Supporting Information

Copper-Mediated Trifluoromethylation of Propiolic Acids: Facile Synthesis of α-Trifluoromethyl Ketones

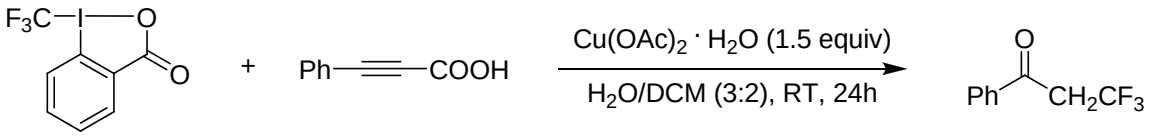
Zhengbiao He, Rui Zhang, Mingyou Hu, Lingchun Li, Chuanfa Ni, and Jinbo Hu*

Key Laboratory of Organofluorine Chemistry
Shanghai Institute of Organic Chemistry
Chinese Academy of Sciences
345 Ling-Ling Road, Shanghai, 200032 (China)
Fax: (+86) 21-64166128
E-mail: jinbohu@sioc.ac.cn

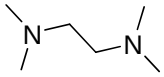
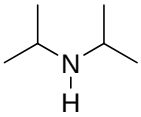
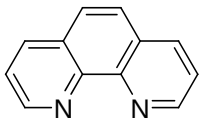
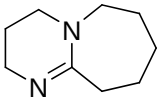
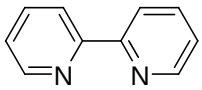
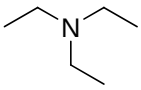
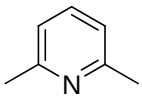
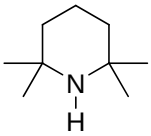
General Methods

Unless otherwise mentioned, solvents and reagents were purchased from commercial sources and used without further purification. The water was used after distillation .All the melting points were uncorrected. ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded on a 400 MHz or 300 MHz NMR spectrometer. ^{1}H NMR chemical shifts were determined relative to intermal $(CH_3)_4Si$ (TMS) at δ 0.0 or to the signal of a residual protonated solvent: $CDCl_3$ δ 7.26. ^{13}C NMR chemical shifts were determined relative to internal TMS at δ 0.0. ^{19}F NMR chemical shifts were determined relative to $CFCl_3$ at δ 0.0 . Data for ^{1}H, ^{13}C and ^{19}F NMR are recorded as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, q = quartet, br = broad). Mass spactra were obtained on a mass spectrometer. High-resolution mass data were recorded on a high–resolution mass spectrometer in the EI, ESI or MALDL mode.

Table S1. Survey of the additive for the trifluoromethyldecarboxylation reaction of 2a



1(1.5 equiv) **2a** (1.0 equiv) **3a**

Entry	Additive (1.0 equiv)	Yield [%][a]	Entry	Additive (1.0 equiv)	Yield [%][a]
1		70	5		37
2		53	6		51
3		45	7		40
4		10	8		61

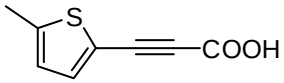
[a] Determined by ^{19}F NMR spectroscopy using $PhCF_3$ as an internal standard.

Supporting Information

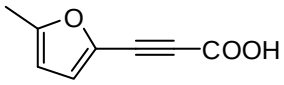
Preparation of substituted propiolic acids

The substituted propiolic acids were prepared according to the literature procedures.[1.] The compounds **2a–2m, 4a-4h, 4l** are known compounds.

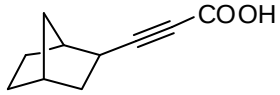
Charaterization data of substituted propiolic acids



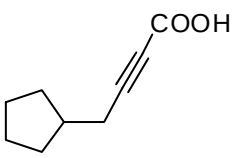
3-(5-Methylthiophen-2-yl)propiolic acid (2o): 65% yield, yellow solid. Mp= 127–129℃. ^{1}H NMR (300 MHz, $CDCl_3$/TMS): δ 10.1 (br, 1H), 7.36 (d, *J* = 3.7 Hz, 1H), 6.73(d, *J* = 3.7 Hz, 1H), 2.52 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$/TMS): δ 158.8, 147.9, 138.2, 126.3, 116.3, 84.3, 84.2, 15.7; R (film):2814, 2607, 2545, 2196, 1671, 1529, 1460, 1409, 1380, 1342, 1283, 1221, 1181, 1160, 1048, 915, 881, 801, 743, 695, 665, 610 cm^{-1}; MS (EI, *m/z*): 166(M^+, 100.00), 121 (97.96); HRMS (EI): exact mass calcd for $C_8H_6O_2S$ (M^+): 166.0089, found: 166.0091.



3-(5-Methylfuran-2-yl)propiolic acid (2p) : 60% yield, yellow solid. Mp = 101–103℃. ^{1}H NMR (300 MHz, $CDCl_3$/TMS): δ 10.2 (br, 1H), 6.93 (d, *J* = 3.4 Hz, 1H), 6.10(d, *J* = 3.4 Hz, 1H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$/TMS): δ 158.4, 157.9, 132.6, 124.0, 108.3, 85.9, 80.5, 14.1; IR (film): 2807, 2579, 1667, 1585, 1526, 1409, 1376, 1357, 1298, 1263, 1233, 1200, 1026, 952, 910, 881, 800, 740, 689, 639, 611cm^{-1}; MS (EI, *m/z*): 150(M^+, 100.00); HRMS (EI): exact mass calcd for $C_8H_6O_3$ (M^+): 150.0317, found: 150.0316.

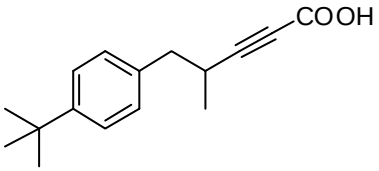


3-(Bicyclo[2.2.1]heptan-2-yl)propiolic acid(4i): 50% yield**,** yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$/TMS): δ 10.8 (br, 1H), 2.75 (d, *J* = 5.1Hz, 0.66 H), 2.40-2.27 (m, 2.23H), 2.00-1.80 (m, 1.55H), 1.66-1.18 (m, 6.63H); ^{13}C NMR (100 MHz, $CDCl_3$/TMS): δ 159.0, 158.8, 97.1, 96.3, 72.9, 72.2, 43.1, 41.1, 39.2, 38.0, 37.1, 36.9, 36.8, 36.1, 32.7, 31.4, 29.4, 28.7, 28.5, 24.2; IR (film): 2959, 2874, 2647, 2231, 1683, 1455, 1412, 1328, 1281, 1145, 1125, 1085, 884, 855, 826, 777, 756,732 cm^{-1}; MS (EI, *m/z*): 164(M^+, 2.93); HRMS (EI): exact mass calcd for $C_{10}H_{12}O_2$ (M^+): 164.0837, found: 164.0835.



4-Cyclopentylbut-2-ynoic acid (4j): 65% yield**,** yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$/TMS): δ 10.8 (br, 1H), 2.37 (d, *J* = 6.8 Hz, 2H), 2.22-2.03(m, 1H), 1.92-1.75 (m, 2H), 1.72-1.48 (m, 4H), 1.37-1.18 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$/TMS): δ 158.7, 92.3, 72.7, 38.0, 32.0, 25.0, 24.4; IR (film): 2955, 2870,

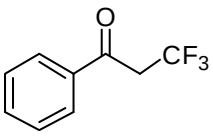
2237, 1686, 1452, 1412, 1282, 1076, 912, 786, 756 cm^{-1}; MS (ESI, *m/z*): 151($M-H^+$); HRMS (ESI): exact mass calcd for $C_9H_{11}O_2$($M-H^+$): 151.07645, found: 151.07670



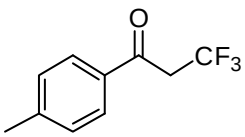
5-(4-Tert-butylphenyl)-4-methylpent-2-ynoic acid: 70% yield, colorless solid. Mp= 81–83℃. ^1H NMR (300 MHz, $CDCl_3$/TMS): δ 11.2 (br, 1H), 7.32 (d, *J* = 8.1Hz, 2 H), 7.13(d, *J* = 8.1Hz, 2 H), 2.92-2.65 (m, 3H), 1.30 (s, 9H), 1.22 (d, *J* = 6.5Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$/TMS): δ 158.8, 149.5, 135.1, 128.8, 125.3, 96.0, 73.4, 41.3, 34.4, 31.4, 28.0, 19.2; IR (film):2965, 2653, 2523, 2228, 1686, 1516, 1459, 1408, 1377, 1364, 1277, 1127, 1107, 1020, 982, 911, 860, 835, 805, 768, 731, 604, 583 cm^{-1}; MS (EI, *m/z*): 244(M^+, 4.61), 147 (100.00); HRMS (EI): exact mass calcd for $C_{16}H_{20}O_2$ (M^+): 244.1463, found: 244. 1464.

General procedure for trifluoromethylation of substituted propiolic acids (Table 2) A Schlenk test tube with a magnetic stirring bar was charged with **1** (0.8 mmol, 2.0 equiv), **2** (0.4mmol, 1.0 equiv), $Cu(OAc)_2 \cdot H_2O$ (0.8 mmol), TMEDA (1.0 mmol), followed by DCM (3 mL) and H_2O (4.5 mL). The reaction mixture was stirred at room temperature. After stirring for 24 h, the reaction mixture was extracted with CH_2Cl_2 (15 mL × 3), dried over $MgSO_4$., filtered and concentrated. The residue was purified with silica gel chromatography to provide pure product **3**.

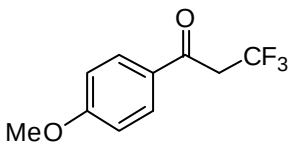
Charaterization data of compounds 3



3,3,3-Trifluoro-1-phenylpropan-1-one (3a): 90% yield, colorless liquid. ^1H NMR (300 MHz, $CDCl_3$/TMS): δ 7.94 (d, *J* = 7.4 Hz, 2H), 7.67–7.61 (m, 1H), 7.54–7.49 (m, 2H), 3.80 (q, *J* = 10.0 Hz, 2H); ^{19}F NMR (282 MHz , $CDCl_3/CFCl_3$): δ – 61.8 (t, *J* = 10.0 Hz, 3F); MS (EI, *m/z*): 188(M^+, 23.05), 105 (100.00), 77 (66.29). The data are consistent with the previous report[2].

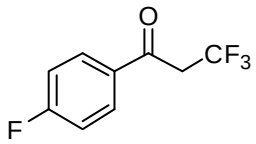


3,3,3-Trifluoro-1-p-tolylpropan-1-one (3b): 91% yield, colorless solid. ^1H NMR (300 MHz, $CDCl_3$/TMS): δ 7.84 (d, *J* = 7.8 Hz, 2H), 7.30 (d, *J* = 7.8 Hz, 2H), 3.77 (q, *J* = 10.0 Hz, 2H), 2.44 (s, 3H); ^{19}F NMR (282 MHz , $CDCl_3/CFCl_3$): δ – 61.8 (t, *J* = 10.0 Hz, 3F); MS (EI, *m/z*): 202(M^+, 23.47), 119 (100.00), 91(63.09); The data are consistent with the previous report[3].

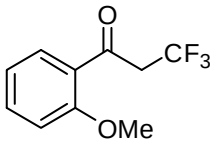


3,3,3-Trifluoro-1-(4-methoxyphenyl)propan-1-one (3c): 90% yield, yellow liquid. ^1H NMR (300 MHz, $CDCl_3$/TMS): δ 7.92 (d, *J* = 8.9 Hz, 2H),

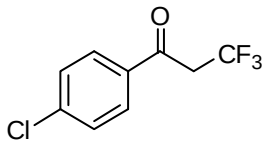
6.97 (d, J = 8.9 Hz, 2H), 3.89 (s, 3H), 3.74 (q, J = 10.1 Hz, 2H); ^{19}F NMR (282 MHz , $CDCl_3/CFCl_3$): δ – 61.7 (t, J = 10.1 Hz, 3F); MS (EI, *m/z*): 218(M^+, 24.57), 135 (100.00); The data are consistent with the previous report[2].



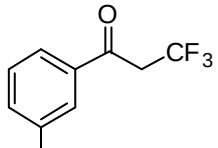
3,3,3-Trifluoro-1-(4-fluorophenyl)propan-1-one (3d): 89 % yield**,** yellow liquid. ^{1}H NMR (300 MHz, $CDCl_3$/TMS): δ 7.98 (dd, J_1 = 7.4 Hz, J_2 = 5.5 Hz, 2H); 7.19 (t, J = 8.1 Hz, 2H), 3.77 (q, J = 9.9 Hz, 2H); ^{19}F NMR (282 MHz , $CDCl_3/CFCl_3$): δ – 61.7 (t, J = 9.9 Hz, 3F), –102.6 (m, 1F); MS (EI, *m/z*): 206(M^+, 14.50), 123 (100.00), 95 (59.39); The data are consistent with the previous report[2].



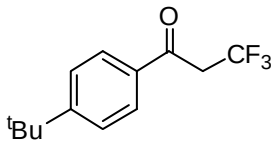
3,3,3-Trifluoro-1-(2-methoxyphenyl)propan-1-one (3e): 88% yield, colorless solid. ^{1}H NMR (300 MHz, $CDCl_3$/TMS): δ 7.82 (dd, J_1 = 7.8 Hz, J_2 = 1.6 Hz, 1H), 7.53 (td, J_1 = 7.8 Hz, J_2 = 1.8 Hz, 1H), 7.04 (t, J = 7.9 Hz, 1H), 6.99 (d, J = 8.4 Hz, 1H), 3.95 (s, 3H), 3.88 (q, J = 10.3 Hz, 2H) ; ^{19}F NMR (282 MHz , $CDCl_3/CFCl_3$): δ – 61.8 (t, J = 10.3 Hz, 3F); MS (EI, *m/z*): 218(M^+, 15.92), 135 (100.00); The data are consistent with the previous report[4].



1-(4-Chlorophenyl)-3,3,3-trifluoropropan-1-one (3f) : 86% yield, white solid. ^{1}H NMR (300 MHz, $CDCl_3$/TMS): δ 7.88 (d, J = 8.5 Hz, 2H); 7.49 (d, J = 8.5 Hz, 2H), 3.77 (q, J = 9.9 Hz, 2H); ^{19}F NMR (282 MHz , $CDCl_3/CFCl_3$): δ – 61.7 (t, J = 9.9 Hz, 3F); MS (EI, *m/z*): 222(M^+, 22.36), 139 (100.00), 111 (52.26); The data are consistent with the previous report[2].

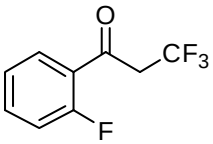


3,3,3-Trifluoro-1-m-tolylpropan-1-one (3g) : 84% yield, yellow liquid. ^{1}H NMR (300 MHz, $CDCl_3$/TMS): δ 7.75–7.71 (m, 2H), 7.46–7.39 (m, 2H), 3.78 (q, J = 10.0 Hz, 2H), 2.43 (s, 3H); ^{19}F NMR (282 MHz , $CDCl_3/CFCl_3$): δ – 62.0 (t, J = 10.0 Hz, 3F); MS (EI, *m/z*): 202(M^+, 27.87), 119 (100.00), 91 (66.96); The data are consistent with the previous report[5].

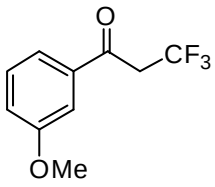


1-(4-Tert-butylphenyl)-3,3,3-trifluoropropan-1-one (3h): 84% yield, yellow liquid. ^{1}H NMR (300 MHz, $CDCl_3$/TMS): δ 7.88 (d, J = 8.4 Hz, 2H), 7.52 (d, J = 8.4 Hz, 2H), 3.77 (q, J = 10.1 Hz, 2H), 1.35 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$/TMS): δ 189.3, 158.2, 133.4, 128.4, 125.9, 124.2 (q, J = 277.1 Hz), 42.0 (q, J = 28.2 Hz), 35.2, 31.0; ^{19}F NMR (282 MHz , $CDCl_3/CFCl_3$): δ – 61.8 (t, J = 10.1 Hz, 3F); IR (film): 2967, 2909, 2873, 1698, 1606, 1567, 1466, 1417, 1371, 1339, 1271, 1257, 1235, 1197,

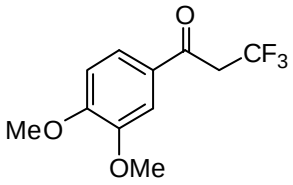
1135, 1105, 1020, 998, 920, 866, 854, 843, 817, 727, 642, 597 cm^{-1}; MS (EI, *m/z*): 244(M^+, 20.27), 229 (100.00); HRMS (EI): exact mass calcd for $C_{13}H_{15}OF_3$ (M^+): 244.1075, found: 244.1072.



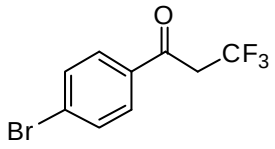
3,3,3-Trifluoro-1-(2-fluorophenyl)propan-1-one (3i): 80% yield, white solid. Mp= 68–70℃. ^{1}H NMR (300 MHz, $CDCl_3$/TMS): δ 7.94 (t, *J* = 7.6 Hz, 1H), 7.61 (dd, J_1 = 13.8 Hz, J_2 = 6.7 Hz, 1H), 7.28 (d, *J* = 7.9 Hz, 1H), 7.18 (dd, J_1 = 11.4 Hz, J_2 = 8.5 Hz, 1H), 3.84 (qd, J_1 = 9.8 Hz, J_2 = 2.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$/TMS): δ 187.6, 162.1 (d, *J* = 254.2 Hz), 135.9 (d, *J* = 9.2 Hz), 130.9 (d, *J* = 1.9 Hz), 124.9 (d, *J* = 3.2 Hz), 124.4 (dd, J_1 = 11.1 Hz, J_2 = 1.1 Hz), 123.8(qd, J_1 = 276.8 Hz, J_2 = 2.8 Hz), 116.80 (d, *J* = 23. 8 Hz), 46.60 (qd, J_1 = 28.4 Hz, J_2 = 9.7 Hz); ^{19}F NMR (282 MHz , $CDCl_3$/$CFCl_3$): δ – 62.4 (td, J_1 = 9.8 Hz, J_2 = 1.6 Hz, 3F), – 109.5 (m, 1F); IR (film): 3370, 2987, 2956, 2924, 1695, 1653, 1610, 1579, 1484, 1457, 1419, 1379, 1288, 1278, 1262, 1217, 1161, 1117, 1104, 1044, 1000, 966, 920, 860, 839, 797, 769, 674, 618, 592 cm^{-1}; MS (EI, *m/z*): 206(M^+, 14.85), 123 (100.00); HRMS (EI): exact mass calcd for $C_9H_6OF_4$ (M^+): 206.0355, found: 206.0354.



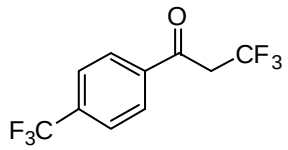
3,3,3-Trifluoro-1-(3-methoxyphenyl)propan-1-one (3j): 80% yield, colorless liquid. ^{1}H NMR (300 MHz, $CDCl_3$/TMS): δ 7.54–7.35 (m, 3H), 7.18 (d, *J* = 8.7 Hz, 1H), 3.87 (s, 3H), 3.78 (q, *J* = 10.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$/TMS): δ 189.5, 160.1, 137.2, 129.9, 124.0 (q, *J* = 277.0 Hz), 121.0, 120.7, 112.6, 55.5, 42.2 (q, *J* = 28.2 Hz); ^{19}F NMR (282 MHz , $CDCl_3$/$CFCl_3$): δ – 61.8 (t, *J* = 10.0 Hz, 3F); IR (film): 3079, 2946, 2841, 1699, 1599, 1585, 1488, 1466, 1454, 1432, 1417, 1372, 1337, 1317, 1259, 1206, 1179, 1128, 1104, 1049, 1023, 927, 873, 853, 778, 735, 684, 619 cm^{-1}; MS (EI, *m/z*): 218(M^+, 43.71), 135 (100.00); HRMS (EI): exact mass calcd for $C_{10}H_9O_2F_3$ (M^+): 218.0555, found: 218.0556.



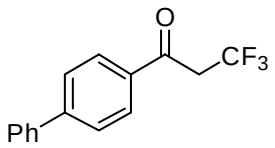
1-(3,4-Dimethoxyphenyl)-3,3,3-trifluoropropan-1-one (3k): 83% yield, colorless solid. Mp= 100–102℃. ^{1}H NMR (300 MHz, $CDCl_3$/TMS): δ 7.70–7.41 (m, 2H), 6.92 (d, *J* = 8.1Hz, 1H), 3.97 (s, 3H), 3.95 (s, 3H), 3.76 (q, *J* = 10.1 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$/TMS): δ 188.2, 154.3, 149.4, 129.1, 124.2 (q, *J* = 276.9 Hz), 123.4, 110.2, 110.1, 56.1, 56.0, 41.6 (q, *J* = 28.1 Hz); ^{19}F NMR (282 MHz , $CDCl_3$/$CFCl_3$): δ – 61.7 (t, *J* = 10.1 Hz, 3F); IR (film): 3082, 2975, 2946, 2849, 1686, 1587, 1519, 1470, 1456, 1443, 1424, 1362, 1284, 1262, 1208, 1172, 1157, 1103, 1020, 933, 912, 873, 854, 800, 784, 765, 659, 635,625, 585 cm^{-1}; MS (EI, *m/z*): 248(M^+, 28.65), 165 (100.00); HRMS (EI): exact mass calcd for $C_{11}H_{11}O_3F_3$ (M^+): 248.0660, found: 248.0663.



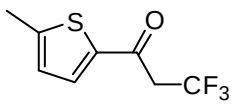
1-(4-Bromophenyl)-3,3,3-trifluoropropan-1-one (3l): 78% yield, colorless solid. ^{1}H NMR (300 MHz, $CDCl_3$/TMS): 7.80 (d, J = 8.2 Hz, 2H), 7.66 (d, J = 8.2 Hz, 2H), 3.76 (q, J = 9.9 Hz, 2H); ^{19}F NMR (282 MHz , $CDCl_3$/$CFCl_3$): δ – 61.8 (t, J = 9.9 Hz, 3F); MS (EI, *m/z*): 266(M^+, 17.80), 183 (100.00); The data are consistent with the previous report[2].



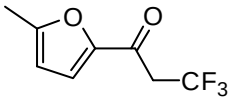
3,3,3-Trifluoro-1-(4-(trifluoromethyl)phenyl)propan-1-one (3m) : 74 % yield. colorless solid. Mp = 68–71℃. ^{1}H NMR (300 MHz, $CDCl_3$/TMS): δ 8.05 (d, J = 7.7 Hz, 2H), 7.79 (d, J = 7.7 Hz, 2H), 3.84 (q, J = 9.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$/TMS): δ 188.9 (d, J = 2.5Hz), 138.4, 135.5 (q, J = 32.9 Hz), 128.7, 126.0 (q, J = 3.6 Hz), 123.7 (q, J = 277.1 Hz), 123.3 (q, J = 272.4 Hz), 42.4 (q, J = 28.7 Hz); ^{19}F NMR (282 MHz , $CDCl_3$/$CFCl_3$): δ – 61.8 (t, J = 9.8 Hz, 3F), – 63.1 (s, 3F); IR (film): 3068, 2956, 1705, 1584, 1515, 1421, 1380, 1327, 1278, 1229, 1167, 1137, 1101, 1065, 1017, 1000, 920, 858, 834, 770, 696, 631, 609 cm^{-1}; MS (EI, *m/z*): 256(M^+, 4.81), 173 (100.00), 145 (67.58); HRMS (EI): exact mass calcd for $C_{10}H_6OF_6$ (M^+): 256.0323, found: 256.0326.



1-(Biphenyl-4-yl)-3,3,3-trifluoropropan-1-one (3n): 68% yield, colorless solid. Mp = 135–137℃. ^{1}H NMR (300 MHz, $CDCl_3$/TMS): δ 8.01 (d, J = 8.5 Hz, 2H), 7.74–7.71(m, 2H), 7.65–7.62 (m, 2H), 7.51–7.42 (m, 3H), 3.83 (q, J = 10.1 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$/TMS): δ 189.3, 146.9, 139.4, 134.6, 129.1, 129.0, 128.6, 127.5, 127.3, 124.1 (q, J = 277.0 Hz), 42.2 (q, J = 28.4 Hz); ^{19}F NMR (282 MHz , $CDCl_3$/$CFCl_3$): δ – 61.8 (t, J = 10.0 Hz, 3F); IR (film): 3067, 2966, 2938, 1686, 1651, 1604, 1582, 1559, 1451, 1416, 1371, 1277, 1228, 1198, 1138, 1102, 1023, 999, 968, 914, 853, 841, 822, 767, 749, 724, 698, 664, 618, 594 cm^{-1}; MS (EI, *m/z*): 264(M^+, 27.02), 181 (100.00), 152 (62.39); HRMS (EI): exact mass calcd for $C_{15}H_{11}OF_3$ (M^+): 264.0762, found: 264.0763.



3,3,3-Trifluoro-1-(5-methylthiophen-2-yl)propan-1-one (3o): 70% yield, colorless solid. Mp= 55–58℃. ^{1}H NMR (300 MHz, $CDCl_3$/TMS): δ 7.55 (d, J = 3.7 Hz, 1H), 6.85 (d, J = 3.7 Hz, 1H), 3.65 (d, J = 10.2 Hz, 2H), 2.56 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$/TMS): δ 181.6, 152.2, 141.0, 134.2, 127.3, 123.8 (q, J = 277.3 Hz), 42.6 (q, J = 28.6 Hz), 16.1; ^{19}F NMR (282 MHz , $CDCl_3$/$CFCl_3$): δ – 62.4 (t, J = 10.2 Hz, 3F); IR (film): 3099, 2918, 2849, 1667, 1538, 1456, 1372, 1343, 1242, 1130, 1068, 1008, 960, 944, 919, 851, 805, 783, 635, 618, 599 cm^{-1}; MS (EI, *m/z*): 208(M^+, 21.31), 125 (100.00); HRMS (EI): exact mass calcd for $C_8H_7OSF_3$ (M^+): 208. 0170, found: 208. 0167.

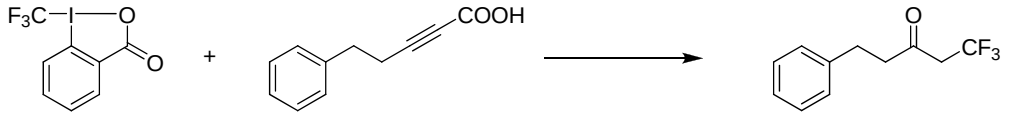


3,3,3-Trifluoro-1-(5-methylfuran-2-yl)propan-1-one(3p):72% yield, colorless solid. Mp = 57–59℃. ^{1}H NMR (300 MHz, $CDCl_3$/TMS): δ 7.23 (d, *J* = 3.4 Hz, 1H), 6.24 (d, *J* = 3.4 Hz, 1H), 3.61 (q, *J* = 10.3 Hz, 2H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$/TMS): 177.2, 159.3, 150.8, 123.9 (q, *J* = 277.1 Hz), 121.0, 109.9, 41.9 (q, *J* = 28.7 Hz), 14.0 ; ^{19}F NMR (282 MHz , $CDCl_3$/$CFCl_3$): δ – 62.4 (t, *J* = 10.3 Hz, 3F); IR (film): 3127, 2960, 1752, 1674, 1589, 1515, 1415, 1379, 1267, 1212, 1144, 1107, 1054, 1031, 963, 917, 851, 795, 736, 637, 623 cm^{-1}; MS (EI, *m/z*): 192(M^+, 29.85), 109 (100.00); HRMS (EI): exact mass calcd for $C_8H_7O_2F_3$ (M^+): 192.0398, found: 192.0400.

Screens for the Trifluoromethyldecarboxylation reaction of 4a. A Schlenk test tube with a magnetic stirring bar and a reflux condensing tube was charged with **1**, 4a, and catalyst followed by solvent. The reaction mixture was stirred and heated for 12 h. The reaction mixture was cooled to ambient temperature, extracted with CH_2Cl_2 (15 mL × 3) and $PhOCF_3$ was added. The yield was determined by ^{19}F NMR. The results are summarized in **Table S-1**.

Table S2. Screens for the Trifluoromethyldecarboxylation reaction of 4a

Supporting Information



1 **4a**(1.0 equiv) **5a**

entry	**1**(equiv)	solvent[a]	metal (equiv)	T (^{o}C)	yield (%)[b]
1	2.0	H_2O/CCl_4 (3:2)	$CuF_2 \cdot 2H_2O$ (2.0)	80	29
2	2.0	H_2O/CCl_4 (3:2)	$Cu(OH)_2$ (2.0)	80	24
3	2.0	H_2O/CCl_4 (3:2)	$Cu(HCOO)_2 \cdot 4H_2O$ (2.0)	80	30
4	2.0	H_2O/CCl_4 (3:2)	Bis(2,4–pentanedionato)copper (II)(2.0)	80	44
5	2.0	H_2O/CCl_4 (3:2)	copper(II) gluconate (2.0)	80	45
6	2.0	H_2O/DMF(3:2)	copper(II) gluconate (2.0)	80	22
7	2.0	H_2O/DCE(3:2)	copper(II) gluconate (2.0)	80	32
8	2.0	H_2O/DBE(3:2)	copper(II) gluconate (2.0)	80	43
9	2.0	H_2O/CH_2Br_2(3:2)	copper(II) gluconate (2.0)	80	40
10	2.0	H_2O/Dioxane(3:2)	copper(II) gluconate (2.0)	80	12
11	2.0	H_2O/CH_3CN(3:2)	copper(II) gluconate (2.0)	80	27
12	2.0	H_2O/DMSO(3:2)	copper(II) gluconate (2.0)	80	26
13	2.0	H_2O/DME(3:2)	copper(II) gluconate (2.0)	80	14
14	2.0	H_2O/CCl_4 (3:2)	copper(II) gluconate (1.0)	80	38
15	2.0	H_2O/CCl_4 (3:2)	copper(II) gluconate (0.5)	80	10
16	3.0	H_2O/CCl_4 (3:2)	copper(II) gluconate (2.0)	80	58
17	3.0	H_2O/CCl_4 (3:2)	copper(II) gluconate (2.0)	60	53
18	3.0	H_2O/CCl_4 (2:1)	copper(II) gluconate (2.0)	80	56
19	3.0	H_2O/CCl_4 (1:4)	copper(II) gluconate (2.0)	80	37

[a] The data in the parentheses refers to the volume ratio. [b] Determined by ^{19}F NMR spectroscopy using $PhOCF_3$ as an internal standard.

General procedure for the trifluoromethylative decarboxylation reaction of 4 (for Table 3 in manuscript)

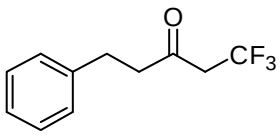
General procedure for **4a**-**4g**: Into a reaction flask equipped with a magnetic stirring bar and a reflux condenser, was added **1** (2.4 mmol, 3.0 equiv), **4a** (0.8 mmol, 1.0 equiv), copper(II) gluconate (1.6

mmol, 2.0 equiv), CCl_4 (3 mL), and H_2O (4.5 mL). The reaction mixture was stirred and heated to 80 ℃. After stirring at this temperature for 12 h, the reaction mixture was cooled to ambient temperature and extracted with CH_2Cl_2 (15 mL × 3), dried over $MgSO_4$., filtered and concentrated under vacuum. The residue was purified with silica gel chromatography to provide pure product.

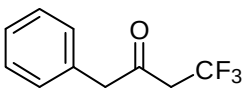
General procedure for **4h-4j**:Into a reaction flask equipped with a magnetic stirring bar and a reflux condenser, was added **1** (2.4 mmol, 3.0 equiv), **4h** (0.8 mmol, 1.0 equiv), copper(II) gluconate (1.6 mmol, 2.0 equiv), DMSO (3 mL), and H_2O (4.5 mL). The reaction mixture was stirred and heated to 80 ℃. After stirring at this temperature for 12 h, the reaction mixture was cooled to ambient temperature and extracted with ether (15 mL × 3), dried over $MgSO_4$., filtered and concentrated under vacuum. The residue was purified with silica gel chromatography to provide pure product.

General procedure for **4k-4l**: Into a reaction flask equipped with a magnetic stirring bar and a reflux condenser, was added **1** (0.6 mmol, 3.0 equiv), **4h** (0.2 mmol, 1.0 equiv), $CuC_4H_4O_6{\cdot}3H_2O$ (cupric tartrate) (0.2 mmol, 1.0 equiv), DMSO (2 mL), and H_2O (3 mL). The reaction mixture was stirred and heated to 80 ℃. After stirring at this temperature for 12 h, the reaction mixture was cooled to ambient temperature and extracted with ether (15 mL × 3), dried over $MgSO_4$., filtered and concentrated under vacuum. The residue was purified with silica gel chromatography to provide pure product.

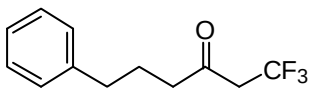
Charaterization data of compounds 5



1,1,1-Trifluoro-5-phenylpentan-3-one (5a): 54% yield**,** colorless liquid. ^{1}H NMR (300 MHz, $CDCl_3$/TMS): δ 7.32-7.16 (m, 5H), 3.19 (q, J = 10.4Hz, 2H), 2.99-2.78 (m, 4H); ^{19}F NMR (282 MHz , $CDCl_3$/$CFCl_3$): δ – 62.3 (t, J = 10.3 Hz, 3F); MS (EI, *m/z*): 216(M^+, 64.71), 105 (100.00); The data are consistent with the previous report[6]

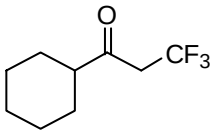


4,4,4-Trifluoro-1-phenylbutan-2-one (5b): 50% yield**,** colorless liquid. ^{1}H NMR (300 MHz, $CDCl_3$/TMS): δ 7.39-7.30 (m, 3H), 7.20 (d, J = 7.0Hz, 2H), 3.80 (s, 2H), 3.23 (q, J = 10.3Hz, 2H); ^{19}F NMR (282 MHz , $CDCl_3$/$CFCl_3$): δ – 62.4 (t, J = 10.3 Hz, 3F); MS (EI, *m/z*): 202(M^+, 22.22), 91 (100.00); The data are consistent with the previous report[7]

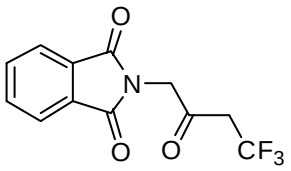


1,1,1-Trifluoro-6-phenylhexan-3-one (5c): 40% yield, colorless liquid. ^{1}H

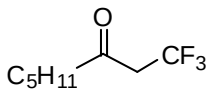
NMR (300 MHz, $CDCl_3$/TMS): δ 7.32-7.14 (m, 5H), 3.17 (q, *J* = 10.5Hz, 2H), 2.64 (t, *J* = 7.5Hz, 2H), 2.53 (t, *J* = 7.2Hz, 2H), 1.99-1.89 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$/TMS): δ 199.9, 141.1, 128.5, 128.4, 126.1, 123.6 (q, *J* = 276.9Hz), 46.2 (q, *J* = 28.1Hz), 42.5 (q, *J* = 1.9Hz), 34.6, 24.5; ^{19}F NMR (282 MHz , $CDCl_3$/$CFCl_3$): δ – 62.4 (t, *J* = 10.4 Hz, 3F); IR (film): 3443, 3087, 3064, 3029, 2940, 2864, 1732, 1604, 1497, 1455, 1418, 1375, 1271, 1153, 1099, 1016, 911, 735, 701, 649 cm^{-1}; MS (EI, *m/z*): 230(M^+, 5.82), 104 (100.00); HRMS (EI): exact mass calcd for $C_{12}H_{13}OF_3$ (M^+): 230.0918, found: 230.0916.



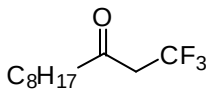
1-Cyclohexyl-3,3,3-trifluoropropan-1-one (5d): 51% yield, colorless liquid. ^1H NMR (300 MHz, $CDCl_3$/TMS): δ 3.26 (q, *J* = 10.3Hz, 2H), 2.41 (t, *J* = 9.0Hz, 1H), 2.00-1.08 (m, 10H); ^{19}F NMR (282 MHz , $CDCl_3$/$CFCl_3$): δ – 62.4 (t, *J* = 10.3Hz, 3F); MS (EI, *m/z*): 194(M^+, 20.30), 83 (100.00); The data are consistent with the previous report[6]



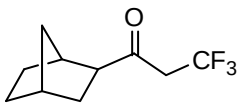
2-(4,4,4-Trifluoro-2-oxobutyl)isoindoline-1,3-dione (**5e**): 50% yield, colorless solid. Mp = 166–168℃. ^1H NMR (300 MHz, $CDCl_3$/TMS): δ 7.93-7.85 (m, 2H), 7.81-7.72 (m, 2H), 4.59 (s, 2H), 3.39 (q, *J* = 10.2Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$/TMS): δ 192.2, 167.3, 134.4, 131.8, 123.7, 123.2 (q, *J* = 277.2Hz), 46.7 (q, *J* = 2.6Hz), 44.2 (q, *J* = 29.6Hz); ^{19}F NMR (282 MHz , $CDCl_3$/$CFCl_3$): δ – 61.9(t, *J* = 10.2Hz, 3F); IR (film): 3484, 2981, 2950, 1786, 1743, 1709, 1618, 1470, 1422, 1376, 1357, 1329, 1279, 1193, 1154, 1077, 1055, 1017, 960, 909, 874, 845, 799, 750, 716, 708, 661, 600 cm^{-1}; MS (EI, *m/z*): 271(M^+, 1.66), 160 (100.00); HRMS (EI): exact mass calcd for $C_{12}H_8NO_3F_3$ (M^+): 271.0456, found: 271.0451.



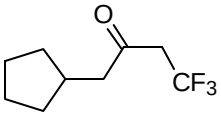
1,1,1-Trifluorooctan-3-one (5g): 45% yield, yellow oil. ^1H NMR (300 MHz, $CDCl_3$/TMS): δ 3.21 (q, *J* = 10.5Hz, 2H), 2.53 (t, *J* = 7.3Hz, 2H), 1.66-1.56 (m, 2H), 1.34-1.25 (m, 4H), 0.90 (t, *J* = 6.8Hz, 3H); ^{19}F NMR (282 MHz , $CDCl_3$/$CFCl_3$): δ – 62.4(t, *J* = 10.6Hz, 3F); MS (EI, *m/z*): 182(M^+, 3.20), 126(100.00);The data are consistent with the previous report[8]



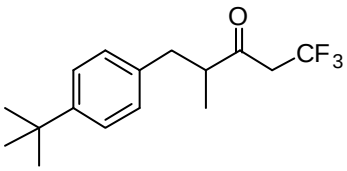
1,1,1-Trifluoroundecan-3-one (5h): 49% yield,colorless oil. ^1H NMR (300 MHz, $CDCl_3$/TMS): δ 3.22 (q, *J* = 10.5Hz, 2H), 2.52 (t, *J* = 7.3Hz, 2H), 1.61-1.58 (m, 2H), 1.36-1.19 (m, 10H), 0.88 (t, *J* = 6.5 Hz, 3H); ^{19}F NMR (282 MHz , $CDCl_3$/$CFCl_3$): δ – 62.4(t, *J* = 10.5Hz, 3F); MS (EI, *m/z*): 224(M^+, 5.13), 126 (88.04) , 110 (100.00); The data are consistent with the previous report[6]



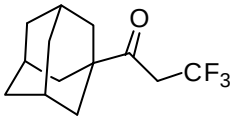
1-(Bicyclo[2.2.1]heptan-2-yl)-3,3,3-trifluoropropan-1-one (5i): 50% yield, yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$/TMS): δ 3.31-3.15 (m, 2H), 2.93-2.88 (m, 0.68H), 2.63 (br, 0.68H), 2.52-2.46 (m, 0.68H), 2.33-2.28 (m, 1H), 1.83-1.77 (m, 1H), 1.61-1.10 (m, 7H); ^{13}C NMR (100 MHz, $CDCl_3$/TMS): δ 201.22 (q, *J* = 2.1 Hz), 202. 18 (q, *J* = 2.0 Hz), 123.8 (q, *J* = 276.9 Hz), 123.7 (q, *J* = 276.9 Hz), 54.7 (q, *J* = 1.6 Hz), 54.6 (q, *J* = 1.6 Hz), 45.2 (q, *J* = 27.6 Hz), 44.7 (q, *J* = 27.8 Hz), 40.6, 40.2, 39.7, 37.1, 36.0, 35.8, 32.1, 29.6, 29.5, 28.9, 28.6, 24.3; ^{19}F NMR (282 MHz , $CDCl_3$/$CFCl_3$): δ – 62.30(t, *J* = 10.2Hz, 1.78F), 62.32 (t, *J* = 10.1Hz, 1.22F); IR (film): 2959, 2876, 1726, 1455, 1415, 1371, 1265, 1159, 1125, 1098, 1056, 954, 911, 850, 805, 735 cm^{-1}; MS (EI, *m/z*): 206(M^+, 3.01), 95 (100.00); HRMS (EI): exact mass calcd for $C_{10}H_{13}OF_3$ (M^+): 206.0918, found: 206.0914.



1-Cyclopentyl-4,4,4-trifluorobutan-2-one (5j): 46% yield, yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$/TMS): δ 3.21 (q, *J* = 10.5Hz, 2H), 2.55 (d, *J* = 7.1Hz, 2H), 2.39-2.16 (m, 1H), 1.89-1.79 (m, 2H), 1.68-1.49(m, 4H), 1.14-1.02 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$/TMS): δ 200.0 (q, *J* = 2.1Hz), 123.6 (q, *J* = 276.9Hz), 49.7 (q, *J* = 1.8Hz), 46.1 (q, *J* = 28.0Hz), 34.9, 32.3, 24.8; ^{19}F NMR (282 MHz , $CDCl_3$/$CFCl_3$): δ – 62.4(t, *J* = 10.6Hz, 3F); IR (film): 2956, 2872, 1731, 1454, 1420, 1366, 1263, 1148, 1114, 1039, 912, 848, 805, 645 cm^{-1}; MS (EI, *m/z*): 194(M^+, 0.63), 68(100.00); HRMS (EI): exact mass calcd for $C_9H_{13}OF_3$ (M^+): 194.0918, found: 194.0914.



5-(4-Tert-butylphenyl)-1,1,1-trifluoro-4-methylpentan-3-one (5k): 63% yield, colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$/TMS): δ 7.31 (d, *J* = 8.0Hz, 2H), 7.07 (d, *J* = 8.0Hz, 2H), 3.27-2.80 (m, 4H), 2.62-2.56 (m, 1H), 1.30 (s, 9H), 1.13 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$/TMS): δ 203.6, 149.5, 135.7, 128.6, 125.5, 123.8 (q, *J* = 276.9Hz), 48.7 (q, *J* = 1.5Hz), 44.9 (q, *J* = 27.8Hz), 38.4, 34.4, 31.3, 15.8; ^{19}F NMR (282 MHz , $CDCl_3$/$CFCl_3$): δ – 62.4(t, *J* = 10.2Hz, 3F); IR (film): 2966, 2872, 1730, 1510, 1460, 1412, 1367, 1268, 1159, 1118, 1024, 838, 805, 628, 567 cm^{-1}; MS (EI, *m/z*): 286(M^+, 19.38), 271(100.00); HRMS (EI): exact mass calcd for $C_{16}H_{21}OF_3$ (M^+): 286.1545, found: 286.1547.

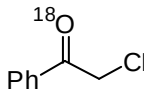


1-(Adamantan-1-yl)-3,3,3-trifluoropropan-1-one (5l): 60% yield. colorless solid. Mp = 60–62℃. ^{1}H NMR (300 MHz, $CDCl_3$/TMS): δ 3.28 (q, *J* = 10.1Hz, 2H), 2.07 (br, 3H), 1.80-1.67 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$/TMS): δ 204.8 (q, *J* = 1.6Hz), 124.2 (q, *J* = 276.8Hz), 46.9 (q, *J* = 1.5Hz), 39.3 (q, *J* = 27.6Hz), 37.5, 36.2, 27.6; ^{19}F NMR (282 MHz , $CDCl_3$/$CFCl_3$): δ – 62.2(t, *J* = 10.1Hz, 3F); IR (film): 2962, 2910, 2854, 1716, 1453,

1413, 1365, 1317, 1260, 1201, 1176, 1096, 1014, 937, 910, 871, 850, 802, 736, 620 cm^{-1}; MS (EI, *m/z*): 246(M^+, 1.77), 135(100.00); HRMS (EI): exact mass calcd for $C_{13}H_{17}OF_3$ (M^+): 246.1232, found: 246.1237.

The isotopic labeling experiment: A Schlenk test tube with a magnetic stirring bar was charged with **1** (0.8 mmol, 2.0 equiv), **2a** (0.4 mmol, 1.0 equiv), $Cu(OAc)_2$ (0.8 mmol), TMEDA (1.0 mmol), followed by DCM (2 mL) and $H_2{}^{18}O$ (3 mL, with 97% abundance of ^{18}O). The reaction mixture was stirred at room temperature. After stirring for 24 h, the reaction mixture was extracted with CH_2Cl_2 (15 mL × 3), dried over $MgSO_4$, filtered and concentrated. The residue was purified with silica gel chromatography to provide pure product **3a'** in 86% yield**.** The abundance of ^{18}O in **3a'** was determined by EI-MS, which was shown in page 73.

Charaterization data of compound 3a'



3,3,3-Trifluoro-1-phenylpropan-1-one (3a'): 86% yield, colorless solid. Mp = 31–33℃. ^1H NMR (300 MHz, $CDCl_3$/TMS): δ 7.94 (d, *J* = 7.3 Hz, 2H), 7.64 (t, *J* = 7.3 Hz, 1H), 7.51 (t, *J* = 7.8 Hz, 2H), 3.80 (q, *J* = 10.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$/TMS): δ 189.7 (q, *J* = 2.4 Hz), 135.7 (q, *J* = 1.7 Hz), 134.2, 128.9, 128.3, 124.0 (q, *J* = 276.9 Hz), 42.0 (q, *J* = 28.2 Hz); ^{19}F NMR (282 MHz , $CDCl_3/CFCl_3$): δ – 62.1 (t, *J* = 10.0 Hz, 3F); MS (EI, *m/z*): 190(M^+, 36.34), 188 (M^+-2, 4.73), 107 (100.00), 105 (18.78), 77 (56.46). HRMS (EI): exact mass calcd for $C_9H_7{}^{18}OF_3$ (M^+): 190.0491, found: 190.0488.

Reference:

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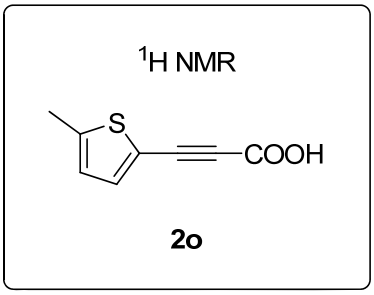
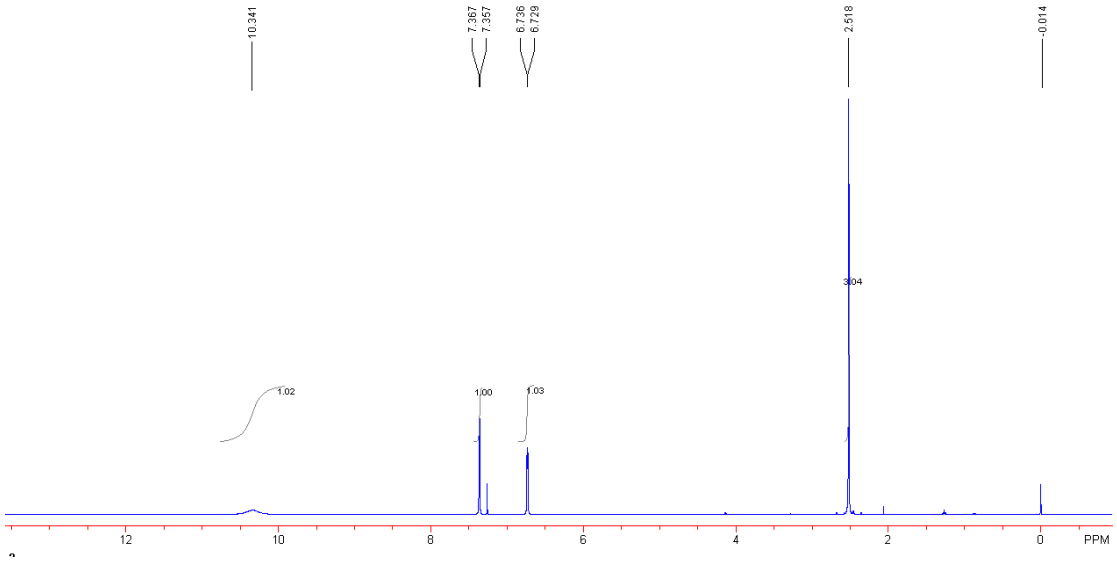
3. C. P. Zhan, Z. L. Wang, Q. Y. Chen, C. T. Zhang, Y. C. Gu, J. C. Xiao, *Chem. Commun*. **2011**. *47*. 6632.
4. N. Yoneda, S. Matsuoka, N. Miyaura, T. Fukuhara, A. Suzuki, *Bull. Chem. Soc. Jpn*., **1990**, *63*, 2124.
5. R. A. Cox, E. Grant, T. Whitaker, T. T. Tidwell, *Can. J. Chem*. **1990**. *68*. 1876.
6. B. Morandi, E. K. Carreira, *Angew. Chem.* **2011**, *123*, 9251; *Angew. Chem., Int.Ed.* **2011**, *50*, 9085.
7. Y. Kamitori, M. Hojo, R. Masuda, S.Ohara, Y. Kawamura, T. Ebisu, *Synthesis*, **1989**, 43.
8. L. Xiao, T. Kitazume, *J. Fluorine Chem.* **1997**, *86*, 99.

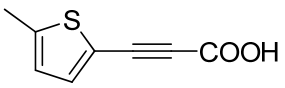
Supporting Information

1H, 13C NMR and 19F spectra of all new products:

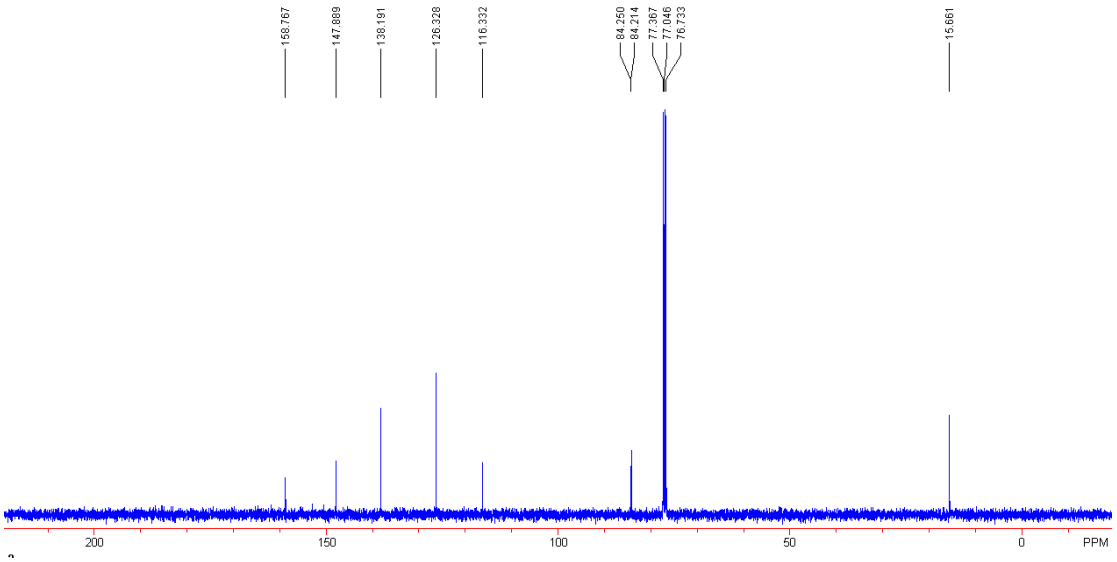




^{13}C NMR

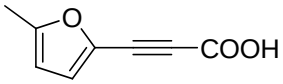


2o

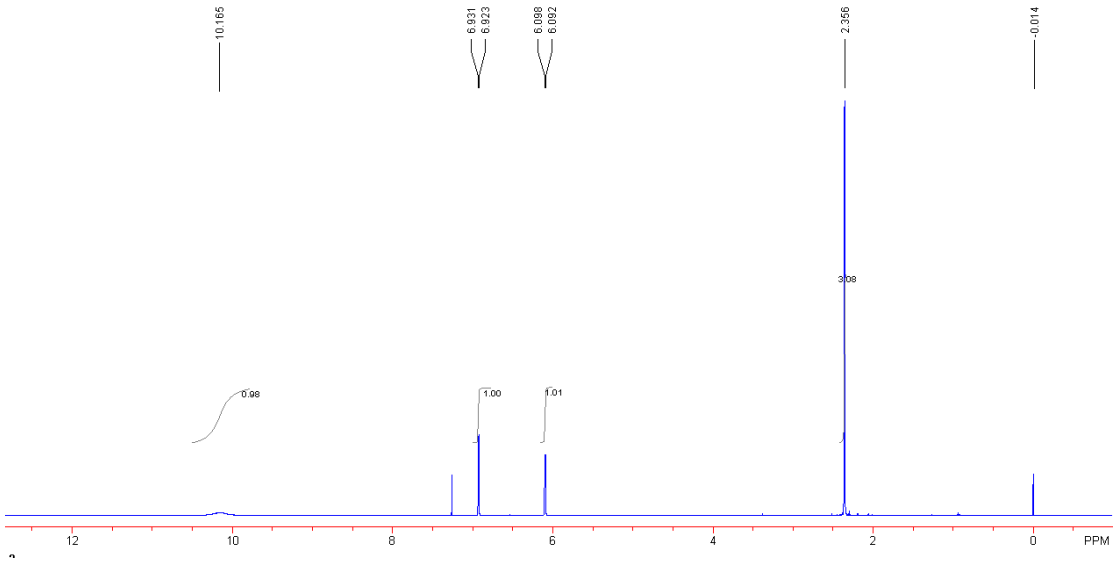


Supporting Information

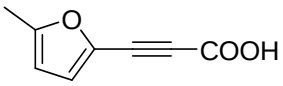
^{1}H NMR



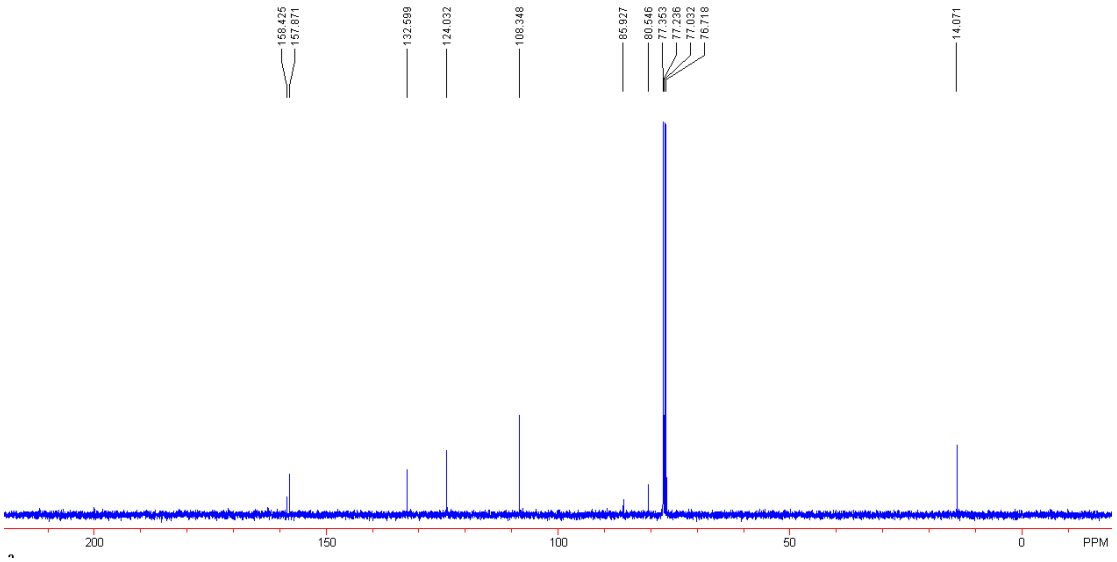
2p



^{13}C NMR


O
COOH

2p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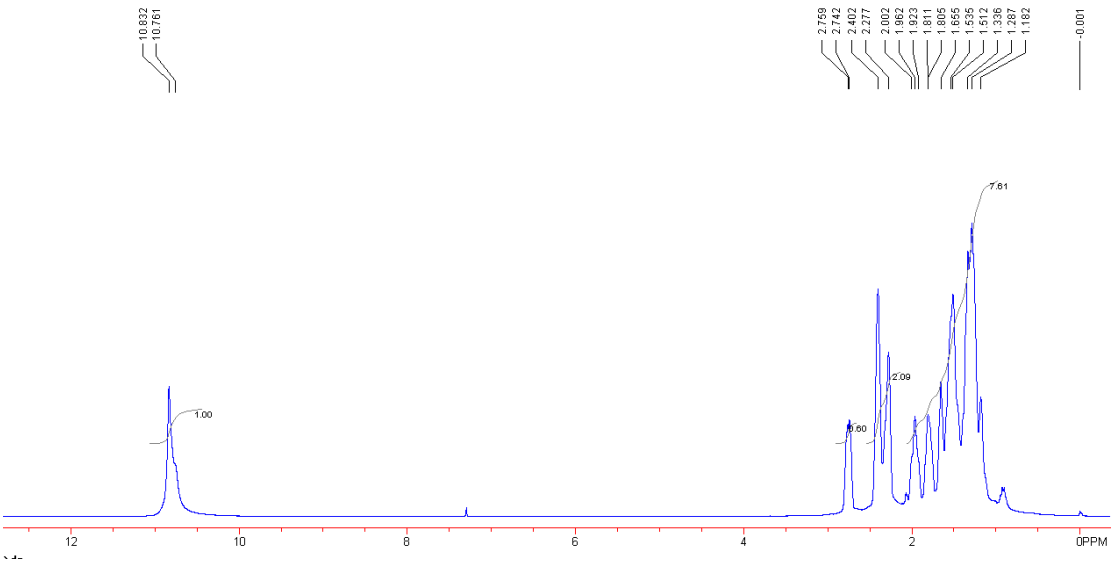
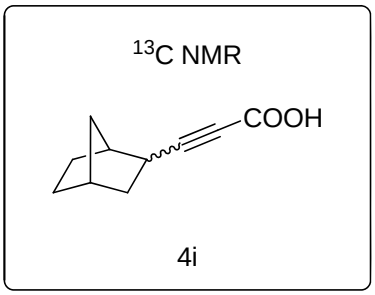
157.871
132.599
124.032
108.348
85.927
80.546
77.353
77.236
77.032
76.718
14.071
200
150
100
50
0
PPM

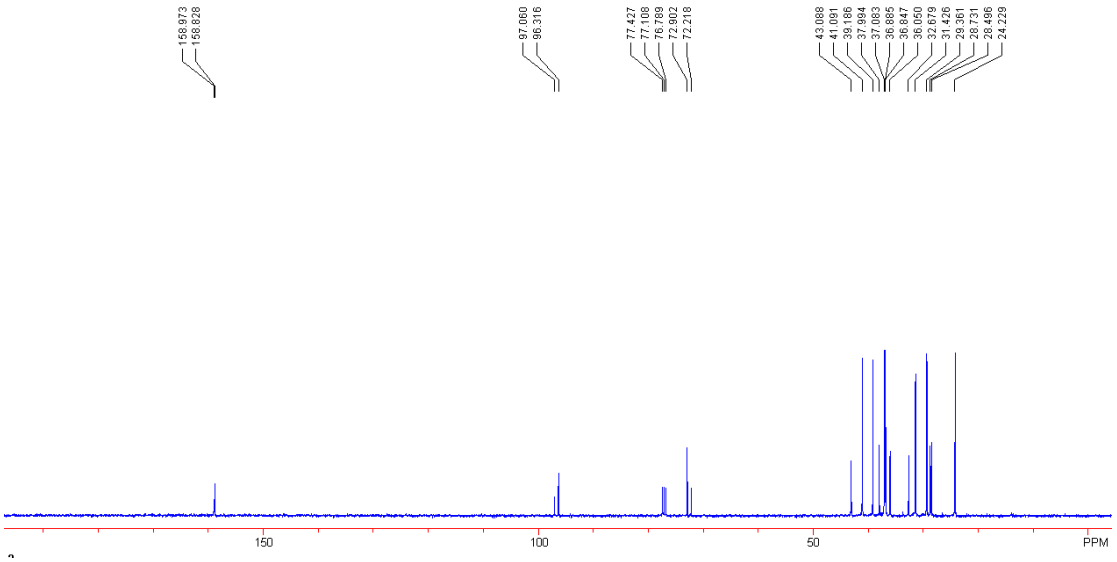
Supporting Information

^{1}H NMR

4i







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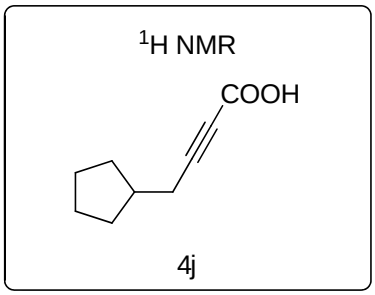

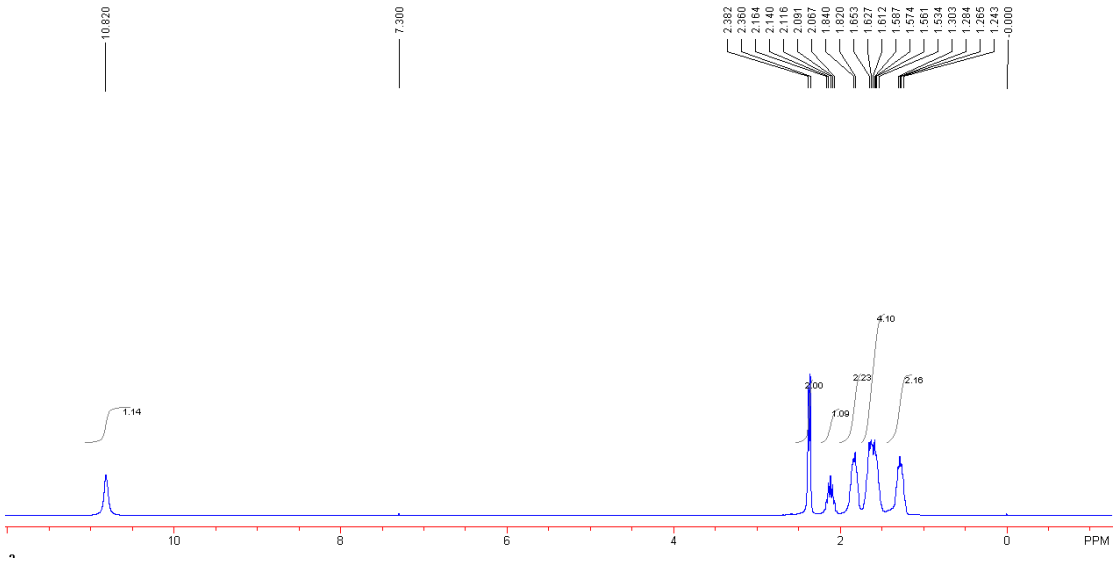

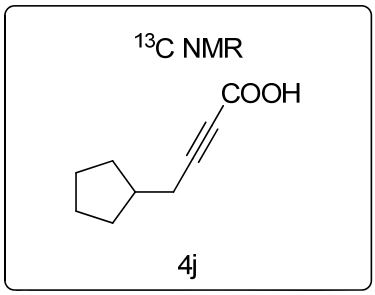

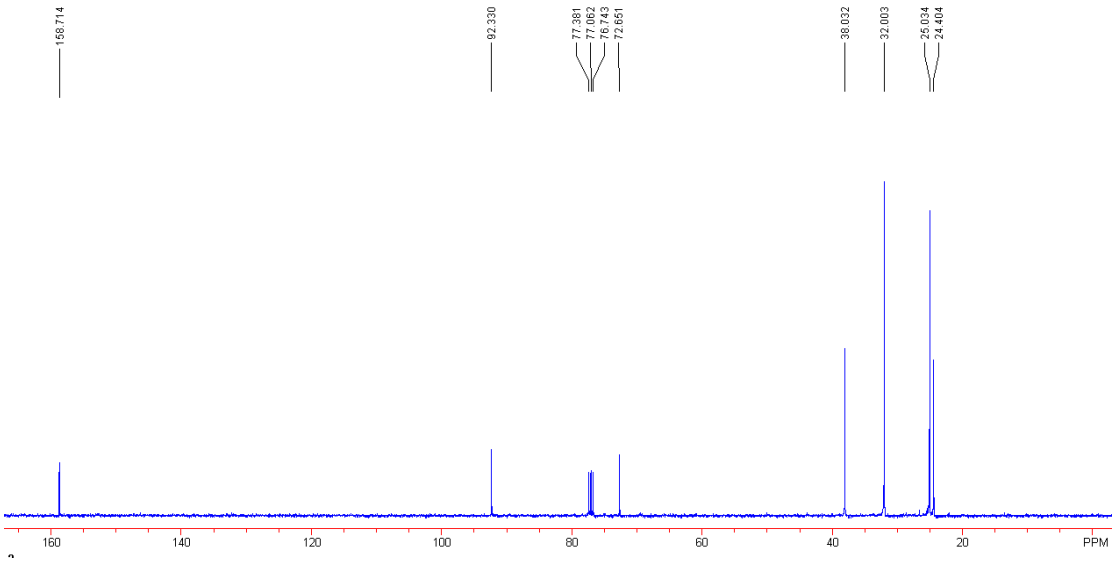

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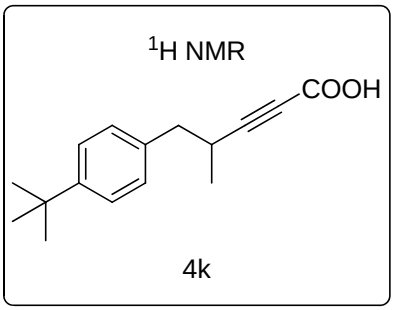
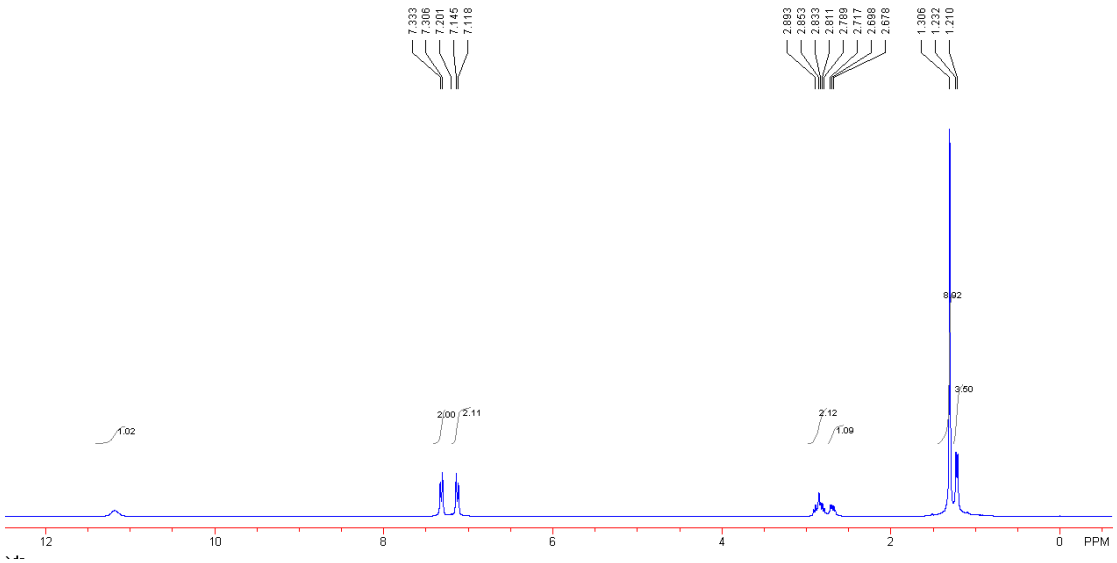
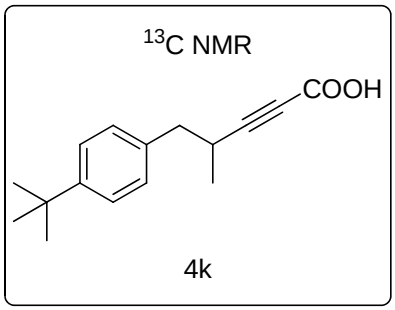
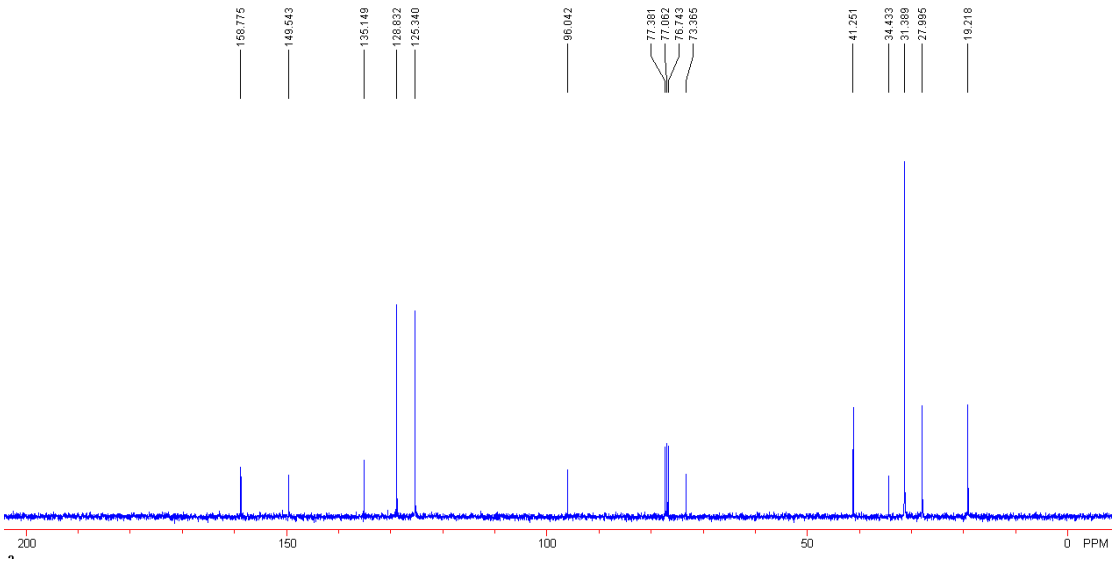


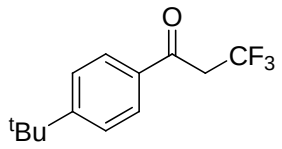




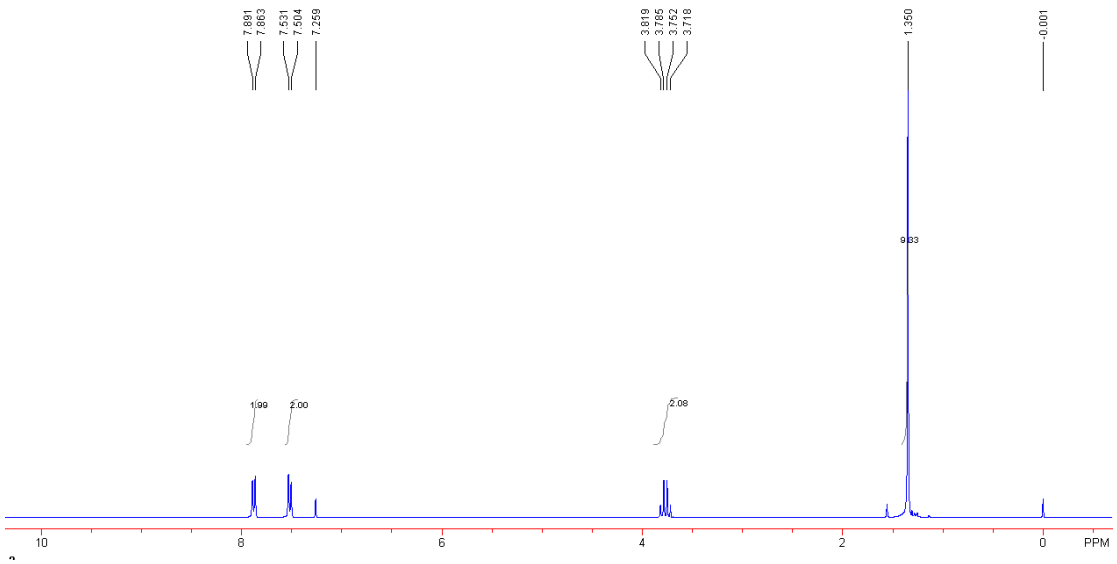


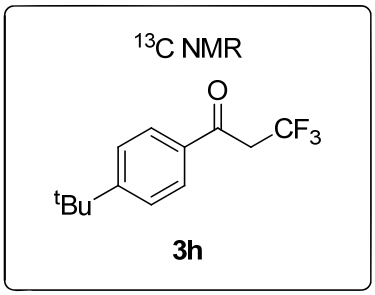
Supporting Information

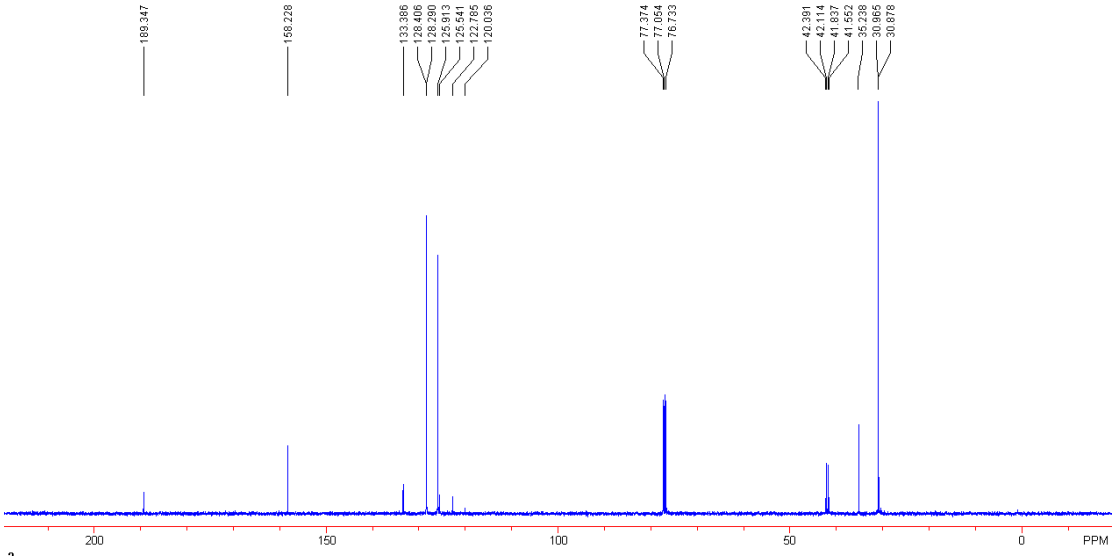
^{1}H NMR



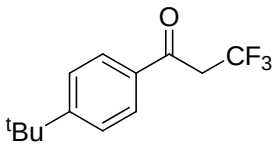
3h



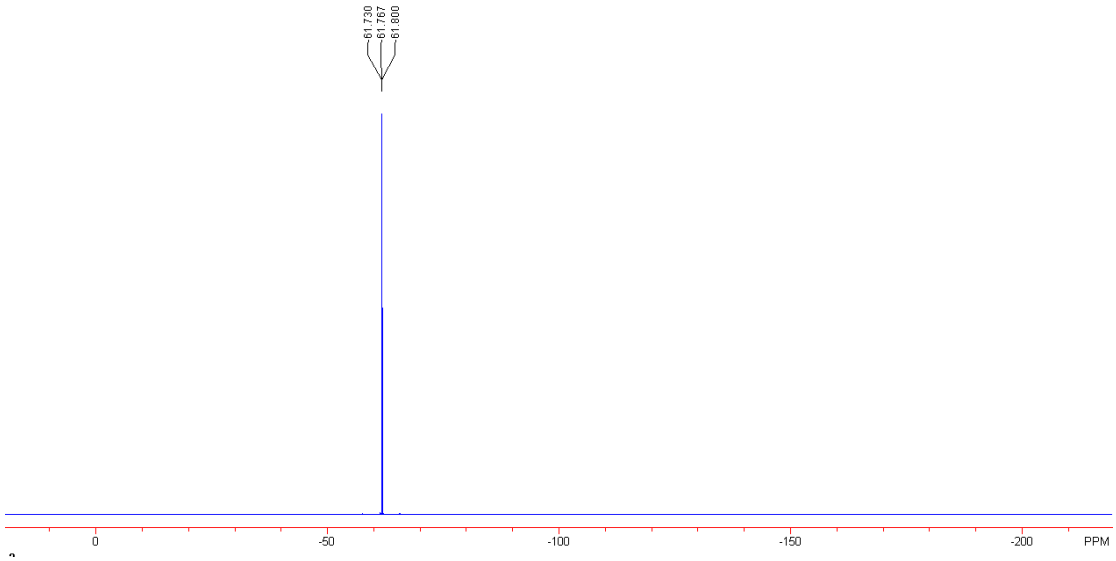


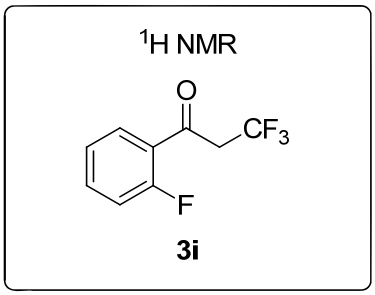


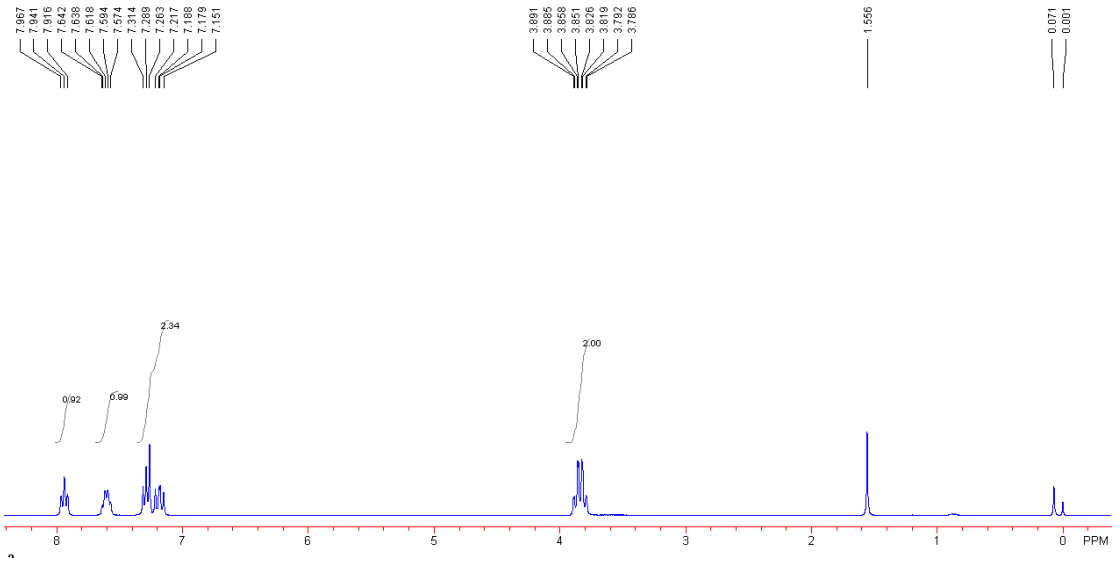
^{19}F NMR



3h




1H NMR
O
CF3
F
3i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7.179
7.151
3.891
3.885
3.858
3.851
3.826
3.819
3.792
3.786
1.556
0.071
0.001
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7
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3
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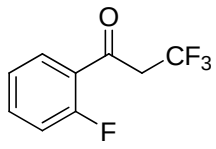
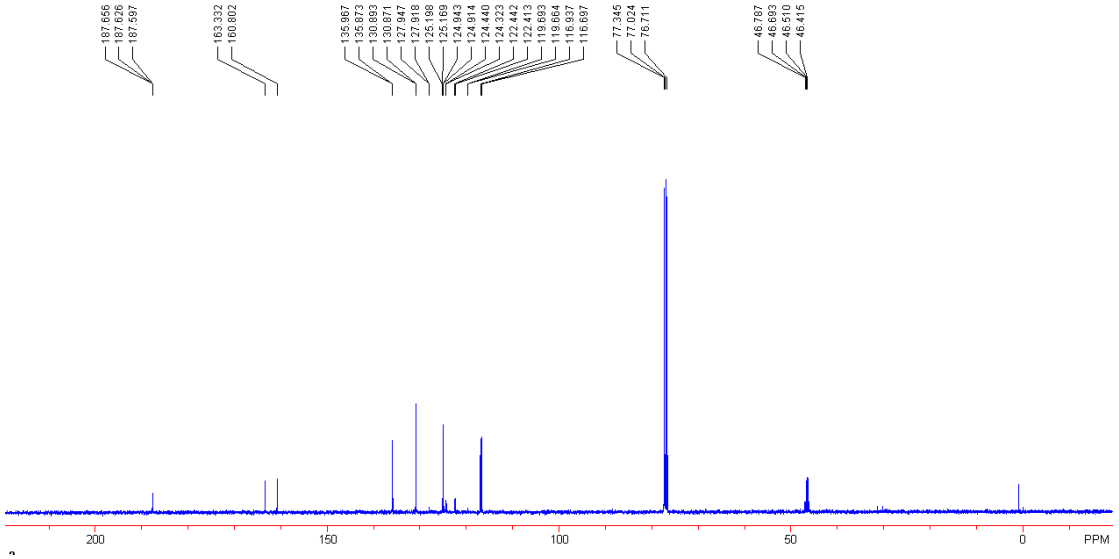
PPM

Supporting Information

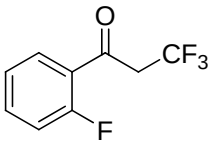
^{13}C NMR



3i



^{19}F NMR



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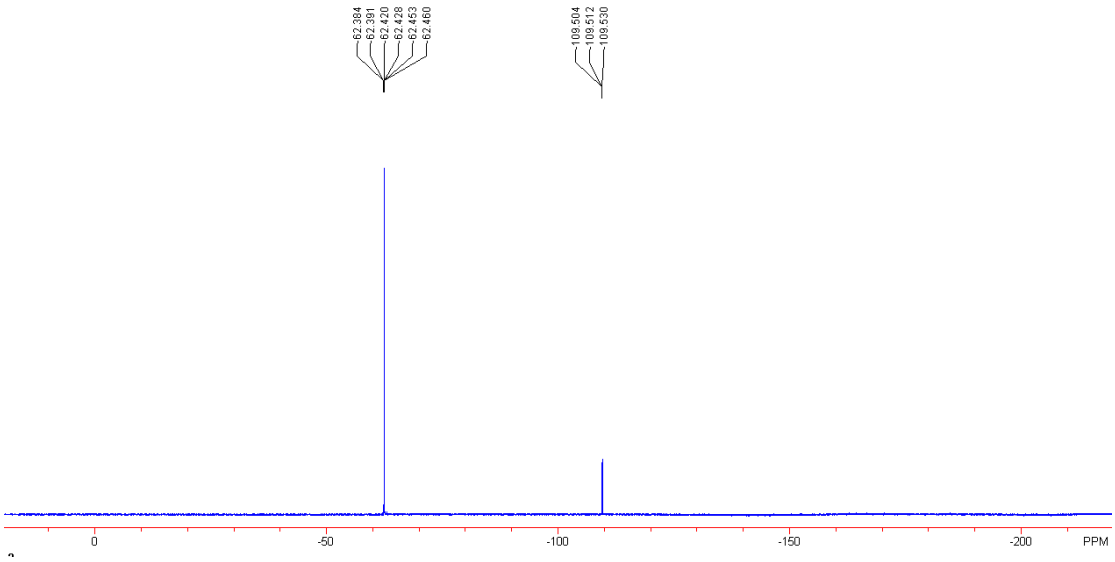
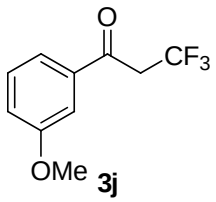


Supporting Information

^{1}H NMR



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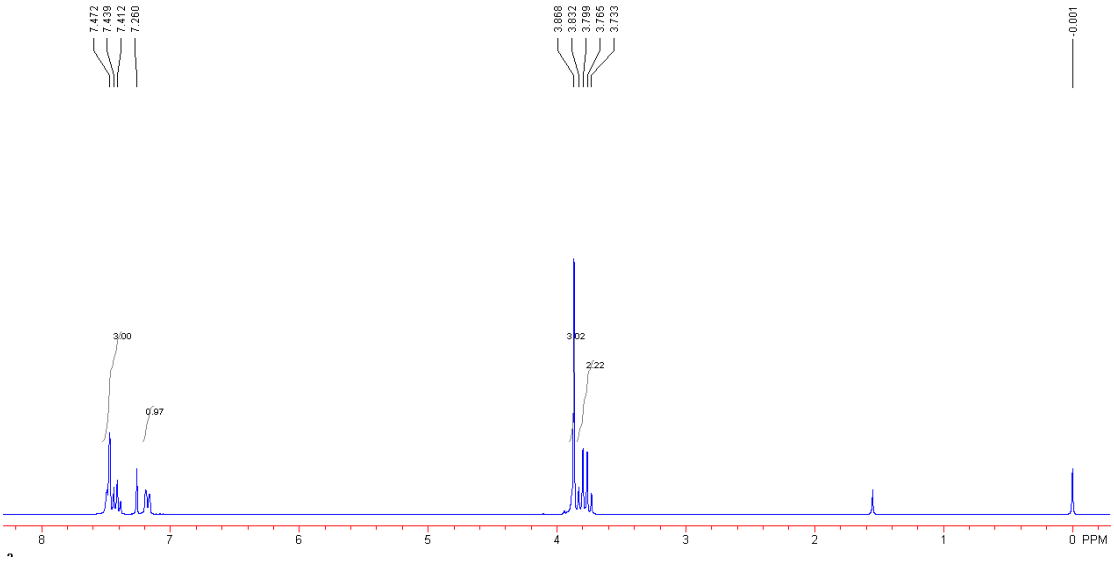
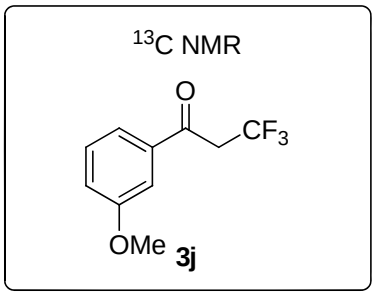
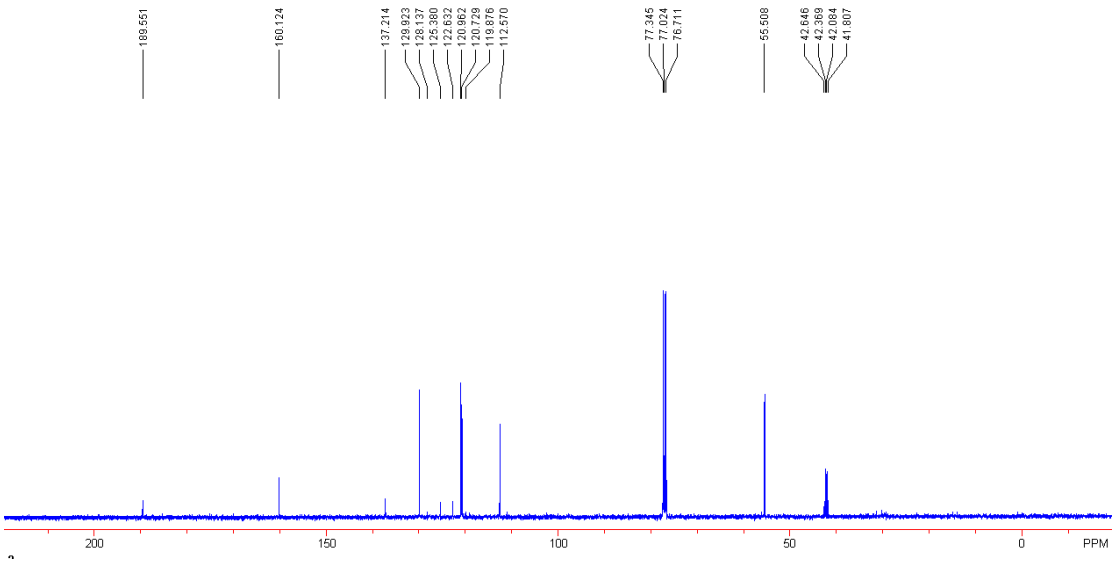
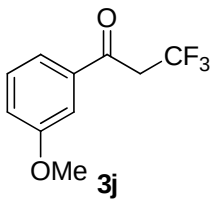






Supporting Information

^{19}F NMR



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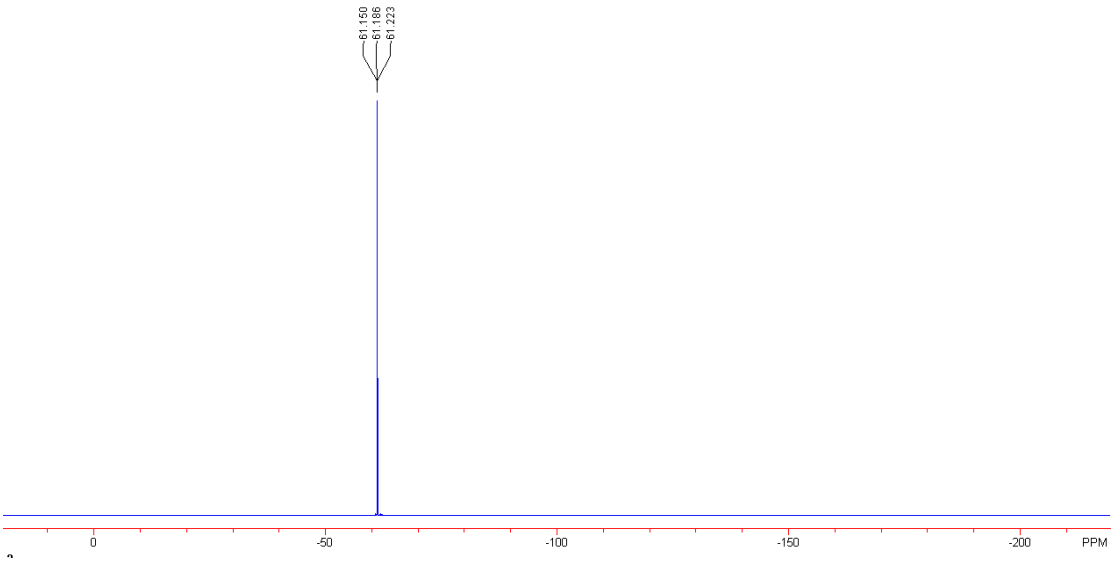
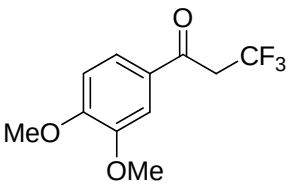


^{1}H NMR



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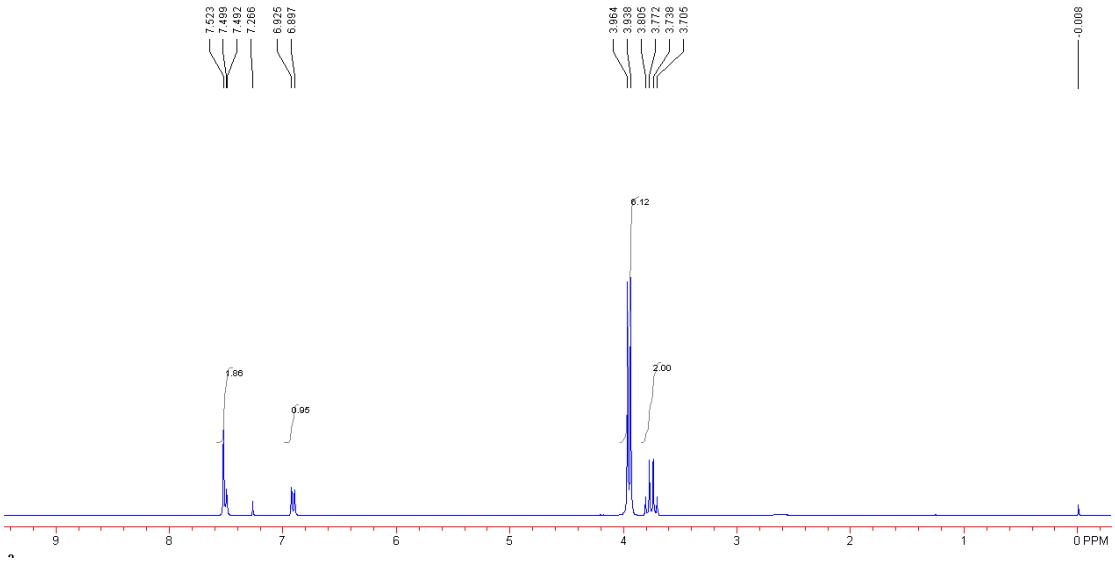
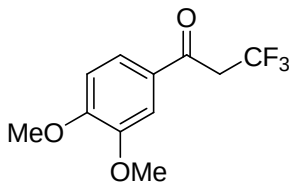


Supporting Information

^{13}C NMR



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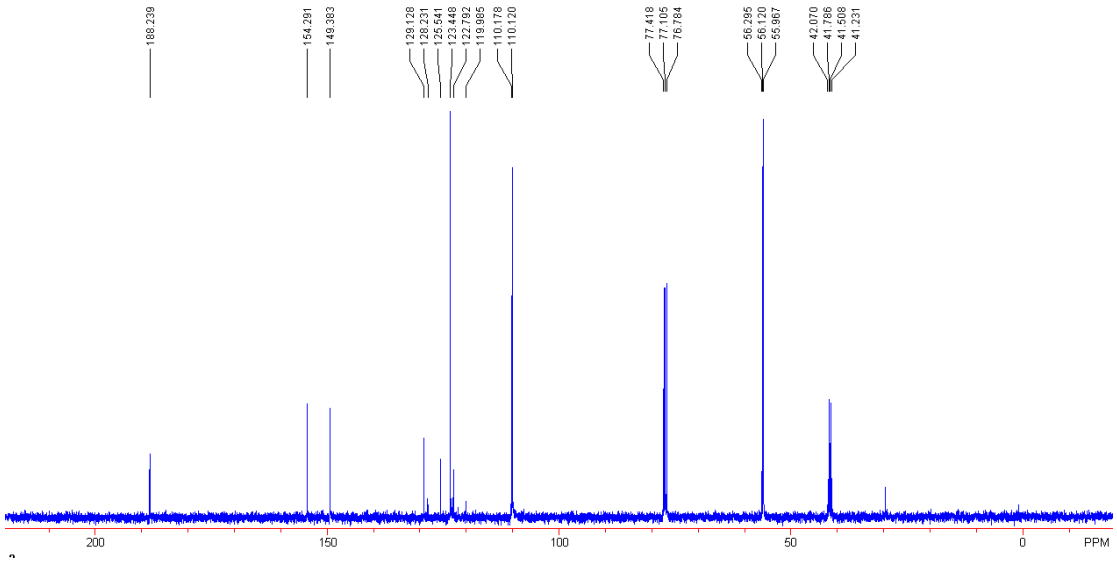

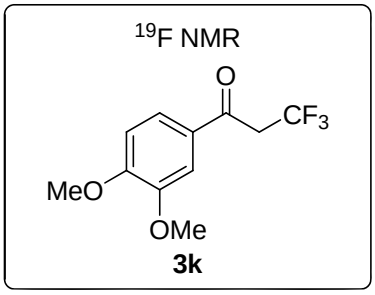

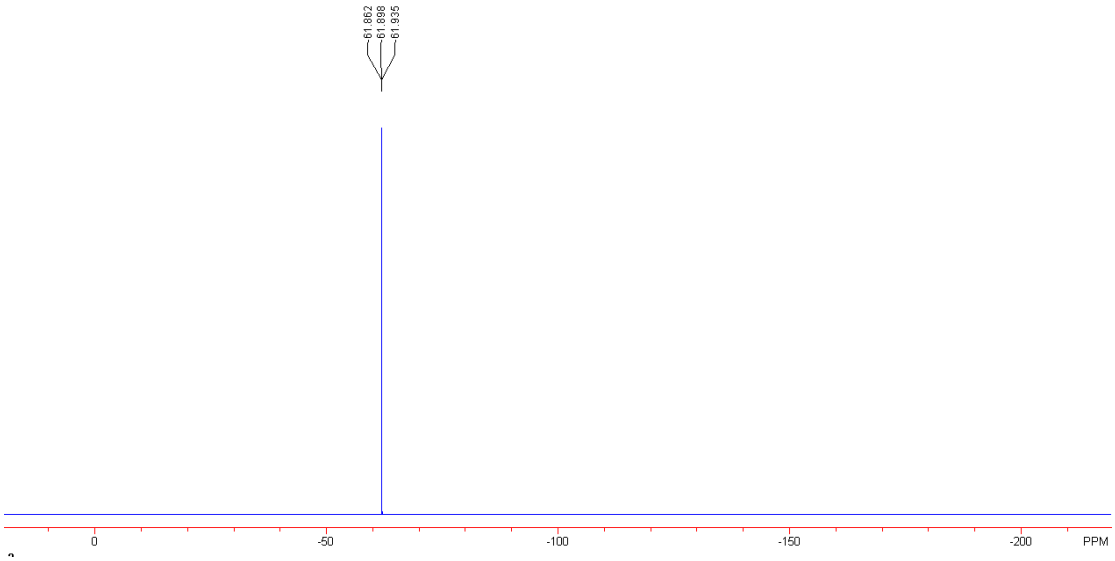

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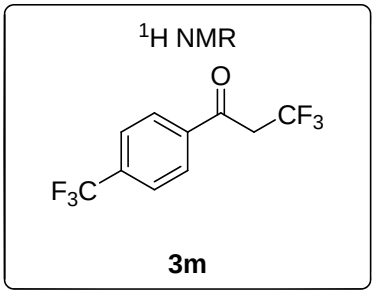
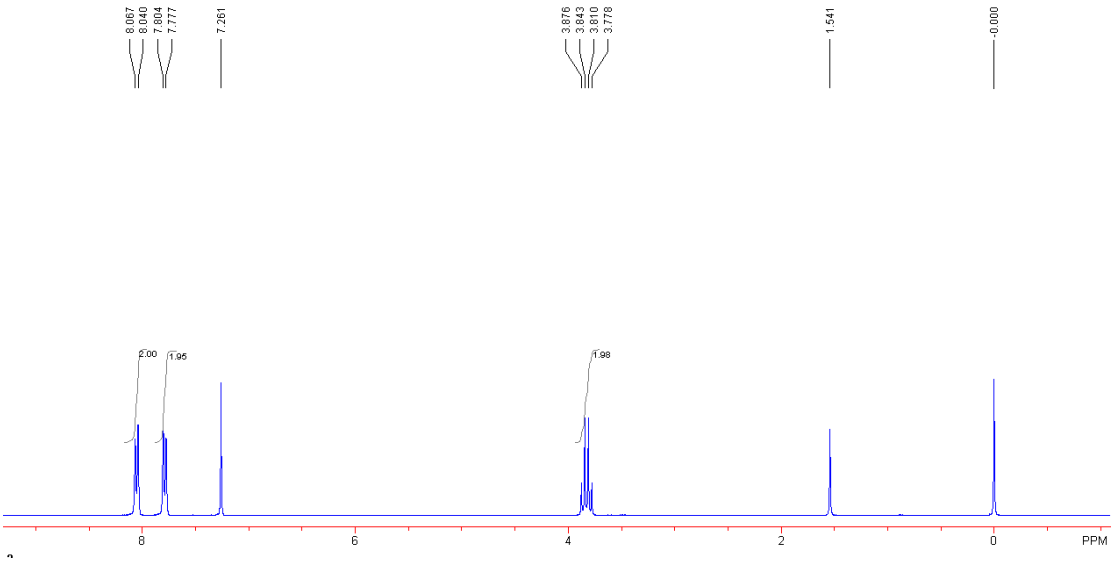
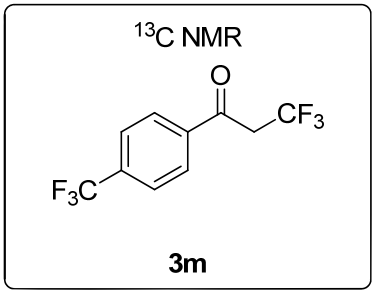
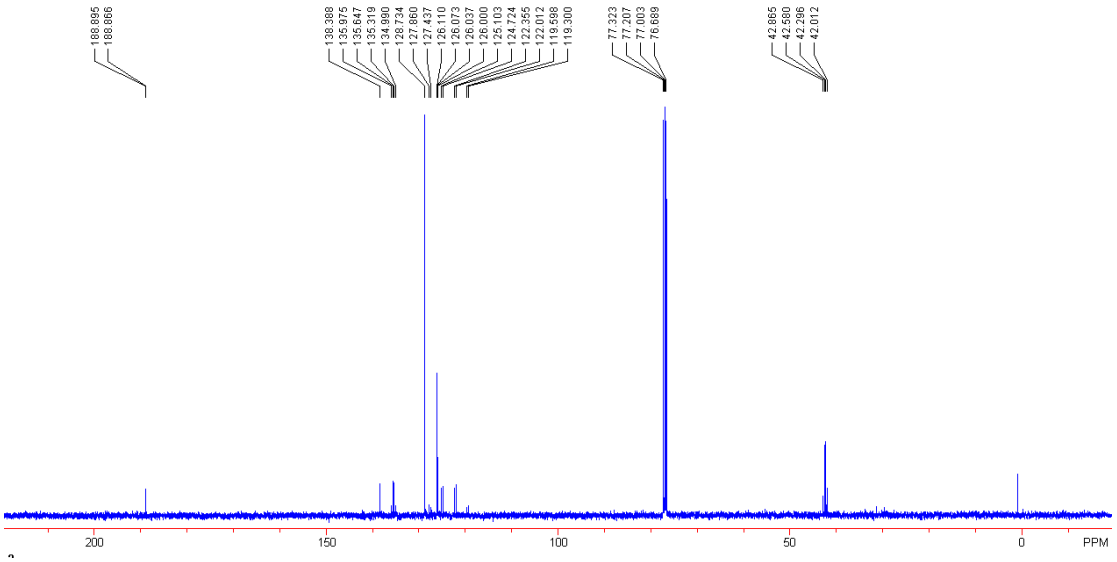
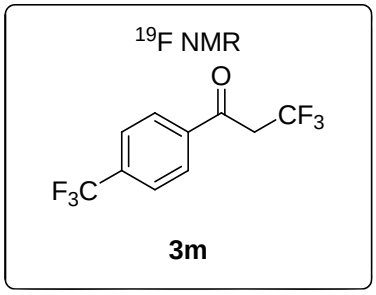
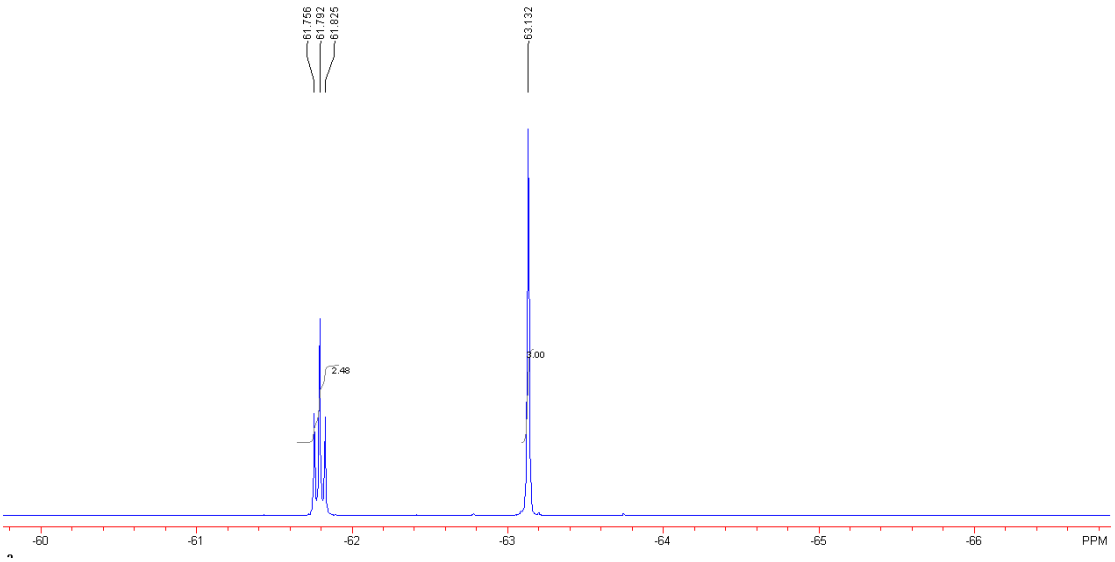









19F NMR
O
CF3
F3C
3m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3.00
-60
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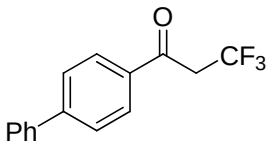
-63
-64
-65
-66
PPM

^{1}H NMR



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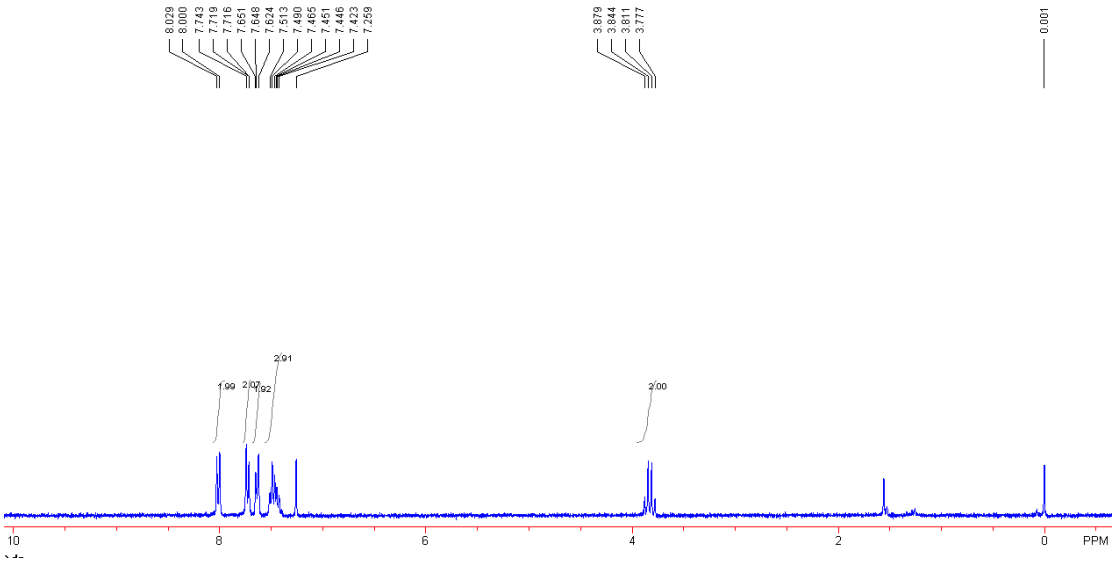
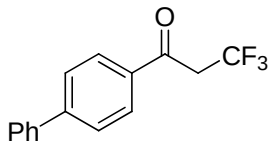


Supporting Information

^{13}C NMR



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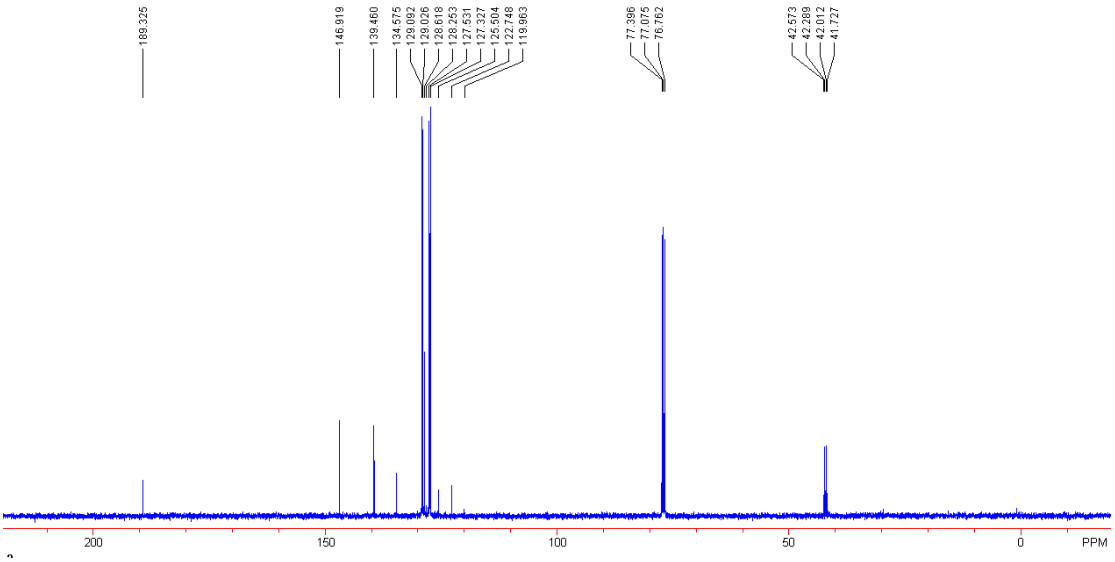
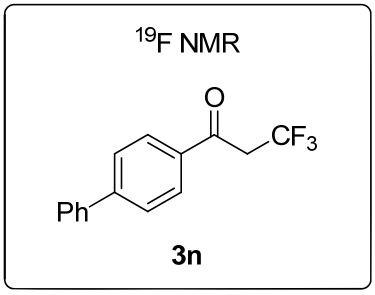
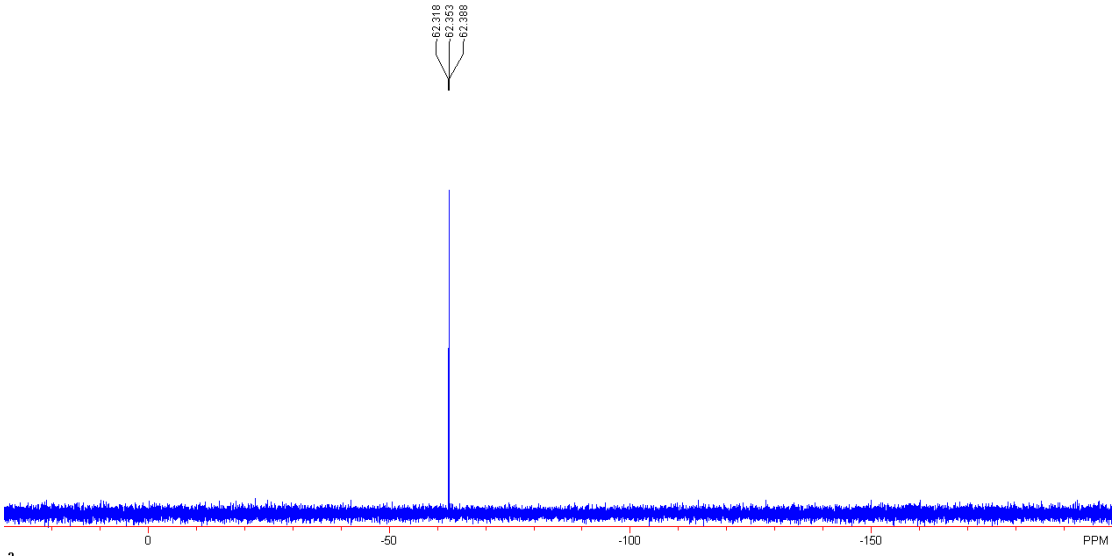
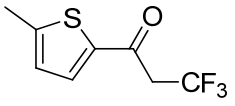






Supporting Information

^{1}H NMR



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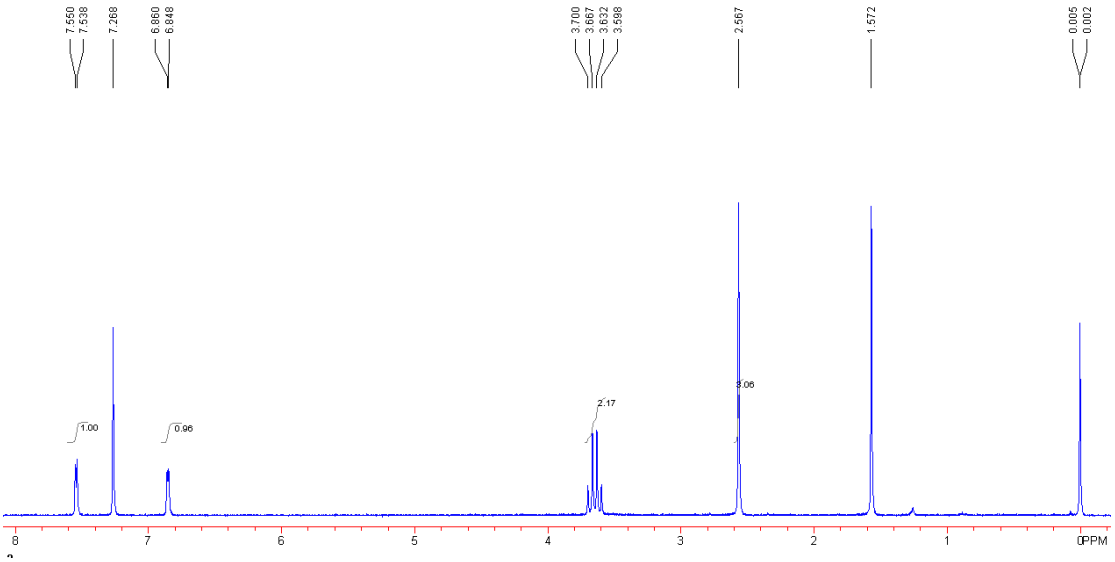
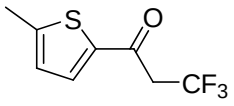


^{13}C NMR



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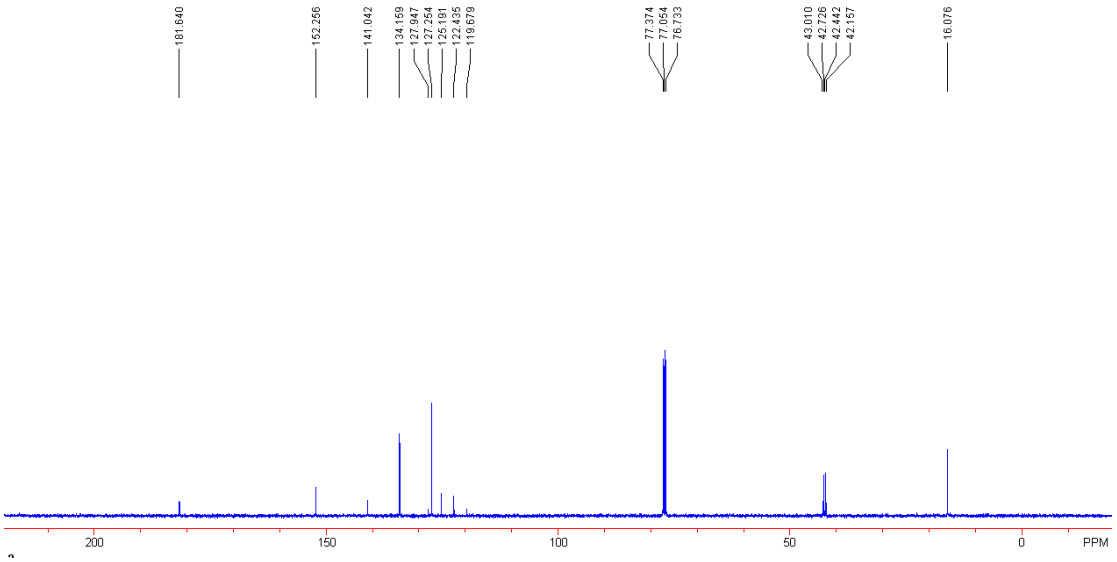
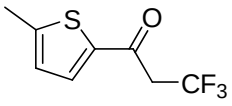


Supporting Information

^{19}F NMR



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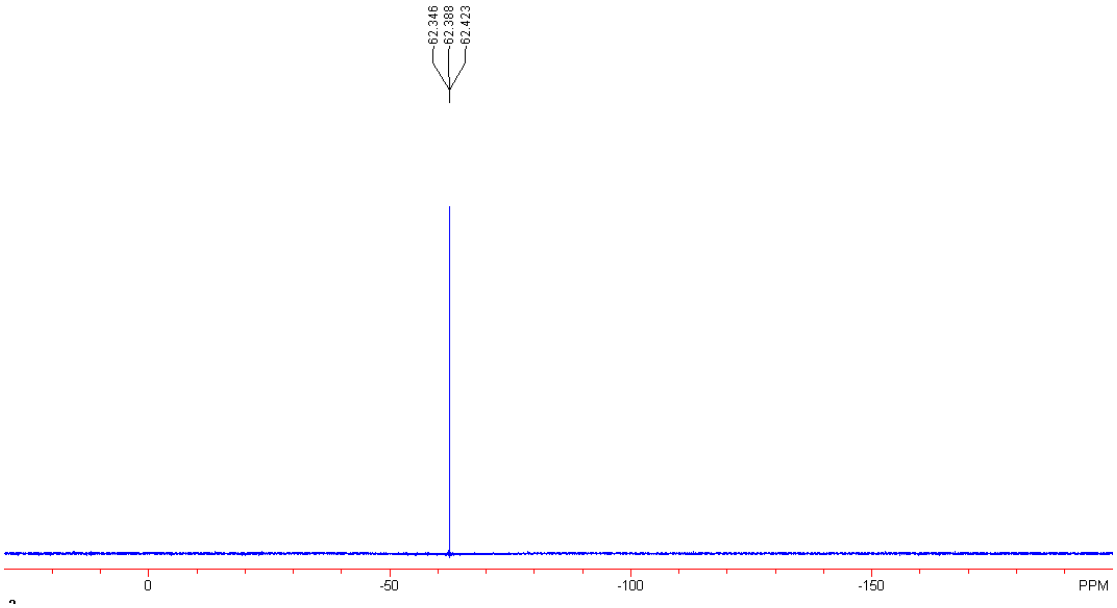

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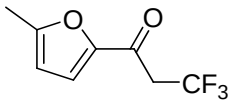

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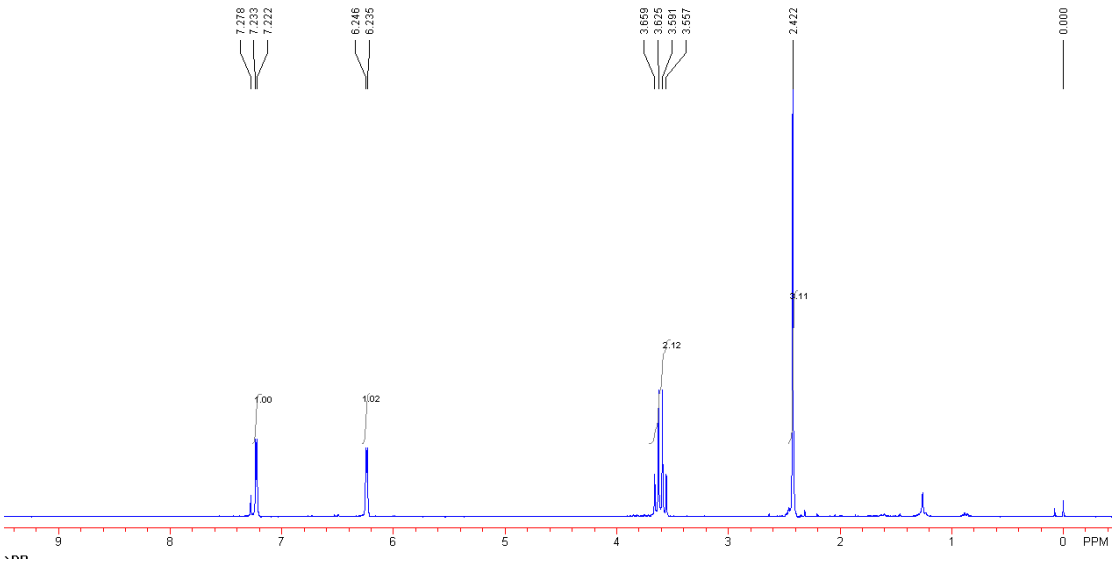
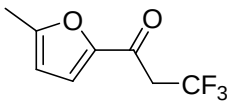


Supporting Information

^{13}C NMR



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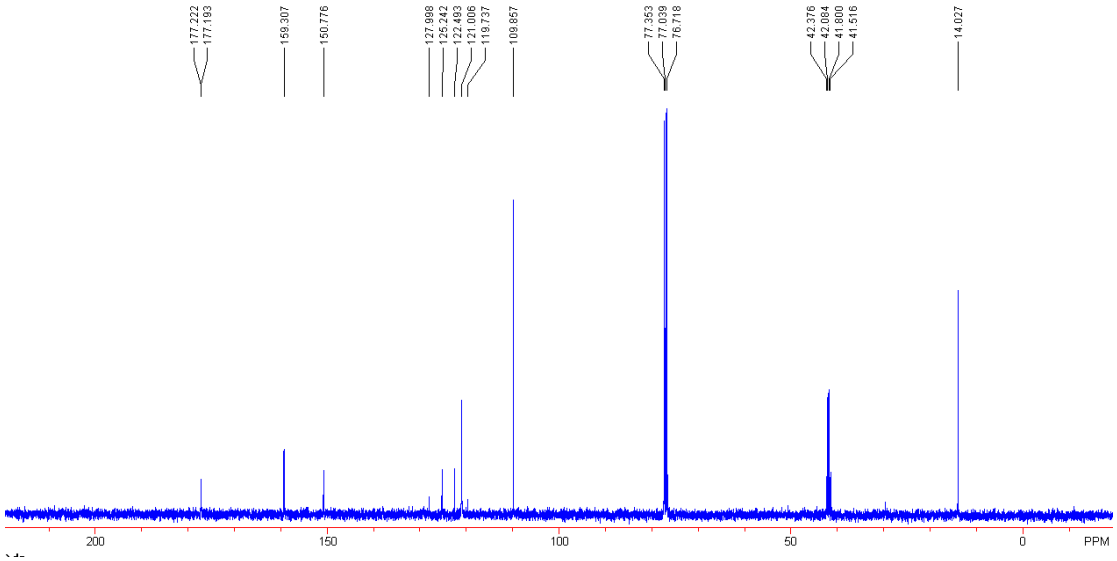
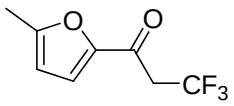


^{19}F NMR



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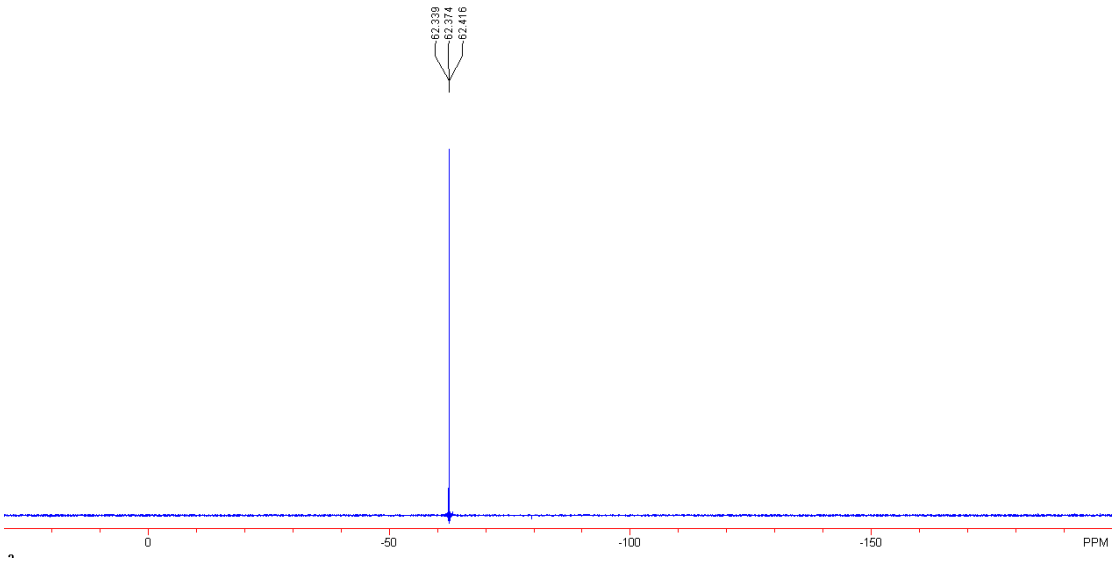
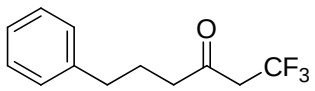
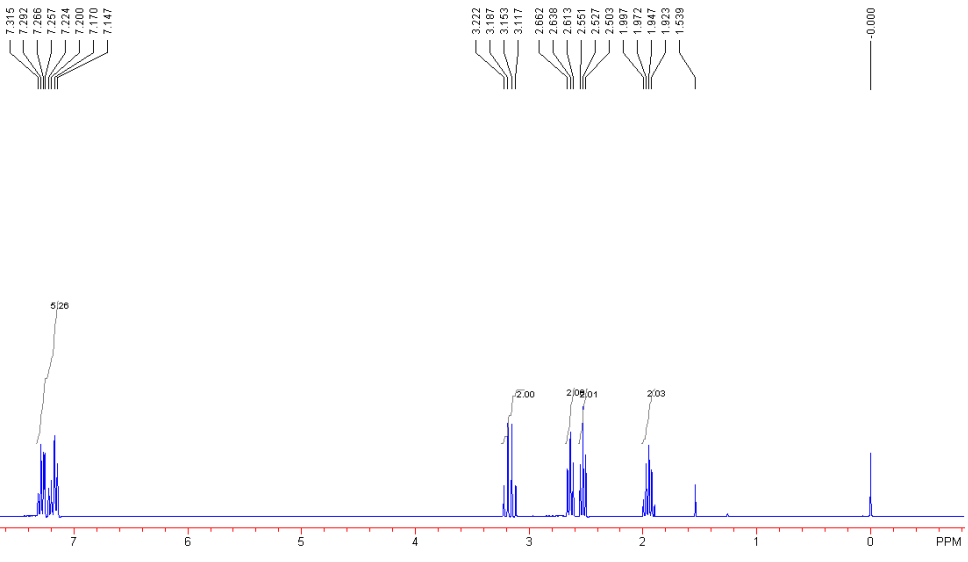


Supporting Information

^{1}H NMR



5c



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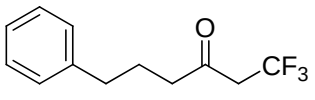

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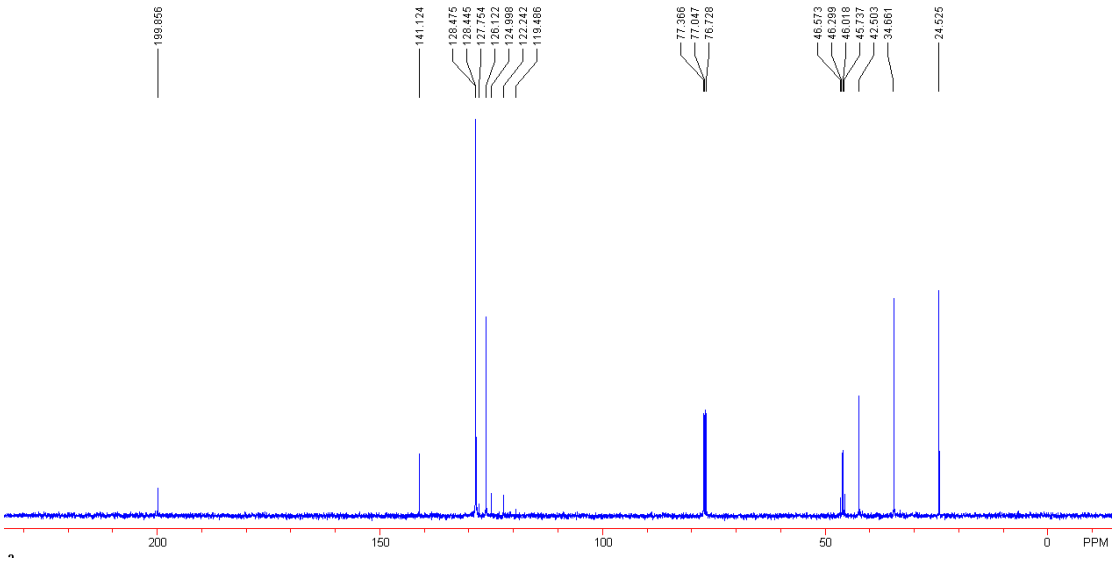
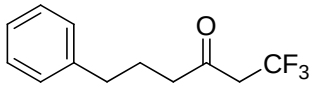


Supporting Information

^{19}F NMR



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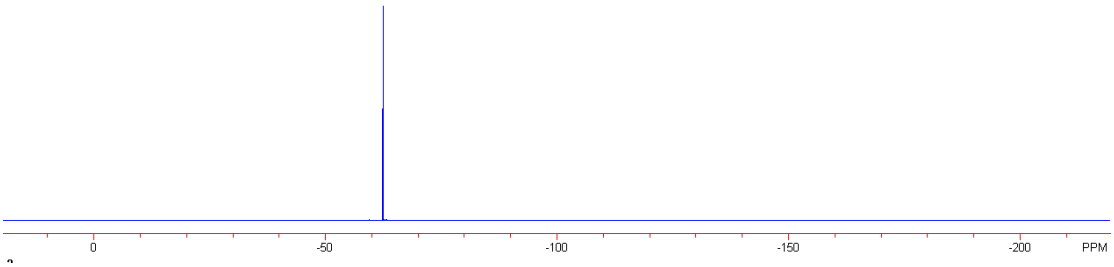
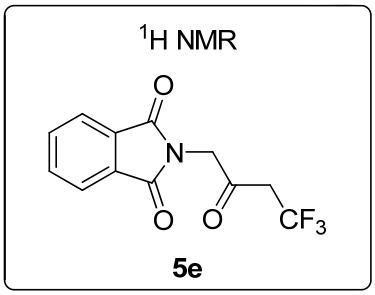
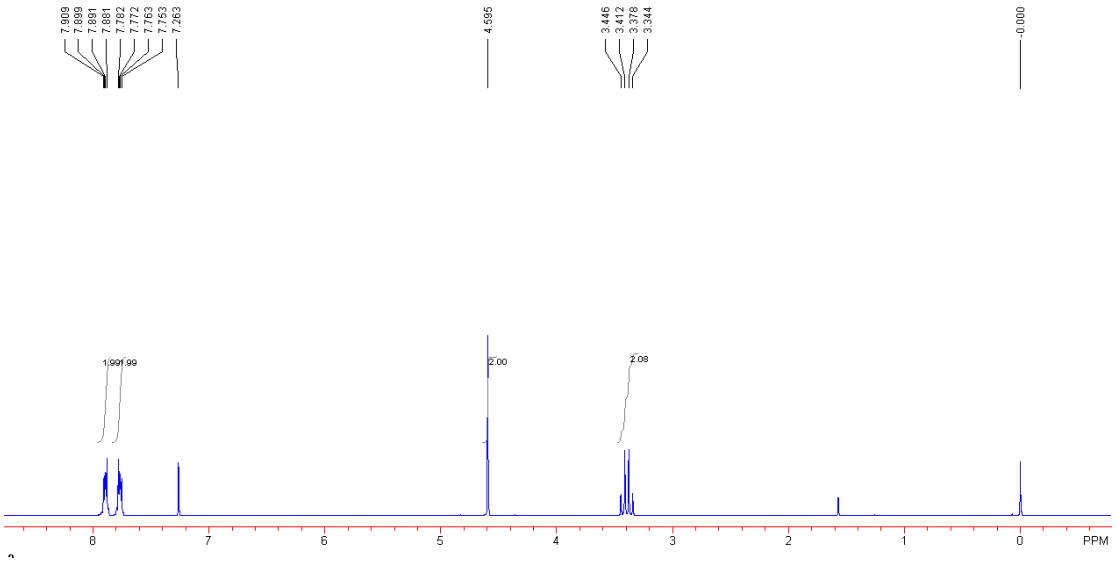
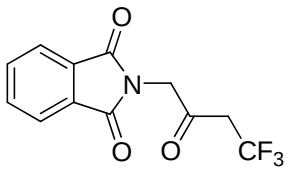






^{13}C NMR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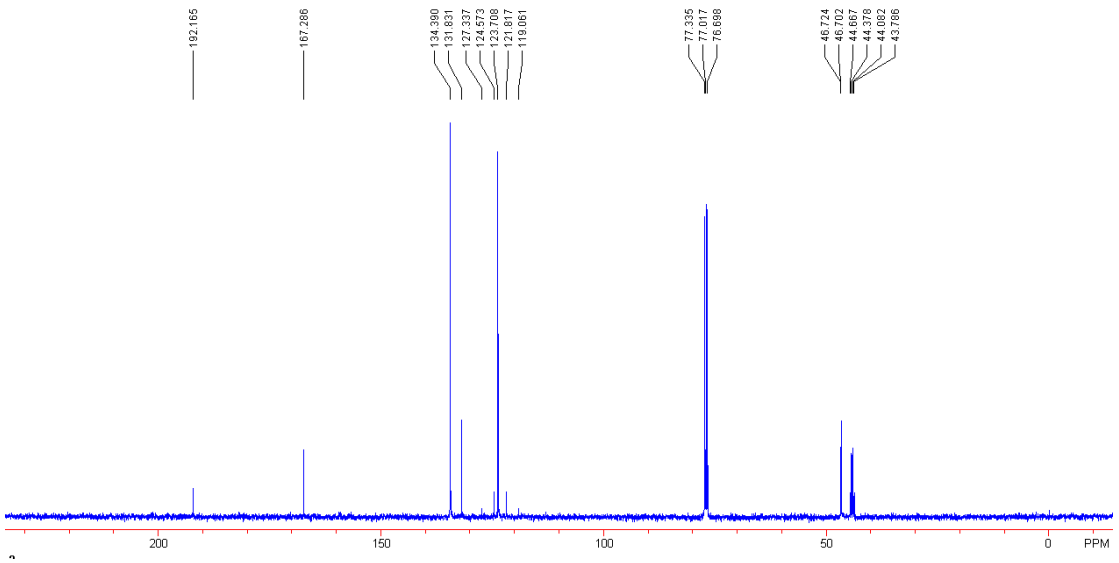
N
O
O
CF3

5e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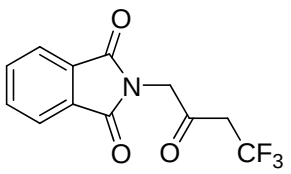
PPM

^{19}F NMR



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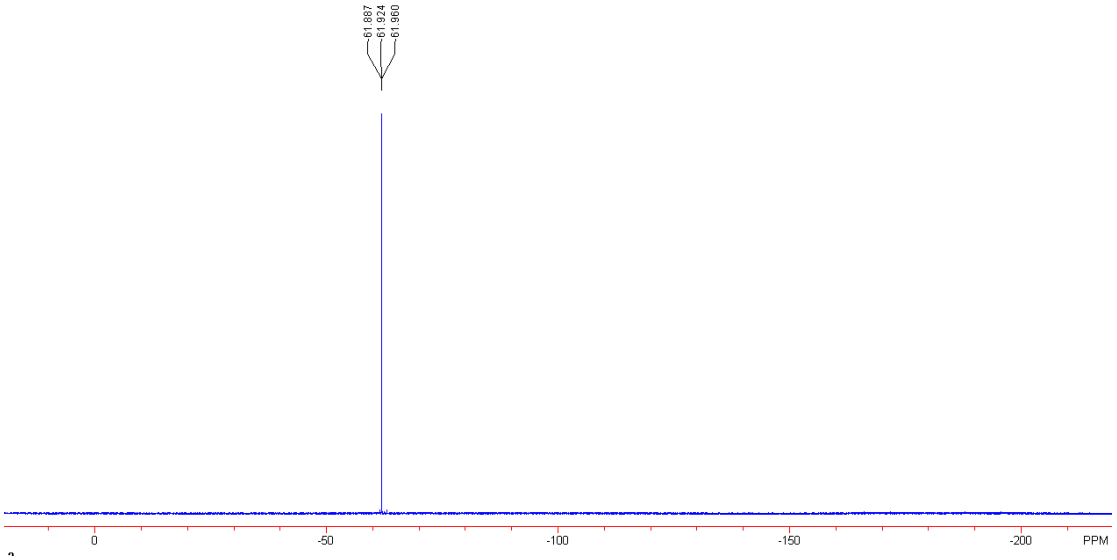
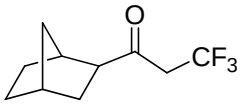
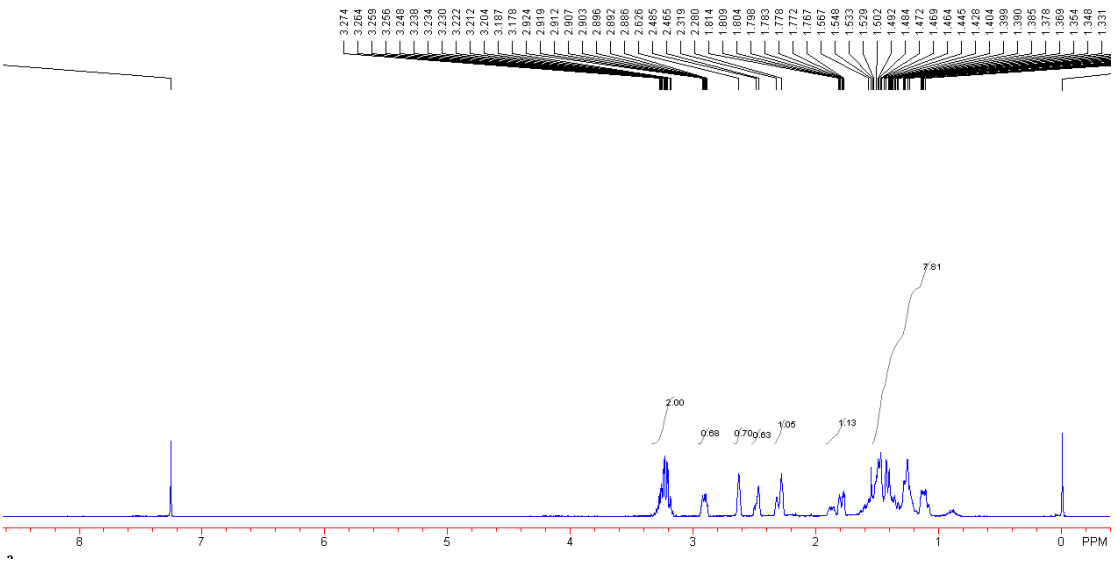


Supporting Information

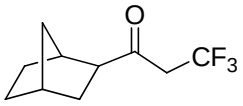
^{1}H NMR



5i



^{13}C NMR



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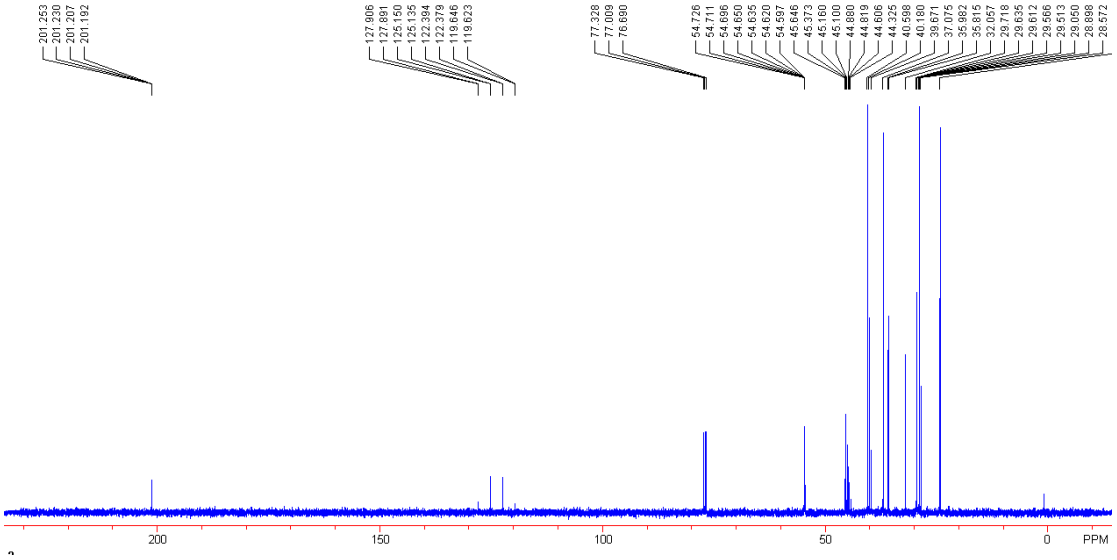
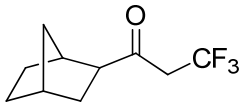


^{19}F NMR



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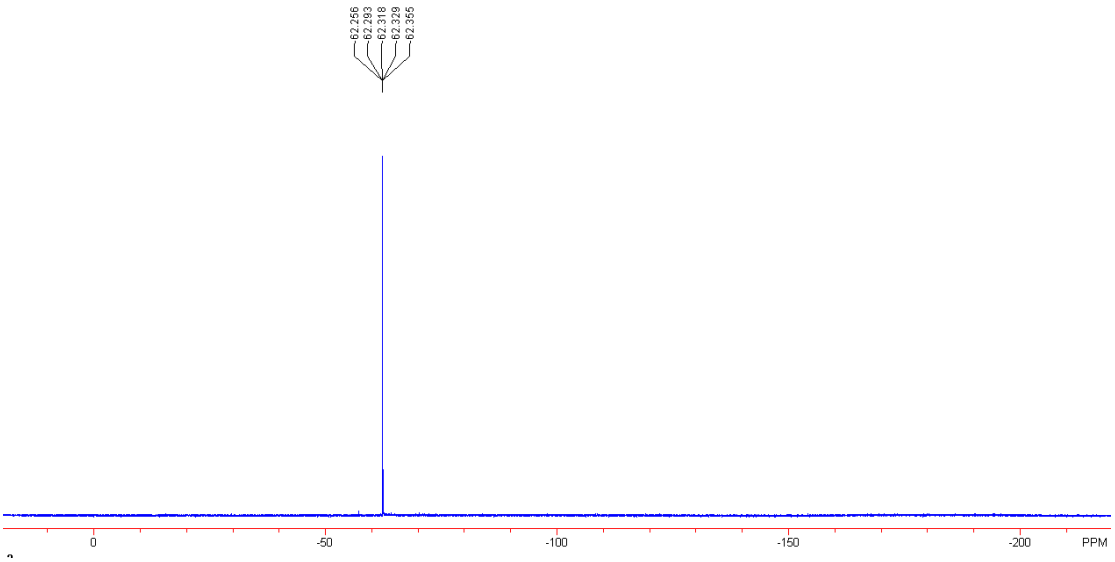
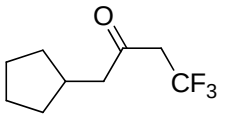


^{1}H NMR



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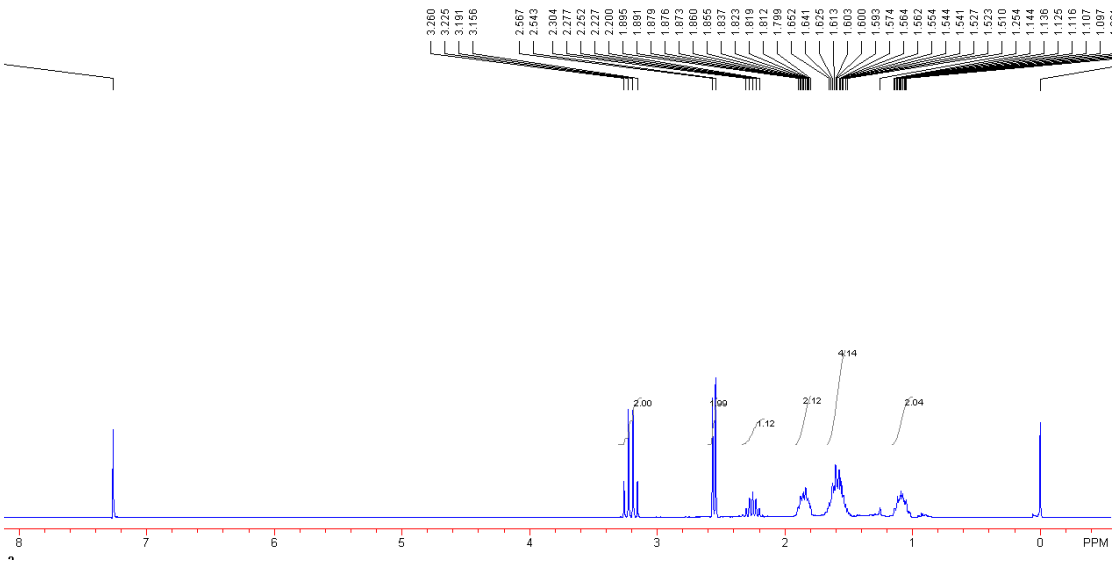
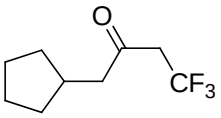


Supporting Information

^{13}C NMR



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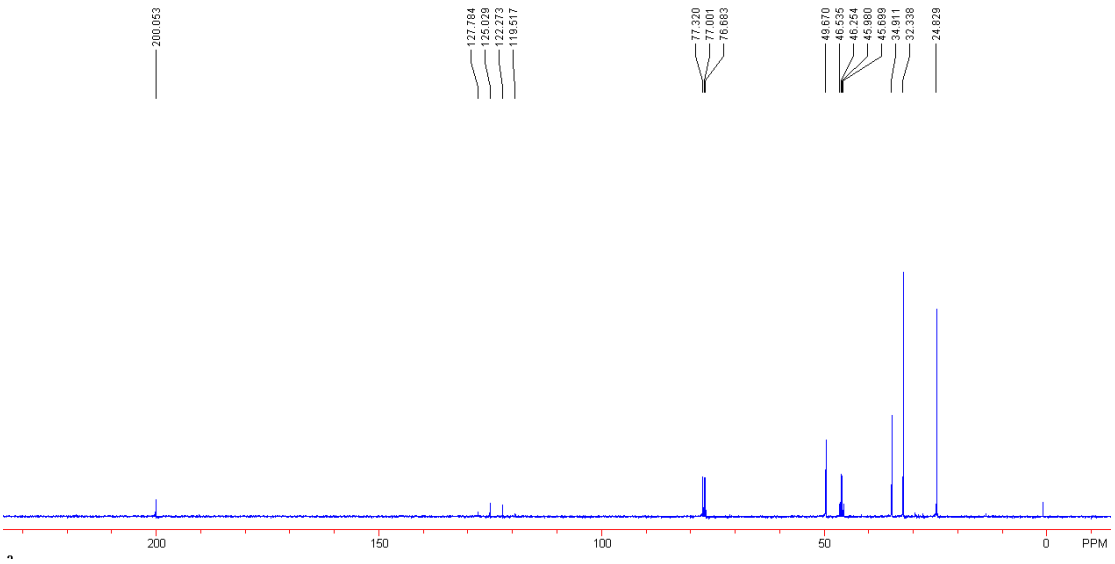
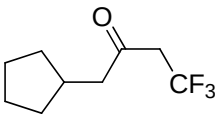


^{19}F NMR



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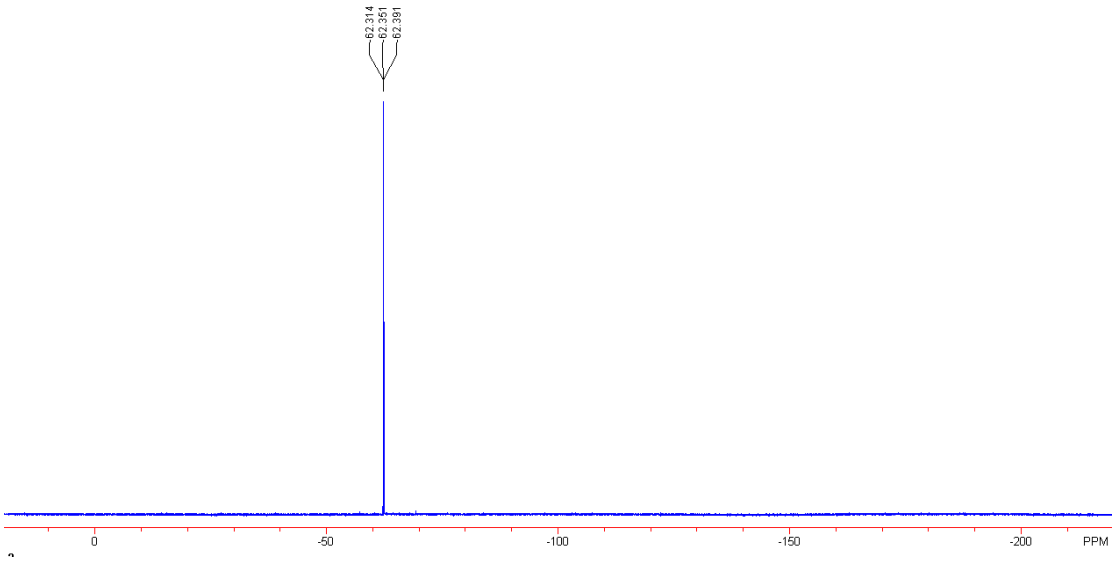

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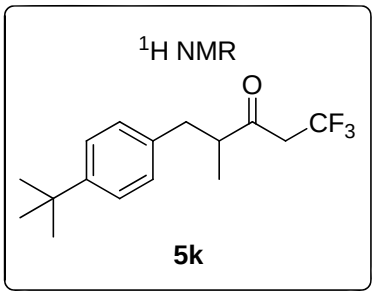

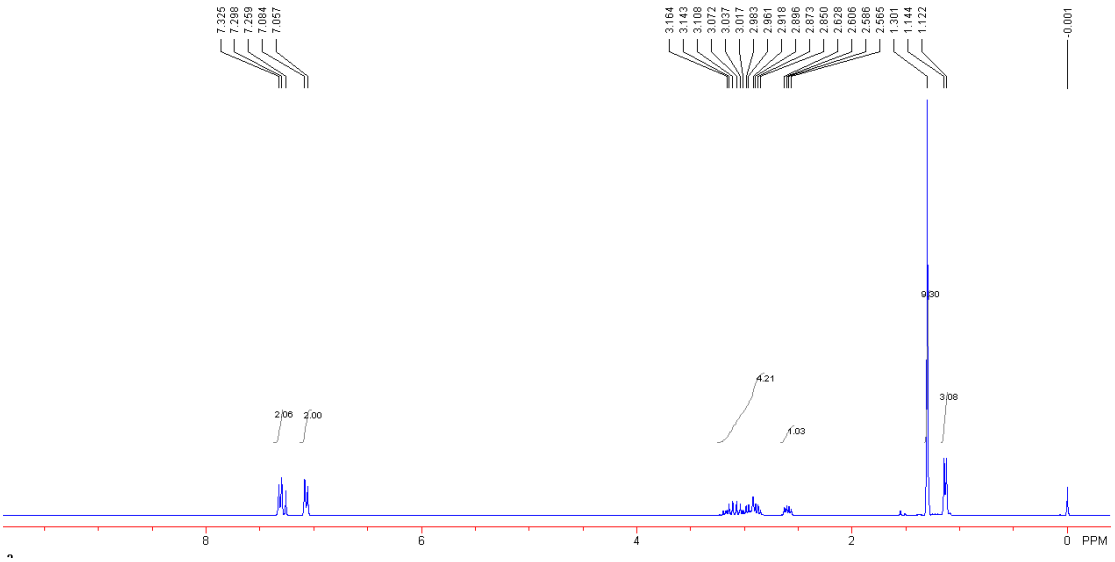

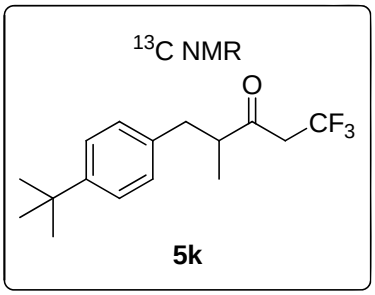

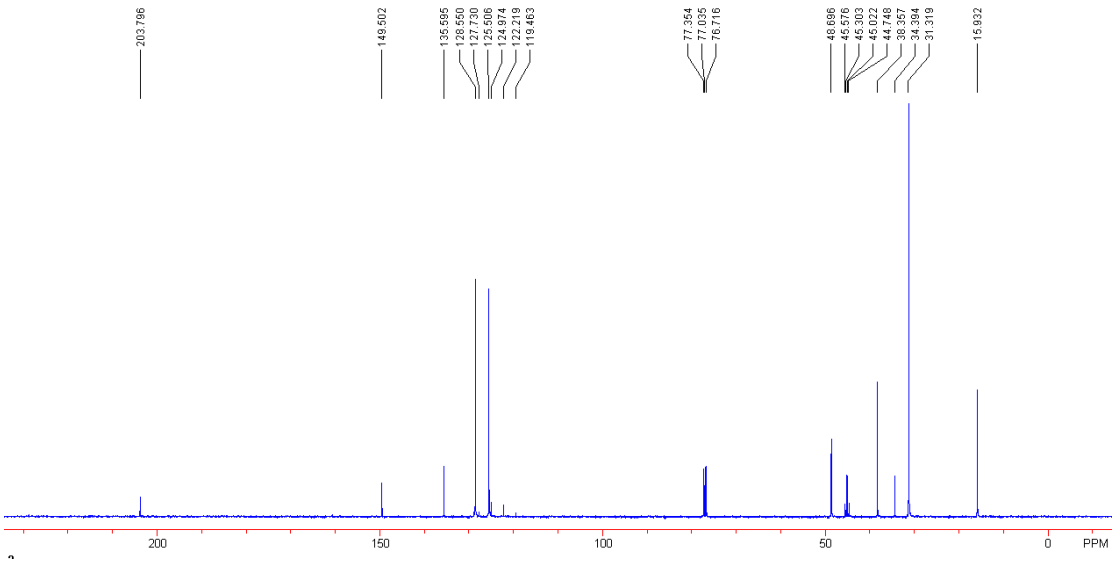

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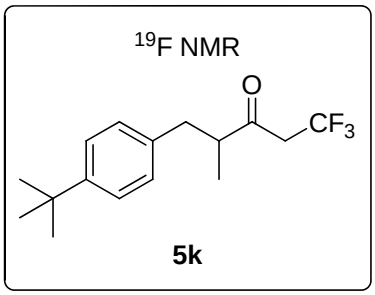
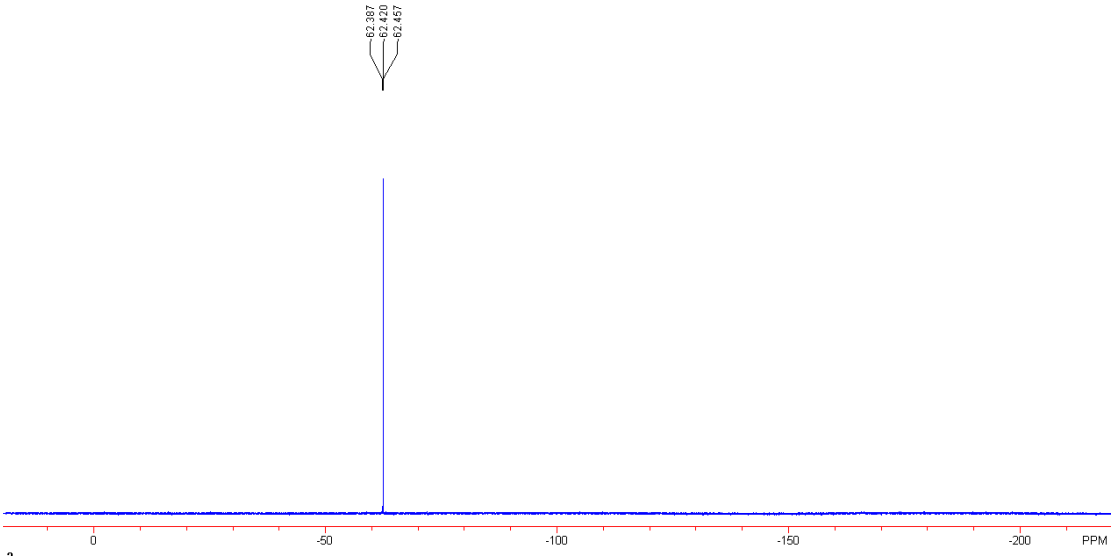
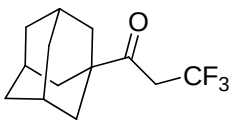




^{1}H NMR



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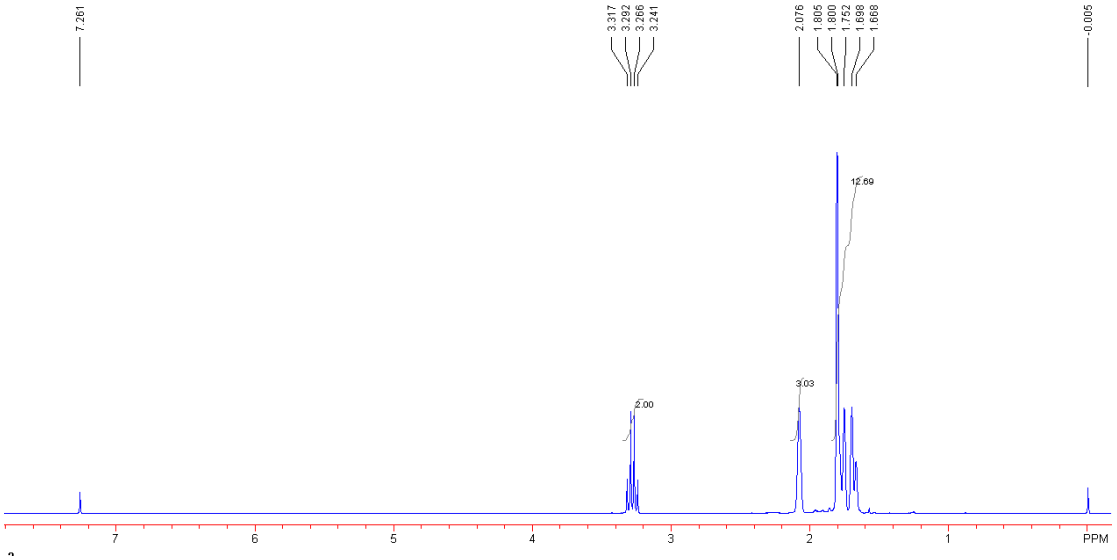
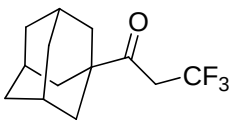


Supporting Information

^{13}C NMR



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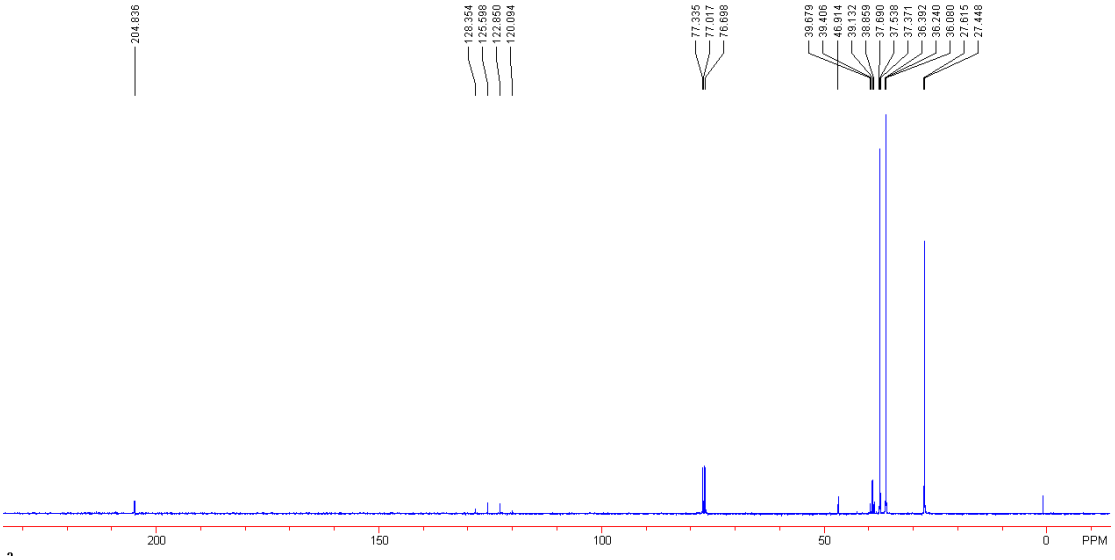
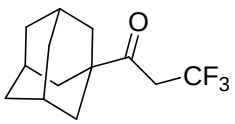


^{19}F NMR



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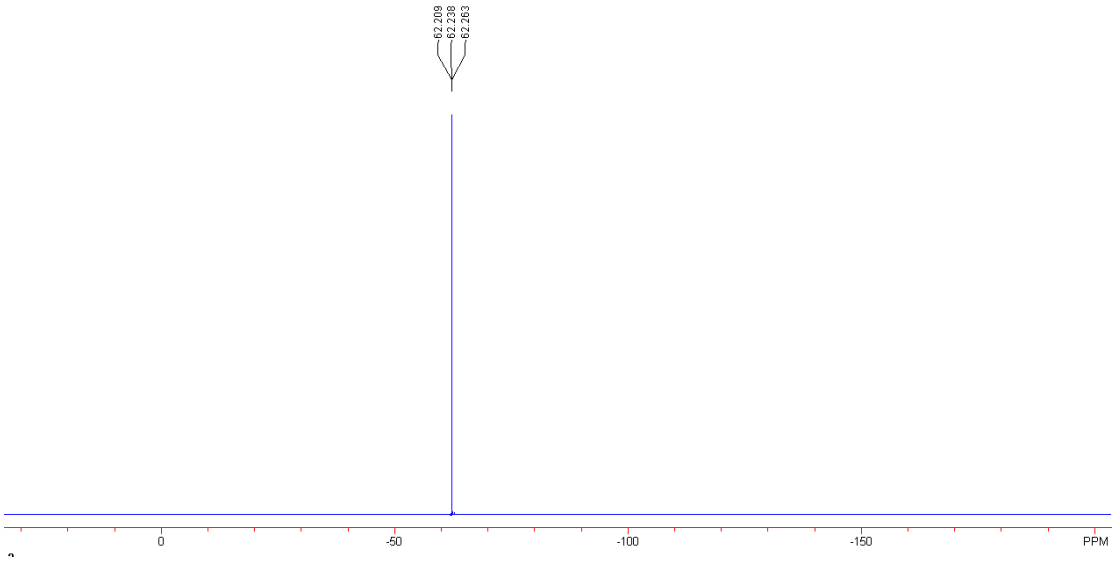
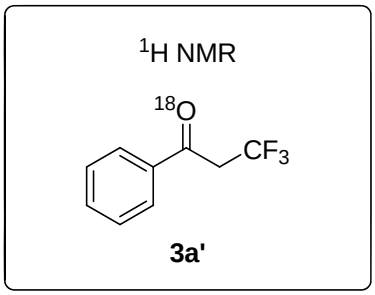
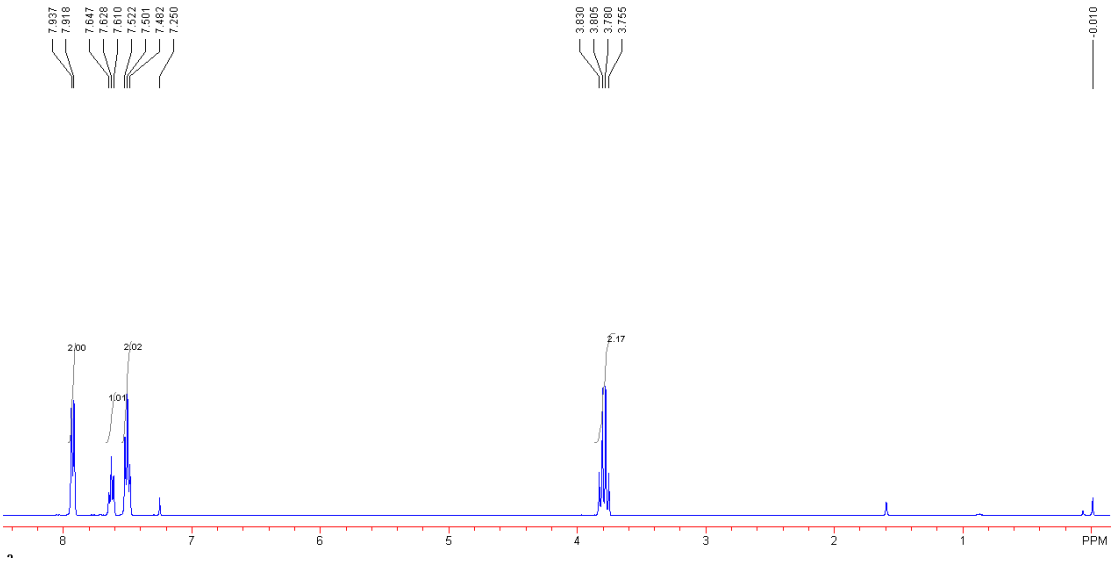
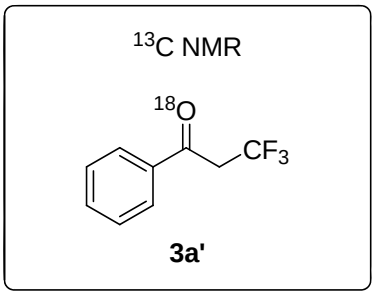
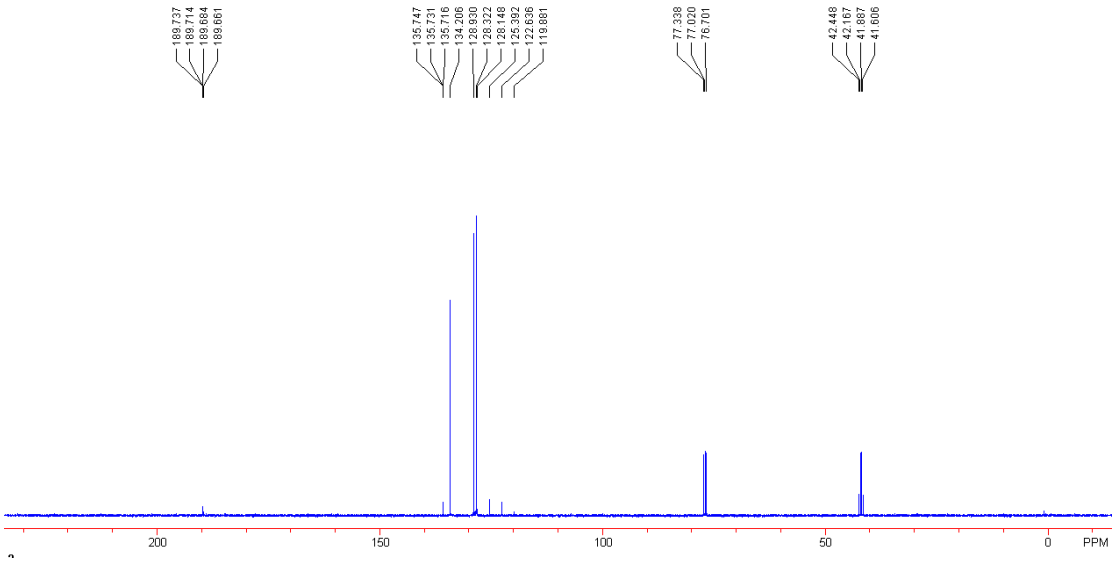


Supporting Information









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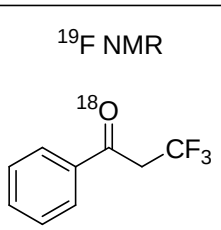
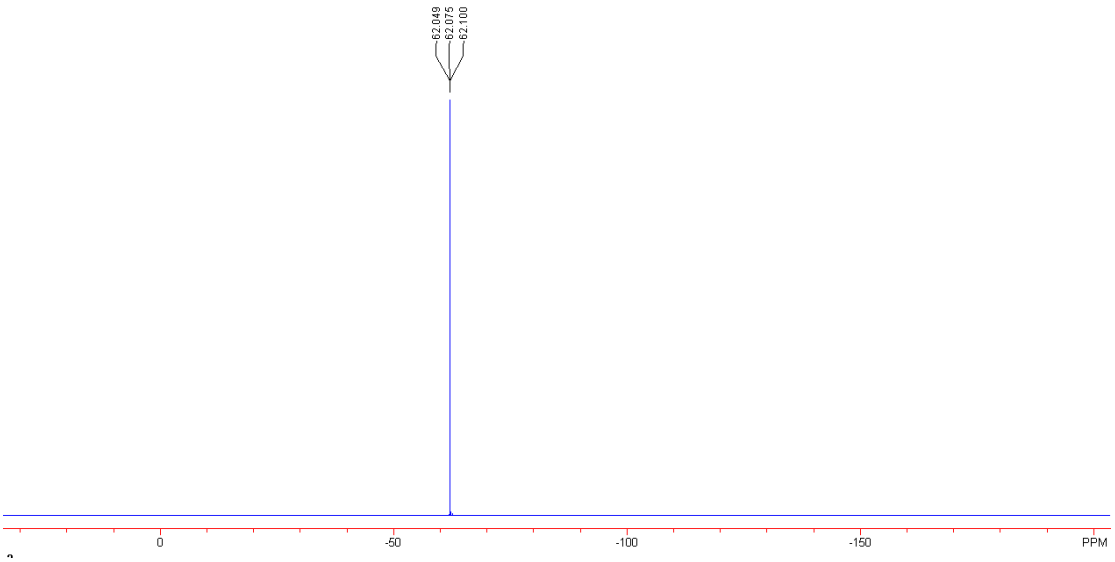


3a'



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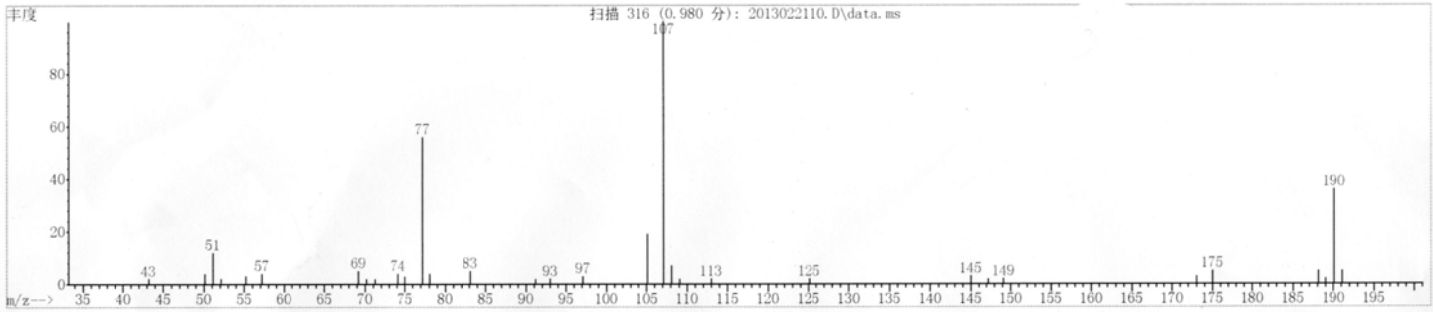
Acquired : 22 Feb 2013 9:53
Sample Name : 2012042H03-30 M.W.190
Instrument : Agilent Technologies 5973N
: Shanghai Mass spectrometry Center, Shanghai Institute of Organic Chemistry

Base m/z:107.1 Inten:9307



m/z	RA%	m/z	RA%	m/z	RA%	m/z	RA%	m/z	RA%	m/z	RA%	m/z	RA%	m/z	RA%	m/z	RA%
43	1.95	50	4.39	51	11.55	52	1.65	55	2.86	57	3.55	69	4.8	70	2.33	71	1.84
74	3.7	75	2.73	77	56.46	78	3.71	83	5.09	91	2.15	93	2.36	97	3.09	105	18.78
107	100	108	6.76	109	2.2	113	2.47	125	1.71	145	2.91	147	1.81	149	2.38	173	2.78
175	4.84	188	4.73	189	1.74	190	36.34	191	5.03								

8 Peak Value:

107 100 77 56.46 190 36.34 105 18.78 51 11.55 108 6.76 83 5.09 191 5.03