Red-Light-Induced Highly Efficient Aerobic Oxidation of Organoboron Compounds Using Spinach as Photocatalyst

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Supporting Information

1. General methods

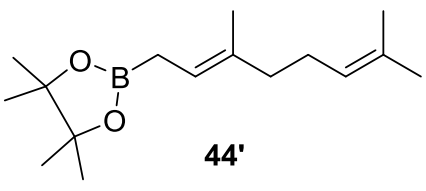
^{1}H NMR or ^{13}C NMR spectra were recorded on Agilent 600 or 150 MHz NMR spectrometer, respectively (Chemical shifts were reported in ppm from tetramethylsilane with the solvent resonance as the internal standard in $CDCl_3$ solution, unless otherwise noted). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, td = triple doublet, dt = double triplet, m = multiplet, and coupling constants (*J*) are reported in Hertz (Hz). ESI-HRMS was recorded on a Waters SYNAPT G2. Column chromatography was performed on silica gel (300-400 mesh) eluting with ethyl acetate and petroleum ether or dichloromethane (CH_2Cl_2)/methanol (MeOH). TLC was performed on glass-backed silica plates. UV light, I_2, cerium molybdate, phosphomolybdic acid and $KMnO_4$ were used to visualize products or the starting materials. All chemicals were used without purification as commercially available unless otherwise noted. Petroleum ether (60–90 °C) was redistilled. Unless otherwise noted, all reactions were carried out under ambient atmosphere.

2. General procedure for extraction of chlorophyll

Fresh spinach leaves was simply removed from the excess water, and was chopped into the wall breaker along with a small amount of calcium carbonate. Added an appropriate amount of ethanol, and then turned on the wall breaker for juice extraction. Added petroleum ether to extract the spinach juice and filtered to remove the residue. The crude extract was then quickly passed through the column with 100-200 mesh silica gel to collect the dark green band, which was subsequently concentrated to obtain chlorophyll as photocatalyst.

3. General procedure for preparation of organoborons

Most of the arylboronic acid reported in this paper was commercially available from bidepharmatech®. Other substrates were prepared according to reported methods.[1-4] ^{1}H and ^{13}C NMR spectra data for the reported ones showed good agreement with the literature data. Belows are summarized characterization data for the newly synthesized organoboron.



44'

(*E*)-2-(3,7-dimethylocta-2,6-dien-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

^{1}H NMR (600 MHz, $CDCl_3$) δ 5.26–5.19 (t, 1H), 5.07 (td, *J* = 6.1, 5.4, 3.4 Hz, 1H), 2.03 (t, *J* = 7.2 Hz, 2H), 1.97 (dd, *J* = 9.1, 6.2 Hz, 2H), 1.64 (d, *J* = 1.8 Hz, 3H), 1.60–1.51 (m, 8H), 1.21 (s, 12H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 134.9, 130.9, 124.4, 118.5, 82.9, 39.7, 26.8, 25.6, 24.7, 17.6, 15.8.

4. General procedure for photooxidation of organoborons

General procedure (**GP**): Organoborons (0.2 mmol, 1.0 equiv), chlorophyll (0.004 mmol, 2.0 mol%) and Et_3N (0.2 mmol, 1.0 equiv) were dissolved with anhydrous ethanol (2.0 mL) in a transparent reaction tube. Then, the reaction mixture was stirred and irradiated by 30 W red LEDs at room temperature under air atmosphere for 12-24 h (**Figure S1**). After completion, the solvent was removed under reduced pressure and the residue was purified by flash column chromatography on silica gel to afford the products.

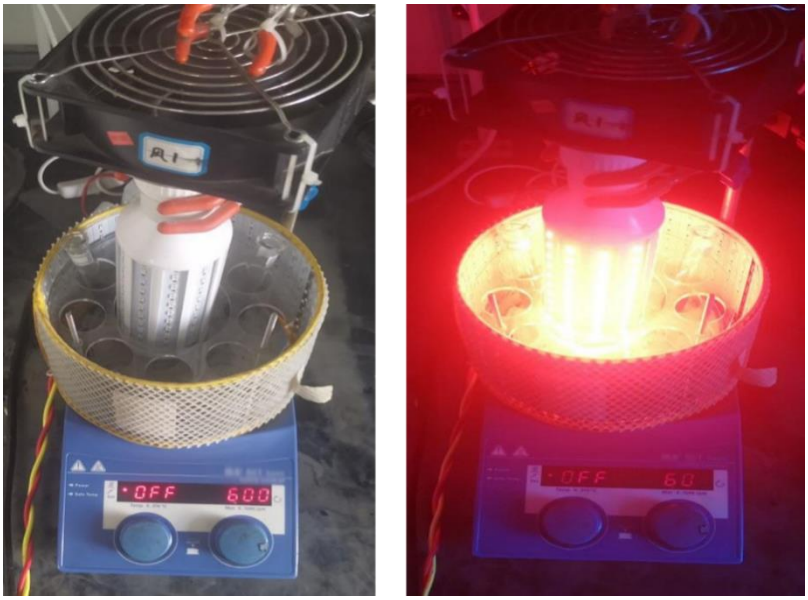
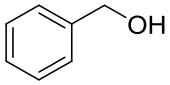


Figure S1 Reaction setup (30 W red LEDs)



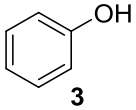
2

Phenylmethanol

According to **GP** with 2-benzyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (43.6 mg, 0.2 mmol, 1.0 equiv), chlorophyll (4.0 mg, 0.004mmol, 2.0 mol%), and Et_3N (28.0 μL, 0.2 mmol, 1.0 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 10/1) to afford the

desired product **2** as yellow oil (21.3 mg, 99%).

According to **GP** with potassium benzyltrifluoroborate (39.6 mg, 0.2 mmol, 1.0 equiv), chlorophyll (4.0 mg, 0.004 mmol, 2.0 mol%), and Et_3N (28.0 μL, 0.2 mmol, 1.0 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 10/1) to afford the desired product **2** as yellow oil (5.1 mg, 70%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.39–7.34 (m, 4H), 7.32–7.28 (m, 1H), 4.64 (s, 2H), 2.37 (s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 140.9, 128.5, 127.6, 127.0, 65.2. This characterization data are in accordance with the reported literature.[2]

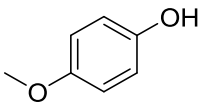


3

Phenol

According to **GP** with phenylboronic acid (24.4 mg, 0.2 mmol, 1.0 equiv), chlorophyll (4.0 mg, 0.004 mmol, 2.0 mol%), and Et_3N (28.0 μL, 0.2 mmol, 1.0 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 10/1) to afford the desired product **3** as white solid (17.1 mg, 91%).

According to **GP** with potassium trifluoro(phenyl)borate (36.8 mg, 0.2 mmol, 1.0 equiv), chlorophyll (4.0 mg, 0.004 mmol, 2.0 mol%), and Et_3N (28.0 μL, 0.2 mmol, 1.0 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 10/1) to afford the desired product **3** as white solid (17.8 mg, 95%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.28–7.22 (m, 2H), 6.95 (t, J = 7.4 Hz, 1H), 6.85 (d, J = 7.7 Hz, 2H), 5.00 (s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 155.4, 129.7, 129.7, 129.7, 120.9, 115.3. This characterization data are in accordance with the reported literature.[2]

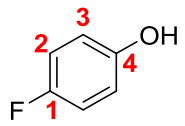


4

4-Methoxyphenol

According to **GP** with (4-methoxyphenyl)boronic acid (30.4 mg, 0.2 mmol, 1.0 equiv), chlorophyll (4.0 mg, 0.004 mmol, 2.0 mol%), and Et_3N (28.0 μL, 0.2 mmol, 1.0 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 15/1) to afford the desired product **4** as white solid (23.5 mg, 95%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.83–6.74 (m, 4H), 4.69 (s,

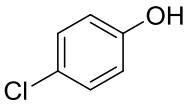
1H), 3.77 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 153.7, 149.4, 116.0, 114.8, 55.7. This characterization data are in accordance with the reported literature.[5]



5

4-Fluorophenol

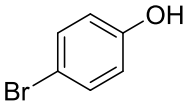
According to **GP** with (4-fluorophenyl)boronic acid (28 mg, 0.2 mmol, 1.0 equiv), chlorophyll (4.0 mg, 0.004 mmol, 2.0 mol%), and Et_3N (28.0 μL, 0.2 mmol, 1.0 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 20/1) to afford the desired product **5** as yellow oil (22.1 mg, 99%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.93 (t, J = 8.6 Hz, 2H), 6.80–6.73 (m, 2H), 4.91 (d, J = 30.8 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 157.2 (d, $^1J_{C\text{-}F}$ = 238.0 Hz), 151.4, 116.2 (d, $^3J_{C\text{-}F}$ = 8.1 Hz), 115.9 (d, $^2J_{C\text{-}F}$ = 23.4 Hz). This characterization data are in accordance with the reported literature.[6]



6

4-Chlorophenol

According to **GP** with (4-chlorophenyl)boronic acid (31.2 mg, 0.2 mmol, 1.0 equiv), chlorophyll (4.0 mg, 0.004 mmol, 2.0 mol%), and Et_3N (28.0 μL, 0.2 mmol, 1.0 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 20/1) to afford the desired product **6** as yellow oil (22.7 mg, 89%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.19 (d, J = 8.8 Hz, 2H), 6.77 (d, J = 8.9 Hz, 2H), 5.32 (s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 154.1, 129.4, 125.6, 116.6. This characterization data are in accordance with the reported literature.[7]

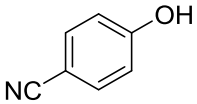


7

4-Bromophenol

According to **GP** with (4-bromophenyl)boronic acid (40.0 mg, 0.2 mmol, 1.0 equiv), chlorophyll (4.0 mg, 0.004 mmol, 2.0 mol%), and Et_3N (28.0 μL, 0.2 mmol, 1.0 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 20/1) to afford the desired product **7** as

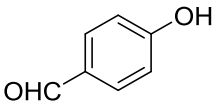
yellow oil (32.6 mg, 95%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.33 (d, *J* = 8.9 Hz, 2H), 6.72 (d, *J* = 8.9 Hz, 2H), 4.99 (s, 1H).^{13}C NMR (150 MHz, $CDCl_3$) δ 154.6, 132.4, 117.1, 112.8. This characterization data are in accordance with the reported literature.[8]



8

4-Hydroxybenzonitrile

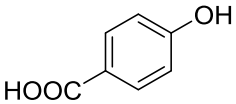
According to **GP** with (4-cyanophenyl)boronic acid (29.4 mg, 0.2 mmol, 1.0 equiv), chlorophyll (4.0 mg, 0.004 mmol, 2.0 mol%), and Et_3N (28.0 μL, 0.2 mmol, 1.0 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 10/1) to afford the desired product **8** as white solid (23.0 mg, 97%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.54 (d, *J* = 2.2 Hz, 2H), 7.06 (s, 1H), 6.93 (d, *J* = 2.2 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 160.3, 134.2, 119.2, 116.4, 102.7. This characterization data are in accordance with the reported literature.[9]



9

4-Hydroxybenzaldehyde

According to **GP** with (4-formylphenyl)boronic acid (30 mg, 0.2 mmol, 1.0 equiv), chlorophyll (4.0 mg, 0.004 mmol, 2.0 mol%), and Et_3N (28.0 μL, 0.2 mmol, 1.0 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 10/1) to afford the desired product **9** as yellow solid (24.1 mg, 99%). ^{1}H NMR (600 MHz, DMSO-d^6) δ 10.60 (s, 1H), 9.79 (s, 1H), 7.76 (d, *J* = 8.8 Hz, 2H), 6.93 (d, *J* = 8.5 Hz, 2H). ^{13}C NMR (150 MHz, DMSO-d^6) δ 191.4, 163.8, 132.6, 128.9, 116.3. This characterization data are in accordance with the reported literature.[2]

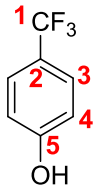


10

4-hydroxybenzoic acid

According to **GP** with 4-boronobenzoic acid (33.2 mg, 0.2 mmol, 1.0 equiv), Chlorophyll (4.0 mg, 0.004 mmol, 2.0 mol%), and Et_3N (28.0 μL, 0.2 mmol, 1.0 equiv). The crude reaction mixture was purified by flash silica gel column

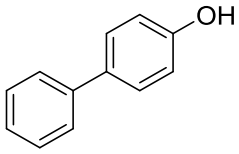
chromatography (petroleum ether/EtOAc = 10/1) to afford the desired product **10** as white solid (25.4 mg, 92%). ^{1}H NMR (600 MHz, DMSO-d6) δ 12.46 (s, 1H), 10.25 (s, 1H), 7.79 (d, *J* = 8.8 Hz, 2H), 6.82 (d, *J* = 8.8 Hz, 2H). ^{13}C NMR (150 MHz, DMSO-d6) δ 167.6, 162.0, 131.9, 121.7, 115.5. This characterization data are in accordance with the reported literature.[10]



11

4-(trifluoromethyl)phenol

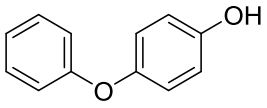
According to **GP** with (4-(trifluoromethyl)phenyl)boronic acid (38 mg, 0.2 mmol, 1.0 equiv), chlorophyll (4.0 mg, 0.004 mmol, 2.0 mol%), and Et_3N (28.0 μL, 0.2 mmol, 1.0 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 10/1) to afford the desired product **11** as yellow solid (32 mg, 99%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.51 (d, *J* = 8.4 Hz, 2H), 6.90 (d, *J* = 8.3 Hz, 2H), 5.25 (s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 158.1, 127.1 (q, $^{3}J_{C\text{-}F}$ = 3.6 Hz), 124.3 (q, $^{1}J_{C\text{-}F}$ = 271.1 Hz), 123.2 (q, $^{2}J_{C\text{-}F}$ = 32.7 Hz), 115.4. This characterization data are in accordance with the reported literature.[11]



12

[1,1'-biphenyl]-4-ol

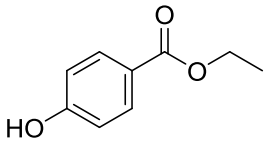
According to **GP** with [1,1'-biphenyl]-4-ylboronic acid (39.6 mg, 0.2 mmol, 1.0 equiv), chlorophyll (4.0 mg, 0.004 mmol, 2.0 mol%), and Et_3N (28.0 μL, 0.2 mmol, 1.0 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 10/1) to afford the desired product **10** as white solid (33.6 mg, 99%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.54 (d, *J* = 7.0 Hz, 2H), 7.48 (d, *J* = 8.7 Hz, 2H), 7.41 (t, *J* = 7.8 Hz, 2H), 7.31 (t, *J* = 7.4 Hz, 1H), 6.91 (d, *J* = 8.6 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 155.0, 140.7, 134.0, 128.7, 128.3, 126.7, 115.6. This characterization data are in accordance with the reported literature.[10]



13

4-phenoxyphenol

According to **GP** with (4-(phenylthio)phenyl)boronic acid (46 mg, 0.2 mmol, 1.0 equiv), chlorophyll (4.0 mg, 0.004 mmol, 2.0 mol%), and Et_3N (28.0 μL, 0.2 mmol, 1.0 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 10/1) to afford the desired product **13** as white solid (39.6 mg, 98%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.34–7.29 (m, 2H), 7.06 (t, *J* = 7.9 Hz, 1H), 6.99–6.92 (m, 4H), 6.83 (d, *J* = 9.0 Hz, 2H), 5.19 (s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 158.3, 151.6, 150.2, 129.6, 122.5, 121.0, 117.6, 116.3. This characterization data are in accordance with the reported literature.[10]



14

ethyl 4-hydroxybenzoate

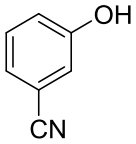
According to **GP** with (4-(ethoxycarbonyl)phenyl)boronic acid (38.8 mg, 0.2 mmol, 1.0 equiv), chlorophyll (4.0 mg, 0.004 mmol, 2.0 mol%), and Et_3N (28.0 μL, 0.2 mmol, 1.0 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 10/1) to afford the desired product **14** as white solid (32 mg, 98%).

According to **GP** with ethyl 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoate (55.2 mg, 0.2 mmol, 1.0 equiv), chlorophyll (4.0 mg, 0.004 mmol, 2.0 mol%), and Et_3N (28.0 μL, 0.2 mmol, 1.0 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 10/1) to afford the desired product **14** as white solid (32 mg, 98%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.6 Hz, 2H), 7.47 (s, 1H), 6.91 (d, *J* = 8.6 Hz, 2H), 4.36 (q, *J* = 7.1 Hz, 2H), 1.38 (t, *J* = 7.1 Hz, 3H).^{13}C NMR (150 MHz, $CDCl_3$) δ 167.4, 160.7, 131.9, 122.0, 115.3, 61.1, 14.2. This characterization data are in accordance with the reported literature.[12]

15

3-bromophenol

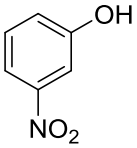
According to **GP** with (3-bromophenyl)boronic acid (39.8 mg, 0.2 mmol, 1.0 equiv), chlorophyll (4.0 mg, 0.004 mmol, 2.0 mol%), and Et_3N (28.0 μL, 0.2 mmol, 1.0 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 10/1) to afford the desired product **15** as white solid (28.2 mg, 82%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.09 (dt, *J* = 16.4, 8.1 Hz, 2H), 7.03–7.01 (m, 1H), 6.77 (d, *J* = 9.1 Hz, 1H), 5.29 (s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 156.3, 130.7, 123.9, 122.7, 118.7, 114.2. This characterization data are in accordance with the reported literature.[12]



16

3-hydroxybenzonitrile

According to **GP** with (3-cyanophenyl)boronic acid (29.4 mg, 0.2 mmol, 1.0 equiv), chlorophyll (4.0 mg, 0.004 mmol, 2.0 mol%), and Et_3N (28.0 μL, 0.2 mmol, 1.0 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 10/1) to afford the desired product **16** as white solid (22.3 mg, 94%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.32 (t, *J* = 8.0 Hz, 1H), 7.23–7.19 (m, 1H), 7.16–7.13 (m, 1H), 7.10 (ddd, *J* = 8.3, 2.5, 0.9 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 156.3, 130.6, 124.4, 120.8, 118.7, 118.6, 112.6. This characterization data are in accordance with the reported literature.[10]

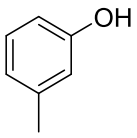


17

3-nitrophenol

According to **GP** with (3-nitrophenyl)boronic acid (33.4 mg, 0.2 mmol, 1.0 equiv), chlorophyll (4.0 mg, 0.004 mmol, 2.0 mol%), and Et_3N (28.0 μL, 0.2 mmol, 1.0 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 10/1) to afford the desired product **17** as

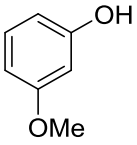
white solid (26.1 mg, 94%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.81 (ddd, *J* = 8.1, 2.1, 0.9 Hz, 1H), 7.70 (t, *J* = 2.3 Hz, 1H), 7.41 (t, *J* = 8.1 Hz, 1H), 7.18 (ddd, *J* = 8.2, 2.5, 0.8 Hz, 1H), 5.71 (s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 156.3, 149.1, 130.2, 121.9, 115.8, 110.5. This characterization data are in accordance with the reported literature.[11]



18

***m*-cresol**

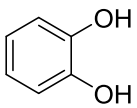
According to **GP** with m-tolylboronic acid (27.2 mg, 0.2 mmol, 1.0 equiv), chlorophyll (4.0 mg, 0.004 mmol, 2.0 mol%), and Et_3N (28.0 μL, 0.2 mmol, 1.0 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 10/1) to afford the desired product **18** as white solid (19.4 mg, 90%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.16 (t, *J* = 7.7 Hz, 1H), 6.80 (d, *J* = 7.5 Hz, 1H), 6.70 (d, *J* = 11.9 Hz, 2H), 5.68 (s, 1H), 2.33 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 155.2, 139.9, 129.5, 121.7, 116.1, 112.3, 21.3. This characterization data are in accordance with the reported literature.[13]



19

3-methoxyphenol

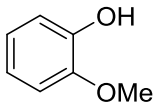
According to **GP** with (3-methoxyphenyl)boronic acid (30.4mg, 0.2 mmol, 1.0 equiv), chlorophyll (4.0 mg, 0.004 mmol, 2.0 mol%), and Et_3N (28.0 μL, 0.2 mmol, 1.0 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 10/1) to afford the desired product **19** as white solid (22.5 mg, 91%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.14 (t, *J* = 8.1 Hz, 1H), 6.51 (ddd, *J* = 8.3, 2.3, 0.9 Hz, 1H), 6.46–6.42 (m, 2H), 5.52 (s, 1H), 3.78 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ160.8, 156.6, 130.1, 107.8, 106.4, 101.5, 55.2. This characterization data are in accordance with the reported literature.[11]



20

Pyrocatechol

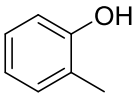
According to **GP** with (2-hydroxyphenyl)boronic acid (27.6mg, 0.2 mmol, 1.0 equiv), chlorophyll (4.0 mg, 0.004 mmol, 2% mol), and Et_3N (28.0 μL, 0.2 mmol, 1.0 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 10/1) to afford the desired product **20** as white solid (15.4 mg, 70%). ^{1}H NMR (600 MHz, DMSO-d^6) δ 8.83 (s, 2H), 6.74 (dt, J = 7.4, 3.7 Hz, 2H), 6.60 (dq, J = 7.3, 3.7 Hz, 2H). ^{13}C NMR (150 MHz, DMSO-d^6) δ 150.4, 124.5, 120.9. This characterization data are in accordance with the reported literature.[14]



21

2-methoxyphenol

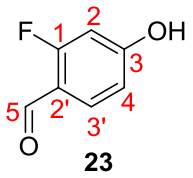
According to **GP** with (2-methoxyphenyl)boronic acid (30.4mg, 0.2 mmol, 1.0 equiv), chlorophyll (4.0 mg, 0.004 mmol, 2.0 mol%), and Et_3N (28.0 μL, 0.2 mmol, 1.0 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 10/1) to afford the desired product **21** as white solid (17.3 mg, 70%).^{1}H NMR (600 MHz, $CDCl_3$) δ 6.95 (d, J = 6.8 Hz, 1H), 6.88 (d, J = 7.2 Hz, 3H), 5.69 (s, 1H), 3.89 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 146.6, 145.6, 121.4, 120.2, 114.5, 110.7, 77.3, 77.1, 76.8, 55.9. This characterization data are in accordance with the reported literature.[11]



22

o-cresol

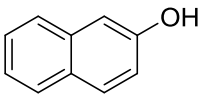
According to **GP** with o-tolylboronic acid (27.2mg, 0.2 mmol, 1.0 equiv), chlorophyll (4.0 mg, 0.004 mmol, 2.0 mol%), and Et_3N (28.0 μL, 0.2 mmol, 1.0 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 10/1) to afford the desired product **22** as white solid (21.5 mg, 99%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.15 (d, J = 7.4 Hz, 1H), 7.11 (t, J = 7.7 Hz, 1H), 6.88 (t, J = 7.4 Hz, 1H), 6.79 (d, J = 8.0 Hz, 1H), 4.96 (s, 1H), 2.28 (s, 3H).^{13}C NMR (150 MHz, $CDCl_3$) δ 153.7, 131.0, 127.1, 123.8, 120.7, 114.9, 15.7. This characterization data are in accordance with the reported literature.[9]



23

2-fluoro-4-hydroxybenzaldehyde

According to **GP** with (3-fluoro-4-formylphenyl)boronic acid (33.6mg, 0.2 mmol, 1.0 equiv), chlorophyll (4.0 mg, 0.004 mmol, 2.0 mol%), and Et_3N (28.0 μL, 0.2 mmol, 1.0 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 10/1) to afford the desired product **23** as white solid (19.3 mg, 69%). ^{1}H NMR (600 MHz, DMSO-d^6) δ 9.98 (s, 1H), 7.67 (t, J = 8.5 Hz, 1H), 6.74 (dd, J = 8.7, 2.2 Hz, 1H), 6.64 (dd, J = 12.9, 2.3 Hz, 1H). ^{13}C NMR (150 MHz, DMSO-d^6) δ 186.2 (d, $^5J_{C\text{-}F}$ = 4.5 Hz), 165.7 (d, $^1J_{C\text{-}F}$ = 255.0 Hz) , 165.8 (d, $^3J_{C\text{-}F}$ = 13.5 Hz) , 131.4 (d, $^{3'}J_{C\text{-}F}$ = 4.5 Hz), 116.4 (d, $^{2'}J_{C\text{-}F}$ = 7.5 Hz), 113.2 (d, $^4J_{C\text{-}F}$ = 3.0 Hz), 103.2 (d, $^2J_{C\text{-}F}$ = 22.5 Hz). This characterization data are in accordance with the reported literature.[15]

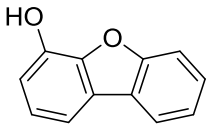


24

naphthalen-2-ol

According to **GP** with naphthalen-2-ylboronic acid (34.4 mg, 0.2 mmol, 1.0 equiv), chlorophyll (4.0 mg, 0.004 mmol, 2.0 mol%), and Et_3N (28.0 μL, 0.2 mmol, 1.0 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 10/1) to afford the desired product **24** as white solid (22.3 mg, 74%).

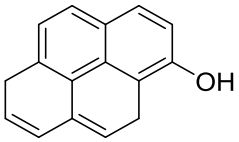
According to **GP** with 4,4,5,5-tetramethyl-2-(naphthalen-2-yl)-1,3,2-dioxaborolane (50.8 mg, 0.2 mmol, 1.0 equiv), chlorophyll (4.0 mg, 0.004 mmol, 2.0 mol%), and Et_3N (28.0 μL, 0.2 mmol, 1.0 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 10/1) to afford the desired product **24** as white solid (21 mg, 73%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.80–7.74 (m, 2H), 7.69 (d, J = 8.2 Hz, 1H), 7.44 (t, J = 7.8 Hz, 1H), 7.37–7.31 (m, 1H), 7.17–7.14 (m, 1H), 7.11 (dd, J = 8.8, 2.5 Hz, 1H), 5.05 (s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 153.3, 134.5, 129.8, 128.9, 127.7, 126.5, 126.3, 123.6, 117.7, 109.4. This characterization data are in accordance with the reported literature.[13]



25

dibenzo[*b*,*d*]furan-4-ol

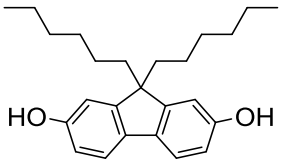
According to **GP** with dibenzo[*b*,*d*]furan-4-ylboronic acid (42.4 mg, 0.2 mmol, 1.0 equiv), chlorophyll (4.0 mg, 0.004 mmol, 2.0 mol%), and Et_3N (28.0 μL, 0.2 mmol, 1.0 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 10/1) to afford the desired product **25** as white solid (25 mg, 68%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.94 (d, *J* = 7.7 Hz, 1H), 7.59 (d, *J* = 8.2 Hz, 1H), 7.53 (d, *J* = 7.5 Hz, 1H), 7.47 (t, *J* = 7.8 Hz, 1H), 7.36 (t, *J* = 7.4 Hz, 1H), 7.23 (t, *J* = 7.8 Hz, 1H), 7.03 (d, *J* = 7.8 Hz, 1H), 5.47 (s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 156.0, 144.0, 141.1, 127.2, 125.7, 124.5, 123.6, 122.9, 121.0, 113.5, 112.8, 111.7. This characterization data are in accordance with the reported literature.[2]



26

6,10-dihydropyren-1-ol

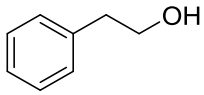
According to **GP** with (6,10-dihydropyren-1-yl)boronic acid (49.6 mg, 0.2 mmol, 1.0 equiv), chlorophyll (4.0 mg, 0.004 mmol, 2.0 mol%), and Et_3N (28.0 μL, 0.2 mmol, 1.0 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 10/1) to afford the desired product **26** as white solid (43.1 mg, 98%). ^{1}H NMR (600 MHz, DMSO-d6) δ 10.65 (s, 1H), 8.34 (d, *J* = 9.1 Hz, 1H), 8.12 (t, *J* = 7.3 Hz, 3H), 8.02 (dd, *J* = 18.3, 9.0 Hz, 2H), 7.96 (t, *J* = 7.6 Hz, 1H), 7.89 (d, *J* = 8.8 Hz, 1H), 7.60 (d, *J* = 8.3 Hz, 1H). ^{13}C NMR (150 MHz, DMSO-d6) δ 152.1, 131.3, 131.2, 127.3, 126.1, 126.1, 125.4, 125.4, 124.4, 123.8, 123.7, 123.5, 123.5, 121.3, 118.0, 113.2. This characterization data are in accordance with the reported literature.[16]



27

9,9-dihexyl-9*H*-fluorene-2,7-diol

According to **GP** with (9,9-dihexyl-9*H*-fluorene-2,7-diyl)diboronic acid (84.4 mg, 0.2 mmol, 1.0 equiv), The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 10/1) to afford the desired product **27** as white solid (68 mg, 93%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.43 (d, *J* = 8.0 Hz, 2H), 6.80–6.72 (m, 4H), 4.81 (s, 2H), 1.89–1.83 (m, 4H), 1.12 (q, *J* = 7.0 Hz, 4H), 1.08–1.00 (m, 8H), 0.77 (t, *J* = 7.3 Hz, 6H), 0.63 (dtd, *J* = 14.2, 7.1, 4.1 Hz, 4H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 154.4, 152.3, 134.2, 119.5, 113.7, 110.0, 54.9, 40.6, 31.52, 29.7, 23.6, 22.5, 13.9.HRMS (ESI) calculated for $C_{25}H_{34}O_2$ $[M+K]^+$ m/z 389.2451, found 389.2449.



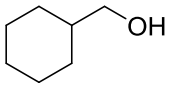
28

2-Phenylethanol

According to **GP** with 4,4,5,5-tetramethyl-2-phenethyl-1,3,2-dioxaborolane (46.4 mg, 0.2 mmol, 1.0 equiv), chlorophyll (4.0 mg, 0.004 mmol, 2.0 mol%), and Et_3N (28.0 μL, 0.2 mmol, 1.0 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 10/1) to afford the desired product **28** as yellow oil (21.9 mg, 90%).

According to **GP** with phenethylboronic acid (30.0 mg, 0.2mmol, 1.0 equiv), chlorophyll (4.0 mg, 0.004 mmol, 2.0 mol%), and Et_3N (28.0 μL, 0.2 mmol, 1.0 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 10/1) to afford the desired product **28** as white solid (21.9 mg, 90%).

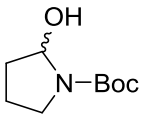
According to **GP** with potassium trifluoro(phenethyl)borate (42.4 mg, 0.2 mmol, 1.0 equiv), chlorophyll (4.0 mg, 0.004 mmol, 2.0 mol%), and Et_3N (28.0 μL, 0.2 mmol, 1.0 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 10/1) to afford the desired product **28** as yellow oil (19.5 mg, 80%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.34–7.30 (m, 2H), 7.26–7.22 (m, 3H), 3.87 (t, *J* = 6.6 Hz, 2H), 2.88 (t, *J* = 6.6 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 138.4, 129.0, 128.5, 126.4, 63.6, 39.1. This characterization data are in accordance with the reported literature.[2]



29

Cyclohexylmethanol

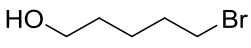
According to **GP** with (cyclohexylmethyl)boronic acid (28.4 mg, 0.2 mmol, 1.0 equiv), chlorophyll (4.0 mg, 0.004 mmol, 2.0 mol%), and Et_3N (28.0 μL, 0.2 mmol, 1.0 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 10/1) to afford the desired product **29** as white solid (21.9 mg, 96%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.43 (d, *J* = 6.4 Hz, 2H), 1.74 (ddt, *J* = 16.7, 10.9, 2.5 Hz, 4H), 1.67 (dddt, *J* = 12.1, 5.4, 3.6, 1.9 Hz, 1H), 1.52–1.43 (m, 2H), 1.24 (qt, *J* = 12.3, 3.6 Hz, 2H), 1.19–1.12 (m, 1H), 0.92 (qd, *J* = 13.5, 12.7, 3.9 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 68.7, 40.4, 29.5, 26.5, 25.8. This characterization data are in accordance with the reported literature.[17]



30

***tert*-butyl 2-hydroxypyrrolidine-1-carboxylate**

According to **GP** with (1-(*tert*-butoxycarbonyl)pyrrolidin-2-yl)boronic acid (43 mg, 0.2 mmol, 1.0 equiv), chlorophyll (4.0 mg, 0.004 mmol, 2.0 mol%), and Et_3N (28.0 μL, 0.2 mmol, 1.0 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 10/1) to afford the desired product **30** as white solid (28 mg, 75%). Compound **30** is a mixture of two isomers with a *dr* value of 1:0.6. **Isomer 1**: ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.47 (dt, *J* = 5.0, 2.3 Hz, 1H), 3.71 (s, 1H), 3.47 (dt, *J* = 7.4, 4.0 Hz, 1H), 3.27–3.21 (m, 1H), 2.02–2.05 (m, 2H), 1.99–1.91 (m, 2H), 1.46 (s, 9H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 155.11, 81.73, 80.02, 45.91, 32.64, 28.43, 22.71. **Isomer 2**:^{1}H NMR (600 MHz, $CDCl_3$) δ 5.42–5.33 (m, 1H), 3.53 (ddd, *J* = 10.8, 7.9, 3.1 Hz, 1H), 3.33–3.28 (m, 1H), 2.90 (s, 1H), 1.90–1.84 (m, 2H), 1.83– .80 (m, 2H), 1.49 (s, 9H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 153.5, 81.4, 80.3, 45.7, 33.4, 28.5, 22.0. This characterization data are in accordance with the reported literature.[18]

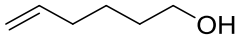


31

5-bromopentan-1-ol

According to **GP** with (5-bromopentyl)boronic acid (38.8 mg, 0.2 mmol, 1.0 equiv), chlorophyll (4.0 mg, 0.004 mmol, 2.0 mol%), and Et_3N (28.0 μL, 0.2 mmol, 1.0 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 10/1) to afford the desired product **31** as

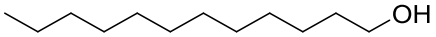
white solid (17.3mg, 52%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.66 (t, *J* = 6.4 Hz, 2H), 3.42 (t, *J* = 6.8 Hz, 2H), 1.89 (dt, *J* = 14.3, 6.8 Hz, 2H), 1.59 (dt, *J* = 13.6, 6.6 Hz, 2H), 1.55–1.48 (m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 62.5, 33.7, 32.4, 31.7, 24.4. This characterization data are in accordance with the reported literature.[19]



32

hex-5-en-1-ol

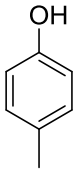
According to **GP** with hex-5-en-1-ylboronic acid (25.6 mg, 0.2 mmol, 1.0 equiv), chlorophyll (4.0 mg, 0.004 mmol, 2.0 mol%), and Et_3N (28.0 μL, 0.2 mmol, 1.0 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 10/1) to afford the desired product **32** as white solid (10.8 mg, 54%). ^{1}H NMR (600 MHz, CD_3OD) δ 5.77 (ddt, *J* = 17.0, 10.2, 6.7 Hz, 1H), 4.95 (dd, *J* = 17.1, 1.7 Hz, 1H), 4.90–4.85 (m, 1H), 3.49 (t, *J* = 6.6 Hz, 2H), 2.02 (q, *J* = 7.2 Hz, 2H), 1.52–1.46 (m, 2H), 1.43–1.37 (m, 2H). ^{13}C NMR (150 MHz, CD_3OD) δ 138.4, 113.5, 61.3, 33.2, 31.6, 24.8. This characterization data are in accordance with the reported literature.[2]



33

dodecan-1-ol

According to **GP** with dodecylboronic acid (42.8 mg, 0.2 mmol, 1.0 equiv), chlorophyll (4.0 mg, 0.004 mmol, 2.0 mol%), and Et_3N (28.0 μL, 0.2 mmol, 1.0 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 10/1) to afford the desired product **33** as white solid (30.4 mg, 76%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.62 (t, *J* = 6.7 Hz, 2H), 1.59–1.51 (m, 2H), 1.46 (s, 1H), 1.36–1.19 (m, 18H), 0.87 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 63.0, 32.7, 31.8, 29.6, 29.6, 29.5, 29.5, 29.4, 29.3, 25.7, 22.6, 14.0. This characterization data are in accordance with the reported literature.[20]



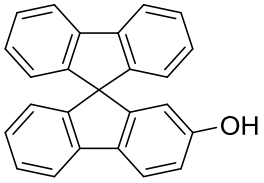
34

***p*-cresol**

According to **GP** with 4,4,5,5-tetramethyl-2-(p-tolyl)-1,3,2-dioxaborolane (43.6 mg, 0.2 mmol, 1.0 equiv), chlorophyll (4.0 mg, 0.004 mmol, 2.0 mol%), and Et_3N

(28.0 μL, 0.2 mmol, 1.0 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 10/1) to afford the desired product **34** as white solid (17.2 mg, 80%).

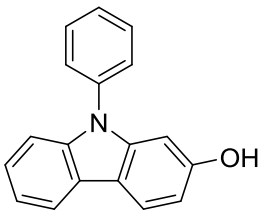
According to **GP** with 5,5-dimethyl-2-(*p*-tolyl)-1,3,2-dioxaborinane (40.8 mg, 0.2 mmol, 1.0 equiv), chlorophyll (4.0 mg, 0.004 mmol, 2.0 mol%), and Et_3N (28.0 μL, 0.2 mmol, 1.0 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 10/1) to afford the desired product **34** as white solid (17.2 mg, 80%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.05 (d, *J* = 8.1 Hz, 2H), 6.75 (d, *J* = 8.4 Hz, 2H), 5.04 (s, 1H), 2.29 (s, 3H).^{13}C NMR (150 MHz, $CDCl_3$) δ 153.1, 130.0, 130.0, 115.0, 20.4. The characterization data are in accordance with the reported literature.[10]



35

9,9'-spirobi[fluoren]-2-ol

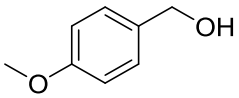
According to **GP** with 2-(9,9'-spirobi[fluoren]-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (88.4 mg, 0.2 mmol, 1.0 equiv), chlorophyll (4.0 mg, 0.004 mmol, 2.0 mol%), and Et_3N (28.0 μL, 0.2 mmol, 1.0 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 10/1) to afford the desired product **35** as white solid (59.7 mg, 90%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.84 (dt, *J* = 7.7, 0.9 Hz, 2H), 7.74 (dt, *J* = 7.8, 0.9 Hz, 1H), 7.70 (d, *J* = 8.3 Hz, 1H), 7.35 (dtd, *J* = 20.6, 7.5, 1.1 Hz, 3H), 7.12 (td, *J* = 7.5, 1.1 Hz, 2H), 7.04 (td, *J* = 7.5, 1.1 Hz, 1H), 6.84 (dd, *J* = 8.3, 2.4 Hz, 1H), 6.76 (dt, *J* = 7.6, 0.9 Hz, 2H), 6.70 (dt, *J* = 7.6, 0.9 Hz, 1H), 6.17 (d, *J* = 2.4 Hz, 1H), 4.71 (s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 155.6, 150.8, 148.8, 148.1, 141.6, 141.6, 134.7, 127.8, 127.7, 127.7, 126.6, 124.1, 123.8, 120.9, 119.9, 119.1, 115.0, 111.0, 65.7. The characterization data are in accordance with the reported literature.[21]



36

9-phenyl-9*H*-carbazol-2-ol

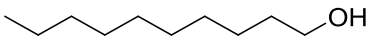
According to **GP** with 9-phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9*H*-carbazole (73.8 mg, 0.2 mmol, 1.0 equiv), chlorophyll (4.0 mg, 0.004 mmol, 2.0 mol%), and Et_3N (28.0 μL, 0.2 mmol, 1.0 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 10/1) to afford the desired product **36** as white solid (44.8 mg, 81%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.06 (d, *J* = 7.7 Hz, 1H), 7.97 (d, *J* = 8.4 Hz, 1H), 7.58 (t, *J* = 7.7 Hz, 2H), 7.54 (d, *J* = 7.1 Hz, 2H), 7.45 (t, *J* = 7.3 Hz, 1H), 7.36 (d, *J* = 6.3 Hz, 2H), 7.31–7.25 (m, 1H), 6.85 (d, *J* = 2.1 Hz, 1H), 6.80 (dd, *J* = 8.3, 2.2 Hz, 1H), 5.16 (s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 154.7, 142.3, 141.0, 137.5, 129.8, 127.5, 127.0, 124.7, 123.5, 121.2, 120.0, 119.4, 117.4, 109.5, 109.0, 96.1. This characterization data are in accordance with the reported literature.[22]



37

(4-Methoxyphenyl)methanol

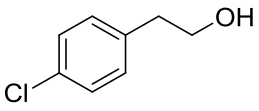
According to **GP** with 2-(4-methoxybenzyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (49.6 mg, 0.2 mmol, 1.0 equiv), chlorophyll (4.0 mg, 0.004 mmol, 2.0 mol%), and Et_3N (28.0 μL, 0.2 mmol, 1.0 equiv). The crude reaction mixture was purified byflash silica gel column chromatography (petroleum ether/EtOAc = 5/1) to afford the desired product **37** as colorless oil (27 mg, 98%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.25 (d, *J* = 8.7 Hz, 2H), 6.86 (d, *J* = 8.6 Hz, 2H), 4.56 (s, 2H), 3.78 (s, 3H), 2.08 (s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 159.1, 133.1, 128.6, 113.9, 64.8, 55.2. This characterization data are in accordance with the reported literature.[2]



38

decan-1-ol

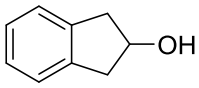
According to **GP** with 9-phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9H-carbazole (53.6 mg, 0.2 mmol, 1.0 equiv), chlorophyll (4.0 mg, 0.004 mmol, 2.0 mol%), and Et_3N (28.0 μL, 0.2 mmol, 1.0 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 10/1) to afford the desired product **38** as white solid (29 mg, 92%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.63 (t, *J* = 6.7 Hz, 2H), 1.55 (dt, *J* = 8.2, 6.6 Hz, 2H), 1.44–1.16 (m, 16H), 0.87 (t, *J* = 7.0 Hz, 3H). 13C NMR (150 MHz, $CDCl_3$) δ 63.0, 32.7, 31.8, 29.5, 29.5, 29.4, 29.3, 25.7, 22.6, 14.0. This characterization data are in accordance with the reported literature.[22]



39

2-(4-chlorophenyl)ethan-1-ol

According to **GP** with 2-(4-chlorophenethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (53.2 mg, 0.2 mmol, 1.0 equiv), chlorophyll (4.0 mg, 0.004 mmol, 2.0 mol%), and Et_3N (28.0 μL, 0.2 mmol, 1.0 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 10/1) to afford the desired product **39** as yellow oil (30.8 mg, 99%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.28 (d, *J* = 8.4 Hz, 2H), 7.16 (d, *J* = 8.4 Hz, 2H), 3.83 (t, *J* = 6.6 Hz, 2H), 2.83 (t, *J* = 6.5 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 137.0, 132.2, 130.3, 128.6, 63.4, 38.4. This characterization data are in accordance with the reported literature.[23]

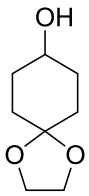


40

2,3-dihydro-1*H*-inden-2-ol

According to **GP** with 2-(2,3-dihydro-1*H*-inden-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (28.8 mg, 0.2 mmol, 1.0 equiv), chlorophyll (4.0 mg, 0.004 mmol, 2.0 mol%), and Et_3N (28.0 μL, 0.2 mmol, 1.0 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 10/1) to afford the desired product **40** as white solid (26.2 mg, 98%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.28–7.23 (m, 2H), 7.18 (dd, *J* = 5.4, 3.2 Hz, 2H), 4.70 (tt, *J* = 6.0, 3.2 Hz, 1H), 3.22 (dd, *J* = 16.3, 5.9 Hz, 2H), 2.92 (dd, *J* = 16.2, 3.1 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 140.7, 126.6,

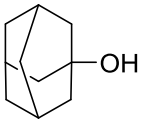
125.0, 73.2, 42.6. This characterization data are in accordance with the reported literature.[2]



41

1,4-dioxaspiro[4.5]decan-8-ol

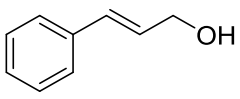
According to **GP** with 4,4,5,5-tetramethyl-2-(1,4-dioxaspiro[4.5]decan-8-yl)-1,3,2-dioxaborolane (53.6 mg, 0.2 mmol, 1.0 equiv), chlorophyll (4.0 mg, 0.004 mmol, 2.0 mol%), and Et_3N (28.0 μL, 0.2 mmol, 1.0 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 10/1) to afford the desired product **41** as white solid (28.1 mg, 89%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.99–3.90 (m, 4H), 3.79 (tt, *J* = 8.3, 3.7 Hz, 1H), 1.87 (dqd, *J* = 11.9, 3.9, 2.0 Hz, 2H), 1.80 (ddd, *J* = 14.9, 5.9, 3.0 Hz, 2H), 1.64 (tdd, *J* = 12.2, 8.3, 3.5 Hz, 2H), 1.56 (ddd, *J* = 13.7, 10.3, 4.1 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 108.2, 68.1, 64.2, 64.2, 31.9, 31.5. This characterization data are in accordance with the reported literature.[24]



42

adamantan-1-ol

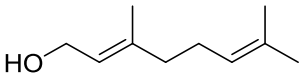
According to **GP** with 2-(adamantan-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (49.4 mg, 0.2 mmol, 1.0 equiv), chlorophyll (4.0 mg, 0.004 mmol, 2.0 mol%), and Et_3N (28.0 μL, 0.2 mmol, 1.0 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 10/1) to afford the desired product **42** as white solid (26.8 mg, 88%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.12 (t, *J* = 3.5 Hz, 3H), 1.69 (d, *J* = 2.5 Hz, 6H), 1.62–1.54 (m, 6H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 45.3, 36.0, 30.6. This characterization data are in accordance with the reported literature.[2]



43

(*E*)-3-phenylprop-2-en-1-ol

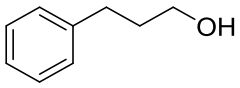
According to **GP** with 2-cinnamyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (48.8 mg, 0.2 mmol, 1.0 equiv), chlorophyll (4.0 mg, 0.004 mmol, 2.0 mol%), and Et_3N (28.0 μL, 0.2 mmol, 1.0 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 10/1) to afford the desired product **43** as white solid (11.2 mg, 42%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.37 (d, *J* = 7.7 Hz, 2H), 7.31 (t, *J* = 7.6 Hz, 2H), 7.25 (t, *J* = 7.3 Hz, 1H), 6.60 (d, *J* = 15.9 Hz, 1H), 6.34 (dt, *J* = 15.9, 5.7 Hz, 1H), 4.29 (dd, *J* = 5.7, 1.5 Hz, 2H), 2.72 (s, 1H). ^{13}C NMR (150 MHz, Chloroform-d) δ 136.7, 130.9, 128.6, 128.6, 127.6, 126.5, 63.4. This characterization data are in accordance with the reported literature.[17]



44

(*E*)-3,7-dimethylocta-2,6-dien-1-ol

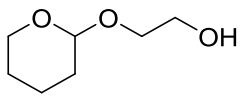
According to **GP** with (*E*)-2-(3,7-dimethylocta-2,6-dien-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (52.8 mg, 0.2 mmol, 1.0 equiv), chlorophyll (4.0 mg, 0.004 mmol, 2% mol), and Et_3N (28.0 μL, 0.2 mmol, 1.0 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 10/1) to afford the desired product **44** as white solid (14.4 mg, 47%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.40 (t, *J* = 7.5 Hz, 1H), 5.08 (t, *J* = 6.2 Hz, 1H), 4.14 (d, *J* = 7.0 Hz, 2H), 2.09 (q, *J* = 7.0 Hz, 2H), 2.06–1.98 (m, 2H), 1.67 (d, *J* = 4.4 Hz, 6H), 1.59 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 139.6, 131.6, 123.8, 123.3, 59.3, 39.5, 26.3, 25.6, 17.6, 16.2. This characterization data are in accordance with the reported literature.[25]



45

3-phenylpropan-1-ol

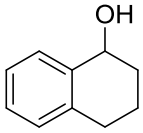
According to **GP** with potassium trifluoro(3-phenylpropyl)borate (45.2 mg, 0.2 mmol, 1.0 equiv), chlorophyll (4.0 mg, 0.004 mmol, 2% mol), and Et_3N (28.0 μL, 0.2 mmol, 1.0 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 10/1) to afford the desired product **45** as white solid (26.1 mg, 96%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.29 (dd, *J* = 8.2, 7.0 Hz, 2H), 7.23–7.17 (m, 3H), 3.68 (t, *J* = 6.4 Hz, 2H), 2.75–2.68 (m, 2H), 1.94–1.87 (m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 141.8, 128.4, 128.4, 125.8, 62.2, 34.2, 32.0. This characterization data are in accordance with the reported literature.[2]



46

2-((tetrahydro-2*H*-pyran-2-yl)oxy)ethan-1-ol

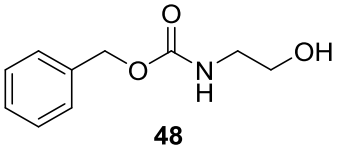
According to **GP** with potassium trifluoro(2-((tetrahydro-2*H*-pyran-2-yl)oxy)ethyl)borate (47.2 mg, 0.2 mmol, 1.0 equiv), chlorophyll (4.0 mg, 0.004 mmol, 2% mol), and Et_3N (28.0 μL, 0.2 mmol, 1.0 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 10/1) to afford the desired product **46** as white solid (28 mg, 96%). ^{1}H NMR (600 MHz, CD_3OD) δ 4.59 (dd, *J* = 4.5, 2.8 Hz, 1H), 3.85 (ddd, *J* = 11.6, 8.3, 3.2 Hz, 1H), 3.73 (dt, *J* = 10.8, 4.8 Hz, 1H), 3.68–3.60 (m, 2H), 3.50–3.44 (m, 2H), 1.81 (td, *J* = 8.3, 7.8, 3.7 Hz, 1H), 1.72–1.64 (m, 1H), 1.60–1.43 (m, 4H). ^{13}C NMR (150 MHz, CD_3OD) δ 99.1, 68.8, 61.9, 60.9, 30.2, 25.1, 19.1. This characterization data are in accordance with the reported literature.[26]



47

1,2,3,4-tetrahydronaphthalen-1-ol

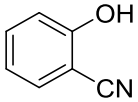
According to **GP** with potassium trifluoro(1,2,3,4-tetrahydronaphthalen-1-yl)borate (47.6 mg, 0.2 mmol, 1.0 equiv), chlorophyll (4.0 mg, 0.004 mmol, 2% mol), and Et_3N (28.0 μL, 0.2 mmol, 1.0 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 10/1) to afford the desired product **47** as white solid (26.1 mg, 88%). ^{1}H NMR (300 MHz, CDCl3) δ7.46–7.41 (m, 1H), 7.23–7.18 (m, 2H), 7.14–7.09 (m, 1H), 4.78 (d, *J* = 5.0 Hz, 1H), 2.83 (dt, *J* = 16.7, 5.6 Hz, 1H), 2.73 (ddd, *J* = 16.5, 8.1, 5.5 Hz, 1H), 1.98 (dddd, *J* = 17.6, 12.6, 8.0, 4.0 Hz, 2H), 1.94–1.88 (m, 1H), 1.85 (d, *J* = 5.7 Hz, 1H), 1.82–1.75 (m, 1H). ^{13}C NMR (75 MHz, CDCl3) δ 138.7, 137.0, 128.9, 128.6, 127.5, 126.1, 68.1, 32.2, 29.1, 18.7.This characterization data are in accordance with the reported literature.[2]



48

Benzyl (2-hydroxyethyl)carbamate

According to **GP** with potassium (2-(((benzyloxy)carbonyl)amino)ethyl)trifluoroborate (57 mg, 0.2 mmol, 1.0 equiv), chlorophyll (4.0 mg, 0.004 mmol, 2% mol), and Et_3N (28.0 μL, 0.2 mmol, 1.0 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 10/1) to afford the desired product **48** as white solid (37 mg, 95%). ^{1}H NMR (600 MHz, CD_3OD) δ 7.32 (d, *J* = 6.9 Hz, 4H), 7.29–7.25 (m, 1H), 5.05 (s, 2H), 3.56 (t, *J* = 5.9 Hz, 2H), 3.21 (t, *J* = 5.9 Hz, 2H). ^{13}C NMR (150 MHz, CD_3OD) δ 157.6, 136.9, 128.0, 127.5, 127.4, 66.0, 60.4, 42.8. This characterization data are in accordance with the reported literature.[27]

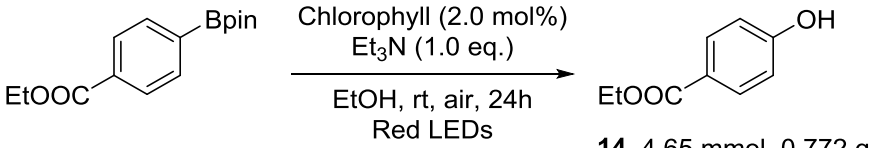


49

2-hydroxybenzonitrile

According to **GP** with 2-(5,5-dimethyl-1,3,2-dioxaborinan-2-yl)benzonitrile (43 mg, 0.2 mmol, 1.0 equiv), chlorophyll (4.0 mg, 0.004 mmol, 2% mol), and Et_3N (28.0 μL, 0.2 mmol, 1.0 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 10/1) to afford the desired product **49** as white solid (20.9 mg,88%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.50 (d, *J* = 7.8 Hz, 1H), 7.46 (t, *J* = 7.9 Hz, 1H), 7.03 (d, *J* = 8.4 Hz, 1H), 6.97 (t, *J* = 7.6 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 158.8, 134.8, 133.0, 120.7, 116.6, 116.5, 99.2. This characterization data are in accordance with the reported literature.[2]

5. Larger Scale Reaction

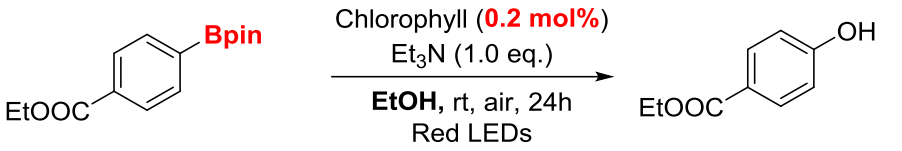


50, **5 mmol, 1.38 g**

14, 4.65 mmol, 0.772 g
93%

According to **GP** with ethyl 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoate (1.38 g, 5.0 mmol, 1.0 equiv), chlorophyll (100 mg, 0.1 mmol, 2.0 mol%), and Et_3N (750 μL, 5.0 mmol, 1.0 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 10/1) to afford the desired product **14** as white solid (772 mg, 93%).

6. Evaluation of green chemistry metrics



50, 1 mmol, 276 mg

14, 0.93 mmol, 154.8 mg
93.2 %

In order to explore the greater potential of chlorophyll, its equivalent was further reduced to 1.0 % mmol. Surprisingly, the reaction still proceeded well, and based on this, the green chemistry parameters were calculated.

According to **GP** with ethyl 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoate (276 mg, 1 mmol, 1.0 equiv), chlorophyll (2.0 mg, 0.002 mmol, 0.2 mol%), and Et_3N (140 μL, 1.0 mmol, 1.0 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 10/1) to afford the desired product **14** as white solid (154.8 mg, 93%).

Based on the above advanced reaction, green chemistry metrics were calculated as follows.

6.1 Green chemistry metrics

The green chemistry metrics including Effective Mass Yield (EMY), Atom Economy (AE), Atom Efficiency (AEf), Reaction Mass Efficiency (RME), Optimum Efficiency (OE), Process Mass Intensity (PMI), Mass Intensity (MI), Mass Productivity (MP), E-factor, Solvent Intensity (SI) and Water Intensity (WI), Turnover Number (TON), and Turnover Frequency (TOF) were calculated according to the reported method.[10] EcoScale was calculated according to the reported method.[28]

6.2 Calculations of green chemistry metrics for this method

$$\text{EMY}\ (\%) = \frac{\text{Mass of product}}{\text{Mass of non} - \text{benign reagents}} \times 100 = \frac{0.155\ g}{0.276\ g + 0.101\ \text{g} + 0.002\ \text{g}} \times 100 = 40.8\%$$

$$\text{AE}\ (\%) = \frac{\text{Molecular weight of product}}{\text{Total molecular weight of reagents}} \times 100 = \frac{166.1}{276.2 + 101.2 + 878.5 \times 0.002} \times 100 = 43.8\%$$

$$\text{AEf}\ (\%) = \text{AE} \times \text{Yield}\% = 43.8 \times 93.2\% = 40.8\%$$

$$\text{RME}\ (\%) = \frac{\text{Mass of isolated product}}{\text{Total mass of reagents}} \times 100 = \frac{0.155\ g}{0.276\ g + 0.101\ \text{g} + 0.032\ \text{g} + 0.002\ \text{g}} \times 100 = 37.7\%$$

$$\text{OE}\ (\%) = \frac{RME}{\text{AE}} \times 100 = \frac{37.7\%}{43.8\%} \times 100 = 85.9\%$$

$$\text{PMI} = \frac{\text{Total mass of input material in the whole process (including solvents)}}{\text{Mass of products}}$$

$$= \frac{0.276\ g + 0.101\ g + 0.032\ g + 0.002\ g + 3.9\ g}{0.155\ g} = 28.1$$

$$\mathrm{MI} = \frac{\text{Total mass of input material in the whole process (excluding water)}}{\text{Mass of products}}$$

$$= \frac{0.276\ g + 0.101\ g + 0.032\ g + 0.002\ g + 3.9\ g}{0.155\ g} = 28.1$$

$$\mathrm{MP}\ (\%) = \frac{1}{\mathrm{MI}} \times 100 = \frac{1}{28.1} \times 100 = 3.6\%$$

$$\mathrm{E-factor} = \frac{\text{Total mass of waste}}{\text{Mass of products}} = \frac{0.276\ g + 0.101\ g + 0.032\ g + 0.002\ g + 3.9\ g - 0.155\ g}{0.155\ g} = 27.1$$

$$\mathrm{TON} = \frac{Amout\ of\ desired\ product\ (mmol\ scale)}{Amout\ of\ catalyst\ used\ (mmol\ scale)} = \frac{0.932}{0.002} = 466$$

$$\mathrm{TOF} = \frac{TON}{\text{Time (hour)}} = \frac{466}{24\ h} = 19.4/h$$

6.3 Comparison of metrics with the same type of reaction

In order to further demonstrate the advantages of this method in green chemistry, the relevant parameters of the same type of reactions were also calculated and compared to ours. The comparative examples were selected from the similar photooxidation processes and were listed below.[2, 10, 22, 29-37] The detailed calculation parameters were summarized **Table S1**. The comparison of each metric sees **Figure S2-S12**.

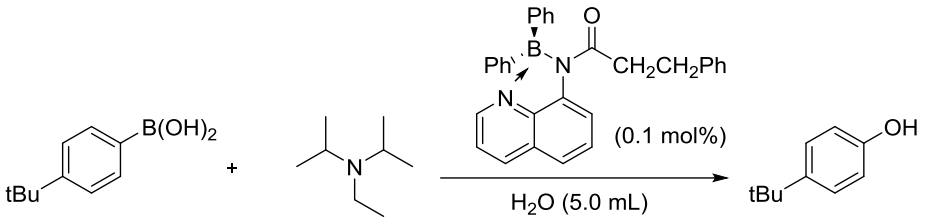
Except for Optimum Efficiency (OE), all other metrics of this method are at the upstream level. The use of low doses of catalysts and additives, accompanied by less waste losses, results in a high Effective Mass Yield (EMY), Atom Economy (AE), and Reaction Mass Efficiency (RME), while at the same time the Process Mass Intensity (PMI), Mass Intensity (MI) and E-factor are at a lower level. Low dosage of catalyst and less reaction time result in satisfactory TON and TOF, indicating that chlorophyll has a very high catalytic efficiency for the photooxidation of organoborons.

6.4 Calculations of EcoScale

EcoScale was calculated according to the reported method and summarized at Table S3.[28] The score drops significantly due to the use of the toxic reagent triethylamine, but it is still an acceptable green synthesis method. And the EcoScale of this method (70.6) is also better than that of the Ref 10 (61).

In conclusion, this method can be regarded as an efficient green synthesis method through green chemistry metrics calculations and horizontal comparison.

1
Ref 10

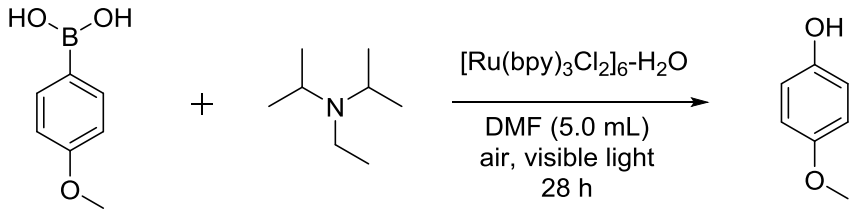


MW: 178.11
3.0 mmol

MW: 129.25
3.5 equiv

MW: 150.10
82%

2
Ref 29

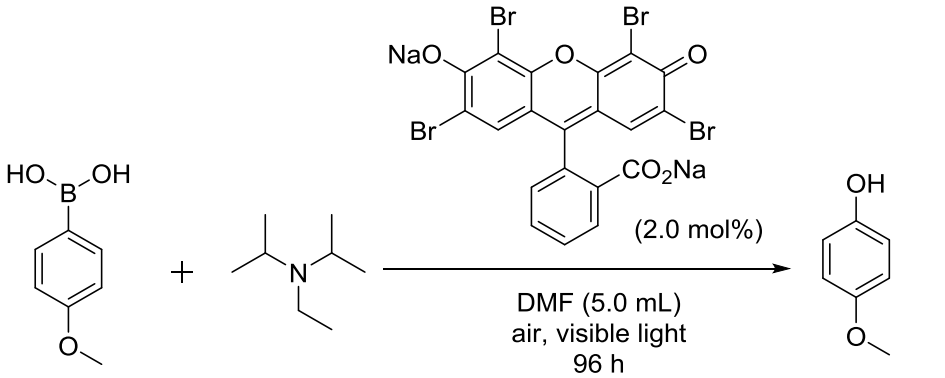


MW: 151.96
0.5 mmol

MW: 129.25
2.0 equiv

MW: 124.14
93%

3
Ref 29

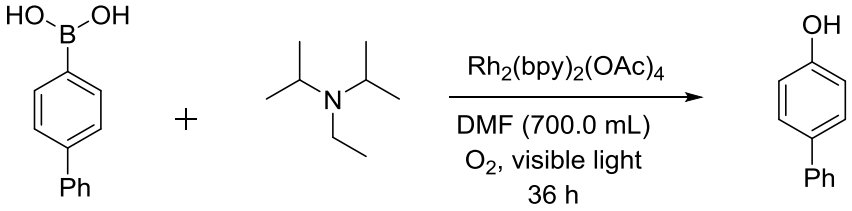


MW: 151.96
0.5 mmol

MW: 129.25
2.0 equiv

MW: 124.14
90%

4
Ref 30

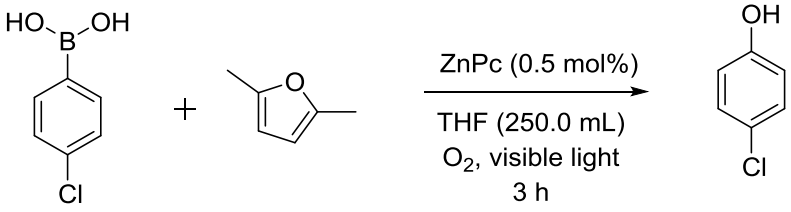


MW: 198.03
7.0 mmol

MW: 129.25
2.0 equiv

MW: 170.12
99%

5
Ref 22

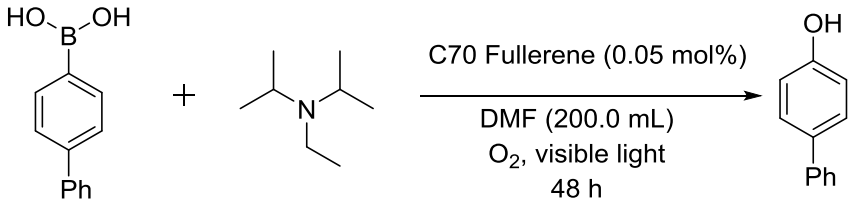


MW: 156.37
20.0 mmol

MW: 96.13
2.0 equiv

MW: 128.56
93%

6
Ref 31

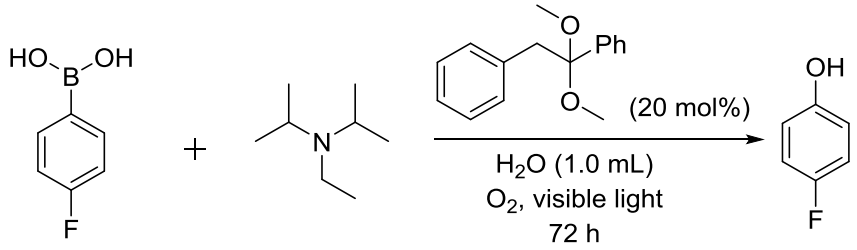


MW: 198.03
10.0 mmol

MW: 129.25
2.0 equiv

MW: 170.12
91%

7
Ref 32

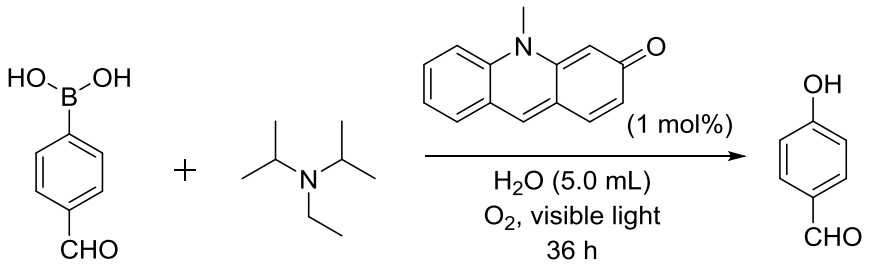


MW: 139.92
0.6 mmol

MW: 129.25
7.5 equiv

MW: 170.12
57%

8
Ref 33

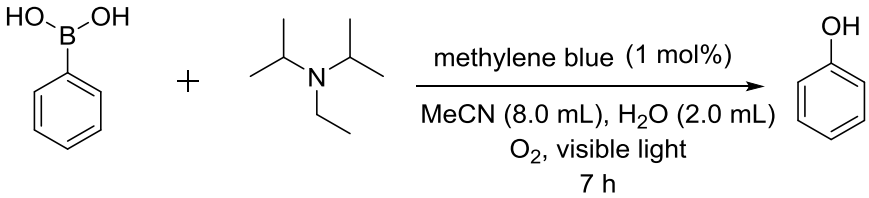


MW: 149.94
0.5 mmol

MW: 129.25
5.0 equiv

MW: 122.12
98%

9
Ref 34

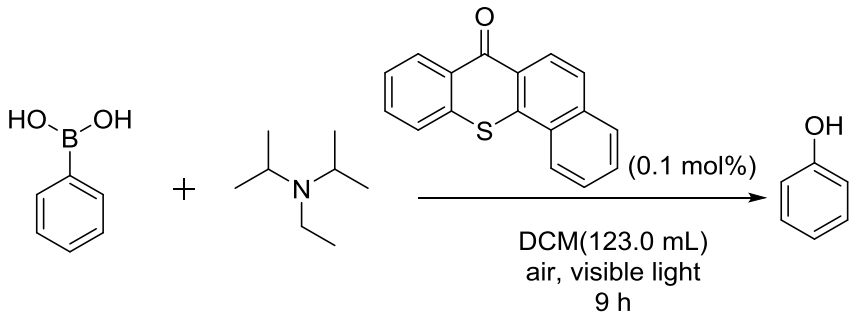


MW: 121.93
0.6 mmol

MW: 129.25
5.0 equiv

MW: 94.11
94%

10
Ref 35

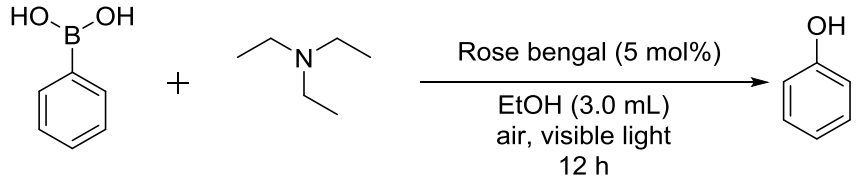


MW: 121.93
12.3mmol

MW: 129.25
2.0 equiv

MW: 94.11
87%

11
Ref 2

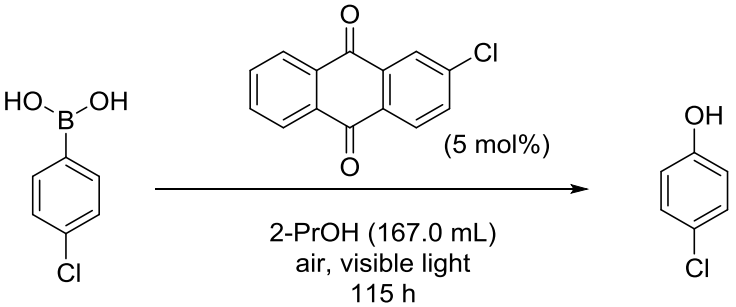


MW: 121.93
0.5 mmol

MW: 101.19
0.4 equiv

MW: 94.11
97%

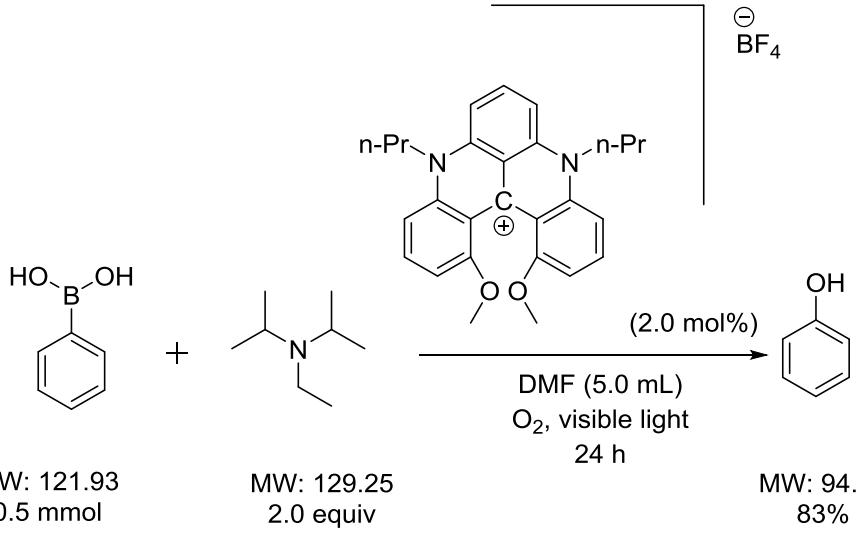
12
Ref 36



MW: 156.37
0.5 mmol

MW: 128.56
91%

13
Ref 37



MW: 121.93
0.5 mmol

MW: 129.25
2.0 equiv

MW: 94.11
83%

Table S1. Calculated green metrics

Entry			This	1	2	3	4	5	6	7	8	9	10	11	12	13
Reference			This	10	29	29	30	22	31	32	33	34	35	2	36	37
Atomsphere			air	air	air	air	O_2	O_2	O_2	O_2	O_2	O_2	air	air	air	air
Borides	M	mmol	1	3	0.5	0.5	7	20	10	0.6	0.5	0.6	12.3	0.5	10	0.5
	MW	g/mmol	276.2	178.04	151.96	151.96	198.03	156.37	198.03	139.92	149.94	121.93	121.93	121.93	156.37	121.93
	Weight	mg	276.2	534.1	76	76	1386.2	3127.4	1980.3	84	75	73.2	1499.71	61	1563.71	61
Additive	MW	g/mmol	101.2	129.25	129.25	129.25	129.25	100.16	129.25	129.25	129.25	129.25	129.25	101.19	0	129.25
	Weight	mg	101.2	1357.1	129.3	129.3	1809.5	4006.4	2585	581.6	323.1	387.8	3179.6	20.2	0	129.3
O_2	MW	g/mmol	32	32	32	32	32	32	32	32	32	32	32	32	32	32
	Weight	mg	32	96	16	16	224	640	320	19.2	16	19.2	393.6	16	320	16
Catalyst	M	mmol	0.002	0.003	0.01	0.01	0.14	0.1	0.005	0.12	0.005	0.006	0.0123	0.025	0.5	0.01
	MW	g/mmol	878.5	440.35	748.62	691.86			840.77	256.3	209.25	319.85	262.33	973.67	242.66	544.44
	Weight	mg	1.757	1.3	7.5	6.9	112	60	4.2	30.8	1	1.9	3.2	24.3	121.3	5.4
Solvent(not water)	Solvent		EtOH		DMF	DMF	DMF	THF	CHCl3			MeCN	DMC	EtOH	iPrOH	DMF
	Densty	mg/mL	789		944	944	944	889	1490			786	1070	789	786	944
	Volume	mL	5		5	5	700	250	200			8	123	3	167	5
	Weight	mg	3945	0	4720	4720	660800	222250	298000	0	0	6288	131610	2367	131262	4720
Water	Weight	mg	0	5000	0	0	0	0	0	1000	5000	2000	0	0	0	0
Co-solvent	Weight	mg			0	0	0	0	7282	0	0	0	0	0	0	0
Product	MW	g/mmol	166.1	150.22	124.14	124.14	170.21	128.56	170.21	112.1	122.12	94.11	94.11	94.11	128.56	94.11
	M	mmol	0.932	2.46	0.465	0.465	6.93	18.6	9.1	0.342	0.49	0.564	10.701	0.485	9.1	0.415
	AW	mg	154.8	369.5	57.7	55.9	1179.6	2391.2	1548.9	38.3	59.8	53.1	1007.1	45.6	1169.9	39.1
	Yield		93.20%	82%	93%	90%	99%	93%	91%	57%	98%	94%	87%	97%	91%	83%
Effective Mass Yield		**EMY**	40.80%	19.53%	27.14%	26.33%	35.66%	33.24%	33. 90%	5.51%	14.99%	11.47%	21.51%	43.25%	69.43%	19.96%
Atom Economy		**AE**	43.80%	22.68%	28.06%	28.06%	34.84%	33.08%	34.84%	9.82%	14.75%	11.76%	22.82%	48.41%	68.25%	22.82%
Atom Efficiency		**AEF**	43.80%	18.60%	26.09%	25.25%	34.49%	30.76%	31.71%	5.60%	14.45%	11.06%	19.85%	46.96%	62.11%	18.94%
Reaction Mass Efficiency		**RME**	37.65%	18.58%	25.24%	24.49%	33.40%	30.52%	31.68%	5.36%	14.41%	11.01%	19.84%	37.55%	58.35%	18.45%
Optimum Efficiency		**OE**	85.94%	81.95%	89.96%	87.27%	95.86%	92.29%	90.92%	54.55%	97.75%	93.63%	86.94%	77.57%	85.49%	80.87%
Process Mass Intensty		**PMI**	28.14	18.91	85.73	88.58	563.21	96.22	200.25	44.75	90.5	165.23	135.73	54.52	113.91	126.27
Mass Intensity		**MI**	28.13	5.38	85.73	88.58	563.21	96.22	200.25	18.66	6.94	127.55	135.73	54.52	113.91	126.27
Mass Productivity		**MP**	3.55%	18.58%	1.17%	1.13%	0.18%	1.04%	0.50%	5.36%	14.41%	0.78%	0.74%	1.83%	0.88%	0.79%
E-factor			27.13	17.91	84.73	87.58	562.21	95.22	199.25	43.75	89.5	164.23	134.73	53.52	112.91	125.27
Solvent Intensity		**SI**	25.48	0	81.77	84.49	560.21	92.94	197.09	0	0	118.47	130.69	51.86	112.2	120.85
Turnover Number		**TON**	466	820	46.5	45	49.5	186	1820	2.85	98	94	870	19.4	18.2	41.5
Reaction time		**h**	24	36	28	96	36	3	48	72	36	7	9	12	115	24
Turmover Frequency		**/h**	19.41	22.778	1.66	0.47	1.38	6200	37.92	0.04	2.72	13.43	96.67	1.62	0.16	1.73

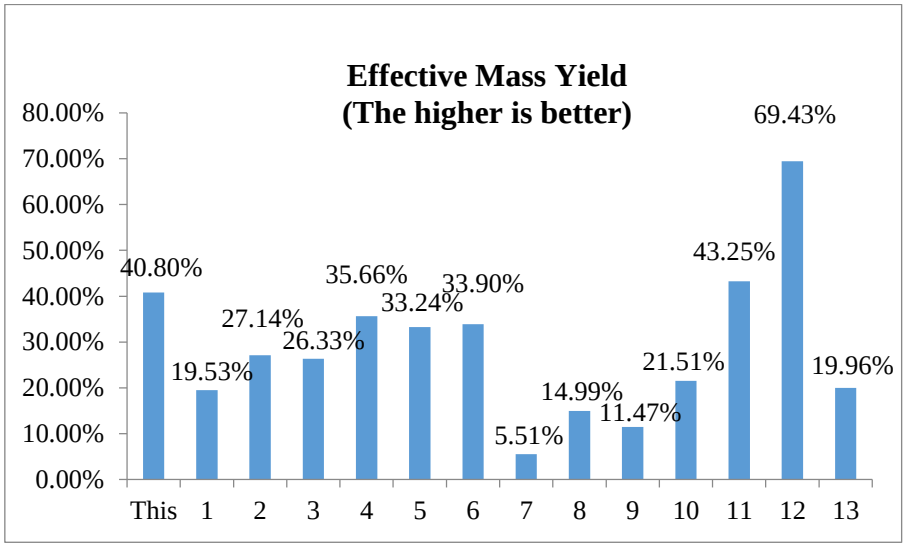


Figure S2. The comparison of Effective Mass Yield

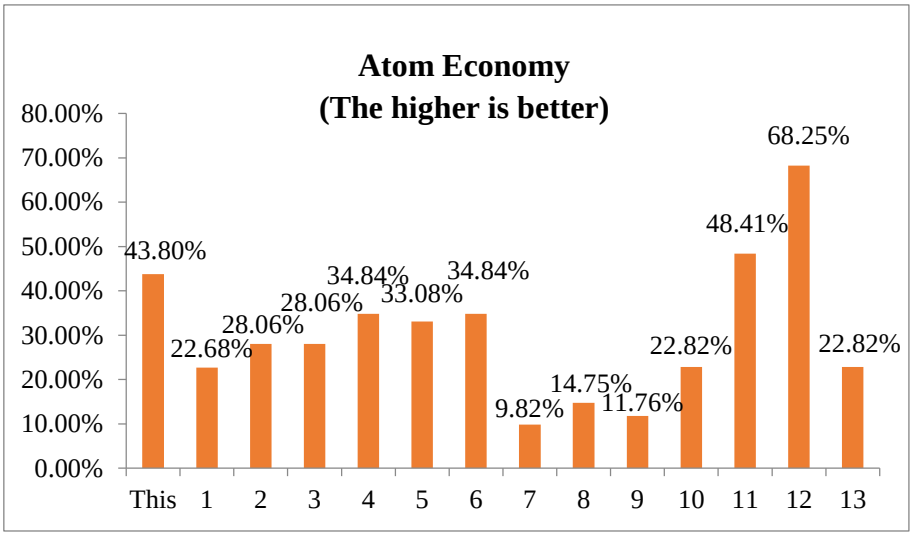


Figure S3. The comparison of Atom Economy

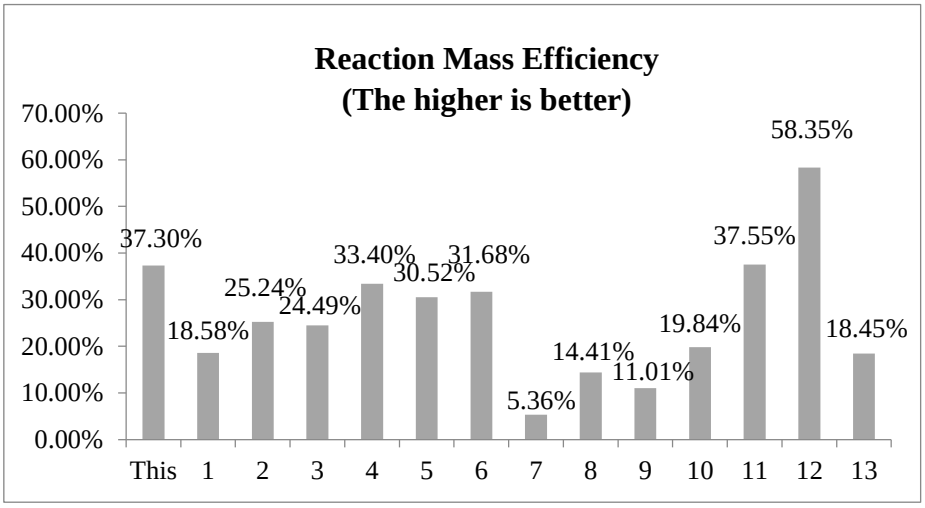


Figure S4. The comparison of Reaction Mass Efficiency

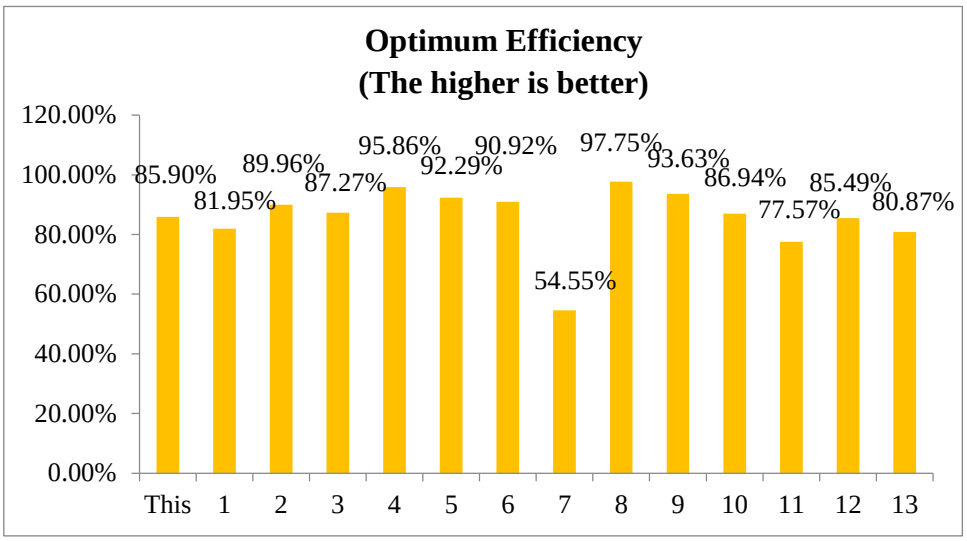


Figure S5. The comparison of Optimum Efficiency

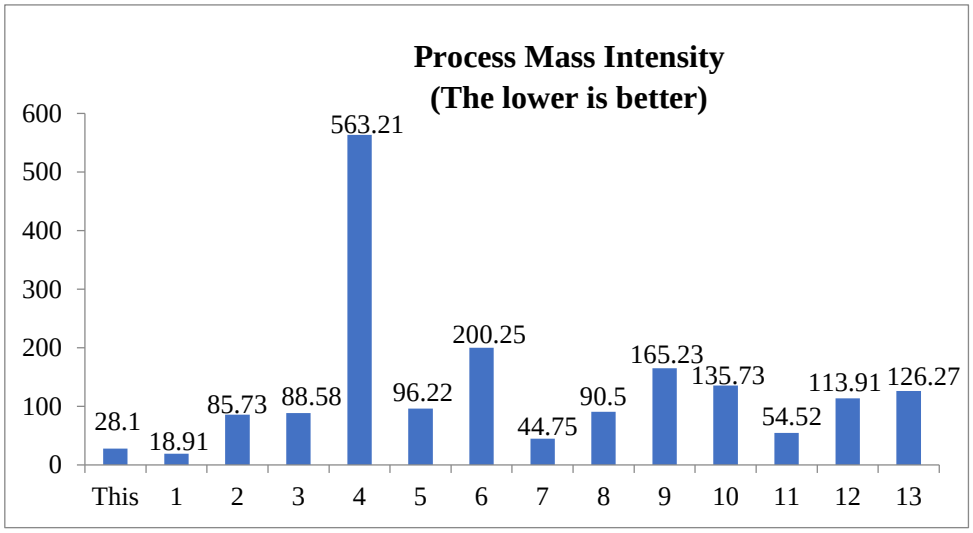


Figure S6. The comparison of Process Mass Intensity

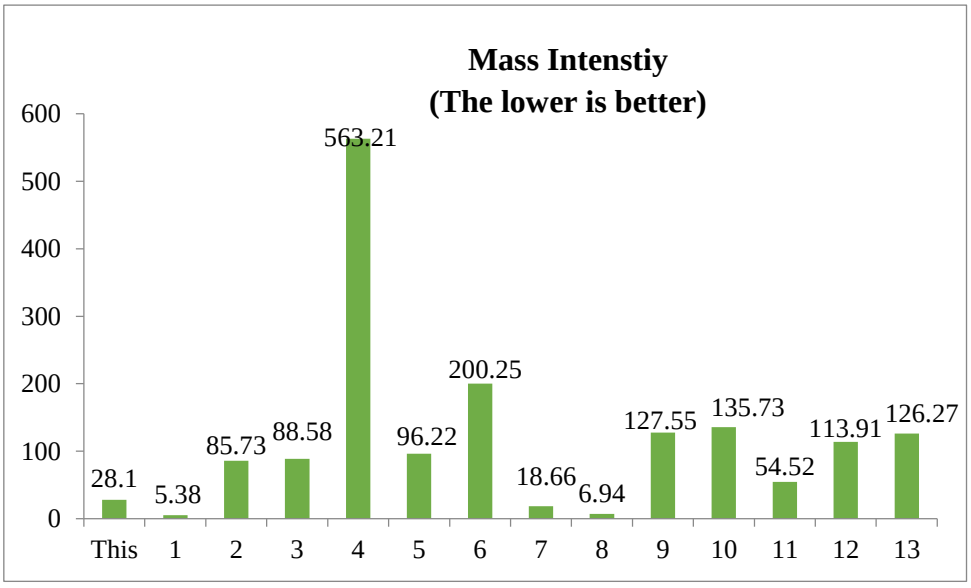


Figure S7. The comparison of Mass Intensity

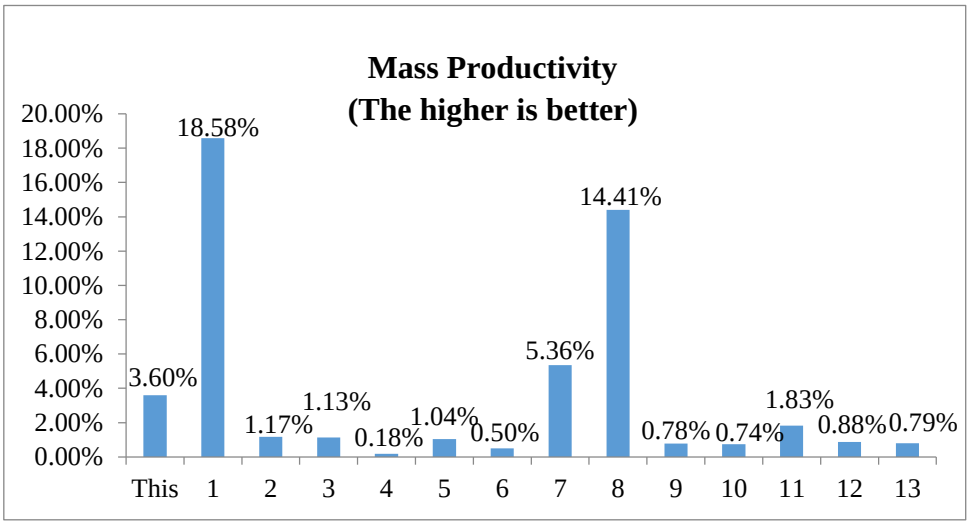


Figure S8. The comparison of Mass Productivity

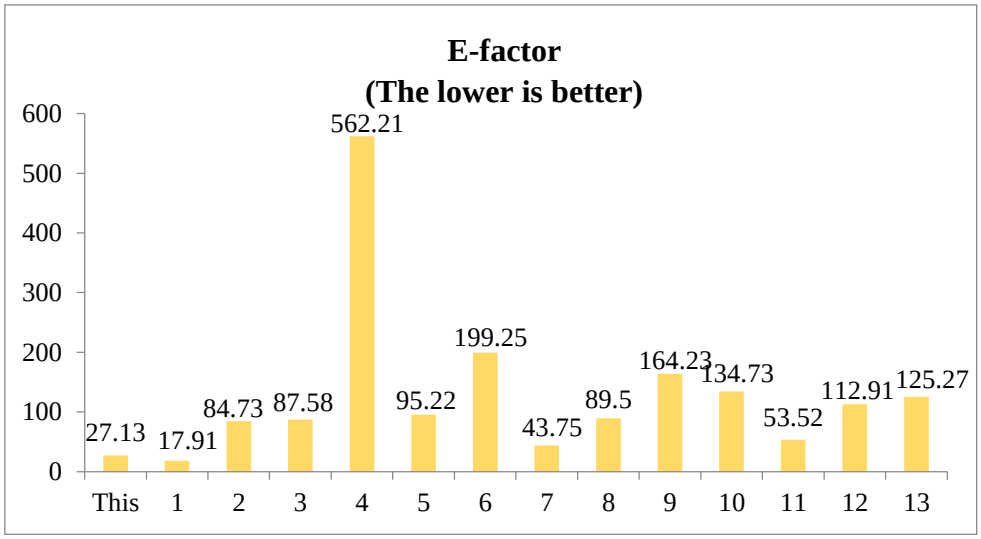


Figure S9. The comparison of E-factor

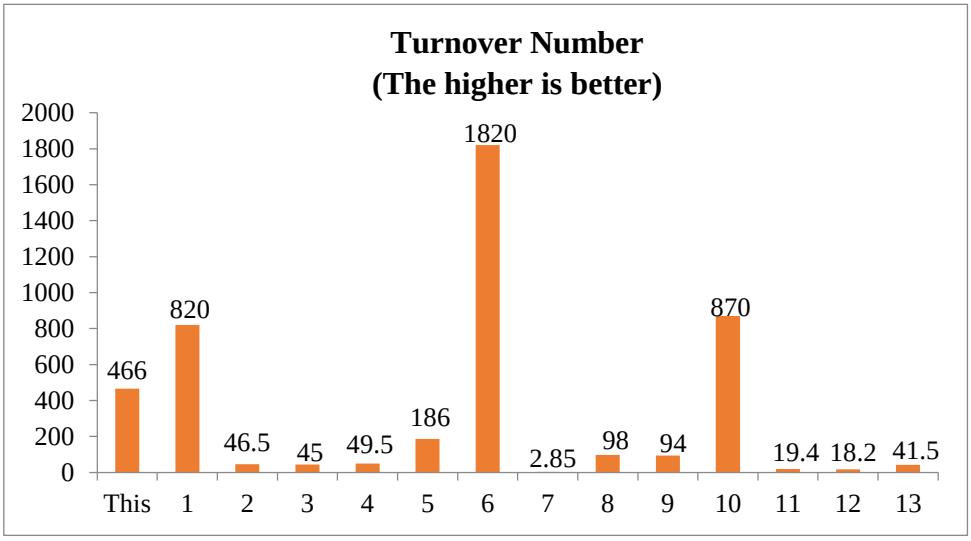


Figure S10. The comparison of Turnover Number

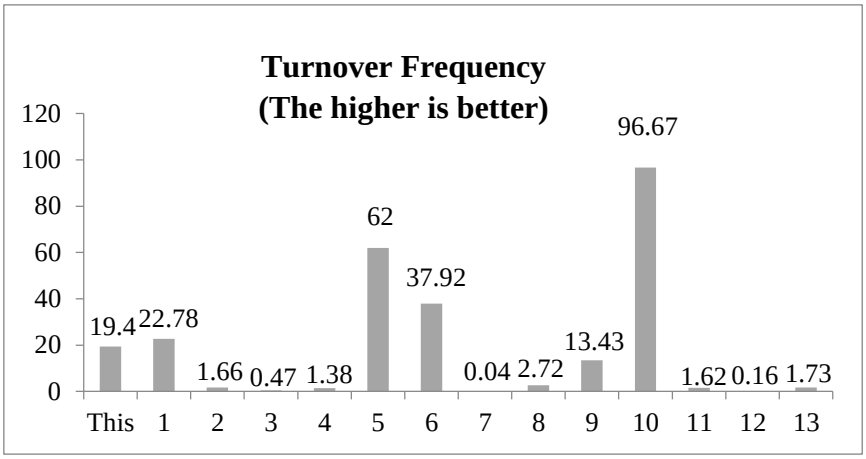


Figure S11. The comparison of Turnover Frequency

Table S2. The summary of green chemistry metrics

Photo-catalysts	EMY	AE	RME	OE	PMI	MI	MP	E-factor	TON	TOF
This	40.8%	43.8%	37.3%	85.9%	28.1	28.1	3.6%	27.1	466	19.40
1	19.5%	22.7%	18.6%	82.0%	18.9	5.4	18.6%	17.9	820	22.78
2	27.1%	28.1%	25.2%	90.0%	85.7	85.7	1.2%	84.7	47	1.66
3	26.3%	28.1%	24.5%	87.3%	88.6	88.6	1.1%	87.6	45	0.47
4	35.7%	34.8%	33.4%	95.9%	563.2	563.2	0.2%	562.2	50	1.38
5	33.2%	33.1%	30.5%	92.3%	96.2	96.2	1.0%	95.2	186	62.00
6	33.9%	34.8%	31.7%	90.9%	200.3	200.3	0.5%	199.3	1820	37.92
7	5.5%	9.8%	5.4%	54.6%	44.8	18.7	5.4%	43.8	3	0.04
8	15.0%	14.8%	14.4%	97.8%	90.5	6.9	14.4%	89.5	98	2.72
9	11.5%	11.8%	11.0%	93.6%	165.2	127.6	0.8%	164.2	94	13.43
10	21.5%	22.8%	19.8%	86.9%	135.7	135.7	0.7%	134.7	870	96.67
11	43.3%	48.4%	37.6%	77.6%	54.5	54.5	1.8%	53.5	19	1.62
12	69.4%	68.3%	58.4%	85.5%	113.9	113.9	0.9%	112.9	18	0.16
13	20.0%	22.8%	18.5%	80.9%	126.3	126.3	0.8%	125.3	42	1.73

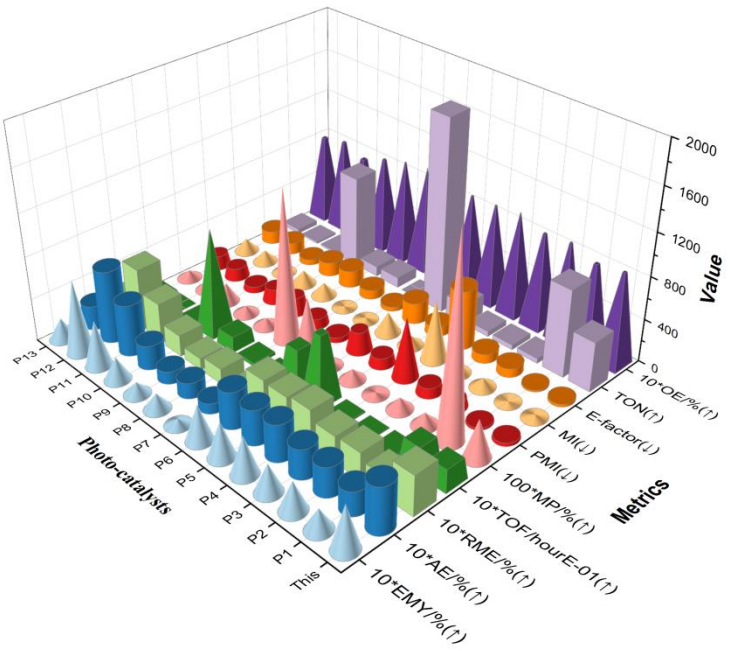


Figure S12. The summary of the green chemistry metrics

Table S3.The calculation of EcoScale

EcoScale = 100- Sum of individual penalties Score on EcoScale: > 75, Excellent; >50, Acceptable; <50, Inadequate		
A) Calculation of penalty points:		
Parameters		Penalty points
1. Yield	(100-100*yield)/2 = (100-93.2)/2 = 3.4	3.4
2. Price of reaction components (To obtain 10 mmol of end product)	(a) Substrate X = 2.96 g < $30	
	(b) PC = 2.0 mg < $1	
	(c) Et_3N = 1.09 g < $1	
	Total price < $ 32	
	Expensive (> $10 and < $50)	3
3. Safety	Et_3N	
	Toxic (T)	5
	Highly flammable (F)	5
4. Technical Setup	Inconventional activation technique (Photochemical reaction)	2
5. Temperature and time	Room temperature and < 24h	1
6. Workup and purification	Classical chromatography	10
Total Penalty Points		29.4
B) EcoScale calculation:		
EcoScale	= 100- Total Penalty Points	70.6

7. Experiment using kitchen things

Interestingly, the reaction can be carried out entirely with kitchen equipment and ingredients. 200 g fresh spinach leaves with 50 ml edible alcohol (52% Vol), crushed with a juicer. Then, substrate **50** (276 mg) and baking soda (312 mg) were added to the filtered spinach juice. The juice was exposed to sunlight for 5 hours. Egg-whisk can be used as an alternative to a magnetic stirrer during the reaction. Finally, 60% of the arylboronic acid **50** was converted to phenol **14** by ^{1}H-NMR detection.

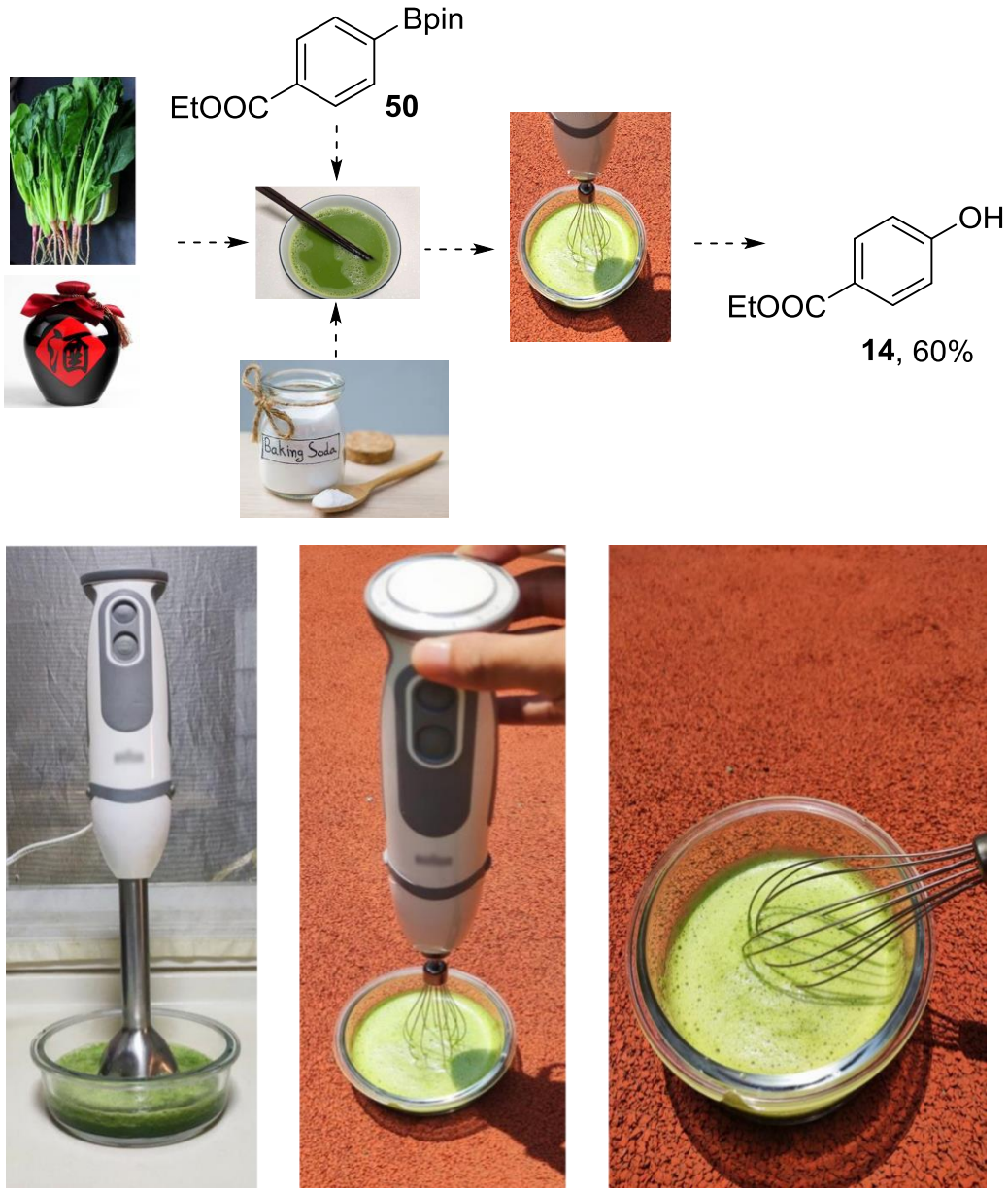
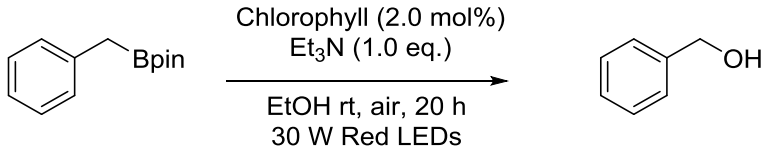


Figure S13. Experiment using kitchen things

8. Mechanistic studies

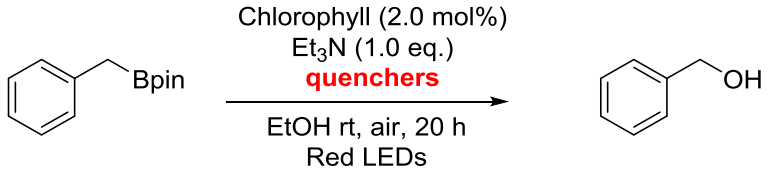
8.1 Control experiments



entry	visible light	chlorophyll	air	Et_3N	Yield (%)	NOTE
1	yes	yes	yes	yes	97	
2	no	yes	yes	yes	0	
3	yes	no	yes	yes	0	
4	yes	yes	no	yes	0	
5	yes	yes	yes	no	15	
6	no	no	yes	yes	0	
7	yes	no	yes	no	0	
8	no	yes	yes	yes	0	heated to 50 ℃

The above control experiments showed that the photocatalyst, amine, air, and visible light are all necessary for the success of this transformation. And the thermal effect of red light is irrelevant to the reaction

8.2 Control experiments with quenchers



Quenchers	equivalents	yields/%	note
$CuCl_2$	1.0/5.0	31/6	electron scav.
Benzoquinone	1.0/5.0/10.0	90/42/12	superoxide radical anion scav.
Catalase	100 mg	84%	peroxide radical scav.

2-benzyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (43.6 mg, 0.2 mmol, 1.0 equiv), chlorophyll (4.0 mg, 0.004 mmol, 2.0 mol%), and Et_3N (28.0 μL, 0.2 mmol, 1.0 equiv) and different kind of quenchers were placed in a 10 mL Schlenk tube. Then EtOH (2.0 mL) was added with a syringe. The reaction mixture was stirred and irradiated by using 30 W Red LEDs at room temperature under air atmosphere for 20 h. After completion of the reaction, the solvent was removed under reduced pressure and yield by ^1H NMR. The above results suggest that single-electron transfer, and superoxide anion radicals are closely related to the reaction.

8.3 Kinetic curve determination

12 sets of reactions were carried out in parallel, each of which was used 2-benzyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (43.6 mg, 0.2mmol, 1.0 equiv) as substrate through the general procedure. Then, the ^{1}H NMR yields were measured by sampling at 0 h, 2 h, 4 h, 6 h, 8 h, 10 h, 12 h, 15 h, 18 h, 21 h and 24 h.

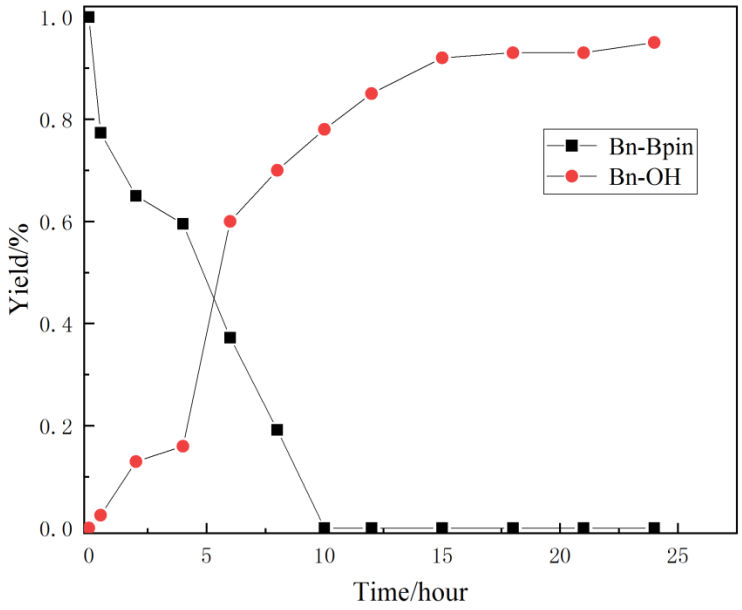


Figure S14. Kinetic experiments

8.4 Light "on/off" experiments

2-benzyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (21.8 mg, 0.1 mmol, 1.0 equiv), chlorophyll (2.0 mg, 0.004 mmol, 2.0 mol%), and Et_3N (14 μL, 0.1 mmol, 1.0 equiv) were placed in a NMR tubes. 1,3,5-Trimethoxybenzene (8.4 mg, 0.05 mmol) was added as internal standard add, and CD_3OD (0.5ml) was added as solvent. Then the NMR tubes was irradiated by using 30 W Red LEDs at the appropriate time under room temperature. The ^{1}H NMR yields were measured at a specific time interval.

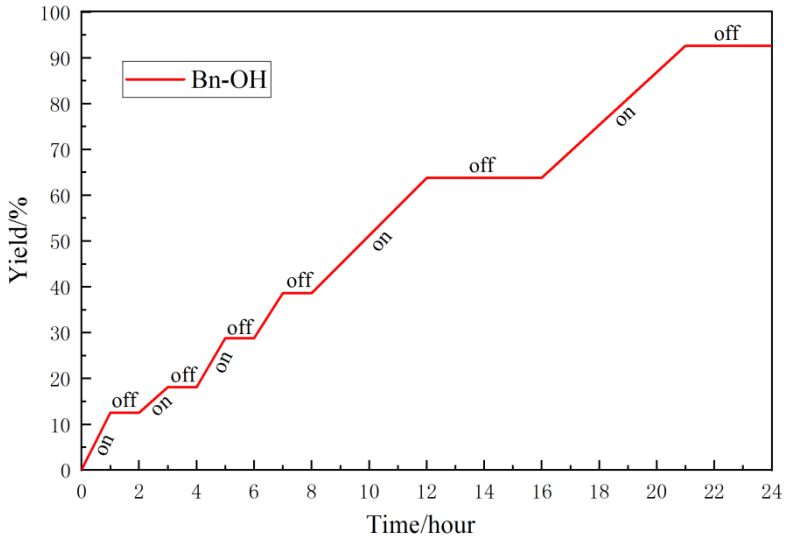


Figure S15. Light on-off experiment

8.5. Fluorescence Quenching Experiments

Fluorescence spectra were collected on Hitachi F-7000 Fluorescence Spectrophotometer. All chlorophyll solutions were excited at 610 nm and the emission intensity was collected at 686 nm. Photocatalyst chlorophyll (44.7 mg) was dissolved in EtOH (50 mL) to give a 1.0 mM solution. Et_3N (101 mg, 138.7 μL, 1.0 mmol) was dissolved in EtOH (1.0 mL) to give a 1.0 M solution. Bn-Bpin (218 mg, 1.0 mmol) was dissolved in EtOH (1.0 mL) to give a 1.0 M solution. A quartz cuvette was charged with 4.0 mL chlorophyll solution (1.0 mM). Then different concentration solution (2.0 μL, 4.0 μL, 8.0 μL, 12.0 μL, 16.0 μL, 20.0 μL, 40.0 μL Et_3N (1.0 mM); 2.0 μL, 4.0 μL, 8.0 μL, 12.0 μL, 16.0 μL, 20.0 μL, 40.0 μL Bn-Bpin (1.0 mM); and 2.0 μL, 4.0 μL, 8.0 μL, 12.0 μL, 16.0 μL, 20.0 μL, 40.0 μL Et_3N (1.0 mM)+ Bn-Bpin (1.0 mM)) was added to investigate the quenching effect. Oxygen was bubbled into the solution to investigate the quenching effect of chlorophyll fluorescence. The emission spectra of the samples were collected, respectively.

(a) Chlorophyll quenched by O_2 in EtOH.

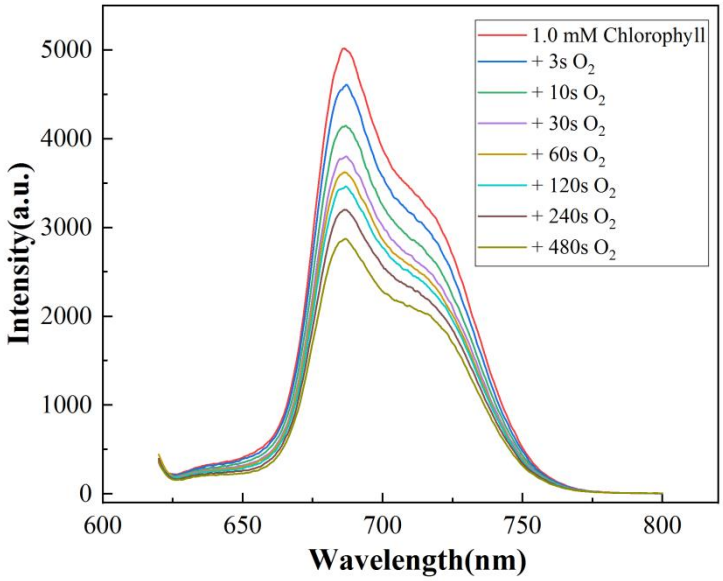


Figure S16. Chlorophyll quenched by O_2 in EtOH

(b) Chlorophyll quenched by Et_3N in EtOH.

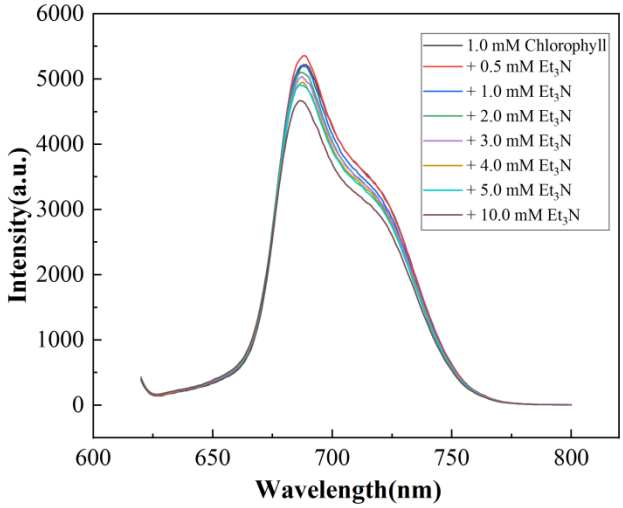


Figure S17. Chlorophyll quenched by Et_3N in EtOH

(c) Chlorophyll quenched by Bn-Bpin in EtOH.

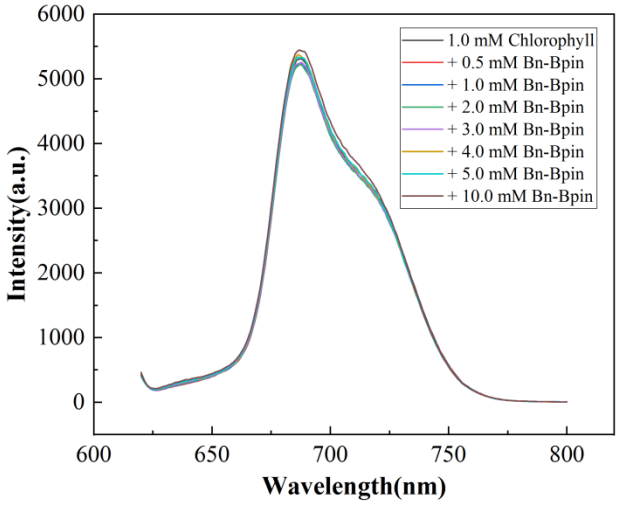


Figure S18. Chlorophyll quenched by Bn-Bpin in EtOH

(d) Chlorophyll quenched by Et_3N + Bn-Bpin in EtOH.

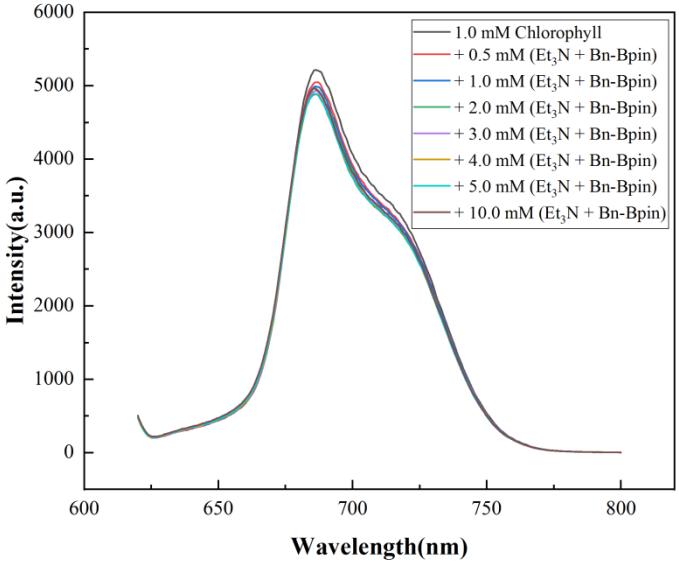


Figure S19. Chlorophyll quenched by Et_3N + Bn-Bpin in EtOH

(e) Chlorophyll quenched by O_2 + Et_3N + Bn-Bpin in EtOH.

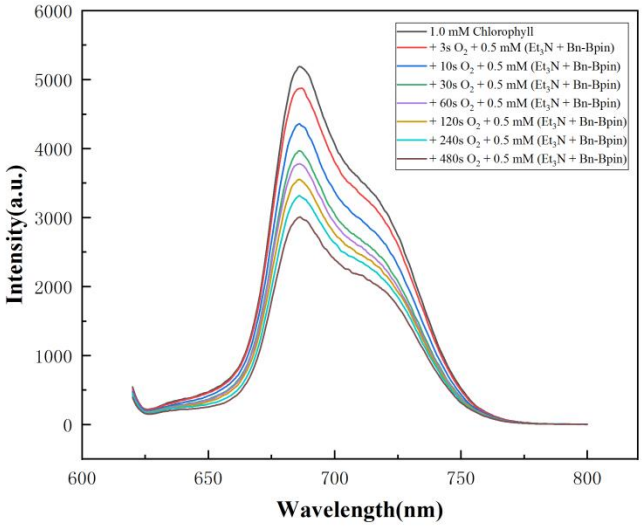


Figure S20. Chlorophyll quenched by O_2 + Et_3N + Bn-Bpin in EtOH

8.6 EPR spectrum

Electron paramagnetic resonance spectroscopy spectra were measured on Chinainstru&Quantumtech (Hefei) EPR200-Plus with continues-wave X band frequency. The EPR spectrum was measured by sampling after ten minutes of light irradiation. When a mixture of chlorophyll and DMPO in MeOH was irradiated with red LED under air atmosphere, the corresponding EPR spectrum exhibited a new triplet signal with a few detectable hyperfine splitting, which proved the existence of free radicals in reaction. In addition, the EPR signal of excited chlorophyll and air disappeared only in the presence of Et_3N. It has been reported that the excited chlorophyll could undergo oxidative quenching readily by donating electron to substrate, resulting in *pi*-radical cation of chlorophyll $Chl^{\bullet+}$. Considering that the organoborons does not appear to have a direct interaction with chlorophyll (derived from fluorescence quenching experiments and EPR studies), the presence of superoxide anion is a relatively plausible explanation based on existing experiments, even though the EPR signal is not captured due to its very short duration.

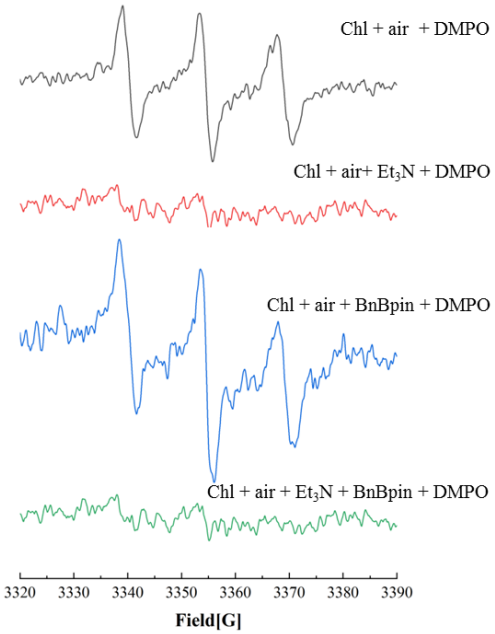


Figure S21. The EPR spectrum

8.7 DFT calculation

In this section, all calculations were performed by Gaussian 09 software packages.[38] The conformations of intermediates were generated by SYBYL-X 2.0 GA Conf. search module and manual adjustment.[39] The recently developed M06-2X functional[40] together with the standard 6-31+G(d) basis set,[41] were used for optimizing the geometry of all the minima and transition states. The optimized structures or transition structures were confirmed by normal vibrational mode analysis. The optimized structures were no imaginary frequency but transition structure had only one imaginary frequency. Considering the influence of solvation effect, SMD implicit solvent model[42] was used at M06-2X/6-311++G (2d, p) theoretical level[43] to obtain high accuracy single point energy in EtOH. This method has been applied successfully to investigate the mechanisms of several organic reaction, which is generally considered to be more accurate for energetic. Solution-phase single-point energies corrected by the gas-phase Gibbs free energy corrections were used to describe all the reaction energetics.

The reaction process after the formation of superoxide anion radical was studied by DFT calculation to prove the rationality of the speculated mechanism. First, superoxide anion radicals ($\mathbf{O_2^{\bullet-}}$) attacked phenylboronic acid ($PhB(OH)_2$) to give **INT1** *via* **TS1**. Due to the high activity of $\mathbf{O_2^{\bullet-}}$, the energy barrier of **TS1** is only 6.3 kcal/mol. Next, **INT1** abstracted the $\mathbf{H^{\bullet}}$ from triethylamine cation radical ($\mathbf{Et_3N^{+\bullet}}$) to

obtain **INT2** and imine cation. Then **INT2** underwent intramolecular oxygen transfer rearrangement to give **INT3** *via* **TS2** with the energy barrier of 25.6 kcal/mol. The final hydroxylated product was obtained by hydrolysis, which was a process that has been reported in many literatures before. The above calculation results demonstrate that the reaction process mediated by $\mathbf{O_2^{\bullet-}}$ is thermodynamically feasible.

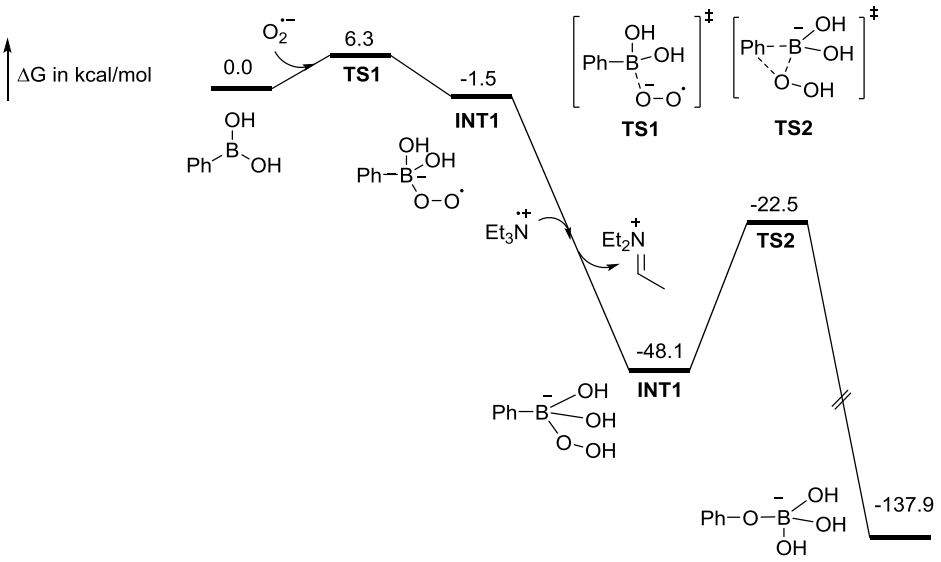


Figure S22.Computed potential energy profiles. Relative Gibbs free energies were computed at the M06-2X/ 6-311++G(2d,p) // M06-2X/ 6-31+G(d) level of theory with unit in kcal/mol.

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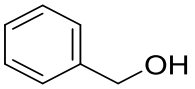
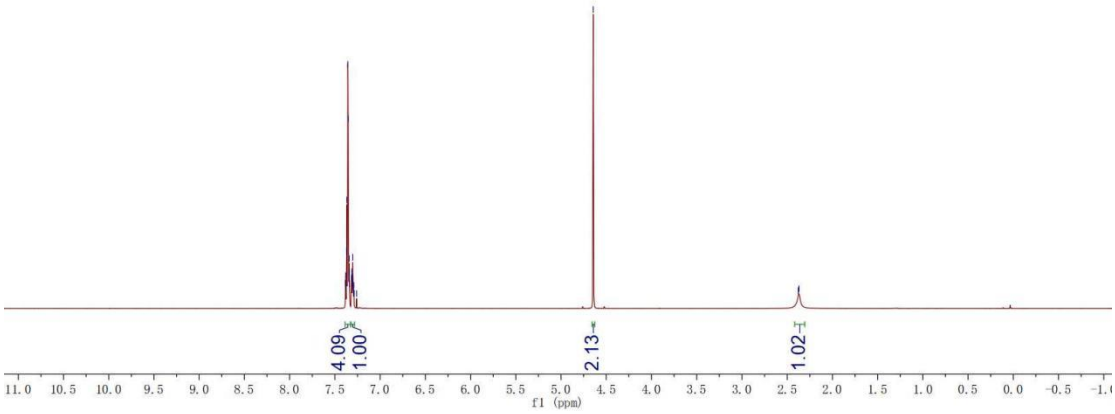
10. NMR (^{1}H and ^{13}C) Spectra

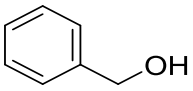
^{1}H NMR spectrum of compound **2**



2 (600 MHz, $CDCl_3$)



^{13}C NMR spectrum of compound **2**



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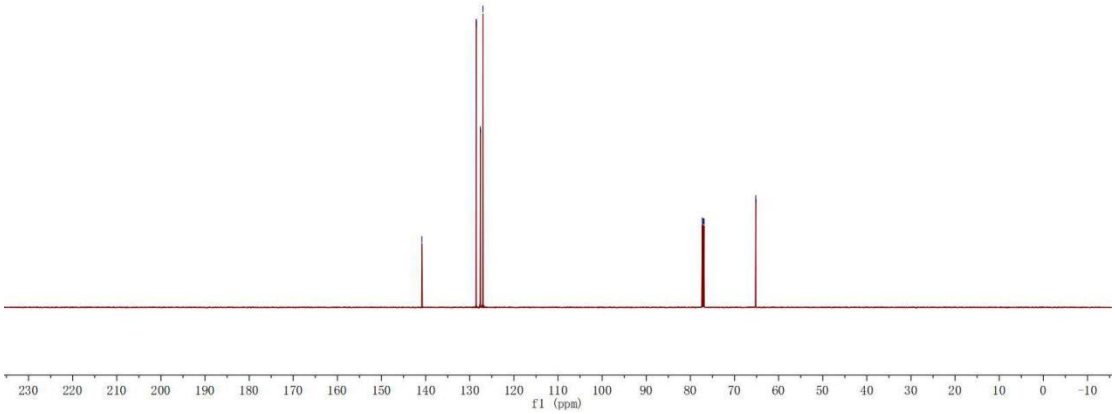
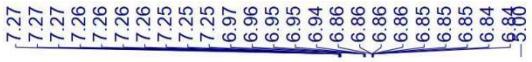
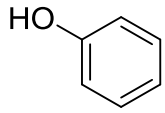
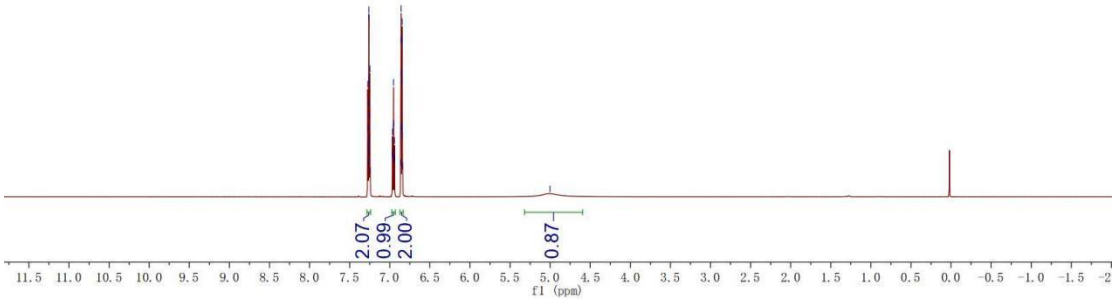


^{1}H NMR spectrum of compound **3**

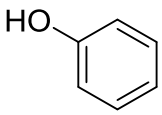




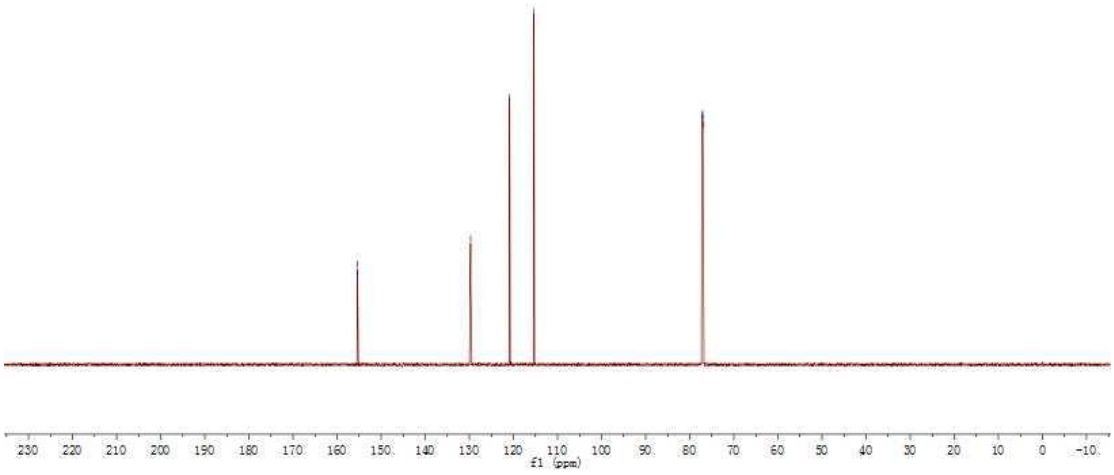
3 (600 MHz, $CDCl_3$)



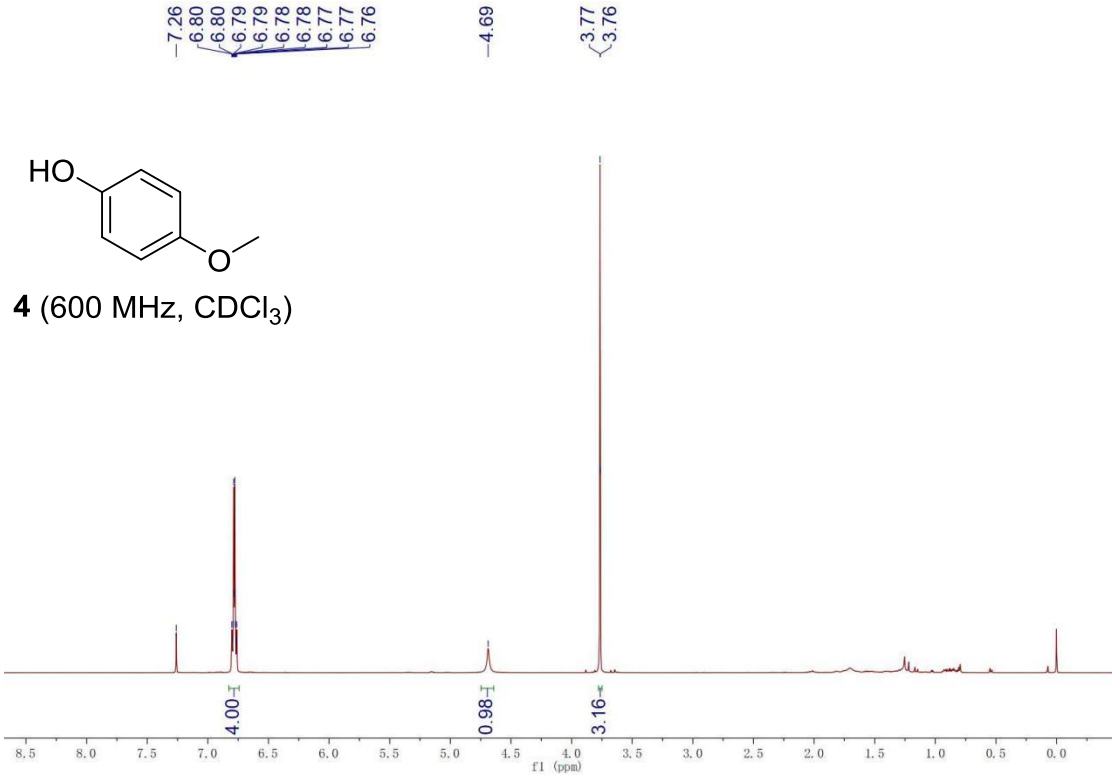
^{13}C NMR spectrum of compound **3**



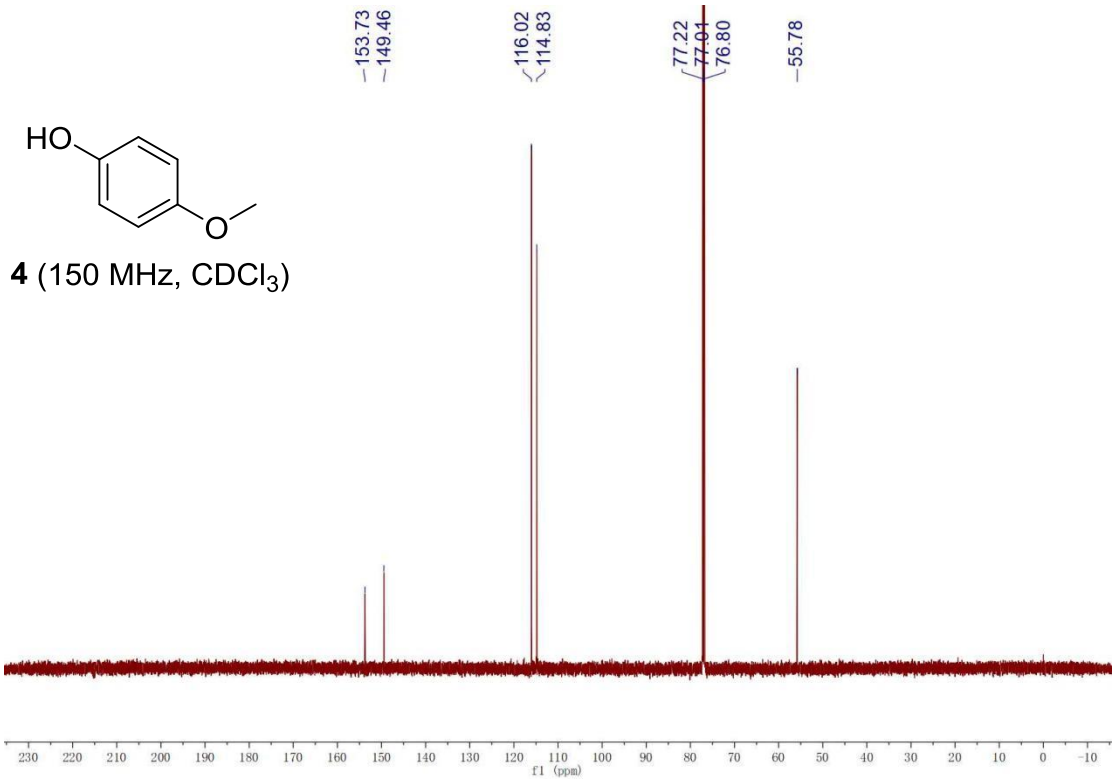
3 (150 MHz, $CDCl_3$)



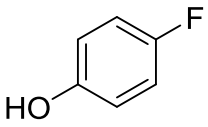
^{1}H NMR spectrum of compound **4**



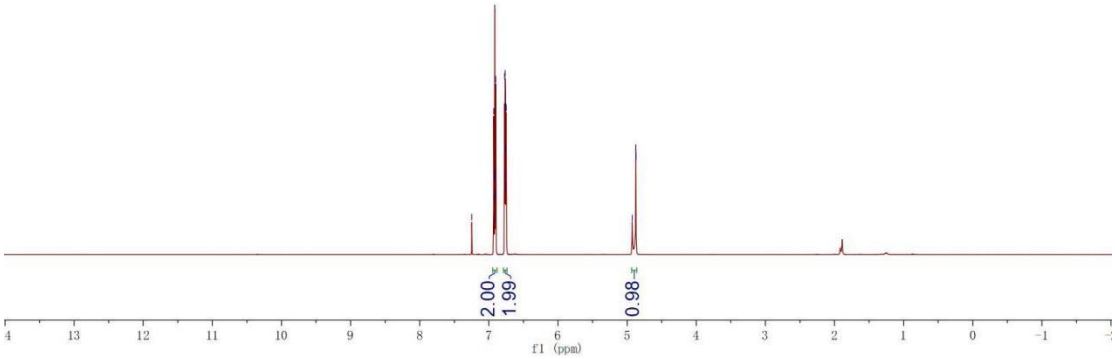
^{13}C NMR spectrum of compound **4**



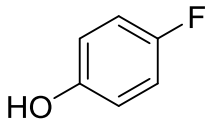
^{1}H NMR spectrum of compound **5**



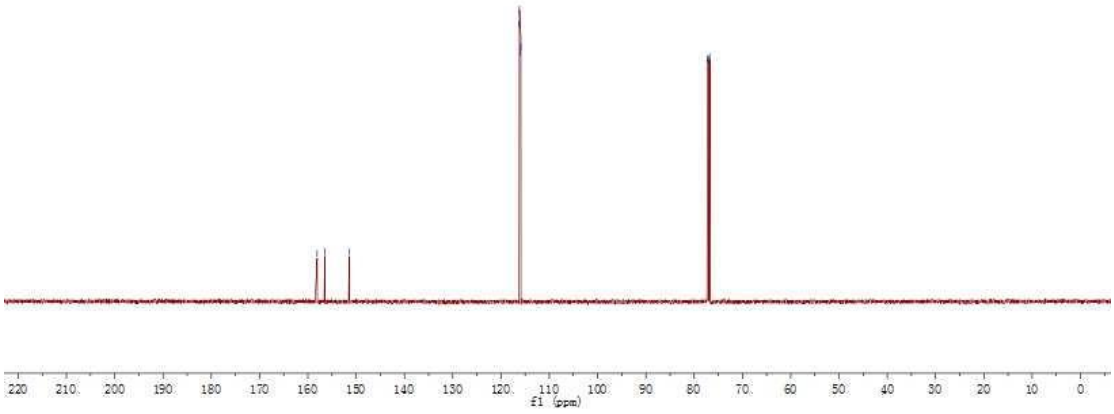
5 (600 MHz, $CDCl_3$)



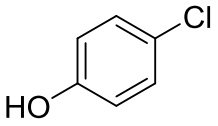
^{13}C NMR spectrum of compound **6w**



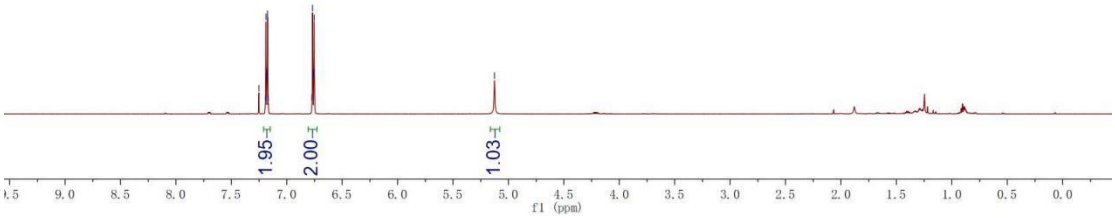
5 (150 MHz, $CDCl_3$)



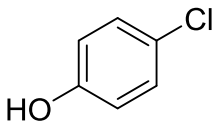
^{1}H NMR spectrum of compound **6**



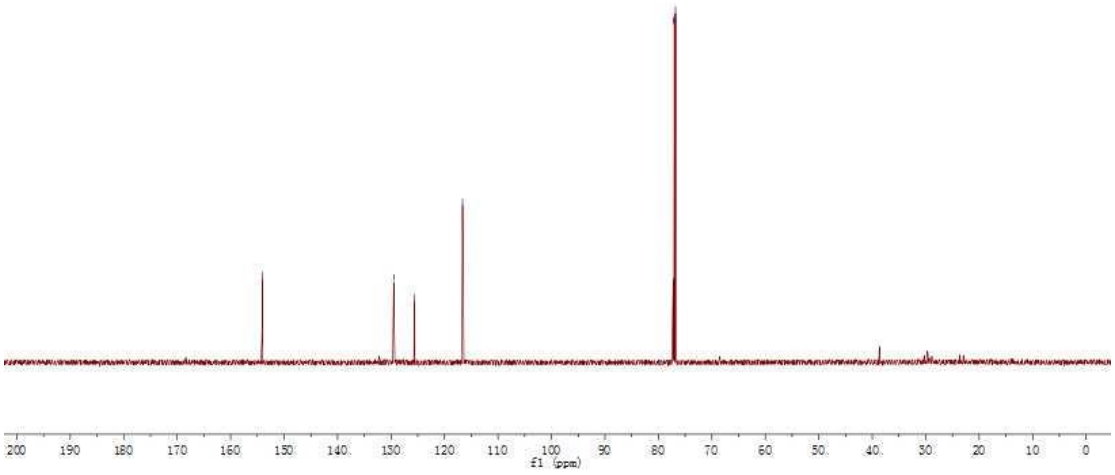
6 (600 MHz, $CDCl_3$)



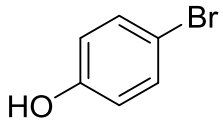
^{13}C NMR spectrum of compound **6**



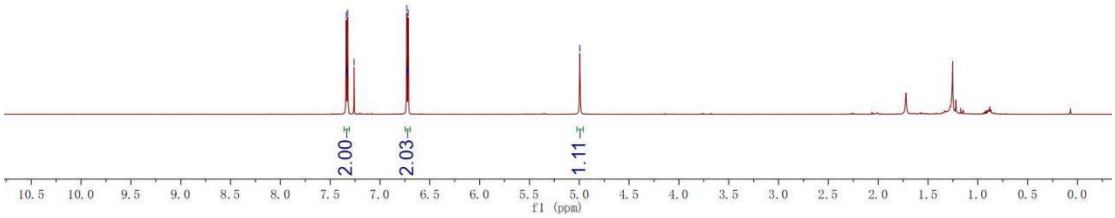
6 (150 MHz, $CDCl_3$)



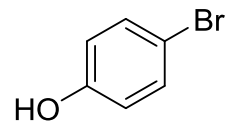
^{1}H NMR spectrum of compound **7**



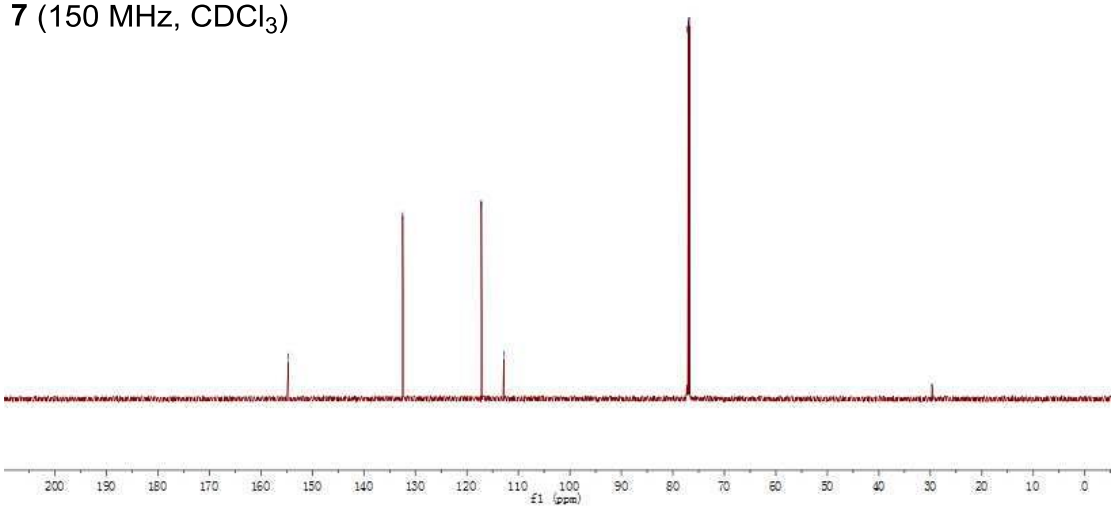
7 (600 MHz, $CDCl_3$)



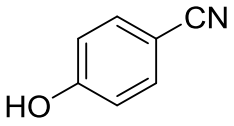
^{13}C NMR spectrum of compound **7**



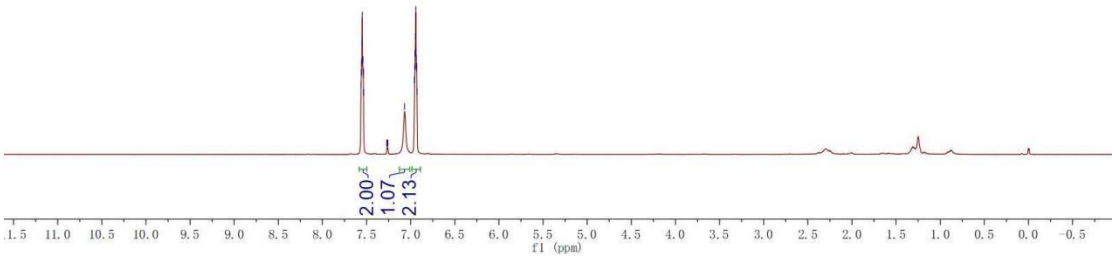
7 (150 MHz, $CDCl_3$)



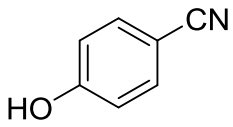
^{1}H NMR spectrum of compound **8**



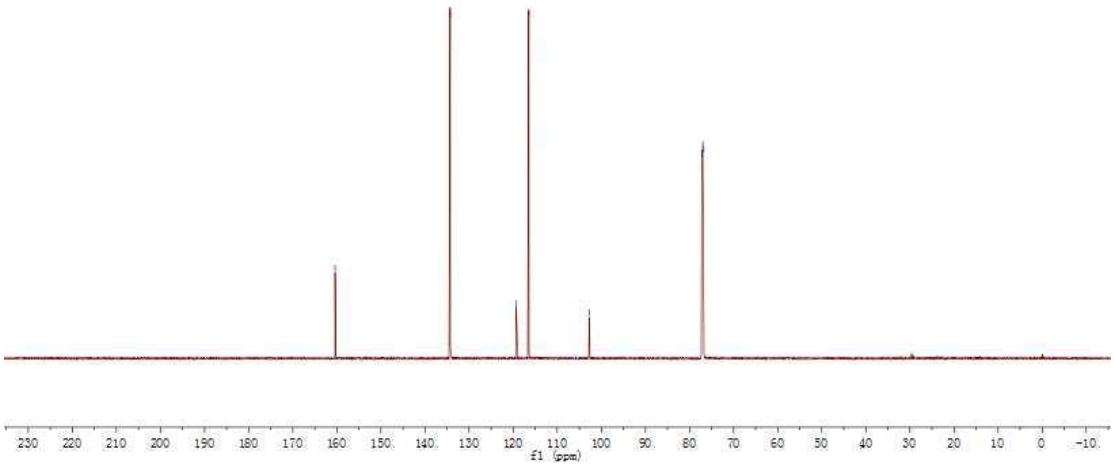
8 (600 MHz, $CDCl_3$)



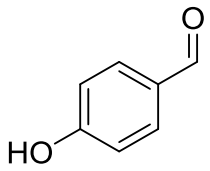
^{13}C NMR spectrum of compound **8**



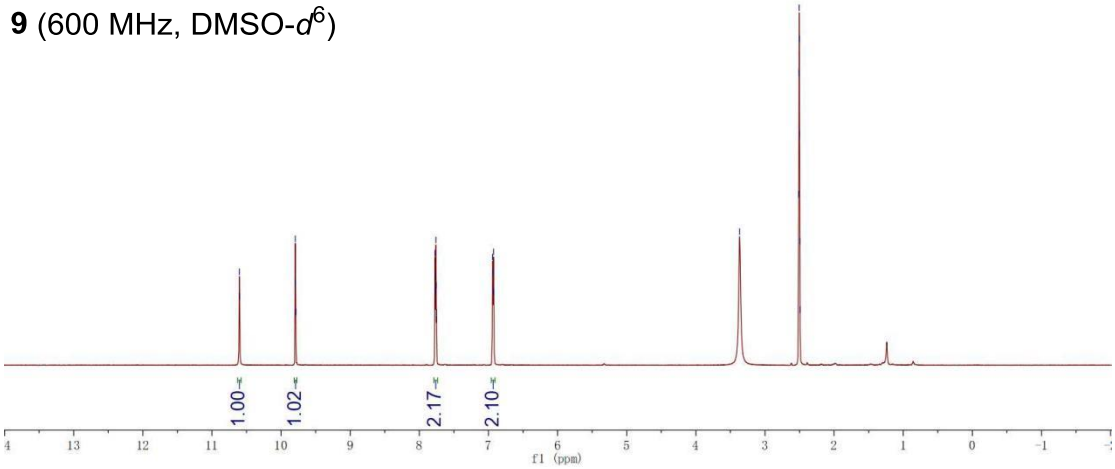
8 (150 MHz, $CDCl_3$)



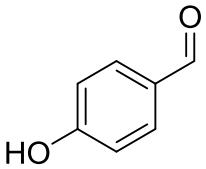
^{1}H NMR spectrum of compound **9**



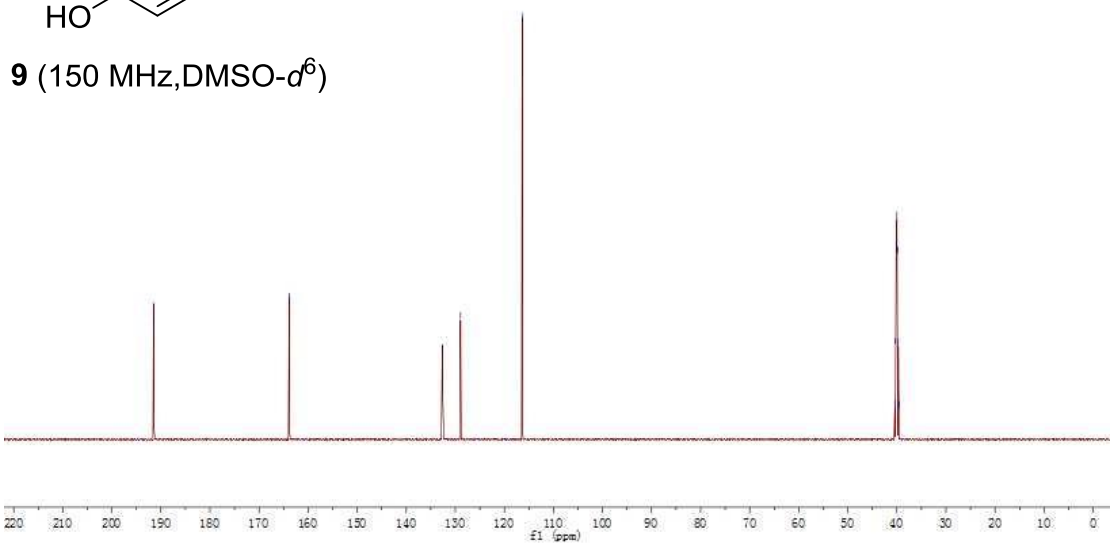
9 (600 MHz, DMSO-d^6)



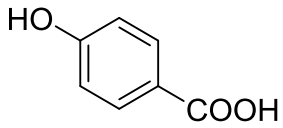
^{13}C NMR spectrum of compound **9**



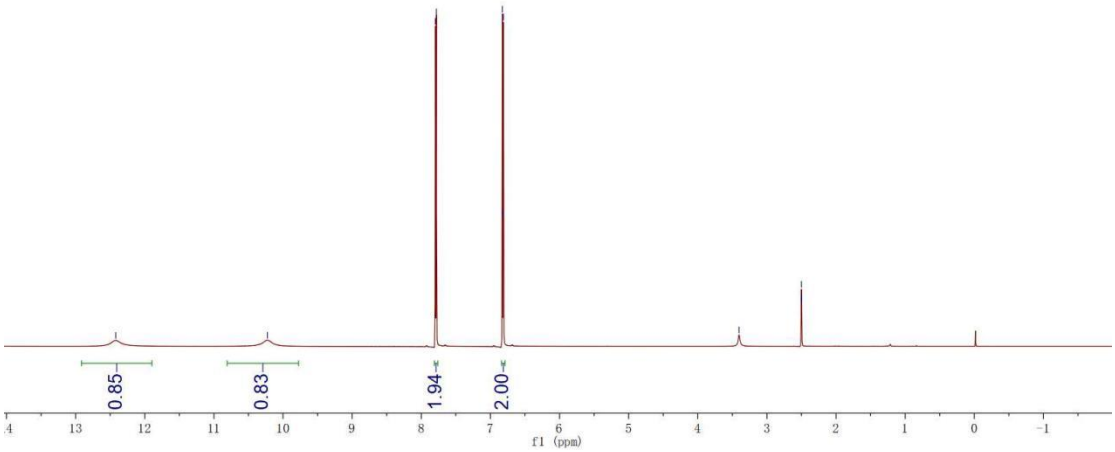
9 (150 MHz,DMSO-d^6)



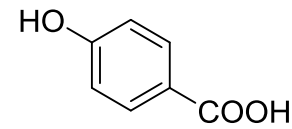
^{1}H NMR spectrum of compound **10**



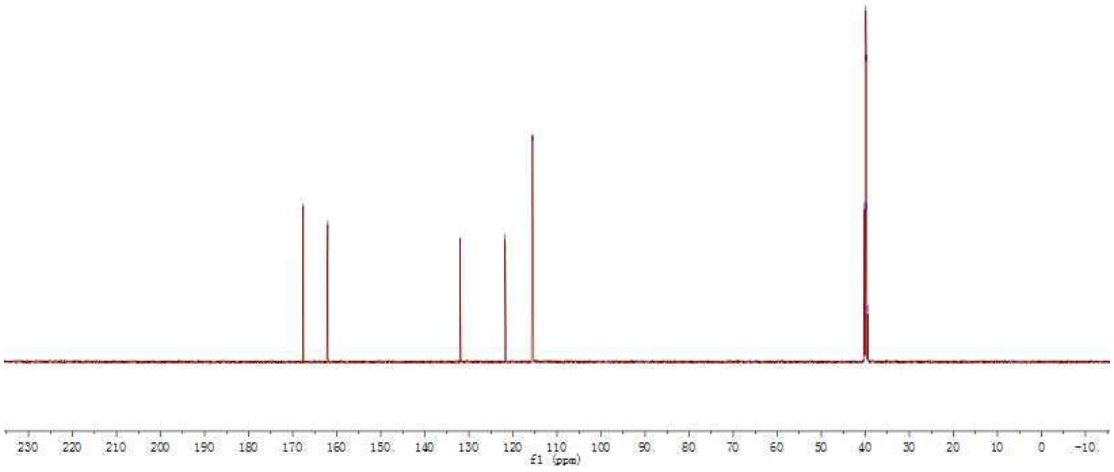
10 (600 MHz, DMSO-d^6)



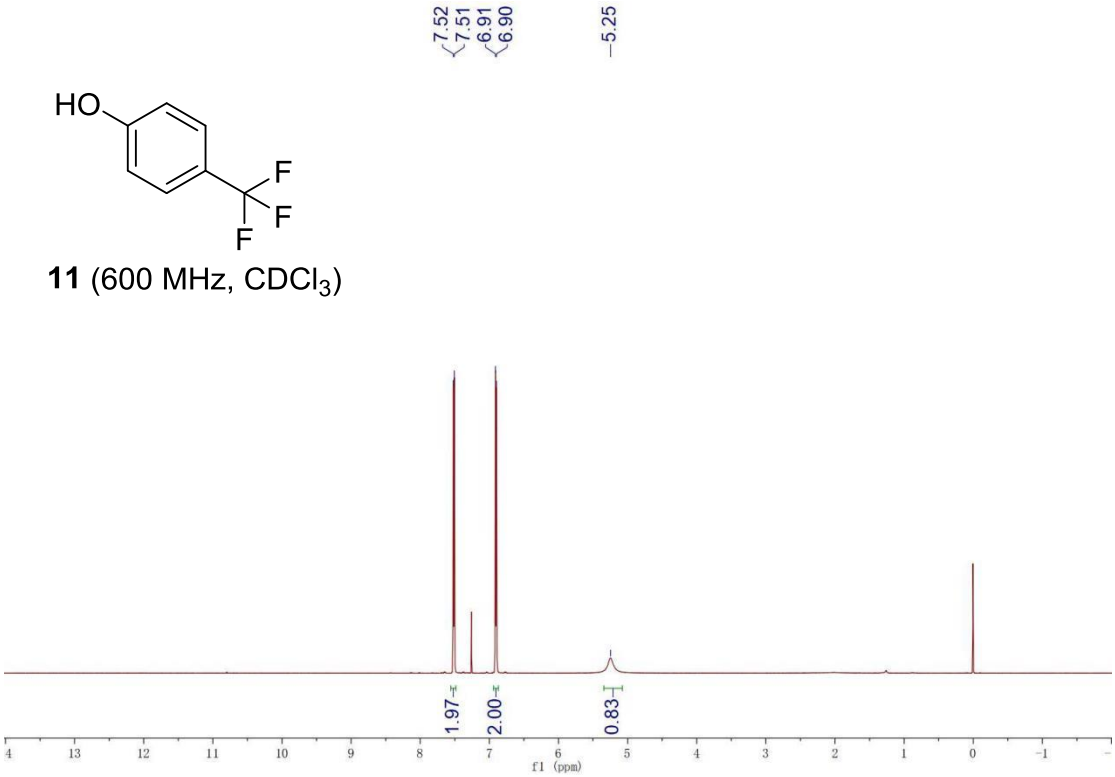
^{13}C NMR spectrum of compound **10**



10 (150 MHz, DMSO-d^6)

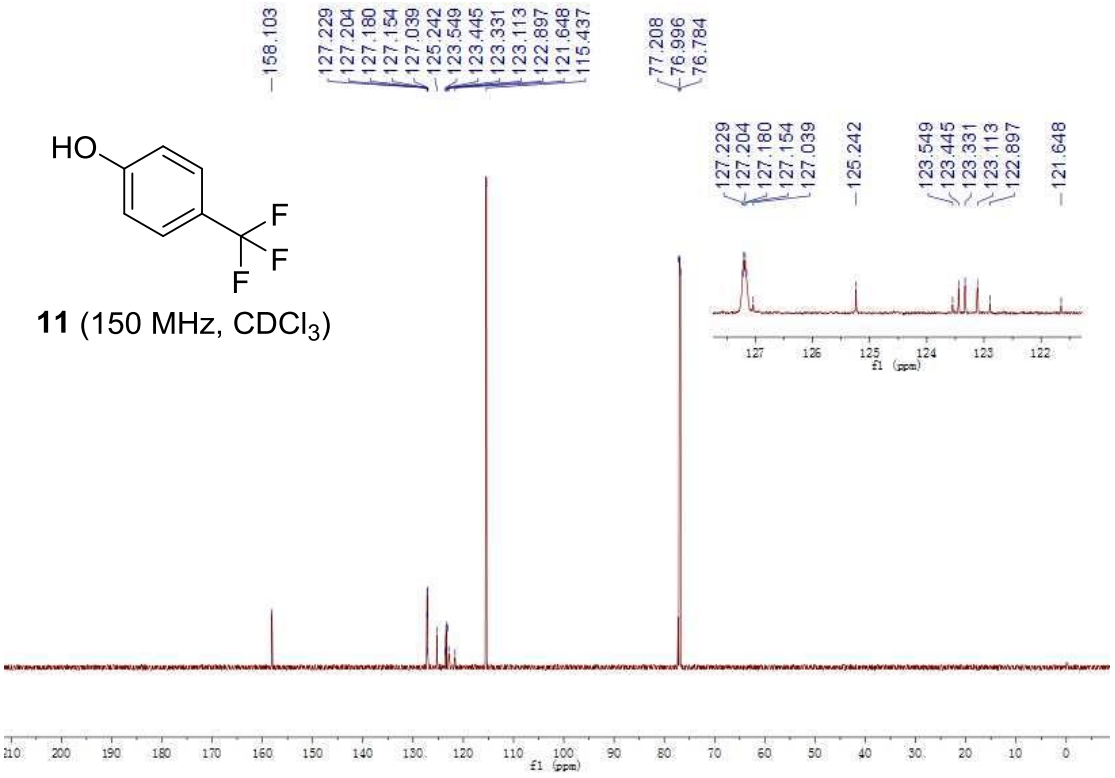


^{1}H NMR spectrum of compound **11**



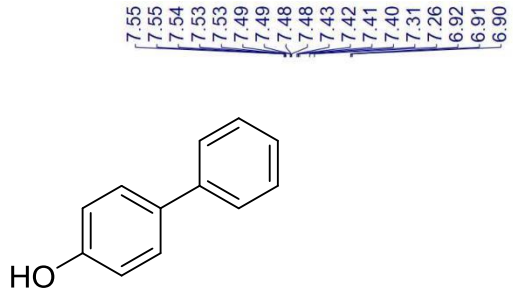
11 (600 MHz, $CDCl_3$)

^{13}C NMR spectrum of compound **11**

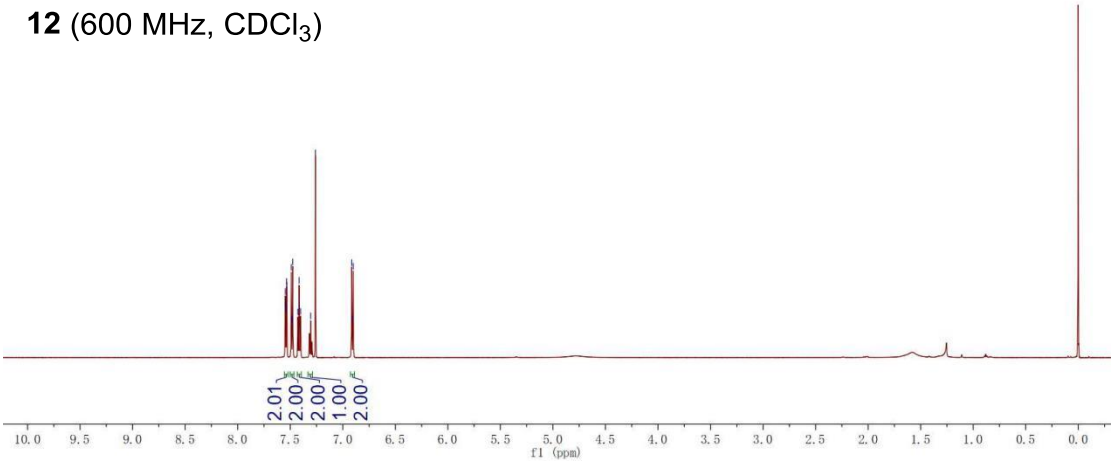


11 (150 MHz, $CDCl_3$)

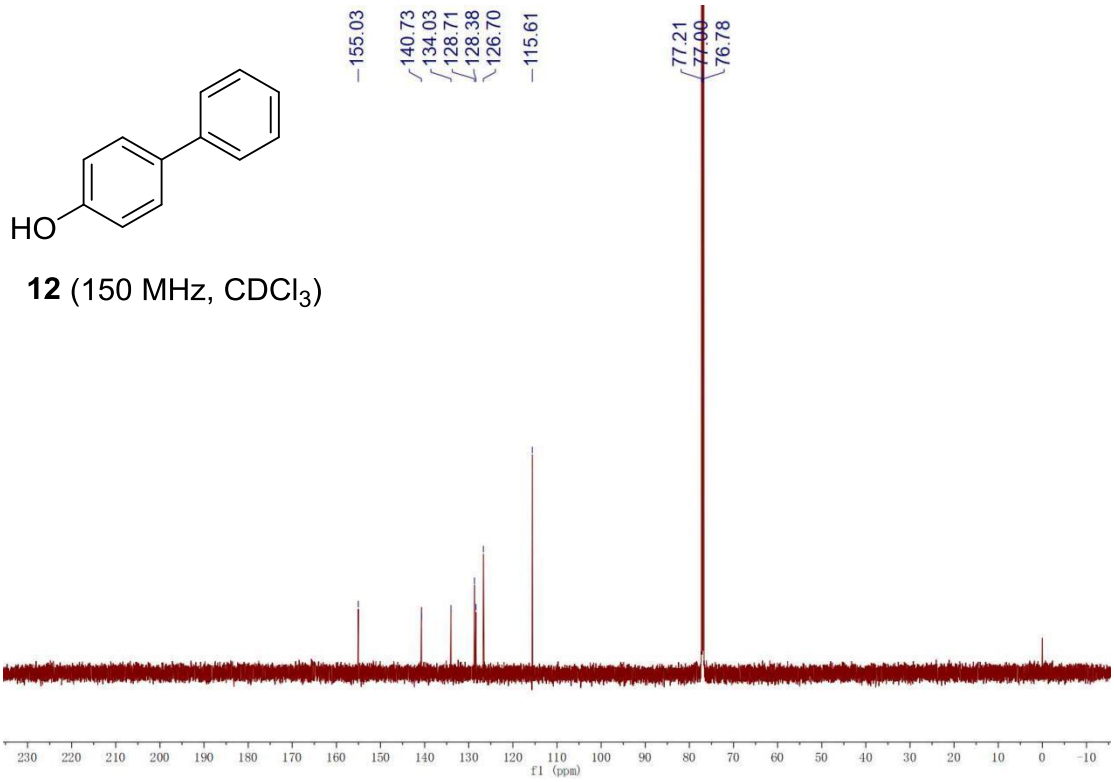
^{1}H NMR spectrum of compound **12**



12 (600 MHz, $CDCl_3$)

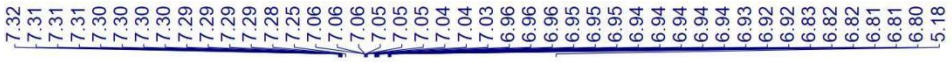


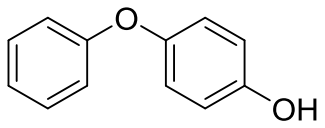
^{13}C NMR spectrum of compound **12**



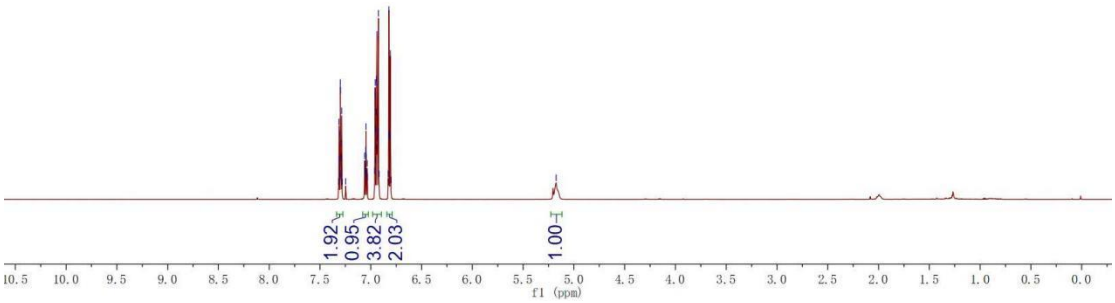
12 (150 MHz, $CDCl_3$)

^{1}H NMR spectrum of compound **13**

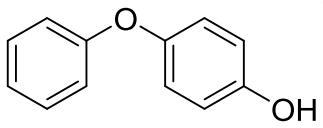




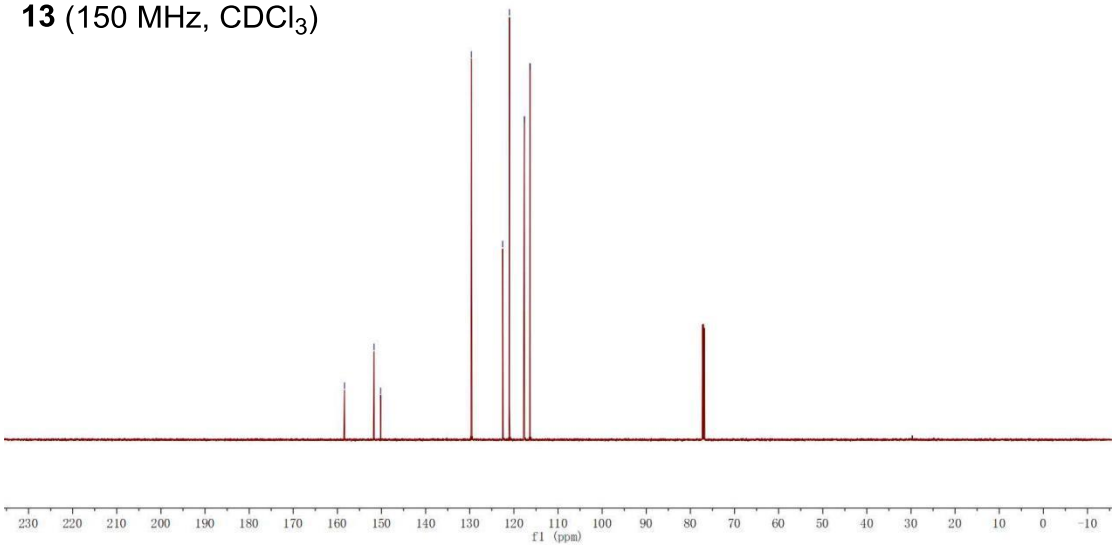
13 (600 MHz, $CDCl_3$)



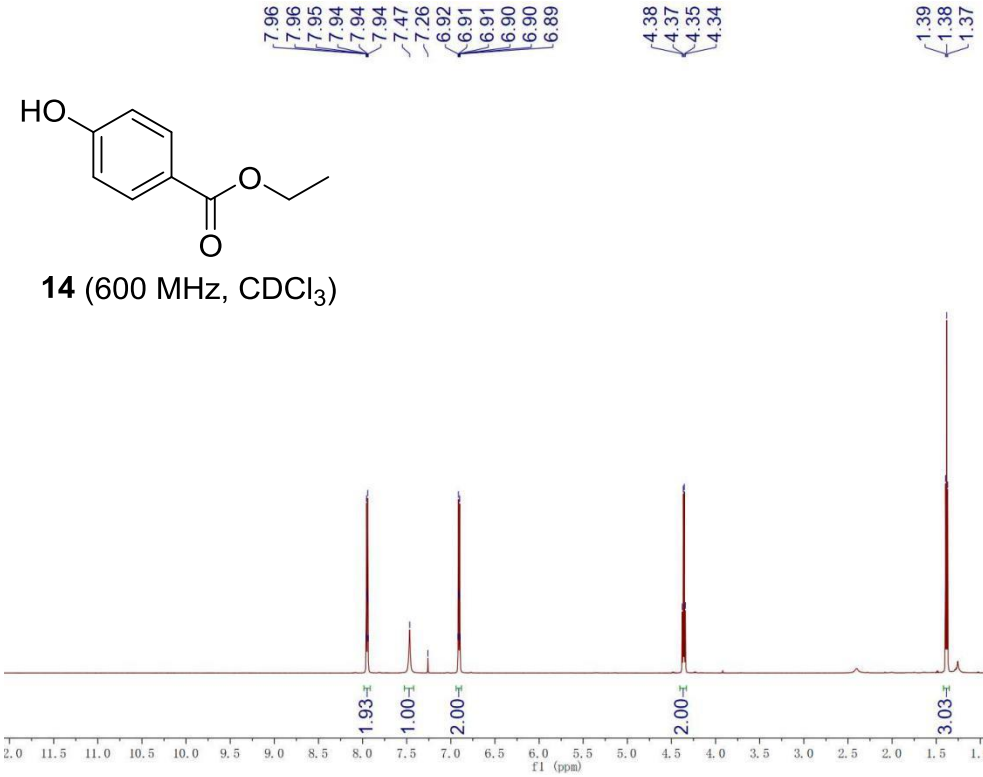
^{13}C NMR spectrum of compound **13**



13 (150 MHz, $CDCl_3$)

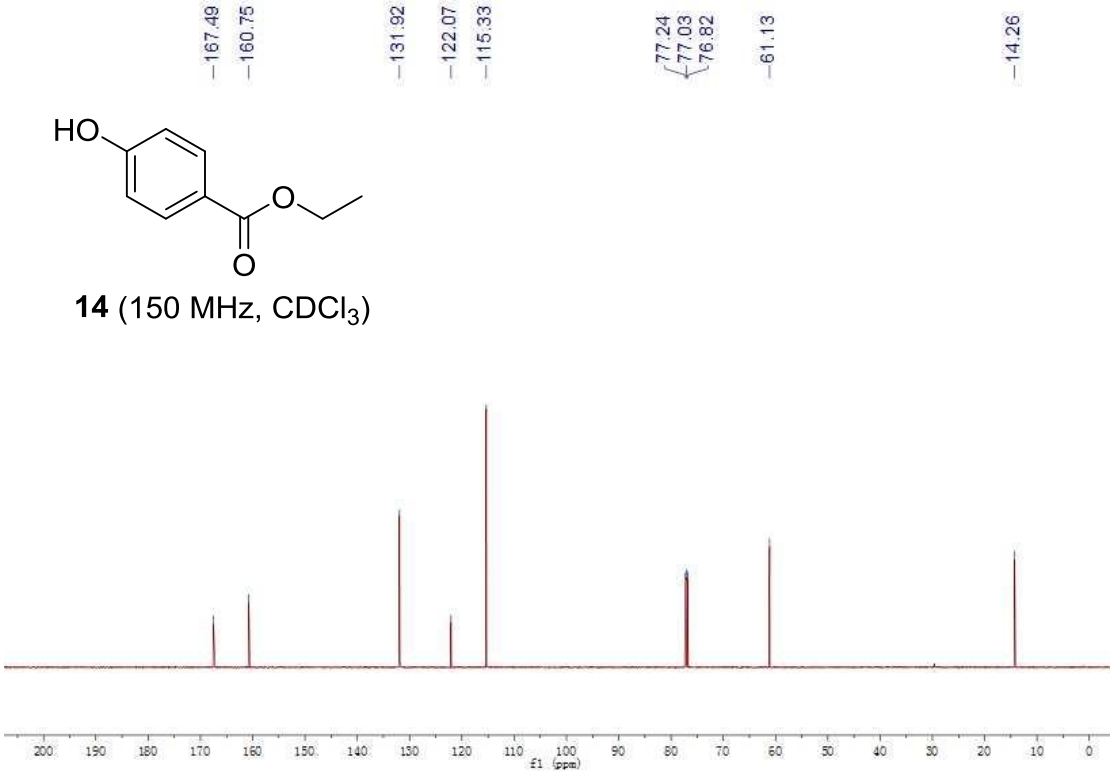


^{1}H NMR spectrum of compound **14**



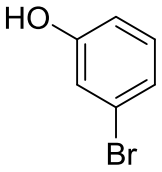
14 (600 MHz, $CDCl_3$)

^{13}C NMR spectrum of compound **14**

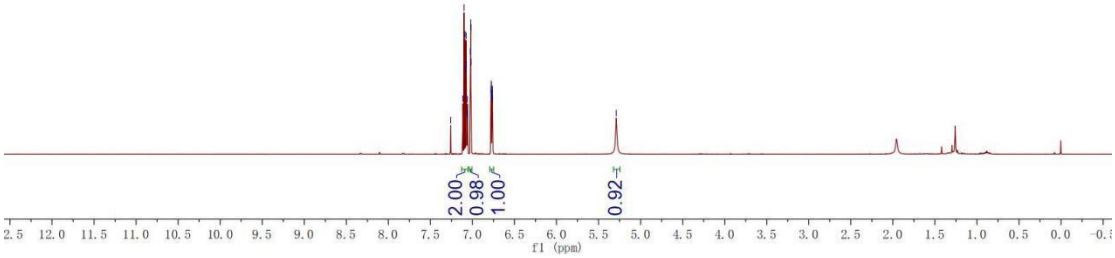


14 (150 MHz, $CDCl_3$)

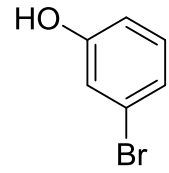
^{1}H NMR spectrum of compound **15**



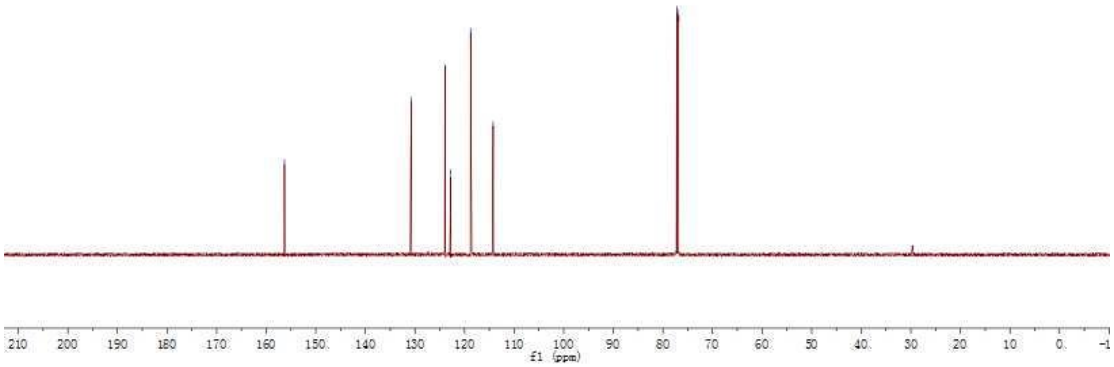
15 (600 MHz, $CDCl_3$)



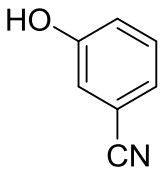
^{13}C NMR spectrum of compound **15**



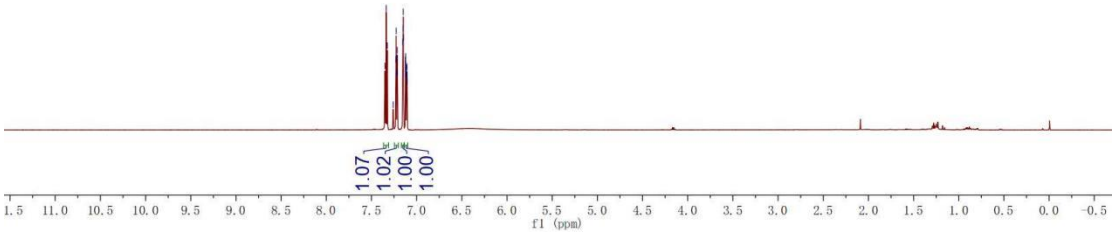
15 (150 MHz, $CDCl_3$)



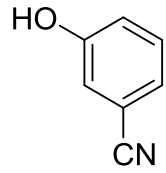
^{1}H NMR spectrum of compound **16**



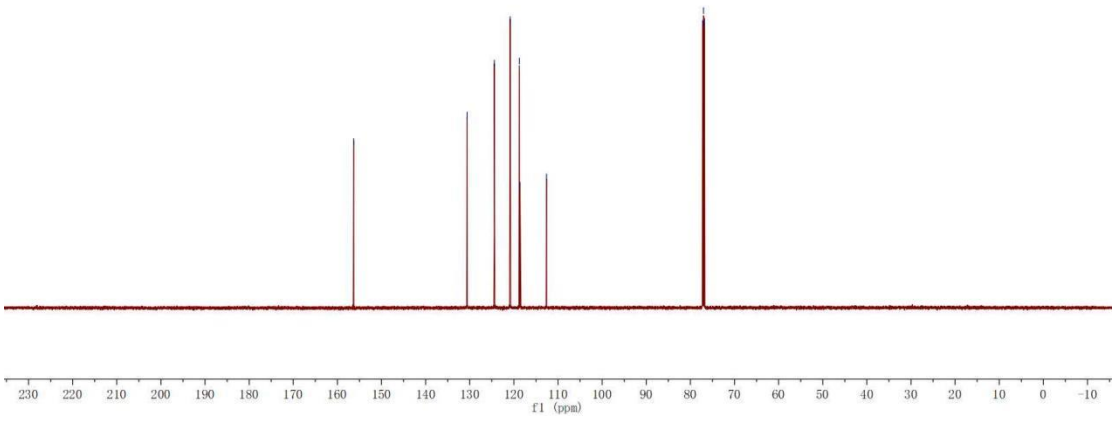
16 (600 MHz, $CDCl_3$)



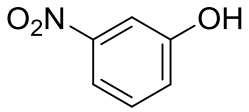
^{13}C NMR spectrum of compound **16**



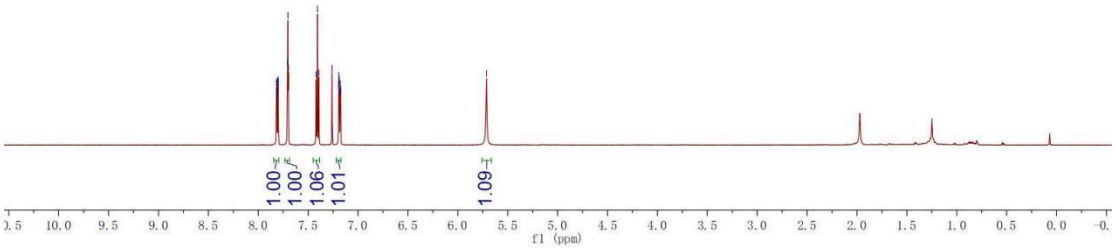
16 (150 MHz, $CDCl_3$)



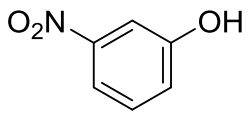
^{1}H NMR spectrum of compound **17**



17 (600 MHz, $CDCl_3$)

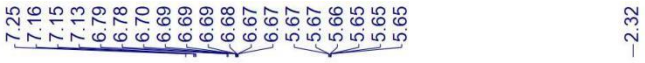


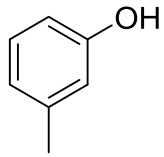
^{13}C NMR spectrum of compound **17**



17 (150 MHz, $CDCl_3$)

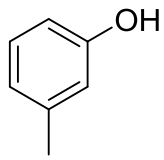
^{1}H NMR spectrum of compound **18**



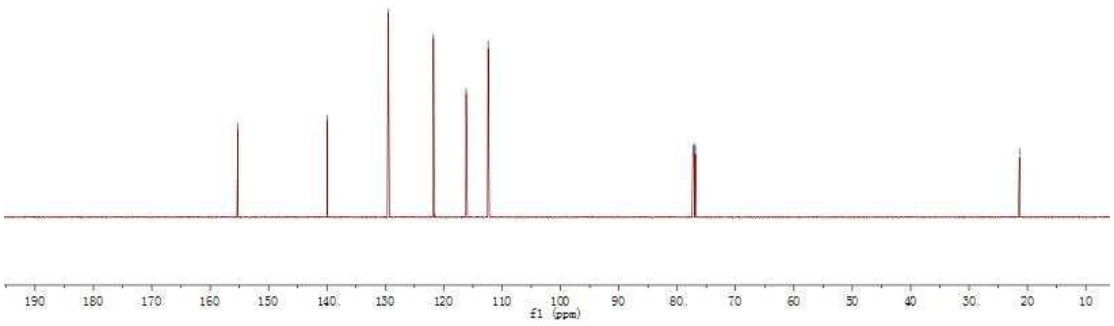


18 (600 MHz, $CDCl_3$)

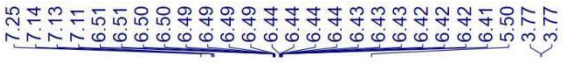
^{13}C NMR spectrum of compound **18**

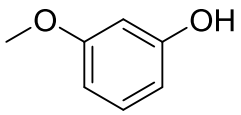


18 (150 MHz, $CDCl_3$)

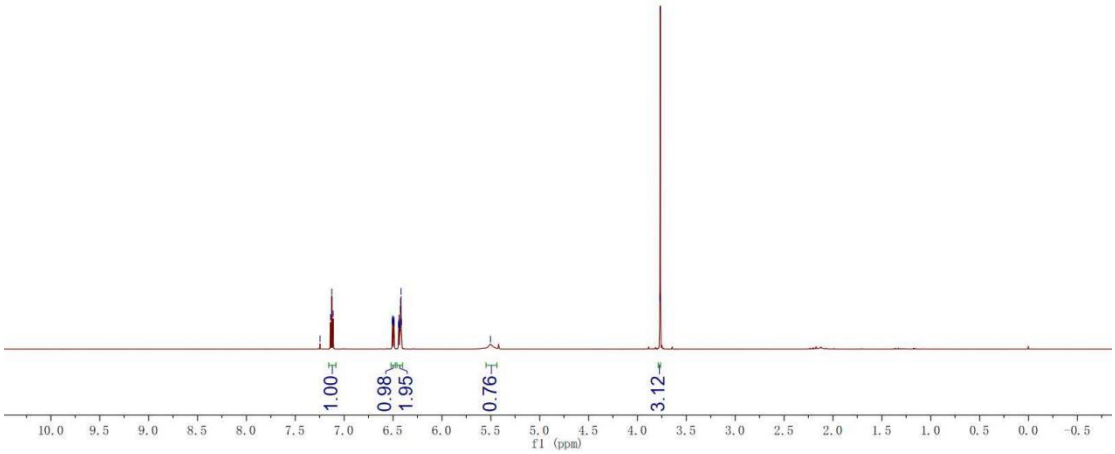


^{1}H NMR spectrum of compound **19**

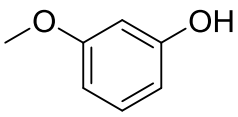




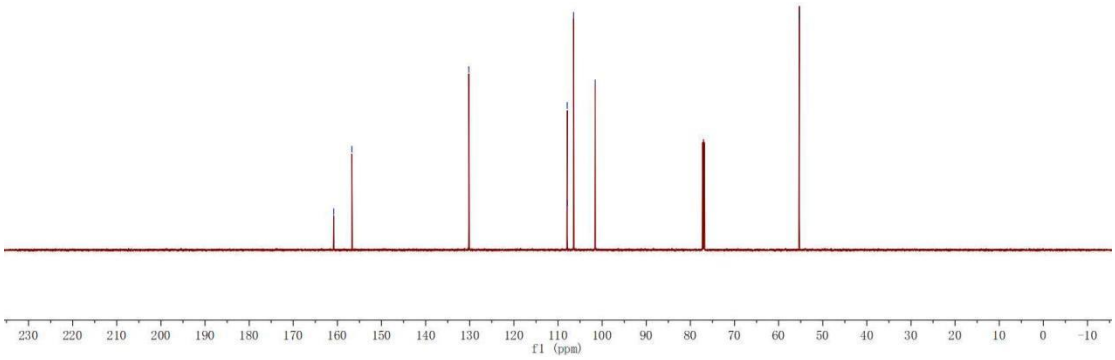
19 (600 MHz, $CDCl_3$)



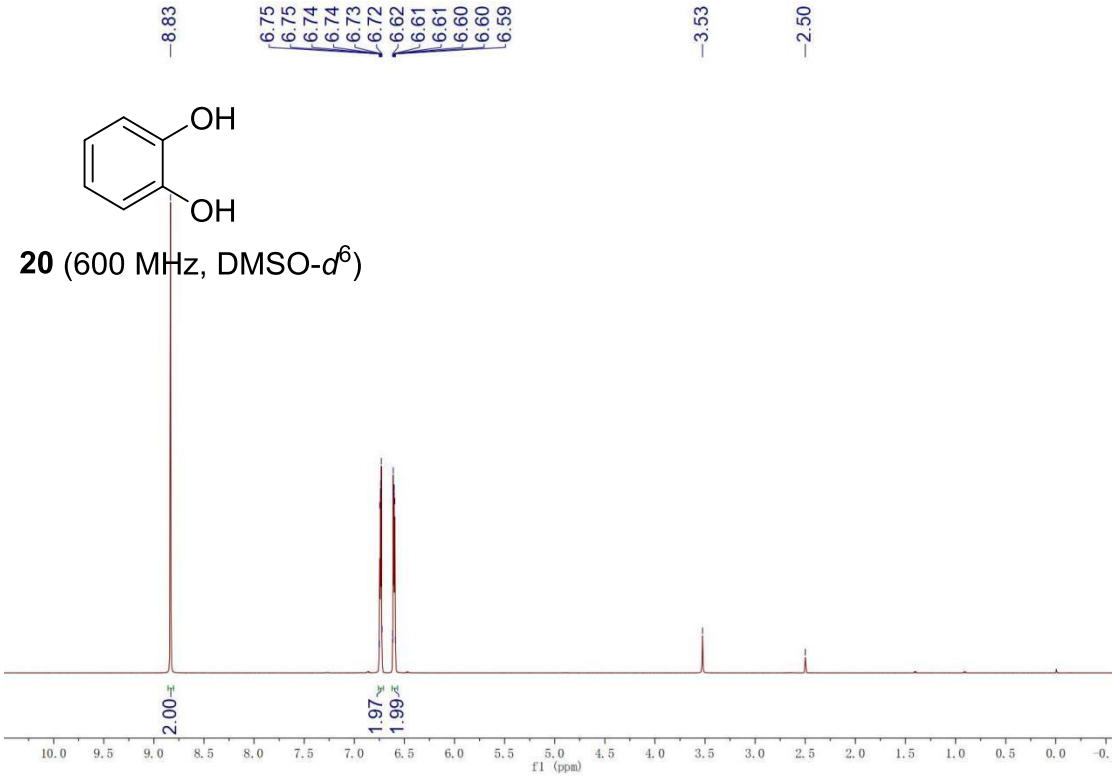
^{13}C NMR spectrum of compound **19**



19 (150 MHz, $CDCl_3$)

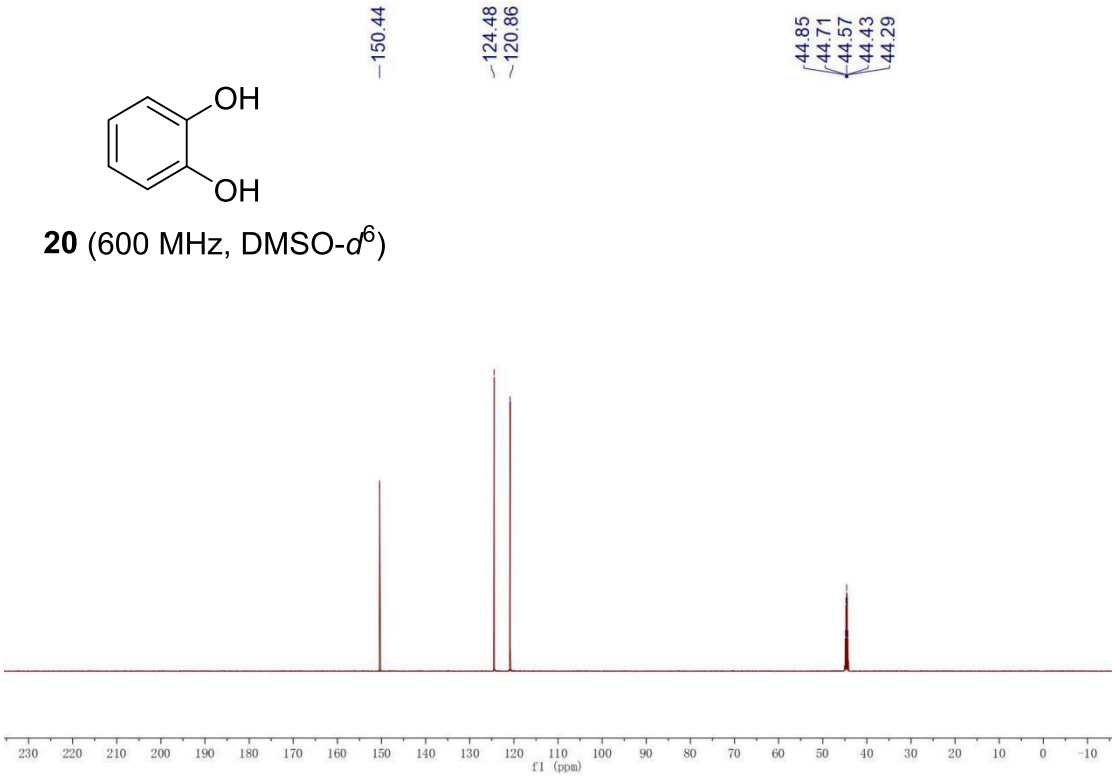


^{1}H NMR spectrum of compound **20**



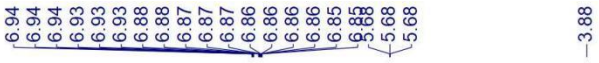
20 (600 MHz, DMSO-d^6)

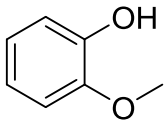
^{13}C NMR spectrum of compound **20**



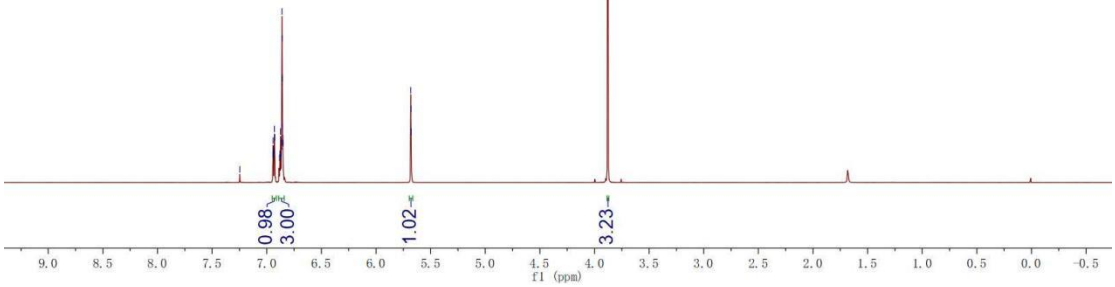
20 (600 MHz, DMSO-d^6)

^{1}H NMR spectrum of compound **21**

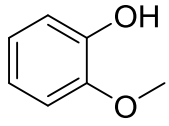




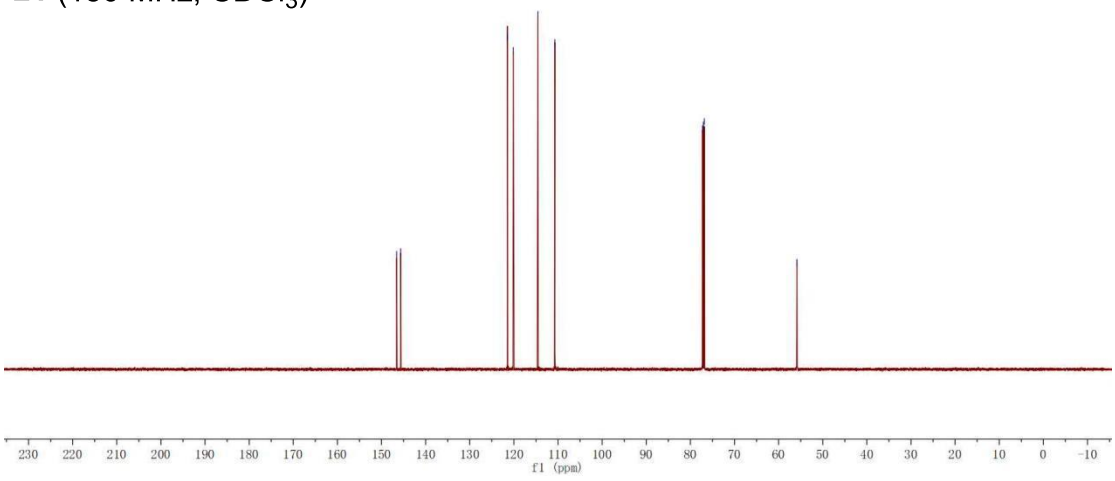
21 (600 MHz, $CDCl_3$)



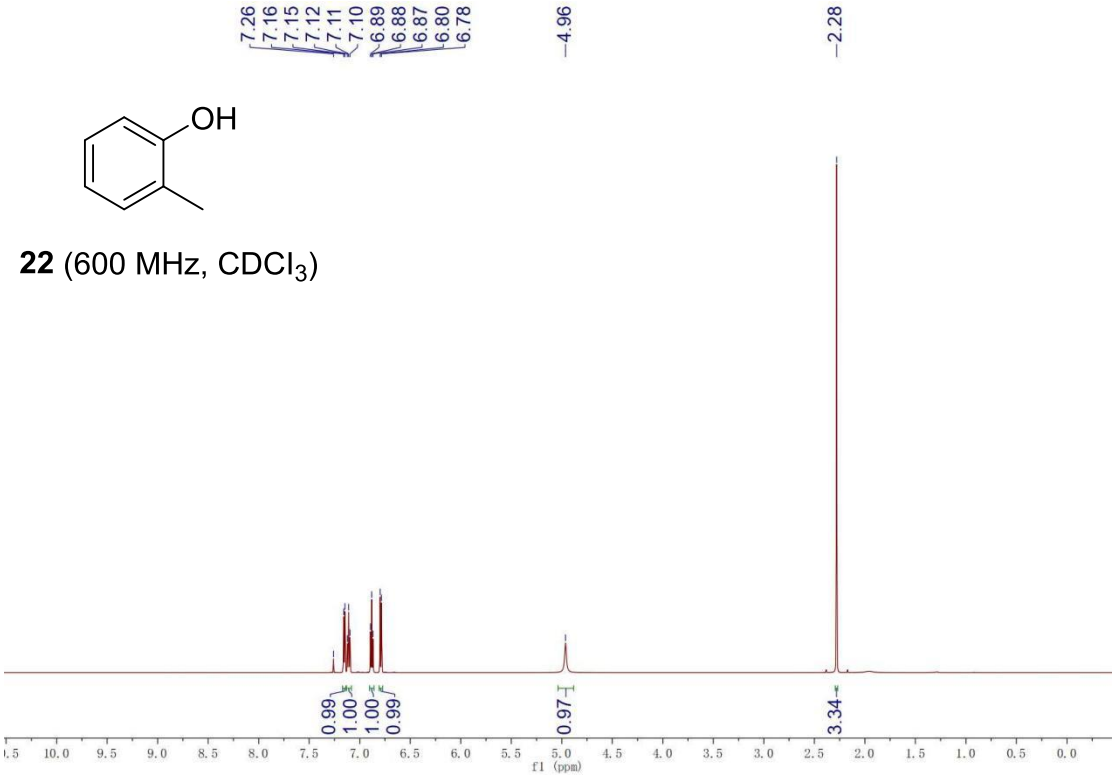
^{13}C NMR spectrum of compound **21**



21 (150 MHz, $CDCl_3$)

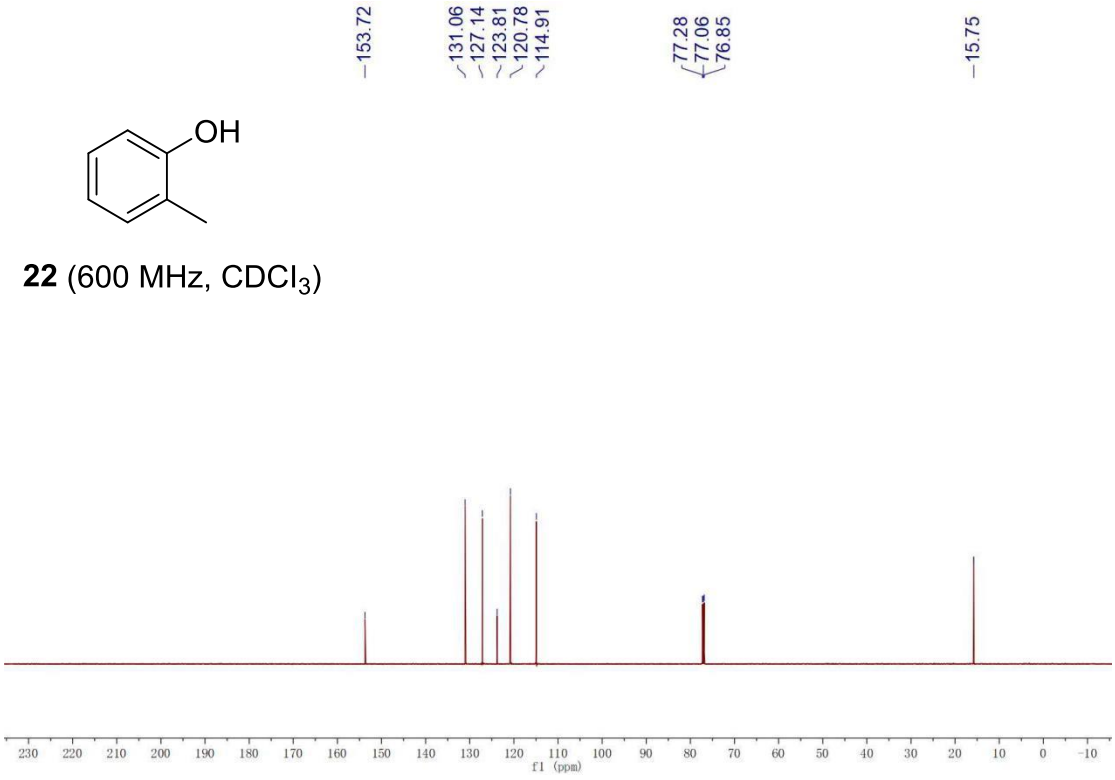


^{1}H NMR spectrum of compound **22**



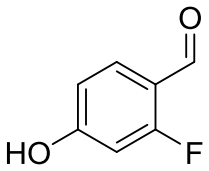
22 (600 MHz, $CDCl_3$)

^{13}C NMR spectrum of compound **22**

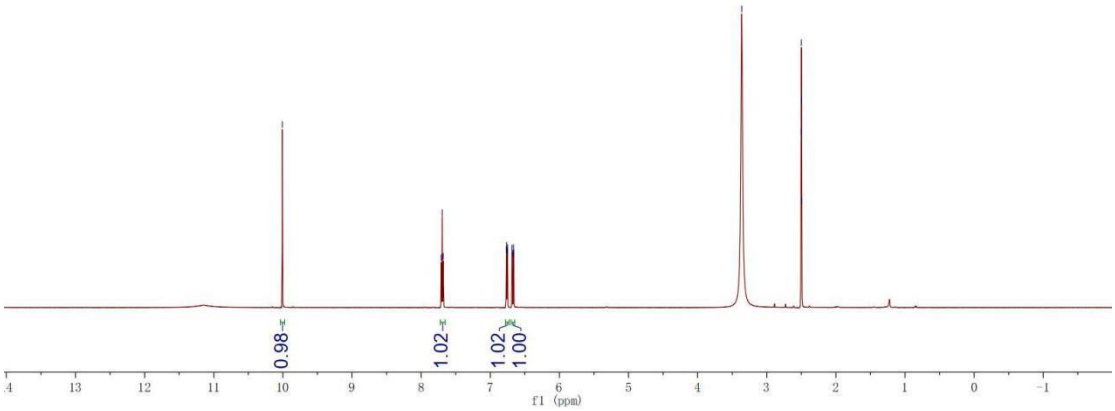


22 (600 MHz, $CDCl_3$)

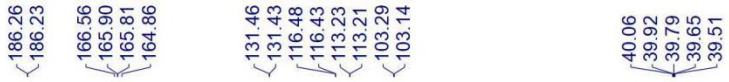
^{1}H NMR spectrum of compound **23**

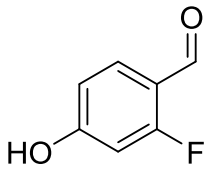


23 (600 MHz, DMSO-d^6)

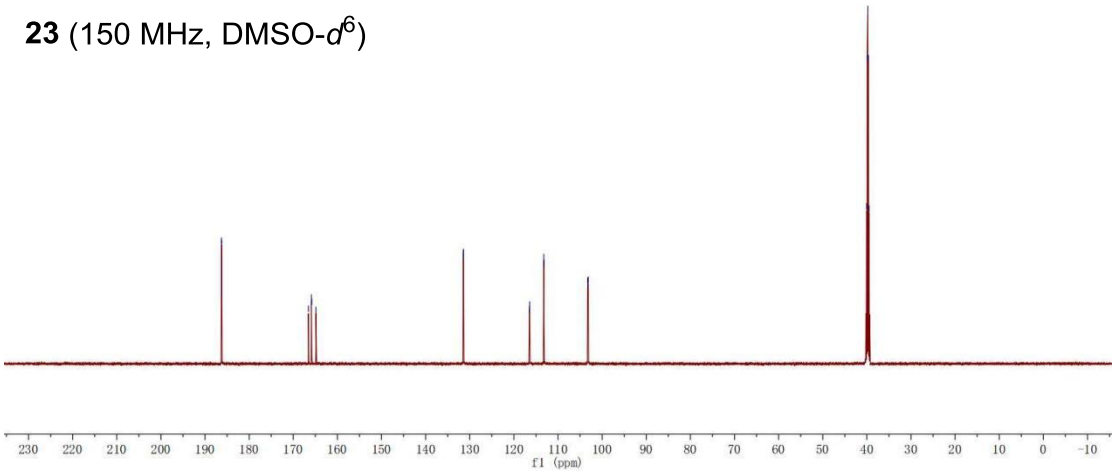


^{13}C NMR spectrum of compound **23**

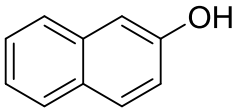




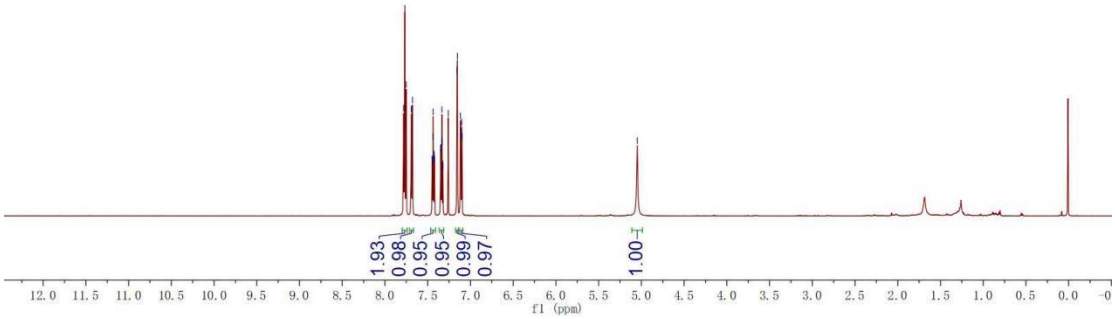
23 (150 MHz, DMSO-d^6)



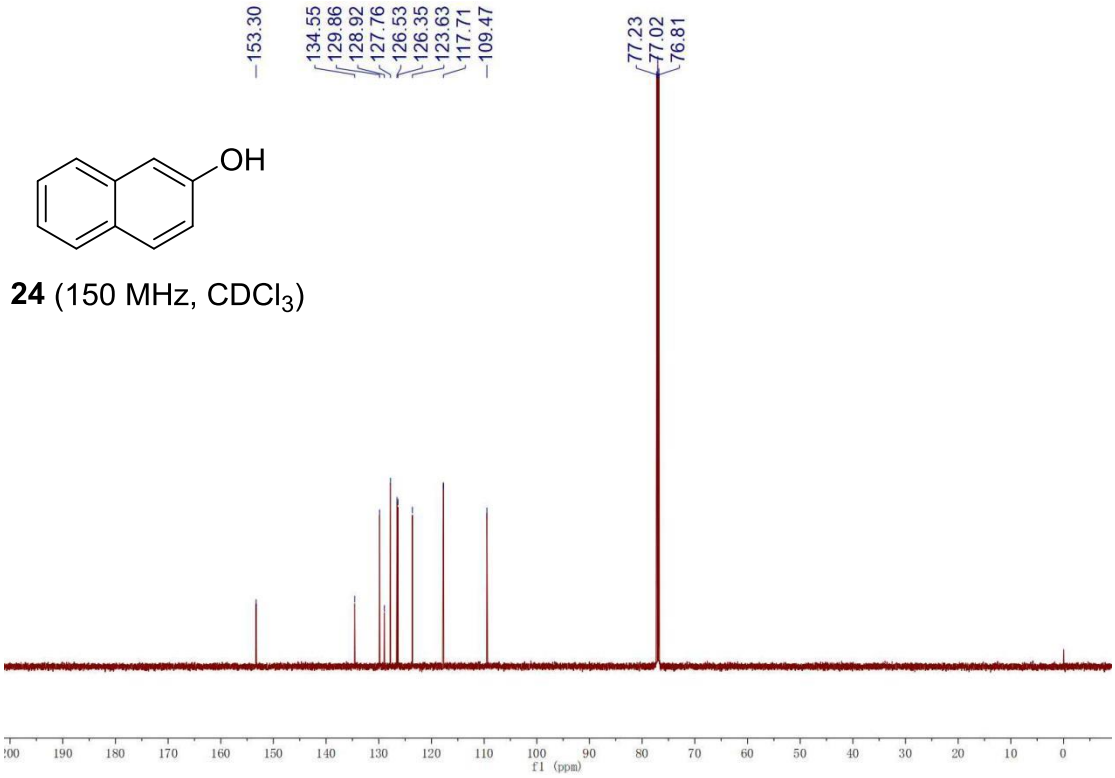
^{1}H NMR spectrum of compound **24**



24 (600 MHz, $CDCl_3$)

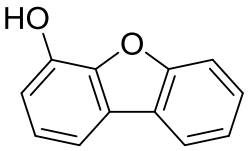


^{13}C NMR spectrum of compound **24**

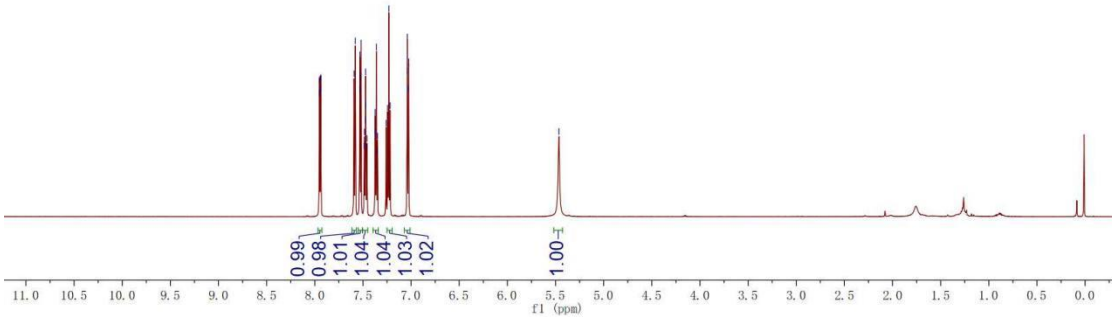


24 (150 MHz, $CDCl_3$)

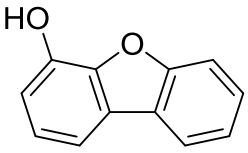
^{1}H NMR spectrum of compound **25**



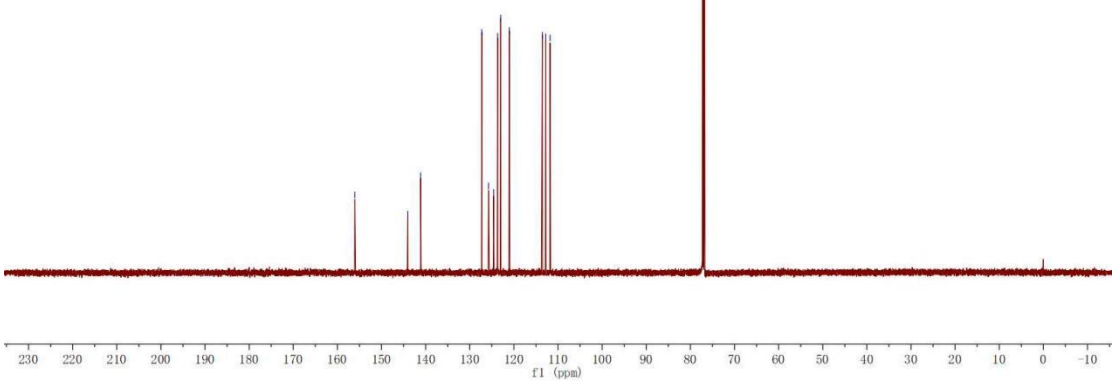
25 (600 MHz, $CDCl_3$)



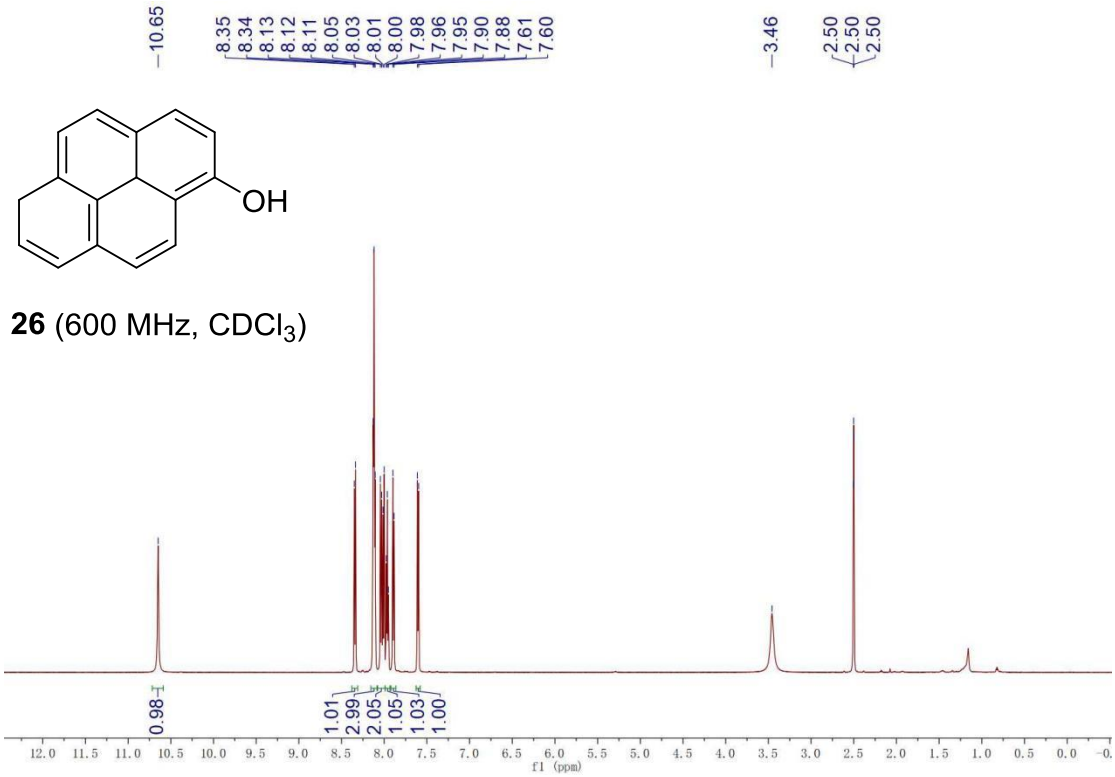
^{13}C NMR spectrum of compound **25**



25 (150 MHz, $CDCl_3$)

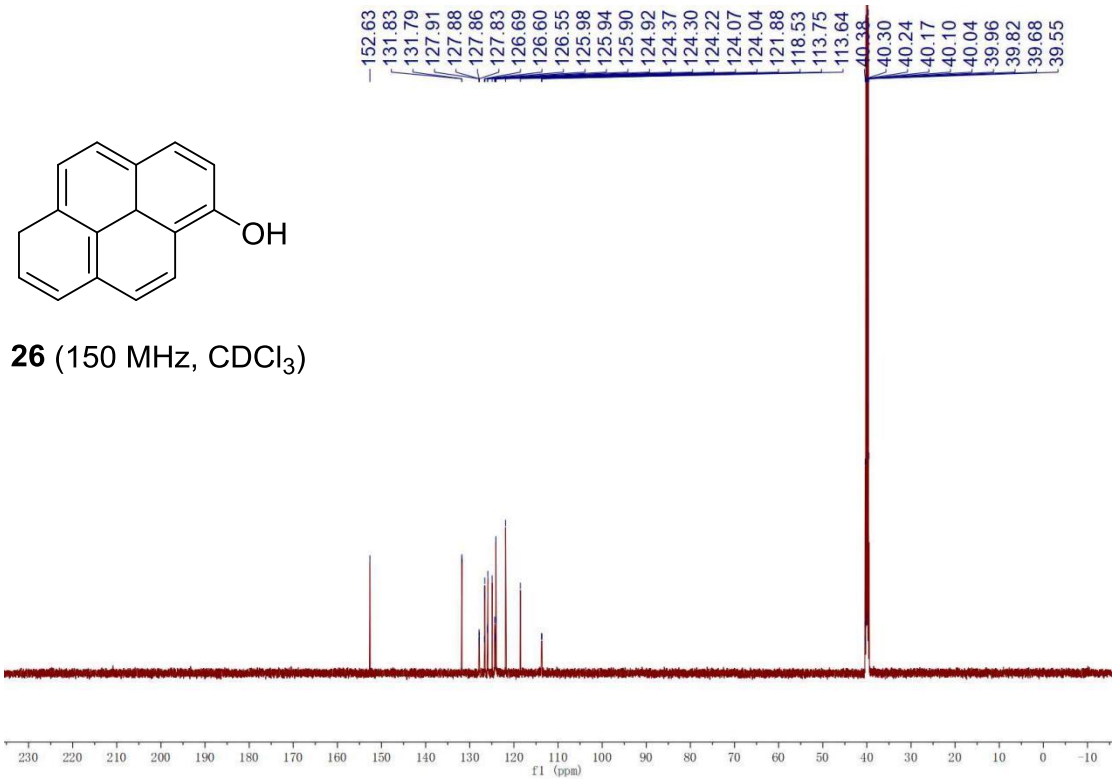


^{1}H NMR spectrum of compound **26**



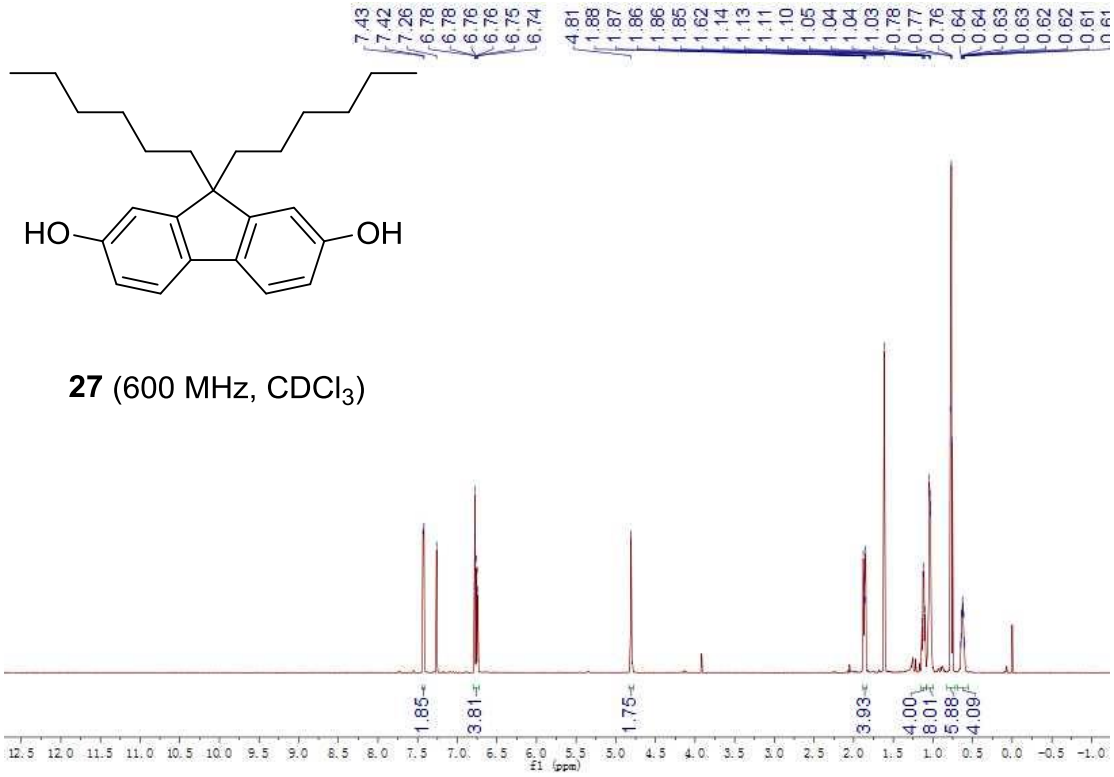
26 (600 MHz, $CDCl_3$)

^{13}C NMR spectrum of compound **26**

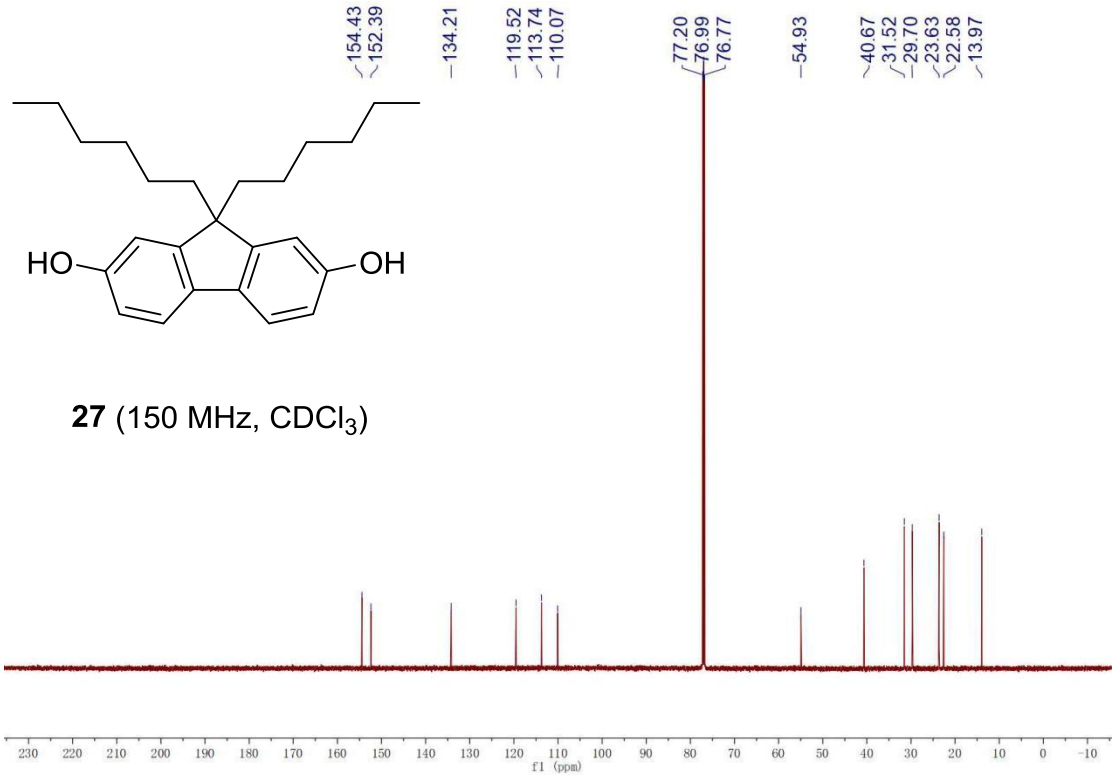


26 (150 MHz, $CDCl_3$)

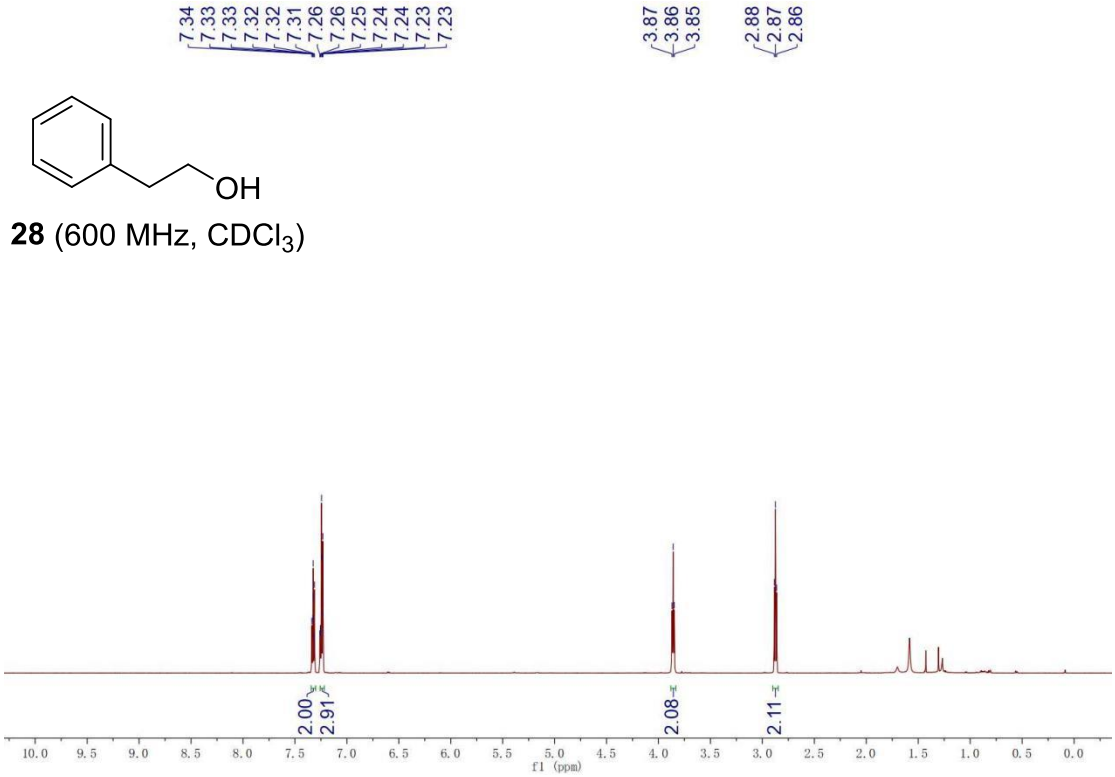
^{1}H NMR spectrum of compound **27**



^{13}C NMR spectrum of compound **27**

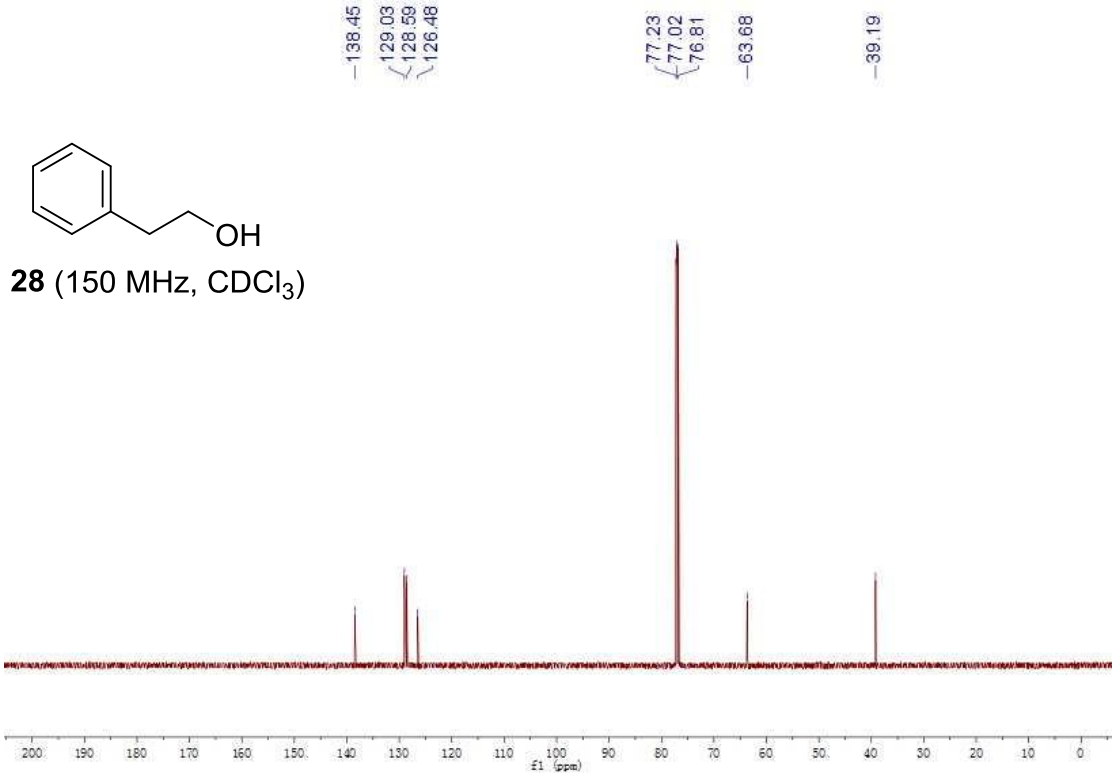


^{1}H NMR spectrum of compound **28**



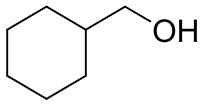
28 (600 MHz, $CDCl_3$)

^{13}C NMR spectrum of compound **28**

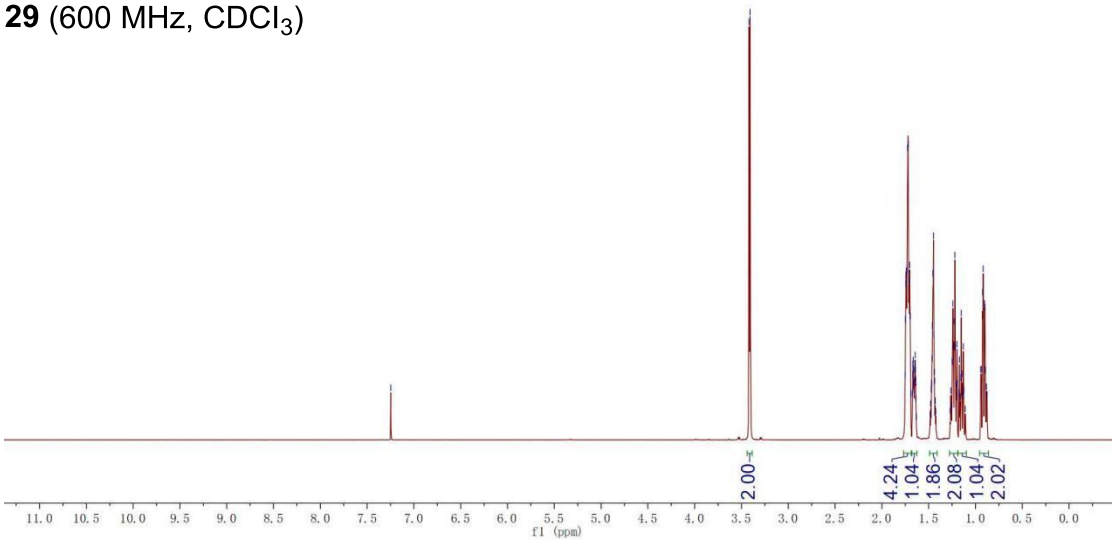


28 (150 MHz, $CDCl_3$)

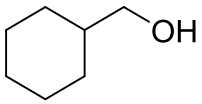
^{1}H NMR spectrum of compound **29**



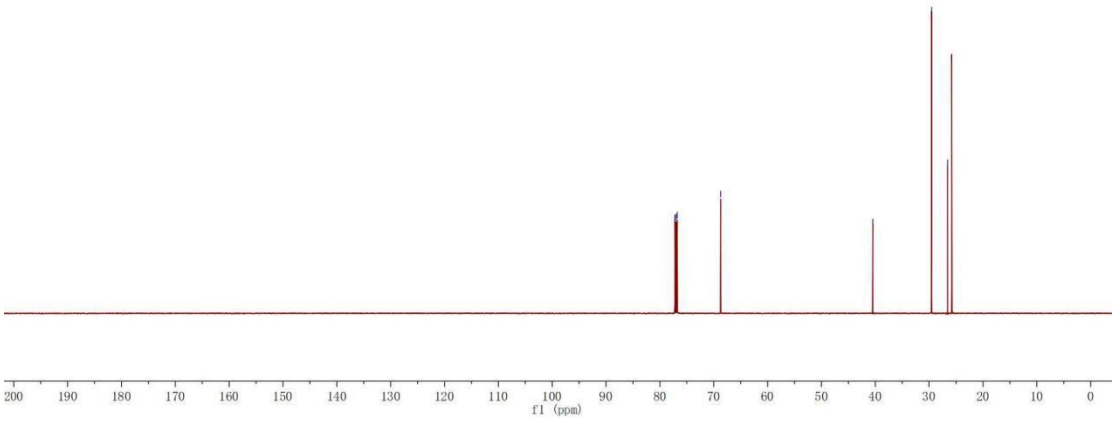
29 (600 MHz, $CDCl_3$)



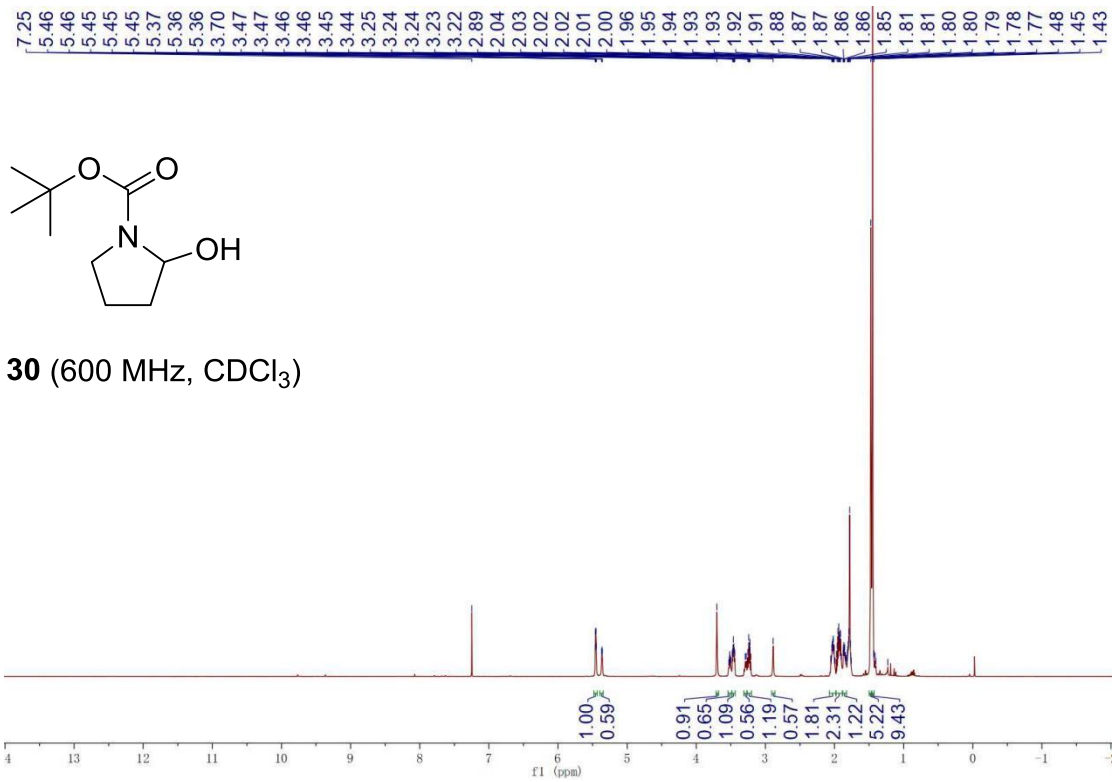
^{13}C NMR spectrum of compound **29**



29 (150 MHz, $CDCl_3$)

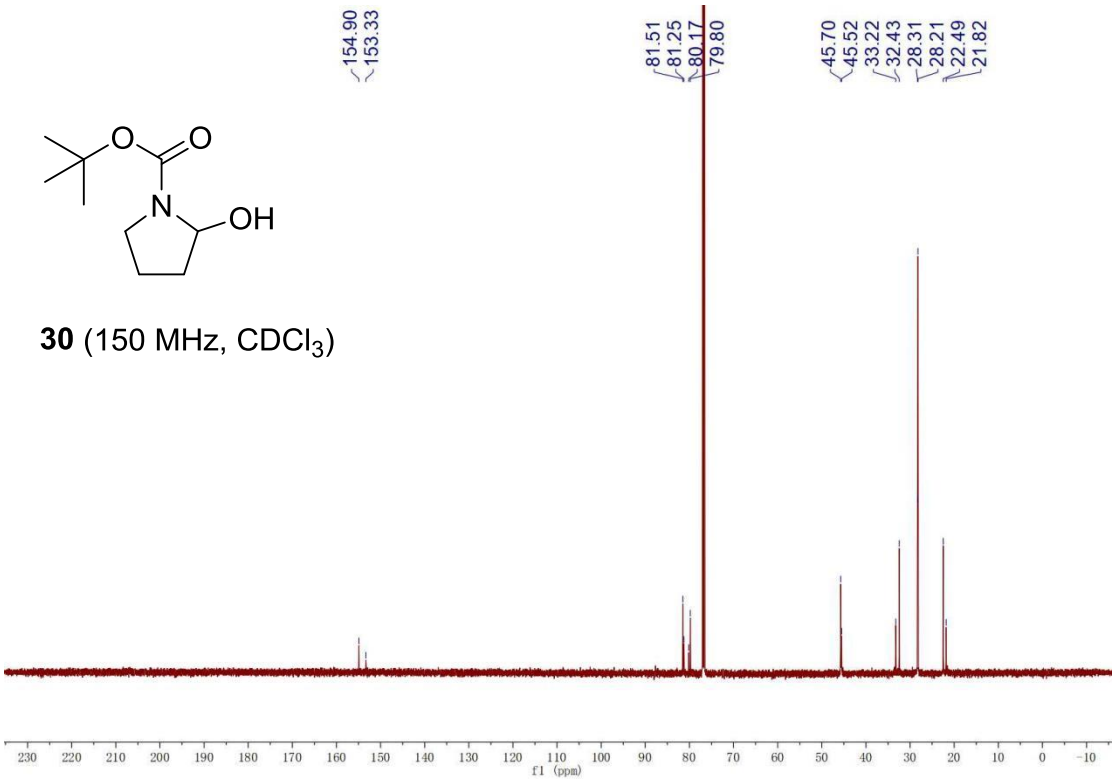


^{1}H NMR spectrum of compound **30**



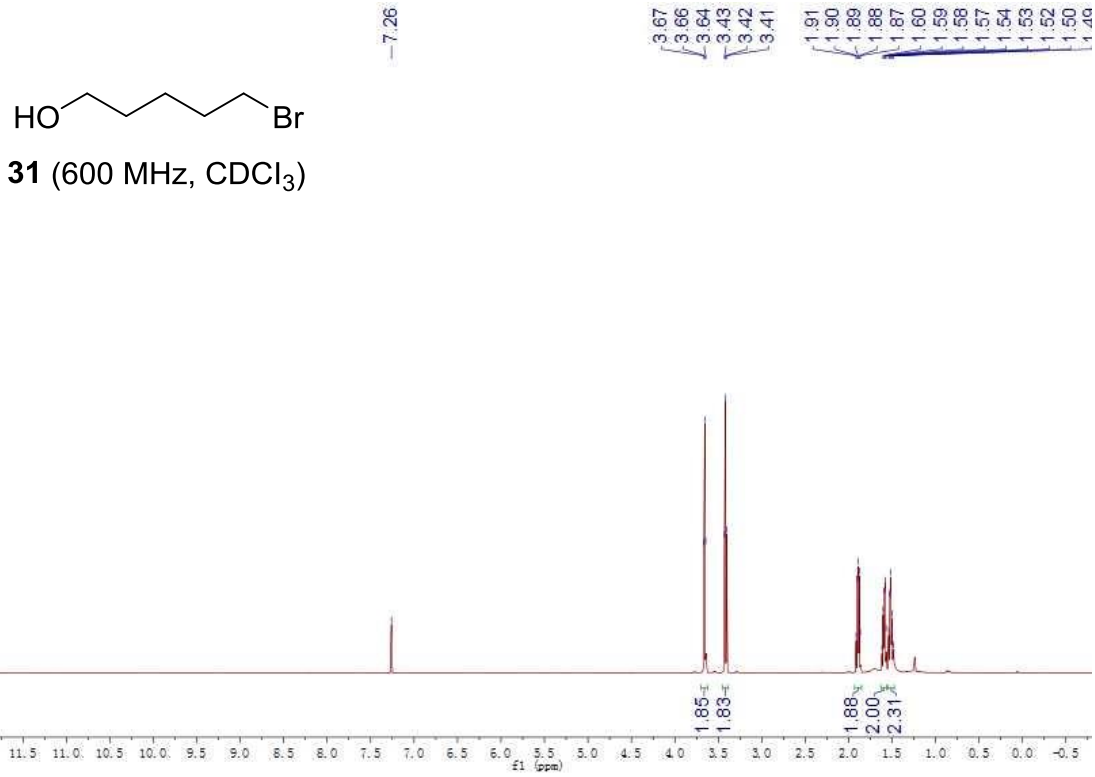
30 (600 MHz, $CDCl_3$)

^{13}C NMR spectrum of compound **30**

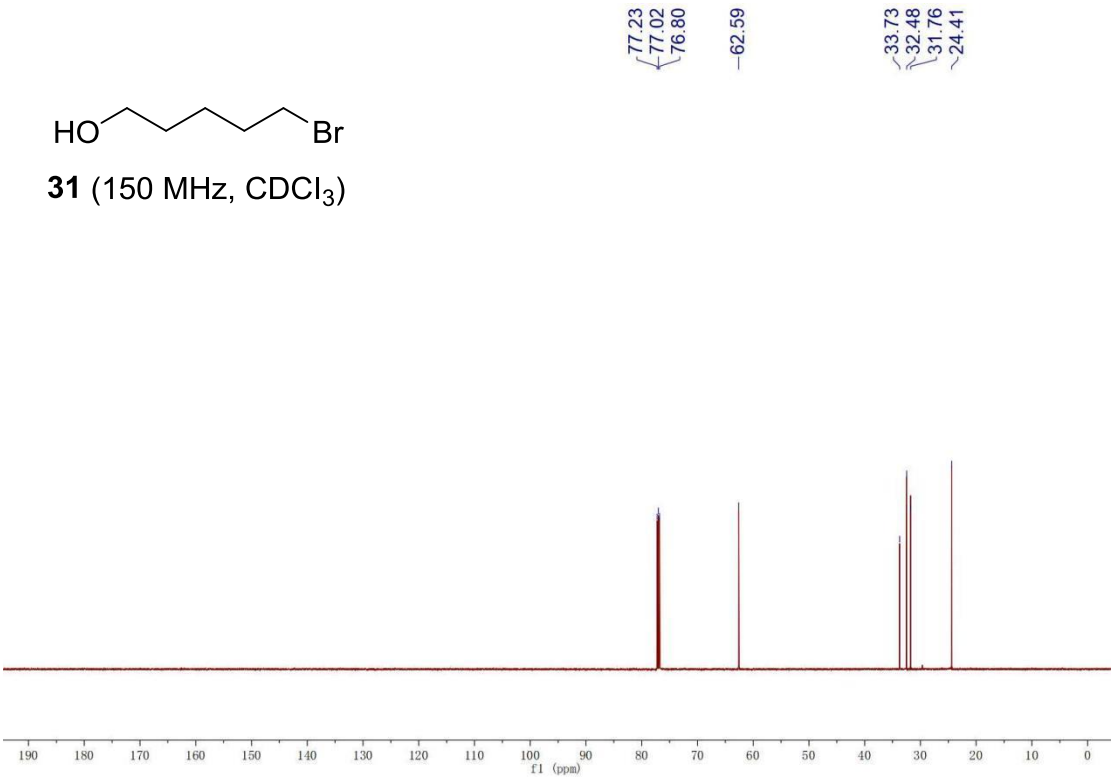


30 (150 MHz, $CDCl_3$)

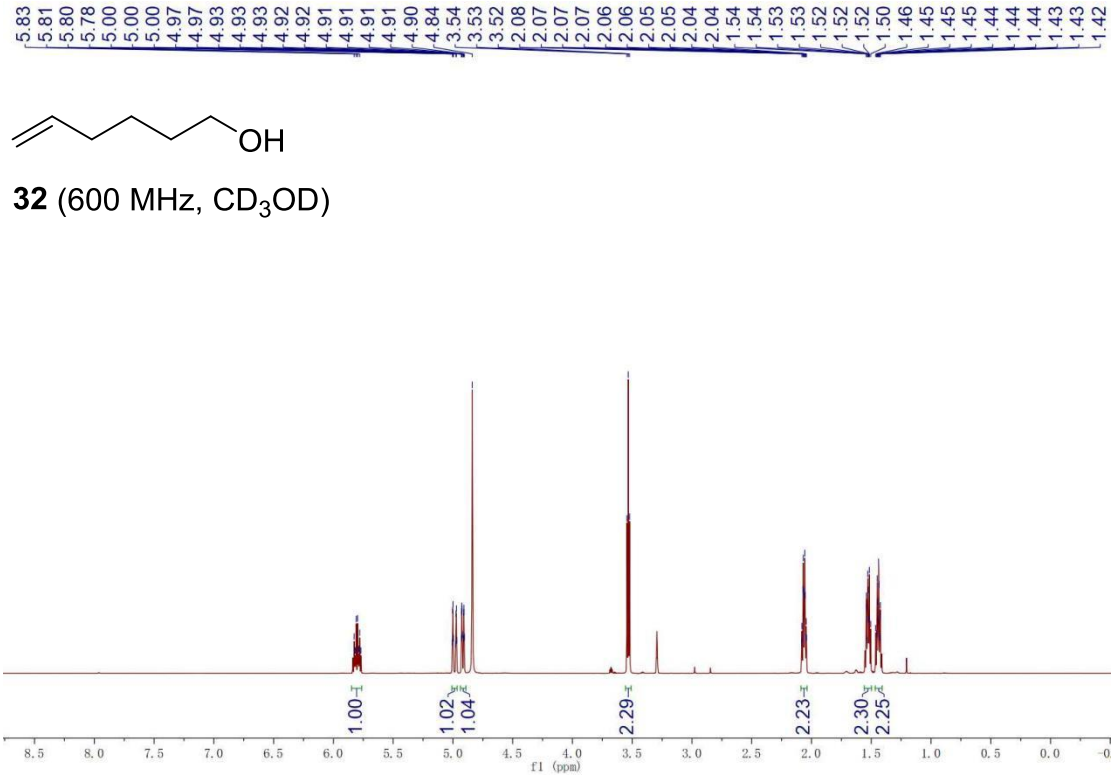
^{1}H NMR spectrum of compound **31**



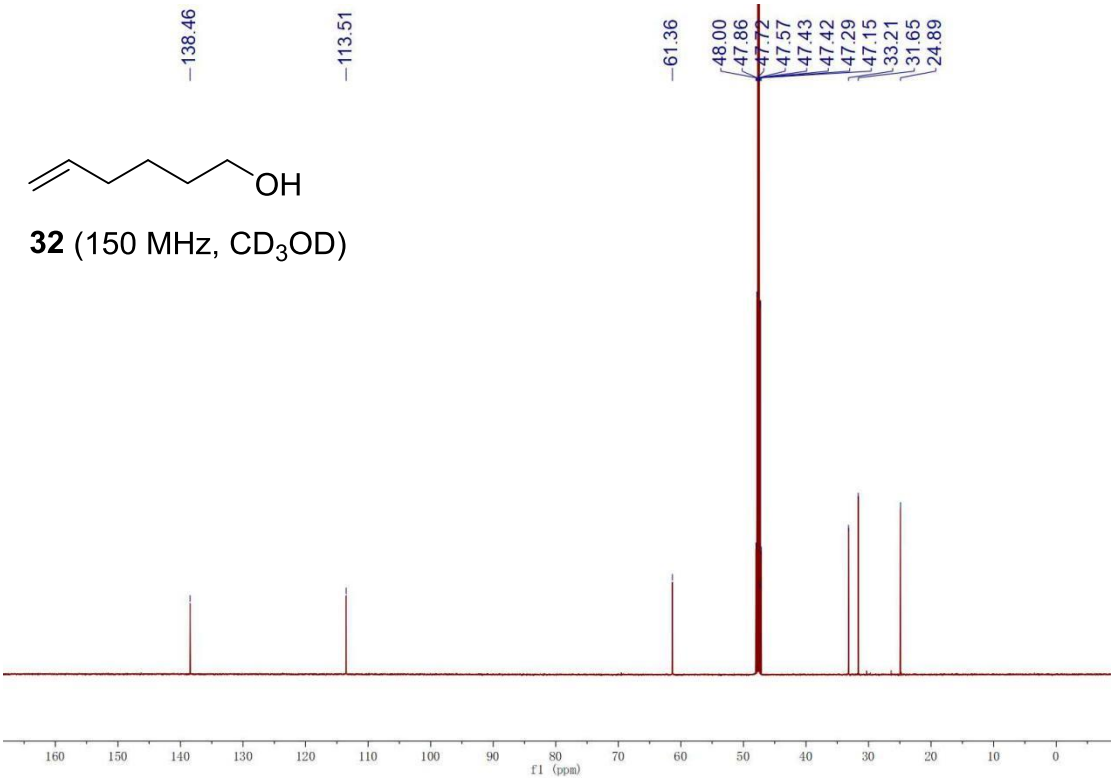
^{13}C NMR spectrum of compound **31**



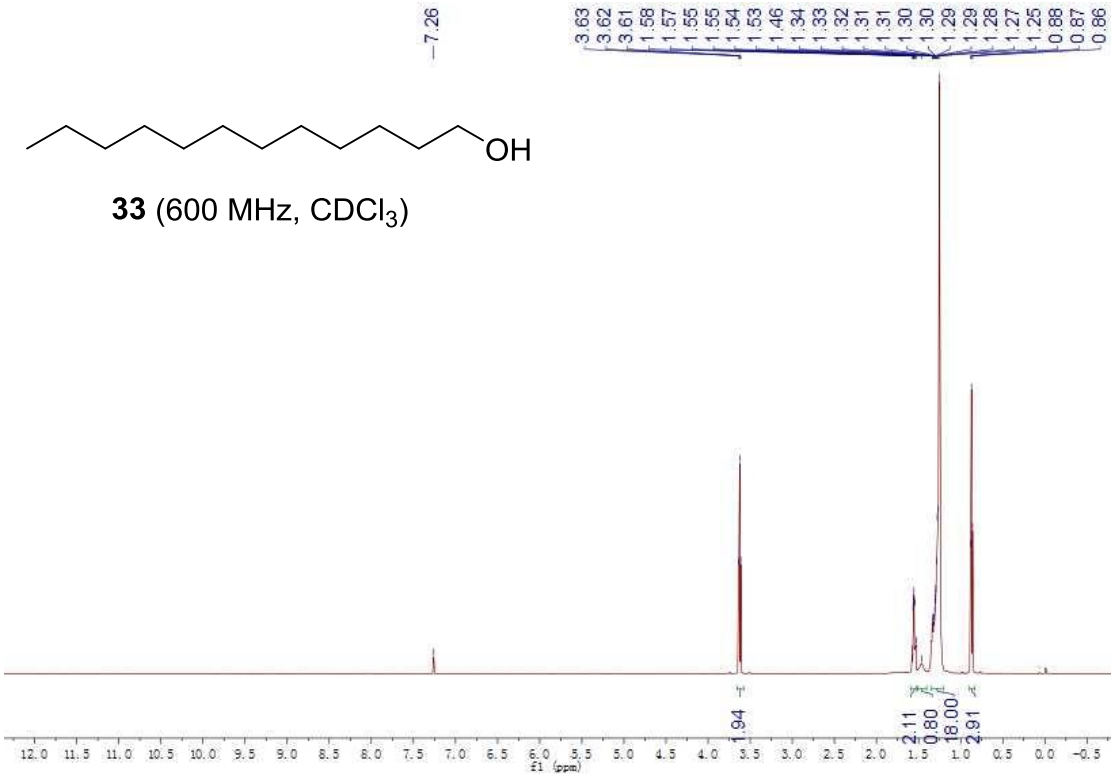
^{1}H NMR spectrum of compound **32**



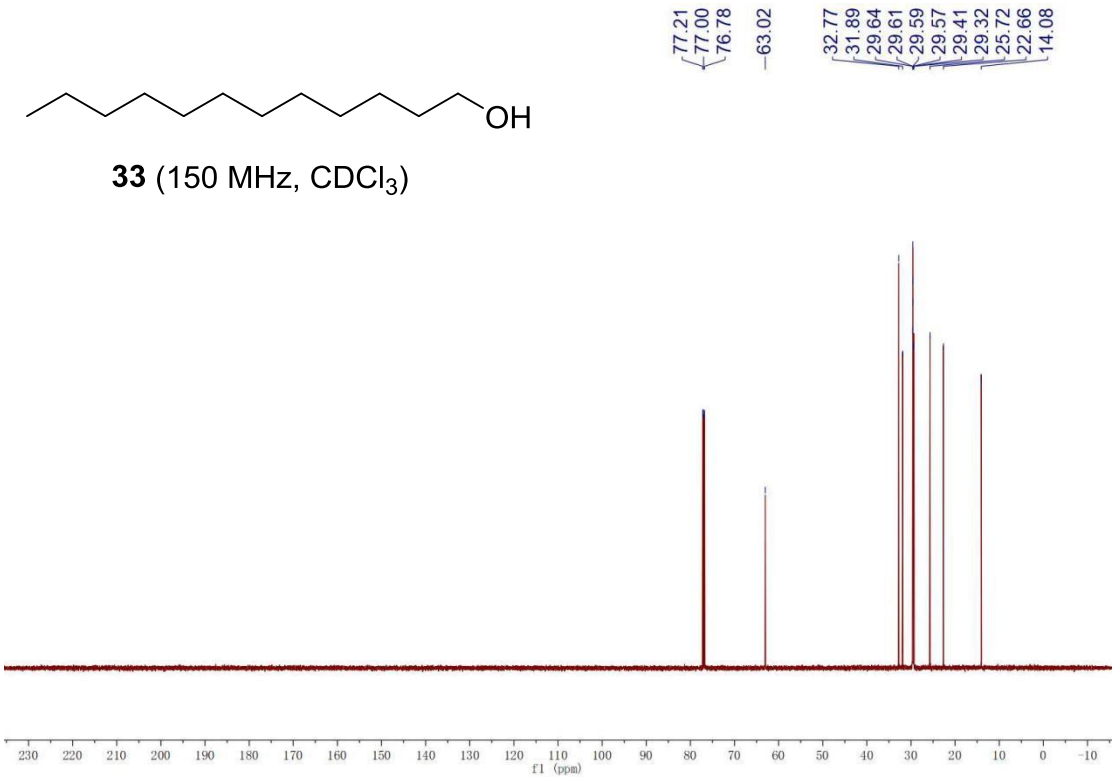
^{13}C NMR spectrum of compound **32**



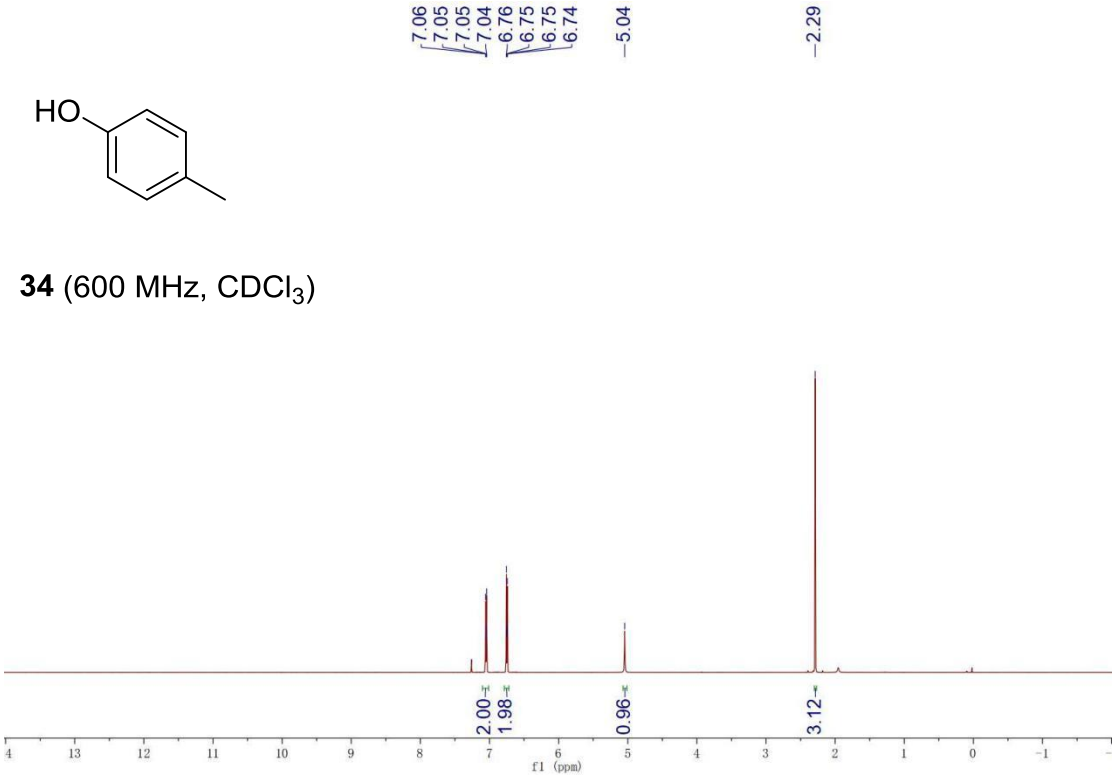
^{1}H NMR spectrum of compound **33**



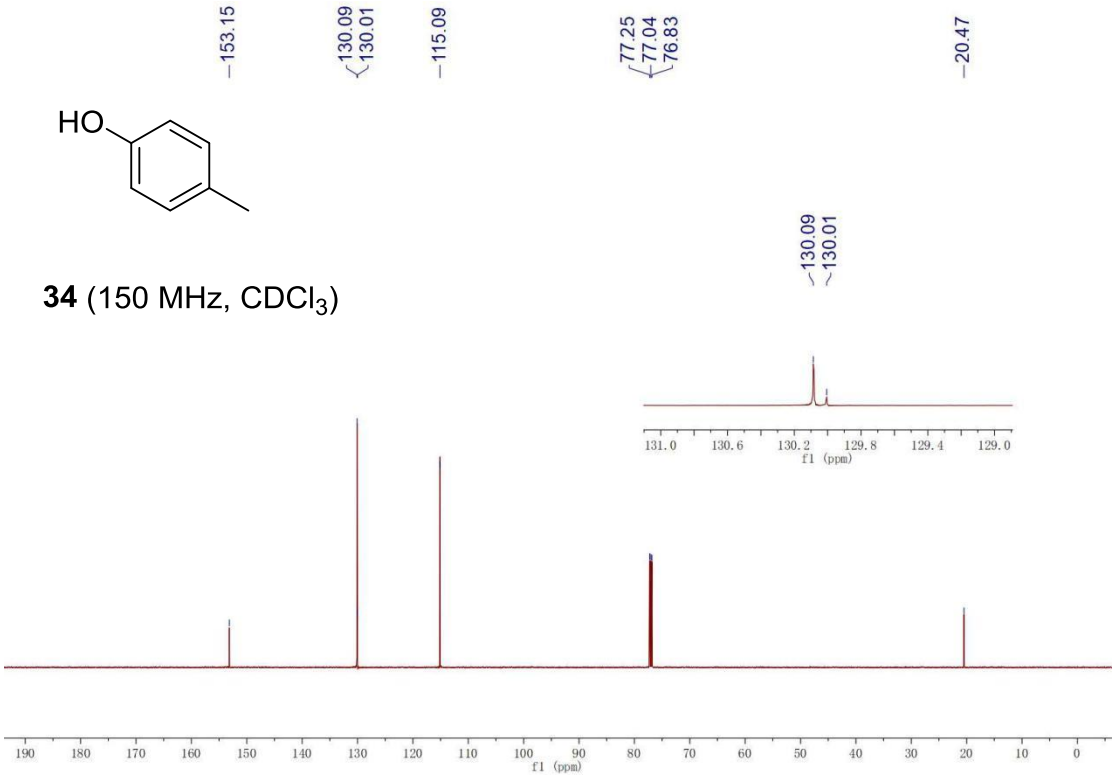
^{13}C NMR spectrum of compound **33**



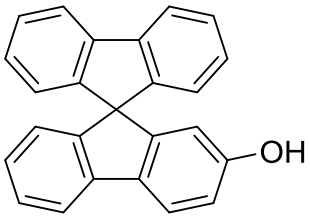
^{1}H NMR spectrum of compound **34**



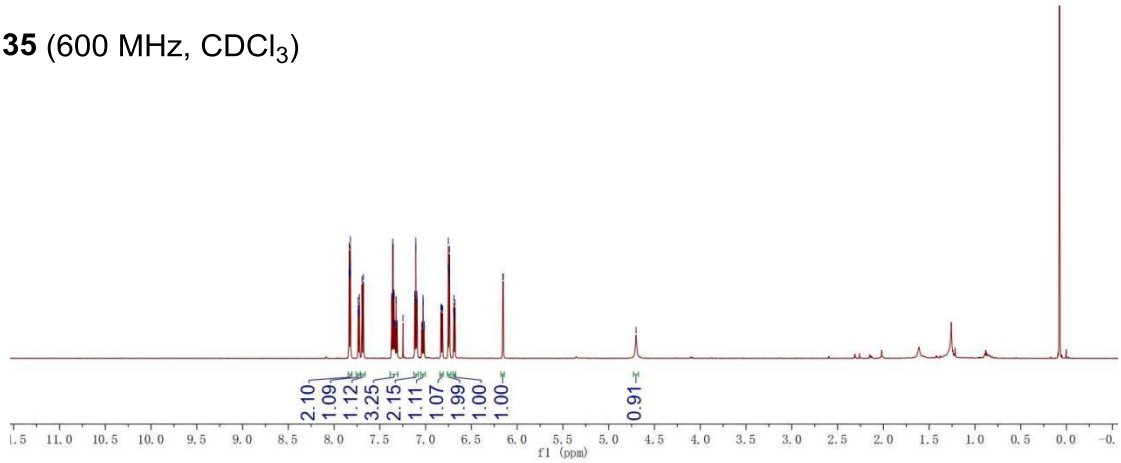
^{13}C NMR spectrum of compound **34**



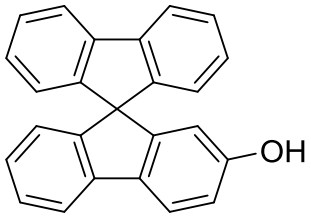
^{1}H NMR spectrum of compound **35**



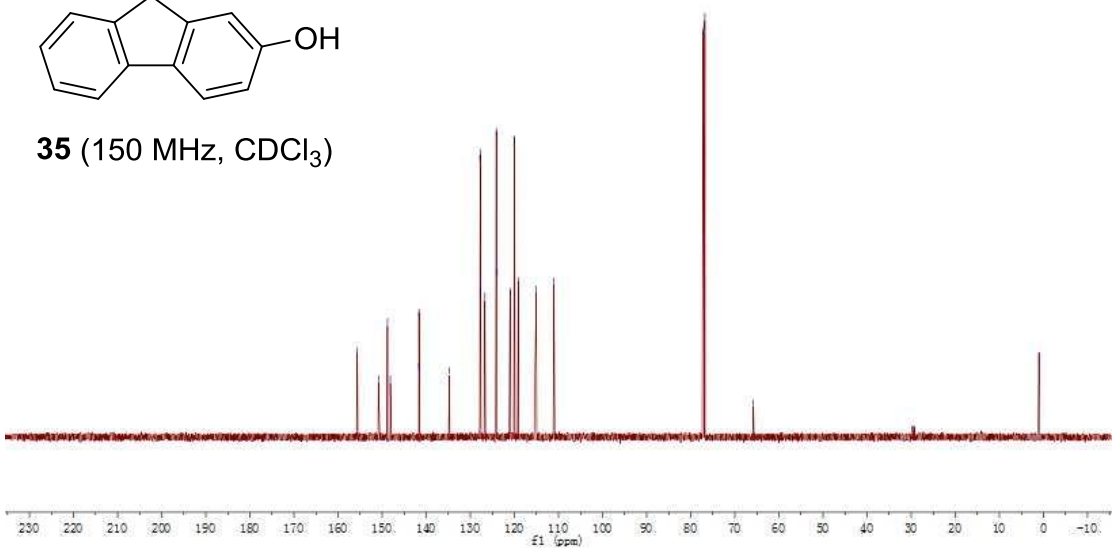
35 (600 MHz, $CDCl_3$)



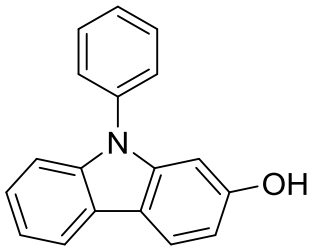
^{13}C NMR spectrum of compound **35**



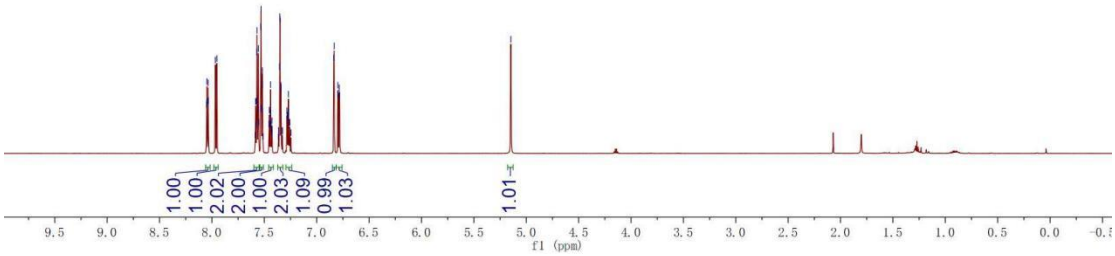
35 (150 MHz, $CDCl_3$)



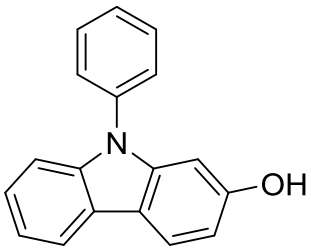
^{1}H NMR spectrum of compound **36**



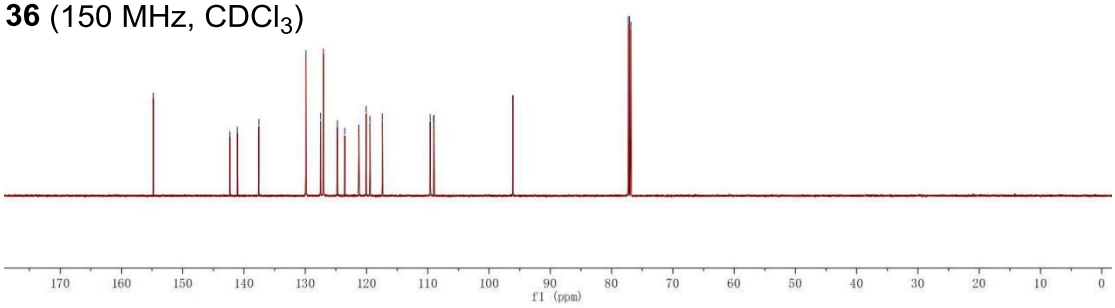
36 (600 MHz, $CDCl_3$)



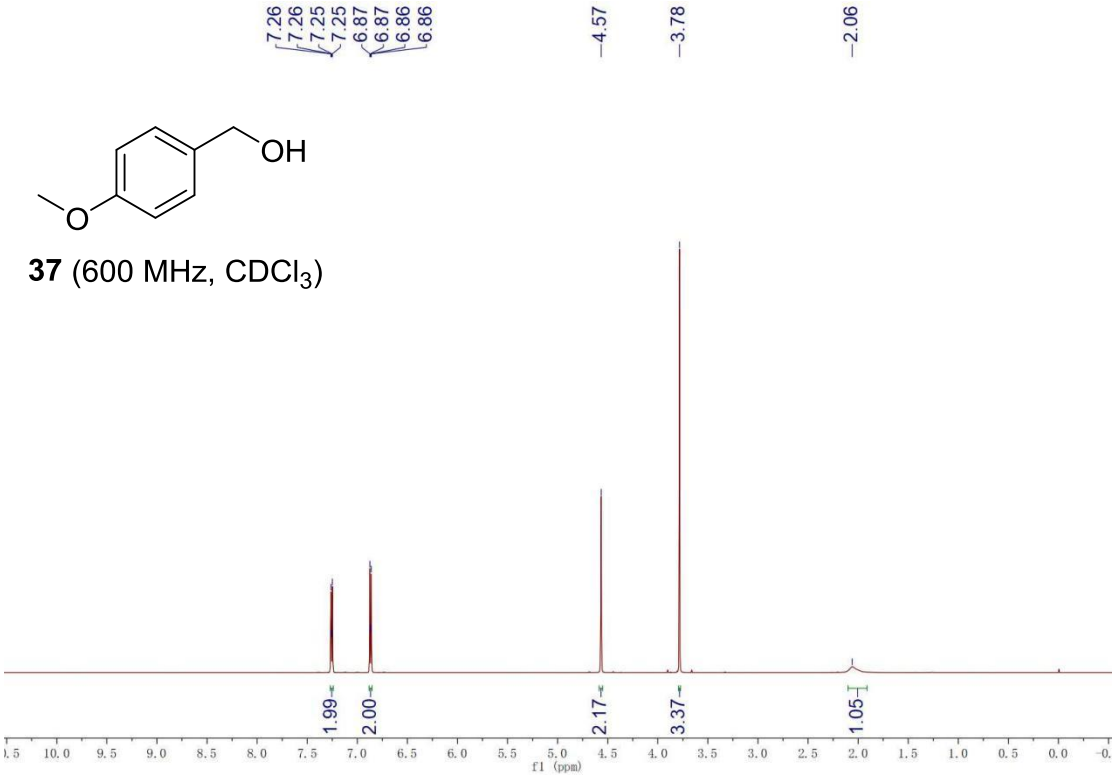
^{13}C NMR spectrum of compound **36**



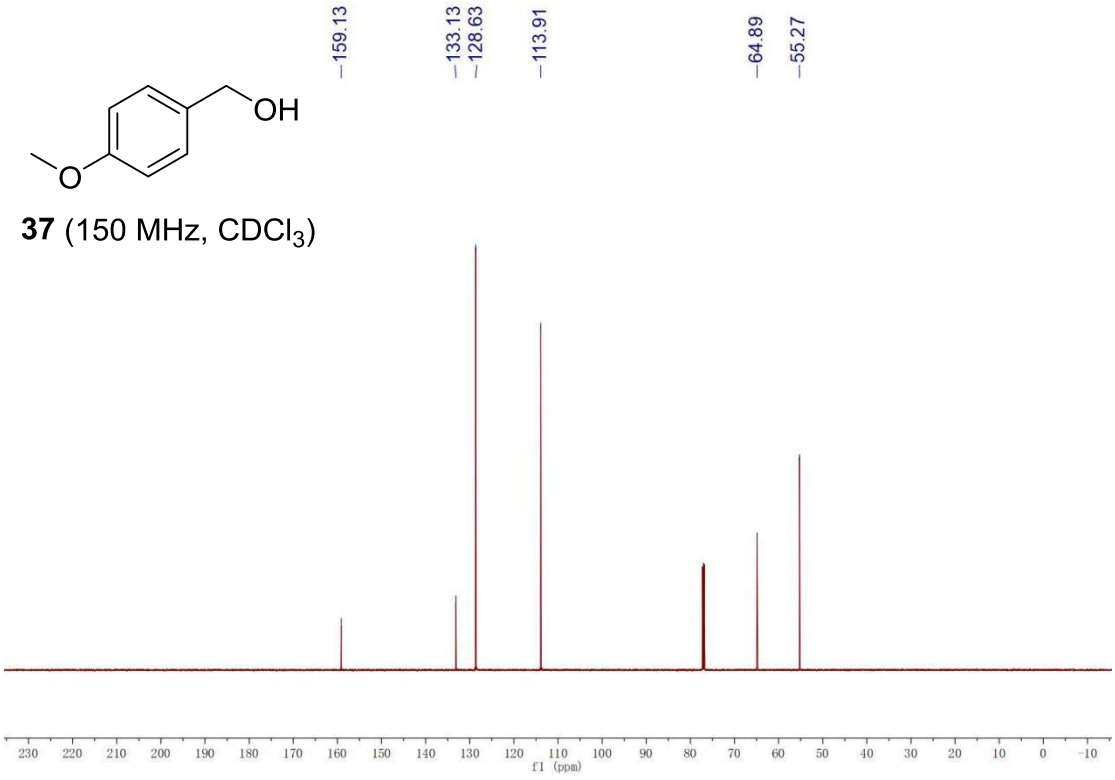
36 (150 MHz, $CDCl_3$)



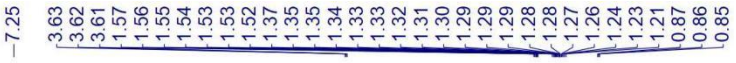
^{1}H NMR spectrum of compound **37**

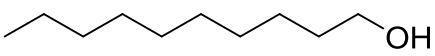


^{13}C NMR spectrum of compound **37**

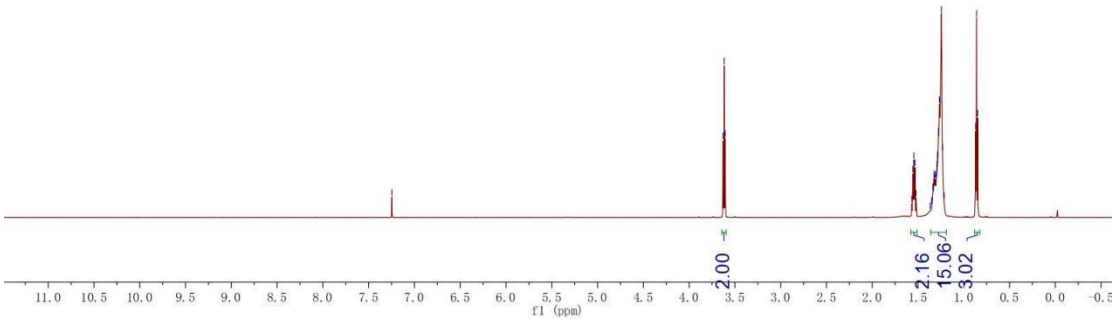


^{1}H NMR spectrum of compound **38**

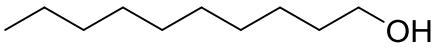




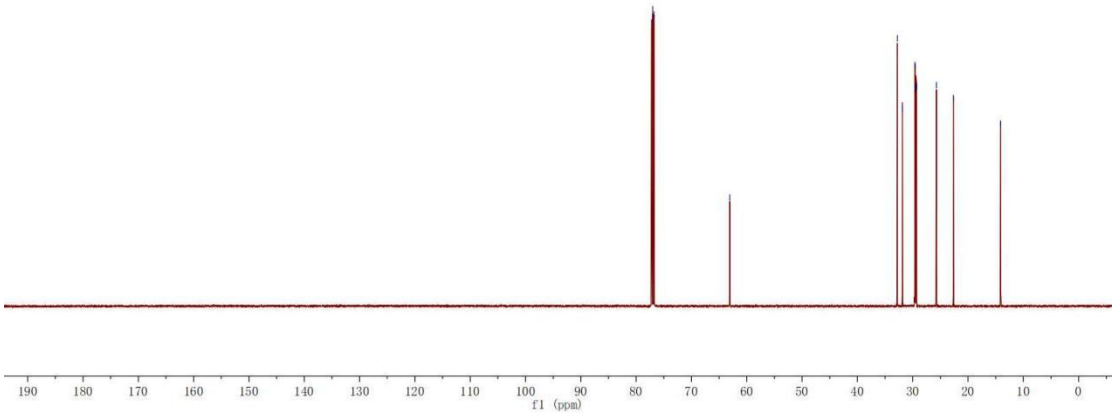
38 (600 MHz, $CDCl_3$)



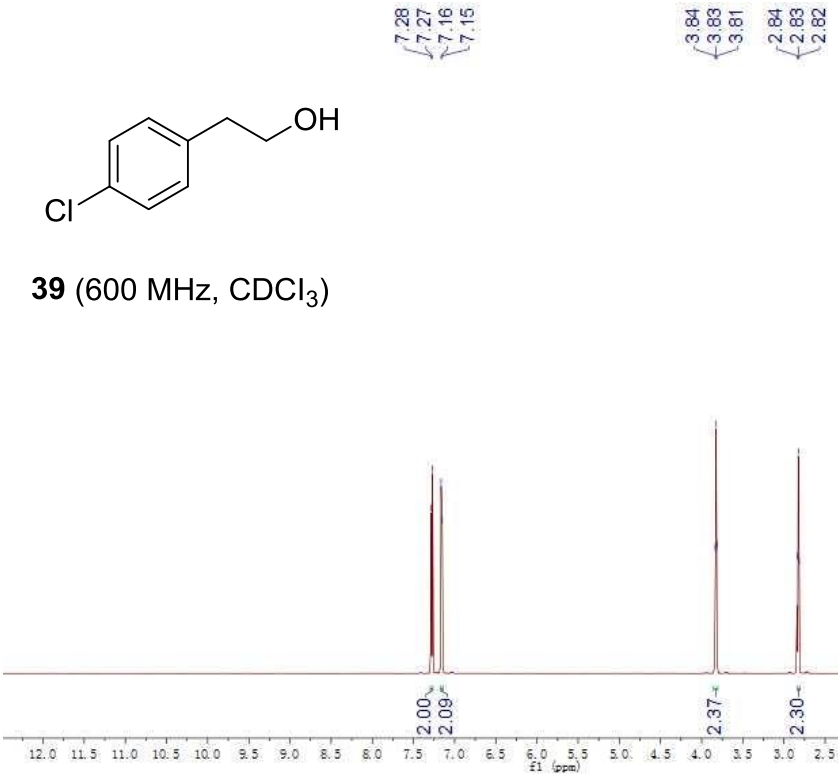
^{13}C NMR spectrum of compound **38**



38 (150 MHz, $CDCl_3$)

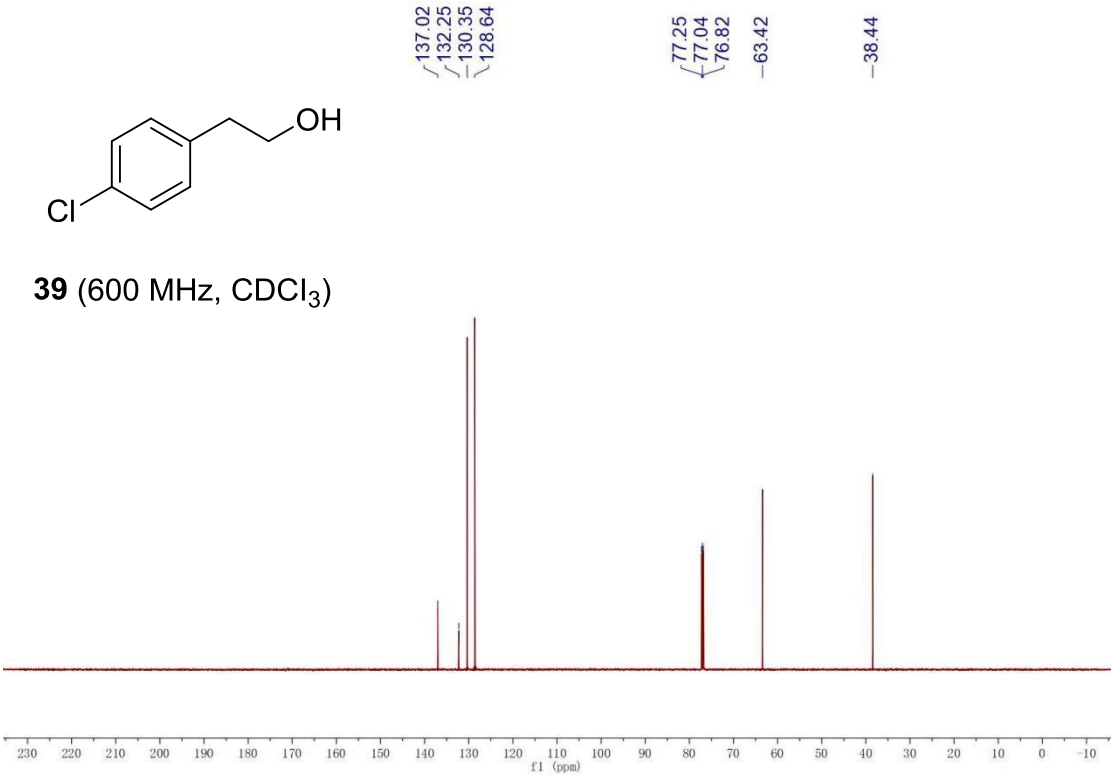


^{1}H NMR spectrum of compound **39**



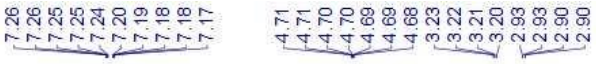
39 (600 MHz, $CDCl_3$)

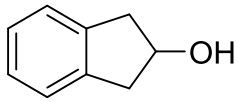
^{13}C NMR spectrum of compound **39**



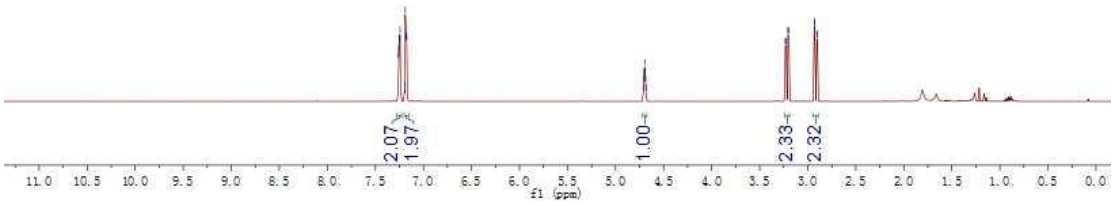
39 (600 MHz, $CDCl_3$)

^{1}H NMR spectrum of compound **40**

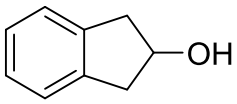




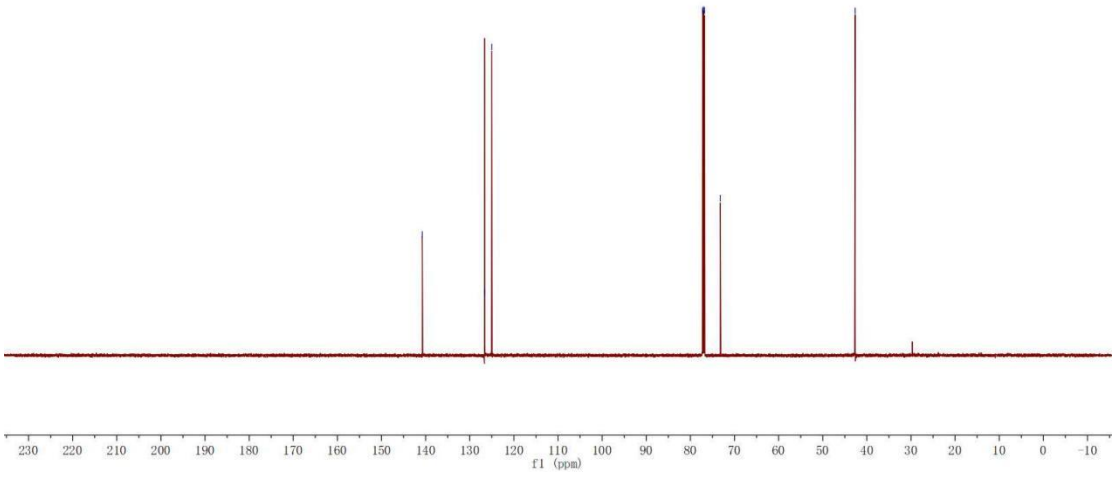
40 (600 MHz, $CDCl_3$)



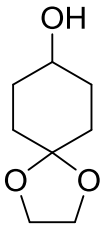
^{13}C NMR spectrum of compound **40**



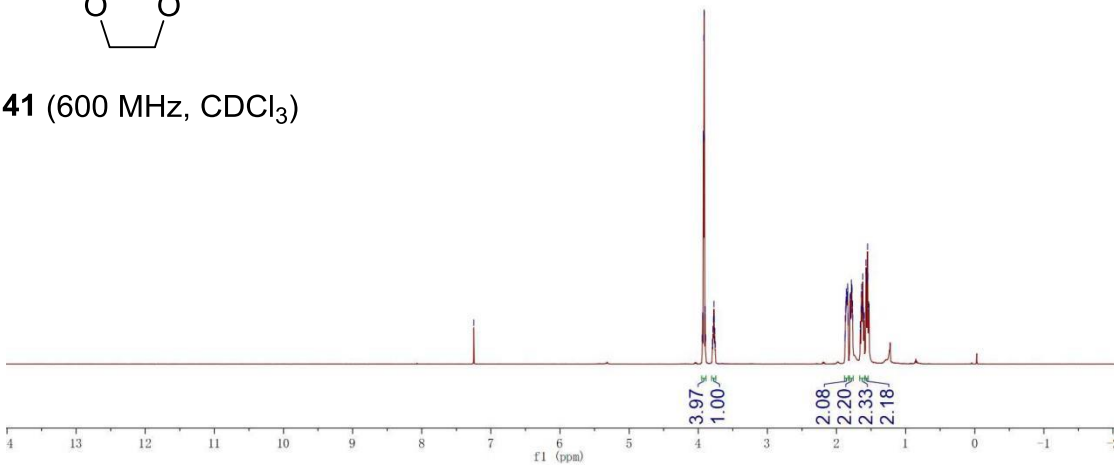
40 (150 MHz, $CDCl_3$)



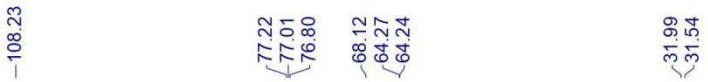
^{1}H NMR spectrum of compound **41**

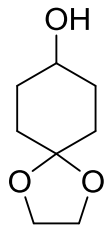


41 (600 MHz, $CDCl_3$)

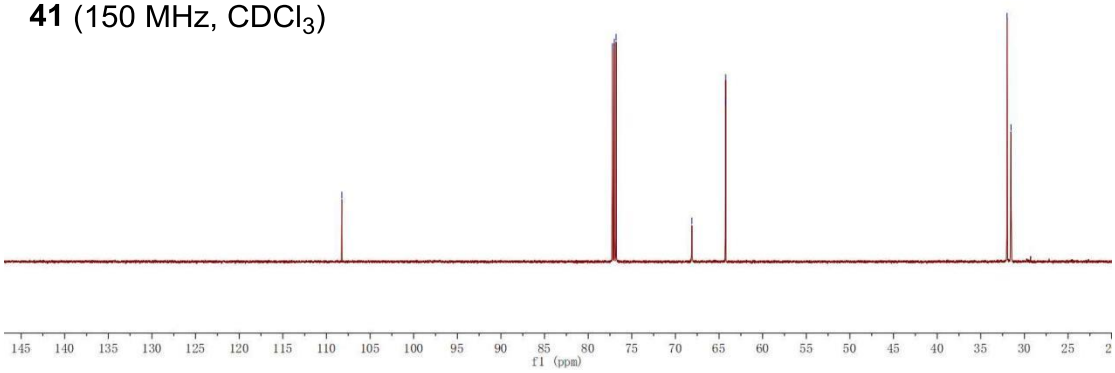


^{13}C NMR spectrum of compound **41**

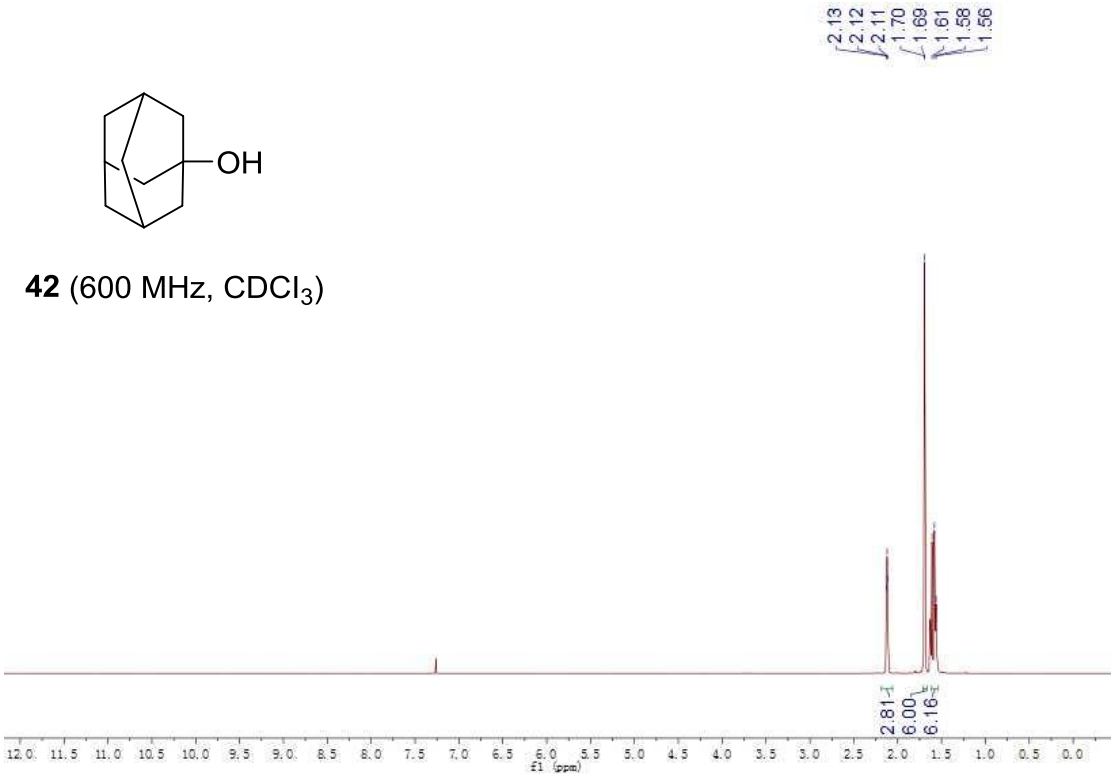




41 (150 MHz, $CDCl_3$)

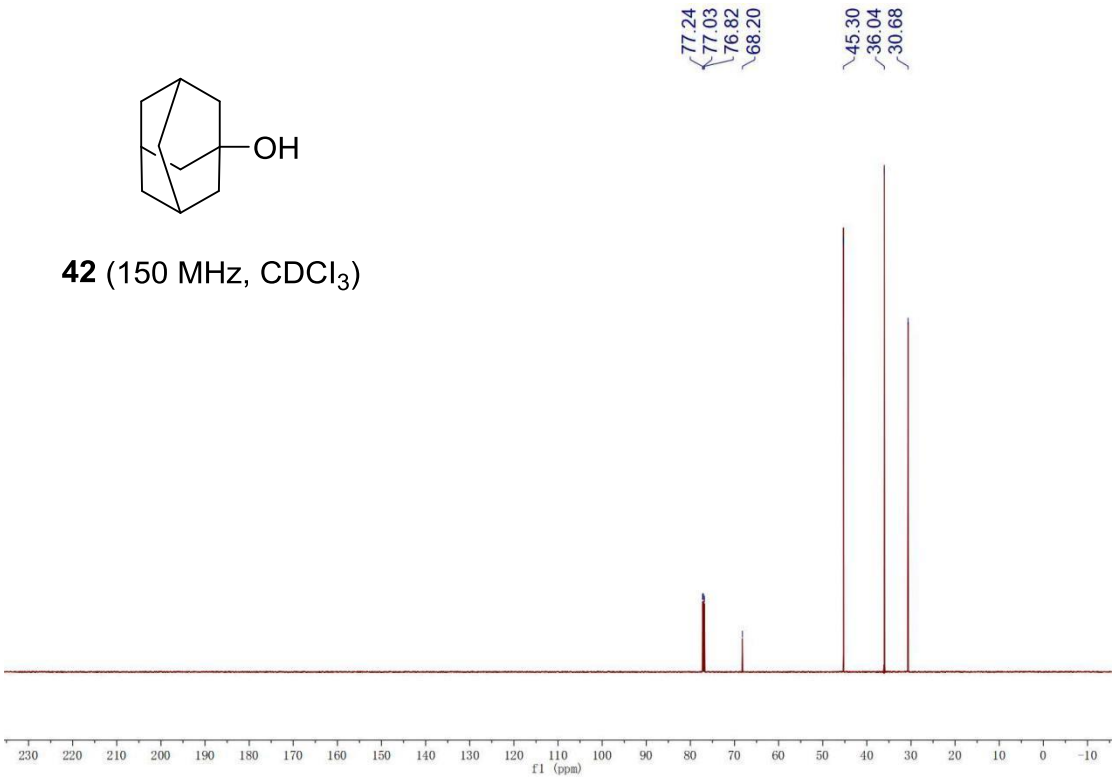


^{1}H NMR spectrum of compound **42**



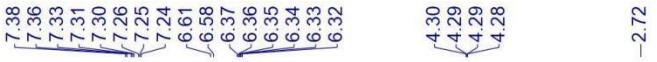
42 (600 MHz, $CDCl_3$)

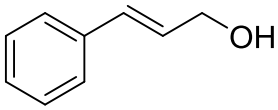
^{13}C NMR spectrum of compound **42**



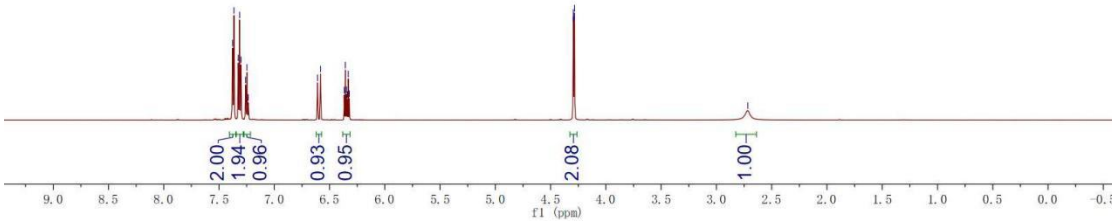
42 (150 MHz, $CDCl_3$)

^{1}H NMR spectrum of compound **43**

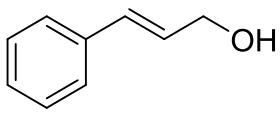




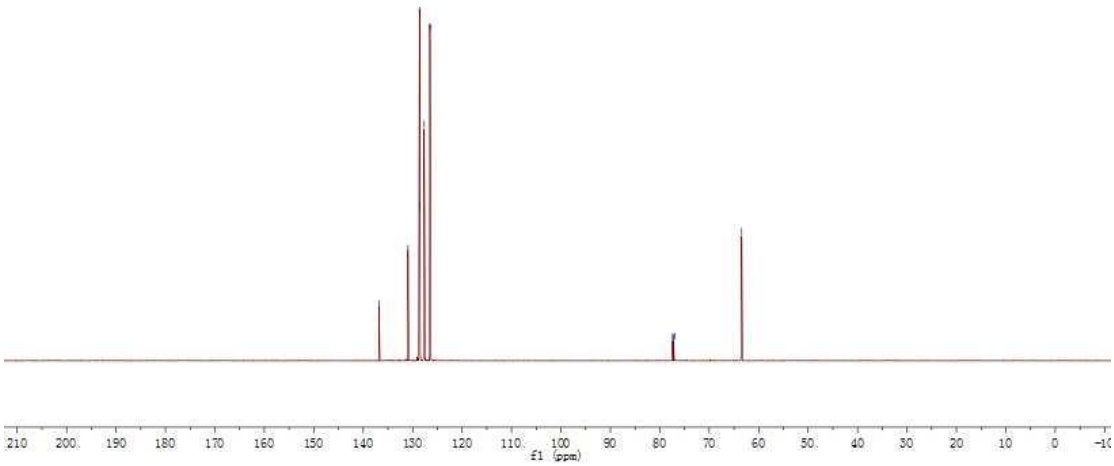
43 (600 MHz, $CDCl_3$)



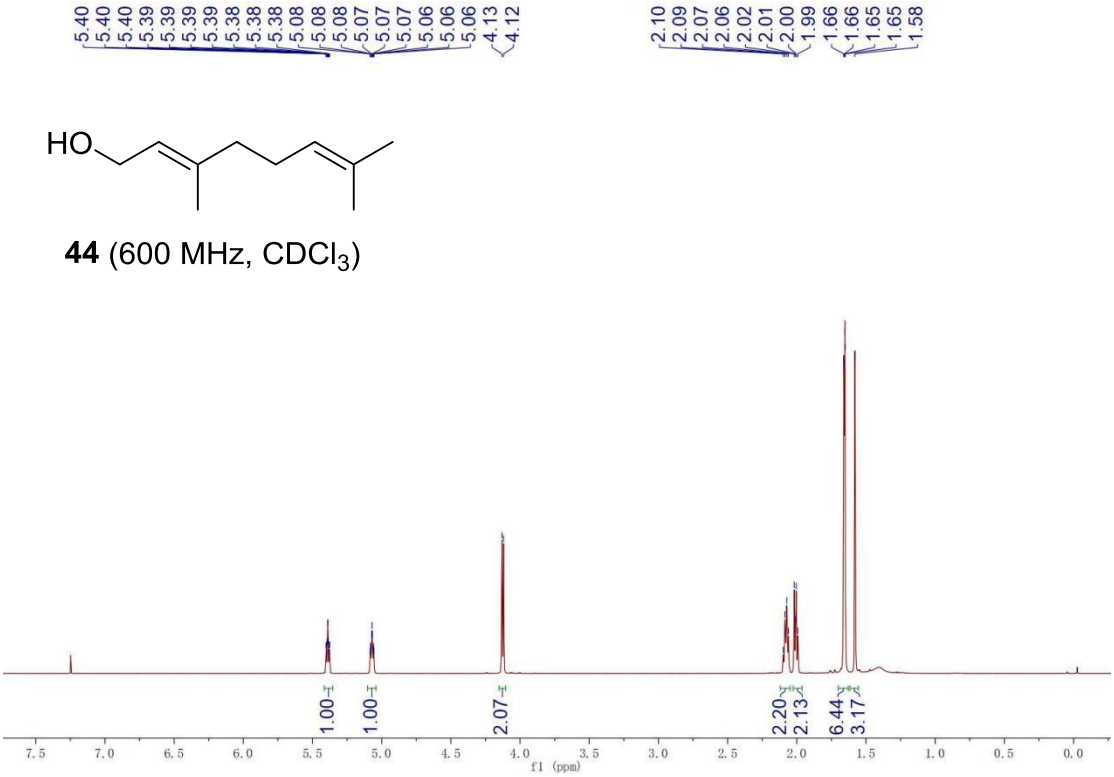
^{13}C NMR spectrum of compound **43**



43 (150 MHz, $CDCl_3$)

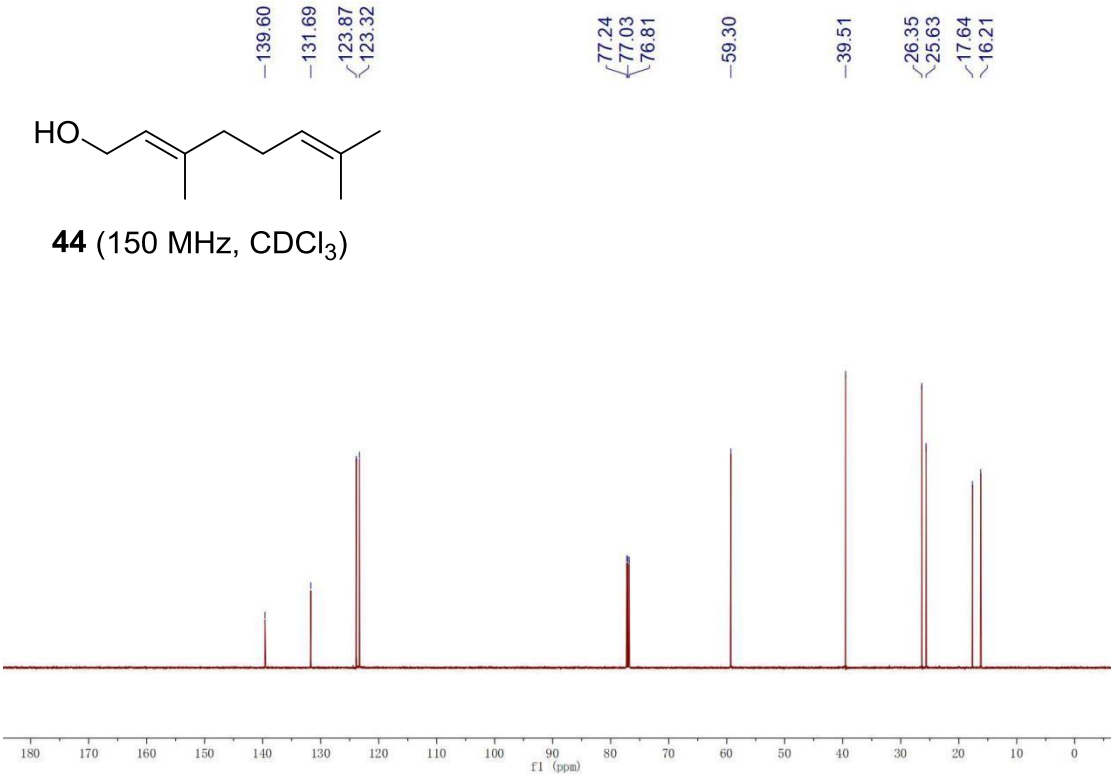


^{1}H NMR spectrum of compound **44**



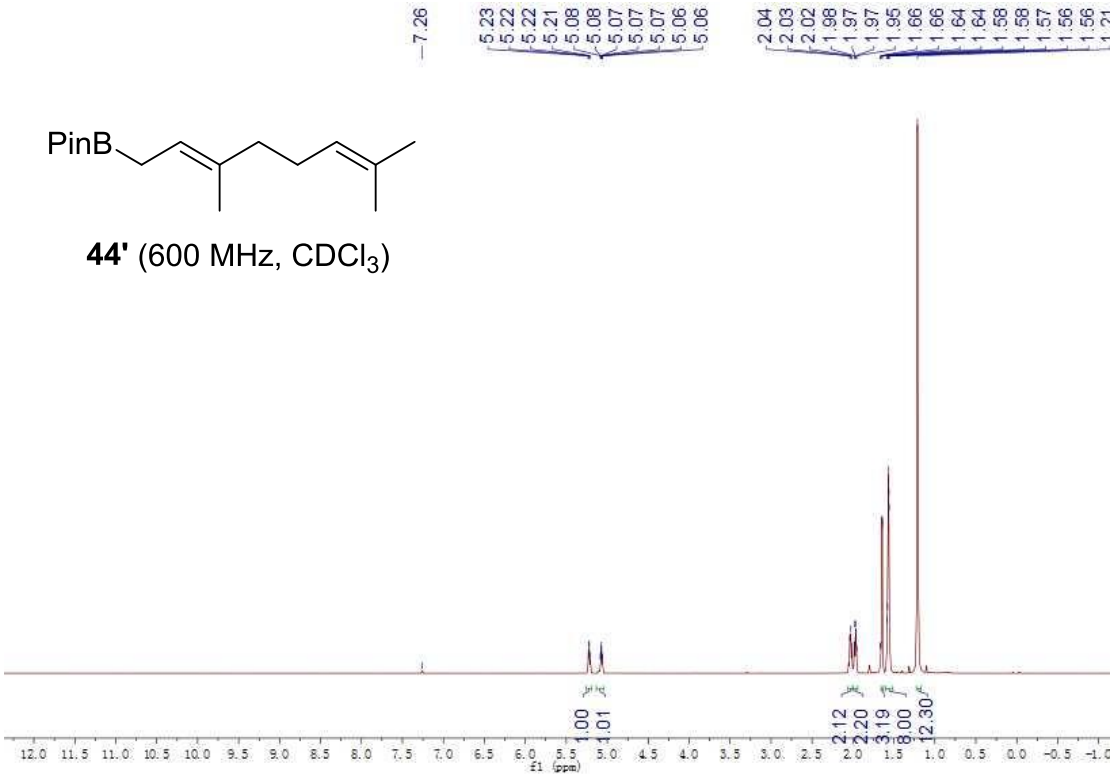
44 (600 MHz, $CDCl_3$)

^{13}C NMR spectrum of compound **44**



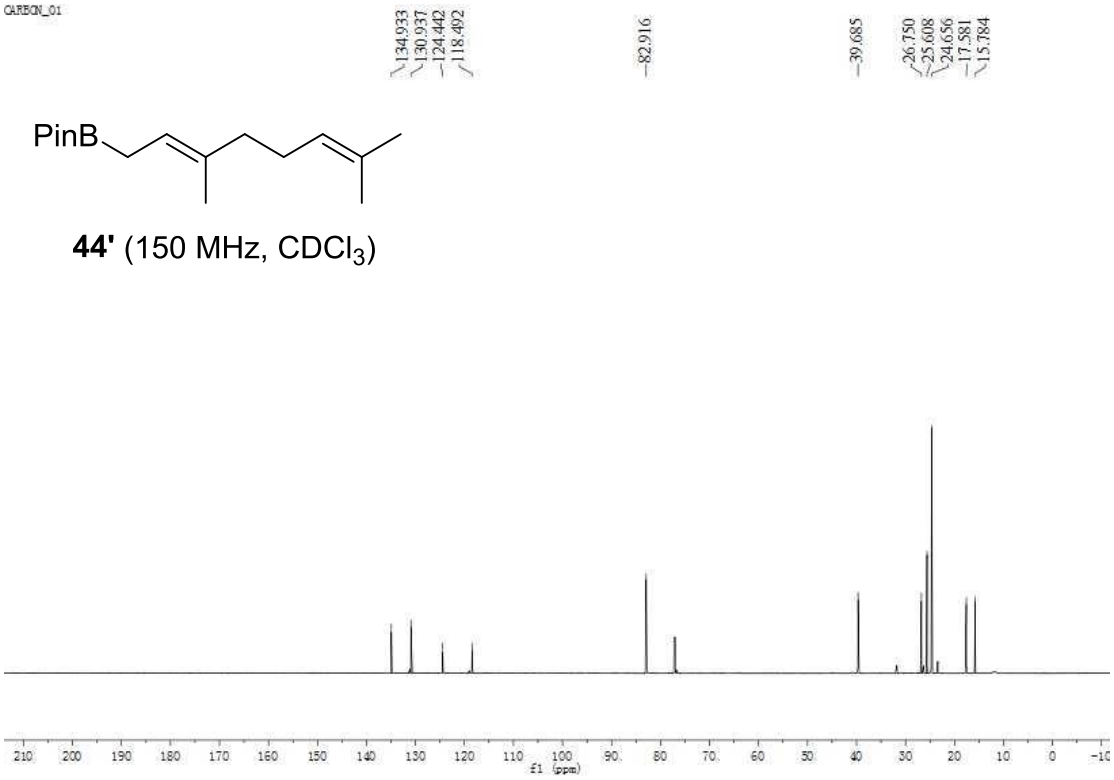
44 (150 MHz, $CDCl_3$)

^{1}H NMR spectrum of compound **44'**



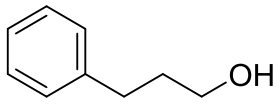
44' (600 MHz, $CDCl_3$)

^{13}C NMR spectrum of compound **44'**

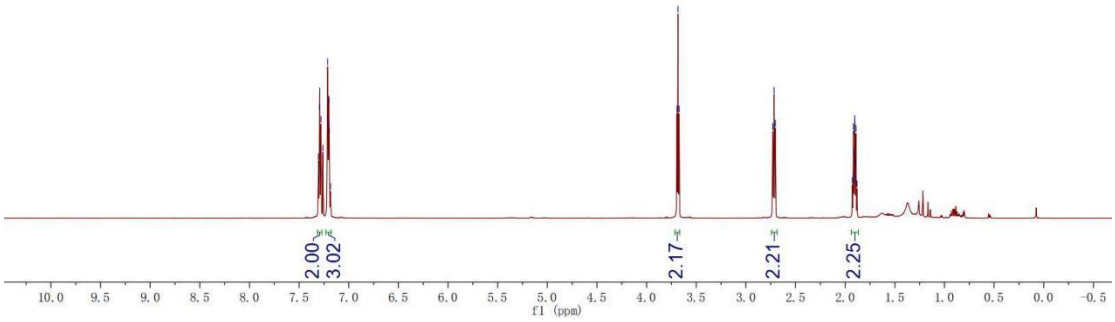


44' (150 MHz, $CDCl_3$)

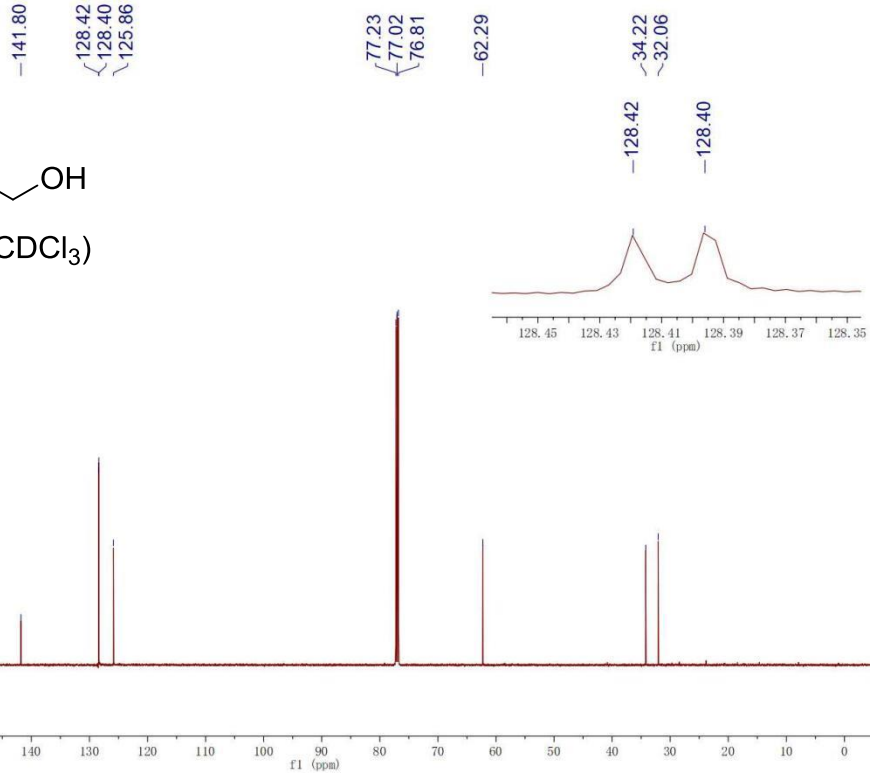
^{1}H NMR spectrum of compound **45**

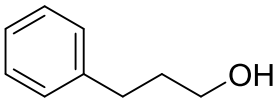


45 (600 MHz, $CDCl_3$)



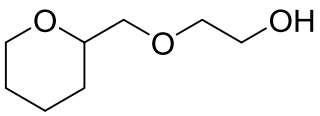
^{13}C NMR spectrum of compound **45**



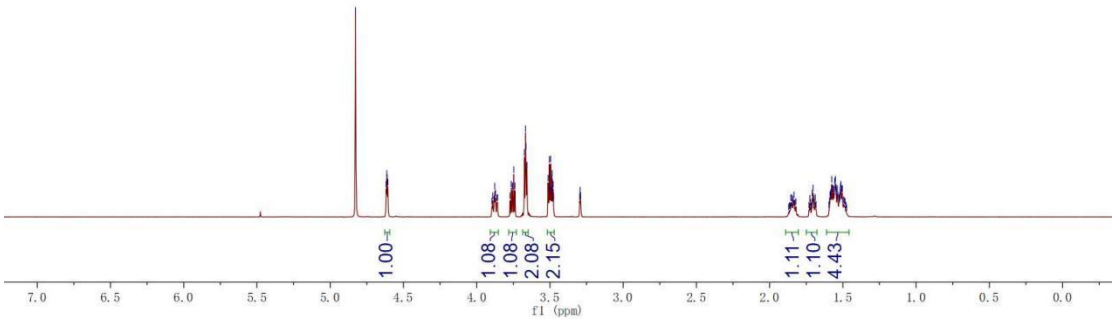


45 (150 MHz, $CDCl_3$)

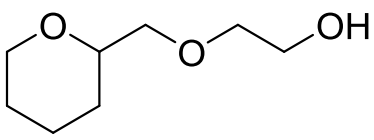
^{1}H NMR spectrum of compound **46**



46 (600 MHz, CD_3OD)

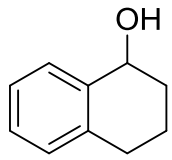


^{13}C NMR spectrum of compound **46**

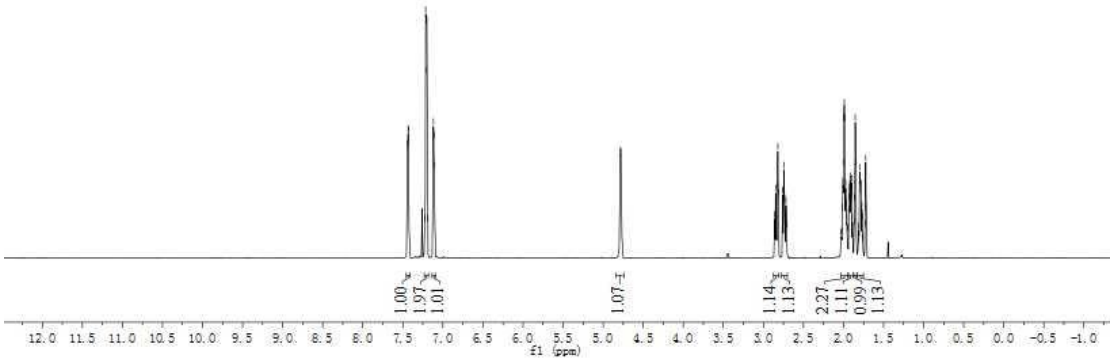


46 (150 MHz, CD_3OD)

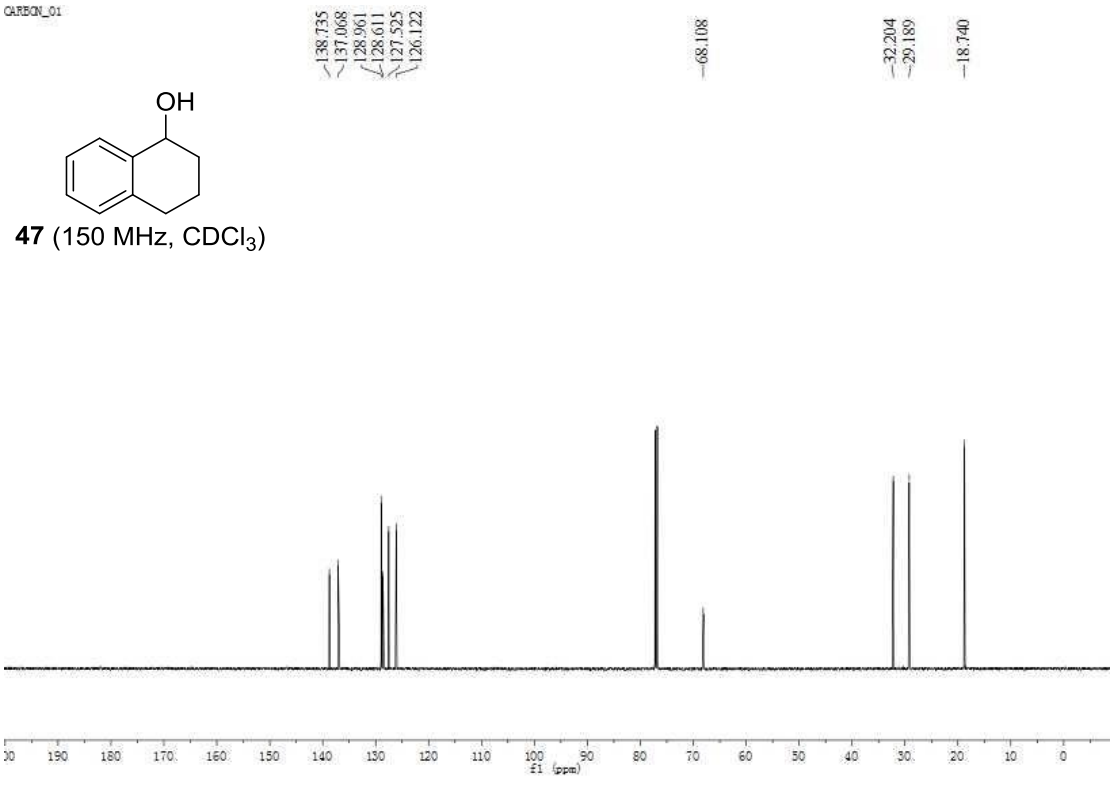
^{1}H NMR spectrum of compound **47**



47 (600 MHz, $CDCl_3$)

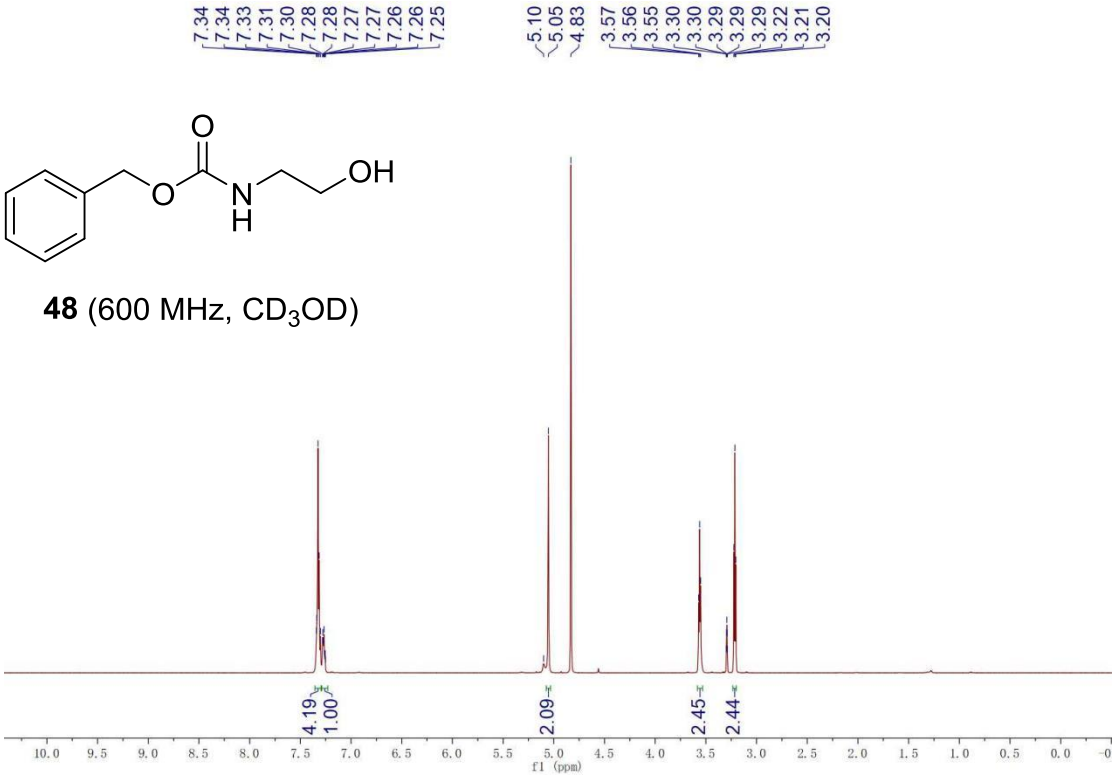


^{1}H NMR spectrum of compound **47**



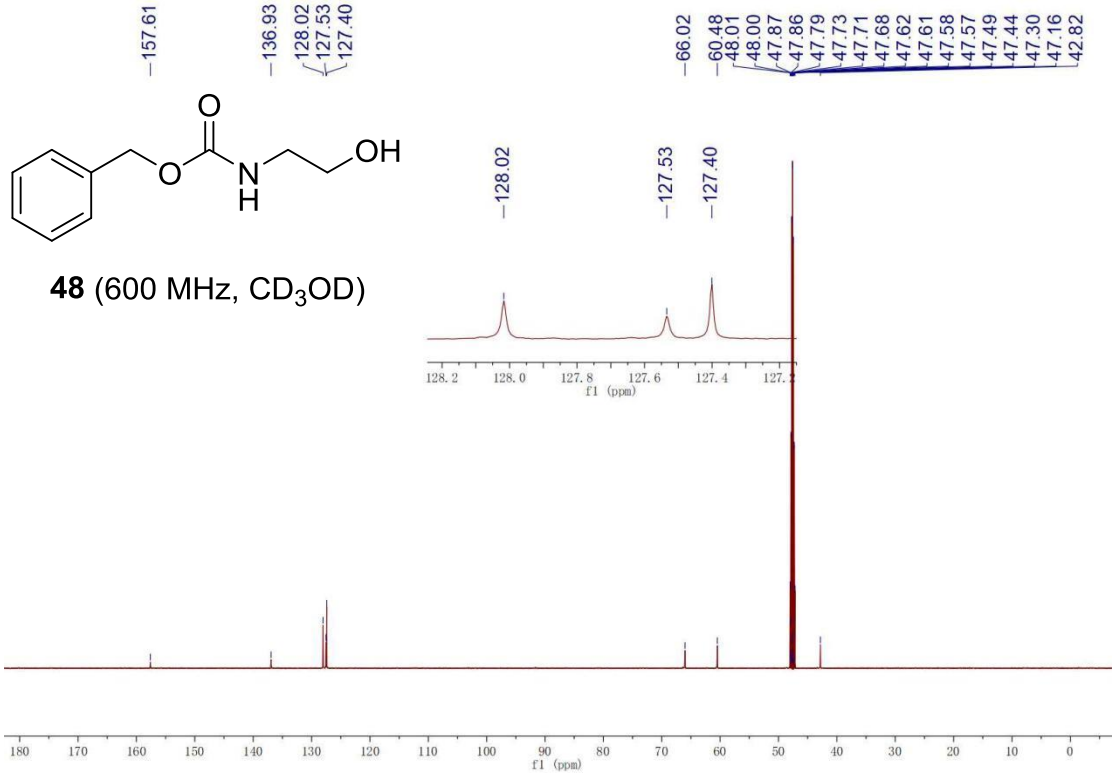
47 (150 MHz, $CDCl_3$)

^{1}H NMR spectrum of compound **48**



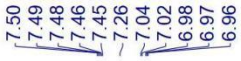
48 (600 MHz, CD_3OD)

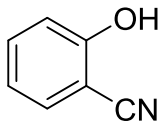
^{13}C NMR spectrum of compound **48**



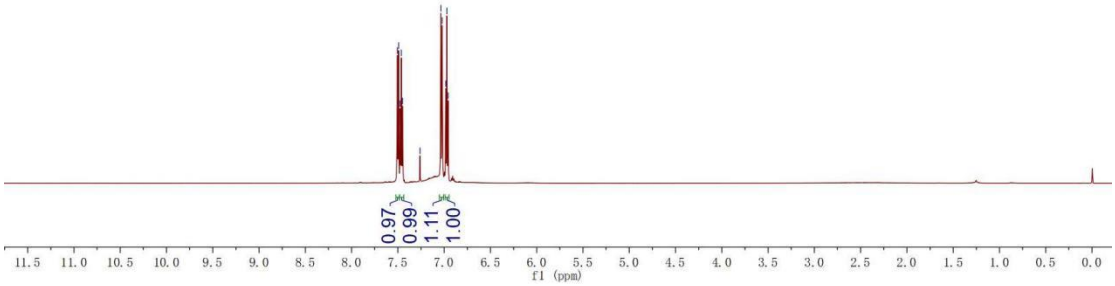
48 (600 MHz, CD_3OD)

^{1}H NMR spectrum of compound **49**

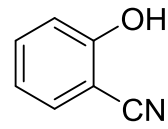




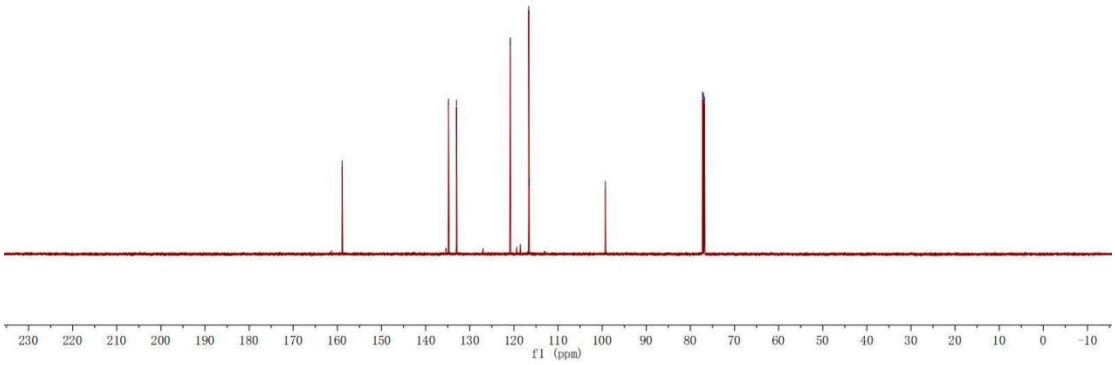
49 (600 MHz, $CDCl_3$)



^{13}C NMR spectrum of compound **49**



49 (150 MHz, $CDCl_3$)



11. Computational data

Phenylboronic acid

Zero-point correction= 0.126016 (Hartree/Particle)
Thermal correction to Energy= 0.133844
Thermal correction to Enthalpy= 0.134788
Thermal correction to Gibbs Free Energy= 0.093330
E(solvent) = -408.255484663 A.U.

C	2.637979	0.000007	0.000015
C	1.940702	1.208365	0.000081
C	0.547395	1.204750	0.000029
C	-0.169445	-0.000012	-0.000012
C	0.547397	-1.204769	-0.000041
C	1.940693	-1.208360	-0.000073
H	3.724496	-0.000005	0.000032
H	2.483597	2.149238	0.000121
H	0.001360	2.144591	-0.000016
H	0.001364	-2.144616	-0.000044
H	2.483603	-2.149224	-0.000117
B	-1.731223	-0.000014	-0.000048
O	-2.376461	1.211310	-0.000088
H	-3.341428	1.190006	-0.000072
O	-2.376505	-1.211318	0.000099
H	-3.341477	-1.189730	0.000258

Superoxide anions

Zero-point correction= 0.002926 (Hartree/Particle)
Thermal correction to Energy= 0.005298
Thermal correction to Enthalpy= 0.006243
Thermal correction to Gibbs Free Energy= -0.016838
E(solvent) = -150.449032272 A.U.

O	0.000000	-0.000000	0.663126
O	0.000000	-0.000000	-0.663126

TS1

Zero-point correction= 0.129109 (Hartree/Particle)
Thermal correction to Energy= 0.139074

Thermal correction to Enthalpy= 0.140018
Thermal correction to Gibbs Free Energy= 0.091865
E(solvent) = -558.709829699 A.U.

C	3.043649	-0.529628	0.069491
C	2.063076	-1.392112	-0.426573
C	0.746790	-0.952725	-0.555090
C	0.372224	0.348276	-0.191241
C	1.369166	1.195506	0.309834
C	2.692443	0.768302	0.439864
H	4.072262	-0.869463	0.170469
H	2.327669	-2.409464	-0.706928
H	-0.019676	-1.629347	-0.926229
H	1.093144	2.205865	0.603427
H	3.449248	1.445175	0.831617
B	-1.128994	0.839614	-0.372548
O	-1.384114	2.129923	0.088634
H	-2.316239	2.312488	-0.093752
O	-2.040724	0.219029	-1.172450
H	-2.307396	-0.678603	-0.721316
O	-1.891014	-0.854233	1.276668
O	-2.481414	-1.644774	0.410616

INT1

Zero-point correction= 0.130295 (Hartree/Particle)
Thermal correction to Energy= 0.140831
Thermal correction to Enthalpy= 0.141775
Thermal correction to Gibbs Free Energy= 0.092575
E(solvent) = -558.723039321 A.U.

C	-3.211372	0.000008	-0.236402
C	-2.513295	-1.204594	-0.134350
C	-1.131136	-1.196268	0.064668
C	-0.407434	-0.000025	0.167176
C	-1.131101	1.196225	0.064655
C	-2.513277	1.204582	-0.134361
H	-4.288635	-0.000000	-0.391013
H	-3.049574	-2.149220	-0.208836
H	-0.586184	-2.133746	0.153462
H	-0.586152	2.133703	0.153436
H	-3.049509	2.149234	-0.208856
B	1.196834	0.000019	0.362647

O	1.648785	1.235005	0.971885
H	2.604215	1.298433	0.831802
O	1.648867	-1.234783	0.972200
H	2.604289	-1.298196	0.832039
O	1.810477	-0.000132	-1.112142
O	3.118505	-0.000072	-1.047391

$Et_3N^{\bullet+}$

Zero-point correction= 0.208190 (Hartree/Particle)
Thermal correction to Energy= 0.217849
Thermal correction to Enthalpy= 0.218793
Thermal correction to Gibbs Free Energy= 0.173062
E(solvent) = -292.166365209 A.U.

N	0.137537	0.041562	0.107740
C	-0.329451	1.401000	0.320942
H	-0.347521	1.571821	1.405422
H	0.394036	2.080915	-0.132856
C	-1.732079	1.608808	-0.270074
H	-2.011661	2.653508	-0.116795
H	-1.739465	1.402095	-1.343207
H	-2.476889	0.982572	0.226630
C	-0.550267	-1.075910	0.731356
H	0.219032	-1.718048	1.177989
H	-1.190784	-0.682513	1.523600
C	-1.367482	-1.875022	-0.299201
H	-1.851354	-2.703382	0.223336
H	-2.139384	-1.254351	-0.758290
H	-0.730664	-2.292413	-1.082337
C	1.328425	-0.199466	-0.685337
H	1.328939	-1.245793	-0.997133
H	1.279548	0.444893	-1.569686
C	2.584204	0.121800	0.147808
H	3.461819	-0.074955	-0.472072
H	2.604943	1.170626	0.452734
H	2.636561	-0.513177	1.035525

$Et_2N^{+}=CHCH_3$

Zero-point correction= 0.198305 (Hartree/Particle)
Thermal correction to Energy= 0.207511
Thermal correction to Enthalpy= 0.208455
Thermal correction to Gibbs Free Energy= 0.164524
E(solvent) = -291.609285935 A.U.

N	0.117445	-0.144362	0.105733
C	-0.566440	-1.215900	0.285442
H	-0.072609	-1.999176	0.860941
C	-1.938594	-1.484936	-0.205061
H	-1.911573	-2.373774	-0.846810
H	-2.567131	-1.746171	0.654393
H	-2.395776	-0.658381	-0.745845
C	-0.395720	1.041336	-0.627823
H	0.481968	1.578474	-0.991073
H	-0.953629	0.695091	-1.498750
C	-1.238484	1.918934	0.291048
H	-1.564702	2.804560	-0.259213
H	-2.126998	1.389395	0.645800
H	-0.662526	2.253101	1.158427
C	1.493706	-0.017607	0.652316
H	1.571629	0.992930	1.062663
H	1.588428	-0.727521	1.476317
C	2.537682	-0.272776	-0.427284
H	3.532845	-0.147421	0.006042
H	2.458458	-1.292640	-0.813342
H	2.446595	0.427754	-1.261510

INT2

Zero-point correction= 0.140773 (Hartree/Particle)
Thermal correction to Energy= 0.150753
Thermal correction to Enthalpy= 0.151697
Thermal correction to Gibbs Free Energy= 0.104582
E(solvent) = -559.357732432 A.U.

C	3.253955	0.000074	0.255830
C	2.555623	-1.204550	0.150831
C	1.173882	-1.195671	-0.053642
C	0.449615	-0.000029	-0.160547
C	1.173816	1.195666	-0.053782
C	2.555556	1.204646	0.150691
H	4.330959	0.000113	0.414133

H	3.092114	-2.149362	0.227156
H	0.626688	-2.131654	-0.145741
H	0.626570	2.131608	-0.145990
H	3.091995	2.149498	0.226906
B	-1.164080	-0.000085	-0.359763
O	-1.588727	1.234543	-1.029739
H	-2.517081	1.382469	-0.804469
O	-1.588673	-1.234813	-1.029593
H	-2.516984	-1.382819	-0.804199
O	-1.715760	-0.000021	1.062667
O	-3.165155	0.000230	0.904077
H	-3.422040	0.000237	1.835433

TS2

Zero-point correction= 0.138340 (Hartree/Particle)
Thermal correction to Energy= 0.149536
Thermal correction to Enthalpy= 0.150480
Thermal correction to Gibbs Free Energy= 0.101326
E(solvent) = -559.313766520 A.U.

C	3.200054	-0.089029	0.136371
C	2.439555	-1.257132	0.040116
C	1.047632	-1.186018	-0.009826
C	0.394022	0.049486	0.007942
C	1.162300	1.211078	0.118011
C	2.554838	1.148473	0.178581
H	4.285189	-0.142885	0.181470
H	2.936147	-2.225115	0.007575
H	0.447310	-2.089409	-0.086728
H	0.668255	2.180616	0.165561
H	3.138680	2.063207	0.262363
B	-1.393005	0.021381	-0.536996
O	-1.694673	1.147924	-1.348937
H	-1.408770	1.944151	-0.884463
O	-1.835370	-1.208431	-1.060622
H	-2.313041	-1.599499	-0.309628
O	-1.246557	0.126053	0.844902
O	-3.002468	-0.097736	1.482014
H	-3.346603	0.758400	1.182808

INT3

Zero-point correction= 0.143136 (Hartree/Particle)
Thermal correction to Energy= 0.153632
Thermal correction to Enthalpy= 0.154576
Thermal correction to Gibbs Free Energy= 0.107095
E(solvent) = -559.503384774 A.U.

C	3.225925	0.400650	-0.000005
C	2.187467	1.336448	0.000003
C	0.850746	0.948523	0.000024
C	0.511149	-0.423487	0.000046
C	1.565421	-1.362489	0.000020
C	2.895631	-0.956449	0.000003
H	4.264524	0.721175	-0.000008
H	2.423019	2.399352	-0.000017
H	0.051023	1.679204	0.000021
H	1.298277	-2.416006	0.000022
H	3.682939	-1.708458	-0.000008
B	-1.949410	0.014531	-0.000034
O	-1.963926	0.889761	1.167815
H	-1.972975	0.319897	1.946620
O	-1.963638	0.889788	-1.167781
H	-1.972705	0.320091	-1.946695
O	-0.726981	-0.889750	0.000063
O	-3.043978	-0.965142	-0.000139
H	-3.856903	-0.444335	0.000036