Supporting Information

Metal-free oxidative direct C(sp^3)-H bond functionalization of ethers with α,α-diaryl allylic alcohols

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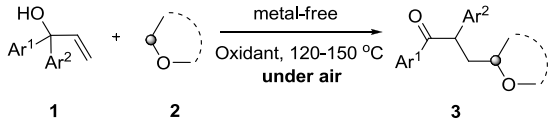
Table of Contents

Experimental Section:

General

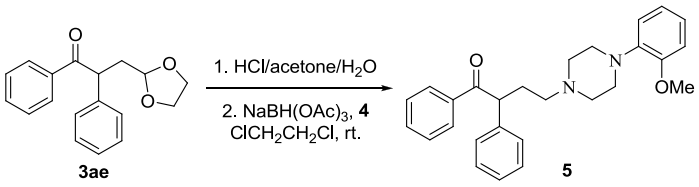
Unless otherwise stated, all reagents were purchased from commercial suppliers and used without further purification. All reactions were carried out in air and using undistilled solvent, without any precautions to exclude air and moisture unless otherwise noted. Melting points were recorded on an Electrothermal digital melting point apparatus. IR spectra were recorded on a FT-IR spectrophotometer using KBr optics. ^{1}H, ^{13}C NMR spectra were recorded in $CDCl_3$ on 400 MHz spectometers. Tetramethylsilane (TMS) served as internal standard for ^{1}H NMR and ^{13}C NMR. High resolution mass spectra were obtained using a commercial apparatus (ESI or EI Source).

General procedure for alkylation of α,α-diaryl allylic alcohols



α,α-Diaryl allylic alcohol **1** (0.3 mmol), **2** ether (1 mL) and *tert*-butylperoxybenzoate (0.6 mmol) was stirred at 120°C or 150°C under air for 9-24h. Upon completion of the reaction (indicated by TLC), it was then removal of the organic solvent in vacuum and followed by flash silica gel column chromatographic purification afforded pure product **3** with petroleum/ethyl acetate.

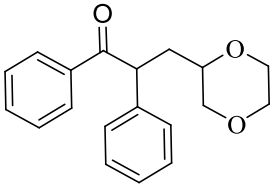
General procedure for the synthesis of serotonin antagonist 5



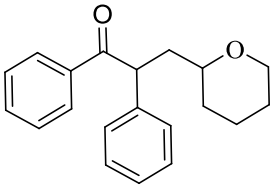
Step 1: ketone **3ae** (0.41 mmol) was dissolved in 5 mL acetone and an excess of 2M hydrochloric acid (6 mL) was slowly added to the reaction mixture. The reaction mixture was then stirred at room temperature for 6 hours. Upon completion of the reaction, a sat. aq. $NaHCO_3$ solution (10 mL) was added and the mixture was extracted with ethyl acetate (3×10 mL). The combined organic extracts were dried with sodium sulfate and concentrated to give the crude keto-aldehyde which was used directly without further purification.

Step 2: A solution of the crude keto-aldehyde obtained above in dichloroethane (2 mL) was added a solution of 1-(2-methoxyphenyl)piperazine **4** (0.49 mmol) in dichloroethane (2 mL). To this mixture triacetoxysodium borohydride (0.82 mmol) was added and the mixture was then stirred at room temperature for 6 h. Upon completion of the reaction, a sat. aq. $NaHCO_3$ solution (5 mL) was added and the mixture was extracted with ethyl acetate (3×5 mL). The combined organic extracts were dried with sodium sulfate and concentrated. The pure product **5** was obtained after purification of the residue by column chromatography (silica gel, ethyl acetate/petroleum ether) as a colourless oil.

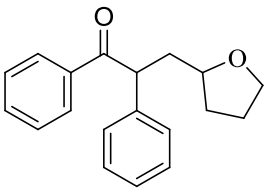
Analytical and spectral data for compounds:



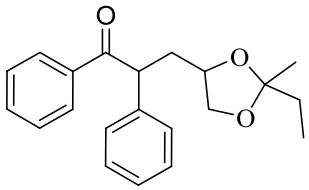
3-(1,4-dioxan-2-yl)-1,2-diphenylpropan-1-one (3aa): Yield = 95% (2:3 dr). Colorless oil. IR (KBr) ν = 2953, 2853, 1723, 1677, 1596, 1492, 1447, 1360, 1120, 1076, 940, 913, 869, 760, 742, 696 cm^{-1}. ^{1}H NMR (400MHz, $CDCl_3$): δ = 8.00–7.93 (m, 2H), 7.51–7.43 (m, 1H), 7.41–7.33 (m, 2H), 7.31–7.24 (m, 4H), 7.23–7.16 (m, 1H), 4.94 (dd, *J* = 11.0, 3.6 Hz, 0.4H), 4.88 (dd, *J* = 10.2, 4.5 Hz, 0.6H), 3.80–3.71 (m, 1.3H), 3.67–3.53 (m, 4H), 3.35–3.21 (m, 1.7H), 2.45–2.36 (m, 0.4H), 2.12–2.04 (m, 0.6H), 1.97–1.89 (m, 0.6H), 1.71–1.64 (m, 0.4H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 199.8, 199.7, 139.9, 138.8, 137.1, 136.7, 133.1, 133.0, 129.2, 129.2, 129.0, 129.0, 128.7, 128.7, 128.6, 128.2, 127.4, 127.3, 73.6, 72.7, 71.6 ,71.5, 66.9, 66.9, 66.7, 66.7, 49.0, 48.6, 36.3, 35.0 ppm. HRMS m/z: calcd for $C_{19}H_{21}O_3$ $[M+H]^+$ 297.1491, found: 297.1489.



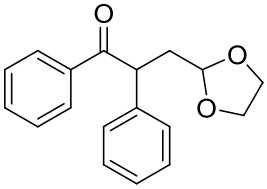
1,2-diphenyl-3-(tetrahydro-2H-pyran-2-yl)propan-1-one (3ab): Yield = 63% (1:1.3 dr). Colorless oil. IR (KBr) ν = 2933, 2846, 1719, 1679, 1597, 1580, 1493, 1447, 1272, 1239, 1206, 1175, 1086, 1048, 1032, 757, 742, 696 cm^{-1}. ^{1}H NMR (400MHz, $CDCl_3$): δ = 8.02–7.94 (m, 2H), 7.50–7.43 (m, 1H), 7.43–7.33 (m, 3H), 7.32–7.27 (m, 3H), 7.24–7.14 (m, 1H), 5.01 (dd, *J* = 11.1, 3.5 Hz, 0.4H), 4.95–4.89 (m, 0.6H), 4.01–3.95 (m, 0.6H), 3.95–3.89 (m, 0.4H), 3.34–3.20 (m, 2H), 3.01–2.93 (m, 0.6H), 2.52–2.44 (m, 0.4H), 2.19–2.10 (m, 0.4H), 2.05–1.97 (m, 0.6H), 1.81–1.62 (m, 2H), 1.57–1.23 (m, 4H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 200.7, 200.4, 140.3, 139.4, 137.5, 136.9, 133.0, 132.8, 129.1, 129.0, 129.0, 128.9, 128.8, 128.7, 128.6, 128.3, 127.1, 127.1, 75.9, 74.7, 68.6, 68.5, 49.5, 49.0, 41.7, 40.1, 32.6, 32.4, 26.3, 26.3, 23.6, 23.6 ppm. HRMS m/z: calcd for $C_{20}H_{23}O_2$ $[M+H]^+$ 295.1698, found: 295.1703.



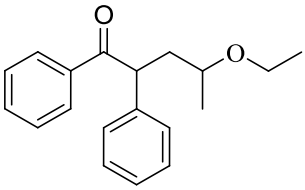
1,2-diphenyl-3-(tetrahydrofuran-2-yl)propan-1-one (3ac): Yield = 70% (1:1.2 dr). Colorless oil. IR (KBr) ν = 2925, 1717, 1678, 1597, 1580 ,1493, 1448, 1249, 1174, 1066, 1027, 954, 758, 697 cm^{-1}. ^1H NMR (400MHz, $CDCl_3$): δ = 7.99 (t, J = 7.8 Hz, 2H), 7.50–7.43 (m, 1H), 7.41–7.34 (m, 3H), 7.33–7.26 (m, 3H), 7.23–7.15 (m, 1H), 4.91 (dd, J = 10.5, 3.9 Hz, 0.45H), 4.86 (dd, J = 9.7, 4.7 Hz, 0.55H), 3.88–3.60 (m, 3H), 2.63–2.54 (m, 0.45H), 2.24–2.16 (m, 0.55H), 2.13–2.07 (m, 0.45H), 2.07–1.99 (m, 0.55H), 1.93–1.76 (m, 3H), 1.54–1.42 (m, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 200.2, 200.2, 140.3, 139.2, 137.3, 136.8, 133.1, 132.9, 129.2, 129.1, 129.0, 128.9, 128.7, 128.6, 128.3, 127.2, 127.2, 77.4, 76.3, 67.8, 67.7, 50.9, 50.6, 40.7, 39.8, 32.0, 31.8, 25.9, 25.9 ppm. HRMS m/z: calcd for $C_{19}H_{21}O_2$ $[M+H]^+$ 281.1542, found: 281.1538.



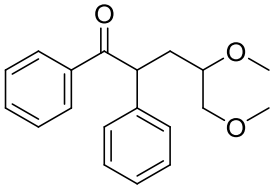
3-(2-ethyl-2-methyl-1,3-dioxolan-4-yl)-1,2-diphenylpropan-1-one (3ad): Yield = 61% (3:4:4:4 dr). Colorless oil. IR (KBr) ν = 2976, 2935, 2880, 1724, 1680, 1597, 1492, 1447, 1374, 1249, 1177, 1067, 1030, 1001, 971, 923, 886, 757, 697 cm^{-1}. ^1H NMR (400MHz, $CDCl_3$): δ = 8.01–7.95 (m, 2H), 7.49–7.44 (m, 1H), 7.40–7.35 (m, 2H), 7.35–7.32 (m, 2H), 7.30–7.27 (m, 2H), 7.24–7.19 (m, 1H), 4.92–4.81 (m, 1H), 4.12–3.99 (m, 1H), 3.90–3.76 (m, 1H), 3.57–3.40 (m, 1H), 2.64–2.54 (m, 0.5H), 2.27–2.12 (m, 1H), 1.95–1.80 (m, 0.5H), 1.70–1.54 (m, 2H), 1.33 (s, 0.8H), 1.33 (s, 0.8H), 1.25 (s, 0.8H), 1.22 (s, 0.6H), 1.00–0.79 (m, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 199.9, 199.7, 199.6, 146.0, 143.7, 140.0, 139.9, 138.8, 138.8, 137.1, 137.0, 136.6, 136.6, 133.2, 133.1, 133.1, 129.3, 129.3, 129.2, 129.2, 129.1, 129.1, 129.0, 128.8, 128.7, 128.7, 128.7, 128.4, 128.2, 128.2, 127.5, 127.1, 114.2, 111.2, 111.1, 111.1, 110.9, 74.7, 74.1, 73.7, 73.1, 70.1, 70.0, 69.9, 69.7, 50.6, 50.6, 50.2, 50.2, 38.8, 38.6, 37.5, 37.1, 33.0, 33.0, 32.2, 32.1, 24.8, 24.8, 23.9, 23.8, 8.7, 8.6, 8.5, 8.4 ppm. HRMS m/z: calcd for $C_{21}H_{24}O_3$ $[M]^+$ 324.1725, found: 324.1718.



3-(1,3-dioxolan-2-yl)-1,2-diphenylpropan-1-one (3ae): Yield = 43%. White soild. M.p. 36.0–38.0 °C. IR (KBr) ν = 2957, 2929, 1681, 1597, 1447, 1279, 1251, 1175, 1069, 1026, 983, 762, 694 cm^{-1}. ^1H NMR (400MHz, $CDCl_3$): δ = 8.01–7.96 (m, 2H), 7.64–7.59 (m, 1H), 7.50–7.49 (m, 2H), 7.39–7.33 (m, 3H), 7.30–7.28 (m, 1H), 7.22–7.16 (m, 1H), 4.90–4.85 (m, 1H), 4.83–4.79 (m, 1H), 3.98–3.91 (m, 1H), 3.89–3.74 (m, 3H), 2.73–2.64 (m, 1H), 2.21–2.12 (m, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 199.4, 139.2, 136.9, 134.0, 133.0, 130.4, 129.2, 129.0, 128.7, 128.5, 127.3, 102.8, 65.1, 65.0, 48.6, 38.0 ppm. HRMS m/z: calcd for $C_{18}H_{19}O_3$ $[M+H]^+$ 283.1334, found: 283.1342.

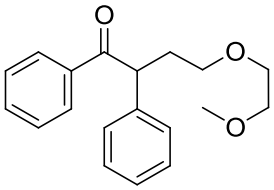


4-ethoxy-1,2-diphenylpentan-1-one (3af): Yield = 45% (1:1.4 dr). Colorless oil. IR (KBr) ν = 3412, 3027, 2971, 1680, 1597, 1493, 1447, 1372, 1269, 1249, 1140, 1094, 1073, 757, 697 cm^{-1}. ^1H NMR (400MHz, $CDCl_3$): δ = 7.99 (t, J = 7.2 Hz, 2H), 7.51–7.44 (m, 1H), 7.43–7.35 (m, 2H), 7.34–7.30 (m, 2H), 7.29–7.25 (m, 2H), 7.23–7.15 (m, 1H), 4.99 (dd, J = 10.5, 4.1 Hz, 0.4H), 4.88 (dd, J = 9.1, 5.3 Hz, 0.6H), 3.61–3.46 (m, 1H), 3.43–3.37 (m, 0.4H), 3.28–3.09 (m, 1.6H), 2.51–2.42 (m, 0.4H), 2.31–2.22 (m, 0.6H), 2.06–1.97 (m, 0.6H), 1.88–1.79 (m, 0.4H), 1.18 (t, J = 7.0 Hz, 3H), 1.13–1.01 (m, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 200.5, 200.2, 140.1, 139.5, 137.4, 137.0, 133.1, 132.9, 129.1, 129.0, 129.0, 128.8, 128.8, 128.7, 128.6, 128.4, 127.2, 127.1, 73.2, 72.6, 63.9, 63.8, 50.1, 49.3, 42.2, 41.2, 20.2, 20.0, 15.9, 15.7 ppm. HRMS m/z: calcd for $C_{19}H_{23}O_2$ $[M+H]^+$ 283.1698, found: 283.1699.

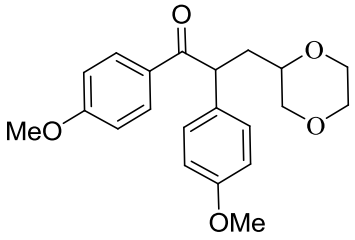


4,5-dimethoxy-1,2-diphenylpentan-1-one (3ag): Yield = 42% (1:1.3 dr). Colorless oil. IR (KBr) ν = 2925, 2828, 1723, 1697, 1597, 1448, 1356, 1175, 1124, 1093, 1076, 1058, 925, 759, 697 cm^{-1}. ^1H NMR (400MHz, $CDCl_3$): δ = 8.01–7.95 (m, 2H), 7.49–7.43 (m, 1H), 7.42–7.35 (m, 2H),

7.34–7.26 (m, 4H), 7.22–7.17 (m, 1H), 4.92 (dd, *J* = 10.2, 4.4 Hz, 0.45H), 4.87 (dd, *J* = 8.8, 5.6 Hz, 0.55H), 3.91–3.86 (m, 0.45H), 3.62–3.56 (m, 0.45H), 3.48 (dd, *J* = 10.1, 3.8 Hz, 0.55H), 3.42 (dd, *J* = 5.5, 2.3 Hz, 0.55H), 3.38 (s, 1.5H), 3.35 (s, 1.5H), 3.34–3.32 (m, 0.45H), 3.27 (s, 1.5H), 3.27 (s, 1.5H), 3.16–3.09 (m, 0.55H), 2.54–2.44 (m, 0.45H), 2.40–2.31 (m, 0.55H), 2.11–2.02 (m, 0.55H), 2.00–1.91 (m, 0.45H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 200.2, 199.9, 140.0, 139.3, 137.2, 136.9, 133.1, 132.9, 130.0, 129.1, 129.0, 128.9, 128.8, 128.7, 128.7, 128.4, 127.3, 127.2, 78.0, 77.3, 74.9, 74.5, 59.4, 59.3, 57.8, 57.7, 49.7, 49.3, 36.7, 36.1 ppm. HRMS m/z: calcd for $C_{19}H_{23}O_3$ $[M+H]^+$ 299.1647, found: 299.1646.

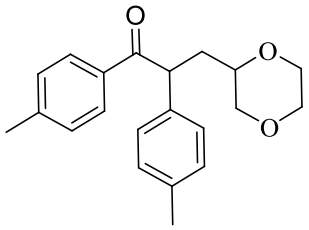


4-(2-methoxyethoxy)-1,2-diphenylbutan-1-one (3ag'): Yield = 21%. Colorless oil. IR (KBr) ν = 2955, 2850, 1680, 1597, 1448, 1352, 1266, 1101, 1081, 964, 756, 741, 697 cm^{-1}. ^{1}H NMR (400MHz, $CDCl_3$): δ = 8.01–7.94 (m, 2H), 7.47 (t, *J* = 7.4 Hz, 1H), 7.37 (t, *J* = 7.6 Hz, 2H), 7.33–7.26 (m, 4H), 7.22–7.16 (m, 1H), 4.87 (t, *J* = 7.3 Hz, 1H), 3.54–3.44 (m, 5H), 3.38 (dd, *J* = 6.2, 3.5 Hz, 1H), 3.36 (d, *J* = 4.7 Hz, 3H), 2.48 (dd, *J* = 13.2, 6.1 Hz, 1H), 2.16–2.02 (m, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 200.1, 139.4, 137.1, 133.0, 129,1, 129.0, 128.7, 127.2, 72.1, 70.2, 68.7, 59.2, 49.9, 33.8 ppm. HRMS m/z: calcd for $C_{19}H_{23}O_3$ $[M+H]^+$ 299.1647, found: 299.1642.

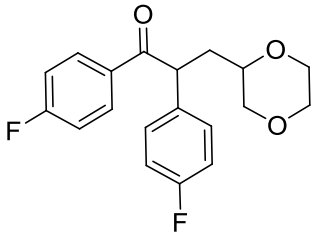


3-(1,4-dioxan-2-yl)-1,2-bis(4-methoxyphenyl)propan-1-one (3ba): Yield = 80% (1:1.2 dr). Colorless oil. IR (KBr) ν = 2956, 2914, 2849, 1720, 1669, 1598, 1574, 1509, 1456, 1420, 1245, 1167, 1119, 1028, 935, 870, 829, 786, 713 cm^{-1}. ^{1}H NMR (400MHz, $CDCl_3$): δ = 7.99–7.92 (m, 2H), 7.23–7.18 (m, 2H), 6.89–6.78 (m, 4H), 4.84 (dd, *J* = 10.9, 3.6 Hz, 0.45H), 4.78 (dd, *J* = 10.3, 4.4 Hz, 0.55 H), 3.82 (s, 1.3H), 3.81 (s, 1.7H), 3.75 (s, 1.7H), 3.74 (s, 1.3H), 3.72–3.49 (m, 5.5H), 3.35–3.32 (m, 1.5H), 2.40–2.32 (m, 0.45H), 2.06–1.97 (m, 0.55H), 1.93–1.85 (m, 0.55H), 1.68–1.59 (m, 0.45H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 198.4, 198.2, 163.3, 163.2, 158.7, 158.6, 132.2,

131.1, 131.1, 131.0, 129.9, 129.4, 129.4, 129.0, 114.4, 113.7, 113.6, 73.6, 72.6, 71.4, 71.3, 66.8, 66.7, 66.5, 66.5, 55.4, 55.4, 55.2, 47.5, 47.1, 36.2, 34.8 ppm. HRMS m/z: calcd for $C_{21}H_{25}O_5$ $[M+H]^+$ 357.1702, found: 357.1689.

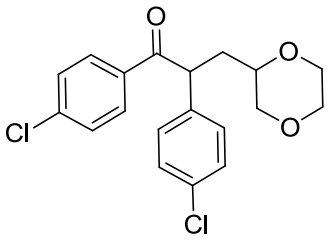


3-(1,4-dioxan-2-yl)-1,2-dip-tolylpropan-1-one (3ca): Yield = 89% (1:1.5 dr). Colorless oil. IR (KBr) ν = 2955, 2918, 2852, 1724, 1675, 1606, 1510, 1408, 1447, 1242, 1199, 1175, 1121, 1078, 935, 814, 761 cm^{-1}. ^1H NMR (400MHz, $CDCl_3$): δ = 7.91–7.84 (m, 2H), 7.20–7.13 (m, 4H), 7.11–7.04 (m, 2H), 4.87 (dd, *J* = 10.9, 3.6 Hz, 0.4H), 4.80 (dd, *J* = 10.7, 3.6 Hz, 0.6H), 3.79–3.70 (m, 1H), 3.67–3.50 (m, 4H), 3.35–3.32 (m, 2H), 2.40 (dd, *J* = 9.8, 6.6 Hz, 0.4H), 2.35 (s, 1.2H), 2.33 (s, 1.8H), 2.28 (s, 1.8H), 2.26 (s, 1.2H), 2.08–1.99 (m, 0.6H), 1.93–1.85 (m, 0.6H), 1.68–1.60 (m, 0.4H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 199.6, 199.4, 143.9, 143.7, 137.1, 137.0, 136.9, 136.0, 134.6, 134.1, 129.9, 129.9, 129.4, 129.3, 129.1, 129.1, 128.5, 128.1, 73.7, 72.7, 71.6, 71.5, 67.0, 66.9, 66.7, 66.7, 48.4, 48.1, 36.3, 35.0, 21.8, 21.8, 21.2, 21.2 ppm. HRMS m/z: calcd for $C_{21}H_{25}O_3$ $[M+H]^+$ 325.1804, found: 325.1810.

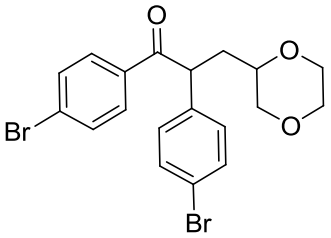


3-(1,4-dioxan-2-yl)-1,2-bis(4-fluorophenyl)propan-1-one (3da): Yield = 70% (1:1.3 dr). Colorless oil. IR (KBr) ν = 2958, 2917, 2854, 1725, 1680, 1596, 1506, 1409, 1225, 1121, 1078, 993, 912, 833, 799, 773, 685 cm^{-1}. ^1H NMR (400MHz, $CDCl_3$): δ = 8.02–7.94 (m, 2H), 7.27–7.21 (m, 2H), 7.10–6.94 (m, 4H), 4.89 (dd, *J* = 11.0, 3.5 Hz, 0.43H), 4.83 (dd, *J* = 10.2, 4.4 Hz, 0.57H), 3.80–3.49 (m, 5.5H), 3.35–3.20 (m, 1.5H), 2.41–2.32 (m, 0.43H), 2.08–2.00 (m, 0.57H), 1.92–1.84 (m, 0.57H), 1.68–1.60 (m, 0.43H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 198.2, 198.2, 167.1 (d, $J_{C\text{-}F}$ = 12.9 Hz), 164.6 (d, $J_{C\text{-}F}$ = 12.5 Hz), 163.4 (d, $J_{C\text{-}F}$ = 10.4 Hz), 161.0 (d, $J_{C\text{-}F}$ = 10.2 Hz), 135.5 (d, $J_{C\text{-}F}$ = 3.3 Hz), 134.3 (d, $J_{C\text{-}F}$ = 3.2 Hz),, 133.3 (d, $J_{C\text{-}F}$ = 3.0 Hz), 132.8 (d, $J_{C\text{-}F}$ = 3.0 Hz), 131.6 (d, $J_{C\text{-}F}$ = 9.3 Hz), 131.6 (d, $J_{C\text{-}F}$ = 9.3 Hz), 130.2 (d, $J_{C\text{-}F}$ = 8.0 Hz), 129.7 (d, $J_{C\text{-}F}$ = 8.0 Hz), 116.3 (d, $J_{C\text{-}F}$ = 8.0

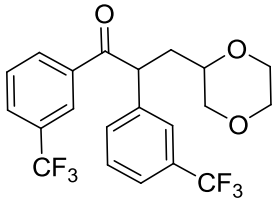
Hz), 116.2 (d, $J_{C\text{-}F}$ = 21.3 Hz), 116.2 (d, $J_{C\text{-}F}$ = 21.4 Hz), 115.9 (d, $J_{C\text{-}F}$ = 21.7 Hz), 115.9 (d, $J_{C\text{-}F}$ = 21.7 Hz), 73.5, 72.5, 71.5, 71.5, 67.0, 66.9, 66.7, 48.1, 47.7, 36.4, 35.0 ppm. HRMS m/z: calcd for $C_{19}H_{19}F_2O_3$ $[M+H]^+$ 333.1302, found: 333.1306.



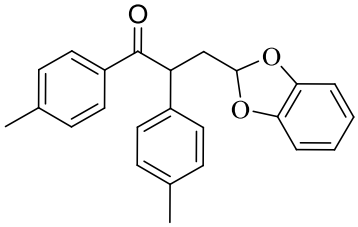
1,2-bis(4-chlorophenyl)-3-(1,4-dioxan-2-yl)propan-1-one (3ea): Yield = 82% (1:1.3 dr). Colorless oil. IR (KBr) ν = 2962, 2922, 2859, 1728, 1688, 1611, 1491, 1449, 1327, 1256, 1163, 1118, 1071, 895, 806, 702, 693 cm^{-1}. ^1H NMR (400MHz, $CDCl_3$): δ = 8.28–8.20 (m, 1H), 8.12 (t, J = 8.7 Hz, 1H), 7.81–7.73 (m, 1H), 7.61–7.41 (m, 5H), 5.04 (dd, J = 11.2, 3.3 Hz, 0.4H), 4.95 (dd, J = 9.9, 4.7 Hz, 0.6H), 3.81–3.51 (m, 5.4H), 3.35–3.19 (m, 1.6H), 2.48–2.39 (m, 0.4H), 2.16–2.08 (m, 0.6H), 1.98–1.90 (m, 0.6H), 1.74–1.66 (m, 0.4H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 198.4, 198.4, 138.6, 137.5, 135.5, 135.1, 132.5, 132.2, 132.1, 139.5, 130.4, 139.3, 129.9, 128.7, 128.5, 121,7, 121.6, 73.4, 72.4, 71.5, 71.4, 67.0, 66.9, 66.6, 48.4, 47.9, 36.1, 34.8 ppm. HRMS m/z: calcd for $C_{19}H_{19}Cl_2O_3$ $[M+H]^+$ 365.0711, found: 365.0714.



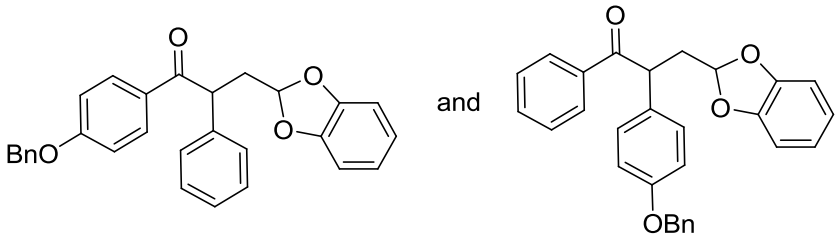
1,2-bis(4-bromophenyl)-3-(1,4-dioxan-2-yl)propan-1-one (3fa): Yield = 78% (1:1.3 dr). Colorless oil. IR (KBr) ν = 2956, 2913, 2851, 1719, 1680, 1584, 1567, 1447, 1396, 1341, 1277, 1121, 1070, 1009, 959, 870, 817, 734, 684 cm^{-1}. ^1H NMR (400MHz, $CDCl_3$): δ = 7.92–7.84 (m, 2H), 7.40–7.33 (m, 2H), 7.31–7.25 (m, 2H), 7.23–7.18 (m, 2H), 4.87 (dd, J = 11.0, 3.5 Hz, 0.43H), 4.81 (dd, J = 10.2, 4.4 Hz, 0.57H), 3.79–3.51 (m, 5.4H), 3.34–3.21 (m, 1.6H), 2.41–2.32 (m, 0.43H), 2.09–2.00 (m, 0.57H), 1.91–1.83 (m, 0.57H), 1.67–1.58 (m, 0.43H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 198.3, 198.3, 139.9, 139.7, 138.1, 137.0, 135.2, 134.7, 133.6, 133.5, 130.4, 130.3, 130.0, 129.5, 129.2, 129.1, 73.4, 72.5, 71.5, 71.4, 67.0, 66.9, 66.7, 48.3, 47.9, 36.2, 34.8 ppm. HRMS m/z: calcd for $C_{19}H_{19}Br_2O_3$ $[M+H]^+$ 452.9701, found: 452.9721.



3-(1,4-dioxan-2-yl)-1,2-bis(3-(trifluoromethyl)phenyl)propan-1-one (3ga): Yield = 76% (1:1 dr). Colorless oil. IR (KBr) ν = 2957, 2915, 2853, 1724, 1680, 1588, 1488, 1399, 1262, 1121, 1090, 1078, 1013, 960, 870, 745, 713, 690 cm^{-1}. ^1H NMR (400MHz, $CDCl_3$): δ = 7.83–7.76 (m, 2H), 7.56–7.50 (m, 2H), 7.46–7.38 (m, 2H), 7.18–7.11 (m, 2H), 4.85 (dd, *J* = 11.0, 3.5 Hz, 0.43H), 4.79 (dd, *J* = 10.2, 4.4 Hz, 0.57H), 3.78–3.48 (m, 5.3H), 3.34–3.20 (m, 1.6H), 2.40–2.32 (m, 0.43H), 2.09–2.01 (m, 0.57H), 1.91–1.83 (m, 0.57H), 1.67–1.59 (m, 0.43H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 198.3, 197.9, 140.2, 139.2, 137.4, 136.8, 132.0, 131.9, 131.9, 131.8, 131.7, 131.6, 131.6, 131.4, 131.4, 130.0, 129.9, 129.9, 129.9, 129.8, 129.8, 129.7, 129.7, 129.6, 129.5, 125.9 (m), 125.6 (dd, $J_{C\text{-}F}$ = 7.4, 3.7 Hz), 125.1 (dd, $J_{C\text{-}F}$ = 7.6, 3.7 Hz), 124.7 (m), 73.2, 72.5, 71.4, 66.9, 66.9, 66.7, 48.9, 48.3, 36.4, 35.0 ppm. HRMS m/z: calcd for $C_{21}H_{19}F_6O_3$ $[M+H]^+$ 433.1238, found: 433.1231.

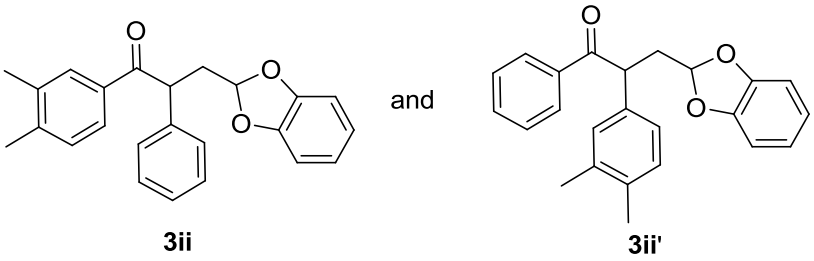


3-(benzo[*d*][1,3]dioxol-2-yl)-1,2-dip-tolylpropan-1-one (3ci): Yield = 71%. Colorless oil. IR (KBr) ν = 2922, 2855, 1676, 1606, 1482, 1460, 1231, 1176, 1096, 1018, 964, 813, 737, 681 cm^{-1}. ^1H NMR (400MHz, $CDCl_3$): δ = 7.85 (d, *J* = 8.2 Hz, 2H), 7.70 (d, *J* = 8.0 Hz, 1H), 7.22 (d, *J* = 8.0 Hz, 2H), 7.16 (d, *J* = 8.3 Hz, 2H), 7.11–7.08 (m, 1H), 6.80–6.72 (m, 3H), 6.72–6.68 (m, 1H), 6.02–5.98 (m, 1H), 4.88 (t, *J* = 7.3 Hz, 1H), 2.84 (dd, *J* = 13.9, 7.6 Hz, 1H), 2.43– 2.38 (m, 1H), 2.33 (s, 3H), 2.27 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 198.3, 147.7, 144.0, 143.1, 137.3, 135.7, 133.9, 130.4, 130.1, 129.4, 129.1, 128.3, 121.6, 110.2, 108.8, 108.7, 47.7, 38.5, 21.8, 21.2 ppm. HRMS m/z: calcd for $C_{24}H_{23}O_3$ $[M+H]^+$ 359.1647, found: 359.1655.



3hi **3hi'**

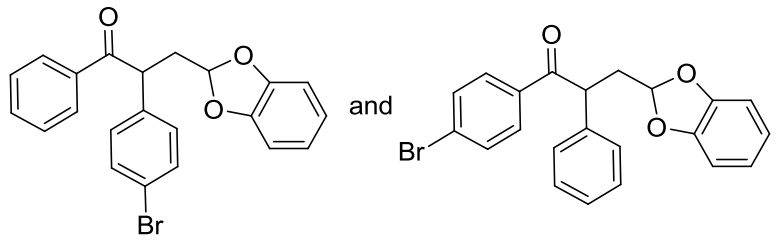
3-(benzo[*d*][1,3]dioxol-2-yl)-1-(4-(benzyloxy)phenyl)-2-phenylpropan-1-one (3hi) and 3-(benzo[*d*][1,3]dioxol-2-yl)-2-(4-(benzyloxy)phenyl)-1-phenylpropan-1-one (3hi'): Yield = 49% (**3hi**:**3hi'**=4:1). Colorless oil. IR (KBr) ν = 3062, 3031, 2927, 1673, 1597, 1508, 1482, 1453, 1351, 1230, 1167, 1096, 1005, 965, 831, 803, 735, 696 cm^{-1}. The ^{1}H NMR spectrum of the isolated product showed a 4:1 mixture of **3hi** and its isomer **3hi'**. ^{1}H NMR (400MHz, $CDCl_3$) **3hi**: δ = 7.95–7.92 (m, 2H), 7.48–7.42 (m, 1H), 7.39–7.37 (m, 4H), 7.36–7.34 (m, 2H), 7.34–7.32 (m, 2H), 7.31–7.28 (m, 2H), 7.23–7.18 (m, 1H), 6.78–6.75 (m, 3H), 6.70–6.67 (m, 1H), 6.02 (t, *J* = 2.2 Hz, 1H), 5.07 (s, 2H), 4.89 (t, *J* = 4.9 Hz, 1H), 2.91–2.85 (m, 1H), 2.47–2.42 (m, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 198.8, 197.1, 162.8, 158.4, 147.7, 147.7, 147.6, 138.9, 136.4, 136.3, 131.4, 129.6, 129.5, 129.4, 129.0, 128.9, 128.8, 128.7, 128.5, 128.4, 128.2, 128.7, 127.7, 127.6, 121.6, 115.7, 114.8, 114.6, 110.1, 108.8, 108.7, 70.3, 70.2, 47.9, 47.3, 38.7, 38.6 ppm. HRMS m/z: calcd for $C_{29}H_{25}O_4$ $[M+H]^+$ 437.1753, found: 437.1742.



3ii **3ii'**

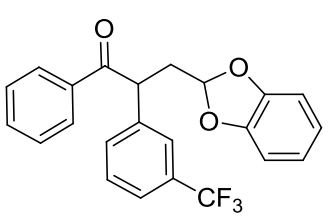
3-(benzo[*d*][1,3]dioxol-2-yl)-1-(3,4-dimethylphenyl)-2-phenylpropan-1-one (3ii) and 3-(benzo[*d*][1,3]dioxol-2-yl)-2-(3,4-dimethylphenyl)-1-phenylpropan-1-one (3ii'): Yield = 53% (**3ii**:**3ii'**=1.6:1). Colorless oil. IR (KBr) ν = 2921, 1676, 1727, 1482, 1448, 1351, 1231, 1117, 1096, 1021, 970, 862, 809, 735, 699 cm^{-1}. The ^{1}H NMR spectrum of the isolated product showed a 1.6:1 mixture of **3ii** and its isomer **3ii'**. ^{1}H NMR (400MHz, $CDCl_3$) **3ii** and **3ii'**: δ = 7.95 (dd, *J* = 5.2, 3.3 Hz, 0.7H), 7.80–7.76 (m, 0.3H), 7.74–7.71 (m, 0.5H), 7.68 (m, 0.5H), 7.63–7.44 (m, 1H), 7.39–7.32 (m, 2H), 7.31–7.27(m, 1H), 7.23–7.17 (m, 0.7H), 7.13–7.05 (m, 1.3H), 6.79–6.72 (m, 3H), 6.71–6.66 (m, 1H), 6.03–6.00 (m, 0.6H), 6.01–5.99 (m, 0.4H), 4.93 (t, *J* = 7.3 Hz, 0.6H), 4.88 (t, *J* = 7.3 Hz, 0.4H),

2.92–2.86 (m, 0.6H), 2.87–2.82 (m, 0.4H), 2.48–2.42 (m, 0.6H), 2.44–2.39 (m, 0.4H), 2.25 (s,2H), 2.24 (s, 2H), 2.20 (s, 1H), 2.18 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) **3ii** and **3ii'**: δ = 198.8, 198.5, 147.7, 147.7, 142.9, 138.8, 137.7, 137.1, 136.5, 136.0, 135.8, 134.2, 133.1, 130.6, 130.2, 129.9, 129.4, 129.3, 129.0, 128.7, 128.4, 127.5, 126.8, 125.9, 121.6, 110.2, 110.1, 108.8, 108.8, 108.7, 48.0, 47.8, 38.6, 38.6, 20.2, 20.2, 20.0, 20.0 ppm. HRMS m/z: calcd for $C_{24}H_{23}O_3$ $[M+H]^+$ 359.1647, found: 359.1633.



3ji **3ji'**

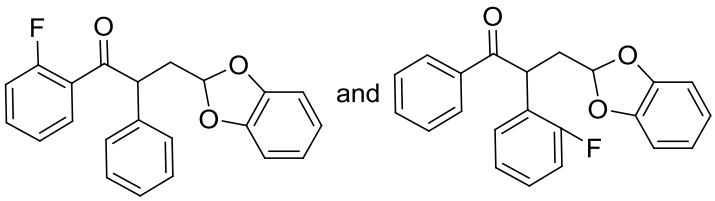
3-(benzo[*d*][1,3]dioxol-2-yl)-2-(4-bromophenyl)-1-phenylpropan-1-one (3ji) and 3-(benzo[*d*][1,3]dioxol-2-yl)-1-(4-bromophenyl)-2-phenylpropan-1-one (3ji'): Yield = 60% (**3ji**:**3ji'**=1.1:1). Colorless oil. IR (KBr) ν = 2926, 1718, 1681, 1584, 1482, 1447, 1396, 1265, 1231, 1174, 1096, 1070, 1010, 989, 964, 805, 737, 700, 669 cm^{-1}. The ^{1}H NMR spectrum of the isolated product showed a 1.1:1 mixture of **3ji** and its isomer **3ji'**. ^{1}H NMR (400MHz, $CDCl_3$) **3ji** and **3ji'**: δ = 7.93–7.88 (m, 1H), 7.80–7.76 (m, 0.6H), 7.70–7.58 (m, 0.6H), 7.53–7.46 (m, 1.4H), 7.45–7.36 (m, 2.6H), 7.31–7.29 (m, 1H), 7.24–7.19 (m, 1.4H), 7.16–7.11 (m, 0.4H), 6.88–6.72 (m, 3H), 6.69–6.66 (m, 1H), 6.04–6.02 (m, 0.5H), 6.02–5.98 (m, 0.5H), 4.93 (t, J = 7.2 Hz, 0.5H), 4.89–4.85 (m, 0.5H), 2.94–2.85 (m, 1H), 2.48–2.39 (m, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) **3ji** and **3ji'**: δ = 198.3, 197.6, 147.6, 147.5, 138.2, 137.5, 136.1, 135.1, 133.5, 132.9, 132.5, 132.1, 131.8, 131.6, 131.6, 130.5, 130.2, 129.9, 129.5, 129.0, 128.8, 128.6, 128.5, 128.5, 128.4, 127.9, 127.8, 121.8, 121.7, 109.9, 109.8, 108.8, 108.8, 108.7, 48.2, 47.4, 38.5, 38.4 ppm. HRMS m/z: calcd for $C_{22}H_{18}BrO_3$ $[M+H]^+$ 409.0439, found: 409.0454/411.0439.



3ki

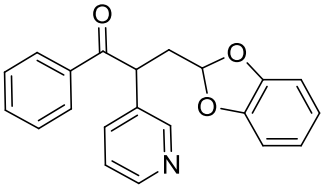
3-(benzo[*d*][1,3]dioxol-2-yl)-1-phenyl-2-(3-(trifluoromethyl)phenyl)propan-1-one (3ki): Yield = 43%. Colorless oil. IR (KBr) ν = 3065, 2933, 1682, 1596, 1483, 1448, 1351, 1327, 1164, 1121,

1096, 1073, 964, 799, 737, 700, 685, 657 cm^{-1}. The ^1H NMR spectrum of the crude product showed a 2.2:1 mixture of **3ki** and its isomer **3ki'**, flash chromatography on silica gel afforded ketone **3ki**. ^1H NMR (400MHz, $CDCl_3$): δ = 7.95–7.91 (m, 2H), 7.62–7.60 (m, 1H), 7.56–7.47 (m, 3H), 7.45–7.37 (m, 3H), 6.80–6.72 (m, 3H), 6.68–6.64 (m, 1H), 6.05 (dd, *J* = 8.8, 4.2 Hz, 1H), 5.05 (dd, *J* = 7.7, 6.7 Hz, 1H), 3.02–2.93 (m, 1H), 2.50–2.42 (m, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 198.2, 147.5, 147.5, 139.6, 136.0, 133.6, 131.8, 129.8, 128.9, 128.9, 125.3 (dd, J_{C-F} = 7.6, 3.7 Hz), 124.6 (dd, J_{C-F} = 7.3, 3.8 Hz), 121.8, 121.8, 109.6, 108.8, 108.8, 47.4, 38.7 ppm. HRMS m/z: calcd for $C_{23}H_{18}F_3O_3$ $[M+H]^+$ 399.1208, found: 399.1216.



3li **3li'**

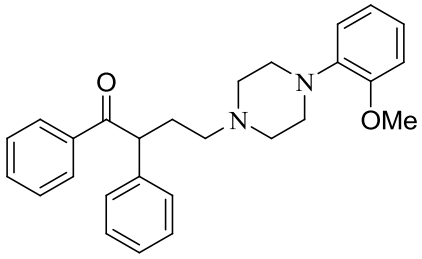
3-(benzo[*d*][1,3]dioxol-2-yl)-1-(2-fluorophenyl)-2-phenylpropan-1-one (3li) and 3-(benzo[*d*][1,3]dioxol-2-yl)-2-(2-fluorophenyl)-1-phenylpropan-1-one (3li'): Yield = 48% (**3li**:**3li'**=2.7:1). Colorless oil. IR (KBr) ν = 2930, 1682, 1608, 1481, 1449, 1351, 1273, 1230, 1096, 1033, 966, 736, 698 cm^{-1}. The ^1H NMR spectrum of the isolated product showed a 1.1:1 mixture of **3li** and its isomer **3li'**. ^1H NMR (400MHz, $CDCl_3$) **3li** and **3li'**: δ = 7.98–7.93 (m, 0.5H), 7.77–7.71 (m, 0.5H), 7.50–7.35 (m, 2H), 7.28 (m, 3H), 7.23–6.98 (m, 3H), 6.87–6.72 (m, 3H), 6.72–6.66 (m, 1H), 6.09 (t, *J* = 4.9 Hz, 0.3H), 6.05–6.00 (m, 0.7H), 5.34–5.29 (m, 0.3H), 4.88 (t, *J* = 7.3 Hz, 0.7H), 2.98–2.88 (m, 1H), 2.46–2.37 (m, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) **3li** and **3li'**: δ = 197.6, 197.6, 147.7, 147.6, 147.6, 137.6, 134.6, 134.5, 133.5, 131.4, 131.3, 129.5, 129.4, 129.1, 128.8, 127.7, 125.1, 125.1, 121.7, 121.6, 121.6, 121.6, 117.0, 116.7, 116.2, 116.0, 110.0, 109.8, 108.8, 108.7, 52.1, 52.1, 38.4 ppm. HRMS m/z: calcd for $C_{22}H_{18}FO_3$ $[M+H]^+$ 349.1240, found: 349.1241.



3mi

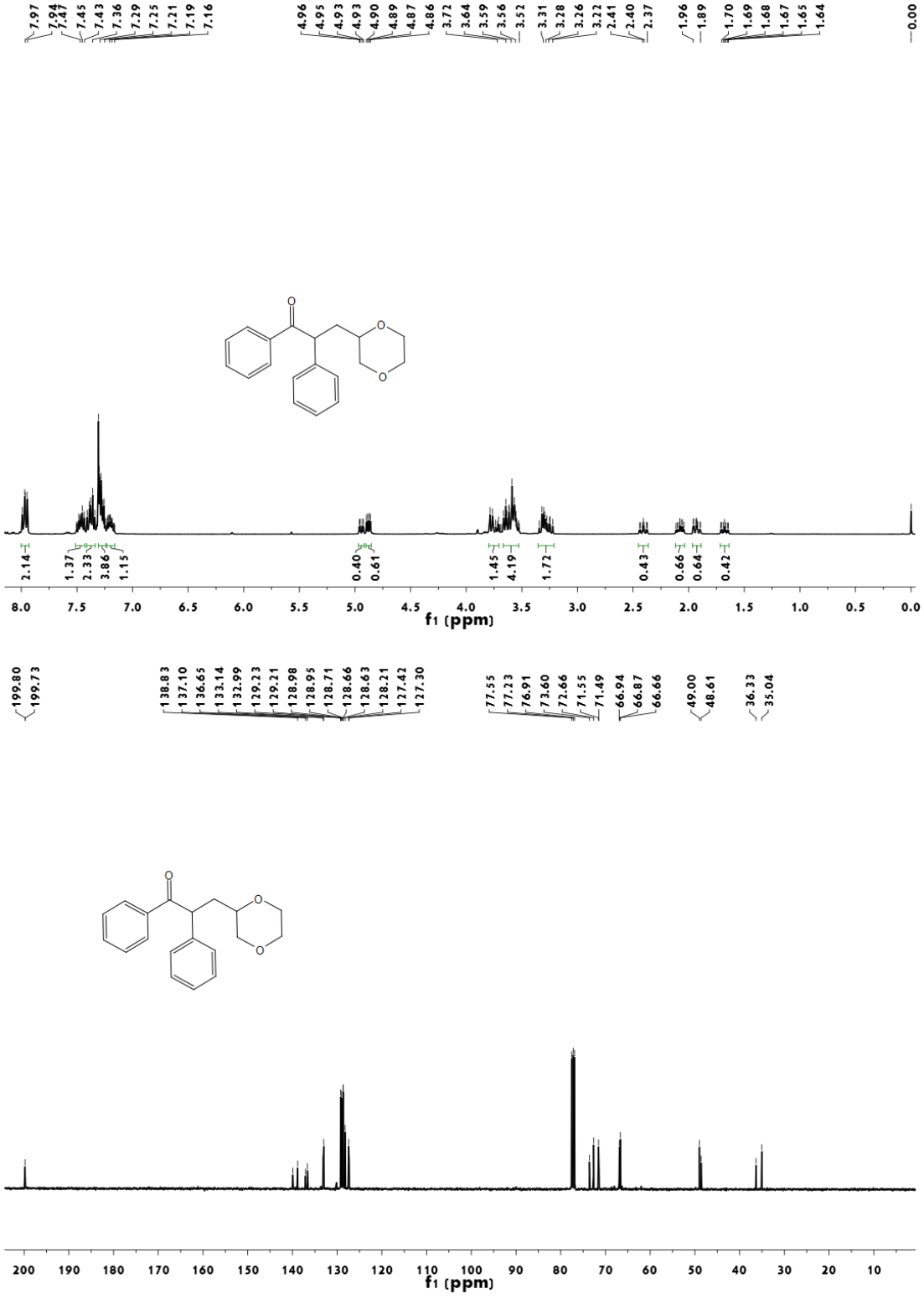
3-(benzo[*d*][1,3]dioxol-2-yl)-1-phenyl-2-(3-(trifluoromethyl)phenyl)propan-1-one (3mi): Yield

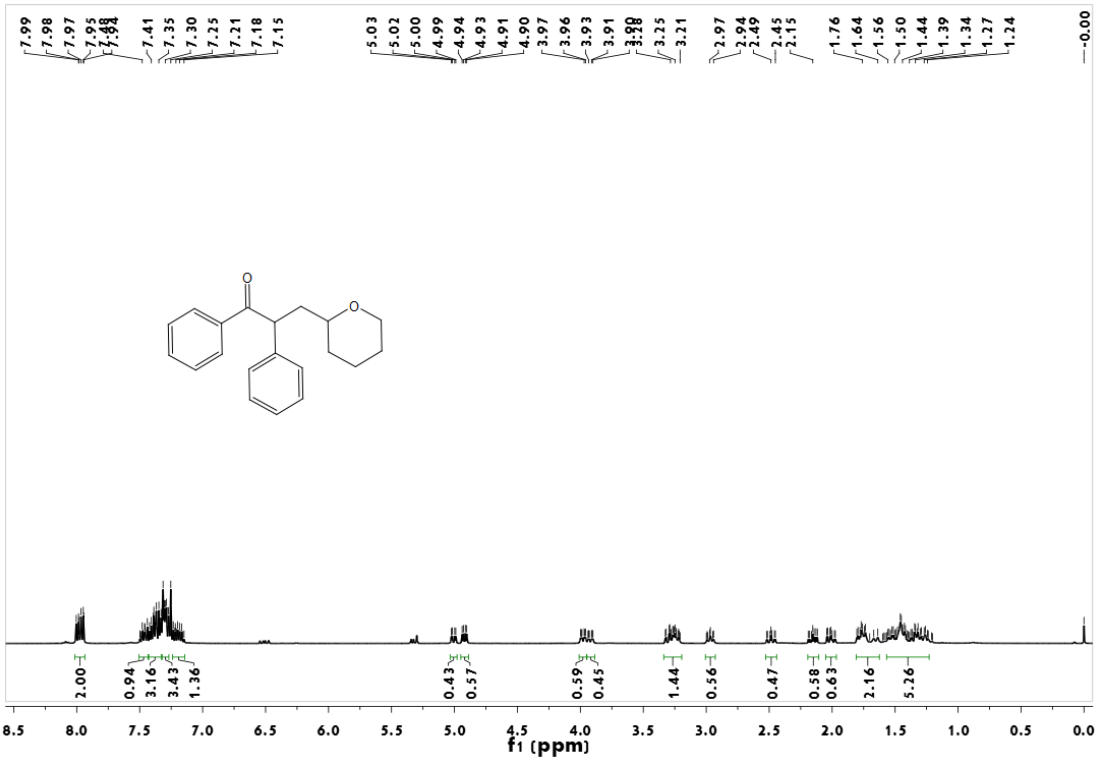
= 60%. White solid. M.p. = 148.8-149.9 ℃. IR (KBr) ν = 2961, 2911, 1680, 1485, 1338, 1261, 1231, 1175, 1123, 1075, 873, 799, 759, 718, 669 cm^{-1}. The ^{1}H NMR spectrum of the crude product showed a 2.3:1 mixture of **3mi** and its isomer **3mi'**, flash chromatography on silica gel afforded ketone **3mi**. ^{1}H NMR (400MHz, $CDCl_3$): δ = 8.64 (d, *J* = 1.9 Hz, 1H), 8.48 (dd, *J* = 4.7, 1.4 Hz, 1H), 7.95–7.90 (m, 2H), 7.70–7.64 (m, 1H), 7.54–7.48 (m, 1H), 7.39 (dd, *J* = 10.6, 4.8 Hz, 2H), 7.23 (dd, *J* = 7.9, 4.9 Hz, 1H), 6.82–6.72 (m, 3H), 6.69–6.65 (m, 1H), 6.07 (t, *J* = 4.7 Hz, 1H), 5.02 (dd, *J* = 7.6, 6.7 Hz, 1H), 3.02–2.93 (m, 1H), 2.50–2.42 (m, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 198.1, 150.2, 149.1, 147.5, 147.4, 135.9, 135.6, 134.4, 133.7, 129.0, 128.9, 124.2, 121.8, 121.8, 109.5, 108.9, 108.8, 45.0, 38.4 ppm. HRMS m/z: calcd for $C_{21}H_{18}NO_3$ $[M+H]^+$ 332.1287, found: 332.1279.



4-(4-(2-methoxyphenyl)piperazin-1-yl)-1,2-diphenylbutan-1-one (5): Yield = 54%. Colorless oil. IR (KBr) ν = 2935, 2813, 1678, 1595, 1499, 1447, 1238, 1138, 1024, 746, 696 cm^{-1}. ^{1}H NMR (400MHz, $CDCl_3$): δ = 7.99 (d, *J* = 7.4 Hz, 2H), 7.47 (t, *J* = 7.3 Hz, 1H), 7.38 (t, *J* = 7.5 Hz, 2H), 7.34 (d, *J* = 7.2 Hz, 2H), 7.28 (t, *J* = 7.6 Hz, 2H), 7.19 (t, *J* = 7.2 Hz, 1H), 7.00–6.95 (m, 1H), 6.93–6.88 (m, 2H), 6.84 (d, *J* = 8.0 Hz, 1H), 4.74 (t, *J* = 7.0 Hz, 1H), 3.83 (s, 3H), 3.08–2.89 (m, 4H), 2.68–2.47 (m, 5H), 2.44–2.36 (m, 2H), 2.02–1.94 (m, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 199.7, 152.4, 141.6, 139.8, 137.3, 132.9, 129.0, 128.9, 128.6, 128.5, 127.2, 123.0, 121.1, 118.3, 111.4, 56.4, 55.5, 53.4, 51.5, 50.7, 31.5 ppm. HRMS m/z: calcd for $C_{27}H_{31}N_2O_2$ $[M+H]^+$ 415.2386, found: 415.2387.

The ^{1}H , ^{13}C spectra of compounds:

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7.41
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7.30
7.25
7.21
7.18
7.15
5.03
5.02
5.00
4.99
4.94
4.93
4.91
4.90
3.97
3.96
3.93
3.91
3.90
3.88
3.25
3.21
2.97
2.94
2.49
2.45
2.15
1.76
1.64
1.56
1.50
1.44
1.39
1.34
1.27
1.24
0.00
2.00
0.94
3.16
3.43
1.36
0.43
0.57
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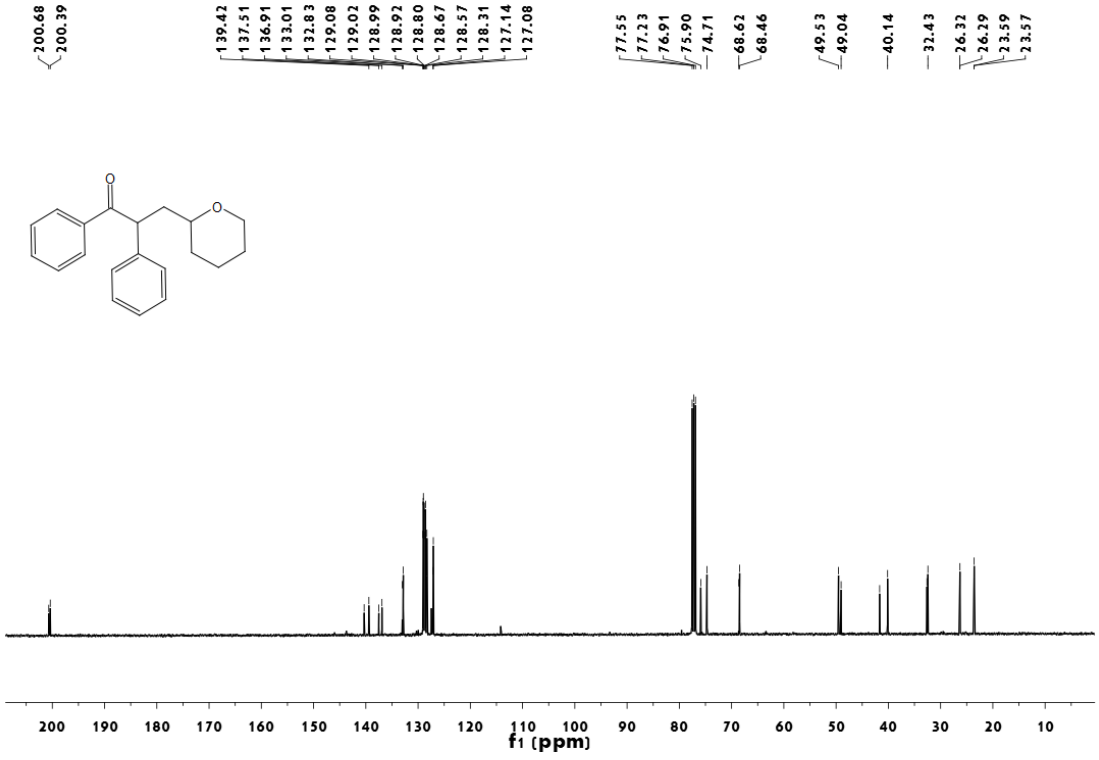
0.45
1.44
0.56
0.47
0.58
0.63
2.16
5.26
f1 (ppm)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129.02
128.99
128.92
128.80
128.67
128.57
128.31
127.14
127.08
77.55
77.23
76.91
75.90
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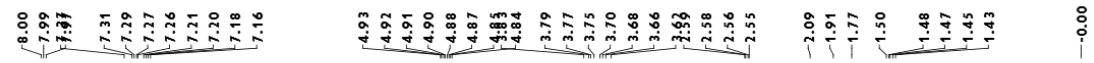
40.14
32.43
26.32
26.29
23.59
23.57
f1 (ppm)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7.99
7.31
7.29
7.27
7.26
7.21
7.20
7.18
7.16
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4.92
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4.88
4.87
4.84
3.79
3.77
3.75
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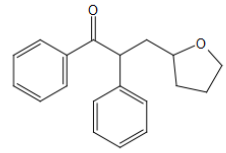
1.45
1.43
0.00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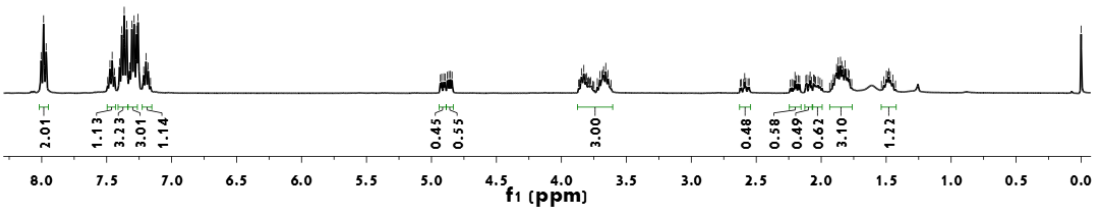
O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3.23
3.01
1.14
0.45
0.55
3.00
0.48
0.58
0.49
0.62
3.10
1.22
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


200.19
200.17
140.25
139.24
137.28
136.84
133.07
132.93
129.16
129.09
129.00
128.86
128.69
128.64
128.26
127.22
127.17
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77.41
77.23
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76.28
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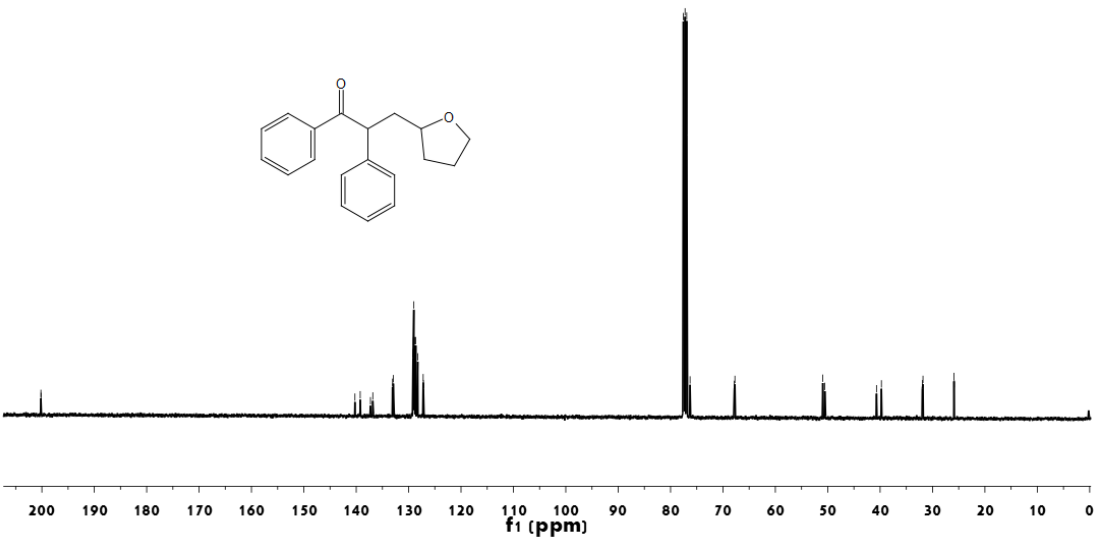
39.75
31.82
25.90
25.86

O
O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190
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90
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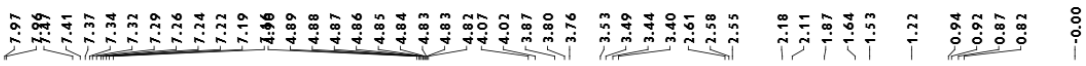
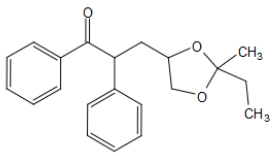
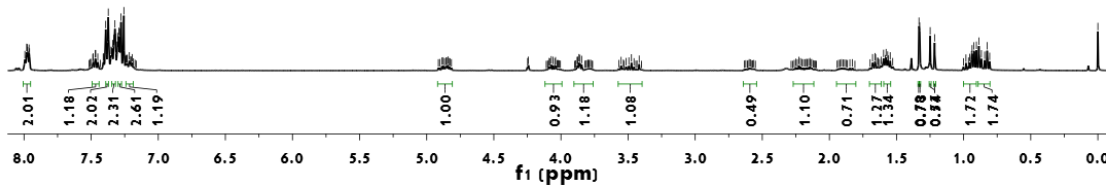
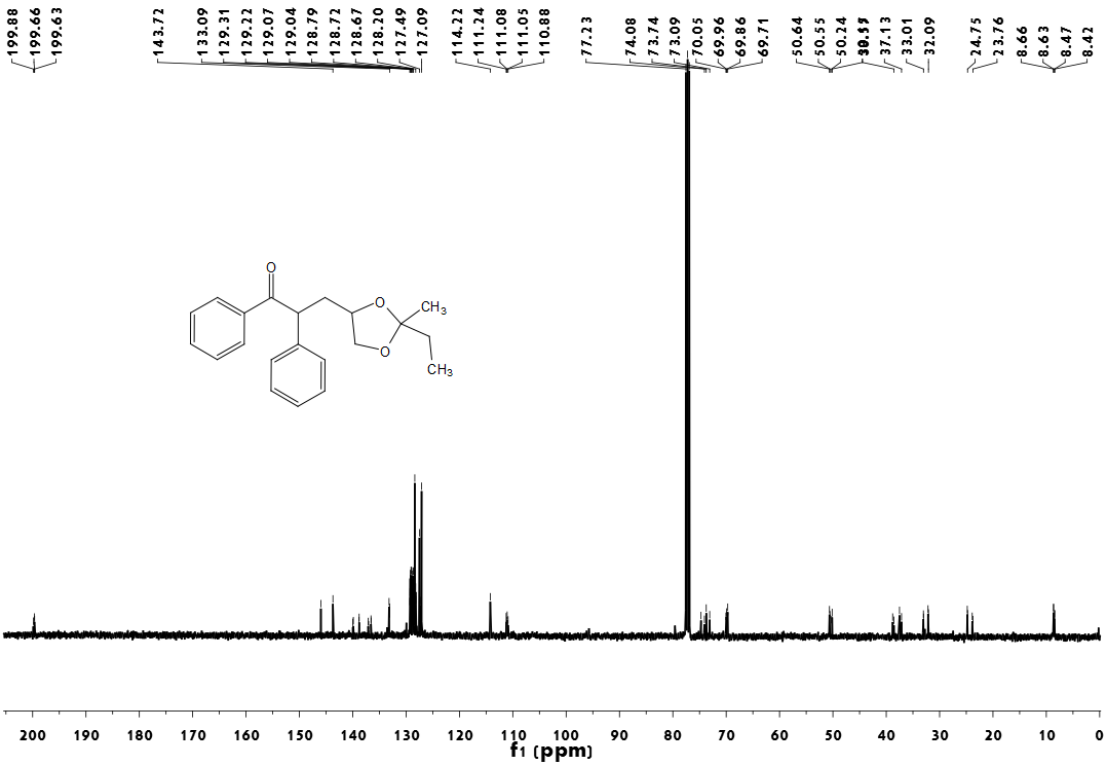
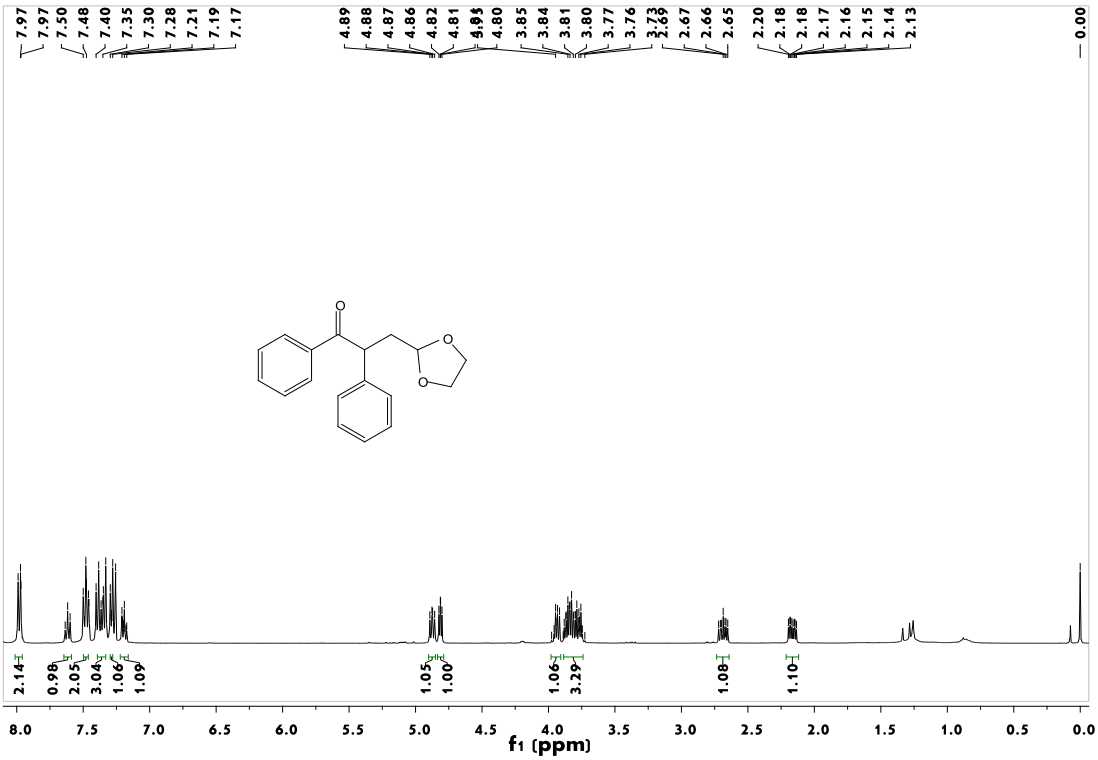
50
40
30
20
10
0
f1 (ppm)







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7.97
7.50
7.48
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7.35
7.30
7.28
7.21
7.19
7.17
4.89
4.88
4.87
4.86
4.82
4.81
4.80
3.85
3.84
3.81
3.80
3.77
3.76
2.67
2.66
2.65
2.20
2.18
2.18
2.17
2.16
2.15
2.14
2.13
0.00
2.14
0.98
2.05
3.04
1.06
1.09
1.05
1.00
1.06
3.29
1.08
1.10
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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3.5
3.0
2.5
2.0
1.5
1.0
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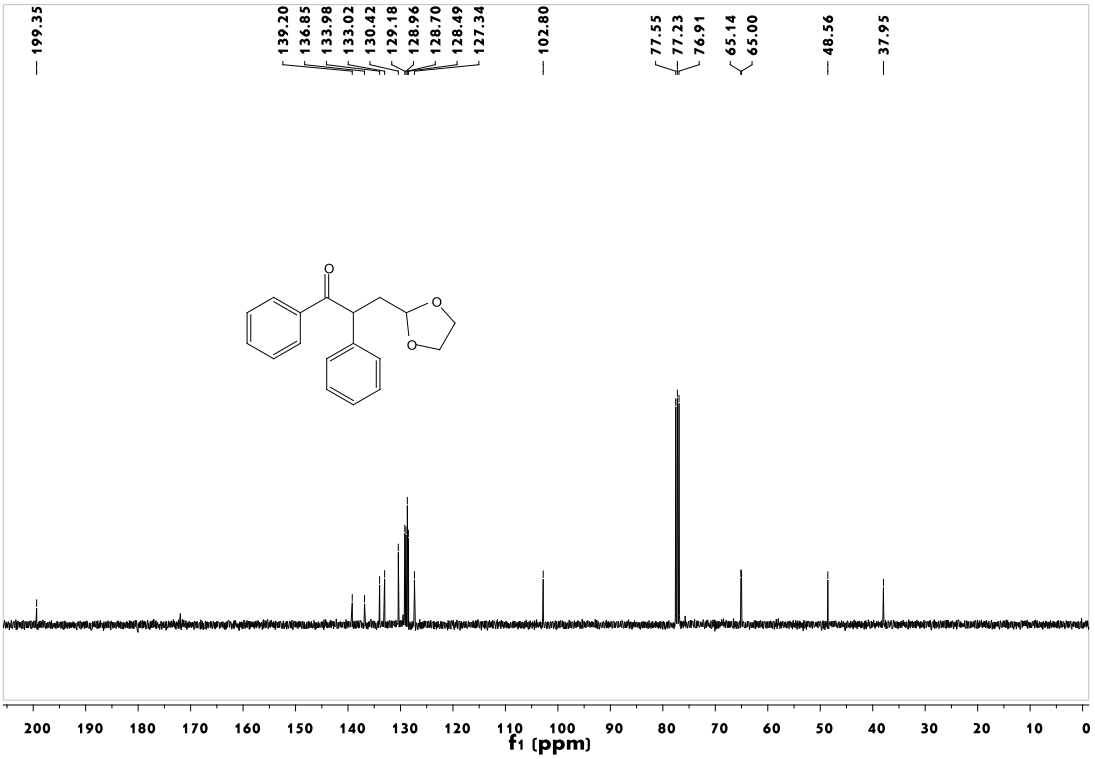
0.0
f1 (ppm)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133.02
130.42
129.18
128.96
128.70
128.49
127.34
102.80
77.55
77.23
76.91
65.14
65.00
48.56
37.95
200
190
180
170
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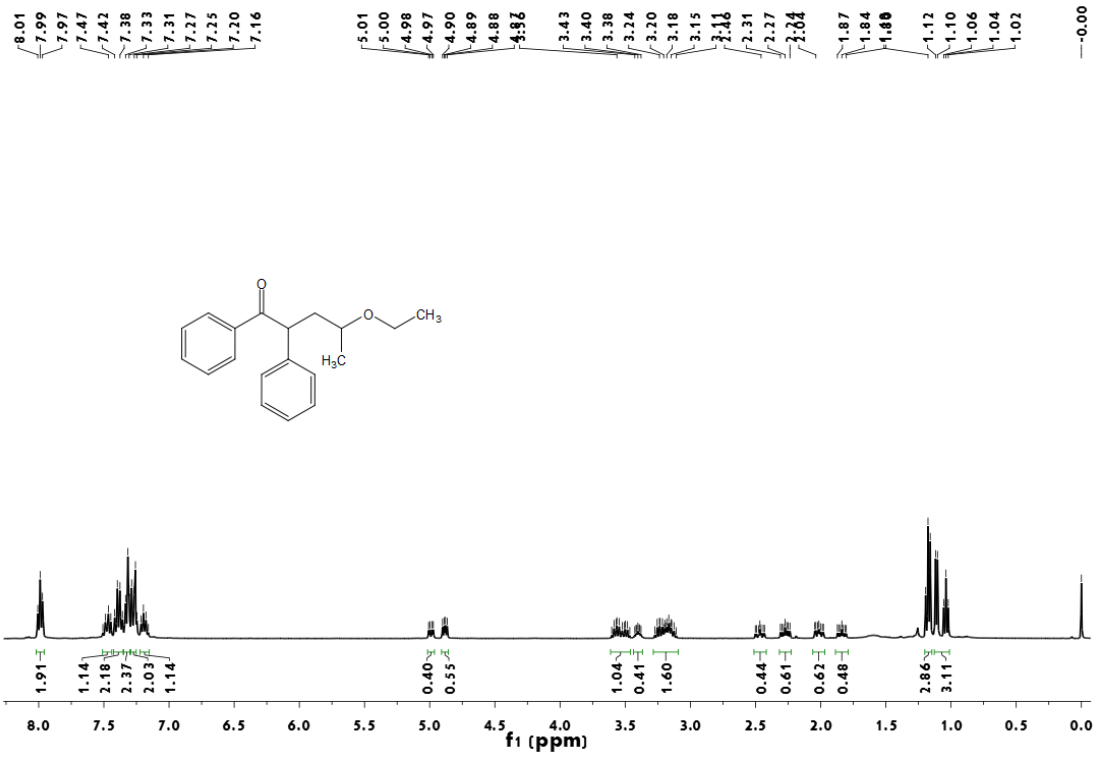
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.99
7.97
7.47
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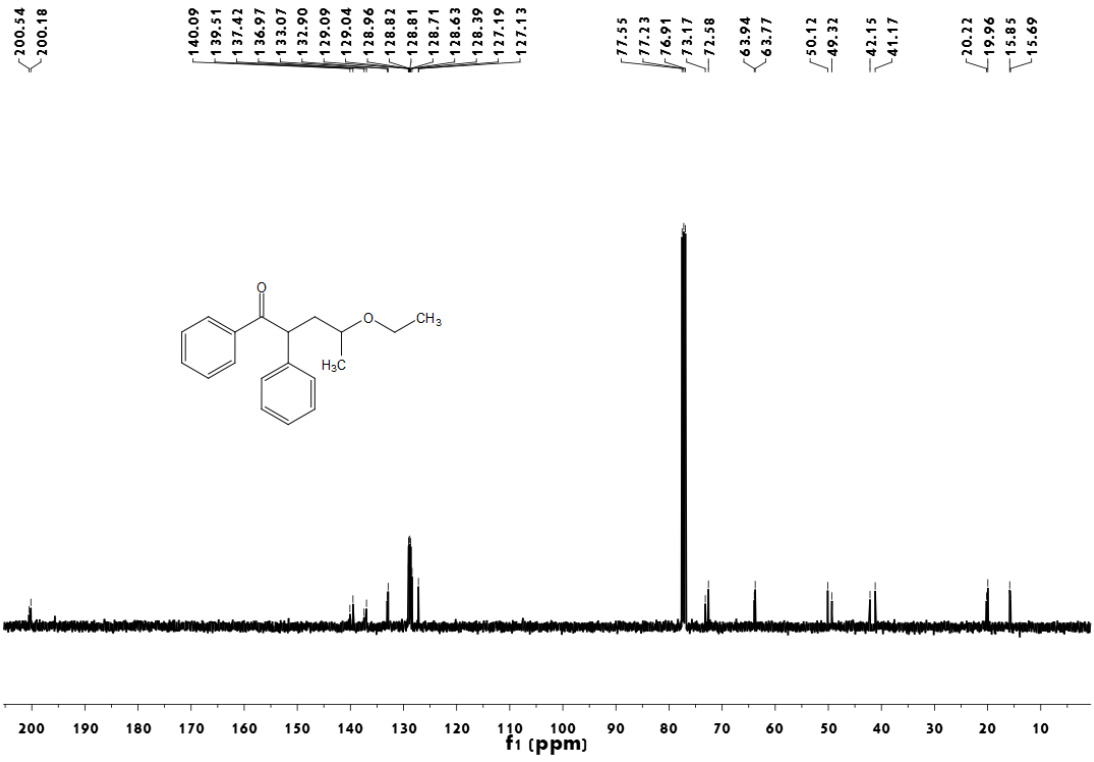
7.38
7.33
7.31
7.27
7.25
7.20
7.16
5.01
5.00
4.98
4.97
4.90
4.89
4.88
3.43
3.40
3.38
3.24
3.20
3.18
3.15
2.31
2.27
1.87
1.84
1.12
1.10
1.06
1.04
1.02
-0.00
O
O
CH3
H3C
1.91
1.14
2.18
2.37
2.03
1.14
0.40
0.55
1.04
0.41
1.60
0.44
0.61
0.62
0.48
2.86
3.11
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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129.04
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128.63
128.39
127.19
127.13
77.55
77.23
76.91
73.17
72.58
63.94
63.77
50.12
49.32
42.15
41.17
20.22
19.96
15.85
15.69
O
O
CH3
H3C
200
190
180
170
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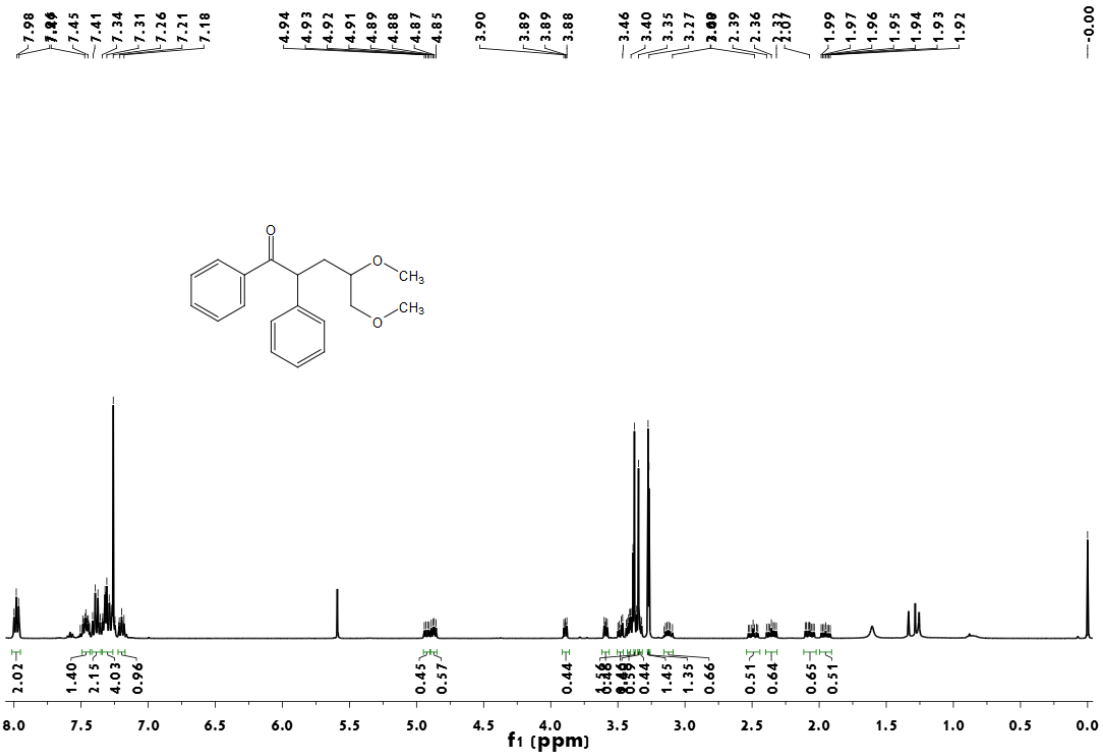
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)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4.94
4.93
4.92
4.91
4.89
4.88
4.87
4.85
3.90
3.89
3.89
3.88
3.46
3.40
3.35
3.27
2.39
2.36
1.99
1.97
1.96
1.95
1.94
1.93
1.92
0.00
O
O
CH3
O
CH3
2.02
1.40
2.15
4.03
0.96
0.45
0.57
0.44
1.45
1.35
0.66
0.51
0.64
0.65
0.51
8.0
7.5
7.0
6.5
6.0
5.5
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2.0
1.5
1.0
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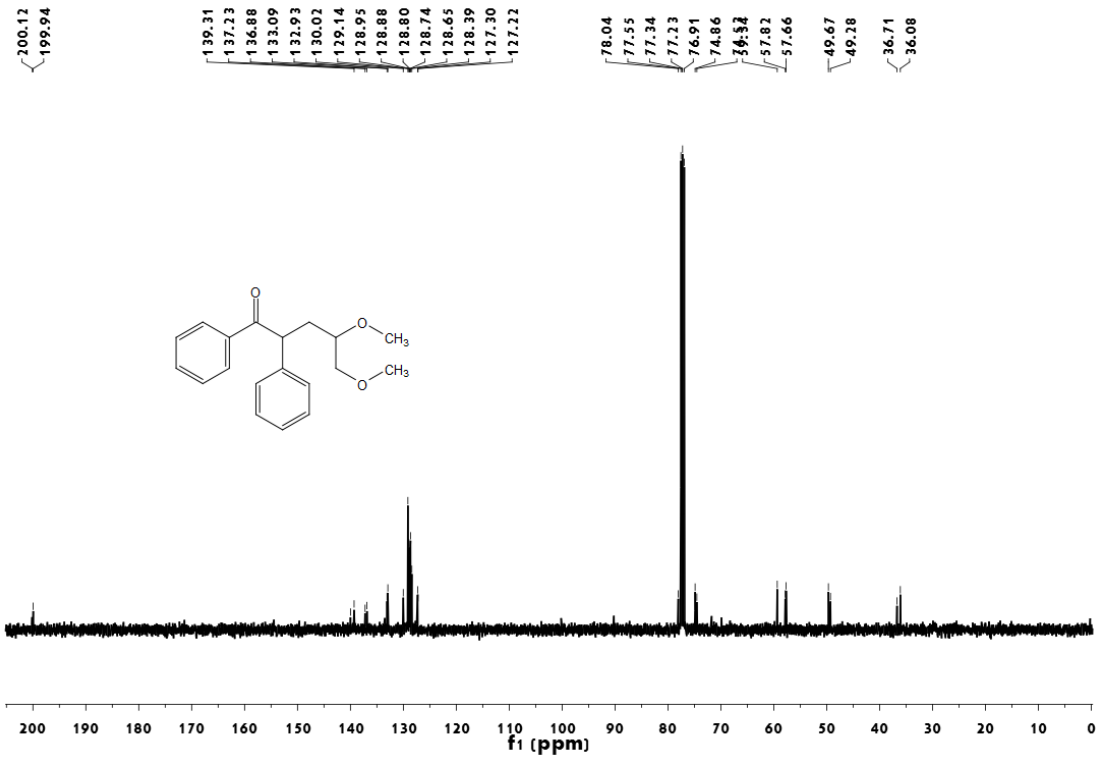
0.0
f1 (ppm)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128.80
128.74
128.65
128.39
127.30
127.22
78.04
77.55
77.34
77.23
76.91
74.86
57.82
57.66
49.67
49.28
36.71
36.08
O
O
CH3
O
CH3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
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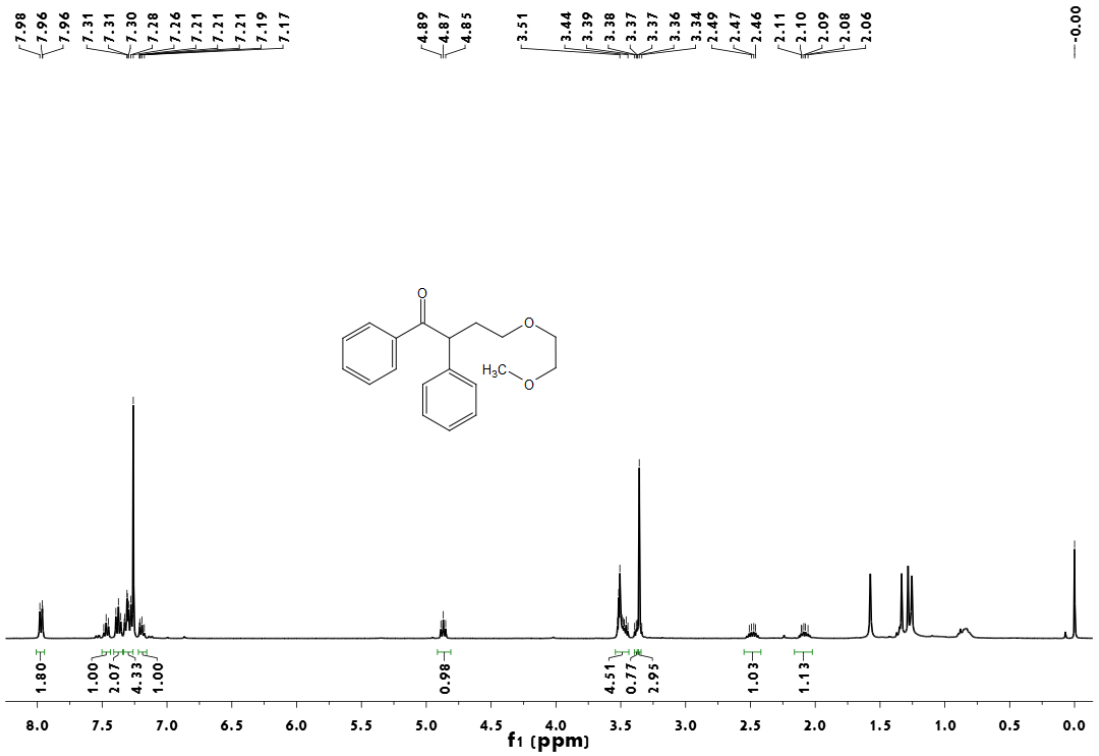
20
10
0
f1 (ppm)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7.21
7.21
7.19
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4.85
3.51
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3.37
3.37
3.36
3.34
2.49
2.47
2.46
2.11
2.10
2.09
2.08
2.06
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O
H3C
O
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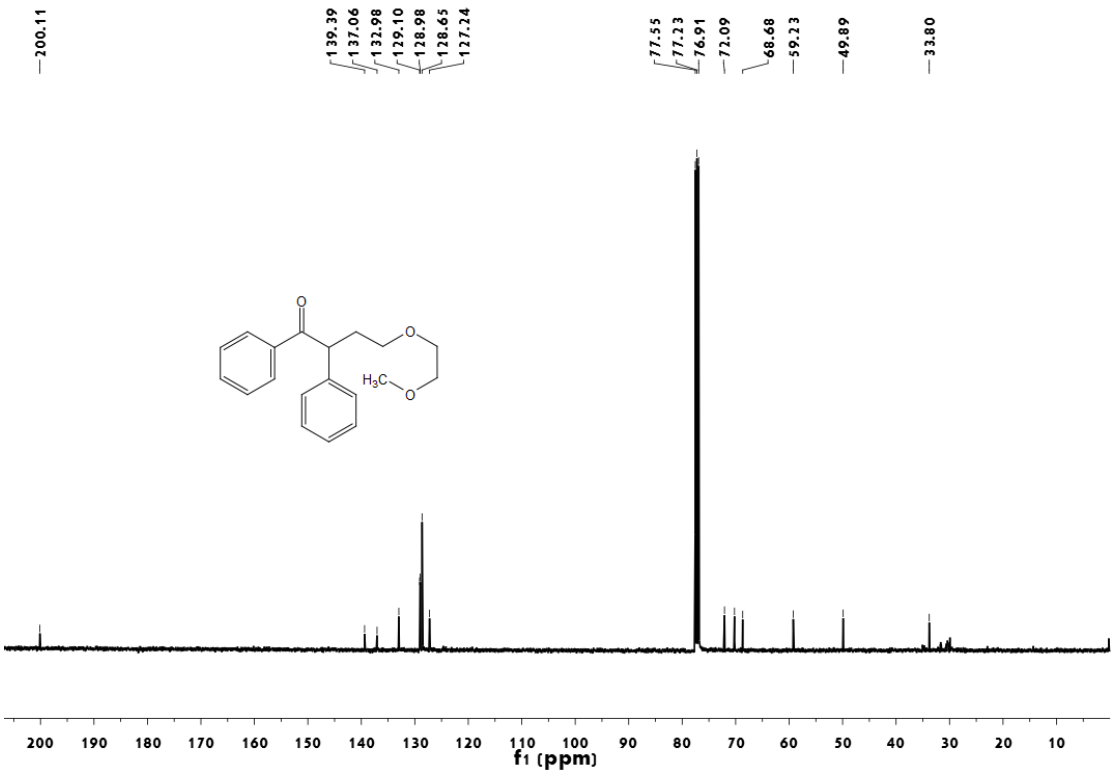
1.00
2.07
4.33
1.00
0.98
4.51
0.77
2.95
1.03
1.13
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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127.24
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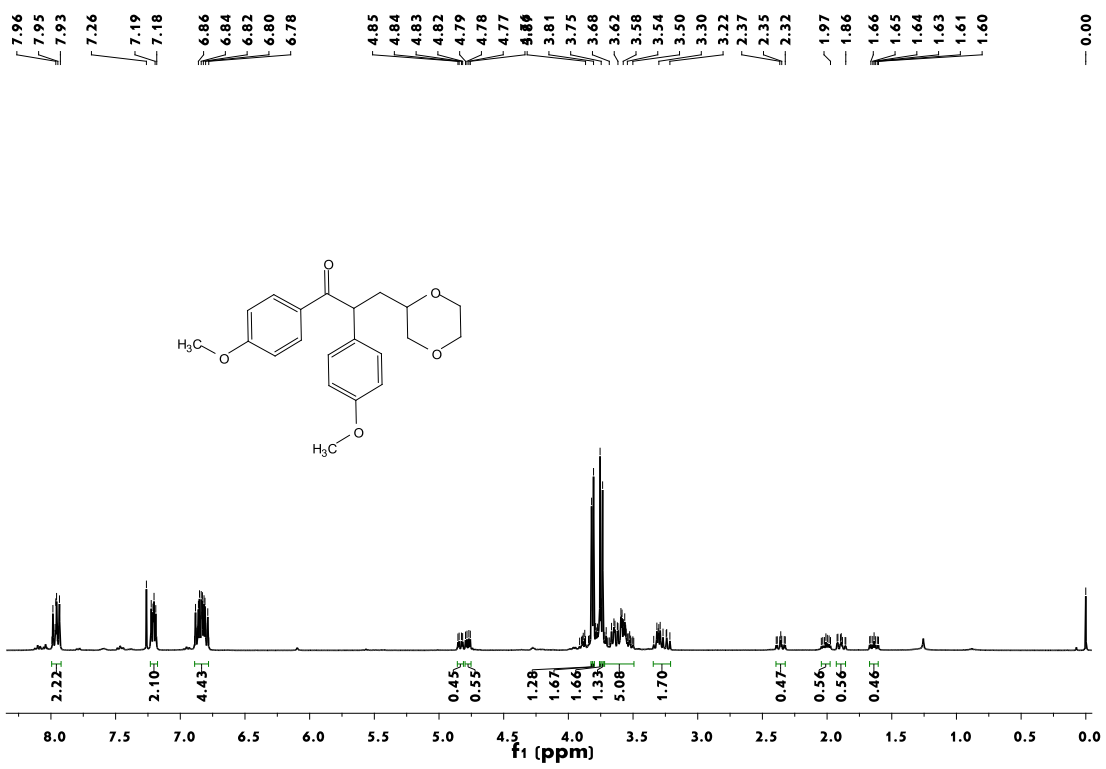
77.23
76.91
72.09
68.68
59.23
49.89
33.80
O
O
H3C
O
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)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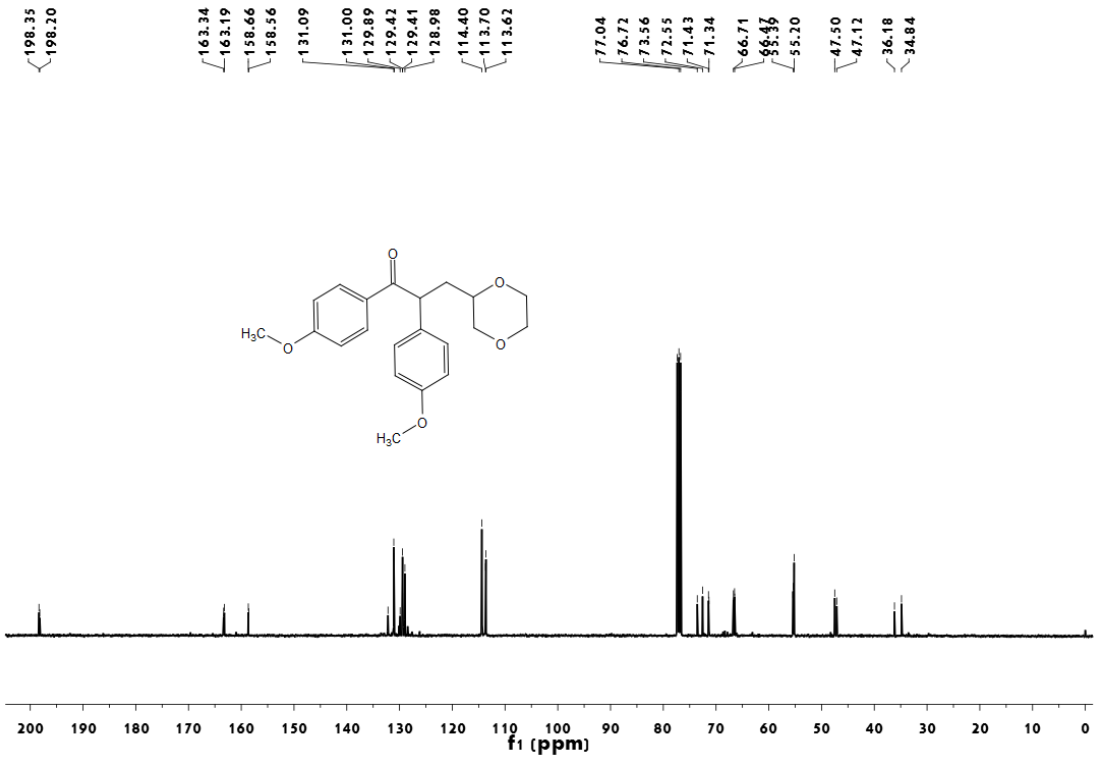
4.85 4.84 4.83 4.82 4.79 4.78 4.77 3.81 3.75 3.68 3.62 3.58 3.54 3.50 3.30 3.22 2.37 2.35 2.32
1.97 1.86 1.66 1.65 1.64 1.63 1.61 1.60 0.00
O
O
O
H3C
O
O
H3C
2.22 2.10 4.43 0.45 0.55 1.28 1.67 1.66 1.33 5.08 1.70 0.47 0.56 0.56 0.46
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


198.35 198.20
163.34 163.19 158.66 158.56 131.09 131.00 129.89 129.42 129.41 128.98 114.40 113.70 113.62
77.04 76.72 73.56 72.55 71.43 71.34 66.71 55.20 47.50 47.12 36.18 34.84
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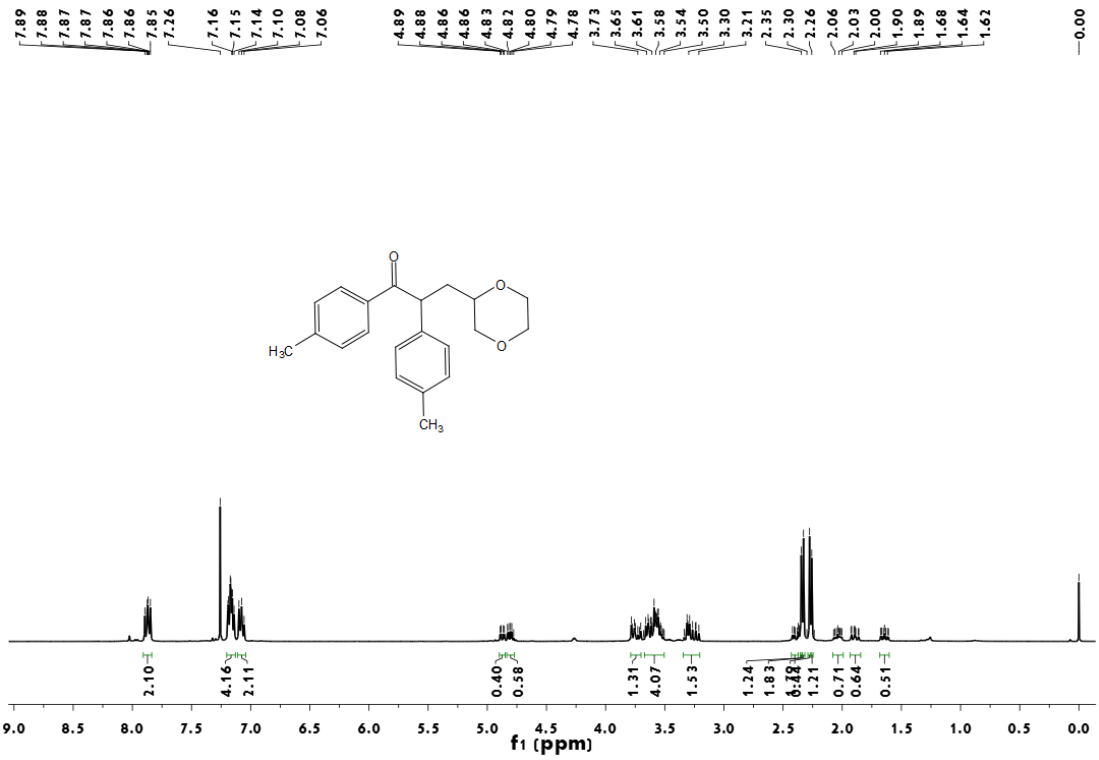
O
O
H3C
O
O
H3C
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.87
7.87
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7.86
7.85
7.26
7.16
7.15
7.14
7.10
7.08
7.06
4.89
4.88
4.86
4.86
4.83
4.82
4.80
4.79
4.78
3.73
3.65
3.61
3.58
3.54
3.50
3.30
3.21
2.35
2.30
2.26
2.06
2.03
2.00
1.90
1.89
1.68
1.64
1.62
0.00
O
O
O
H3C
CH3
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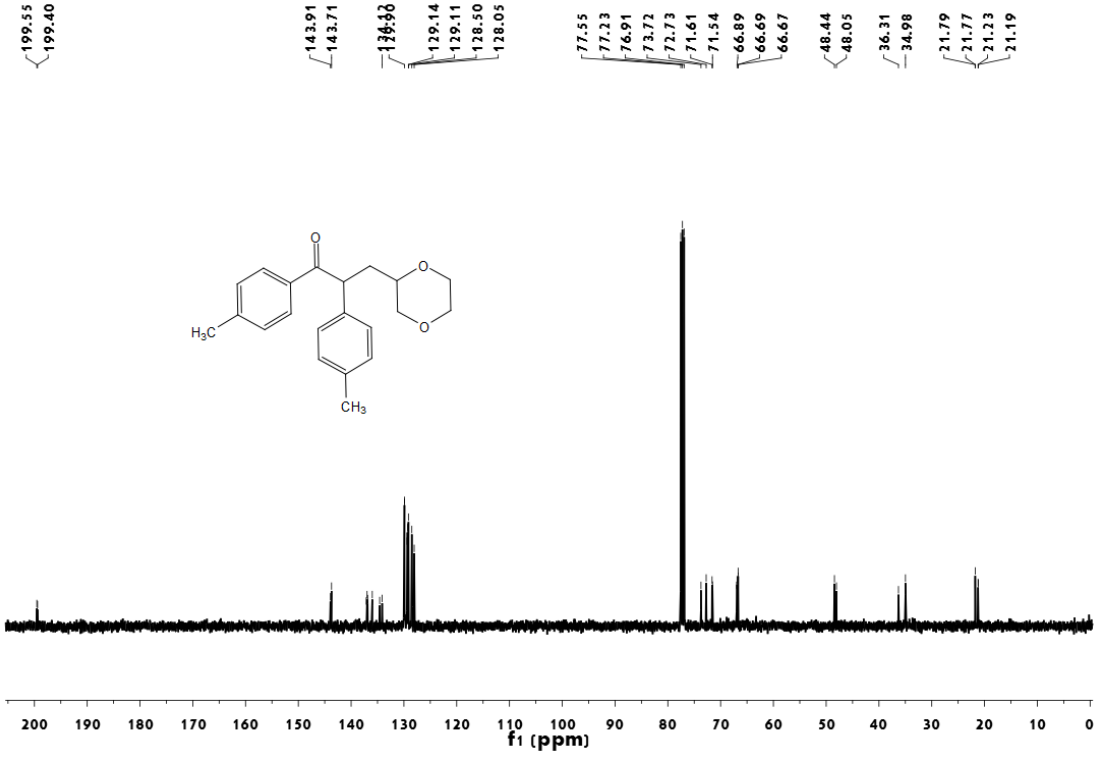
4.16
2.11
0.40
0.58
1.31
4.07
1.53
1.24
1.83
1.21
0.71
0.64
0.51
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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199.40
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143.71
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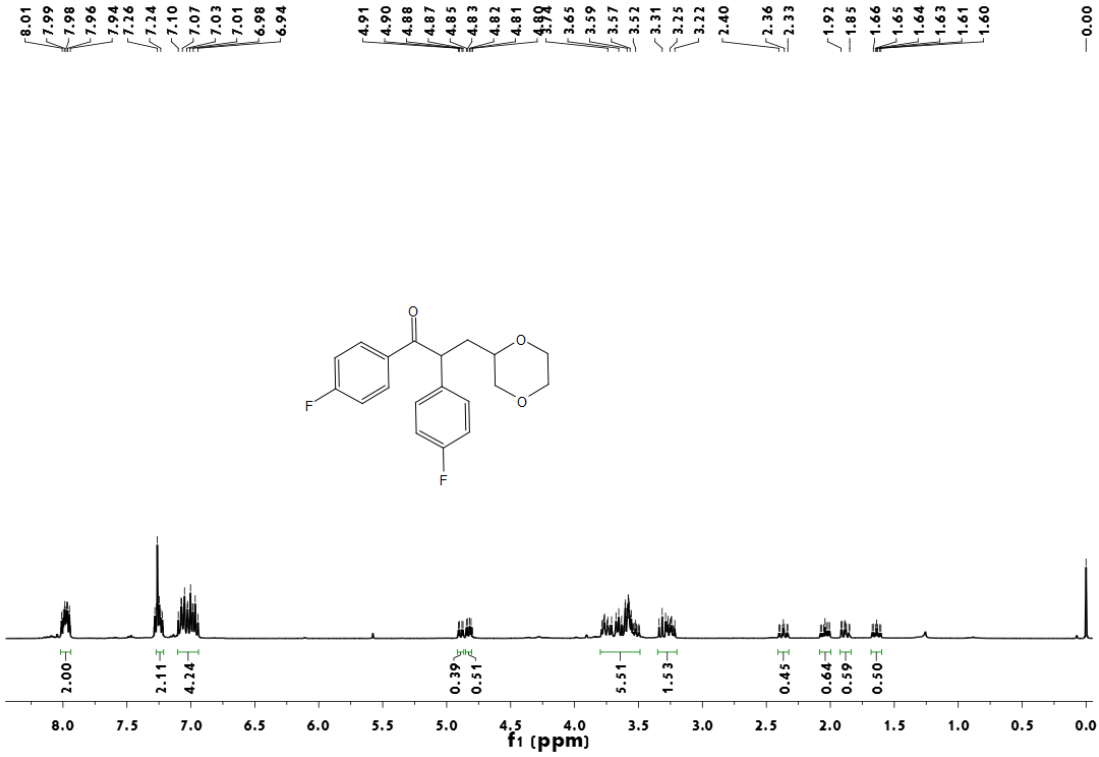
129.11
128.50
128.05
77.55
77.23
76.91
73.72
72.73
71.61
71.54
66.89
66.69
66.67
48.44
48.05
36.31
34.98
21.79
21.77
21.23
21.19
O
O
O
H3C
CH3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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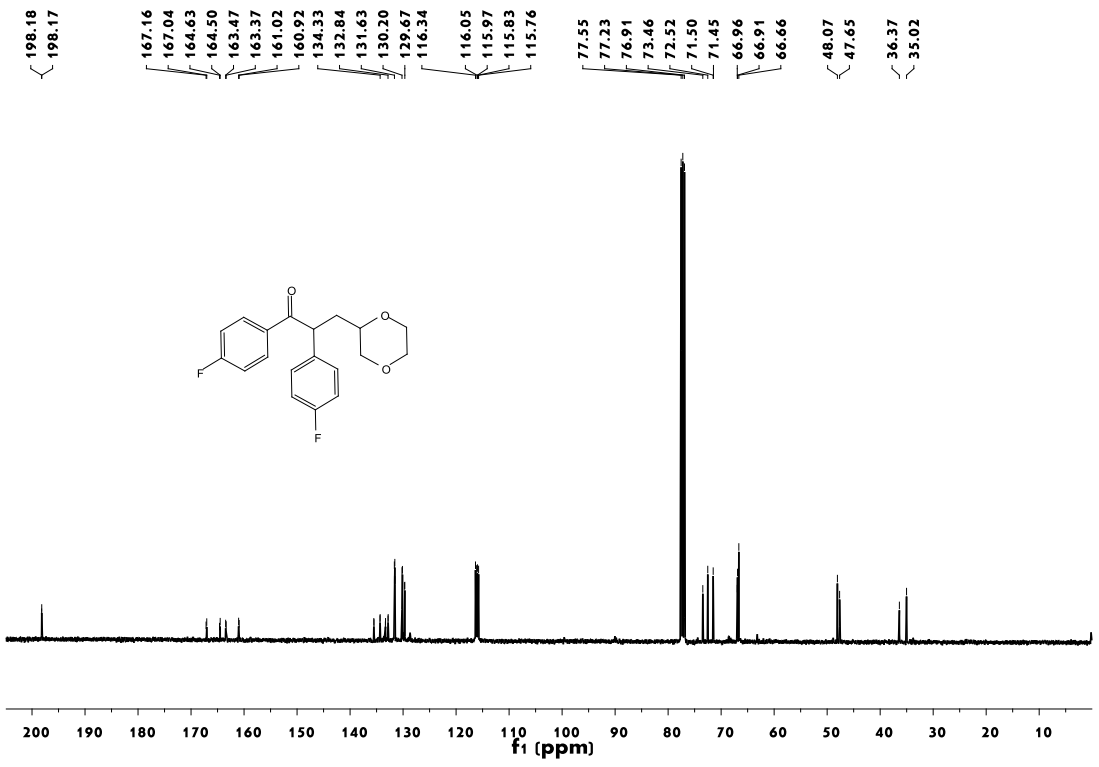
4.91 4.90 4.88 4.87 4.85 4.83 4.82 4.81 3.65 3.59 3.57 3.52 3.31 3.25 3.22 2.40 2.36 2.33 1.92 1.85 1.66 1.65 1.64 1.63 1.61 1.60 0.00
O
O
O
F
F
2.00 2.11 4.24 0.39 0.51 5.51 1.53 0.45 0.64 0.59 0.50
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


198.18 198.17 167.16 167.04 164.63 164.50 163.47 163.37 161.02 160.92 134.33 132.84 131.63 130.20 129.67 116.34 116.05 115.97 115.83 115.76 77.55 77.23 76.91 73.46 72.52 71.50 71.45 66.96 66.91 66.66 48.07 47.65 36.37 35.02
O
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O
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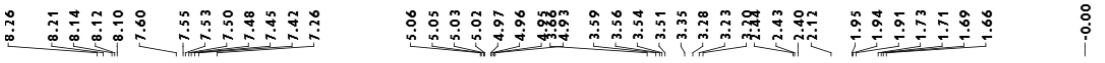
f1 (ppm)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7.53
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7.48
7.45
7.42
7.26
5.06
5.05
5.03
5.02
4.97
4.96
3.59
3.56
3.54
3.51
3.35
3.28
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2.12
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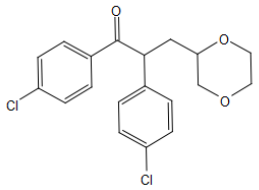
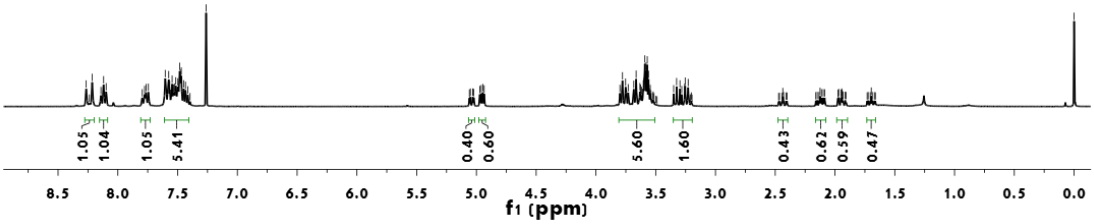
1.94
1.91
1.73
1.71
1.69
1.66
0.00


O
O
O
Cl
Cl


1.05
1.04
1.05
5.41
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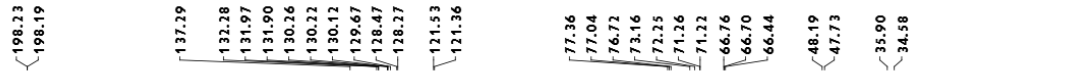
0.60
5.60
1.60
0.43
0.62
0.59
0.47
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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198.19
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129.67
128.47
128.27
121.53
121.36
77.36
77.04
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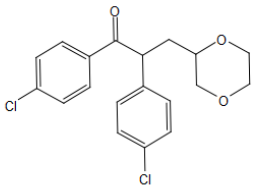
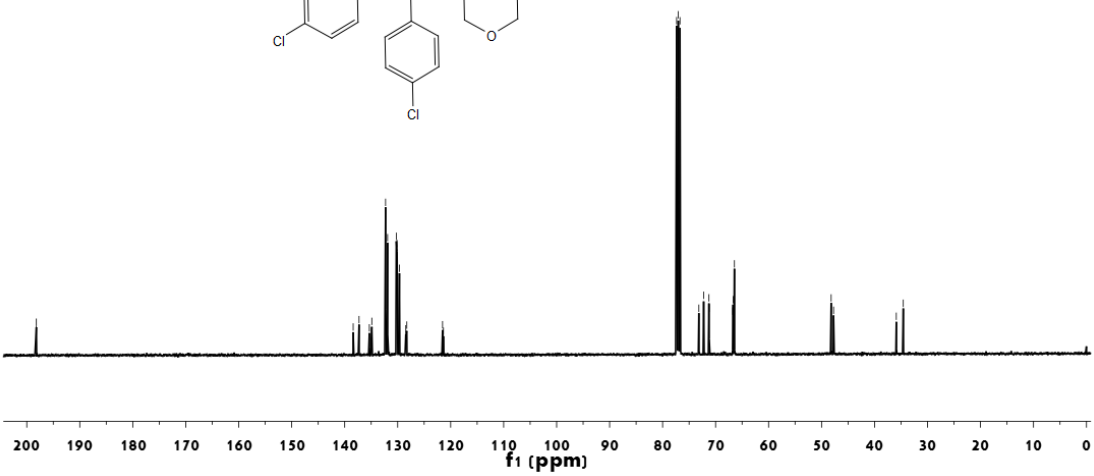
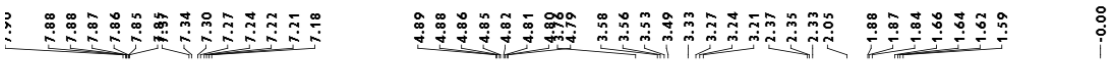
71.26
71.22
66.76
66.70
66.44
48.19
47.73
35.90
34.58


O
O
O
Cl
Cl


200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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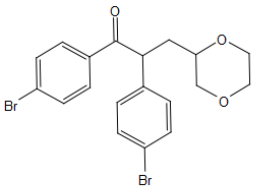
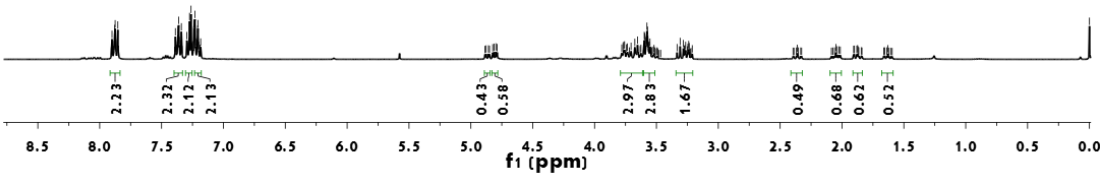
7.88
7.87
7.86
7.85
7.34
7.30
7.27
7.24
7.22
7.21
7.18
4.89
4.88
4.86
4.85
4.82
4.81
3.58
3.56
3.53
3.49
3.33
3.27
3.24
3.21
2.37
2.35
2.33
2.05
1.88
1.87
1.84
1.66
1.64
1.62
1.59
0.00


O
O
O
Br
Br


2.23
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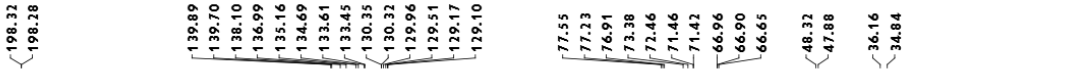
2.12
2.13
0.43
0.58
2.97
2.83
1.67
0.49
0.68
0.62
0.52
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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198.28
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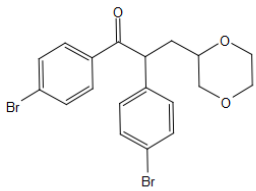
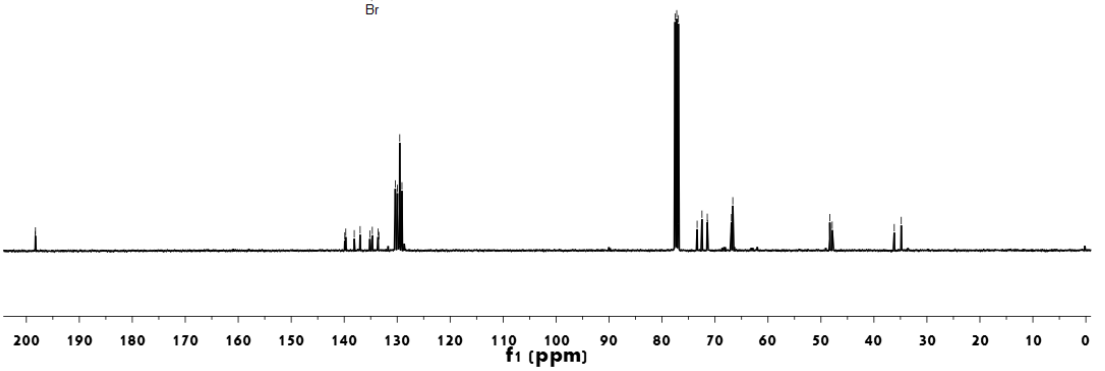
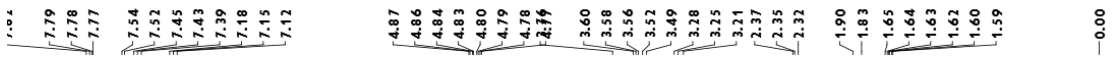
139.70
138.10
136.99
135.16
134.69
133.61
133.45
130.35
130.32
129.96
129.51
129.17
129.10
77.55
77.23
76.91
73.38
72.46
71.46
71.42
66.96
66.90
66.65
48.32
47.88
36.16
34.84


O
O
O
Br
Br


200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.79
7.78
7.77
7.54
7.52
7.45
7.43
7.39
7.18
7.15
7.12
4.87
4.86
4.84
4.83
4.80
4.79
4.78
3.60
3.58
3.56
3.52
3.49
3.28
3.25
3.21
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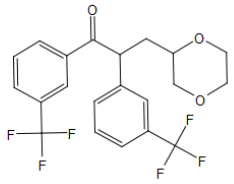
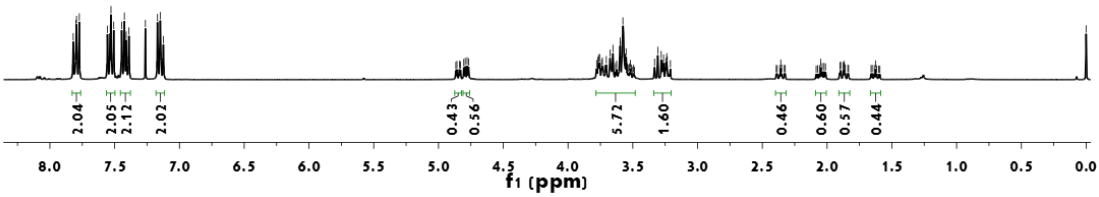
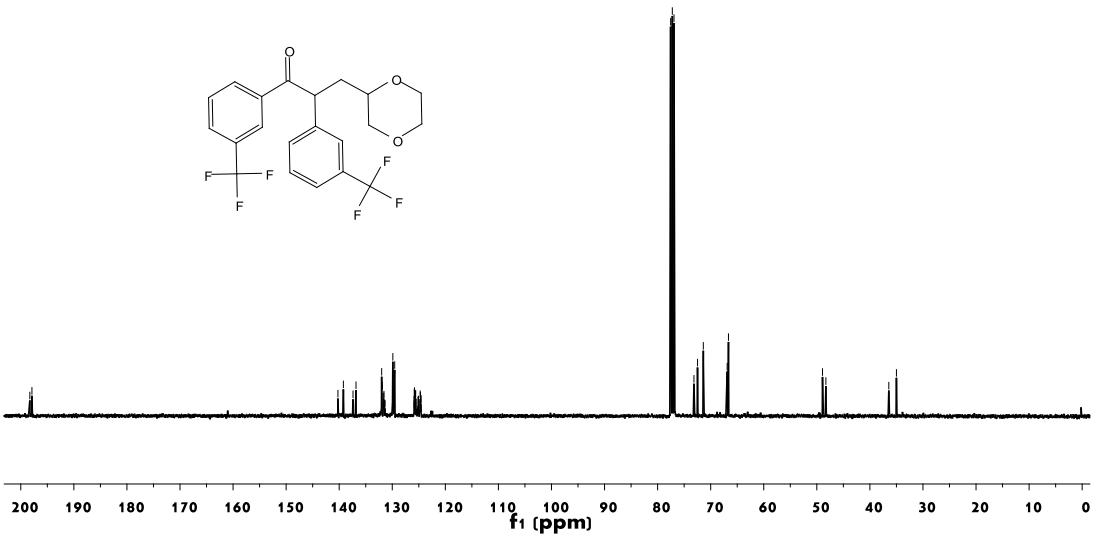
2.32
1.90
1.83
1.65
1.64
1.63
1.62
1.60
1.59
0.00

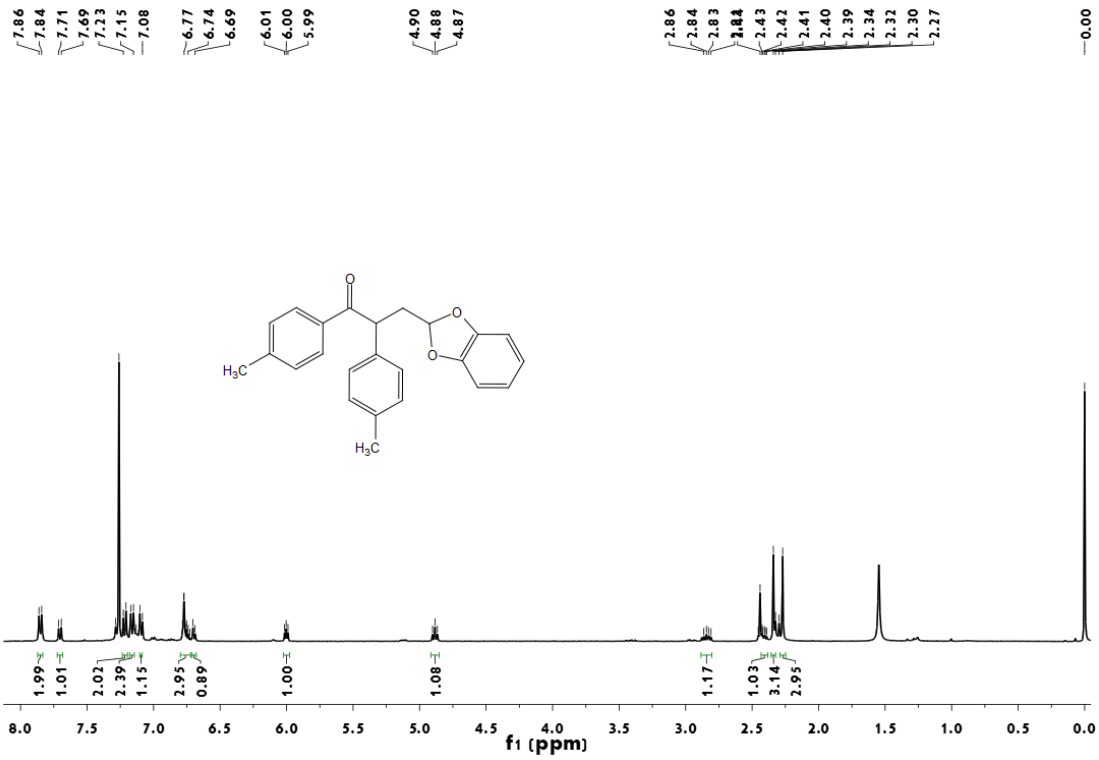

O
O
O
F
F
F
F
F
F

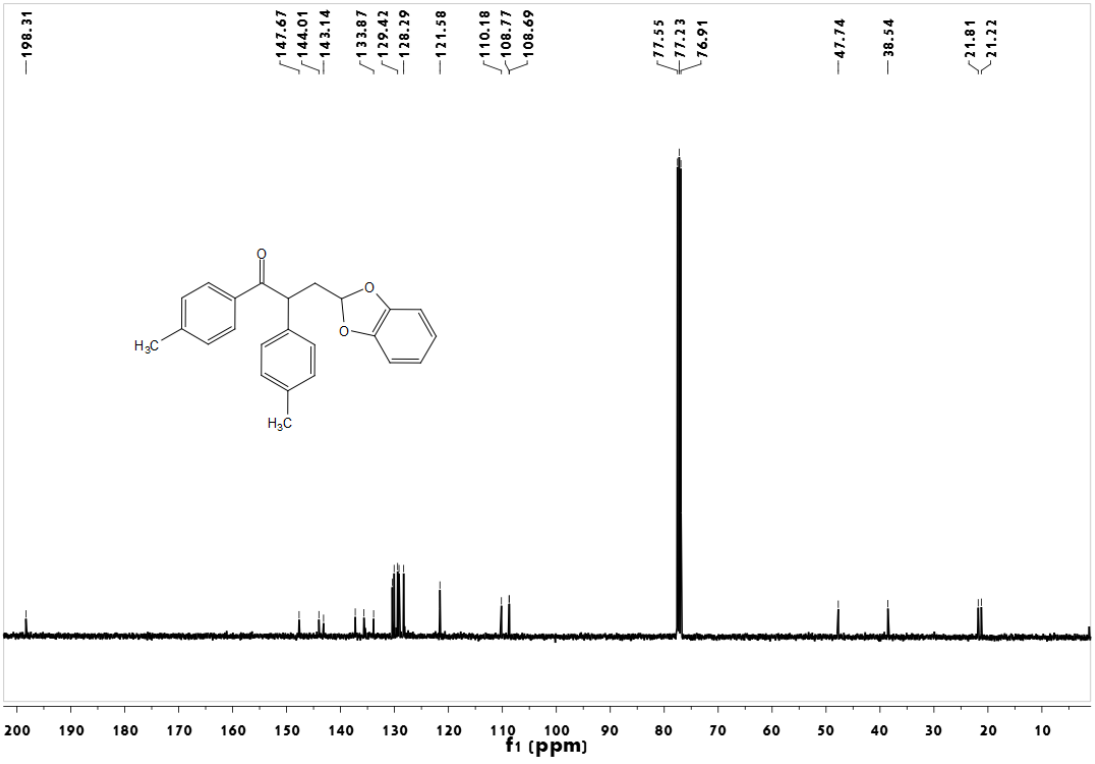

2.04
2.05
2.12
2.02
0.43
0.56
5.72
1.60
0.46
0.60
0.57
0.44
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


198.29
197.90
140.24
139.21
137.40
136.83
132.00
129.74
125.82
125.59
124.77
124.55
77.55
77.23
76.91
73.15
72.48
71.39
66.94
66.89
66.65
48.93
48.29
36.44
35.00

O
O
O
F
F
F
F
F
F


200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.86
7.84
7.71
7.69
7.23
7.15
7.08
6.77
6.74
6.69
6.01
6.00
5.99
4.90
4.88
4.87
2.86
2.84
2.83
2.43
2.42
2.41
2.40
2.39
2.34
2.32
2.30
2.27
0.00
O
O
O
H3C
H3C
1.99
1.01
2.02
2.39
1.15
2.95
0.89
1.00
1.08
1.17
1.03
3.14
2.95
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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143.14
133.87
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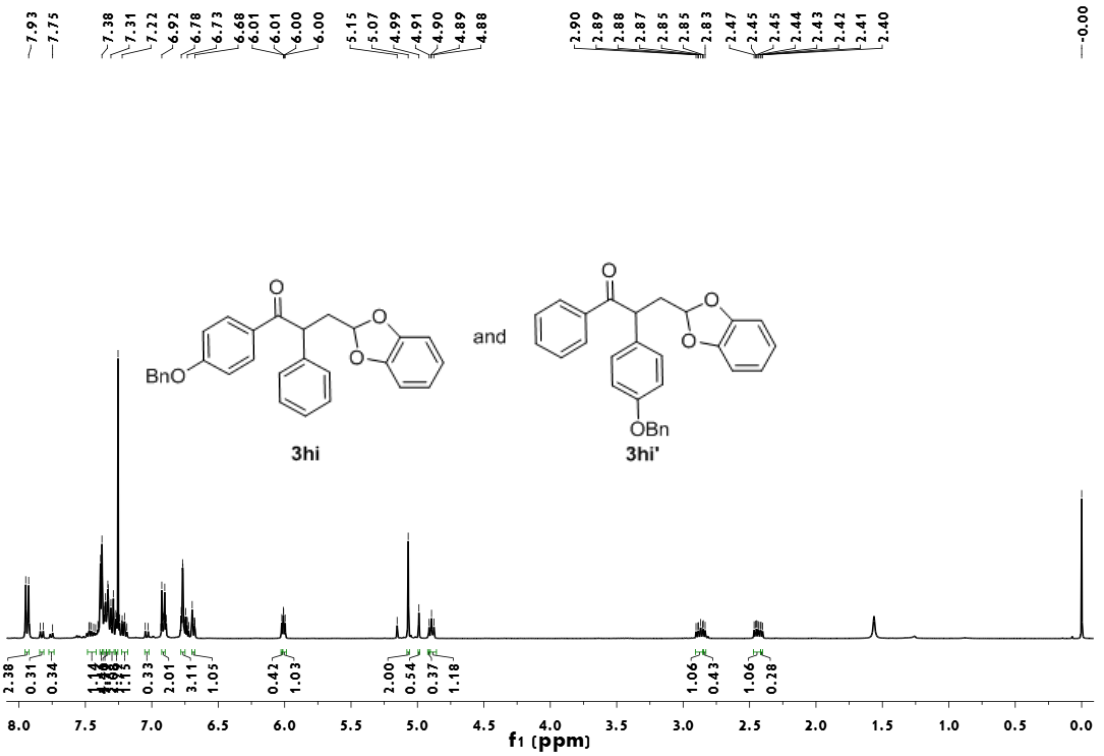
121.58
110.18
108.77
108.69
77.55
77.23
76.91
47.74
38.54
21.81
21.22
O
O
O
H3C
H3C
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)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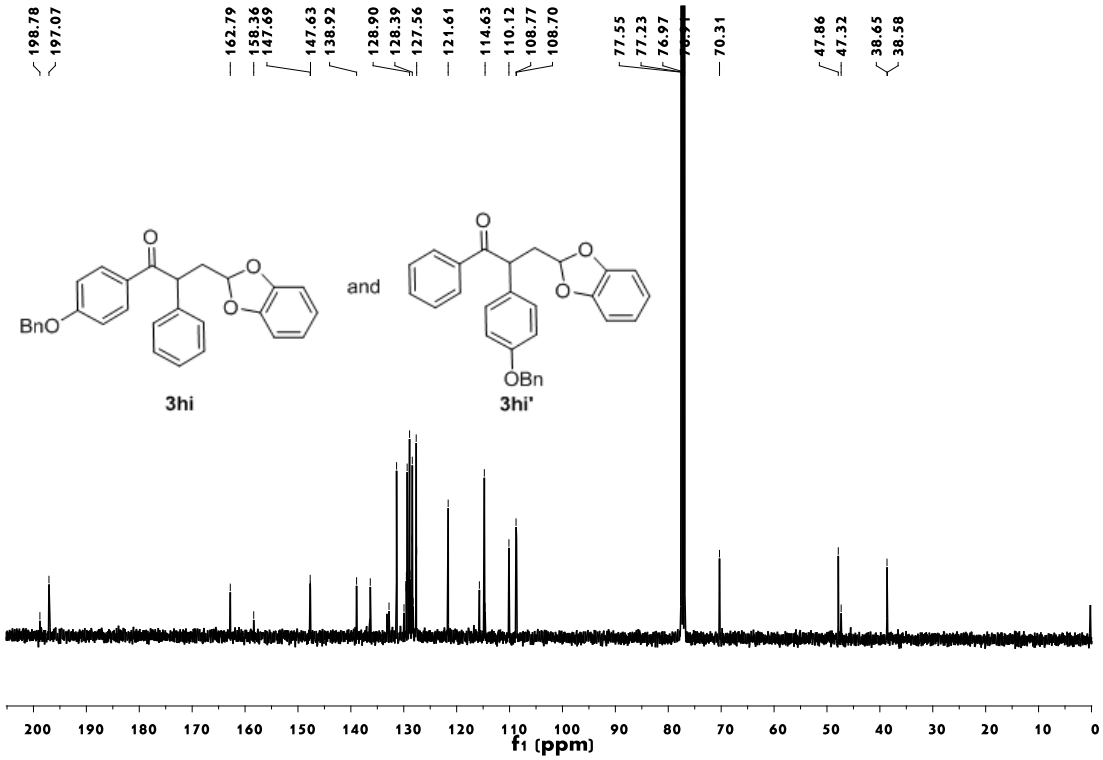
7.38
7.31
7.22
6.92
6.78
6.73
6.68
6.01
6.01
6.00
6.00
5.15
5.07
4.99
4.91
4.90
4.89
4.88
2.90
2.89
2.88
2.87
2.85
2.85
2.83
2.47
2.45
2.45
2.44
2.43
2.42
2.41
2.40
0.00
BnO
3hi
and
OBn
3hi'
2.38
0.31
0.34
1.14
0.33
2.01
3.11
1.05
0.42
1.03
2.00
0.54
0.37
1.18
1.06
0.43
1.06
0.28
f1 (ppm)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147.63
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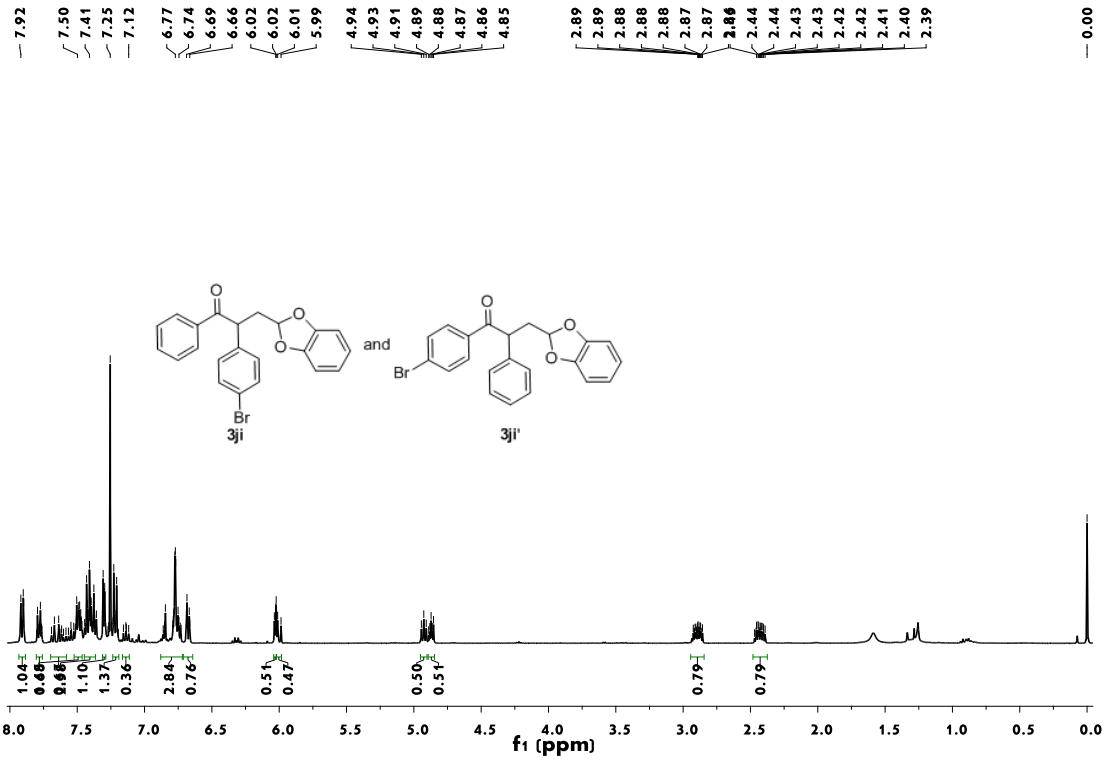
128.90
128.39
127.56
121.61
114.63
110.12
108.77
108.70
77.55
77.23
76.97
70.31
47.86
47.32
38.65
38.58
BnO
3hi
and
OBn
3hi'
f1 (ppm)


7.72
7.58
7.49
7.45
7.30
7.20
7.06
6.74
6.67
6.02
6.01
6.01
6.00
4.95
4.93
4.91
4.90
4.88
4.86
2.90
2.89
2.88
2.87
2.86
2.85
2.84
2.82
2.43
2.42
2.41
2.40
2.39
2.25
2.24
2.20
2.18
-0.00
and
3ii
3ii'
0.69
0.65
0.43
0.62
0.39
0.63
0.47
0.68
0.50
1.86
1.91
0.97
0.88
198.76
198.47
147.70
147.66
137.10
134.23
129.94
128.70
125.91
121.59
110.15
110.13
108.79
108.70
77.55
76.91
47.99
47.83
38.64
38.60
20.24
20.19
20.03
20.00
and
3ii
3ii'
f1 (ppm)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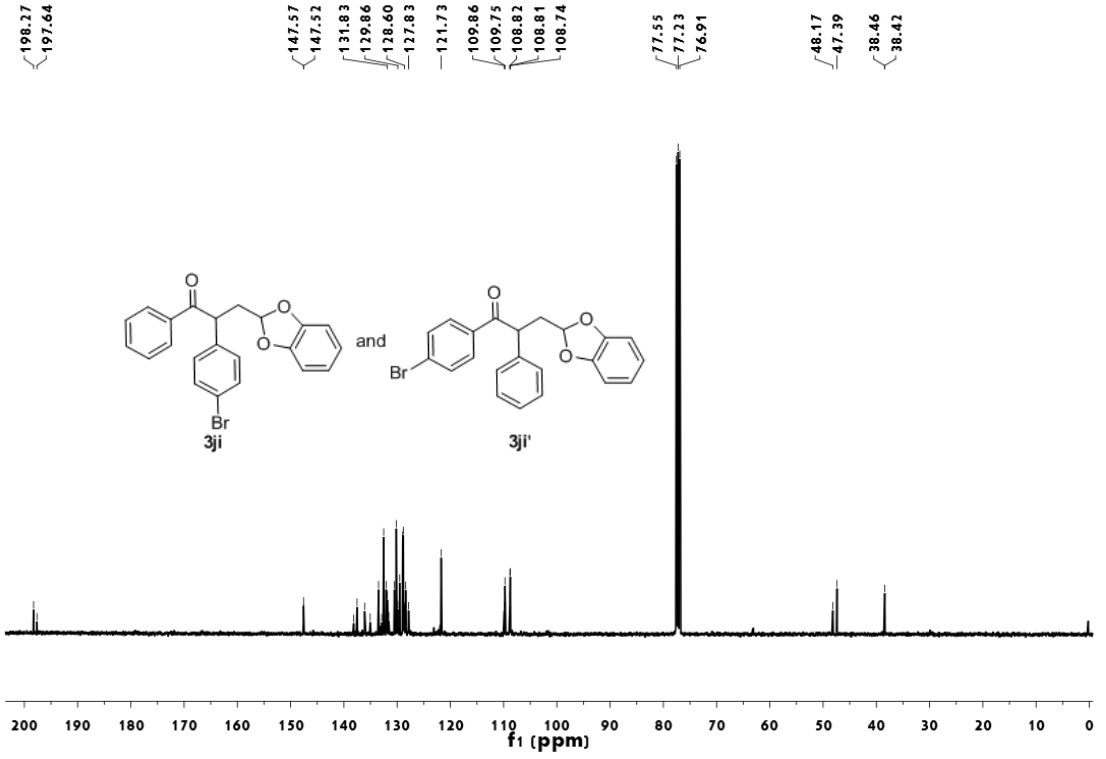
7.50
7.41
7.25
7.12
6.77
6.74
6.69
6.66
6.02
6.02
6.01
5.99
4.94
4.93
4.91
4.89
4.88
4.87
4.86
4.85
2.89
2.89
2.88
2.88
2.88
2.87
2.87
2.44
2.44
2.43
2.43
2.42
2.42
2.41
2.40
2.39
0.00
and
Br
3ji
Br
3ji'
1.04
1.10
1.37
0.36
2.84
0.76
0.51
0.47
0.50
0.51
0.79
0.79
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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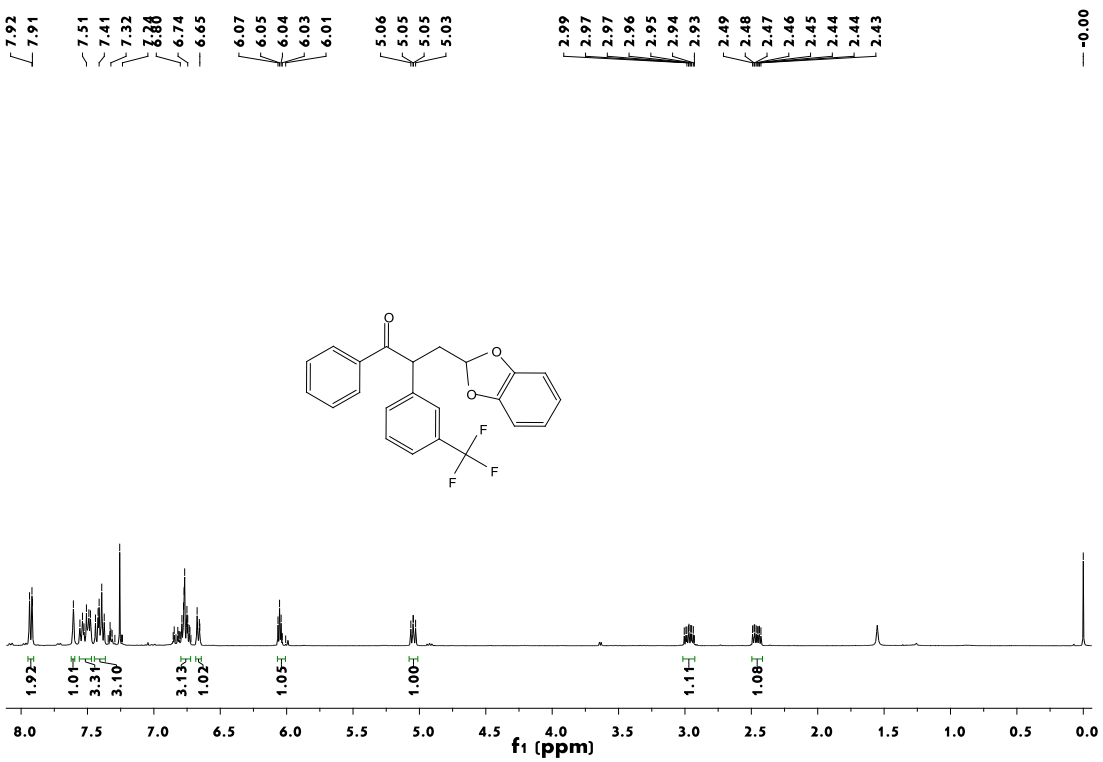
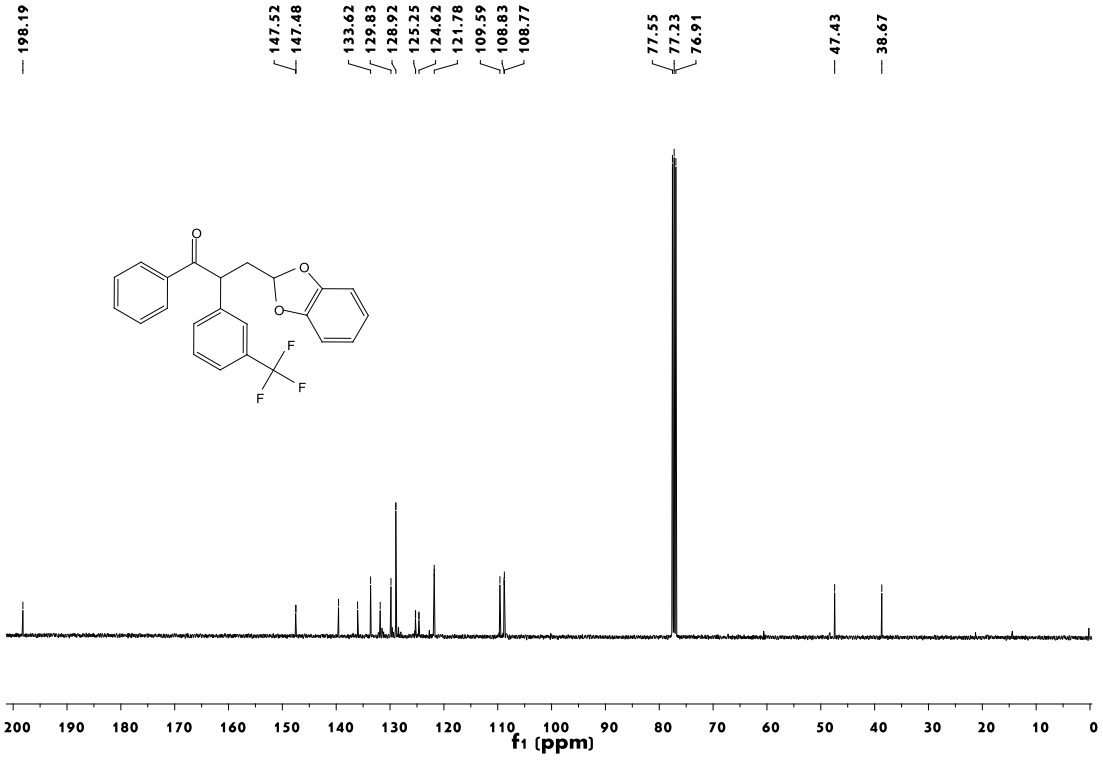
127.83
121.73
109.86
109.75
108.82
108.81
108.74
77.55
77.23
76.91
48.17
47.39
38.46
38.42
and
Br
3ji
Br
3ji'
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.92
7.91
7.51
7.41
7.32
6.74
6.65
6.07
6.05
6.04
6.03
6.01
5.06
5.05
5.05
5.03
2.99
2.97
2.97
2.96
2.95
2.94
2.93
2.49
2.48
2.47
2.46
2.45
2.44
2.44
2.43
-0.00
O
O
O
F
F
F
1.92
1.01
3.31
3.10
3.13
1.02
1.05
1.00
1.11
1.08
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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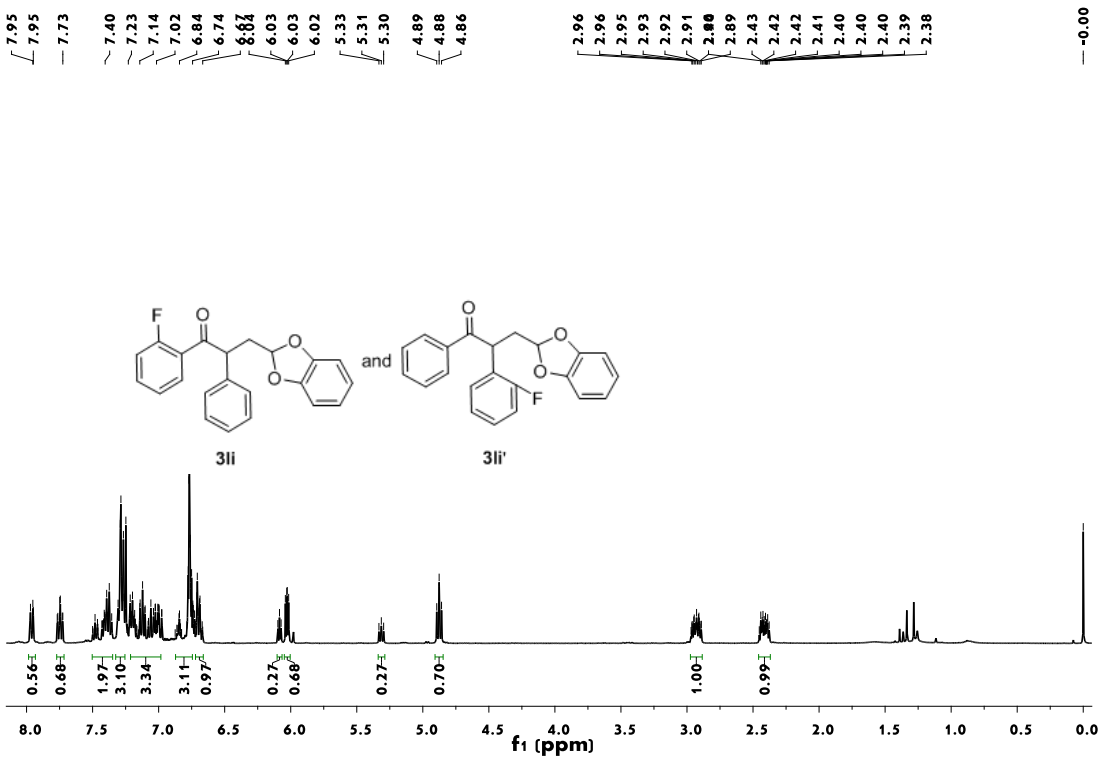
147.52
147.48
133.62
129.83
128.92
125.25
124.62
121.78
109.59
108.83
108.77
77.55
77.23
76.91
47.43
38.67
O
O
O
F
F
F
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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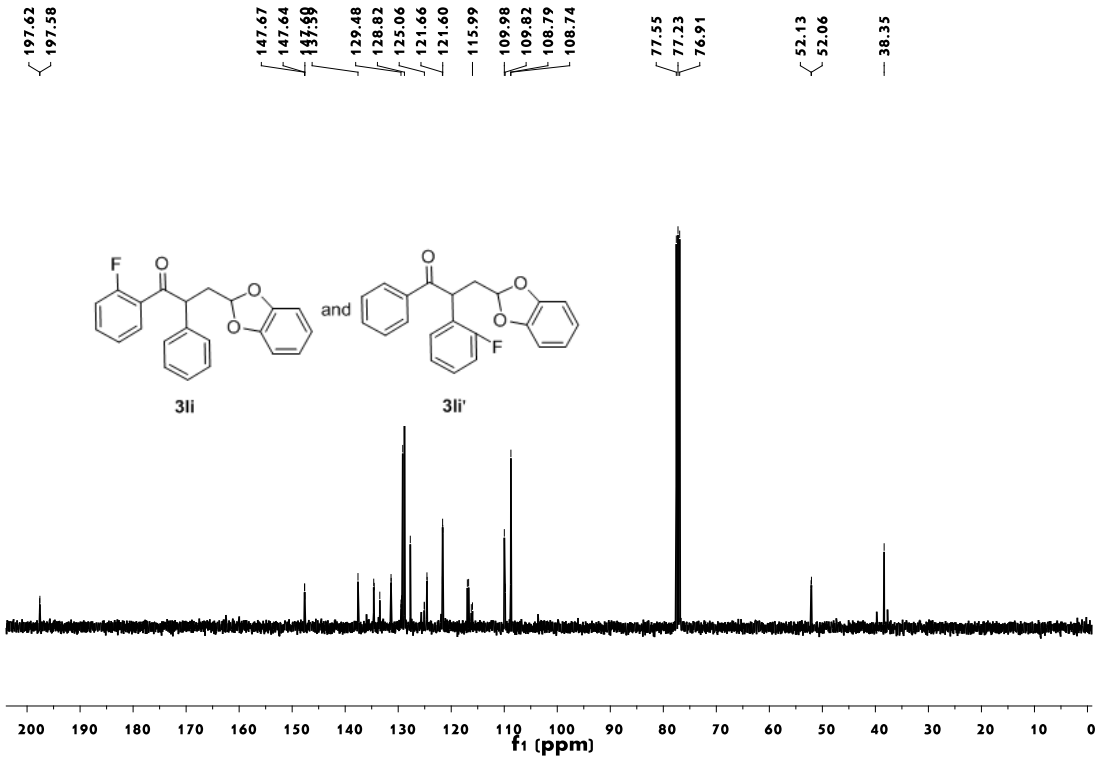
7.95
7.73
7.40
7.23
7.14
7.02
6.84
6.74
6.03
6.03
6.02
5.33
5.31
5.30
4.89
4.88
4.86
2.96
2.96
2.95
2.93
2.92
2.91
2.89
2.43
2.42
2.42
2.41
2.40
2.40
2.40
2.39
2.38
-0.00
F
O
O
O
and
O
O
F
3li
3li'
0.56
0.68
1.97
3.10
3.34
3.11
0.97
0.27
0.68
0.27
0.70
1.00
0.99
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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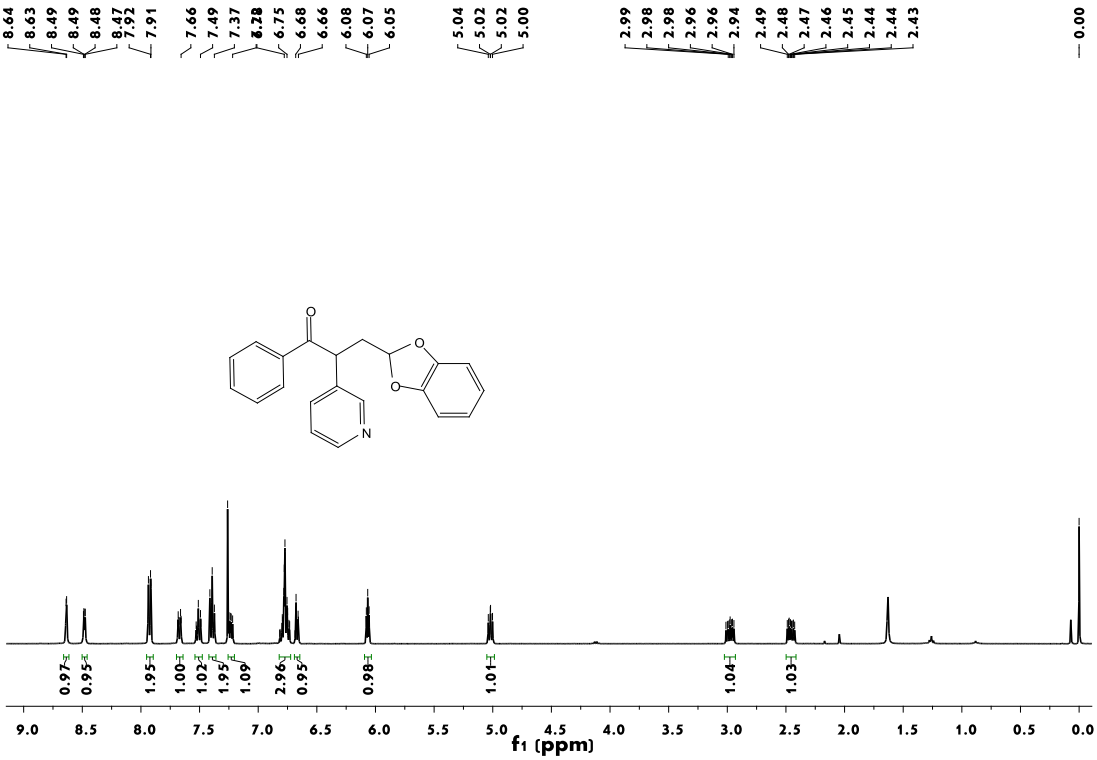
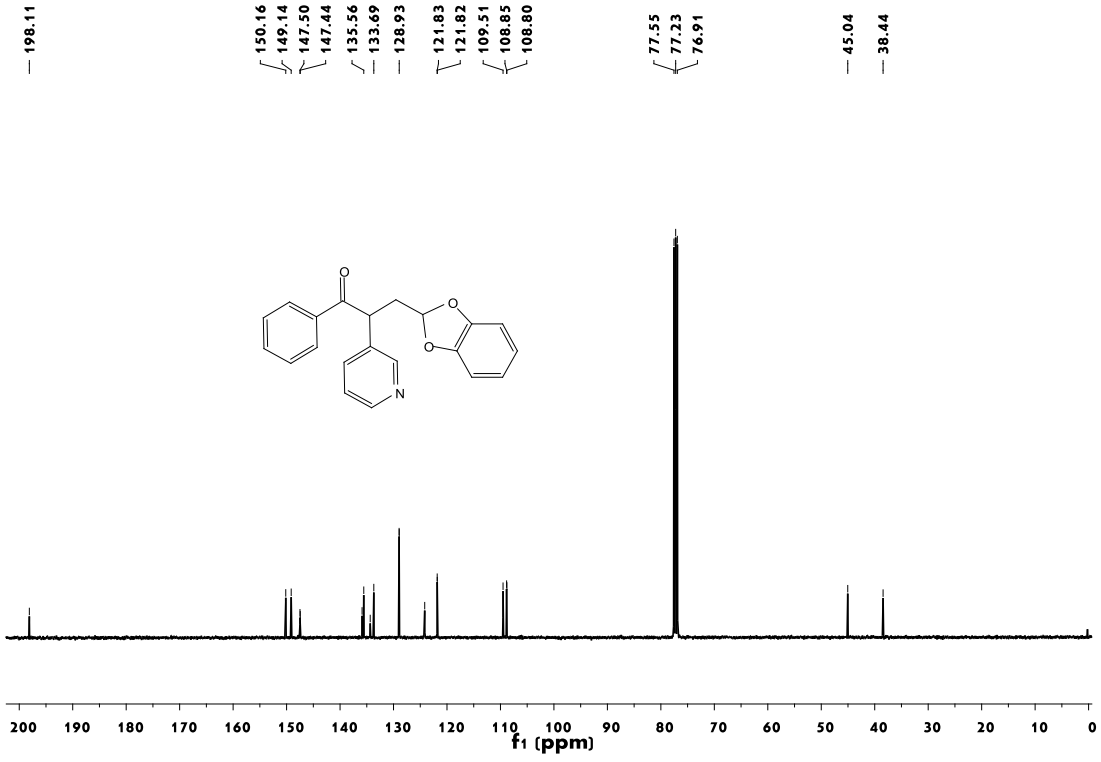
197.58
147.67
147.64
129.48
128.82
125.06
121.66
121.60
115.99
109.98
109.82
108.79
108.74
77.55
77.23
76.91
52.13
52.06
38.35
F
O
O
O
and
O
O
F
3li
3li'
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.64
8.63
8.49
8.49
8.48
8.47
7.92
7.91
7.66
7.49
7.37
6.75
6.68
6.66
6.08
6.07
6.05
5.04
5.02
5.02
5.00
2.99
2.98
2.98
2.96
2.96
2.94
2.49
2.48
2.47
2.46
2.45
2.44
2.44
2.43
0.00
O
O
O
N
0.97
0.95
1.95
1.00
1.02
1.95
1.09
2.96
0.95
0.98
1.01
1.04
1.03
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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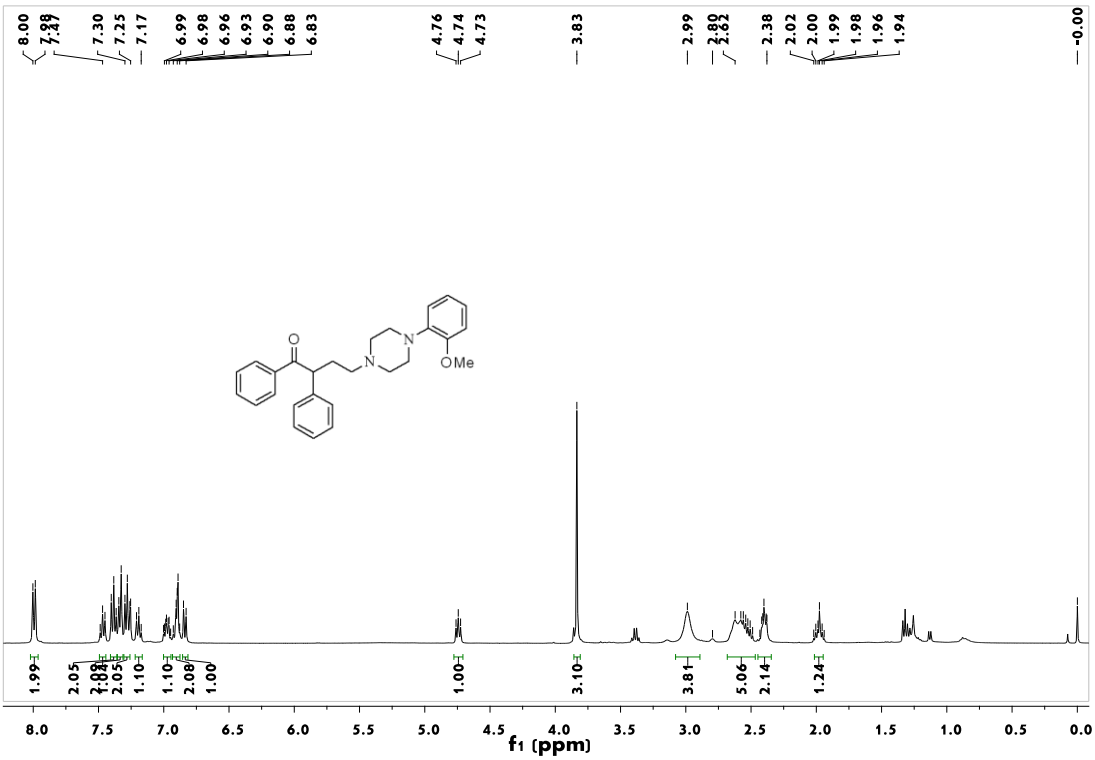
150.16
149.14
147.50
147.44
135.56
133.69
128.93
121.83
121.82
109.51
108.85
108.80
77.55
77.23
76.91
45.04
38.44
O
O
O
N
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.00
7.98
7.47
7.45
7.30
7.25
7.17
6.99
6.98
6.96
6.93
6.90
6.88
6.83
4.76
4.74
4.73
3.83
2.99
2.80
2.82
2.38
2.02
2.00
1.99
1.98
1.96
1.94
-0.00
OMe
1.99
2.05
2.08
2.05
1.10
1.10
2.08
1.00
1.00
3.10
3.81
5.06
2.14
1.24
f1 (ppm)

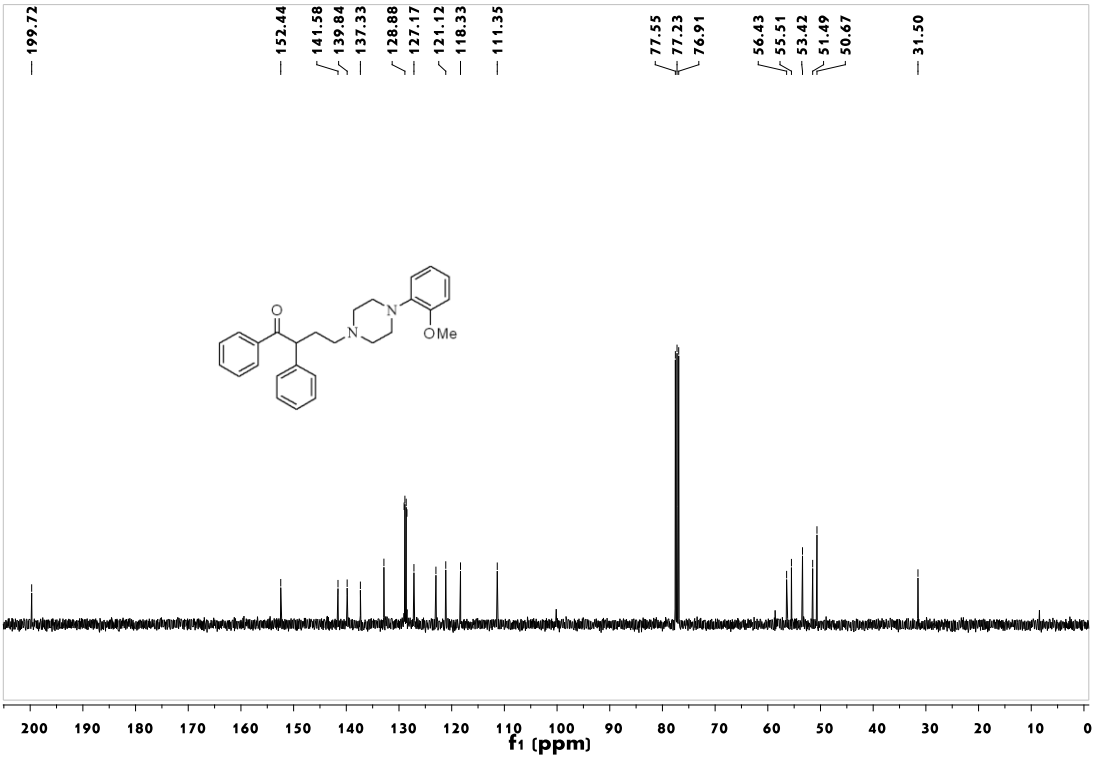
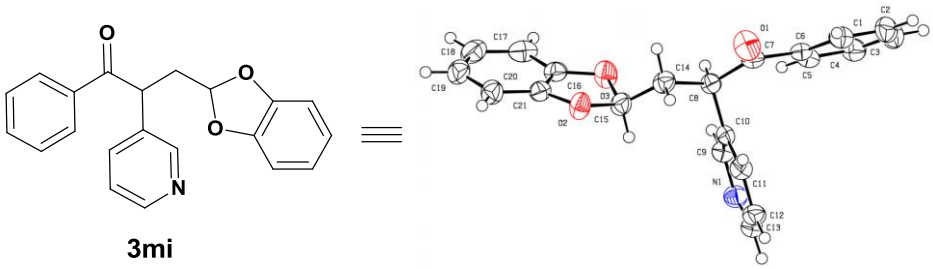

199.72
152.44
141.58
139.84
137.33
128.88
127.17
121.12
118.33
111.35
77.55
77.23
76.91
56.43
55.51
53.42
51.49
50.67
31.50
OMe
f1 (ppm)

Figure 1. X-ray structure of **3mi**



Crystal Number: CCDC 1006442

Empirical formula: $C_{21}H_{17}NO_3$

Formula weight: 357.4019

Unit cell parameters: a = 10.2758 (3) Å, b = 8.6059 (15) Å, c = 10.5383 (3) Å, α = 90.00, β = 118.016(4), γ = 90.00, space group P 1 21 1.

Temperature: 223(2) K

Wavelength: 1.54184 Å

Crystal system: Monoclinic

Volume: 822.72(4) $Å^3$

Z: 2

Calculated density: 1.338 Mg/m^3

Absorption coefficient: 0.725 mm^{-1}

F (000): 348

Crystal size: 0.80×0.60×0.50 mm^3

Correction-type: multi-scan

h, k, l max: 11, 7, 12

Tmin,Tmax: 0.73309/ 1.00000

R_1 = 0.0456, **wR_2** = 0.1061.