Supporting Information

Oxidative Trifluoromethylselenolation of 1,3-Dicarbonyls with $[Me_4N][SeCF_3]$

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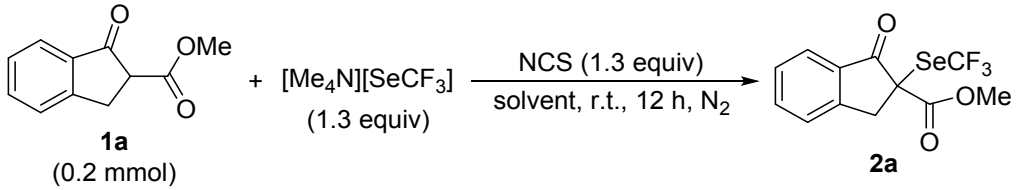
1. General information

All reactions were carried out under a nitrogen atmosphere. Unless otherwise specified, NMR spectra were recorded in $CDCl_3$ on a 500 MHz (for ^1H), 471 MHz (for ^{19}F), and 126 MHz (for ^{13}C) spectrometer. All chemical shifts were reported in ppm relative to TMS (0 ppm) for ^1H NMR and $PhOCF_3$ (-58.0 ppm) for ^{19}F NMR as an internal or external standard. The HPLC experiments were carried out on a Wufeng LC-100 II instrument (column: Shodex, C18, 5 μm, 4.6 × 250 mm), and yields of the product were determined by using the corresponding pure compound as the external standard. Melting points of the products were measured and uncorrected. MS experiments were performed on a TOF-Q ESI instrument. $[Me_4N][SeCF_3]$, $[Me_4N][SCF_3]$ and $CsOCF_3$ were prepared according to the literatures.[1] The starting materials (**1a-h**[2] and **1o**[3]) were synthesized according to the literatures. Solvents were dried before use according to the literature.[4] Other reagents in the reactions were all purchased from the commercial sources and used without further purification.

2. Screening of the optimal reaction conditions for trifluoromethylselenolation of 1a by $[Me_4N][SeCF_3]$.

Table S1 The solvent effects on trifluoromethylselenolation of **1a** by $[Me_4N][SeCF_3]$ in the presence of NCS.

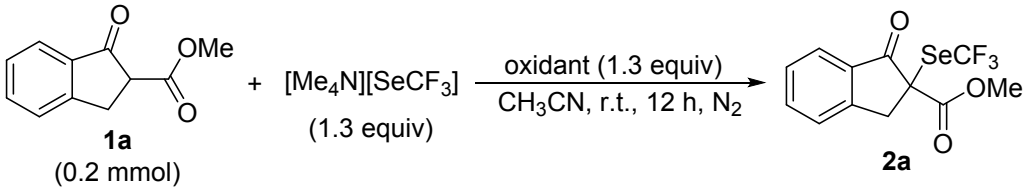


Entry [a]	Solvent	Yield (**2a**, %) [b]
1	CH_2Cl_2	67
2	CH_3CN	81
3	THF	72
4	toluene	16
5	DMF	13
6	DMSO	0

[a] Reaction conditions: a sealed tube was charged with **1a** (0.2 mmol), $[Me_4N][SeCF_3]$ (0.26 mmol) and solvent (1 mL), followed by addition of NCS (0.26 mmol) in solvent (1 mL), with vigorous stirring. The mixture was reacted at room temperature under N_2

for 12 h. [b] Yields were determined by HPLC using **2a** as an external standard (t_R = 5.30 min, λ_{max} = 210 nm, water/methanol (v/v) = 20:80).

Table S2. Trifluoromethylselenolation of **1a** by $[Me_4N][SeCF_3]$ in the presence of different oxidants.

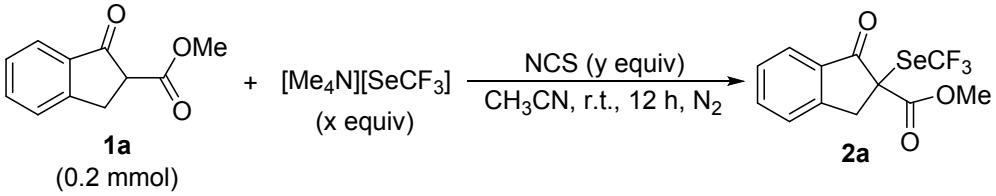


Entry [a]	Oxidant	Yield (**2a**, %) [b]
1	$PhI(OAc)_2$	73
2	$PhI(OCOCF_3)_2$	52
3	$PhICl_2$	16
4	NCS	81
5	NBS	82
6	NIS	72
7	NFSI	81
8	Selectfluor	55
9 [c]	TCCA	87
10	*t*-BuOCl	54
11	DDQ	38
12	NHS	0
13	DMP	0
14	$KMnO_4$	0
15	$K_2S_2O_8$	0
16	$AgNO_3$	0
17	TBHP	trace
18	H_2O_2	trace
19	*m*-CPBA	0
20 [d]	O_2	0

[a] Reaction conditions: a sealed tube was charged with **1a** (0.2 mmol), $[Me_4N][SeCF_3]$ (0.26 mmol) and CH_3CN (1 mL), followed by addition of oxidant (0.26 mmol) in CH_3CN (1 mL), with vigorous stirring. The mixture was reacted at room temperature

under N_2 for 12 h. [b] Yields were determined by HPLC using **2a** as an external standard (t_R = 5.30 min, λ_{max} = 210 nm, water/methanol (v/v) = 20:80). [c] TCCA (0.087 mmol). [d] An O_2 balloon (1 atm) was used.

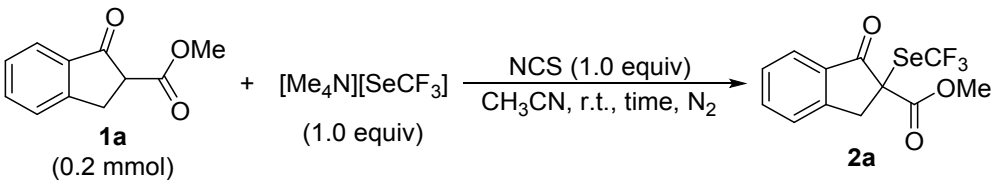
Table S3. Trifluoromethylselenolation of **1a** by $[Me_4N][SeCF_3]$ and NCS with different reactant ratios.



Entry [a]	x/y	Yield (**2a**, %) [b]
1	1.3/1.3	81
2	1.5/1.5	90
3	1.5/1.3	52
4	1.3/1.5	89
5	1.3/1.7	66
6	1.0/1.0	91
7	1.0/1.3	80
8	1.3/1.0	22
9	1.1/1.1	89

[a] Reaction conditions: a sealed tube was charged with **1a** (0.2 mmol), $[Me_4N][SeCF_3]$ (0.26, 0.3, 0.2 or 0.22 mmol) and CH_3CN (1 mL), followed by addition of NCS (0.26, 0.3, 0.34, 0.2 or 0.22 mmol) in CH_3CN (1 mL), with vigorous stirring. The mixture was reacted at room temperature under N_2 for 12 h. [b] Yields were determined by HPLC using **2a** as an external standard (t_R = 5.30 min, λ_{max} = 210 nm, water/methanol (v/v) = 20:80).

Table S4 Trifluoromethylselenolation of **1a** by $[Me_4N][SeCF_3]$ and NCS at different reaction times.

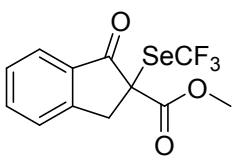


Entry [a]	Time	Yield (**2a**, %) [b]
1	2 min	60
2	5 min	56
3	15 min	83
4	1 h	86 (84)
5	3 h	85
6	6 h	88
7	9 h	85
8	12 h	91
9 [c]	1 h	(88)

[a] Reaction conditions: a sealed tube was charged with **1a** (0.2 mmol), $[Me_4N][SeCF_3]$ (0.2 mmol) and CH_3CN (1 mL), followed by addition of NCS (0.2 mmol) in CH_3CN (1 mL), with vigorous stirring. The mixture was reacted at room temperature under N_2 for times as described above. [b] Yields were determined by HPLC using **2a** as an external standard (t_R = 5.30 min, λ_{max} = 210 nm, water/methanol (v/v) = 20:80). Isolated yields are depicted in the parenthesis. [c] The reaction was run under an air atmosphere. Besides 88% of **2a**, 4% of methyl 2-chloro-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate (**2a'**) was also obtained in this reaction.

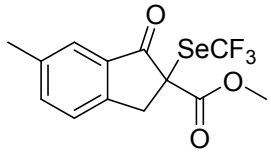
3. General procedures for oxidative trifluoromethylchalcogenation of 1 by $[Me_4N][XCF_3]$ and NCS.

Procedure A: In a nitrogen-filled glovebox, a sealed tube was charged with **1** (0.2 mmol), $[Me_4N][SeCF_3]$ (44.4 mg, 0.2 mmol) and CH_3CN (1 mL), followed by addition of NCS (26.7 mg, 0.2 mmol) in CH_3CN (1 mL), with vigorous stirring. The mixture was reacted at room temperature for 1 h and concentrated to dryness under reduced pressure. The residue was purified by flash column chromatography on silica gel using a mixture of petroleum ether/ethyl acetate or hexane/diethyl ether as eluents to give the trifluoromethylselenolated products (**2**).

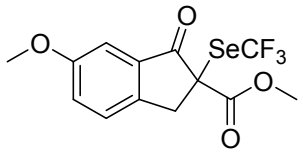


Methyl 1-oxo-2-((trifluoromethyl)selanyl)-2,3-dihydro-1*H*-indene-2-carboxylate (**2a**).

Yellow liquid (56.6 mg, 84% yield), petroleum ether/ethyl acetate = 10:1 (v/v) as eluents for column chromatography. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 (d, *J* = 7.8 Hz, 1H), 7.70 (t, *J* = 7.4 Hz, 1H), 7.50 (d, *J* = 7.7 Hz, 1H), 7.45 (t, *J* = 7.5 Hz, 1H), 4.20 (d, *J* = 18.1 Hz, 1H), 3.78 (s, 3H), 3.78 (d, *J* = 18.1 Hz, 1H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -31.6 (s, 3F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 196.2, 168.3, 151.5, 136.3, 133.2, 128.5, 126.2, 125.6, 122.5 (q, *J* = 333.2 Hz), 60.1, 54.2, 40.7. IR (KBr): 3084, 3041, 2958, 2922, 2848, 1732, 1715, 1602, 1588, 1479, 1466, 1330, 1301, 1273, 1261, 1215, 1185, 1158, 1138, 1122, 1102, 1068, 1022, 1004, 962, 941, 883, 876, 846, 818, 784, 752, 738, 691, 684, 623, 596, 558 cm^{-1}. HRMS-ESI (m/z) calcd. for $C_{12}H_9F_3NaO_3Se$ ($[M + Na]^+$): 360.9561; found: 360.9568.

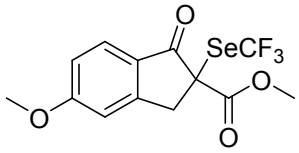


Methyl 6-methyl-1-oxo-2-((trifluoromethyl)selanyl)-2,3-dihydro-1*H*-indene-2-carboxylate (**2b**). Yellow solid (51.3 mg, 73% yield), petroleum ether/ethyl acetate = 10:1 (v/v) as eluents for column chromatography. M.p.: 85-87 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63 (s, 1H), 7.52 (d, *J* = 7.9 Hz, 1H), 7.38 (d, *J* = 7.8 Hz, 1H), 4.15 (d, *J* = 18.0 Hz, 1H), 3.78 (s, 3H), 3.73 (d, *J* = 18.0 Hz, 1H), 2.43 (s, 3H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -31.6 (s, 3F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 196.3, 168.4, 148.9, 138.7, 137.7, 133.4, 125.9, 125.4, 122.5 (q, *J* = 333.3 Hz), 60.5, 54.2, 40.4, 21.1. IR (KBr): 3039, 2966, 2941, 2926, 2853, 1733, 1711, 1681, 1614, 1582, 1558, 1493, 1476, 1442, 1432, 1386, 1325, 1281, 1264, 1220, 1187, 1150, 1125, 1102, 1070, 1022, 991, 947, 929, 894, 854, 832, 823, 817, 759, 737, 688, 632, 581 cm^{-1}. HRMS-ESI (m/z) calcd. for $C_{13}H_{12}F_3O_3Se$ ($[M + H]^+$): 352.9898; found: 352.9899.

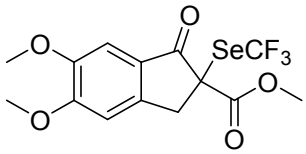


Methyl 6-methoxy-1-oxo-2-((trifluoromethyl)selanyl)-2,3-dihydro-1*H*-indene-2-carboxylate (**2c**). Yellow solid (57.2 mg, 75% yield), petroleum ether/ethyl acetate = 10:1 (v/v) as eluents for column chromatography. M.p.: 99-101 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 (d, *J* = 8.5 Hz, 1H), 7.29 (dd, *J* = 8.4 Hz, *J* = 2.6 Hz, 1H), 7.24

(d, J = 2.5 Hz, 1H), 4.12 (d, J = 17.8 Hz, 1H), 3.85 (s, 3H), 3.79 (s, 3H), 3.70 (d, J = 17.8 Hz, 1H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -31.6 (s, 3F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 196.2, 168.4, 160.2, 144.4, 134.4, 126.9, 126.0, 122.5 (q, J = 333.2 Hz), 106.3, 60.8, 55.7, 54.2, 40.2. IR (KBr): 3096, 3005, 2960, 2923, 2845, 1732, 1707, 1614, 1587, 1495, 1470, 1445, 1442, 1436, 1346, 1300, 1280, 1259, 1229, 1201, 1167, 1147, 1127, 1099, 1062, 1022, 973, 950, 939, 864, 849, 835, 818, 768, 747, 680, 645, 596, 540 cm^{-1}. HRMS-ESI (m/z) calcd. for $C_{13}H_{12}F_3O_4Se$ ([M + H]$^+$): 368.9847; found: 368.9845.

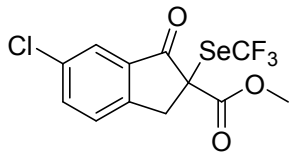


Methyl 5-methoxy-1-oxo-2-((trifluoromethyl)selanyl)-2,3-dihydro-1*H*-indene-2-carboxylate (**2d**). Yellow solid (59.6 mg, 81% yield), petroleum ether/ethyl acetate = 5:1 (v/v) as eluents for column chromatography. M.p.: 175-177 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 (d, J = 8.6 Hz, 1H), 6.97 (d, J = 8.6 Hz, 1H), 6.91 (s, 1H), 4.17 (d, J = 18.1 Hz, 1H), 3.91 (s, 3H), 3.78 (s, 3H), 3.72 (d, J = 18.1 Hz, 1H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -31.7 (s, 3F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 194.1, 168.5, 166.7, 154.8, 127.3, 126.2, 122.6 (q, J = 333.5 Hz), 116.7, 109.2, 60.7, 55.9, 54.2, 40.7. IR (KBr): 3018, 3004, 2953, 2844, 1727, 1703, 1595, 1490, 1472, 1348, 1305, 1270, 1261, 1197, 1186, 1138, 1098, 1026, 1017, 927, 878, 855, 738, 659, 551 cm^{-1}. HRMS-ESI (m/z) calcd. for $C_{13}H_{12}F_3O_4Se$ ([M + H]$^+$): 368.9847; found: 368.9848.

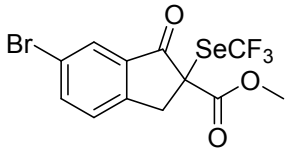


Methyl 5,6-dimethoxy-1-oxo-2-((trifluoromethyl)selanyl)-2,3-dihydro-1*H*-indene-2-carboxylate (**2e**). Yellow solid (59.6 mg, 75% yield), petroleum ether/ethyl acetate = 4:1 (v/v) as eluents for column chromatography. M.p.: 180-182 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.02 (s, 1H), 6.89 (s, 1H), 4.12 (d, J = 17.9 Hz, 1H), 3.99 (s, 3H), 3.91 (s, 3H), 3.78 (s, 3H), 3.69 (d, J = 17.9 Hz, 1H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -31.8 (s, 3F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 194.5, 168.6, 157.0, 150.3, 147.4, 125.9, 122.6 (q, J = 333.5 Hz), 106.9, 105.4, 60.7, 56.5, 56.2, 54.2, 40.5. IR (KBr): 3090,

3008, 2956, 2928, 2875, 1740, 1716, 1593, 1506, 1467, 1454, 1442, 1257, 1223, 1197, 1179, 1153, 1145, 1112, 1097, 1025, 959, 875, 856, 800, 760, 748, 738, 654, 591, 561 cm^{-1}. HRMS-ESI (m/z) calcd. for $C_{14}H_{14}F_3O_5Se$ ($[M + H]^+$): 398.9953; found: 398.9951.

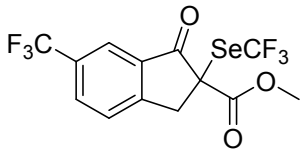


Methyl 6-chloro-1-oxo-2-((trifluoromethyl)selanyl)-2,3-dihydro-1*H*-indene-2-carboxylate (**2f**). Yellowish liquid (49.4 mg, 66% yield), petroleum ether/ethyl acetate = 20:1 (v/v) as eluents for column chromatography. ^1H NMR (500 MHz, $CDCl_3$) δ 7.80 (d, *J* = 1.8 Hz, 1H), 7.66 (dd, *J* = 8.2 Hz, *J* = 2.0 Hz, 1H), 7.45 (d, *J* = 8.2 Hz, 1H), 4.16 (d, *J* = 18.3 Hz, 1H), 3.79 (s, 3H), 3.73 (d, *J* = 18.3 Hz, 1H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -31.5 (s, 3F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 195.20, 167.9, 149.5, 136.4, 135.0, 134.7, 127.4, 125.2, 122.4 (q, *J* = 333.0 Hz), 60.2, 54.4, 40.3. IR (KBr): 3060, 2960, 2931, 2874, 1728, 1663, 1618, 1595, 1571, 1488, 1444, 1391, 1342, 1288, 1259, 1209, 1197, 1184, 1161, 1127, 1106, 1075, 1040, 1001, 963, 883, 774, 744, 693, 649, 621 cm^{-1}. HRMS-ESI (m/z) calcd. for $C_{12}H_8ClF_3NaO_3Se$ ($[M + Na]^+$): 394.9171; found: 394.9172.

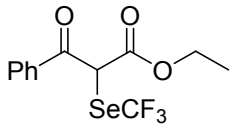


Methyl 6-bromo-1-oxo-2-((trifluoromethyl)selanyl)-2,3-dihydro-1*H*-indene-2-carboxylate (**2g**). Yellowish liquid (54.5 mg, 66% yield), petroleum ether/ethyl acetate = 20:1 (v/v) as eluents for column chromatography. ^1H NMR (500 MHz, $CDCl_3$) δ 7.96 (d, *J* = 1.6 Hz, 1H), 7.80 (dd, *J* = 8.2 Hz, *J* = 1.9 Hz, 1H), 7.40 (d, *J* = 8.2 Hz, 1H), 4.14 (d, *J* = 18.3 Hz, 1H), 3.79 (s, 3H), 3.71 (d, *J* = 18.3 Hz, 1H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -31.5 (s, 3F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 195.0, 167.9, 150.0, 139.1, 135.0, 128.3, 127.7, 122.7, 122.4 (q, *J* = 331.6 Hz), 60.1, 54.4, 40.4. IR (KBr): 3062, 2958, 2931, 2874, 1740, 1727, 1599, 1581, 1531, 1470, 1434, 1416, 1279, 1253, 1198, 1182, 1123, 1100, 1077, 1026, 964, 897, 862, 822, 739, 699 cm^{-1}. HRMS-ESI (m/z) calcd. for $C_{12}H_8BrF_3NaO_3Se$ ($[M + Na]^+$): 438.8666; found:

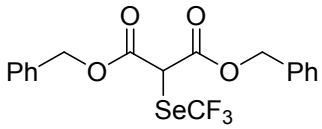
438.8667.



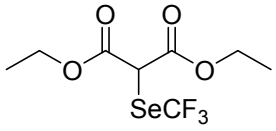
Methyl 1-oxo-6-(trifluoromethyl)-2-((trifluoromethyl)selanyl)-2,3-dihydro-1*H*-indene-2-carboxylate (**2h**). Yellowish liquid (51.8 mg, 64% yield), petroleum ether/ethyl acetate = 20:1 (v/v) as eluents for column chromatography. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.11 (s, 1H), 7.95 (d, J = 8.0 Hz, 1H), 7.66 (d, J = 8.2 Hz, 1H), 4.28 (d, J = 18.6 Hz, 1H), 3.85 (m, 1H), 3.81 (m, 3H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -31.4 (s, 3F), -62.8 (s, 3F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 195.3, 167.7, 154.5, 133.7, 132.7 (q, $^{3}J_{(C,F)}$ = 3.3 Hz), 131.5 (q, $^{2}J_{(C,F)}$ = 33.5 Hz), 127.1, 123.4 (q, $^{1}J_{(C,F)}$ = 273.9 Hz), 122.8 (q, $^{3}J_{(C,F)}$ = 3.9 Hz), 122.4 (q, J = 333.0 Hz), 59.9, 54.5, 40.7. IR (KBr): 3066, 2961, 2932, 2874, 1727, 1668, 1626, 1600, 1584, 1486, 1448, 1383, 1328, 1276, 1224, 1201, 1185, 1165, 1132, 1102, 1075, 1059, 1040, 997, 964, 941, 910, 832, 778, 744, 715, 704, 689 cm^{-1}. HRMS-ESI (m/z) calcd. for $C_{13}H_8F_6NaO_3Se$ ([M + Na]$^{+}$): 428.9435; found: 428.9435.



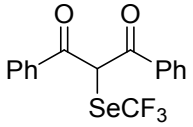
Ethyl 3-oxo-3-phenyl-2-((trifluoromethyl)selanyl)propanoate (**2i**). Yellowish liquid (54.0 mg, 80% yield), petroleum ether/ethyl acetate = 40:1 (v/v) as eluents for column chromatography. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01 (d, J = 8.2 Hz, 2H), 7.66 (t, J = 7.5 Hz, 1H), 7.52 (t, J = 7.9 Hz, 2H), 5.77 (s, 1H), 4.23 (m, 2H), 1.21 (t, J = 7.1 Hz, 3H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -33.6 (s, 3F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 189.7, 167.1, 134.6, 134.0, 129.1, 129.1, 122.8 (q, J = 332.4 Hz), 63.1, 51.2, 13.7. IR (KBr): 3066, 2984, 2922, 2851, 1738, 1682, 1598, 1581, 1467, 1450, 1393, 1369, 1339, 1321, 1284, 1269, 1234, 1186, 1136, 1100, 1074, 1025, 1001, 993, 877, 773, 739, 718, 687, 592 cm^{-1}. HRMS-ESI (m/z) calcd. for $C_{12}H_{11}F_3NaO_3Se$ ([M + Na]$^{+}$): 362.9718; found: 362.9718.



Dibenzyl 2-((trifluoromethyl)selanyl)malonate (**2j**). Yellowish liquid (70.8 mg, 82% yield), petroleum ether/ethyl acetate = 20:1 (v/v) as eluents for column chromatography. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36-7.35 (m, 6H), 7.31 (m, 4H), 5.22 (m, 4H), 4.89 (s, 1H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -33.9 (s, 3F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.6, 134.4, 128.7, 128.7, 128.4, 122.2 (q, J = 331.9 Hz), 68.8, 44.5. IR (KBr): 3092, 3067, 3035, 2958, 2922, 2851, 1734, 1660, 1663, 1587, 1499, 1469, 1456, 1377, 1292, 1273, 1224, 1137, 1096, 1075, 1002, 906, 740, 696, 644, 583 cm^{-1}. HRMS-ESI (m/z) calcd. for $C_{18}H_{15}F_3NaO_4Se$ ([M + Na]$^+$): 454.9980; found: 454.9988.

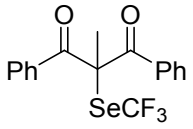


Diethyl 2-((trifluoromethyl)selanyl)malonate (**2k**). Yellowish liquid (46.8 mg, 76% yield), hexane/diethyl ether = 20:1 (v/v) as eluents for column chromatography. ^{1}H NMR (500 MHz, DMSO-d_6) δ 5.39 (s, 1H), 4.21 (q, J = 7.1 Hz, 4H), 1.20 (t, J = 7.1 Hz, 6H). ^{19}F NMR (471 MHz, DMSO-d_6) δ -32.8 (s, 3F). ^{13}C NMR (126 MHz, DMSO-d_6) δ 166.3, 122.8 (q, J = 332.7 Hz), 63.2, 45.7, 14.1. IR (KBr): 2254, 2127, 1726, 1654, 1257, 1051, 1026, 1006, 825, 763, 629 cm^{-1}. HRMS-ESI (m/z) calcd. for $C_8H_{11}F_3NaO_4Se$ ([M + Na]$^+$): 330.9667; found: 330.9667.

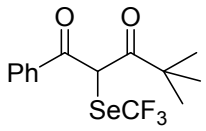


1,3-Diphenyl-2-((trifluoromethyl)selanyl)propane-1,3-dione (**2l**). Yellowish liquid (52.5 mg, 71% yield), petroleum ether/ethyl acetate = 20:1 (v/v) as eluents for column chromatography. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 (d, J = 7.8 Hz, 4H), 7.59 (t, J = 7.4 Hz, 2H), 7.45 (t, J = 7.8 Hz, 4H), 6.54 (s, 1H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -33.1 (s, 3F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 191.3, 134.5, 134.3, 129.3, 129.0, 122.8 (q, J = 330.9 Hz), 56.2. IR (KBr): 3071, 2960, 2939, 1728, 1677, 1652, 1595, 1576, 1450, 1380, 1321, 1308, 1259, 1234, 1185, 1145, 1131, 1122, 1098, 1057, 1028, 1000,

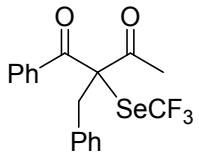
969, 954, 940, 819, 789, 737, 708, 693, 688, 664, 587 cm^{-1}. HRMS-ESI (m/z) calcd. for $C_{16}H_{11}F_3NaO_2Se$ ($[M + Na]^+$): 394.9769; found: 394.9769.



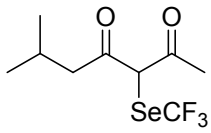
2-Methyl-1,3-diphenyl-2-((trifluoromethyl)selanyl)propane-1,3-dione (**2m**). Yellowish liquid (61.5 mg, 80% yield), petroleum ether/ethyl acetate = 20:1 (v/v) as eluents for column chromatography. ^1H NMR (500 MHz, $CDCl_3$) δ 7.90 (d, *J* = 7.9 Hz, 4H), 7.46 (t, *J* = 7.4 Hz, 2H), 7.33 (t, *J* = 7.9 Hz, 4H), 2.41 (s, 3H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -32.1 (s, 3F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 194.6, 134.0, 134.0, 129.7, 128.8, 122.9 (q, *J* = 335.4 Hz), 70.4, 26.6. IR (KBr): 3069, 2962, 2937, 2874, 1727, 1676, 1652, 1595, 1576, 1449, 1380, 1321, 1306, 1277, 1258, 1233, 1185, 1121, 1099, 1077, 1057, 1028, 1001, 968, 953, 940, 819, 789, 737, 709, 692, 688, 664, 586 cm^{-1}. HRMS-ESI (m/z) calcd. for $C_{17}H_{13}F_3NaO_2Se$ ($[M + Na]^+$): 408.9925; found: 408.9925.



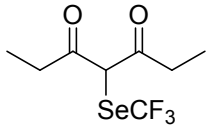
4,4-Dimethyl-1-phenyl-2-((trifluoromethyl)selanyl)pentane-1,3-dione (**2n**). Yellowish liquid (56.2 mg, 80% yield), petroleum ether/ethyl acetate = 20:1 (v/v) as eluents for column chromatography. ^1H NMR (500 MHz, $CDCl_3$) δ 8.00 (d, *J* = 7.6 Hz, 2H), 7.65 (t, *J* = 7.4 Hz, 1H), 7.52 (t, *J* = 7.8 Hz, 2H), 6.14 (s, 1H), 1.19 (s, 9H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -33.6 (s, 3F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 205.7, 191.0, 134.5, 134.3, 129.1, 129.1, 122.7 (q, *J* = 330.0 Hz), 51.7, 45.7, 26.8. IR (KBr): 3075, 3002, 2971, 2933, 2873, 1702, 1669, 1595, 1581, 1479, 1469, 1450, 1397, 1367, 1325, 1278, 1267, 1215, 1191, 1163, 1144, 1119, 1108, 1073, 1055, 1003, 997, 973, 937, 806, 738, 730, 692, 687, 605, 561 cm^{-1}. HRMS-ESI (m/z) calcd. for $C_{14}H_{15}F_3NaO_2Se$ ($[M + Na]^+$): 375.0082; found: 375.0082.



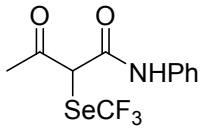
2-Benzyl-1-phenyl-2-((trifluoromethyl)selanyl)pentane-1,3-dione (**2o**). Yellowish liquid (49.5 mg, 62% yield), petroleum ether/ethyl acetate = 20:1 (v/v) as eluents for column chromatography. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 (d, *J* = 7.5 Hz, 2H), 7.68 (t, *J* = 7.5 Hz, 1H), 7.53 (t, *J* = 7.7 Hz, 2H), 7.22-7.15 (m, 3H), 6.92 (d, *J* = 7.2 Hz, 2H), 3.87 (m, 2H), 2.43 (s, 3H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -32.1 (s, 3F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 200.6, 193.6, 134.7, 134.5, 134.1, 130.5, 129.4, 129.4, 128.0, 127.4, 122.7 (q, *J* = 334.5 Hz), 80.9, 39.8, 27.7. IR (KBr): 3065, 3033, 2925, 2852, 1716, 1661, 1596, 1579, 1497, 1449, 1438, 1358, 1323, 1254, 1184, 1174, 1122, 1098, 1069, 1030, 1001, 992, 913, 782, 755, 737, 698, 653, 617, 589, 514 cm^{-1}. HRMS-ESI (m/z) calcd. for $C_{18}H_{15}F_3NaO_2Se$ ([M + Na]$^+$): 423.0082; found: 423.0081.



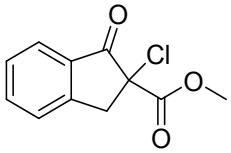
6-Methyl-3-((trifluoromethyl)selanyl)heptane-2,4-dione (**2p**). Yellow liquid (35.8 mg, 62% yield), hexane/diethyl ether = 40:1 (v/v) as eluents for column chromatography. ^{1}H NMR (500 MHz, DMSO-d_6) δ 17.74 (s, 0.89H), 5.63 (s, 0.16H, keto), 2.74 (d, *J* = 7.0 Hz, 2H), 2.63 (m, 0.40H, keto), 2.49 (s, 3H), 2.35 (s, 0.59H, keto), 2.14-2.05 (m, 1.24H), 0.93 (d, *J* = 6.7 Hz, 6H), 0.88 (d, *J* = 6.7 Hz, 1.25H, keto). ^{19}F NMR (471 MHz, DMSO-d_6) δ -32.3 (s, 0.47F, keto), -36.6 (s, 0.02F), -38.5 (s, 3F). ^{13}C NMR (126 MHz, DMSO-d_6) δ 201.9, 200.6, 200.3, 198.9, 130.6 (q, *J* = 365.1 Hz), 123.0 (q, *J* = 336.2 Hz), 97.6, 62.1, 49.7, 46.6, 28.8, 26.6, 26.0, 24.0, 22.9, 22.4, 22.4, 14.3, 11.2. IR (KBr): 3396, 3193, 2957, 2923, 2850, 1716, 1662, 1647, 1567, 1469, 1449, 1418, 1401, 1379, 1327, 1257, 1173, 1123, 1100, 1048, 913, 804, 755, 737, 698, 652, 516 cm^{-1}. HRMS-ESI (m/z) calcd. for $C_9H_{13}F_3NaO_2Se$ ([M + Na]$^+$): 312.9925; found: 312.9925. *Note*: the characteristic downfield signal at 17.74 ppm (s) in ^{1}H NMR was assigned to the enol forms which contain OH groups with strong hydrogen bonding interaction with the adjacent C=O groups, while the signal at 5.63 ppm (s) corresponded to the keto form according to the chemical shifts of the active α-proton in other diketone products. Other ^{1}H NMR signals were assigned on the basis of these two integrals. Since **2p** is an asymmetric 1,3-diketone, there are two possible enol forms, which give two different peaks at -36.6 ppm (s) and -38.5 ppm (s) in ^{19}F NMR and complicated resonances in ^{13}C NMR.



4-((Trifluoromethyl)selanyl)heptane-3,5-dione (**2q**). Yellow liquid (40.3 mg, 73% yield), hexane/diethyl ether = 40:1 (v/v) as eluents for column chromatography. ^{1}H NMR (500 MHz, DMSO-d_6) δ 17.75 (s, 0.83H), 5.68 (s, 0.39H, keto), 2.87 (q, J = 7.3 Hz, 4H), 2.73 (m, 1.81H, keto), 1.09 (t, J = 7.4 Hz, 6H), 0.97 (t, J = 7.1 Hz, 2.66H, keto). ^{19}F NMR (471 MHz, DMSO-d_6) δ -32.4 (s, 1.28F, keto), -38.6 (s, 3F). ^{13}C NMR (126 MHz, DMSO-d_6) δ 203.1(keto), 201.5, 197.6, 123.1 (q, J = 332.4 Hz, keto), 123.0 (q, J = 336.4 Hz), 96.3, 60.8 (keto), 34.5, 31.6, 30.4 (keto), 9.7, 8.8 (keto), 8.2. IR (KBr): 3420, 2254, 2127, 1653, 1051, 1026, 1005, 825, 763, 629 cm^{-1}. HRMS-ESI (m/z) calcd. for $C_8H_{10}F_3O_2Se$ ([M – H]$^-$): 274.9804; found: 274.9809. *Note*: the enol/keto assignment was made in a manner similar to that for **2p**.



3-Oxo-*N*-phenyl-2-((trifluoromethyl)selanyl)butanamide (**2r**). Yellowish liquid (51.8, 80% yield), petroleum ether/ethyl acetate = 20:1 (v/v) as eluents for column chromatography. ^{1}H NMR (500 MHz, DMSO-d_6) δ 10.73 (s, 1H), 7.57 (d, J = 7.8 Hz, 2H), 7.36 (t, J = 7.8 Hz, 2H), 7.14 (t, J = 7.4 Hz, 1H), 5.45 (s, 1H), 2.37 (s, 3H). ^{19}F NMR (471 MHz, DMSO-d_6) δ -32.6 (s, 3F). ^{13}C NMR (126 MHz, DMSO-d_6) δ 199.4, 163.9, 138.6, 129.4, 124.9, 123.3 (q, J = 331.7 Hz), 120.2, 58.1, 27.3. IR (KBr): 3365, 3140, 3059, 3038, 2959, 2926, 2853, 1716, 1600, 1579, 1544, 1491, 1446, 1379, 1338, 1327, 1314, 1304, 1238, 1213, 1159, 1147, 1128, 1102, 1051, 1029, 983, 969, 904, 855, 795, 758, 735, 689, 628, 602, 509 cm^{-1}. HRMS-ESI (m/z) calcd. for $C_{11}H_{11}F_3NO_2Se$ ([M + H]$^+$): 325.9902; found: 325.9901.

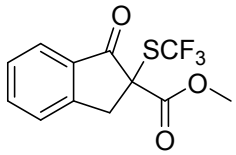


Methyl 2-chloro-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate (**2a'**).[5] Yellow liquid, petroleum ether/ethyl acetate = 10:1 (v/v) as eluents for column chromatography. ^{1}H

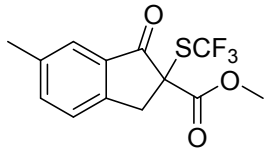
NMR (500 MHz, $CDCl_3$) δ 7.87 (d, *J* = 7.6 Hz, 1H), 7.71 (t, *J* = 7.9 Hz, 1H), 7.50-7.46 (m, 2H), 4.12 (d, *J* = 17.7 Hz, 1H), 3.82 (s, 3H), 3.58 (d, *J* = 17.7 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 195.0, 167.7, 150.6, 136.5, 132.5, 128.7, 126.3, 126.0, 67.9, 54.1, 43.4.

Procedure B: In a nitrogen-filled glovebox, a sealed tube was charged with $[Me_4N][SCF_3]$ (45.5 mg, 0.26 mmol), NCS (34.7 mg, 0.26 mmol) and CH_3CN (1 mL) with stirring. After 1 h a solution of **1** (0.2 mmol) in CH_3CN (1 mL) was added. The mixture was reacted at room temperature or 60 °C for 1, 24 or 48 h, and concentrated to dryness under reduced pressure. The residue was purified by flash column chromatography on silica gel using a mixture of petroleum ether/ethyl acetate or hexane/dichloromethane as eluents to give the trifluoromethylthiolated products (**3**).

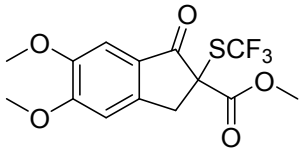
Procedure C: In a nitrogen-filled glovebox, a sealed tube was charged with $[Me_4N][SCF_3]$ (35.0 mg, 0.2 mmol), NCS (26.7 mg, 0.2 mmol) and CH_3CN (1 mL) with stirring. After 5 min a solution of **1** (0.2 mmol) in CH_3CN (1 mL) was added. The mixture was reacted at room temperature or 60 °C for 1, 24 or 48 h, and concentrated to dryness under reduced pressure. The residue was purified by flash column chromatography on silica gel using a mixture of petroleum ether/ethyl acetate or hexane/dichloromethane as eluents to give the trifluoromethylthiolated products (**3**).



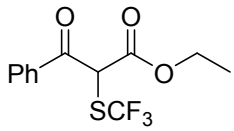
Methyl 1-oxo-2-((trifluoromethyl)thio)-2,3-dihydro-1*H*-indene-2-carboxylate (**3a**).[6] Yellow liquid (36.6 mg, 63% yield (**Procedure B**); 48.2 mg, 83% (**Procedure C**)), petroleum ether/ethyl acetate = 10:1 (v/v) as eluents for column chromatography. ^1H NMR (500 MHz, $CDCl_3$) δ 7.83 (d, *J* = 7.7 Hz, 1H), 7.71 (t, *J* = 7.7 Hz, 1H), 7.52 (d, *J* = 7.7 Hz, 1H), 7.46 (t, *J* = 7.5 Hz, 1H), 4.21 (d, *J* = 17.7 Hz, 1H), 3.80 (s, 3H), 3.67 (d, *J* = 17.7 Hz, 1H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -37.2 (s, 3F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 194.7, 167.3, 151.7, 136.6, 132.8, 129.8 (q, *J* = 309.1 Hz), 128.5, 126.3, 125.7, 63.4, 54.3, 40.4.



Methyl 6-methyl-1-oxo-2-((trifluoromethyl)thio)-2,3-dihydro-1*H*-indene -2-carboxy-late (**3b**).[6] Yellow liquid (35.9 mg, 59% yield (**Procedure B**); 30.5 mg, 50% (**Procedure C**)), petroleum ether/ethyl acetate = 10:1 (v/v) as eluents for column chromatography. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62 (s, 1H), 7.52 (d, *J* = 7.9 Hz, 1H), 7.40 (d, *J* = 7.9 Hz, 1H), 4.14 (d, *J* = 17.5 Hz, 1H), 3.79 (s, 3H), 3.61 (d, *J* = 17.5 Hz, 1H), 2.43 (s, 3H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -37.2 (s, 3F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 194.8, 167.4, 149.2, 138.7, 137.9, 133.0, 129.8 (q, *J* = 309.3 Hz), 125.9, 125.5, 63.7, 54.3, 40.1, 21.1.



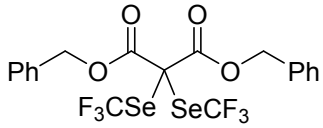
Methyl 5,6-dimethoxy-1-oxo-2-((trifluoromethyl)thio)-2,3-dihydro-1*H*-indene-2-carboxylate (**3c)**.[6] Yellow solid (26.6 mg, 38% yield (**Procedure B**); 25.2 mg, 36% (**Procedure C**); 23.8 mg, 34% (**Procedure C**)), petroleum ether/ethyl acetate = 4:1 (v/v) as eluents for column chromatography. M.p.: 181-183 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.19 (s, 1H), 6.91 (s, 1H), 4.11 (d, *J* = 17.4 Hz, 1H), 4.00 (s, 3H), 3.91 (s, 3H), 3.80 (s, 3H), 3.58 (d, *J* = 17.4 Hz, 1H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -37.4 (s, 3F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 192.9, 167.6, 157.2, 150.3, 147.8, 129.9 (q, *J* = 309.1 Hz), 125.4, 107.0, 105.5, 63.8, 56.5, 56.2, 54.3, 40.2.



Ethyl 3-oxo-3-phenyl-2-((trifluoromethyl)thio)propanoate (**3d**).[7] Yellow liquid (9.9 mg, 17% yield (**Procedure B**); 9.4 mg, 16% (**Procedure C**)), hexane/dichloromethane = 9:1 (v/v) as eluents for column chromatography. ^{1}H NMR (500 MHz, $CDCl_3$) δ 14.54 (s, 0.85H), 8.03 (d, *J* = 7.3 Hz, 0.82H, keto), 7.66 (t, *J* = 7.5 Hz, 0.50H, keto), 7.60 (m, 1.98H), 7.48 (m, 4.15H), 5.63 (s, 0.38H, keto), 4.40 (q, *J* = 7.1 Hz, 2.06H), 4.24 (m, 0.88H, keto), 1.40 (t, *J* = 7.1 Hz, 3H), 1.21 (t, *J* = 7.1 Hz,

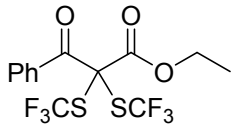
1.29H, keto). ^{19}F NMR (471 MHz, $CDCl_3$) δ -40.5 (s, 1.22F, keto), -45.2 (s, 3F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 188.5 (keto), 184.5, 173.2, 165.9 (keto), 134.7 (keto), 133.9, 133.8 (keto), 130.9, 130.1 (q, J = 307.8 Hz, keto), 129.2 (q, J = 311.0 Hz), 129.1 (keto), 129.1 (keto), 129.0, 127.9, 86.7 (d, J = 1.9 Hz), 63.3 (keto), 62.5, 55.0 (d, J = 1.6 Hz, keto), 14.0, 13.7 (keto). *Note*: the NMR data of **3d** including enol/keto assignment were in accordance with the data reported in the literature.[20]

Procedure D: In a nitrogen-filled glovebox, a sealed tube was charged with **1j** (56.9 mg, 0.2 mmol), $[Me_4N][SeCF_3]$ (133.2 mg, 0.6 mmol) and CH_3CN (2 mL), followed by addition of NCS (80.1 mg, 0.6 mmol) in CH_3CN (2 mL), with vigorous stirring. The mixture was reacted at room temperature for 1 h and concentrated to dryness under reduced pressure. The residue was purified by flash column chromatography on silica gel using a mixture of petroleum ether/ethyl acetate = 20:1 (v/v) as eluents to give the doubly trifluoromethylselenolated product (**4**) as a yellow liquid (75.4 mg, 65% yield).



Dibenzyl 2,2-bis((trifluoromethyl)selanyl)malonate (**4**). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35-7.31 (m, 6H), 7.25 (m, 4H), 5.19 (s, 4H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -33.7 (s, 6F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.4, 133.6, 129.0, 128.7, 128.5, 122.3 (q, J = 334.4 Hz), 70.2. IR (KBr): 3093, 3069, 3037, 2962, 2917, 2853, 1727, 1608, 1588, 1499, 1457, 1376, 1266, 1204, 1147, 1095, 1023, 970, 907, 845, 825, 740, 696, 613, 582 cm^{-1}. HRMS-ESI (m/z) calcd. for $C_{19}H_{14}F_6NaO_4Se_2$ ($[M + Na]^+$): 602.9019; found: 602.9019.

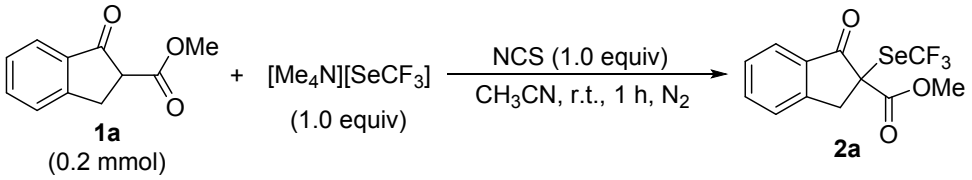
Procedure E: In a nitrogen-filled glovebox, a sealed tube was charged with $[Me_4N][SCF_3]$ (175 mg, 0.6 mmol), NCS (80.1 mg, 0.6 mmol) and CH_3CN (2 mL) with stirring. After 5 min a solution of **1i** (38.4 mg, 0.2 mmol) in CH_3CN (2 mL) was added. The mixture was reacted at room temperature for 1 h and concentrated to dryness under reduced pressure. The residue was purified by flash column chromatography on silica gel using a mixture of hexane/dichloromethane = 9:1 (v/v) as eluents to give the doubly trifluoromethylthiolated product (**5**) as a yellow liquid (11.8 mg, 15% yield).



Ethyl 3-oxo-3-phenyl-2,2-bis((trifluoromethyl)thio)propanoate (**5**). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07 (d, *J* = 7.5 Hz, 2H), 7.64 (t, *J* = 7.4 Hz, 1H), 7.48 (t, *J* = 7.6 Hz, 2H), 4.25 (q, *J* = 7.2 Hz, 2H), 1.09 (t, *J* = 7.1 Hz, 3H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -37.4 (s, 3F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 186.5, 165.7, 134.7, 131.8, 129.6, 128.9, 128.7 (q, *J* = 309.9 Hz), 73.4, 65.1, 13.3. IR (KBr): 3071, 2987, 2964, 2933, 2852, 1743, 1687, 1597, 1581, 1467, 1449, 1393, 1370, 1300, 1256, 1217, 1154, 1102, 1021, 1005, 936, 908, 841, 822, 808, 782, 758, 744, 701, 686, 653, 609 cm^{-1}. HRMS-ESI (m/z) calcd. for $C_{13}H_{10}F_6NaO_3S_2$ ($[M + Na]^+$): 414.9868; found: 414.9866.

4. The control experiments for mechanistic insights

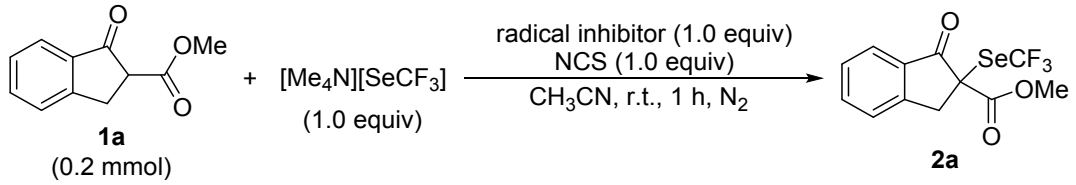
Table S5. Trifluoromethylselenolation of **1a** by $[Me_4N][SeCF_3]$ and NCS at room temperature with different charging sequence.



Entry	Yield (**2a**, %) [a]
1 [b]	84
2 [c]	82
3 [d]	88

[a] Isolated yields. [b] Reaction conditions: a sealed tube was charged with **1a** (0.2 mmol), $[Me_4N][SeCF_3]$ (0.2 mmol) and CH_3CN (1 mL) with stirring, and after 5 minutes a solution of NCS (0.2 mmol) in CH_3CN (1 mL) was added. The mixture was reacted at room temperature under N_2 for 1 h. [c] Reaction conditions: a sealed tube was charged with **1a** (0.2 mmol), NCS (0.2 mmol) and CH_3CN (1 mL) with stirring, and after 5 minutes a solution of $[Me_4N][SeCF_3]$ (0.2 mmol) in CH_3CN (1 mL) was added. The mixture was reacted at room temperature under N_2 for 1 h. [d] Reaction conditions: a sealed tube was charged with $[Me_4N][SeCF_3]$ (0.2 mmol), NCS (0.2 mmol) and CH_3CN (1 mL) with stirring, and after 5 minutes a solution of **1a** (0.2 mmol) in CH_3CN (1 mL) was added. The mixture was reacted at room temperature under N_2 for 1 h.

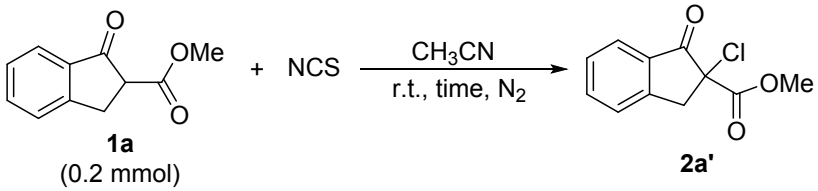
Table S6. Trifluoromethylselenolation of **1a** by $[Me_4N][SeCF_3]$ and NCS in the presence of different radical inhibitors.



Entry [a]	Radical inhibitor	Yield (**2a**, %) [b]
1	*trans*-stilbene	88
2	1,3-dinitrobenzene	90
3	1,4-dinitrobenzene	89
4	BHT	85
5	TEMPO	92

[a] Reaction conditions: a sealed tube was charged with **1a** (0.2 mmol), $[Me_4N][SeCF_3]$ (0.2 mmol), radical inhibitor (0.2 mmol) and CH_3CN (1 mL), followed by addition of NCS (0.2 mmol) in CH_3CN (1 mL), with vigorous stirring. The mixture was reacted at room temperature under N_2 for 1 h. [b] Yields were determined by HPLC using **2a** as an external standard (t_R = 5.30 min, λ_{max} = 210 nm, water/methanol (v/v) = 20:80).

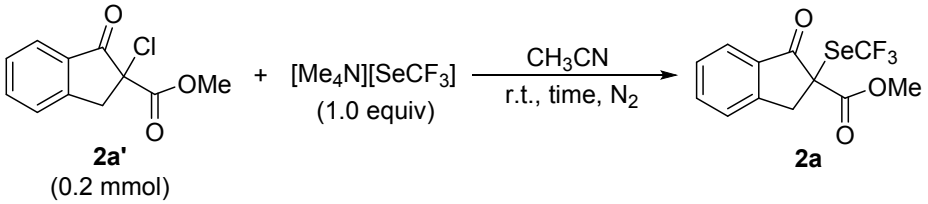
Table S7. Chlorination of **1a** by NCS in the absence of $[Me_4N][SeCF_3]$.



Entry [a]	Time	Yield (**2a'**, %) [b]
1	5 min	73
2	10 min	92
3	20 min	98

[a] Reaction conditions: a sealed tube was charged with **1a** (0.2 mmol), NCS (0.2 mmol) and CH_3CN (2 mL) with stirring. The mixture was reacted at room temperature under N_2 for times as described above. [b] Isolated yields.

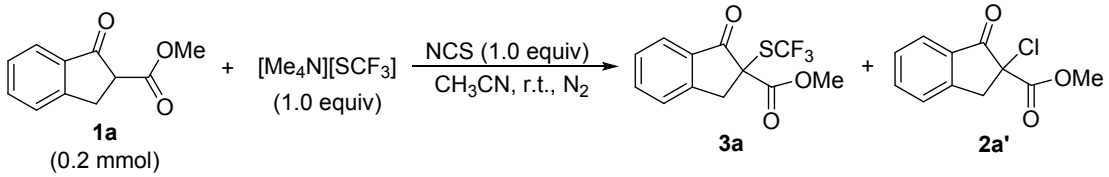
Table S8. Nucleophilic trifluoromethylselenolation of **2a'** by $[Me_4N][SeCF_3]$.



Entry [a]	Time	Yield (**2a**, %) [b]
1	5 min	50
2	10 min	85
3	20 min	87

[a] Reaction conditions: a sealed tube was charged with **2a'** (0.2 mmol), $[Me_4N][SeCF_3]$ (0.2 mmol) and CH_3CN (2 mL) with vigorous stirring. The mixture was reacted at room temperature under N_2 for times as described above. [b] Isolated yields.

Table S9. Trifluoromethylthiolation of **1a** by $[Me_4N][SCF_3]$ and NCS at room temperature with different charging sequence.

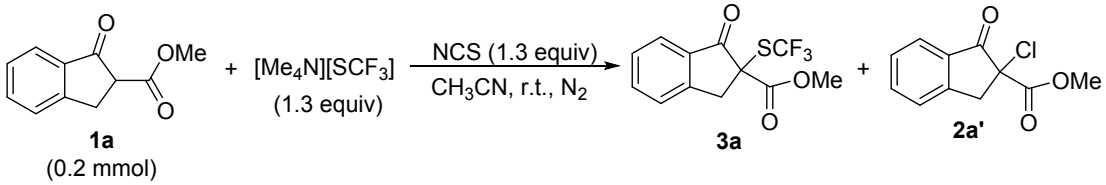


Entry	Yield (**3a**, %) [a]	Yield (**2a'**, %) [a]
1 [b]	64	27
2 [c]	40	20
3 [d]	**83**	**12**

[a] Isolated yields. [b] Reaction conditions: a sealed tube was charged with **1a** (0.2 mmol), NCS (0.2 mmol) and CH_3CN (1 mL) with stirring, and after 5 minutes a solution of $[Me_4N][SCF_3]$ (0.2 mmol) in CH_3CN (1 mL) was added. The mixture was reacted at room temperature under N_2 for 1 h. [c] Reaction conditions: a sealed tube was charged with **1a** (0.2 mmol), $[Me_4N][SCF_3]$ (0.2 mmol) and CH_3CN (1 mL) with stirring, and after 5 minutes a solution of NCS (0.2 mmol) in CH_3CN (1 mL) was added. The mixture was reacted at room temperature under N_2 for 1 h. [d] Reaction conditions: a sealed tube was charged with $[Me_4N][SCF_3]$ (0.2 mmol), NCS (0.2

mmol) and CH_3CN (1 mL) with stirring, and after 5 minutes a solution of **1a** (0.2 mmol) in CH_3CN (1 mL) was added. The mixture was reacted at room temperature under N_2 for 1 h.

Table S10. Trifluoromethylthiolation of **1a** by a mixture of $[Me_4N][SCF_3]$/NCS that was already treated at room temperature for times.

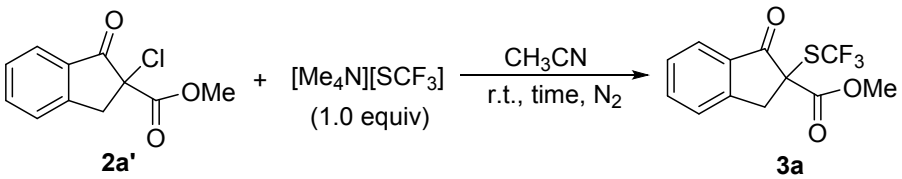


1a (0.2 mmol) **3a** **2a'**

Entry	Yield (**3a**, %) [a]	Yield (**2a'**, %) [a]
1 [b]	70	5
2 [c]	63	-
3 [d]	65	-

[a] Isolated yields. [b] Reaction conditions: a sealed tube was charged with $[Me_4N][SCF_3]$ (0.26 mmol), NCS (0.26 mmol) and CH_3CN (1 mL) with stirring, and after 5 minutes a solution of **1a** (0.2 mmol) in CH_3CN (1 mL) was added. The mixture was reacted at room temperature under N_2 for 1 h. [c] Reaction conditions: a sealed tube was charged with $[Me_4N][SCF_3]$ (0.26 mmol), NCS (0.26 mmol) and CH_3CN (1 mL) with stirring, and after 1 hour a solution of **1a** (0.2 mmol) in CH_3CN (1 mL) was added. The mixture was reacted at room temperature under N_2 for 1 h. [d] Reaction conditions: a sealed tube was charged with $[Me_4N][SCF_3]$ (0.26 mmol), NCS (0.26 mmol) and CH_3CN (1 mL) with stirring, and after 2 hours a solution of **1a** (0.2 mmol) in CH_3CN (1 mL) was added. The mixture was reacted at room temperature under N_2 for 1 h.

Table S11. Nucleophilic trifluoromethylthiolation of **2a'** by $[Me_4N][SCF_3]$.



2a' (0.2 mmol) **3a**

Entry [a]	Time	Yield (**3a**, %) [b]
1	5 min	13
2	10 min	18
3	20 min	33

[a] Reaction conditions: a sealed tube was charged with **2a'** (0.2 mmol), $[Me_4N][SCF_3]$ (0.2 mmol), and CH_3CN (2 mL), with vigorous stirring. The mixture was reacted at room temperature under N_2. [b] Isolated yield.

Figure S1. ^{19}F NMR spectrum of a mixture of $[Me_4N][SeCF_3]$ (0.2 mmol) and NCS (0.2 mmol) in CD_3CN that was reacted at room temperature for 5 minutes ($PhOCF_3$ (37.6 mg, 0.23 mmol) as an internal standard)

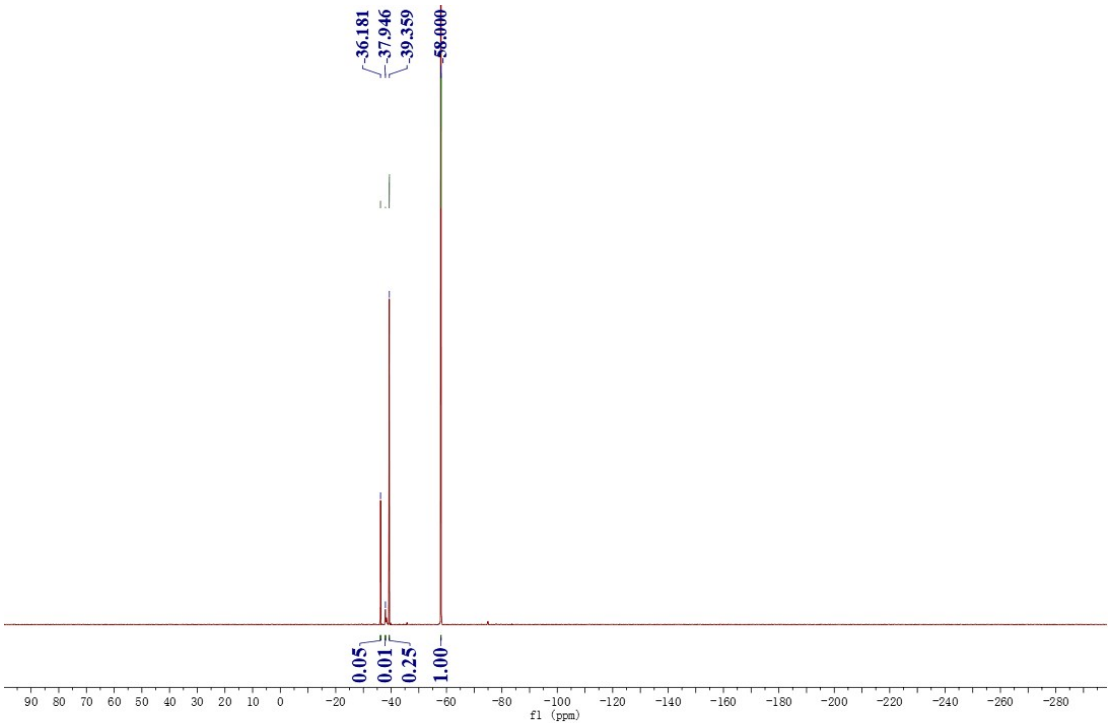


Figure S2. ^{19}F NMR spectrum of a mixture of $[Me_4N][SeCF_3]$ (0.2 mmol) and NCS (0.2 mmol) in CD_3CN that was reacted at room temperature for 1 hour ($PhOCF_3$ (34.9 mg, 0.22 mmol) as an internal standard)

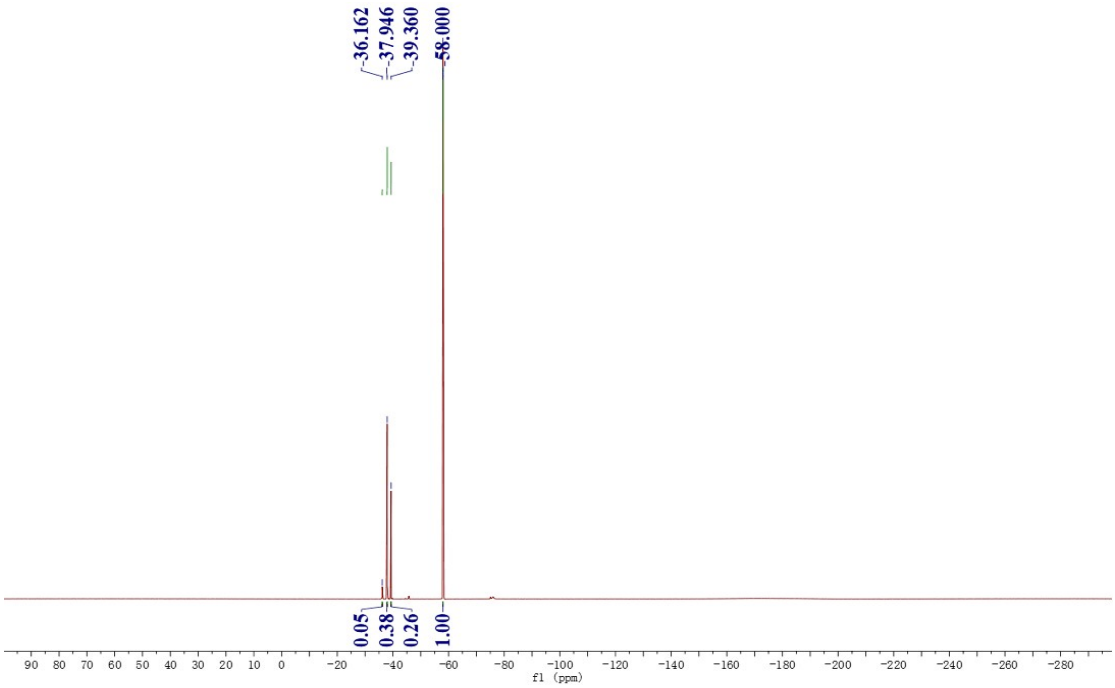


Figure S3. ^{19}F NMR spectrum of a mixture of **1a** (0.2 mmol), $[Me_4N][SeCF_3]$ (0.2 mmol) and NCS (0.2 mmol) in CH_3CN that was reacted at room temperature for 5 minutes ($PhOCF_3$ (30.7 mg, 0.19 mmol) as an internal standard)

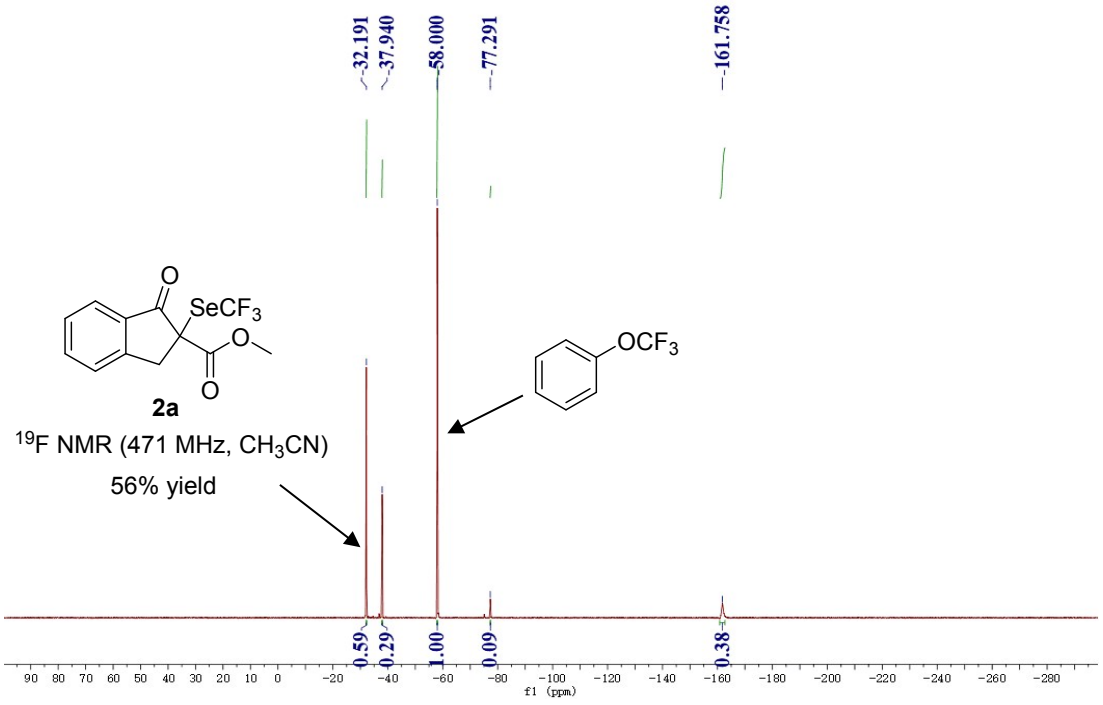


Figure S4. ^{19}F NMR spectrum of a mixture of **1a** (0.2 mmol), $[Me_4N][SeCF_3]$ (0.2 mmol) and NCS (0.2 mmol) in CH_3CN that was reacted at room temperature for 1 hour ($PhOCF_3$ (33.8 mg, 0.21 mmol) as an internal standard)

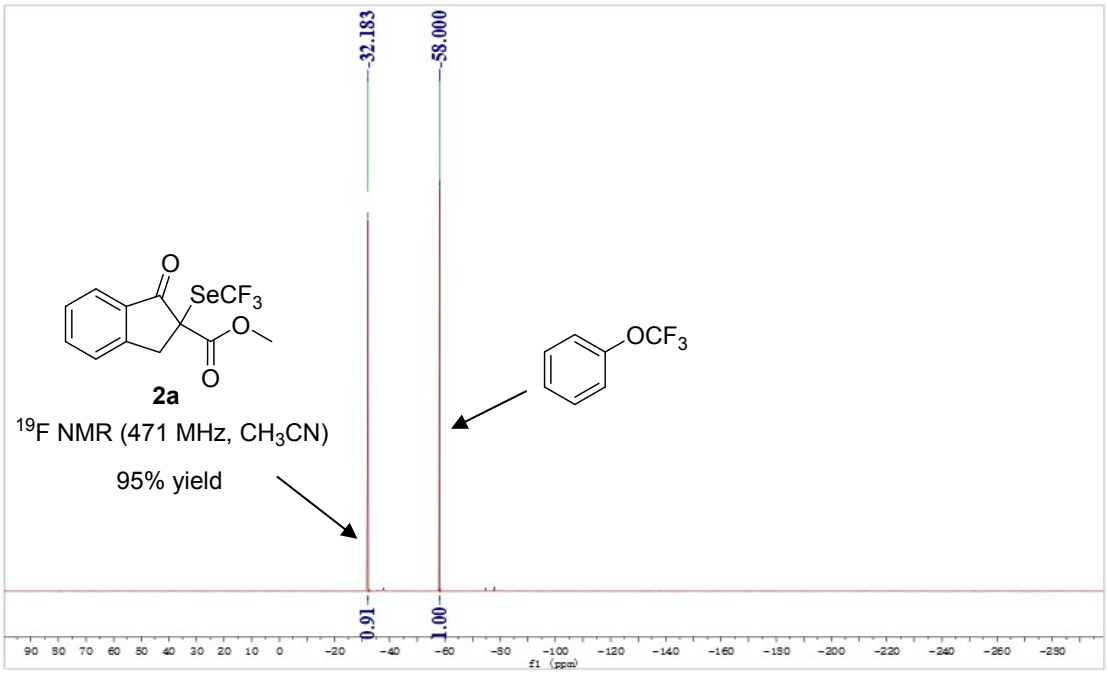


Figure S5. ^{19}F NMR spectrum of a mixture of **1a** (0.2 mmol), $[Me_4N][SeCF_3]$ (0.2 mmol) and NCS (0.2 mmol) in CH_3CN that was reacted at room temperature for 12 hours ($PhOCF_3$ (32.6 mg, 0.20 mmol) as an internal standard)

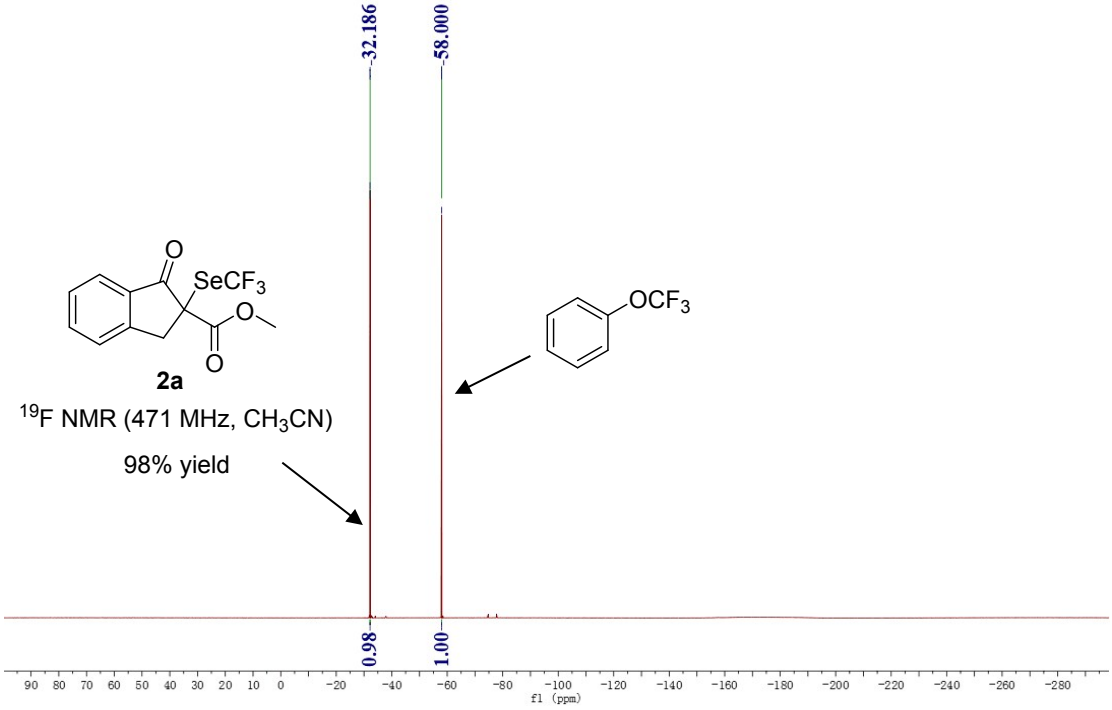


Figure S6. Combination of the above spectra (**Figures 1 and 3-5**)

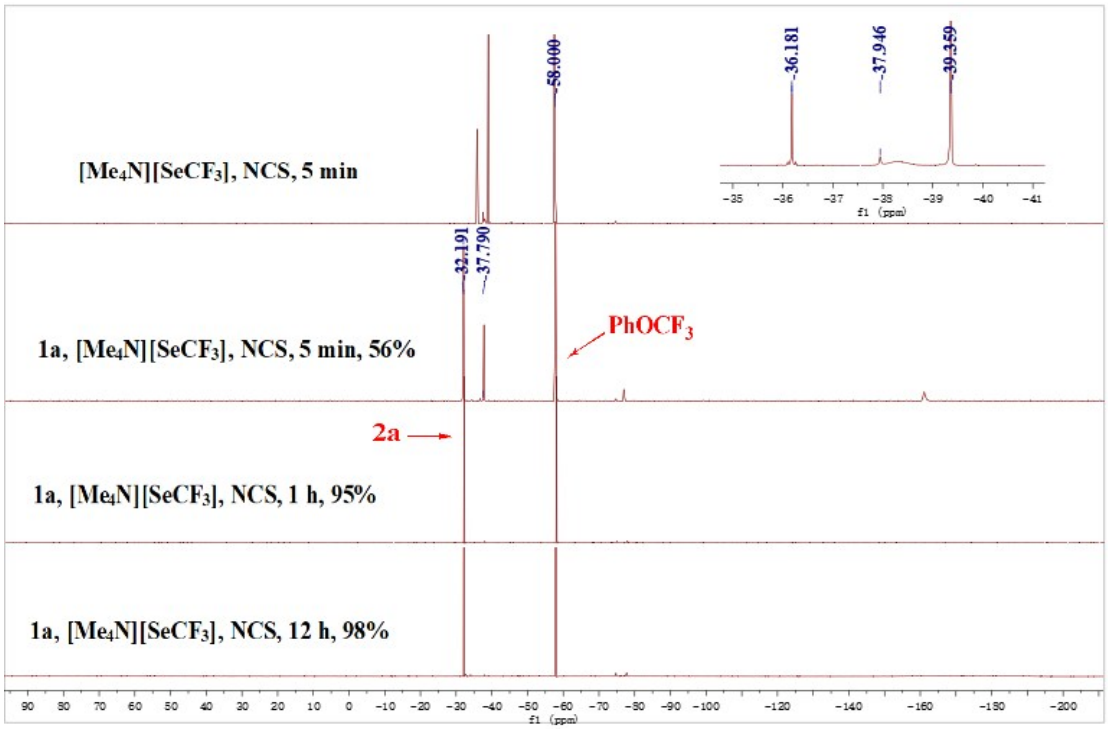


Figure S7. ^{19}F NMR spectrum of a mixture of $[Me_4N][SCF_3]$ (0.2 mmol) and NCS (0.2 mmol) in CD_3CN that was reacted at room temperature for 5 minutes ($PhOCF_3$ (28.6 mg, 0.18 mmol) as an internal standard)

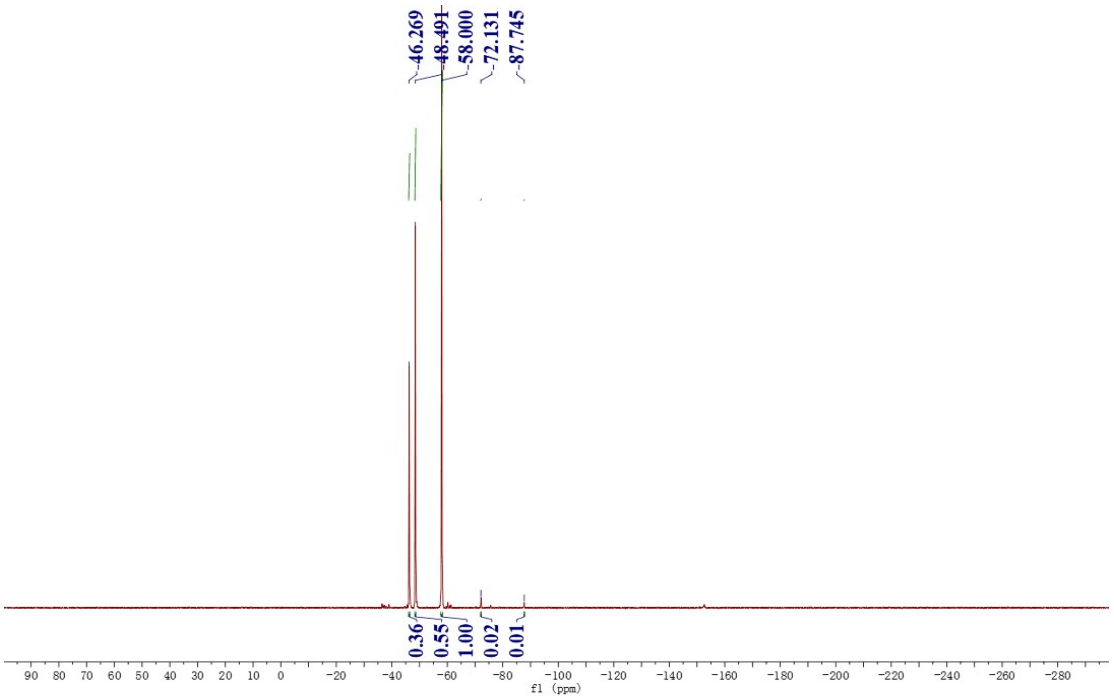


Figure S8. ^{19}F NMR spectrum of a mixture of **1a** (0.2 mmol), $[Me_4N][SCF_3]$ (0.2 mmol) and NCS (0.2 mmol) in CH_3CN that was reacted at room temperature for 5

minutes ($PhOCF_3$ (29.2 mg, 0.18 mmol) as an internal standard)

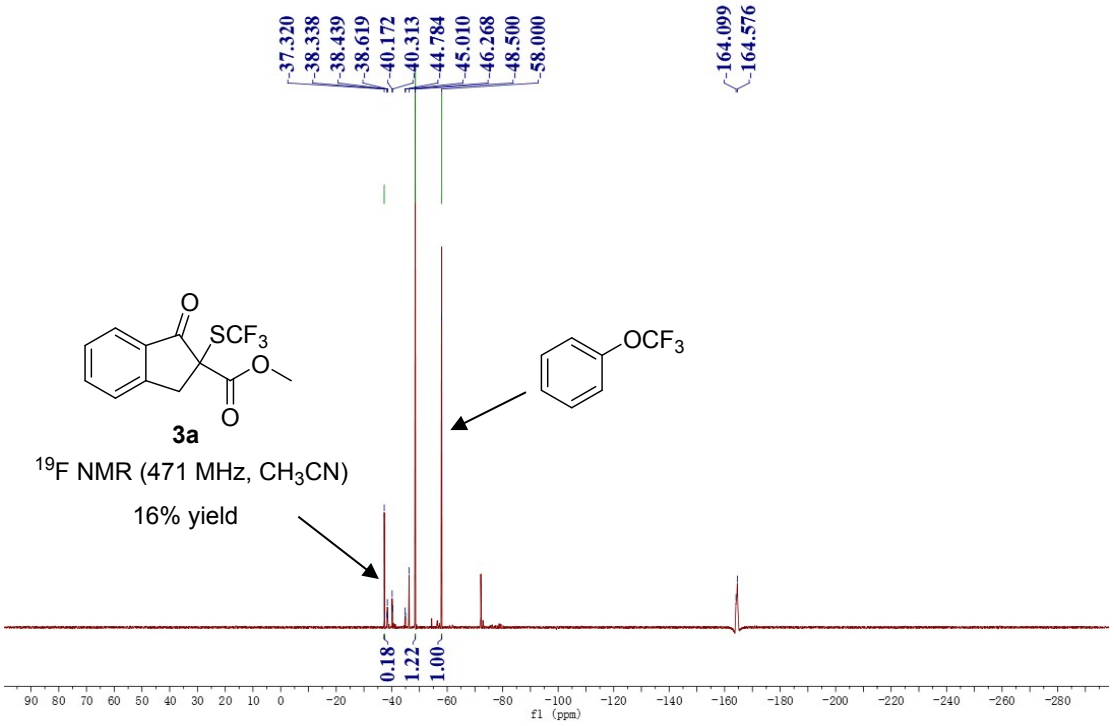


Figure S9. ^{19}F NMR spectrum of a mixture of **1a** (0.2 mmol), $[Me_4N][SCF_3]$ (0.2 mmol) and NCS (0.2 mmol) in CH_3CN that was reacted at room temperature for 1 hour ($PhOCF_3$ (32.1 mg, 0.20 mmol) as an internal standard)

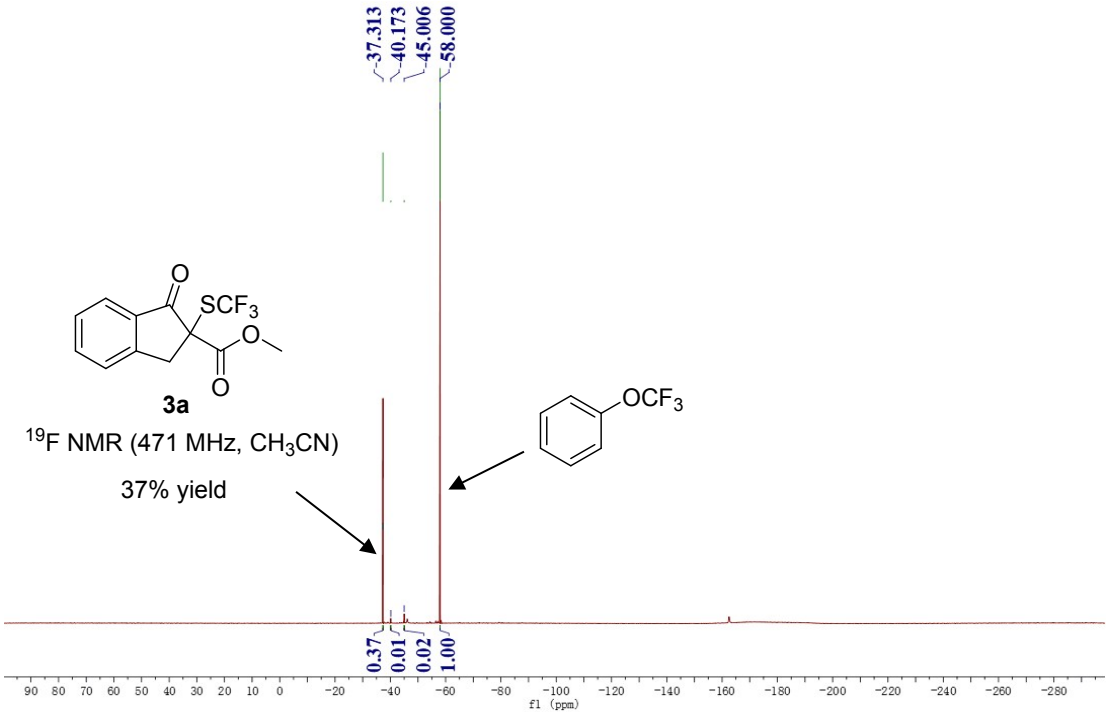


Figure S10. ^{19}F NMR spectrum of a mixture of **1a** (0.2 mmol), $[Me_4N][SCF_3]$ (0.2

mmol) and NCS (0.2 mmol) in CH_3CN that was reacted at room temperature for 12 hours ($PhOCF_3$ (36.9 mg, 0.23 mmol) as an internal standard)

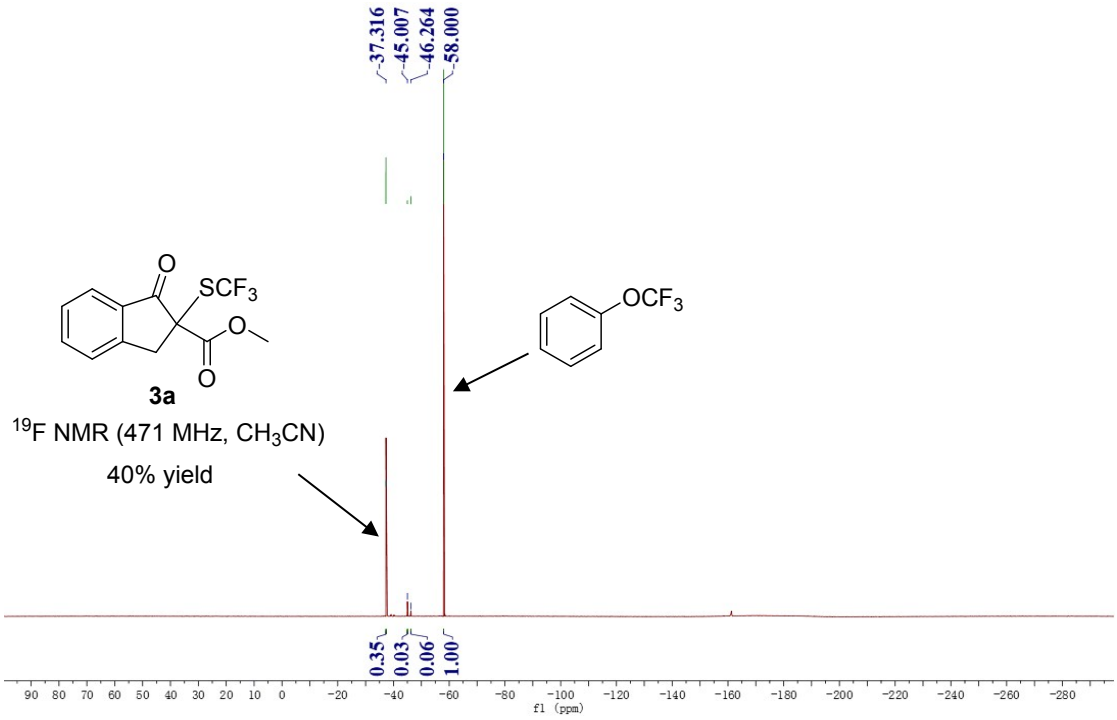
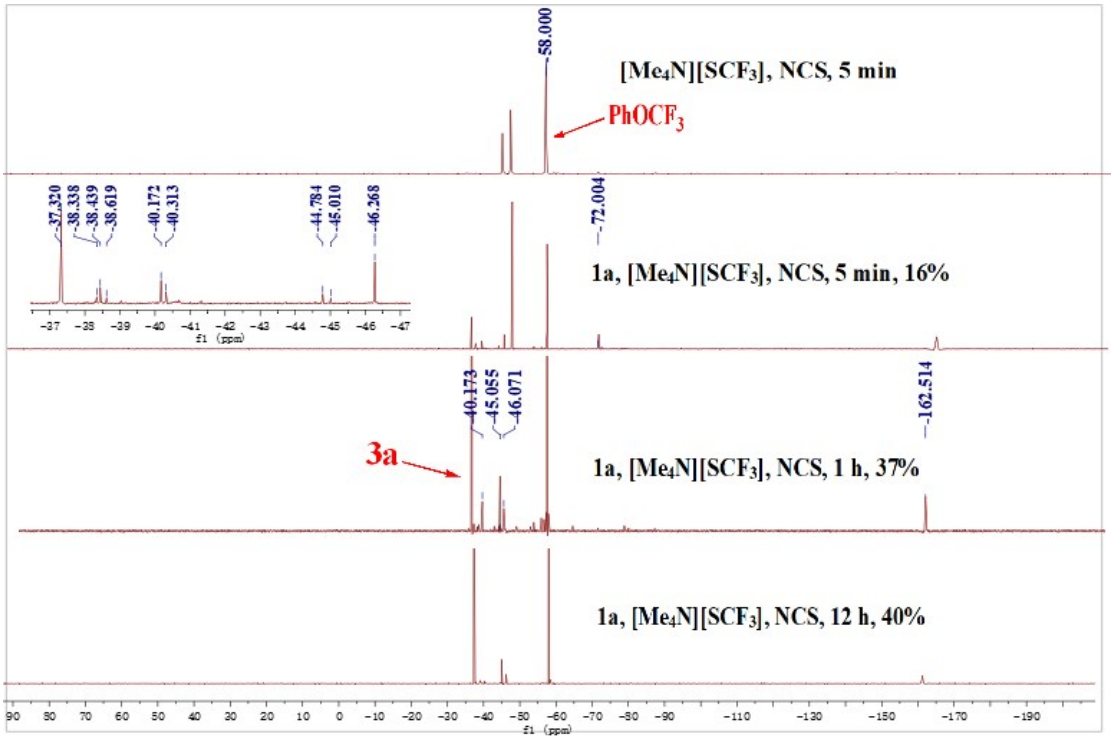


Figure S11. Combination of the above spectra (**Figures 7-10**)



Reference:

[1] (a) W. Tyrra, D. Naumann, Y. L. Yagupolskii, *J. Fluorine Chem.* **2003**, *123*, 183-

187. (b) T. Dong, J. He, Z.-H. Li, C.-P. Zhang, *ACS Sustainable Chem. Eng*. **2018**, *6*, 1327-1335. (c) W. Tyrra, D. Naumann, B. Hoge, Y.L. Yagupolskii, *J. Fluorine Chem.* **2003**, *119*, 101-107. (d) X.-X. Qi, P.-H. Chen, G.-S. Liu, *Angew. Chem. Int. Ed.* **2017**, *56*, 9517-9521.

[2] I. Geibel, J. Christoffers, *Eur. J. Org. Chem*. **2016**, 918-920.

[3] P. Gogoi, T. Kotipalli, K. Indukuri, S. Bondalapati, P. Saha, A. K. Saikia, *Tetrahedron* **2012**, *53*, 2726-2729.

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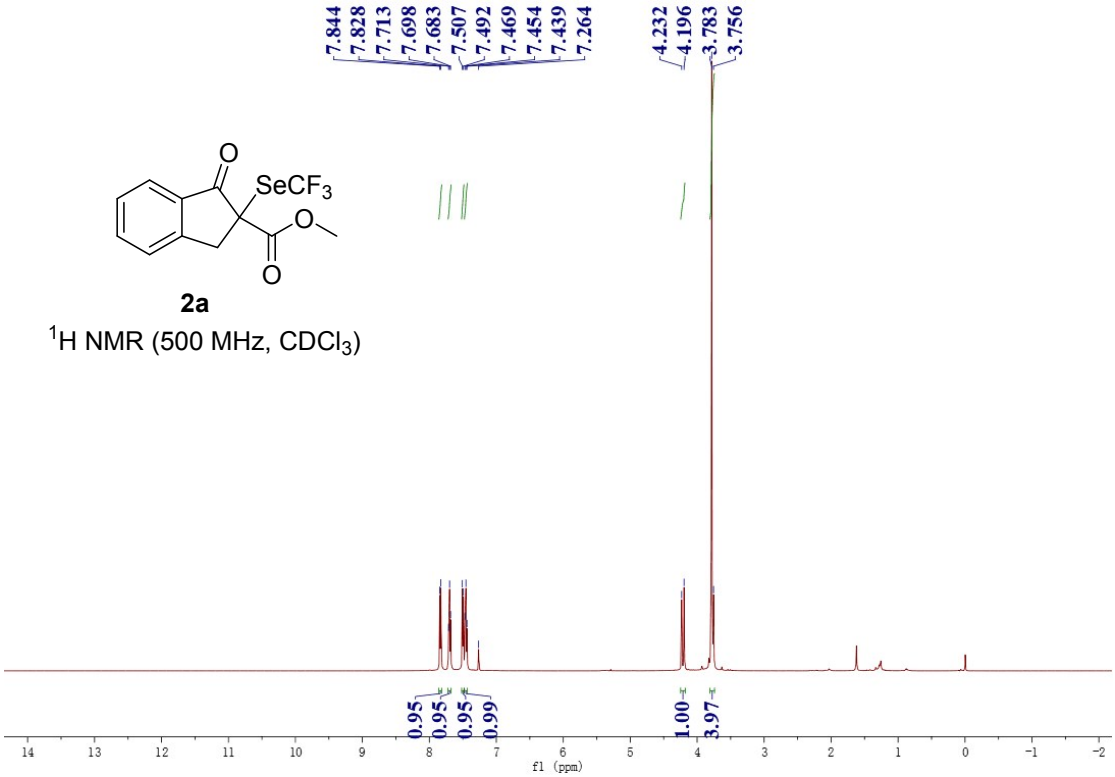
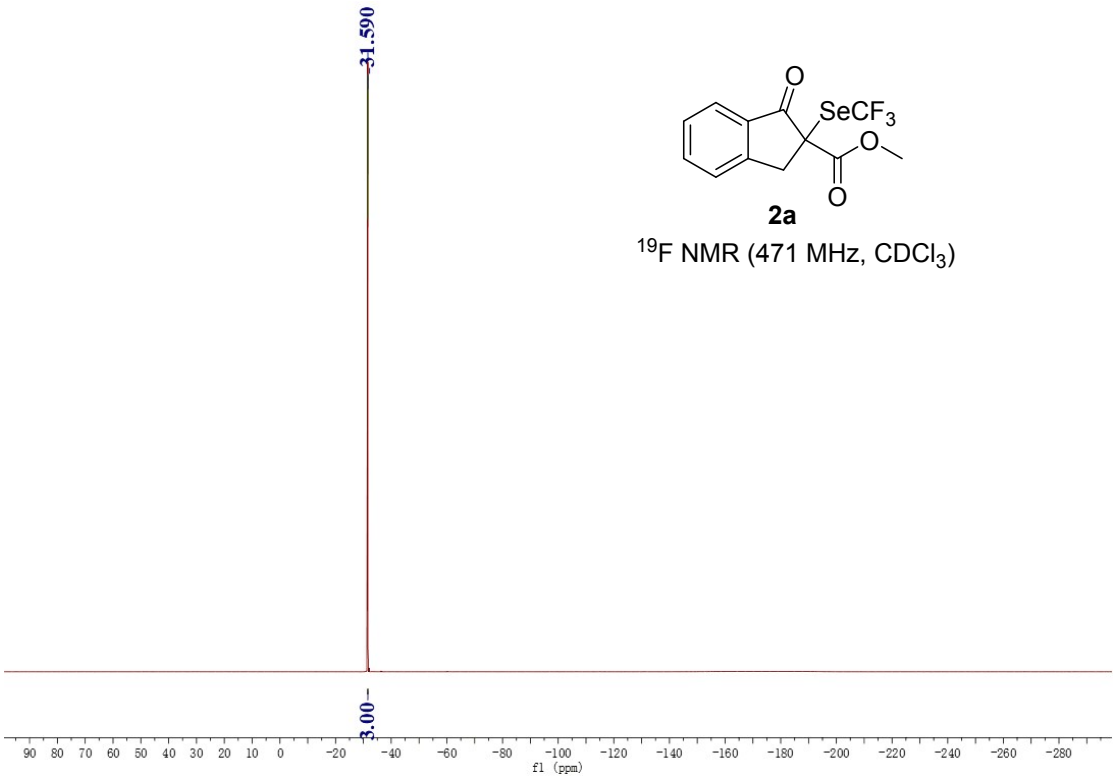
5. NMR spectra of the products



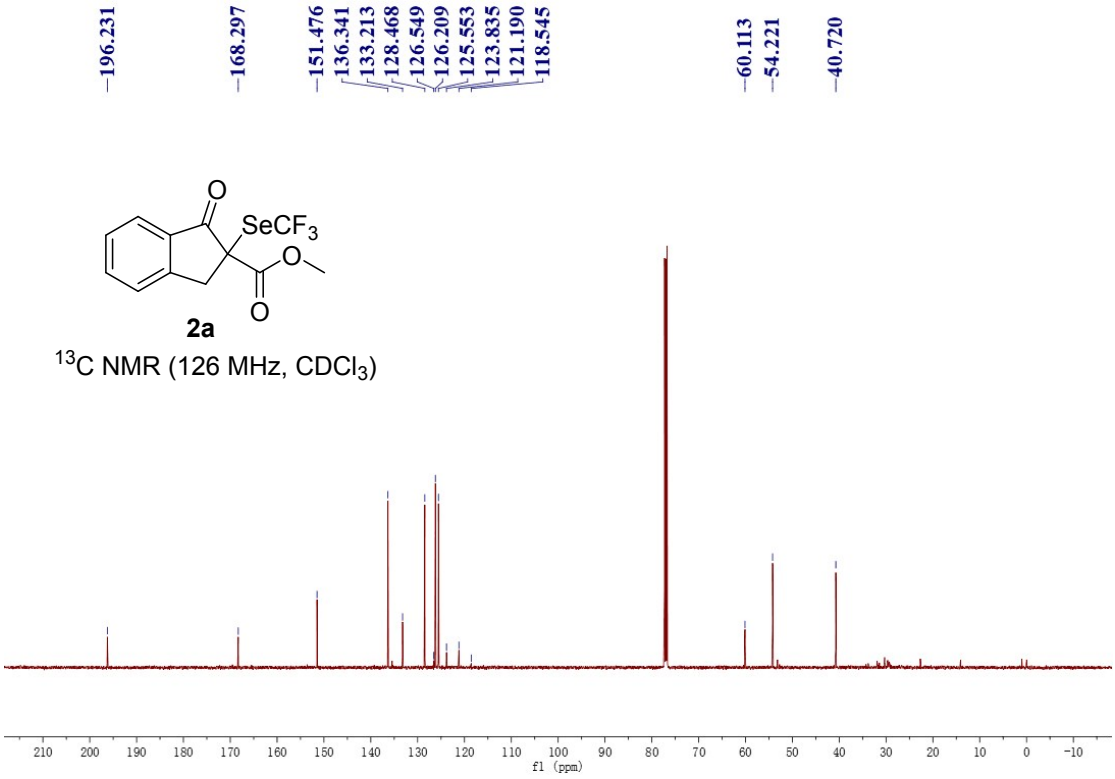
2a

^{1}H NMR (500 MHz, $CDCl_3$)



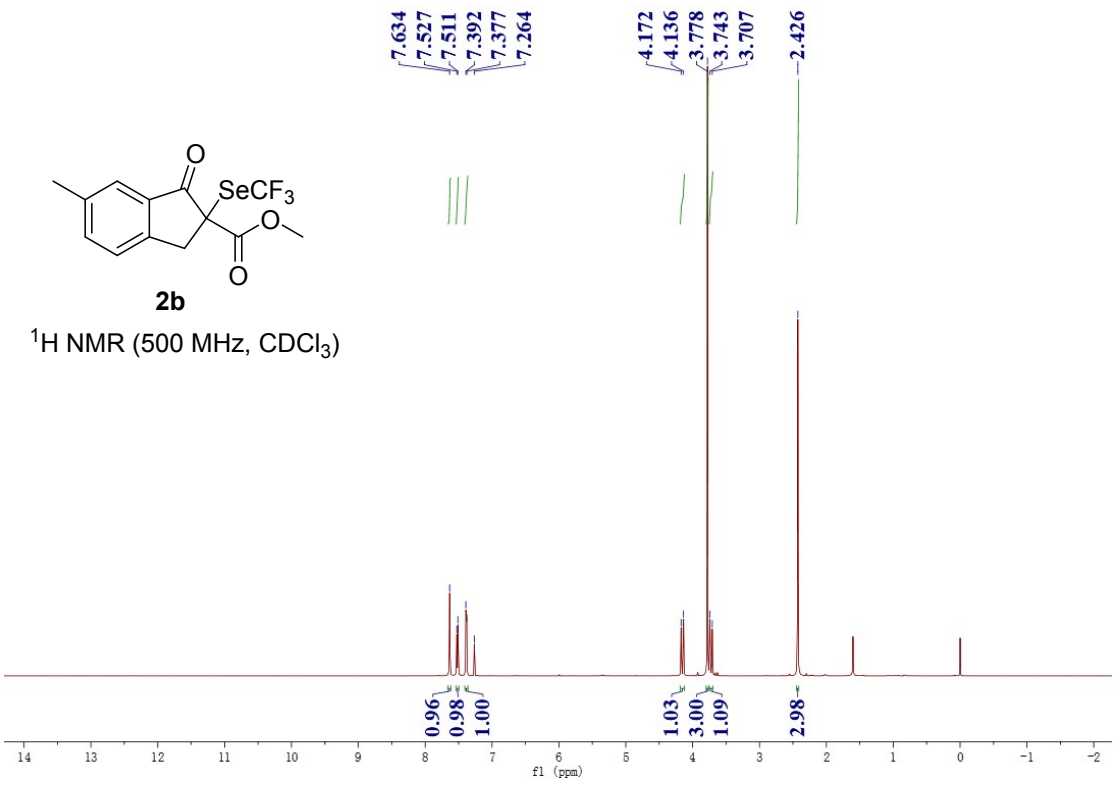
2a

^{19}F NMR (471 MHz, $CDCl_3$)



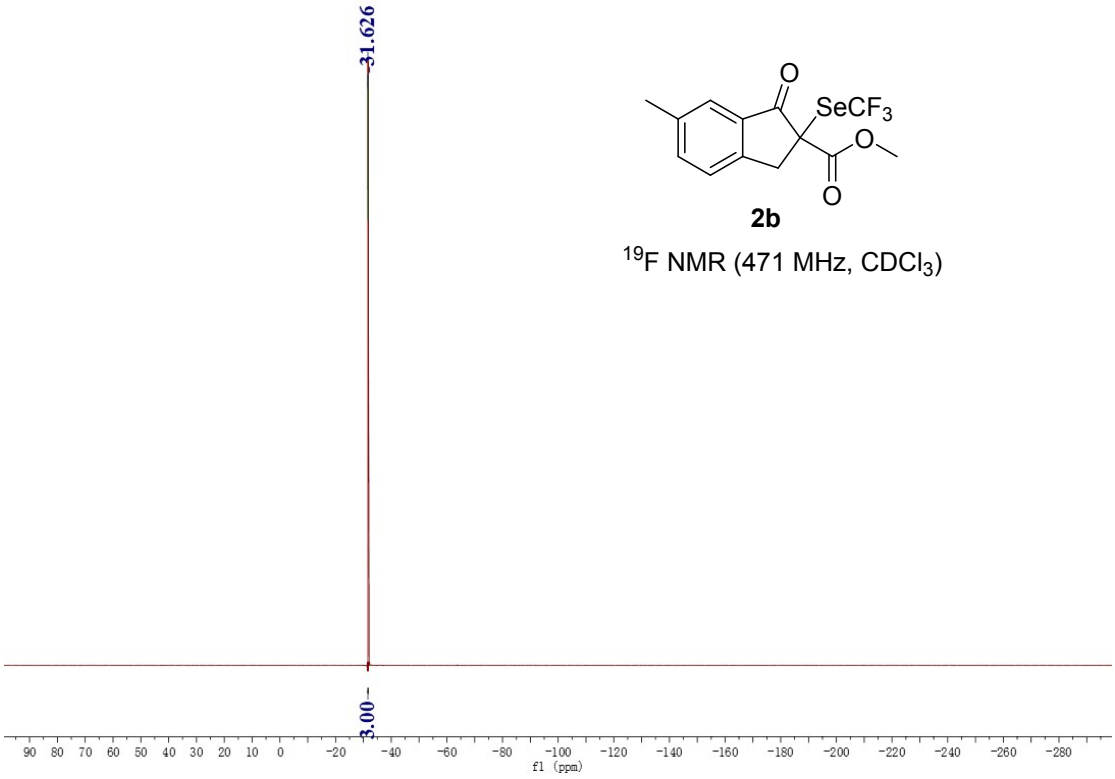
2a

^{13}C NMR (126 MHz, $CDCl_3$)



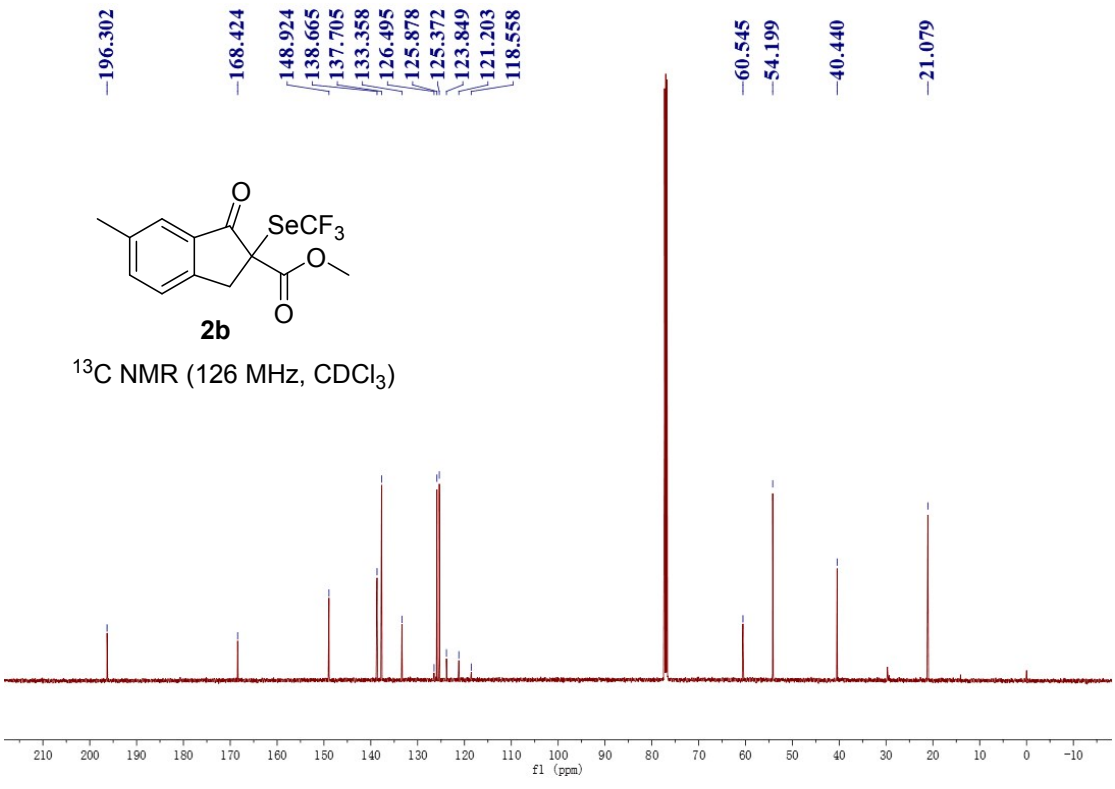
2b

^{1}H NMR (500 MHz, $CDCl_3$)



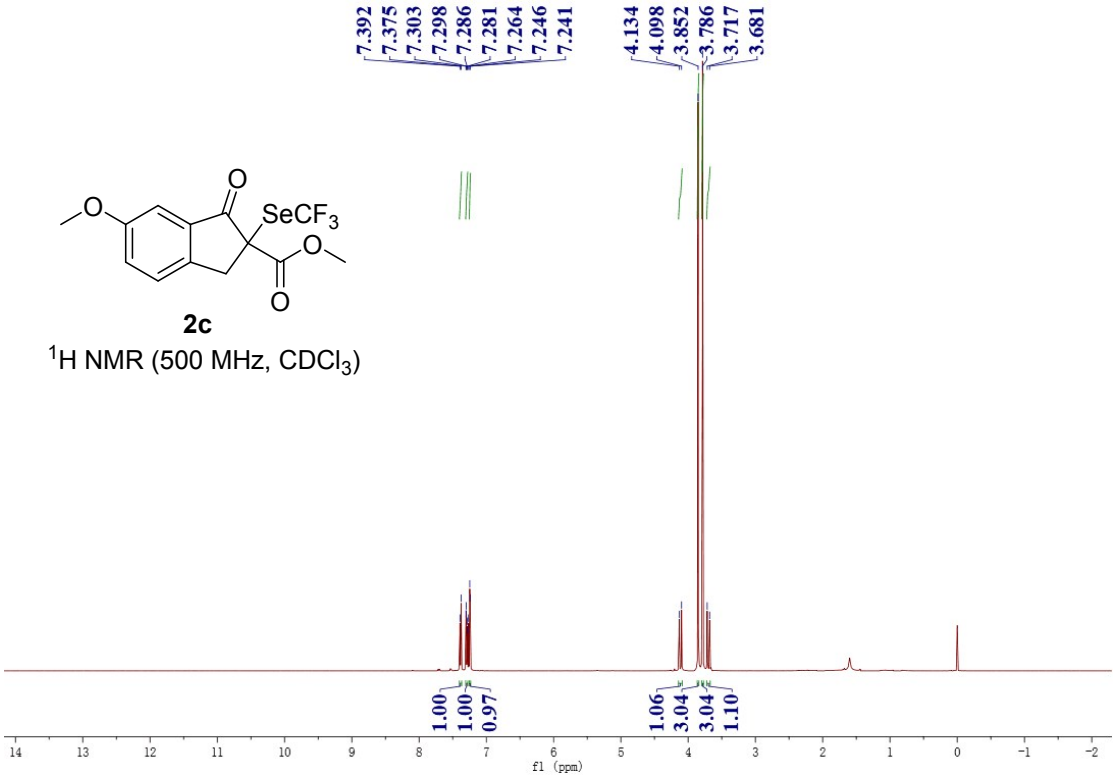
2b

^{19}F NMR (471 MHz, $CDCl_3$)



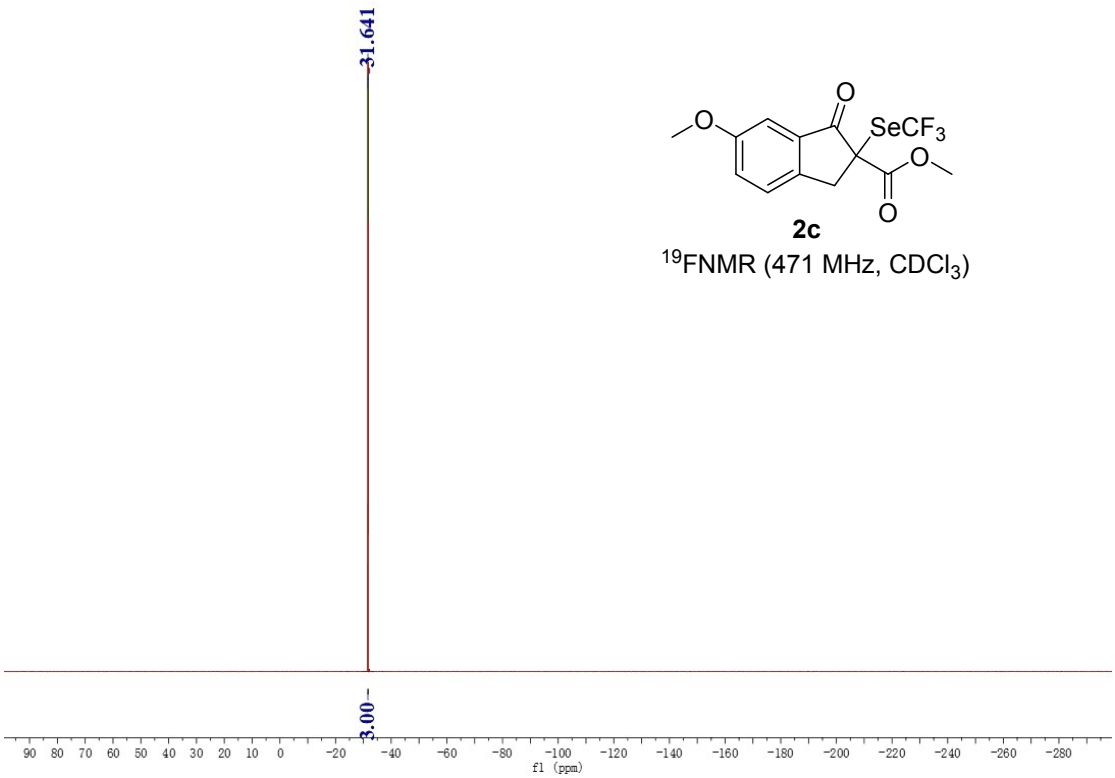
2b

^{13}C NMR (126 MHz, $CDCl_3$)



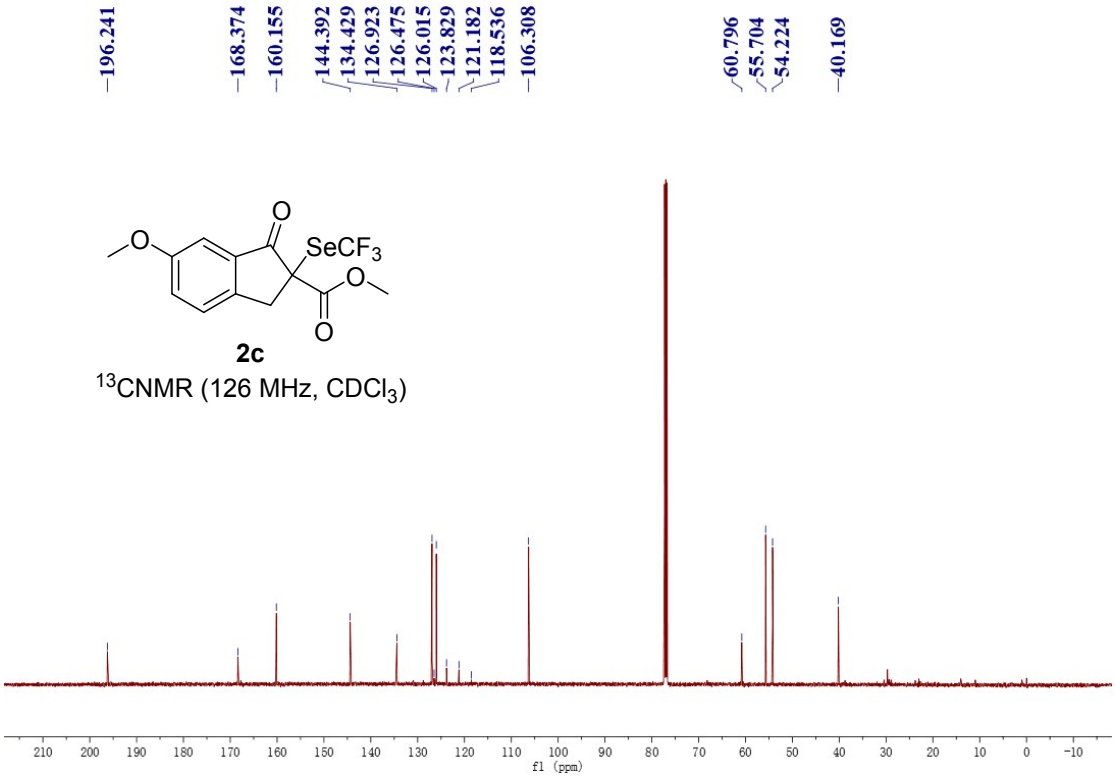
2c

^{1}H NMR (500 MHz, $CDCl_3$)



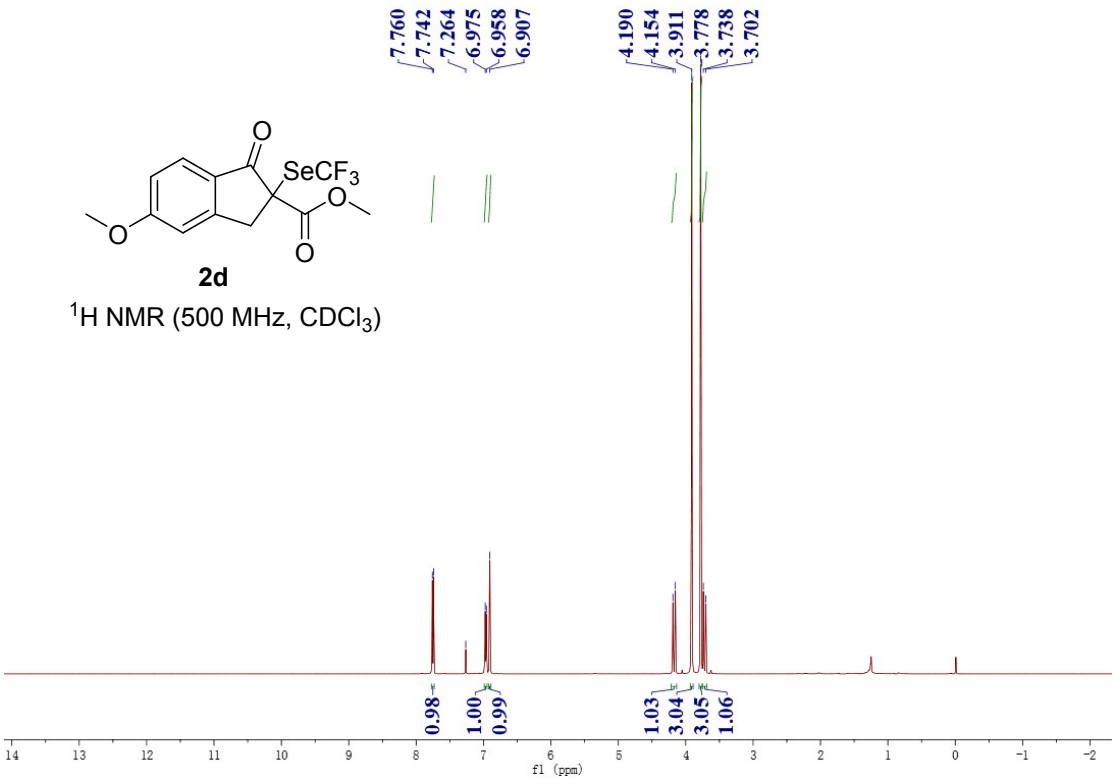
2c

^{19}FNMR (471 MHz, $CDCl_3$)



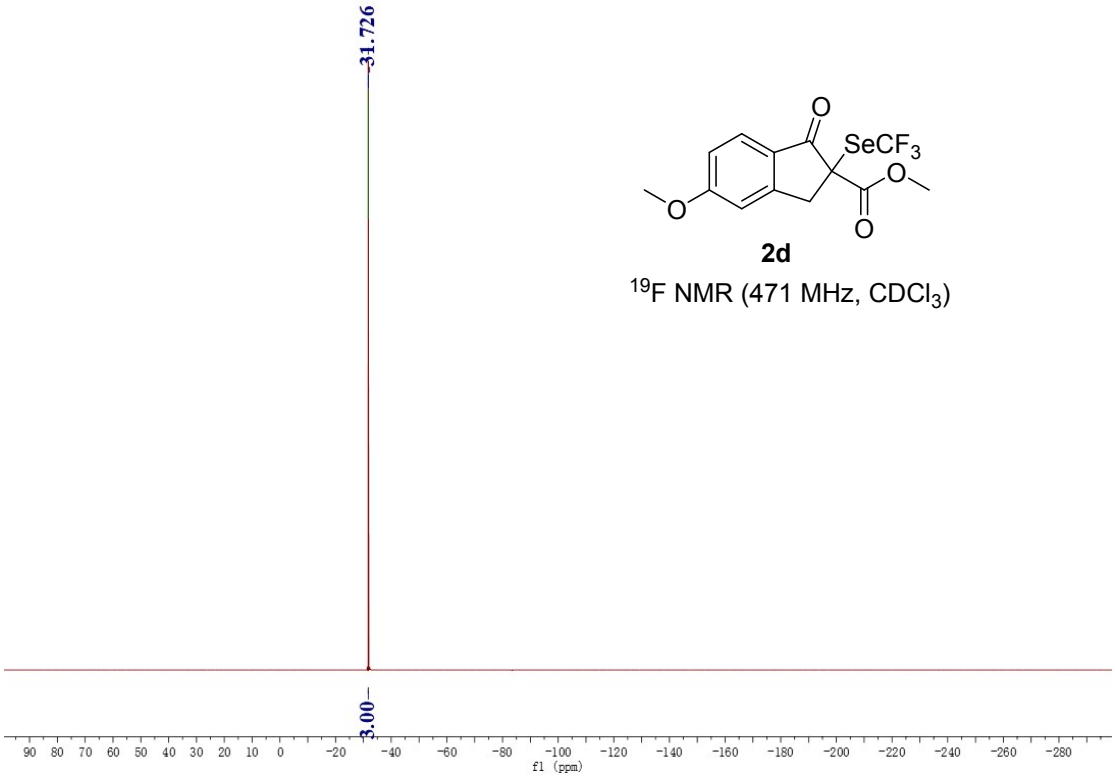
2c

^{13}CNMR (126 MHz, $CDCl_3$)



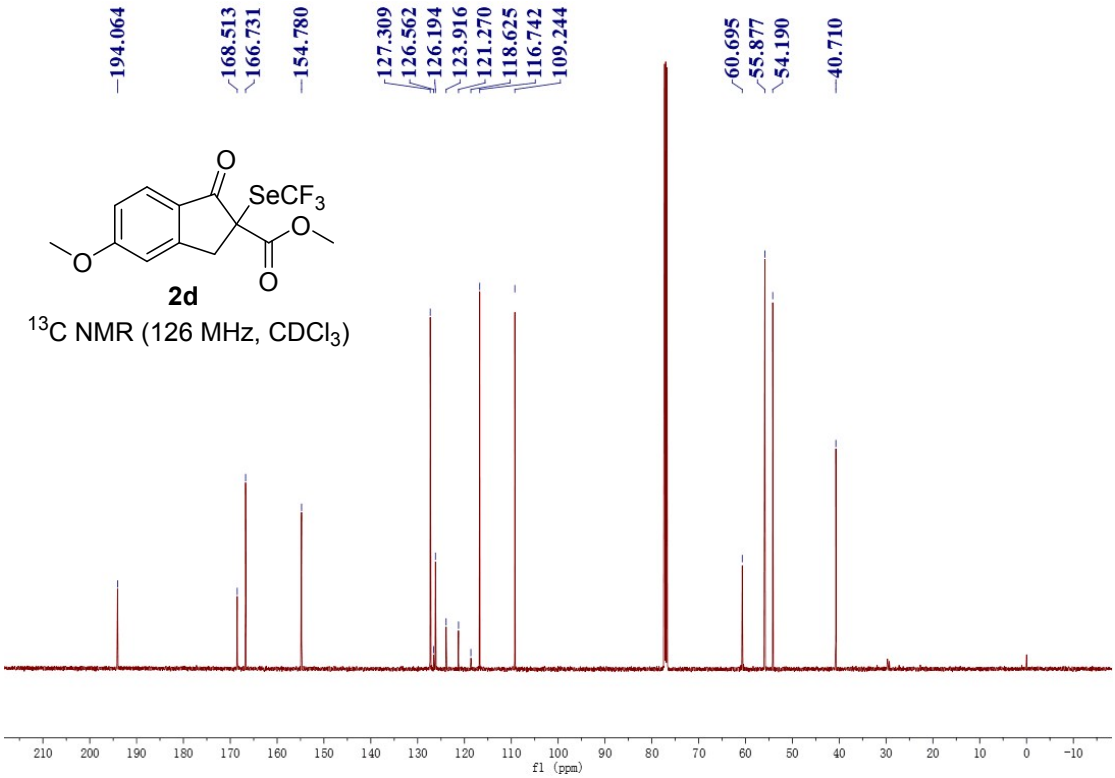
2d

^{1}H NMR (500 MHz, $CDCl_3$)



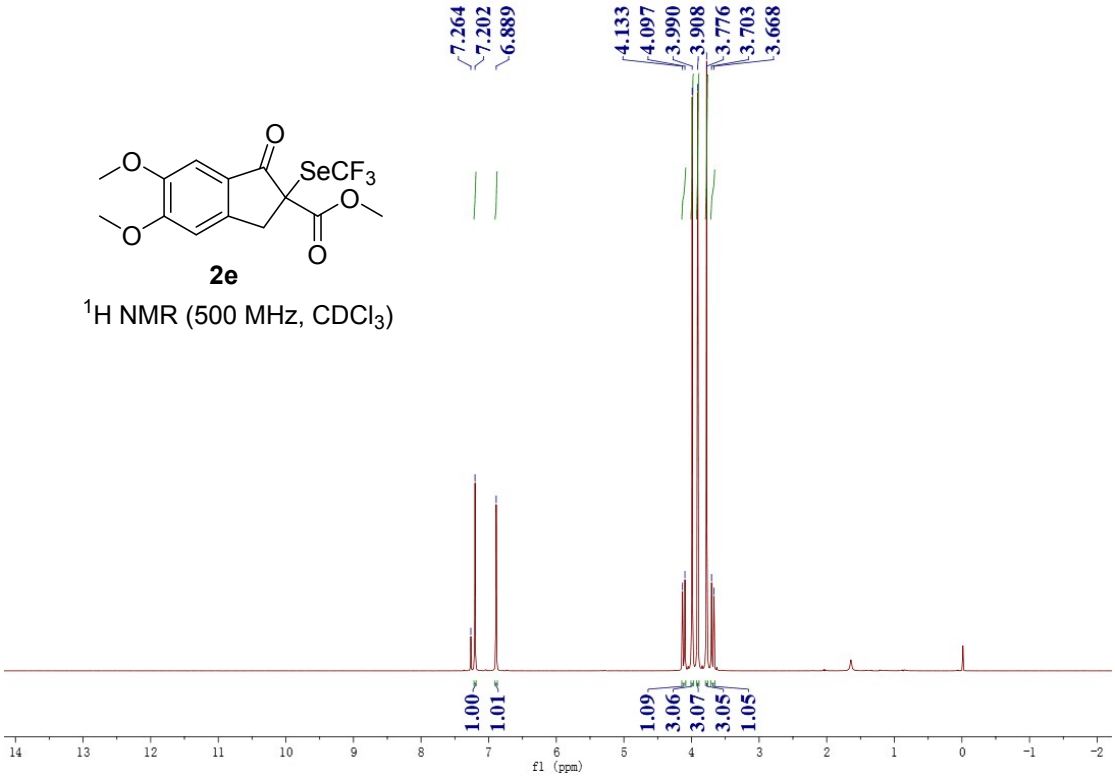
2d

^{19}F NMR (471 MHz, $CDCl_3$)



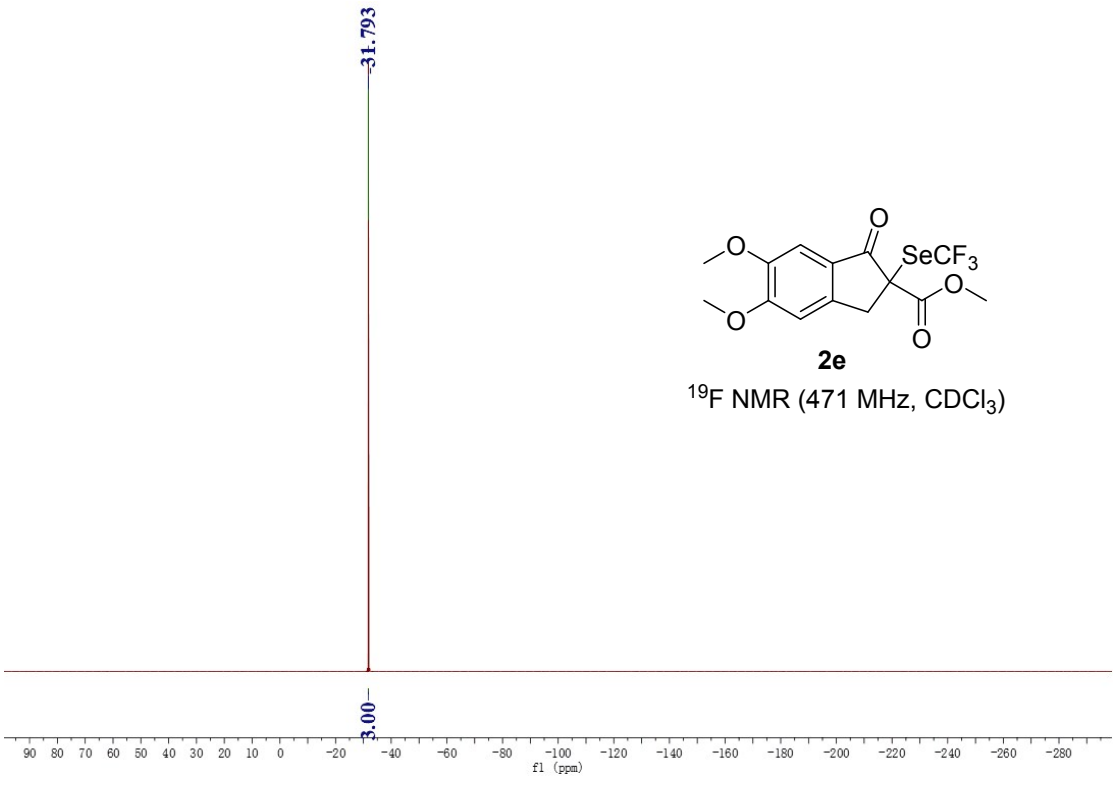
2d

^{13}C NMR (126 MHz, $CDCl_3$)



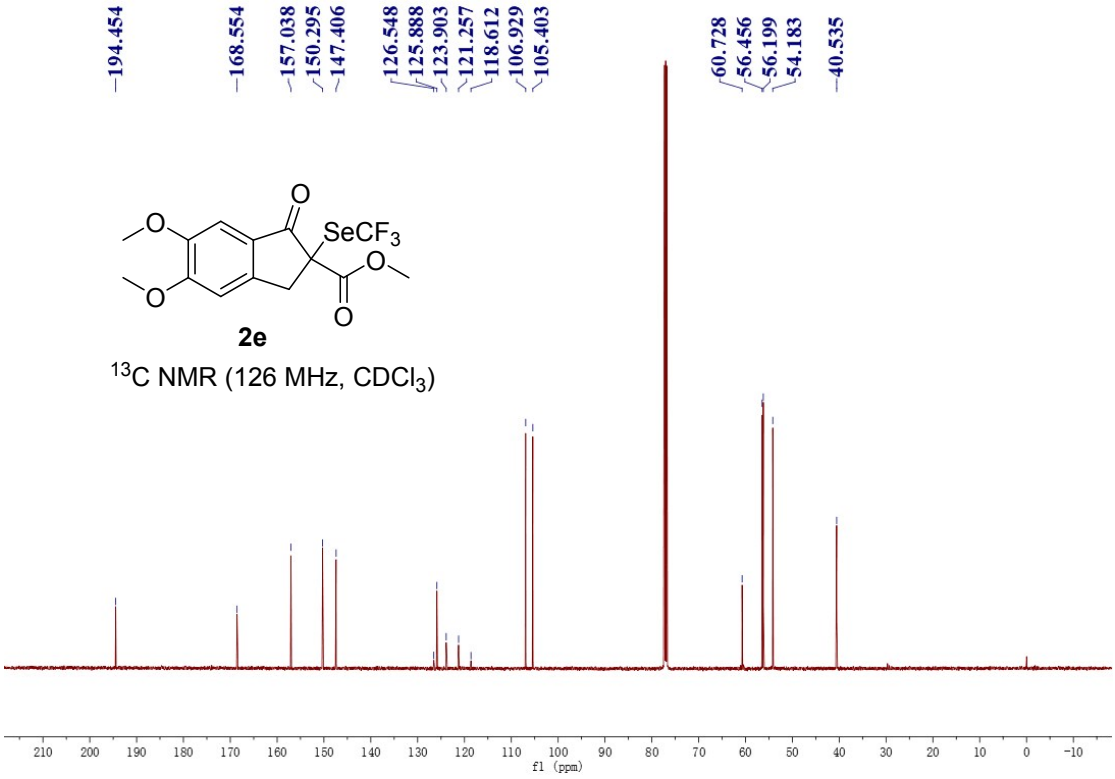
2e

^{1}H NMR (500 MHz, $CDCl_3$)



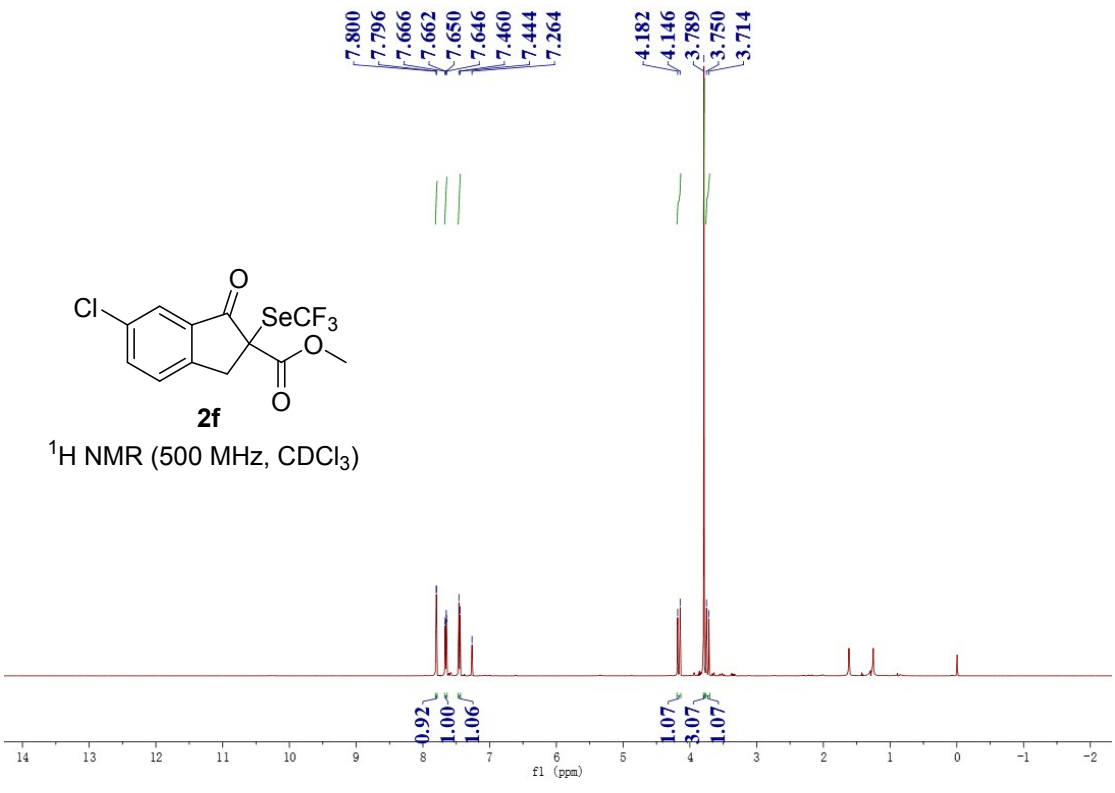
2e

^{19}F NMR (471 MHz, $CDCl_3$)



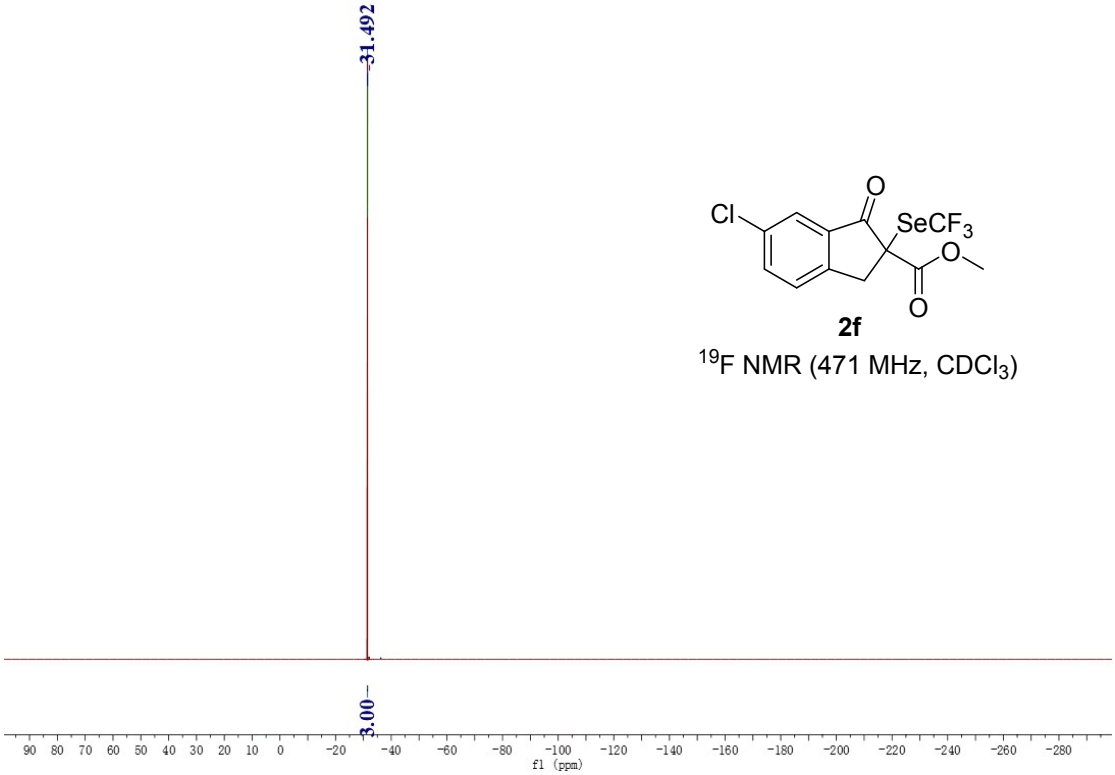
2e

^{13}C NMR (126 MHz, $CDCl_3$)



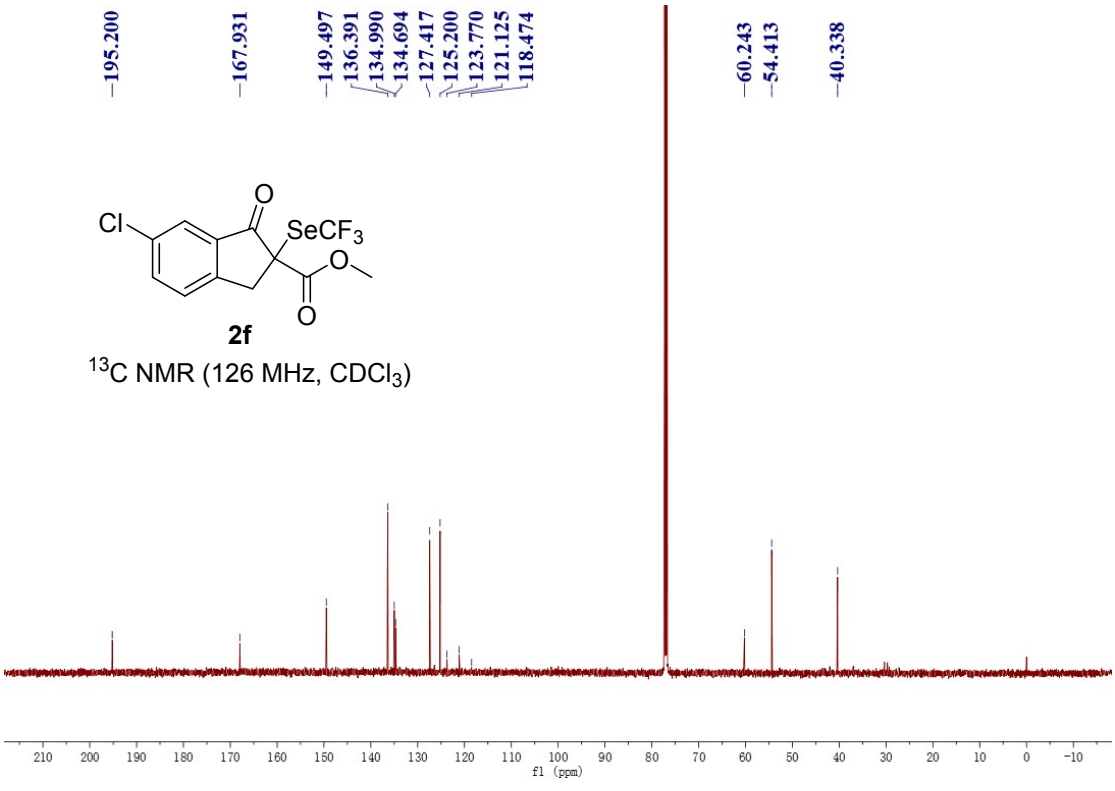
2f

^{1}H NMR (500 MHz, $CDCl_3$)



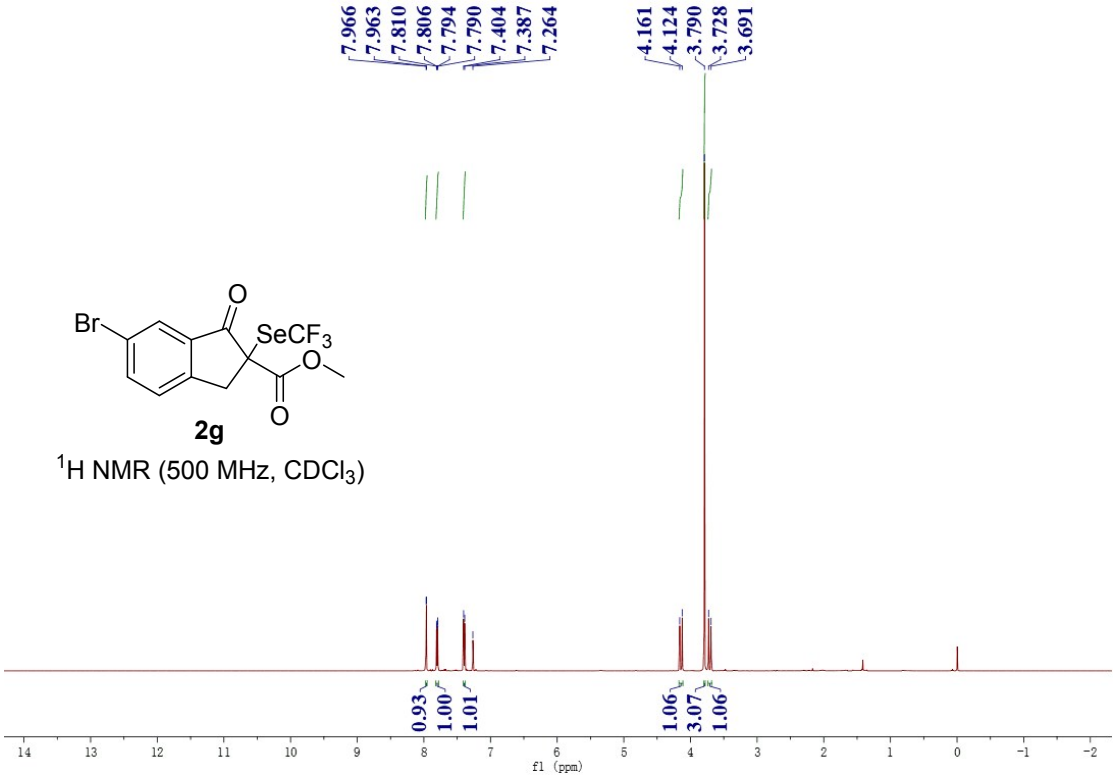
2f

^{19}F NMR (471 MHz, $CDCl_3$)



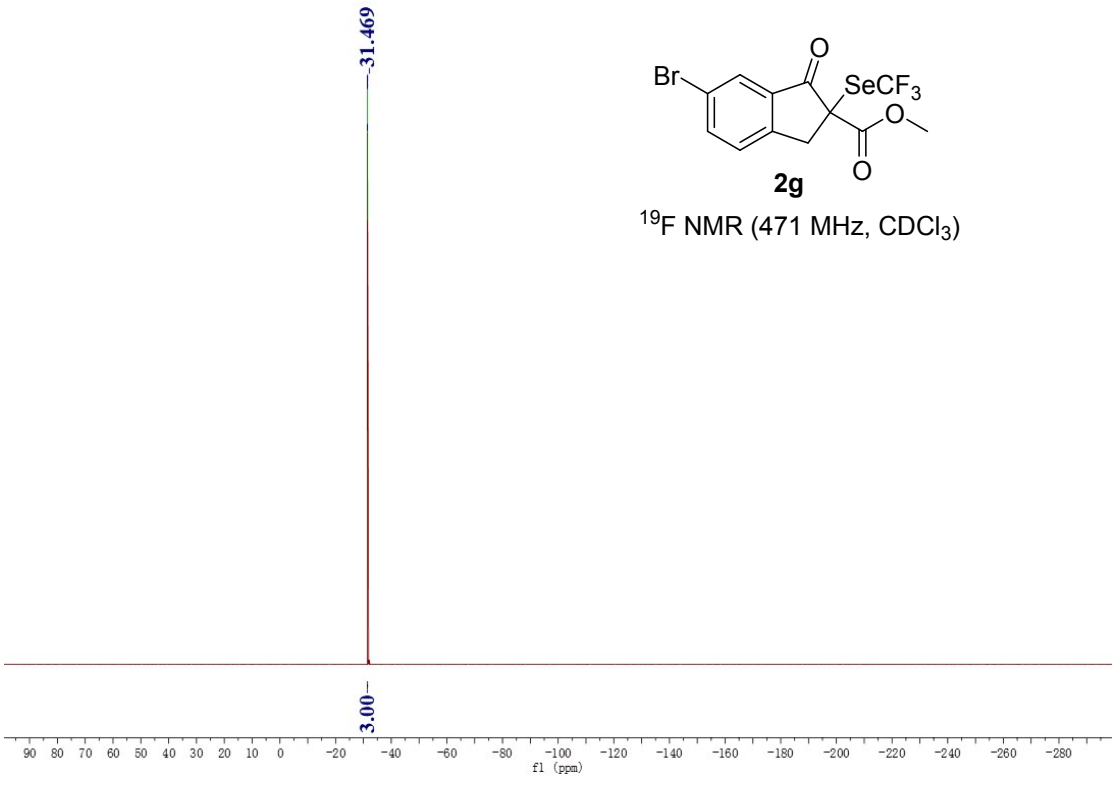
2f

^{13}C NMR (126 MHz, $CDCl_3$)



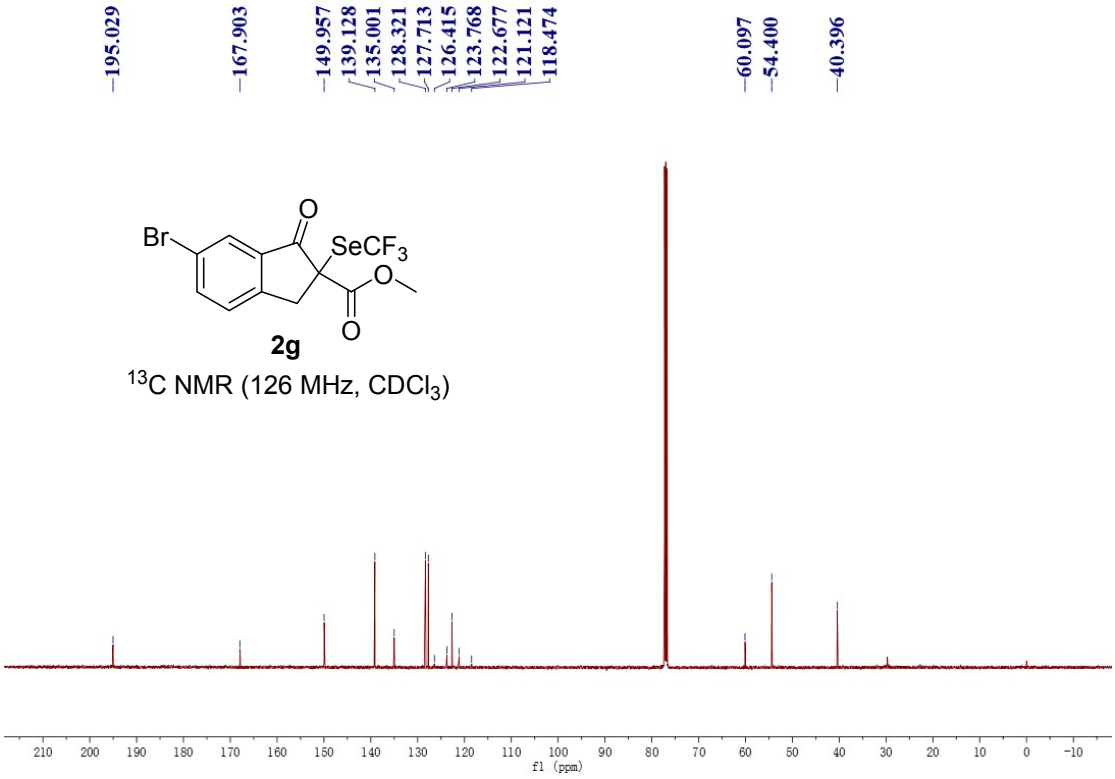
2g

^{1}H NMR (500 MHz, $CDCl_3$)



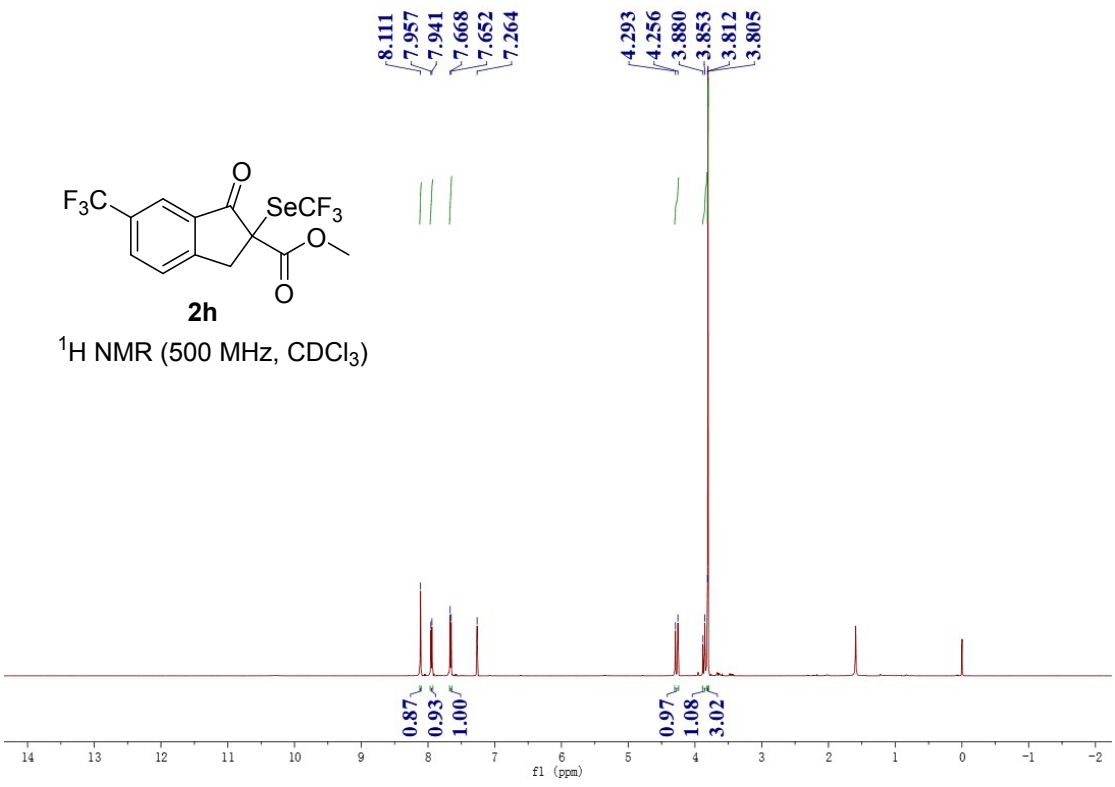
2g

^{19}F NMR (471 MHz, $CDCl_3$)



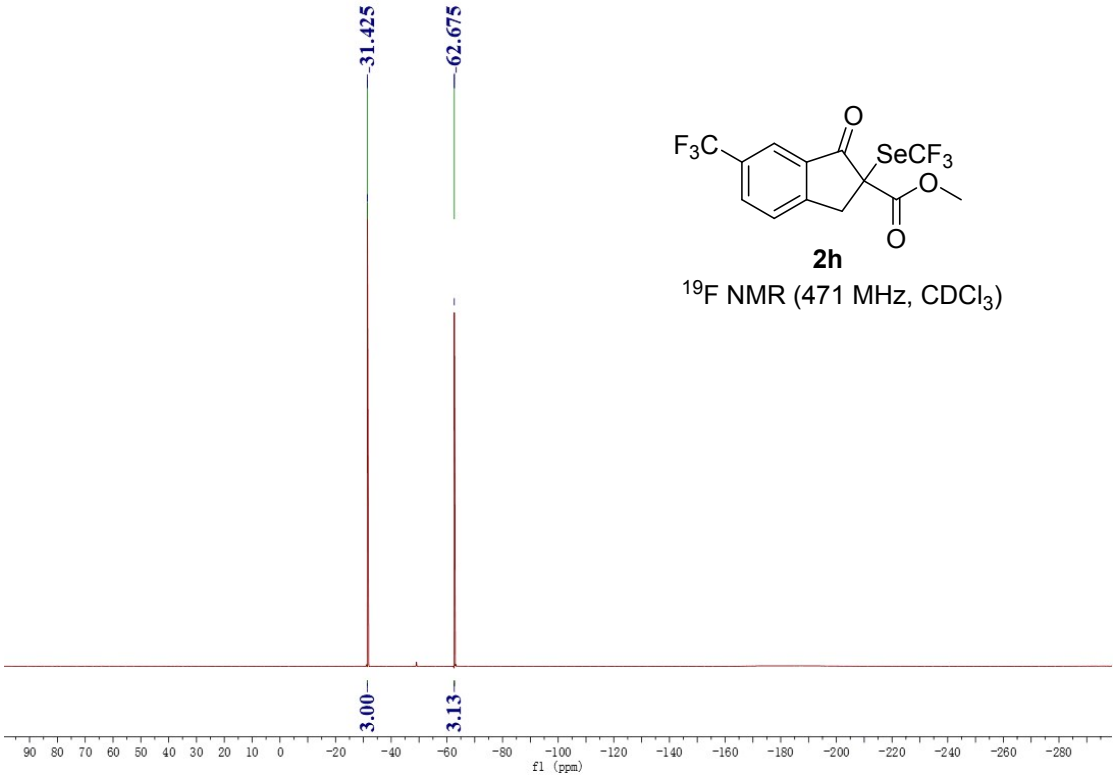
2g

^{13}C NMR (126 MHz, $CDCl_3$)



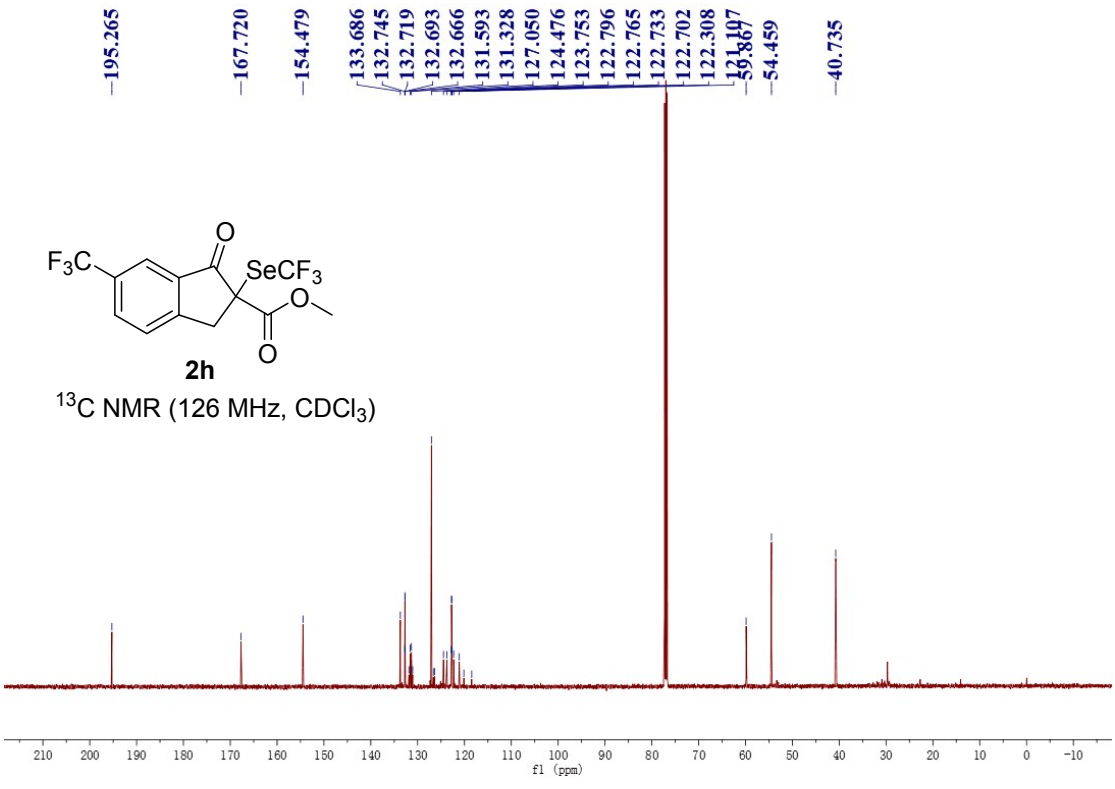
2h

^{1}H NMR (500 MHz, $CDCl_3$)



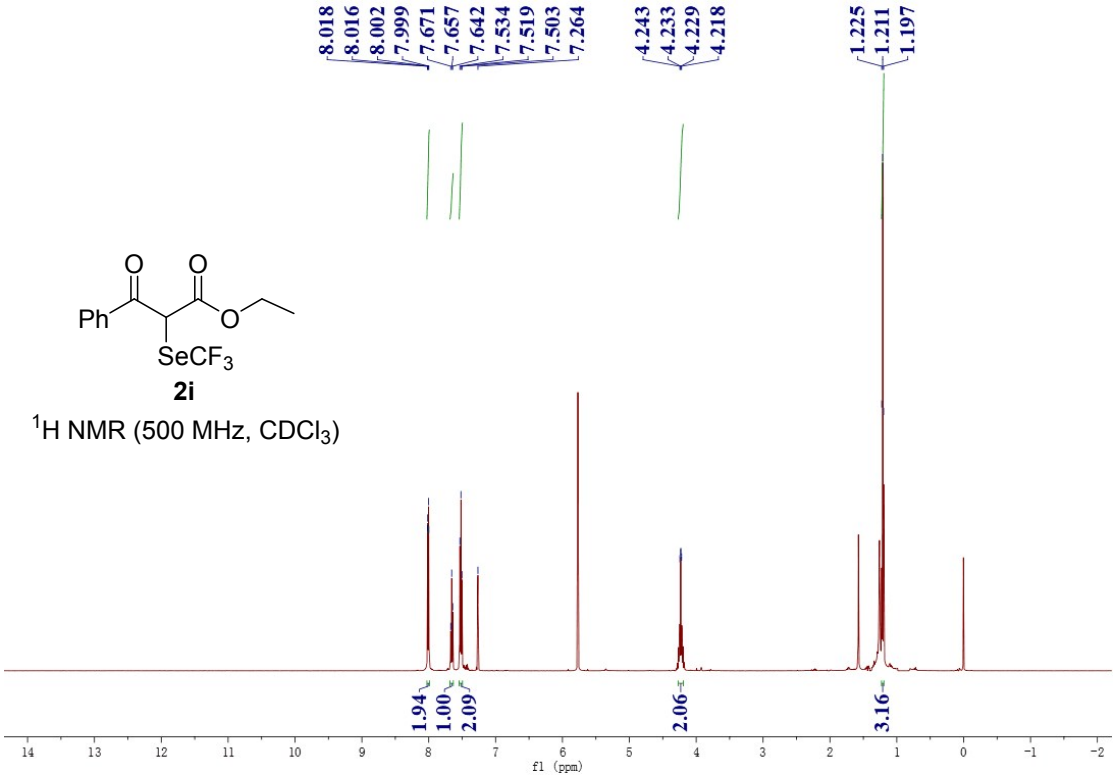
2h

^{19}F NMR (471 MHz, $CDCl_3$)



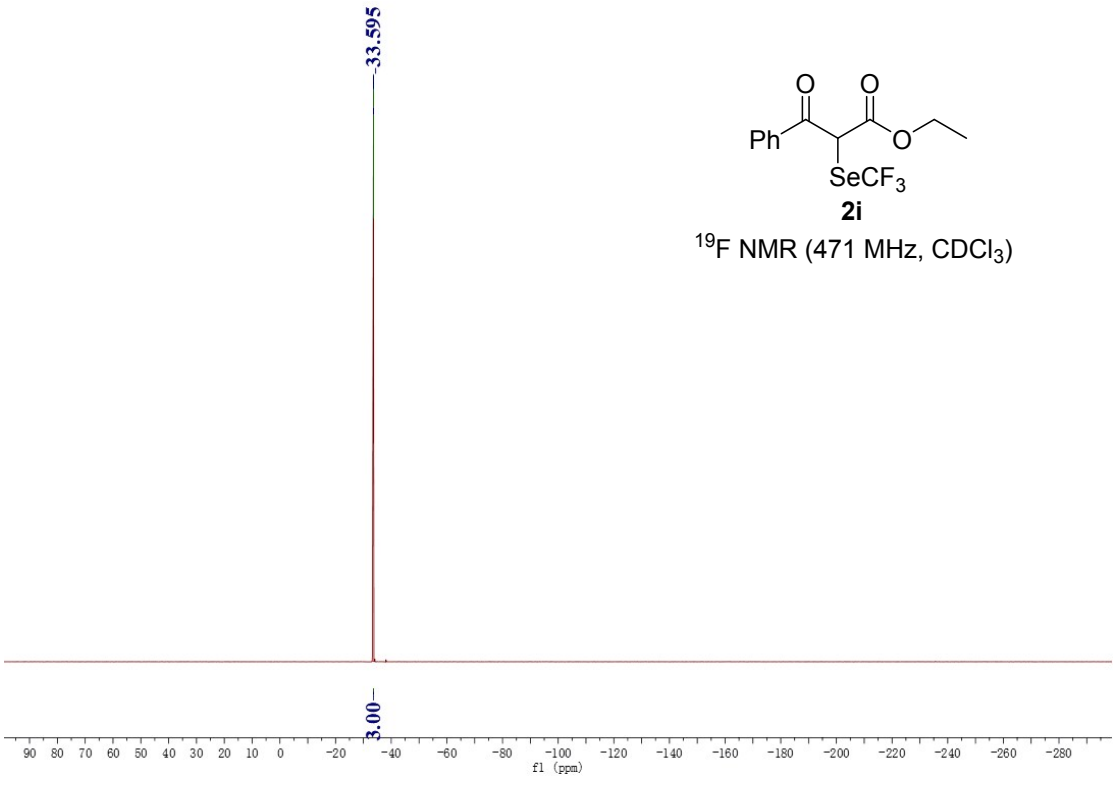
2h

^{13}C NMR (126 MHz, $CDCl_3$)



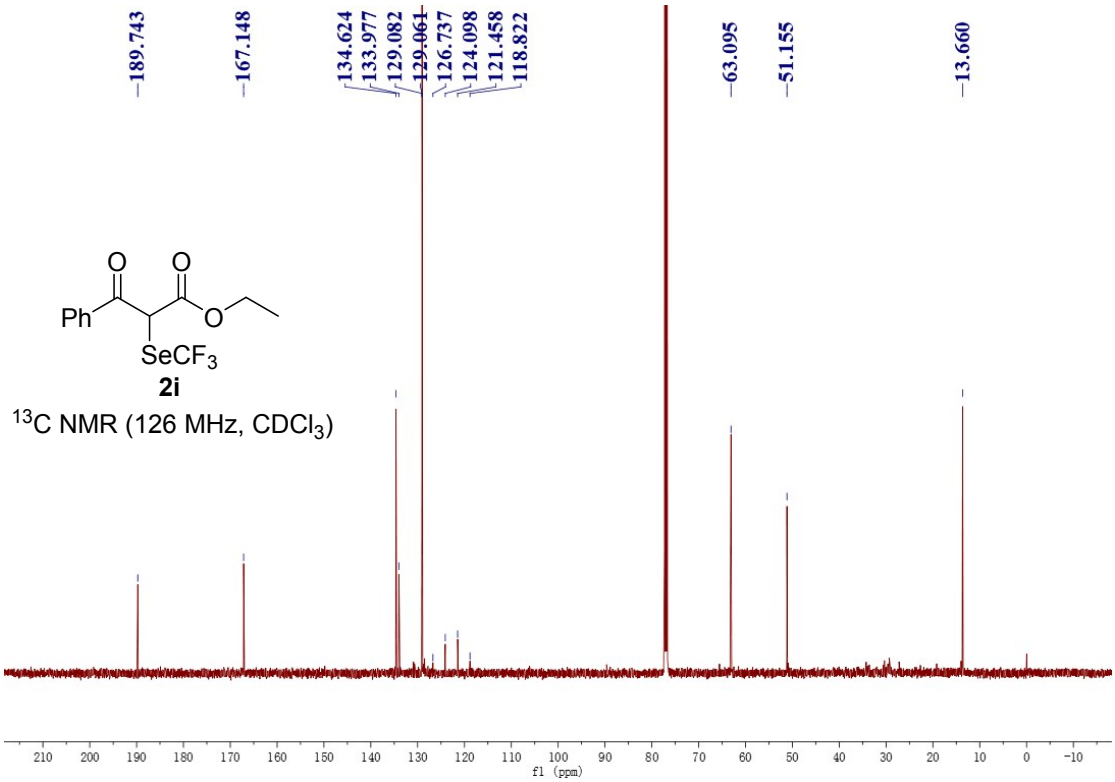
2i

^{1}H NMR (500 MHz, $CDCl_3$)



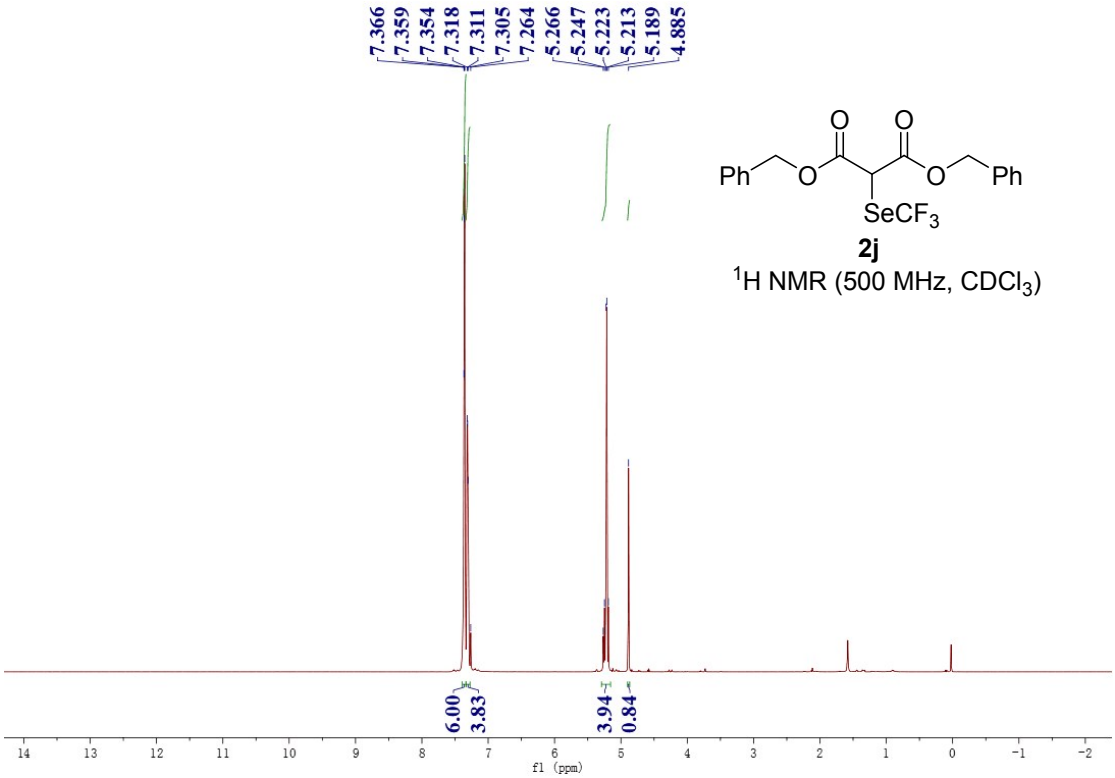
2i

^{19}F NMR (471 MHz, $CDCl_3$)



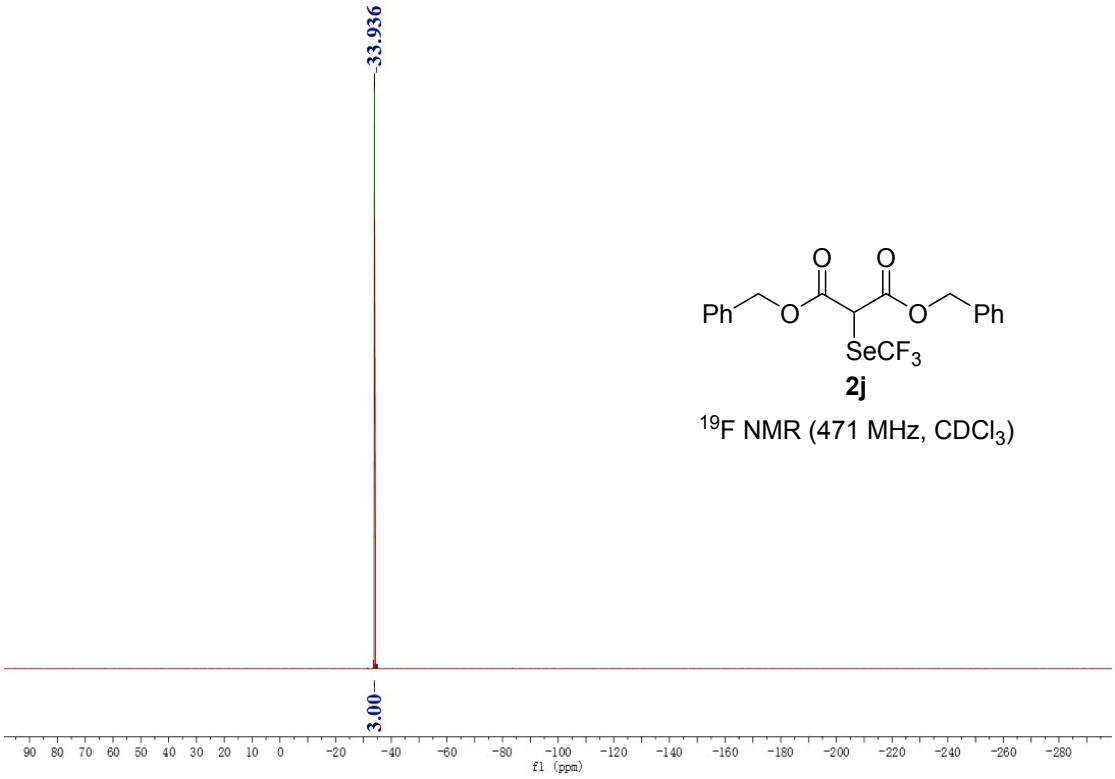
2i

^{13}C NMR (126 MHz, $CDCl_3$)



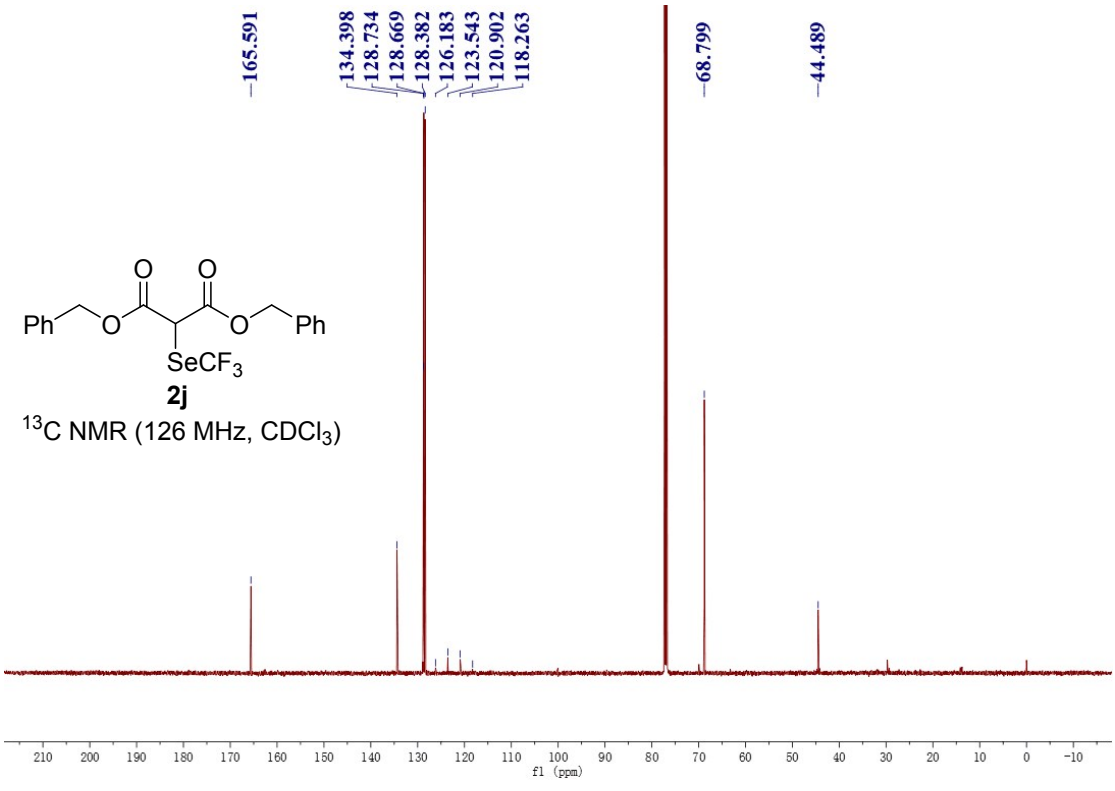
2j

^{1}H NMR (500 MHz, $CDCl_3$)



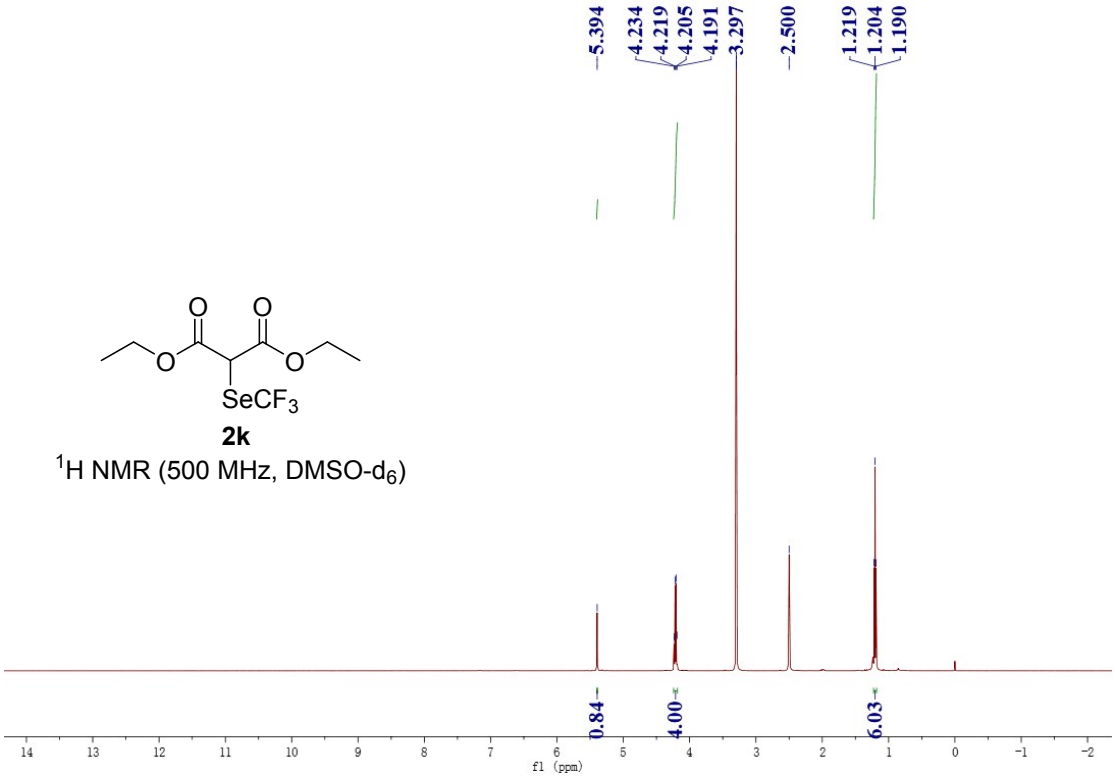
2j

^{19}F NMR (471 MHz, $CDCl_3$)



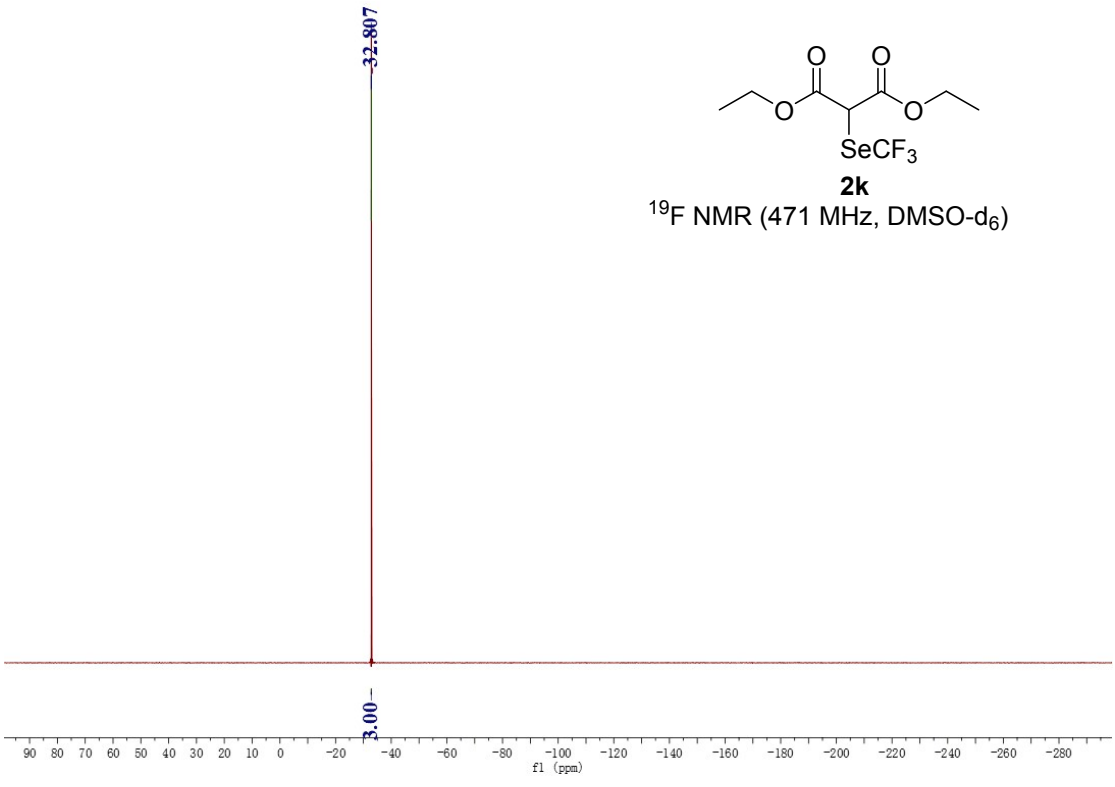
2j

^{13}C NMR (126 MHz, $CDCl_3$)



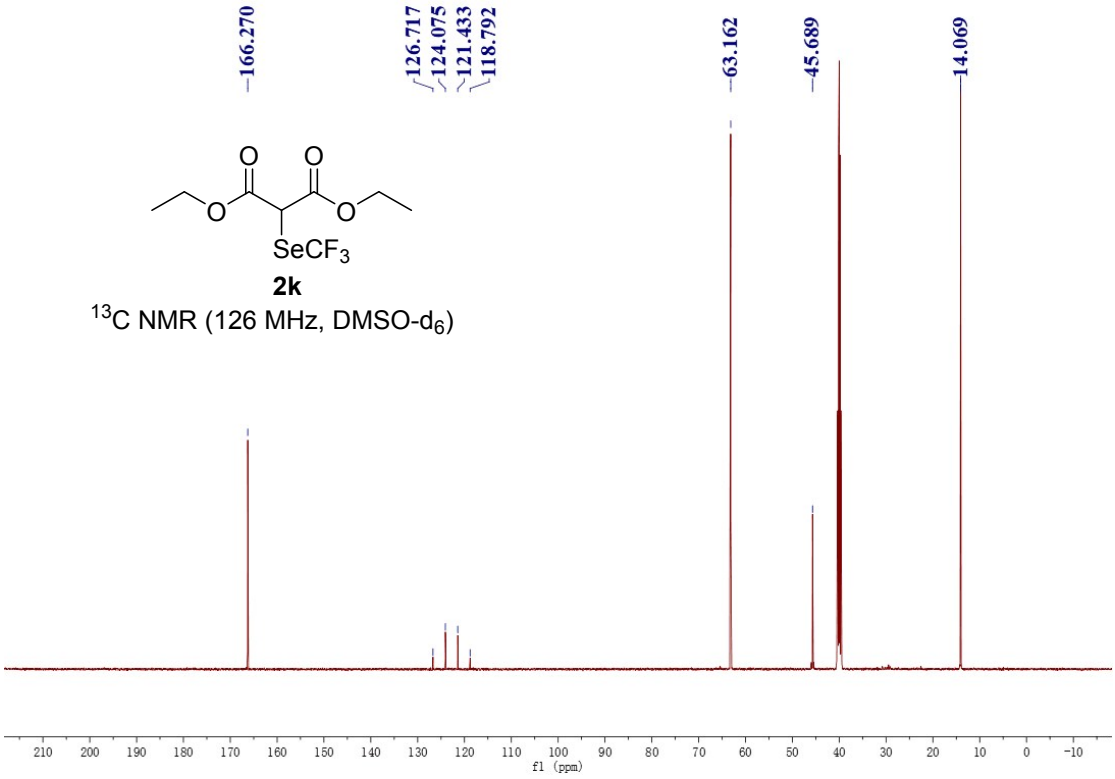
2k

^{1}H NMR (500 MHz, DMSO-d_6)



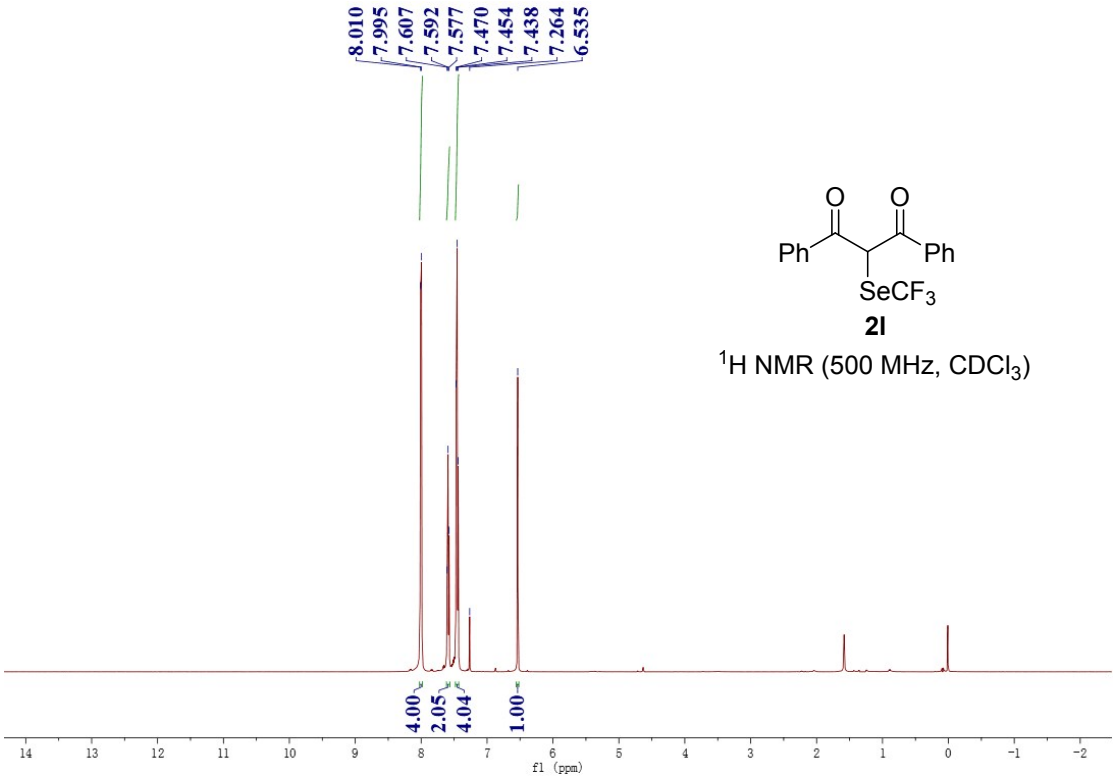
2k

^{19}F NMR (471 MHz, DMSO-d_6)



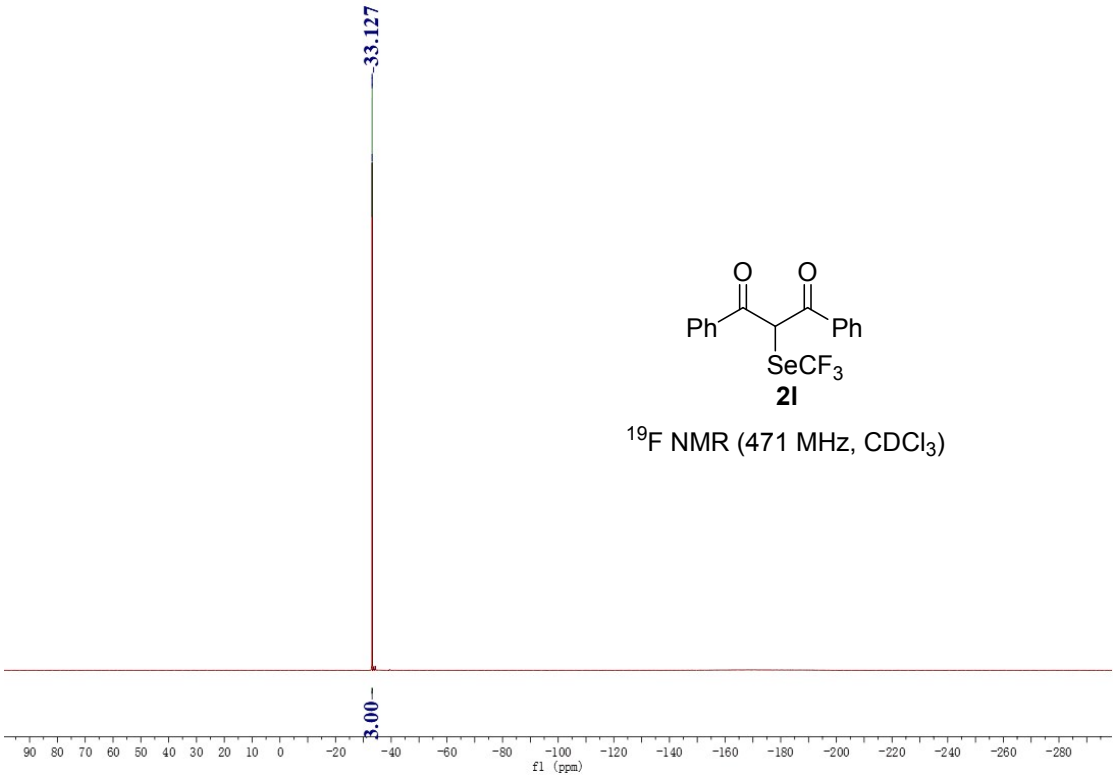
2k

^{13}C NMR (126 MHz, DMSO-d_6)



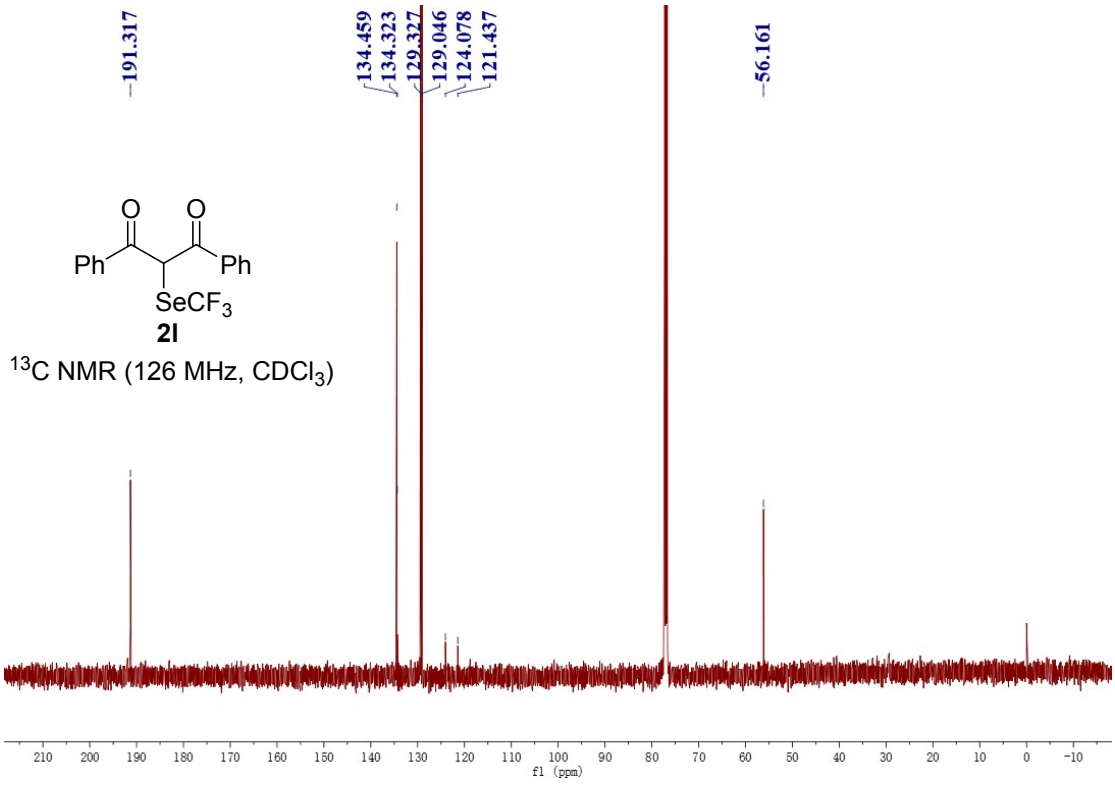
2l

^{1}H NMR (500 MHz, $CDCl_3$)



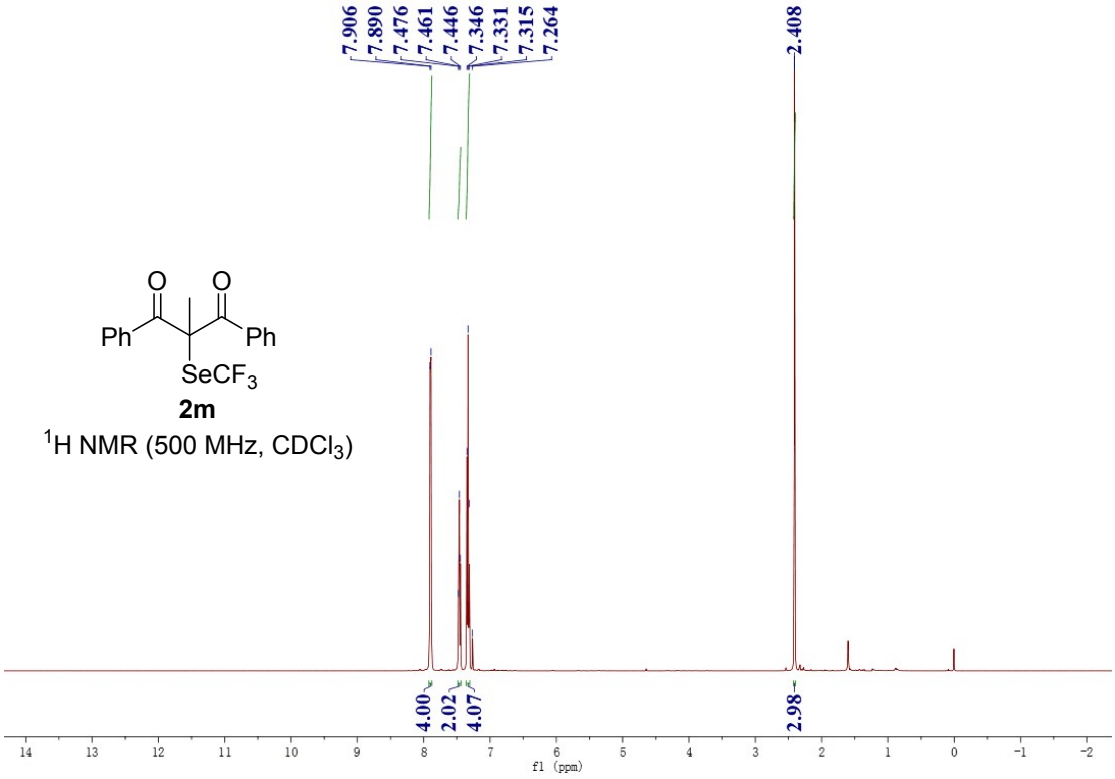
2l

^{19}F NMR (471 MHz, $CDCl_3$)



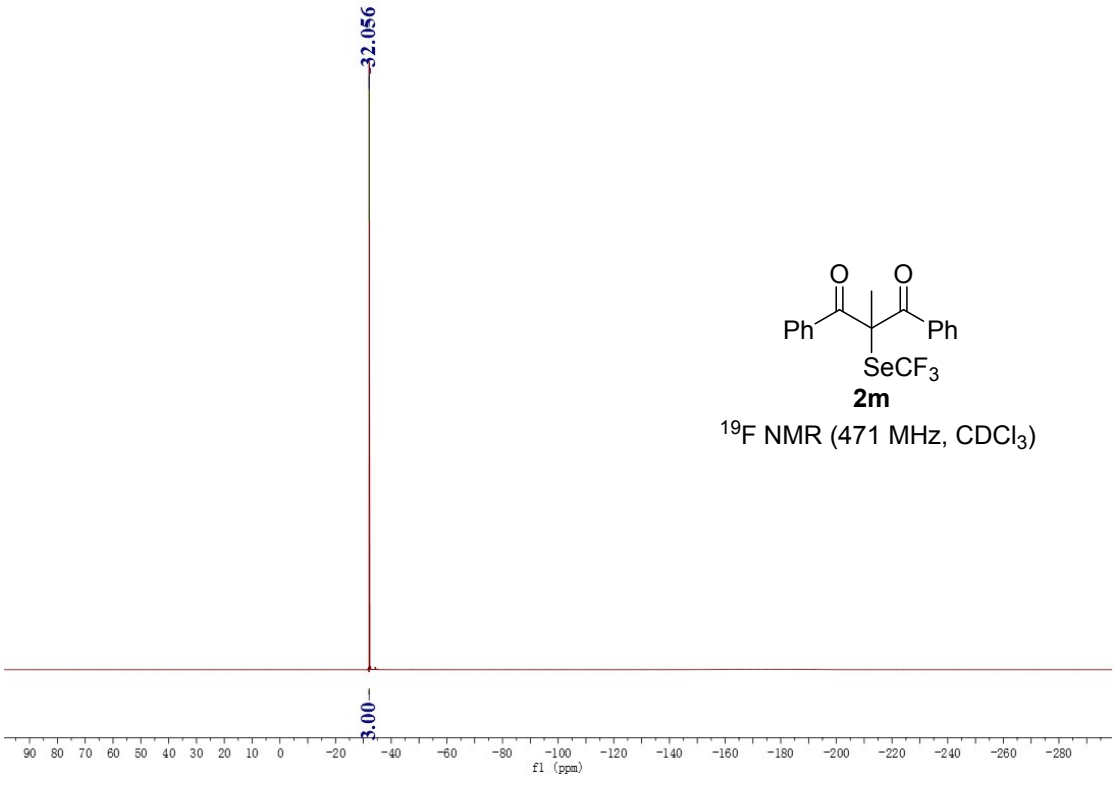
2l

^{13}C NMR (126 MHz, $CDCl_3$)



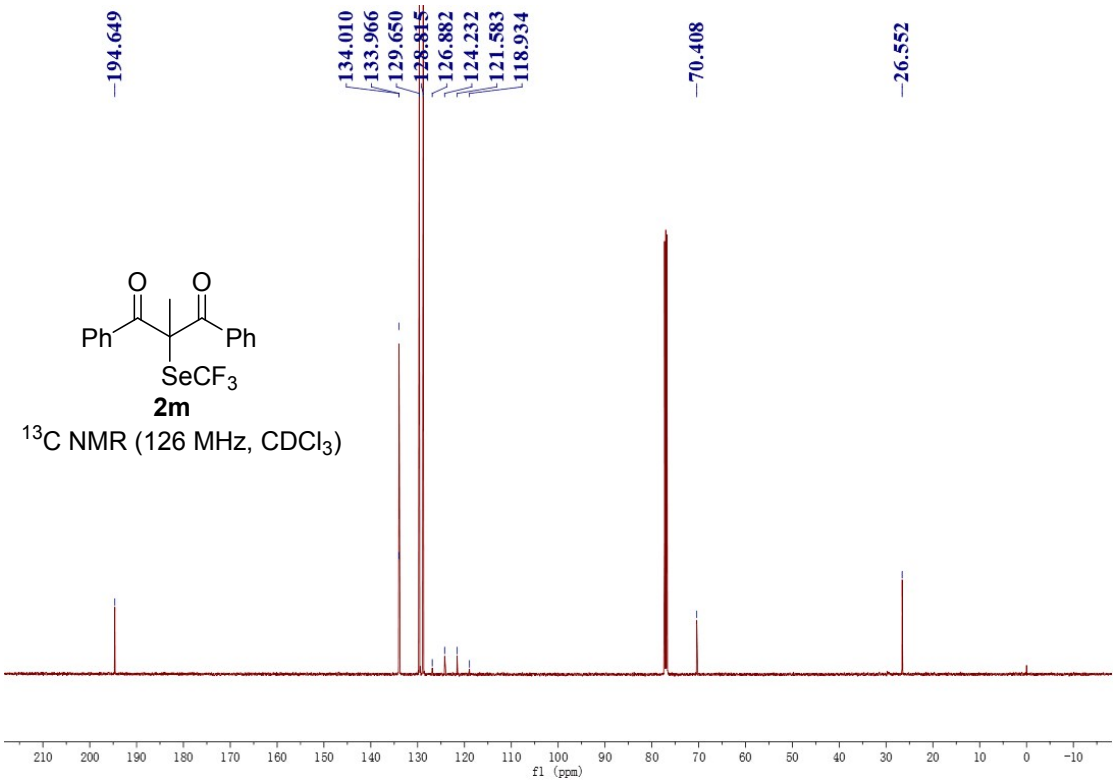
2m

^{1}H NMR (500 MHz, $CDCl_3$)



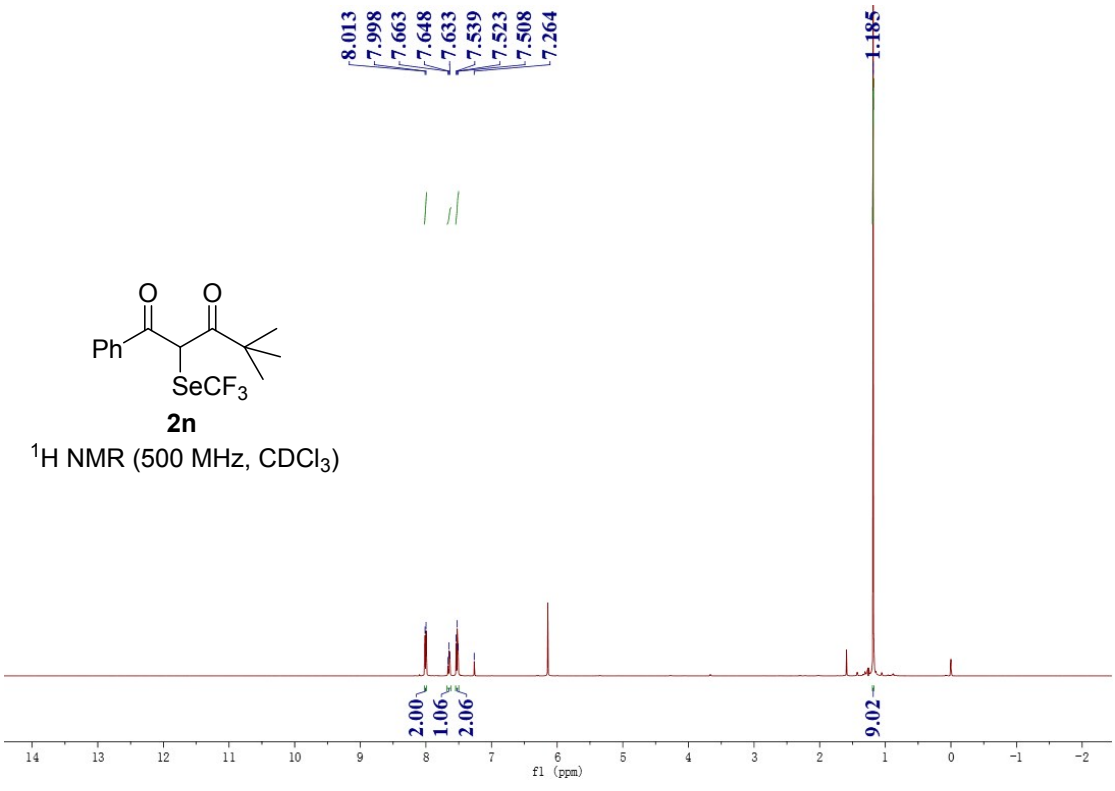
2m

^{19}F NMR (471 MHz, $CDCl_3$)



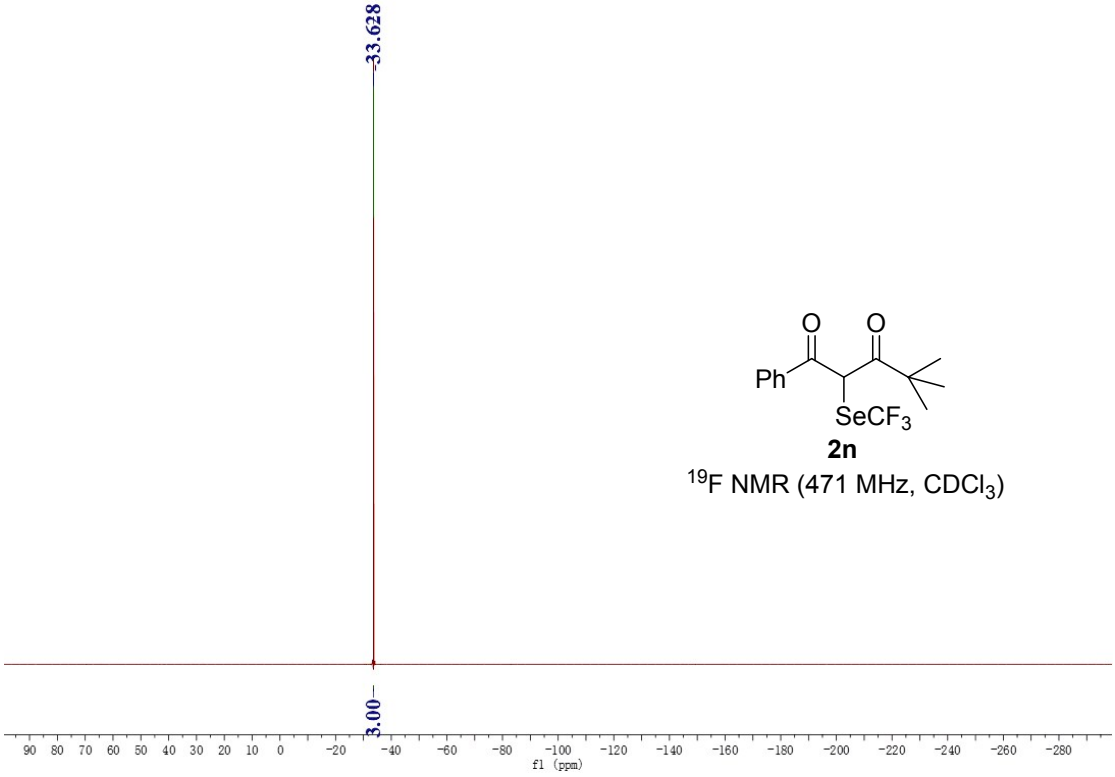
2m

^{13}C NMR (126 MHz, $CDCl_3$)



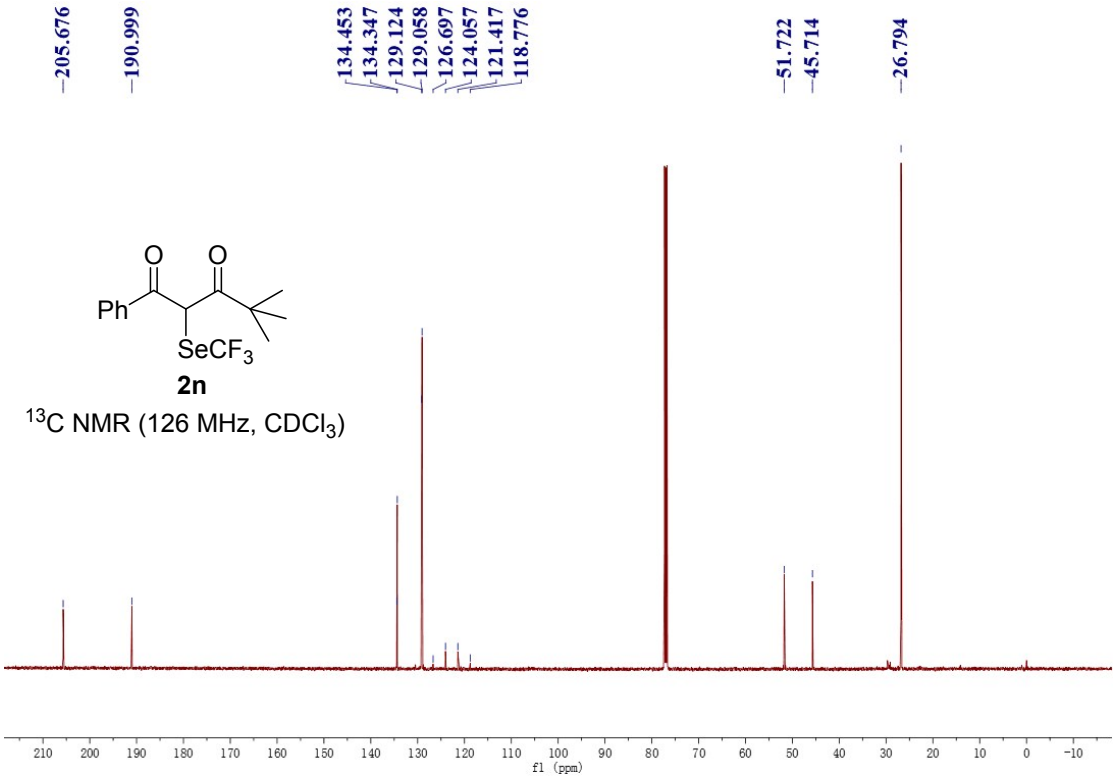
2n

^{1}H NMR (500 MHz, $CDCl_3$)



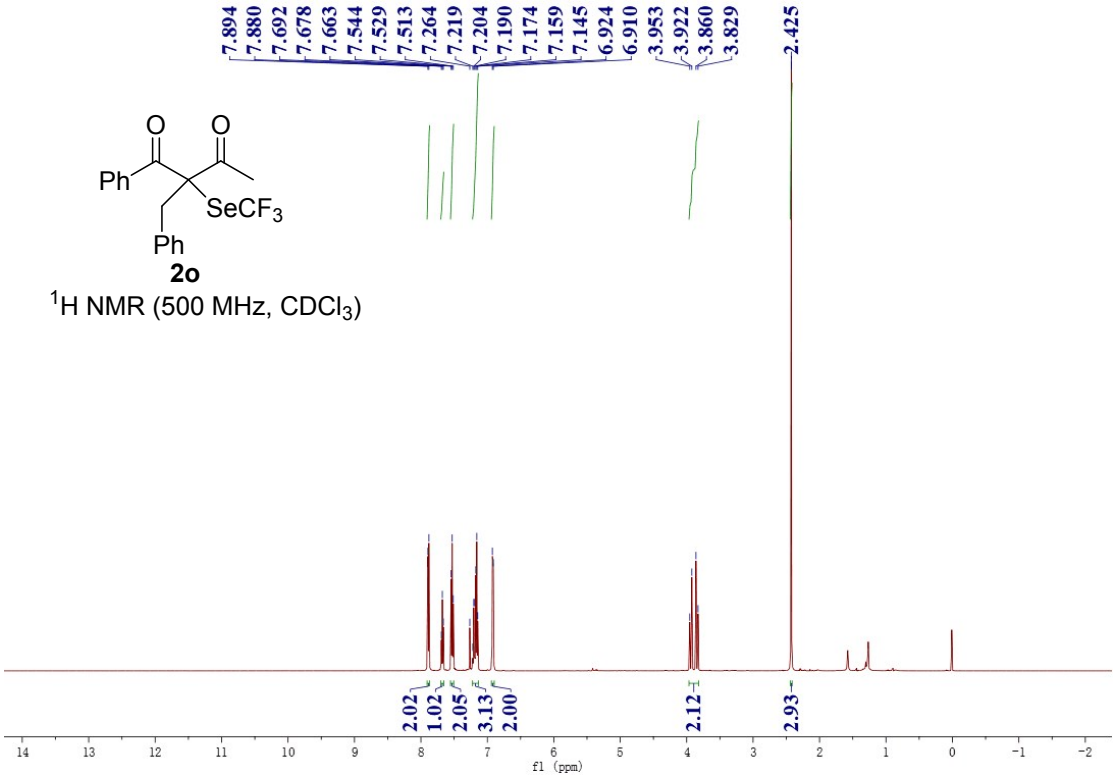
2n

^{19}F NMR (471 MHz, $CDCl_3$)



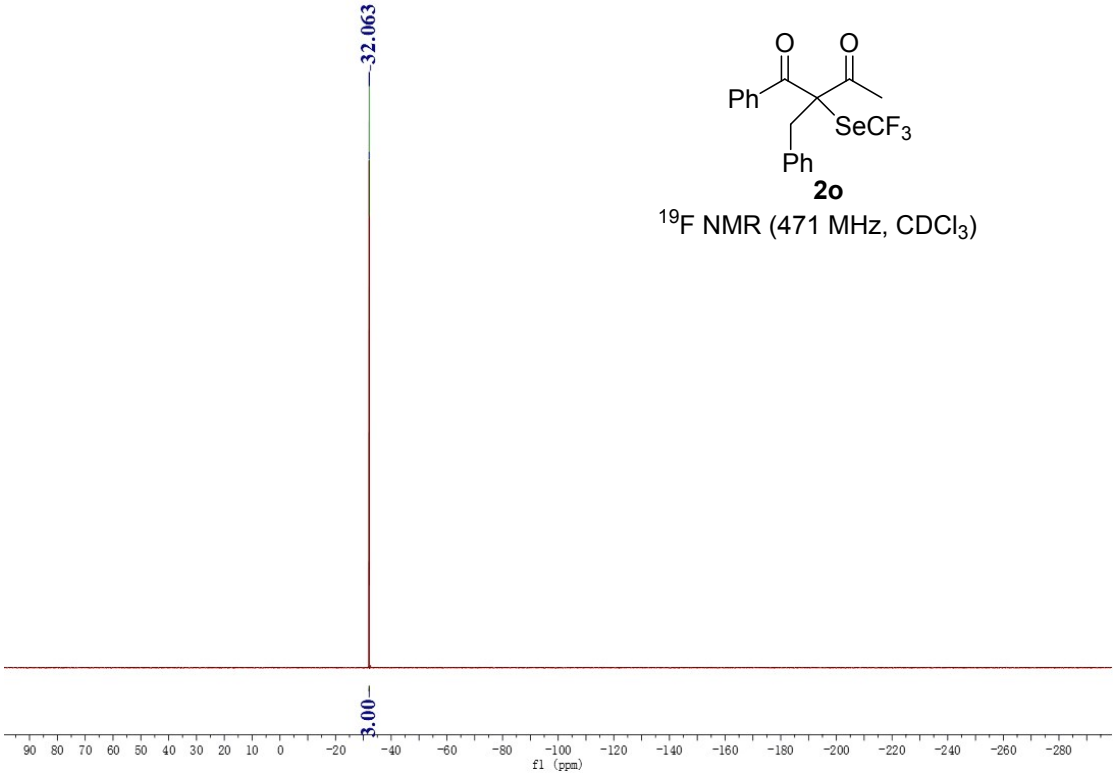
2n

^{13}C NMR (126 MHz, $CDCl_3$)



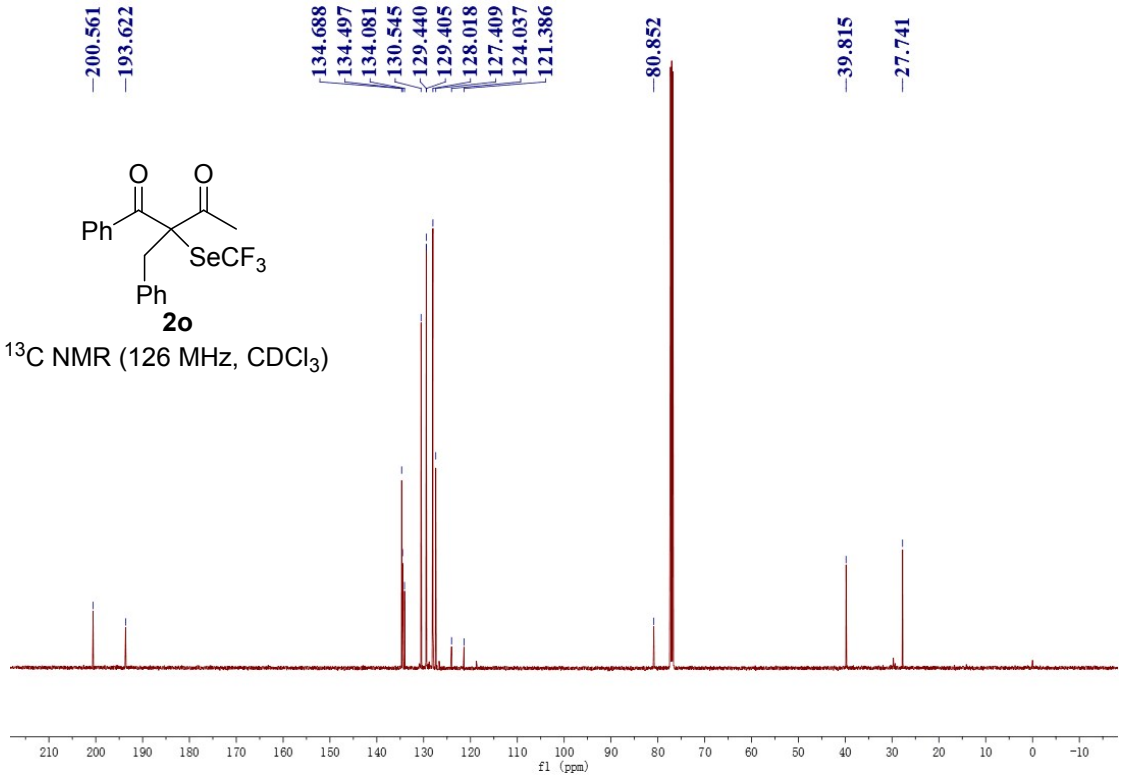
2o

^{1}H NMR (500 MHz, $CDCl_3$)



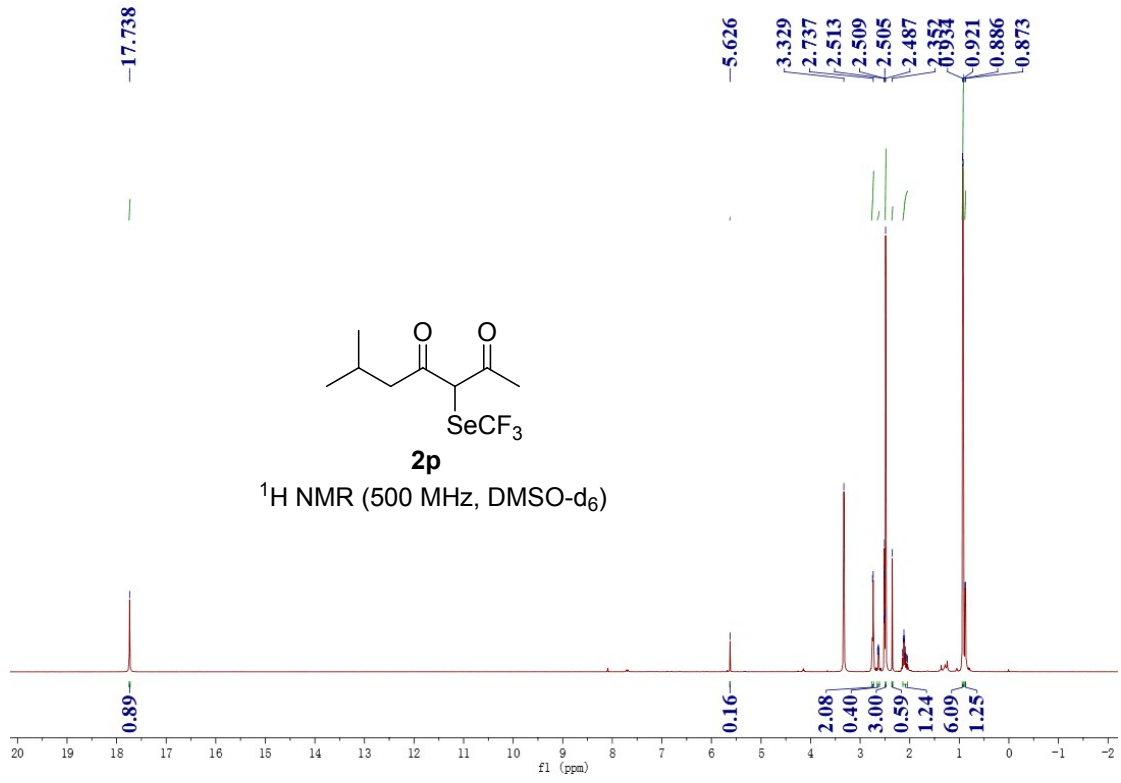
2o

^{19}F NMR (471 MHz, $CDCl_3$)



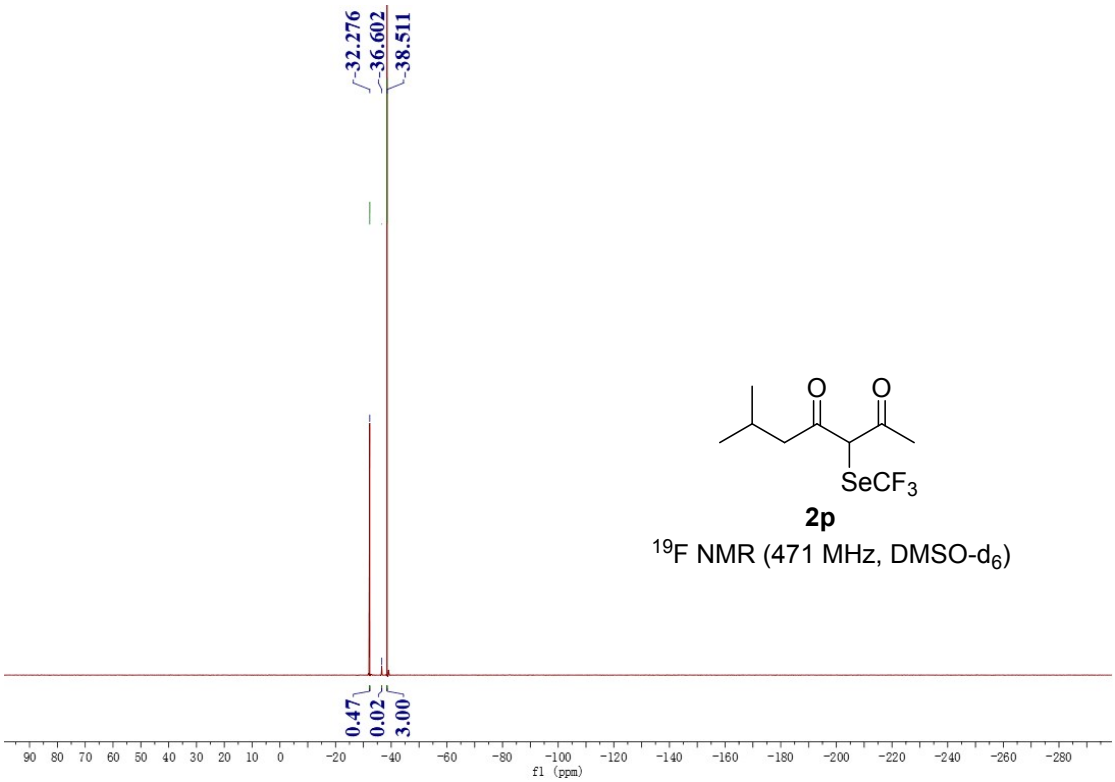
2o

^{13}C NMR (126 MHz, $CDCl_3$)



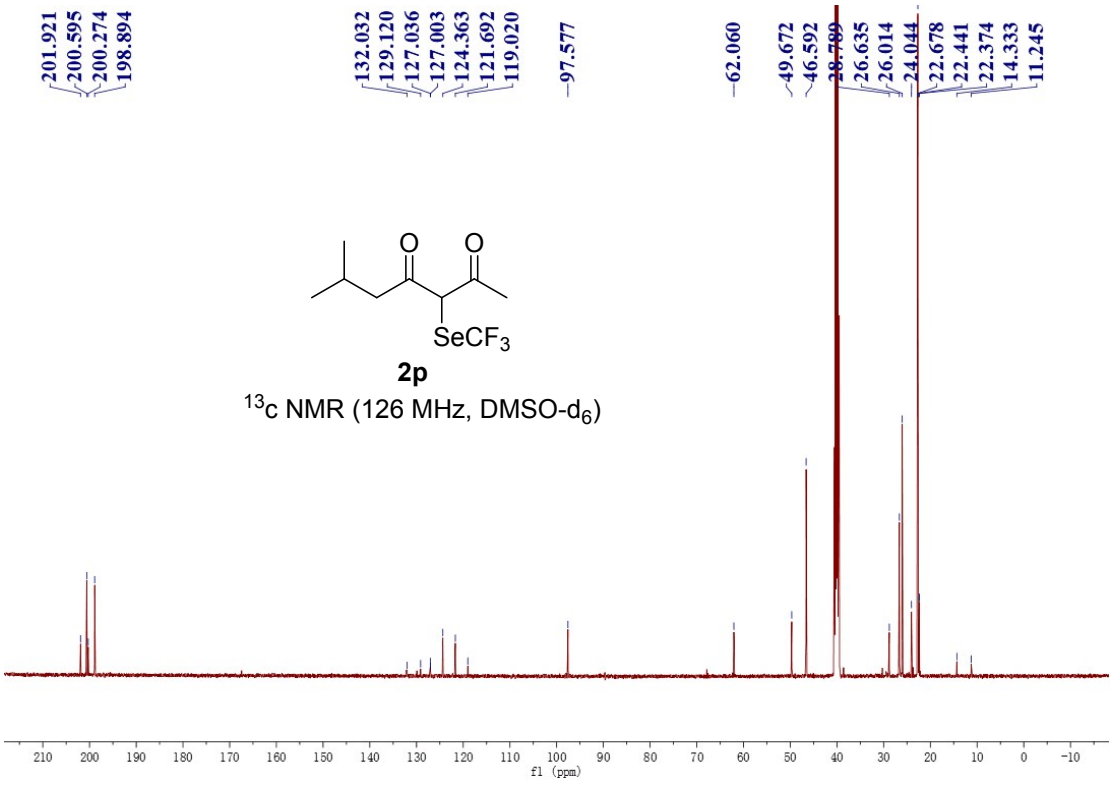
2p

^{1}H NMR (500 MHz, DMSO-d_6)



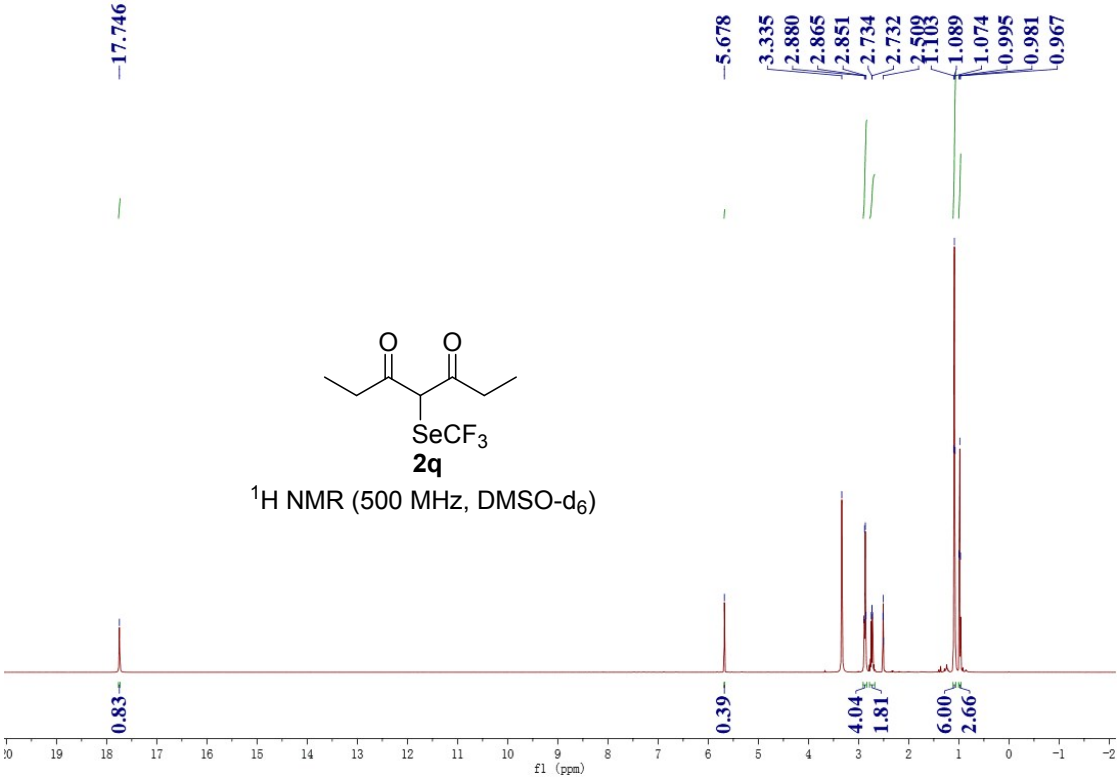
2p

^{19}F NMR (471 MHz, DMSO-d_6)



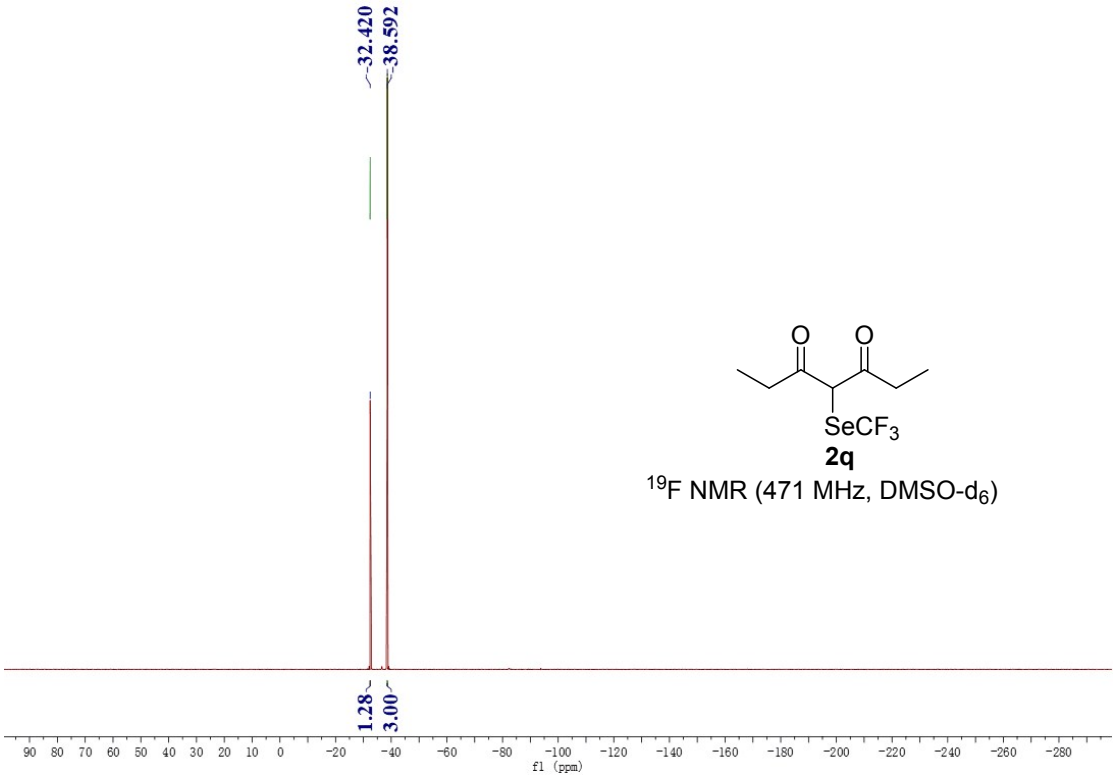
2p

^{13}c NMR (126 MHz, DMSO-d_6)



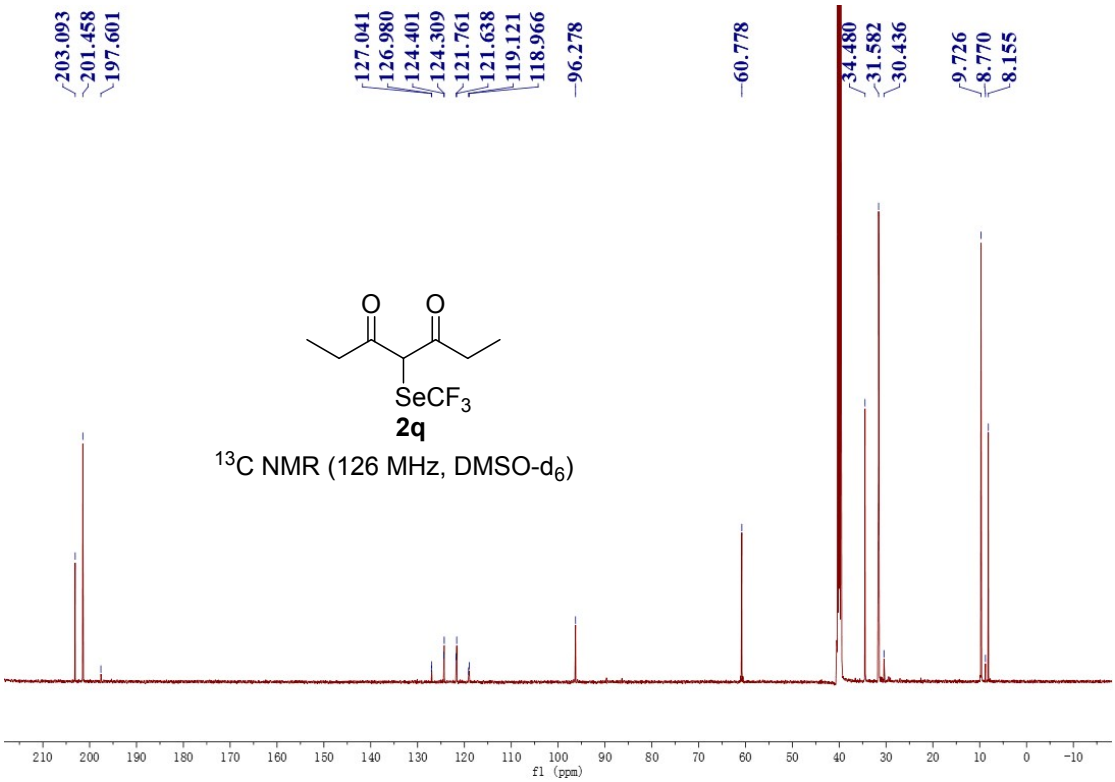
2q

^{1}H NMR (500 MHz, DMSO-d_6)



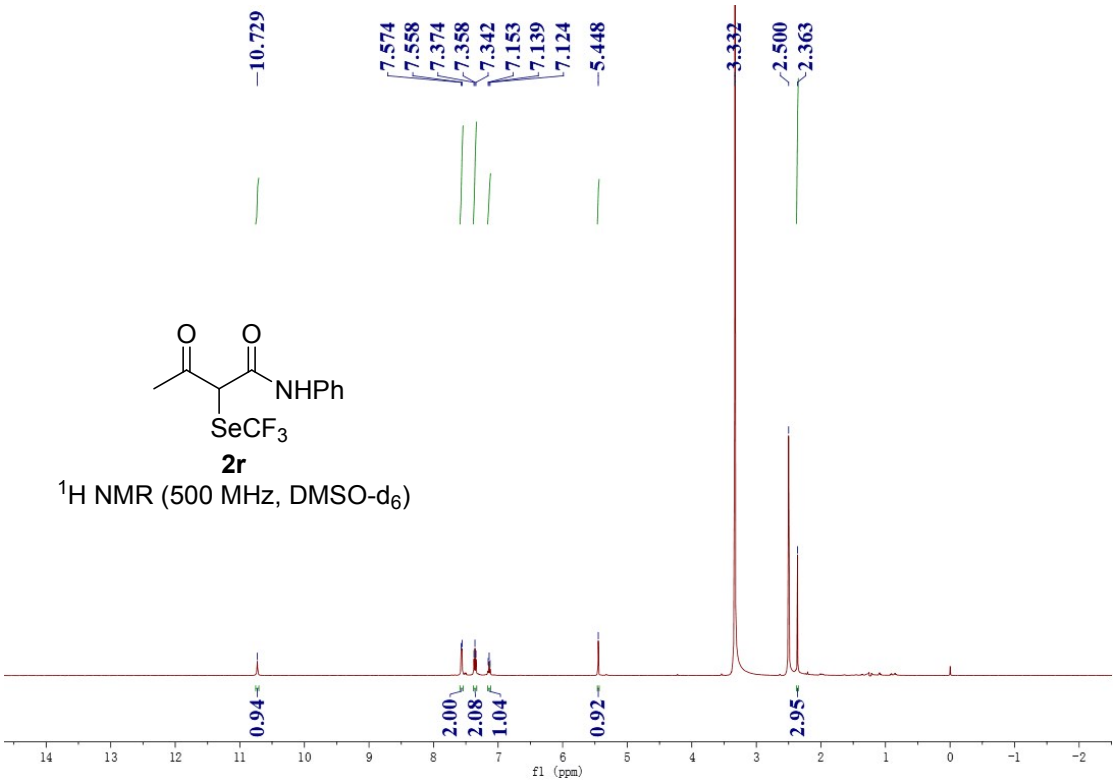
2q

^{19}F NMR (471 MHz, DMSO-d_6)



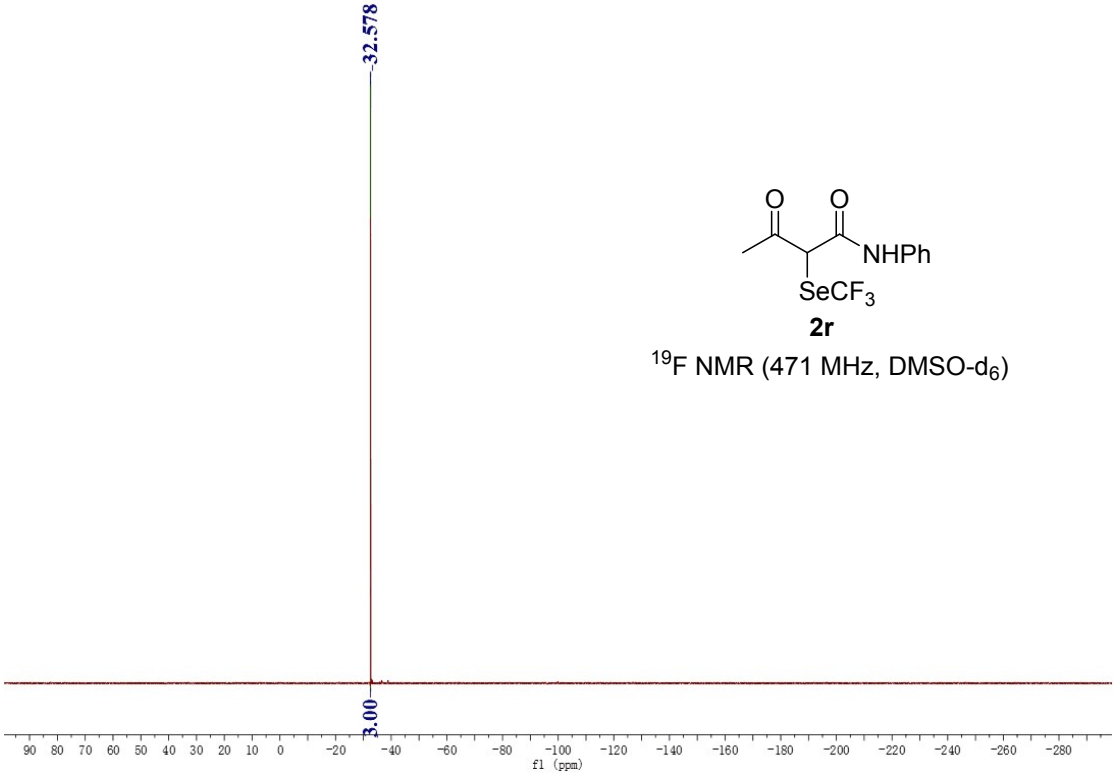
2q

^{13}C NMR (126 MHz, DMSO-d_6)



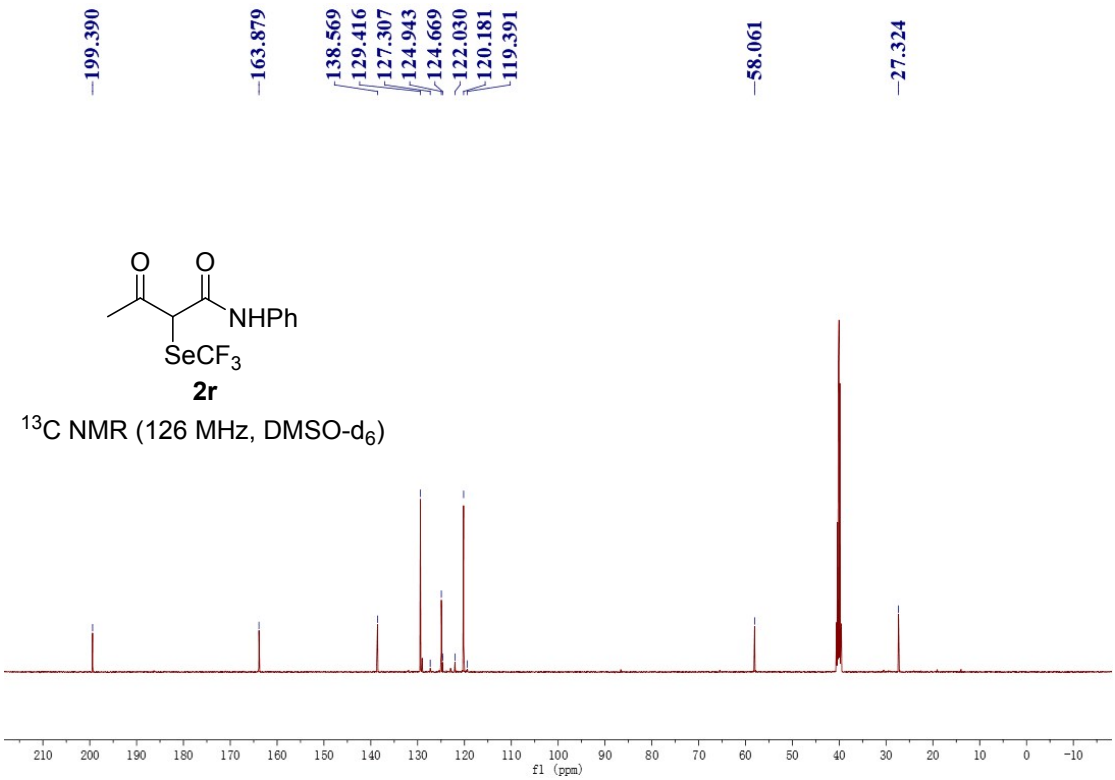
2r

^{1}H NMR (500 MHz, DMSO-d_6)



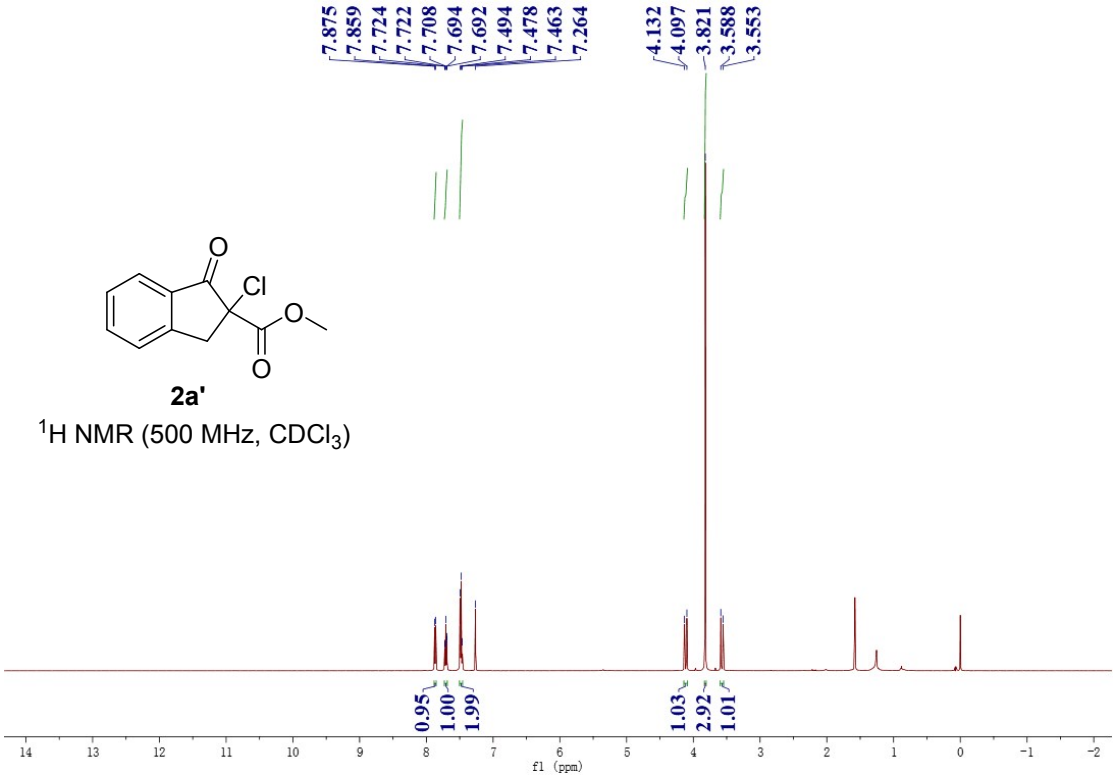
2r

^{19}F NMR (471 MHz, DMSO-d_6)



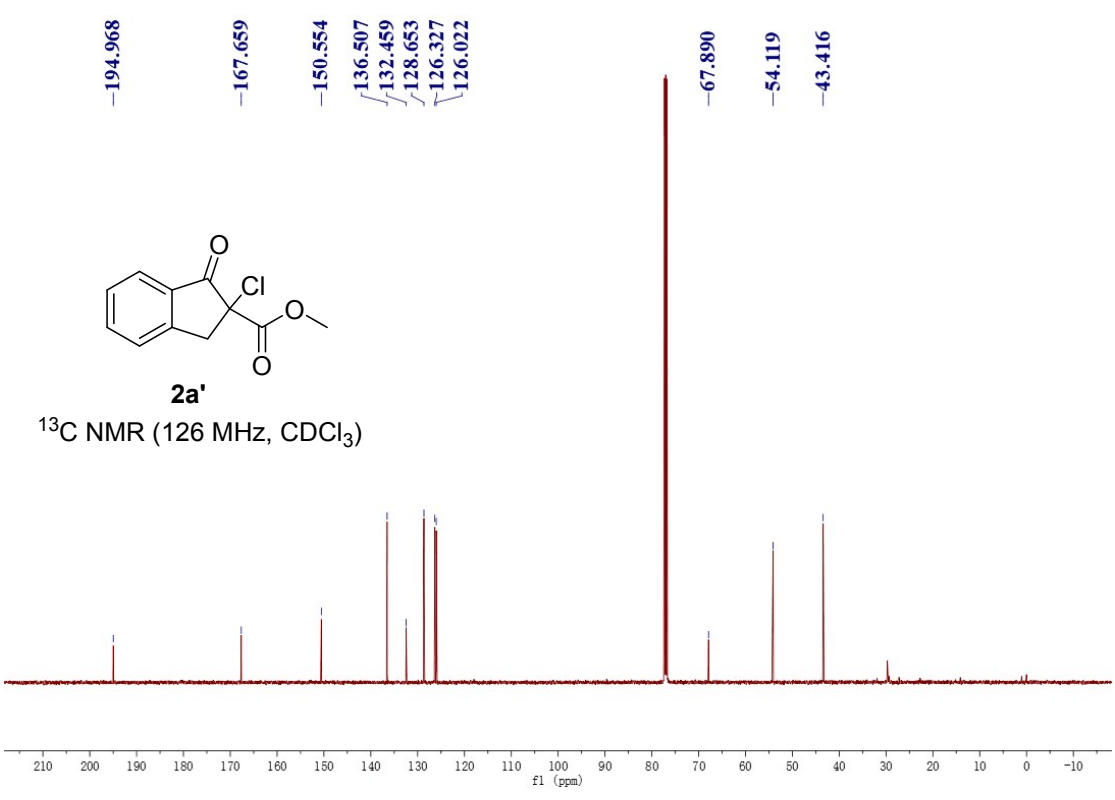
2r

^{13}C NMR (126 MHz, DMSO-d_6)



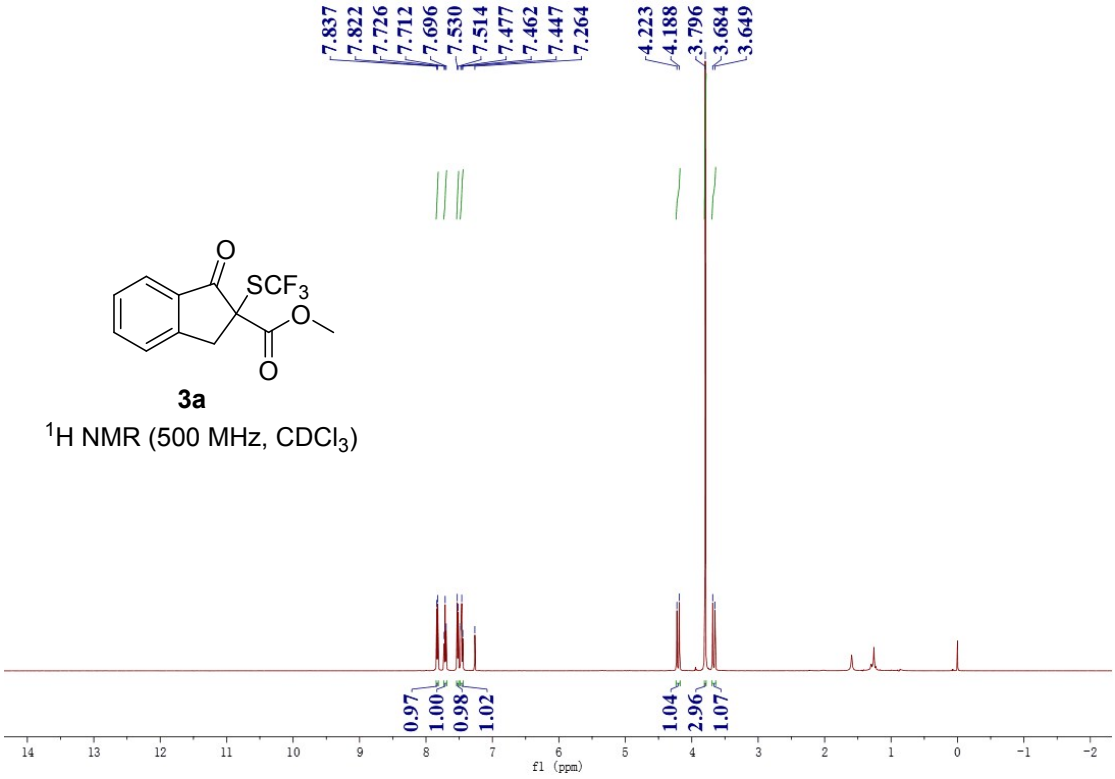
2a'

^{1}H NMR (500 MHz, $CDCl_3$)



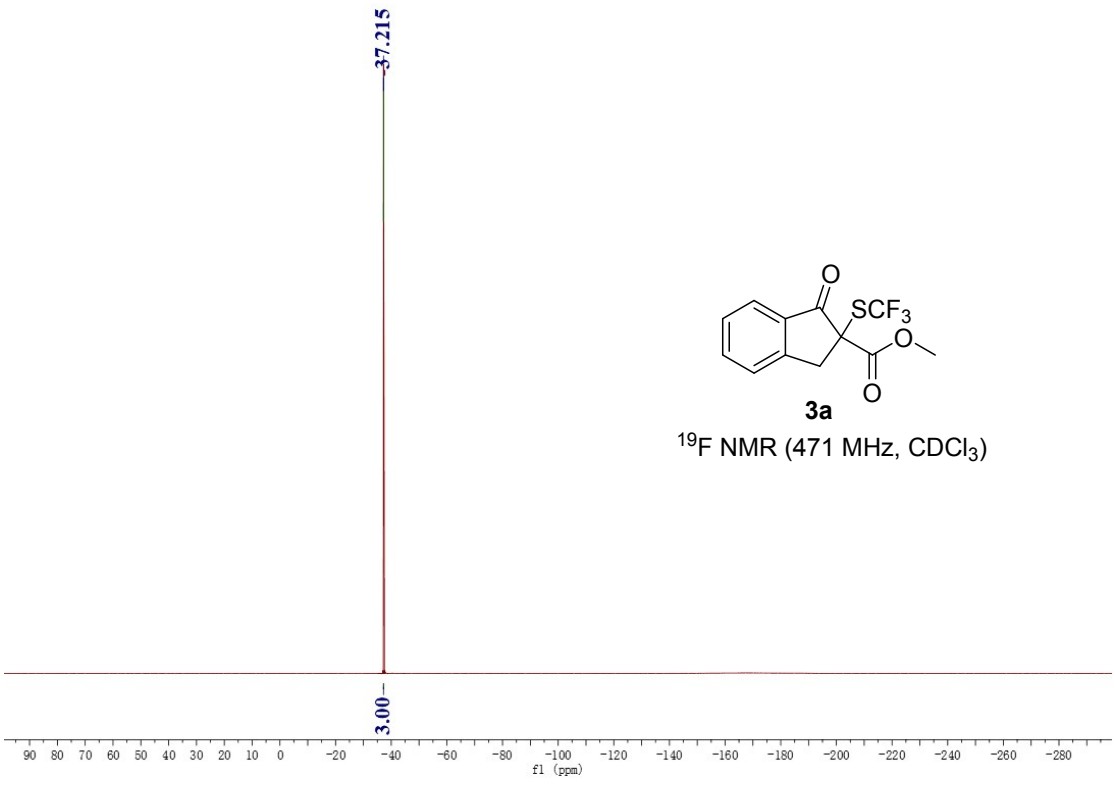
2a'

^{13}C NMR (126 MHz, $CDCl_3$)



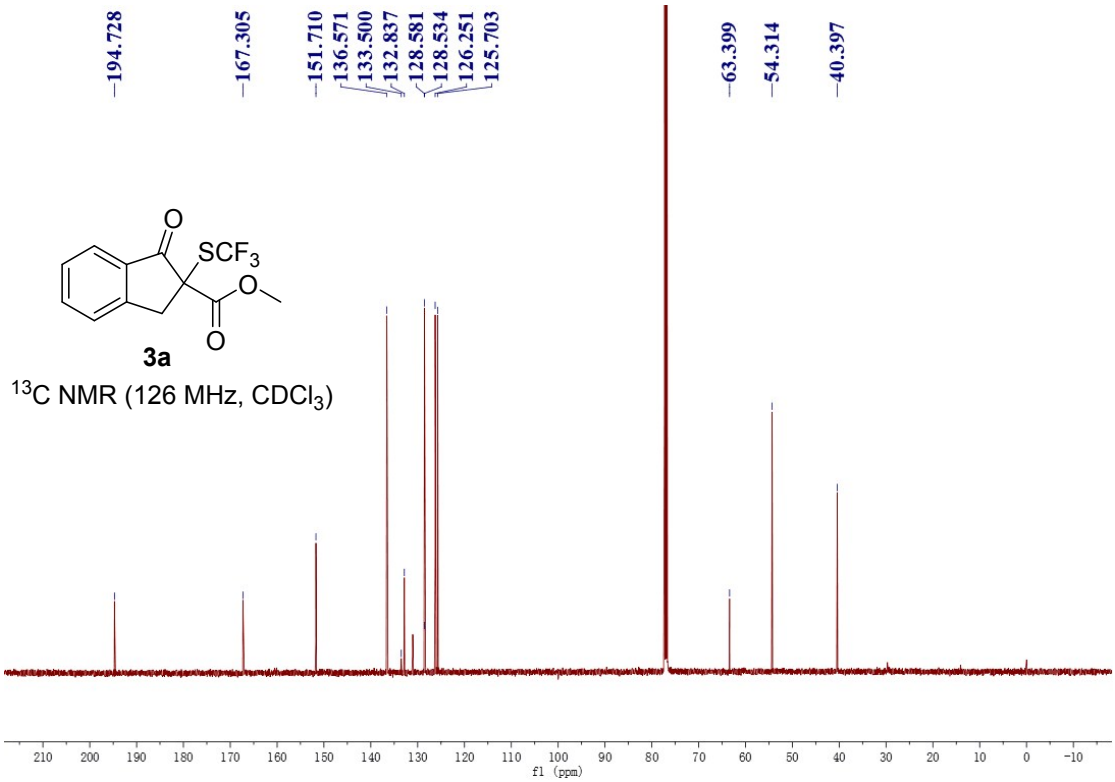
3a

^{1}H NMR (500 MHz, $CDCl_3$)



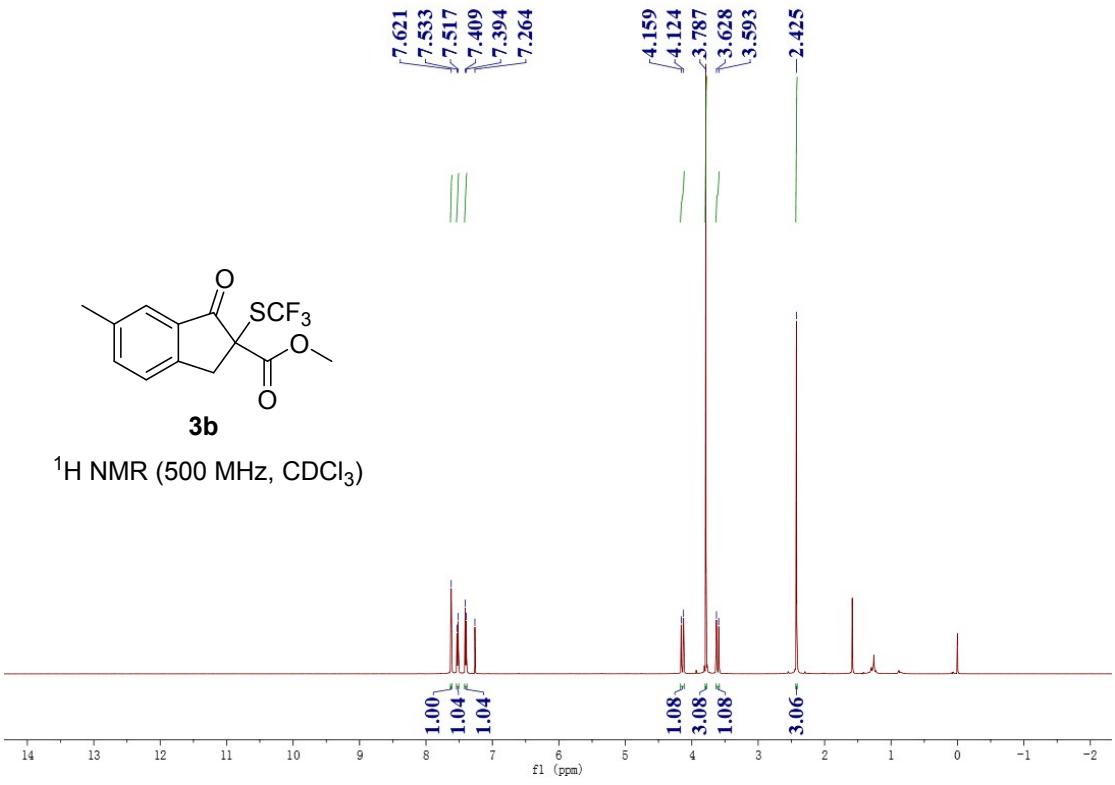
3a

^{19}F NMR (471 MHz, $CDCl_3$)



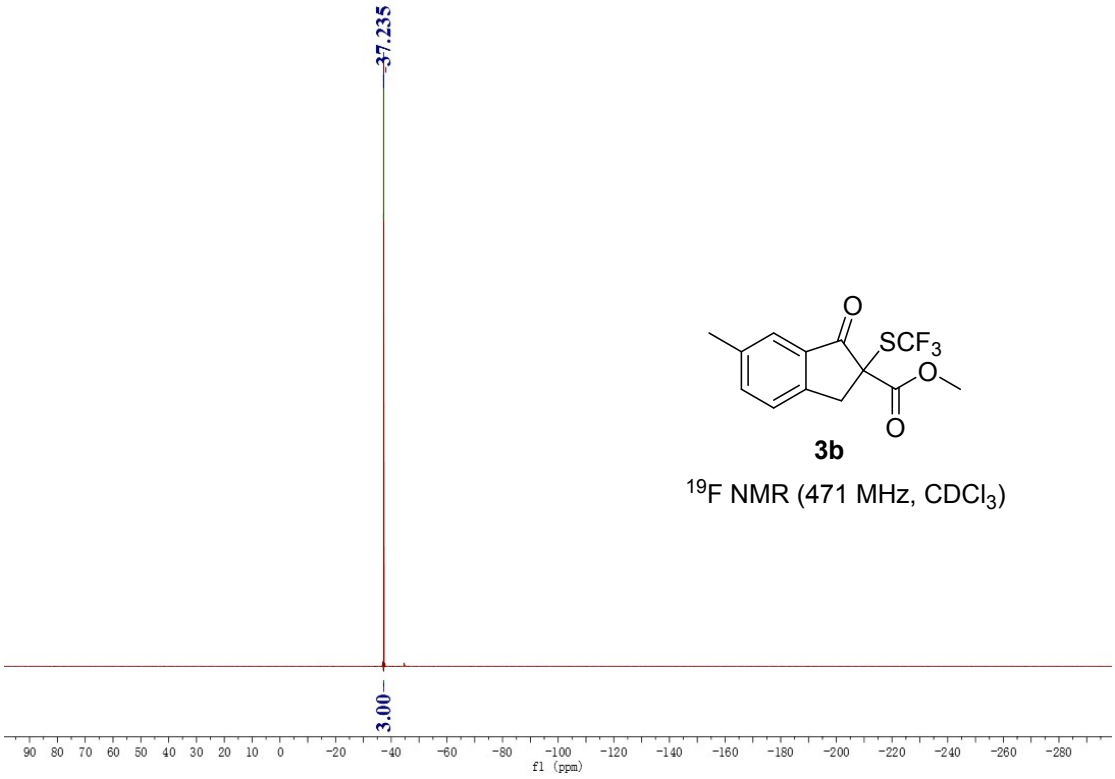
3a

^{13}C NMR (126 MHz, $CDCl_3$)



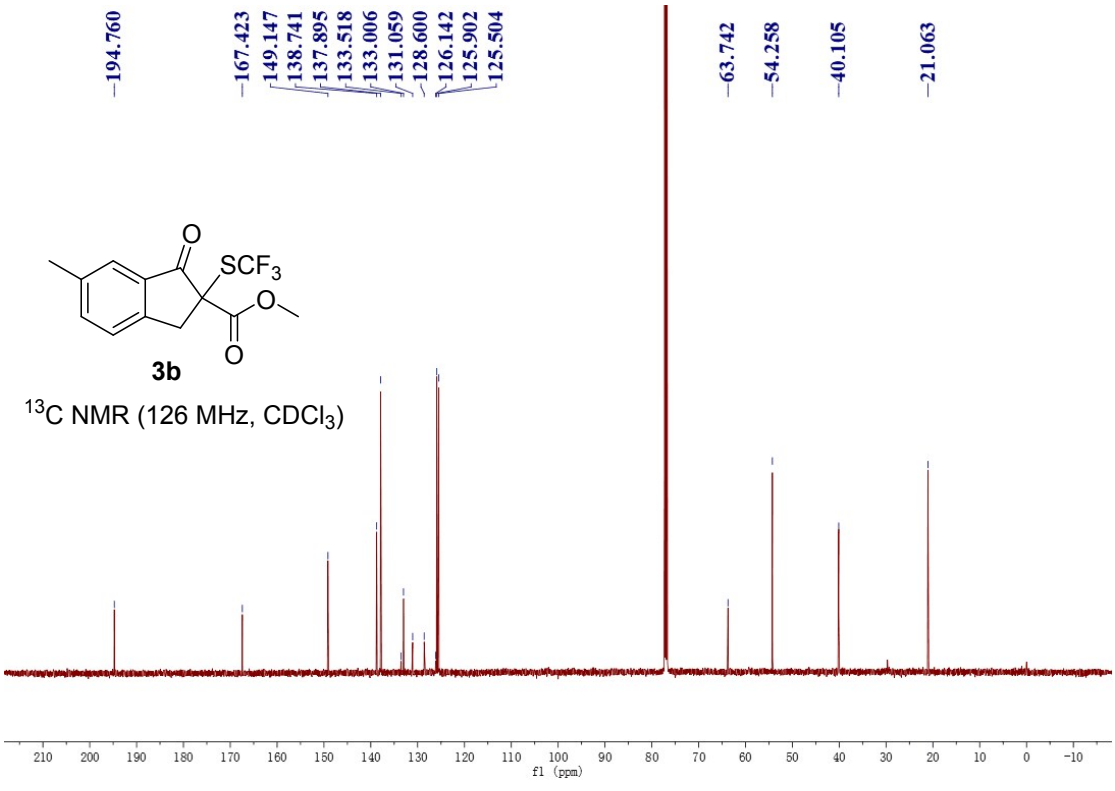
3b

^{1}H NMR (500 MHz, $CDCl_3$)



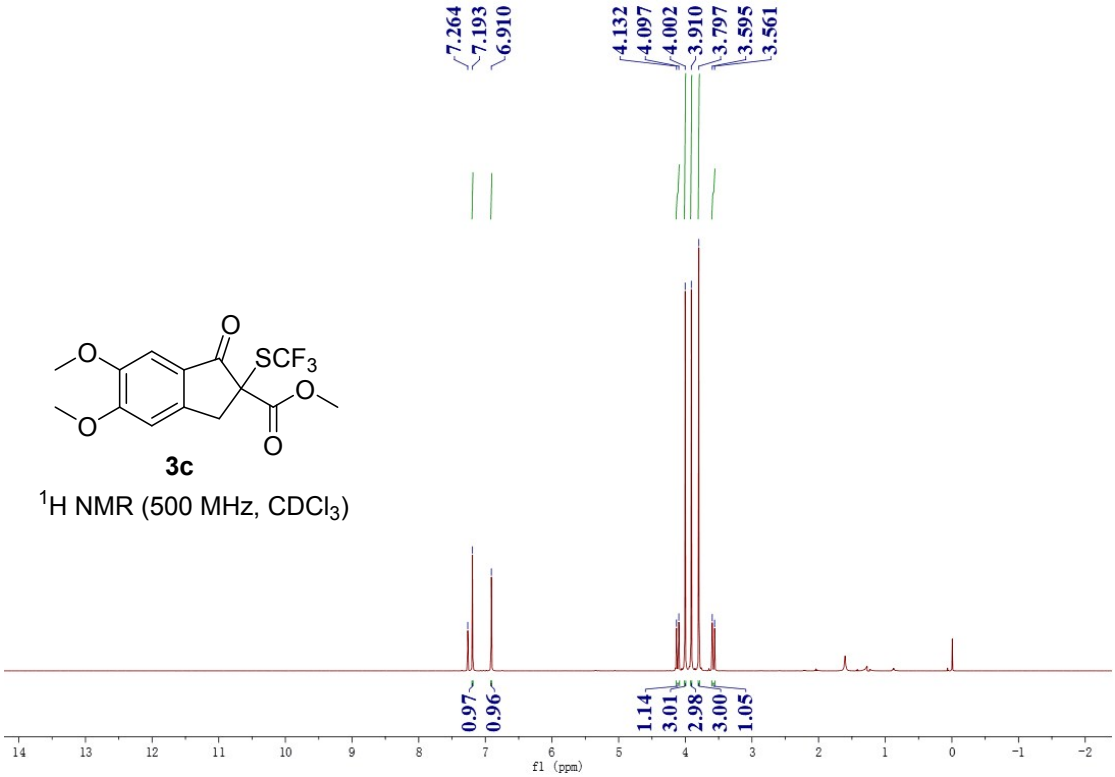
3b

^{19}F NMR (471 MHz, $CDCl_3$)



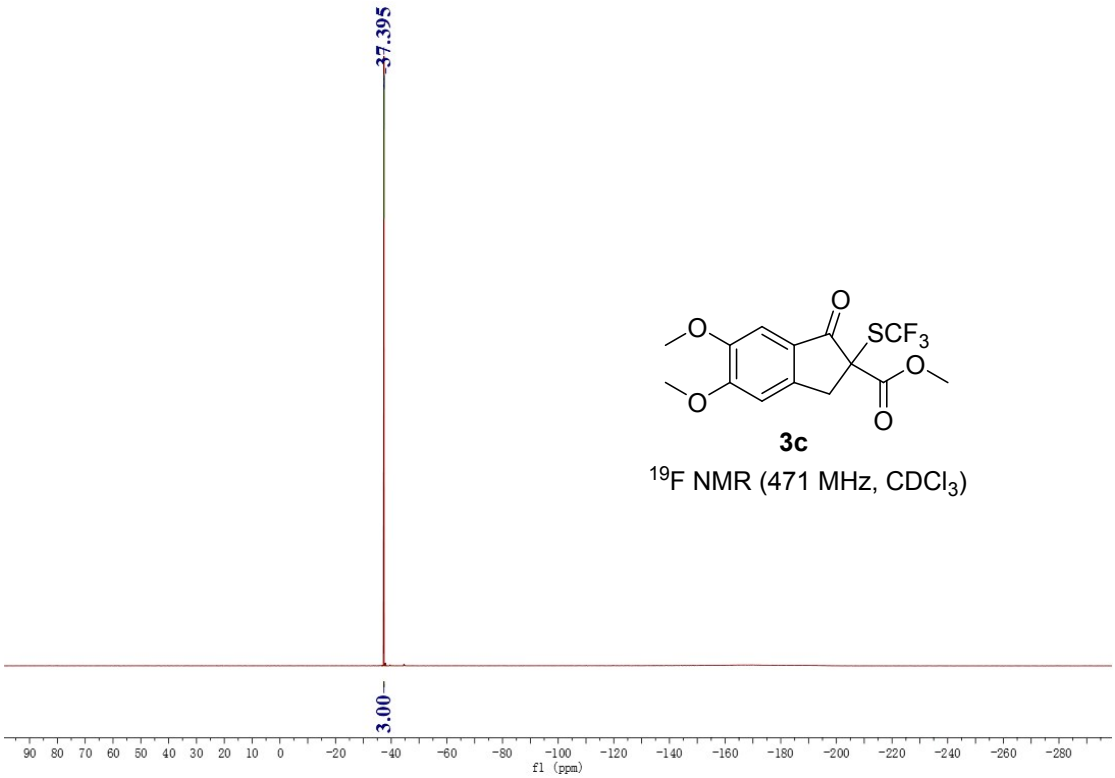
3b

^{13}C NMR (126 MHz, $CDCl_3$)



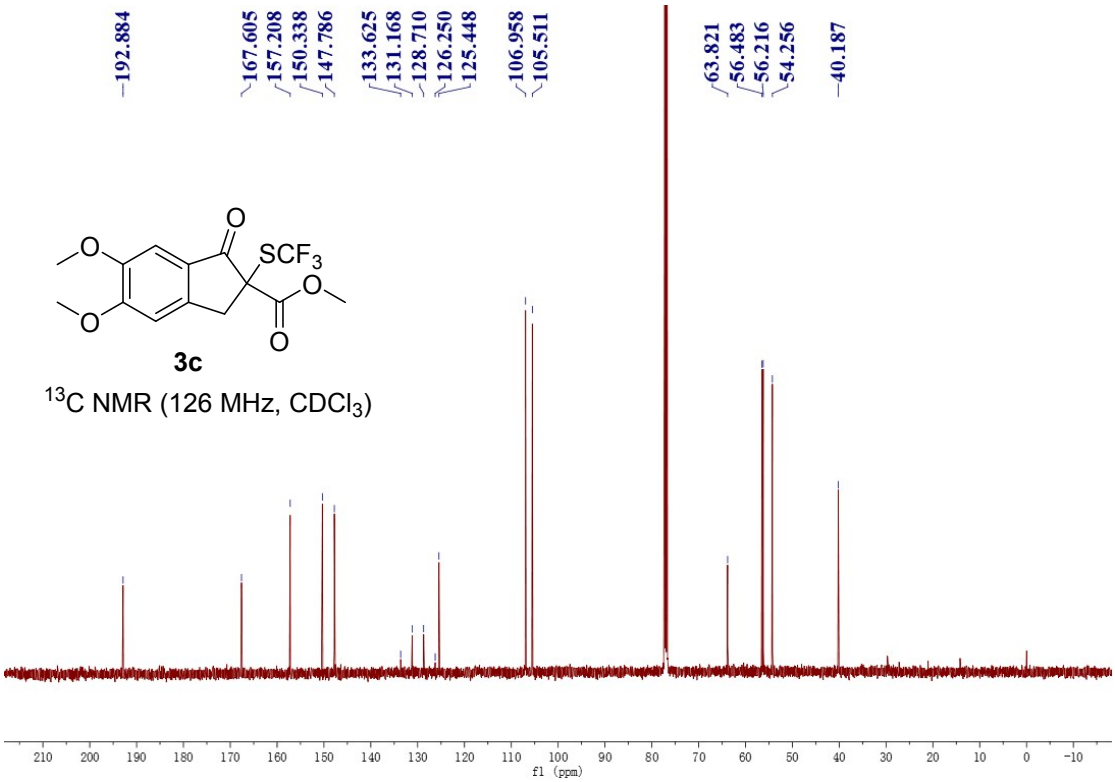
3c

^{1}H NMR (500 MHz, $CDCl_3$)



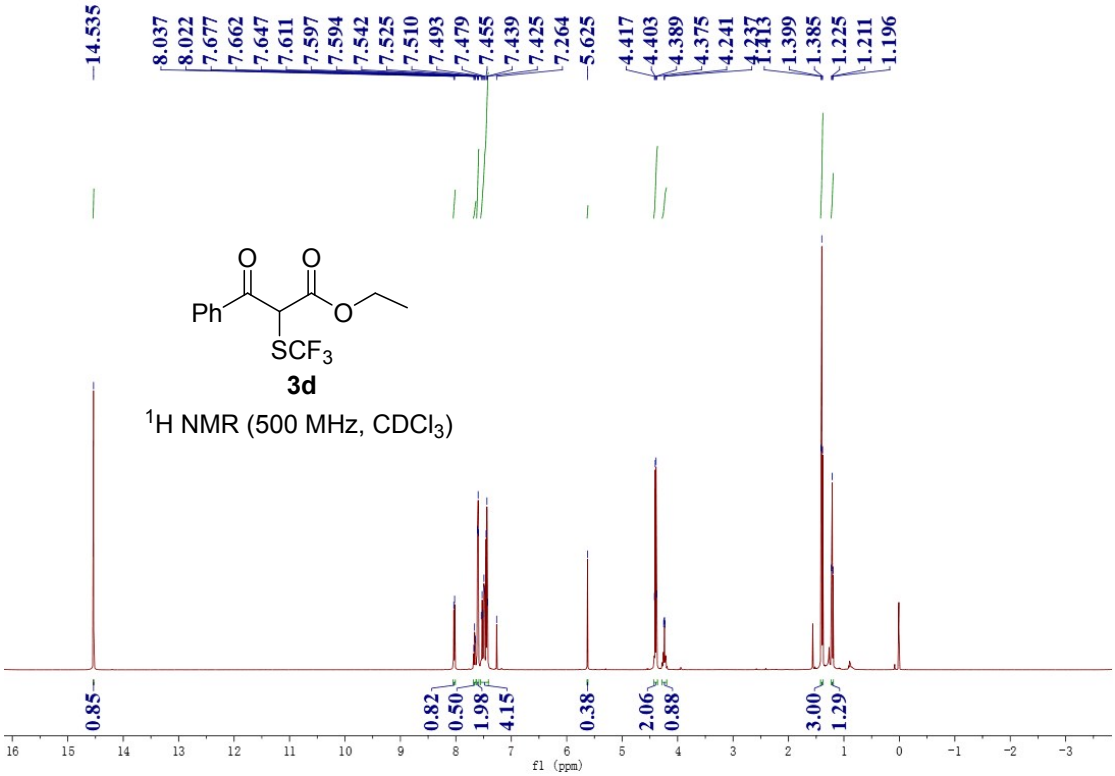
3c

^{19}F NMR (471 MHz, $CDCl_3$)



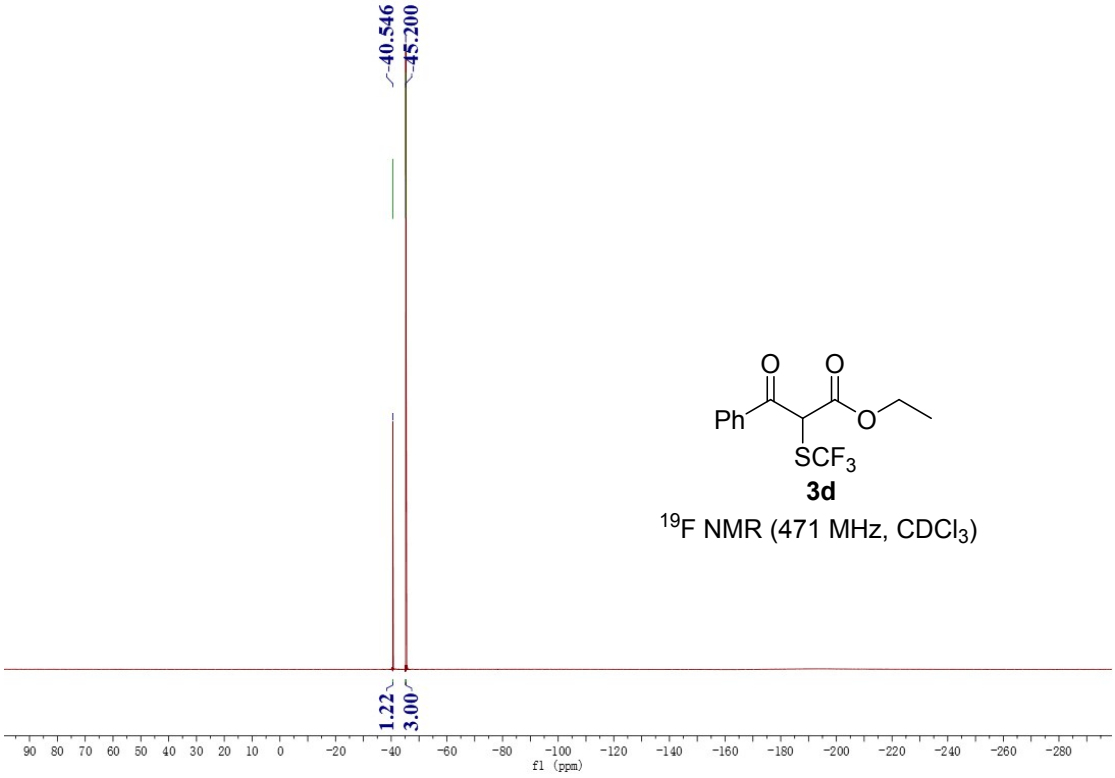
3c

^{13}C NMR (126 MHz, $CDCl_3$)



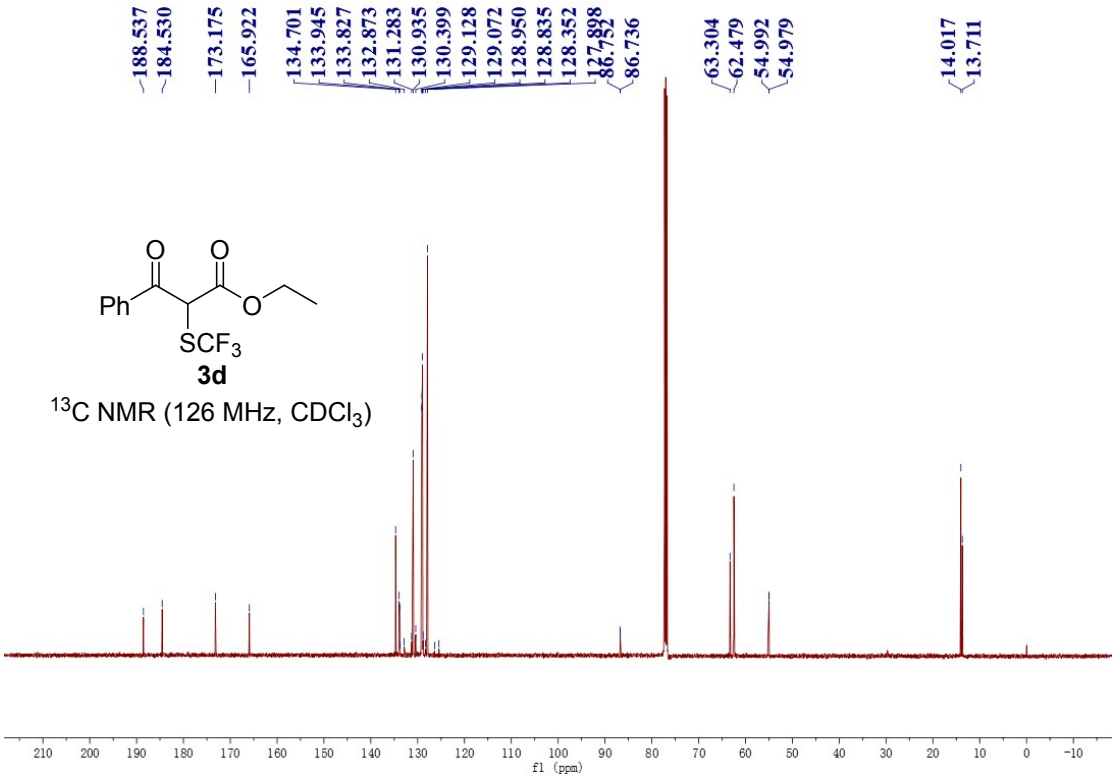
3d

^{1}H NMR (500 MHz, $CDCl_3$)



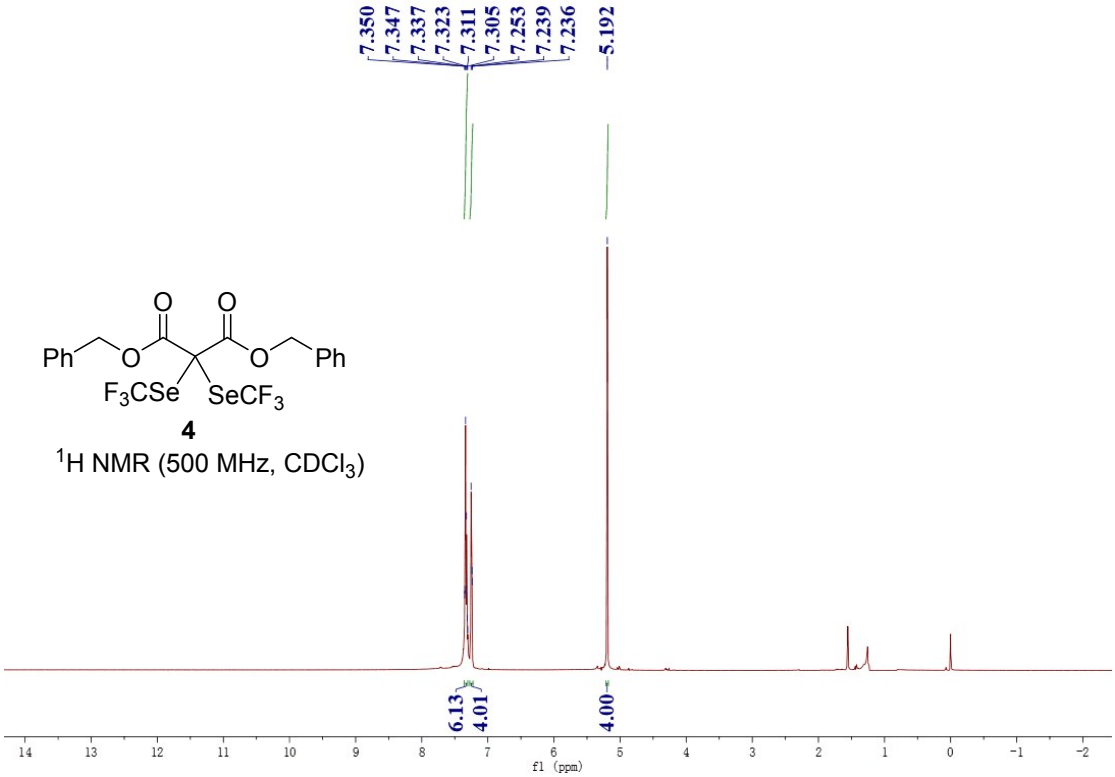
3d

^{19}F NMR (471 MHz, $CDCl_3$)



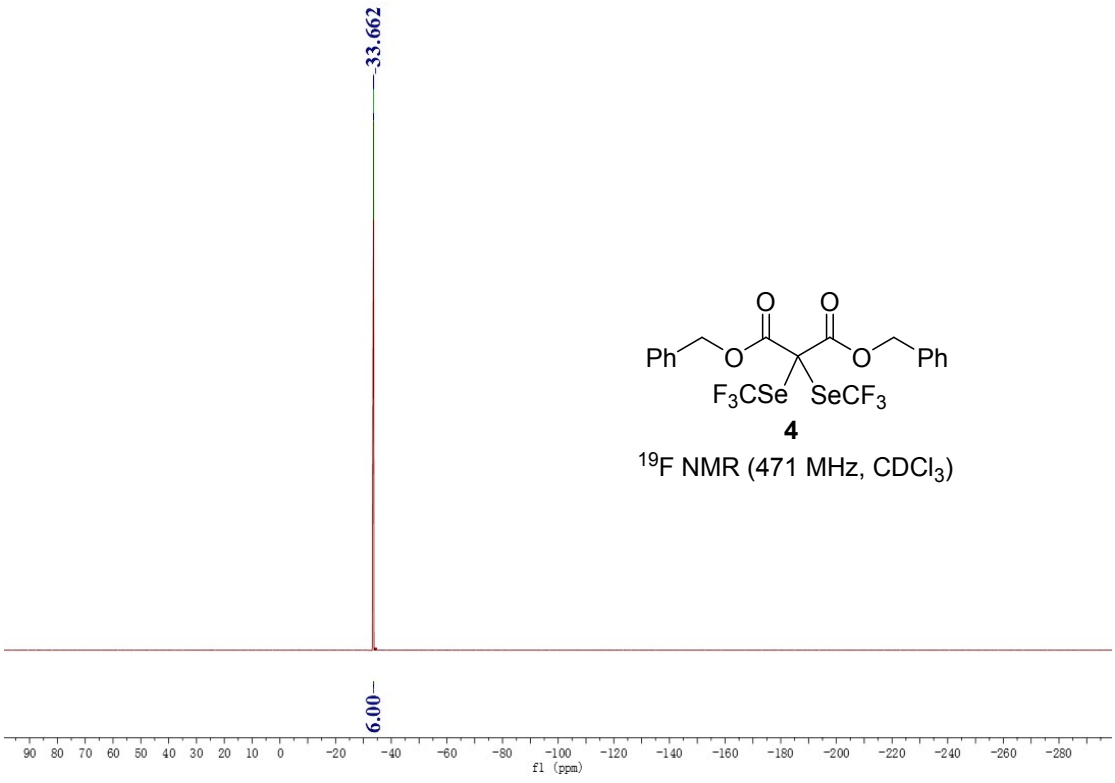
3d

^{13}C NMR (126 MHz, $CDCl_3$)



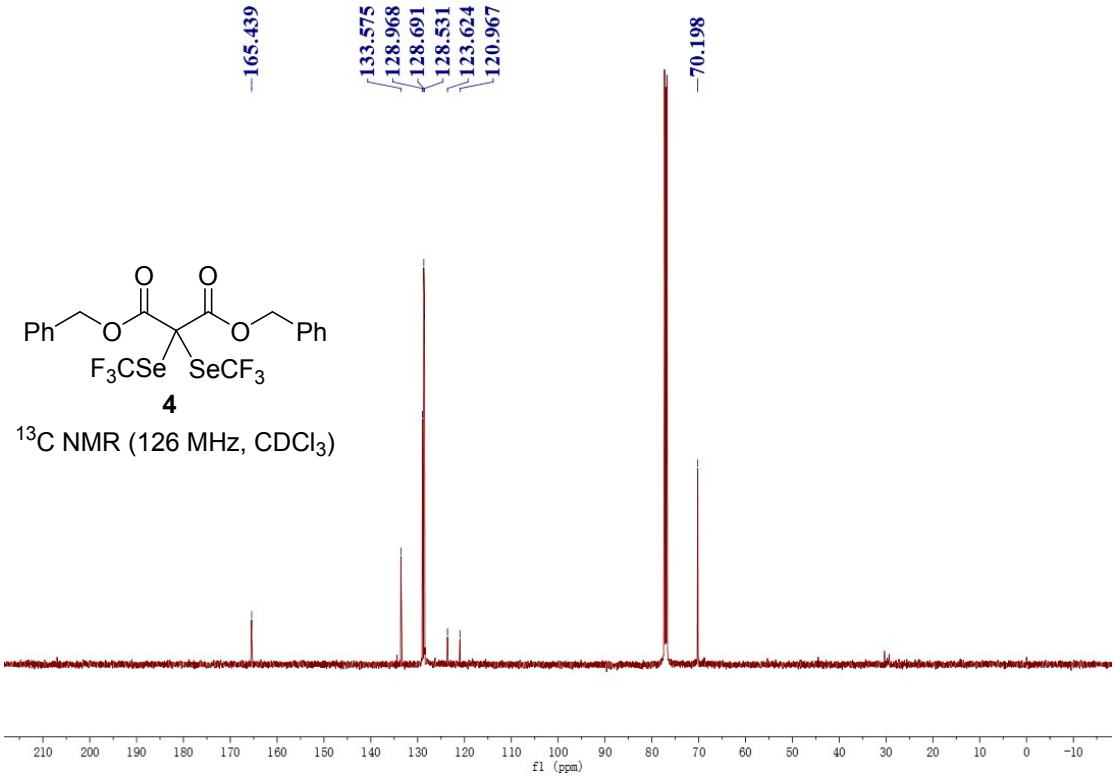
4

^{1}H NMR (500 MHz, $CDCl_3$)



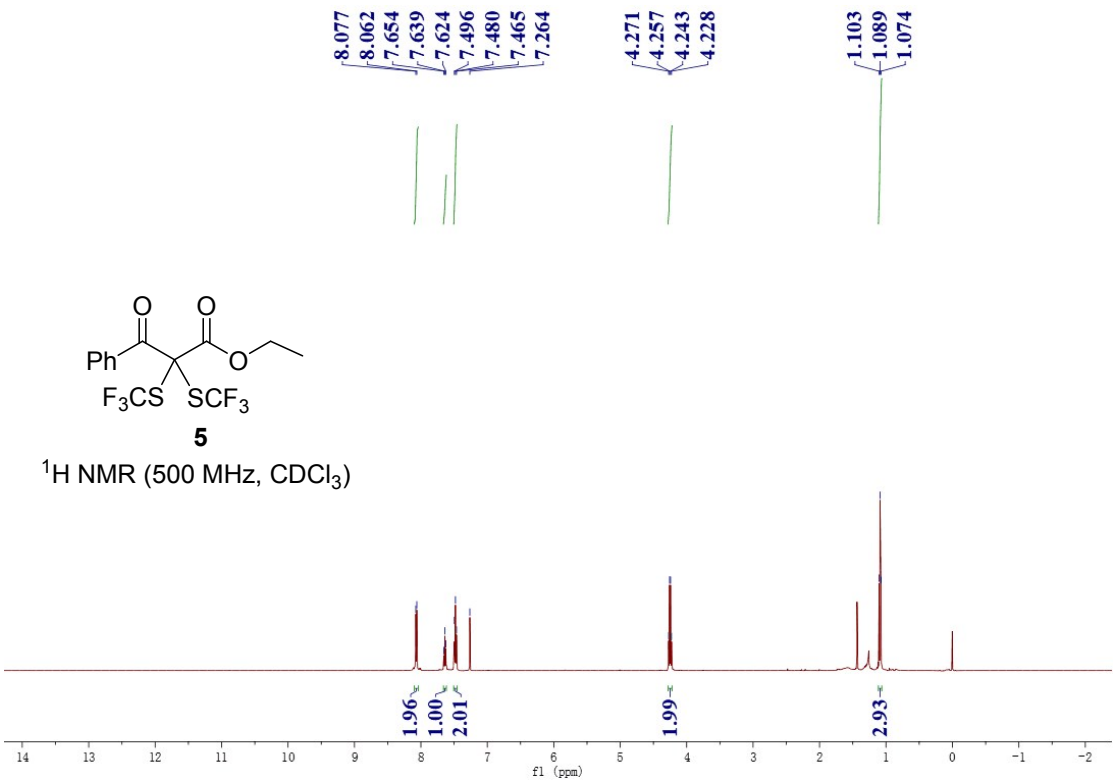
4

^{19}F NMR (471 MHz, $CDCl_3$)



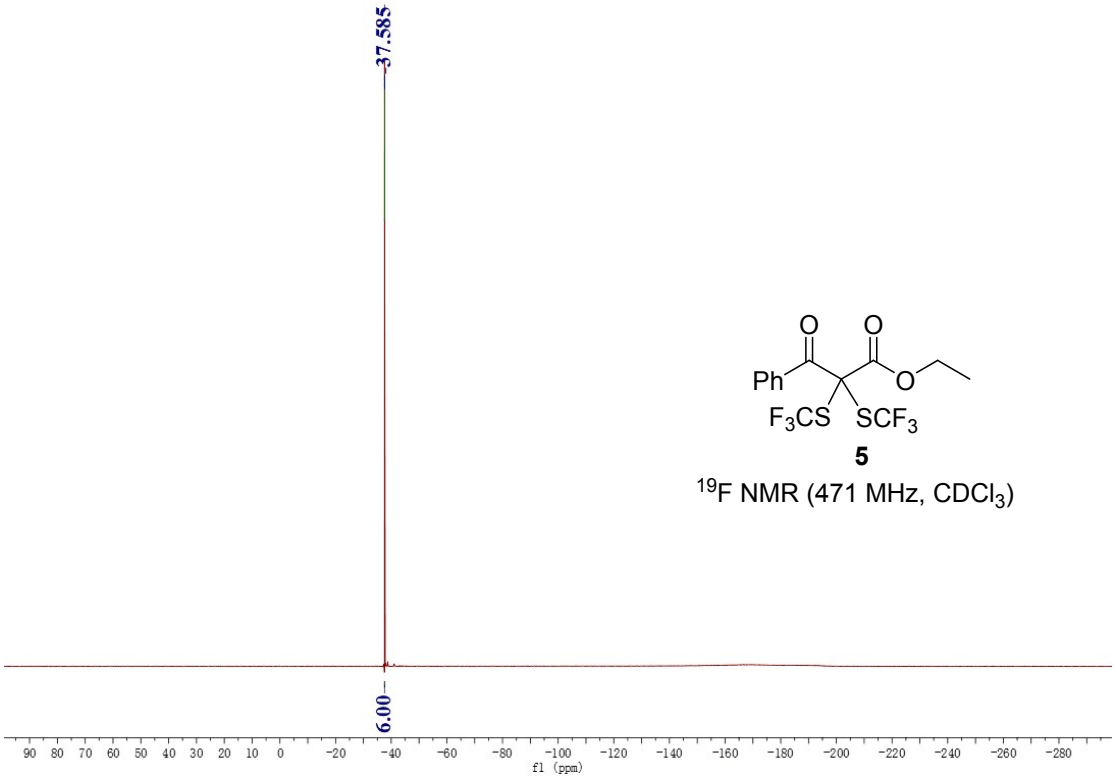
4

^{13}C NMR (126 MHz, $CDCl_3$)



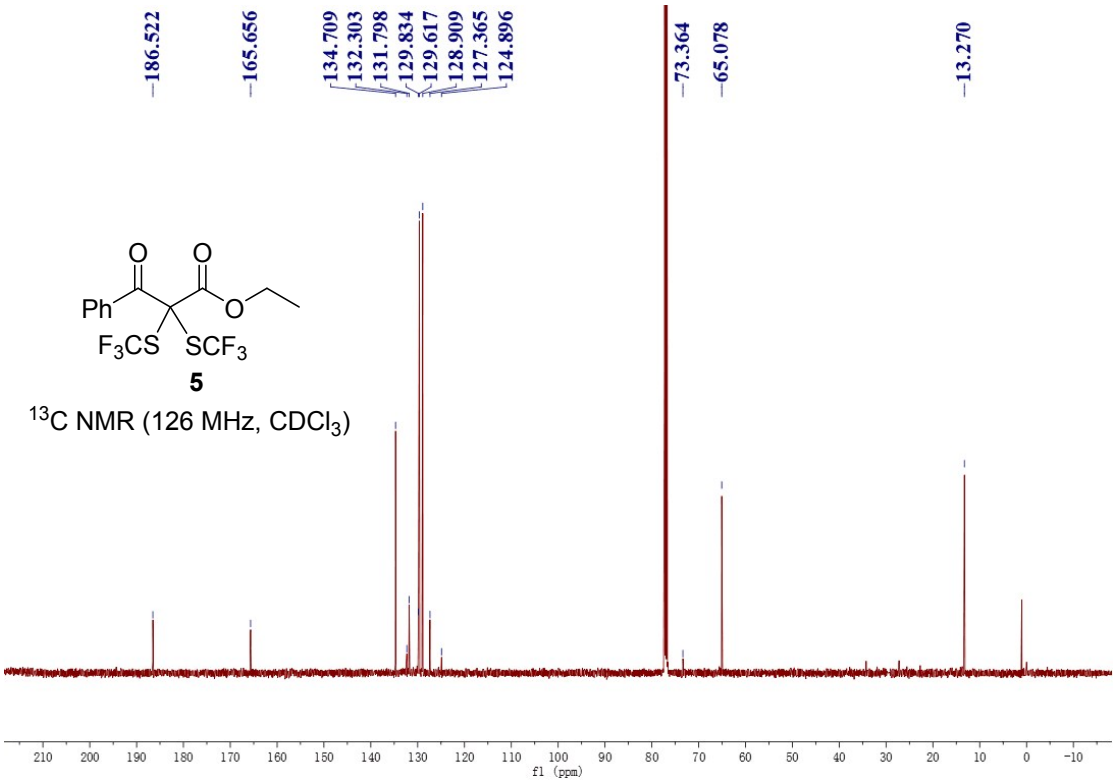
5

^{1}H NMR (500 MHz, $CDCl_3$)



5

^{19}F NMR (471 MHz, $CDCl_3$)



5

^{13}C NMR (126 MHz, $CDCl_3$)