Supporting Information

Consecutive Regulation of Catalytic Activities of $B(C_6F_5)_3 \cdot H_2O$: Direct Nucleophilic Substitution of Benzyl Fluorides with Alcohols via Dual Activation

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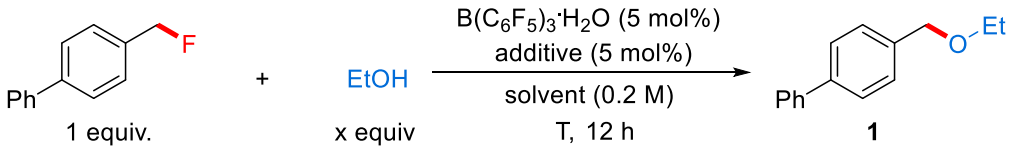
Content

1. General Remarks.

The ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded on a Bruker AV-400 spectrometer with TMS as internal reference in $CDCl_3$. High resolution mass spectra were recorded using analyses by Bruker Daltonics SolariX 7.0T. Organic solvents were dried by standard methods when necessary. Commercially obtained reagents were used without further purification. Flash column chromatography was performed using 300-400 mesh silica gel. For thin-layer chromatography (TLC), silica gel plates (Huanghai GF254) were used.

2. Table S1. Screening the reaction conditions.



Entry	equiv (x)	additive	T (^{o}C)	solvent	yield (%)
1	1.5	-	60	THF	37
2	1.5	-	60	dibutyl ether	48
3	1.5	-	60	isopropl ether	28
4	1.5	TMP	60	DCE	N.D.
5	1.5	PMP	60	DCE	N.D.
6	1.5	Ph_3P	60	DCE	34
7	1.5	$(4\text{-}FPh)_3P$	60	DCE	38
8[b]	1.5	-	60	dibutyl ether/DCE	17
9[c]	1.5	-	60	THF/DCE	70
10[d]	1.5	-	60	THF/DCE	58
11[e]	1.5	-	60	THF/toluene	39
12[f]	1.5	-	60	THF/$CHCl_3$	26
13	***1.5***	***-***	***60***	***THF/DCE***	***90***
14	1.5	-	60	DCE	28
15	1.5	-	25	THF/DCE	<5
16	1.5	-	40	THF/DCE	<5
17	1	-	60	THF/DCE	40
18	2	-	60	THF/DCE	51
19	5	-	60	THF/DCE	35
20[g]	1.5	-	60	THF/DCE	N.R.
21[h]	1.5	-	60	THF/DCE	trace
22[i]	1.5	-	60	THF/DCE	N.D.
23[j]	1.5	-	60	THF/DCE	N.D.
24[k]	1.5	-	60	THF/DCE	N.D.
25[l]	1.5	-	60	THF/DCE	79
26[m]	1.5	-	60	THF/DCE	75

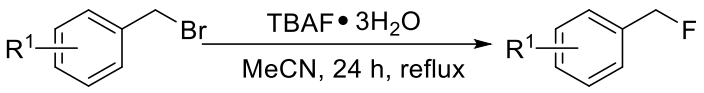
[a] All the reaction was carried out on a 0.2 mmol scale. Entries 13-24, THF/DCE = 1:4. [b] Dibutyl ether/DCE = 1:1. [c] THF/DCE = 1:1. [d]THF/DCE = 4:1. [e]THF/toluene = 1:4. [f] THF/$CHCl_3$ = 1:4. [g] Without $B(C_6F_5)_3{\cdot}H_2O$. [h] TsOH (20 mol%) instead $B(C_6F_5)_3{\cdot}H_2O$. [i] PhCOOH (20 mol%) instead $B(C_6F_5)_3{\cdot}H_2O$. [j] CH_3COOH (20 mol%) instead $B(C_6F_5)_3{\cdot}H_2O$. [k] HFIP (20 mol%) instead $B(C_6F_5)_3{\cdot}H_2O$. [l] H_2O (0.05 mL) was added. [m] H_2O (0.1 mL) was added. TMP = 2,2,6,6-tetramethylpiperidine. PMP = 1,2,2,6,6-pentamethylpiperidine.

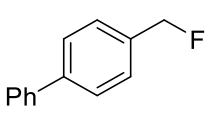
We began our investigation by examining the reaction of 4-(fluoromethyl)-1,1'-biphenyl (**S1**) with the ethanol in THF with 5 mol% of $B(C_6F_5)_3$ at 60 ^{o}C, and the reaction went on smoothly to give the desired

ether **1** in 37% yields (Table S1, entry 1). While performing the reaction in dibutyl ether and isopropyl ether, corresponding product **1** was obtained in 48% and 28% yields (Table S1, entries 2 and 3). Next, several phosphine or amine Brønsted bases (5 mol%) were used instead of ethers. Using DCE as solvent, the reactions were inhibited in the presence of 2,2,6,6-tetramethylpiperidine (TMP) or 1,2,2,6,6-pentamethylpiperidine (PMP) but gave corresponding product **1** in 34% and 38% yields when phosphines were used (Table S1, entries 4-7). Therefore, ethers were selected as the Brønsted base. Considering that the interaction of BCF and ether is too strong, different diluted ethereal solvents were investigated, and it was found that the mixed solvent of THF/DCE (1:4) was the most suitable for the transformation and delivered product **1** in 90% yields (Table S1, entries 8-13). If the reaction was performed in DCE without THF, the yield of **1** decreased to 28%, indicating that THF is crucial to this transformation (Table S1, entry 14). Temperature effect was also evaluated, as conducting the reaction at 25 °C and 40 °C, only trace amount of the product was observed (Table S1, entries 15-16). Increasing or decreasing the amount of EtOH did not benefit the reaction outcomes (Table S1, entries 17–19). It has to be mentioned that, no reaction occurred in the absence of $B(C_6F_5)_3 \cdot H_2O$ (Table S1, entry 20). When the Brønsted acids were used as catalyst, no desired product **1** was obtained (Table S1, entry 21-23). The polymerization of benzyl fluoride was not observed by using hexafluoroisopropanol (HFIP) as catalyst (Table S1, entry 24). Besides, the yield was decreased to 79% and 75% when the H_2O was added (Table S1, entries 25-26), and the 4-biphenylmethanol produced by water insertion of **1** was monitored.

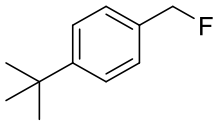
3. General procedure for the preparation of benzyl fluorides

Typical Procedures for the Synthesis of Primary benzylic fluorides.[1]

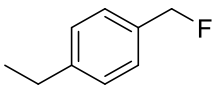




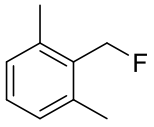
S1



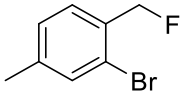
S2



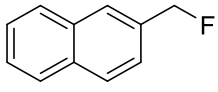
S3



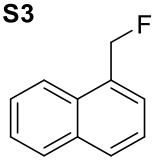
S4



S5



S6

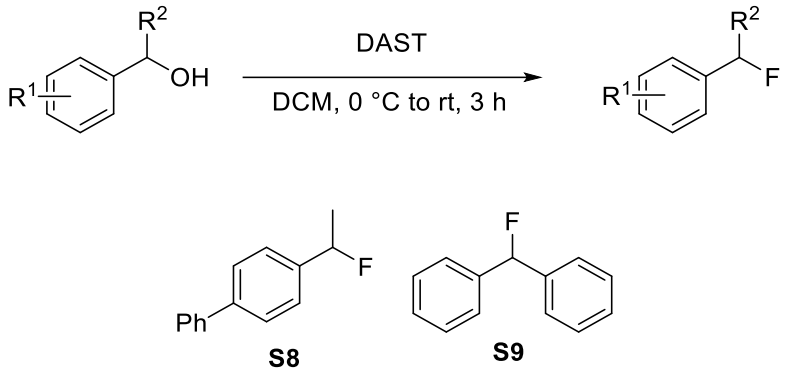


S7

To a stirred solution of the benzylic bromide (5.0 mmol, 1.0 eq.) in anhydrous CH_3CN (0.5 M) was added tetrabutylammonium fluoride trihydrate (10.0 mmol, 2.0 eq.). The reaction mixture was refluxed for 24 h. After completion, the reaction was quenched with water and extracted with EA three times. The combined organic extracts were washed with brine, dried with Na_2SO_4, filtered and concentrated under

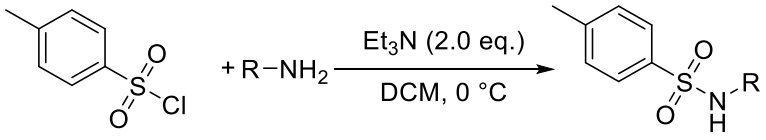
vacuum. Column chromatography followed to give pure product. In addition, **S1**-**S4, S6**-**S7** are known compounds.[1-3]

Typical Procedures for the Synthesis of Secondary benzylic fluorides.[4]



To a solution of the alcohol (5.0 mmol, 1.0 eq.) in the dry DCM (0.5 M), DAST (6.0 mmol, 1.2 eq.) was added at 0˚C. The reaction was slowly warmed to room temperature and the mixture was stirred for 3 h. Water was added to the reaction mixture, and then a saturated aqueous solution of sodium hydrogencarbonate was added and the mixture was extracted with EA. The combined organic layers were washed with brine and dried with Na_2SO_4. After filtration, the mixture was dried and the residue was purified by silica gel column chromatography to give pure product. In addition, **S8**, **S9** are known compound.[4,5]

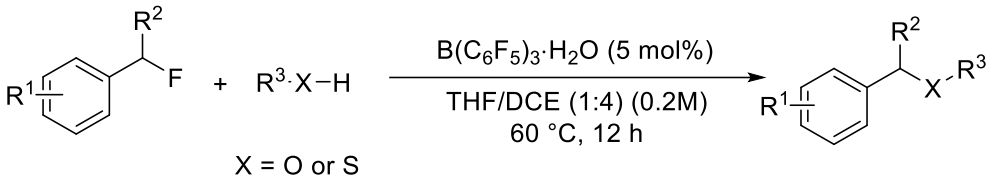
4. General procedure for the preparation of N-(arylsulfonyl)acrylamide.[6]



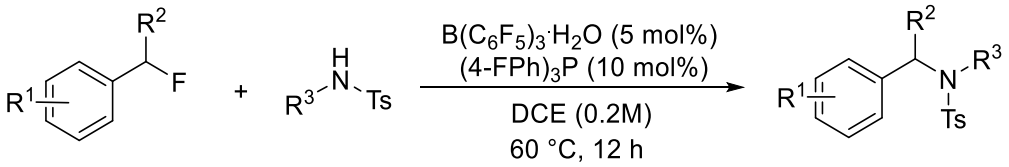
Amine (6.0 mmol, 1.2 eq.) and Et_3N (10.0 mmol, 2.0 eq.) were added to a flame-dried flask, then 4-methylbenzenesulfonyl chloride (5.0 mmol, 1.0 eq.) in dichloromethane was injected by syringe. The mixture was stirred at 0 ˚C until TLC showed that arylsulfonyl chloride was totally consumed. Water was added to the reaction mixture and extracted with dichloromethane. The combined organic layers

were dried over Na_2SO_4, concentrated under reduced pressure. The residue was purified by silica gel column chromatography to give pure product.

5. General procedure for the nucleophilic substitution of benzylic fluorides



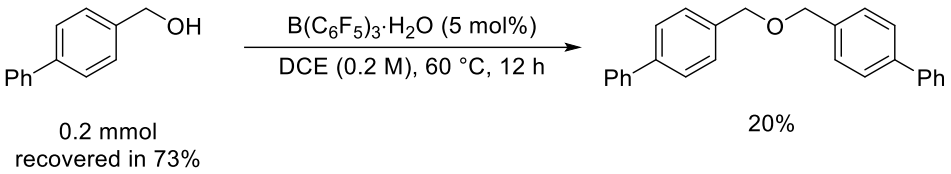
To a stirred solution of benzylic fluorides (0.2 mmol, 1.0 eq.) in mixed solvent (THF:DCE = 1:4) were added the nucleophiles (0.3 mmol, 1.5 eq.) and $B(C_6F_5)_3 \cdot H_2O$ (5 mol%). The resulting solution was stirred at 60 ˚C for 12 h. The reaction was quenched with water and extracted with DCM for three times. The organic phases were washed with brine, dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by silica gel column chromatography to give pure product.



To a stirred solution of benzylic fluorides (0.2 mmol, 1.0 eq.) in DCE was added N-(arylsulfonyl)acrylamide (0.4 mmol, 2.0 eq.), followed by the addition of $B(C_6F_5)_3 \cdot H_2O$ (5 mol%) and phosphine catalyst (10 mol%). The resulting solution was stirred for 12 h at 60 ˚C. The reaction was quenched with water and extracted with DCM for three times. The organic phases were washed with brine, dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by silica gel column chromatography.

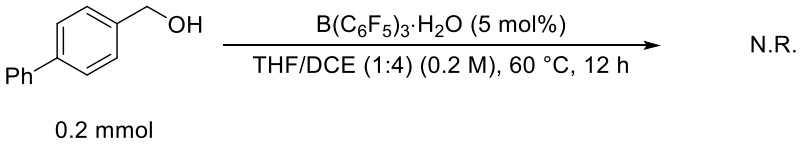
6. Control experiments

Experiment (a):



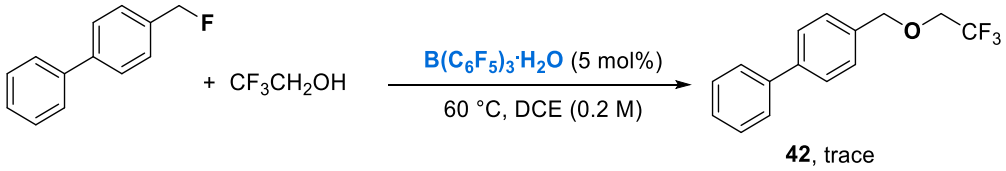
To a stirred solution of 4-biphenylmethanol (36.8 mg, 0.2 mmol) in DCE (1 ml) was added $B(C_6F_5)_3{\cdot}H_2O$ (5 mol%). The resulting solution was stirred at 60 ˚C for 12 h. The corresponding ether was obtained in 20% (7.0 mg), and the 4-biphenylmethanol was recovered in 73% (27.1 mg).

Experiment (b):



To a stirred solution of 4-biphenylmethanol (36.8 mg, 0.2 mmol) in mixed solvent (THF:DCE = 1:4, 1.0 mL) was added $B(C_6F_5)_3{\cdot}H_2O$ (5 mol%). The resulting solution was stirred at 60 ˚C for 12 h. No reaction was observed.

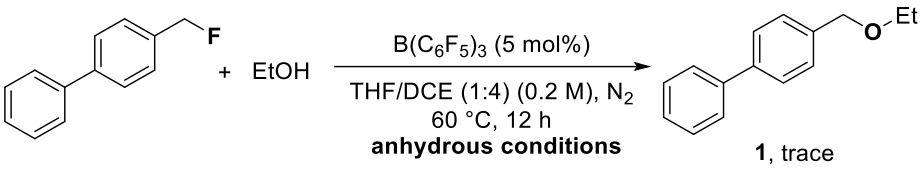
Experiment (c):



To a stirred solution of benzylic fluorides (37.2 mg, 0.2 mmol, 1.0 eq.) in DCE (1.0 mL) was added the CF_3CH_2OH (1.5 eq.) and $B(C_6F_5)_3{\cdot}H_2O$ (5 mol%). The resulting solution was stirred at 60 ˚C for 12 h. The reaction was complex.

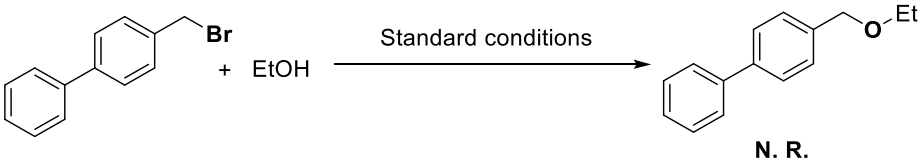
Investigations of the influence of water:

Experiment (d):



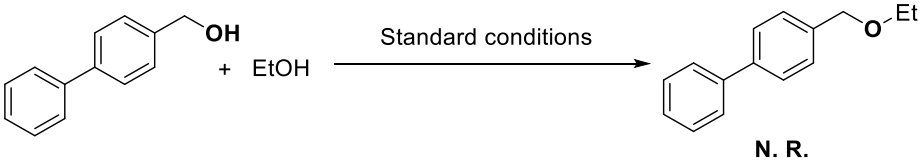
In glovebox, to a stirred solution of benzylic fluorides (37.2 mg, 0.2 mmol, 1.0 eq.) in mixed anhydrous solvent (THF:DCE = 1:4, 1.0 mL) were added the anhydrous ethanol (1.5 eq.) and $B(C_6F_5)_3 \cdot H_2O$ (5 mol%), the reaction was protected by N_2. The resulting solution was stirred at 60 °C for 12 h. Only trace amount of **1** was observed (TLC).

Experiment (e):



To a stirred solution of benzylic bromide (49.4 mg, 0.2 mmol, 2.0 eq.) in mixed solvent (THF:DCE = 1:4, 1.0 mL) were added ethanol (1.5 eq.) and $B(C_6F_5)_3 \cdot H_2O$ (5 mol%). The resulting solution was stirred at 60 °C for 12 h. No product was found.

Experiment (f):



To a stirred solution of 4-biphenylmethanol (36.8 mg, 0.2 mmol, 1.0 eq.) in mixed solvent (THF:DCE = 1:4, 1.0 mL) were added ethanol (1.5 eq.) and $B(C_6F_5)_3 \cdot H_2O$ (5 mol%). The resulting solution was stirred at 60 °C for 12 h. No product was found.

7. NMR experiments

0.05 mmol $B(C_6F_5)_3 \cdot H_2O$ was dissolved in $CDCl_3$. The solution was measured by ^{19}F NMR the result shows in Figure S1. Subsequently, 1.0 eq. THF was added, the result shows in Figure S2. Last, 1.0 eq. 1-(tert-butyl)-4-(fluoromethyl)benzene was added, the result shows in Figure S3.

^{19}F NMR Experiments:

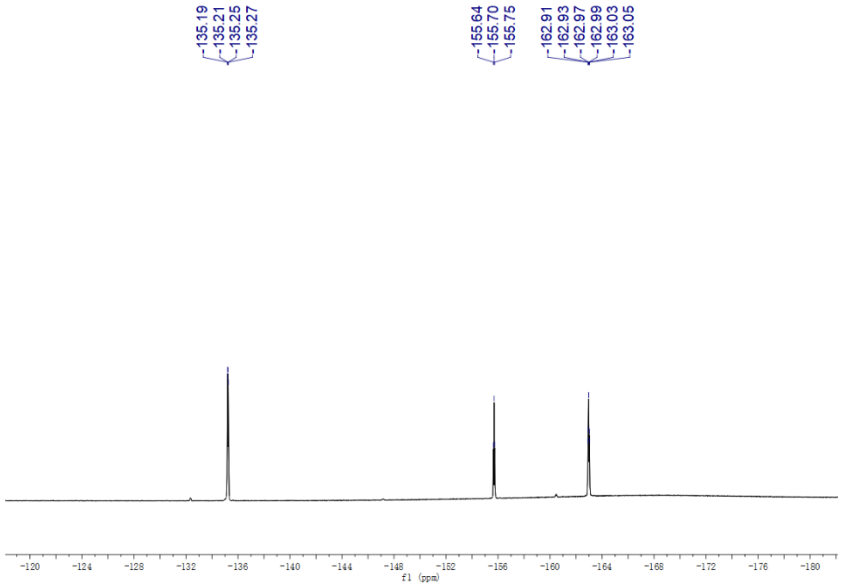


Figure S1. ^{19}F NMR of $B(C_6F_5)_3 \cdot H_2O$.

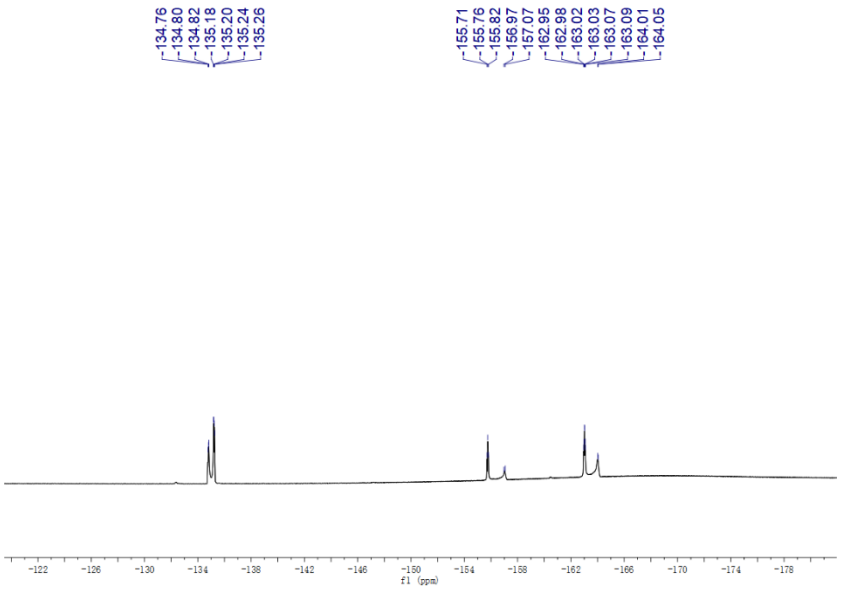


Figure S2. ^{19}F NMR of $B(C_6F_5)_3 \cdot H_2O$ and THF (1:1).

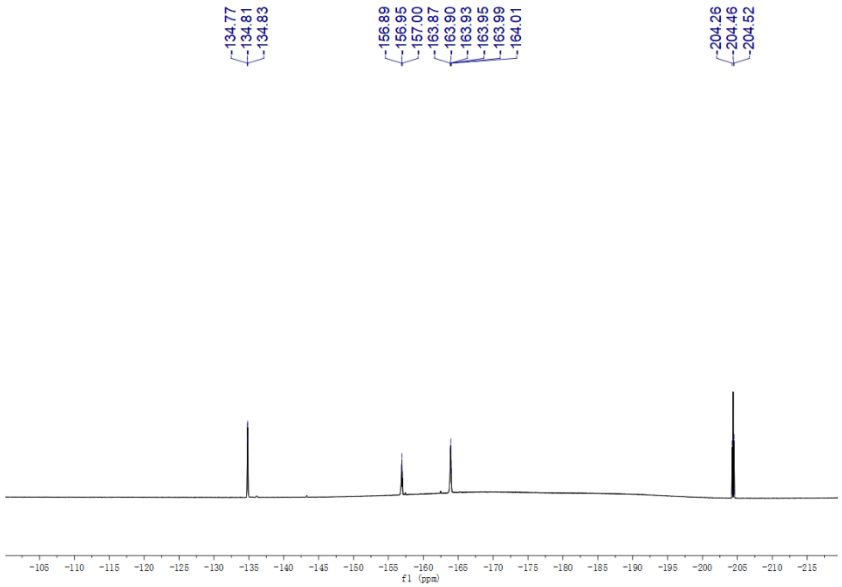


Figure S3. ^{19}F NMR of $B(C_6F_5)_3 \cdot H_2O$, THF and1-(tert-butyl)-4-(fluoromethyl)benzene (1:1:1).

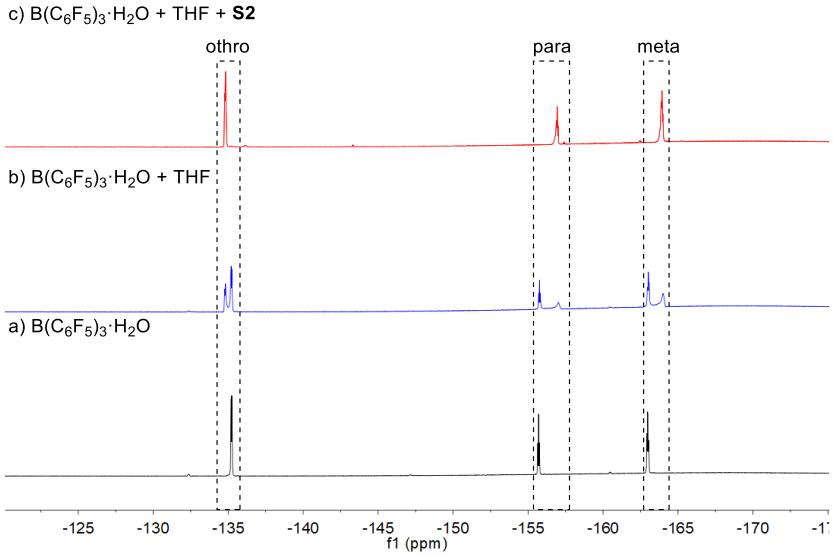
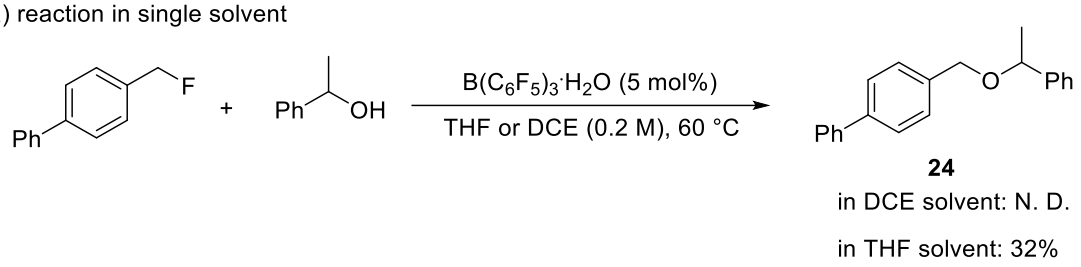


Figure S4. Variation in ^{19}F NMR chemical shifts of $B(C_6F_5)_3 \cdot H_2O$.

Nucleophilic reaction of aryl fluorides.

a) reaction in single solvent

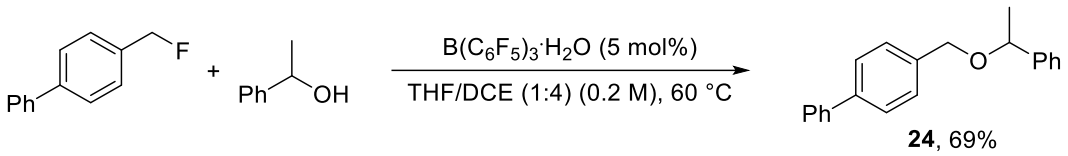


24

in DCE solvent: N. D.

in THF solvent: 32%

b) reaction in mixed solvents



24, 69%

To a stirred solution of 4-(fluoromethyl)-1,1'-biphenyl (**S1**) (0.2 mmol) in solvent (1 mL) were added the α-methylbenzyl alcohol (0.3 mmol) and boron catalyst (5 mol%). The resulting solution was stirred at 60 ℃. In DCE, **S1** disappeared in 5 mins and product **24** was not determined. In THF, product **24** was obtained in 32% yield for 12 h. In mixed solvents, **24** was obtained in 69% yield for 12 h. The reaction solution was concentrated under reduced pressure and dissolved by deuterated chloroform for crude ^{1}H NMR measurement.

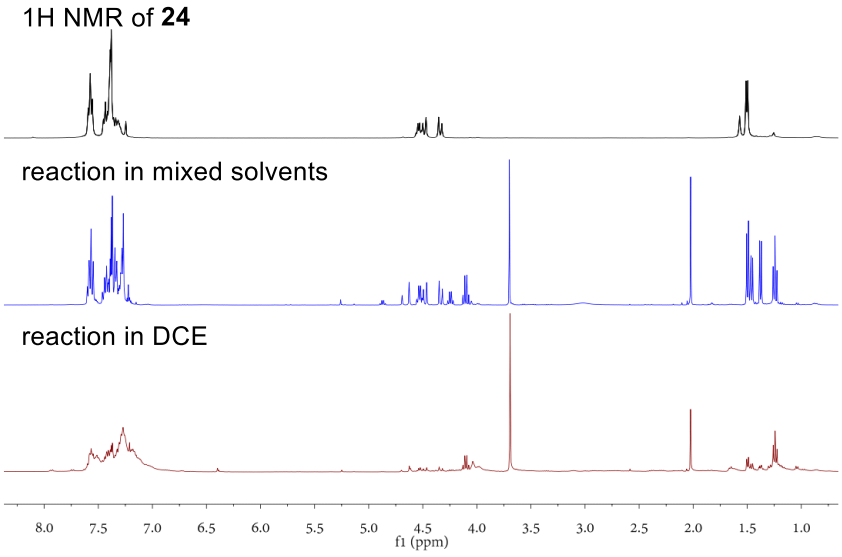


Figure S5. Crude ^{1}H NMR after reaction.

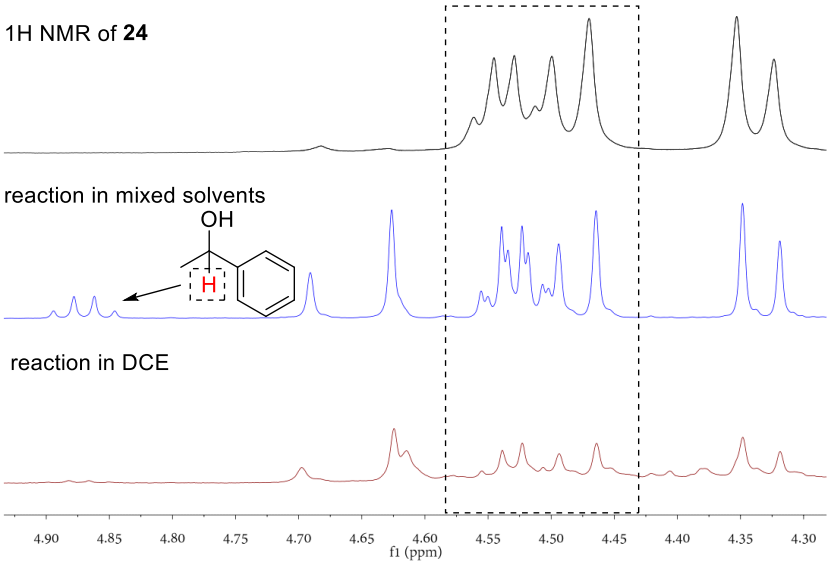


Figure S6. Detail of crude ^{1}H NMR after reaction.

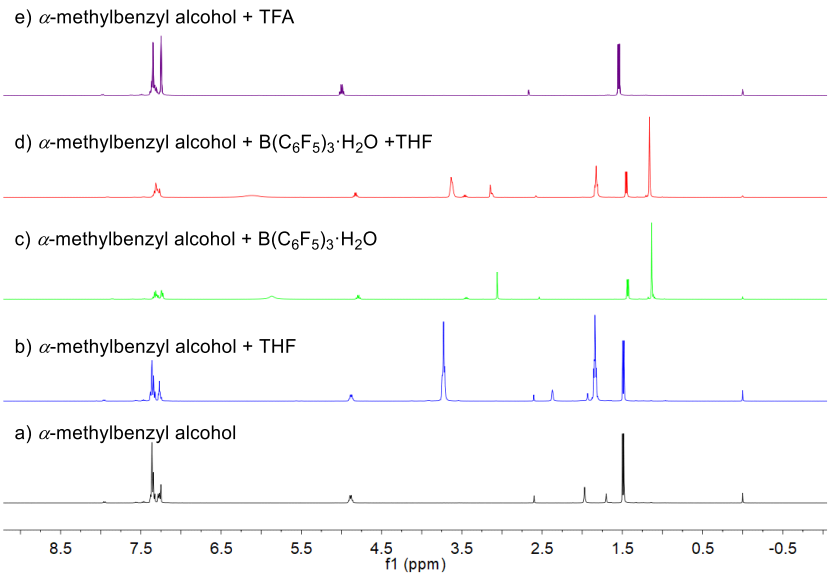


Figure S7. *α*-methylbenzyl alcohol with acids. a) α-methylbenzyl alcohol (0.05 mmol) in $CDCl_3$ (0.6 mL); b) α-methylbenzyl alcohol (0.05 mmol) and THF (0.05 mmol) in $CDCl_3$ (0.6 mL); c) α-methylbenzyl alcohol (0.05 mmol) and $B(C_6F_5)_3{\cdot}H_2O$ (0.05 mmol) in $CDCl_3$ (0.6 mL); d) α-methylbenzyl alcohol (0.05 mmol), THF (0.05 mmol) and $B(C_6F_5)_3{\cdot}H_2O$ (0.05 mmol) in $CDCl_3$ (0.6 mL); e) α-methylbenzyl alcohol (0.05 mmol) and TFA (0.05 mmol) in $CDCl_3$ (0.6 mL).

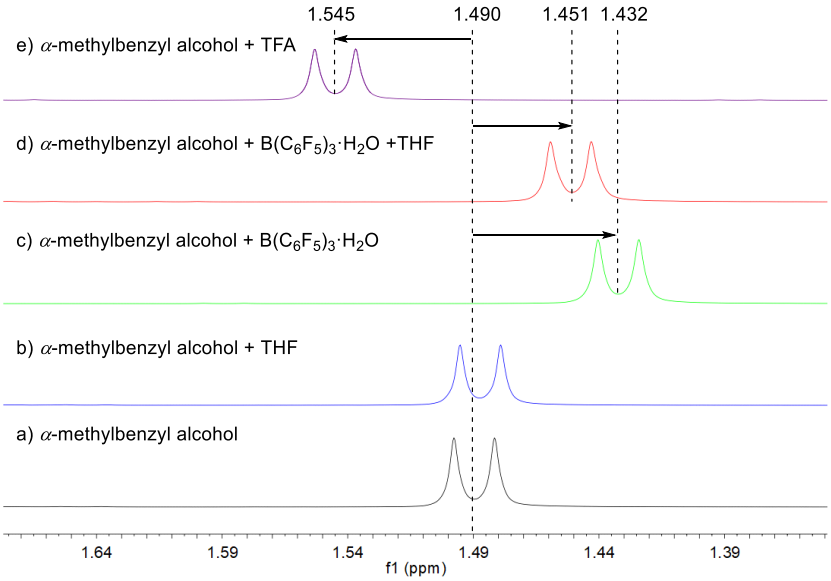


Figure S8. Variation in ^{1}H NMR chemical shifts of CH_3 group of α-methylbenzyl alcohol.

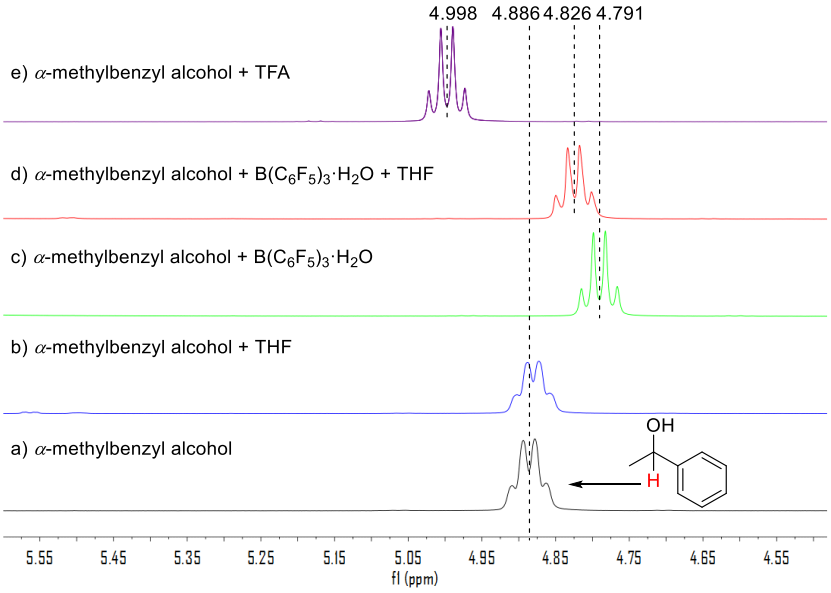


Figure S9. Variation in ^{1}H NMR chemical shifts of CH group of α-methylbenzyl alcohol.

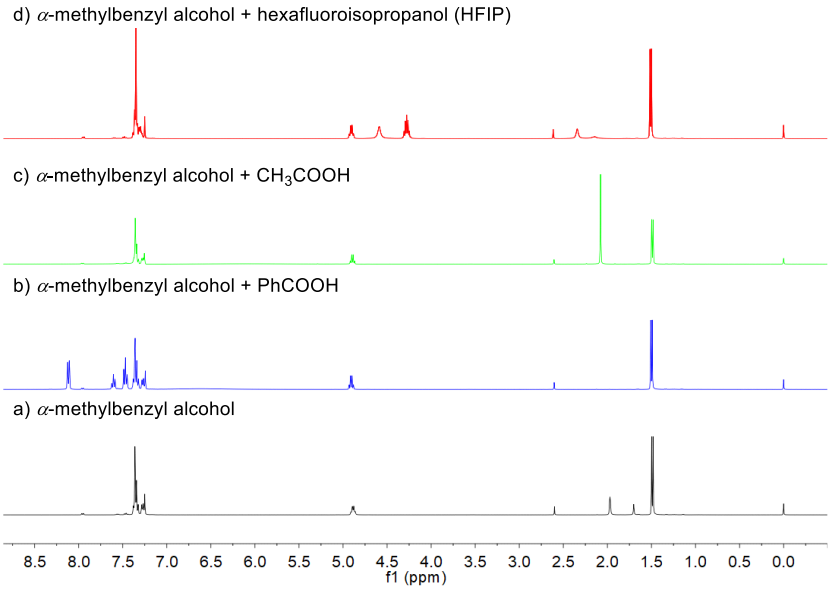


Figure S10.*α*-methylbenzyl alcohol with different acids. a) *α*-methylbenzyl alcohol (0.05 mmol) in $CDCl_3$ (0.6 mL); b) *α*-methylbenzyl alcohol (0.05 mmol) and PhCOOH (0.05 mmol) in $CDCl_3$ (0.6 mL); c) *α*-methylbenzyl alcohol (0.05 mmol) and CH_3COOH (0.05 mmol) in $CDCl_3$ (0.6 mL); d) *α*-methylbenzyl alcohol (0.05 mmol) and HFIP (0.05 mmol) and $B(C_6F_5)_3 \cdot H_2O$ (0.05 mmol) in $CDCl_3$ (0.6 mL).

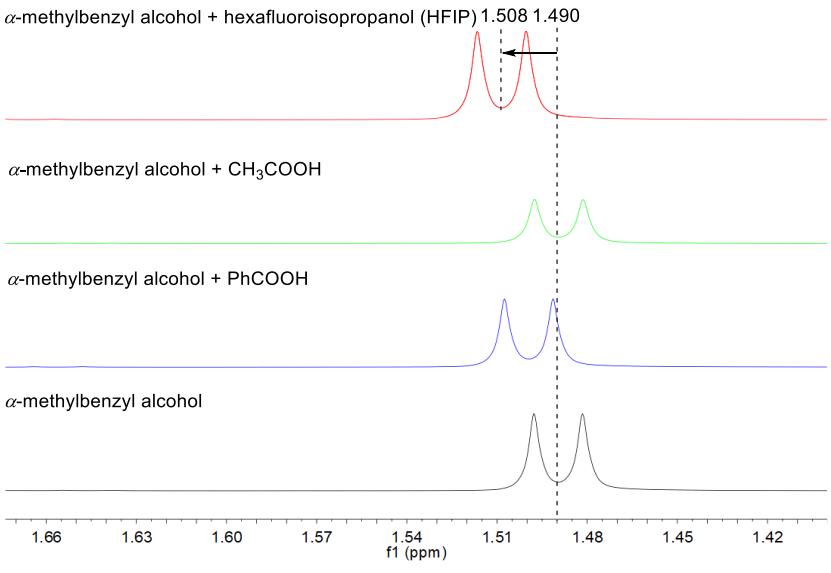


Figure S11. Variation in ^{1}H NMR chemical shifts of CH_3 group of *α*-methylbenzyl alcohol with different acids.

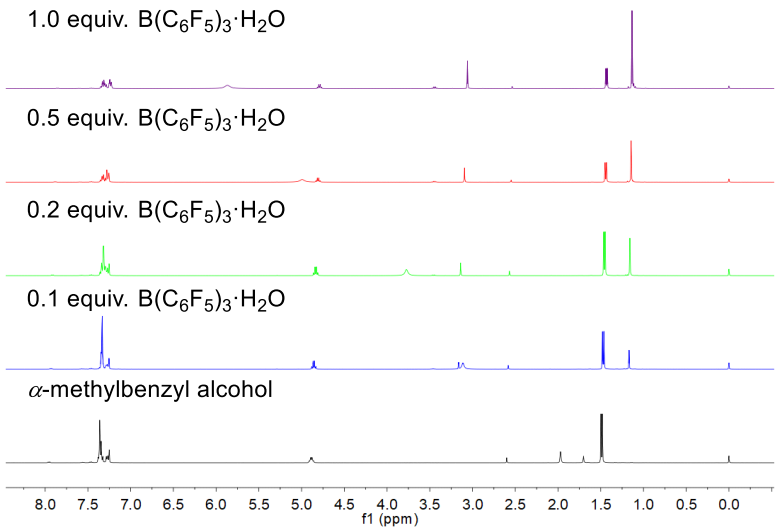


Figure S12. ^{1}H NMR titration experiments of α-methylbenzyl alcohol with $B(C_6F_5)_3 \cdot H_2O$. α-methylbenzyl alcohol (0.05 mmol) in $CDCl_3$ (0.6 mL).

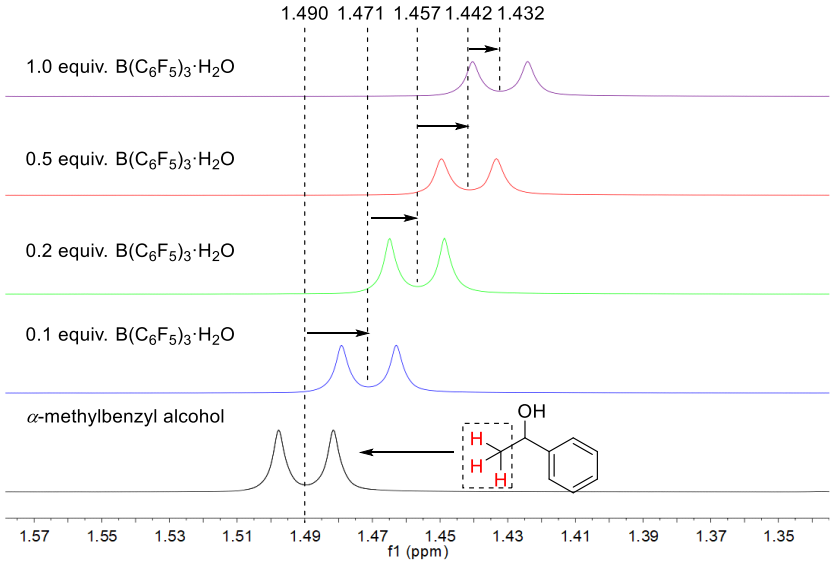


Figure S13. Variation of CH_3 group of α-methylbenzyl alcohol with $B(C_6F_5)_3 \cdot H_2O$.

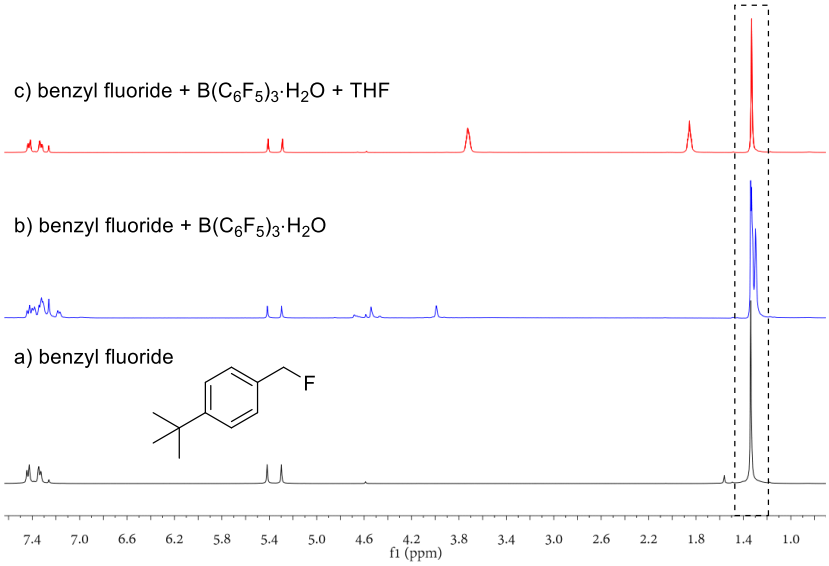


Figure S14. Variation in ^{1}H NMR chemical shifts of of 1-(*tert*-butyl)-4-(fluoromethyl)benzene. a) benzyl flouride (0.05 mmol) in $CDCl_3$ (0.6 mL); b) benzyl flouride (0.05 mmol) and $B(C_6F_5)_3{\cdot}H_2O$ (0.05 mmol) in $CDCl_3$ (0.6 mL); c) benzyl flouride (0.05 mmol) THF (0.05 mmol) and $B(C_6F_5)_3{\cdot}H_2O$ (0.05 mmol) in $CDCl_3$ (0.6 mL).

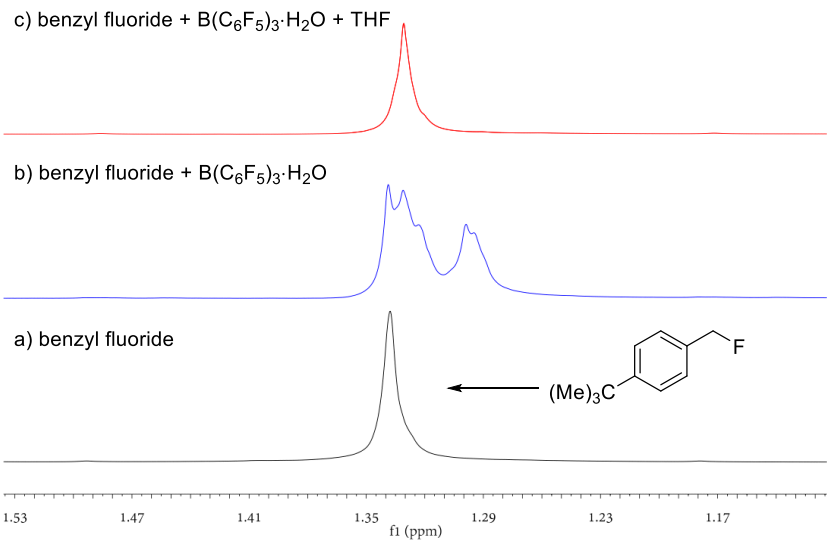


Figure S15. Variation in ^{1}H NMR chemical shifts of *tert*-butyl group of 1-(*tert*-butyl)-4-(fluoromethyl)benzene.

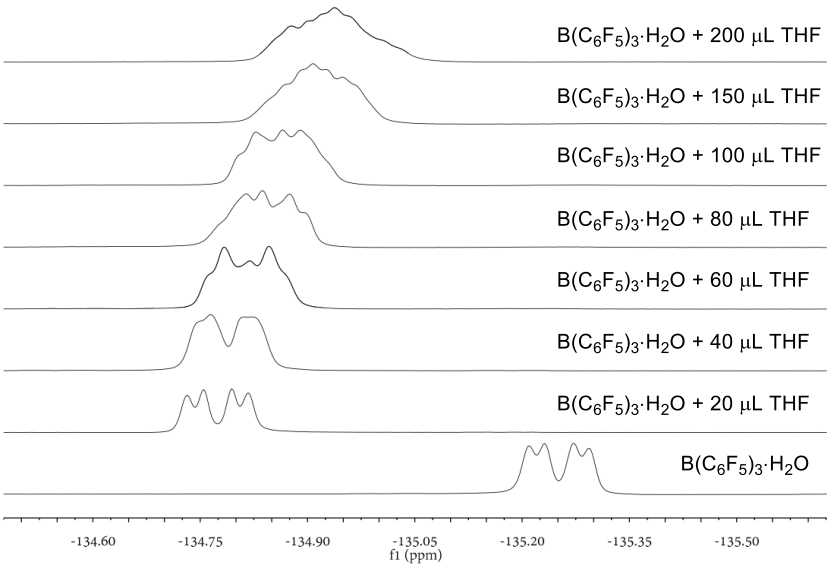


Figure S16. ^{19}F NMR titration experiments of $B(C_6F_5)_3 \cdot H_2O$. $B(C_6F_5)_3 \cdot H_2O$ (0.03 mmol) in $CDCl_3$ (0.6 mL). ^{19}F NMR changes of *othro*-F.

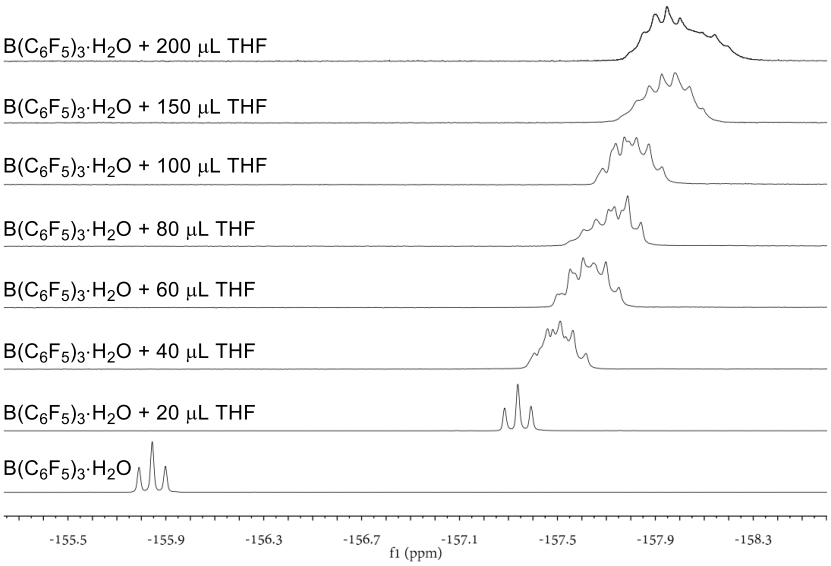


Figure S17. ^{19}F NMR titration experiments of $B(C_6F_5)_3 \cdot H_2O$. $B(C_6F_5)_3 \cdot H_2O$ (0.03 mmol) in $CDCl_3$ (0.6 mL). ^{19}F NMR changes of *para*-F.

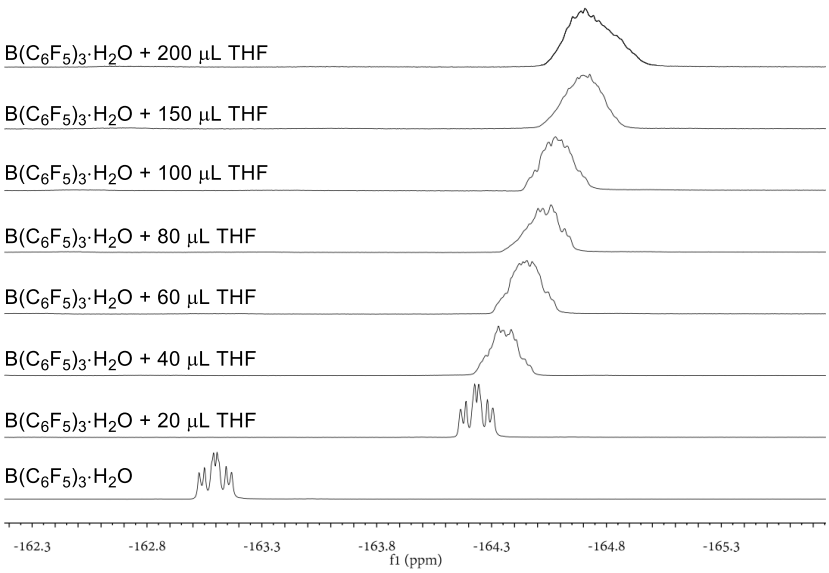


Figure S18. ^{19}F NMR titration experiments of $B(C_6F_5)_3 \cdot H_2O$. $B(C_6F_5)_3 \cdot H_2O$ (0.03 mmol) in $CDCl_3$ (0.6 mL). ^{19}F NMR changes of *meta*-F.

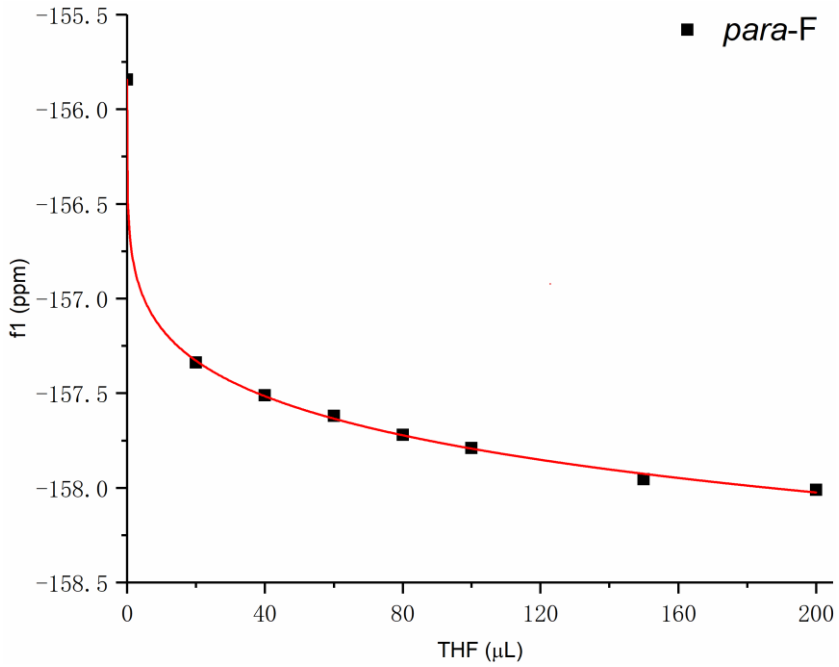


Figure S19. ^{19}F NMR changes of *para*-F of $B(C_6F_5)_3 \cdot H_2O$.

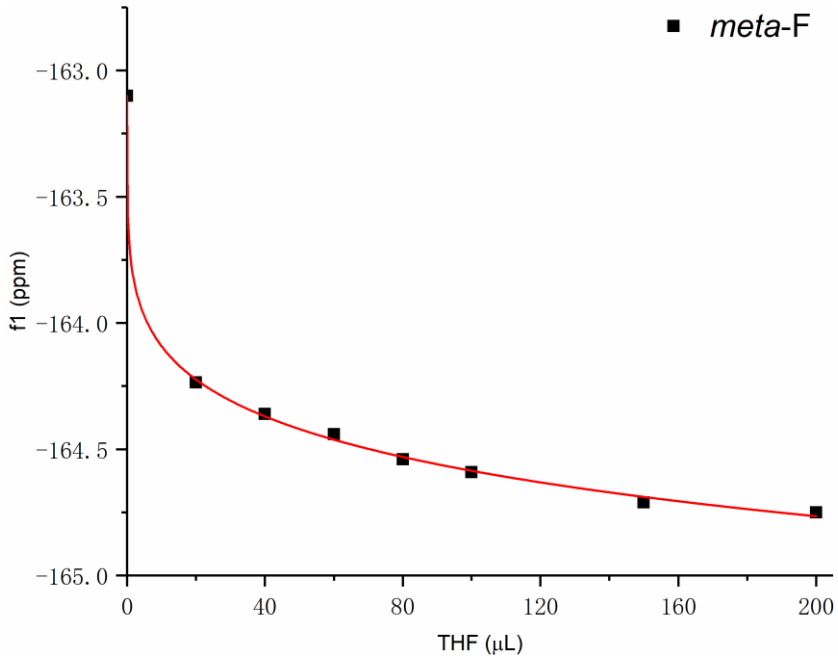
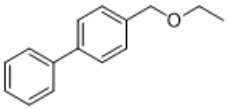
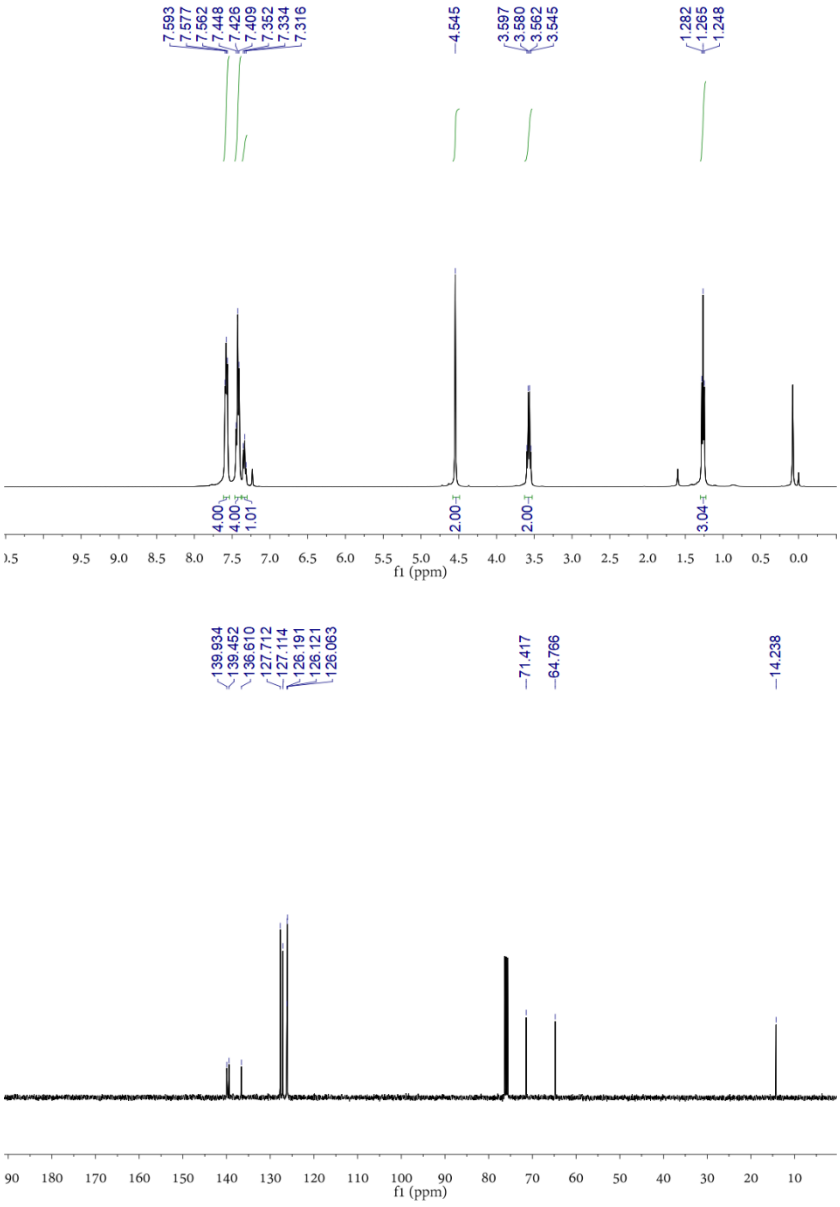


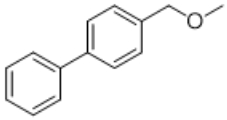
Figure S20. ^{19}F NMR changes of *meta*-F of $B(C_6F_5)_3 \cdot H_2O$.

8. Spectroscopic data

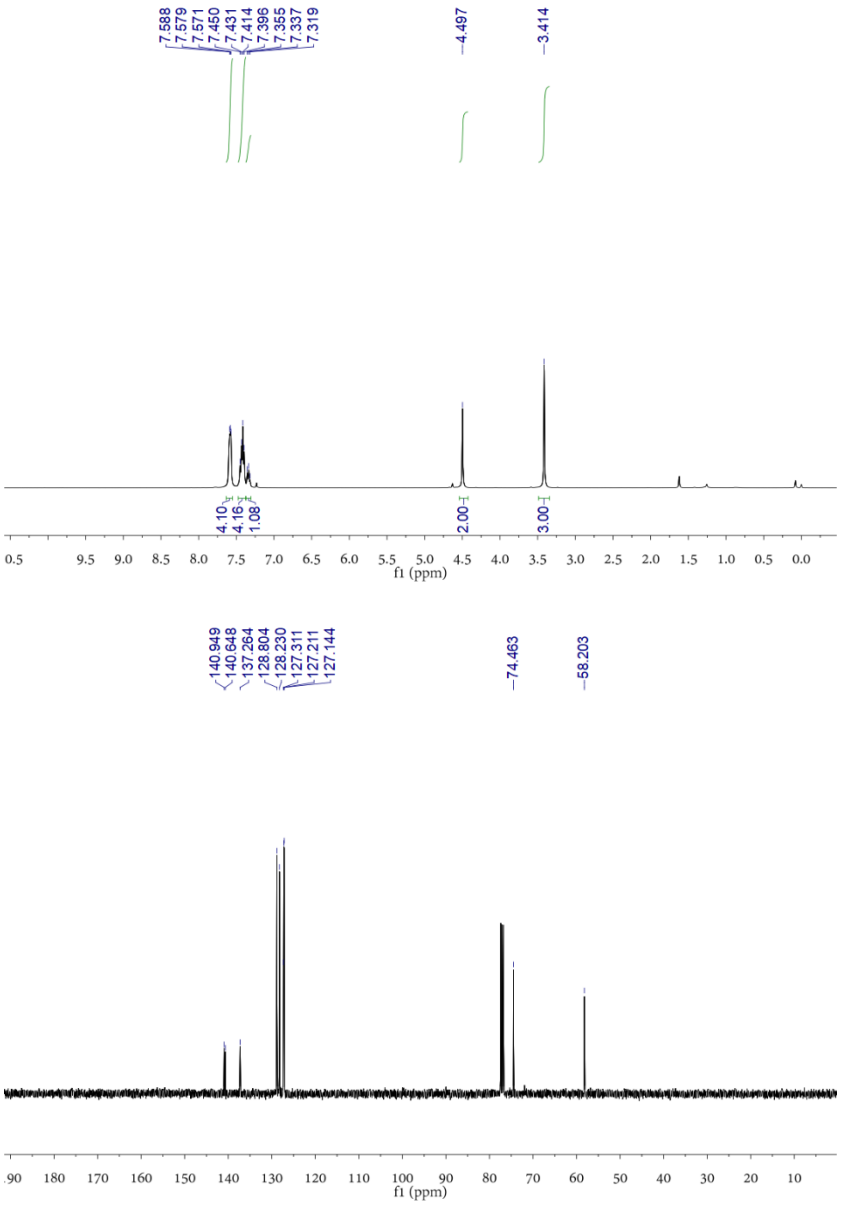


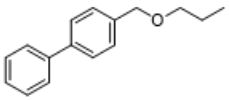
4-(Ethoxymethyl)-1,1'-biphenyl (1): colorless oil (38.1 mg, 90% yield). ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.27 (t, J = 6.8 Hz, 3H), 3.57 (q, J = 6.8 Hz, 2H), 4.55 (s, 2H), 7.33 (dd, J_1 = J_2 = 7.2 Hz, 1H), 7.40-7.45 (m, 4H), 7.56-7.59 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 14.2, 64.8, 71.4, 126.06, 126.12, 126.2, 127.1, 127.7, 136.6, 139.5, 139.9. IR ν 3031, 2985, 2925, 2821, 2737, 1487, 1096, 761 cm^{-1}. HRMS (EI) calcd. for $C_{15}H_{16}O$, ([M]): 212.1201, found: 212.1204.



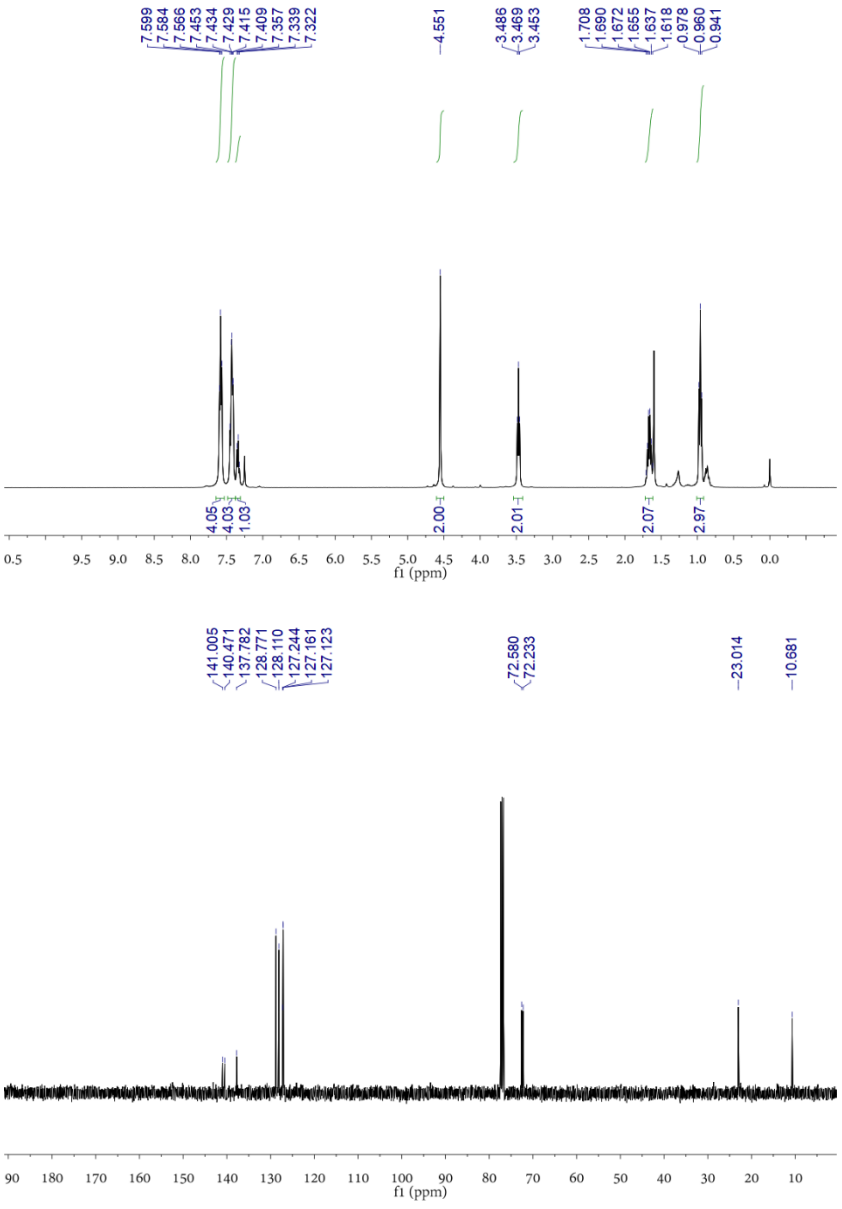


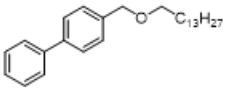
4-(Methoxymethyl)-1,1'-biphenyl (2): orange oil (24.1mg, 61% yield). ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 3.41 (s, 3H), 4.50 (s, 2H), 7.34 (dd, $J_1 = J_2 = 7.2$ Hz, 1H), 7.39-7.47 (m, 4H), 7.56-7.59 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 58.2, 74.5, 127.1, 127.2, 127.3, 128.2, 128.8, 137.3, 140.7, 141.0. IR ν 3030, 2983, 2925, 2821, 2735, 1487, 1100, 761 cm^{-1}. HRMS (EI) calcd. for $C_{14}H_{14}O$, ([M]): 198.1045, found: 198.1047. Known compound.[7]



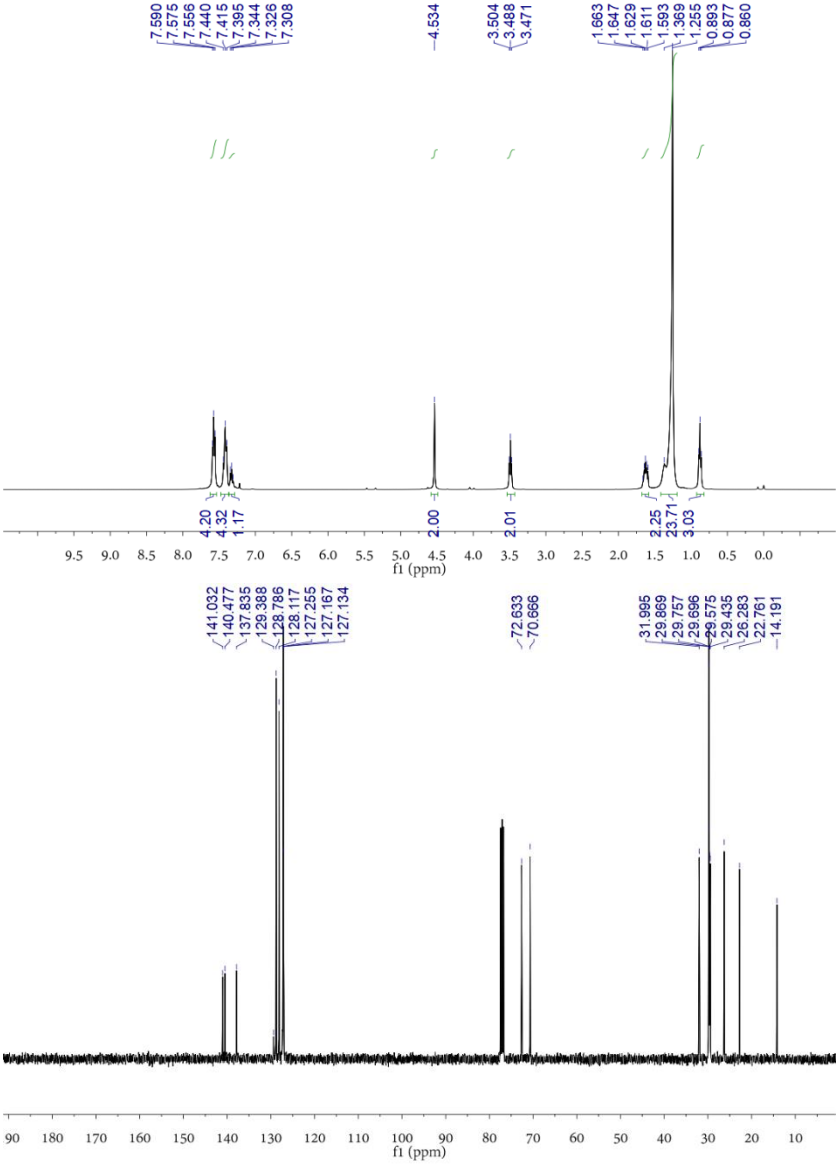


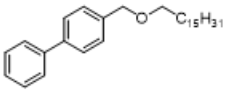
4-(Propoxymethyl)-1,1'-biphenyl (3): colorless oil (37.0 mg, 82% yield). ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 0.96 (t, *J* = 7.2 Hz, 3H), 1.61-1.71 (m, 2H), 3.47 (t, *J* = 6.8 Hz, 2H), 4.55 (s, 2H), 7.32-7.36 (m, 1H), 7.40-7.46 (m, 4H), 7.56-7.60 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 10.7, 23.0, 72.2, 72.6, 127.1, 127.2, 127.3, 128.1, 128.8, 137.8, 140.5, 141.0. IR ν 3066, 3029, 2963, 2931, 2855, 1486, 1098, 698 cm^{-1}. HRMS (EI) calcd. for $C_{16}H_{18}O$, ([M]): 226.1358, found: 226.1364. Known compound.[8]



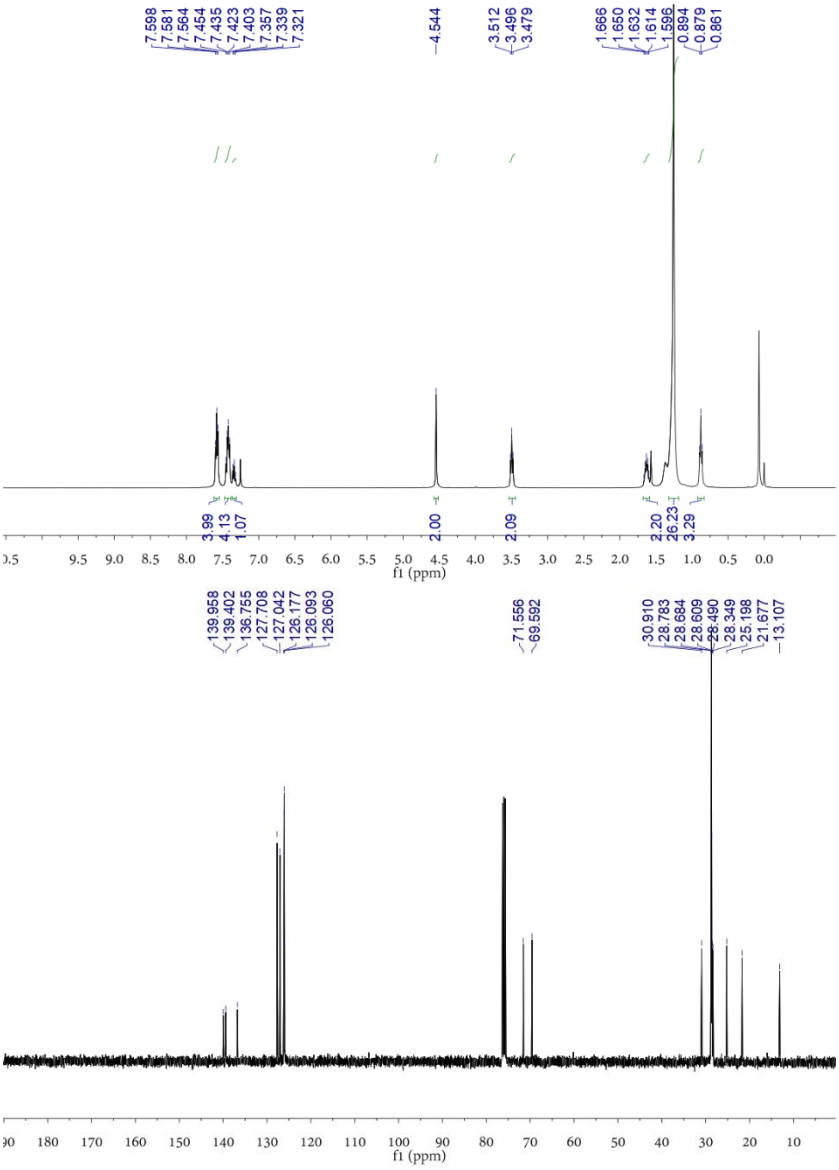


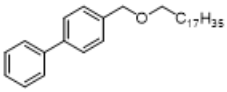
4-((Tetradecyloxy)methyl)-1,1'-biphenyl (4): white solid (54.7 mg, 72% yield). m.p. 46-50 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 0.88 (t, J = 6.4 Hz, 3H), 1.26 (s, 22H), 1.59-1.67 (m, 2H), 3.49 (t, J = 6.4 Hz, 2H), 4.53 (s, 2H), 7.30-7.35 (m, 1H), 7.39-7.44 (m, 4H), 7.55-7.60 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 14.9, 22.8, 26.3, 29.4, 29.6, 29.7, 29.76, 29.87, 32.0, 70.7, 72.6, 127.1, 127.3, 127.4, 128.2, 128.8, 137.8, 140.5, 141.0. IR ν 3058, 3033, 2956, 2918, 2849, 2794, 1466, 755 cm^{-1}. HRMS (ESI) calcd. for $C_{27}H_{44}NO$, ($[M + NH_4]^+$): 398.3415, found: 398.3417.



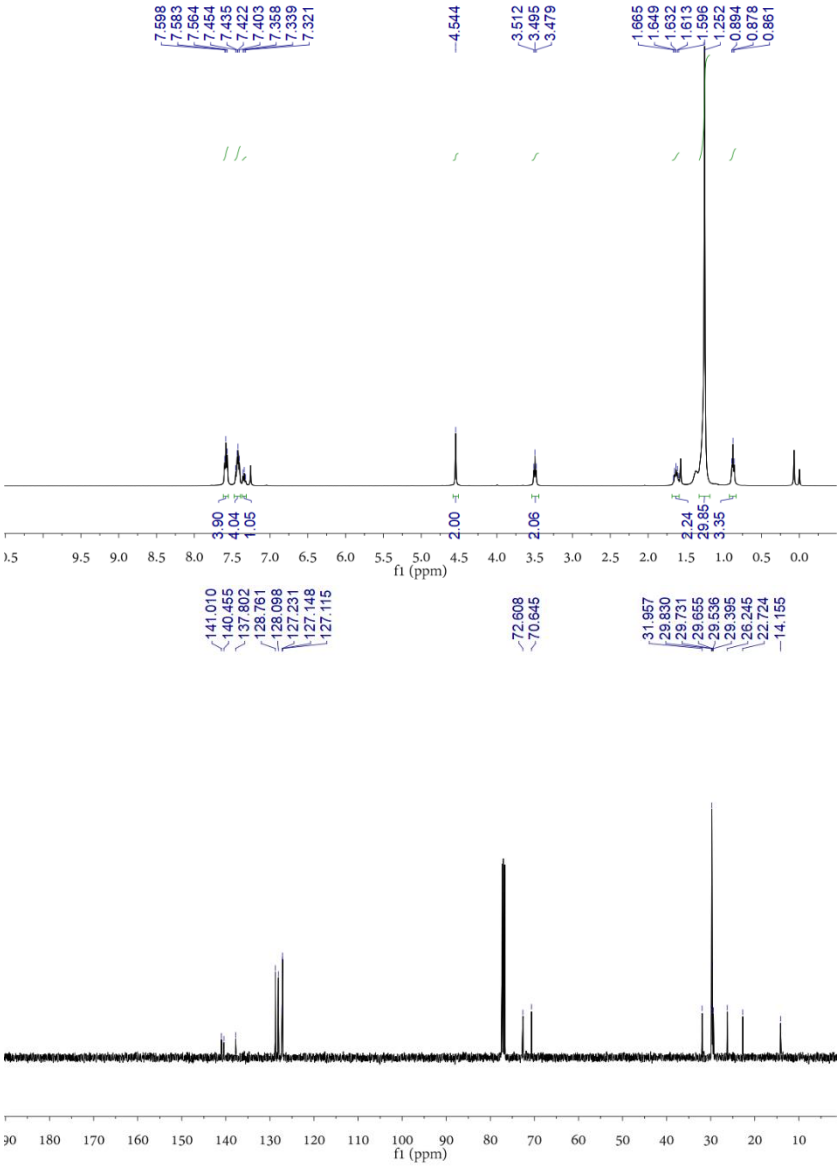


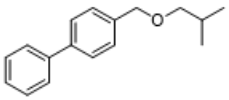
4-((Hexadecyloxy)methyl)-1,1'-biphenyl (5): white solid (57.9 mg, 71% yield). m.p. 55-57 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 0.88 (t, J = 6.4 Hz, 3H), 1.25 (s, 26H), 1.59-1.67 (m, 2H), 3.50 (t, J = 6.8 Hz, 2H), 4.54 (s, 2H), 7.32-7.36 (m, 1H), 7.40-7.46 (m, 4H), 7.56-7.60 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 13.1, 21.7, 25.2, 28.4, 28.5, 28.6, 28.7, 28.8, 30.9, 69.6, 71.6, 126.06, 126.09, 126.2, 127.0, 127.7, 136.8, 139.4, 140.0. IR ν 3034, 2957, 2918, 2849, 2794, 1465, 1116, 755 cm^{-1}. HRMS (EI) calcd. for $C_{29}H_{44}O$, ([M]): 408.3392, found: 408.3391



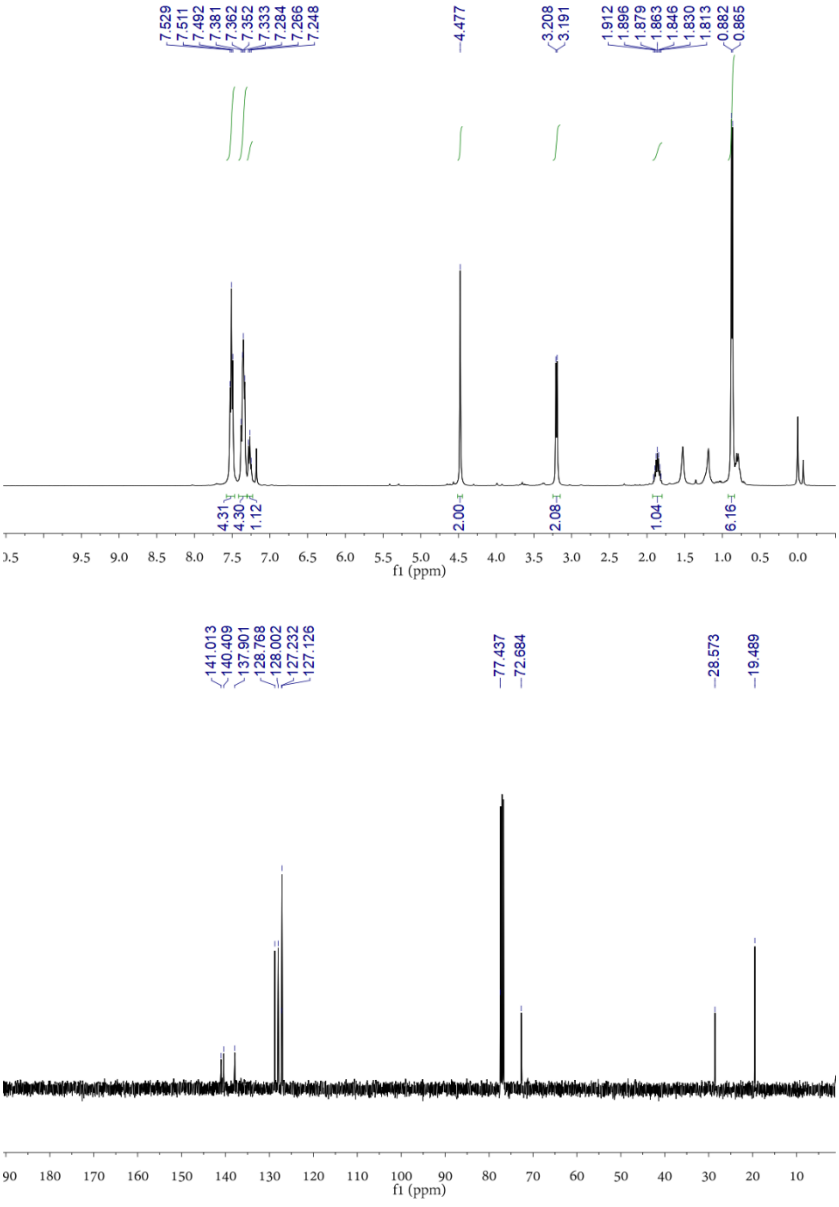


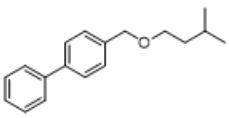
4-((Octadecyloxy)methyl)-1,1'-biphenyl (6): white solid (55.8 mg, 64% yield). m.p. 59-61 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 0.88 (t, J = 6.4 Hz, 3H), 1.25 (s, 30H), 1.59-1.67 (m, 2H), 3.50 (t, J = 6.8 Hz, 2H), 4.54 (s, 2H), 7.32-7.36 (m, 1H), 7.40-7.46 (m, 4H), 7.56-7.60 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 14.2, 22.7, 26.3, 29.4, 29.5, 29.66, 29.73, 29.8, 32.0, 70.7, 72.6, 127.12, 127.15, 127.23, 128.1, 137.8, 140.5, 141.0. IR ν 3034, 2956, 2918, 2849, 2794, 1464, 1117, 755 cm^{-1}. HRMS (EI) calcd. for $C_{31}H_{48}O$, ([M]): 436.3705, found: 436.3707.



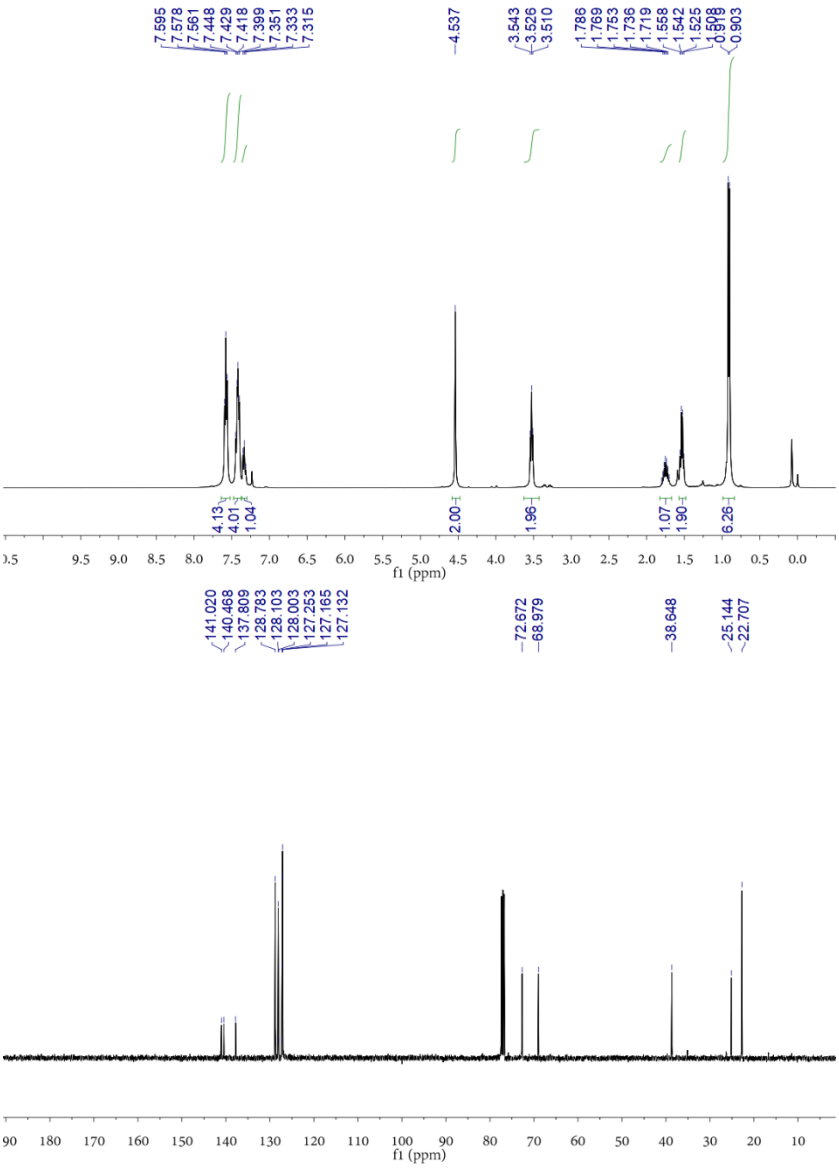


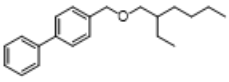
4-(Isobutoxymethyl)-1,1'-biphenyl (7): colorless oil (27.8 mg, 58% yield). ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 0.95 (d, J = 6.8 Hz, 6H), 1.88-1.99 (m, 1H), 3.27 (d, J = 6.8 Hz, 2H), 4.55 (s, 2H), 7.34 (dd, $J_1 = J_2$ = 7.2 Hz, 1H), 7.40-7.46 (m, 4H), 7.56-7.61 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 19.5, 28.6, 72.7, 77.4, 127.1, 127.2, 128.0, 128.8, 137.9, 140.4, 141.0. IR ν 3057, 3029, 2957, 2928, 2870, 1486, 1096, 761 cm^{-1}. HRMS (EI) calcd. for $C_{17}H_{20}O$, ([M]): 240.1514, found: 240.1517.



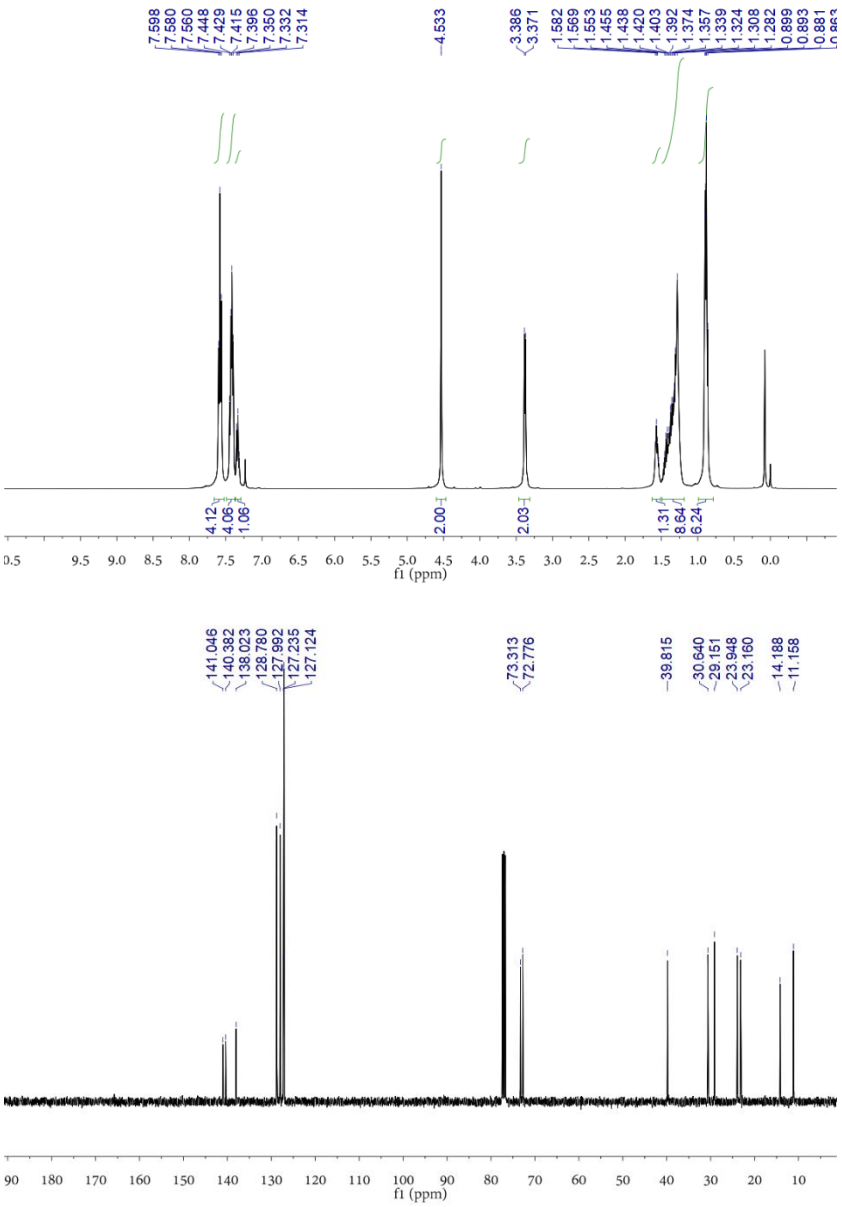


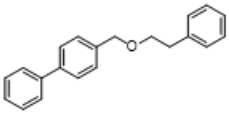
4-((Isopentyloxy)methyl)-1,1'-biphenyl (8): colorless oil (36.0 mg, 71% yield). ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 0.91 (d, *J* = 6.4 Hz, 6H), 1.53 (q, *J* = 6.4 Hz, 2H), 1.70-1.80 (m, 1H), 3.53 (t, *J* = 6.4 Hz, 2H), 4.54 (s, 2H), 7.31-7.36 (m, 1H), 7.39-7.45 (m, 4H), 7.56-7.60 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 22.7, 25.1, 38.7, 69.0, 72.7, 127.1, 127.2, 127.3, 128.0, 128.1, 128.8, 137.8, 140.5, 141.0. IR ν 3057, 3029, 2956, 2867, 1487, 1364, 1097, 824 cm^{-1}. HRMS (EI) calcd. for $C_{18}H_{22}O$, ([M]): 254.1671, found: 254.1672.



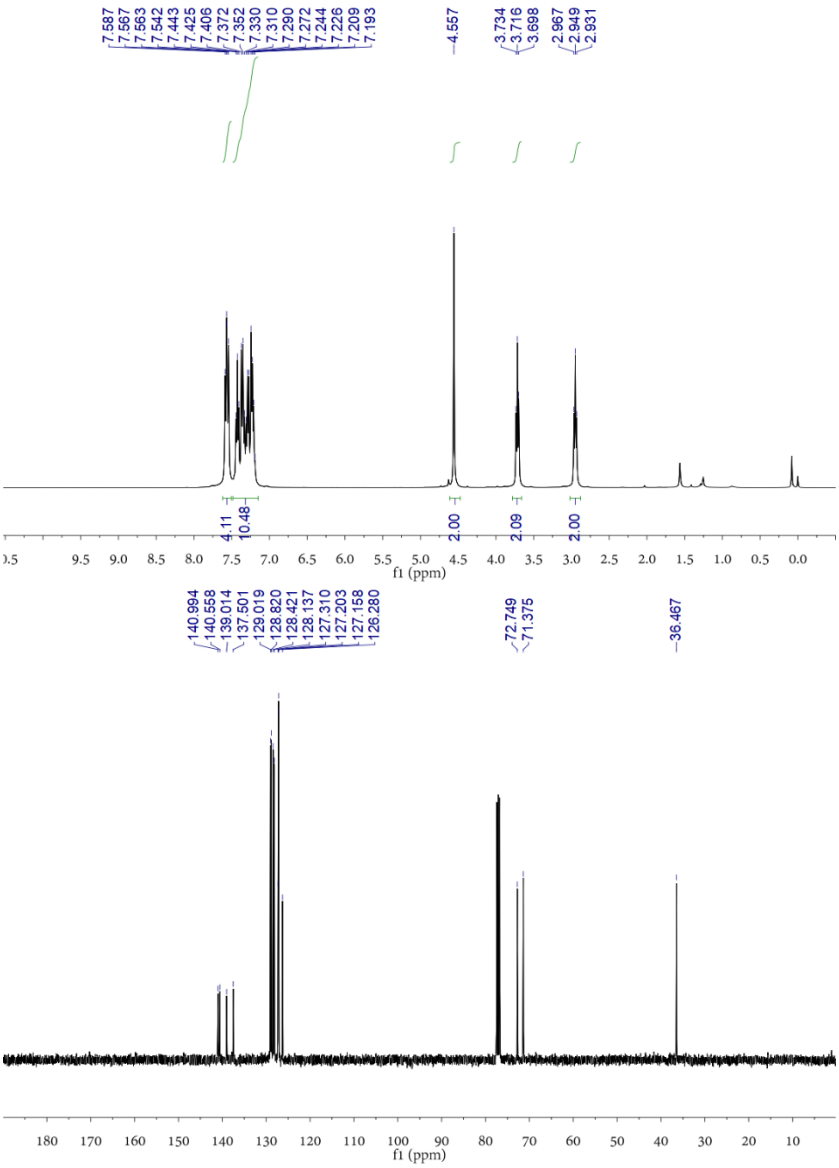


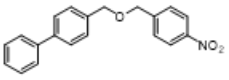
4-(((2-Ethylhexyl)oxy)methyl)-1,1'-biphenyl (9): colorless oil (43.2 mg, 73% yield). ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 0.86-0.90 (m, 6H), 1.28-1.48 (m, 8H), 1.53-1.59 (m, 1H), 3.38 (d, *J* = 7.0 Hz, 2H), 4.53 (s, 2H), 7.31-7.35 (m, 1H), 7.39-7.45 (m, 4H), 7.56-7.60 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 11.2, 14.2, 23.2, 24.0, 29.2, 30.6, 39.8, 72.8, 73.3, 127.1, 127.2, 128.0, 128. 8, 138.0, 140.4, 141.1. IR ν 3058, 3029, 2959, 2858, 1486, 1461, 1096, 760 cm^{-1}. HRMS (EI) calcd. for $C_{21}H_{28}O$, ([M]): 296.2140, found: 296.2141.



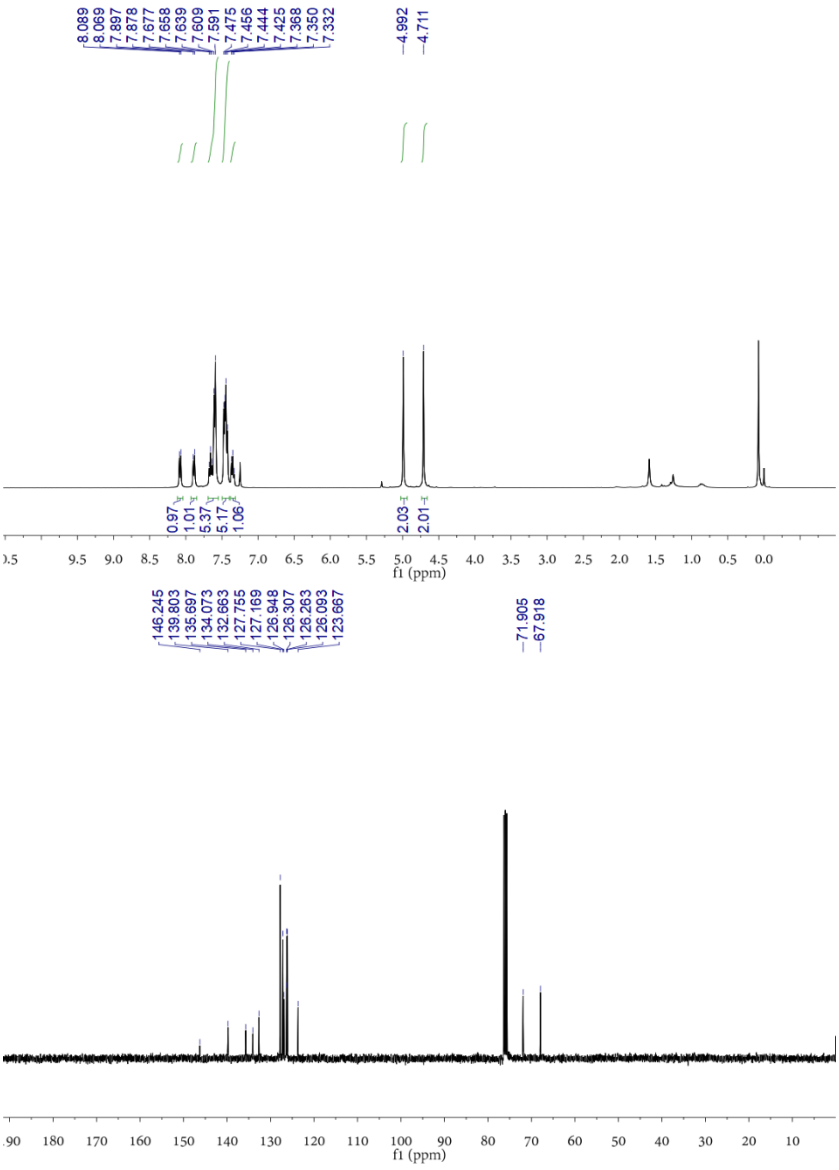


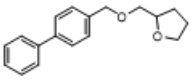
4-(Phenethoxymethyl)-1,1'-biphenyl (10): colorless oil (33.4 mg, 58% yield). ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 2.95 (t, *J* = 7.2 Hz, 2H), 3.72 (t, *J* = 7.2 Hz, 2H), 4.56 (s, 2H), 7.19-7.25 (m, 3H), 7.27-7.38 (m, 5H), 7.40-7.45 (m, 2H), 7.54-7.59 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 36.5, 71.4, 72.8, 126.3, 127.16, 127.2, 127.3, 128.1, 128.4, 128.8, 129.0, 137.5, 139.0, 140.6, 141.0. IR ν 3059, 3028, 2923, 2857, 1489, 1098, 759, 699 cm^{-1}. HRMS (EI) calcd. for $C_{21}H_{20}O$, ([M]): 288.1514, found: 288.1515. Known compound.[9]



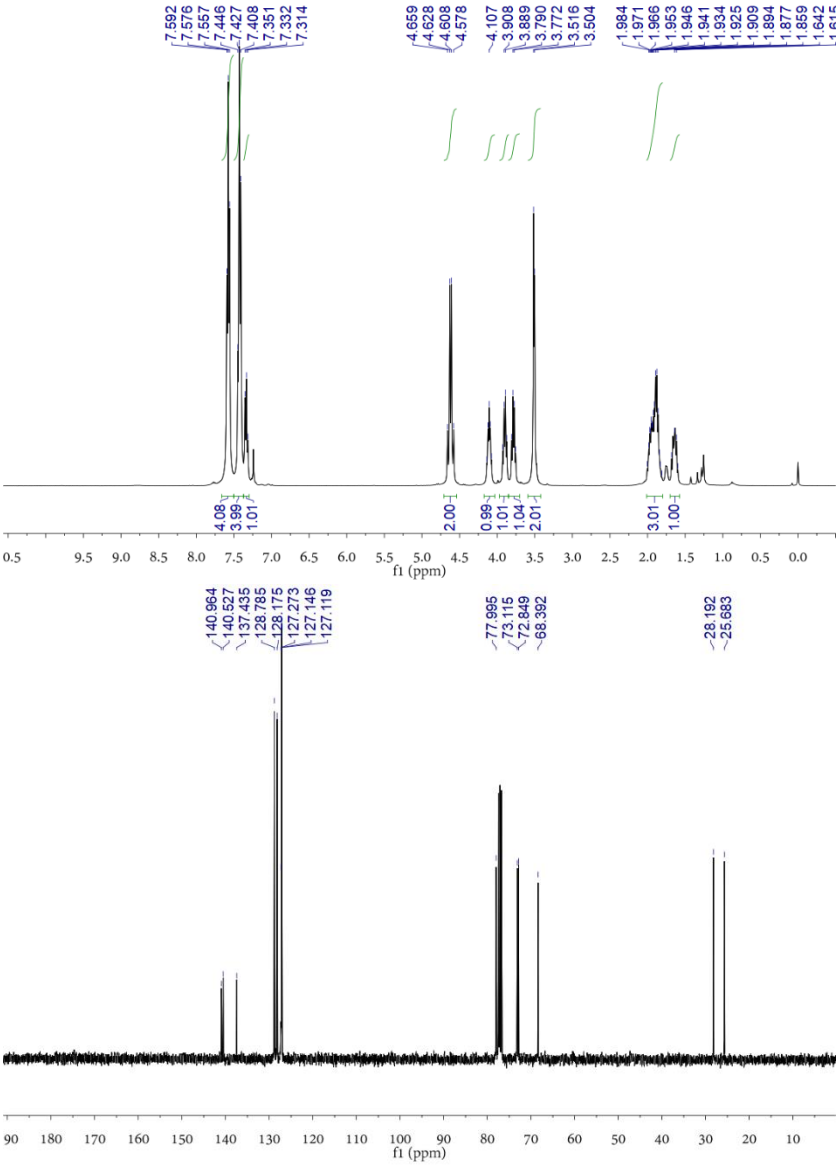


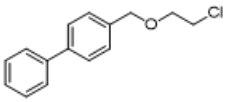
4-(((4-Nitrobenzyl)oxy)methyl)-1,1'-biphenyl (11): brown oil (35.7 mg, 56% yield). ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 4.71 (s, 2H), 4.99 (s, 2H), 7.32-7.37 (m, 1H), 7.42-7.48 (m, 5H), 7.59-7.68 (m, 5H), 7.89 (d, *J* = 7.6 Hz, 1H), 8.08 (d, *J* = 7.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 67.9, 71.9, 123.7, 126.1, 126.26, 126.31, 127.0, 127.2, 127.8, 132.7, 134.1, 135.7, 139.8, 146.3. IR ν 3029, 2923, 2850, 1521, 1331, 1073, 757, 723 cm^{-1}. HRMS (EI) calcd. for $C_{20}H_{17}NO_3$, ([M]): 319.1208, found: 319.1210.



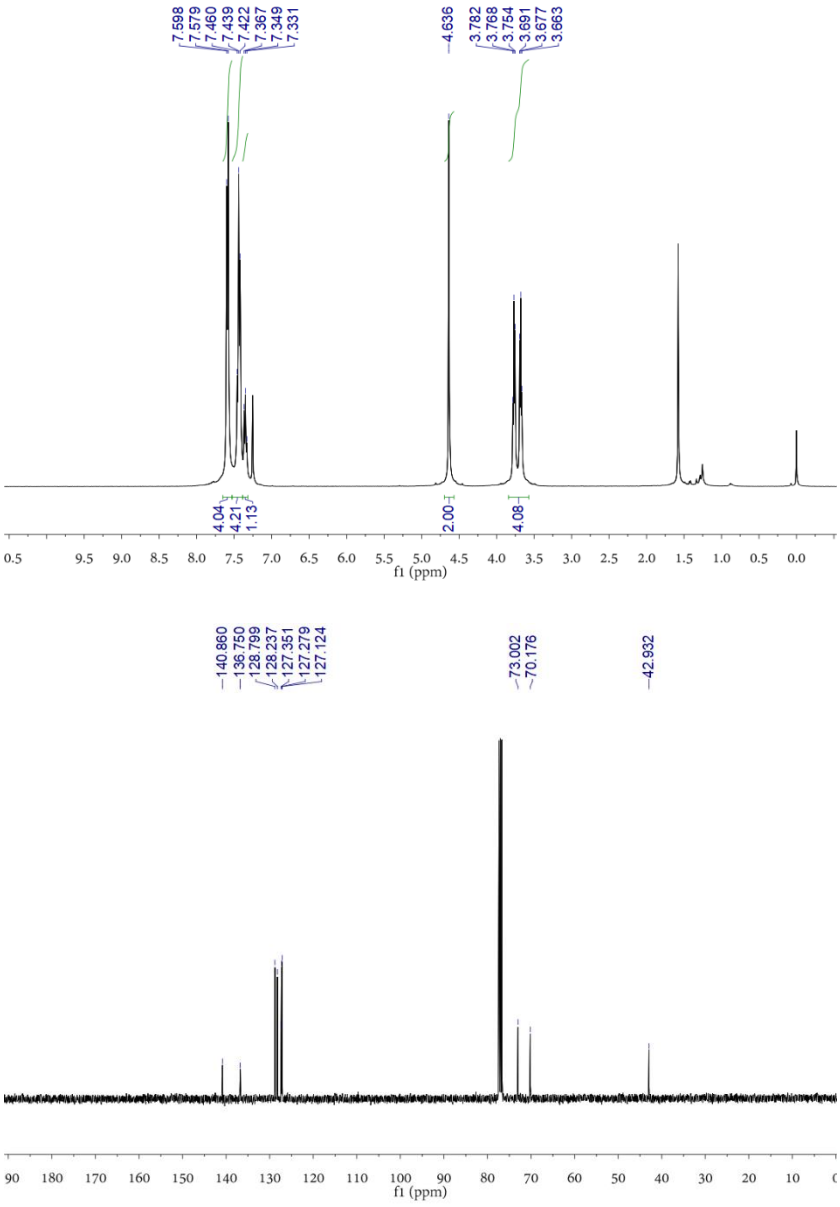


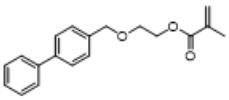
2-(([1,1'-Biphenyl]-4-ylmethoxy)methyl)tetrahydrofuran (12): colorless oil (38.5 mg, 72% yield)**.** ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.59-1.69 (m, 1H), 1.82-2.01 (m, 3H), 3.51 (d, J = 4.8 Hz, 2H), 3.78 (q, J = 7.2 Hz, 1H), 3.90 (q, J = 7.2 Hz, 1H), 4.07-4.14 (m, 1H), 4.57-4.66 (m, 2H), 7.33 (dd, $J_1 = J_2$ = 7.6 Hz, 1H), 7.43 (dd, $J_1 = J_2$ = 7.6 Hz, 4H), 7.58 (dd, $J_1 = J_2$ = 7.6 Hz, 4H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 25.7, 28.2, 68.4, 72.9, 73.1, 78.0, 127.12, 127.15, 127.3, 128.2, 128.8, 137.4, 140.5, 141.0. IR ν 3056, 3029, 2971, 2926, 2861, 1487, 1082, 762 cm^{-1}. HRMS (EI) calcd. for $C_{18}H_{20}O_2$, ([M]): 268.1463, found: 268.1460. Known compound.[9]



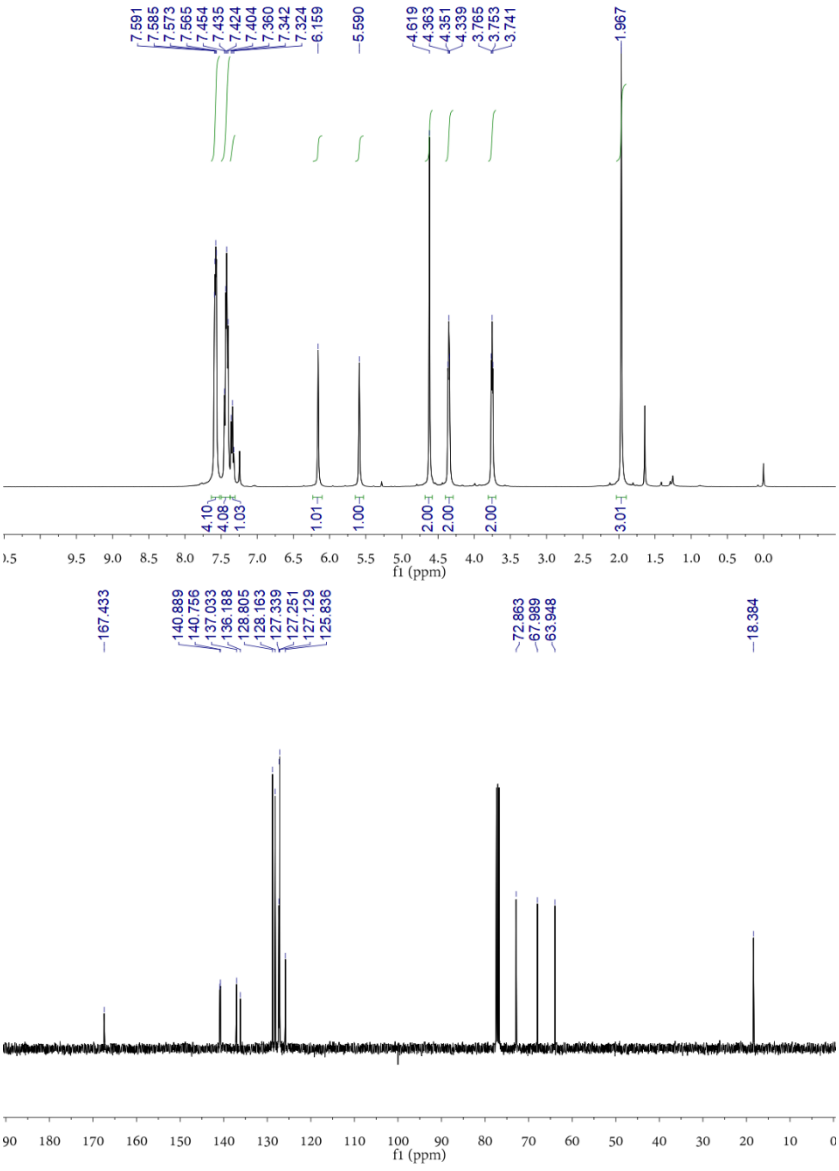


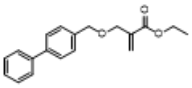
4-((2-Chloroethoxy)methyl)-1,1'-biphenyl (13): colorless oil (32.4 mg, 66% yield). ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 3.68 (t, *J* = 5.6 Hz, 2H), 3.77 (t, *J* =5.6 Hz, 3H), 4.67 (s, 2H), 7.33-7.37 (m, 1H), 7.42-7.60 (m, 4H), 7.57-7.60 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 42.9, 70.2, 73.0, 127.1, 127.3, 127.4, 128.2, 128.8, 136.8, 140.9. HRMS (EI) calcd. for $C_{15}H_{15}OCl$, ([M]): 246.0811, found: 246.0812.



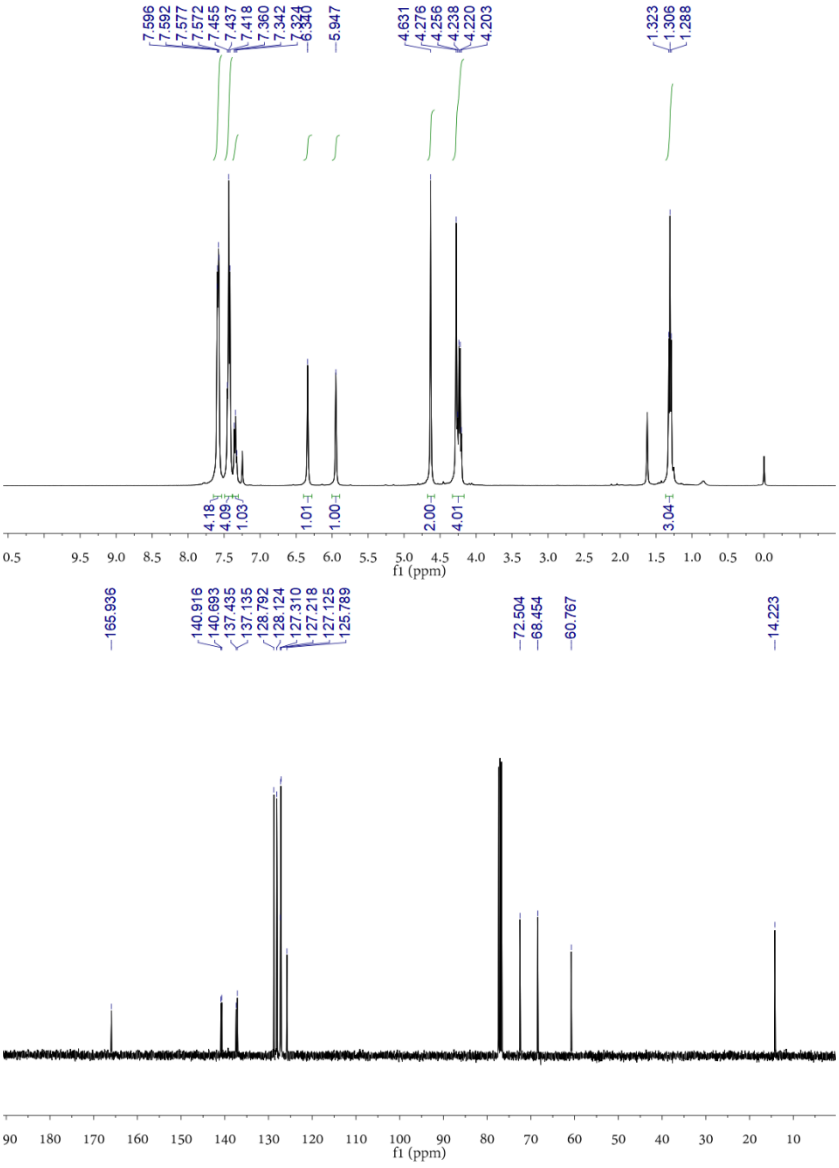


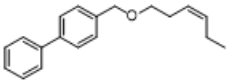
2-([1,1'-Biphenyl]-4-ylmethoxy)ethyl methacrylate (14): colorless oil (40.2 mg, 68% yield). ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.97 (s, 3H), 3.75 (t, *J* = 4.8 Hz, 2H), 4.35 (t, *J* = 4.8 Hz, 2H), 4.62 (s, 2H), 5.59 (s, 1H), 6.16 (s, 1H), 7.32-7.36 (m, 1H), 7.40-7.46 (m, 4H), 7.56-7.60 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 18.4, 64.0, 68.0, 72.9, 125.8, 127.1, 127.25, 127.34, 128.2, 128.8, 136.2, 137.0, 140.8, 140.9, 167.4. IR ν 3030, 2955, 2927, 2862, 1910, 1719, 1452, 1296, 1038 cm^{-1}. HRMS (EI) calcd. for $C_{19}H_{20}O_3$, ([M]): 296.1412, found: 296.1420.



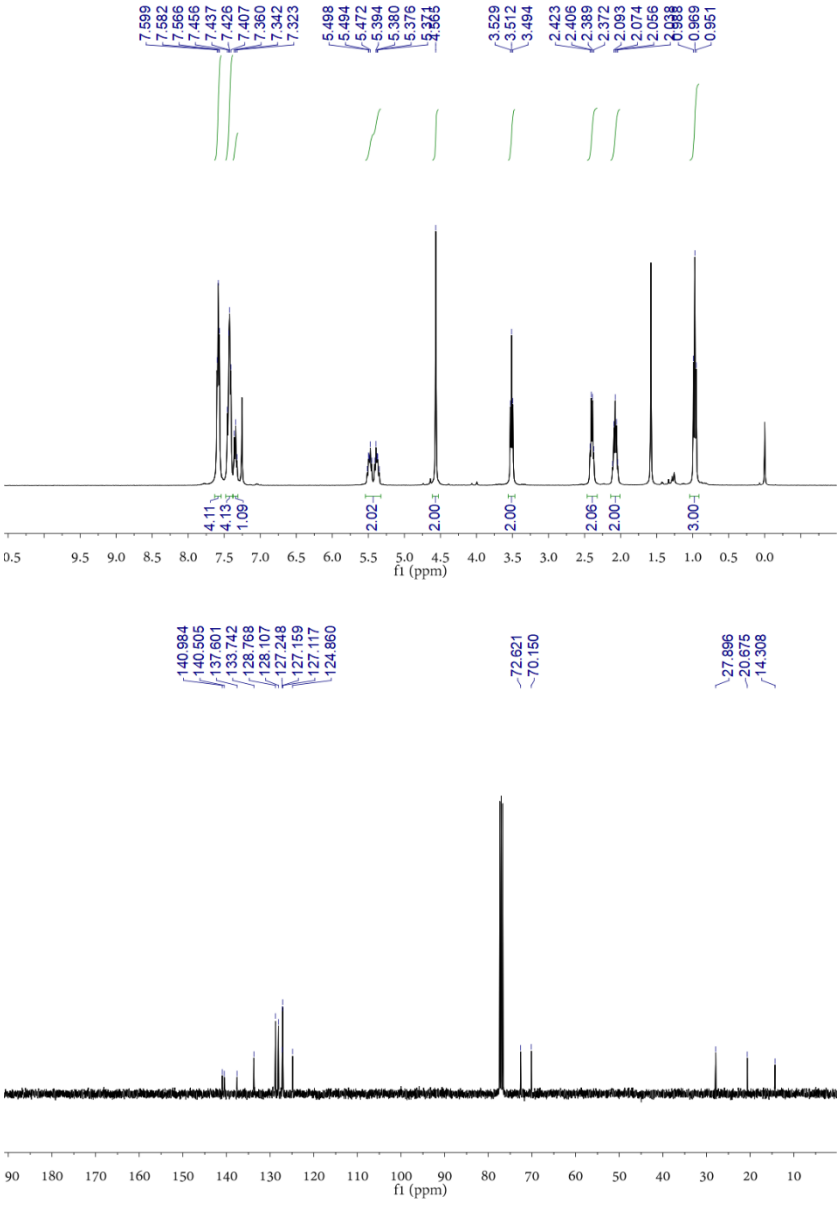


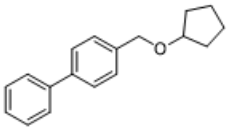
Ethyl 2-(([1,1'-biphenyl]-4-ylmethoxy)methyl)acrylate (15): colorless oil (39.6 mg, 67% yield). ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.31 (t, J = 6.8 Hz, 3H), 4.23 (q, J = 6.8 Hz, 2H), 4.28 (s, 2H), 4.63 (s, 2H), 5.95 (s, 1H), 6.34 (s, 1H), 7.34 (dd, $J_1 = J_2$ = 7.2 Hz, 1H), 7.44 (dd, $J_1 = J_2$ = 7.2 Hz, 4H), 7.57-7.60 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 14.2, 60.8, 68.5, 72.5, 125.8, 127.1, 127.2, 127.3, 128.1, 128.8, 137.1, 137.4, 140.7, 140.9, 165.9. IR ν 3030, 2982, 2929, 2860, 1716, 1369, 1271, 1096 cm^{-1}. HRMS (EI) calcd. for $C_{19}H_{20}O_3$, ([M]): 296.1412, found: 296.1420.



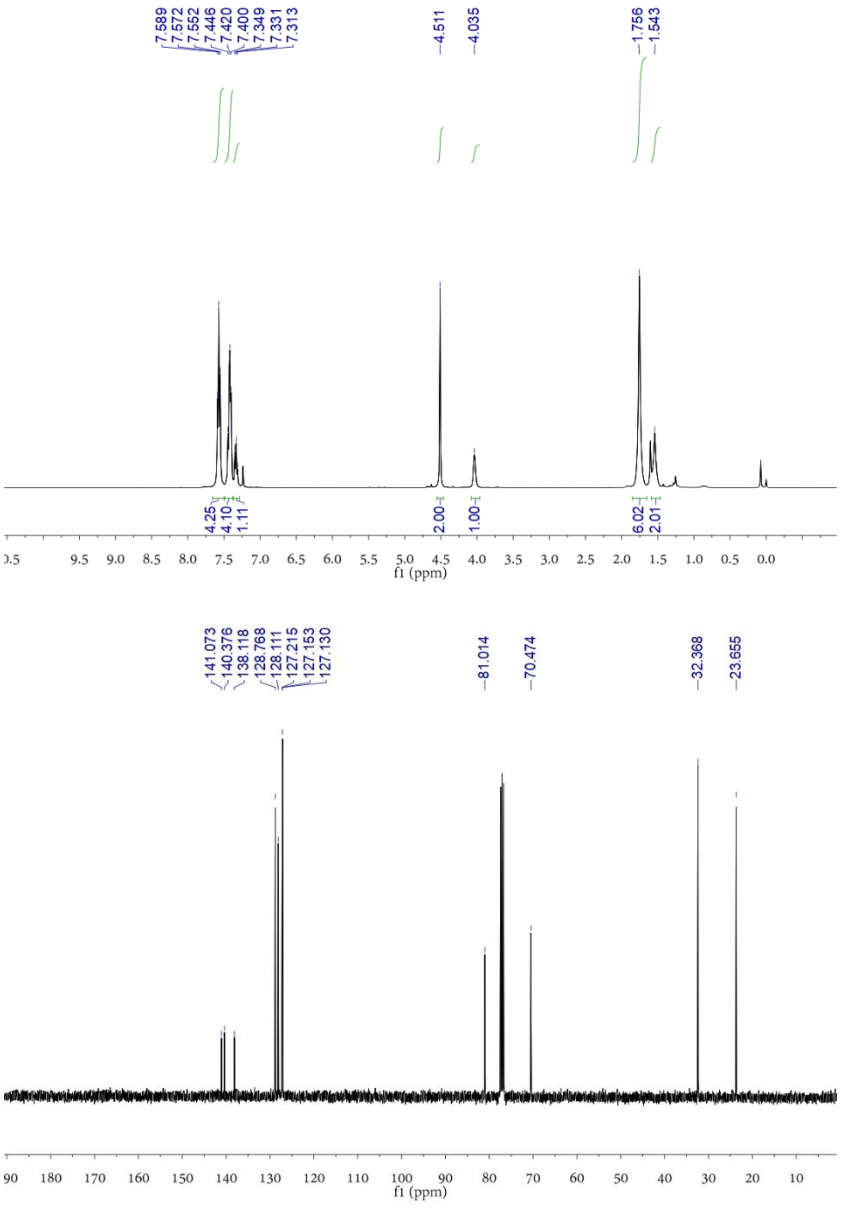


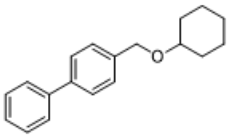
(Z)-4-((hex-3-en-1-yloxy)methyl)-1,1'-biphenyl (16): colorless oil (35.6 mg, 67% yield). ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 0.97 (t, *J* = 7.6 Hz, 3H), 2.03-2.11 (m, 2H), 2.40 (q, *J* = 6.8 Hz, 2H), 3.51 (t, *J* = 6.8 Hz, 2H), 4.57 (s, 2H), 5.35-5.52 (m, 2H), 7.23-7.36 (m, 1H), 7.40-7.46 (m, 4H), 7.56-7.60 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 14.3, 20.7, 27.9, 70.2, 72.6, 124.9, 127.1, 127.2, 127.3, 128.1, 128.8, 133.7, 137.6, 140.5, 141.0. IR ν 3057, 3009, 2963, 2931, 2856, 1487, 1098, 761 cm^{-1}. HRMS (EI) calcd. for $C_{19}H_{22}O$, ([M]): 266.1671, found: 266.1673.



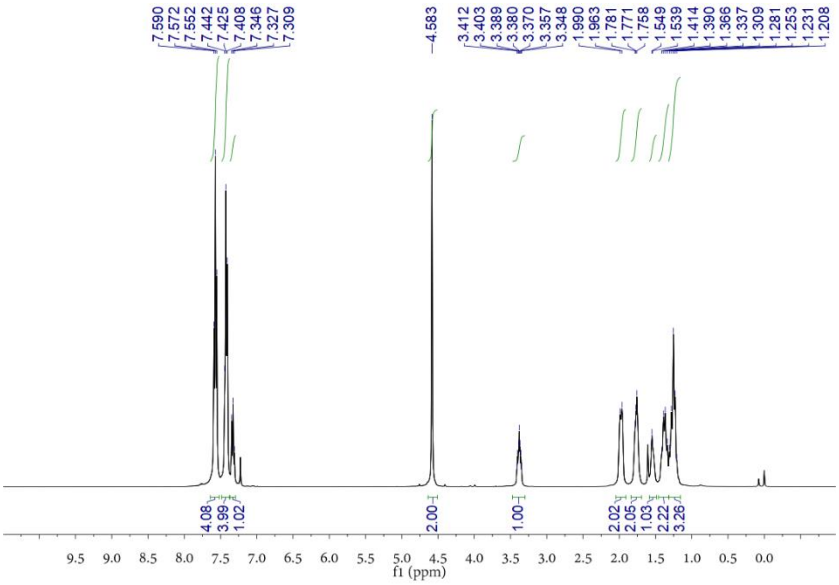


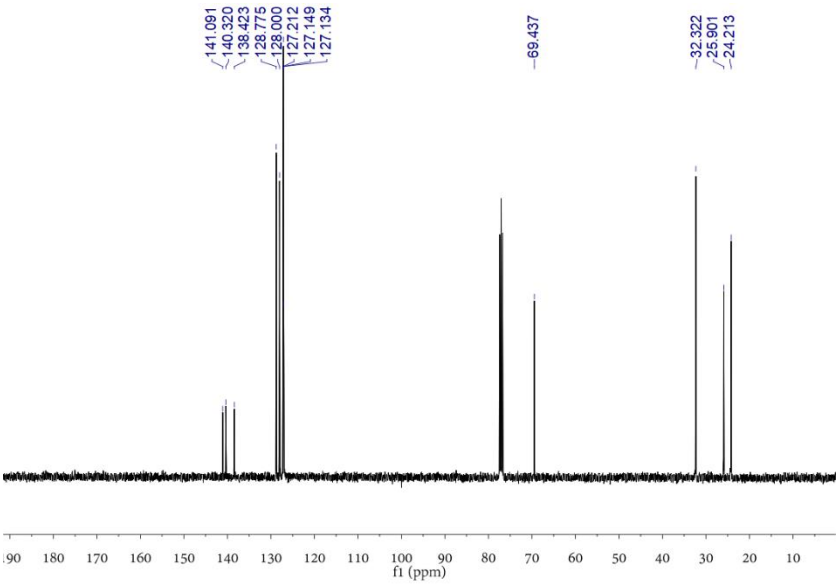
4-((Cyclopentyloxy)methyl)-1,1'-biphenyl (17): colorless oil (41.8 mg, 83% yield). ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.54 (s, 2H), 1.76 (s, 6H), 4.04 (s, 1H), 4.51 (s, 2H), 7.33 (dd, $J_1 = J_2$ = 7.2 Hz, 1H), 7.40-7.45 (m, 4H), 7.55-7.59 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 23.7, 32.4, 70.5, 81.0, 127.13, 127.15, 127.22, 128.1, 128.8, 138.1, 140.4, 141.1. IR ν 3056, 3029, 2958, 2869, 1487, 1348, 1090, 760 cm^{-1}. HRMS (EI) calcd. for $C_{18}H_{20}O$, ([M]): 252.1514, found: 252.1510.

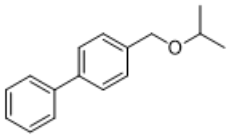




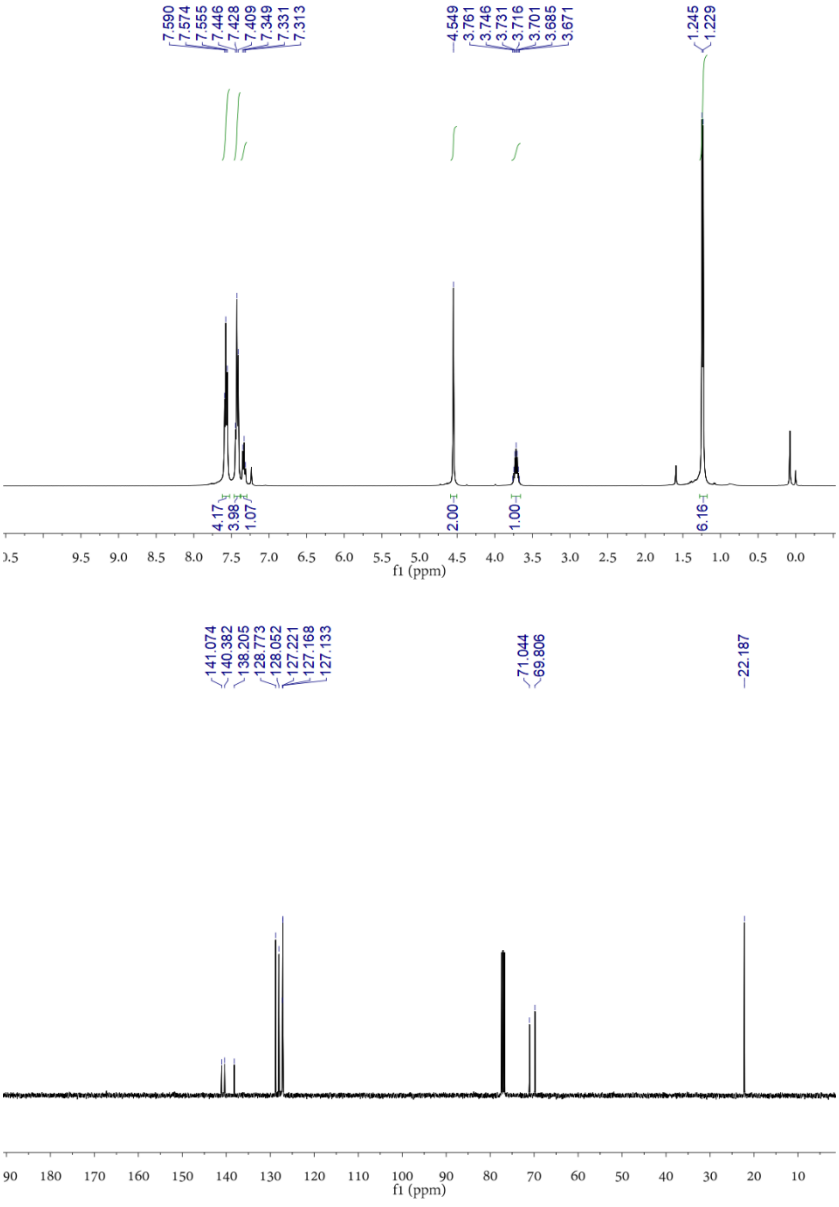
4-((Cyclohexyloxy)methyl)-1,1'-biphenyl (18): colorless oil (41.5 mg, 78% yield). ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.18-1.31 (m, 3H), 1.30-1.42 (m, 2H), 1.53-1.55 (m, 1H), 1.75-1.79 (m, 2H), 1.96-1.99 (m, 2H), 3.34-3.42 (m, 1H), 4.58 (s, 2H), 7.30-7.35 (m, 1H), 7.40-7.45 (m, 4H), 7.55-7.59 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 24.2, 25.9, 32.3, 69.4, 127.13, 127.15, 127.21, 128.0, 128.8, 138.4, 140.3, 141.1. IR ν 3057, 3029, 2932, 2855, 2660, 1487, 1450, 1092 cm^{-1}. HRMS (EI) calcd. for $C_{19}H_{22}O$, ([M]): 266.1671, found: 266.1664. Known compound.[9]

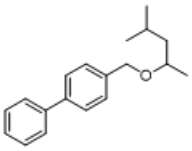




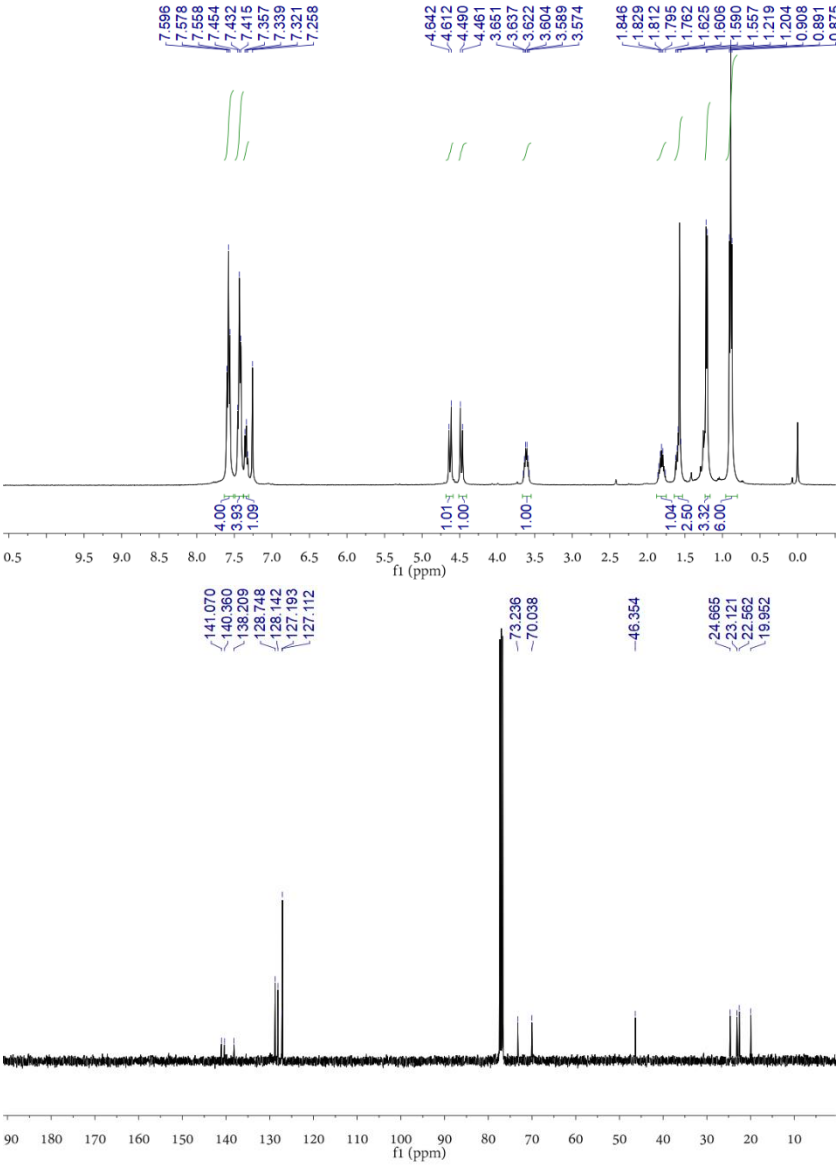


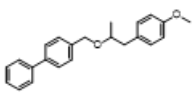
4-(Isopropoxymethyl)-1,1'-biphenyl (19): colorless oil (36.1 mg, 80% yield). ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.24 (d, *J* = 6.4 Hz, 6H), 3.67-3.77 (m, 1H), 4.55 (s, 2H), 7.31-7.35 (m, 1H), 7.40-7.45 (m, 4H), 7.55-7.59 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 22.2, 69.8, 71.1, 127.13, 127.17, 127.22, 128.1, 128.8, 138.2, 140.4, 141.1. IR ν 3057, 2971, 2929, 2867, 2629, 1126, 1076, 760 cm^{-1}.HRMS (EI) calcd. for $C_{16}H_{18}O$, ([M]): 226.1358, found: 226. 1360. Known compound.[8]



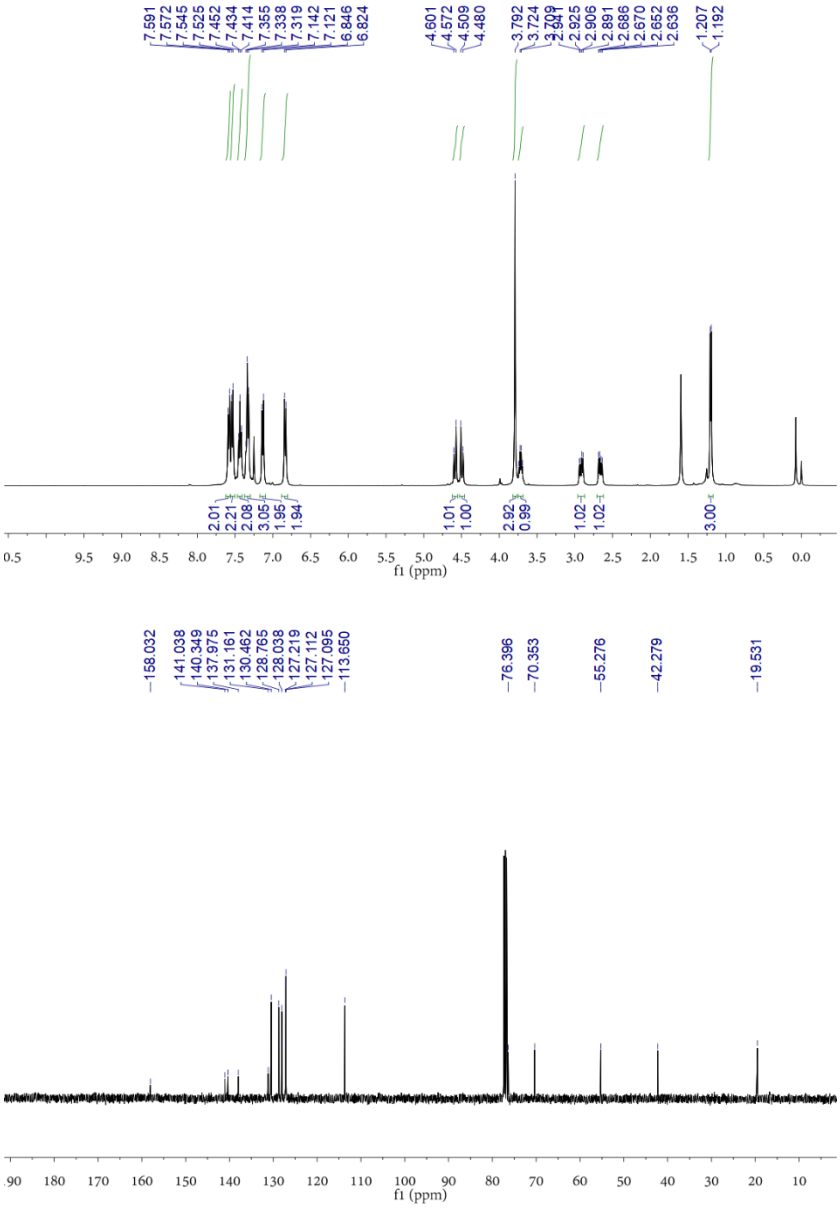


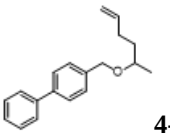
4-(((4-Methylpentan-2-yl)oxy)methyl)-1,1'-biphenyl (20): colorless oil (47.7 mg, 89% yield). ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 0.89 (d, *J* = 6.8 Hz, 6H), 1.21 (d, *J* = 7.0 Hz, 3H), 1.55-1.63 (m, 2H), 1.76-1.87 (m, 1H), 3.57-3.66 (m, 1H), 4.48 (d, *J* = 11.6 Hz, 1H), 4.63 (d, *J* = 11.6 Hz, 1H), 7.23-7.36 (m, 1H), 7.41-7.46 (m, 4H), 7.55-7.60 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 20.0, 22.6, 23.1, 24.7, 46.4, 70.0, 73.2, 127.1, 127.2, 128.1, 128.8, 138.2, 140.4, 141.1. IR ν 3029, 2959, 2926, 2869, 1488, 1465, 1079, 822 cm^{-1}. HRMS (EI) calcd. for $C_{19}H_{24}O$, ([M]): 268.1827, found: 268.1834.



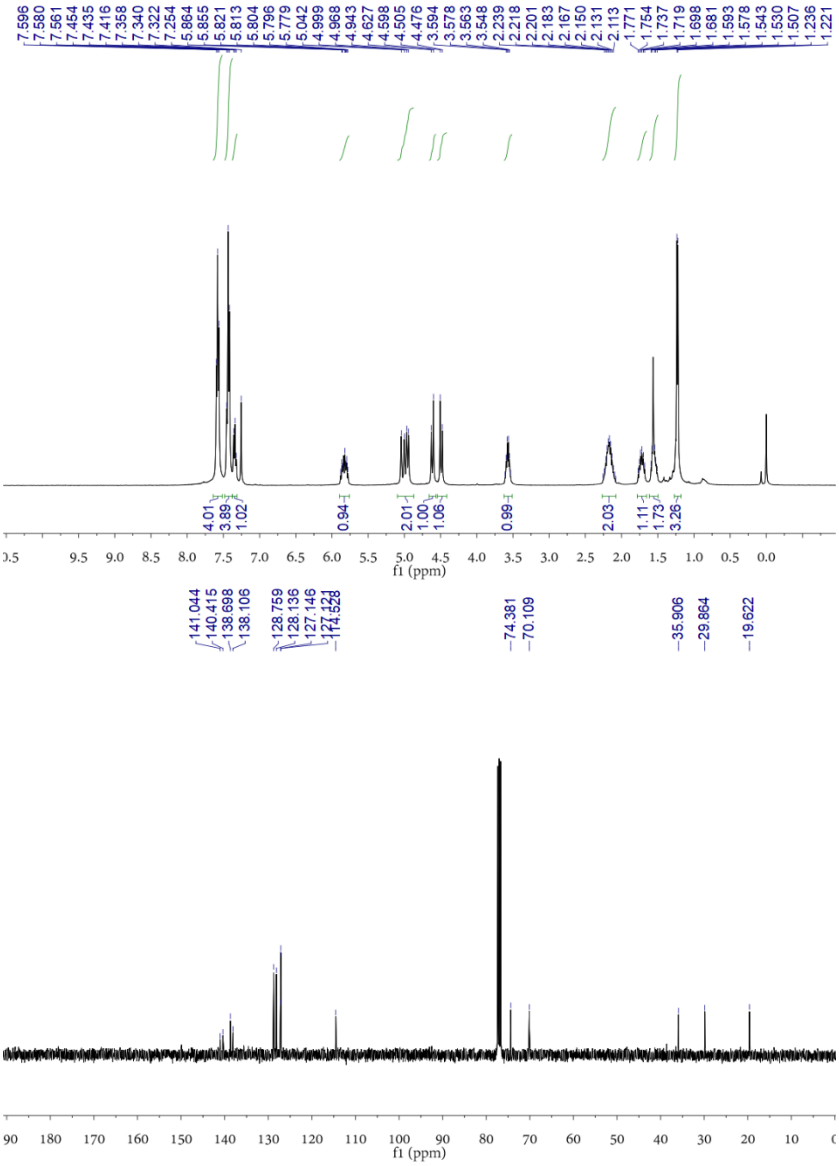


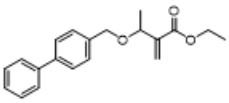
4-(((1-(4-Methoxyphenyl)propan-2-yl)oxy)methyl)-1,1'-biphenyl (21): white solid (35.8 mg, 54% yield). m.p. 44-45 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.20 (d, J = 6.0 Hz, 3H), 2.66 (dd, J_1 = 13.6 Hz, J_2 = 6.4 Hz, 1H), 2.92 (dd, J_1 = 13.6 Hz, J_2 = 6.4 Hz, 1H), 3.68-3.76 (m, 1H), 3.79 (s, 3H), 4.49 (d, J = 11.6 Hz, 1H), 4.58 (d, J = 11.6 Hz, 1H), 6.83 (d, J = 8.8 Hz, 2H), 7.13 (d, J = 8.4 Hz, 2H), 7.31-7.36 (m, 3H), 7.41-7.46 (m, 2H), 7.54 (d, J = 8.0 Hz, 2H), 7.58 (d, J = 7.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 19.5, 42.3, 55.3, 70.4, 76.4, 113.7, 127.10, 127.11, 127.2, 128.0, 128.8, 130.5, 131.2, 138.0, 140.4, 141.0, 158.0. IR ν 3029, 2967, 2857, 2837, 1512, 1247, 1090, 1036 cm^{-1}. HRMS (EI) calcd. for $C_{23}H_{24}O$, ([M]): 332.1776, found: 332.1778.



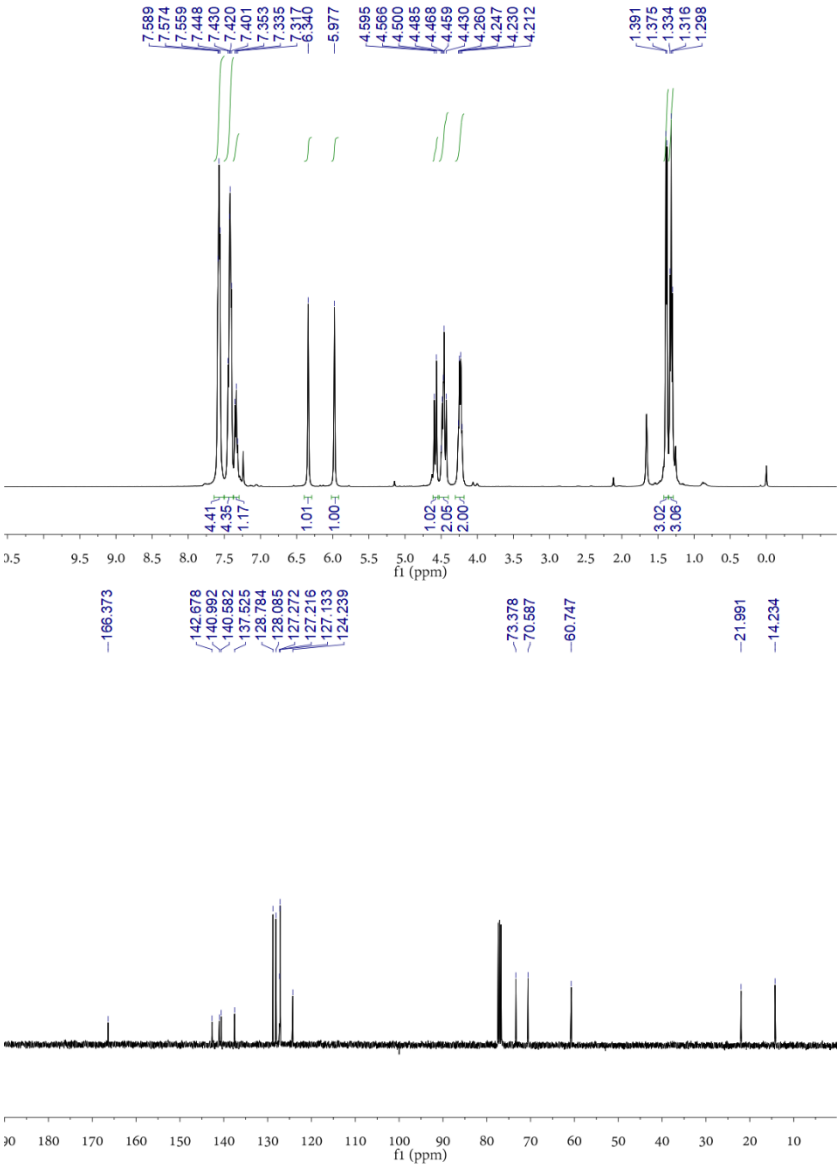


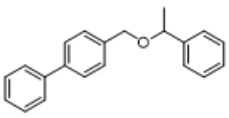
4-((Hex-5-en-2-yloxy)methyl)-1,1'-biphenyl (22): colorless oil (35.6 mg, 67% yield). ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.23 (d, *J* = 7.0 Hz, 3H), 1.50-1.60 (m, 1H), 1.68-1.78 (m, 1H), 2.08-2.26 (m, 2H), 3.53-3.61 (m, 1H), 4.49 (d, *J* = 11.6 Hz, 1H), 4.61 (d, *J* = 11.6 Hz, 1H), 4.95 (d, *J* = 10.0 Hz, 1H), 5.02 (d, *J* = 17.2 Hz, 1H), 5.77-5.88 (m, 1H), 7.32-7.36 (m, 1H), 7.41-7.46 (m, 4H), 7.56-7.60 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 19.6, 29.9, 35.9, 70.1, 74.4, 114.5, 127.12, 127.15, 127.2, 128.1, 128.8, 138.1, 138.7, 140.4, 141.0. IR ν 3075, 3030, 2971, 2929, 2859, 1488, 1375, 1134, 1081 cm^{-1}. HRMS (EI) calcd. for $C_{19}H_{22}O$, ([M]): 266.1671, found: 266.1670.



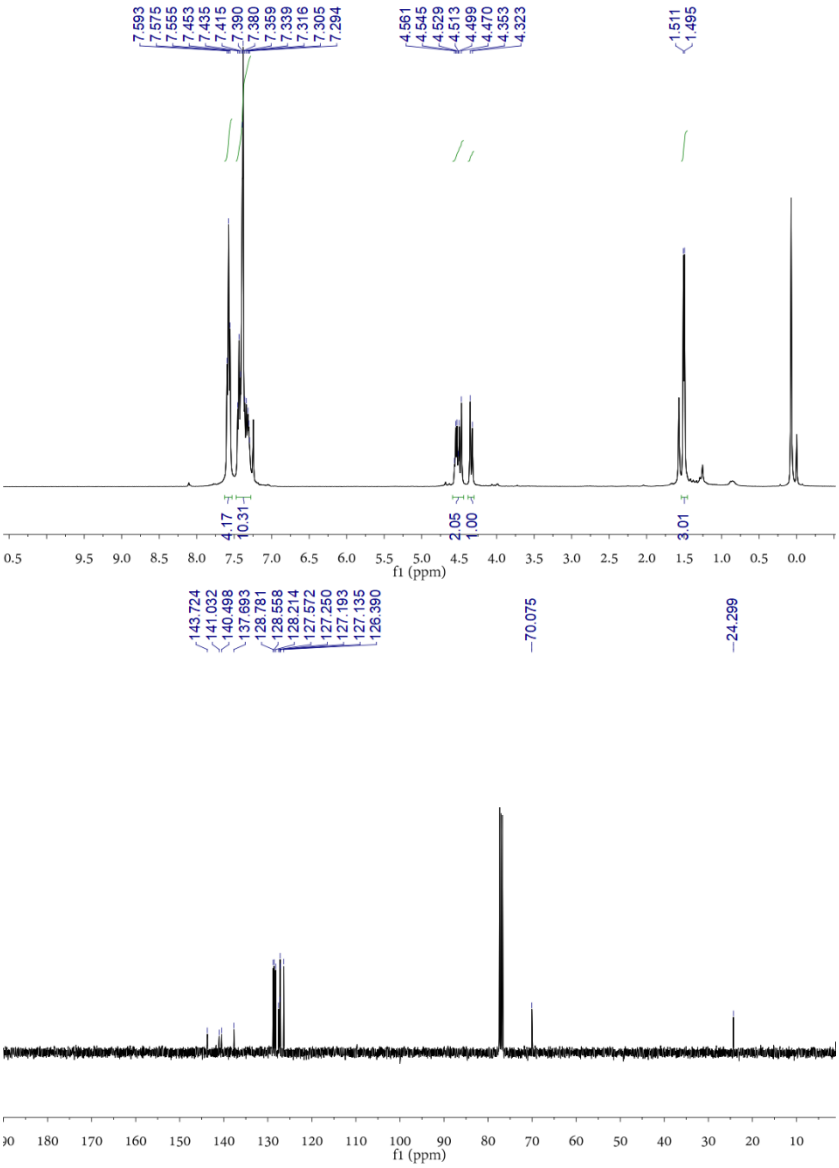


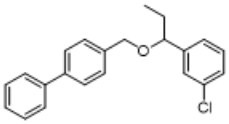
Methyl 3-([1,1'-biphenyl]-4-ylmethoxy)-2-methylenebutanoate (23): colorless oil (42.8 mg, 69% yield). ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.32 (t, J = 7.2 Hz, 3H), 1.38 (d, J = 6.4 Hz, 3H), 4.18-4.30 (m, 2H), 4.43-4.50 (m, 2H), 4.58 (d, J = 11.6 Hz, 1H), 5.98 (s, 1H), 6.34 (s, 1H), 7.34 (dd, J_1 = J_2 = 7.2 Hz, 1H), 7.40-7.45 (m, 4H), 7.55-7.59 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 11.2, 22.0, 60.8, 70.6, 73.4, 124.2, 127.1, 127.2, 127.3, 128.1, 128.8, 137.5, 140.6, 141.0, 142.7, 166.4. IR ν 3030, 2980, 2932, 2902, 2869, 1714, 1371, 1287, 1096 cm^{-1}. HRMS (ESI) calcd. for $C_{20}H_{26}NO_3$, ($[M+NH_4]^+$): 328.1913, found: 328.1907.



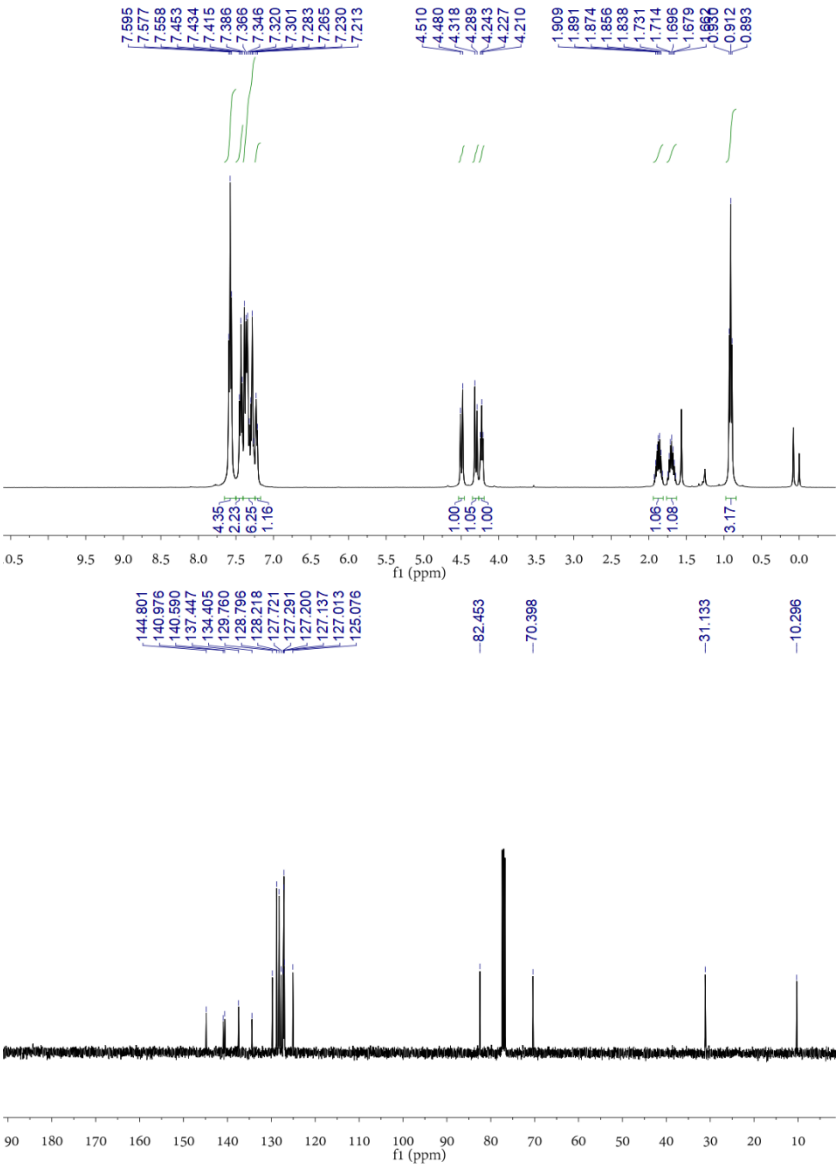


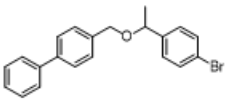
4-((1-Phenylethoxy)methyl)-1,1'-biphenyl (24): colorless oil (39.7 mg, 69% yield). ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.50 (d, *J* = 6.4 Hz, 3H), 4.34 (d, *J* = 12.0 Hz, 1H), 4.48 (d, *J* = 12.0 Hz, 1H), 4.54 (q, *J* = 6.4 Hz, 1H), 7.29-7.45 (m, 10H), 7.55-7.59 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 24.3, 70.1, 126.4, 127.1, 127.2, 127.3, 127.6, 128.2, 128.6, 128.8, 137.7, 140.5, 141.0, 143.7. IR ν 3059, 3029, 2973, 2927, 2861, 1489, 1095, 761 cm^{-1}. HRMS (EI) calcd. for $C_{21}H_{20}O$, ([M]): 288.1514, found: 288.1516.



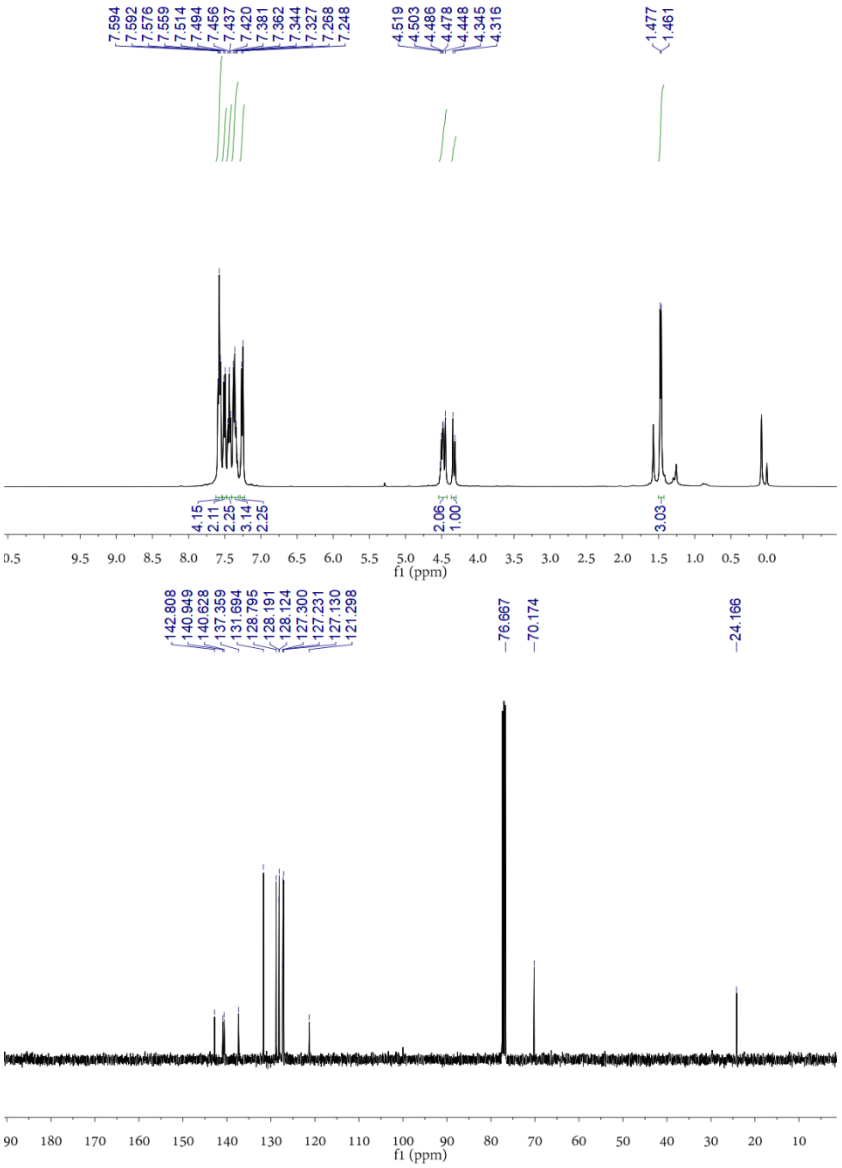


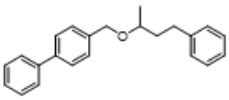
4-((1-(3-Chlorophenyl)propoxy)methyl)-1,1'-biphenyl (25): Colorless oil (33.6 mg, 50% yield). ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 0.91 (t, *J* = 7.2 Hz, 3H), 1.64-1.75 (m, 1H), 1.82-1.93 (m, 1H), 4.23 (t, *J* = 6.8 Hz, 1H), 4.31 (d, *J* = 12.0 Hz, 1H), 4.50 (d, *J* = 12.0 Hz, 1H), 7.21-7.24 (m, 1H), 7.26-7.39 (m, 6H), 7.34 (dd, $J_1 = J_2$ = 7.6 Hz, 2H), 7.55-7.60 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 10.3, 31.1, 70.4, 82.4, 125.1, 127.0, 127.1, 127.2, 127.3, 127.7, 128.2, 128.8, 129.8, 134.4, 137.4, 140.6, 141.0, 144.8. IR ν 3058, 2967, 2932, 2871, 1485, 1341, 760, 697 cm^{-1}. HRMS (EI) calcd. for $C_{21}H_{21}OCl$, ([M]): 336.1281, found: 336.1276.



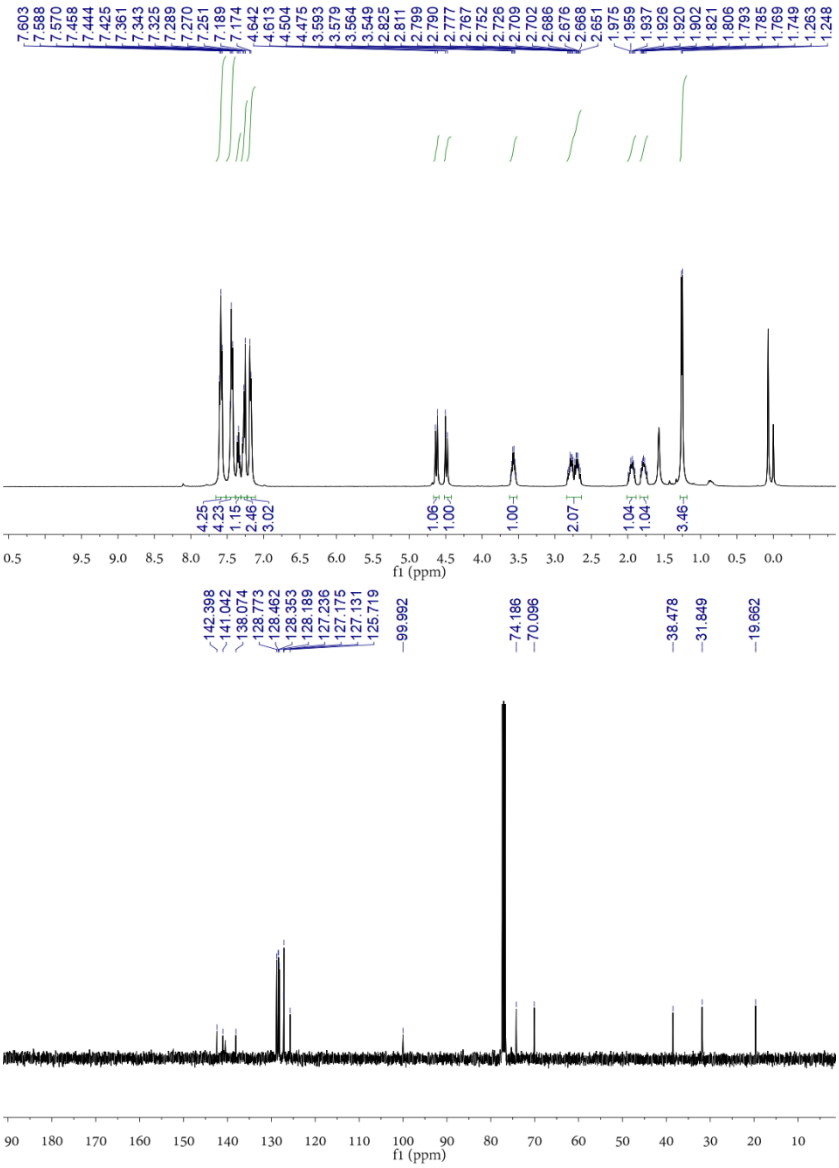


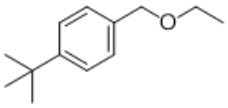
4-((1-(4-Bromophenyl)ethoxy)methyl)-1,1'-biphenyl (26): colorless oil (44.0 mg, 60% yield). ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.47 (d, *J* = 6.4 Hz, 3H), 4.33 (d, *J* = 12.0 Hz, 1H), 4.46 (d, *J* = 12.0 Hz, 1H), 4.49 (q, *J* = 6.4 Hz, 2H), 7.26 (d, *J* = 8.0 Hz, 2H), 7.32-7.39 (m, 3H), 7.42-7.46 (m, 2H), 7.50 (d, *J* = 8.0 Hz, 2H), 7.55-7.60 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 24.2, 70.2, 76.7, 121.3, 127.1, 127.2, 127.3, 128.1, 128.2, 128.8, 131.7, 137.4, 140.6, 141.1, 142.8. IR ν 3056, 3029, 2975, 2927, 2860, 1486, 1406, 1092, 824 cm^{-1}. HRMS (EI) calcd. for $C_{21}H_{19}OBr$, ([M]): 366.0619, found: 366.0618.



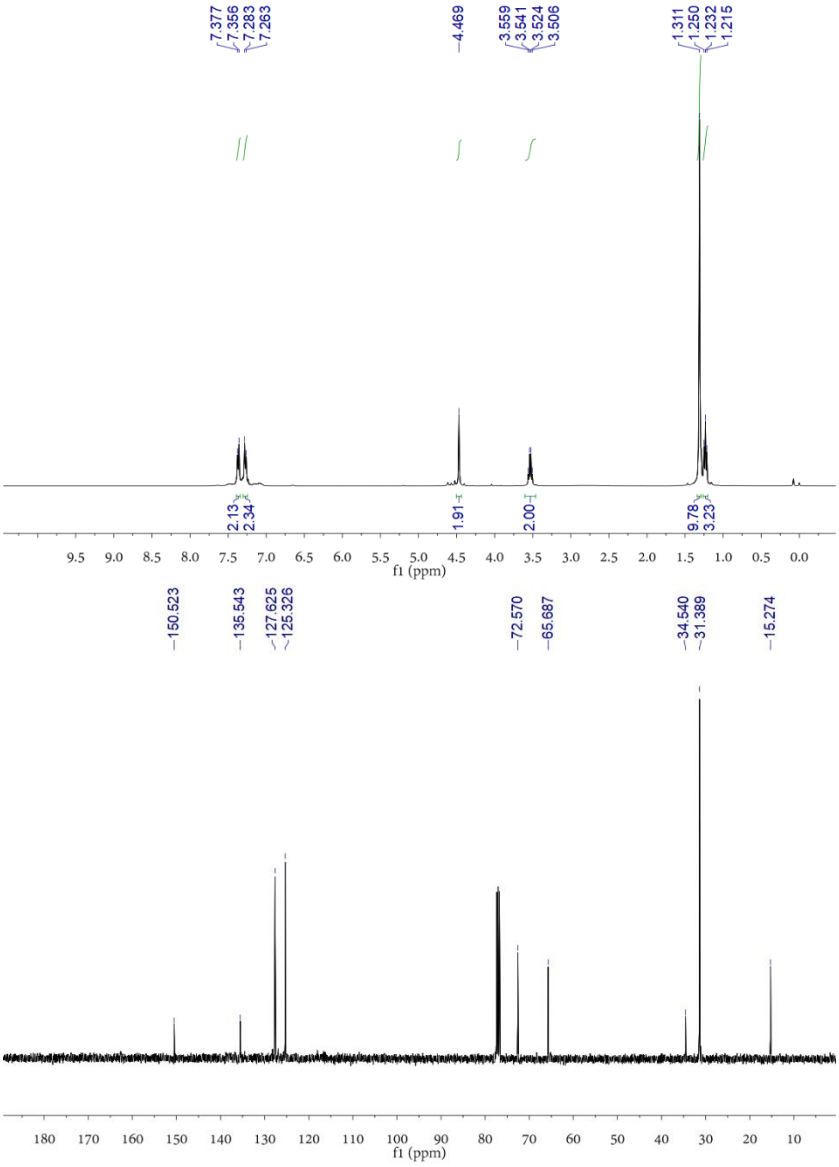


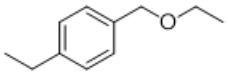
4-(((4-Phenylbutan-2-yl)oxy)methyl)-1,1'-biphenyl (27): colorless oil (55.6 mg, 88% yield). ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.26 (d, *J* = 6.0 Hz, 3H), 1.73-1.82 (m, 1H), 1.90-1.94 (m, 1H), 2.65-2.73 (m, 1H), 2.75-2.83 (m, 1H), 3.53-3.61 (m, 1H), 4.49 (d, *J* = 11.6 Hz, 1H), 4.63 (d, *J* = 11.6 Hz, 1H), 7.17-7.20 (m, 3H), 7.25-7.29 (m, 2H), 7.32-7.37 (m, 1H), 7.42-7.46 (m, 4H), 7.57-7.61 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 19.7, 31.9, 38.5, 70.1, 74.2, 100.0, 125.7, 127.13, 127.18, 127.2, 128.2, 128.4, 128.5, 128.8, 138.1, 141.0, 142.4. IR ν 3059, 3028, 2967, 2927, 1453, 1072, 759, 698 cm^{-1}. HRMS (EI) calcd. for $C_{23}H_{24}O$, ([M]): 316.1827, found: 316.1817.



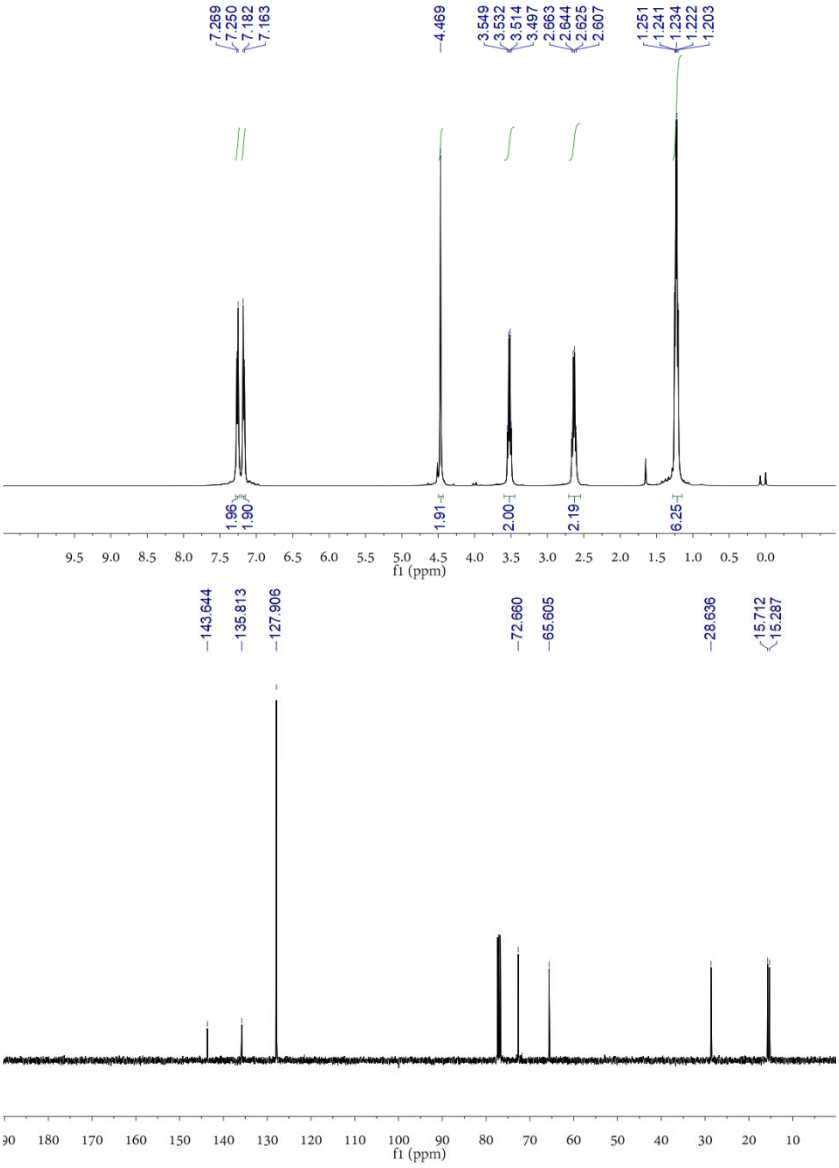


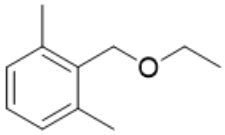
1-(1,1-Dimethylethyl)-4-(ethoxymethyl)benzene (28): colorless oil (33.0 mg, 86% yield). ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.23 (t, *J* = 7.2 Hz, 3H), 1.31 (s, 9H), 3.53 (q, *J* = 7.2 Hz, 2H), 4.47 (s, 2H), 7.27 (d, *J* = 8.0 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 15.3, 31.4, 34.5, 65.7, 72.6, 125.3, 127.6, 135.5, 150.5. IR ν 3096, 3058,2966, 2904, 2868, 1465, 1103, 831 cm^{-1}. HRMS (EI) calcd. for $C_{13}H_{20}O$, ([M]): 192.1514, found: 192.1513.



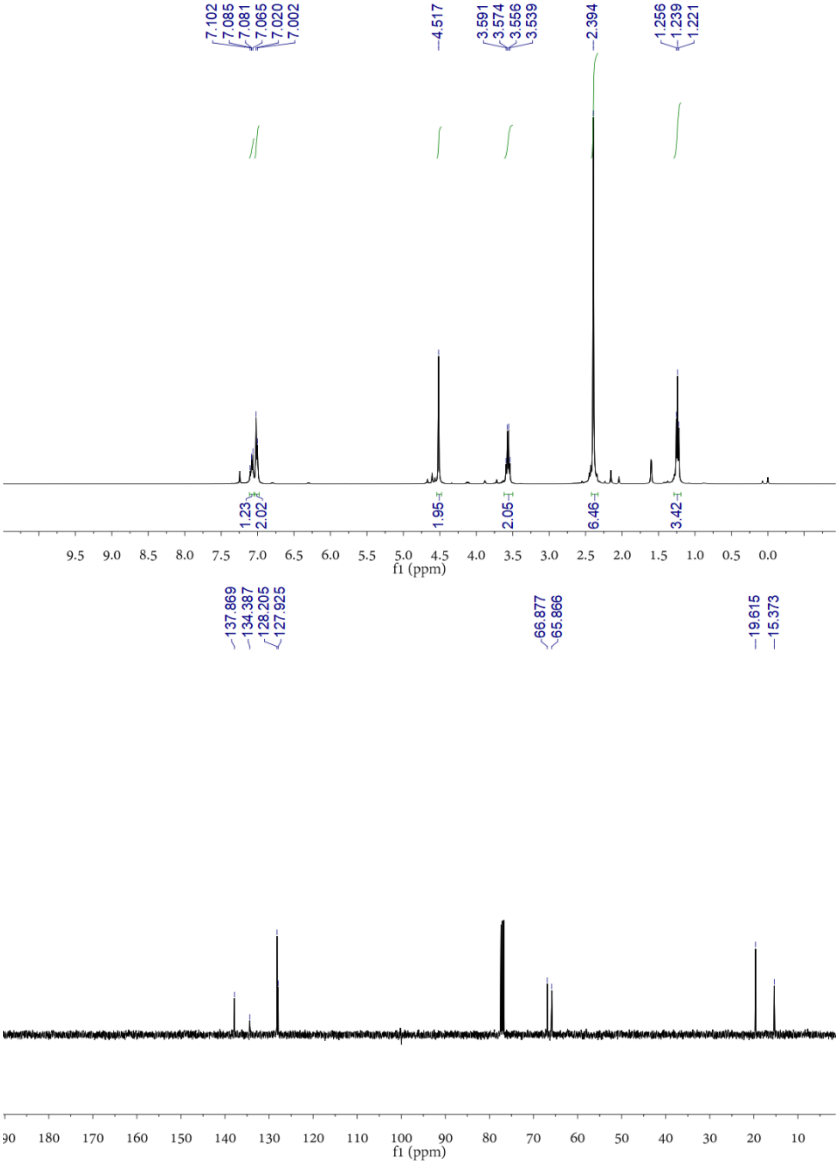


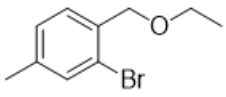
1-(Ethoxymethyl)-4-ethylbenzene (29): colorless oil (24.3 mg, 74% yield). ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.20-1.26 (m, 6H), 2.64 (q, *J* = 7.6 Hz, 2H), 3.52 (q, *J* = 6.8 Hz, 2H), 4.47 (s, 2H), 7.17 (d, *J* = 7.6 Hz, 2H), 7.26 (d, *J* = 7.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 15.3, 15.7, 28.6, 65.6, 72.7, 127.9, 135.8, 143.6. IR ν 3093, 3016, 2970, 2931, 2865, 1456, 1102, 818 cm^{-1}. HRMS (EI) calcd. for $C_{11}H_{16}O$, ([M]): 164.1201, found: 164.1203.



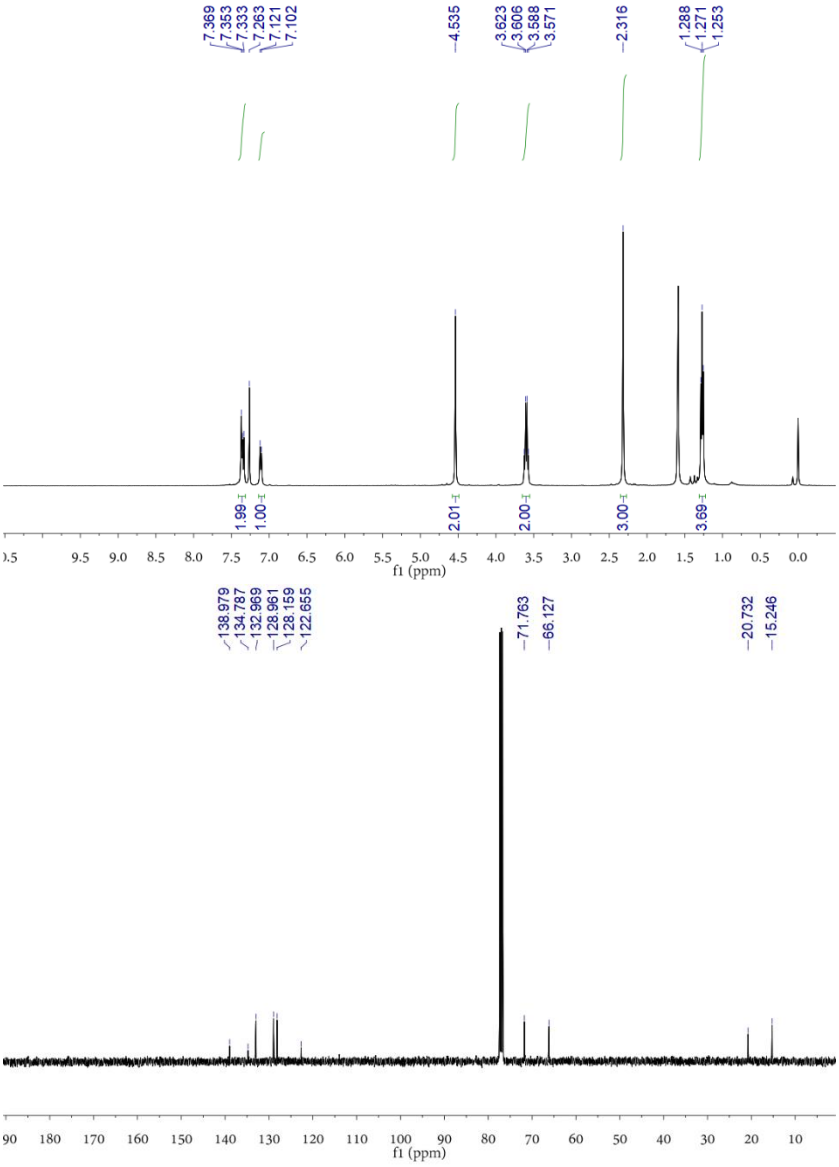


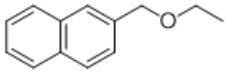
2-(Ethoxymethyl)-1,3-dimethylbenzene (30): orange oil (19.3 mg, 59% yield). ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.24 (t, J = 6.8 Hz, 3H), 2.40 (s, 6H), 3.56 (q, J = 6.8 Hz, 2H), 4.52 (s, 2H), 7.01 (d, J = 7.2 Hz, 2H), 7.06-7.11 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 15.4, 19.6, 65.9, 66.9, 127.9, 128.2, 134.4, 137.9. IR ν 3069, 3024, 2973, 2926, 1741, 1094, 770 cm^{-1}. HRMS (EI) calcd. for $C_{11}H_{16}O$, ([M]):164.1201, found: 164.1204.



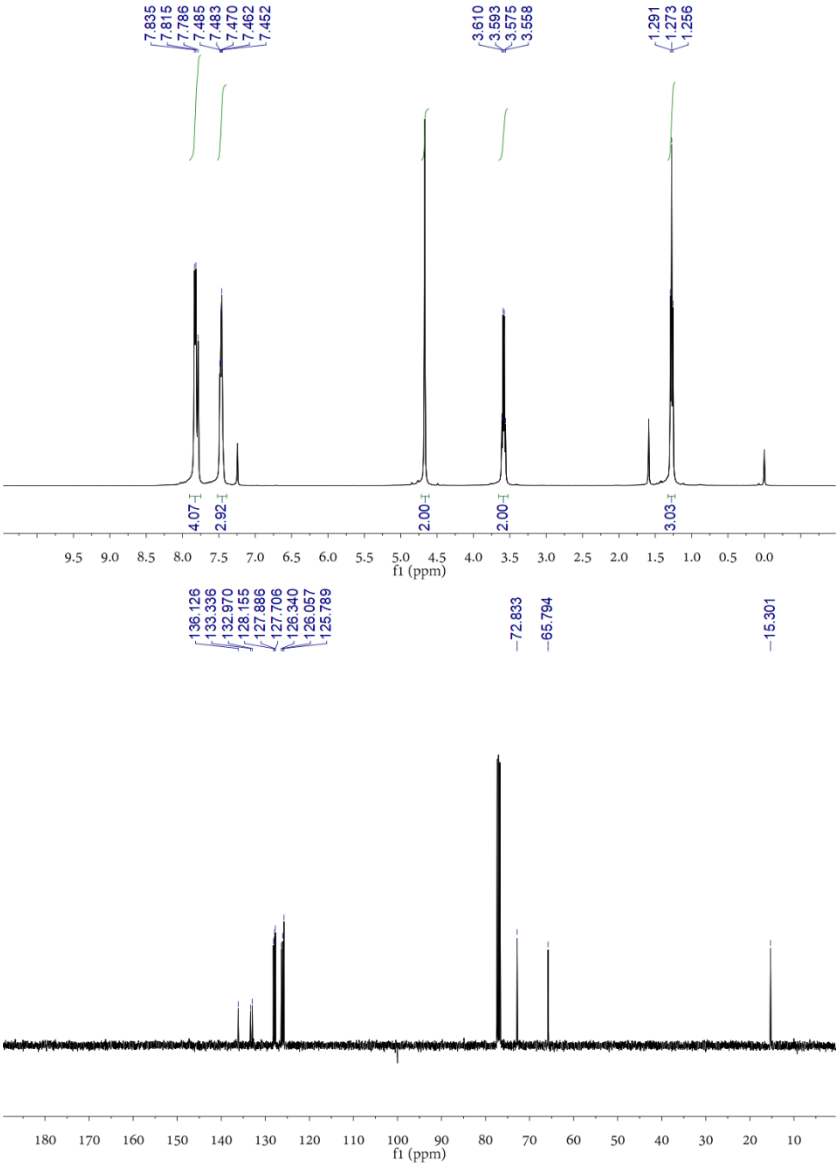


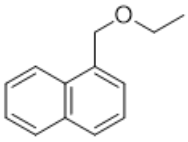
2-Bromo-1-(ethoxymethyl)-4-methylbenzene (31): colorless oil (28.7 mg, 63% yield). ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.27 (t, *J* = 6.8 Hz, 3H), 2.32 (s, 3H), 3.60 (q, *J* = 6.8 Hz, 2H), 4.54 (s, 2H), 7.11 (d, *J* = 7.6 Hz, 1H), 7.33-7.37 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 15.3, 20.7, 66.1, 71.8, 122.7, 128.2, 129.0, 133.0, 134.8, 139.0. IR ν 2974, 2926, 2861, 2797, 1118, 1039, 816 cm^{-1}. HRMS (EI) calcd. For $C_{10}H_{13}OBr$, ([M]): 228.0150, found: 228.0150.



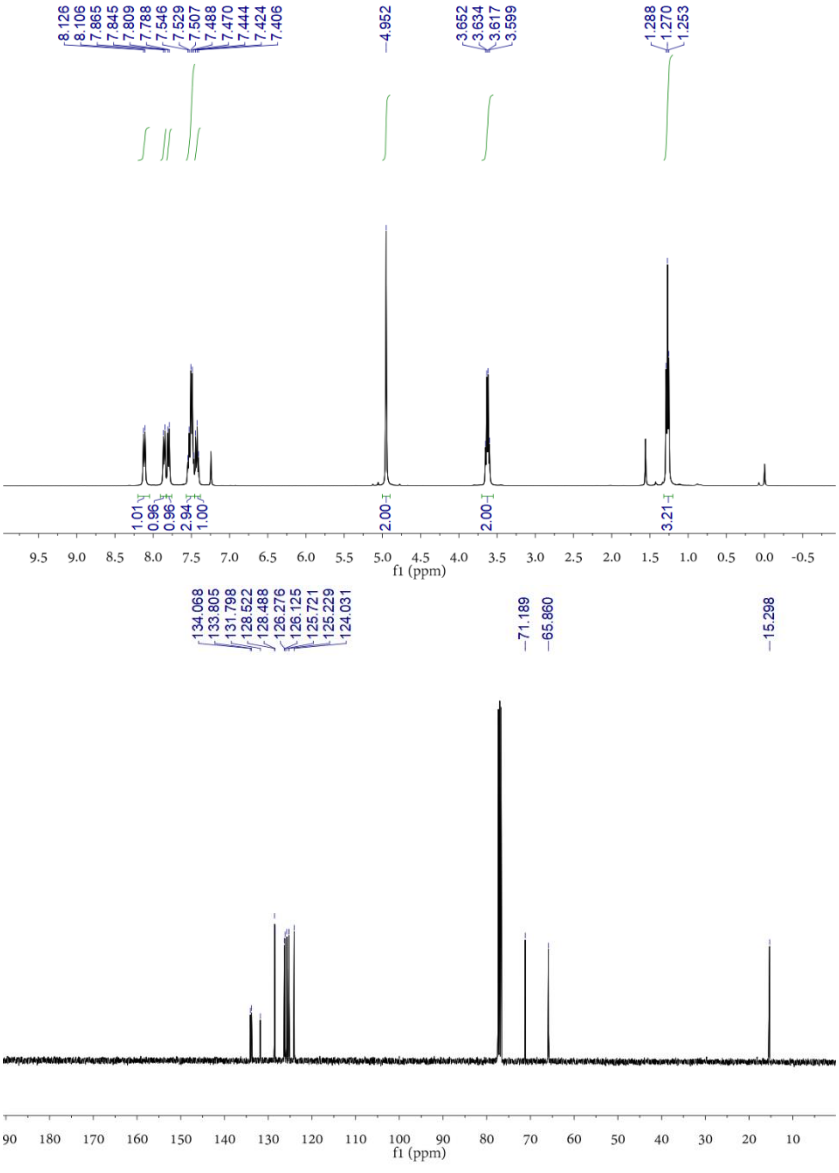


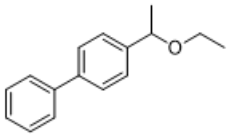
2-(Ethoxymethyl)naphthalene (32): colorless oil (26.1 mg, 70% yield). ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.27 (t, J = 6.8 Hz, 3H), 3.58 (q, J = 6.8 Hz, 2H), 4.67 (s, 2H), 7.45-7.49 (m, 3H), 7.78-7.84 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 15.3, 65.8, 72.8, 125.8, 126.1, 126.3, 127.7, 127.9, 128.2, 133.0, 133.3, 136.1. IR ν 3055, 3022, 2974 ,2929, 2862, 1377, 1101, 816 cm^{-1}. HRMS (EI) calcd. for $C_{13}H_{14}O$, ([M]): 186.1045, found: 186.1048. Known compound.[7]



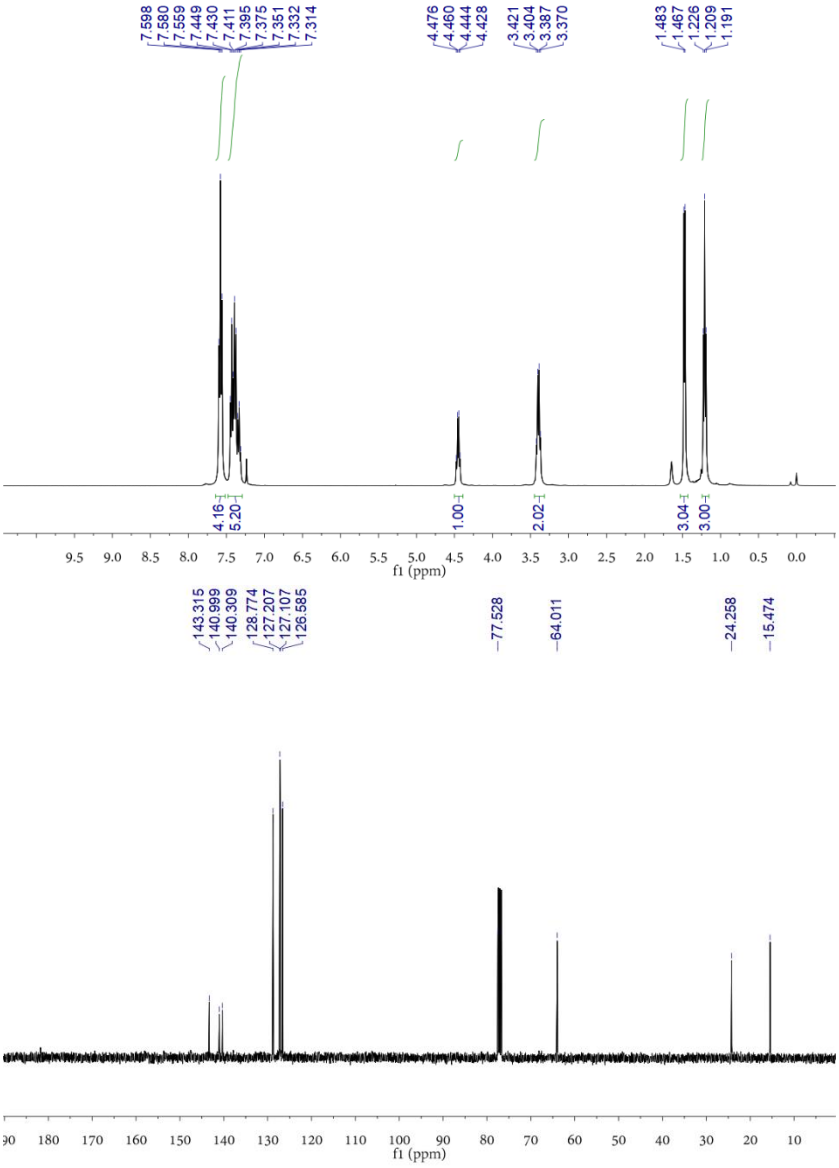


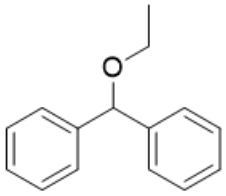
1-(Ethoxymethyl)naphthalene (33): colorless oil (24.9 mg, 67% yield). ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.27 (t, *J* = 6.8 Hz, 3H), 3.62 (q, *J* = 6.8 Hz, 2H), 4.95 (s, 2H), 7.40-7.55 (m, 4H), 7.80 (d, *J* = 8.4 Hz, 1H), 7.86 (d, *J* = 8.0 Hz, 1H), 8.12 (d, *J* = 8.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 15.3, 65.9, 71.2, 124.0, 125.2, 125.7, 126.1, 126.3, 128.49, 128.52, 131.8, 133.8, 134.1. IR ν 3048, 2974, 2929, 2863, 1511, 1118, 1098, 796 cm^{-1}. HRMS (EI) calcd. for $C_{13}H_{14}O$, ([M]): 186.1045, found: 186.1048.



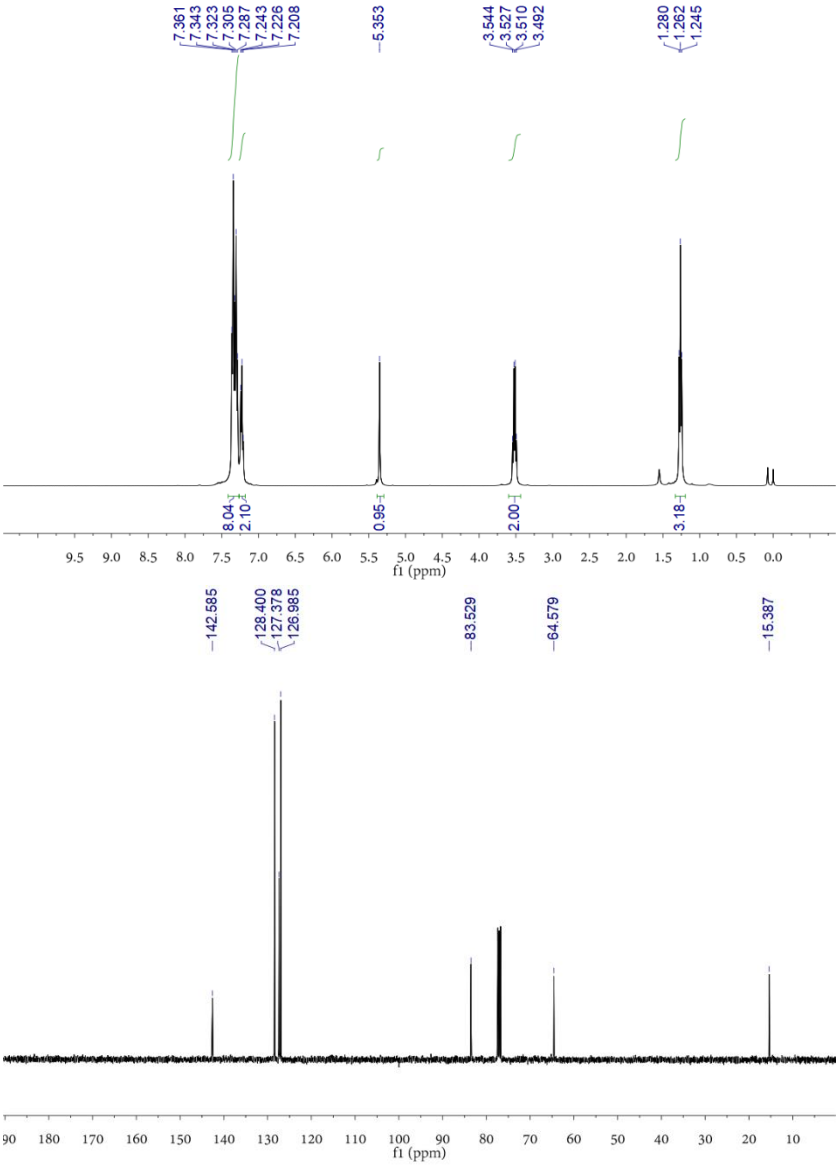


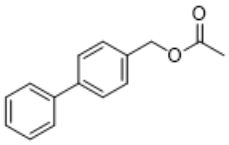
4-(1-Ethoxyethyl)-1,1'-biphenyl (34): colorless oil (34.8 mg, 77% yield). ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.21 (t, J = 6.8 Hz, 3H), 1.47 (d, J = 6.4 Hz, 3H), 3.39 (q, J = 6.8 Hz, 2H), 4.45 (q, J = 6.4 Hz, 1H), 7.31-7.45 (m, 5H), 7.55-7.60 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 15.5, 24.3, 64.0, 77.5, 126.6, 127.1, 127.2, 128.8, 140.3, 141.0, 143.3. IR ν 3056, 3029, 2975, 2929, 2779, 1486, 1099, 839 cm^{-1}. HRMS (EI) calcd. for $C_{16}H_{18}O$, ([M]): 226.1358, found: 226.1366.



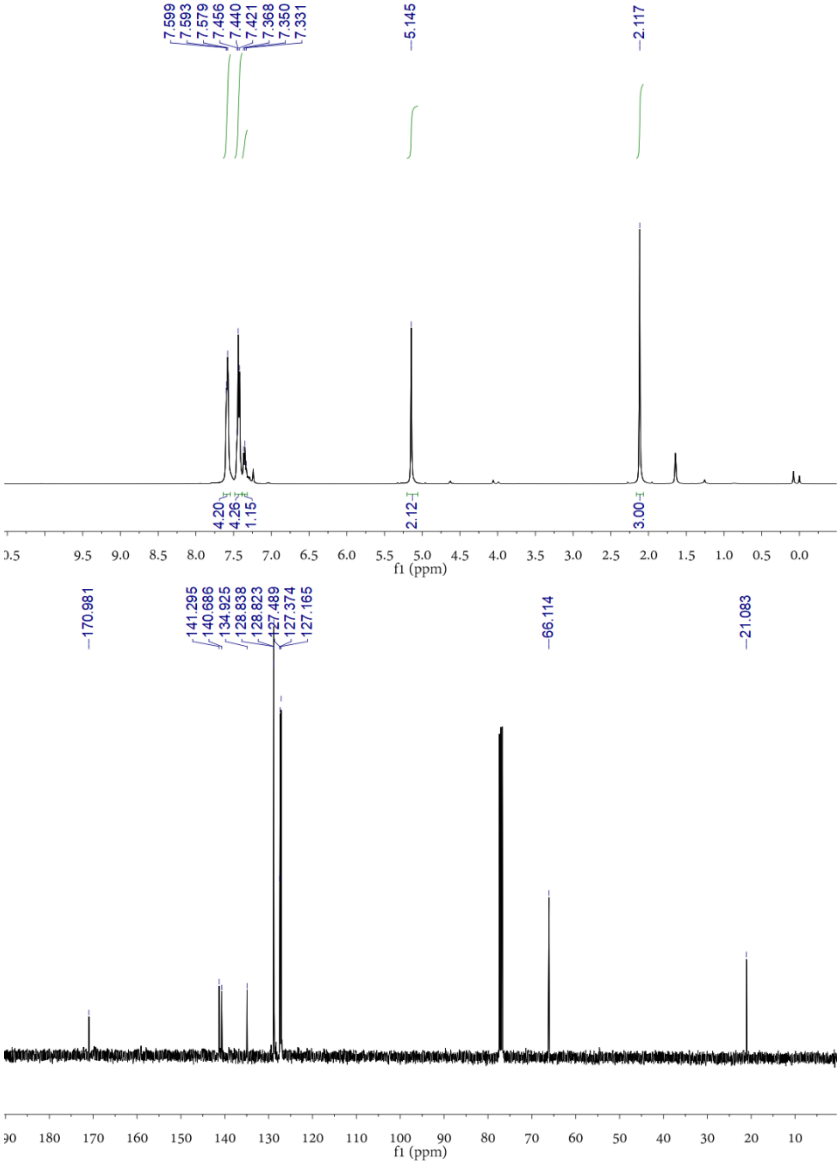


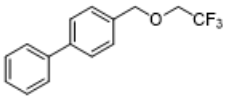
(Ethoxymethylene)dibenzene (35): colorless oil (33.1 mg, 78% yield). ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.26 (t, J = 6.8 Hz, 3H), 3.52 (q, J = 6.8 Hz, 2H), 5.35 (s, 1H), 7.20-7.24 (m, 2H), 7.28-7.37 (m, 8H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 15.4, 64.6, 83.5, 127.0, 127.4, 128.4, 142.6. IR ν 3085, 3062, 2975, 2867, 2782, 1451, 1097, 700 cm^{-1}. HRMS (EI) calcd. for $C_{15}H_{16}O$, ([M]): 212.1201, found: 212.1206. Known compound.[10]



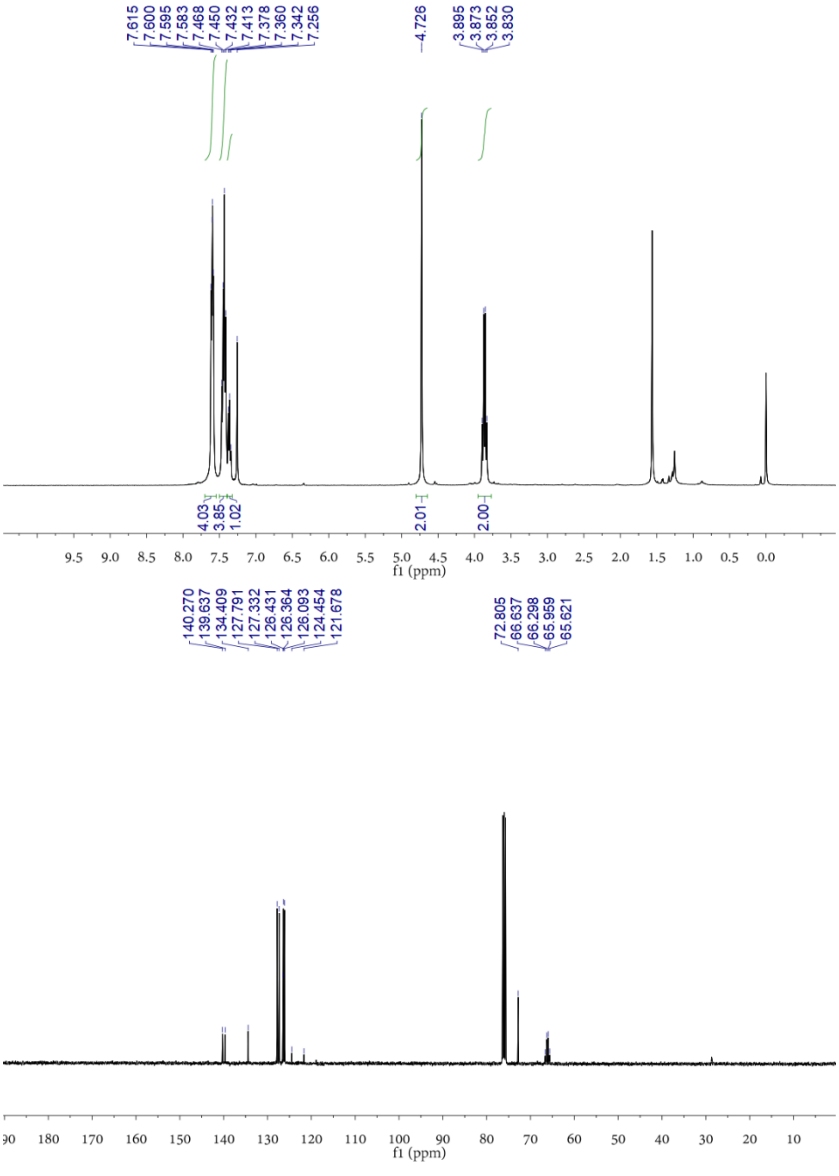


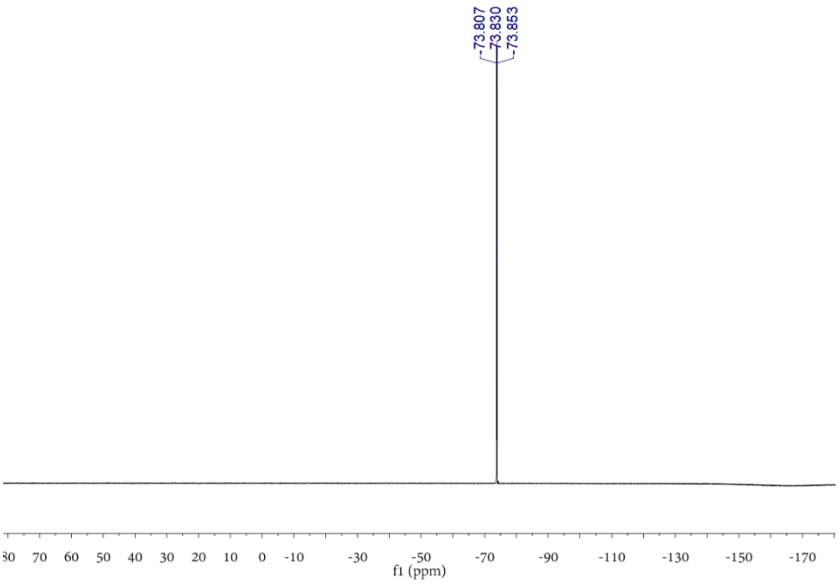
[1,1'-Biphenyl]-4-ylmethyl acetate (36): colorless oil (31.2 mg, 69% yield). ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 2.12 (s, 3H), 5.15 (s, 2H), 7.35 (dd, $J_1 = J_2 = 7.2$ Hz, 1H), 7.42-7.46 (m, 4H), 7.57-7.60 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 21.1, 66.1, 127.2, 127.4, 127.5, 128.82, 128.84, 134.9, 140.7, 141.3, 171.0. IR ν 3057, 3031, 2955, 2891, 1741, 1379, 1364, 1229, 1028 cm^{-1}. HRMS (EI) calcd. for $C_{15}H_{14}O_2$, ([M]): 226.0994, found: 226.1000. Known compound.[11]

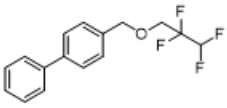




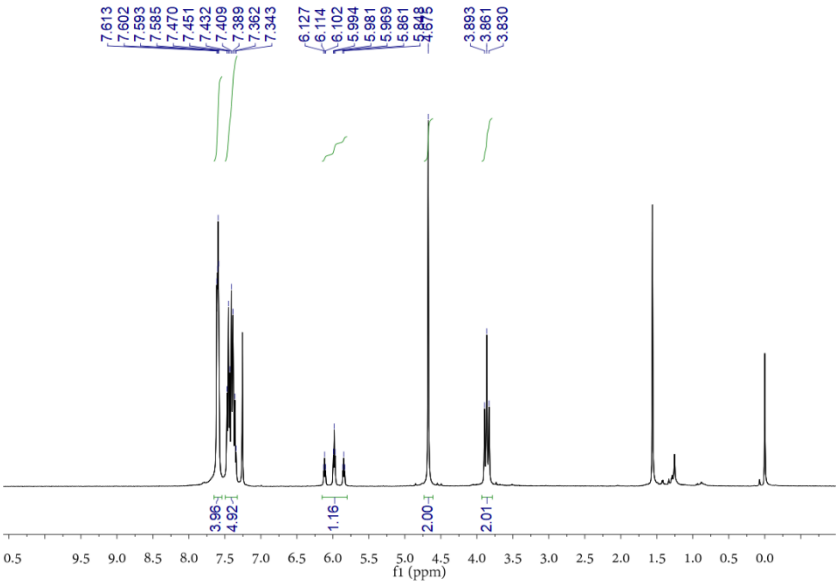
4-((2,2,2-Trifluoroethoxy)methyl)-1,1'-biphenyl (37): white solid (23.9 mg, 45% yield). m.p. 40-45 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 3.86 (q, J = 8.8 Hz, 2H), 4.73 (s, 2H), 7.34-7.38 (m, 1H), 7.41-7.47 (m, 4H), 7.58-7.62 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 66.1 (q, J = 68.4 Hz), 72.8, 123.1 (q, J = 277.7 Hz), 126.1, 126.37, 126.43, 127.3, 127.8, 134.4, 139.6, 140.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ -73.83 (t, J = 8.6 Hz). IR ν 2963, 2927, 1736, 1410, 1162, 1077, 967, 762 cm^{-1}. HRMS (EI) calcd. for $C_{15}H_{13}OF_3$, ([M]): 266.0918, found: 266.0920.

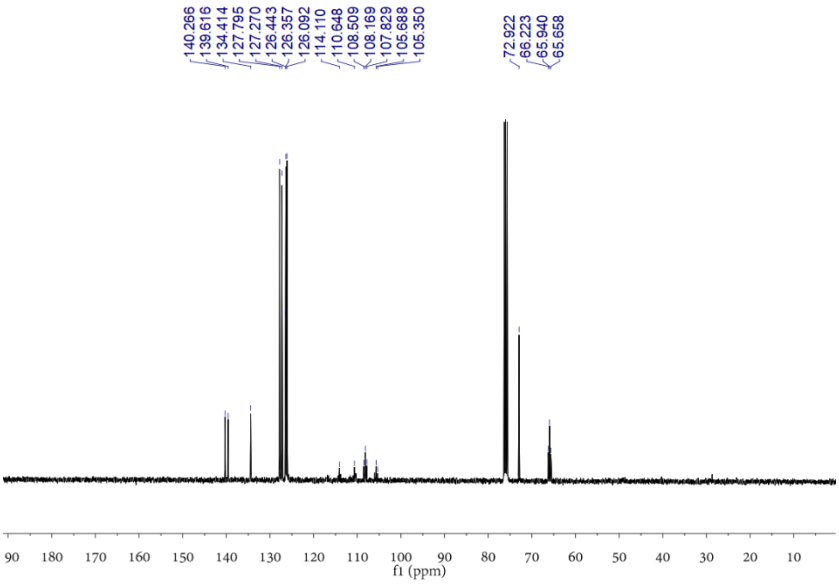






4-((2,2,3,3-Tetrafluoropropoxy)methyl)-1,1'-biphenyl (38): colorless oil (26.2 mg, 44% yield). ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 3.86 (t, J = 12.0 Hz, 2H), 4.68 (s, 2H), 5.98 (tt, J_1 = 53.2 Hz, J_2 = 4.8 Hz, 1H), 7.34-7.47 (m, 5H), 7.58-7.62 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 65.9 (t, J = 28.6 Hz), 72.9, 108.2 (tt, J_1 = 247.9 Hz, J_2 = 34.3 Hz), 126.1, 126.36, 126.44, 127.3, 127.8, 134.4, 139.6, 140.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ -139.86 (d, J = 53.4 Hz, 2F), -125.22 to -125.12 (m, 2F). IR ν 3058, 3031, 2927, 2877, 1488, 1203, 1107, 830 cm^{-1}. HRMS (EI) calcd. for $C_{16}H_{14}OF_4$, ([M]): 298.0981, found: 298.0990.

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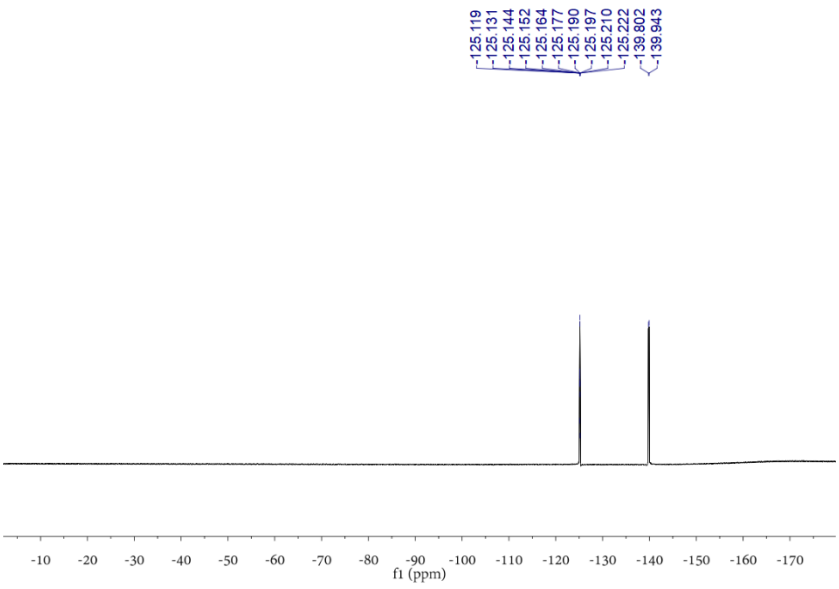
72.922
66.223
65.940
65.658
90 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)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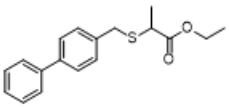
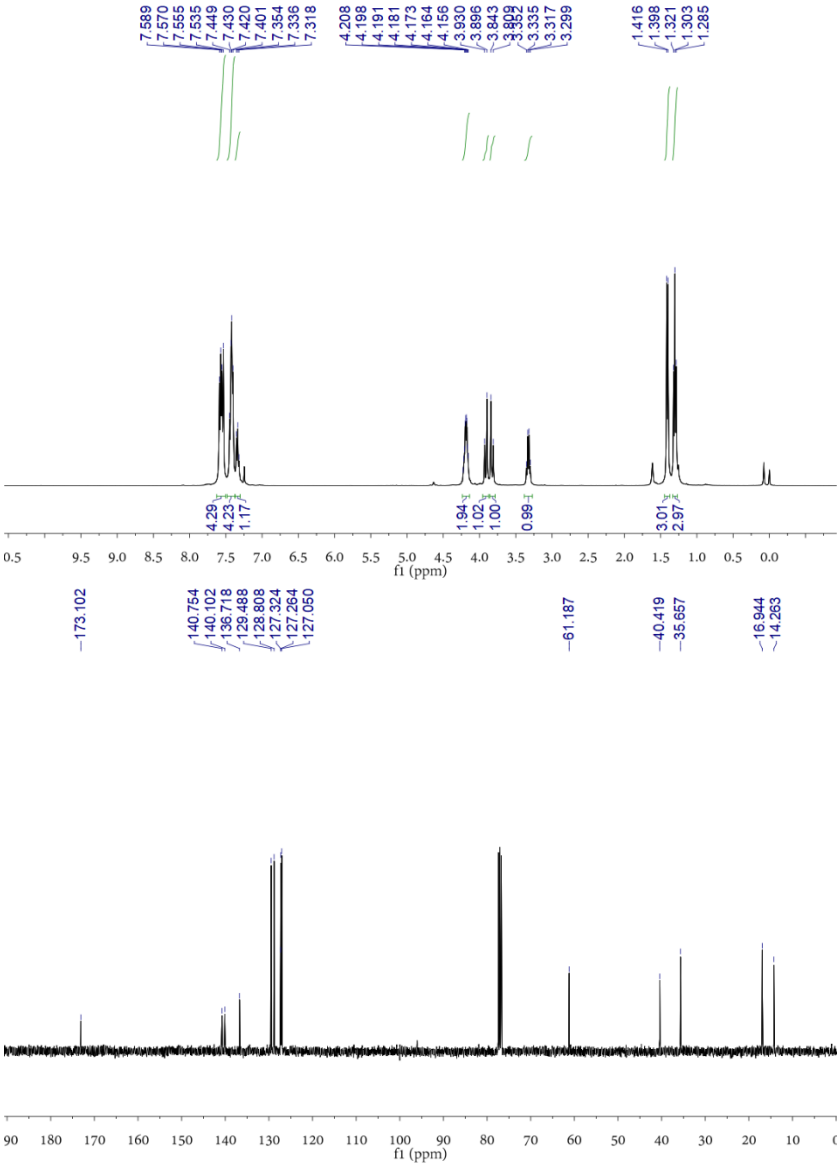
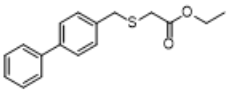
-139.943
-10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170
f1 (ppm)

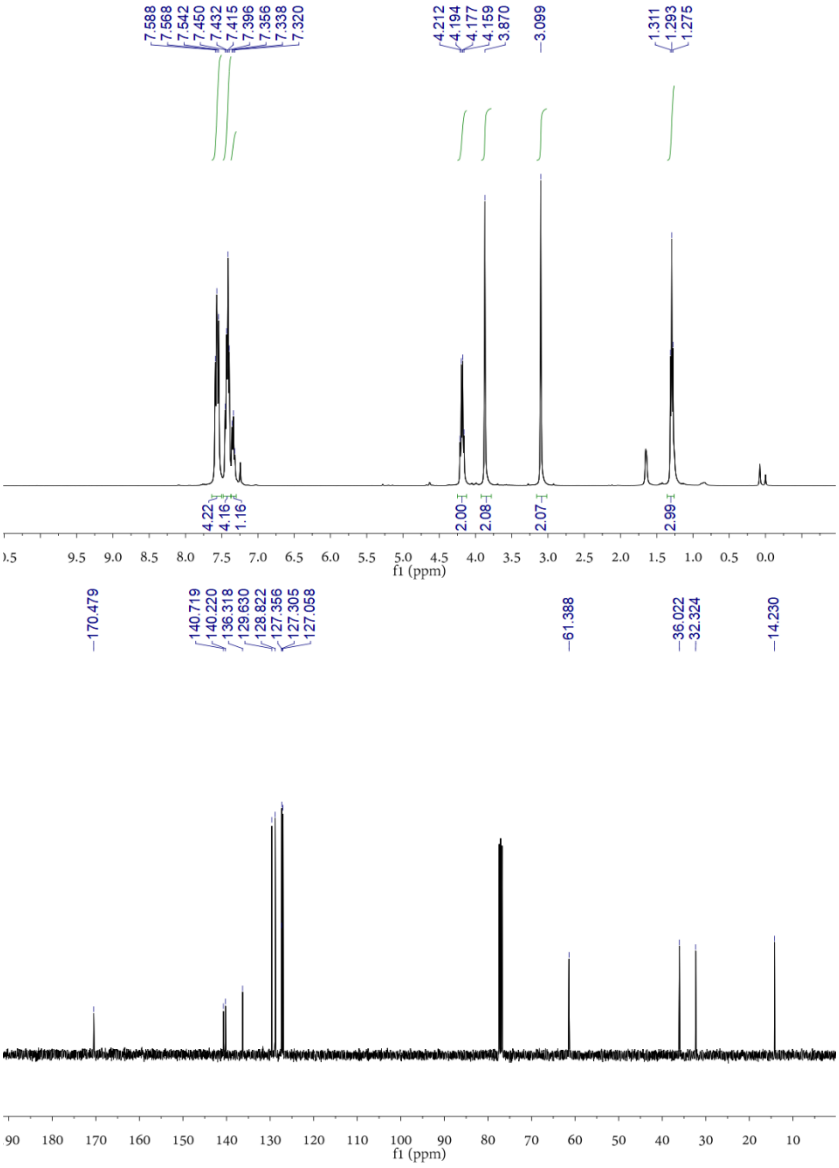


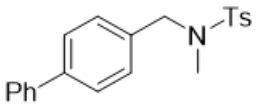
Ethyl 2-(([1,1'-biphenyl]-4-ylmethyl)thio)propanoate (39): colorless oil (40.8 mg, 68% yield). ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.30 (t, *J* = 7.2 Hz, 3H), 1.41 (d, *J* = 7.2 Hz, 3H), 3.33 (q, *J* = 7.2 Hz, 1H), 3.82 (d, *J* = 13.6 Hz, 1H), 3.92 (d, *J* = 13.6 Hz, 1H), 4.15-4.23 (m, 2H), 7.31-7.36 (m, 1H), 7.40-7.45 (m, 4H), 7.53-7.59 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 14.3, 16.9, 35.7, 40.4, 61.2, 127.1, 127.26, 127.32, 128.8, 129.5, 136.7, 140.1, 140.8, 173.1. IR ν 3659, 3447, 3029, 2932, 2872, 1732, 1486, 1161 cm^{-1}. HRMS (EI) calcd. for $C_{18}H_{20}O_2S$, ([M]): 300.1184, found: 300.1187.



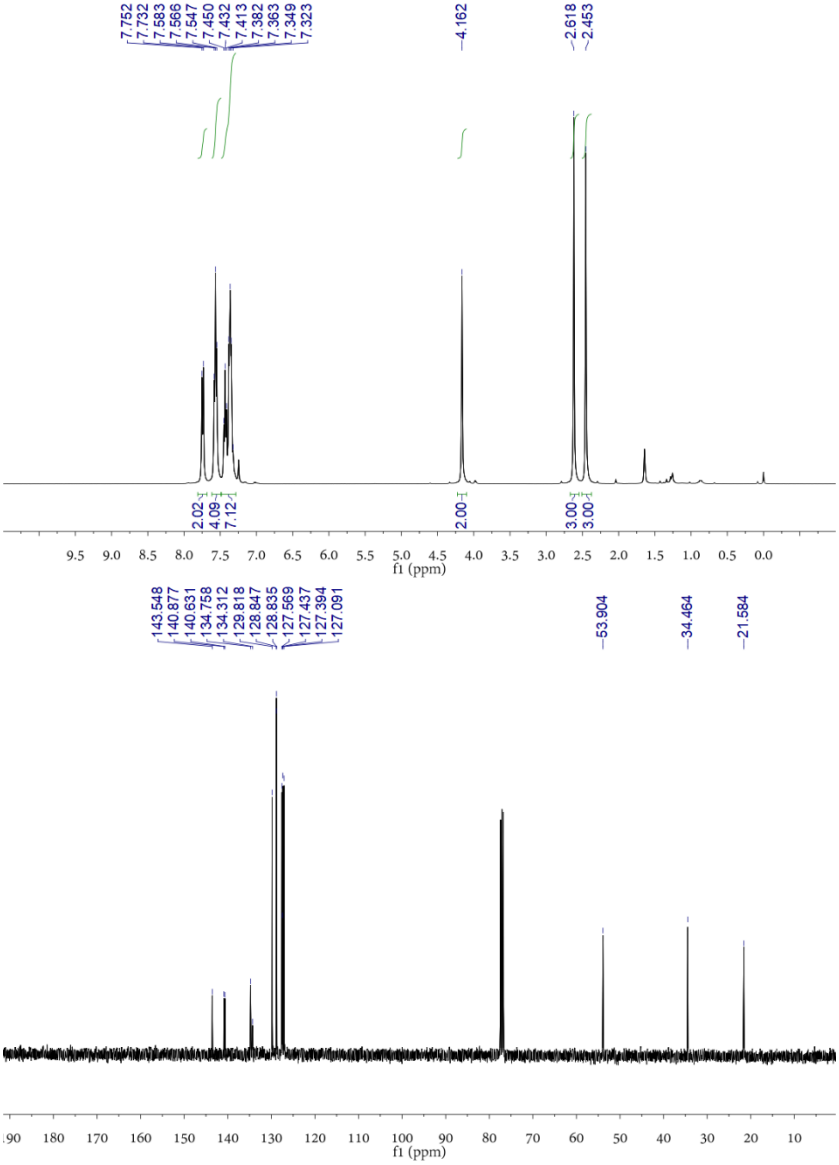


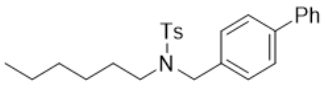
Ethyl 2-(([1,1'-biphenyl]-4-ylmethyl)thio)acetate (40): colorless oil (40.1 mg, 70% yield). ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.29 (t, J = 7.2 Hz, 3H), 3.10 (s, 2H), 3.87 (s, 2H), 4.19 (q, J = 7.2 Hz, 2H), 7.34 (dd, J_1 = J_2 = 7.6 Hz, 1H), 7.39-7.45 (m, 4H), 7.54-7.59 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 14.2, 32.3, 36.0, 61.4, 127.1, 127.31, 127.36, 128.8, 129.6, 136.3, 140.2, 140.7, 170.5. IR ν 3651, 3445, 2982, 2930, 1732, 1486, 1274, 1127, 842 cm^{-1}. HRMS (EI) calcd. for $C_{17}H_{18}O_2S$, ([M]): 286.1028, found: 286.1024.



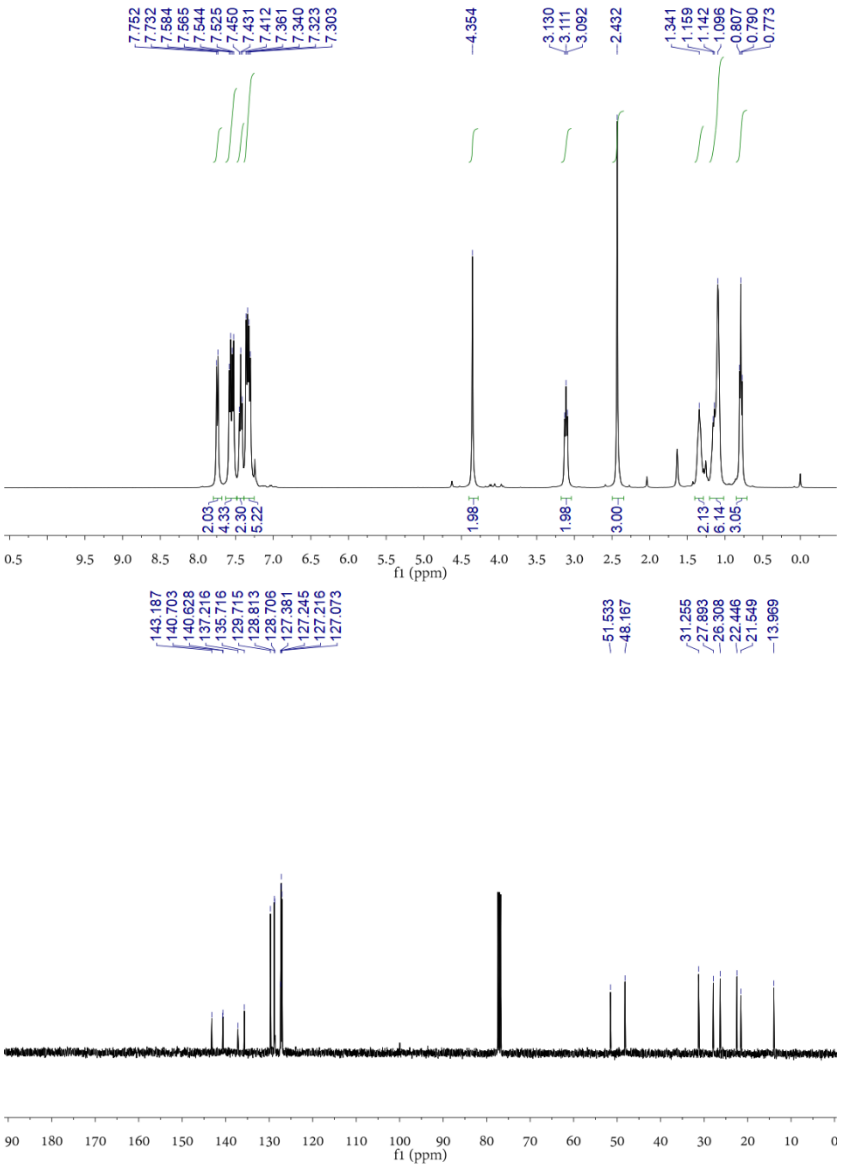


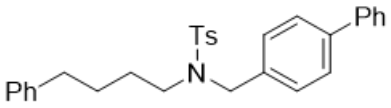
***N*-([1,1'-biphenyl]-4-ylmethyl)-N,4-dimethylbenzenesulfonamide (41):** white solid (44.9 mg, 64% yield). m.p. 154-158 °C ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 2.45 (s, 3H), 2.62 (s, 3H), 4.16 (s, 2H), 7.32-7.45 (m, 7H), 7.54-7.59 (m, 4H), 7.74 (d, J = 8.0Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 21.6, 34.5, 53.9, 127.1, 127.39, 127.44, 127.6, 128.83, 128.84, 129.8, 134.3, 134.8, 140.6, 140.9, 143.6. IR ν 3058, 3031, 2920, 2810, 1452, 1338, 1161, 745 cm^{-1}. HRMS (EI) calcd. for $C_{21}H_{21}NO_2S$, ([M]): 351.1293, found: 351.1288.



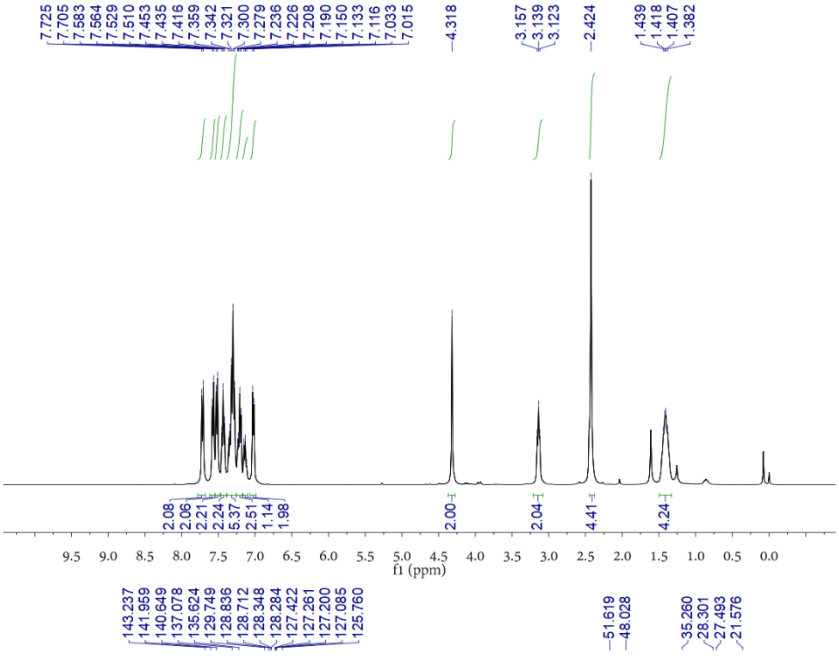


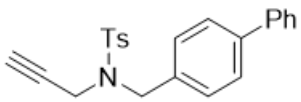
***N*-([1,1'-biphenyl]-4-ylmethyl)-*N*-hexyl-4-methylbenzenesulfonamide (42):** colorless oil (36.2 mg, 43% yield). ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 0.79 (t, *J* = 6.8 Hz, 3H), 1.09-1.16 (m, 6H), 1.30-1.40 (m, 2H), 2.43 (s, 3H), 3.11 (t, *J* = 7.6 Hz, 2H), 4.35 (s, 2H), 7.30-7.37 (m, 5H), 7.43 (dd, J_1 = J_2 = 7.6 Hz, 2H), 7.52-7.59 (m, 4H), 7.74 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 14.0, 21.6, 22.5, 26.3, 27.9, 31.3, 48.2, 51.5, 127.1, 127.2, 127.3, 127.4, 128.7, 128.8, 129.7, 135.7, 137.2, 140.6, 140.7, 143.2. IR ν 3058, 3030, 2955, 2928, 2859, 1339, 1159, 755 cm^{-1}. HRMS (EI) calcd. for $C_{26}H_{31}NO_2S$, ([M]): 421.2075, found: 421.2078.



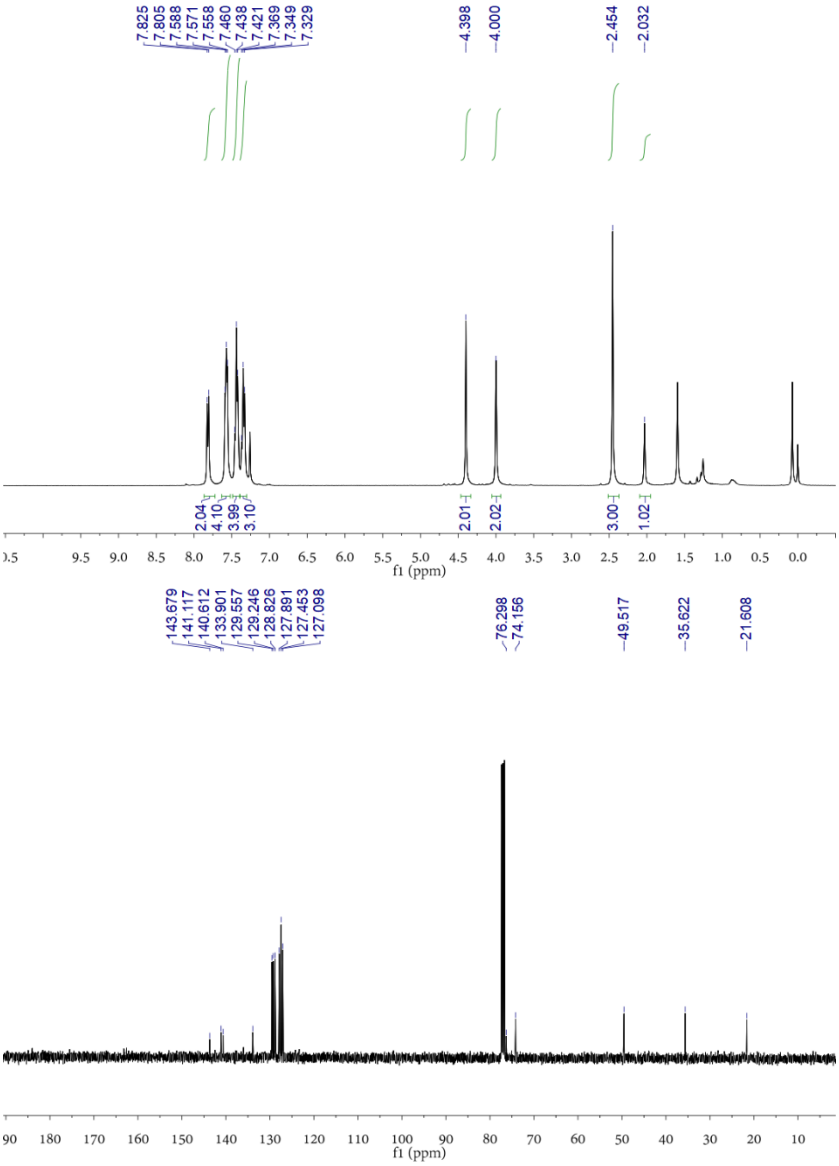


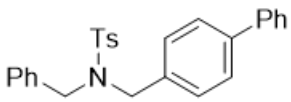
***N*-([1,1'-biphenyl]-4-ylmethyl)-4-methyl-*N*-(4-phenylbutyl)benzenesulfonamide (43): purified by silica gel chromatography (petroleum ether/ethyl acetate 10:1 as the eluent).** White solid (33.7 mg, 36% yield). 91-95 ˚C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.35-1.48 (m, 4H) 2.42-2.46 (m, 5H), 3.14 (t, J = 7.2 Hz, 2H), 4.32 (s, 2H), 7.02 (d, J = 7.2 Hz, 2H), 7.11-7.15 (m, 1H), 7.19-7.24 (m, 2H), 7.27-7.36 (m, 5H), 7.35 (dd, $J_1 = J_2$ = 7.2 Hz, 2H), 7.52 (d, J = 7.2 Hz, 2H), 7.57 (d, J = 7.2 Hz, 2H), 7.72 (d, J = 7.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 21.6, 27.5, 28.3, 35.3, 48.0, 51.6, 125.8, 127.1, 127.2, 127.3, 127.4, 128.3, 128.4, 128.7, 128.8, 129.8, 135.62, 137.0, 140.7, 142.0, 143.2. IR ν 3084, 3029, 2924, 2872, 1600, 1322, 1151, 738 cm^{-1}. HRMS (EI) calcd. for $C_{30}H_{31}NO_2S$, ([M]): 469.2075, found: 469.2068.



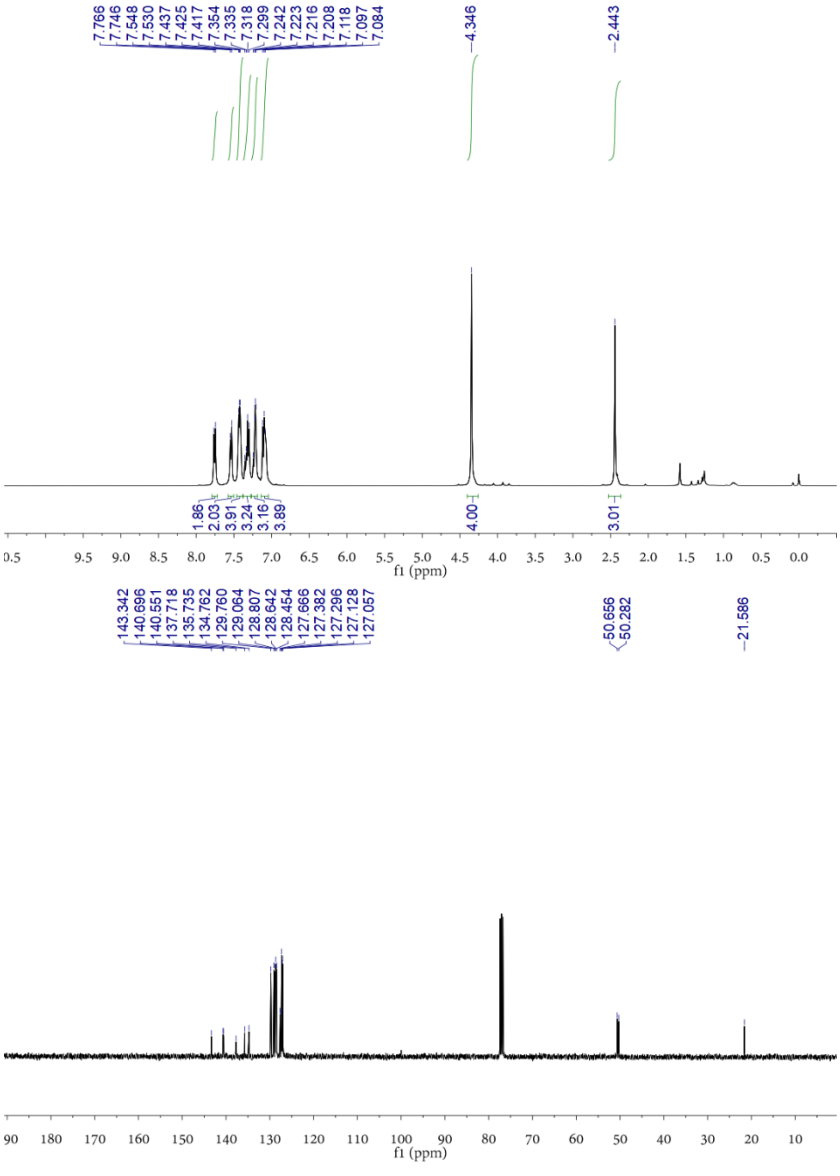


***N*-([1,1'-biphenyl]-4-ylmethyl)-4-methyl-N-(prop-2-yn-1-yl)benzenesulfonamide (44):** white solid (29.2 mg, 39% yield). 113-114 ˚C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 2.03 (s, 1H), 2.45 (s, 3H), 4.00 (s, 2H), 4.40 (s, 2H), 7.35 (dd, $J_1 = J_2 = 8.0$ Hz, 3H), 7.42-7.46 (m, 4H), 7.55-7.59 (m, 4H), 7.82 (d, $J = 8.0$ Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 21.6, 35.6, 49.5, 74.2, 76.3, 127.1, 127.5, 127.9, 128.8, 129.3, 129.6, 133.9, 140.6, 141.1, 143.7. IR ν 3265, 2963, 2913, 2854, 1598, 1339, 1160, 1094 cm^{-1}. HRMS (EI) calcd. for $C_{23}H_{21}NO_2S$, ([M]): 375.1293, found: 375.1292.





***N*-([1,1'-biphenyl]-4-ylmethyl)-N-benzyl-4-methylbenzenesulfonamide (45):** colorless oil (35.0 mg, 41% yield). ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 2.44 (s, 3H), 4.35 (s, 4H), 7.08-7.12 (m, 4H), 7.20-7.22 (m, 3H), 7.29-7.36 (m, 3H), 7.41-7.44 (m, 4H), 7.54 (d, *J* = 7.2 Hz, 2H), 7.76 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 21.6, 50.3, 50.7, 127.06, 127.13, 127.3, 127.4, 127.7, 128.5, 128.6, 128.8, 129.1, 129.8, 134.8, 135.7, 137.7, 140.6, 140.7, 143.3. IR ν 3059, 3029, 2921, 2855, 1490, 1154, 756, 656 cm^{-1}. HRMS (EI) calcd. for $C_{27}H_{25}NO_2S$, ([M]): 427.1606, found: 427.1600.



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