Supporting Information

Ru(dppbsa)-catalyzed hydrodeoxygenation and reductive etherification of ketones and aldehydes

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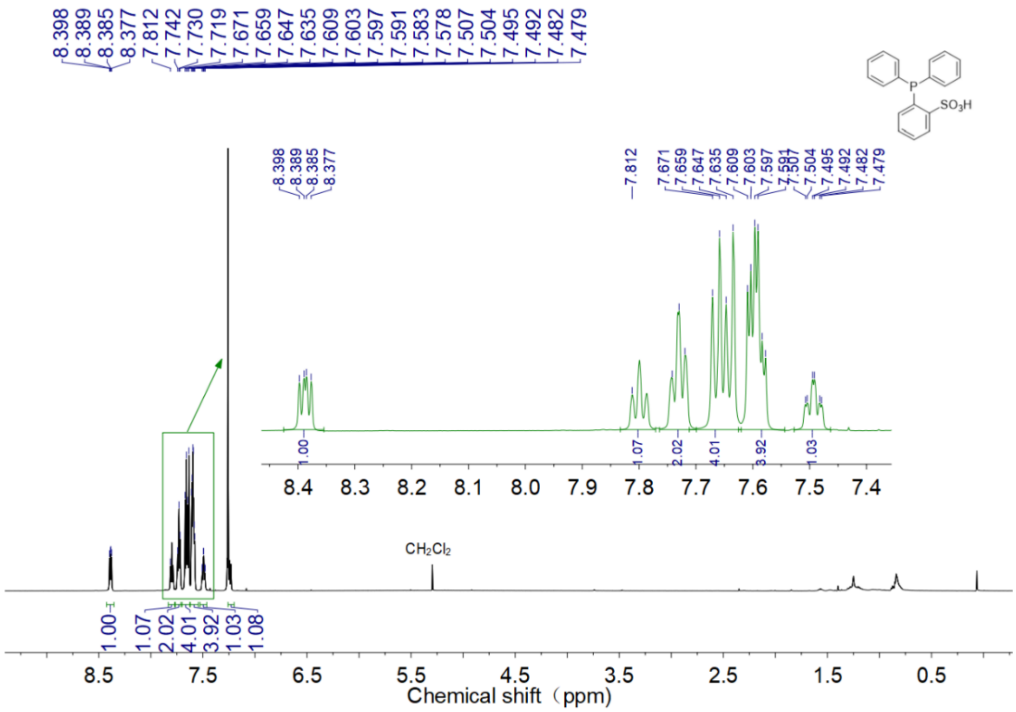
1. General experimental information

Unless specified, all substrates (aldehydes and ketones), Ru precursor was obtained commercially and their purity has been checked before use. All reactions were done under argon using a standard glove box and the solvents were dried before use unless otherwise noted. In particular, the Schlenk techniques were used in the synthesis of the Ru catalyst. All catalytic reactions were carried out in 25 mL autoclaves (Wuzhou Dingchuang (Beijing) Technology Co., Ltd.). GC-7890B equipped with a capillary column (DB-FFAP, 30 m × 0.32 mm) using a flame ionization detector. GC-MS was performed using Shimadzu GCMS-QP2020, column Rtx-5MS 30 m × 0.25 mm × 0.25 μm. GC was recorded on an Agilent 8890N instrument. ^{1}H, ^{13}C, ^{31}P NMR data were recorded on a Bruker ASCEND spectrometer (^{1}H, 600 MHz; $^{13}C\{^{1}H\}$, 151 MHz) using $CDCl_3$ or CD_3OD as solvents. ^{1}H NMR and ^{13}C NMR, chemical shift δ is given relative to TMS and referenced to the solvent signal. Chemical shifts were reported in ppm with the internal TMS signal at 0.0 ppm as a standard. The spectra are interpreted as: s = singlet, d = doublet, t = triplet, m = multiplet, dd = doublet of doublets, dt = doublet of triplets, ddd = doublet of doublet of doublets, coupling constant (s) *J* are reported in Hz and relative integrations are reported. Column chromatography was performed using silica gel. Analytical TLC was done using pre-coated silica gel 60 F254 plates.

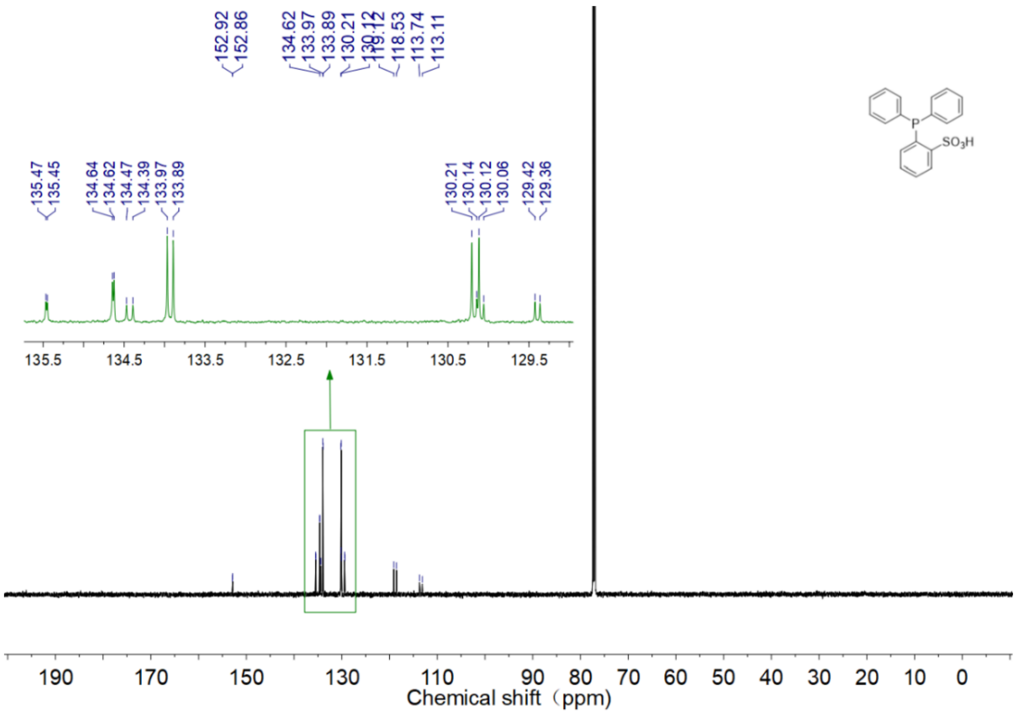
2. Preparation and characterization of Ru(dppbsa)

Preparation of dppbsa Ligand

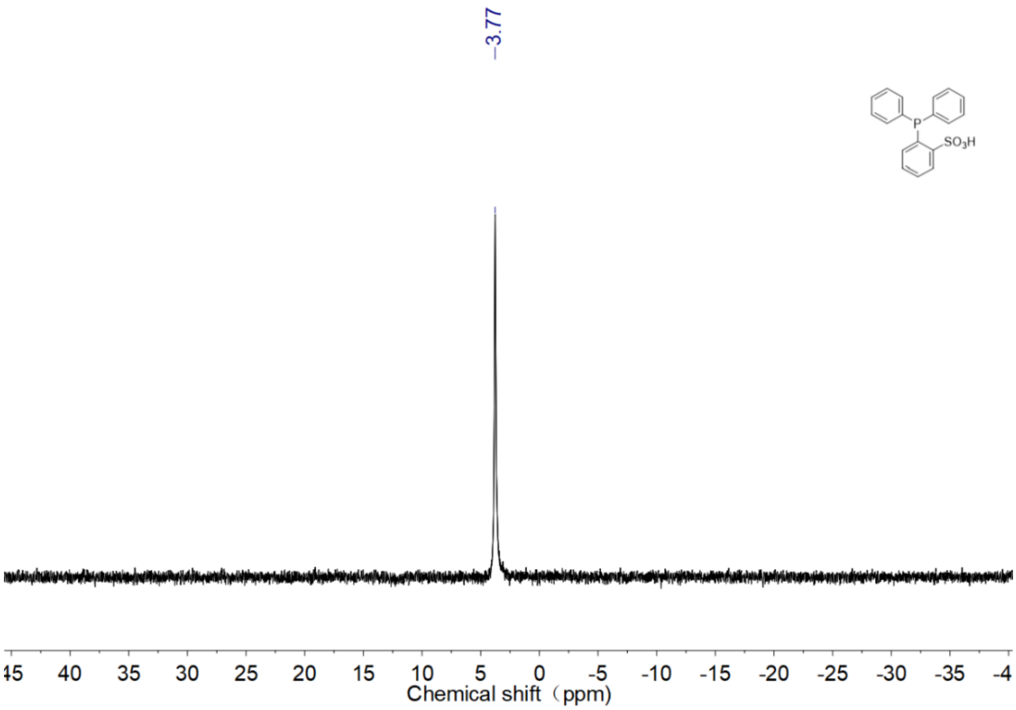
According to the literature,[S1] benzenesulfonic acid (0.80 g, 5 mmol) was dissolved in a Schleck tube with 25 mL of THF, *n*-BuLi (2.5 M in hexanes; 4 mL, 10 mmol) was added at 0 °C. After stirring for 1 h at room temperature; the solution was cooled to 0 °C again, a solution of chlorodi-phenylphosphane (1.10 g, 5 mmol) in THF (10 mL) was added dropwise to the Schleck tube and stirred at room temperature overnight. After the reaction, the solvent was removed in vacuo to obtain a pale-yellow solid. The solid was dissolved in dichloromethane (50 mL) and extracted with aqueous HCl (2 M, 30 mL), and then deionized water (30 mL) was added twice. The crude product was dissolved in dichloromethane and recrystallized with ether at -32 °C to obtain 1.05 g of white solid with a yield of 62%. **^{1}H NMR** (600 MHz, 298K, $CDCl_3$): δ = 8.39 (m, 1H), 7.80 (m, 1H), 7.73 (m, 2H), 7.66 (m, 2H), 7.64 (m, 2H), 7.59 (m, 4H), 7.49 (m, 1H), 7.25 (m, 1H), N.O. (-SO_3H). **^{13}C{^{1}H} NMR** (151 MHz, 298K, $CDCl_3$): δ = 152.9 (J_{PC} = 8.9 Hz, *i*-Ph-SO_3H), 135.5 (J_{PC} = 3.2 Hz, *i*-Ph), 134.6 (J_{PC} = 3.0 Hz, 2 × *i*-Ph), 134.5, 134.4, 134.0, 133.9, 130.2, 130.1 (4), 130.1 (1), 130.0 (5), 129.4 (2), 129.3 (6), 119.1, 118.5, 113.7, 113.1 (Ph). **^{31}P{^{1}H} NMR** (243 MHz, 298K, $CDCl_3$): δ = 3.8.



^{1}H NMR (600 MHz, $CDCl_3$, 298 K) of dppbsa



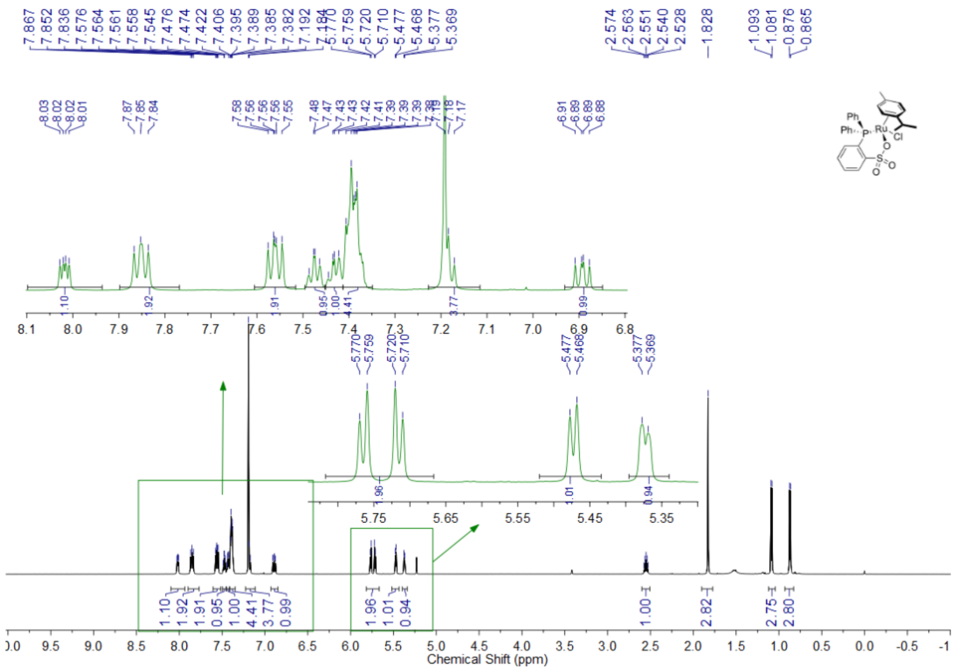
^{13}C NMR (151 MHz, $CDCl_3$, 298 K) of dppbsa



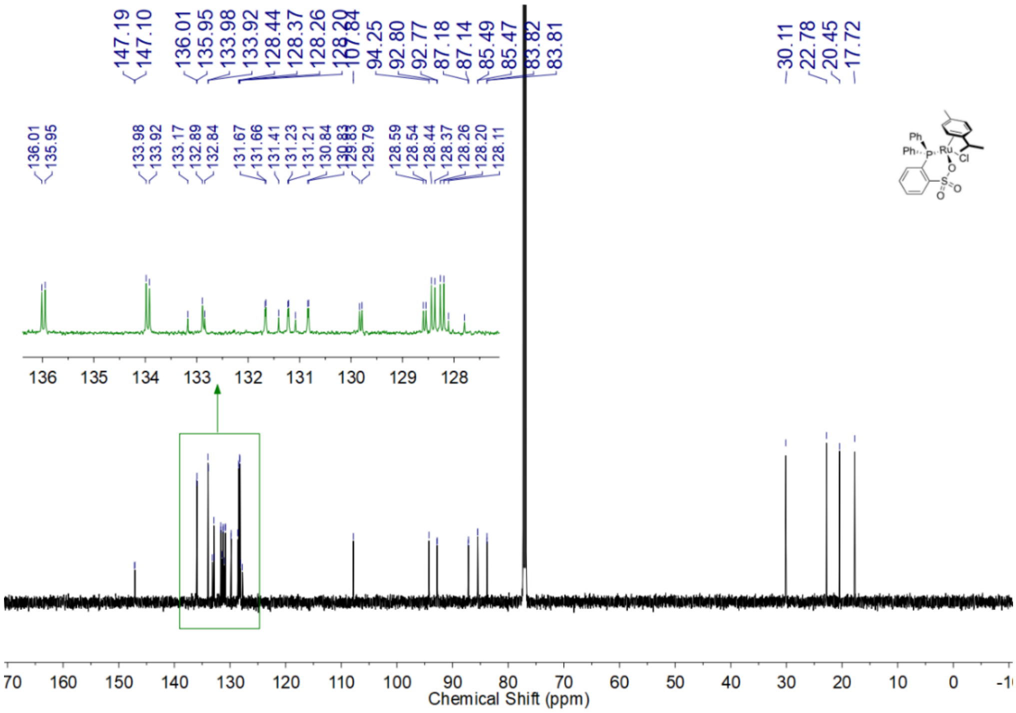
^{31}P NMR (243 MHz, $CDCl_3$, 298 K) of dppbsa

Preparation of Ru(dppbsa) Complex

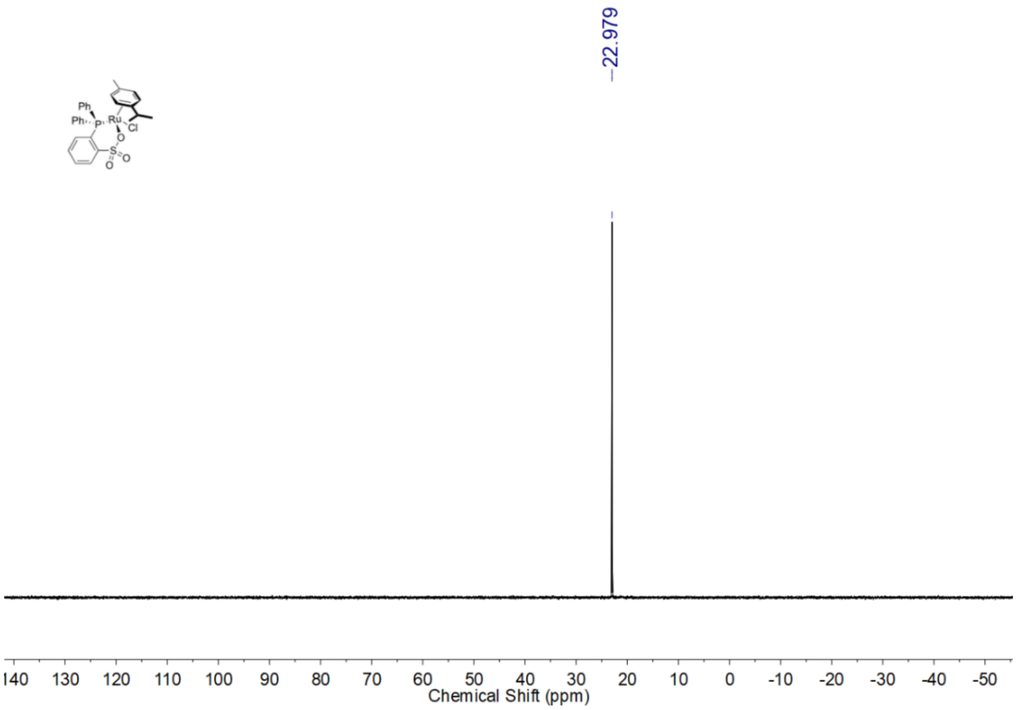
According to the literature,[S2] dppbsa ligand (164.2 mg, 0.46 mmol) and *t*-BuOK (58.2 mg, 0.51 mmol, 1.1 equiv.) were added to a 25 mL Schlenk tube, 10 mL of degassed MeOH was added, and the mixture was stirred at room temperature for 30 min; [Ru(*p*-cymene)Cl_2]$_2$ (144.5 mg, 0.22 mmol, 0.5 equiv.) was added and stirred at room temperature for 16 h; after the MeOH was removed in vacuo, the solid was dissolved in dichloromethane. Filter and recrystallize in *n*-hexane/dichloromethane solution to obtain 262.2 mg of dark red solid, with a yield of 90%. **^{1}H NMR** (600 MHz, 298 K, $CDCl_3$): δ = 8.08 (m, 1H), 7.92 (m, 2H), 7.64 (m, 1H), 7.62 (m, 1H), 7.54 (m, 1H), 7.50 (m, 1H), 7.46 (m, 4H), 7.44 (m, 1H), 7.25 (m, 1H), 6.96 (m, 1H), 5.83 (d, $^3J_{HH}$ = 6.5 Hz, 1H), 5.78 (d, $^3J_{HH}$ = 6.5 Hz, 1H), 5.54 (d, $^3J_{HH}$ = 5.5 Hz, 1H), 5.44 (d, $^3J_{HH}$ = 5.5 Hz, 1H), 2.62 (sept, $^3J_{HH}$ = 6.8 Hz, $^3J_{HH}$ = 6.8 Hz, 1H), 1.89 (s, 3H, CH_3), 1.15 (d, $^3J_{HH}$ = 6.8 Hz, 3H), 0.94 (d, $^3J_{HH}$ = 6.8 Hz, 3H). **^{13}C{^{1}H} NMR** (151 MHz, 298K, $CDCl_3$): δ = 147.2 (J_{PC} = 12.8 Hz, *i*-Ph-SO_3Ru), 136.1 (J_{PC} = 9.8 Hz), 134.1 (J_{PC} = 9.8 Hz), 133.3, 133.0(0), 132.9(6), 131.8 (J_{PC} = 2.5 Hz), 131.5, 131.3 (J_{PC} = 2.0 Hz), 131.2, 131.0 (J_{PC} = 2.5 Hz), 129.9 (J_{PC} = 6.8 Hz), 128.7 (J_{PC} = 8.3 Hz), 128.5 (J_{PC} = 9.7 Hz), 128.4 (J_{PC} = 10.3 Hz), 128.2, 128.1, 108.0, 94.4, 92.9 (J_{PC} = 5.3 Hz), 87.3 (J_{PC} = 7.7 Hz), 85.6 (J_{PC} = 2.2 Hz), 83.9 (J_{PC} = 2.2 Hz), 30.2, 22.9, 20.5, 17.8. **^{31}P{^{1}H} NMR** (243 MHz, 298K, $CDCl_3$): δ = 22.9.



[1]H NMR (600 MHz, $CDCl_3$, 298 K) of Ru(dppbsa)



[13]C NMR (151 MHz, $CDCl_3$, 298 K) of Ru(dppbsa)



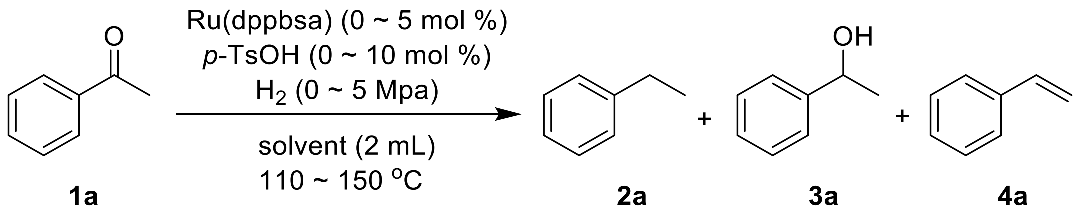
[31]P NMR (243 MHz, $CDCl_3$, 298 K) of Ru(dppbsa)

3. Ruthenium-catalyzed deoxygenation and etherification reactions

General Procedure: In a typical experiment, combination of substrate (0.2 mmol), Ru(dppbsa) (6.1 mg, 10 μmol) and *p*-TsOH (3.4 mg, 20 μmol) was dissolved in toluene (2 mL) in a reaction vessel equipped with a Teflon lining and a stir bar in the glove box. After addition of the above reactants, the reaction vessel was filled with H_2 (3 MPa). The solution was stirred at 150 °C. At the end of the reaction, the pressure of reaction vessel was gradually released, and the reaction mixture was diluted with ethyl acetate (20 mL) for analysis. The structures of the products were determined by GC-MS analysis, and yields determined by GC analysis. For some selected examples, the solvent was removed under vacuum to provide a crude product for ^{1}H NMR (600 MHz, 298 K, $CDCl_3$) analysis. The structures of the products were determined by ^{1}H NMR and ^{13}C NMR, with spectra matching those reported in the literature or authentic samples.

Screening Conditions for Catalytic Hydrogenation of Acetophenone (1a).

Table S1: Ru(dppbsa)-catalyzed hydrogenation of acetophenone (**1a**)

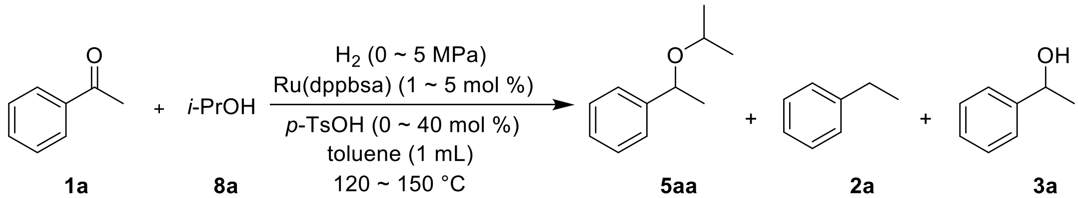


Entry	Ru(dppbsa) (mol %)	Temp. (°C)	*P*-TsOH (mol %)	H_2 (MPa)	solvent	Conv. (%)	Yield (%)[a]		
							2a	**3a**	**4a**
1	5	150	10	5	toluene	98	90	1	7
2	5	150	10	5	heptane	74	66	1	6
3	5	150	10	5	1,4-dioxane	87	66	1	9
4	5	150	10	5	THF	77	62	3	7
5[b]	5	150	10	5	*i*-PrOH	100	54	0	0
6	5	150	10	5	1,1,2,2-TeCA	31	0	2	6
7	5	150	10	5	n-Dodecane	98	69	1	5
8	0	150	10	5	toluene	8	0	0	0
9	3	150	10	5	toluene	77	70	0	6
10	5	150	10	0	toluene	15	4	0	5
11	5	150	10	1	toluene	77	47	0	9
12	**5**	**150**	**10**	**3**	**toluene**	**94**	**91**	**0**	**3**
13	5	150	0	5	toluene	92	80	0	10
14	5	110	10	3	toluene	70	42	7	5
15	5	130	10	3	toluene	98	80	0	6
16[c]	5	150	10	3	toluene	81	62	0	0
17[d]	5	150	10	3	toluene	87	78	0	0
18[e]	5	150	10	3	toluene	96	78	0	0
19[f]	5	150	-	5	toluene	87	45	2	4
20[g]	5	150	-	5	toluene	66	19	33	3
21[h]	-	150	10	3	toluene	11	0	0	0
22[i]	-	150	10	3	toluene	57	45	0	0

[a] General conditions: **1a** (0.2 mmol), 20 h, under argon, in autoclave; yields determined by GC wherein biphenyl was used as internal standard; [b] 46% of **5aa** were found in the product; [c] Reaction time was 8 h; [d] Reaction time was 12 h; [e] Reaction time was 16 h; [f] $AgBF_4$ (10 mol %); [g] $AlCl_3$ (10 mol %); [h] dppbsa (5 mol %); [i] $[Ru(p\text{-cymene})Cl_2]_2$ (2.5 mol %).

Screening Conditions for Catalytic Etherification of Acetophenone (1a).

Table S2. Catalytic etherification of acetophenone (**1a**) with *i*-PrOH (**8a**) in the presence of Ru(dppbsa)[a]

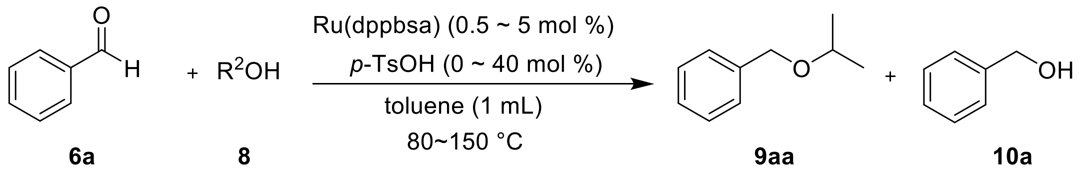


Entry	[Ru] (mol %)	Temp. (°C)	*p*-TsOH (mol %)	H_2 (MPa)	Conv.	Yield (%)[a]		
						5aa	**2a**	**3a**
1	5	150	10	5	100	46	54	0
2	1	150	40	5	94	3	91	0
3	3	150	40	5	89	2	87	0
4	**5**	**150**	**40**	**5**	**85**	**55**	**25**	**3**
5	5	150	0	5	90	43	20	16
6	5	150	20	5	92	0	92	0
7	5	150	40	0	27	7	20	0
8	5	150	40	1	80	3	77	0
9	5	150	40	2	86	3	82	1
10	5	150	40	3	87	6	80	1
11	5	150	40	4	87	43	40	3
12	5	120	40	0	0	0	0	0

[a] General conditions: **1a** (0.2 mmol), **8a** (1 mL), toluene (1 mL), 20 h, under argon, in autoclave; yields determined by GC.

Screening Conditions for Catalytic Etherification of Benzaldehyde (6a).

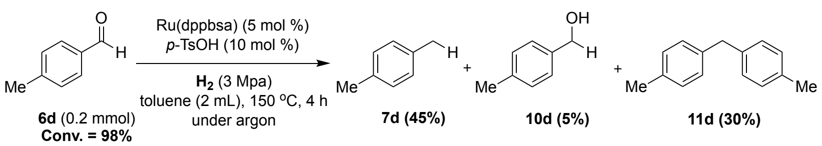
Table S3. Catalytic etherification of benzaldehyde (**6a**) with alcohols (**8**) in the presence of Ru(dppbsa) complex[a]



Entry	[Ru] (mol %)	**8**	Temp. (°C)	*p*-TsOH (mol %)	Conv.	Yield (%)[a]	
						9aa	**10a**
1	0.5	*i*-PrOH	150	40	59	49	10
2	1	*i*-PrOH	150	40	100	85	15
3	3	*i*-PrOH	150	40	100	95	5
4	5	*i*-PrOH	150	40	100	93	0
5	5	*i*-PrOH	80	40	10	6	4
6	5	*i*-PrOH	100	40	100	39	61
7	5	*i*-PrOH	120	40	99	49	50
8	5	*i*-PrOH	150	0	29	23	5
9	3	*i*-PrOH	150	5	100	82	17
10	5	*i*-PrOH	150	10	100	90	10
11	**3**	***i*-PrOH**	**150**	**20**	**100**	**96**	**4**
12	5	MeOH	150	40	60	3	2
13	5	EtOH	150	40	100	89	11
14[b]	3	*i*-PrOH	150	40	94	53	1

[a] General conditions: **6a** (0.2 mmol), **8** (1 mL), toluene (1 mL), 20 h, under argon, in autoclave; yields determined by GC; [b] **8a** (10 equiv.).

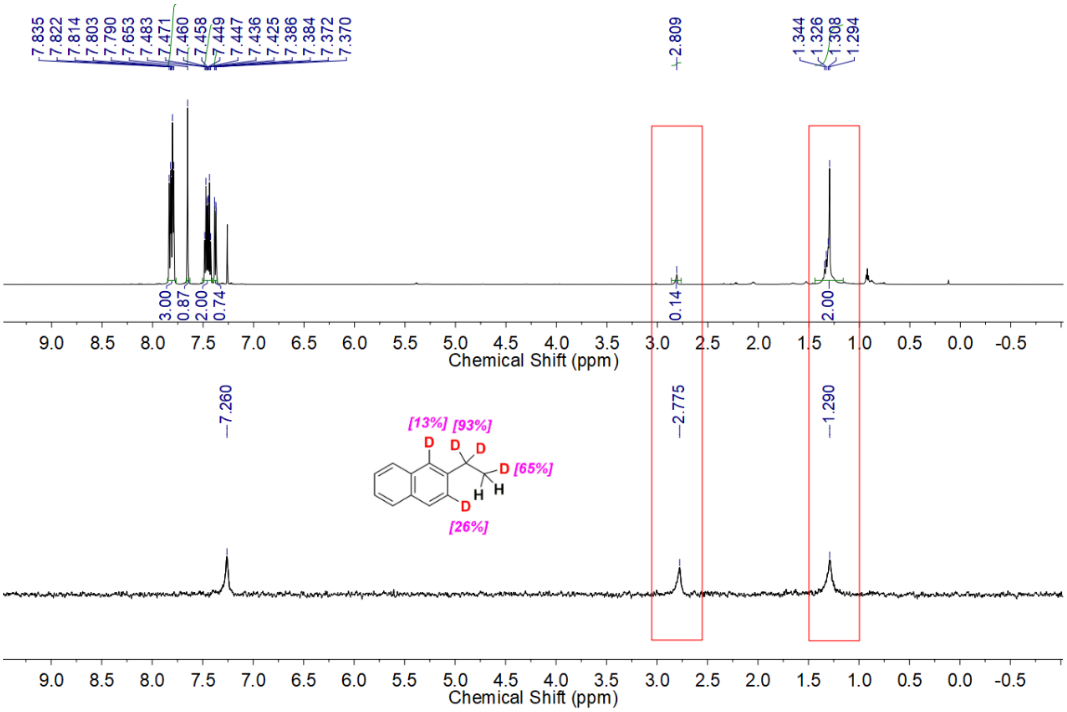
4. Hydrodeoxygenation of aldehydes in toluene



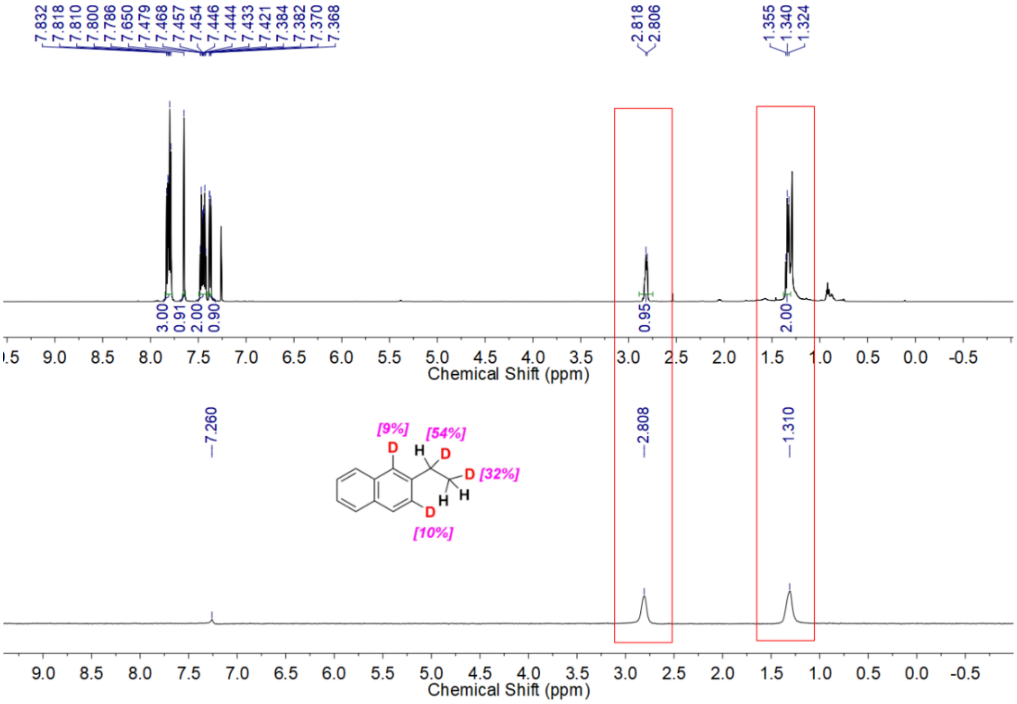
Scheme S1 Hydrodeoxygenation of aldehydes in toluene

5. Hydrodeoxygenation of 1a/3a/4a with D_2

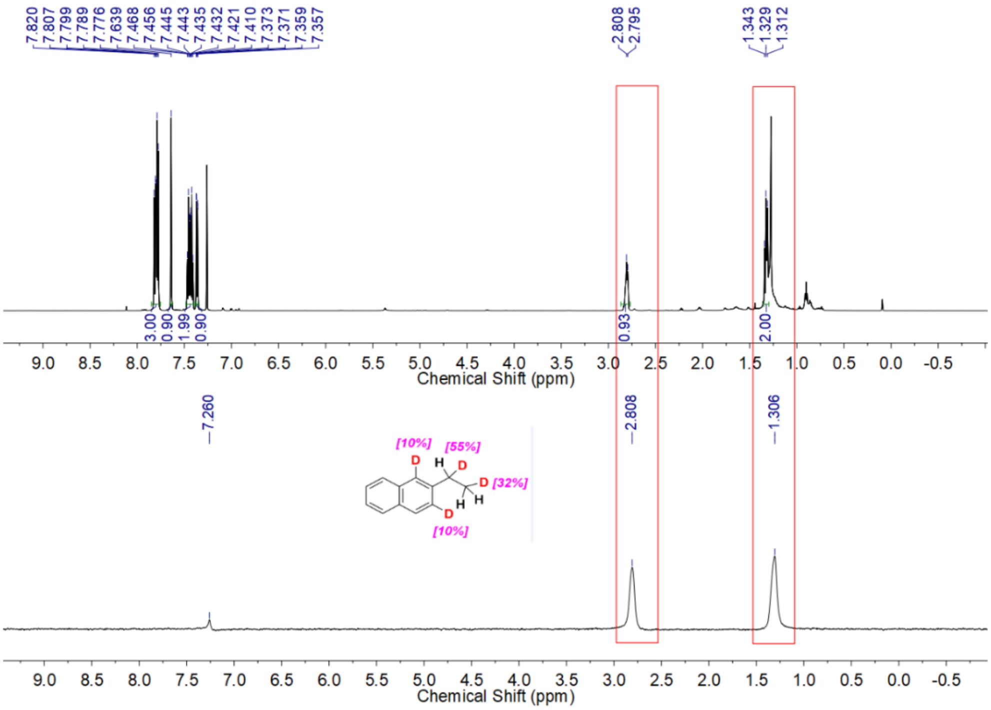
Ru(dppbsa) (5 mol %), *p*-TsOH (10 mol %) were dissolved with toluene (2 mL) in a reaction vessel equipped with a Teflon lining and a stir bar. After **1a/3a/4a** (0.2 mmol) was added, the reaction vessel was filled with D_2 (3 MPa). The mixture was stirred at 150 ^oC for 20 h. Thereafter, the pressure of reaction vessel was gradually released, and the reaction solution was diluted with ethyl acetate (20 mL) for analysis. The distribution of the product was determined by GC analysis.



^2H NMR and ^1H NMR (600 MHz, $CDCl_3$, 298 K) of product of **1j** with D_2



^{2}H NMR and ^{1}H NMR (600 MHz, $CDCl_3$, 298 K) of product of **3j** with D_2



^{2}H NMR and ^{1}H NMR (600 MHz, $CDCl_3$, 298 K) of product of **4j** with D_2

6. Hammett study

The reactions were performed in parallel reaction vessel for designated time on multi-zone reaction platform. In a glove box, Ru(dppbsa) (5 mol %), *p*-TsOH (10 mol %) were dissolved with solvent (2 mL) in a reaction vessel equipped with a Teflon lining and a stir bar. After *p*-Y-acetophenone or *p*-Y-benzaldehyde (Y = OMe, Me, H, Cl, CF_3) was added, the reaction vessel was filled with H_2 (3 MPa). The mixture was stirred at 150 °C for 2~4 h. Thereafter, the pressure of reaction vessel was gradually released, and the reaction solution was diluted with ethyl acetate (20 mL) for analysis. The distribution of the product was determined by GC analysis. The k_{obsd} of each catalytic reaction is determined from a first-order plot of [(*p*-Y-ethylbenzene)$_t$] (Fig. S1A) or [(*p*-Y-methyl benzene)$_t$] (Fig. S1B) *vs.* time.

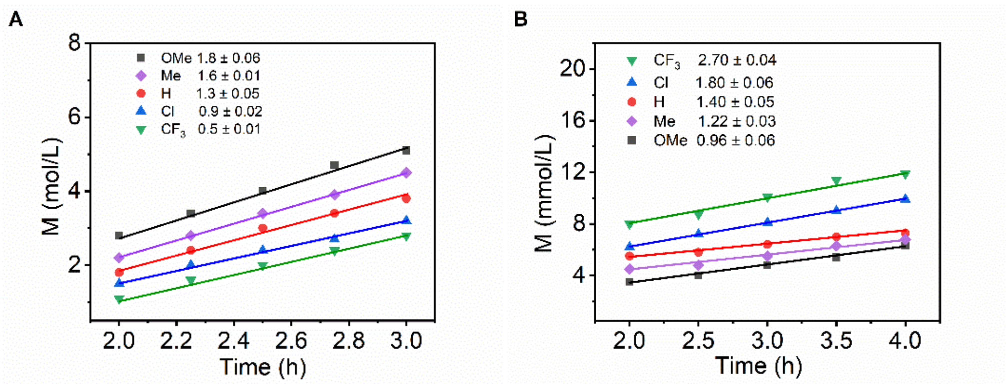


Fig. S1 First-order plot of [(*p*-Y-ethylbenzene)$_t$] (A) or [(*p*-Y-methylbenzene)$_t$] (B) vs. time

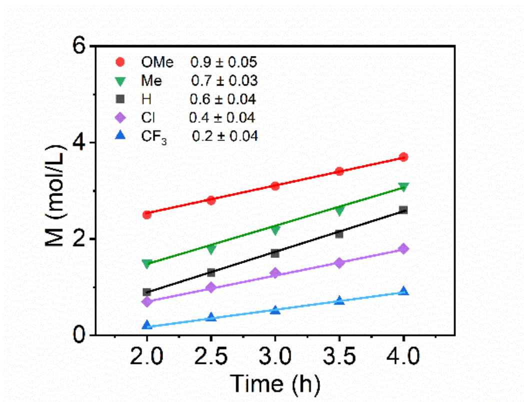


Fig. S2 First-order plot of [(*p*-Y-ethylbenzene)$_t$] vs. time (solvent: heptane) (Y = OMe, Me, H, Cl, CF_3)

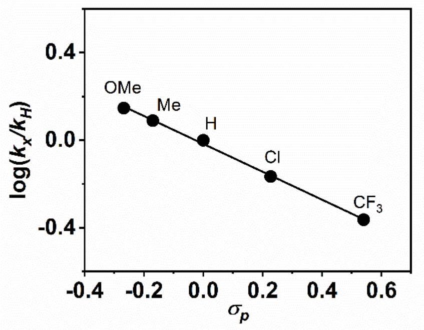


Fig. S3 Hammett plot of the Ru(dppbsa)-catalyzed hydrodeoxygenation of *p*-Y-acetophenone (solvent: heptane) (Y = OMe, Me, H, Cl, CF_3)

7. Detection of *p*-cymene

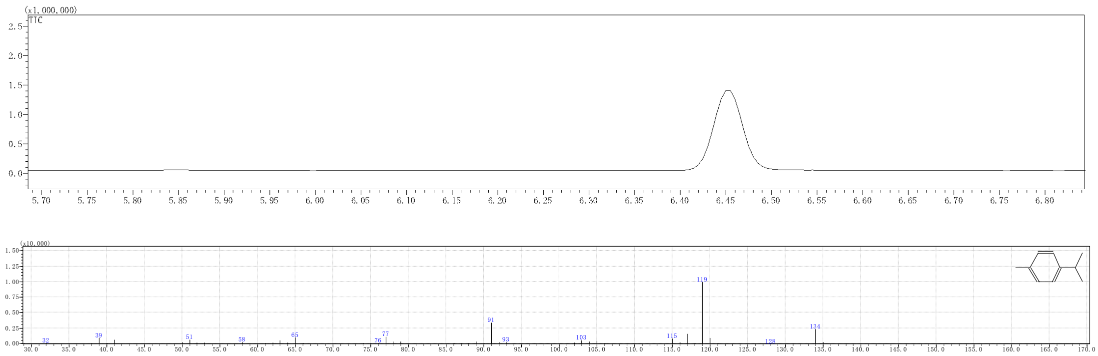


Fig. S4 GC-MS analysis of *p*-cymene in the evaluation of catalytic performance

8. Deuterium isotope effect study

The reactions were performed in parallel reaction vessel for designated time on multi-zone reaction platform. In a glove box, Ru(dppbsa) (5 mol %), *p*-TsOH (10 mol %) were dissolved with toluene (2 mL) in a reaction vessel equipped with a Teflon lining and a stir bar. After **1a** or **6a** (0.2 mmol) was added, the reaction vessel was filled with H_2 or D_2 (3 MPa). The mixture was stirred at 150 °C for 2~4 h. Thereafter, the pressure of reaction vessel was gradually released, and the reaction solution was diluted with ethyl acetate (20 mL) for analysis. The distribution of the product was determined by GC analysis using biphenyl as an internal standard. The k_{obsd} was determined from a first-order plot of −ln[$(\mathbf{1a})_t/(\mathbf{1a})_0$] or −ln[$(\mathbf{6a})_t/(\mathbf{6a})_0$] *vs.* time, and k_H/k_D was calculated from the ratio of the slopes.

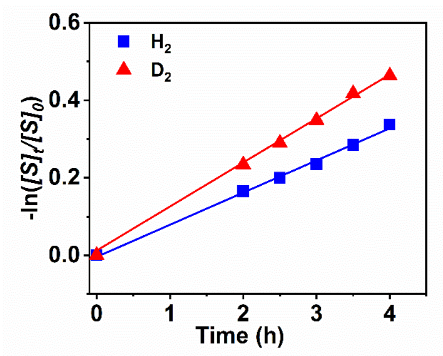


Fig. S5 First-order plot for the hydrogenolysis of **1a** (solvent: heptane) with H_2 (■) and with D_2 (▲) catalyzed by Ru(dppbsa).

9. Empirical rate measurements

Catalyst concentration dependence study.

Ru(dppbsa) (2.5 ~ 10 mol %), *p*-TsOH (10 mol %) were dissolved with solvent (2 mL) in a reaction vessel equipped with a Teflon lining and a stir bar. After **1a** or **10a** (0.2 mmol) was added, the reaction vessel was filled with H_2 (3 MPa). The mixture was stirred at the different temperature (150 °C) for 2~4 h. Thereafter, the pressure of reaction vessel was gradually released, and the reaction solution was diluted with ethyl acetate (20 mL) for analysis. The distribution of the product was determined by GC analysis. Linear regression of the rates versus concentration of **1a** or **10a** indicates a first-order dependence on Ru(dppbsa) (Figures S1~S2).

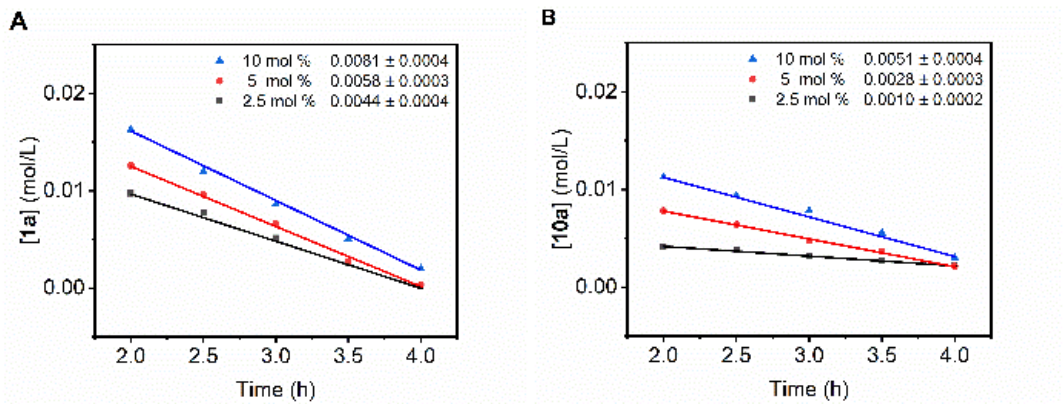


Fig. S6 Experiments measuring the concentration of **1a** or **10a** with respect to time for a series of reactions at varied concentrations of Ru(dppbsa).

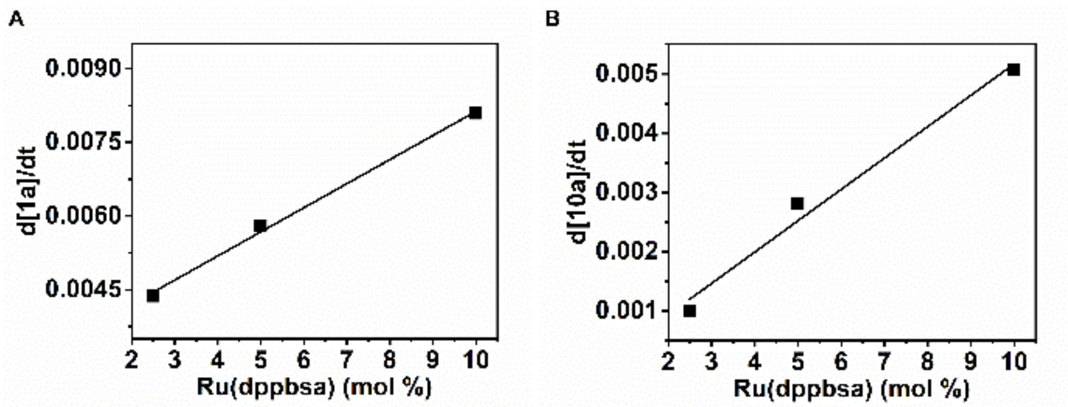


Fig. S7 Reaction rate with respect to concentration of Ru(dppbsa).

Ketone and aldehyde substrate dependence study.

Ru(dppbsa) (5 mol %), *p*-TsOH (10 mol %) were dissolved with solvent (2 mL) in a reaction vessel equipped with a Teflon lining and a stir bar. After a series of varying concentration of **1a** or **10a** was added, the reaction vessel was filled with H_2 (3 MPa). The mixture was stirred at the different temperature (150 °C) for 2~4 h. Thereafter, the pressure of reaction vessel was gradually released, and the reaction solution was diluted with ethyl acetate (20 mL) for analysis. The distribution of the product was determined by GC analysis. Linear regression of the rates versus concentration of **1a** or **10a** indicates a first-order dependence on the substrate (Figures S3~S4).

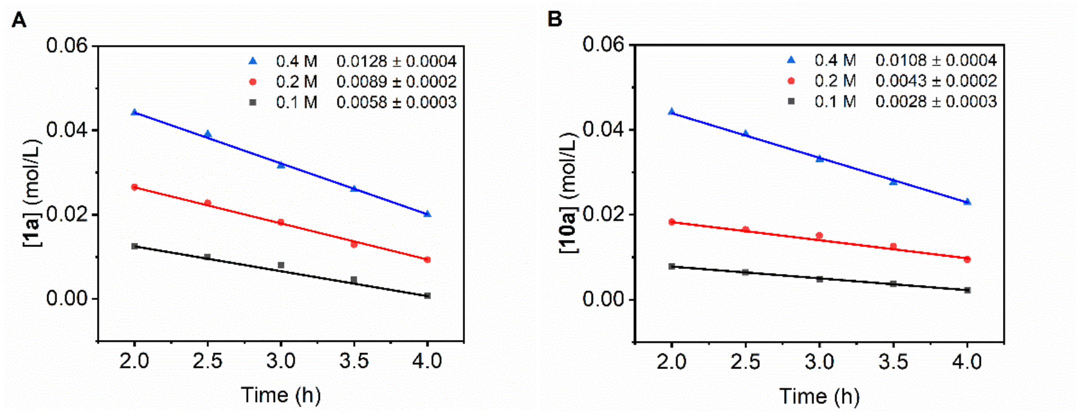


Fig. S8 Experiments measuring the concentration of **1a** or **10a** with respect to time for a series of reactions at varied concentrations of **1a** or **10a** .

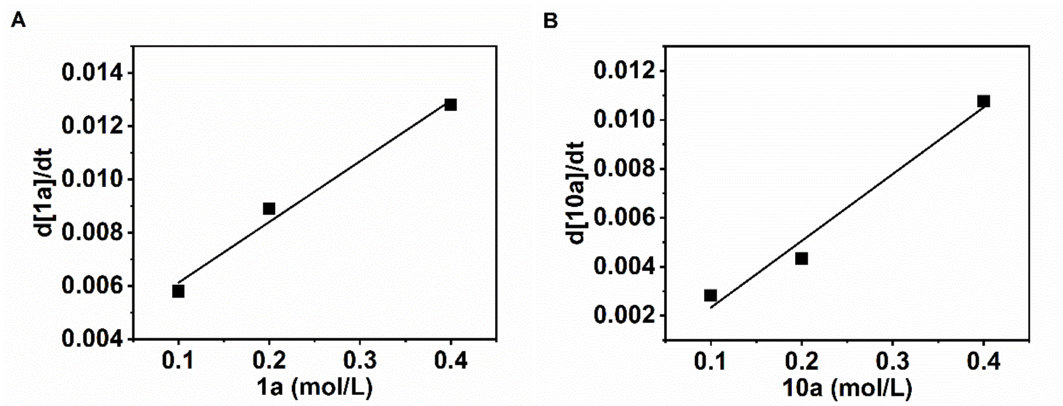


Fig. S9 Reaction rate with respect to concentration of **1a** or **10a**.

Hydrogen pressure dependence study.

Ru(dppbsa) (5 mol %), *p*-TsOH (10 mol %) were dissolved with solvent (2 mL) in a reaction vessel equipped with a Teflon lining and a stir bar. After **1a** or **10a** (0.2 mmol) was added, the reaction vessel was filled with H_2 (1~ 5 MPa). The mixture was stirred at the different temperature (150 °C) for 2~4 h. Thereafter, the pressure of reaction vessel was gradually released, and the reaction solution was diluted with ethyl acetate (20 mL) for analysis. The distribution of the product was determined by GC analysis. Linear regression of the rates versus concentration of **1a** or **10a** indicates a first-order dependence on the hydrogen pressure (Figures S5~S6).

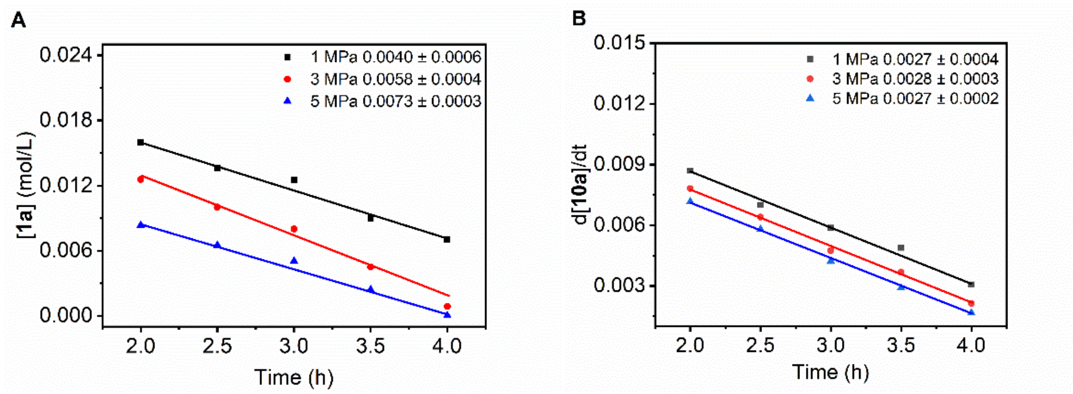


Fig. S10 Experiments measuring the concentration of **1a** or **10a** with respect to time for a series of reactions at varied pressure of H_2.

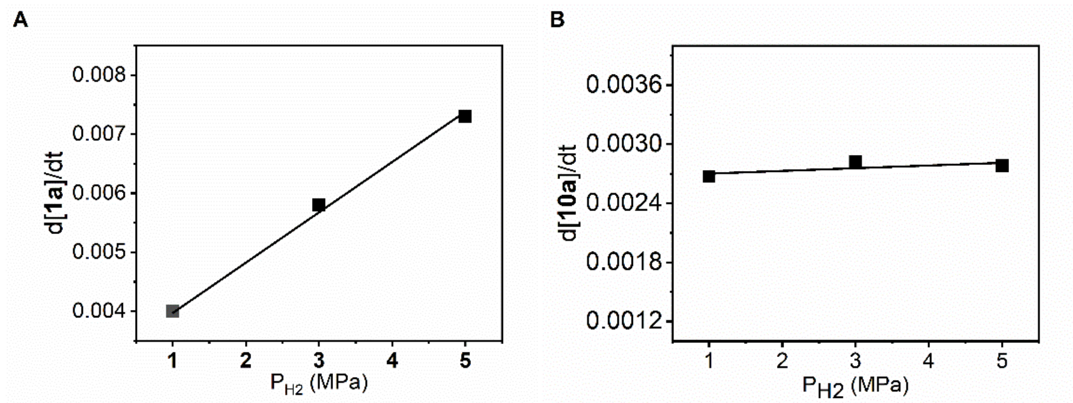
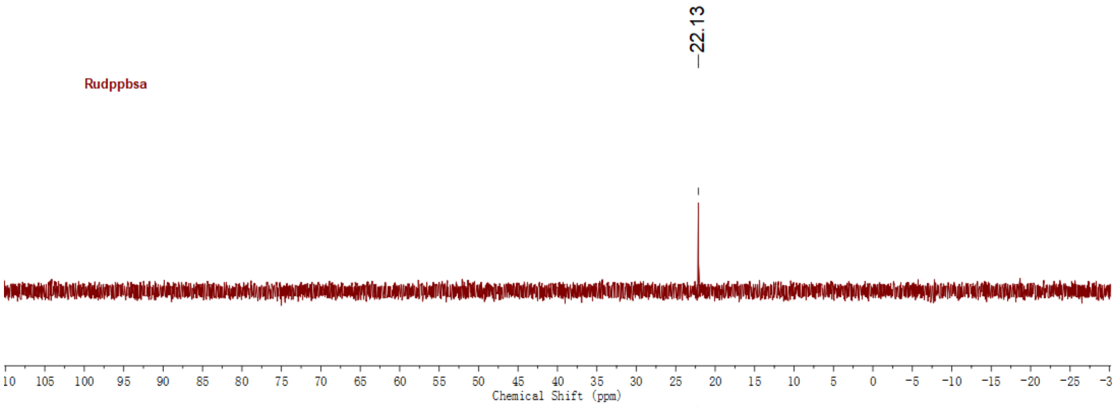


Fig. S11 Reaction rate with respect to pressure of H_2.

10.^{31}P NMR experiment on Ru(dppbsa) with or without 1a and *p*-TsOH



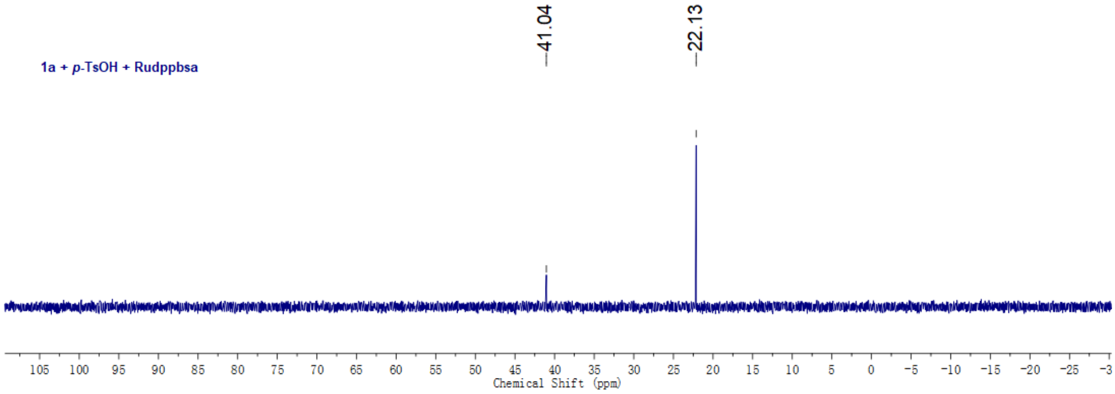
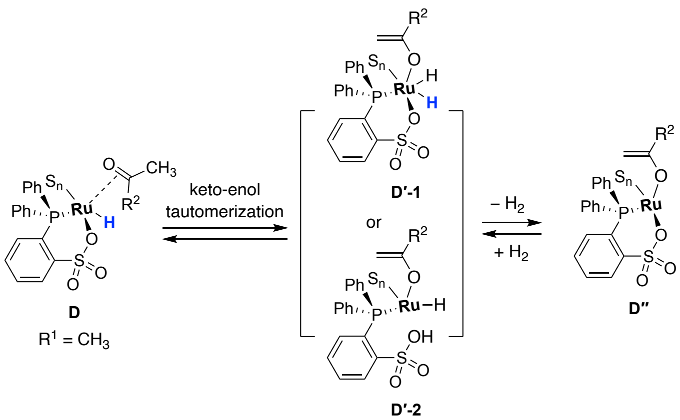


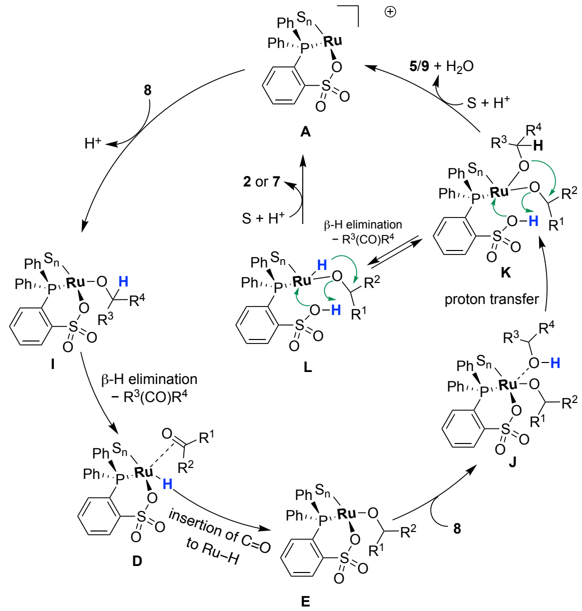
Fig. S12 ^{31}P NMR (243 MHz, C_6D_6, 298 K) of Rudppbsa and solution of **1a**, *p*-TsOH, and Ru(dppbsa)

11.The path of keto-enol tautomerization



Scheme S2 The path of keto-enol tautomerization (taking complex D as an example).

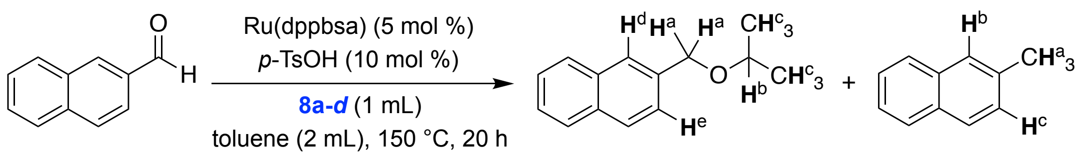
12. Proposed reaction pathway for the the reductive etherification of carbonyl compounds.



Scheme S3 Proposed reaction pathway for the the reductive etherification of carbonyl compounds.

13. Etherification of 6n with *i*-PrOH-d_7 and *i*-PrOH-d_8

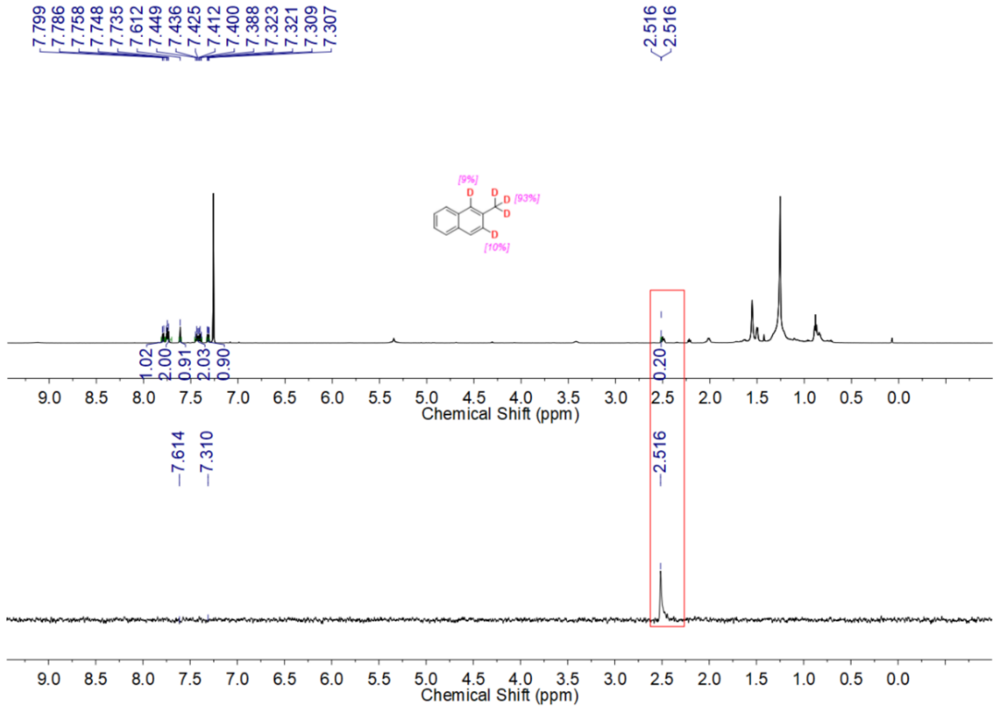
Table S4 Deuterium labeling study on the Ru(dppbsa)-catalyzed reductive etherification of aldehydes[a]



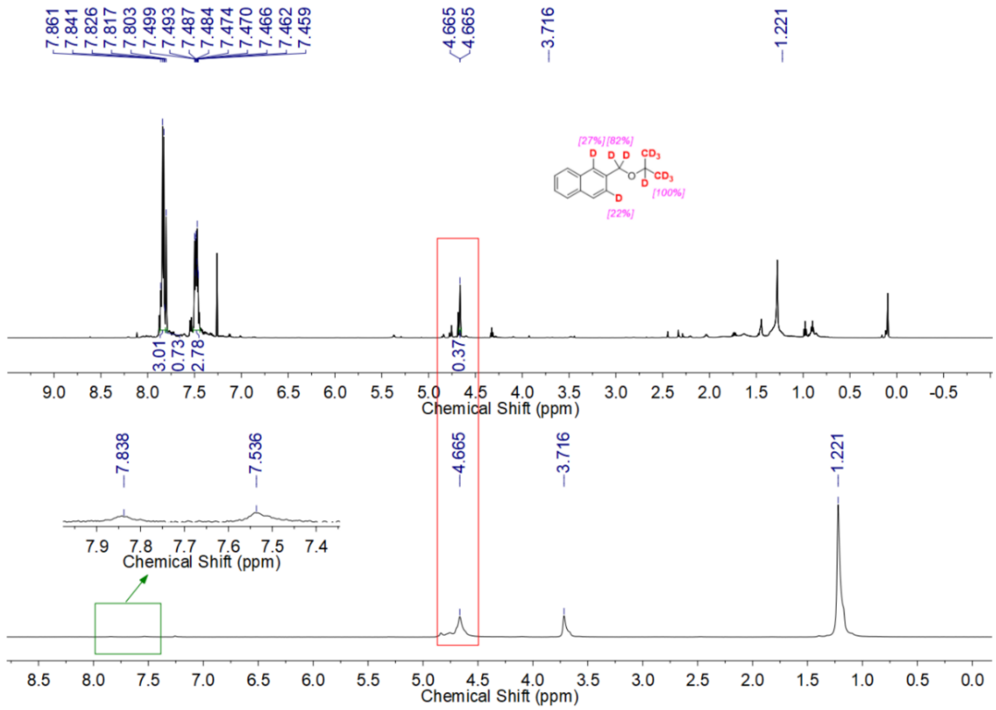
6n 9na-*d* 7n-*d*

8a	Yield (%)		D occupation (D%)							
			9na-*d*					7n-*d*		
	9na	7n	H^a	H^b	H^c	H^d	H^e	H^a	H^b	H^c
d_0	85	8	0	0	0	0	0	0	0	0
d_8	68	22	73	100	100	11	21	93	8	10
d_7	49	41	82	100	100	27	22	93	9	10

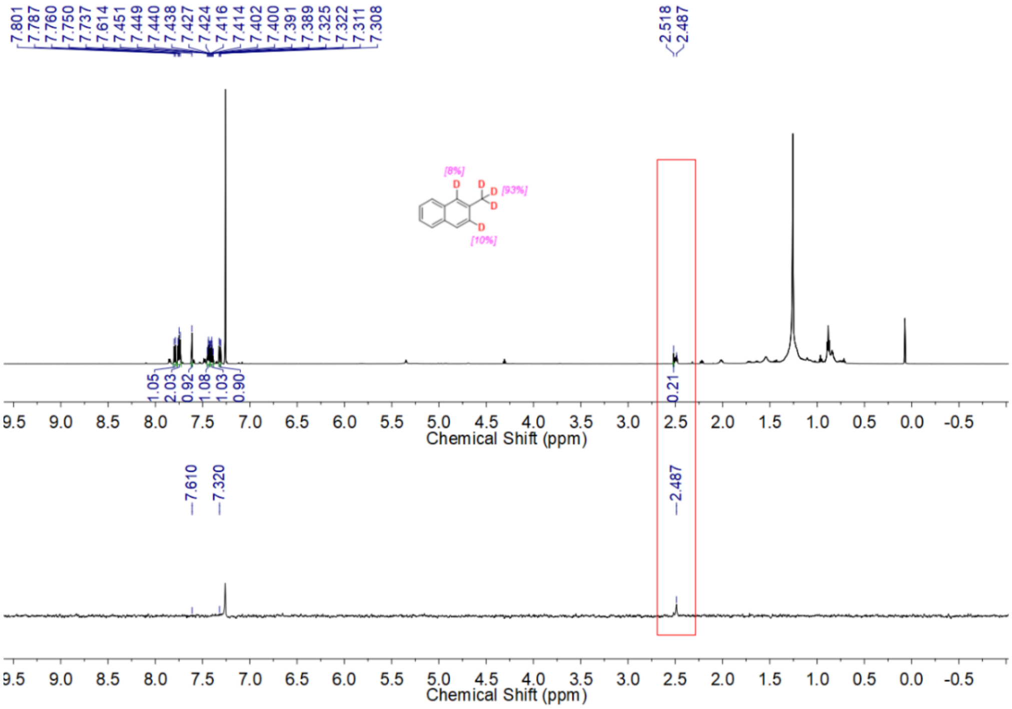
[a] General conditions: **6n** (0.2 mmol), under argon, in autoclave; [b] GC yield.



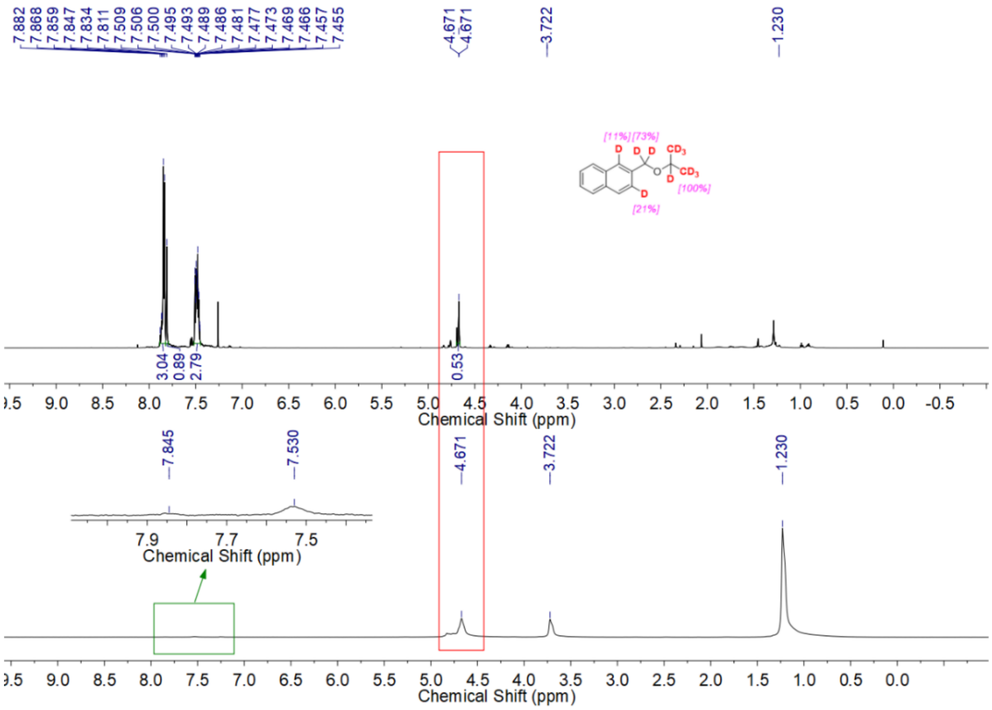
^{2}H NMR and ^{1}H NMR (600 MHz, $CDCl_3$, 298 K) of **7n**-*d* of **6n** with *i*-PrOH-d_7



^{2}H NMR and ^{1}H NMR (600 MHz, $CDCl_3$, 298 K) of **9na**-*d* of **6n** with *i*-PrOH-d_7



^{2}H NMR and ^{1}H NMR (600 MHz, $CDCl_3$, 298 K) of **7n**-*d* of **6n** with *i*-PrOH-*d*$_8$



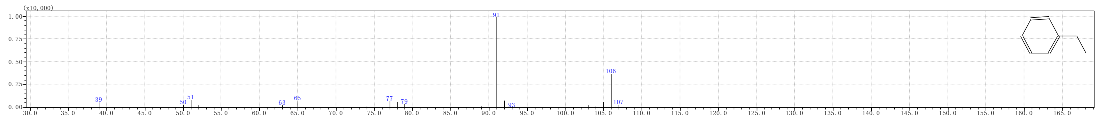
^{2}H NMR and ^{1}H NMR (600 MHz, $CDCl_3$, 298 K) of **9na**-*d* of **6n** with *i*-PrOH-*d*$_8$

14. NMR, GC and GC-MS data

1. Ethylbenzene (2a)

Analytically pure product was isolated by a column chromatography on silica gel (hexanes/EtOAc = 50:1). Colorless liquid, Yield: 18.2 mg, 86%. **^{1}H NMR** (600 MHz, $CDCl_3$, 298 K): δ = 7.43 (t, $^3J_{HH}$ = 7.5 Hz, 2H, Ph), 7.33 (m, 3H, Ph), 2.81 (q, $^3J_{HH}$ = 7.7 Hz, 2H, CH_2), 1.41 (t, $^3J_{HH}$ = 7.7 Hz, 3H, CH_3). **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$, 298 K): δ = 143.2, 127.3 (2C), 126.8 (2C), 124.5, 27.9, 14.6.

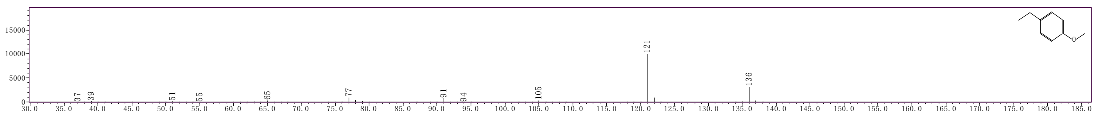
GC: **2a**: 3.979 min. Biphenyl: 8.858 min. GC-MS (m/z): Calcd. 106; Found 106.



2. 1-Ethyl-4-Methoxybenzene (2b)

Analytically pure product was isolated by a column chromatography on silica gel (hexanes/EtOAc = 50:1). Colorless liquid, Yield: 24.5 mg, 90%. **^{1}H NMR** (600 MHz, $CDCl_3$, 298 K): δ = 7.12 (d, $^3J_{HH}$ = 7.1 Hz, 2H, Ph), 6.83 (d, $^3J_{HH}$ = 6.8 Hz, 2H, Ph), 3.79 (s, 3H, CH_3), 2.56 (q, $^3J_{HH}$ = 7.6 Hz, 2H, CH_2), 1.21 (t, $^3J_{HH}$ = 7.7 Hz, 3H, CH_3). **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$, 298 K): δ = 157.6, 136.4, 128.7 (2C), 113.7 (2C), 55.3, 27.9, 15.9.

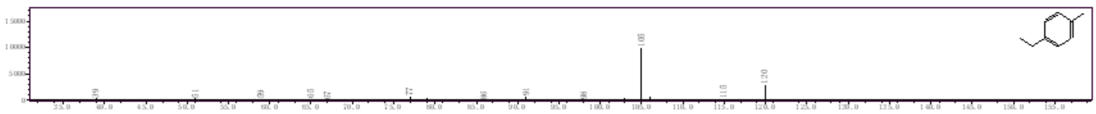
GC: **2b**: 6.689 min. GC-MS (m/z): Calcd. 136; Found 136.



3. 1-Ethyl-4-Methylbenzene (2c)

Analytically pure product was isolated by a column chromatography on silica gel (hexanes/EtOAc = 50:1). Colorless liquid, Yield: 21.1 mg, 88%. **^{1}H NMR** (600 MHz, $CDCl_3$, 298 K): δ = 7.11 (s, 4H, Ph), 2.63 (q, $^3J_{HH}$ = 7.6 Hz, 2H, CH_2), 2.33 (s, 3H, CH_3). **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$, 298 K): δ = 141.2, 135.0, 129.0 (2C), 127.7 (2C), 28.4, 20.9, 15.7.

GC: **2c**: 4.725 min. GC-MS (m/z): Calcd. 120; Found 120.

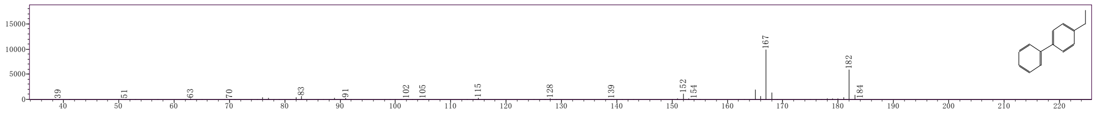


4. 4-Ethyl-1,1'-Biphenyl (2d)

Analytically pure product was isolated by a column chromatography on silica gel (hexanes/EtOAc = 50:1). Colorless liquid, Yield: 32.0 mg, 88%. **^{1}H NMR** (600 MHz, $CDCl_3$, 298 K): δ = 7.59 (dd, $^3J_{HH}$ = 8.4 Hz, 2H, Ph), 7.53 (dt, $^3J_{HH}$ = 8.4 Hz, 2H, Ph), 7.43 (t, $^3J_{HH}$

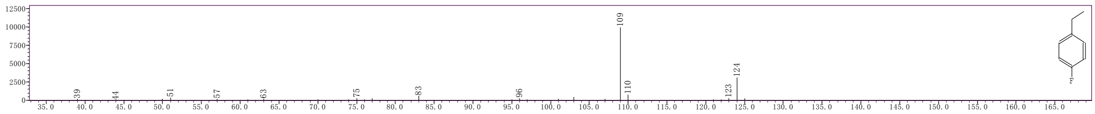
= 7.5 Hz, 2H, Ph), 7.33 (m, 1H, Ph), 7.28 (d, $^3J_{HH}$ = 8.2 Hz, 2H, Ph), 2.71 (q, $^3J_{HH}$ = 7.8 Hz, 2H, CH_2), 1.29 (t, $^3J_{HH}$ = 7.3 Hz, 3H, CH_3). **$^{13}C\{^1H\}$ NMR** (151 MHz, $CDCl_3$, 298 K): δ = 143.4, 141.2, 138.6, 128.7 (2C), 128.3 (2C), 127.1 (2C), 127.0 (2C), 126.9, 28.5, 15.6.

GC: **2d**: 9.670 min. GC-MS (m/z): Calcd. 182; Found 182.



5. 1-Ethyl-4-Fluorobenzene (2e)

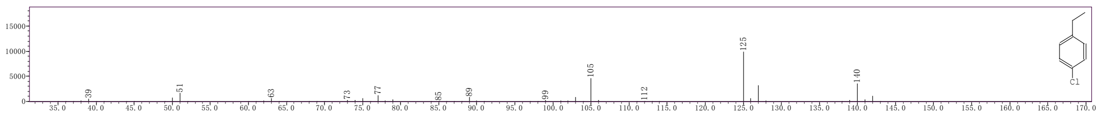
GC: **2e**: 4.315 min. GC-MS (m/z): Calcd. 124; Found 124.



6. 1-Ethyl-4-Chlorobenzene (2f)

Analytically pure product was isolated by a column chromatography on silica gel (hexanes/EtOAc = 50:1). Colorless liquid, Yield: 24.1 mg, 86%. **^1H NMR** (600 MHz, $CDCl_3$, 298 K): δ = 7.27 (m, 2H, Ph), 7.14 (d, $^3J_{HH}$ = 8.6 Hz, 2H, Ph), 2.64 (q, $^3J_{HH}$ = 7.5 Hz, 2H, CH_2), 1.24 (t, $^3J_{HH}$ = 7.5 Hz, 3H, CH_3). **$^{13}C\{^1H\}$ NMR** (151 MHz, $CDCl_3$, 298 K): δ = 142.6, 131.2, 129.2 (2C), 128.3 (2C), 28.2, 15.5.

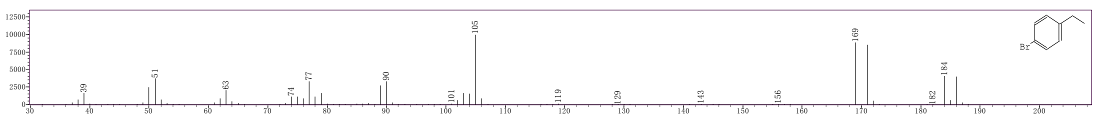
GC: **2f**: 5.988 min. GC-MS (m/z): Calcd. 140; Found 140.



7. 1-Ethyl-4-Bromobenzene (2g)

Analytically pure product was isolated by a column chromatography on silica gel (hexanes/EtOAc = 50:1). Colorless liquid, Yield: 29.6 mg, 80%. **^1H NMR** (600 MHz, $CDCl_3$, 298 K): δ = 7.39 (d, $^3J_{HH}$ = 8.3 Hz, 2H, Ph), 7.07 (d, $^3J_{HH}$ = 8.3 Hz, 2H, Ph), 2.60 (q, $^3J_{HH}$ = 7.7 Hz, 2H, CH_2), 1.21 (t, $^3J_{HH}$ = 7.9 Hz, 3H, CH_3). **$^{13}C\{^1H\}$ NMR** (151 MHz, $CDCl_3$, 298 K): δ = 143.1, 131.3 (2C), 129.6 (2C), 119.27, 28.3, 15.4.

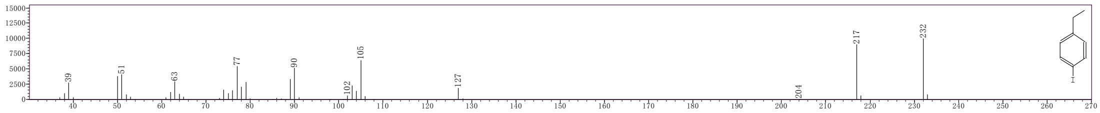
GC: **2g**: 6.766 min. GC-MS (m/z): Calcd. 185; Found 185.



8. 1-Ethyl-4-Iodobenzene (2h)

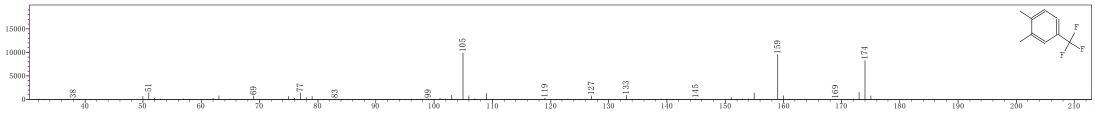
Analytically pure product was isolated by a column chromatography on silica gel (hexanes/EtOAc = 50:1). Colorless liquid, Yield: 23.2 mg, 50%. **^1H NMR** (600 MHz, $CDCl_3$, 298 K): δ = 7.59 (m, 2H, Ph), 6.95 (d, $^3J_{HH}$ = 8.3 Hz, 2H, Ph), 2.59 (q, $^3J_{HH}$ = 7.4 Hz, 2H, CH$_2$), 1.21 (t, $^3J_{HH}$ = 7.4 Hz, 3H, CH$_3$). **^{13}C{^{1}H} NMR** (151 MHz, CDCl$_3$, 298 K): δ = 143.8, 137.3 (2C), 130.0 (2C), 90.5, 28.4, 15.4.

GC: **2h**: 7.652 min. GC-MS (m/z): Calcd. 232; Found 232.



9. 1-Ethyl-4-(Trifluoromethyl)benzene (2i)

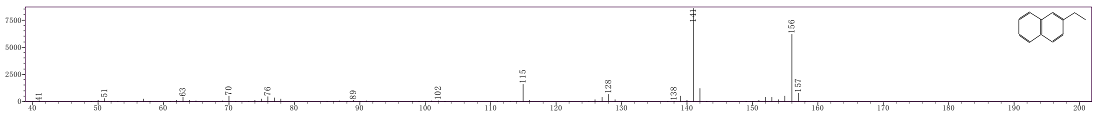
GC: **2i**: 4.175 min. GC-MS (m/z): Calcd. 174; Found 174.



10. 2-Ethylnaphthalene (2j)

Analytically pure product was isolated by a column chromatography on silica gel (hexanes/EtOAc = 100:1). Colorless liquid, Yield: 27.7 mg, 89%. **^{1}H NMR** (600 MHz, CDCl$_3$, 298 K): δ = 7.77 (m, 3H, Ph), 7.62 (s, 1H, Ph), 7.38 (m, 2H, Ph), 7.34 (dd, $^3J_{HH}$ = 8.4, 1.6 Hz, 1H, Ph), 2.81 (q, $^3J_{HH}$ = 7.9 Hz, 2H, CH$_2$), 1.32 (t, $^3J_{HH}$ = 7.7 Hz, 3H, CH$_3$). **^{13}C{^{1}H} NMR** (151 MHz, CDCl$_3$, 298 K): δ = 141.7, 133.7, 131.9, 127.8, 127.6, 127.4, 127.1, 125.8, 125.5, 125.0, 29.0, 15.5.

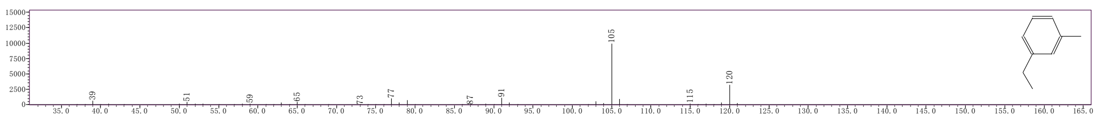
GC: **2j**: 8.692 min. GC-MS (m/z): Calcd. 156; Found 156.



11. 1-Ethyl-3-Methylbenzene (2k)

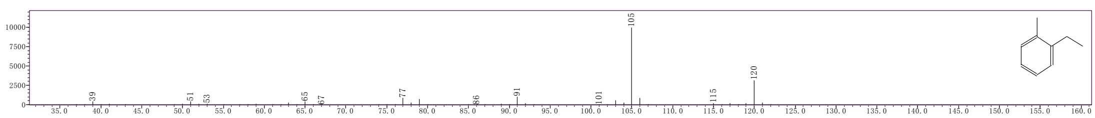
Analytically pure product was isolated by a column chromatography on silica gel (hexanes/EtOAc = 50:1). Colorless liquid, Yield: 20.4 mg, 85%. **^{1}H NMR** (600 MHz, CDCl$_3$, 298 K): δ = 7.18 (m, 3H, Ph), 7.13 (m, 1H, Ph), 2.67 (q, $^3J_{HH}$ = 7.5 Hz, 2H, CH$_2$), 2.34 (s, 3H, CH$_3$), 1.25 (t, $^3J_{HH}$ = 7.7 Hz, 3H, CH$_3$). **^{13}C{^{1}H} NMR** (151 MHz, CDCl$_3$, 298 K): δ = 142.3, 135.7 130.0, 127.9, 126.0, 125.7, 26.2, 19.1, 14.4.

GC: **2k**: 4.745 min. GC-MS (m/z): Calcd. 120; Found 120.



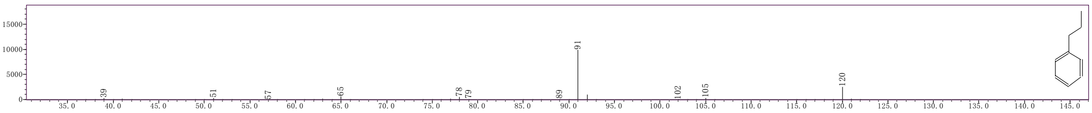
12. 1-Ethyl-2-Methylbenzene (2l)

GC: **2l**: 6.023 min. GC-MS (m/z): Calcd. 120; Found 120.



13. n-Propylbenzene (2m)

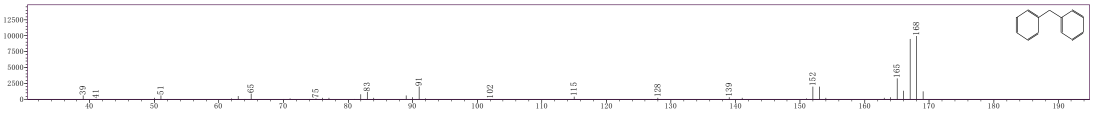
GC: **2m**: 4.632 min. GC-MS (m/z): Calcd. 120; Found 120.



14. Diphenylmethylene (2n)

Analytically pure product was isolated by a column chromatography on silica gel (hexanes/EtOAc = 100:1). Colorless liquid, Yield: 5.7 mg, 17%. **^{1}H NMR** (600 MHz, $CDCl_3$, 298 K): δ = 7.29 (m, 4H, Ph), 7.21 (m, 6H, Ph), 3.99 (s, 2H, CH_2). **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$, 298 K): δ = 141.1 (2C), 128.9 (4C), 128.4 (4C), 126.0 (2C), 41.9.

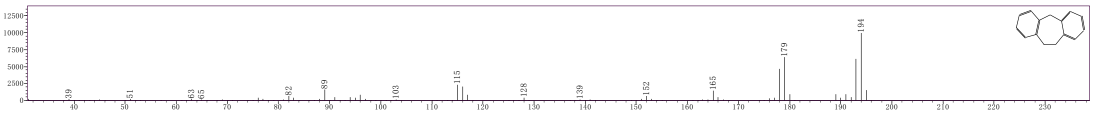
GC: **2n**: 8.938 min. GC-MS (m/z): Calcd. 168; Found 168.



15. 10,11-Dihydro-5*H*-Dibenzo[*a,d*]cycloheptene (2o)

Analytically pure product was isolated by a column chromatography on silica gel (hexanes/EtOAc = 20:1). White solid, Yield: 7.7 mg, 20%. **^{1}H NMR** (600 MHz, $CDCl_3$, 298 K): δ = 7.30 (m, 1H, Ph), 7.20 (dd, $^3J_{HH}$ = 7.3 Hz, 2H, Ph), 7.12 (m, 5H, Ph), 4.13 (s, 2H, CH_2), 3.19 (s, 4H, CH_2). **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$, 298 K): δ = 139.3 (2C), 138.9 (2C), 129.6 (2C), 129.0 (2C), 126.6 (2C), 126.1 (2C), 41.0, 32.5 (2C).

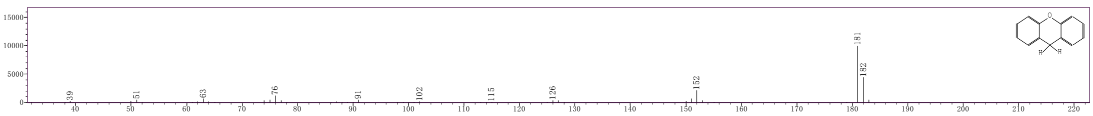
GC: **2o**: 11.071 min. GC-MS (m/z): Calcd. 194; Found 194.



16. 9*H*-Xanthene (2p)

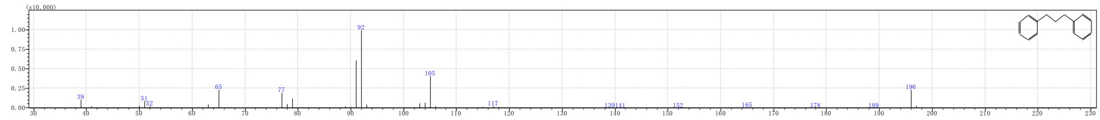
Analytically pure product was isolated by a column chromatography on silica gel (hexanes/EtOAc = 20:1). White solid, Yield: 2.9 mg, 8%. **^{1}H NMR** (600 MHz, $CDCl_3$, 298 K): δ = 7.17 (q, $^3J_{HH}$ = 8.0 Hz, 4H, Ph), 7.02 (q, $^3J_{HH}$ = 8.5 Hz, 4H, Ph), 4.06 (s, 2H, CH_2). **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$, 298 K): δ = 150.9, 127.8 (2C), 126.6 (2C), 121.9 (2C), 119.5, 115.4 (2C), 28.6, 26.9 (2C).

GC: **2p**: 10.574 min. GC-MS (m/z): Calcd. 182; Found 182.



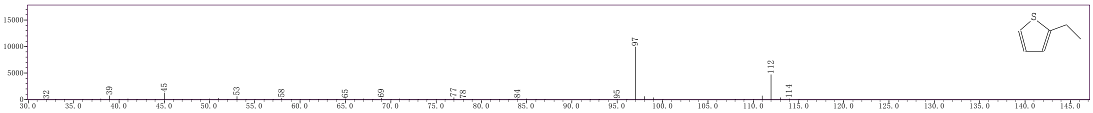
17. 1,3-Diphenylpropane (2q)

GC: **2q**: 9.021 min. GC-MS (m/z): Calcd. 196; Found 196.



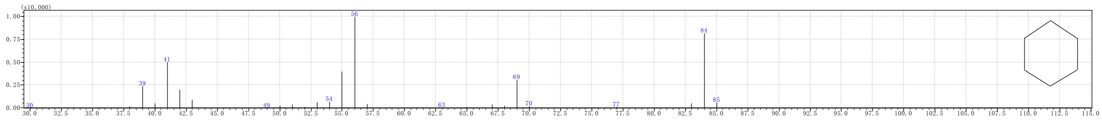
18. 2-Ethylthiophene (2r)

GC: **2r**: 4.347 min. GC-MS (m/z): Calcd. 114; Found 114.



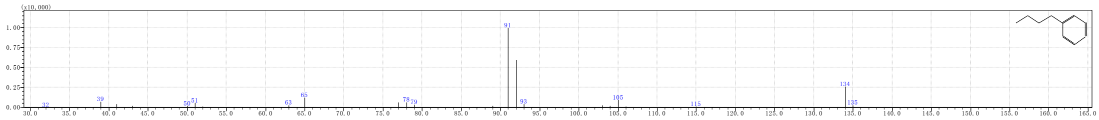
19. Cyclohexane (2s)

GC: **2s**: 1.657 min. GC-MS (m/z): Calcd. 84; Found 84.

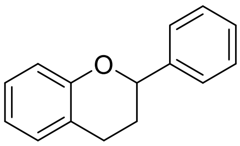


20. n-Butylbenzene (2t)

GC: **2t**: 5.385 min. GC-MS (m/z): Calcd. 134; Found 134.



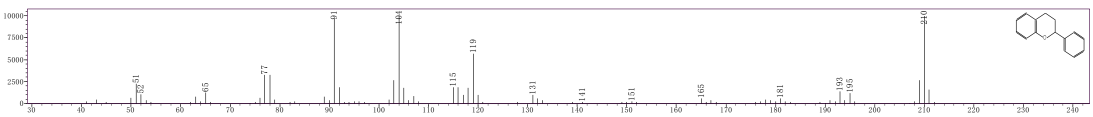
21. Flavan (2u)



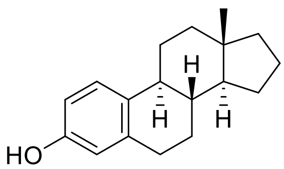
2u

Analytically pure product was isolated by a column chromatography on silica gel (hexanes/EtOAc = 10:1). Yellow solid, Yield: 33.1 mg, 79%. **^{1}H NMR** (600 MHz, $CDCl_3$, 298 K): δ = 7.98 (dd, $^3J_{HH}$ = 8.1, 1.3 Hz, 2H, Ph), 7.89 (s, 1H, Ph), 7.57 (t, $^3J_{HH}$ = 7.5 Hz, 1H, Ph), 7.45 (t, $^3J_{HH}$ = 7.9 Hz, 2H, Ph), 7.11 (m, 2H, Ph), 6.91 (d, $^3J_{HH}$ = 8.0 Hz, 1H, Ph), 6.85 (td, $^3J_{HH}$ = 7.4, 1.0 Hz, 1H, CH), 3.45 (t, $^3J_{HH}$ = 6.1 Hz, 2H, CH_2), 3.04 (t, $^3J_{HH}$ = 6.3 Hz, 2H, CH_2). **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$, 298 K): δ = 202.0, 154.5, 136.1, 133.8, 130.6, 128.7 (2C), 128.3 (2C), 128.0, 127.7, 120.7, 117.5, 40.4, 23.4.

GC: **2u**: 11.485 min. GC-MS (m/z): Calcd. 210; Found 210.



22. 1, 3, 5 (10)-estratrien-3-ol (2v)

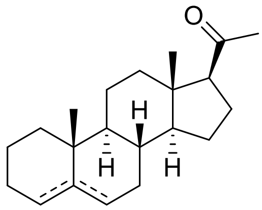


2v

Analytically pure product was isolated by a column chromatography on silica gel (CH_2Cl_2/MeOH = 10:1). White solid, Yield: 16.9 mg, 33%. **^{1}H NMR** (600 MHz, $CDCl_3$, 298 K): δ = 7.14 (d, $^3J_{HH}$ = 8.4 Hz, 1H, Ph), 6.62 (dd, $^3J_{HH}$ = 8.5, 2.6 Hz, 1H, Ph), 6.55 (d, $^3J_{HH}$ = 2.7 Hz, 1H, Ph), 4.68 (t, $^3J_{HH}$ = 8.5 Hz, 1H, Cy), 2.81 (m, 2H, Cy), 2.26

(m, 1H, Cy), 2.19 (m, 1H, Cy), 2.05 (s, 2H, Cy), 1.87 (m, 2H, Cy), 1.73 (m, 1H, Cy), 1.54 (s, 2H, Cy), 1.25 (s, 6H, CH_2), 0.82 (s, 3H, CH_3). **$^{13}C\{^1H\}$ NMR** (151 MHz, $CDCl_3$, 298 K): δ = 152.0, 136.9, 129.1, 124.1, 113.8, 111.9, 109.2, 52.6, 42.0, 41.9, 37.9, 37.8, 34.5, 30.1, 28.6, 27.3, 21.3, 13.1.

23. Pregn-4-en-20-one and Pregn-5-en-20-one (2w)



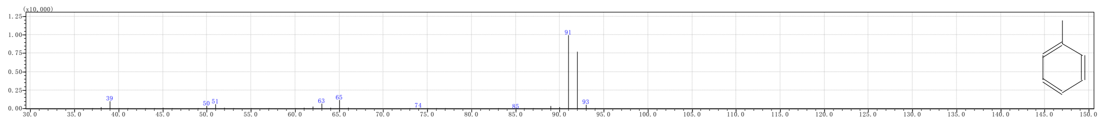
2w

Analytically pure product was isolated by a column chromatography on silica gel (CH_2Cl_2/MeOH = 10:1). White solid, Yield: 28.7 mg, 48% (isomers were not separated). **^1H NMR** (600 MHz, $CDCl_3$, 298 K): δ = 5.28 (br s, 1H), 5.24 (d, 1H), 2.51 (q, $^3J_{HH}$ = 9.1 Hz, 2H), 2.12-2.23 (m, 4H), 2.10 (s, 2H), 2.11 (d, $^3J_{HH}$ = 2.6 Hz, 4H), 0.93-2.07 (m, 40 H), 0.90 (m, 3H), 0.76 (s, 3H), 0.6 (m, 6H). **$^{13}C\{^1H\}$ NMR** (151 MHz, $CDCl_3$, 298 K): δ = 209.6, 209.6, 144.5, 143.5, 119.2, 118.6, 63.9, 63.8, 56.8, 56.77, 54.5, 46.9, 44.3, 43.5, 40.4, 39.3, 39.1, 38.6, 37.5, 36.2, 35.8, 35.4, 32.0, 28.9, 28.8, 27.3, 27.1, 26.9, 26.7, 26.5, 24.4, 24.3, 24.1, 22.8, 22.6, 22.1, 21.2, 20.7, 20.75, 13.4, 13.36, 12.1. ^1H and ^{13}C NMR spectral data are in good agreement with the literature data.[S3]

24. Toluene (7a)

Analytically pure product was isolated by a column chromatography on silica gel (hexanes/EtOAc = 50:1). White solid, Yield: 14.7 mg, 80%. **^1H NMR** (600 MHz, $CDCl_3$, 298 K): δ = 7.28 (t, $^3J_{HH}$ = 7.4 Hz, 2H, Ph), 7.19 (m, 3H, Ph), 2.38 (s, 3H, CH_3). **$^{13}C\{^1H\}$ NMR** (151 MHz, $CDCl_3$, 298 K): δ = 137.9, 129.0 (2C), 128.2 (2C), 125.3, 21.4.

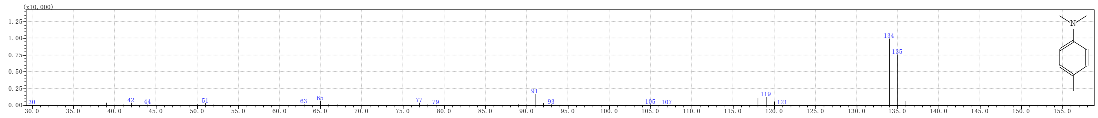
GC: **7a**: 3.210 min. GC-MS (m/z): Calcd. 92; Found 92.



25. 4,N,N-Trimethylaniline (7b)

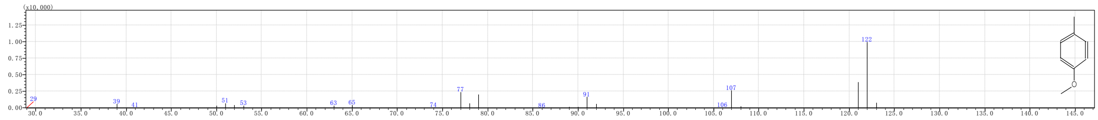
Analytically pure product was isolated by a column chromatography on silica gel (hexanes/EtOAc = 50:1). Light yellow liquid, Yield: 17.8 mg, 66%. **^1H NMR** (600 MHz, $CDCl_3$, 298 K): δ = 7.07 (dd, $^3J_{HH}$ = 8.1 Hz, 2H, Ph), 6.71 (dd, $^3J_{HH}$ = 8.1 Hz, 2H, Ph), 2.91 (s, 6H, CH_3), 2.27 (s, 3H, CH_3). **$^{13}C\{^1H\}$ NMR** (151 MHz, $CDCl_3$, 298 K): δ = 148.7, 129.6 (4C), 113.3, 41.1, 20.2 (2C).

GC: **7b**: 7.167 min. GC-MS (m/z): Calcd. 135; Found 135.



26. 1-Methoxy-4-Methylbenzene (7c)

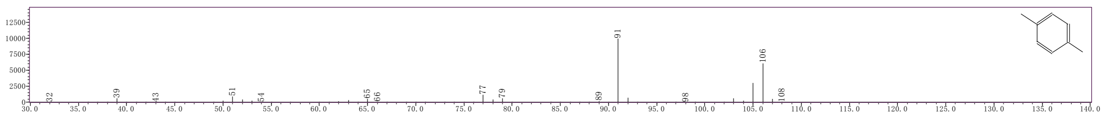
GC: **7c**: 6.204 min. GC-MS (m/z): Calcd. 122; Found 122.



27. *p*-Xylene (7d)

Analytically pure product was isolated by a column chromatography on silica gel (hexanes/EtOAc = 50:1). Colorless liquid, Yield: 16.7 mg, 79%. **^{1}H NMR** (600 MHz, $CDCl_3$, 298 K): δ = 7.12 (s, 4H, Ph), 2.37 (s, 6H, CH_3). **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$, 298 K): δ = 134.7 (2C), 128.9 (4C), 21.0 (2C).

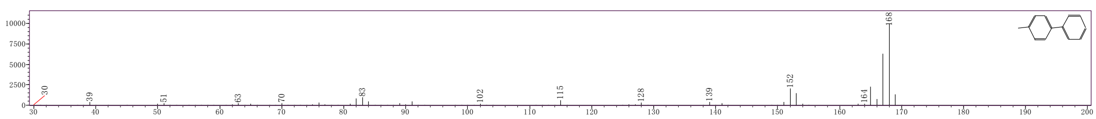
GC: **7d**: 4.024 min. GC-MS (m/z): Calcd. 106; Found 106.



28. 4-Phenyltoluene (7e)

Analytically pure product was isolated by a column chromatography on silica gel (hexanes/EtOAc = 100:1). Colorless liquid, Yield: 26.9 mg, 80%. **^{1}H NMR** (600 MHz, $CDCl_3$, 298 K): δ = 7.58 (d, $^{3}J_{HH}$ = 7.9 Hz, 2H, Ph), 7.49 (d, $^{3}J_{HH}$ = 7.5 Hz, 2H, Ph), 7.42 (t, $^{3}J_{HH}$ = 7.5 Hz, 2H, Ph), 7.32 (t, $^{3}J_{HH}$ = 7.4 Hz, 2H, Ph), 7.25 (m, 2H, Ph), 2.40 (s, 3H, CH_3). **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$, 298 K): δ = 141.1, 138.3, 137.0, 129.4 (2C), 128.7 (2C), 127.0 (2C), 126.9 (3C), 21.1.

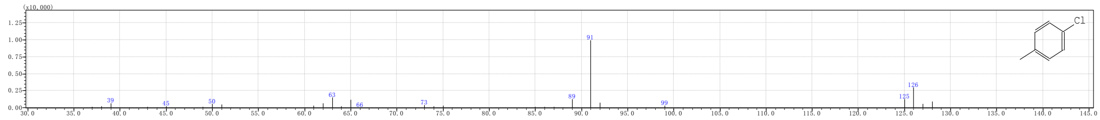
GC: **7e**: 9.286 min. GC-MS (m/z): Calcd. 168; Found 168.



29. 4-Chlorotoluene (7f)

Analytically pure product was isolated by a column chromatography on silica gel (hexanes/EtOAc = 50:1). Colorless liquid, Yield: 19.6 mg, 78%. **^{1}H NMR** (600 MHz, $CDCl_3$, 298 K): δ = 7.21 (dd, $^{3}J_{HH}$ = 8.3 Hz, 2H, Ph), 7.09 (dd, $^{3}J_{HH}$ = 8.1 Hz, 2H, Ph), 2.32 (s, 3H, CH_3). **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$, 298 K): δ = 136.2, 131.0, 130.3 (2C), 128.2 (2C), 20.8.

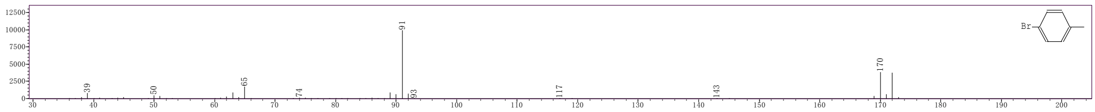
GC: **7f**: 5.449 min. GC-MS (m/z): Calcd. 126; Found 126.



30. 4-Bromotoluene (7g)

Analytically pure product was isolated by a column chromatography on silica gel (hexanes/EtOAc = 50:1). Light yellow liquid, Yield: 30.1 mg, 88%. **^{1}H NMR** (600 MHz, $CDCl_3$, 298 K): δ = 7.37 (dd, $^3J_{HH}$ = 8.3 Hz, 2H, Ph), 7.03 (dd, $^3J_{HH}$ = 8.3 Hz, 2H, Ph), 2.30 (s, 3H, CH_3). **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$, 298 K): δ = 136.7, 131.2 (2C), 130.8 (2C), 119.0, 21.0.

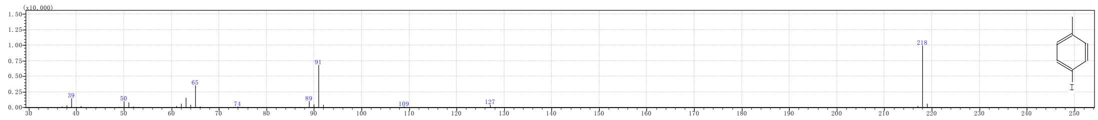
GC: **7g**: 6.257 min. GC-MS (m/z): Calcd. 171; Found 171.



31. 4-Iodotoluene (7h)

Analytically pure product was isolated by a column chromatography on silica gel (hexanes/EtOAc = 50:1). Colorless liquid, Yield: 38.3 mg, 88%. **^{1}H NMR** (600 MHz, $CDCl_3$, 298 K): δ = 7.56 (d, $^3J_{HH}$ = 8.5 Hz, 2H, Ph), 6.93 (d, $^3J_{HH}$ = 8.5 Hz, 2H, Ph), 2.29 (s, 3H, CH_3). **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$, 298 K): δ = 137.4, 137.2 (2C), 131.2 (2C), 90.2, 21.0.

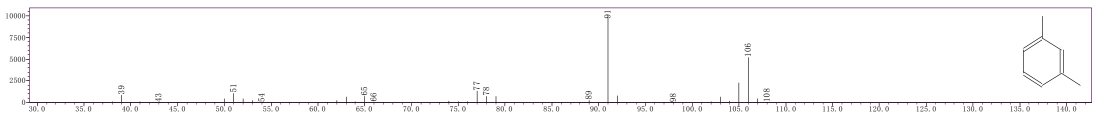
GC: **7h**: 7.192 min. GC-MS (m/z): Calcd. 218; Found 218.



32. *m*-Xylene (7j)

Analytically pure product was isolated by a column chromatography on silica gel (hexanes/EtOAc = 50:1). Colorless liquid, Yield: 14.4 mg, 68%. **^{1}H NMR** (600 MHz, $CDCl_3$, 298 K): δ = 7.17 (t, $^3J_{HH}$ = 7.6 Hz, 1H, Ph), 7.01 (t, $^3J_{HH}$ = 7.6 Hz, 3H, Ph), 2.34 (s, 3H, CH_3). **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$, 298 K): δ = 137.8 (2C), 129.9, 128.1, 126.0 (2C), 21.3.

GC: **7j**: 4.076 min. GC-MS (m/z): Calcd. 106; Found 106.

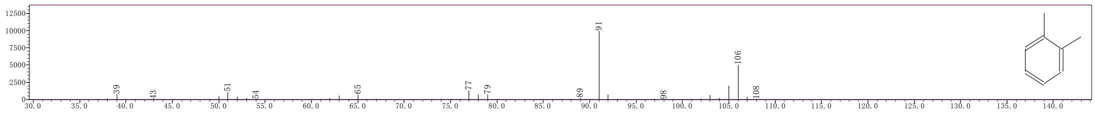


33. *o*-Xylene (7k)

Analytically pure product was isolated by a column chromatography on silica gel (hexanes/EtOAc = 50:1). Colorless liquid, Yield: 10.6 mg, 50%. **^{1}H NMR** (600 MHz, $CDCl_3$, 298 K): δ = 7.15 (m, 2H, Ph), 7.11 (m, 2H, Ph), 2.28 (s, 6H, CH_3). **^{13}C{^{1}H} NMR** (151 MHz,

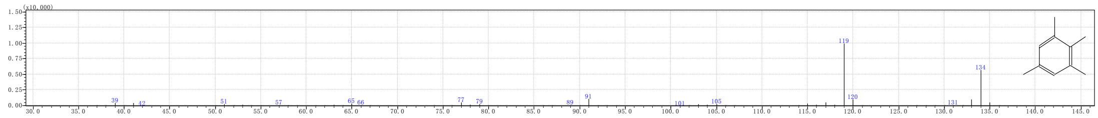
$CDCl_3$, 298 K): δ = 136.5 (2C), 129.5 (2C), 125.7 (2C), 19.7 (2C).

GC: **7k**: 4.438 min. GC-MS (m/z): Calcd. 106; Found 106.



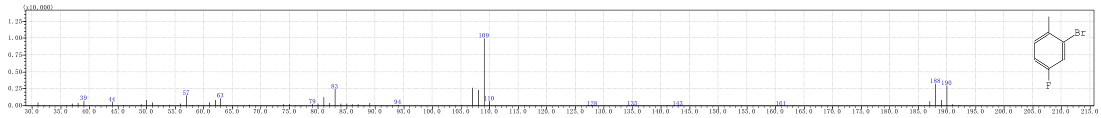
34. 1,2,3,5-Tetramethylbenzene (7l)

GC: **7l**: 6.165 min. GC-MS (m/z): Calcd. 134; Found 134.



35. 2-Bromo-4-Fluorotoluene (7m)

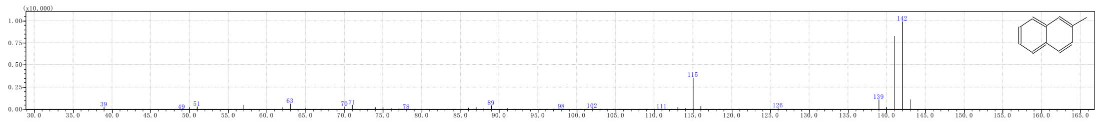
GC: **7m**: 6.017 min. GC-MS (m/z): Calcd. 189; Found 189.



36. 2-Methylnaphthalene (7n)

Analytically pure product was isolated by a column chromatography on silica gel (hexanes/EtOAc = 100:1). White solid, Yield: 24.4 mg, 86%. **^{1}H NMR** (600 MHz, $CDCl_3$, 298 K): δ = 7.79 (dd, $^3J_{HH}$ = 7.7 Hz, 1H, Ph), 7.75 (t, $^3J_{HH}$ = 6.3 Hz, 2H, Ph), 7.61 (s, 1H, Ph), 7.42 (m, 2H, Ph), 7.32 (d, $^3J_{HH}$ = 8.4 Hz, 1H, Ph), 2.52 (s, 3H, CH_3). **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$, 298 K): δ = 135.4 (2C), 133.6, 131.7, 128.1, 127.7, 127.6, 127.2, 126.8, 125.8, 124.9, 21.7.

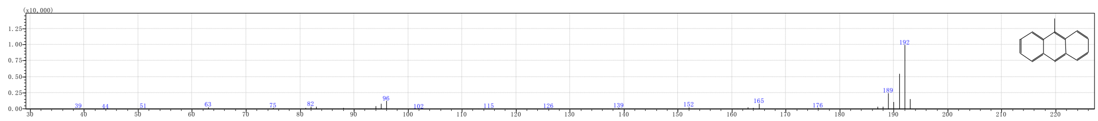
GC: **7n**: 8.318 min. GC-MS (m/z): Calcd. 142; Found 142.



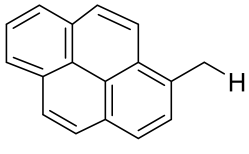
37. 9-Methylanthracene (7o)

Analytically pure product was isolated by a column chromatography on silica gel (hexanes/EtOAc = 100:1). Yellow solid, Yield: 26.5 mg, 69%. **^{1}H NMR** (600 MHz, $CDCl_3$, 298 K): δ = 8.34 (s, 1H, Ph), 8.29 (d, $^3J_{HH}$ = 8.5 Hz, 2H, Ph), 8.00 (d, $^3J_{HH}$ = 8.5 Hz, 1H, Ph), 7.52 (m, 2H, Ph), 7.46 (m, 2H, Ph), 3.11 (s, 3H, CH_3). **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$, 298 K): δ = 130.4 (2C), 129.0 (2C), 128.0 (4C), 124.2 (2C), 123.7 (2C), 123.6 (2C), 12.9.

GC: **7o**: 13.397 min. GC-MS (m/z): Calcd. 192; Found 192.



38. 1-Methylpyrene (7p)

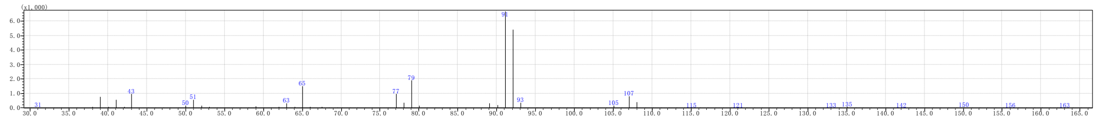


7p

Analytically pure product was isolated by a column chromatography on silica gel (hexanes/EtOAc = 20:1). White solid, Yield: 27.2 mg, 63%. **^{1}H NMR** (600 MHz, $CDCl_3$, 298 K): δ = 8.25 (d, $^3J_{HH}$ = 8.9 Hz, 1H, Ph), 8.19 (d, $^3J_{HH}$ = 7.3 Hz, 1H, Ph), 8.15 (d, $^3J_{HH}$ = 8.3 Hz, 1H, Ph), 8.12 (d, $^3J_{HH}$ = 9.2 Hz, 1H, Ph), 8.08 (s, 1H, Ph), 8.03 (q, $^3J_{HH}$ = 8.9 Hz, 2H, Ph), 7.99 (t, $^3J_{HH}$ = 7.3 Hz, 1H, Ph), 7.87 (d, $^3J_{HH}$ = 7.7 Hz, 1H, Ph), 2.99 (s, 3H, CH_3). **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$, 298 K): δ = 127.8, 127.5, 127.4 (2C), 127.1, 126.4, 125.8, 125.7, 124.9 (2C), 124.8 (3C), 124.7, 124.6, 123.7, 19.8. ^{1}H and ^{13}C NMR spectral data are in good agreement with the literature data.[S4]

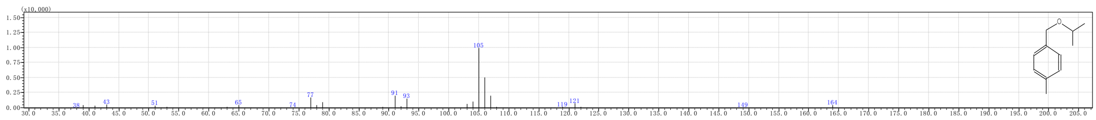
39. Propan-2-Yloxymethylbenzene (9aa)

GC: **9aa**: 8.281 min. GC-MS (m/z): Calcd. 150; Found 150. HRMS (ESI) m/z calcd for $C_{10}H_{15}O^+$ $(M+H)^+$: 151.1014; found: 151.1006.



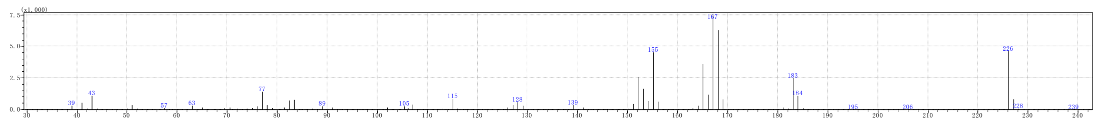
40. 1-Methyl-4-[(1-Methylethoxy)methyl]benzene (9da)

GC: **9da**: 9.493 min. GC-MS (m/z): Calcd. 164; Found 164. HRMS (ESI) m/z calcd for $C_{11}H_{17}O^+$ $(M+H)^+$: 165.1236; found: 165.1241.



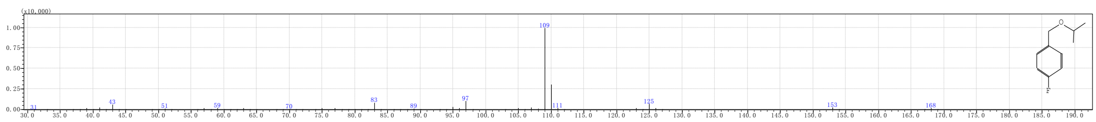
41. 4-[(1-Methylethoxy)methyl]-1,1'-Biphenyl (9ea)

GC: **9ea**: 18.226 min. GC-MS (m/z): Calcd. 226; Found 226. HRMS (ESI) m/z calcd for $C_{16}H_{19}O^+$ $(M+H)^+$: 227.1459; found: 227.1450.



42. 1-Fluoro-4-[(1-Methylethoxy)methyl]benzene (9qa)

GC: **9qa**: 8.651 min. GC-MS (m/z): Calcd. 168; Found 168. HRMS (ESI) m/z calcd for $C_{10}H_{14}FO^+$ $(M+H)^+$: 169.1028; found: 169.1022.

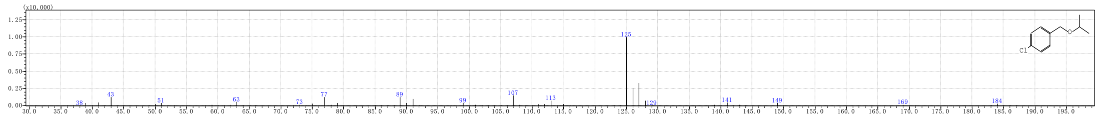


43. 1-Chloro-4-[(1-Methylethoxy)methyl]benzene (9fa)

Analytically pure product was isolated by a column chromatography on silica gel (hexanes/EtOAc = 100:1). Yellow liquid, Yield: 29.4 mg, 80%. **^{1}H NMR** (600 MHz, $CDCl_3$, 298 K): δ = 7.30 (m, 4H, Ph), 4.47 (s, 2H, CH_2), 3.67 (m, 1H, CH), 1.21 (d, 6H, CH_3). **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$, 298 K): δ = 137.6, 133.0, 128.8 (2C), 128.4 (2C), 71.1, 69.2, 22.1 (2C).

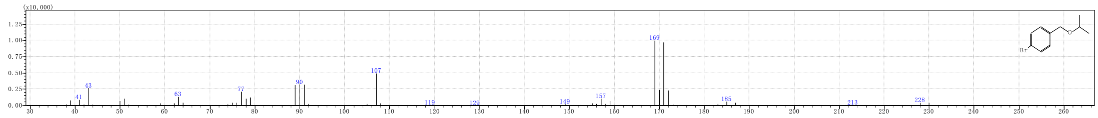
GC: **9fa**: 10.884 min. GC-MS (m/z): Calcd. 184; Found 184. HRMS (ESI) m/z calcd for

$C_{10}H_{14}ClO^+$ $(M+H)^+$: 185.0761; found: 185.0755.



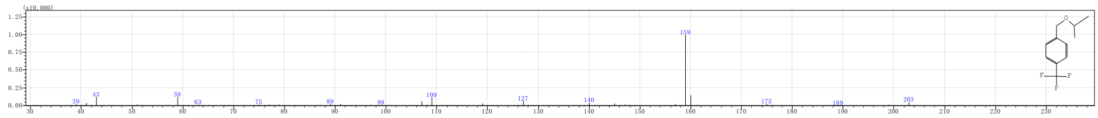
44. 1-Bromo-4-[(1-Methylethoxy)methyl]benzene (9ga)

GC: **9ga**: 11.724 min. GC-MS (m/z): Calcd. 229; Found 229. HRMS (ESI) m/z calcd for $C_{10}H_{14}BrO^+$ $(M+H)^+$: 229.0274; found: 229.0268.



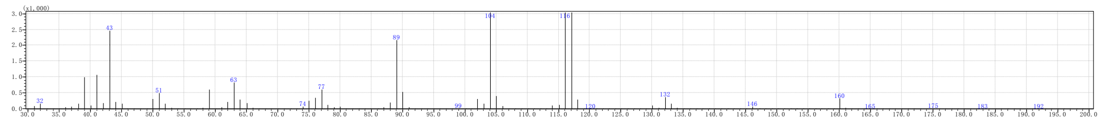
45. 1-Trifluoromethyl-4-[(1-Methylethoxy)methyl]benzene (9ra)

GC: **9ra**: 12.046 min. GC-MS (m/z): Calcd. 218; Found 218. HRMS (ESI) m/z calcd for $C_{11}H_{14}F_3O^+$ $(M+H)^+$: 219.1066; found: 219.1070.



46. 4-[(1-Methylethoxy)methyl]benzonitrile (9ia)

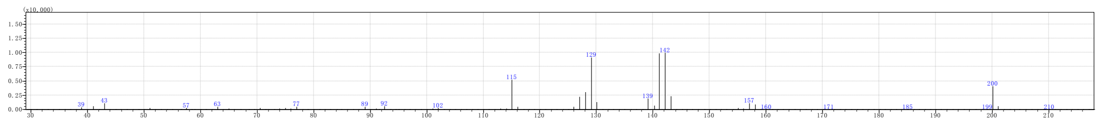
GC: **9ia**: 13.267 min. GC-MS (m/z): Calcd. 175; Found 175. HRMS (ESI) m/z calcd for $C_{11}H_{14}NO^+$ $(M+H)^+$: 176.1023; found: 176.1015.



47. 2-[(1-Methylethoxy)methyl]naphthalene (9na)

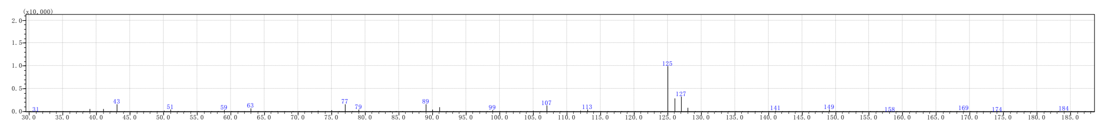
Analytically pure product was isolated by a column chromatography on silica gel (hexanes/EtOAc = 100:1). Yellow liquid, Yield: 32.0 mg, 99%. **^{1}H NMR** (600 MHz, $CDCl_3$, 298 K): δ = 7.49 (m, 4H, Ph), 7.34 (t, $^3J_{HH}$ = 8.1 Hz, 3H, Ph), 7.25 (t, $^3J_{HH}$ = 7.9 Hz, 1H, Ph), 4.47 (s, 2H, CH_2), 3.63 (m, 1H, CH), 1.16 (d, 6H, CH_3). **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$, 298 K): δ = 140.0, 139.3, 137.1, 127.7 (2C), 126.9 (2C), 126.1 (2C), 126.0, 69.9, 68.7, 21.1 (2C).

GC: **9na**: 14.664 min. GC-MS (m/z): Calcd. 200; Found 200. HRMS (ESI) m/z calcd for $C_{14}H_{17}O^+$ $(M+H)^+$: 201.1268; found: 201.1263.



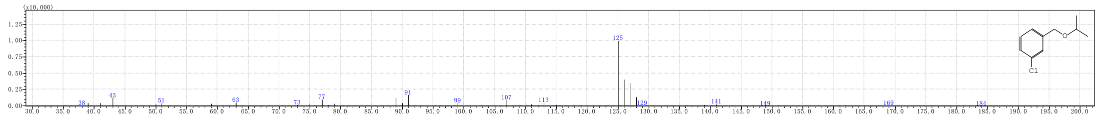
48. 1-Chloro-2-[(1-Methylethoxy)methyl]benzene (9sa)

GC: **9sa**: 12.273 min. GC-MS (m/z): Calcd. 184; Found 184. HRMS (ESI) m/z calcd for $C_{10}H_{14}ClO^+$ $(M+H)^+$: 185.0778; found: 185.0766.



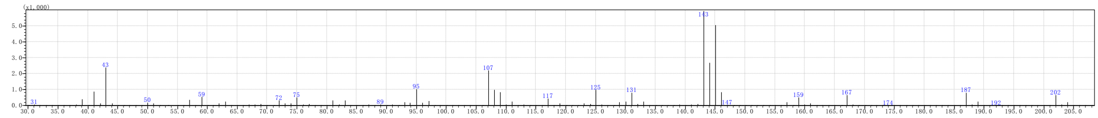
49. 1-Chloro-3-[(1-Methylethoxy)methyl]benzene (9ta)

GC: **9ta**: 10.826 min. GC-MS (m/z): Calcd. 184; Found 184. HRMS (ESI) m/z calcd for $C_{10}H_{14}ClO^+$ $(M+H)^+$: 185.0755; found: 185.0748.



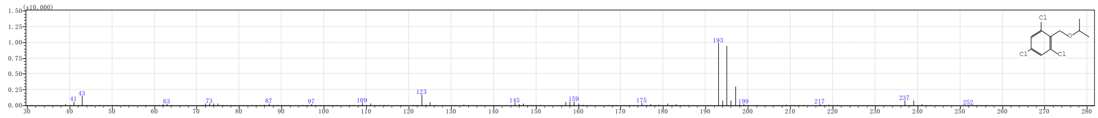
50. 1-Chloro-3-Fluoro-4-[(1-Methylethoxy)methyl]benzene (9ua)

GC: **9ua**: 10.170 min. GC-MS (m/z): Calcd. 202; Found 202. HRMS (ESI) m/z calcd for $C_{10}H_{13}ClFO^+$ $(M+H)^+$: 203.0677; found: 203.0669.



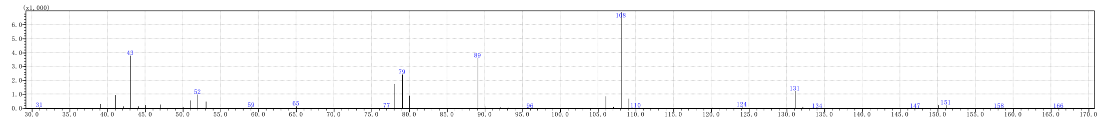
51. 1-[(1-Methylethoxy)methyl]-2,4,6-Trichlorophenylbenzene (9va)

GC: **9va**: 12.296 min. GC-MS (m/z): Calcd. 253; Found 253. HRMS (ESI) m/z calcd for $C_{10}H_{12}Cl_3O^+$ $(M+H)^+$: 253.9816; found: 253.9820.



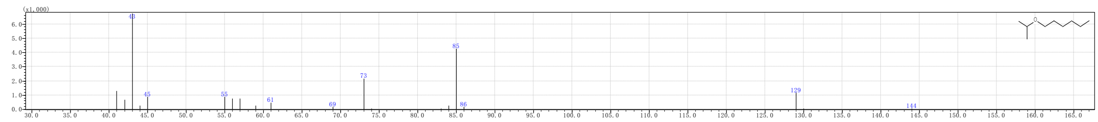
52. 2-[(1-Methylethoxy)methyl]pyridine (9wa)

GC: **9wa**: 12.284 min. GC-MS (m/z): Calcd. 151; Found 151. HRMS (ESI) m/z calcd for $C_9H_{14}NO^+$ $(M+H)^+$: 152.1043; found: 152.1038.



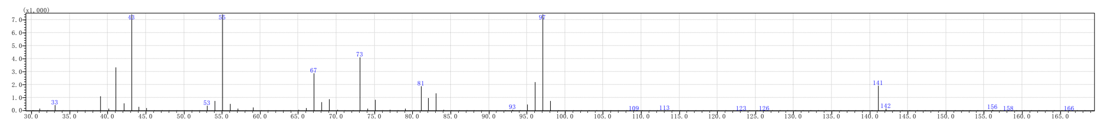
53. 1-Isopropoxyhexane (9xa)

GC: **9xa**: 11.512 min. GC-MS (m/z): Calcd. 144; Found 144. HRMS (ESI) m/z calcd for $C_9H_{21}O^+$ $(M+H)^+$: 145.1529; found: 145.1521.



54. [(1-Methylethoxy)methyl]cyclohexane (9ya)

GC: **9ya**: 9.430 min. GC-MS (m/z): Calcd. 156; Found 156. HRMS (ESI) m/z calcd for $C_{10}H_{21}O^+$ $(M+H)^+$: 157.1591; found: 157.1588.

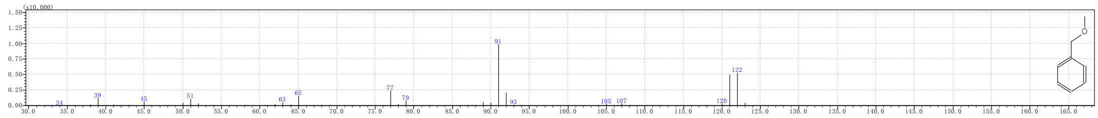


55. (Methoxymethyl)benzene (9ab)

Analytically pure product was isolated by a column chromatography on silica gel (hexanes/EtOAc = 100:1). Colorless liquid, Yield: 2.4 mg, 10%. **^{1}H NMR** (600 MHz, $CDCl_3$, 298 K): δ = 7.35 (m, 4H, Ph), 7.30 (m, 1H, Ph), 4.47 (s, 2H, CH_2), 3.40 (s, 3H, CH_3). **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$, 298 K): δ = 138.2, 128.4 (2C), 127.7 (2C), 127.6, 74.7, 58.1.

GC: **9ab**: 10.595 min. GC-MS (m/z): Calcd. 122; Found 122. HRMS (ESI) m/z calcd for

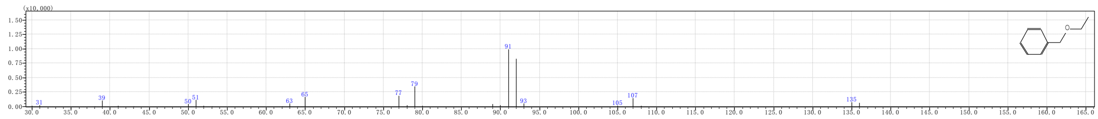
$C_8H_{11}O^+$ $(M+H)^+$: 123.0865; found: 123.0858.



56. (Ethoxymethyl)benzene (9ac)

Analytically pure product was isolated by a column chromatography on silica gel (hexanes/EtOAc = 100:1). Colorless liquid, Yield: 21.7 mg, 80%. **^{1}H NMR** (600 MHz, $CDCl_3$, 298 K): δ = 7.35 (m, 4H, Ph), 7.29 (m, 1H, Ph), 4.52 (s, 2H, CH_2), 3.55 (q, $^3J_{HH}$ = 7.0 Hz, 2H, CH_2), 1.26 (t, $^3J_{HH}$ = 7.0 Hz, 3H, CH_3). **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$, 298 K): δ = 138.6, 128.3 (2C), 127.7 (2C), 127.5, 72.7, 65.7, 15.2.

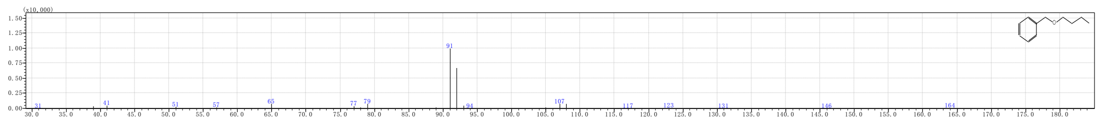
GC: **9ac**: 12.410 min. GC-MS (m/z): Calcd. 136; Found 136. HRMS (ESI) m/z calcd for $C_9H_{13}O^+$ $(M+H)^+$: 137.0976; found: 137.0964.



57. (Butoxymethyl)benzene (9ad)

Analytically pure product was isolated by a column chromatography on silica gel (hexanes/EtOAc = 100:1). Colorless liquid, Yield: 24.9 mg, 76%. **^{1}H NMR** (600 MHz, $CDCl_3$, 298 K): δ = 7.34 (d, $^3J_{HH}$ = 4.8 Hz, 4H, Ph), 7.28 (m, 1H, Ph), 4.51 (s, 2H, CH_2), 3.48 (t, $^3J_{HH}$ = 6.5 Hz, 2H, CH_2), 1.60 (m, 2H, CH_2), 1.41 (m, 2H, CH_2), 0.92 (t, $^3J_{HH}$ = 7.4 Hz, 3H, CH_3). **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$, 298 K): δ = 138.7, 128.3 (2C), 127.6 (2C), 127.4, 72.8, 70.2, 31.8, 19.4, 13.9.

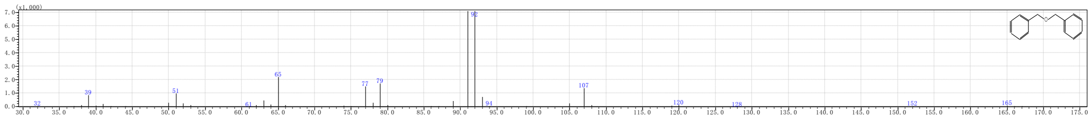
GC: **9ad**: 12.410 min. GC-MS (m/z): Calcd. 164; Found 164. HRMS (ESI) m/z calcd for $C_{11}H_{16}O^+$ $(M+H)^+$: 165.1294; found: 165.1282.



58. Dibenzyl ether (9ae)

Analytically pure product was isolated by a column chromatography on silica gel (hexanes/EtOAc = 100:1). Colorless liquid, Yield: 29.3 mg, 74%. **^{1}H NMR** (600 MHz, $CDCl_3$, 298 K): δ = 7.39 (m, 8H, Ph), 7.32 (m, 2H, Ph), 4.59 (s, 4H, CH_2). **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$, 298 K): δ = 138.3 (2C), 128.4 (4C), 127.8 (4C), 127.6 (2C), 72.1 (2C).

GC: **9ae**: 11.740 min. GC-MS (m/z): Calcd. 198; Found 198. HRMS (ESI) m/z calcd for $C_{14}H_{15}O^+$ $(M+H)^+$: 199.1125; found: 199.1116.


(x1,000)
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1.0
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107
120
128
152
165
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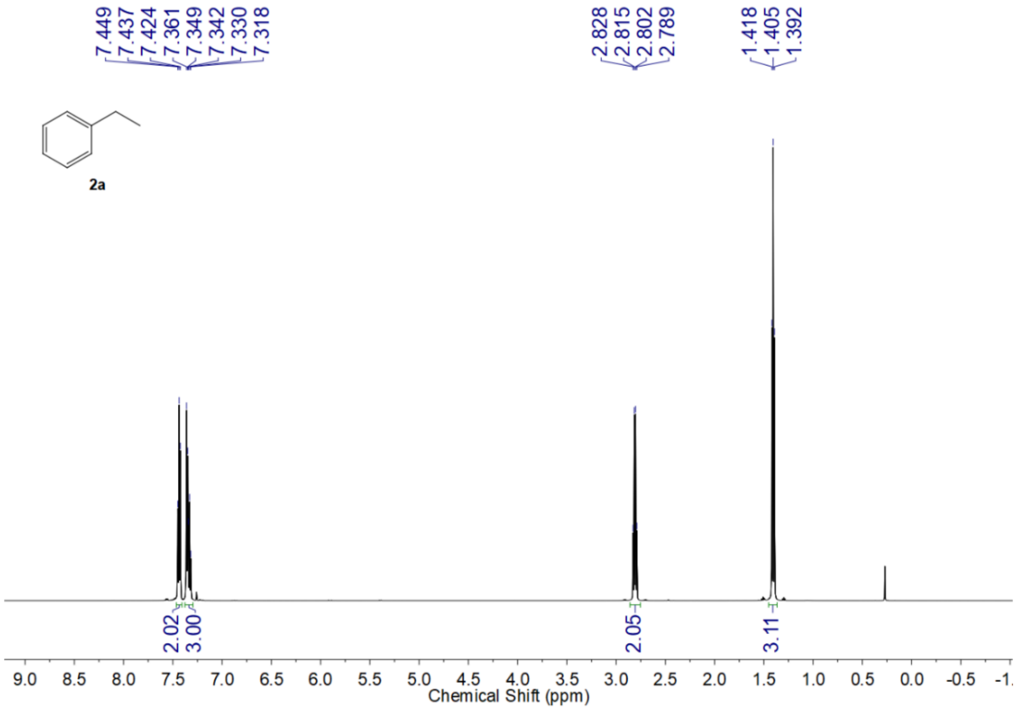
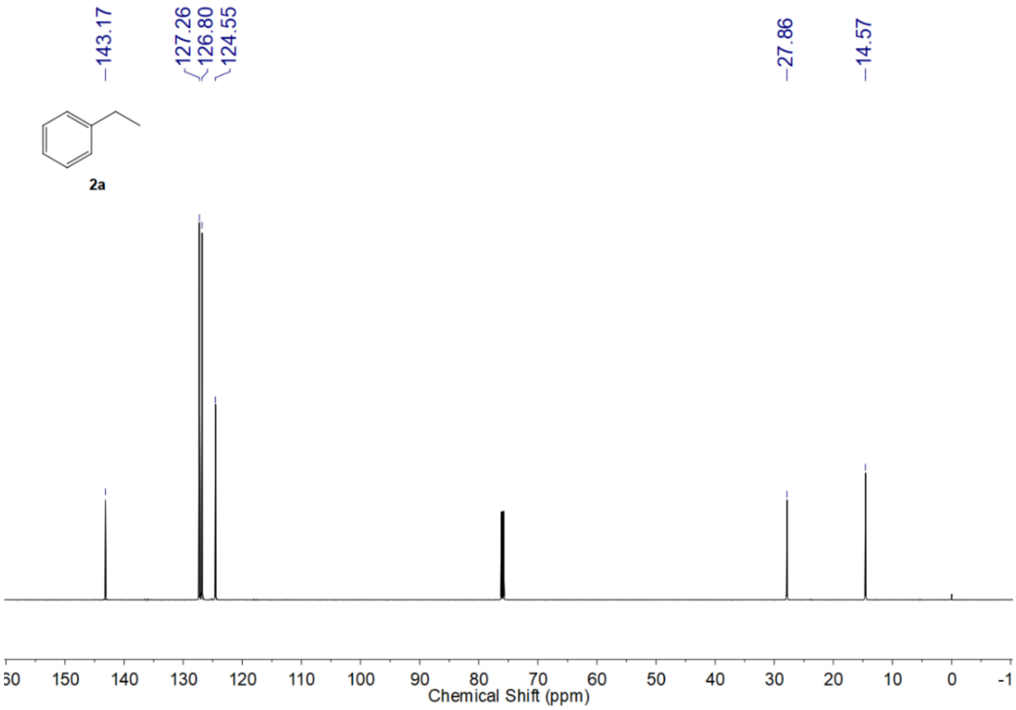
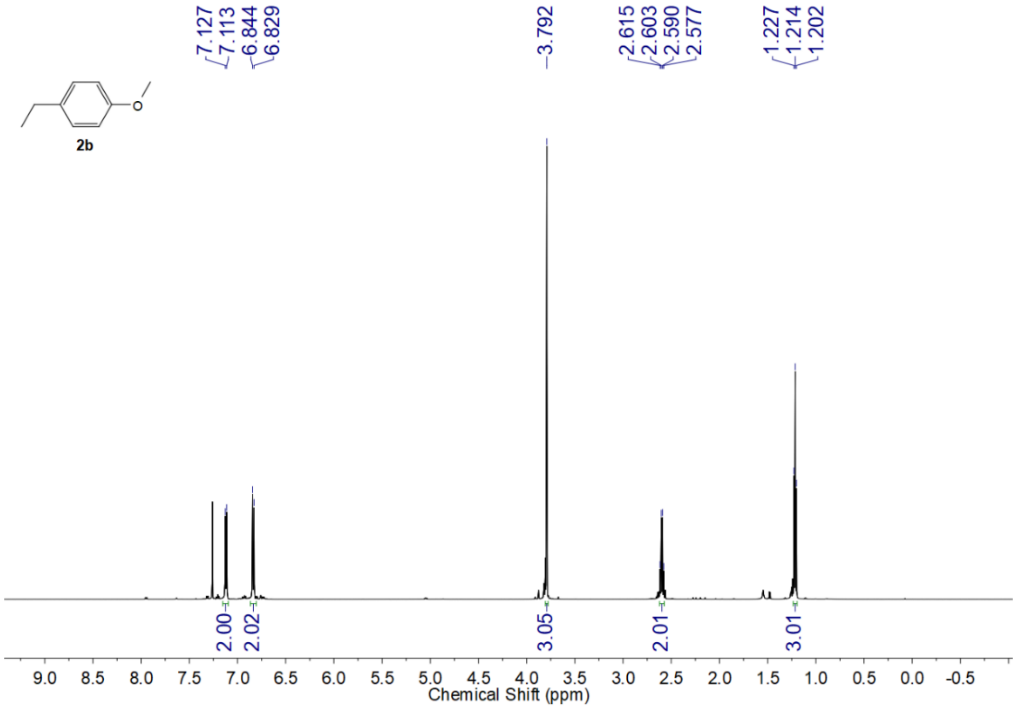
15. NMR spectra



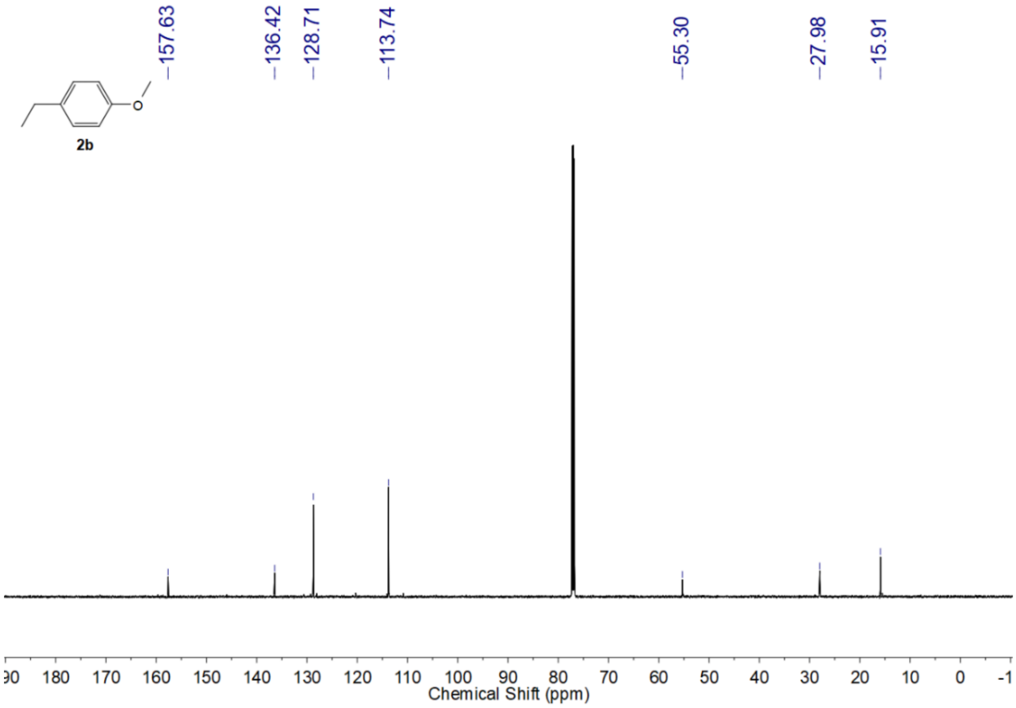
^{1}H NMR (600 MHz, 298K, $CDCl_3$) of **2a**



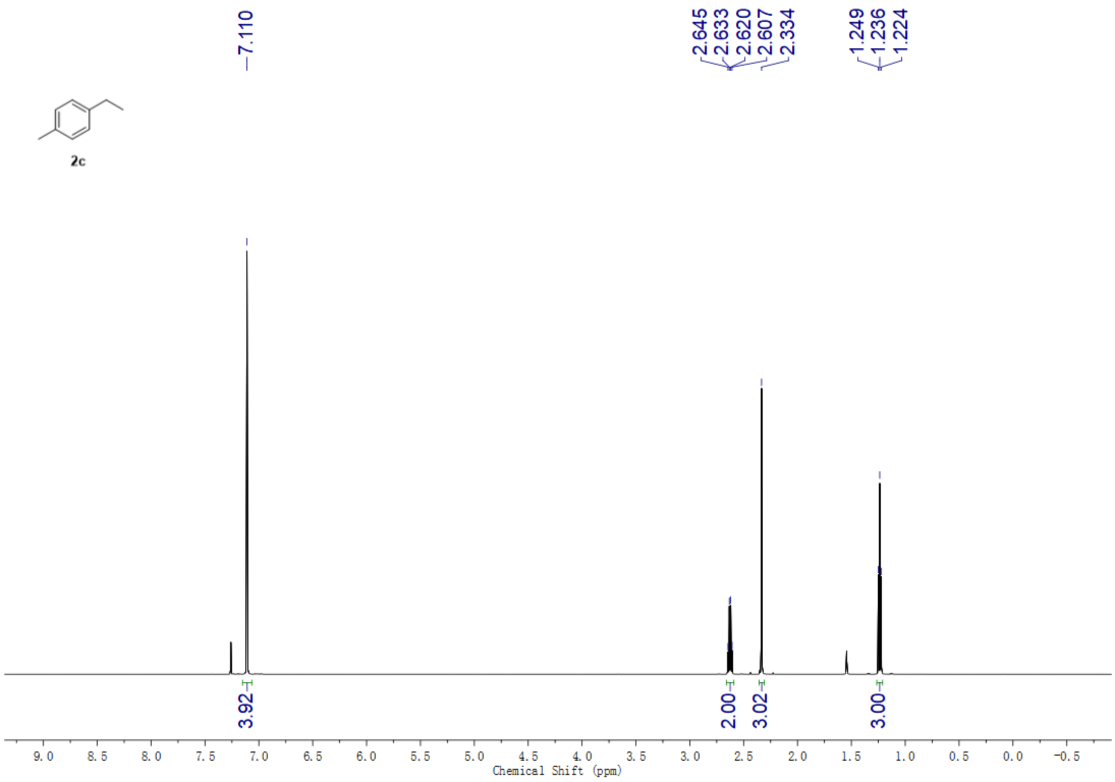
^{13}C NMR (151 MHz, 298 K, $CDCl_3$) of **2a**



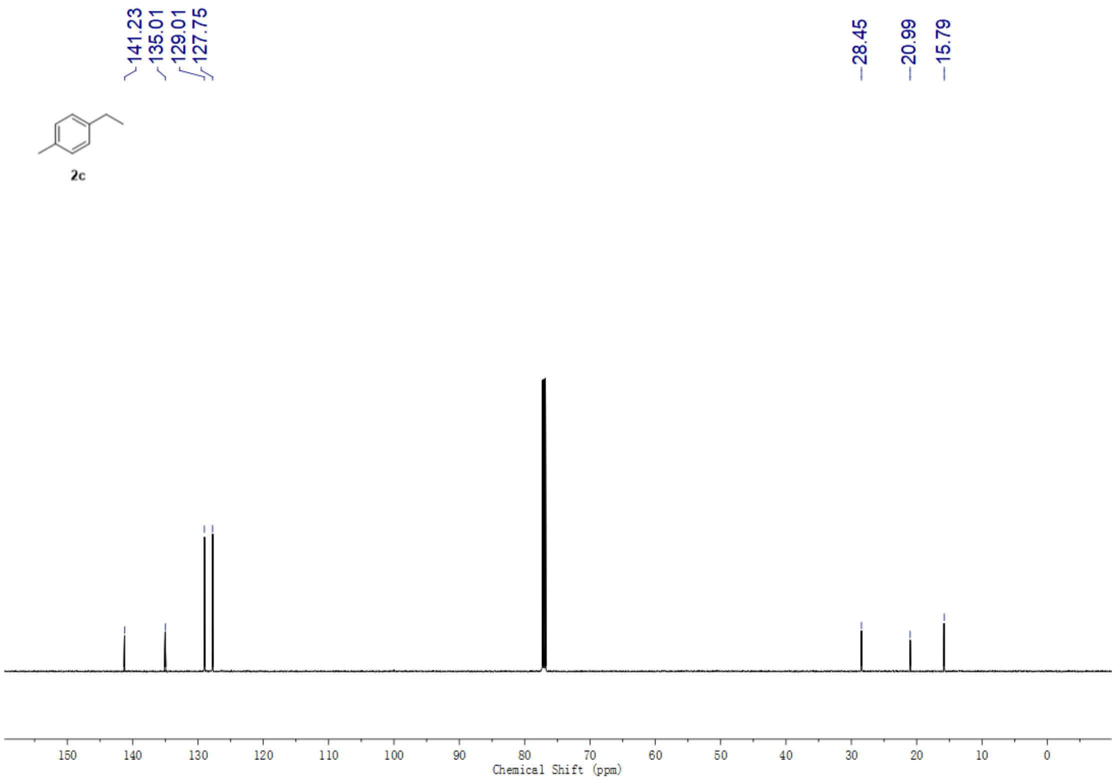
^{1}H NMR (600 MHz, 298K, $CDCl_3$) of **2b**



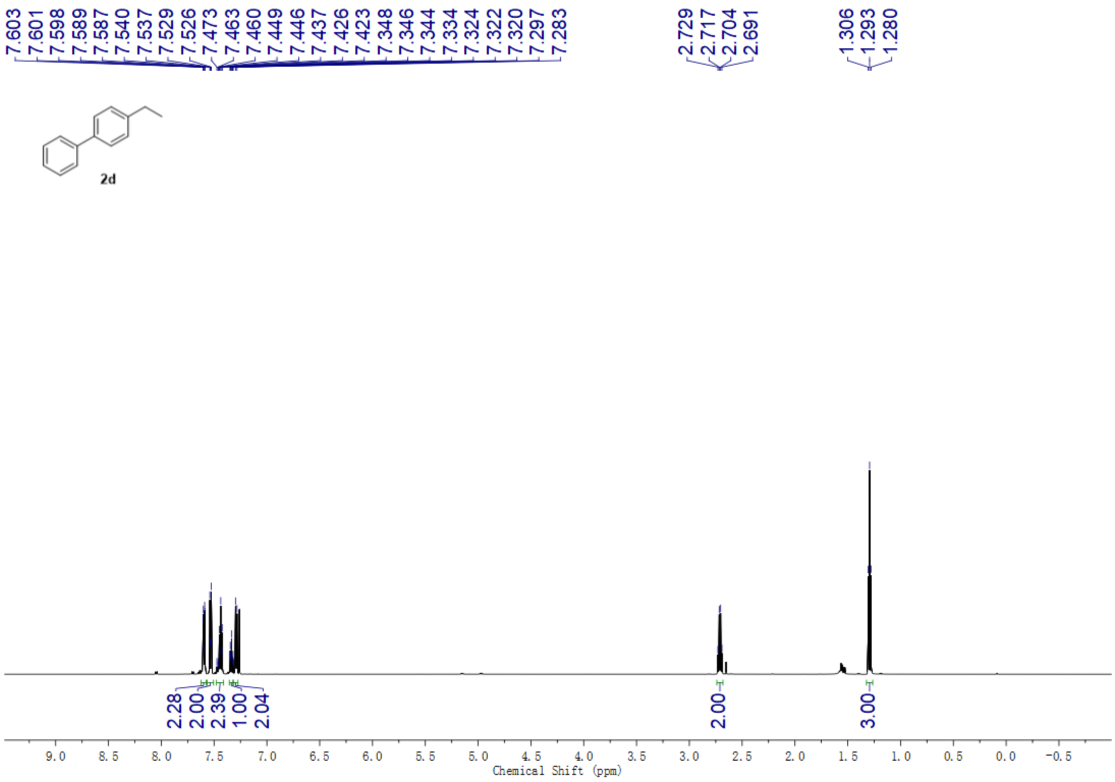
^{13}C NMR (151 MHz, 298 K, $CDCl_3$) of **2b**



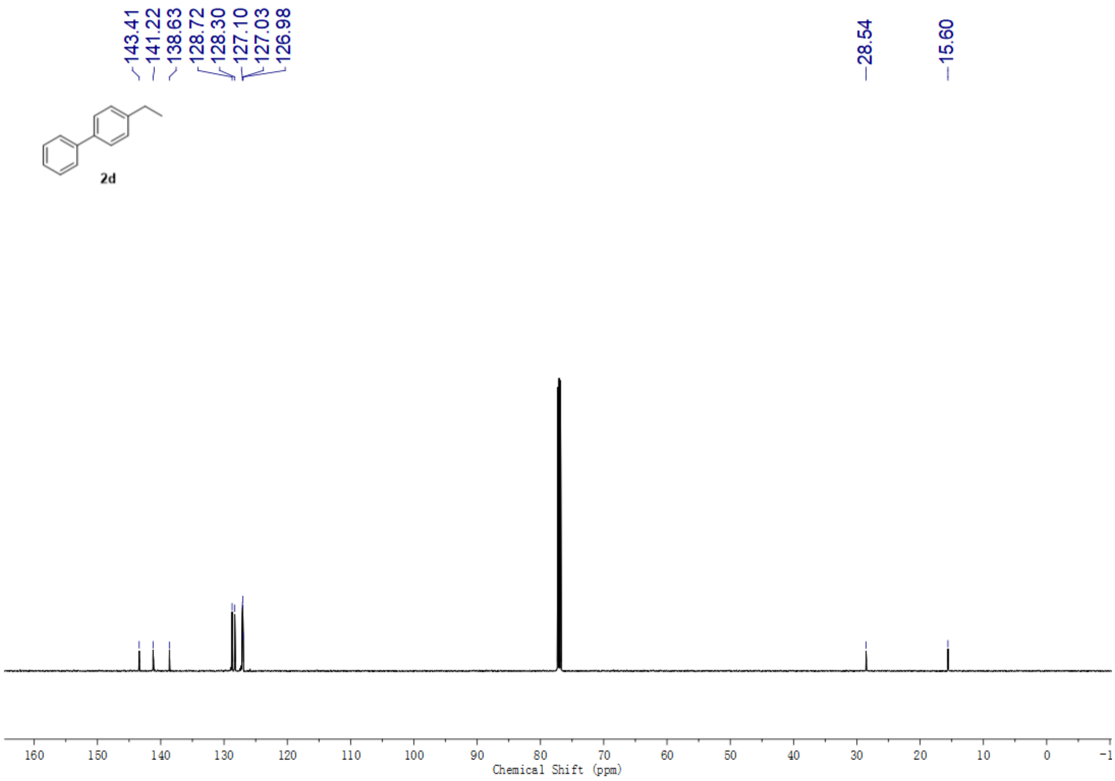
^{1}H NMR (600 MHz, 298K, $CDCl_3$) of **2c**



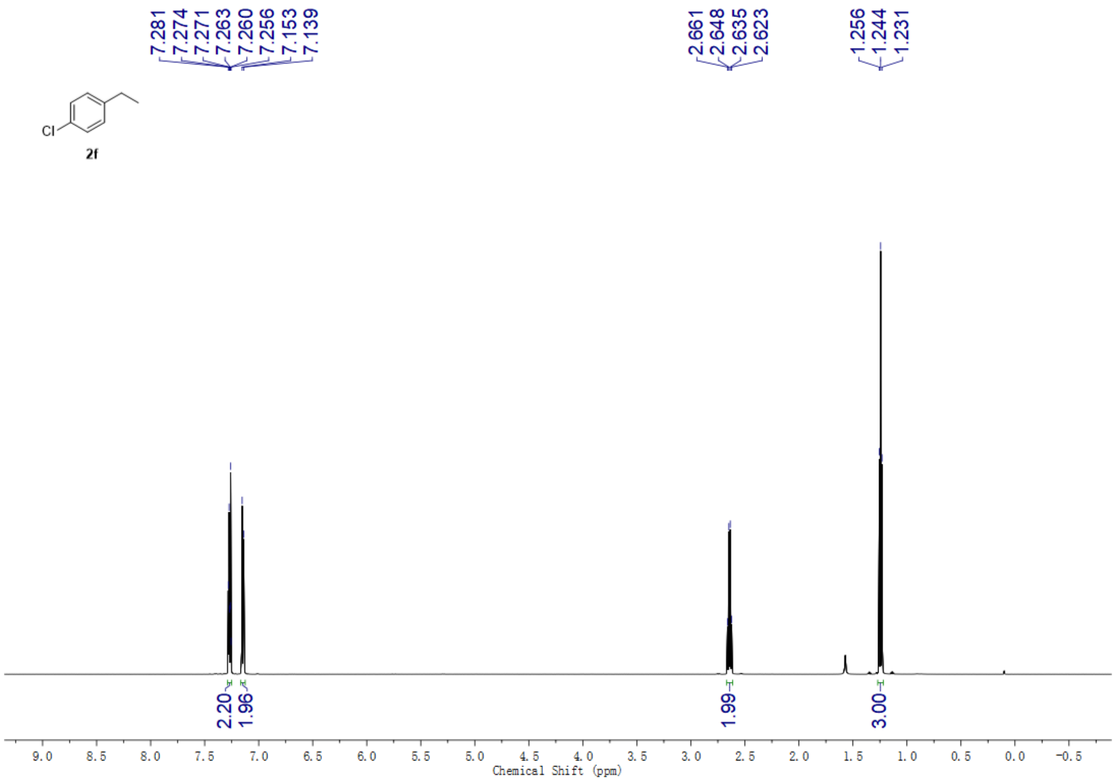
^{13}C NMR (151 MHz, 298 K, $CDCl_3$) of **2c**



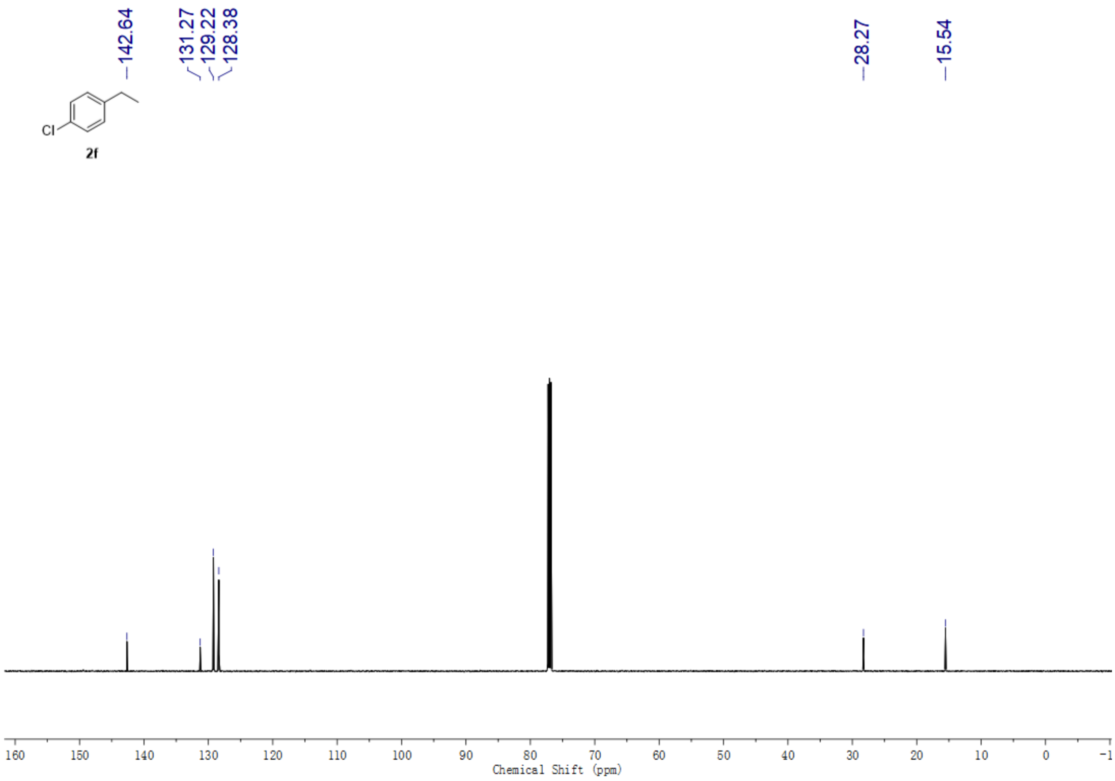
^{1}H NMR (600 MHz, 298K, $CDCl_3$) of **2d**



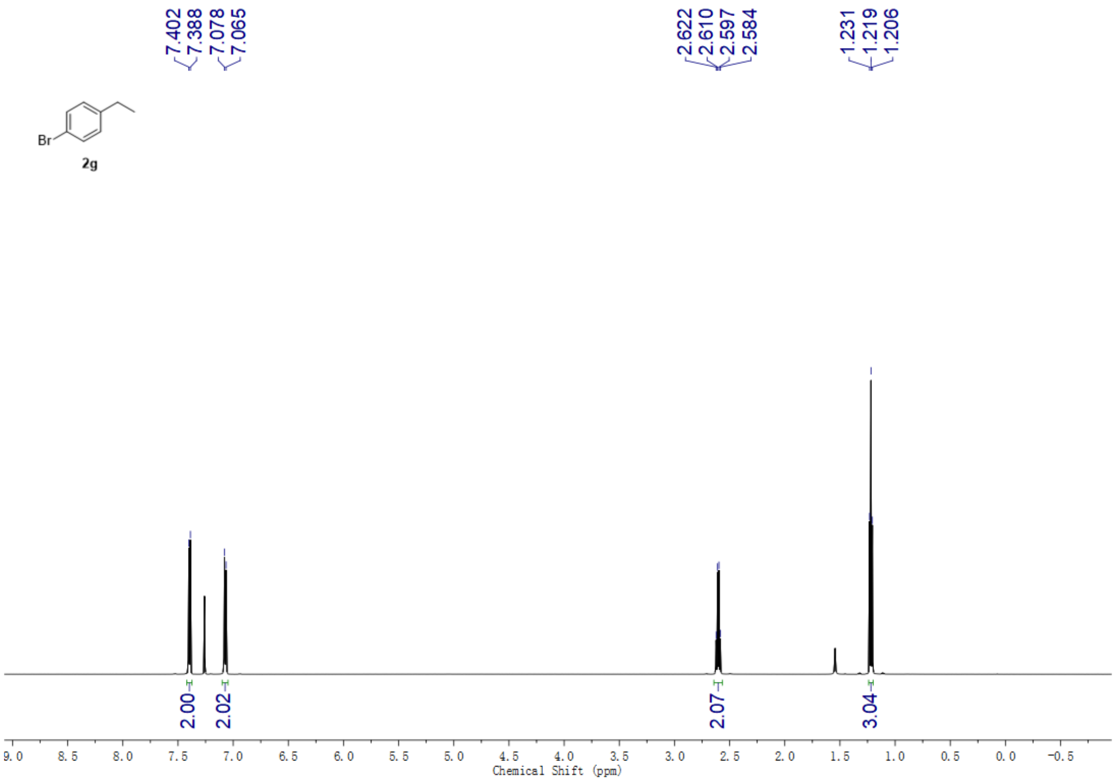
^{13}C NMR (151 MHz, 298 K, $CDCl_3$) of **2d**



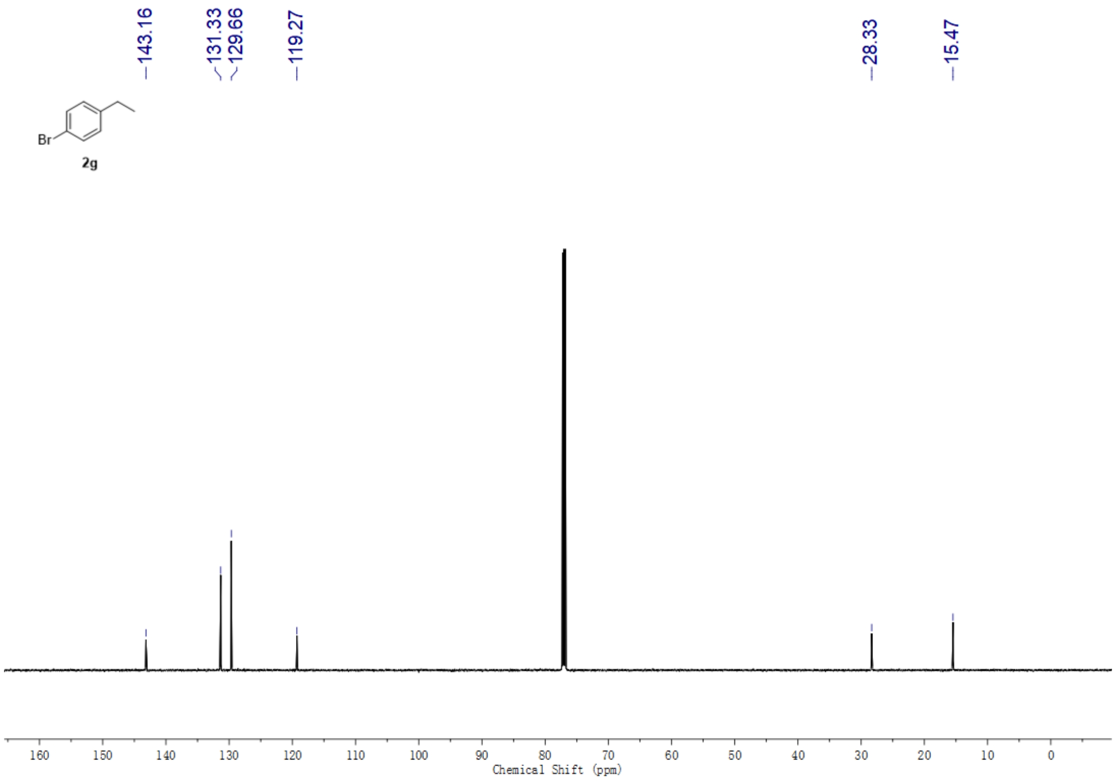
^{1}H NMR (600 MHz, 298K, $CDCl_3$) of **2f**



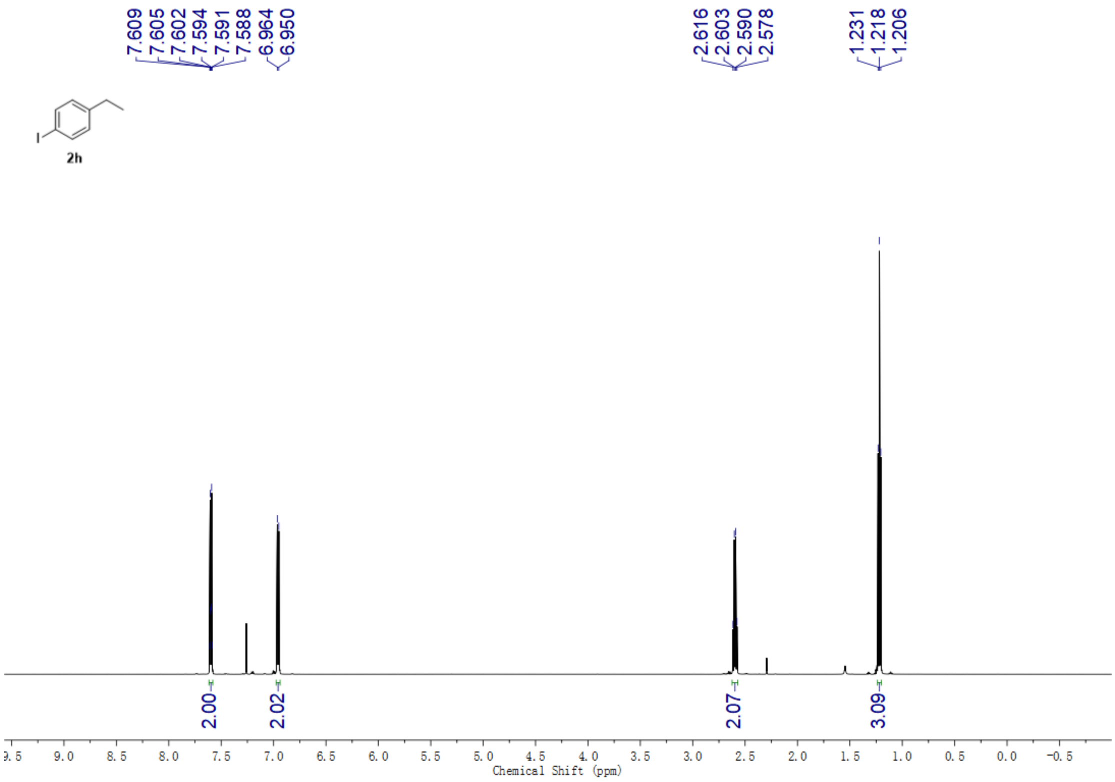
^{13}C NMR (151 MHz, 298 K, $CDCl_3$) of **2f**



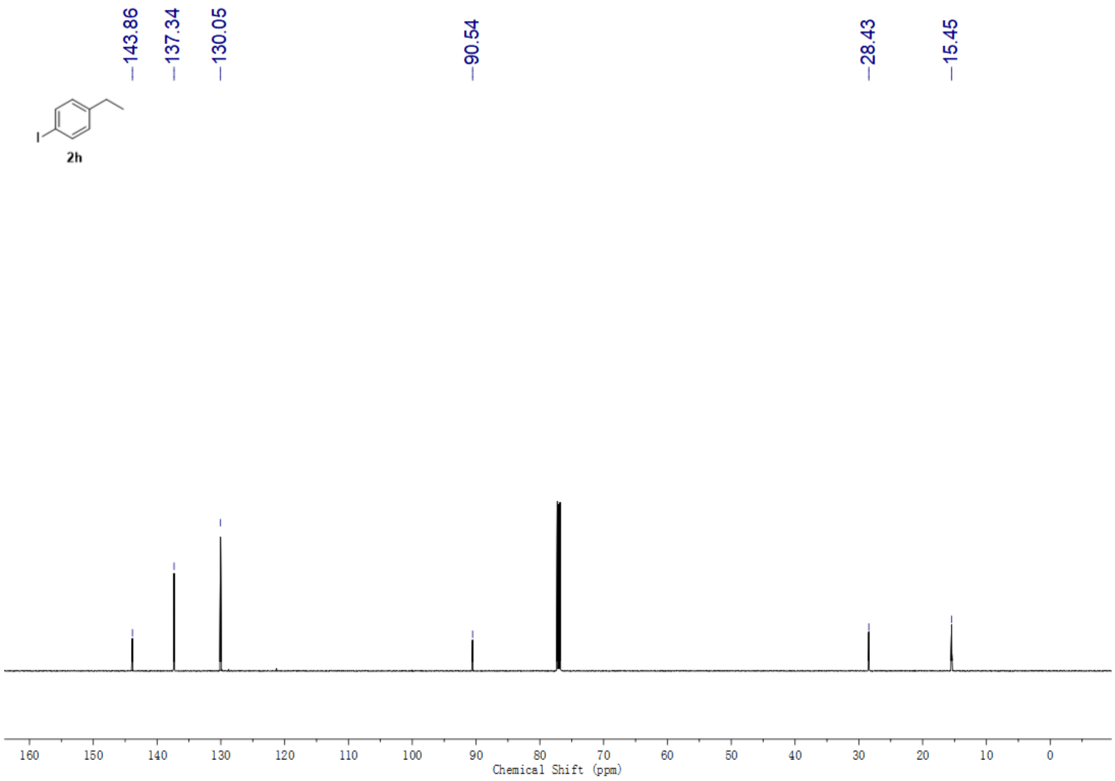
[1]H NMR (600 MHz, 298K, $CDCl_3$) of **2g**



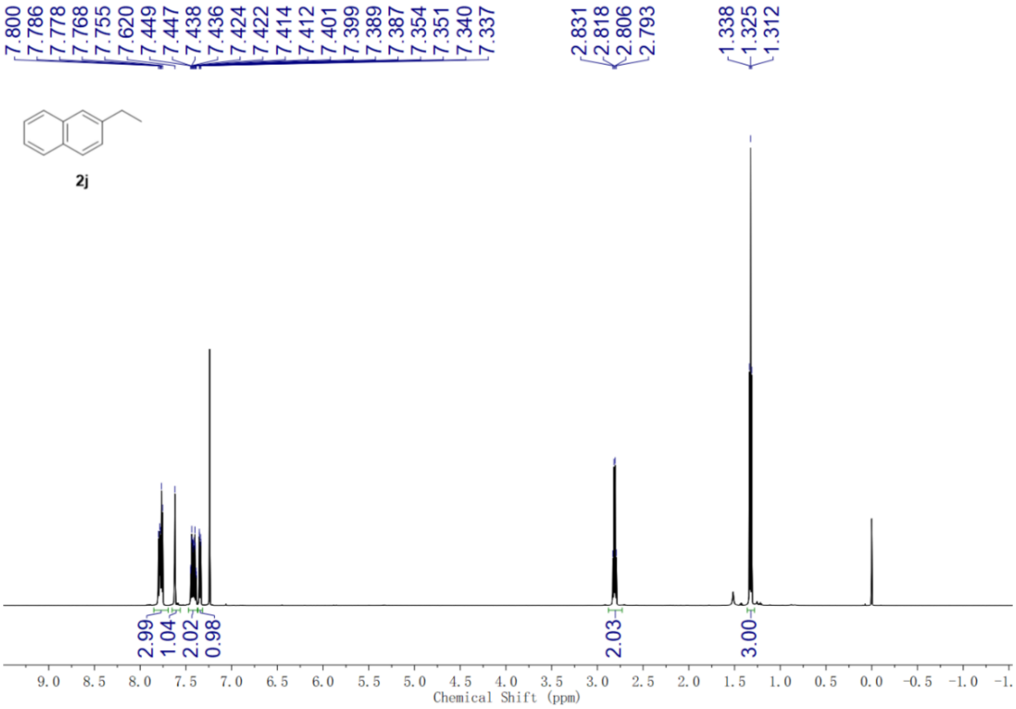
[13]C NMR (151 MHz, 298 K, $CDCl_3$) of **2g**



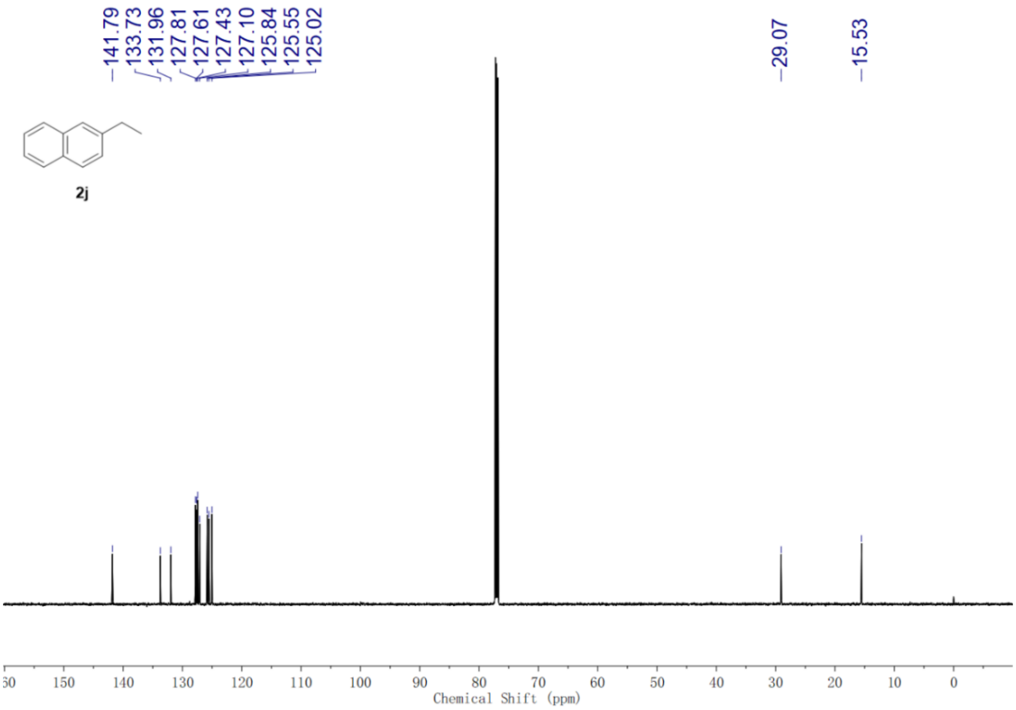
^{1}H NMR (600 MHz, 298K, $CDCl_3$) of **2h**



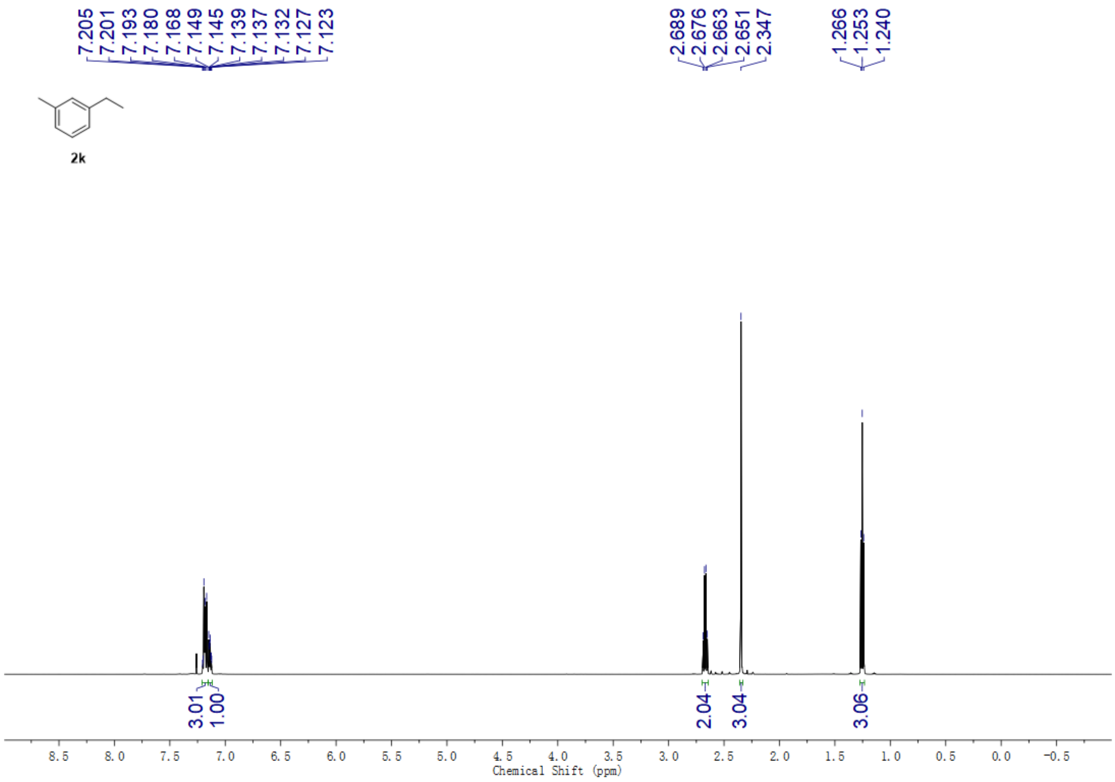
^{13}C NMR (151 MHz, 298 K, $CDCl_3$) of **2h**



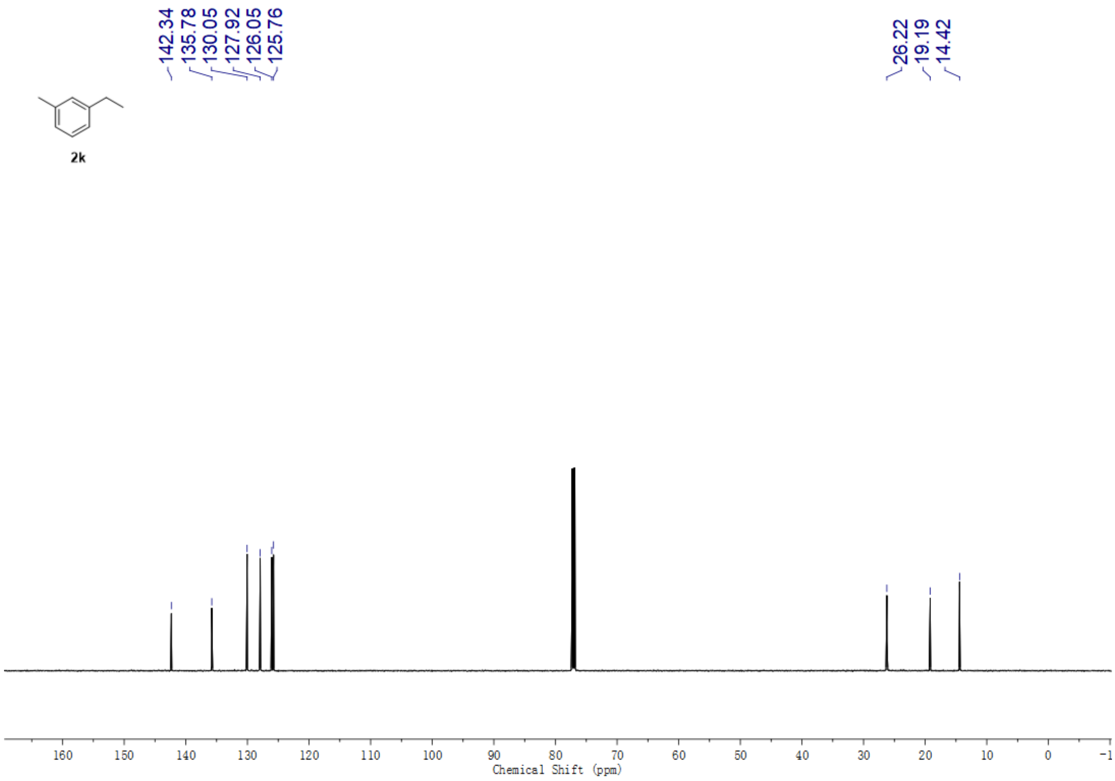
^{1}H NMR (600 MHz, 298K, $CDCl_3$) of **2j**



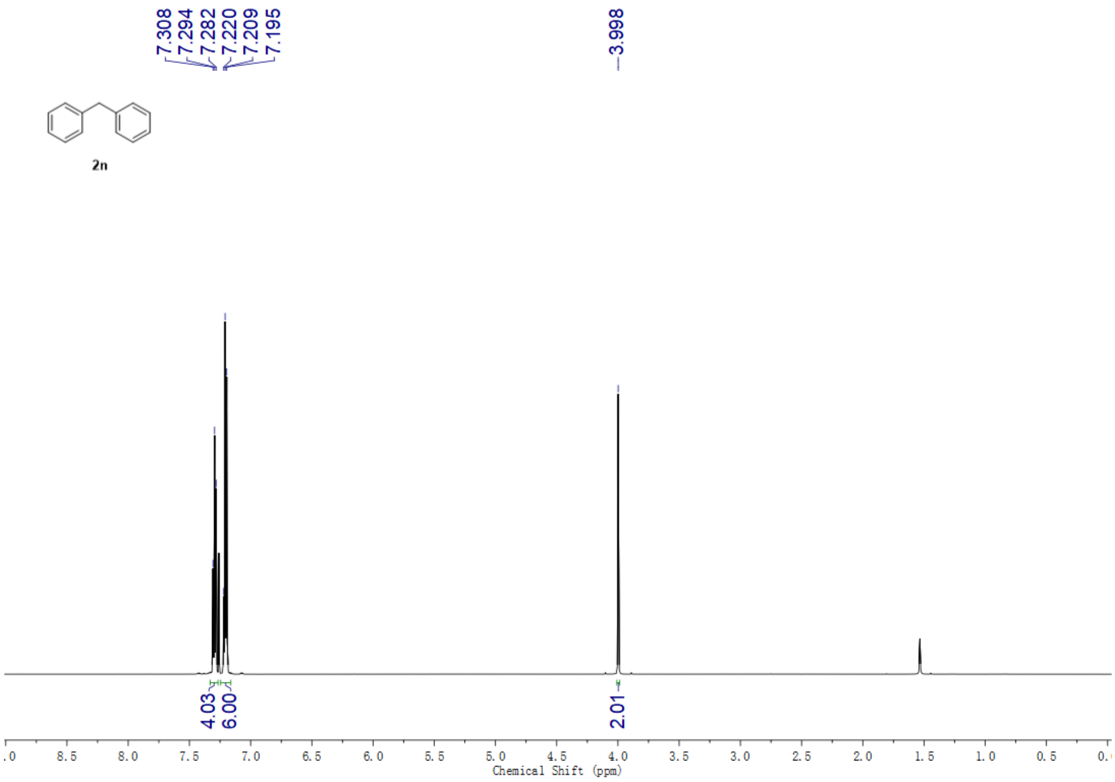
^{13}C NMR (151 MHz, 298 K, $CDCl_3$) of **2j**



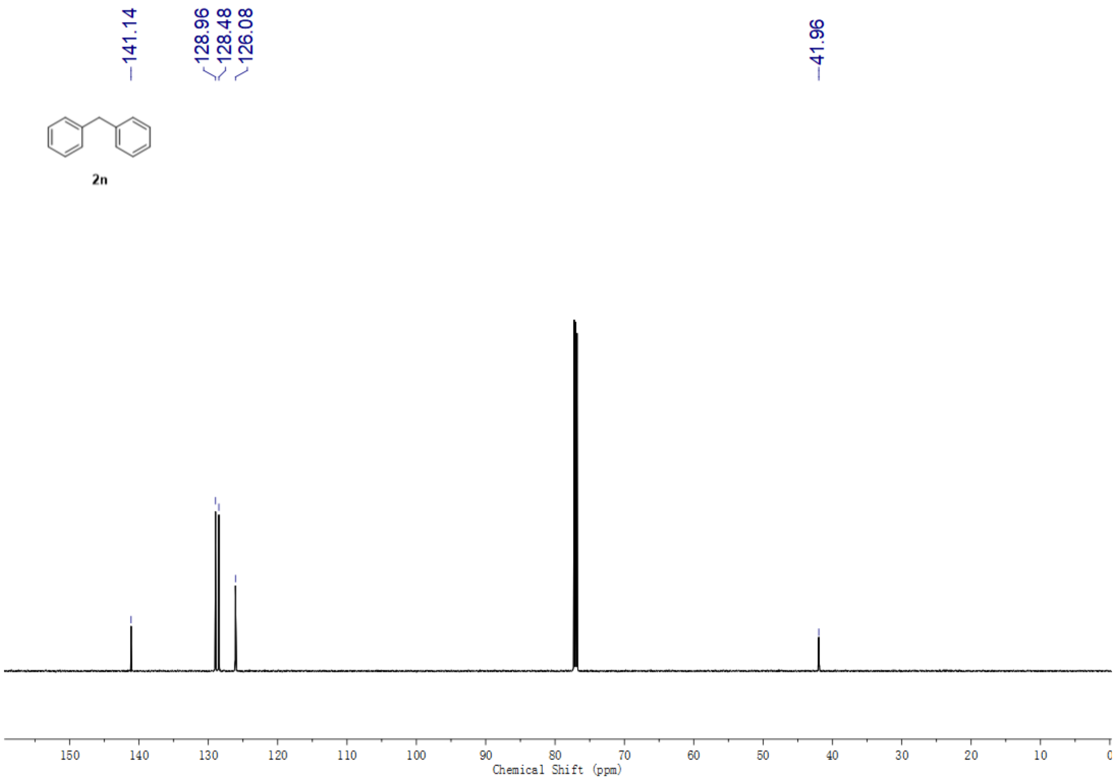
^{1}H NMR (600 MHz, 298K, $CDCl_3$) of **2k**



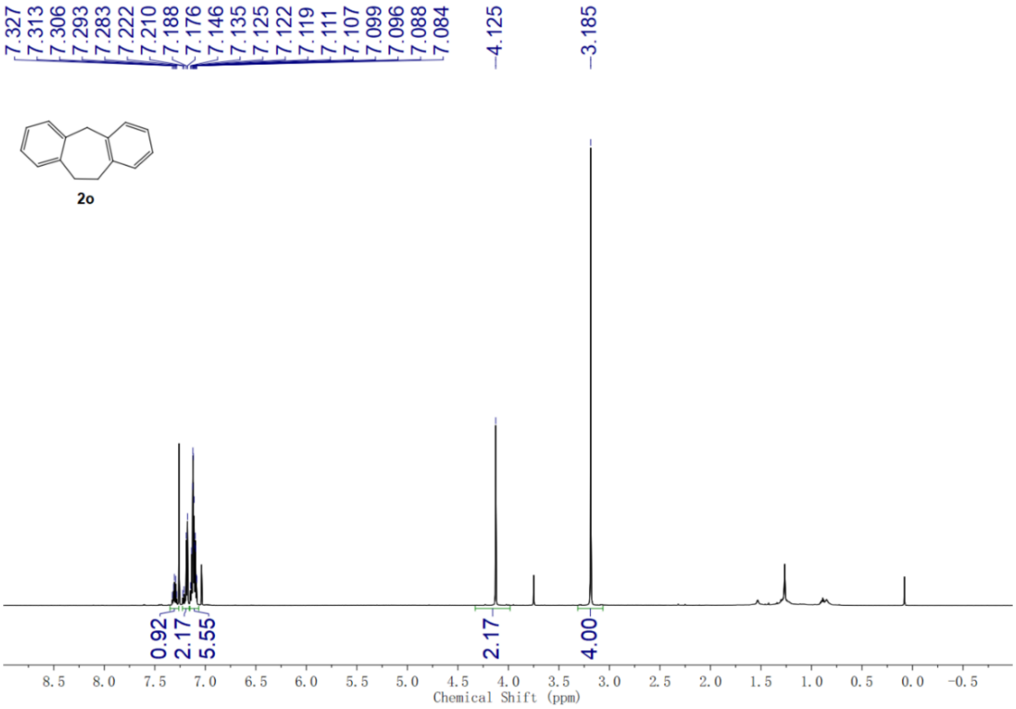
^{13}C NMR (151 MHz, 298 K, $CDCl_3$) of **2k**



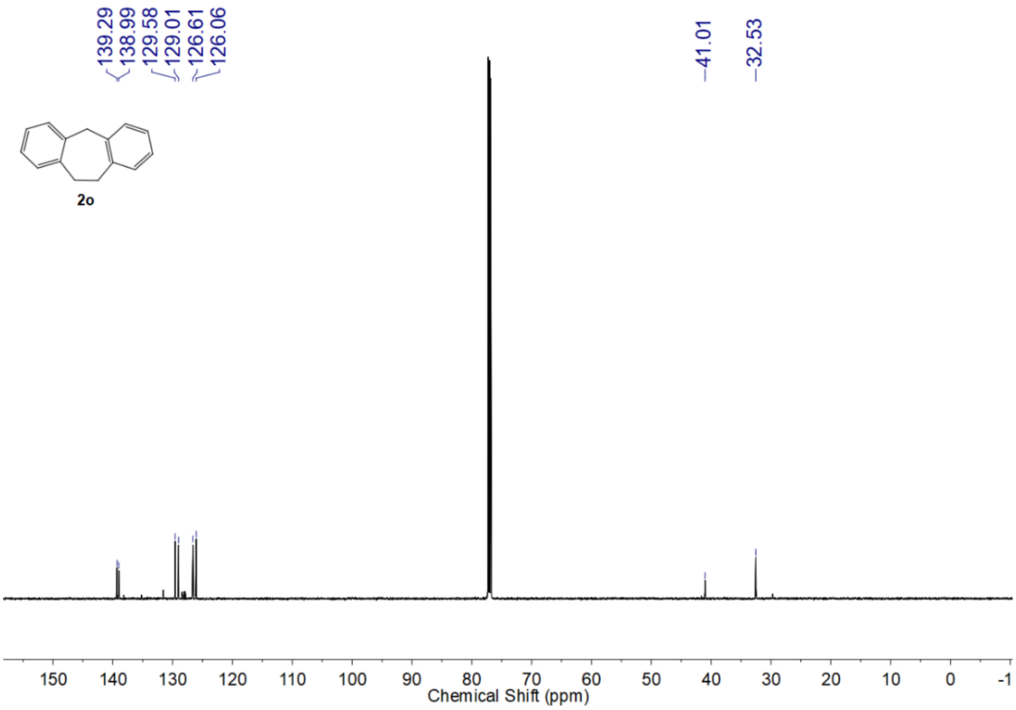
^{1}H NMR (600 MHz, 298K, $CDCl_3$) of **2n**



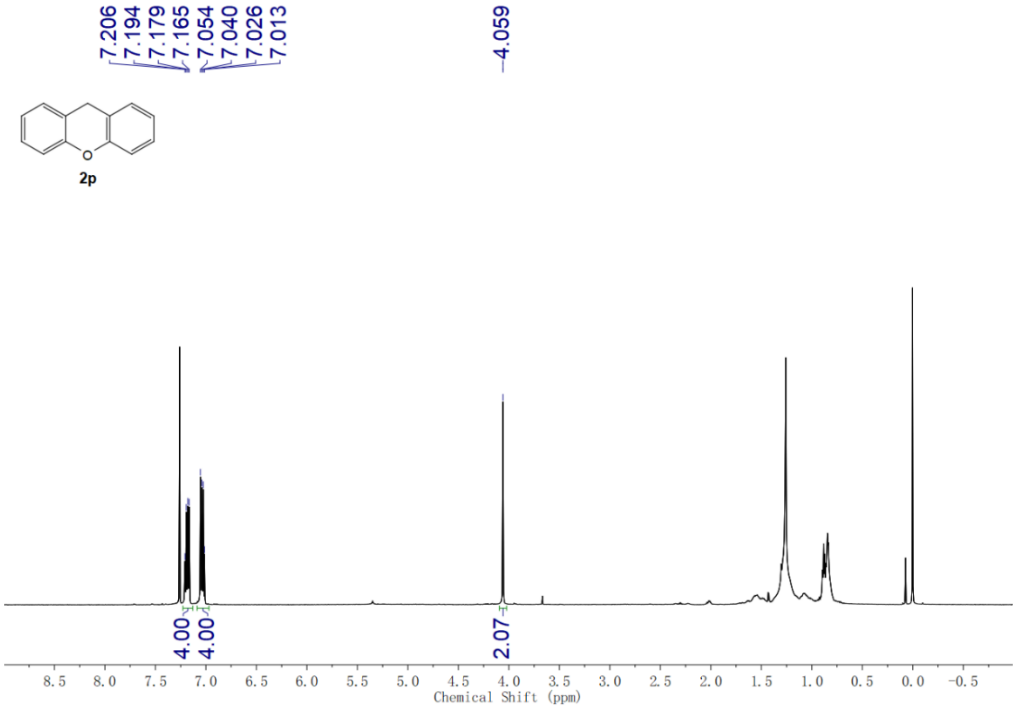
^{13}C NMR (151 MHz, 298 K, $CDCl_3$) of **2n**



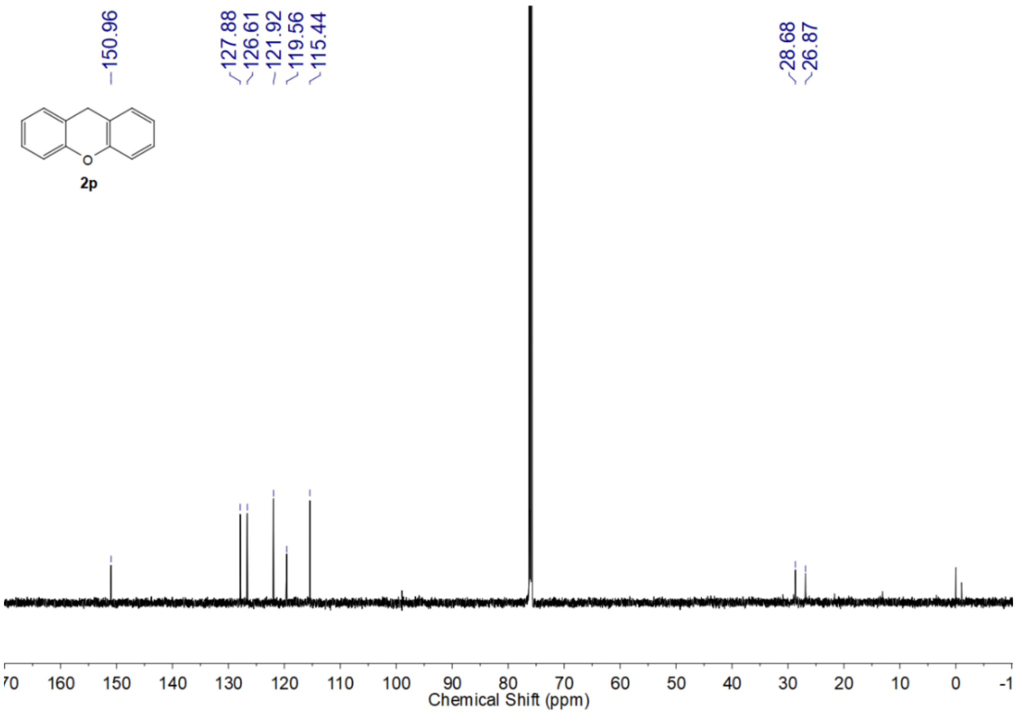
^{1}H NMR (600 MHz, 298K, $CDCl_3$) of **2o**



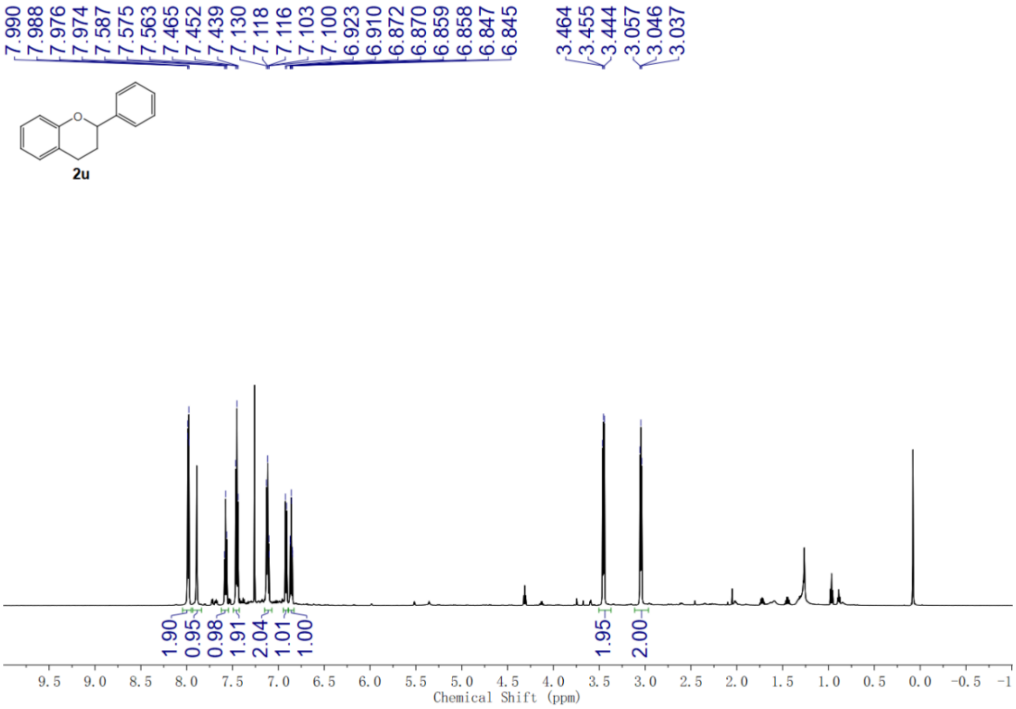
^{13}C NMR (151 MHz, 298 K, $CDCl_3$) of **2o**



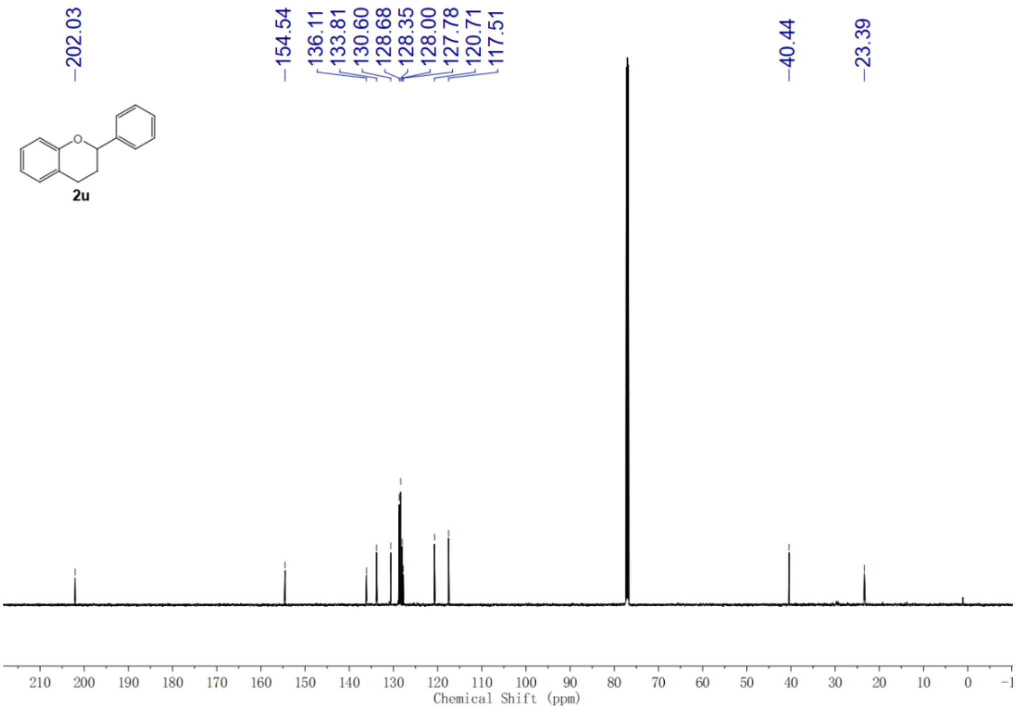
[1]H NMR (600 MHz, 298K, $CDCl_3$) of **2p**



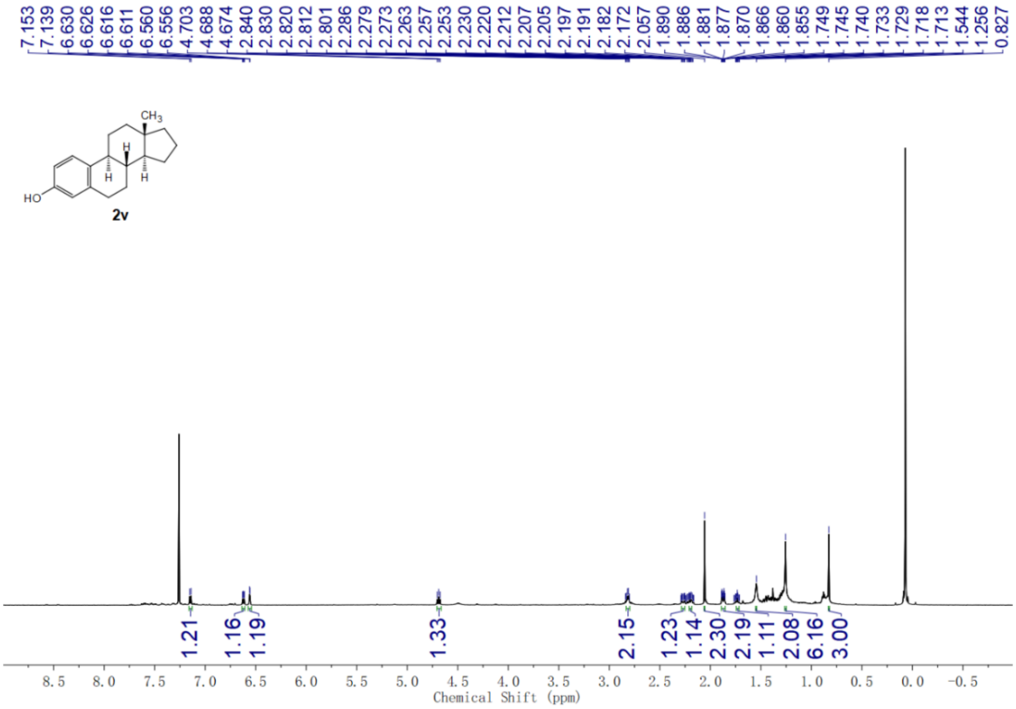
[13]C NMR (151 MHz, 298 K, $CDCl_3$) of **2p**



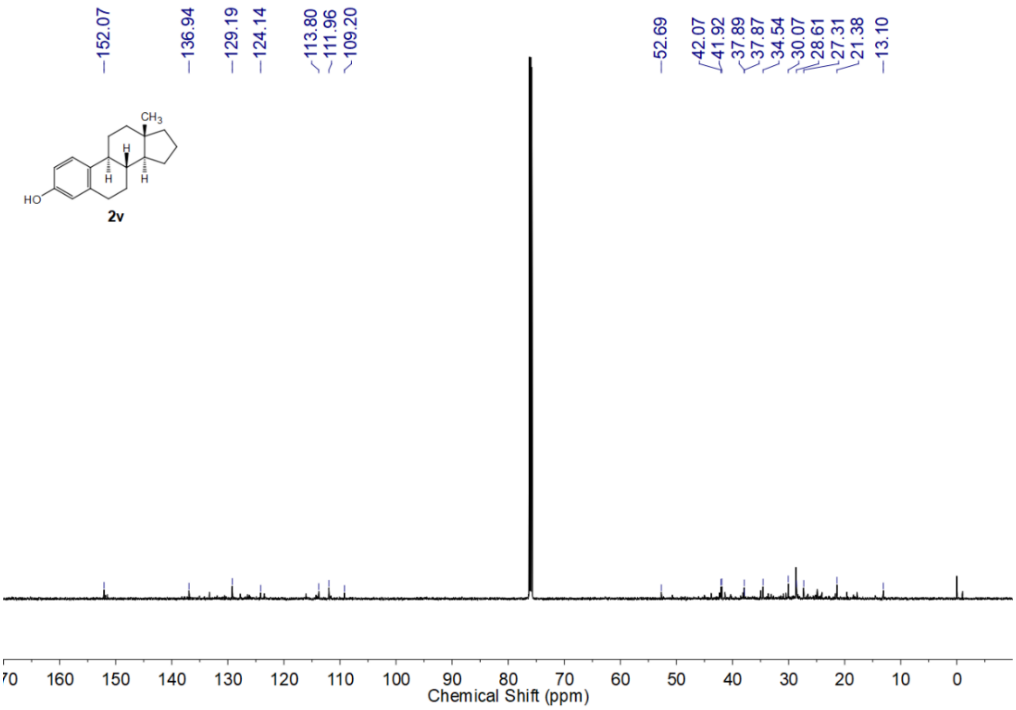
^{1}H NMR (600 MHz, 298K, $CDCl_3$) of **2u**



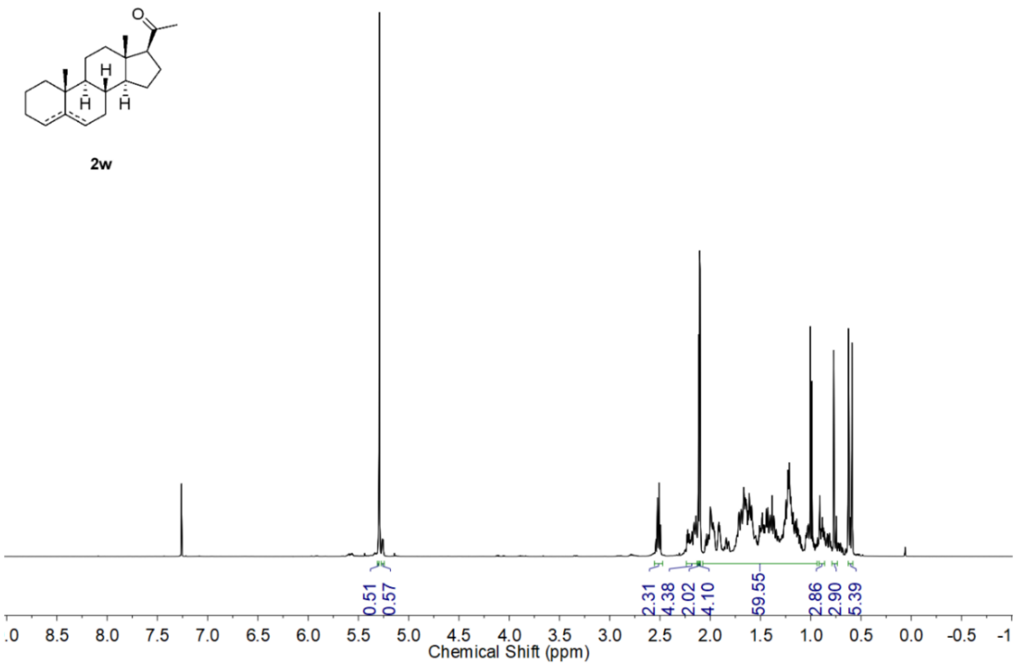
^{13}C NMR (151 MHz, 298 K, $CDCl_3$) of **2u**



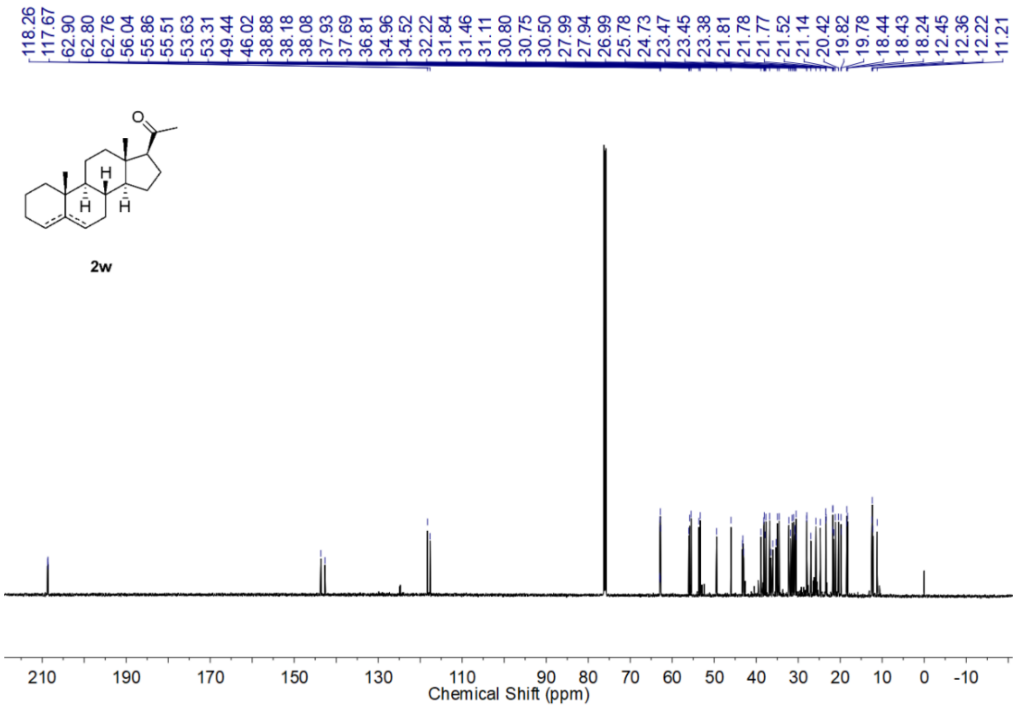
^{1}H NMR (600 MHz, 298K, $CDCl_3$) of **2v**



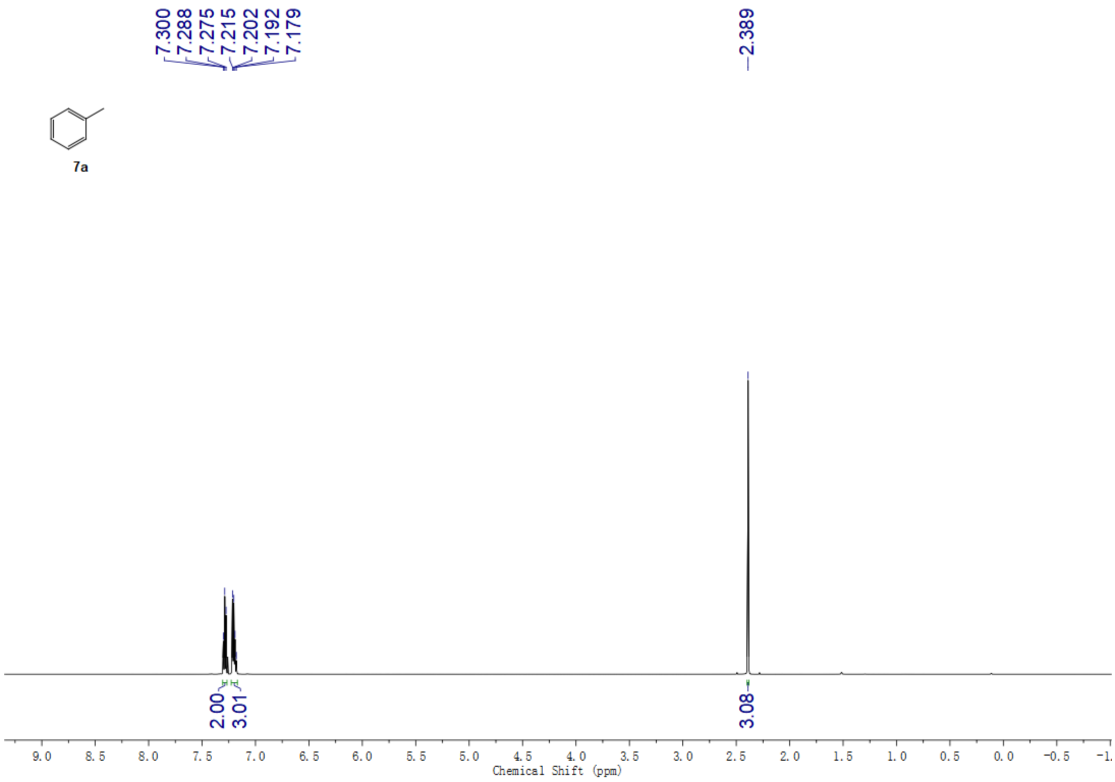
^{13}C NMR (151 MHz, 298 K, $CDCl_3$) of **2v**



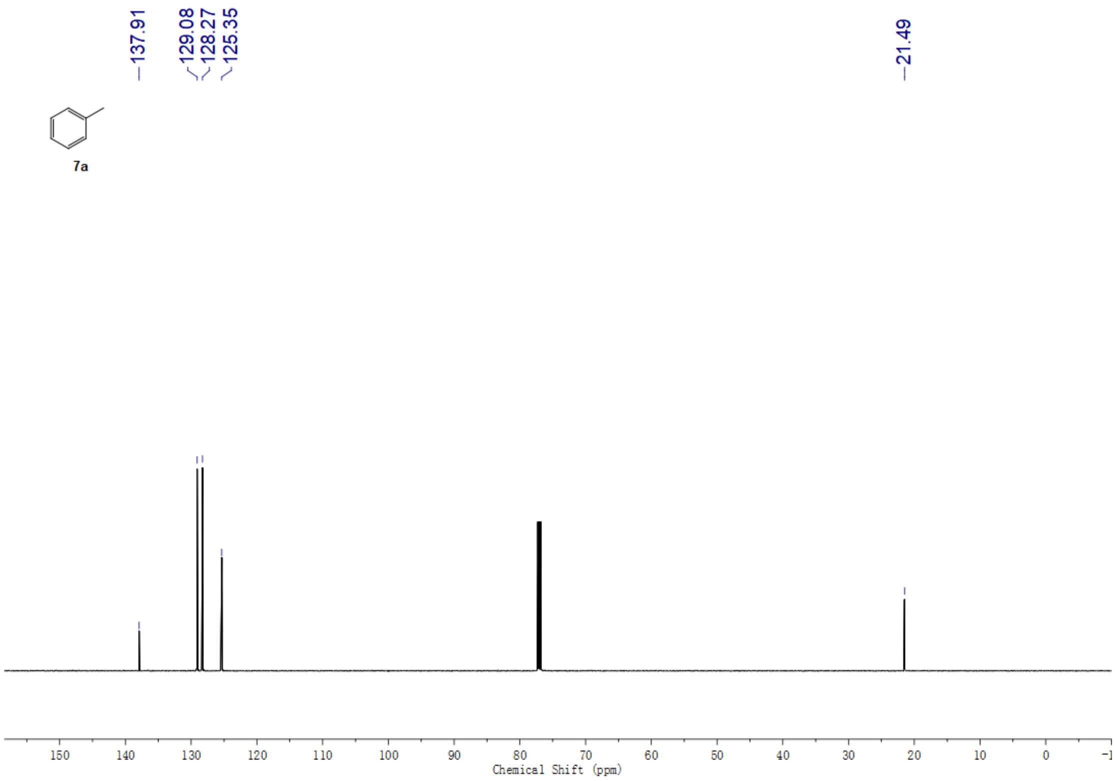
^{1}H NMR (600 MHz, 298K, $CDCl_3$) of **2w**



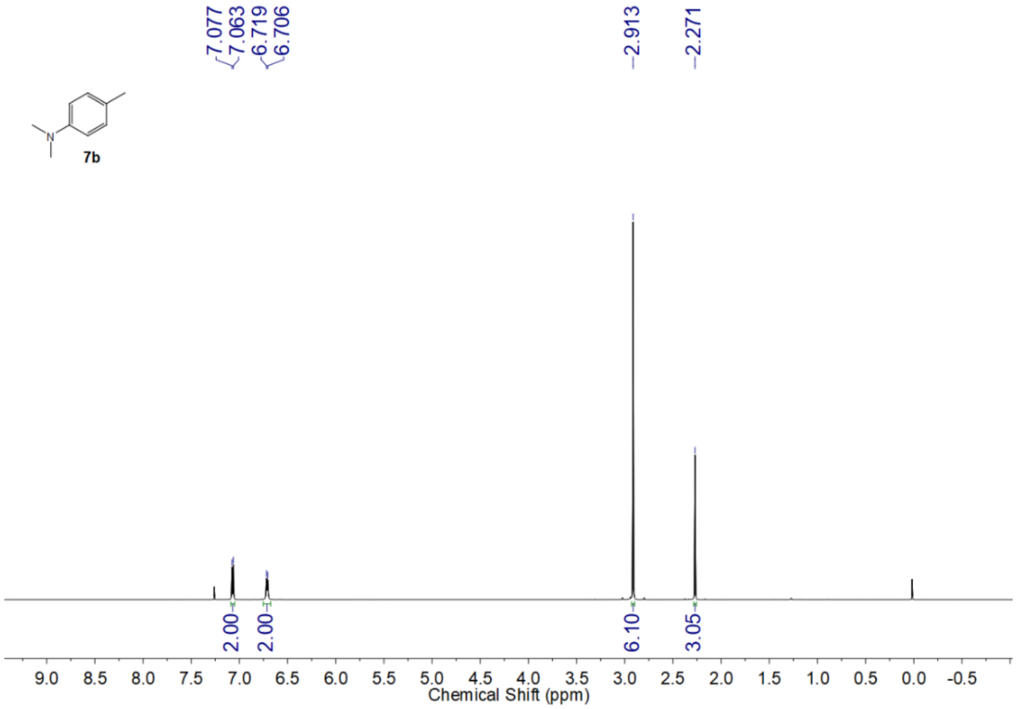
^{13}C NMR (151 MHz, 298 K, $CDCl_3$) of **2w**



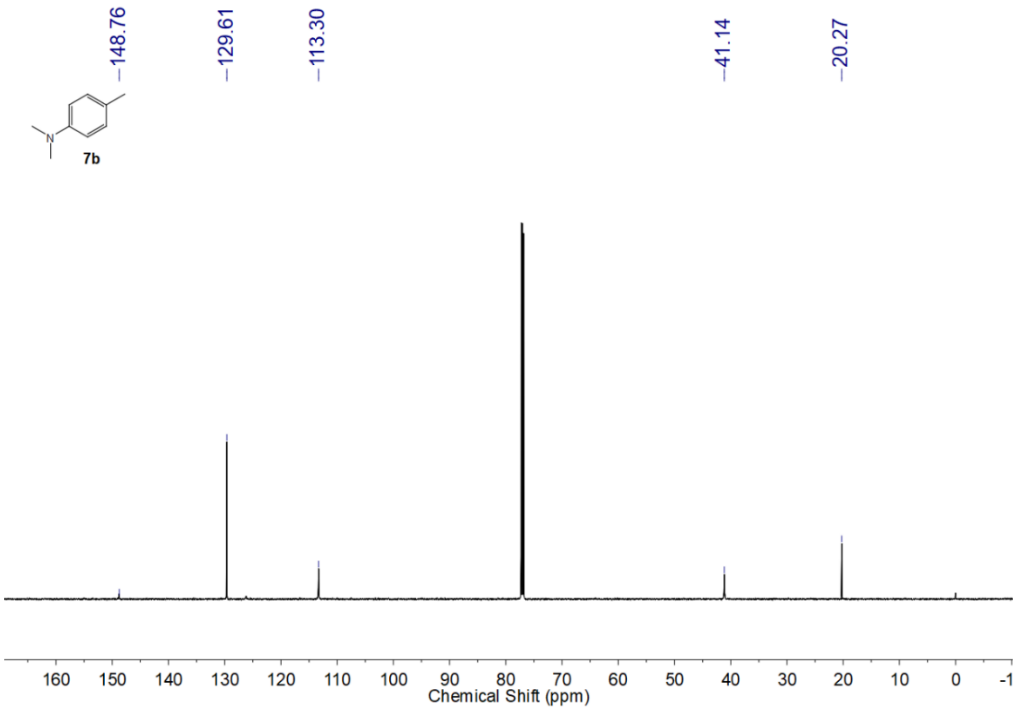
[1]H NMR (600 MHz, 298K, $CDCl_3$) of **7a**



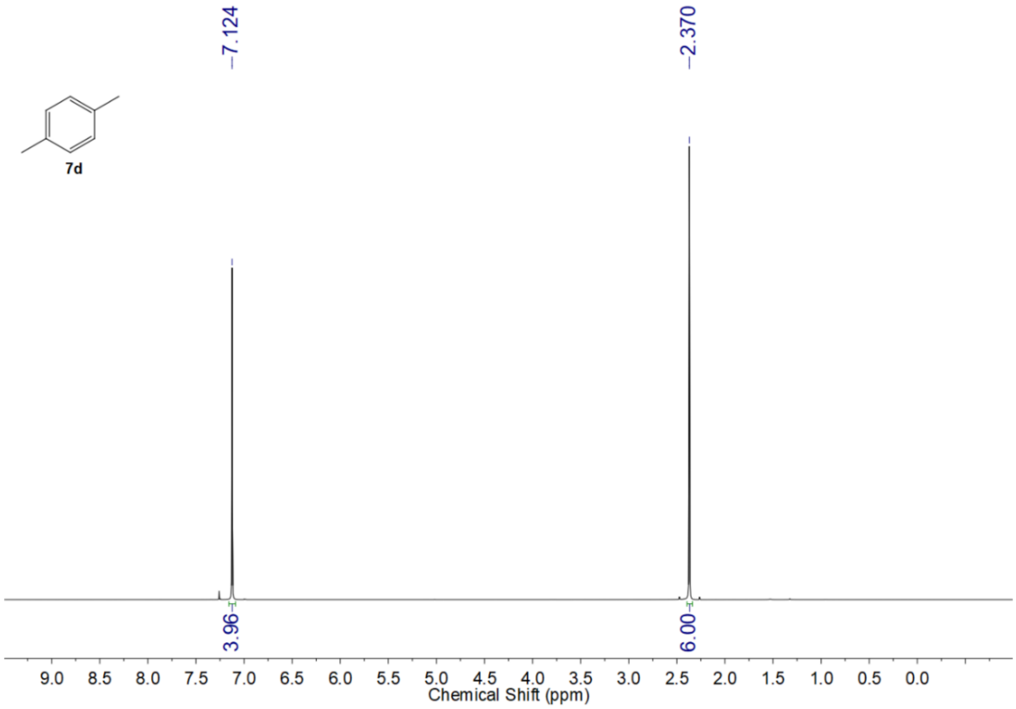
[13]C NMR (151 MHz, 298 K, $CDCl_3$) of **7a**



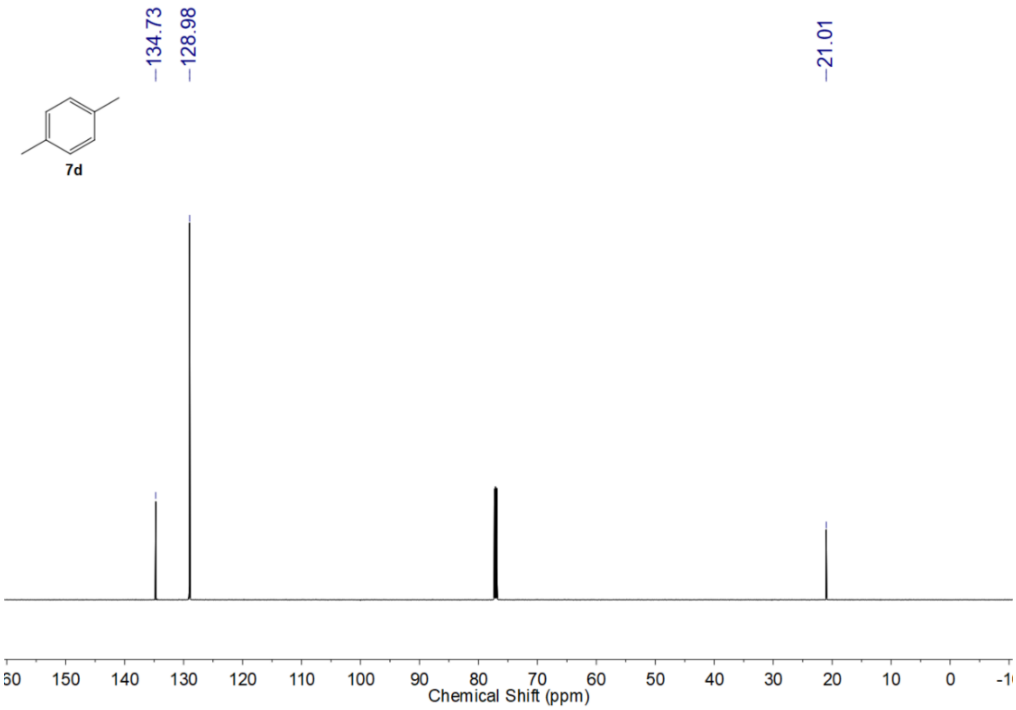
^{1}H NMR (600 MHz, 298K, $CDCl_3$) of **7b**



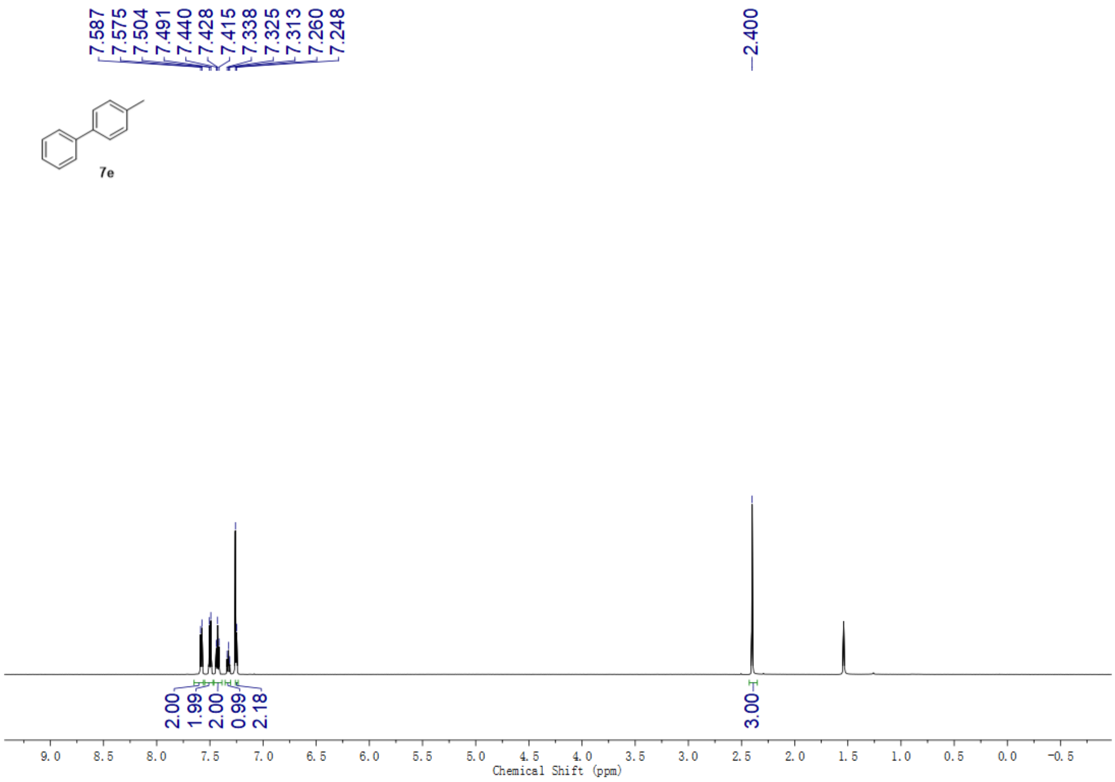
^{13}C NMR (151 MHz, 298 K, $CDCl_3$) of **7b**



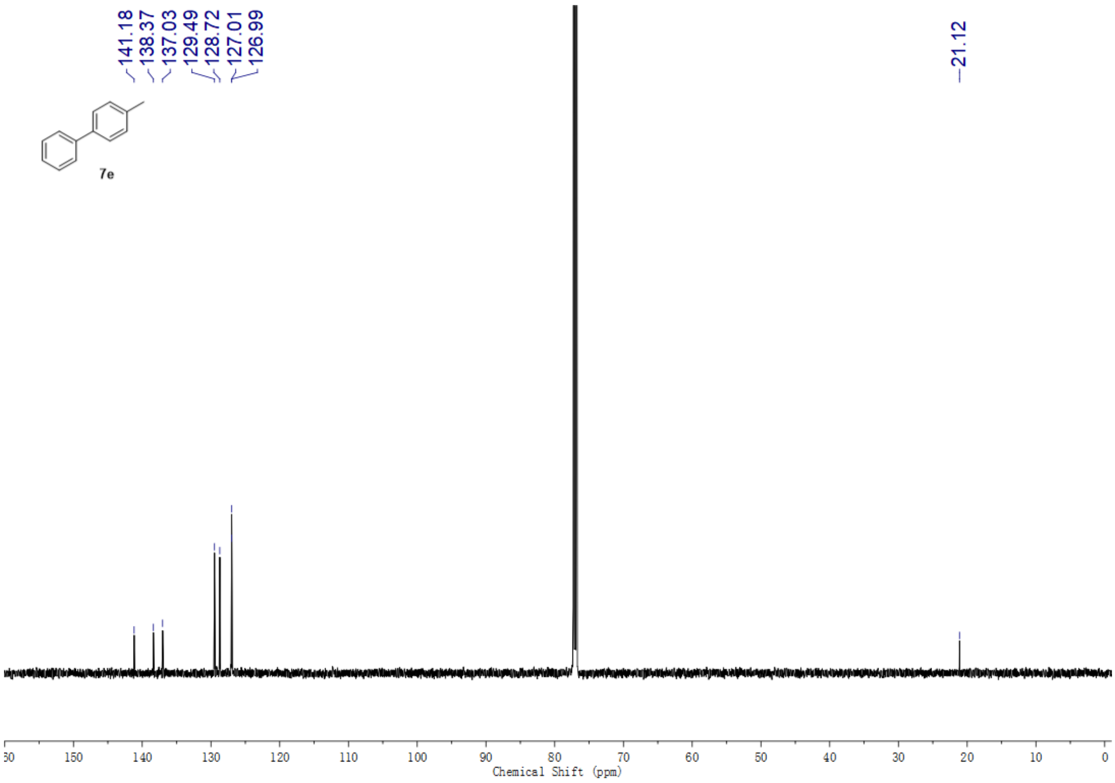
[1]H NMR (600 MHz, 298K, $CDCl_3$) of **7d**



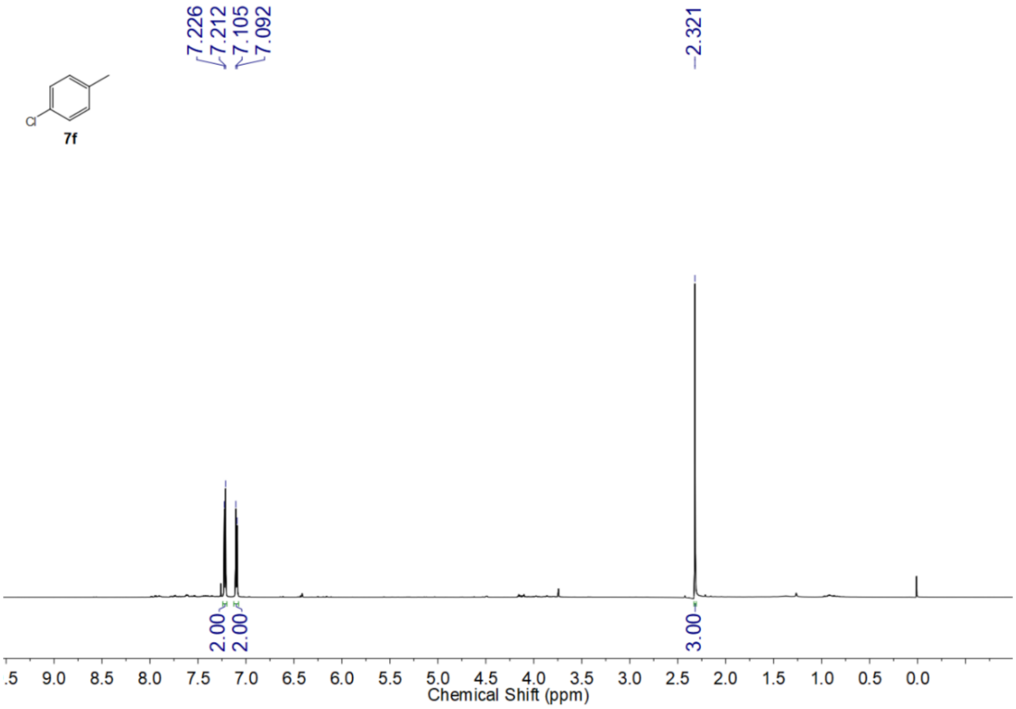
[13]C NMR (151 MHz, 298 K, $CDCl_3$) of **7d**



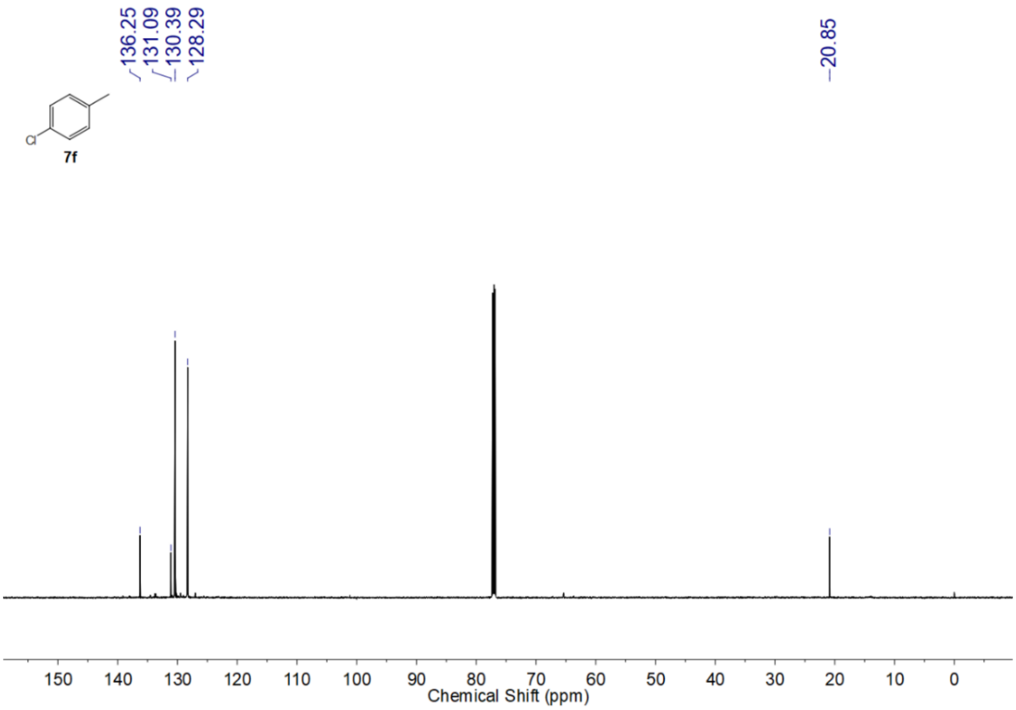
^{1}H NMR (600 MHz, 298K, $CDCl_3$) of **7e**



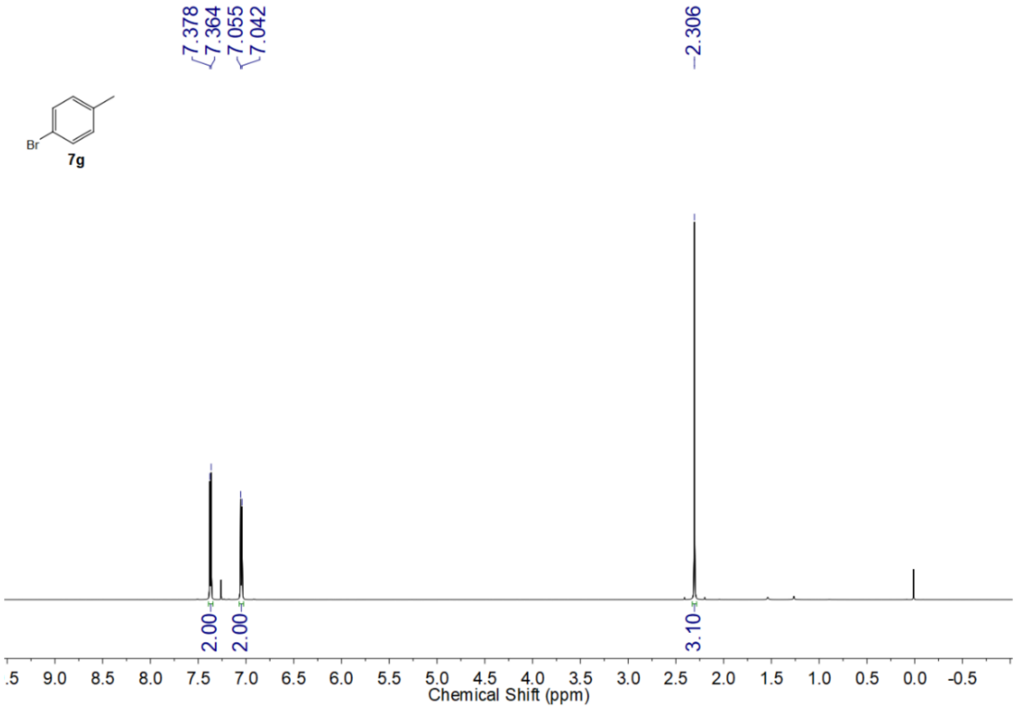
^{13}C NMR (151 MHz, 298 K, $CDCl_3$) of **7e**



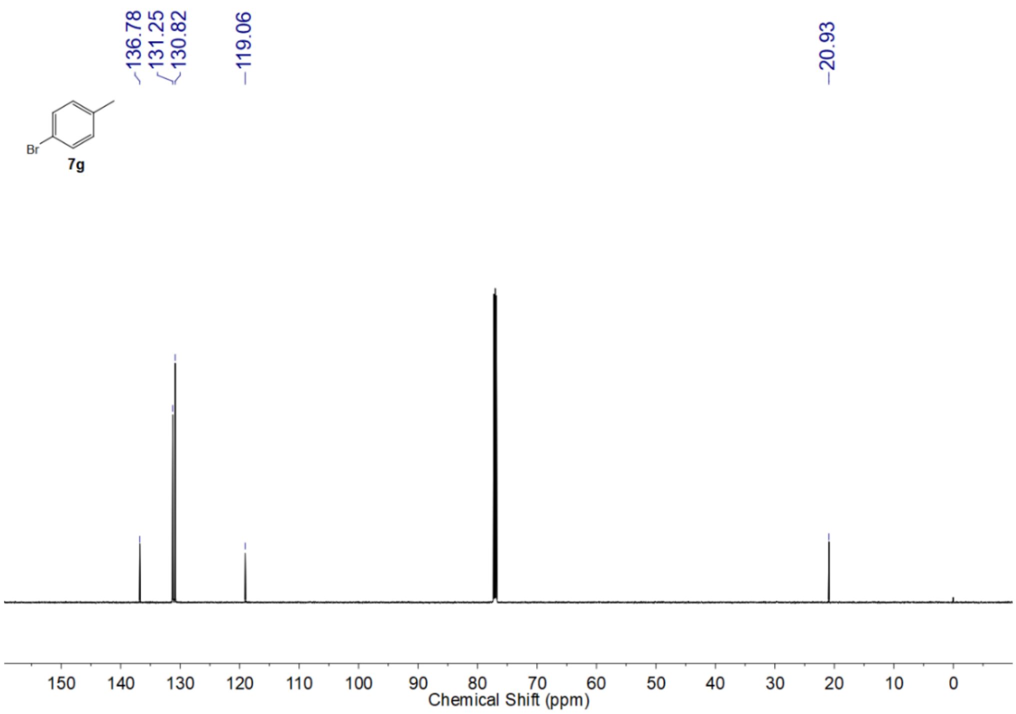
^{1}H NMR (600 MHz, 298K, $CDCl_3$) of **7f**



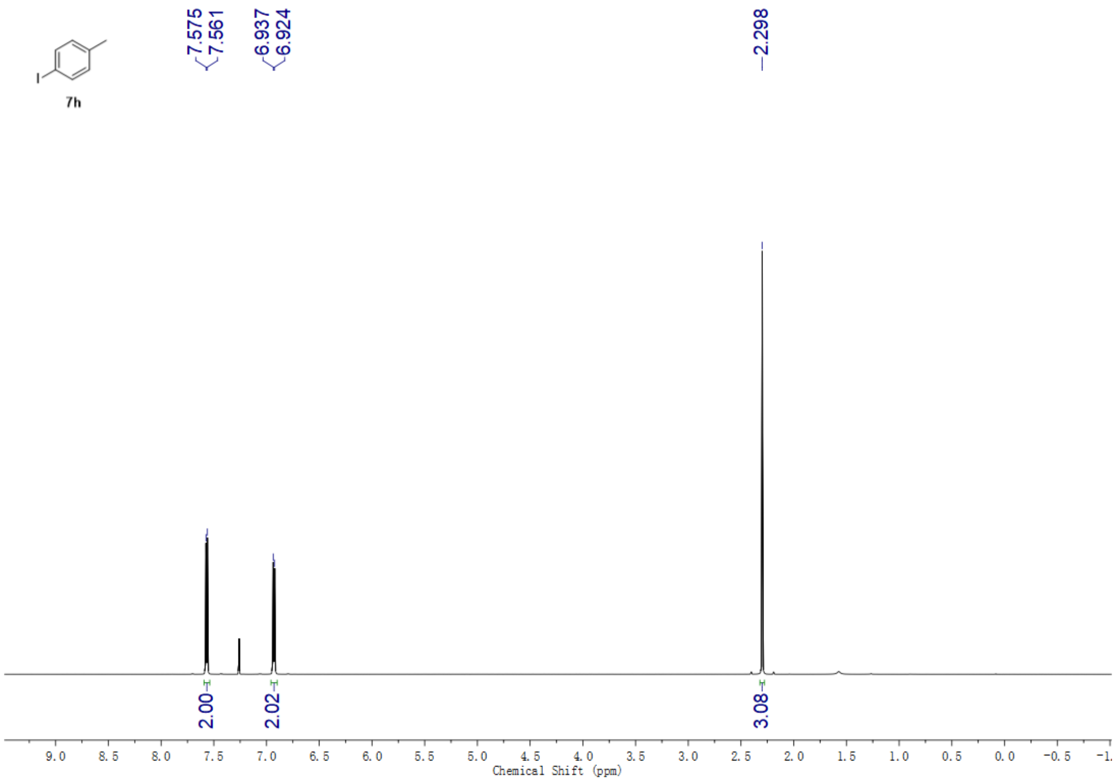
^{13}C NMR (151 MHz, 298 K, $CDCl_3$) of **7f**



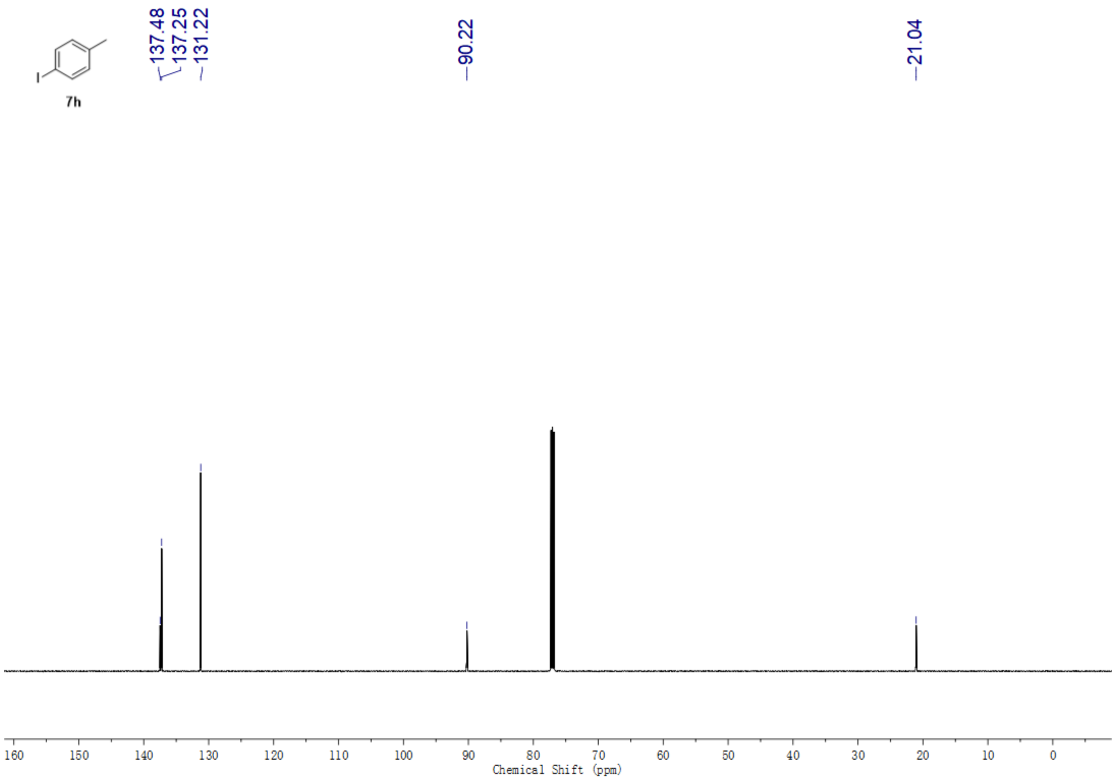
^{1}H NMR (600 MHz, 298K, $CDCl_3$) of **7g**



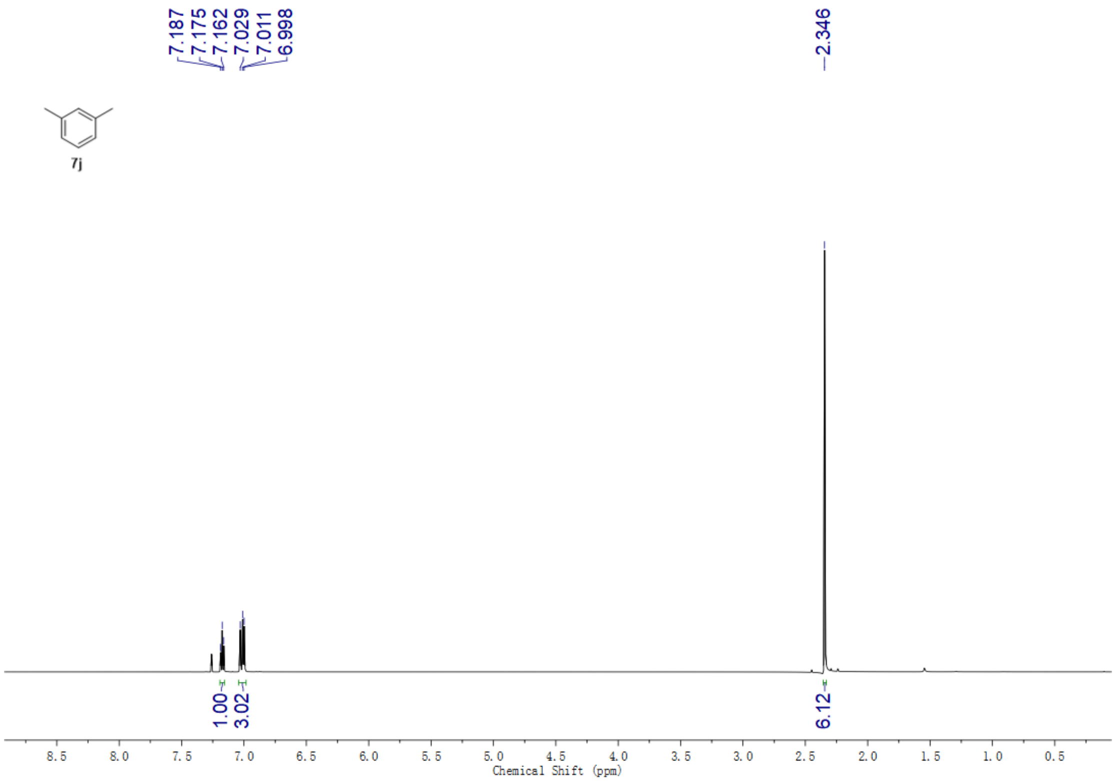
^{13}C NMR (151 MHz, 298 K, $CDCl_3$) of **7g**



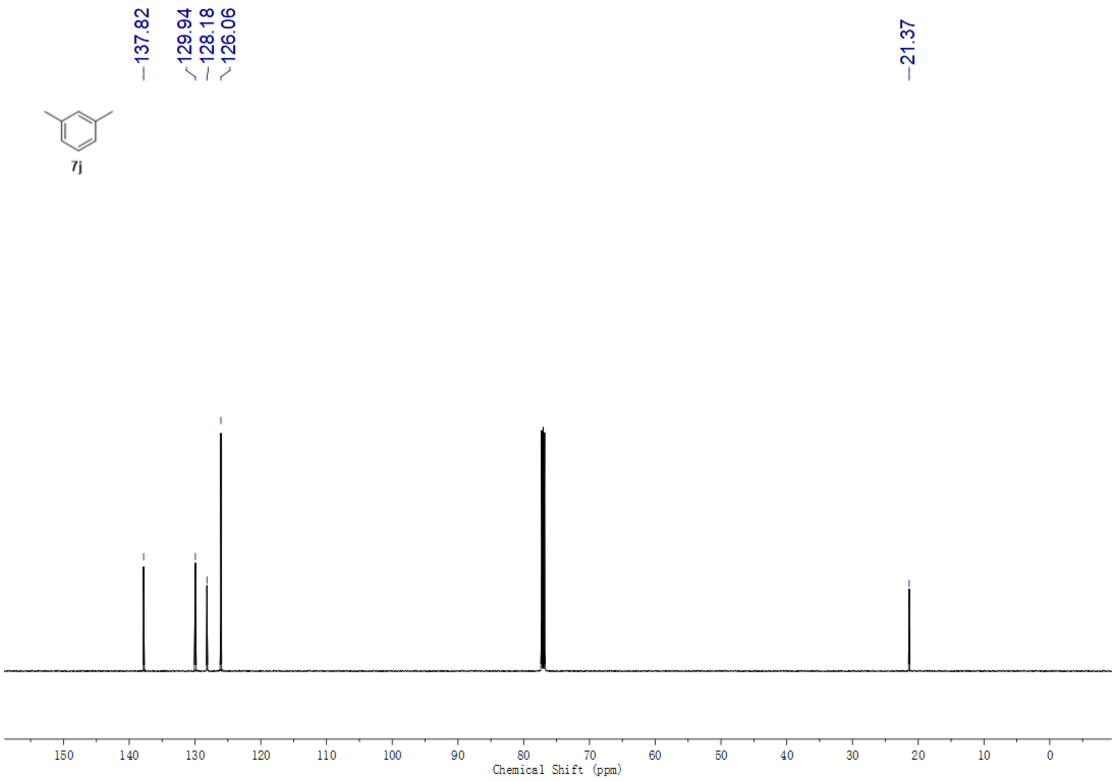
^{1}H NMR (600 MHz, 298K, $CDCl_3$) of **7h**



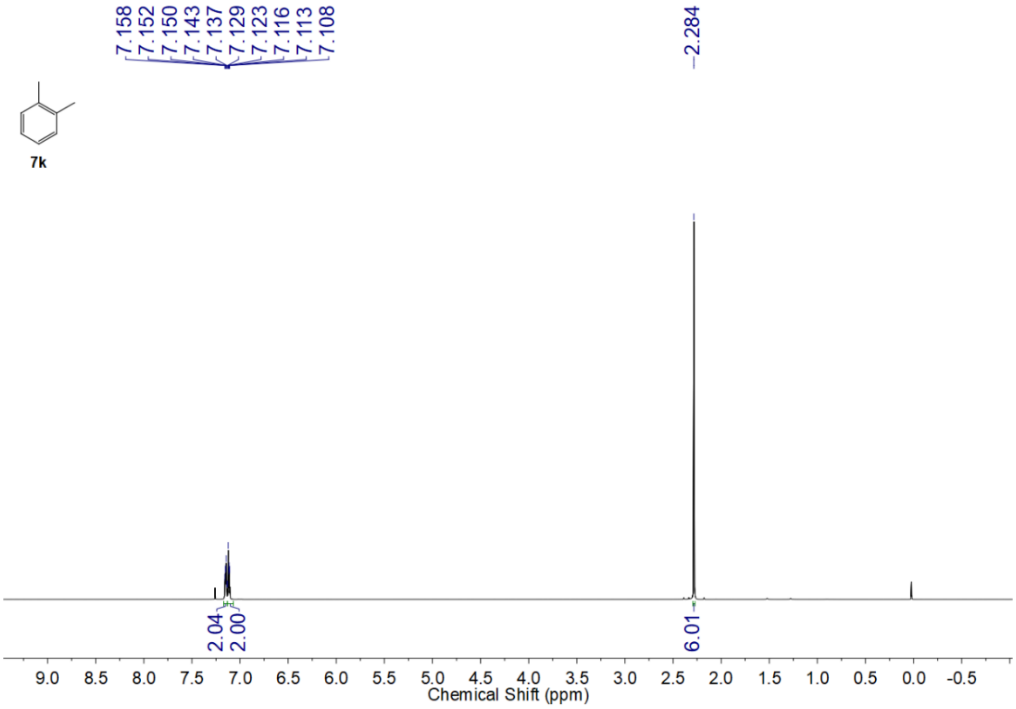
^{13}C NMR (151 MHz, 298 K, $CDCl_3$) of **7h**



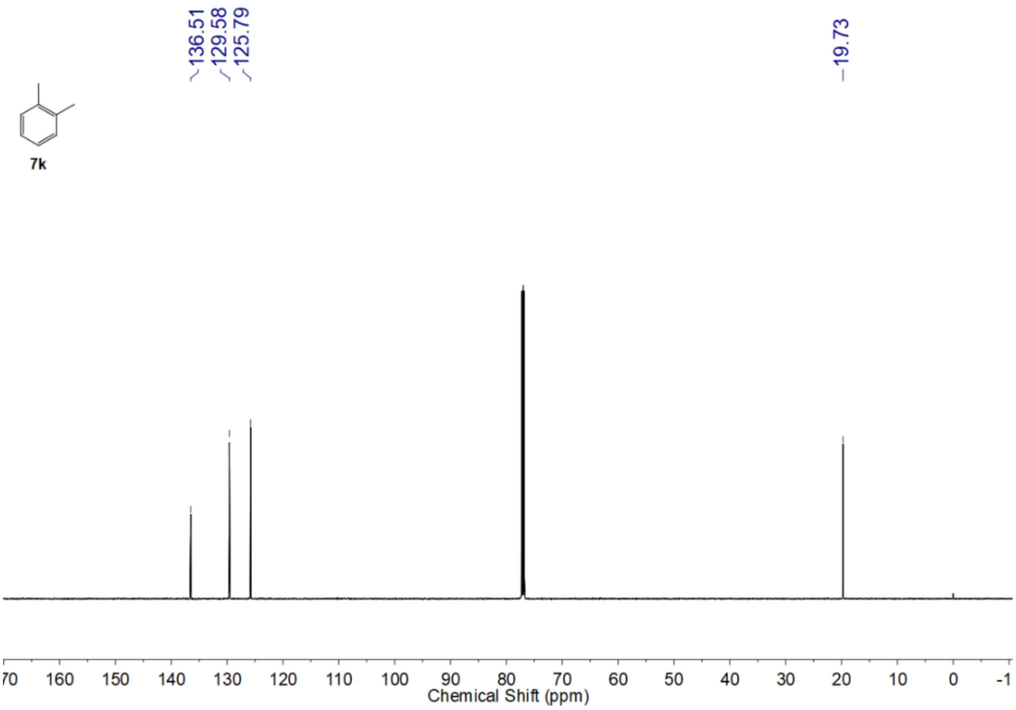
^{1}H NMR (600 MHz, 298K, $CDCl_3$) of **7j**



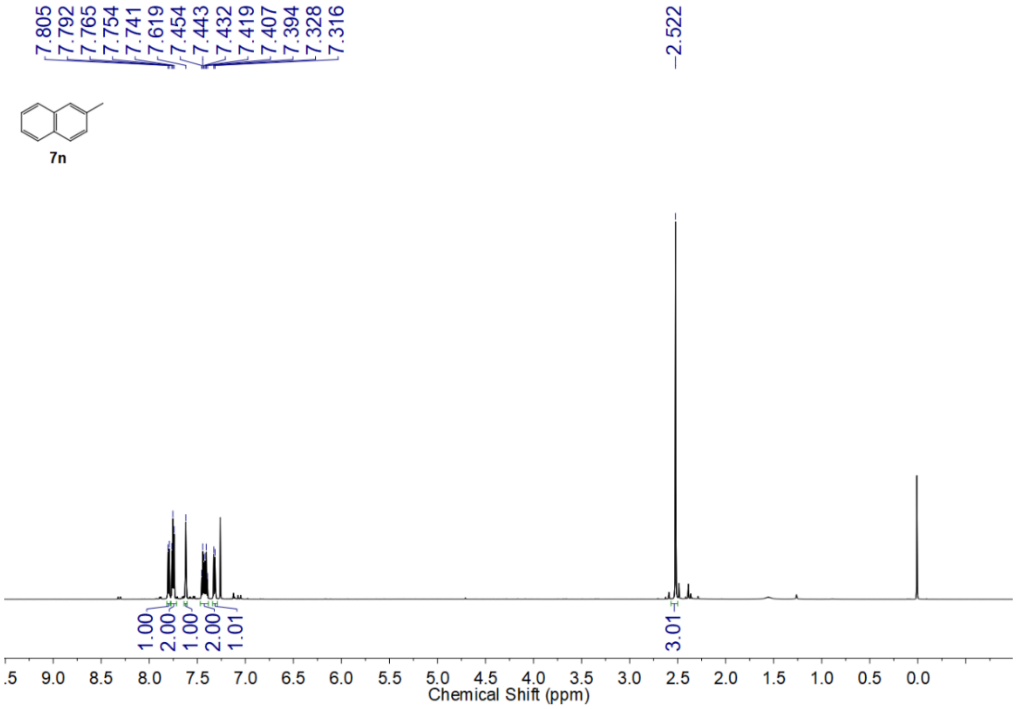
^{13}C NMR (151 MHz, 298 K, $CDCl_3$) of **7j**



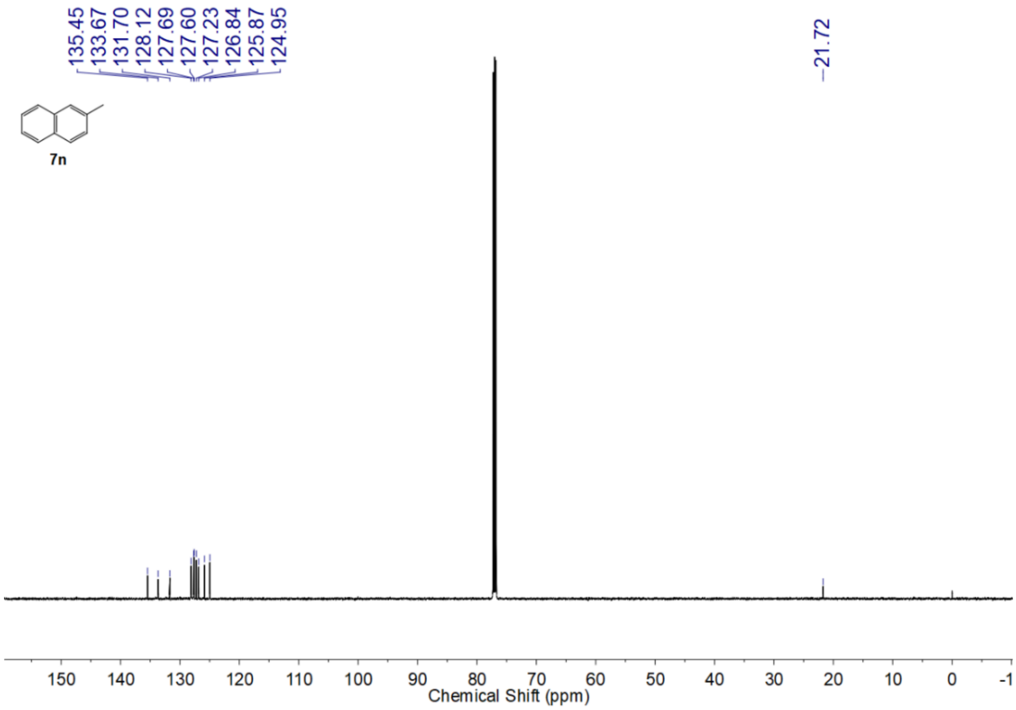
^{1}H NMR (600 MHz, 298K, $CDCl_3$) of **7k**



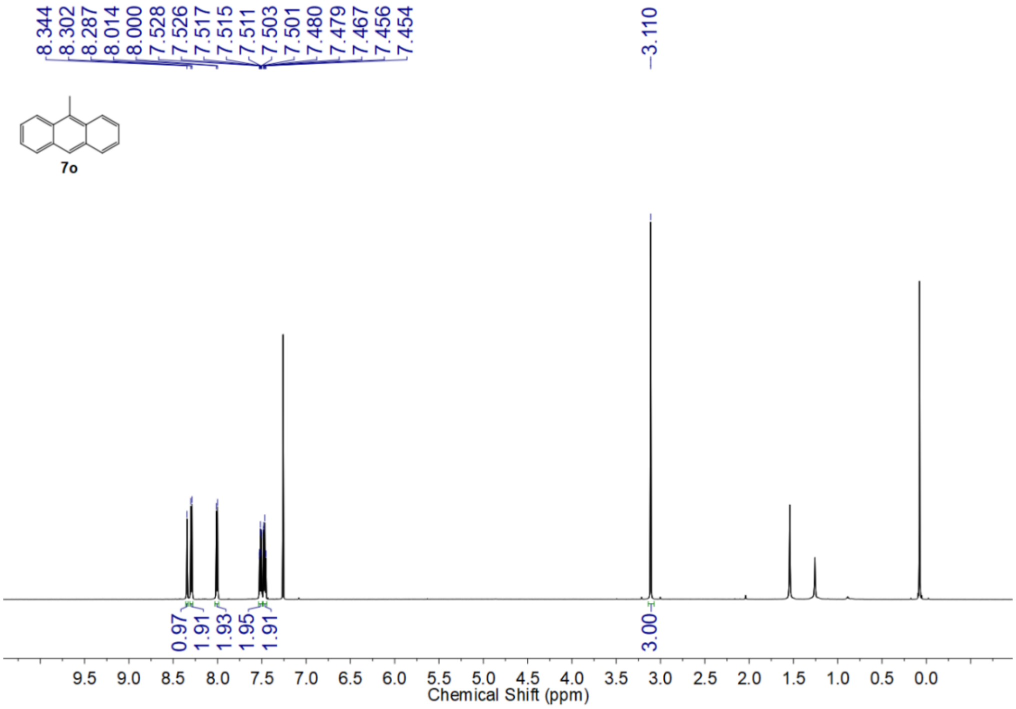
^{13}C NMR (151 MHz, 298 K, $CDCl_3$) of **7k**



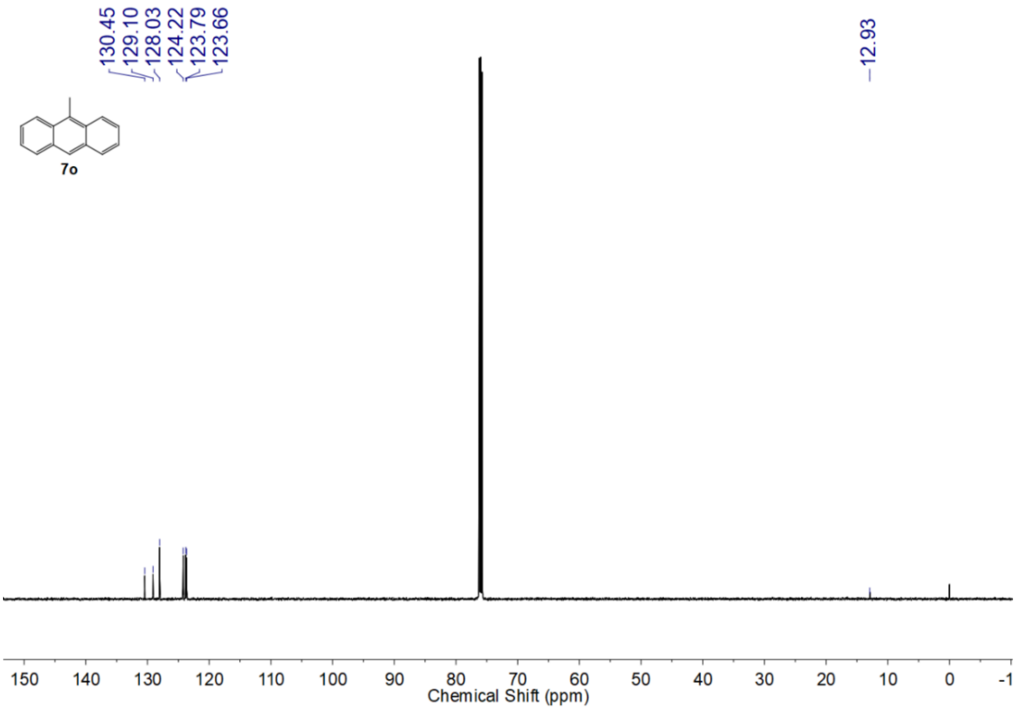
^{1}H NMR (600 MHz, 298K, $CDCl_3$) of **7n**



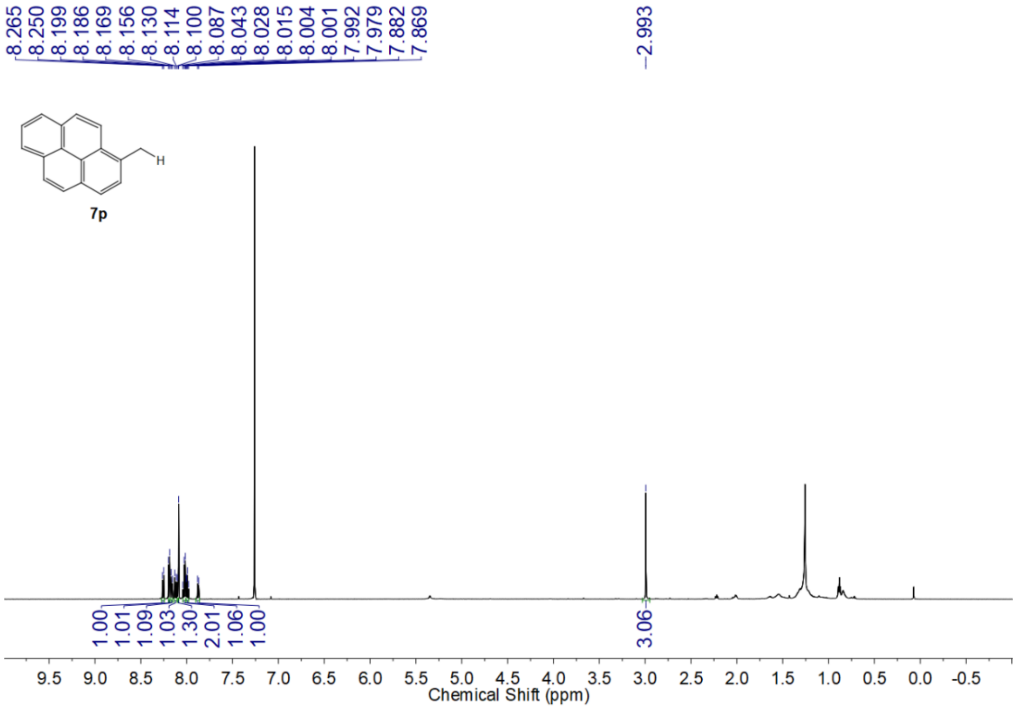
^{13}C NMR (151 MHz, 298 K, $CDCl_3$) of **7n**



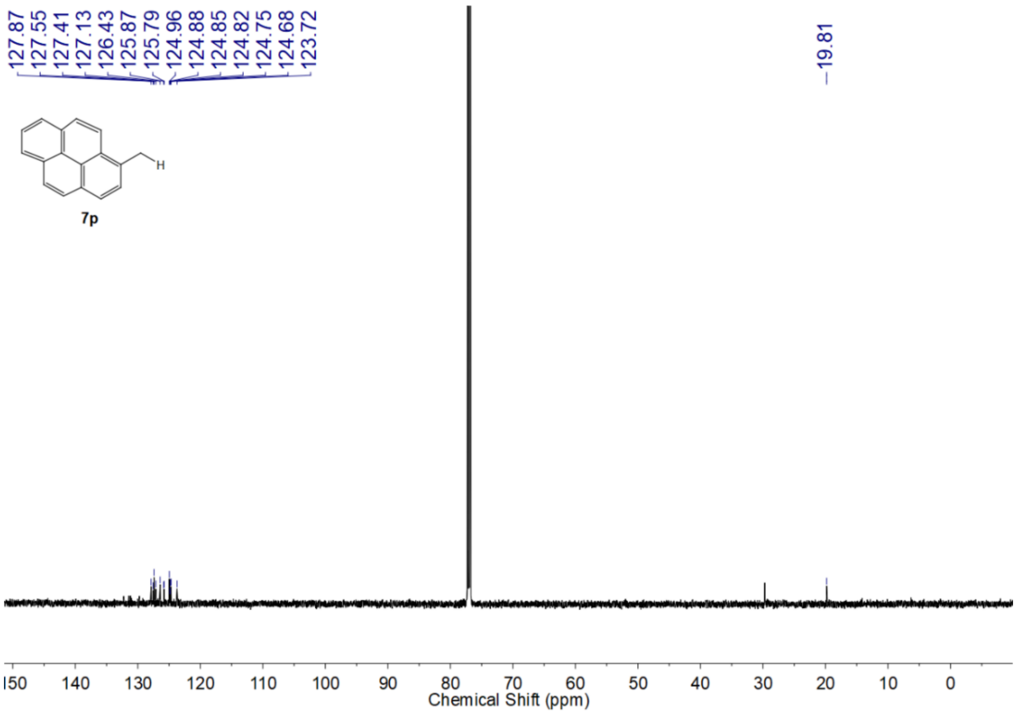
¹H NMR (600 MHz, 298K, $CDCl_3$) of **7o**



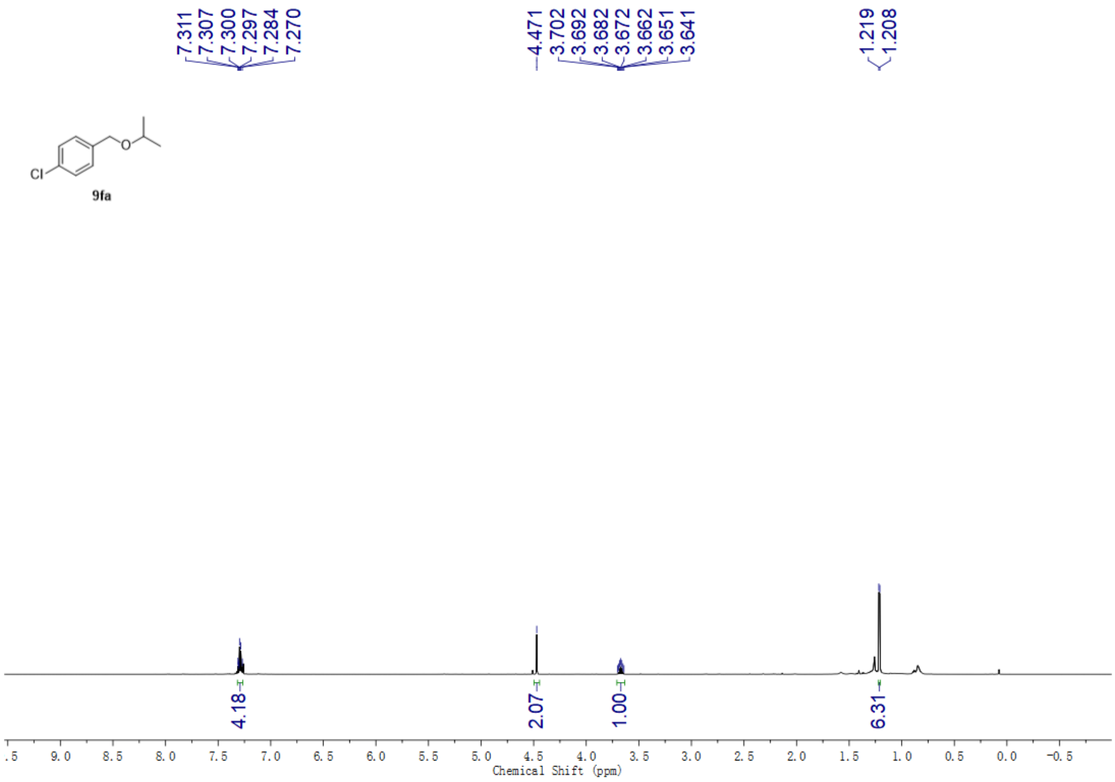
^{13}C NMR (151 MHz, 298 K, $CDCl_3$) of **7o**



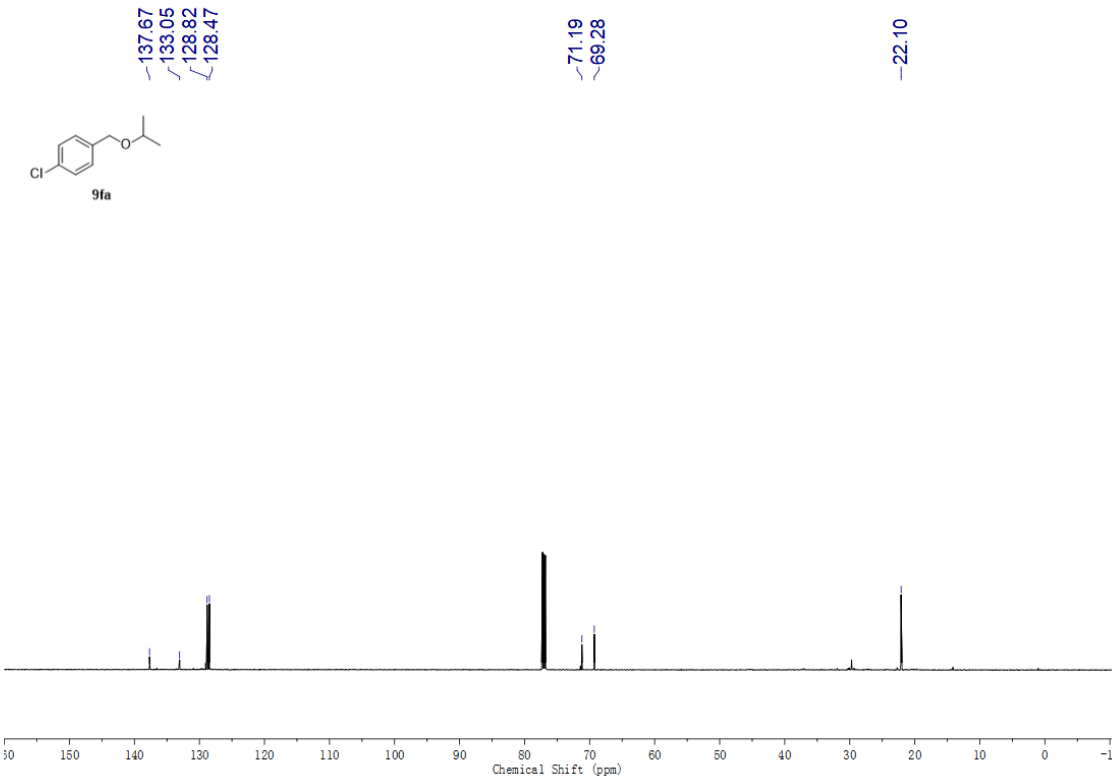
^{1}H NMR (600 MHz, 298K, $CDCl_3$) of **7p**



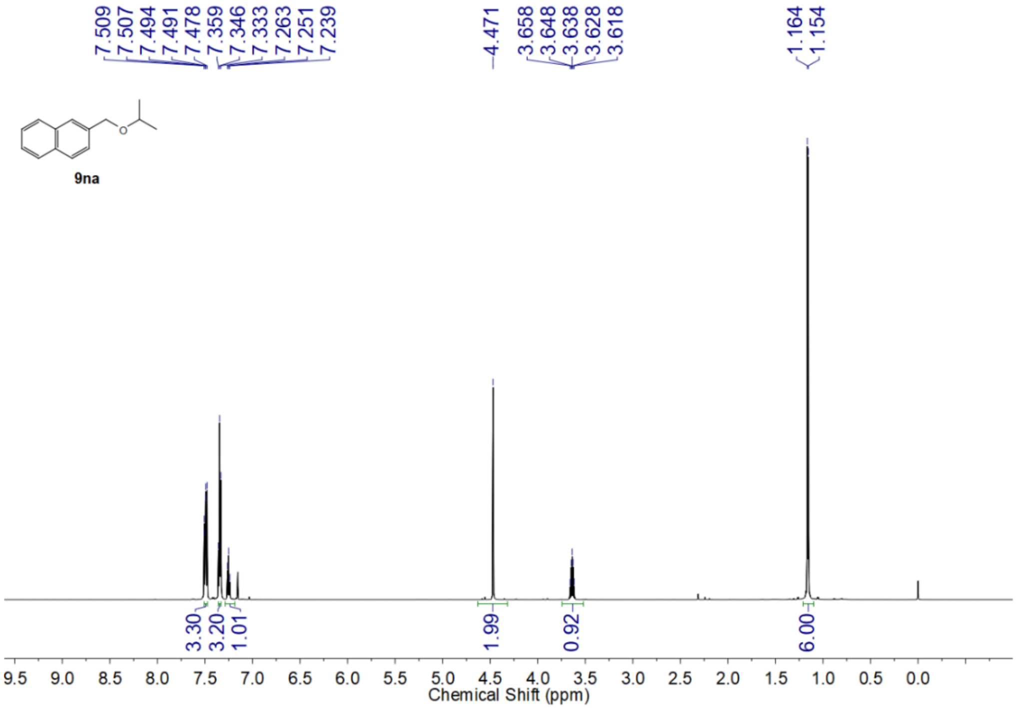
^{13}C NMR (151 MHz, 298 K, $CDCl_3$) of **7p**



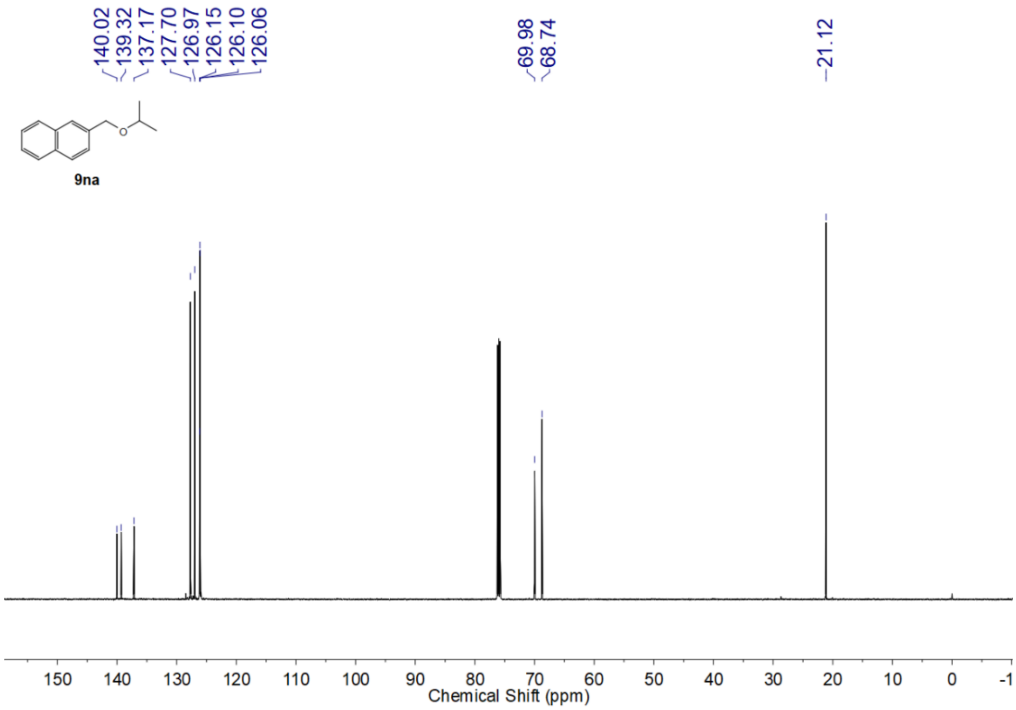
^{1}H NMR (600 MHz, 298K, $CDCl_3$) of **9fa**



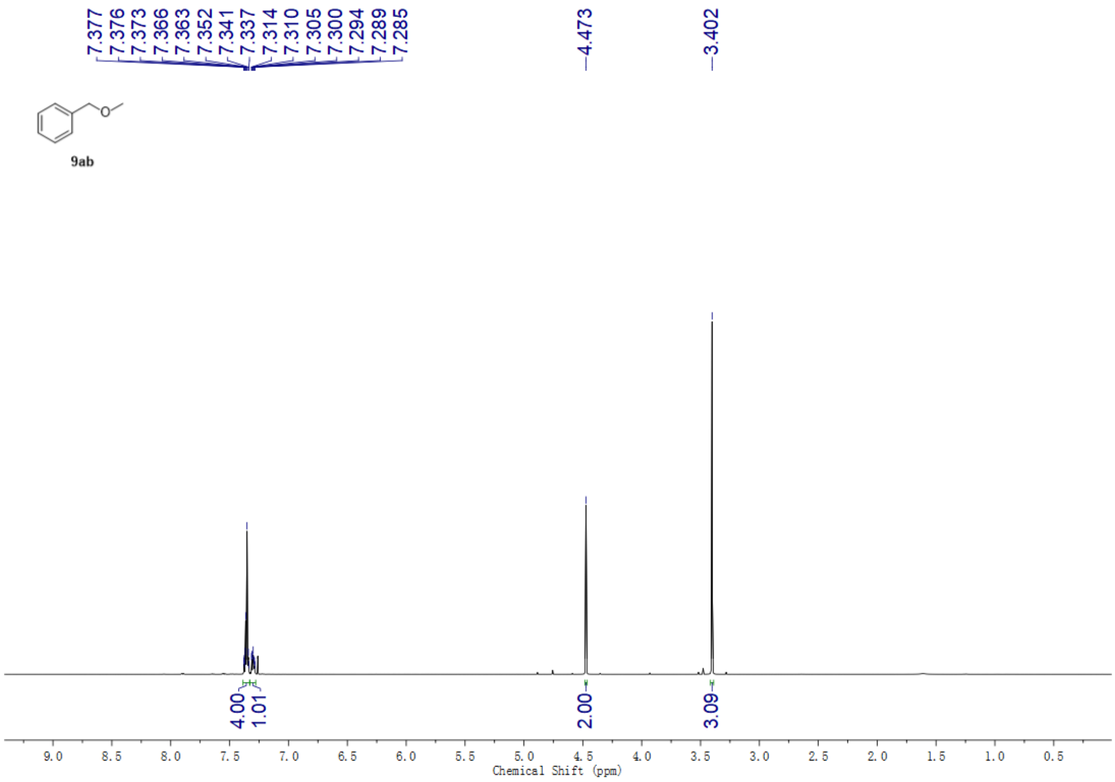
^{13}C NMR (151 MHz, 298 K, $CDCl_3$) of **9fa**



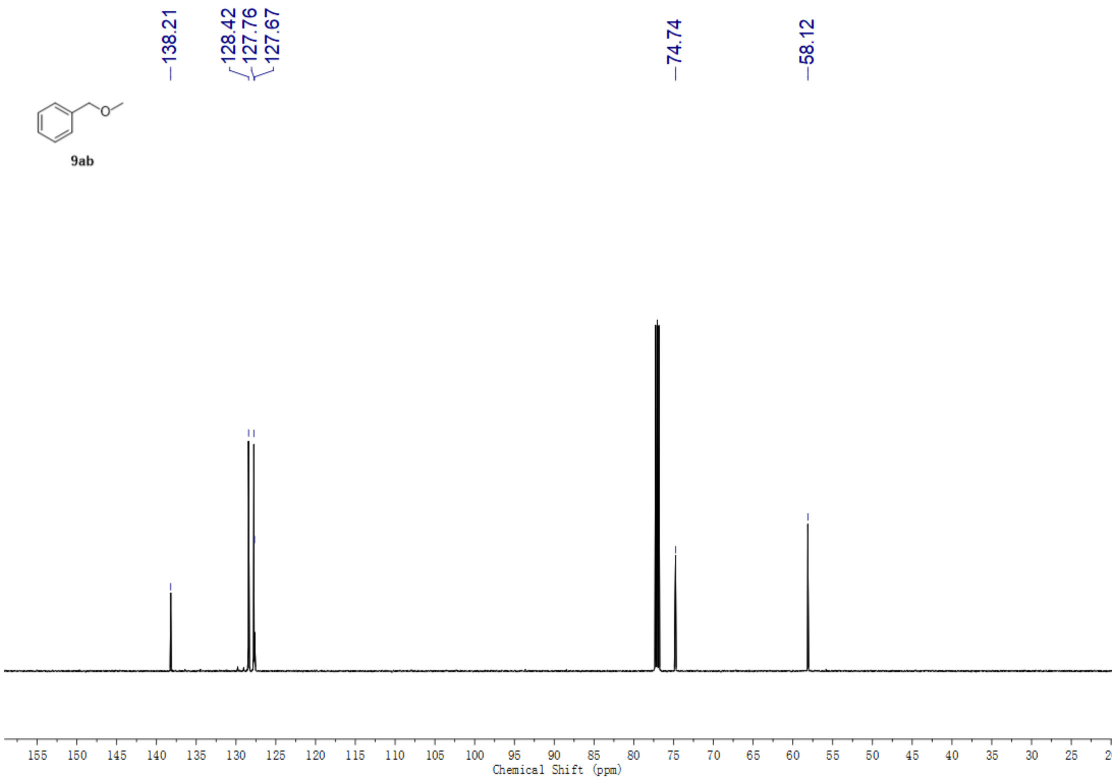
^{1}H NMR (600 MHz, 298K, $CDCl_3$) of **9na**



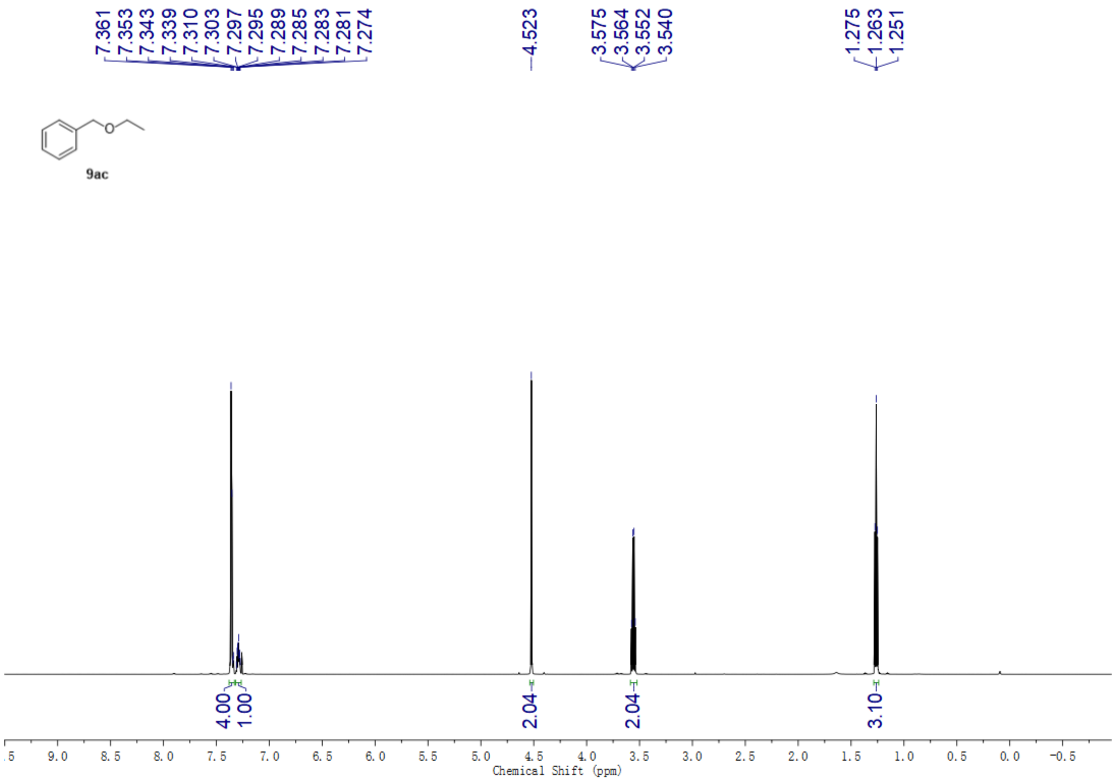
^{13}C NMR (151 MHz, 298 K, $CDCl_3$) of **9na**



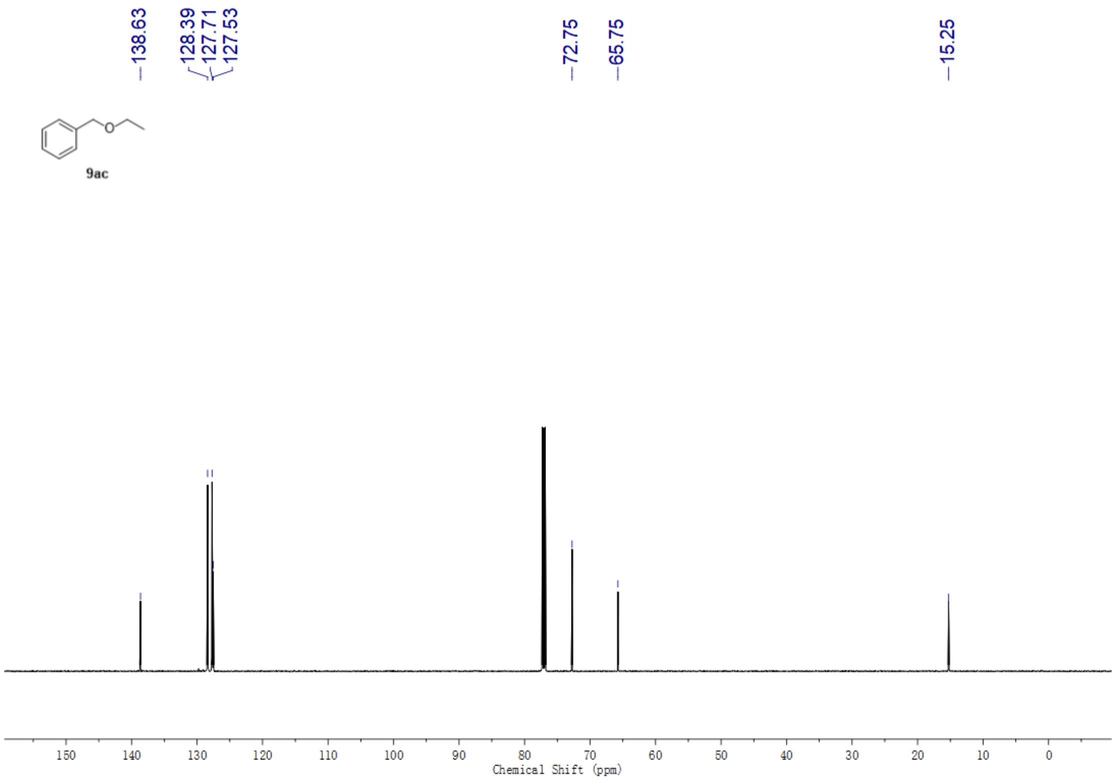
^1H NMR (600 MHz, 298K, $CDCl_3$) of **9ab**



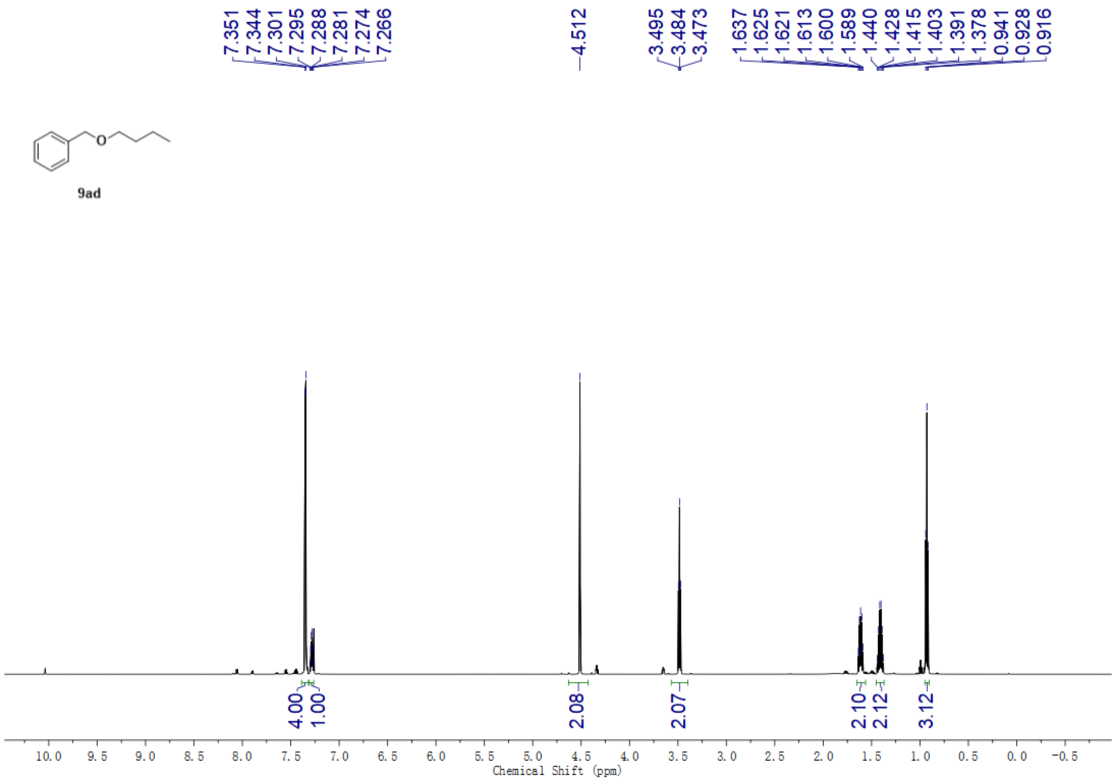
^{13}C NMR (151 MHz, 298 K, $CDCl_3$) of **9ab**



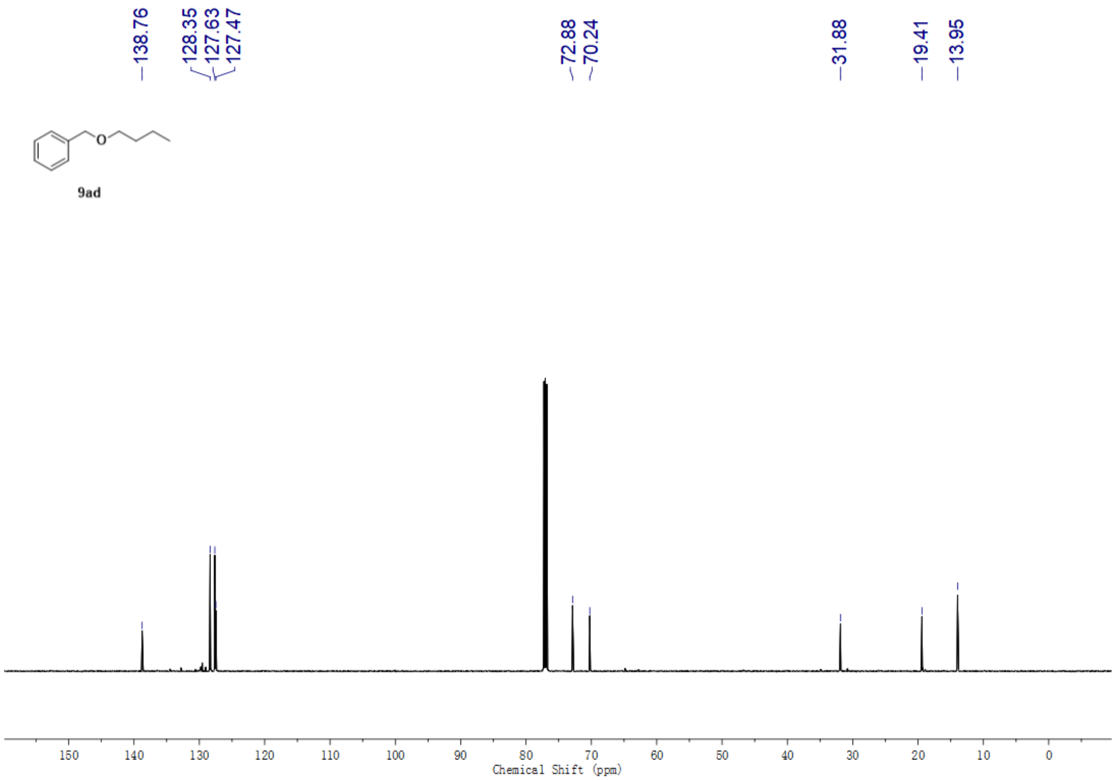
^{1}H NMR (600 MHz, 298K, $CDCl_3$) of **9ac**



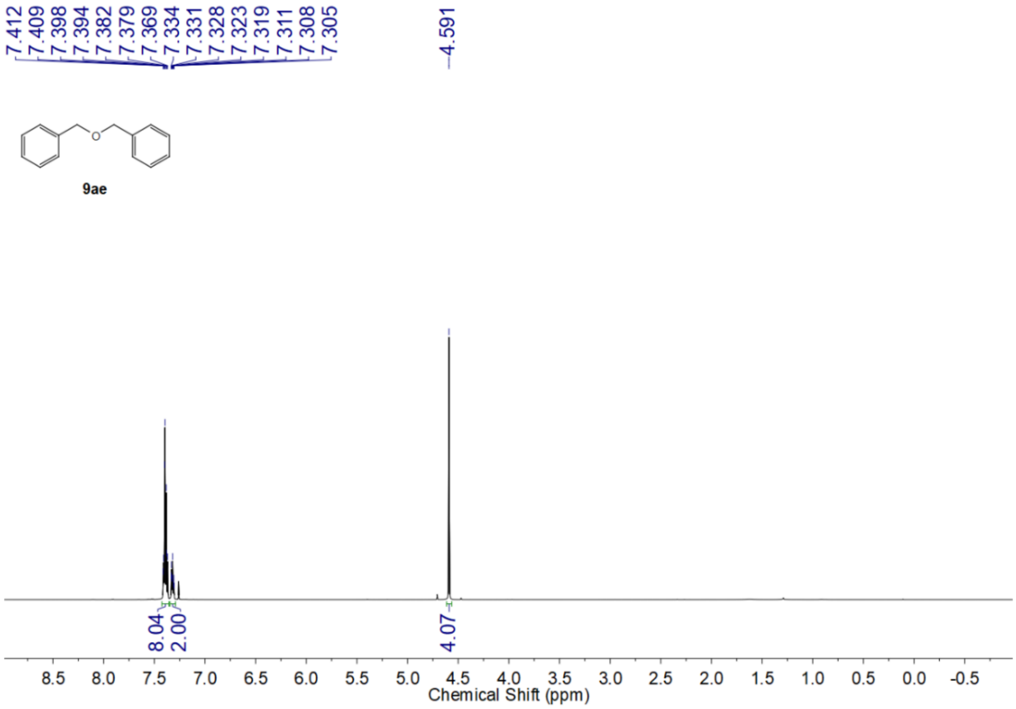
^{13}C NMR (151 MHz, 298 K, $CDCl_3$) of **9ac**



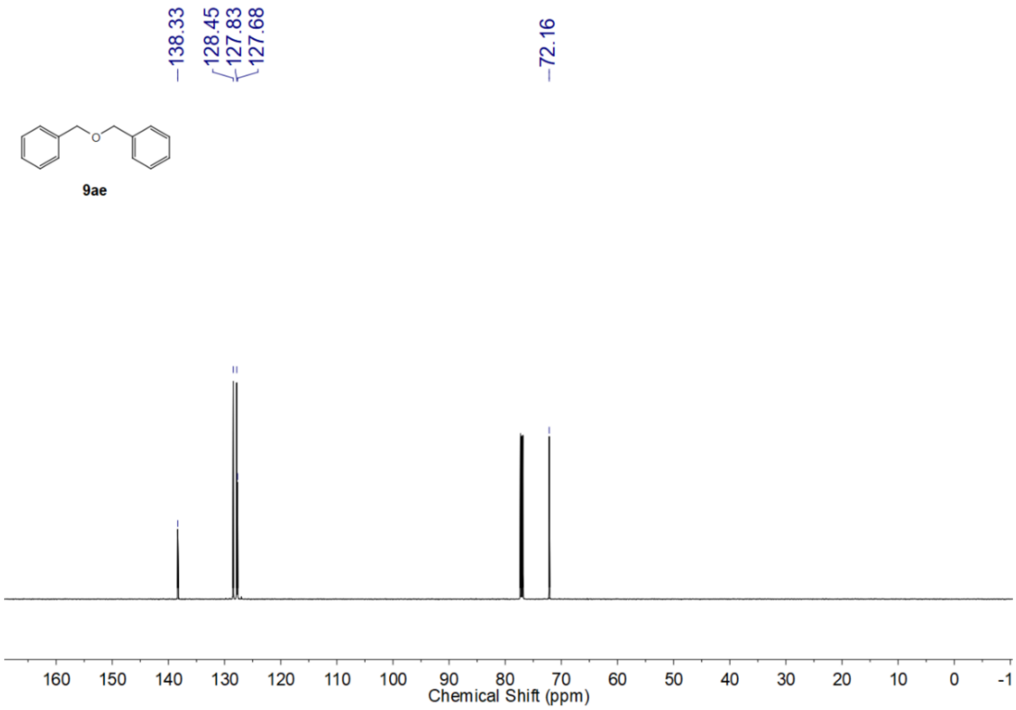
^{1}H NMR (600 MHz, 298K, $CDCl_3$) of **9ad**



^{13}C NMR (151 MHz, 298 K, $CDCl_3$) of **9ad**



^{1}H NMR (600 MHz, 298K, $CDCl_3$) of **9ae**



^{13}C NMR (151 MHz, 298 K, $CDCl_3$) of **9ae**

16. References

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