Electronic Supplementary Material (ESI) for Green Chemistry.

Palladium nano-particles as recyclable catalyst for C-O bond formation under solvent free conditions

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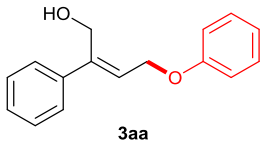
General experimental details

Analytical thin-layer chromatography (TLC) was carried out using 0.2 mm commercial silica gel plates (Yantai Jiangyou Silica Gel Development Co., Ltd., silica gel HSGF 254). Preparative column chromatography employing silica gel (Qingdao Shenghai Fine Silica Gel Chemical Co., Ltd., 200-300 mesh) was performed according to the method of Still. Solvents for the chromatography are listed as volume/volume ratios. High-resolution mass spectra (HRMS) were performed at Instrumental Analysis Center of Xi'an Jiao Tong University using ESI method. Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded with a Varian Mercuryplus 400 (400 MHz) spectrometer. Chemical shifts are reported in delta (δ) units, parts per million (ppm) downfield from tetramethylsilane or ppm relative to the center of the singlet at 7.26 ppm for deuteriochloroform. Coupling constants are reported in Hertz (Hz). Carbon-13 nuclear magnetic resonance (^{13}C NMR) spectra were recorded with a Varian Gemini 400 (100 MHz) spectrometer. Chemical shifts are reported in delta (δ) units, ppm relative to the center of the triplet at 77.0 ppm for deuteriochloroform. ^{13}C NMR spectra were routinely run with broadband decoupling. $Pd_2(dba)_3$ and other palladium catalysts were purchased from Energy Chemicals and Aladin/Sigma-Aldrich companies and used as received. Substituted vinyl ethylene carbonates (VECs) were synthesized according to the previously reported procedure.[1] All other chemicals were used as received from commercial resources.

General procedure for PdNPs catalyzed cross coupling of vinyl cyclic carbonate 1a with phenol (2a)

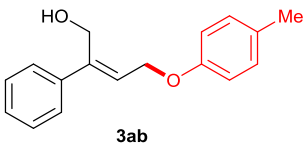
To an oven dried screw-cap reaction tube equipped with a magnetic stir bar, $Pd_2(dba)_3$ (2.5 mol%), vinyl cyclic carbonate **1a** (0.2 mmol) and phenol **2a** (0.3 mmol). The resulting mixture was stirred at room temperature for 15 hours. After the completion of reaction, the product **3aa** was isolated by using flash column chromatography using PE/EA (10:1) as a solvent. The *Z*/*E* ratio of the product was determined by ^{1}H-NMR analysis.

Scale-up Experiment: To an oven dried screw-cap reaction tube equipped with a magnetic stir bar, $Pd_2(dba)_3$ (2.5 mol%), vinyl cyclic carbonate **1a** (10.0 mmol, 1.9g) and phenol **2a** (15 mmol, 1.41g) were added. The resulting mixture was stirred at room temperature for 15 hours. After the completion of reaction, the residue was filtered, washed with ethanol, concentrated and purified by flash column chromatography to afford the product **3aa** in 81% yield (1.94g). The upper solid layer was further recycled and examined for TEM analysis.



3aa

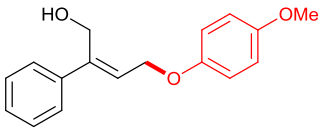
(*Z*)-4-phenoxy-2-phenylbut-2-en-1-ol (3aa)[2] was prepared according to the general procedure from **1a** and **2a**. The crude product was purified by flash column chromatography (Petroleum ether/EtOAc = 3:1) on silica gel to provide the title compound as a light-yellow oil in 93% yield (44.7 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49–7.45 (m, 2H), 7.38–7.28 (m, 5H), 6.99–6.93 (m, 3H), 6.15 (t, *J* = 6.4 Hz, 1H), 4.80 (d, *J* = 6.4 Hz, 2H), 4.61 (s, 2H), 1.89 (brs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.3, 143.2, 139.9, 129.5, 128.6, 127.9, 126.4, 126.2, 121.1, 114.8, 64.4, 60.3; HRMS (ESI-MS): Calcd. for $C_{16}H_{16}O_2$ (M + Na): 263.1048, Found: 263.1054.



3ab

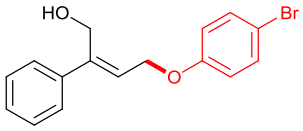
(*Z*)-2-phenyl-4-(p-tolyloxy)but-2-en-1-ol (3ab) was prepared according to the general procedure from **1a** and **2b**. The crude product was purified by flash column chromatography (Petroleum ether/EtOAc = 3:1) on silica gel to provide the title compound as a colorless oil in 91% yield (46.3 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49–7.45 (m, 2H), 7.37–7.27 (m, 3H), 7.11–7.08 (m, 2H), 6.87–6.83 (m, 2H), 6.15 (t, *J* = 6.4 Hz, 1H), 4.77 (d, *J* = 6.4 Hz, 2H), 4.60 (s, 2H), 2.29 (s, 3H), 1.87 (brs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.2, 143.2, 139.9, 130.4,

130.0, 128.5, 127.8, 126.4, 126.3, 114.7, 64.6, 60.3, 20.5; HRMS (ESI-MS): Calcd. for $C_{17}H_{18}O_2$ (M + Na): 277.1204, Found: 277.1208.



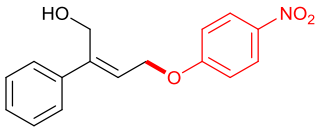
3ac

(*Z*)-4-(4-methoxyphenoxy)-2-phenylbut-2-en-1-ol (3ac)[2] was prepared according to the general procedure from **1a** and **2c**. The crude product was purified by flash column chromatography (Petroleum ether/EtOAc = 3:1) on silica gel to provide the title compound as a white solid in 96% yield (52.0 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49–7.46 (m, 2H), 7.38–7.28 (m, 3H), 6.92–6.83 (m, 4H), 6.15 (t, *J* = 6.4 Hz, 1H), 4.75 (d, *J* = 6.4 Hz, 2H), 4.60 (s, 2H), 3.77 (s, 3H), 1.84 (brs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.1，152.4，143.2，139.9，128.6，127.8， 126.4，126.3, 115.9, 114.7, 65.2, 60.3, 55.7; HRMS (ESI-MS): Calcd. for $C_{17}H_{18}O_3$ (M + Na): 293.1154, Found: 293.1162.



3ad

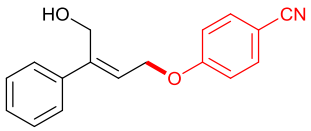
(*Z*)-4-(4-bromophenoxy)-2-phenylbut-2-en-1-ol (3ad) was prepared according to the general procedure from **1a** and **2d**. The crude product was purified by flash column chromatography (Petroleum ether/EtOAc = 3:1) on silica gel to provide the title compound as a white solid in 88% yield (56.2 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48–7.44 (m, 2H), 7.41–7.29 (m, 5H), 6.85–6.81 (m, 2H), 6.11 (t, *J* = 6.4 Hz, 1H), 4.78 (d, *J* = 6.4 Hz, 2H), 4.62 (s, 2H), 1.75 (brs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.5, 143.3, 139.7, 132.3, 128.6, 128.0, 126.5, 125.7, 116.5, 113.3, 64.7, 60.4; HRMS (ESI-MS): Calcd. for $C_{16}H_{15}BrO_2$ (M + Na): 341.0153, Found: 341.0147.



3ae

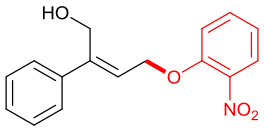
(*Z*)-4-(4-nitrophenoxy)-2-phenylbut-2-en-1-ol (3ae) was prepared according to the general procedure from **1a** and **2e**. The crude product was purified by flash column chromatography (Petroleum ether/EtOAc = 3:1) on silica gel to provide the title compound as a light yellow solid in 92% yield (52.5 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23–8.19 (m, 2H), 7.48–7.45 (m, 2H), 7.42–7.31 (m, 3H), 7.04–7.00 (m, 2H), 6.10 (t, *J* = 6.4 Hz, 1H), 4.94 (d, *J* = 6.4 Hz, 2H), 4.66 (s, 2H), 1.78 (brs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.5, 143.6, 141.7, 139.4, 128.7, 128.2,

126.5, 126.0, 124.8, 114.7, 65.3, 60.5; HRMS (ESI-MS): Calcd. for $C_{16}H_{15}NO_4$ (M + Na): 308.0899, Found: 308.0906.



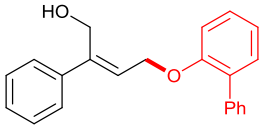
3af

(*Z*)-4-((4-hydroxy-3-phenylbut-2-en-1-yl)oxy)benzonitrile (3af) was prepared according to the general procedure from **1a** and **2f**. The crude product was purified by flash column chromatography (Petroleum ether/EtOAc = 3:1) on silica gel to provide the title compound as a white solid in 93% yield (49.3 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62–7.59 (m, 2H), 7.48–7.45 (m, 2H), 7.41–7.34 (m, 3H), 7.03–6.99 (m, 2H), 6.10 (t, *J* = 6.4 Hz, 1H), 4.89 (d, *J* = 6.4 Hz, 2H), 4.66 (s, 2H), 1.63 (brs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.7, 143.6, 139.5, 134.1, 128.7, 128.2, 126.5, 125.0, 119.1, 115.4, 104.3, 64.8, 60.5; HRMS (ESI-MS): Calcd. for $C_{17}H_{15}NO_2$ (M + Na): 288.1000, Found: 288.1008.



3ag

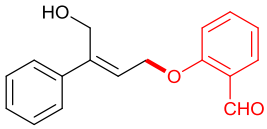
(*Z*)-4-(2-nitrophenoxy)-2-phenylbut-2-en-1-ol (3ag) was prepared according to the general procedure from **1a** and **2g**. The crude product was purified by flash column chromatography (Petroleum ether/EtOAc = 3:1) on silica gel to provide the title compound as a light yellow solid in 84% yield (48.0 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (dd, *J* = 1.6, 8.0 Hz, 1H), 7.57–7.47 (m, 3H), 7.40–7.31 (m, 3H), 7.17 (dd, *J* = 1.2, 8.0 Hz, 1H), 7.08–7.04 (m, 1H), 6.16 (t, *J* = 6.4 Hz, 1H), 4.97 (d, *J* = 6.4 Hz, 2H), 4.64 (s, 2H), 2.07 (brs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.8, 145.0, 140.1, 139.6, 134.2, 128.6, 128.1, 126.5, 125.9, 124.1, 120.7, 114.8, 65.8, 60.6; HRMS (ESI-MS): Calcd. for $C_{16}H_{15}NO_4$ (M + Na): 308.0899, Found: 308.0907.



3ah

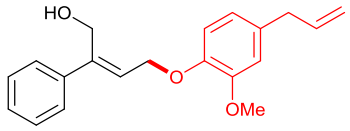
(*Z*)-4-([1,1'-biphenyl]-2-yloxy)-2-phenylbut-2-en-1-ol (3ah) was prepared according to the general procedure from **1a** and **2h**. The crude product was purified by flash column chromatography (Petroleum ether/EtOAc = 3:1) on silica gel to provide the title compound as a white solid in 89% yield (56.3 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56–7.52 (m, 2H), 7.42–7.38 (m, 4H), 7.36–7.29 (m, 6H), 7.09–7.04 (m, 2H), 6.08 (t, *J* = 6.4 Hz, 1H), 4.77 (d, *J* = 6.4 Hz, 2H), 4.45 (s, 2H), 1.55 (brs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.3, 143.2, 139.9,

138.3, 131.4, 131.1, 129.5, 128.6, 128.5, 128.1, 127.8, 127.0, 126.4, 126.0, 121.6, 113.4, 65.1, 60.3; HRMS (ESI-MS): Calcd. for $C_{22}H_{20}O_2$ (M + Na): 339.1361, Found: 339.1354.



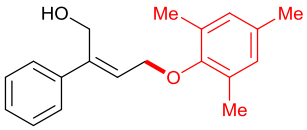
3ai

(*Z*)-2-((4-hydroxy-3-phenylbut-2-en-1-yl)oxy)benzaldehyde (3ai) was prepared according to the general procedure from **1a** and **2i**. The crude product was purified by flash column chromatography (Petroleum ether/EtOAc = 3:1) on silica gel to provide the title compound as a light-yellow oil in 82% yield (44.0 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.45 (s, 1H), 7.84 (dd, *J* = 1.6, 8.0 Hz, 1H), 7.58–7.47 (m, 3H), 7.40–7.32 (m, 3H), 7.08–7.04 (m, 2H), 6.16 (t, *J* = 6.4 Hz, 1H), 4.95 (d, *J* = 6.4 Hz, 2H), 4.66 (s, 2H), 2.04 (brs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.0, 160.6, 143.6, 139.6, 135.9, 129.5, 128.7, 128.1, 126.5, 125.1, 125.0, 121.0, 112.8, 65.0, 60.4; HRMS (ESI-MS): Calcd. for $C_{17}H_{16}O_3$ (M + Na): 291.0997, Found: 291.1005.



3aj

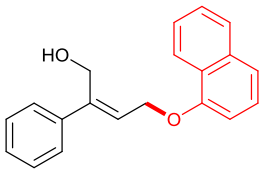
(*Z*)-4-(4-allyl-2-methoxyphenoxy)-2-phenylbut-2-en-1-ol (3aj) was prepared according to the general procedure from **1a** and **2j**. The crude product was purified by flash column chromatography (Petroleum ether/EtOAc = 3:1) on silica gel to provide the title compound as a white solid in 90% yield (55.8 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55–7.50 (m, 2H), 7.37–7.27 (m, 3H), 6.88 (d, *J* = 8.6 Hz, 1H), 6.75–6.72 (m, 2H), 6.24 (t, *J* = 6.4 Hz, 1H), 6.01–5.91 (m, 1H), 5.12–5.05 (m, 2H), 4.78 (d, *J* = 6.4 Hz, 2H), 4.54 (s, 2H), 3.86 (s, 3H), 3.34 (d, *J* = 6.4 Hz, 2H), 2.77 (brs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.2, 145.9, 145.2, 140.5, 137.5, 133.5, 128.5, 127.7, 126.3, 125.5, 120.4, 115.7, 113.3, 111.9, 65.1, 60.7, 55.7, 39.8; HRMS (ESI-MS): Calcd. for $C_{20}H_{22}O_3$ (M + Na): 333.1467, Found: 333.1475.



3ak

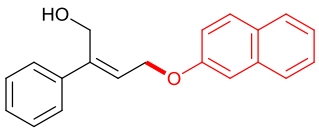
(*Z*)-4-(mesityloxy)-2-phenylbut-2-en-1-ol (3ak) was prepared according to the general procedure from **1a** and **2k**. The crude product was purified by flash column chromatography (Petroleum ether/EtOAc = 3:1) on silica gel to provide the title compound as a light-yellow oil in 72% yield (40.7 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52–7.49 (m, 2H), 7.43–7.31 (m, 3H), 6.84 (s, 2H), 6.25 (t, *J* = 6.4 Hz, 1H), 4.56 (d, *J* = 6.8 Hz, 2H), 4.55 (d, *J* = 6.8 Hz, 2H), 2.29 (s, 6H), 2.24 (s, 3H), 1.74 (brt, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.0, 143.5, 140.2, 133.5,

130.6, 129.5, 128.6, 127.8, 126.5, 126.4, 68.4, 60.2, 20.6, 16.5; HRMS (ESI-MS): Calcd. for $C_{19}H_{22}O_2$ (M + Na): 305.1517, Found: 305.1524.



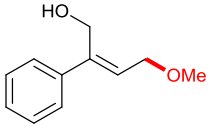
3al

(*Z*)-4-(naphthalen-1-yloxy)-2-phenylbut-2-en-1-ol (3al) was prepared according to the general procedure from **1a** and **2l**. The crude product was purified by flash column chromatography (Petroleum ether/EtOAc = 3:1) on silica gel to provide the title compound as a yellow solid in 94% yield (54.6 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30–8.27 (m, 1H), 7.82–7.78 (m, 1H), 7.52–7.44 (m, 5H), 7.39–6.31 (m, 4H), 6.87 (d, *J* = 7.6 Hz, 1H), 6.28 (t, *J* = 6.4 Hz, 1H), 4.98 (d, *J* = 6.4 Hz, 2H), 4.67 (s, 2H), 1.74 (brs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.2, 142.9, 139.8, 134.5, 128.6, 127.9, 127.5, 126.5, 126.4, 126.3, 125.8, 125.7, 125.3, 121.9, 120.7, 105.2, 64.8, 60.3; HRMS (ESI-MS): Calcd. for $C_{20}H_{18}O_2$ (M + Na): 313.1204, Found: 313.1206.



3am

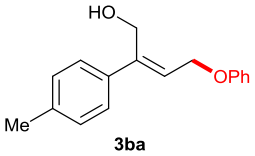
(*Z*)-4-(naphthalen-2-yloxy)-2-phenylbut-2-en-1-ol (3am) was prepared according to the general procedure from **1a** and **2m**. The crude product was purified by flash column chromatography (Petroleum ether/EtOAc = 3:1) on silica gel to provide the title compound as a light yellow solid in 92% yield (53.4 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.78–8.73 (m, 3H), 7.51–7.42 (m, 3H), 7.39–7.31 (m, 4H), 7.21–6.17 (m, 2H), 6.22 (t, *J* = 6.4 Hz, 1H), 4.92 (d, *J* = 6.4 Hz, 2H), 4.67 (s, 2H), 1.79 (brs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.3, 143.2, 139.8, 134.5, 129.6, 129.1, 128.6, 127.9, 127.7, 126.8, 126.5, 126.4, 126.1, 123.8, 118.9, 107.1, 64.5, 60.4; HRMS (ESI-MS): Calcd. for $C_{20}H_{18}O_2$ (M + Na): 313.1204, Found: 313.1208.



3an

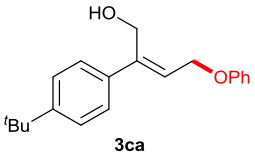
(*Z*)-4-methoxy-2-phenylbut-2-en-1-ol (3an) was prepared according to the general procedure from **1a** and **2n**. The crude product was purified by flash column chromatography (Petroleum ether/EtOAc = 3:1) on silica gel to provide the title compound as a colorless oil in 78% yield (27.8 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48–7.44 (m, 2H), 7.39–7.27 (m, 3H), 6.05 (t, *J* = 6.4 Hz, 1H), 4.54 (s, 2H), 4.18 (d, *J* = 6.4 Hz, 2H), 3.41 (s, 3H), 2.22 (brs, 1H); ^{13}C NMR

(100 MHz, $CDCl_3$) δ 144.0, 140.4, 128.5, 127.7, 127.0, 126.3, 68.6, 60.5, 58.3; HRMS (ESI-MS): Calcd. for $C_{11}H_{14}O_2$ (M + Na): 201.0891, Found: 201.0898.



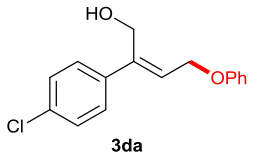
3ba

(*Z*)-4-phenoxy-2-(p-tolyl)but-2-en-1-ol (3ba)[2] was prepared according to the general procedure from **1b** and **2a**. The crude product was purified by flash column chromatography (Petroleum ether/EtOAc = 3:1) on silica gel to provide the title compound as a colorless oil in 90% yield (45.7 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38–7.35 (m, 2H), 7.32–7.27 (m, 2H), 7.17–7.15 (m, 2H), 6.99–6.93 (m, 3H), 6.12 (t, *J* = 6.4 Hz, 1H), 4.78 (d, *J* = 6.4 Hz, 2H), 4.59 (s, 2H), 2.34 (s, 3H), 1.83 (brs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.4, 143.0, 137.7, 136.9, 129.5, 129.3, 126.3, 125.3, 121.1, 114.8, 64.4, 60.3, 21.1; HRMS (ESI-MS): Calcd. for $C_{17}H_{18}O_2$ (M + Na): 277.1204, Found: 277.1208.



3ca

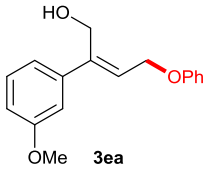
(*Z*)-2-(4-(tert-butyl)phenyl)-4-phenoxybut-2-en-1-ol (3ca) was prepared according to the general procedure from **1c** and **2a**. The crude product was purified by flash column chromatography (Petroleum ether/EtOAc = 3:1) on silica gel to provide the title compound as a white solid in 92% yield (54.5 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43–7.35 (m, 4H), 7.31–7.27 (m, 2H), 6.98–6.94 (m, 3H), 6.14 (t, *J* = 6.4 Hz, 1H), 4.79 (d, *J* = 6.4 Hz, 2H), 4.61 (s, 2H), 1.87 (brs, 1H), 1.32 (s, 9); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.3, 151.0, 142.9, 136.8, 129.5, 126.1, 125.5, 125.4, 121.1, 114.8, 64.4, 60.2, 34.5, 31.3; HRMS (ESI-MS): Calcd. for $C_{20}H_{24}O_2$ (M + Na): 319.1674, Found: 319.1668.



3da

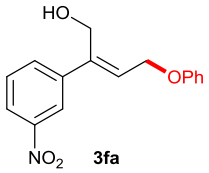
(*Z*)-2-(4-chlorophenyl)-4-phenoxybut-2-en-1-ol (3da) was prepared according to the general procedure from **1d** and **2a**. The crude product was purified by flash column chromatography (Petroleum ether/EtOAc = 3:1) on silica gel to provide the title compound as a colorless oil in 82% yield (45.0 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42–7.39 (m, 2H), 7.33–7.27 (m, 4H), 6.97–6.92 (m, 3H), 6.14 (t, *J* = 6.4 Hz, 1H), 4.78 (d, *J* = 6.4 Hz, 2H), 4.57 (s, 2H), 2.03 (brs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.2, 142.1, 138.4, 133.7, 129.6, 128.7, 127.8, 126.6,

121.3, 114.7, 64.3, 60.2; HRMS (ESI-MS): Calcd. for $C_{16}H_{15}ClO_2$ (M + Na): 297.0658, Found: 297.0664.



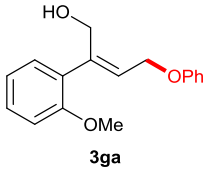
3ea

(*Z*)-2-(3-methoxyphenyl)-4-phenoxybut-2-en-1-ol (3ea) was prepared according to the general procedure from **1e** and **2a**. The crude product was purified by flash column chromatography (Petroleum ether/EtOAc = 3:1) on silica gel to provide the title compound as a yellow solid in 88% yield (47.6 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31–7.23 (m, 3H), 7.06–6.93 (m, 5H), 6.85–6.82 (m, 1H), 6.14 (t, *J* = 6.4 Hz, 1H), 4.77 (d, *J* = 6.4 Hz, 2H), 4.57 (s, 2H), 3.79 (s, 3H), 2.01 (brs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.7, 158.3, 142.9, 141.4, 129.5, 126.3, 121.1, 118.9, 114.7, 113.2, 112.3, 64.4, 60.3, 55.2; HRMS (ESI-MS): Calcd. for $C_{17}H_{18}O_3$ (M + Na): 293.1154, Found: 293.1148.



3fa

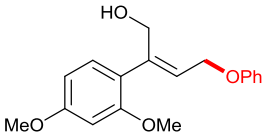
(*Z*)-2-(3-nitrophenyl)-4-phenoxybut-2-en-1-ol (3fa) was prepared according to the general procedure from **1f** and **2a**. The crude product was purified by flash column chromatography (Petroleum ether/EtOAc = 3:1) on silica gel to provide the title compound as a yellow solid in 84% yield (48.0 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (t, *J* = 1.9 Hz, 1H), 8.17–8.14 (m, 1H), 7.85–7.82 (m, 1H), 7.53 (t, *J* = 8.0 Hz, 1H), 7.34–7.30 (m, 2H), 7.02–6.95 (m, 3H), 6.29 (t, *J* = 6.4 Hz, 1H), 4.84 (d, *J* = 6.4 Hz, 2H), 4.66 (s, 2H), 1.95 (brs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.1, 148.4, 141.8, 141.1, 132.5, 129.6, 129.4, 128.7, 122.5, 121.4, 114.7, 64.2, 60.0; HRMS (ESI-MS): Calcd. for $C_{16}H_{15}NO_4$ (M + Na): 308.0899, Found: 308.0897.



3ga

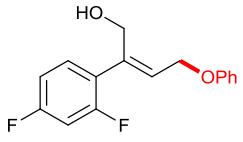
(*Z*)-2-(2-methoxyphenyl)-4-phenoxybut-2-en-1-ol (3ga) was prepared according to the general procedure from **1g** and **2a**. The crude product was purified by flash column chromatography (Petroleum ether/EtOAc = 3:1) on silica gel to provide the title compound as a yellow solid in 85% yield (46.0 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31–7.20 (m, 4H), 6.98–6.88 (m, 5H), 5.94 (t, *J* = 6.4 Hz, 1H), 4.84 (d, *J* = 6.4 Hz, 2H), 4.41 (s, 2H), 3.41 (s, 3H), 2.53 (brs, 1H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 158.5, 156.3, 142.5, 130.8, 130.3, 129.4, 129.1, 129.0, 121.2, 120.8, 114.8, 110.5, 64.4, 61.4, 55.7; HRMS (ESI-MS): Calcd. for $C_{17}H_{18}O_3$ (M + Na): 293.1154, Found: 293.1161.



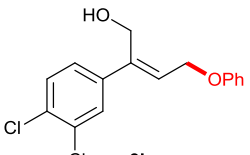
3ha

(*Z*)-2-(2,4-dimethoxyphenyl)-4-phenoxybut-2-en-1-ol (3ha) was prepared according to the general procedure from **1h** and **2a**. The crude product was purified by flash column chromatography (Petroleum ether/EtOAc = 3:1) on silica gel to provide the title compound as a white solid in 92% yield (55.2 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34–7.28 (m, 2H), 7.17–7.16 (m, 1H), 7.01–6.99 (m, 3H), 6.53–6.49 (m, 2H), 5.93 (t, *J* = 6.4 Hz, 1H), 4.85 (d, *J* = 6.4 Hz, 2H), 4.43 (d, *J* = 5.8 Hz, 2H), 3.87 (s, 3H), 3.84 (s, 3H), 2.44 (brt, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.7, 158.5, 157.3, 142.2, 130.8, 129.44, 128.3, 123.6, 120.8, 114.8, 104.6, 98.6, 64.4, 61.5, 55.6, 55.4; HRMS (ESI-MS): Calcd. for $C_{18}H_{20}O_4$ (M + Na): 323.1259, Found: 323.1265.



3ia

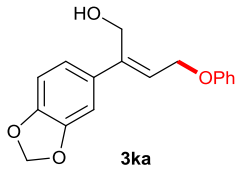
(*Z*)-2-(2,4-difluorophenyl)-4-phenoxybut-2-en-1-ol (3ia) was prepared according to the general procedure from **1i** and **2a**. The crude product was purified by flash column chromatography (Petroleum ether/EtOAc = 3:1) on silica gel to provide the title compound as a yellow solid in 87% yield (48.0 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33–7.27 (m, 3H), 6.99–6.93 (m, 3H), 6.87–6.78 (m, 2H), 6.01 (t, *J* = 6.4 Hz, 1H), 4.80 (d, *J* = 6.4 Hz, 2H), 4.51 (s, 2H), 2.11 (brs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.7, 163.6, 161.3, 161.3, 161.1, 158.7, 158.6, 158.3, 138.4, 131.2, 131.1, 129.7, 129.5, 124.7, 124.6, 124.5, 121.2, 114.7, 104.3, 104.0, 103.7, 64.2, 60.9; HRMS (ESI-MS): Calcd. for $C_{16}H_{14}F_2O_2$ (M + Na): 299.0860, Found: 299.0866.



3ja

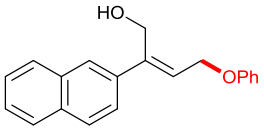
(*Z*)-2-(3,4-dichlorophenyl)-4-phenoxybut-2-en-1-ol (3ja) was prepared according to the general procedure from **1j** and **2a**. The crude product was purified by flash column chromatography (Petroleum ether/EtOAc = 3:1) on silica gel to provide the title compound as a white solid

in 91% yield (56.3 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 2.2 Hz, 1H), 7.44 (d, *J* = 2.2 Hz, 1H), 7.37–7.33 (m, 3H), 7.05–6.96 (m, 3H), 6.21 (t, *J* = 6.4 Hz, 1H), 4.81 (d, *J* = 6.4 Hz, 2H), 4.59 (s, 2H), 1.96 (brs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.1, 141.1, 140.0, 132.6, 131.8, 130.4, 129.6, 128.4, 127.7, 125.8, 121.4, 114.7, 64.2, 60.0; HRMS (ESI-MS): Calcd. for $C_{16}H_{14}Cl_2O_2$ (M + Na): 331.0269, Found: 331.0262.



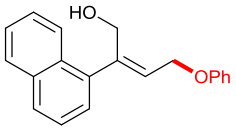
3ka

(*Z*)-2-(benzo[d][1,3]dioxol-5-yl)-4-phenoxybut-2-en-1-ol (3ka) was prepared according to the general procedure from **1k** and **2a**. The crude product was purified by flash column chromatography (Petroleum ether/EtOAc = 3:1) on silica gel to provide the title compound as a white solid in 90% yield (51.2 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32–7.27 (m, 2H), 6.99–6.93 (m, 5H), 6.78 (d, *J* = 1.2, 7.4 Hz, 1H), 6.07 (t, *J* = 6.4 Hz, 1H), 5.95 (s, 2H), 4.76 (d, *J* = 6.4 Hz, 2H), 4.55 (s, 2H), 1.83 (brs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.3, 147.9, 147.4, 142.9, 134.1, 129.5, 125.0, 121.2, 120.1, 114.8, 108.3, 107.0, 101.1, 64.3, 60.4; HRMS (ESI-MS): Calcd. for $C_{17}H_{16}O_4$ (M + Na): 307.0946, Found: 307.0952.



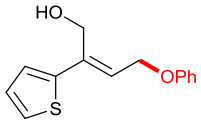
3la

(*Z*)-2-(naphthalen-2-yl)-4-phenoxybut-2-en-1-ol (3la) was prepared according to the general procedure from **1k** and **2a**. The crude product was purified by flash column chromatography (Petroleum ether/EtOAc = 3:1) on silica gel to provide the title compound as a yellow solid in 92% yield (53.4 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 1.2 Hz, 1H), 7.83–7.79 (m, 3H), 7.59 (dd, *J* = 1.2, 7.4 Hz, 1H), 7.49–7.43 (m, 2H), 7.33–7.28 (m, 2H), 7.00–6.95 (m, 3H), 6.29 (t, *J* = 6.4 Hz, 1H), 4.82 (d, *J* = 6.4 Hz, 2H), 4.69 (s, 2H), 2.02 (brs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.3, 143.0, 137.1, 133.3, 132.9, 129.6, 128.2, 128.1, 127.5, 126.6, 126.3, 126.1, 125.4, 124.5, 121.2, 114.8, 64.4, 60.3; HRMS (ESI-MS): Calcd. for $C_{20}H_{18}O_2$ (M + Na): 313.1204, Found: 313.1198.



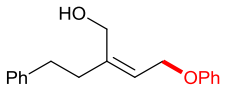
3ma

(*Z*)-2-(naphthalen-1-yl)-4-phenoxybut-2-en-1-ol (3ma) was prepared according to the general procedure from **1m** and **2a**. The crude product was purified by flash column chromatography (Petroleum ether/EtOAc = 3:1) on silica gel to provide the title compound as a yellow solid in 89% yield (52.7 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94–7.78 (m, 3H), 7.49–7.41 (m, 3H), 7.35–7.29 (m, 3H), 7.02–6.97 (m, 3H), 5.98 (t, *J* = 6.4 Hz, 1H), 4.91 (d, *J* = 6.4 Hz, 2H), 4.59 (s, 2H), 1.90 (brs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.3, 143.1, 138.8, 133.7, 131.5, 129.5, 128.7, 128.4, 128.0, 126.2, 126.1, 125.9, 125.4, 125.3, 121.2, 114.9, 64.3, 62.4; HRMS (ESI-MS): $C_{20}H_{18}O_2$ (M + Na): 313.1204, Found: 313.1198.



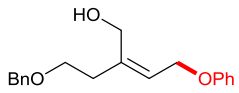
3na

(*E*)-4-phenoxy-2-(thiophen-2-yl)but-2-en-1-ol (3na) was prepared according to the general procedure from **1n** and **2a**. The crude product was purified by flash column chromatography (Petroleum ether/EtOAc = 3:1) on silica gel to provide the title compound as a light-yellow oil in 90% yield (44.3 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (dd, *J* = 1.2, 2.8 Hz, 1H), 7.33–7.27 (m, 4H), 7.02–6.94 (m, 3H), 6.26 (t, *J* = 6.4 Hz, 1H), 4.79 (d, *J* = 6.4 Hz, 2H), 4.58 (s, 2H), 1.82 (brs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.3, 140.9, 137.9, 129.6, 126.0, 125.7, 124.6, 121.5, 121.2, 114.8, 64.2, 60.3; HRMS (ESI-MS): Calcd. for $C_{14}H_{14}O_2S$ (M + Na): 269.0612, Found: 269.0618.



3oa

(*Z*)-2-phenethyl-4-phenoxybut-2-en-1-ol (3oa) was prepared according to the general procedure from **1p** and **2a**. The crude product was purified by flash column chromatography (Petroleum ether/EtOAc = 3:1) on silica gel to provide the title compound as a colorless oil in 73% yield (39.2 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30–7.24 (m, 5H), 7.21–7.17 (m, 3H), 6.98–6.88 (m, 2H), 5.69 (t, *J* = 6.4 Hz, 1H), 4.61 (d, *J* = 6.4 Hz, 2H), 4.22 (s, 2H), 2.83–2.78 (m, 2H), 2.53–2.48 (m, 2H), 1.56 (brs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.4, 143.8, 141.6, 129.5, 128.5, 128.4, 126.0, 133.3, 121.0, 114.8, 64.0, 61.0, 37.0, 34.6; HRMS (ESI-MS): Calcd. for $C_{18}H_{20}O_2$ (M + Na): 291.1361, Found: 291.1368.



3pa

(*Z*)-2-(2-(benzyloxy)ethyl)-4-phenoxybut-2-en-1-ol (3pa) was prepared according to the general procedure from **1q** and **2a**. The crude product was purified by flash column chromatography (Petroleum ether/EtOAc = 3:1) on silica gel to provide the title compound as a colorless oil in 78% yield (46.6 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37–7.25 (m, 8H), 6.97–6.89 (m, 2H), 5.68 (t, *J* = 6.4 Hz, 1H), 4.60 (d, *J* = 6.4 Hz, 2H), 4.19 (s, 2H), 3.64 (t, *J* = 6.4 Hz, 2H), 2.50 (t, *J* = 6.4 Hz, 2H), 1.63 (brs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.5, 142.2, 137.5, 129.5, 128.5, 128.9, 127.8, 124.5, 120.9, 114.7, 73.3, 70.4, 63.9, 60.8, 36.1; HRMS (ESI-MS): Calcd. for $C_{18}H_{20}O_3$ (M + Na): 307.1310, Found: 307.1316.

References:

1. (a) A. Khan, R. Zheng, Y. Kan, J. Ye, J. Xing, Y. J. Zhang, *Angew. Chem. Int. Ed*. **2014**, *53*, 6439; (b) A. Khan, L. Yang, J. Xu, L. Y. Jin, Y. J. Zhang, *Angew. Chem. Int. Ed*. **2014**, *53*, 11257.

2. J. Xie, W. Guo, A. Cai, E. C. Escudero-Adán and A. W. Kleij, *Org. Lett*. **2017**, *19*, 6388.

TEM study of PdNPs for the coupling reaction of **1a** with **2a**.

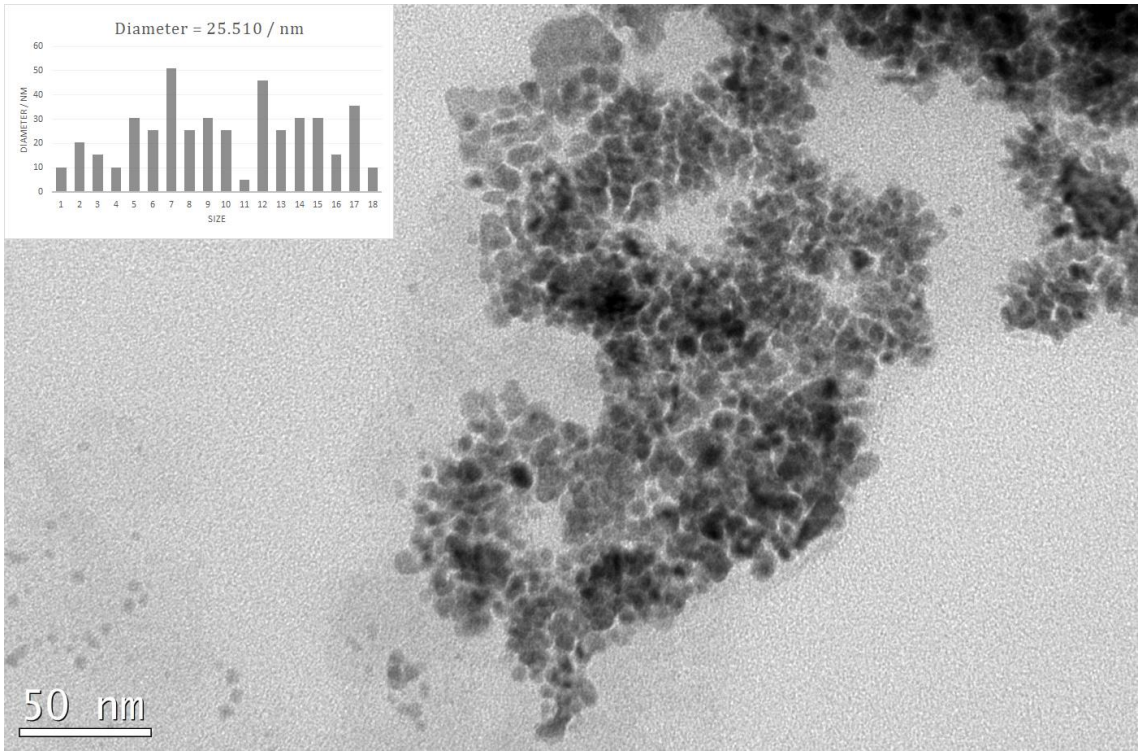


Figure S1. TEM image. A sample taken after 30 minutes.

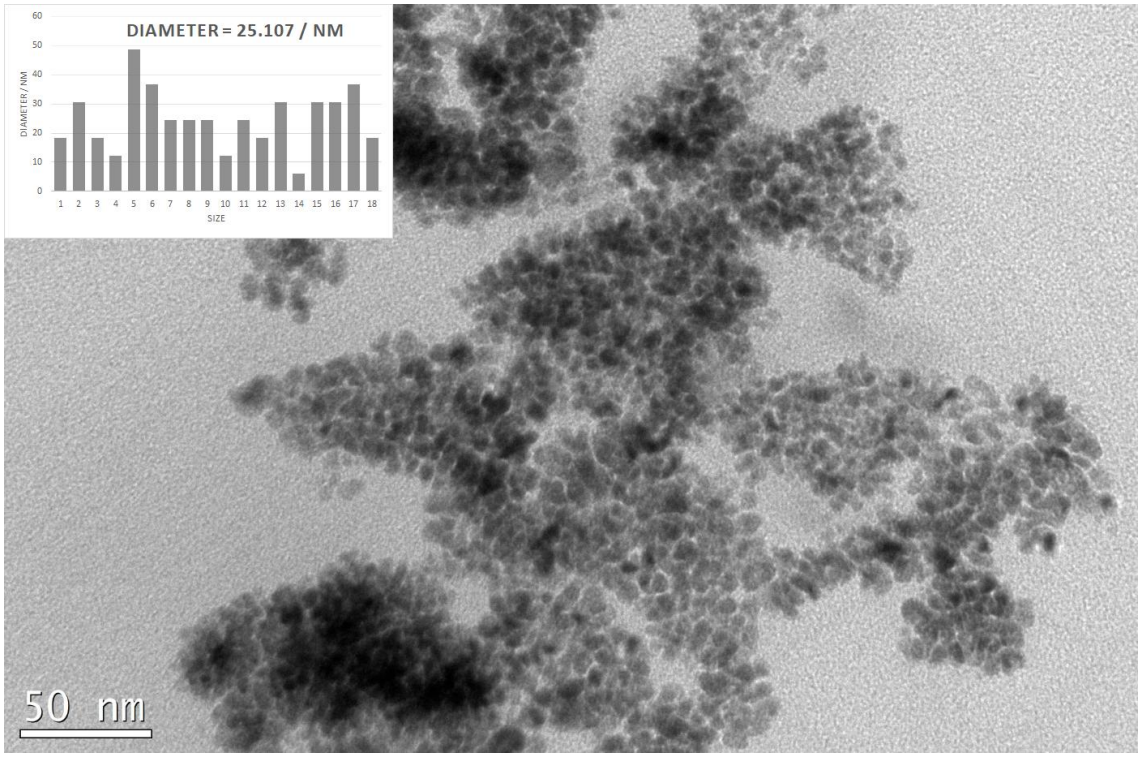


Figure S2. TEM image. A sample taken after 15 hours of the reaction mixture.

TEM study of PdNPs for the coupling reaction of **1a** with **2a** after recycling experiments.

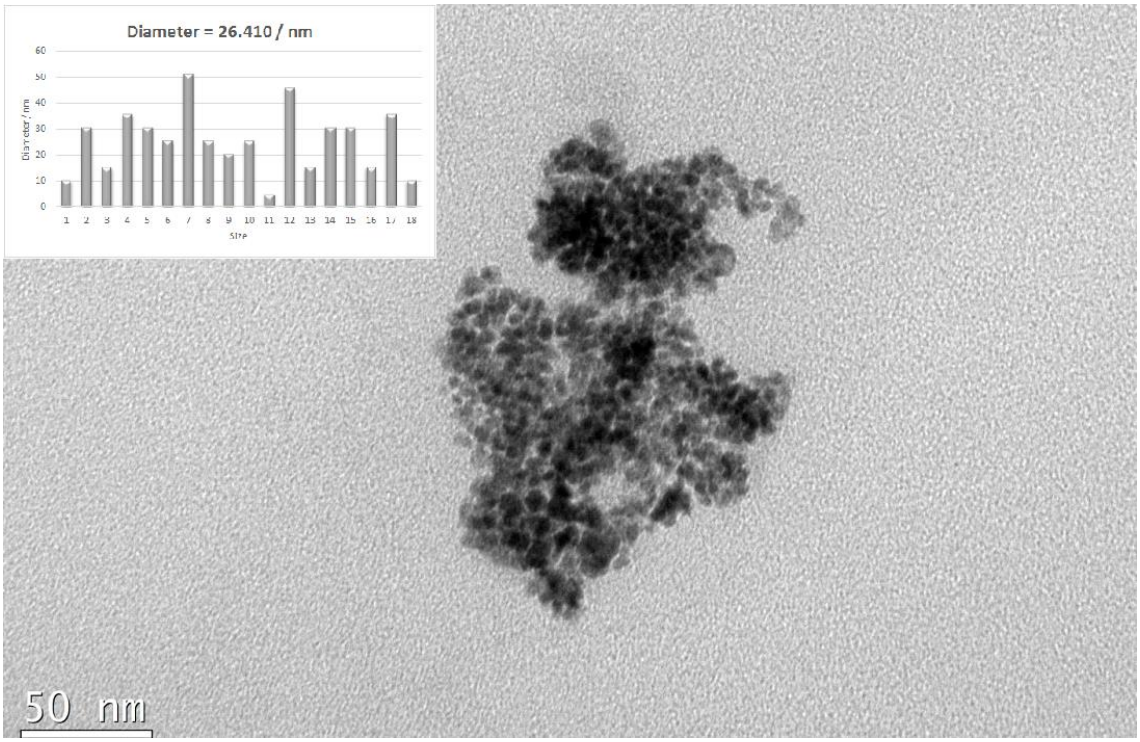


Figure S3. TEM image. A sample taken after third cycle of the reaction mixture.

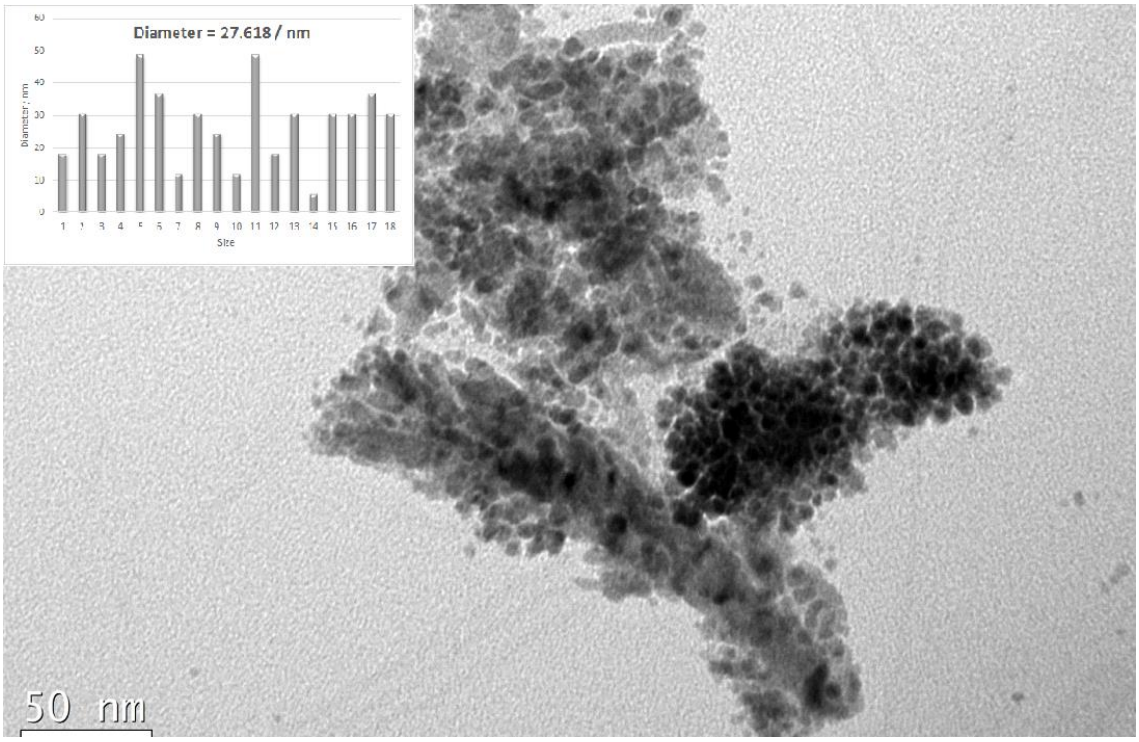


Figure S4. TEM image. A sample taken after fifth cycle of the reaction mixture.

Kinetic Curves for recycling study and hot filtration test experiments.

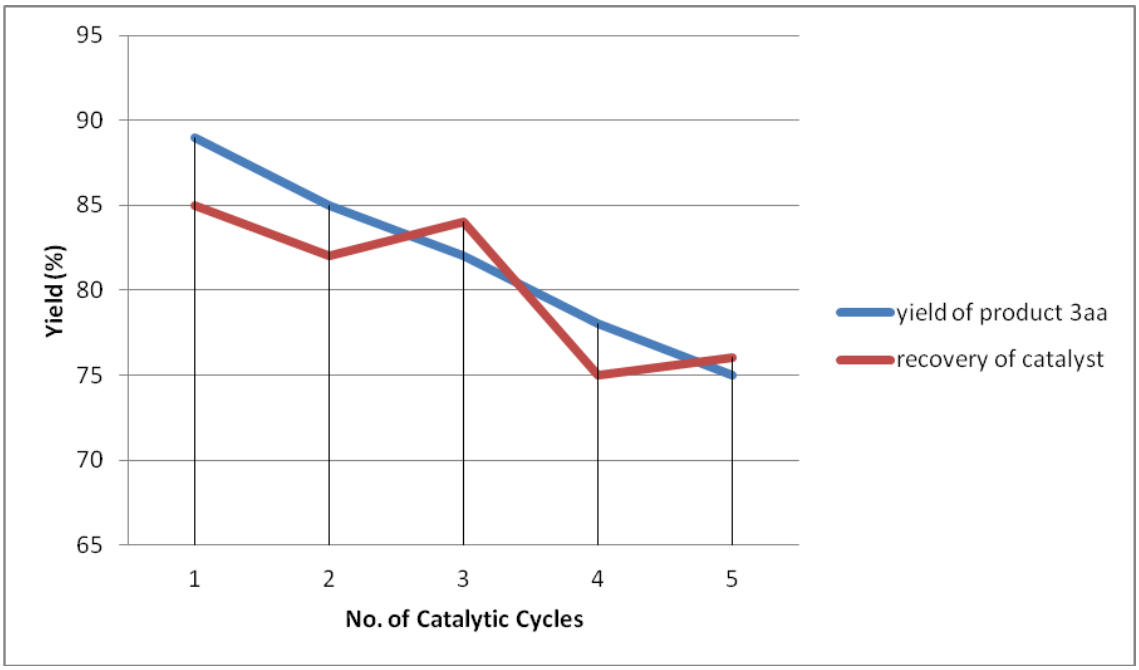


Figure S5. Kinetic curve for PdNPs recovery cycle and effect on the yields.

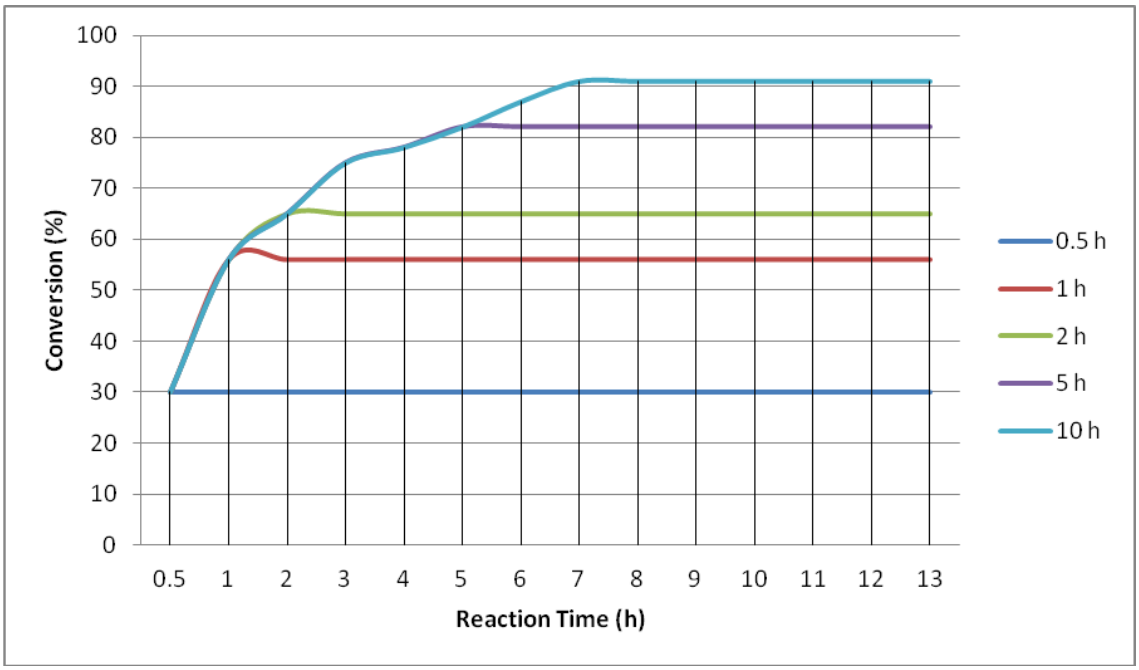
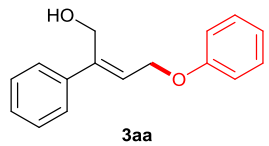
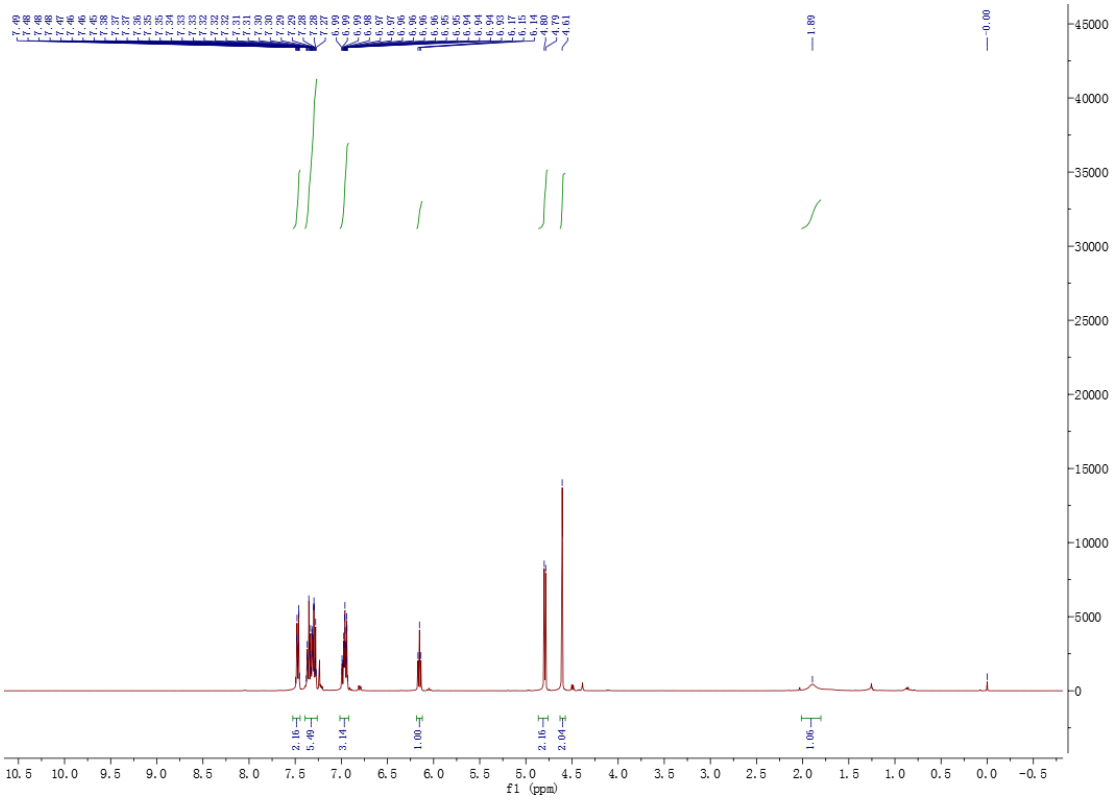


Figure S6. Kinetic curve for the effect of hot filtration on the yields of reaction.


HO
O

3aa


7.49
7.48
7.48
7.48
7.47
7.46
7.46
7.45
7.38
7.37
7.37
7.36
7.35
7.34
7.33
7.32
7.32
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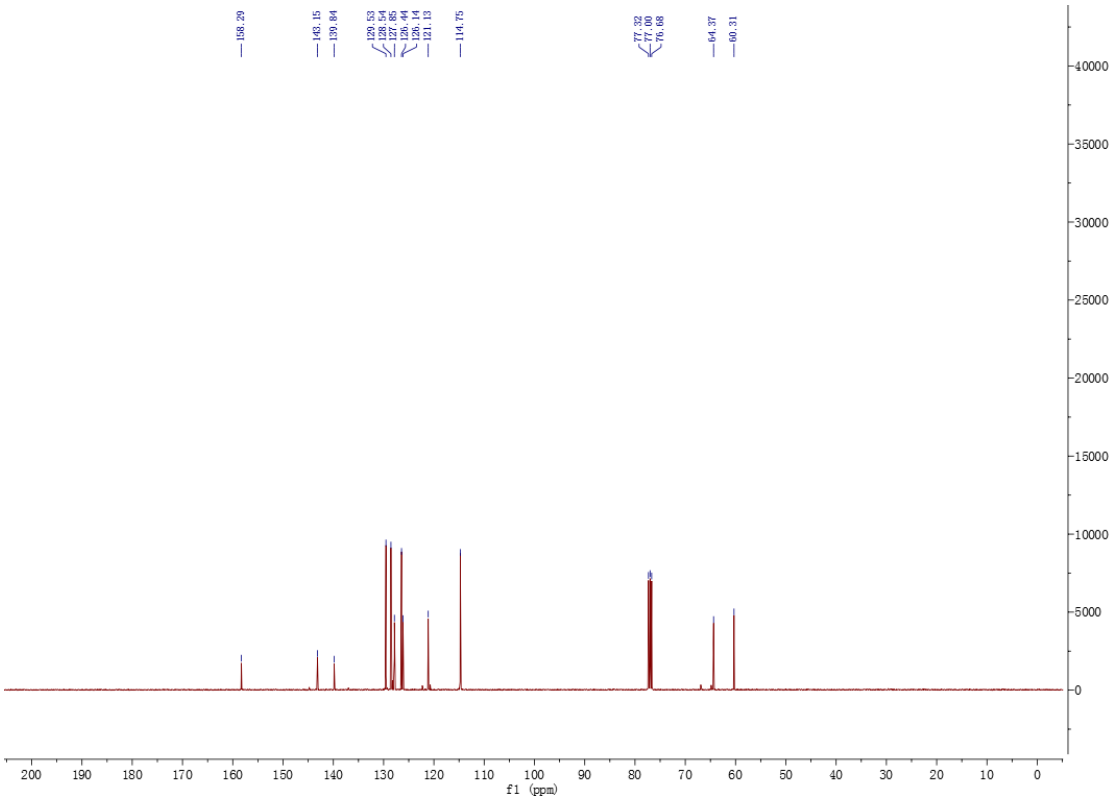
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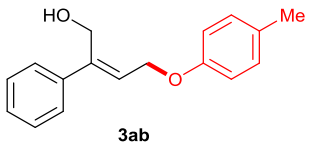
60.31
f1 (ppm)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Me
O

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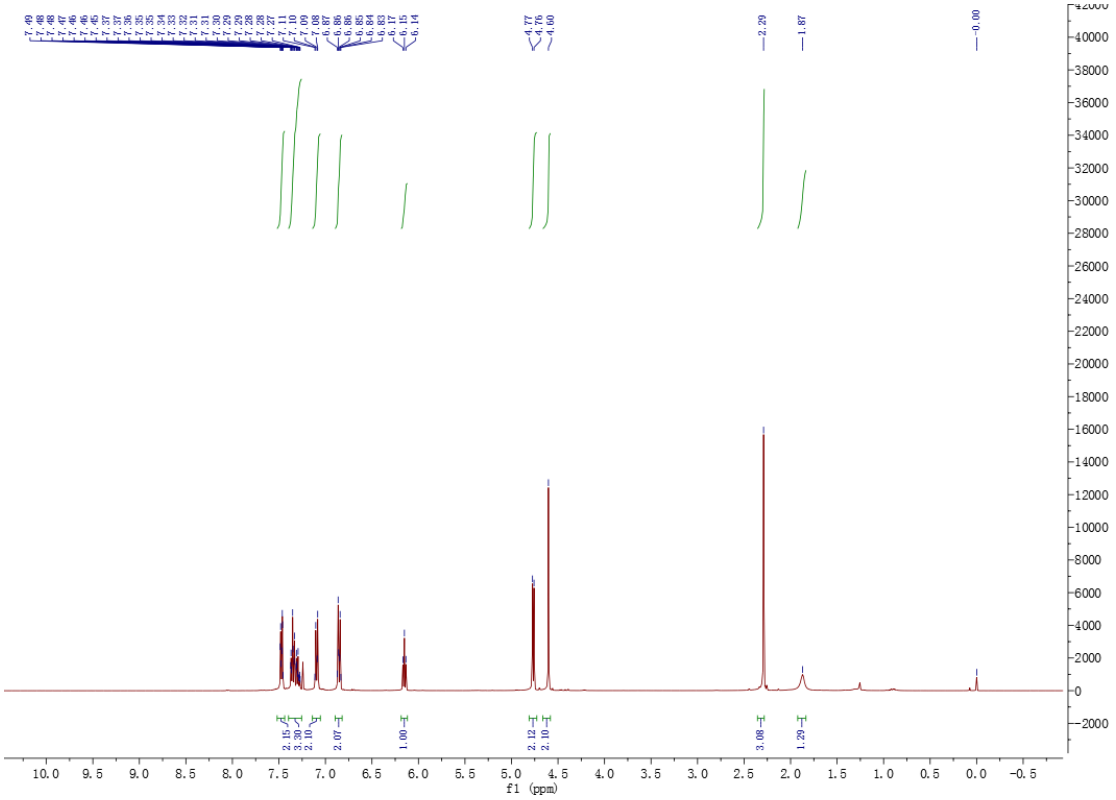
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7.28
7.27
7.11
7.10
7.09
7.08
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6.86
6.85
6.84
6.83
6.17
6.15
6.14
4.77
4.76
4.60
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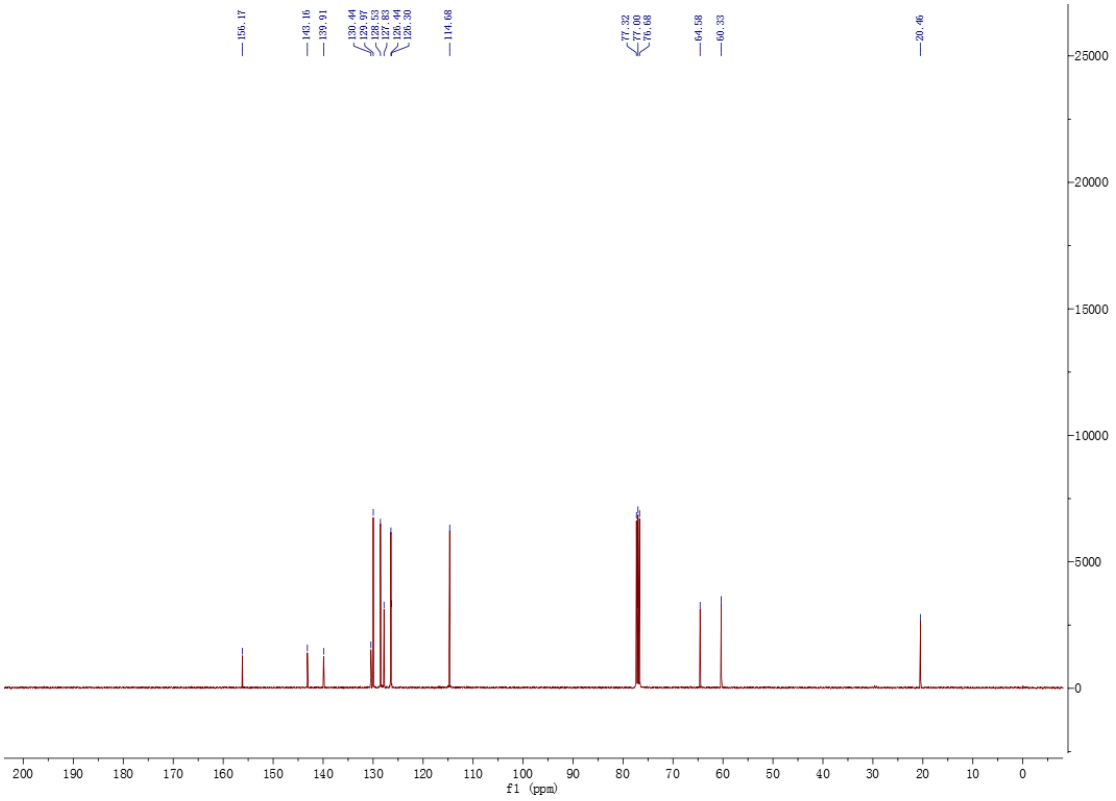
1.29
f1 (ppm)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77.32
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76.68
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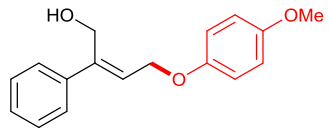
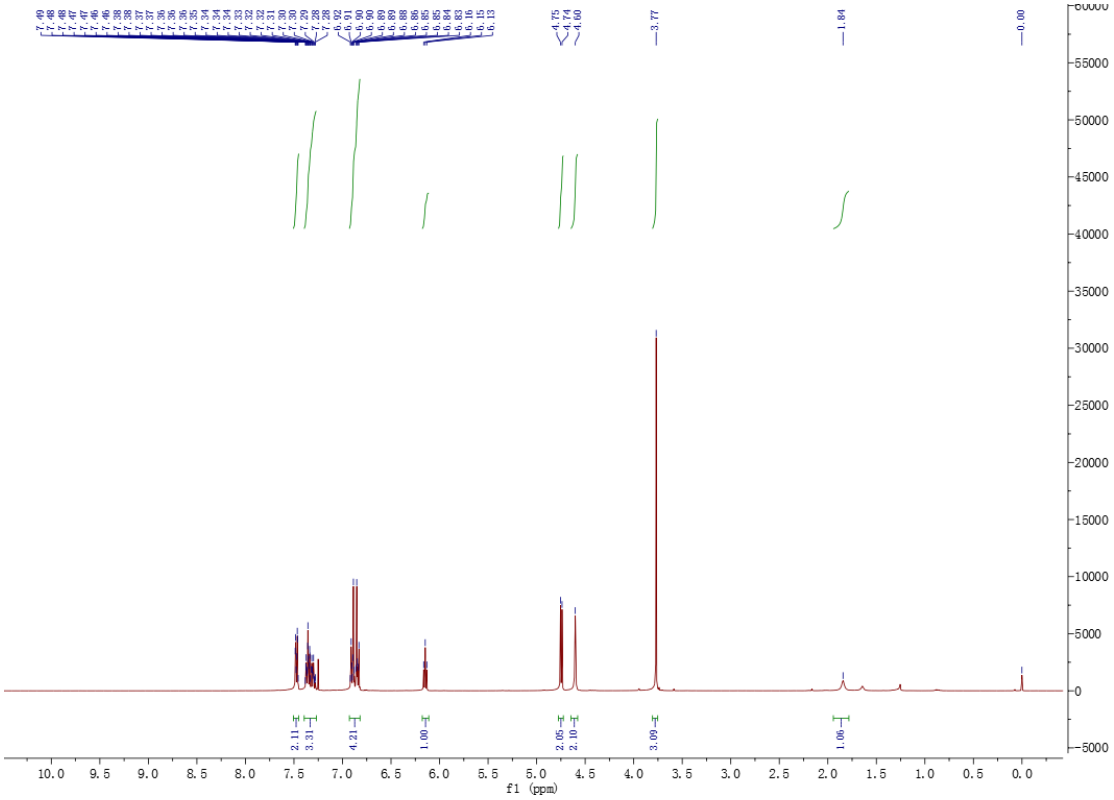
20.46
f1 (ppm)


HO
OMe
O

3ac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7.34
7.34
7.34
7.33
7.32
7.31
7.30
7.30
7.29
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6.91
6.90
6.90
6.89
6.89
6.88
6.86
6.85
6.85
6.84
6.83
6.16
6.15
6.13
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4.60
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2.10
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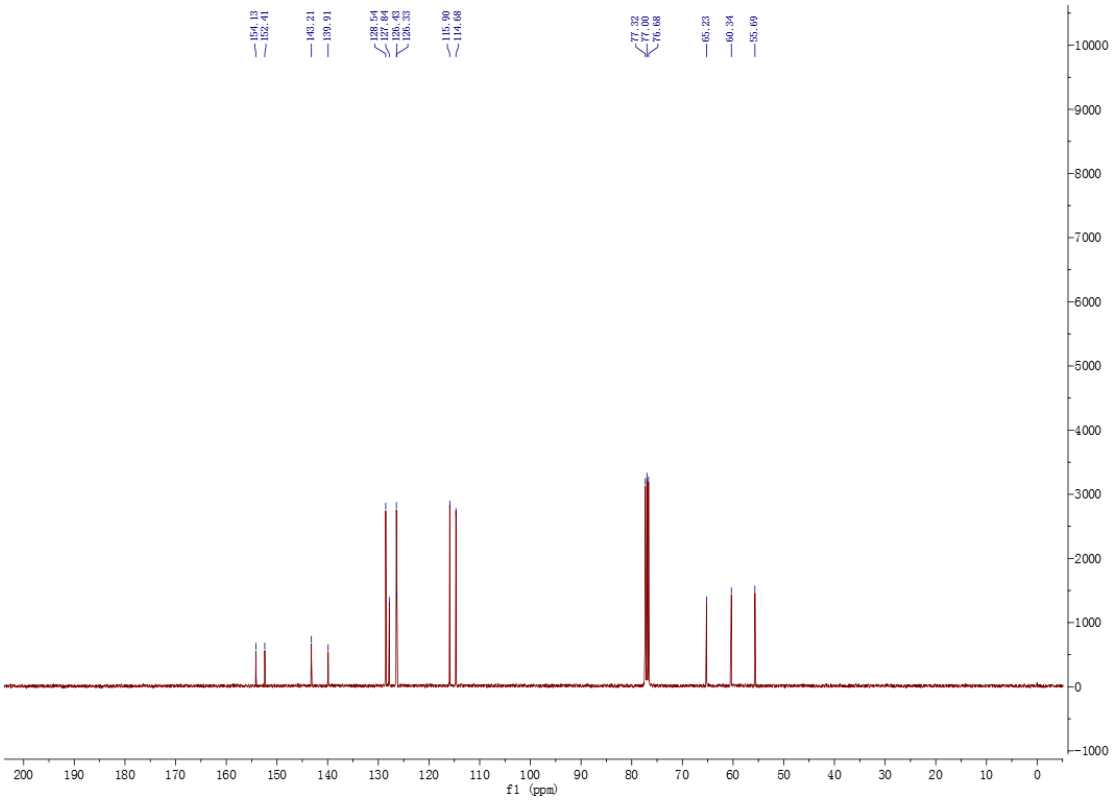
1.06
f1 (ppm)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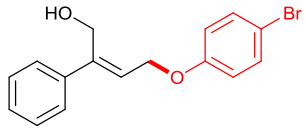
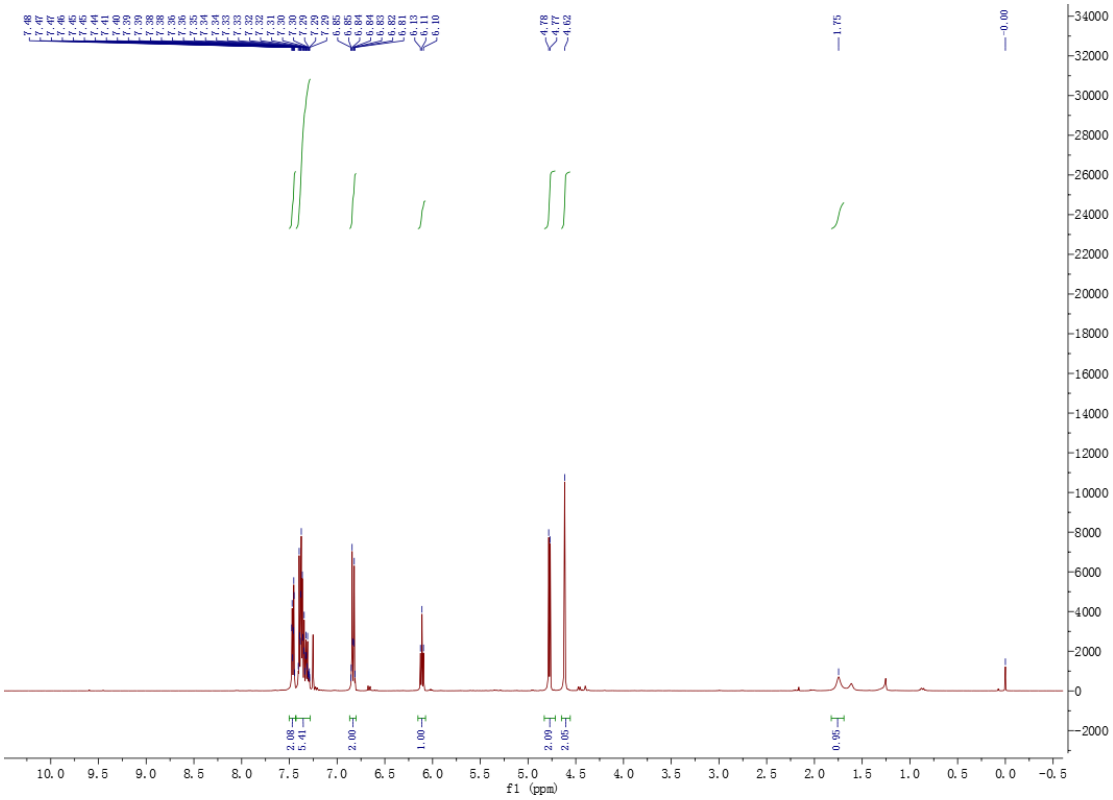
55.69
f1 (ppm)


HO
Br
O

3ad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7.33
7.32
7.31
7.30
7.29
7.29
6.85
6.84
6.83
6.82
6.81
6.13
6.11
6.10
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4.62
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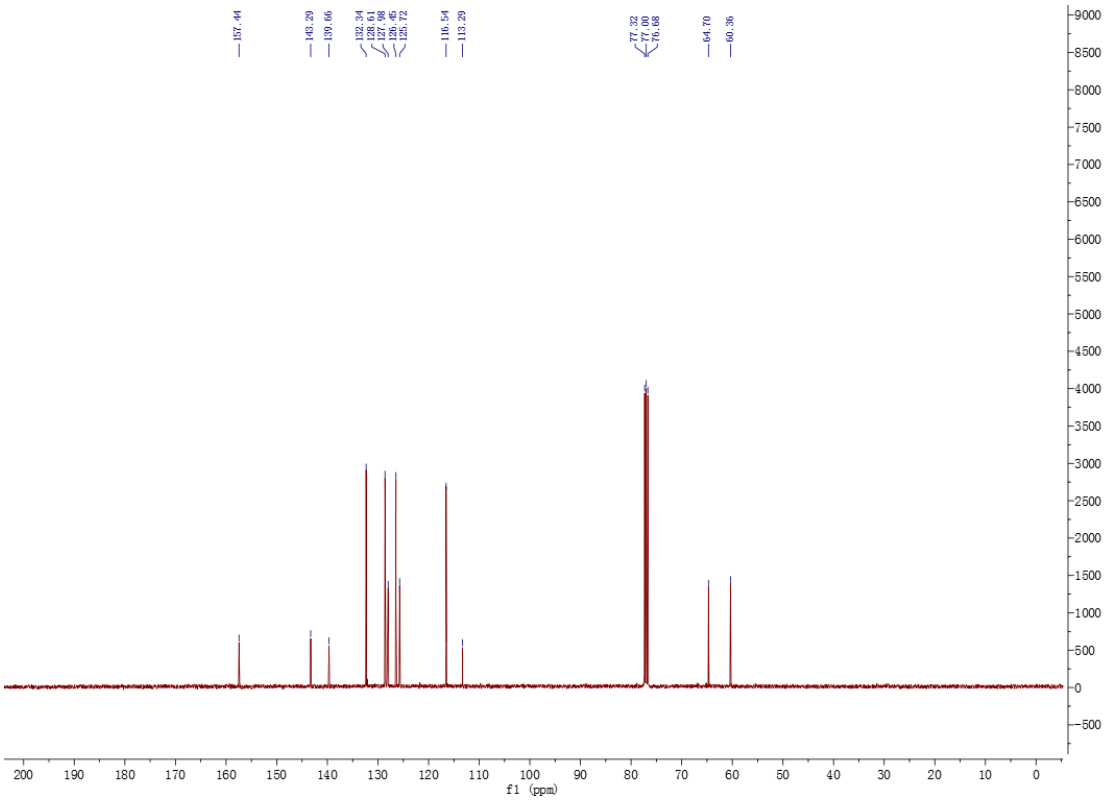
5.41
2.00
1.00
2.09
2.05
0.95
f1 (ppm)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113.29
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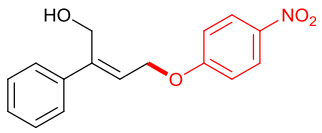
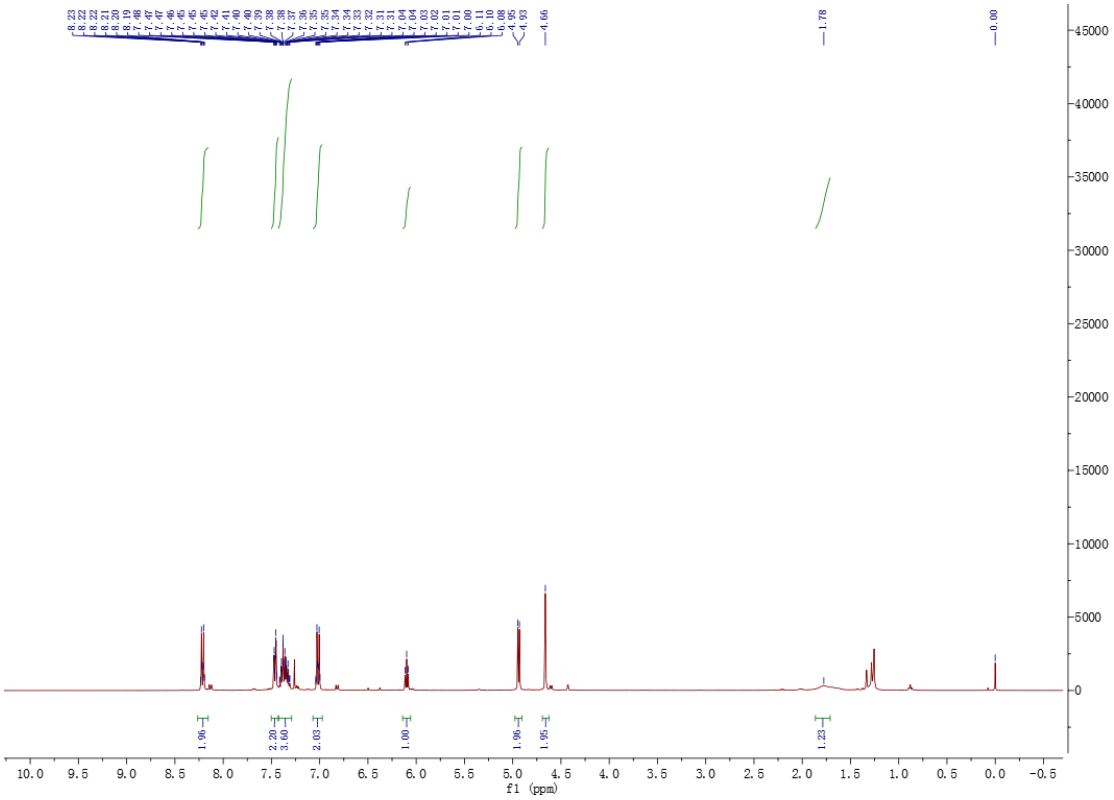
76.68
64.70
60.36
f1 (ppm)


HO
NO2
O

3ae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7.37
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7.31
7.04
7.04
7.03
7.02
7.01
7.01
7.00
6.11
6.10
6.08
4.95
4.93
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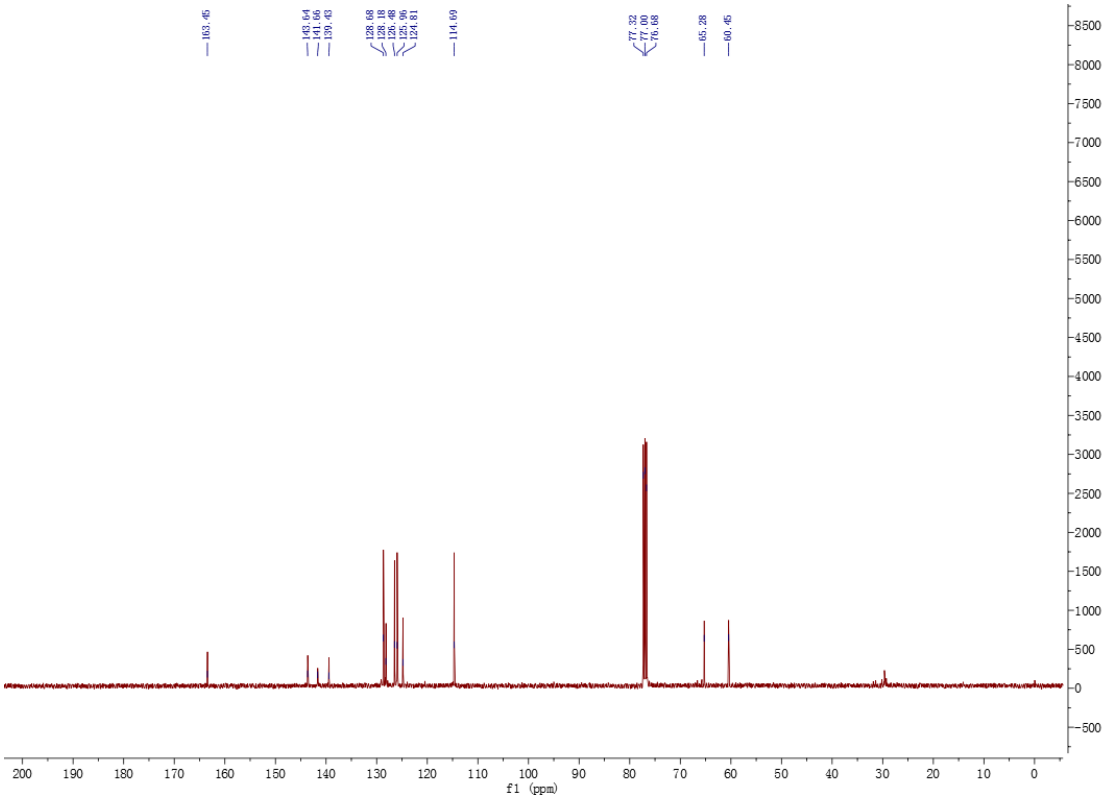
3.60
2.03
1.00
1.96
1.95
1.23
f1 (ppm)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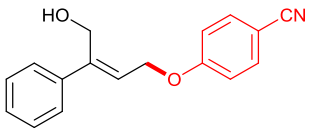
124.81
114.69
77.32
77.00
76.68
65.28
60.45
f1 (ppm)



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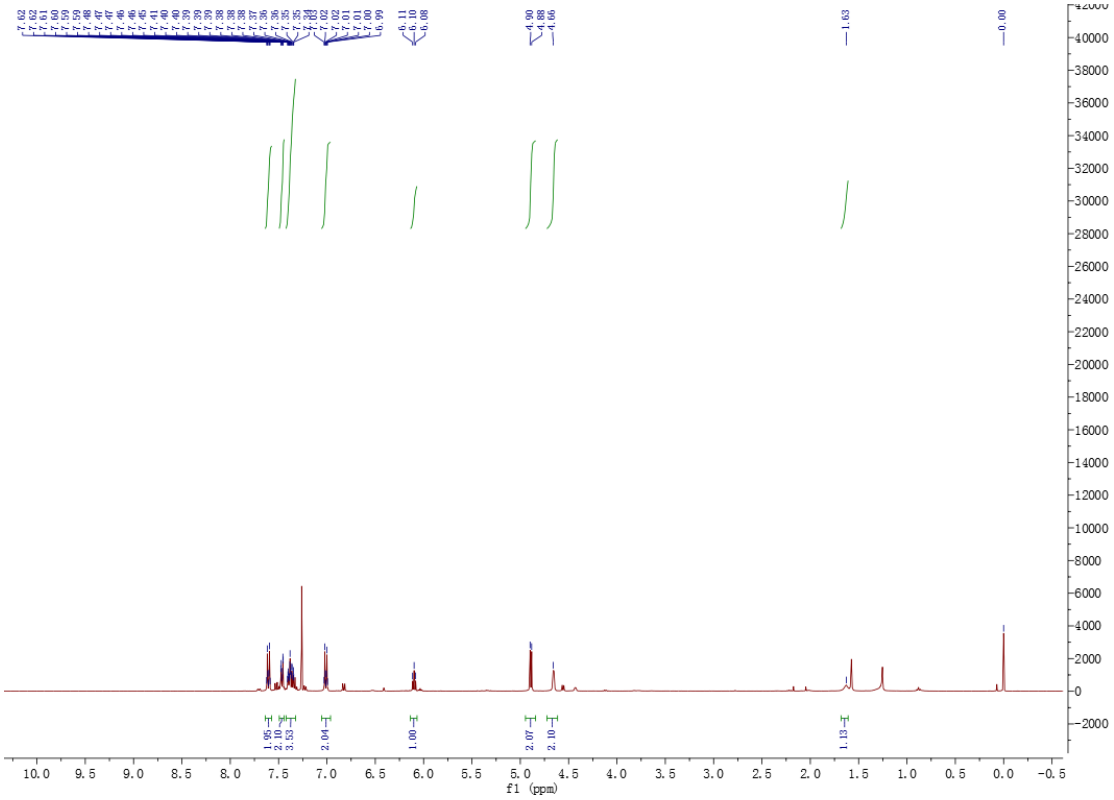

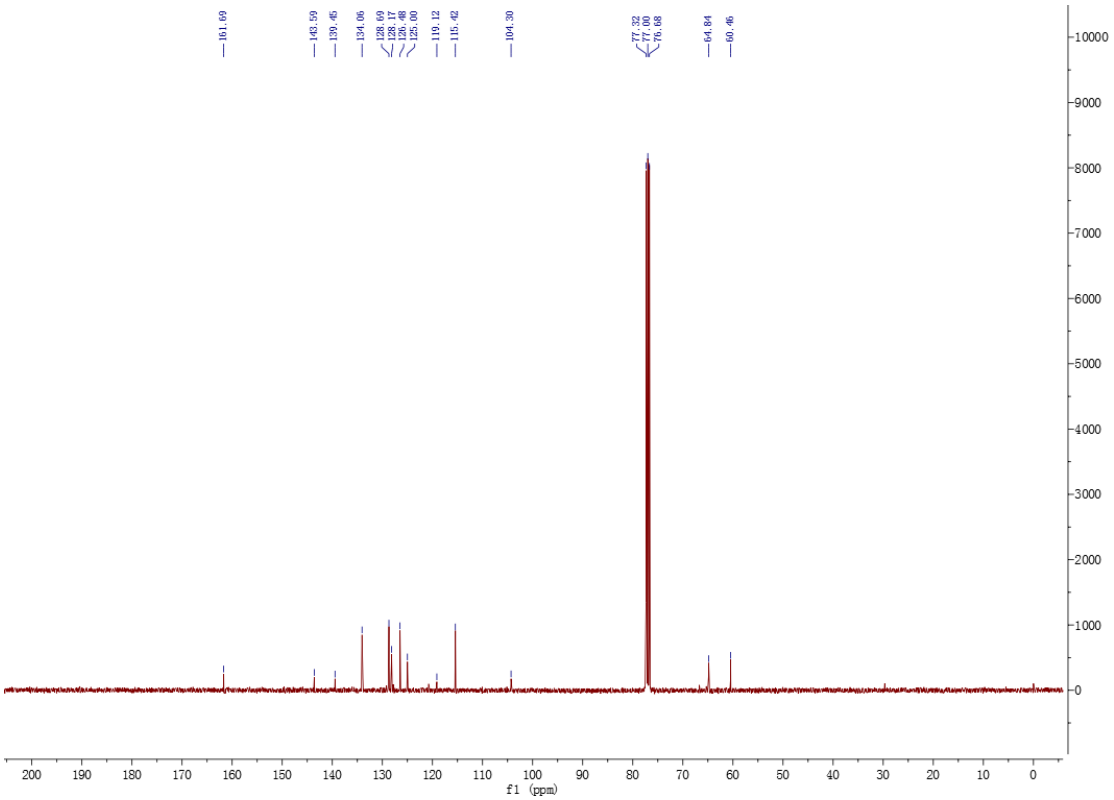

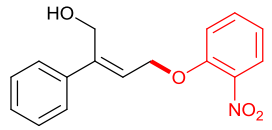

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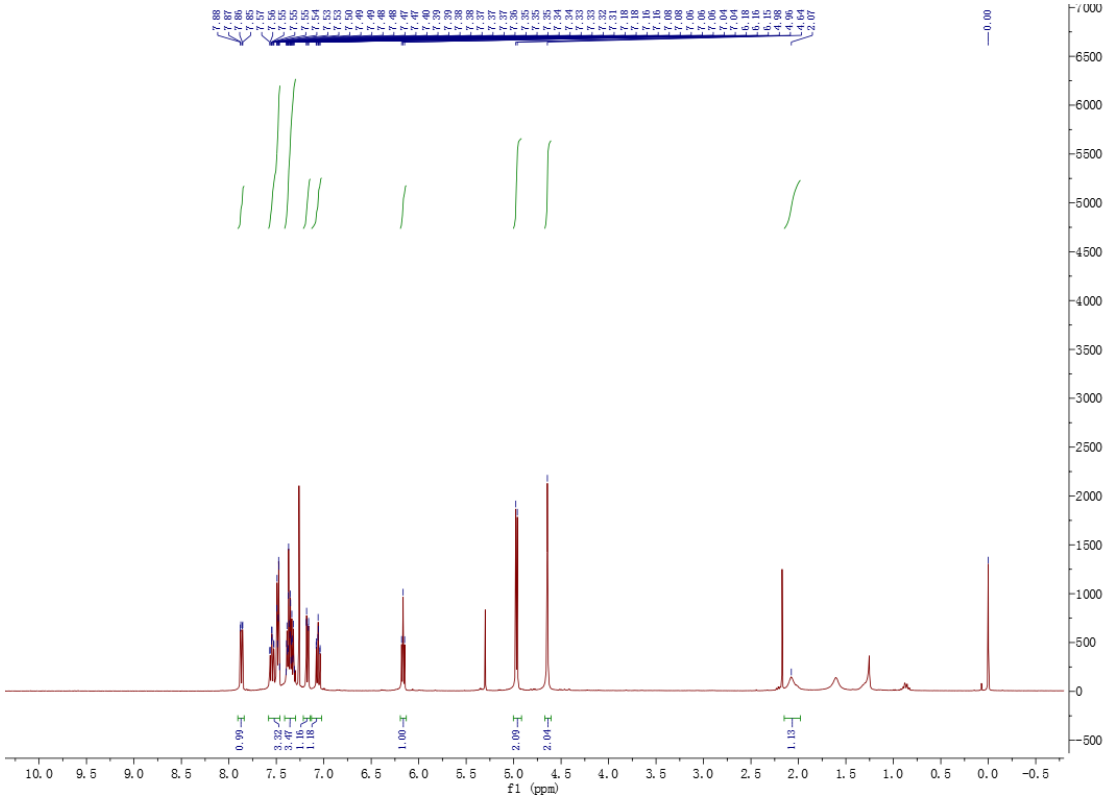

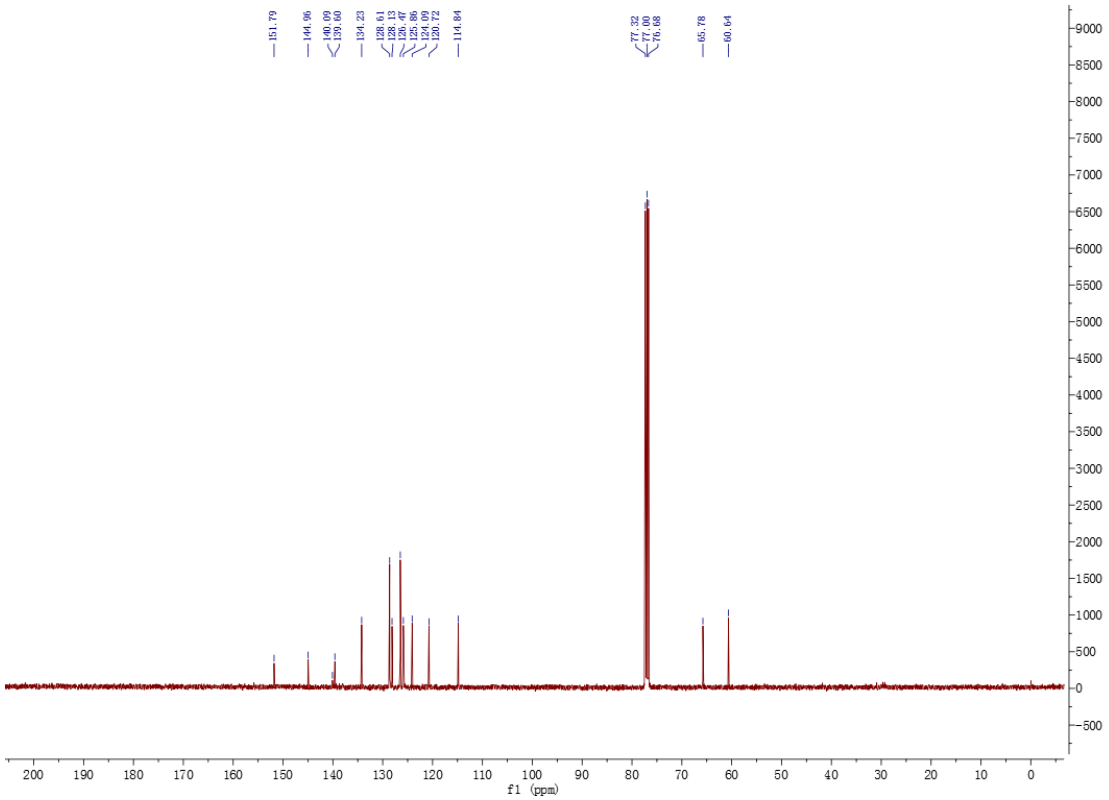

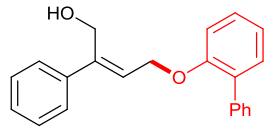

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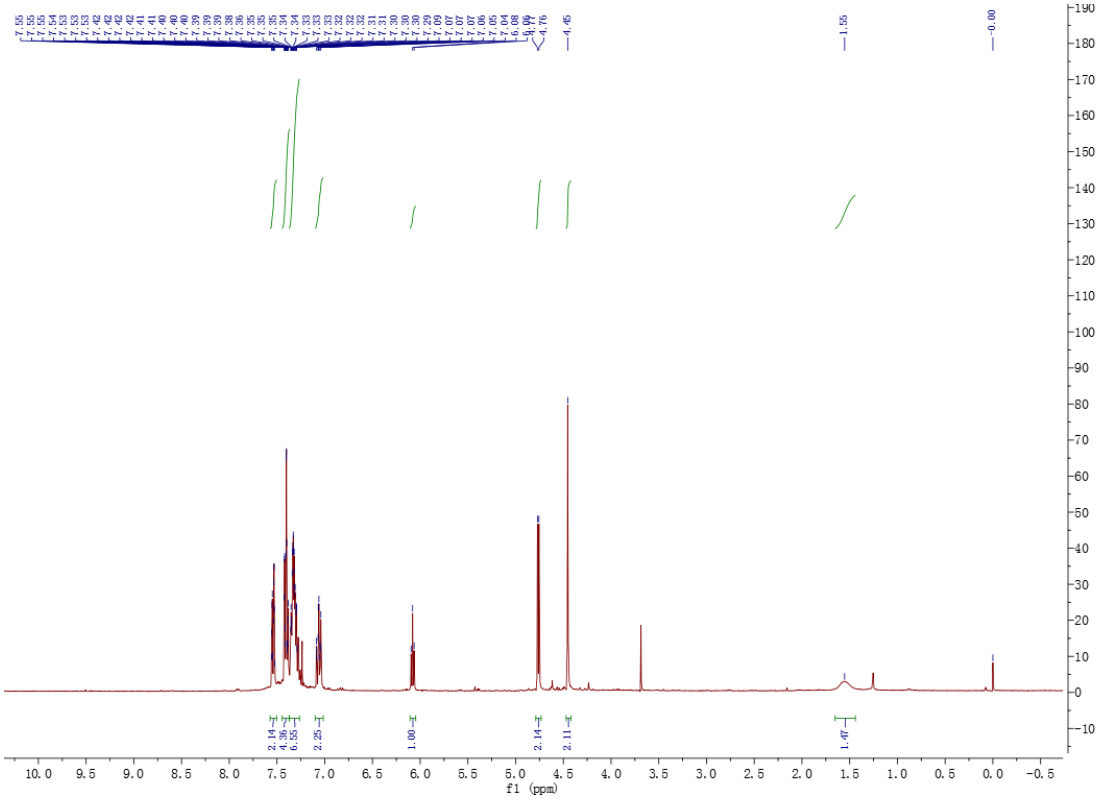
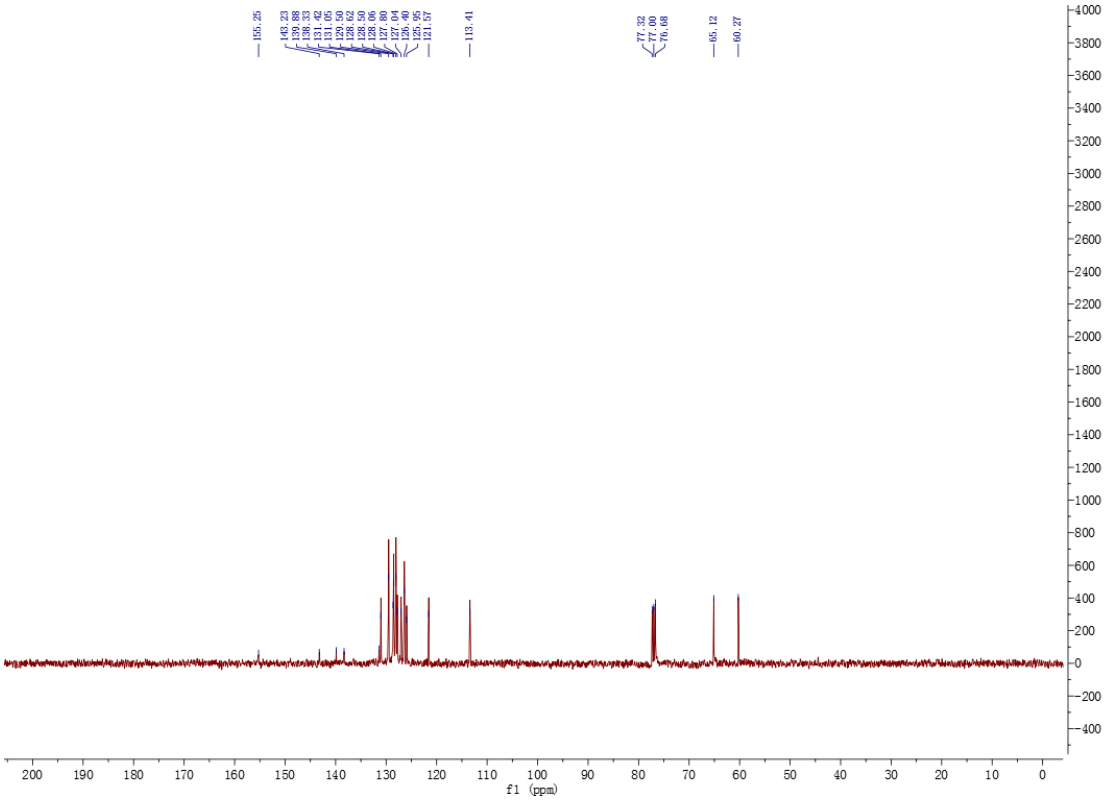
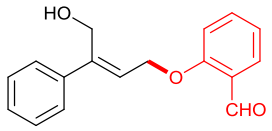
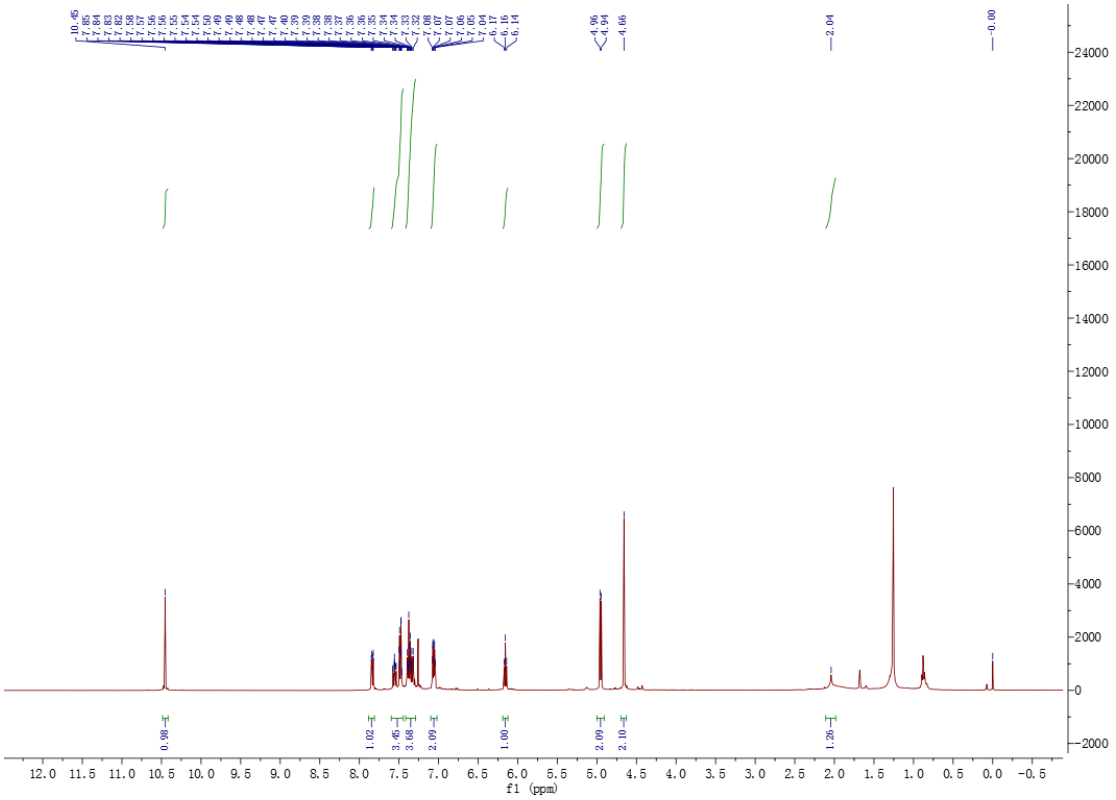





HO
O
CHO

3ai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7.38
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7.36
7.35
7.34
7.34
7.33
7.08
7.07
7.07
7.06
7.05
7.04
6.17
6.16
6.14
4.96
4.94
4.66
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3.68
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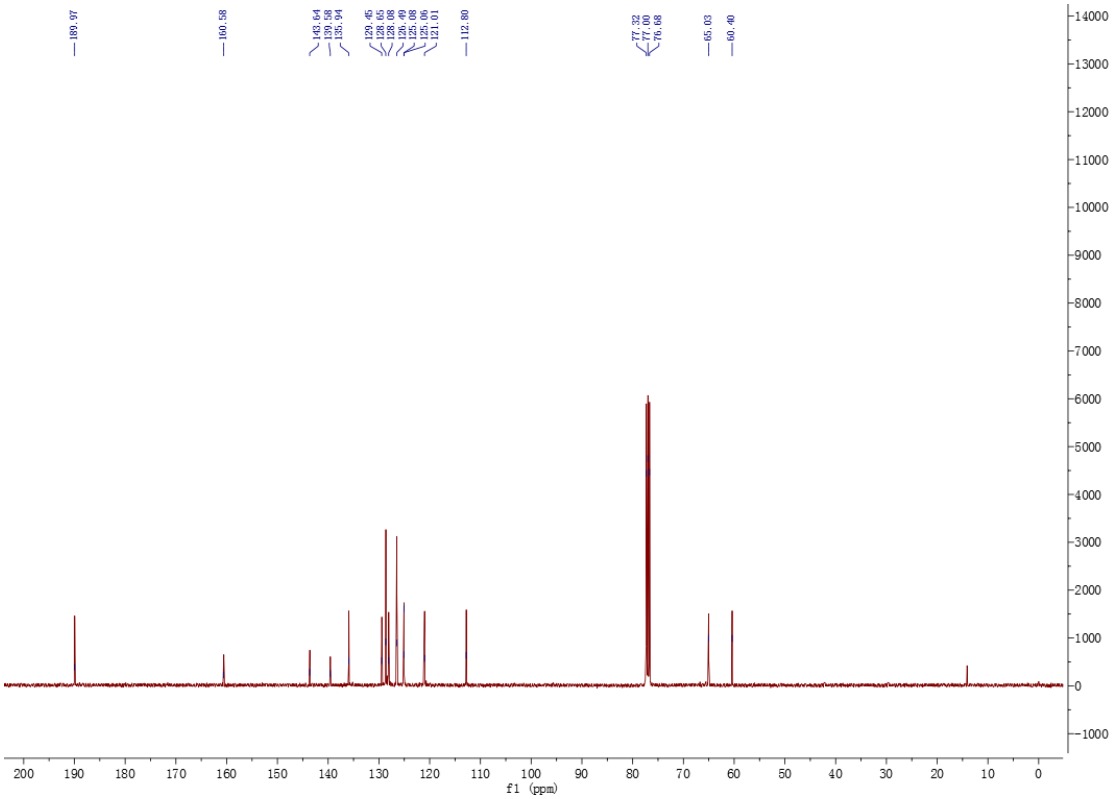
1.00
2.09
2.10
1.26
f1 (ppm)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76.68
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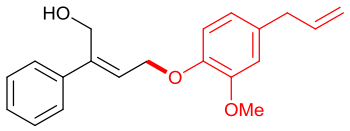
60.40
f1 (ppm)



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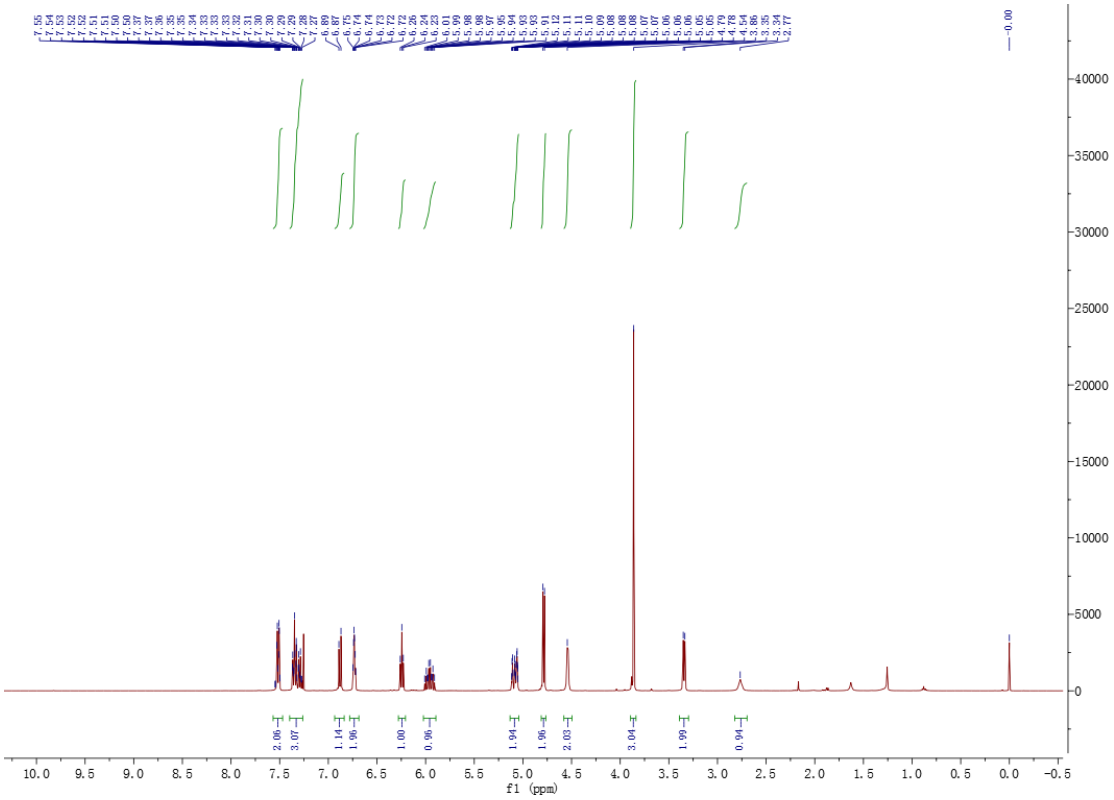
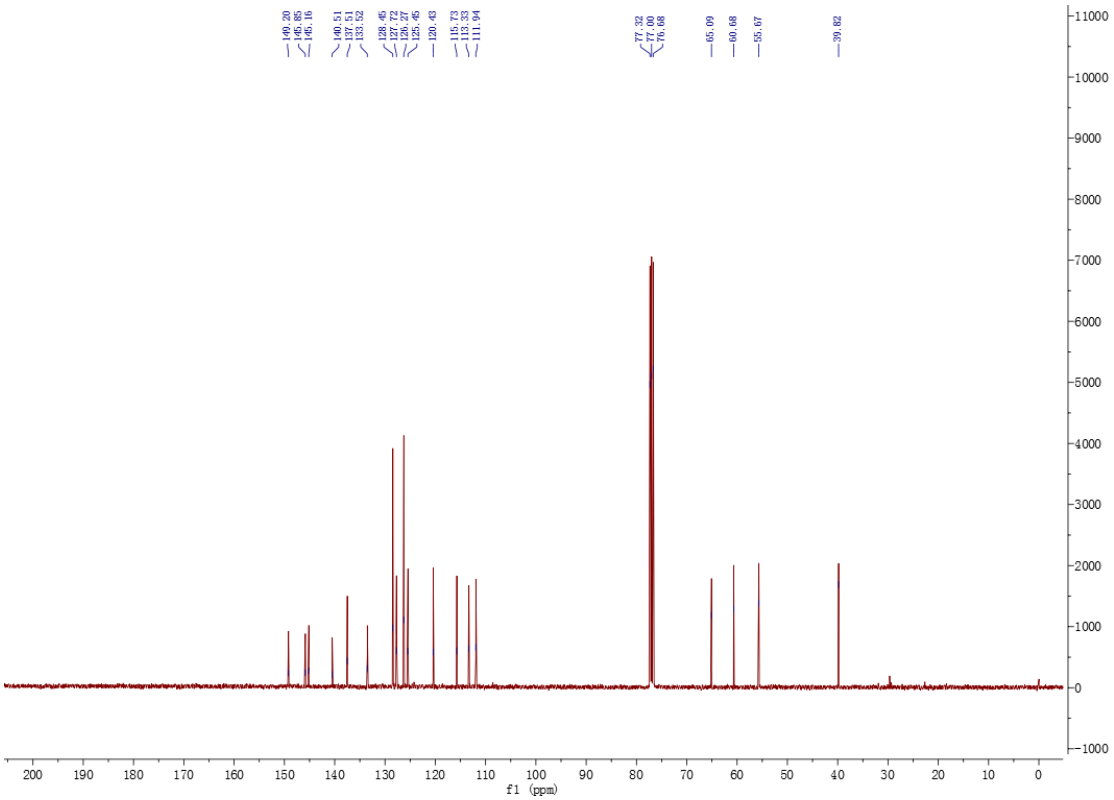
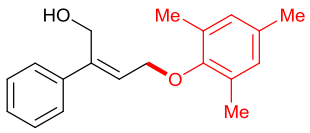
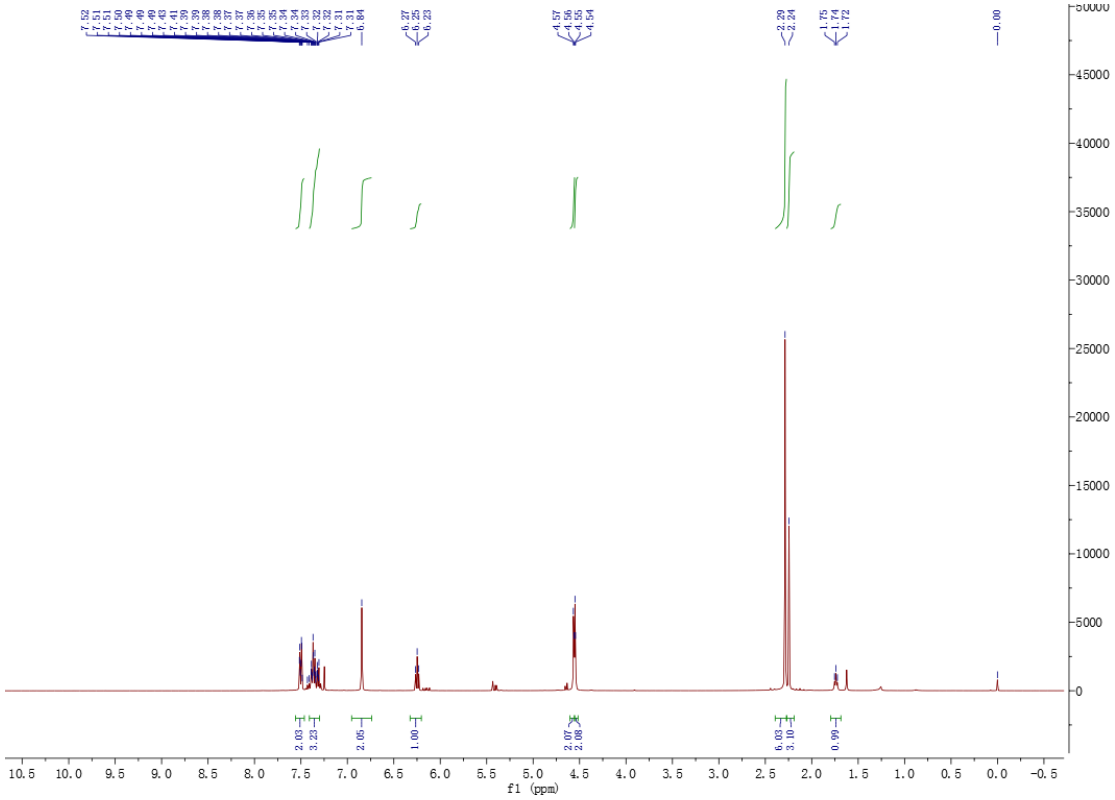





HO
Me
Me
O
Me

3ak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1.74
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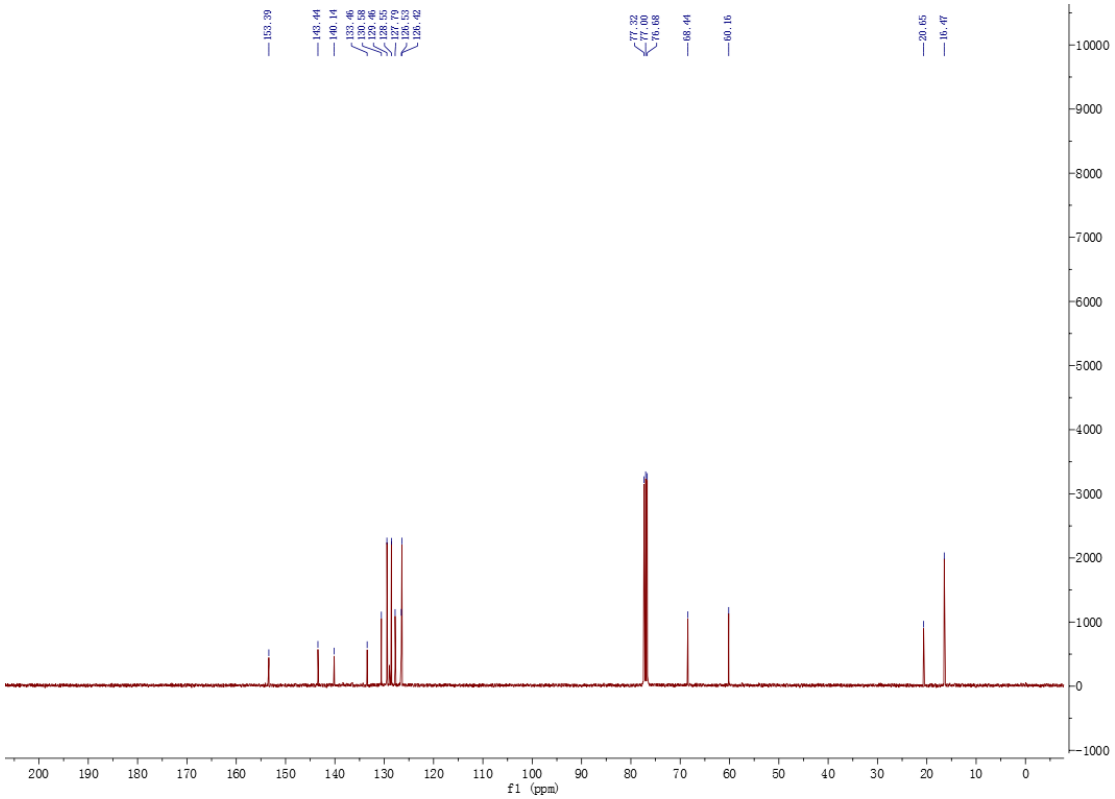
2.08
6.03
3.10
0.99
f1 (ppm)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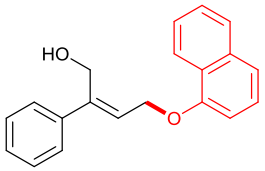
16.47
f1 (ppm)



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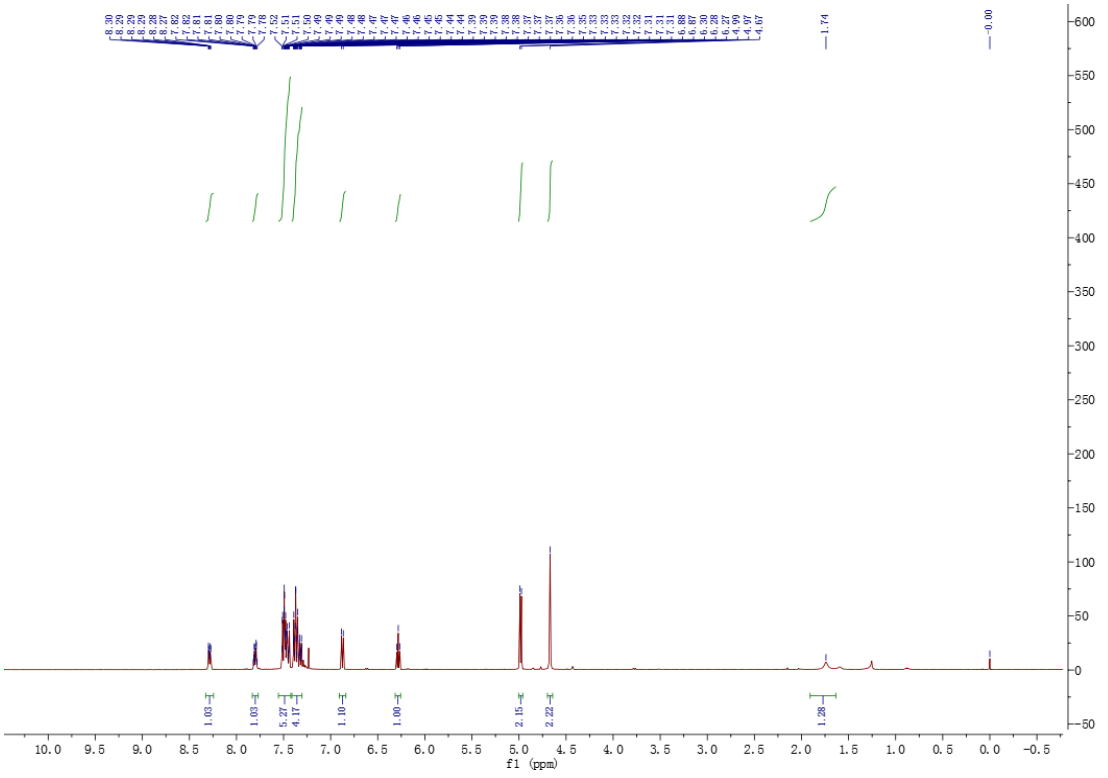
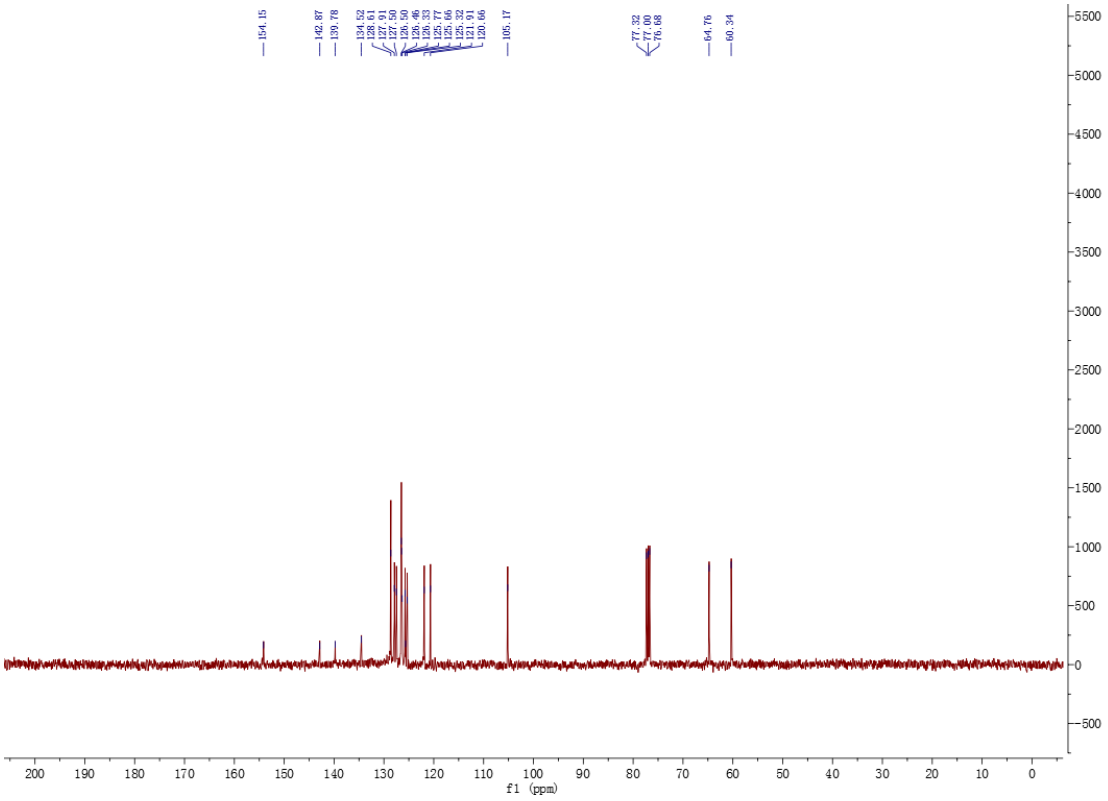
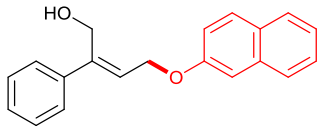
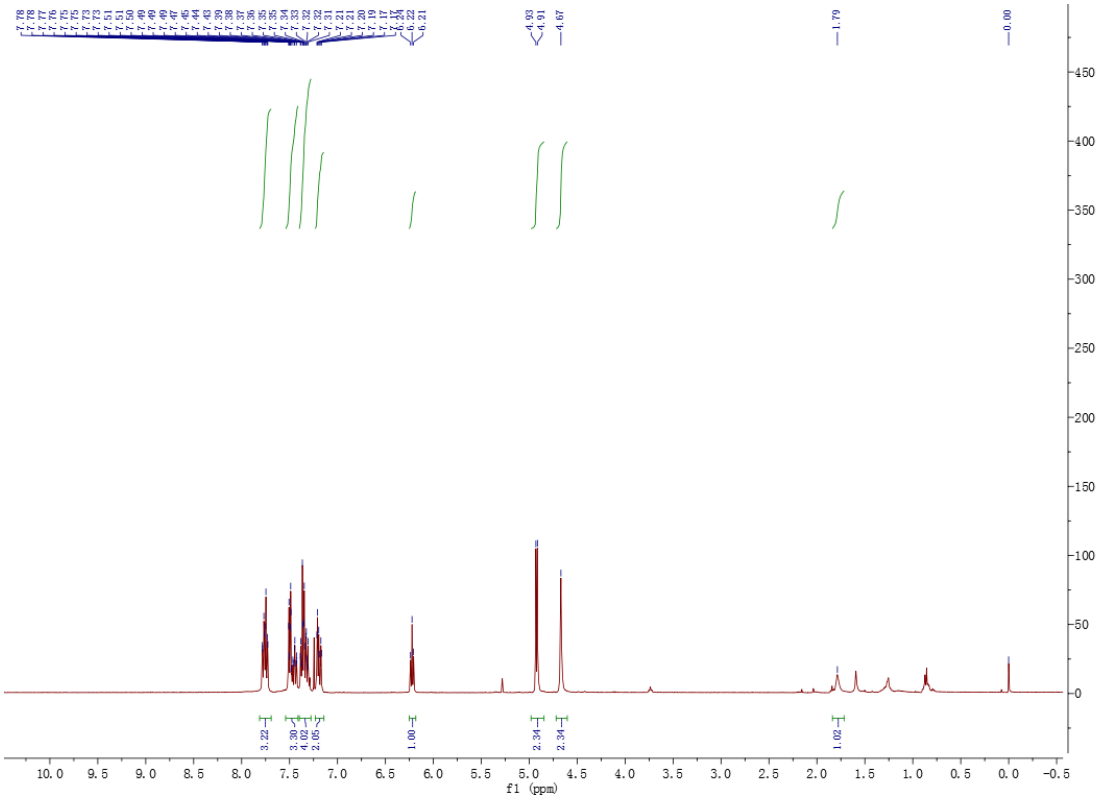





HO
O

3am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7.19
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6.21
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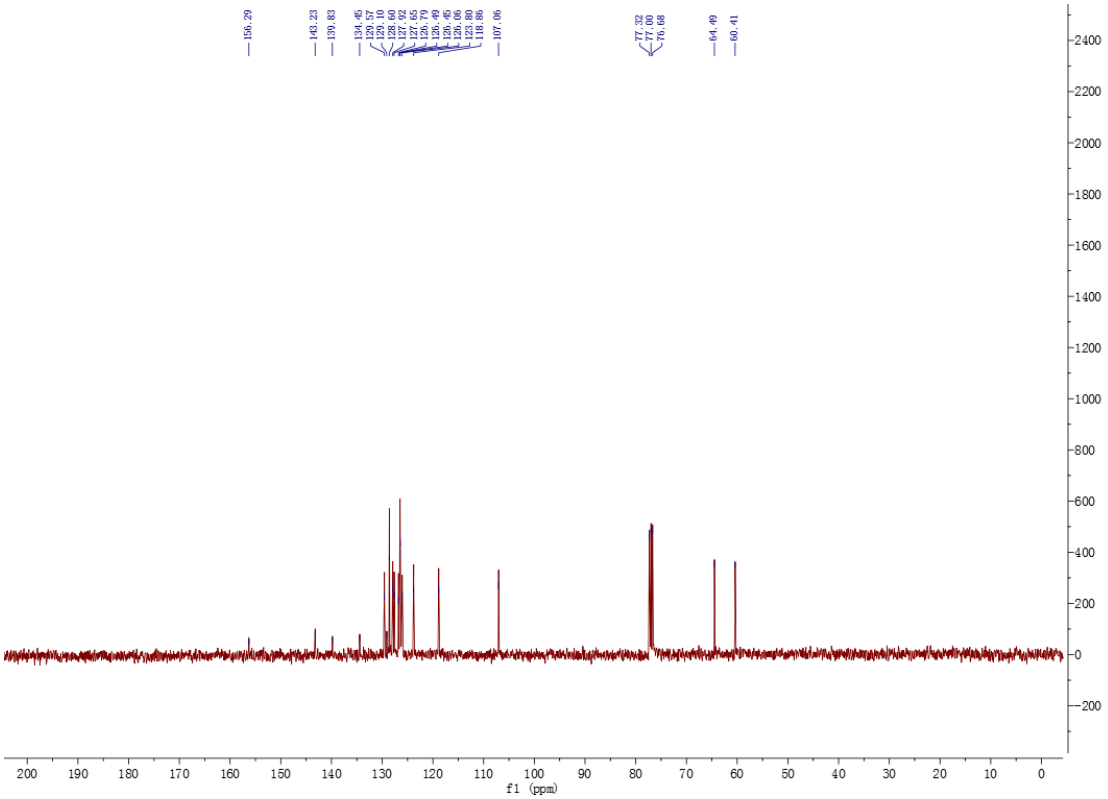
1.00
2.34
2.34
1.02
f1 (ppm)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126.79
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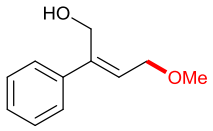
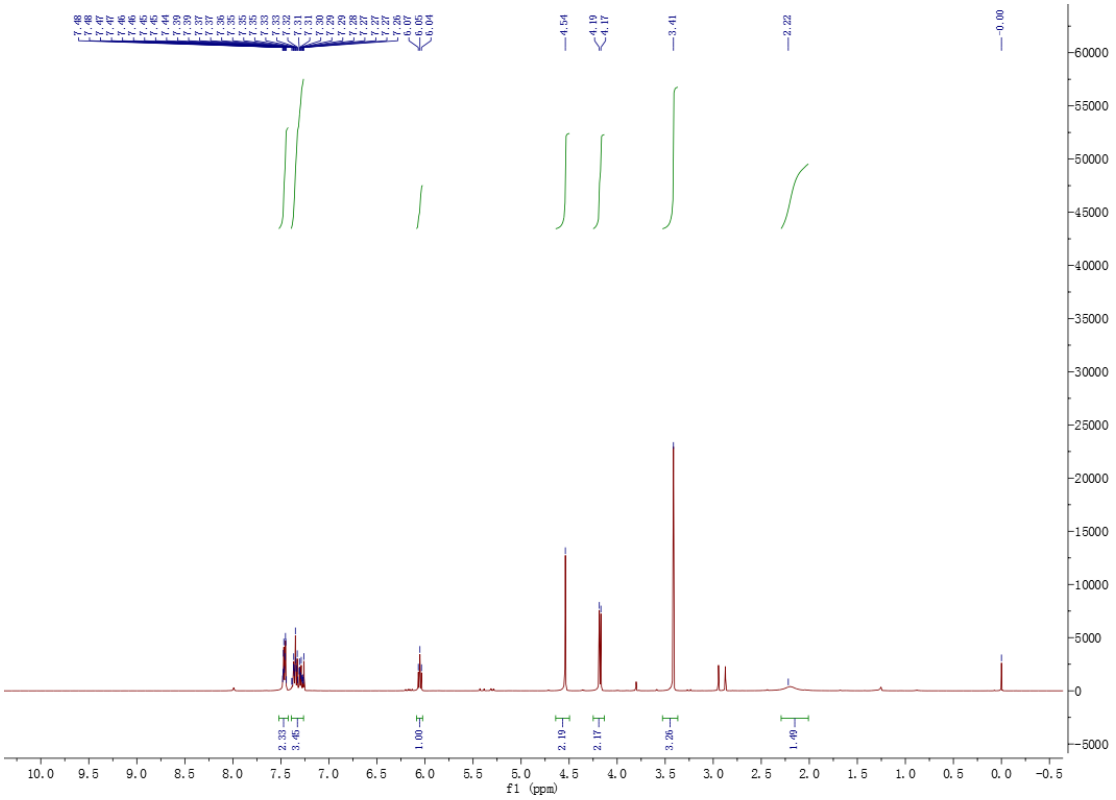
60.41
f1 (ppm)


HO
OMe

3an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7.29
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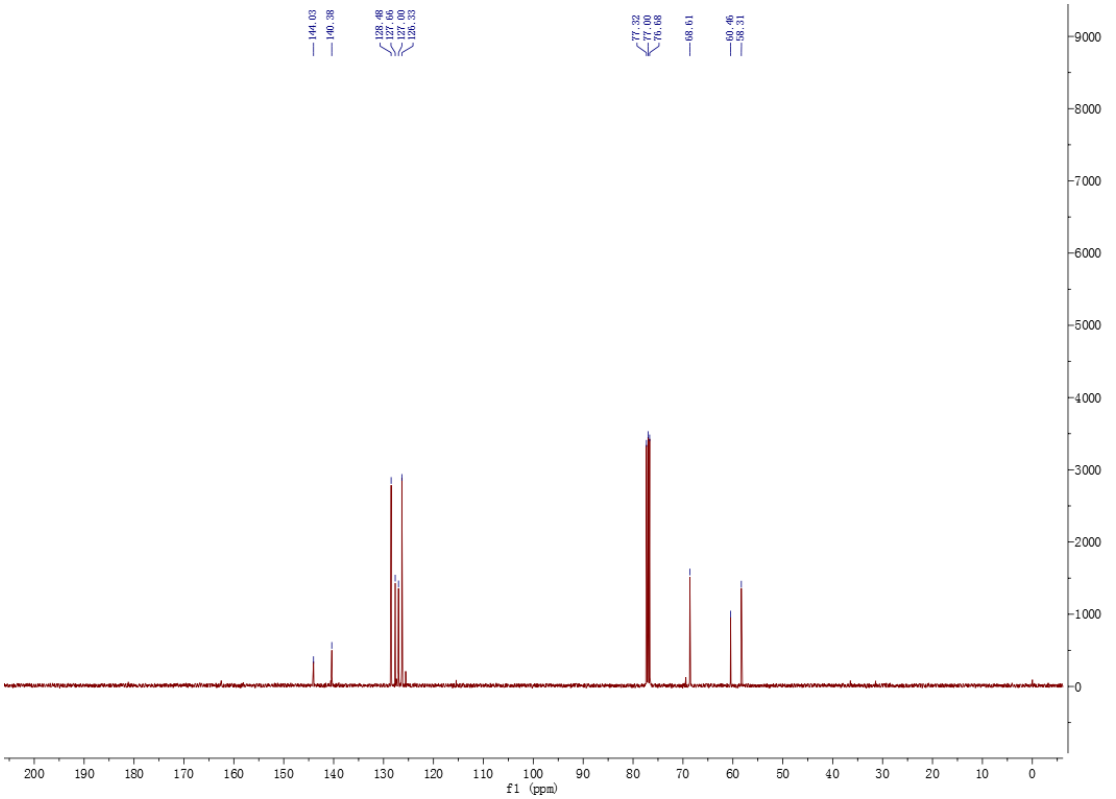
7.27
7.26
6.07
6.05
6.04
4.54
4.19
4.17
3.41
2.22
0.00
2.33
3.45
1.00
2.19
2.17
3.26
1.49
f1 (ppm)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77.00
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68.61
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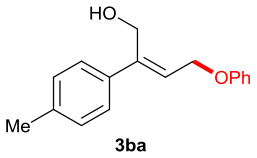
f1 (ppm)



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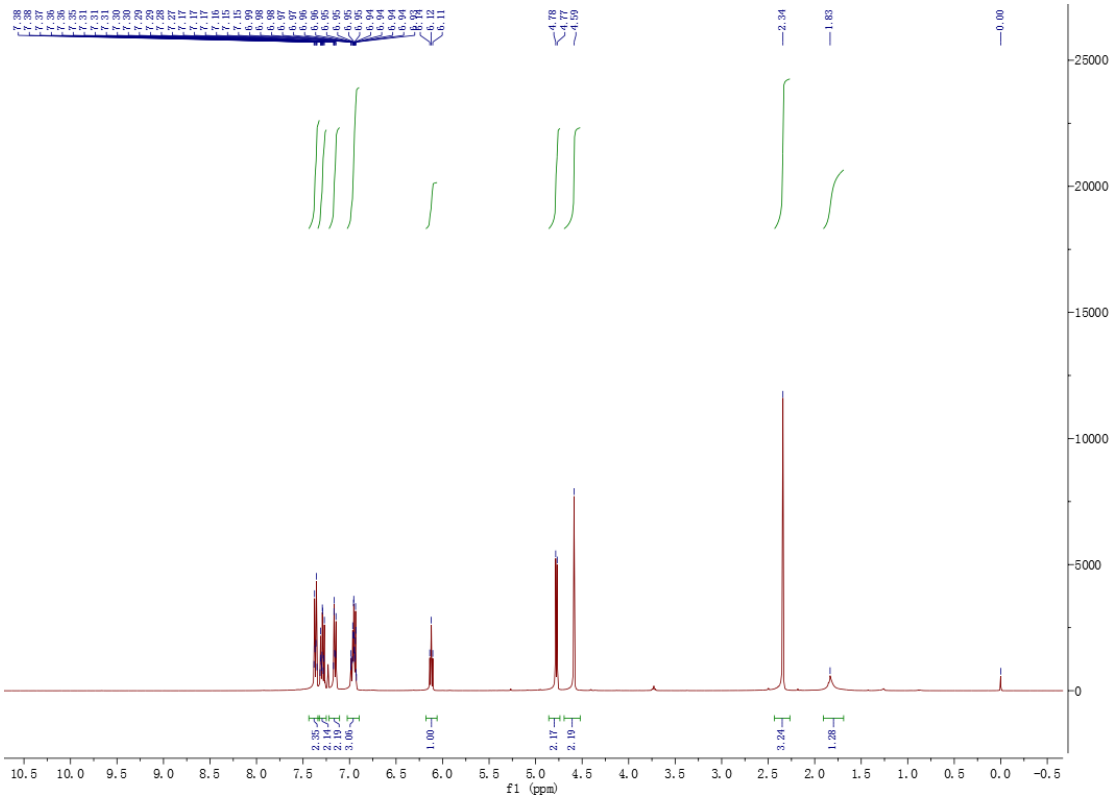
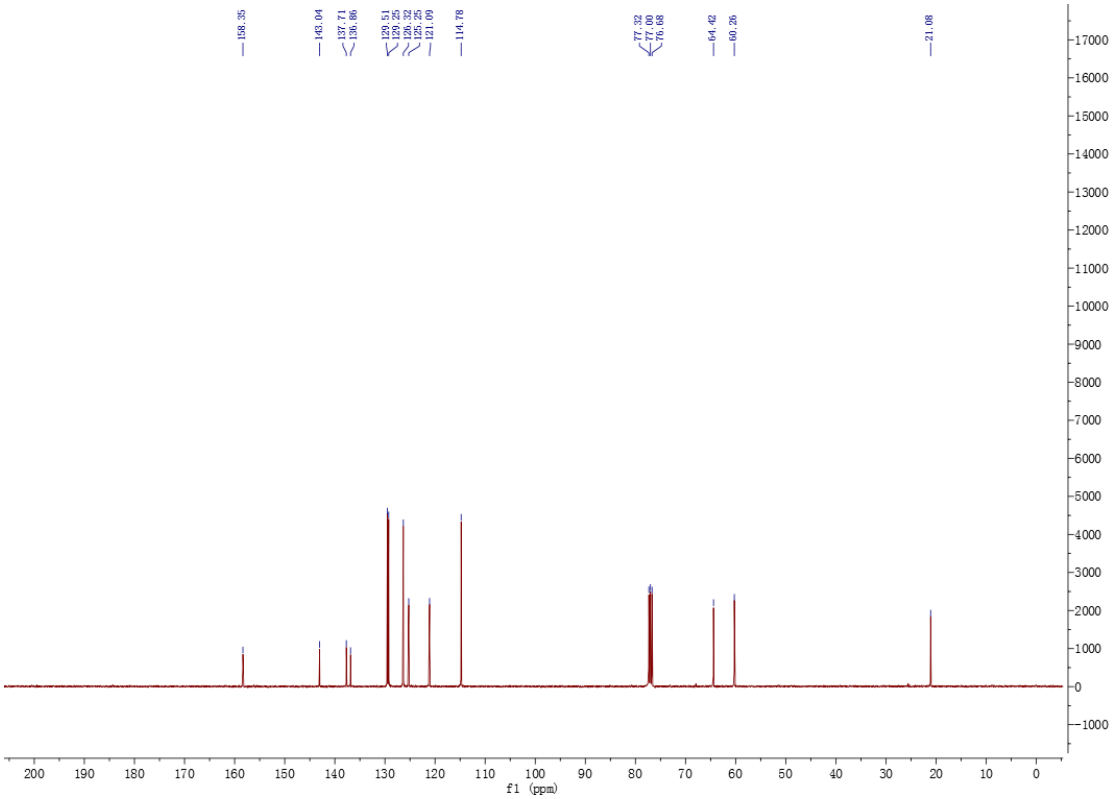
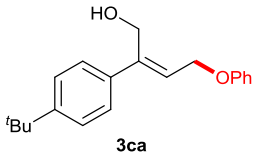
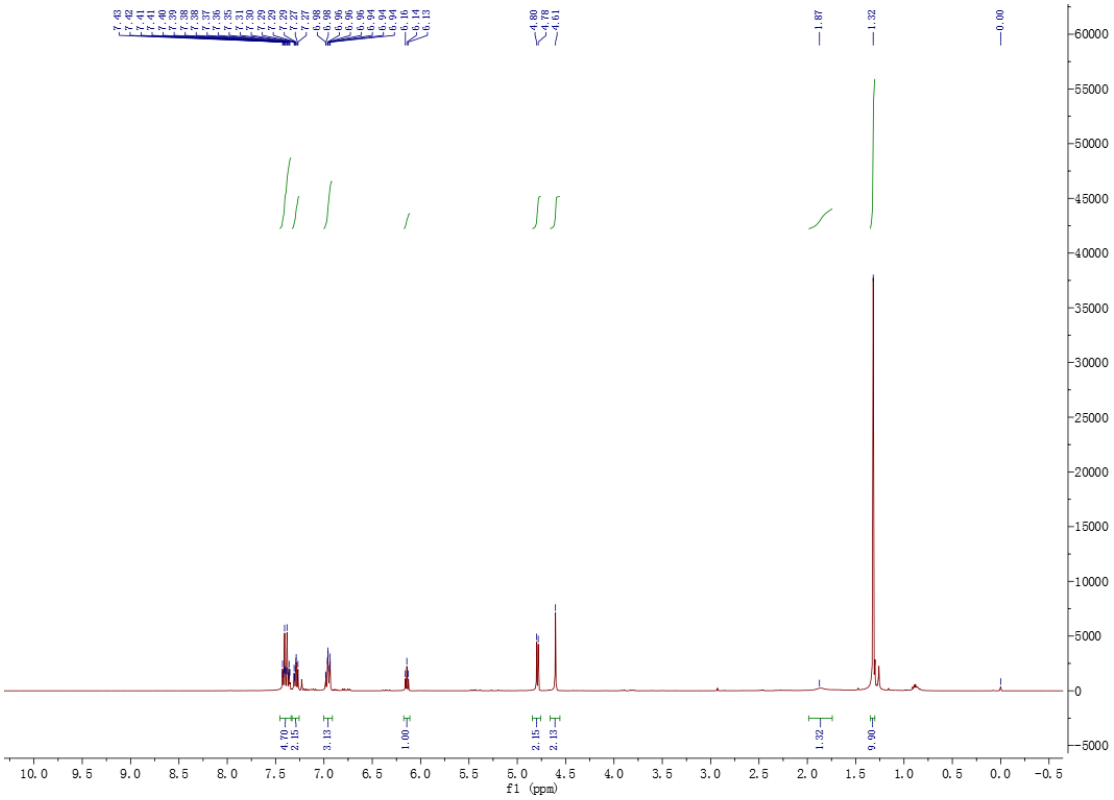





HO
OPh
tBu

3ca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6.96
6.94
6.94
6.16
6.14
6.13
4.80
4.78
4.61
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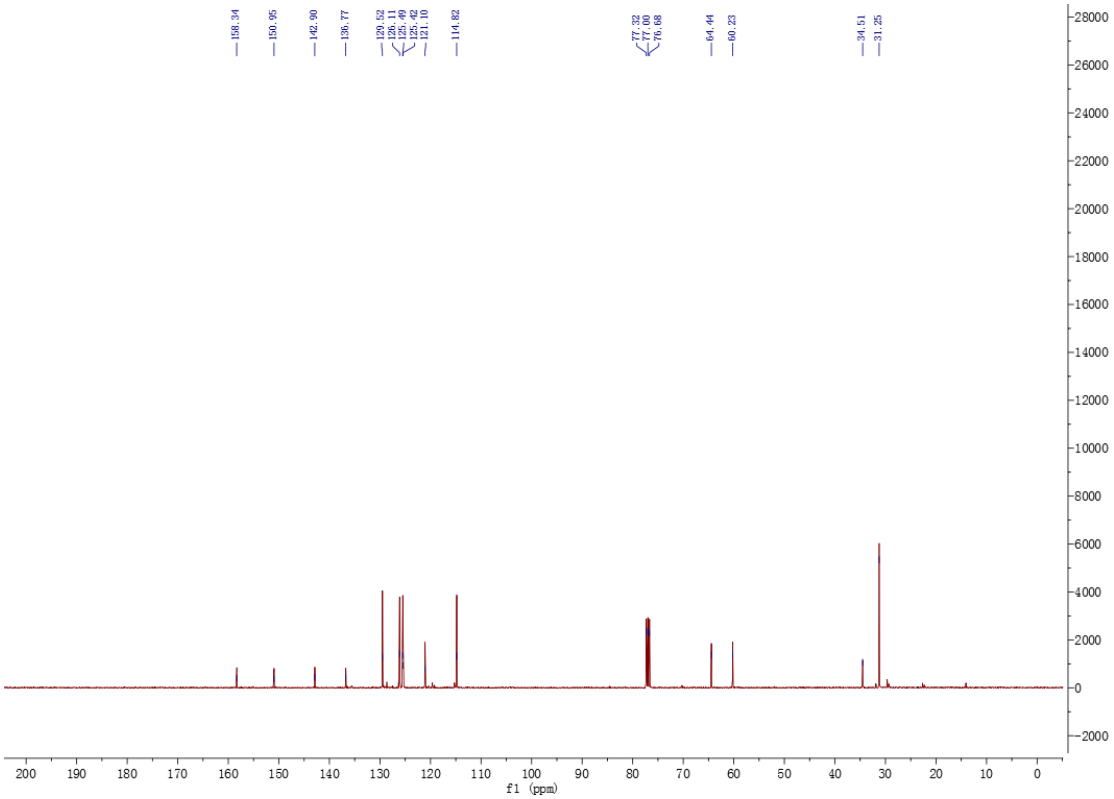
2.15
2.13
1.32
9.90
f1 (ppm)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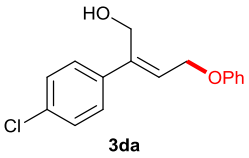
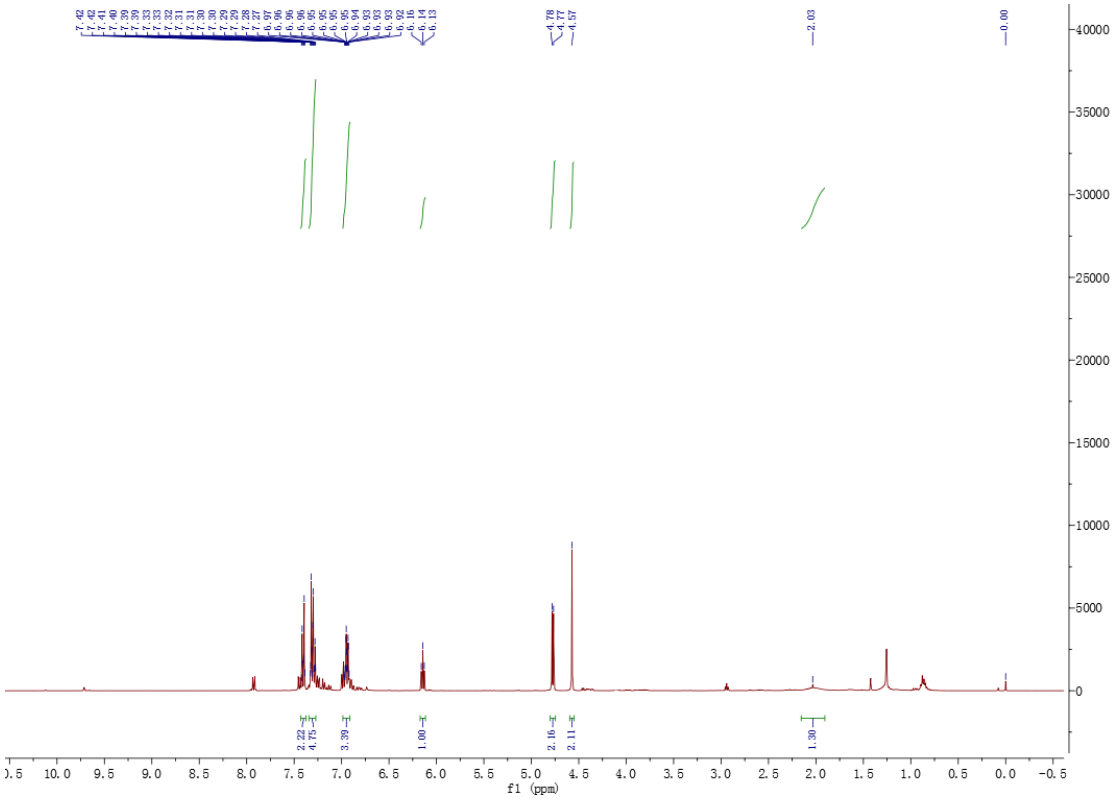
60.23
34.51
31.25
f1 (ppm)


HO
OPh
Cl

3da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6.94
6.93
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6.93
6.92
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6.14
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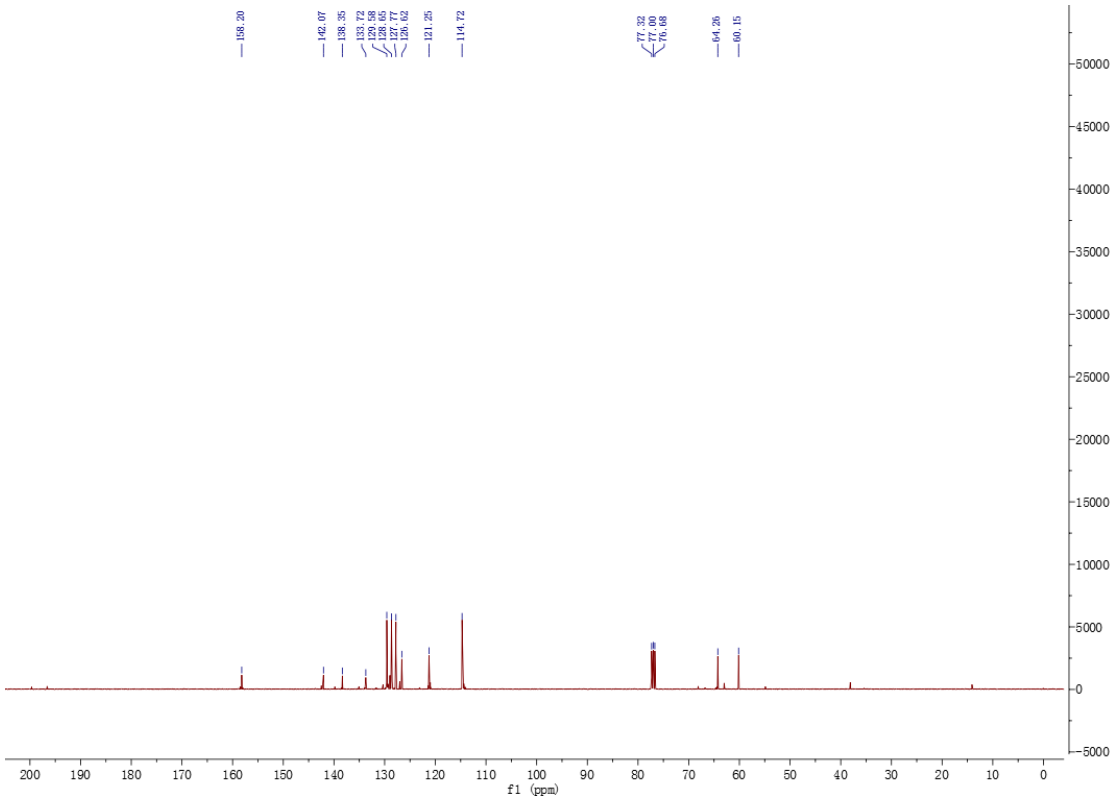
f1 (ppm)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77.00
76.68
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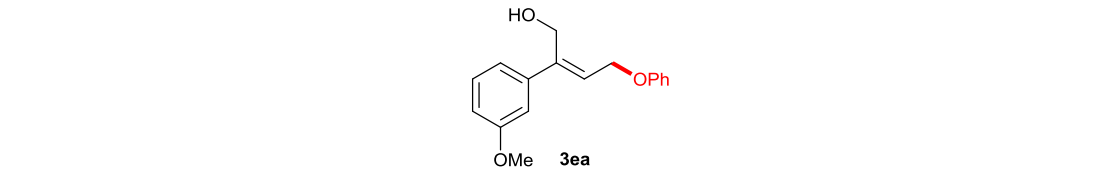
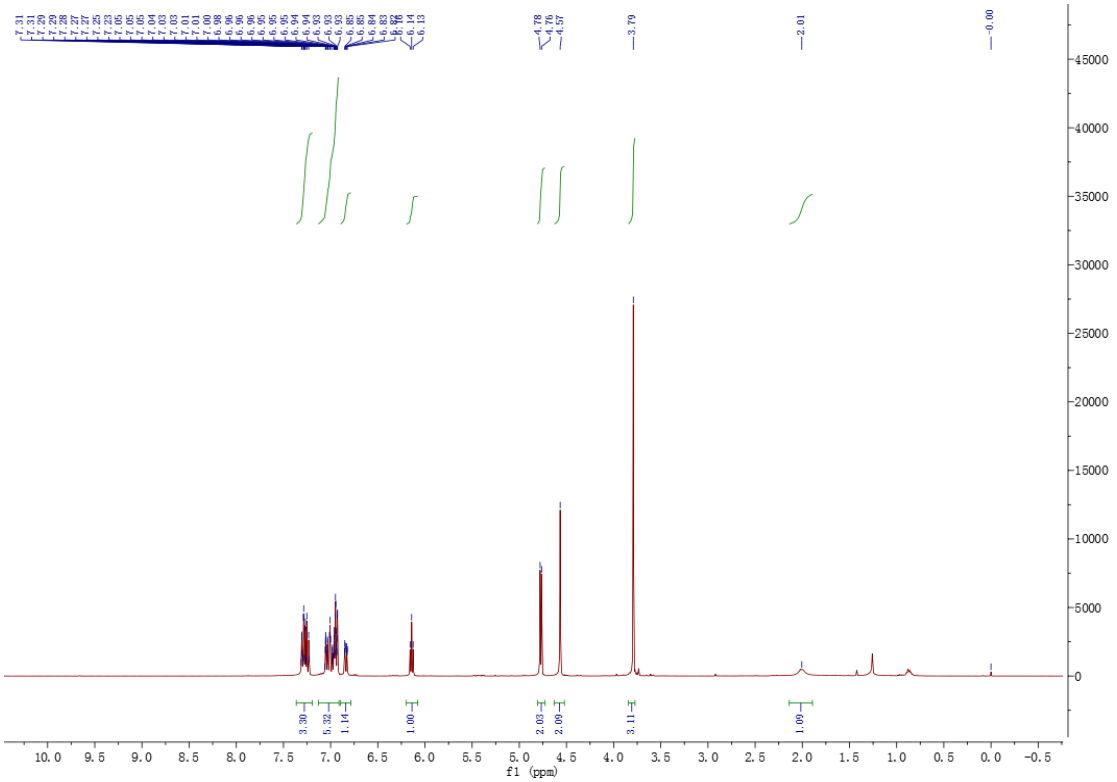
60.15
f1 (ppm)


HO
OPh
OMe

3ea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6.96
6.95
6.95
6.94
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6.93
6.93
6.85
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6.16
6.14
6.13
4.78
4.76
4.57
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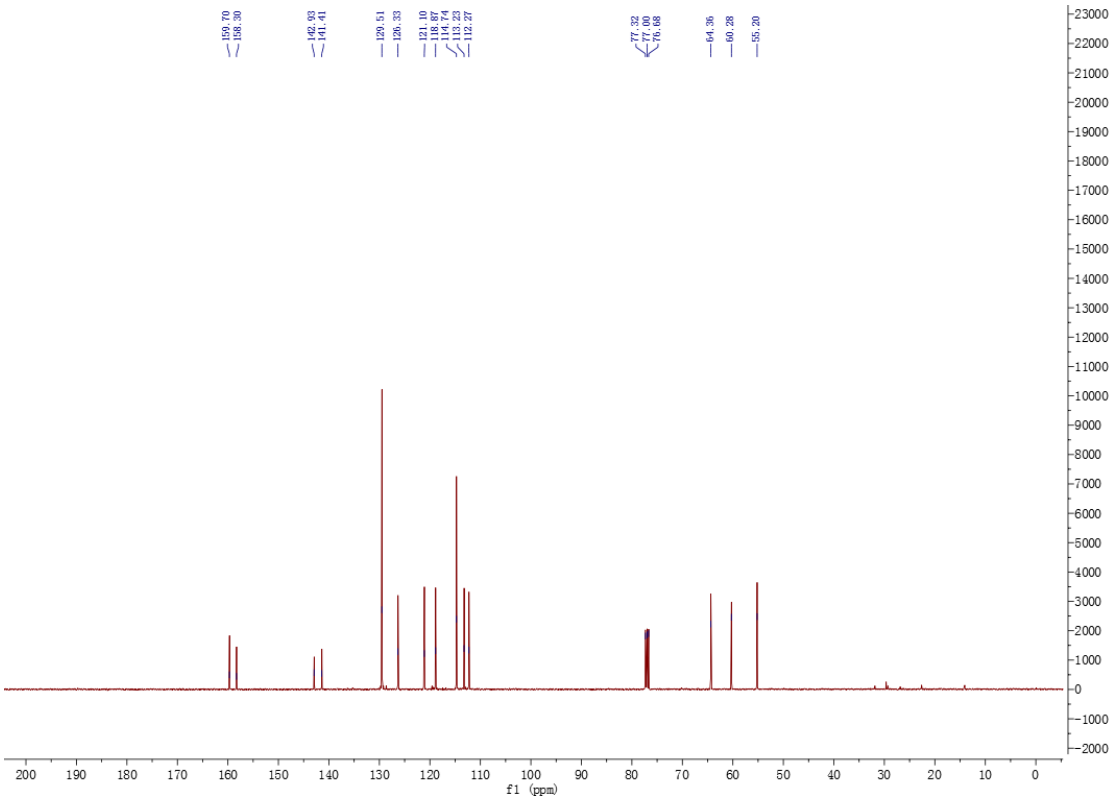
1.14
1.00
2.03
2.09
3.11
1.09
f1 (ppm)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119.87
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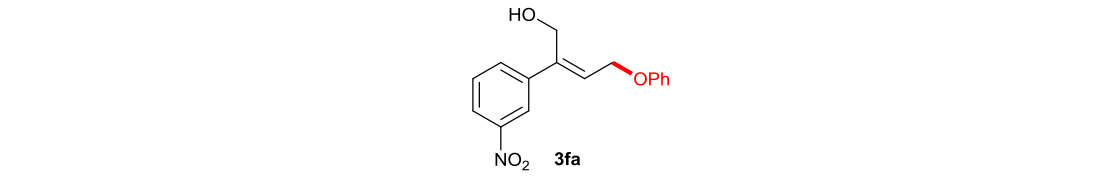
77.32
77.00
76.68
64.36
60.28
55.20
f1 (ppm)



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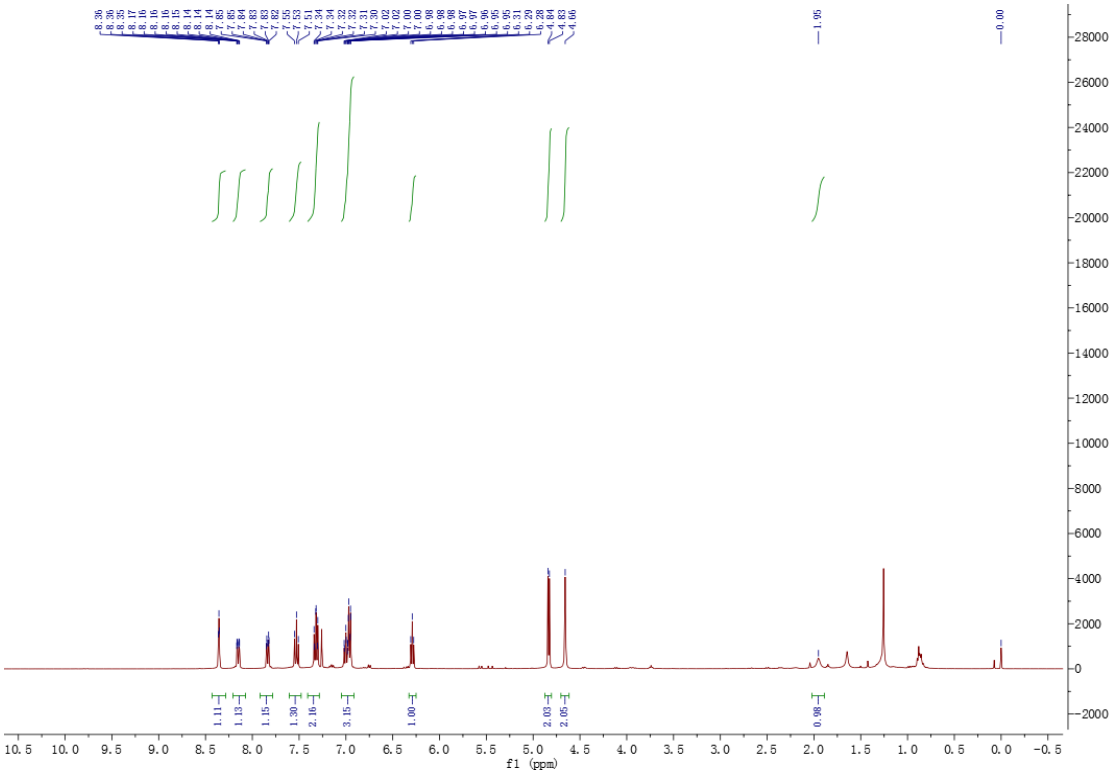
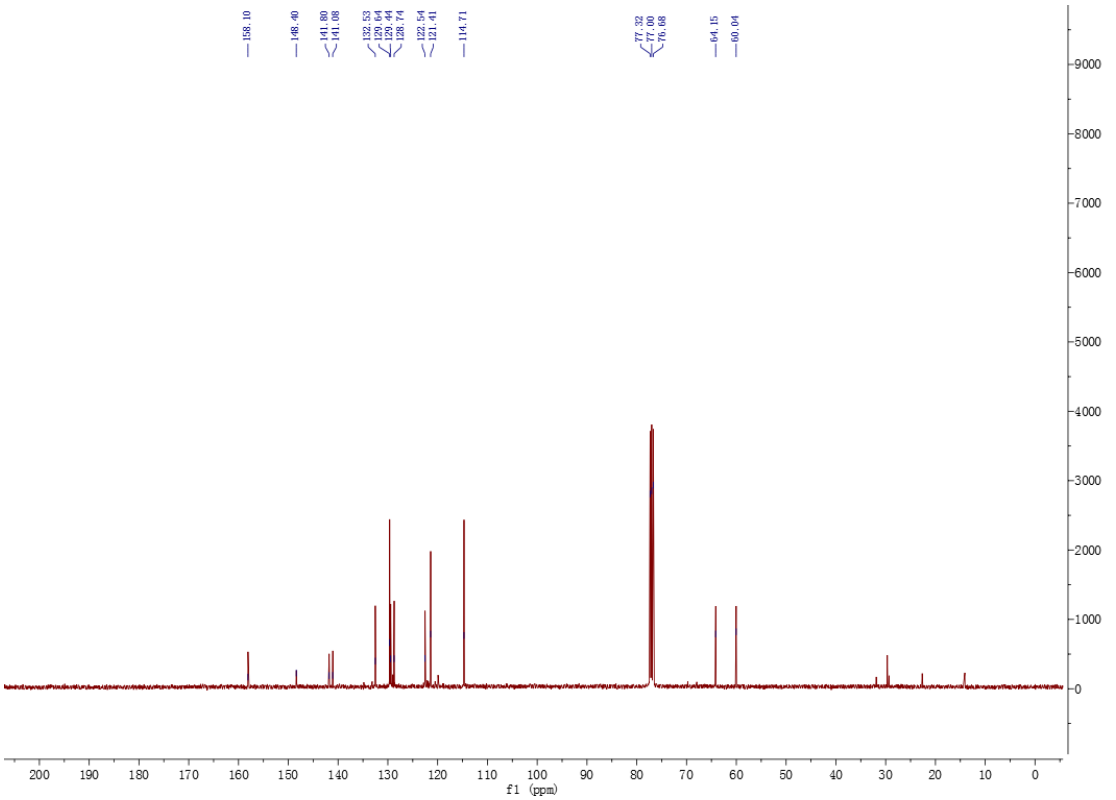
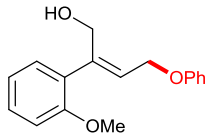
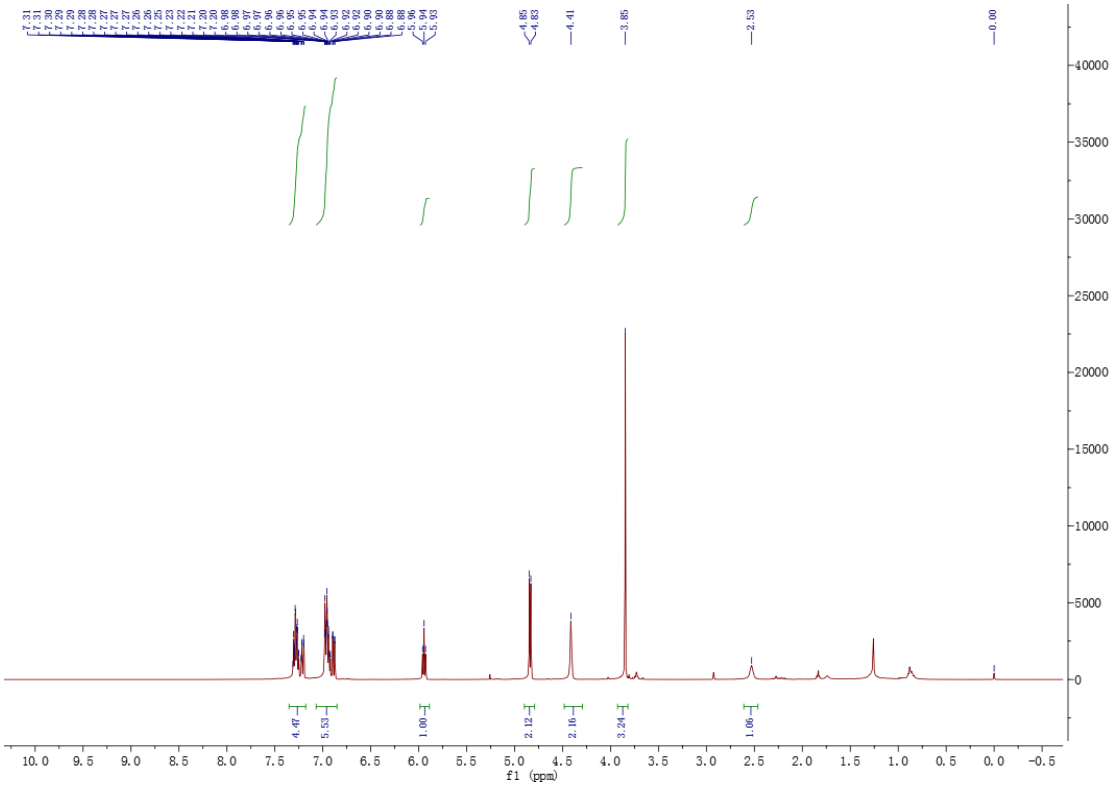





HO
OPh
OMe

3ga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6.92
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5.93
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5.53
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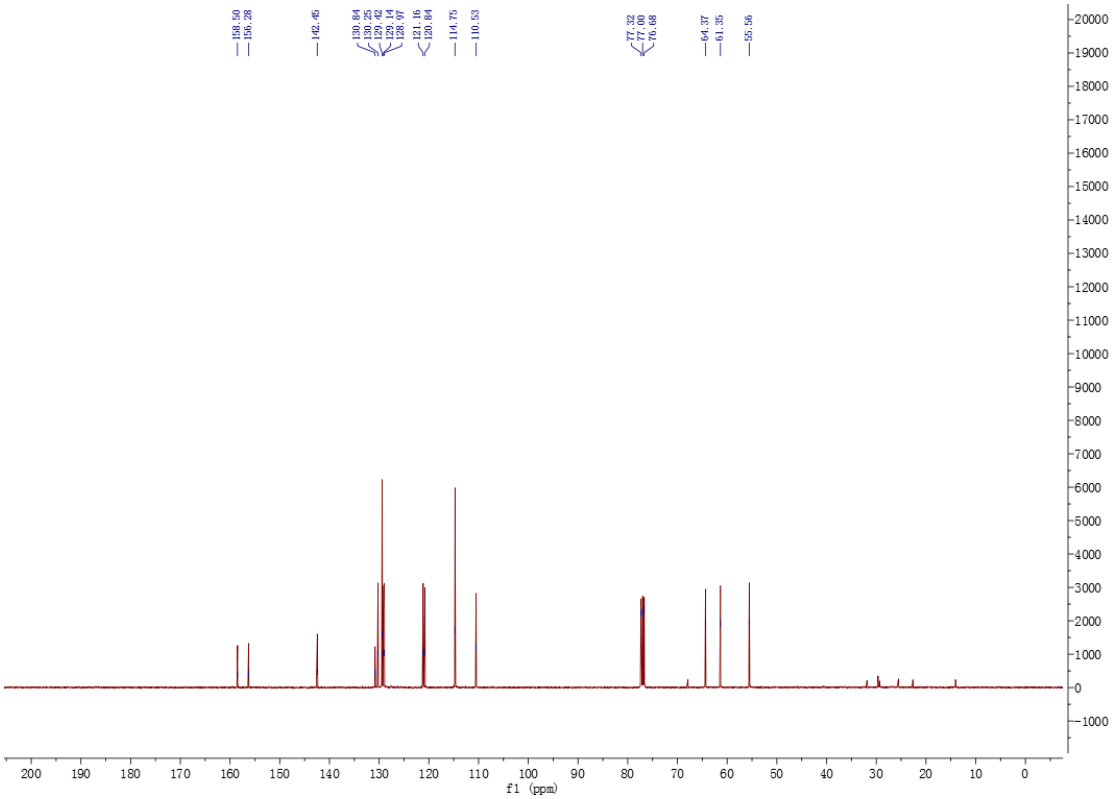
1.06
f1 (ppm)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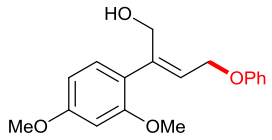
55.56
f1 (ppm)



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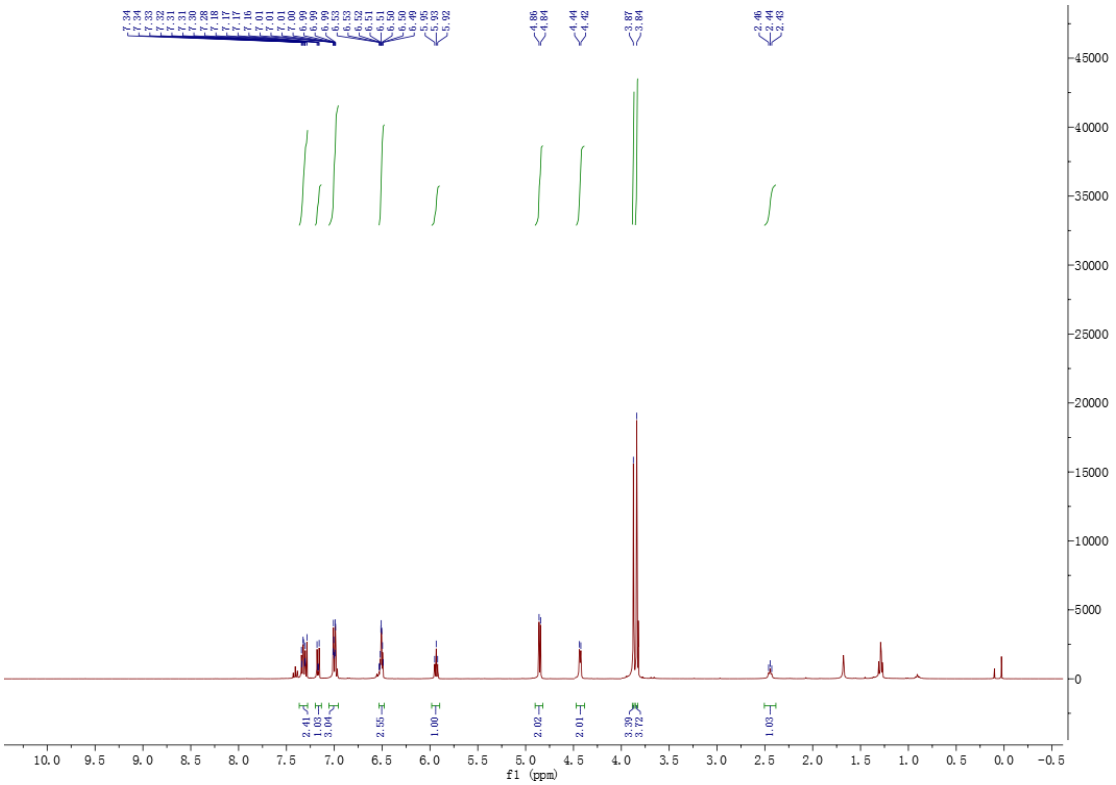
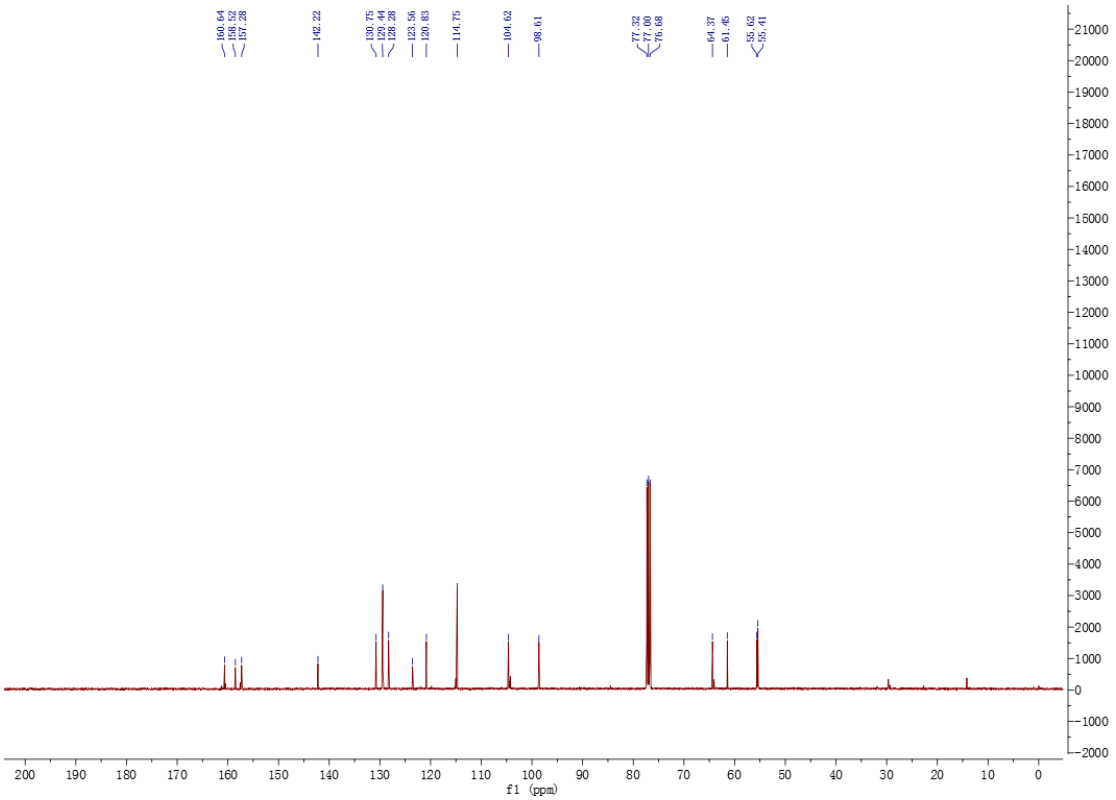
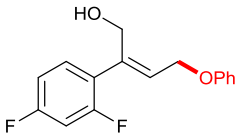
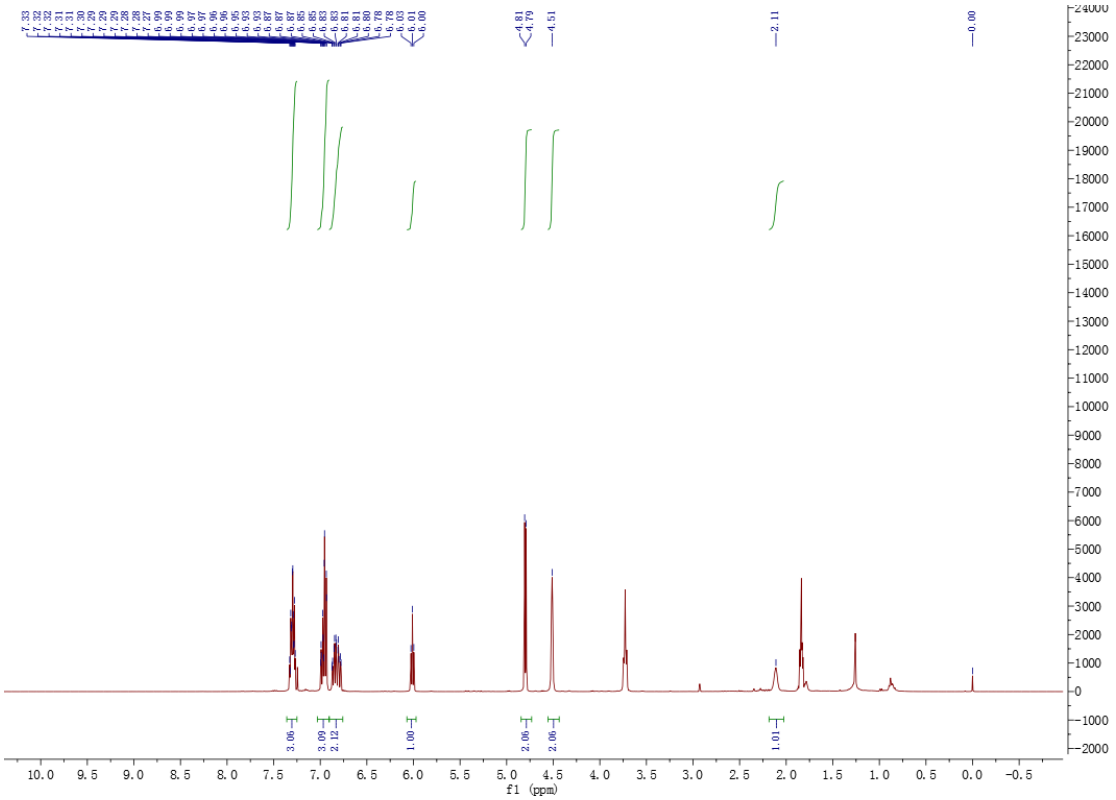





HO
OPh
F
F

3ia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6.80
6.78
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6.00
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3.09
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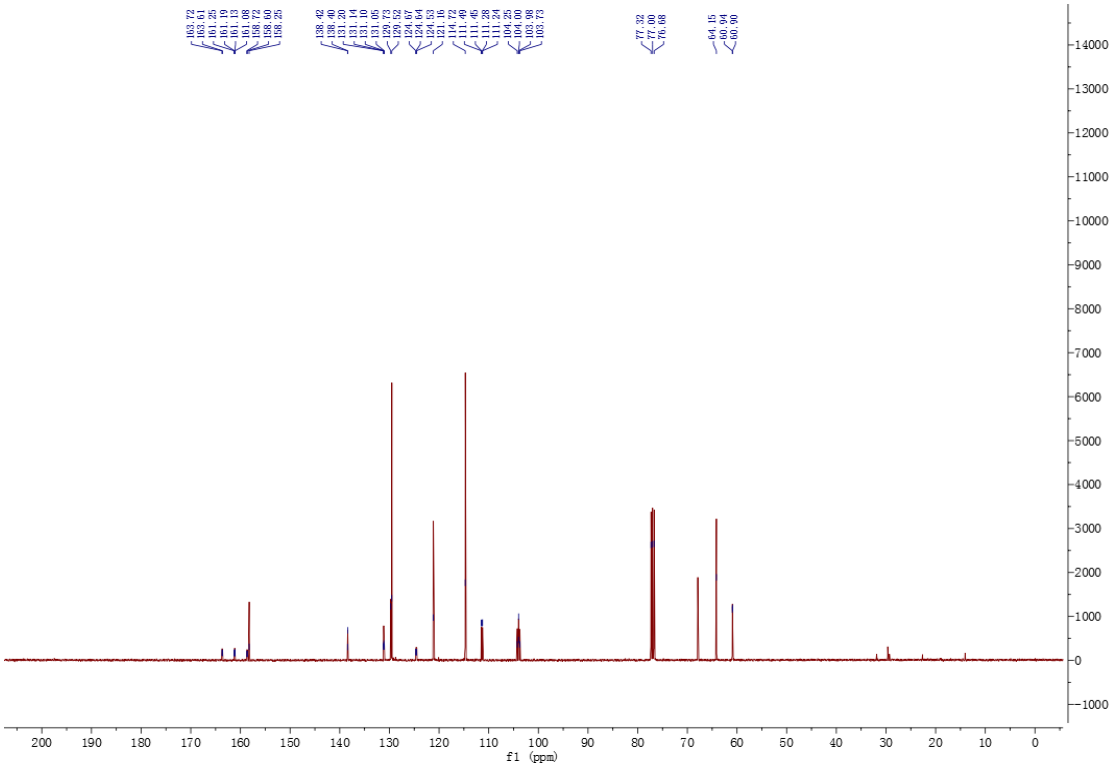
2.06
2.06
1.01
f1 (ppm)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131.10
131.05
129.73
129.52
124.67
124.64
124.53
121.16
114.72
114.46
111.46
111.28
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77.00
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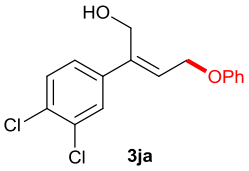
60.90
f1 (ppm)



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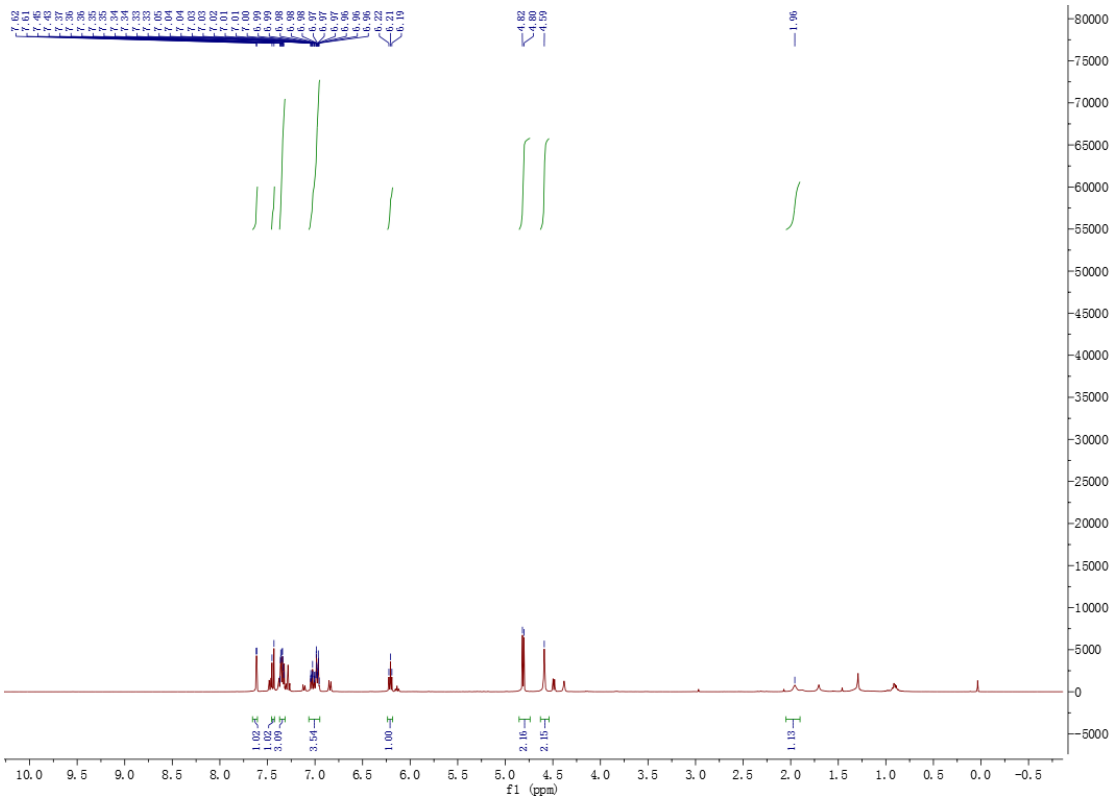

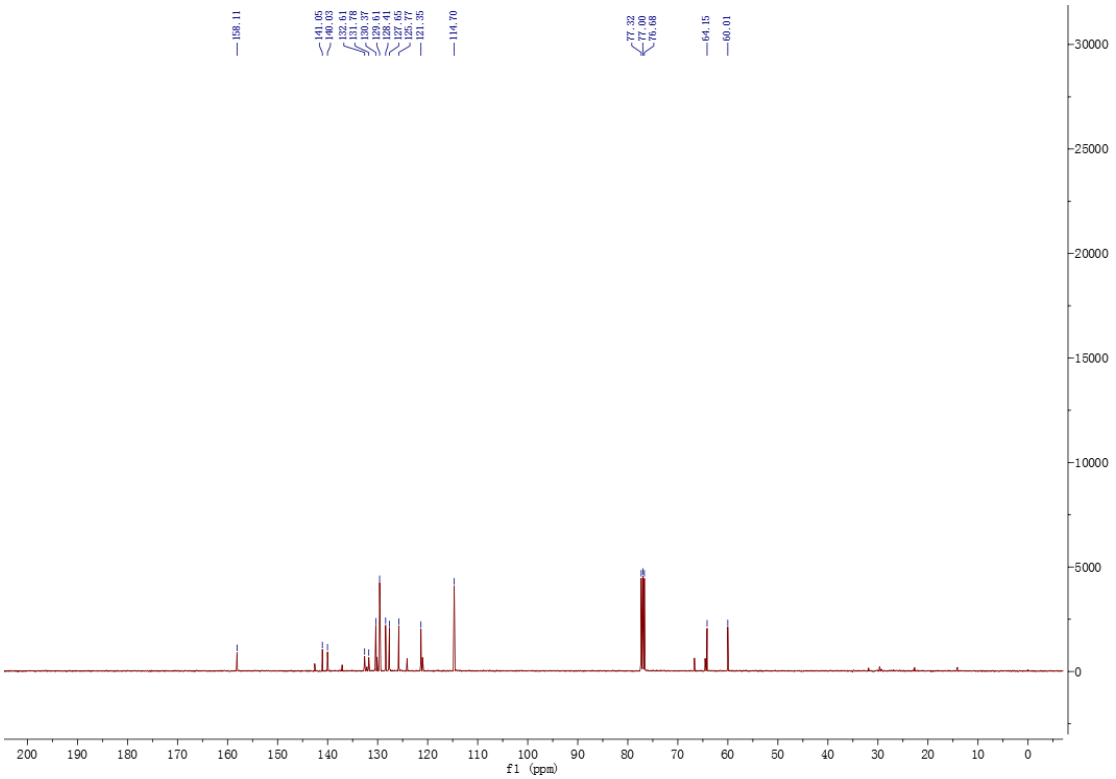

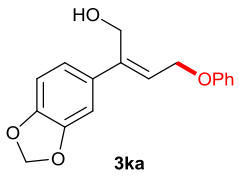

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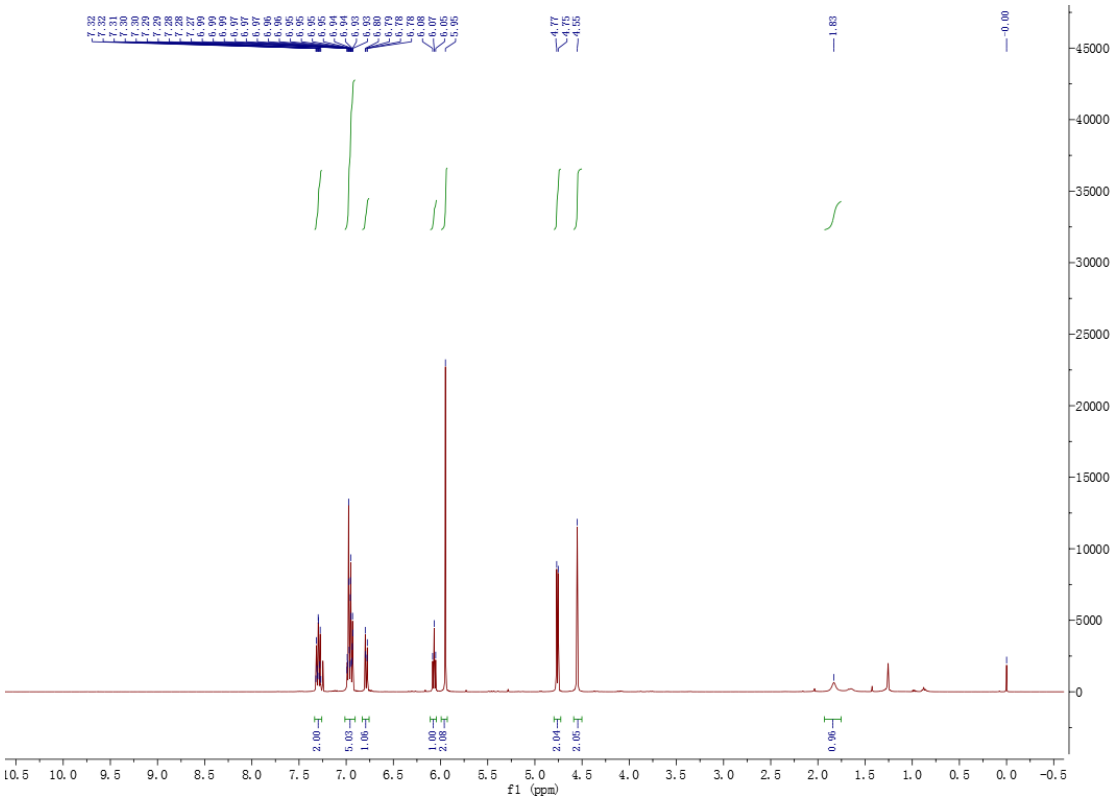

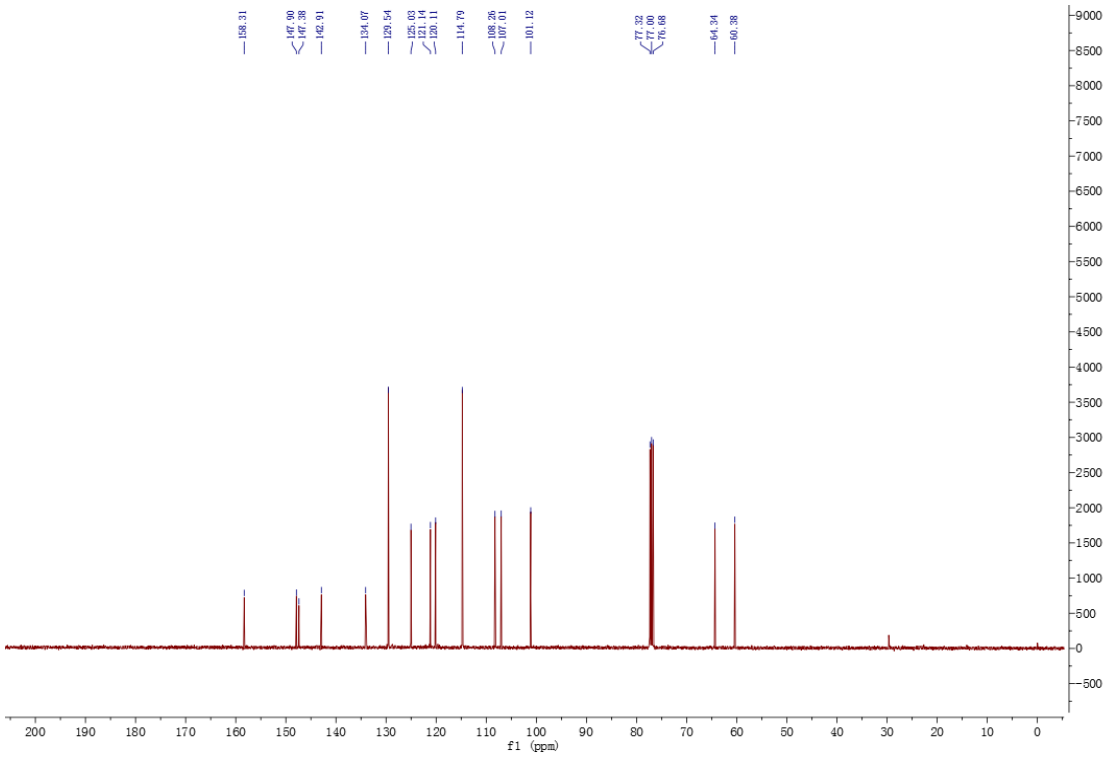

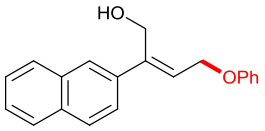

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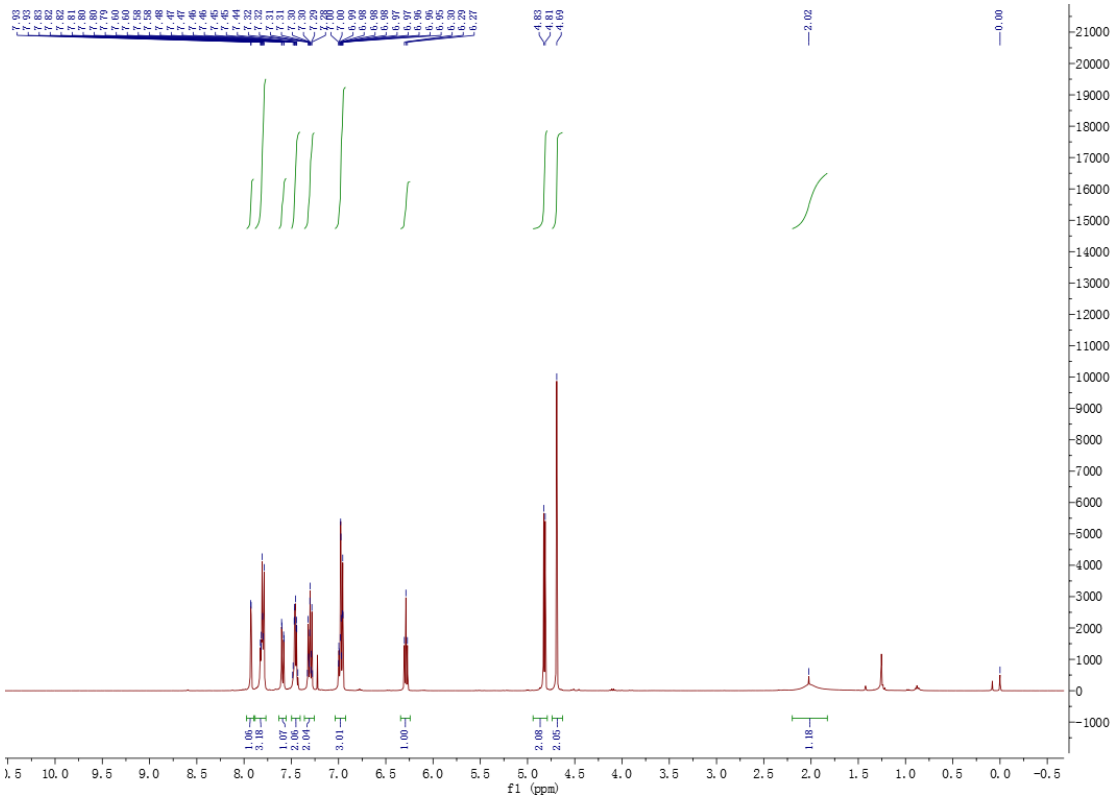

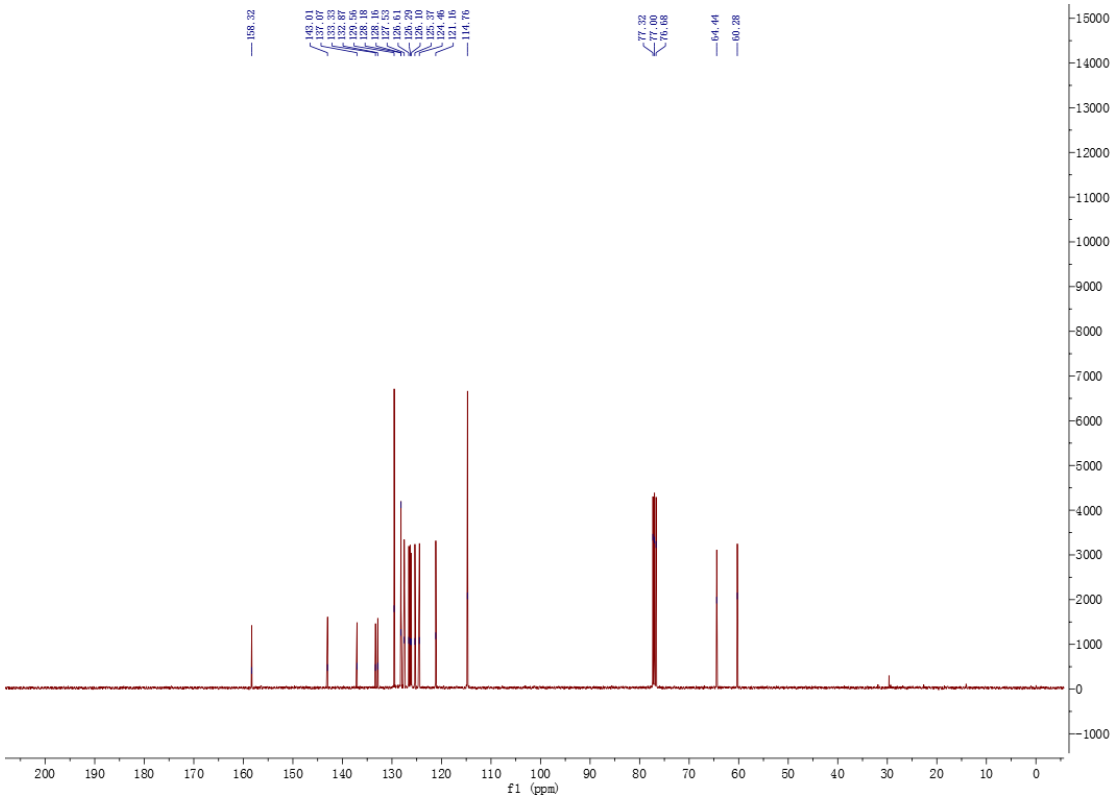

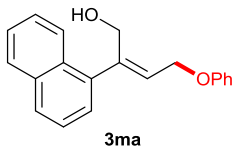

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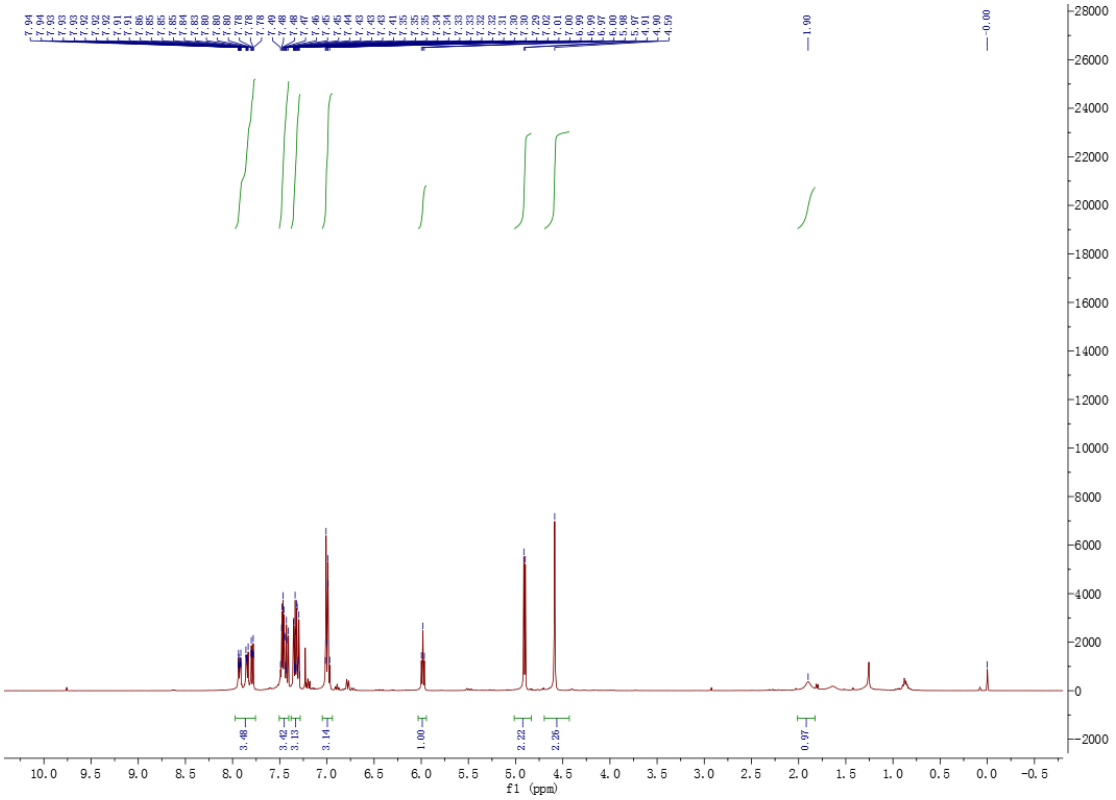
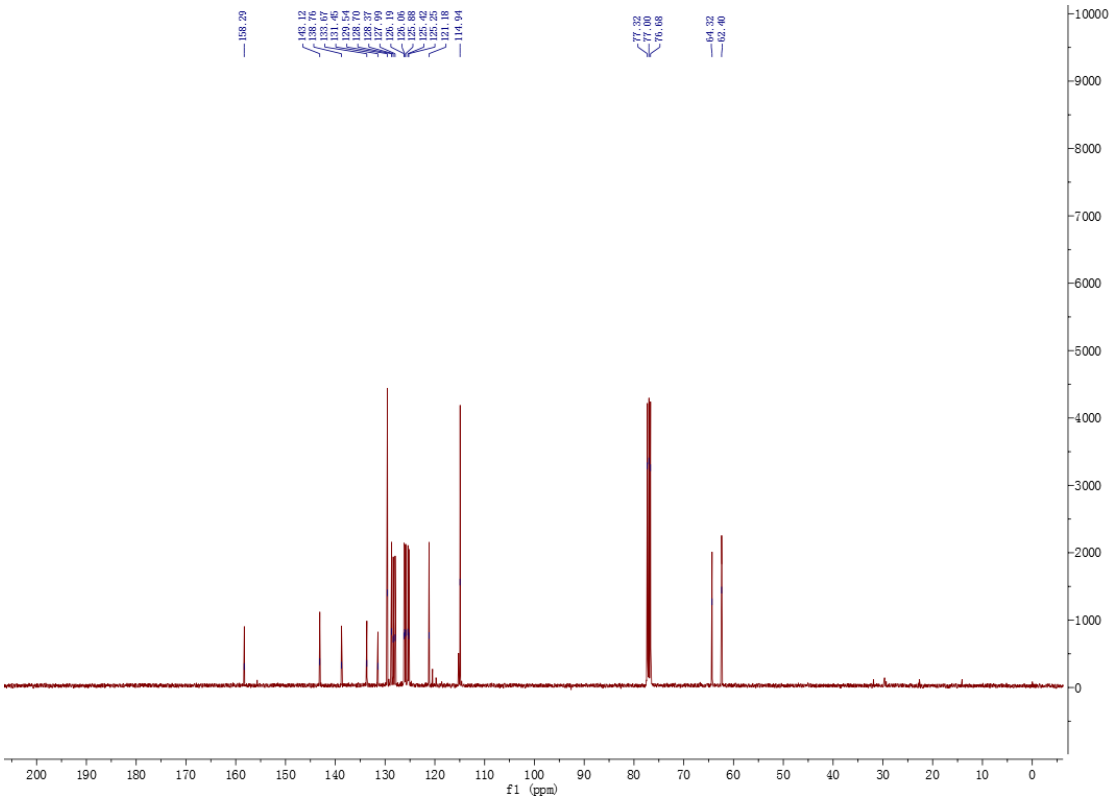
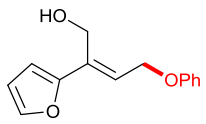
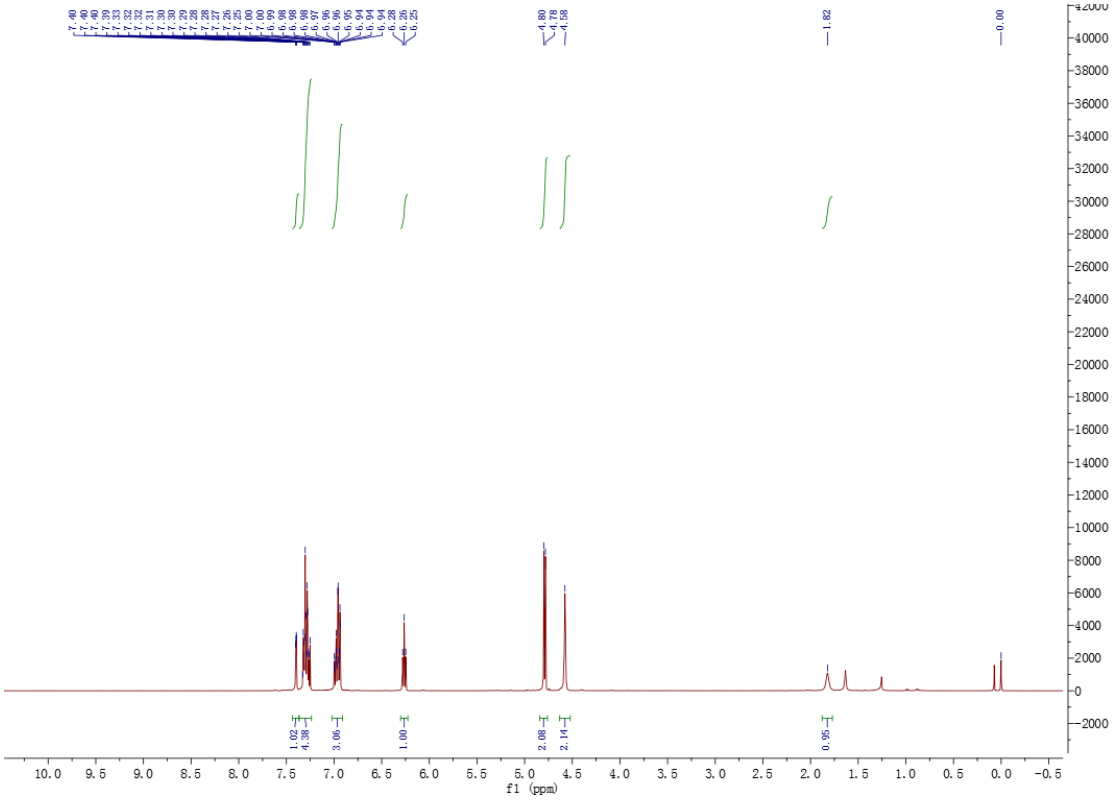





HO
OPh
O

3na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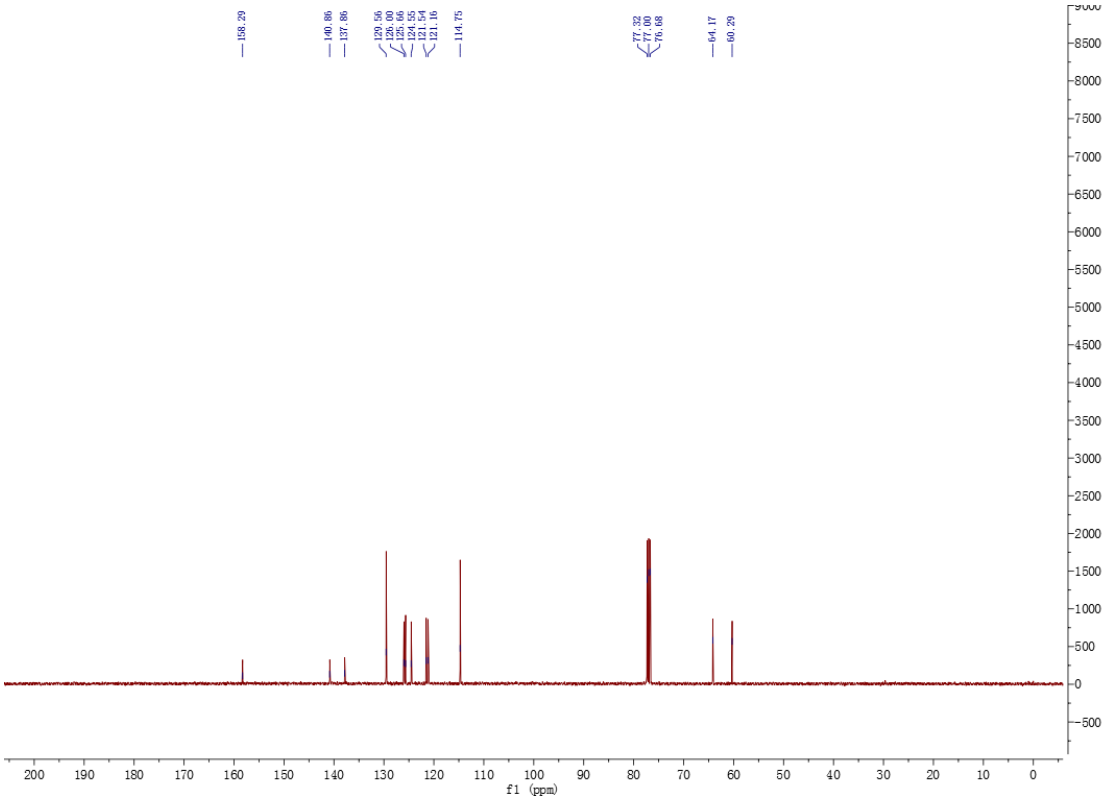
f1 (ppm)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76.68
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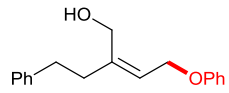
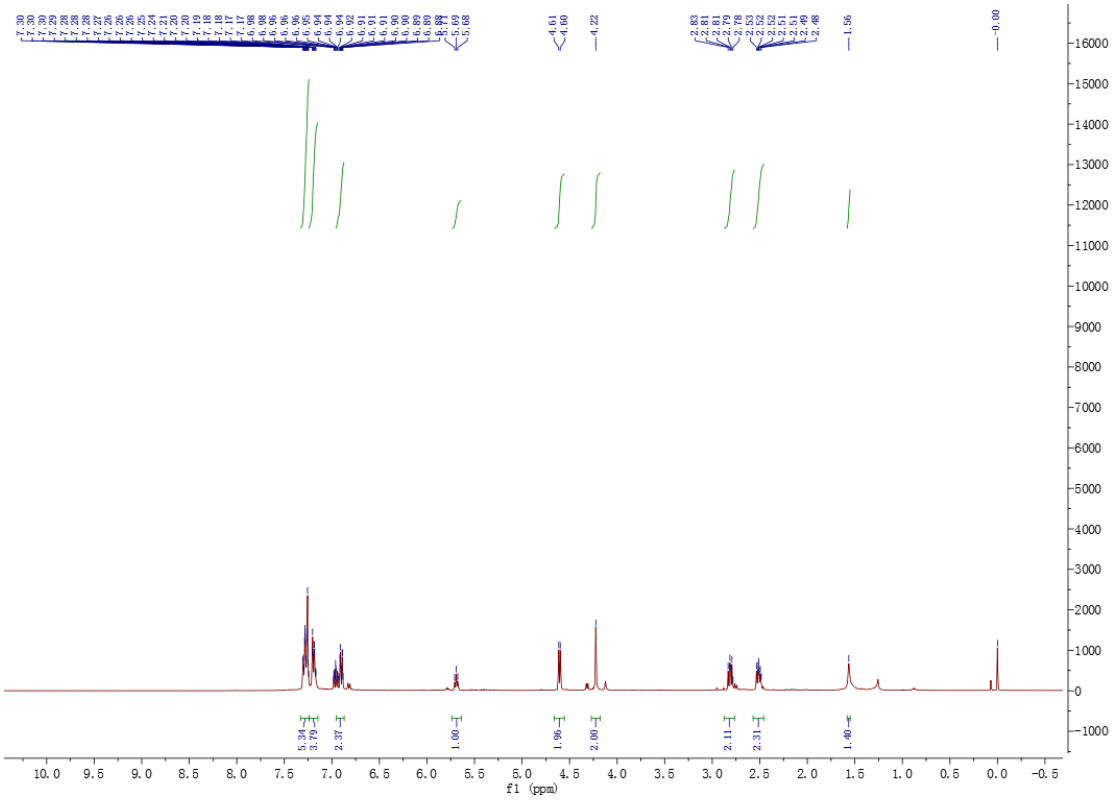
60.29
f1 (ppm)


HO
Ph
OPh

3oa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2.78
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2.48
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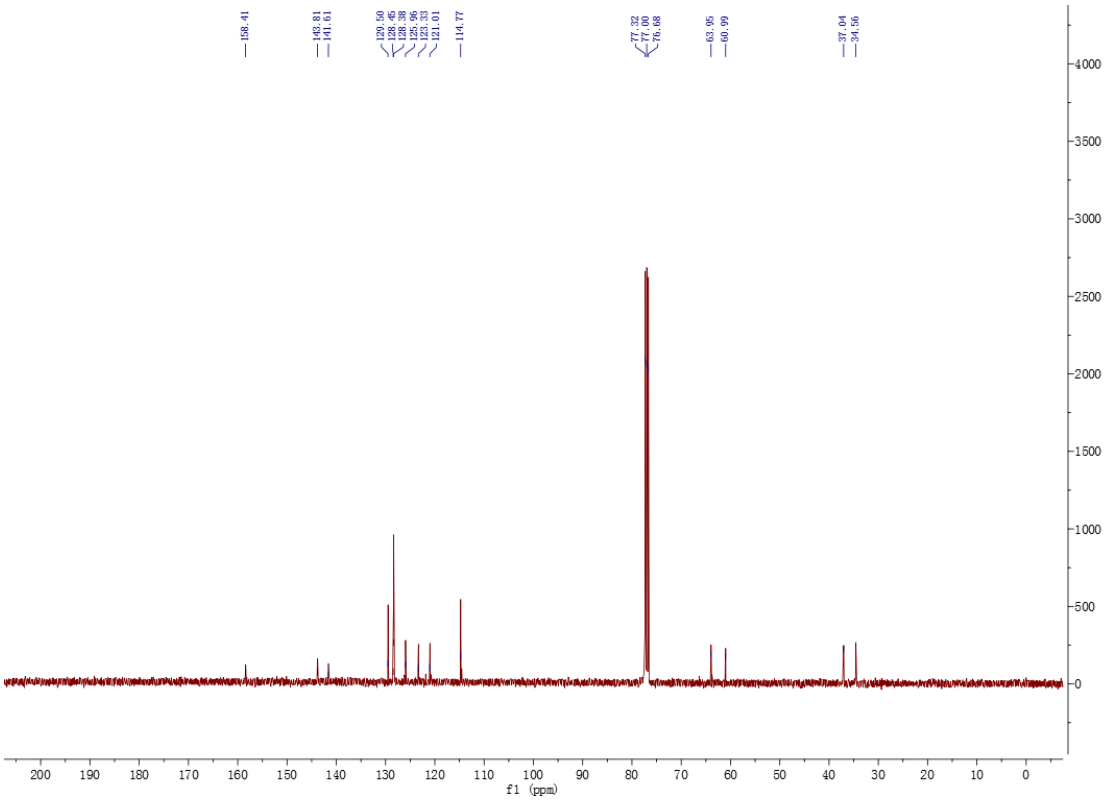
f1 (ppm)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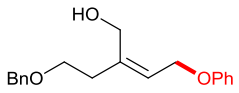
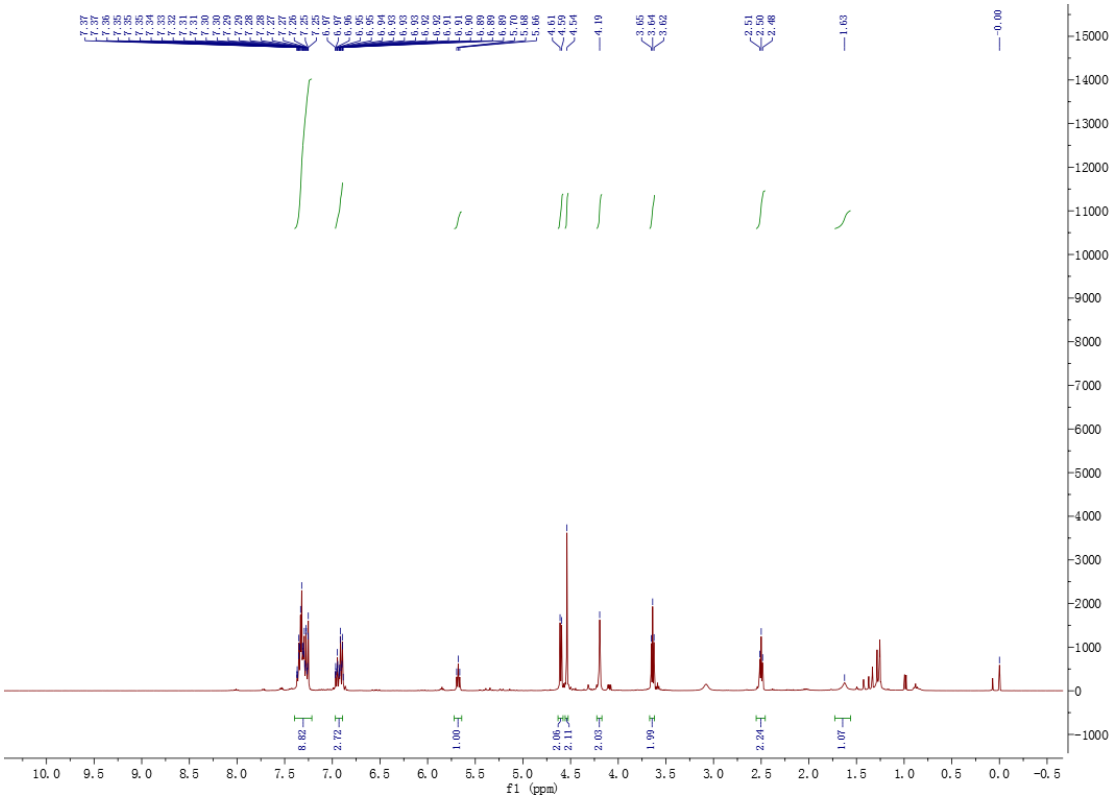
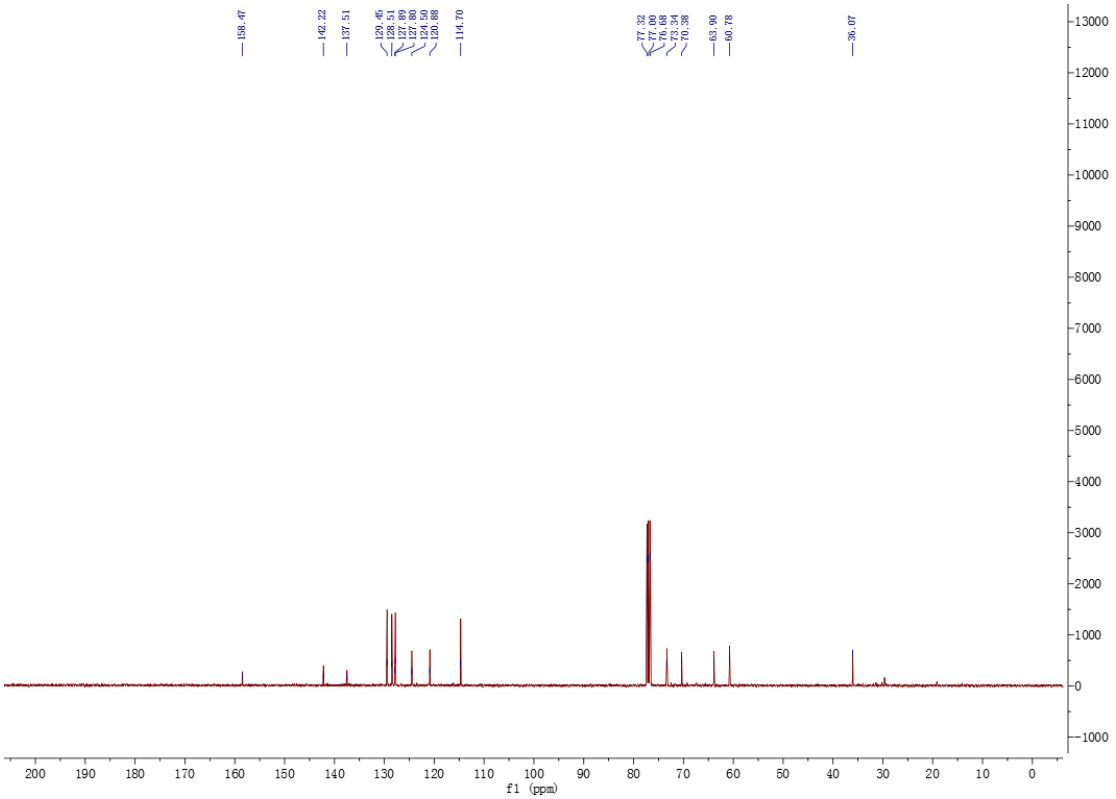
114.77
77.32
77.00
76.68
63.95
60.99
37.04
34.56
f1 (ppm)


HO
BnO
OPh

3pa


7.37
7.36
7.35
7.34
7.33
7.32
7.31
7.30
7.29
7.28
7.27
7.26
7.25
6.97
6.96
6.95
6.94
6.93
6.92
6.91
6.90
5.89
5.89
5.89
5.70
5.68
5.66
4.61
4.59
4.54
4.19
3.65
3.64
3.62
2.51
2.50
2.48
1.63
0.00
8.82
2.72
1.00
2.06
2.11
2.03
1.99
2.24
1.07
f1 (ppm)


158.47
142.22
137.51
129.46
128.51
127.89
127.80
124.50
120.88
114.70
77.32
77.00
76.68
73.34
70.38
63.90
60.78
36.07
f1 (ppm)