Supplementary Information

Anodic Oxidation Triggered Divergent 1,2- and 1,4-Group Transfer Reactions of β-Hydroxycarboxylic Acids Enabled by Electrochemical Regulation

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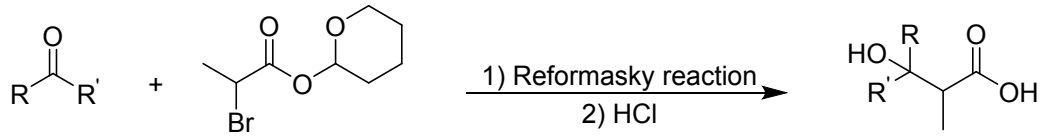
Contents

1. General information

Unless otherwise noted, chemicals and solvents were purchased with the highest purity grade available and were used without further purification. Purification of products was conducted by column chromatography on silica gel (200-300 mesh, from Qingdao, China). NMR spectra were measured on a Bruker ARX400 (^{1}H at 400 MHz, ^{13}C at 101 MHz，^{19}F at 376 MHz) magnetic resonance spectrometer. Chemical shifts (δ) are reported in ppm using tetramethylsilane as internal standard (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, td = triplet of doublets, dt = doublet of triplets, ddd = doublet of doublet of doublets, m = multiplet), and coupling constants (J) were reported in Hertz (Hz). HRMS data were obtained on a VG ZAB-HS mass spectrometer, Brucker Apex IV FTMS spectrometer.

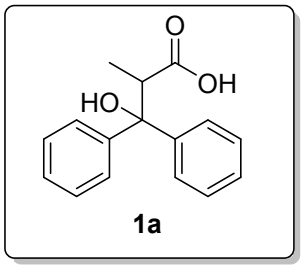
Materials: Pt electrodes were purchased from Tianjin Aida Corp. IKA Electrasyn 2.0 was as the potentiostat, and its kit electrodes were used during the optimization of the reaction conditions.

2. Synthesis and characterization of starting materials

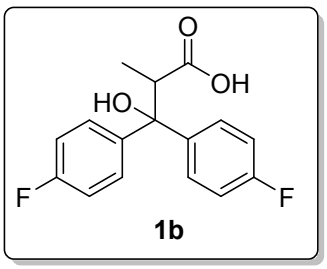


S-1 **S-2** **1**

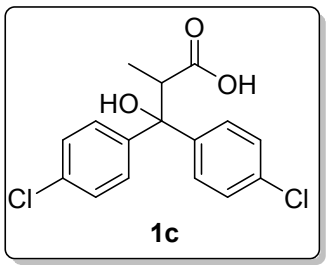
The starting acid **1** was synthesized using a modified method reported by Arsenijevic.[1] Esters **S-2** (10 mmol) were added to a mixture of Zn (10 mmol), ketone **S-1** (10 mmol) and small amounts of $HgCl_2$ or I_2 (2 mmol) in 20 ml dry THF dropwise over a period of 30 min. The reaction mixture was cooled in ice bath and stirred constantly, until the whole Zn was disappeared (2 days usually). Then THF was removed under reduced pressure, 20 ml of benzene was added. The reaction mixture was cooled to 0 °C in ice bath, 1 M HCl (aq. 15ml) was added dropwise. After stirring over 3 h, the organic layer was separated and the aqueous solution was extracted with benzene. The combined organic layer was washed with water, brine and dried over anhydrous sodium sulfate, concentrated under reduced pressure. The residue was chromatographed through silica gel to give the desired product **1**. Note: some carboxylic acids contain two diastereoisomers.



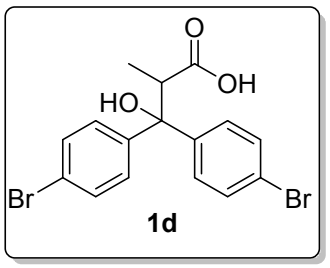
3-Hydroxy-2-methyl-3,3-diphenylpropanoic acid (**1a**).[2] White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62 – 7.48 (m, 2H), 7.48 – 7.38 (m, 2H), 7.32 – 7.24 (m, 5H), 7.24 – 7.12 (m, 2H), 4.35 (s, 1H), 3.66 (q, J = 7.1 Hz, 1H), 1.19 (d, J = 7.1 Hz, 3H).



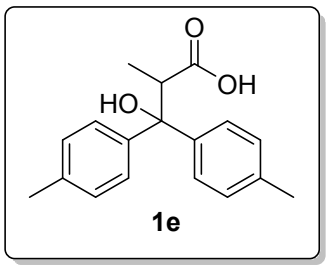
3,3-Bis(4-fluorophenyl)-3-hydroxy-2-methylpropanoic acid (**1b**). White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50 (dd, J = 8.9, 5.2 Hz, 2H), 7.37 (dd, J = 8.9, 5.3 Hz, 2H), 7.08 – 6.90 (m, 4H), 4.54 (s, 1H), 3.58 (q, J = 7.1 Hz, 1H), 1.18 (d, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 178.62, 162.55, 162.38, 160.14, 144.52, 144.49, 141.64, 141.61, 127.85, 127.77, 127.69, 115.27, 115.24, 115.06, 115.03, 77.64, 46.10, 13.26. HRMS (ESI): calcd for $C_{16}H_{13}F_2O_3^-$ [M-H]$^-$: 291.0838; found: 291.0855.



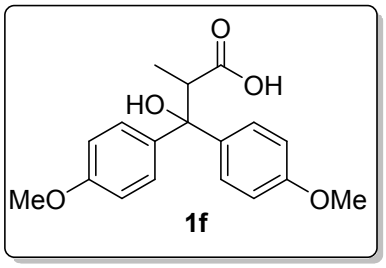
3,3-Bis(4-chlorophenyl)-3-hydroxy-2-methylpropanoic acid (**1c**). White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50 – 7.41 (m, 2H), 7.37 – 7.31 (m, 2H), 7.28 (d, J = 6.7 Hz, 2H), 7.24 (d, J = 1.9 Hz, 2H), 4.46 (s, 1H), 3.59 (d, J = 7.1 Hz, 1H), 1.19 (d, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 178.30, 147.06, 144.29, 131.83, 131.67, 128.51, 128.46, 127.75, 127.69, 77.69, 45.85, 13.23. HRMS (ESI): calcd for $C_{16}H_{13}Cl_2O_3^-$ [M-H]$^-$: 323.0247; found: 323.0262.



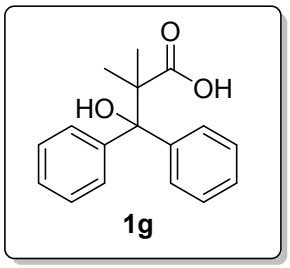
3,3-Bis(4-bromophenyl)-3-hydroxy-2-methylpropanoic acid (**1d**). White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46 – 7.37 (m, 6H), 7.27 (d, J = 8.2 Hz, 2H), 3.57 (q, J = 7.1 Hz, 1H), 1.19 (d, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 178.23, 147.44, 144.68, 131.45, 131.39, 128.12, 128.07, 120.43, 120.28, 77.79, 45.76, 13.23. HRMS (ESI): calcd for $C_{16}H_{13}Br_2O_3^-$ [M-H]$^-$: 412.9216; found: 412.9217.



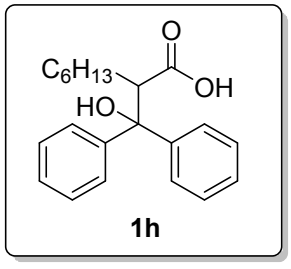
3-Hydroxy-2-methyl-3,3-di-*p*-tolylpropanoic acid (**1e**). White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40 (d, J = 8.3 Hz, 2H), 7.28 (d, J = 8.2 Hz, 2H), 7.08 (dd, J = 8.1, 6.2 Hz, 4H), 4.27 (s, 1H), 3.62 (q, J = 7.1 Hz, 1H), 2.27 (d, J = 3.5 Hz, 6H), 1.19 (d, J = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 179.09, 145.83, 142.73, 135.86, 135.61, 129.01, 128.98, 125.61, 125.51, 77.86, 45.99, 20.95, 20.92, 13.38. HRMS (ESI): calcd for $C_{18}H_{19}O_3^-$ [M-H]$^-$: 283.1340; found: 283.1355.



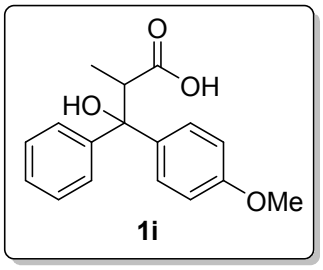
3-Hydroxy-3,3-bis(4-methoxyphenyl)-2-methylpropanoic acid (**1f**). White solid. ^{1}H NMR (400 MHz, DMSO): δ 7.46 (d, J = 8.9 Hz, 2H), 7.36 (d, J = 8.9 Hz, 2H), 6.82 (dd, J = 8.9, 2.5 Hz, 4H), 5.18 (s, 1H), 3.70 (m, 7H), 1.02 (d, J = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 179.13, 158.15, 157.93, 140.90, 137.87, 126.85, 126.77, 113.71, 113.68, 77.55, 55.40, 55.36, 46.14, 13.40. HRMS (ESI): calcd for $C_{18}H_{19}O_5^-$ [M-H]$^-$: 315.1238; found: 315.1230.



3-Hydroxy-2,2-dimethyl-3,3-diphenylpropanoic acid (**1g**).[2] White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37 – 7.22 (m, 10H), 4.56 (s, 1H), 1.36 (s, 6H).

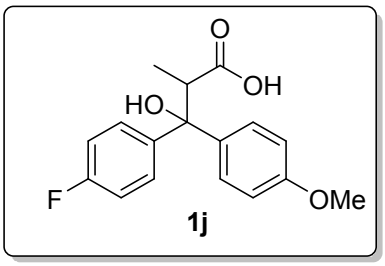


2-(Hydroxydiphenylmethyl)octanoic acid (**1h**). White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62 – 7.51 (m, 2H), 7.50 – 7.40 (m, 2H), 7.33 – 7.22 (m, 5H), 7.17 (t, J = 7.3 Hz, 2H), 4.39 (s, 1H), 3.55 (dd, J = 10.9, 3.4 Hz, 1H), 1.95 – 1.71 (m, 1H), 1.49 – 1.36 (m, 1H), 1.36 – 1.04 (m, 8H), 0.83 (t, J = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 179.07, 149.04, 146.28, 128.35, 128.26, 126.64, 126.46, 126.01, 125.55, 78.32, 52.52, 31.59, 29.19, 28.29, 27.71, 22.48, 14.39. HRMS (ESI): calcd for $C_{21}H_{25}O_3^-$ [M-H]$^-$: 325.1809; found: 325.1822.



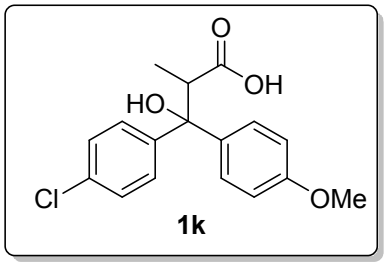
1i

3-Hydroxy-3-(4-methoxyphenyl)-2-methyl-3-phenylpropanoic acid (**1i**). White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55 – 7.47 (m, 1H), 7.48 – 7.42 (m, 1H), 7.42 – 7.36 (m, 1H), 7.31 (dd, J = 9.3, 2.6 Hz, 1H), 7.29 – 7.23 (m, 2H), 7.22 – 7.12 (m, 1H), 6.86 – 6.77 (m, 2H), 4.32 (s, 1H), 3.75 (d, J = 3.9 Hz, 3H), 3.60 (q, J = 7.1 Hz, 1H), 1.18 (dd, J = 10.3, 7.1 Hz, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 179.07, 158.25, 145.83, 140.63, 128.40, 126.95, 126.60, 125.56, 113.78, 77.79, 55.41, 46.05, 13.40. HRMS (ESI): calcd for $C_{17}H_{17}O_4^-$ [M-H]$^-$: 285.1132; found: 285.1152.



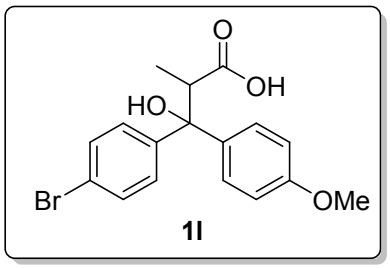
1j

3-(4-Fluorophenyl)-3-hydroxy-3-(4-methoxyphenyl)-2-methylpropanoic acid (**1j**). White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48 (dd, J = 8.7, 5.4 Hz, 1H), 7.45 – 7.39 (m, 1H), 7.35 (dd, J = 8.8, 5.4 Hz, 1H), 7.32 – 7.27 (m, 1H), 6.95 (td, J = 8.7, 7.4 Hz, 2H), 6.82 (dd, J = 8.9, 7.3 Hz, 2H), 4.32 (s, 1H), 3.76 (d, J = 4.6 Hz, 3H), 3.56 (qd, J = 7.1, 2.0 Hz, 1H), 1.18 (dd, J = 10.4, 7.1 Hz, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 178.93, 178.82, 158.30, 158.07, 140.37, 137.45, 127.77, 127.69, 127.61, 126.93, 126.84, 115.13, 115.10, 114.92, 114.89, 113.82, 113.81, 77.62, 77.57, 55.40, 55.37, 46.21, 46.04, 13.35, 13.32. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -115.80, -116.46. HRMS (ESI): calcd for $C_{17}H_{16}FO_4^-$ [M-H]$^-$: 303.1038; found: 303.1027.



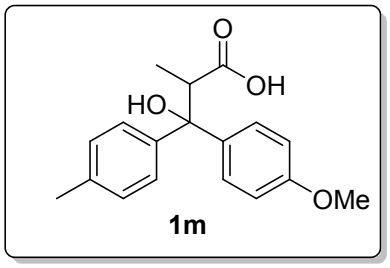
1k

3-(4-Chlorophenyl)-3-hydroxy-3-(4-methoxyphenyl)-2-methylpropanoic acid (**1k**). White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44 (dd, J = 15.4, 8.4 Hz, 2H), 7.34 (d, J = 8.3 Hz, 1H), 7.29 – 7.21 (m, 3H), 6.82 (dd, J = 8.7, 7.3 Hz, 2H), 4.34 (s, 1H), 3.76 (d, J = 3.9 Hz, 3H), 3.57 (q, J = 7.1 Hz, 1H), 1.19 (dd, J = 11.6, 7.1 Hz, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 180.34, 180.31, 158.01, 157.82, 149.35, 146.08, 141.53, 138.21, 130.83, 128.16, 128.05, 127.94, 127.55, 127.19, 126.71, 113.69, 113.62, 77.46, 55.35, 55.33, 46.93, 46.68, 13.83. HRMS (ESI): calcd for $C_{17}H_{16}ClO_4^-$ [M-H]$^-$: 319.0743; found: 319.0731.



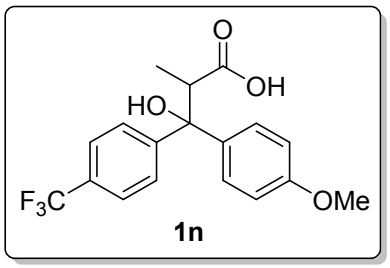
1l

3-(4-Bromophenyl)-3-hydroxy-3-(4-methoxyphenyl)-2-methylpropanoic acid (**1l**). White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46 – 7.35 (m, 4H), 7.28 (dd, J = 8.9, 6.6 Hz, 2H), 6.86 – 6.77 (m, 2H), 4.33 (s, 1H), 3.76 (d, J = 4.4 Hz, 3H), 3.56 (q, J = 7.1 Hz, 1H), 1.18 (dd, J = 11.1, 7.2 Hz, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 180.48, 180.43, 157.84, 157.65, 150.52, 147.27, 142.20, 138.80, 130.96, 130.81, 128.56, 128.05, 127.37, 126.72, 119.09, 113.60, 113.46, 77.37, 55.34, 47.60, 47.33, 14.20, 14.17. HRMS (ESI): calcd for $C_{17}H_{16}BrO_4^-$ [M-H]$^-$: 363.0237; found: 363.0254.



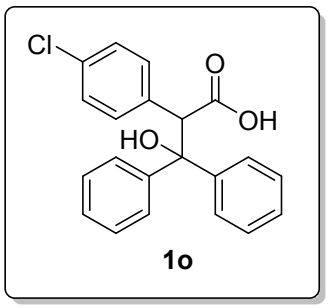
1m

3-Hydroxy-3-(4-methoxyphenyl)-2-methyl-3-(p-tolyl)propanoic acid (**1m**). White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41 (dd, J = 14.9, 8.4 Hz, 2H), 7.35 – 7.26 (m, 2H), 7.08 (t, J = 7.7 Hz, 2H), 6.80 (dd, J = 8.7, 6.3 Hz, 2H), 4.26 (s, 1H), 3.75 (d, J = 2.7 Hz, 3H), 3.59 (qd, J = 7.1, 1.7 Hz, 1H), 2.28 (d, J = 4.0 Hz, 3H), 1.19 (dd, J = 7.2, 2.9 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 183.23 (br), 158.13, 158.08, 145.92, 142.03, 140.97, 137.05, 136.36, 136.01, 129.12, 128.92, 126.82, 126.60, 125.55, 125.32, 113.72, 113.53, 77.96, 55.25, 55.20, 48.09 (br), 21.07, 20.92, 13.41, 13.36. HRMS (ESI): calcd for $C_{18}H_{19}O_4^-$ [M-H]$^-$: 299.1289; found: 299.1310.



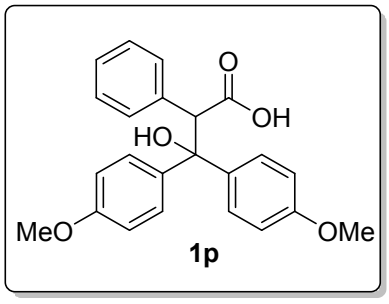
1n

3-Hydroxy-3-(4-methoxyphenyl)-2-methyl-3-(4-(trifluoromethyl)phenyl)propanoic acid (**1n**). White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65 (d, J = 8.2 Hz, 1H), 7.54 (d, J = 11.0 Hz, 3H), 7.44 (d, J = 8.8 Hz, 1H), 7.31 (d, J = 8.9 Hz, 1H), 6.83 (dd, J = 8.9, 6.7 Hz, 2H), 3.76 (d, J = 3.1 Hz, 3H), 3.63 (qd, J = 7.1, 5.8 Hz, 1H), 1.19 (dd, J = 23.4, 7.1 Hz, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 179.27, 158.08, 154.18, 137.21, 127.22 (q, J = 31.7 Hz), 126.81, 126.58, 124.77 (q, J = 272.8 Hz), 125.21 (q, J = 3.8 Hz), 113.87, 77.82, 55.38, 46.35, 13.39. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -62.48. HRMS (ESI): calcd for $C_{18}H_{16}F_3O_4^-$ [M-H]$^-$: 353.1006; found: 353.1029.



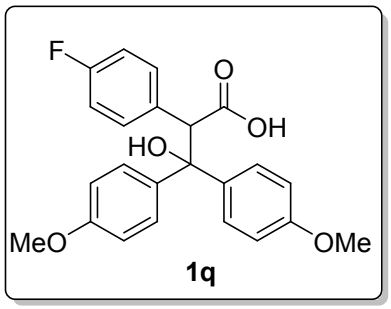
1o

2-(4-Chlorophenyl)-3-hydroxy-3,3-diphenylpropanoic acid (**1o**). White solid. ^{1}H NMR (400 MHz, $CDCl_3$ and CD_3OD): δ 7.71 – 7.60 (m, 2H), 7.40 – 7.33 (m, 2H), 7.31 – 7.21 (m, 1H), 7.15 – 6.99 (m, 9H), 4.65 (s, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 176.08, 148.61, 144.69, 134.76, 132.36, 132.31, 128.68, 127.98, 127.95, 127.21, 126.57, 125.92, 125.90, 78.94, 56.55. HRMS (ESI): calcd for $C_{21}H_{16}ClO_3^-$ [M-H]$^-$: 351.0793; found: 351.0807.

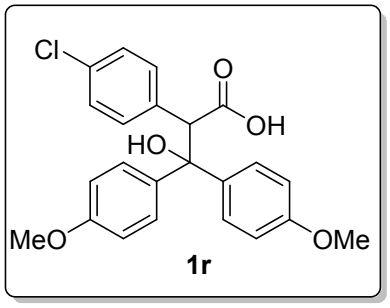


1p

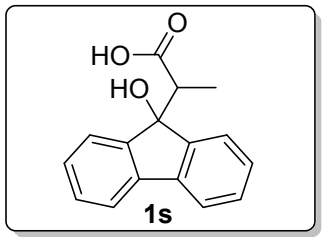
3-Hydroxy-3,3-bis(4-methoxyphenyl)-2-phenylpropanoic acid (**1p**). White solid. ^{1}H NMR (400 MHz, DMSO-d6) δ 7.67 – 7.56 (m, 2H), 7.32 – 7.09 (m, 7H), 6.96 – 6.84 (m, 2H), 6.69 – 6.55 (m, 2H), 5.68 (s, 1H), 4.94 (s, 1H), 3.74 (s, 3H), 3.60 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 176.62, 158.33, 157.66, 141.22, 137.34, 135.72, 130.59, 127.98, 127.40, 127.15, 127.10, 113.88, 113.05, 78.55, 57.54, 55.46, 55.22. HRMS (ESI): calcd for $C_{23}H_{21}O_5^-$ [M-H]$^-$: 377.1394; found: 377.1374.



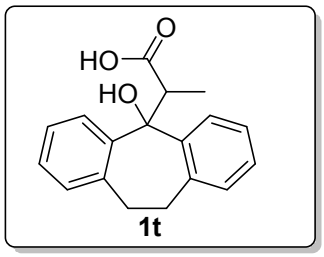
2-(4-Fluorophenyl)-3-hydroxy-3,3-bis(4-methoxyphenyl)propanoic acid (**1q**). White solid. ^{1}H NMR (400 MHz, DMSO-d6) δ13.04 (s, 1H), 7.60 (d, J = 8.9 Hz, 2H), 7.27 – 7.22 (m, 2H), 7.15 – 7.11 (m, 2H), 6.98 (t, J = 8.9 Hz, 2H), 6.93 – 6.83 (m, 2H), 6.61 (d, J = 8.9 Hz, 2H), 5.65 (s, 1H), 4.98 (s, 1H), 3.73 (s, 3H), 3.60 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 176.60, 158.27, 157.62, 141.15, 137.42, 132.40, 132.32, 127.13, 127.07, 114.76, 114.55, 113.81, 113.08, 78.45, 56.75, 55.45, 55.24. ^{19}F NMR (376 MHz, DMSO-d_6) δ -116.00. HRMS (ESI): calcd for $C_{23}H_{20}FO_5^-$ [M-H]$^-$: 395.1300; found: 395.1285.



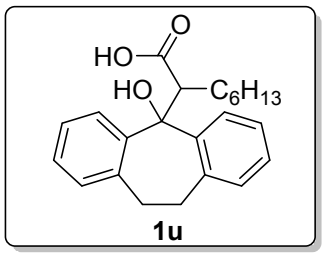
2-(4-Chlorophenyl)-3-hydroxy-3,3-bis(4-methoxyphenyl)propanoic acid(**1r**). White solid. ^{1}H NMR (400 MHz, DMSO-d6) δ 7.60 (d, J = 8.8 Hz, 2H), 7.40 – 7.10 (m, 6H), 6.89 (d, J = 8.8 Hz, 2H), 6.63 (d, J = 8.9 Hz, 2H), 5.67 (s, 1H), 5.01 (s, 1H), 3.73 (s, 3H), 3.61 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 176.19, 158.34, 157.70, 140.93, 137.19, 134.94, 132.34, 132.24, 127.99, 127.06, 113.87, 113.16, 78.45, 56.74, 55.47, 55.24. HRMS (ESI): calcd for $C_{23}H_{20}ClO_5^-$ [M-H]$^-$: 411.1005; found: 411.1015.



2-(9-Hydroxy-9*H*-fluoren-9-yl)propanoic acid (**1s**). White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66 – 7.61 (m, 2H), 7.60 (d, J = 7.5 Hz, 1H), 7.52 – 7.46 (m, 1H), 7.40 (tt, J = 7.4, 1.4 Hz, 2H), 7.36 – 7.31 (m, 1H), 7.29 (td, J = 7.6, 1.2 Hz, 1H), 3.32 (q, J = 7.1 Hz, 1H), 0.70 (d, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 175.29, 149.17, 147.51, 140.29, 140.07, 129.05, 129.02, 128.11, 127.68, 125.94, 124.36, 120.12, 120.05, 82.45, 48.03, 13.06. HRMS (ESI): calcd for $C_{16}H_{13}O_3^-$ [M-H]$^-$: 253.0870; found: 253.0876.

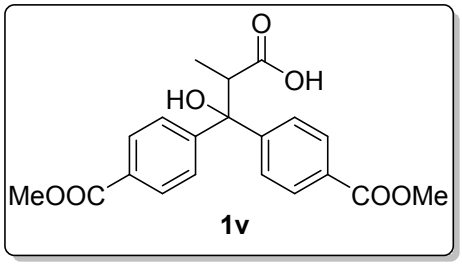


2-(5-Hydroxy-10,11-dihydro-5*H*-dibenzo[*a,d*][7]annulen-5-yl)propanoic acid (**1t**). White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95 (dd, J = 7.6, 1.8 Hz, 1H), 7.75 – 7.65 (m, 1H), 7.14 (dddd, J = 25.3, 20.8, 11.5, 7.1 Hz, 6H), 4.42 (s, 1H), 3.94 (q, J = 7.0 Hz, 1H), 3.68 (ddd, J = 15.9, 9.5, 6.2 Hz, 1H), 3.43 (dt, J = 16.5, 6.0 Hz, 1H), 3.04 (dddd, J = 34.0, 16.0, 11.2, 6.4 Hz, 2H), 1.12 (d, J = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 145.75, 141.49, 137.87, 136.30, 131.08, 130.73, 127.30, 126.22, 125.95, 125.84, 77.74, 46.64, 33.35, 33.24, 13.70.



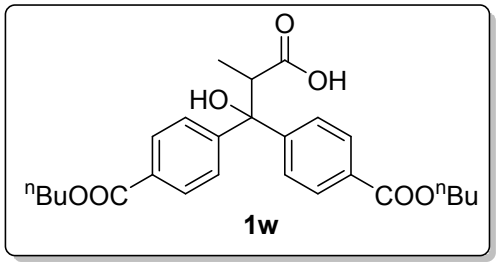
1u

2-(5-Hydroxy-10,11-dihydro-5*H*-dibenzo[*a,d*][7]annulen-5-yl)octanoic acid (**1u**). White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95 (dd, J = 7.5, 2.0 Hz, 1H), 7.67 (dd, J = 7.6, 1.9 Hz, 1H), 7.22 – 7.04 (m, 6H), 4.40 (s, 1H), 3.83 (dd, J = 11.2, 3.4 Hz, 1H), 3.71 (ddd, J = 16.0, 9.4, 6.4 Hz, 1H), 3.45 (dt, J = 16.5, 6.1 Hz, 1H), 3.09 (ddd, J = 16.3, 9.3, 6.6 Hz, 1H), 2.99 (dt, J = 16.0, 6.2 Hz, 1H), 1.79 (dt, J = 13.4, 9.9 Hz, 1H), 1.41 – 1.27 (m, 1H), 1.27 – 1.03 (m, 8H), 0.83 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 177.07, 145.01, 142.66, 137.43, 136.71, 131.47, 131.01, 127.68, 127.65, 127.12, 126.38, 126.05, 125.85, 77.67, 52.75, 32.78, 32.75, 31.38, 28.92, 27.74, 27.62, 22.41, 14.33. HRMS (ESI): calcd for $C_{23}H_{27}O_3^-$ [M-H]$^-$: 351.1966; found: 351.1935.



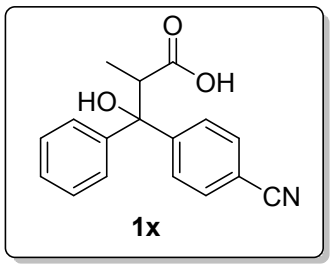
1v

3-Hydroxy-3,3-bis(4-(methoxycarbonyl)phenyl)-2-methylpropanoic acid (**1v**). White solid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.95 (dd, *J* = 8.6, 5.1 Hz, 4H), 7.63 (d, *J* = 8.6 Hz, 2H), 7.51 (d, *J* = 8.6 Hz, 2H), 4.66 (s, 1H), 3.87 (s, 6H), 3.71 (q, *J* = 7.0 Hz, 1H), 1.18 (d, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 181.13, 166.95, 166.94, 151.69, 148.20, 129.97, 129.73, 129.11, 128.80, 125.45, 125.36, 78.00, 52.27, 52.21, 46.07, 12.95. HRMS (ESI): calcd for $C_{20}H_{24}NO_7^+$ [M+NH_4]$^+$: 390.1547; found: 390.1552.



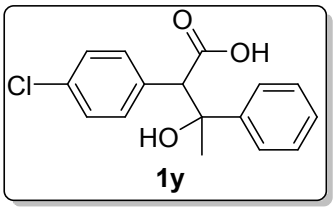
1w

3,3-Bis(4-(butoxycarbonyl)phenyl)-3-hydroxy-2-methylpropanoic acid (**1w**). White solid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.96 (t, *J* = 8.1 Hz, 4H), 7.63 (d, *J* = 8.5 Hz, 2H), 7.51 (d, *J* = 8.6 Hz, 2H), 4.28 (t, *J* = 6.6 Hz, 4H), 3.72 (q, *J* = 7.1 Hz, 1H), 1.71 (p, *J* = 6.7 Hz, 4H), 1.44 (h, *J* = 7.4 Hz, 4H), 1.20 (d, *J* = 7.1 Hz, 4H), 0.95 (t, *J* = 7.4 Hz, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 181.00, 166.59, 151.74, 148.26, 129.93, 129.68, 129.38, 129.07, 125.44, 125.34, 78.03, 65.03, 64.97, 46.06, 30.70, 19.23, 13.73, 12.96. HRMS (ESI): calcd for $C_{26}H_{36}NO_7^+$ [M+NH_4]$^+$: 474.2486; found: 474.2501.



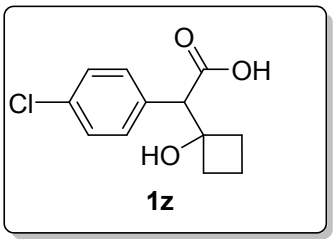
1x

3-(4-Cyanophenyl)-3-hydroxy-2-methyl-3-phenylpropanoic acid (**1x**). White solid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.71 – 7.55 (m, 4H), 7.53 – 7.37 (m, 2H), 7.36 – 7.17 (m, 4H), 4.52 (s, 1H), 3.66 (p, *J* = 7.1 Hz, 1H), 1.19 (dd, *J* = 19.2, 7.1 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 181.71, 181.58, 152.70, 149.35, 142.45, 132.39, 132.18, 128.81, 128.55, 127.75, 127.32, 126.26, 126.21, 125.27, 125.15, 118.62, 110.81, 77.93, 77.90, 46.27, 46.07, 13.00, 12.97. HRMS (ESI): calcd for $C_{17}H_{19}N_2O_3^+$ [M+NH_4]$^+$: 299.1390; found: 299.1396.



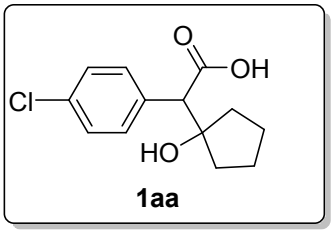
1y

2-(4-Chlorophenyl)-3-hydroxy-3-phenylbutanoic acid (**1y**). White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50 (d, J = 7.7 Hz, 2H), 7.42 – 7.32 (m, 6H), 7.30 (m, 1H), 4.18 (s, 1H), 1.26 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 174.42, 148.41, 135.28, 132.50, 132.34, 128.16, 128.11, 126.90, 125.77, 75.15, 59.89, 27.88. HRMS (ESI): calcd for $C_{16}H_{14}ClO_3^-$ [M-H]$^-$: 289.0637; found: 289.0631.



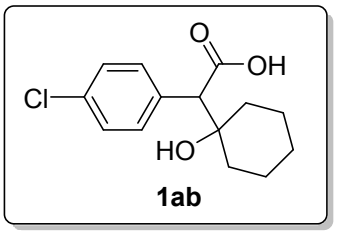
1z

2-(4-Chlorophenyl)-2-(1-hydroxycyclobutyl)acetic acid (**1z**). White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ7.38 – 7.29 (m, 4H), 3.85 (s, 1H), 2.22 (ddd, J = 8.5, 5.3, 2.6 Hz, 2H), 2.07 – 1.81 (m, 3H), 1.70 – 1.52 (m, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 173.66, 136.26, 132.16, 132.04, 128.01, 76.16, 57.69, 36.16, 34.42, 12.46. HRMS (ESI): calcd for $C_{12}H_{12}ClO_3^-$ [M-H]$^-$: 239.0480; found: 239.0464.



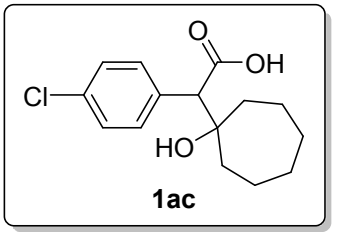
1aa

2-(4-Chlorophenyl)-2-(1-hydroxycyclopentyl)acetic acid (**1aa**). White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40 – 7.18 (m, 4H), 3.62 (s, 1H), 1.94 – 1.31 (m, 8H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 174.44, 136.99, 131.98, 131.88, 128.06, 82.32, 59.06, 38.53, 37.61, 23.46, 23.32. ^{13}C NMR (101 MHz, DMSO-d_6) δ 174.44, 136.99, 131.98, 131.88, 128.06, 82.32, 59.06, 38.53, 37.61, 23.46, 23.32. HRMS (ESI): calcd for $C_{13}H_{14}ClO_3^-$ [M-H]$^-$: 253.0637; found: 253.0623.



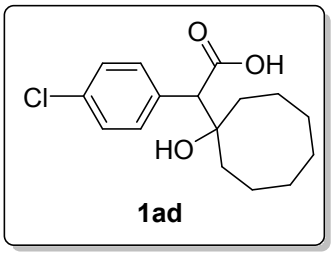
1ab

2-(4-Chlorophenyl)-2-(1-hydroxycyclohexyl)acetic acid (**1ab**).[3] White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36 (d, J = 8.6 Hz, 2H), 7.29 (d, J = 8.5 Hz, 2H), 3.62 (s, 1H), 1.86 – 1.08 (m, 11H).



1ac

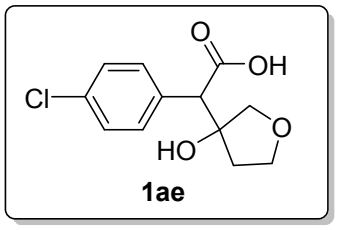
2-(4-Chlorophenyl)-2-(1-hydroxycycloheptyl)acetic acid (**1ac**). White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36 (d, J = 8.2 Hz, 2H), 7.32 – 7.22 (m, 2H), 3.63 (s, 1H), 1.90 (dd, J = 14.4, 8.6 Hz, 1H), 1.80 (dd, J = 14.4, 9.6 Hz, 1H), 1.76 – 1.59 (m, 2H), 1.60 – 1.38 (m, 5H), 1.32 (dq, J = 17.4, 11.5, 8.2 Hz, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 174.83, 135.98, 132.23, 132.17, 128.04, 75.74, 60.44, 39.97, 38.50, 29.50, 21.99, 21.78. HRMS (ESI): calcd for $C_{15}H_{18}ClO_3^-$ [M-H]$^-$: 281.0950; found: 281.0945.



1ad

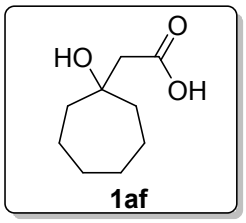
2-(4-Chlorophenyl)-2-(1-hydroxycyclooctyl)acetic acid (**1ad**). White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40 (d, J = 8.1 Hz, 2H), 7.30 (d, J = 8.1 Hz, 2H), 3.69 (s, 1H), 2.00 (dd, J = 14.6, 9.8 Hz, 1H), 1.84 – 1.33 (m, 11H), 1.23 (dd, J = 13.1, 7.8 Hz, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 174.79, 135.91, 132.36, 132.22,

128.03, 75.35, 58.50, 35.26, 34.15, 28.38, 27.99, 24.79, 22.19, 21.55. HRMS (ESI): calcd for $C_{16}H_{20}ClO_3^-$ [M-H]$^-$: 295.1106; found: 295.1108.



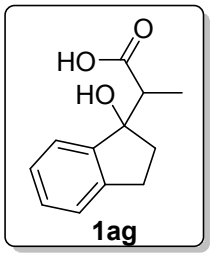
1ae

2-(4-Chlorophenyl)-2-(3-hydroxytetrahydrofuran-3-yl)acetic acid (**1ae**). White solid. ^{1}H NMR (400 MHz, DMSO): δ 12.56 (s, 1H), 7.46 – 7.15 (m, 4H), 5.09 (s, 1H), 3.86 – 3.62 (m, 3H), 3.57 (d, J = 9.2 Hz, 1H), 2.07 – 1.87 (m, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 173.50, 173.41, 136.72, 136.02, 132.42, 132.17, 131.88, 128.34, 128.12, 81.39, 81.25, 78.44, 76.57, 67.03, 66.68, 57.37, 57.11, 39.04, 38.84. HRMS (ESI): calcd for $C_{12}H_{12}ClO_4^-$ [M-H]$^-$: 255.0430; found: 255.0429.



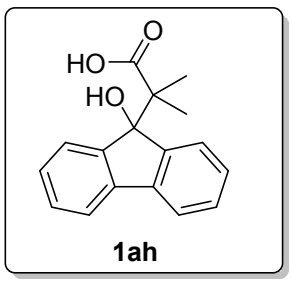
1af

2-(1-Hydroxycycloheptyl)acetic acid (**1af**). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.56 (s, 2H), 1.81 (td, J = 11.6, 10.2, 8.0 Hz, 2H), 1.75 – 1.58 (m, 6H), 1.57 – 1.47 (m, 2H), 1.46 – 1.33 (m, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 173.35, 73.39, 48.14, 40.89, 29.56, 22.14. HRMS (ESI): calcd for $C_9H_{15}O_3^-$ [M-H]$^-$: 171.1027; found: 171.1026.



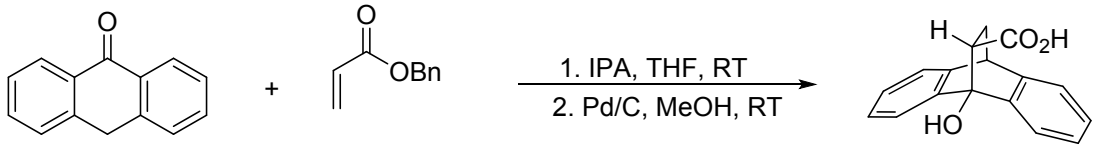
1ag

2-(1-Hydroxy-2,3-dihydro-1*H*-inden-1-yl)propanoic acid (**1ag**). White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34 – 7.24 (m, 4H), 3.19 – 2.99 (m, 2H), 2.87 (ddd, J = 15.7, 8.7, 5.7 Hz, 1H), 2.50 (ddd, J = 13.9, 8.7, 5.2 Hz, 1H), 2.16 (ddd, J = 14.3, 8.9, 5.8 Hz, 1H), 1.09 (d, J = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 176.50, 147.12, 143.81, 128.34, 126.80, 124.98, 123.67, 84.28, 48.25, 35.40, 30.07, 13.79. HRMS (ESI): calcd for $C_{12}H_{13}O_3^-$ [M-H]$^-$: 205.0870; found: 205.0850.



1ah

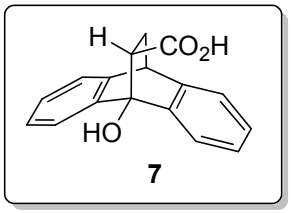
2-(9-Hydroxy-9*H*-fluoren-9-yl)-2-methylpropanoic acid (**1ah**).[2] White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61 (d, J = 7.5 Hz, 2H), 7.51 (d, J = 7.6 Hz, 2H), 7.38 (td, J = 7.5, 1.1 Hz, 2H), 7.26 (td, J = 7.5, 1.2 Hz, 2H), 1.11 (s, 6H).



4 **5** **7**

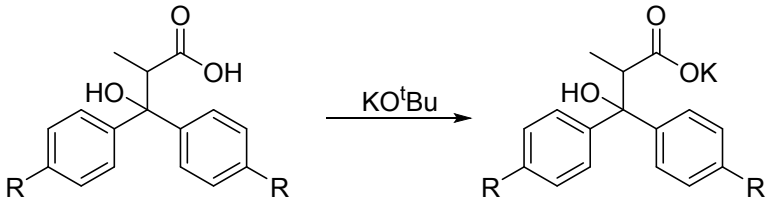
The addition of 0.10 mL of isopropylamine (1.17 mmol) to a mixture of enthrone (677 mg, 3.49 mmol) and benzyl acrylate (559mg, 3.45 mmol) in 10 mL of THF caused the clear colorless solution to turn yellow. After 16 h at ambient temperature, volatiles were removed in vacuo (foaming) to give 1.12g (91%) of essentially pure intermediate as an off-white solid. To a solution of the crude product obtained above (1.12 g, 3.1 mmol) in methanol (10 mL) was added Pd/C (10 % wt, 400 mg,

0.37 mmol) under nitrogen atmosphere at rt. Upon completion, the reaction flask was charged with H_2 via a T-type stopcock and the reaction mixture was stirred at rt until complete conversion of the starting material. Then the reaction mixture was filtered through a celite® pad and the filtrate was evaporated under reduced pressure. The residue thus obtained was purified by flash column chromatography to afford a carboxylic acid intermediate (0.66g, 80% yield).



7

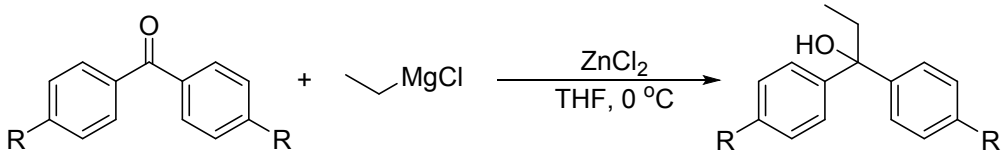
9-Hydroxy-9,10-dihydro-9,10-ethanoanthracene-12-carboxylic acid (**7**). White solid. ^{1}H NMR (400 MHz, DMSO): δ 12.07 (s, 1H), 7.48 (dd, J = 23.0, 7.3 Hz, 2H), 7.29 (t, J = 7.2 Hz, 2H), 7.11 (td, J = 15.3, 14.8, 7.1 Hz, 4H), 6.54 (s, 1H), 4.35 (s, 1H), 2.68 (dd, J = 10.3, 5.2 Hz, 1H), 2.13 – 1.95 (m, 1H), 1.87 (ddd, J = 12.2, 5.4, 2.5 Hz, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 174.93, 145.93, 142.60, 142.51, 126.11, 125.85, 125.63, 125.47, 123.28, 122.77, 121.96, 120.32, 77.41, 48.92, 42.22, 33.07. HRMS (ESI): calcd for $C_{17}H_{13}O_3^-$ $[M-H]^-$: 265.0870; found: 265.0856.



R = H, **1a** Cl, **1c** OMe, **1f**

R = H, **1a'** Cl, **1c'** OMe, **1f'**

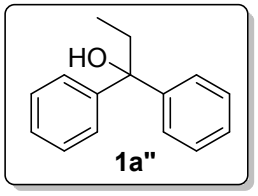
Carboxylate compounds **1a'**, **1c'** and **1f'** were synthesized *in situ* without isolation, and directly electrolyzed for CV studies. In an electrolysis cell, to a solution of compound 1a (6.4 mg, 0.025 mmol) in 5 mL mixed solvent ($MeCN/H_2O$ = 3/1), KO^{t}Bu (28 mg, 0.250 mmol) were added, the resulting solution of **1a'** was used for the CV studies. Compound **1c'** and **1f'** were synthesized by the same method.



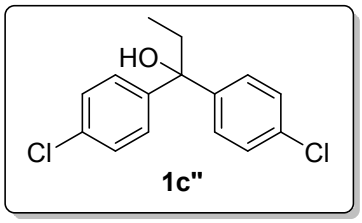
R = H, **S-1a** Cl, **S-1c** OMe, **S-1f**

R = H, **1a''** Cl, **1c''** OMe, **1f''**

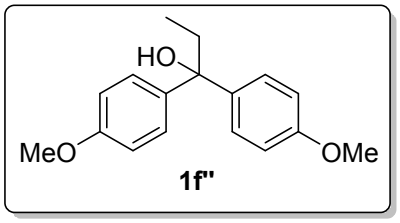
Tertiary alcohols **1a''**, **1c''** and **1f''** were synthesized according to literature reported by Ishihara.[4] To a solution of EtMgCl (1.0 M in THF, 3.90 mL, 3.90 mmol) was added $ZnCl_2$ (40.8 mg, 0.30 mmol) at room temperature under nitrogen atmosphere. This solution was stirred at that temperature for 1 h. Then, the solution was cooled to 0 °C, and benzophenone (**S-1**) (3.00 mmol) was added at 0 °C. The mixture was stirred for 8 h at 0 °C, and the reaction was monitored by TLC. The resulting mixture was quenched by saturated aqueous NH_4Cl (5 mL), extracted with EtOAc (10 mL×3), and washed by brine (5 mL). The combined extracts were dried over $MgSO_4$. The organic phase was concentrated under reduced pressure and the resultant residue was purified by silica gel column chromatography to give the desired product.



1,1-Diphenylpropan-1-ol (**1a''**), 482 mg, 76% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.46 – 7.39 (m, 4H), 7.31 (dd, *J* = 8.5, 6.9 Hz, 4H), 7.25 – 7.19 (m, 2H), 2.32 (q, *J* = 7.3 Hz, 2H), 2.06 (s, 1H), 0.88 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 146.93, 128.14, 126.78, 126.14, 78.48, 34.47, 8.18.

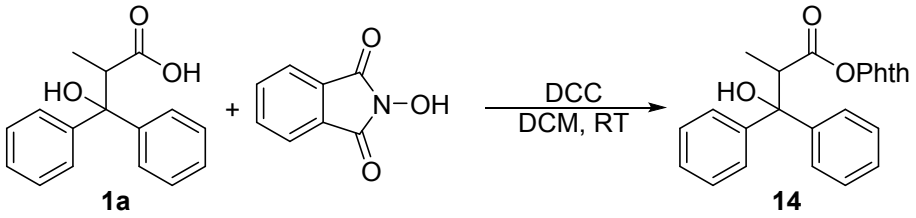


1,1-Bis(4-chlorophenyl)propan-1-ol (**1c''**), 374 mg, 44% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.36 – 7.24 (m, 8H), 2.26 (q, *J* = 7.3 Hz, 2H), 2.01 (s, 1H), 0.86 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 145.00, 132.87, 128.36, 127.53, 77.82, 34.36, 7.99.



1f''

1,1-Bis(4-methoxyphenyl)propan-1-ol (**1f''**), 700 mg, 86% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.34 – 7.27 (m, 4H), 6.88 – 6.79 (m, 4H), 3.78 (s, 6H), 2.26 (d, *J* = 7.3 Hz, 2H), 1.97 (s, 1H), 0.86 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 158.26, 139.48, 127.36, 113.36, 77.98, 55.24, 34.69, 8.30.



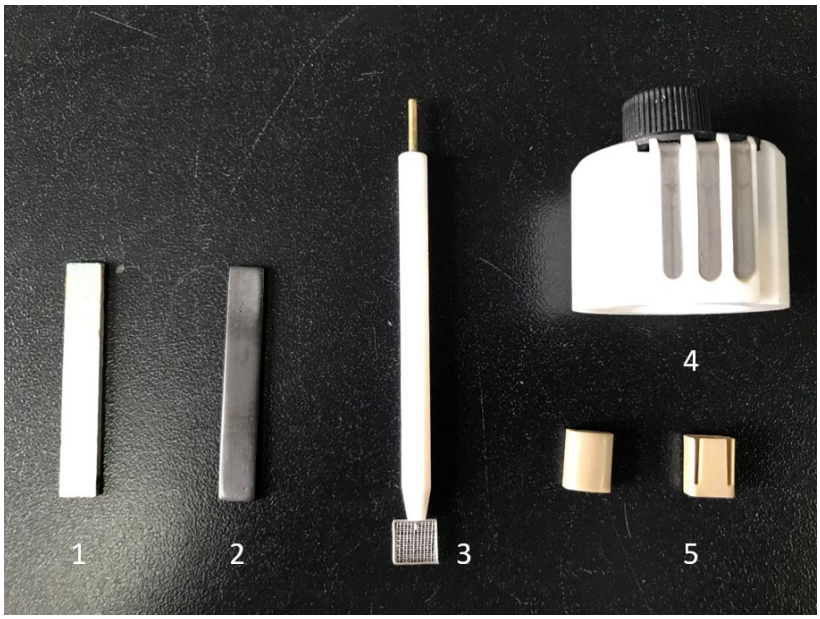
1a **14**

Compound **14** were synthesized according to literature reported by Aggarwal.[5] To a solution of 1a (256 mg, 1.00 mmol) and N-hydroxyphthalimide (171 mg, 1.05 mmol) in DCM (10 mL) at 0 °C was added DCC (217 mg, 1.05 mmol). The reaction was removed from the ice bath and stirred at r.t. for 1 h. The mixture was filtered through Celite, eluting with DCM, and the filtrate was concentrated in vacuo. Purification by flash column chromatography gave N-hydroxyphthalimide ester **14** (303 mg) in 75% yield as a white solid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.83 (dt, *J* = 7.4, 3.8 Hz, 2H), 7.75 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.67 – 7.60 (m, 2H), 7.47 (dd, *J* = 8.4, 1.3 Hz, 2H), 7.39 (dd, *J* = 8.5, 7.1 Hz, 2H), 7.34 – 7.24 (m, 3H), 7.23 – 7.16 (m, 1H), 4.01 (q, *J* = 7.1 Hz, 1H), 3.79 (s, 1H), 1.41 (d, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 173.48, 161.62, 146.23, 143.42, 134.83, 128.82, 128.72, 128.30, 127.56, 126.95, 125.60, 125.44, 124.03, 78.28, 44.93, 13.24. HRMS (ESI): calcd for $C_{24}H_{23}N_2O_5^+$ $[M+NH_4]^+$: 419.1601; found: 419.1600.

3. Electrochemical reactions and characterization

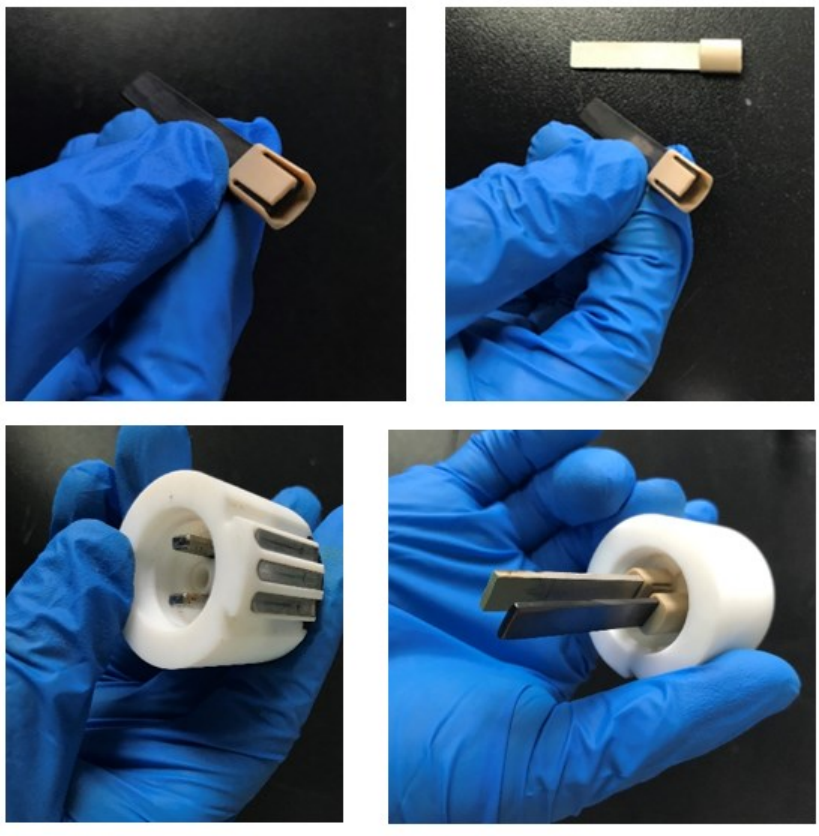
Schematic diagram of the connection of electrochemical set-up

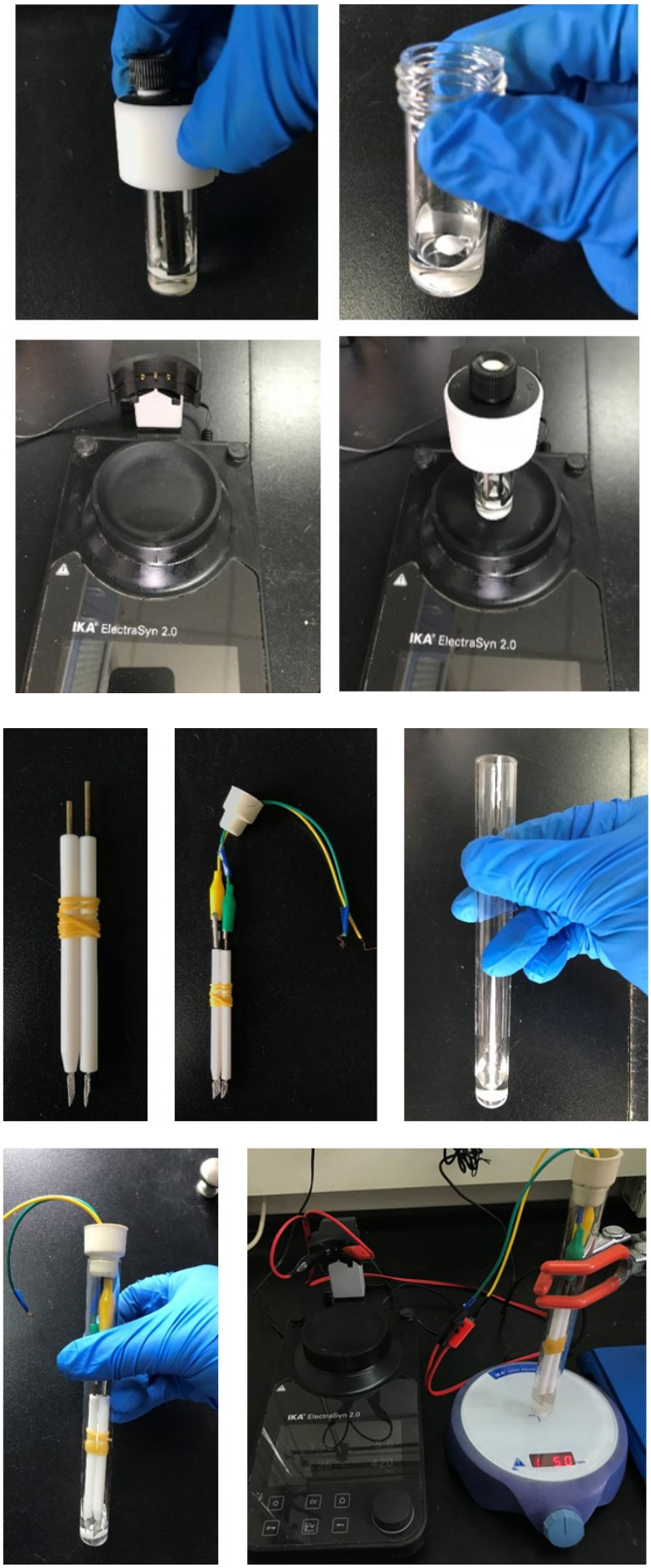
Materials:



1. Pt plate electrode; 2. Graphite electrode; 3. Pt net electrode; 4. Connector; 5. Connector.

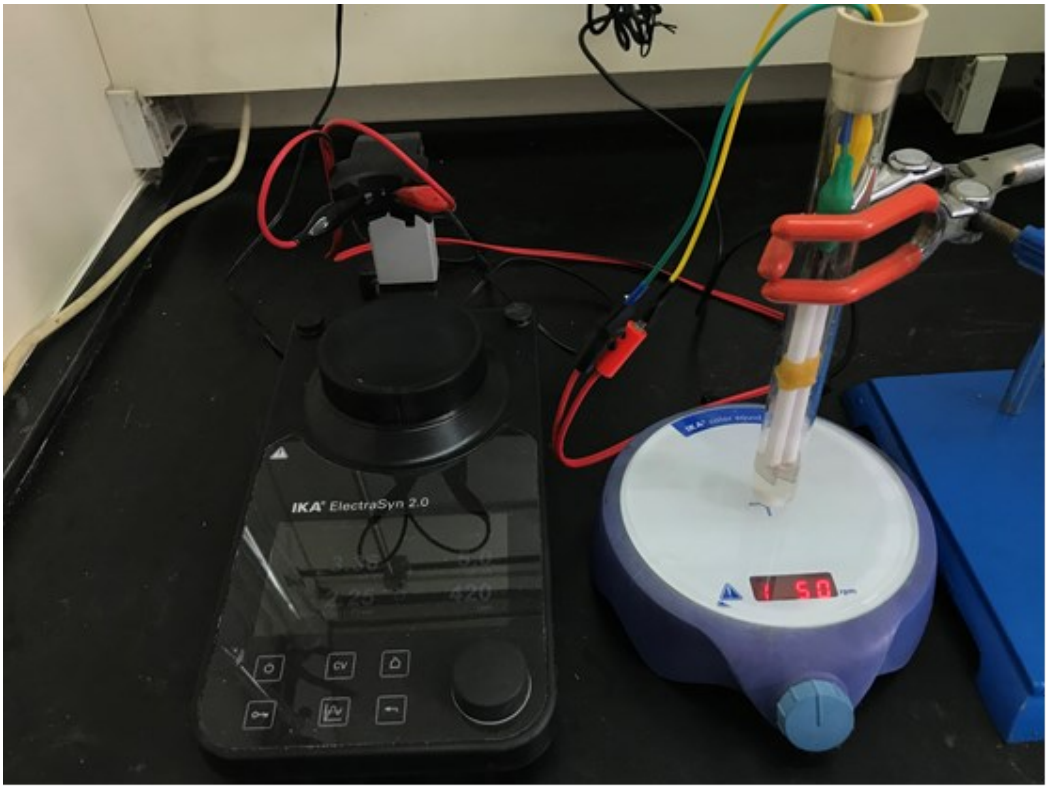
Setting up for 1,2-migration electrochemical experiments





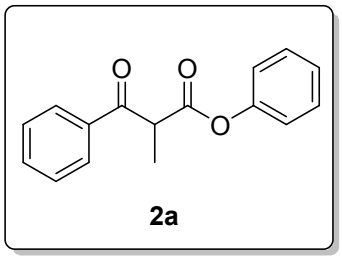
Setting up for 1,4-migration electrochemical experiments

General procedure for the 0.3 mmol scale 1,4-migration electrochemical experiments

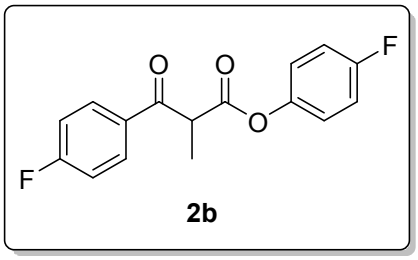


To a 15 mL test tube with a stir bar was charged with 0.3 mmol acid **1**, followed by 3 mL acetonitrile and 1 mL aqueous NaOH solution (0.03 M, 0.03 mmol). Two platinum net electrodes (1.0 cm × 1.0 cm) were set up in the tube. Make sure that the electrodes be totally immersed. The resulting mixture was electrolyzed using IKA Electrasyn 2.0 as a power supply at constant current mode with a current of 5 mA under ambient temperature. The reaction was monitored by TLC or GC. The reaction mixture was concentrated under reduced pressure. The residue was chromatographed through silica gel eluting with PE/EA to give the desired product **2**.

Characterization of the ester-type products

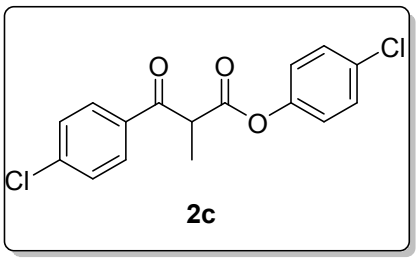


Phenyl 2-methyl-3-oxo-3-phenylpropanoate (**2a**), [6] colorless oil, 59mg, 78% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.09 – 8.00 (m, 2H), 7.65 – 7.57 (m, 1H), 7.51 (dd, *J* = 8.3, 7.1 Hz, 2H), 7.37 – 7.27 (m, 2H), 7.22 – 7.15 (m, 1H), 7.02 – 6.93 (m, 2H), 4.61 (q, *J* = 7.1 Hz, 1H), 1.62 (d, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): 169.63, 135.66, 133.75, 129.44, 128.93, 128.69, 126.08, 121.29, 48.50, 13.88.



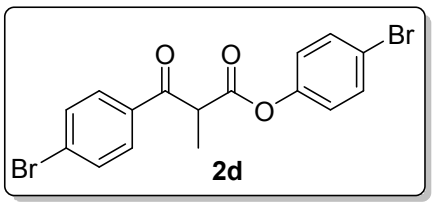
2b

4-Fluorophenyl 3-(4-fluorophenyl)-2-methyl-3-oxopropanoate (**2b**), colorless solid, 61mg, 70% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.08 (ddd, *J* = 8.9, 5.3, 1.6 Hz, 2H), 7.20 (td, *J* = 8.5, 1.6 Hz, 2H), 7.03 (td, *J* = 8.6, 8.1, 1.5 Hz, 2H), 6.96 (ddd, *J* = 9.0, 4.5, 1.5 Hz, 2H), 4.57 (qd, *J* = 7.1, 1.4 Hz, 1H), 1.61 (dd, *J* = 7.2, 1.4 Hz, 3H).^{13}C NMR (101 MHz, $CDCl_3$): 193.99, 166.14 (d, *J* = 256.1 Hz), 160.38 (d, *J* = 244.6 Hz), 146.28 (d, *J* = 2.6 Hz), 131.91 (d, *J* = 3.2 Hz), 131.40 (d, *J* = 9.5 Hz), 122.68 (d, *J* = 8.3 Hz), 116.27, 116.05 (d, *J* = 3.1 Hz), 48.34, 13.85. HRMS (ESI): calcd for $C_{16}H_{13}F_2O_3^+$ $[M+H]^+$: 291.0827; found: 291.0826.



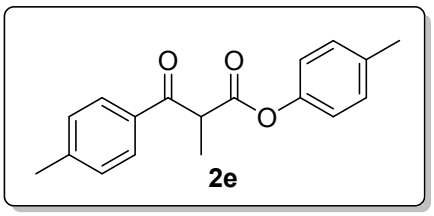
2c

4-Chlorophenyl 3-(4-chlorophenyl)-2-methyl-3-oxopropanoate (**2c**), white solid, 72mg, 75% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06 – 7.90 (m, 2H), 7.49 (dd, *J* = 8.5, 1.6 Hz, 2H), 7.30 (dd, *J* = 8.8, 1.6 Hz, 2H), 6.95 (dd, *J* = 8.6, 1.5 Hz, 2H), 4.56 (qd, *J* = 7.2, 1.4 Hz, 1H), 1.61 (dd, *J* = 7.1, 1.4 Hz, 3H).^{13}C NMR (101 MHz, $CDCl_3$): 194.36, 169.11, 148.91, 140.46, 133.76, 131.57, 130.08, 129.55, 129.33, 122.64, 48.37, 13.82. HRMS (ESI): calcd for $C_{16}H_{13}Cl_2O_3^+$ $[M+NH_4]^+$: 323.0236; found: 323.0236



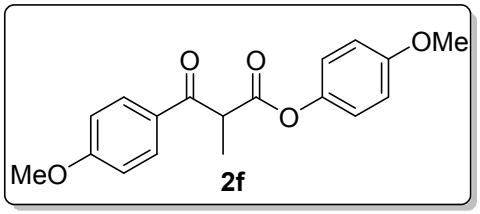
2d

4-Bromophenyl 3-(4-bromophenyl)-2-methyl-3-oxopropanoate (**2d**), white solid, 100mg, 81% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89 (d, *J* = 8.2 Hz, 2H), 7.66 (d, *J* = 8.2 Hz, 2H), 7.45 (d, *J* = 8.3 Hz, 2H), 6.90 (d, *J* = 8.3 Hz, 2H), 4.56 (q, *J* = 7.1 Hz, 1H), 1.60 (d, *J* = 7.2 Hz, 3H).^{13}C NMR (101 MHz, $CDCl_3$): 194.58, 169.01, 149.47, 134.15, 132.54, 132.33, 130.16, 129.24, 123.09, 119.30, 48.35, 13.83. HRMS (ESI): calcd for $C_{16}H_{13}Br_2O_3^+$ $[M+H]^+$: 410.9226; found: 410.9226.



2e

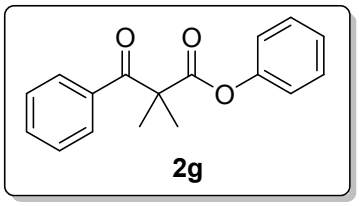
p-Tolyl 3-hydroxy-2-methyl-3-(p-tolyl)propanoate (**2e**), colorless oil, 70mg, 83% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03 – 7.83 (m, 2H), 7.30 (d, *J* = 7.8 Hz, 2H), 7.12 (d, *J* = 8.0 Hz, 2H), 6.92 – 6.77 (m, 2H), 4.57 (qd, *J* = 7.1, 1.4 Hz, 1H), 2.43 (s, 3H), 2.30 (s, 3H), 1.60 (dd, *J* = 7.1, 1.4 Hz, 3H).^{13}C NMR (101 MHz, $CDCl_3$): 195.26, 169.94, 148.36, 144.67, 135.67, 129.91, 129.59, 128.83, 120.96, 48.39, 21.73, 20.88, 13.93. HRMS (ESI): calcd for $C_{18}H_{19}O_3^+$ $[M+H]^+$: 283.1329; found: 183.1328.



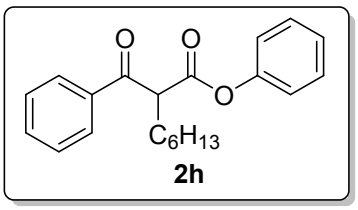
2f

4-Methoxyphenyl 3-(4-methoxyphenyl)-2-methyl-3-oxopropanoate (**2f**), white solid, 73mg, 77% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ8.08 – 7.99 (m, 2H), 7.02 – 6.95 (m, 2H), 6.95 – 6.88 (m, 2H), 6.88 – 6.78 (m, 2H), 4.55 (q, *J* = 7.1 Hz, 1H), 3.89 (s, 3H), 3.77 (s, 3H), 1.60

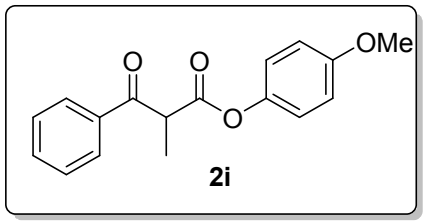
(d, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): 194.10, 170.19, 163.98, 131.07, 128.60, 122.07, 114.41, 114.07, 77.28, 55.58, 48.16, 13.98. HRMS (ESI): calcd for $C_{18}H_{19}O_5^+$ $[M+H]^+$: 315.1227; found: 315.1221.



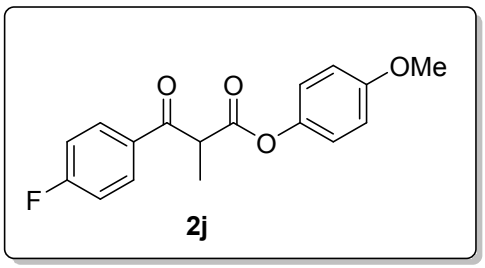
Phenyl 2,2-dimethyl-3-oxo-3-phenylpropanoate (**2g**), colorless oil, 37mg, 46% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97 (d, J = 8.0 Hz, 2H), 7.58 (t, J = 7.3 Hz, 1H), 7.48 (t, J = 7.6 Hz, 2H), 7.32 – 7.26 (m, 2H), 7.22 – 7.14 (m, 1H), 6.76 (d, J = 8.1 Hz, 2H), 1.71 (s, 6H).^{13}C NMR (101 MHz, $CDCl_3$): 197.17, 173.77,150.36, 135.33, 133.02, 129.41, 128.74, 128.70, 126.12, 121.01, 53.49, 23.95. HRMS (ESI): calcd for $C_{17}H_{17}O_3^+$ $[M+H]^+$: 269.1172; found: 269.1169.



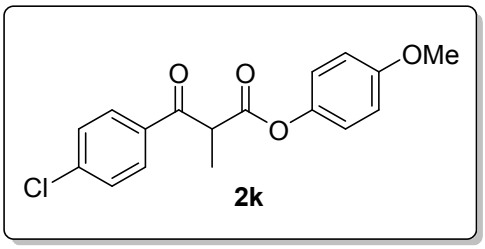
Phenyl 2-benzoyloctanoate (**2h**), colorless oil, 75mg, 77% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06 (d, J = 7.2 Hz, 2H), 7.62 (t, J = 7.4 Hz, 1H), 7.52 (t, J = 7.7 Hz, 2H), 7.33 (t, J = 7.9 Hz, 2H), 7.20 (t, J = 7.4 Hz, 1H), 6.97 (d, J = 7.9 Hz, 2H), 4.51 (dd, J = 8.0, 6.2 Hz, 1H), 2.23 – 2.00 (m, 2H), 1.51 – 1.21 (m, 8H), 0.96 – 0.79 (m, 3H).^{13}C NMR (101 MHz, $CDCl_3$): 194.99,168.85, 150.52, 136.16, 133.69, 129.42, 128.91, 128.63, 126.05, 121.30, 54.43, 31.55, 29.11, 29.04, 27.65, 22.56, 14.06. HRMS (ESI): calcd for $C_{21}H_{25}O_3^+$ $[M+H]^+$: 325.1798; found: 325.1798.



4-Methoxyphenyl 2-methyl-3-oxo-3-phenylpropanoate (**2i**), [7] white solid, 67mg, 79% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.08 – 8.01 (m, 2H), 7.65 – 7.58 (m, 1H), 7.51 (dd, J = 8.4, 7.0 Hz, 2H), 6.95 – 6.87 (m, 2H), 6.86 – 6.79 (m, 2H), 4.59 (q, J = 7.1 Hz, 1H), 3.76 (s, 3H), 1.61 (d, J = 7.2 Hz, 3H).^{13}C NMR (101 MHz, $CDCl_3$): 195.71, 170.00, 157.41, 144.05, 135.68, 133.72, 128.91, 128.67, 122.04, 114.43, 55.58, 48.46, 13.86.

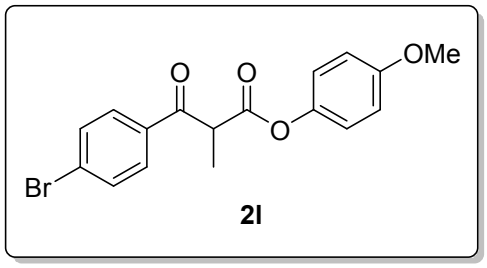


4-Methoxyphenyl 3-(4-fluorophenyl)-2-methyl-3-oxopropanoate (**2j**). 72mg, 79%. White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.12 – 8.04 (m, 2H), 7.22 – 7.14 (m, 2H), 6.94 – 6.87 (m, 2H), 6.87 – 6.80 (m, 2H), 4.55 (q, J = 7.1 Hz, 1H), 3.76 (s, 3H), 1.61 (d, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): 194.06, 169.80, 166.07 (d, J = 256.0 Hz), 157.46, 143.96, 132.08 (d, J = 3.0 Hz), 131.40 (d, J = 9.5 Hz), 121.99, 116.09 (d, J = 22.0 Hz). 114.45, 55.58, 48.40, 13.82. HRMS (ESI): calcd for $C_{17}H_{16}FO_4^+$ $[M+H]^+$: 303.1027; found: 303.1027.



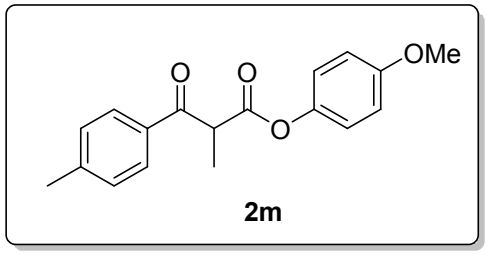
4-Methoxyphenyl 3-(4-chlorophenyl)-2-methyl-3-oxopropanoate (**2k**). 78mg, 82%. Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99 (d, J = 8.6 Hz, 2H), 7.49 (d, J = 8.6 Hz, 2H), 6.94 – 6.87 (m, 2H), 6.87 – 6.80 (m, 2H), 4.54 (q, J = 7.1 Hz, 1H), 3.77 (s, 3H),

1.61 (d, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): 194.41, 169.70, 157.47, 143.92, 140.28, 133.99, 130.08, 129.26, 121.97, 114.46, 55.59, 48.44, 13.77. HRMS (ESI): calcd for $C_{17}H_{16}ClO_4^+$ $[M+H]^+$: 319.0732; found: 319.0729.



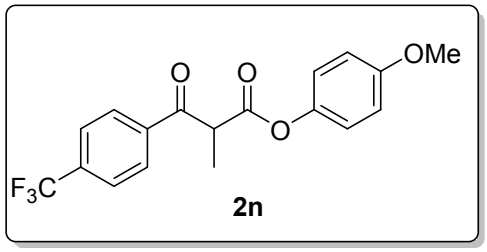
2l

4-Methoxyphenyl 3-(4-bromophenyl)-2-methyl-3-oxopropanoate (**2l**). 80mg, 73%. Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90 (d, J = 8.6 Hz, 2H), 7.65 (d, J = 8.6 Hz, 2H), 6.94 – 6.87 (m, 2H), 6.87 – 6.80 (m, 2H), 4.53 (q, J = 7.1 Hz, 1H), 3.76 (s, 3H), 1.60 (d, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): 194.63, 169.67, 157.47, 143.92, 134.40, 132.25, 130.16, 129.04, 121.97, 114.47, 55.59, 48.42, 13.76. HRMS (ESI): calcd for $C_{17}H_{16}BrO_4^+$ $[M+H]^+$: 363.0227; found: 363.0231.



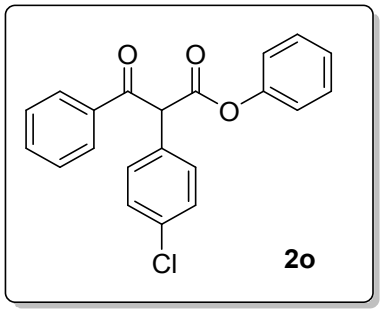
2m

4-Methoxyphenyl 3-(4-bromophenyl)-2-methyl-3-oxopropanoate (**2m**). 58mg, 65%. Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95 (d, J = 8.2 Hz, 2H), 7.31 (d, J = 8.0 Hz, 2H), 6.96 – 6.88 (m, 2H), 6.87 – 6.79 (m, 2H), 4.57 (q, J = 7.1 Hz, 1H), 3.77 (s, 3H), 2.44 (s, 3H), 1.60 (d, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): 195.30, 144.70, 144.07, 133.13, 129.59, 128.82, 122.07, 114.41, 55.59, 48.35, 21.74, 13.93. HRMS (ESI): calcd for $C_{18}H_{19}O_4^+$ $[M+H]^+$: 299.1278; found: 299.1280.

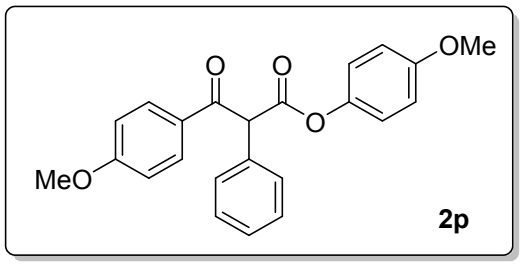


2n

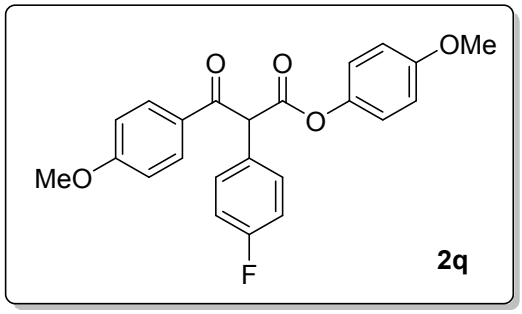
4-Methoxyphenyl 2-methyl-3-oxo-3-(4-(trifluoromethyl)phenyl)propanoate(**2n**). 79mg, 75%. Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95 (d, J = 8.2 Hz, 2H), 7.31 (d, J = 8.0 Hz, 2H), 6.96 – 6.88 (m, 2H), 6.87 – 6.79 (m, 2H), 4.57 (q, J = 7.1 Hz, 1H), 3.77 (s, 3H), 2.44 (s, 3H), 1.60 (d, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): 194.69, 169.46, 157.52, 143.85, 138.41, 134.94 (q, J = 32.8 Hz), 128.99, 125.98 (q, J = 3.7 Hz), 123.48 (q, J = 272.4 Hz), 121.91, 114.48, 55.59, 48.71, 13.65. HRMS (ESI): calcd for $C_{18}H_{16}F_3O_4^+$ $[M+H]^+$: 353.0995; found: 353.0999.



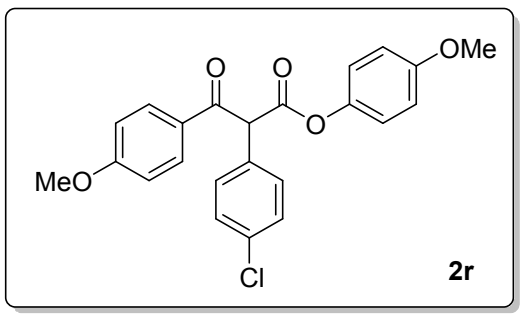
Phenyl 2-(4-chlorophenyl)-3-oxo-3-phenylpropanoate (**2o**), colorless oil, 37mg, 35% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.01 (d, *J* = 7.8 Hz, 2H), 7.60 (s, 1H), 7.46 (dd, *J* = 17.8, 8.3 Hz, 4H), 7.39 – 7.33 (m, 4H), 7.23 (d, *J* = 7.8 Hz, 1H), 7.09 (d, *J* = 8.0 Hz, 2H), 5.82 (s, 1H).^{13}C NMR (101 MHz, $CDCl_3$): 192.70, 167.28， 150.65，135.23, 134.59, 133.98, 131.06, 130.89, 129.50, 129.25, 129.04, 128.96, 126.22, 121.30, 59.84. HRMS (ESI): calcd for $C_{21}H_{16}ClO_3^+$ $[M+H]^+$: 351.0782; found: 351.0786.



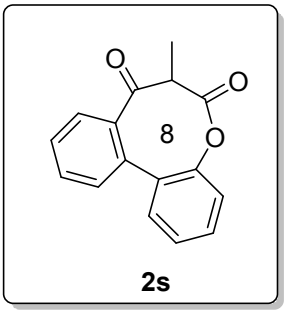
4-Methoxyphenyl 3-(4-methoxyphenyl)-3-oxo-2-phenylpropanoate (**2p**), white solid, 71mg, 63% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99 (d, *J* = 8.5 Hz, 2H), 7.47 (d, *J* = 7.3 Hz, 2H), 7.38 (t, *J* = 7.4 Hz, 2H), 7.35 – 7.29 (m, 1H), 7.03 (d, *J* = 8.7 Hz, 2H), 6.91 (d, *J* = 8.5 Hz, 2H), 6.85 (d, *J* = 8.7 Hz, 2H), 5.78 (s, 1H), 3.84 (s, 3H), 3.78 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$): 191.63, 168.15, 163.93, 157.37, 144.35, 132.93, 131.47, 129.63, 128.95, 128.37, 128.26, 122.19, 114.39, 114.02, 60.43, 55.60, 55.55. HRMS (ESI): calcd for $C_{23}H_{21}O_5^+$ $[M+H]^+$: 377.1384; found: 377.1385.



4-Methoxyphenyl 3-(4-methoxyphenyl)-3-oxo-2-(p-tolyl)propanoate (**2q**), white solid, 70mg, 59% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98 (d, *J* = 8.9 Hz, 2H), 7.52 – 7.39 (m, 2H), 7.06 (t, *J* = 8.5 Hz, 2H), 7.01 (d, *J* = 8.8 Hz, 2H), 6.96 – 6.89 (m, 2H), 6.85 (d, *J* = 8.9 Hz, 2H), 5.77 (s, 1H), 3.85 (s, 3H), 3.77 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$): 191.45, 168.06, 164.06, 162.66 (d, *J* = 247.4 Hz), 157.44, 144.25, 131.46, 131.37 (d, *J* = 8.4 Hz), 128.70 (d, *J* = 3.6 Hz), 128.17, 122.13, 115.93 (d, *J* = 21.5 Hz), 114.43, 114.10, 59.39, 55.60, 55.58. HRMS (ESI): calcd for $C_{23}H_{20}FO_5^+$ $[M+H]^+$: 395.1289; found: 395.1289.

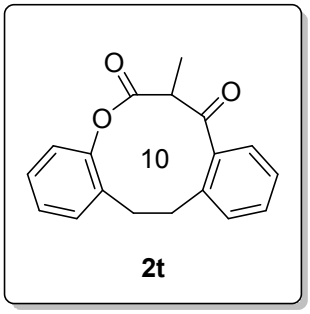


4-Methoxyphenyl 2-(4-chlorophenyl)-3-(4-methoxyphenyl)-3-oxopropanoate (**2r**), white solid, 75mg, 61% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03 – 7.89 (m, 2H), 7.48 – 7.38 (m, 2H), 7.33 (dd, *J* = 8.4, 1.4 Hz, 2H), 7.10 – 6.96 (m, 2H), 6.96 – 6.89 (m, 2H), 6.85 (dd, *J* = 9.0, 1.2 Hz, 2H), 5.76 (s, 1H), 3.83 (d, *J* = 1.2 Hz, 3H), 3.76 (d, *J* = 1.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): 191.27, 167.88, 164.13, 157.47, 144.24, 134.38, 131.47, 131.41, 131.03, 129.14, 128.10, 122.13, 114.45, 114.14, 59.53, 55.59. HRMS (ESI): calcd for $C_{23}H_{20}ClO_5^+$ $[M+H]^+$: 411.0994; found: 411.0989.



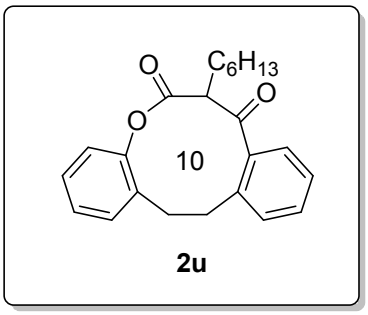
2s

7-Methyl-7,8-dihydro-6H-dibenzo[b,d]oxocin-6-one (**2s**), colorless solid, 45mg, 63% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.64 (td, *J* = 7.6, 1.5 Hz, 1H), 7.53 (dtd, *J* = 9.0, 4.7, 2.9 Hz, 2H), 7.45 – 7.35 (m, 2H), 7.31 – 7.26 (m, 2H), 3.91 (q, *J* = 6.5 Hz, 1H), 1.46 (d, *J* = 6.5 Hz, 3H).^{13}C NMR (101 MHz, $CDCl_3$): 194.52, 169.46, 149.44,137.13, 135.39, 133.74, 133.18, 132.62, 131.70, 130.66, 129.79, 129.04, 127.08, 120.62, 49.98, 12.35. HRMS (ESI): calcd for $C_{16}H_{13}O_3^+$ $[M+H]^+$: 253.0859; found: 253.0857.



2t

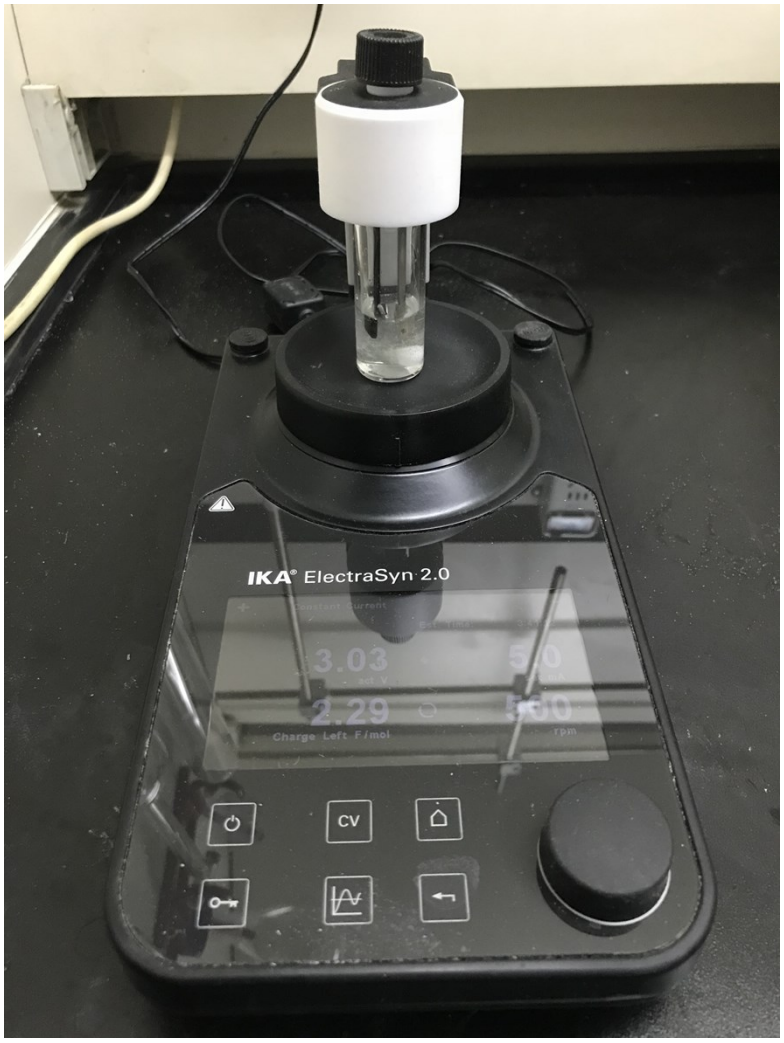
7-Methyl-13,14-dihydro-6H-dibenzo[b,f]oxecine-6,8(7H)-dione (**2t**), colorless oil, 53mg, 63% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47 – 6.94 (m, 8H), 4.29 (q, *J* = 6.9 Hz, 1H), 3.18 (ddd, *J* = 14.0, 6.2, 4.5 Hz, 1H), 2.98 (ddd, *J* = 14.0, 9.8, 6.2 Hz, 1H), 2.88 (ddd, *J* = 14.0, 9.8, 6.2 Hz, 1H), 2.75 (ddd, *J* = 14.0, 6.2, 4.5 Hz, 1H), 1.63 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): 202.43, 167.26, 149.93, 140.38, 138.34, 132.02, 130.91, 130.66, 129.92, 127.52, 126.08, 126.04, 125.45, 121.80, 55.38, 32.76, 32.25, 11.89. HRMS (ESI): calcd for $C_{18}H_{20}NO_3^+$ $[M+NH_4]^+$: 298.1438; found: 298.1437.



2u

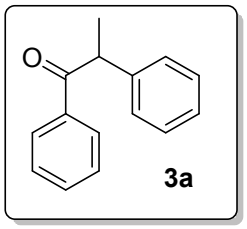
7-Hexyl-13,14-dihydro-6H-dibenzo[b,f]oxecine-6,8(7H)-dione (**2u**), colorless oil, 54mg, 51% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.24 – 6.98 (m, 8H), 4.09 (t, *J* = 7.3 Hz, 1H), 3.09 – 2.99 (m, 1H), 2.96 (dd, *J* = 15.0, 6.3 Hz, 1H), 2.90 – 2.79 (m, 1H), 2.68 – 2.58 (m, 1H), 2.14 (dt, *J* = 14.9, 7.4 Hz, 1H), 2.03 (dq, *J* = 14.7, 7.3 Hz, 1H), 1.47 – 1.32 (m, 4H), 1.28 (dt, *J* = 8.3, 4.0 Hz, 4H), 0.89 – 0.80 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): 202.00, 166.55, 149.85, 140.74, 138.55, 132.22, 130.80, 130.51, 129.96, 127.47, 126.04, 125.21, 121.93, 61.43, 32.59, 32.49, 31.59, 29.15, 27.48, 27.24, 22.60, 14.10. HRMS (ESI): calcd for $C_{23}H_{27}O_3^+$ $[M+H]^+$: 351.1955; found: 351.1958.

General procedure for the 0.3 mmol scale 1,2-migration electrochemical experiments

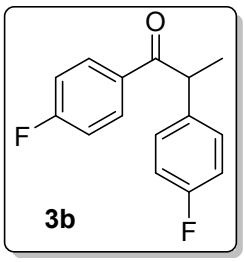


These reactions were set up with IKA Electrasyn 2.0. To a 10 mL tube with a stir bar was charged with 0.3 mmol acid **1**, followed by 3 mL H_2O and 1 mL pyridine. Graphite SK-50 was used as the working electrode, platinum plate was used as the counter electrode. The resulting mixture was electrolyzed at constant current mode with a current of 5 mA under ambient temperature. The reaction was monitored by TLC or GC-MS. The reaction mixture was concentrated under reduced pressure. The residue was chromatographed through silica gel eluting with PE/EA to give the desired product **3**.

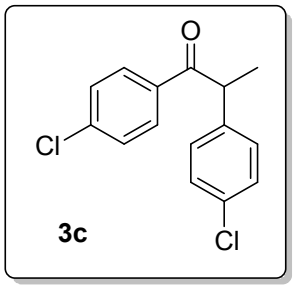
Characterization of the ketone-type products



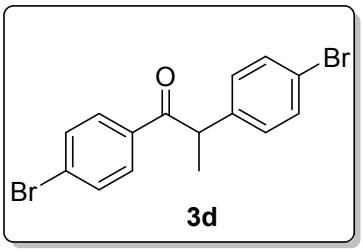
1,2-Diphenylpropan-1-one (**3a**), [8] colorless oil, 47mg, 74% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99 – 7.92 (m, 2H), 7.50 – 7.43 (m, 1H), 7.37 (dd, *J* = 8.2, 6.8 Hz, 2H), 7.28 (d, *J* = 4.4 Hz, 4H), 7.19 (ddd, *J* = 8.7, 5.0, 3.8 Hz, 1H), 4.68 (q, *J* = 6.9 Hz, 1H), 1.53 (d, *J* = 6.9 Hz, 3H).^{13}C NMR (101 MHz, $CDCl_3$): 200.35, 141.50, 136.50, 132.79, 129.00, 128.79, 128.50, 127.79, 126.91, 47.92, 19.52.



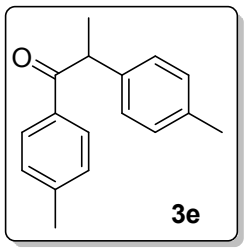
1,2-Bis(4-fluorophenyl)propan-1-one (**3b**), [8] colorless oil, 59mg, 80% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00 – 7.92 (m, 2H), 7.26 – 7.20 (m, 2H), 7.12 – 7.02 (m, 2H), 7.02 – 6.94 (m, 2H), 4.63 (q, *J* = 6.8 Hz, 1H), 1.51 (d, *J* = 6.9 Hz, 3H).^{13}C NMR (101 MHz, $CDCl_3$): 198.60, 165.54 (d, *J* = 255.2 Hz), 161.83 (d, *J* = 245.7 Hz), 136.99 (d, *J* = 3.6 Hz), 132.65 (d, *J* = 3.0 Hz), 131.37 (d, *J* = 9.5 Hz), 129.23 (d, *J* = 7.9 Hz), 115.93 (d, *J* = 21.3 Hz), 115.68 (d, *J* = 21.7 Hz), 47.02, 19.56.



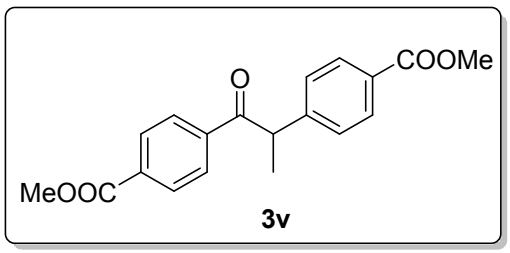
1,2-Bis(4-chlorophenyl)propan-1-one (**3c**), [8] colorless oil, 63mg, 75% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91 – 7.80 (m, 2H), 7.40 – 7.33 (m, 2H), 7.30 – 7.24 (m, 2H), 7.22 – 7.15 (m, 2H), 4.60 (q, *J* = 6.9 Hz, 1H), 1.51 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): 198.70, 139.59, 139.46, 134.50, 133.01, 130.14, 129.26, 129.07, 128.92, 47.29, 19.36.



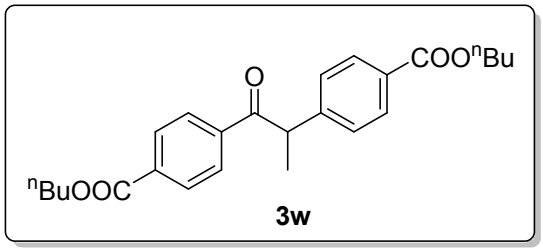
1,2-Bis(4-bromophenyl)propan-1-one (**3d**), [8] colorless oil, 82mg, 75% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77 (d, *J* = 7.6 Hz, 2H), 7.53 (d, *J* = 7.7 Hz, 2H), 7.42 (d, *J* = 7.8 Hz, 2H), 7.13 (d, *J* = 7.8 Hz, 2H), 4.58 (q, *J* = 6.9 Hz, 1H), 1.50 (d, *J* = 6.7 Hz, 3H).^{13}C NMR (101 MHz, $CDCl_3$): 198.81, 140.08, 132.23, 131.93, 130.25, 129.44, 47.35, 19.31.



1,2-Di-*p*-tolylpropan-1-one (**3e**), [8] colorless oil, 52mg, 73% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85 (d, *J* = 8.3 Hz, 2H), 7.16 (d, *J* = 8.0 Hz, 4H), 7.08 (d, *J* = 8.0 Hz, 2H), 4.63 (q, *J* = 6.8 Hz, 1H), 2.34 (s, 3H), 2.27 (s, 3H), 1.50 (d, *J* = 6.9 Hz, 3H).^{13}C NMR (101 MHz, $CDCl_3$): 200.10, 143.48, 138.73, 136.42, 133.99, 129.66, 129.17, 128.92, 127.61, 47.33, 21.59, 21.03, 19.52.

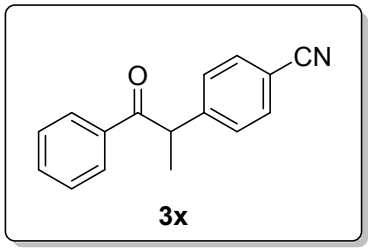


Dimethyl 4,4'-(1-oxopropane-1,2-diyl)dibenzoate (3v), white solid, 14mg, 14% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.04 (d, *J* = 8.6 Hz, 2H), 8.00 – 7.92 (m, 4H), 7.34 (d, *J* = 8.3 Hz, 2H), 4.73 (q, *J* = 6.8 Hz, 1H), 3.91 (s, 3H), 3.88 (s, 3H), 1.56 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 199.25, 166.68, 166.09, 146.02, 139.48, 133.75, 130.42, 129.80, 129.07, 128.61, 127.85, 52.46, 52.13, 48.36, 19.18. HRMS (ESI): calcd for $C_{19}H_{19}O_5^+$ $[M+H]^+$: 327.1227; found: 327.1231.



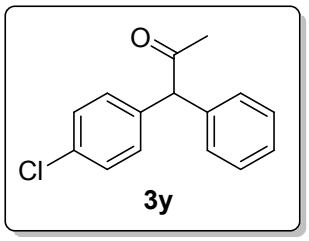
3w

Dibutyl 4,4'-(1-oxopropane-1,2-diyl)dibenzoate (**3w**), colorless oil, 20mg, 16% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.04 (d, *J* = 7.8 Hz, 2H), 7.96 (t, *J* = 7.3 Hz, 4H), 7.32 (s, 2H), 4.73 (q, *J* = 6.8 Hz, 1H), 4.39 – 4.23 (m, 4H), 1.72 (h, *J* = 6.7 Hz, 5H), 1.63 – 1.53 (m, 3H), 1.52 – 1.40 (m, 4H), 0.96 (ddt, *J* = 7.5, 4.2, 2.1 Hz, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 199.24, 166.26, 165.67, 145.95, 139.40, 134.13, 130.39, 129.73, 129.44, 128.59, 127.80, 65.29, 64.85, 48.41, 30.75, 30.67, 19.24, 19.23, 19.16, 13.74. HRMS (ESI): calcd for $C_{25}H_{34}NO_5^+$ $[M+NH_4]^+$: 428.2432; found: 428.2430.



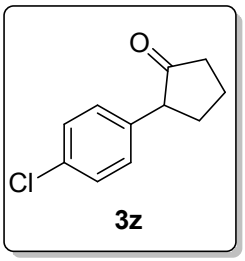
3x

4-(1-Oxo-1-phenylpropan-2-yl)benzonitrile (**3x**), [9] colorless oil, 5mg, 7% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.92 (d, *J* = 8.2 Hz, 2H), 7.60 (d, *J* = 7.9 Hz, 2H), 7.53 (t, *J* = 7.3 Hz, 1H), 7.48 – 7.35 (m, 4H), 4.77 (q, *J* = 6.9 Hz, 1H), 1.55 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 199.26, 146.66, 135.94, 133.37, 132.76, 128.76, 128.68, 118.66, 110.98, 47.65, 19.31.



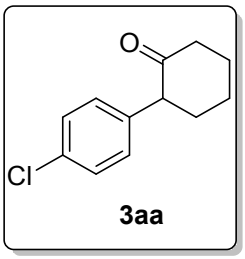
3y

1-(4-Chlorophenyl)-1-phenylpropan-2-one (**3y**), [10] colorless oil, 52mg, 71% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34 (dd, *J* = 8.0, 6.3 Hz, 2H), 7.31 – 7.23 (m, 3H), 7.23 – 7.18 (m, 2H), 7.14 (d, *J* = 8.4 Hz, 2H), 5.08 (s, 1H), 2.23 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): 206.08, 137.84, 136.91, 133.21, 130.36, 128.99, 128.90, 128.82, 127.57, 64.27, 30.09.



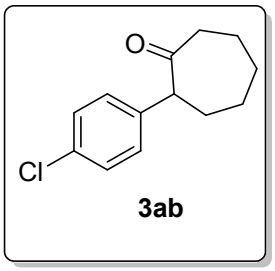
3z

2-(4-Chlorophenyl)cyclopentan-1-one (**3z**), [11] colorless oil, 41mg, 70% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29 (d, *J* = 7.9 Hz, 2H), 7.12 (d, *J* = 8.0 Hz, 2H), 3.28 (dd, *J* = 11.5, 8.2 Hz, 1H), 2.48 (dddd, *J* = 18.2, 9.8, 7.8, 4.0 Hz, 2H), 2.36 – 2.21 (m, 1H), 2.21 – 2.10 (m, 1H), 2.04 (td, *J* = 11.8, 5.9 Hz, 1H), 1.92 (tdd, *J* = 18.5, 17.2, 8.7, 5.7 Hz, 1H).^{13}C NMR (101 MHz, $CDCl_3$): 217.44, 136.79, 132.73, 129.51, 128.70, 54.67, 38.28, 31.55, 20.78.



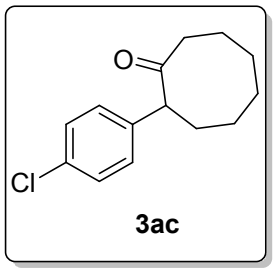
3aa

2-(4-Chlorophenyl)cyclohexan-1-one (**3aa**), [12] colorless oil, 44mg, 71% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30 (d, *J* = 8.5 Hz, 2H), 7.07 (d, *J* = 8.4 Hz, 2H), 3.58 (dd, *J* = 12.4, 5.2 Hz, 1H), 2.60 – 2.39 (m, 2H), 2.33 – 2.21 (m, 1H), 2.15-2.25 (m, 1H), 2.07 – 1.90 (m, 2H), 1.90 – 1.73 (m, 2H).^{13}C NMR (101 MHz, $CDCl_3$): 209.83, 137.23, 132.70, 129.95, 128.50, 56.82, 42.21, 35.28, 27.80, 25.39.



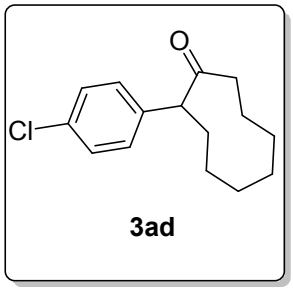
3ab

2-(4-Chlorophenyl)cycloheptanone (**3ab**), [13] colorless oil, 41mg, 61% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ7.28 (d, *J* = 8.5 Hz, 2H), 7.15 (d, *J* = 8.4 Hz, 2H), 3.71 (dd, *J* = 11.3, 3.8 Hz, 1H), 2.64 (ddd, *J* = 14.7, 11.8, 3.3 Hz, 1H), 2.54 (ddt, *J* = 13.7, 6.5, 3.3 Hz, 1H), 2.18 – 1.84 (m, 5H), 1.66 (qd, *J* = 12.1, 11.3, 6.9 Hz, 1H), 1.46 (q, *J* = 11.1 Hz, 2H).^{13}C NMR (101 MHz, $CDCl_3$): 212.91, 138.93, 132.70, 129.31, 128.59, 57.88, 42.88, 32.17, 29.77, 28.72, 24.98.



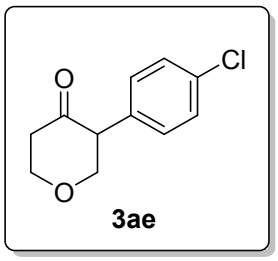
3ac

2-(4-Chlorophenyl)cyclooctan-1-one (**3ac**), colorless oil, 47mg, 67% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.27 (m, 4H), 3.79 (dd, *J* = 12.2, 3.0 Hz, 1H), 2.55 (td, *J* = 12.6, 3.9 Hz, 1H), 2.35 – 2.22 (m, 2H), 2.07 – 1.82 (m, 3H), 1.74 (tt, *J* = 10.5, 4.9 Hz, 2H), 1.50 (m, 4H).^{13}C NMR (101 MHz, $CDCl_3$): 216.06, 137.93, 132.88, 129.22, 128.61, 56.34, 40.73, 32.27, 26.92, 26.43, 26.39, 24.59. HRMS (EI): calcd for $C_{14}H_{17}ClO$ [M]: 236.0968; found: 236.0965.



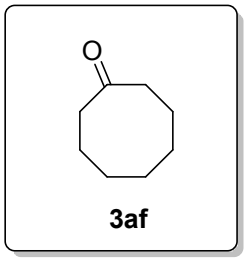
3ad

2-(4-Chlorophenyl)cyclononan-1-one (**3ad**), colorless oil, 55mg, 73% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.26 (s, 4H), 3.91 (dd, *J* = 11.8, 2.7 Hz, 1H), 2.51 – 2.21 (m, 3H), 2.01 – 1.67 (m, 4H), 1.65 – 1.39 (m, 7H). ^{13}C NMR (101 MHz, $CDCl_3$): 215.82, 138.18, 132.91, 129.25, 128.67, 57.99, 42.02, 32.09, 25.68, 25.44, 25.41, 24.03. HRMS (ESI): calcd for $C_{15}H_{20}ClO^+$ $[M+H]^+$: 251.1197; found: 251.1196.



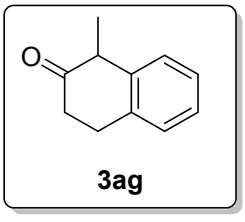
3ae

3-(4-Chlorophenyl)tetrahydro-4H-pyran-4-one (**3ae**), [14] white solid, 36mg, 57% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ7.32 (d, *J* = 8.1 Hz, 2H), 7.17 (d, *J* = 8.0 Hz, 2H), 4.24 (dt, *J* = 10.9, 5.3 Hz, 2H), 4.03 – 3.86 (m, 2H), 3.78 (dd, *J* = 9.0, 6.0 Hz, 1H), 2.68 (ddd, *J* = 15.6, 9.7, 6.2 Hz, 1H), 2.57 (dt, *J* = 14.6, 4.2 Hz, 1H).^{13}C NMR (101 MHz, $CDCl_3$): 205.30, 133.56, 133.25, 130.28, 128.87, 77.30, 73.06, 68.60, 57.39, 41.92.



3af

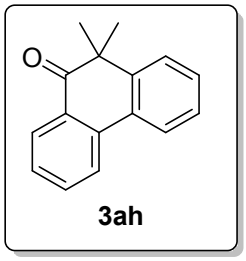
Cyclooctanone (**3af**), [15] colorless oil, 22mg, 58% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.47 – 2.35 (m, 4H), 1.88 (p, *J* = 6.4 Hz, 4H), 1.55 (p, *J* = 6.0 Hz, 4H), 1.38 (p, *J* = 6.2 Hz, 2H).^{13}C NMR (101 MHz, $CDCl_3$): 218.38, 41.95, 27.16, 25.66, 24.70.



3ag

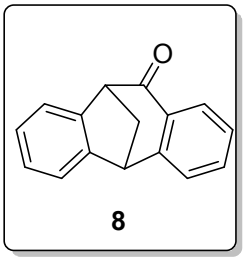
1-Methyl-3,4-dihydronaphthalen-2(1H)-one (**3ag**), [16] colorless oil, 32mg, 67% yield. ^{1}H NMR (400

MHz, $CDCl_3$): δ 8.04 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.45 (td, *J* = 7.5, 1.5 Hz, 1H), 7.30 (t, *J* = 7.5 Hz, 1H), 7.23 (d, *J* = 7.6 Hz, 1H), 3.02 (dddd, *J* = 22.7, 16.7, 11.6, 4.6 Hz, 2H), 2.59 (dqd, *J* = 11.4, 6.8, 4.5 Hz, 1H), 2.20 (dq, *J* = 13.2, 4.4 Hz, 1H), 1.89 (dddd, *J* = 13.2, 11.9, 10.9, 4.8 Hz, 1H), 1.27 (d, *J* = 6.8 Hz, 3H).^{13}C NMR (101 MHz, $CDCl_3$): 200.84, 144.22, 133.10, 132.40, 128.72, 127.41, 126.56, 42.66, 31.39, 28.85, 15.46.



3ah

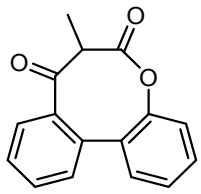
10,10-Dimethylphenanthren-9(10H)-one (**3ah**), [17] colorless oil, 36mg, 54% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.11 – 8.05 (m, 1H), 8.04 – 8.00 (m, 1H), 7.99 (dd, *J* = 5.4, 2.2 Hz, 1H), 7.67 (ddd, *J* = 8.1, 7.2, 1.5 Hz, 1H), 7.55 – 7.49 (m, 1H), 7.47 – 7.40 (m, 1H), 7.40 – 7.33 (m, 2H), 1.55 (s, 6H).^{13}C NMR (101 MHz, $CDCl_3$): 203.16, 144.05, 137.09, 134.23, 129.15, 128.89, 128.15, 127.86, 127.05, 126.34, 123.98, 122.90, 47.37, 29.72, 27.30.



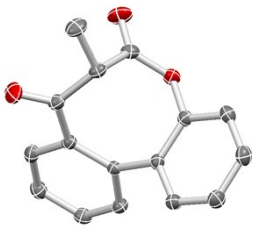
8

5,10-Dihydro-11H-5,10-methanodibenzo[a,d][7]annulen-11-one (**8**), [18] colorless oil, 43mg, 65% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87 (d, *J* = 7.7 Hz, 1H), 7.51 – 7.33 (m, 2H), 7.35 – 7.25 (m, 3H), 7.09 (dt, *J* = 5.9, 1.5 Hz, 2H), 4.18 (d, *J* = 4.5 Hz, 1H), 4.04 (d, *J* = 4.4 Hz, 1H), 3.00 – 2.90 (m, 1H), 2.83 (d, *J* = 11.0 Hz, 1H).^{13}C NMR (101 MHz, $CDCl_3$): 195.77, 150.14，148.37, 140.15, 133.50, 128.54，128.45, 127.51, 126.97, 125.35, 124.80, 123.15, 57.22, 48.20.

4. X-ray data of compound 2s



2s



Bond precision: C-C = 0.0014 A Wavelength=0.71073

Cell: a=8.0221(2) b=11.8060(3) c=13.2172(3)
alpha=90 beta=102.032(2) gamma=90

Temperature: 180 K

	Calculated	Reported
Volume	1224.29(5)	1224.29(5)
Space group	P 21/n	P 1 21/n 1
Hall group	-P 2yn	-P 2yn
Moiety formula	C16 H12 O3	C16 H12 O3
Sum formula	C16 H12 O3	C16 H12 O3
Mr	252.26	252.26
Dx,g cm-3	1.369	1.369
Z	4	4
Mu (mm-1)	0.094	0.094
F000	528.0	528.0
F000'	528.28	
h,k,lmax	11,16,18	11,16,18
Nref	3705	3403
Tmin,Tmax	0.991,0.991	0.845,1.000
Tmin'	0.991	

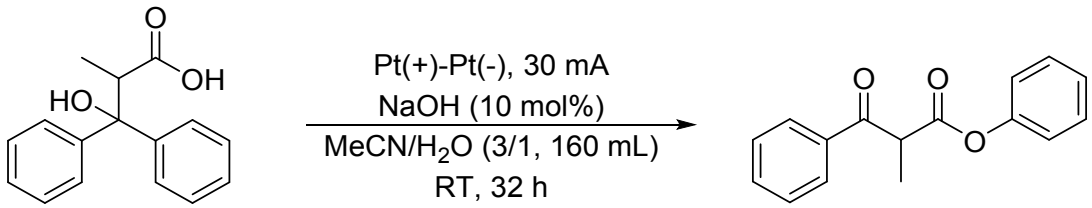
Correction method= # Reported T Limits: Tmin=0.845 Tmax=1.000 AbsCorr = MULTI-SCAN

Data completeness= 0.918 Theta(max)= 30.418

R(reflections)= 0.0374(3122) wR2(reflections)= 0.1033(3403)

S = 1.040 Npar= 173

5. Large-scale synthesis

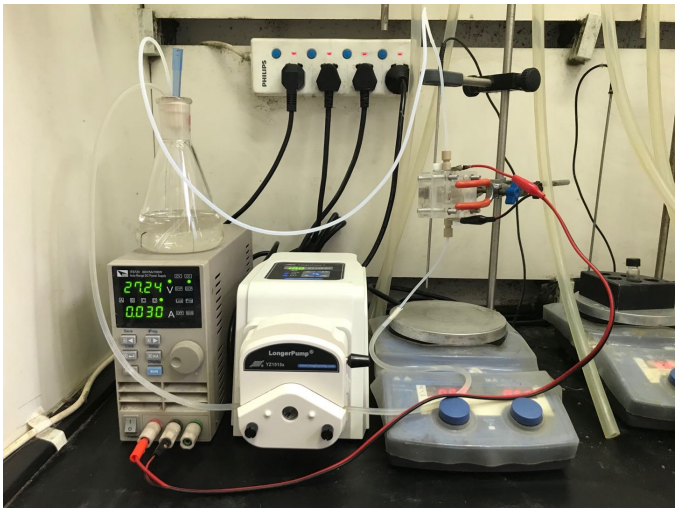


12 mmol
(88% conversion)

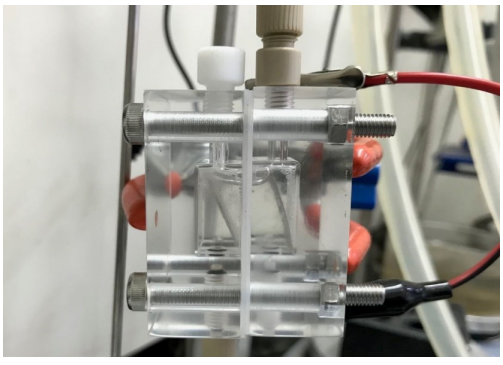
49 % NMR yield

To a 250 mL conical flask was charged with the substrate (3.075 g, 12 mmol, 1.0 eq.), followed by 120 mL acetonitrile and 40 mL aqueous NaOH solution (0.03 M, 1.2 mmol). Facilitated by peristaltic pump, the resulting mixture was pumped into a reaction cell which contained two platinum net electrodes (2.0 cm × 2.0 cm), and flowed out of the cell to the conical flask to complete a circulation. A constant current of 30 mA was applied to the reaction cell, after 32 h, the solvent was removed and 1,3,5-trimethoxybenzene was added as internal standard. NMR ananlysis showed the yield of the ester was 49% and 12% starting material remained.

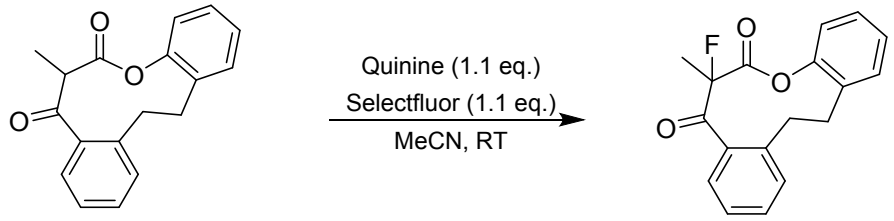
The whole set-up



The reaction cell

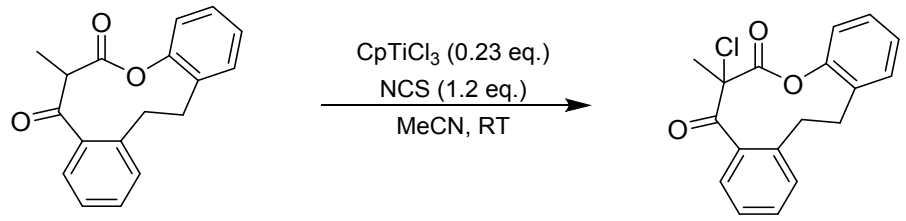


6. Versatile transformations of medium-sized lactone 2t



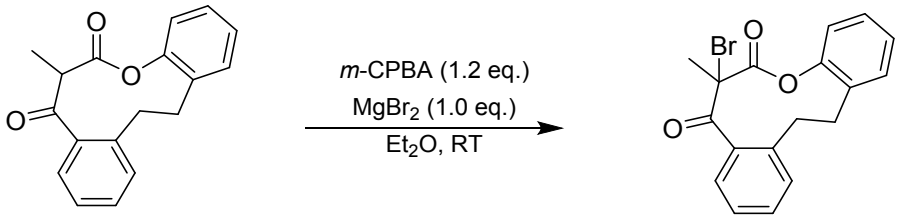
2t **9,** 58%

A mixture of Selectfluor (116 mg, 0.33 mmol) and quinine (107mg, 0.33 mmol) in CH_3CN was stirred at rt for 1 h, **2t** (84mg, 0.3mmol) was added. After stirring of the mixture at rt for 48 h, the reaction was quenched with H_2O. After extraction with EtOAc. The organic layer was washed with aqueous HCl (2 M, 5 mL) and H_2O (5 mL), and then dried over Na_2SO_4. After evaporation of the solvent, the residue was purified by flash column chromatography to give **9** (52mg, 58%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36 (td, *J* = 7.4, 1.5 Hz, 1H), 7.33 – 7.29 (m, 1H), 7.28 – 7.20 (m, 5H), 7.18 (d, *J* = 7.1 Hz, 1H), 3.05 – 2.89 (m, 2H), 2.84 – 2.69 (m, 1H), 2.67 – 2.54 (m, 1H), 2.07 (d, *J* = 21.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): 199.44 (d, *J* = 27.1 Hz), 164.58 (d, *J* = 27.1 Hz), 149.36, 139.30, 136.51 (d, *J* = 2.2 Hz), 132.70, 130.59, 129.90, 127.88, 126.95 (d, *J* = 5.1 Hz), 126.75, 125.79, 121.88, 98.47 (d, *J* = 197.3 Hz), 33.99, 32.22, 19.99 (d, *J* = 22.8 Hz). ^{19}F NMR(471 MHz, $CDCl_3$): -156.09 (q, *J* = 22.5 Hz). HRMS (ESI): calcd for $C_{18}H_{19}FNO_3^+$ $[M+NH_4]^+$: 316.1343; found: 316.1341.



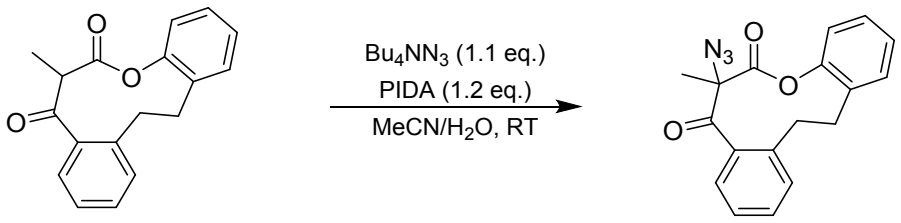
2t **10,** 81%

$CpTiCl_3$ (58 mg, 0.07 mmol) was added to a solution of **2t** (84mg, 0.3 mmol) in 2mL acetonitrile and the mixture was stirred until a clear yellow solution was obtained. To this was added NCS (48mg, 0.36mmol) and the reaction mixture was stirred until complete conversion (TLC) followed by extraction with TBME. The organic phase was dried over $MgSO_4$ and evaporated. The residue was purified by flash chromatography to give **10** (77mg 81%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48 – 7.39 (m, 1H), 7.22 (dtt, *J* = 20.4, 13.0, 7.2 Hz, 7H), 3.07 – 2.98 (m, 1H), 2.95 (t, *J* = 6.5 Hz, 2H), 2.87 (dd, *J* = 13.3, 6.0 Hz, 1H), 2.20 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): 197.13, 164.60, 149.63, 138.49, 137.02, 131.58, 130.76, 130.32, 129.92, 127.86, 127.60, 126.44, 125.56, 121.63, 72.84, 33.14, 31.76, 25.28. HRMS (ESI): calcd for $C_{18}H_{19}ClNO_3^+$ $[M+NH_4]^+$: 332.1048; found: 332.1048.



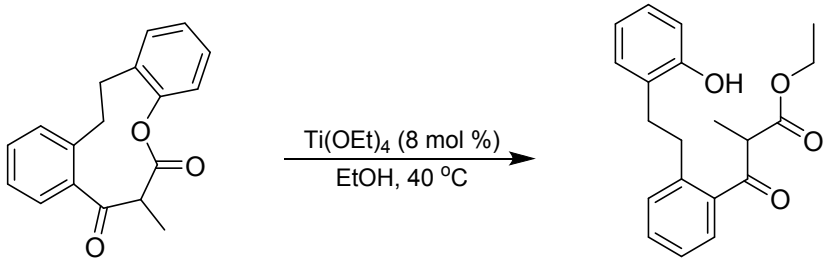
2t **11,** 91%

m-Chloroperbenzoic acid (60 mg, 85 %) was added to a solution of **2t** (84mg, 0.3 mmol) and anhydrous magnesium bromide: tetrahydrofuran complex (144 mg, 0.3mmol), in ether (3 mL) and the reaction mixture was stirred until complete conversion (TLC) followed by addition of saturated aqueous sodium bicarbonate, the reaction mixture was extracted with DCM, separated and dried. After removal of solvent the residue was chromatographed to afford **11** (98 mg, 91 %) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44 (d, J = 7.7 Hz, 1H), 7.32 – 7.11 (m, 7H), 2.99 (t, J = 5.0 Hz, 4H), 2.34 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): 197.08, 164.71, 149.62, 138.22, 137.17, 131.11, 130.91, 130.24, 129.76, 127.87, 127.50, 126.37, 125.67, 121.73, 64.97, 33.05, 31.54, 26.34. HRMS (ESI): calcd for $C_{18}H_{19}BrNO_3^+$ $[M+NH_4]^+$: 376.0543; found: 376.0543.



2t **12,** 67%

In a sample vial fitted with a stirrer bar was placed $TBAN_3$ (94mg, 0.33mmol). PIDA (116mg, 0.36mmol) and MeCN/H_2O (9:1, 2mL) were added. Stirring was initiated and subsequent addition of **2t** (84mg, 0.3mmol) was carried out immediately, after disappearance of the starting material as judged by TLC analysis, the reaction mixture was diluted with Et_2O (5 mL) and washed with H_2O (3 mL). The aqueous layer was extracted with Et_2O (3 x 5 mL) and the organic layers were combined, dried over Na_2SO_4 and concentrated in vacuo. The crude product was purified by flash column chromatography on silica gel to afford **12** (65mg 67%) as a pale yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44 (d, J = 7.7 Hz, 1H), 7.41 – 7.12 (m, 8H), 3.01 – 2.73 (m, 4H), 1.92 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): 199.36, 165.39, 149.49, 138.96, 137.12, 132.20, 130.66, 130.42, 129.99, 127.80, 127.02, 126.69, 125.89, 121.84, 74.44，33.91, 31.83, 20.06. HRMS (ESI): calcd for $C_{18}H_{19}BrN_4O_3^+$ $[M+NH_4]^+$: 339.1452; found: 339.1449.



2t **13**, 66%

A solution of **2t** (84 mg, 0.3 mmol) in ethanol (2 mL) was added $Ti(OEt)_4$ (5 uL, 0.024 mmol) heated under 40°C for 12h at N_2 atmosphere. The reaction was cooled down to room temperature, Ethylacetate (5 mL) was added for extraction. The organic layer was washed with saturated $NaHCO_3$ (5mL), water and brine. After the removal of solvent, the residue was carefully purified by and purified by flash column chromatography to afford the product **13** (65 mg, 66%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81 (d, *J* = 7.9 Hz, 1H), 7.49 (t, *J* = 7.5 Hz, 1H), 7.39 – 7.31 (m, 2H), 7.16 (dd, *J* = 13.3, 6.0 Hz, 3H), 6.94 (d, *J* = 8.1 Hz, 1H), 6.85 (t, *J* = 7.3 Hz, 1H), 4.37 (q, *J* = 7.1 Hz, 1H), 4.11 (q, *J* = 7.1 Hz, 2H), 3.00 – 2.82 (m, 4H), 1.51 (d, *J* = 7.1 Hz, 3H), 1.11 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): 200.68, 170.74, 154.79, 143.09, 135.56，132.80, 132.01, 130.22, 129.63, 127.99, 126.53, 126.51, 120.20, 116.21, 61.48, 50.72, 36.05, 34.04, 13.93, 13.77. HRMS (ESI): calcd for $C_{20}H_{26}NO_4^+$ $[M+NH_4]^+$: 344.1856; found: 344.1856.

7. Cyclic voltammetry study

Cyclic voltammograms of different compounds were measured in 0.1 M $LiClO_4$ in $MeCN/H_2O$ (3/1) using Pt disk (Φ 3 mm) as the working electrode, silver wire as the counter electrode and $Ag/AgNO_3$ (0.1 M in CH_3CN) as the reference electrode, at a scan rate of 0.1 V/s. The concentration of all tested compounds was 5 mM. Background (black line): 0.1 M $LiClO_4$ in $MeCN/H_2O$ (3:1). All the potential measured was recorded vs ferrocene ($Fc^{+/0}$).

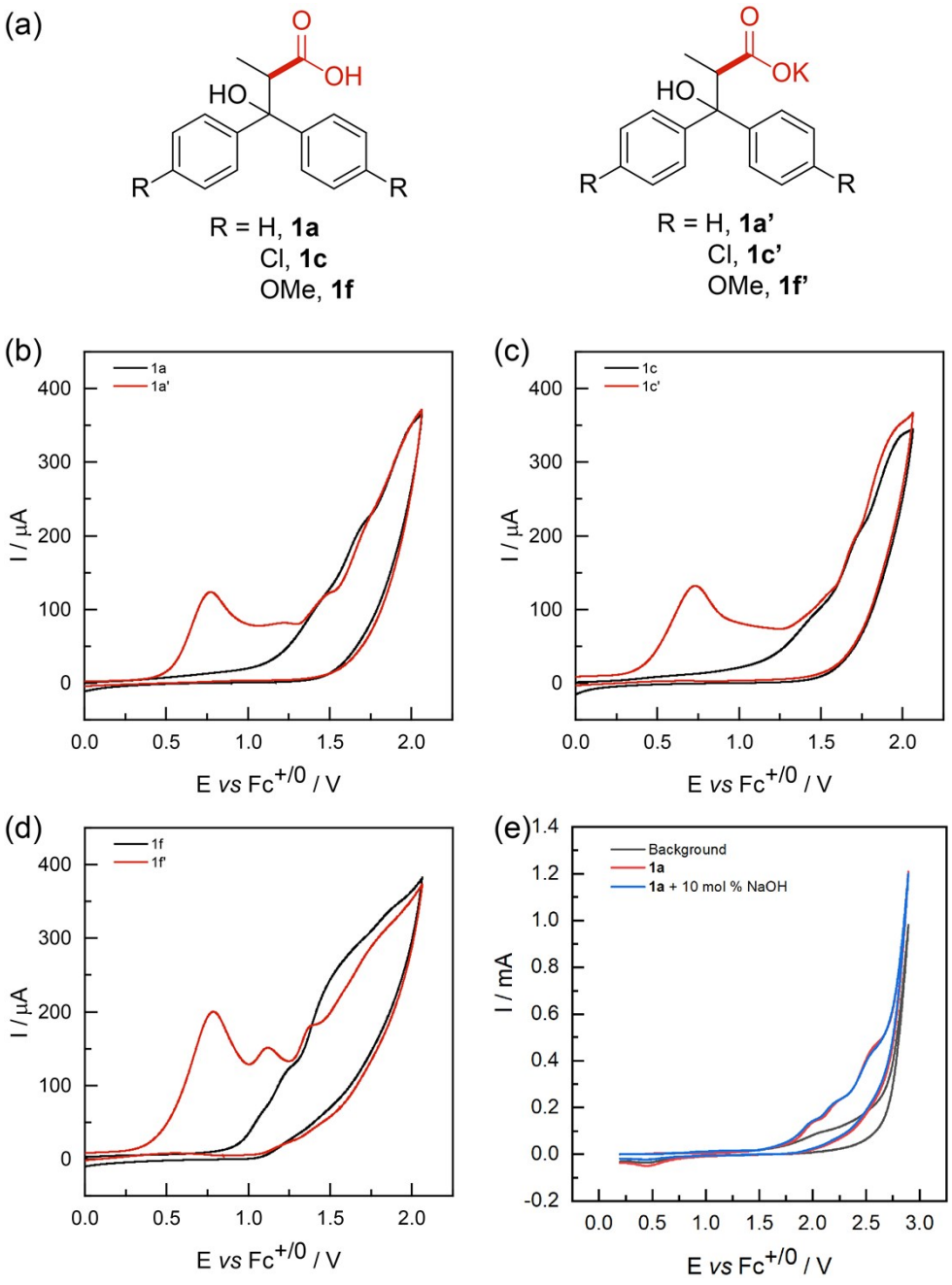
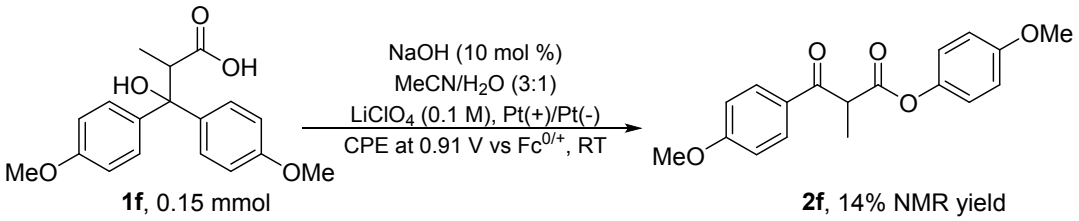


Figure S1. CV studies of **1a-1f** and **1a'-1f'**.

8. Controlled potential electrolysis (CPE)

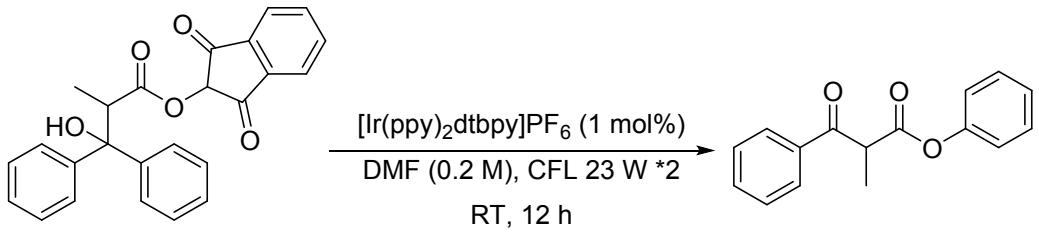


1f, 0.15 mmol

2f, 14% NMR yield

To a 5 mL test tube with a stir bar was charged with acid **1f** (47 mg, 0.15 mmol), 2 mL solution of 0.1 M $LiClO_4$ in $MeCN/H_2O$ (3/1), followed by NaOH (0.6 mg, 0.015 mmol). Two platinum net electrodes (1.0 cm × 1.0 cm) and a reference electrode [$Ag/AgNO_3$ (0.1 M in CH_3CN)] were set up in the tube, and connected to an electrochemical workstation (Potentiostat/Galvanostat) as working electrode, counter electrode and reference electrode respectively. *Bulk Electrolysis with Coulometry (BE)* mode was applied, electrolytic potential was set as 0.91V vs $Fc^{0/+}$. When electrolytic current decreased to 1% of the initial electrolytic current, the reaction was stopped, and 8.1762 C electric charge was consumed. The resulting mixture was extract by EtOAc after adding of water, and the organic phase was collected, concentrated under reduced pressure. Crude NMR showed 14% **2f** was formed with adding 1,3,5-trimethoxybenzene as internal standard.

9. Verification of mechanism by photochemistry



14, 0.2 mmol

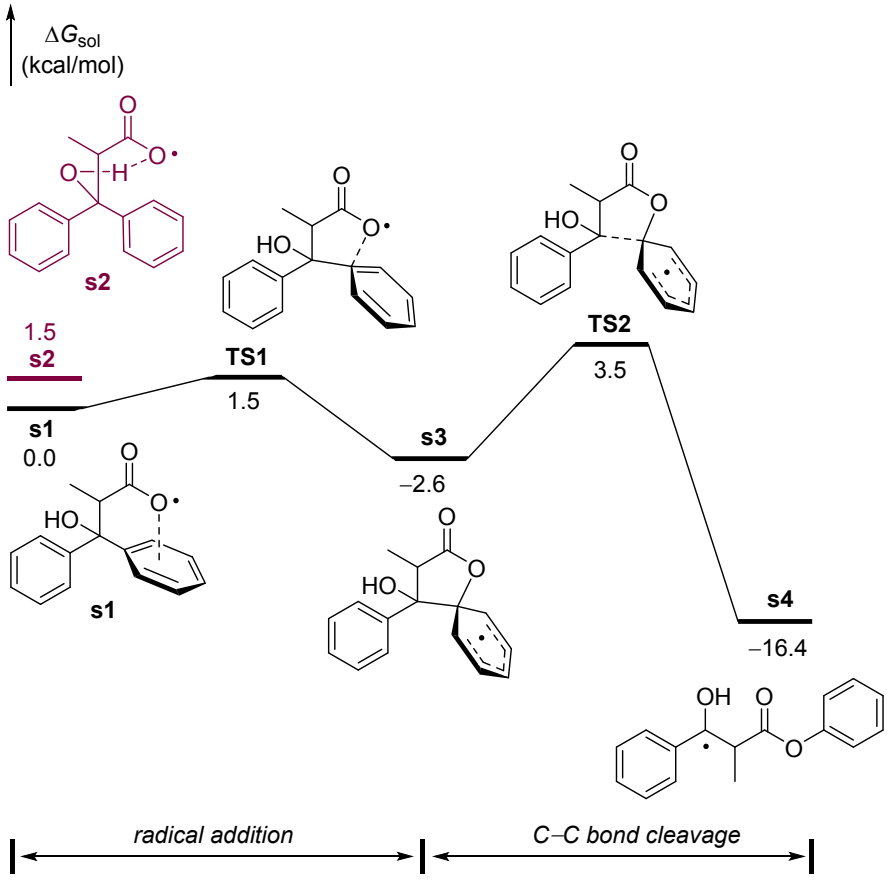
2a, 10% NMR yield

The reaction was carried out according to a modified literature procedure.[19] A solution of **14** (80 mg, 0.2 mmol) and $[Ir(ppy)_2(dtbpy)]PF_6$ (1 mol%) in DMF (1.0 mL) was added into a quartz test tube containing a magnetic stirring bar and the mixture was purged with N_2 for 10 min. The reaction mixture was irradiated using two 25 W CFL for 12 h. The resulting mixture was extract by EtOAc after adding of water, the organic phase was collected, concentrated under reduced pressure. Crude NMR showed 10% **2a** was formed with adding 1,3,5-trimethoxybenzene as internal standard.

10. DFT calculations

All DFT calculations were performed with Gaussian 09.[20] Geometry optimizations were performed in the gas phase with the uB3LYP functional and a basis set of 6-31G(d). Single point energies were calculated with the uB3LYP-D3 and a basis set of 6-311+G(d,p). Solvation energy corrections were calculated using the SMD model[21] with acetonitrile as the solvent.

The computed energy profile for 1,4-aryl migration is shown in Figure S2. The carboxylate radical can interact with the phenyl ring (**s1**) and form hydrogen bonding interaction with the hydroxyl group (**s2**). The higher stability of **s1** than **s2** is mostly due to the electrophilic nature of carboxylate radical. The carboxylate radical can easily add to the phenyl ring via **TS1** to generate a dearomatization intermediate (**s3**), which undergoes C–C bond cleavage with a low barrier (**TS2**)



to deliver the 1,4-aryl migration product.

Figure S2. Energy profile of 1,4-aryl migration initiated by the carboxylate radical.

Cartesian coordinates (Å) and energies of the optimized structures

s1

UB3LYP SCF energy: -844.34444299 a.u.
UB3LYP enthalpy: -844.054543 a.u.
UB3LYP free energy: -844.118432 a.u.
UB3LYP-D3 SCF energy in solution: -844.64293562 a.u.
UB3LYP-D3 enthalpy in solution: -844.353036 a.u.
UB3LYP-D3 free energy in solution: -844.416925 a.u.
Three lowest frequencies (cm-1): 34.7625 43.3488 45.5527

Cartesian coordinates

ATOM	X	Y	Z
H	-2.191007	-0.389189	2.075597
C	-2.455552	0.001329	1.100610
C	-3.131141	1.006850	-1.411319
C	-1.479336	0.059332	0.099549
C	-3.755698	0.444191	0.847180
C	-4.100151	0.945819	-0.407521
C	-1.832014	0.570151	-1.157769
H	-4.500760	0.393911	1.636997
H	-5.112661	1.288595	-0.602796
H	-1.085959	0.643513	-1.944448
H	-3.383952	1.400450	-2.392265
C	-0.048880	-0.431279	0.362962
C	0.939018	0.730711	0.132345
C	2.625912	2.964815	-0.203724
C	1.595085	0.964563	-1.089646
C	1.138608	1.649698	1.178781
C	1.973802	2.749351	1.015007
C	2.431104	2.069038	-1.253825
H	1.469469	0.283624	-1.924967
H	0.628484	1.487253	2.122164
H	2.116071	3.443925	1.838511
H	2.934775	2.222448	-2.204162
H	3.278876	3.823800	-0.330840
O	0.009640	-0.833768	1.734517
H	0.948995	-0.989584	1.934433
C	0.271179	-1.682090	-0.518400
H	0.282597	-1.390581	-1.576659
C	-0.740030	-2.827455	-0.355852
H	-0.391049	-3.713859	-0.892914
H	-1.714492	-2.536868	-0.755963

H	-0.859738	-3.084681	0.699904
C	1.667679	-2.186485	-0.197738
O	2.069312	-3.346058	-0.427107
O	2.543903	-1.451922	0.376785

s2

UB3LYP SCF energy: -844.34510930 a.u.
UB3LYP enthalpy: -844.055147 a.u.
UB3LYP free energy: -844.119399 a.u.
UB3LYP-D3 SCF energy in solution: -844.64021434 a.u.
UB3LYP-D3 enthalpy in solution: -844.350252 a.u.
UB3LYP-D3 free energy in solution: -844.414504 a.u.
Three lowest frequencies (cm-1): 30.0555 37.6634 46.8235

Cartesian coordinates

ATOM	X	Y	Z
H	2.295495	0.496699	1.997553
C	2.521959	0.073304	1.026564
C	3.099260	-1.017365	-1.474242
C	1.498423	-0.054842	0.080515
C	3.820317	-0.344752	0.724804
C	4.115590	-0.887688	-0.525078
C	1.801642	-0.608622	-1.171256
H	4.602194	-0.242381	1.472929
H	5.126572	-1.210822	-0.758289
H	1.016567	-0.741368	-1.910802
H	3.313704	-1.445719	-2.449767
C	0.070105	0.412659	0.396247
C	-0.919399	-0.750580	0.179364
C	-2.641985	-2.960950	-0.115889
C	-1.669517	-0.923941	-0.991170
C	-1.043988	-1.707137	1.198702
C	-1.896102	-2.799252	1.054270
C	-2.525437	-2.019517	-1.136089
H	-1.611547	-0.206000	-1.802793
H	-0.467851	-1.580903	2.109301
H	-1.978189	-3.526204	1.858050
H	-3.103919	-2.127859	-2.049579
H	-3.308998	-3.811273	-0.228420
O	0.056533	0.804358	1.769036

H	-0.852423	1.089364	1.972986
C	-0.270961	1.670603	-0.485573
H	-0.195858	1.409094	-1.546258
C	0.672049	2.861598	-0.209639
H	0.385225	3.724826	-0.818758
H	1.699070	2.586044	-0.460899
H	0.637169	3.143555	0.844893
C	-1.686636	2.119099	-0.241541
O	-2.221115	2.249395	0.889821
O	-2.489060	2.454652	-1.170117

TS1

UB3LYP SCF energy: -844.33855643 a.u.
UB3LYP enthalpy: -844.049616 a.u.
UB3LYP free energy: -844.110484 a.u.
UB3LYP-D3 SCF energy in solution: -844.64260768 a.u.
UB3LYP-D3 enthalpy in solution: -844.353667 a.u.
UB3LYP-D3 free energy in solution: -844.414535 a.u.
Three lowest frequencies (cm-1): -316.2227 25.7808 58.5312
Imaginary frequency: -316.2227 cm-1

Cartesian coordinates

ATOM	X	Y	Z
H	1.946787	-0.048003	2.200067
C	2.321091	-0.125992	1.186656
C	3.294349	-0.297627	-1.417395
C	1.471536	0.190852	0.118216
C	3.638512	-0.523493	0.955304
C	4.131167	-0.612998	-0.346491
C	1.978027	0.101696	-1.186265
H	4.281326	-0.760617	1.799011
H	5.157769	-0.920693	-0.525810
H	1.352612	0.348752	-2.038657
H	3.665361	-0.355755	-2.437184
C	0.021031	0.595635	0.387407
C	-0.952218	-0.593070	0.133331
C	-1.986217	-3.201488	-0.322484
C	-1.147810	-1.111874	-1.200885
C	-1.198639	-1.511765	1.217779
C	-1.729238	-2.762535	0.989408
C	-1.678688	-2.367058	-1.410763

H	-0.918907	-0.482408	-2.053270
H	-0.965644	-1.184855	2.223881
H	-1.932435	-3.422425	1.828156
H	-1.854818	-2.713883	-2.424884
H	-2.404313	-4.188879	-0.494758
O	-0.060392	0.960659	1.764456
H	-0.999601	1.133396	1.951909
C	-0.506999	1.767820	-0.474909
H	-0.365039	1.535779	-1.538262
C	0.125946	3.129471	-0.193771
H	-0.420209	3.901731	-0.742204
H	1.175064	3.144060	-0.505278
H	0.082246	3.366718	0.872257
C	-2.023694	1.756037	-0.233281
O	-2.765470	2.706383	-0.402808
O	-2.467780	0.588633	0.222587

s3

UB3LYP SCF energy: -844.34759491 a.u.
UB3LYP enthalpy: -844.058032 a.u.
UB3LYP free energy: -844.119562 a.u.
UB3LYP-D3 SCF energy in solution: -844.64902393 a.u.
UB3LYP-D3 enthalpy in solution: -844.359461 a.u.
UB3LYP-D3 free energy in solution: -844.420991 a.u.
Three lowest frequencies (cm-1): 29.7688 44.3508 70.0800

Cartesian coordinates

ATOM	X	Y	Z
H	-1.044325	-1.310530	-1.913577
C	-1.700899	-1.047478	-1.090200
C	-3.442373	-0.405076	0.981483
C	-1.172314	-0.689988	0.157705
C	-3.079918	-1.081393	-1.301366
C	-3.957045	-0.759342	-0.266271
C	-2.064484	-0.371197	1.192072
H	-3.465415	-1.366166	-2.276715
H	-5.031041	-0.788842	-0.429171
H	-1.670344	-0.108076	2.166291
H	-4.115130	-0.156704	1.798139
C	0.323320	-0.610546	0.413157
C	0.957762	0.821159	0.069102

C	-0.121698	3.484200	-0.390116
C	0.583122	1.344094	-1.284072
C	0.759827	1.830120	1.153127
C	0.240838	3.071736	0.915003
C	0.075691	2.598639	-1.475933
H	0.756553	0.694899	-2.137081
H	1.030964	1.530898	2.158672
H	0.110253	3.760208	1.746068
H	-0.170025	2.925687	-2.483009
H	-0.528823	4.475959	-0.558452
O	0.517210	-0.881515	1.801768
H	1.462503	-0.777416	2.002944
C	1.234752	-1.538055	-0.421398
H	0.962324	-1.458647	-1.481450
C	1.262119	-3.013975	-0.030479
H	2.051102	-3.527154	-0.587376
H	0.301587	-3.488089	-0.254000
H	1.458488	-3.135343	1.037593
C	2.592189	-0.846368	-0.294461
O	3.686109	-1.331682	-0.433346
O	2.414931	0.464465	0.037453

TS2

UB3LYP SCF energy: -844.33654572 a.u.
UB3LYP enthalpy: -844.048365 a.u.
UB3LYP free energy: -844.109252 a.u.
UB3LYP-D3 SCF energy in solution: -844.63868741 a.u.
UB3LYP-D3 enthalpy in solution: -844.350507 a.u.
UB3LYP-D3 free energy in solution: -844.411394 a.u.
Three lowest frequencies (cm-1): -506.7414 42.9400 55.9196
Imaginary frequency: -506.7414 cm-1

Cartesian coordinates

ATOM	X	Y	Z
H	-0.785958	-1.342571	-1.921854
C	-1.471895	-1.217054	-1.090123
C	-3.285299	-0.922741	1.003053
C	-0.988955	-0.889313	0.190834
C	-2.834604	-1.395996	-1.317184
C	-3.749208	-1.250482	-0.272641
C	-1.924275	-0.741934	1.234079

H	-3.181307	-1.654719	-2.314169
H	-4.811444	-1.394043	-0.450843
H	-1.569271	-0.490768	2.226163
H	-3.987271	-0.808217	1.824892
C	0.445168	-0.665932	0.457880
C	0.995781	1.215162	-0.021465
C	-1.190153	2.988108	-0.308734
C	0.468603	1.545832	-1.324026
C	0.547886	2.026076	1.082525
C	-0.563578	2.830622	0.942604
C	-0.639129	2.359977	-1.440713
H	0.939168	1.116168	-2.203905
H	1.056230	1.931877	2.035992
H	-0.936951	3.378341	1.803895
H	-1.065045	2.547603	-2.422848
H	-2.058021	3.632338	-0.408366
O	0.714140	-0.772752	1.819805
H	1.645206	-0.546467	1.980883
C	1.520809	-1.292131	-0.413245
H	1.203584	-1.223528	-1.460608
C	1.862116	-2.752953	-0.093685
H	2.718147	-3.075305	-0.692254
H	1.005830	-3.397663	-0.312703
H	2.118370	-2.874860	0.962446
C	2.743668	-0.378956	-0.293008
O	3.897073	-0.702633	-0.411846
O	2.399678	0.906898	0.009088

s4

UB3LYP SCF energy: -844.38029213 a.u.
UB3LYP enthalpy: -844.089386 a.u.
UB3LYP free energy: -844.155429 a.u.
UB3LYP-D3 SCF energy in solution: -844.66791781 a.u.
UB3LYP-D3 enthalpy in solution: -844.377012 a.u.
UB3LYP-D3 free energy in solution: -844.443055 a.u.
Three lowest frequencies (cm-1): 12.7209 18.4989 42.1212

Cartesian coordinates

ATOM	X	Y	Z
H	3.682729	-0.549448	2.050481
C	3.875581	-0.575406	0.984224

C	4.361088	-0.642350	-1.765089
C	2.879390	-0.068583	0.097830
C	5.065299	-1.095594	0.499209
C	5.324383	-1.137713	-0.877521
C	3.165351	-0.116219	-1.297064
H	5.804371	-1.475809	1.200431
H	6.258559	-1.546958	-1.251216
H	2.447488	0.266109	-2.016415
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C	1.667422	0.455387	0.623451
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C	-5.566704	-0.996600	-0.071059
C	-3.209847	-1.226459	0.451493
C	-3.958852	0.488930	-1.101636
C	-5.277145	0.064554	-0.930558
C	-4.533121	-1.637601	0.615475
H	-2.402134	-1.718356	0.980406
H	-3.708069	1.308930	-1.766989
H	-6.075490	0.565287	-1.470850
H	-4.753557	-2.465340	1.283491
H	-6.593450	-1.324963	0.061955
O	1.556977	0.543065	1.979281
H	0.606458	0.655624	2.197530
C	0.554584	1.071100	-0.195045
H	0.632282	0.744127	-1.232348
C	0.596147	2.624869	-0.154955
H	-0.226195	3.057126	-0.736199
H	1.544005	2.972928	-0.575103
H	0.523222	2.980499	0.876724
C	-0.800551	0.614598	0.326798
O	-1.111431	0.603348	1.504538
O	-1.630303	0.256601	-0.679782

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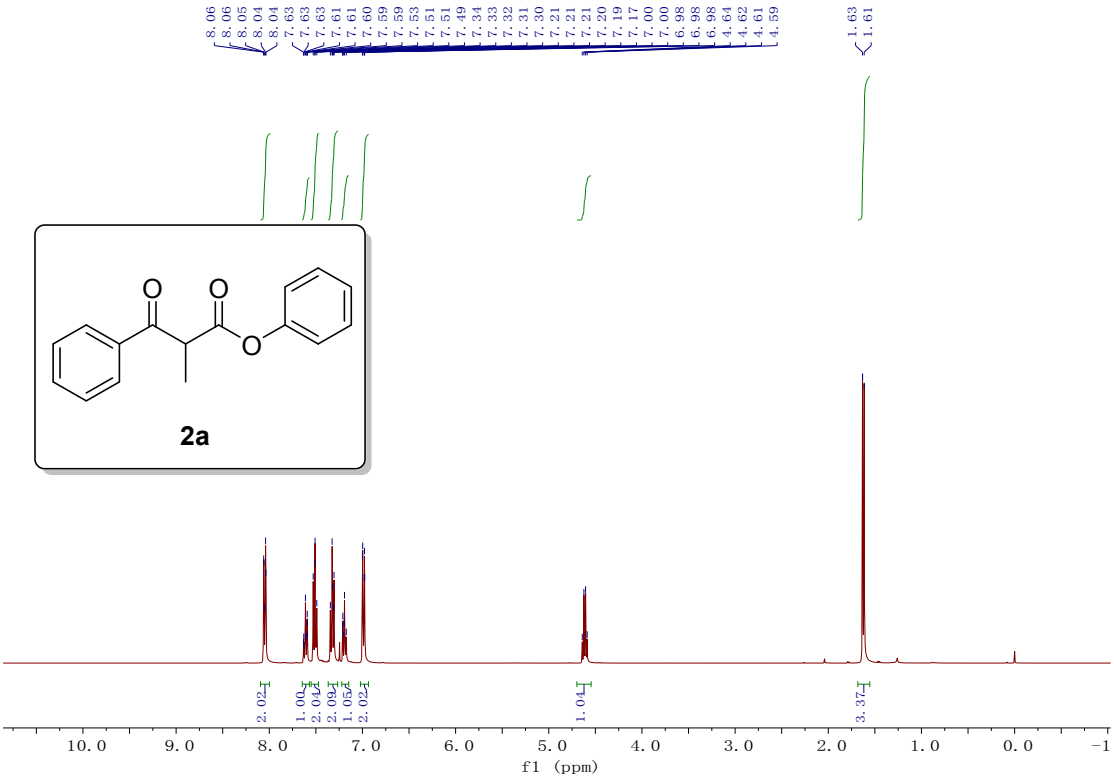
12. Spectra


8.06
8.06
8.05
8.04
8.04
7.63
7.63
7.63
7.61
7.61
7.60
7.59
7.59
7.59
7.53
7.51
7.51
7.49
7.34
7.33
7.32
7.31
7.30
7.21
7.21
7.21
7.20
7.19
7.17
7.00
7.00
6.98
6.98
6.98
4.64
4.62
4.61
4.59
1.63
1.61
O
O
O
2a
2.02
1.00
2.04
2.09
1.05
2.02
1.04
3.37
10.0
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4.0
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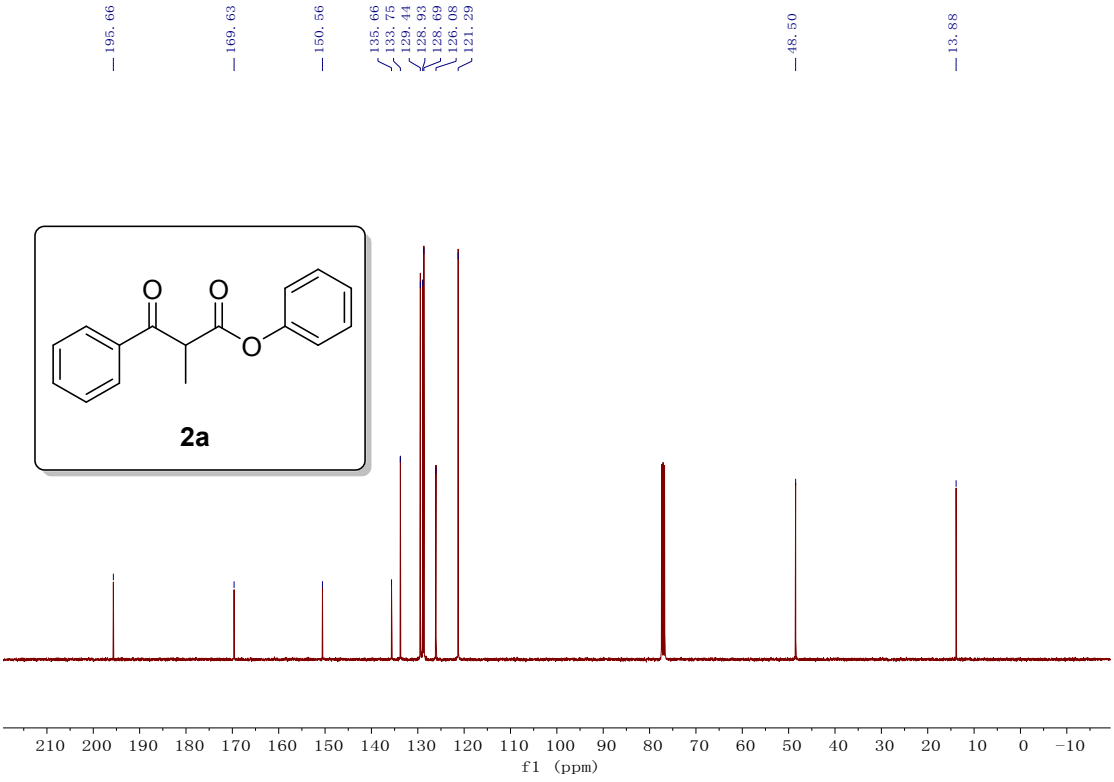
f1 (ppm)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128.69
126.08
121.29
48.50
13.88
O
O
O
2a
210
200
190
180
170
160
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100
90
80
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60
50
40
30
20
10
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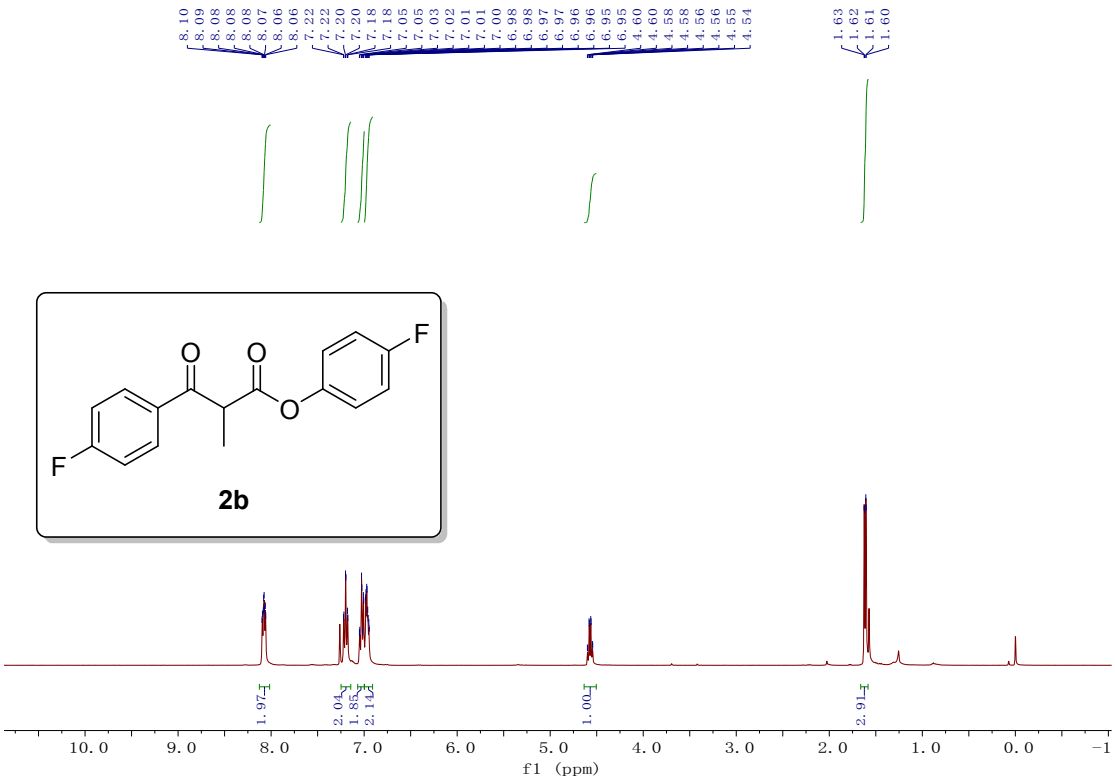
−10
f1 (ppm)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7.18
7.18
7.05
7.05
7.03
7.02
7.01
7.01
7.00
6.98
6.98
6.97
6.96
6.96
6.96
6.95
6.95
4.60
4.60
4.58
4.58
4.56
4.56
4.55
4.54
1.63
1.62
1.61
1.60
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O
O
F
F
2b
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1.85
2.14
1.00
2.91
10.0
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4.0
3.0
2.0
1.0
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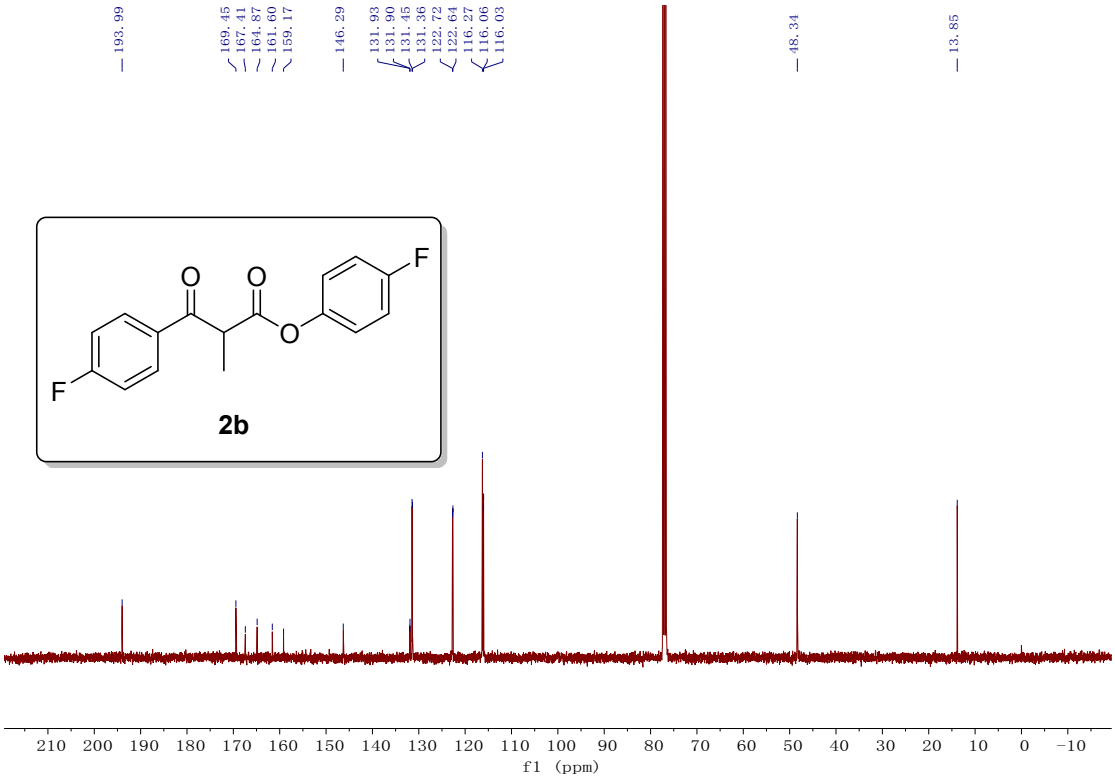
−1
f1 (ppm)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131.45
131.36
122.72
122.64
116.27
116.06
116.03
48.34
13.85
O
O
O
F
F
2b
210
200
190
180
170
160
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100
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80
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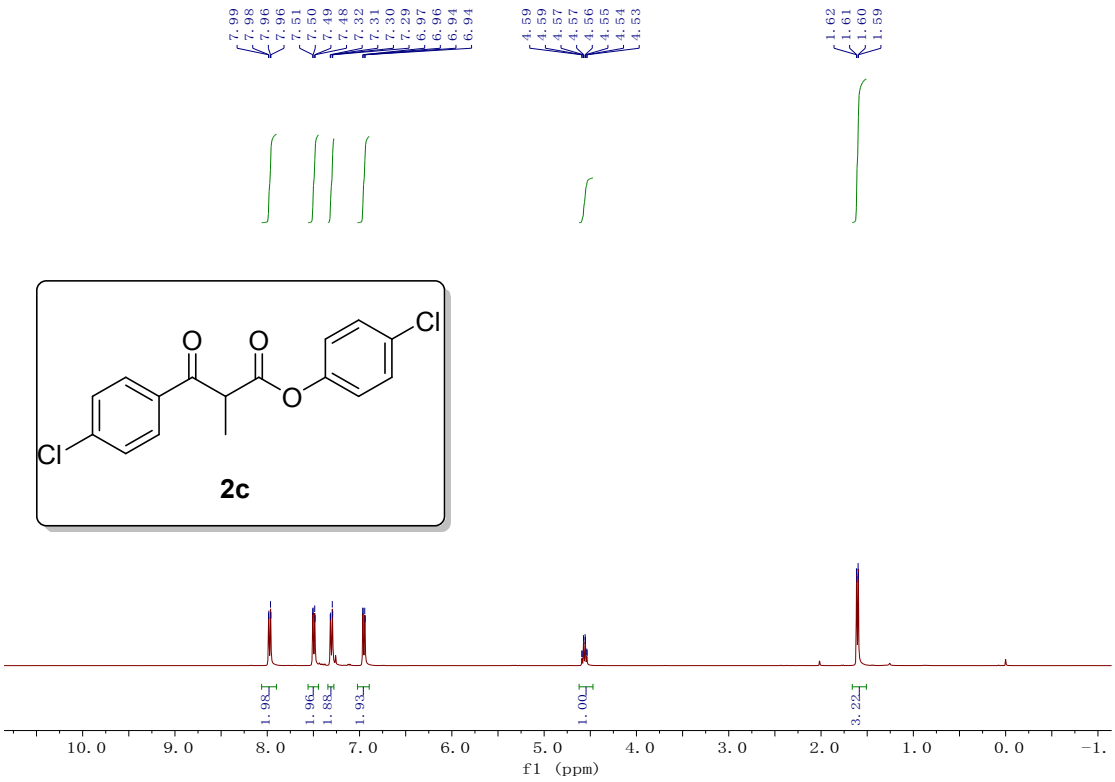
50
40
30
20
10
0
−10
f1 (ppm)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7.30
7.29
6.97
6.96
6.94
6.94
4.59
4.59
4.57
4.57
4.56
4.55
4.54
4.53
1.62
1.61
1.60
1.59
O
O
O
Cl
Cl
2c
1.98
1.96
1.88
1.93
1.00
3.22
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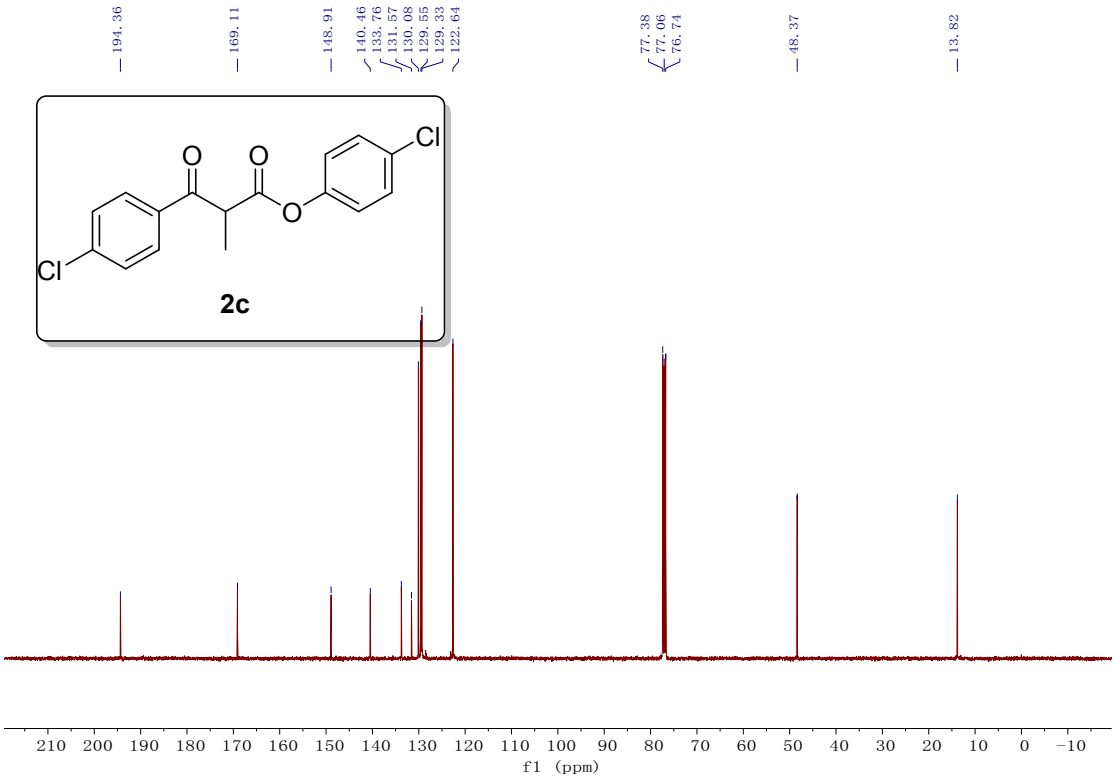
f1 (ppm)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169.11
148.91
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131.57
130.08
129.55
129.33
122.64
77.38
77.06
76.74
48.37
13.82
O
O
O
Cl
Cl
2c
210
200
190
180
170
160
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140
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120
110
100
90
80
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60
50
40
30
20
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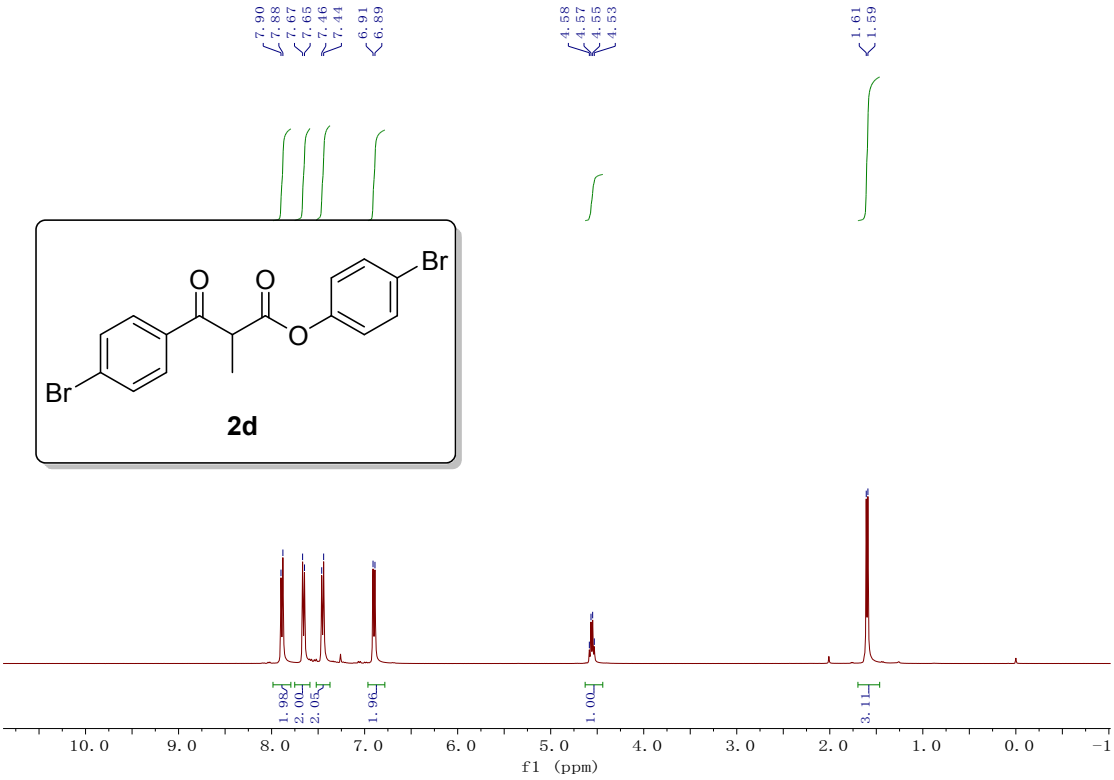
0
−10
f1 (ppm)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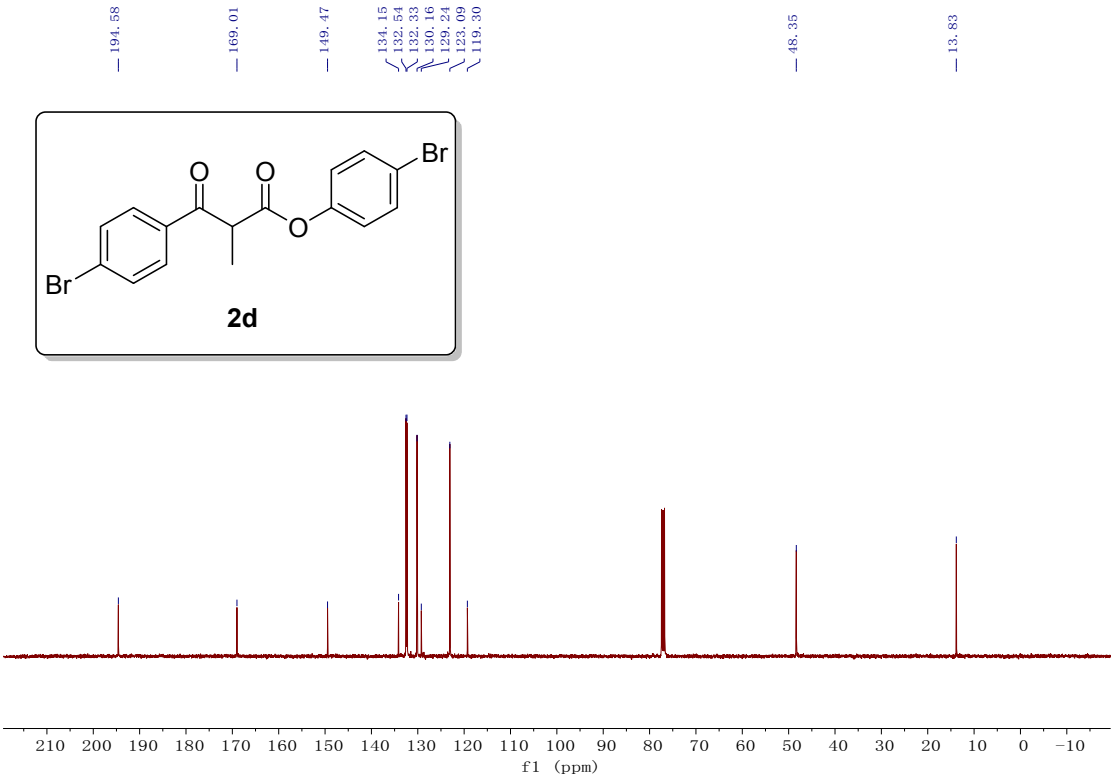
7.44
6.91
6.89
4.58
4.57
4.55
4.53
1.61
1.59
Br
O
O
O
Br
2d
1.98
2.00
2.05
1.96
1.00
3.11
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
−1
f1 (ppm)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149.47
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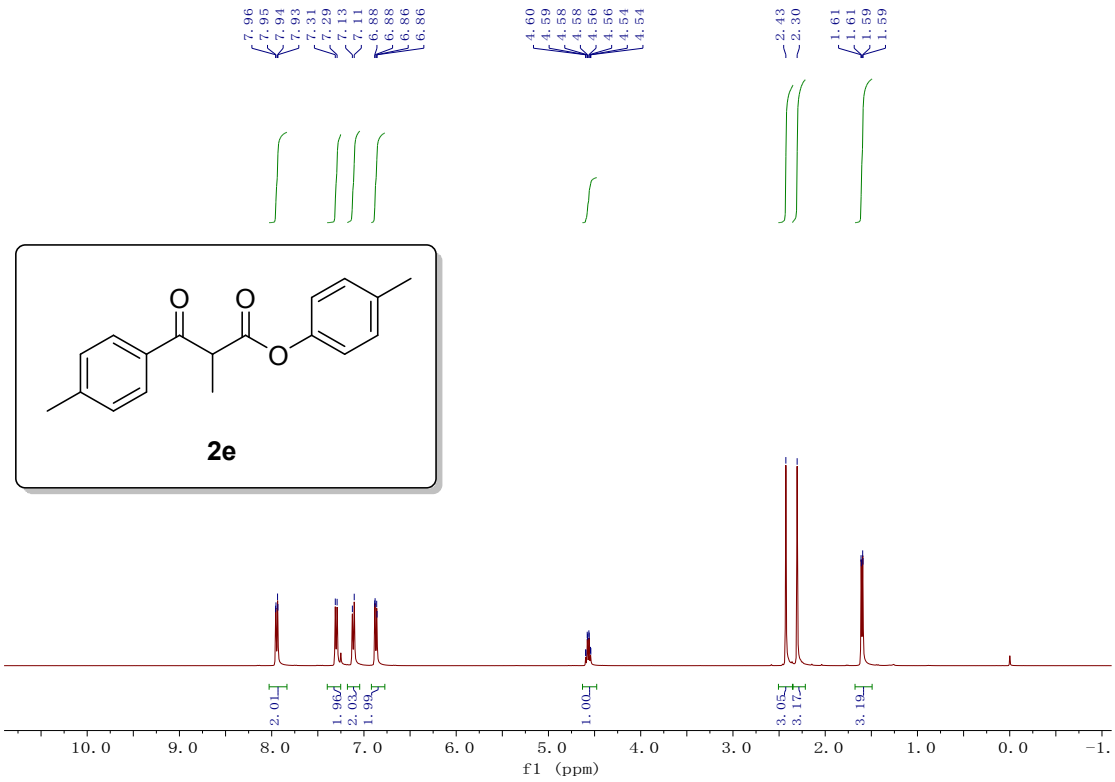
132.54
132.33
130.16
129.24
123.09
119.30
48.35
13.83
Br
O
O
O
Br
2d
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)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7.93
7.31
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7.13
7.11
6.88
6.88
6.86
6.86
4.60
4.59
4.58
4.58
4.56
4.56
4.54
4.54
2.43
2.30
1.61
1.61
1.59
1.59
O
O
O
2e
2.01
1.96
2.03
1.99
1.00
3.05
3.17
3.19
10.0
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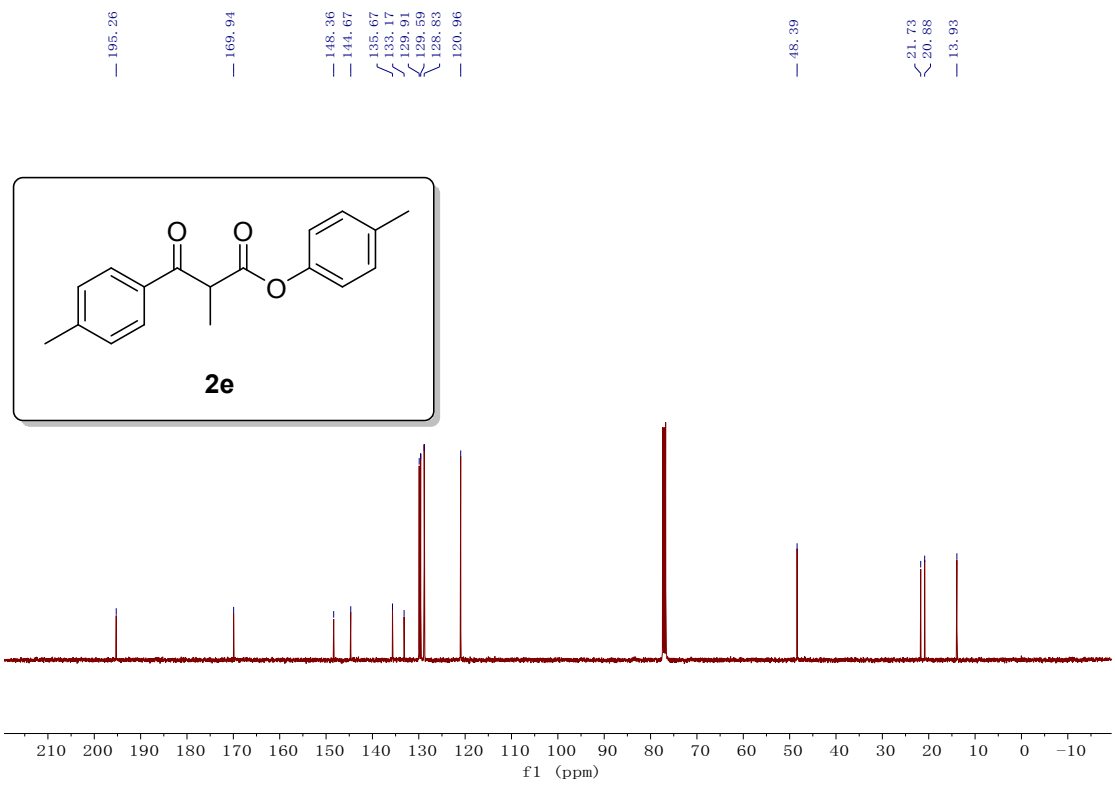
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
−1.
f1 (ppm)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133.17
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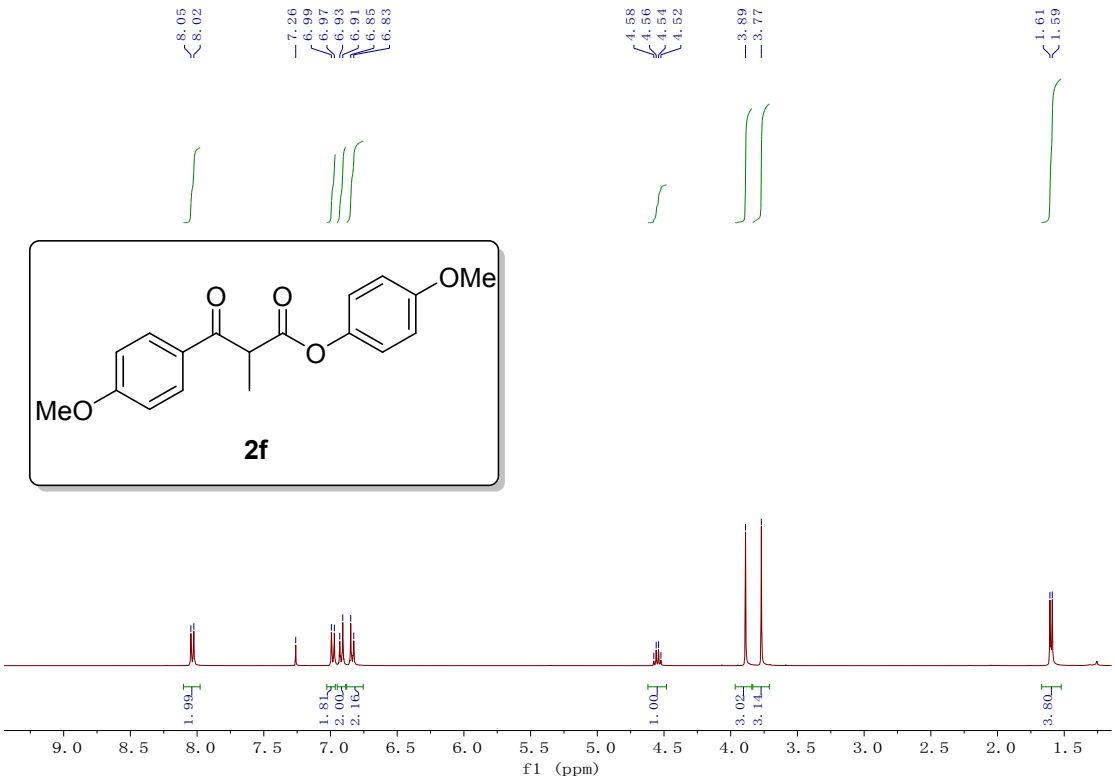
129.59
128.83
120.96
48.39
21.73
20.88
13.93
O
O
O
2e
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)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7.26
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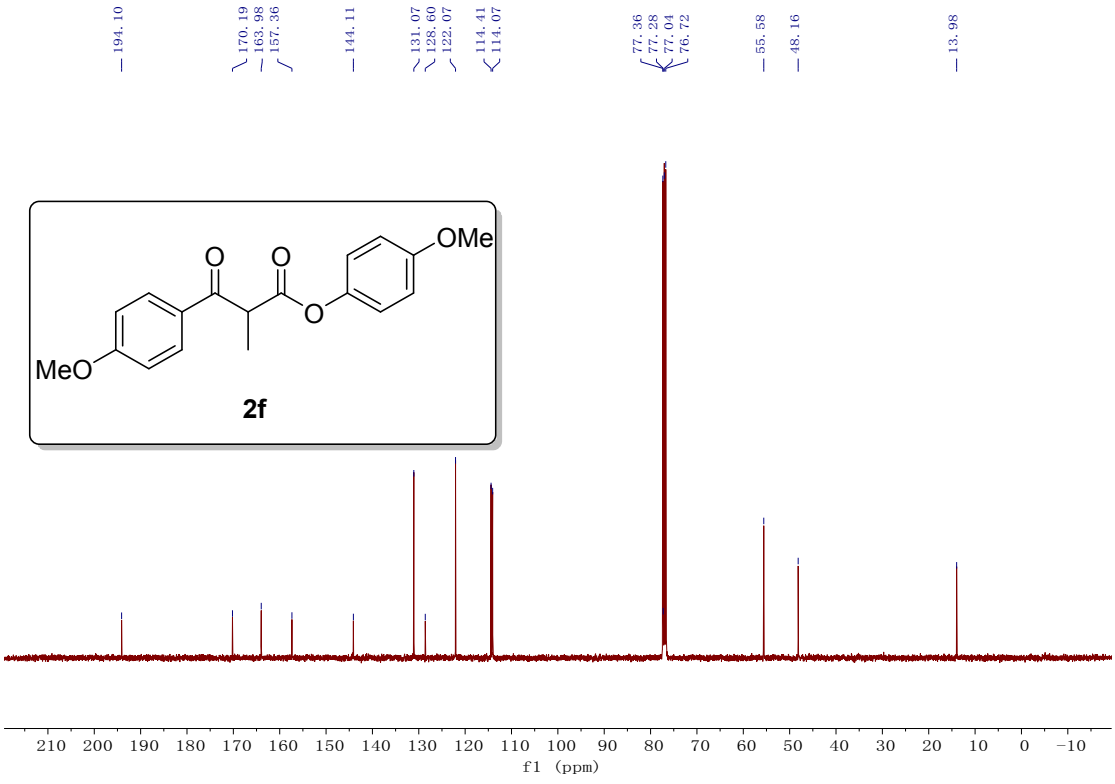
6.97
6.93
6.91
6.85
6.83
4.58
4.56
4.54
4.52
3.89
3.77
1.61
1.59
OMe
MeO
2f
1.99
1.81
2.00
2.16
1.00
3.02
3.14
3.80
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5
f1 (ppm)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170.19
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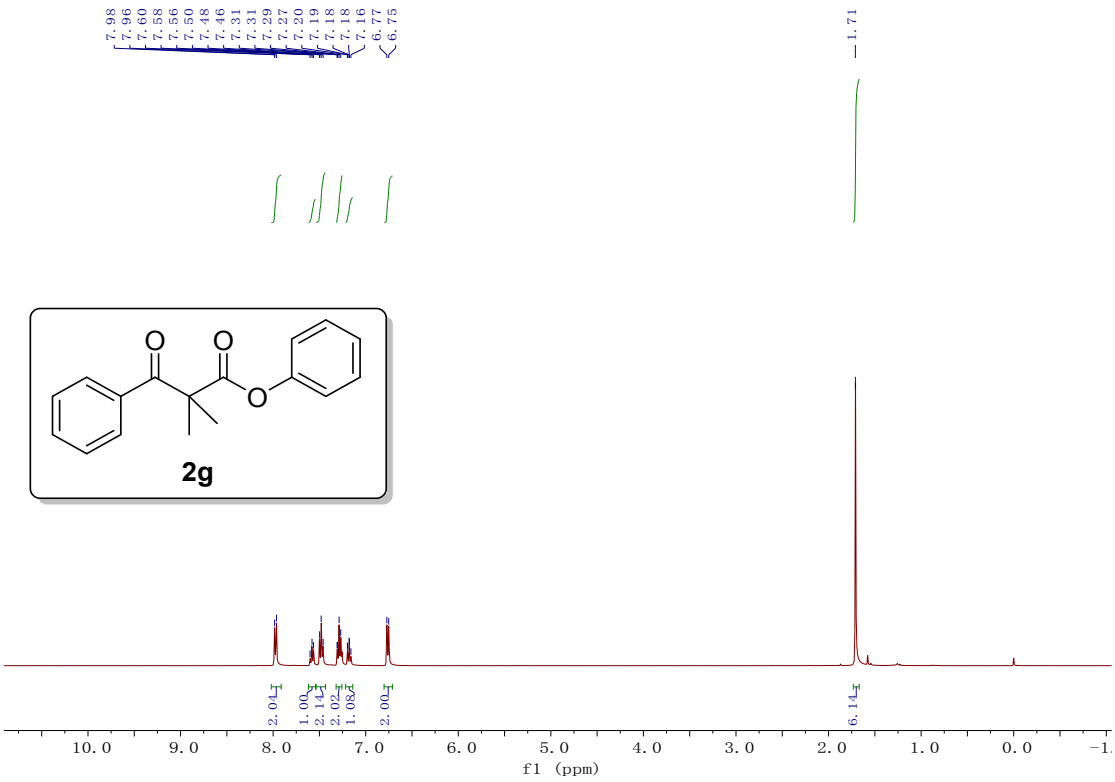
157.36
144.11
131.07
128.60
122.07
114.41
114.07
77.36
77.28
77.04
76.72
55.58
48.16
13.98
OMe
MeO
2f
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)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7.50
7.48
7.46
7.31
7.29
7.27
7.20
7.19
7.18
7.18
7.16
6.77
6.75
1.71
2g
2.04
1.00
2.14
2.02
1.08
2.00
6.14
10.0
9.0
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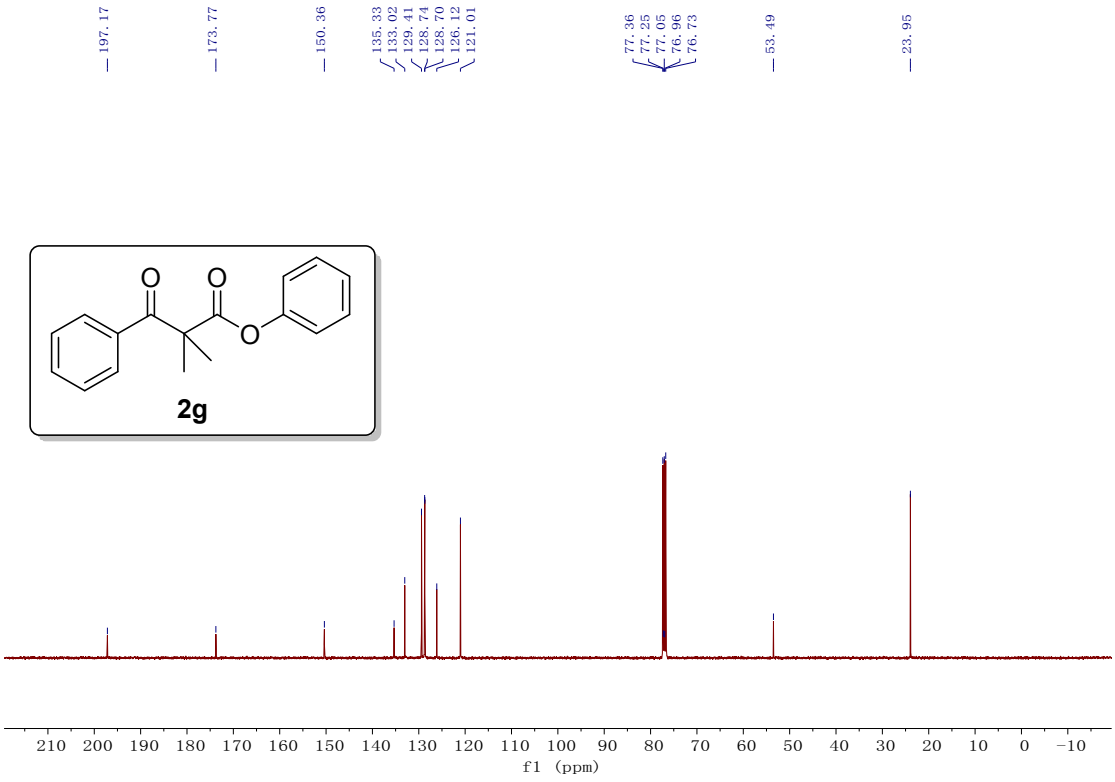
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)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129.41
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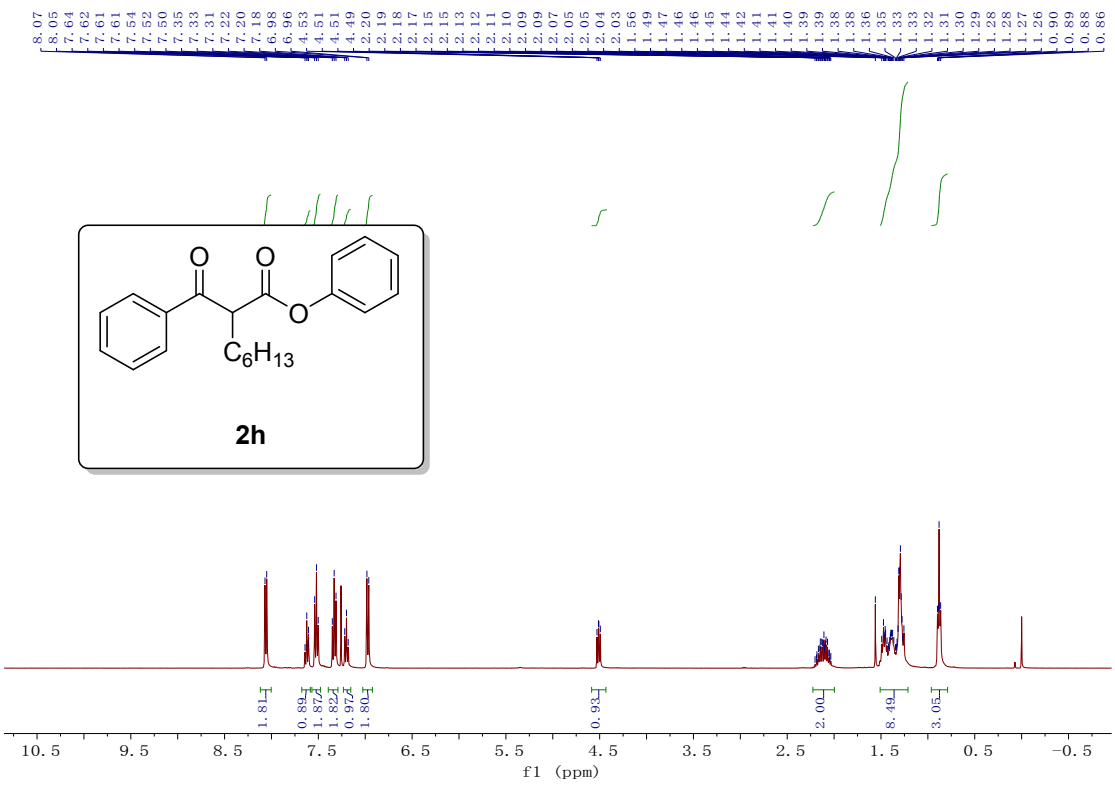
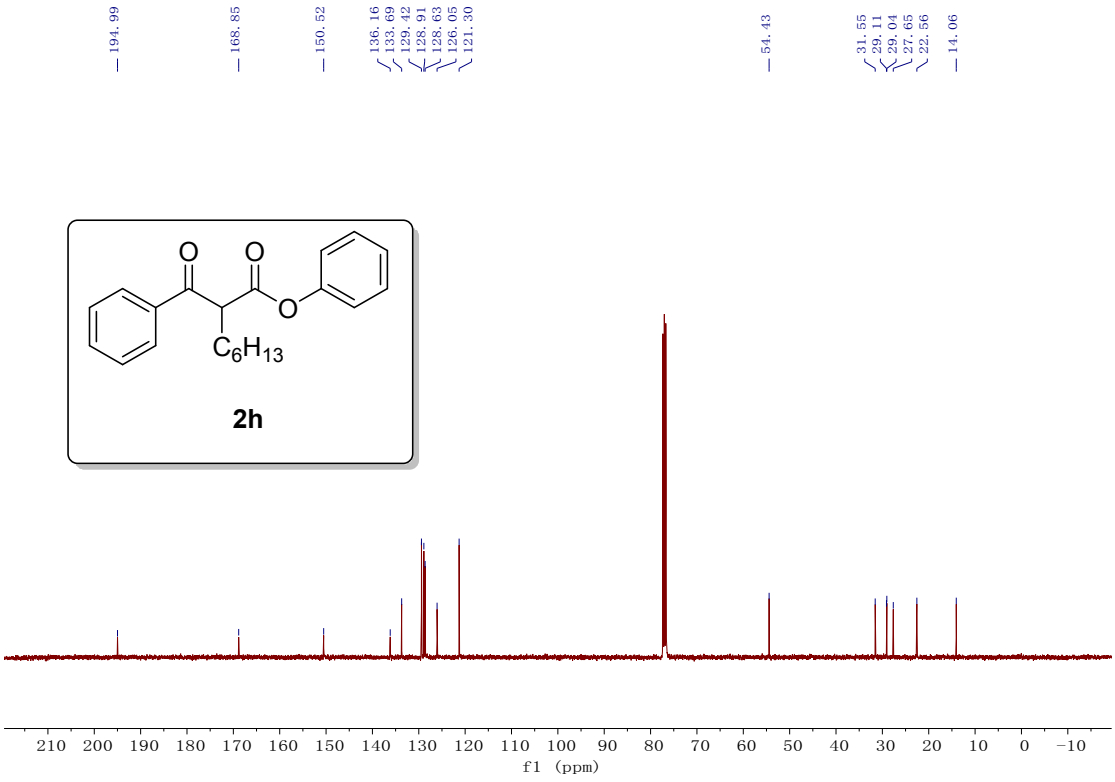
128.70
126.12
121.01
77.36
77.25
77.05
76.96
76.73
53.49
23.95
2g
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)


8.07 8.05 7.64 7.62 7.61 7.61 7.54 7.52 7.50 7.35 7.33 7.31 7.22 7.20 7.18 6.98 6.96 4.53 4.51 4.51 4.49 2.20 2.19 2.18 2.17 2.15 2.15 2.13 2.12 2.11 2.10 2.09 2.09 2.07 2.05 2.05 2.04 2.03 1.56 1.49 1.47 1.46 1.46 1.45 1.44 1.42 1.41 1.41 1.40 1.39 1.39 1.38 1.38 1.36 1.35 1.33 1.33 1.32 1.31 1.30 1.29 1.28 1.28 1.27 1.26 0.90 0.89 0.88 0.86
O
O
O
C6H13
2h
1.81
0.89
1.87
1.82
0.97
1.80
0.93
2.00
8.49
3.05
10.5 9.5 8.5 7.5 6.5 5.5 4.5 3.5 2.5 1.5 0.5 −0.5
f1 (ppm)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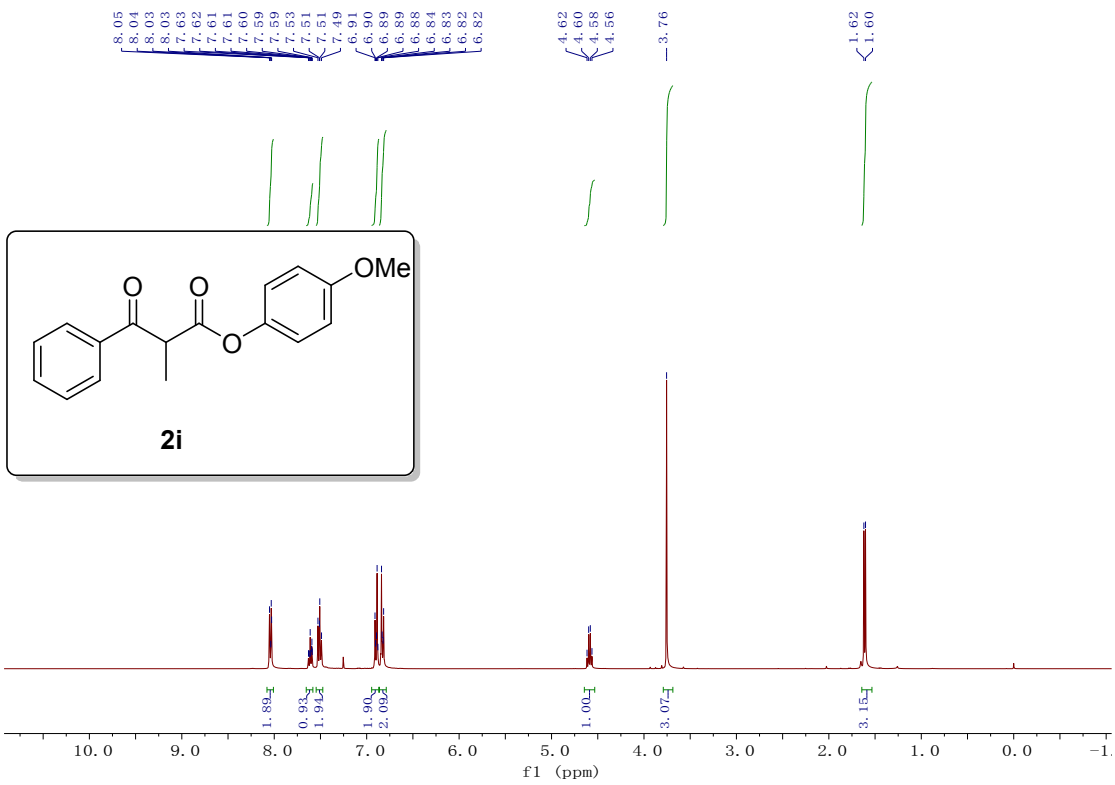
128.91
128.63
126.05
121.30
54.43
31.55
29.11
29.04
27.65
22.56
14.06
O
O
O
C6H13
2h
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)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8.04
8.03
8.03
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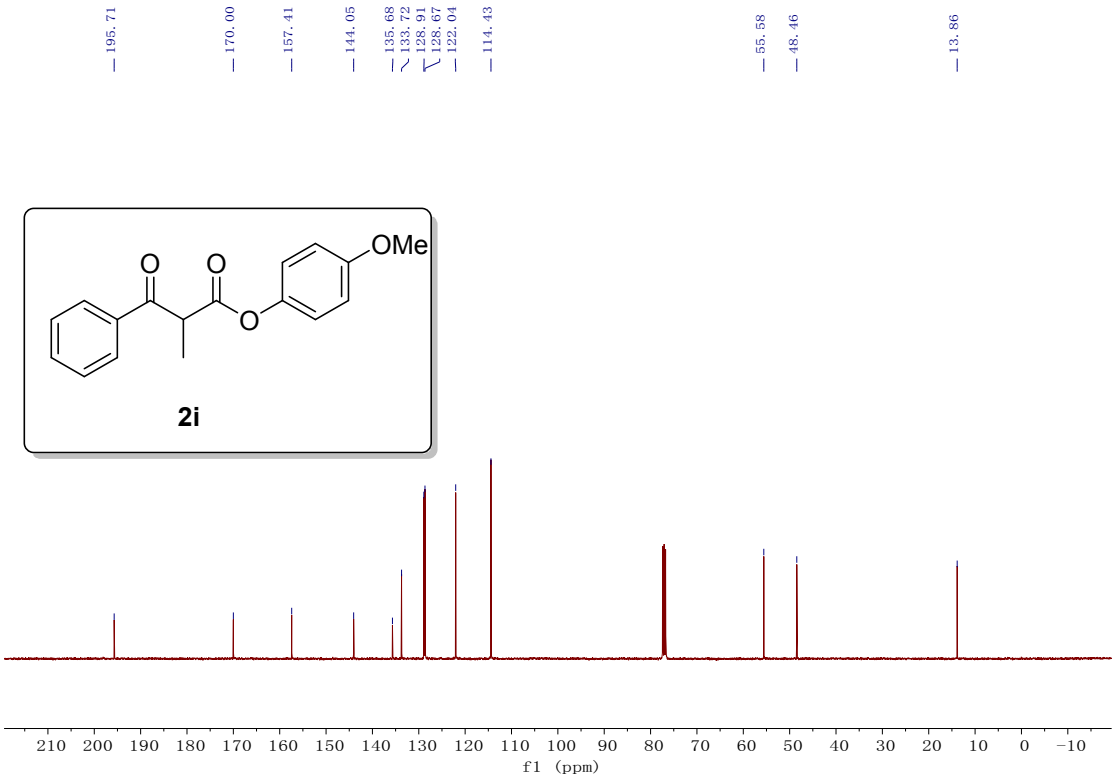
7.61
7.60
7.59
7.59
7.53
7.51
7.51
7.49
6.91
6.90
6.89
6.89
6.88
6.84
6.83
6.82
6.82
4.62
4.60
4.58
4.56
3.76
1.62
1.60
OMe
O
O
O
2i
1.89
0.93
1.94
1.90
2.09
1.00
3.07
3.15
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)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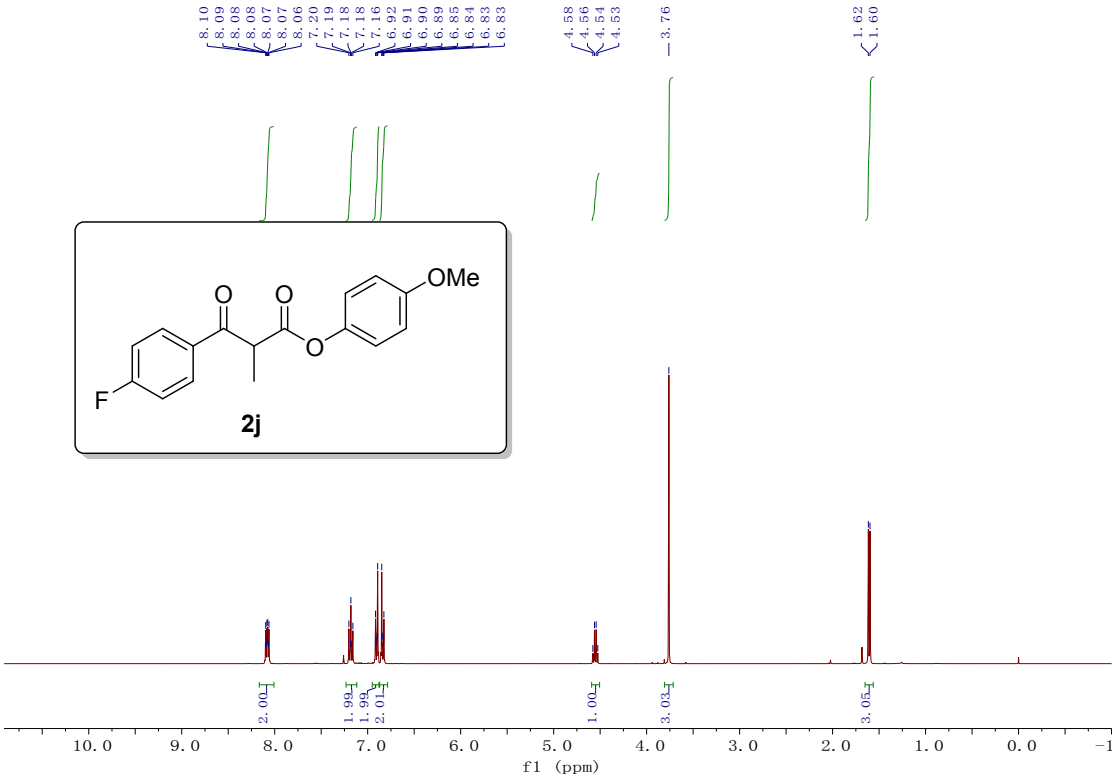
133.72
128.91
128.67
122.04
114.43
55.58
48.46
13.86
OMe
O
O
O
2i
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)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8.09
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8.08
8.07
8.07
8.06
7.20
7.19
7.18
7.18
7.16
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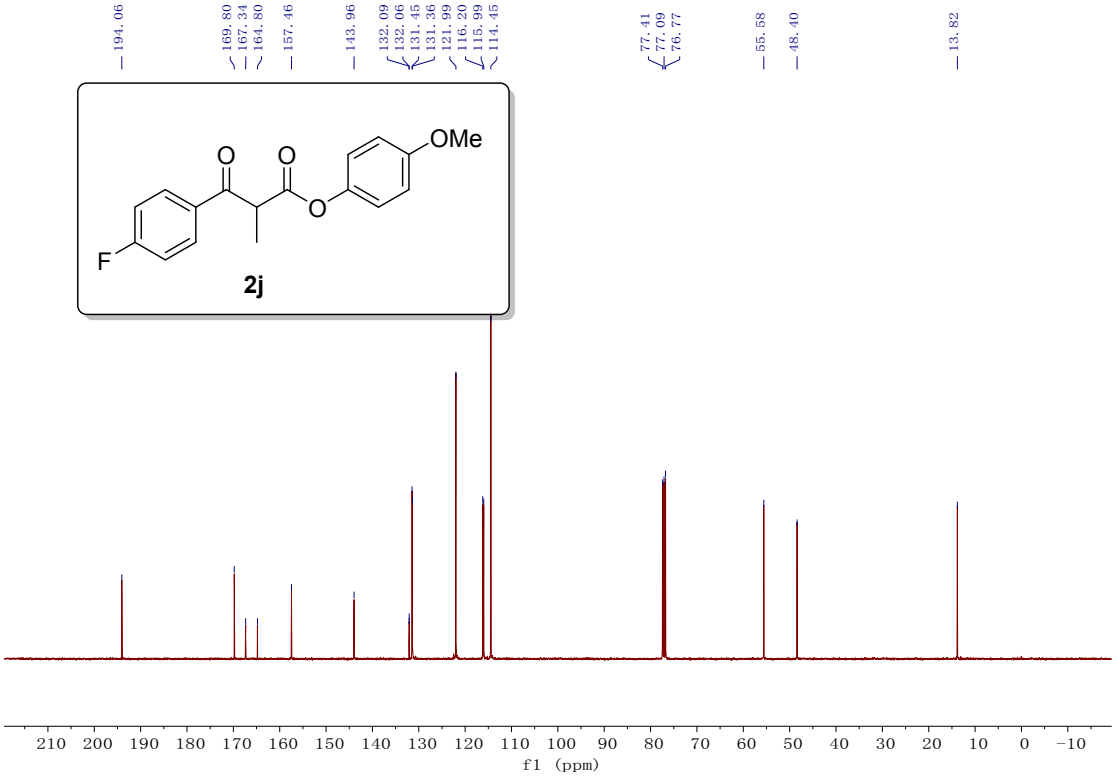
6.91
6.90
6.89
6.85
6.84
6.83
6.83
4.58
4.56
4.54
4.53
3.76
1.62
1.60
OMe
O
O
O
F
2j
2.00
1.99
1.99
2.01
1.00
3.03
3.05
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
−1
f1 (ppm)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132.06
131.45
131.36
121.99
116.20
115.99
114.45
77.41
77.09
76.77
55.58
48.40
13.82
OMe
O
O
O
F
2j
210
200
190
180
170
160
150
140
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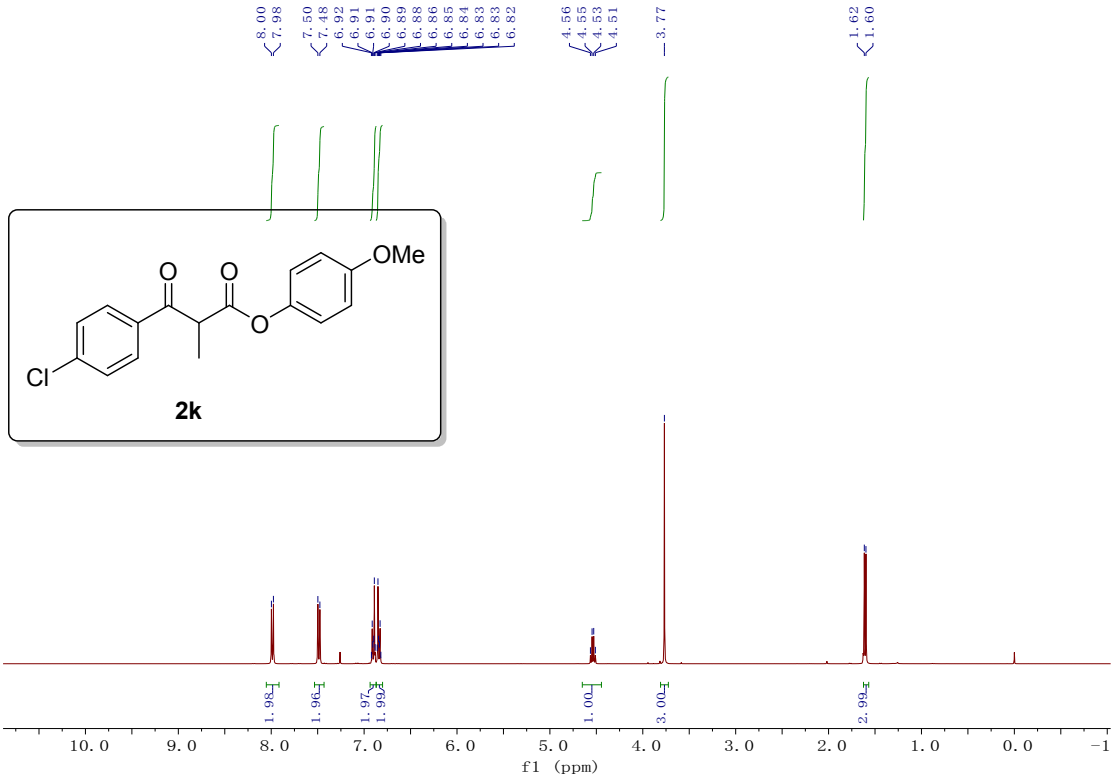
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)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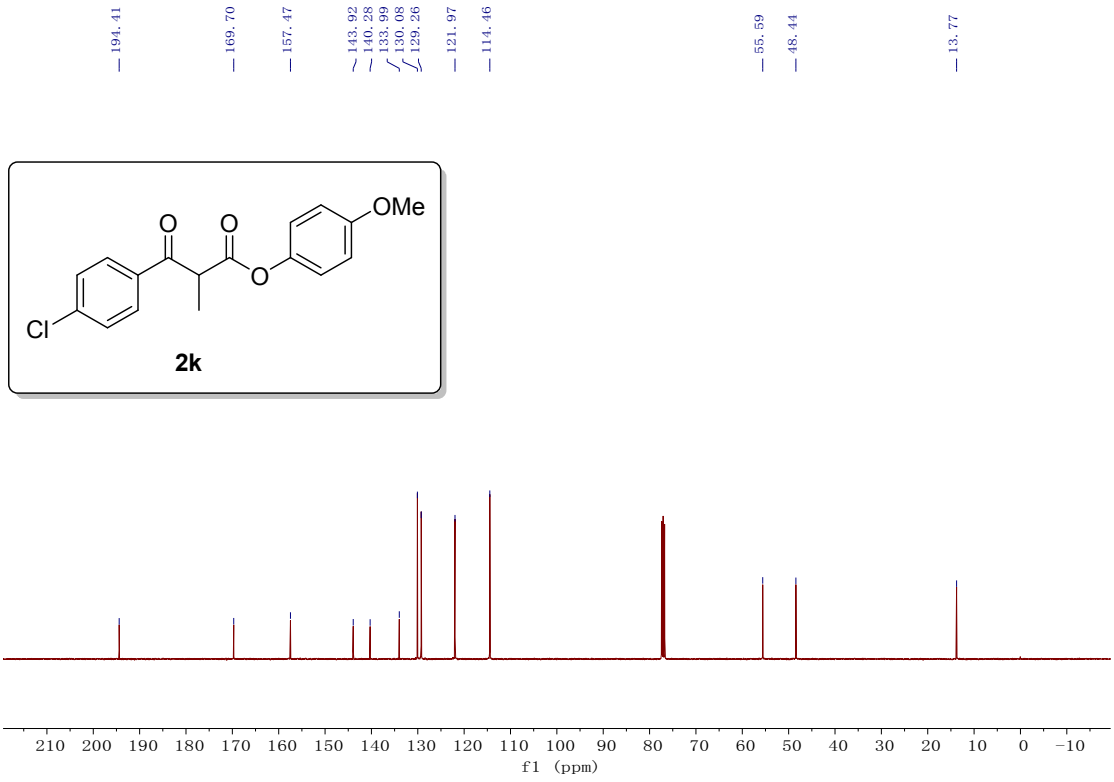
6.91
6.91
6.90
6.89
6.88
6.86
6.85
6.84
6.83
6.83
6.82
4.56
4.55
4.53
4.51
3.77
1.62
1.60
OMe
O
O
O
Cl
2k
1.98
1.96
1.97
1.92
1.00
3.00
2.99
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
−1
f1 (ppm)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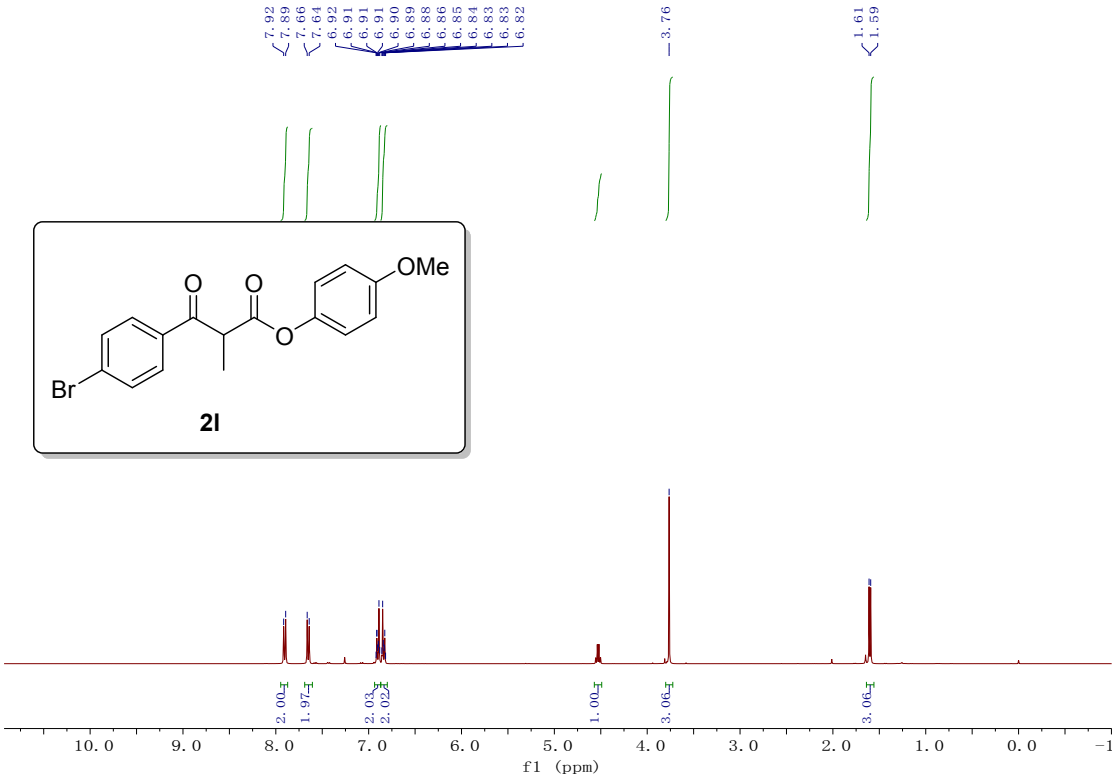
114.46
55.59
48.44
13.77
OMe
O
O
O
Cl
2k
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)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7.89
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7.64
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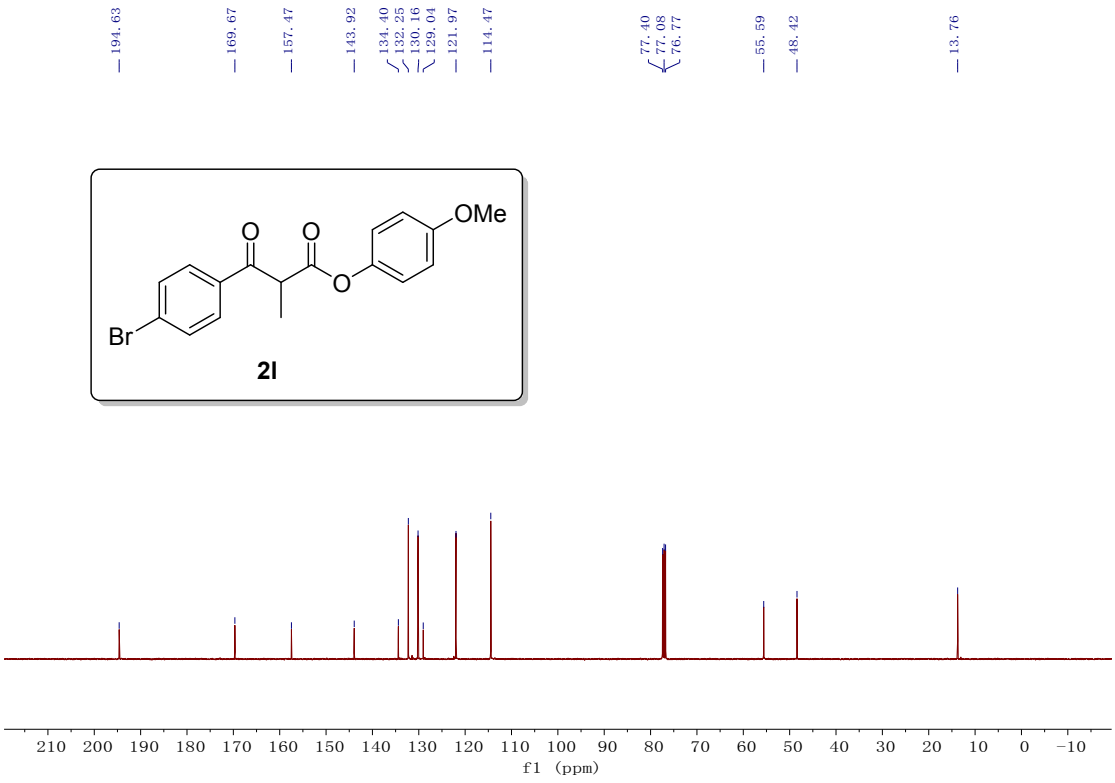
6.91
6.91
6.91
6.90
6.89
6.89
6.88
6.86
6.85
6.84
6.83
6.83
6.82
3.76
1.61
1.59
OMe
O
O
O
Br
2l
2.00
1.97
2.03
2.02
1.00
3.06
3.06
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
−1
f1 (ppm)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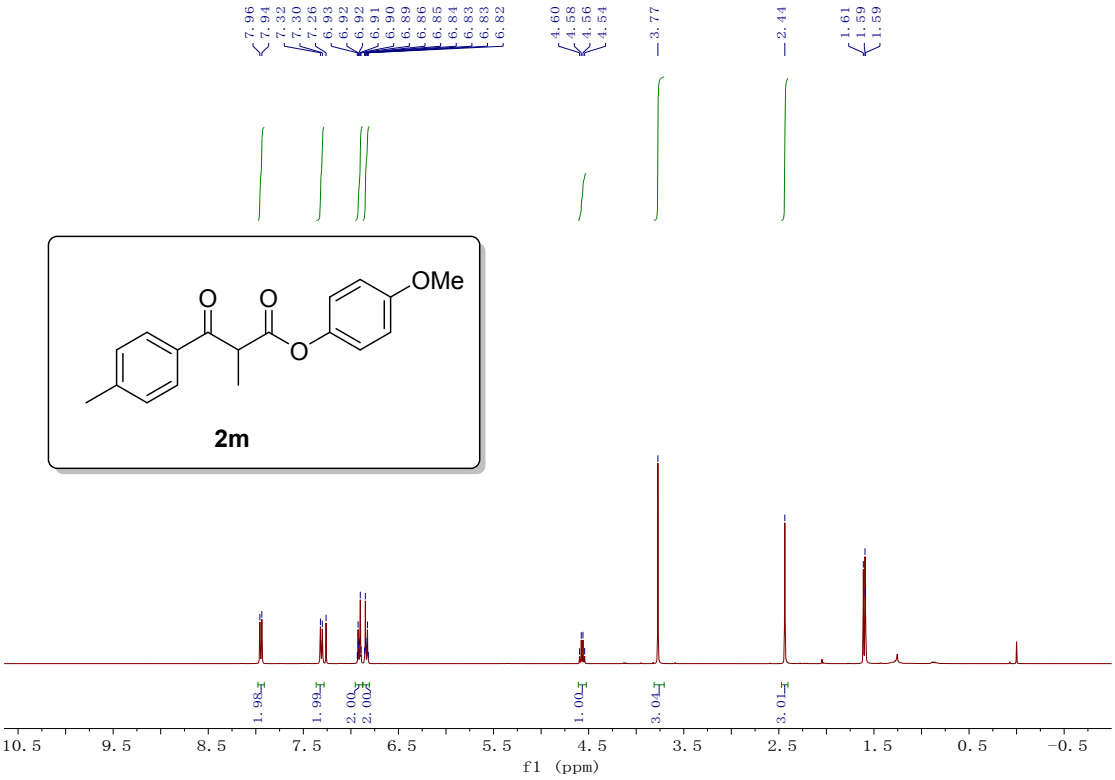
130.16
129.04
121.97
114.47
77.40
77.08
76.77
55.59
48.42
13.76
OMe
O
O
O
Br
2l
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)


7.96
7.94
7.32
7.30
7.26
6.93
6.92
6.92
6.91
6.90
6.89
6.86
6.85
6.84
6.83
6.83
6.82
4.60
4.58
4.56
4.54
3.77
2.44
1.61
1.59
1.59
OMe
O
O
O
2m
1.98
1.99
2.00
2.00
1.00
3.04
3.01
10.5
9.5
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6.5
5.5
4.5
3.5
2.5
1.5
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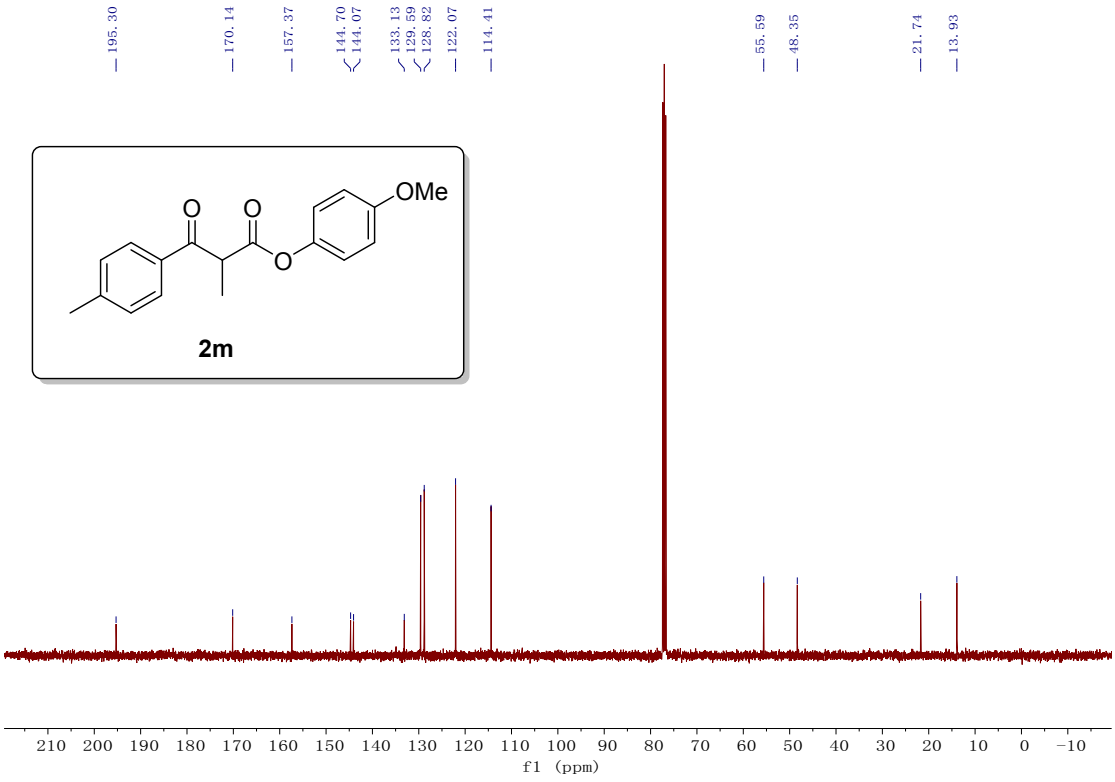
f1 (ppm)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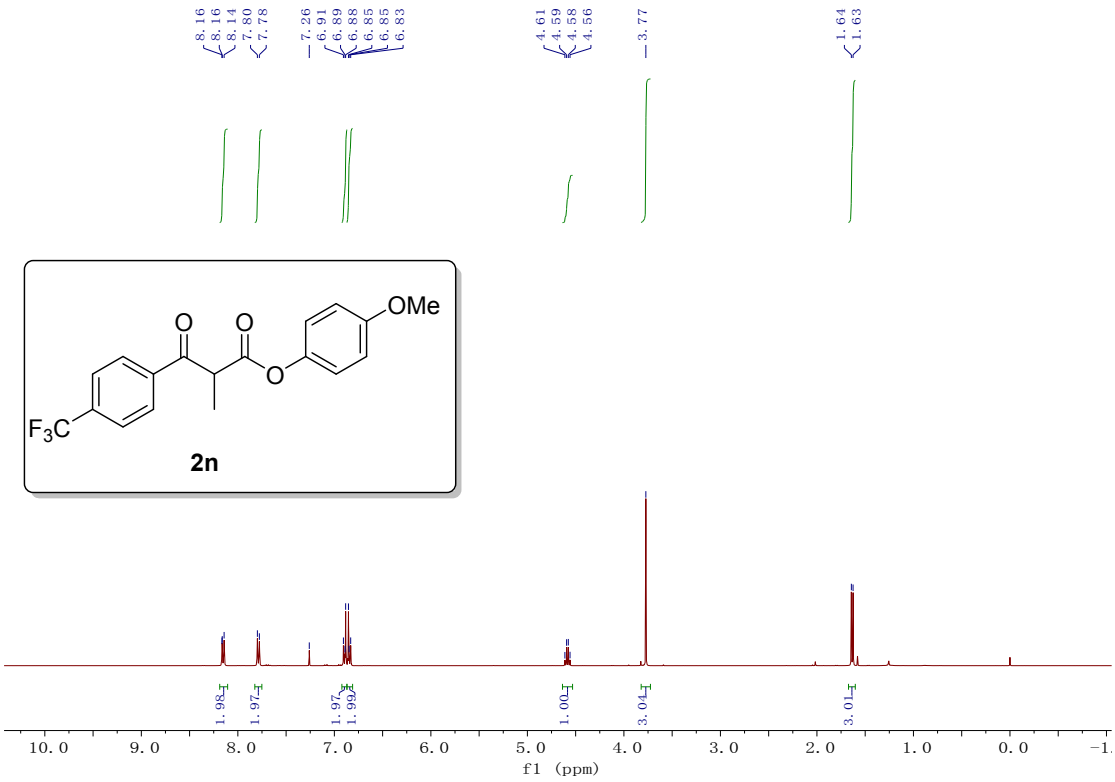
157.37
144.70
144.07
133.13
129.59
128.82
122.07
114.41
55.59
48.35
21.74
13.93
OMe
O
O
O
2m
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)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6.89
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6.85
6.85
6.83
4.61
4.59
4.58
4.56
3.77
1.64
1.63
OMe
O
O
O
F3C
2n
1.98
1.97
1.97
1.93
1.00
3.04
3.01
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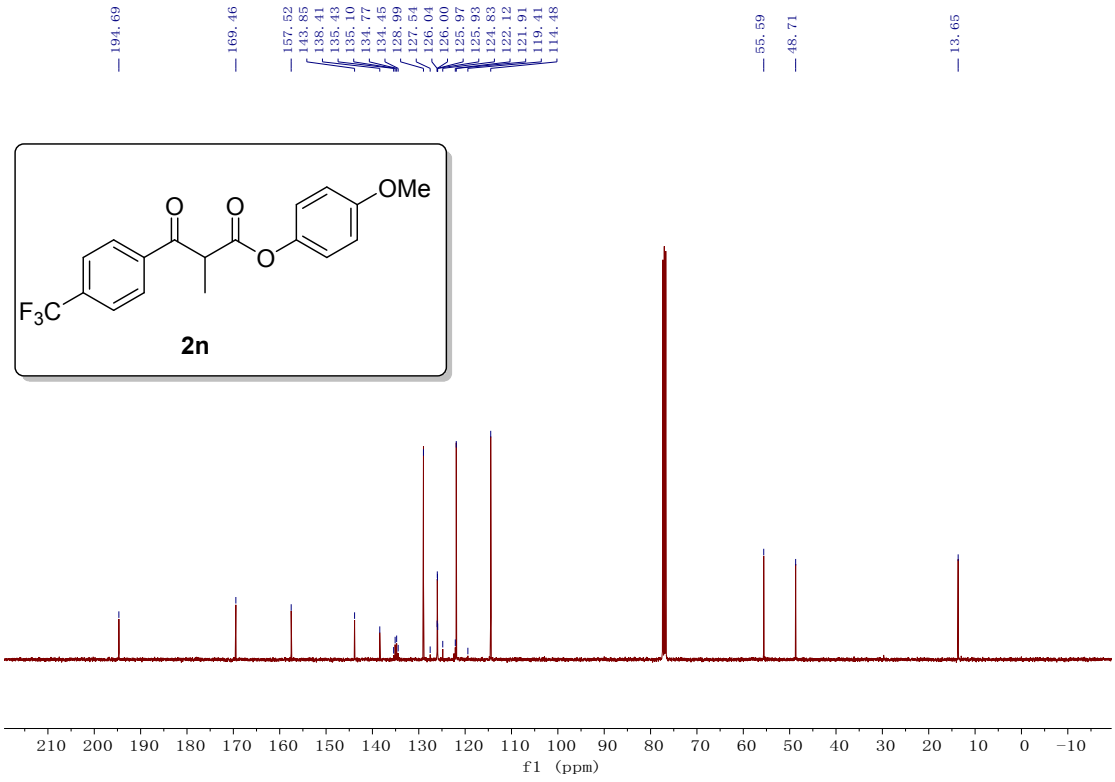
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)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134.77
134.45
128.99
127.54
126.04
126.00
125.97
125.93
124.83
122.12
121.91
119.41
114.48
55.59
48.71
13.65
OMe
O
O
O
F3C
2n
210
200
190
180
170
160
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120
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100
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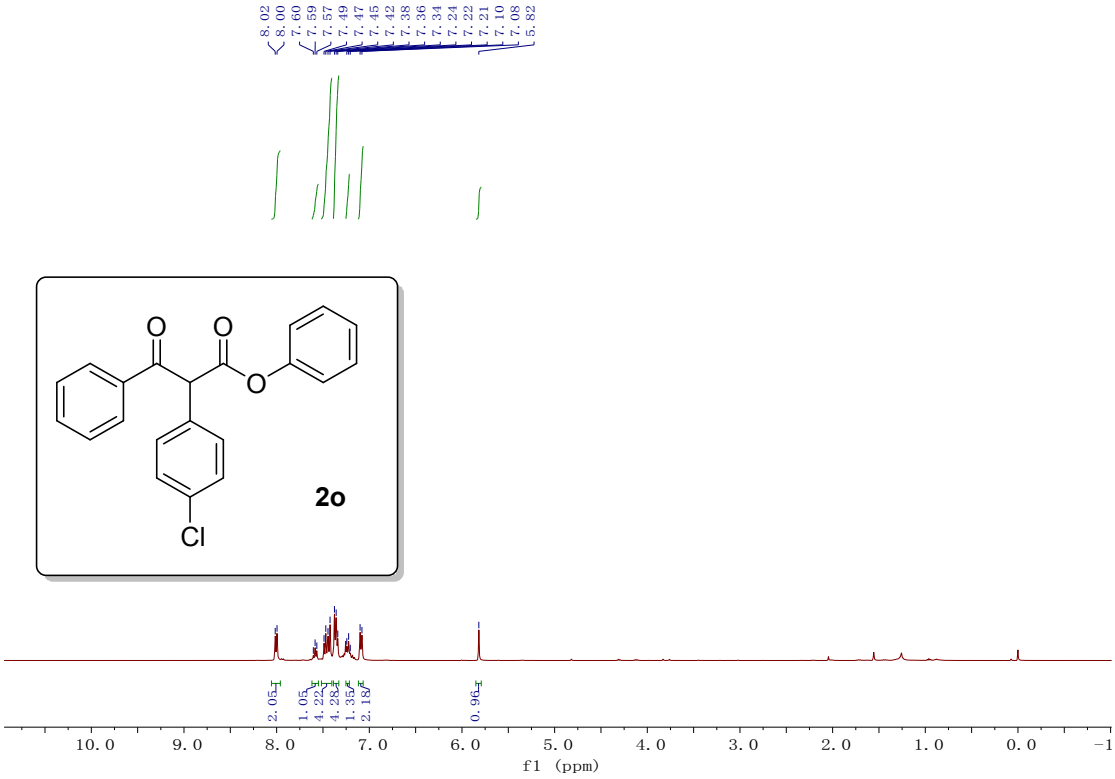
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)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8.00
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7.59
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7.47
7.45
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7.36
7.34
7.24
7.22
7.21
7.10
7.08
5.82
O
O
O
Cl
2o
2.05
1.05
4.22
4.28
1.35
2.18
0.96
10.0
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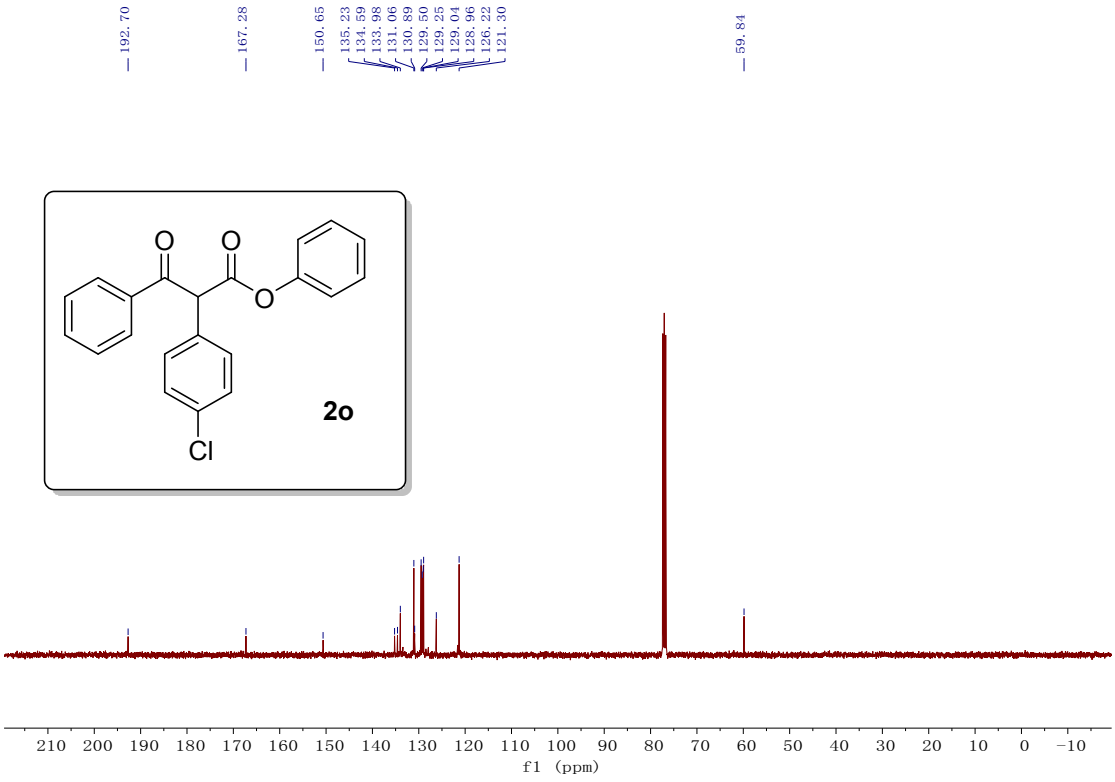
4.0
3.0
2.0
1.0
0.0
−1
f1 (ppm)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150.65
135.23
134.59
133.98
131.06
130.89
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129.25
129.04
128.96
126.22
121.30
59.84
O
O
O
Cl
2o
210
200
190
180
170
160
150
140
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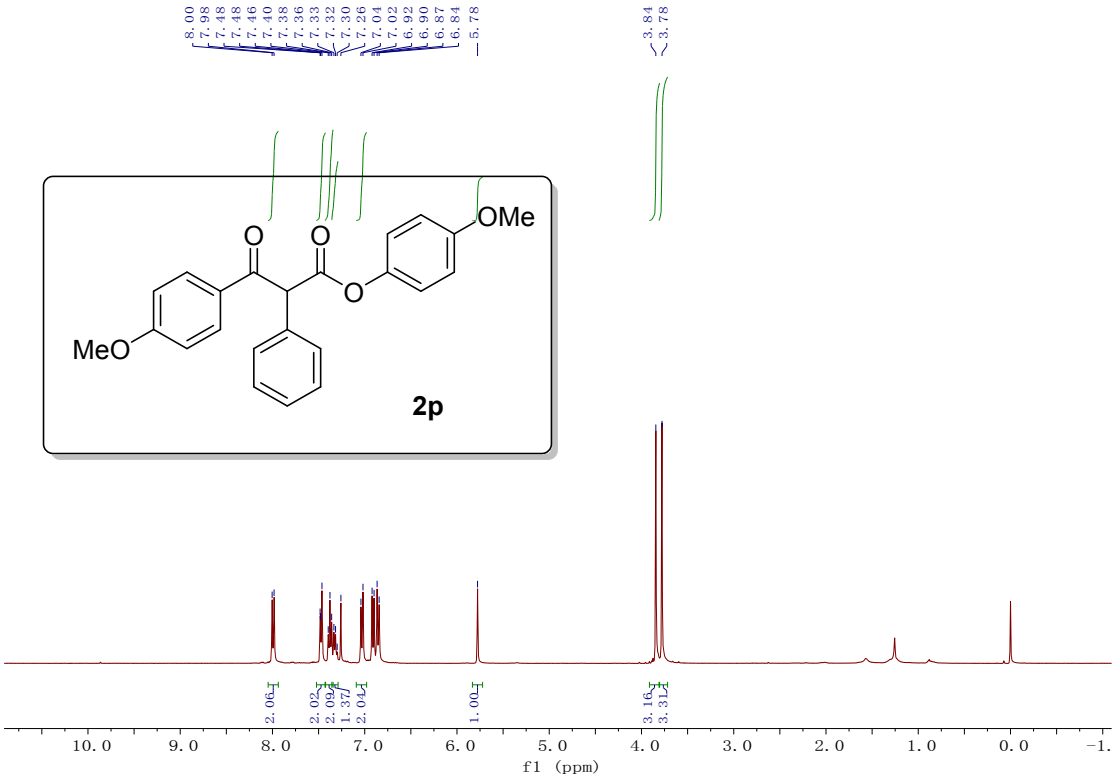
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)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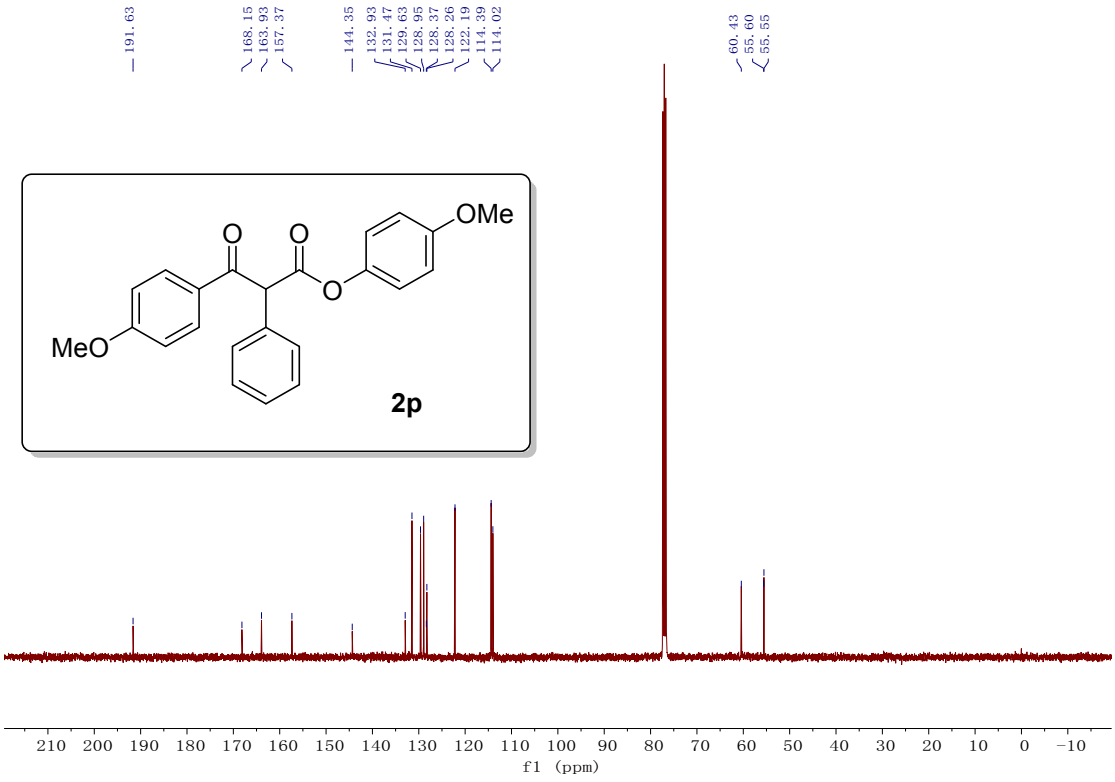
7.40
7.38
7.36
7.33
7.32
7.30
7.26
7.04
7.02
6.92
6.90
6.87
6.84
5.78
3.84
3.78
OMe
O
O
O
MeO
2p
2.06
2.02
2.09
1.37
2.04
1.00
3.16
3.31
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)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163.93
157.37
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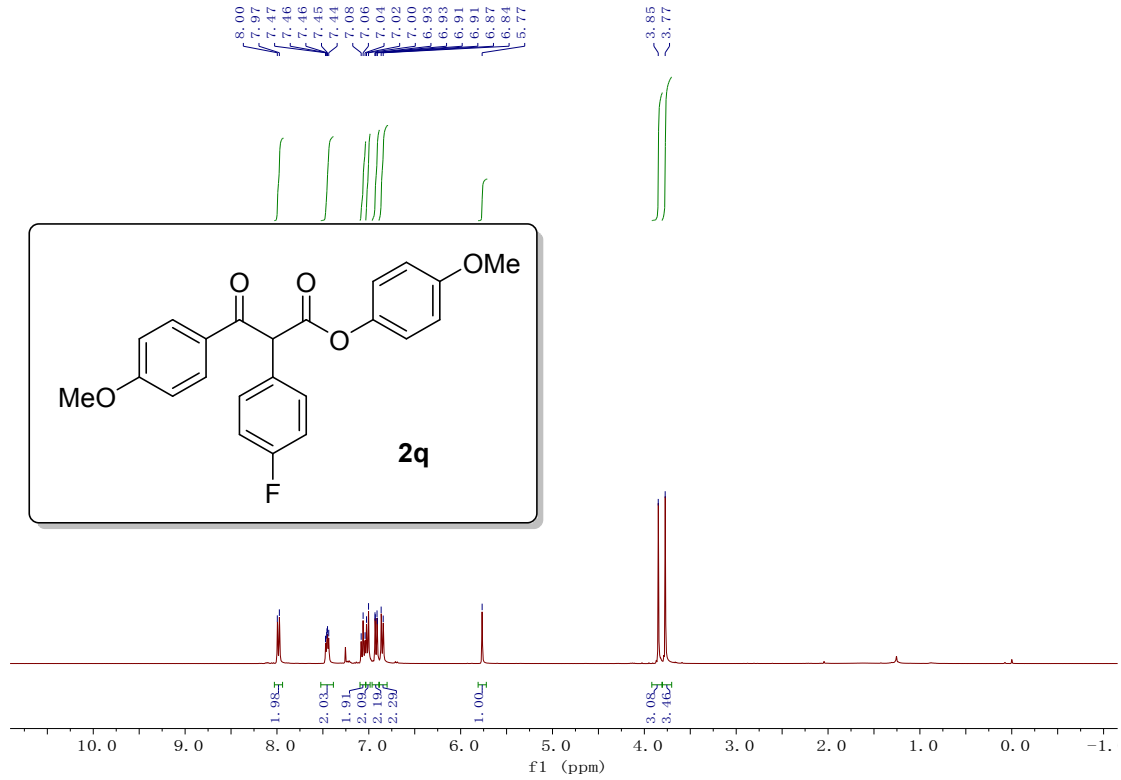
132.93
131.47
129.63
128.95
128.37
128.26
122.19
114.39
114.02
60.43
55.60
55.55
OMe
O
O
O
MeO
2p
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)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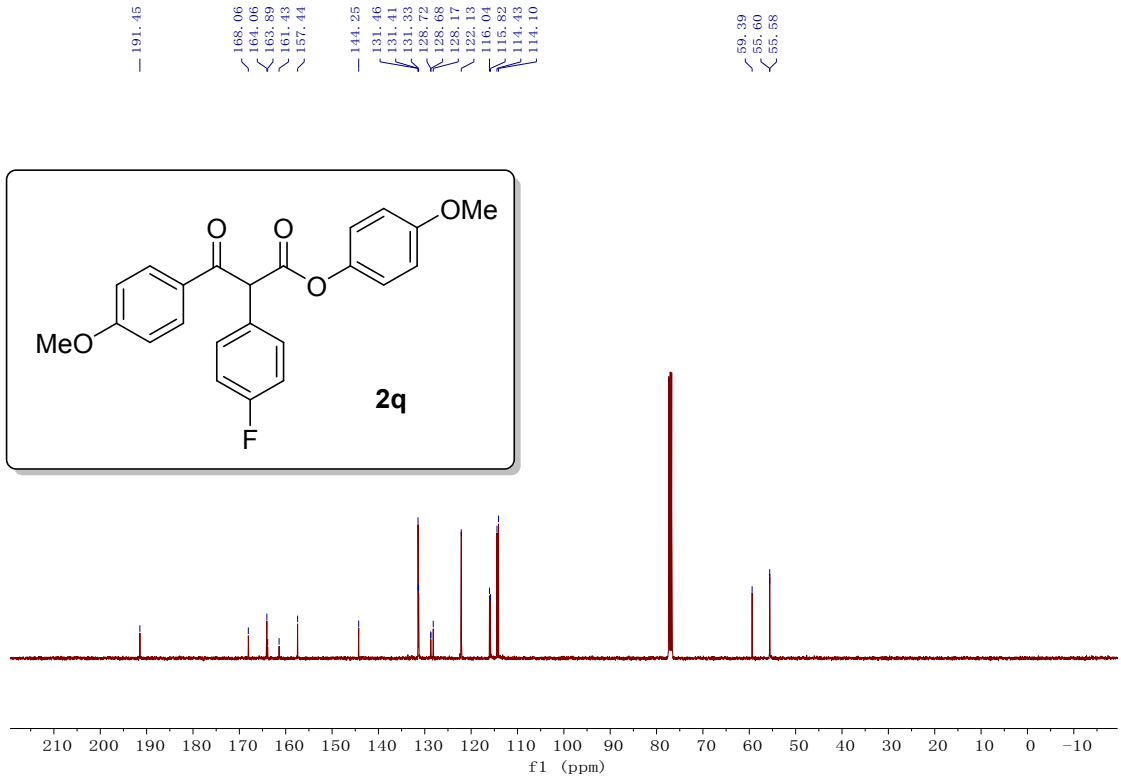
7.97
7.47
7.46
7.46
7.45
7.44
7.08
7.06
7.04
7.02
7.00
6.93
6.91
6.91
6.87
6.84
5.77
3.85
3.77
OMe
O
O
O
MeO
F
2q
1.98
2.03
1.91
2.09
2.19
2.29
1.00
3.08
3.46
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)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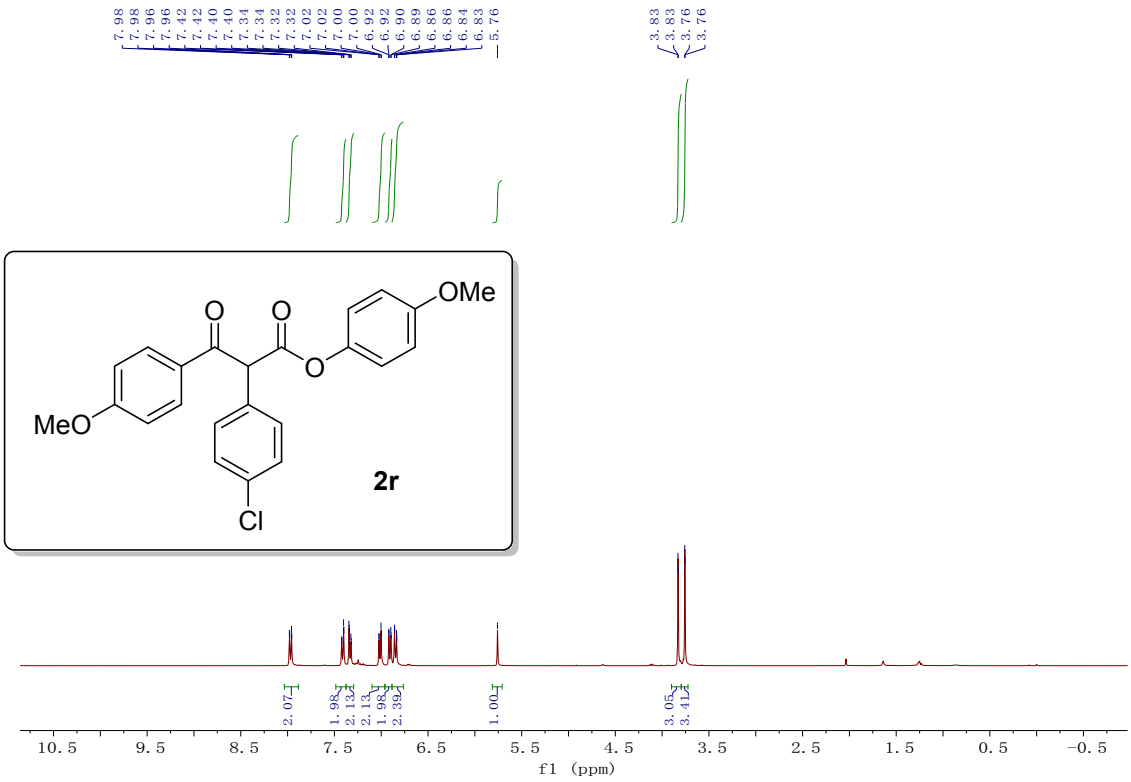
157.44
144.25
131.46
131.41
131.33
128.72
128.68
128.17
122.13
116.04
115.82
114.43
114.10
59.39
55.60
55.58
OMe
O
O
O
MeO
F
2q
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)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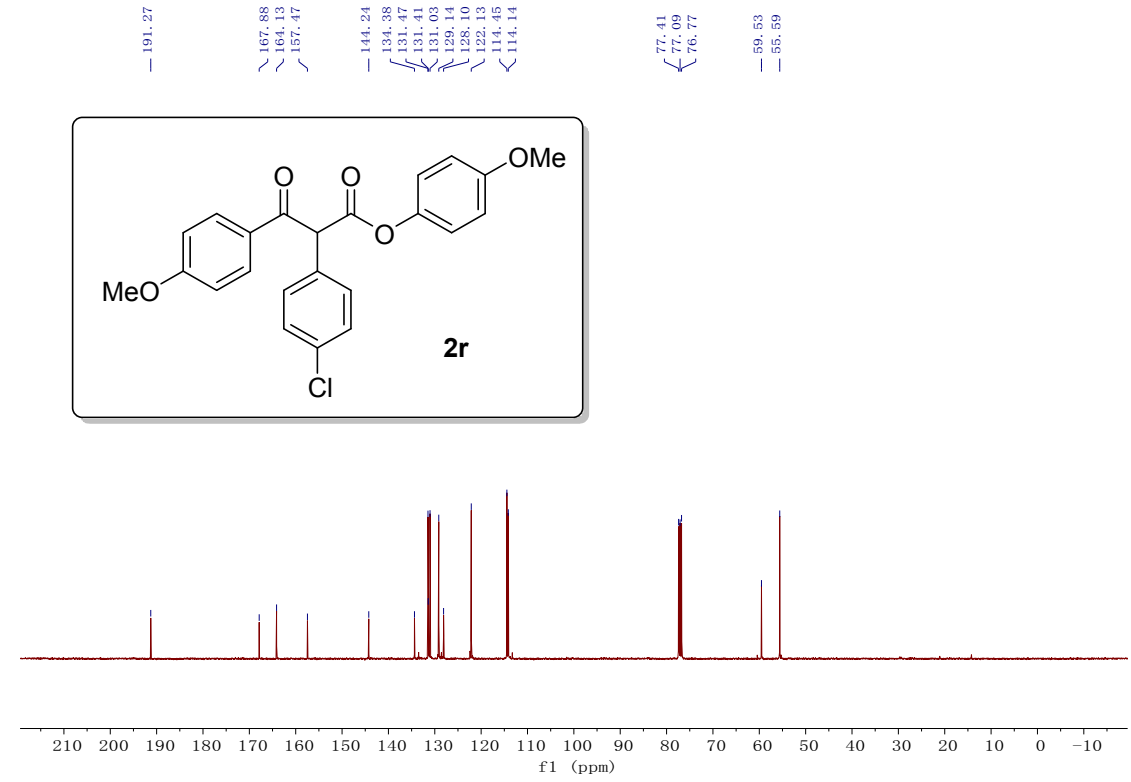
7.98
7.96
7.96
7.42
7.42
7.40
7.40
7.34
7.32
7.32
7.02
7.02
7.00
7.00
6.92
6.92
6.90
6.89
6.86
6.86
6.84
6.83
5.76
3.83
3.83
3.76
3.76
OMe
O
O
O
MeO
Cl
2r
2.07
1.98
2.13
1.98
2.39
1.00
3.05
3.41
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
−0.5
f1 (ppm)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144.24
134.38
131.47
131.41
131.03
129.14
128.10
122.13
114.45
114.14
77.41
77.09
76.77
59.53
55.59
OMe
O
O
O
MeO
Cl
2r
210
200
190
180
170
160
150
140
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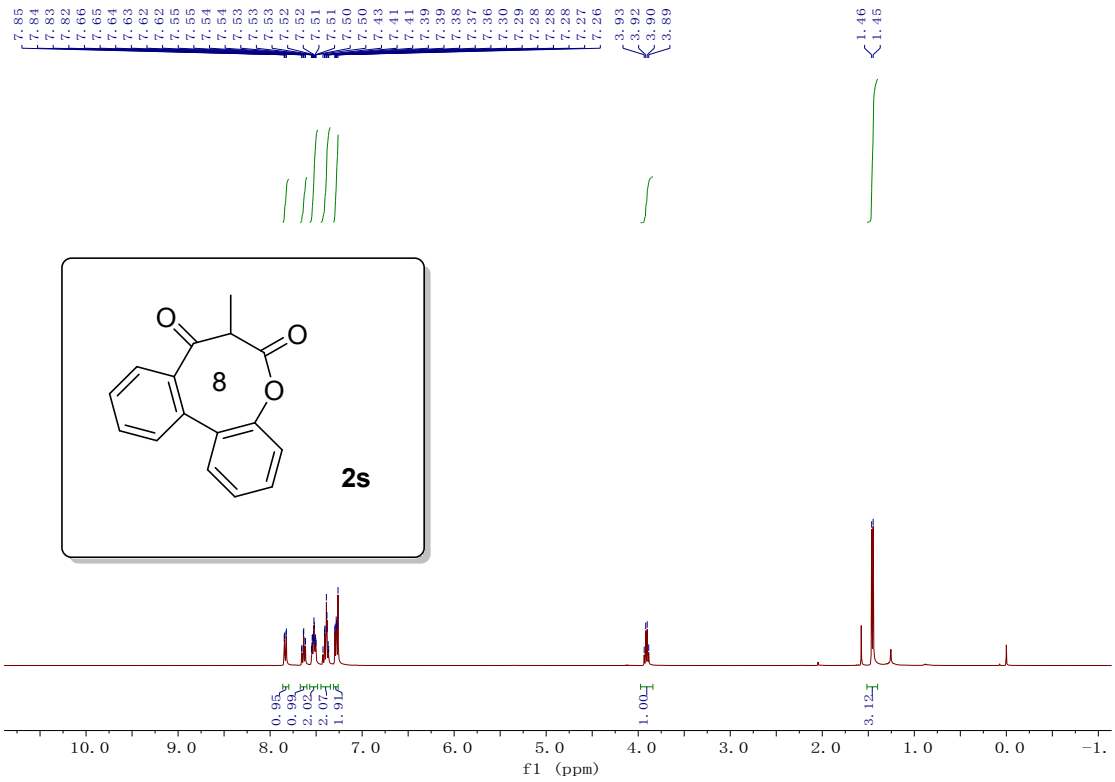
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)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7.84
7.83
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7.62
7.62
7.55
7.55
7.54
7.54
7.53
7.53
7.52
7.52
7.51
7.51
7.50
7.50
7.43
7.41
7.41
7.39
7.39
7.38
7.37
7.36
7.30
7.29
7.28
7.28
7.27
7.26
3.93
3.92
3.90
3.89
1.46
1.45
O
O
O
8
2s
0.95
0.99
2.02
2.07
1.91
1.00
3.12
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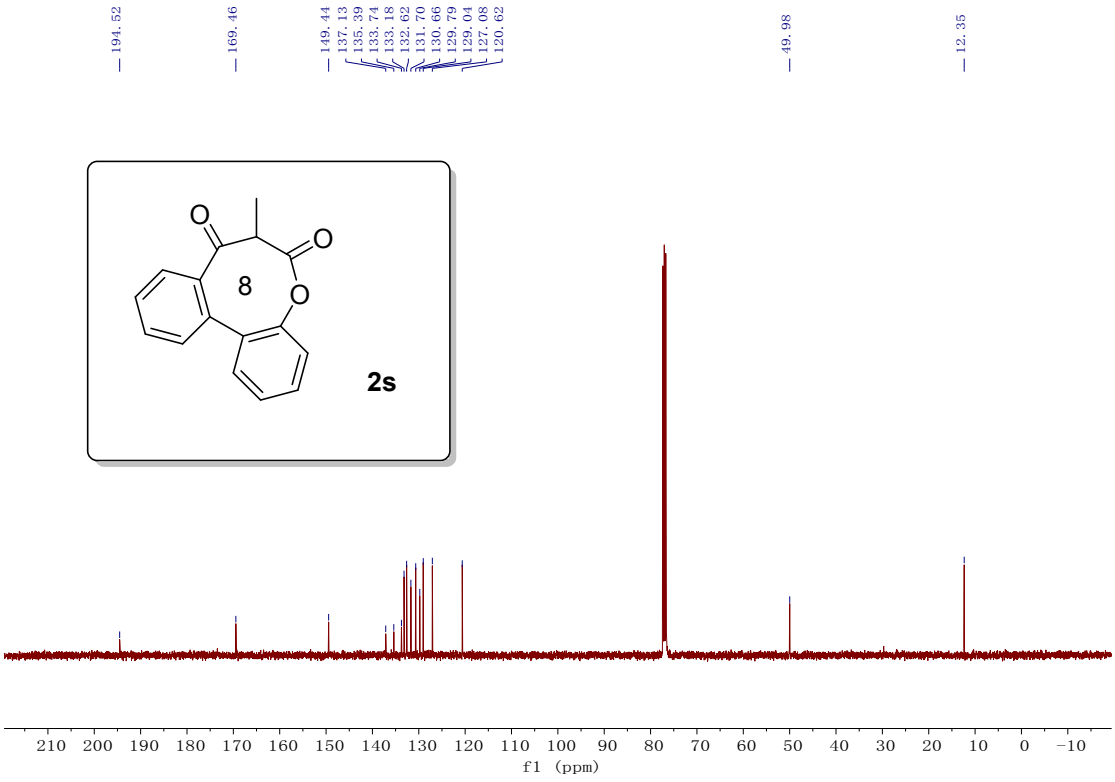
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)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169.46
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137.13
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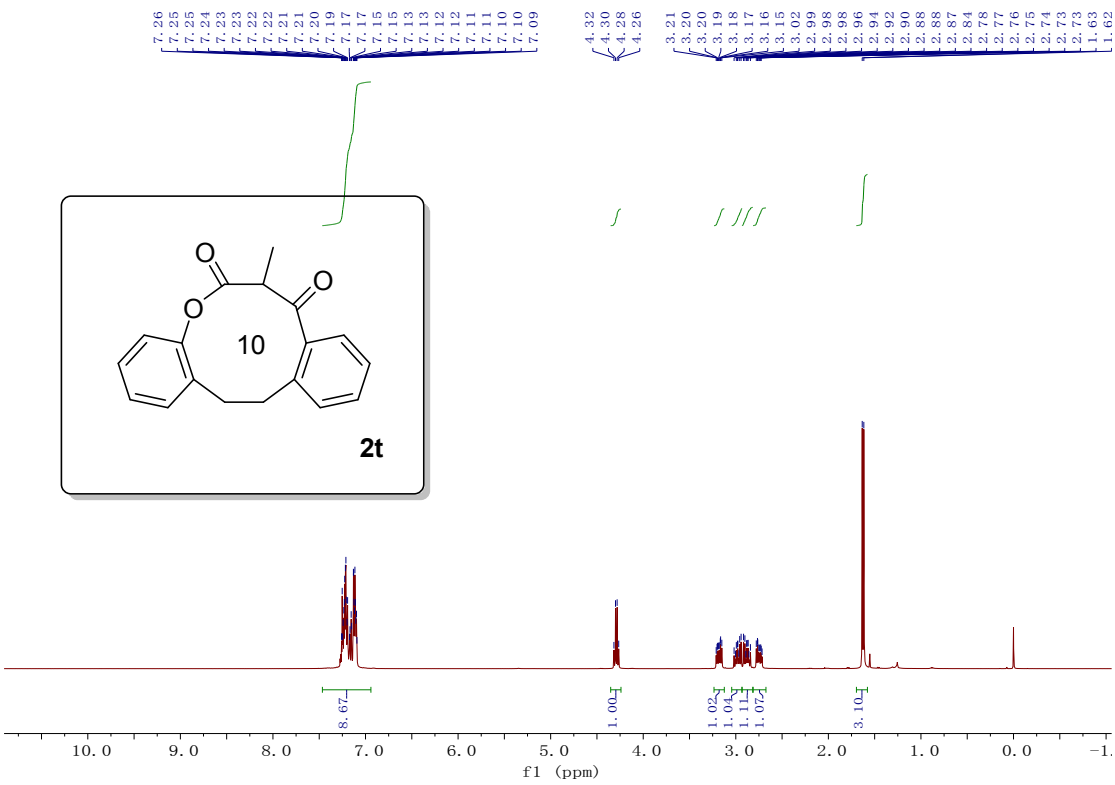
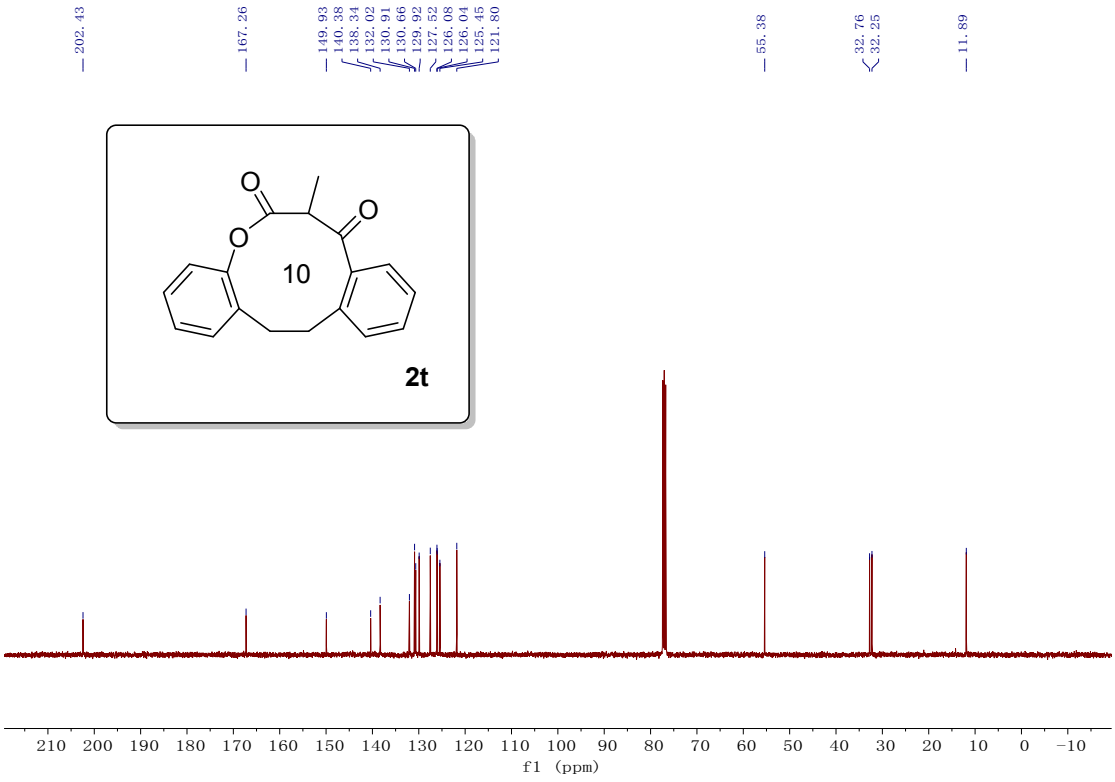
133.18
132.62
131.70
130.66
129.79
129.04
127.08
120.62
49.98
12.35
O
O
O
8
2s
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)


7.26 7.25 7.25 7.24 7.23 7.23 7.22 7.22 7.21 7.21 7.20 7.19 7.17 7.17 7.15 7.15 7.13 7.12 7.12 7.11 7.11 7.10 7.10 7.09
4.32 4.30 4.28 4.26
3.21 3.20 3.20 3.19 3.18 3.17 3.16 3.15 3.02 2.99 2.98 2.98 2.96 2.94 2.92 2.90 2.88 2.88 2.87 2.84 2.78 2.77 2.76 2.75 2.74 2.73 2.73 1.63 1.62
O
O
O
10
2t
8.67
1.00
1.02
1.04
1.11
1.07
3.10
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
f1 (ppm)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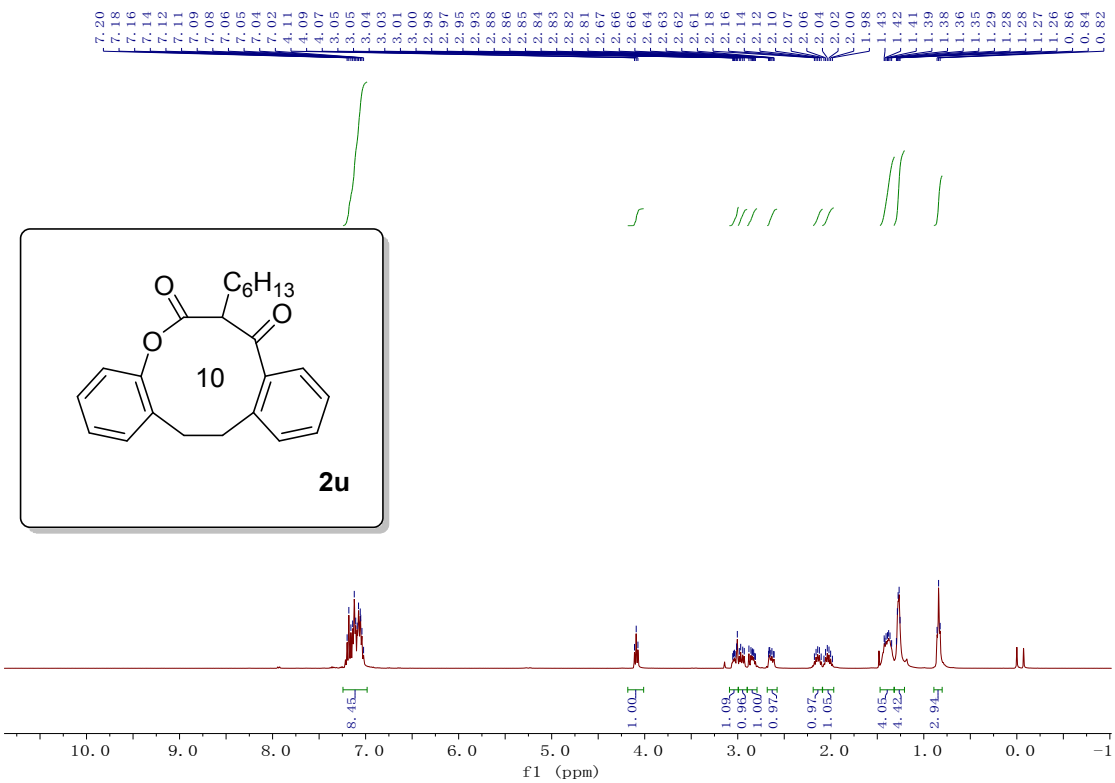
130.66
129.92
127.52
126.08
126.04
125.45
121.80
55.38
32.76
32.25
11.89
O
O
O
10
2t
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)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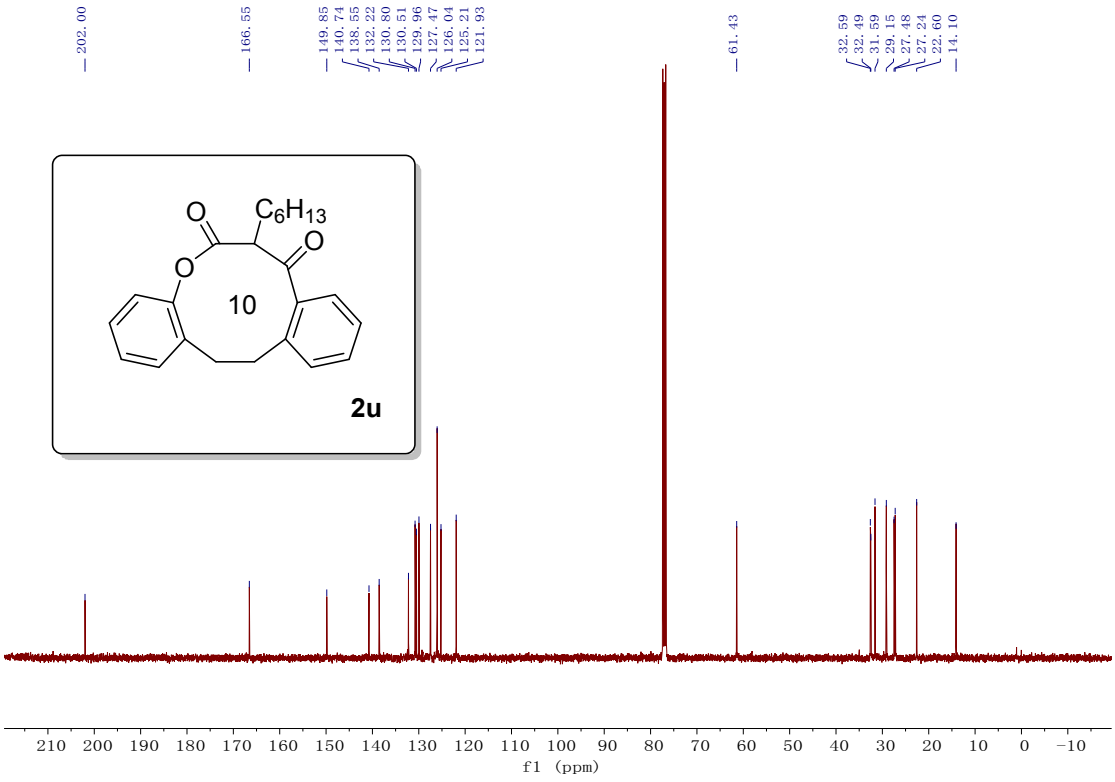
O
C6H13
O
O
10
2u
8.45
1.00
1.09
0.96
1.00
0.97
0.97
1.05
4.05
4.42
2.94
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 −1
f1 (ppm)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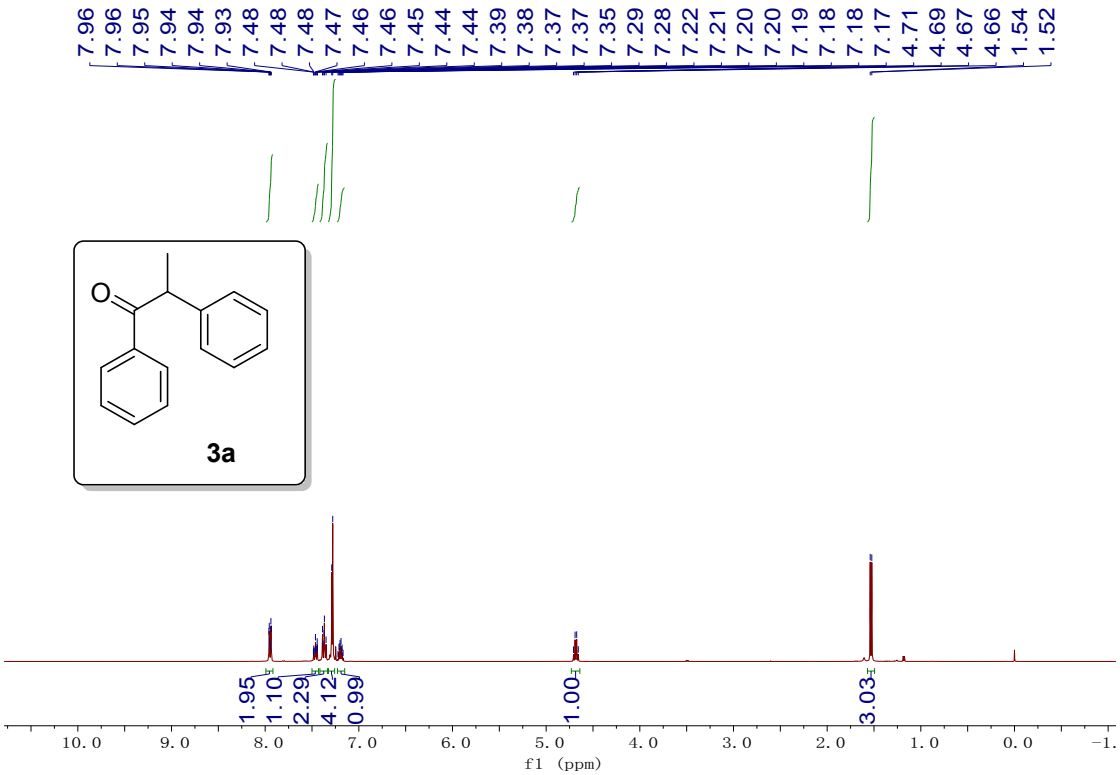
127.47
126.04
125.21
121.93
61.43
32.59
32.49
31.59
29.15
27.48
27.24
22.60
14.10
O
C6H13
O
O
10
2u
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)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7.96
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7.93
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7.48
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7.44
7.44
7.39
7.38
7.37
7.37
7.35
7.29
7.28
7.22
7.21
7.20
7.20
7.19
7.18
7.18
7.17
4.71
4.69
4.67
4.66
1.54
1.52
O
3a
1.95
1.10
2.29
4.12
0.99
1.00
3.03
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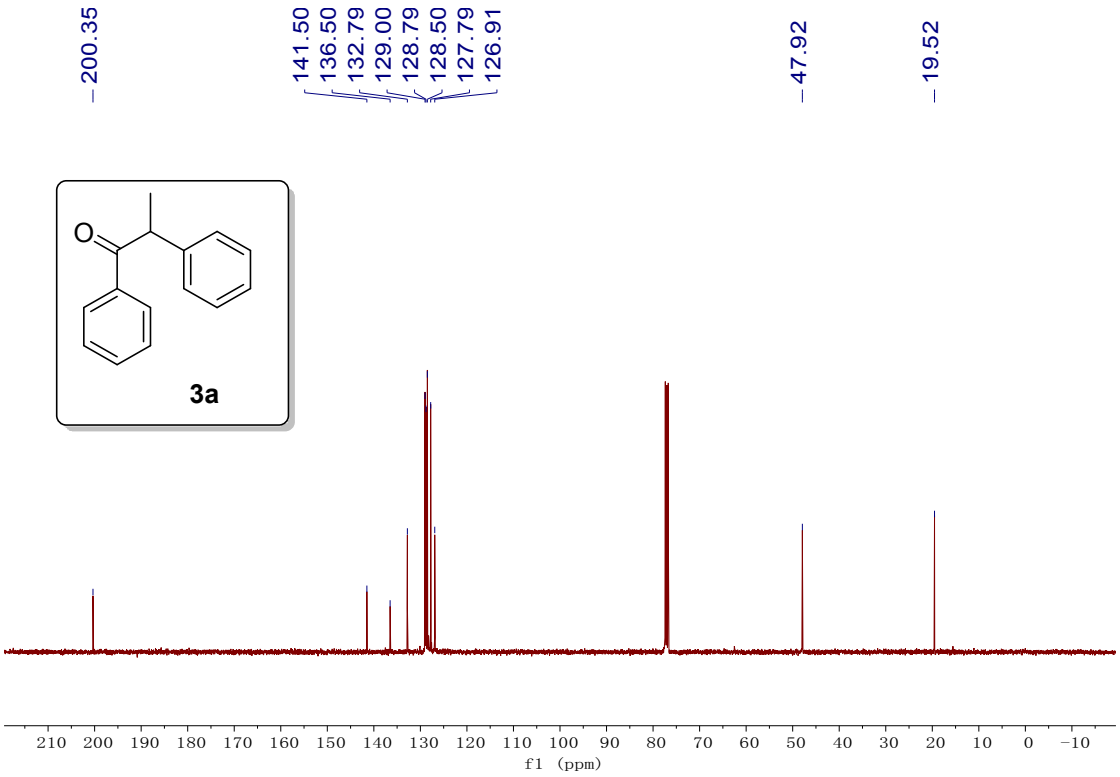
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)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128.79
128.50
127.79
126.91
47.92
19.52
O
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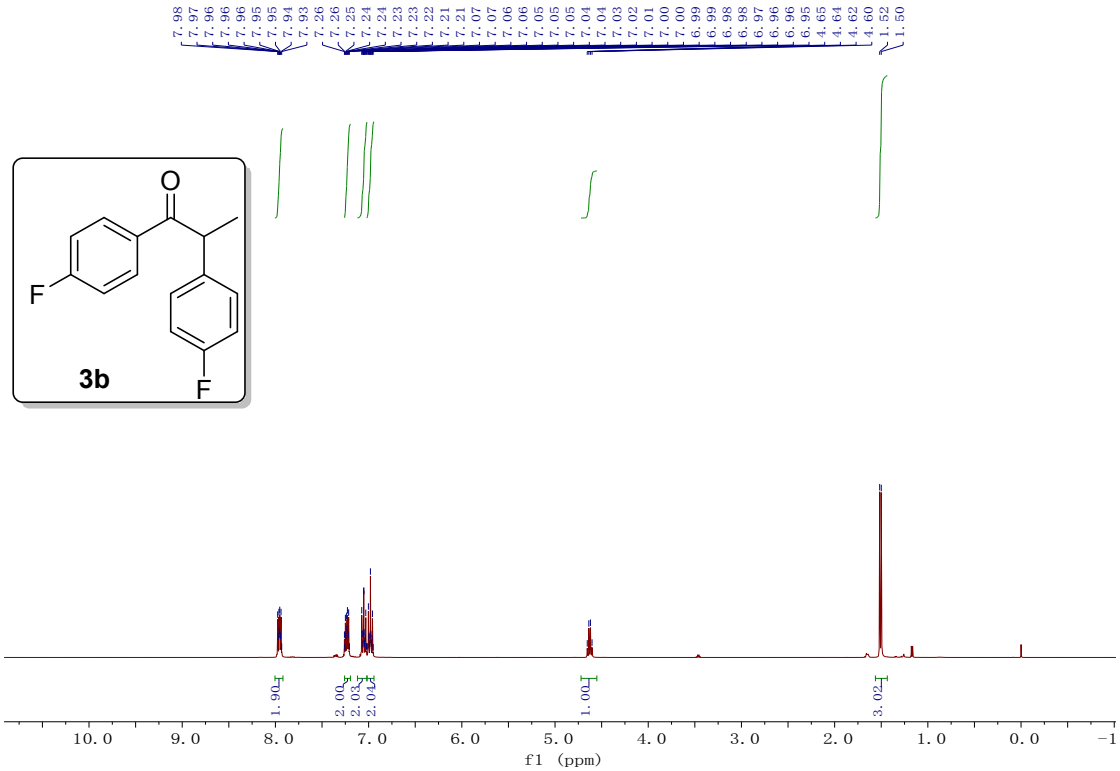
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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7.96
7.96
7.96
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7.94
7.93
7.26
7.25
7.24
7.24
7.23
7.23
7.22
7.21
7.21
7.07
7.07
7.06
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7.05
7.05
7.05
7.04
7.04
7.03
7.02
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7.00
7.00
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6.96
6.95
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4.62
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O
F
F
3b
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2.04
1.00
3.02
10.0
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8.0
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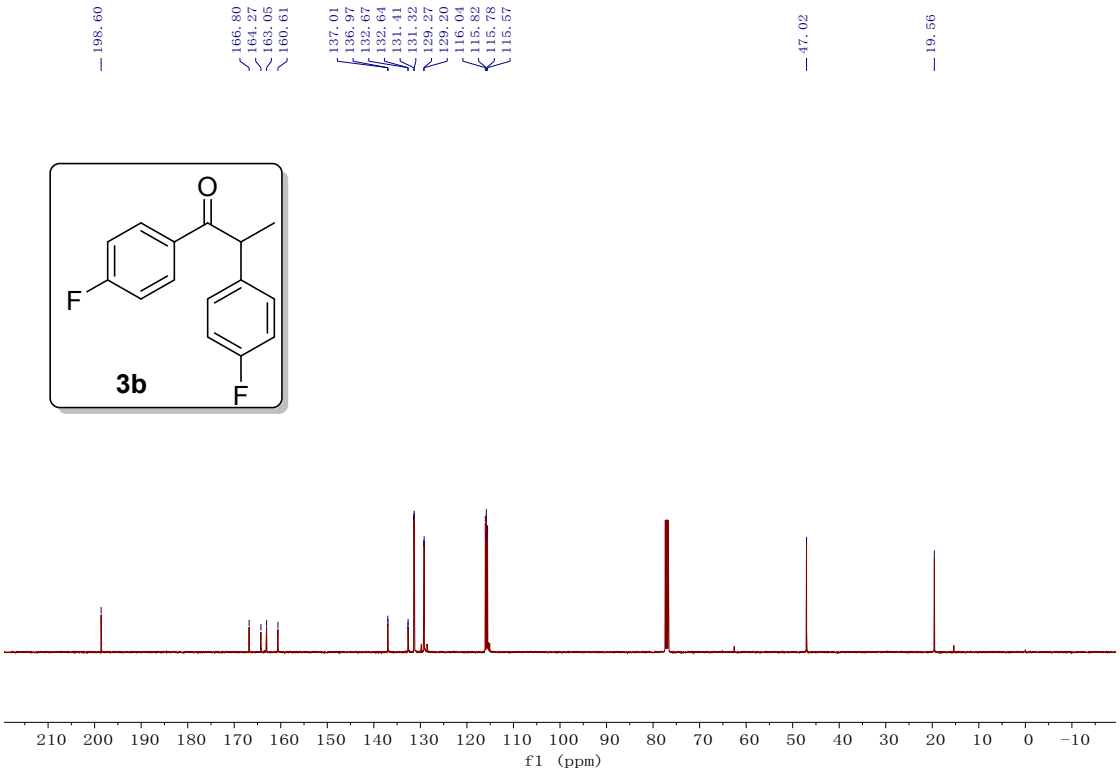
6.0
5.0
4.0
3.0
2.0
1.0
0.0
−1
f1 (ppm)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132.67
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131.41
131.32
129.27
129.20
116.04
115.82
115.78
115.57
47.02
19.56
O
F
F
3b
210
200
190
180
170
160
150
140
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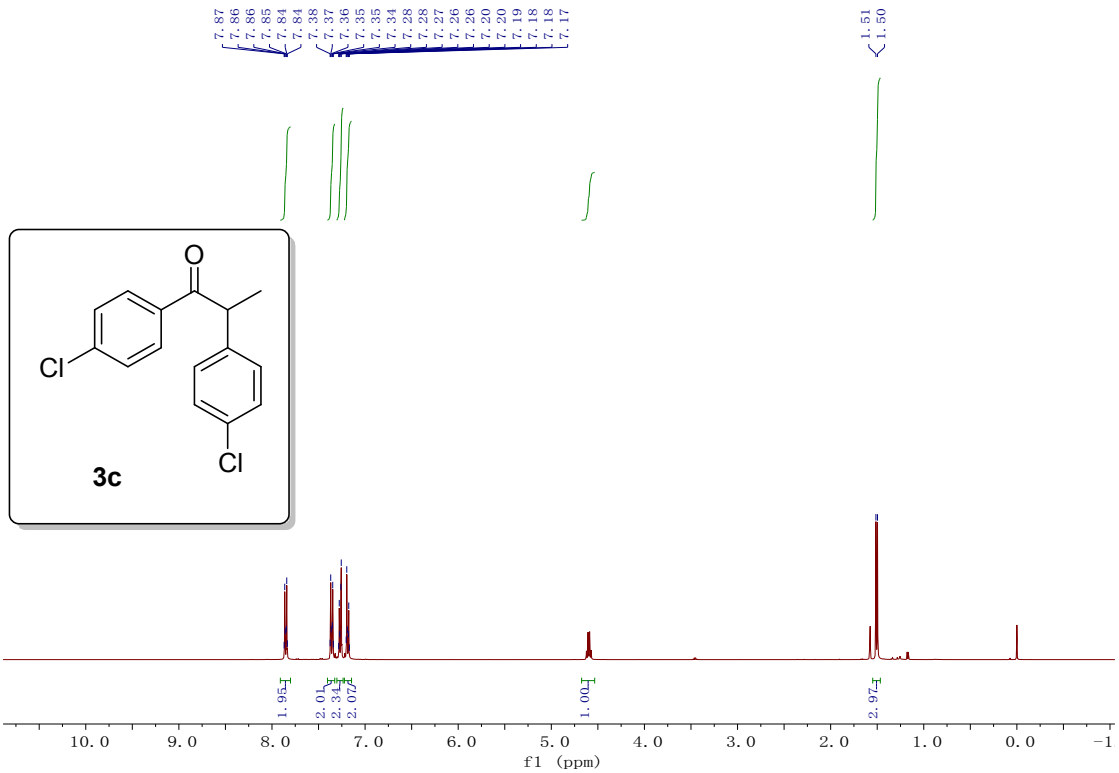
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)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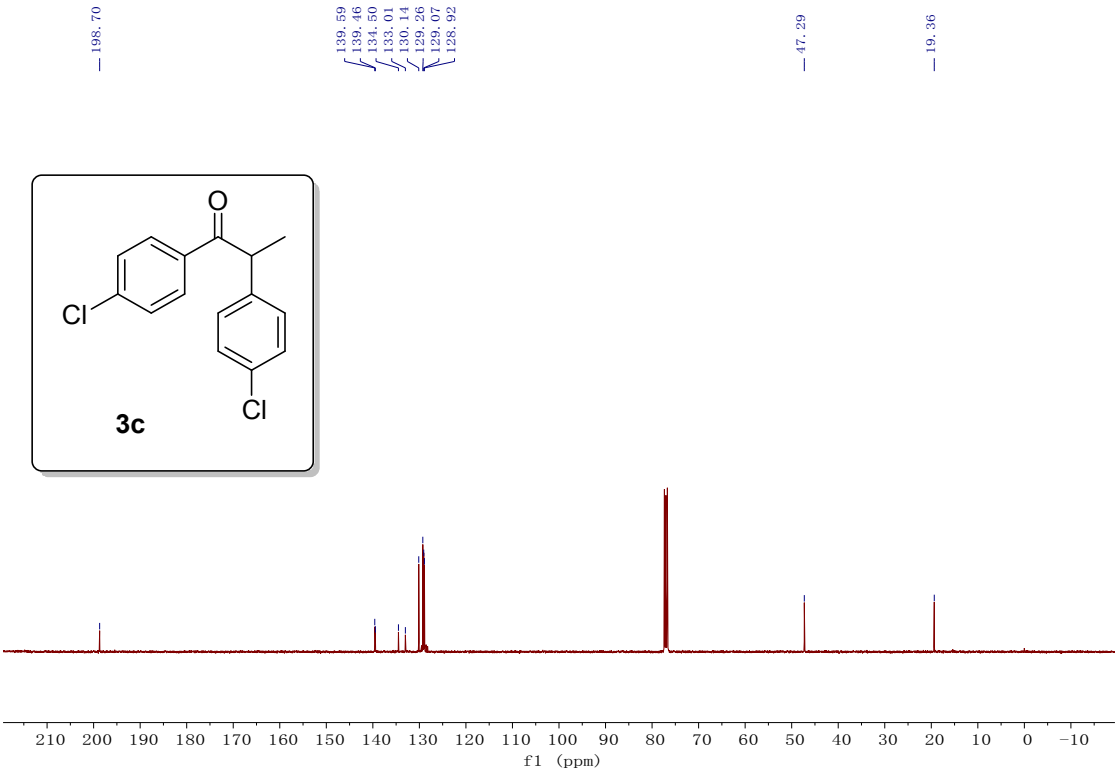
7.35
7.35
7.34
7.28
7.28
7.27
7.26
7.26
7.20
7.20
7.19
7.18
7.18
7.17
1.51
1.50
O
Cl
Cl
3c
1.95
2.01
2.34
2.72
1.00
2.97
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
−1
f1 (ppm)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134.50
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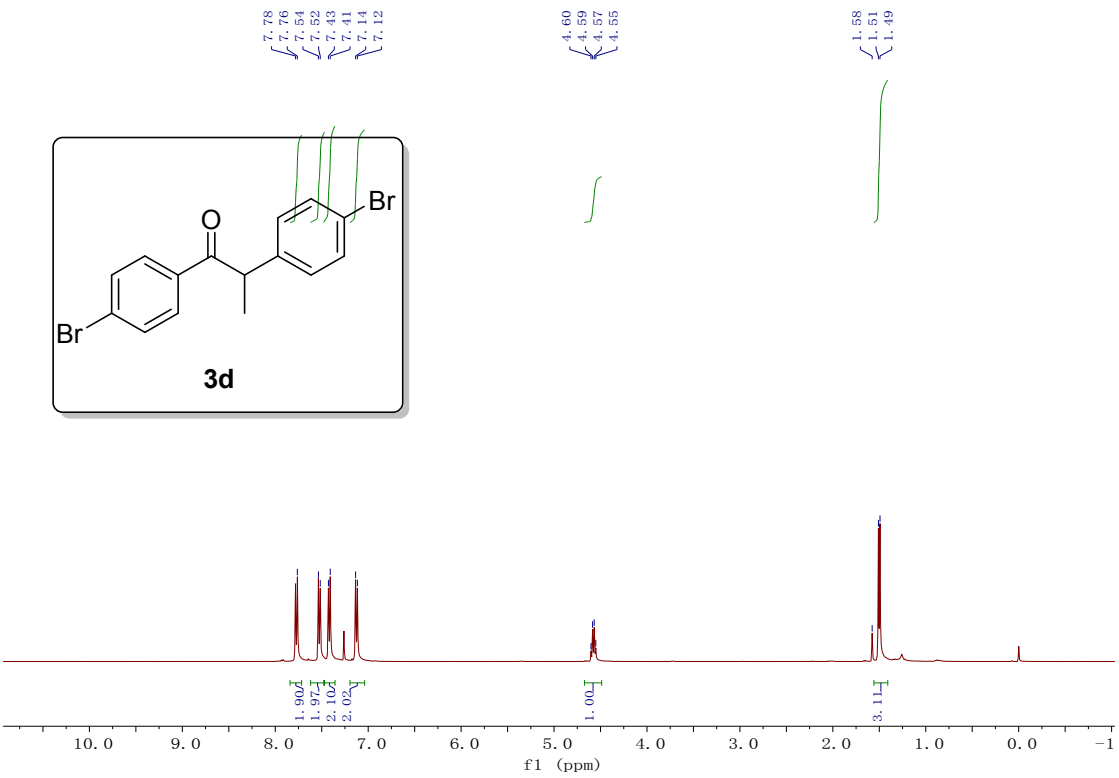
129.26
129.07
128.92
47.29
19.36
O
Cl
Cl
3c
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)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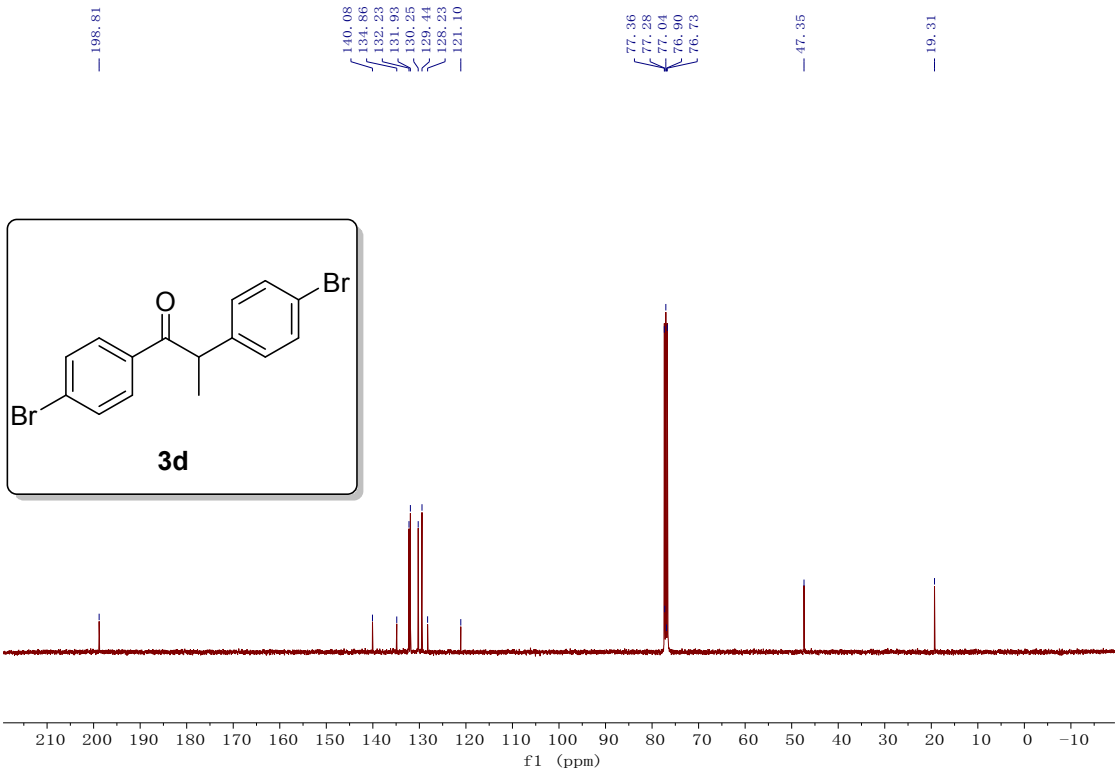
7.76
7.54
7.52
7.43
7.41
7.14
7.12
4.60
4.59
4.57
4.55
1.58
1.51
1.49
Br
O
Br
3d
1.90
1.97
2.10
2.02
1.00
3.11
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
−1
f1 (ppm)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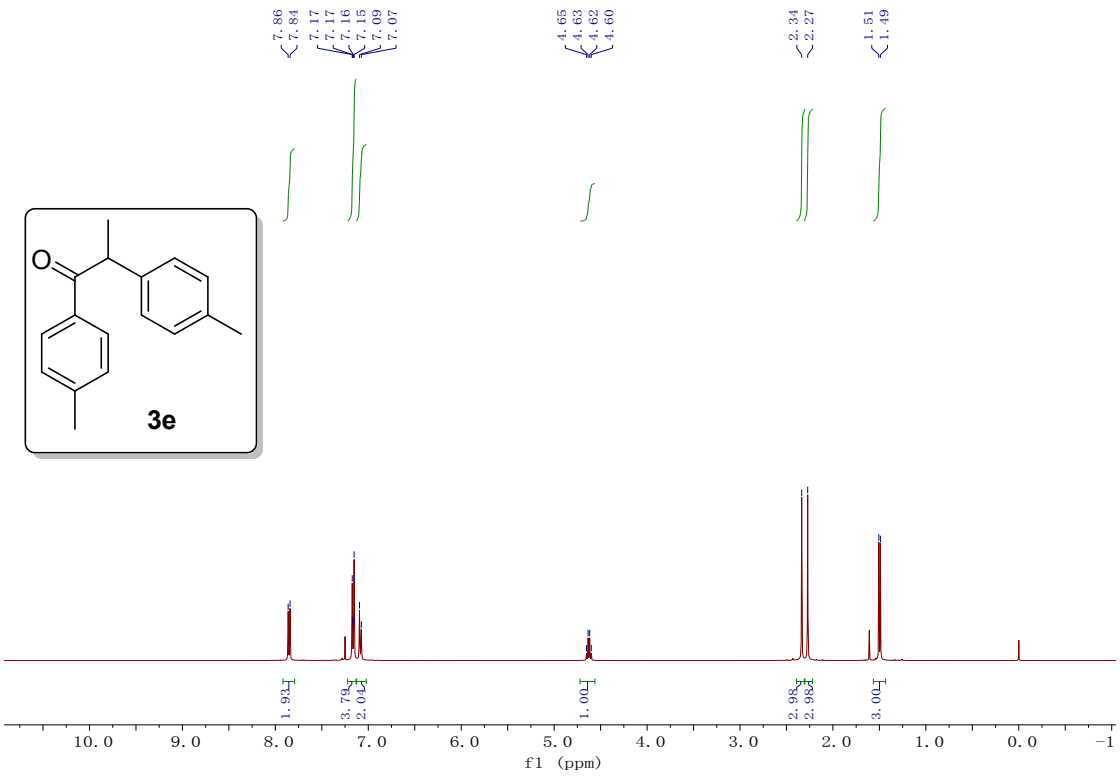
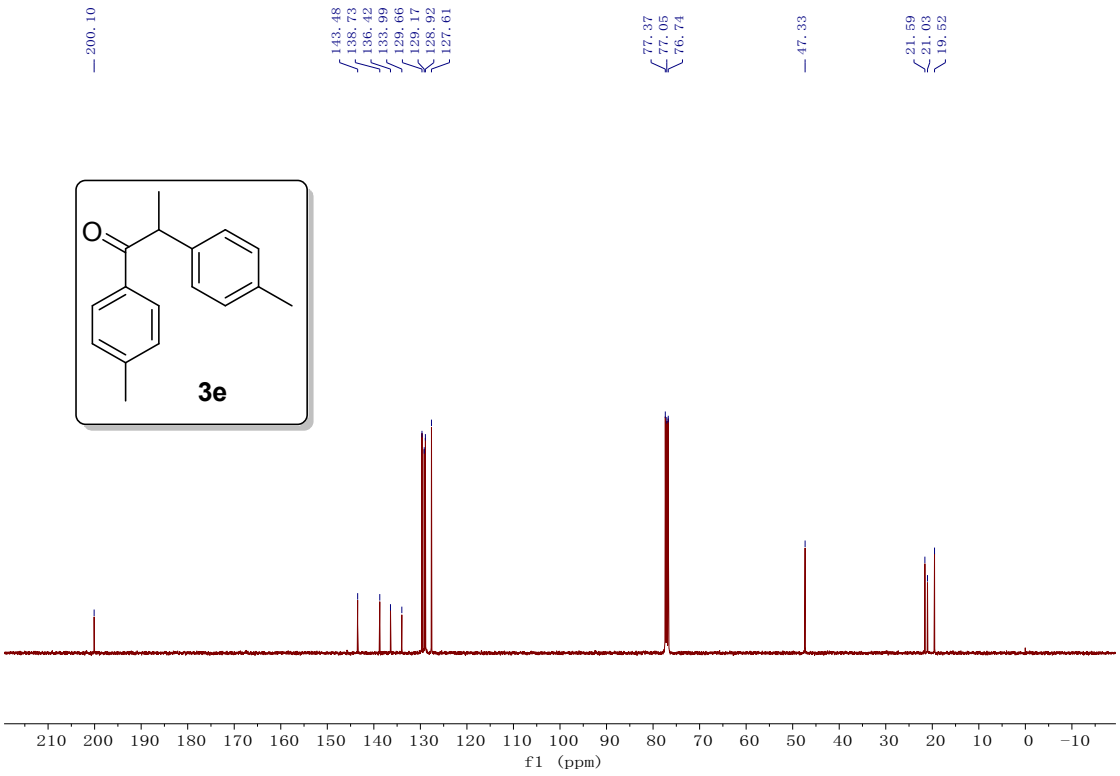
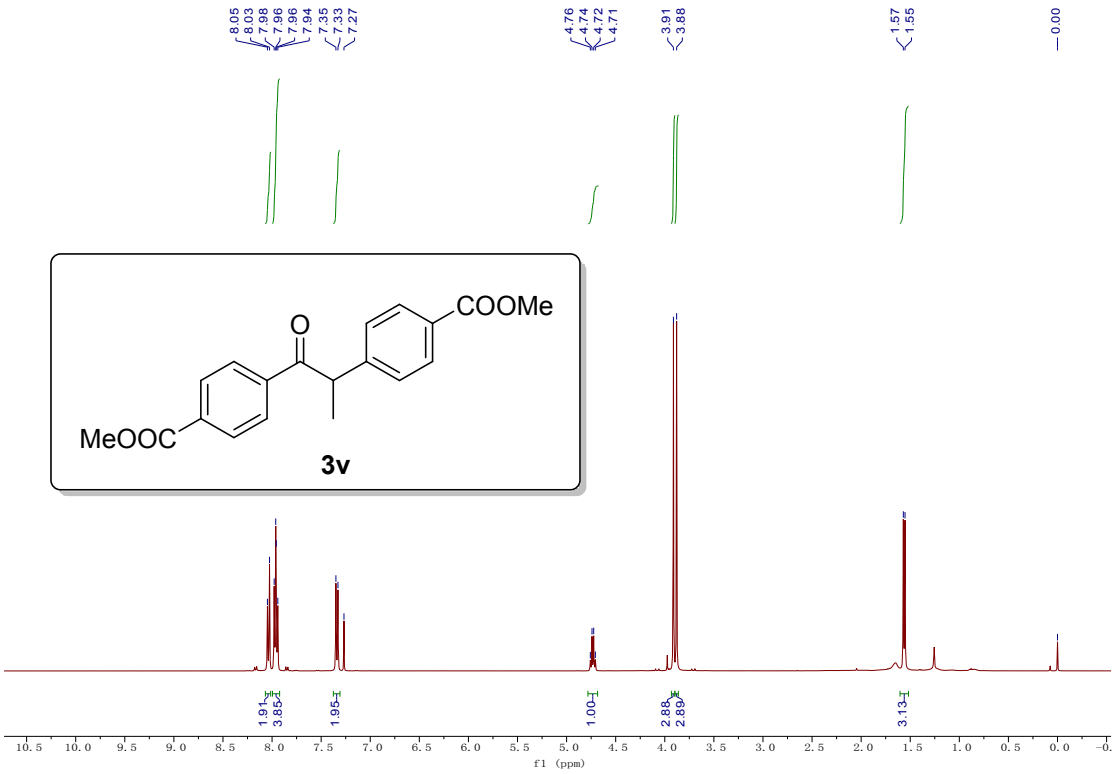
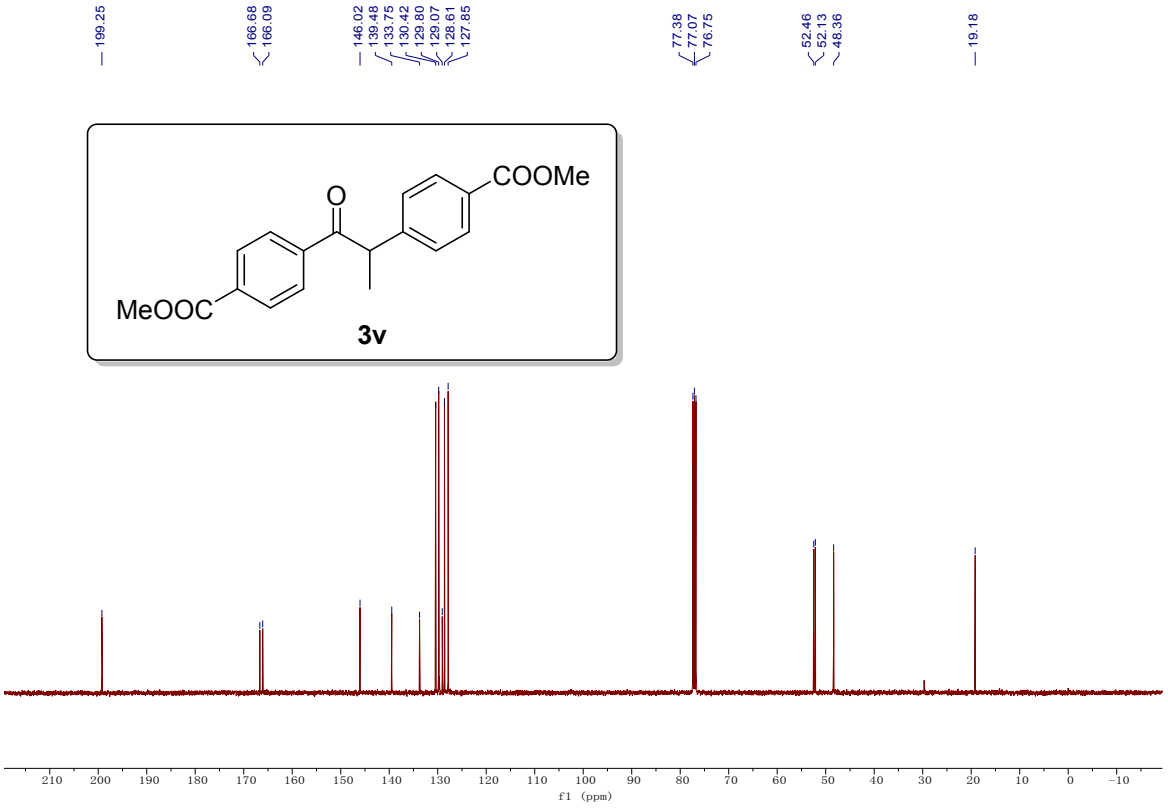
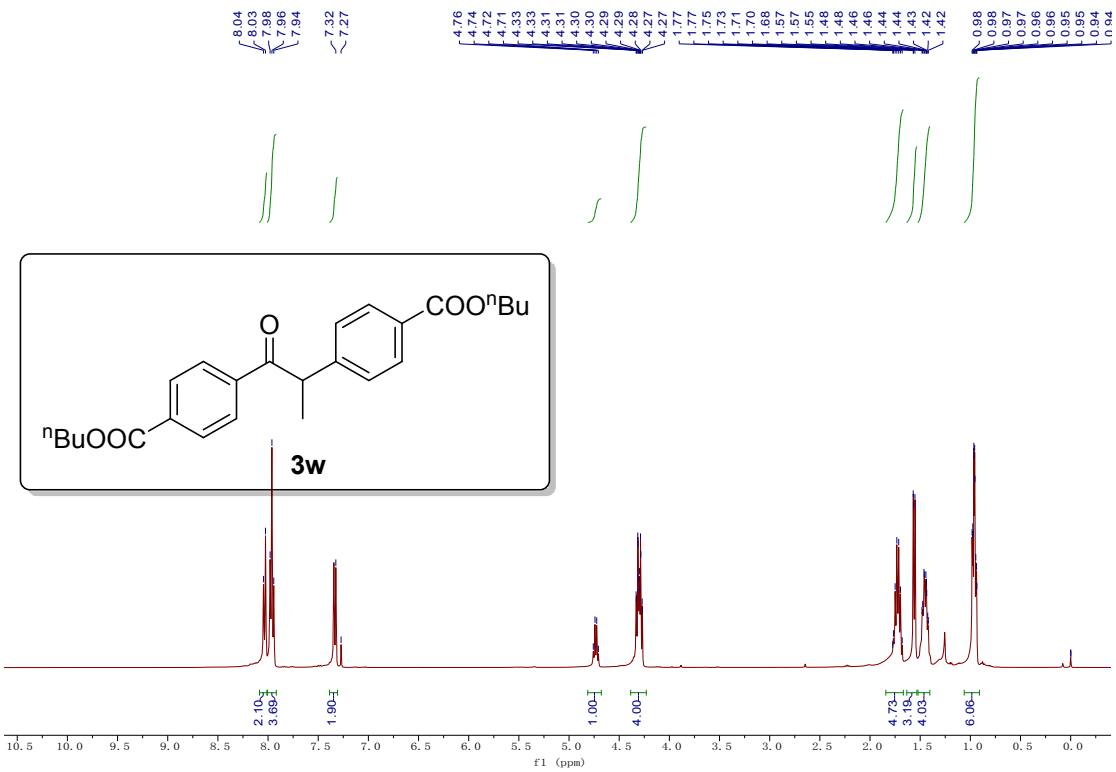
140.08
134.86
132.23
131.93
130.25
129.44
128.23
121.10
77.36
77.28
77.04
76.90
76.73
47.35
19.31
Br
O
Br
3d
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

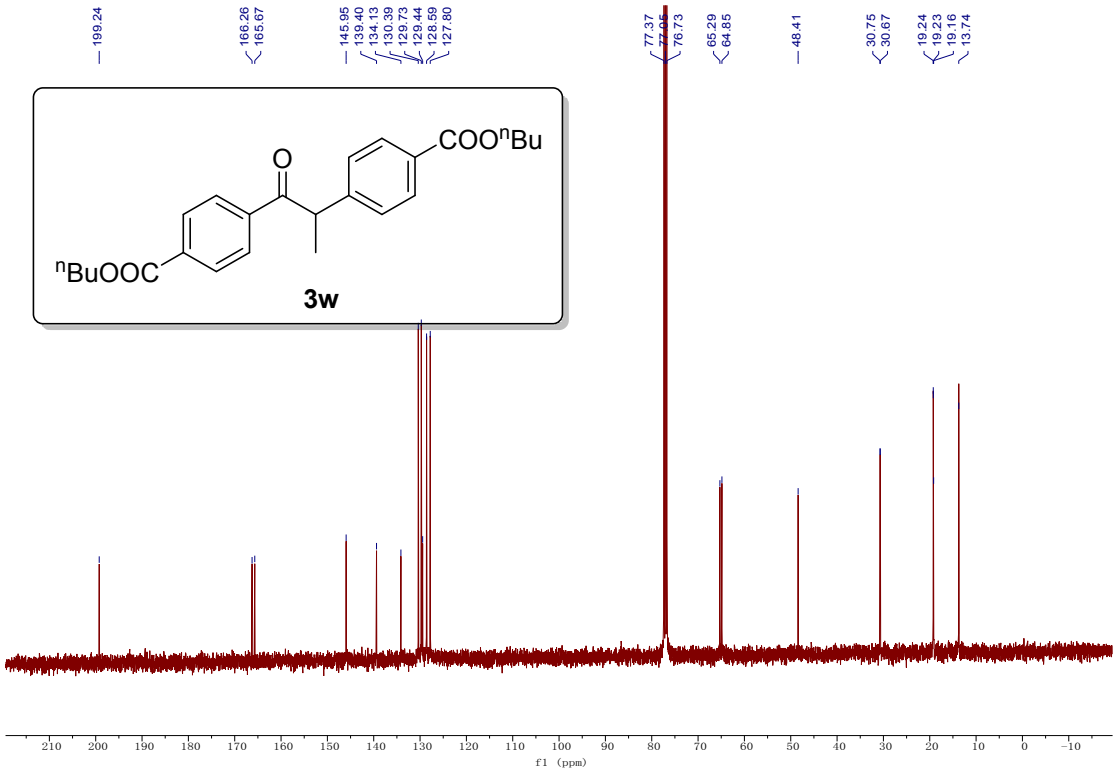

7.86
7.84
7.17
7.17
7.16
7.15
7.09
7.07
4.65
4.63
4.62
4.60
2.34
2.27
1.51
1.49
O
3e
1.93
3.79
2.04
1.00
2.98
2.98
3.00
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
−1
f1 (ppm)

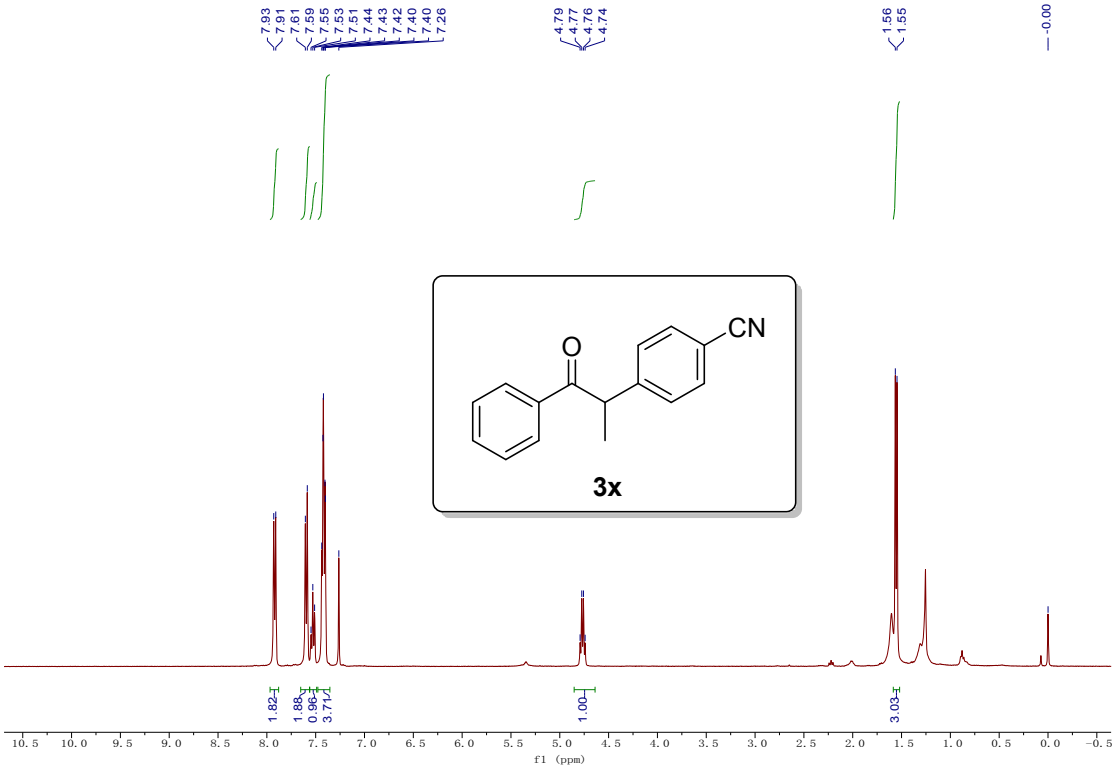

200.10
143.48
138.73
136.42
133.99
129.66
129.17
128.92
127.61
77.37
77.05
76.74
47.33
21.59
21.03
19.52
O
3e
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)


8.05
8.03
7.98
7.96
7.96
7.96
7.94
7.35
7.33
7.27
4.76
4.74
4.72
4.71
3.91
3.88
1.57
1.55
0.00
COOMe
O
MeOOC
3v
1.91
3.85
1.95
1.00
2.88
2.89
3.13
f1 (ppm)


199.25
166.68
166.09
146.02
139.48
133.75
130.42
129.80
129.07
128.61
127.85
77.38
77.07
76.75
52.46
52.13
48.36
19.18
COOMe
O
MeOOC
3v
f1 (ppm)


8.04
8.03
7.98
7.96
7.94
7.32
7.27
4.76
4.74
4.72
4.71
4.33
4.31
4.30
4.29
4.28
4.27
1.77
1.75
1.73
1.71
1.70
1.68
1.57
1.55
1.48
1.46
1.44
1.43
1.42
0.98
0.97
0.96
0.95
0.94
COO^{n}Bu
O
^{n}BuOOC
3w
2.10
3.69
1.90
1.00
4.00
4.73
3.19
4.03
6.06
f1 (ppm)


199.24
166.26
165.67
145.95
139.40
134.13
130.39
129.73
129.44
128.59
127.80
77.37
77.05
76.73
65.29
64.85
48.41
30.75
30.67
19.24
19.23
19.16
13.74
COO^{n}Bu
O
^{n}BuOOC
3w
f1 (ppm)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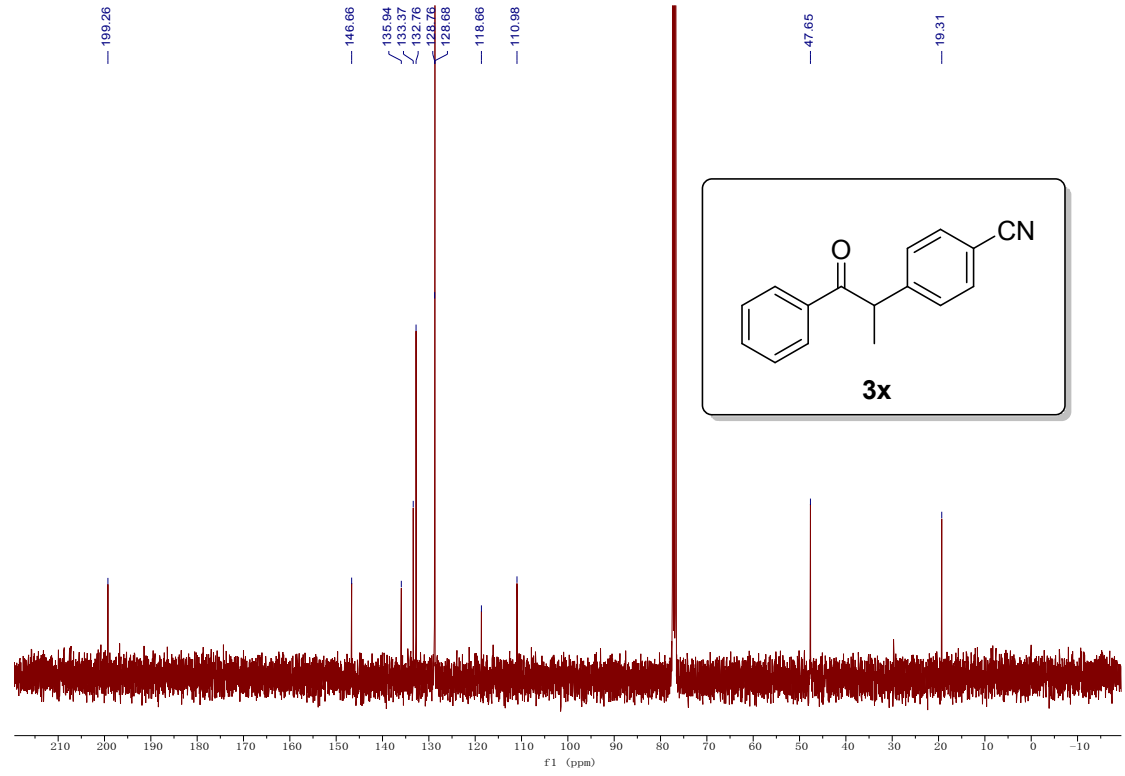
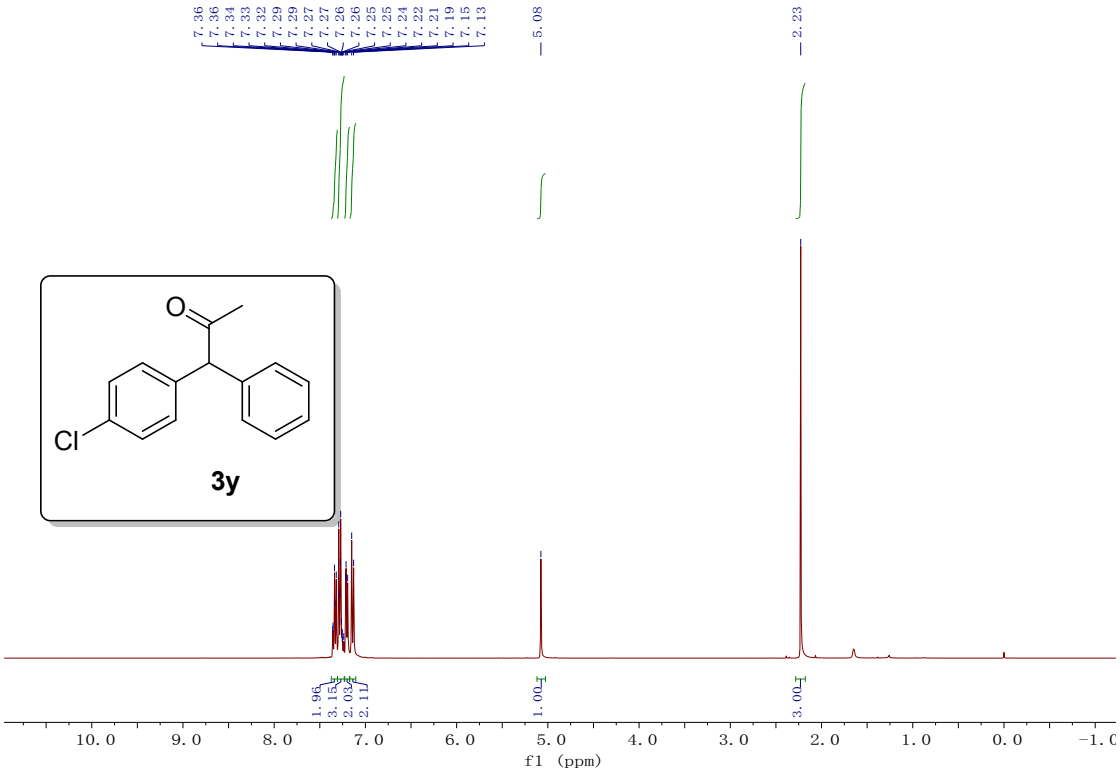
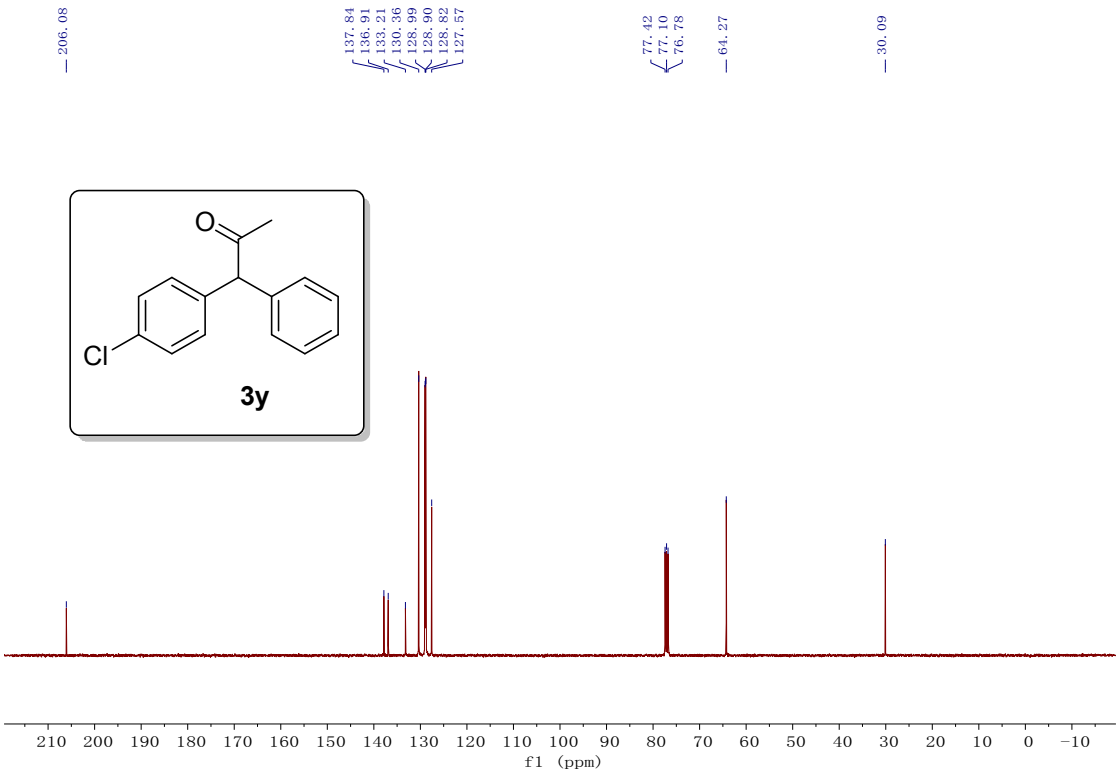
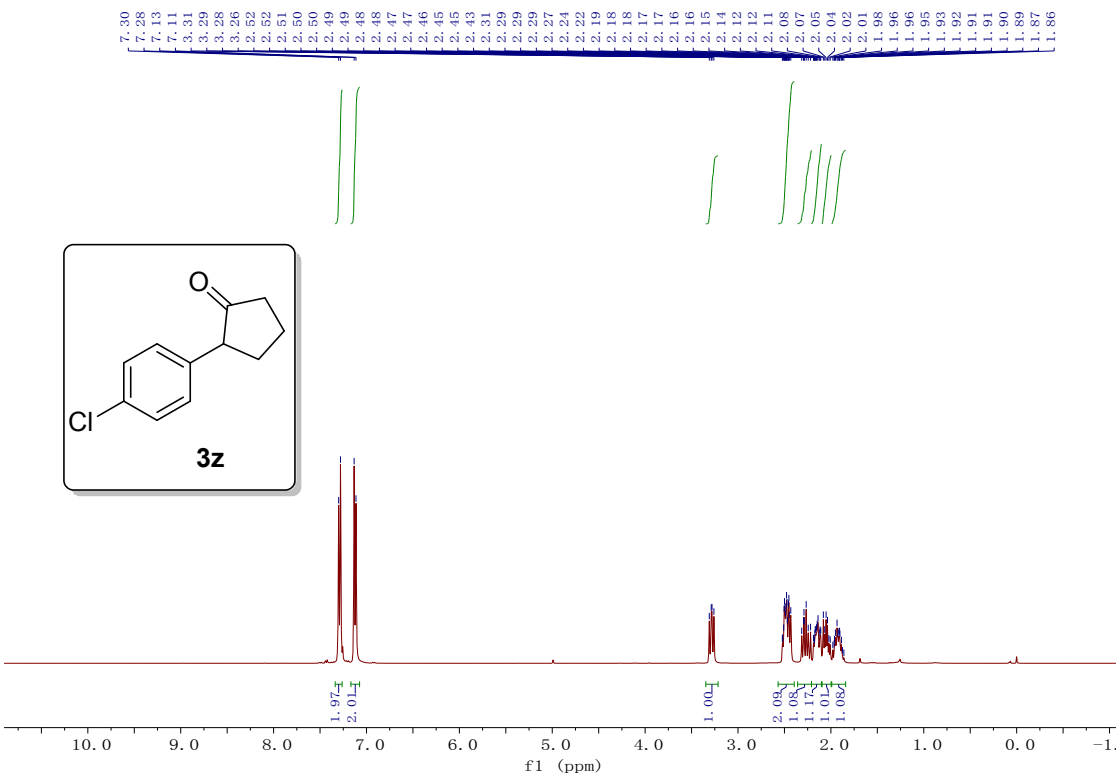
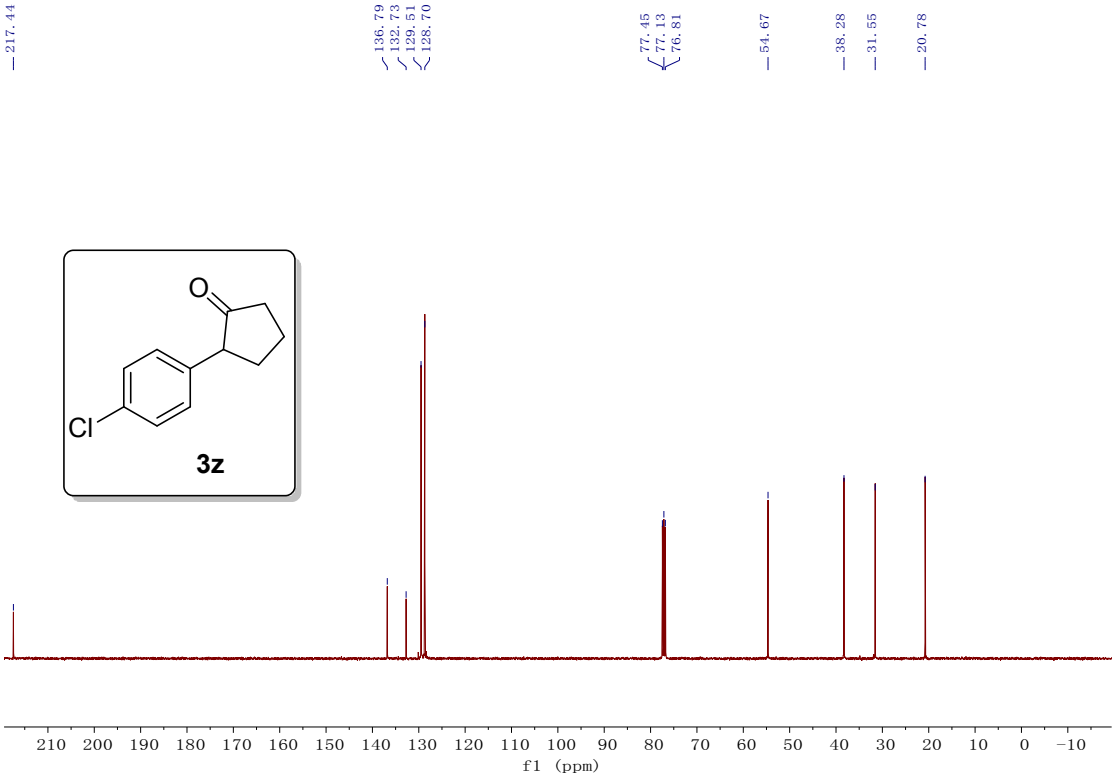
7.91
7.61
7.59
7.55
7.53
7.51
7.44
7.43
7.42
7.40
7.40
7.26
4.79
4.77
4.76
4.74
1.56
1.55
-0.00
O
CN
3x
1.82
1.88
0.96
3.71
1.00
3.03
f1 (ppm)

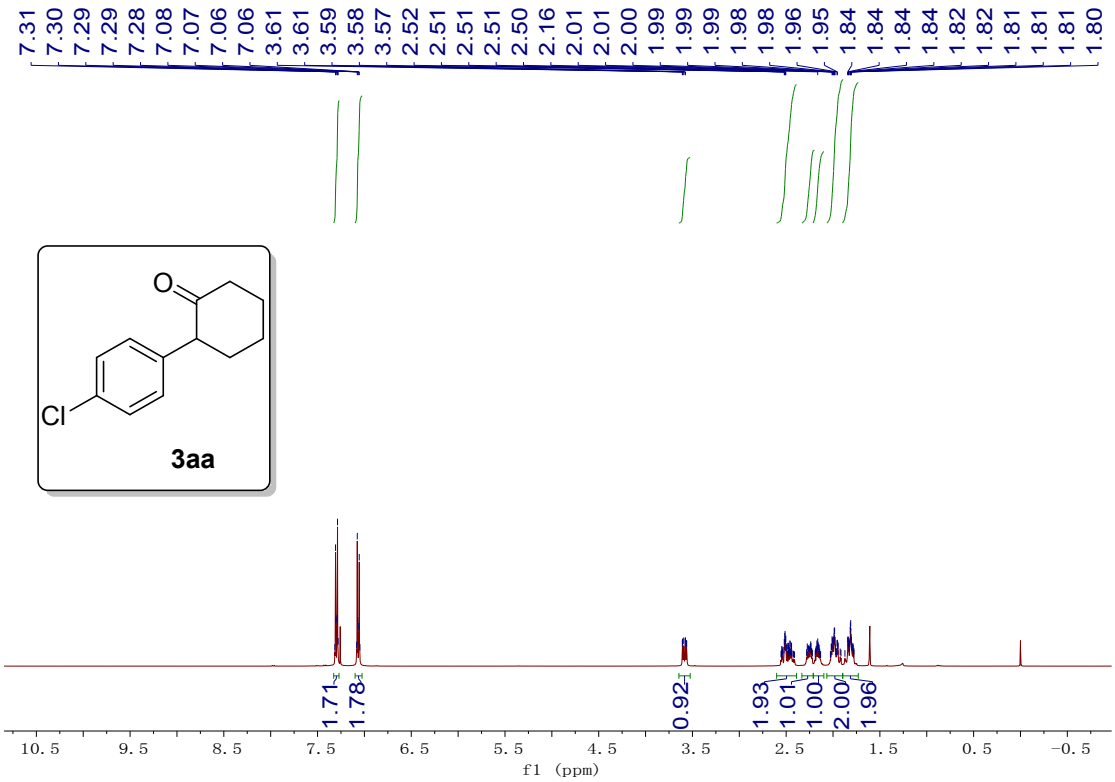

199.26
146.66
135.94
133.37
132.76
128.76
128.68
118.66
110.98
47.65
19.31
O
CN
3x
f1 (ppm)

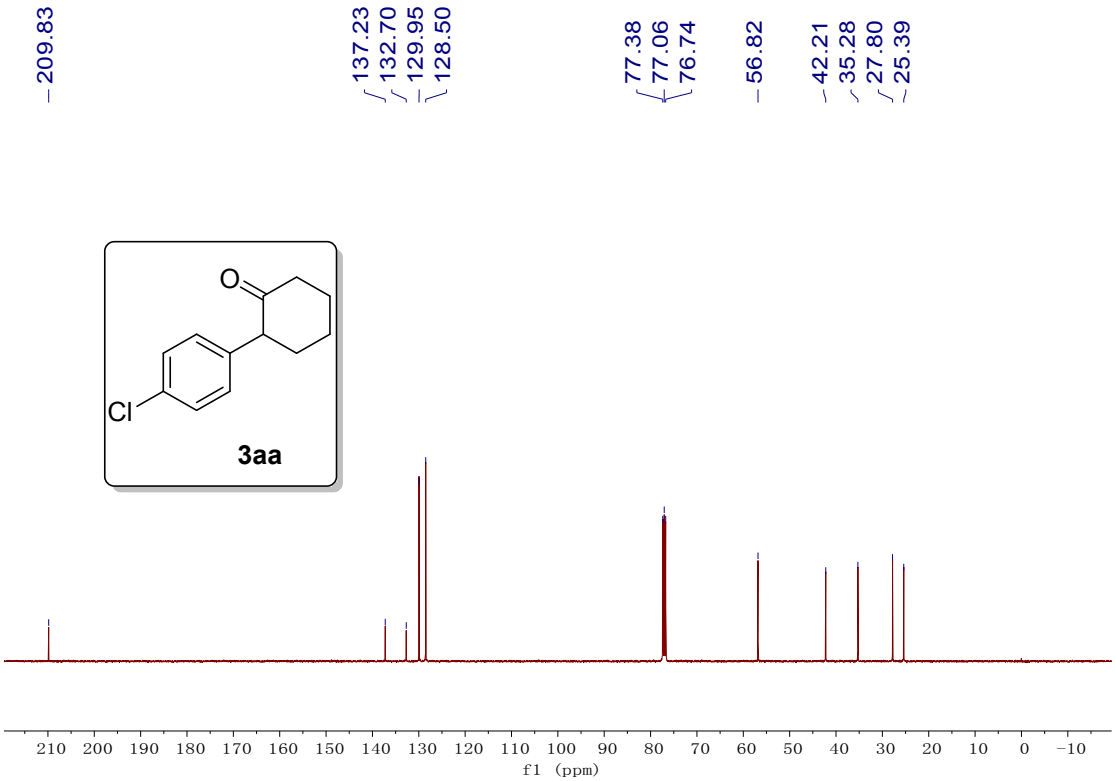

7.36
7.36
7.34
7.33
7.32
7.29
7.29
7.27
7.27
7.26
7.26
7.25
7.25
7.24
7.22
7.21
7.19
7.15
7.13
5.08
2.23
O
Cl
3y
1.96
3.15
2.03
2.11
1.00
3.00
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

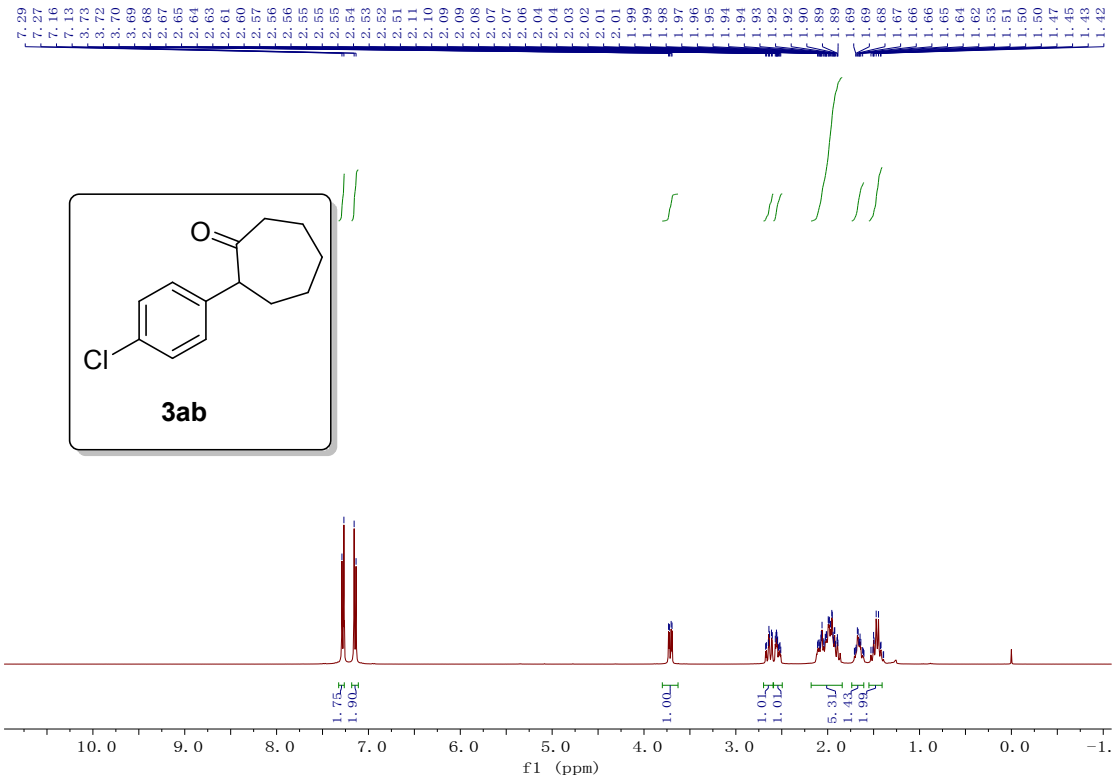

206.08
137.84
136.91
133.21
130.36
128.99
128.90
128.82
127.57
77.42
77.10
76.78
64.27
30.09
O
Cl
3y
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

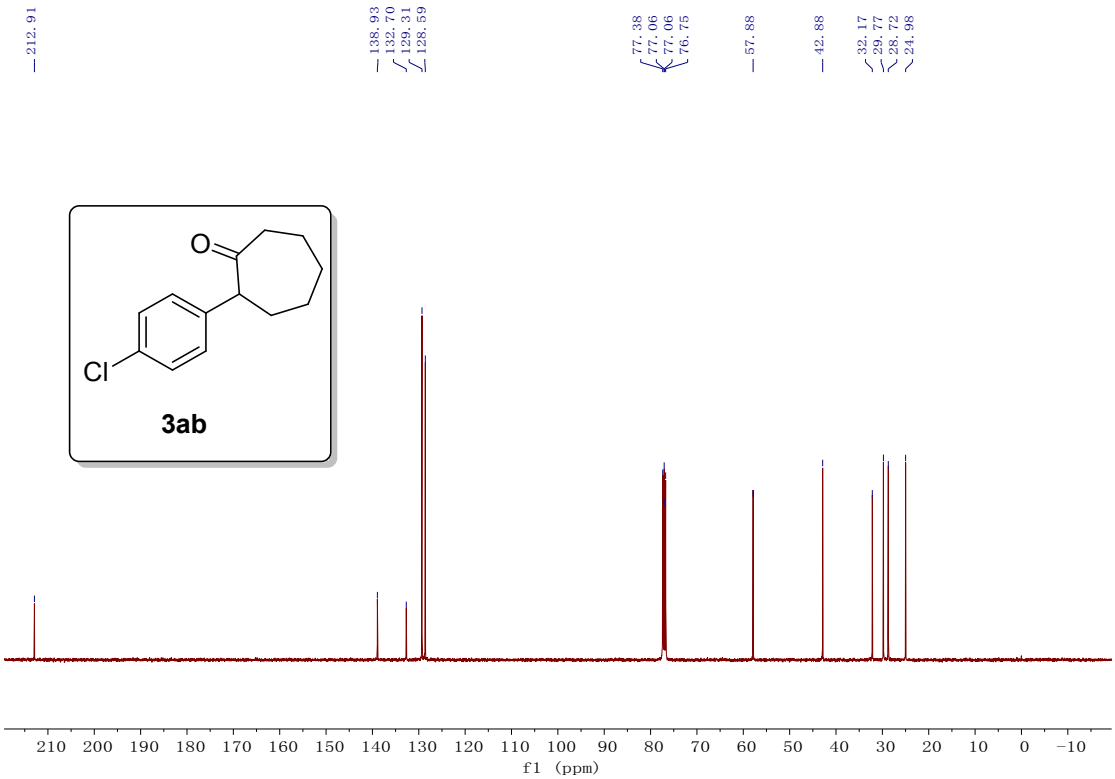

7.30 7.28 7.13 7.11 3.31 3.29 3.28 3.26 2.52 2.52 2.51 2.50 2.50 2.49 2.49 2.48 2.48 2.47 2.47 2.46 2.45 2.45 2.43 2.31 2.29 2.29 2.29 2.27 2.24 2.22 2.19 2.18 2.18 2.17 2.17 2.16 2.16 2.15 2.14 2.12 2.12 2.11 2.08 2.07 2.05 2.04 2.02 2.01 1.98 1.96 1.96 1.95 1.93 1.92 1.91 1.91 1.90 1.89 1.87 1.86
O
Cl
3z
1.97
2.01
1.00
2.09
1.08
1.17
1.01
1.08
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
f1 (ppm)

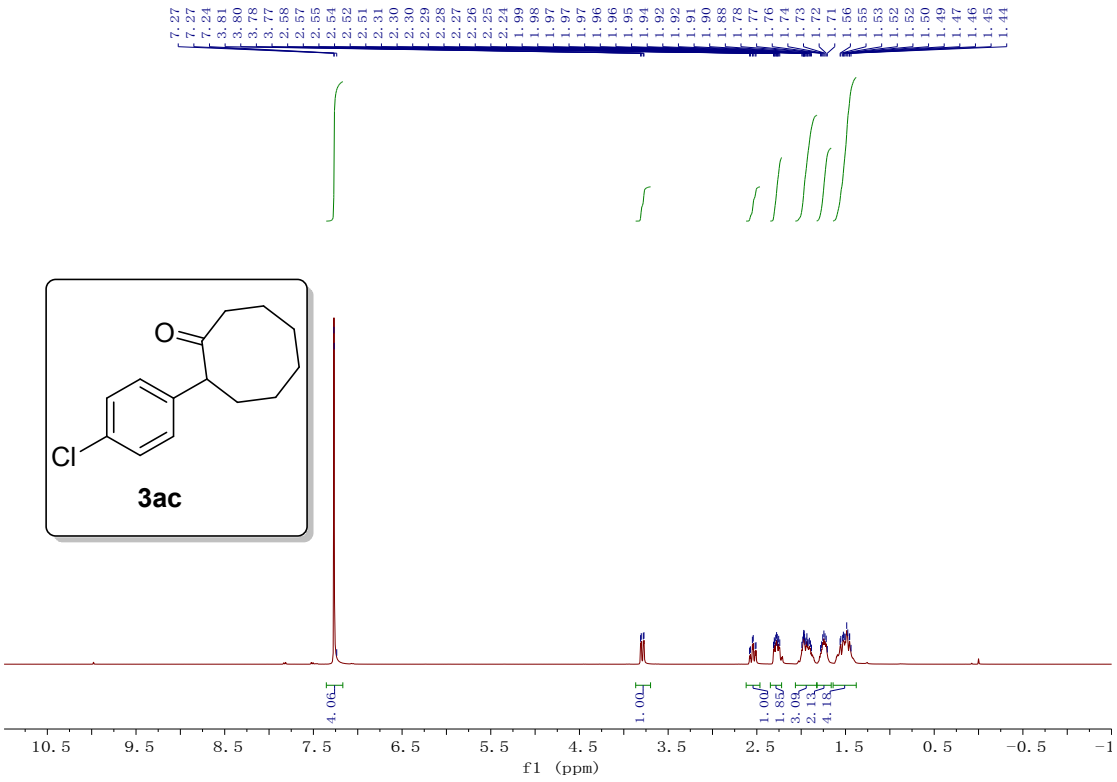

217.44
136.79
132.73
129.51
128.70
77.45
77.13
76.81
54.67
38.28
31.55
20.78
O
Cl
3z
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.31 7.30 7.29 7.29 7.28 7.08 7.07 7.06 7.06 3.61 3.61 3.59 3.58 3.57 2.52 2.51 2.51 2.51 2.50 2.16 2.01 2.01 2.00 1.99 1.99 1.99 1.98 1.98 1.96 1.95 1.84 1.84 1.84 1.84 1.82 1.82 1.81 1.81 1.81 1.80
O
Cl
3aa
1.71 1.78 0.92 1.93 1.01 1.00 2.00 1.96
10.5 9.5 8.5 7.5 6.5 5.5 4.5 3.5 2.5 1.5 0.5 −0.5
f1 (ppm)


209.83
137.23 132.70 129.95 128.50
77.38 77.06 76.74
56.82
42.21 35.28 27.80 25.39
O
Cl
3aa
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)


O
Cl
3ab
f1 (ppm)


O
Cl
3ab
f1 (ppm)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7.27
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3.77
3.77
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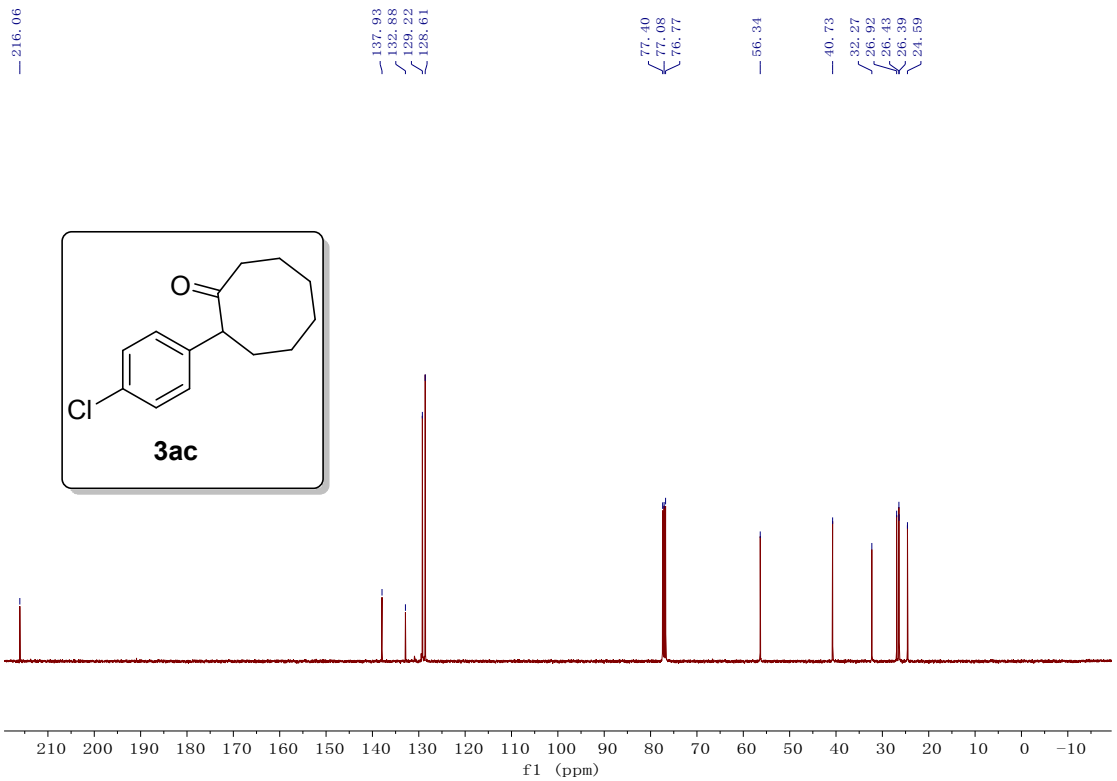
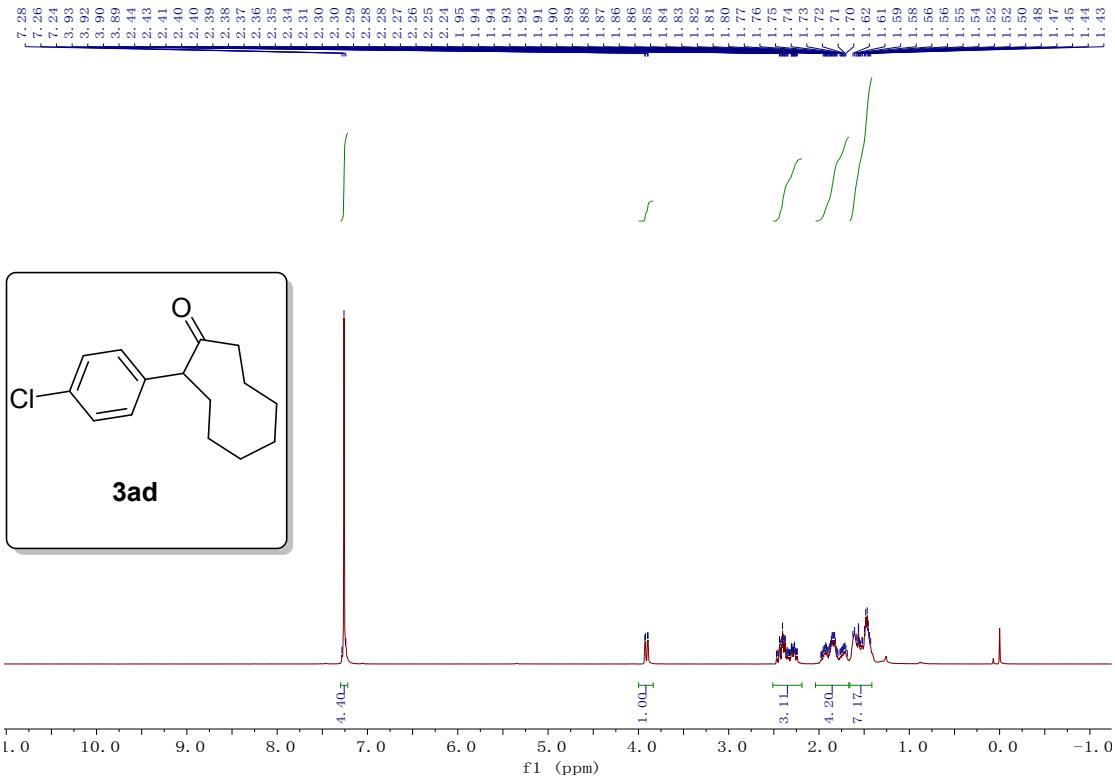
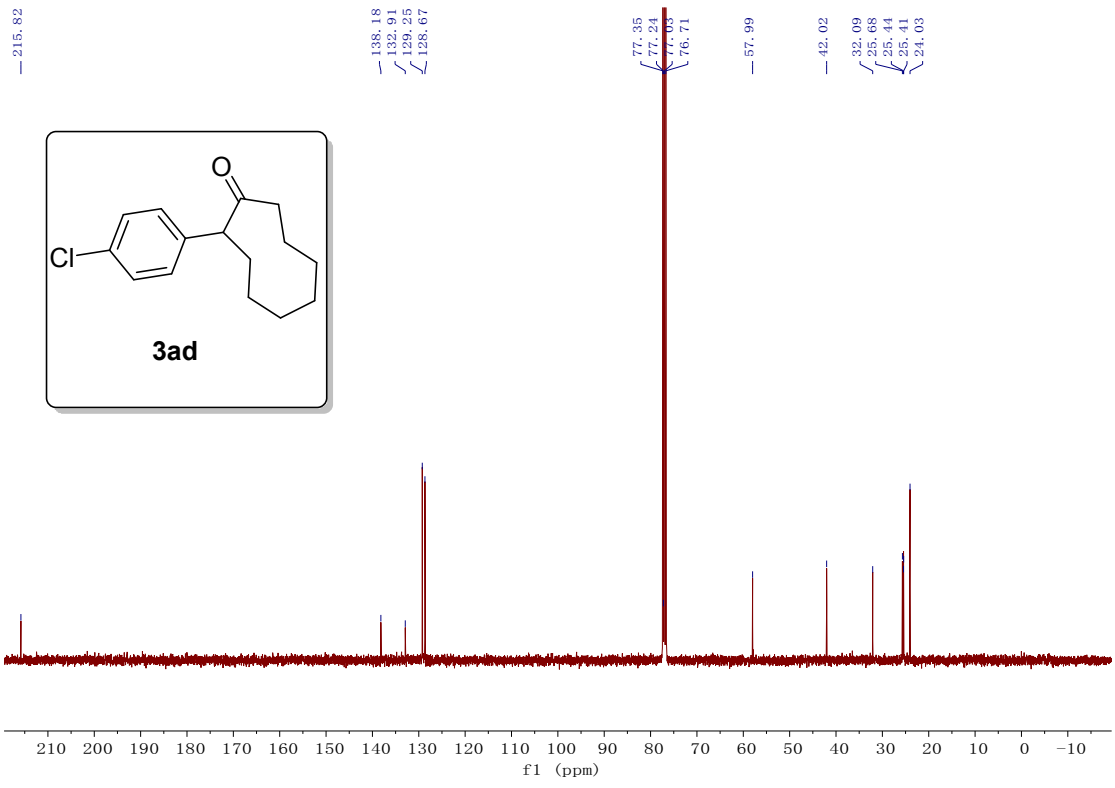
2.57
2.55
2.54
2.52
2.51
2.31
2.30
2.29
2.28
2.27
2.26
2.25
2.24
1.99
1.98
1.97
1.97
1.97
1.96
1.96
1.95
1.94
1.92
1.92
1.91
1.90
1.88
1.78
1.77
1.76
1.74
1.73
1.72
1.71
1.56
1.55
1.53
1.52
1.52
1.50
1.49
1.47
1.46
1.45
1.44
O
Cl
3ac
4.06
1.00
1.00
1.85
3.09
2.13
4.18
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
−0.5
−1
f1 (ppm)


216.06
137.93
132.88
129.22
128.61
77.40
77.08
76.77
56.34
40.73
32.27
26.92
26.43
26.39
24.59
O
Cl
3ac
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)


7.28 7.26 7.24 3.93 3.92 3.90 3.89 2.44 2.43 2.41 2.40 2.40 2.39 2.38 2.37 2.36 2.35 2.34 2.31 2.30 2.30 2.29 2.28 2.28 2.27 2.26 2.25 2.24 1.95 1.94 1.94 1.93 1.92 1.91 1.90 1.89 1.88 1.87 1.86 1.86 1.85 1.84 1.83 1.82 1.81 1.80 1.77 1.76 1.75 1.74 1.73 1.72 1.71 1.70 1.62 1.61 1.59 1.58 1.56 1.56 1.55 1.54 1.52 1.50 1.48 1.47 1.45 1.44 1.43
O
Cl
3ad
4.40
1.00
3.11
4.20
7.17
f1 (ppm)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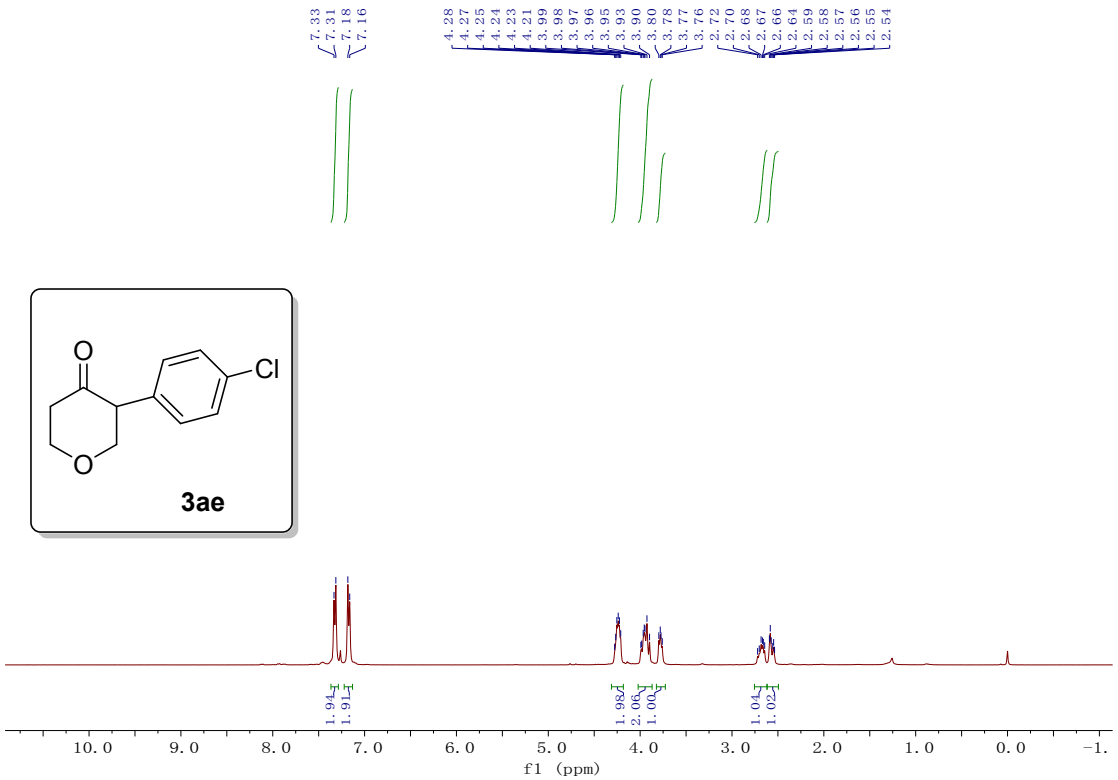
129.25
128.67
77.35
77.24
77.03
76.71
57.99
42.02
32.09
25.68
25.44
25.41
24.03
O
Cl
3ad
f1 (ppm)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7.18
7.16
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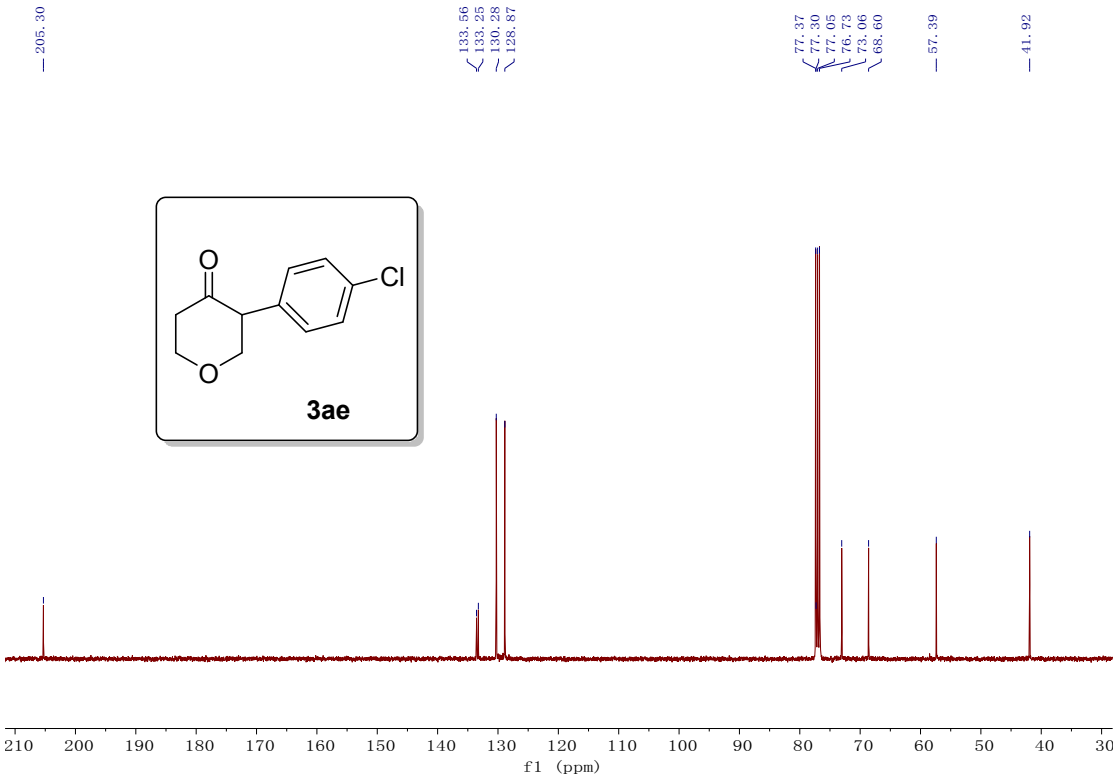
4.27
4.25
4.24
4.23
4.21
3.99
3.98
3.97
3.96
3.95
3.93
3.90
3.80
3.78
3.77
3.76
2.72
2.70
2.68
2.67
2.66
2.64
2.59
2.58
2.57
2.56
2.55
2.54
O
Cl
O
3ae
1.94
1.91
1.98
2.06
1.00
1.04
1.02
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)


205.30
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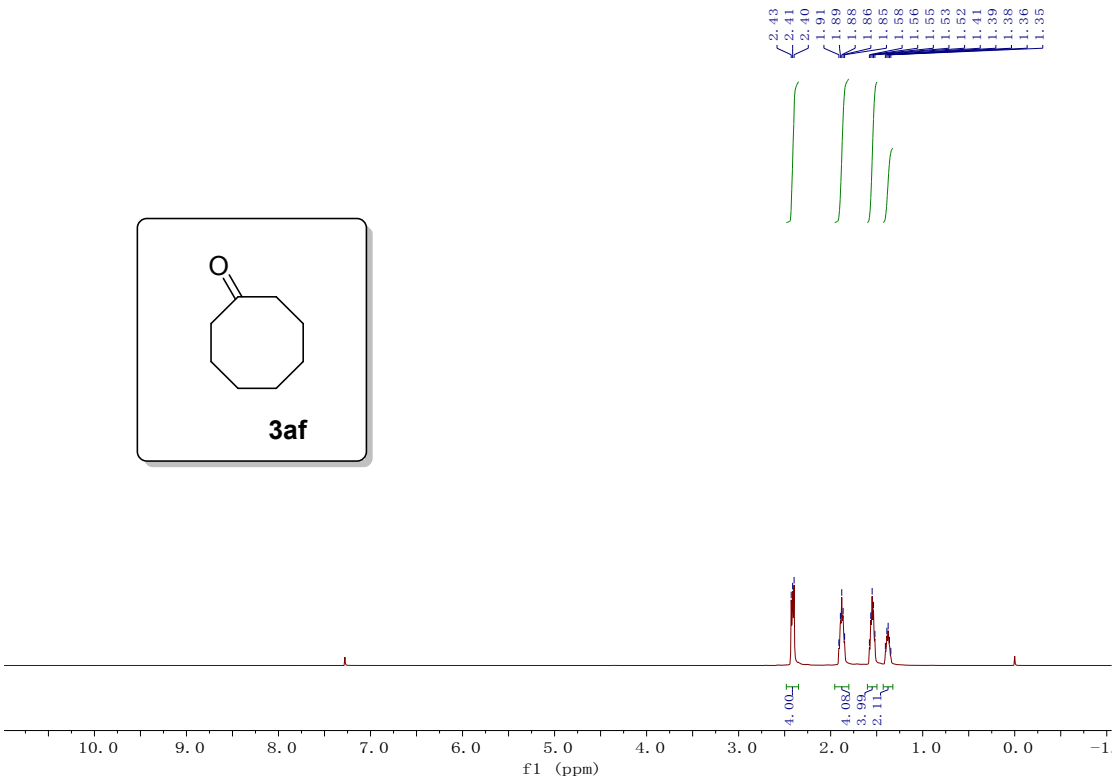
133.25
130.28
128.87
77.37
77.30
77.05
76.73
73.06
68.60
57.39
41.92
O
Cl
O
3ae
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
f1 (ppm)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2.41
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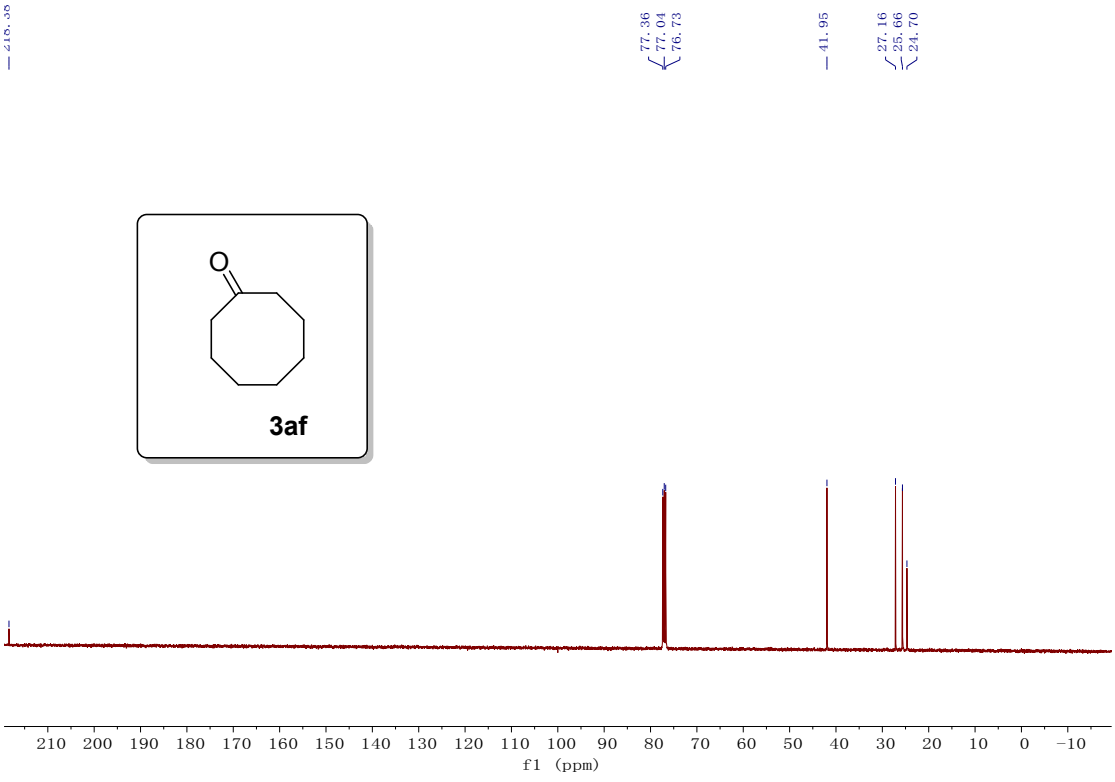
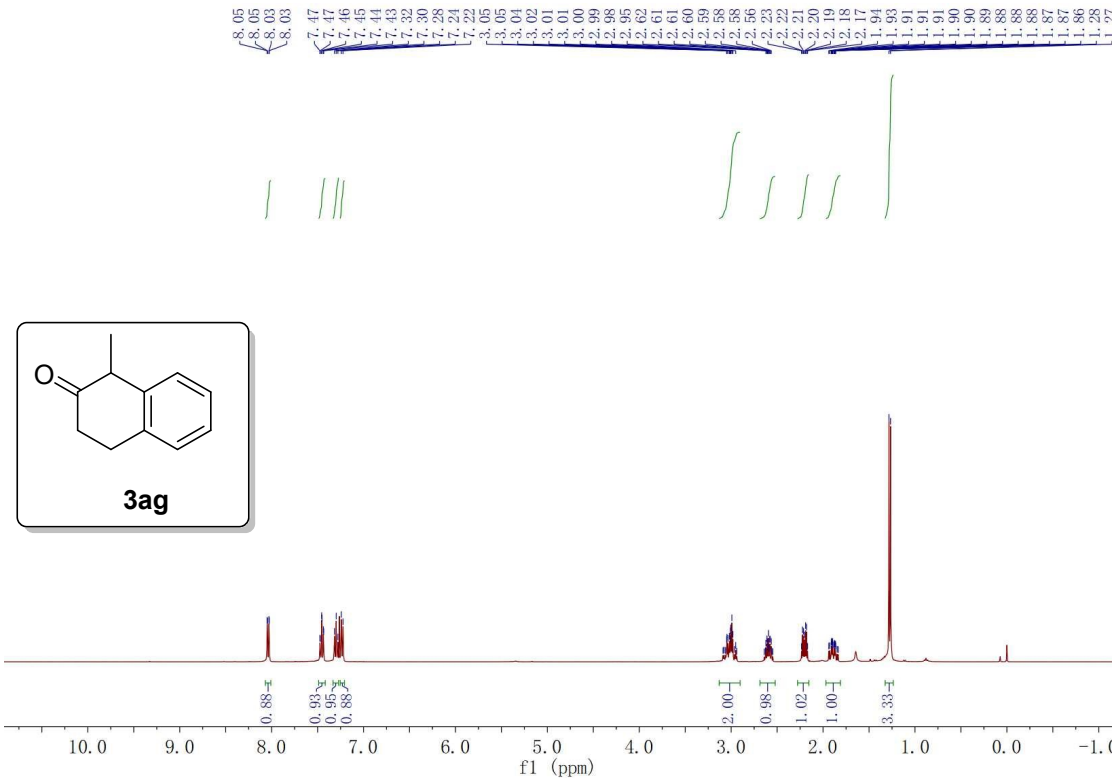
1.89
1.88
1.86
1.85
1.58
1.56
1.55
1.53
1.52
1.41
1.39
1.38
1.36
1.35
O
3af
4.00
4.08
3.99
2.11
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)


77.36
77.04
76.73
41.95
27.16
25.66
24.70
O
3af
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)


8.05
8.03
7.47
7.46
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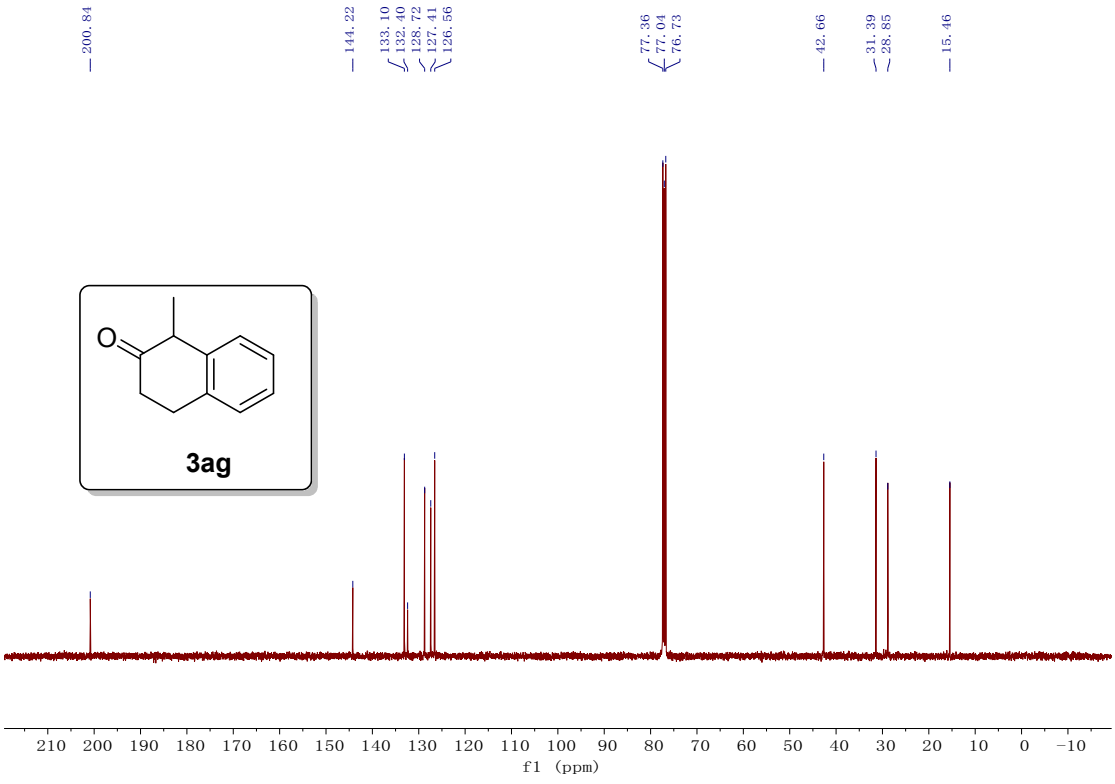
7.44
7.43
7.32
7.30
7.28
7.24
7.22
3.05
3.04
3.02
3.01
3.00
2.99
2.98
2.95
2.62
2.61
2.60
2.59
2.58
2.56
2.23
2.22
2.21
2.20
2.19
2.18
2.17
1.94
1.93
1.91
1.91
1.91
1.90
1.90
1.89
1.88
1.88
1.88
1.87
1.87
1.86
1.28
O
3ag
0.88
0.93
0.95
0.88
2.00
0.98
1.02
1.00
3.33
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)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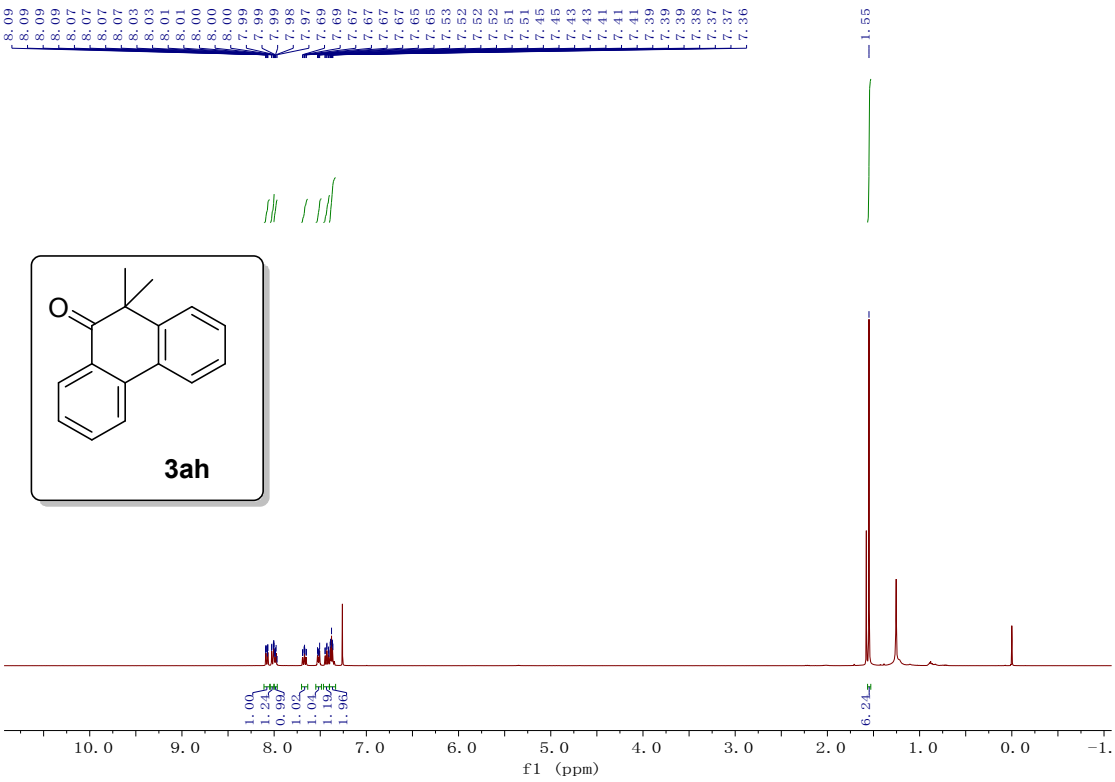
144.22
133.10
132.40
128.72
127.41
126.56
77.36
77.04
76.73
42.66
31.39
28.85
15.46
O
3ag
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)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8.09
8.09
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8.07
8.07
8.07
8.03
8.03
8.01
8.01
8.00
8.00
8.00
7.99
7.99
7.99
7.98
7.97
7.69
7.69
7.67
7.67
7.67
7.67
7.65
7.65
7.53
7.52
7.52
7.51
7.51
7.45
7.45
7.43
7.41
7.41
7.41
7.39
7.39
7.39
7.38
7.37
7.37
7.36
1.55
O
3ah
1.00
1.24
0.99
1.02
1.01
1.19
1.96
6.24
10.0
9.0
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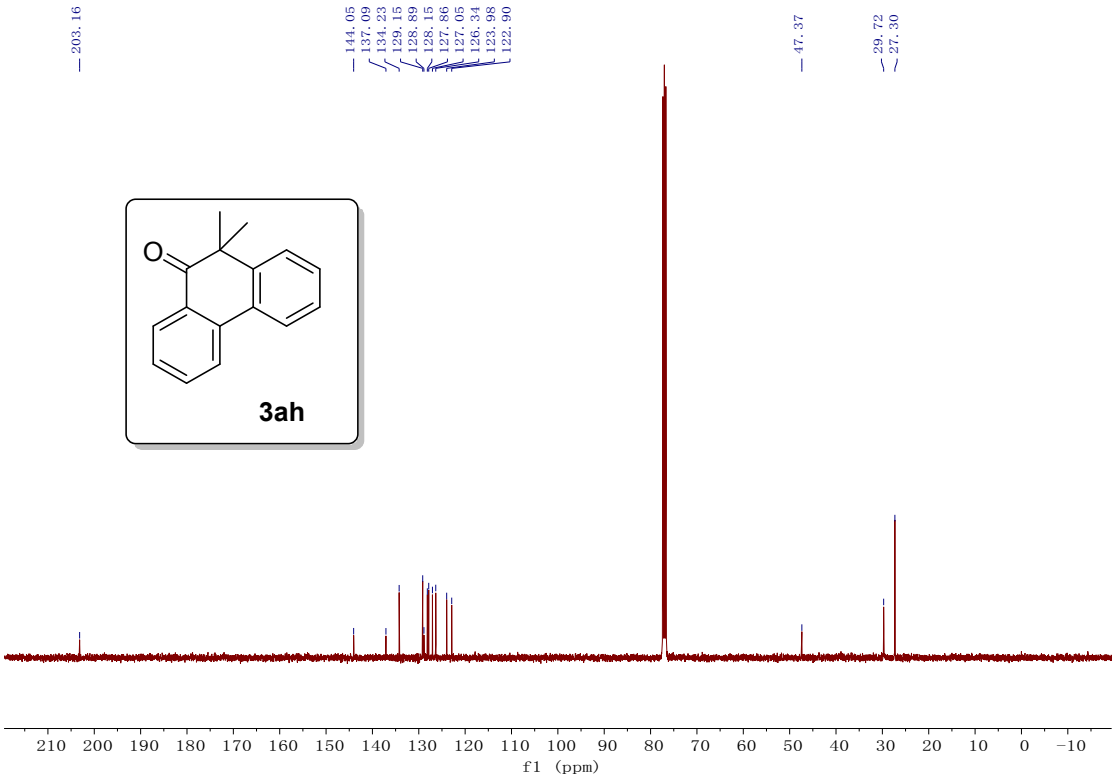
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
−1.
f1 (ppm)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137.09
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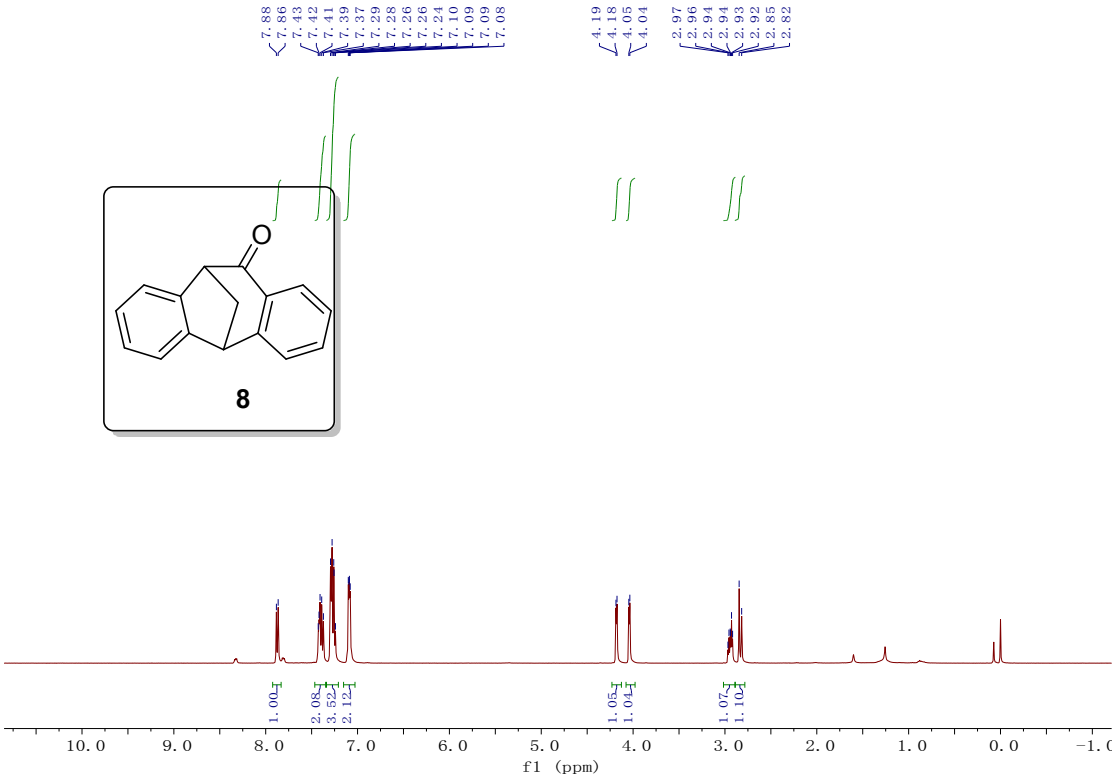
128.89
128.15
127.86
127.05
126.34
123.98
122.90
47.37
29.72
27.30
O
3ah
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)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7.29
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7.26
7.26
7.24
7.10
7.09
7.09
7.08
4.19
4.18
4.05
4.04
2.97
2.96
2.94
2.94
2.93
2.92
2.85
2.82
O
8
1.00
2.08
3.52
2.12
1.05
1.04
1.07
1.10
10.0
9.0
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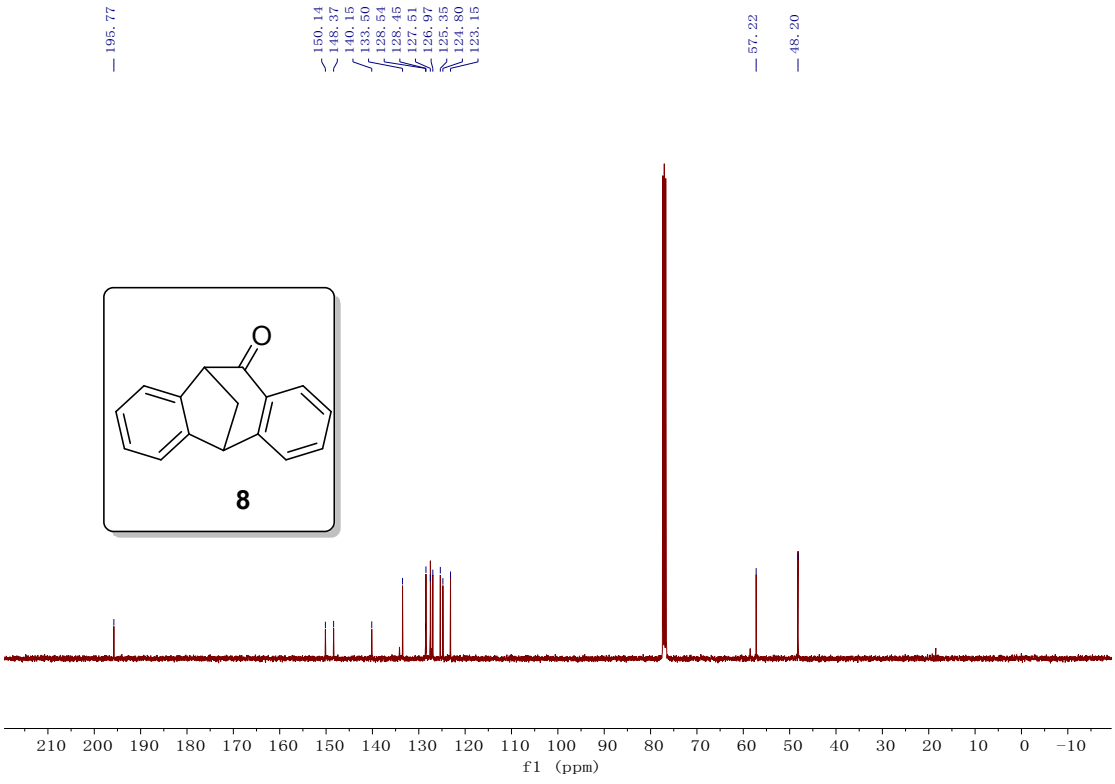
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)


195.77
150.14
148.37
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133.50
128.54
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127.51
126.97
125.35
124.80
123.15
57.22
48.20
O
8
210
200
190
180
170
160
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140
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120
110
100
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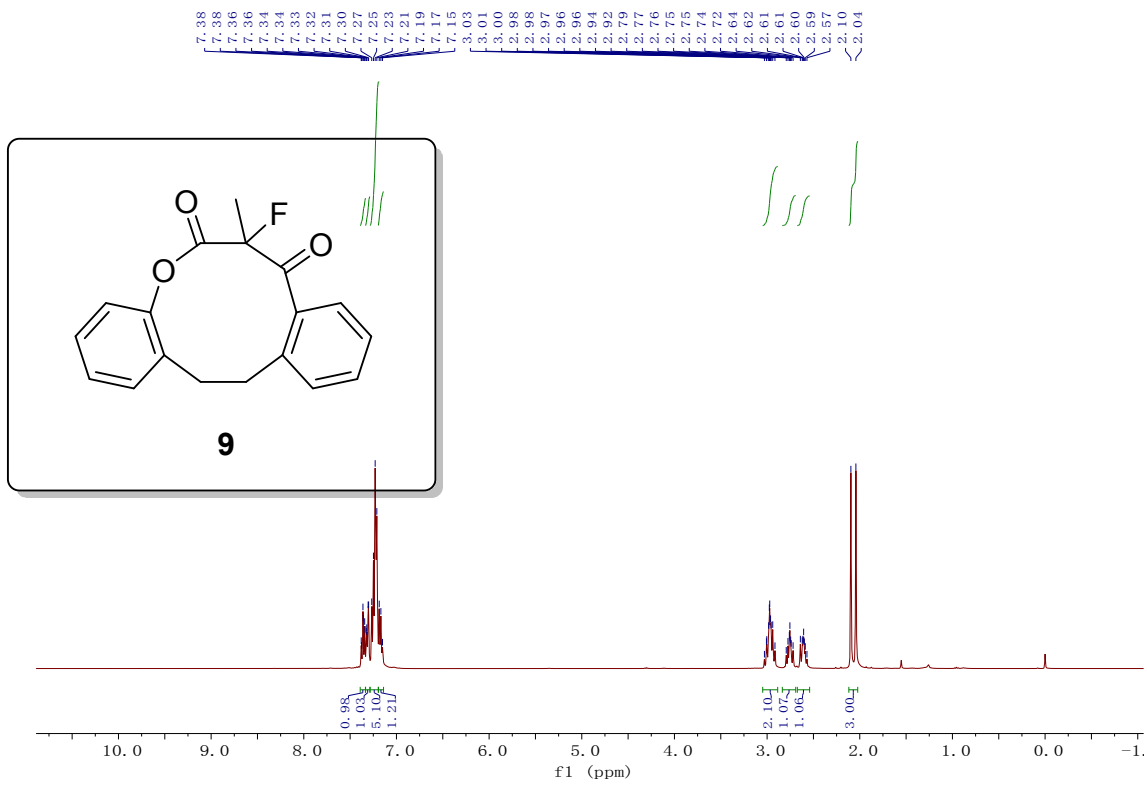
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)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7.38
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7.33
7.32
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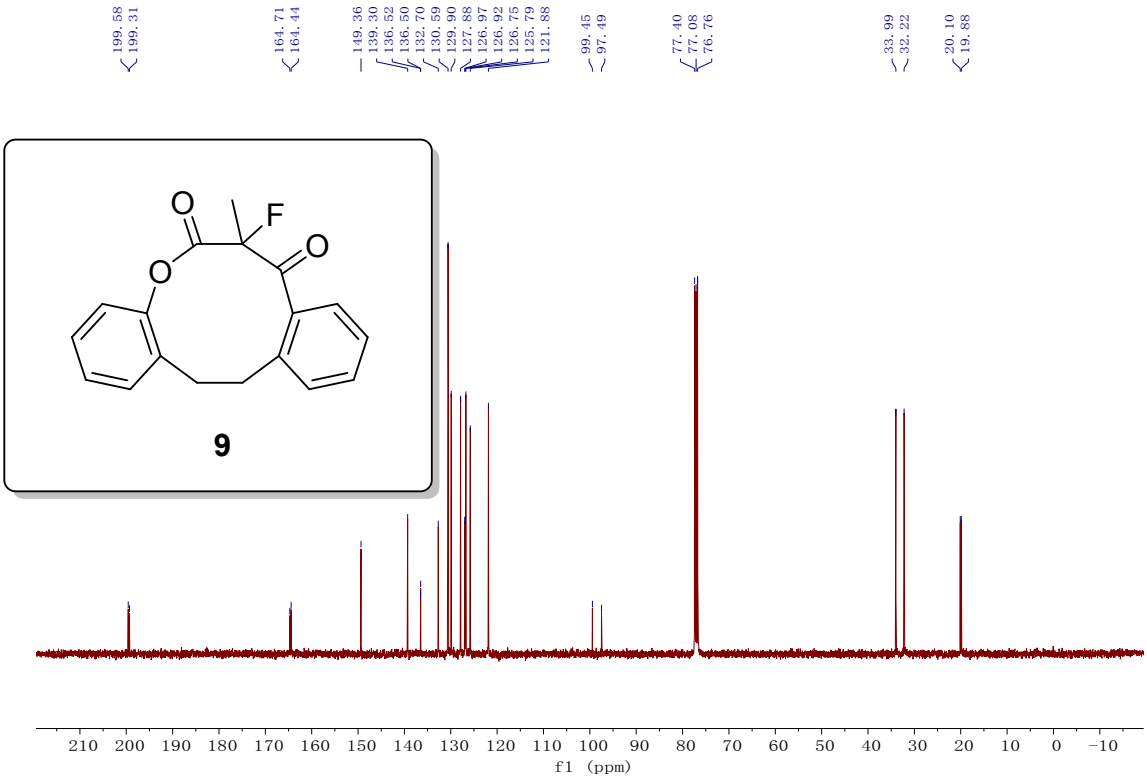
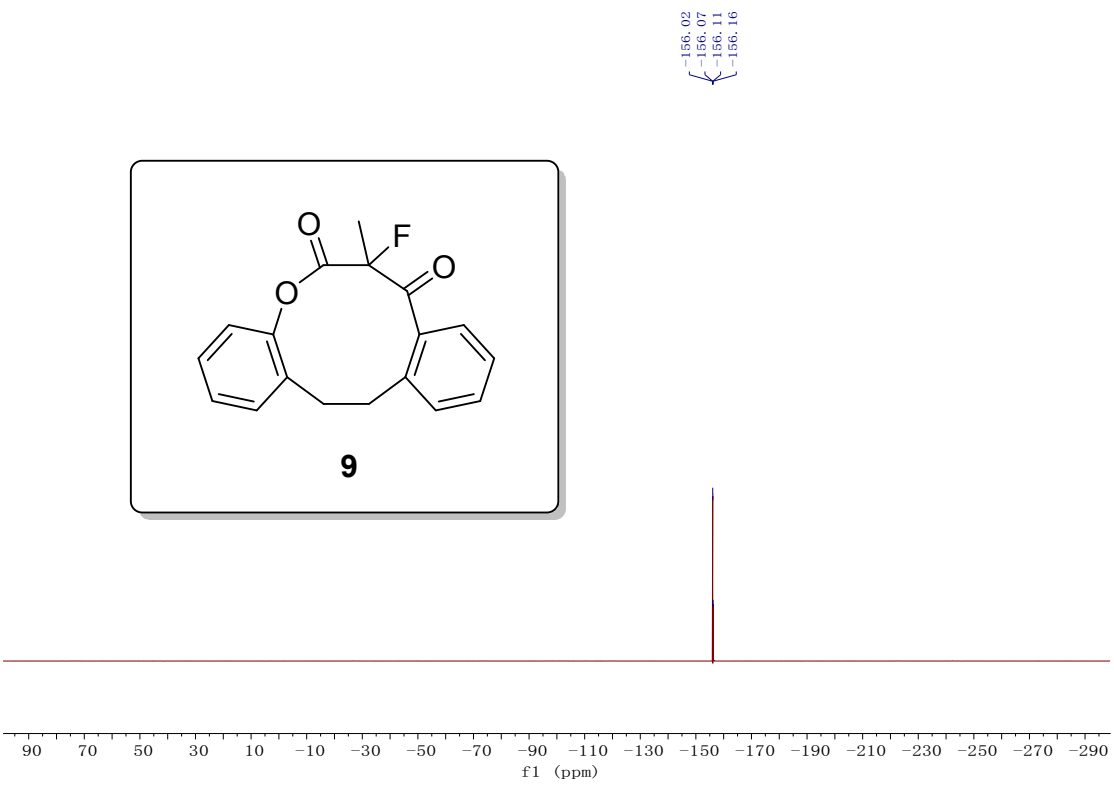
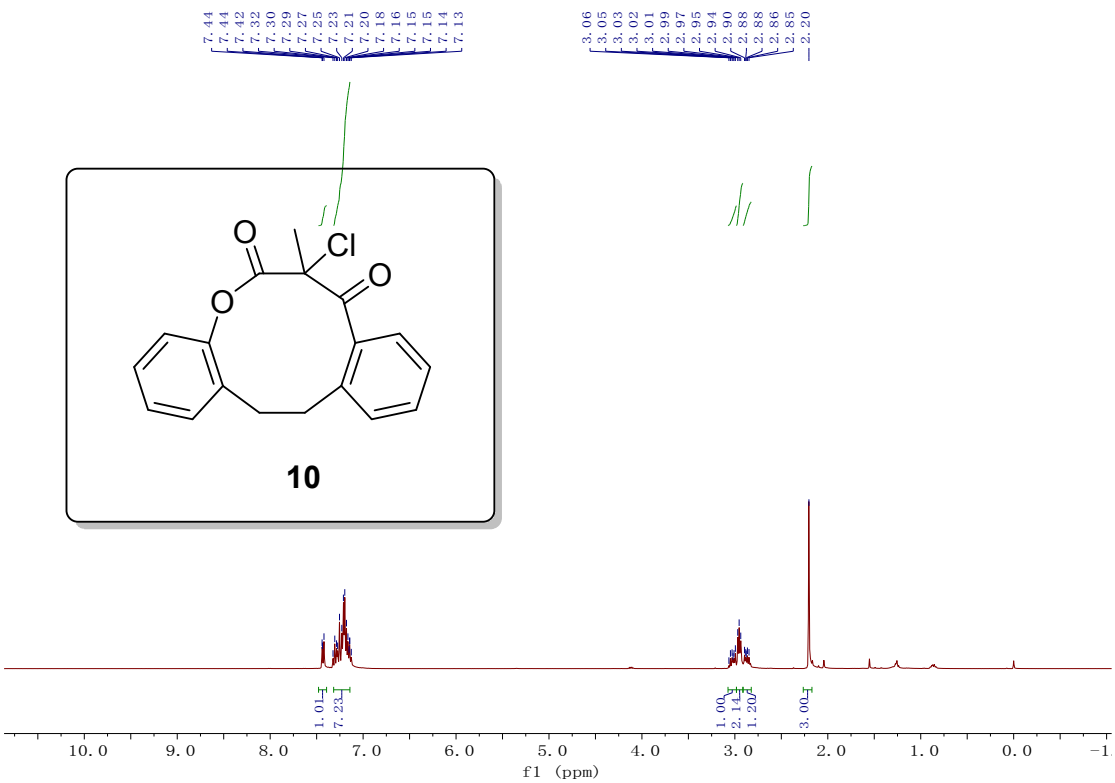
7.30
7.27
7.25
7.23
7.21
7.19
7.17
7.15
3.03
3.01
3.00
2.98
2.98
2.97
2.96
2.96
2.94
2.92
2.79
2.77
2.76
2.75
2.75
2.74
2.72
2.64
2.62
2.61
2.61
2.60
2.59
2.57
2.10
2.04
O
F
O
O
9
0.98
1.03
5.10
1.21
2.10
1.07
1.06
3.00
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)


199.58
199.31
164.71
164.44
149.36
139.30
136.52
136.50
132.70
130.59
129.90
127.88
126.97
126.92
126.75
125.79
121.88
99.45
97.49
77.40
77.08
76.76
33.99
32.22
20.10
19.88
O
F
O
O
9
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)


−156.02
−156.07
−156.11
−156.16
O
F
O
O
9
90 70 50 30 10 −10 −30 −50 −70 −90 −110 −130 −150 −170 −190 −210 −230 −250 −270 −290
f1 (ppm)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7.42
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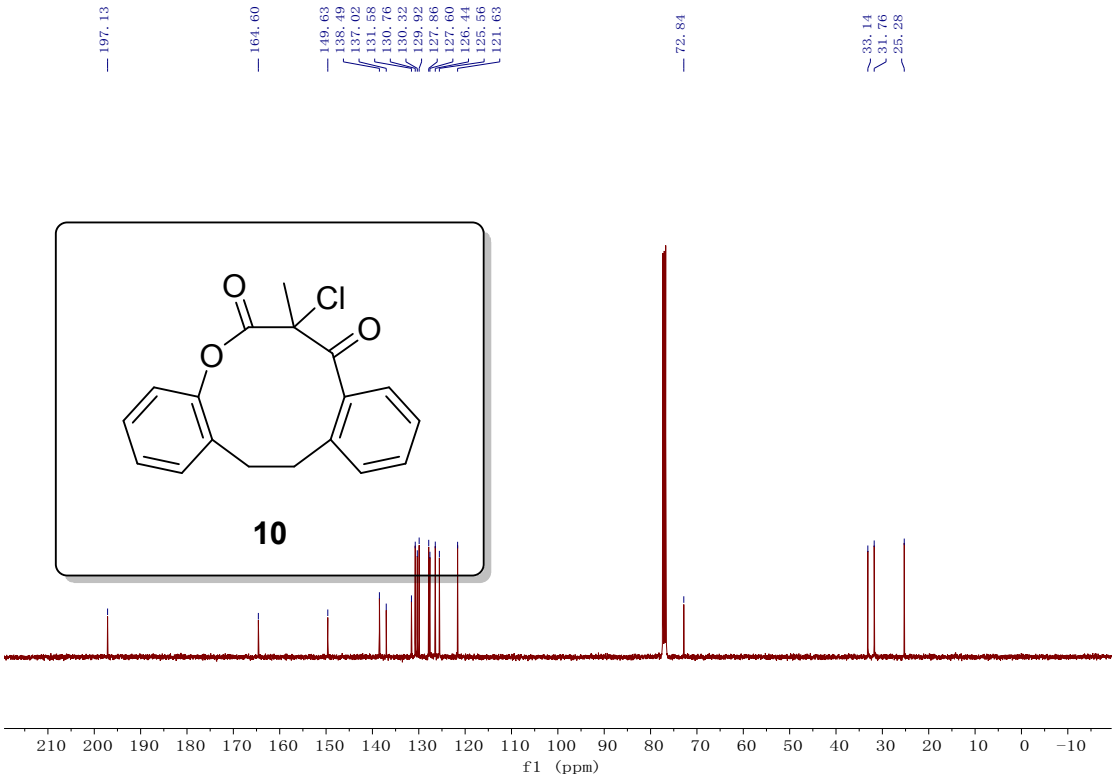
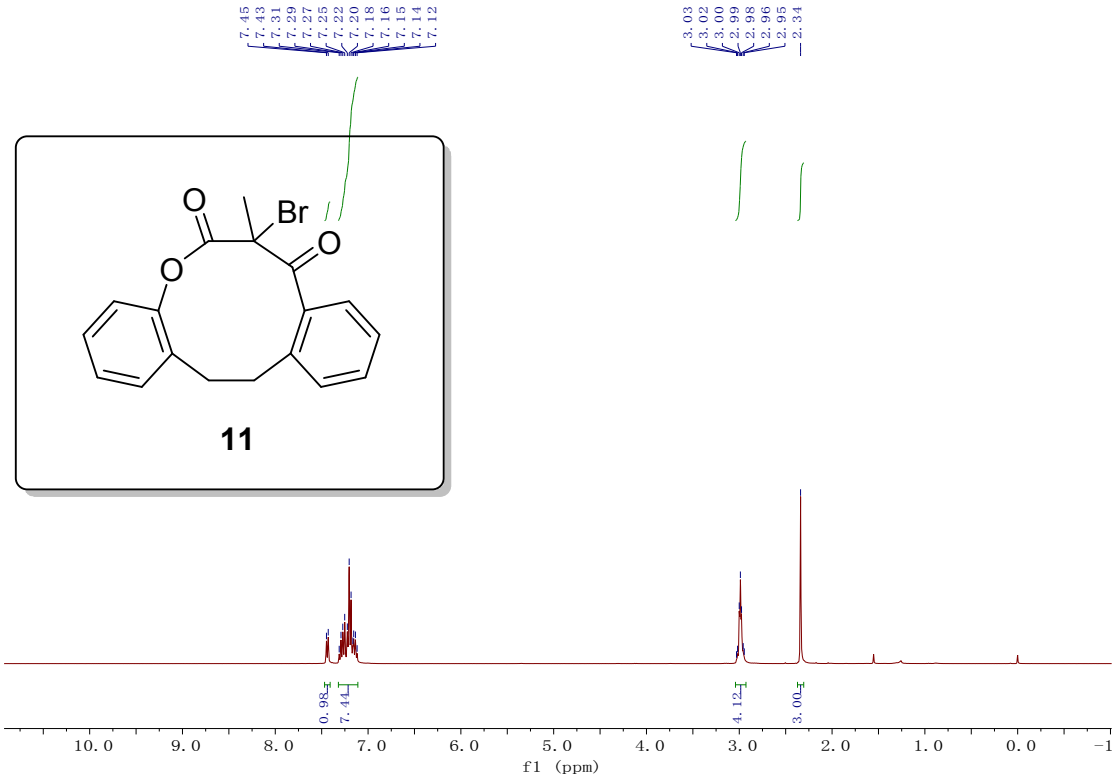
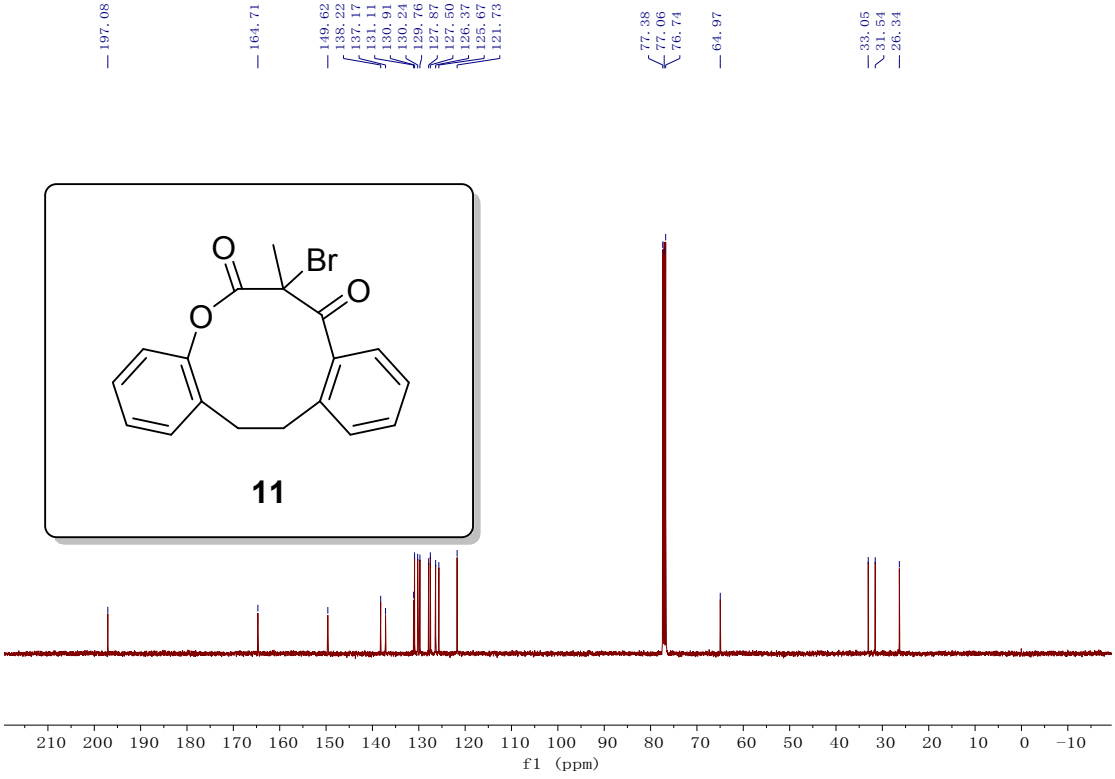
7.29
7.27
7.25
7.23
7.21
7.20
7.18
7.16
7.15
7.15
7.14
7.13
3.06
3.05
3.03
3.02
3.01
2.99
2.97
2.95
2.94
2.90
2.88
2.88
2.86
2.85
2.20
O
Cl
O
O
10
1.01
7.23
1.00
2.14
1.20
3.00
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)


197.13
164.60
149.63
138.49
137.02
131.58
130.76
130.32
129.92
127.86
127.60
126.44
125.56
121.63
72.84
33.14
31.76
25.28
O
Cl
O
O
10
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)


7.45
7.43
7.31
7.29
7.27
7.25
7.22
7.20
7.18
7.16
7.15
7.14
7.12
3.03
3.02
3.00
2.99
2.98
2.96
2.95
2.34
O
Br
O
O
11
0.98
7.44
4.12
3.00
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)


197.08
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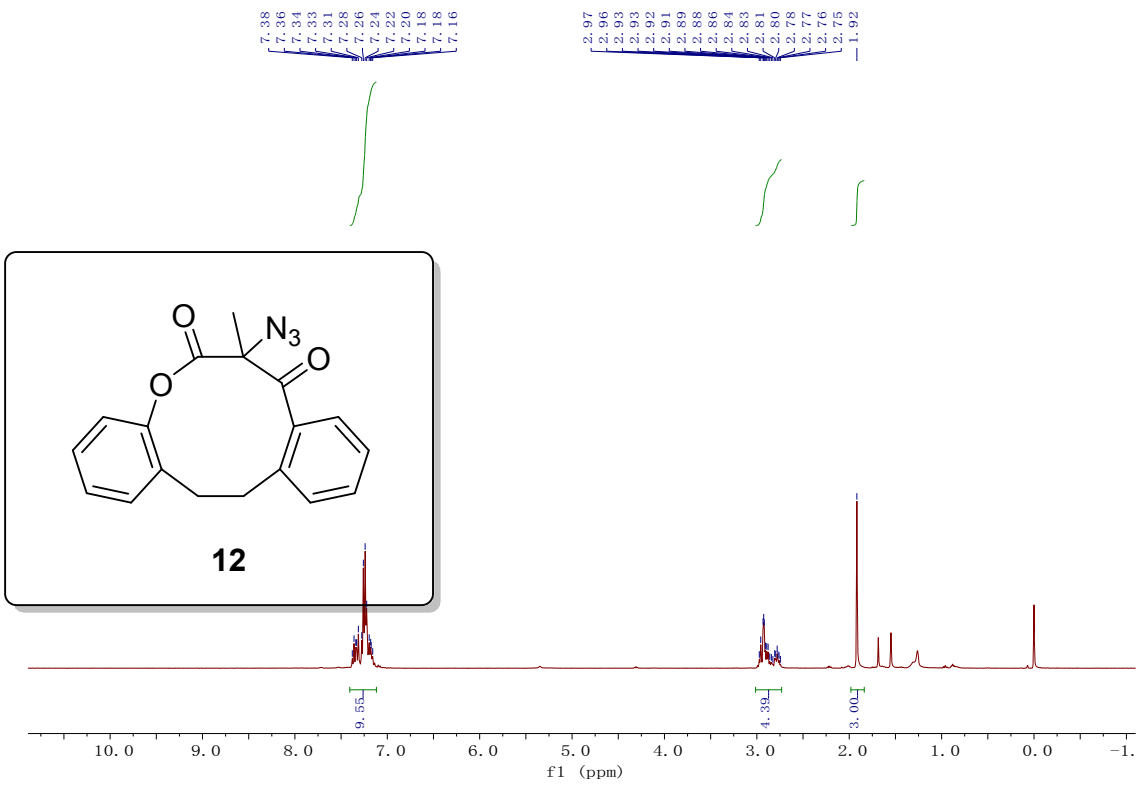
137.17
131.11
130.91
130.24
129.76
127.87
127.50
126.37
125.67
121.73
77.38
77.06
76.74
64.97
33.05
31.54
26.34
O
Br
O
O
11
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)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7.36
7.34
7.33
7.31
7.28
7.26
7.24
7.22
7.20
7.18
7.18
7.16
2.97
2.96
2.93
2.93
2.92
2.91
2.89
2.88
2.86
2.84
2.83
2.81
2.80
2.78
2.77
2.76
2.75
1.92
O
N3
O
O
12
9.55
4.39
3.00
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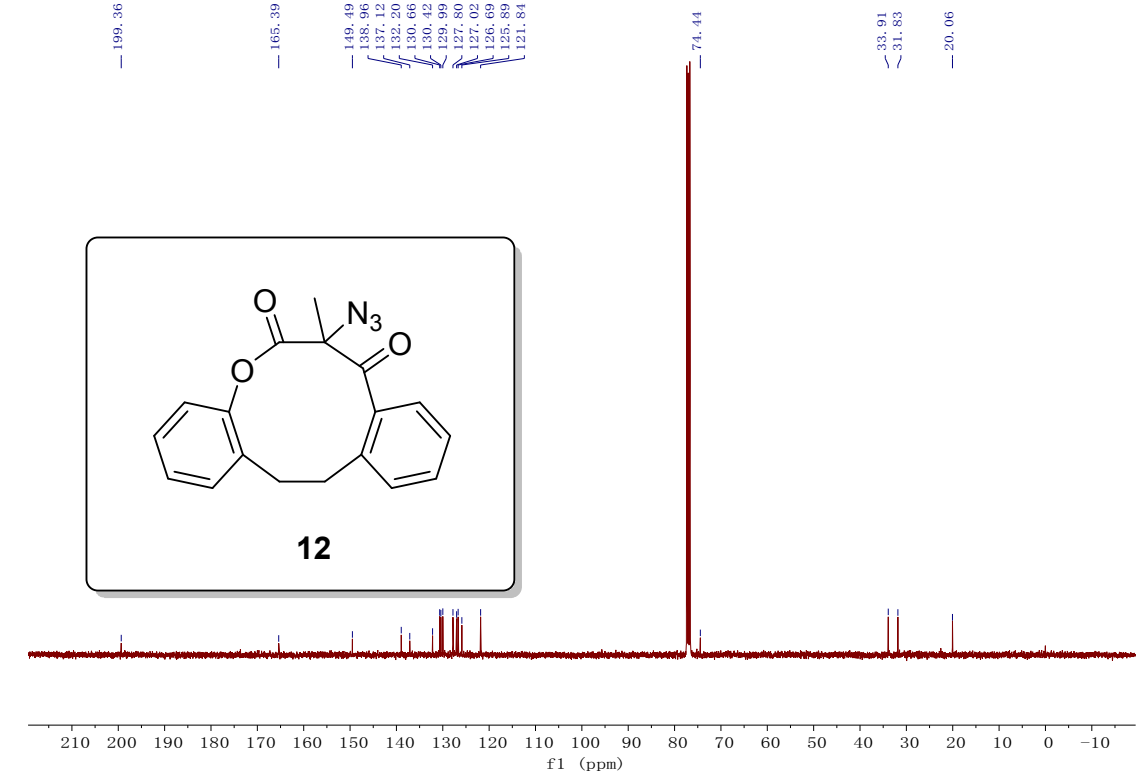
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)


199.36
165.39
149.49
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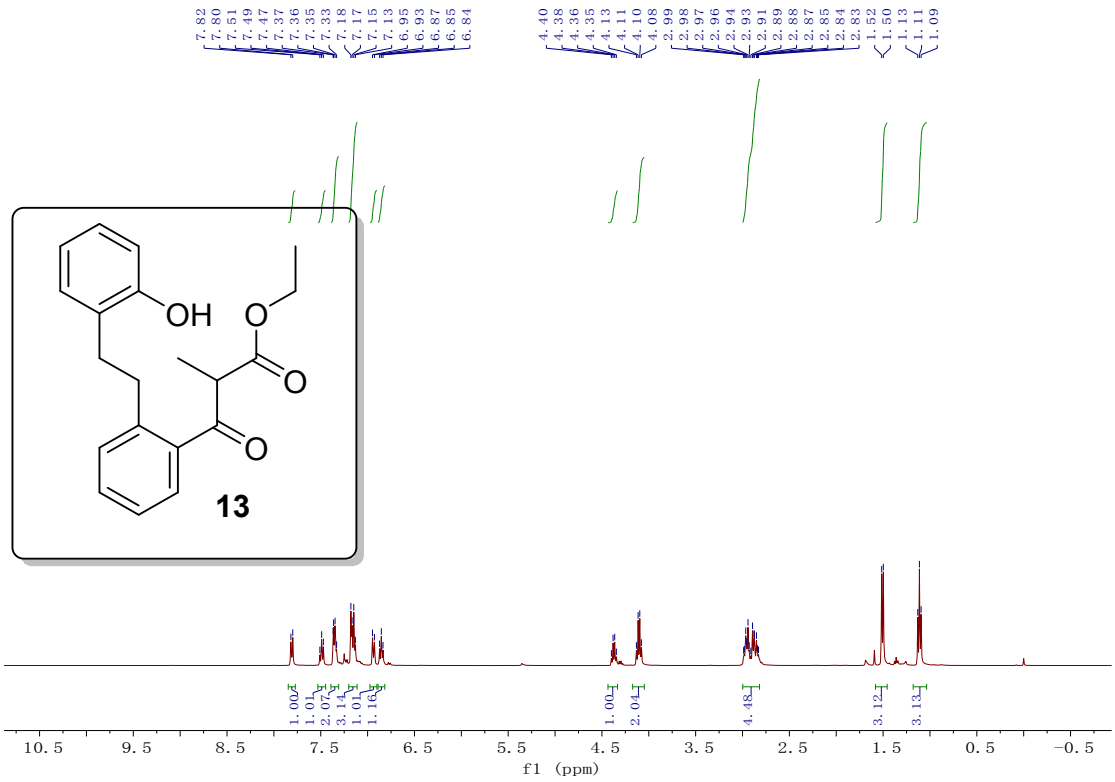
137.12
132.20
130.66
130.42
129.99
127.80
127.02
126.69
125.89
121.84
74.44
33.91
31.83
20.06
O
N3
O
O
12
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)


7.82
7.80
7.51
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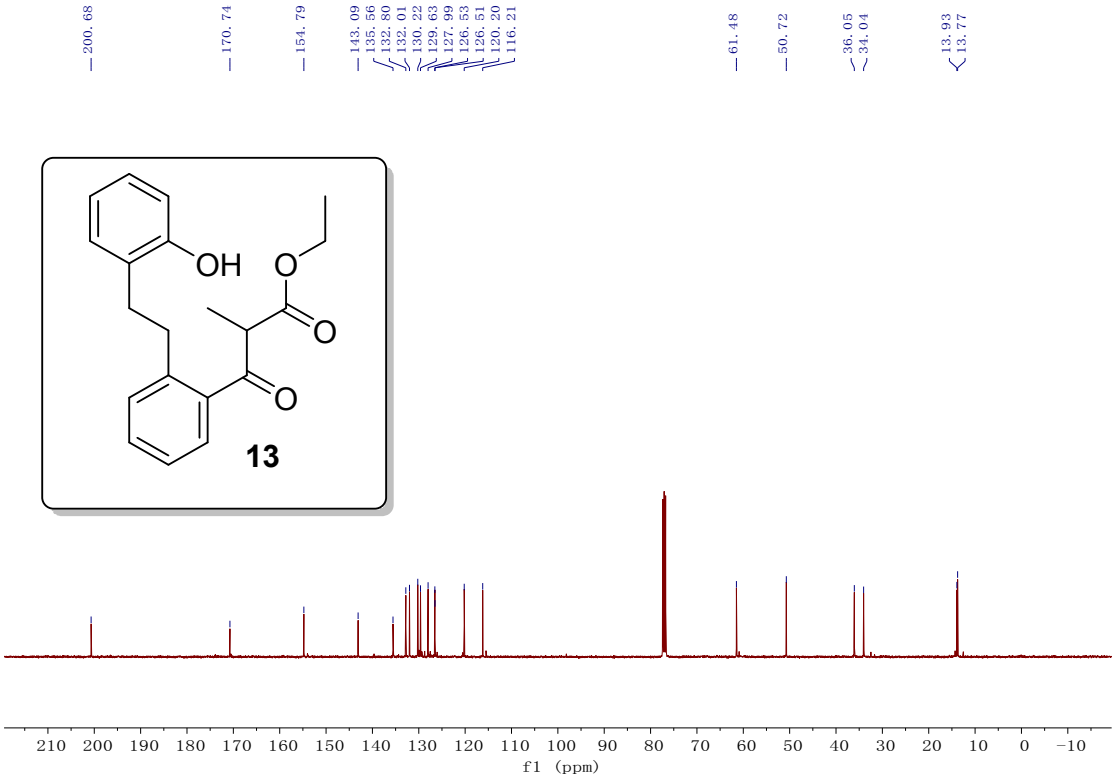
7.37
7.36
7.35
7.33
7.18
7.17
7.15
7.13
6.95
6.93
6.87
6.85
6.84
4.40
4.38
4.36
4.35
4.13
4.11
4.10
4.08
2.99
2.98
2.97
2.96
2.94
2.93
2.91
2.89
2.88
2.87
2.85
2.84
2.83
1.52
1.50
1.13
1.11
1.09
OH
O
O
O
13
1.00
1.01
2.07
3.14
1.01
1.16
1.00
2.04
4.48
3.12
3.13
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
−0.5
f1 (ppm)


200.68
170.74
154.79
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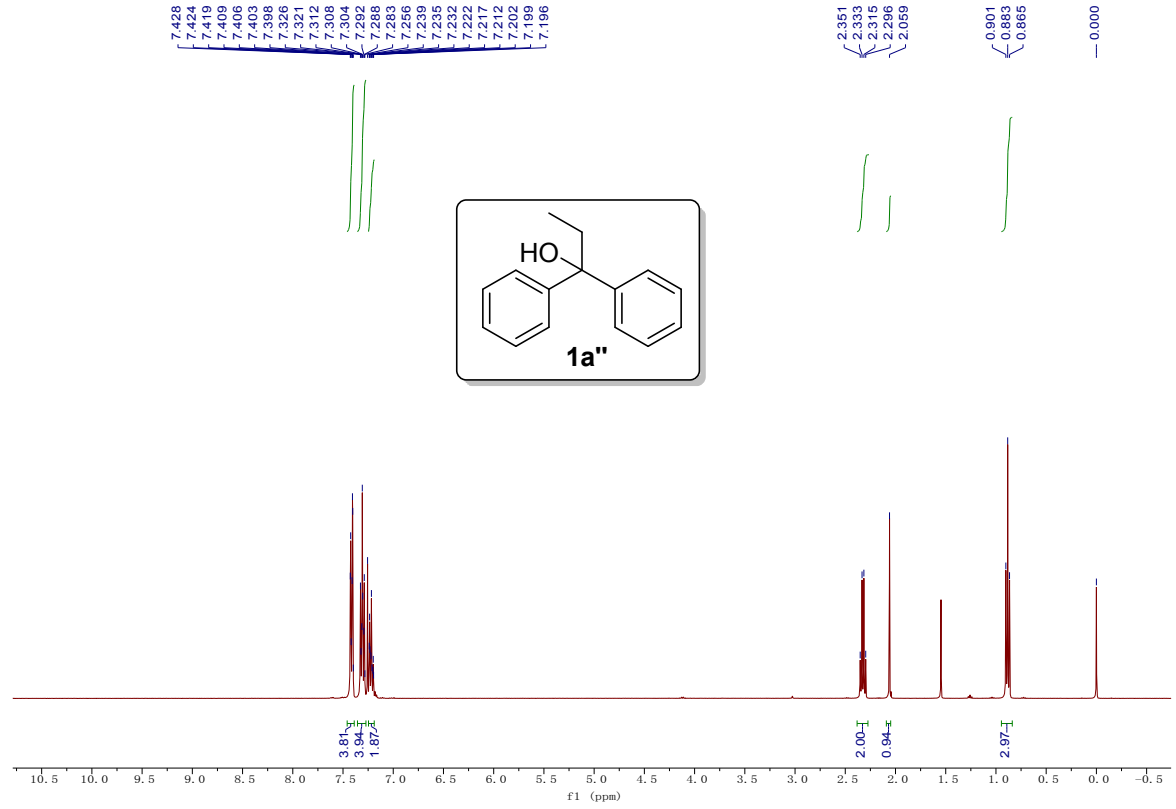
135.56
132.80
132.01
130.22
129.63
127.99
126.53
126.51
120.20
116.21
61.48
50.72
36.05
34.04
13.93
13.77
OH
O
O
O
13
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)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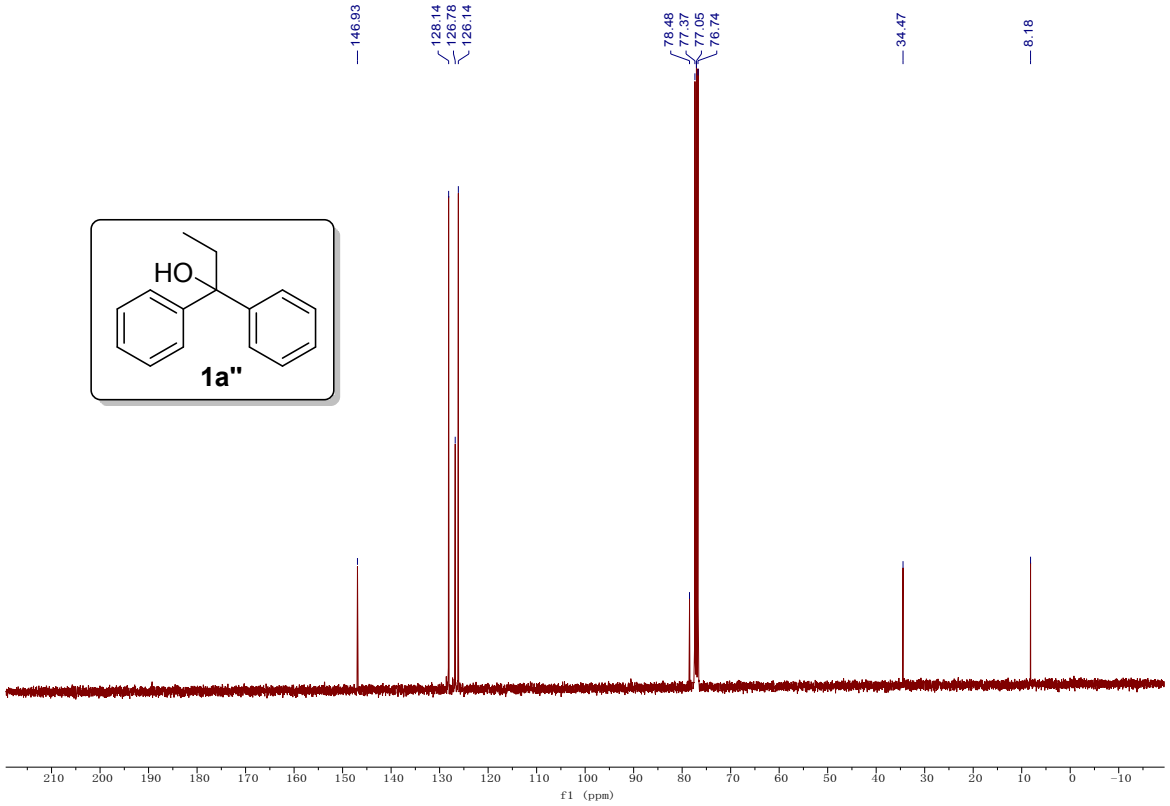
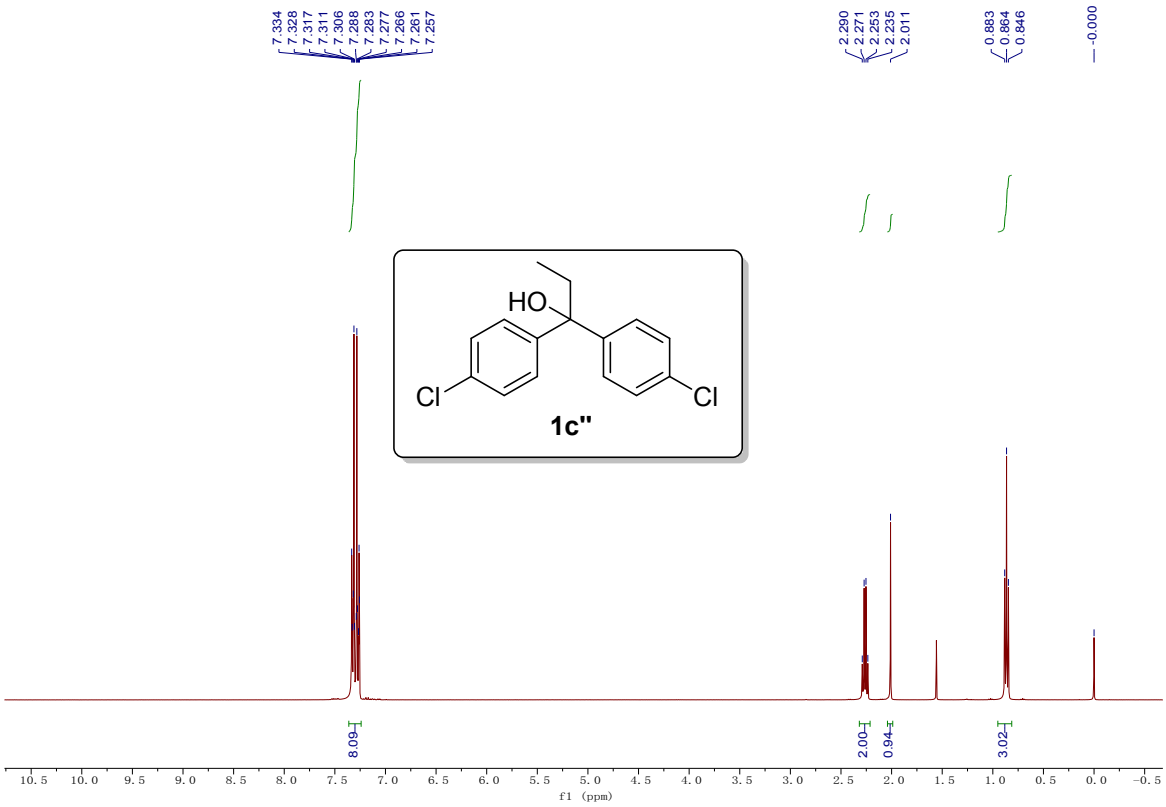
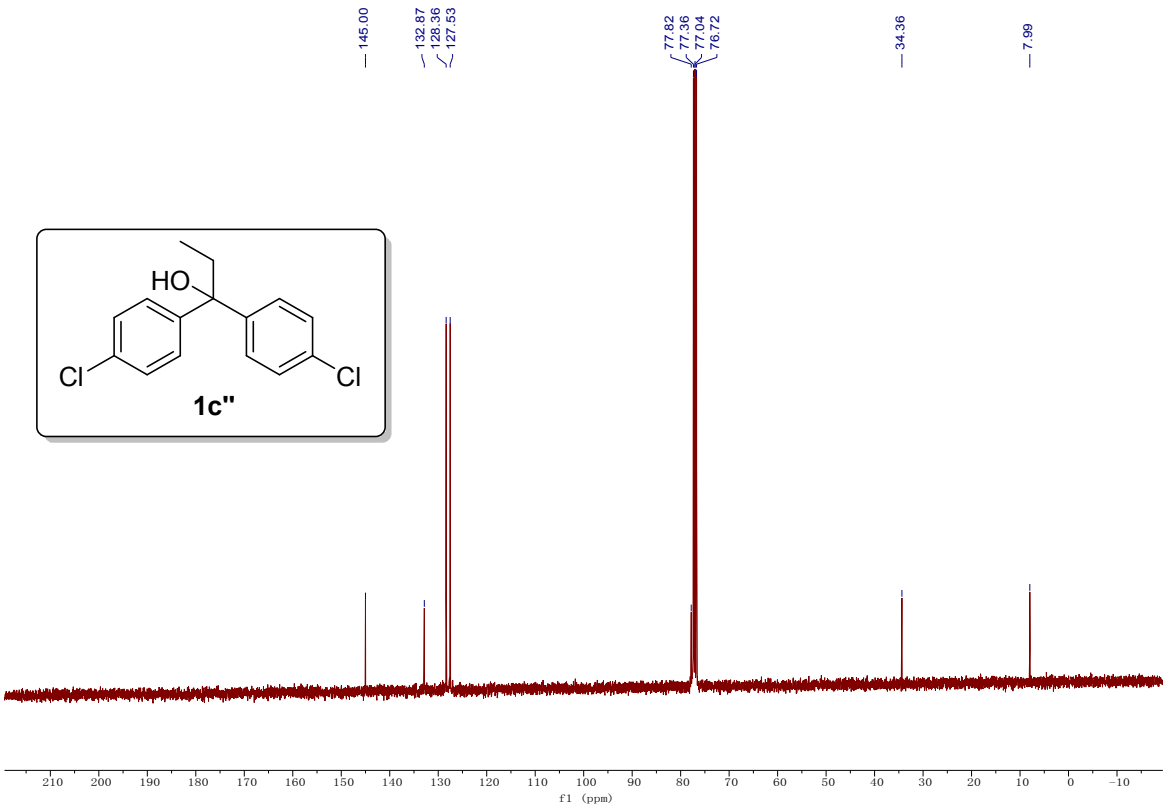
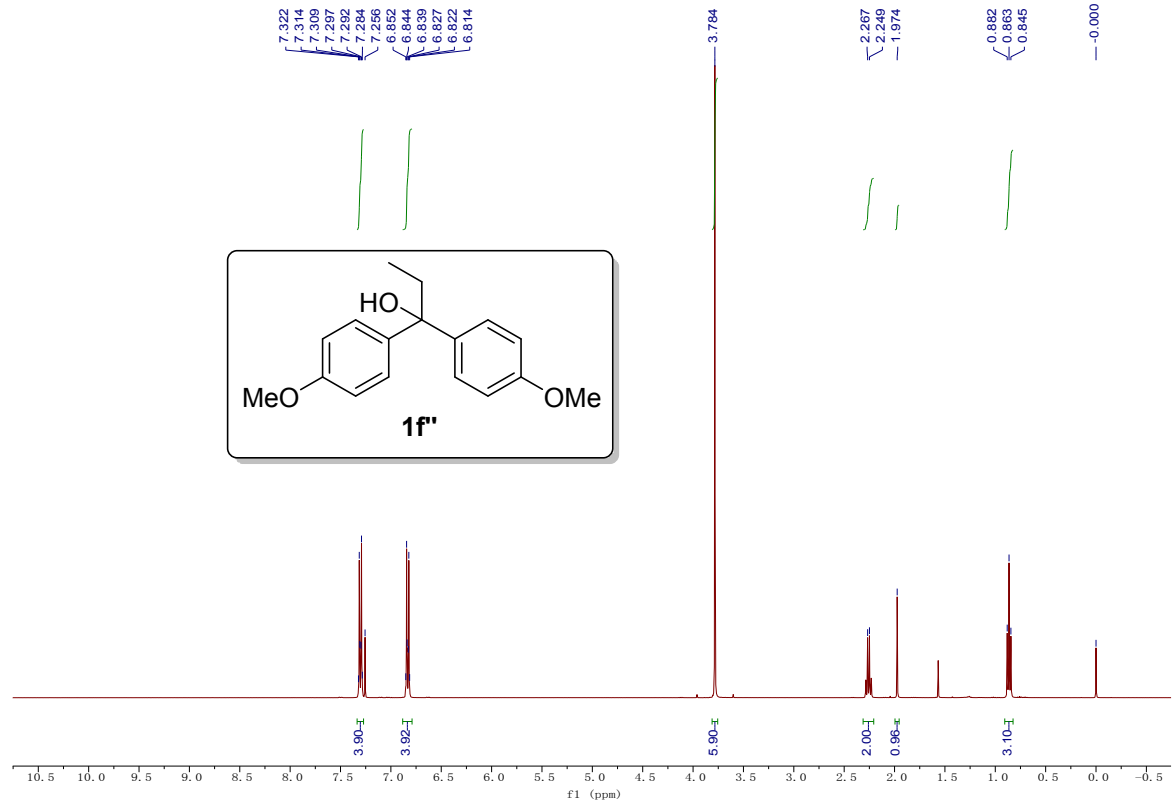
7.409
7.406
7.403
7.398
7.326
7.321
7.312
7.308
7.304
7.292
7.288
7.283
7.256
7.239
7.235
7.232
7.222
7.217
7.212
7.202
7.199
7.196
2.351
2.333
2.315
2.296
2.059
0.901
0.883
0.865
0.000
HO
1a"
3.81
3.94
1.87
2.00
0.94
2.97
f1 (ppm)


146.93
128.14
126.78
126.14
78.48
77.37
77.05
76.74
34.47
8.18
HO
1a"
f1 (ppm)


7.334
7.328
7.317
7.311
7.306
7.288
7.283
7.277
7.266
7.261
7.257
2.290
2.271
2.253
2.235
2.011
0.883
0.864
0.846
-0.000
HO
Cl
Cl
1c"
8.09
2.00
0.94
3.02
f1 (ppm)


145.00
132.87
128.36
127.53
77.82
77.36
77.04
76.72
34.36
7.99
HO
Cl
Cl
1c"
f1 (ppm)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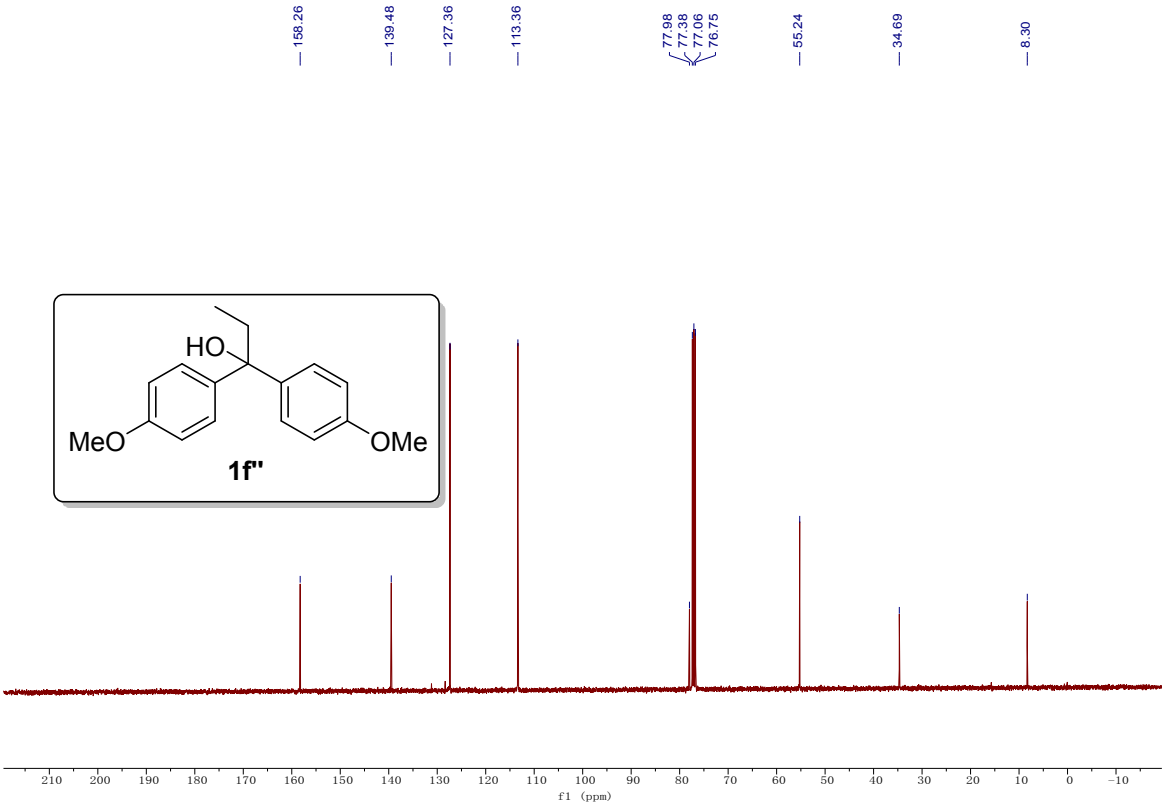
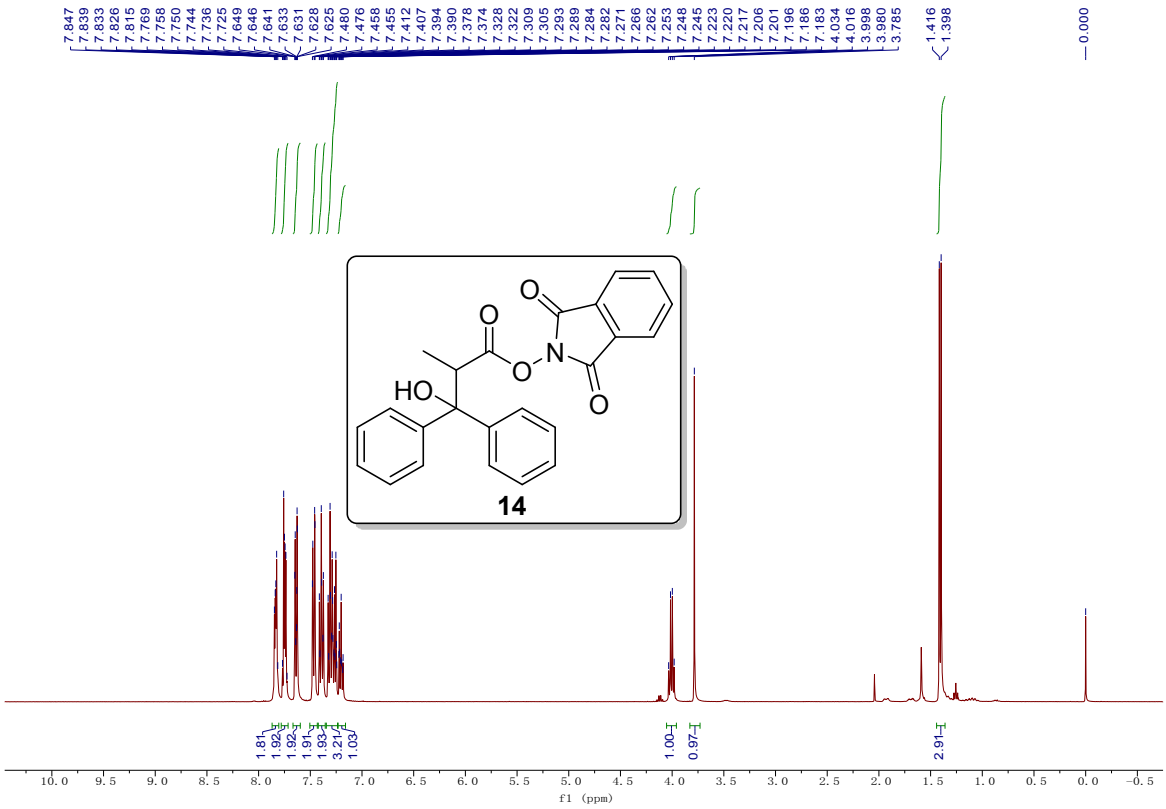
7.314
7.309
7.297
7.292
7.284
7.256
6.852
6.844
6.839
6.827
6.822
6.814
3.784
2.267
2.249
1.974
0.882
0.863
0.845
-0.000
HO
MeO
OMe
1f''
3.90
3.92
5.90
2.00
0.96
3.10
f1 (ppm)


158.26
139.48
127.36
113.36
77.98
77.38
77.06
76.75
55.24
34.69
8.30
HO
MeO
OMe
1f''
f1 (ppm)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7.750
7.744
7.736
7.725
7.649
7.646
7.641
7.633
7.631
7.628
7.625
7.480
7.476
7.458
7.455
7.412
7.407
7.394
7.390
7.378
7.374
7.328
7.322
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7.305
7.293
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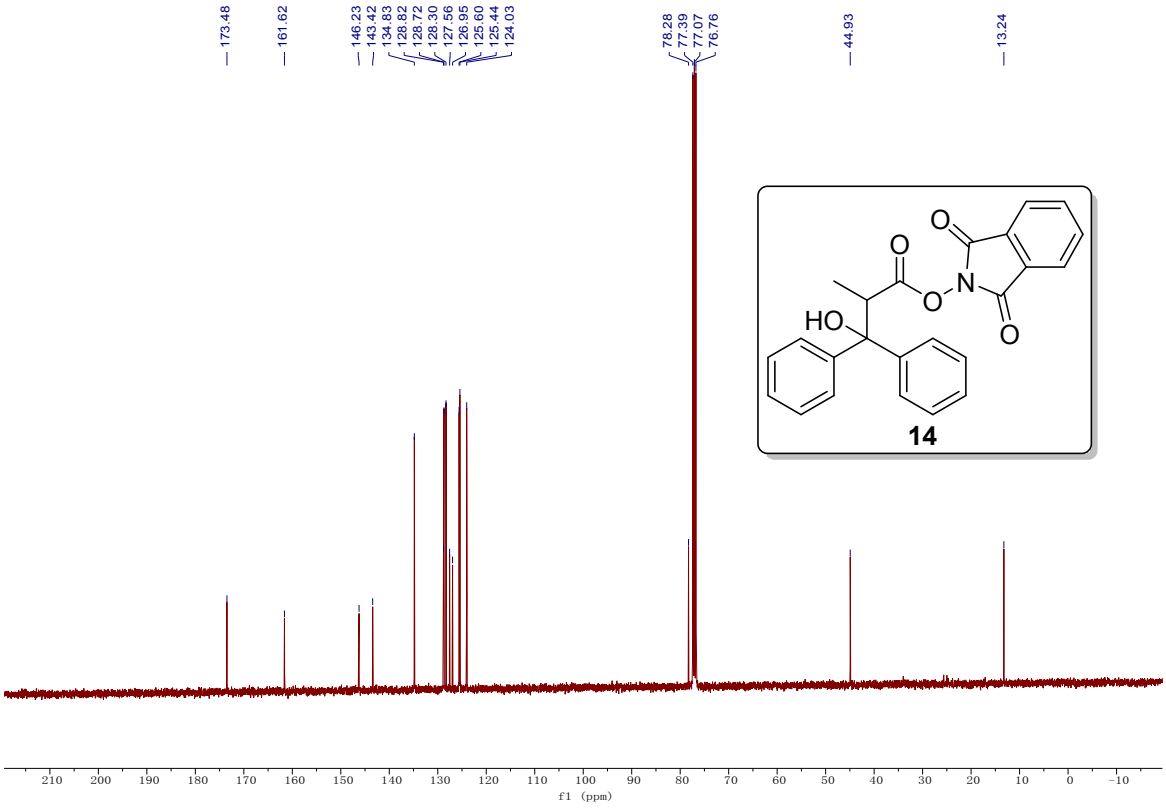
7.284
7.282
7.271
7.266
7.262
7.253
7.248
7.245
7.223
7.220
7.217
7.206
7.201
7.196
7.186
7.183
4.034
4.016
3.998
3.980
3.785
1.416
1.398
0.000
HO
O
N
14
1.81
1.92
1.92
1.91
1.93
3.21
1.03
1.00
0.97
2.91
f1 (ppm)


173.48
161.62
146.23
143.42
134.83
128.82
128.72
128.30
127.56
126.95
125.60
125.44
124.03
78.28
77.39
77.07
76.76
44.93
13.24
HO
O
N
14
f1 (ppm)