Supporting Information

for

Umpolung of Proton from H_2O: A Metal-free Selective Reduction of Carbonyl Compounds Mediated by Diboron Reagents

Qingqing Xuan[a], Cong Zhao [a] and Qiuling Song[a, *]

[a] Institute of Next Generation Matter Transformation, College of Chemical Engineering at Huaqiao University, Xiamen, Fujian, 361021, P. R. China
Email: qsong@hqu.edu.cn

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I. **General Methods**

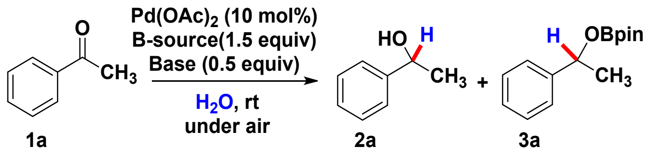
Unless otherwise noted, otherwise noted, all reagents were obtained from commercial suppliers and were used without further purification. ^1H, ^{13}C spectra were recorded in $CDCl_3$ on a Bruker AVIII-500M spectrometers. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard. The following abbreviations were used to designate chemical shift multiplicities: s = singlet, d = doublet, t = triplet, m = multiplet. Column chromatography was performed using silica gel (200-300 mesh).

General Optimization Procedure: To a reaction tube equipped with a stir bar, 76.2 mg of B_2pin_2 (0.3 mmol), 4.5mg $Pd(OAc)_2$ (0.02 mmol) and base (0.02 mmol) were added. Next, 24.0mg (0.2 mmol) of acetophenone (**1a**) and H_2O (2ml) was added via syringe, then sealed the reaction tube. The mixture was stired at 60^{o}C for about 10h. After the reaction was finished, the mixture was extracted with ethyl acetate, repeat three times. The combined organic layer was evaporated under reduced pressure, and the product was purified by column chromatography.

II. **Hydrogenation of Ketones in the Presence of $Pd(OAc)_2$**

The reaction was first carried out with $Pd(OAc)_2$ under N_2, the solvents, bases were also screened (Table 2). Protic solvent, for example ethanol could also offered excellent result (Entry 2). However, aprotic solvent was detrimental to our reaction, only trace amount product was detected by GC-MS (Entry 3). Other bases, such as DIPEA, DBU were also investigated, both of them could afforded satisfied conversions; however the ratio of **2a** and **3a** was affected largely by different bases (Entry 1& 4-5). The influence of Lewic acid was also considered, when $MgSO_4$ was added to our catalytic system, the conversion suffered a little decrement, however the ratio of **2a** and **3a** was affected largrly, that **3a** was changed to the major product.

Table S1 Hydrogenation of Ketones in the Presence of $Pd(OAc)_2$



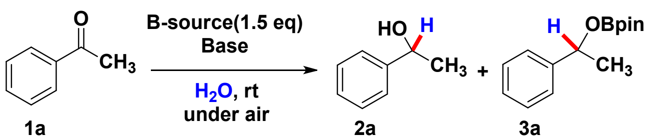
Entry	B-Source	Base	Solvent	Conversion [a]	Ratio of A/B (%) [a]
1	B_2pin_2	Cs_2CO_3	H_2O	quantively	63/37
2	B_2pin_2	Cs_2CO_3	EtOH	quantively	57/43
3	B_2pin_2	Cs_2CO_3	CH_3CN	trace	-
4	B_2pin_2	DIPEA	H_2O	quantively	54/46
5	B_2pin_2	DBU	H_2O	quantively	85/15
6 [b]	B_2pin_2	Cs_2CO_3	H_2O	88%	30/70

[a] Determined by GC-MS. [b] $MgSO_4$(0.5 eq) was added

III. **Hydrogenation of Ketones under Metal-free Conditions**

Under metal-free conditions the kinds of bases and the their amounts was investigated. It showed that stoichiometric bases and diboron compounds were necessary. With stoichiometric diboron compounds, different ambient atmospheres had little effect on the conversion of **1a** (entry 1 vs 2). However, when B_2pin_2 was reduced to 0.5 equiv, the conversion was reduced to 23% (Entry 8). When further reduced the amount of B_2pin_2, the conversion suffered a lot, less than 10% (entry 9).

Table S2 Hydrogenation of Ketones under Metal-free Conditions

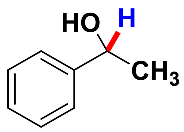


Entry	Base	B-Source	Conversion [b]	Ratio(2a/3a)(%) [b]
1 [c]	Cs_2CO_3 (0.5 equiv)	B_2pin_2	51%	78/22
2	Cs_2CO_3 (0.5 equiv)	B_2pin_2	52%	81/19
3	Cs_2CO_3 (1.0 equiv)	B_2pin_2	78%	80/20
4[d]	Cs_2CO_3 (1.0 equiv)	B_2pin_2	95%	85/15

5[d]	DBU (1.0 equiv)	B_2pin_2	98%	86/14
6[d]	DBU (0.5 equiv)	B_2pin_2	71%	ND[e]
7[d]	DBU (0.2 equiv)	B_2pin_2	25%	ND[e]
8[d]	DBU (1.0 equiv)	B_2pin_2 (0.5 equiv)	23%	ND[e]
9[d,c]	DBU (1.0 equiv)	B_2pin_2 (0.2 equiv)	< 10%	ND[e]

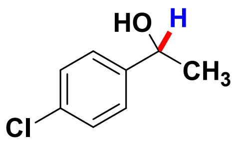
[a] General procedure: **1a** (0.2 mmol), B-source (0.24 mmol), H_2O (2ml), under air. [b] Determined by GC-MS. [c] The reactions were carried out under N_2. [d]The reaction was carried out at 60 °C.[e]Not detected.

IV. Analytic data of products



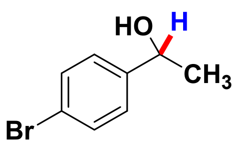
1-phenylethan-1-ol (2a): shallow yellow oil (89% yield, 21.7 mg); ^1H NMR (500 MHz, $CDCl_3$) δ 7.40 (dd, *J* = 9.2, 6.9 Hz, 4H), 7.33 – 7.28 (m, 1H), 4.93 (q, *J* = 6.4 Hz, 1H), 1.94 (s, 1H), 1.53 (d, *J* = 6.5 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.73 (s), 128.52 (s), 127.50 (s), 125.39 (s), 25.04 (s).

Wei, S.; Du, H. *J. Am. Chem. Soc.* **2014**, *136*, 12261.



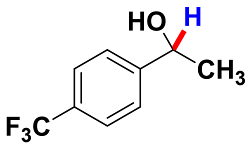
1-(4-chlorophenyl)ethan-1-ol (2b): Shallow yellow liquid (86% yield, 26.8 mg); ^1H NMR (500 MHz, $CDCl_3$) δ 7.35 – 7.30 (m, 4H), 4.88 (q, *J* = 6.4 Hz, 1H), 2.10 (s, 1H), 1.48 (d, *J* = 6.5 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.24 (s), 133.05 (s), 128.60 (s), 126.80 (s), 69.74 (s), 25.27 (s).

Wei, S.; Du, H. *J. Am. Chem. Soc.* **2014**, *136*, 12261.



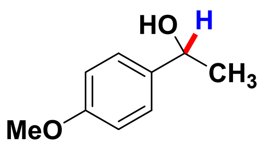
1-(4-bromophenyl)ethan-1-ol (2c): Shallow yellow liquid (85% yield, 34.1 mg) ^1H NMR (500 MHz, $CDCl_3$) δ 7.50 – 7.46 (m, 2H), 7.25 (t, *J* = 5.4 Hz, 2H), 4.87 (q, *J* = 6.4 Hz, 1H), 2.12 (s, 1H), 1.48 (d, *J* = 6.5 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.77 (s), 131.55 (s), 127.16 (s), 121.15 (s), 69.77 (s), 25.25 (s).

Xu, W.; Wu, G.; Yao, W.; Fan, H.; Wu, J.; Chen, P. *Chem. Eur. J.* **2012**, *18*, 13885.



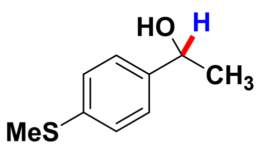
1-(4-(trifluoromethyl)phenyl)ethan-1-ol (2d): Shallow yellow liquid (81%, 30.8 mg) ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62 (d, J = 8.1 Hz, 2H), 7.49 (d, J = 8.0 Hz, 2H), 4.96 (q, J = 6.4 Hz, 1H), 2.32 (s, 1H), 1.51 (d, J = 6.5 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.68 (s), 129.60 (q, J = 32.3 Hz), 125.64 (s), 125.42 (q, J = 3.8 Hz), 124.16 (q, J = 271.9 Hz), 69.79 (s), 25.33 (s).

Gladiali, S.; Alberico, E. *Chem. Soc. Rev.* **2006**, *35*, 226.



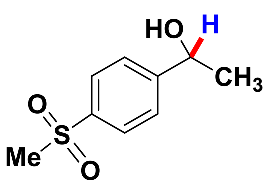
1-(4-methoxyphenyl)ethan-1-ol (2e): Colour less liquid (80% yield, 24.3 mg) ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 – 7.28 (m, 2H), 6.95 – 6.85 (m, 2H), 4.84 (q, J = 6.4 Hz, 1H), 3.81 (s, 3H), 2.32 (s, 1H), 1.48 (d, J = 6.5 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.91 (s), 138.07 (s), 126.68 (s), 113.82 (s), 69.89 (s), 55.29 (s), 25.03 (s).

Xu, W.; Wu, G.; Yao, W.; Fan, H.; Wu, J.; Chen, P. *Chem. Eur. J.* **2012**, *18*, 13885.



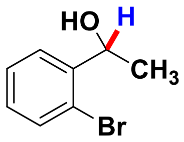
1-(4-(methylthio)phenyl)ethan-1-ol (2f): Shallow yellow liquid (82% yield, 27.6 mg) ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 – 7.29 (m, 2H), 7.28 – 7.24 (m, 2H), 4.87 (q, J = 6.4 Hz, 1H), 2.50 (s, 3H), 2.02 (s, 1H), 1.49 (d, J = 6.5 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.79 (s), 137.41 (s), 126.83 (s), 125.99 (s), 69.99 (s), 25.10 (s), 16.02 (s).

Yu, J.; Jiao, L.; Yang, Y.; Wu, W.; Xue, P.; Chung, L. W.; Dong, X.-Q.; Zhang, X. *Org. Lett.* **2017**, *19*, 690.



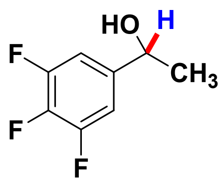
1-(4-(methylsulfonyl)phenyl)ethan-1-ol (2g): White solide (80% yield, 32.0 mg) ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 (d, J = 8.4 Hz, 2H), 7.57 (d, J = 8.2 Hz, 2H), 5.00 (q, J = 6.4 Hz, 1H), 3.05 (s, 3H), 2.45 (s, 1H), 1.51 (d, *J* = 6.5 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.28 (s), 139.15 (s), 127.54 (s), 126.30 (s), 69.53 (s), 44.55 (s), 25.47 (s).

Mahdi, T.; Stephan, D. W. *Angew. Chem., Int. Ed.* **2015**, *54*, 8511.



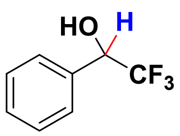
1-(2-bromophenyl)ethan-1-ol (2h): Shallow yellow liquid (83% yield, 33 mg) ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.54 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.36 (dd, *J* = 10.9, 4.2 Hz, 1H), 7.15 (td, *J* = 7.8, 1.7 Hz, 1H), 5.26 (q, *J* = 6.4 Hz, 1H), 2.10 (s, 1H), 1.51 (d, *J* = 6.4 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.64 (s), 132.65 (s), 128.76 (s), 127.85 (s), 126.67 (s), 121.71 (s), 69.18 (s), 23.60 (s).

Vega, E.; Lastra, E.; Gamasa, M. P., *Inorg. Chem*. **2013**, 52, 6193.



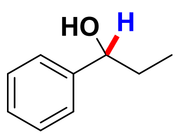
1-(3,4,5-trifluorophenyl)ethan-1-ol (2i): Shallow yellow liquid (79% yield, 27.8 mg) ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.02 (dd, *J* = 7.8, 7.0 Hz, 2H), 4.86 (q, *J* = 6.3 Hz, 1H), 2.00 (s, 1H), 1.48 (d, *J* = 6.5 Hz, 3H). ^{13}C NMR (126 MHz, CDCl3) δ 152.18 (dd, J = 10.0, 3.9 Hz), 150.19 (dd, J = 10.0, 3.8 Hz), 142.09 (d, J = 4.3 Hz), 138.73 (d, J = 250.4 Hz), 109.32 (dd, J = 16.5, 5.0 Hz), 69.06 (s), 25.35 (s).

Brandt, P.; Roth, P.; Andersson, P. G. *J. Org. Chem.* **2004**, *69*, 4885.



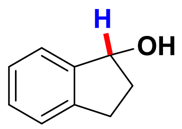
2,2,2-trifluoro-1-phenylethan-1-ol (2j): Shallow yellow liquid (91% yield, 32.0 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 – 7.48 (m, 2H), 7.48 – 7.41 (m, 3H), 5.02 (s, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 134.08 (s), 129.52 (s), 128.61 (s), 127.47 (s), 124.30 (d, *J* = 282.1 Hz), 72.76 (q, *J* = 31.9 Hz).

Gladiali, S.; Alberico, E. *Chem. Soc. Rev.* **2006**, *35*, 226.



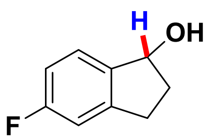
1-phenylpropan-1-ol (2k): Colour less liquid (89% yield, 24.2 mg) ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 – 7.34 (m, 4H), 7.31 (ddd, *J* = 8.4, 5.5, 3.3 Hz, 1H), 4.61 (t, *J* = 6.6 Hz, 1H), 2.01 (s, 1H), 1.88 – 1.81 (m, 1H), 1.81 – 1.74 (m, 1H), 0.94 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.59 (s), 128.41 (s), 127.50 (s), 125.98 (s), 76.04 (s), 31.89 (s), 10.16 (s).

Vega, E.; Lastra, E.; Gamasa, M. P., *Inorg. Chem*. **2013**, 52, 6193.



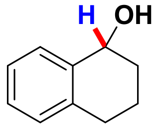
2,3-dihydro-1H-inden-1-ol (2l): Shallow yellow liquid 5-fluoro-2,3-dihydro-1H-inden-1-ol ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 – 7.41 (m, 1H), 7.32 – 7.24 (m, 3H), 5.26 (t, *J* = 6.0 Hz, 1H), 3.08 (ddd, *J* = 15.9, 8.5, 4.8 Hz, 1H), 2.90 – 2.79 (m, 1H), 2.51 (dddd, *J* = 13.2, 8.3, 6.9, 4.8 Hz, 1H), 2.04 (s, 1H), 2.00 – 1.92 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.99 (s), 143.33 (s), 128.32 (s), 126.71 (s), 124.91 (s), 124.21 (s), 76.43 (s), 35.93 (s), 29.81 (s).

Wei, S.; Du, H. *J. Am. Chem. Soc.* **2014**, *136*, 12261.



5-fluoro-2,3-dihydro-1H-inden-1-ol (2m): Shallow yellow liquid (85% yield, 25.8 mg) ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 – 7.33 (m, 1H), 6.94 (dd, *J* = 12.5, 5.7 Hz, 2H), 5.29 – 5.17 (m, 1H), 3.07 (ddd, *J* = 15.7, 8.4, 5.1 Hz, 1H), 2.88 – 2.78 (m, 1H), 2.53 (dddd, *J* = 13.4, 8.4, 6.8, 5.1 Hz, 1H), 2.00 (dddd, *J* = 13.4, 8.5, 6.3, 5.0 Hz, 1H), 1.84 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.26 (d, *J* = 245.3 Hz), 145.77 (d, *J* = 8.5 Hz), 140.63 (s), 125.45 (d, *J* = 9.2 Hz), 113.82 (d, *J* = 22.8 Hz), 111.73 (d, *J* = 22.0 Hz), 75.65 (s), 36.36 (s), 29.86 (d, *J* = 2.1 Hz).

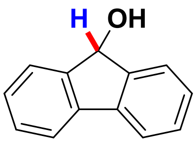
Adcock, W.; Gupta, B. D.; Kitching, W.; Doddrell, D. *J. Organomet. Chem.* **1975**, *102*, 297.



1,2,3,4-tetrahydronaphthalen-1-ol (2n): Shallow yellow liquid (78% yield, 23.2 mg) ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 (dd, *J* = 5.8, 3.2 Hz, 1H), 7.28 – 7.20 (m, 2H), 7.18 – 7.09 (m, 1H), 4.80 (d, *J* = 4.4 Hz, 1H), 2.86 (dt, *J* = 16.4, 5.3 Hz, 1H), 2.75 (dt, *J* = 16.6, 6.8 Hz, 1H), 2.06 – 1.97 (m, 2H), 1.94 (ddd, *J* = 4.9, 4.4, 3.5 Hz, 1H), 1.87 (s, 1H), 1.85 – 1.78 (m, 1H). ^{13}C NMR (126

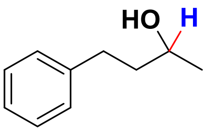
MHz, $CDCl_3$) δ 138.80 (s), 137.13 (s), 129.02 (s), 128.67 (s), 127.59 (s), 126.18 (s), 68.16 (s), 32.28 (s), 29.26 (s), 18.81 (s).

Gladiali, S.; Alberico, E. *Chem. Soc. Rev.* **2006**, *35*, 226.



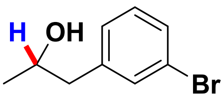
9H-fluoren-9-ol (2o): White solide (65% yield, 23.7 mg) ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66 (t, J = 7.3 Hz, 4H), 7.42 (t, J = 7.5 Hz, 2H), 7.38 – 7.31 (m, 2H), 5.59 (d, J = 6.7 Hz, 1H), 1.99 (d, J = 8.4 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.64 (s), 140.00 (s), 129.08 (s), 127.82 (s), 125.14 (s), 119.98 (s), 75.24 (s).

Kuroda, Y.; Harada, S.; Oonishi, A.; Kiyama, H.; Yamaoka, Y.; Yamada, K.-i.; Takasu, K. *Angew. Chem., Int. Ed.* **2016**, *55*, 13137.



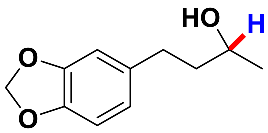
4-phenylbutan-2-ol (2p): Colour less liquid (82% yield, 24.6 mg) ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 (t, J = 7.5 Hz, 2H), 7.22 (dd, J = 12.3, 7.2 Hz, 3H), 3.86 (dq, J = 12.4, 6.2 Hz, 1H), 2.84 – 2.75 (m, 1H), 2.70 (ddd, J = 13.8, 9.2, 7.1 Hz, 1H), 1.86 – 1.76 (m, 2H), 1.64 – 1.49 (m, 1H), 1.26 (d, J = 6.2 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.07 (s), 128.41 (s), 125.83 (s), 67.54 (s), 40.86 (s), 32.16 (s), 23.64 (s).

Mahdi, T.; Stephan, D. W. *J. Am. Chem. Soc.* **2014**, *136*, 15809.



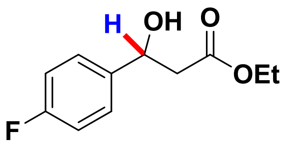
1-(3-bromophenyl)propan-2-ol (2q): Shallow yellow liquid (84% yield, 35.9 mg) ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 (d, J = 7.7 Hz, 2H), 7.19 (dt, J = 15.8, 4.1 Hz, 2H), 4.04 (dq, J = 12.4, 6.1 Hz, 1H), 2.77 (dd, J = 13.6, 4.8 Hz, 1H), 2.69 (dd, J = 13.6, 7.9 Hz, 1H), 1.66 (s, 1H), 1.27 (d, J = 6.2 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 140.97 (s), 132.39 (s), 130.04 (s), 129.59 (s), 128.07 (s), 122.57 (s), 68.68 (s), 45.28 (s), 22.93 (s).

Hu, X.; Zhang, G.; Bu, F.; Lei, A. *ACS Catal.* **2017**, *7*, 1432.



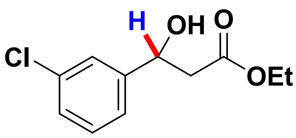
4-(benzo[d][1,3]dioxol-5-yl)butan-2-ol (2r): Shallow yellow liquid (87% yield, 34.6 mg) ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.77 – 6.70 (m, 2H), 6.67 (d, J = 7.9 Hz, 1H), 5.94 (s, 2H), 3.83 (dq, J = 12.4, 6.2 Hz, 1H), 2.73 – 2.59 (m, 2H), 1.80 – 1.72 (m, 2H), 1.24 (d, J = 6.2 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.58 (s), 145.59 (s), 135.88 (s), 121.06 (s), 108.87 (s), 108.17 (s), 100.76 (s), 67.40 (s), 41.06 (s), 31.88 (s), 23.66 (s).

Yi, J.; Lu, X.; Sun, Y.-Y.; Xiao, B.; Liu, L. *Angew. Chem., Int. Ed.* **2013**, *52*, 12409.



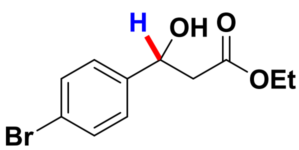
ethyl 3-(4-fluorophenyl)-3-hydroxypropanoate (2s): Shallow yellow liquid (85% yield, 36.0 mg) ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 – 7.31 (m, 2H), 7.11 – 6.96 (m, 2H), 5.13 (dd, J = 5.5, 3.2 Hz, 1H), 4.20 (q, J = 7.1 Hz, 2H), 3.42 (d, J = 3.0 Hz, 1H), 2.72 (qd, J = 16.4, 6.4 Hz, 2H), 1.28 (t, J = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.33 (s), 162.28 (d, J = 245.8 Hz), 138.28 (s), 127.38 (d, J = 8.1 Hz), 115.37 (d, J = 21.5 Hz), 69.69 (s), 60.97 (s), 43.33 (s), 14.14 (s).

Ariger, M. A.; Carreira, E. M. *Org. Lett.* **2012**, *14*, 4522.



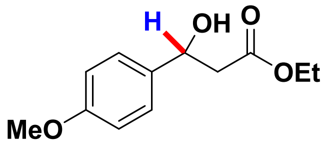
ethyl 3-(3-chlorophenyl)-3-hydroxypropanoate (2t): Shallow yellow liquid (85% yield, 37.8 mg) ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 (d, J = 1.6 Hz, 1H), 7.32 – 7.24 (m, 3H), 5.17 – 5.05 (m, 1H), 4.20 (q, J = 7.1 Hz, 2H), 3.53 (d, J = 3.2 Hz, 1H), 2.75 – 2.69 (m, 2H), 1.28 (t, J = 7.2 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.22 (s), 144.58 (s), 134.45 (s), 129.82 (s), 127.88 (s), 125.95 (s), 123.81 (s), 69.65 (s), 61.04 (s), 43.18 (s), 14.14 (s).

Niu, Z.; Chen, J.; Chen, Z.; Ma, M.; Song, C.; Ma, Y. *J. Org. Chem.* **2015**, *80*, 602.



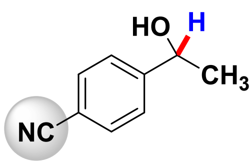
ethyl 3-(4-bromophenyl)-3-hydroxypropanoate(2u): Shallow yellow liquid (81% yield, 44.1 mg) ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52 – 7.48 (m, 2H), 7.28 (d, J = 8.1 Hz, 2H), 5.14 – 5.07 (m, 1H), 4.20 (q, J = 7.1 Hz, 2H), 3.44 (d, J = 2.6 Hz, 1H), 2.71 (dd, J = 6.4, 3.0 Hz, 2H), 1.29 (t, J = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.25 (s), 141.51 (s), 131.63 (s), 127.43 (s), 121.59 (s), 69.67 (s), 61.03 (s), 43.14 (s), 14.15 (s).

Ariger, M. A.; Carreira, E. M. *Org. Lett.* **2012**, *14*, 4522



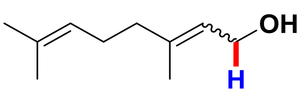
ethyl 3-hydroxy-3-(4-methoxyphenyl)propanoate (2v): Shallow yellow liquid (79% yield, 35.4 mg) ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 – 7.29 (m, 2H), 6.98 – 6.85 (m, 2H), 5.10 (d, J = 9.1 Hz, 1H), 4.19 (q, J = 7.1 Hz, 2H), 3.82 (s, 3H), 3.28 (d, J = 2.4 Hz, 1H), 2.77 (dd, J = 16.2, 9.3 Hz, 1H), 2.69 (dd, J = 16.2, 3.7 Hz, 1H), 1.28 (t, J = 7.1 Hz, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.44 (s), 159.18 (s), 134.73 (s), 126.98 (s), 113.90 (s), 69.97 (s), 60.85 (s), 55.29 (s), 43.35 (s), 14.16 (s).

Ariger, M. A.; Carreira, E. M. *Org. Lett.* **2012**, *14*, 4522



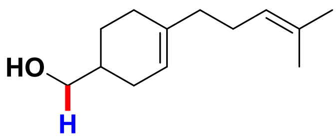
4-(1-hydroxyethyl)benzonitrile (2w): Shallow yellow liquid (89% yield, 26.2 mg) ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66 (d, J = 8.4 Hz, 2H), 7.51 (d, J = 8.1 Hz, 2H), 4.99 (q, J = 6.5 Hz, 1H), 1.52 (d, J = 6.5 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 151.04 (s), 132.37 (s), 126.06 (s), 118.86 (s), 111.13 (s), 69.70 (s), 25.44 (s).

Kallmeier, F.; Irrgang, T.; Dietel, T.; Kempe, R. *Angew. Chem., Int. Ed.* **2016**, *55*, 11806.



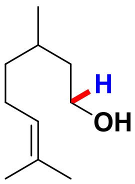
Geraniol (2x): Shallow yellow liquid (74% yield, 22.8mg) ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.44 (ddd, J = 10.5, 8.1, 4.2 Hz, 1H), 5.16 – 5.09 (m, 1H), 4.14 (dd, J = 31.5, 7.0 Hz, 2H), 2.15 – 2.03 (m, 4H), 1.77 – 1.69 (m, 6H), 1.62 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.97 (s), 139.76 (s), 132.45 (s), 131.74 (s), 124.40 (s), 123.85 (d, J = 8.9 Hz), 123.31 (s), 59.39 (s), 58.97 (s), 39.54 (s), 31.96 (s), 26.45 (d, J = 17.5 Hz), 25.67 (d, J = 2.4 Hz), 23.42 (s), 17.67 (d, J = 3.8 Hz), 16.27 (s).

C. Milone, M. L. Tropeano, G. Gulino, G. Neri, R. Ingoglia and S. Galvagno, *Chem. Commun.*, **2002**, 868.



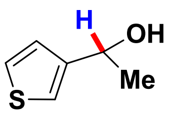
myrac alcohol (2y): Shallow yellow liquid (78% yield, 24.3 mg) ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.45 – 5.38 (m, 1H), 5.12 (dddd, J = 7.0, 5.6, 2.7, 1.3 Hz, 1H), 3.62 – 3.51 (m, 2H), 2.13 – 1.96 (m, 7H), 1.89 – 1.71 (m, 4H), 1.70 (d, J = 0.9 Hz, 3H), 1.62 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 137.81 (s), 131.39 (s), 124.34 (s), 119.44 (s), 67.86 (s), 37.71 (s), 36.36 (s), 28.22 (s), 27.80 (s), 26.47 (s), 25.72 (s), 25.66 (s), 17.70 (s).

Mimoun, H. *J. Org. Chem.* **1999**, *64*, 2582.



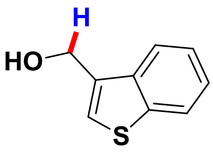
Citronellol (2z): Shallow yellow liquid (79% yield, 30.7mg) ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.12 (tdd, J = 5.8, 2.8, 1.4 Hz, 1H), 3.77 – 3.64 (m, 2H), 2.01 (td, J = 15.8, 7.1 Hz, 2H), 1.70 (d, J = 1.0 Hz, 3H), 1.66 (dd, J = 7.3, 5.6 Hz, 1H), 1.63 (d, J = 3.7 Hz, 3H), 1.60 – 1.55 (m, 1H), 1.45 – 1.39 (m, 1H), 1.39 – 1.32 (m, 2H), 0.93 (d, J = 6.6 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 131.29 (s), 124.70 (s), 61.23 (s), 39.91 (s), 37.21 (s), 29.16 (s), 25.73 (s), 25.46 (s), 19.53 (s), 17.66 (s).

Hua, Y.; Guo, Z.; Han, H.; Wei, X. *Organometallics* **2017**, *36*, 877.



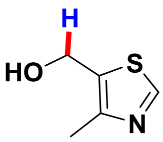
1-(thiophen-3-yl)ethan-1-ol (2aa): Shallow yellow liquid (89% yield, 22.8mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.27 (dd, J = 4.9, 1.3 Hz, 1H), 7.03 – 6.98 (m, 2H), 5.20 – 5.12 (m, 1H), 2.02 (d, J = 4.2 Hz, 1H), 1.63 (d, J = 6.4 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.85 (s), 126.67 (s), 124.46 (s), 123.20 (s), 66.29 (s), 25.28 (s).

Polshettiwar, V.; Varma, R. S. *Green Chem.* **2009**, *11*, 1313.



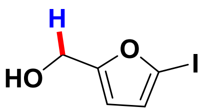
benzo[b]thiophen-3-ylmethanol (2ab): Shallow yellow liquid (85% yield, 27.9 mg); [1]H NMR (500 MHz, $CDCl_3$) δ 7.89 (ddd, J = 5.8, 5.4, 1.5 Hz, 2H), 7.45 – 7.38 (m, 3H), 4.96 (d, J = 0.6 Hz, 2H), 1.90 (s, 1H). [13]C NMR (126 MHz, $CDCl_3$) δ 140.81 (s), 137.67 (s), 135.97 (s), 124.60 (s), 124.23 (s), 123.86 (s), 122.90 (s), 121.95 (s), 59.85 (s).

Huang, H.-M.; Procter, D. J. *J. Am. Chem. Soc.* **2017**, *139*, 1661.



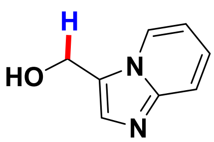
(4-methylthiazol-5-yl)methanol (2ac): Shallow yellow liquid (79% yield, 20.4 mg); [1]H NMR (500 MHz, $CDCl_3$) δ 8.67 (s, 1H), 4.85 (s, 2H), 2.46 (s, 3H), 2.29 (s, 1H). [13]C NMR (126 MHz, $CDCl_3$) δ 151.20 (s), 149.89 (s), 130.96 (s), 56.69 (s), 14.95 (s).

Russell, M. G. N.; Carling, R. W.; Atack, J. R.; Bromidge, F. A.; Cook, S. M.; Hunt, P.; Isted, C.; Lucas, M.; McKernan, R. M.; Mitchinson, A.; Moore, K. W.; Narquizian, R.; Macaulay, A. J.; Thomas, D.; Thompson, S.-A.; Wafford, K. A.; Castro, J. L. *J. Med. Chem.* **2005**, *48*, 1367.



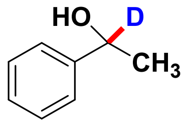
(5-iodofuran-2-yl)methanol (2ad): Shallow yellow liquid (87% yield, 38.9 mg); [1]H NMR (500 MHz, $CDCl_3$) δ 6.52 (d, J = 3.2 Hz, 1H), 6.25 (d, J = 3.2 Hz, 1H), 4.63 (s, 2H), 1.90 (s, 1H). [13]C NMR (126 MHz, $CDCl_3$) δ 159.53 (s), 120.95 (s), 110.87 (s), 87.85 (s), 57.26 (s).

CAS: 773868-46-5



imidazo[1,2-a]pyridin-3-ylmethanol (2ae): light brown solid (78% yield, 23.1 mg). [1]H NMR (500 MHz, $CDCl_3$) δ 8.11 – 8.03 (m, 1H), 7.56 (d, J = 9.0 Hz, 2H), 7.16 (ddd, J = 9.3, 6.8, 1.2 Hz, 1H), 6.77 (dt, J = 7.6, 3.8 Hz, 1H), 4.86 (s, 2H). [13]C NMR (126 MHz, $CDCl_3$) δ 146.88 (s), 145.31 (s), 125.74 (s), 124.80 (s), 117.24 (s), 112.36 (s), 109.56 (s), 58.50 (s).

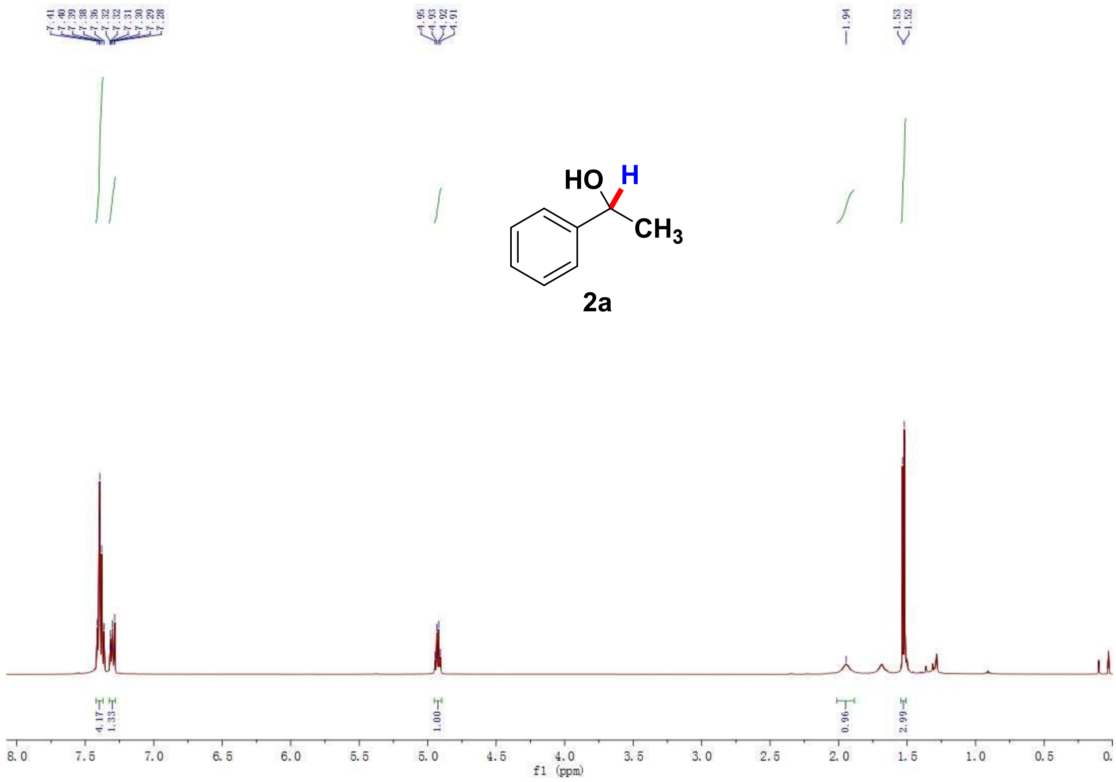
Chandra Mohan, D.; Nageswara Rao, S.; Adimurthy, S. *J. Org. Chem.* **2013**, *78*, 1266.

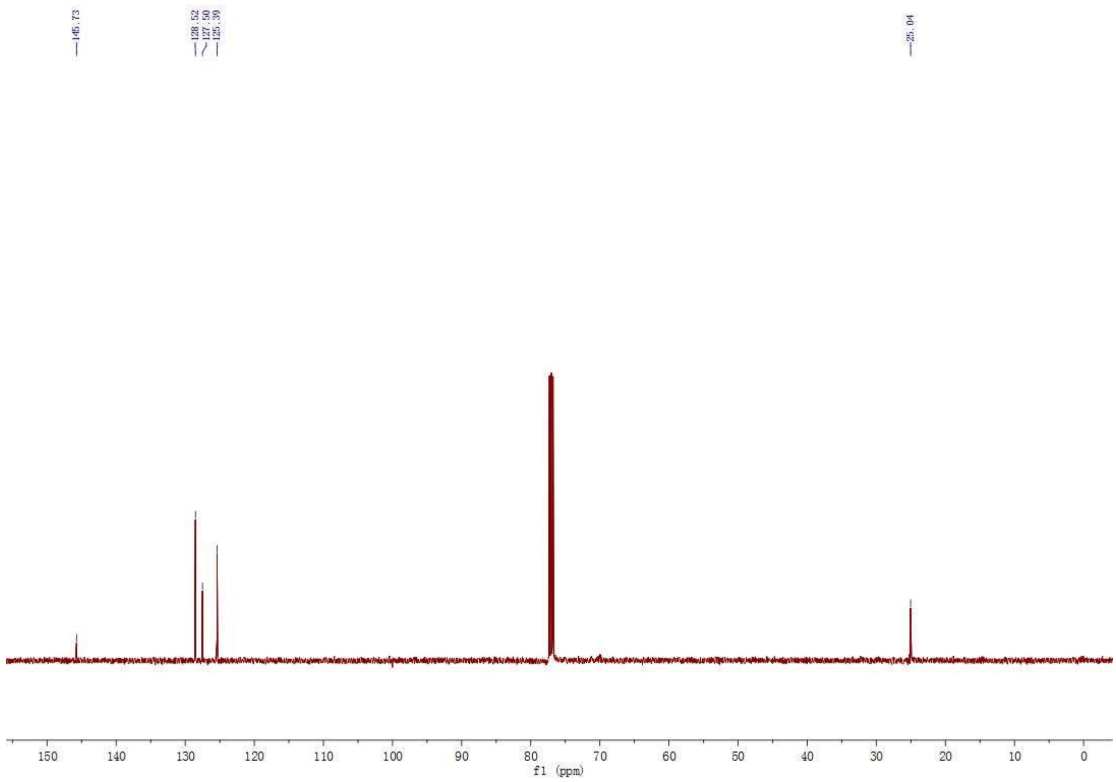


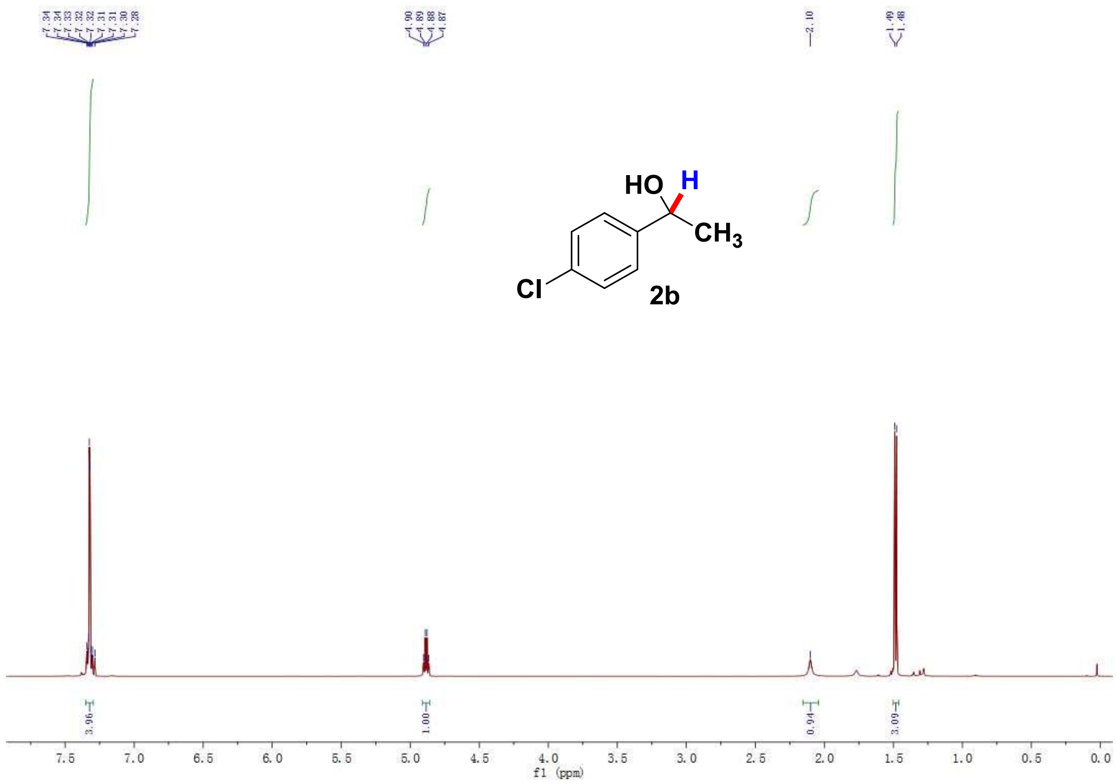
1-phenylethan-1-d-1-ol (4) shallow yellow oil (90% yield, 22.1 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 (dd, *J* = 9.4, 7.0 Hz, 4H), 7.31 (d, *J* = 6.9 Hz, 1H), 1.89 (s, 1H), 1.52 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.73 (s), 128.52 (s), 127.50 (s), 125.39 (s), 25.04 (s).

Li, C.; Zhang, Y.; Sun, Q.; Gu, T.; Peng, H.; Tang, W. *J. Am. Chem. Soc.* **2016**, *138*, 10774.

V. ^{1}H and ^{13}C NMR spectra of products



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7.32
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7.31
7.31
7.30
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4.90
4.89
4.88
4.87
2.10
1.49
1.48
HO
H
CH_3
Cl
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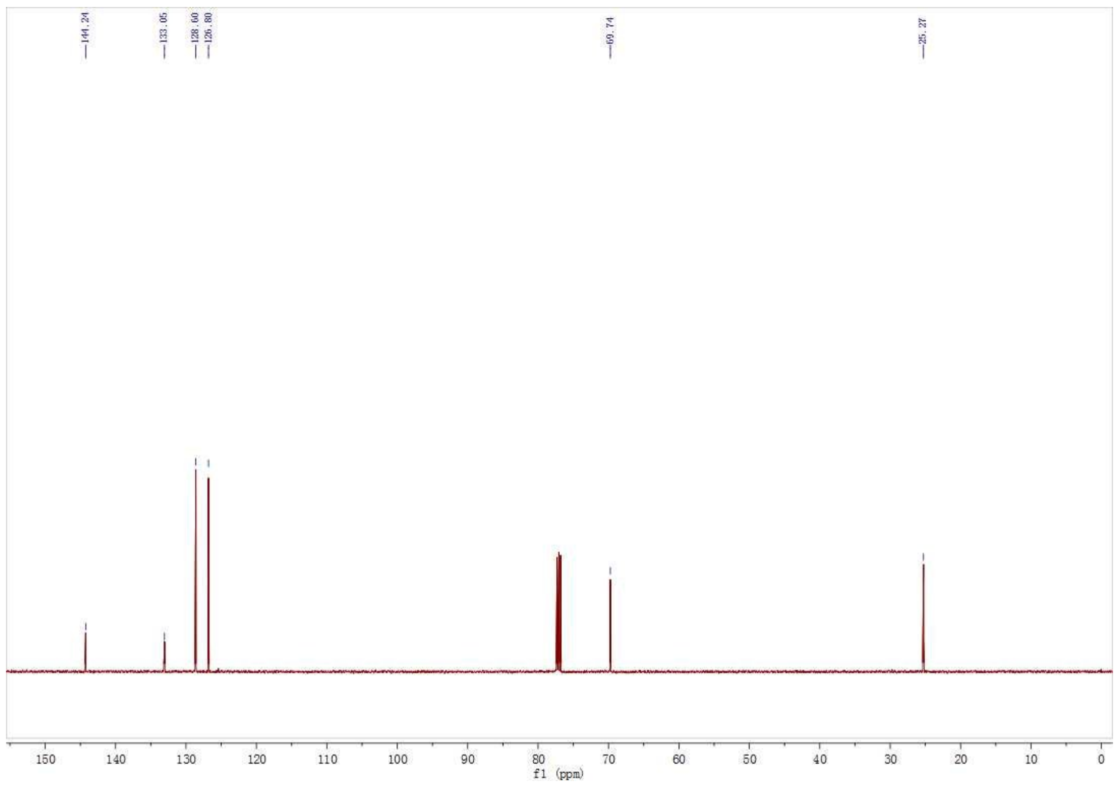
1.00
0.94
3.09
f1 (ppm)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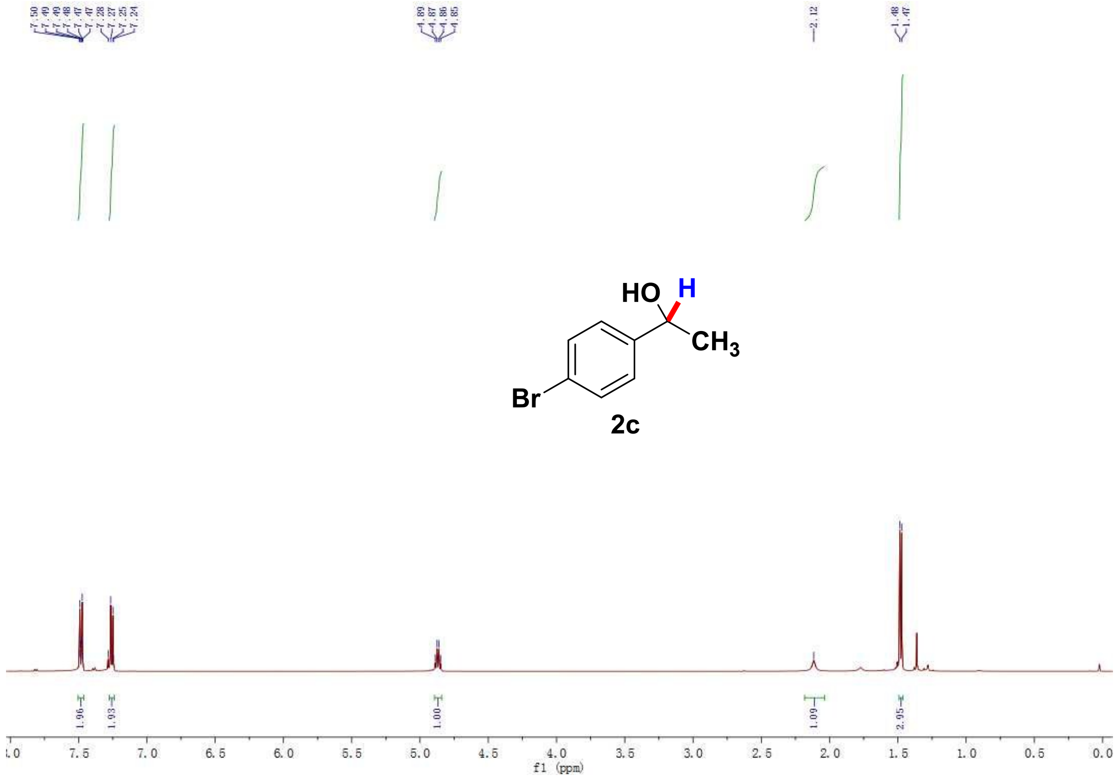
126.80
69.74
25.27
f1 (ppm)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4.89 4.87 4.86 4.85
2.12
1.48 1.47
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Br
2c
1.96
1.93
1.00
1.09
2.95
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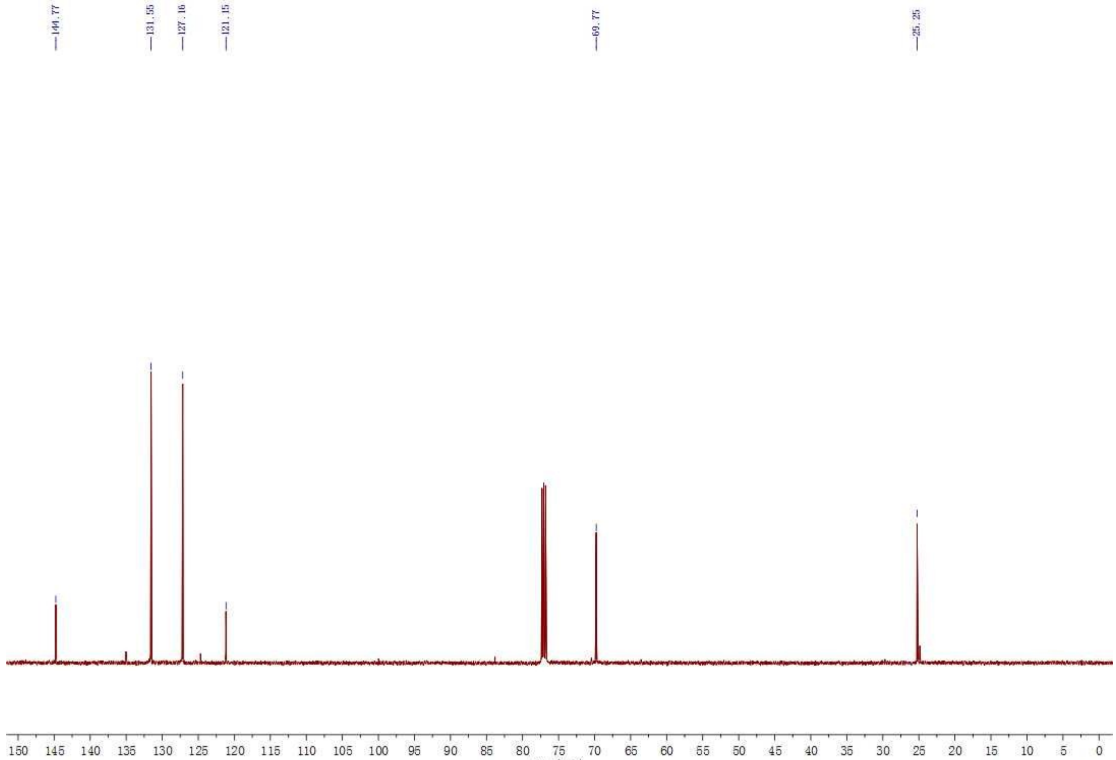
f1 (ppm)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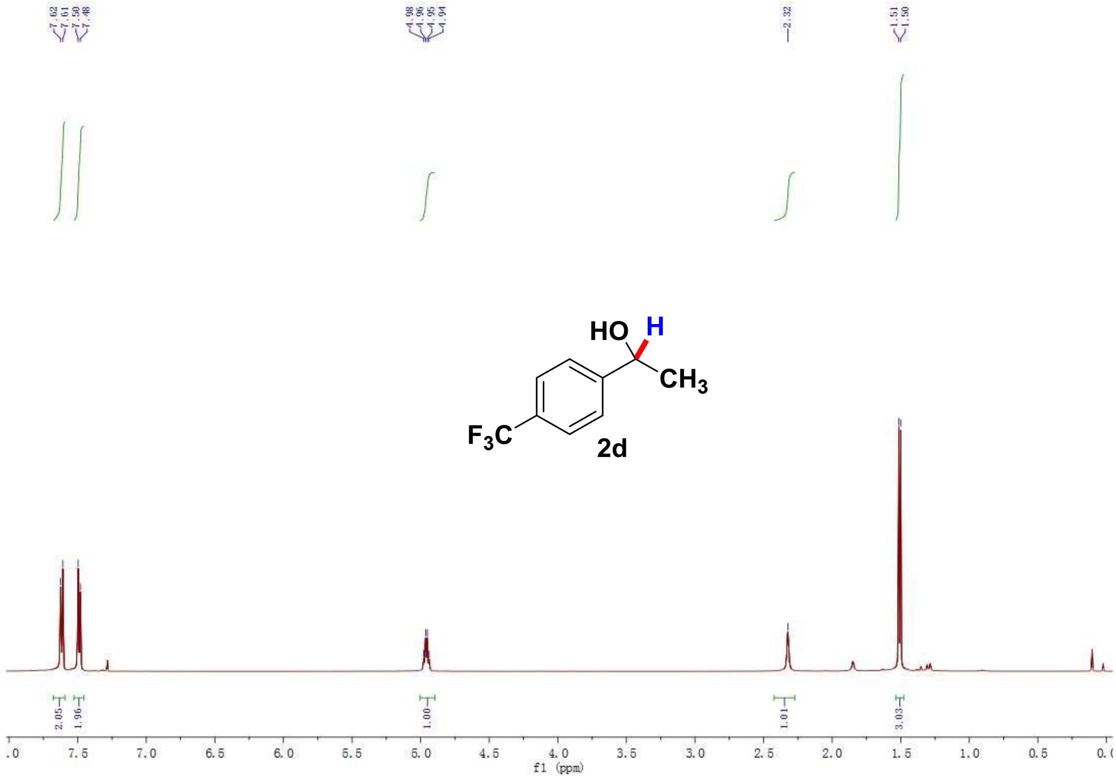
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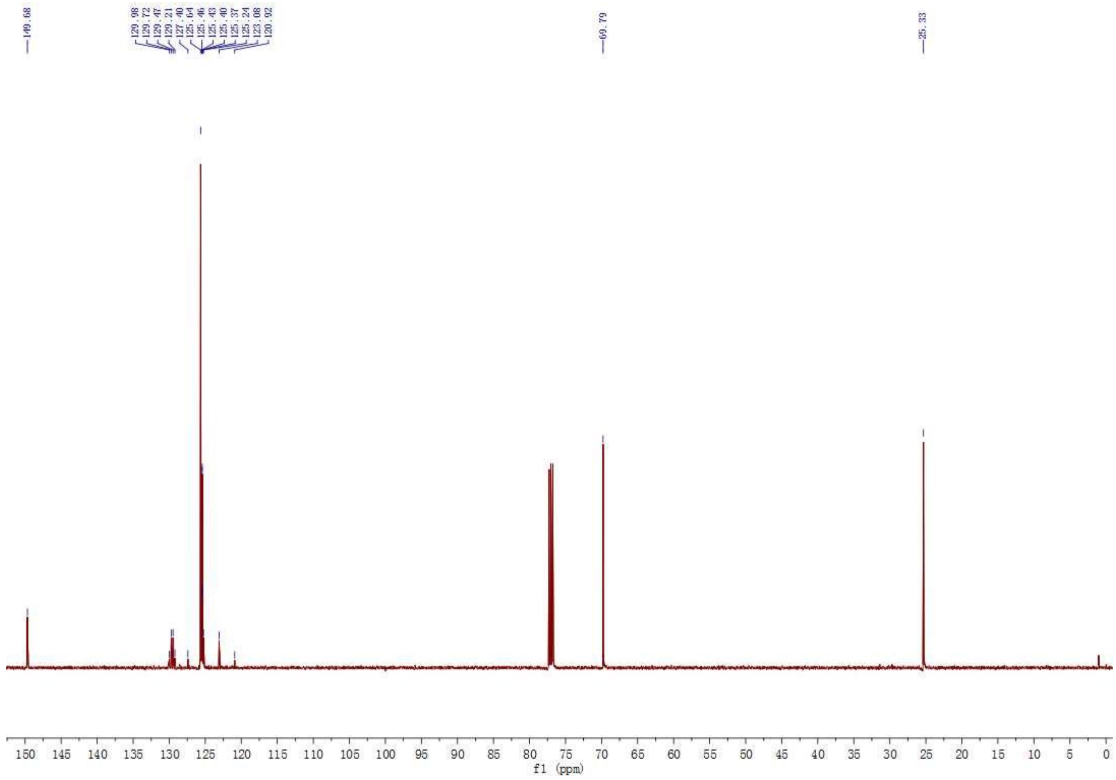
3.03
f1 (ppm)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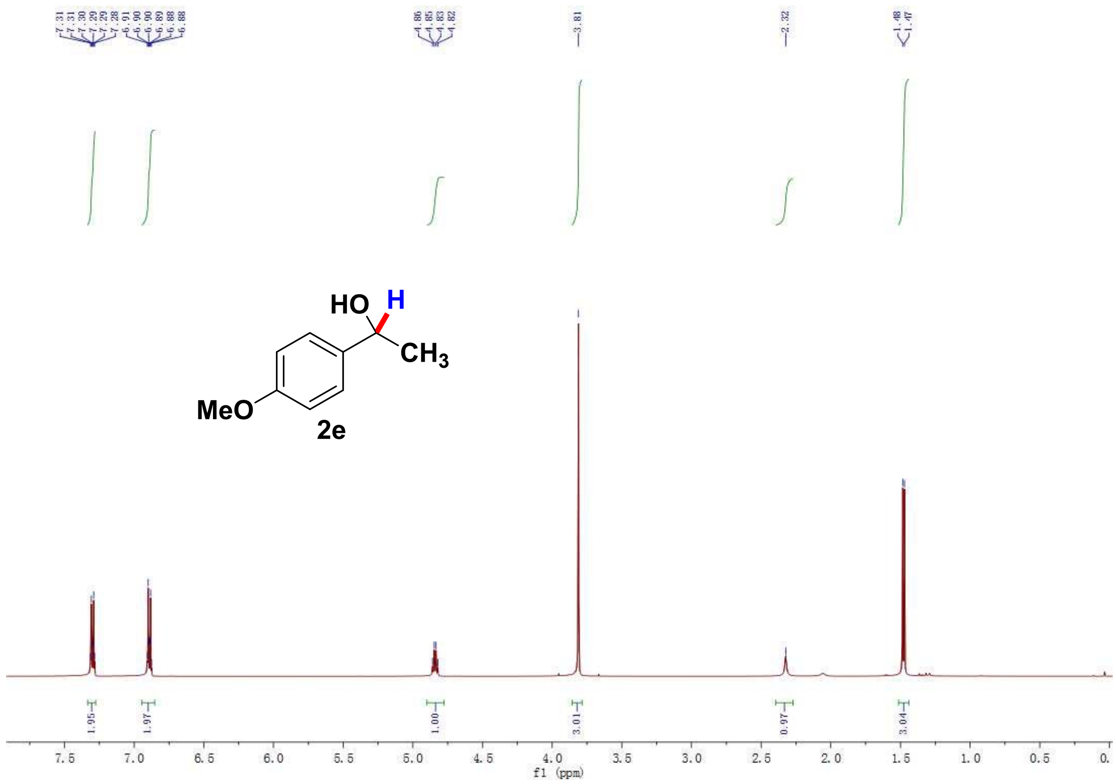
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3.81
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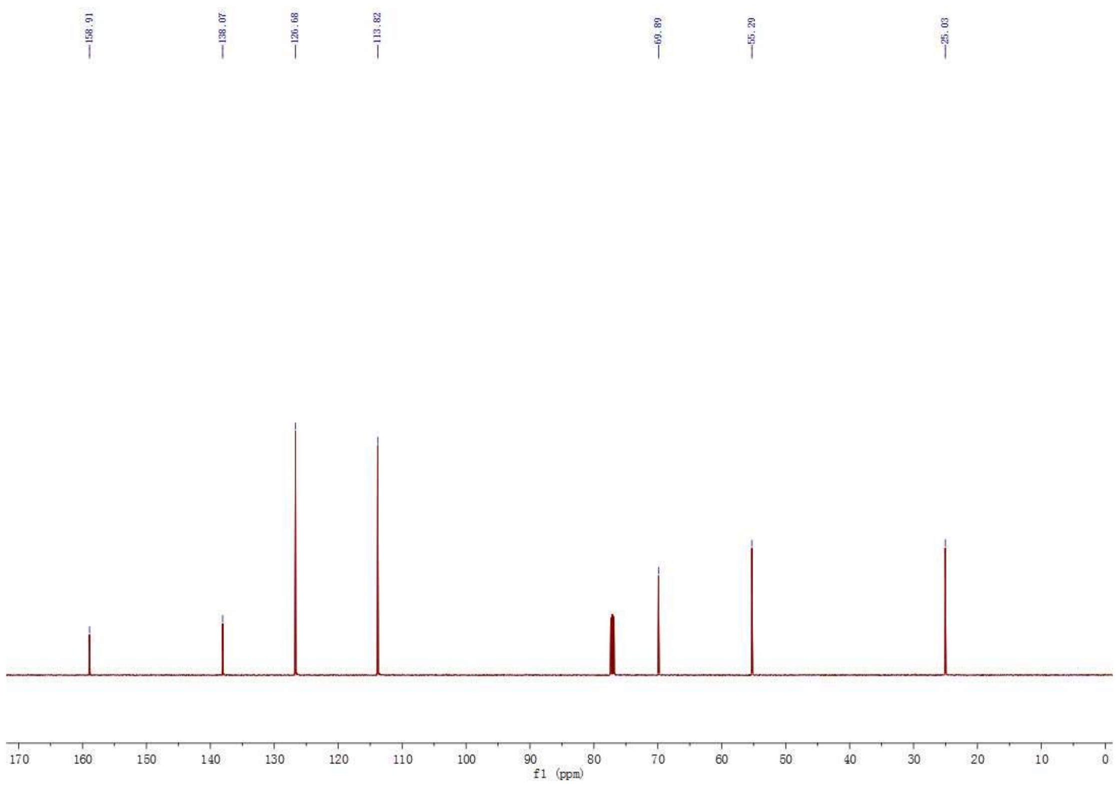
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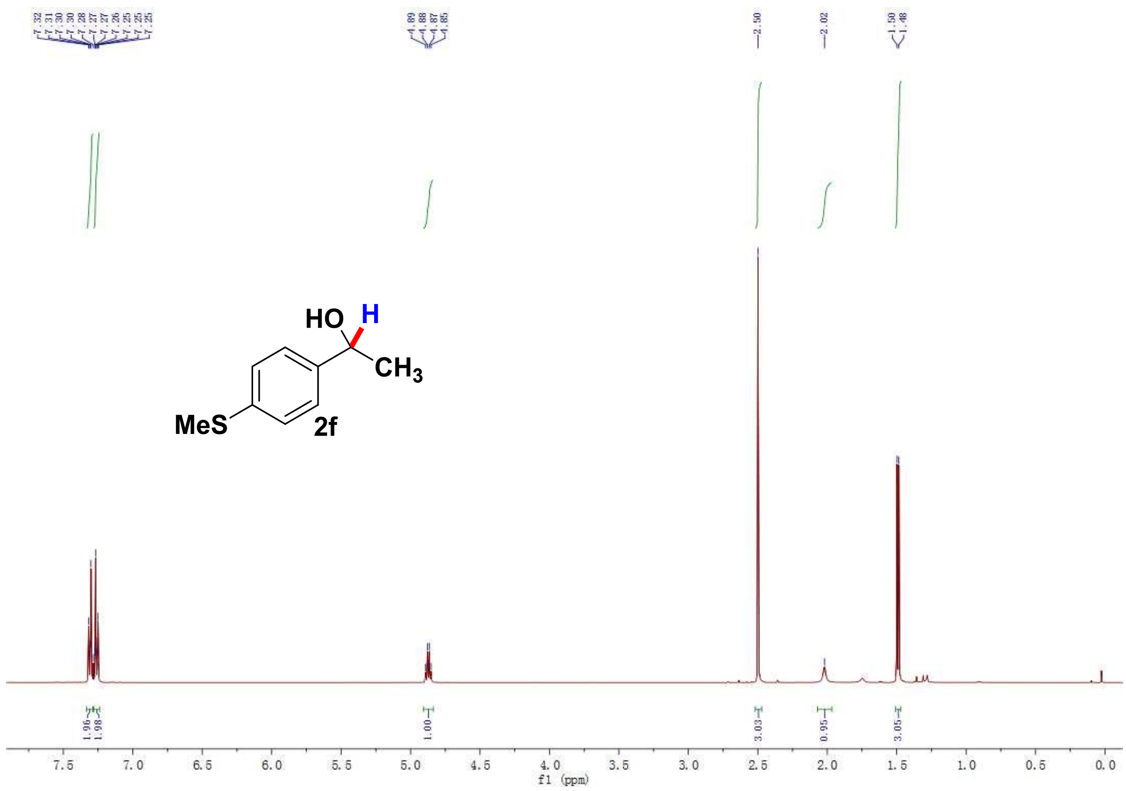
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4.89 4.88 4.87 4.85
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2.02
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MeS
2f
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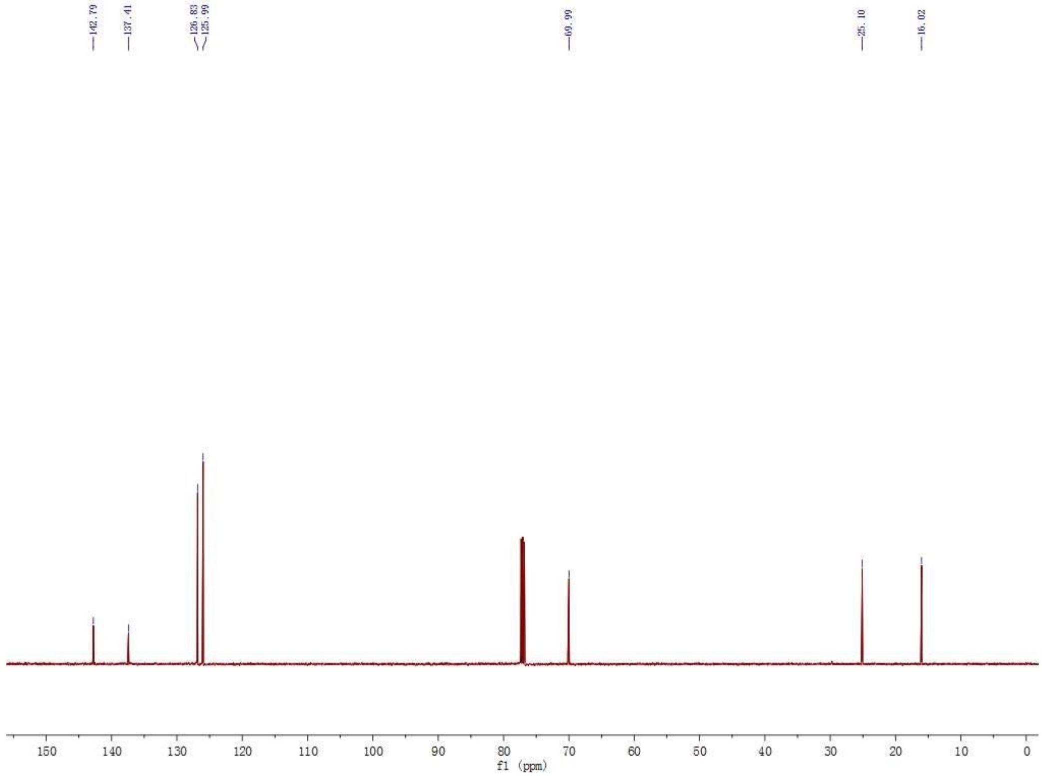
1.00
3.03
0.95
3.05
f1 (ppm)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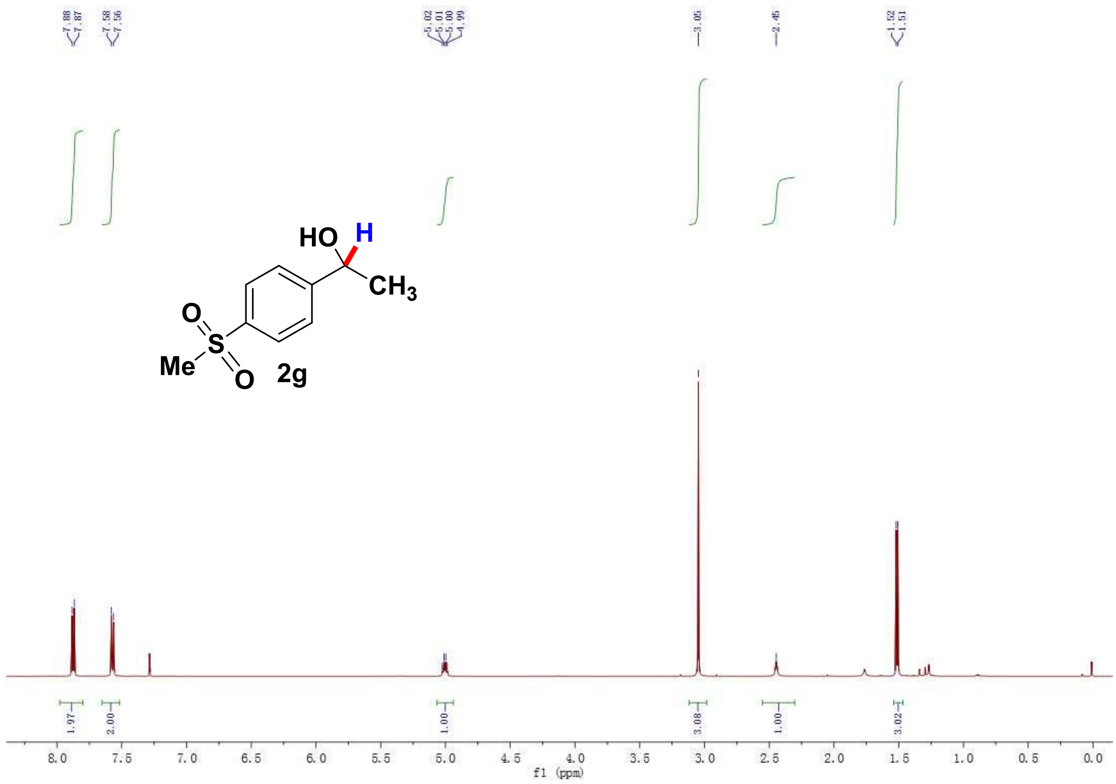
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1.52
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H
CH3
O
S
Me
O
2g
1.97
2.00
1.00
3.08
1.00
3.02
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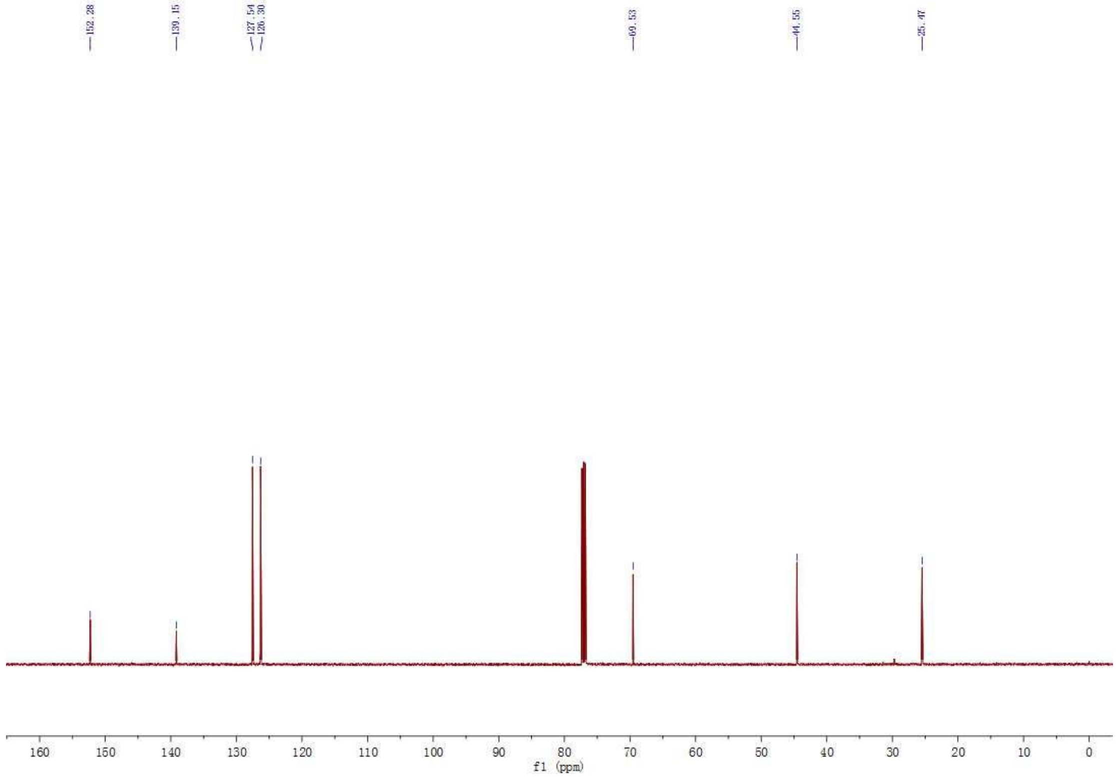
f1 (ppm)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44.55
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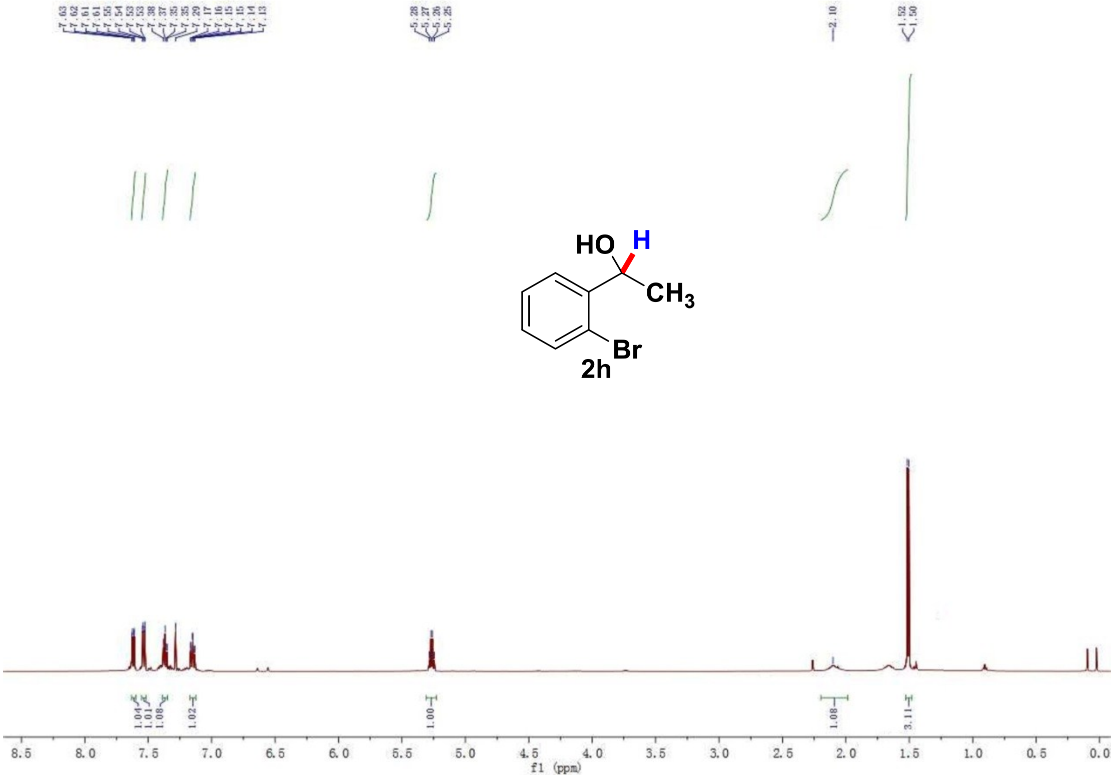
f1 (ppm)



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Br
2h
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1.00
1.08
3.11
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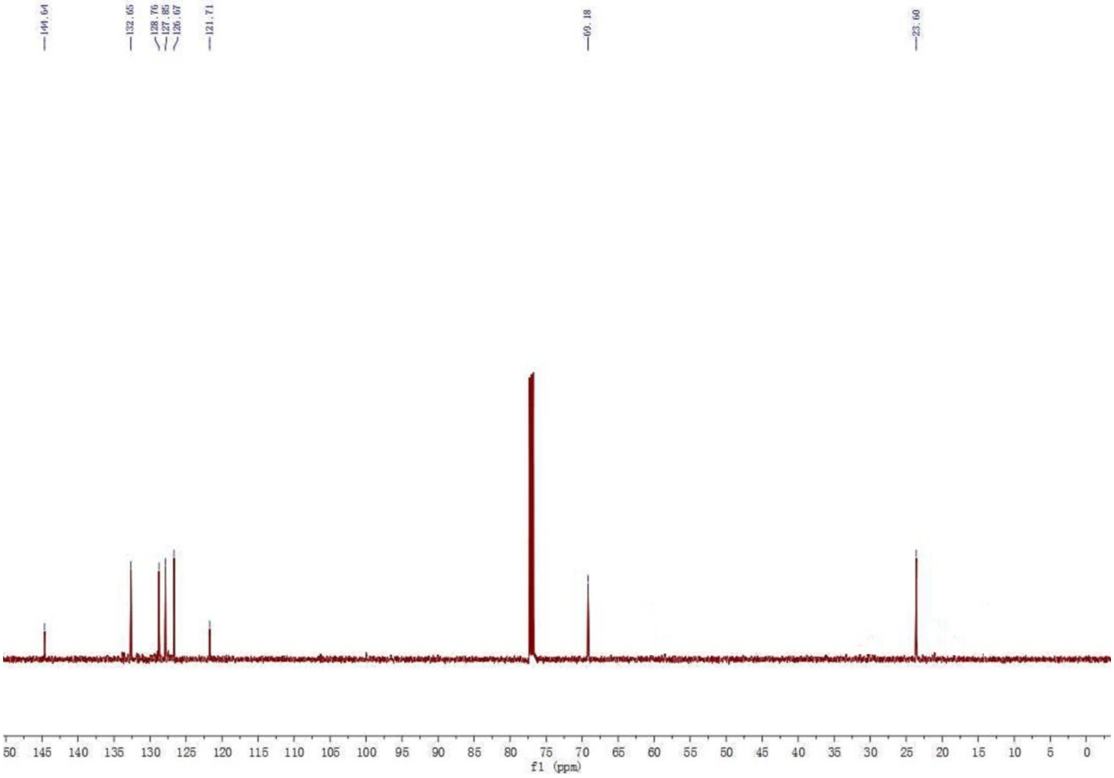
f1 (ppm)



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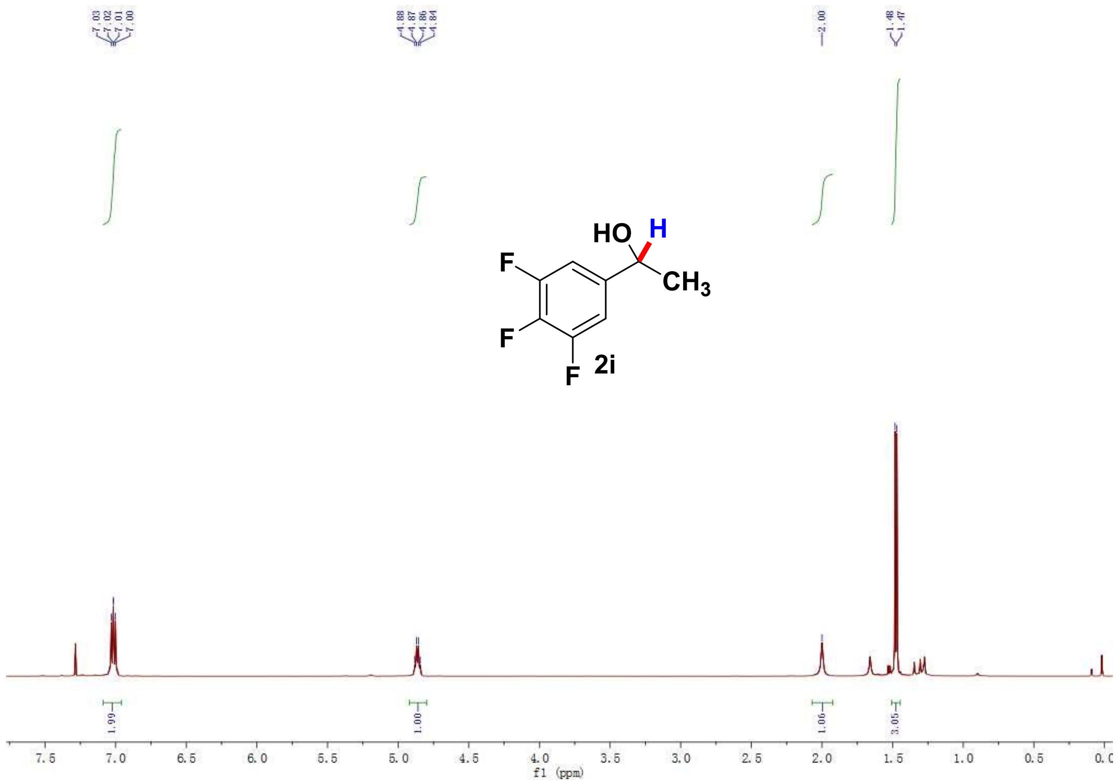
132.65
128.76 127.85 126.67
121.71
69.18
23.60
150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0
f1 (ppm)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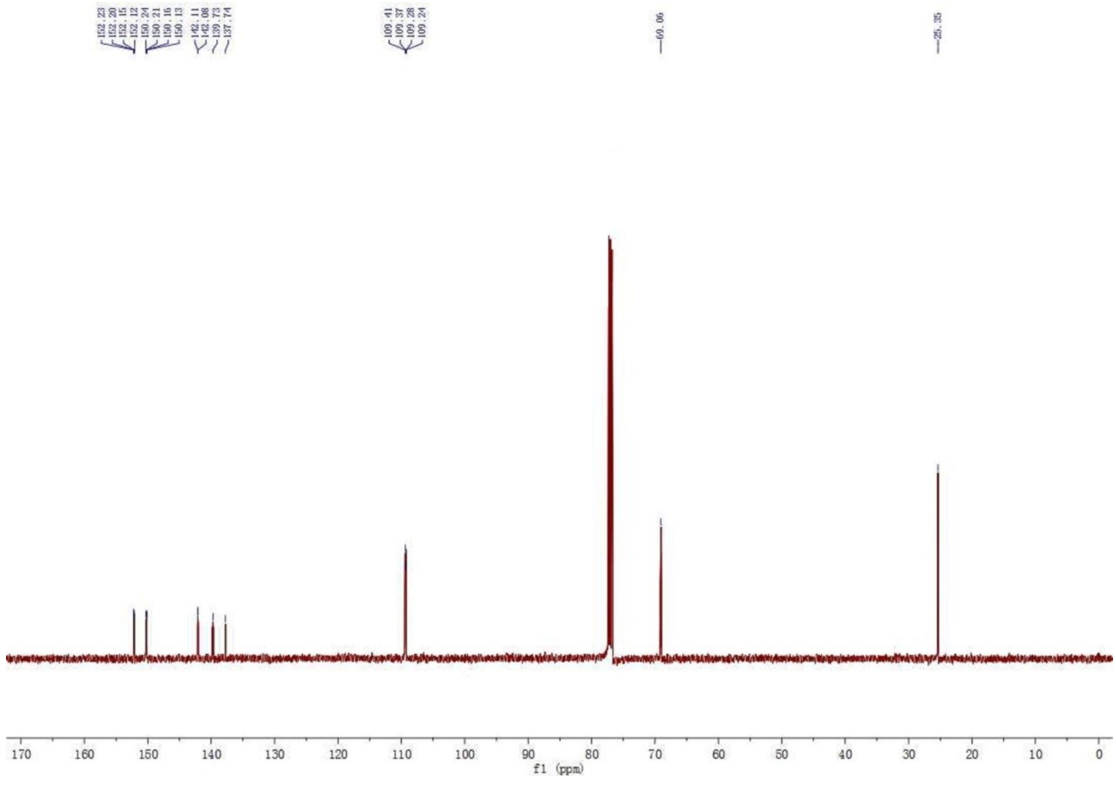
7.02
7.01
7.00
4.88
4.87
4.86
4.84
2.00
1.48
1.47
HO
H
CH_3
F
F
F
2i
1.99
1.00
1.06
3.05
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


152.23
152.20
152.15
152.12
150.24
150.21
150.16
150.13
142.11
142.08
139.73
137.74
109.41
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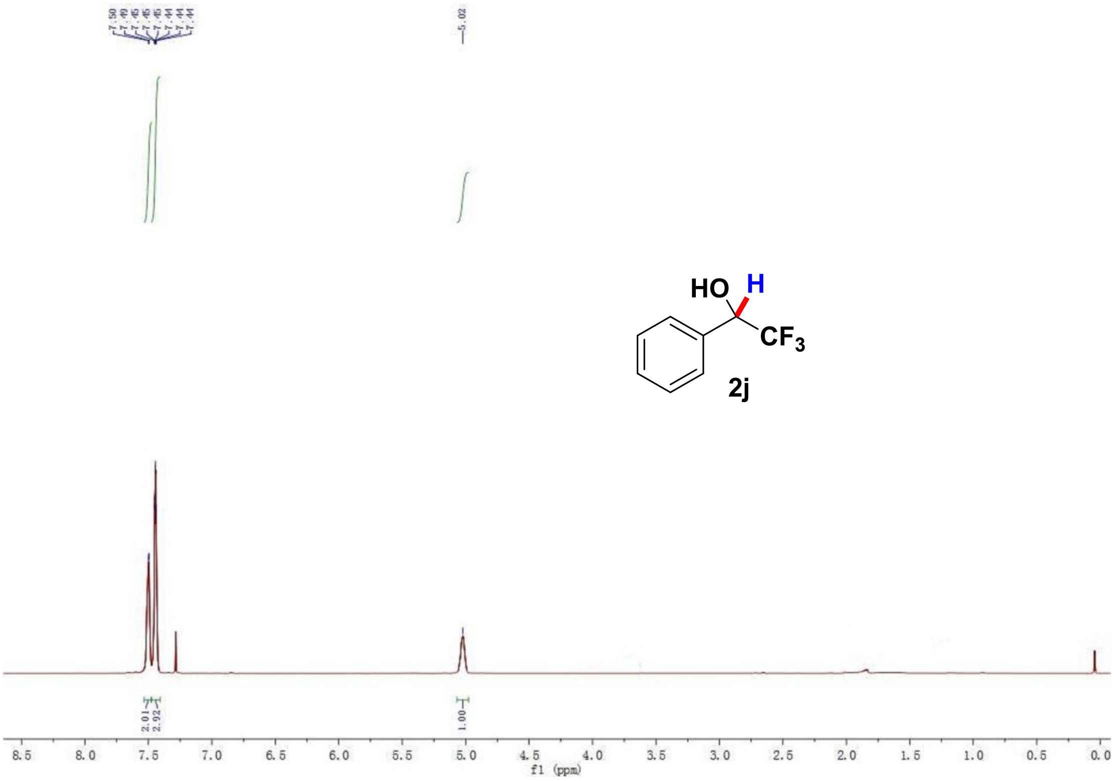
109.28
109.24
69.06
25.35
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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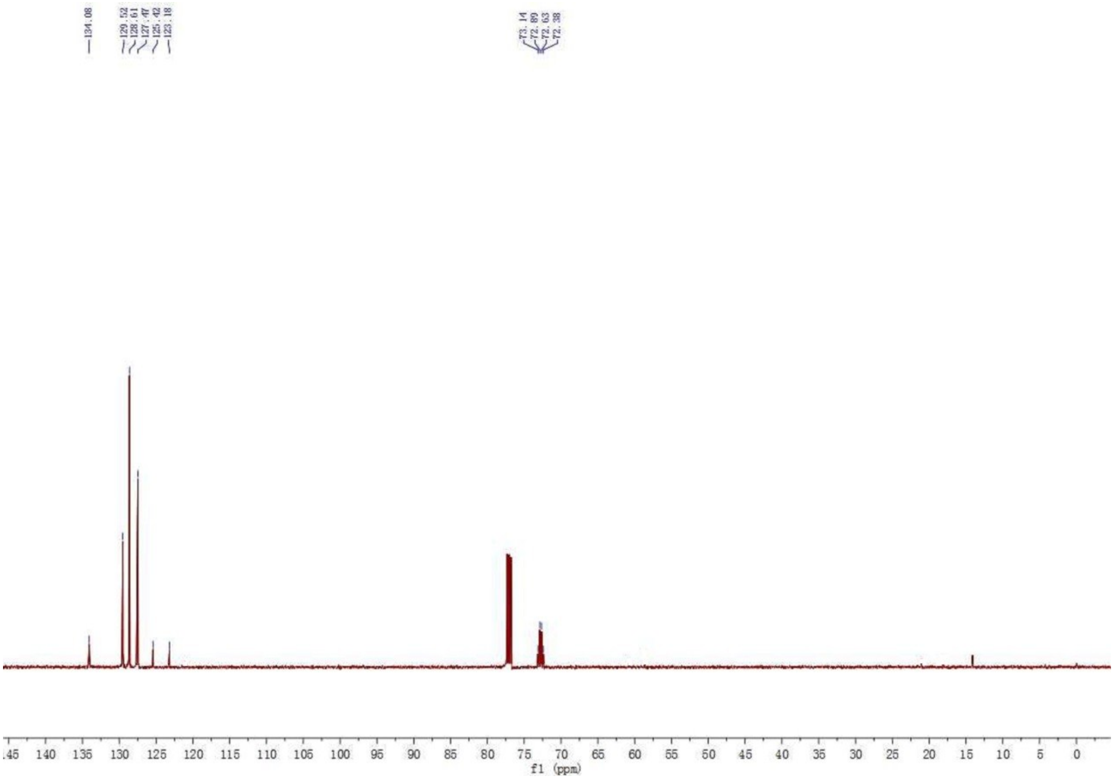
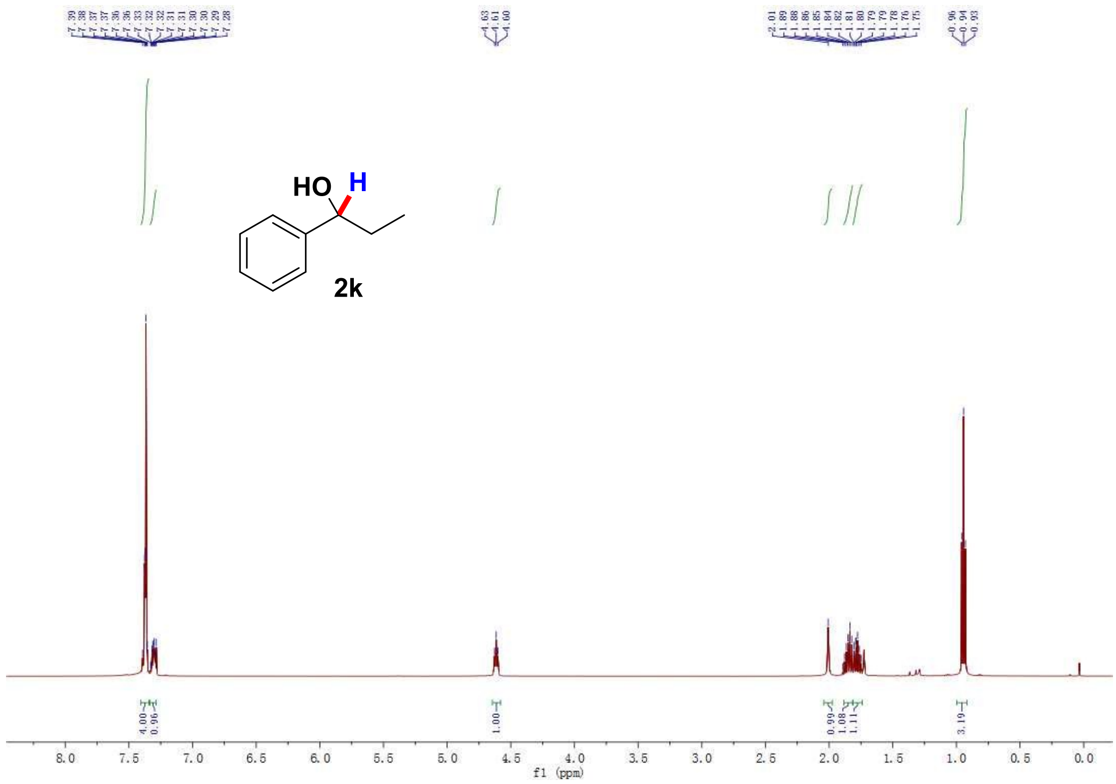
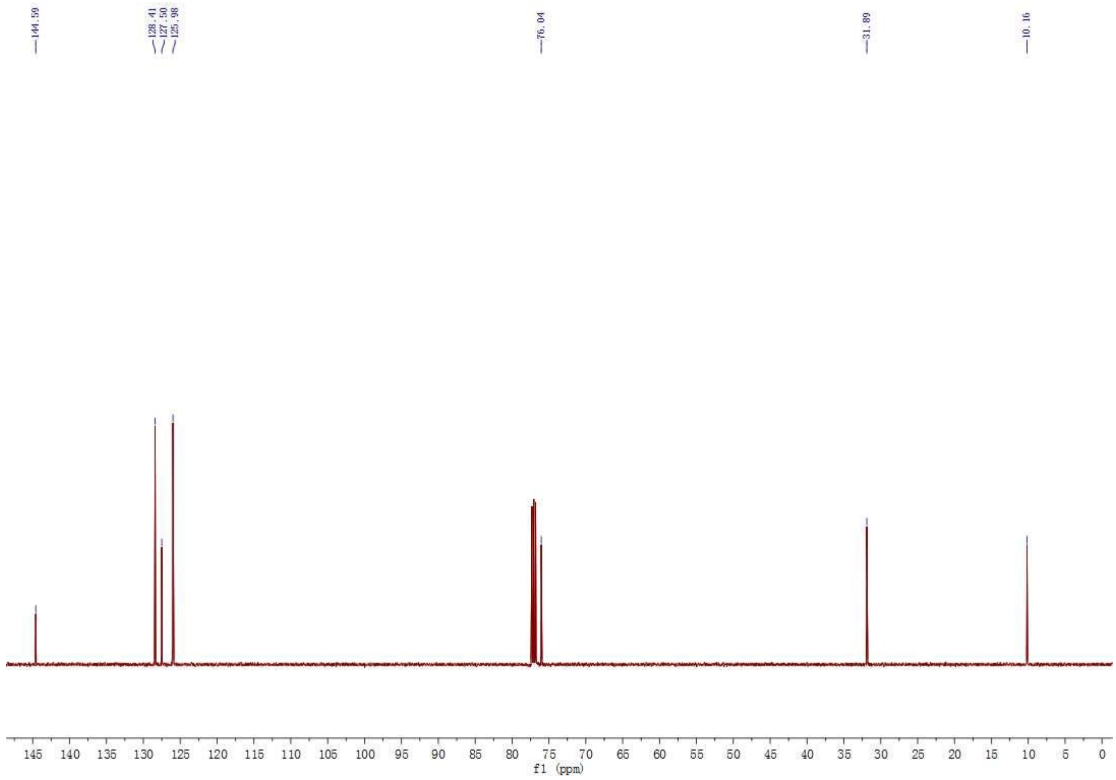
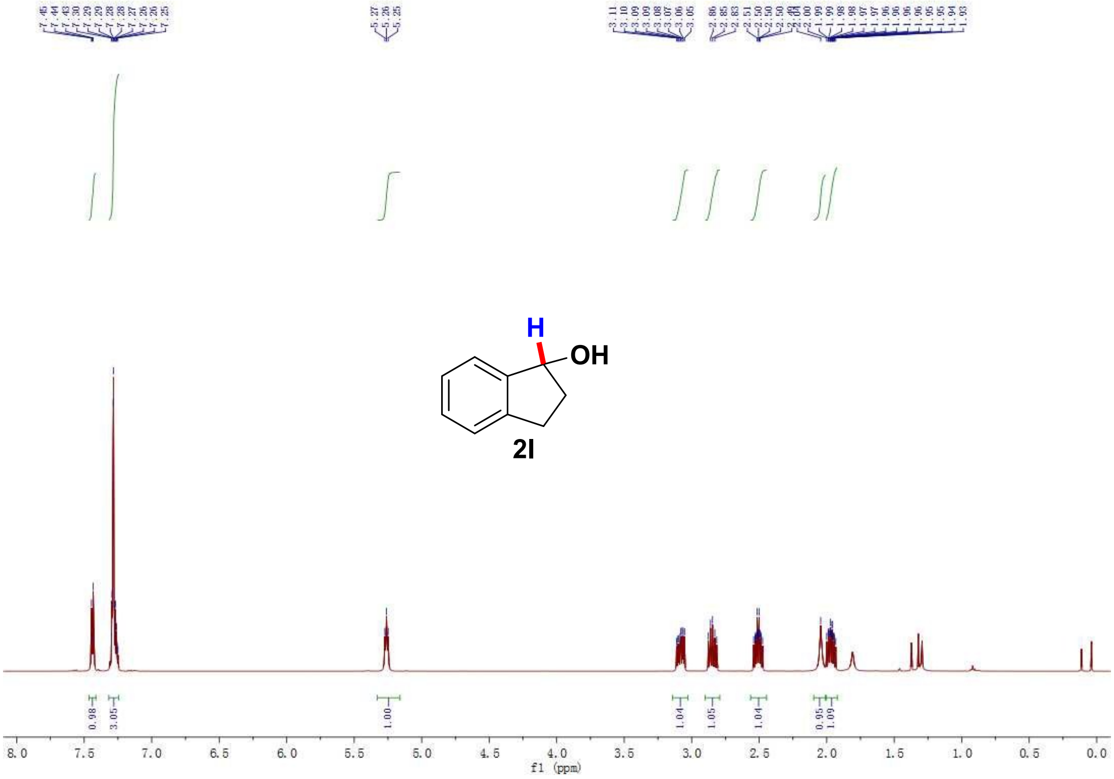
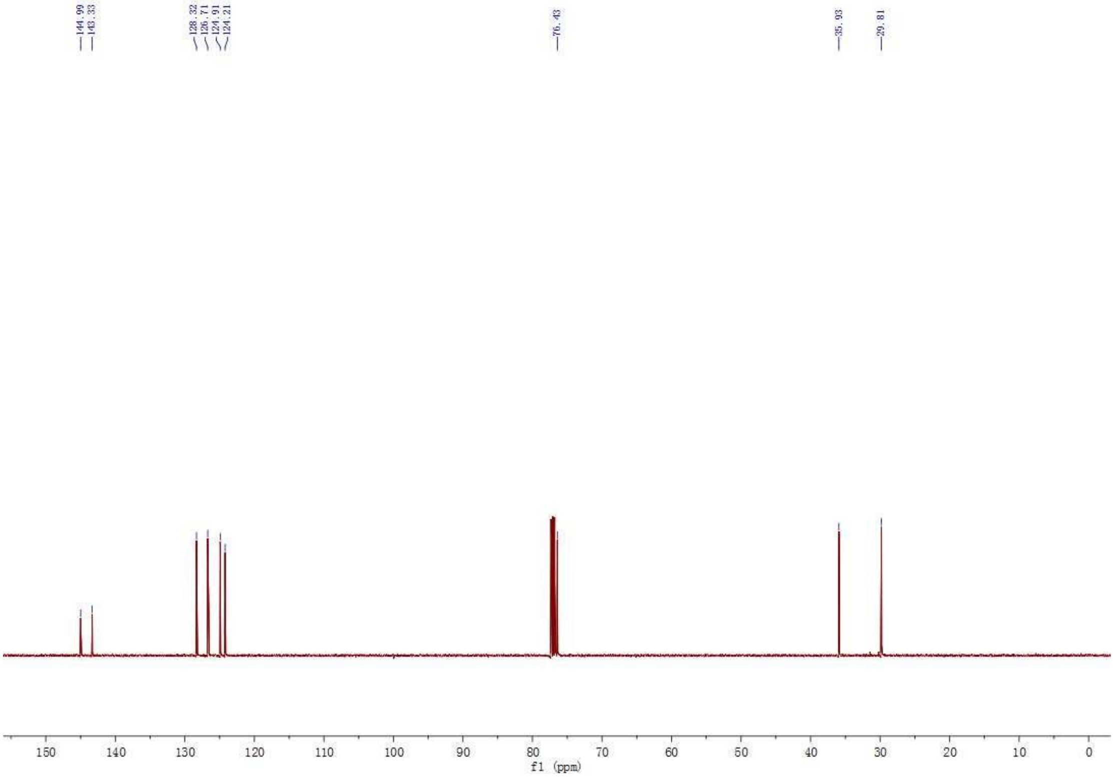
7.49
7.46
7.45
7.45
7.44
7.44
7.44
5.02
2.01
2.92
1.00
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
HO
H
CF_3
2j


134.08
129.52
128.61
127.47
125.42
123.18
73.14
72.89
72.63
72.38
145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0
f1 (ppm)


HO
H
2k
f1 (ppm)


f1 (ppm)


H
OH
2l
f1 (ppm)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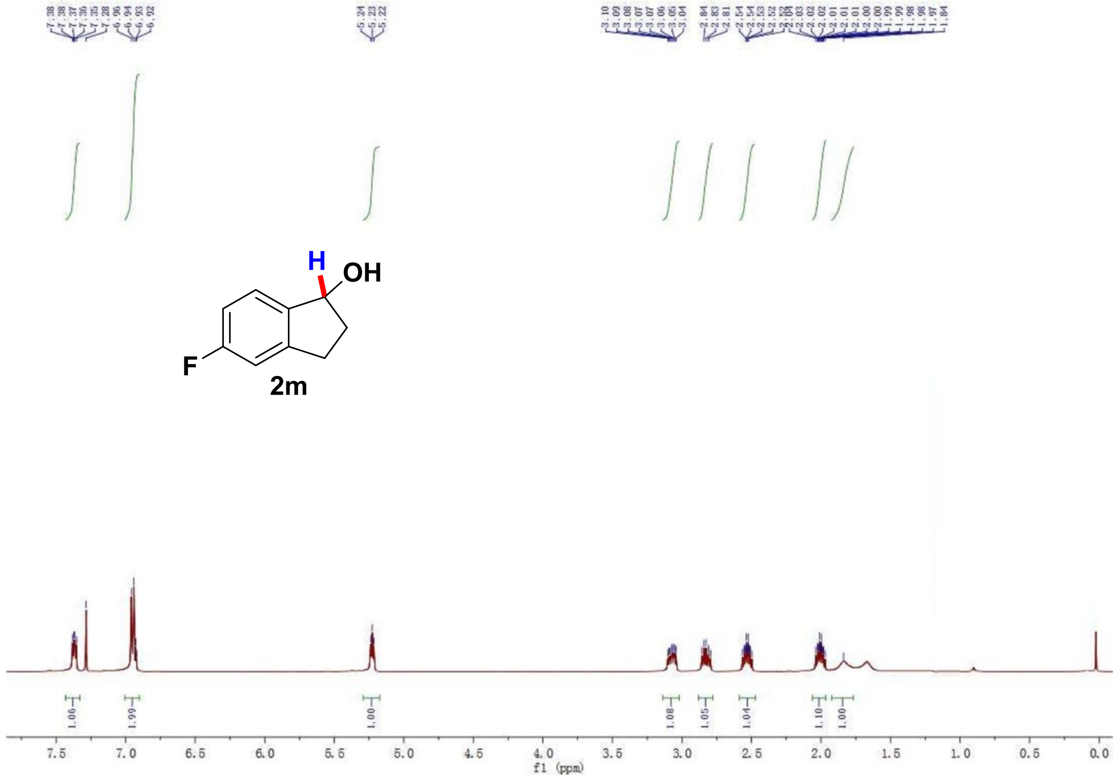
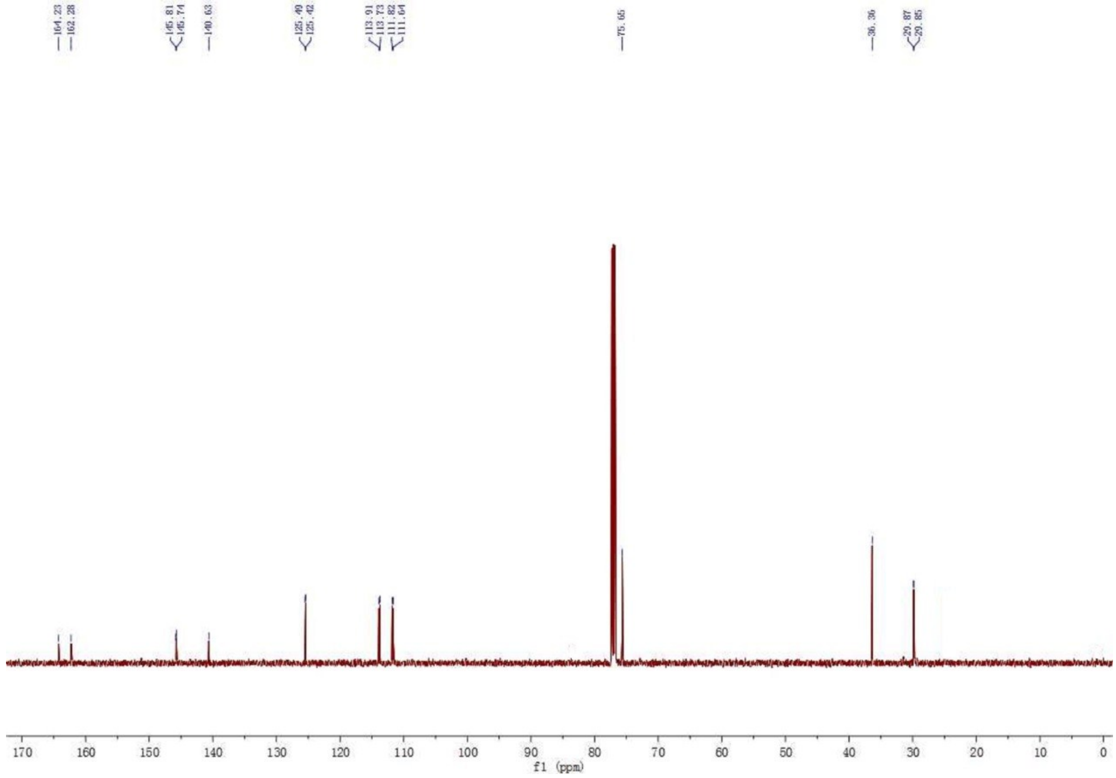
143.33
128.32
126.71
124.91
124.21
76.43
35.93
29.81
f1 (ppm)


H
OH
F
2m
f1 (ppm)


164.23
162.28
145.81
145.74
140.63
125.49
125.42
113.91
113.73
111.82
111.64
75.65
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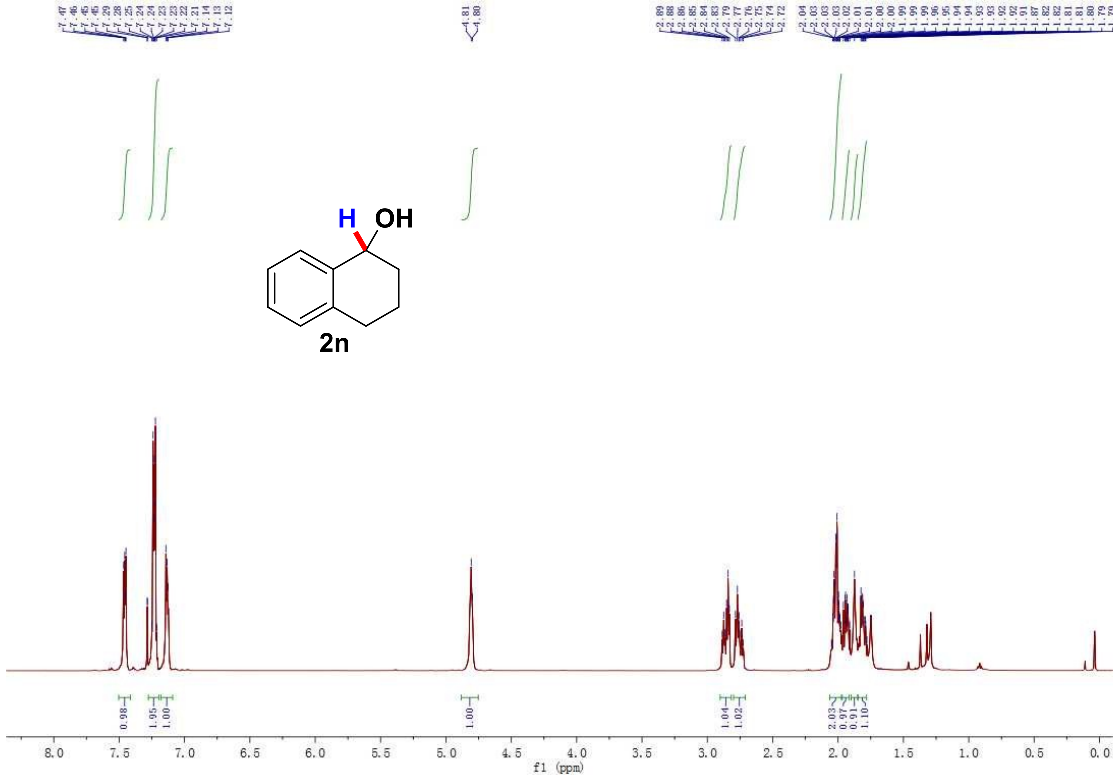
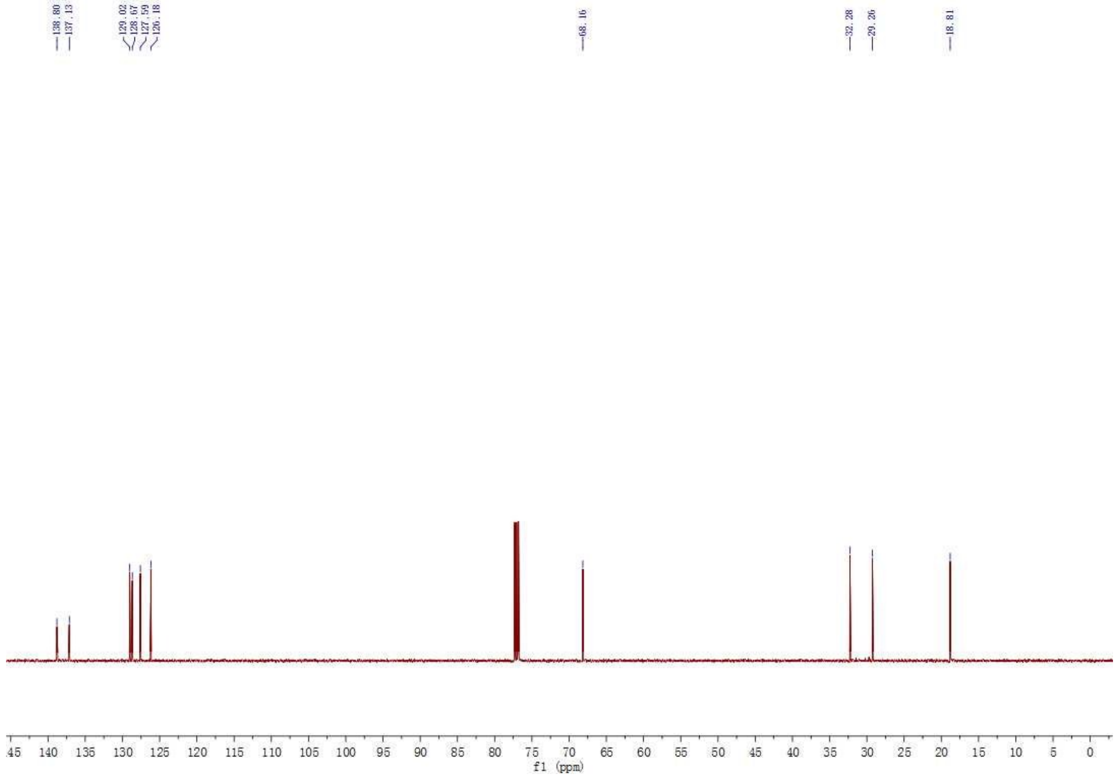
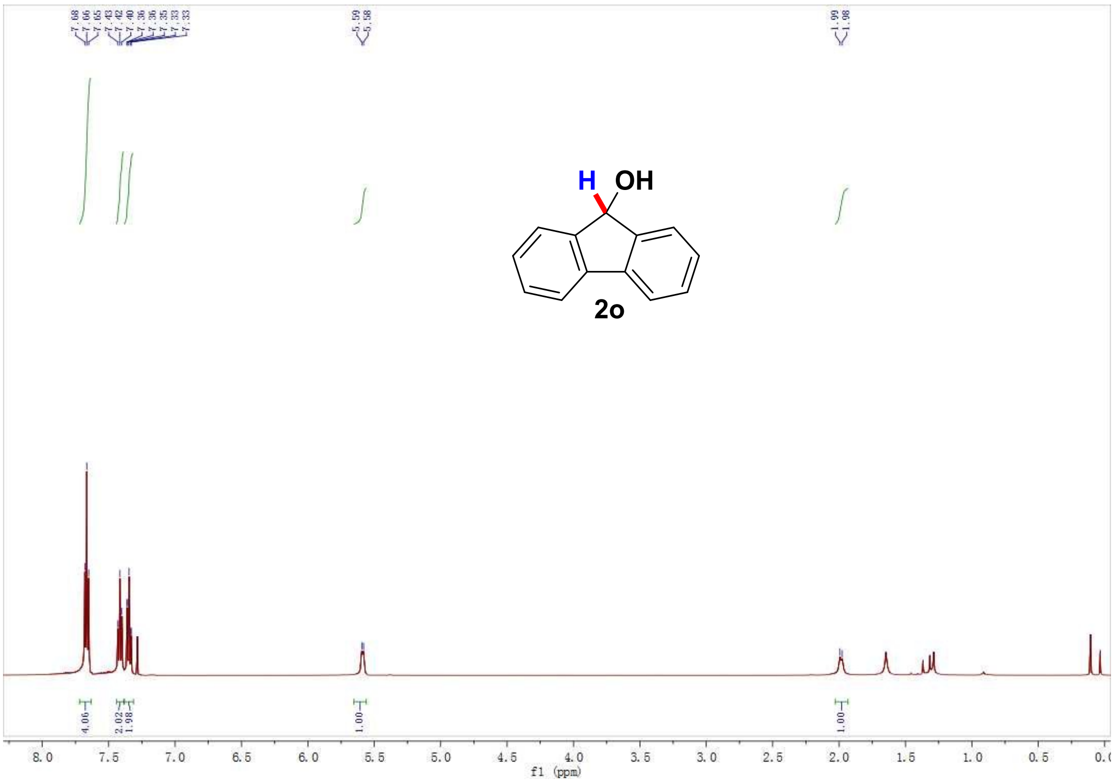
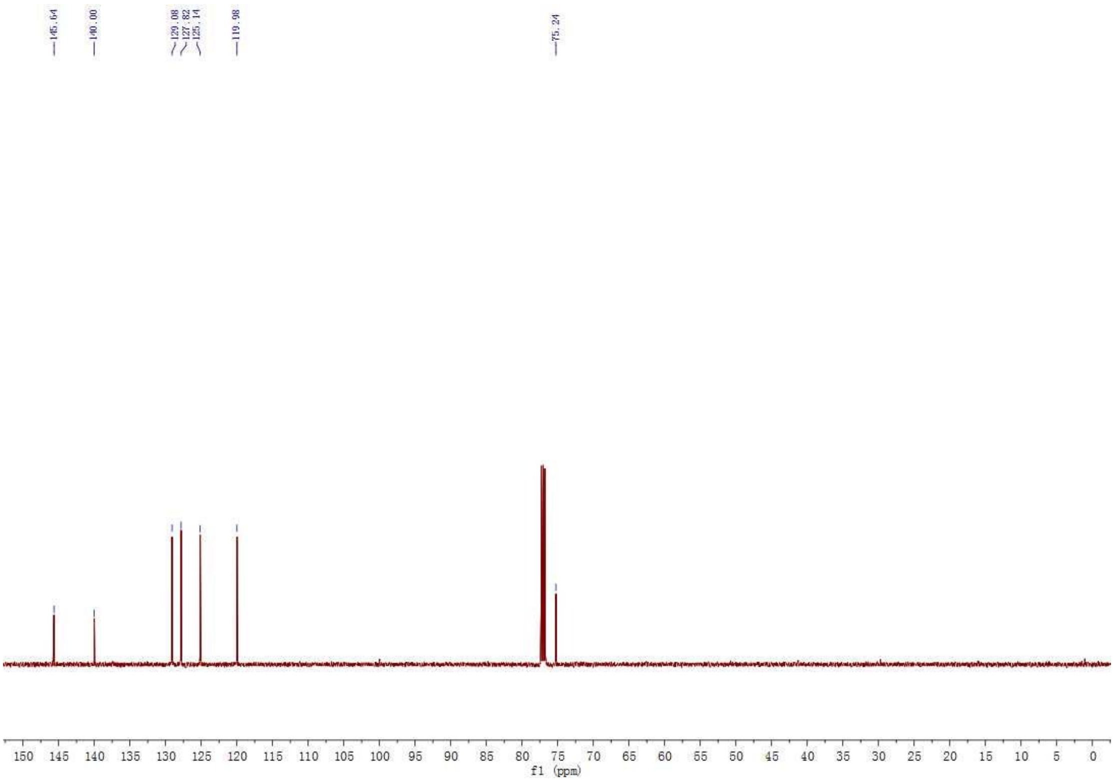
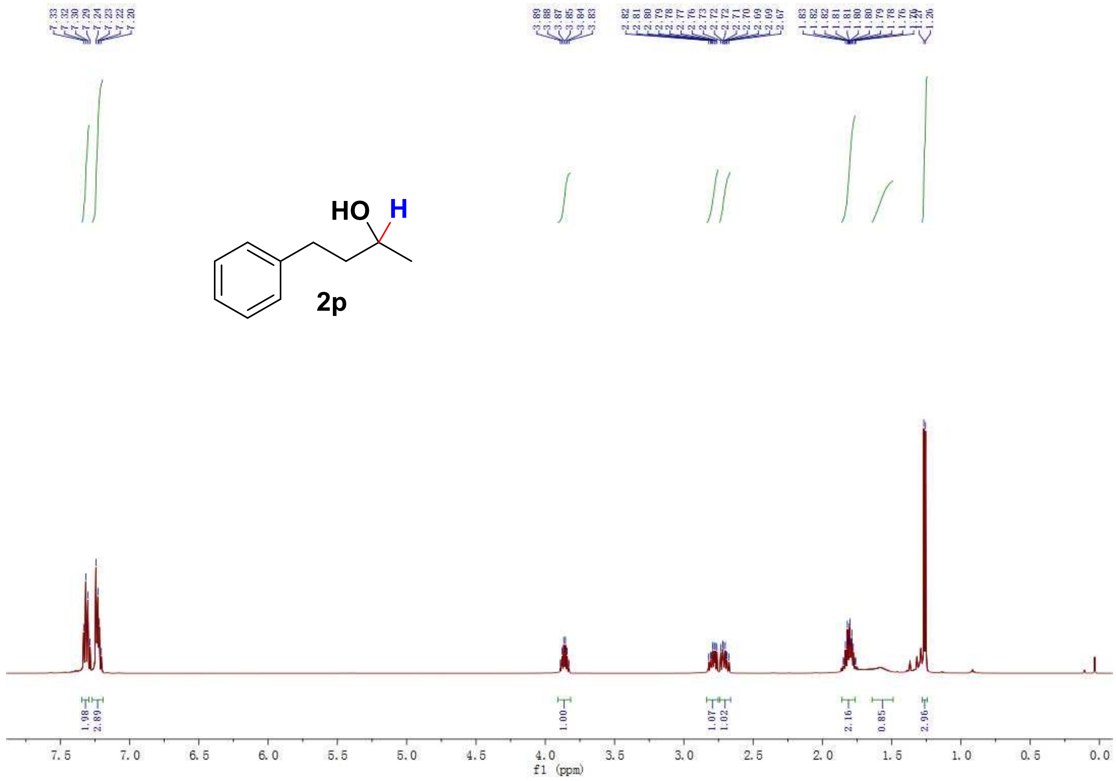
29.87
29.85
f1 (ppm)

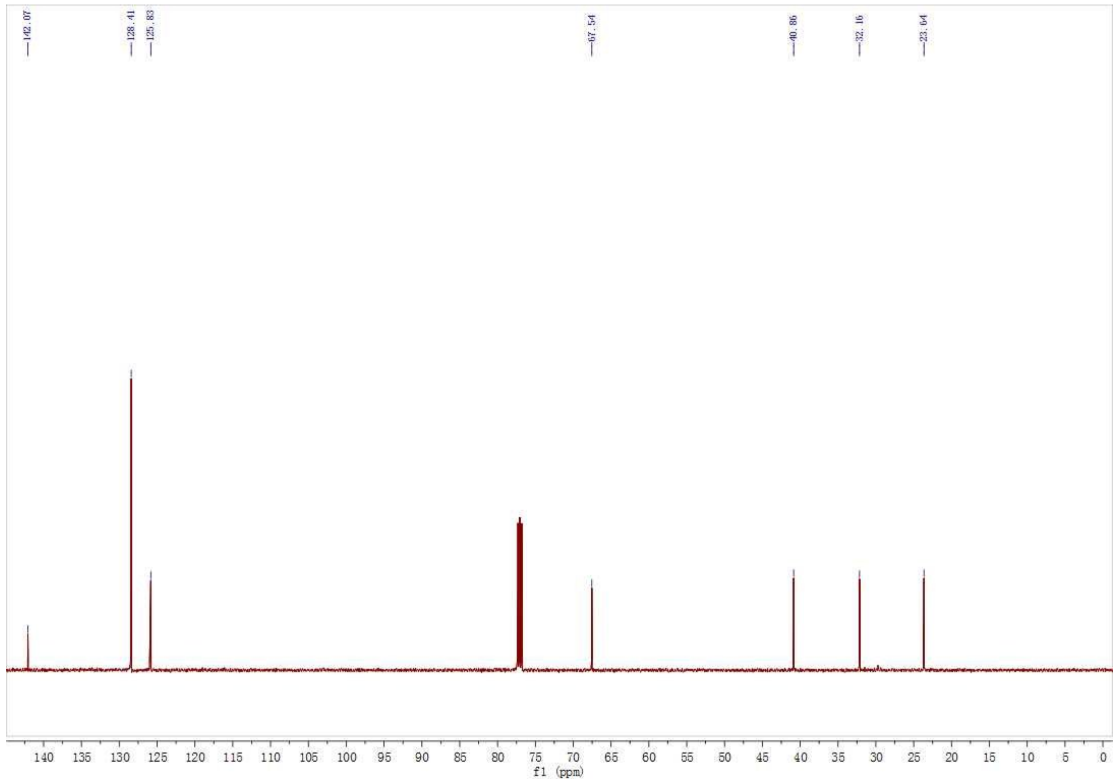

H OH
2n
f1 (ppm)

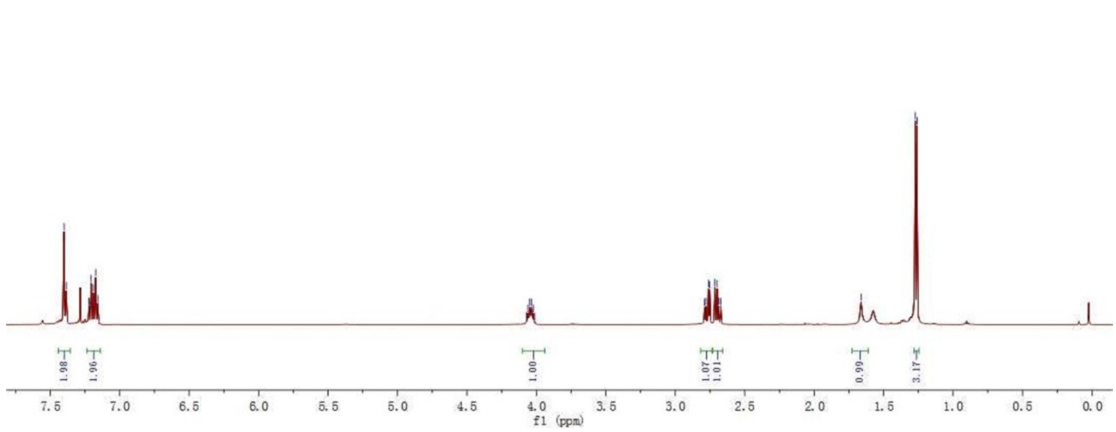

f1 (ppm)

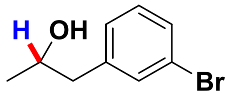

H
OH
2o
f1 (ppm)


145.64
140.00
129.08
127.82
125.14
119.98
75.24
f1 (ppm)

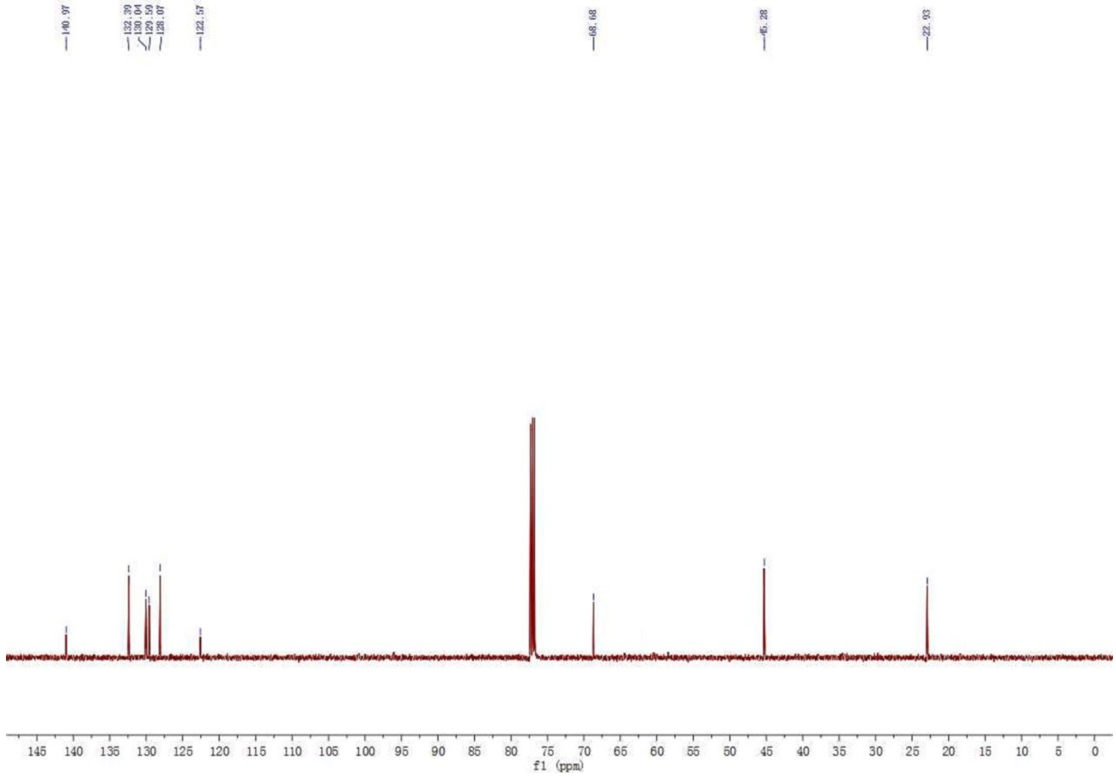

HO H
2p
7.33 7.32 7.30 7.29 7.24 7.23 7.22 7.20
3.89 3.88 3.87 3.85 3.84 3.83
2.82 2.81 2.80 2.79 2.78 2.77 2.76 2.73 2.72 2.72 2.71 2.70 2.69 2.69 2.67
1.83 1.82 1.82 1.81 1.81 1.80 1.80 1.79 1.78 1.76 1.27 1.26
1.98 2.89 1.00 1.07 1.02 2.16 0.85 2.96
f1 (ppm)

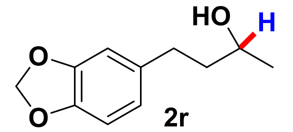

142.07 128.41 125.83 67.54 40.86 32.16 23.64
f1 (ppm)


7.40 7.39 7.22 7.21 7.19 7.17 7.16
4.07 4.06 4.05 4.04 4.02 4.01
2.79 2.78 2.76 2.75 2.72 2.70 2.69 2.67
1.66
1.27 1.26
1.98 1.96 1.00 1.07 1.01 0.99 3.17
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


H
OH
Br

2q


140.97
132.39 130.04 129.59 128.07
122.57
68.68
45.28
22.93
145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0
f1 (ppm)



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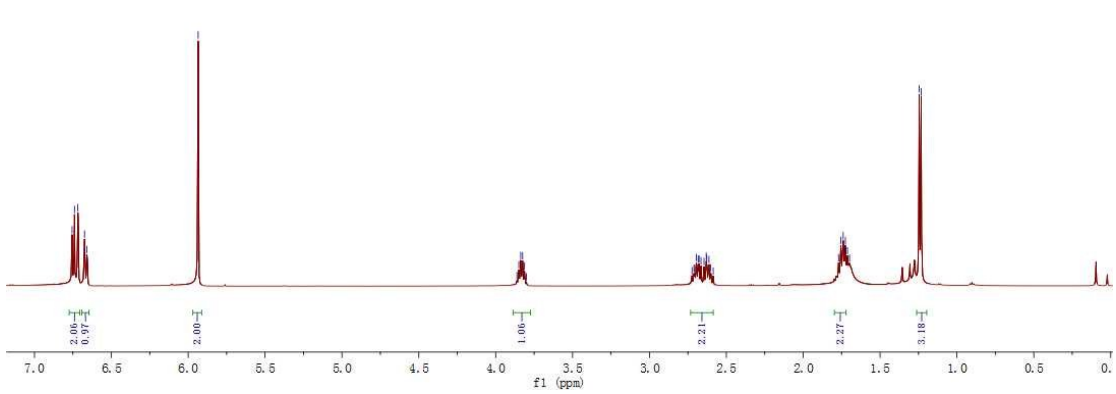

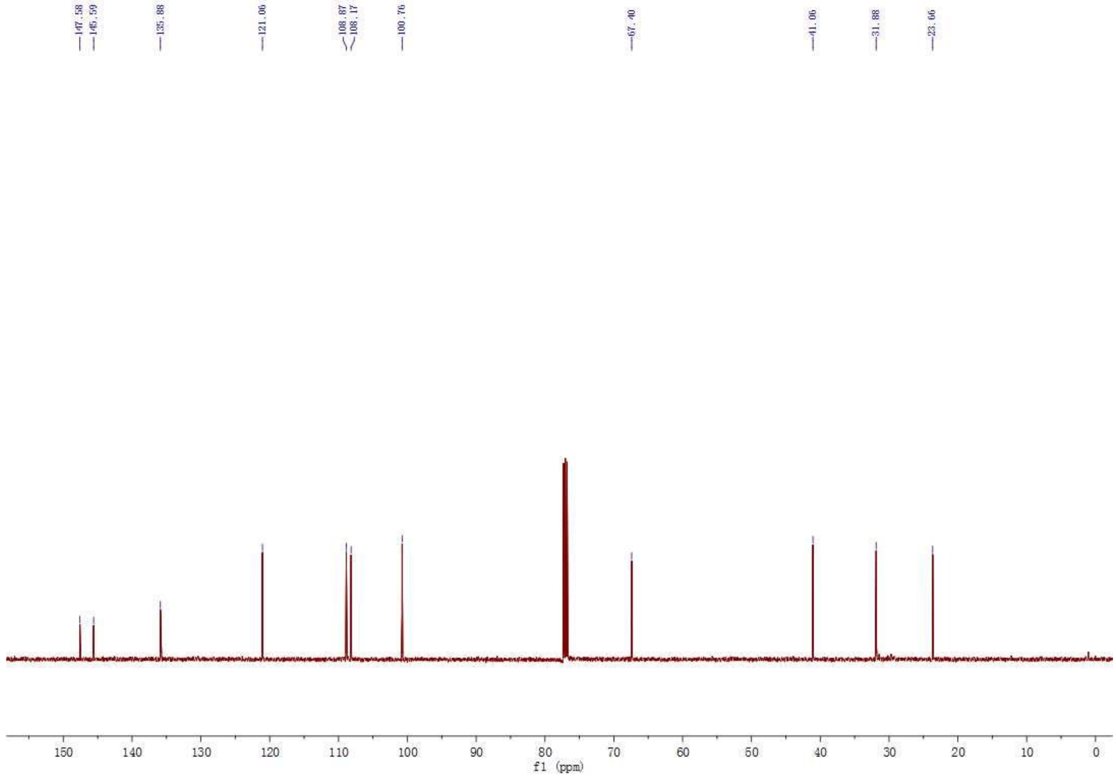

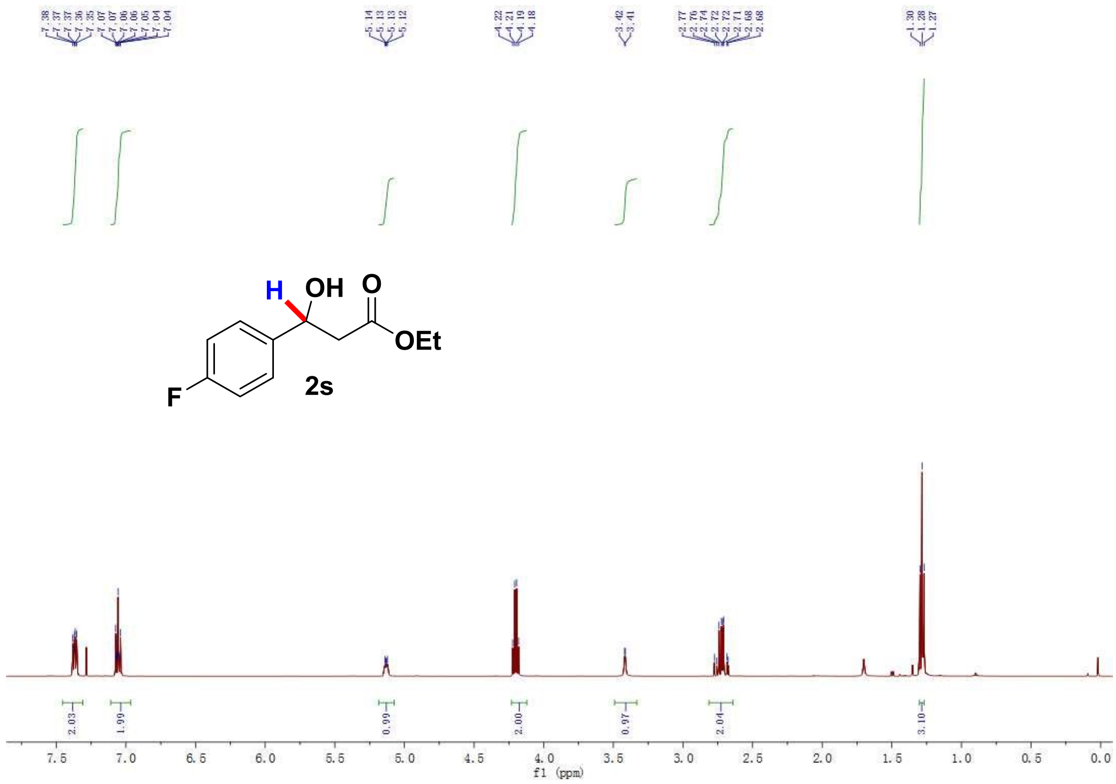
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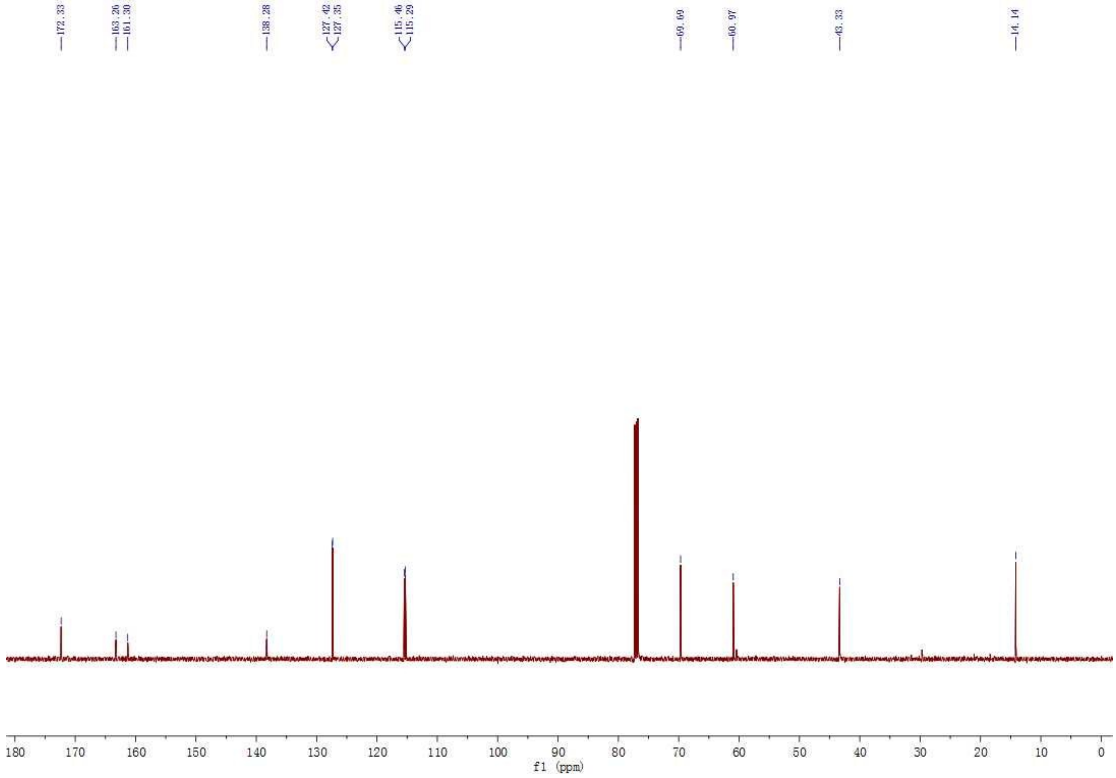
5.14 5.13 5.13 5.12
4.22 4.21 4.19 4.18
3.42 3.41
2.77 2.76 2.74 2.72 2.72 2.71 2.68 2.68
1.30 1.28 1.27
H OH O
OEt
F
2s
2.03 1.99 0.99 2.00 0.97 2.04 3.10
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


172.33
163.26 161.30
138.28
127.42 127.35
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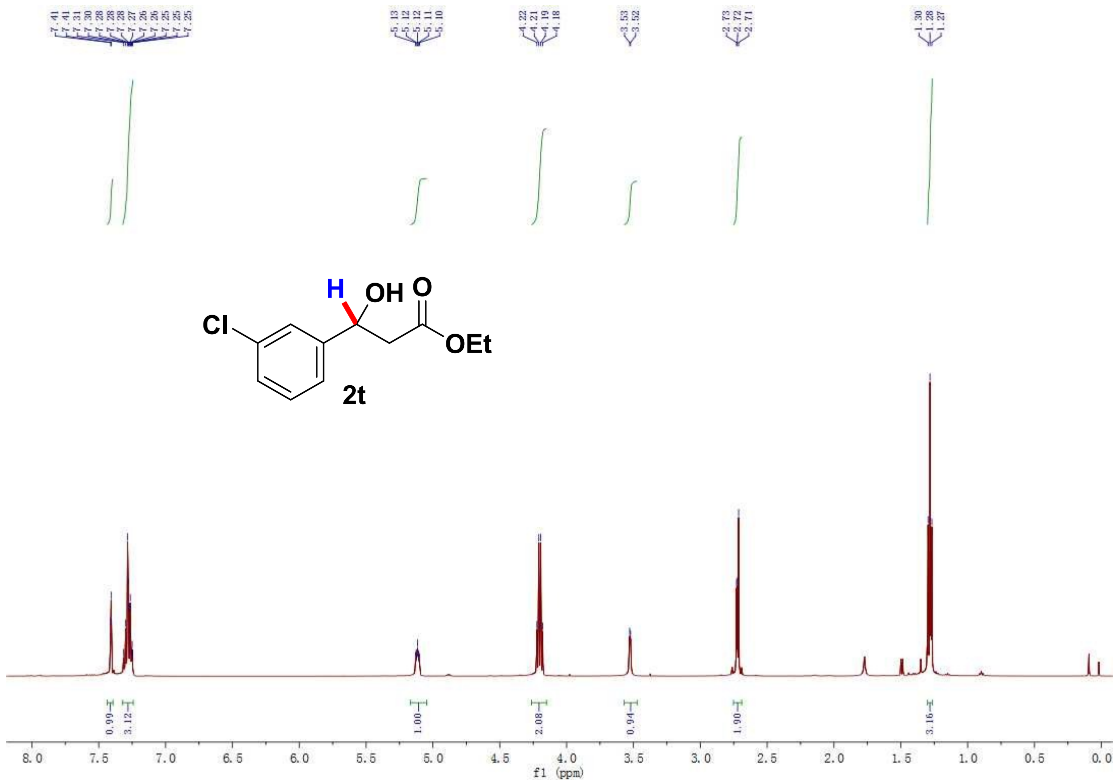
69.69
60.97
43.33
14.14
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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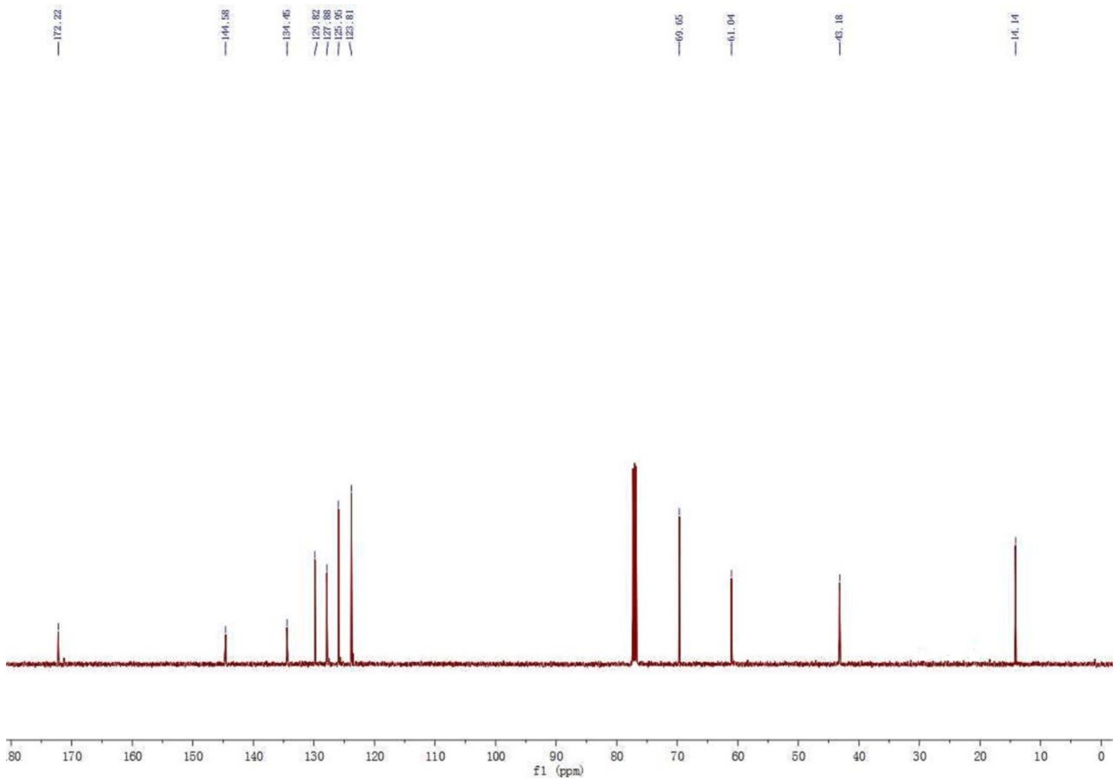
O
Cl
OEt
2t
f1 (ppm)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125.95
123.81
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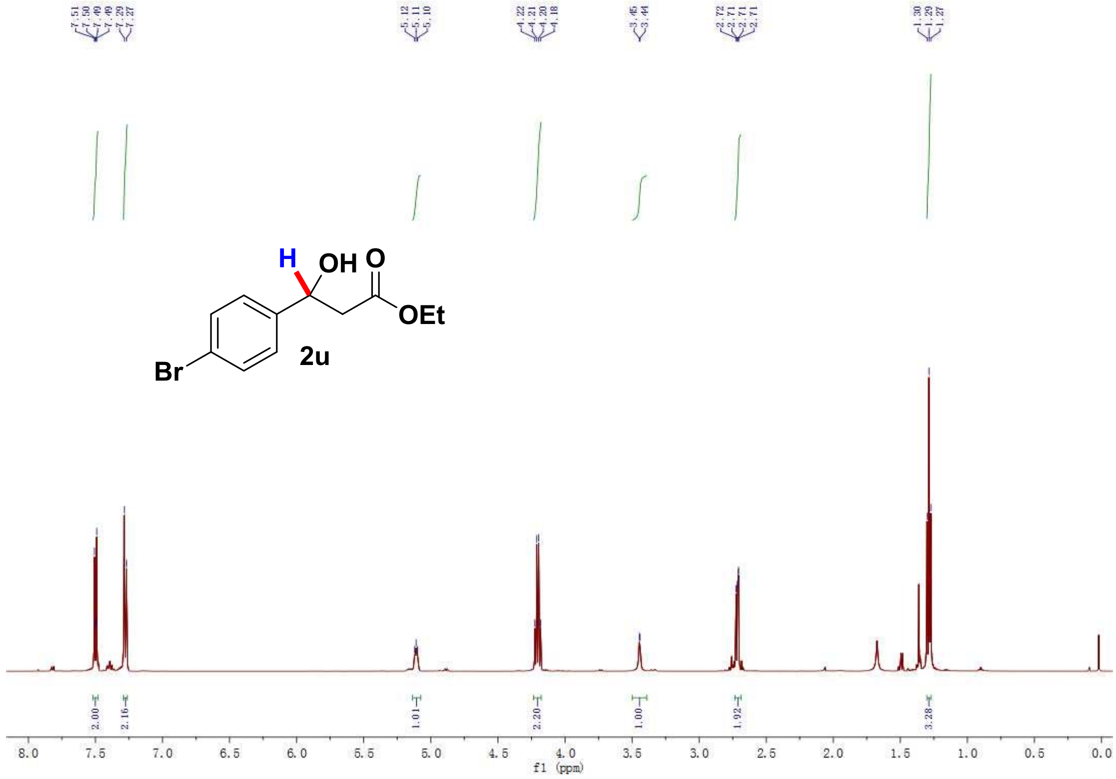
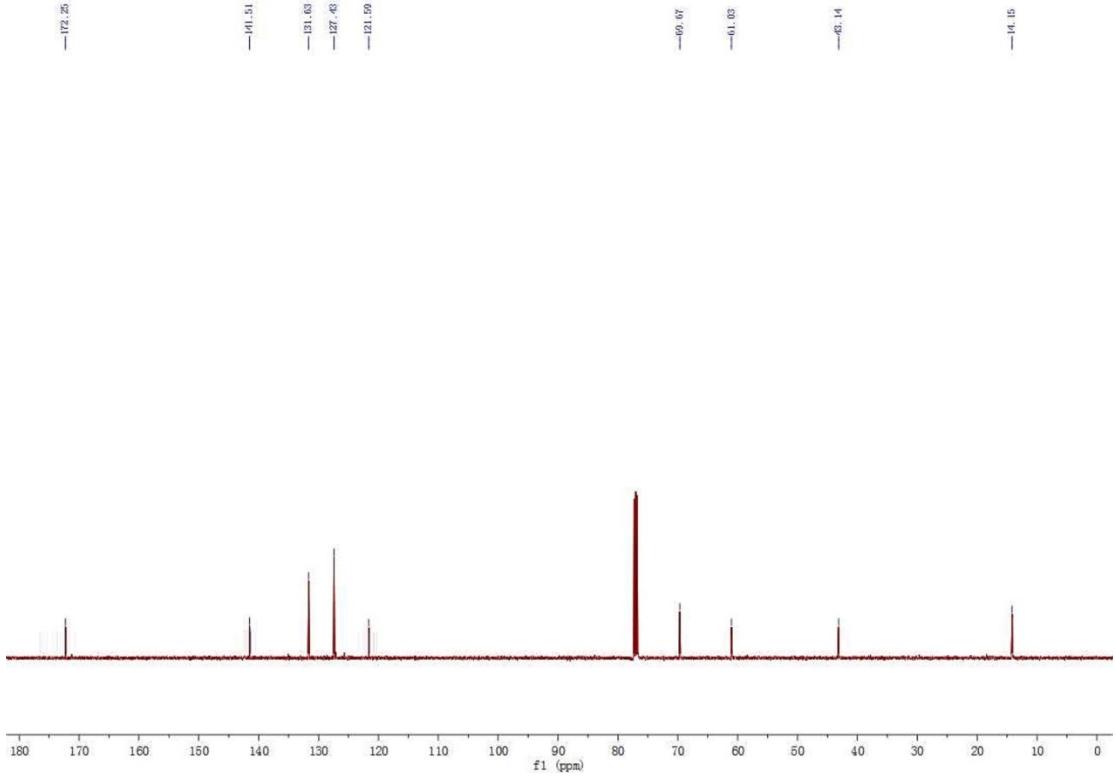
43.18
14.14
f1 (ppm)


H
OH
O
OEt
Br
2u
f1 (ppm)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127.43
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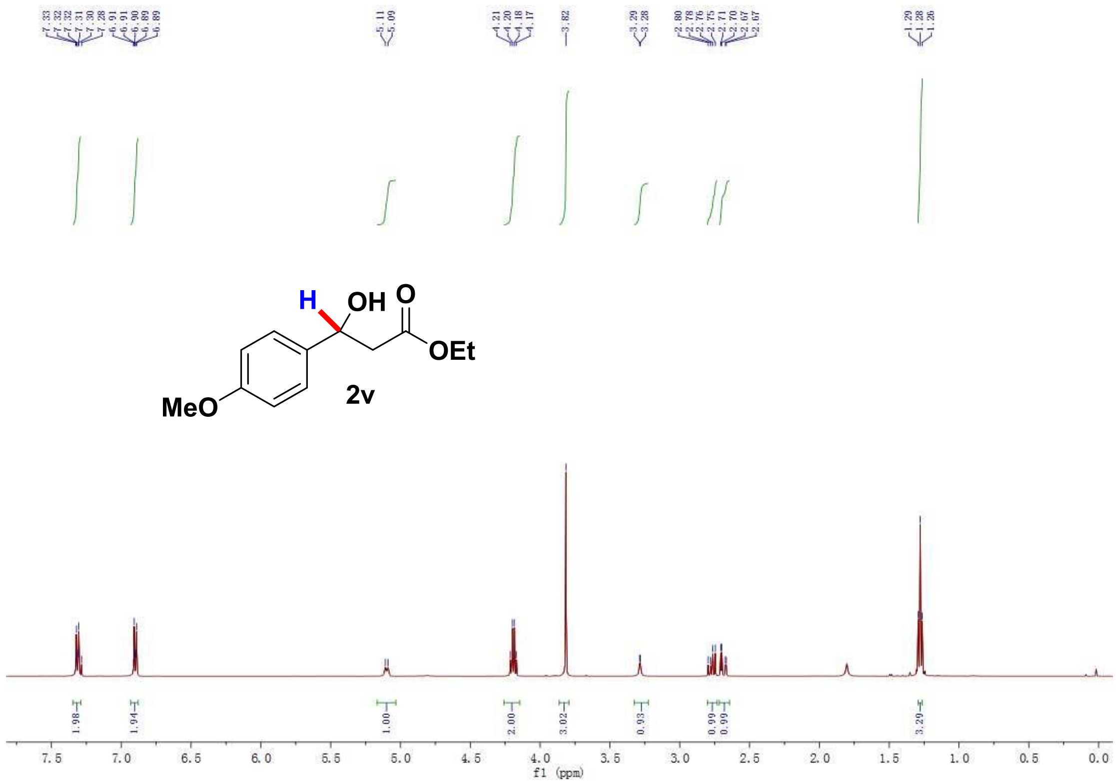
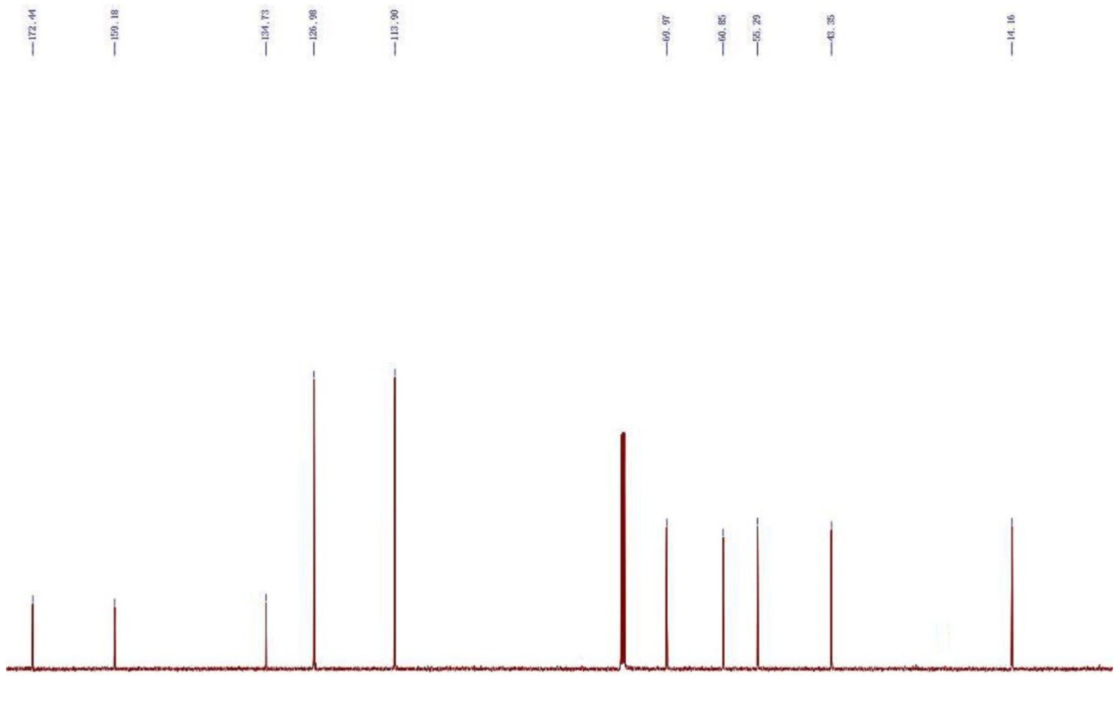
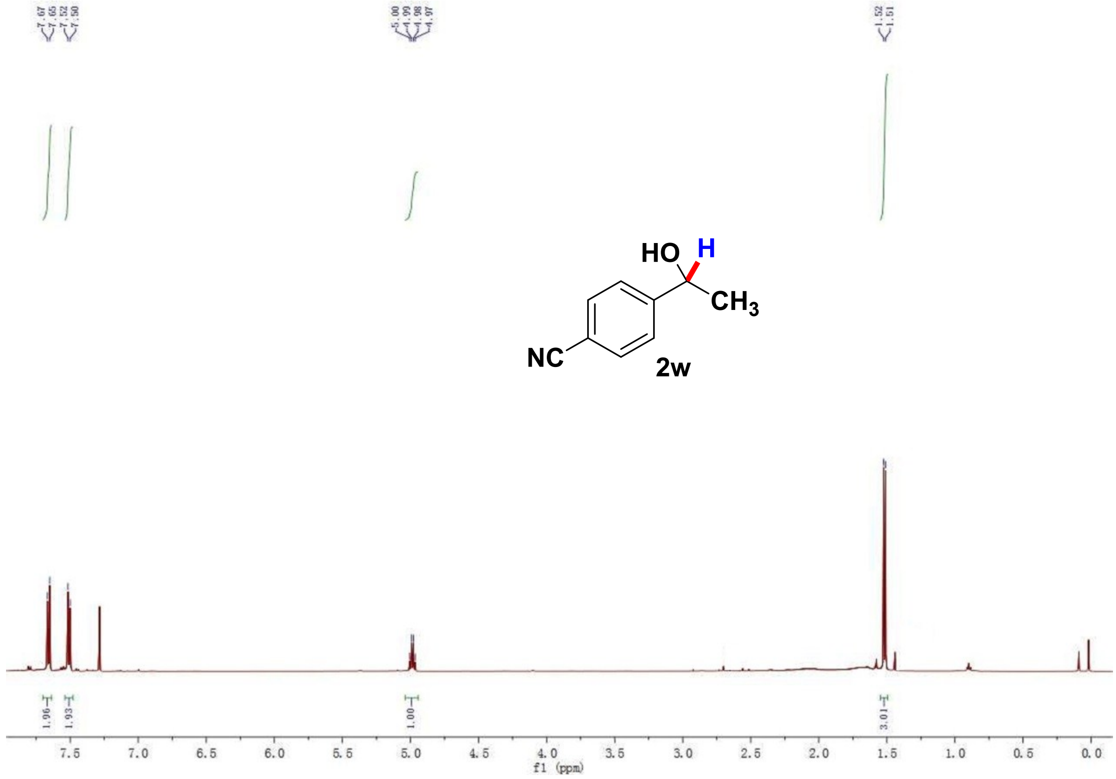
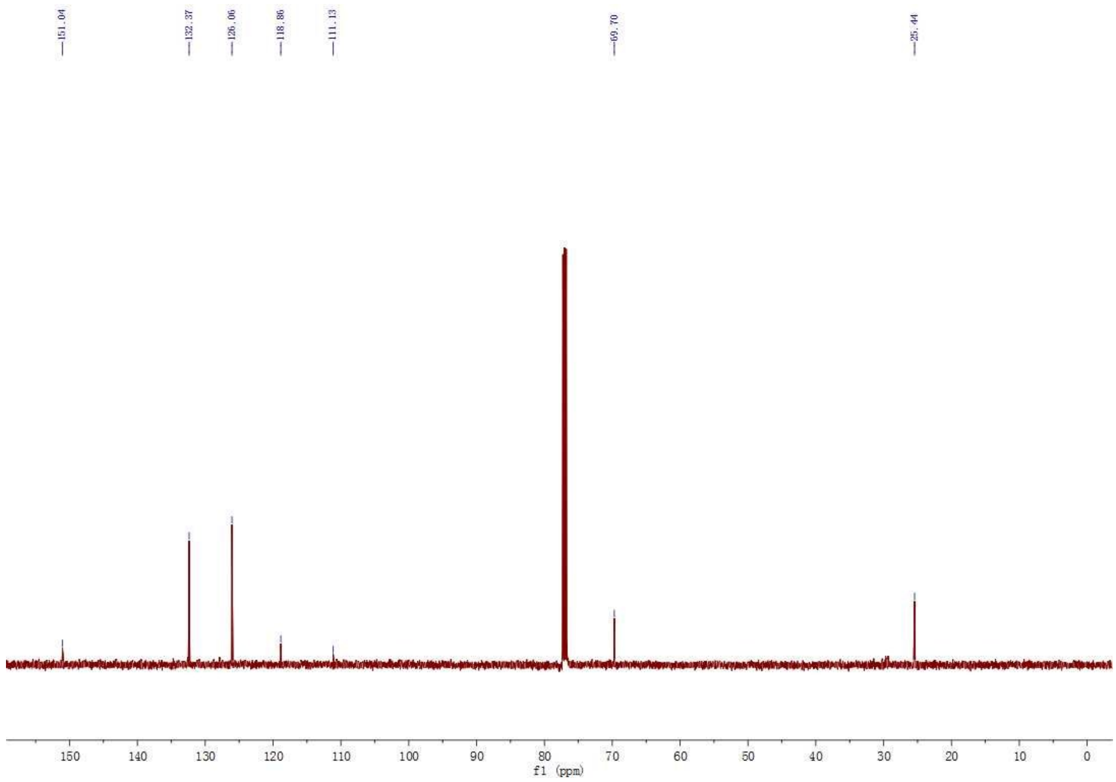
43.14
14.15
f1 (ppm)






7.67
7.65
7.52
7.50
5.00
4.99
4.98
4.97
1.52
1.51
HO
H
CH3
NC
2w
1.96
1.93
1.00
3.01
f1 (ppm)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126.06
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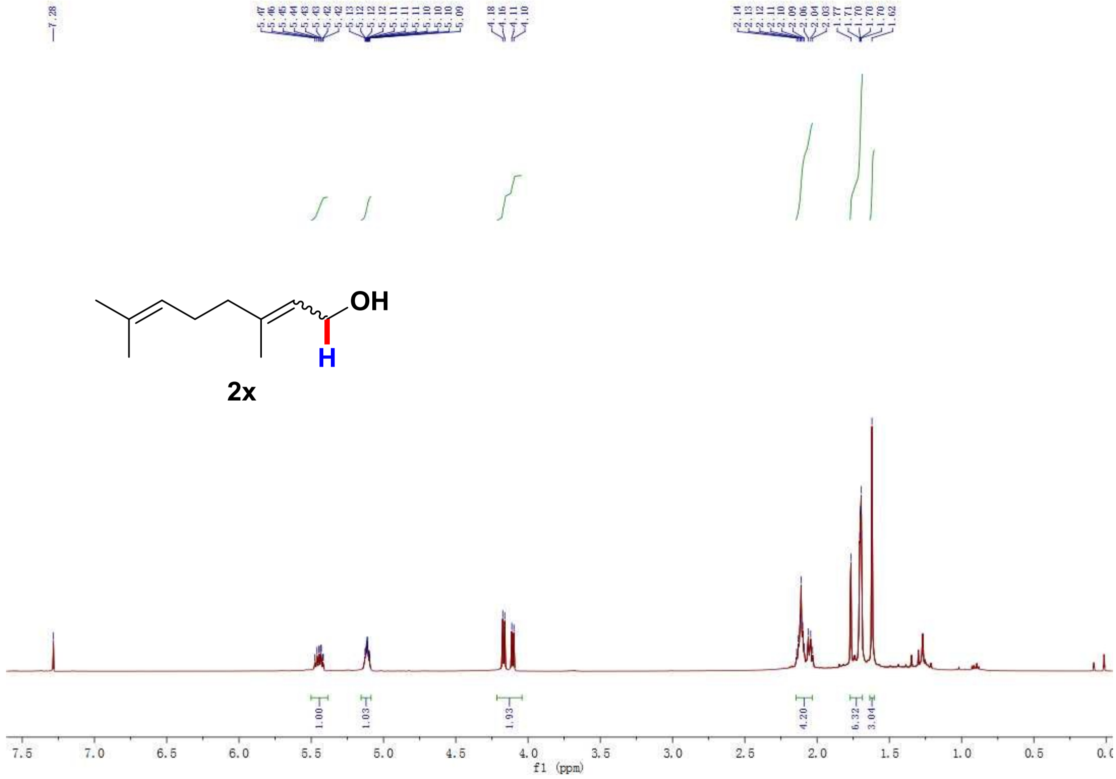
25.44
f1 (ppm)



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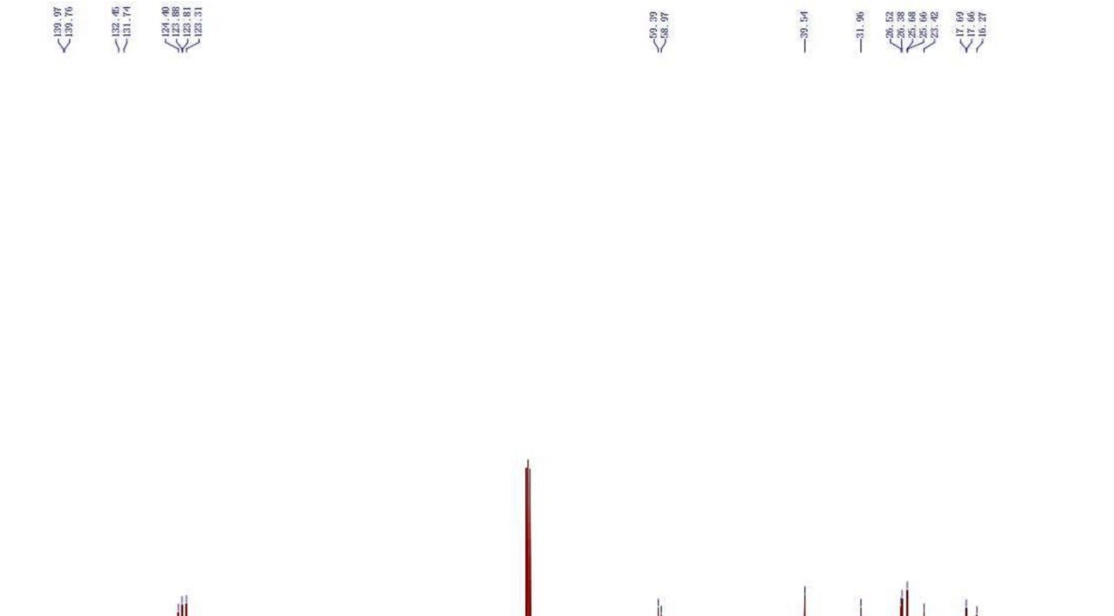
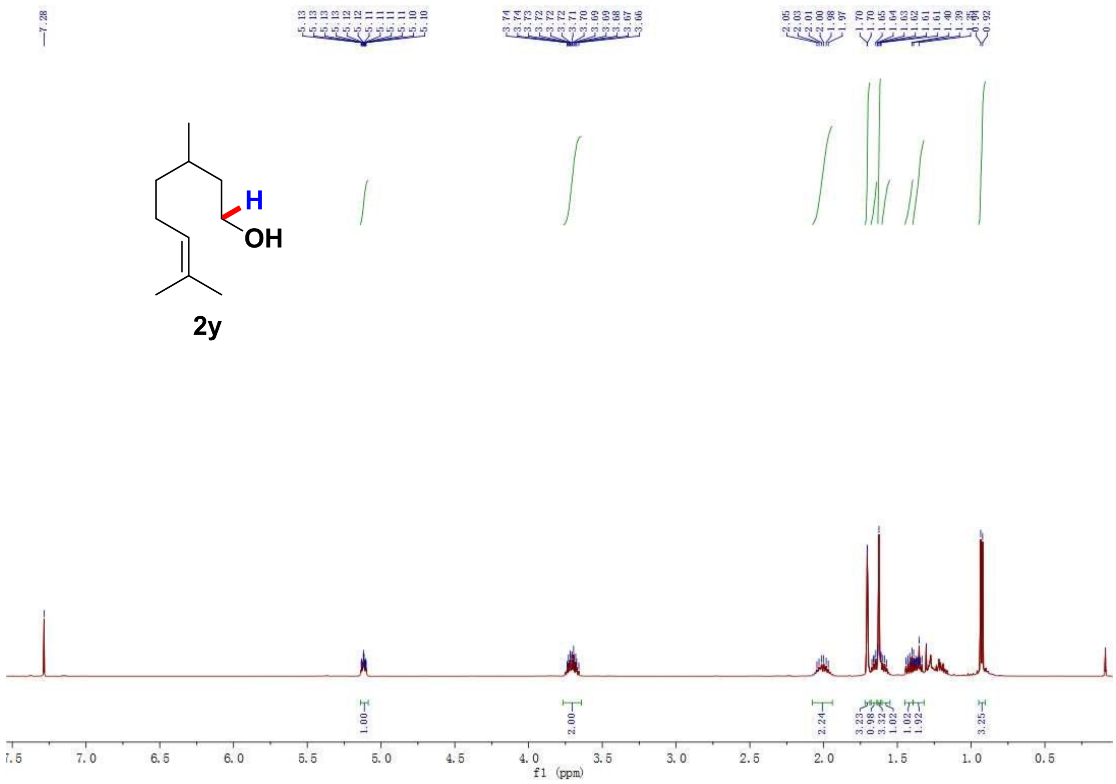
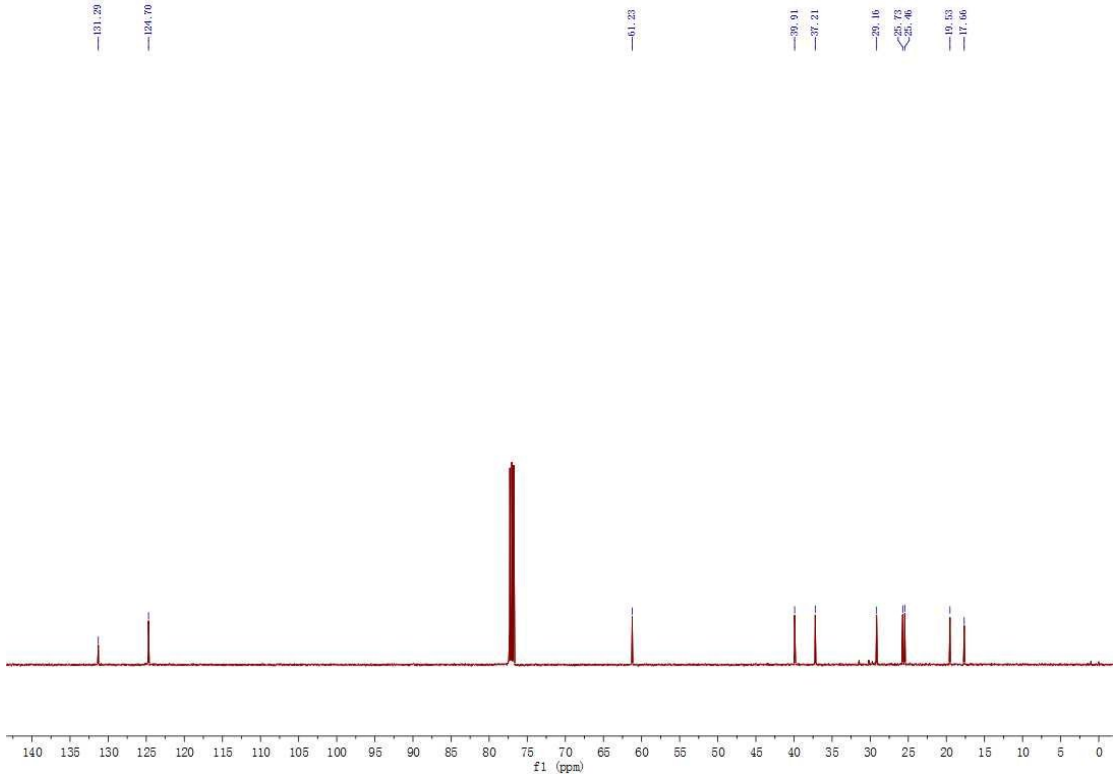



H
OH
2y
f1 (ppm)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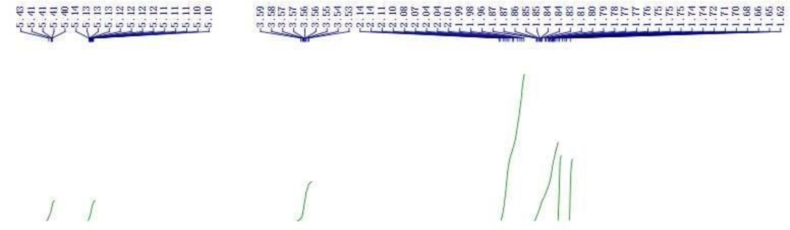
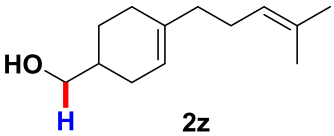
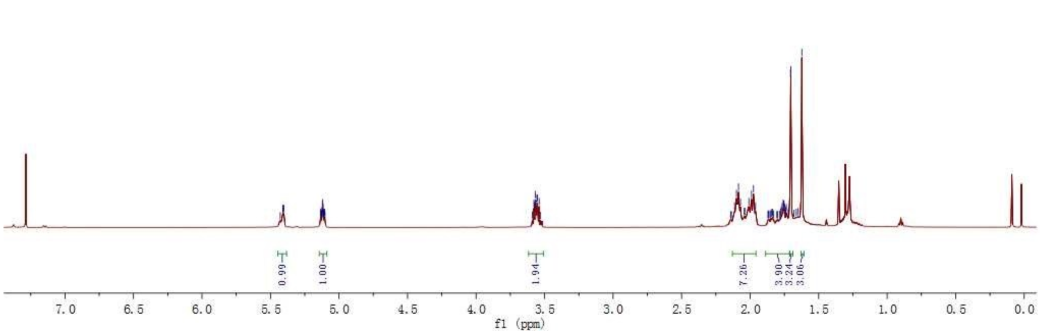
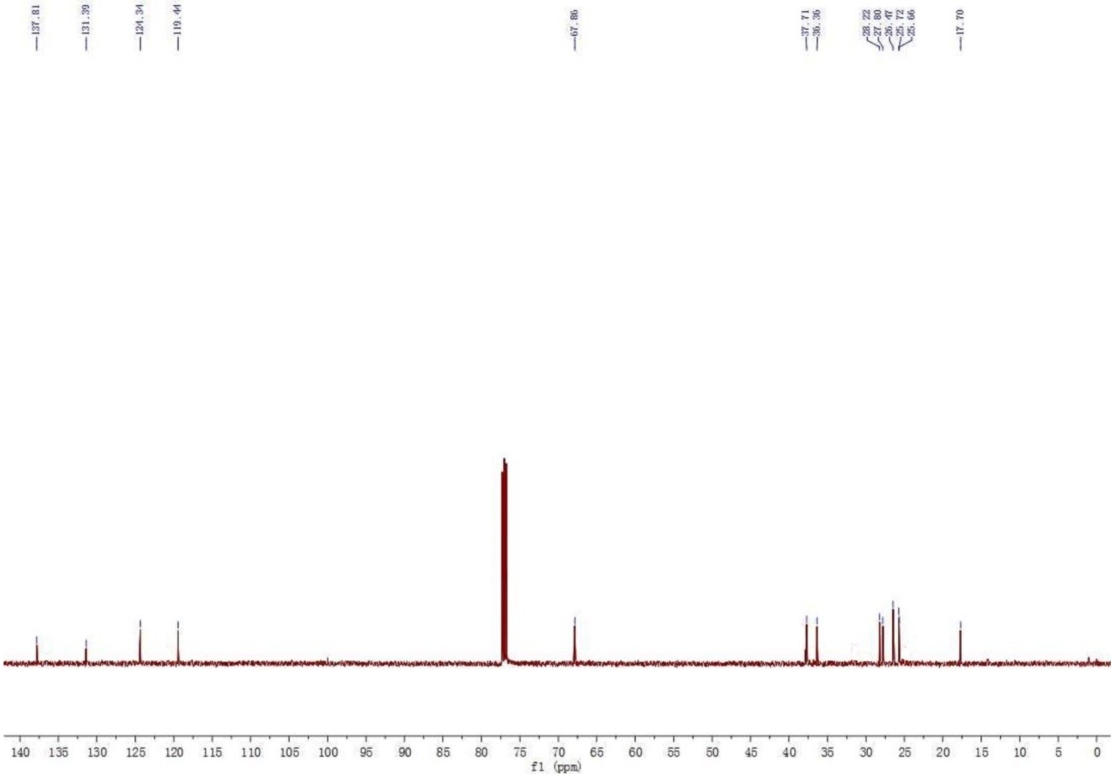
25.46
19.53
17.66
f1 (ppm)

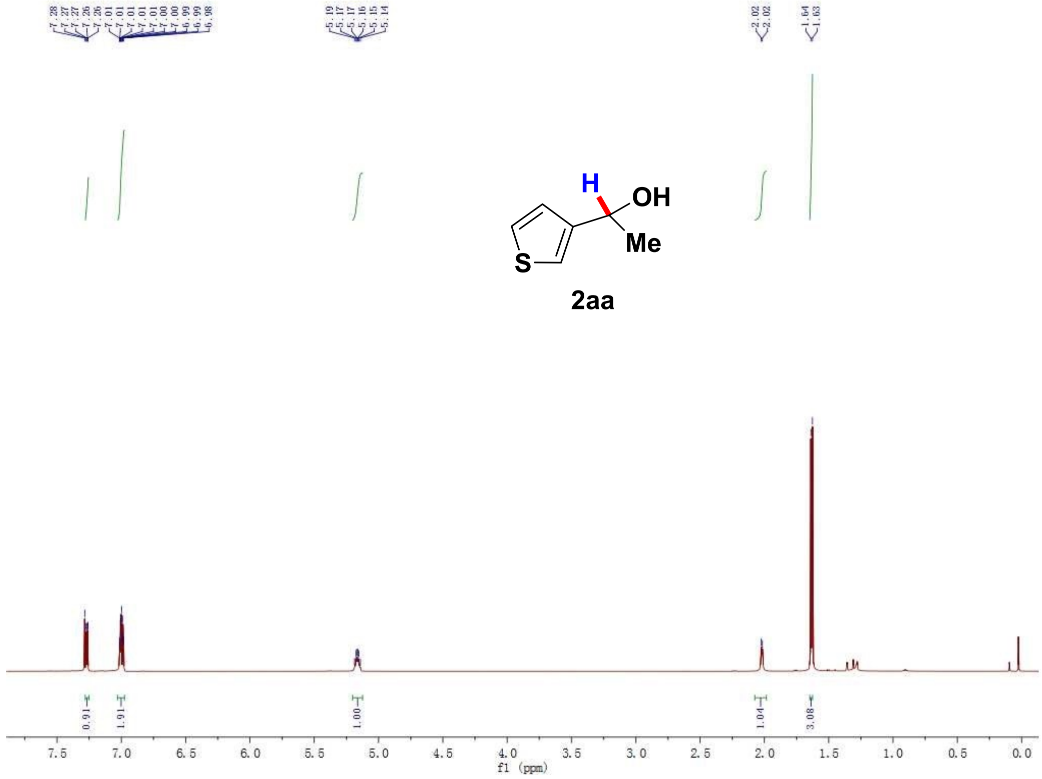




2z



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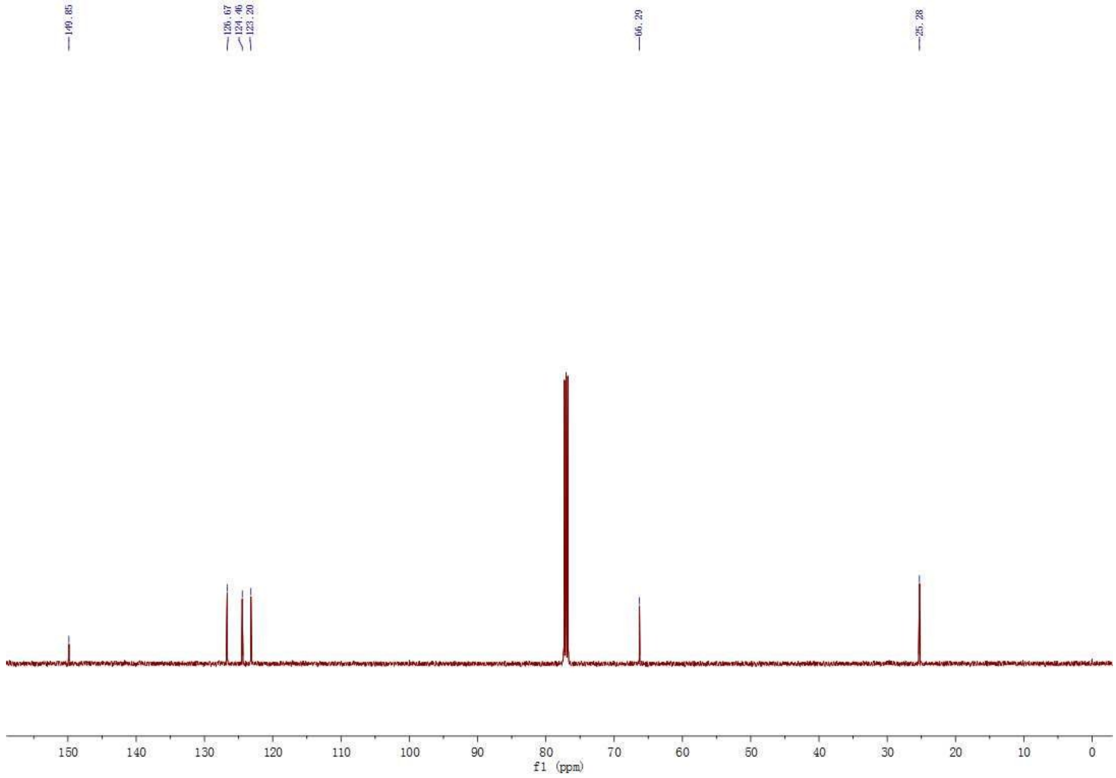
7.27
7.27
7.26
7.26
7.01
7.01
7.01
7.01
7.00
6.99
6.99
6.98
5.19
5.17
5.17
5.16
5.15
5.14
2.02
2.02
1.64
1.63
H
OH
Me
S
2aa
0.91
1.91
1.00
1.04
3.08
f1 (ppm)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126.67
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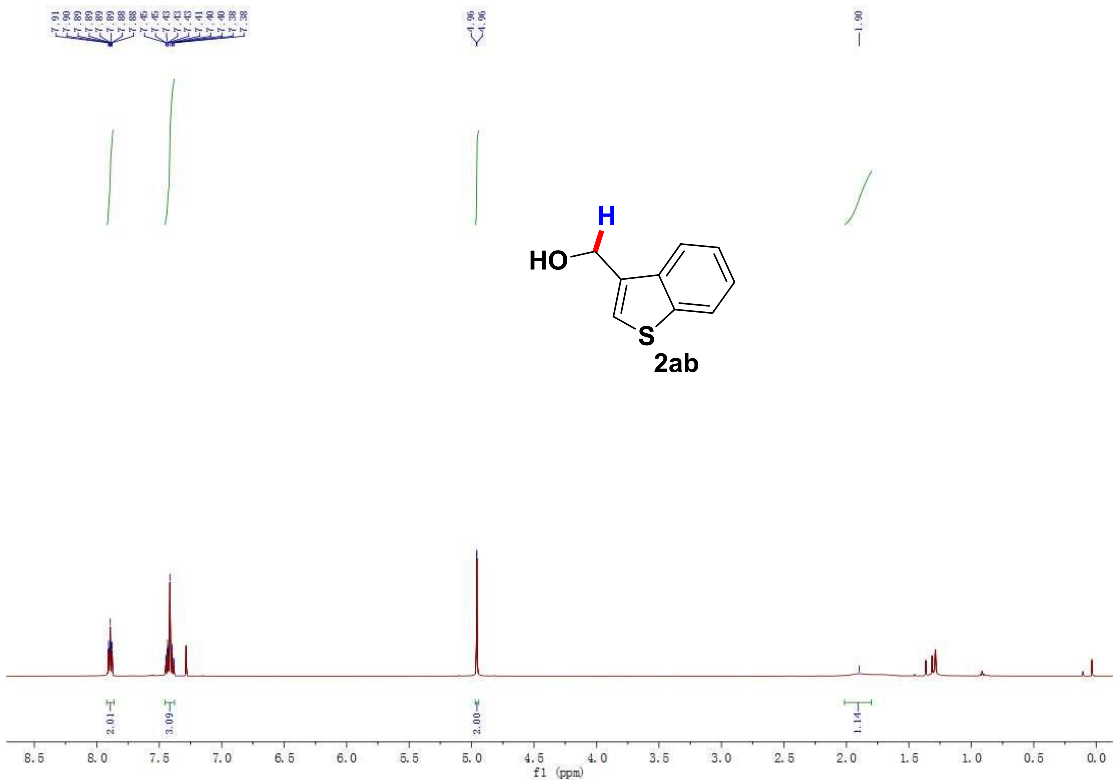
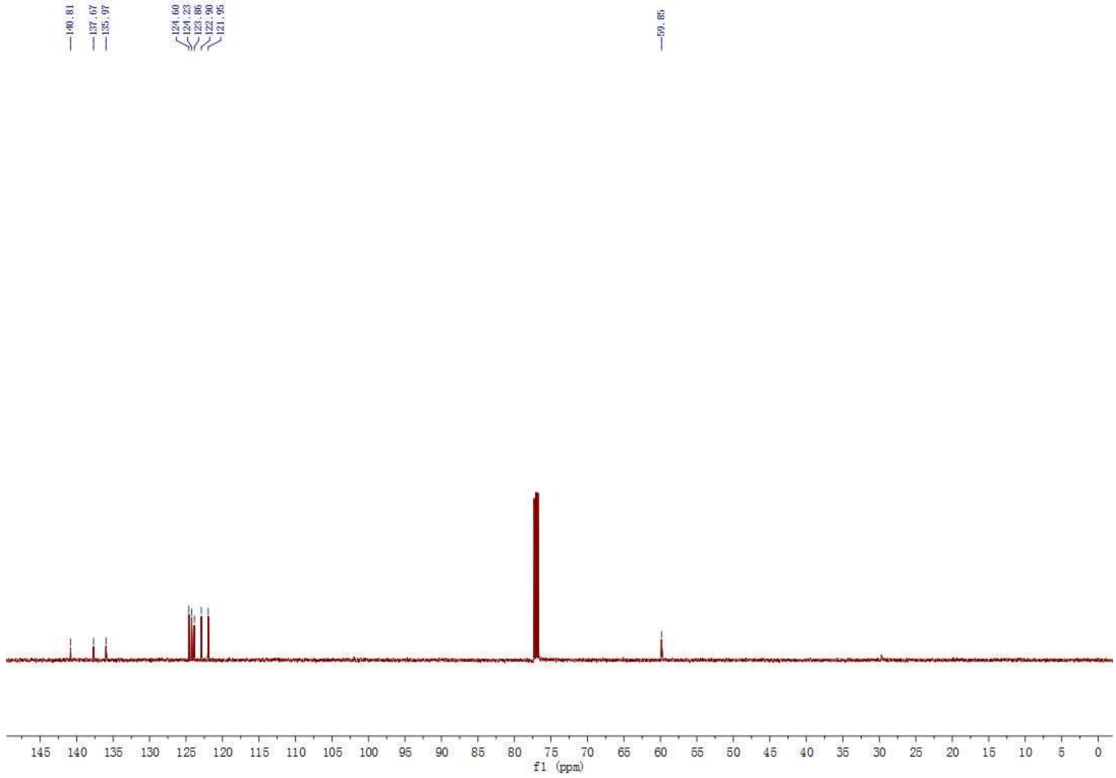
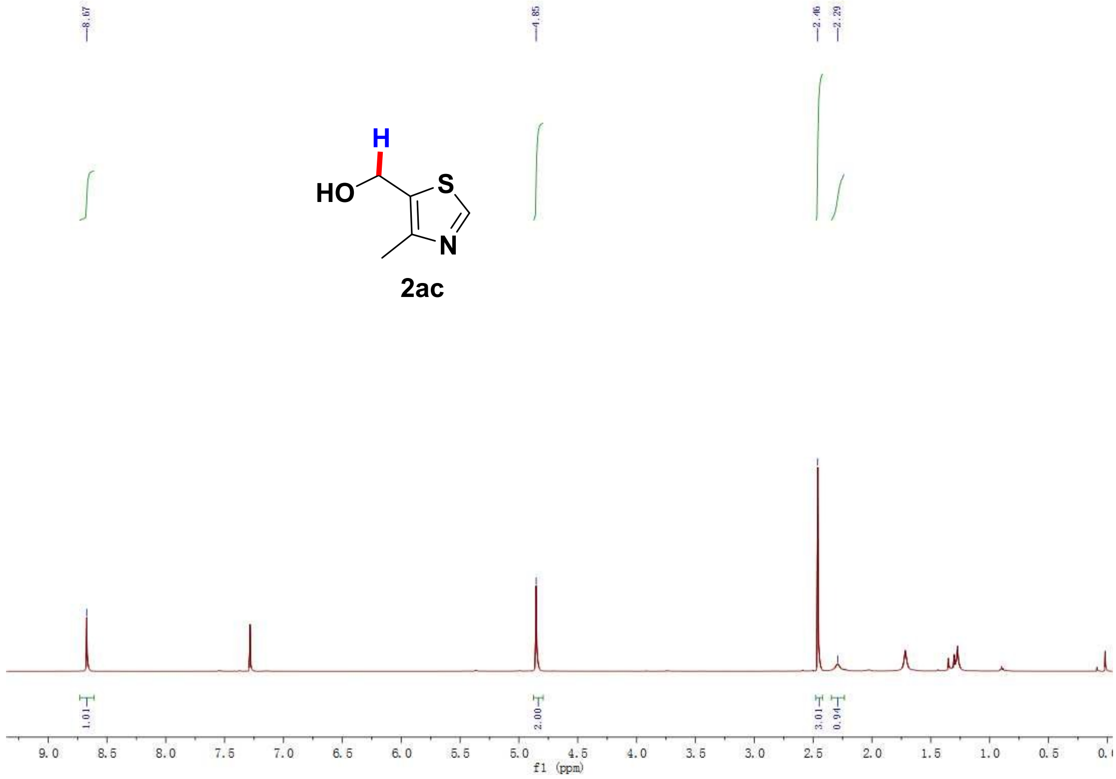
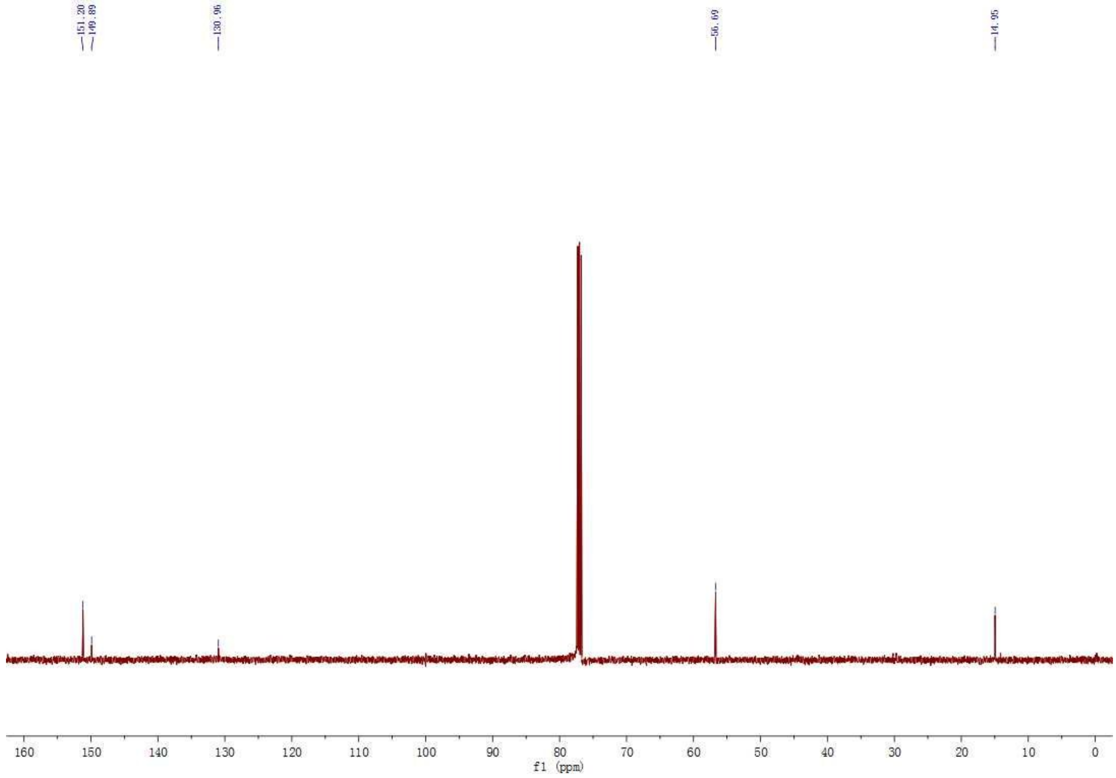
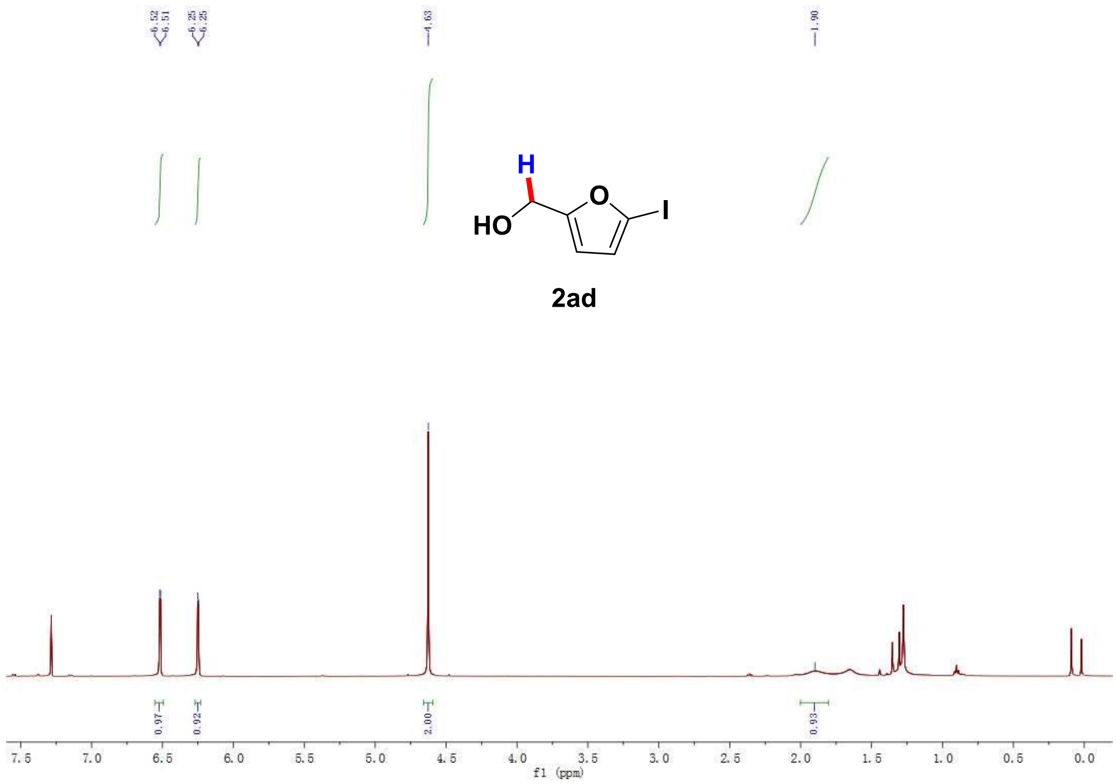
f1 (ppm)


7.91 7.90 7.89 7.89 7.89 7.89 7.88 7.45 7.45 7.43 7.43 7.41 7.40 7.40 7.38 7.38
4.96 4.96
1.90
HO
H
S
2ab
2.01
3.09
2.00
1.14
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


140.81 137.67 135.97
124.60 124.23 123.86 122.90 121.95
59.85
145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0
f1 (ppm)

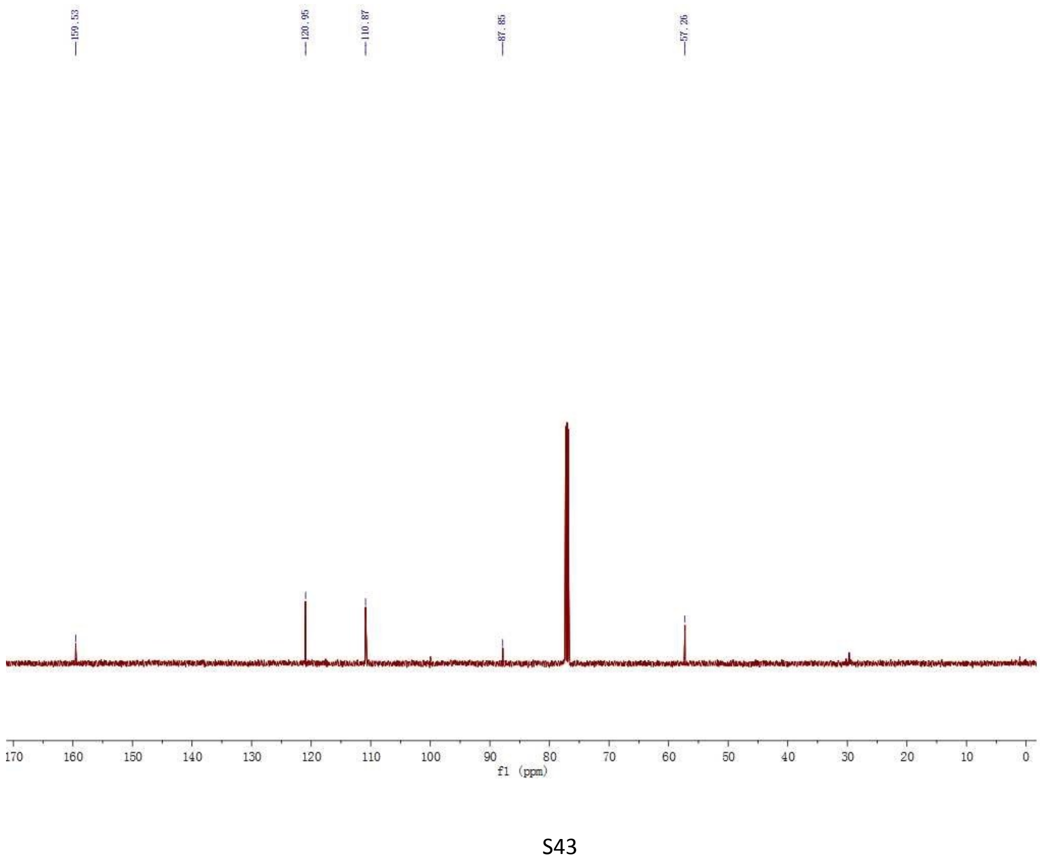

8.67
4.85
2.46
2.29
HO
H
S
N
2ac
1.01
2.00
3.01
0.94
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


151.20
149.89
130.96
56.69
14.95
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

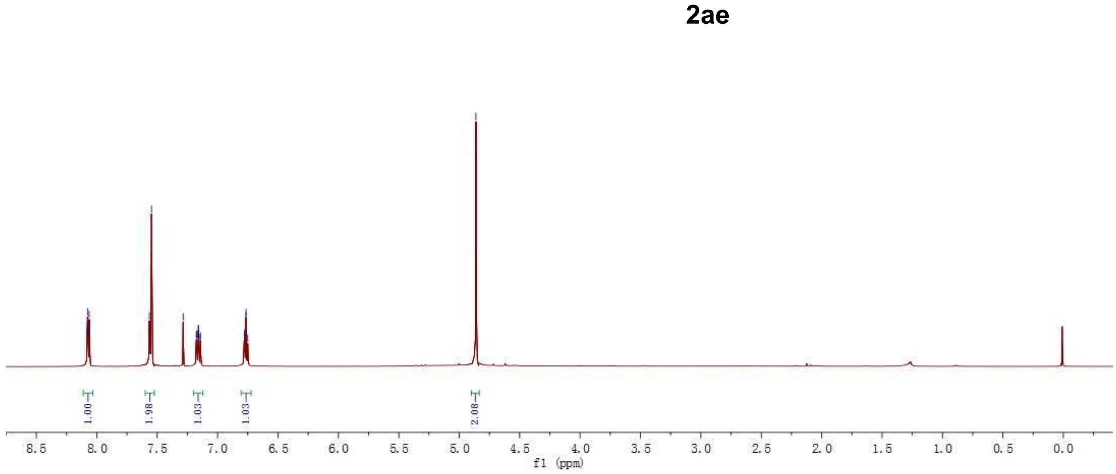


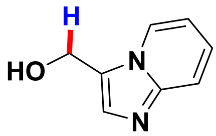
6.52
6.51
6.25
6.25
4.63
1.90
HO
O
I
H
0.97
0.92
2.00
0.93
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

2ad



159.53
120.95
110.87
87.85
57.26
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)





2ae