC R_f = 0.70 (PE), 79% yield (26.4 mg), r.r. = 94:6, *Z*/*E* > 98:2.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (dd, *J* = 5.1, 1.3 Hz, 1H, Ar-H), 7.00 (dd, *J* = 5.1, 3.6 Hz, 1H, Ar-H), 6.97 (dd, *J* = 3.6, 1.3 Hz, 1H, Ar-H),5.58 (t, *J* = 7.0 Hz, 1H, =CH), 2.41 (q, *J* = 7.2 Hz, 2H, CH_2), 1.53 – 1.38 (m, 4H, CH_2CH_2), 0.93 (t, *J* = 7.2 Hz, 3H, CH_3).

^{13}C NMR (101 MHz, $CDCl_3$) δ 140.77 (1C, Ar-C), 131.11 (1C, Ar-C), 126.95 (1C, =C), 126.65 (1C, Ar-C), 124.82 (1C, Ar-C), 121.31 (t, *J* = 24.2 Hz, 1C, =CD), 31.62 (1C, CH_2), 28.97 (1C, CH_2), 22.49 (1C, CH_2), 13.98 (1C, CH_3).

HRMS (EI) calcd for [M, $C_{10}H_{13}DS]^+$: 167.0879; found 167.0874.

(*Z*)-5-(hex-1-en-1-yl-1-D)-1H-indole (2bd)



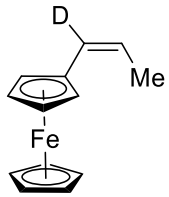
Serial number: Lwt-3-116A. colorless oil, TLC R_f = 0.75 (PE/EA = 2:1), 98% yield (39.2 mg), r.r. = 97:3, *Z*/*E* = 97:3.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (br, 1H, NH), 7.57 (d, *J* = 1.5 Hz, 1H, Ar-H), 7.31 (d, *J* = 8.4 Hz, 1H, Ar-H), 7.19 – 7.10 (m, 2H, Ar-H), 6.53 (t, *J* = 2.6 Hz, 1H, Ar-H), 5.60 (tt, *J* = 7.2, 1.6 Hz, 1H, =CH), 2.40 (q, *J* = 7.3 Hz, 2H, CH_2), 1.48 – 1.42 (m, 2H, CH_2), 1.40 – 1.31 (m, 2H, CH_2), 0.90 (t, *J* = 7.2 Hz, 3H, CH_3).

^{13}C NMR (101 MHz, $CDCl_3$) δ 134.52 (1C, Ar-C), 130.94 (1C, =C), 129.70 (1C, Ar-C), 129.17 (t, *J* = 23.2 Hz, 1C, =CD), 127.78 (1C, Ar-C), 124.44 (1C, Ar-C), 123.53 (1C, Ar-C), 120.70 (1C, Ar-C), 110.52 (1C, Ar-C), 102.74 (1C, Ar-C), 32.35 (1C, CH_2), 28.39 (1C, CH_2), 22.46 (1C, CH_2), 14.02 (1C, CH_3).

HRMS (EI) calcd for [M, $C_{14}H_{16}DN$]$^+$: 200.1424; found 200.1416.

(*Z*)-1-(prop-1-en-1-yl-1-D)ferrocene (2be)



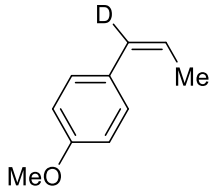
Serial number: Lwt-4-147C. **C1h** was used instead, orange oil, TLC R_f = 0.6 (PE/EA = 50:1), 87% yield (39.5 mg), r.r. = 93:7, *Z*/*E* = 97:3.

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.56 (ddd, *J* = 8.4, 6.7, 5.1 Hz, 1H, =CH), 4.33 (t, *J* = 1.9 Hz, 2H, Ar-H), 4.19 (t, *J* = 1.9 Hz, 2H, Ar-H), 4.10 (s, 5H, Ar-H), 1.82 (d, *J* = 7.0 Hz, 3H, CH_3).

^{13}C NMR (101 MHz, $CDCl_3$) δ 126.51 (t, *J* = 24.2 Hz, 1C, =CD), 123.37 (1C, =C), 82.29 (1C, Ar-C), 69.03 (2C, Ar-C), 68.99 (5C, Ar-C), 68.19 (2C, Ar-C), 14.76 (1C, CH_3).

HRMS (ESI) calcd for [M, $C_{13}H_{13}DFe$]$^+$: 227.0508; found 227.0501.

(*Z*)-1-methoxy-4-(prop-1-en-1-yl-1-D)benzene (2ca)



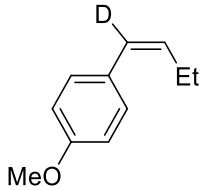
Serial number: Lwt-3-56. colorless oil, TLC R_f = 0.48 (PE/EA = 50:1), 87% yield (26.0 mg), r.r. = 92:8, *Z*/*E* = 98:2.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (d, *J* = 8.7 Hz, 2H, Ar-H), 6.92 – 6.85 (m, 2H, Ar-H), 5.69 (tdd, *J* = 8.0, 5.2, 2.1 Hz, 1H, =CH), 3.80 (s, 3H, OCH_3), 1.88 (dd, *J* = 7.2, 2.2 Hz, 3H, CH_3).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.08 (1C, OAr-C), 130.25 (1C, Ar-C), 129.96 (2C, Ar-C), 128.91 (t, *J* = 23.2 Hz, 1C, =CD), 124.89 (1C, =C), 113.52 (2C, Ar-C), 55.20 (1C, OCH_3), 14.53 (1C, CH_3).

HRMS (EI) calcd for [M, $C_{10}H_{11}DO$]$^+$: 149.0951; found 149.0943.

(*Z*)-1-(but-1-en-1-yl-1-D)-4-methoxybenzene (2cb)



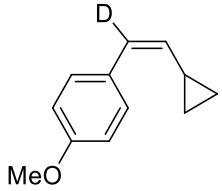
Serial number: Lwt-3-49. colorless oil, TLC R_f = 0.48 (PE/EA = 50:1), 91% yield (29.8 mg), r.r. = 90:10, *Z*/*E* = 98:2.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (d, *J* = 8.7 Hz, 2H, Ar-H), 6.86 (d, *J* = 8.7 Hz, 2H, Ar-H), 5.57 (tt, *J* = 7.2, 1.7 Hz, 1H, =CH), 3.80 (s, 3H, OCH_3), 2.34 (p, *J* = 7.4 Hz, 2H, CH_2), 1.06 (t, *J* = 7.5 Hz, 3H, CH_3).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.12 (1C, OAr-C), 133.00 (1C, =C), 130.37 (1C, Ar-C), 129.87 (2C, Ar-C), 127.28 (t, *J* = 23.2 Hz, 1C, =CD), 113.51 (2C, Ar-C), 55.21 (1C, OCH_3), 21.91 (1C, CH_2), 14.51 (1C, CH_3).

HRMS (EI) calcd for [M, $C_{11}H_{13}DO]^+$: 163.1107; found 163.1100.

(*Z*)-1-(2-cyclopropylvinyl-1-D)-4-methoxybenzene (2cc)



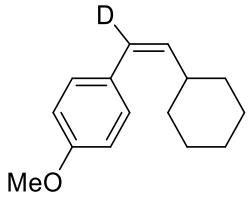
Serial number: Lwt-3-60. colorless oil, TLC R_f = 0.40 (PE/EA = 50:1), 98% yield (34.3 mg), r.r. = 87:13, *Z*/*E* > 98:2.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.33 (m, 2H, Ar-H), 6.87 (d, *J* = 8.7 Hz, 2H, Ar-H), 4.99 (dd, *J* = 9.7, 1.6 Hz, 1H, =CH), 3.80 (s, 3H, OCH_3), 1.90 – 1.81 (m, 1H, CH), 0.83 – 0.79 (m, 2H, CH_2), 0.44 (dt, *J* = 6.5, 4.3 Hz, 2H, CH_2).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.07 (1C, OAr-C), 134.90 (1C, =C), 130.52 (1C, Ar-C), 129.76 (2C, Ar-C), 126.59 (t, *J* = 23.2 Hz, 1C, =CD), 113.54 (2C, Ar-C), 55.21 (1C, OCH_3), 10.94 (1C, CH), 7.96 (2C, CH_2).

HRMS (EI) calcd for [M, $C_{12}H_{13}DO]^+$: 175.1107; found 175.1100.

(*Z*)-1-(2-cyclohexylvinyl-1-D)-4-methoxybenzene (2cd)



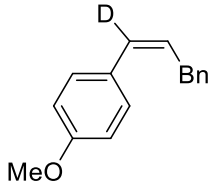
Serial number: Lwt-4-42A. colorless oil, TLC *Rf* = 0.50 (PE/EA = 50:1), 99% yield (43.0 mg), r.r. = 88:12, *Z*/*E* = 96:4.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 – 7.19 (m, 2H, Ar-H), 6.88 – 6.86 (m, 2H, Ar-H), 5.40 (d, *J* = 12 Hz, 1H, =CH), 3.81 (s, 3H, OCH_3), 2.56 (dddd, *J* = 11.0, 7.6, 5.3, 2.3 Hz, 1H, CH), 1.79 – 1.63 (m, 4H, CH_2CH_2), 1.36 – 1.08 (m, 6H, CH_2).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.15 (1C, OAr-C), 137.43 (1C, =C), 130.53 (1C, Ar-C), 129.77 (2C, Ar-C), 125.90 (t, *J* = 23.2 Hz, 1C, =CD), 113.62 (2C, Ar-C), 55.26 (1C, OCH_3), 36.88 (1C, CH), 33.34 (2C, CH_2CH_2), 26.09 (1C, CH_2), 25.78 (2C, CH_2CH_2).

HRMS (EI) calcd for [M, $C_{15}H_{19}DO]^+$: 217.1577; found 217.1570.

(*Z*)-1-methoxy-4-(3-phenylprop-1-en-1-yl-1-D)benzene (2ce)



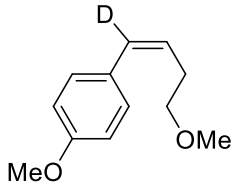
Serial number: Lwt-4-31A. colorless oil, TLC R_f = 0.66 (PE/EA = 50:1), 99% yield (44.6 mg), r.r. = 93:7, *Z*/*E* = 95:5.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.27 (m, 4H, Ar-H), 7.25 – 7.19 (m, 3H, Ar-H), 6.89 (d, *J* = 8.8 Hz, 2H, Ar-H), 5.77 (dd, *J* = 8.2, 6.7 Hz, 1H, =CH), 3.82 (s, 3H, OCH_3), 3.68 (d, *J* = 7.4 Hz, 2H, CH_2).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.42 (1C, OAr-C), 140.91 (1C, =C), 129.87 (2C, Ar-C), 129.78 (1C, Ar-C), 129.29 (1C, =CD), 128.97 (1C, Ar-C), 128.47 (2C, Ar-C), 128.31 (2C, Ar-C), 125.99 (1C, Ar-C), 113.65 (2C, Ar-C), 55.21 (1C, OCH_3) , 34.62 (1C, CH_2).

HRMS (EI) calcd for [M, $C_{16}H_{15}DO]^+$: 225.1264; found 225.1257.

(*Z*)-1-methoxy-4-(4-methoxybut-1-en-1-yl-1-D)benzene (2cf)



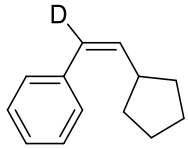
Serial number: Lwt-4-32B-2. **C1h** was used instead, colorless oil, TLC *Rf* = 0.39 (PE/EA = 20:1), 95% yield (36.8 mg), r.r. = 91:9, *Z*/*E* = 96:4.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 – 7.20 (m, 2H, Ar-H), 6.90 – 6.83 (m, 2H, Ar-H), 5.59 (t, *J* = 7.2 Hz, 1H, =CH), 3.80 (s, 3H, OCH_3), 3.48 (td, *J* = 6.7, 1.3 Hz, 2H, OCH_2), 3.35 (s, 3H, OCH_3), 2.62 (qd, *J* = 6.9, 1.4 Hz, 2H, CH_2).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.33 (1C, OAr-C), 130.00 (1C, =C), 129.94 (2C, Ar-C), 129.66 (t, *J* = 23.2 Hz, 1C, =CD), 126.86 (1C, Ar-C), 113.60 (2C, Ar-C), 72.40 (1C, OCH_2), 58.67 (1C, OCH_3), 55.24 (1C, OCH_3), 29.15 (1C, CH_2).

HRMS (EI) calcd for [M, $C_{12}H_{15}DO_2$]$^+$: 193.1213; found 193.1207.

(*Z*)-(2-cyclopentylvinyl-1-D)benzene (2cg)



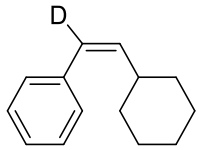
Serial number: Lwt-7-182. colorless oil, TLC R_f = 0.8 (PE), 81% yield (28 mg), r.r. = 95:5, *Z*/*E* = 95:5.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.25 (m, 4H, Ar-H), 7.24 – 7.16 (m, 1H, Ar-H), 5.57 (dd, *J* = 10.1, 2.0 Hz, 1H, =CH), 3.04 – 2.88 (m, 1H, CH), 1.87 (dq, *J* = 10.0, 5.6, 4.9 Hz, 2H, CH_2), 1.76 – 1.65 (m, 2H, CH_2), 1.59 (ddt, *J* = 12.8, 9.7, 4.2 Hz, 2H, CH_2), 1.42 – 1.28 (m, 2H, CH_2).

^{13}C NMR (101 MHz, $CDCl_3$) δ 138.22 (1C, =C), 137.84 (1C, Ar-C), 128.62 (2C, Ar-C), 128.07 (2C, Ar-C), 126.97 (t, *J* = 23.2 Hz, 1C, =CD), 126.37 (1C, Ar-C), 38.77 (1C, CH), 34.19 (2C, $2CH_2$), 25.56 (2C, $2CH_2$).

HRMS (EI) calcd for [M, $C_{13}H_{15}D$]$^+$: 173.1315; found 173.1310.

(*Z*)-(2-cyclohexylvinyl-1-D)benzene (2ch)



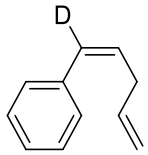
Serial number: Lwt-7-189. colorless oil, TLC R_f = 0.8 (PE), 98% yield (39 mg), r.r. = 93:7, *Z*/*E* = 93:7.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.25 (m, 4H, Ar-H), 7.24 – 7.16 (m, 1H, Ar-H), 5.57 (dd, *J* = 10.1, 2.0 Hz, 1H, =CH), 3.04 – 2.88 (m, 1H, CH), 1.87 (dq, *J* = 10.0, 5.6, 4.9 Hz, 2H, CH_2), 1.76 – 1.65 (m, 2H, CH_2), 1.59 (ddt, *J* = 12.8, 9.7, 4.2 Hz, 2H, CH_2), 1.42 – 1.28 (m, 2H, CH_2).

^{13}C NMR (101 MHz, $CDCl_3$) δ 138.84 (1C, Ar-C), 137.86 (1C, =C), 128.56 (2C, Ar-C), 128.15 (2C, Ar-C), 126.45 (t, *J* = 23.2 Hz, 1C, =CD), 126.22 (1C, Ar-C), 36.87 (1C, CH_2), 33.24 (2C, CH_2), 26.02 (1C, CH_2), 25.67 (2C, CH_2).

HRMS (EI) calcd for [M, $C_{14}H_{17}D]^+$: 187.1471; found 187.1465.

(*Z*)-(penta-1,4-dien-1-yl-1-D)benzene (2ci)



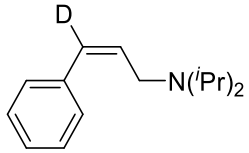
Serial number: Lwt-4-48B. **C1h** was used instead, colorless oil, TLC R_f = 0.55 (PE), 75 yield (21.8 mg), r.r. = 92:8, *Z*/*E* = 97:3.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.15 (m, 5H, Ar-H), 5.91 (ddt, *J* = 16.3, 10.1, 6.0 Hz, 1H, =CH), 5.70 (tt, *J* = 7.6, 1.7 Hz, 1H, =CH), 5.13 (dq, *J* = 17.1, 1.7 Hz, 1H, =CH), 5.06 (dq, *J* = 10.2, 1.7 Hz, 1H, =CH), 3.11 – 3.02 (m, 2H, CH_2).

^{13}C NMR (101 MHz, $CDCl_3$) δ 137.20 (1C, Ar-C), 136.64 (1C, =C), 129.69 (1C, *J* = 22.7 Hz, =CD), 129.31 (1C, =C), 128.61 (2C, Ar-C), 128.15 (2C, Ar-C), 126.69 (1C, Ar-C), 115.26 (1C, =C), 32.66 (1C, CH_2).

HRMS (EI) calcd for [M, $C_{11}H_{11}D]^+$: 145.1002; found 145.0995.

(*Z*)-*N*,*N*-diisopropyl-3-phenylprop-2-en-1-amine-3-D (2cj)



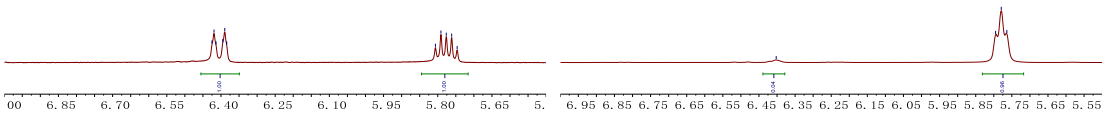
Serial number: Lwt-4-26A. 4 h, colorless oil, TLC R_f = 0.5 (EA), 89% yield (39 mg), r.r. = 96:4, *Z*/*E* > 98:2.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (t, *J* = 7.6 Hz, 2H, Ar-H), 7.27 – 7.19 (m, 3H, Ar-H), 5.82 (t, *J* = 6.2 Hz, 1H, =CH), 3.38 (d, *J* = 6.0 Hz, 2H, NCH_2), 3.13 – 3.03 (m, 2H, NCH), 1.02 (dd, *J* = 6.6, 1.6 Hz, 12H, $4CH_3$).

^{13}C NMR (101 MHz, $CDCl_3$) δ 137.56 (1C, Ar-C), 135.36 (1C, =C), 128.90 (2C, Ar-C), 128.07 (2C, Ar-C), 127.95 (1C, *J* = 24.2 Hz, =CD), 126.52 (1C, Ar-C), 48.87 (2C, NCH), 43.44 (1C, NCH_2), 20.73 (4C, CH_3).

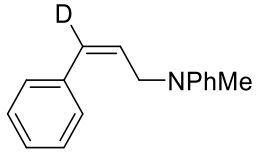
HRMS (EI) calcd for [M, $C_{15}H_{22}DN$]$^+$: 218.1893; found 218.1890.

The r.r. (**2cj**/**3cj**) and *Z*/*E* (**2cj-*Z***/**2cj-*E***) was determined by analysis of 400 MHz ^{1}H NMR spectra of the protonated sample (below left) with deuterated product (below right). The corresponding data of **2ca**-**2ci** and **2ck**-**2cm** were obtained similarly.



Peak	Chem shift (ppm)	Area	Area (%)	Product	Chem shift (ppm)	Area	Area (%)
1	6.40	1.00	50	**3cj-*Z***	6.40	0.04	4
2	5.78	1.00	50	**2cj- *Z***	5.78	0.96	96

(*Z*)-N-methyl-N-(3-phenylallyl-3-D)aniline (2ck)



Serial number: Lwt-4-128A. **C1h** was used instead, 4 h, colorless oil, TLC *Rf* = 0.5

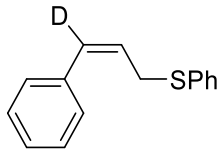
(EA), 98% yield (44.0 mg), r.r. = 90:10, *Z*/*E* > 98:2.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.35 (m, 2H, Ar-H), 7.26 (dt, *J* = 8.0, 1.3 Hz, 3H, Ar-H), 7.24 – 7.15 (m, 2H, Ar-H), 6.75 – 6.64 (m, 3H, Ar-H), 5.69 (td, 1H, *J* = 6.0, 3.0 Hz, =CH), 4.22 (d, *J* = 6.0 Hz, 2H, CH_2), 2.91 (s, 3H, CH_3).

^{13}C NMR (101 MHz, $CDCl_3$) δ 149.25 (1C, NAr-C), 136.82 (1C, =C), 131.02 (t, *J* =23.2 Hz, 1C, =CD), 129.44 (1C, Ar-C), 129.09 (2C, Ar-C), 128.90 (2C, Ar-C), 128.27 (2C, Ar-C), 127.03 (1C, Ar-C), 116.66 (1C, Ar-C), 112.91 (2C, Ar-C), 50.99 (1C, NCH_2), 38.29 (1C, NCH_3).

HRMS (EI) calcd for [M, $C_{16}H_{16}DN$]$^+$: 224.1424; found 224.1419.

(*Z*)-phenyl(3-phenylallyl-3-d)sulfane (2cl)



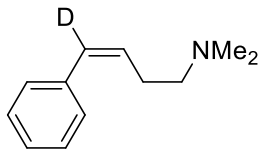
Serial number: Lwt-8-170B. 4 h, yellow oil, TLC R_f = 0.3 (PE), 95% yield (43.1 mg), r.r. = 83:17, *Z*/*E* = 97:3.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.34 (m, 2H, Ar-H), 7.32 – 7.24 (m, 7H, Ar-H), 7.22 – 7.17 (m, 1H, Ar-H), 5.82 (t, *J* = 7.8 Hz, 1H, =CH), 3.82 (d, *J* = 7.7 Hz, 2H, CH_2).

^{13}C NMR (101 MHz, $CDCl_3$) δ 136.30 (1C, Ar-C), 135.97 (1C, Ar-C), 131.63 (t, *J* = 22.2 Hz, 1C, =CD), 129.32 (2C, Ar-C), 128.77 (2C, Ar-C), 128.69 (2C, Ar-C), 128.28 (2C, Ar-C), 127.14 (1C, Ar-C), 126.84 (1C, Ar-C), 126.01 (1C, =C), 31.95 (d, *J* = 9.09 Hz, 1C, CH_2).

HRMS (EI) calcd for [M, $C_{15}H_{13}DS$]$^+$: 227.0879; found 227.0872.

(*Z*)-N,N-dimethyl-4-phenylbut-3-en-1-amine-4-d (2cm)



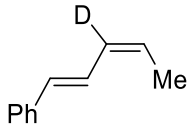
Serial number: Lwt-8-170C. 12 h, yellow oil, TLC R_f = 0.3 (EA), 98% yield (34.9 mg), r.r. = 87:13, *Z*/*E* = 98:2.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.25 (m, 4H, Ar-H), 7.21 (td, *J* = 6.8, 1.8 Hz, 1H, Ar-H), 5.67 (tt, *J* = 7.1, 1.6 Hz, 1H, =CH), 2.57 – 2.48 (m, 2H, CH_2), 2.40 (t, *J* = 7.1 Hz, 2H, CH_2), 2.22 (s, 6H, $N(CH_3)_2$).

^{13}C NMR (101 MHz, $CDCl_3$) δ 137.41 (1C, Ar-C), 130.03 (1C, Ar-C), 129.50 (t, *J* = 22.7 Hz, 1C, =CD), 128.63 (2C, Ar-C), 128.09 (2C, Ar-C), 126.53 (1C, =C), 59.49 (1C, CH_2), 45.35 (2C, $N(CH_3)_2$), 26.98 (1C, CH_2).

HRMS (ESI) calcd for [M+H, $C_{12}H_{17}DN$]$^+$: 177.1496; found 177.1496.

((1*E*,3*Z*)-penta-1,3-dien-1-yl-3-D)benzene (2da)



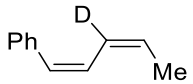
Serial number:Lwt-3-51. **C1h** was used instead, colorless oil, TLC R_f = 0.85 (PE), 82% yield (23.8 mg), r.r. = 84:16, *Z*/*E* = 97:3.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 8.2 Hz, 2H, Ar-H), 7.34 – 7.28 (m, 2H, Ar-H), 7.24 – 7.19 (m, 1H, Ar-H), 7.09 (d, *J* = 15.7 Hz, 1H, =CH), 6.52 (d, *J* = 15.6 Hz, 1H, =CH), 5.60 (q, *J* = 7.3 Hz, 1H, =CH), 1.86 (dd, *J* = 7.1, 1.4 Hz, 3H, CH_3).

^{13}C NMR (101 MHz, $CDCl_3$) δ 137.66 (1C, Ar-C), 131.78 (1C, =C), 129.28 (t, *J* = 17.2 Hz, 1C, =CD), 128.55 (2C, Ar-C),127.29 (1C, =C), 127.01 (1C, Ar-C), 126.29 (2C, Ar-C), 124.10 (1C, =C), 13.58 (1C, CH_3).

HRMS (EI) calcd for [M, $C_{11}H_{11}D$]$^+$: 145.1002; found 145.1017.

((1*Z*,3*Z*)-penta-1,3-dien-1-yl-3-D)benzene (2db)



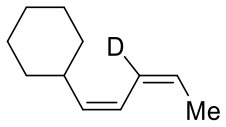
Serial number:Lwt-3-144C-2. **C1h** was used instead, colorless oil, TLC R_f = 0.70 (PE), 99% yield (28.8 mg), r.r. = 92:8, *Z*/*E* >98:2.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.30 (m, 4H, Ar-H), 7.24 – 7.21 (m, 1H, Ar-H), 6.59 – 6.50 (m, 1H, =CH), 6.45 (dd, *J* = 11.7, 1.5 Hz, 1H, =CH), 5.66 (dt, *J* = 7.2, 1.6 Hz, 1H, =CH), 1.83 (d, *J* = 7.1 Hz, 3H, CH_3).

^{13}C NMR (101 MHz, $CDCl_3$) δ 137.55 (1C, Ar-C), 129.26 (1C, =C), 129.08 (2C, Ar-C), 128.78 (1C, =C), 128.12 (2C, Ar-C), 126.80 (1C, Ar-C), 125.31 (t, *J* = 23.2 Hz, 1C, =CD), 124.96 (1C, =C), 13.36 (1C, CH_3).

HRMS (EI) calcd for [M, $C_{11}H_{11}D]^+$: 145.1002; found 145.0997.

((1*Z*,3*Z*)-penta-1,3-dien-1-yl-3-D)cyclohexane (2dc)



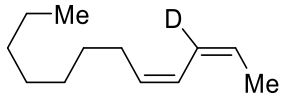
Serial number: Lwt-6-101B. **C1h** was used instead, colorless oil, TLC R_f = 0.78 (PE), 76% yield (23.1 mg), r.r. = 93:7, *Z*/*E* >98:2

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.27 (dt, *J* = 10.7 Hz, 1H, =CH), 5.62 – 5.40 (m, 2H, =CH, =CH), 2.16 (d, *J* = 7.3 Hz, 2H, $=CHCH_2$), 1.74 (d, *J* = 7.0 Hz, 3H, $=CHCH_3$), 1.43 – 1.19 (m, 10H, $5CH_2$), 0.88 (t, *J* = 6.7 Hz, 3H, CH_3).

^{13}C NMR (101 MHz, $CDCl_3$) δ 137.85 (1C, =C), 125.77 (1C, =C), 124.45 (1C, *J* = 23.2 Hz, =CD), 121.32 (1C, =C), 36.55 (1C, CH_2), 33.23 (2C, $2CH_2$), 26.02 (1C, CH_2), 25.90 (2C, $2CH_2$), 13.05 (1C, CH_3).

HRMS (EI) calcd for [M, $C_{11}H_{17}D]^+$: 151.1471; found 151.1467.

(2*Z*,4*Z*)-dodeca-2,4-diene-3-D (2dd)



Serial number: Lwt-6-109B. **C1h** was used instead, colorless oil, TLC R_f = 0.70 (PE), 90% yield (30.0 mg), r.r. = 97:3, *Z*/*E* =97:3.

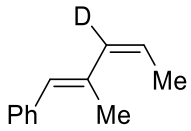
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.17 (dt, *J* = 11.0, 1.5 Hz, 1H, =CH), 5.57 – 5.45 (m, 1H, =CH), 5.31 (t, *J* = 10.2 Hz, 1H, =CH), 2.52 – 2.36 (m, 1H, CH), 1.74 (d, *J* = 7.1 Hz, 5H, CH_2), 1.72 – 1.59 (m, 3H, CH_2), 1.29 (qt, *J* = 11.8, 2.9 Hz, 2H, CH_2), 1.18 (tt, *J* = 12.5, 3.1 Hz, 1H, CH_2), 1.13 – 1.01 (m, 2H, CH_3).

^{13}C NMR (101 MHz, $CDCl_3$) δ 131.99 (1C, =C), 125.69 (1C, =C), 124.28 (1C, *J* = 23.2 Hz, =CD), 123.18 (1C, =C), 31.85 (1C, CH_2), 29.68 (1C, CH_2), 29.27 (1C, CH_2), 29.21 (1C, $1CH_2$), 27.53 (1C, $1CH_2$), 22.67 (1C, $1CH_2$), 14.09 (1C,

1CH_2), 13.07 (1C, =$CHCH_3$).

HRMS (EI) calcd for [M, $C_{12}H_{21}D]^+$: 167.1784; found 167.1778.

((1*E*,3*Z*)-2-methylpenta-1,3-dien-1-yl-3-D)benzene (2de)



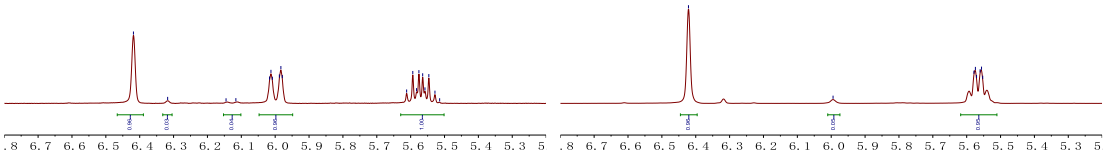
Serial number: Lwt-3-145C. **C1h** was used instead, colorless oil, TLC R_f = 0.70 (PE), 91% yield (29 mg), r.r. = 95:5, *Z*/*E* >98:2.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.28 (m, 4H, Ar-H), 7.24 – 7.19 (m, 1H, Ar-H), 6.42 (s, 1H, =CH), 5.57 (dt, *J* = 7.3, 1.6 Hz, 1H, =CH), 2.05 (s, 3H, CH_3), 1.90 (d, *J* = 7.2 Hz, 3H, CH_3).

^{13}C NMR (101 MHz, $CDCl_3$) δ 137.97 (1C, Ar-C), 135.16 (1C, =C), 133.94 (t, *J* = 23.2 Hz, 1C, =CD), 129.67 (1C, =C), 129.04 (2C, Ar-C), 128.03 (2C, Ar-C), 126.25 (1C, Ar-C), 125.17 (1C, =C), 18.63 (1C, CH_3), 14.95 (1C, CH_3).

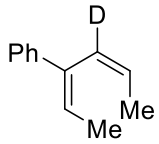
HRMS (EI) calcd for [M, $C_{12}H_{13}D]^+$: 159.1158; found 159.1153.

The r.r. (**2de**/**3de**) and *Z*/*E* (**2de-*Z***/**2de-*E***) was determined by analysis of 400 MHz ^{1}H NMR spectra of the protonated sample (below left) with deuterated product (below right). The corresponding data of **2da**-**2dd** and **2df**-**2di** were obtained similarly.



Peak	Chem shift (ppm)	Area	Area (%)	Product	Chem shift (ppm)	Area	Area (%)
1	5.99	0.96	49.0	**3de-*Z***	5.99	0.05	5
2	5.56	1.00	51.0	**2de-*Z***	5.56	0.95	95

((2*E*,4*Z*)-hexa-2,4-dien-3-yl-4-D)benzene (2df)



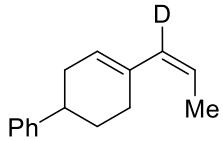
Serial number: Lwt-3-150B. **C1h** was used instead, 3 h, colorless oil, TLC R_f = 0.70 (PE), 63% yield (20.1 mg), r.r. = 96:4, *Z*/*E* = 97:3.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.33 (m, 2H, Ar-H), 7.29 (t, *J* = 7.6 Hz, 2H, Ar-H), 7.25 – 7.14 (m, 1H, Ar-H), 5.98 (q, *J* = 7.0 Hz, 1H, =CH), 5.82 (qt, *J* = 6.9, 1.6 Hz, 1H, =CH), 1.76 (d, *J* = 7.0 Hz, 3H, CH_3), 1.50 (d, *J* = 6.9 Hz, 3H, CH_3).

^{13}C NMR (101 MHz, $CDCl_3$) δ 141.72 (1C, =C), 137.29 (1C, Ar-C), 128.31 (1C, =C), 128.14 (2C, Ar-C), 126.69 (t, *J* = 24.2 Hz, 1C, =CD), 126.59 (1C, Ar-C), 126.37 (2C, Ar-C), 124.47 (1C, =C), 15.49 (1C, CH_3), 14.90 (1C, CH_3).

HRMS (EI) calcd for [M, $C_{12}H_{13}D$]$^+$: 159.1158; found 159.1152.

(*Z*)-4-(prop-1-en-1-yl-1-D)-1,2,3,6-tetrahydro-1,1'-biphenyl (2dg)



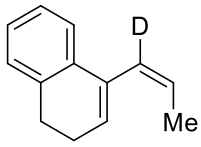
Serial number: Lwt-3-153B. **C1h** was used instead, colorless oil, TLC R_f = 0.70 (PE), 85% yield (33.9 mg), r.r. = 91:9, *Z*/*E* > 98:2.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.28 (m, 2H, Ar-H), 7.26 – 7.15 (m, 3H, Ar-H), 5.72(dq, *J* = 4.6 Hz, 2.4 Hz, 1H, =CH), 5.44 (q, *J* = 7.3 Hz, 1H, =CH), 2.79 (ddt, *J* = 14.9 Hz, 8.0 Hz, 2.8 Hz, 1H, CH), 2.45 – 2.21 (m, 4H, CH_2CH_2), 2.02 – 1.96 (m, 1H, CH), 1.83 (d, *J* = 7.2 Hz, 3H, CH_3), 1.81 –1.73 (m, 1H, CH).

^{13}C NMR (101 MHz, $CDCl_3$) δ 147.01 (1C, Ar-C), 135.13 (1C, =C), 131.71 (t, *J* = 23.2 Hz, 1C, =CD), 128.34 (2C, Ar-C), 126.84 (2C, Ar-C), 126.71 (1C, =C), 125.99 (1C, Ar-C), 123.56 (1C, =C), 39.75 (1C, CH), 33.84 (1C, CH_2), 30.03 (1C, CH_2), 29.63 (1C, CH_2), 14.91 (1C, CH_3).

HRMS (EI) calcd for [M, $C_{15}H_{17}D$]$^+$: 199.1471; found 199.1466.

(*Z*)-4-(prop-1-en-1-yl-1-D)-1,2-dihydronaphthalene (2dh)



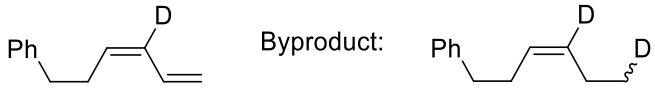
Serial number: Lwt-3-174B. **C1h** was used instead, colorless oil, TLC *Rf* = 0.80 (PE), 82% yield (28.1 mg), r.r. = 89:11, *Z*/*E* > 98:2.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 – 7.13 (m, 4H, Ar-H), 5.94 (t, *J* = 4.7 Hz, 1H, =CH), 5.82 (q, *J* = 7.1 Hz, 1H, =CH), 2.79 (t, *J* = 8.0 Hz, 2H, CH_2), 2.40 – 2.33 (m, 2H, CH_2), 1.74 (dd, *J* = 6.9, 1.1 Hz, 3H, CH_3).

^{13}C NMR (101 MHz, $CDCl_3$) δ 136.20 (1C, =C), 135.02 (1C, Ar-C), 133.58 (1C, Ar-C), 127.84 (t, *J* = 7.1 Hz, 1C, =CD), 127.69 (1C, Ar-C), 127.59 (1C, Ar-C), 127.48 (1C, Ar-C), 126.84 (1C, Ar-C), 126.38 (1C, =C), 124.07 (1C, =C), 28.10 (1C, CH_2), 23.13 (1C, CH_2), 14.73 (1C, CH_3).

HRMS (EI) calcd for [M, $C_{13}H_{13}D$]$^+$: 171.1158; found 171.1151.

(*Z*)-(hexa-3,5-dien-1-yl-4-d)benzene (2di)



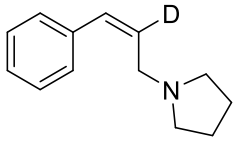
Serial number: Lwt-8-170A. colorless oil, TLC R_f = 0.7 (PE), 72% yield (23 mg), r.r. = 82:18 (5.49 : 6.02 ppm), *Z*/*E* = 98:2. (5% byproduct).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (td, *J* = 7.6, 6.9, 2.4 Hz, 2H, Ar-H), 7.20 (dd, *J* = 7.1, 2.3 Hz, 3H, Ar-H), 5.49 (t, *J* = 7.8Hz, 1H, =CH), 5.25 – 5.15 (m, 1H, =CH), 5.08 (d, *J* = 10.2Hz, 1H, =CH), 2.70 (td, *J* = 8.2, 7.8, 2.2 Hz, 2H, CH_2), 2.51 (qd, *J* = 7.6, 2.3 Hz, 2H, CH_2).

^{13}C NMR (101 MHz, $CDCl_3$) δ 141.65 (1C, Ar-C), 132.01 (1C, Ar-C), 131.39 (2C, Ar-C), 129.35 (t, *J* = 21.2 Hz, 1C, =CD), 128.39 (2C, Ar-C), 128.31 (2C, Ar-C), 125.86 (1C, Ar-C), 117.20 (1C, =C), 35.81 (1C, CH_2), 29.54 (1C, CH_2).

HRMS (EI) calcd for [M, $C_{12}H_{13}D$]$^+$: 159.1158; found 159.1151.

(*Z*)-1-(3-phenylallyl-2-D)pyrrolidine (3ea)



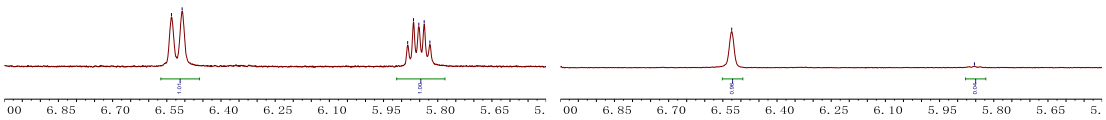
Serial number: Lwt-4-3C. **C1i** was used instead, 10 h, colorless oil, TLC R_f = 0.5 (MeOH), 98% yield (36.9 mg), r.r. = 96:4, *Z*/*E* > 98:2.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.31 (m, 2H, Ar-H), 7.26 – 7.21 (m, 3H, Ar-H), 6.53 (s, 1H, =CH), 3.41 (d, *J* = 2.0 Hz, 2H, NCH_2), 2.59 – 2.49 (m, 4H, $2CH_2$), 1.79 (p, *J* = 3.2 Hz, 4H, CH_2CH_2).

^{13}C NMR (101 MHz, $CDCl_3$) δ 137.51 (1C, Ar-C), 135.32 (1C, =C), 128.85 (2C, Ar-C), 128.02 (2C, Ar-C), 127.91 (t, *J* = 23.2 Hz, 1C, =CD), 126.47 (1C, Ar-C), 48.82 (2C, NCH_2), 43.39 (1C, CH), 20.69 (2C, CH_2).

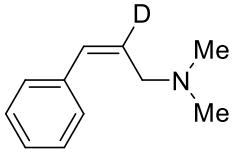
HRMS (EI) calcd for [M, $C_{13}H_{16}DN$]$^+$: 188.1424; found 188.1408.

The r.r. (**3ea**/**2ea**) and *Z*/*E* (**3ea-*Z***/**3ea-*E***) was determined by analysis of 400 MHz ^{1}H NMR spectra of the protonated sample (below left) with deuterated product (below right).



Peak	Chem shift (ppm)	Area	Area (%)	Product	Chem shift (ppm)	Area	Area (%)
1	6.53	1.01	50.2	**3ea-*Z***	6.53	0.96	96
2	5.85	1.00	49.8	**2ea-*Z***	5.85	0.04	4

(*Z*)-*N*,*N*-dimethyl-3-phenylprop-2-en-1-amine-2-D (3eb)



Serial number: Lwt-4-156B. **C1i** was used instead, 10 h, colorless oil, TLC R_f = 0.5

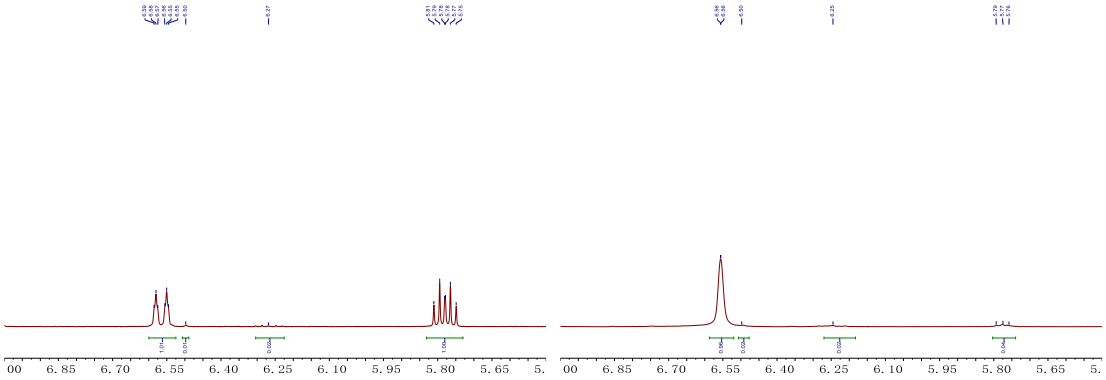
(EA), 98% yield (31.8 mg), r.r. = 94:6, *Z*/*E* > 98:2.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.35 (m, 2H, Ar-H), 7.28 – 7.25 (m, 3H, Ar-H), 6.58 (s, 1H), 3.22 (s, 2H, CH_2), 2.27 (s, 6H, $N(CH_3)_2$).

^{13}C NMR (101 MHz, $CDCl_3$) δ 137.10 (1C, Ar-C), 130.64 (1C, =C), 129.98 (t, *J* = 24.2 Hz, 1C, =CD), 128.83 (2C, Ar-C), 128.03 (2C, Ar-C), 126.73 (1C, Ar-C), 57.27 (2C, CH_2), 45.37 (2C, $N(CH_3)_2$).

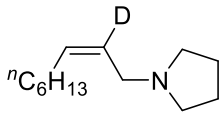
HRMS (EI) calcd for [M, $C_{11}H_{14}DN]^+$: 162.1267; found 162.1262.

The r.r. (**3eb**/**2eb**) and *Z*/*E* (**3eb-*Z***/**3eb-*E***) was determined by analysis of 400 MHz ^{1}H NMR spectra of the protonated sample (below left) with deuterated product (below right).



Peak	Chem shift (ppm)	Area	Area (%)	Product	Chem shift (ppm)	Area	Area (%)
1	6.56	1.01	49.5	**3eb-*Z***	6.56	0.96	92
2	6.50	0.01	0.50	**3eb-*E***	6.50	0.02	2
3	6.27	0.02	1.00	**2eb-*E***	6.25	0.02	2
4	5.78	1.00	49.0	**2eb-*Z***	5.77	0.04	4

(*Z*)-1-(non-2-en-1-yl-2-D)pyrrolidine (3ec)



Serial number: Lwt-4-148A. **C1h** was used instead, 10 h, colorless oil, TLC R_f = 0.5 (EA), 80% yield (31.5 mg), r.r. > 98:2, *Z*/*E* > 98:2.

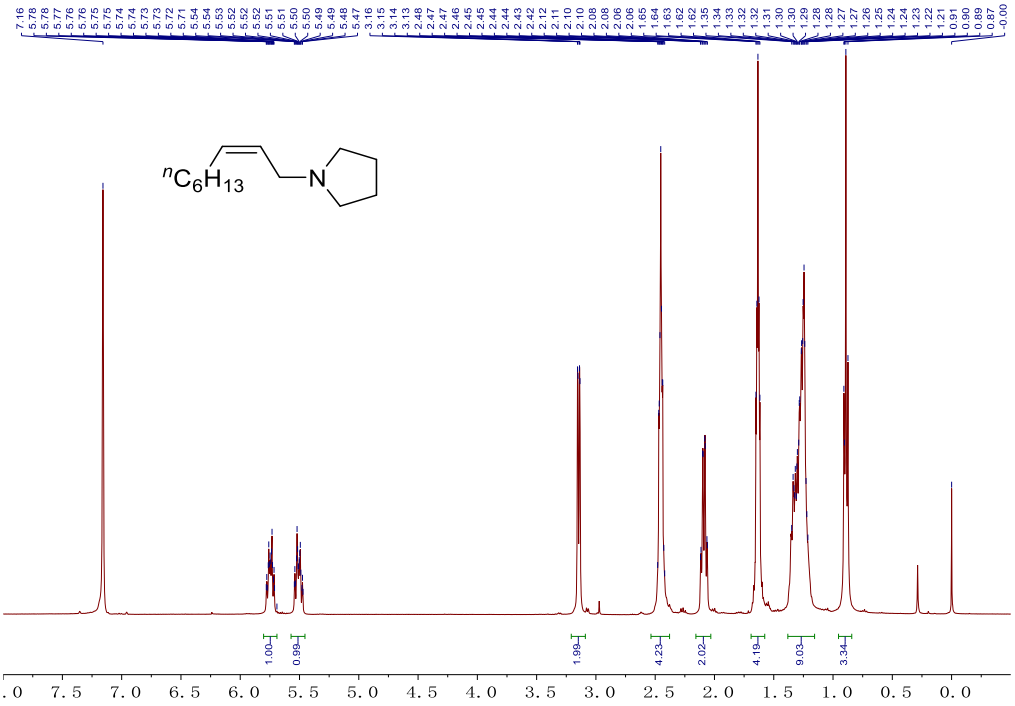
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.48 (t, *J* = 8.0 Hz, 1H, =CH), 3.12 (s, 2H, NCH_2), 2.50 (t, *J* = 8.0 Hz, 4H, NCH_2CH_2), 2.06 (q, *J* = 7.1 Hz, 2H, CH_2), 1.83 – 1.71 (m, 4H, CH_2CH_2), 1.53 – 1.27 (m, 8H, CH_2CH_2), 0.88 (t, *J* = 4.0 Hz, 3H, CH_3).

^{13}C NMR (101 MHz, $CDCl_3$) δ 131.84 (1C, =C), 126.63 (t, *J* = 23.2 Hz, 1C, =CD),

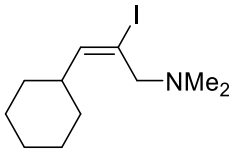
54.08 (2C, NCH_2), 52.48 (1C, NCH_2), 31.75 (1C, CH_2), 29.58 (1C, CH_2), 28.98 (1C, CH_2), 27.47 (1C, CH_2), 23.47 (2C, $2CH_2$), 22.64 (1C, CH_2), 14.10 (1C, CH_3).

HRMS (EI) calcd for [M, $C_{13}H_{24}DN$]$^+$: 196.2050; found 196.2045.

The *Z* configuration of **3ec** was determined according to **3ec-H_2O** (^{1}H NMR in C_6D_6)[10].



(*E*)-3-cyclohexyl-2-iodo-*N*,*N*-dimethylprop-2-en-1-amine (3ed)



Serial number: Lwt-4-169A. **C1i** was used instead, with 0.02 mmol EtMgBr, 10 h, colorless oil, TLC R_f = 0.5 (EA), 67% yield (39.2 mg), r.r. > 98:2, *Z*/*E* < 2:98.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.23 (d, *J* = 9.8 Hz, 1H, =CH), 3.00 (s, 2H, NCH_2), 2.46 – 2.33 (m, 1H, CH), 2.25 (s, 6H, $N(CH_3)_2$), 1.75 – 1.57 (m, 5H, CH_2), 1.32 – 1.04 (m, 5H, CH_2).

^{13}C NMR (101 MHz, $CDCl_3$) δ 150.02 (1C, =C), 100.11 (1C, =C), 64.22 (1C, NCH_2), 44.74 (2C, $N(CH_3)_2$), 40.76 (1C, CH_2), 32.60 (2C, CH_2CH_2), 25.71 (1C, CH_2), 25.62 (2C, CH_2CH_2).

HRMS (EI) calcd for [M, $C_{11}H_{20}IN$]$^+$: 293.0640; found 293.0635.

Stereochemistry of C=C bond was determined by NOESY (**Figure S1**). Because H^c and H^d has NOE interaction, the **3ed** should be with *E* configuration.

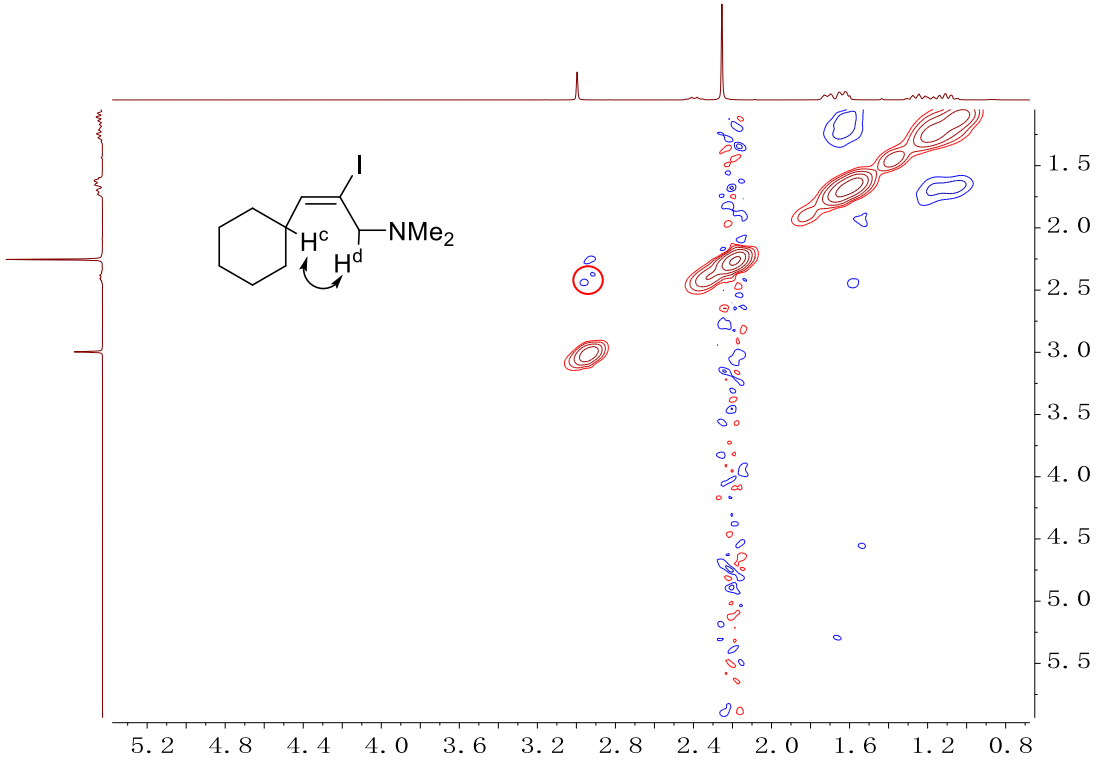
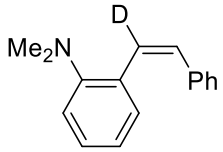


Figure S1. NOESY for 3ed

(*Z*)-*N*,*N*-dimethyl-2-(2-phenylvinyl-1-D)aniline (3ee)



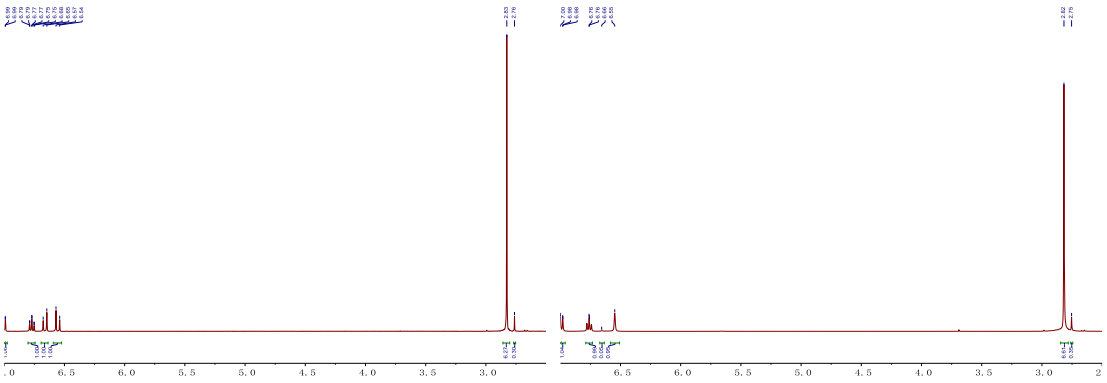
Serial number: Lwt-4-41A. 10 h, colorless oil, TLC R_f = 0.25 (PE/EA= 50:1), 98% yield (44.1 mg), r.r. = 95:5, *Z*/*E* = 95:5.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.29 (m, 2H, Ar-H), 7.23 – 7.13 (m, 5H, Ar-H), 6.99 (dd, *J* = 8.1, 1.2 Hz, 1H, Ar-H), 6.76 (td, *J* = 7.4, 1.2 Hz, 1H, Ar-H), 6.55 (s, 1H, =CH), 2.82 (s, 6H, $N(CH_3)_2$).

^{13}C NMR (101 MHz, $CDCl_3$) δ 152.47 (1C, Ar-C), 137.25 (1C, Ar-C), 130.43 (1C, =C), 129.27 (t, *J* = 23.5 Hz, 1C, =CD), 128.71 (2C, Ar-C), 128.61 (1C, Ar-C), 128.10 (2C, Ar-C), 127.98 (2C, Ar-C),127.79 (1C, Ar-C), 126.83 (1C, Ar-C), 121.14 (1C, Ar-C), 117.18 (1C, Ar-C), 44.14 (2C, $N(CH_3)_2$).

HRMS (EI) calcd for [M, $C_{16}H_{16}DN]^+$: 224.1424; found 224.1415.

The r.r. (**3ee**/**2ee**) and *Z*/*E* (**3ee-*Z***/**3ee-*E***) was determined by analysis of 400 MHz ^{1}H NMR spectra of the protonated sample (below left) with deuterated product (below right).[11]



Peak	Chem shift (ppm)	Area	Area (%)	product	Chem shift (ppm)	Area	Area (%)
1	6.67	1.00	50.0	**2ee-*Z***	6.65	0.05	5
2	6.55	1.00	50.0	**3ee-*Z***	6.55	0.95	95
3	2.83	6.27	95	**3ee-*Z*+2ee-*Z***	2.82	6.61	95
4	2.76	0.30	5	**3ee-*E*+2ee-*E***	2.75	0.35	5

Reaction site was determined by NOESYof protonated **3ee** (**Figure S2**). Because NCH_3 and H^e has NOE interaction.

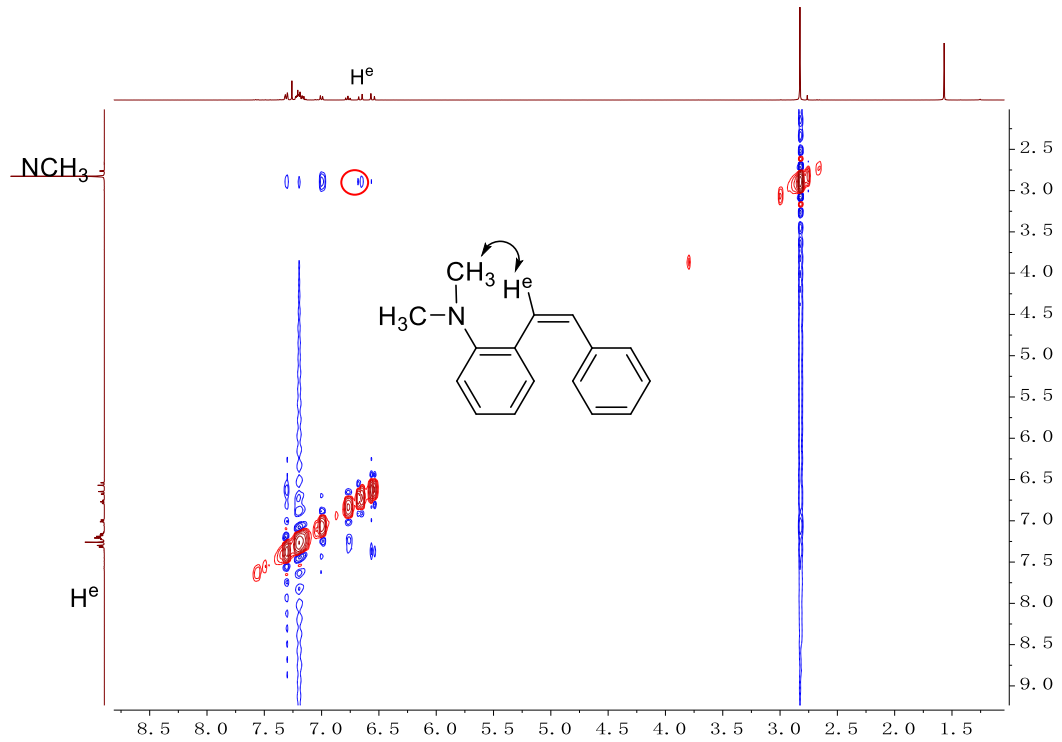
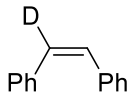


Figure S2. NOESY for protonated 3ee

(*Z*)-(ethene-1,2-diyl-1-D)dibenzene (2fa)[12]

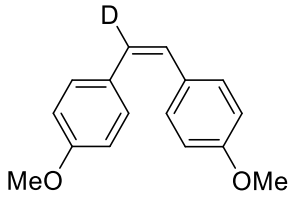


Serial number: Lwt-9-38A. 24 h, colorless oil, TLC R_f = 0.70 (PE), 83% yield (30 mg), *Z*/*E* = 96:4.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 – 7.14 (m, 10H, Ar-H), 6.60 (d, *J* = 2.2 Hz, 1H, =CH).

^{13}C NMR (101 MHz, $CDCl_3$) δ 137.10 (2C, Ar-C), 130.07 (2C, Ar-C), 128.83 (4C, Ar-C), 128.17 (4C, Ar-C), 127.06 (1C, =CH).

(*Z*)-4,4'-(ethene-1,2-diyl-1-D)bis(methoxybenzene) (2fb)[13]

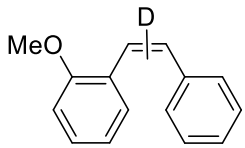


Serial number: Lwt-9-30. 24 h, colorless oil, TLC R_f = 0.60 (PE/EA = 20:1), 95% yield (47 mg), *Z*/*E* = 96:4.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 – 7.16 (m, 4H, Ar-H), 6.80 – 6.73 (m, 4H, Ar-H), 6.43 (s, 1H, =CH),3.76 (s, 6H, OCH_3).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.46 (2C, Ar-C), 129.98 (4C, Ar-C), 128.16 (4C, Ar-C), 127.97 – 127.36 (1C, =C), 113.54 (2C, Ar-C), 55.11 (2C, OCH_3).

(*Z*)-1-methoxy-2-(2-phenylvinyl-1-D)benzene (2fc)[14]

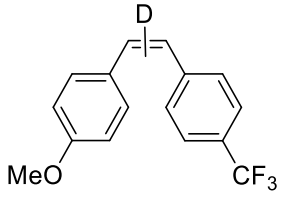


Serial number: Lwt-9-38C. 12 h, colorless oil, TLC R_f = 0.60 (PE/EA = 20:1), 99% yield (47 mg), r.r. = 77:23, *Z*/*E* = 96:4.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 – 7.12 (m, 8H, Ar-H), 6.89 (dd, *J* = 8.2, 1.1 Hz, 1H, Ar-H), 6.75 (td, *J* = 7.5, 1.3 Hz, 1H, Ar-H), 6.63 (s, 1H, =CH), 3.82 (d, J = 1.2 Hz, 3H, OCH_3).

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.12 (1C, Ar-C), 137.24 (1C, Ar-C), 137.16 (1C, Ar-C), 130.03 (1C, Ar-C), 128.78 (2C, Ar-C), 128.54 (1C, Ar-C), 127.98 (2C, Ar-C), 126.85 (1C, Ar-C), 126.50 – 125.39 (1C, =C), 120.12 (1C, =C), 120.12 (1C, Ar-C), 110.56 (1C, Ar-C), 55.36 (1C, OCH_3).

(*Z*)-1-methoxy-4-(2-(4-(trifluoromethyl)phenyl)vinyl-1-D)benzene (2fd)[15]



Serial number: Lwt-9-38B. 24 h, colorless solid, TLC R_f = 0.60 (PE/EA = 20:1), 99% yield (28 mg, 0.1 mmol SM, 5mol% **C1g**), r.r. = 68:32, *Z*/*E* = 87:13.

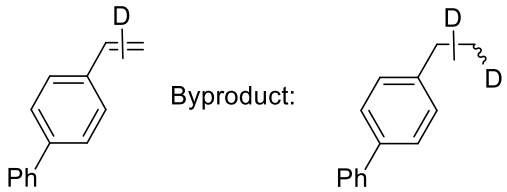
^{1}H NMR (400 MHz, $CDCl_3$) δ7.48 (d, *J* = 8.5 Hz, 2H, Ar-H), 7.36 (d, *J* = 8.1 Hz, 2H, Ar-H), 7.15 (d, *J* = 8.7 Hz, 2H, Ar-H), 6.77 (d, *J* = 9.0 Hz, 2H, Ar-H), 6.64 (s, 1H, =CH), 3.79 (s, 3H, OCH_3).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.99 (1C, Ar-C), 141.20 (1C, Ar-C), 131.66 (1C, Ar-C), 130.13 (2C, Ar-C), 129.03 (2C, Ar-C), 128.85 (q, *J* = 32.3 Hz, 1C, Ar-C), 126.24 (1C, =C), 126.24 (1C, =C), 125.14 (q, *J* = 3.9 Hz, 2C, Ar-C), 124.93 (q, *J* = 210 Hz, 1C, CF_3), 113.74 (2C, Ar-C), 55.17 (1C, OCH_3).

^{19}F NMR (376 MHz, $CDCl_3$) δ -62.47.

HRMS (EI) calcd for [M, $C_{16}H_{12}DF_3O$]$^+$: 279.0981; found 279.0972.

4-(vinyl-1-d)-1,1'-biphenyl (2ga)[16]

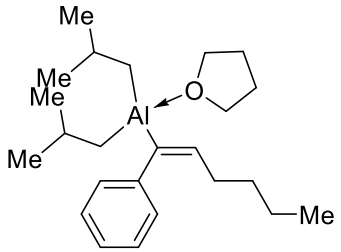


Serial number: Lwt-9-48B. **C1i** was used instead, 6 h, white solid, TLC R_f = 0.65 (PE), 84% NMR yield (36 mg), r.r. = 63:37 (5.26 : 6.75 ppm). (13% byproduct)

^{1}H NMR (400 MHz, $CDCl_3$) δ7.61 – 7.54 (m, 4H, Ar-H), 7.47 (d, *J* = 8.1 Hz, 2H, Ar-H), 7.42 (t, *J* = 7.6 Hz, 2H, Ar-H), 7.33 (t, *J* = 7.3 Hz, 1H, Ar-H), 6.75 (d, *J* = 17.6 Hz, 1H, =CH), 5.99 – 5.64 (m, 1H, =CH), 5.26 (s, 1H, =CH).

^{13}C NMR (101 MHz, $CDCl_3$) δ 140.70 (1C, Ar-C), 140.54 (1C, Ar-C),136.50 (1C, Ar-C), 136.27 (1C, =C), 128.75 (2C, Ar-C), 127.28 (1C, Ar-C), 127.19 (2C, Ar-C), 126.93 (2C, Ar-C),126.60 (2C, Ar-C), 113.71 (1C, =C).

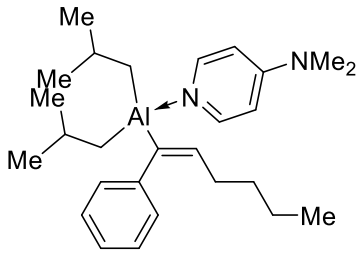
(*E*)-diisobutyl(1-phenylhex-1-en-1-yl)aluminum tetrahydrofuran adduct (2aa'-THF)



^{1}H NMR (400 MHz, C_6D_6) δ 7.23 (t, *J* = 7.5 Hz, 2H, Ar-H), 7.11 (d, *J* = 7.6 Hz, 2H, Ar-H), 7.01 (t, *J* = 7.4 Hz, 1H, Ar-H), 6.20 (t, *J* = 6.7 Hz, 1H, =CH), 3.34 (d, *J* = 6.4 Hz, 4H, OCH_2), 2.21 (dq, *J* = 20.5, 6.8 Hz, 4H, 2CH+CH_2), 1.52 – 1.38 (m, 2H, CH_2), 1.36 – 1.31 (m, 2H, CH_2), 1.27 (d, *J* = 6.5 Hz, 12H, 4CH_3), 0.86 (br, 4H, 2CH_2), 0.83 (t, *J* = 7.3 Hz, 3H, CH_3), 0.31 (d, *J* = 7.3 Hz, 4H, 2CH_2).

^{13}C NMR (101 MHz, C_6D_6) δ149.83 (1C, =C), 141.68 (1C, Ar-C), 128.08 (2C, Ar-C), 127.14 (2C, Ar-C), 123.54 (1C, =C), 70.99 (2C, OCH_2), 32.89 (2C, 2CH_2), 30.27 (2C, 2CH_2), 28.93 (4C, 4CH_3), 27.07 (2C, 2CH), 24.76 (2C, 2CH_2), 22.79 (2C, 2CH_2), 14.26 (1C, CH_3).

(*E*)-diisobutyl(1-phenylhex-1-en-1-yl)aluminum DMAP adduct (2aa'-DMAP)



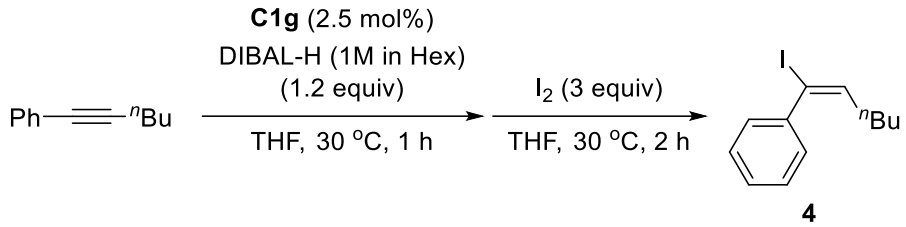
^{1}H NMR (400 MHz, C_6D_6) δ 8.03 (br, 2H, DMAP-H), 7.25 (ddt, *J* = 12.3, 8.0, 4.1 Hz, 4H, Ar-H), 7.08 – 6.95 (m, 1H, Ar-H), 6.43 (t, *J* = 6.8 Hz, 1H, =CH), 5.72 – 5.51 (m, 2H, DMAP-H), 2.35 (m, 4H, 2CH+CH_2), 1.87 (s, 6H, NMe_2), 1.54

(ddd, J = 12.4, 8.7, 6.5 Hz, 2H, CH_2), 1.40 – 1.36 (m, 2H, CH_2), 1.36 (d, J = 6.5 Hz, 12H, $4CH_3$), 0.86 (t, J = 7.3 Hz, 3H, CH_3), 0.66 (d, J = 7.1 Hz, 4H, $2Al\text{-}CH_2$).

^{13}C NMR (101 MHz, C_6D_6) δ 155.05 (1C, =C), 150.57 (1C, Ar-C), 146.98 (1C, Ar-C), 140.67 (2C, Ar-C), 127.96 (2C, Ar-C), 127.26 (2C, Ar-C), 123.21 (2C, Ar-C), 106.46 (1C, Ar-C), 38.17 (2C, NMe_2), 33.20 (1C, CH_2), 30.56 (2C, $2CH_2$), 29.25 (1C, CH), 29.21 (2C, $2CH_3$), 27.78 (1C, CH), 27.59 (2C, $2CH_3$), 22.94 (1C, CH_2), 22.80 (1C, CH_2), 14.43 (1C, CH_3).

8. Transformations of Product 2aa'

8.1 Synthesis of (*E*)-(1-iodohex-1-en-1-yl)benzene (4)



4

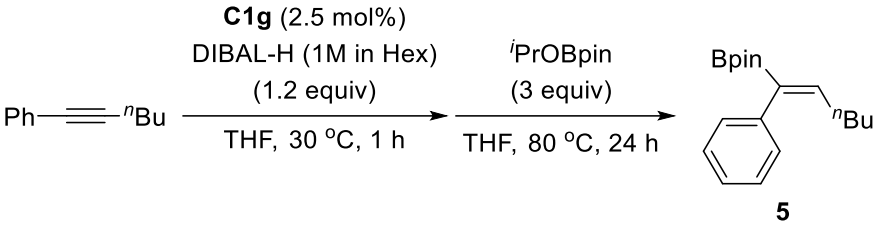
In an argon-filled glovebox, a vial (10 mL) was charged with **C1g** (0.005 mmol), anhydrous THF (1 mL). The reaction mixture was stirred at 30 °C for 1 minute, then internal alkyne **1aa** (0.2 mmol), DIBAL-H (1.0 M in hexanes, 240 μL, 0.24 mmol, 1.2 equiv) was added sequentially. The resulting black solution was allowed to stir for 1 hour. After that, I_2 (153 mg, 0.6 mmol, 3 equiv, in 2mL THF) was added into the reaction solution at 30 °C and stirred for 2 hours before the reaction was quenched with saturated potassium sodium tartrate solution and extracted with EA. The combined organic layer was dried over anhydrous $MgSO_4$, filtered and concentrated under vacumm to afford yellow oil, which was purified by silica gel chromatography (PE) to afford the desired product **4**.

Serial number: Lwt-3-189. colorless oil, TLC R_f = 0.7 (PE), 91% yield (52.1 mg), r.r. = 92:8 (1.98 : 2.55 ppm). The spectroscopic data are in agreement with that previously reported.[17]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.27 (m, 4H, Ar-H), 7.25 – 7.22 (m, 1H, Ar-H), 6.47 (t, *J* = 7.7 Hz, 1H, =CH), 1.98 (q, *J* = 7.4 Hz, 2H, CH_2), 1.36 – 1.22 (m, 4H, CH_2CH_2), 0.82 (t, *J* = 7.2 Hz, 3H, CH_3).

^{13}C NMR (101 MHz, $CDCl_3$) δ 143.68 (1C, =C), 141.79 (1C, Ar-C), 128.68 (2C, Ar-C), 128.09 (2C, Ar-C), 127.87 (1C, Ar-C), 94.47 (1C, =CI), 31.86 (1C, CH_2), 31.25 (1C, CH_2), 22.04 (1C, CH_2), 13.80 (1C, CH_3).

8.2 Synthesis of (*Z*)-4,4,5,5-tetramethyl-2-(1-phenylhex-1-en-1-yl)-1,3,2-dioxaborolane (5)



Prepared according to a literature procedure[18]: In an argon-filled glovebox, a vial (10 mL) was charged with **C1g** (0.005 mmol), anhydrous THF (1 mL). The reaction mixture was stirred at 30 °C for 1 minute, then internal alkyne **1aa** (0.2 mmol), DIBAL-H (1.0 M in hexanes, 240 μL, 0.24 mmol, 1.2 equiv) was added sequentially. The resulting black solution was allowed to stir for 1 hour. After that, 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (^{i}PrO-Bpin; 122.4 μL, 0.60 mmol, 3 equiv) was added dropwise through a syringe into the reaction solution at 30 °C. The vial was removed from the glovebox and allowed to be heated to 80 °C and stirred for 24 hours. The reaction was quenched by dropwise addition of water (3.0 mL) at 0 °C (ice bath) and extracted with with Et_2O (5.0 mL x 3). The combined organic layer was dried over anhydrous $MgSO_4$, filtered and concentrated under vacumm to afford yellow oil, which was purified by silica gel chromatography (PE/EA = 40:1) to afford the desired product **5**. The spectroscopic data are in agreement with that previously reported[19].

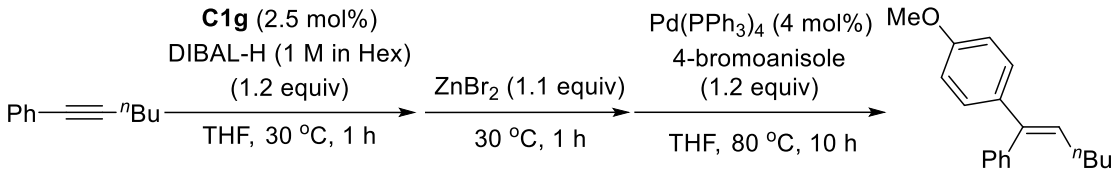
Serial number: Lwt-3-197. colorless oil, TLC *Rf* = 0.6 (PE/EA = 30:1), 86% yield (49.2 mg), r.r. = 91:9 (2.15 : 2.38 ppm).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.28 (m, 2H, Ar-H), 7.22 – 7.17 (m, 1H, Ar-H), 7.16 – 7.10 (m, 2H, Ar-H), 6.58 (td, *J* = 7.3, 1.5 Hz, 1H, =CH), 2.14 (qd, *J* = 7.4, 1.5 Hz, 2H, CH_2), 1.42 – 1.35 (m, 2H, CH_2), 1.31 – 1.30 (m, 2H, CH_2), 1.28 – 1.25 (m, 12H, CH_3), 0.83 (td, *J* = 7.2, 1.5 Hz, 3H, CH_3).

^{13}C NMR (101 MHz, $CDCl_3$) δ 148.48 (1C, =C), 140.24 (1C, Ar-C), 128.93 (2C, Ar-C), 128.01(1C, =C), 127.66 (2C, Ar-C), 125.75 (1C, Ar-C), 83.36 (1C, OC), 31.50 (1C, CH_2), 29.63 (1C, CH_2), 24.76 (4C, CH_3), 22.45 (1C, CH_2), 13.91 (1C, CH_3).

^{11}B NMR (128 MHz, $CDCl_3$) δ 29.80.

8.3 Synthesis of (*E*)-1-methoxy-4-(1-phenylhex-1-en-1-yl)benzene (6)



6

Prepared according to a literature procedure[20]: In an argon-filled glovebox, a vial (10 mL) was charged with **C1g** (0.005 mmol), anhydrous THF (1 mL), The reaction mixture was stirred at 30 °C for 1 minute, then internal alkynes **1aa** (0.2 mmol), DIBAL-H (1.0 M in hexanes, 240 μL, 0.24 mmol, 1.2 equiv) was added sequentially. The resulting black solution was allowed to stir for 1 hour. After that, $ZnBr_2$ (50 mg, 0.22 mmol, 1.1 equiv) was added into the reaction solution at 30 °C. The resulting solution was allowed to stir at 30 °C for 2 hours. $Pd(PPh_3)_4$ (9 mg, 0.008 mmol, 4 mol %), 4-bromoanisole (46 mg, 0.24 mmol, 1.2 equiv) were added sequentially. The vial was allowed to be heated to 80 °C and stirred for 10 hours before the reaction was quenched by dropwise addition of water. The combined organic layer was dried over anhydrous $MgSO_4$, filtered and concentrated under vacumm to afford afford yellow oil, which was purified by silica gel chromatography (PE/EA = 50:1) to afford the desired product **6**. The spectroscopic data are in agreement with that previously reported[21].

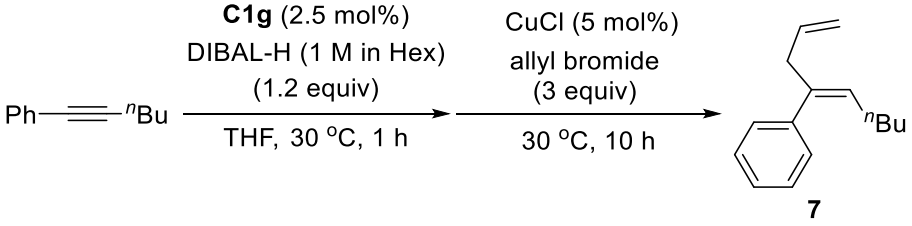
Serial number: Lwt-4-176. TLC Rf = 0.32 (PE/EA = 50:1), 77% yield (41 mg), colorless oil, r.r. = 91:9 (5.98 : 6.64 ppm).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.32 (m, 2H, Ar-H), 7.30 (dd, J = 6.9, 5.3 Hz, 1H, Ar-H), 7.19 – 7.10 (m, 4H, Ar-H), 6.79 (d, J = 8.8 Hz, 2H, Ar-H), 5.98 (t, J = 7.5 Hz, 1H, =CH), 3.78 (s, 3H, OCH_3), 2.08 (q, J = 7.4 Hz, 2H, CH_2), 1.45 – 1.36 (m, 2H, CH_2), 1.35 – 1.25 (m, 2H, CH_2), 0.85 (t, J = 7.2 Hz, 3H, CH_3).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.59 (1C, Ar-C), 140.80 (1C, Ar-C), 140.59 (1C, Ar-C), 135.68 (1C, =C), 129.90 (2C, Ar-C) ,128.61 (1C, Ar-C) , 128.23 (2C, Ar-C) , 128.04 (2C, Ar-C) , 126.69 (1C, =C), 113.43 (2C, Ar-C), 55.26 (1C, OCH_3), 32.27 (1C, CH_2), 29.43 (1C, CH_2), 22.34 (1C, CH_2), 13.97 (1C, CH_3).

HRMS (EI) calcd for [M, $C_{19}H_{22}O$]$^+$: 266.1671; found 266.1662.

8.4 Synthesis of (*Z*)-nona-1,4-dien-4-ylbenzene (7)



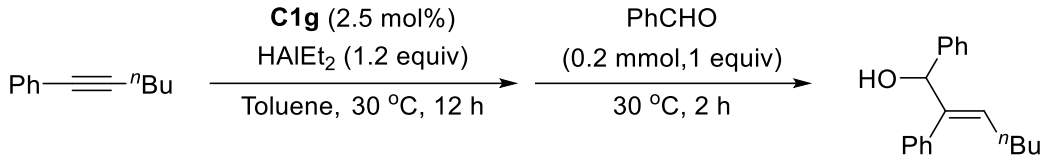
In an argon-filled glovebox, a vial (10 mL) was charged with **C1g** (0.005 mmol), anhydrous THF (1 mL). The reaction mixture was stirred at 30 °C for 1 minute, then internal alkyne **1aa** (0.2 mmol), DIBAL-H (1 M in Hexanes, 240 μL, 0.24 mmol, 1.2 equiv) were added sequentially. The resulting black solution was allowed to stir for 1 hour. After that, CuCl (1 mg, 0.01 mmol, 5 mol %), allyl bromide (52 μL, 0.6 mmol, 3 equiv) were added sequentially into the reaction solution at 30 °C and stirred for 10 hours before the reaction was quenched with saturated potassium sodium tartrate solution and extracted with ethyl acetate. The combined organic layer was dried over anhydrous $MgSO_4$, filtered and concentrated under vacumm to afford yellow oil, which was purified by silica gel chromatography (PE) to afford the desired product **7**. The spectroscopic data are in agreement with that previously reported[22].

Serial number: Lwt-4-178. colorless oil, TLC *Rf* = 0.59 (PE), 82 % yield (33 mg), r.r. = 92:8 (5.48 : 6.28 ppm).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.28 (m, 2H, Ar-H), 7.25 – 7.20 (m, 1H, Ar-H), 7.17 – 7.13 (m, 2H, Ar-H), 5.86 – 5.73 (m, 1H, =CH), 5.46 (tt, *J* = 7.3, 1.3 Hz, 1H, =CH), 5.05 – 4.93 (m, 2H, $=CH_2$), 3.07 (dq, *J* = 6.8, 1.3 Hz, 2H, $=CCH_2$), 1.96 (q, *J* = 7.2 Hz, 2H, $=CHCH_2$), 1.36 – 1.18 (m, 4H, CH_2 CH_2), 0.82 (t, *J* = 7.1 Hz, 3H, CH_3).

^{13}C NMR (101 MHz, $CDCl_3$) δ 141.29 (1C, Ar-C), 138.76 (1C, =C), 136.70 (1C, =C), 128.51(1C, Ar-C), 128.43 (2C, Ar-C), 127.91 (2C, Ar-C), 126.37 (1C, =CH), 115.73 (1C, $=CH_2$), 43.45 (1C, CH_2), 32.25 (1C, CH_2), 28.66 (1C, CH_2), 22.28 (1C, CH_2), 13.95 (1C, CH_3).

8.5 Synthesis of (*E*)- 1,2-diphenylhept-2-en-1-ol (8)



1aa
0.3 mmol

8
37% yield
r.r. = 92:8

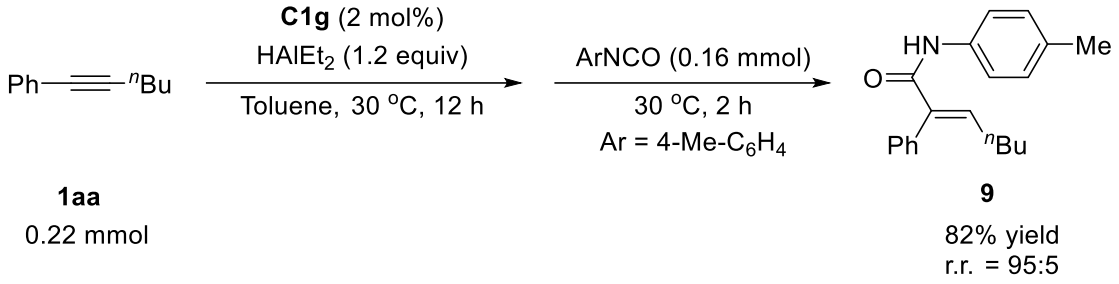
In an argon-filled glovebox, a vial (100 mL) was charged with **C1g** (0.0075 mmol, 4.9 mg), internal alkyne **1aa** (47.5 mg, 0.3 mmol, 1.5 equiv), anhydrous toluene (1.5 mL). The reaction mixture was stirred at 30 °C for 1 minute, then $HAlEt_2$ (1.0 M in toluene, 0.24 mL, 0.24 mmol, 1.2 equiv) was added sequentially. The resulting black solution was allowed to stir for 12 hours. After **1aa** was consumed, the reaction solution was added into PhCHO (21.5 mg, 0.2 mmol, 1.0 equiv, in 1mL toluene) at 0 °C and stirred for 2 hours. After that the resulting mixture was quenched with 3M HCl and extracted with DCM and washed by brine. The combined organic layers was dried over $MgSO_4$, concentrated in vacumm, purified by SiO_2 column chromatography (2:1 hexanes/EA as eluent) to afford allylic alcohols **8**.

Serial number: Lwt-7-191. Colorless oil, TLC R_f = 0.3 (PE/EA = 2:1), 37% yield (27 mg), r.r = 91:9 (5.42:5.33 ppm).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.27 (m, 4H, Ar-H), 7.25 – 7.14 (m, 4H, 4H, Ar-H), 7.02 – 6.78 (m, 2H, 4H, Ar-H), 5.87 – 5.82 (t, J = 8.0 Hz, 1H, =CH), 5.42 (s, 1H, OCH), 2.01 (br, 1H, 4H, OH), 1.92 (q, J = 7.8 Hz, 2H, 4H, CH_2), 1.37 – 1.29 (m, 2H, CH_2), 1.25 (m, 2H, CH_2), 0.82 (t, J = 7.1 Hz, 3H, CH_3).

^{13}C NMR (101 MHz, $CDCl_3$) δ 142.81 (1C, Ar-C), 142.19 (1C, =C), 137.93 (1C, Ar-C), 129.42 (1C, Ar-C), 129.39 (2C, Ar-C), 128.09 (2C, Ar-C), 127.85 (2C, Ar-C), 127.32 (1C, Ar-C), 126.82 (1C, =CH), 126.60 (2C, Ar-C), 78.53 (1C, OCH), 31.90 (1C, CH_2), 28.25 (1C, CH_2), 22.27 (1C, CH_2), 13.91 (1C, CH_3).

8.6 Synthesis of (*E*)-2-phenyl-N-(*p*-tolyl)hept-2-enamide (9)



1aa
0.22 mmol

9
82% yield
r.r. = 95:5

In an argon-filled glovebox, a vial (100 mL) was charged with **C1g** (0.005 mmol, 3.3 mg), internal alkyne **1aa** (31.6 mg, 0.2 mmol, 1.25 equiv), anhydrous toluene (1 mL). The reaction mixture was stirred at 30 °C for 1 minute, then $HAlEt_2$ (1.0 M in toluene, 0.24 mL, 0.24 mmol, 1.2 equiv) was added sequentially. The resulting black solution was allowed to stir for 12 hours. After **1aa** was consumed, p-tolyl isocyanate (21.3 mg, 0.16 mmol, 1.0 equiv) was added into the reaction solution at 30 °C and stirred for 2 hours. After that the resulting mixture was quenched with 3M HCl and extracted with EA and washed by brine. The combined organic layers was dried over $MgSO_4$, concentrated in vacumm, purified by SiO_2 column chromatography (10:1 hexanes/EA as eluent) to afford acrylamide **9**.

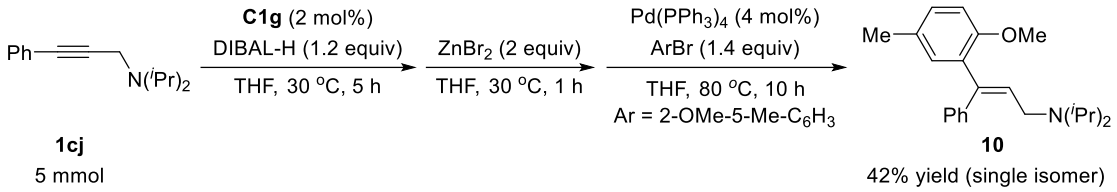
Serial number: Lwt-6-145. Yellow solid, TLC R_f = 0.45 (PE/EA = 10:1), 82% yield (37 mg), r.r. = 95:5 (2.28 : 2.33 ppm).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.37 (m, 3H, Ar-H), 7.31 – 7.27 (m, 4H, Ar-H), 7.15 (t, *J* = 7.8 Hz, 1H, =CH), 7.07 (d, *J* = 8.1 Hz, 2H, Ar-H), 6.98 (s, 1H, NH), 2.28 (s, 3H, CH_3), 2.01 (q, *J* = 7.5 Hz, 2H, CH_2), 1.45 – 1.37 (m, 2H, CH_2), 1.35 – 1.21 (m, 2H, CH_2), 0.83 (t, *J* = 7.1 Hz, 3H, CH_3).

^{13}C NMR (101 MHz, $CDCl_3$) δ 164.54 (1C, =CO), 142.70 (1C, Ar-C), 135.92 (1C, Ar-C), 135.47 (1C, Ar-C), 135.31 (1C, Ar-C), 133.84 (1C, Ar-C), 129.90 (2C, Ar-C), 129.32 (2C, Ar-C), 129.09 (2C, Ar-C), 128.31 (1C, Ar-C), 119.84 (2C, Ar-C), 30.96 (1C, CH_3), 29.15 (1C, CH_2), 22.32 (1C, CH_2), 20.82 (1C, CH_2), 13.80 (1C, CH_3).

HRMS (EI) calcd for [M+Na, $C_{20}H_{23}NONa]^+$: 316.1674; found 316.1675.

8.7 Synthesis of (*E*)-N,N-diisopropyl-3-(2-methoxy-5-methylphenyl)-3-phenylprop-2-en-1-amine (10)



1cj
5 mmol

10
42% yield (single isomer)

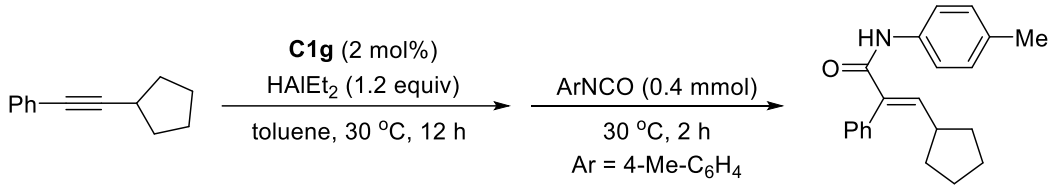
In an argon-filled glovebox, a vial (100 mL) was charged with **C1g** (0.1 mmol, 65 mg), anhydrous THF (15 mL). The reaction mixture was stirred at 30 °C for 1 minute, then internal alkyne **1ch** (1.075 g, 5 mmol), DIBAL-H (1.0 M in hexanes, 6 mL, 6 mmol, 1.2 equiv) was added sequentially. The resulting black solution was allowed to stir for 5 hours. $ZnBr_2$ (2.25 g, 10 mmol, 2 equiv) was added into the reaction solution at 30 °C and stirred for 1 hour. $Pd(PPh_3)_4$ (231 mg, 0.2 mmol, 4 mol %), 3-bromo-4-methoxytoluene (1.41 g, 7 mmol, 1.4 equiv) was added into the reaction solution at 30 °C. Then the reaction mixture was heated up to 80 °C. After stirring 10 hours, the resulting mixture was cooled down to room temperature, quenched with water and extracted with EA and washed by 1 M NaOH solution and brine. The organic layer was concentrated in vacuo, redissolved in Et_2O, and extracted with 3 M HCl (5 mL x 3). The resulting acidic aqueous layer was then basified by the addition of 5M NaOH solution until the pH > 11, extracted with DCM. The combined organic layers was dried over $MgSO_4$, concentrated in vacumm, purified by Al_2O_3 column chromatography (100 g Al_2O_3 + 4 g H_2O, 50:1 hexanes/EA with 0.5% MeOH as eluent) to afford allylic amine **9**. The spectroscopic data are in agreement with that previously reported.[23]

Serial number: Lwt-6-143. colorless oil, TLC R_f = 0.25 (EA), 42% yield (700 mg), single isomer.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 – 7.26 (m, 2H, Ar-H), 7.23 – 7.19 (m, 1H, Ar-H), 7.18 – 7.14 (m, 2H, Ar-H), 7.03 – 7.00 (m, 2H, Ar-H), 6.71 (d, *J* = 8.1 Hz, 1H, Ar-H), 5.89 (t, *J* = 6.4 Hz, 1H, =CH), 3.50 (s, 3H, OCH_3), 3.27 (d, *J* = 6.4 Hz, 2H, CH_2), 3.08-3.01 (m, 2H, 2CH), 2.27 (s, 3H, Ar-CH_3), 0.96 (d, *J* = 6.6, Hz, 12H, 4CH_3).

^{13}C NMR (101 MHz, $CDCl_3$) δ 155.05 (1C, Ar-C), 140.88 (1C, =C), 138.44 (1C, Ar-C), 133.88 (1C, Ar-C), 133.28 (1C, Ar-C), 131.45 (1C, Ar-C), 129.60 (1C, Ar-C), 129.02 (2C, Ar-C), 128.51 (1C, Ar-C), 127.38 (2C, Ar-C), 126.26 (1C, Ar-C), 111.77 (1C, =C), 55.78 (1C, OCH_3), 48.79 (2C, C-H),43.80 (1C, CH_2), 20.75 (4C, CH_3), 20.44 (1C, CH_3).

8.8 Synthesis of (*E*)-3-cyclopentyl-N,2-diphenylacrylamide (11)



1cg
0.5 mmol

11
80% yield (single isomer)

In an argon-filled glovebox, a vial (10 mL) was charged with **C1g** (0.012 mmol, 8 mg), internal alkyne **1cg** (85 mg, 0.5 mmol, 1.25 equiv), anhydrous toluene (2.5 mL). The reaction mixture was stirred at 30 °C for 1 minute, then $HAlEt_2$ (1.0 M in toluene, 0.6 mL, 0.6 mmol, 1.2 equiv) was added sequentially. The resulting black solution was allowed to stir for 12 hours. After **1cg** was consumed, ArNCO (53.3 mg, 10 mmol, 1.0 equiv) was added into the reaction solution at 30 °C and stirred for 2 hours. After that, the resulting mixture was quenched with 3M HCl and extracted with EA and washed by brine. The combined organic layers was dried over $MgSO_4$, concentrated in vacumm, purified by SiO_2 column chromatography (10:1 hexanes/EA as eluent) to afford acrylamide **11**.

Serial number: Lwt-7-183. Light yellow solid, TLC R_f = 0.45 (PE/EA = 10:1), 80% yield (91 mg), single isomer.

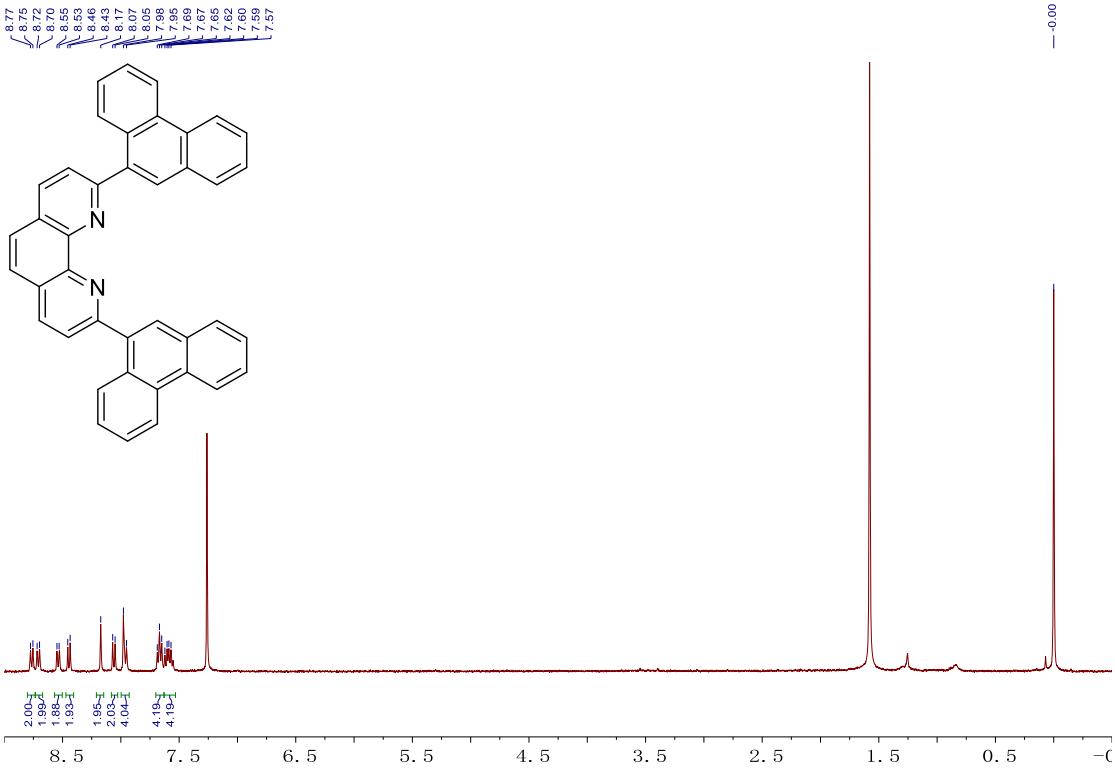
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.41 (m, 3H, Ar-H), 7.31 – 7.26 (m, 4H, Ar-H), 7.07 (d, J = 6.0 Hz, 2H, Ar-H), 7.04 (d, J = 8.2 Hz, 1H, =CH), 6.95(s, br, 1H, N-H), 2.38 – 2.30 (m, 1H, CH), 2.28 (s, 2H, CH_3), 1.70 (ddq, J = 7.6, 5.5, 3.2, 2.8 Hz, 4H, CH_2CH_2), 1.53 – 1.36 (m, 4H, CH_2CH_2).

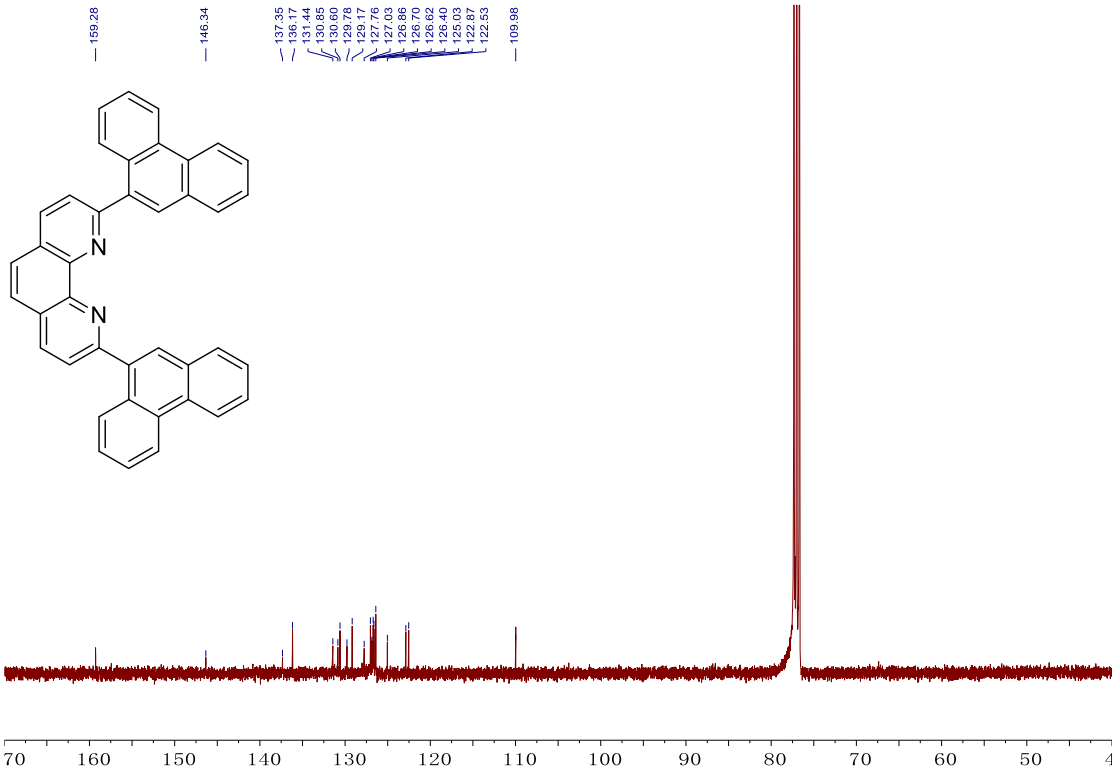
^{13}C NMR (101 MHz, $CDCl_3$) δ 164.69 (1C, C=O) , 147.33 (1C, Ar-C) , 135.73 (1C, =CH), 135.36 (1C, =C), 134.35 (1C, Ar-C), 133.83 (1C, Ar-C), 130.00 (2C, Ar-C), 129.33 (2C, Ar-C), 129.06 (2C, Ar-C), 128.28 (1C, Ar-C), 119.84 (2C, Ar-C), 40.04 (1C, CH), 33.46 (1C, CH_2), 25.61 (1C, CH_2), 20.83 (1C, CH_3).

HRMS (EI) calcd for [M, $C_{21}H_{23}NO]^+$: 305.1774; found 305.1772.

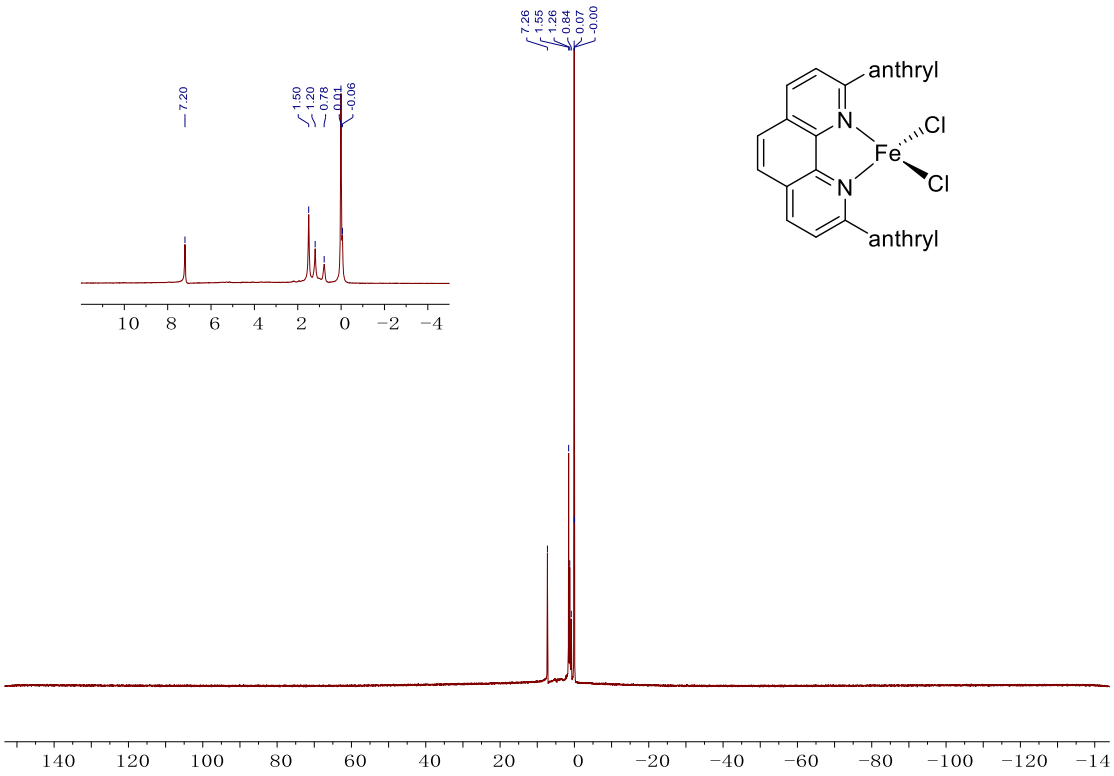
9. NMR Spectra of New Compounds

2,9-di(phenanthren-9-yl)-1,10-phenanthroline (L1h)

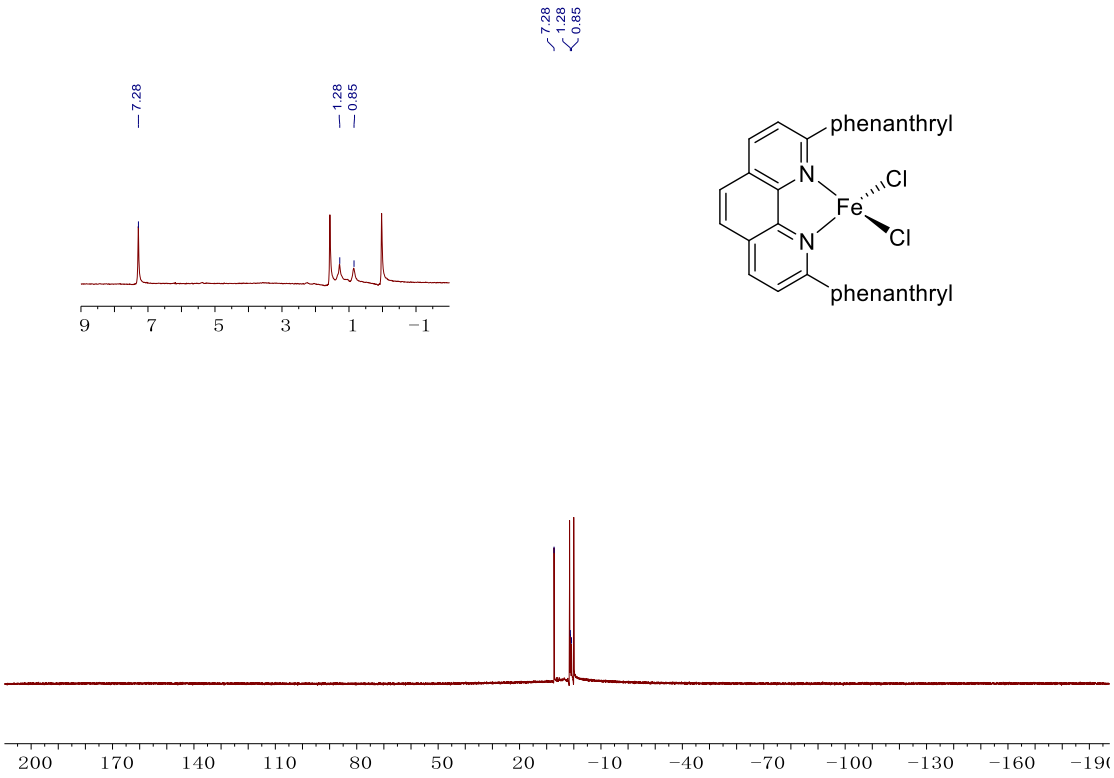




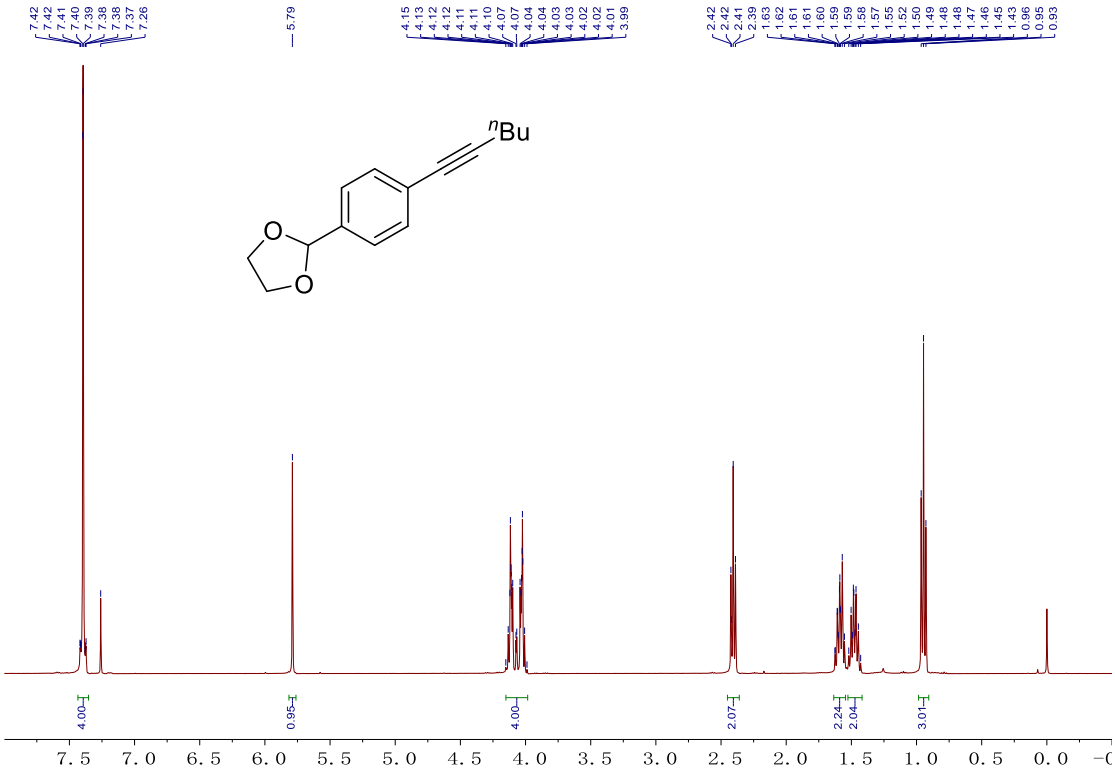
2,9-di(anthracen-9-yl)-1,10-phenanthroline $FeCl_2$ complexe (C1g)

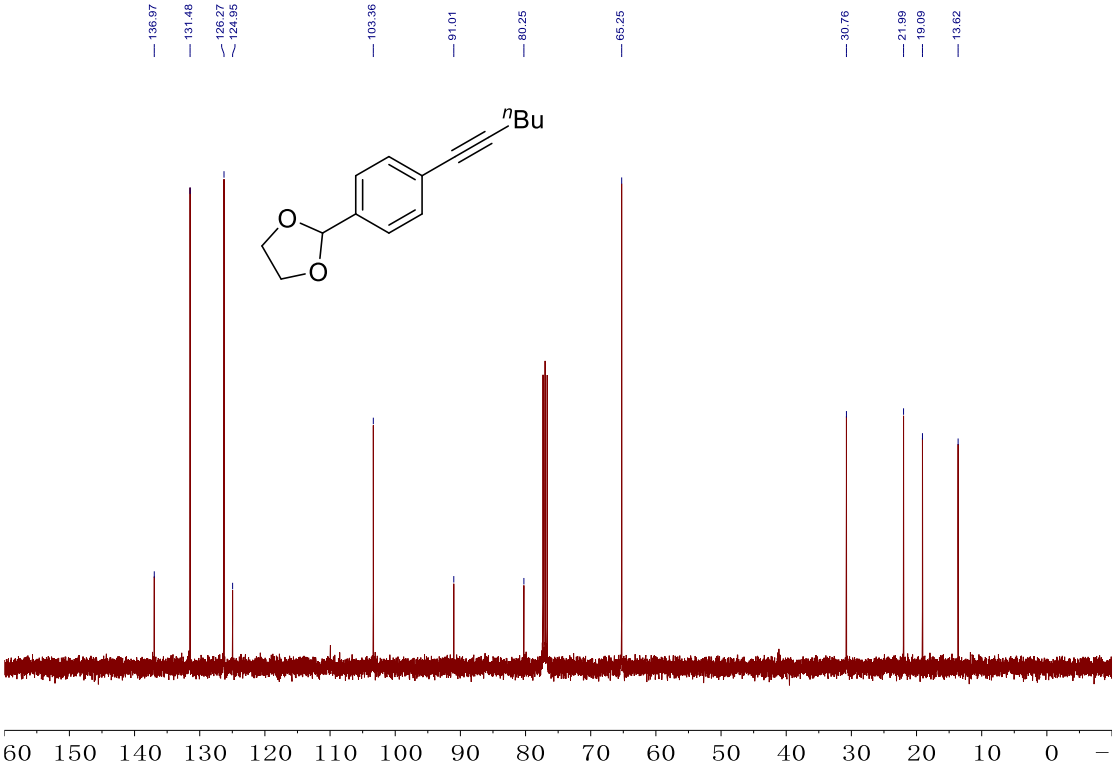


2,9-di(phenanthren-9-yl)-1,10-phenanthroline $FeCl_2$ complexe (C1h)

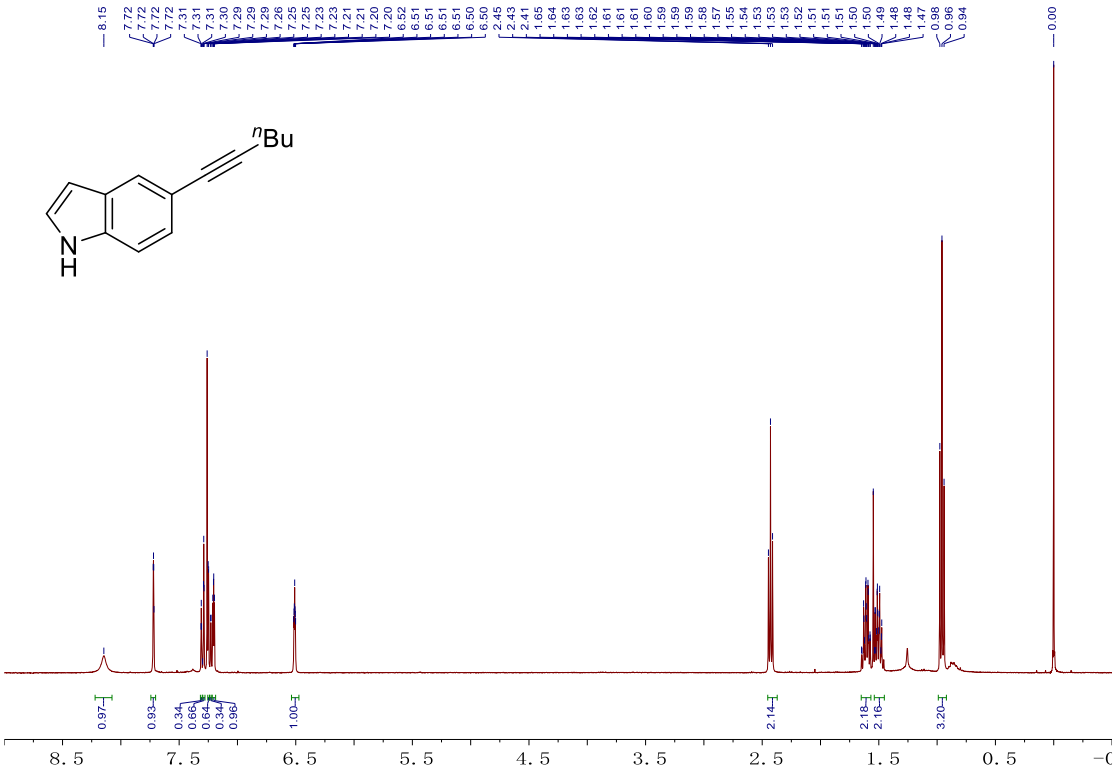


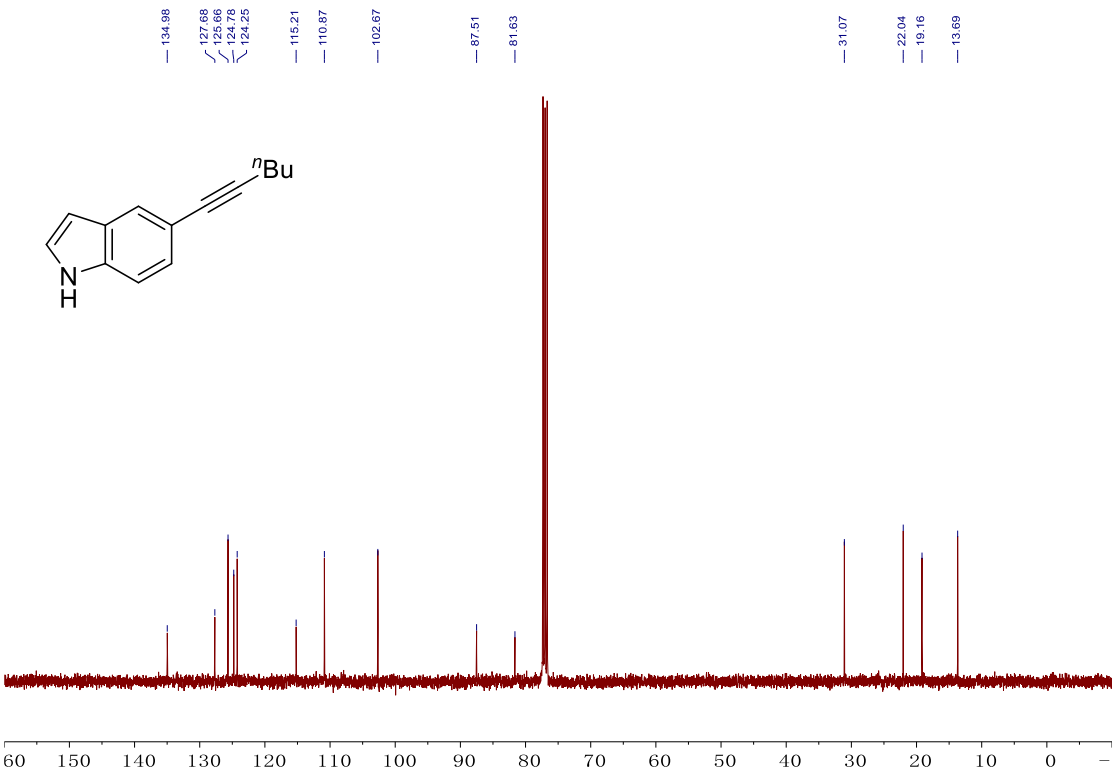
2-(4-(hex-1-yn-1-yl)phenyl)-1,3-dioxolane (1ai)



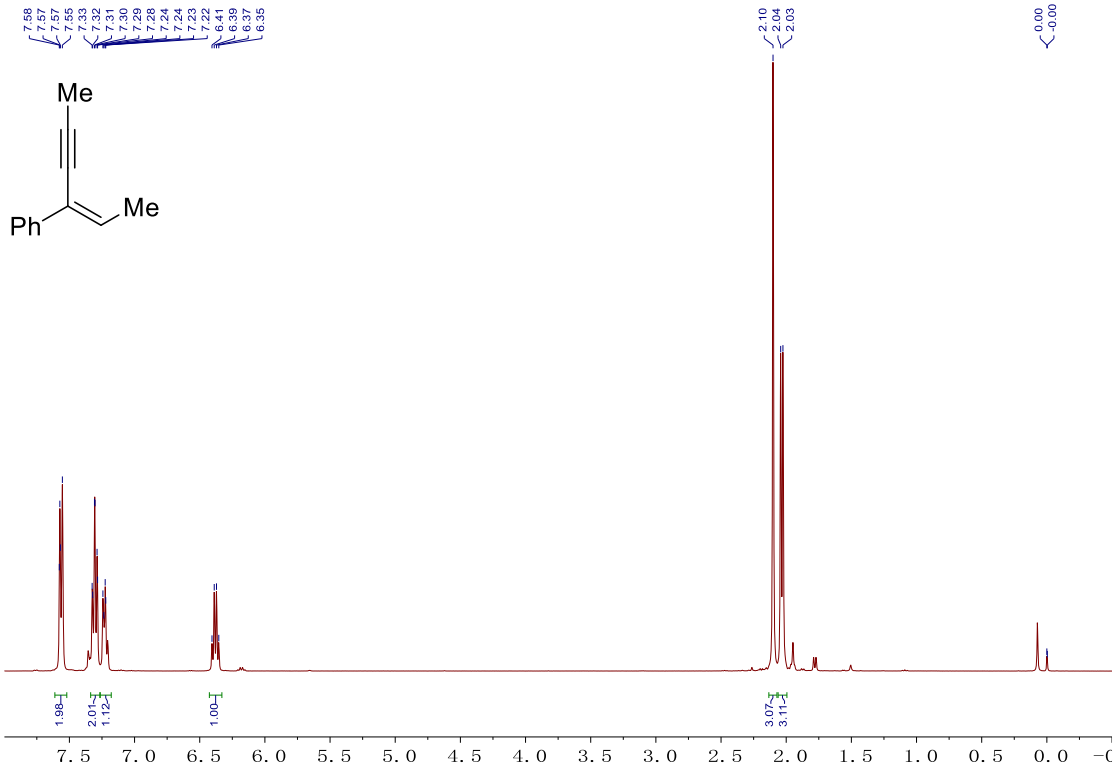


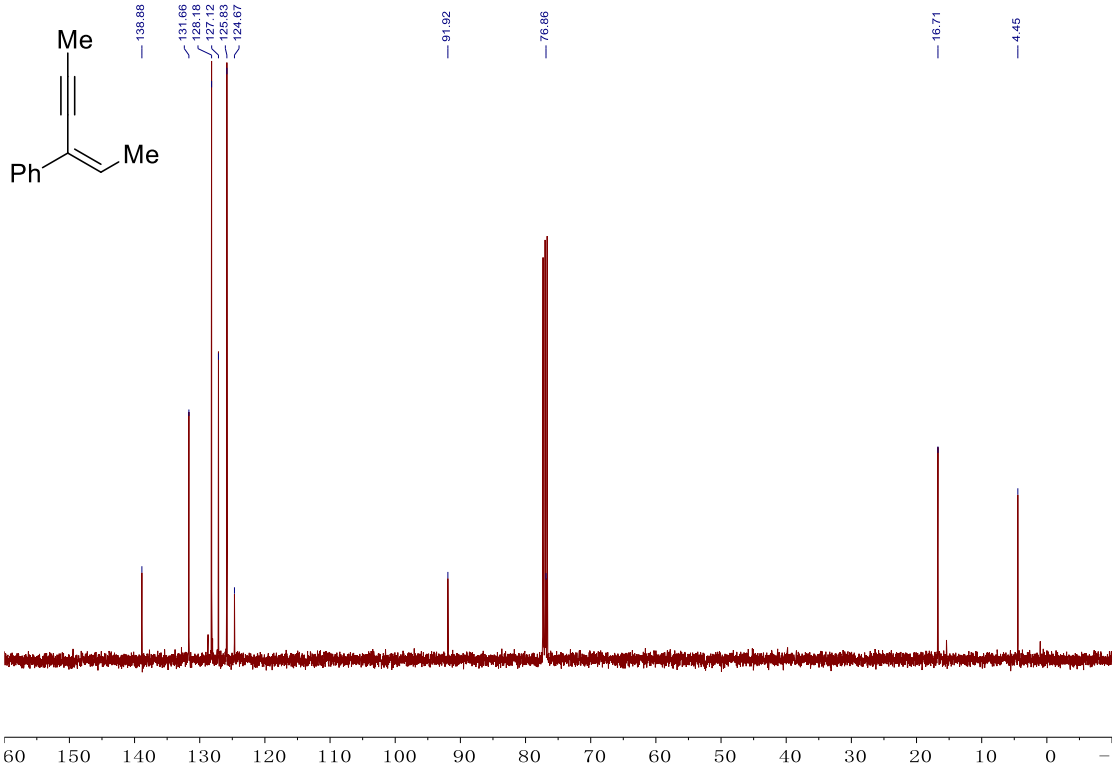
5-(hex-1-yn-1-yl)-1H-indole (1bd)



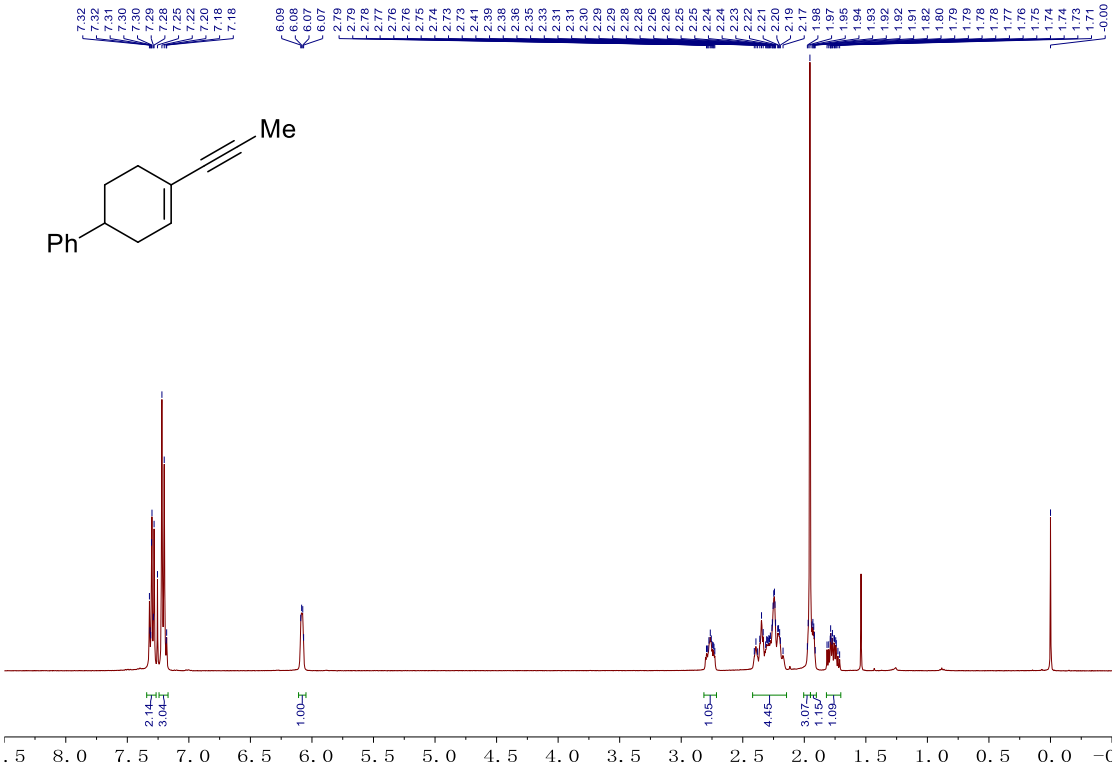


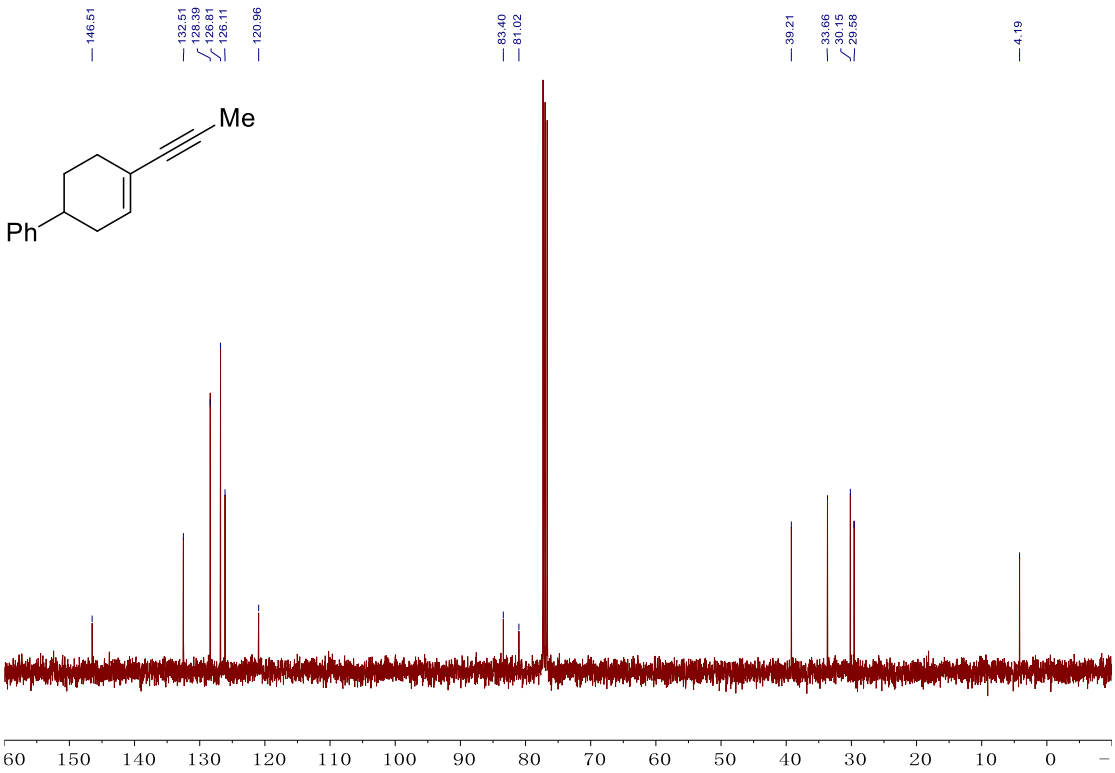
(*Z*)-hex-2-en-4-yn-3-ylbenzene (1df)



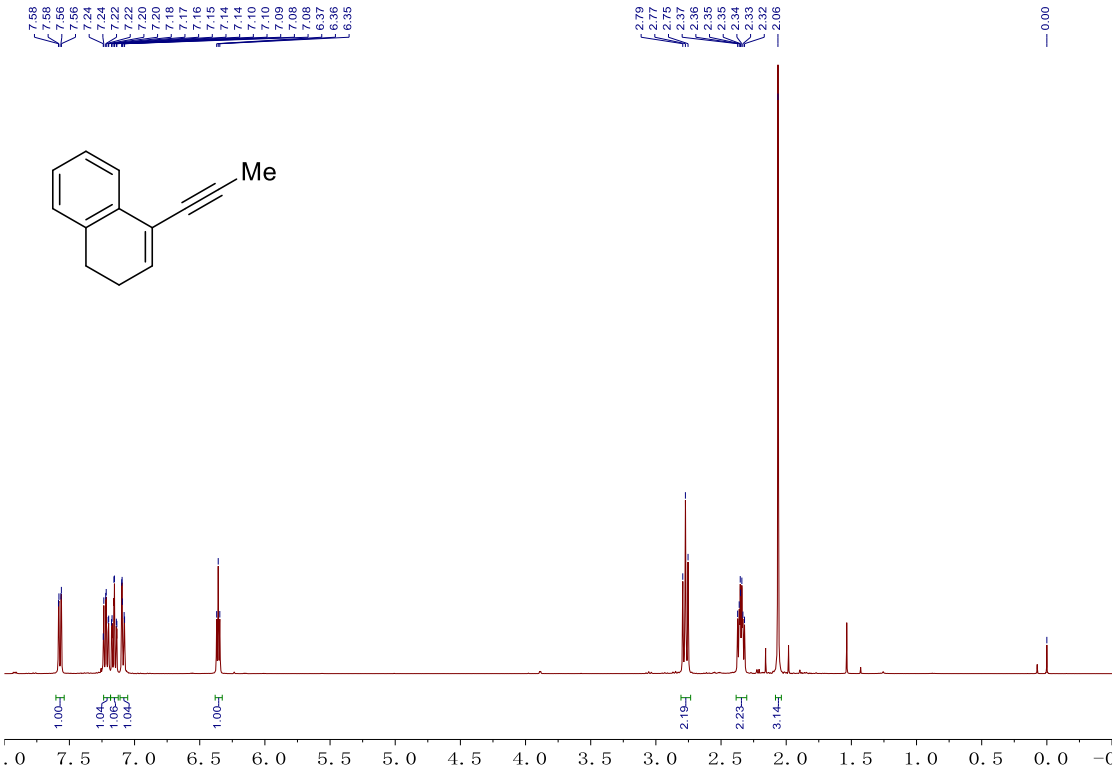


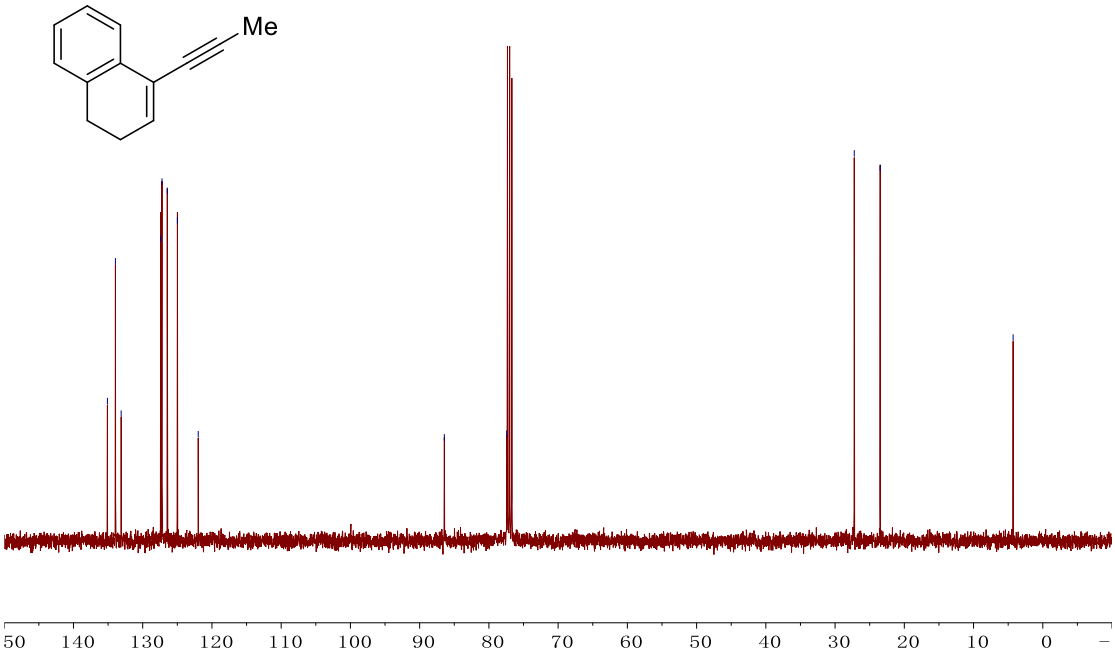
4-(prop-1-yn-1-yl)-1,2,3,6-tetrahydro-1,1'-biphenyl (1dg)



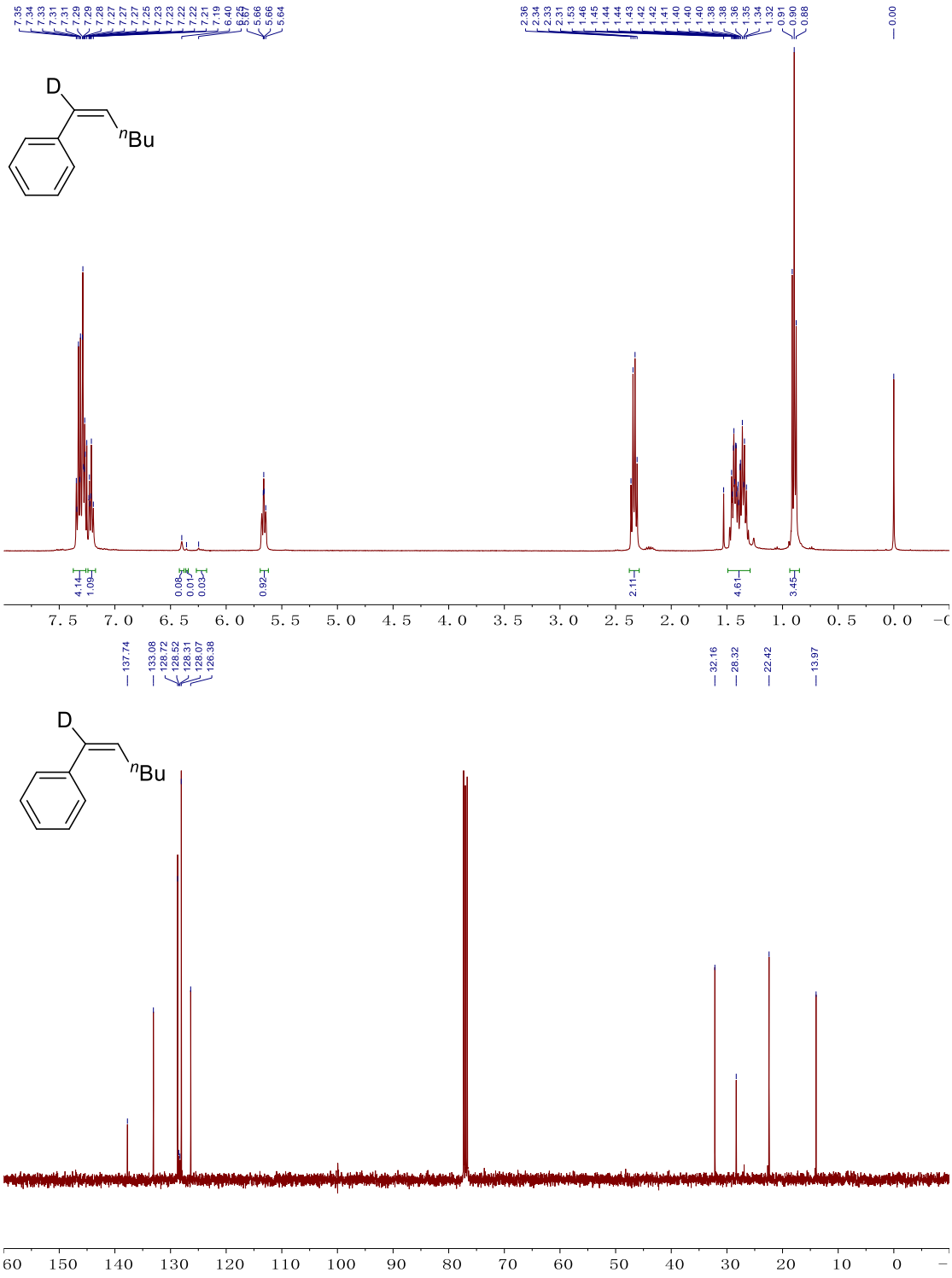


4-(prop-1-yn-1-yl)-1,2-dihydronaphthalene (1dh)

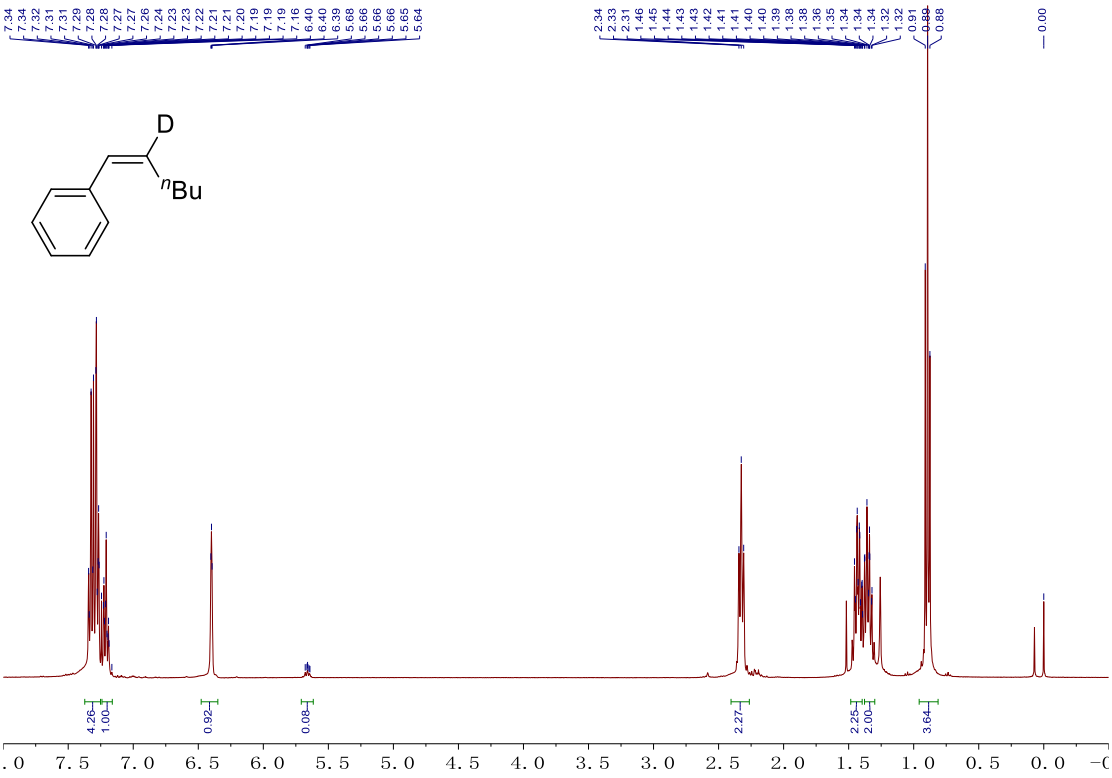


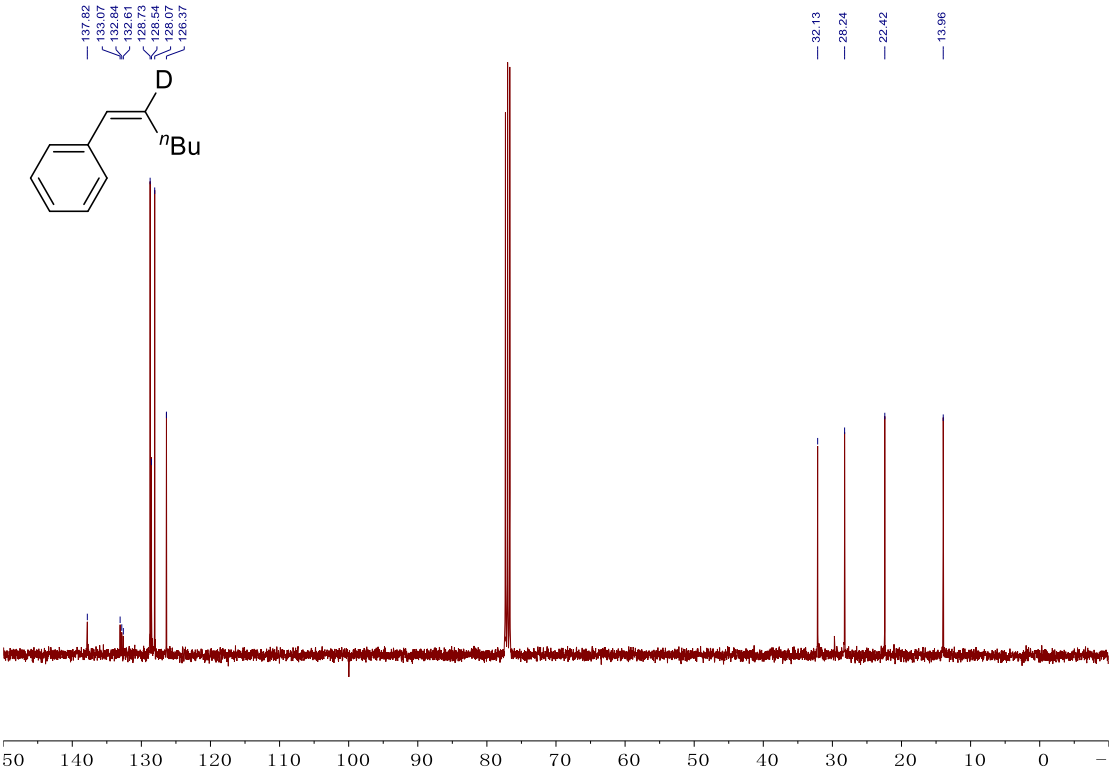


(*Z*)-(hex-1-en-1-yl-1-D)benzene (2aa)

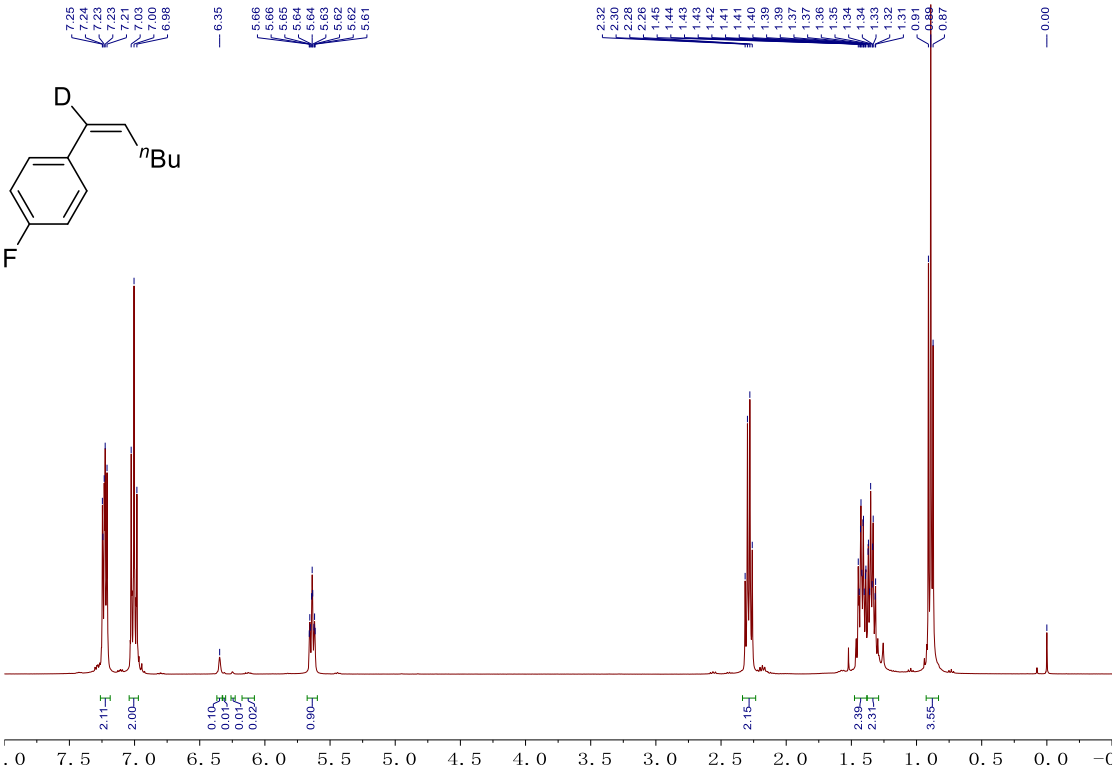


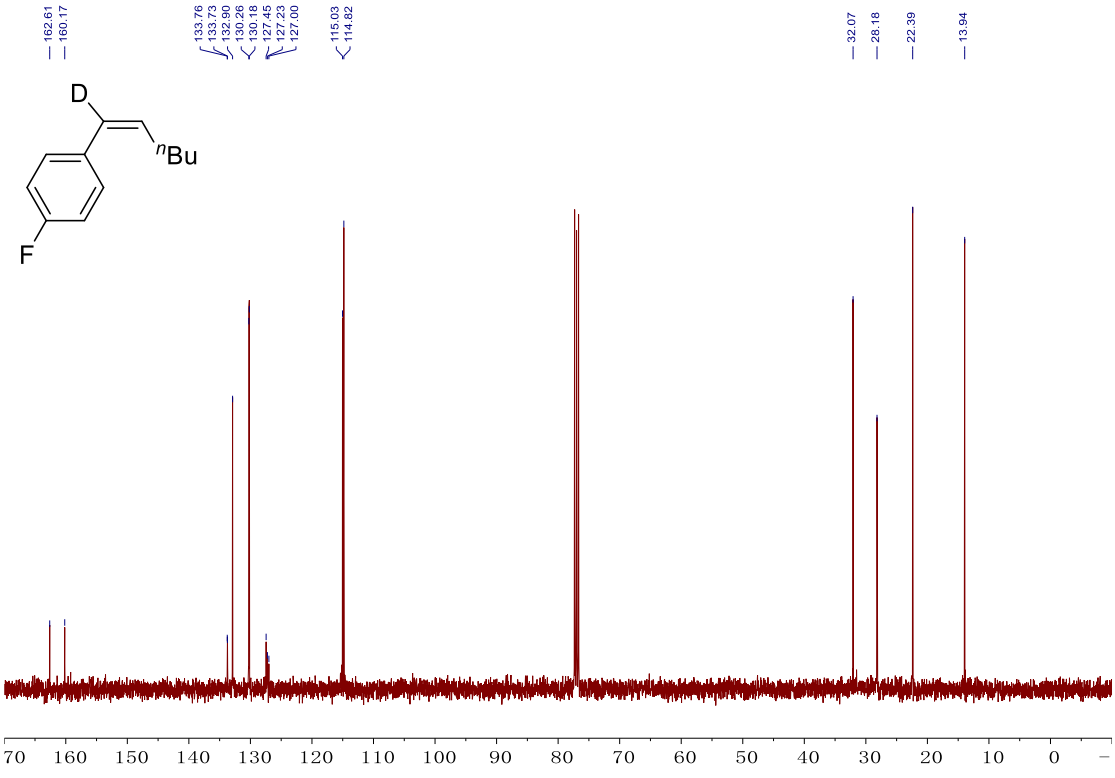
(Z)-(hex-1-en-1-yl-2-D)benzene (3aa)



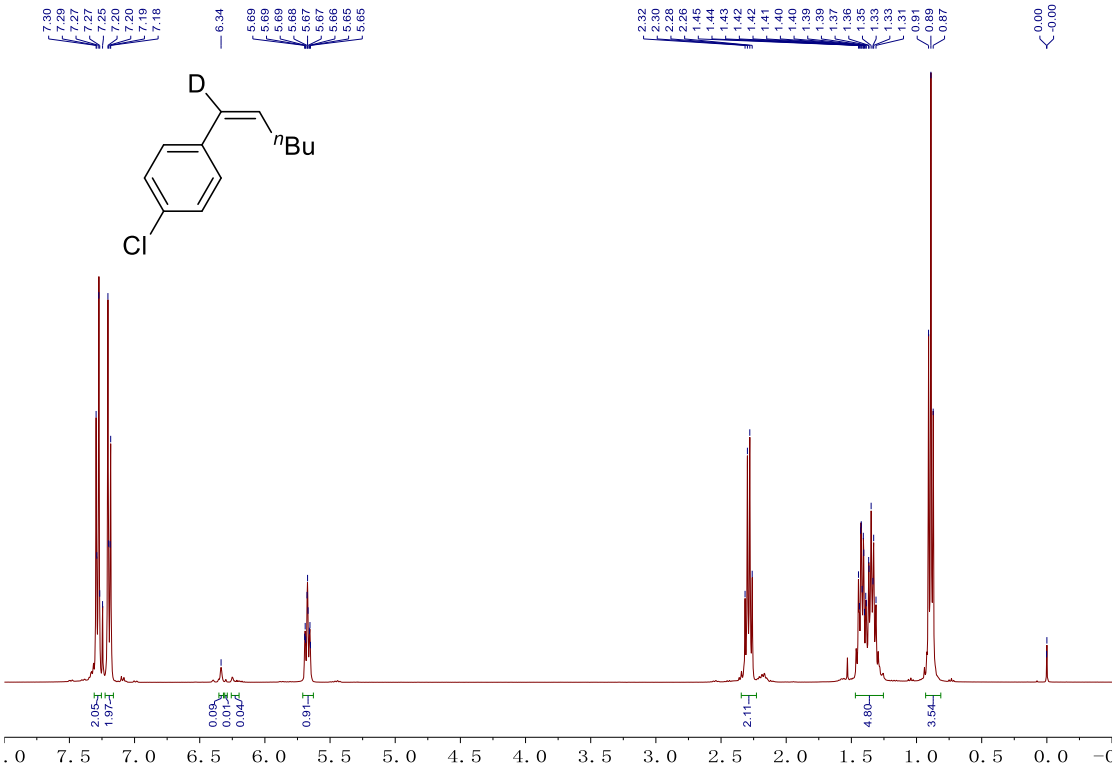


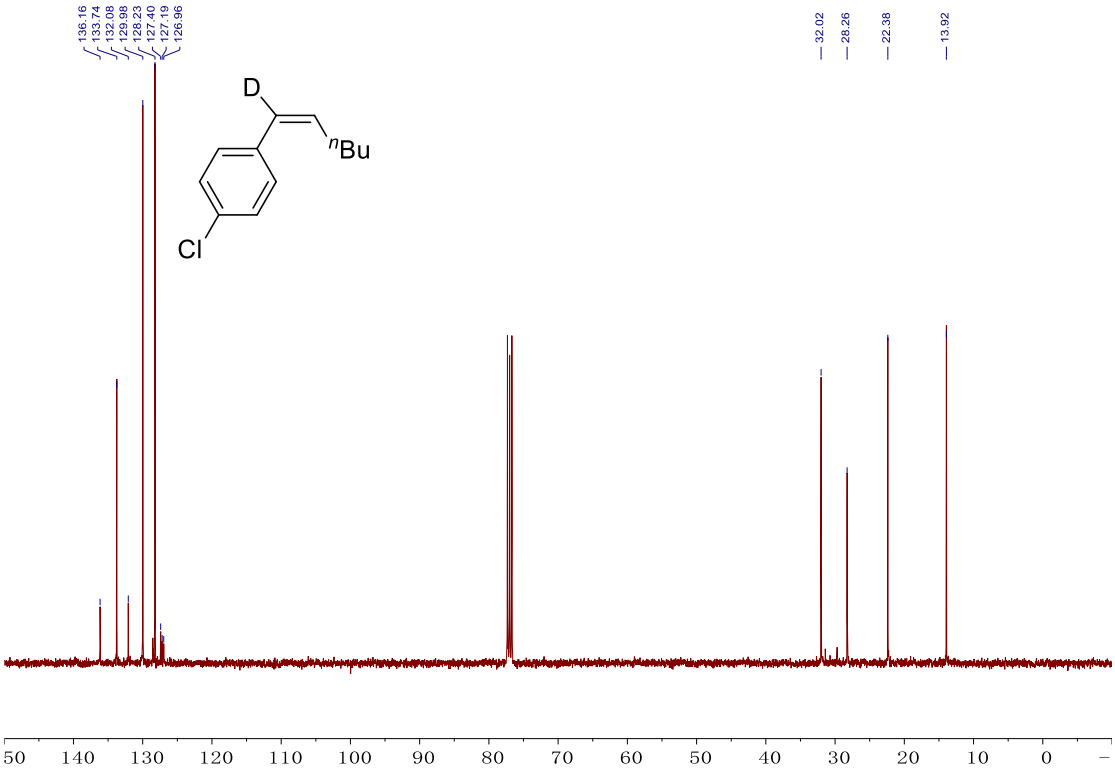
(*Z*)-1-fluoro-4-(hex-1-en-1-yl-1-D)benzene (2ab)



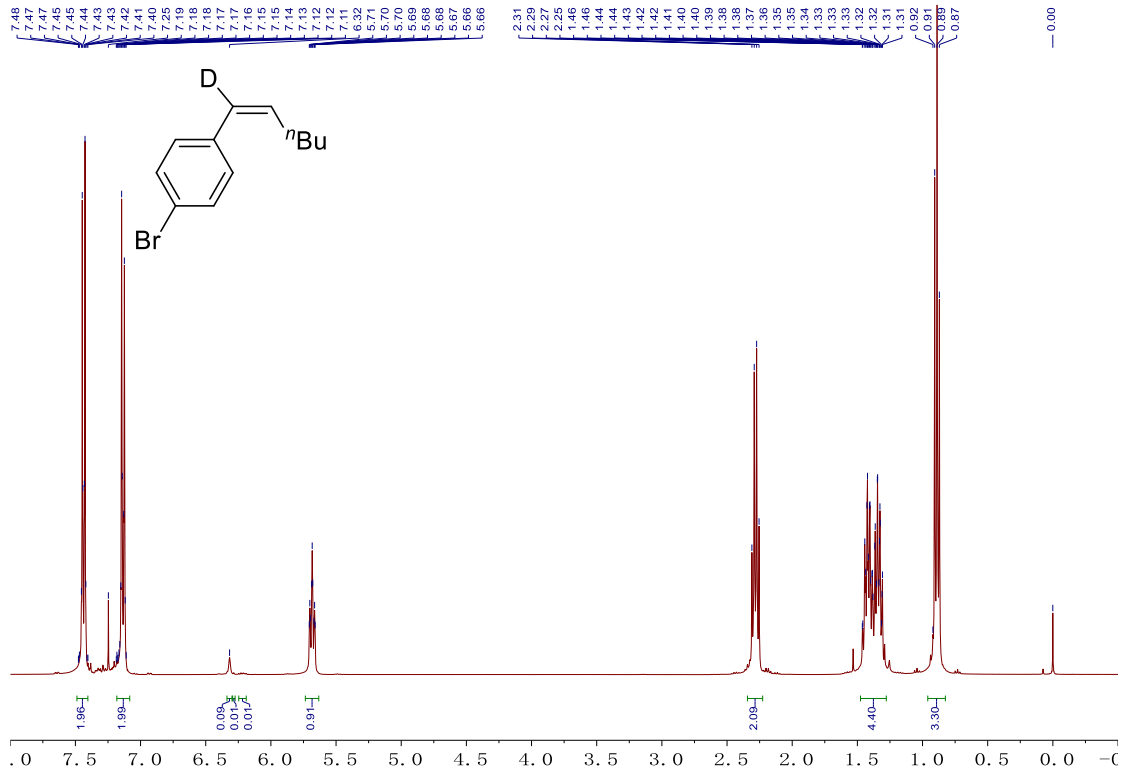


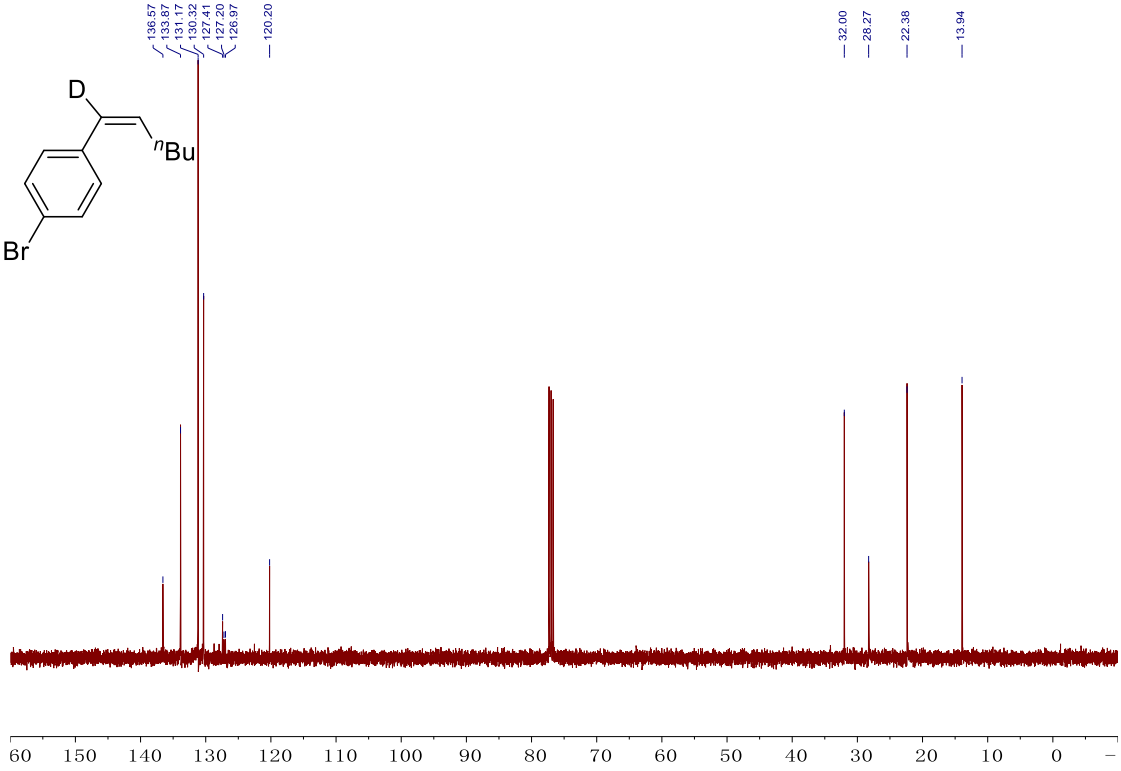
(*Z*)-1-chloro-4-(hex-1-en-1-yl-1-D)benzene (2ac)



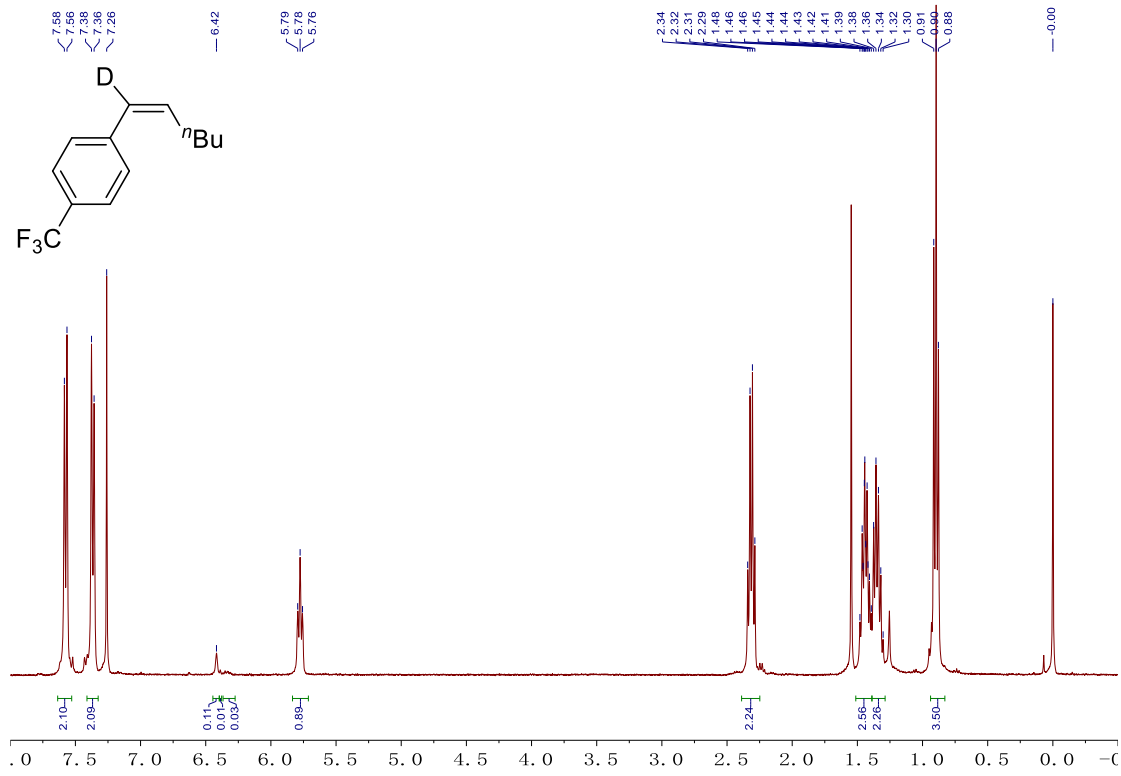


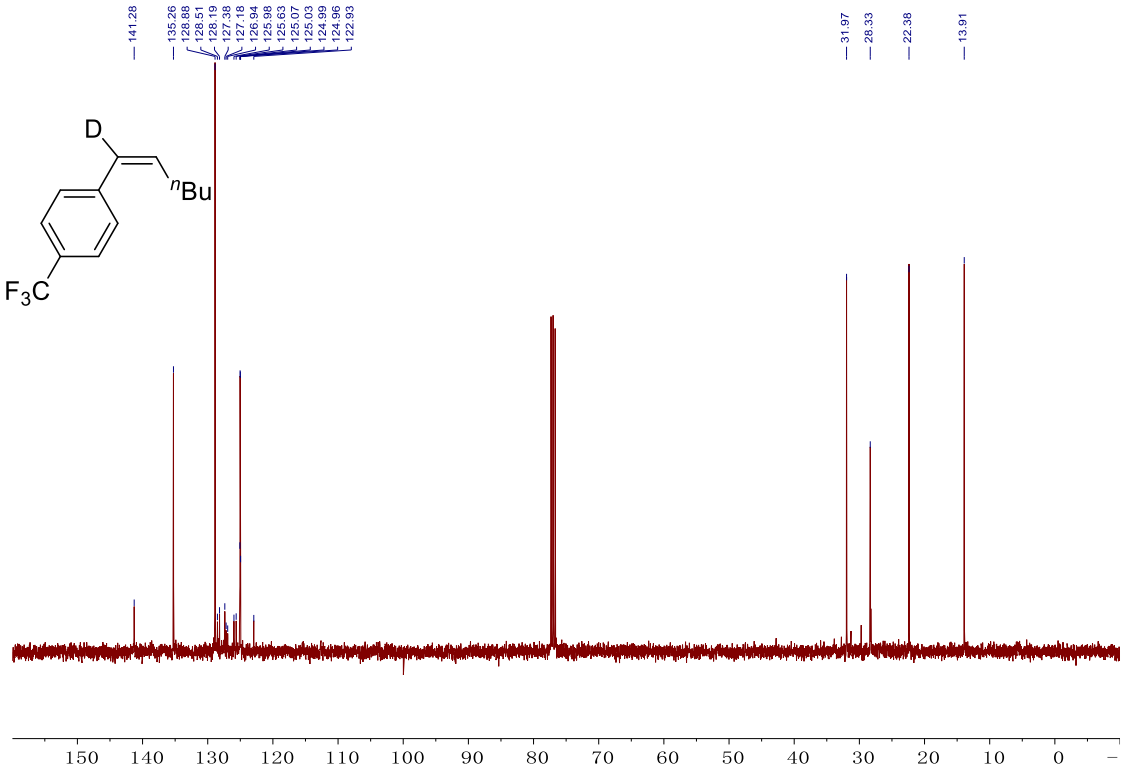
(*Z*)-1-bromo-4-(hex-1-en-1-yl-1-D)benzene (2ad)



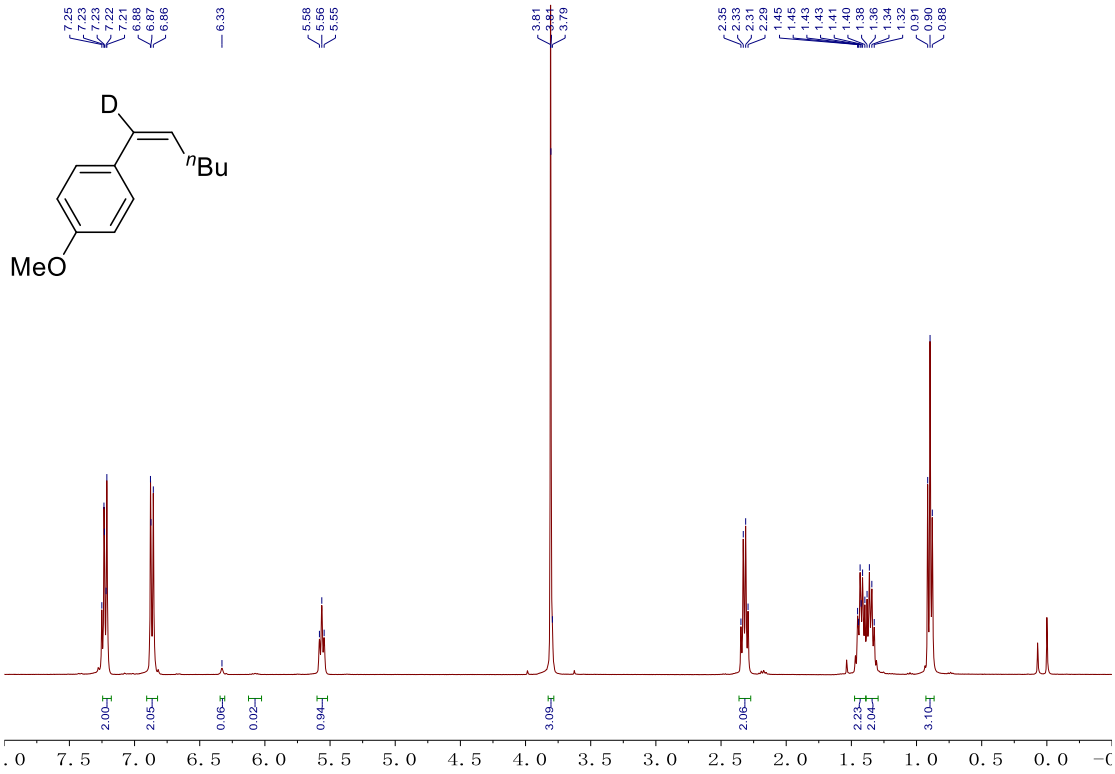


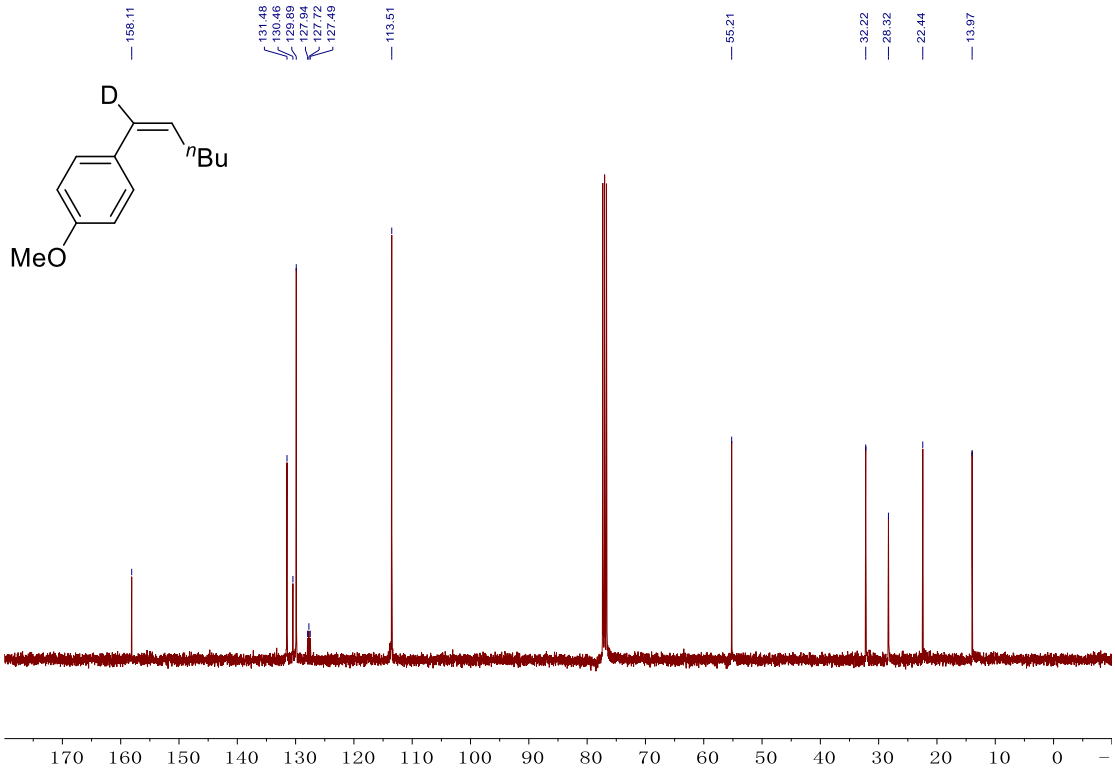
(*Z*)-1-(hex-1-en-1-yl-1-D)-4-(trifluoromethyl)benzene (2ae)



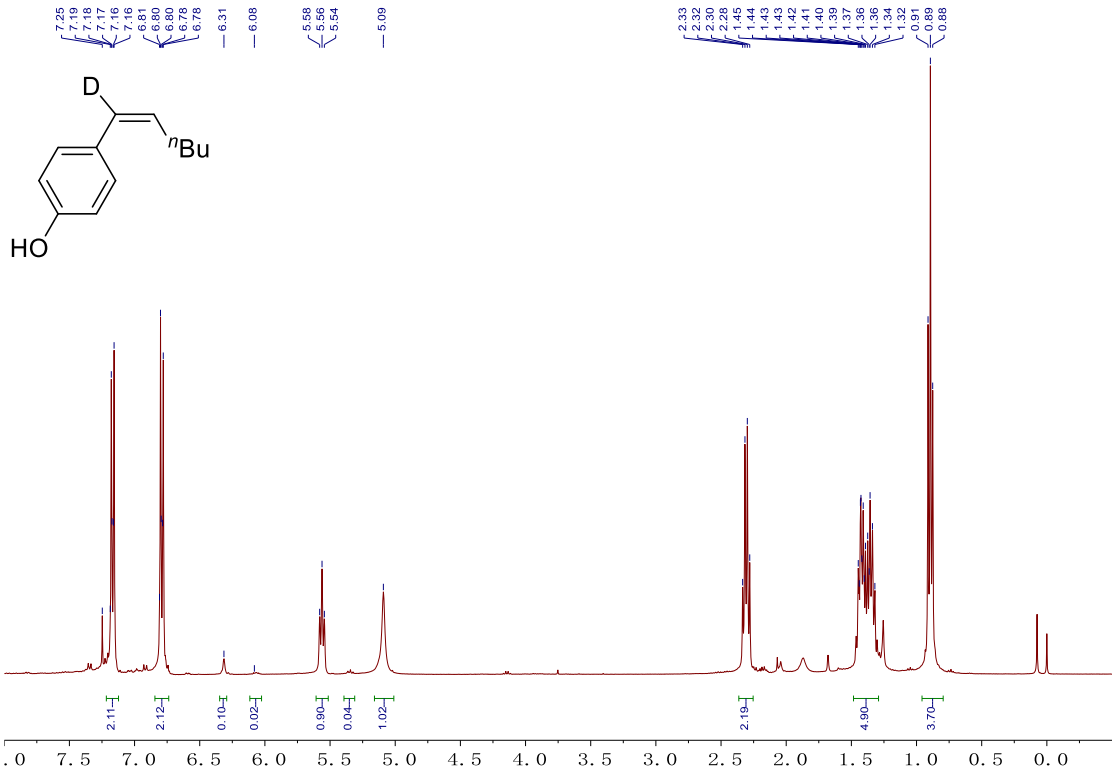


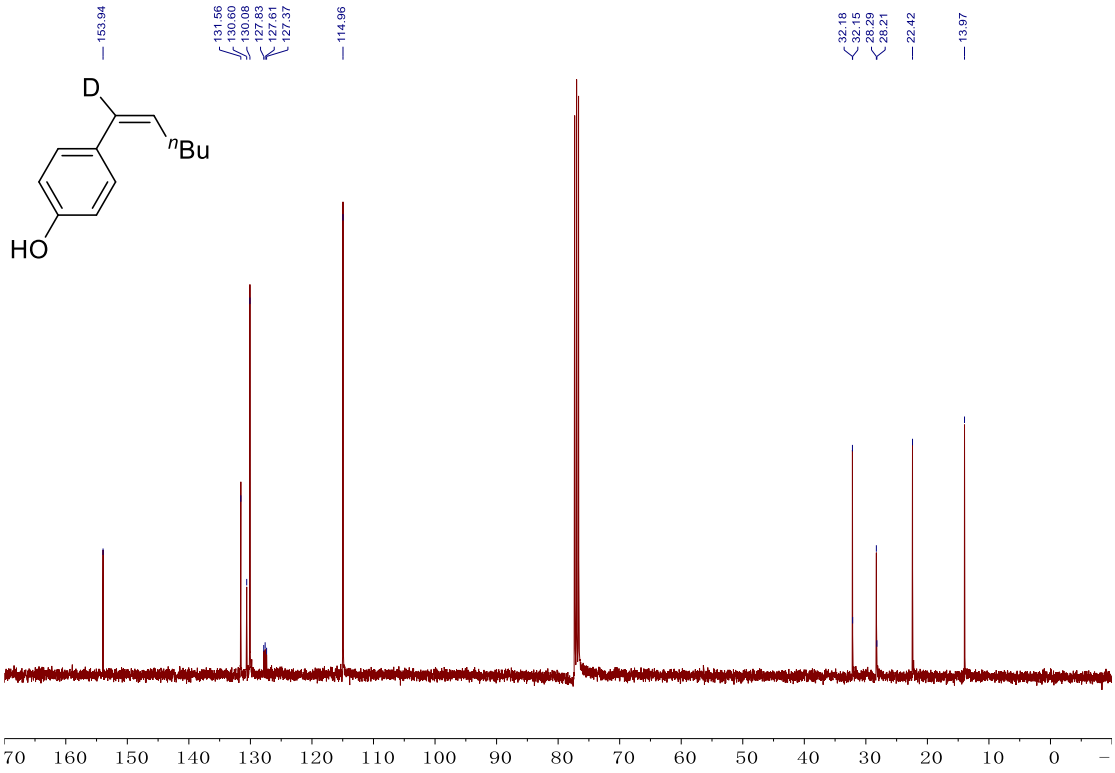
(*Z*)-1-(hex-1-en-1-yl-1-D)-4-methoxybenzene (2af)



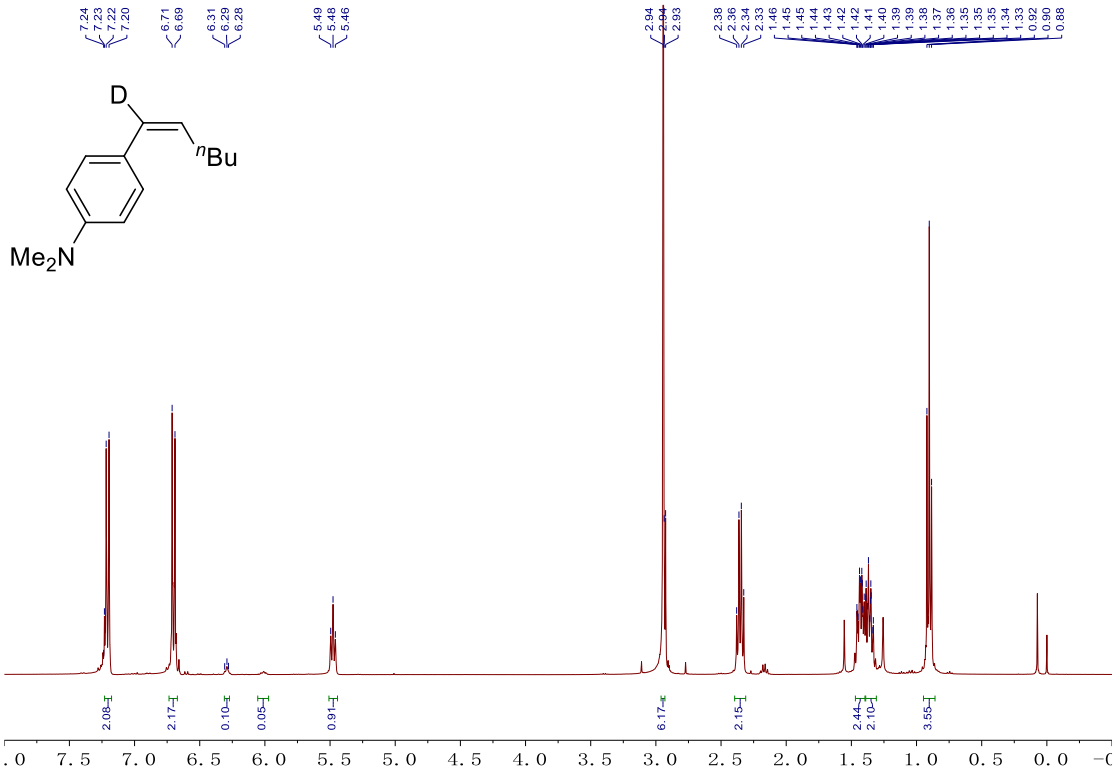


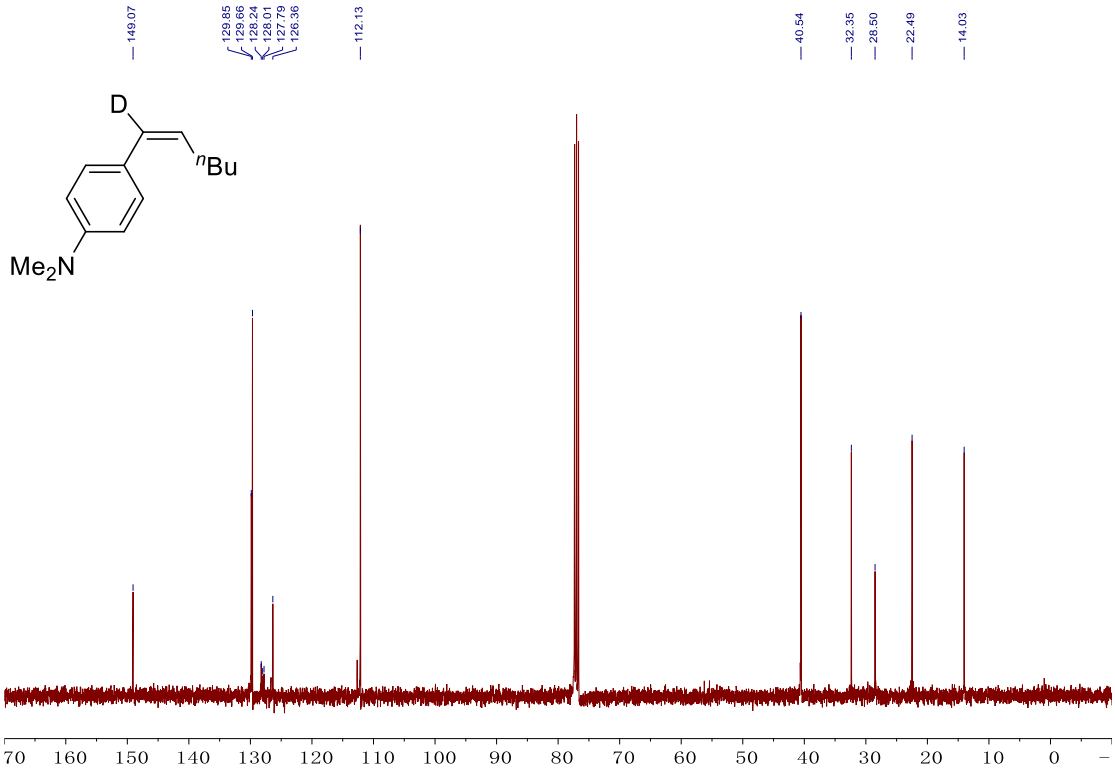
(*Z*)-4-(hex-1-en-1-yl-1-D)phenol (2ag)



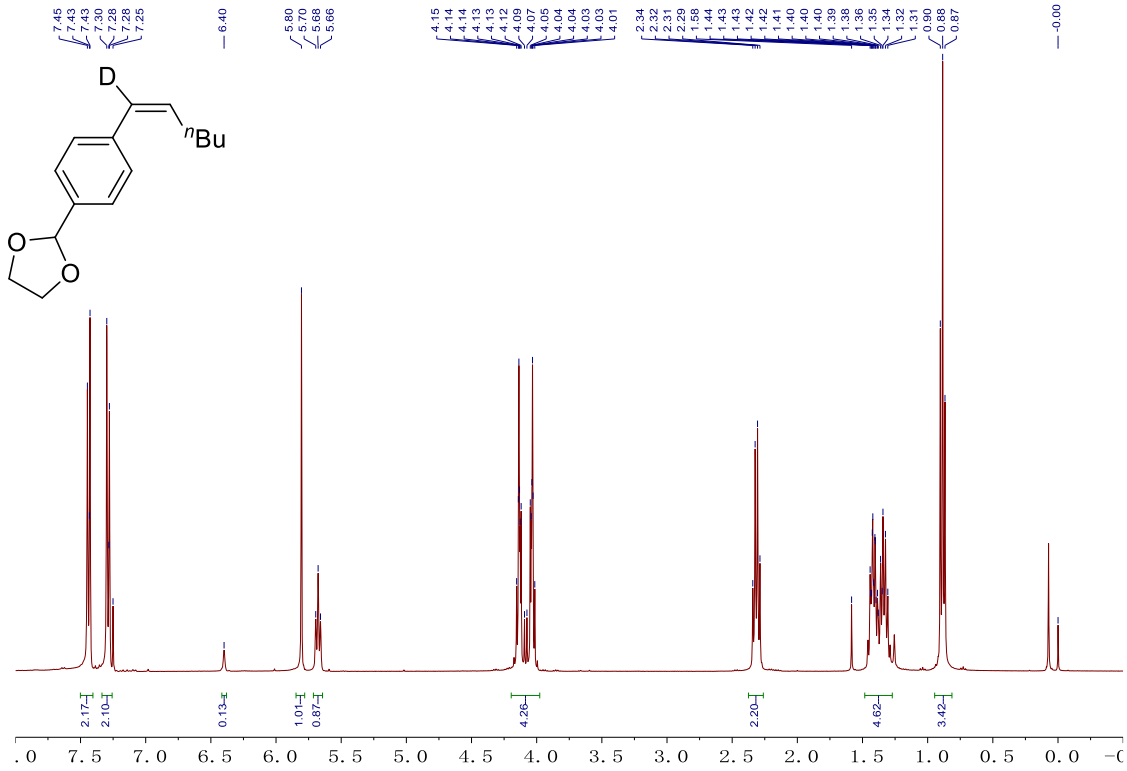


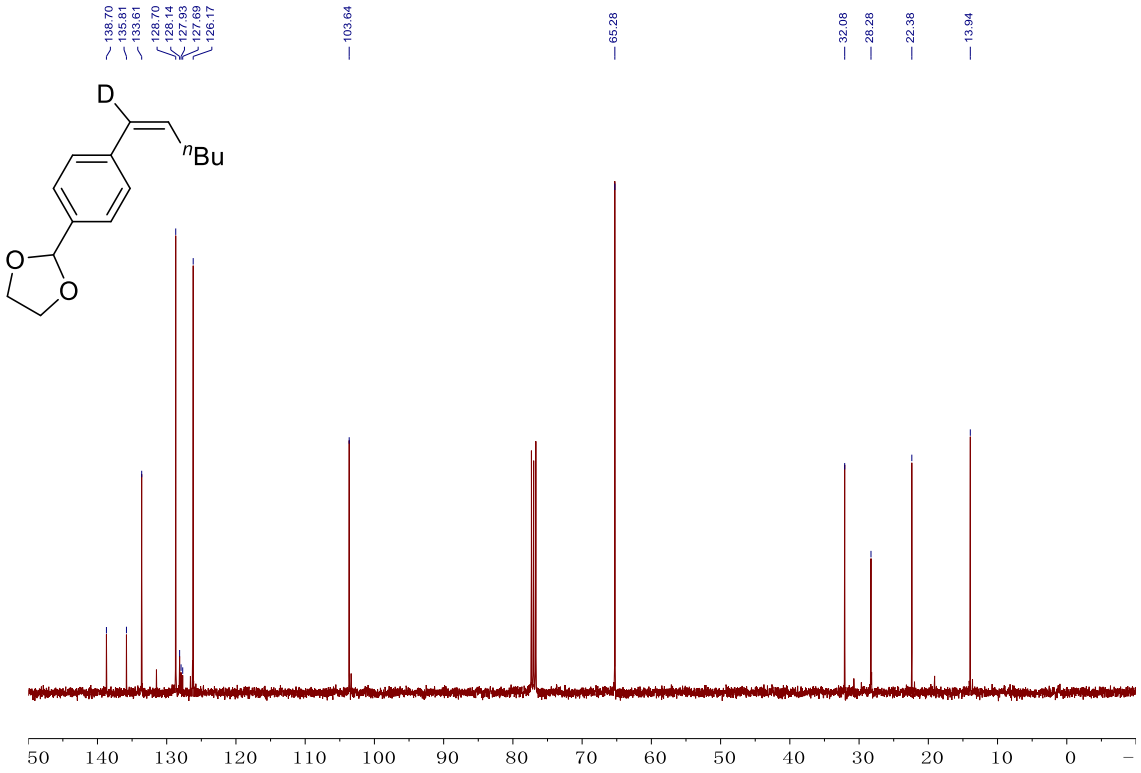
(*Z*)-4-(hex-1-en-1-yl-1-D)-N,N-dimethylaniline (2ah)



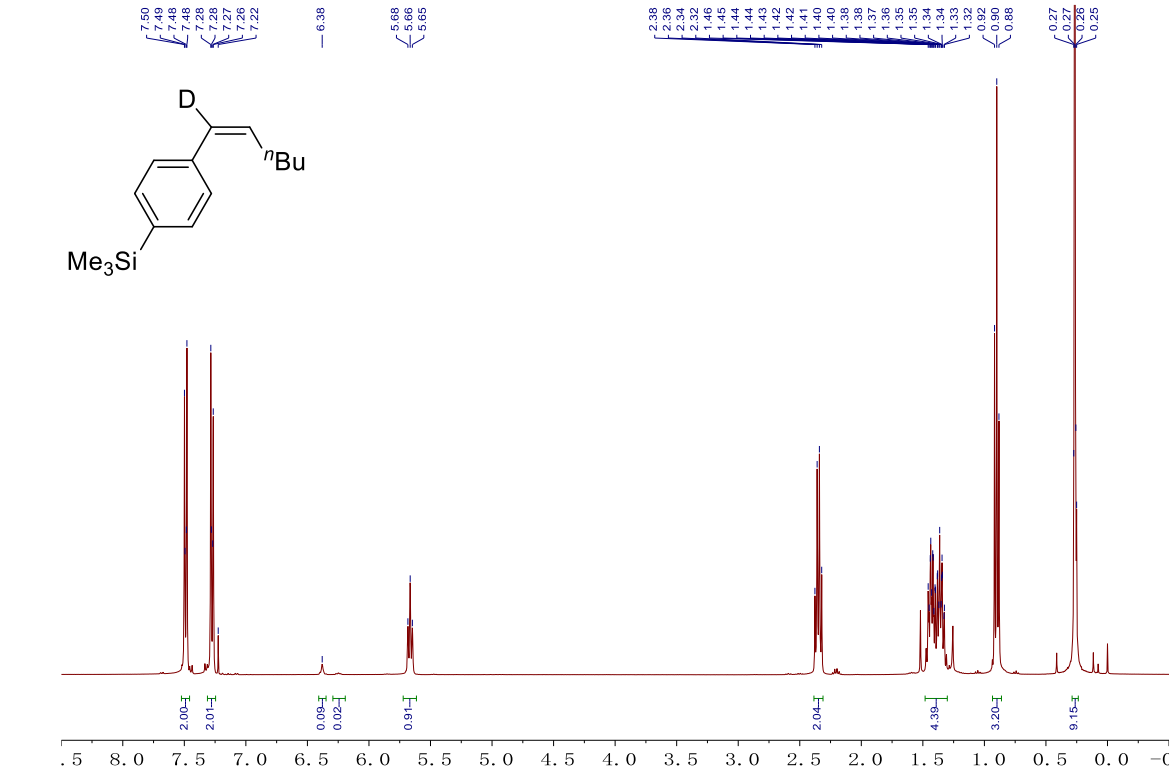


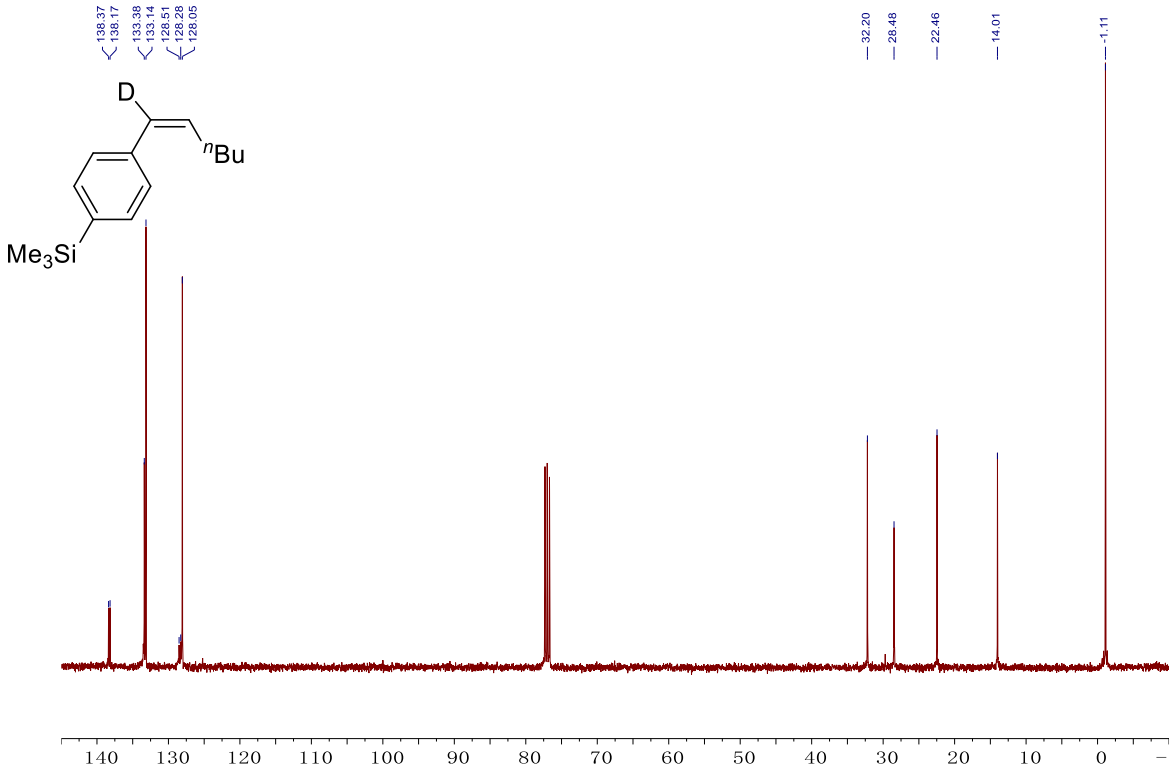
(*Z*)-2-(4-(hex-1-en-1-yl-1-D)phenyl)-1,3-dioxolane (2ai)



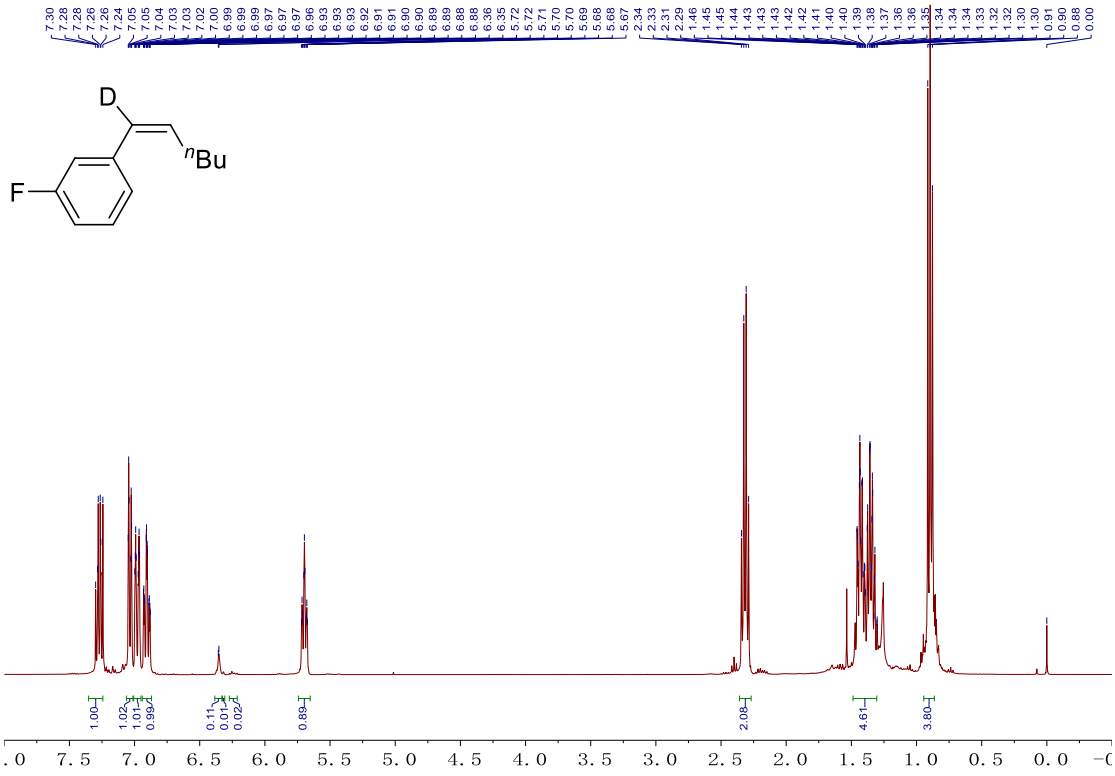


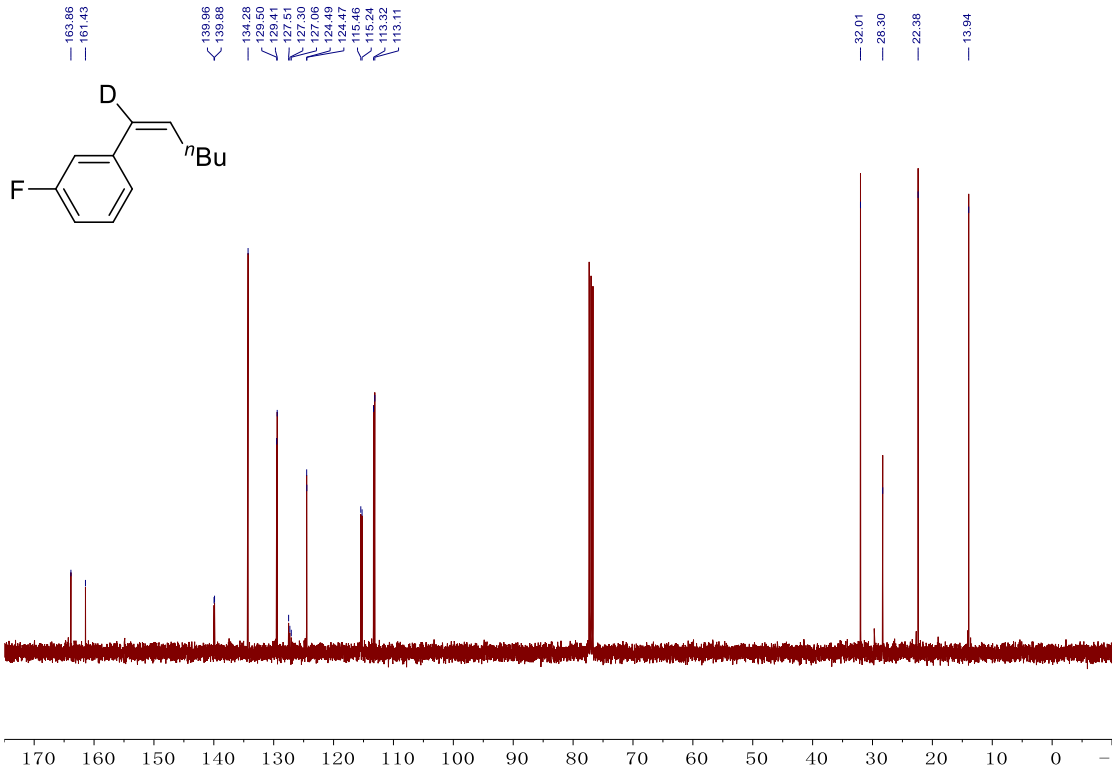
(*Z*)-(4-(hex-1-en-1-yl-1-D)phenyl)trimethylsilane (2aj)



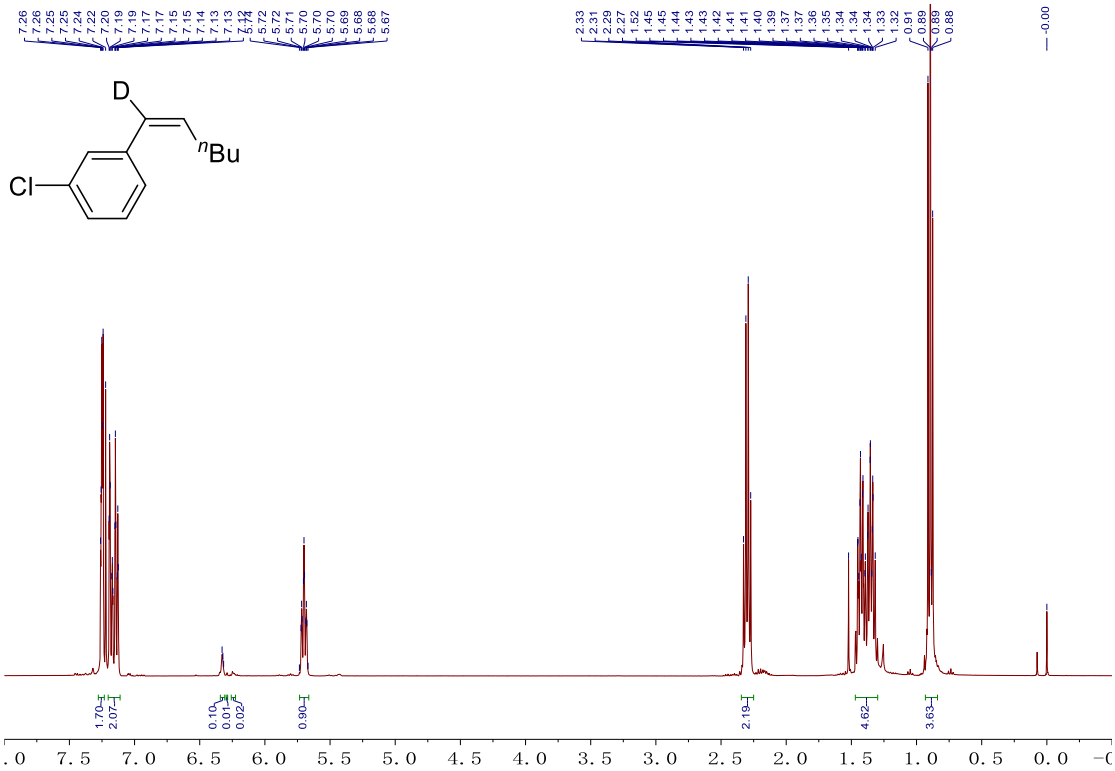


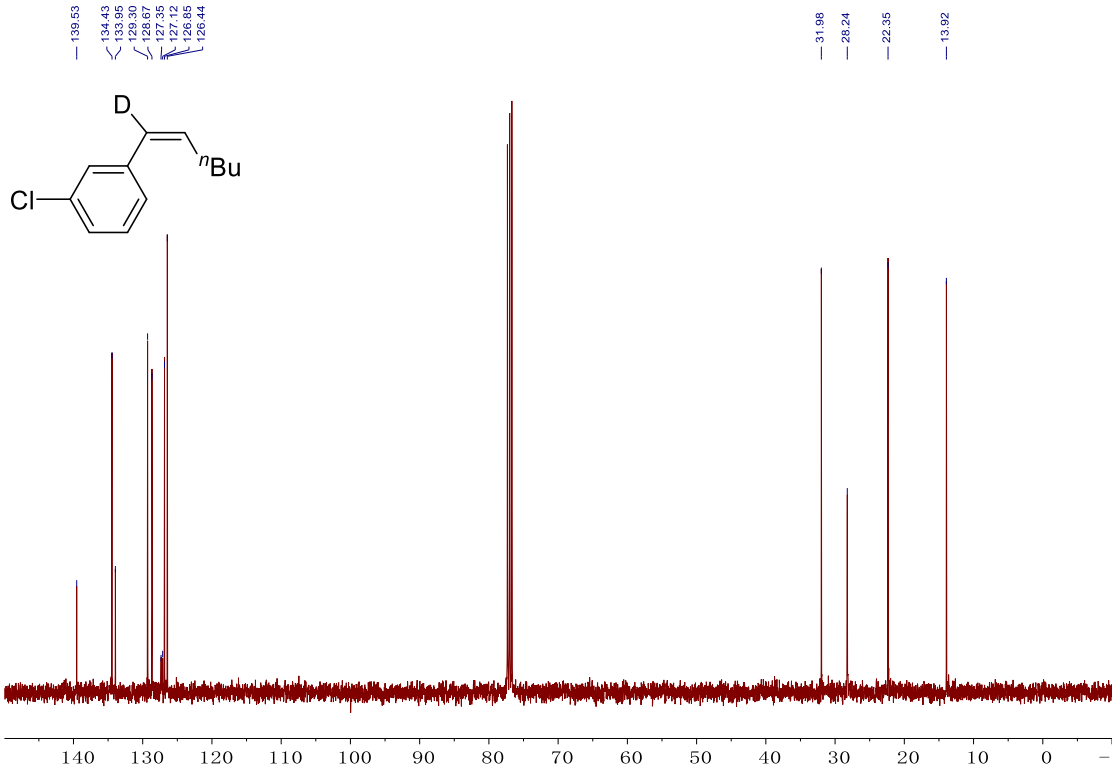
(*Z*)-1-fluoro-3-(hex-1-en-1-yl-1-D)benzene (2ak)



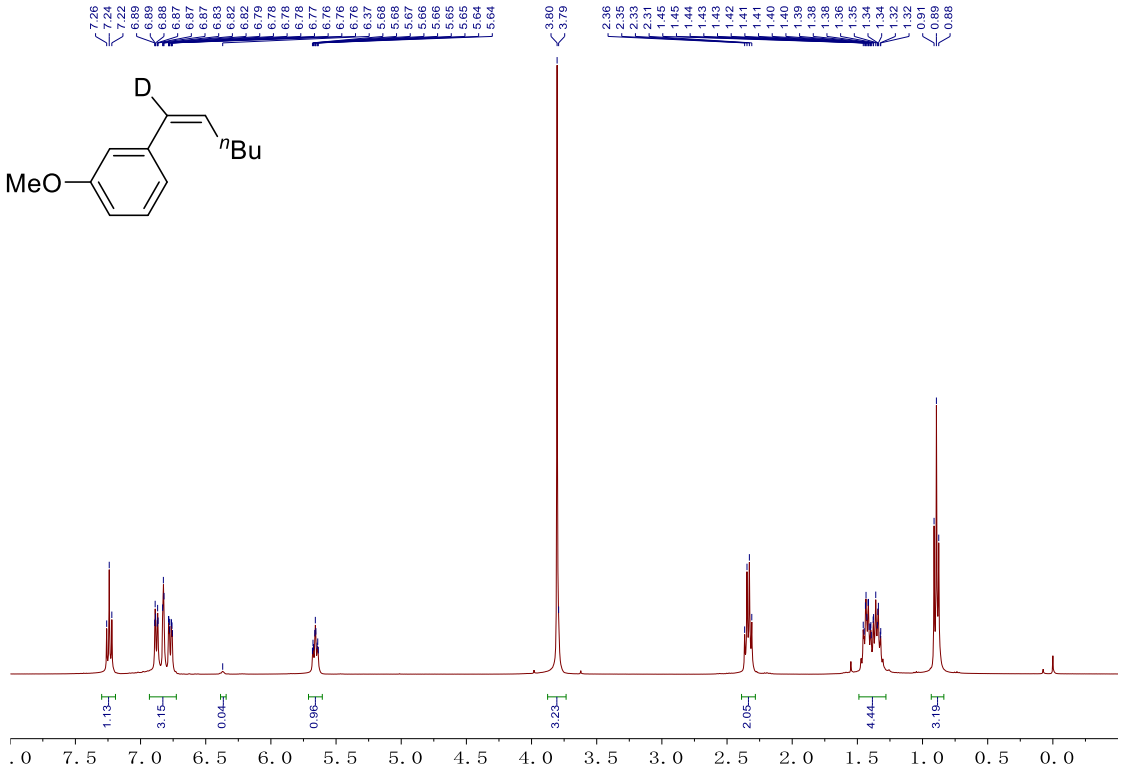


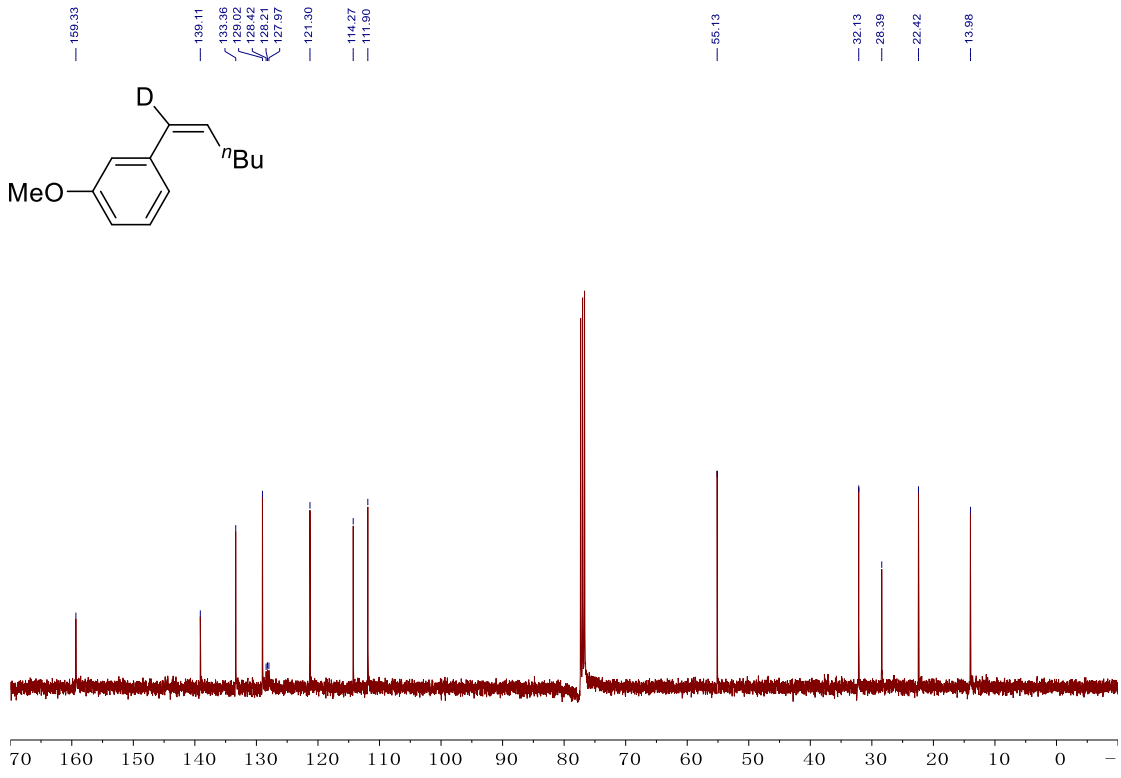
(*Z*)-1-chloro-3-(hex-1-en-1-yl-1-D)benzene (2al)



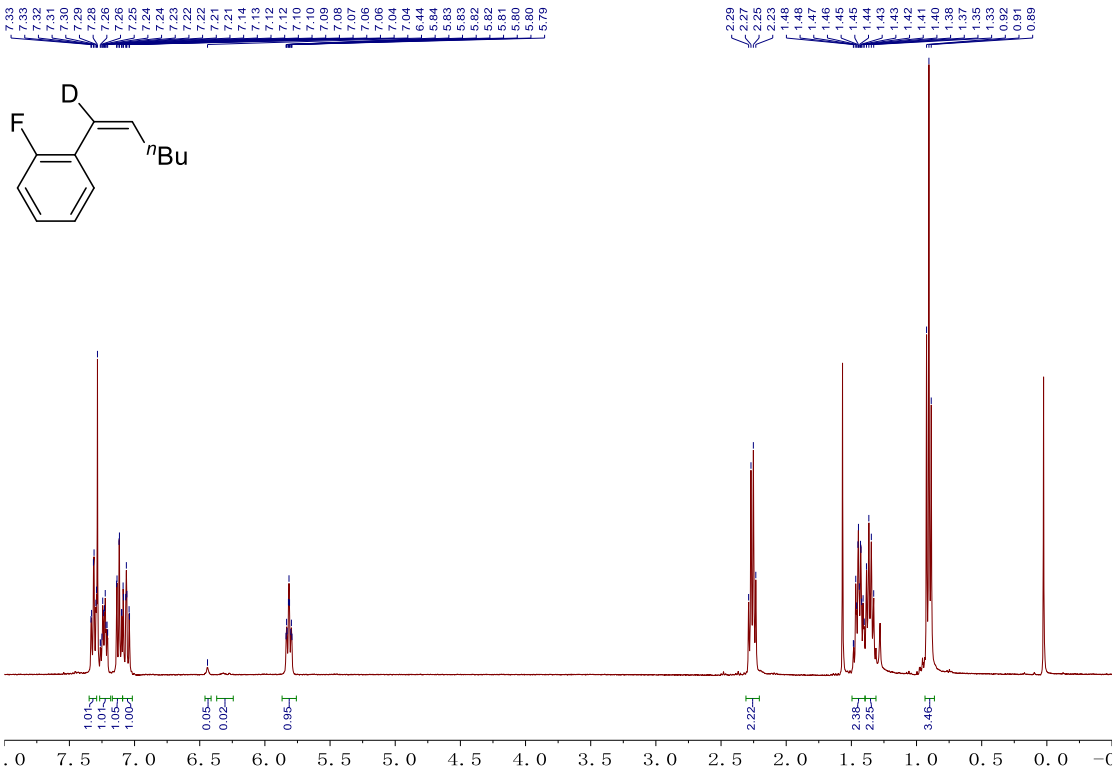


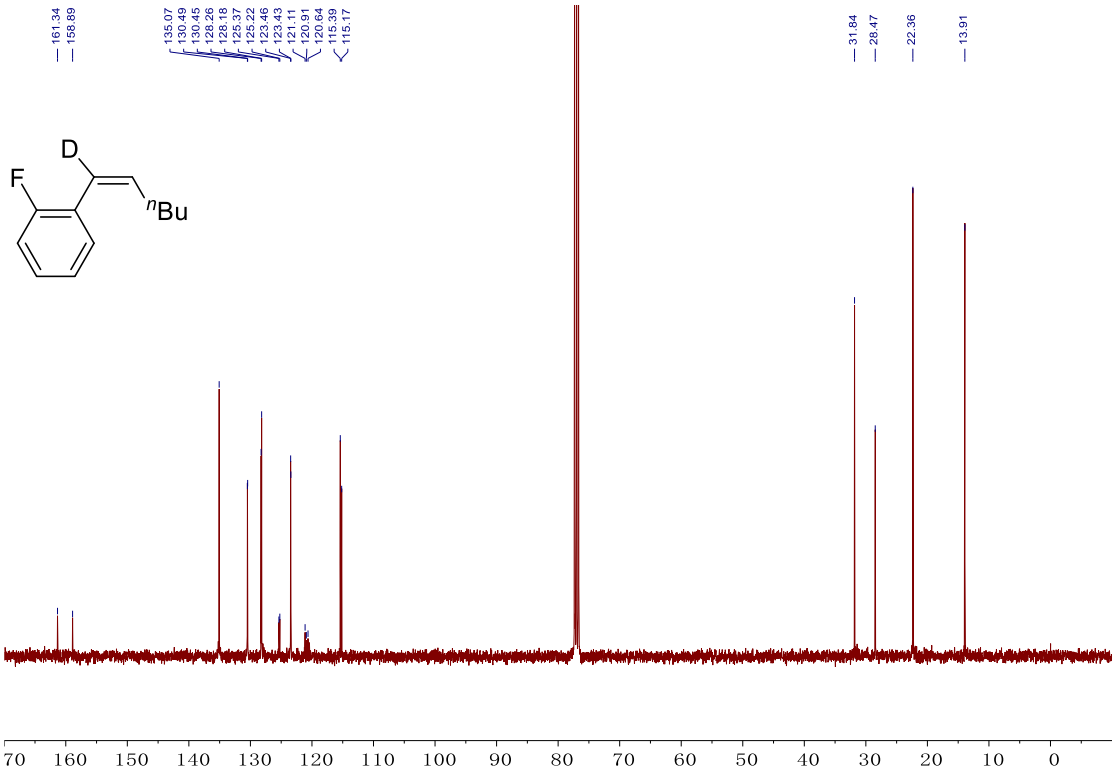
(*Z*)-1-(hex-1-en-1-yl-1-D)-3-methoxybenzene (2am)



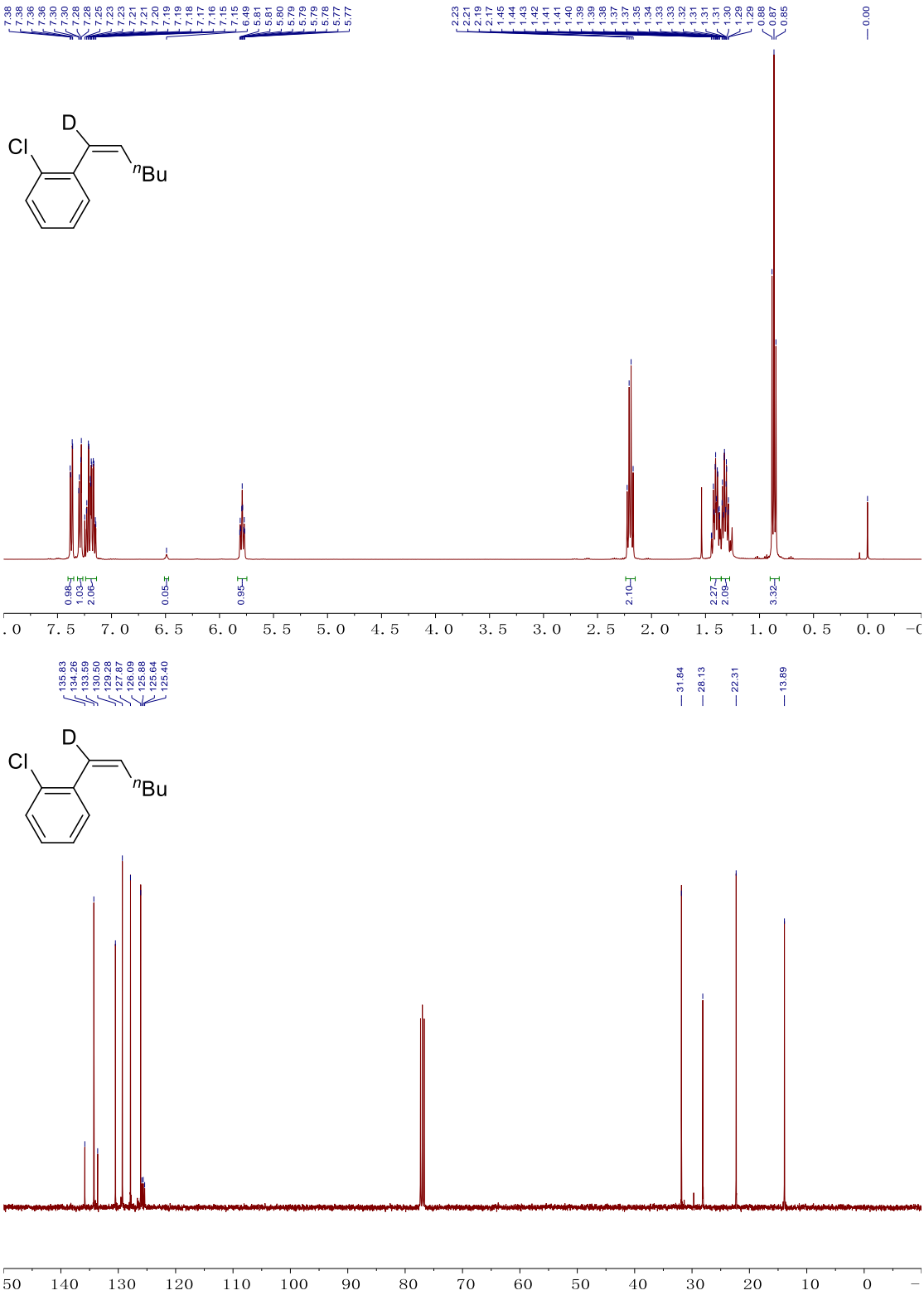


(*Z*)-1-fluoro-2-(hex-1-en-1-yl-1-D)benzene (2an)

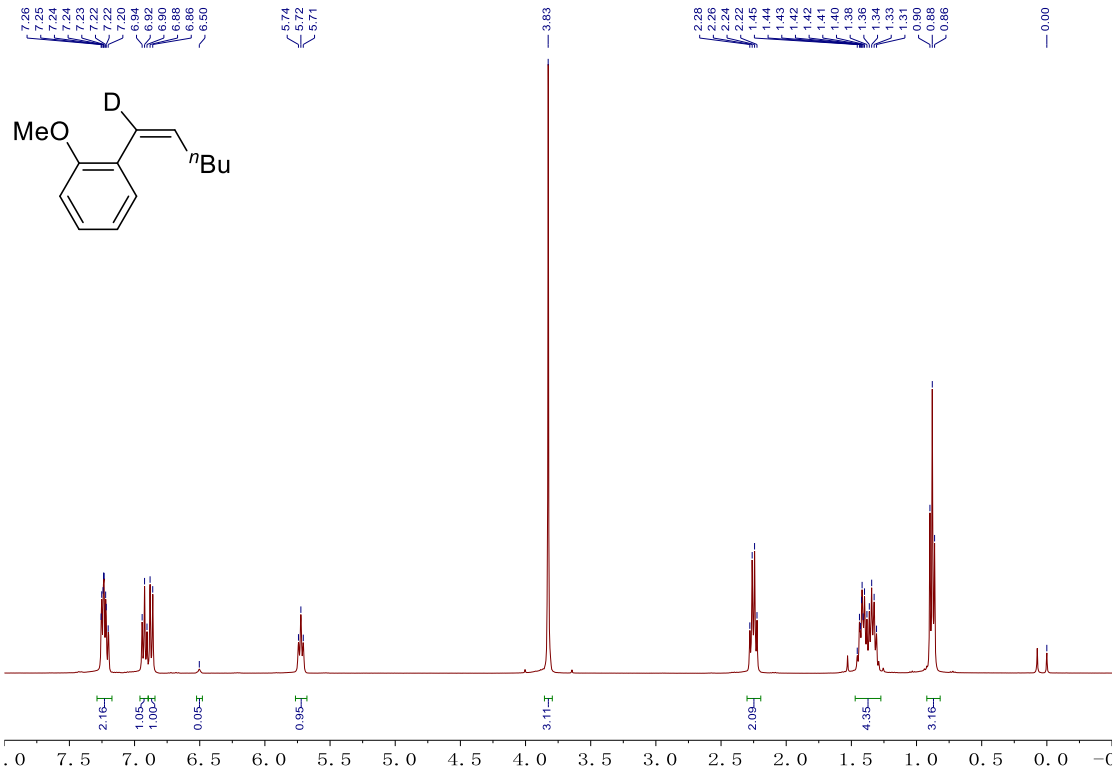


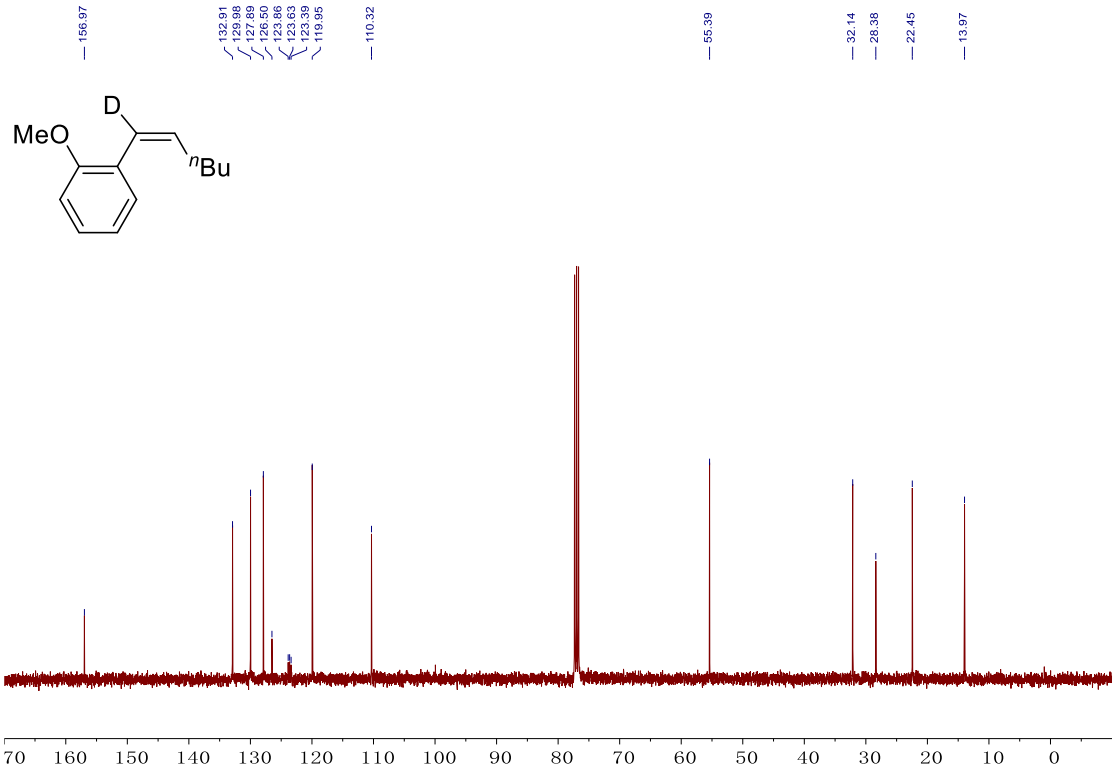


(*Z*)-1-chloro-2-(hex-1-en-1-yl-1-D)benzene (2ao)

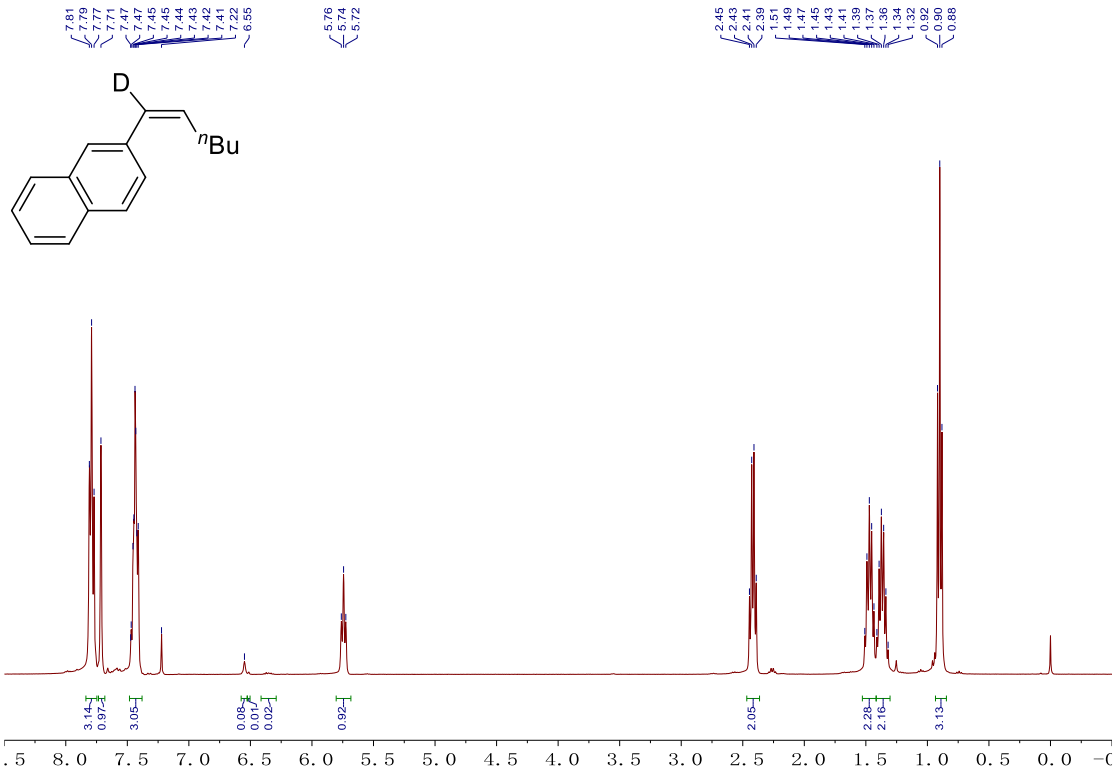


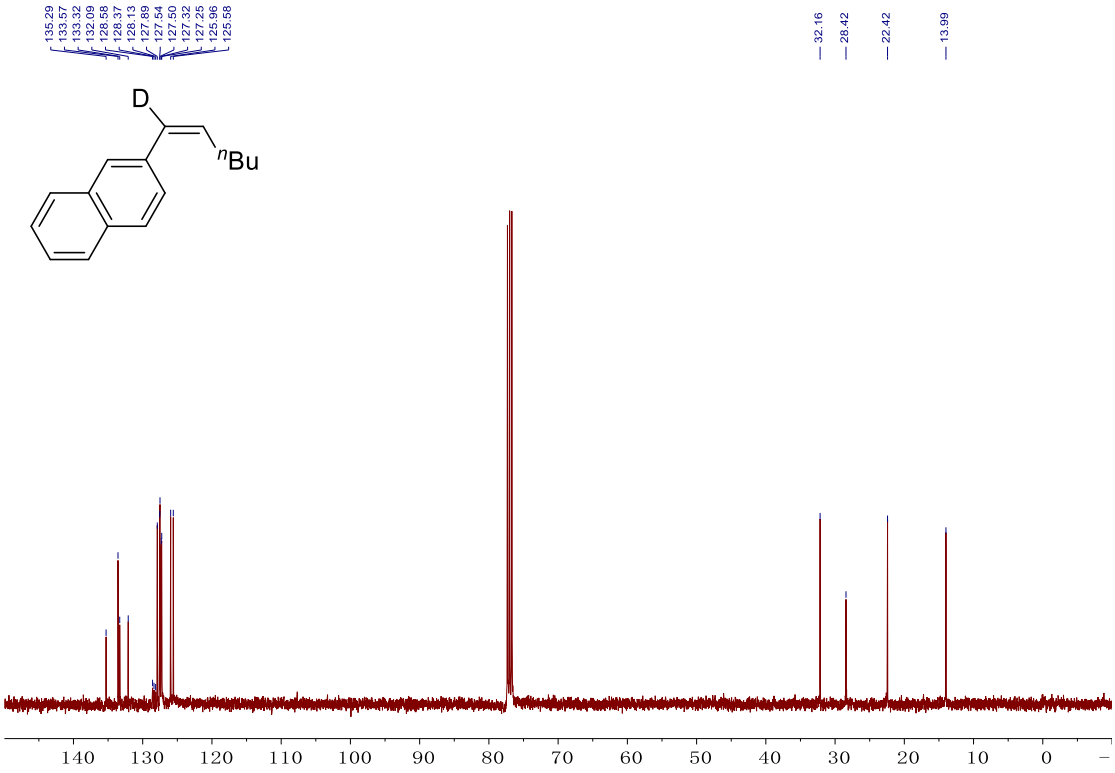
(*Z*)-1-(hex-1-en-1-yl-1-D)-2-methoxybenzene (2ap)



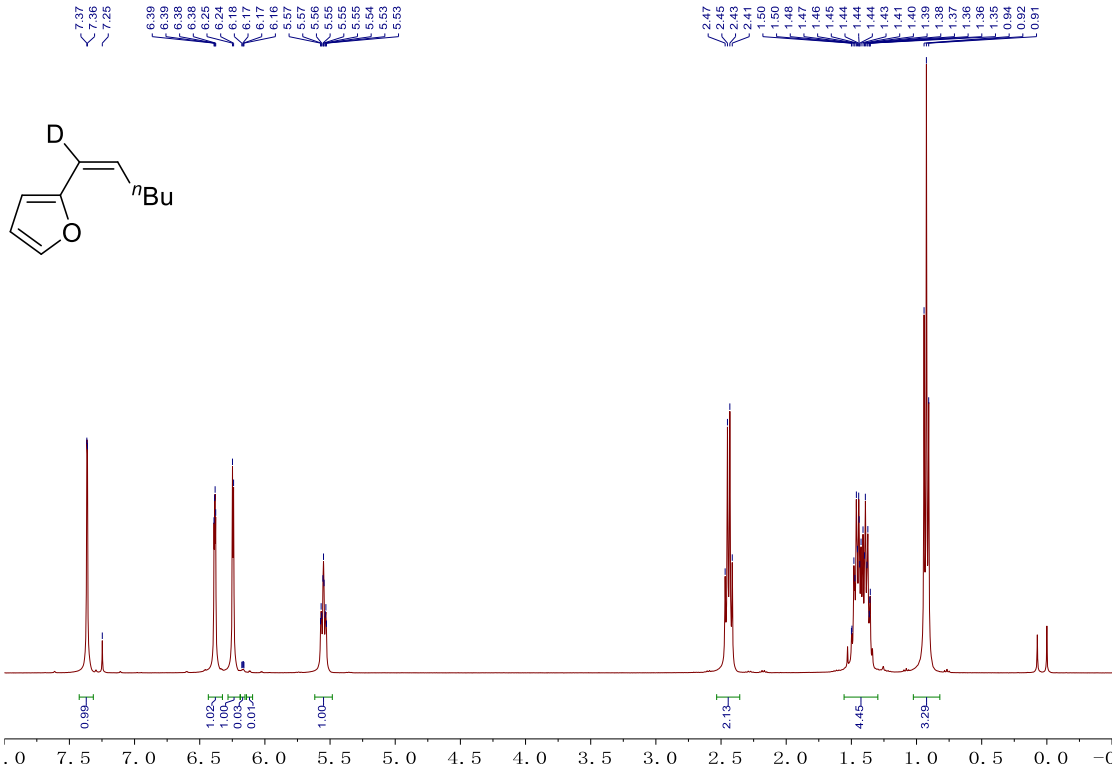


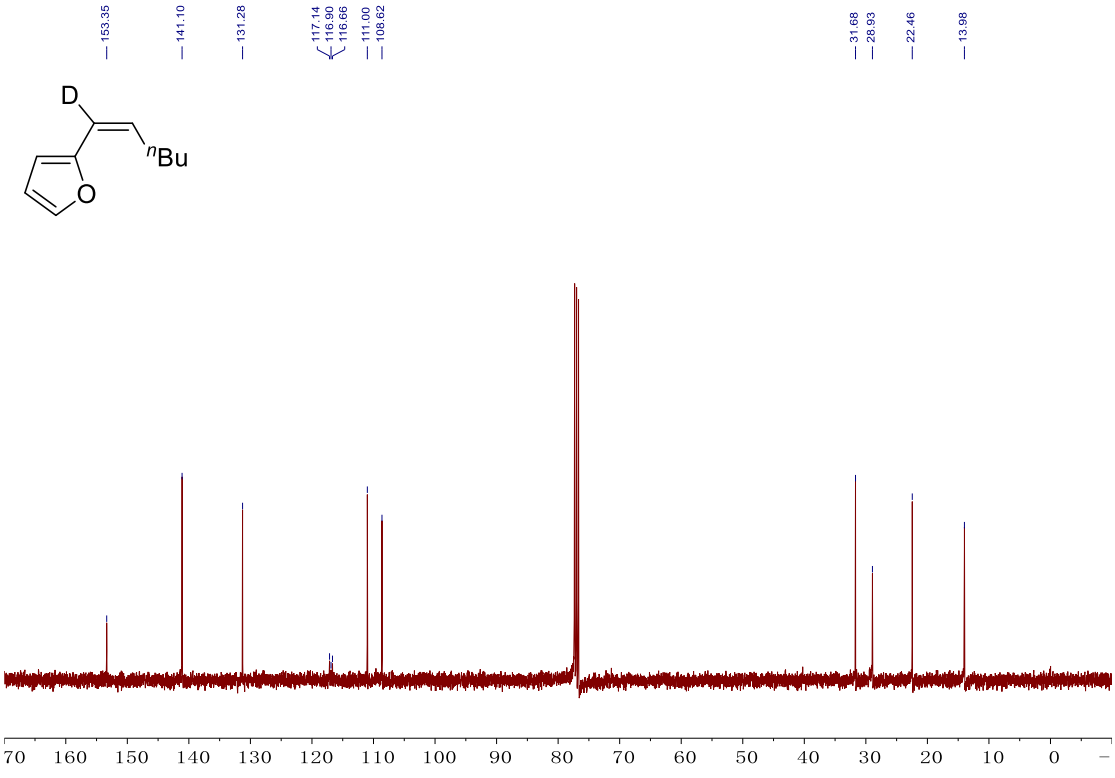
(*Z*)-2-(hex-1-en-1-yl-1-D)naphthalene (2ba)



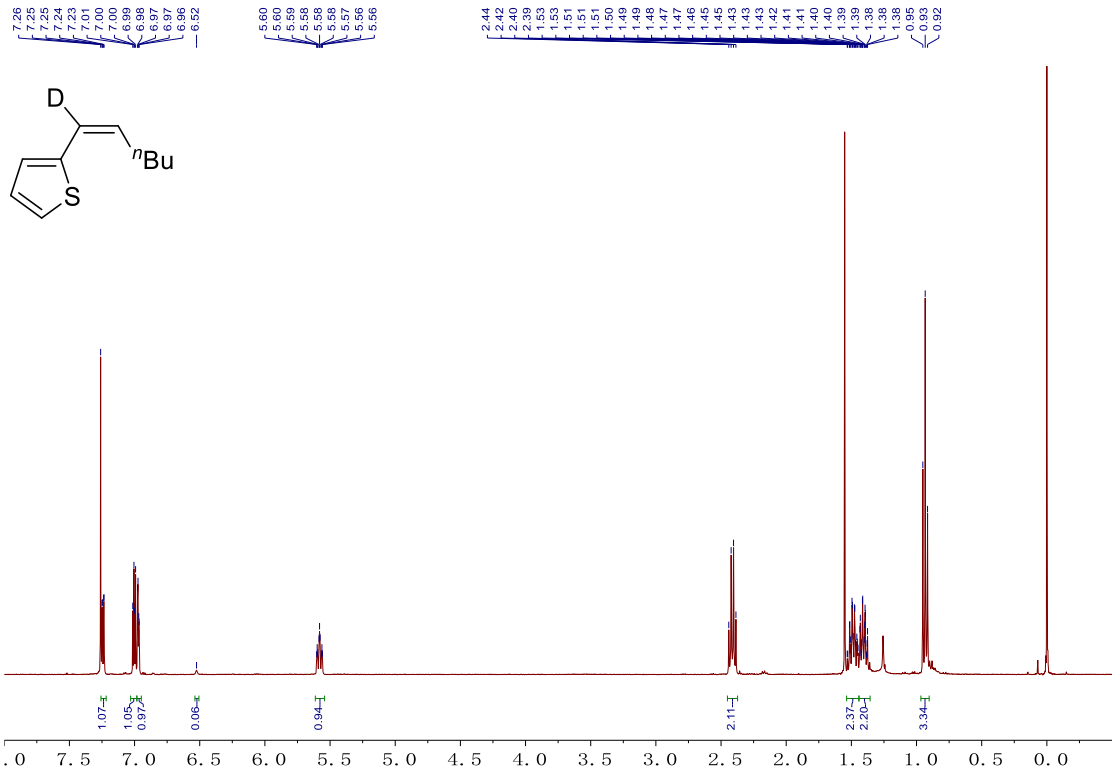


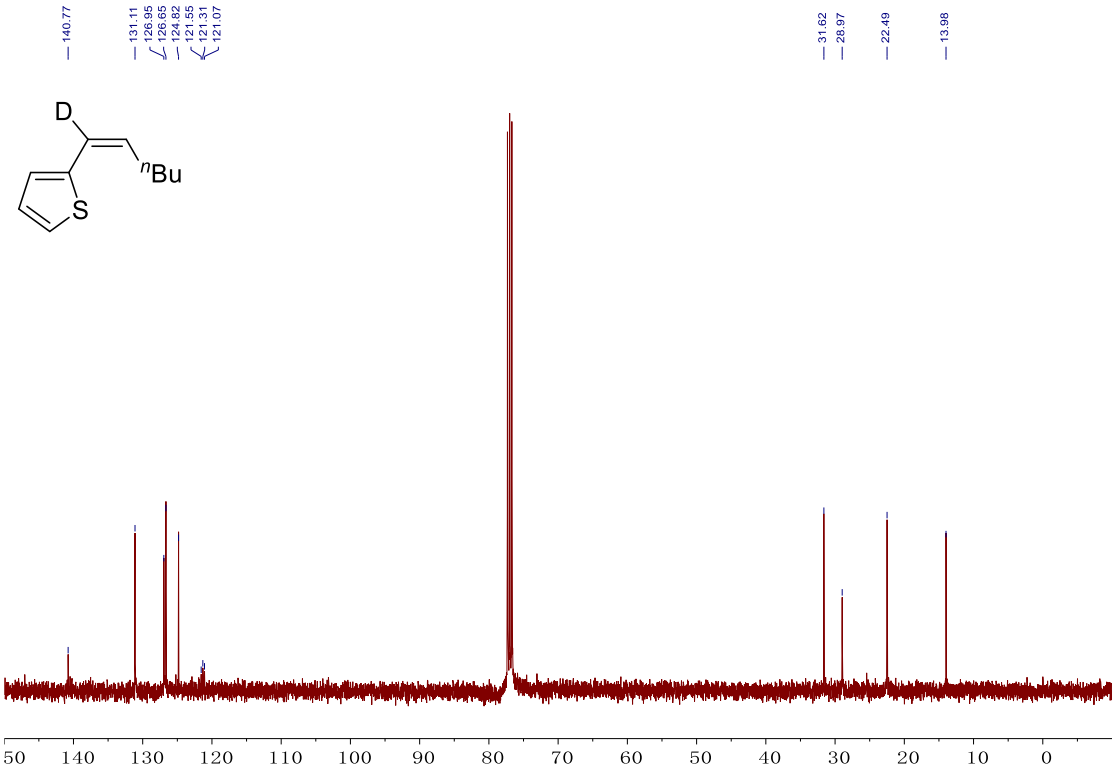
(*Z*)-2-(hex-1-en-1-yl-1-D)furan (2bb)



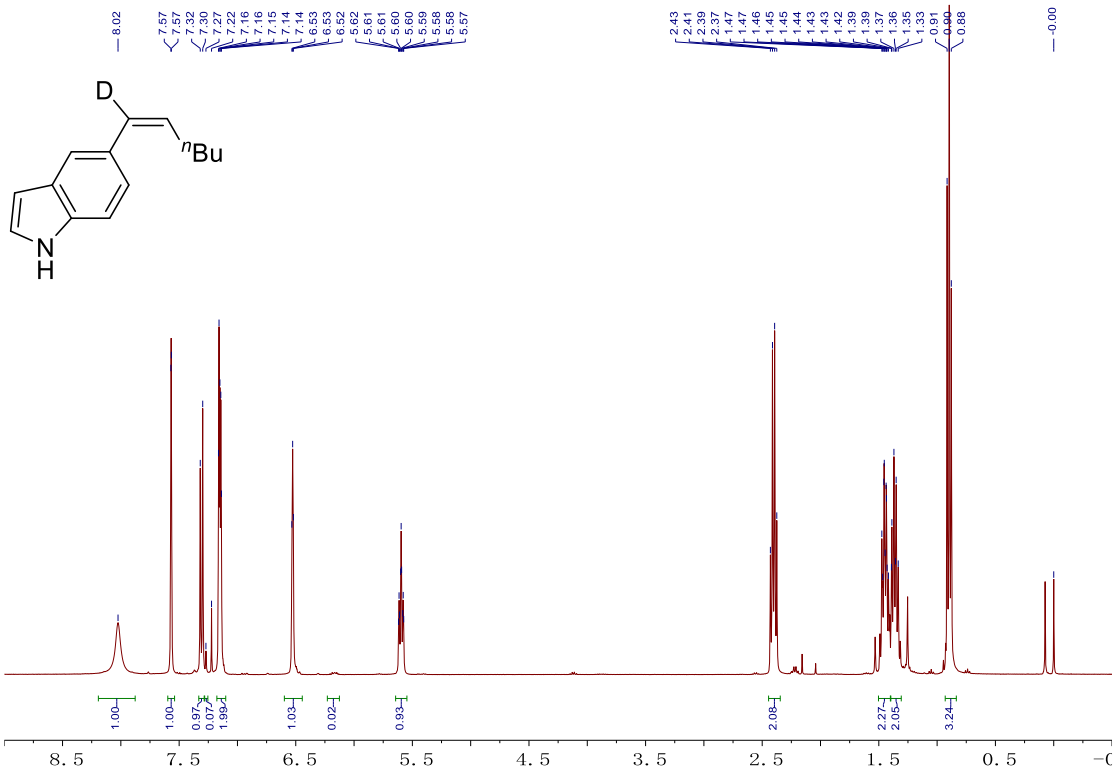


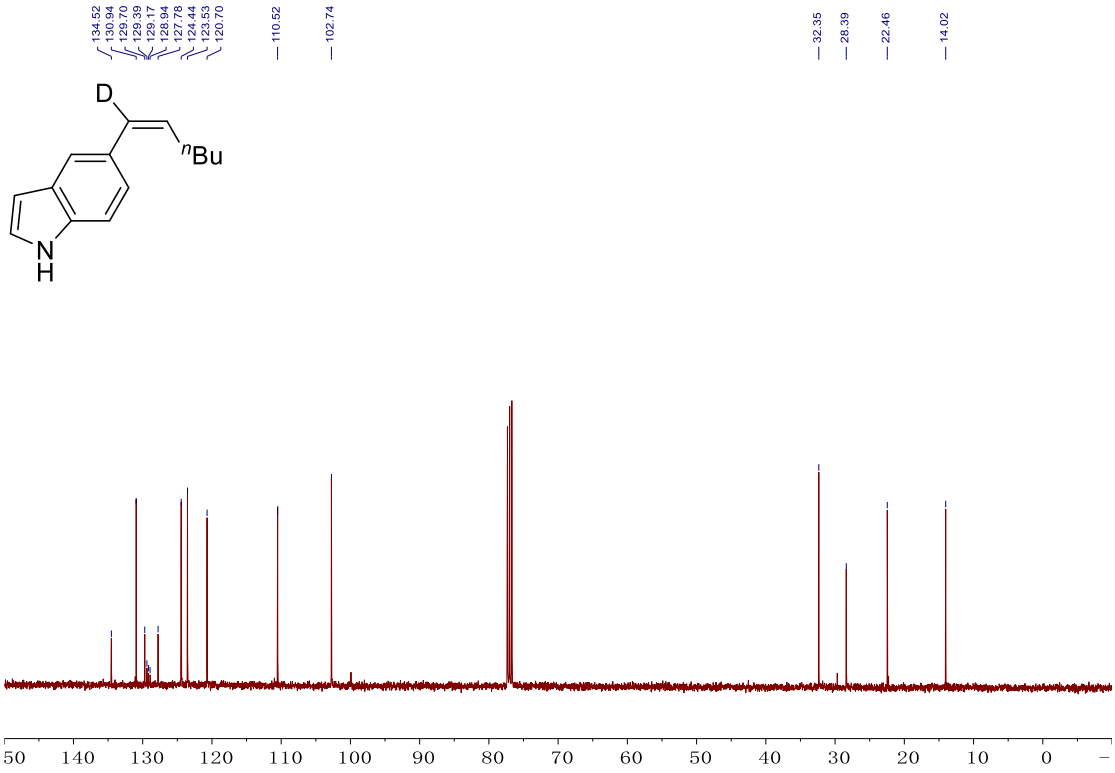
(*Z*)-2-(hex-1-en-1-yl-1-D)thiophene (2bc)



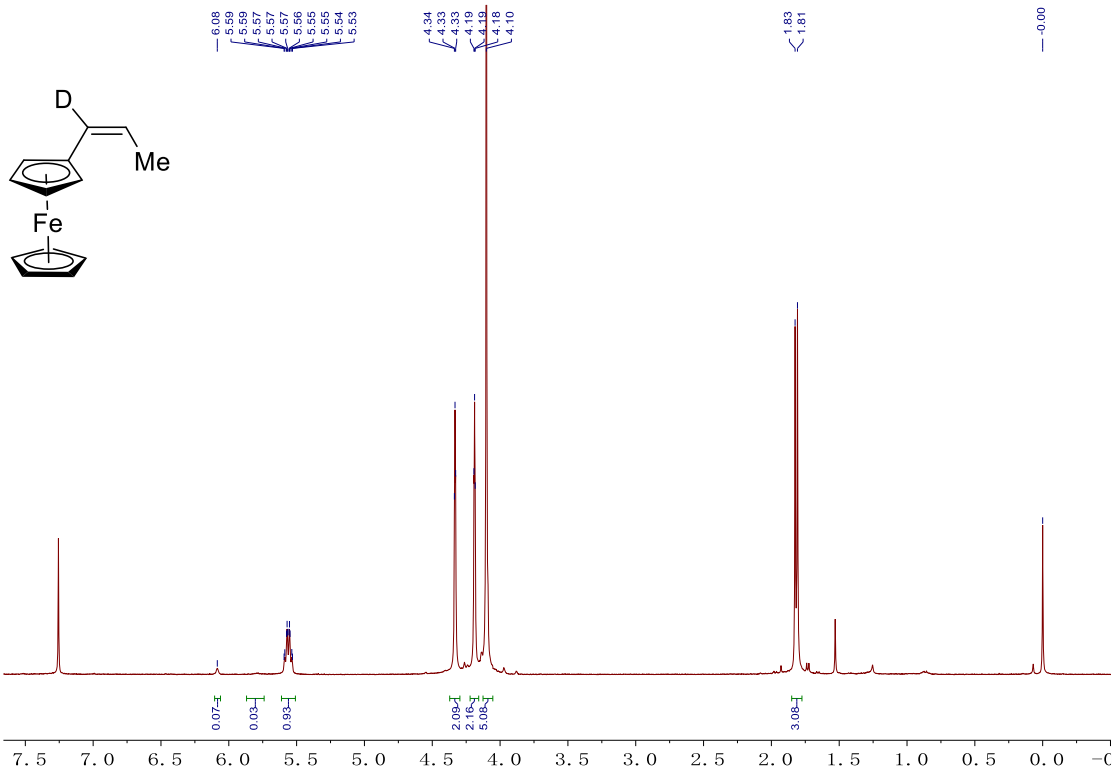


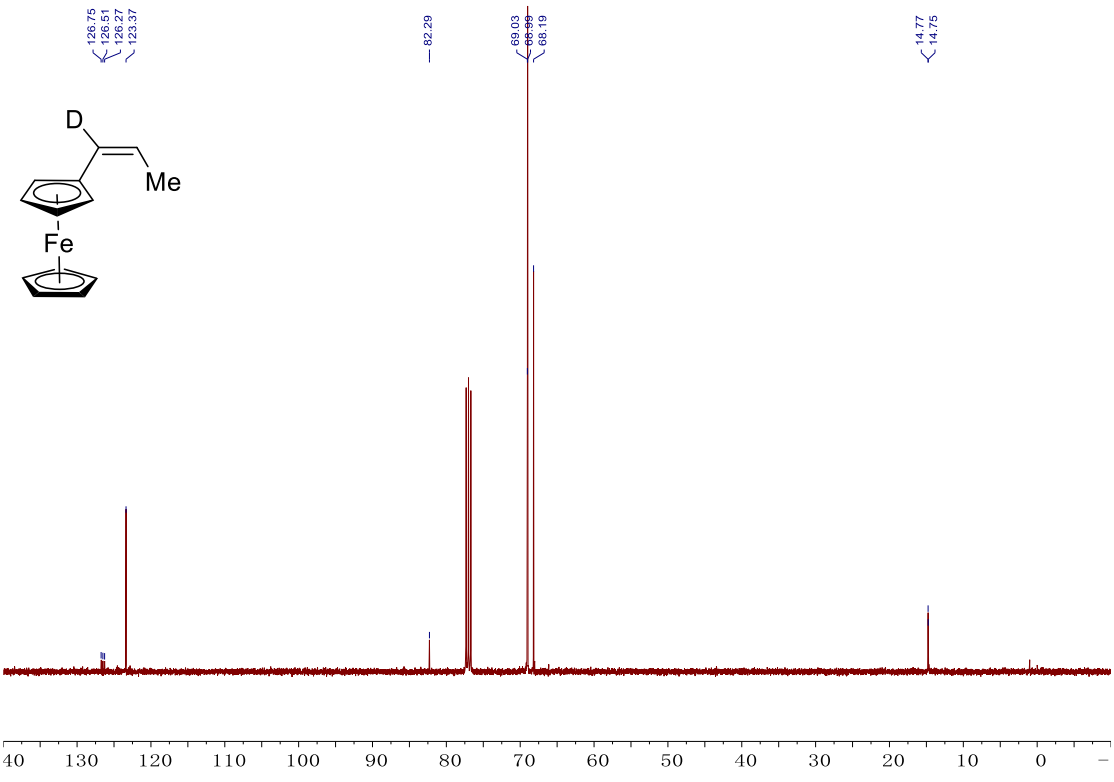
(*Z*)-5-(hex-1-en-1-yl-1-D)-1H-indole (2bd)



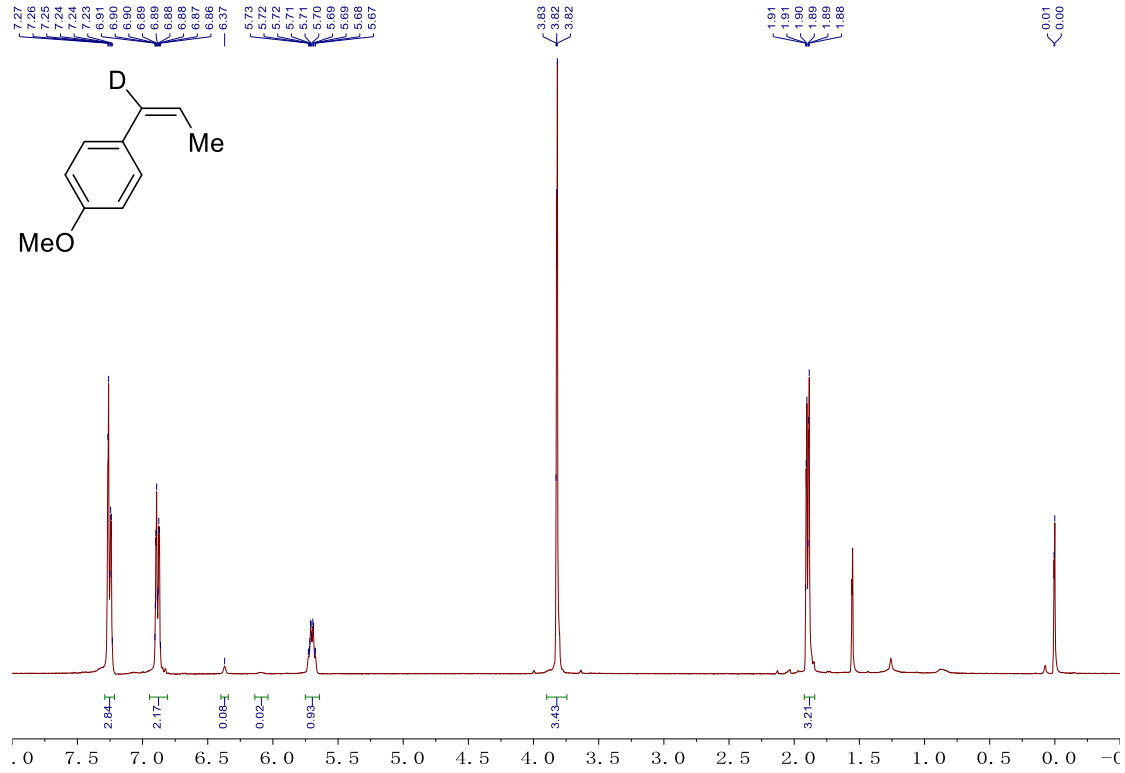


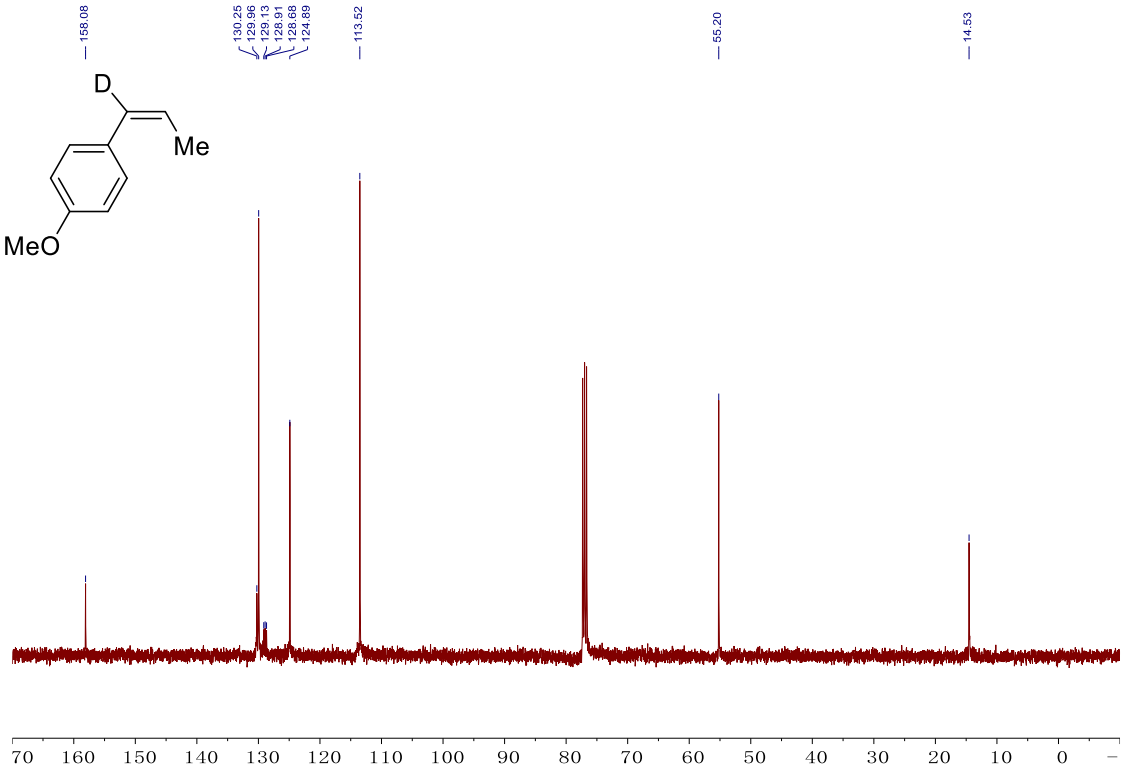
(*Z*)-1-(prop-1-en-1-yl-1-D)ferrocene (2be)



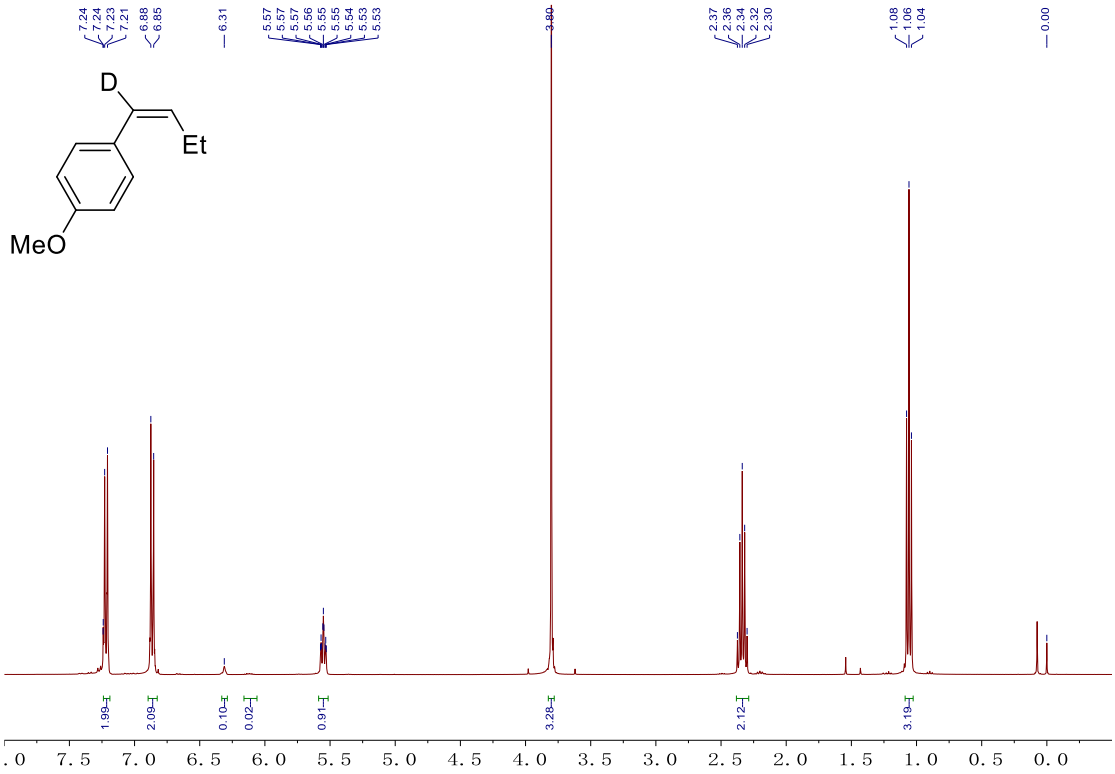


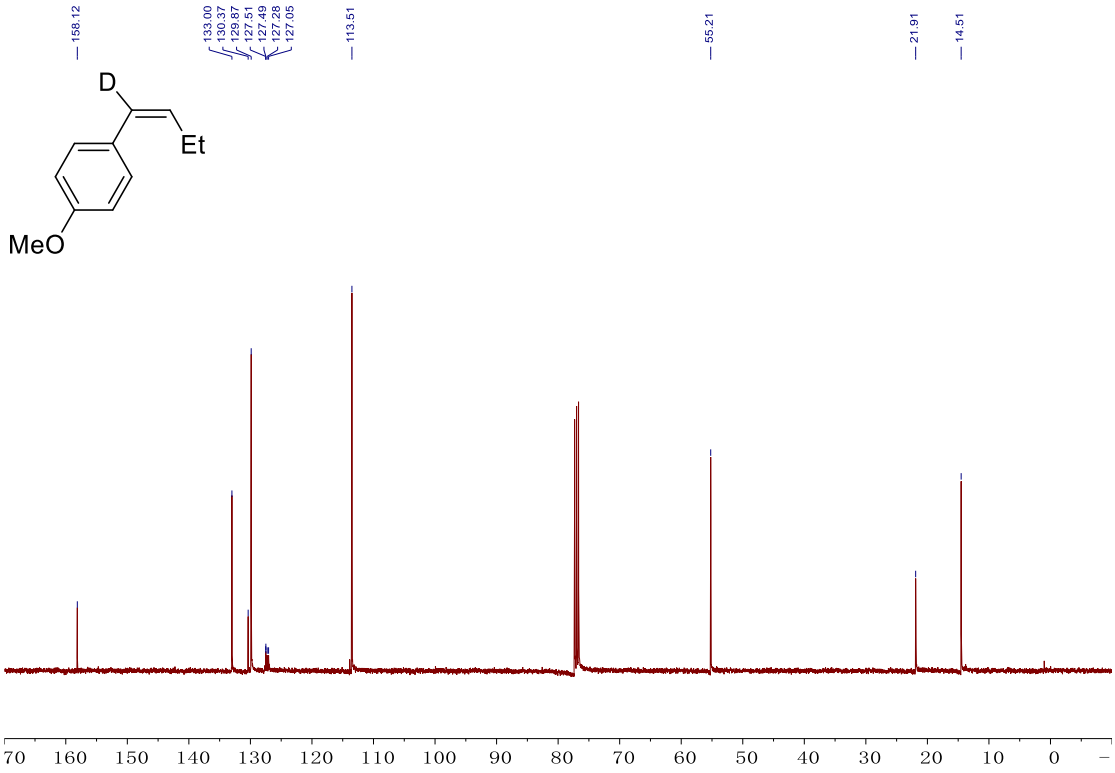
(*Z*)-1-methoxy-4-(prop-1-en-1-yl-1-D)benzene (2ca)



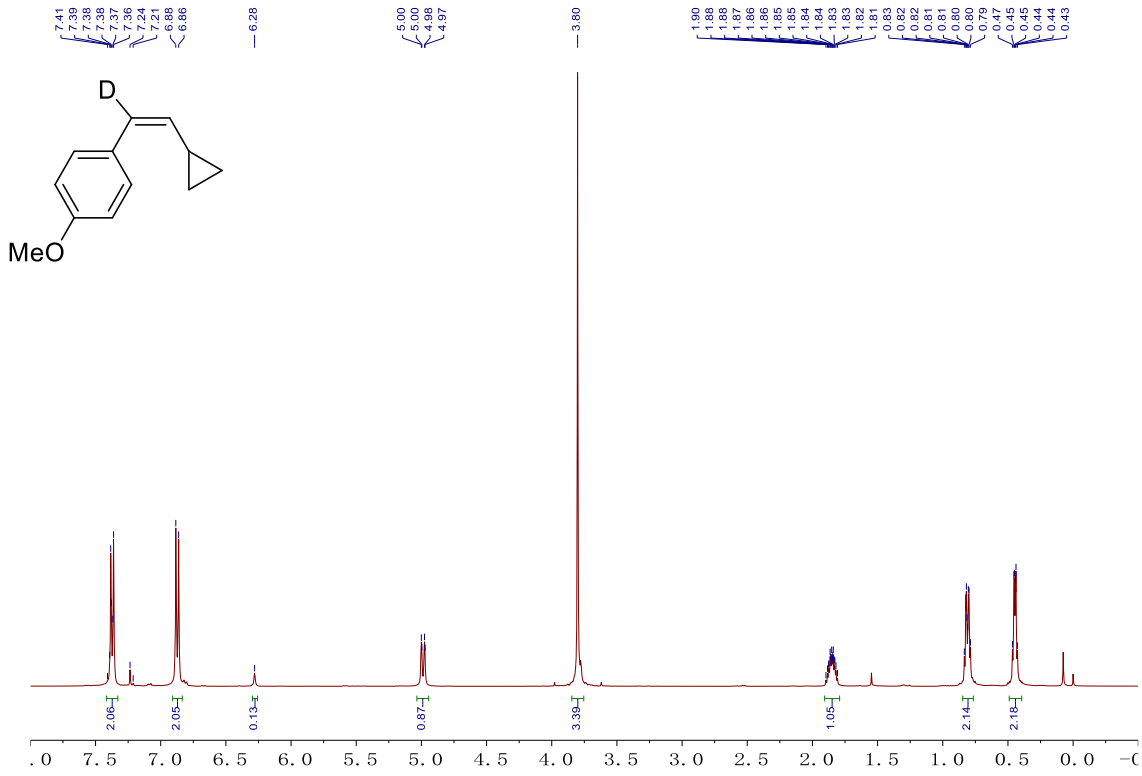


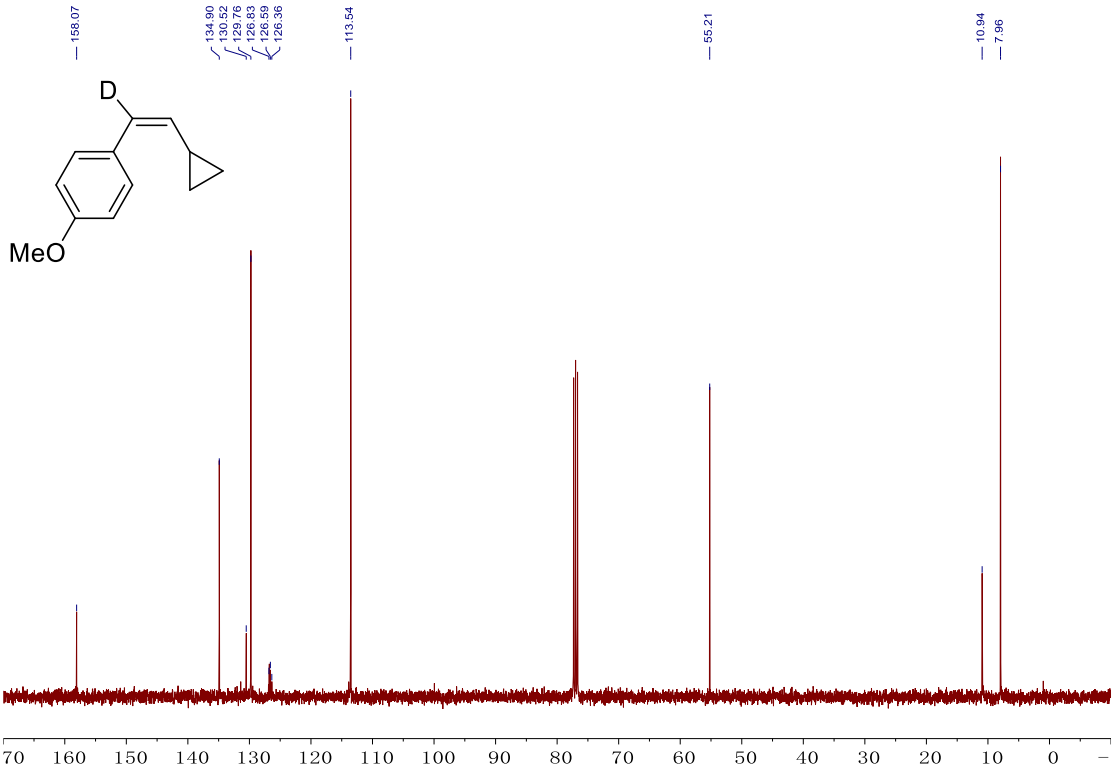
(*Z*)-1-(but-1-en-1-yl-1-D)-4-methoxybenzene (2cb)



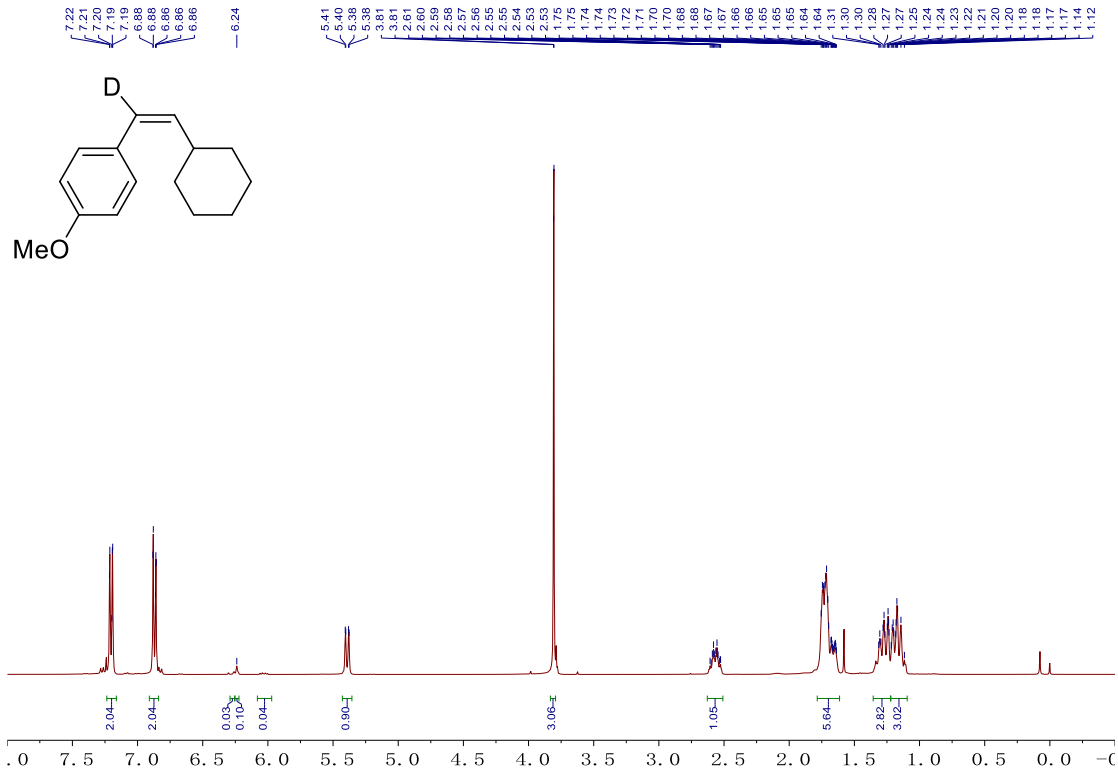


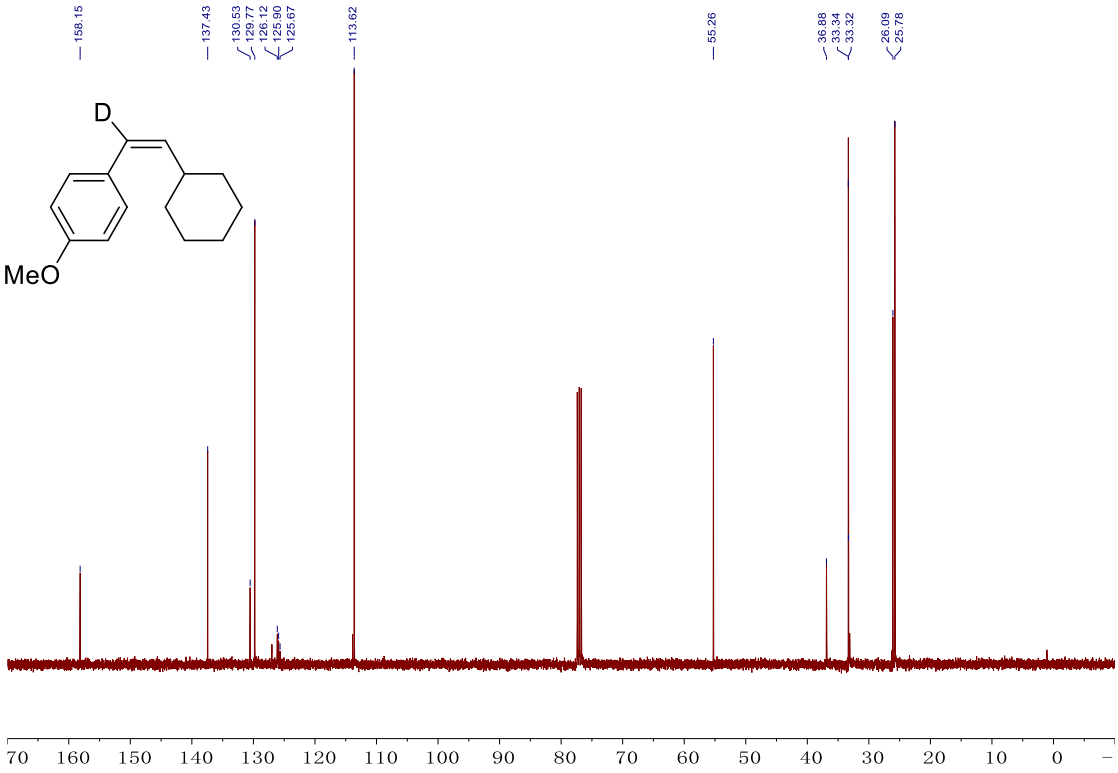
(*Z*)-1-(2-cyclopropylvinyl-1-D)-4-methoxybenzene (2cc)



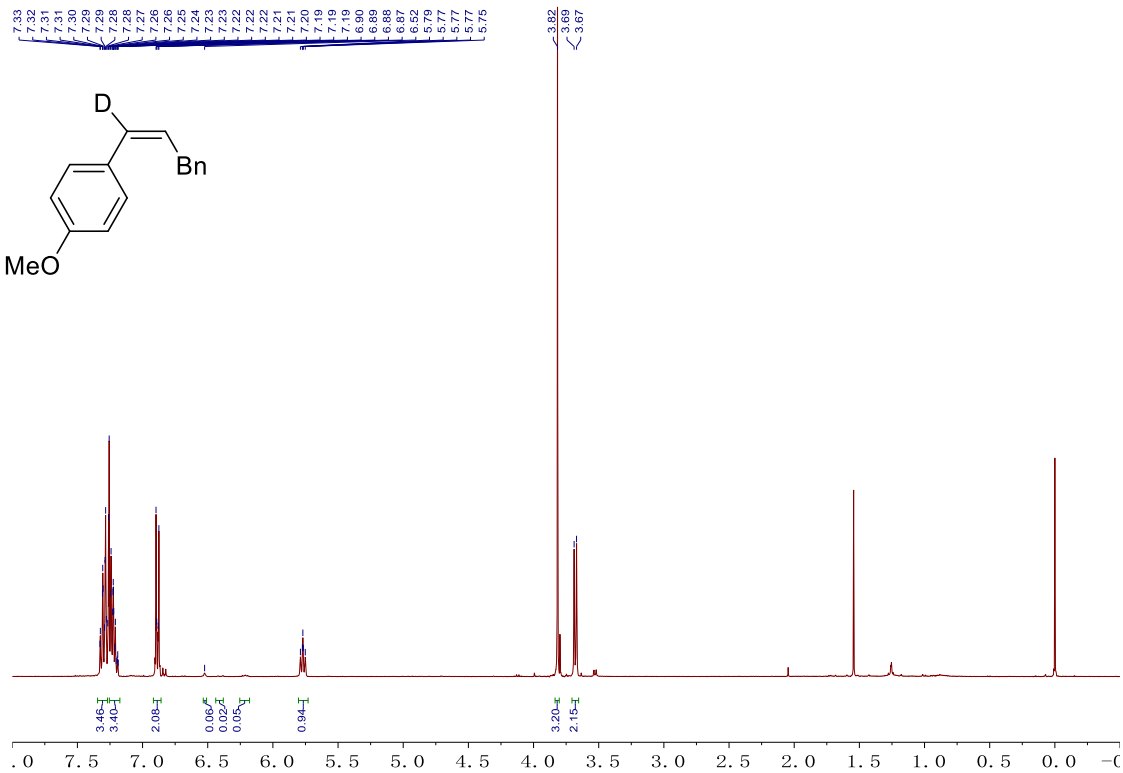


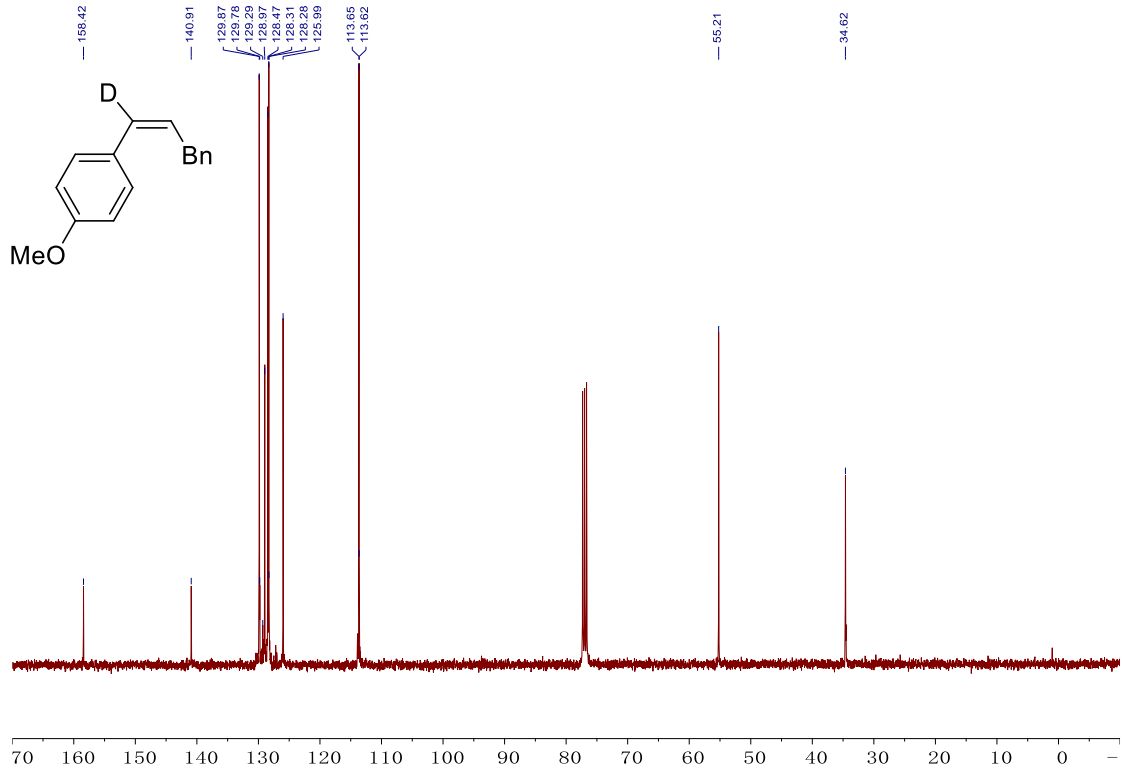
(*Z*)-1-(2-cyclohexylvinyl-1-D)-4-methoxybenzene (2cd)



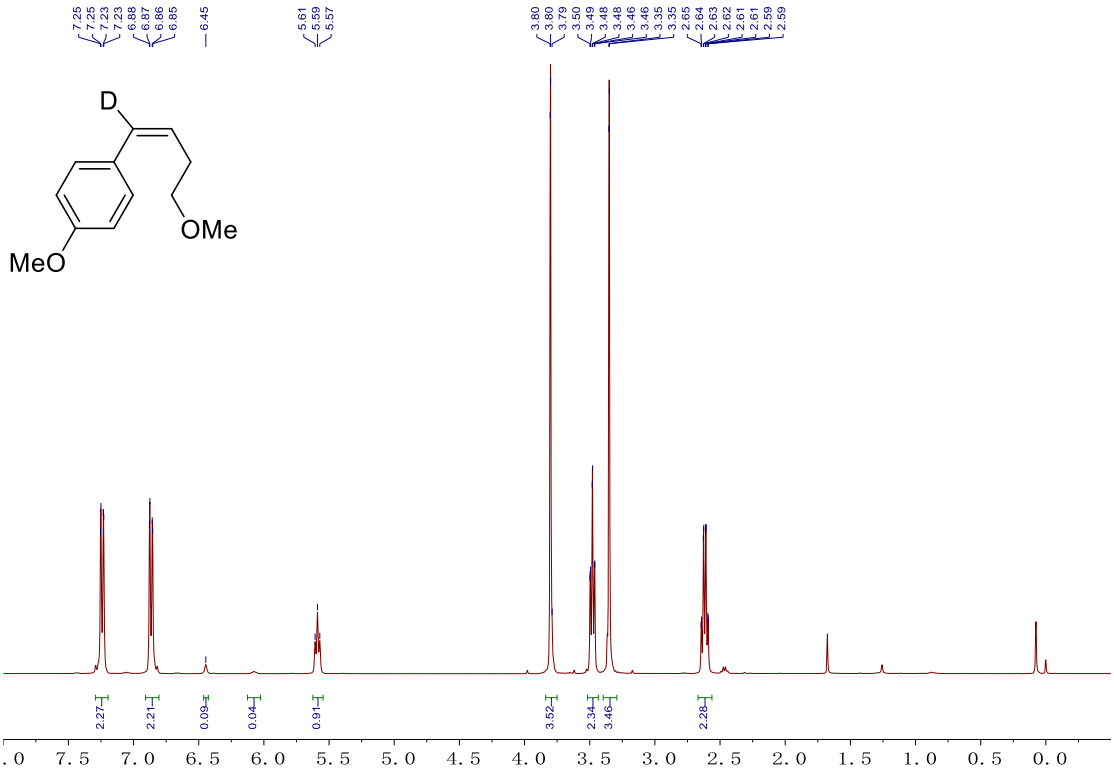


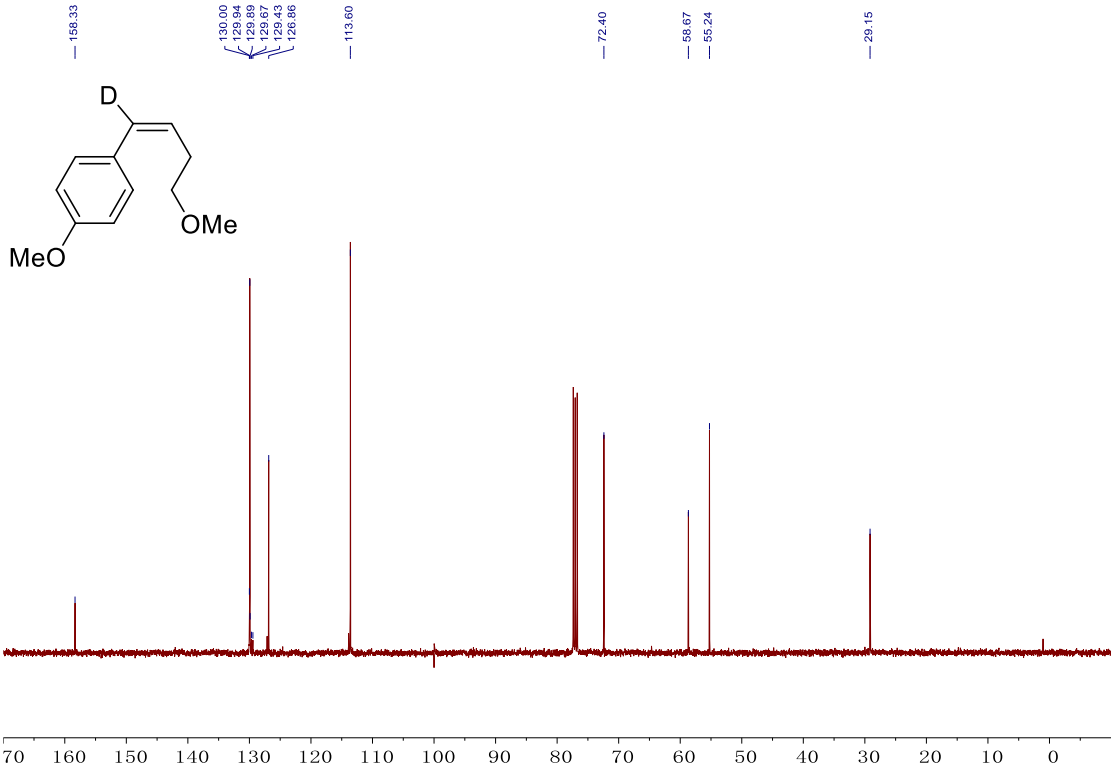
(*Z*)-1-methoxy-4-(3-phenylprop-1-en-1-yl-1-D)benzene (2ce)



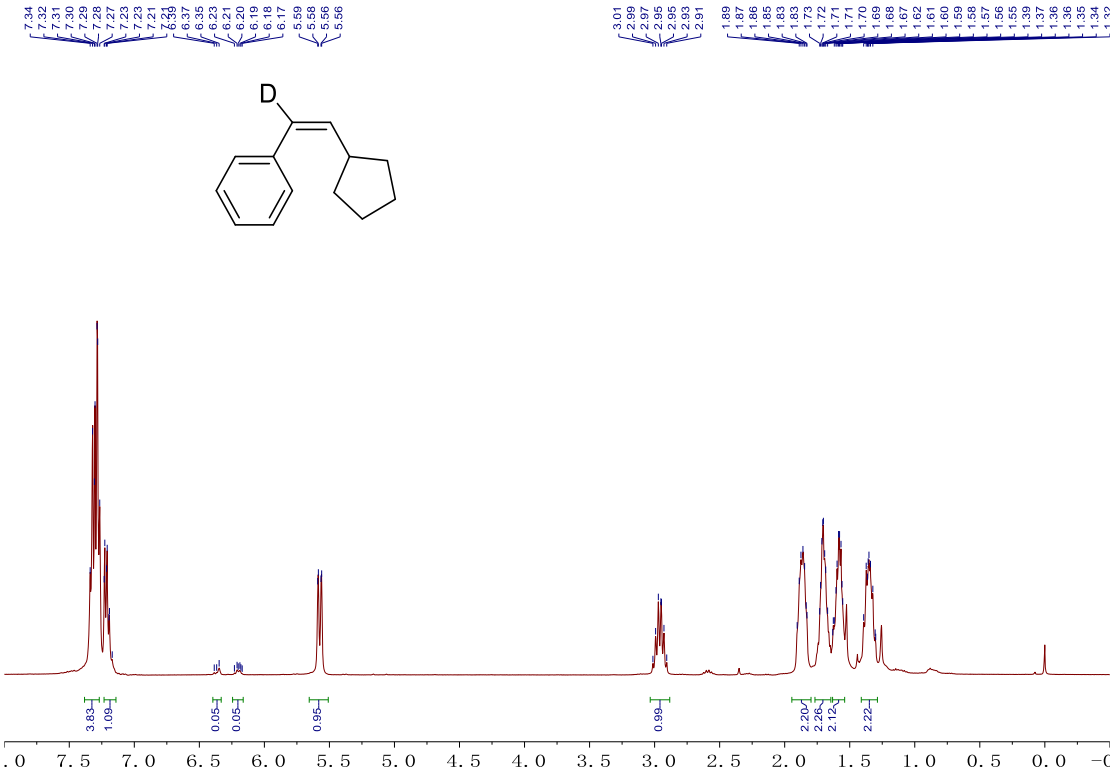


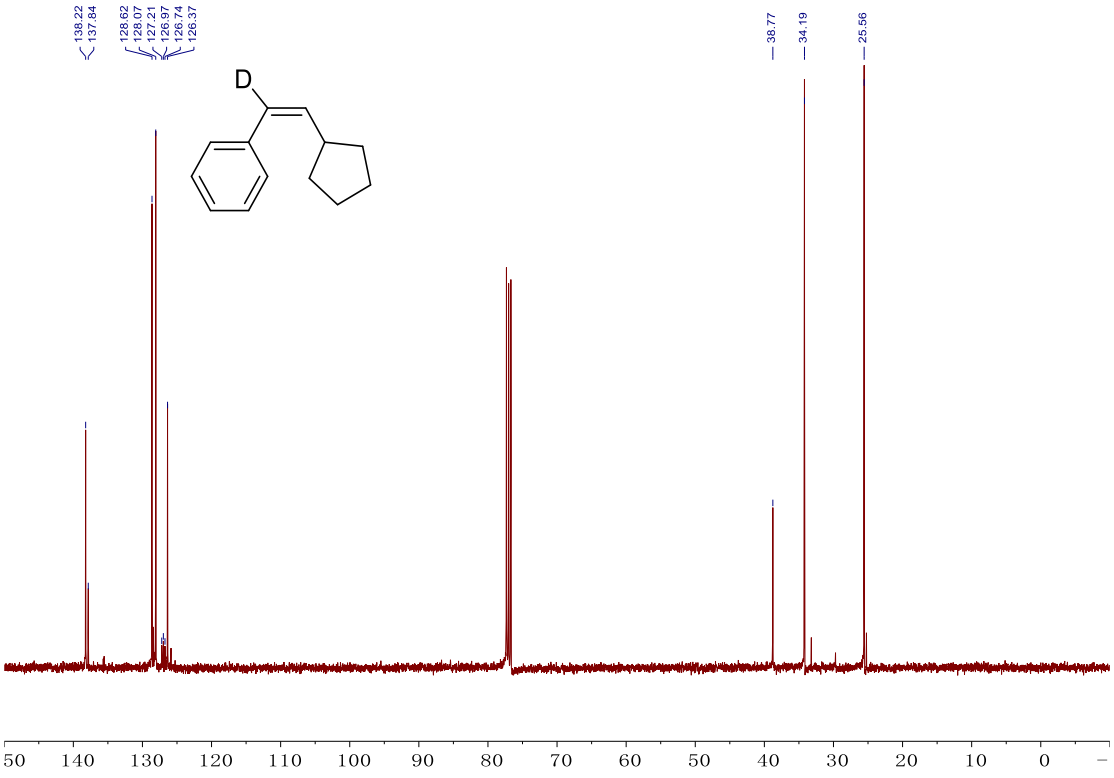
(*Z*)-1-methoxy-4-(4-methoxybut-1-en-1-yl-1-D)benzene (2cf)



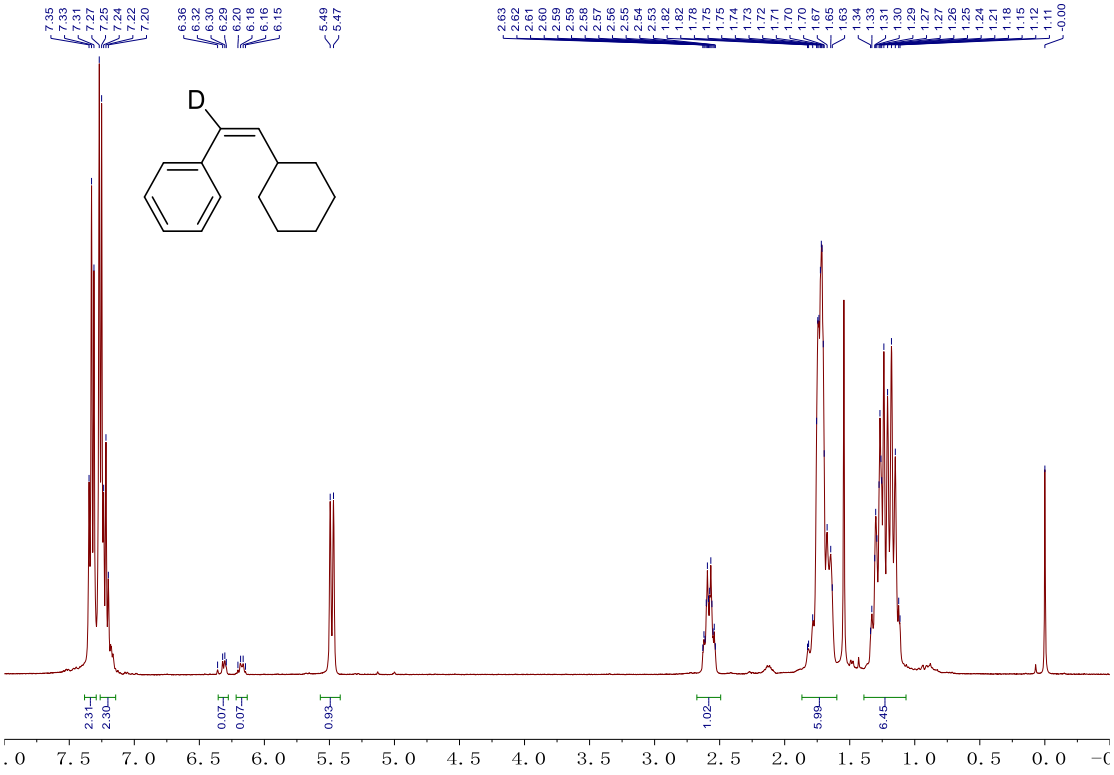


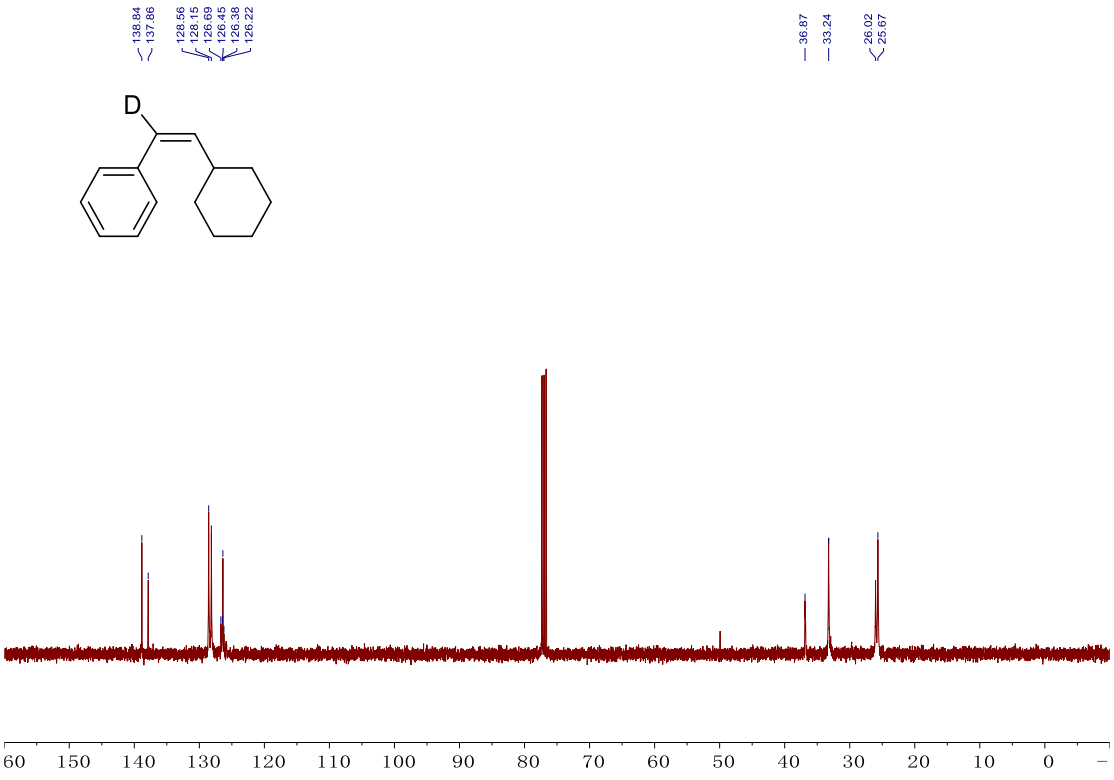
(Z)-(2-cyclopentylvinyl-1-D)benzene (2cg)



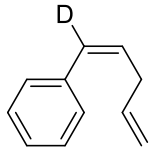


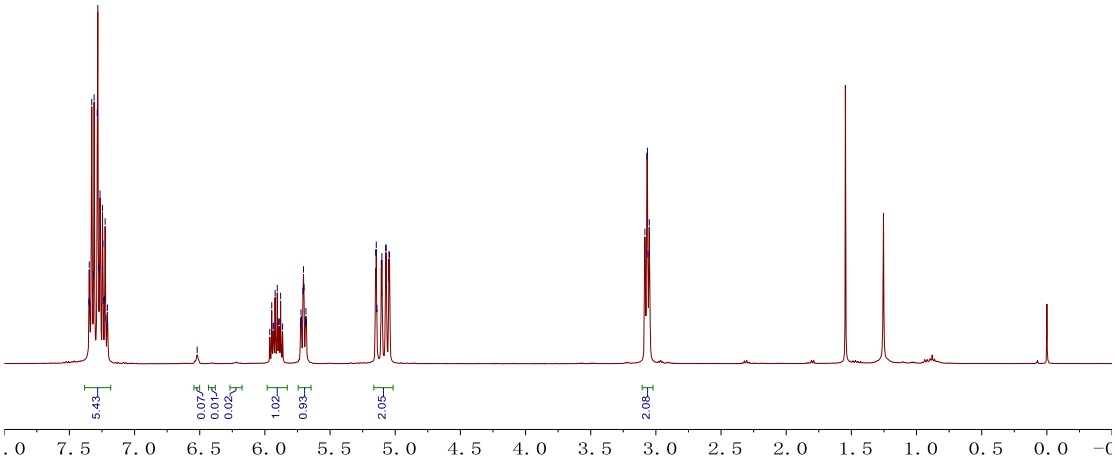
(Z)-(2-cyclohexylvinyl-1-D)benzene (2ch)

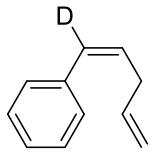




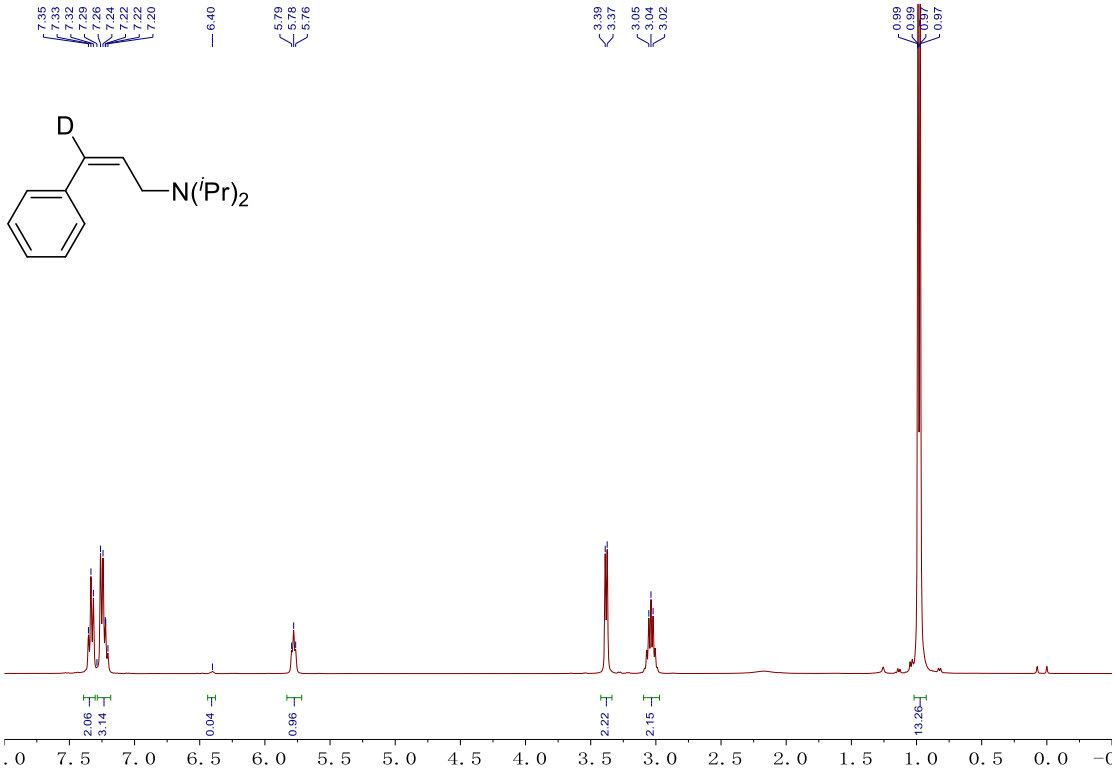
(*Z*)-(penta-1,4-dien-1-yl-1-D)benzene (2ci)

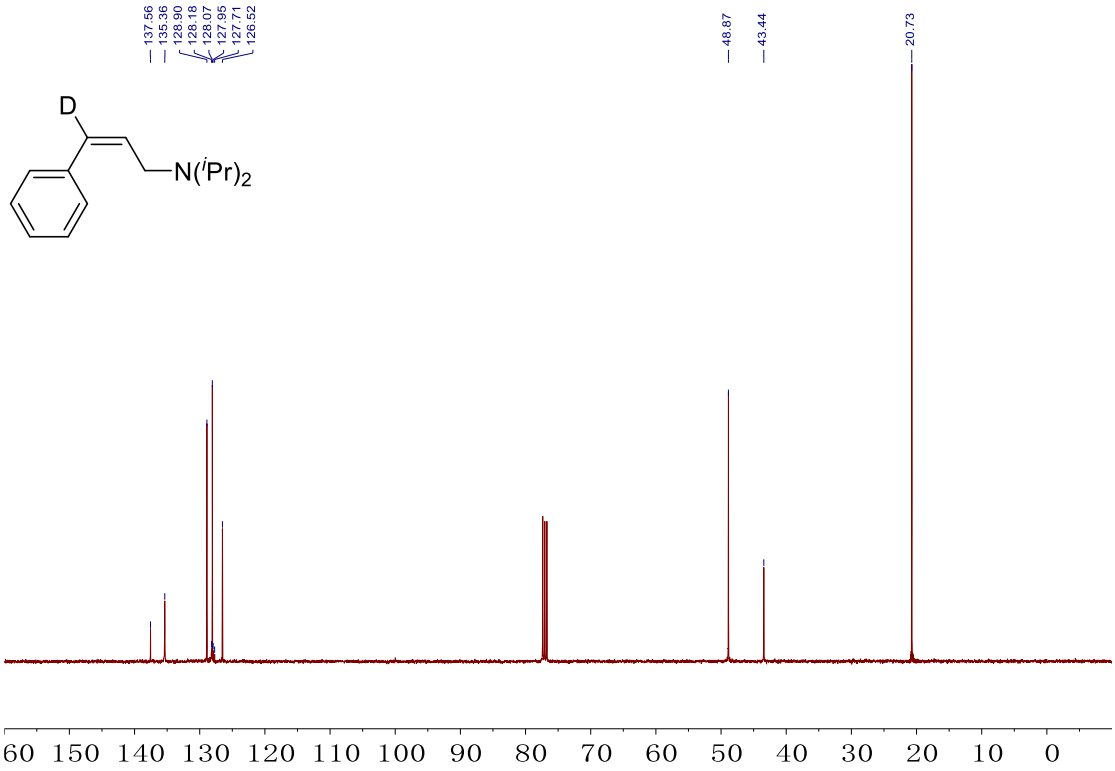




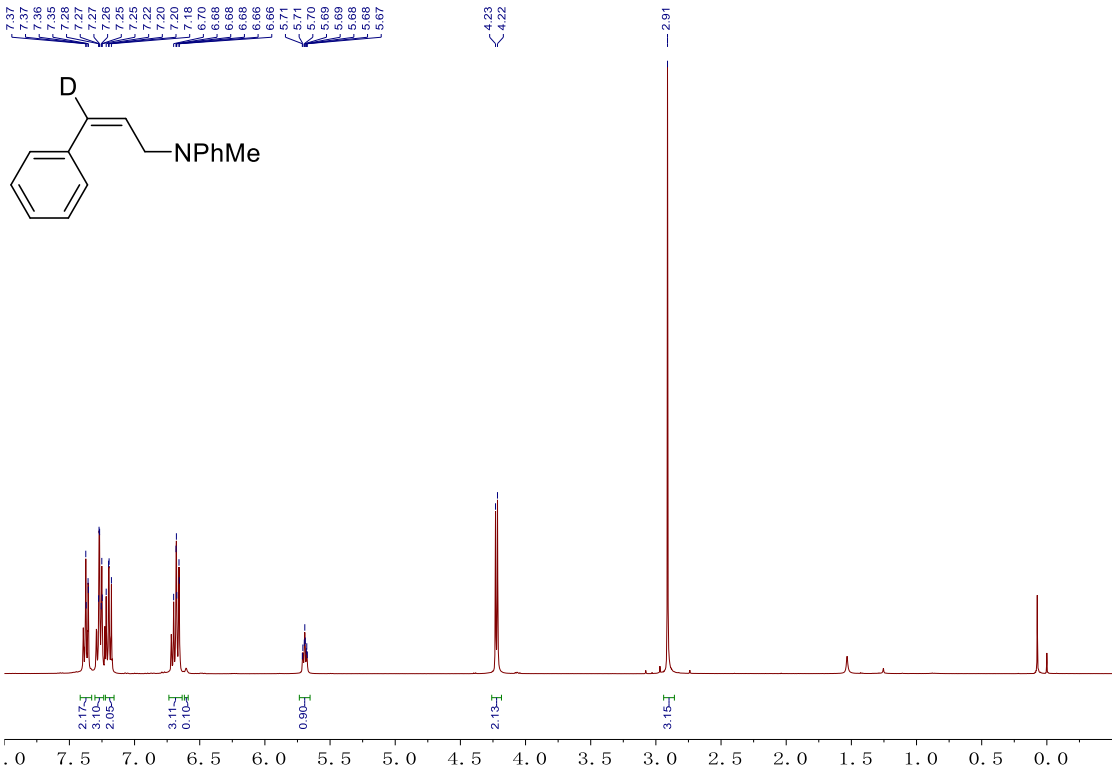


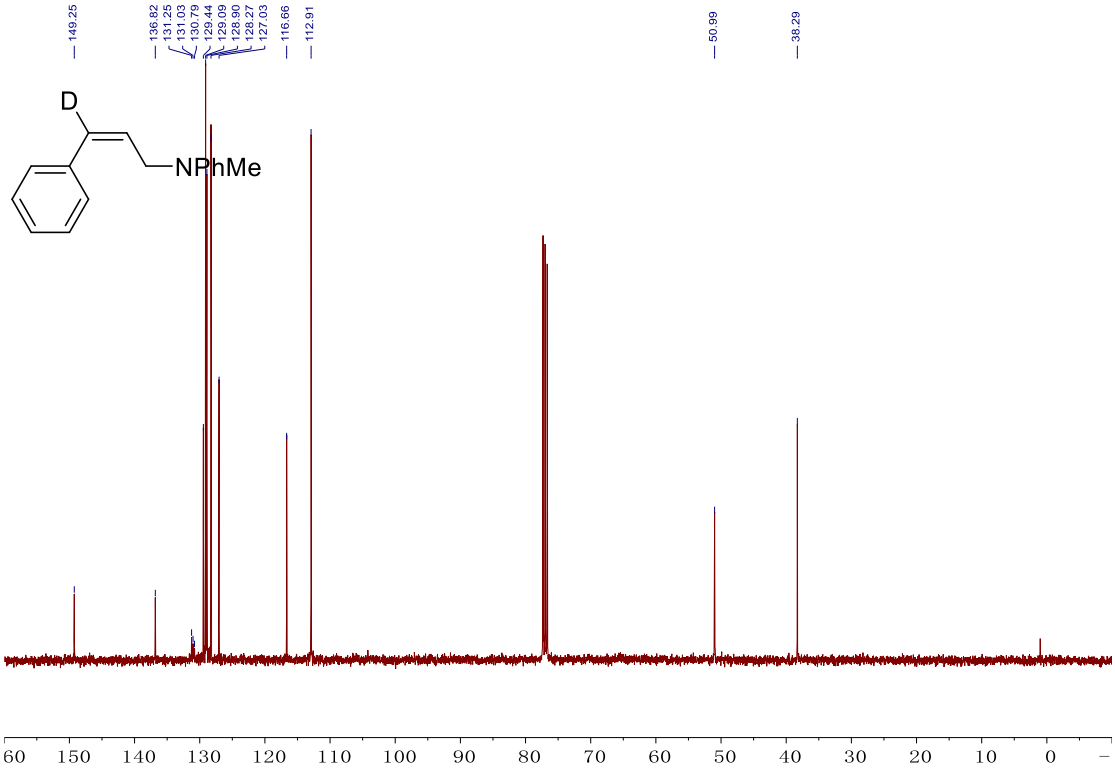
(*Z*)-N,N-diisopropyl-3-phenylprop-2-en-1-amine-3-D (2cj)



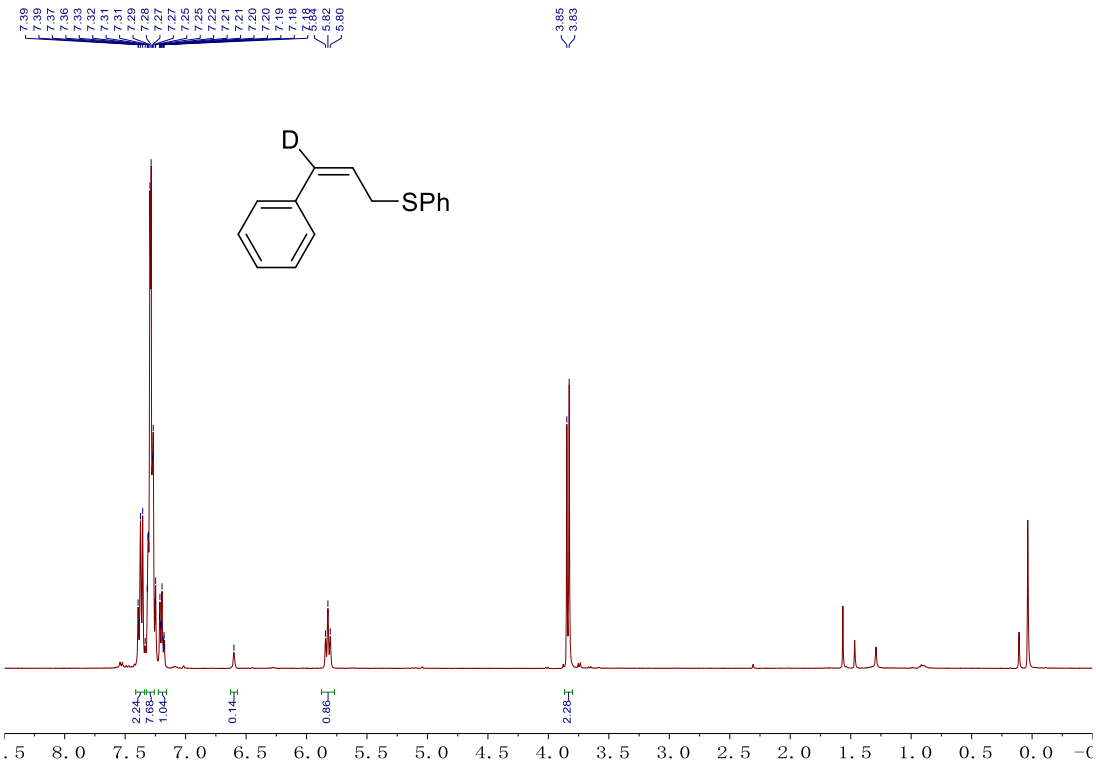


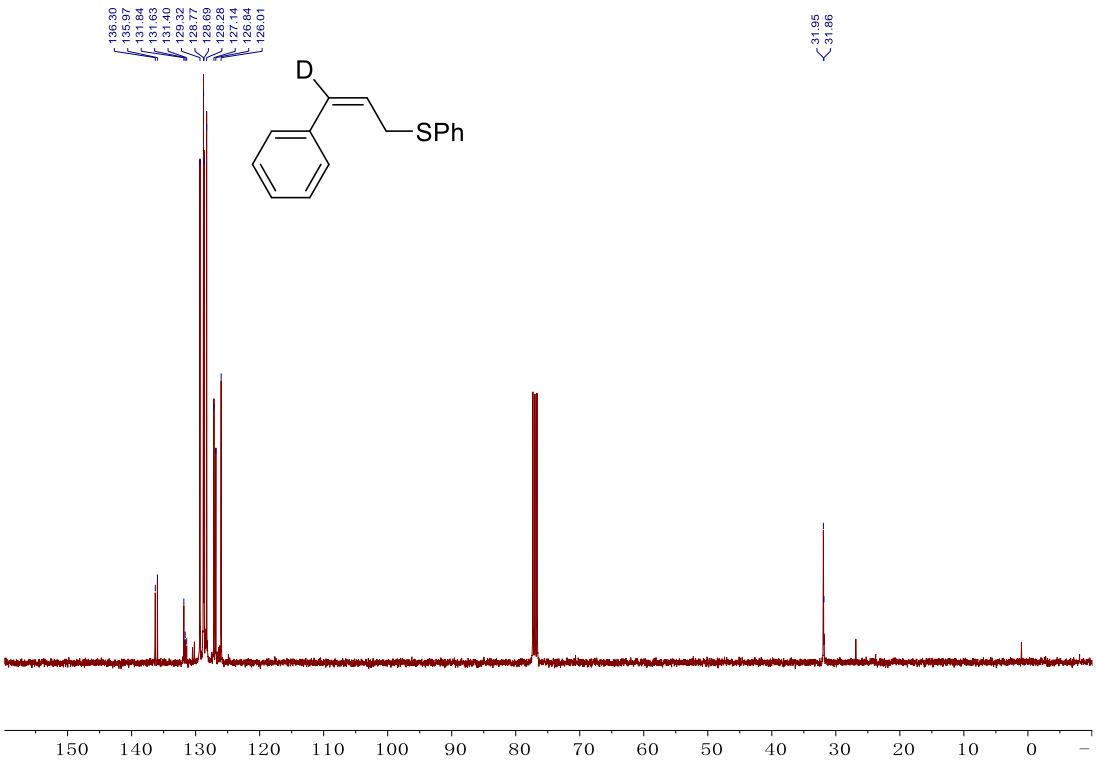
(*Z*)-N-methyl-N-(3-phenylallyl-3-D)aniline (2ck)



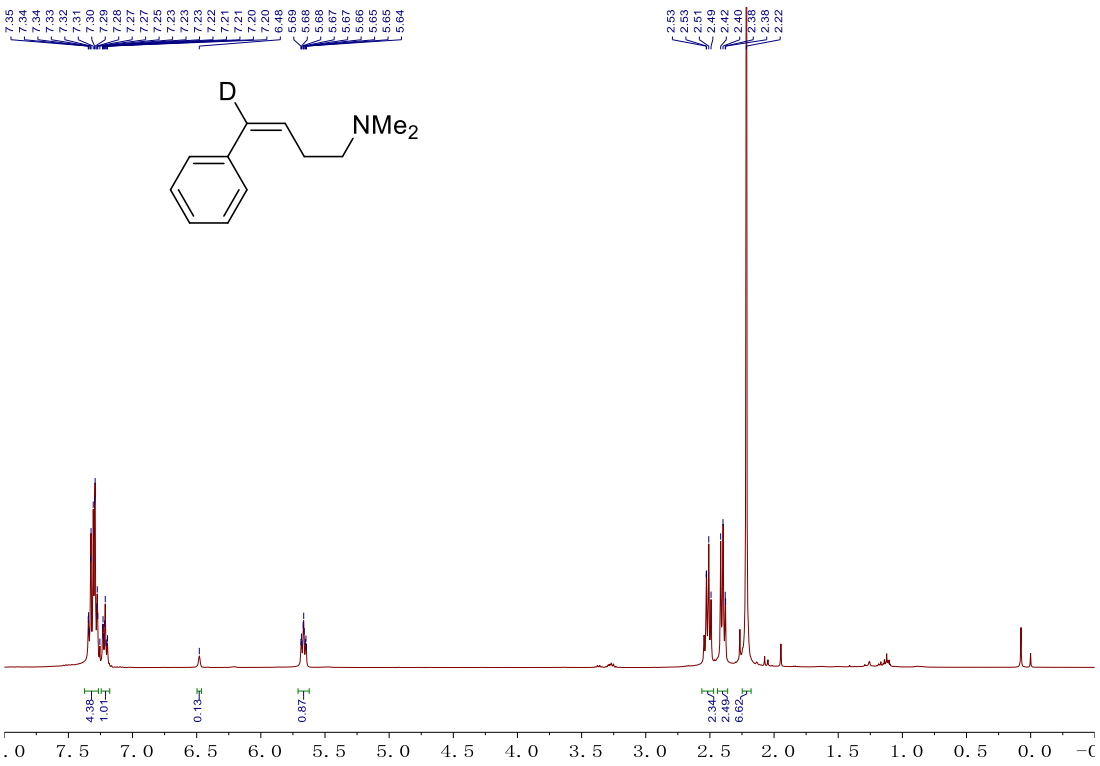


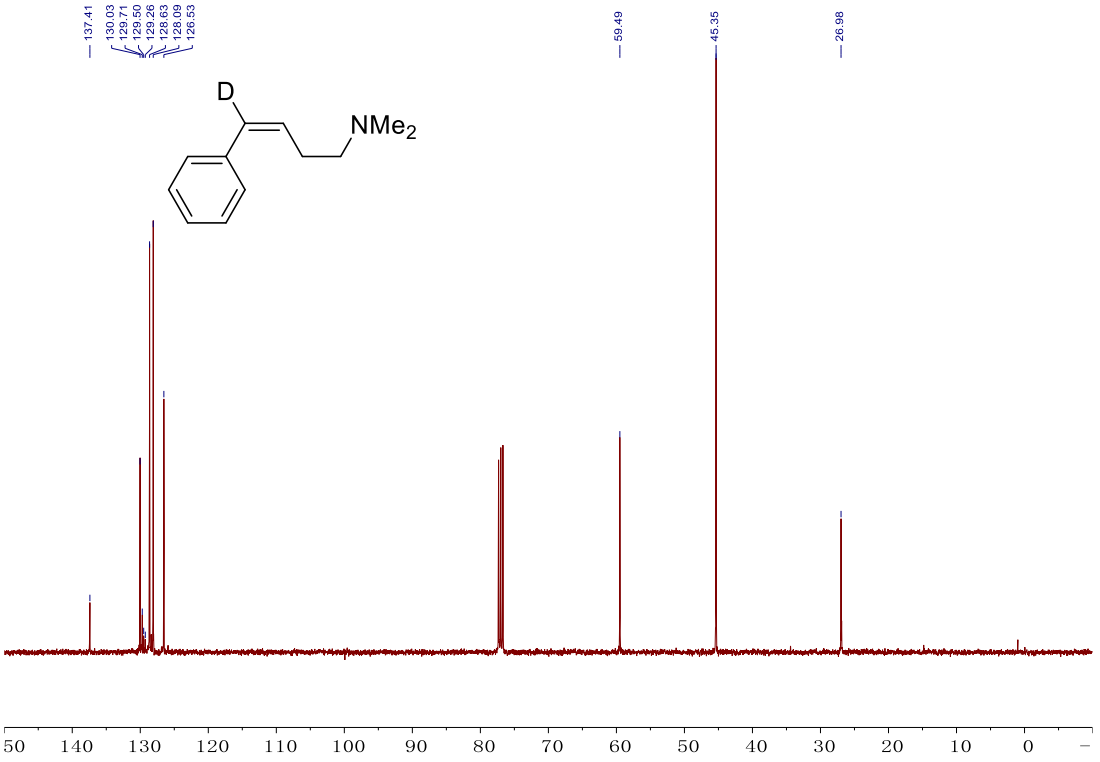
(*Z*)-phenyl(3-phenylallyl-3-d)sulfane (2cl)



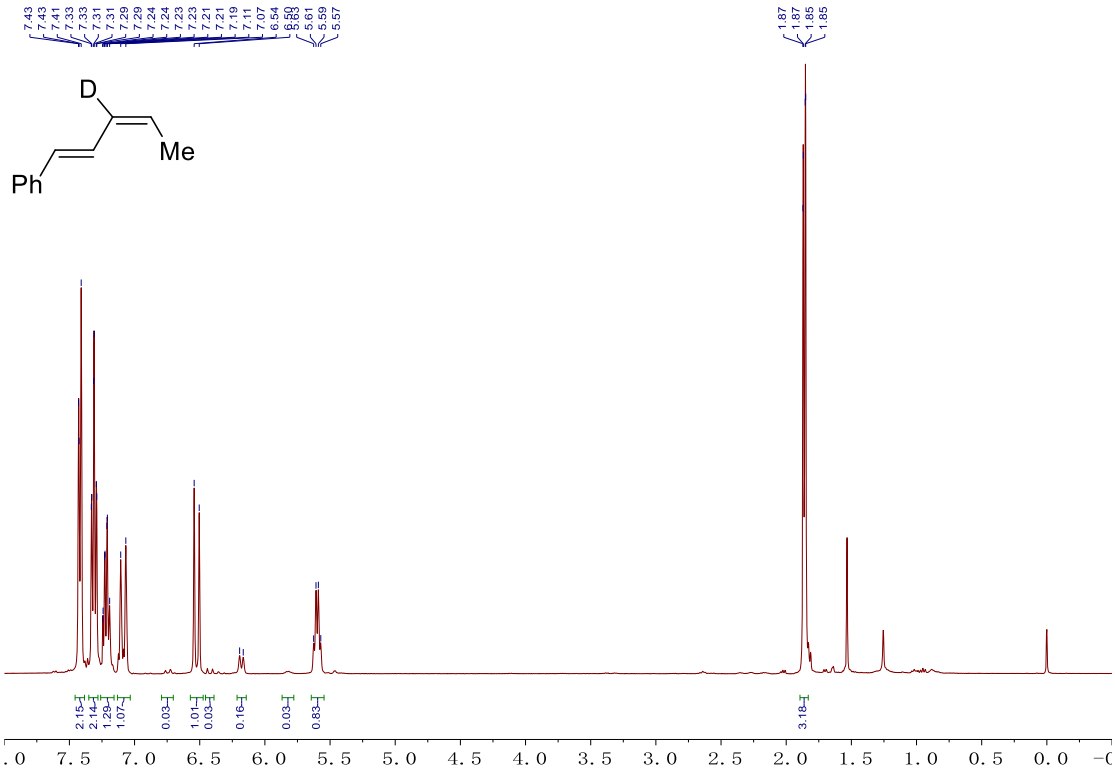


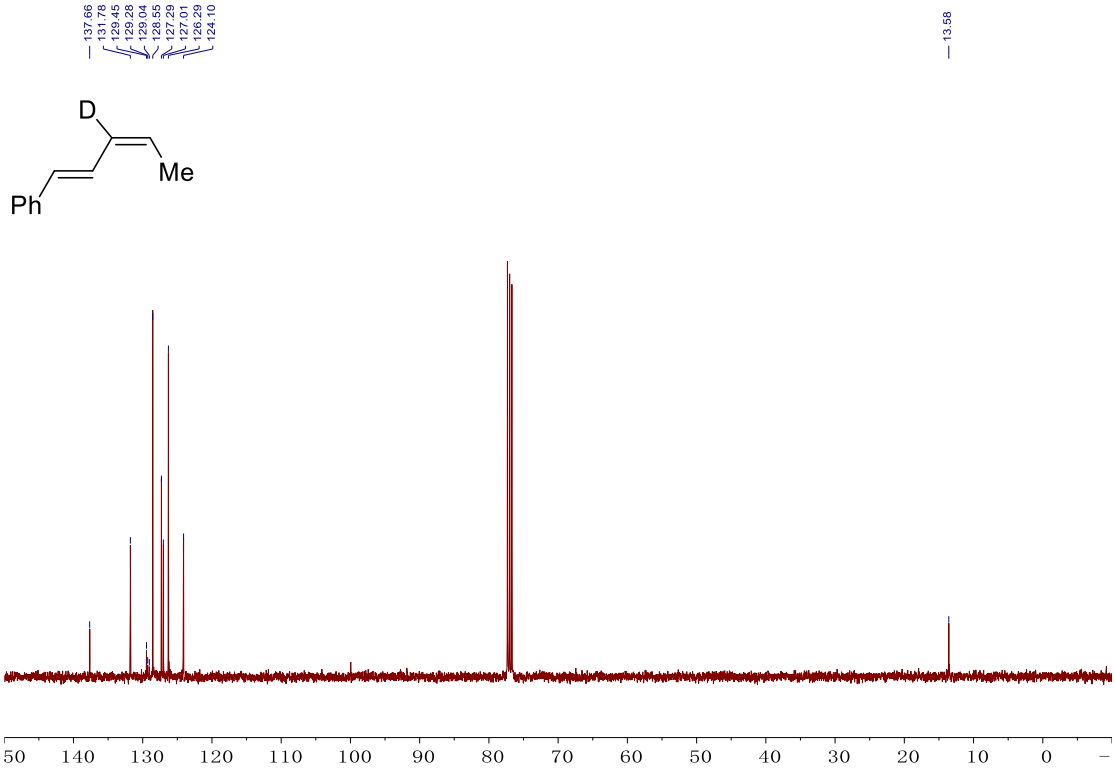
(*Z*)-N,N-dimethyl-4-phenylbut-3-en-1-amine-4-d (2cm)



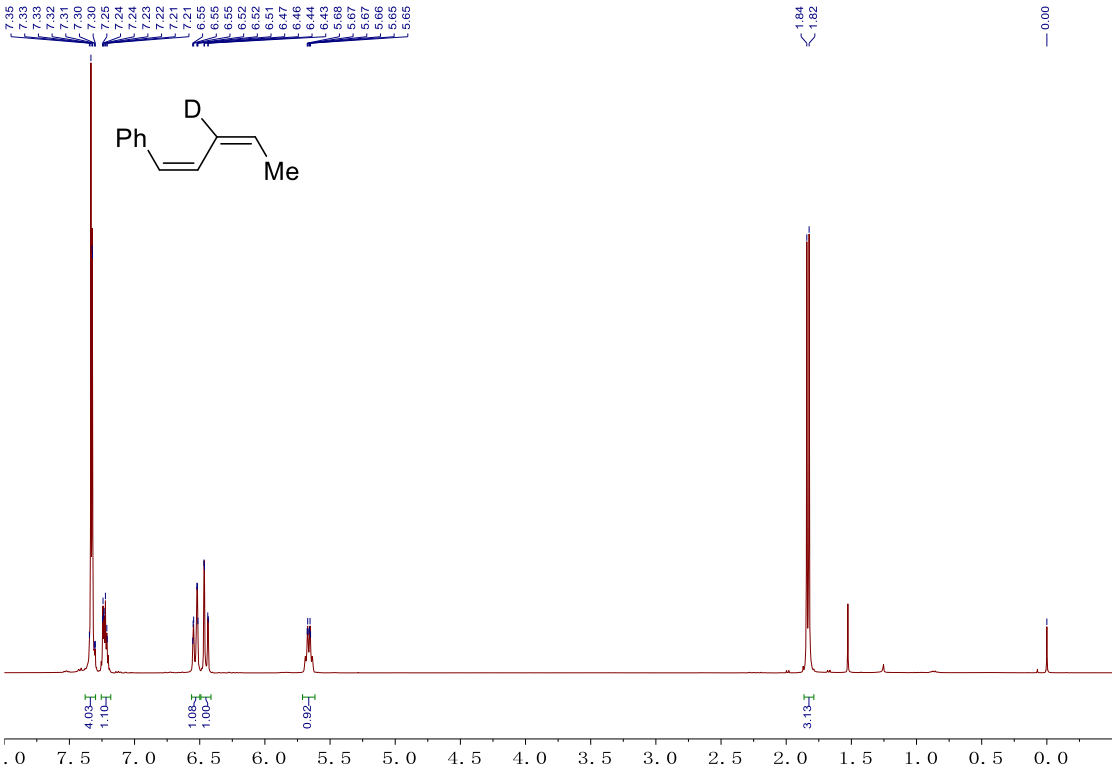


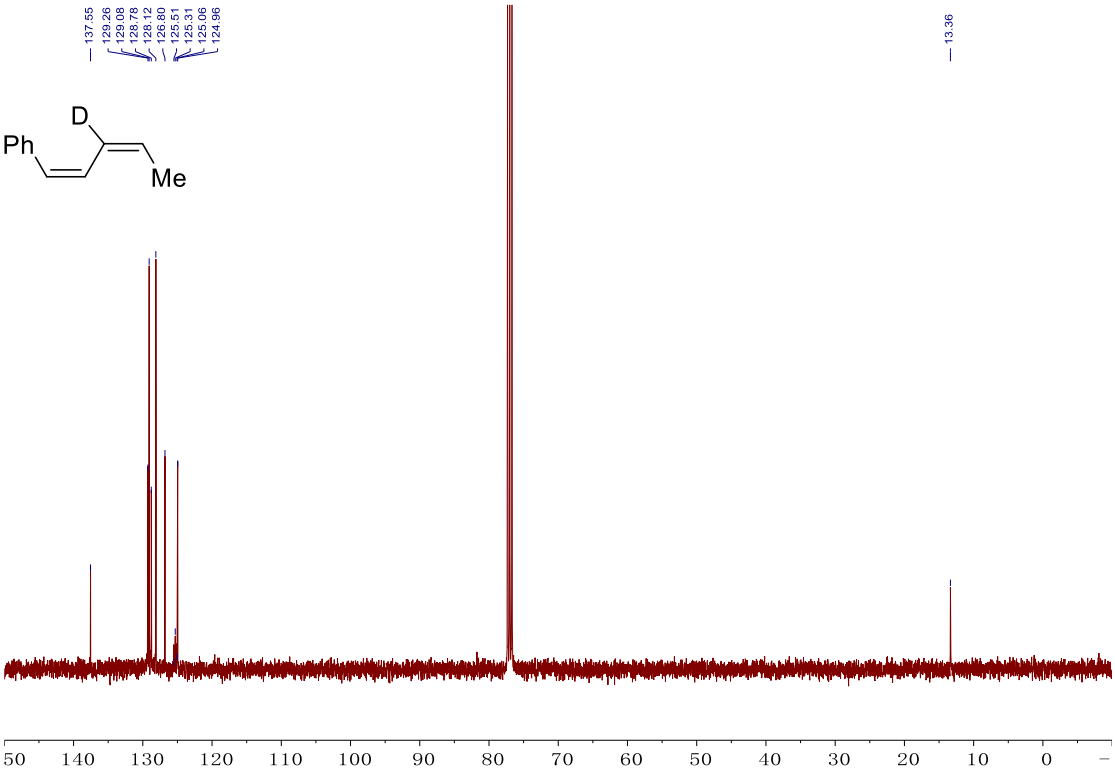
((1*E*,3*Z*)-penta-1,3-dien-1-yl-3-D)benzene (2da)



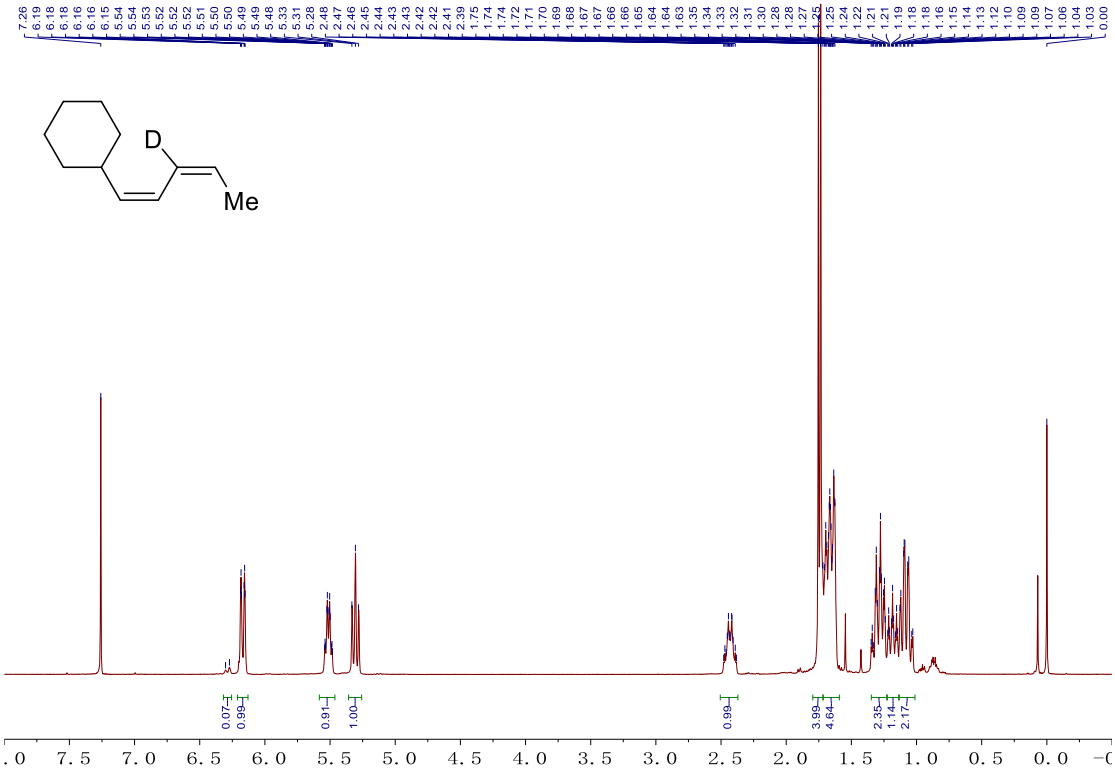


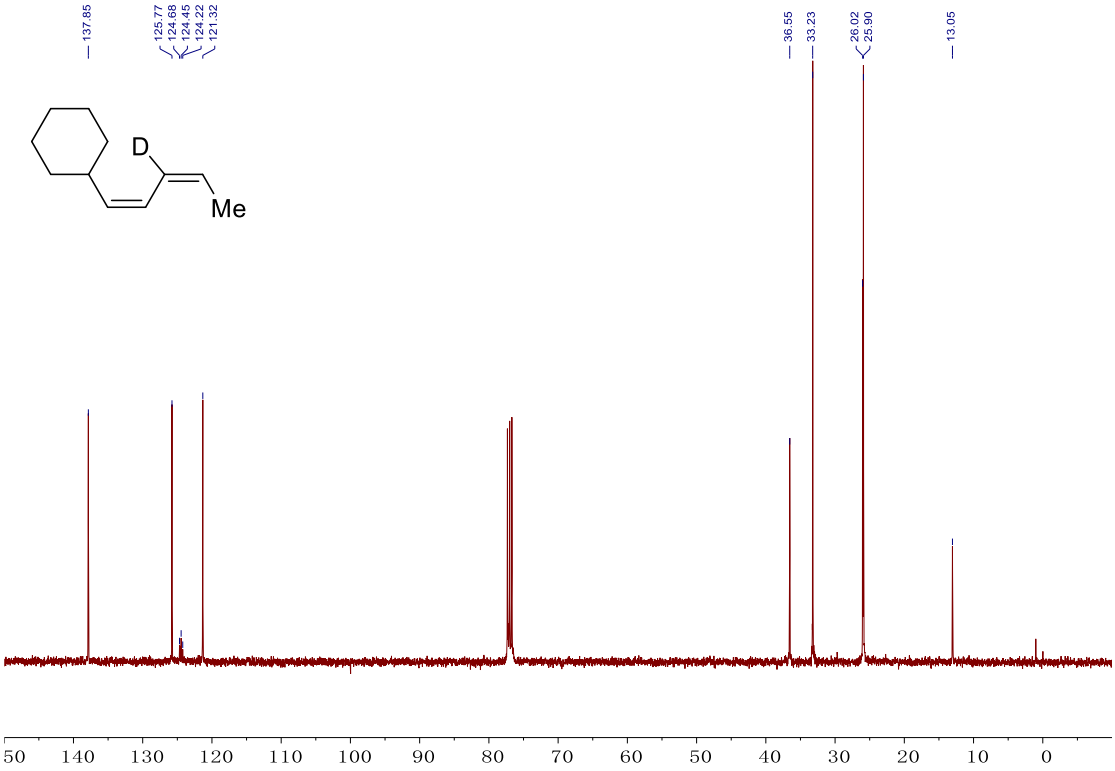
((1*Z*,3*Z*)-penta-1,3-dien-1-yl-3-D)benzene (2db)



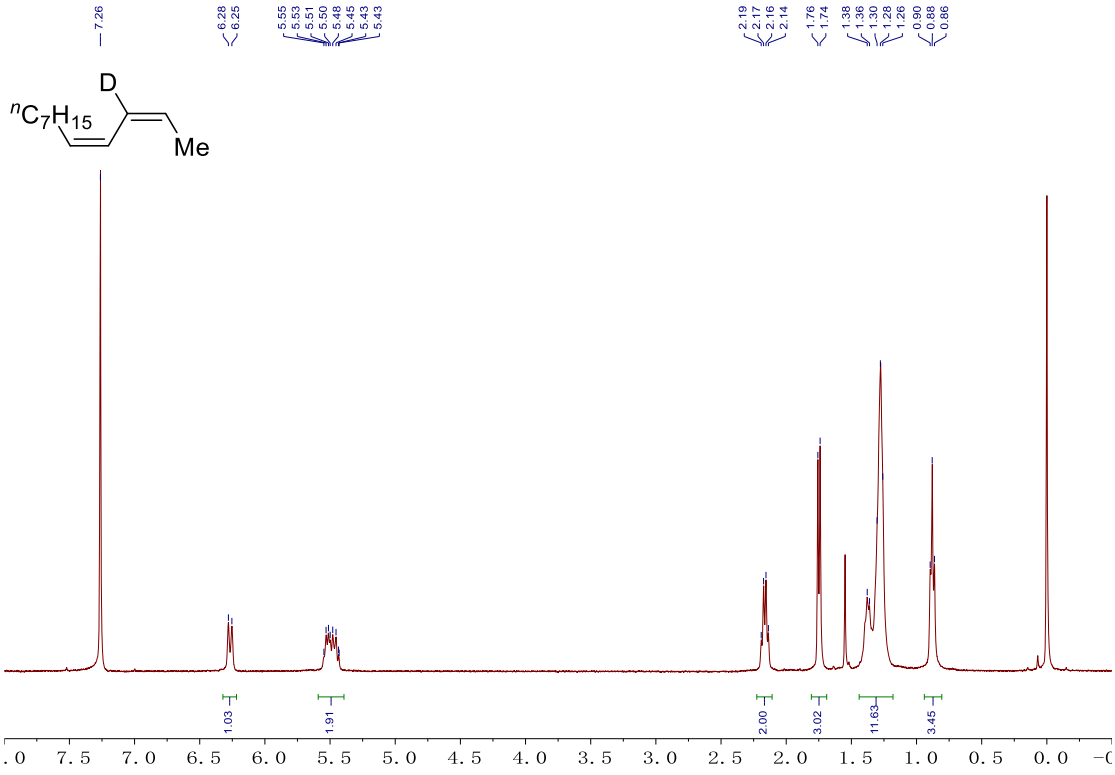


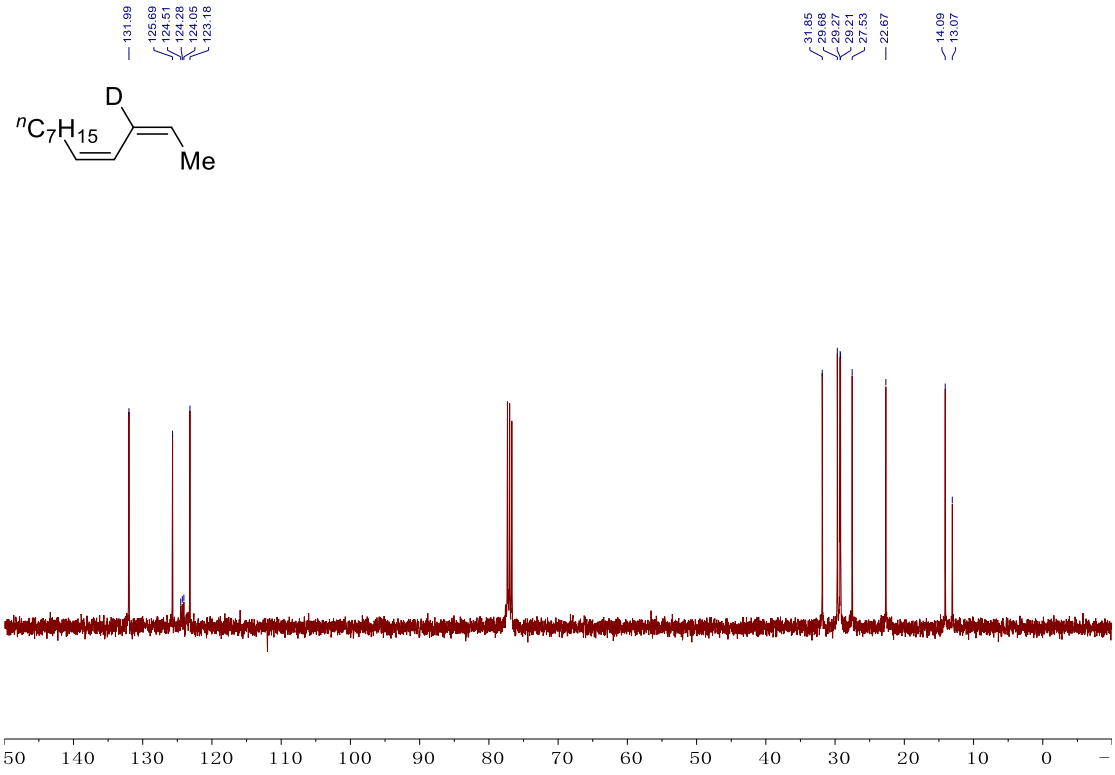
((1*Z*,3*Z*)-penta-1,3-dien-1-yl-3-D)cyclohexane (2dc)



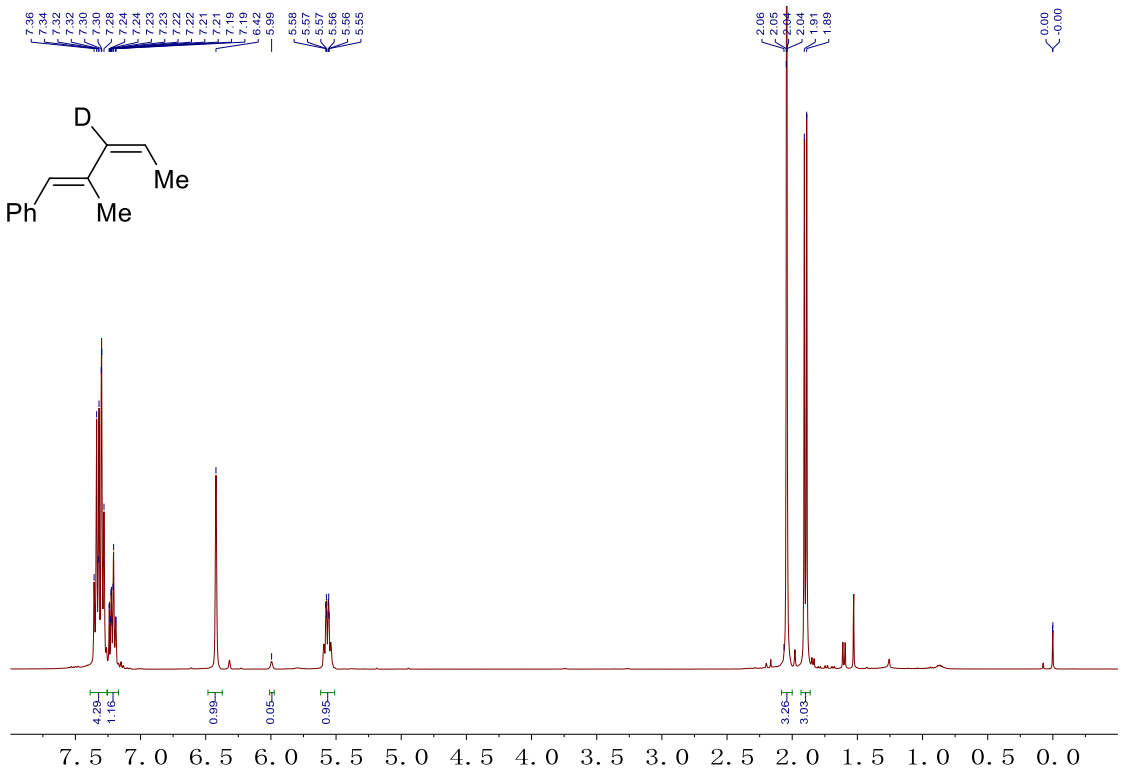


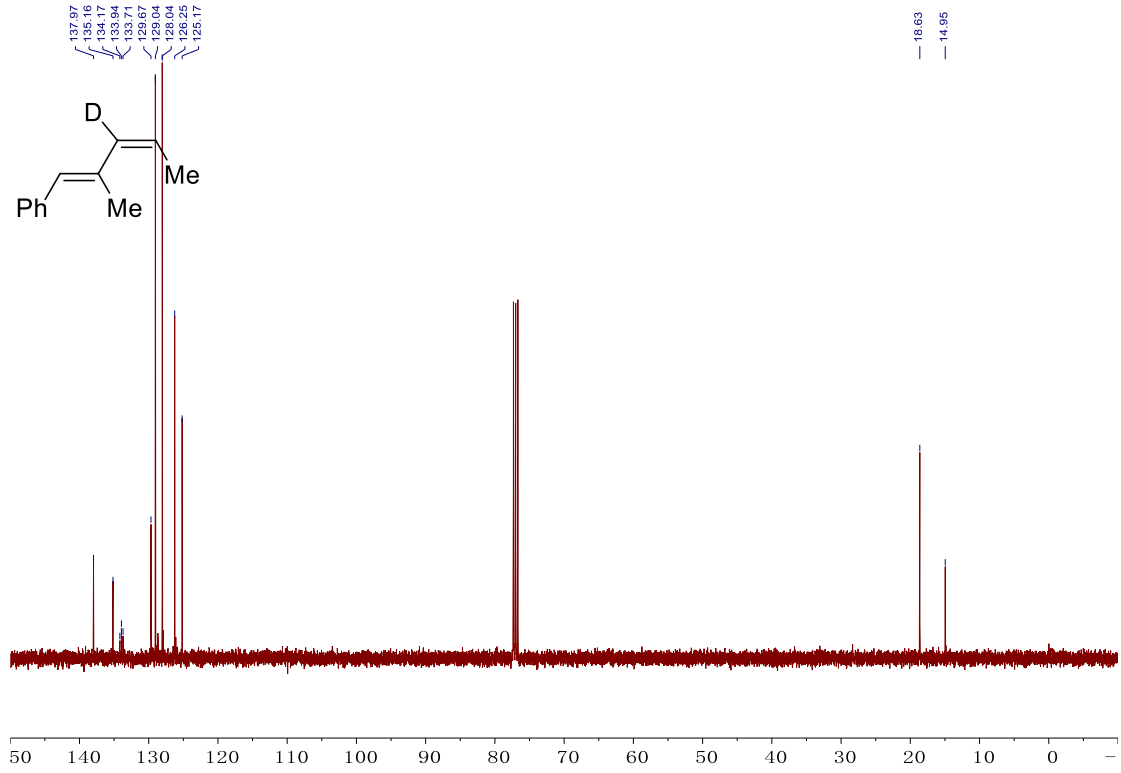
(2*Z*,4*Z*)-dodeca-2,4-diene-3-D (2dd)



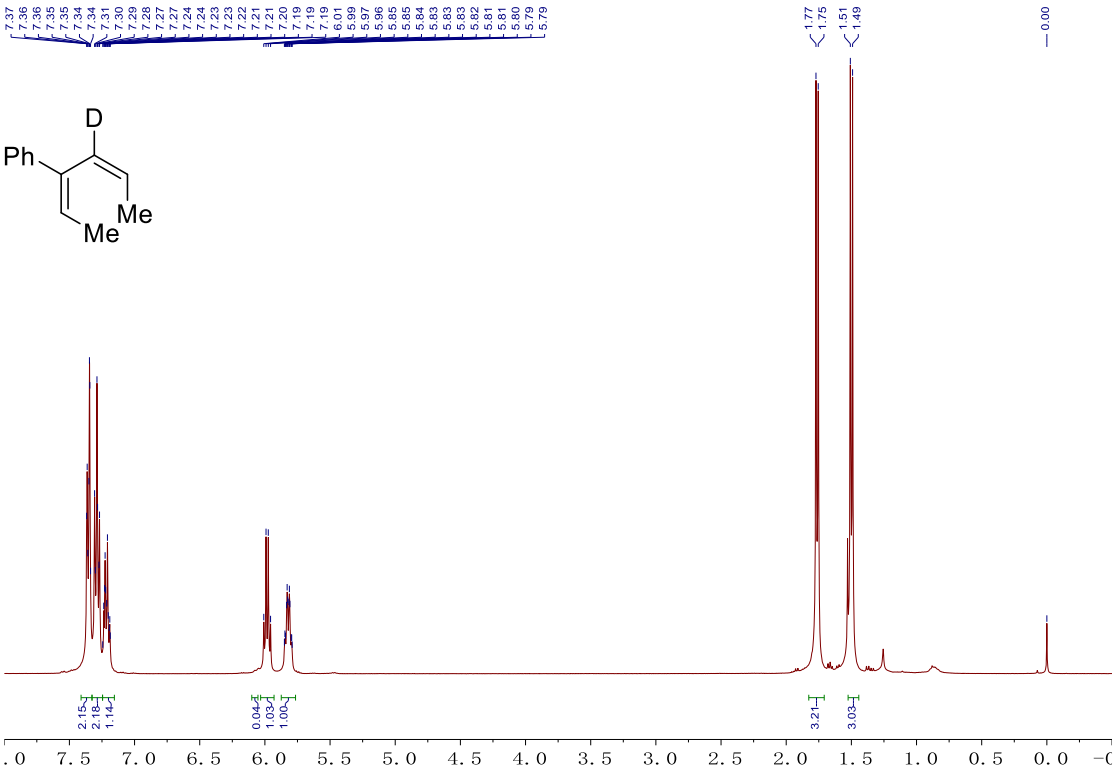


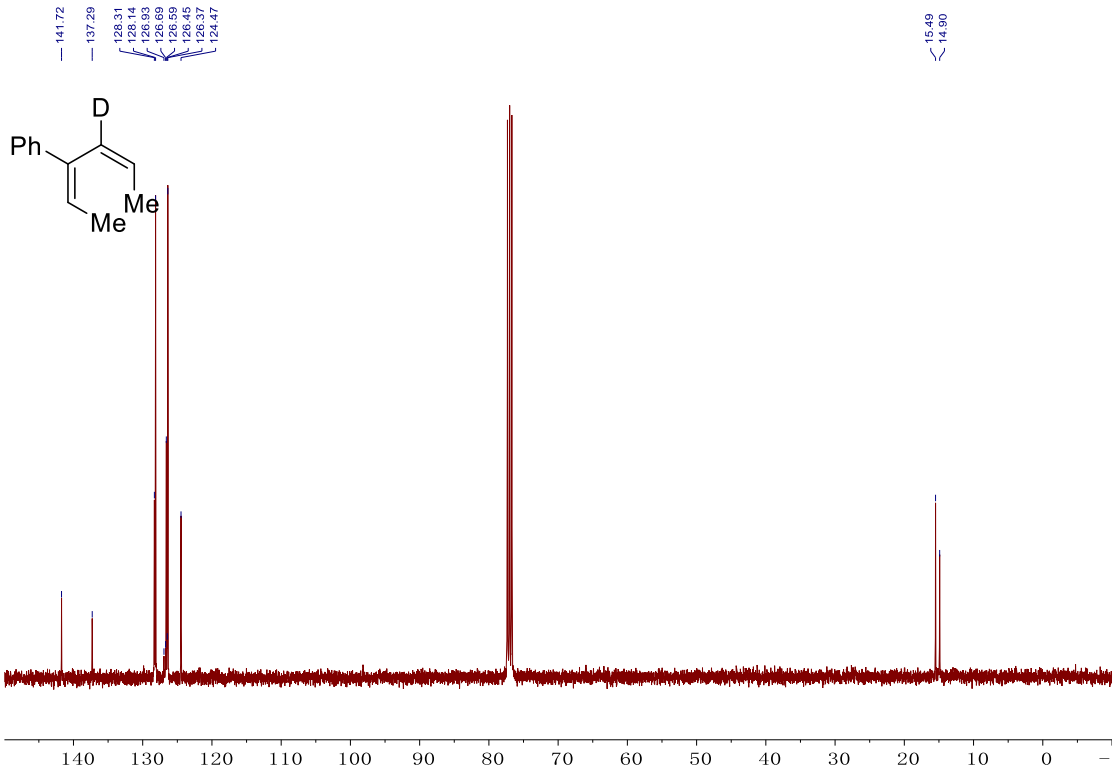
((1*E*,3*Z*)-2-methylpenta-1,3-dien-1-yl-3-D)benzene (2de)



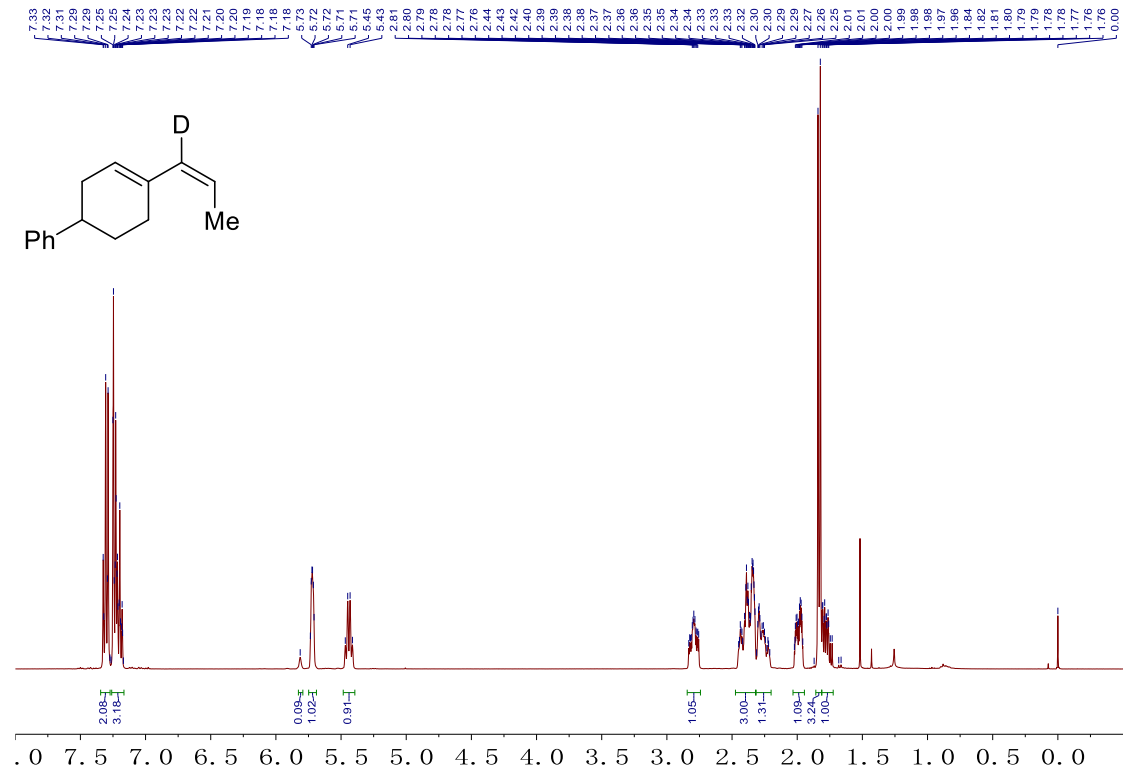


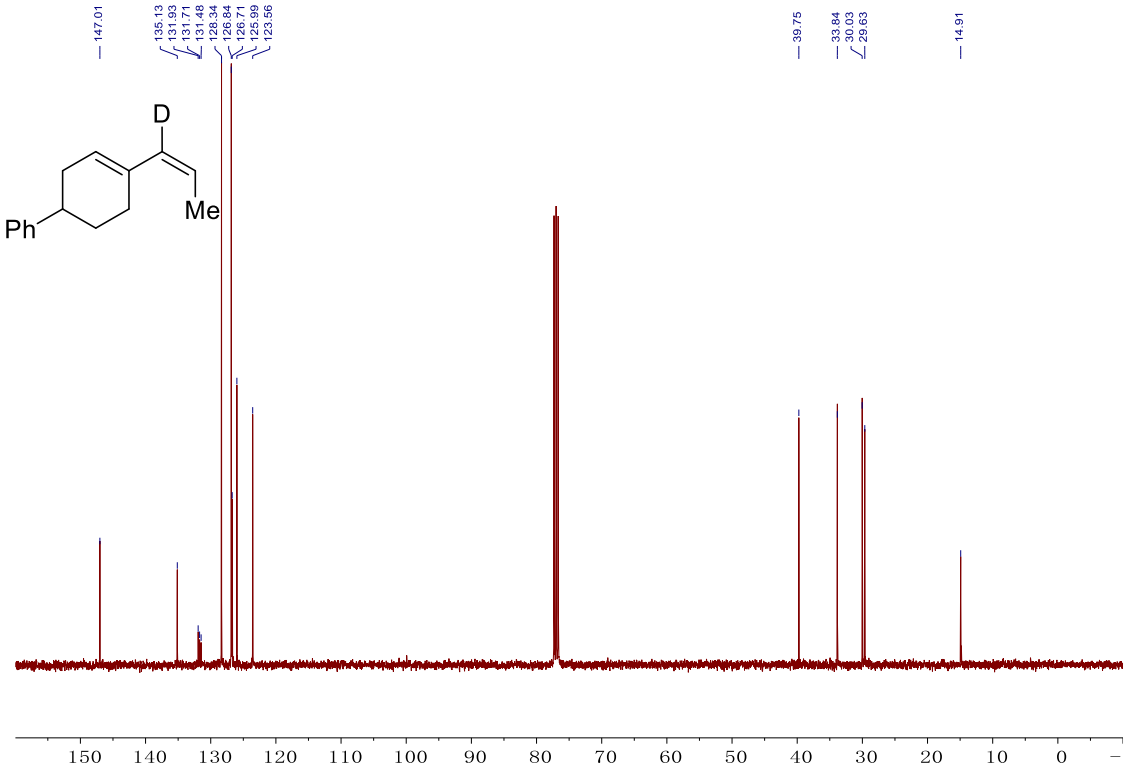
((2*E*,4*Z*)-hexa-2,4-dien-3-yl-4-D)benzene (2df)



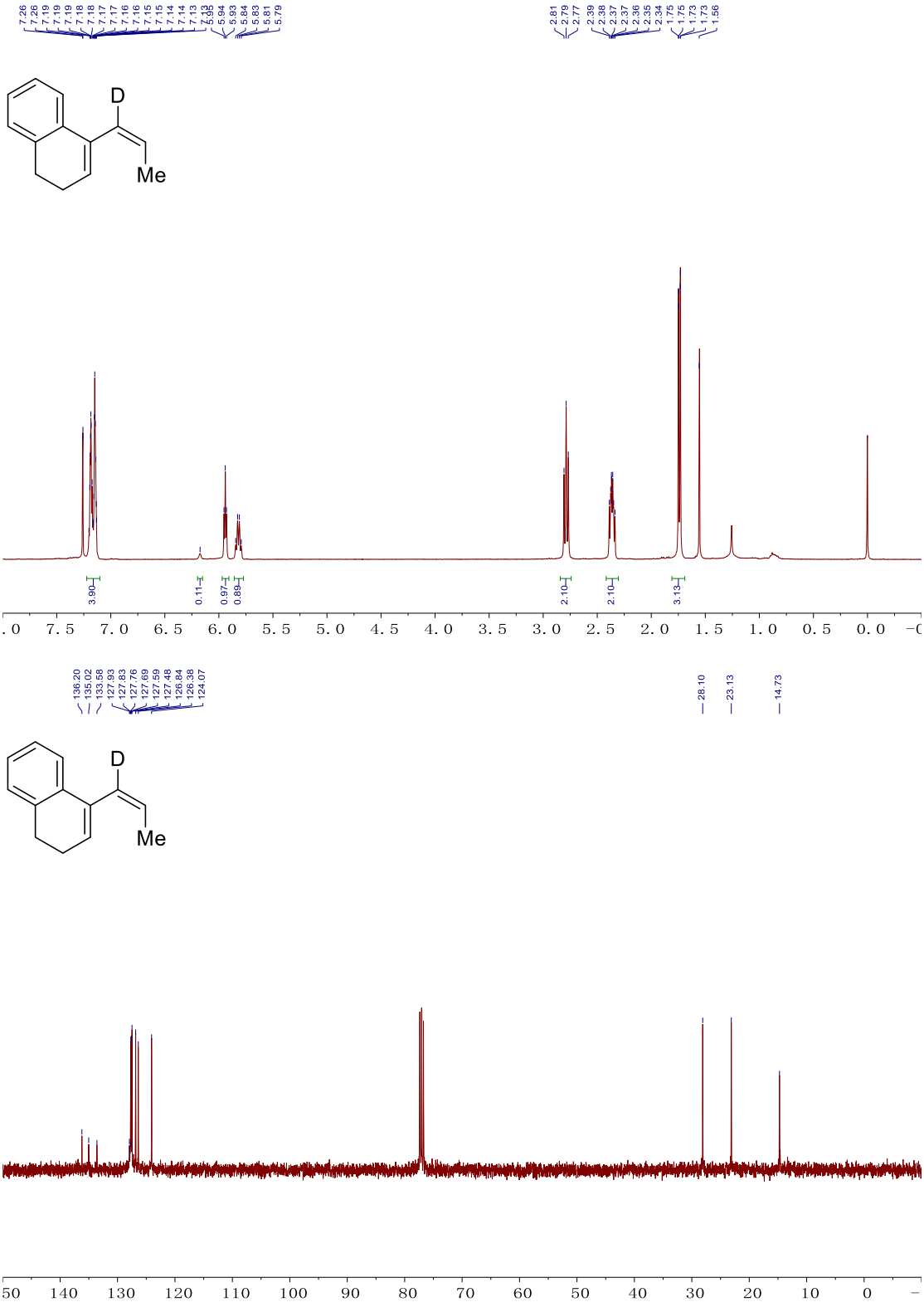


(*Z*)-4-(prop-1-en-1-yl-1-D)-1,2,3,6-tetrahydro-1,1'-biphenyl (2dg)

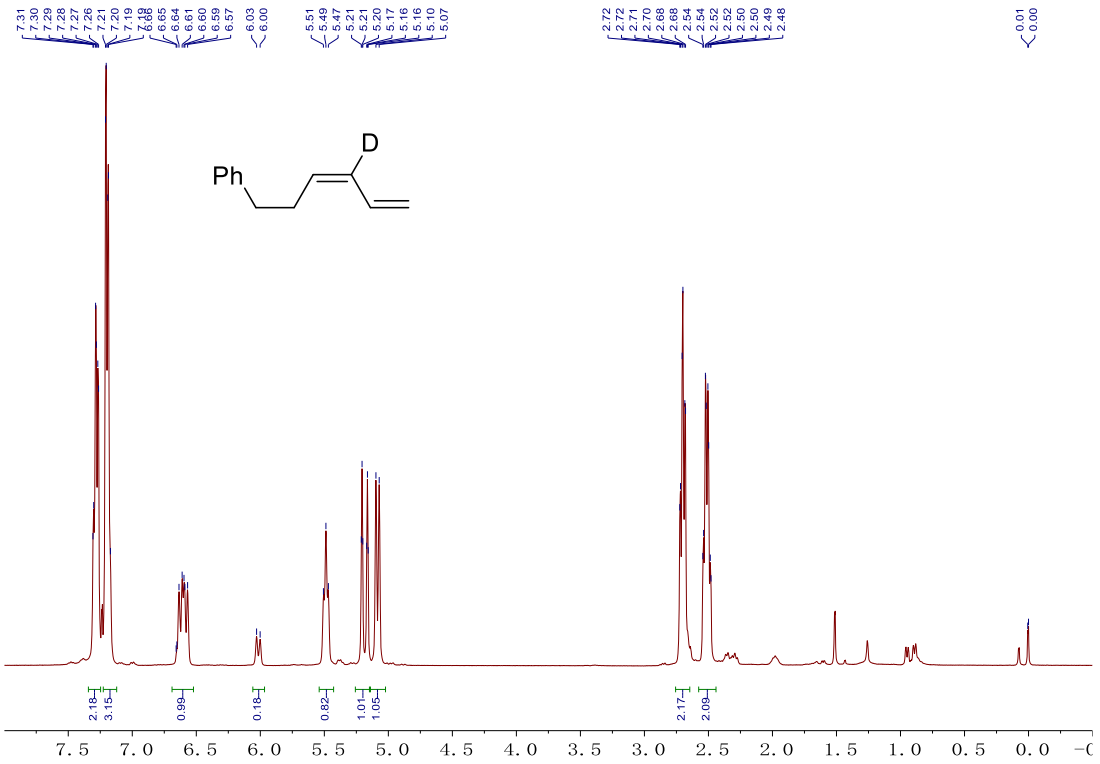


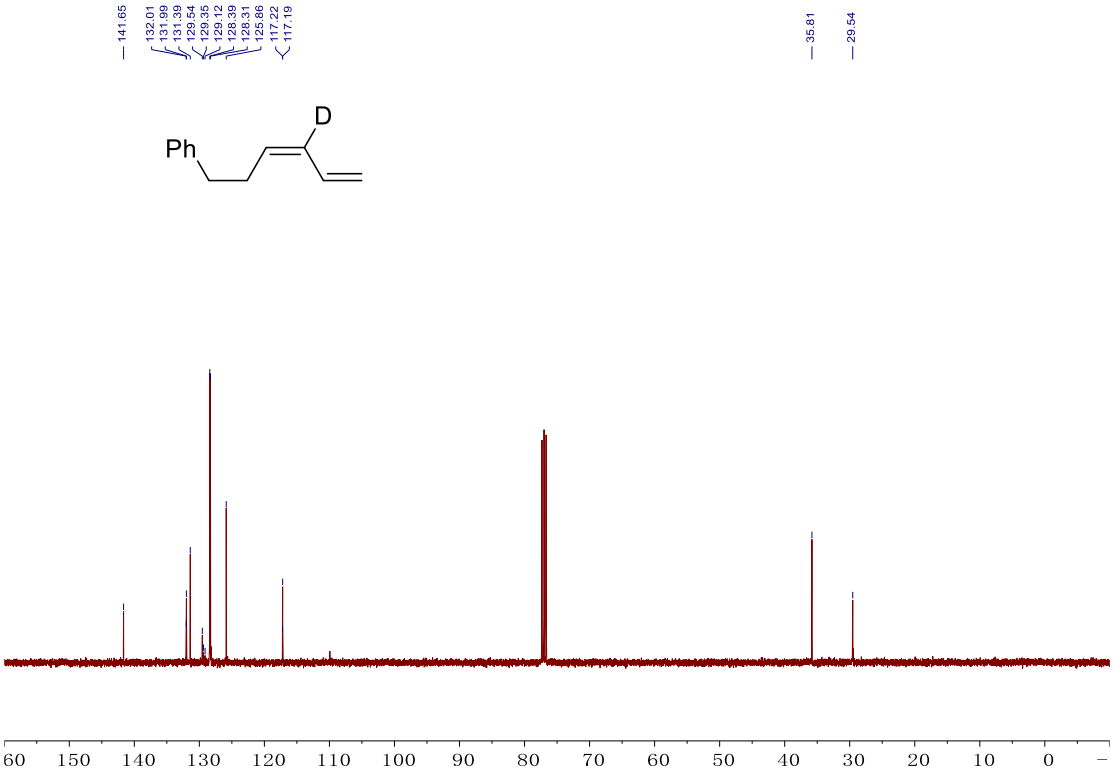


(*Z*)-4-(prop-1-en-1-yl-1-D)-1,2-dihydronaphthalene (2dh)

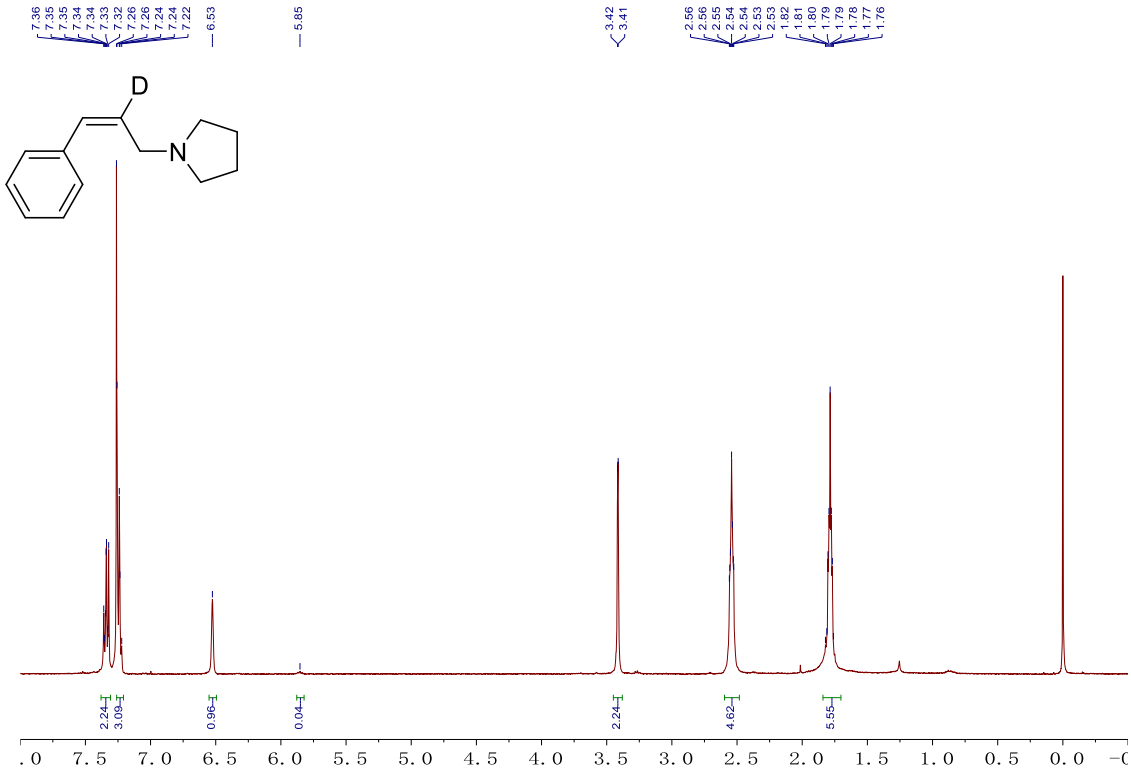


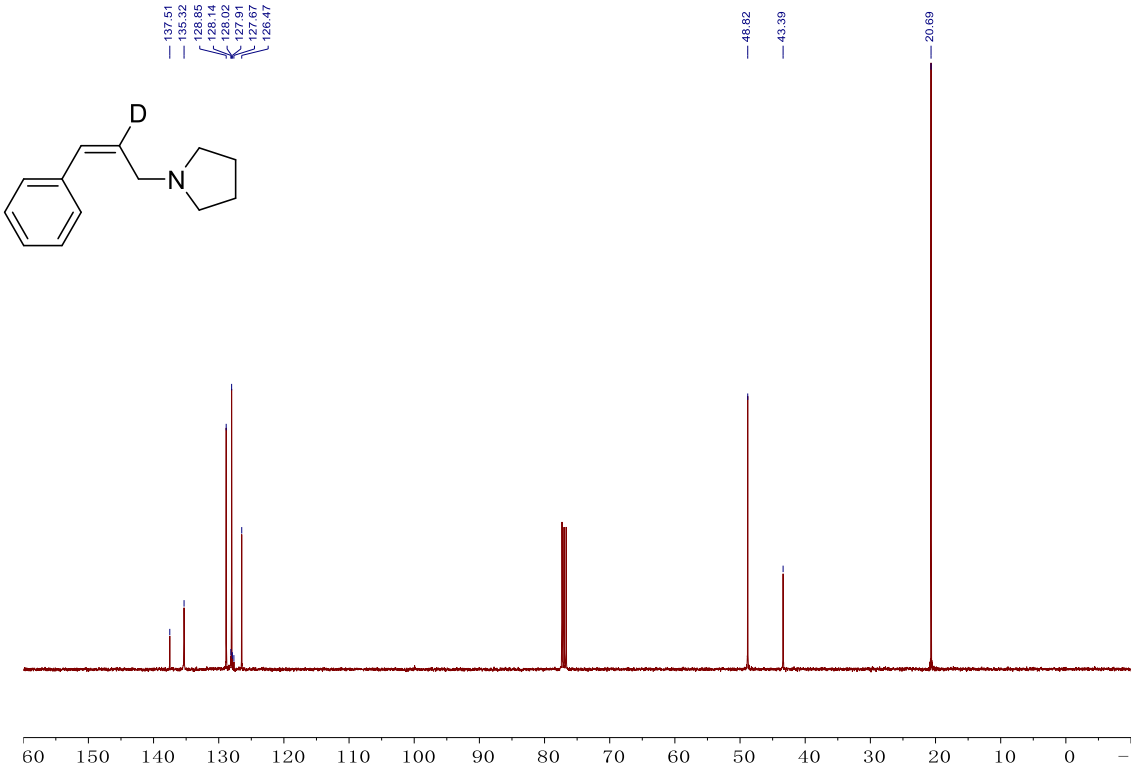
(*Z*)-(hexa-3,5-dien-1-yl-4-d)benzene (2di)



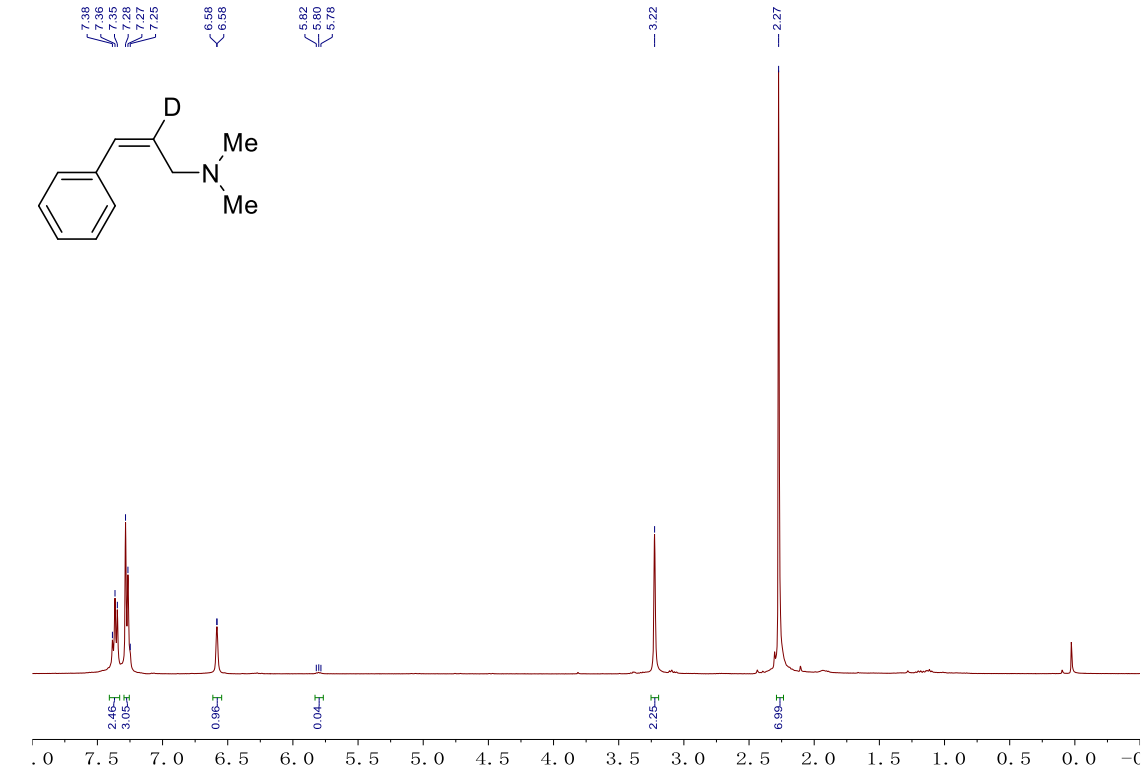


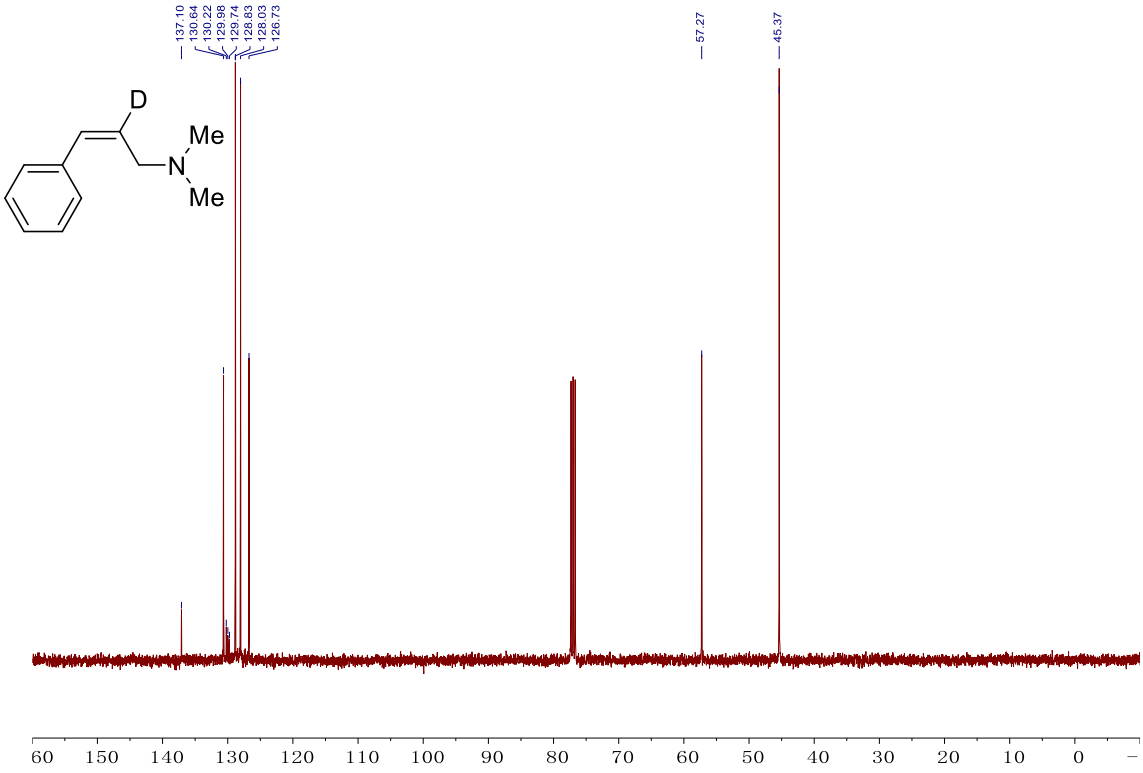
(*Z*)-1-(3-phenylallyl-2-D)pyrrolidine (3ea)



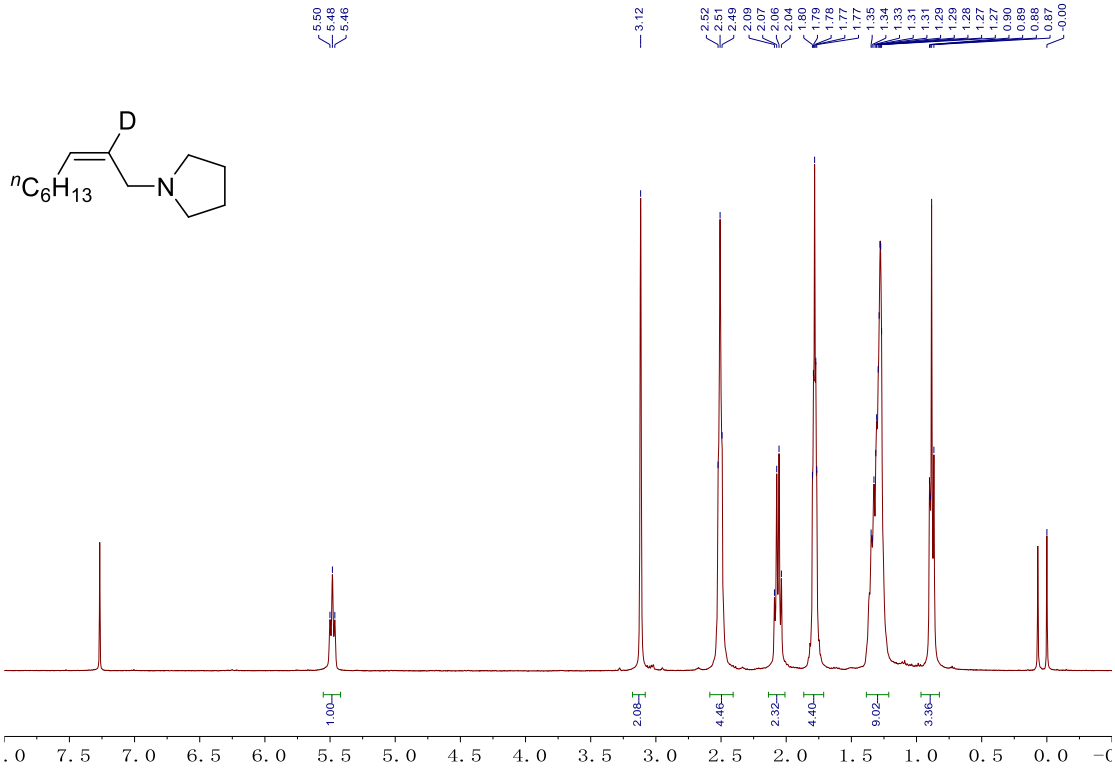


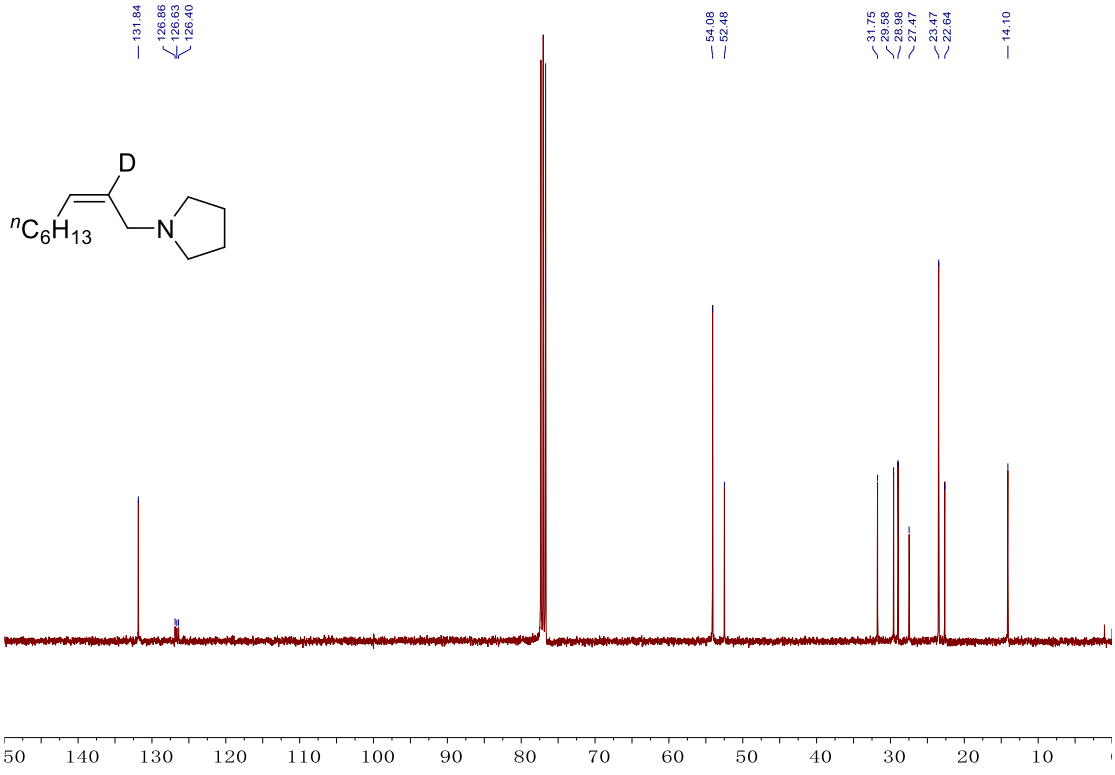
(*Z*)-N,N-dimethyl-3-phenylprop-2-en-1-amine-2-D (3eb)



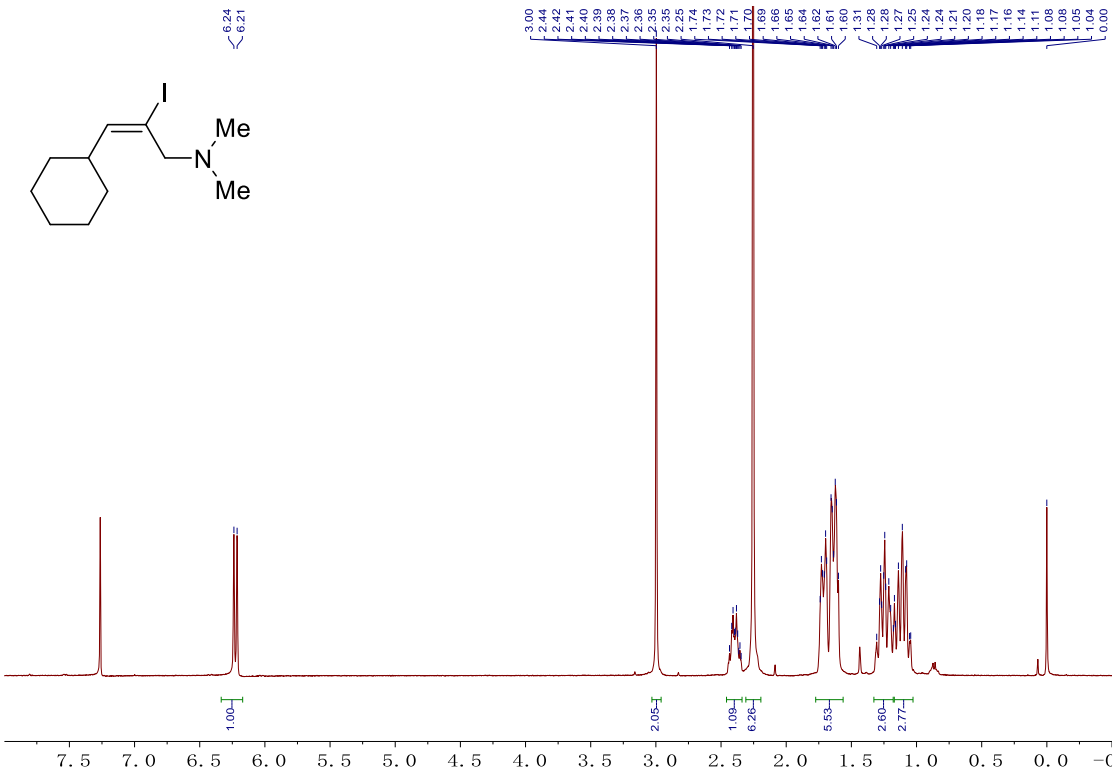


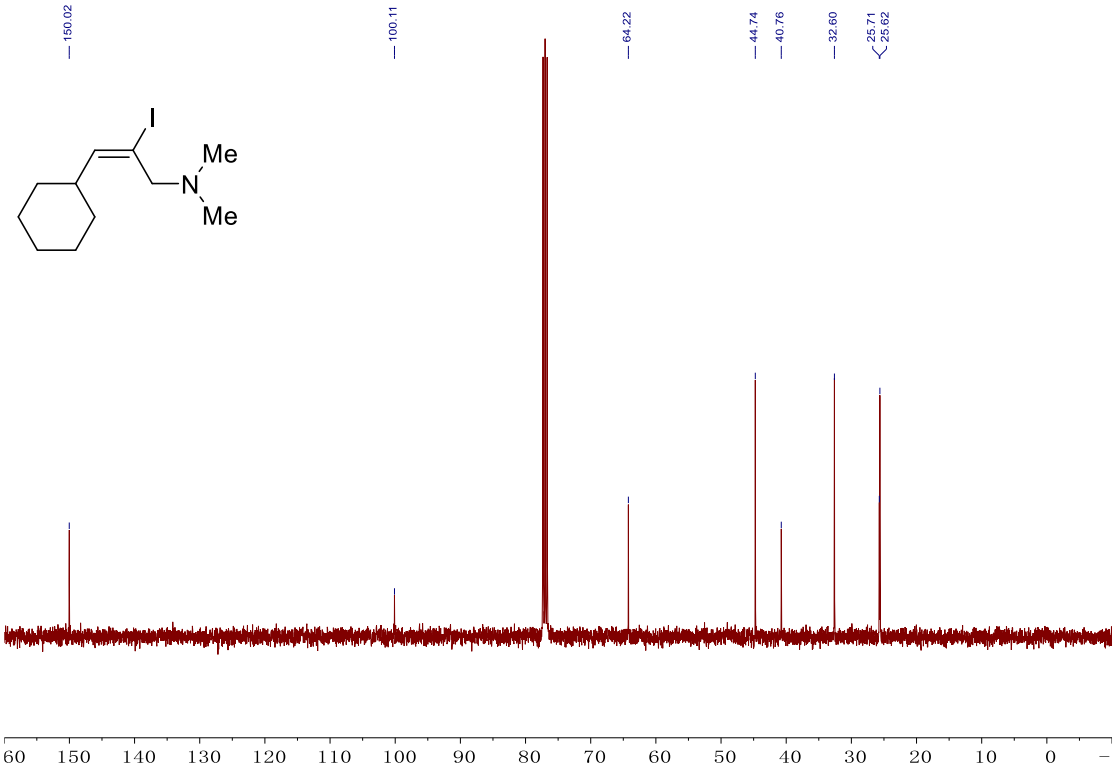
(*Z*)-1-(non-2-en-1-yl-2-D)pyrrolidine (3ec)



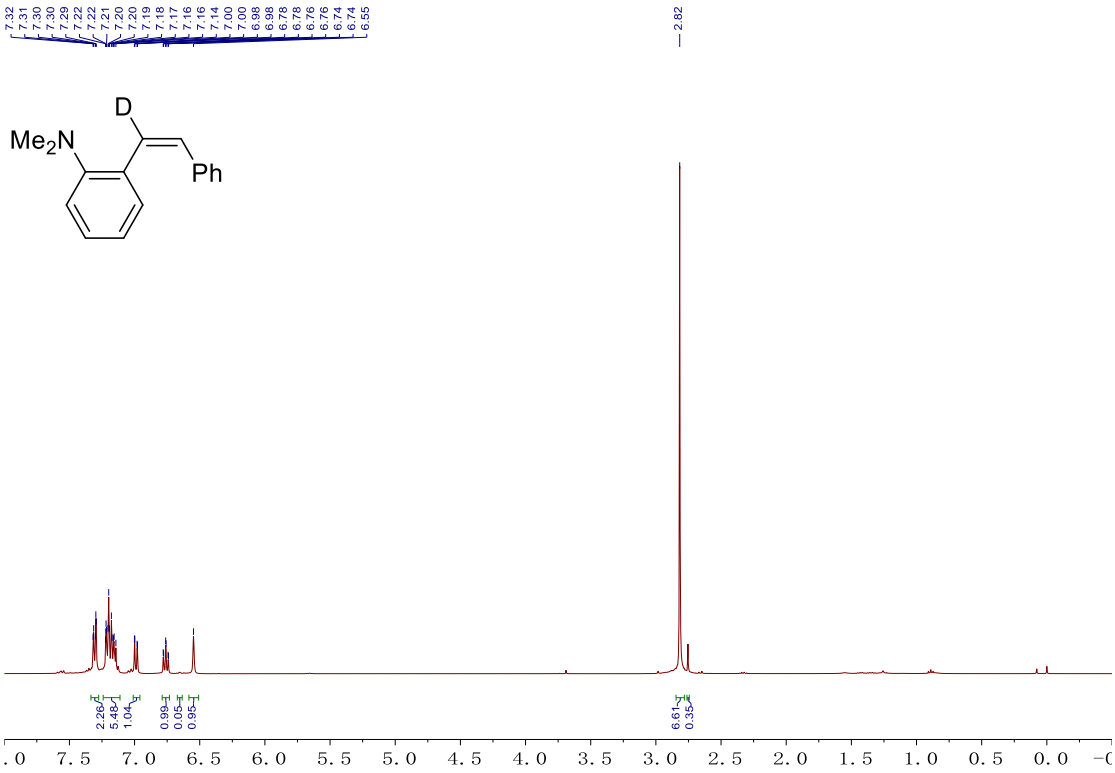


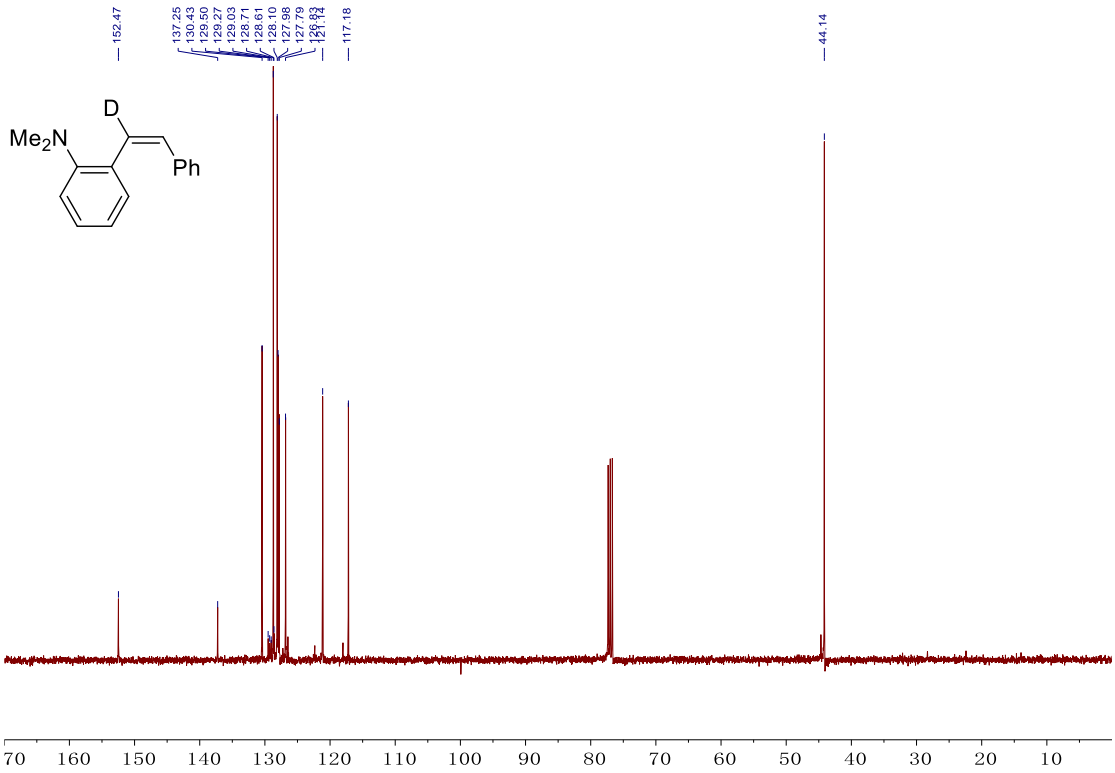
(*E*)-3-cyclohexyl-2-iodo-N,N-dimethylprop-2-en-1-amine (3ed)



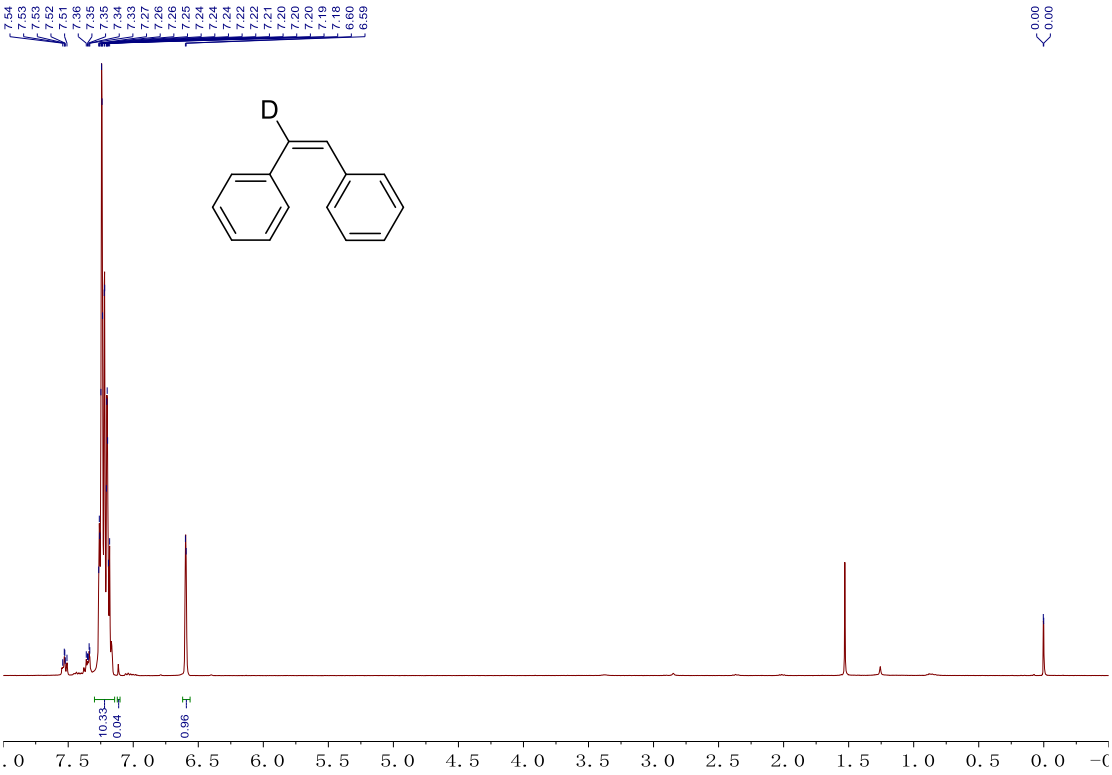


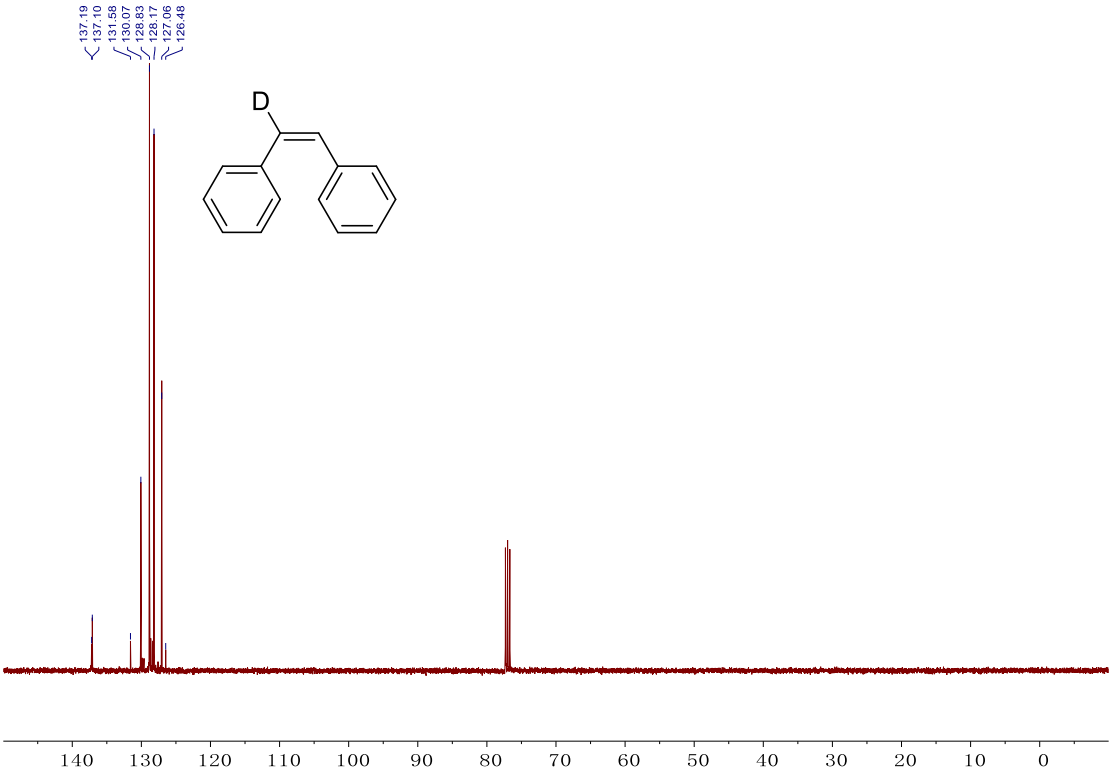
(*Z*)-N,N-dimethyl-2-(2-phenylvinyl-1-D)aniline (3ee)



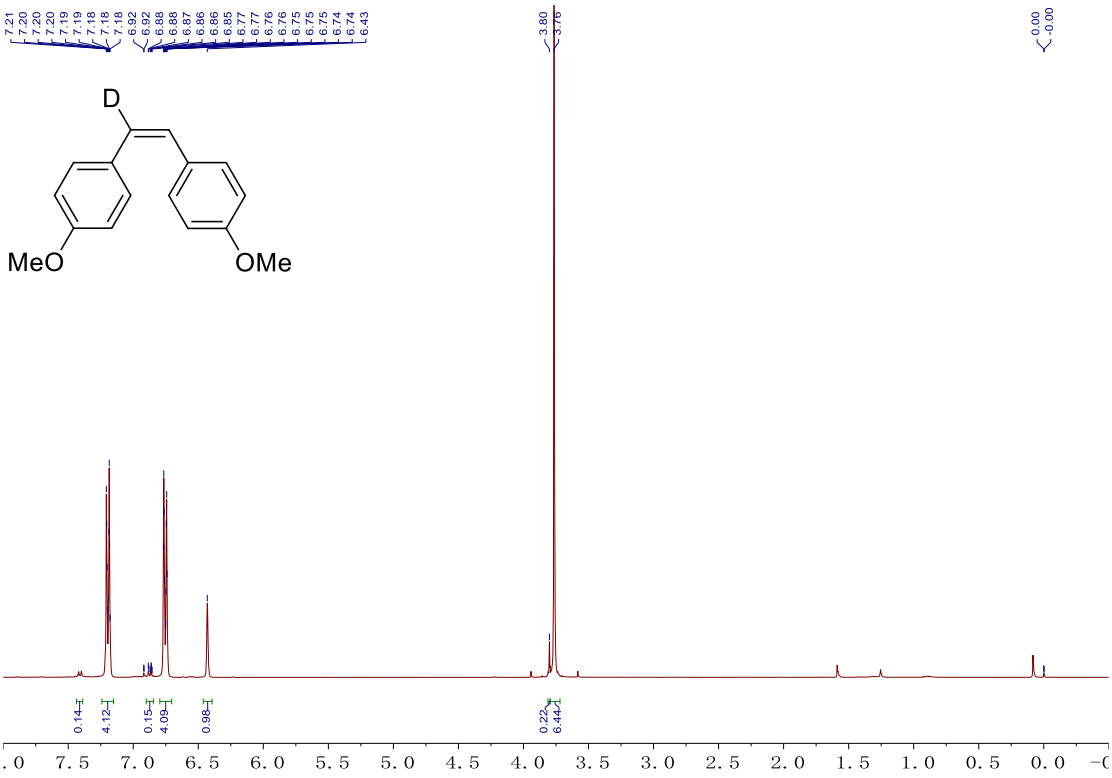


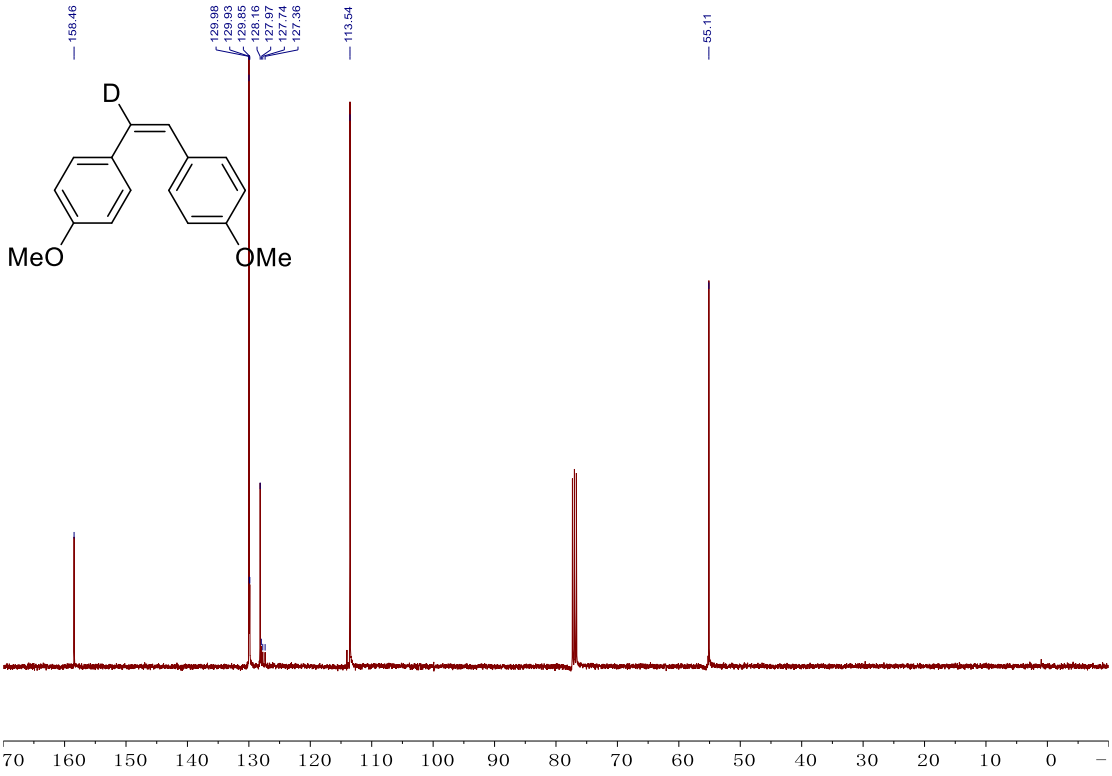
(*Z*)-(ethene-1,2-diyl-1-D)dibenzene (2fa)



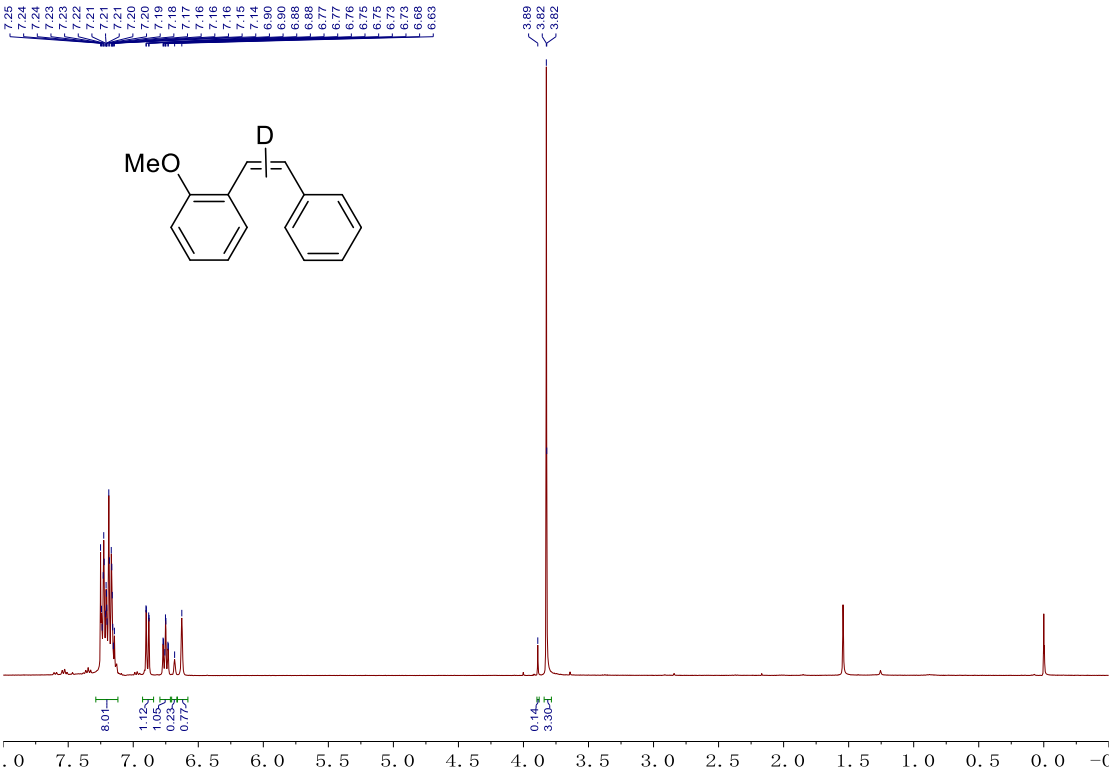


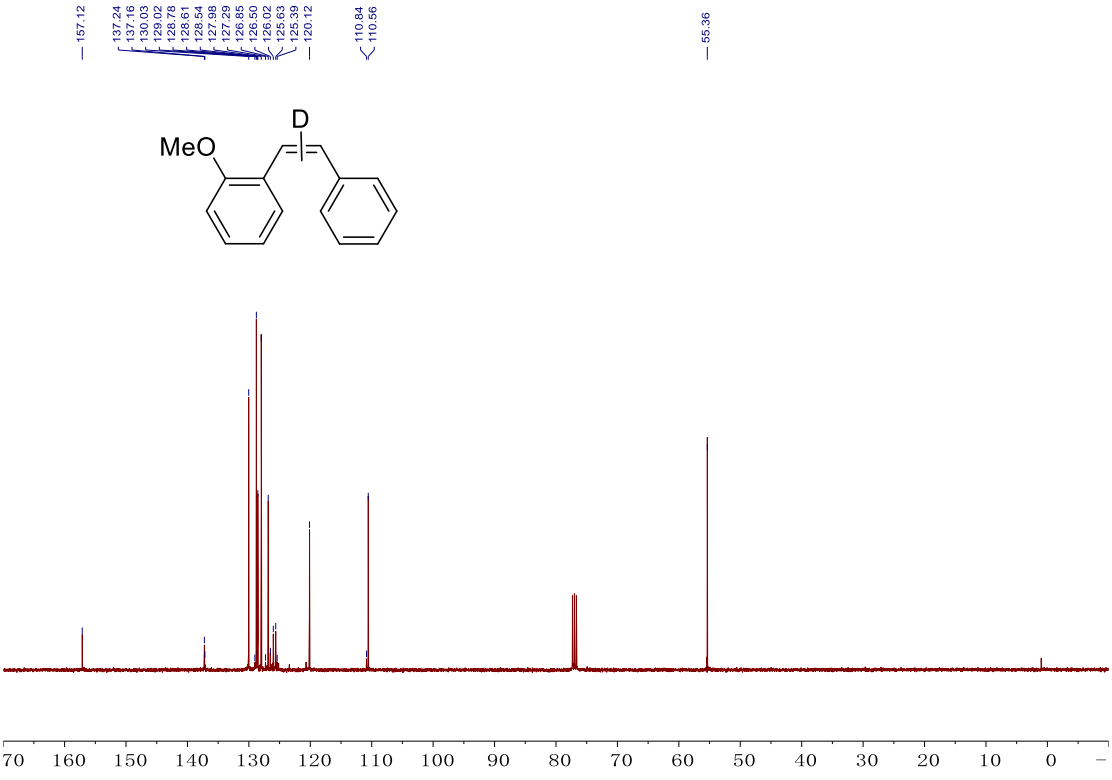
(*Z*)-4,4'-(ethene-1,2-diyl-1-D)bis(methoxybenzene) (2fb)



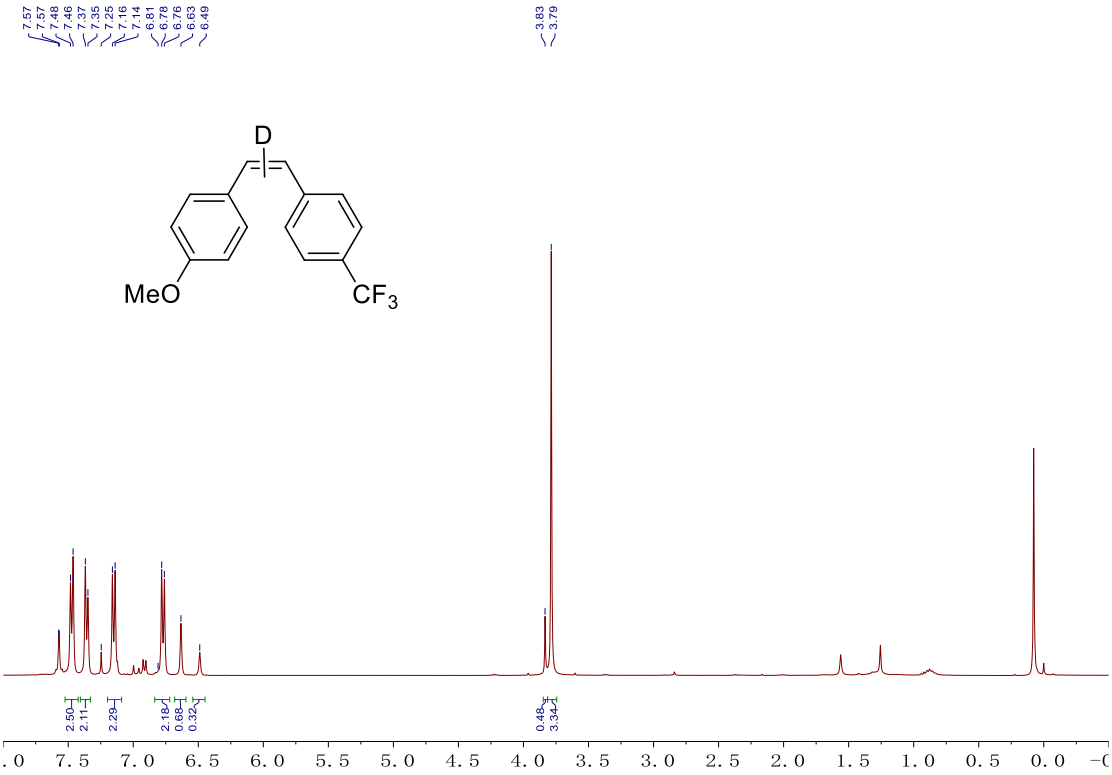


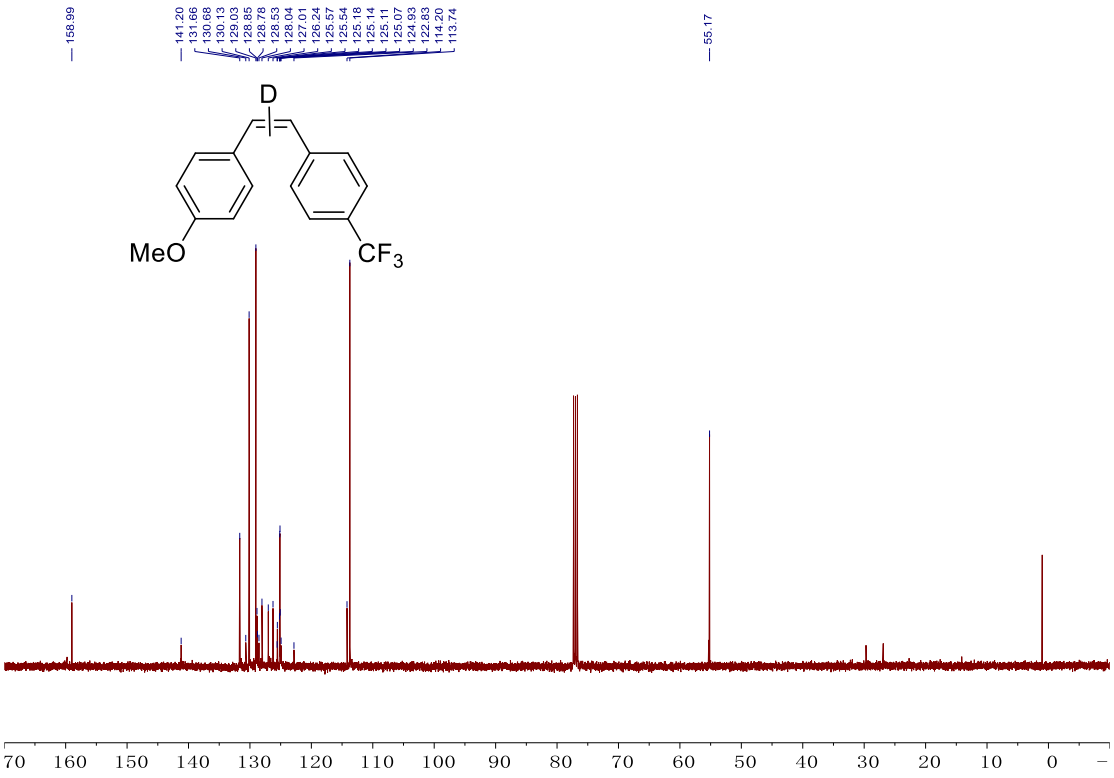
(*Z*)-1-methoxy-2-(2-phenylvinyl-1-D)benzene (2fc)



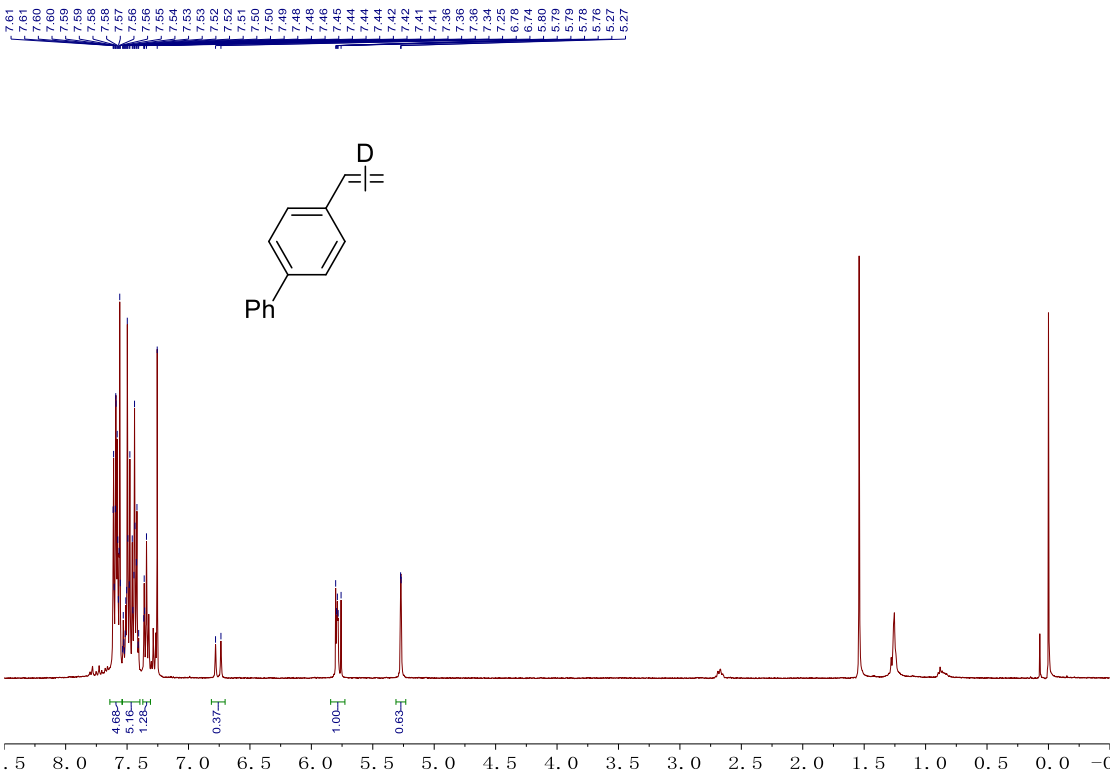


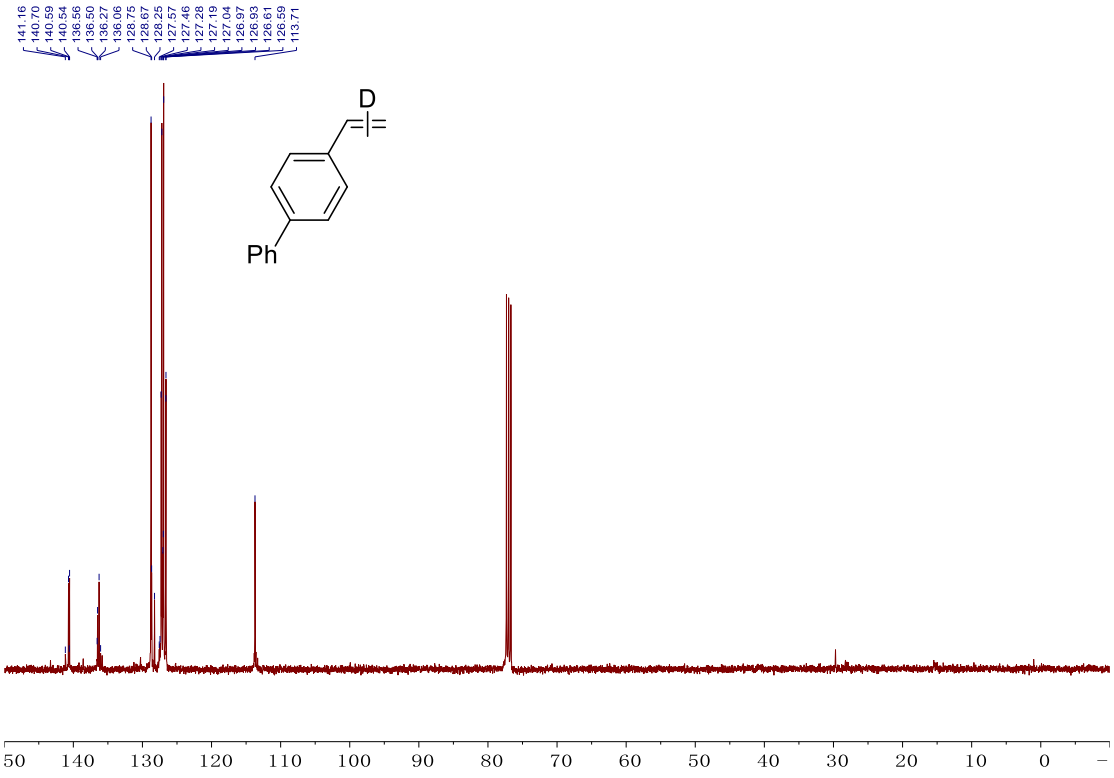
(*Z*)-1-methoxy-4-(2-(4-(trifluoromethyl)phenyl)vinyl-1-D)benzene (2fd)



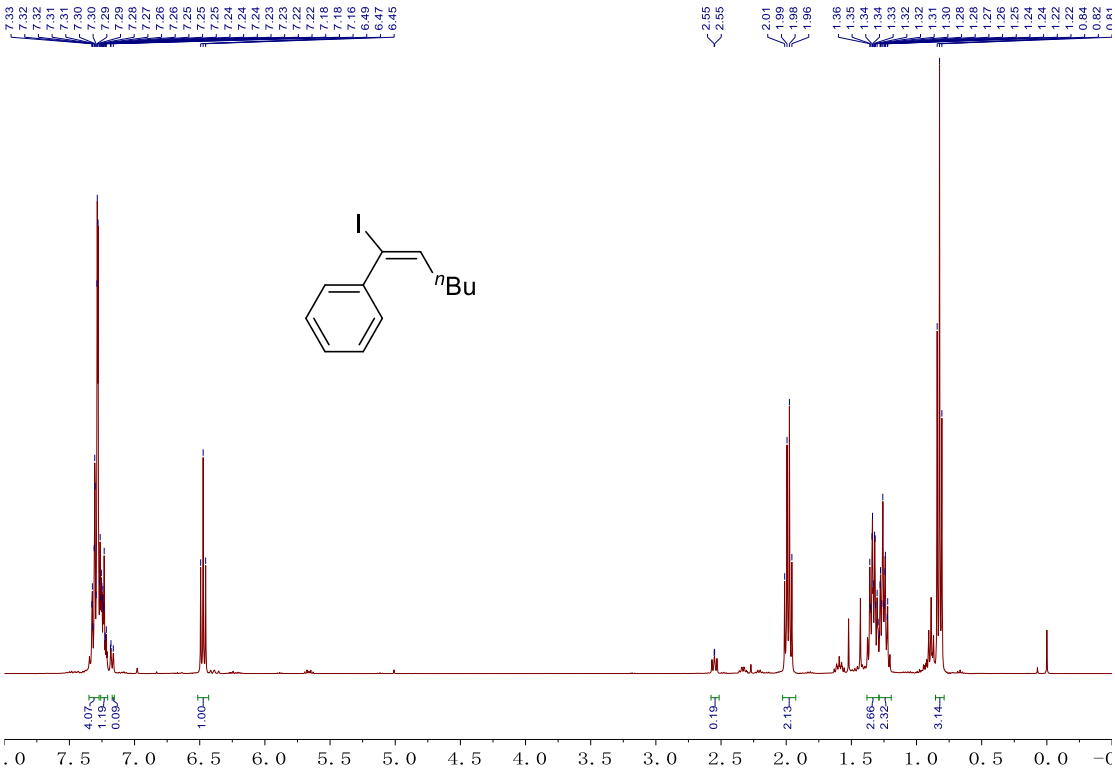


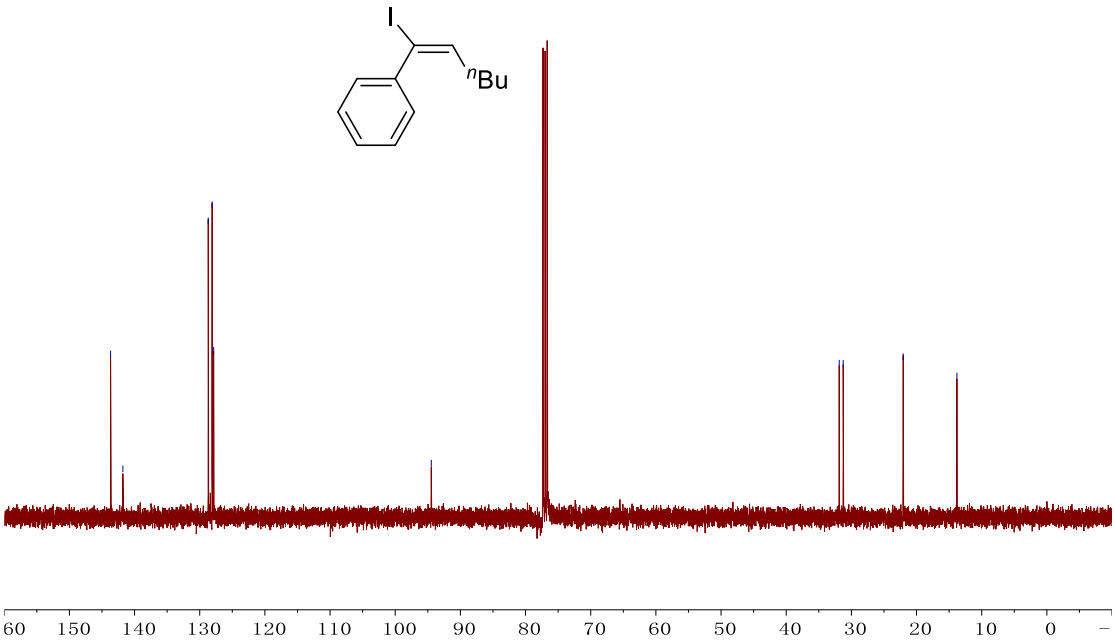
4-(vinyl-1-d)-1,1'-biphenyl (2ga)



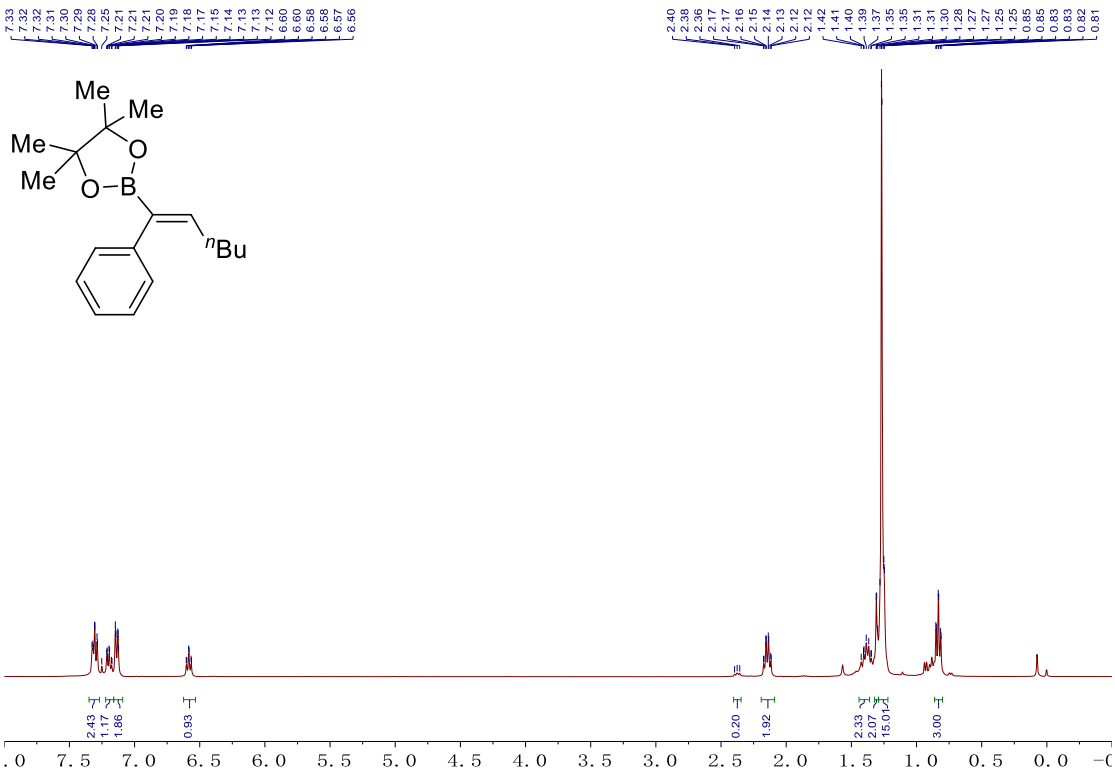


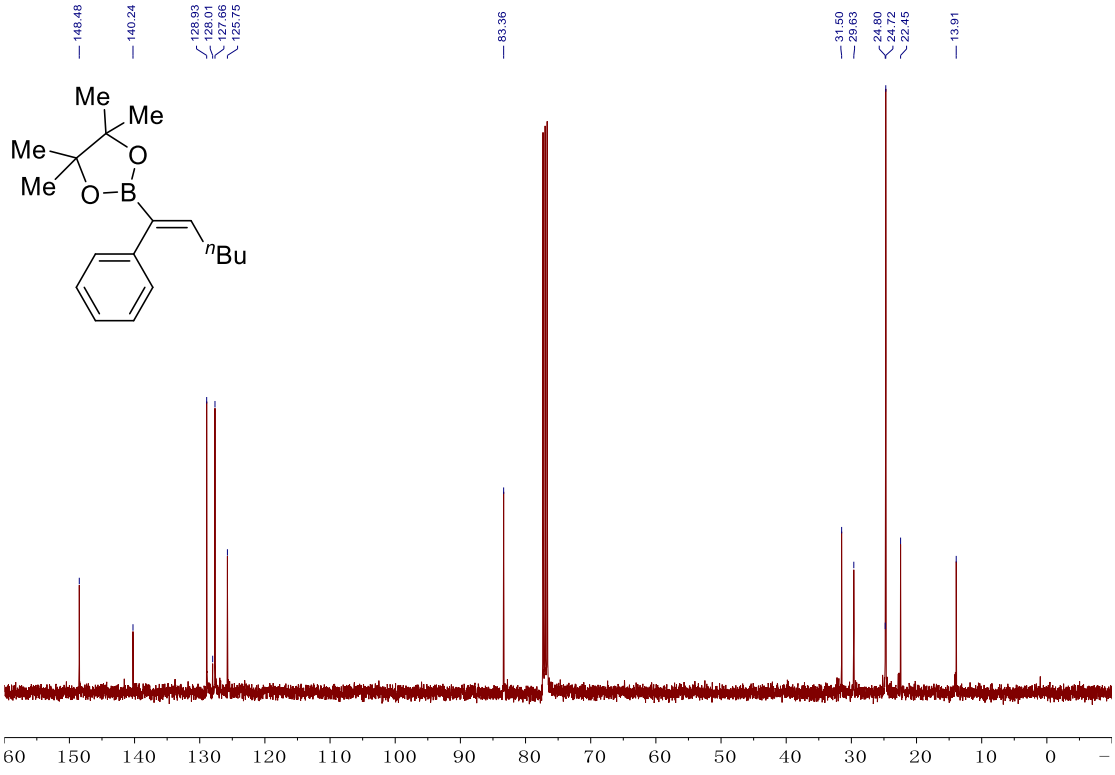
(*E*)-(1-iodohex-1-en-1-yl)benzene (4)



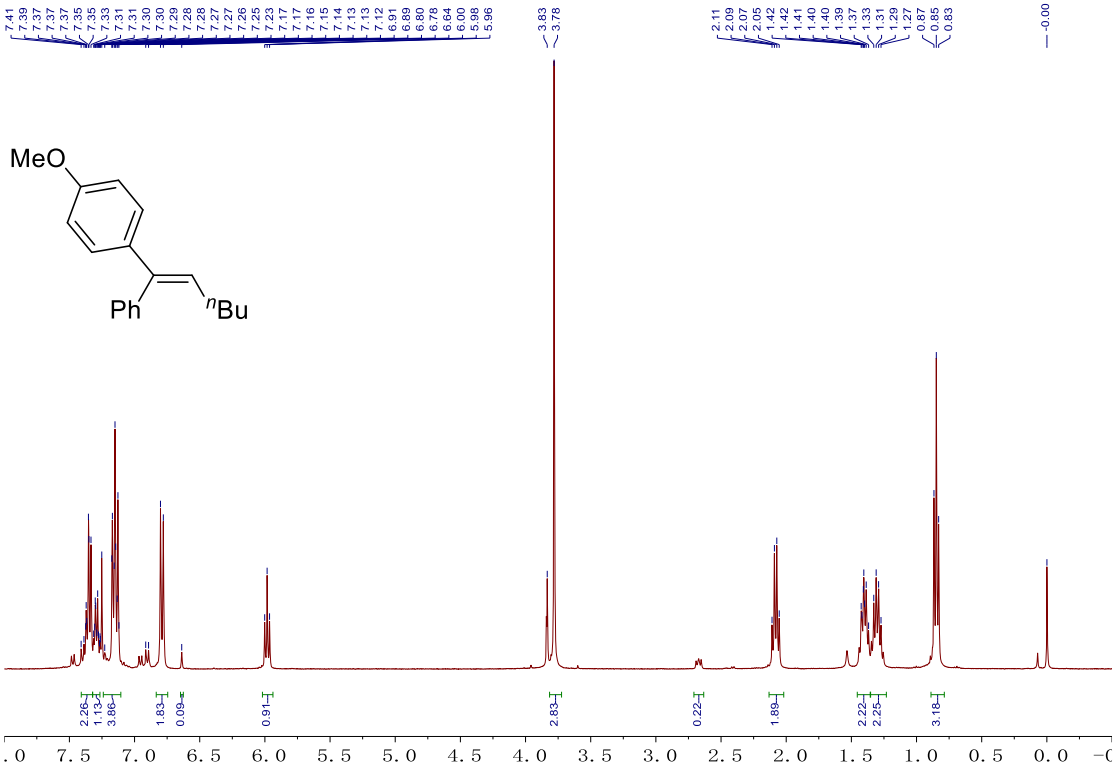


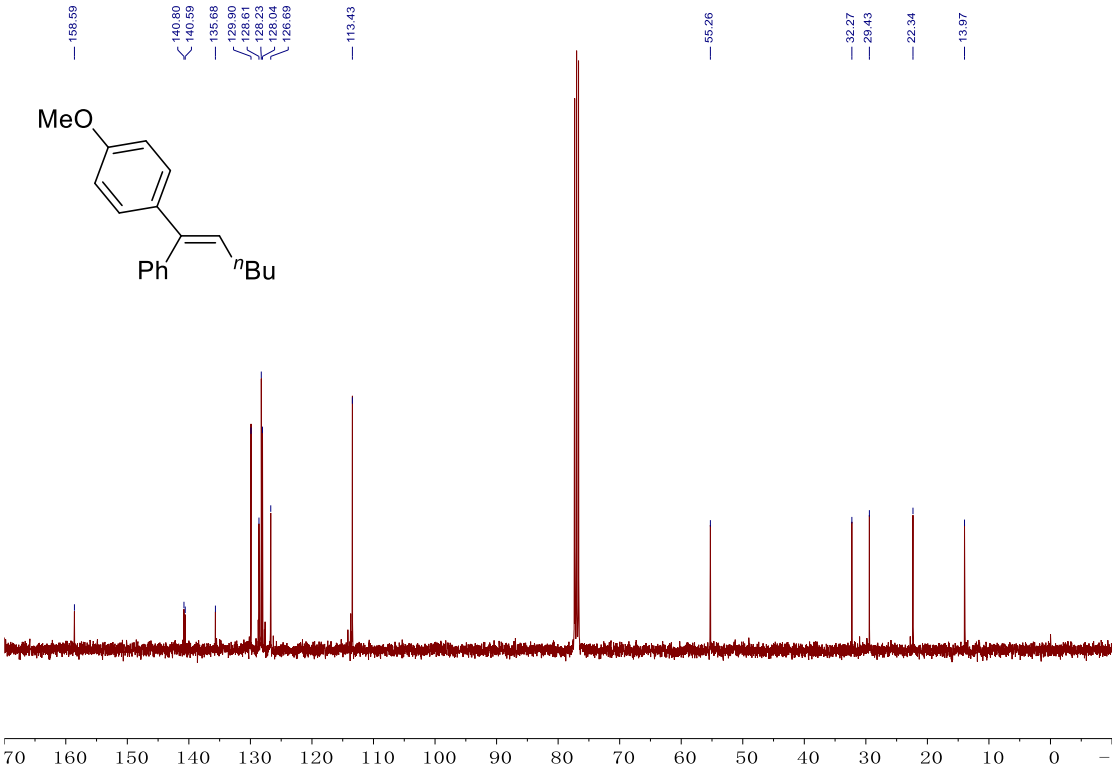
(*Z*)-4,4,5,5-tetramethyl-2-(1-phenylhex-1-en-1-yl)-1,3,2-dioxaborolane (5)



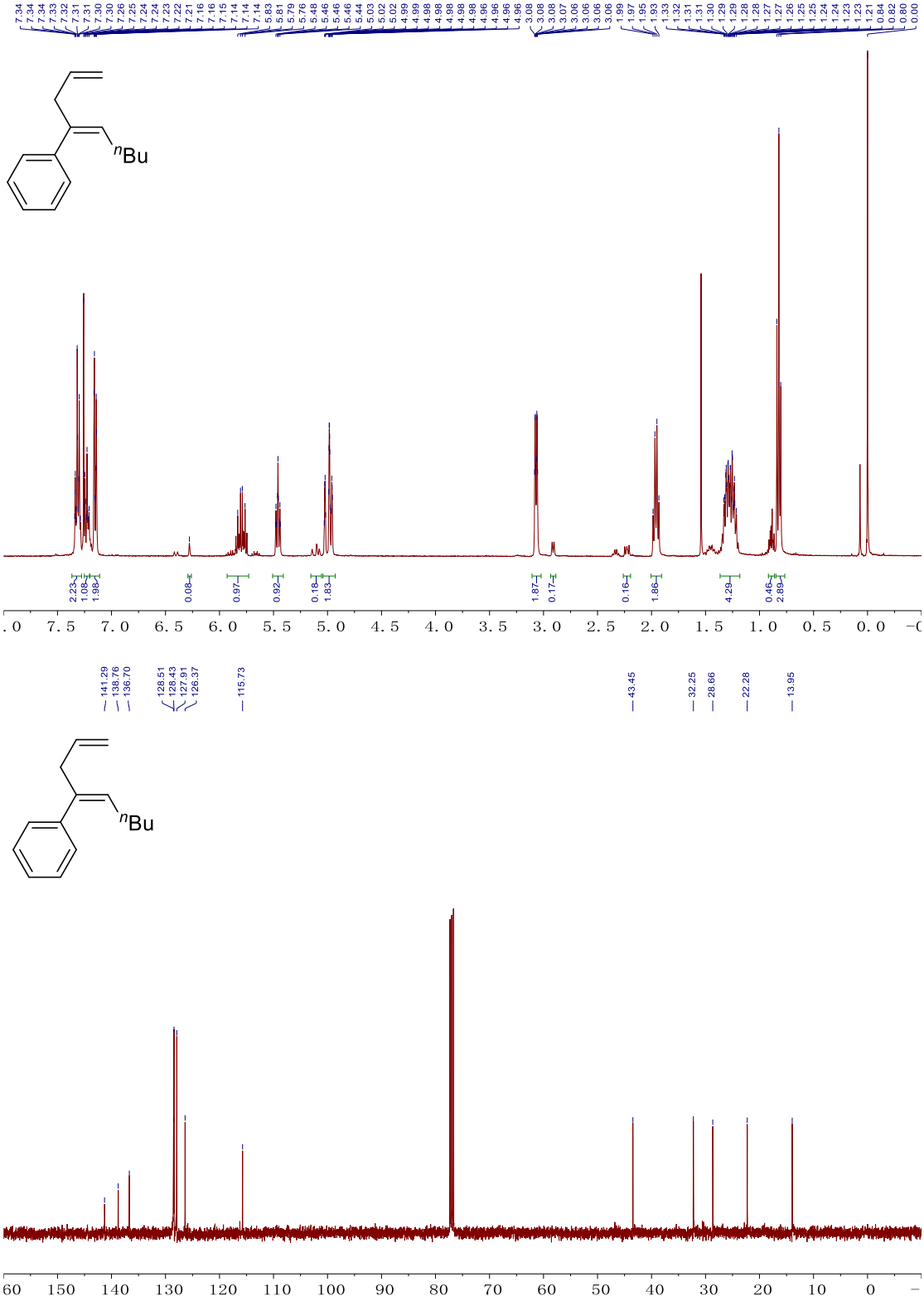


(*E*)-1-methoxy-4-(1-phenylhex-1-en-1-yl)benzene (6)

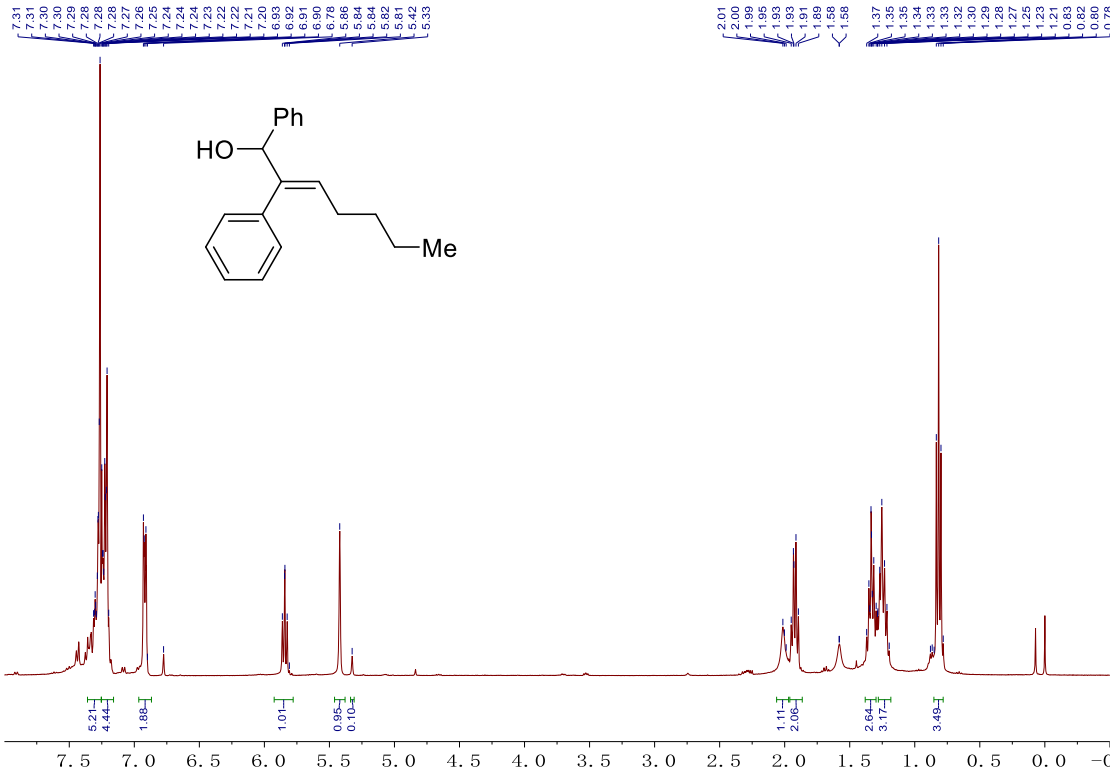


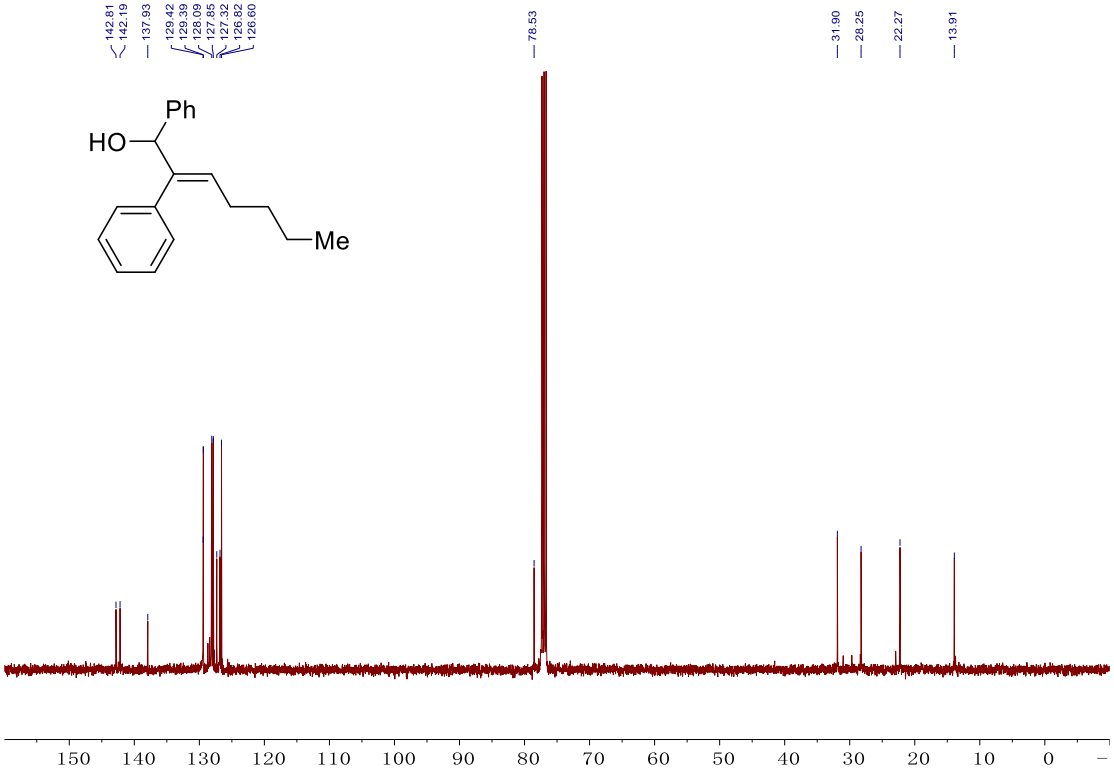


(*Z*)-nona-1,4-dien-4-ylbenzene (7)

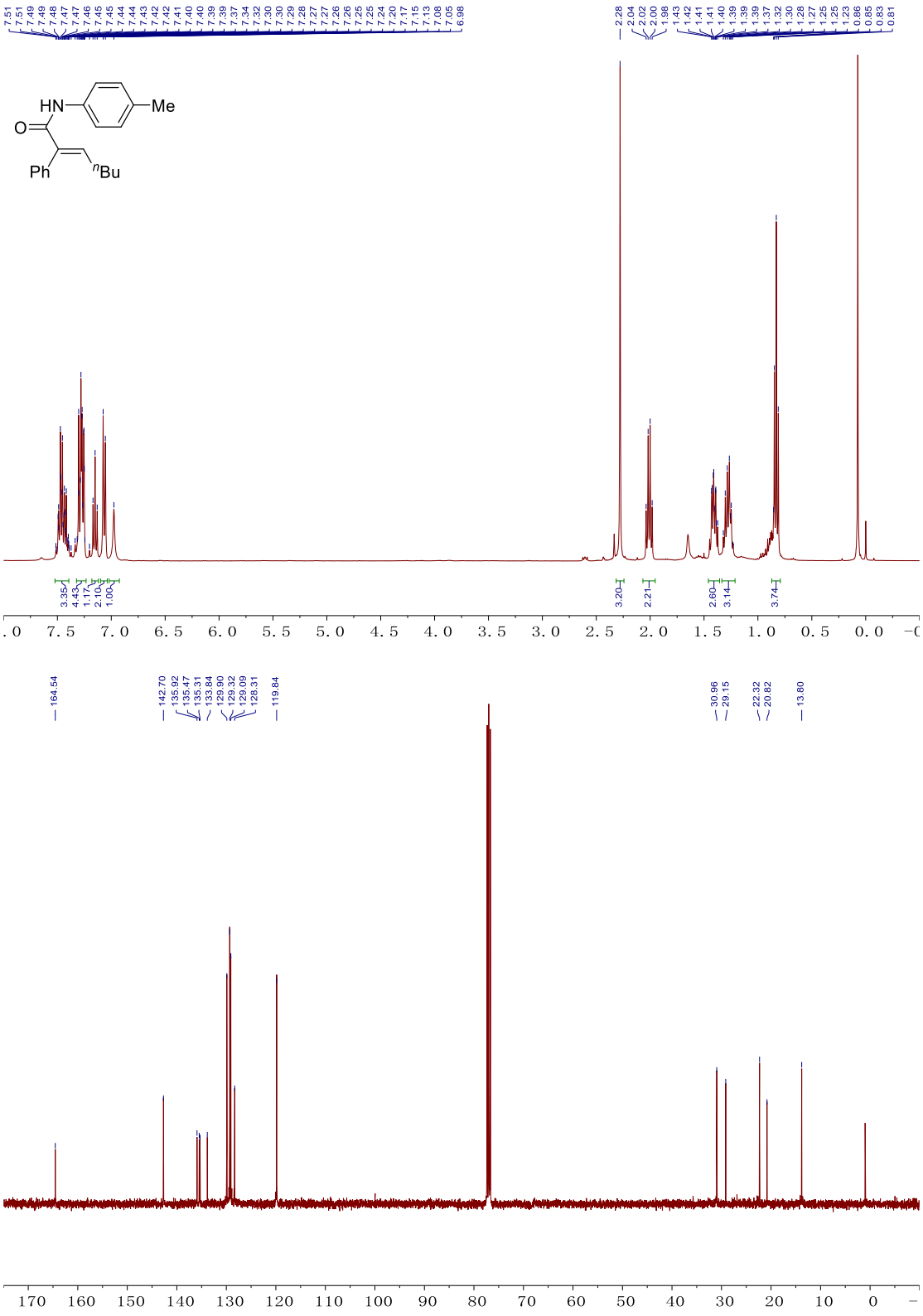


(*E*)-1,2-diphenylhept-2-en-1-ol (8)

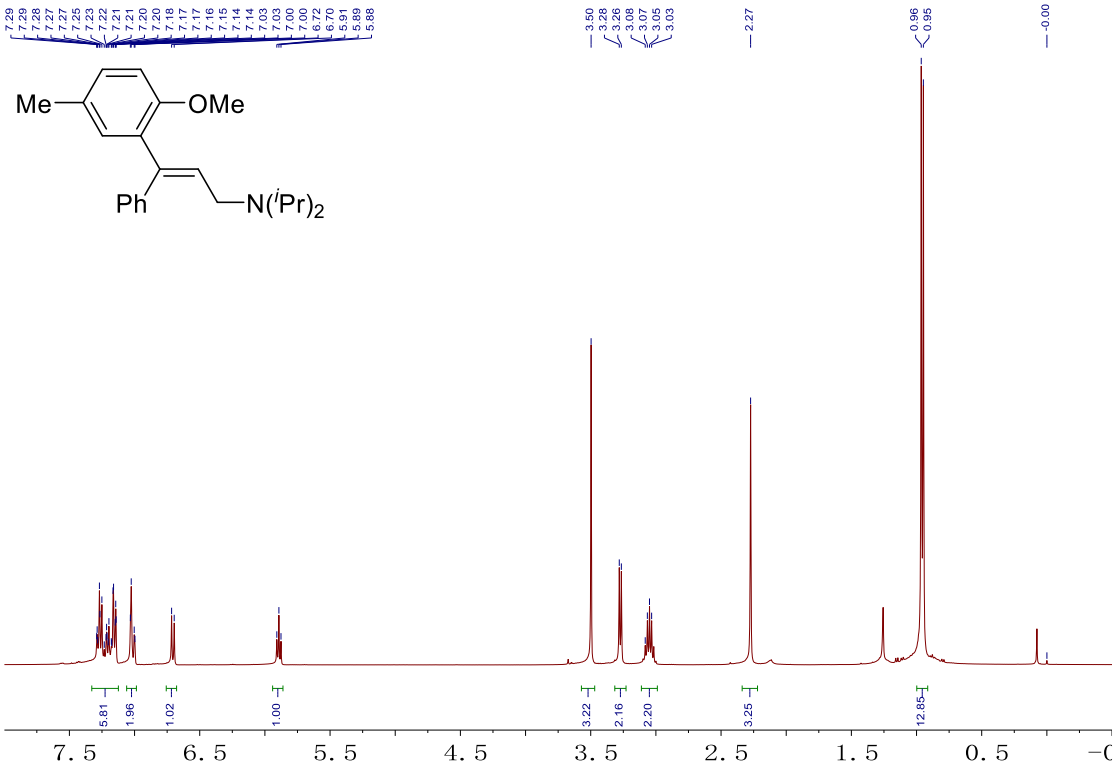


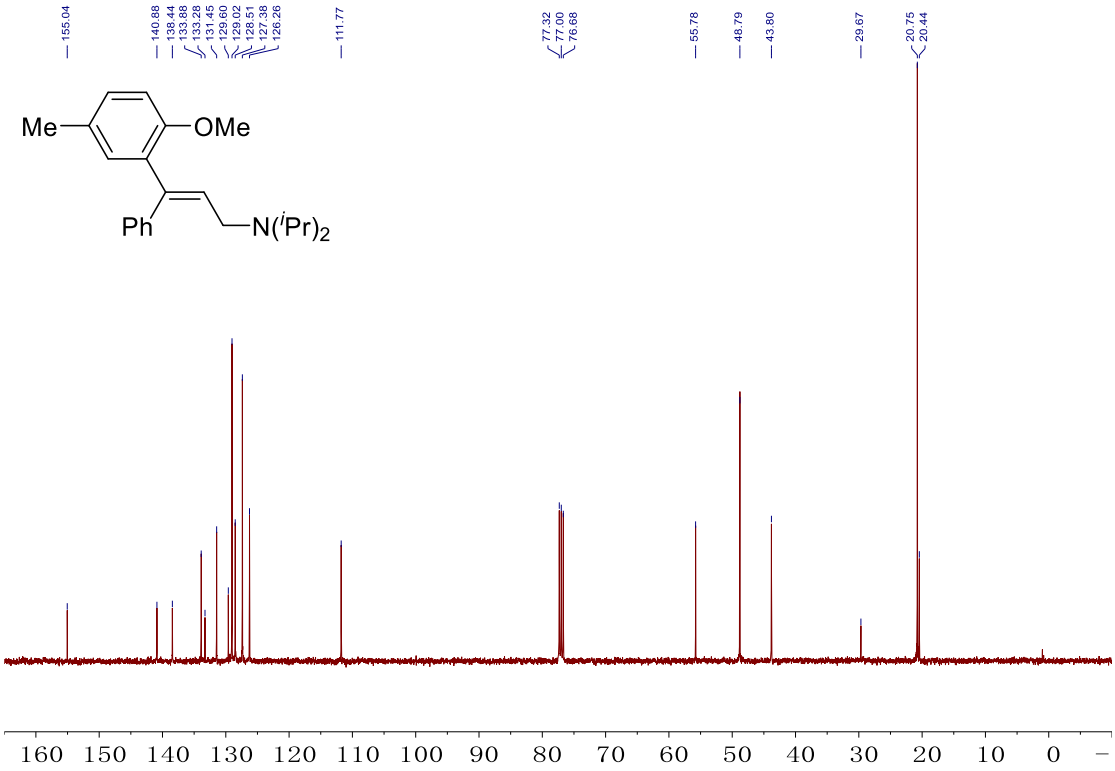


(*E*)-2-phenyl-N-(p-tolyl)hept-2-enamide (9)

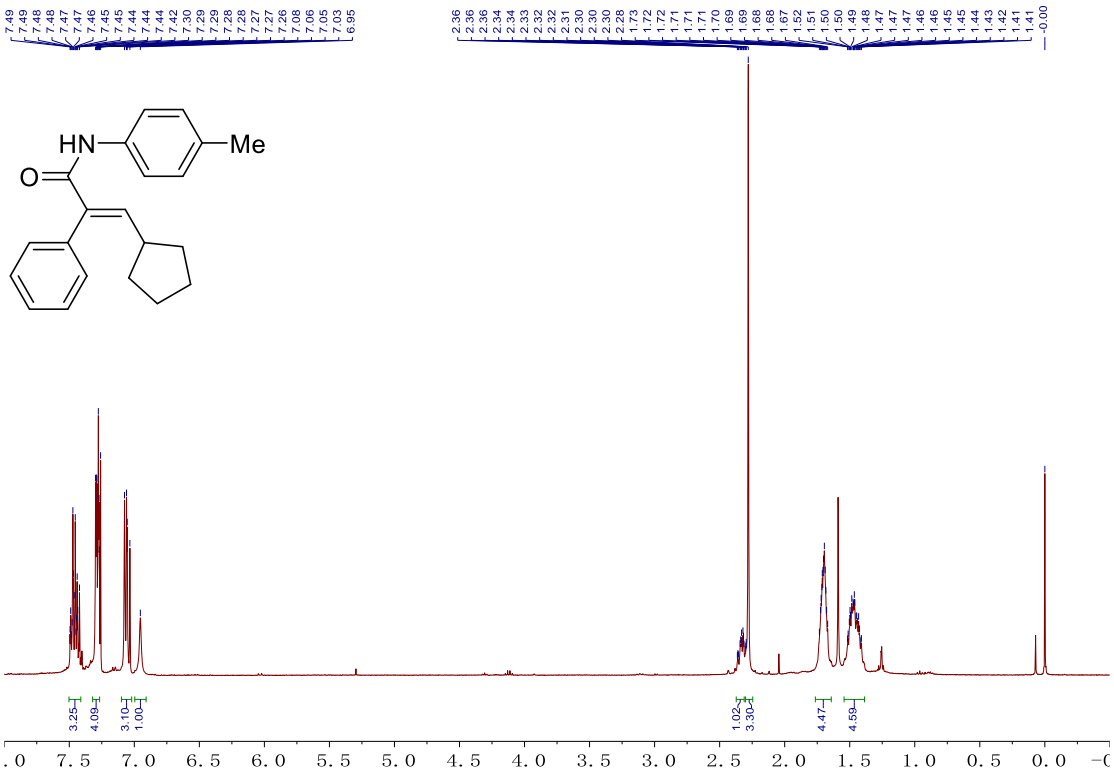


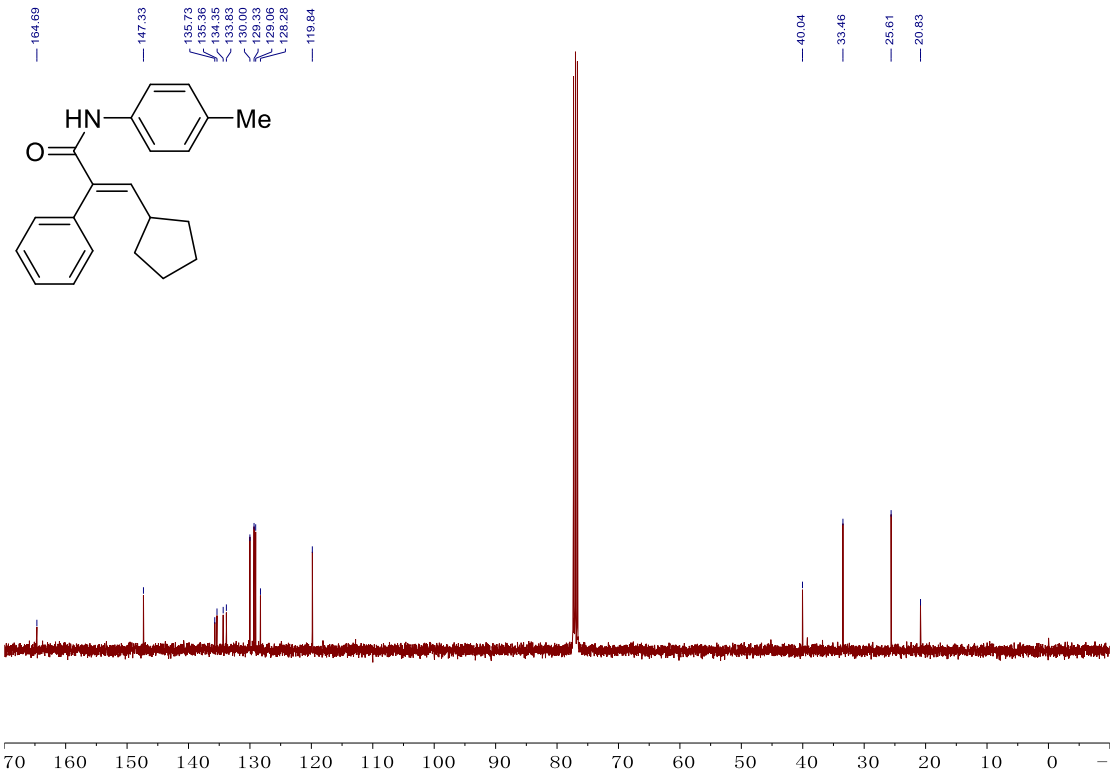
(*E*)-N,N-diisopropyl-3-(2-methoxy-5-methylphenyl)-3-phenylprop-2-en-1-amine (10)



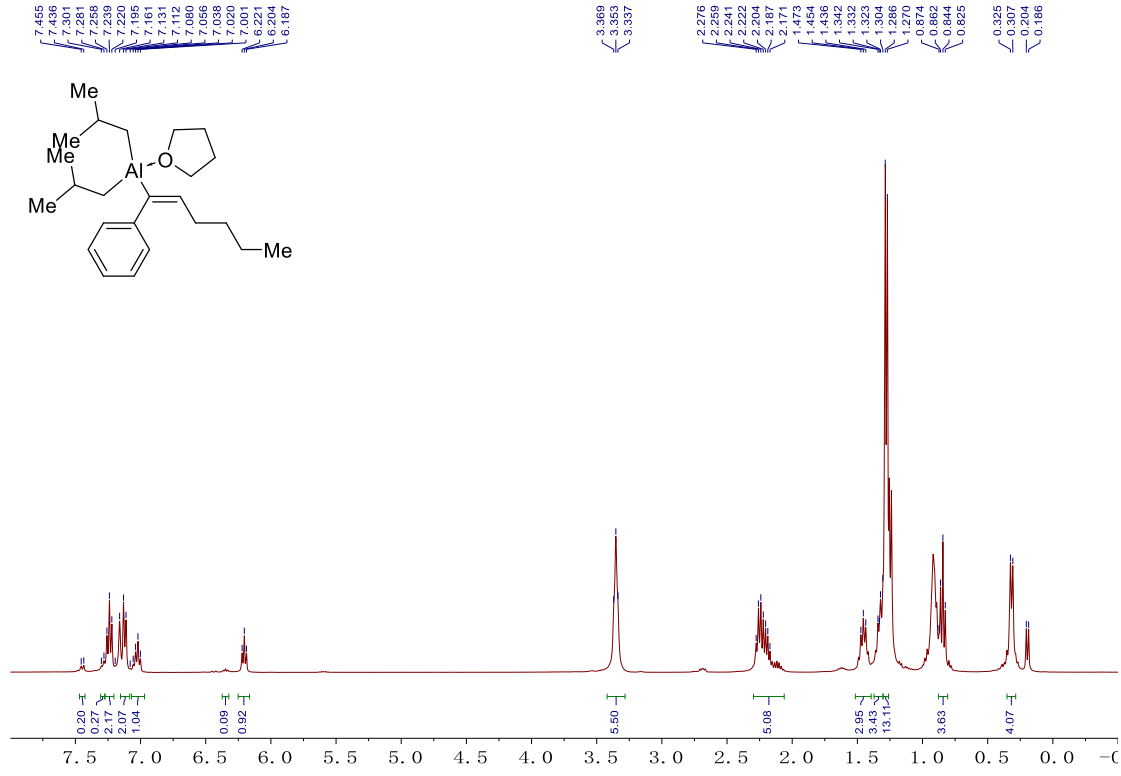


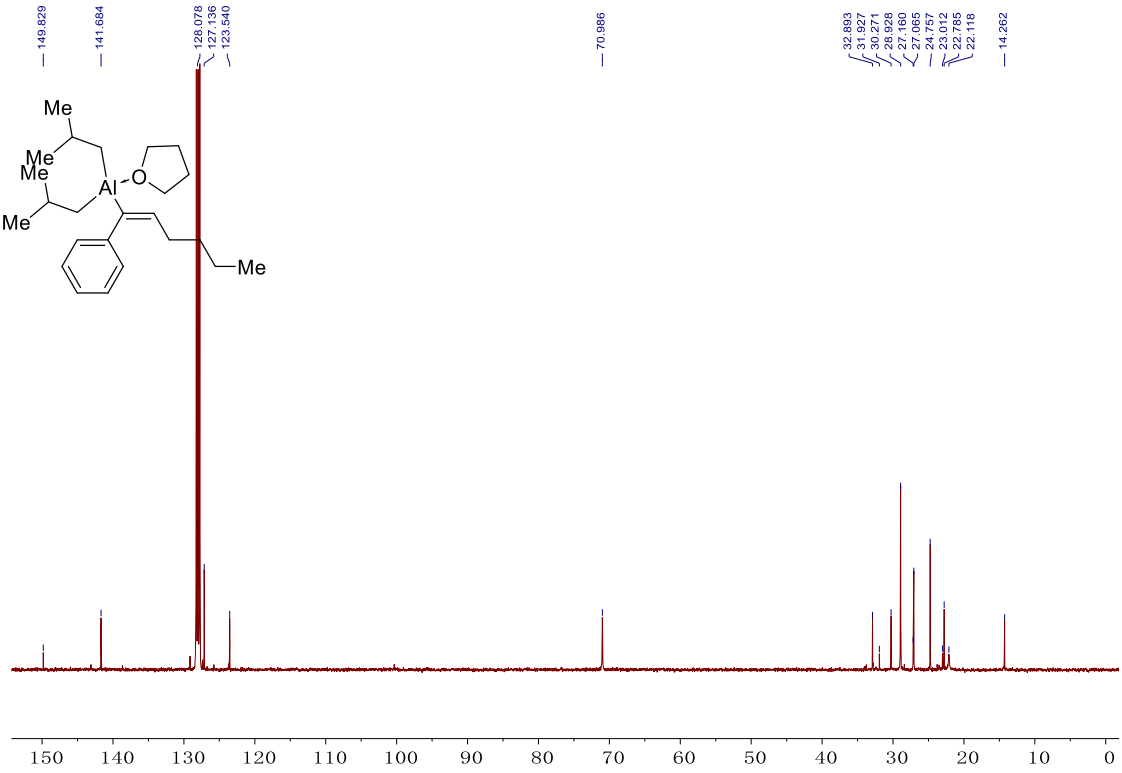
(*E*)-3-cyclopentyl-N,2-diphenylacrylamide (11)

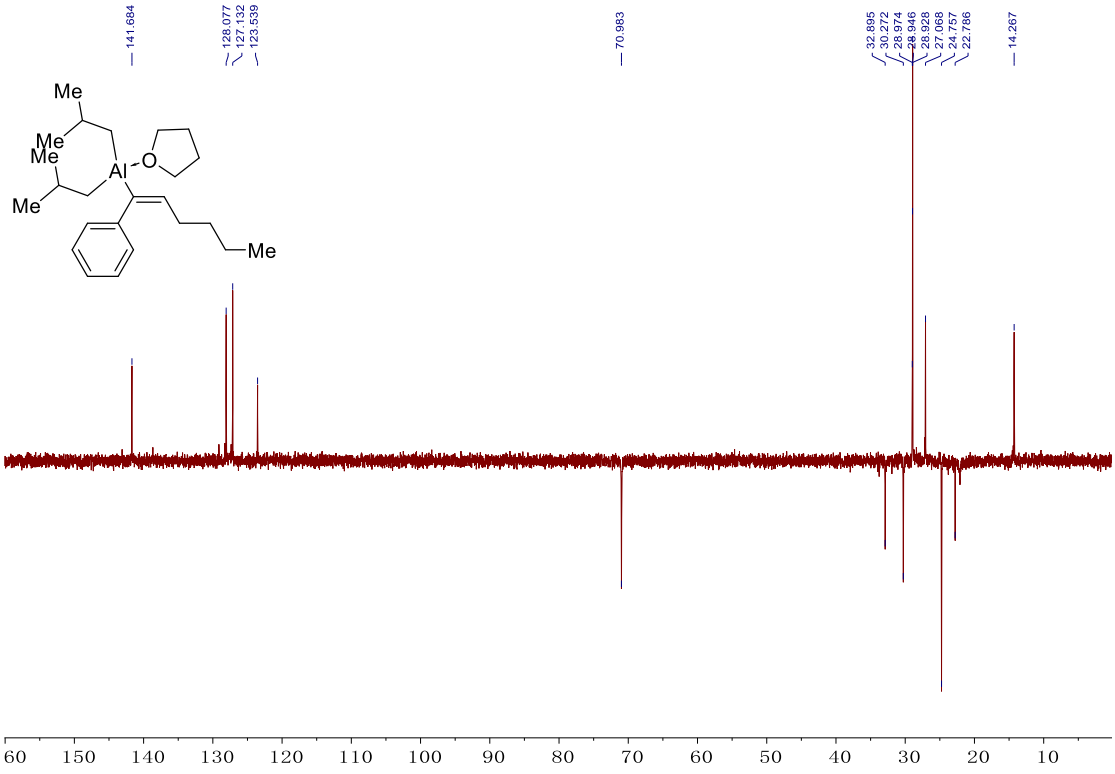




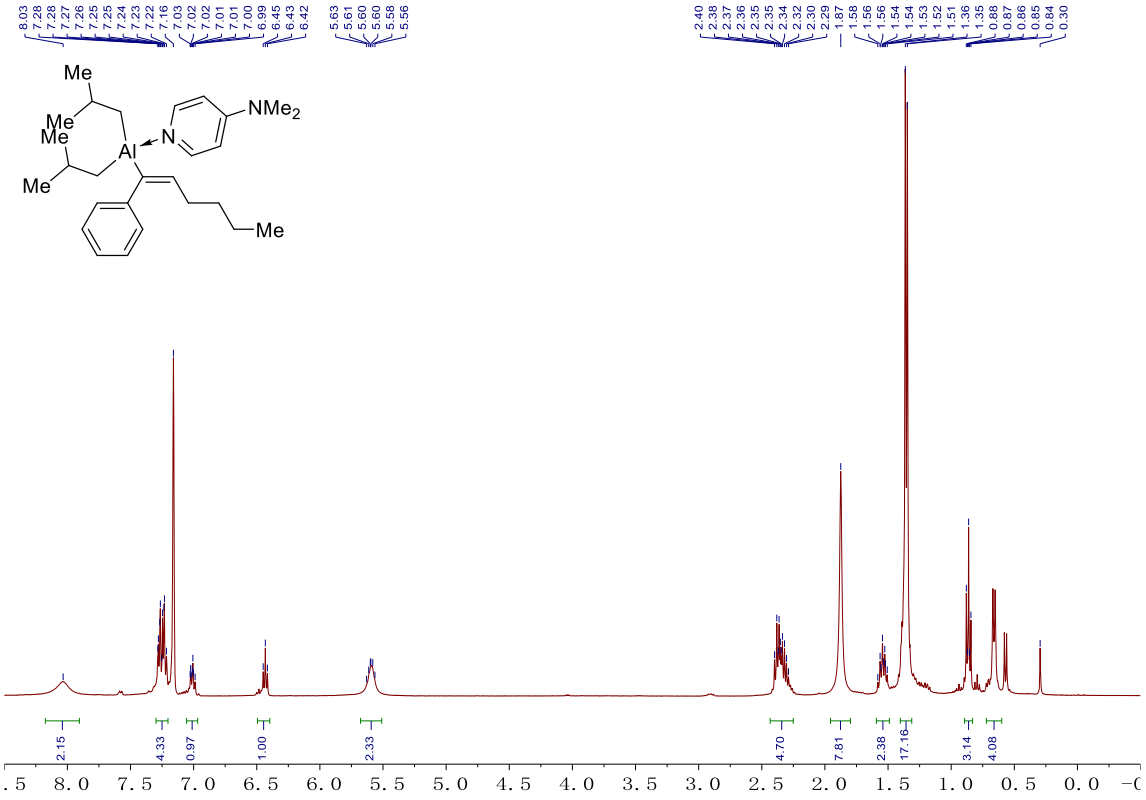
(*E*)-diisobutyl(1-phenylhex-1-en-1-yl)aluminum tetrahydrofuran adduct (2aa'-THF)

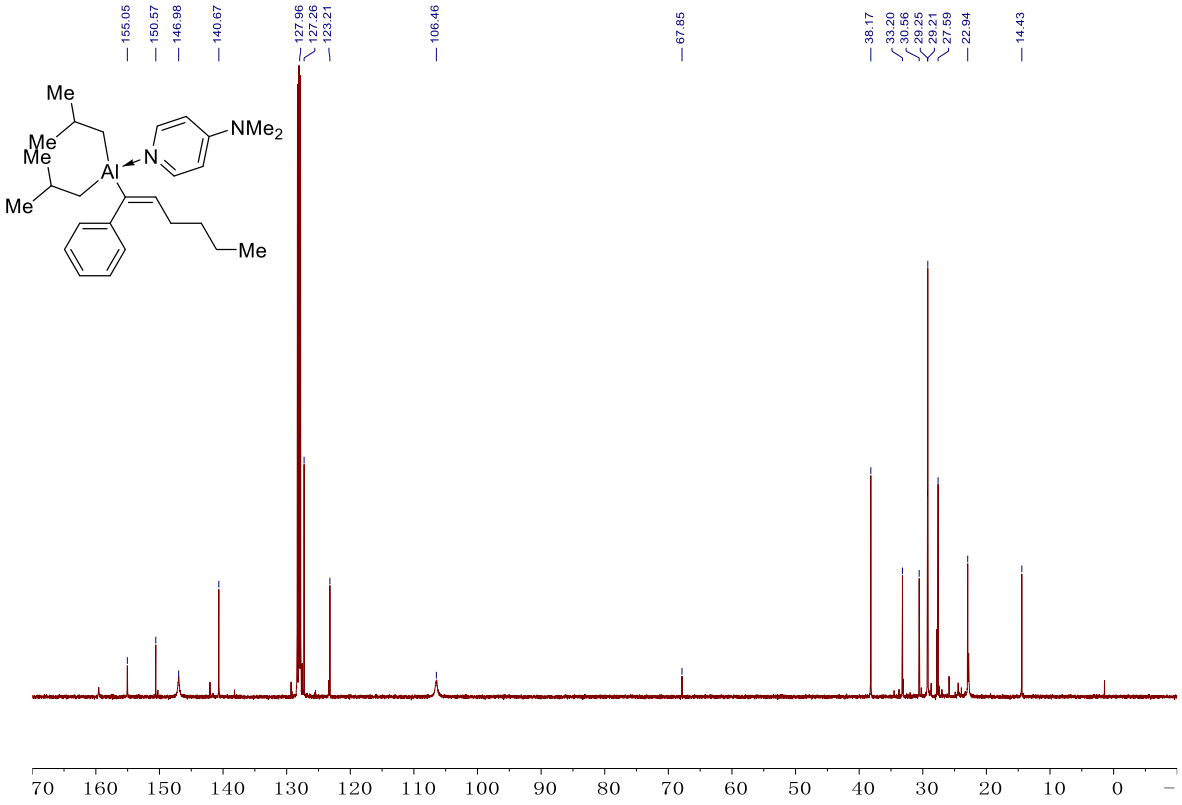




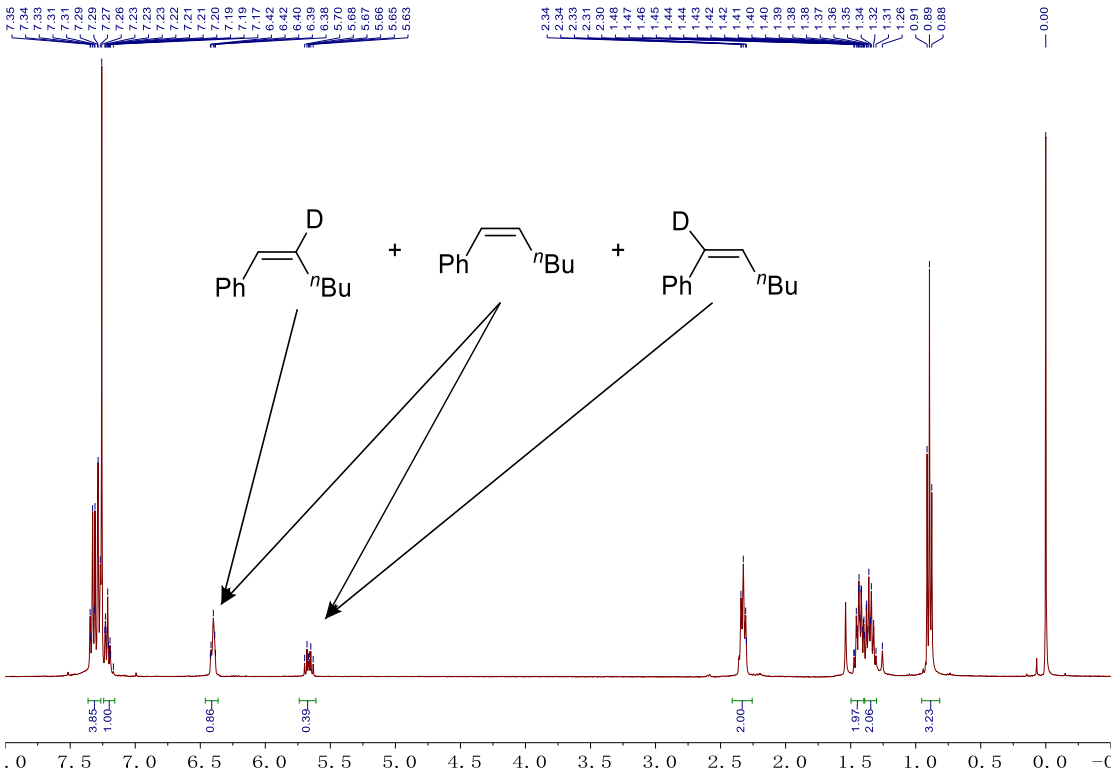


(*E*)-diisobutyl(1-phenylhex-1-en-1-yl)aluminum DMAP adduct (2aa'-DMAP)





Kinetic isotopic effect experiment (Lwt-6-74)



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