Supplementary Information

Direct access to isoindolines through tandem Rh(III)-catalyzed alkenylation and cyclization of *N*-benzyltriflamides

Neeraj Kumar Mishra, Jihye Park, Satyasheel Sharma, Sangil Han, Mirim Kim, Youngmi Shin, Jinbong Jang, Jong Hwan Kwak, Young Hoon Jung, and In Su Kim*

School of Pharmacy, Sungkyunkwan University, Suwon 440-746, Republic of Korea

* Corresponding author. Tel.: +82-31-290-7788; fax: +82-31-292-8800; e-mail: insukim@skku.edu

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General methods

Commercially available reagents were used without additional purification, unless otherwise stated. Sealed tubes (13 × 100 mm^2) were purchased from Fischer Scientific and dried in oven for overnight and cooled at room temperature prior to use. Thin layer chromatography was carried out using plates coated with Kieselgel $60F_{254}$ (Merck). For flash column chromatography, E. Merck Kieselgel 60 (230–400 mesh) was used. Nuclear magnetic resonance spectra (^1H and ^{13}C NMR) were recorded on a Bruker Unity 400 and 700 MHz spectrometer for $CDCl_3$ solution and chemical shifts are reported as parts per million (ppm). Resonance patterns are reported with the notations s (singlet), d (doublet), t (triplet), q (quartet), and m (multiplet). In addition, the notation br is used to indicate a broad signal. Coupling constants (*J*) are reported in hertz (Hz). IR spectra were recorded on a Varian 2000 Infrared spectrophotometer and are reported as cm^{-1}. High-resolution mass spectra (HRMS) were recorded on a JEOL JMS-600 spectrometer.

General procedure for the synthesis of *N*-benzyltriflamides (1a–p)

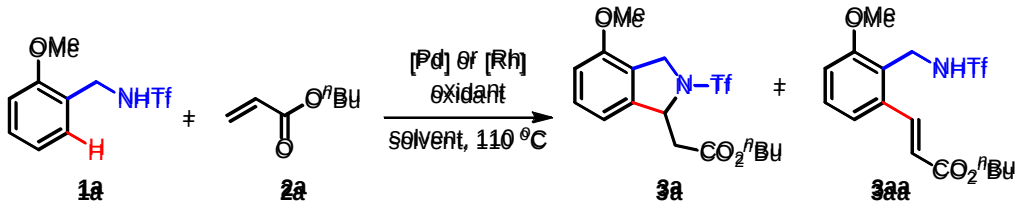
N-Benzyltriflamides were prepared from the corresponding benzylamines and trifluoromethanesulfonic anhydride as described in previous literature.[1]

Typical procedure for the synthesis of isoindolines (3a–p, 4b–j, 5b, 6b and 6c)

To an oven-dried sealed tube charged with *N*-(2-methoxybenzyl)triflamide (**1a**) (80.8 mg, 0.3 mmol, 100 mol %), $[RhCp^*Cl_2]_2$ (4.6 mg, 0.0075 mmol, 2.5 mol %), and $Cu(OAc)_2.H_2O$ (120 mg, 0.6 mmol, 200 mol %) in DMF:AcOH (3:1, 1 mL) was added *n*-butyl acrylate (**2a**) (64 µL, 0.45 mmol, 150 mol %). The reaction mixture was allowed to stir for 24 h at 110 ^oC. The reaction mixture was diluted with EtOAc (10 mL) and washed with water. The aqueous layer was extracted with EtOAc (3 × 10 mL). The combined organic layer was dried over Mg_2SO_4 and concentrated in vacuo. The residue was purified by flash column chromatography (*n*-hexanes/EtOAc = 25:1) to afford isoindoline **3a** (107.9 mg) in 91% yield.

1) Wang, X.; Mei, T.-S.; Yu, J.-Q. *J. Am. Chem. Soc.*, **2009**, *131*, 7520.

Optimization table

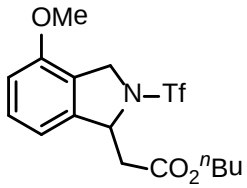


1a **2a** **3a** **3aa**

entry	catalyst (mol %)	Oxidant (mol %)	solvent	yield (%)	
				3a	**3aa**
1	$Pd(OAc)_2$ (10)	$Cu(OAc)_2$ (200)	DCE	trace	27
2	$Pd(OAc)_2$ (10)	AgOAc (200)	DCE	0	0
3	$Pd(OAc)_2$ (10)	$Cu(OAc)_2$ (200)	DMF	17	16
4	$[RhCp^*Cl_2]_2$ (2.5)	$Cu(OAc)_2$ (200)	DMF	53	12
5	$[RhCp^*Cl_2]_2$ (2.5)	$Cu(OAc)_2{\cdot}H_2O$ (200)	DMF	62	10
6	$[RhCp^*Cl_2]_2$ (2.5)	$Cu(OAc)_2{\cdot}H_2O$ (200)	THF	31	39
7	$[RhCp^*Cl_2]_2$ (2.5)	$Cu(OAc)_2{\cdot}H_2O$ (200)	DCE	33	40
8	$[RhCp^*Cl_2]_2$ (2.5)	$Cu(OAc)_2{\cdot}H_2O$ (200)	MeCN	61	8
9	$[RhCp^*Cl_2]_2$ (2.5)	$Cu(OAc)_2{\cdot}H_2O$ (200)	DMF/AcOH (3:1)	**91**	trace
10	$[RhCp^*Cl_2]_2$ (2.5)	$Cu(OAc)_2{\cdot}H_2O$ (200)	MeCN/AcOH (3:1)	7	0
11	$[RhCp^*Cl_2]_2$ (2.5) $AgSbF_6$ (10)	$Cu(OAc)_2{\cdot}H_2O$ (200)	DMF/AcOH (3:1)	82	trace
12	$[RhCp^*Cl_2]_2$ (2.5)	$Cu(OAc)_2{\cdot}H_2O$ (100)	DMF/AcOH (3:1)	69	4

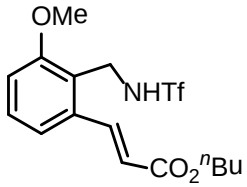
Characterization data for products (3a–p and 4b–j)

Butyl 2-(4-methoxy-2-(trifluoromethylsulfonyl)isoindolin-1-yl)acetate (3a)



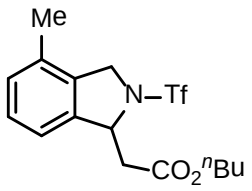
^{1}H NMR (700 MHz, $CDCl_3$) δ 7.27 (t, *J* = 7.9 Hz, 1H), 6.80 (d, *J* = 7.7 Hz, 1H), 6.78 (d, *J* = 8.2 Hz, 1H), 5.55 (br s, 1H), 4.87 (d, *J* = 13.7 Hz, 1H), 4.73 (d, *J* = 13.7 Hz, 1H), 4.05–3.99 (m, 2H), 3.82 (s, 3H), 3.03 (dd, *J* = 16.3, 3.5 Hz, 1H), 2.92 (dd, *J* = 16.3, 7.2 Hz, 1H), 1.52–1.50 (m, 2H), 1.29–1.25 (m, 2H), 0.87 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 169.5, 154.4, 139.6, 130.2, 122.9, 120.1 (q, $J_{C\text{-}F}$ = 322.0 Hz), 114.3, 109.7, 64.6, 63.7, 55.2, 52.8, 41.2, 30.4, 18.9, 13.5 ; IR (KBr) υ 2961, 1733, 1602, 1489, 1388, 1271, 1180, 1062, 1000, 895, 774 cm^{-1}; HRMS (EI) calcd for $C_{16}H_{20}F_3NO_5S$ $[M]^+$ 395.1014, found 395.1017.

(*E*)-Butyl 3-(3-methoxy-2-((trifluoromethylsulfonamido)methyl)phenyl)acrylate (3aa)



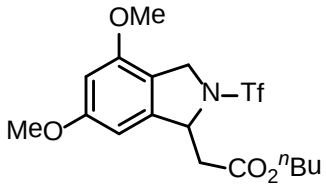
^{1}H NMR (700 MHz, $CDCl_3$) δ 8.01 (d, *J* = 15.6 Hz, 1H), 7.32 (d, *J* = 8.0 Hz, 1H), 7.14 (d, *J* = 7.8 Hz, 1H), 6.92 (d, *J* = 7.8 Hz, 1H), 6.31 (d, *J* = 15.6 Hz, 1H), 5.62 (br s, 1H), 4.54 (d, *J* = 5.8 Hz, 2H), 4.17 (t, *J* = 6.6 Hz, 2H), 3.87 (s, 3H), 1.67–1.65 (m, 2H), 1.43–1.41 (m, 2H), 0.93 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 166.3, 158.0, 140.3, 135.0, 130.0, 122.7, 122.6, 119.9 (q, $J_{C\text{-}F}$ = 320.6 Hz), 119.4, 111.5, 64.6, 55.7, 39.6, 30.6, 19.1, 13.6; IR (KBr) υ 2961, 1695, 1578, 1444, 1372, 1264, 1179, 1142, 1048, 982, 865, 733 cm^{-1}; HRMS (EI) calcd for $C_{16}H_{20}F_3NO_5S$ $[M]^+$ 395.1014, found 395.1015.

Butyl 2-(4-methyl-2-(trifluoromethylsulfonyl)isoindolin-1-yl)acetate (3b)



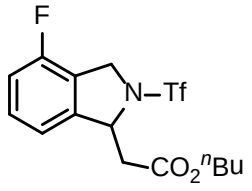
^{1}H NMR (700 MHz, $CDCl_3$) δ 7.22 (t, *J* = 7.5 Hz, 1H), 7.11 (d, *J* = 7.4 Hz, 1H), 7.05 (d, *J* = 7.7 Hz, 1H), 5.58 (br s, 1H), 4.85 (d, *J* = 13.3 Hz, 1H), 4.76 (d, *J* = 13.3 Hz, 1H), 4.04–3.98 (m, 2H), 3.04 (d, *J* = 16.4 Hz, 1H), 2.94 (dd, *J* = 16.5, 7.0 Hz, 1H), 2.24 (s, 3H), 1.51–1.49 (m, 2H), 1.28–1.24 (m, 2H), 0.87 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 169.4, 137.7, 133.8, 132.4, 129.4, 128.6, 120.1 (q, $J_{C\text{-}F}$ = 325.0 Hz), 64.5, 63.6, 53.9, 41.1, 30.3, 18.9, 18.4, 13.5; IR (KBr) υ 2962, 1732, 1467, 1387, 1225, 1180, 1157, 1066, 776 cm^{-1}; HRMS (EI) calcd for $C_{16}H_{20}F_3NO_4S$ $[M]^+$ 379.1065, found 379.1061.

Butyl 2-(4,6-dimethoxy-2-(trifluoromethylsulfonyl)isoindolin-1-yl)acetate (3c)



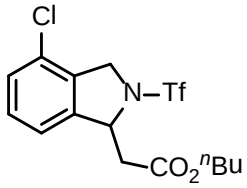
^{1}H NMR (700 MHz, $CDCl_3$) δ 6.35 (d, *J* = 1.9 Hz, 1H), 6.32 (d, *J* = 1.6 Hz, 1H), 5.49 (br s, 1H), 4.78 (d, *J* = 13.0 Hz, 1H), 4.65 (d, *J* = 13.0 Hz, 1H), 4.06–4.01 (m, 2H), 3.78 (s, 3H), 3.75 (s, 3H), 3.03 (dd, *J* = 16.3, 3.6 Hz, 1H), 2.88 (dd, *J* = 16.3, 7.4 Hz, 1H), 1.54–1.51 (m, 2H), 1.30–1.26 (m, 2H), 0.87 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 169.6, 162.0, 155.1, 140.1, 120.2 (q, $J_{C\text{-}F}$ = 323.0 Hz), 115.3, 98.3, 98.2, 64.9, 63.7, 55.5, 55.3, 52.4, 41.3, 30.4, 18.9, 13.5; IR (KBr) υ 2962, 1732, 1610, 1502, 1465, 1388, 1342, 1225, 1200, 1149, 1069, 1001, 935, 836, 735 cm^{-1}; HRMS (EI) calcd for $C_{17}H_{22}F_3NO_6S$ $[M]^+$ 425.1120, found 425.1118.

Butyl 2-(4-fluoro-2-(trifluoromethylsulfonyl)isoindolin-1-yl)acetate (3d)



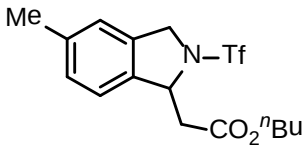
^{1}H NMR (700 MHz, $CDCl_3$) δ 7.31–7.30 (m, 1H), 7.04–7.01 (m, 2H), 5.57 (br s, 1H), 4.97 (d, *J* = 13.7 Hz, 1H), 4.85 (d, *J* = 13.7 Hz, 1H), 4.05–3.99 (m, 2H), 3.05–2.96 (m, 2H), 1.53–1.49 (m, 2H), 1.28–1.25 (m, 2H), 0.87 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 169.2, 157.2 (d, $J_{C\text{-}F}$ = 249.6 Hz), 141.2, 130.7 (d, $J_{C\text{-}F}$ = 6.4 Hz), 122.1 (d, $J_{C\text{-}F}$ = 18.3 Hz), 120.0 (q, $J_{C\text{-}F}$ = 326.9 Hz), 118.2, 115.2 (d, $J_{C\text{-}F}$ = 19.2 Hz), 64.7, 63.4, 51.8, 40.7, 30.4, 18.9, 13.5; IR (KBr) υ 2963, 1733, 1631, 1599, 1480, 1390, 1226, 1184, 1157, 1067, 919, 781 cm^{-1}; HRMS (EI) calcd for $C_{15}H_{17}F_4NO_4S$ $[M]^+$ 383.0814, found 383.0809.

Butyl 2-(4-chloro-2-(trifluoromethylsulfonyl)isoindolin-1-yl)acetate (3e)



^{1}H NMR (700 MHz, $CDCl_3$) δ 7.28 (m, 2H), 7.14 (d, *J* = 7.3 Hz, 1H), 5.60 (br s, 1H), 4.93 (d, *J* = 14.1 Hz, 1H), 4.81 (d, *J* = 14.1 Hz, 1H), 4.04–3.98 (m, 2H), 3.03 (d, *J* = 16.8 Hz, 1H), 2.98 (dd, *J* = 16.8, 7.0 Hz, 1H), 1.51–1.49 (m, 2H), 1.28–1.24 (m, 2H), 0.87 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 169.2, 139.9, 133.8, 130.1, 128.8, 128.7, 120.8, 120.0 (q, $J_{C\text{-}F}$ = 322.0 Hz), 64.7, 63.9, 54.1, 40.7, 30.3, 18.9, 13.5; IR (KBr) υ 2962, 1733, 1586, 1458, 1389, 1227, 1181, 1148, 1065, 995, 861, 777 cm^{-1}; HRMS (EI) calcd for $C_{15}H_{17}ClF_3NO_4S$ $[M]^+$ 399.0519, found 399.0518.

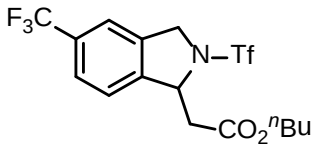
Butyl 2-(5-methyl-2-(trifluoromethylsulfonyl)isoindolin-1-yl)acetate (3f)



^{1}H NMR (700 MHz, $CDCl_3$) δ 7.11 (s, 2H), 7.04 (s, 1H), 5.52 (br s, 1H), 4.86 (d, *J* = 13.3 Hz, 1H), 4.80 (d, *J* = 13.3 Hz, 1H), 4.03–4.00 (m, 2H), 3.01 (dd, *J* = 16.4, 3.5 Hz, 1H), 2.92 (dd, *J* = 16.3, 7.1 Hz, 1H), 2.34 (s, 3H), 1.52–1.50 (m, 2H), 1.29–1.25 (m, 2H), 0.87 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 169.5, 138.7, 135.1, 134.9, 129.2, 122.8, 122.2, 120.1 (q, $J_{C\text{-}F}$ = 323.8 Hz), 64.6, 63.1, 54.3, 41.1, 30.4, 21.2, 18.9, 13.5; IR (KBr) υ 2961, 1732, 1462,

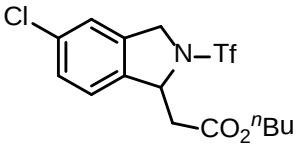
1388, 1225, 1181, 1157, 1064, 971, 818, 776 cm^{-1}; HRMS (EI) calcd for $C_{16}H_{20}F_3NO_4S$ $[M]^+$ 379.1065, found 379.1065.

Butyl 2-(5-(trifluoromethyl)-2-(trifluoromethylsulfonyl)isoindolin-1-yl)acetate (3g)



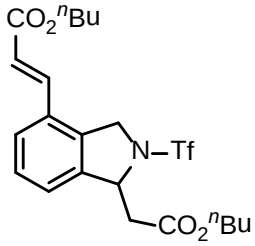
^{1}H NMR (700 MHz, $CDCl_3$) δ 7.59 (d, *J* = 8.1 Hz, 1H), 7.51 (s, 1H), 7.39 (d, *J* = 8.0 Hz, 1H), 5.59 (br s, 1H), 4.96 (d, *J* = 13.7 Hz, 1H), 4.89 (d, *J* = 13.7 Hz, 1H), 4.04–3.99 (m, 2H), 3.08–2.99 (m, 2H), 1.52–1.48 (m, 2H), 1.28–1.23 (m, 2H), 0.87 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 169.2, 141.9, 136.0, 131.4 (q, J_{C-F} = 32.5 Hz), 125.6 (q, J_{C-F} = 3.2 Hz), 123.7 (q, J_{C-F} = 272.3 Hz), 123.2, 120.0 (q, J_{C-F} = 331.3 Hz), 119.7 (q, J_{C-F} = 3.8 Hz), 64.9, 62.9, 54.2, 40.5, 30.4, 18.9, 13.5; IR (KBr) υ 2964, 1732, 1441, 1390, 1326, 1227, 1159, 1125, 1059, 893, 778 cm^{-1}; HRMS (EI) calcd for $C_{16}H_{17}F_6NO_4S$ $[M]^+$ 433.0782, found 433.0784.

Butyl 2-(5-chloro-2-(trifluoromethylsulfonyl)isoindolin-1-yl)acetate (3h)



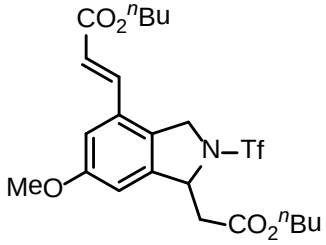
^{1}H NMR (700 MHz, $CDCl_3$) δ 7.28 (dd, *J* = 8.1, 1.8 Hz, 1H), 7.23 (s, 1H), 7.18 (d, *J* = 8.2 Hz, 1H), 5.51 (br s, 1H), 4.87 (d, *J* = 13.7 Hz, 1H), 4.81 (d, *J* = 13.7 Hz, 1H), 4.03–3.99 (m, 2H), 3.02 (dd, *J* = 16.7, 3.0 Hz, 1H), 2.94 (dd, *J* = 16.7, 7.0 Hz, 1H), 1.53–1.49 (m, 2H), 1.29–1.25 (m, 2H), 0.87 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 169.3, 136.9, 136.5, 134.8, 128.7, 123.8, 122.7, 120.0 (q, J_{C-F} = 321.3 Hz), 64.8, 62.8, 54.1, 40.7, 30.4, 18.9, 13.5; IR (KBr) υ 2962, 1731, 1388, 1226, 1183, 1156, 1062, 998, 885, 776 cm^{-1}; HRMS (EI) calcd for $C_{15}H_{17}ClF_3NO_4S$ $[M]^+$ 399.0519, found 399.0494.

(*E*)-Butyl 3-(1-(2-butoxy-2-oxoethyl)-2-(trifluoromethylsulfonyl)isoindolin-4-yl)acrylate (3i)



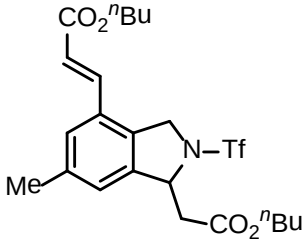
^{1}H NMR (700 MHz, $CDCl_3$) δ 7.54–7.51 (m, 2H), 7.35 (t, *J* = 7.7 Hz, 1H), 7.24 (d, *J* = 7.7 Hz, 1H), 6.31 (d, *J* = 16.0 Hz, 1H), 5.56 (br s, 1H), 5.03 (d, *J* = 13.6 Hz, 1H), 4.94 (d, *J* = 13.6 Hz, 1H), 4.01–3.96 (m, 2H), 3.02–2.96 (m, 2H), 1.69–1.64 (m, 2H), 1.49–1.46 (m, 2H), 1.42–1.39 (m, 2H), 1.25–1.22 (m, 2H), 0.93 (t, *J* = 7.3 Hz, 3H), 0.84 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 169.3, 166.3, 139.9, 139.0, 134.5, 129.6, 129.1, 127.3, 123.8, 121.2, 120.0 (q, $J_{C\text{-}F}$ = 330.6 Hz), 64.73, 64.71, 63.0, 54.1, 40.6, 30.6, 30.3, 19.1, 18.9, 13.6, 13.5; IR (KBr) υ 2961, 1731, 1712, 1640, 1593, 1456, 1389, 1226, 1178, 1160, 1064, 979, 866, 787 cm^{-1}; HRMS (EI) calcd for $C_{22}H_{28}F_3NO_6S$ $[M]^+$ 491.1589, found 491.1591.

(*E*)-Butyl 3-(1-(2-butoxy-2-oxoethyl)-6-methoxy-2-(trifluoromethylsulfonyl)isoindolin-4-yl)acrylate (3j)



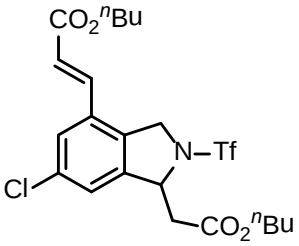
^{1}H NMR (700 MHz, $CDCl_3$) δ 7.46 (d, *J* = 16.0 Hz, 1H), 7.01 (s, 1H), 6.79 (s, 1H), 6.28 (d, *J* = 16.0 Hz, 1H), 5.51 (br s, 1H), 4.95 (d, *J* = 13.0 Hz, 1H), 4.87 (d, *J* = 13.0 Hz, 1H), 4.20–4.18 (m, 2H), 4.05–3.99 (m, 2H), 3.79 (s, 3H), 3.02–2.93 (m, 2H), 1.69–1.62 (m, 2H), 1.52–1.49 (m, 2H), 1.42–1.39 (m, 2H), 1.28–1.22 (m, 2H), 0.94 (t, *J* = 7.4 Hz, 3H), 0.86 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 169.4, 166.3, 160.4, 140.1, 130.3, 129.3, 121.3, 114.3, 112.8, 109.8, 64.8, 64.7, 62.9, 55.6, 53.6, 40.9, 30.6, 30.4, 19.1, 18.9, 13.6, 13.5; IR (KBr) υ 2961, 1728, 1715, 1641, 1466, 1389, 1271, 1226, 1175, 1067, 1042, 975, 850, 735 cm^{-1}; HRMS (EI) calcd for $C_{23}H_{30}F_3NO_7S$ $[M]^+$ 521.1695, found 521.1694.

(*E*)- Butyl 3-(1-(2-butoxy-2-oxoethyl)-6-methyl-2-(trifluoromethylsulfonyl)isoindolin-4-yl)acrylate (3k)



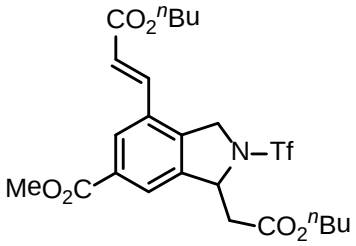
^{1}H NMR (700 MHz, $CDCl_3$) δ 7.50 (d, *J* = 16.0 Hz, 1H), 7.32 (s, 1H), 7.05 (s, 1H), 6.29 (d, *J* = 16.0 Hz, 1H), 5.51 (br s, 1H), 4.97 (d, *J* = 13.4 Hz, 1H), 4.89 (d, *J* = 13.4 Hz, 1H), 4.20–4.17 (m, 2H), 4.04–3.96 (m, 2H), 3.02–2.94 (m, 2H), 2.34 (s, 3H), 1.68–1.64 (m, 2H), 1.50–1.47 (m, 2H), 1.42–1.39 (m, 2H), 1.26–1.23 (m, 2H), 0.93 (t, *J* = 7.3 Hz, 3H), 0.85 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 169.3, 166.4, 140.2, 139.2, 131.7, 129.2, 128.2, 124.5, 120.8, 120.0 (q, $J_{C\text{-}F}$ = 323.7 Hz), 64.6, 64.5, 62.9, 53.9, 40.8, 30.6, 30.4, 21.1, 19.1, 18.9, 13.6, 13.5; IR (KBr) υ 2961, 1728, 1713, 1640, 1463, 1389, 1269, 1226, 1175, 1067, 975, 857, 735 cm^{-1}; HRMS (EI) calcd for $C_{23}H_{30}F_3NO_6S$ $[M]^+$ 505.1746, found 505.1736.

(*E*)- Butyl 3-(1-(2-butoxy-2-oxoethyl)-6-chloro-2-(trifluoromethylsulfonyl)isoindolin-4-yl)acrylate (3l)



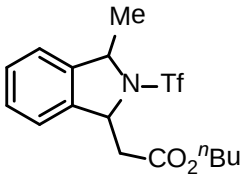
^{1}H NMR (700 MHz, $CDCl_3$) δ 7.49 (s, 1H), 7.44 (d, *J* = 16.0 Hz, 1H), 7.24 (s, 1H), 6.33 (d, *J* = 16.0 Hz, 1H), 5.51 (br s, 1H), 4.97 (d, *J* = 13.7 Hz, 1H), 4.89 (d, *J* = 13.7 Hz, 1H), 4.21–4.18 (m, 2H), 4.05–3.97 (m, 2H), 3.00–2.96 (m, 2H), 1.68–1.64 (m, 2H), 1.51–1.49 (m, 2H), 1.41–1.38 (m, 2H), 1.28–1.24 (m, 2H), 0.93 (t, *J* = 7.3 Hz, 3H), 0.86 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 169.1, 165.9, 140.8, 138.4, 135.1, 133.1, 130.9, 127.1, 123.9, 122.5, 120.0 (q, $J_{C\text{-}F}$ = 332.7 Hz), 64.9, 64.8, 62.6, 53.7, 40.2, 30.6, 30.4, 19.1, 18.9, 13.6, 13.5; IR (KBr) υ 2961, 2046, 1731, 1713, 1643, 1592, 1459, 1389, 1226, 1177, 1160, 1067, 974, 862, 737 cm^{-1}; HRMS (EI) calcd for $C_{22}H_{27}ClF_3NO_6S$ $[M]^+$ 525.1200, found 525.1183.

(*E*)- Methyl 3-(2-butoxy-2-oxoethyl)-7-(3-butoxy-3-oxoprop-1-enyl)-2-(trifluoromethylsulfonyl)isoindoline-5-carboxylate (3m)



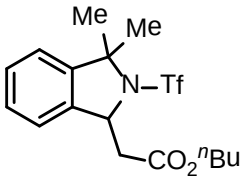
^{1}H NMR (700 MHz, $CDCl_3$) δ 8.22 (s, 1H), 7.88 (s, 1H), 7.53 (d, *J* = 15.9 Hz, 1H), 6.44 (d, *J* = 15.9 Hz, 1H), 5.56 (br s, 1H), 5.06 (d, *J* = 14.2 Hz, 1H), 5.01 (d, *J* = 14.2 Hz, 1H), 4.21 (t, *J* = 6.6 Hz, 2H), 4.03–3.99 (m, 2H), 3.92 (s, 3H), 3.09–3.02 (m, 2H), 1.70–1.66 (m, 2H), 1.50–1.39 (m, 4H), 1.27–1.22 (m, 2H), 0.95 (t, *J* = 7.4 Hz, 3H), 0.84 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 169.0, 166.0, 165.6, 138.7, 131.5, 129.8, 128.5, 124.4, 122.4, 119.9 (q, $J_{C\text{-}F}$ = 315.9 Hz), 64.9, 64.8, 62.9, 54.3, 52.5, 40.0, 30.6, 30.3, 19.1, 18.9, 13.6, 13.5; IR (KBr) υ 2960, 1719, 1644, 1596, 1437, 1390, 1276, 1225, 1179, 1069, 976, 734 cm^{-1}; HRMS (EI) calcd for $C_{24}H_{30}F_3NO_8S$ $[M]^+$ 549.1644, found 549.1649.

Butyl 2-(3-methyl-2-(trifluoromethylsulfonyl)isoindolin-1-yl)acetate (3n)



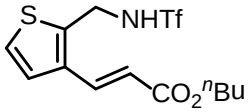
^{1}H NMR (700 MHz, $CDCl_3$) δ 7.35–7.33 (m, 1H), 7.31–7.27 (m, 2H), 7.18 (d, *J* = 7.4 Hz, 1H), 5.56 (br s, 1H), 5.20 (br s, 1H), 4.11 (t, *J* = 6.7 Hz, 2H), 3.17 (d, *J* = 15.1 Hz, 1H), 2.74 (dd, *J* = 15.9, 9.0 Hz, 1H), 1.62 (d, *J* = 6.5 Hz, 3H), 1.59–1.57 (m, 2H), 1.35–1.32 (m, 2H), 0.91 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 169.7, 139.9, 137.5, 128.2, 128.5, 123.0, 122.2, 64.8, 63.1, 62.9, 44.3, 30.4, 25.2, 19.0, 13.6; IR (KBr) υ 2963, 1731, 1461, 1391, 1302, 1225, 1181, 1151, 1061, 980, 751 cm^{-1}; HRMS (EI) calcd for $C_{16}H_{20}F_3NO_4S$ $[M]^+$ 379.1065, found 379.1057.

Butyl 2-(3,3-dimethyl-2-(trifluoromethylsulfonyl)isoindolin-1-yl)acetate (3o)



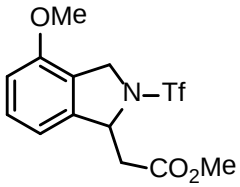
^{1}H NMR (700 MHz, $CDCl_3$) δ 7.34 (t, *J* = 7.8 Hz, 1H), 7.29 (t, *J* = 7.8 Hz, 1H), 7.24 (br s, 1H), 7.12 (d, *J* = 7.7 Hz, 1H), 5.54 (br s, 1H), 4.11(t, *J* = 6.5 Hz, 2H), 3.48 (d, *J* = 15.1 Hz, 1H), 2.70–2.69 (m, 2H), 1.78 (s, 3 H), 1.74 (s, 3 H), 1.59–1.57 (m, 2H), 1.35–1.32 (m, 2H), 0.90 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 170.2, 144.5, 140.7, 128.9, 128.5, 122.6, 121.4, 64.7, 62.9, 53.4, 44.3, 32.7, 30.6, 30.5, 27.4, 19.0, 13.6; IR (KBr) υ 2961, 1730, 1461, 1379, 1221, 1181, 1150, 1040, 941, 737 cm^{-1}; HRMS (EI) calcd for $C_{17}H_{22}F_3NO_4S$ $[M]^+$ 393.1222, found 393.1216.

(*E*)-Butyl 3-(2-((trifluoromethylsulfonamido)methyl)thiophen-3-yl)acrylate (3p)



^{1}H NMR (700 MHz, $CDCl_3$) δ 7.62 (d, *J* = 15.6 Hz, 1H), 7.30 (d, *J* = 5.3 Hz, 1H), 7.22 (d, *J* = 5.3 Hz, 1H), 6.27 (d, *J* = 15.6 Hz, 1H), 5.31 (br s, 1H), 4.70 (d, *J* = 5.7Hz, 2H), 4.17 (t, *J* = 6.6 Hz, 2H), 1.68–1.64 (m, 2H), 1.42–1.39 (m, 2H), 0.94 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 167.0, 138.1, 135.3, 134.0, 126.5, 125.8, 120.0, 64.7, 40.3, 30.6, 19.1, 13.7; IR (KBr) υ 2922, 1689, 1630, 1453, 1376, 1301, 1229, 1183, 1143, 1054, 973, 861, 752 cm^{-1}; HRMS (EI) Calcd for $C_{13}H_{16}F_3NO_4S_2$ $[M]^+$ 371.0473, found 371.0478.

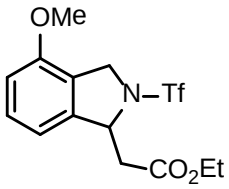
Methyl 2-(4-methoxy-2-(trifluoromethylsulfonyl)isoindolin-1-yl)acetate (4b)



^{1}H NMR (700 MHz, $CDCl_3$) δ 7.28 (t, *J* = 7.9 Hz, 1H), 6.80 (d, *J* = 8.0 Hz, 2H), 5.56 (br s, 1H), 4.87 (d, *J* = 13.7 Hz, 1H), 4.74 (d, *J* = 13.7 Hz, 1H), 3.82 (s, 3H), 3.63 (s, 3H), 3.05 (dd, *J* = 16.3, 3.7 Hz, 1H), 2.90 (dd, *J* = 16.3, 7.4 Hz, 1H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 169.8, 154.4, 139.6, 130.2, 123.0, 120.1 (q, J_{C-F} = 323.2 Hz), 114.2, 109.7, 63.6, 55.2, 52.7, 51.7, 41.0;

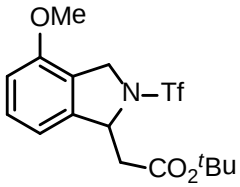
IR (KBr) υ 2955, 1738, 1601, 1489, 1388, 1271, 1224, 1177, 1155, 1061, 999, 892, 775 cm^{-1}; HRMS (EI) calcd for $C_{13}H_{14}F_3NO_5S$ $[M]^+$ 353.0545, found 353.0540.

Ethyl 2-(4-methoxy-2-(trifluoromethylsulfonyl)isoindolin-1-yl)acetate (4c)



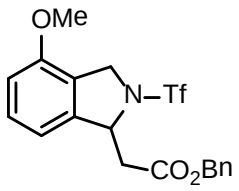
^{1}H NMR (700 MHz, $CDCl_3$) δ 7.28 (t, *J* = 7.9 Hz, 1H), 6.81–6.78 (m, 2H), 5.56 (br s, 1H), 4.87 (d, *J* = 13.7 Hz, 1H), 4.73 (d, *J* = 13.7 Hz, 1H), 4.09–4.07 (m, 2H), 3.82 (s, 3H), 3.03 (dd, *J* = 16.3, 3.4 Hz, 1H), 2.90 (dd, *J* = 16.3, 7.2 Hz, 1H), 1.17 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 169.4, 154.4, 139.6, 130.2, 123.1, 120.0 (q, $J_{C\text{-}F}$ = 321.0 Hz), 114.3, 109.7, 63.7, 60.7, 55.3, 52.8, 41.2, 13.9; IR (KBr) υ 2941, 2056, 1732, 1602, 1489, 1387, 1271, 1225, 1179, 1155, 1062, 872, 774 cm^{-1}; HRMS (EI) calcd for $C_{14}H_{16}F_3NO_5S$ $[M]^+$ 367.0701, found 367.0699.

***tert*-Butyl 2-(4-methoxy-2-(trifluoromethylsulfonyl)isoindolin-1-yl)acetate (4d)**



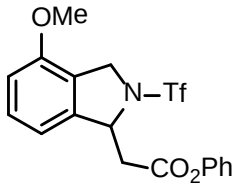
^{1}H NMR (700 MHz, $CDCl_3$) δ 7.28 (t, *J* = 7.9 Hz, 1H), 6.84 (d, *J* = 7.7 Hz, 1H), 6.78 (d, *J* = 8.1 Hz, 1H), 5.53 (br s, 1H), 4.86 (d, *J* = 13.7 Hz, 1H), 4.71 (d, *J* = 13.7 Hz, 1H), 3.82 (s, 3H), 2.96 (dd, *J* = 16.1, 3.3 Hz, 1H), 2.84 (dd, *J* = 16.1, 7.2 Hz, 1H), 1.33 (s, 9H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 168.6, 154.4, 139.9, 130.1, 123.0, 120.2 (q, $J_{C\text{-}F}$ = 326.1 Hz), 114.5, 109.6, 81.2, 64.0, 55.3, 52.8, 42.4, 27.8; IR (KBr) υ 2978, 2057, 1726, 1602, 1489, 1389, 1367, 1271, 1225, 1182, 1145, 1061, 1000, 952, 898, 776 cm^{-1}; HRMS (EI) calcd for $C_{16}H_{20}F_3NO_5S$ $[M]^+$ 395.1014, found 395.1019.

Benzyl 2-(4-methoxy-2-(trifluoromethylsulfonyl)isoindolin-1-yl)acetate (4e)



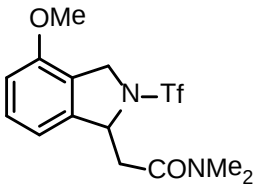
^{1}H NMR (700 MHz, $CDCl_3$) δ 7.33–7.32 (m, 3H), 7.26–7.25 (m, 3H), 6.78 (d, *J* = 8.1 Hz, 1H), 6.74 (d, *J* = 7.7 Hz, 1H), 5.58 (br s, 1H), 5.09 (d, *J* = 12.1 Hz, 1H), 5.04 (d, *J* = 12.1 Hz, 1H), 4.85 (d, *J* = 13.7 Hz, 1H), 4.67 (d, *J* = 13.7 Hz, 1H), 3.83 (s, 3H), 3.10 (dd, *J* = 16.3, 3.7 Hz, 1H), 2.99 (dd, *J* = 16.3, 7.0 Hz, 1H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 169.2, 154.4, 135.2, 130.2, 129.7, 128.5, 128.3, 120.9, 114.3, 110.4, 109.7, 66.6, 63.7, 55.2, 52.8, 41.2; IR (KBr) υ 2941, 2159, 1735, 1602, 1489, 1385, 1270, 1225, 1183, 1156, 1063, 734 cm^{-1}; HRMS (EI) calcd for $C_{19}H_{18}F_3NO_5S$ $[M]^+$ 429.0858, found 429.0848.

Phenyl 2-(4-methoxy-2-(trifluoromethylsulfonyl)isoindolin-1-yl)acetate (4f)



^{1}H NMR (700 MHz, $CDCl_3$) δ 7.34–7.32 (m, 3H), 7.20 (t, *J* = 7.4 Hz, 1H), 6.94–6.89 (m, 3H), 6.82 (d, *J* = 8.1 Hz, 1H), 5.66 (br s, 1H), 4.91 (d, *J* = 13.6 Hz, 1H), 4.79 (d, *J* = 13.6 Hz, 1H), 3.82 (s, 3H), 3.30–3.23 (m, 2H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 168.0, 154.5, 150.1, 139.1, 130.3, 129.4, 126.0, 123.3, 121.3, 114.3, 109.9, 63.3, 55.3, 53.0, 41.0; IR (KBr) υ 2942, 2159, 1757, 1600, 1491, 1388, 1269, 1226, 1187, 1142, 1063, 734 cm^{-1}; HRMS (EI) calcd for $C_{18}H_{16}F_3NO_5S$ $[M]^+$ 415.0701, found 415.0698.

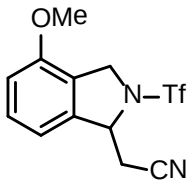
2-(4-Methoxy-2-(trifluoromethylsulfonyl)isoindolin-1-yl)-N,N-dimethylacetamide (4g)



^{1}H NMR (700 MHz, $CDCl_3$) δ 7.24 (t, *J* = 7.9 Hz, 1H), 6.98 (d, *J* = 7.7 Hz, 1H), 6.77 (d, *J* = 8.1 Hz, 1H), 5.72 (br s, 1H), 4.86 (d, *J* = 13.9 Hz, 1H), 4.73 (d, *J* = 13.9 Hz, 1H), 3.81 (s, 3H),

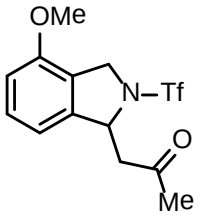
3.13 (d, *J* = 15.9 Hz, 1H), 2.92 (s, 3H), 2.91 (s, 3H), 2.80 (dd, *J* = 16.0, 9.1 Hz, 1H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 168.7, 154.2, 140.9, 130.0, 123.0, 120.2 (q, J_{C-F} = 323.7 Hz), 115.5, 109.4, 64.3, 55.2, 52.5, 40.9, 37.1, 35.3; IR (KBr) υ 2939, 1995, 1643, 1599, 1488, 1385, 1270, 1224, 1180, 1150, 1059, 998, 896, 778 cm^{-1}; HRMS (EI) calcd for $C_{14}H_{17}F_3N_2O_4S$ $[M]^+$ 366.0861, found 366.0845.

2-(4-Methoxy-2-(trifluoromethylsulfonyl)isoindolin-1-yl)acetonitrile (4h)



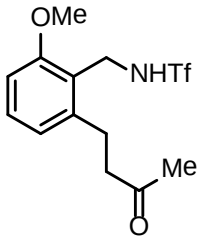
^{1}H NMR (700 MHz, $CDCl_3$) δ 7.38 (t, *J* = 8.0 Hz, 1H), 6.91 (d, *J* = 7.7 Hz, 1H), 6.87 (d, *J* = 8.1 Hz, 1H), 5.42 (br s, 1H), 4.90 (d, *J* = 13.7 Hz, 1H), 4.84 (d, *J* = 13.7 Hz, 1H), 3.84 (s, 3H), 3.11 (dd, *J* = 16.9, 6.0 Hz, 1H), 2.95 (d, *J* = 16.9 Hz, 1H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 154.7, 136.9, 130.8, 123.1, 120.0 (q, J_{C-F} = 323.6 Hz), 115.4, 114.0, 110.6, 63.1, 55.3, 53.2, 26.4; IR (KBr) υ 2945, 2159, 1604, 1491, 1389, 1274, 1225, 1187, 1156, 1062, 1002, 881, 770 cm^{-1}; HRMS (EI) calcd for $C_{12}H_{11}F_3N_2O_3S$ $[M]^+$ 320.0442, found 320.0447.

1-(4-Methoxy-2-(trifluoromethylsulfonyl)isoindolin-1-yl)propan-2-one (4i)



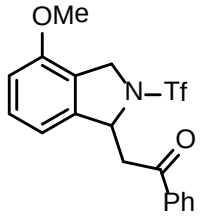
^{1}H NMR (700 MHz, $CDCl_3$) δ 7.25 (t, *J* = 7.9 Hz, 1H), 6.78 (t, *J* = 8.6 Hz, 2H), 5.60 (br s, 1H), 4.85 (d, *J* = 13.7 Hz, 1H), 4.74 (d, *J* = 13.7 Hz, 1H), 3.82 (s, 3H), 3.23 (dd, *J* = 17.8, 2.0 Hz, 1H), 3.03 (dd, *J* = 17.9, 8.1 Hz, 1H), 2.11 (s, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 204.6, 154.4, 140.5, 130.2, 122.7, 120.2 (q, J_{C-F} = 324.2 Hz), 114.5, 109.5, 63.0, 55.3, 52.7, 50.1, 30.6; IR (KBr) υ 2919, 2065, 1713, 1681, 1600, 1490, 1385, 1270, 1225, 1182, 1063, 1027, 883, 778 cm^{-1}; HRMS (EI) calcd for $C_{13}H_{14}F_3NO_4S$ $[M]^+$ 337.0596, found 337.0602.

1,1,1-Trifluoro-N-(2-methoxy-6-(3-oxobutyl)benzyl)methanesulfonamide (4ii)



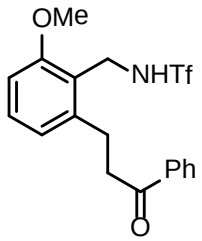
^{1}H NMR (700 MHz, $CDCl_3$) δ 7.22 (t, *J* = 8.0 Hz, 1H), 6.78 (d, *J* = 7.7 Hz, 1H), 6.75 (d, *J* = 8.1 Hz, 1H), 6.16 (br s, 1H), 4.50 (d, *J* = 5.6 Hz, 2H), 3.84 (s, 3H), 2.91 (t, *J* = 7.2 Hz, 2H), 2.80 (t, *J* = 7.1 Hz, 2H), 2.11 (s, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 208.1, 157.9, 140.9, 129.7, 121.9, 121.6, 119.7 (q, J_{C-F} = 321.8 Hz), 108.5, 55.6, 44.3, 39.8, 30.0, 25.7; IR (KBr) υ 2924, 1991, 1707, 1679, 1587, 1440, 1368, 1269, 1226, 1184, 1143, 1091, 1040, 996, 883, 783 cm^{-1}; HRMS (EI) calcd for $C_{13}H_{16}F_3NO_4S$ $[M]^+$ 339.0752, found 339.0751.

2-(4-Methoxy-2-(trifluoromethylsulfonyl)isoindolin-1-yl)-1-phenylethanone (4j)



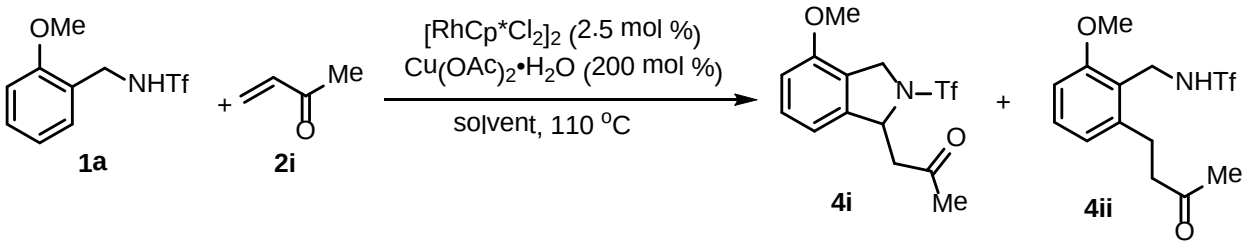
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 7.2 Hz, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.43 (t, *J* = 7.8 Hz, 2H), 7.22 (t, *J* = 8.0 Hz, 1H), 6.83 (d, *J* = 7.7 Hz, 1H), 6.76 (d, *J* = 8.2 Hz, 1H), 5.86 (br s, 1H), 4.91 (d, *J* = 13.9 Hz, 1H), 4.81 (d, *J* = 13.9 Hz, 1H), 3.82 (s, 3H), 3.78 (dd, *J* = 17.8, 2.6 Hz, 1H), 3.58 (dd, *J* = 17.6, 8.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.2, 154.3, 140.6, 136.4, 133.5, 130.1, 128.7, 128.0, 122.7, 115.0, 109.5, 63.5, 55.3, 52.7, 30.9; IR (KBr) υ 2940, 2160, 1683, 1599, 1491, 1385, 1271, 1225, 1183, 1146, 1062, 982, 755 cm^{-1}; HRMS (EI) calcd for $C_{18}H_{16}F_3NO_4S$ $[M]^+$ 399.0752, found 399.0751.

1,1,1-Trifluoro-N-(2-methoxy-6-(3-oxo-3-phenylpropyl)benzyl)methanesulfonamide (4jj)

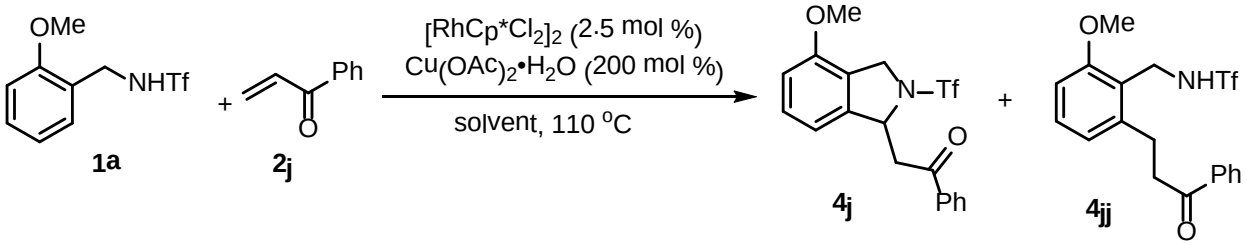


^{1}H NMR (700 MHz, $CDCl_3$) δ 7.96 (dd, *J* = 8.4, 1.1 Hz, 2H), 7.58 (t, *J* = 7.3 Hz, 1H), 7.46 (t, *J* = 8.1 Hz, 1H), 7.27 (t, *J* = 8.0 Hz, 1H), 6.89 (d, *J* = 7.7 Hz, 1H), 6.80 (d, *J* = 8.0 Hz, 1H), 6.38 (br s, 1H), 4.62 (d, *J* = 5.6 Hz, 2H), 3.89 (s, 3H), 3.40 (t, *J* = 7.1 Hz, 2H), 3.16 (t, *J* = 7.0 Hz, 2H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 199.1, 158.0, 141.1, 136.5, 133.3, 129.7, 128.6, 128.1, 122.5, 122.0, 121.7, 120.7 (q, $J_{C\text{-}F}$ = 319.7 Hz), 117.9, 108.5, 55.6, 39.9, 39.5, 26.0; IR (KBr) υ 2943, 2159, 1679, 1586, 1418, 1369, 1266, 1226, 1284, 1142, 1090, 1041, 974, 735 cm^{-1}; HRMS (EI) calcd for $C_{18}H_{18}F_3NO_4S$ $[M]^+$ 401.0909, found 401.0906.

Chemoselectivity between triflamide 1a and α,β-unsaturated ketones 2i and 2j depending on solvents

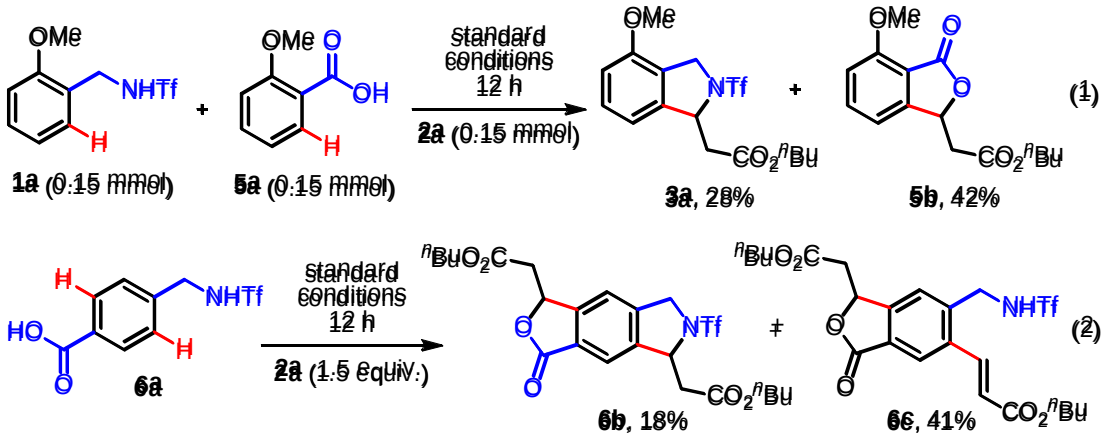


solvent	yield (%) of **4i**	yield (%) of **4ii**
DMF/AcOH (3:1)	4	20
MeCN	54	16
MeCN/AcOH (3:1)	5	7

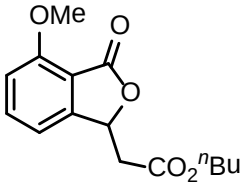


solvent	yield (%) of **4j**	yield (%) of **4jj**
DMF/AcOH (3:1)	16	55
MeCN	52	16

Competition experiments

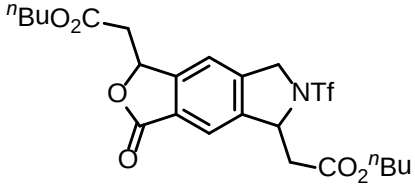


Butyl 2-(4-methoxy-3-oxo-1,3-dihydroisobenzofuran-1-yl)acetate (5b)



^{1}H NMR (700 MHz, $CDCl_3$) δ 7.58 (t, *J* = 7.6 Hz, 1H), 6.97 (d, *J* = 7.5 Hz, 1H), 6.91 (d, *J* = 8.3 Hz, 1H), 5.75 (t, *J* = 6.8 Hz, 1H), 4.12 (t, *J* = 6.7 Hz, 2H), 3.96 (s, 3H), 2.83–2.81 (m, 2H), 1.59–1.57 (m, 2H), 1.35–1.31 (m, 2H), 0.89 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 169.3, 167.8, 158.6, 151.5, 136.5, 113.5, 113.3, 111.1, 75.9, 65.1, 56.0, 39.6, 30.5, 19.0, 13.6; IR (KBr) υ 2960, 2160, 1760, 1730, 1602, 1486, 1315, 1276, 1198, 1170, 1036, 1008, 965, 777 cm^{-1}; HRMS (EI) calcd for $C_{15}H_{18}O_5$ $[M]^+$ 278.1154, found 278.1160.

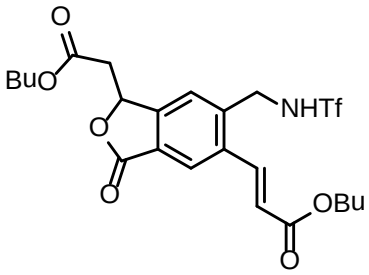
Dibutyl 2,2'-(3-oxo-6-(trifluoromethylsulfonyl)-3,5,6,7-tetrahydro-1H-furo[3,4-f]isoindole-1,5-diyl)diacetate (6b)



^{1}H NMR (700 MHz, $CDCl_3$) δ 7.77 (s, 1H), 7.42 (s, 1H), 5.86 (t, *J* = 6.5 Hz, 1H), 5.61 (br s, 1H), 5.02–4.92 (m, 2H), 4.16 (t, *J* = 6.7 Hz, 2H), 4.05–3.99 (m, 2H), 3.13 (dd, *J* = 17.3, 6.3

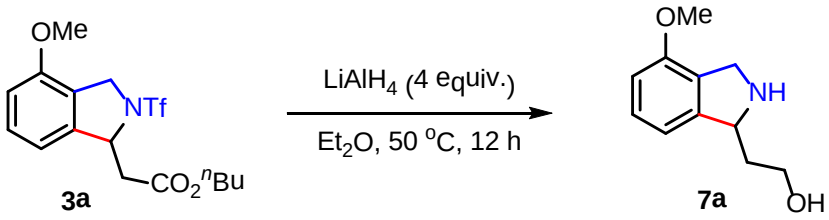
Hz, 1H), 3.08–3.00 (m, 2H), 2.85 (dd, *J* = 16.7, 6.9 Hz, 1H), 1.64–1.60 (m, 2H), 1.55–1.52 (m, 2H), 1.39–1.35 (m, 2H), 1.31–1.26 (m, 2H), 0.94 (t, *J* = 7.4 Hz, 3H), 0.89 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 169.3, 169.2, 168.7, 149.8, 142.6, 140.5, 126.8, 120.1, 116.8, 76.7, 65.3, 65.0, 62.4, 54.4, 39.3, 30.9, 30.5, 19.0, 18.9, 13.7, 13.6; IR (KBr) υ 2961, 2159, 1766, 1729, 1631, 1459, 1389, 1304, 1224, 1179, 1117, 1064, 1006, 789 cm^{-1}; HRMS (EI) calcd for $C_{23}H_{28}F_3NO_8S$ $[M]^+$ 535.1488, found 535.1481.

(*E*)-Butyl 3-(1-(2-butoxy-2-oxoethyl)-3-oxo-6-((trifluoromethylsulfonamido)methyl)-1,3-dihydroisobenzofuran-5-yl)acrylate (6c)



^{1}H NMR (700 MHz, $CDCl_3$) δ 8.33 (d, *J* = 16.0 Hz, 1H), 7.64 (s, 1H), 7.49 (s, 1H), 6.84 (br s, 1H), 6.44 (d, *J* = 16.0 Hz, 1H), 5.71 (t, *J* = 6.4 Hz, 1H), 4.56 (s, 2H), 4.17 (t, *J* = 6.3 Hz, 2H), 4.09 (t, *J* = 6.7 Hz, 2H), 2.88 (t, *J* = 6.1 Hz, 2H), 1.68–1.64 (m, 2H), 1.59–1.55 (m, 2H), 1.42–1.38 (m, 2H), 1.34–1.31 (m, 2H), 0.93 (t, *J* = 7.4 Hz, 3H), 0.90 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 169.3, 168.6, 166.6, 150.7, 143.4, 136.9, 135.0, 125.9, 123.1, 122.9, 122.4, 119.7 (q, $J_{C\text{-}F}$ = 318.9 Hz), 76.2, 65.4, 65.2, 47.4, 38.8, 30.5, 30.4, 19.1, 19.0, 13.6, 13.5 ; IR (KBr) υ 2962, 2160, 2018, 1761, 1732, 1641, 1602, 1459, 1376, 1229, 1183, 1147, 1059, 1016, 871, 734 cm^{-1}; HRMS (EI) Calcd for $C_{23}H_{28}F_3NO_8S$ $[M]^+$ 535.1488, found 535.1486.

General procedure for deprotection of triflamide group

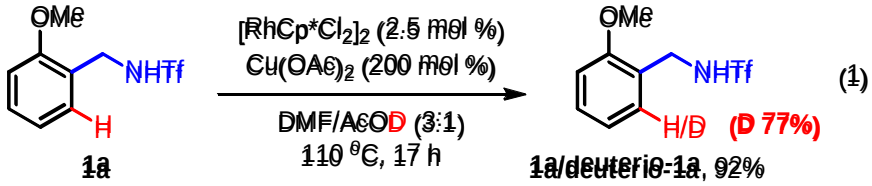


To a stirred solution of **3a** (150.0 mg, 0.38 mmol, 1.0 equiv.) in diethyl ether (4 mL) was added $LiAlH_4$ (57.5 mg, 1.52 mmol, 4.0 equiv.) at 0 ˚C. The reaction mixture was stirred for 12 h at 50˚C. After cooling to room temperature, the reaction mixture was quenched with water and the aqueous layer was extracted with diethyl ether (10 mL × 3). The combined organic layer was dried over Mg_2SO_4 and concentrated in vacuo. The residue was purified by C_{18} reversed-phase silica gel column chromatography (MeOH:H_2O:Et_3N = 90:10:0.2) to afford free (NH)-isoindoline **7a** (53.1 mg) in 72% yield.

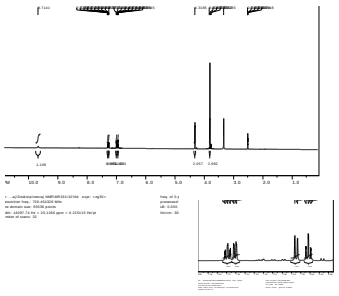
2-(4-Methoxyisoindolin-1-yl)ethanol (7a)

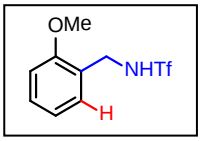
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.26 (t, *J* = 8.0 Hz, 1H), 6.77 (d, *J* = 7.5 Hz, 1H), 6.73 (d, *J* = 8.0 Hz, 1H), 4.70 (br s, 1H), 4.19 (s, 2H), 3.86–3.76 (m, 7H), 2.02–1.96 (m, 1H), 1.84–1.78 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 155.2, 145.9, 129.2, 129.0, 114.5, 108.9, 64.9, 62.0, 55.4, 49.0, 35.9; IR (KBr) υ 3331, 3301, 2926, 2853, 1596, 1546, 1485, 1440, 1267, 1184, 1062, 773 cm^{-1}; LC/MS (ESI) $[M+H]^+$ 194.29.

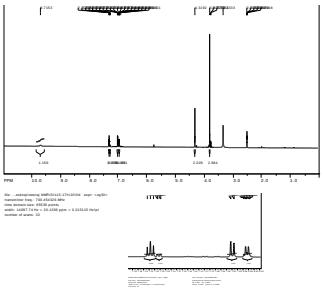
General Procedure of Mechanistic Studies

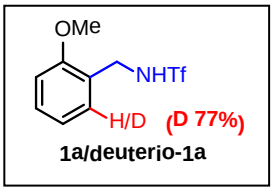


To an oven-dried sealed tube charged with *N*-(2-methoxybenzyl)triflamide (**1a**) (80.8 mg, 0.3 mmol, 100 mol %), $[RhCp^*Cl_2]_2$ (4.6 mg, 0.0075 mmol, 2.5 mol %), and $Cu(OAc)_2$ (108 mg, 0.6 mmol, 200 mol %) in DMF:AcOD (3:1, 1 mL) was allowed to stir for 17 h at 110 ^oC. The reaction mixture was diluted with EtOAc (10 mL) and washed with water. The aqueous layer was extracted with EtOAc (3 × 10 mL). The combined organic layer was dried over Mg_2SO_4 and concentrated in vacuo. The residue was purified by flash column chromatography (*n*-hexanes/EtOAc = 25:1) to afford **1a**/**deutrio-1a** in 92% yield.

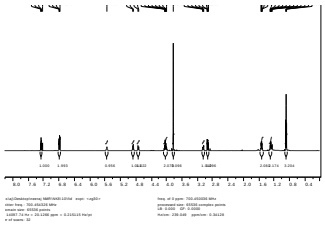


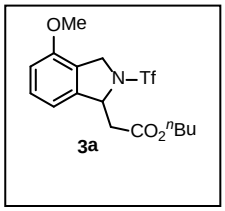


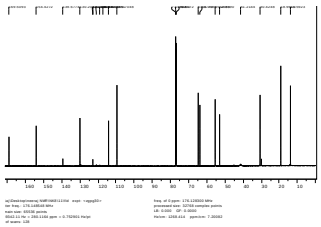


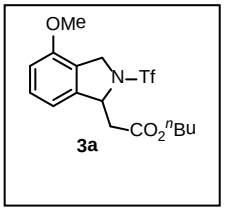


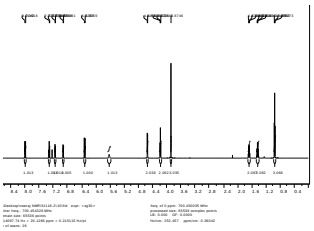
1a/deuterio-1a

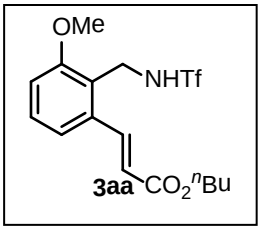


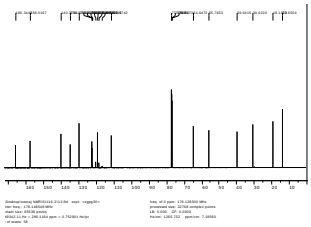

OMe
N–Tf
$CO_2{}^nBu$
3a

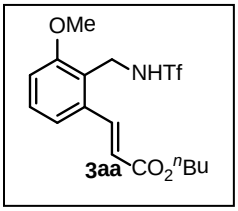


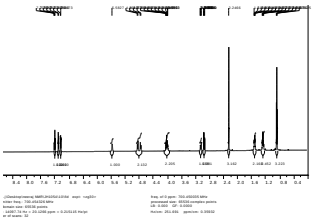

OMe
N–Tf
$CO_2{}^nBu$
3a

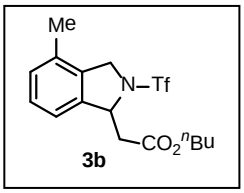



OMe
NHTf
3aa
CO2nBu

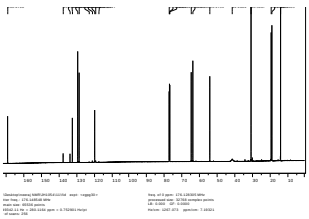


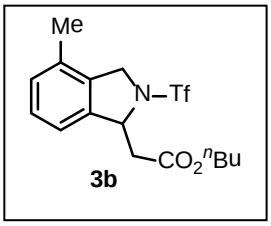

OMe
NHTf
3aa
CO2nBu



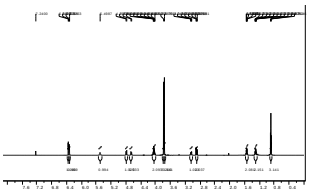


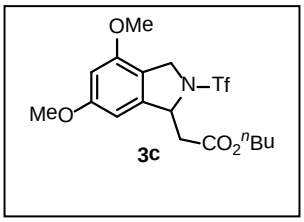
3b

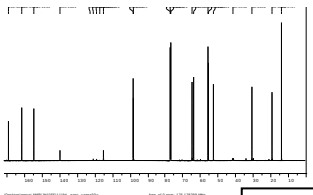


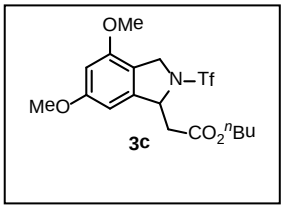


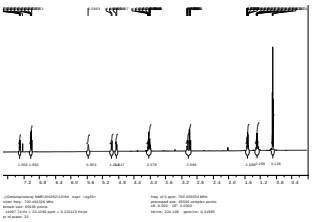
3b

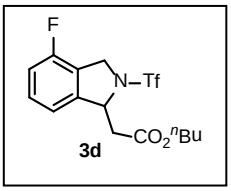


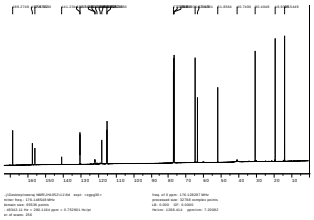

OMe
N–Tf
MeO
$CO_2{}^nBu$
3c

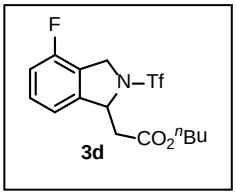


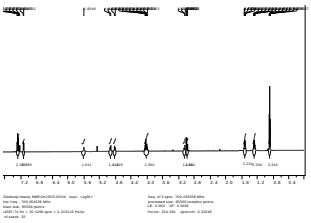

OMe
N–Tf
MeO
$CO_2{}^nBu$
3c

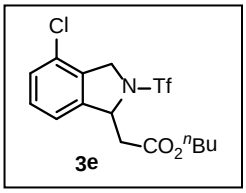


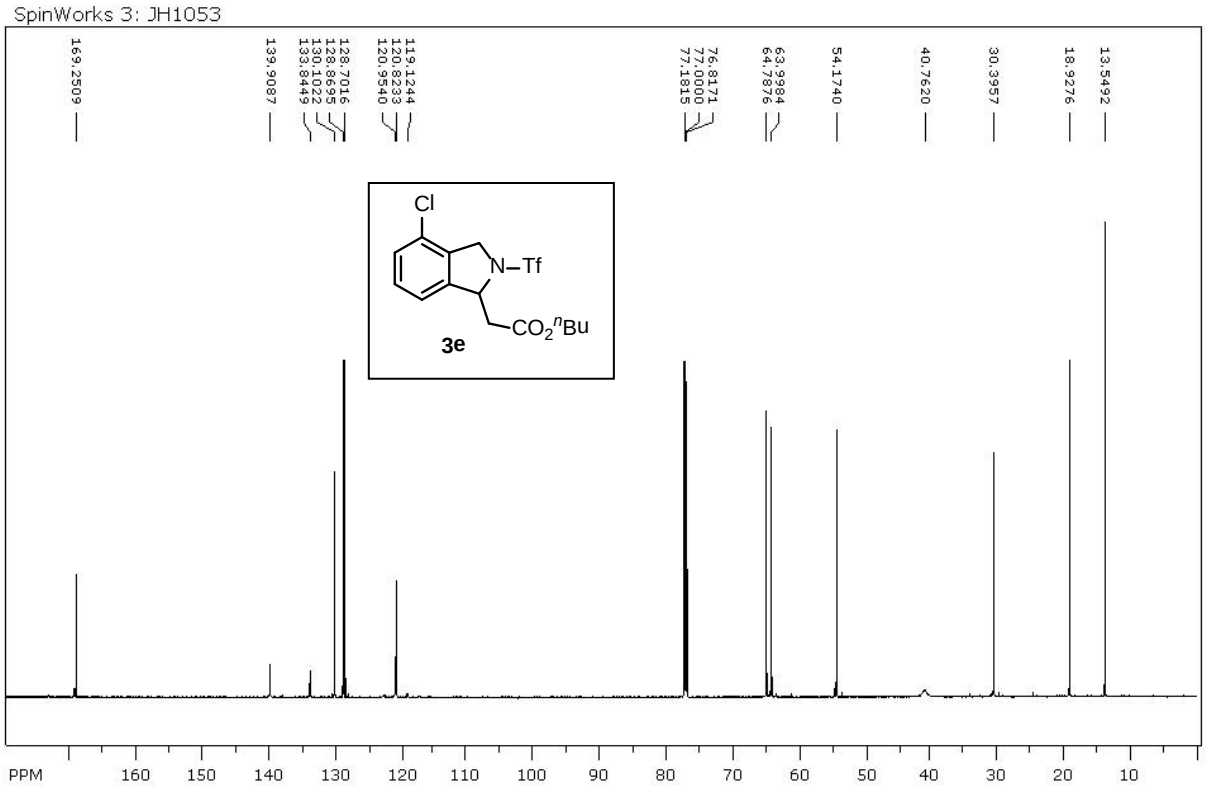

F
N–Tf
$CO_2{}^nBu$
3d




F
N–Tf
$CO_2{}^nBu$
3d




Cl
N–Tf
$CO_2{}^nBu$
3e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120.8233
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77.1815
77.0000
76.8171
64.7876
63.9984
54.1740
40.7620
30.3957
18.9276
13.5492
Cl
N–Tf
$CO_2{}^nBu$
3e
PPM
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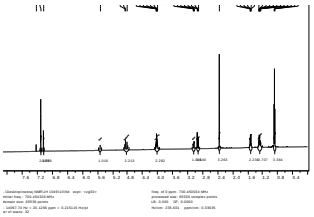

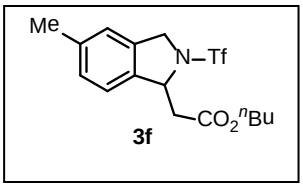

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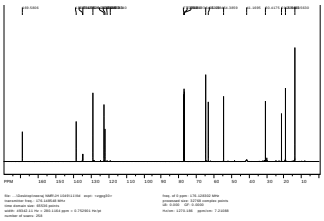

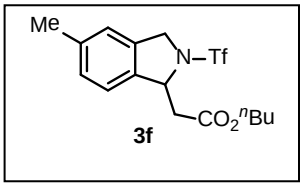

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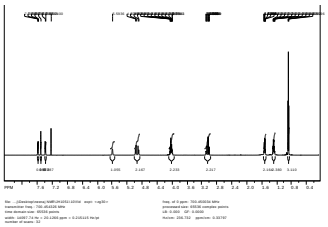

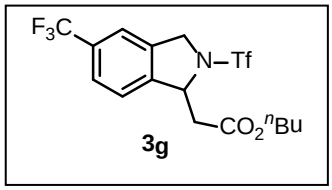

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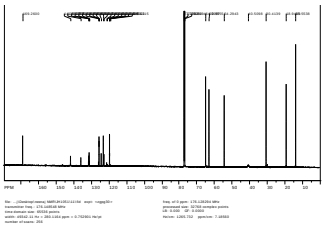

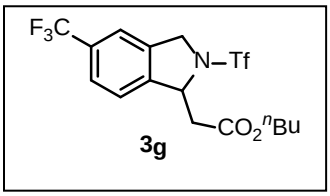

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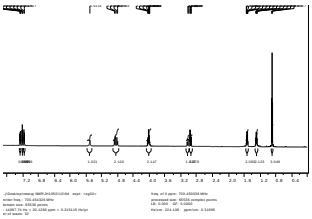

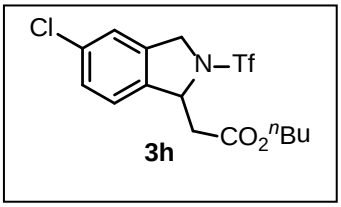

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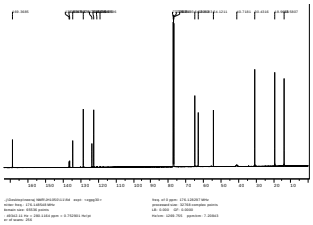

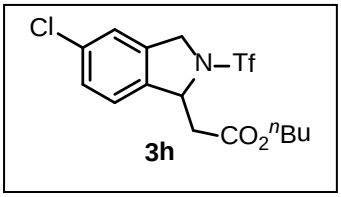

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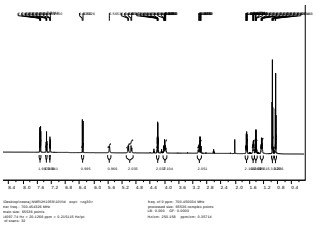
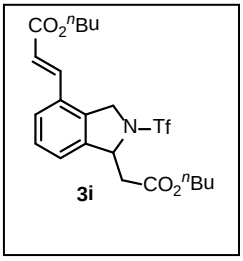
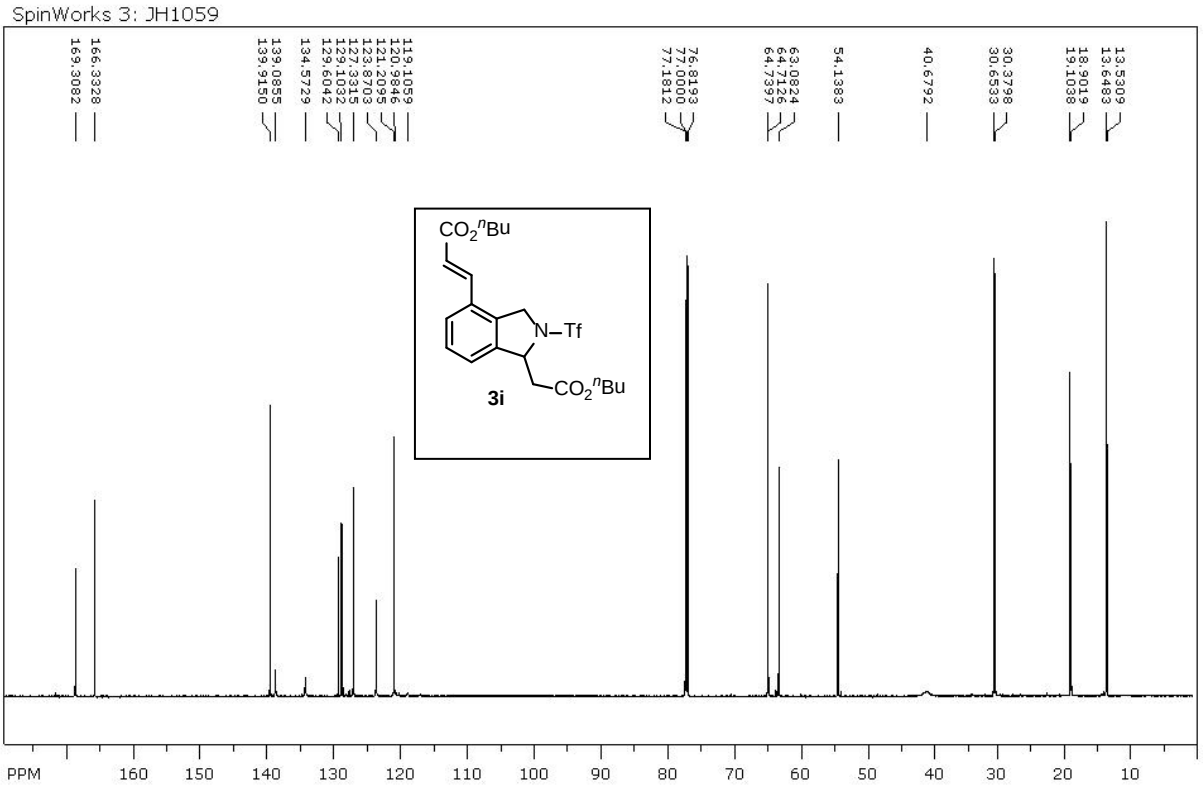



CO2nBu
N–Tf
CO2nBu
3i


SpinWorks 3: JH1059
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139.9150
139.0855
134.5729
129.6042
129.1032
122.3315
123.8703
121.2095
120.9846
119.1059
77.1812
77.0000
76.8193
64.7397
64.7126
63.0824
54.1383
40.6792
30.6533
30.3798
19.1038
18.9019
13.6483
13.5309
CO2nBu
N–Tf
CO2nBu
3i
PPM
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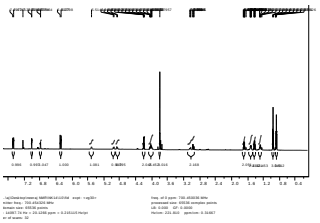
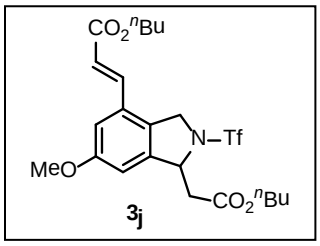
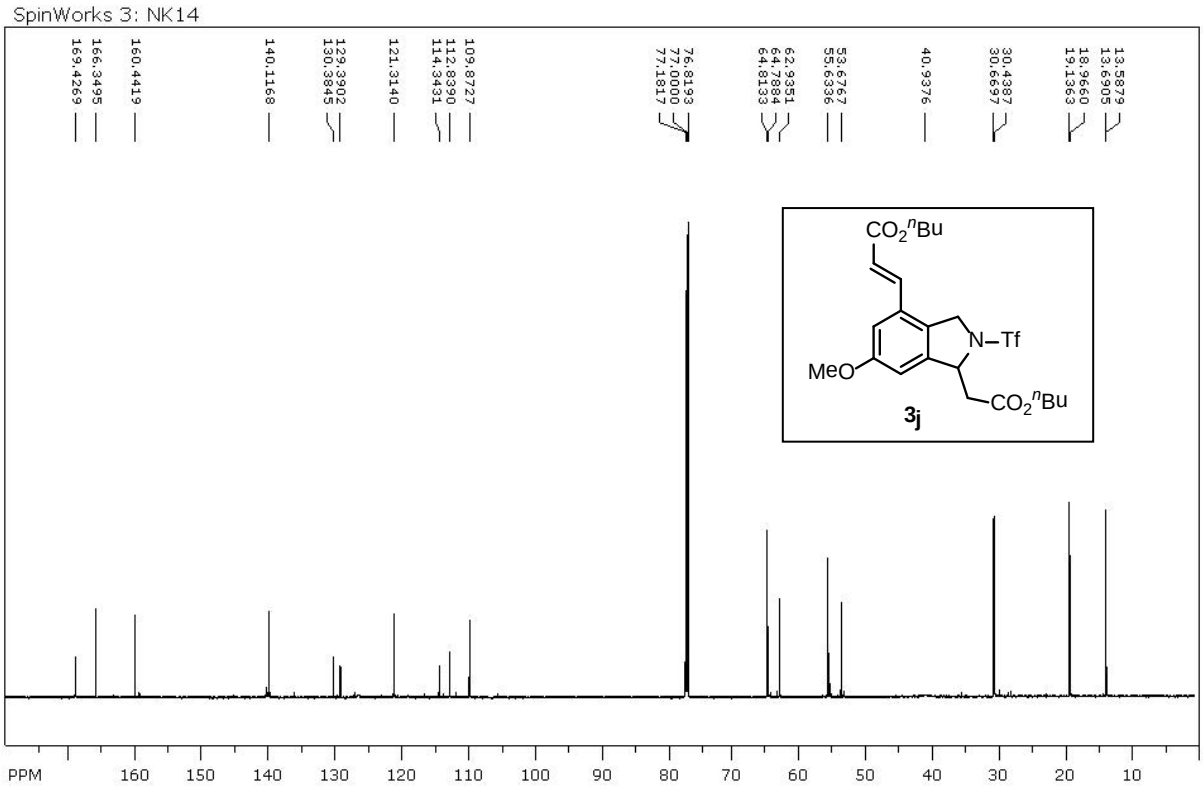



CO2nBu
N–Tf
MeO
CO2nBu
3j


SpinWorks 3: NK14
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129.3902
130.3845
121.3140
112.8390
114.3431
109.8727
76.8193
77.0000
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64.7884
64.8133
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55.6336
53.6767
40.9376
30.4387
30.6697
18.9660
19.1363
13.5879
13.6905
CO2nBu
N–Tf
MeO
CO2nBu
3j
PPM
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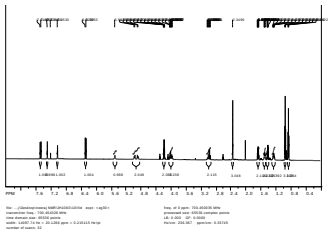
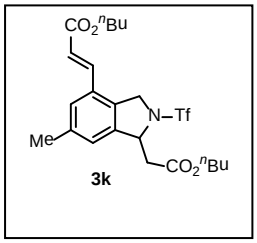
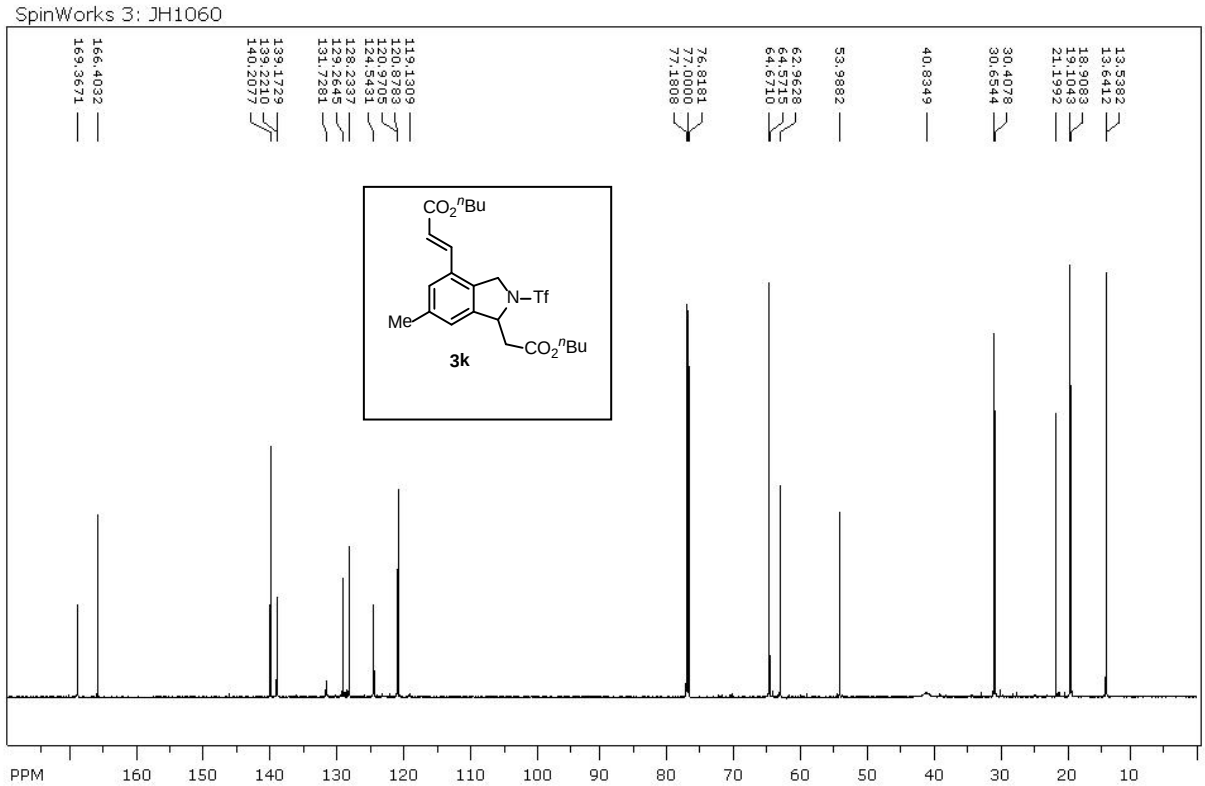
10




CO2nBu
N–Tf
Me
CO2nBu
3k


SpinWorks 3: JH1060
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120.9705
120.8783
119.1309
77.1808
77.0000
76.8181
64.6710
64.5715
62.9628
53.9882
40.8349
30.6544
30.4078
21.1992
19.1043
18.9083
13.6412
13.5382
CO2nBu
N–Tf
Me
CO2nBu
3k
PPM
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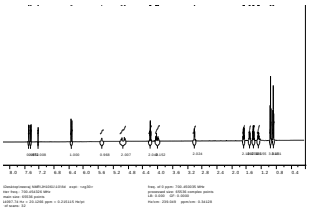
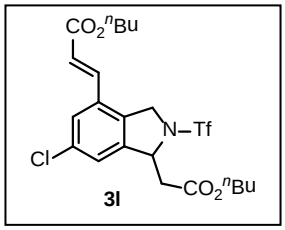
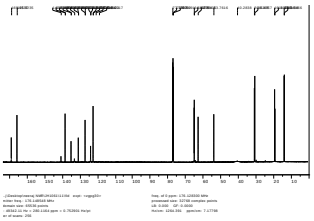
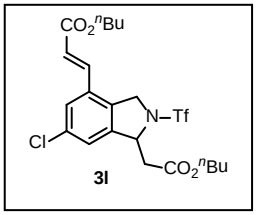




3l





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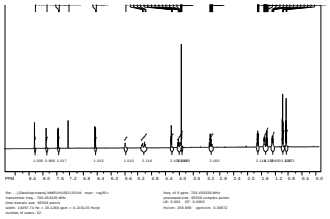
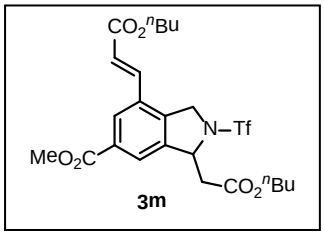
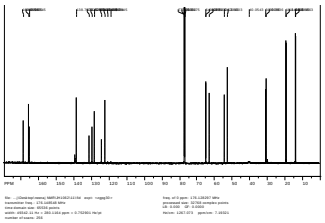
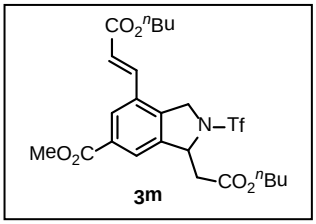




3m





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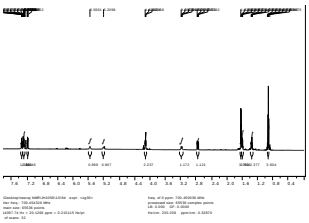

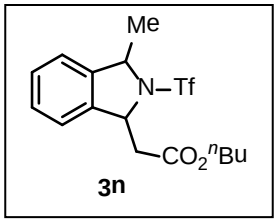

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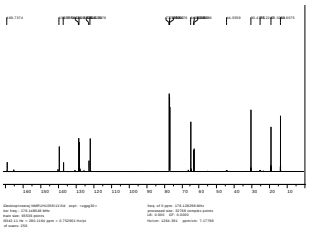

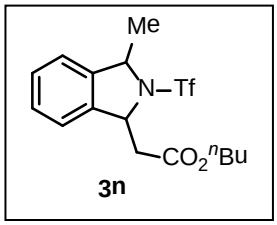

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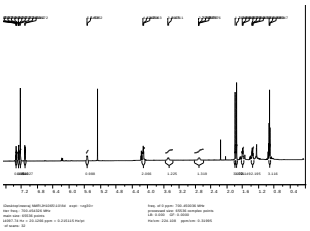
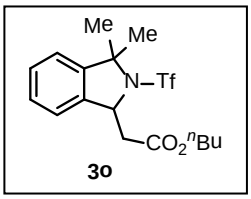
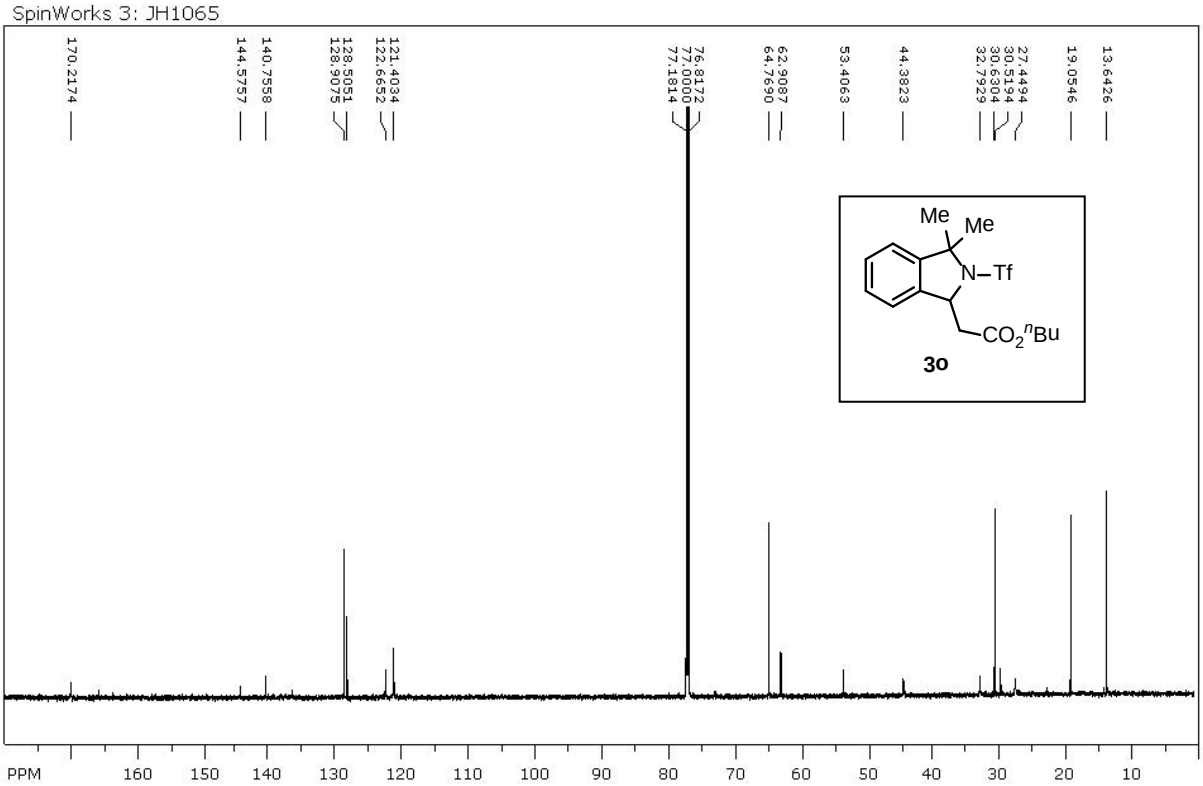



Me
Me
N–Tf
$CO_2{}^nBu$
3o


SpinWorks 3: JH1065
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76.8172
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77.1814
62.9087
64.7690
53.4063
44.3823
27.4494
30.5194
30.6304
32.7929
19.0546
13.6426
Me
Me
N–Tf
$CO_2{}^nBu$
3o
PPM
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150
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120
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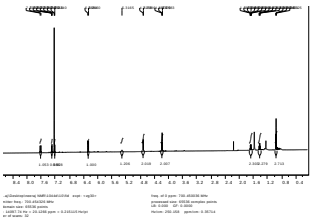
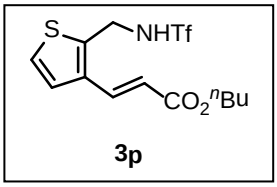
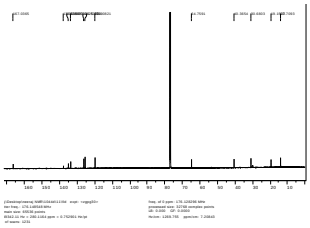
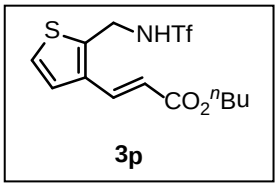


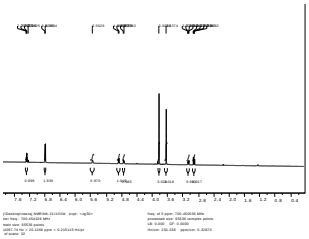


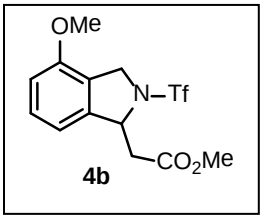
3p



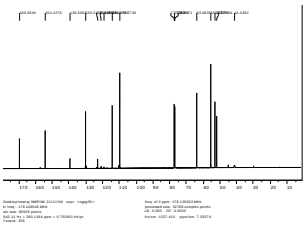


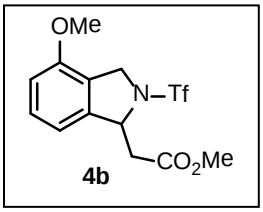
3p



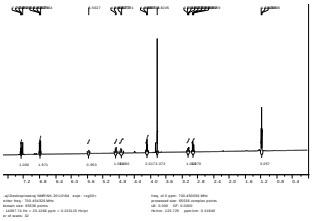


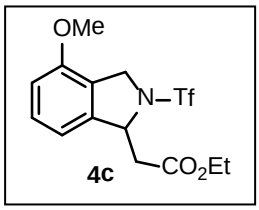
4b

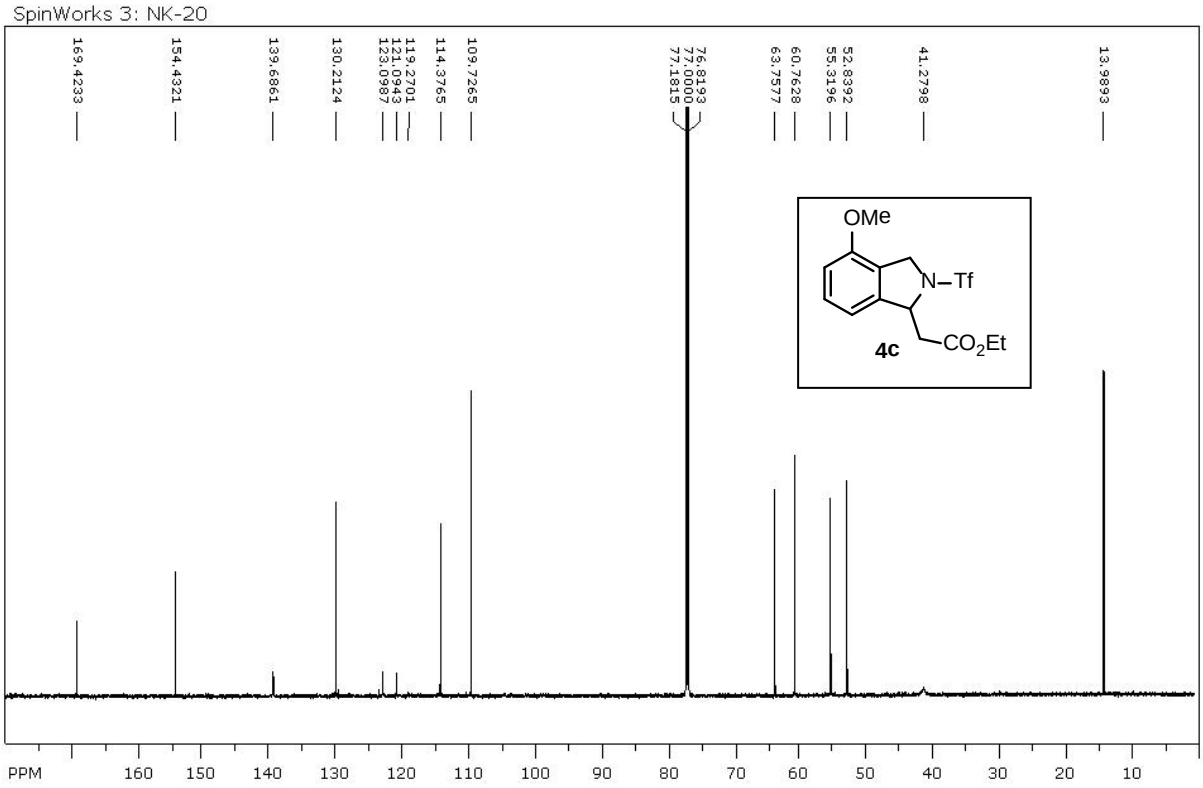




4b




OMe
N–Tf
CO2Et
4c


SpinWorks 3: NK-20
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114.3765
109.7265
77.1815
77.0000
76.8193
63.7577
60.7628
55.3196
52.8392
41.2798
13.9893
OMe
N–Tf
CO2Et
4c
PPM
160
150
140
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120
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100
90
80
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60
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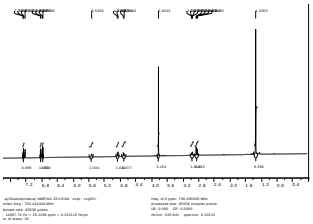
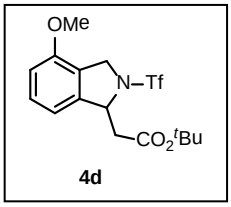
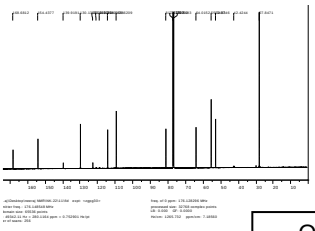
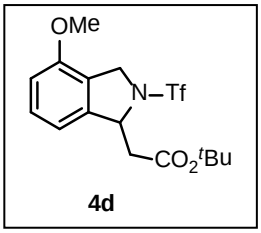
20
10



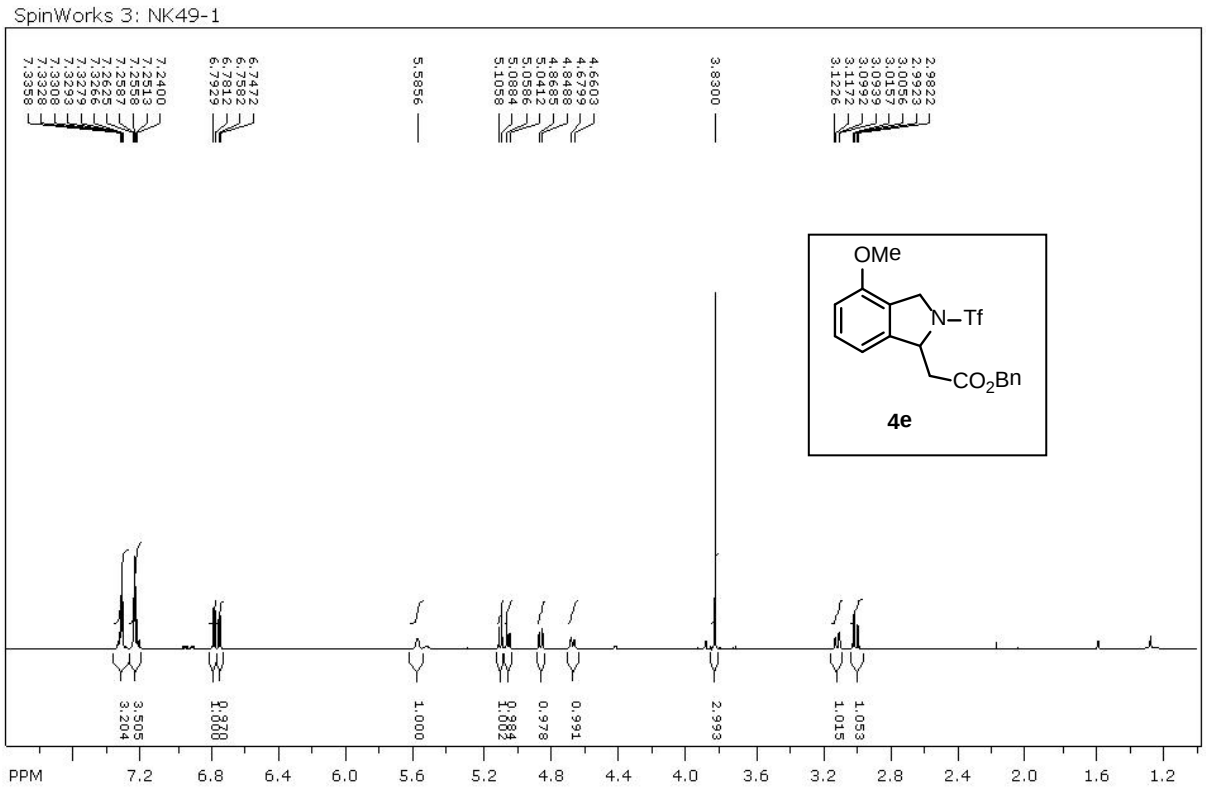


4d





4d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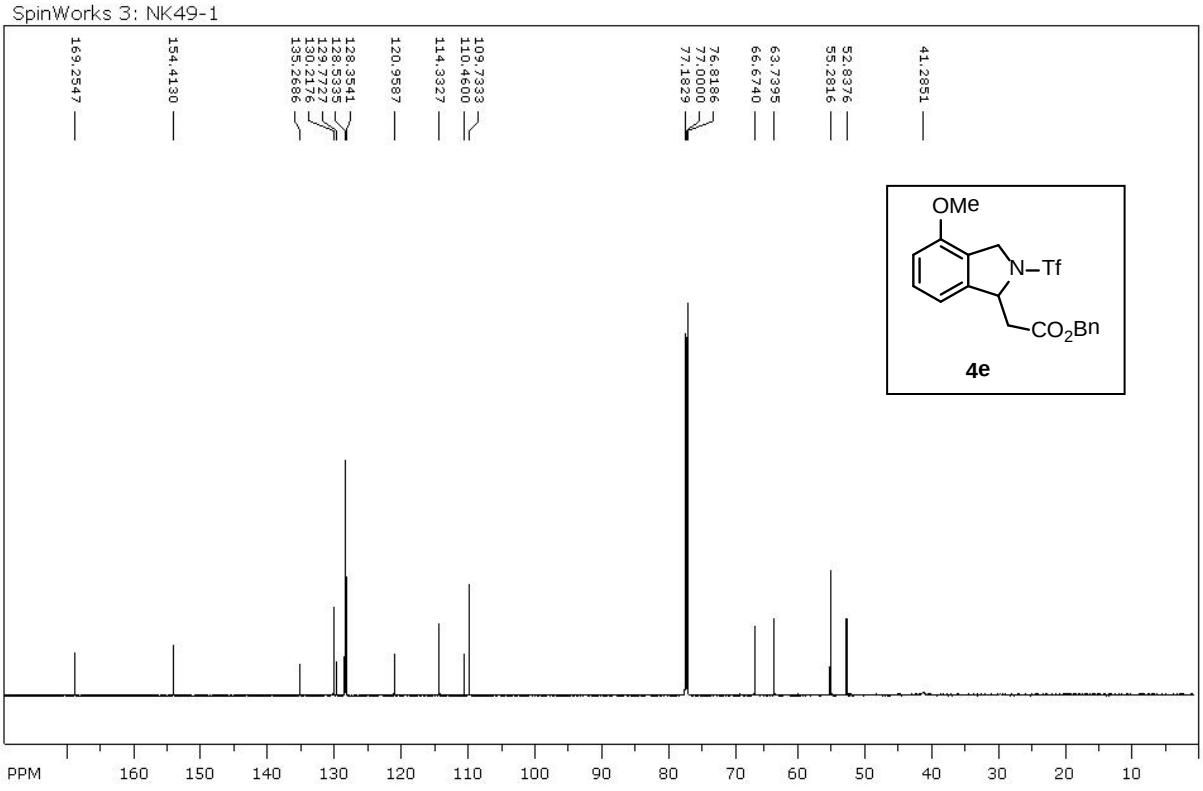
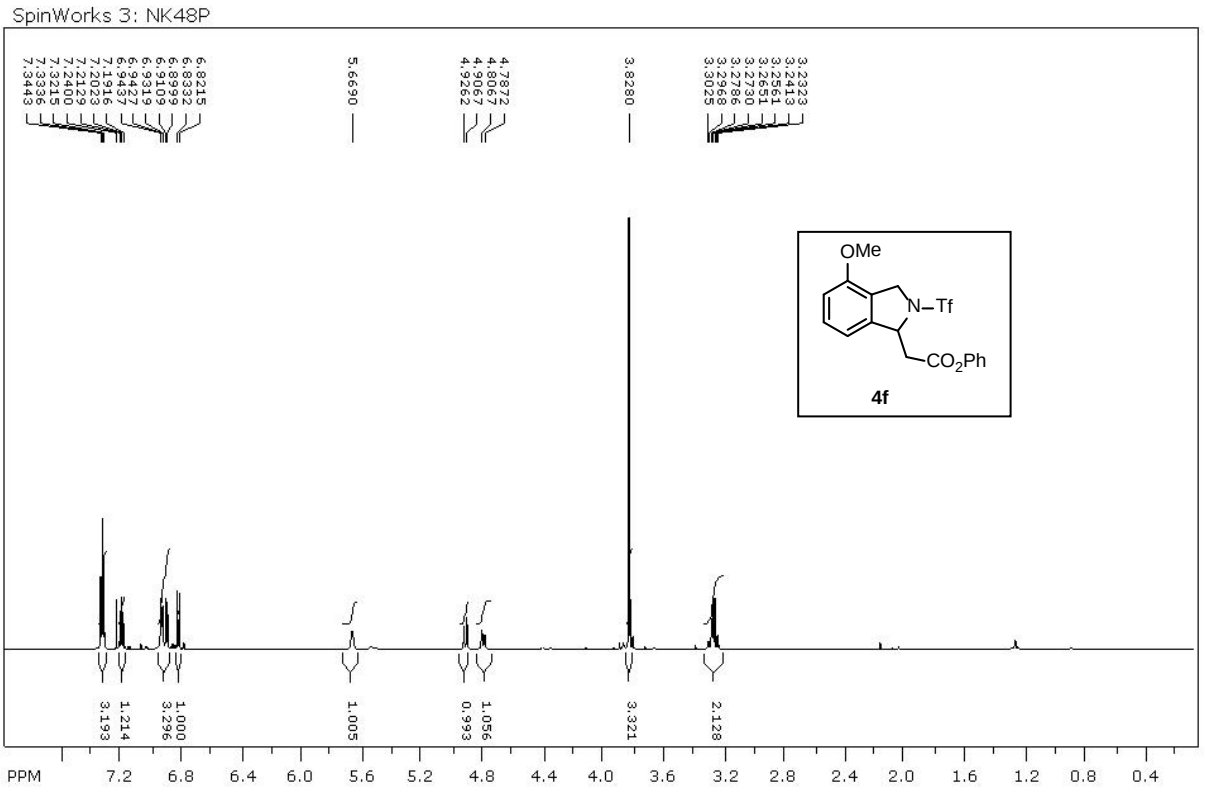
N–Tf
CO2Bn
4e
PPM


SpinWorks 3: NK49-1
OMe
N–Tf
CO2Bn
4e
PPM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7.3215
7.2460
7.2129
7.2015
7.1965
6.9437
6.9427
6.9319
6.9109
6.8999
6.8332
6.8215
5.6690
4.9262
4.9067
4.8067
4.7872
3.8280
3.3025
3.2968
3.2786
3.2730
3.2651
3.2561
3.2413
3.2323
OMe
N–Tf
CO2Ph
4f
3.193
1.214
3.296
1.000
1.005
0.993
1.056
3.321
2.128
PPM
7.2
6.8
6.4
6.0
5.6
5.2
4.8
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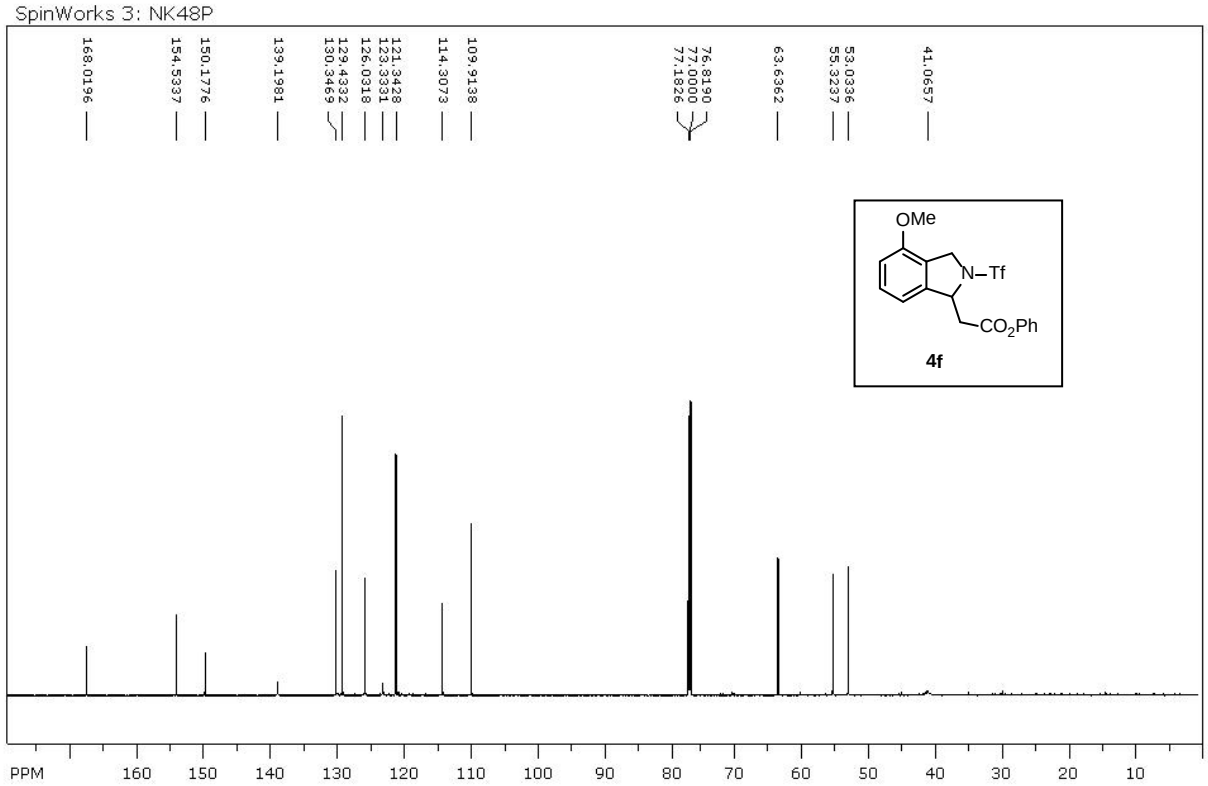
3.2
2.8
2.4
2.0
1.6
1.2
0.8
0.4


SpinWorks 3: NK48P
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150.1776
139.1981
130.3469
129.4332
126.0318
123.3331
121.3428
114.3073
109.9138
77.1826
77.0000
76.8190
63.6362
55.3237
53.0336
41.0657
OMe
N–Tf
CO2Ph
4f
PPM
160
150
140
130
120
110
100
90
80
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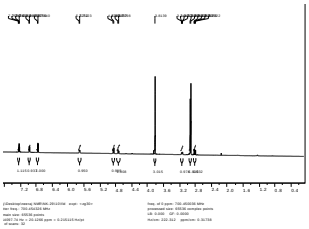
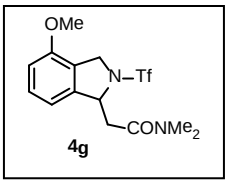
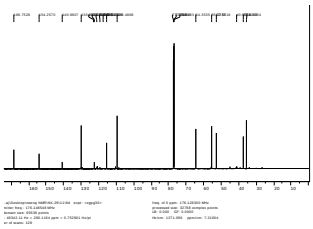
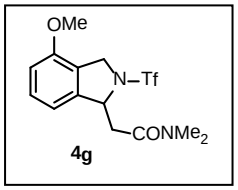
60
50
40
30
20
10



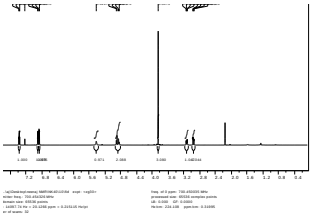


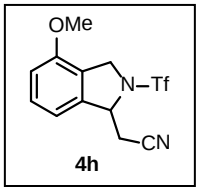
4g

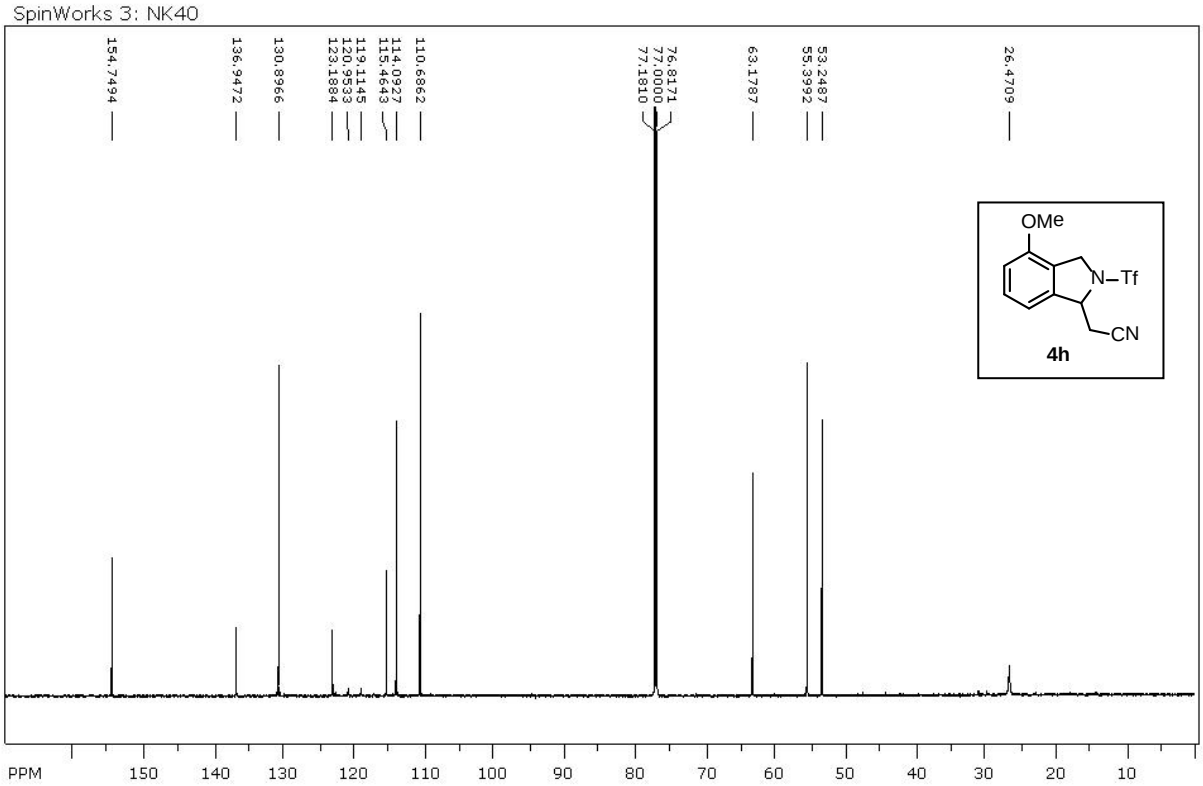




4g




OMe
N–Tf
CN
4h


SpinWorks 3: NK40
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120.9533
119.1145
115.4643
114.0927
110.6862
77.1810
77.0000
76.8171
63.1787
55.3992
53.2487
26.4709
OMe
N–Tf
CN
4h
PPM
150
140
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120
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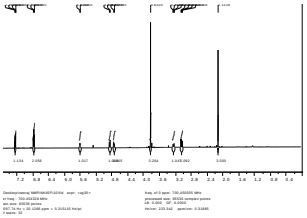
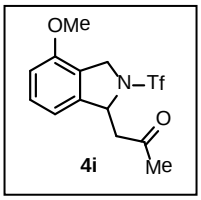
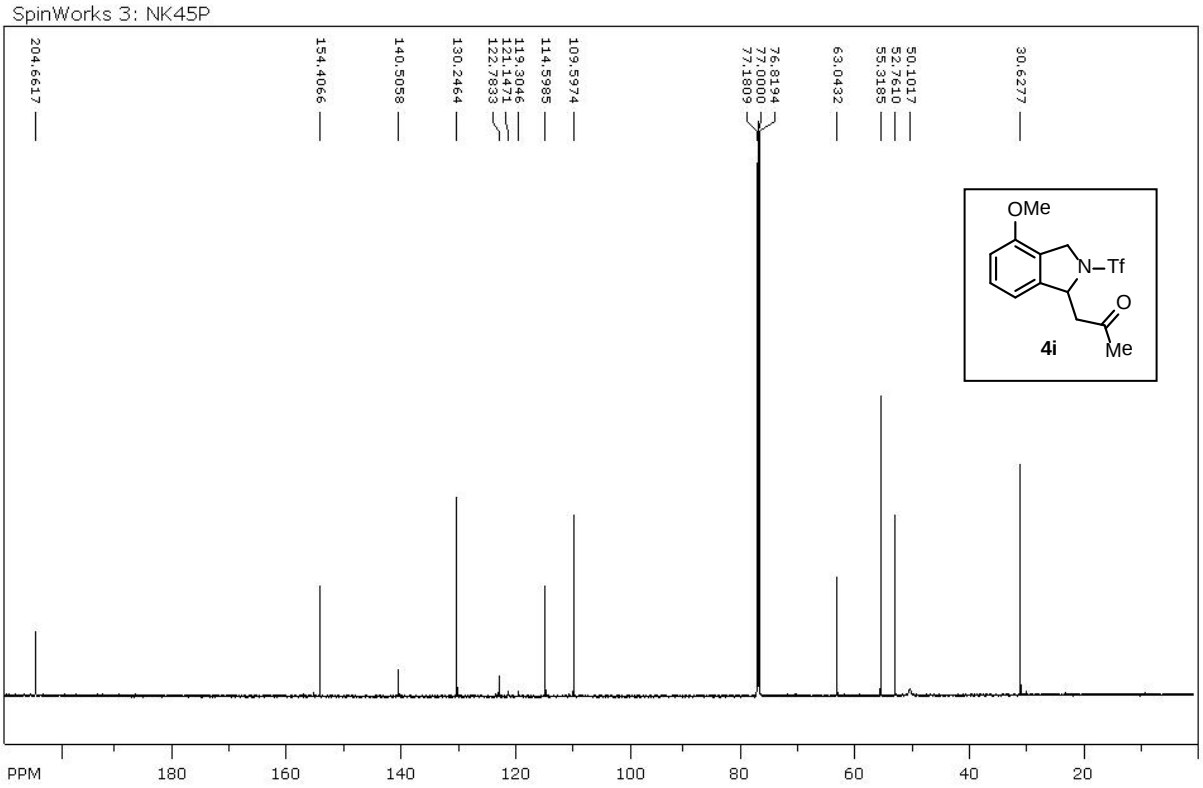
20
10




OMe
N–Tf
O
4i
Me


SpinWorks 3: NK45P
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130.2464
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121.1471
119.3046
114.5985
109.5974
77.1809
77.0000
76.8194
63.0432
55.3185
52.7610
50.1017
30.6277
OMe
N–Tf
O
4i
Me
PPM
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160
140
120
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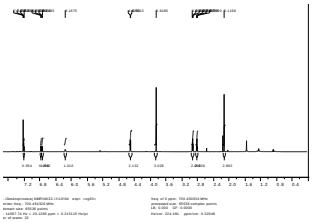
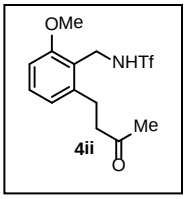
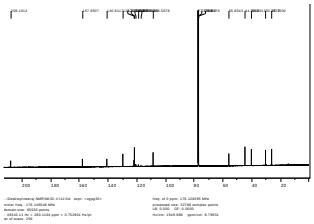
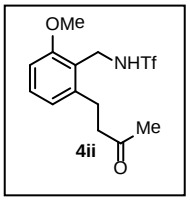
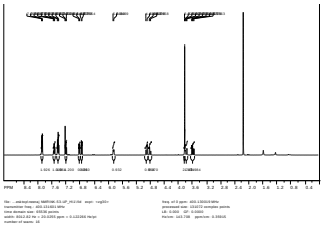
80
60
40
20

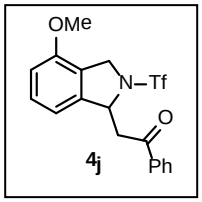


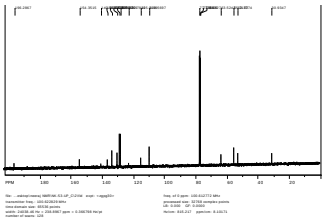

OMe
NHTf
Me
4ii
O

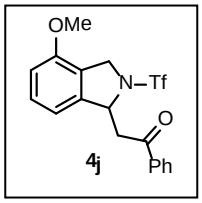


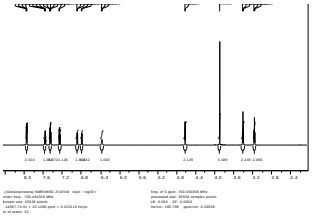

OMe
NHTf
Me
4ii
O

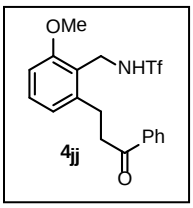


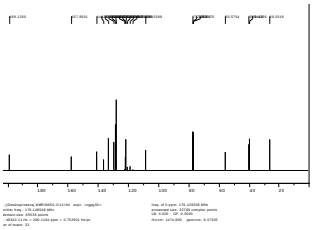

OMe
N–Tf
O
4j
Ph

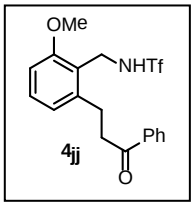


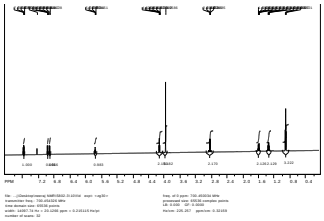

OMe
N–Tf
O
4j
Ph

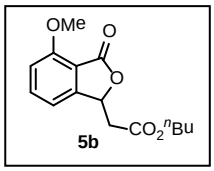



OMe
NHTf
Ph
4jj

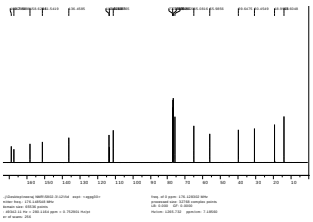


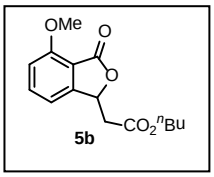

OMe
NHTf
Ph
4jj





5b





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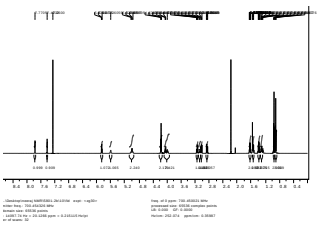

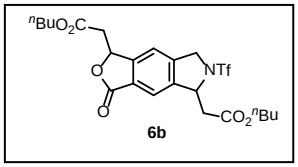

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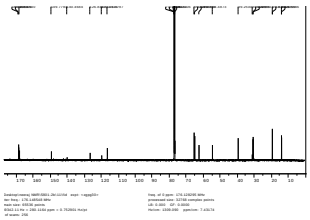

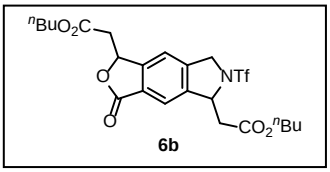

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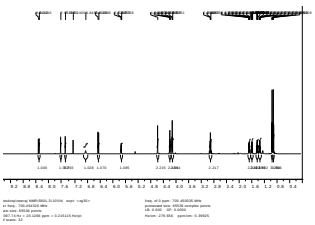

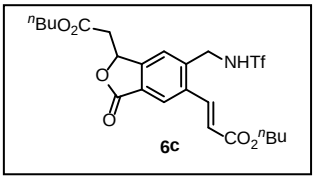
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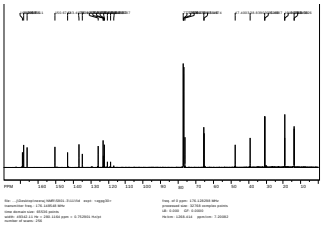
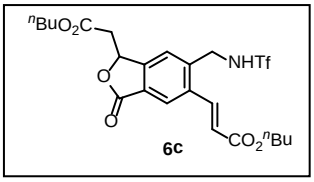
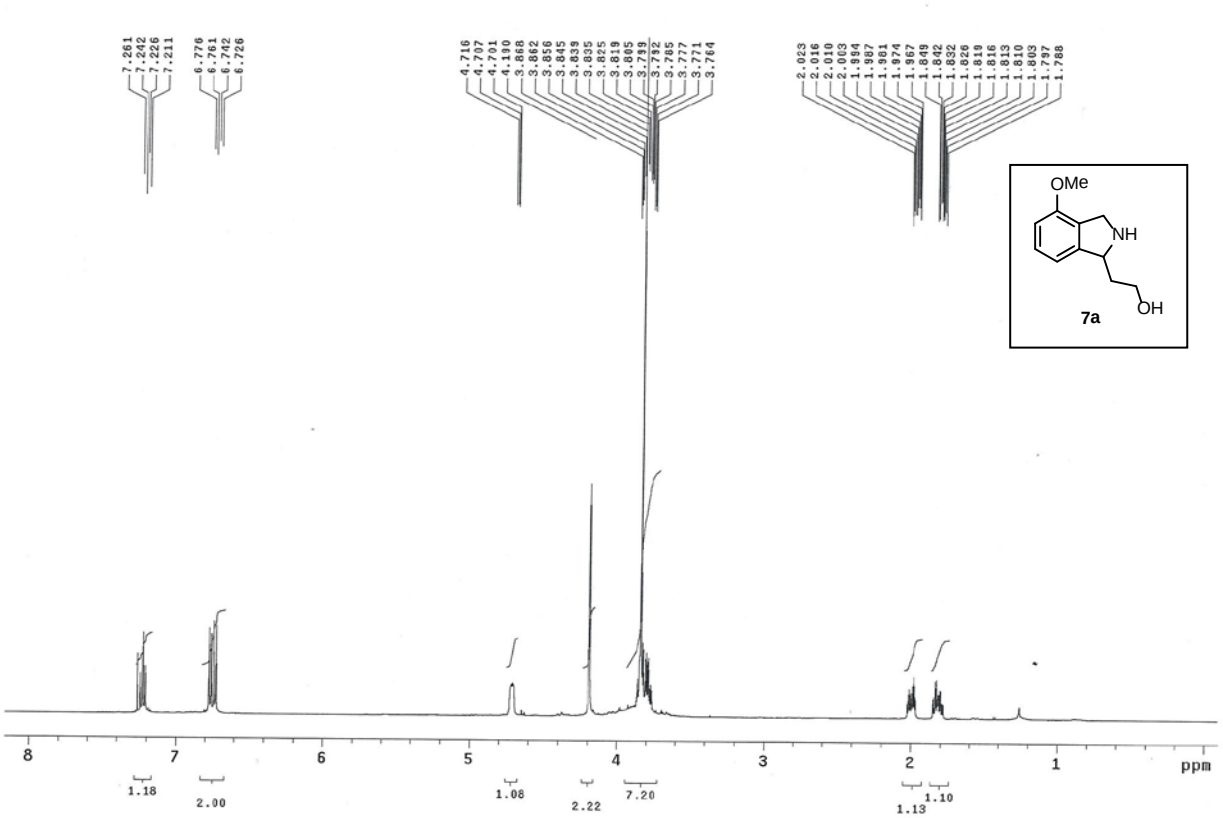
NHTf
O
O
CO$_2$^{n}Bu
6c




^{n}BuO$_2$C
NHTf
O
O
CO$_2$^{n}Bu
6c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4.190
3.868
3.862
3.856
3.845
3.839
3.835
3.825
3.819
3.805
3.792
3.785
3.777
3.771
3.764
2.023
2.016
2.010
2.003
1.994
1.987
1.981
1.974
1.967
1.849
1.842
1.832
1.826
1.819
1.816
1.813
1.810
1.803
1.797
1.788
OMe
NH
OH
7a
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ppm
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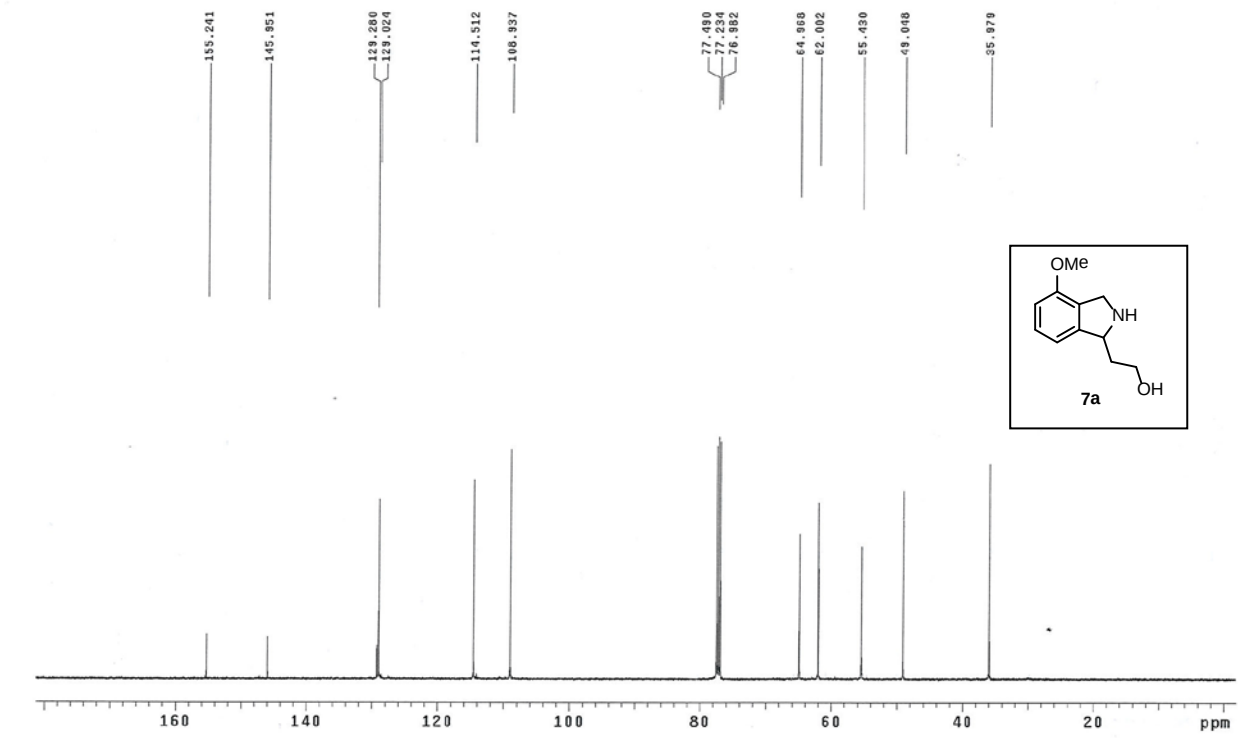
1.08
2.22
7.20
1.13
1.10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129.024
114.512
108.937
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76.982
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62.002
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49.048
35.979
OMe
NH
OH
7a
160
140
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100
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40
20
ppm