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Supporting Information

TfOH-Catalyzed Transfer Hydrogenation Reaction Using 1-Tetralone as A Novel Dihydrogen Source

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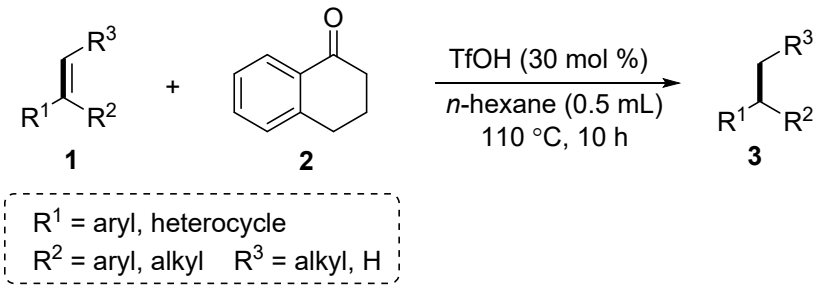
General Information

Reactions were monitored through thin layer chromatography (TLC) on 0.30 mm SiliCycle silica gel plates and visualized under UV light. All known compounds were identified by ^{1}H NMR, ^{13}C NMR and compared with previously reported data. NMR spectra of the new products were recorded using Bruker AC-300, Bruker AC-400, or Bruker AC-500 instruments, with tetramethylsilane as an internal reference. Chemical shifts (δ) and coupling constants (J) were expressed in ppm and Hz, respectively. The following abbreviations indicated the multiplicities: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. Mass spectra were taken on a Finnigan TSQ Quantum-MS instrument in the electron spray ionization (ESI).

Olefins [1, 2] were prepared according to literature procedures. The rest of the chemical reagents were obtained from commercial suppliers.

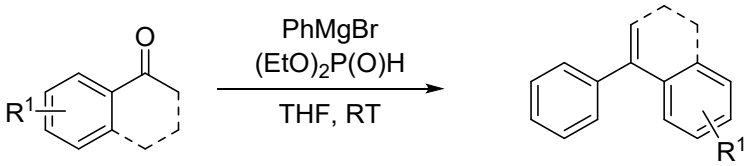
Experimental Procedure

General Procedures for the Synthesis of 3.



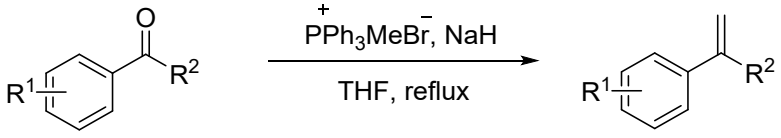
To a solution of olefins **1** (0.20 mmol) in *n*-hexane (0.5 mL) was added 1-tetralone **2** (0.30 mmol) and TfOH (9.0 mg, 5.3 μL, 0.06 mmol). The resulting mixture was stirred at 110 ℃ (oil bath) under air for 10 h, cooled to room temperature, and purified by silica gel chromatography, eluting with petroleum ether to give **3.**

General procedure A. [1]



Phenyl magnesium bromide (1.0 M in THF, 11.0 mL, 2.2 equiv.) was added to a solution of acetophenone (5.0 mmol, 1.0 equiv.) in dry THF (0.083 M). The reaction was stirred at RT for 30 min. Diethyl phosphite (6.0 mmol, 828.0 mg, 1.2 equiv.) was added to the reaction, which was let to stir at RT for 16 h. The reaction was quenched with water and extracted 10 × 3 with EtOAc. The combined organic layers were dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel to give the pure alkene.

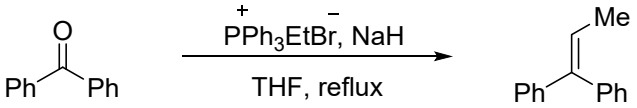
General procedure B. [2]



To a solution of PPh_3MeBr (12.82 g, 36 mmol, 1.2 equiv.) in THF (70 mL) was added NaH (60% dispersion in mineral oil) (1.32g, 33 mmol, 1.1 equiv.), the reaction mixture was refluxed for 1 h. Then the corresponding ketones (30 mmol) in THF (20 mL) were added dropwise at 0 ℃. The mixture was refluxed overnight. When the starting material was consumed (monitored by TLC), the reaction mixture was diluted by petroleum ether and filtered through a pad of

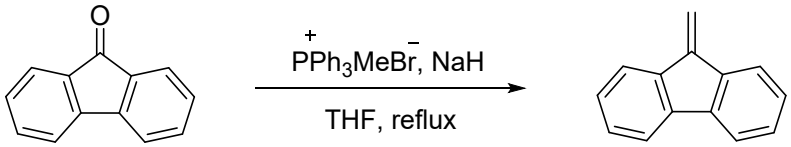
silica gel. The filtrate was concentrated to give a crude product which was distilled or purified through flash column chromatography to obtain the desired product. The known products were identical to the literature.

General procedure C. [2]



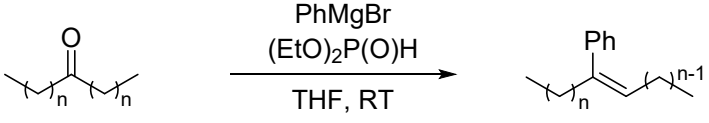
To a solution of PPh_3EtBr (13.32 g, 36 mmol, 1.2 equiv.) in THF (70 mL) was added NaH (60% dispersion in mineral oil) (1.32g, 33 mmol, 1.1 equiv.), the reaction mixture was refluxed for 1 h. Then, benzophenone (5.46g, 30 mmol) in THF (20 mL) were added dropwise at 0 ℃. The mixture was refluxed overnight. When the starting material was consumed (monitored by TLC), the reaction mixture was diluted by petroleum ether and filtered through a pad of silica gel. The filtrate was concentrated to give a crude product which was purified through flash column chromatography to obtain the desired product as a white solid.

General procedure D. [2]



To a solution of PPh_3MeBr (12.82 g, 36 mmol, 1.2 equiv.) in THF (70 mL) was added NaH (60% dispersion in mineral oil) (1.32g, 33 mmol, 1.1 equiv.), the reaction mixture was refluxed for 1 h. Then, 9-fluorenone (5.40 g, 30 mmol) in THF (20 mL) were added dropwise at 0 ℃. The mixture was refluxed overnight. When the starting material was consumed (monitored by TLC), the reaction mixture was diluted by petroleum ether and filtered through a pad of silica gel. The filtrate was concentrated to give a crude product which was purified through flash column chromatography to obtain the desired product, which was identical to the literature.

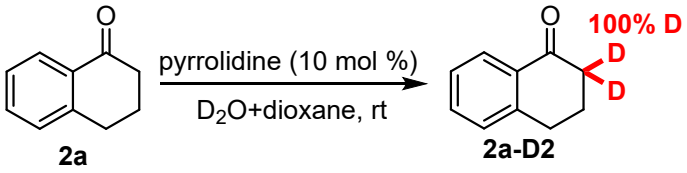
General procedure E. [1]



Phenyl magnesium bromide (1.0 M in THF, 11.0 mL, 2.2 equiv.) was added to a solution of

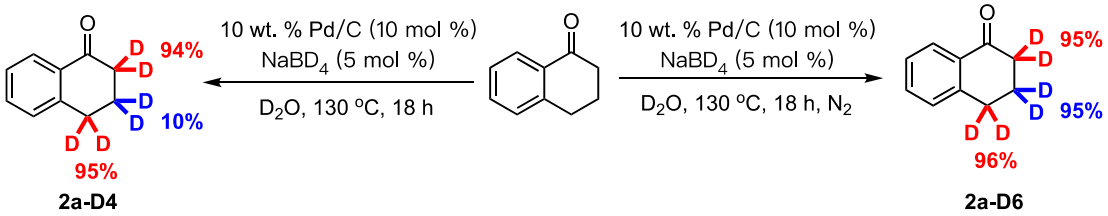
acetophenone (5.0 mmol, 1 equiv.) in dry THF (0.083 M). The reaction was stirred at RT for 30 min. Diethyl phosphite (6.0 mmol, 828.0 mg, 1.2 equiv.) was added to the reaction, which was let to stir at RT for 16 h. The reaction was quenched with water and extracted 10 × 3 with EtOAc. The combined organic layers were dried over Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel to give the pure alkene.

Preparation of *α*-Deuterated 1-tetralone. [3]



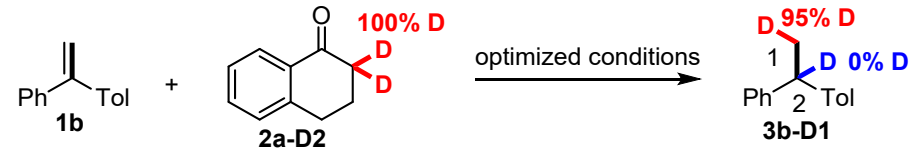
To a solution of 10 mol % of pyrrolidine (35.6 mg, 41.4 μL, 0.50 mmol) in 7.5 mL D_2O with 7.5 mL anhydrous dioxane as cosolvent was added *α*-tetralone (731.2 mg, 0.73 mL, 5.0 mmol). The reaction mixture was stirred at room temperature for 12 h, added water (50 mL), then extracted with diethyl ether (50 × 3 mL). The organic layer was dried over sodium sulfate, and filtered. The filtrate was concentrated to afford *α*-tetralone-D2(**2a-D2**).

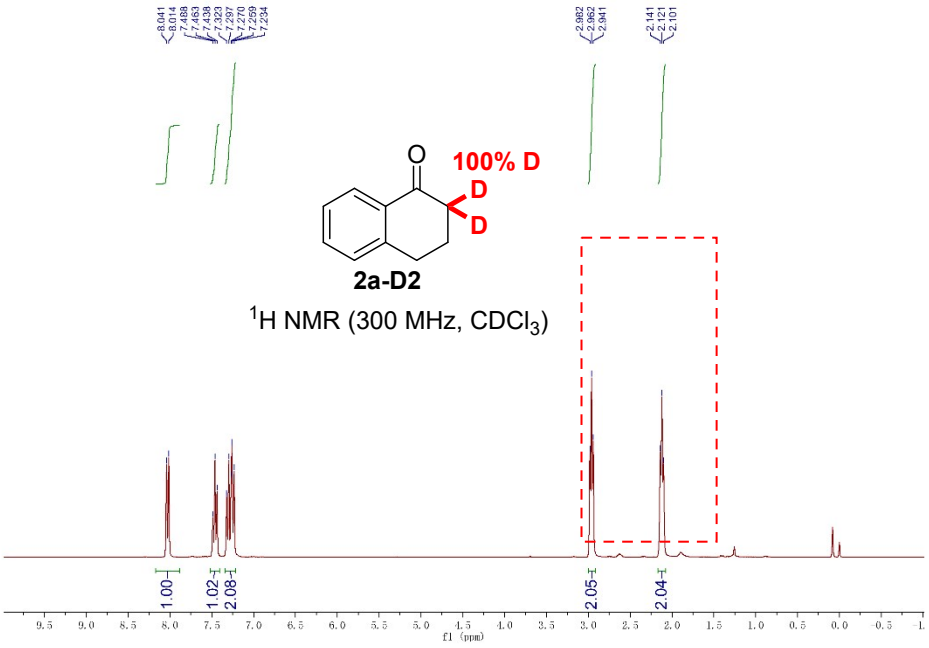
Preparation of polydeuterated 1-tetralone 2a-D4 and 2a-D6. [3]



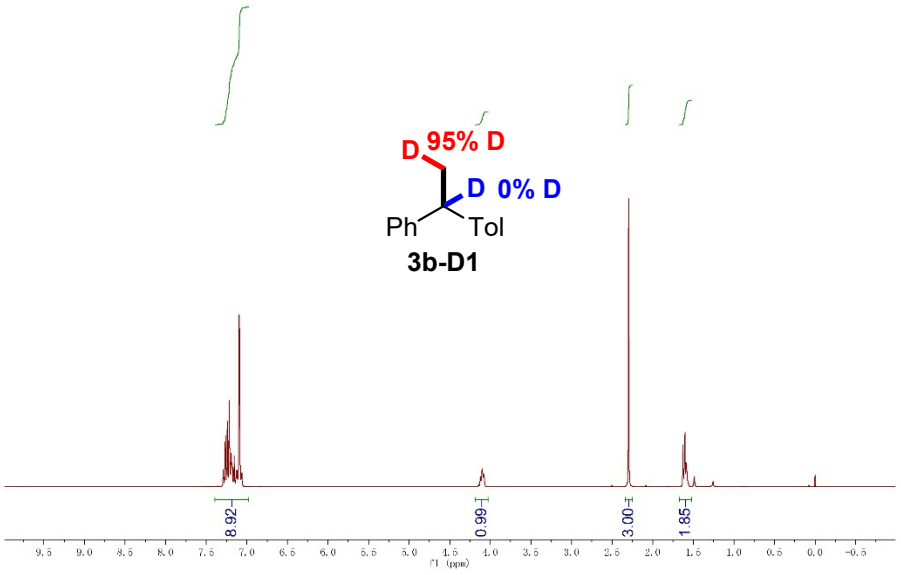
Into a pressure tube filled with nitrogen was placed *α*-tetralone (292.0 mg, 266.4 μL, 2.0 mmol), 10 wt.% Pd/C (212.8 mg, 0.20 mmol), $NaBD_4$ (4.2 mg, 0.10 mmol) and D_2O (3.0 mL). The reaction mixture was heated to 130 °C for 18 h. The mixture was cooled to room temperature and the catalyst was removed by filtration. The product was purified by silica gel chromatography, eluting with petroleum ether/ethyl acetate (5:1 *v/v*) to give **2a-D6** (53 %, 159.6 mg). Without nitrogen, other conditions are the same as above, giving **2a-D4** (45 %, 138.8 mg).

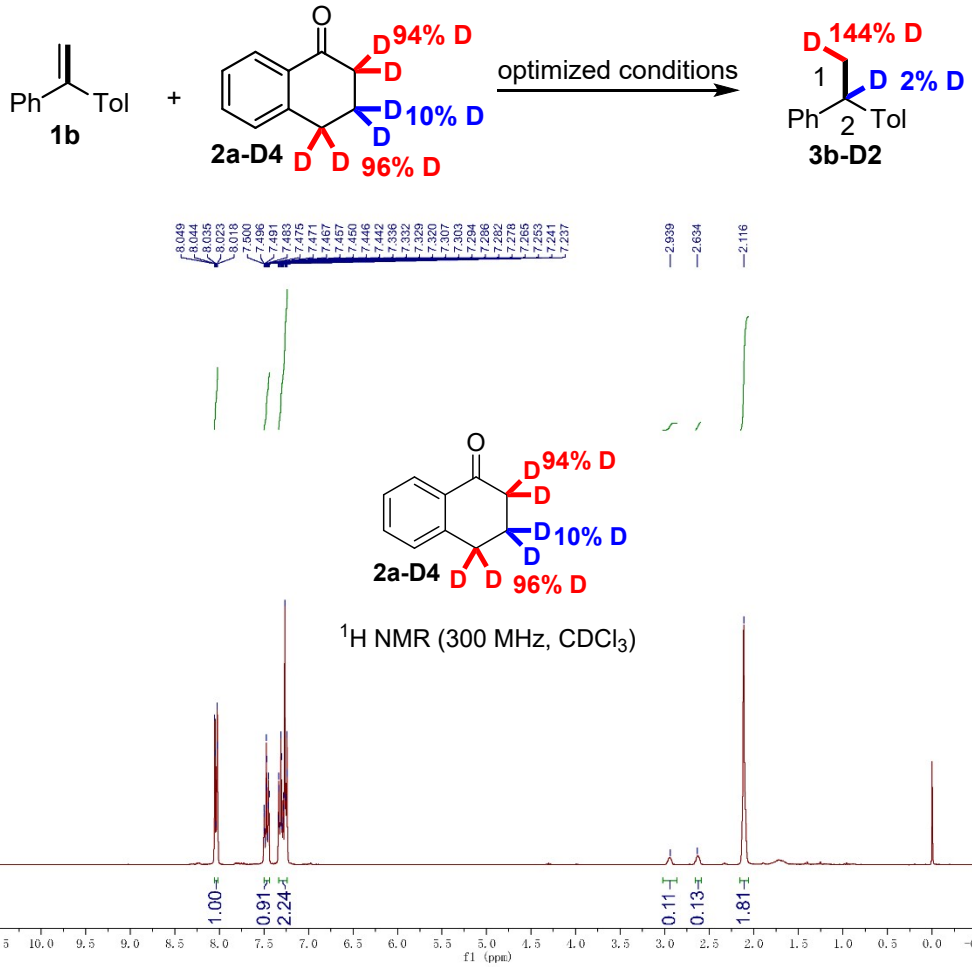
Isotopic Labeling Experiments



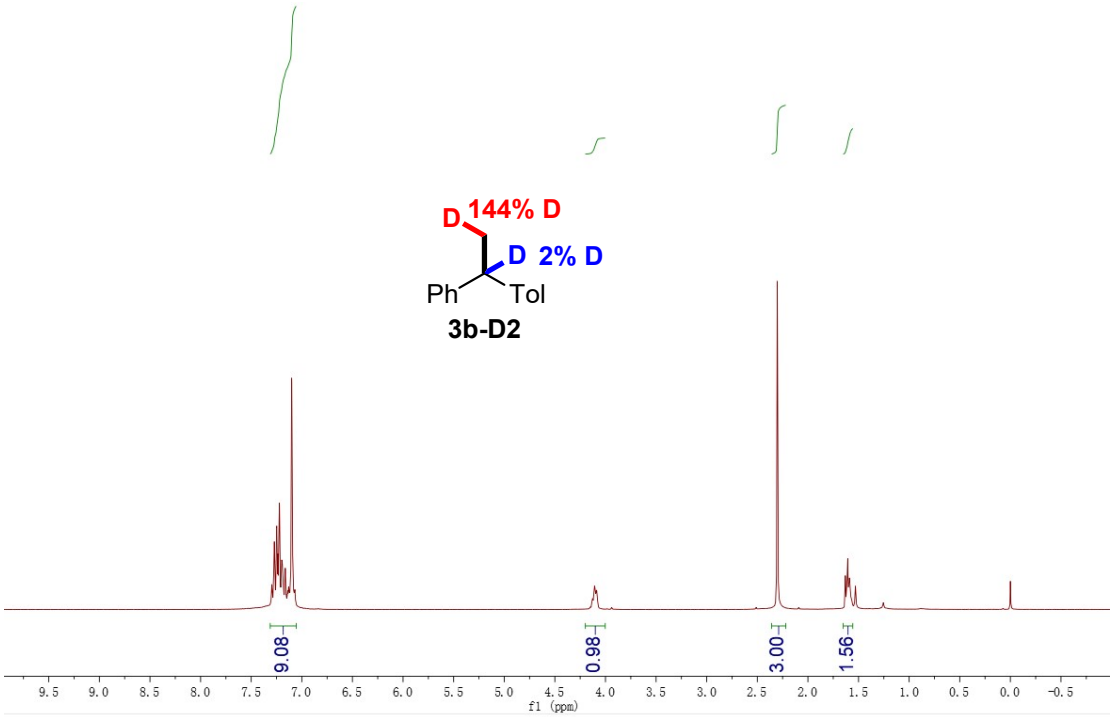


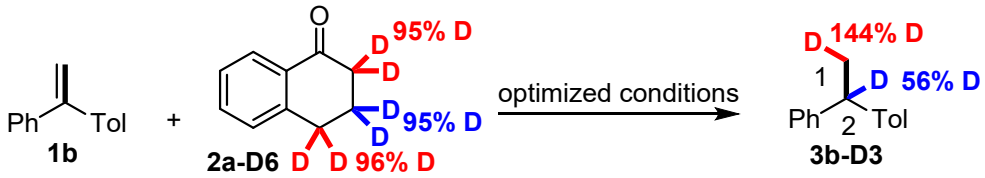
1-methyl-4-(1-phenylethyl-2-*d*)benzene (**3b-D1**), colorless oil (88 %, 34.7 mg); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.30 – 7.04 (m, 9H), 4.11 (q, *J* = 7.0 Hz, 1H), 2.30 (s, 3H), 1.64 – 1.57 (m, 1.96H).

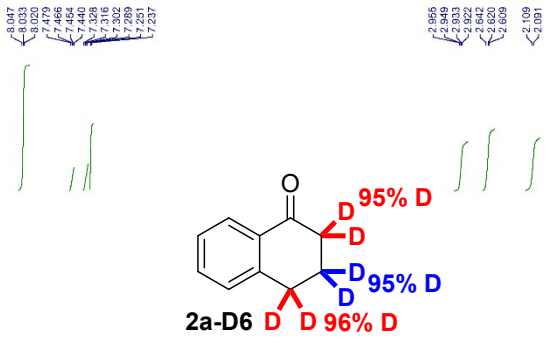




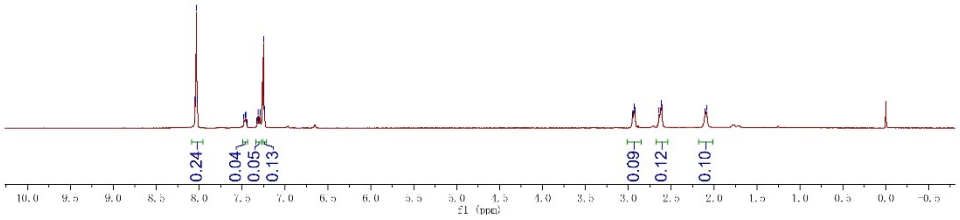
1-methyl-4-(1-phenylethyl-2-*d*)benzene (**3b-D2**), colorless oil (86 %, 34.7 mg); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.30 – 7.04 (m, 9H), 4.11 (q, J = 7.0 Hz, 1H), 2.30 (s, 3H), 1.64 – 1.57 (m, 1.56H).



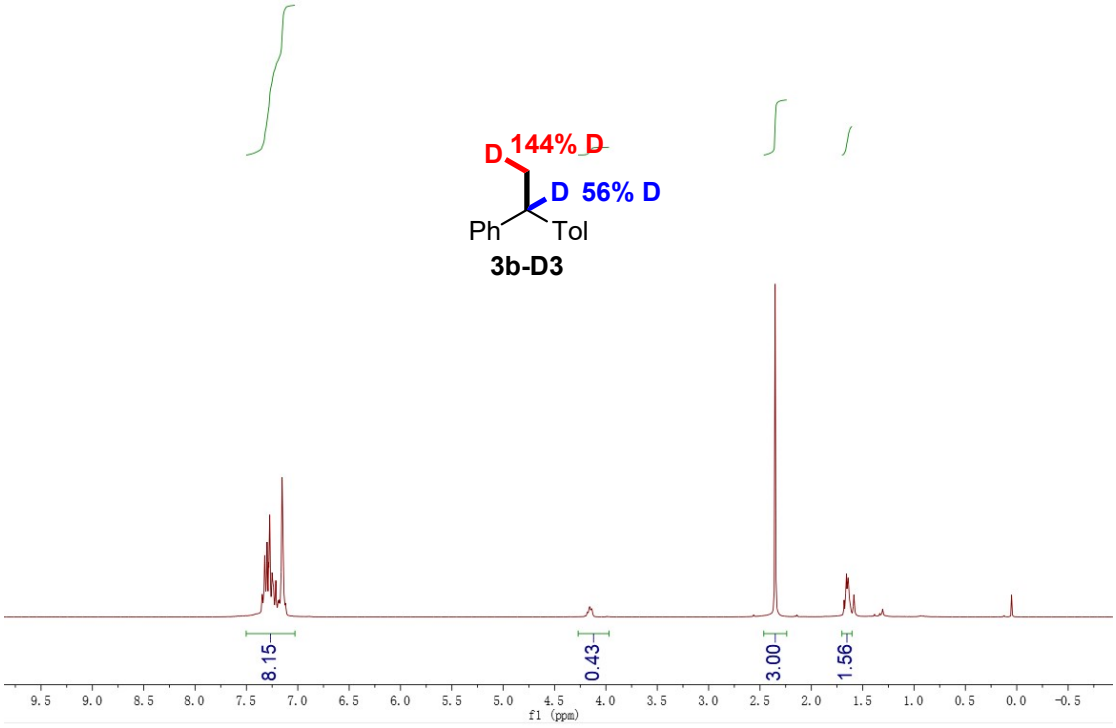


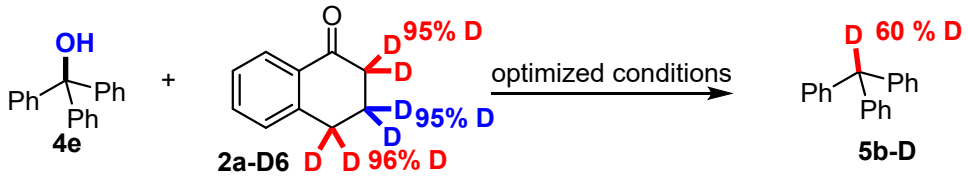


^{1}H NMR (300 MHz, $CDCl_3$)



1-methyl-4-(1-phenylethyl-2-*d*)benzene (**3b-D3**), colorless oil (89 %, 34.7 mg); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.30 – 7.04 (m, 9H), 4.14-4.10 (m, 0.43H), 2.30 (s, 3H), 1.64 – 1.57 (m, 1.56H).





(methanetriyl-*d*)tribenzene (**5b-D**), colorless oil (91 %, 44.7 mg); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.30 – 7.17 (m, 9H), 7.16 – 7.05 (m, 6H), 5.58 – 5.50 (s, 0.42H).

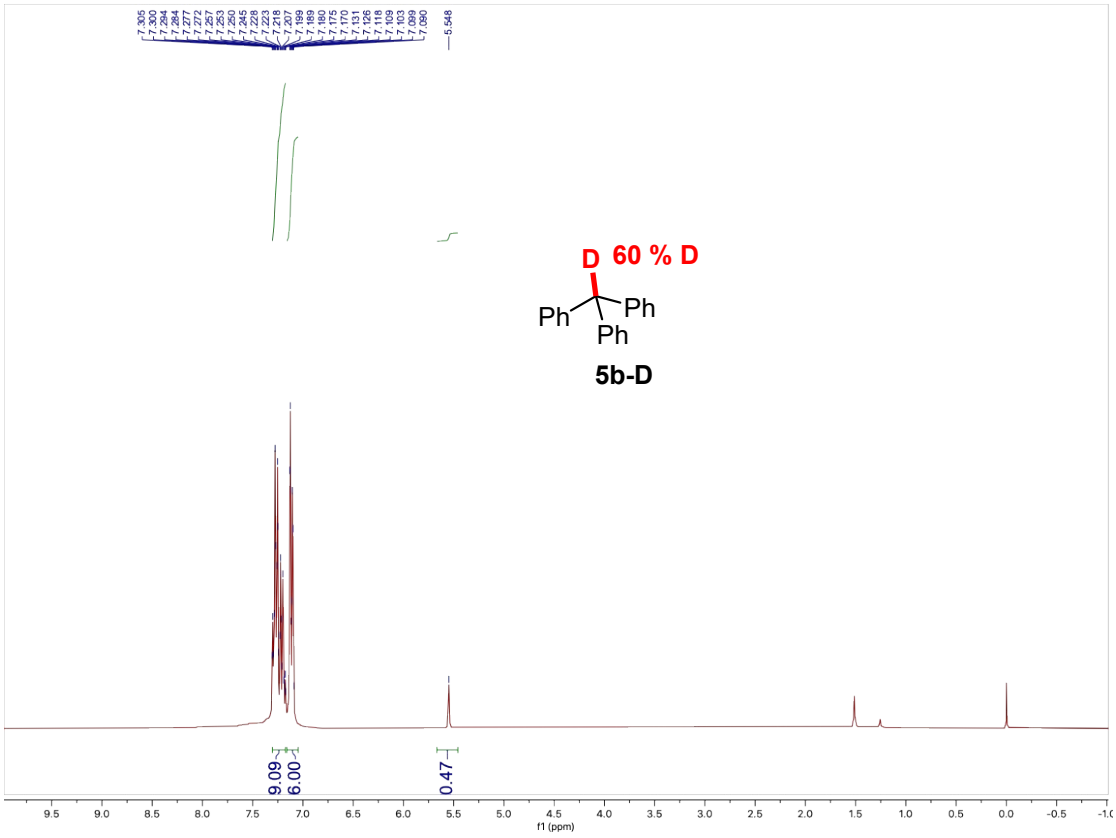
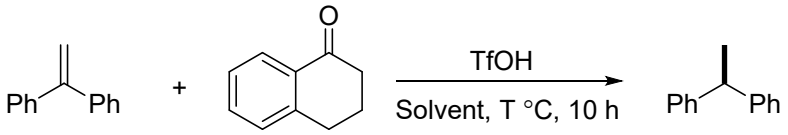


Table S1. Optimization of Reaction Conditions



1a **2a** **1c**

Entry	1a (mmol)	2a (mmol)	Cat. (mol %)	Temp. (°C)	Solvent	Yield (%)[a]
1	0.2	0.3	TfOH (50)	110	*n*-hexane (1.0 mL)	74
2	0.2	0.3	TfOH (50)	110	CH_2Cl_2 (1.0 mL)	39
3	0.2	0.3	TfOH (50)	110	$CHCl_3$ (1.0 mL)	35
4	0.2	0.3	TfOH (50)	110	DCE (1.0 mL)	Trace
5	0.2	0.3	TfOH (50)	110	Toluene (1.0 mL)	42
6	0.2	0.3	TfOH (50)	110	CH_3NO_2 (1.0 mL)	n. d.
7	0.2	0.3	TfOH (50)	110	CH_3CN (1.0 mL)	n. d.
8	0.2	0.3	TfOH (50)	110	EtOH (1.0 mL)	n. d.
9	0.2	0.3	TfOH (50)	110	EtOAc (1.0 mL)	n. d.
10	0.2	0.3	TfOH (50)	110	DMSO (1.0 mL)	n. d.
11	0.2	0.3	TfOH (50)	110	DMF (1.0 mL)	n. d.
12	0.2	0.3	TfOH (50)	110	Dioxane (1.0 mL)	n. d.
13	0.2	0.3	TfOH (50)	110	THF (1.0 mL)	n. d.
14	0.2	0.3	TfOH (50)	110	*n*-hexane (0.5 mL)	71
15	0.2	0.3	TfOH (50)	110	*n*-hexane (1.5 mL)	64
16	0.2	0.3	TfOH (75)	110	*n*-hexane (1.0 mL)	63
17	**0.2**	**0.3**	**TfOH (30)**	**110**	***n*-hexane (1.0 mL)**	**92**
18	0.2	0.3	TfOH (30)	90	*n*-hexane (1.0 mL)	83
19	0.2	0.3	TfOH (10)	110	*n*-hexane (1.0 mL)	74
20	0.2	0.4	TfOH (30)	110	*n*-hexane (1.0 mL)	91
21	0.2	0.3	TFA (30)	110	*n*-hexane (1.0 mL)	n. d.
22	0.2	0.3	TFA (50)	110	*n*-hexane (1.0 mL)	n. d.
23	0.2	0.3	TsOH (50)	110	*n*-hexane (1.0 mL)	n. d.
24[b]	0.2	0.3	TsOH (100)	110	*n*-hexane (1.0 mL)	n. d.
25	0.2	0.3	TfOH (30)	110	*n*-hexane (1.0 mL)	49
26	0.2	0.3	H_2SO_4 (30)	110	*n*-hexane (1.0 mL)	32
27	0.2	0.3	HCl (30)	110	*n*-hexane (1.0 mL)	n. d.
28	0.2	0.3	HOAc (30)	110	*n*-hexane (1.0 mL)	n. d.
29	0.2	0.1	TfOH (30)	110	*n*-hexane (1.0 mL)	37

a. Isolated yield.

b. Under N_2.

n.d., not detected.

X-ray Crystallography

Single crystal growth of compound 6: A solution of compound 6 (10.0 mg) was dissolved in *n*-hexane (2 mL). the solution was allowed to evaporate very slowly at room temperature. After one week, crystals suitable for X-ray structural determination were obtained.

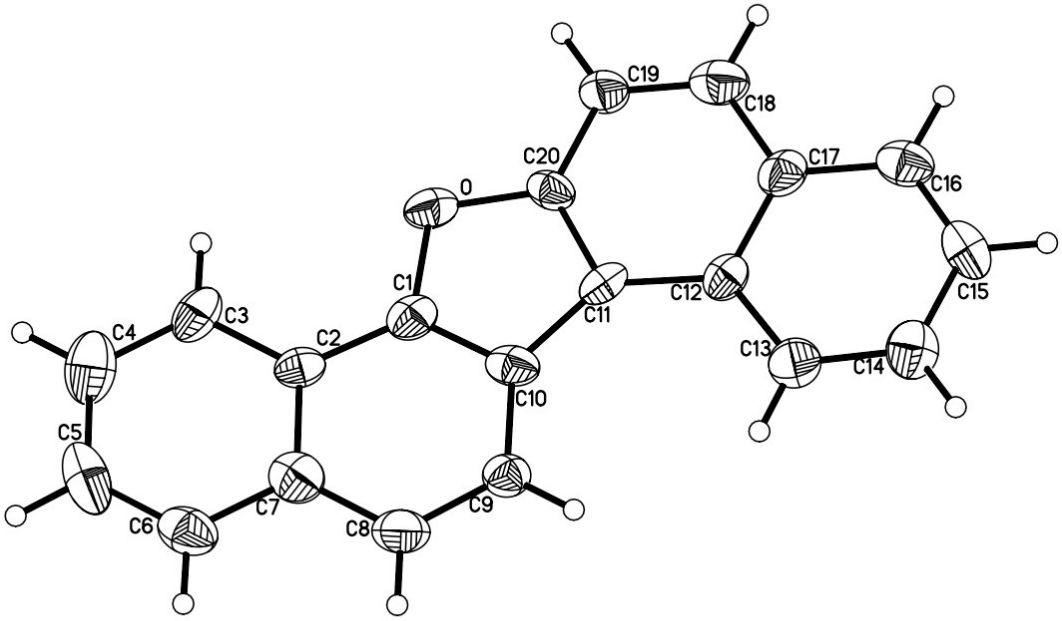


Figure S1. Single crystal of compound **6.**

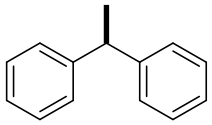
(Complete .cif-data of the compound are available under the CCDC Number: 2300633)

Crystal data of compound 6.

Bond precision	C-C = 0.0113 Å Wavelength = 0.71073
Temperature	293 K
Space Group	$P2_1$

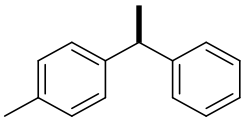
Hall group	P2yb
Cell	a = 12.929(3)Å b = 3.9490(8)Å c = 13.092(3)Å,
	α = 90° β = 103.70(3)° γ = 90°.
Volume	649.4(2)
Sum formula	$C_{20}H_{12}O$
Mr	268.30
Dx ($g \cdot cm^{-3}$)	1.372
Z	2
Mu (mm^{-1})	0.083
F000	280.0
h, k, l_{max}	15, 4, 15
N_{ref}	1388
T_{min},T_{max}	0.971,0.985
Data completeness	1.00/0.58
Theta(max)	25.381
R(reflections)	0.0612(556)
wR2(reflections)	0.1006(1388)
S = 0.931 Npar = 190	

Characterization Data



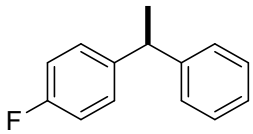
3a

Ethane-1,1-diyldibenzene (**3a**) [4], colorless oil (92 %, 33.5 mg); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35 – 7.11 (m, 10H), 4.14 (q, *J* = 7.2 Hz, 1H), 1.63 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.4, 128.4, 127.6, 126.0, 44.8, 21.9.



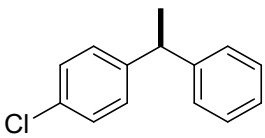
3b

1-Methyl-4-(1-phenylethyl)benzene (**3b**)[4], colorless oil (90 %, 35.3 mg); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.31 – 7.06 (m, 9H), 4.11 (q, *J* = 7.2 Hz, 1H), 2.30 (s, 3H), 1.62 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 146.6, 143.4, 135.5, 129.1, 128.4, 127.6, 127.5, 126.0, 44.4, 22.0, 21.0.



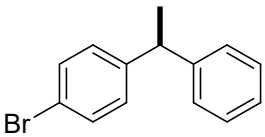
3c

1-Fluoro-4-(1-phenylethyl)benzene (**3c**)[4], colorless oil (84 %, 33.6 mg); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.32 – 7.23 (m, 2H), 7.22 – 7.11 (m, 5H), 7.00 – 6.89 (m, 2H), 4.12 (q, *J* = 7.2 Hz, 1H), 1.61 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.3 (d, *J* = 242.4 Hz), 146.2, 142.1 (d, *J* = 3.2 Hz), 129.1 (d, *J* = 7.7 Hz), 128.5, 127.5, 126.2, 115.1 (d, *J* = 21.0 Hz), 44.1, 22.0.



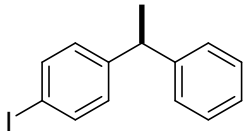
3d

1-Chloro-4-(1-phenylethyl)benzene (**3d**)[5], colorless oil (86 %, 37.3 mg); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40 – 7.13 (m, 9H), 4.17 (q, *J* = 7.2 Hz, 1H), 1.67 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.8, 144.9, 131.8, 129.0, 128.5, 128.5, 127.6, 126.3, 44.2, 21.8.



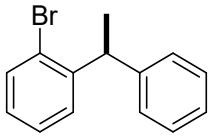
3e

1-Bromo-4-(1-phenylethyl)benzene (**3e**)[6], colorless oil (86 %, 44.9 mg); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.49 – 7.40 (m, 2H), 7.37 – 7.29 (m, 2H), 7.28 – 7.19 (m, 3H), 7.18 – 7.09 (m, 2H), 4.16 (q, *J* = 7.2 Hz, 1H), 1.66 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.7, 145.4, 131.4, 129.4, 128.5, 127.6, 126.3, 119.8, 44.3, 21.8.



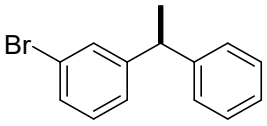
3f

1-Iodo-4-(1-phenylethyl)benzene (**3f**), colorless oil (82 %, 50.5 mg); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.64 – 7.54 (m, 2H), 7.32 – 7.23 (m, 2H), 7.22 – 7.14 (m, 3H), 7.00 – 6.91 (m, 2H), 4.08 (q, *J* = 7.2 Hz, 1H), 1.60 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.1, 145.7, 137.4, 129.8, 128.5, 127.5, 126.3, 91.2, 44.4, 21.7.



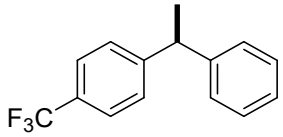
3g

1-Bromo-2-(1-phenylethyl)benzene (**3g**), colorless oil (80 %, 41.8 mg); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.58 – 7.50 (m, 1H), 7.33 – 7.15 (m, 7H), 7.09 – 6.99 (m, 1H), 4.64 (q, *J* = 7.2 Hz, 1H), 1.61 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.4, 144.9, 132.9, 128.8, 128.3, 127.8, 127.6, 127.6, 126.2, 124.8, 43.5, 21.3.



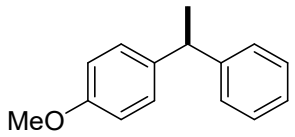
3h

1-Bromo-3-(1-phenylethyl)benzene (**3h**), colorless oil (85 %, 44.4 mg); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.36 (s, 1H), 7.33 – 7.24 (m, 3H), 7.23 – 7.16 (m, 3H), 7.13 (d, *J* = 5.1 Hz, 2H), 4.10 (q, *J* = 7.2 Hz, 1H), 1.61 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.8, 145.5, 130.7, 130.0, 129.2, 128.5, 127.6, 126.4, 126.3, 122.5, 44.6, 21.7.



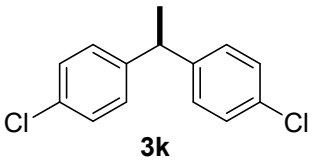
3i

1-(1-Phenylethyl)-4-(trifluoromethyl)benzene (**3i**)[4], colorless oil (79 %, 39.5 mg); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.52 (d, *J* = 8.2 Hz, 2H), 7.38 – 7.24 (m, 4H), 7.24 – 7.15 (m, 3H), 4.20 (q, *J* = 7.2 Hz, 1H), 1.65 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 150.5, 145.3, 128.6, 127.9, 127.6, 126.4, 125.3 (q, *J* = 3.75), 44.7, 21.6.



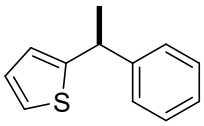
3j

1-Methoxy-4-(1-phenylethyl)benzene (**3j**)[4], colorless oil (65 %, 27.6 mg); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.33 – 7.08 (m, 7H), 6.86 – 6.72 (m, 2H), 4.09 (q, *J* = 7.2 Hz, 1H), 3.75 (s, 3H), 1.60 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.9, 146.8, 138.6, 128.5, 128.4, 127.6, 126.0, 113.8, 55.3, 44.0, 22.1.



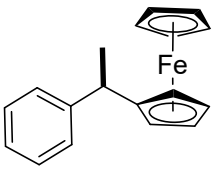
3k

4,4'-(Ethane-1,1-diyl)bis(chlorobenzene) (**3k**)[9], colorless oil (88 %, 44.2 mg); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.24 (d, *J* = 8.3 Hz, 4H), 7.10 (d, *J* = 8.4 Hz, 4H), 4.08 (q, *J* = 7.2 Hz, 1H), 1.58 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.3, 132.0, 128.9, 128.6, 43.6, 21.7.



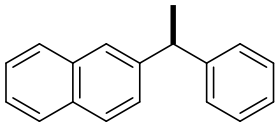
3l

2-(1-Phenylethyl)thiophene (**3l**), colorless oil (52 %, 19.6 mg); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.26 (m, 5H), 7.13 (m, 1H), 6.91 (m, 1H), 6.80-6.77 (m, 1H), 4.34 (q, *J* = 7.1 Hz, 1H), 1.70 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 150.7, 146.1, 128.5, 127.3, 126.5, 123.6, 123.5, 40.8, 23.4.



3m

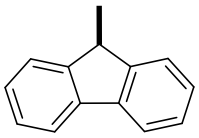
2-(1-Phenylethyl)ferrocene (**3m**), oil (43 %, 25.0 mg); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.30 – 7.07 (m, 5H), 4.12 (s, 8H), 3.98 (s, 1H), 3.83 (q, *J* = 7.2 Hz, 1H), 1.58 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 147.5, 128.2, 127.1, 125.9, 68.8, 68.1, 67.8, 67.1, 66.6, 39.8, 22.6.



3n

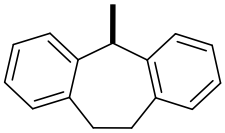
2-(1-Phenylethyl)naphthalene (**3n**)[4], colorless oil (76 %, 35.3 mg); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.83 – 7.66 (m, 4H), 7.43 (ddd, *J* = 6.9, 4.4, 1.7 Hz, 2H), 7.32 – 7.23 (m, 5H), 7.22 – 7.14 (m, 1H), 4.31

(q, J = 7.2 Hz, 1H), 1.73 (d, J = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 146.2, 143.8, 133.5, 132.1, 128.4, 128.0, 127.8, 127.7, 127.6, 126.9, 126.1, 126.0, 125.4, 125.4, 44.9, 21.8.



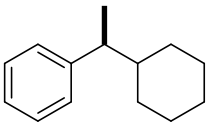
3o

9-Methyl-9H-fluorene (**3o**)[7], colorless oil (82 %, 29.6 mg); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.84 – 7.75 (m, 2H), 7.54 (dd, J = 7.0, 1.0 Hz, 2H), 7.37 (pd, J = 7.3, 1.5 Hz, 4H), 3.98 (q, J = 8.0 Hz, 1H), 1.56 (d, J = 7.4 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.0, 140.5, 126.9, 126.9, 124.0, 119.8, 42.4, 18.2.



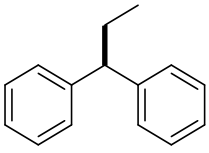
3p

5-Methyl-10,11-dihydro-5H-dibenzo[a, d][7]annulene (**3p**)[4], colorless oil (78 %, 32.5 mg); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.24 – 7.19 (m, 2H), 7.13-7.08 (m, 6H), 4.42 (q, J = 7.4 Hz, 1H), 3.21 (s, 4H), 1.71 (d, J = 8.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.2, 139.3, 130.1, 127.4, 126.3, 126.2, 43.8, 33.3, 22.1.



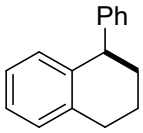
3q

(1-Cyclohexylethyl)benzene (**3q**)[5], colorless oil (42 %, 15.8 mg); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.30 – 7.23 (m, 2H), 7.19 – 7.10 (m, 3H), 2.44 (q, J = 7.2 Hz, 1H), 1.91 – 1.82 (m, 1H), 1.77 – 1.69 (m, 1H), 1.65 – 1.56 (m, 2H), 1.48 – 1.35 (m, 2H), 1.25 – 1.18 (m, 4H), 1.15 – 1.05 (m, 2H), 0.99 – 0.77 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 147.1, 128.0, 127.7, 125.6, 46.0, 44.2, 31.5, 30.6, 26.6, 18.8.



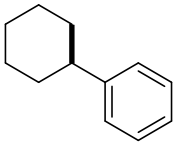
3r

Propane-1,1-diyldibenzene (**3r**)[4], colorless oil (64 %, 25.1 mg); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.25 (h, J = 6.0 Hz, 8H), 7.19 – 7.10 (m, 2H), 3.78 (t, J = 7.8 Hz, 1H), 2.09-2.05 (m, 2H), 0.89 (t, J = 7.3 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.2, 128.4, 128.0, 126.1, 53.3, 28.6, 12.9.



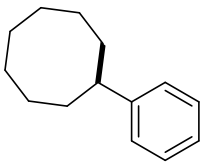
3s

1-Phenyl-1,2,3,4-tetrahydronaphthalene (**3s**)[8], colorless oil (57 %, 23.7 mg); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.62 – 7.58 (m, 1H), 7.48 – 7.41 (m, 1H), 7.39 – 7.29 (m, 1H), 7.29 – 7.23 (m, 2H), 7.22 – 7.17 (m, 1H), 7.17 – 7.06 (m, 4H), 7.06 – 6.98 (m, 1H), 6.83 (d, *J* = 7.6 Hz, 1H), 4.19 – 4.02 (m, 1H), 3.01 – 2.70 (m, 2H), 2.22 – 2.07 (m, 1H), 1.95 – 1.67 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 147.5, 139.4, 137.6, 130.2, 129.0, 128.9, 128.8, 128.2, 127.3, 127.2, 125.9, 125.6, 45.6, 33.3, 29.8, 21.0.



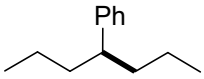
3t

Cyclohexylbenzene (**3t**)[9], colorless oil (45 %, 14.4 mg); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.33 – 7.25 (m, 2H), 7.23 – 7.13 (m, 3H), 2.55 – 2.43 (m, 1H), 1.92 – 1.80 (m, 4H), 1.78 – 1.71 (m, 1H), 1.45 – 1.21 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.1, 128.3, 126.8, 125.8, 44.6, 34.5, 27.0, 26.2.



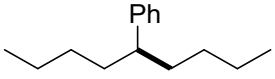
3u

Phenylcyclooctane (**3u**) [9], colorless oil (63 %, 23.7 mg); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.31 – 7.21 (m, 2H), 7.21 – 7.09 (m, 3H), 2.81 – 2.71 (m, 1H), 1.95 – 1.49 (m, 15H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 150.4, 128.3, 127.0, 125.5, 44.7, 34.7, 27.0, 26.4, 26.1.



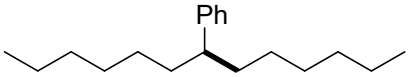
3v

Heptan-4-ylbenzene (**3v**)[10], colorless oil (65 %, 22.9 mg); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.30 – 7.25 (m, 2H), 7.19 – 7.11 (m, 3H), 2.60 – 2.42 (m, 1H), 1.62 – 1.50 (m, 4H), 1.21 – 1.09 (m, 4H), 0.87 – 0.81 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.4, 128.1, 127.7, 125.7, 45.5, 39.2, 20.7, 14.1.



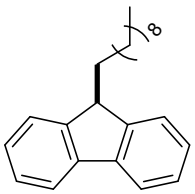
3w

Nonan-5-ylbenzene (**3w**)[11], colorless oil (67 %, 27.4 mg); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.30 – 7.24 (m, 2H), 7.20 – 7.10 (m, 3H), 2.55 – 2.37 (m, 1H), 1.67 – 1.47 (m, 4H), 1.31 – 1.04 (m, 8H), 0.85 – 0.77 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.5, 128.1, 127.7, 125.7, 46.1, 36.7, 29.9, 22.8, 14.1.



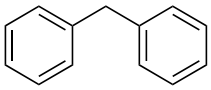
3x

Tridecan-7-ylbenzene (**3x**)[12], colorless oil (70 %, 36.5 mg); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.30 – 7.24 (m, 2H), 7.19 – 7.10 (m, 3H), 2.55 – 2.32 (m, 1H), 1.65 – 1.42 (m, 4H), 1.27 – 1.07 (m, 16H), 0.89 – 0.77 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 146.5, 128.1, 127.7, 125.7, 46.1, 37.0, 31.8, 29.5, 27.6, 22.7, 14.1.



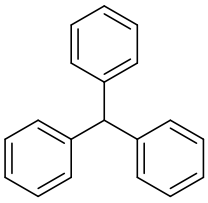
3y

9-Decyl-9*H*-fluorene (**3y**), colorless oil (72 %, 44.1 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, J = 7.0 Hz, 2H), 7.56 (d, J = 7.5 Hz, 2H), 7.43 – 7.32 (m, 4H), 4.01 (t, J = 5.9 Hz, 1H), 2.09 – 1.98 (m, 2H), 1.45 – 1.10 (m, 16H), 0.91 (t, J = 6.9 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.7, 141.1, 126.8, 126.8, 124.4, 119.8, 47.5, 33.1, 31.9, 30.0, 29.6, 29.5, 29.3, 25.7, 22.7, 14.2.



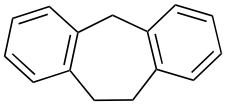
5a

Diphenylmethane (**5a**) [13], colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 – 7.22 (m, 4H), 7.22 – 7.10 (m, 6H), 3.96 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.2, 129.1, 128.6, 126.2, 42.2.



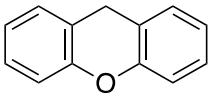
5b

Triphenylmethane (**5b**) [14]; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.37 – 7.24 (m, 9H), 7.22 – 7.12 (m, 6H), 5.60 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.98, 129.54, 128.39, 126.38, 56.91.



5c

10,11-Dihydro-5*H*-dibenzo [*a*, *d*] [7] annulene (**5c**) [15], ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.28 (m, 2H), 7.27 – 7.18 (m, 6H), 4.23 (s, 2H), 3.28 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.4, 139.1, 129.7, 129.1, 126.7, 126.2, 41.1, 32.6.



5d

9*H*-xanthene (**5d**) [16], white powder (68 %, 24.8 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.18 (dd, J = 17.0, 7.7 Hz, 4H), 7.10 – 6.96 (m, 4H), 4.05 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.0, 128.9, 127.7, 123.0, 120.6, 116.5, 27.9.

References

1. T. Wang, Y. Hu, S. Zhang, *Org. Biomol. Chem.* **2010**, *8*, 2312.

2. B. Yang, Z. Lu, *Chem. Commun.* **2017**, *53*, 12634.

3. V. Derdau, J. Atzrodt, W. Holla, *J. Label. Compd. Radiopharm.* **2007**, *50*, 295.

4. J. Wu, B. Yan, J. Meng, E. Yang, X. Ye, Q. Yao, *Org. Biomol. Chem.* **2022**, *20*, 8638.

5. M. L. Czyz, M. S. Taylor, T. H. Horngren, A. Polyzos, *ACS Catal.* **2021**, *11*, 5472.

6. I. Chatterjee, M. Oestreich, *Org. Lett.* **2016**,*18*, 2463.

7. P. Hermange, A. T. Lindhardt, R. H. Taaning, K. Bjerglund, D. Lupp, T. Skrydstrup, *J. Am. Chem. Soc.* **2011**, *133*, 6061.

8. T. N. Gieshoff, U. Chakraborty, M. Villa, A. Jacobi von Wangelin, *Angew. Chem. Int. Ed.* **2017**, *56*, 3585.

9. L. Li, G. Hilt, *Chem. Eur. J.* **2021**, *27*, 11221.

10. A. J. Smith, A. Young, S. Rohrbach, E. F. O'Connor, M. Allison, H.-S. Wang, D. L. Poole, T. Tuttle, J. A. Murphy, *Angew. Chem. Int. Ed.* **2017**, *56*, 13747.

11. Y. Fu, J.-X. Wang, K. Wang, Y. Hu, *Tetrahedron* **2008**, *64*, 11124.

12. A. Cook, H. MacLean, P. St. Onge, S. G. Newman, *ACS Catal.* **2021**, *11*, 13337.

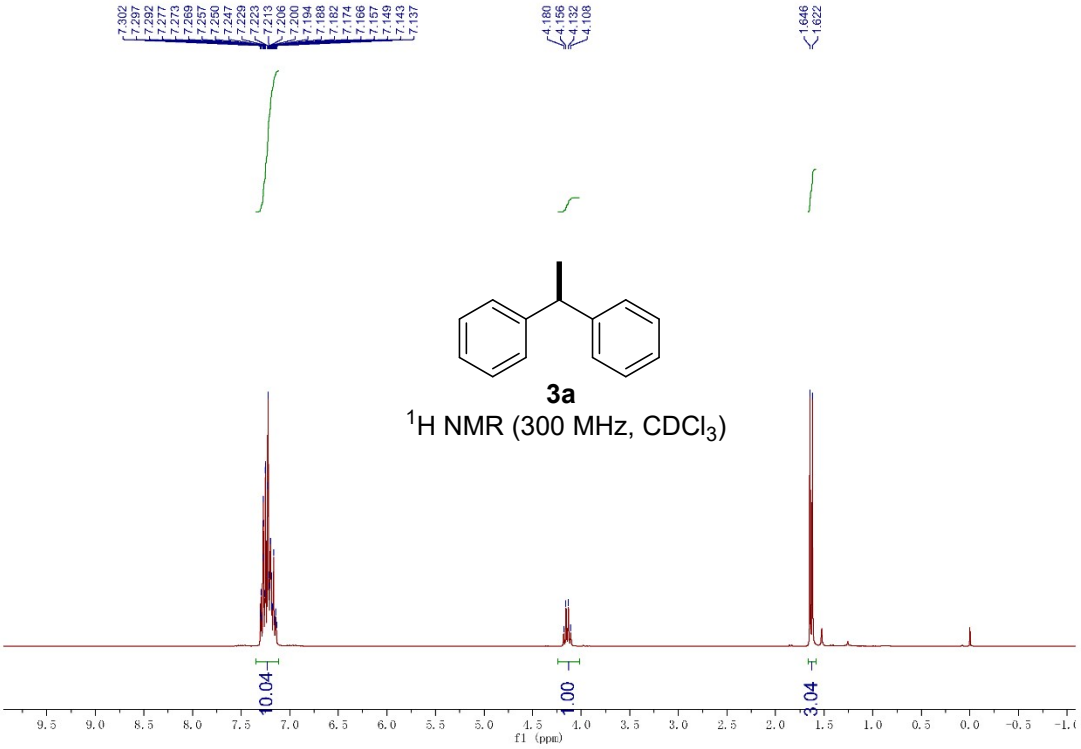
13. J. Xiao, Y. Ma, X. Wu, J. Gao, Z. Tang, L. B. Han, *RSC Adv.* **2019**, *9*, 22343.

14. W. Qiu, S. Shi, R. Li, X. Lin, L. Rao, Z. Sun, *Chin. J. Chem.* **2021**, *39*, 1255.

15. T. Yamada, K. Saito, T. Akiyama, *Adv. Synth. Catal.* **2016**, *358*, 62.

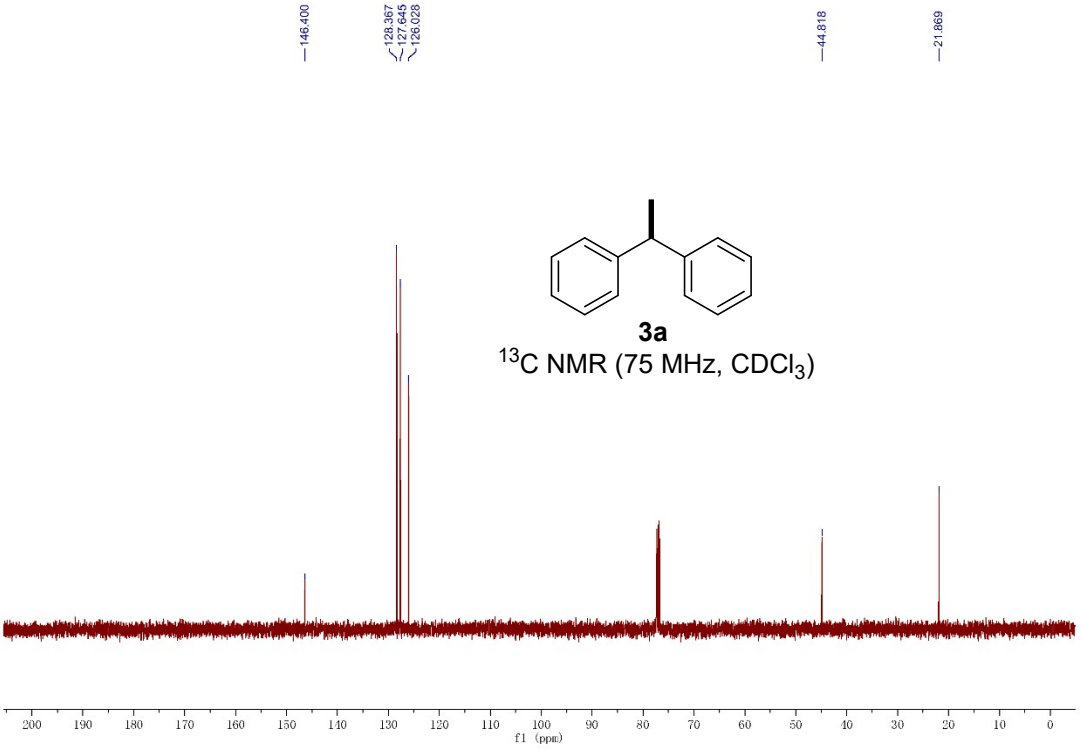
16. Q. H. Luu, J. Li, *Chem. Sci.* **2022**, *13*, 1095.

Copies of ^{1}H NMR, ^{13}C NMR spectra



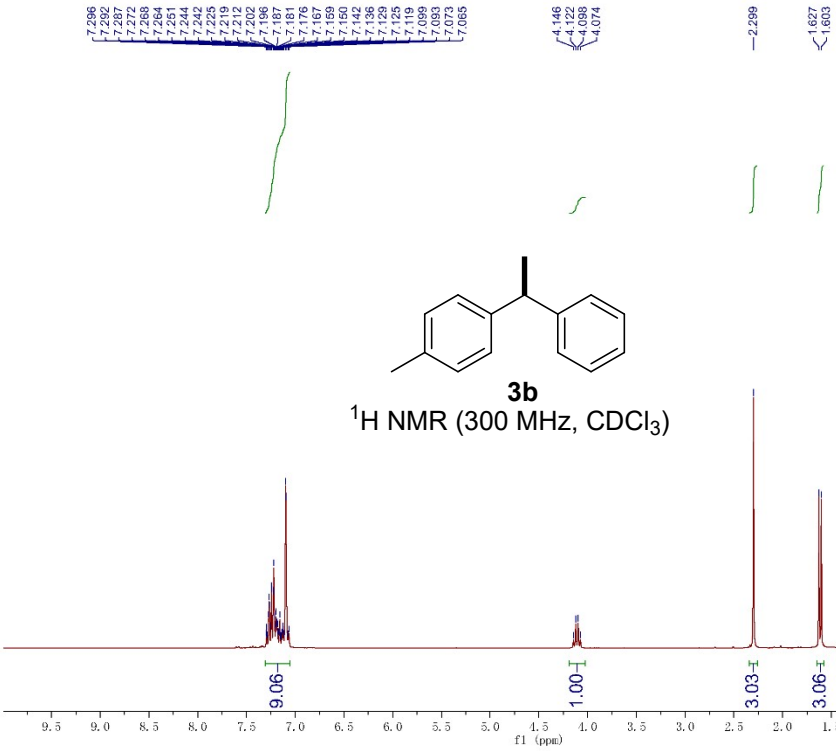
3a

^{1}H NMR (300 MHz, $CDCl_3$)



3a

^{13}C NMR (75 MHz, $CDCl_3$)



3b

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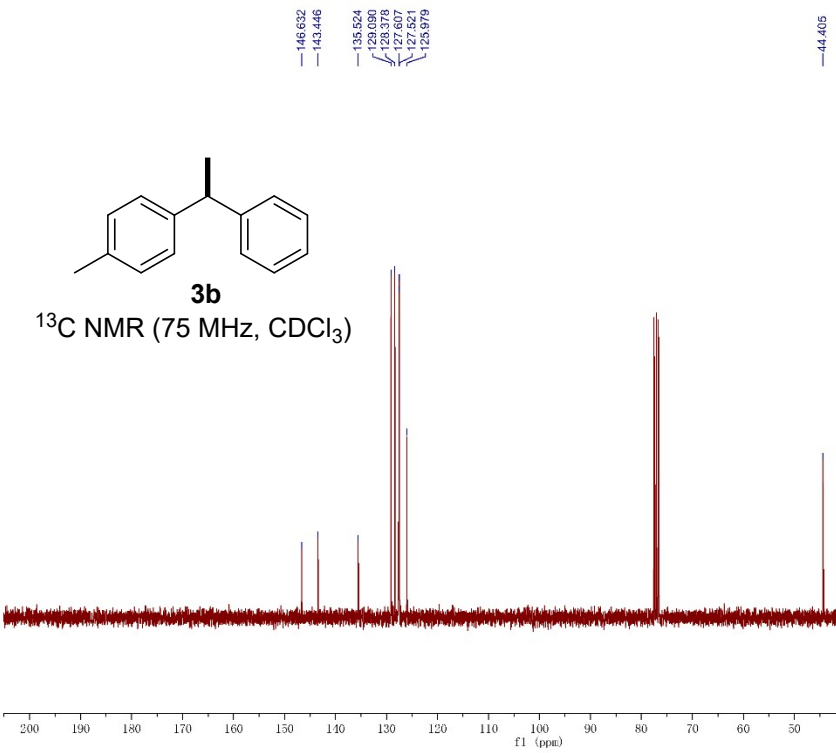
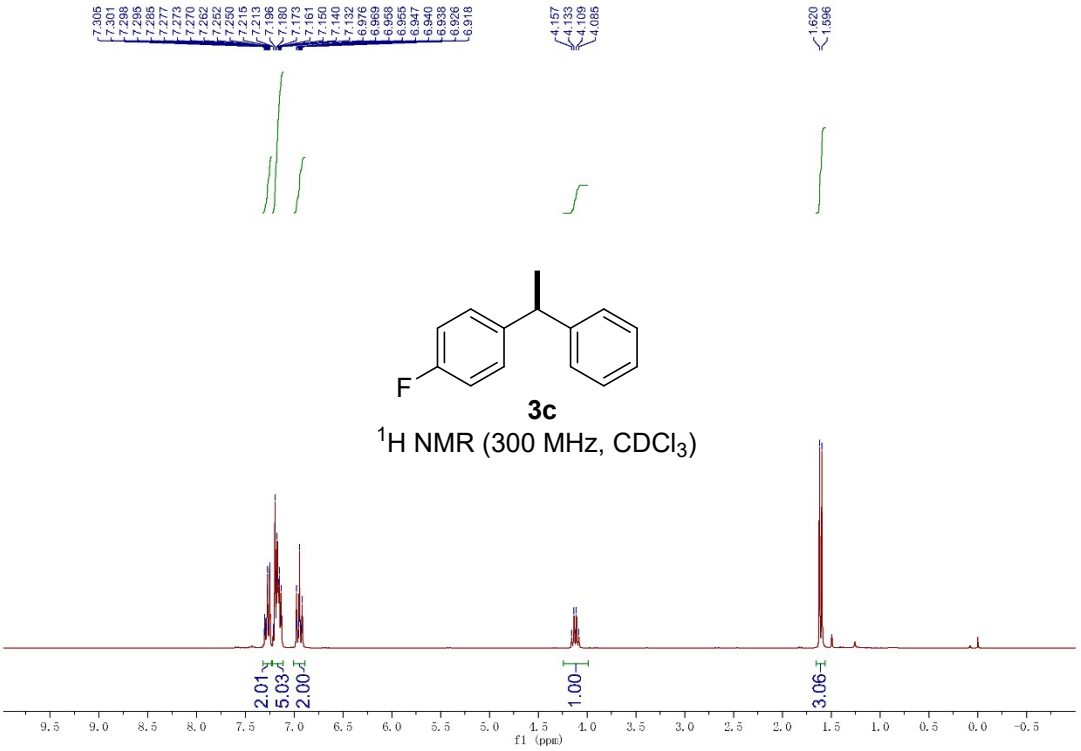
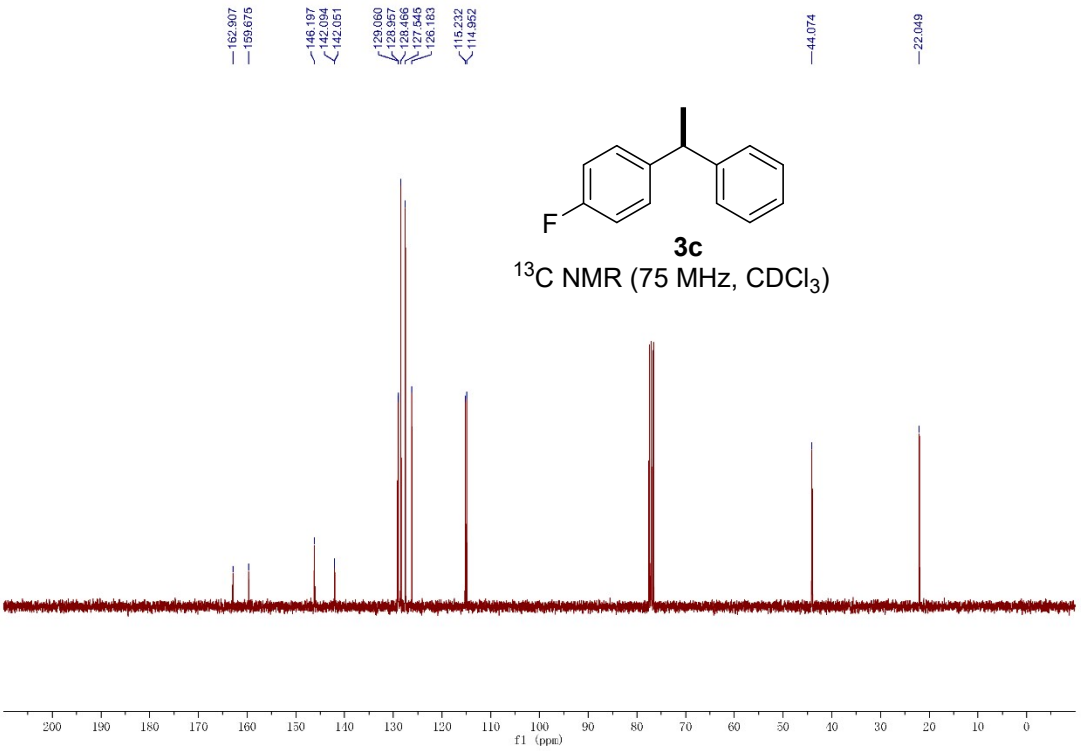
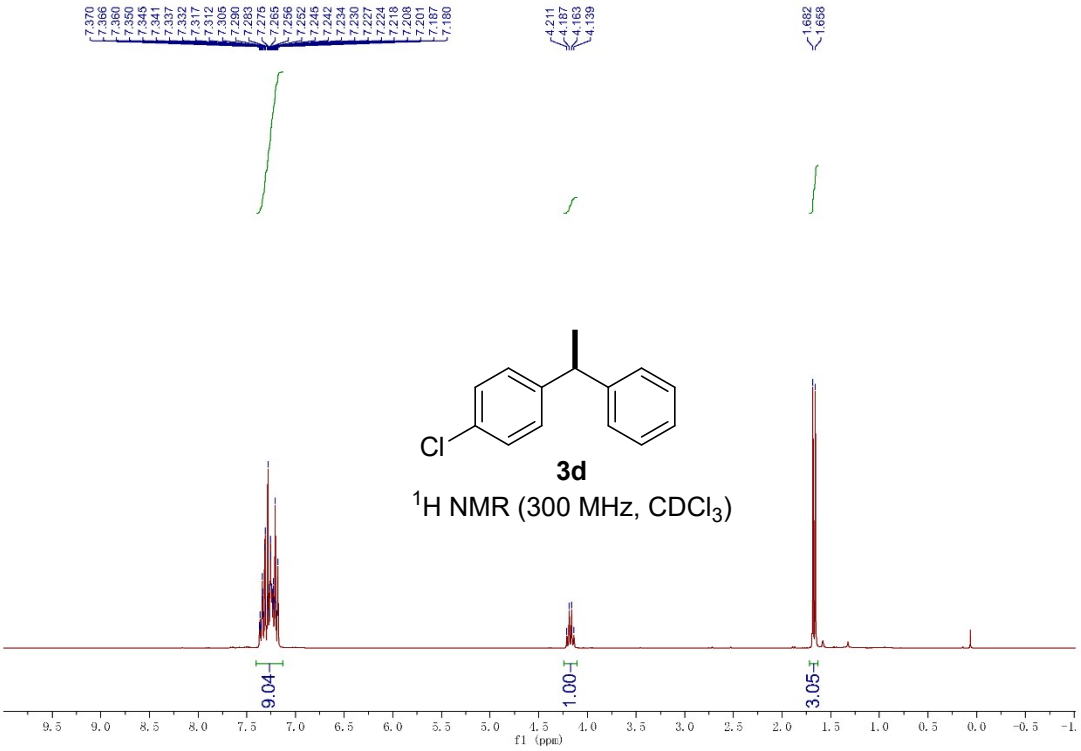


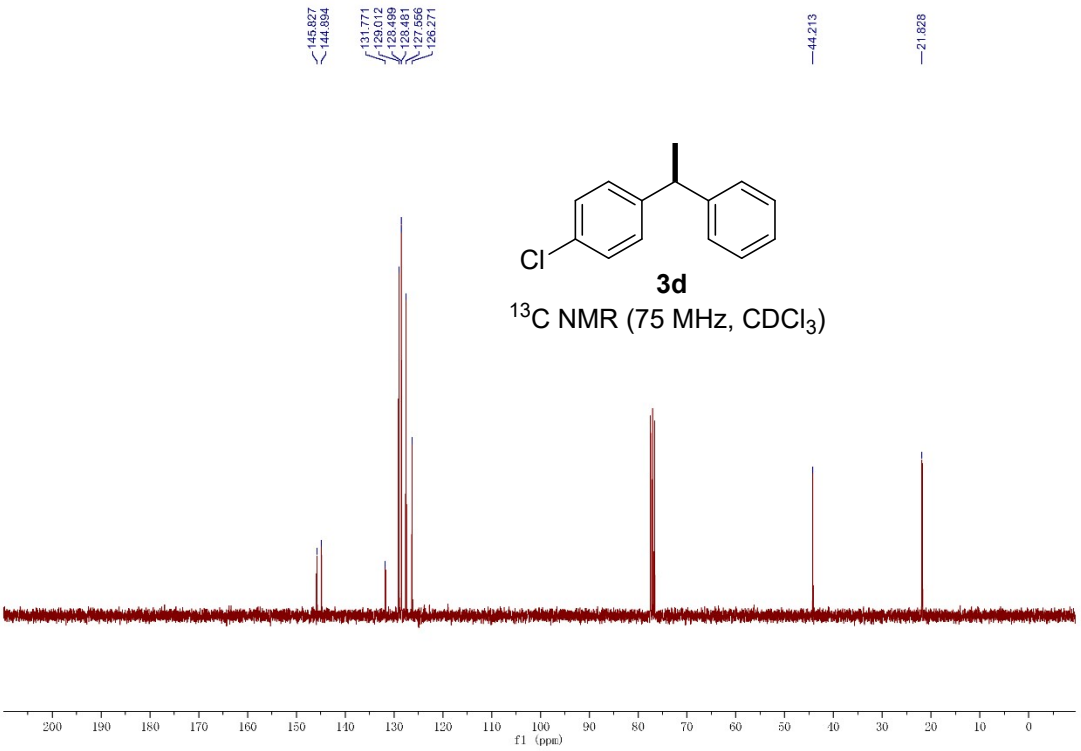
3b

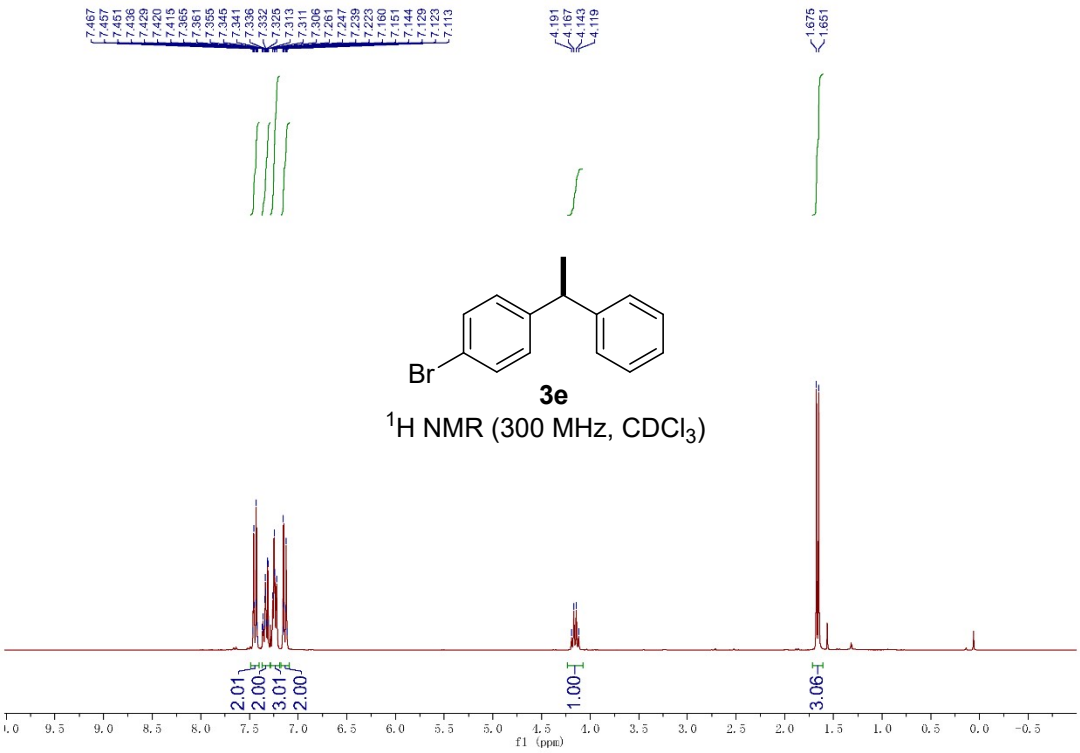
^{13}C NMR (75 MHz, $CDCl_3$)


7.305
7.301
7.298
7.295
7.285
7.277
7.273
7.270
7.262
7.252
7.250
7.215
7.213
7.196
7.180
7.173
7.161
7.150
7.140
7.132
6.976
6.969
6.958
6.955
6.947
6.940
6.938
6.926
6.918
4.157
4.133
4.109
4.085
1.620
1.596
F
3c
1H NMR (300 MHz, CDCl3)
2.01
5.03
2.00
1.00
3.06
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


162.907
159.675
146.197
142.094
142.051
129.060
128.957
128.466
127.545
127.454
126.163
115.232
114.952
44.074
22.049
F
3c
13C NMR (75 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

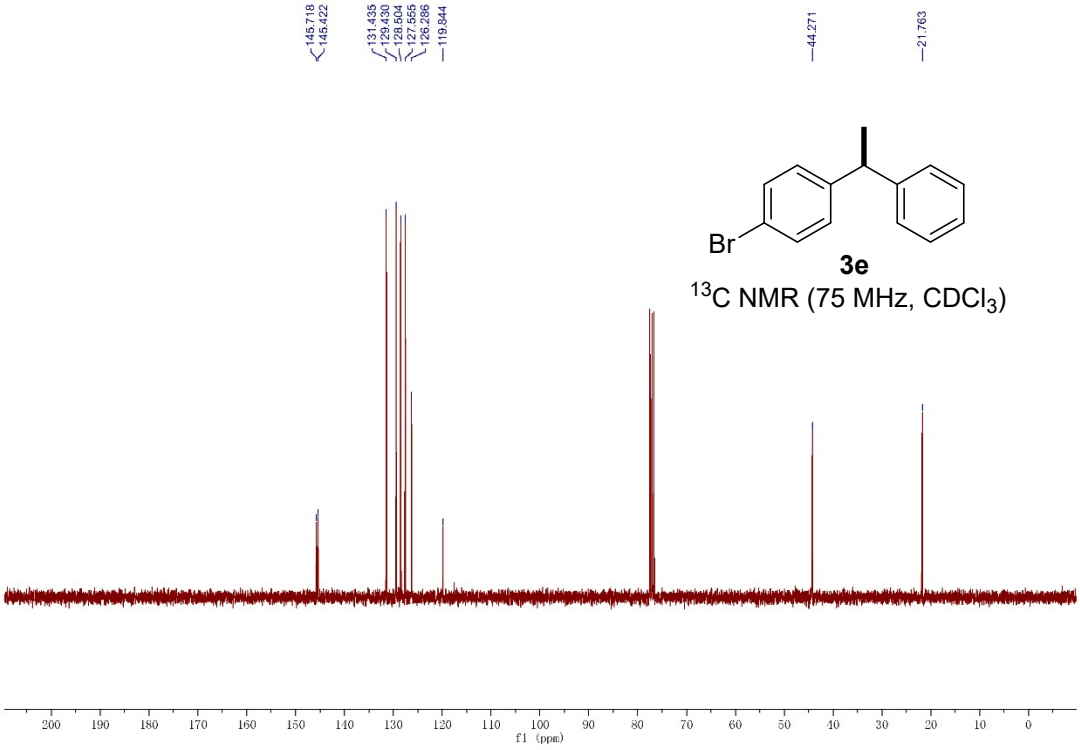

7.370
7.366
7.360
7.350
7.345
7.341
7.337
7.332
7.317
7.312
7.305
7.293
7.283
7.275
7.265
7.256
7.252
7.245
7.242
7.234
7.230
7.227
7.224
7.218
7.208
7.201
7.187
7.180
4.211
4.187
4.163
4.139
1.682
1.658
Cl
3d
1H NMR (300 MHz, CDCl3)
9.04
1.00
3.05
f1 (ppm)


145.827
144.894
131.771
129.012
128.499
128.481
127.566
126.271
44.213
21.828
Cl
3d
13C NMR (75 MHz, CDCl3)
f1 (ppm)



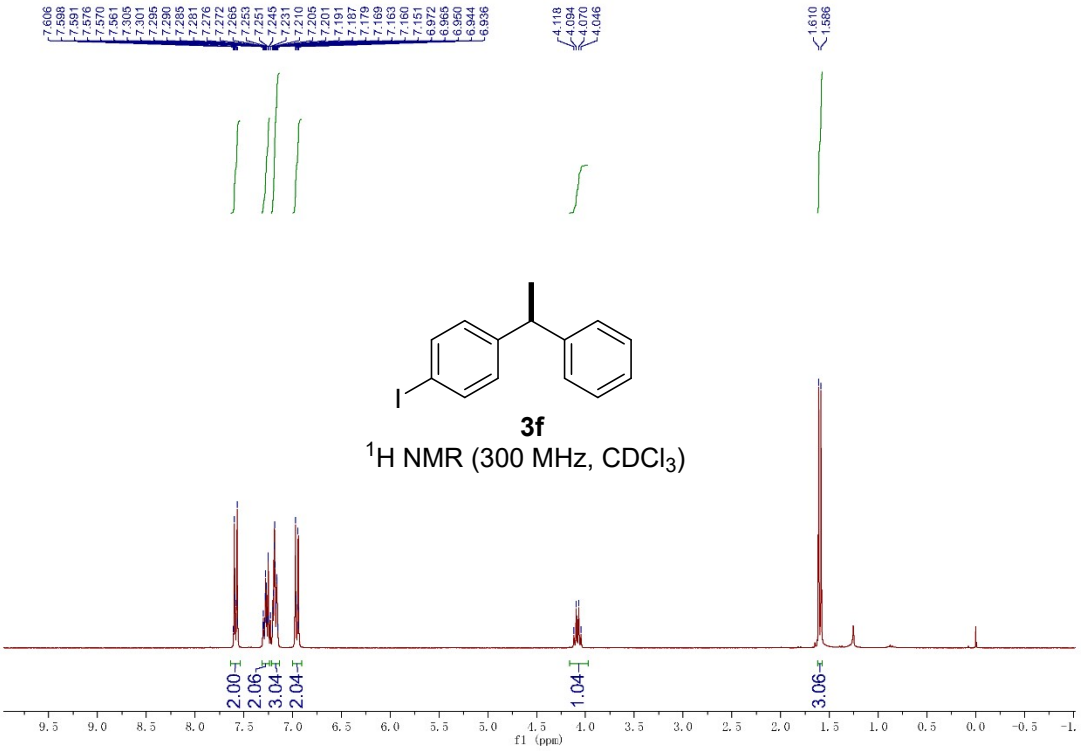
3e

^{1}H NMR (300 MHz, $CDCl_3$)



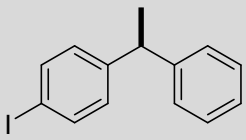
3e

^{13}C NMR (75 MHz, $CDCl_3$)



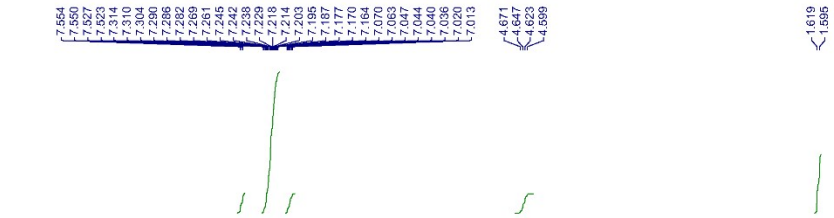
3f

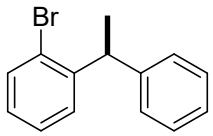
^{1}H NMR (300 MHz, $CDCl_3$)



3f

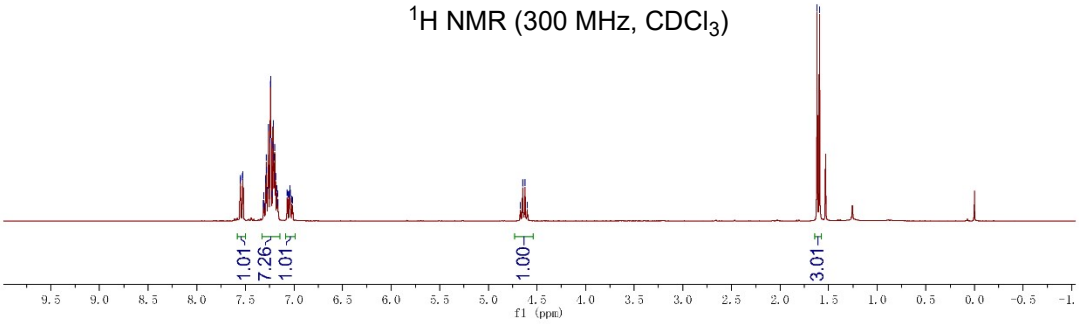
^{13}C NMR (75 MHz, $CDCl_3$)

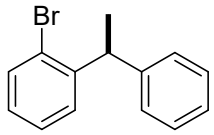




3g

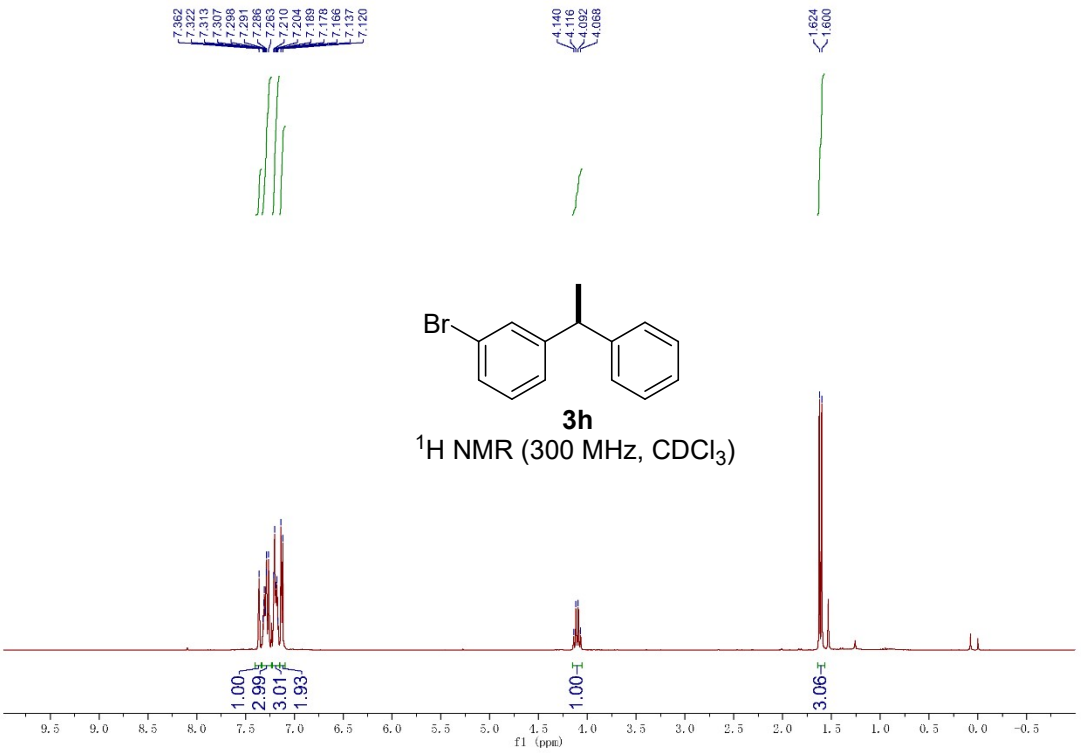
^{1}H NMR (300 MHz, $CDCl_3$)





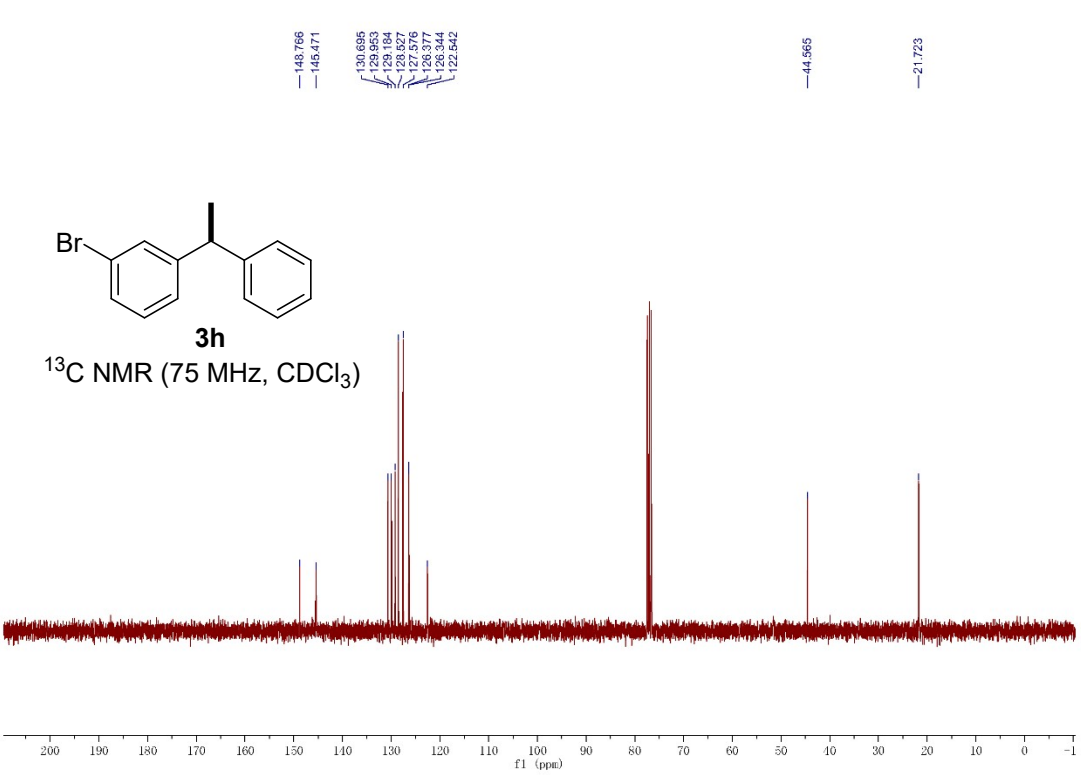
3g

^{13}C NMR (75 MHz, $CDCl_3$)



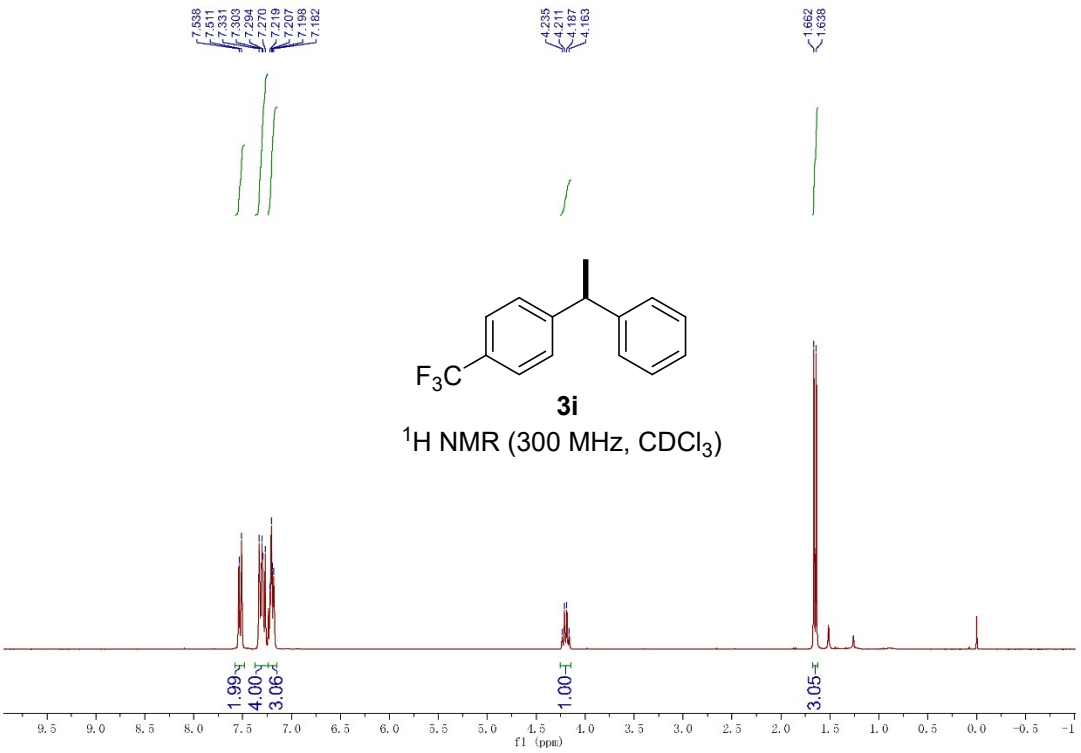
3h

^{1}H NMR (300 MHz, $CDCl_3$)



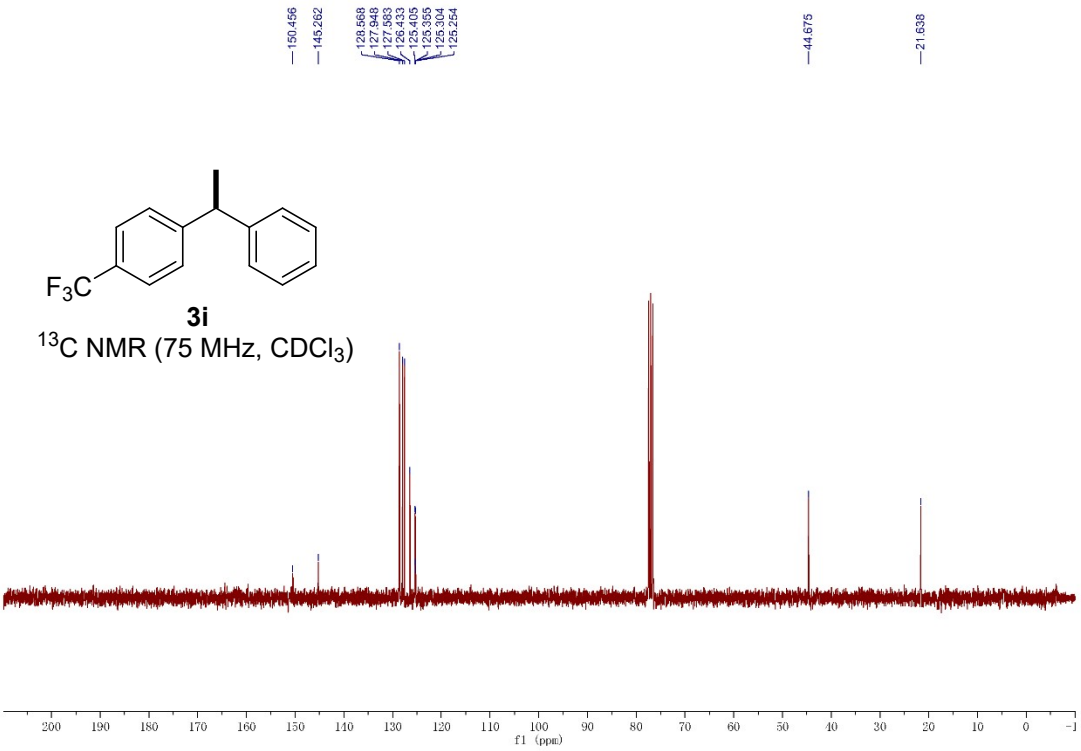
3h

^{13}C NMR (75 MHz, $CDCl_3$)



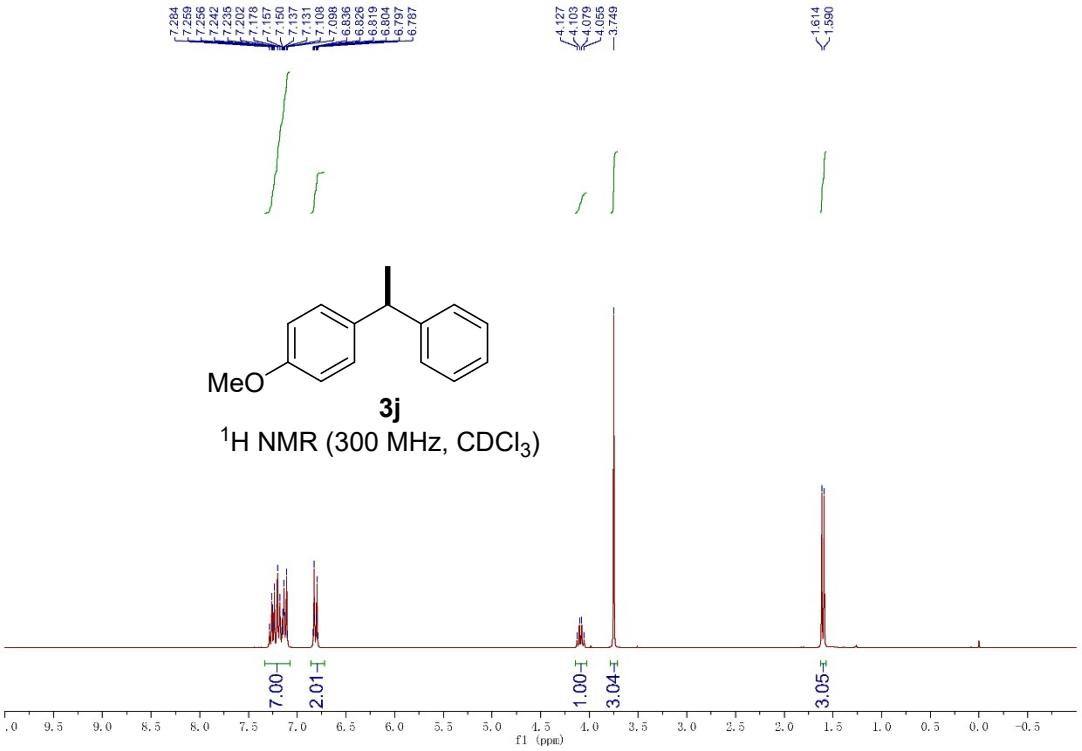
3i

^{1}H NMR (300 MHz, $CDCl_3$)



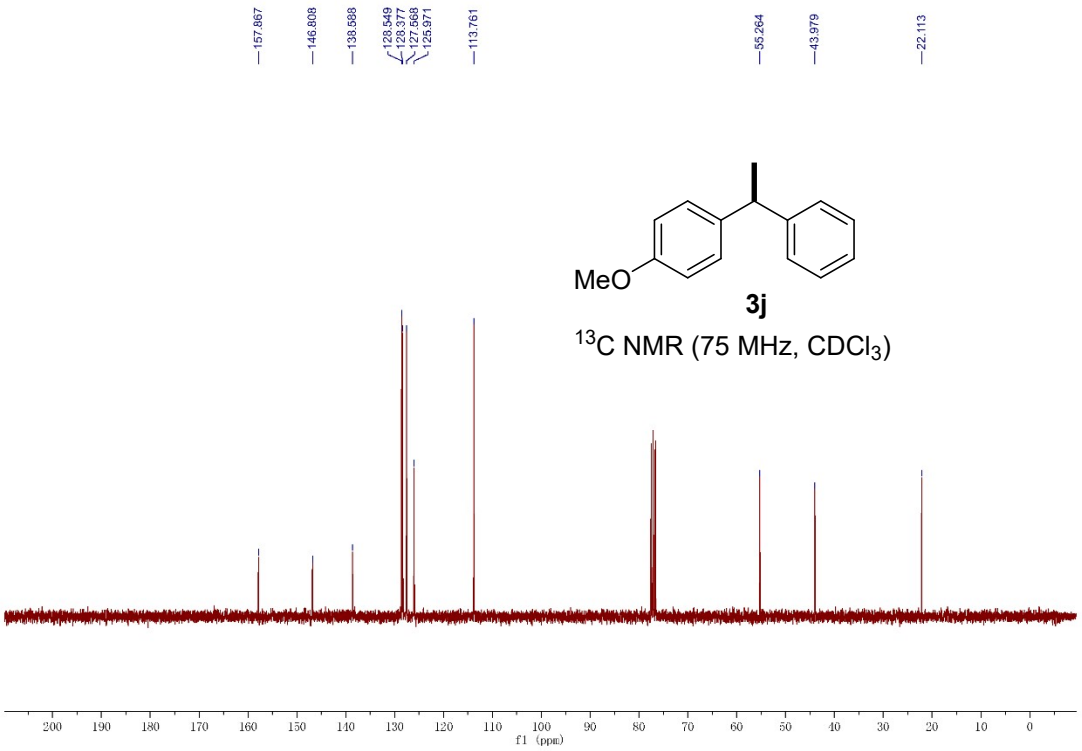
3i

^{13}C NMR (75 MHz, $CDCl_3$)



3j

^{1}H NMR (300 MHz, $CDCl_3$)



3j

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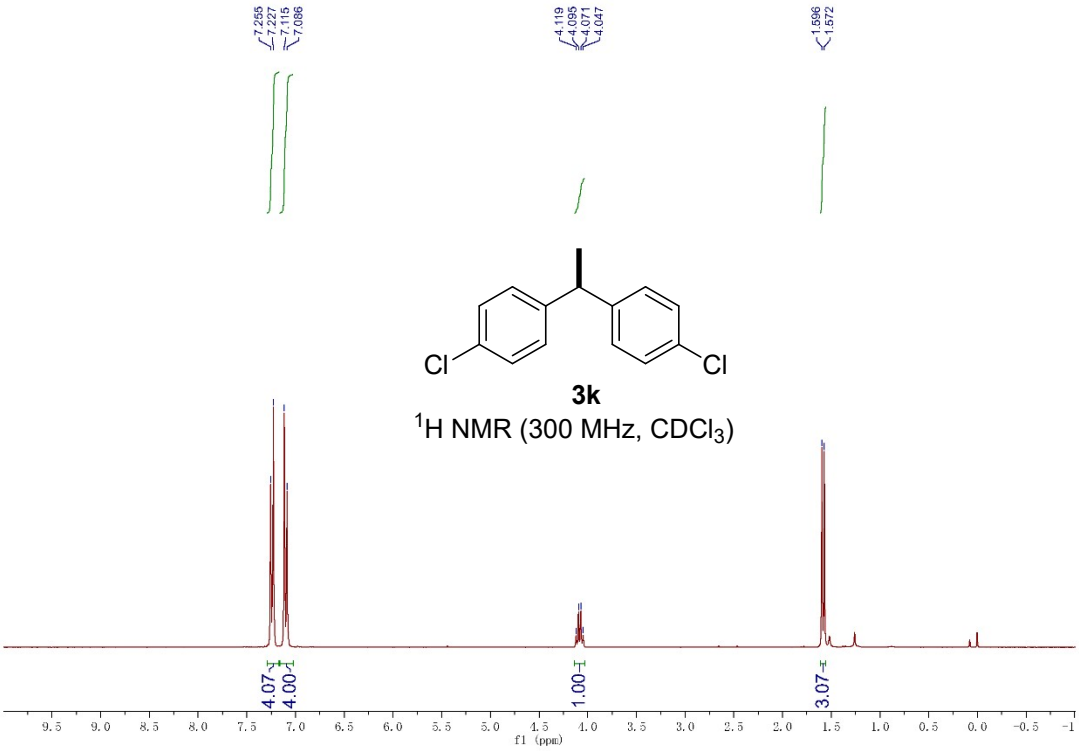

3k

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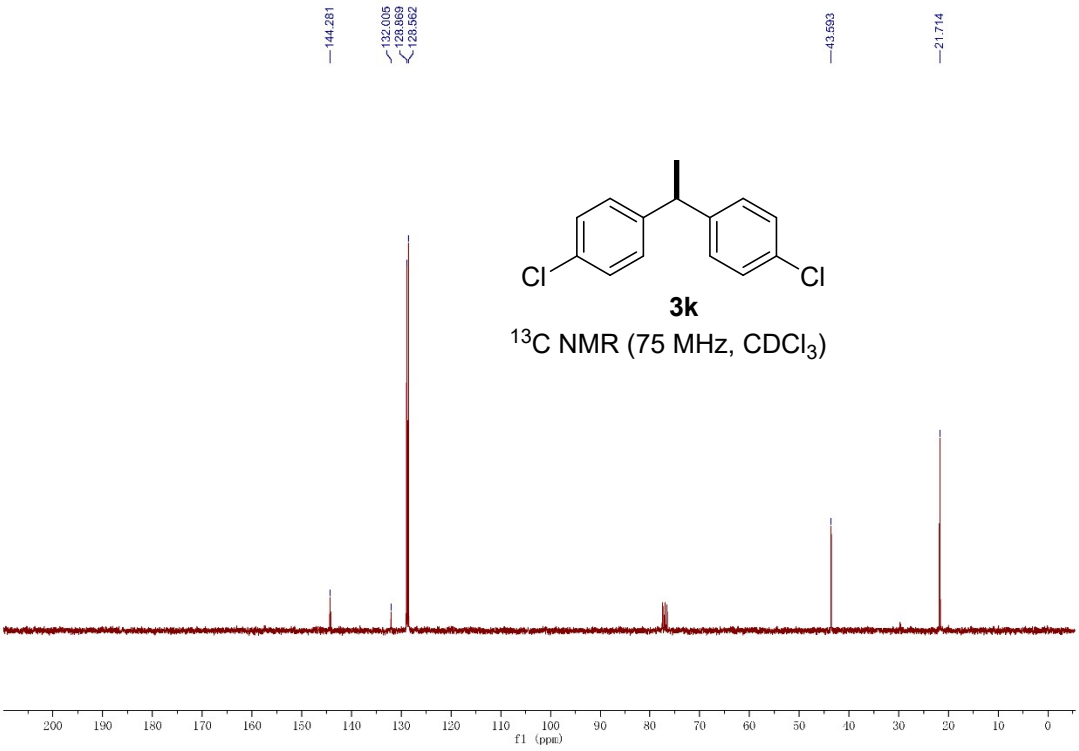

3k

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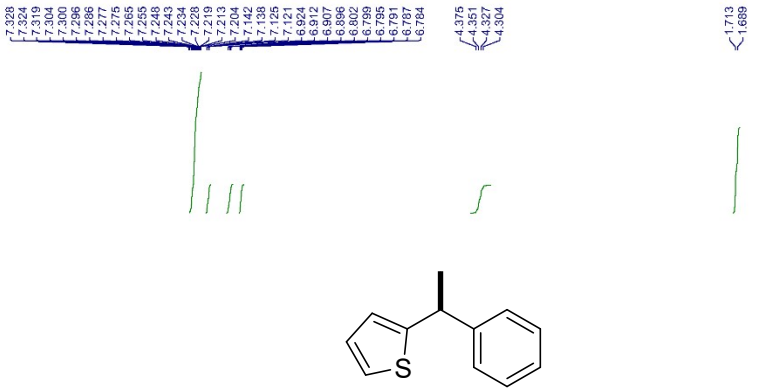

3l

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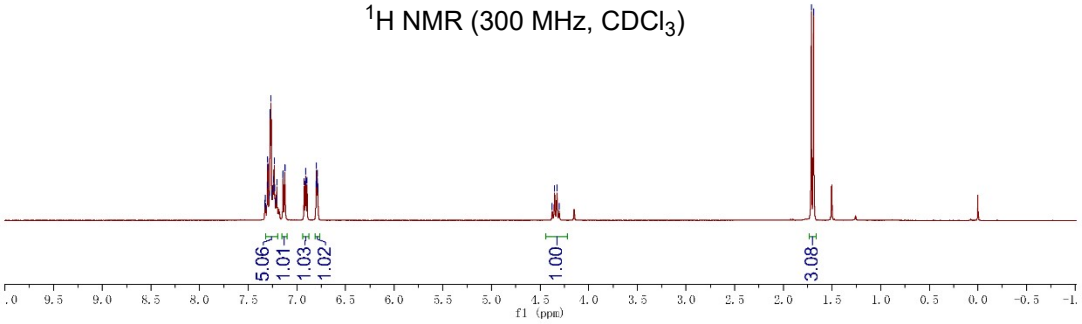
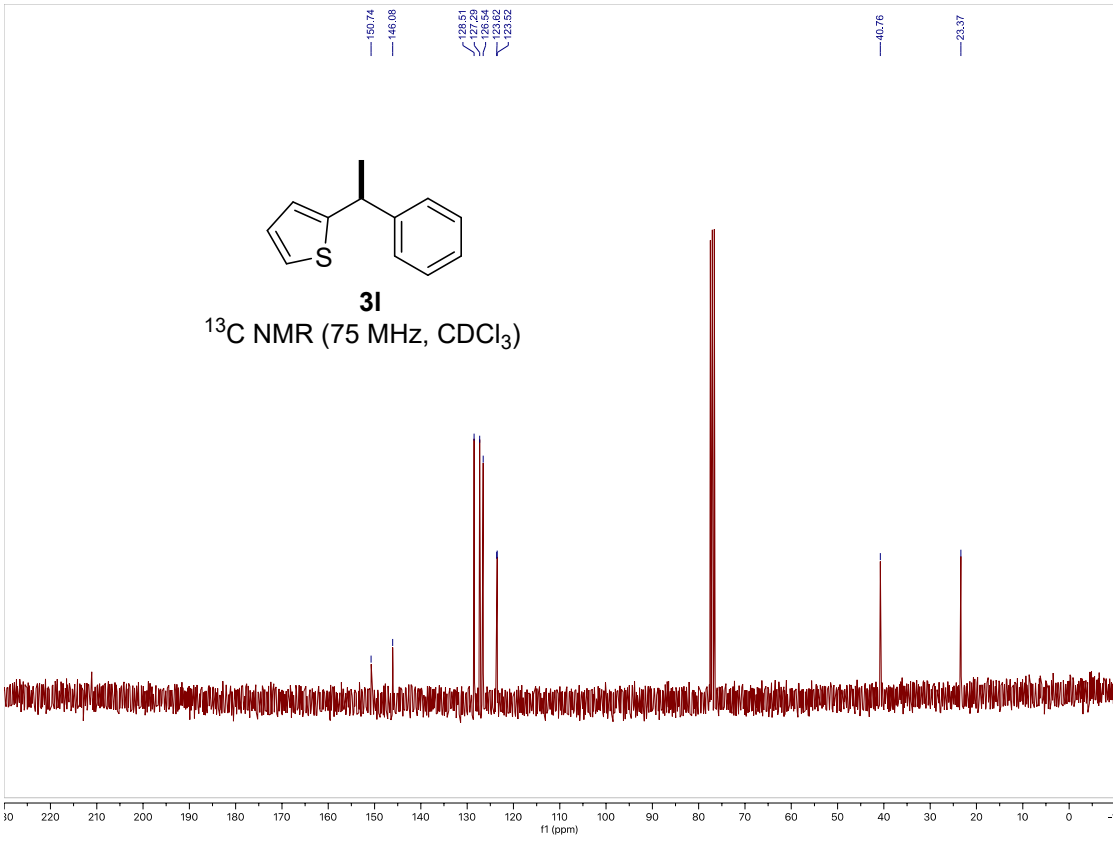
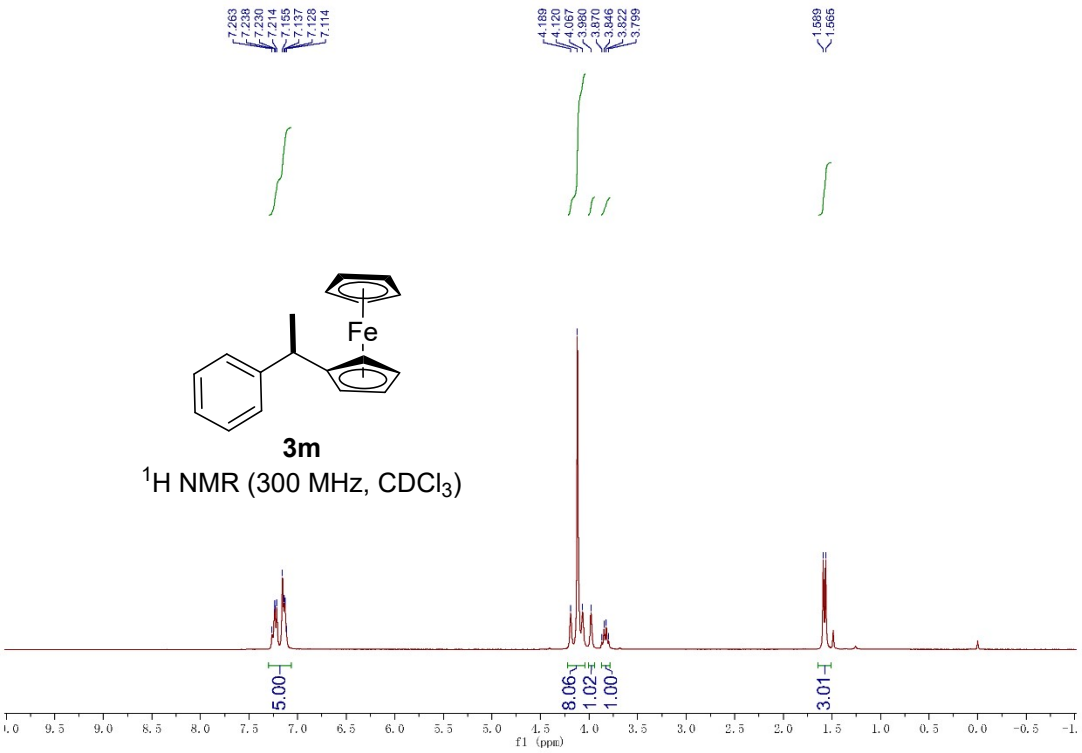




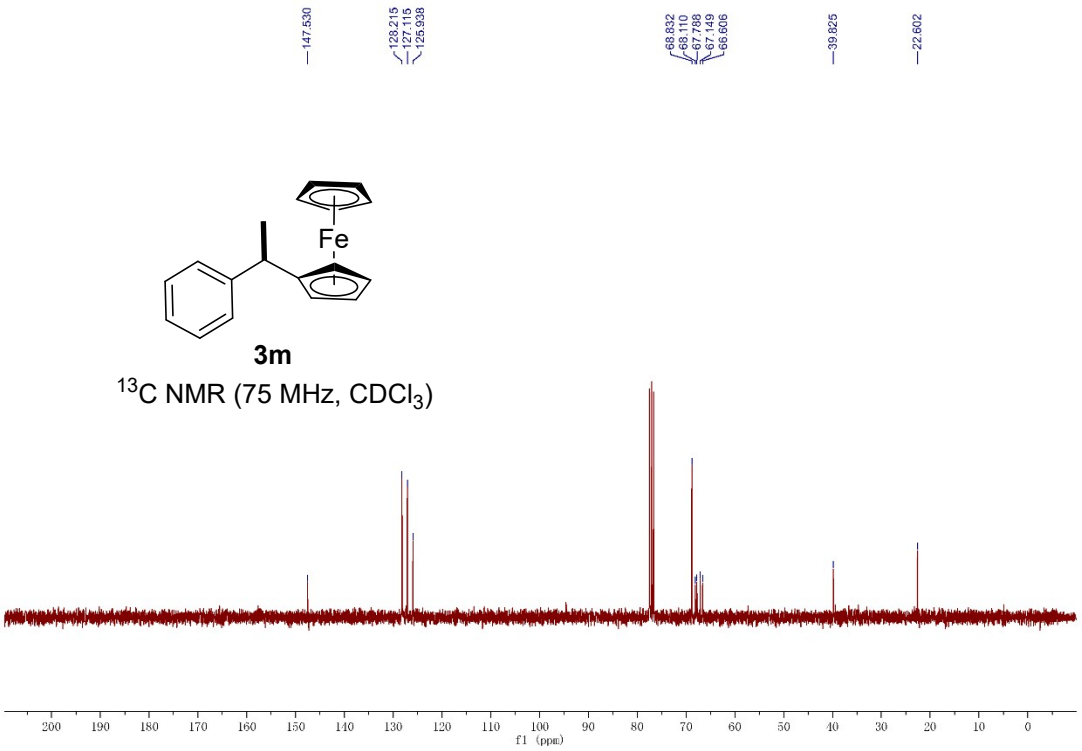
3l

^{13}C NMR (75 MHz, $CDCl_3$)



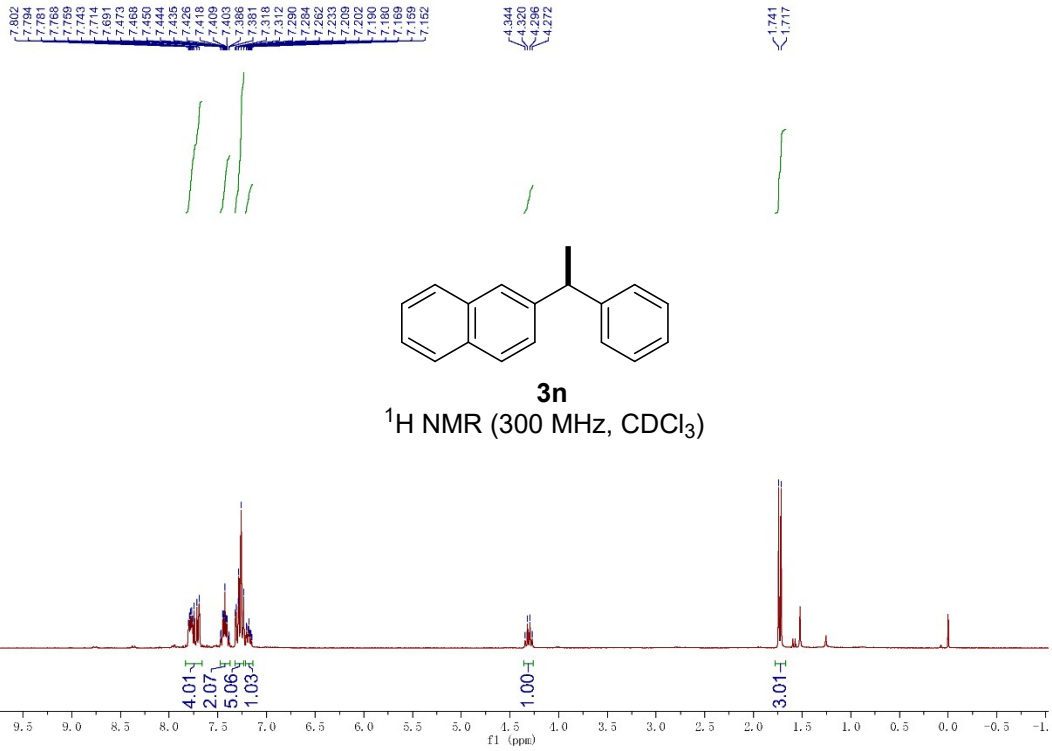
3m

^{1}H NMR (300 MHz, $CDCl_3$)



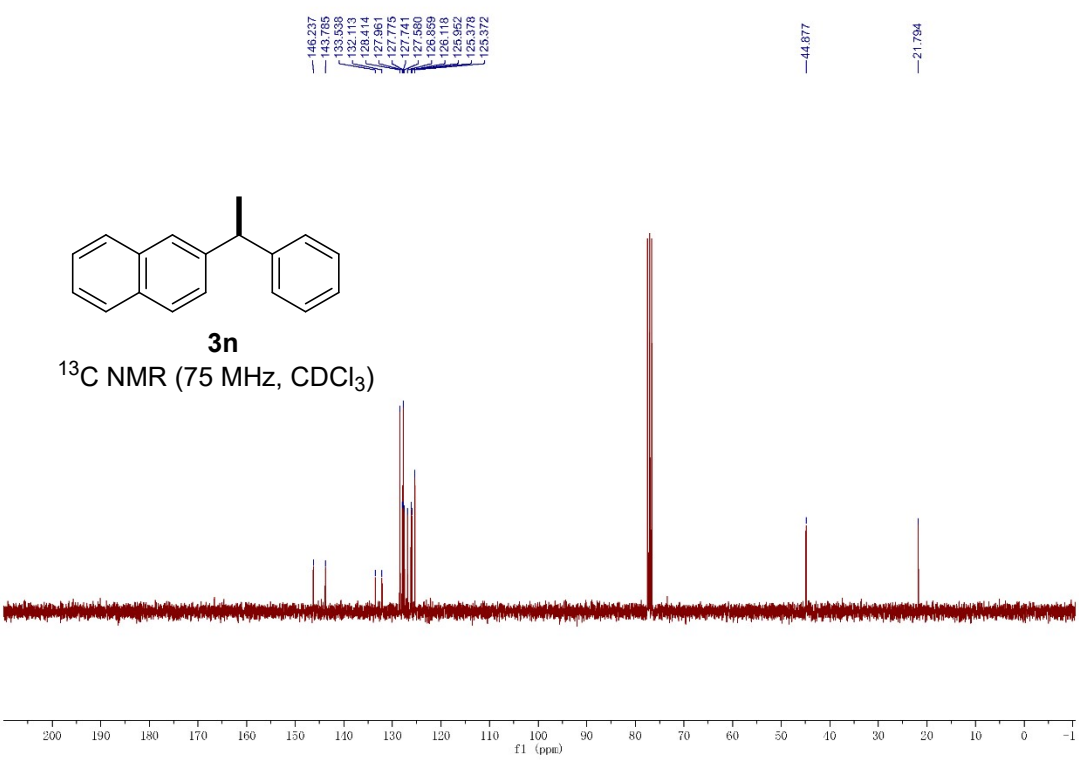
3m

^{13}C NMR (75 MHz, $CDCl_3$)



3n

^{1}H NMR (300 MHz, $CDCl_3$)



3n

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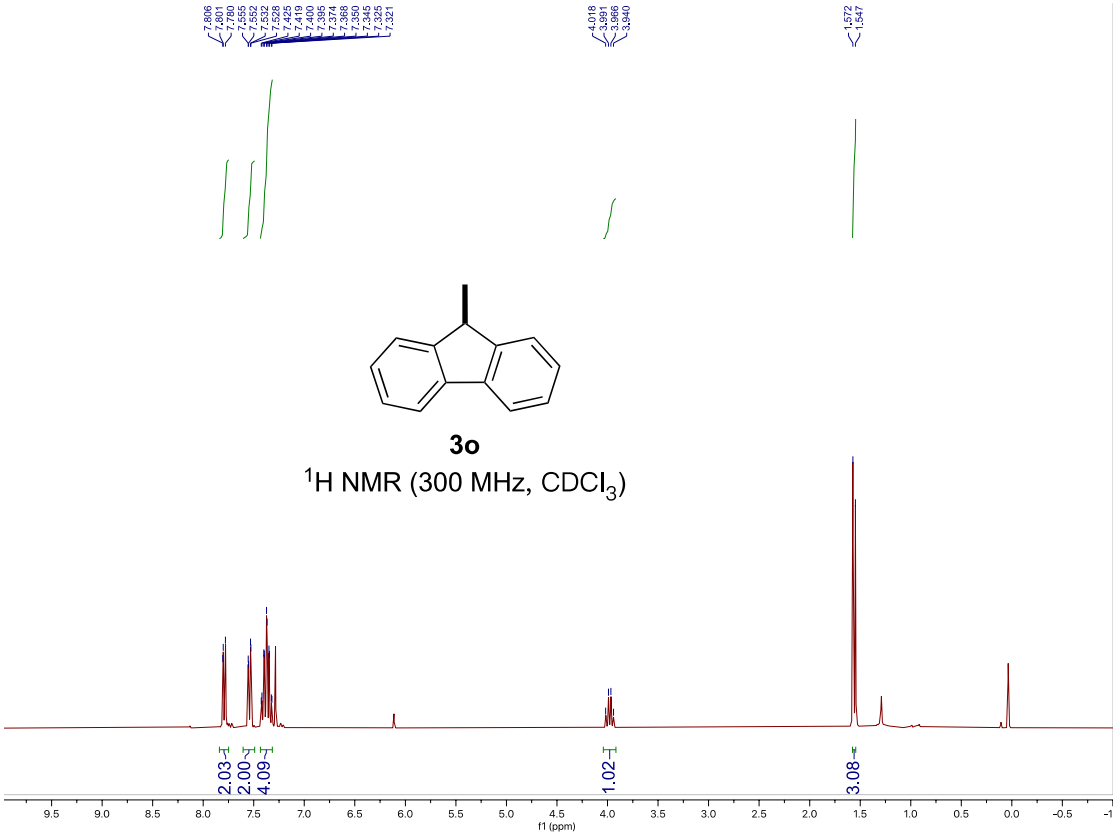

3o

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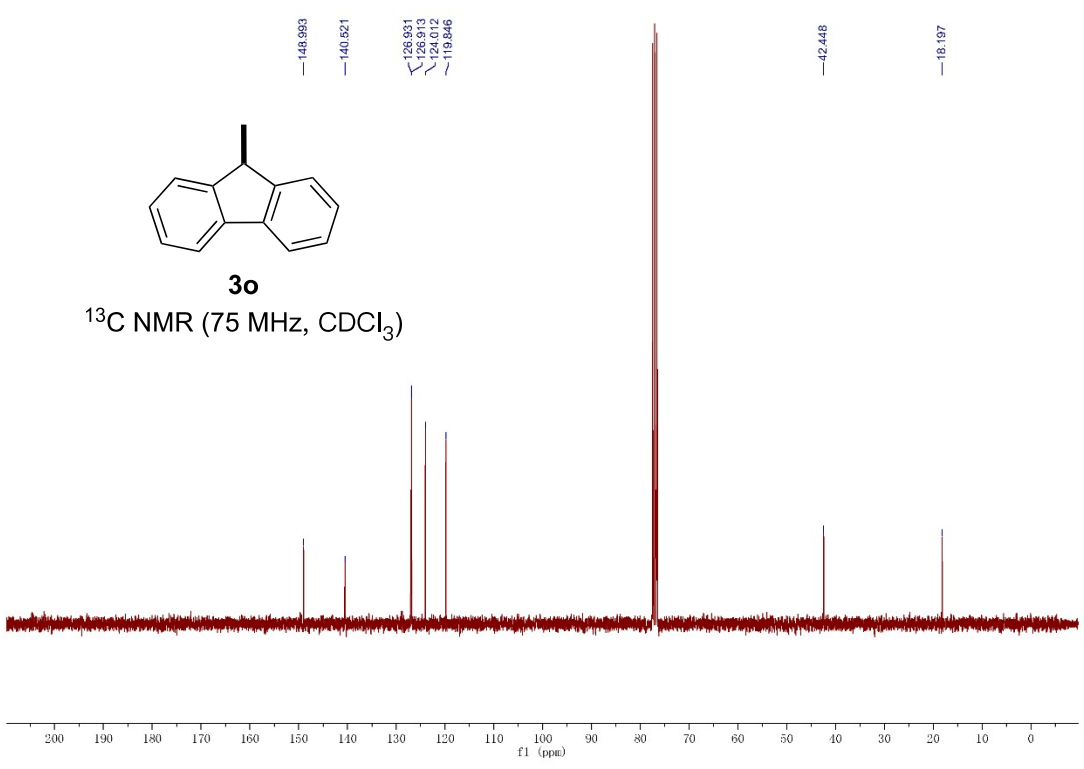

3o

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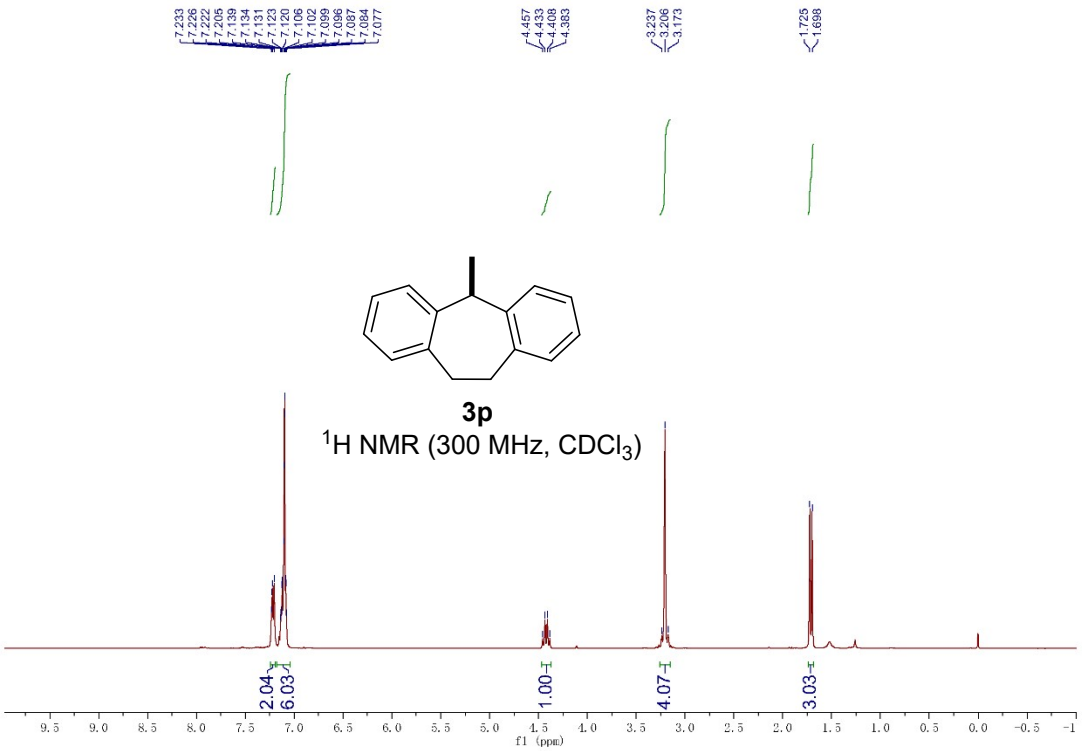
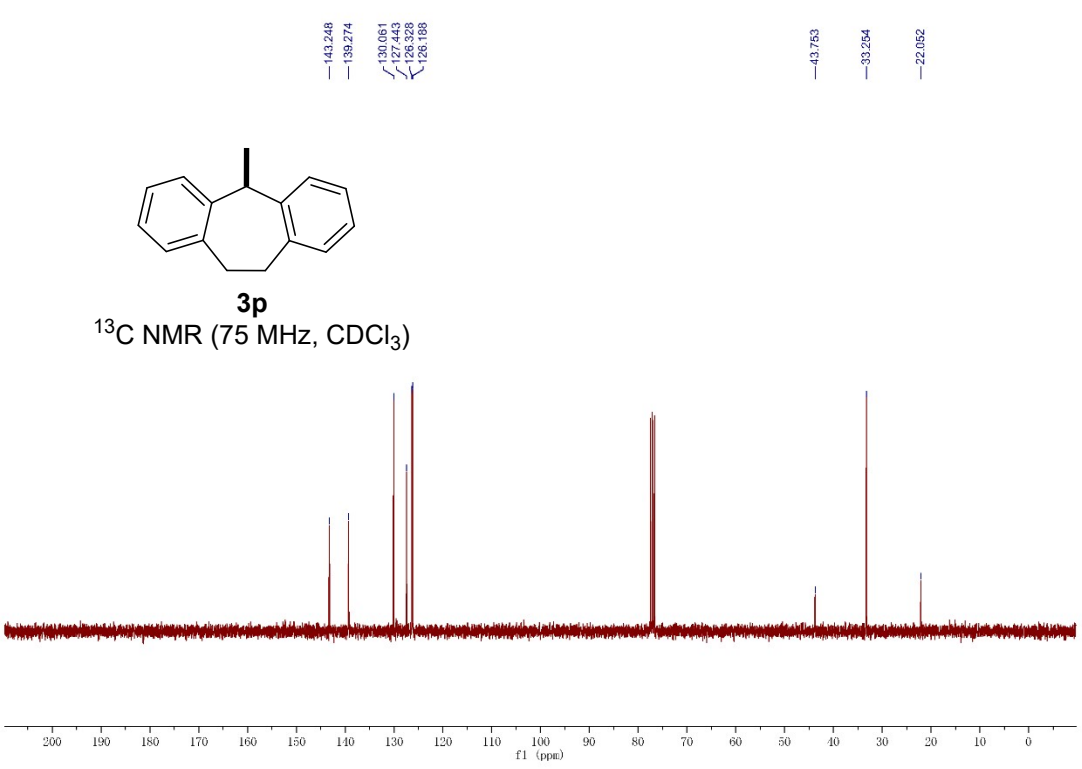


3p

^{1}H NMR (300 MHz, $CDCl_3$)



3p

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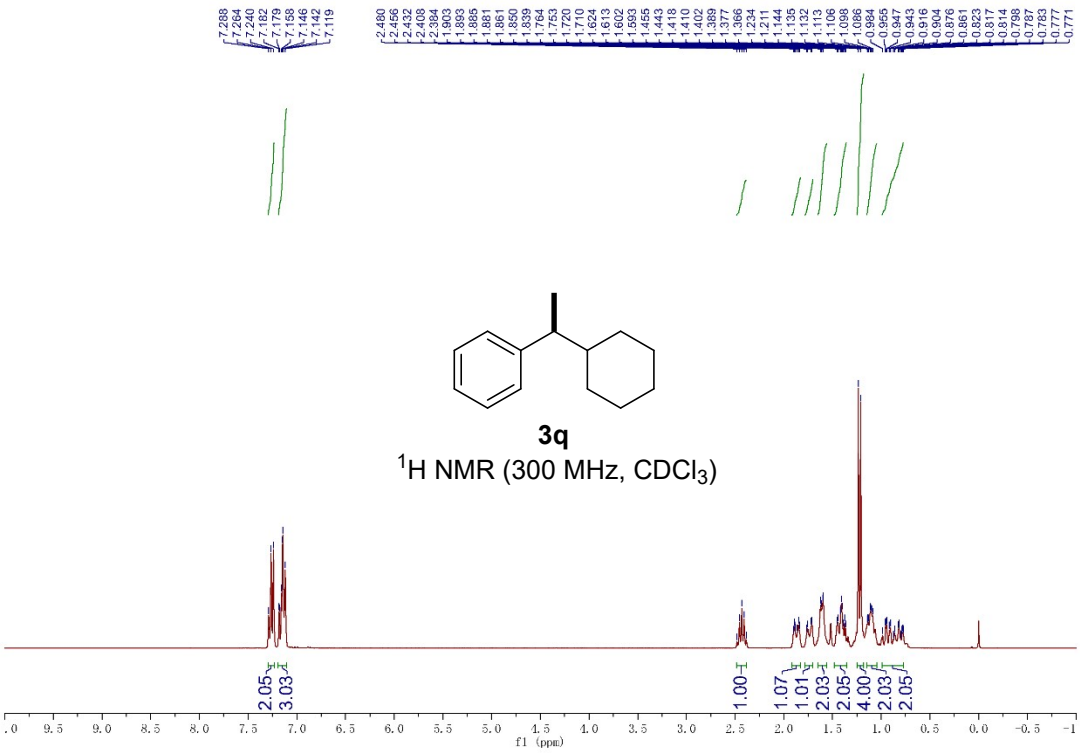
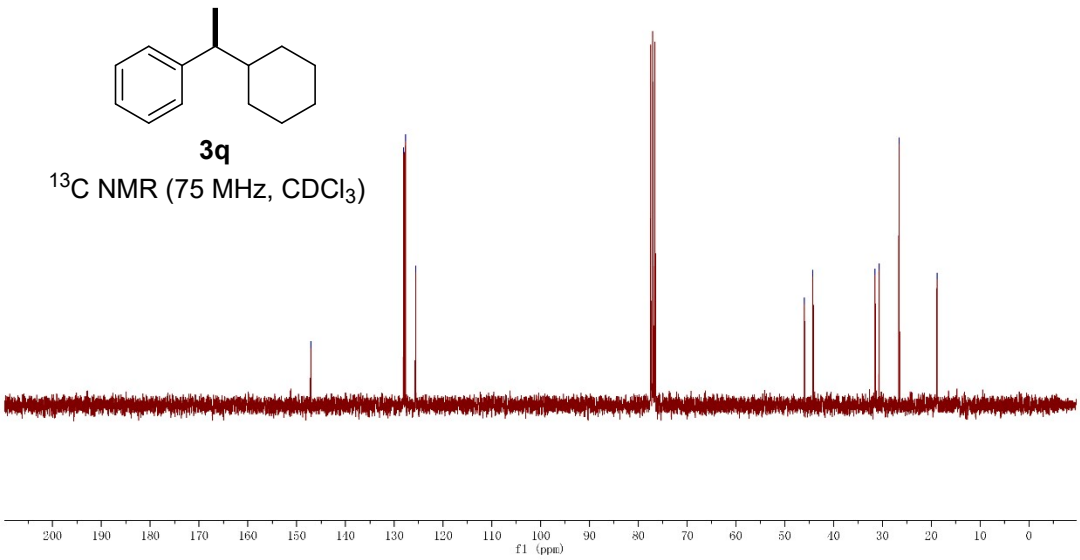


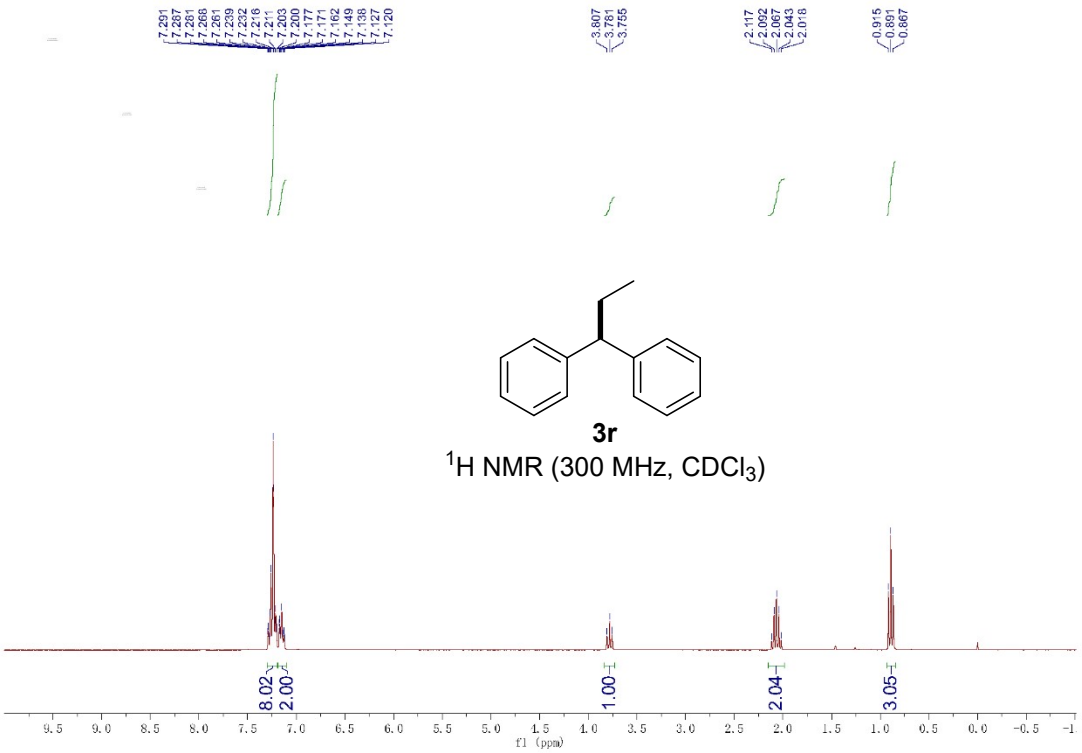
3q

^{1}H NMR (300 MHz, $CDCl_3$)



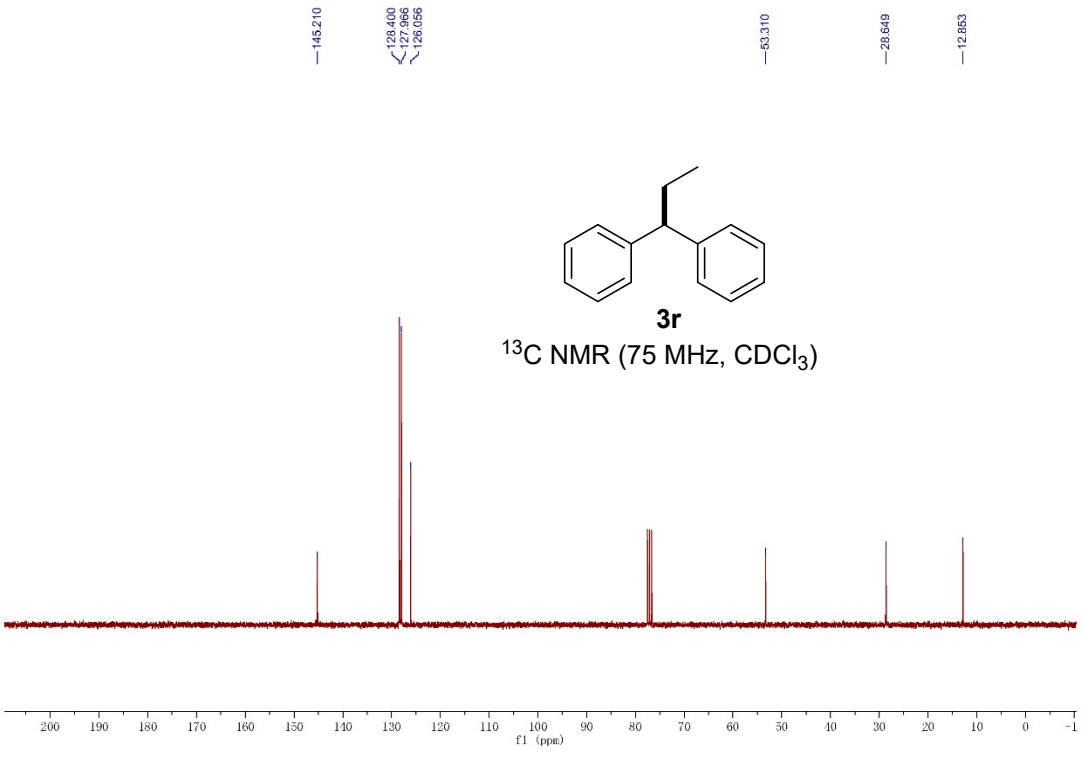
3q

^{13}C NMR (75 MHz, $CDCl_3$)



3r

^{1}H NMR (300 MHz, $CDCl_3$)



3r

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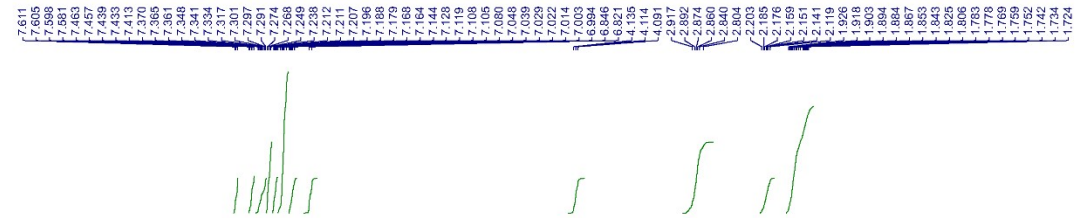

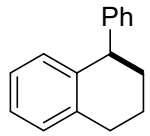

3s

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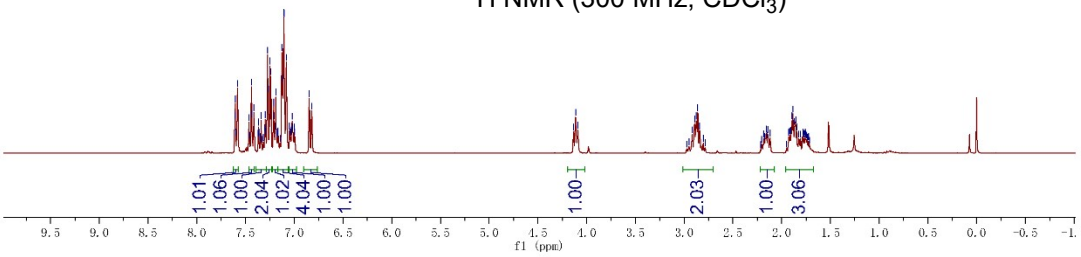

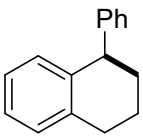

3s

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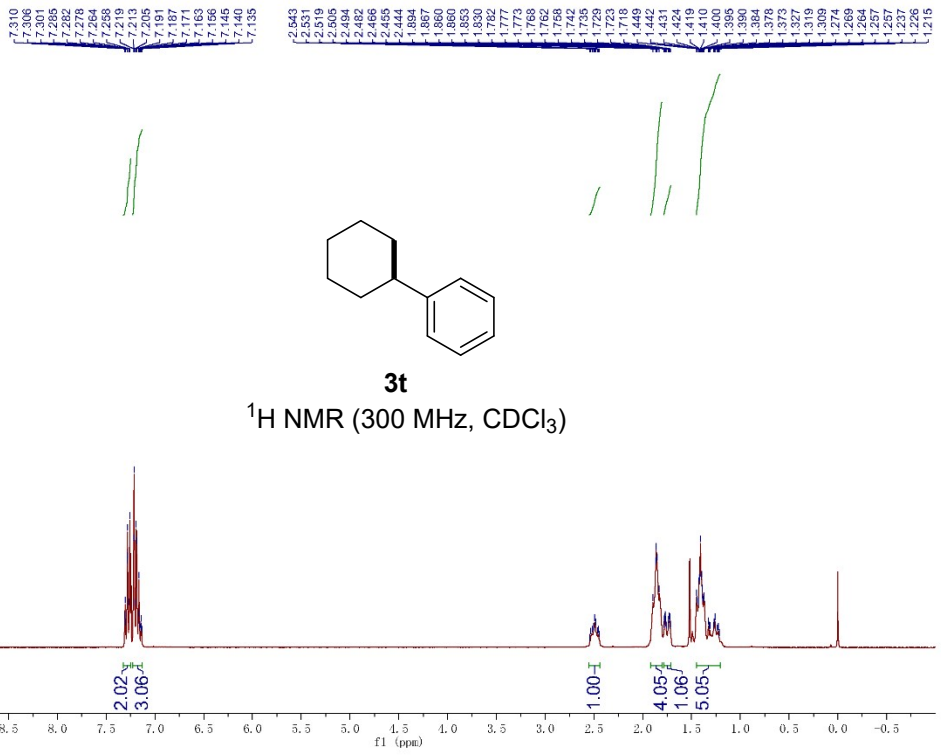
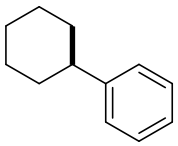


3t

^{1}H NMR (300 MHz, $CDCl_3$)



3t

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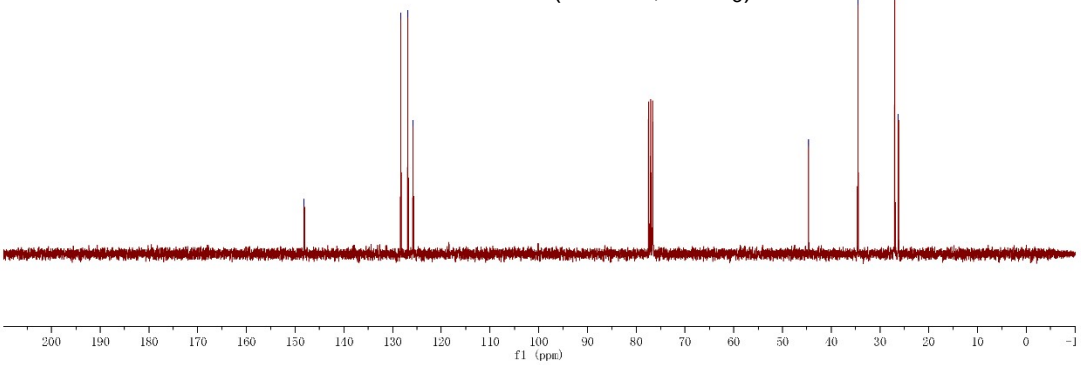

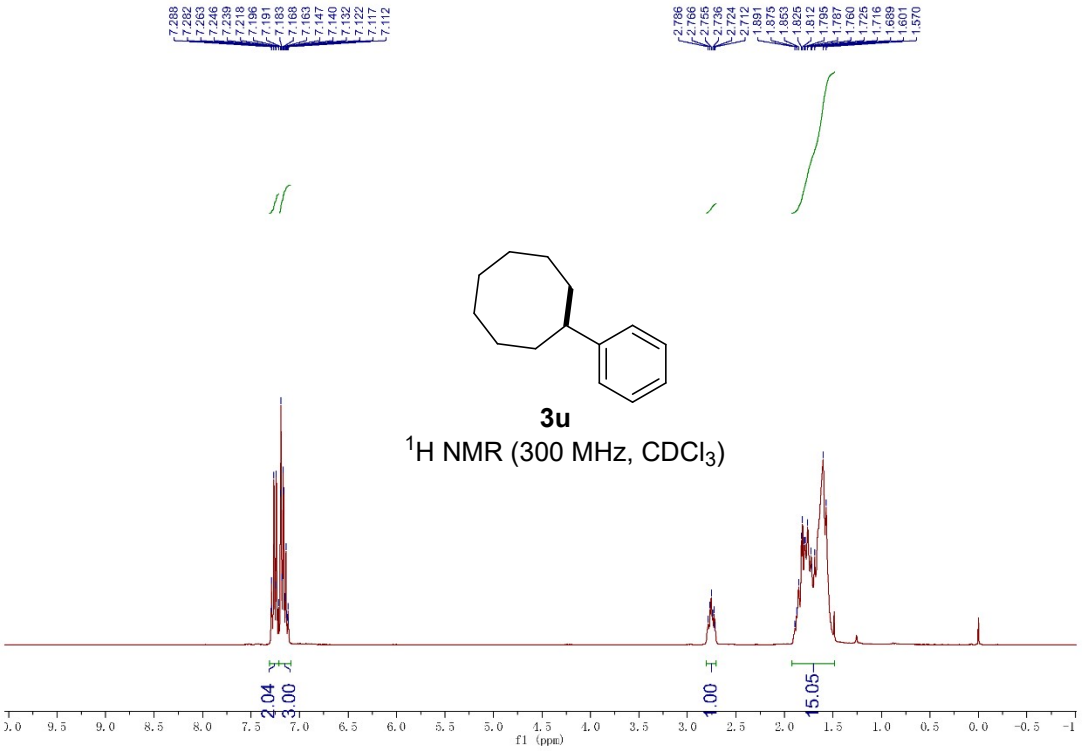

3u

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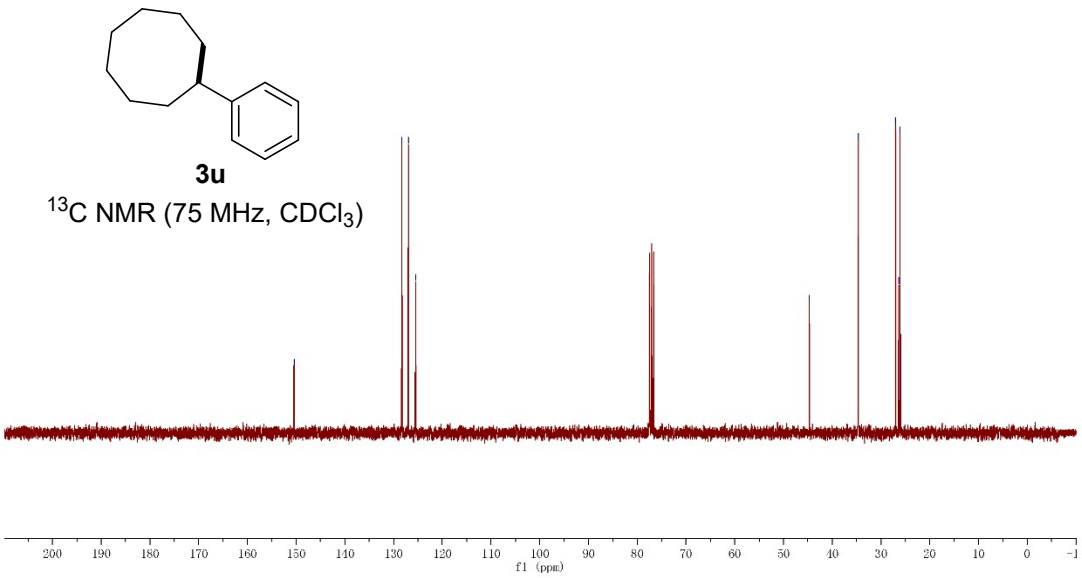
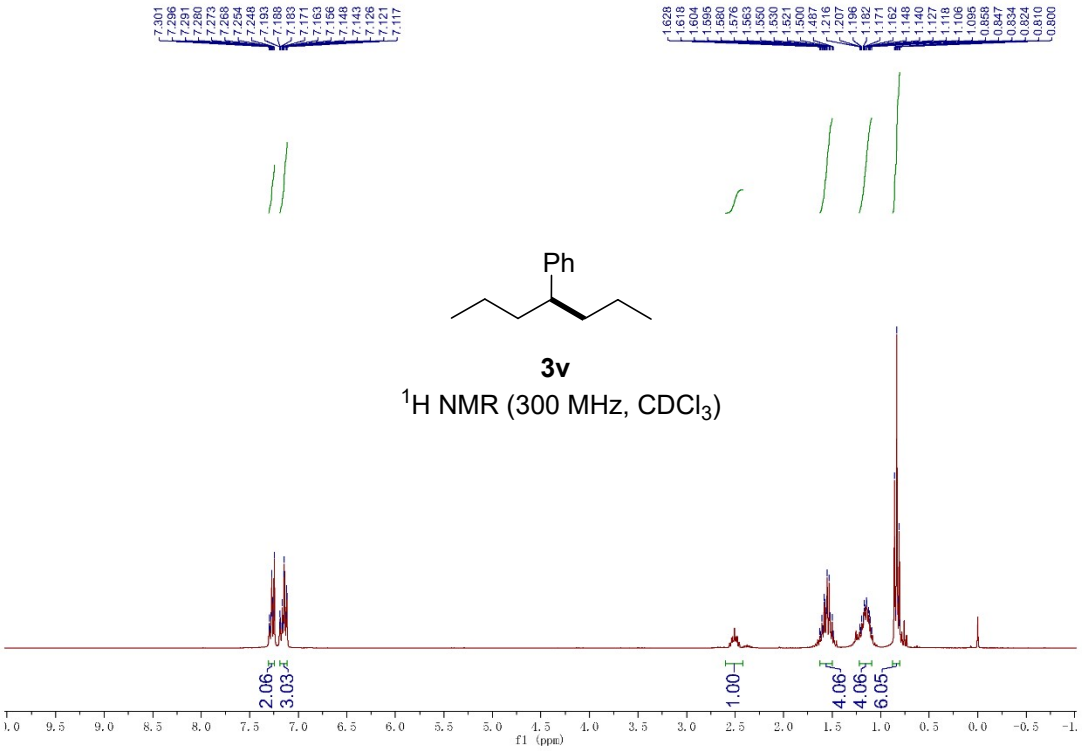


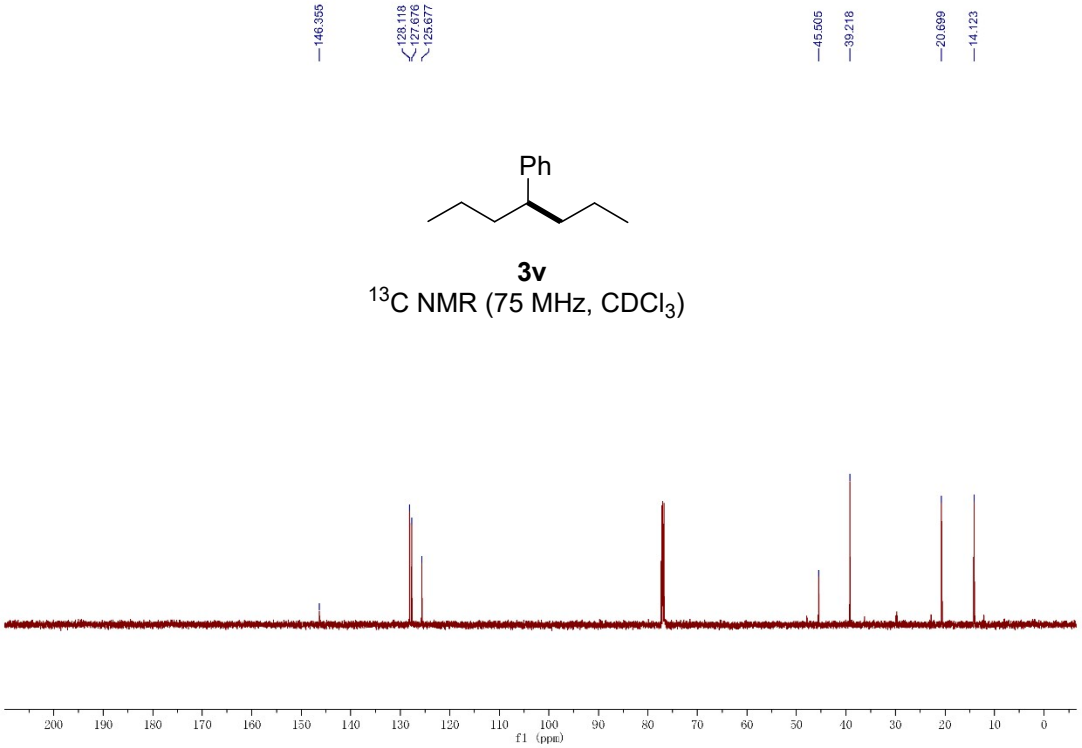
3u

^{13}C NMR (75 MHz, $CDCl_3$)



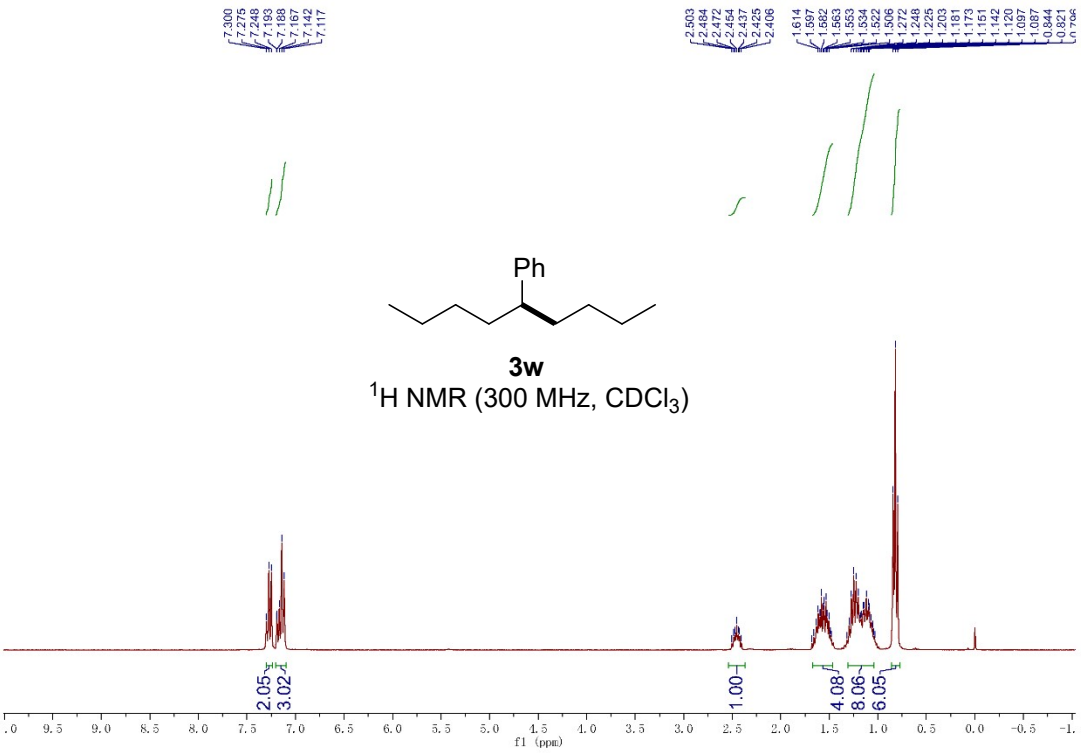
3v

^{1}H NMR (300 MHz, $CDCl_3$)



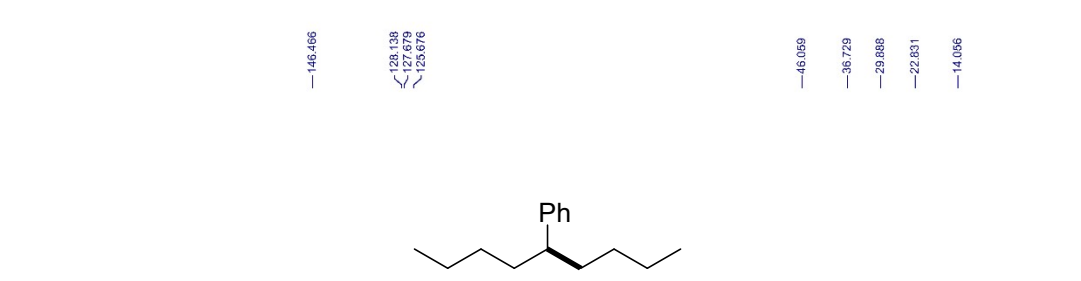
3v

^{13}C NMR (75 MHz, $CDCl_3$)



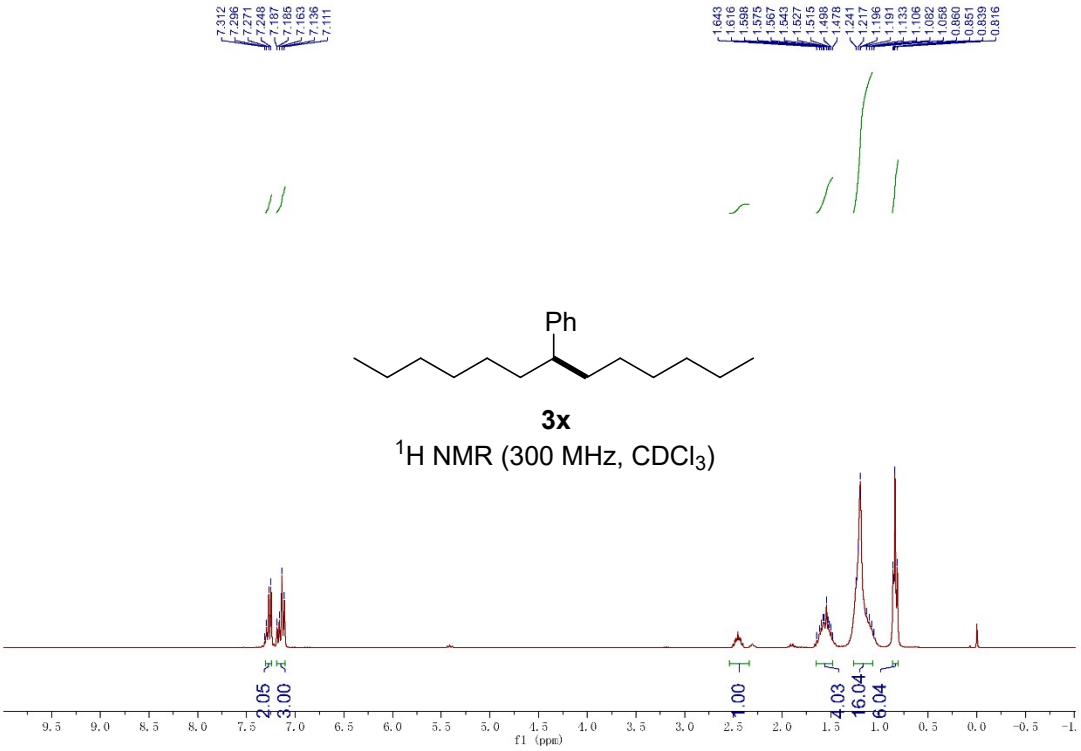
3w

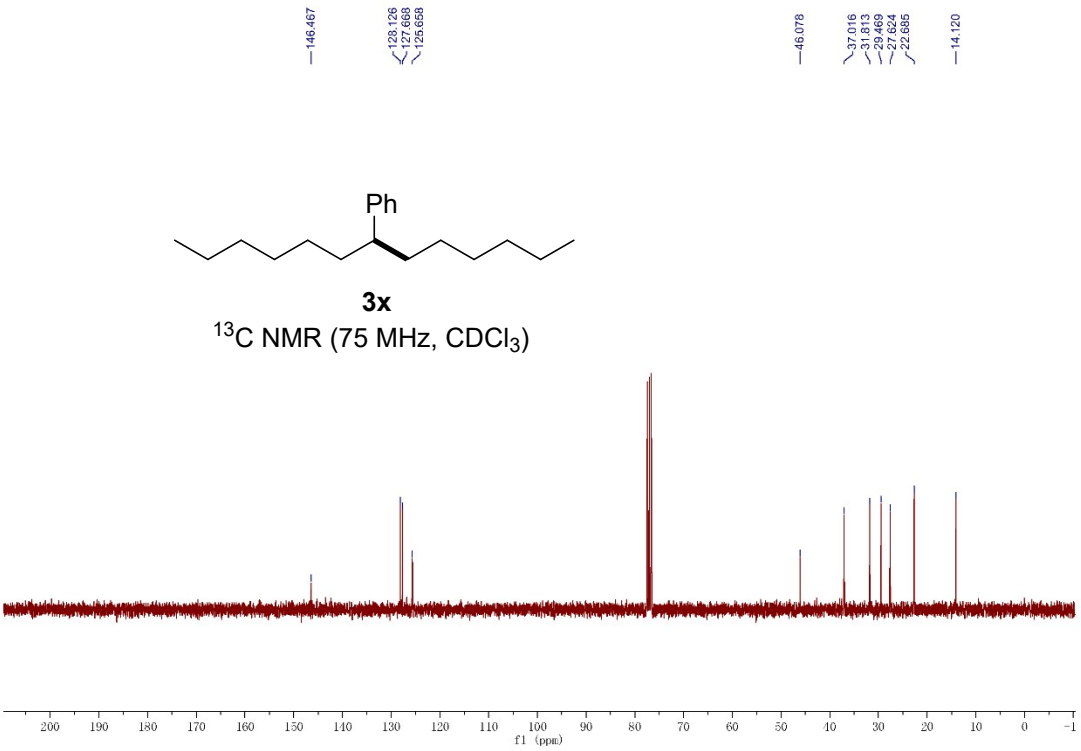
^{1}H NMR (300 MHz, $CDCl_3$)

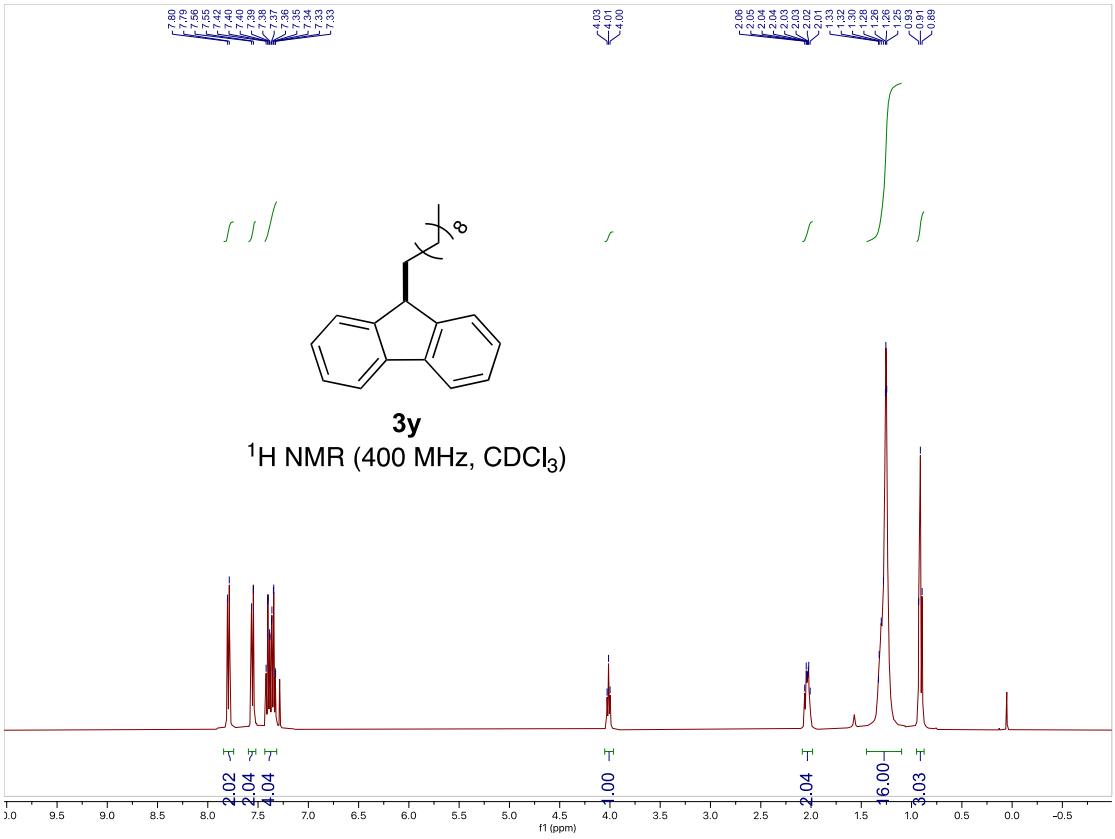


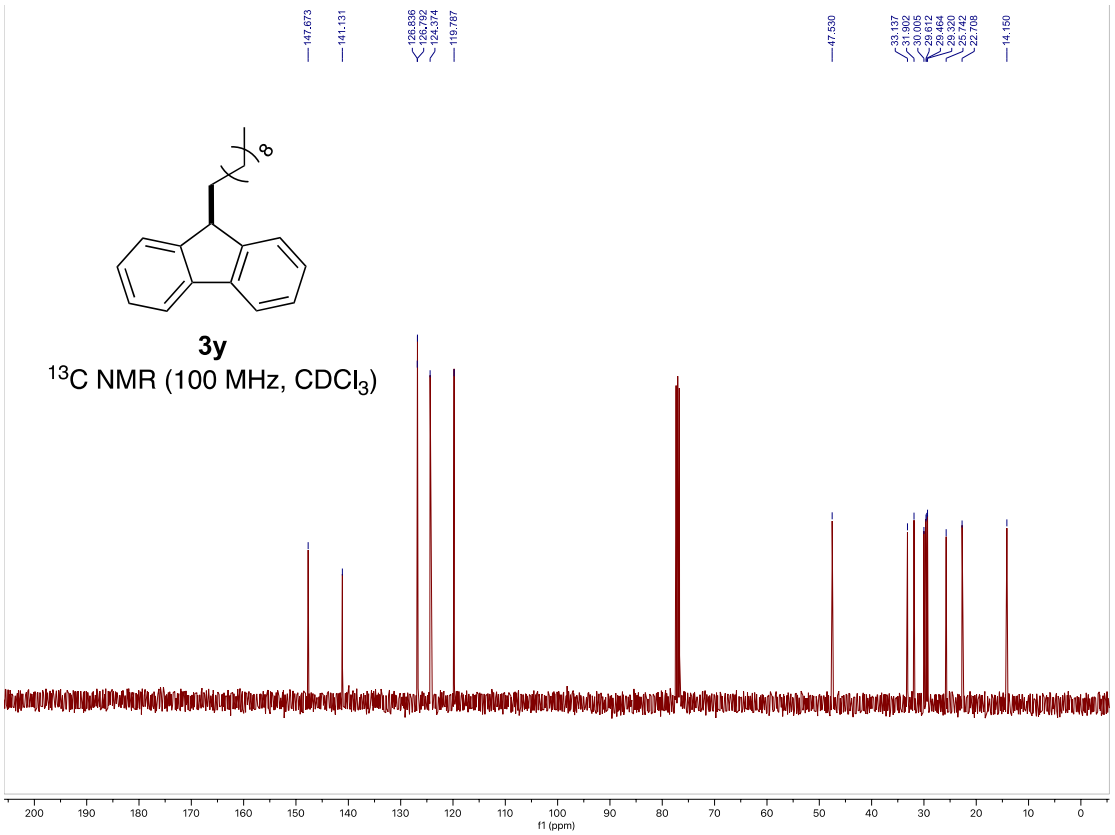
3w

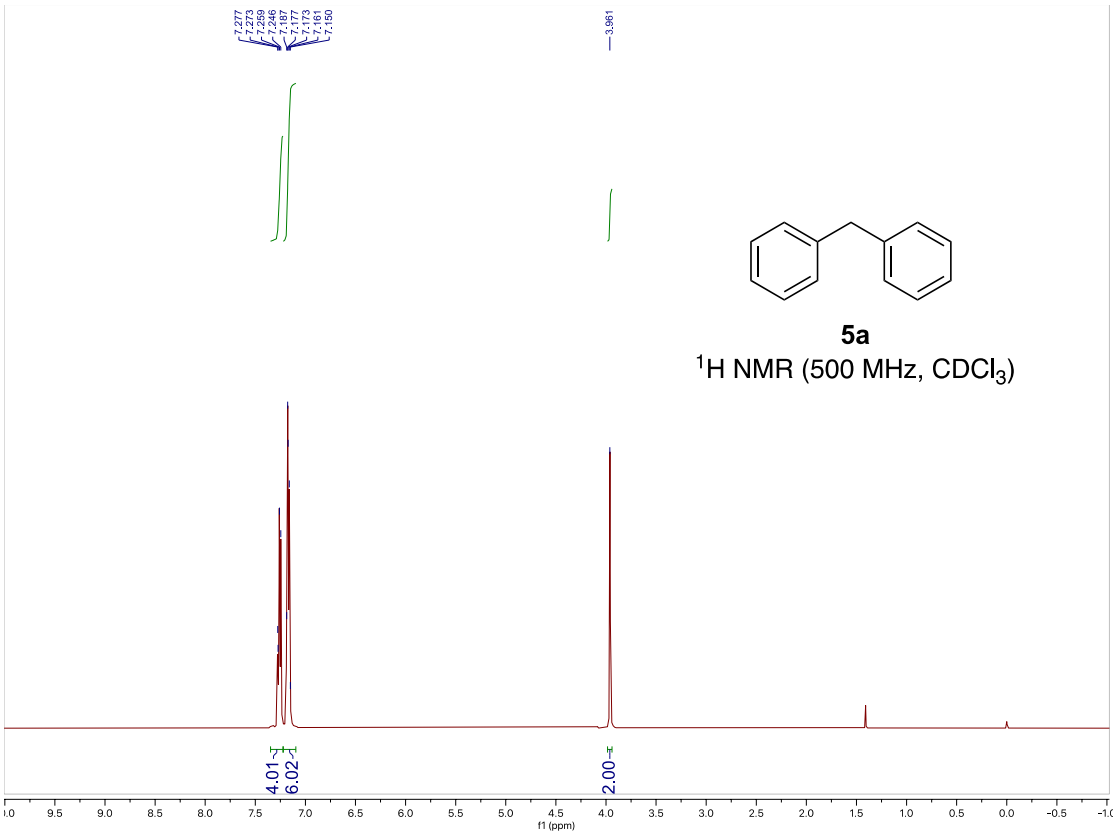
^{13}C NMR (75 MHz, $CDCl_3$)


7.312
7.296
7.271
7.248
7.187
7.185
7.163
7.136
7.111
1.643
1.616
1.598
1.575
1.567
1.543
1.527
1.515
1.498
1.478
1.241
1.217
1.196
1.191
1.133
1.106
1.082
1.058
0.860
0.851
0.839
0.816
Ph
3x
1H NMR (300 MHz, CDCl3)
2.05
3.00
1.00
4.03
16.04
6.04
f1 (ppm)


146.467
128.126
127.668
125.658
46.078
37.016
31.813
29.469
27.624
22.685
14.120
Ph
3x
13C NMR (75 MHz, CDCl3)
f1 (ppm)

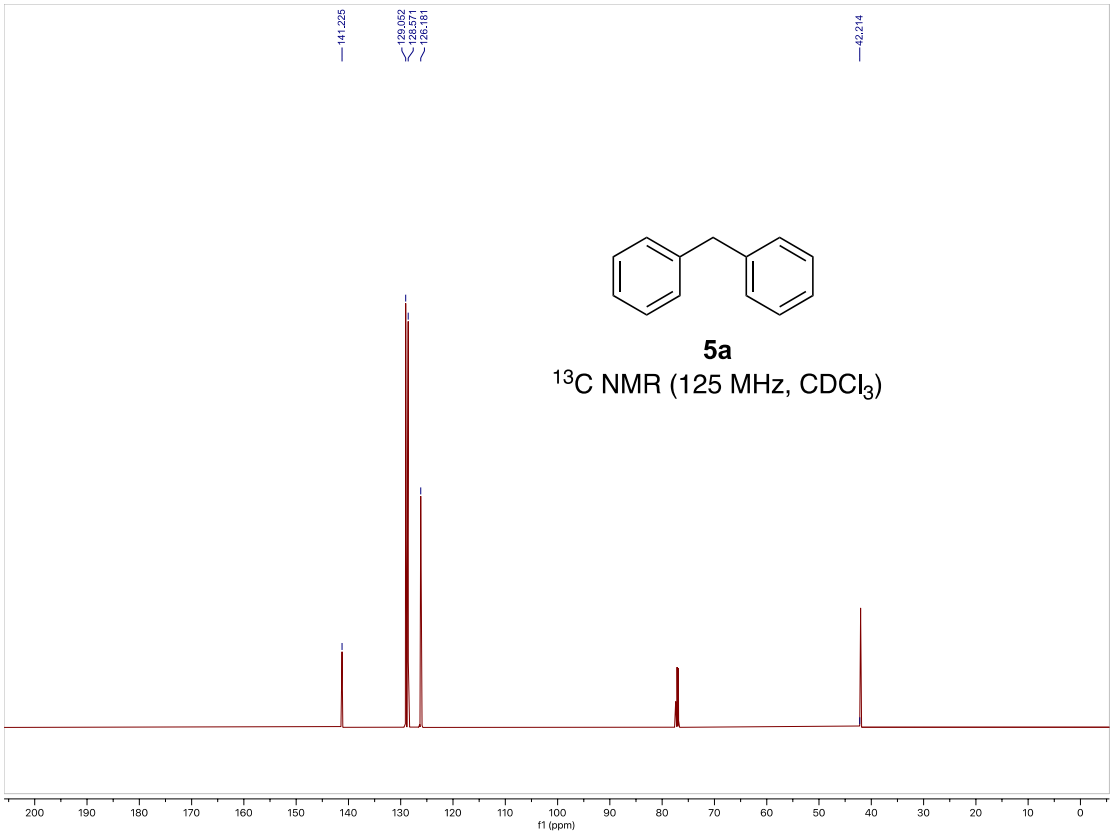

3y
1H NMR (400 MHz, CDCl3)
f1 (ppm)


3y
13C NMR (100 MHz, CDCl3)
f1 (ppm)



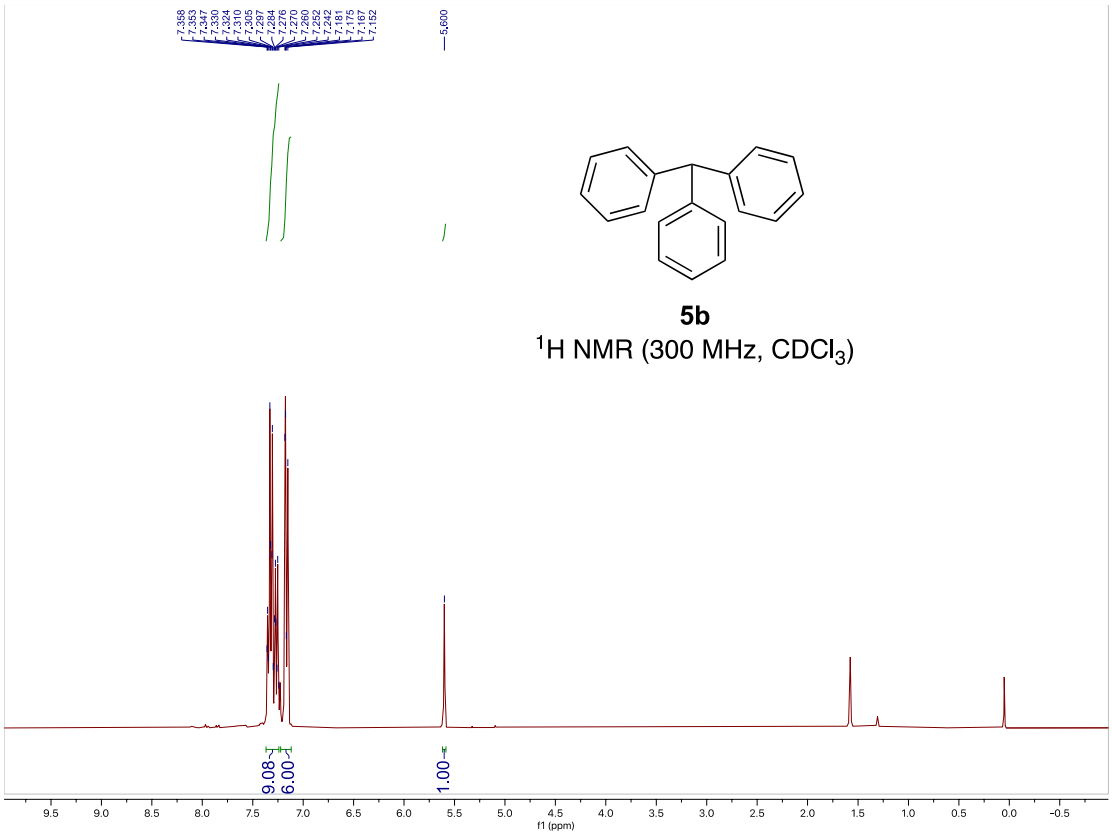
5a

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



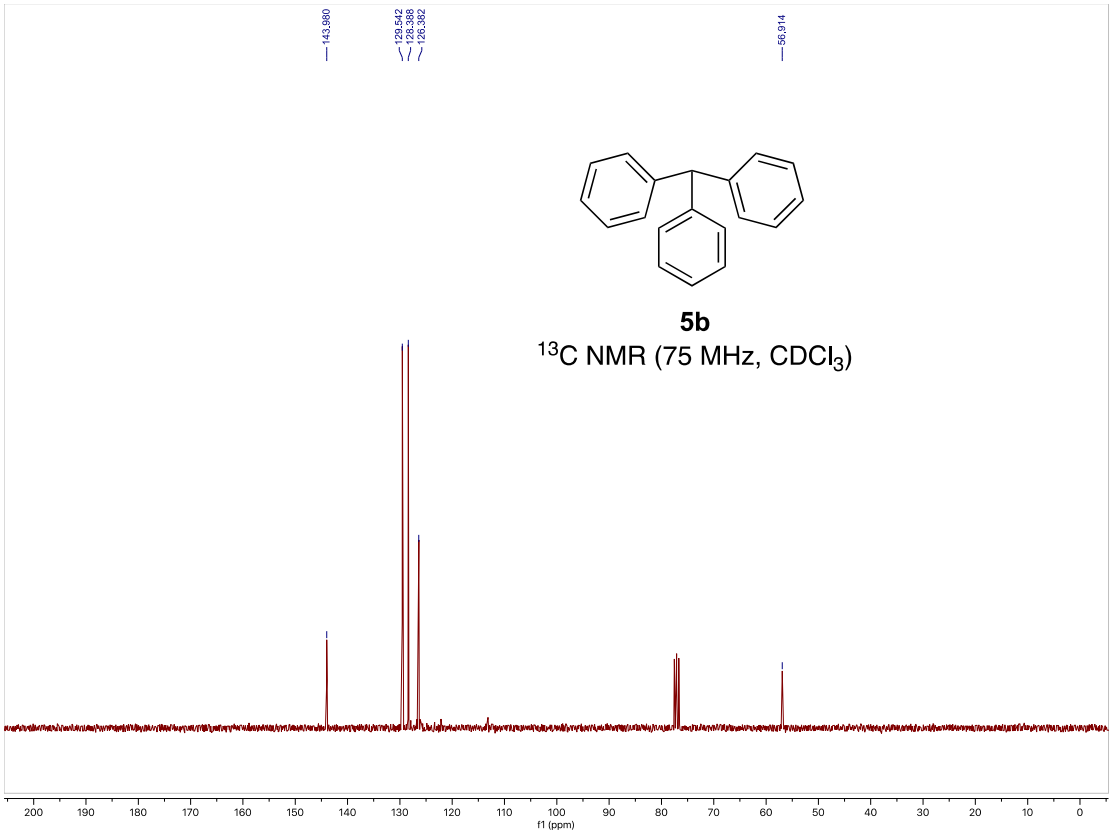
5a

^{13}C NMR (125 MHz, $CDCl_3$)



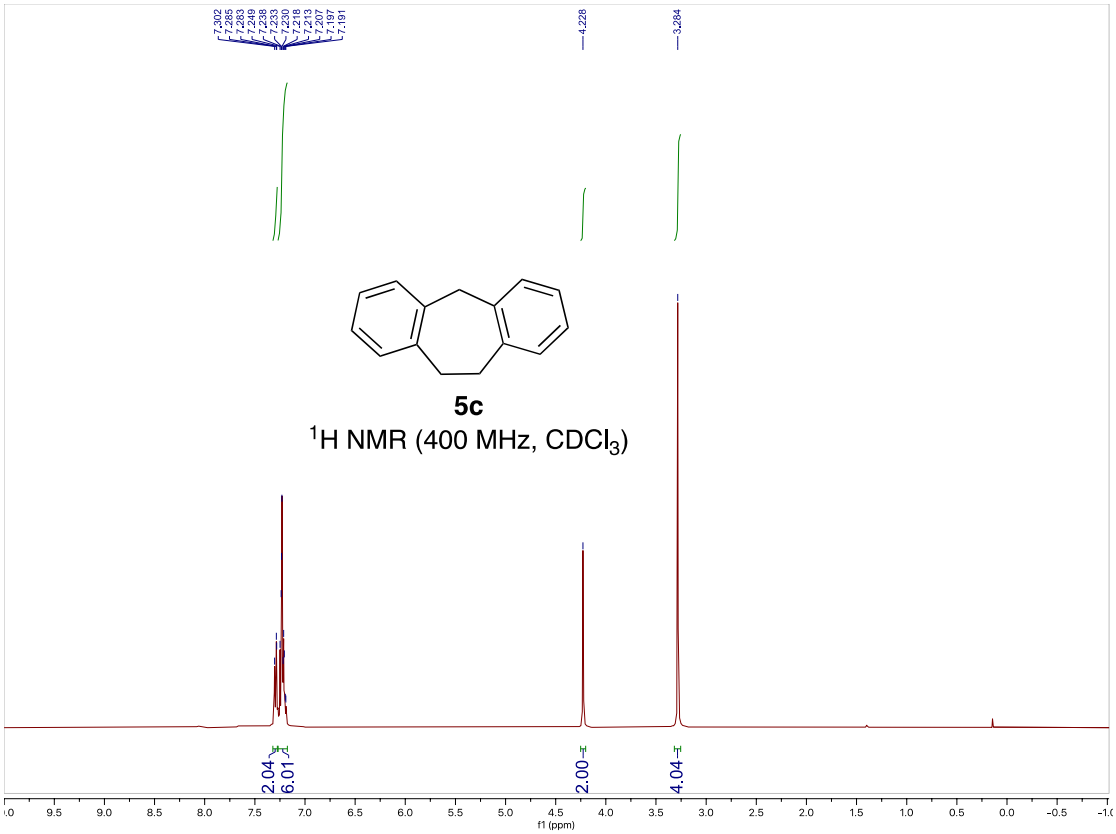
5b

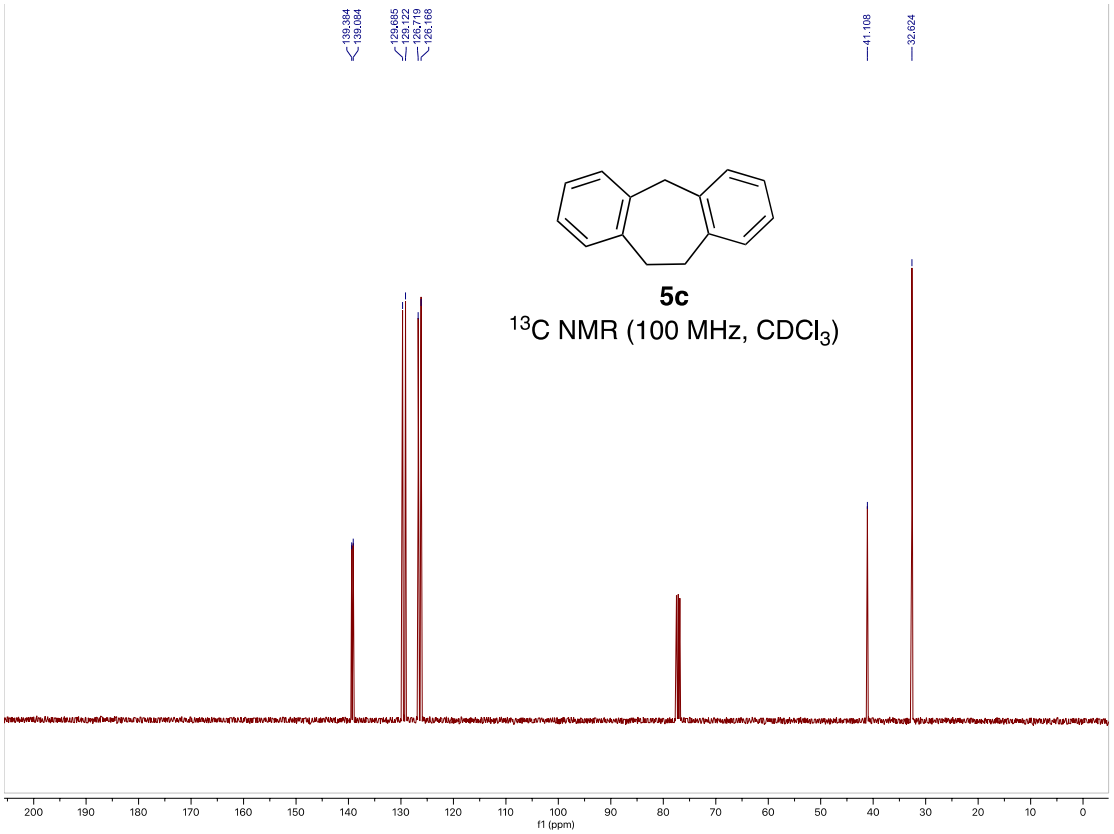
^{1}H NMR (300 MHz, $CDCl_3$)

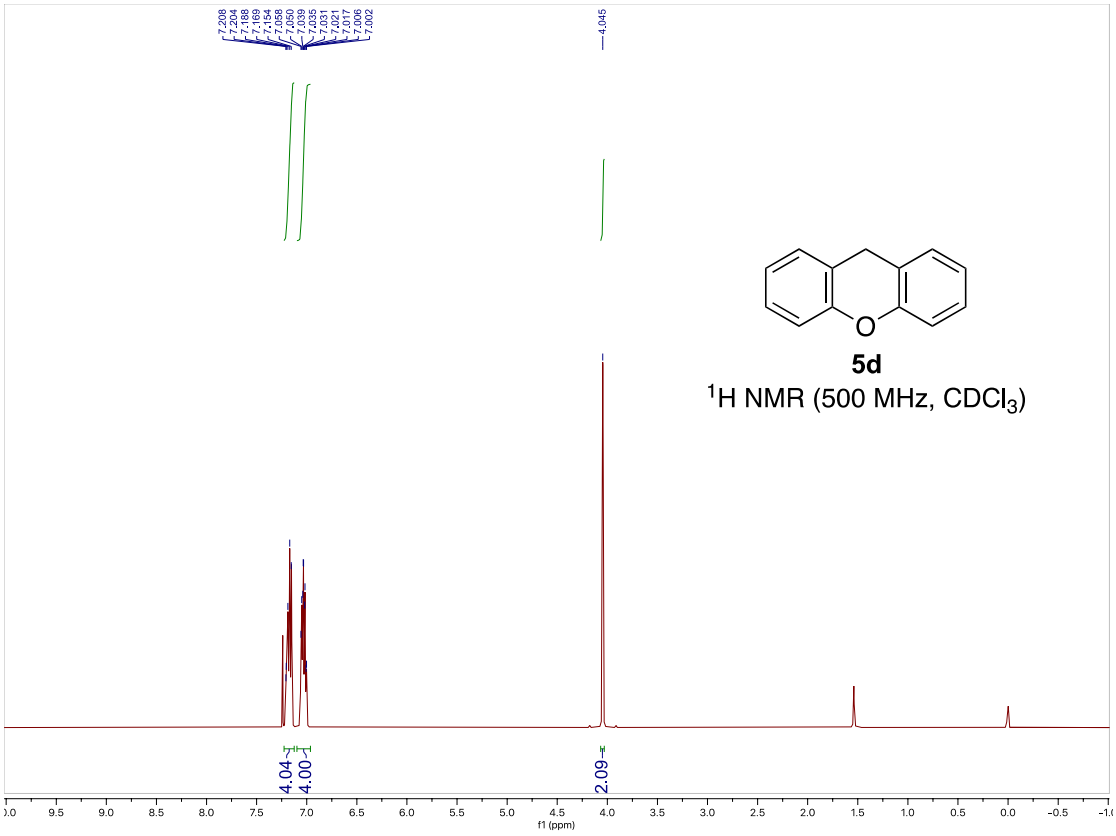


5b

^{13}C NMR (75 MHz, $CDCl_3$)

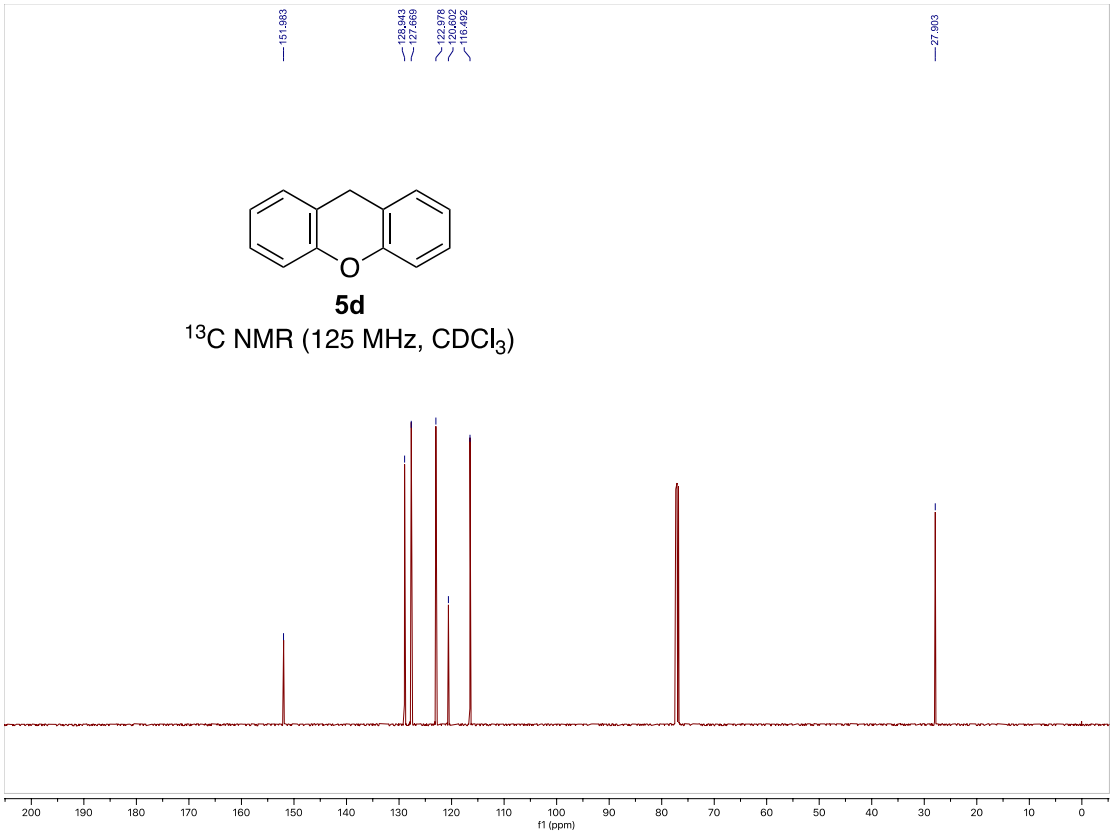

7.302
7.285
7.283
7.249
7.238
7.233
7.230
7.218
7.213
7.207
7.197
7.191
4.228
3.284
5c
1H NMR (400 MHz, CDCl3)
2.04
6.01
2.00
4.04
f1 (ppm)


139.384
139.084
129.685
129.122
126.719
126.168
41.108
32.624
5c
13C NMR (100 MHz, CDCl3)
f1 (ppm)



5d

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



5d

^{13}C NMR (125 MHz, $CDCl_3$)