Supplementary Information for

Rhodium(I)-Catalyzed C-S Bond Formation via Enantioselective Carbenoid S-H Insertion: Catalytic Asymmetric Synthesis of α-Thioesters

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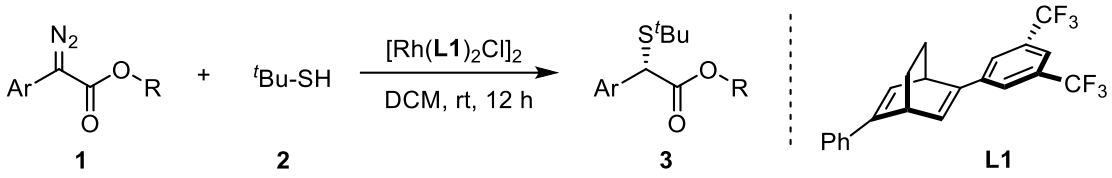
Contents

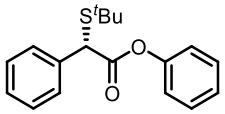
1. General information

All reactions were carried out in dry solvents under argon atmosphere unless otherwise noted. Solvents were dried and distilled before use according to the standard methods. The progress of reactions was monitored by thin layer chromatography to ensure that the reactions had reached completion. NMR spectra were recorded on Varian spectrometers (400 MHz for ^{1}H, and 100 MHz for ^{13}C). Chemical shifts are reported in δ (ppm) referenced to an internal $SiMe_4$ standard for ^{1}H NMR and chloroform-*d* (δ 77.16) for ^{13}C NMR. MS and HRMS were measured in EI or ESI mode, and the mass analyzer type used for HRMS was Magnetic Sector. Chiral HPLC was performed on a SIMADZU 2030C instrument by using Daicel chiral columns with *n*-hexane/*i*-propanol as the eluent at 220 nm. Diazo substrates were prepared according to the literature procedure.

2. General procedure for Rh-catalyzed S-H insertion reaction



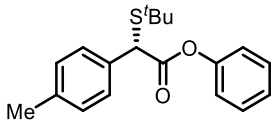
A solution of catalyst [Rh(**L1**)Cl]$_2$ (2.5 mol%, 2.6 mg, 0.005 mmol of [Rh]) in 1 mL of DCM was added into substrate **1** (0.15 mmol), **2** (0.1 mmol) at ambient temperature under argon. After being stirred at ambient temperature for 12 h, the solvent was evaporated in vacuo. The desired product **3** was afforded after purification of the residue by column chromatography.



phenyl (*S*)-2-(*tert*-butylthio)-2-phenylacetate (**3a**).

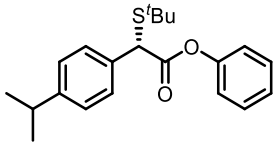
Yellow solid (90% yield); $[\alpha]_D^{25}$ +27.0 (*c* 1.2 $CHCl_3$) for 70% ee; ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.57 (d, *J* = 7.5 Hz, 2H), 7.35 (m, *J* = 15.8, 8.1 Hz, 5H), 7.29 - 7.03 (m, 2H),

7.03 - 6.99 (m, 1H), 4.80 (s, 1H), 1.42 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.7, 150.9, 137.0, 129.5, 129.0, 128.6, 128.2, 126.1, 121.3, 50.2, 45.2, 31.2; HRMS (EI) for $C_{18}H_{20}O_2S$ $[M]^+$: calcd. 300.1179, found 300.1185.



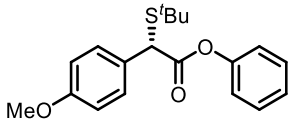
phenyl (*S*)-2-(*tert*-butylthio)-2-(*p*-tolyl)acetate (**3b**).

Yellow solid (94% yield); $[\alpha]_D^{25}$ +35.9 (*c* 1.0 $CHCl_3$) for 61% ee; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, *J* = 7.9 Hz, 2H), 7.35 (d, *J* = 7.9 Hz, 2H), 7.19 (t, *J* = 7.8 Hz, 3H), 7.04 (d, *J* = 7.8 Hz, 2H), 4.78 (s, 1H), 2.35 (s, 3H), 1.42 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.9, 151.0, 138.1, 134.0, 129.7, 129.5, 128.4, 126.1, 121.4, 49.9, 45.2, 31.2, 21.3; HRMS (EI) for $C_{19}H_{22}O_2S$ $[M]^+$: calcd. 314.1335, found 314.1341.



phenyl (*S*)-2-(tert-butylthio)-2-(4-isopropylphenyl)acetate (**3c**)

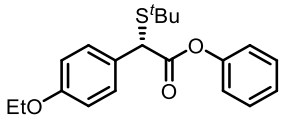
Yellow solid (95% yield); $[\alpha]_D^{25}$ +17.0 (*c* 0.9 $CHCl_3$) for 77% ee; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, *J* = 8.0 Hz, 2H), 7.34 (t, *J* = 7.8 Hz, 2H), 7.19 - 7.23 (m, 3H), 7.04 - 7.07 (m, 2H), 4.78 (s, 1H), 2.87 - 2.94 (m, 1H),1.43 (s, 9H), 1.24 (d, *J* = 6.8 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.0, 150.9, 148.9, 134.1, 129.5, 128.4, 127.0, 126.1, 121.4, 49.9, 45.2, 34.0, 31.2, 24.0; HRMS (ESI) for $C_{21}H_{26}NaO_2S$ $[M+Na]^+$: calcd. 365.1546, found 365.1545.



phenyl (*S*)-2-(*tert*-butylthio)-2-(4-methoxyphenyl)acetate (**3d**).

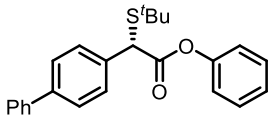
Yellow solid (89% yield); $[\alpha]_D^{25}$ +24.2 (*c* 1.0 $CHCl_3$) for 82% ee; ^{1}H NMR (400 MHz,

$CDCl_3$) δ 7.49 (d, J = 6.6 Hz, 2H), 7.35 (t, J = 6.9 Hz, 2H), 7.21 (t, J = 6.9 Hz, 1H), 7.04 (d, J = 8.2 Hz, 2H), 6.90 (d, J = 6.7 Hz, 2H), 4.77 (s, 1H), 3.81 (s, 3H), 1.42 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.9, 159.6, 151.0, 129.7, 129.5, 129.0, 126.1, 121.4, 114.4, 55.4, 49.5, 45.1, 31.2; HRMS (EI) for $C_{19}H_{22}O_3S$ $[M]^+$ calcd. 330.1284, found 330.1291.



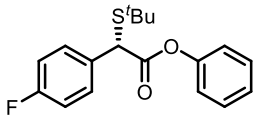
phenyl (*S*)-2-(tert-butylthio)-2-(4-ethoxyphenyl)acetate (**3e**)

Yellow solid (90% yield); $[\alpha]_D^{25}$ +36.7 (*c* 0.98 $CHCl_3$) for 79% ee; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, J = 8.8 Hz, 2H), 7.34 (t, J = 8.0 Hz, 2H), 7.20 (t, J = 7.8 Hz, 2H), 7.04 (d, J = 7.8 Hz, 2H), 6.88 (d, J = 8.8 Hz, 2H), 4.76 (s, 1H), 4.03 (dd, J = 6.8, 7.2 Hz, 2H), 1.41 (s, 9H), 1.39 - 1.42 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.9, 158.9, 151.0, 129.7, 129.5, 128.8, 126.0, 121.4, 114.9, 63.6, 49.6, 45.1, 31.2, 15.0; HRMS (ESI) for $C_{20}H_{24}NaO_3S$ $[M+Na]^+$: calcd. 367.1338, found 367.1341.



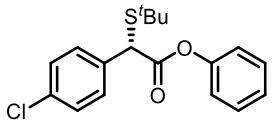
phenyl (*S*)-2-([1,1'-biphenyl]-4-yl)-2-(tert-butylthio)acetate (**3f**)

Yellow solid (79% yield); $[\alpha]_D^{25}$ +27.0 (*c* 0.96 $CHCl_3$) for 63% ee; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, J = 8.4, Hz, 2H), 7.58 - 7.60 (m, 4H), 7.44 (t, J = 7.6, Hz, 2H), 7.34 - 7.38 (m, 3H), 7.22 (t, J = 7.8, Hz, 1H), 7.07 (d, J = 8.0, Hz, 2H), 4.84 (s, 1H), 1.45 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.8, 151.0, 141.2, 140.7, 136.0, 129.6, 129.0, 128.9, 127.7, 127.6, 127.3, 126.2, 121.4, 49.9, 45.4, 31.2; HRMS (ESI) for $C_{24}H_{24}NaO_2S$ $[M+Na]^+$: calcd. 399.1389, found 399.1390.



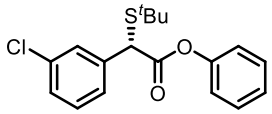
phenyl (*S*)-2-(*tert*-butylthio)-2-(4-fluorophenyl)acetate (**3g**).

Yellow solid (85% yield); $[\alpha]_D^{25}$ +24.9 (*c* 0.9 $CHCl_3$) for 68% ee; ^1H NMR (400 MHz, $CDCl_3$) δ 7.55 (dd, *J* = 8.7, 5.3 Hz, 2H), 7.42 - 7.32 (m, 2H), 7.22 (s, 1H), 7.11 - 7.01 (m, 4H), 4.78 (s, 1H), 1.41 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.6, 162.8 (d, *J* = 245.8 Hz), 150.9, 133.0, 130.4, 130.3, 130.0, 126.2, 121.3, 116.0, 115.8, 49.4, 45.4, 31.2; ^{19}F NMR (400 MHz, $CDCl_3$) δ -113.9; HRMS (EI) for $C_{18}H_{19}FO_2S$ $[M]^+$: calcd. 318.1084, found 318.1091.



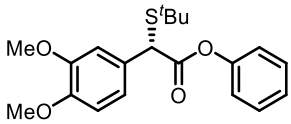
phenyl (*S*)-2-(*tert*-butylthio)-2-(4-chlorophenyl)acetate (**3h**).

Yellow solid (88% yield); $[\alpha]_D^{25}$ +22.2 (*c* 1.1 $CHCl_3$) for 46% ee; ^1H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 8.5 Hz, 2H), 7.35 (d, *J* = 8.4 Hz, 4H), 7.23 (d, *J* = 7.4 Hz, 1H), 7.04 (dd, *J* = 8.6, 1.2 Hz, 2H), 4.76 (s, 1H), 1.41 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.3, 150.8, 135.8, 134.2, 130.0, 129.6, 129.1, 126.2, 121.3, 49.5, 45.5, 31.2; HRMS (EI) for $C_{18}H_{19}ClO_2S$ $[M]^+$: calcd. 334.0789, found 334.0795.



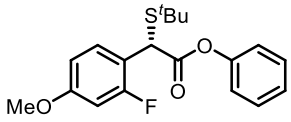
phenyl (*S*)-2-(*tert*-butylthio)-2-(3-chlorophenyl)acetate (**3i**).

Yellow solid (85% yield); $[\alpha]_D^{25}$ +9.4 (*c* 2.2 $CHCl_3$) for 40% ee; ^1H NMR (400 MHz, $CDCl_3$) δ 7.59 (s, 1H), 7.46 (d, *J* = 3.8 Hz, 1H), 7.36 (t, *J* = 7.8 Hz, 2H), 7.31 (d, *J* = 5.0 Hz, 2H), 7.23 (t, *J* = 7.4 Hz, 1H), 7.06 (d, *J* = 7.6 Hz, 2H), 4.75 (s, 1H), 1.42 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.2, 150.8, 139.1, 134.7, 130.1, 129.6, 128.8, 128.5, 126.8, 126.13, 121.3, 49.7, 45.54, 31.1. HRMS (EI) for $C_{18}H_{19}ClO_2S$ $[M^+]$ calcd. 334.0789, found 334.0793.



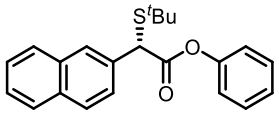
phenyl (*S*)-2-(*tert*-butylthio)-2-(3,4-dimethoxyphenyl)acetate (**3j**).

Yellow solid (98% yield); $[\alpha]_D^{25}$ +46.1 (*c* 1.2 $CHCl_3$) for 71% ee; ^1H NMR (400 MHz, $CDCl_3$) δ 7.35 (t, *J* = 7.9 Hz, 2H), 7.21 (t, *J* = 7.4 Hz, 1H), 7.14 (d, *J* = 2.1 Hz, 1H), 7.09 (dd, *J* = 8.3, 2.1 Hz, 1H), 7.07 - 7.02 (m, 2H), 6.84 (d, *J* = 8.3 Hz, 1H), 4.77 (s, 1H), 3.90 (s, 3H), 3.87 (s, 3H), 1.42 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.8, 150.9, 149.3, 149.0, 129.5, 129.2, 126.1, 121.3, 120.8, 111.4, 111.1, 56.0, 56.0, 49.8, 45.1, 31.1; HRMS (EI) for $C_{20}H_{24}O_4S$ $[M]^+$: calcd. 360.1390, found 360.1396.



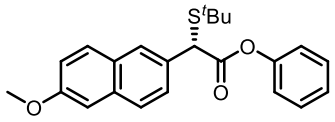
phenyl (*S*)-2-(tert-butylthio)-2-(2-fluoro-4-methoxyphenyl)acetate (**3k**)

Yellow solid (87% yield); $[\alpha]_D^{25}$ +11.3 (*c* 1.05 $CHCl_3$) for 60% ee; ^1H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.8 Hz, 1H), 7.35 (t, *J* = 8.4 Hz, 2H), 7.22 (t, *J* = 7.6 Hz, 1H), 7.08 (d, *J* = 7.8 Hz, 2H), 6.73 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.63 (dd, *J* = 7.8, 2.4 Hz, 1H), 5.07 (s, 1H), 3.80 (s, 1H), 1.41 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.3, 159.8 (d, *J* = 181.8 Hz) 151.0, 130.9, 130.9, 129.5, 126.1, 121.4, 116.6, 110.7, 101.7, 101.4, 55.8, 45.4, 41.6, 31.0; ^{19}F NMR (400 MHz, $CDCl_3$) δ -115.6; HRMS (ESI) for $C_{19}H_{21}FNaO_3S$ $[M+Na]^+$: calcd. 371.1088, found 371.1086.



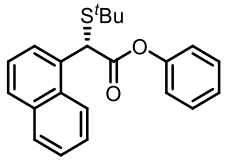
phenyl (*S*)-2-(*tert*-butylthio)-2-(naphthalen-2-yl)acetate (**3l**).

Yellow solid (90% yield); $[\alpha]_D^{25}$ +21.4 (*c* 1.0 $CHCl_3$) for 50% ee; ^1H NMR (400 MHz, $CDCl_3$) δ 8.02 (s, 1H), 7.88 - 7.79 (m, 3H), 7.71 (dd, *J* = 8.5, 1.7 Hz, 1H), 7.50 - 7.43 (m, 2H), 7.32 (t, *J* = 7.9 Hz, 2H), 7.18 (t, *J* = 7.4 Hz, 1H), 7.04 (d, *J* = 7.6 Hz, 2H), 4.98 (s, 1H), 1.43 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.6, 150.9, 134.4, 133.4, 133.1, 129.5, 128.8, 128.1, 127.8, 127.4, 126.5, 126.5, 126.4, 126.1, 121.3, 50.4, 45.3, 31.2; HRMS (EI) for $C_{22}H_{22}O_2S$ $[M]^+$: calcd. 350.1335, found 350.1340.



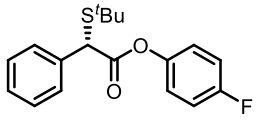
phenyl (*S*)-2-(tert-butylthio)-2-(6-methoxynaphthalen-2-yl)acetate (**3m**)

Yellow solid (93% yield); $[\alpha]_D^{25}$ +53.7 (*c* 0.9 $CHCl_3$) for 78% ee; ^1H NMR (400 MHz, $CDCl_3$) δ 7.93 (s, 1H), 7.74 (t, *J* = 7.2 Hz, 2H), 7.65 (dd, *J* = 8.8, 1.6 Hz, 2H), 7.34 (t, *J* = 6.0 Hz, 2H), 7.12 -7.24 (m, 3H), 7.03 (d, *J* = 8.4 Hz, 2H), 4.94 (s, 1H), 3.91 (s, 1H), 1.43 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.8, 158.2, 150.9, 134.4, 132.0, 129.7, 129.5, 127.7, 127.3, 126.9, 126.1, 121.4, 119.3, 105.8, 55.5, 50.3, 45.3, 31.2; HRMS (ESI) for $C_{23}H_{24}NaO_3S$ $[M+Na]^+$: calcd. 403.1338, found 403.1337.



phenyl (*S*)-2-(tert-butylthio)-2-(naphthalen-1-yl)acetate (**3n**)

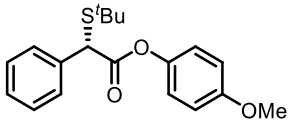
Yellow solid (79% yield); $[\alpha]_D^{25}$ +6.7 (*c* 0.95 $CHCl_3$) for 51% ee; ^1H NMR (600 MHz, $CDCl_3$) δ 8.27 (d, *J* = 6.8 Hz, 1H), 7.93 (d, *J* = 7.2 Hz, 1H), 7.90 (d, *J* = 7.8 Hz, 1H), 7.84 (d, *J* = 7.8 Hz, 1H), 7.61 (t, *J* = 7.2 Hz, 1H), 7.49 - 7.54 (m, 2H), 7.31 (t, *J* = 7.8 Hz, 2H), 7.18 (t, *J* = 7.2 Hz, 1H), 6.98 (d, *J* = 7.2 Hz, 1H), 5.55 (s, 1 H), 1.47 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.9, 151.1, 134.2, 132.6, 131.1, 129.5, 129.3, 129.0, 127.2, 126.9, 125.8, 123.0, 121.3 121.3, 46.6, 45.4, 31.2; HRMS (ESI) for $C_{22}H_{22}NaO_2S$ $[M+Na]^+$: calcd. 373.1233, found 373.1232.



4-fluorophenyl (*S*)-2-(*tert*-butylthio)-2-phenylacetate (**3o**).

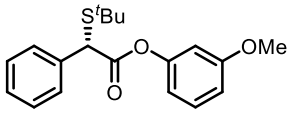
Yellow solid (93% yield); $[\alpha]_D^{25}$ +20.4 (*c* 3.9 $CHCl_3$) for 54% ee; ^1H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 7.7 Hz, 2H), 7.40 - 7.30 (m, 3H), 7.06 - 6.99 (m, 4H), 4.79 (s, 1H), 1.42 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.8, 160.4 (d, *J* = 243 Hz), 146.7, 136.9, 129.0, 128.5, 128.3, 122.8 (d, *J* = 9 Hz), 116.2 (d, *J* = 23.3 Hz), 50.1, 45.3, 31.1; ^{19}F NMR (400 MHz, $CDCl_3$) δ -116.7; HRMS (EI) for $C_{18}H_{19}FO_2S$ $[M]^+$: calcd.

318.1084, found 318.1091



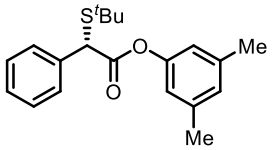
4-methoxyphenyl (*S*)-2-(*tert*-butylthio)-2-phenylacetate (**3p**).

Yellow solid (94% yield); $[\alpha]_D^{25}$ +24.1 (*c* 1.0 $CHCl_3$) for 51% ee; ^1H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, J = 7.6 Hz, 2H), 7.39 - 7.31 (m, 3H), 6.96 (d, J = 7.2 Hz, 2H), 6.85 (d, J = 7.2 Hz, 2H), 4.79 (s, 1H), 3.78 (s, 3H), 1.42 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.0, 157.5, 144.4, 137.1, 128.9, 128.6, 128.2, 122.1, 114.5, 55.7, 50.2, 45.2, 31.2; HRMS (EI) for $C_{19}H_{22}O_3S$ $[M]^+$: calcd. 330.1284, found 330.1291.



3-methoxyphenyl (*S*)-2-(*tert*-butylthio)-2-phenylacetate (**3q**).

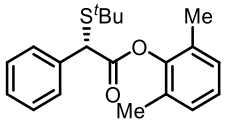
Yellow solid (83% yield); $[\alpha]_D^{25}$ +18.9 (*c* 3.3 $CHCl_3$) for 68% ee; ^1H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, J = 7.9 Hz, 2H), 7.37 (t, J = 6.8 Hz, 2H), 7.32 (d, J = 6.9 Hz, 1H), 7.26 - 7.21 (m, 1H), 6.76 (d, J = 8.3 Hz, 1H), 6.65 (d, J = 8.0 Hz, 1H), 6.60 (s, 1H), 4.79 (s, 1H), 3.77 (s, 3H), 1.42 (s, 9H); 13C NMR (101 MHz, $CDCl_3$) δ 170.6, 160.6, 151.9, 137.0, 129.9, 129.0, 128.6, 128.3, 113.5, 111.9, 107.5, 55.6, 50.2, 45.2, 31.2; HRMS (EI) calcd. for $C_{19}H_{22}O_3S$ $[M]^+$: 330.1284, found 330.1290.



phenyl (*S*)-2-(4-bromophenyl)-2-(*tert*-butylthio)acetate (**3r**).

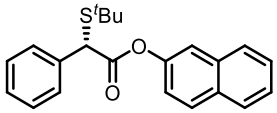
Yellow solid (78% yield); $[\alpha]_D^{25}$ +23.1 (*c* 1.6 $CHCl_3$) for 74% ee; ^1H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, J = 7.1 Hz, 2H), 7.41 - 7.28 (m, 3H), 6.84 (s, 1H), 6.65 (s, 2H), 4.78 (s, 1H), 2.29 (s, 6H), 1.42 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.9, 150.8, 139.4, 137.2, 128.9, 128.6, 127.8, 118.8, 50.2, 45.2, 31.2, 21.3; HRMS (ESI) for $C_{20}H_{25}O_2S$

$[M+H]^+$: calcd. 329.1570, found 329.1564.



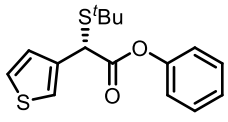
2,6-dimethylphenyl (*S*)-2-(*tert*-butylthio)-2-phenylacetate (**3s**).

Yellow solid (59% yield); $[\alpha]_D^{25}$ -20.6 (*c* 1.6 $CHCl_3$) for 30% ee; ^1H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, J = 7.2 Hz, 2H), 7.42 - 7.29 (m, 3H), 6.99 (s, 3H), 4.83 (d, J = 1.8 Hz, 1H), 1.94 (s, 6H), 1.39 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.3, 148.0, 137.9, 130.5, 128.8, 128.7, 128.2, 126.0, 50.5, 45.2, 31.3, 16.2; HRMS (EI) for $C_{20}H_{24}O_2S$ $[M]^+$: calcd. 328.1492, found 328.1497.



naphthalen-2-yl (*S*)-2-(*tert*-butylthio)-2-phenylacetate (**3t**).

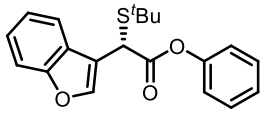
Yellow solid (99% yield); $[\alpha]_D^{25}$ +21.5 (*c* 1.0 $CHCl_3$) for 59% ee; ^1H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, J = 8.8 Hz, 2H), 7.80-7.75 (m, 1H), 7.62 (d, J = 7.3 Hz, 2H), 7.53 (d, J = 2.0 Hz, 1H), 7.49 - 7.45 (m, 2H), 7.41 (t, J = 7.4 Hz, 2H), 7.35 (d, J = 7.1 Hz, 1H), 7.18 (dd, J = 8.9, 2.2 Hz, 1H), 4.87 (s, 1H), 1.46 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.9, 148.6, 137.1, 133.8, 131.7, 129.6, 129.0, 128.6, 128.3, 127.9, 127.8, 126.7, 125.9, 120.8, 118.4, 50.3, 45.3, 31.2; HRMS (EI) calcd. for $C_{22}H_{22}O_2S$ $[M]^+$: 350.1335, found 350.1340.



phenyl (*S*)-2-(tert-butylthio)-2-(thiophen-3-yl)acetate (**3u**)

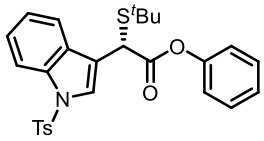
Yellow oil (75% yield); $[\alpha]_D^{25}$ +10.5 (*c* 1.0 $CHCl_3$) for 40% ee; ^1H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, J = 2.4 Hz, 1H), 7.40 (t, J = 7.6 Hz, 2H), 7.36 (dd, J = 7.8 Hz, dd, J = 2.8 Hz, 1H), 7.28 (d, J = 6.2 Hz, 1H), 7.25(t, J = 7.8 Hz, 1H), 7.10 (d, J = 7.6 Hz, 1H), 4.93 (d, J = 1.8 Hz, 1H), 1.46 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.6, 150.9,

136.7, 129.6, 127.7, 126.5, 126.2, 123.5, 121.3, 45.4, 45.3, 31.1; HRMS (ESI) for $C_{16}H_{18}NaO_2S_2$ $[M+Na]^+$: calcd. 329.0640, found 329.0637.



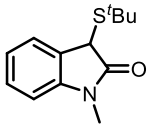
phenyl (*S*)-2-(benzofuran-3-yl)-2-(tert-butylthio)acetate (**3v**)

White soild (91% yield); $[\alpha]_D^{25}$ -12.9 (*c* 1.0 $CHCl_3$) for 58% ee; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (s, 1H), 7.77 (d, *J* = 8.0 Hz, 1H), 7.39-7.32 (m, 3 H), 7.29 (t, *J* = 8.0 Hz, 1H), 7.23 (t, *J* = 7.6 Hz, 1H), 7.07 (d, *J* = 7.6 Hz, 1H), 4.95 (s, 1H), 1.49 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.4, 155.7, 150.8, 143.7, 129.6, 126.3, 126.2, 125.0, 123.0, 121.3, 120.3, 116.8, 111.9, 45.4, 40.7, 31.1; HRMS (ESI) for $C_{20}H_{20}NaO_3S$ $[M+Na]^+$: calcd. 363.1025, found 363.1023.



phenyl (*S*)-2-(tert-butylthio)-2-(1-tosyl-1H-indol-3-yl)acetate (**3w**)

White soild (78% yield); $[\alpha]_D^{25}$ -46.6 (*c* 1.0 $CHCl_3$) for 69% ee; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.2 Hz, 1H), 7.82 (s, 1H), 7.75 (d, *J* = 7.8 Hz, 2H), 7.69 (d, *J* = 7.8 Hz, 1H), 7.36-7.33 (m, 3H), 7.27 (t, *J* = 7.2 Hz, 1H), 7.22 (t, *J* = 7.2 Hz, 1H), 7.18 (d, *J* = 7.8 Hz, 2H), 7.01 (d, *J* = 7.8 Hz, 2H), 4.94 (s, 1H), 2.31 (s, 1H), 1.45 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.3, 150.8, 145.2, 135.5, 135.2, 130.0, 129.6, 129.1, 127.0, 125.7, 125.3, 123.6, 121.3, 120.0, 118.2, 114.0, 45.4, 41.6, 31.1, 21.7; HRMS (ESI) for $C_{27}H_{27}NNaO_4S_2$ $[M+Na]^+$: calcd. 516.1274, found 516.1271.



3-(*tert*-butylthio)-1-methylindolin-2-one (**3x**)

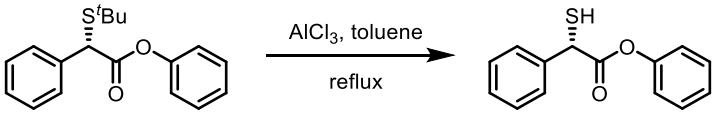
Pink solid (98% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 7.6 Hz, 1H), 7.30 (t,

J = 8.8 Hz, 1H), 7.09 (d, J = 8.0 Hz, 1H), 6.81 (d, J = 7.6 Hz, 1H), 4.30 (s, 1H), 3.23 (s, 2H), 1.52 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.5, 143.9, 128.9, 127.7, 125.5, 122.9, 108.2, 45.1, 44.3, 31.9, 26.7; HRMS (ESI) for $C_{13}H_{18}NOS$ $[M+H]^+$: calcd. 236.1104, found 236.1102.

3. Gram-scale synthesis of 3a

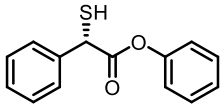
A solution of catalyst [Rh(**L1**)Cl]$_2$ (2.5 mol%, 106.5 mg, 0.2 mmol of [Rh]) in 20 mL of DCM was added into substrate **1a** (6.0 mmol, 1.4 g), *tert*-butyl mercaptan (4.0 mmol) at ambient temperature under argon. After being stirred at ambient temperature for 12 h, the solvent was evaporated in vacuo. The desired product **3a** was afforded after purification of the residue by column chromatography (PE/EA = 200/1). 0.93 g **3a** was obtained (77% yield, 70% ee). The optical purity was improved to 95% ee after simple recrystallization from MTBE under -20 ºC.

4. The synthesis of 4a



3a **4a**

Substrate **3a** (0.2 mmol, 60 mg, 95% ee) and $AlCl_3$ (0.4 mmol, 53.2 mg) was solved in 2.0 mL toluene under argon atmosphere. After being stirred at 80 ℃ for 5 minutes, the mixture was evaporated in vacuo. The residue was purified by column chromatography as a white solid **4a** (43.5 mg, 89% yield, 95% ee).



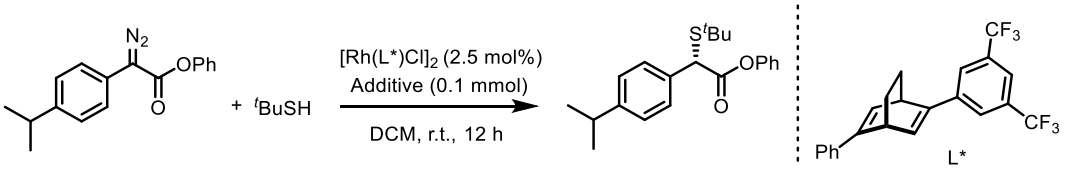
phenyl (*S*)-2-mercapto-2-phenylacetate (**4a**).

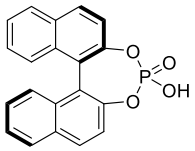
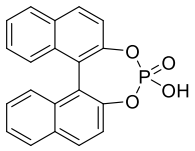
Yellow solid (89% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, J = 7.3 Hz, 2H), 7.45-7.29 (m, 5H), 7.24 (d, J = 7.2 Hz, 1H), 7.06 (d, J = 7.6 Hz, 2H), 4.91 (d, J = 7.9 Hz, 1H), 2.72 (d, J = 7.9 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.2, 150.8, 137.8, 129.6,

129.1, 128.6, 128.0, 126.3, 121.3, 45.9; HRMS (EI) for $C_{14}H_{12}O_2S$ $[M]^+$ calcd. 244.0553, found 244.0555.

5. The effect of adding an external proton source

Table S1 [a]



Entry	Additive	Yield [%] [b]	ee [%] [c]
1	none	95	77
2	Benzyl acid	48	13
3		26	18
4		19	20
5	Phenol	65	74
6	H_2O	73	77

[a] Conditions: diazo compound (0.15 mmol), *tert*-butyl mercaptan (0.1 mmol), [Rh(**L1**)Cl]$_2$ (2.5 mol%) and additive (0.1 mmol) in DCM (2.0 mL) for 12 h at 25 °C; [b] isolated yields; [c] ee determined by chiral HPLC analysis.

6. Computational Details

We performed DFT calculations using Gaussian 16. All calculations were performed at M06/def2svp level with solvent (DCM) corrections under 298 K. All reported Gibbs free energies throughout the text are in kcal/mol after correction. Structures were generated using CYLview software.

References:

[1] Gaussian 16, Revision A.03, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2016.

[2] CYLview, 1.0b; Legault, C. Y., Université de Sherbrooke, 2009 (http://www.cylview.org).

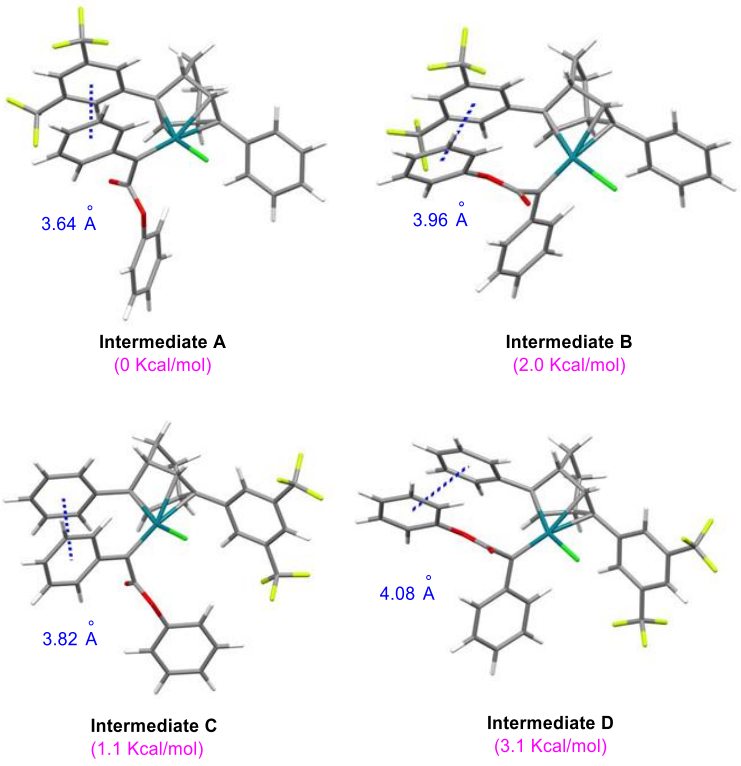


Figure S1. Computed energies of intermediates A~D

Table S2. Summary of computed energies of intermediates A~D

Intermediate	G (Hartree)	ΔG (Hartree)	ΔG (Kcal/mol)
Intermediate A	-2704.355994	0	0
Intermediate B	-2704.352762	0.003232	2.03
Intermediate C	-2704.354208	0.001786	1.12
Intermediate D	-2704.351035	0.004959	3.11

Intermediate A

0 1

C	0.60760500	1.98134700	-0.36655400
C	-1.20287500	0.85325000	-1.70650100
C	-1.67202600	-0.25772800	-2.44468400
C	-2.86849600	-0.18626100	-3.14105700
C	-3.63101800	0.98334800	-3.09506900
C	-3.18705800	2.09249100	-2.37051300
C	-1.97886800	2.03593400	-1.69279100
O	0.21242600	2.46915900	0.66523200
H	-1.05954500	-1.16454900	-2.46678500
H	-3.21837100	-1.04618900	-3.71758400
H	-4.58198300	1.03223400	-3.63322300
H	-3.78922500	3.00411100	-2.33769800
H	-1.63981000	2.89880600	-1.11266600
Rh	0.98237900	-0.78683500	-0.45170400
Cl	1.97557000	-1.21517600	-2.54938700
C	1.40537900	-2.91010300	0.44995600
H	1.50669800	-3.63817800	-0.36074000
C	2.44592100	-2.13389300	0.90086500
C	2.05790800	-1.31759900	2.12441900
H	2.87035600	-0.65531400	2.45458400

C	0.84277200	-0.53396300	1.67810700
H	0.70780700	0.50481800	1.99894300
C	-0.22607200	-1.34889200	1.24769800
C	0.15184100	-2.82568800	1.29250800
H	-0.64182700	-3.47376400	0.89693100
C	0.49278400	-3.18513600	2.75495600
H	-0.41225500	-3.05042400	3.37118900
H	0.75791600	-4.25336400	2.80680100
C	3.82560600	-2.18197700	0.38935000
C	4.33167200	-3.35078600	-0.19731100
H	3.70630100	-4.24752600	-0.24055300
C	5.62620000	-3.38776300	-0.70585500
H	6.00601400	-4.30995300	-1.15474000
C	6.43876200	-2.25686000	-0.63842700
C	5.94913800	-1.08939100	-0.05416400
H	6.57730500	-0.19570700	-0.00242800
C	4.65684300	-1.05415000	0.45941100
H	4.27576000	-0.12446200	0.89349000
C	-1.63074000	-0.90458800	1.13915100
C	-2.05177600	0.31505200	1.68273300
H	-1.35418500	0.93014900	2.25745400
C	-3.34529700	0.78060300	1.46670300
C	-4.25942900	0.03846100	0.72448500
C	-3.85242700	-1.18483200	0.19774500
C	-2.55840900	-1.65293300	0.40385500
H	-2.25285200	-2.59442800	-0.06260100
H	7.45585600	-2.28600300	-1.03934500
H	-5.27069200	0.41327000	0.55136900
C	1.64506600	-2.29621600	3.24648100

H	1.35303800	-1.71296100	4.13482500
H	2.52339100	-2.89734000	3.53453400
C	0.02936300	0.76163200	-0.97168200
O	1.65030400	2.44403000	-1.08002600
C	2.47635500	3.41033900	-0.52288900
C	2.65957400	4.59770800	-1.21929800
C	3.14677100	3.15075300	0.66889300
C	3.54043300	5.54944200	-0.70774400
H	2.11690600	4.75857300	-2.15423400
C	4.01955400	4.11116800	1.17193900
H	2.98050000	2.20139800	1.18750600
C	4.21827700	5.30998800	0.48625500
H	3.69605700	6.48639300	-1.24951700
H	4.55196400	3.91879400	2.10744500
H	4.90697300	6.05984200	0.88462100
C	-3.70982300	2.14216600	1.98115000
C	-4.82108000	-2.01931700	-0.58807700
F	-3.26371400	2.33636700	3.22234600
F	-3.17026000	3.10278700	1.22260700
F	-5.02602600	2.34214100	1.99010100
F	-5.76058400	-1.27429900	-1.16922200
F	-5.44781300	-2.90508400	0.19110300
F	-4.20941000	-2.71433600	-1.54884800

Intermediate B

0 1

C	0.91860600	2.78124300	-0.22905400
C	2.07707500	3.01912800	0.54624900
C	2.35396400	4.28317100	1.04020600

C	1.48102600	5.34105300	0.77286100
C	0.33225400	5.13305200	0.00786100
C	0.05207300	3.86887800	-0.48940600
H	2.75418300	2.18114300	0.73990500
H	3.25494700	4.45326700	1.63473100
H	1.70035600	6.33889900	1.16277400
H	-0.34549100	5.96422900	-0.20171500
H	-0.85053900	3.72151600	-1.09061800
Rh	1.69489500	-0.09035800	-0.48753000
Cl	2.96221700	0.22413700	-2.45920500
C	2.48414300	-2.26617300	-0.07562600
H	2.73441400	-2.75645200	-1.02080900
C	3.35246900	-1.44583000	0.60389500
C	2.78873500	-1.01738700	1.94924400
H	3.44926400	-0.31352800	2.47353000
C	1.45465300	-0.38421300	1.61193800
H	1.12160100	0.49917600	2.16870900
C	0.56170100	-1.26211000	0.95956400
C	1.22452400	-2.60823700	0.68443100
H	0.58509000	-3.28126200	0.09900000
C	1.59962800	-3.23359700	2.04547400
H	0.67357500	-3.41972400	2.61607100
H	2.06949700	-4.21478700	1.87037400
C	4.73195400	-1.13499800	0.19404300
C	5.42661200	-1.98165200	-0.68208800
H	4.95323600	-2.90329500	-1.03275900
C	6.71659000	-1.67163200	-1.09896600
H	7.24294900	-2.34673800	-1.77962000
C	7.33897000	-0.50806300	-0.64825700

C	6.66343600	0.33870300	0.22884100
H	7.14271300	1.25431200	0.58647700
C	5.37490000	0.02489900	0.64994500
H	4.85397700	0.70973800	1.32602400
C	-0.91086400	-1.14286600	0.99351000
C	-1.54347000	-0.14324100	1.74312300
H	-0.94794000	0.57972700	2.30963100
C	-2.92848200	-0.02710200	1.75930600
C	-3.73199000	-0.91914900	1.05418600
C	-3.11377700	-1.91982900	0.31271700
C	-1.72528400	-2.02725400	0.27547100
H	-1.27680600	-2.80845900	-0.34501000
H	8.35266700	-0.26345400	-0.97785700
H	-4.81962800	-0.82126400	1.06565100
C	2.54419300	-2.28506900	2.79847500
H	2.12190000	-1.98286800	3.77064400
H	3.51487600	-2.76436000	3.00795100
C	0.64021300	1.46033600	-0.74377500
C	-0.53788600	1.33052300	-1.63721900
O	-0.48974500	1.36092300	-2.83740800
O	-1.66504000	1.20278600	-0.91106800
C	-2.90028100	1.00229600	-1.50693400
C	-3.93985300	1.81483300	-1.06786800
C	-3.11275800	-0.03072000	-2.41414100
C	-5.23017700	1.57545100	-1.53617600
H	-3.72470800	2.60799600	-0.34621600
C	-4.40638000	-0.25424600	-2.87905000
H	-2.27998000	-0.66332200	-2.73218000
C	-5.46560700	0.54002600	-2.43935300

H	-6.05617500	2.20190800	-1.18833000
H	-4.58838900	-1.07339200	-3.58061300
H	-6.47892200	0.34994200	-2.80309700
C	-3.92838100	-2.92962900	-0.44209100
C	-3.52716300	1.10922600	2.53412400
F	-3.92724700	-4.11152500	0.18270200
F	-5.19772700	-2.55628700	-0.57947000
F	-3.43732200	-3.14530100	-1.66548800
F	-4.84675600	1.18510100	2.38830100
F	-3.26957400	1.00376700	3.83962500
F	-3.01454400	2.28182700	2.13963500

Intermediate C

0 1

C	1.71751200	1.97790600	-0.04501400
C	3.27768200	0.59652300	1.36276000
C	3.54818800	-0.56596900	2.11902800
C	4.71311600	-0.66564100	2.86352300
C	5.63545100	0.38304300	2.85293500
C	5.39016800	1.54043100	2.10878000
C	4.21916400	1.65232600	1.37636400
O	2.02520200	2.28686900	-1.16983800
H	2.81020700	-1.37418800	2.11354600
H	4.91136300	-1.56368700	3.45400300
H	6.55676700	0.30075300	3.43653100
H	6.11713800	2.35636300	2.10870900
H	4.02862100	2.55827600	0.79108000
Rh	0.77724800	-0.62936500	0.19517900
Cl	-0.41355600	-0.46838200	2.23313000

C	-0.13801400	-2.66185400	-0.44855200
H	-0.45838900	-3.21401800	0.44030800
C	-0.90517200	-1.69949300	-1.06446400
C	-0.27490100	-1.21167500	-2.35923900
H	-0.85900800	-0.41030600	-2.83206900
C	1.09188500	-0.72484100	-1.92582500
H	1.50609600	0.19561700	-2.34970700
C	1.88711900	-1.72405000	-1.32682900
C	1.11533600	-3.03635900	-1.20643500
H	1.68240300	-3.80977600	-0.67303600
C	0.73728600	-3.49883500	-2.62968600
H	1.66639200	-3.69760300	-3.19034400
H	0.19329500	-4.45486800	-2.56385500
C	-2.24241900	-1.27225200	-0.62082000
C	-3.05111900	-2.11650400	0.14289800
H	-2.71578700	-3.13211700	0.37473400
C	-4.29094100	-1.68379600	0.60975200
C	-4.75331600	-0.40656100	0.31955300
C	-3.95493300	0.43693600	-0.45415000
C	-2.71745400	0.01292300	-0.92172700
H	-2.09763300	0.70102100	-1.50462900
C	3.36041800	-1.67479700	-1.21075800
C	4.09608100	-0.62828600	-1.79210300
H	3.57999000	0.15215100	-2.35858400
C	5.47622800	-0.55579500	-1.64352100
C	6.16056900	-1.53237600	-0.91847900
C	5.44643100	-2.58015400	-0.34299400
C	4.06242700	-2.64870900	-0.48597700
H	3.52193600	-3.46727600	-0.00151100

H	-5.72781200	-0.07167600	0.68251700
H	7.24697400	-1.47629100	-0.80588700
C	-0.11127800	-2.41561200	-3.31189300
H	0.35805600	-2.06465100	-4.24512800
H	-1.11032000	-2.79638000	-3.58166200
C	2.06483800	0.69509100	0.60227100
O	0.97155100	2.73526200	0.78249900
C	0.29688200	3.83488000	0.26775100
C	0.98517000	4.97699300	-0.12447700
C	-1.08964300	3.75671000	0.20470100
C	0.25692100	6.06755400	-0.59515700
H	2.07604200	5.00330800	-0.05756800
C	-1.80685000	4.85446700	-0.26632300
H	-1.58717600	2.84049600	0.53855600
C	-1.13495400	6.00852600	-0.66746300
H	0.78423300	6.97319700	-0.90760500
H	-2.89774400	4.80053300	-0.31650600
H	-1.69927400	6.86919800	-1.03665900
H	6.02557600	0.27068000	-2.10374100
H	5.96843400	-3.35134000	0.23098000
C	-4.42985900	1.83460600	-0.72349400
C	-5.11446800	-2.64420800	1.41670700
F	-6.25776500	-2.10740700	1.83314800
F	-4.44990100	-3.06440500	2.49474000
F	-5.41803400	-3.73377300	0.70542900
F	-5.74426500	1.87794000	-0.93452900
F	-4.18066700	2.63762800	0.32063200
F	-3.83175100	2.37697000	-1.78163300

Intermediate D

0 1

C	1.18323900	2.48740300	0.04120100
C	0.00948800	2.85601200	-0.65521500
C	-0.22431000	4.17408800	-1.01059400
C	0.71245500	5.15777000	-0.68262200
C	1.88041300	4.82022900	0.00318700
C	2.11559400	3.50127500	0.36317500
H	-0.71630700	2.07411000	-0.89892800
H	-1.14254200	4.44136700	-1.53956100
H	0.52824900	6.19896600	-0.96160900
H	2.60817700	5.59376500	0.26048700
H	3.03302500	3.25364200	0.90675300
Rh	0.19284800	-0.31495200	0.15267400
Cl	-1.03371400	0.14232700	2.13170800
C	-0.82684300	-2.38727200	-0.22568900
H	-1.14610100	-2.81108300	0.73102700
C	-1.56092200	-1.46410100	-0.93336700
C	-0.94027100	-1.15236500	-2.28701800
H	-1.50307600	-0.38725800	-2.83911900
C	0.45850900	-0.68028700	-1.93995600
H	0.91905400	0.14668500	-2.49377500
C	1.21758400	-1.64428600	-1.24742800
C	0.39219000	-2.89616100	-0.95439800
H	0.95279000	-3.62183600	-0.34956800
C	-0.02877300	-3.49813900	-2.31244300
H	0.88246200	-3.79310000	-2.86047400
H	-0.60742100	-4.41880600	-2.13463900
C	-2.85971900	-0.90987800	-0.51517500

C	-3.67458300	-1.57640700	0.40117900
H	-3.38772000	-2.56558200	0.77118900
C	-4.85743600	-0.99409300	0.85575200
C	-5.24817800	0.26266200	0.41257100
C	-4.44370600	0.92713400	-0.51455600
C	-3.27586600	0.34428300	-0.98405100
H	-2.66113200	0.89081100	-1.70341400
C	2.69131500	-1.73666900	-1.25280200
C	3.44529600	-1.18133400	-2.29586300
H	2.93840200	-0.65389600	-3.10984700
C	4.83107300	-1.31925900	-2.32354900
C	5.48719600	-2.02039300	-1.31369300
C	4.74812100	-2.57510500	-0.26912400
C	3.36498400	-2.43197000	-0.23741300
H	2.79458700	-2.84721000	0.60144800
H	-6.16927100	0.72282100	0.77971000
H	6.57553900	-2.13092400	-1.33648300
C	-0.84679100	-2.46271600	-3.09851000
H	-0.38407800	-2.24046900	-4.07383300
H	-1.86644900	-2.82745900	-3.30594200
C	1.40185600	1.11256400	0.43078200
C	2.61047000	0.84178000	1.24601900
O	2.60465800	0.78502100	2.44749000
O	3.69267300	0.70953300	0.46031600
C	4.97065000	0.53033400	0.96552000
C	5.98132100	1.19631200	0.27855100
C	5.25558500	-0.31309100	2.03633700
C	7.30621600	1.00918600	0.66200700
H	5.71049700	1.84107200	-0.56232200

C	6.58642200	-0.48765400	2.41128100
H	4.45278000	-0.83622700	2.55770000
C	7.61218900	0.16513000	1.72909500
H	8.10401000	1.52617300	0.12154800
H	6.82162900	-1.15011400	3.24917400
H	8.65246500	0.01707200	2.03138100
H	5.25644500	-3.11719800	0.53373700
H	5.40173500	-0.88496000	-3.14971900
C	-5.69273600	-1.76971800	1.83171200
C	-4.88370100	2.27644100	-1.00128300
F	-5.98300200	2.18314200	-1.75445600
F	-5.18215200	3.08674100	0.01461800
F	-3.95018000	2.88032700	-1.73597600
F	-6.11295500	-2.91932400	1.29565000
F	-6.76934200	-1.09647900	2.22704700
F	-4.99363300	-2.08926400	2.92217500

7. Crystal structure of compound 3a

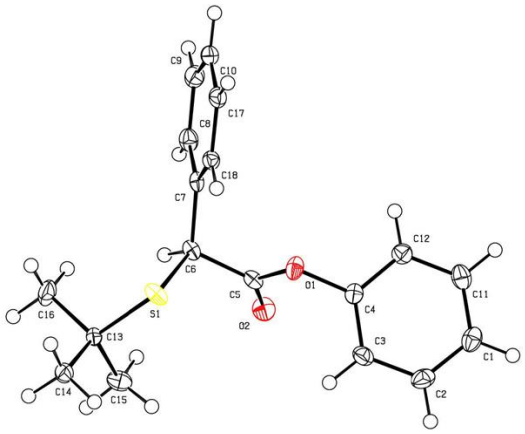


Figure S2. ORTEP representation of compound **3a**

Bond precision: C-C = 0.0029 A Wavelength=0.71073

Cell: a=9.0924(4) b=8.7294(4) c=10.8209(4)
alpha=90 beta=110.726(1) gamma=90
Temperature: 100 K

	Calculated	Reported
Volume	803.29(6)	803.28(6)
Space group	P 21	P 1 21 1
Hall group	P 2yb	P 2yb
Moiety formula	C18 H20 O2 S	C18 H20 O2 S
Sum formula	C18 H20 O2 S	C18 H20 O2 S
Mr	300.40	300.40
Dx,g cm-3	1.242	1.242
Z	2	2
Mu (mm-1)	0.203	0.203
F000	320.0	320.0
F000'	320.38	
h,k,lmax	13,12,15	13,12,15
Nref	4956[2627]	4947
Tmin,Tmax	0.932,0.945	0.689,0.746
Tmin'	0.930	

Correction method= # Reported T Limits: Tmin=0.689 Tmax=0.746
AbsCorr = MULTI-SCAN

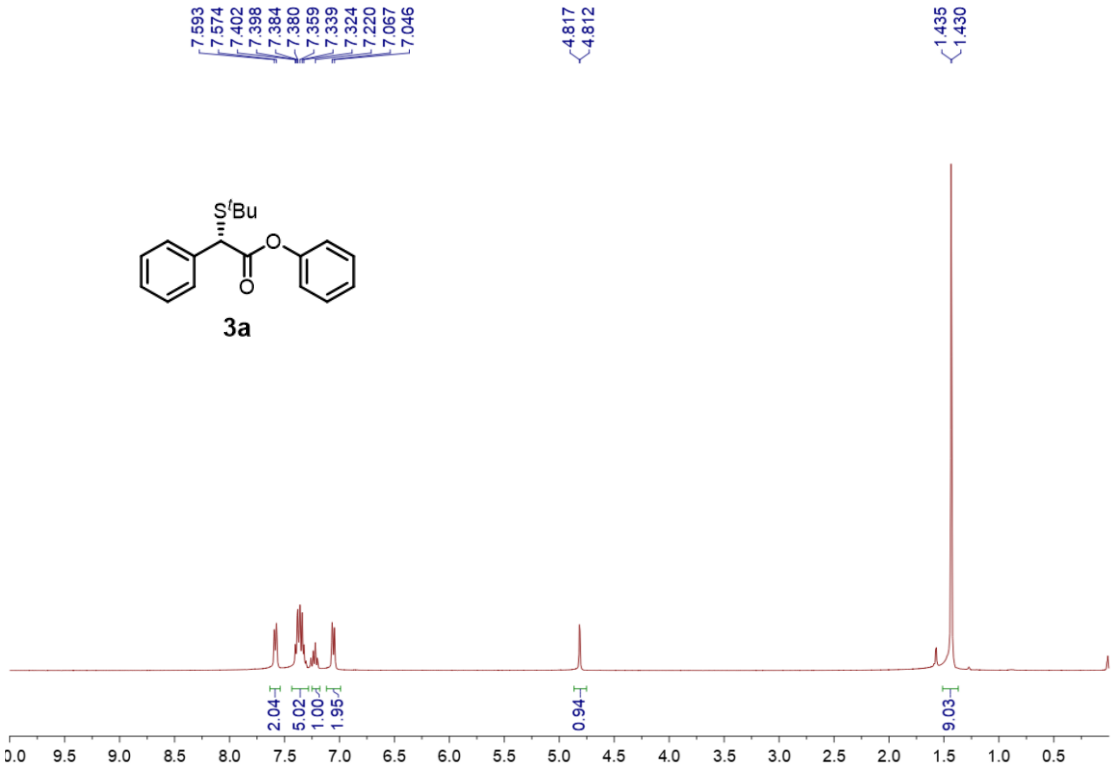
Data completeness= 1.88/1.00 Theta(max)= 30.597

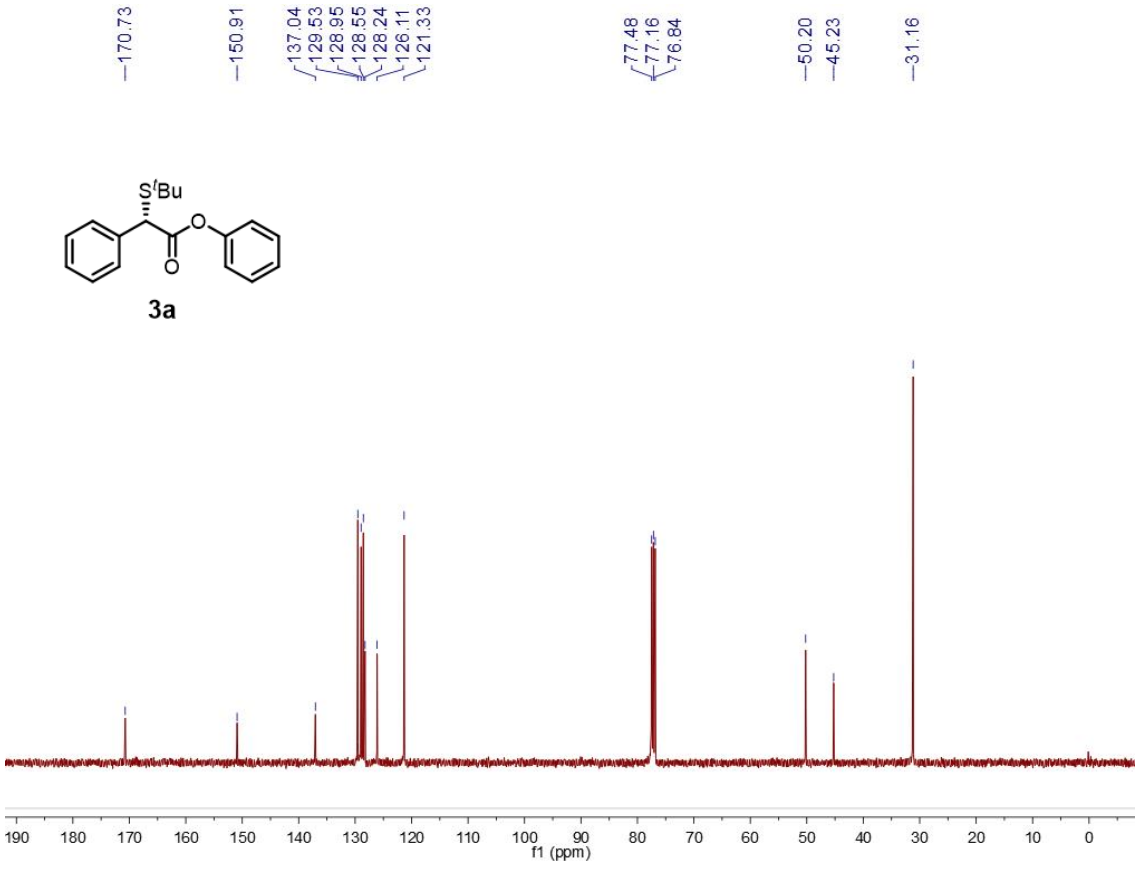
R(reflections)= 0.0326(4686) wR2(reflections)= 0.0842(4947)

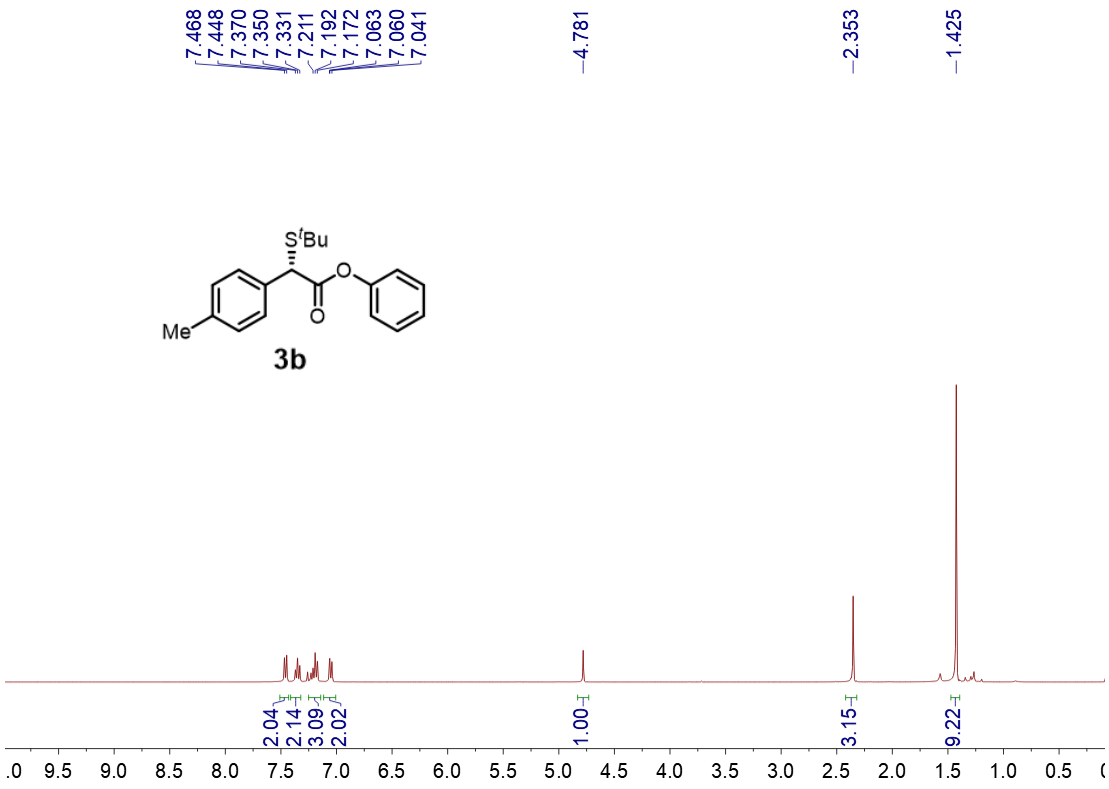
S = 1.053 Npar= 193

Figure S3. Crystal structure parameters

8. NMR spectra



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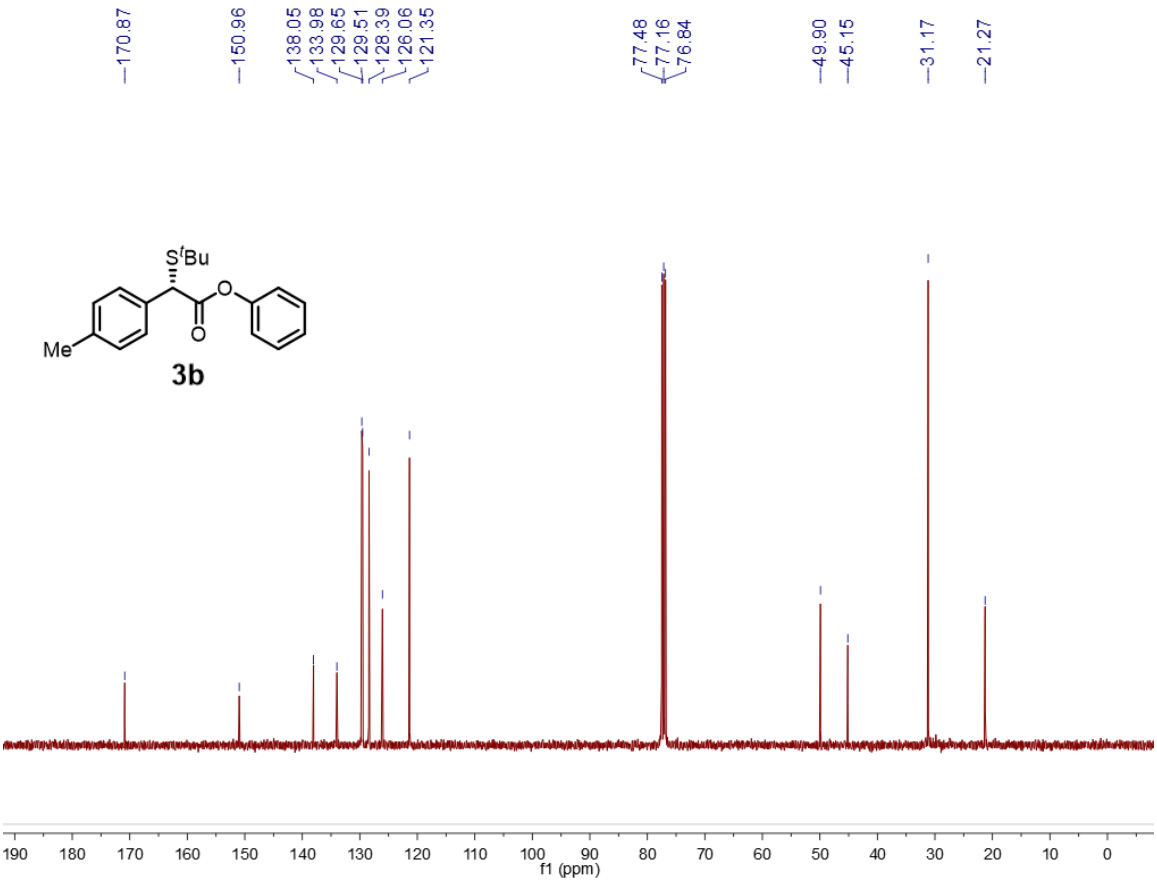
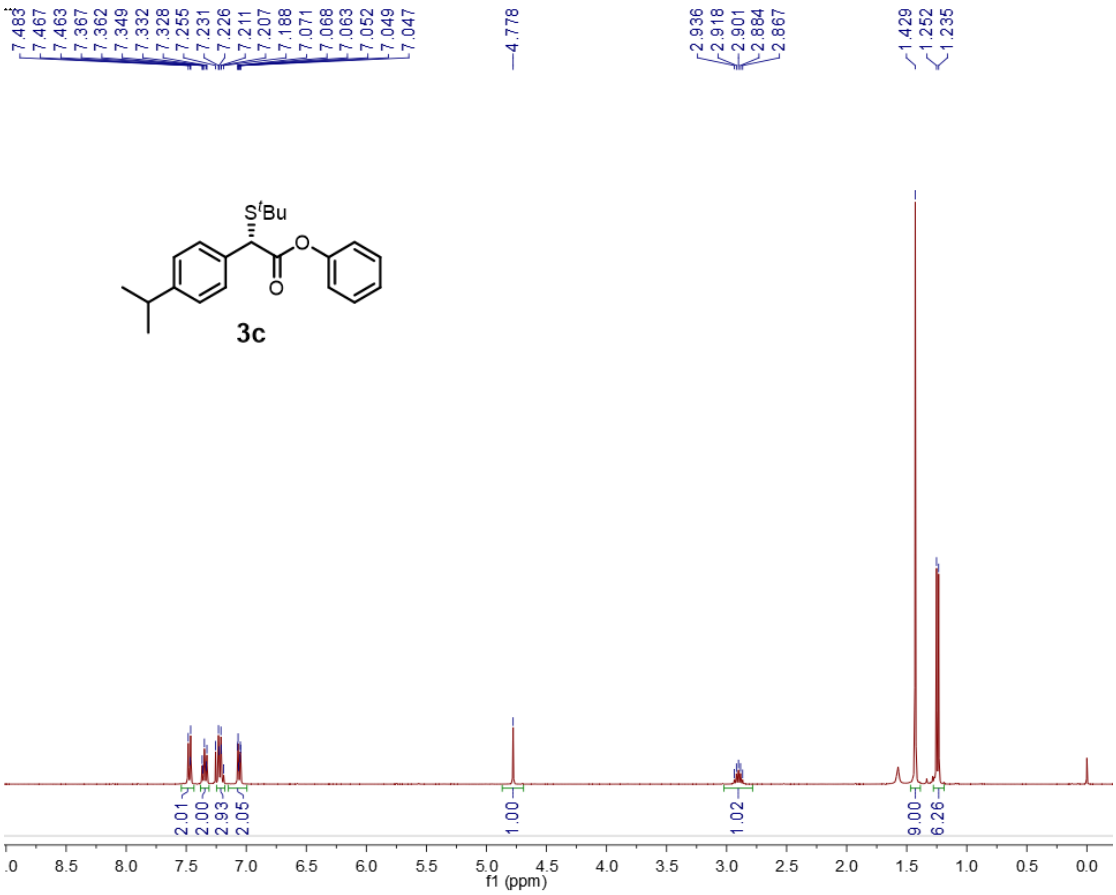
7.370
7.350
7.331
7.211
7.192
7.172
7.063
7.060
7.041
4.781
2.353
1.425
S^{t}Bu
Me
3b
2.04
2.14
3.09
2.02
1.00
3.15
9.22


170.87
150.96
138.05
133.98
129.65
129.51
128.39
126.06
121.35
77.48
77.16
76.84
49.90
45.15
31.17
21.27
S^{t}Bu
Me
3b
f1 (ppm)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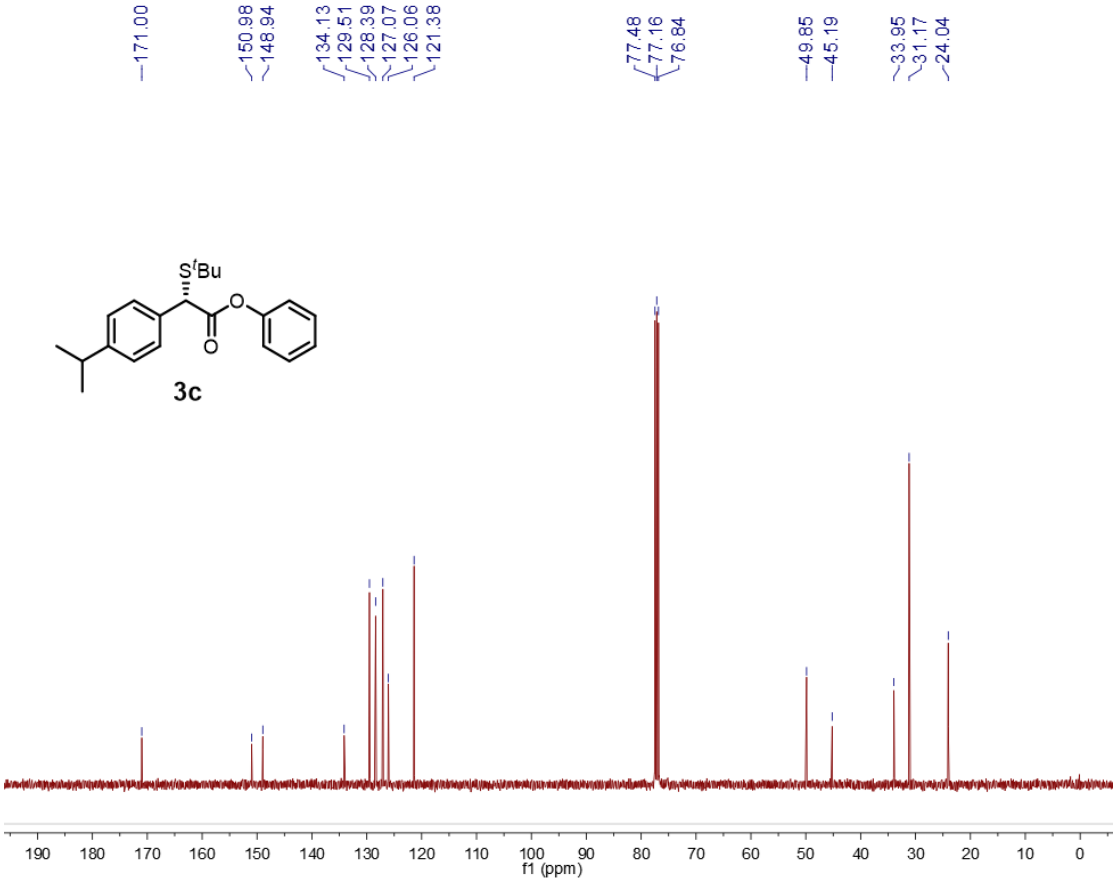
7.467
7.463
7.367
7.362
7.349
7.332
7.328
7.255
7.231
7.226
7.211
7.207
7.188
7.071
7.068
7.063
7.052
7.049
7.047
4.778
2.936
2.918
2.901
2.884
2.867
1.429
1.252
1.235
S^{t}Bu
O
O
3c
2.01
2.00
2.93
2.05
1.00
1.02
9.00
6.26
f1 (ppm)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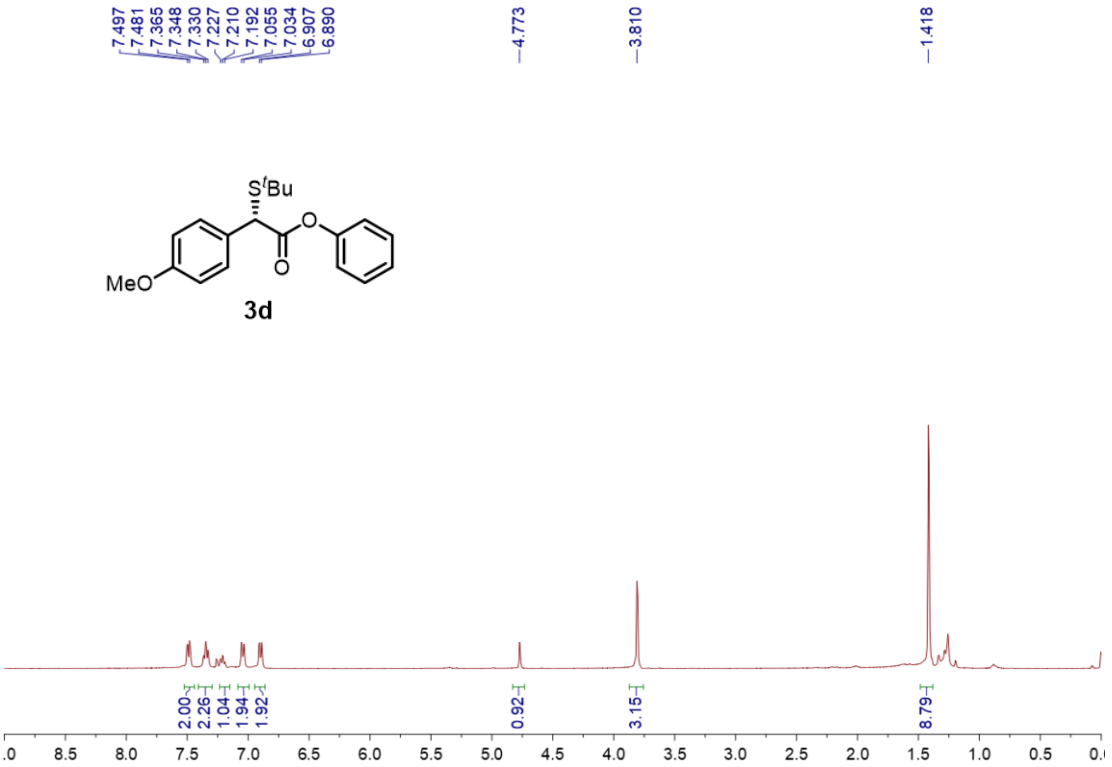
150.98
148.94
134.13
129.51
128.39
127.07
126.06
121.38
77.48
77.16
76.84
49.85
45.19
33.95
31.17
24.04
S^{t}Bu
O
O
3c
f1 (ppm)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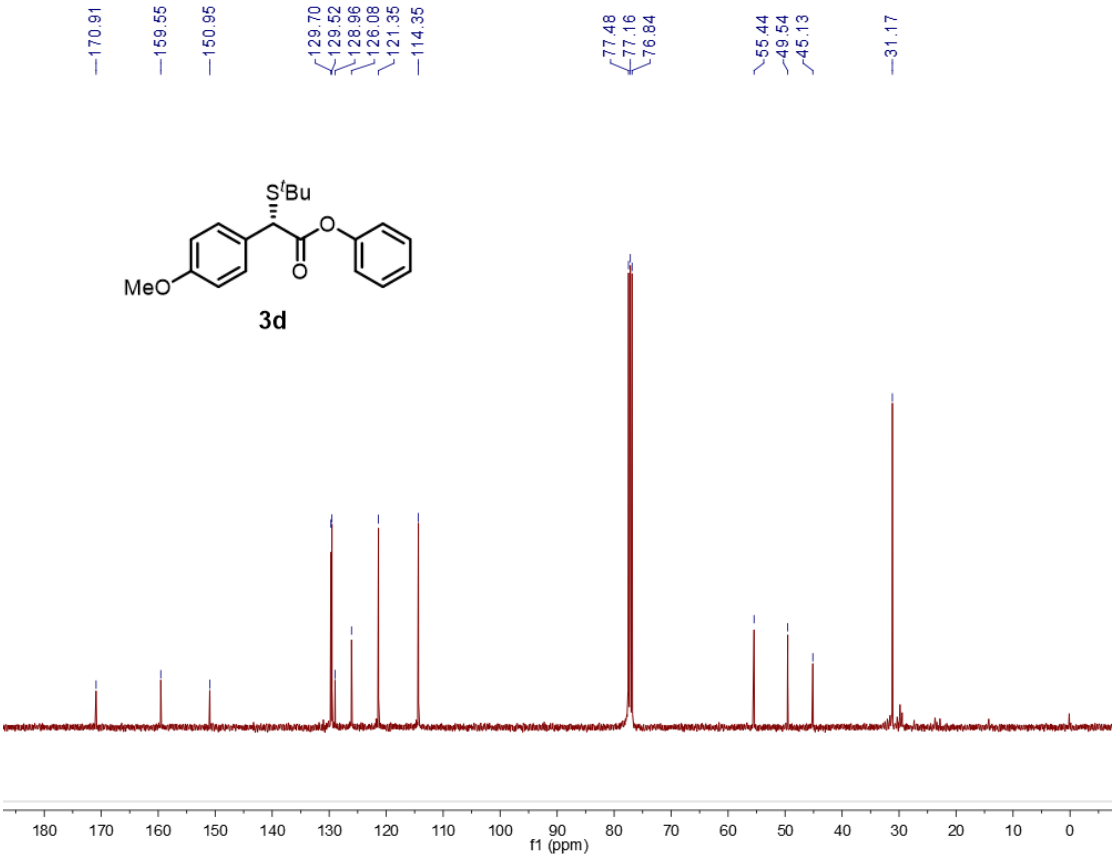
7.330
7.227
7.210
7.192
7.055
7.034
6.907
6.890
4.773
3.810
1.418
S^{t}Bu
MeO
O
O
3d
2.00
2.26
1.04
1.94
1.92
0.92
3.15
8.79
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5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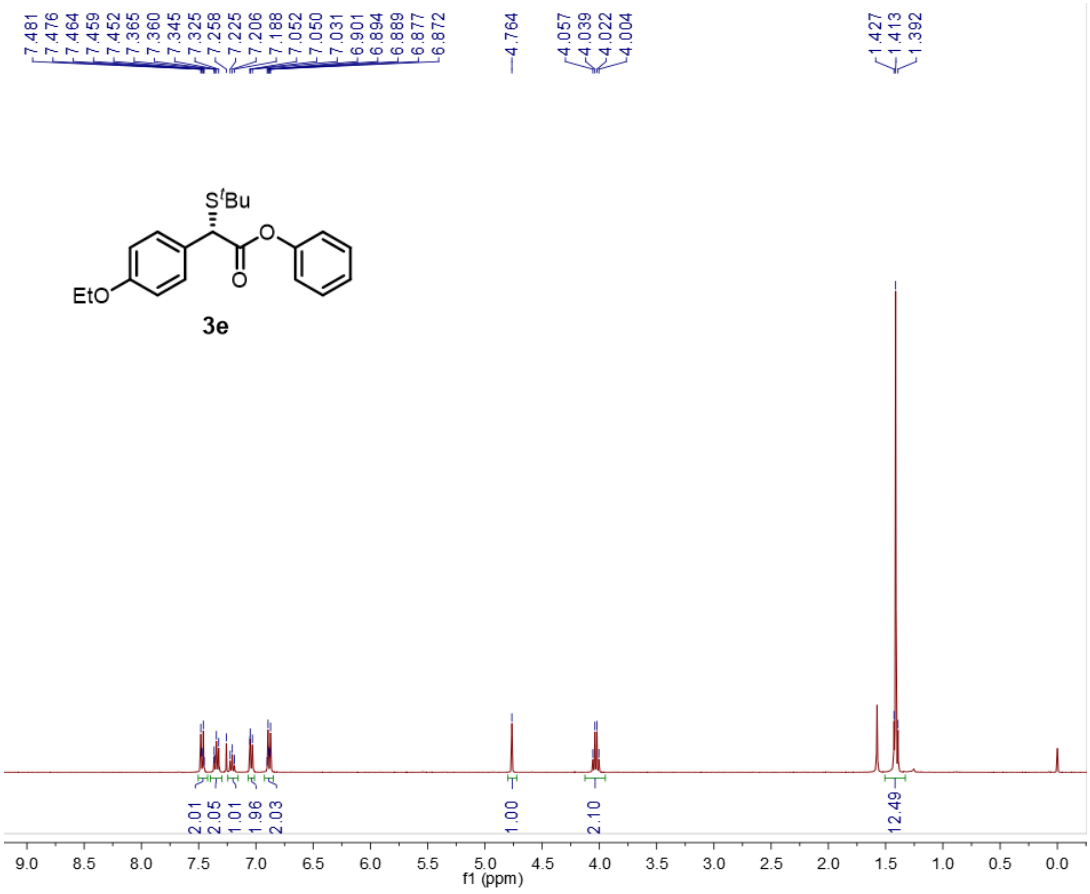
159.55
150.95
129.70
129.52
128.96
126.08
121.35
114.35
77.48
77.16
76.84
55.44
49.54
45.13
31.17
S^{t}Bu
MeO
O
O
3d
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.476
7.464
7.459
7.452
7.365
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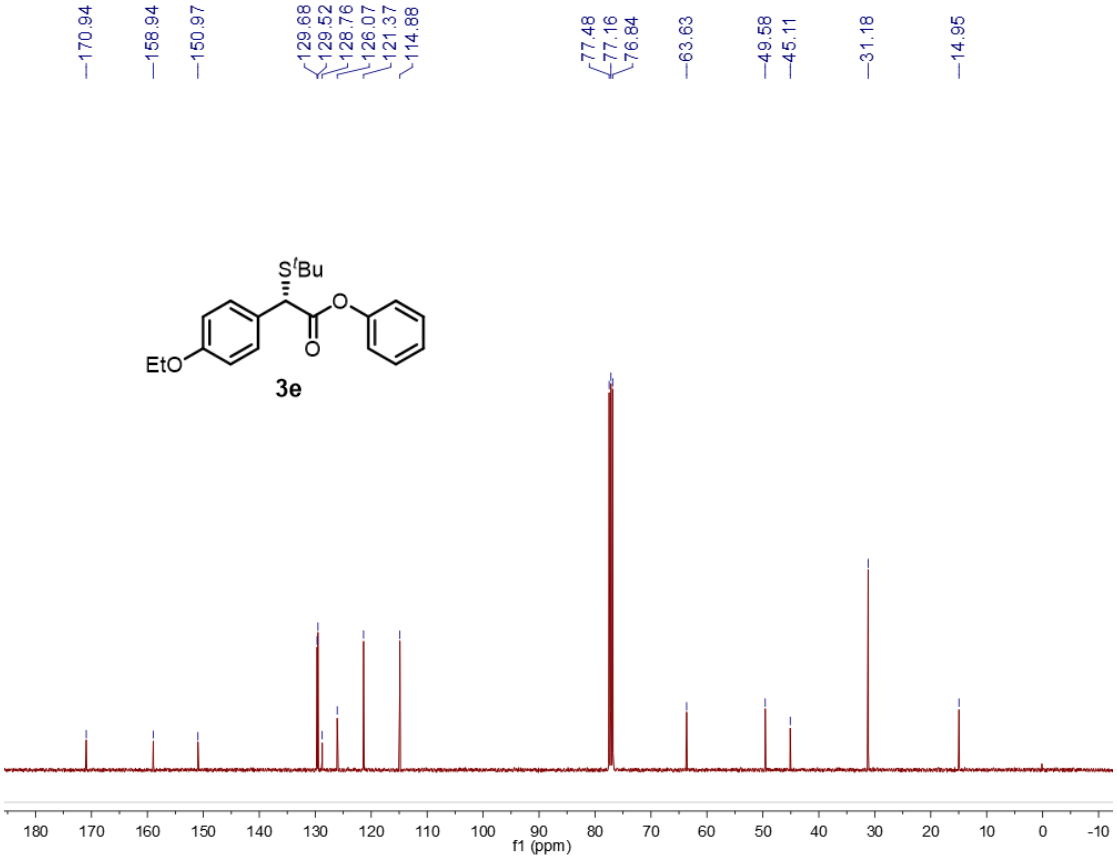
7.345
7.325
7.258
7.225
7.206
7.188
7.052
7.050
7.031
6.901
6.894
6.889
6.877
6.872
4.764
4.057
4.039
4.022
4.004
1.427
1.413
1.392
S^{t}Bu
EtO
O
O
3e
2.01
2.05
1.01
1.96
2.03
1.00
2.10
12.49
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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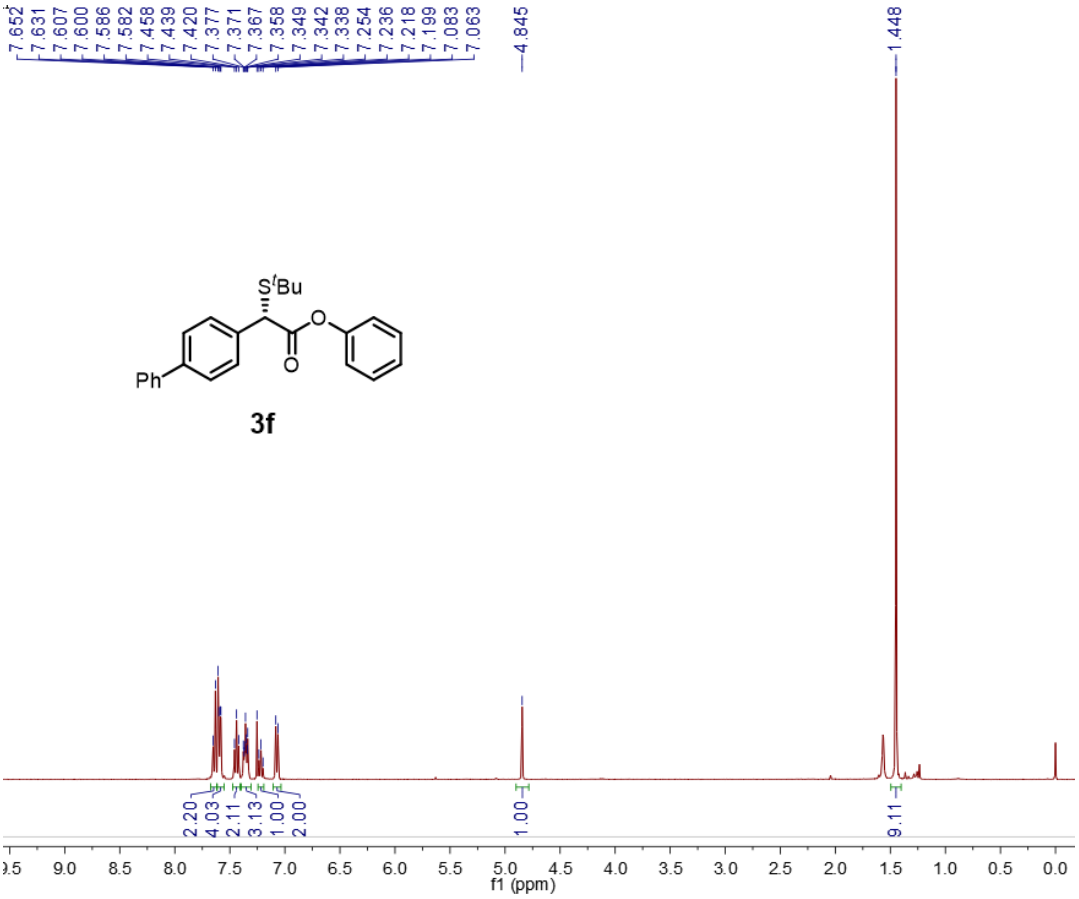
158.94
150.97
129.68
129.52
128.76
126.07
121.37
114.88
77.48
77.16
76.84
63.63
49.58
45.11
31.18
14.95
S^{t}Bu
EtO
O
O
3e
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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7.607
7.600
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7.582
7.458
7.439
7.420
7.377
7.371
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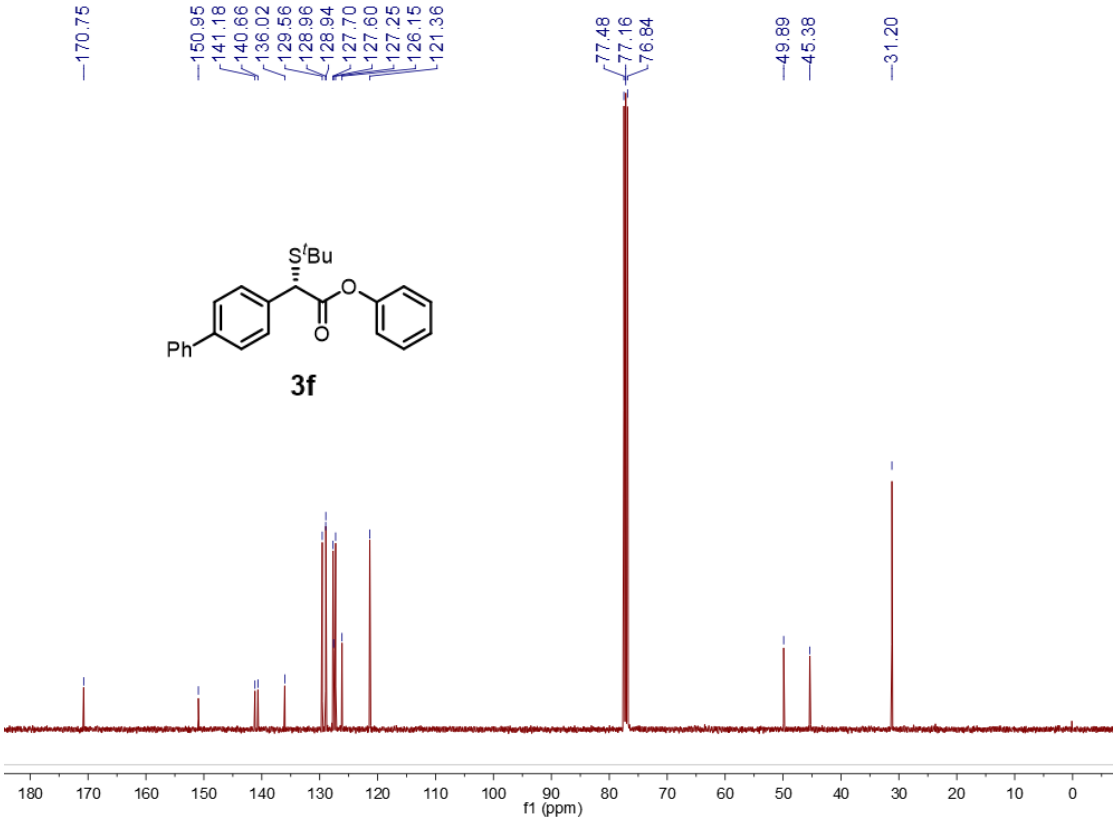
7.358
7.349
7.342
7.338
7.254
7.236
7.218
7.199
7.083
7.063
4.845
1.448
S^{t}Bu
Ph
O
O
2.20
4.03
2.11
3.13
1.00
2.00
1.00
9.11
f1 (ppm)

3f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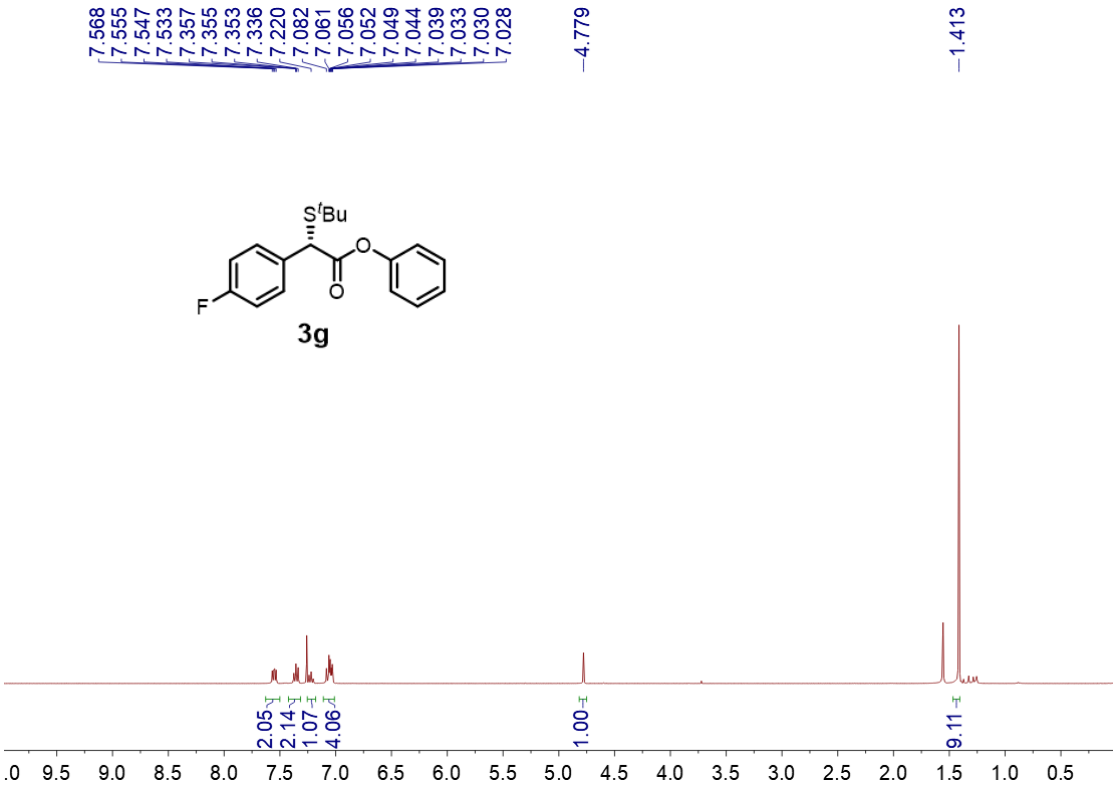
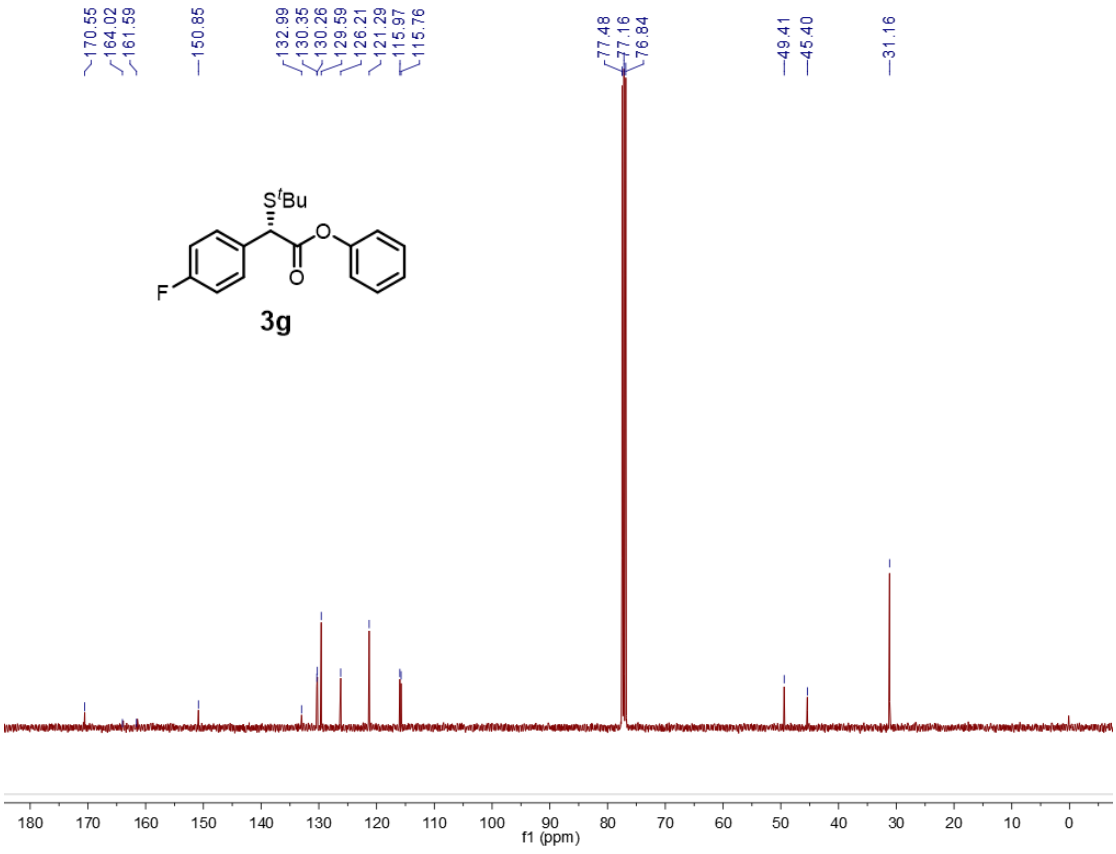
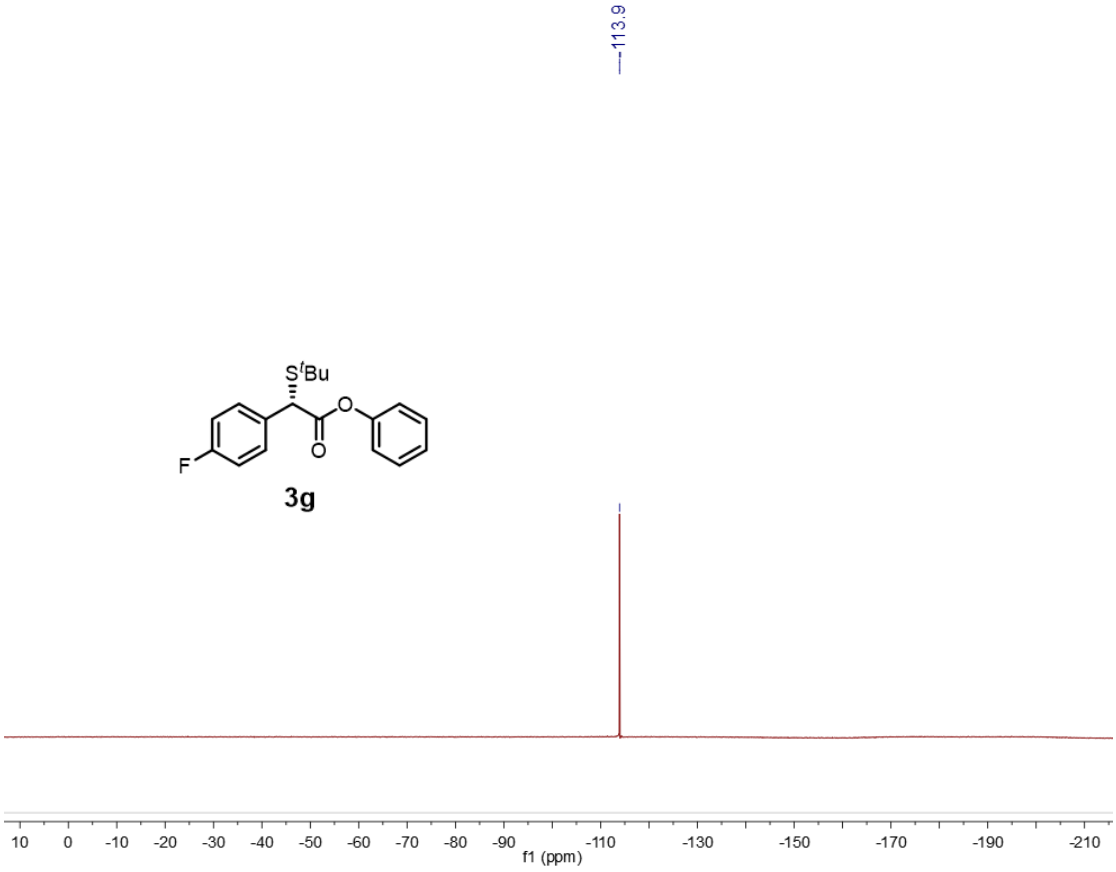
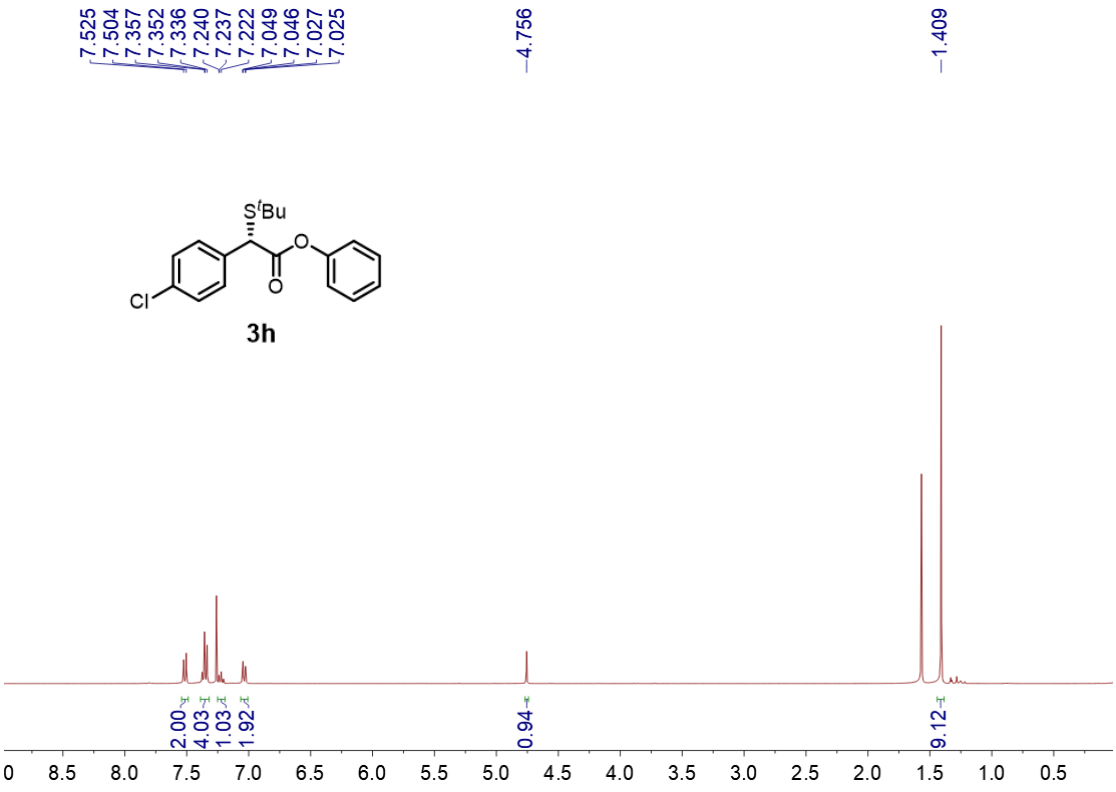
150.95
141.18
140.66
136.02
129.56
128.96
128.94
127.70
127.60
127.25
126.15
121.36
77.48
77.16
76.84
49.89
45.38
31.20
S^{t}Bu
Ph
O
O
f1 (ppm)

3f


7.568
7.555
7.547
7.533
7.357
7.355
7.353
7.336
7.220
7.082
7.061
7.056
7.052
7.049
7.044
7.039
7.033
7.030
7.028
4.779
1.413
S'Bu
O
O
F
3g
2.05
2.14
1.07
4.06
1.00
9.11
.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5


170.55
164.02
161.59
150.85
132.99
130.35
130.26
129.59
126.21
121.29
115.97
115.76
77.48
77.16
76.84
49.41
45.40
31.16
S'Bu
O
O
F
3g
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


113.9
S^{t}Bu
O
O
F
3g
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -110 -130 -150 -170 -190 -210
f1 (ppm)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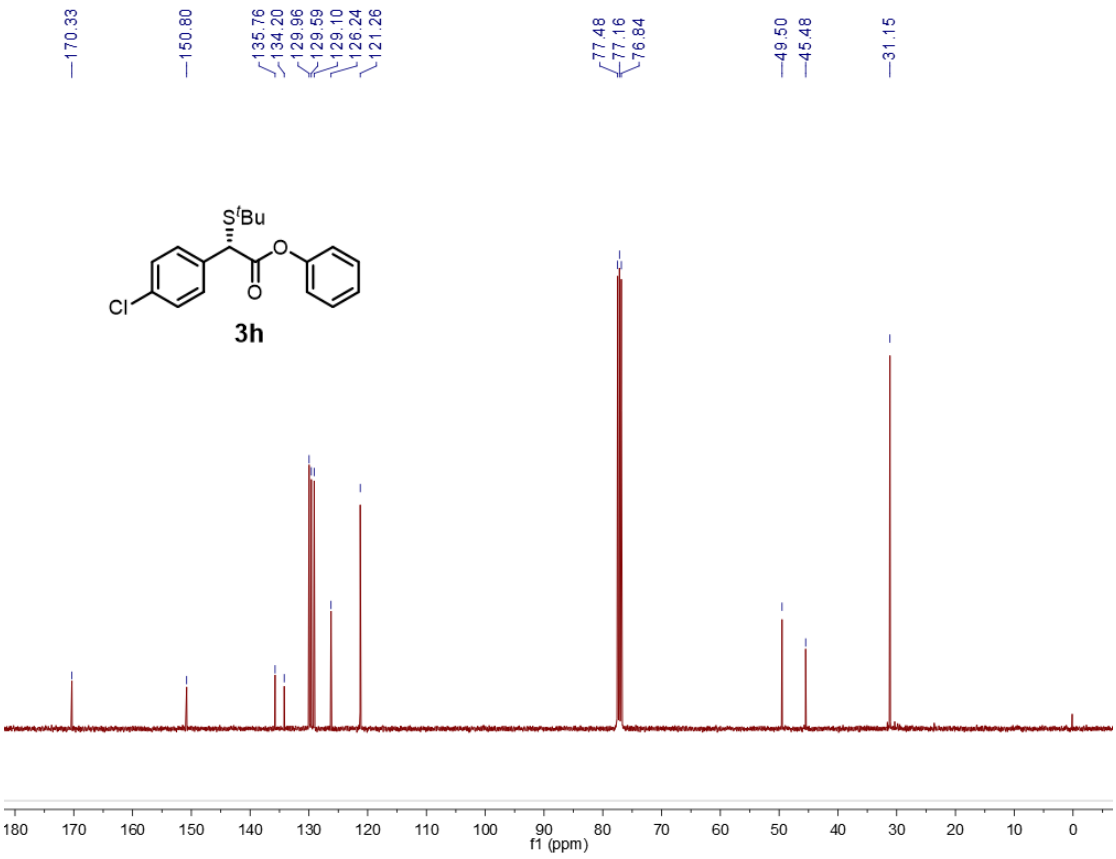
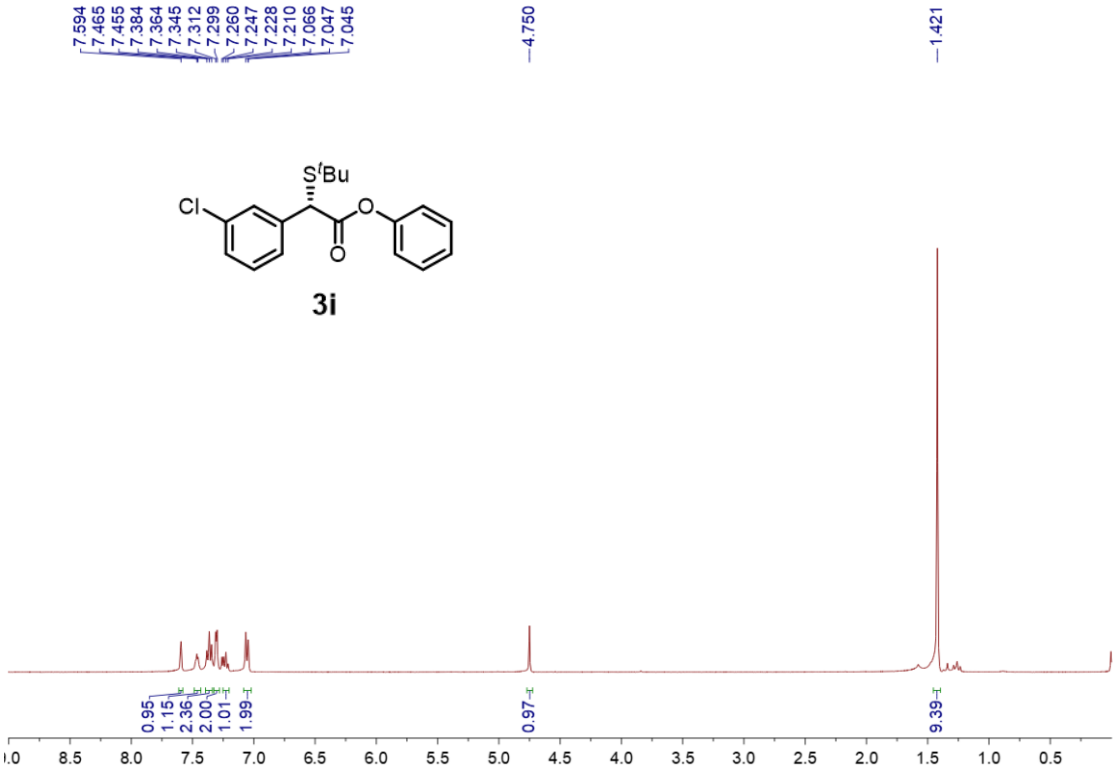
7.504
7.357
7.352
7.336
7.240
7.237
7.222
7.049
7.046
7.027
7.025
4.756
1.409
S^{t}Bu
O
O
Cl
3h
2.00
4.03
1.03
1.92
0.94
9.12
0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5


170.33
150.80
135.76
134.20
129.96
129.59
129.10
126.24
121.26
77.48
77.16
76.84
49.50
45.48
31.15
S^{t}Bu
Cl
O
O
3h
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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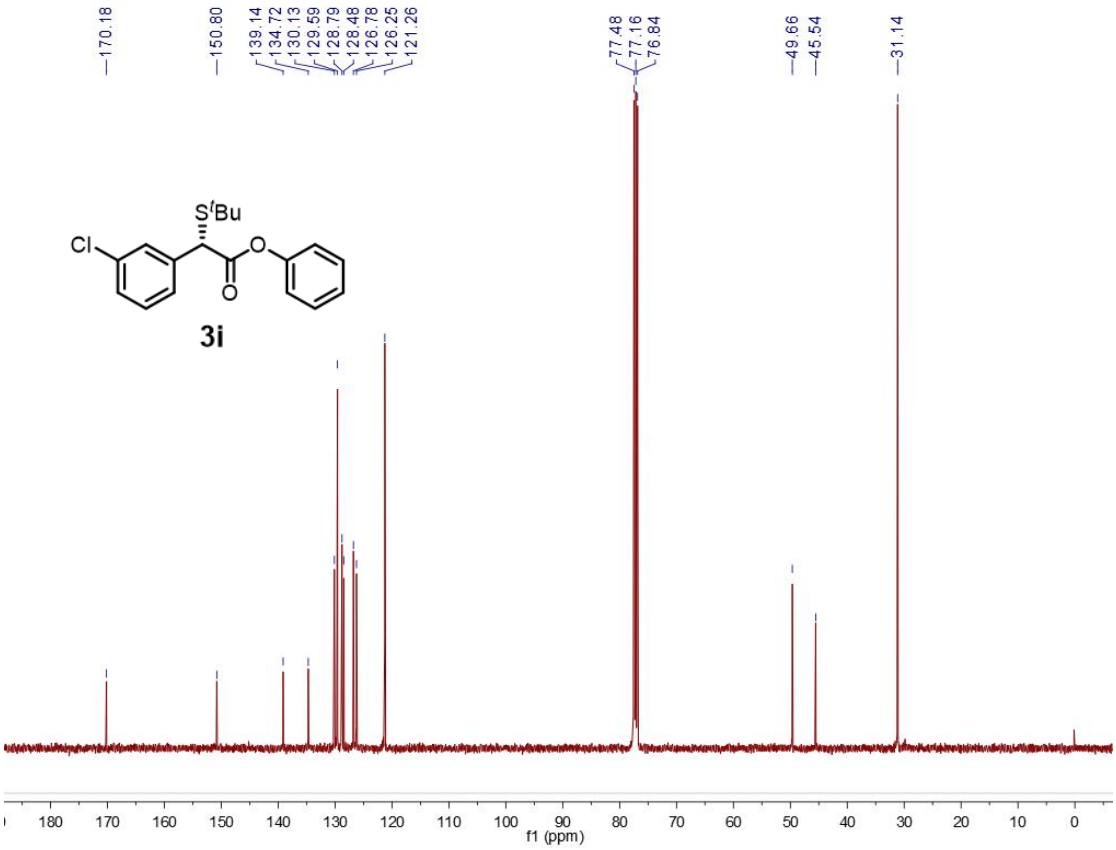
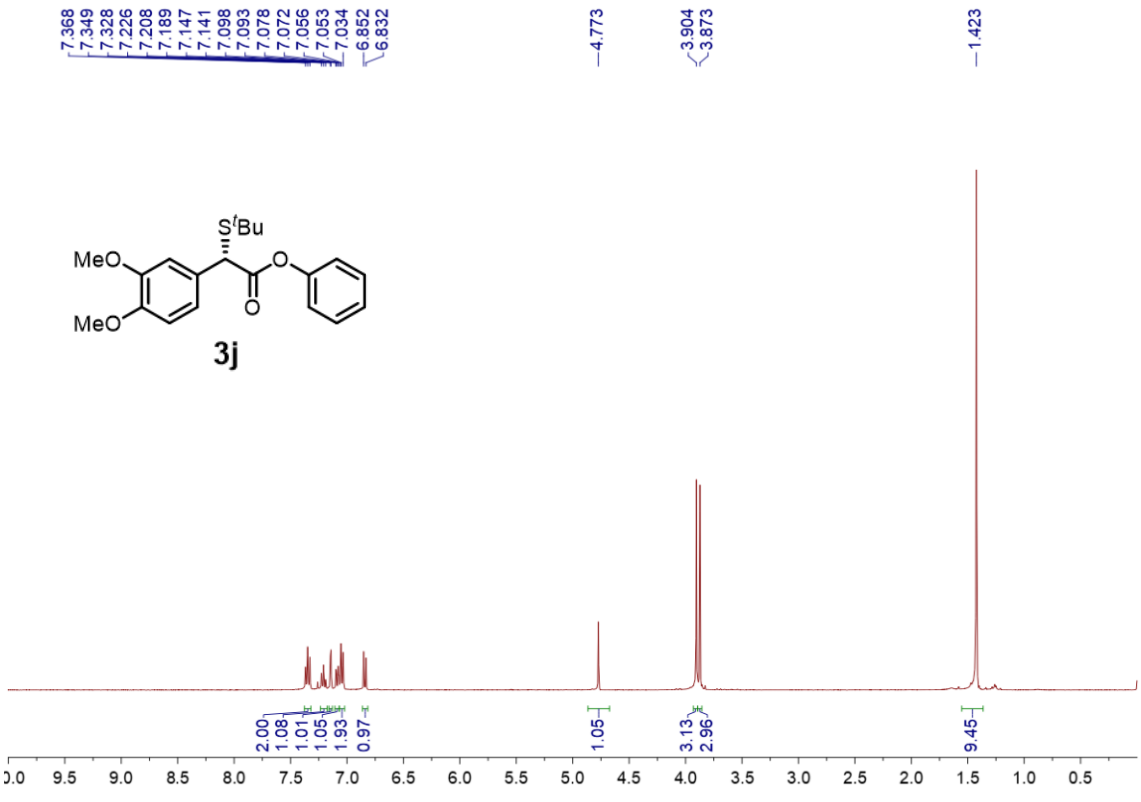
7.465
7.455
7.384
7.364
7.345
7.312
7.299
7.260
7.247
7.228
7.210
7.066
7.047
7.045
4.750
1.421
S^{t}Bu
Cl
O
O
3i
0.95
1.15
2.36
2.00
1.01
1.99
0.97
9.39
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5


170.18
150.80
139.14
134.72
130.13
129.59
128.79
128.48
126.78
126.25
121.26
77.48
77.16
76.84
49.66
45.54
31.14
S^{t}Bu
Cl
O
O
3i
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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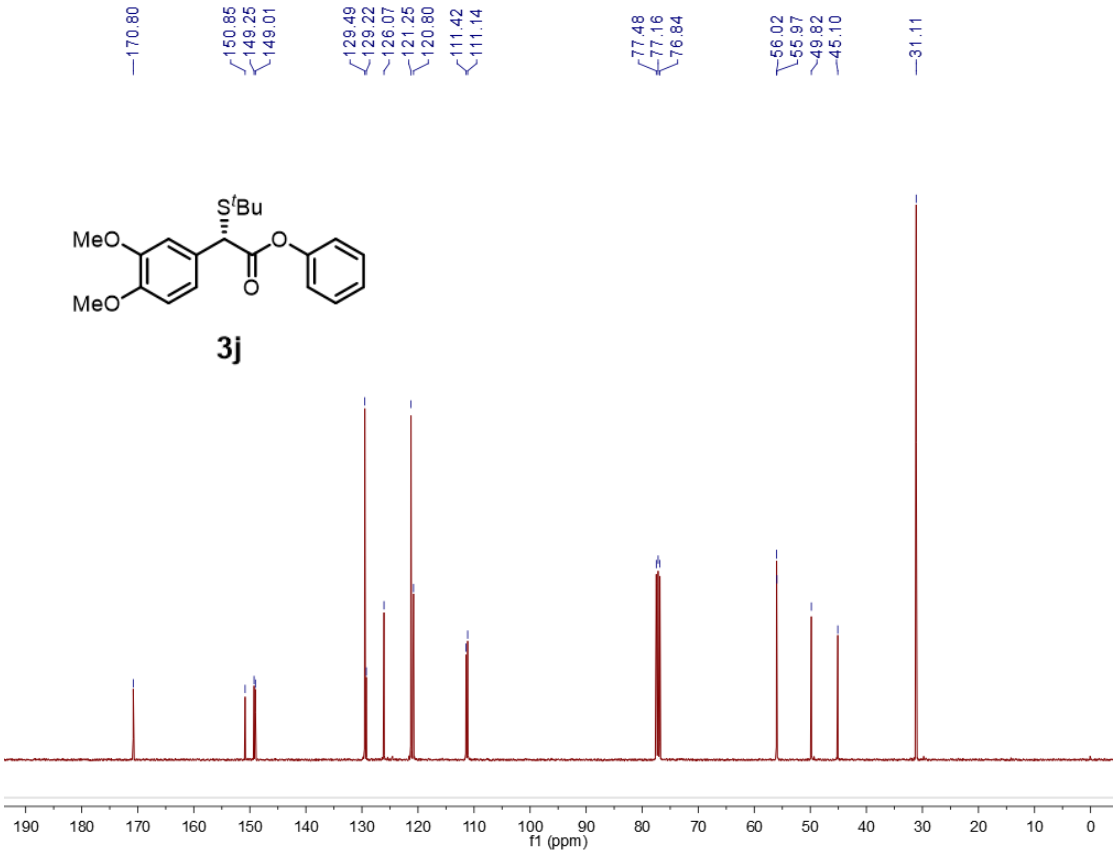
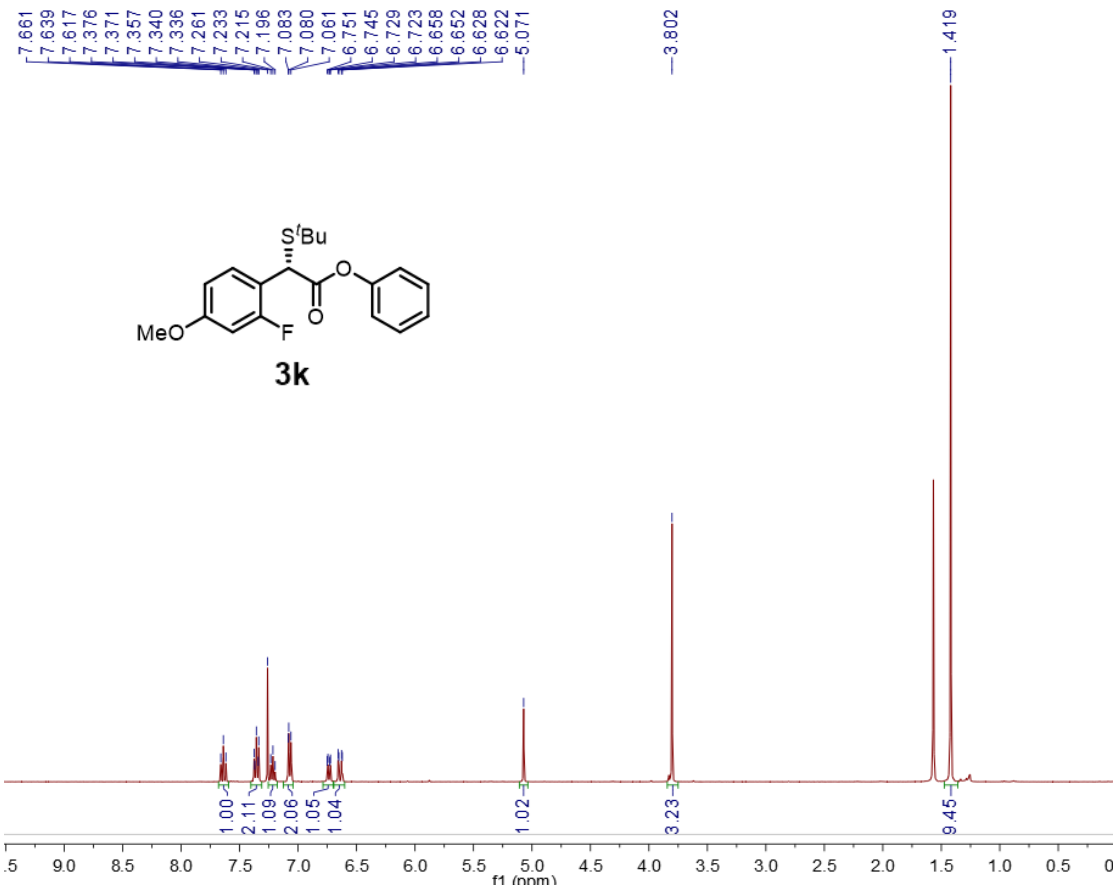
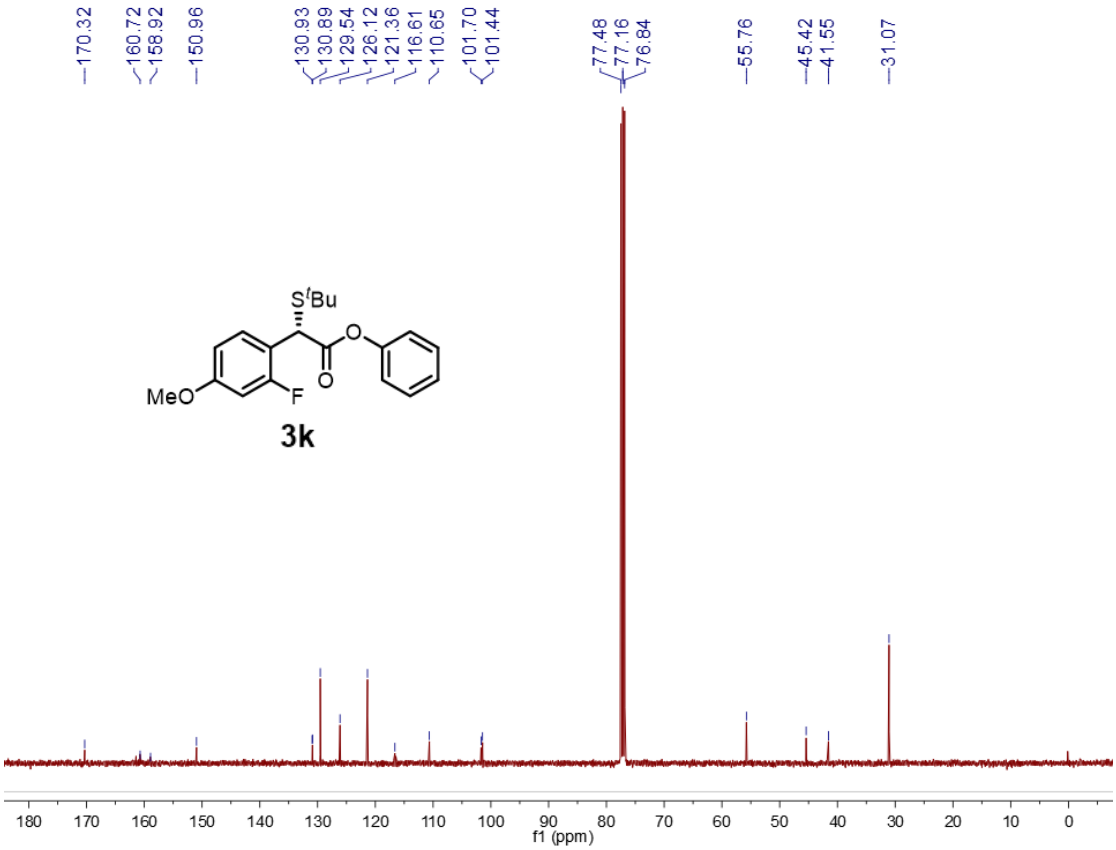
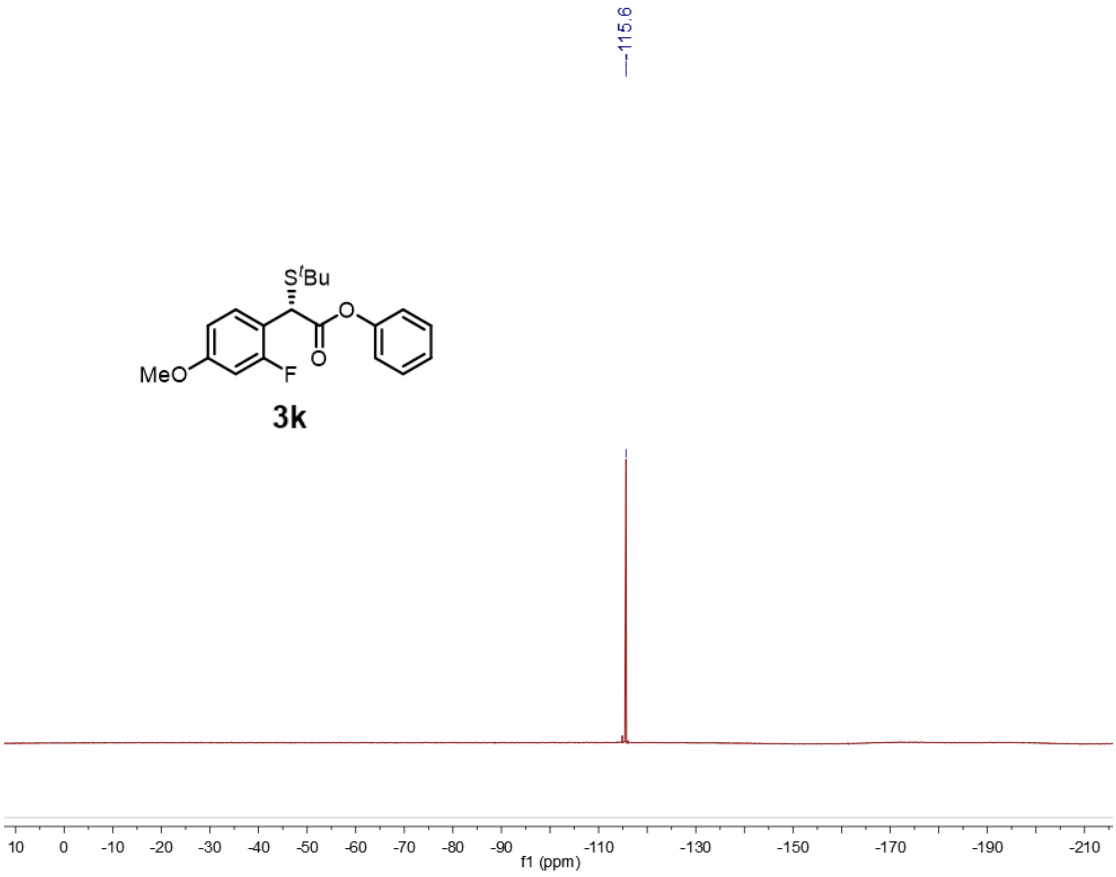
7.349
7.328
7.226
7.208
7.189
7.147
7.141
7.098
7.093
7.078
7.072
7.056
7.053
7.034
6.852
6.832
4.773
3.904
3.873
1.423
S^{t}Bu
MeO
MeO
O
O
3j
2.00
1.08
1.01
1.05
1.93
0.97
1.05
3.13
2.96
9.45
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5


170.80
150.85
149.25
149.01
129.49
129.22
126.07
121.25
120.80
111.42
111.14
77.48
77.16
76.84
56.02
55.97
49.82
45.10
31.11
S^{t}Bu
MeO
MeO
O
O
3j
f1 (ppm)

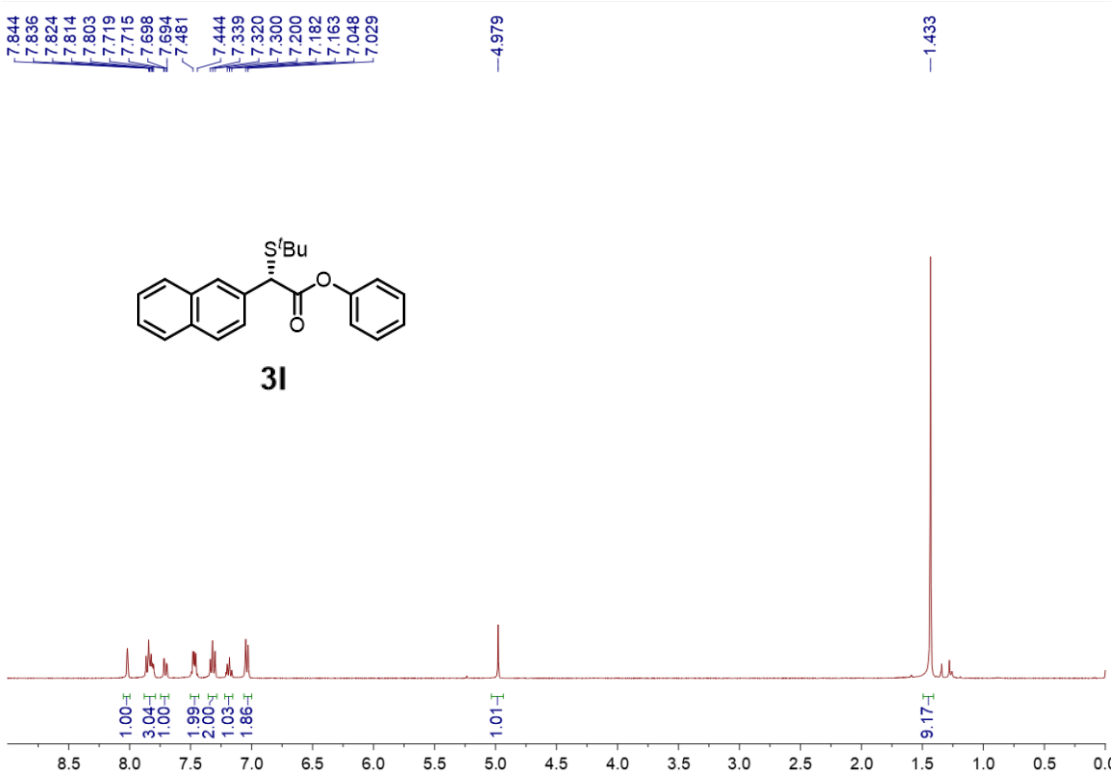

7.661
7.639
7.617
7.376
7.371
7.357
7.340
7.336
7.261
7.233
7.215
7.196
7.083
7.080
7.061
6.751
6.745
6.729
6.723
6.658
6.652
6.628
6.622
5.071
3.802
1.419
S^{t}Bu
MeO
F
O
O
3k
1.00
2.11
1.09
2.06
1.05
1.04
1.02
3.23
9.45
f1 (ppm)


170.32
160.72
158.92
150.96
130.93
130.89
129.54
126.12
121.36
116.61
110.65
101.70
101.44
77.48
77.16
76.84
55.76
45.42
41.55
31.07
S^{t}Bu
O
O
MeO
F
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

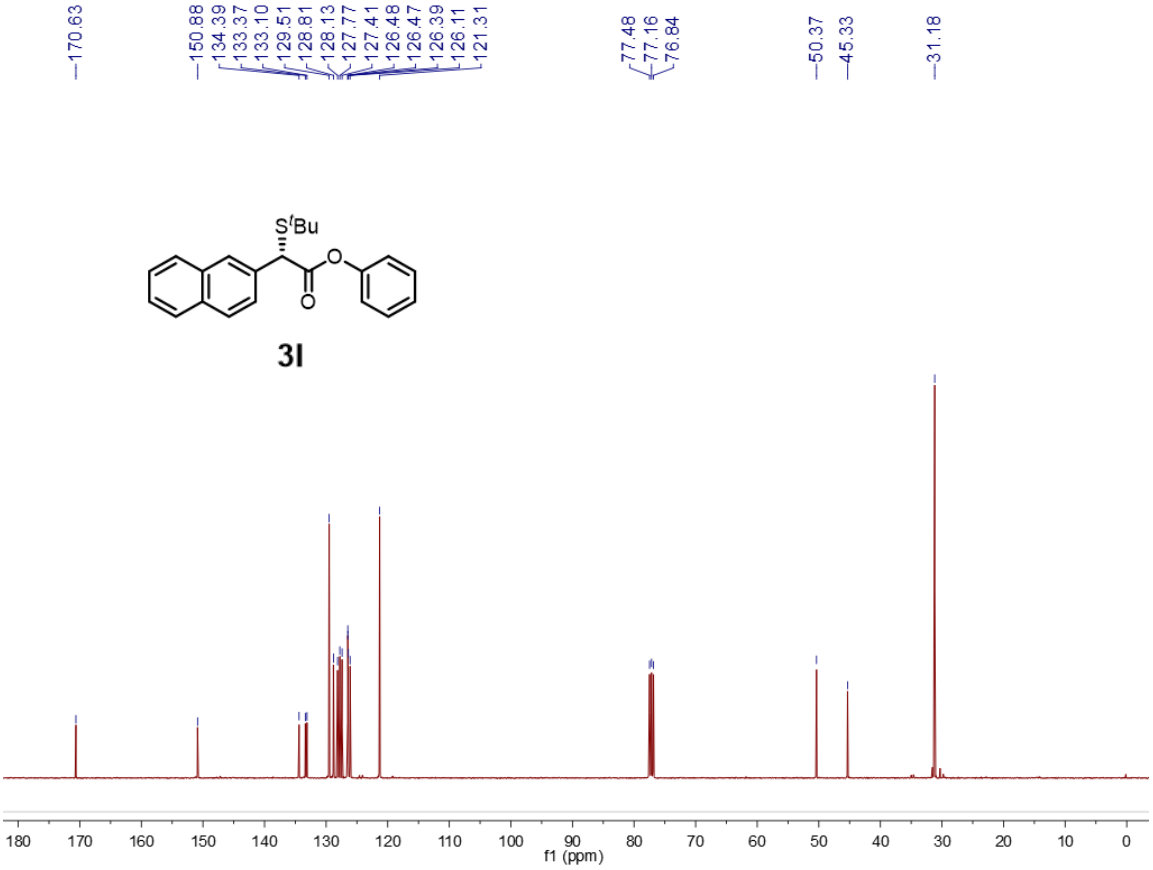
3k


115.6
S^{t}Bu
O
O
MeO
F
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -110 -130 -150 -170 -190 -210
f1 (ppm)

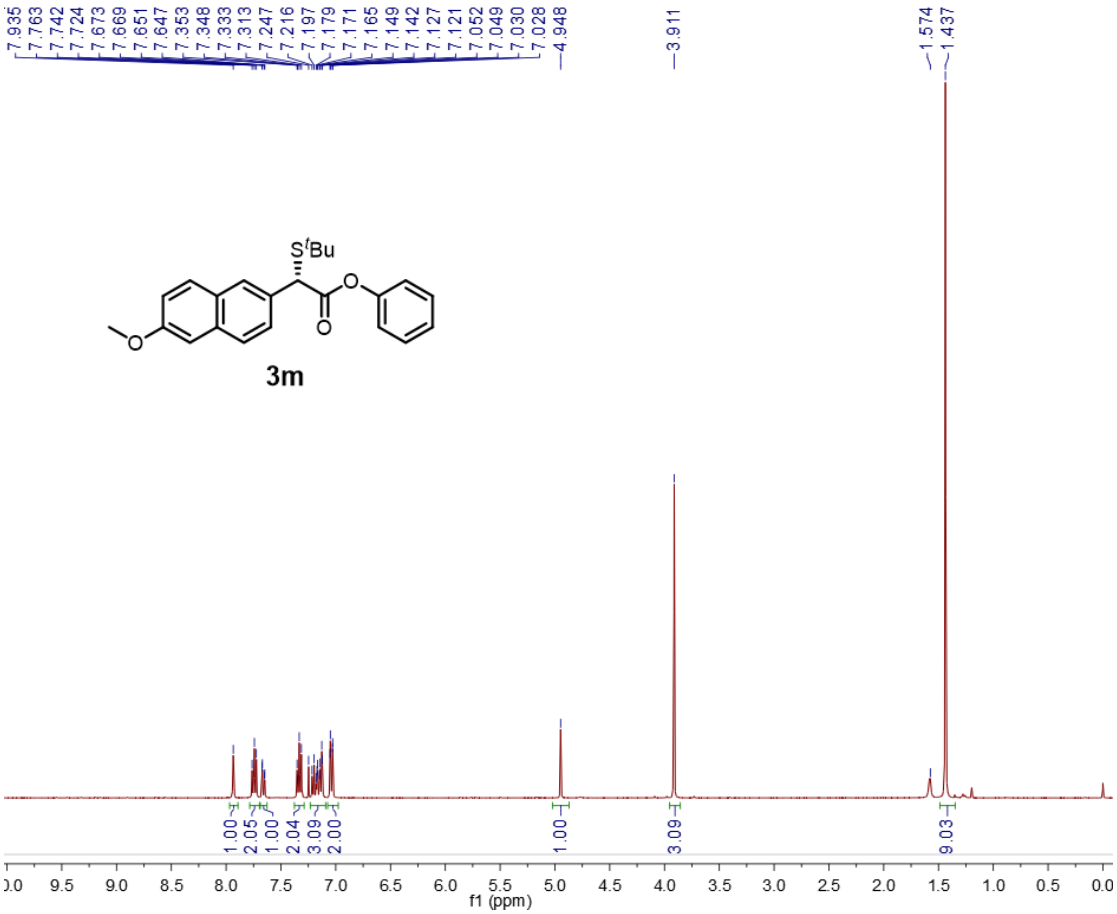
3k


7.844
7.836
7.824
7.814
7.803
7.719
7.715
7.698
7.694
7.481
7.444
7.339
7.320
7.300
7.200
7.182
7.163
7.048
7.029
4.979
1.433
S'Bu
O
O
1.00
3.04
1.00
1.99
2.00
1.03
1.86
1.01
9.17
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5

3l

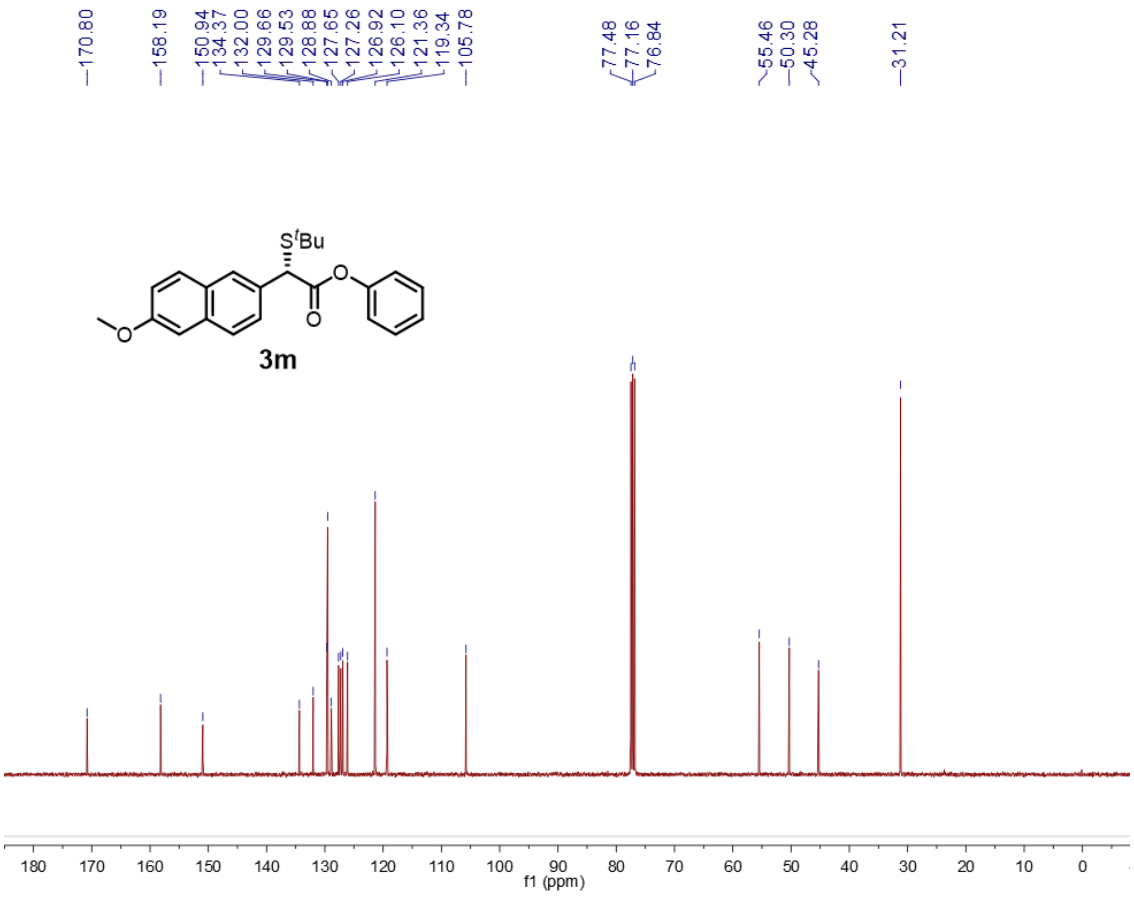

170.63
150.88
134.39
133.37
133.10
129.51
128.81
128.13
127.77
127.41
126.48
126.47
126.39
126.11
121.31
77.48
77.16
76.84
50.37
45.33
31.18
S'Bu
O
O
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

3l


7.935
7.763
7.742
7.724
7.673
7.669
7.651
7.647
7.353
7.348
7.333
7.313
7.247
7.216
7.197
7.179
7.171
7.165
7.149
7.142
7.127
7.121
7.052
7.049
7.030
7.028
4.948
3.911
1.574
1.437
1.00
2.05
1.00
2.04
3.09
2.00
1.00
3.09
9.03
f1 (ppm)

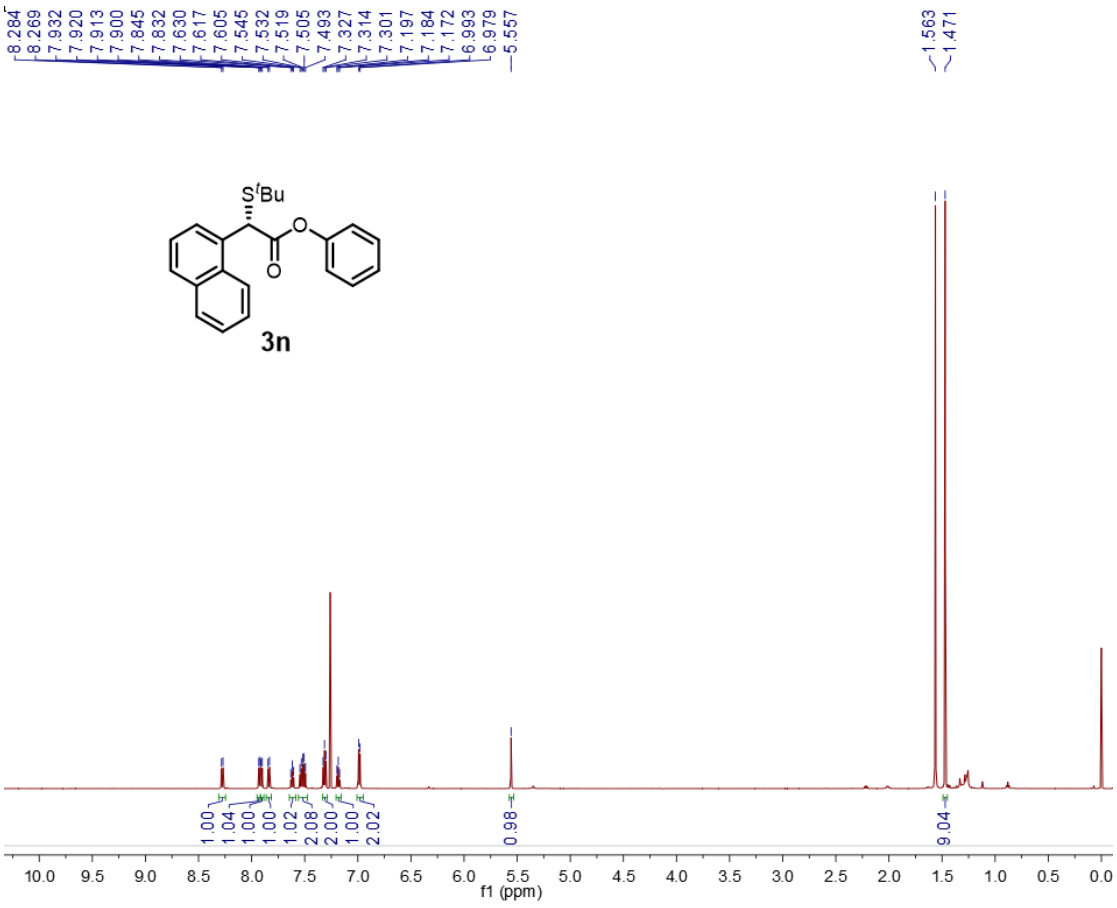
S'Bu
O
O
O

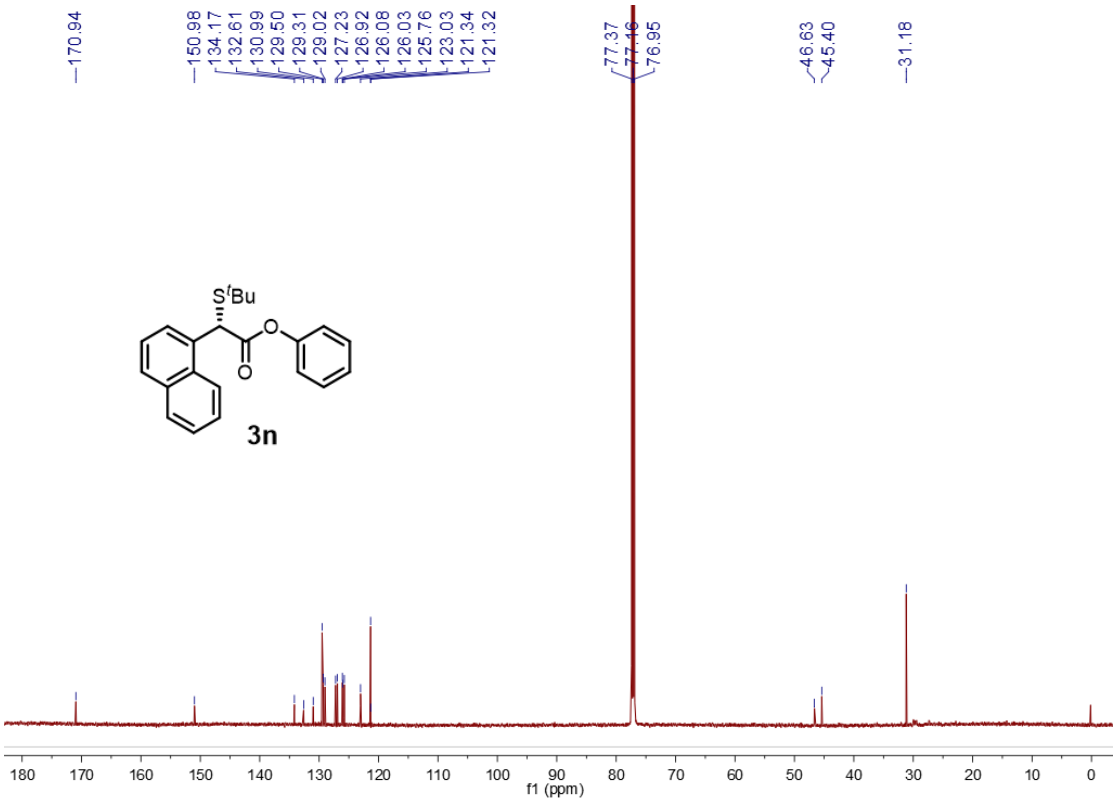
3m

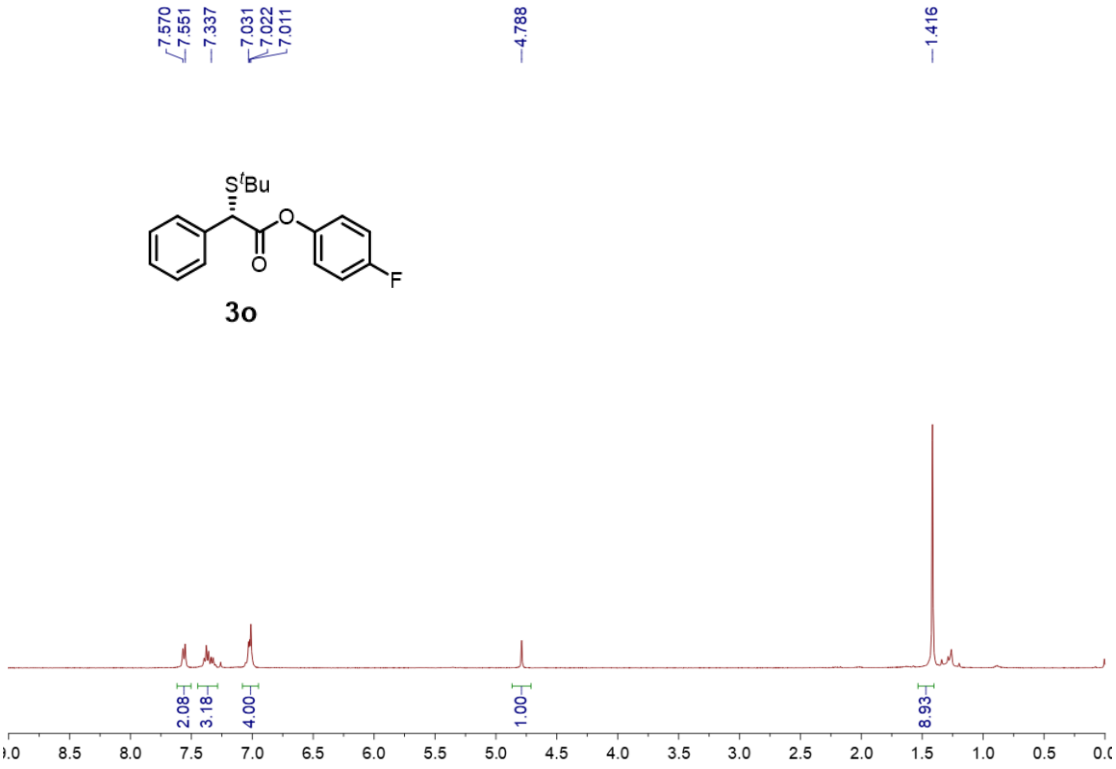

170.80
158.19
150.94
134.37
132.00
129.66
129.53
128.88
127.65
127.26
126.92
126.10
121.36
119.34
105.78
77.48
77.16
76.84
55.46
50.30
45.28
31.21
f1 (ppm)

S'Bu
O
O
O

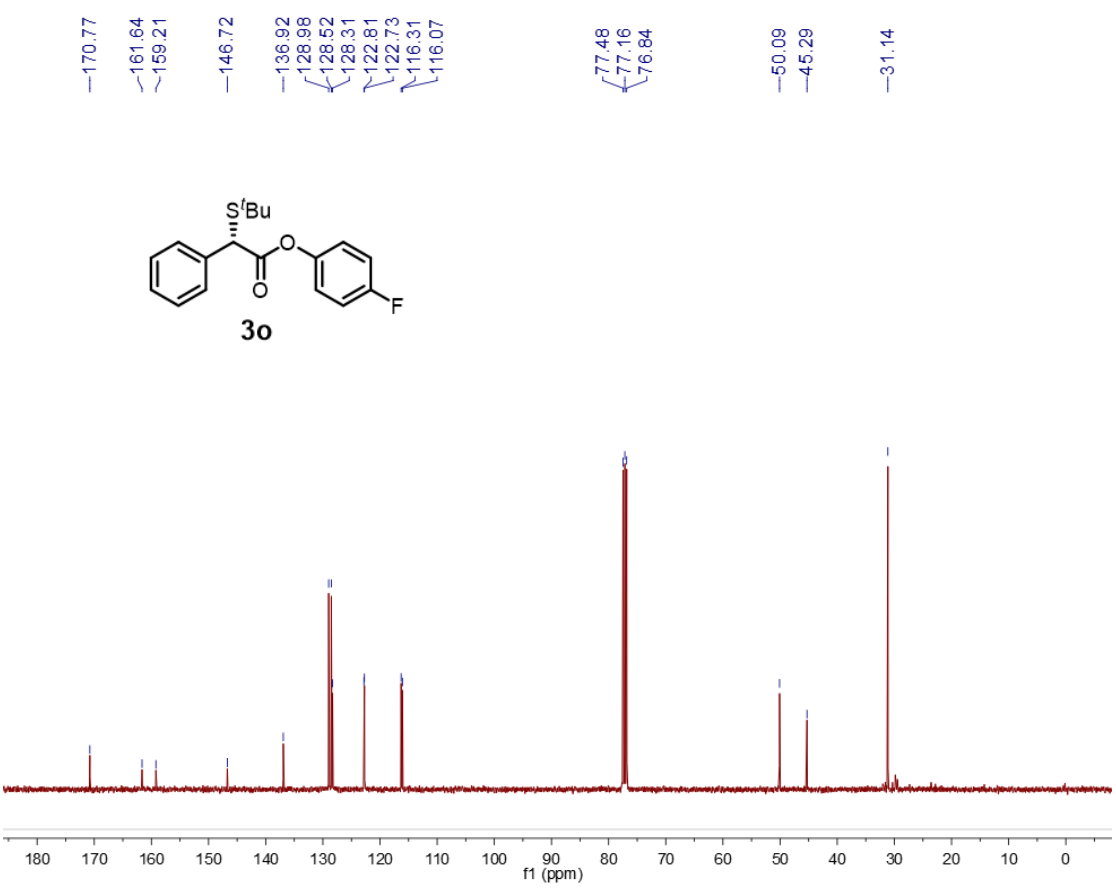
3m


8.284
8.269
7.932
7.920
7.913
7.900
7.845
7.832
7.630
7.617
7.605
7.545
7.532
7.519
7.505
7.493
7.327
7.314
7.301
7.197
7.184
7.172
6.993
6.979
5.557
1.563
1.471
S^{t}Bu
O
O
3n
1.00
1.04
1.00
1.00
1.02
2.08
2.00
1.00
2.02
0.98
9.04
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

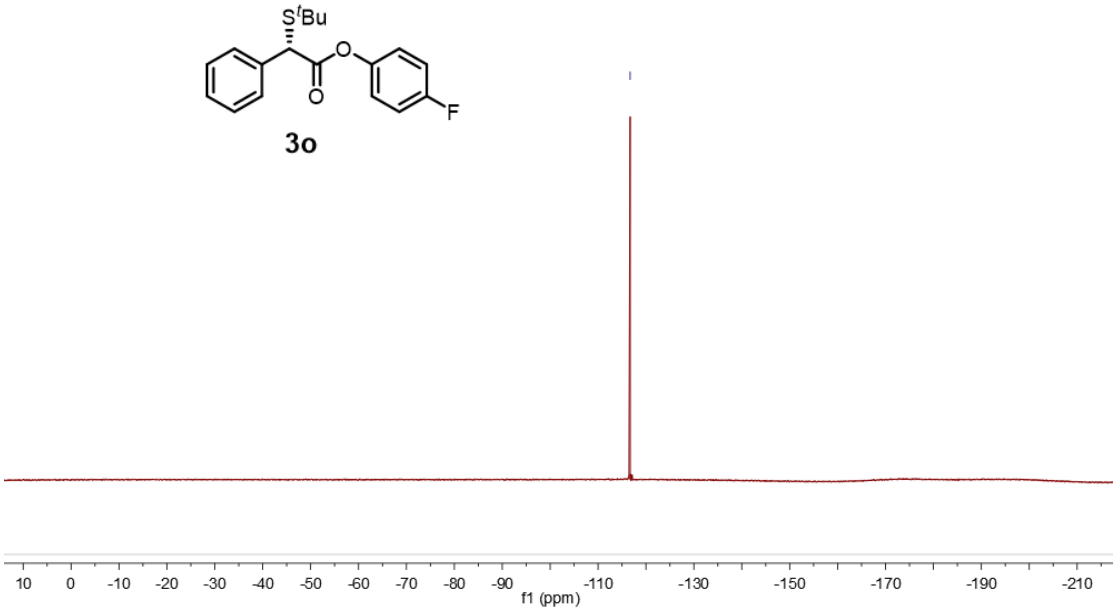

170.94
150.98
134.17
132.61
130.99
129.50
129.31
129.02
127.23
126.92
126.08
126.03
125.76
123.03
121.34
121.32
77.37
77.16
76.95
46.63
45.40
31.18
S^{t}Bu
O
O
3n
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.570
7.551
7.337
7.031
7.022
7.011
4.788
1.416
S^{t}Bu
O
O
F
2.08
3.18
4.00
1.00
8.93
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5

3o

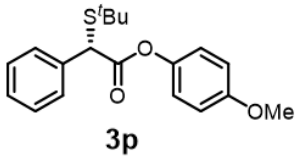

170.77
161.64
159.21
146.72
136.92
128.98
128.52
128.31
122.81
122.73
116.31
116.07
77.48
77.16
76.84
50.09
45.29
31.14
S^{t}Bu
O
O
F
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

3o

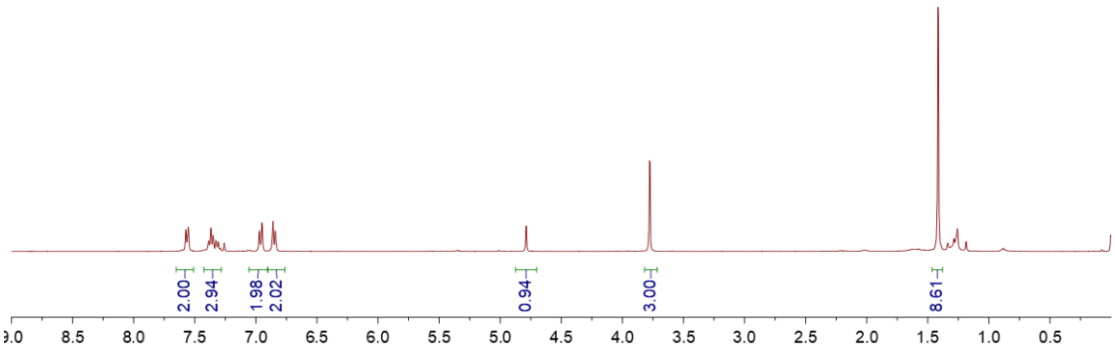

-116.7
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -110 -130 -150 -170 -190 -210
f1 (ppm)

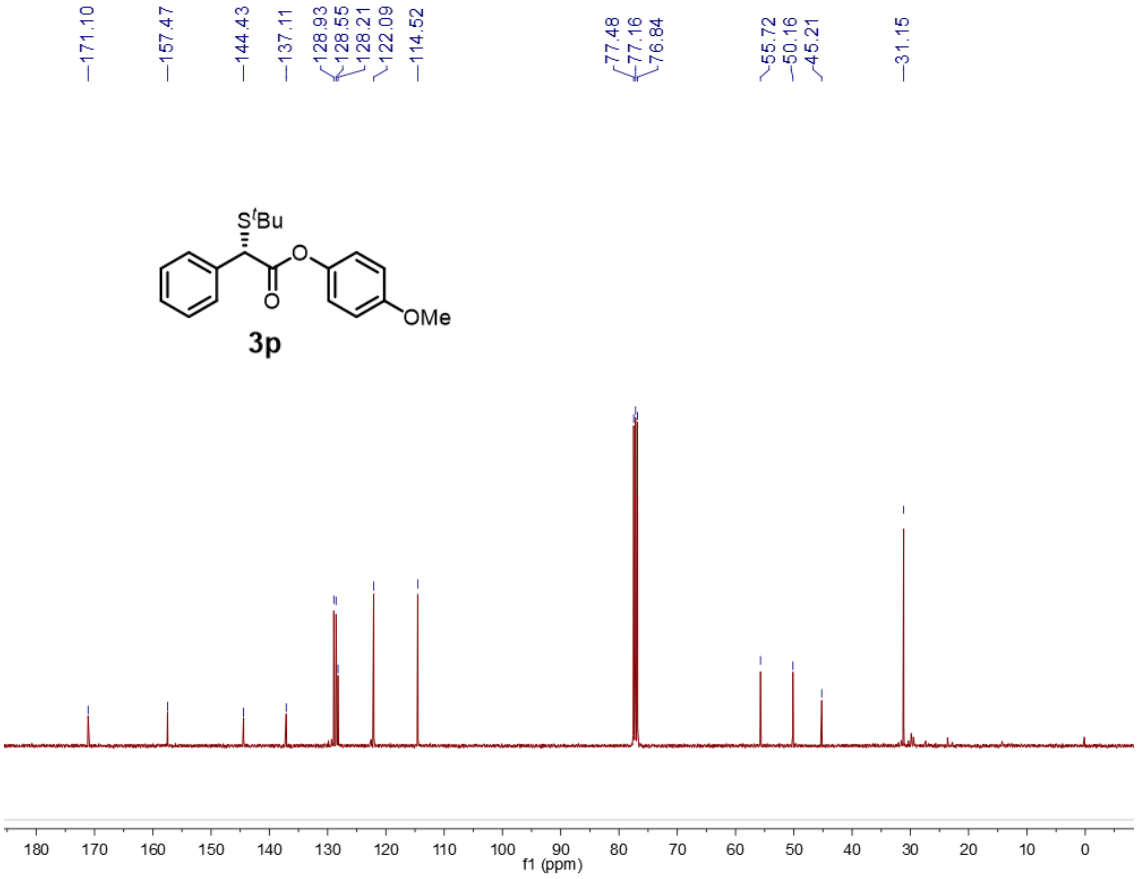
3o

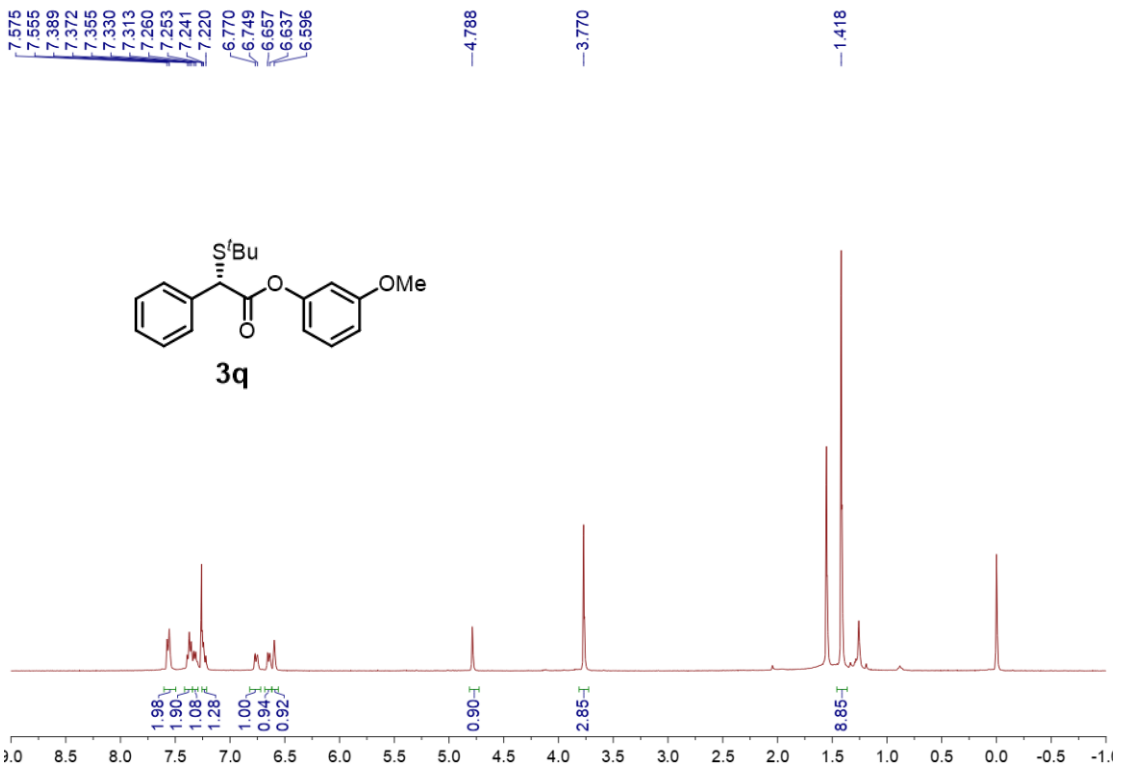

7.573
7.554
7.310
6.969
6.951
6.859
6.841
4.786
3.778
1.417

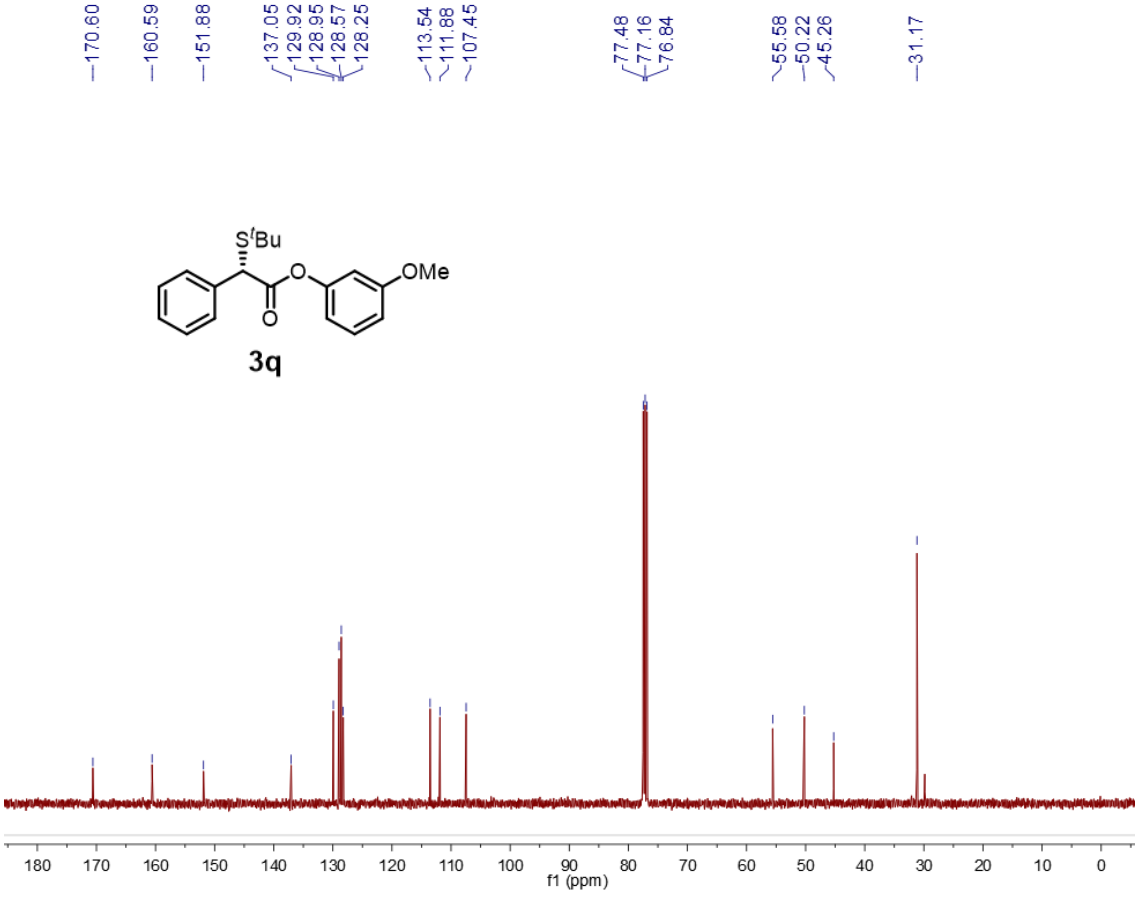


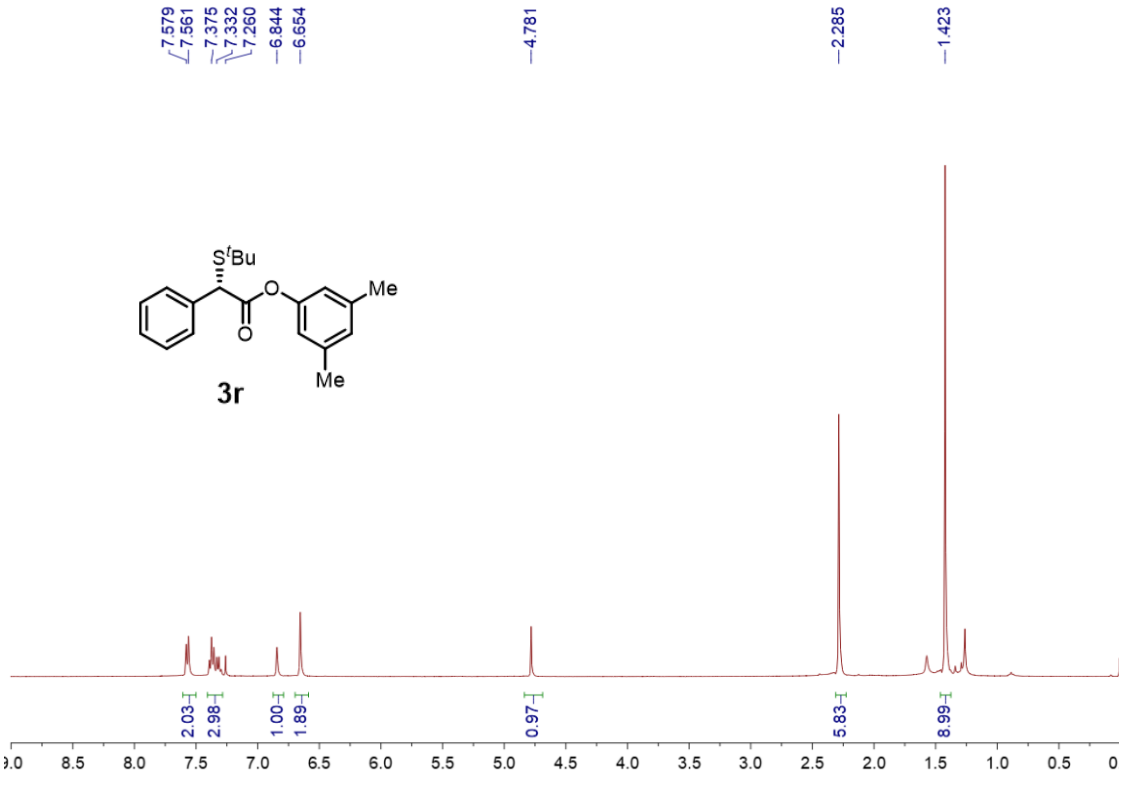
3p

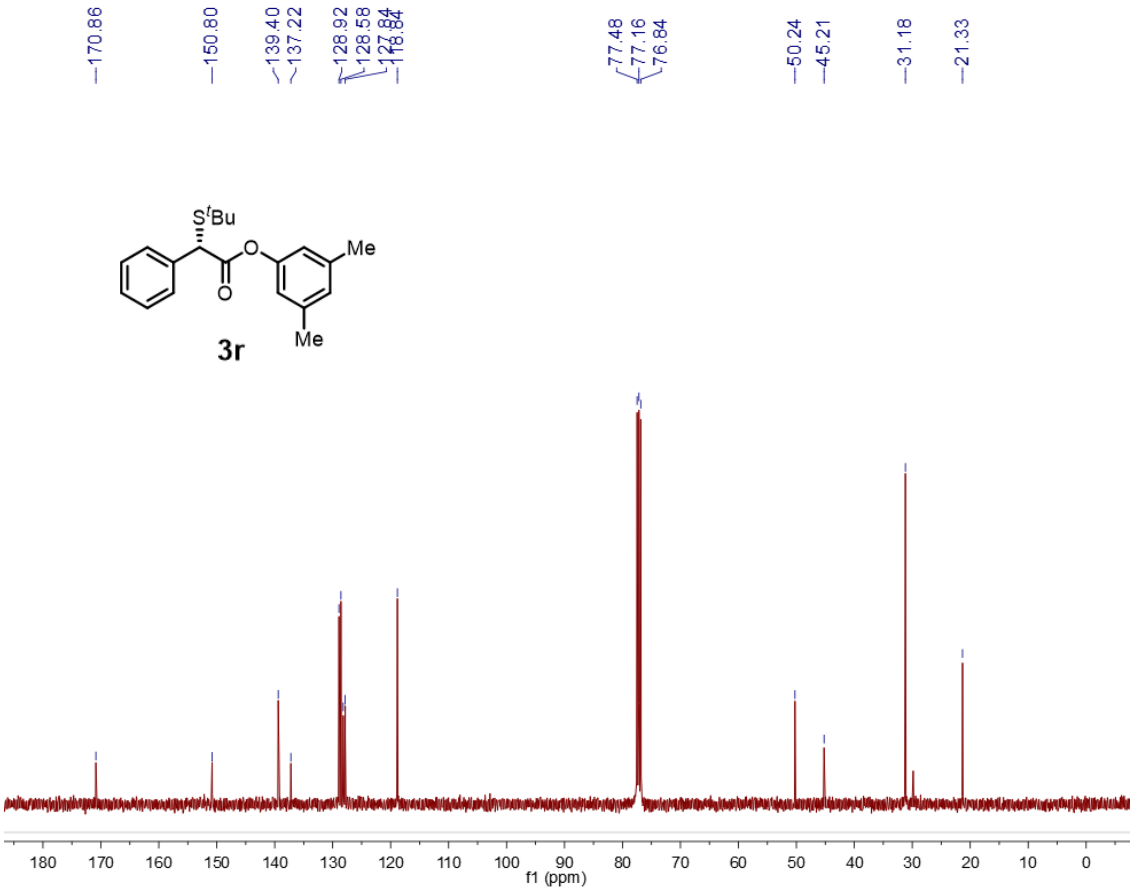

2.00
2.94
1.98
2.02
0.94
3.00
8.61
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5

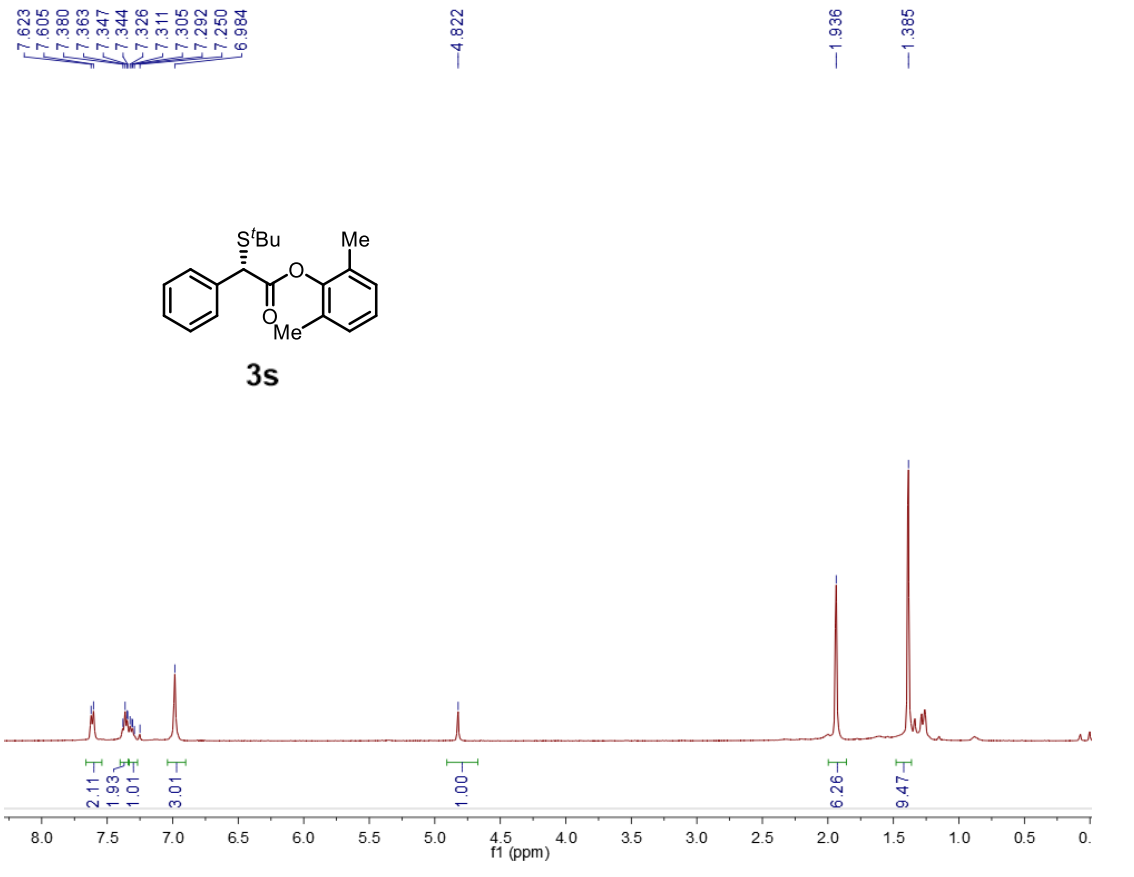

171.10
157.47
144.43
137.11
128.93
128.55
128.21
122.09
114.52
77.48
77.16
76.84
55.72
50.16
45.21
31.15
S^{t}Bu
O
O
OMe
3p
f1 (ppm)

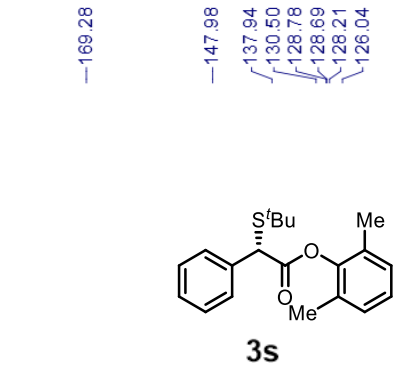

7.575
7.555
7.389
7.372
7.355
7.330
7.313
7.260
7.253
7.241
7.220
6.770
6.749
6.657
6.637
6.596
4.788
3.770
1.418
S^{t}Bu
O
O
OMe
3q
1.98
1.90
1.08
1.28
1.00
0.94
0.92
0.90
2.85
8.85


170.60
160.59
151.88
137.05
129.92
128.95
128.57
128.25
113.54
111.88
107.45
77.48
77.16
76.84
55.58
50.22
45.26
31.17
S^{t}Bu
OMe
O
O
3q
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

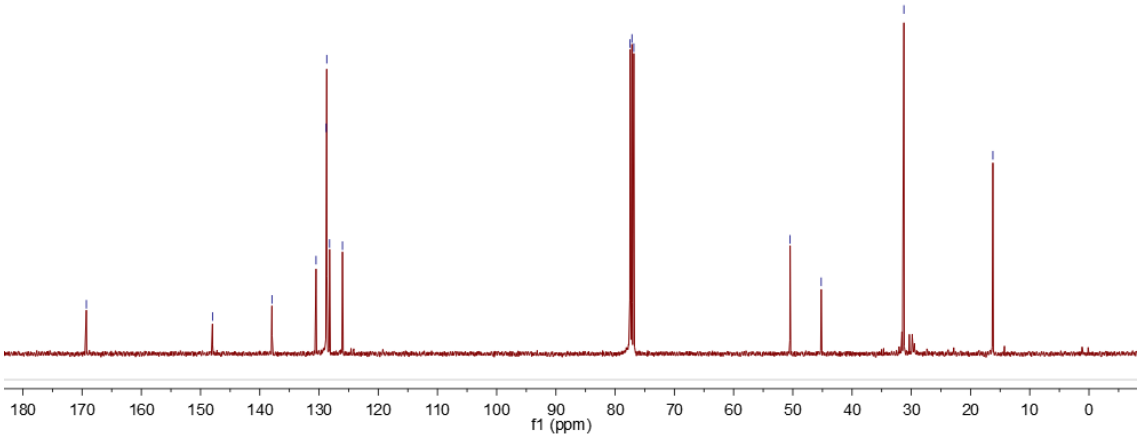

7.579
7.561
7.375
7.332
7.260
6.844
6.654
4.781
2.285
1.423
S^{t}Bu
Me
Me
O
O
3r
2.03
2.98
1.00
1.89
0.97
5.83
8.99
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0

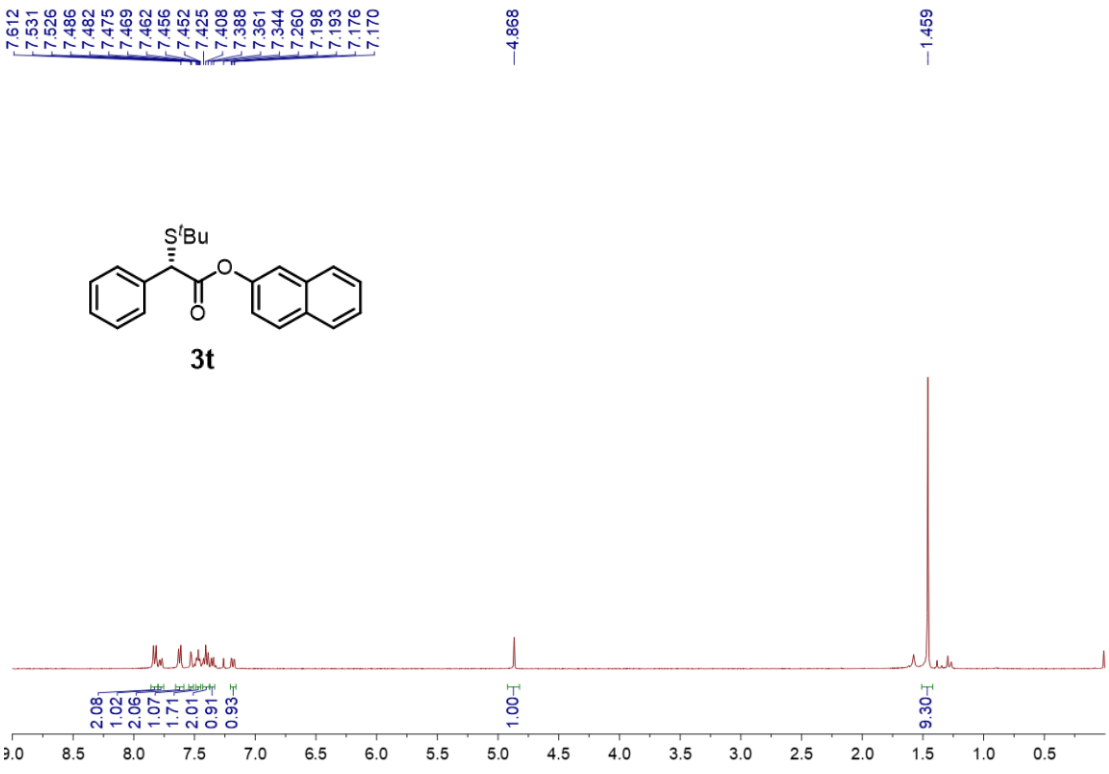

170.86
150.80
139.40
137.22
128.92
128.58
77.48
77.16
76.84
50.24
45.21
31.18
21.33
S^{t}Bu
Me
Me
O
O
3r
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.623
7.605
7.380
7.363
7.347
7.344
7.326
7.311
7.305
7.292
7.250
6.984
4.822
1.936
1.385
S^{t}Bu
Me
O
O
Me
3s
2.11
1.93
1.01
3.01
1.00
6.26
9.47
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.
f1 (ppm)

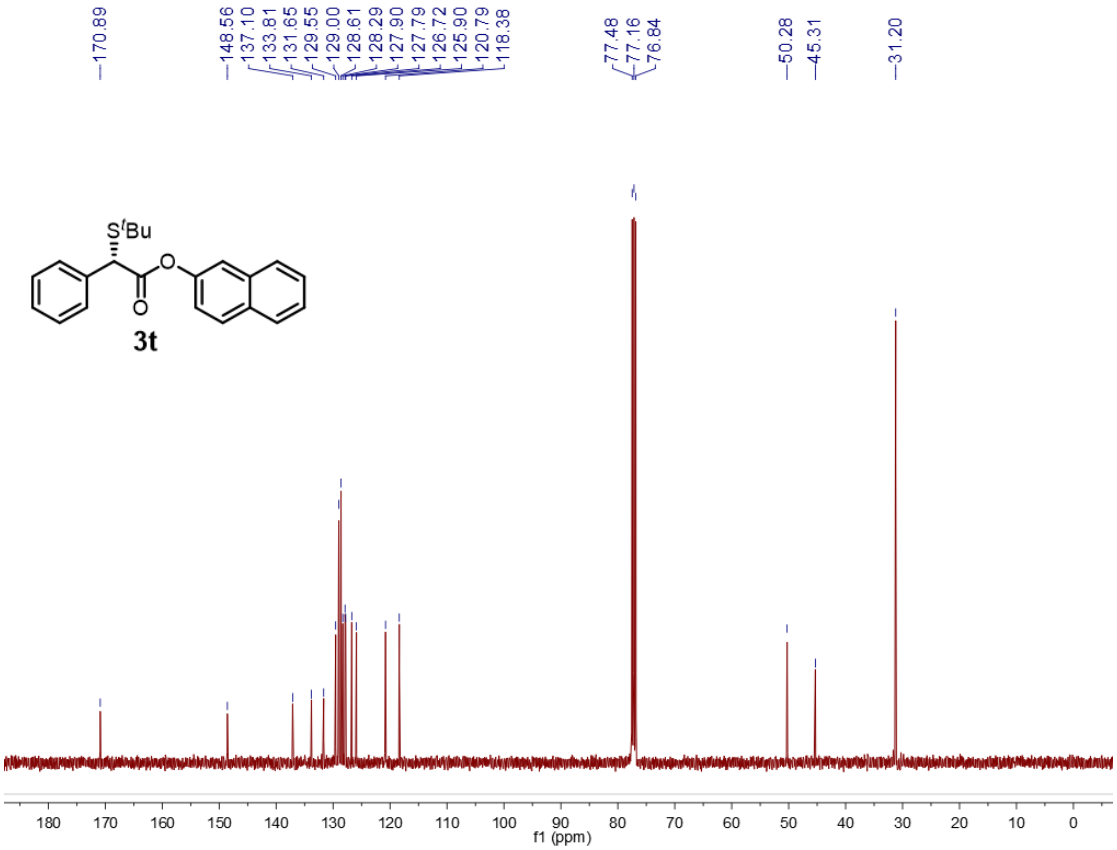

169.28
147.98
137.94
130.50
128.78
128.69
128.21
126.04
77.48
77.16
76.84
50.46
45.21
31.25
16.22
S^{t}Bu
Me
O
O
Me

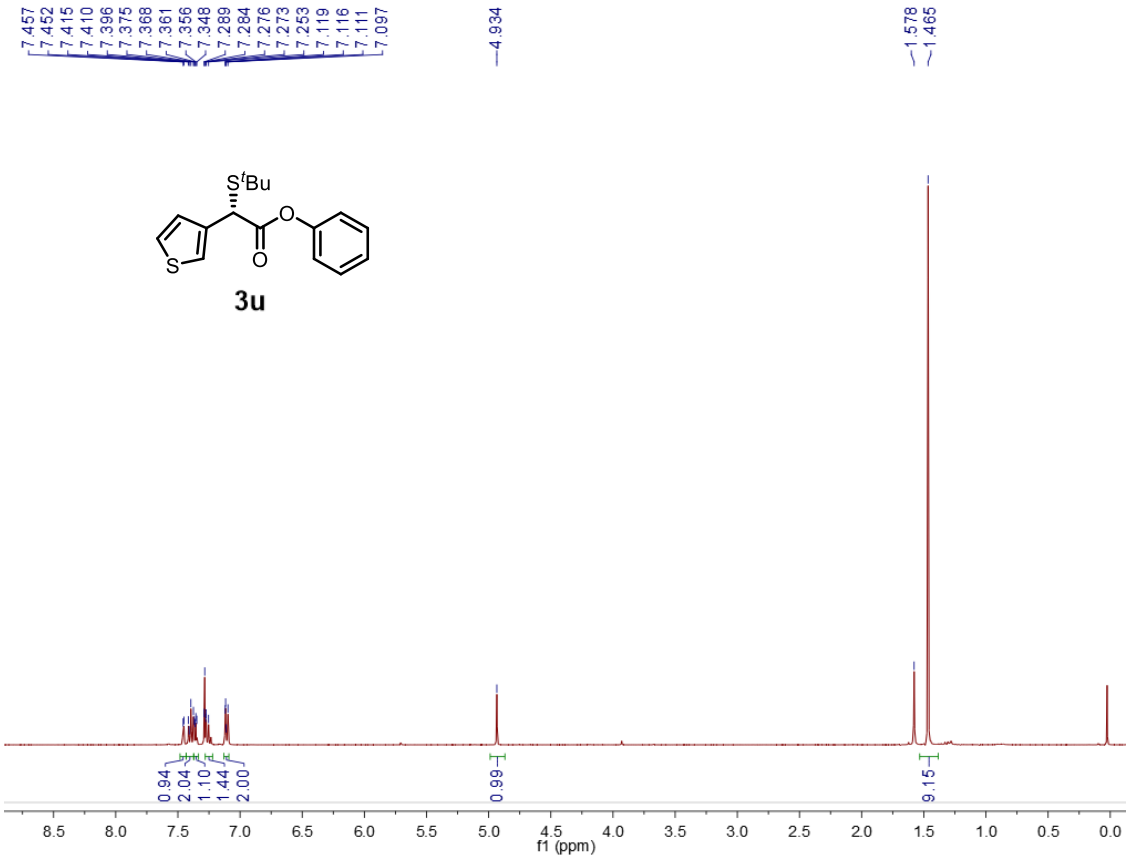
3s

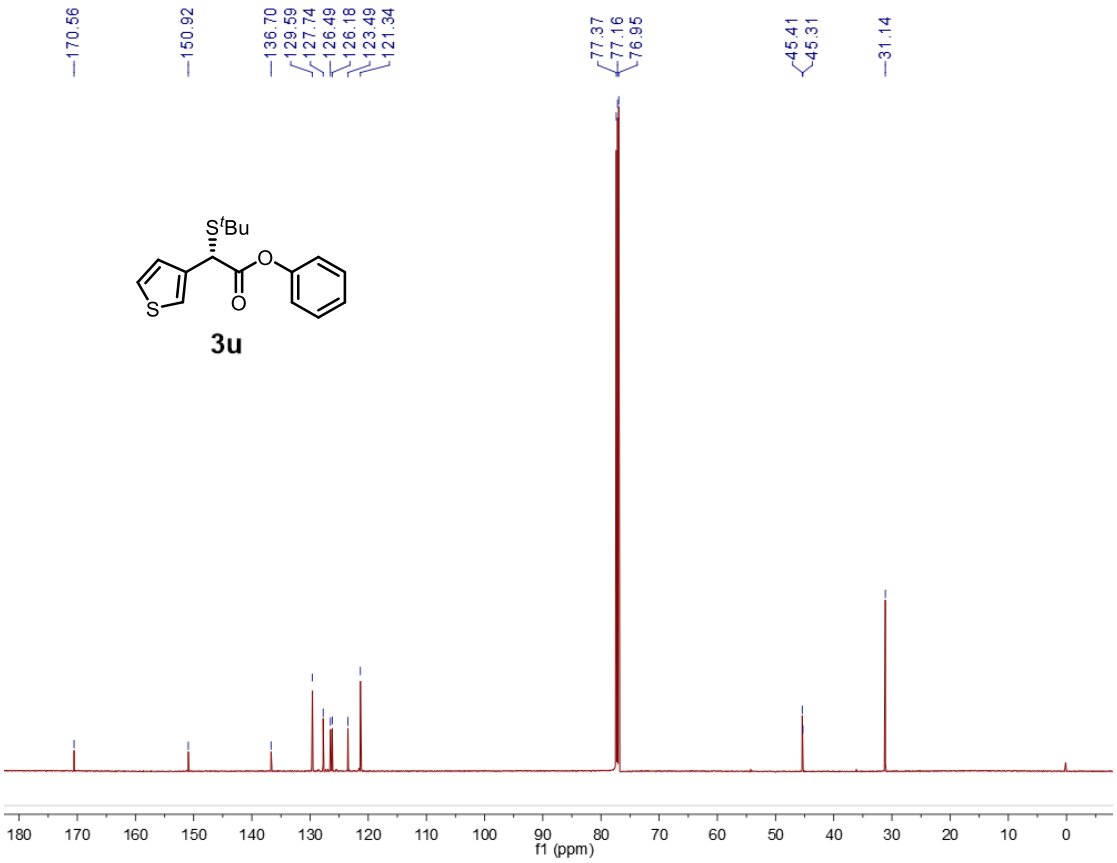

180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

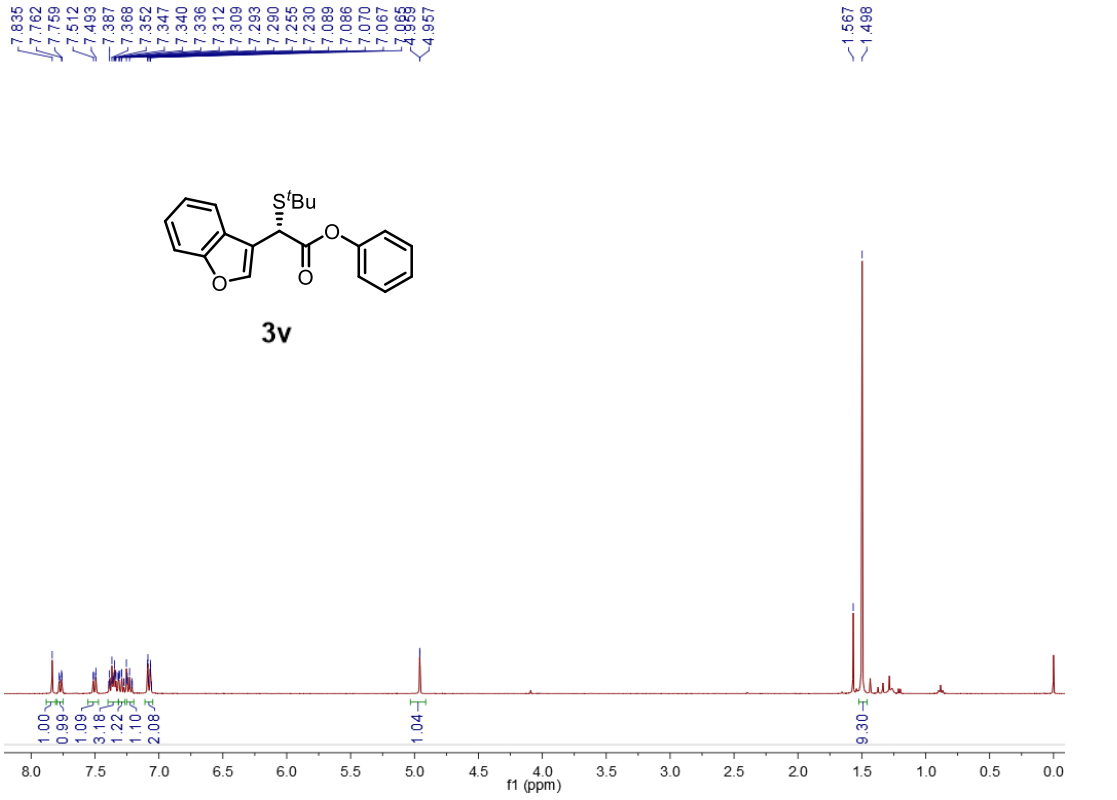

7.612
7.531
7.526
7.486
7.482
7.475
7.469
7.462
7.456
7.452
7.425
7.408
7.388
7.361
7.344
7.260
7.198
7.193
7.176
7.170
4.868
1.459
S^{t}Bu
O
O
2.08
1.02
2.06
1.07
1.71
2.01
0.91
0.93
1.00
9.30
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5

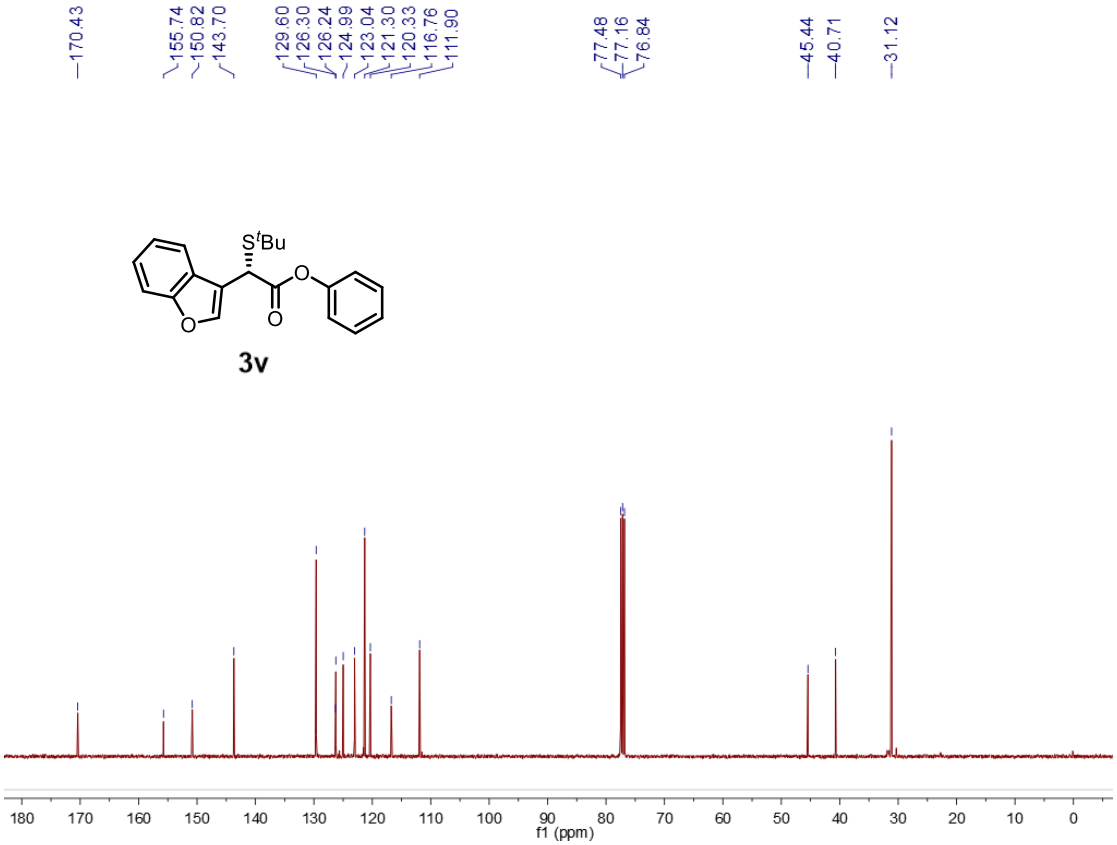
3t

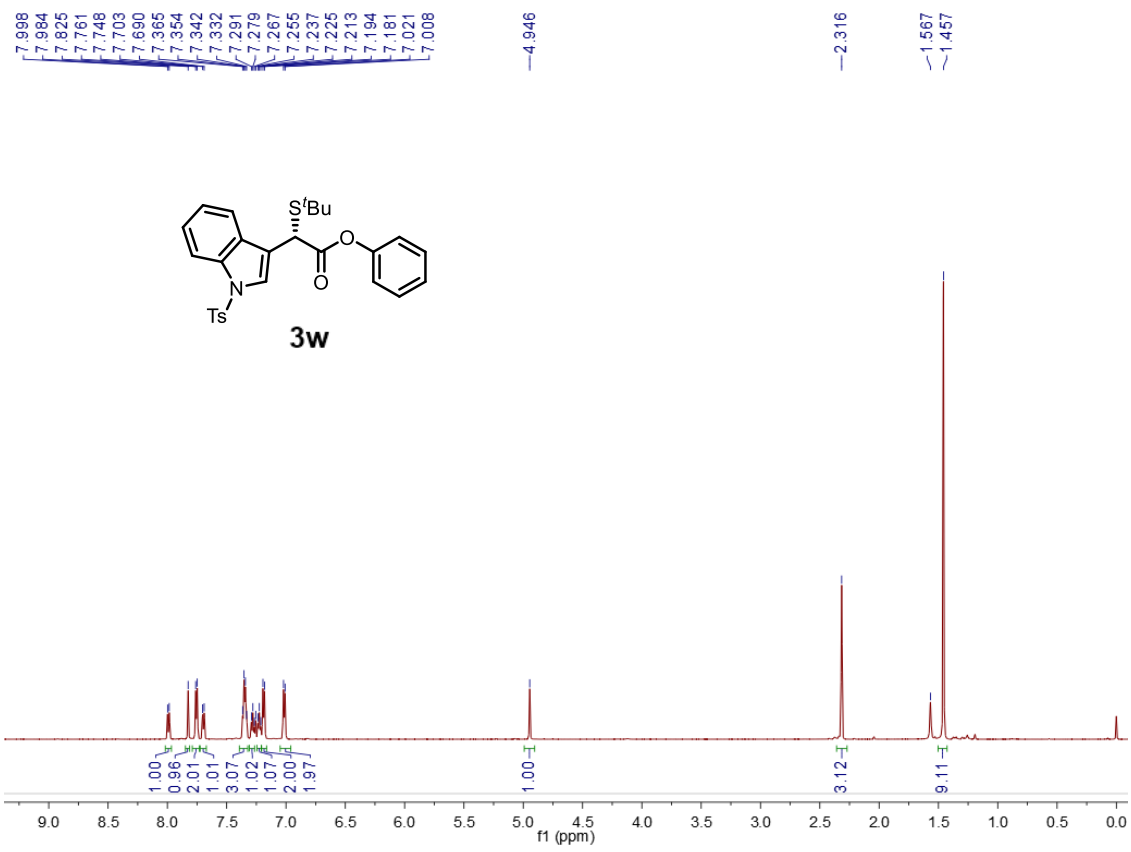

170.89
148.56
137.10
133.81
131.65
129.55
129.00
128.61
128.29
127.90
127.79
126.72
125.90
120.79
118.38
77.48
77.16
76.84
50.28
45.31
31.20
S^{t}Bu
O
O
3t
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.457
7.452
7.415
7.410
7.396
7.375
7.368
7.361
7.356
7.348
7.289
7.284
7.276
7.273
7.253
7.119
7.116
7.111
7.097
4.934
1.578
1.465
S^{t}Bu
O
O
S
3u
0.94
2.04
1.10
1.44
2.00
0.99
9.15
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

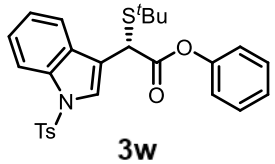

170.56
150.92
136.70
129.59
127.74
126.49
126.18
123.49
121.34
77.37
77.16
76.95
45.41
45.31
31.14
S
tBu
O
O
S
3u
f1 (ppm)


7.835
7.762
7.759
7.512
7.493
7.387
7.368
7.352
7.347
7.340
7.336
7.312
7.309
7.293
7.290
7.255
7.230
7.089
7.086
7.070
7.067
4.957
1.567
1.498
S
tBu
O
O
O
3v
1.00
0.99
1.09
3.18
1.22
1.10
2.08
1.04
9.30
f1 (ppm)

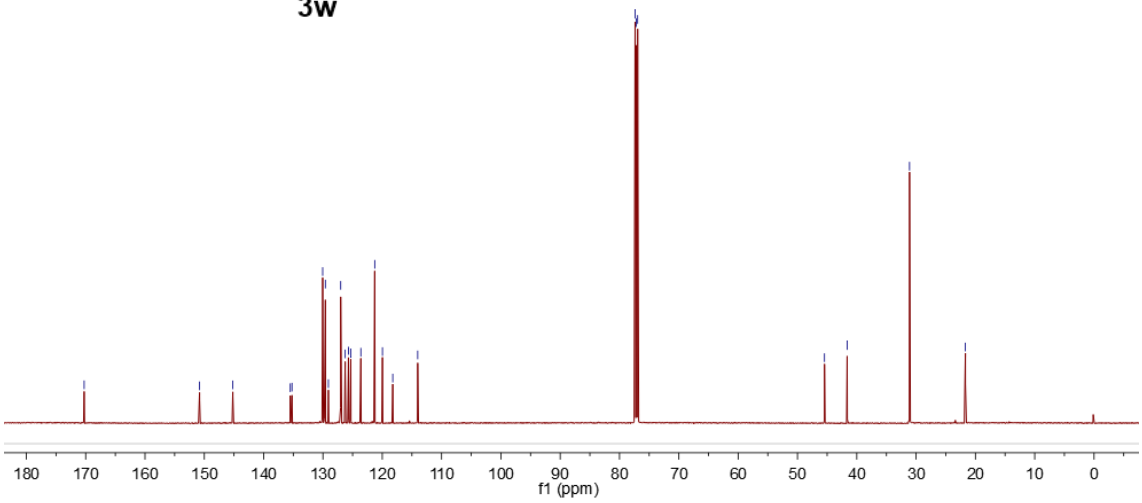

170.43
155.74
150.82
143.70
129.60
126.30
126.24
124.99
123.04
121.30
120.33
116.76
111.90
77.48
77.16
76.84
45.44
40.71
31.12
S^{t}Bu
O
O
O
3v
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.998
7.984
7.825
7.761
7.748
7.703
7.690
7.365
7.354
7.342
7.332
7.291
7.279
7.267
7.255
7.237
7.225
7.213
7.194
7.181
7.021
7.008
4.946
2.316
1.567
1.457
S^{t}Bu
O
O
N
Ts
3w
1.00
0.96
2.01
1.01
3.07
1.02
1.07
2.00
1.97
1.00
3.12
9.11
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

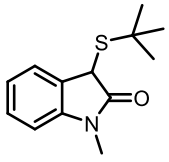

170.26
150.80
145.20
135.51
135.22
130.04
129.59
129.08
127.01
126.25
125.70
125.31
123.61
121.27
119.97
118.23
114.02
77.37
77.16
76.95
45.44
41.63
31.11
21.69


S^{t}Bu
O
O
N
Ts

3w

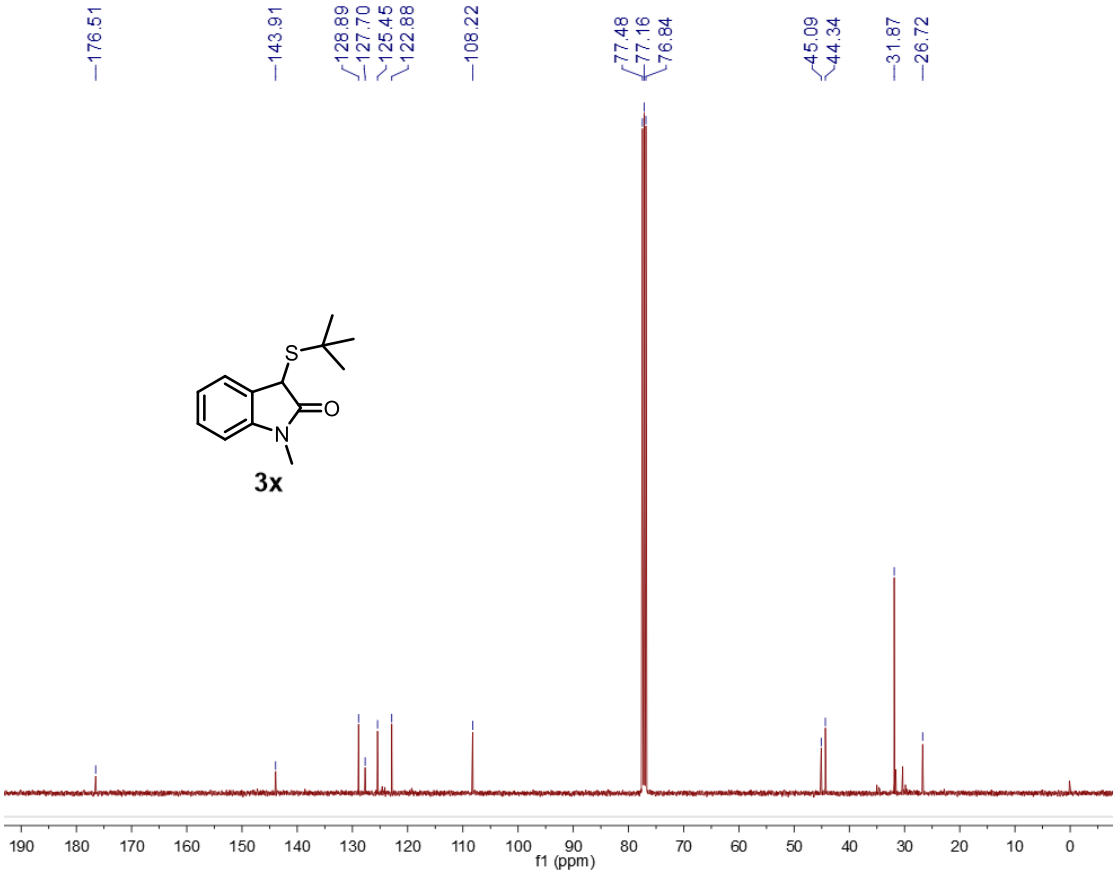

180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.411
7.392
7.322
7.306
7.303
7.300
7.284
7.114
7.112
7.095
7.093
7.077
7.074
6.825
6.806
4.304
3.233
1.609
1.519

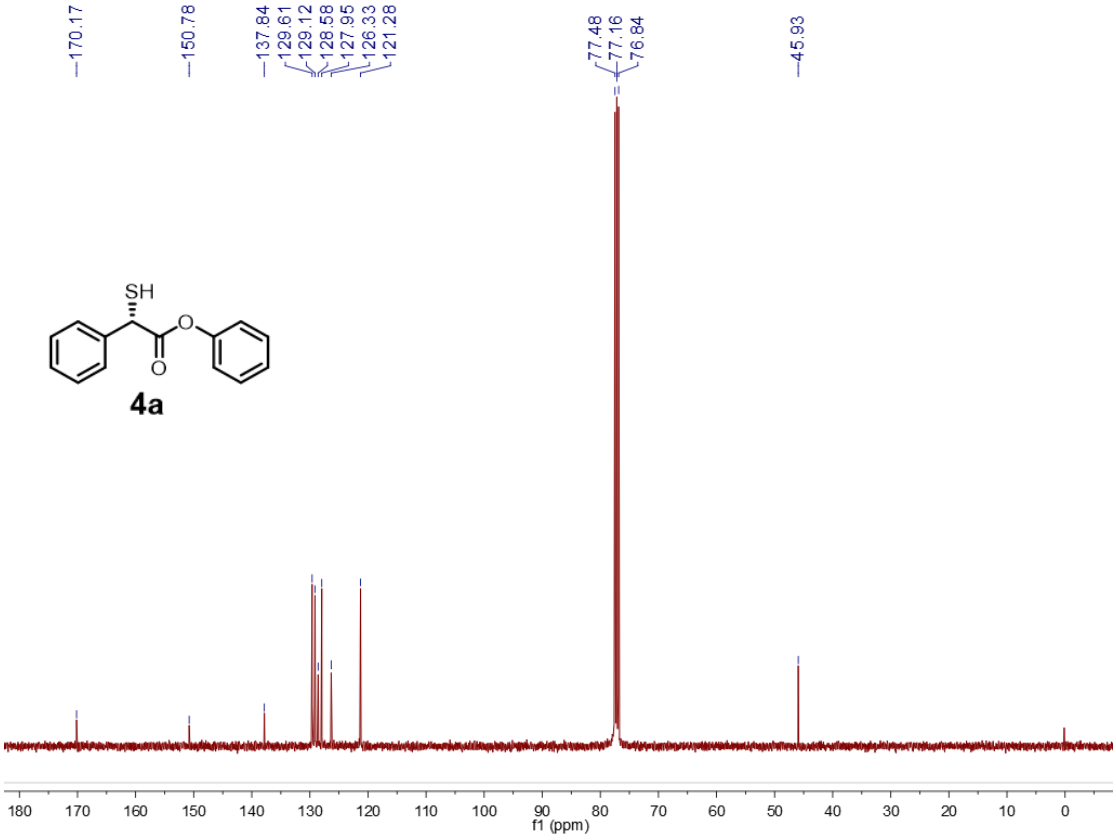

S
O
N

3x

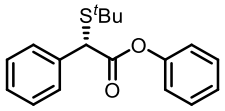
1.09
0.92
1.07
1.04
1.00
3.13
9.42
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5


176.51
143.91
128.89
127.70
125.45
122.88
108.22
77.48
77.16
76.84
45.09
44.34
31.87
26.72
S
O
N
3x
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.553
7.533
7.420
7.401
7.383
7.363
7.344
7.256
7.252
7.231
7.065
7.045
4.917
4.897
2.732
2.712
1.565
SH
O
O
4a
1.07
2.73
0.83
1.00
0.45
0.45
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

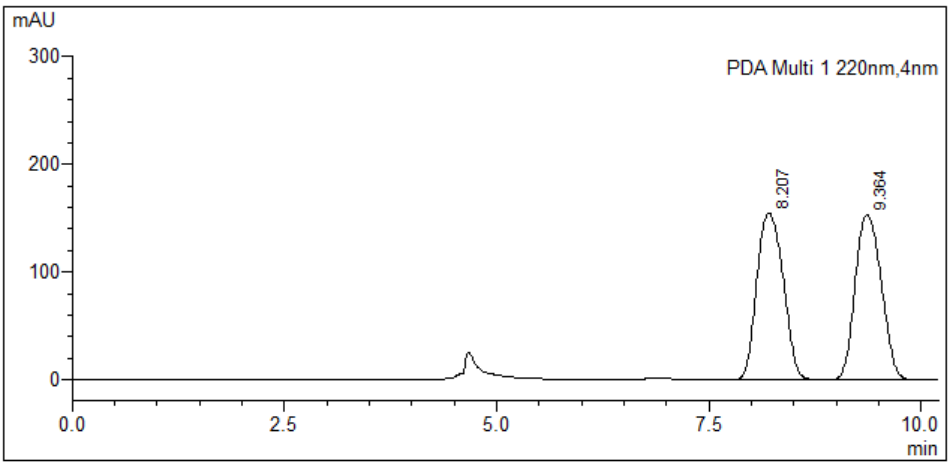

170.17
150.78
137.84
129.61
129.12
128.58
127.95
126.33
121.28
77.48
77.16
76.84
45.93
SH
O
O
4a
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

9. HPLC Spectra



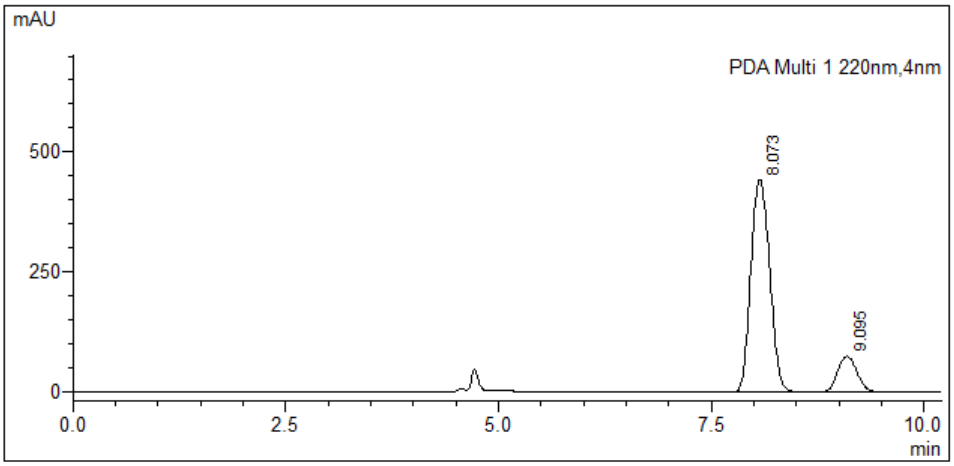
phenyl (*S*)-2-(*tert*-butylthio)-2-phenylacetate (**3a**).

HPLC: Chiralpak OZ-H column (250 mm); detected at 220 nm; hexane/*i*-propanol = 99/1; flow = 0.7 mL/min; Retention time: 8.1 min (major), 9.1 min, 70% ee.



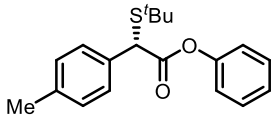
PDA Ch1 220nm

Peak No.	Ret Time	Height	Area	Conc.(%)
1	8.207	154762	3365815	50.272
2	9.364	153813	3329391	49.728



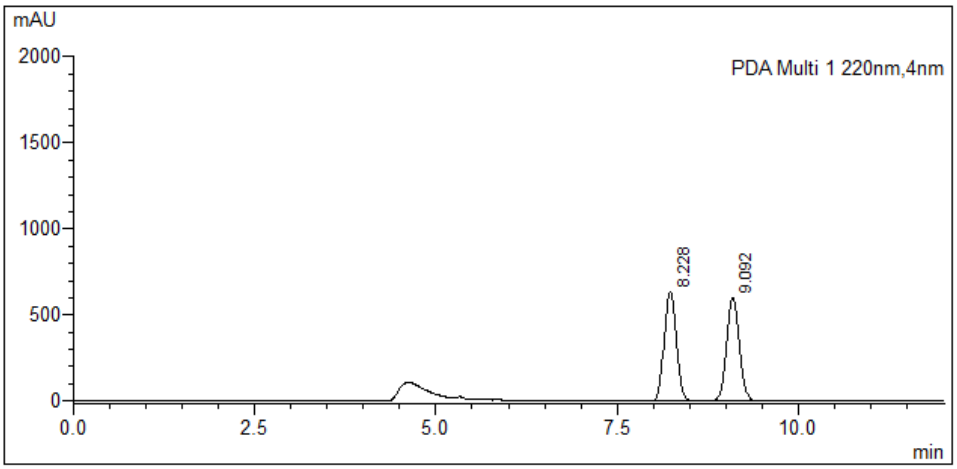
PDA Ch1 220nm

Peak No.	Ret Time	Height	Area	Conc.(%)
1	8.073	442280	6756101	85.301
2	9.095	73921	1164163	14.699



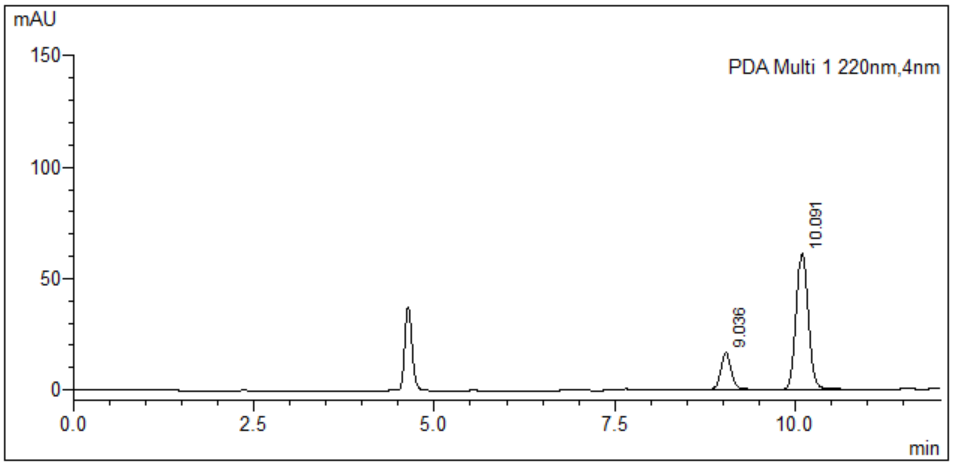
phenyl (*S*)-2-(*tert*-butylthio)-2-(p-tolyl)acetate (**3b**).

HPLC: Chiralpak OZ-H column (250 mm); detected at 220 nm; hexane/*i*-propanol = 99/1; flow = 0.7 mL/min; Retention time: 9.0 min, 10.1 min (major), 61% ee.



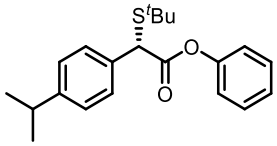
PDA Ch1 220nm

Peak No.	Ret Time	Height	Area	Conc.(%)
1	8.228	637576	7531278	49.963
2	9.092	599648	7542457	50.037



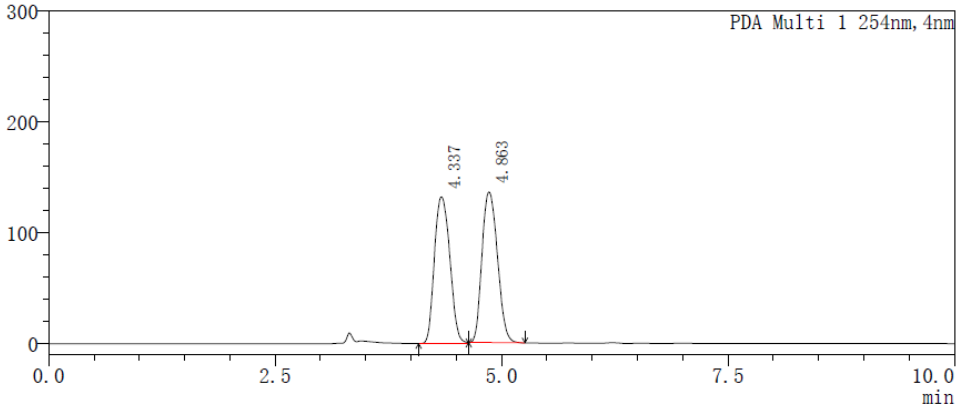
PDA Ch1 220nm

Peak No.	Ret Time	Height	Area	Conc.(%)
1	9.036	16639	168572	19.217
2	10.091	60996	708648	80.783



phenyl (*S*)-2-(tert-butylthio)-2-(4-isopropylphenyl)acetate (**3c**)

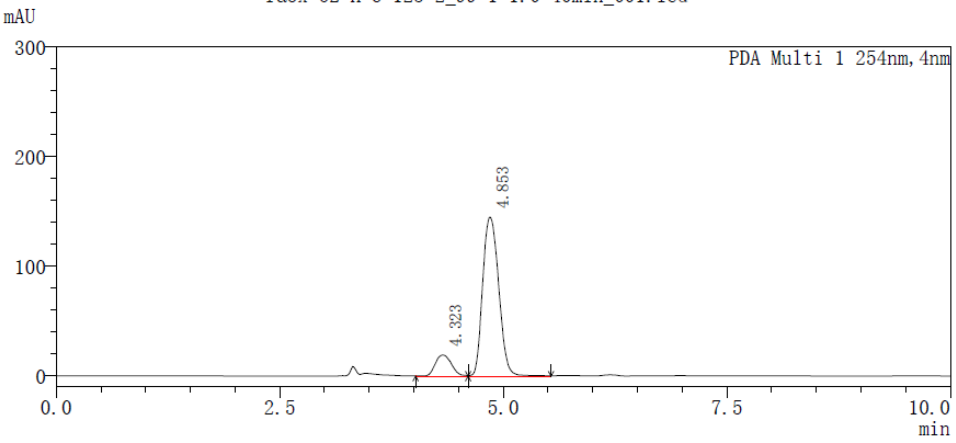
HPLC: Chiralpak OZ-H column (250 mm); detected at 254 nm; hexane/*i*-propanol = 99/1; flow = 1.0 mL/min; Retention time: 4.32 min, 4.85 min (major), 77% ee.



PDA Ch1 254nm

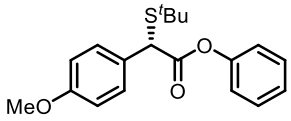
Number	Retention	Area	Height	Area%
1	4.337	1577191	132438	49.288
2	4.863	1622789	135824	50.712

raox-OZ-H-6-125-2_99-1-1.0-40min_001.lcd



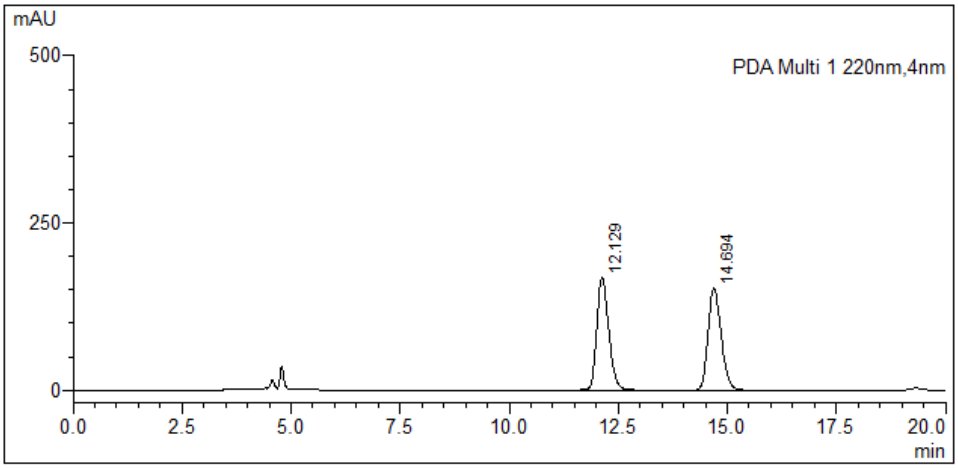
PDA Ch1 254nm

Number	Retention	Area	Height	Area%
1	4.323	242070	19251	11.763
2	4.853	1815884	145115	88.237



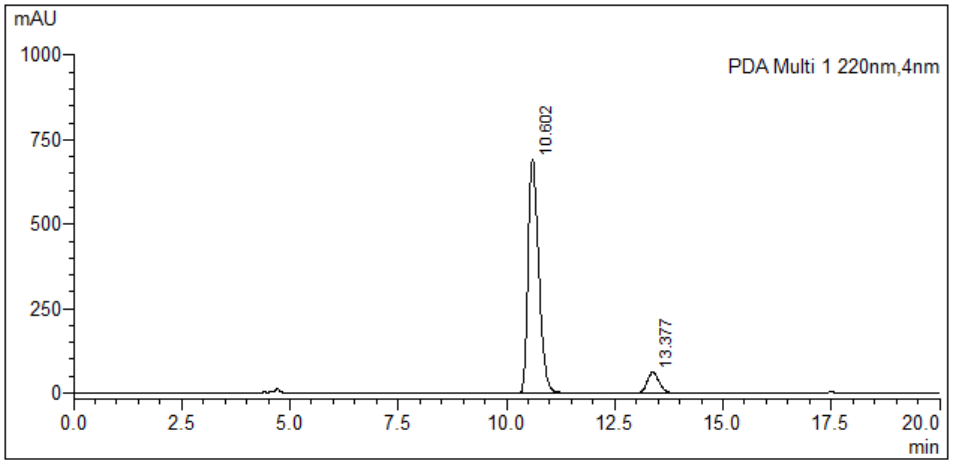
phenyl (*S*)-2-(*tert*-butylthio)-2-(4-methoxyphenyl)acetate (**3d**).

HPLC: Chiralpak OZ-H column (250 mm); detected at 220 nm; hexane/*i*-propanol = 99/1; flow = 0.7 mL/min; Retention time: 10.6 min (major), 13.3 min, 82% ee.



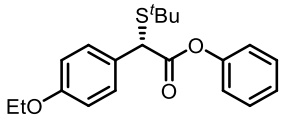
PDA Ch1 220nm

Peak No.	Ret Time	Height	Area	Conc.(%)
1	12.129	168342	3265263	50.203
2	14.694	152518	3238884	49.797



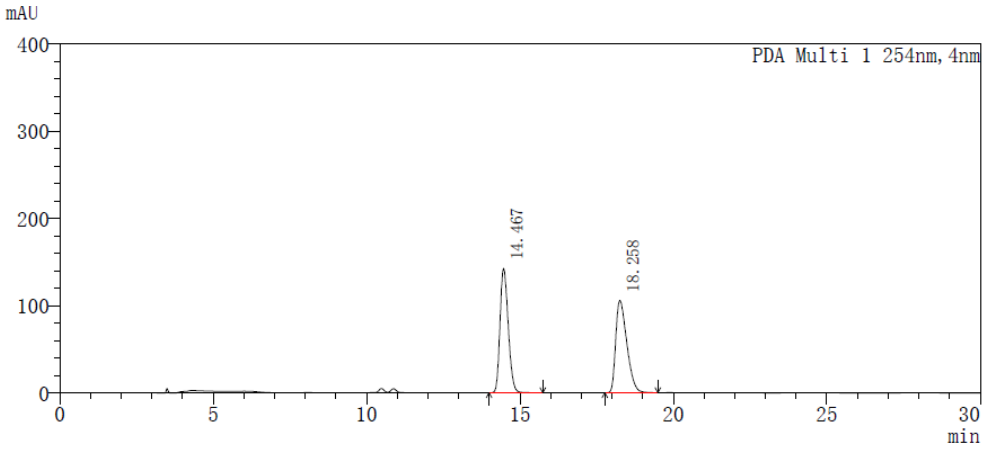
PDA Ch1 220nm

Peak No.	Ret Time	Height	Area	Conc.(%)
1	10.602	690043	11888710	91.003
2	13.377	60851	1175354	8.997



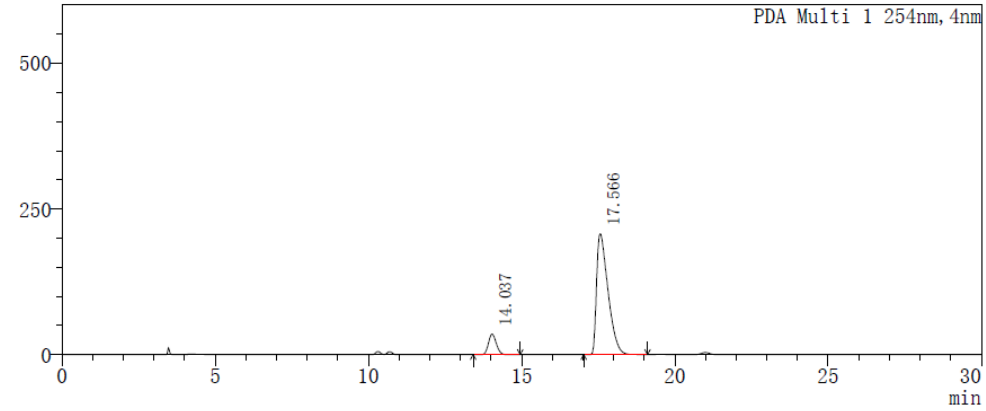
phenyl (*S*)-2-(tert-butylthio)-2-(4-ethoxyphenyl)acetate (**3e**)

HPLC: Chiralpak IC-3 column (250 mm); detected at 254 nm; hexane/*i*-propanol = 99/1; flow = 1.0 mL/min; Retention time: 14.4 min, 18.2 min (major), 79% ee.



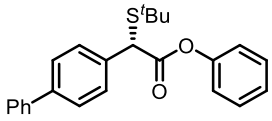
PDA Ch1 254nm

Number	Retention	Area	Height	Area%
1	14.467	2656376	142226	49.901
2	18.258	2666866	105675	50.099



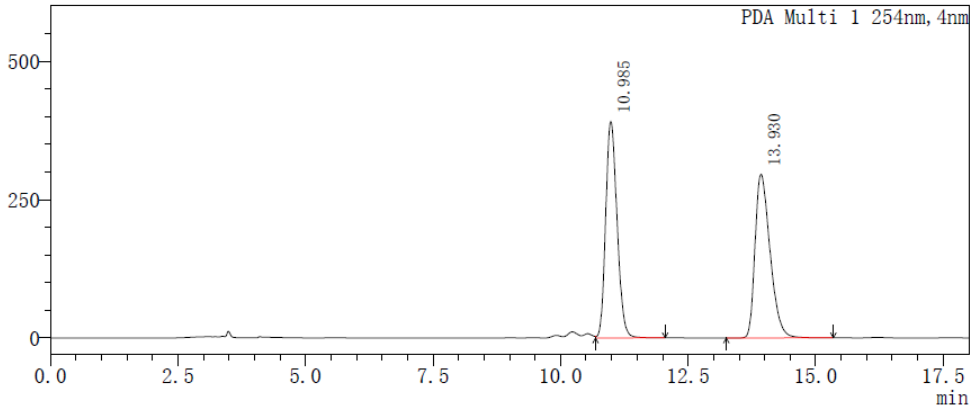
PDA Ch1 254nm

Number	Retention	Area	Height	Area%
1	14.037	638430	35392	10.550
2	17.566	5413235	207724	89.450



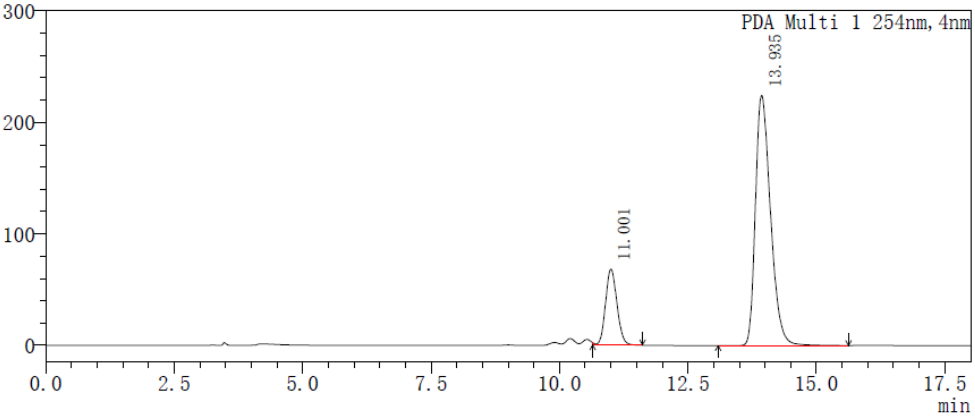
phenyl (*S*)-2-([1,1'-biphenyl]-4-yl)-2-(tert-butylthio)acetate (**3f**)

HPLC: Chiralpak IC-3 column (250 mm); detected at 254 nm; hexane/*i*-propanol = 99/1; flow = 1.0 mL/min; Retention time: 11.0 min, 13.9 min (major), 63% ee.



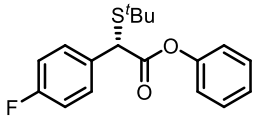
PDA Ch1 254nm

Number	Retention	Area	Height	Area%
1	10.985	6065830	390927	50.026
2	13.930	6059614	295792	49.974



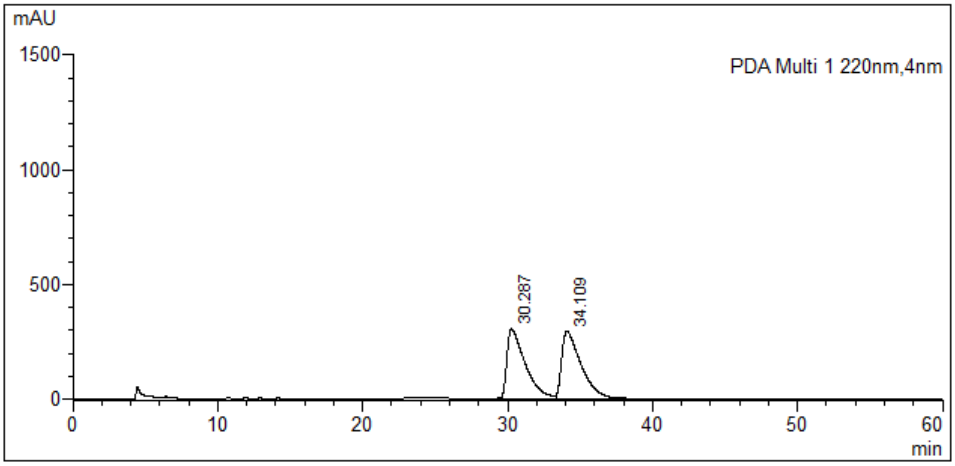
PDA Ch1 254nm

Number	Retention	Area	Height	Area%
1	11.001	1035956	67749	18.439
2	13.935	4582457	224405	81.561



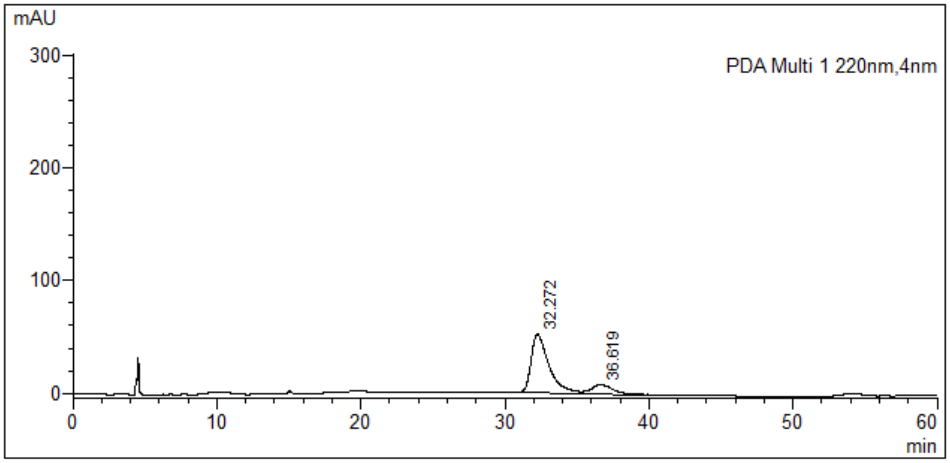
phenyl (*S*)-2-(*tert*-butylthio)-2-(4-fluorophenyl)acetate (**3g**).

HPLC: Chiralpak OJ-3 column (250 mm); detected at 220 nm; hexane/*i*-propanol = 99/1; flow = 0.7 mL/min; Retention time: 32.3 min (major), 36.6 min, 68% ee.



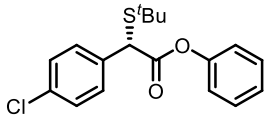
PDA Ch1 220nm

Peak No.	Ret Time	Height	Area	Conc.(%)
1	30.287	302723	26461867	49.299
2	34.109	293680	27214498	50.701



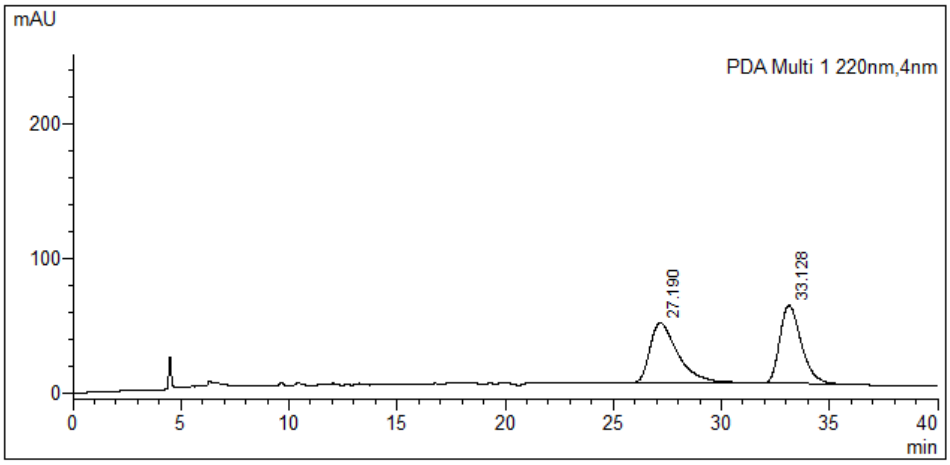
PDA Ch1 220nm

Peak No.	Ret Time	Height	Area	Conc.(%)
1	32.272	51750	4441800	84.294
2	36.619	7884	827595	15.706



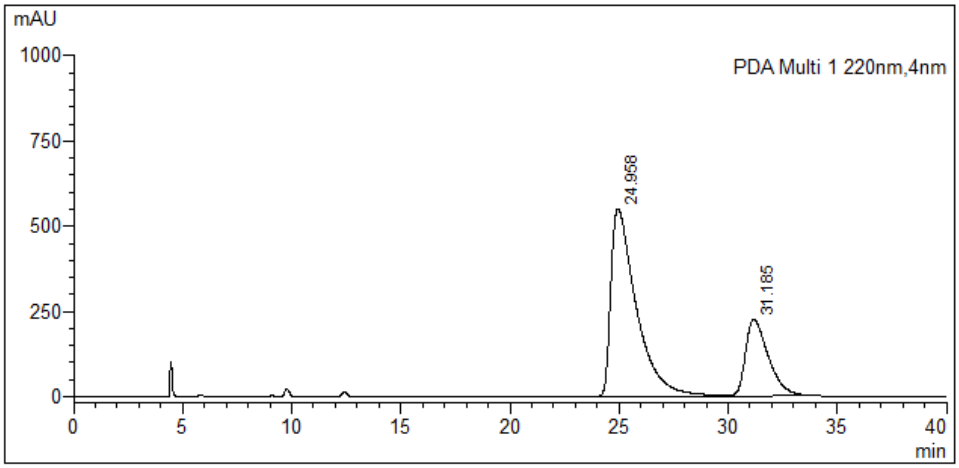
phenyl (*S*)-2-(*tert*-butylthio)-2-(4-chlorophenyl)acetate (**3h**).

HPLC: Chiralpak OJ-3 column (250 mm); detected at 220 nm; hexane/*i*-propanol = 99/1; flow = 0.7 mL/min; Retention time: 25.0 min (major), 31.2 min, 46% ee.



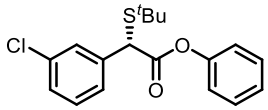
PDA Ch1 220nm

Peak No.	Ret Time	Height	Area	Conc.(%)
1	27.190	44412	4057780	50.008
2	33.128	57964	4056452	49.992



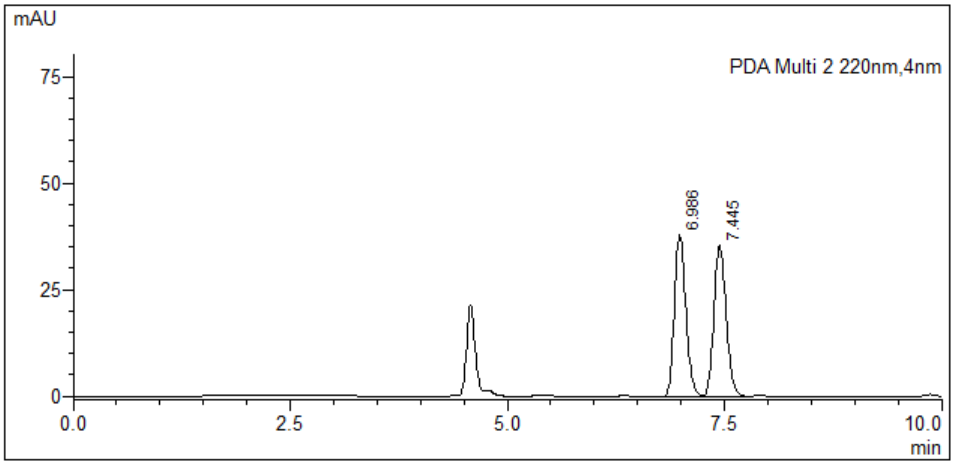
PDA Ch1 220nm

Peak No.	Ret Time	Height	Area	Conc.(%)
1	24.958	551062	44721846	73.252
2	31.185	224572	16330096	26.748



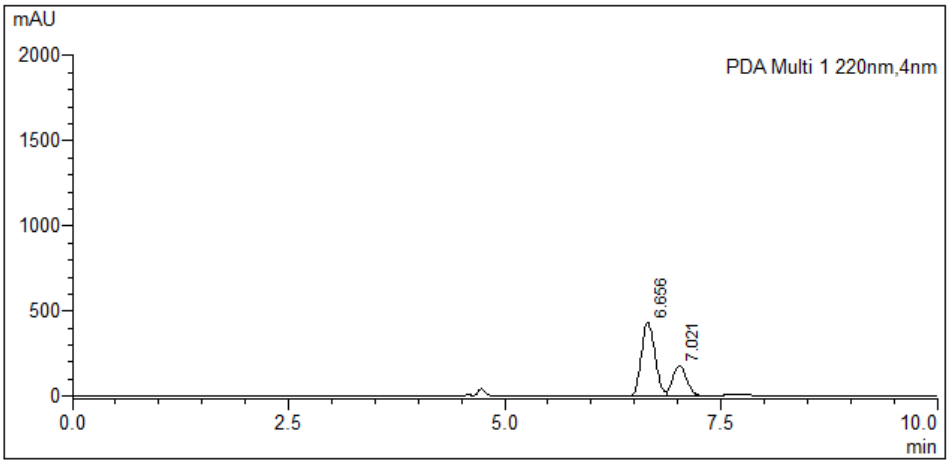
phenyl (*S*)-2-(*tert*-butylthio)-2-(3-chlorophenyl)acetate (**3i**).

HPLC: Chiralpak OZ-H column (250 mm); detected at 220 nm; hexane/*i*-propanol = 99/1; flow = 0.7 mL/min; Retention time: 6.6 min (major), 7.0 min, 40% ee.



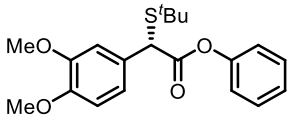
PDA Ch2 220nm

Peak No.	Ret Time	Height	Area	Conc.(%)
1	6.986	37989	350977	49.925
2	7.445	35672	352028	50.075



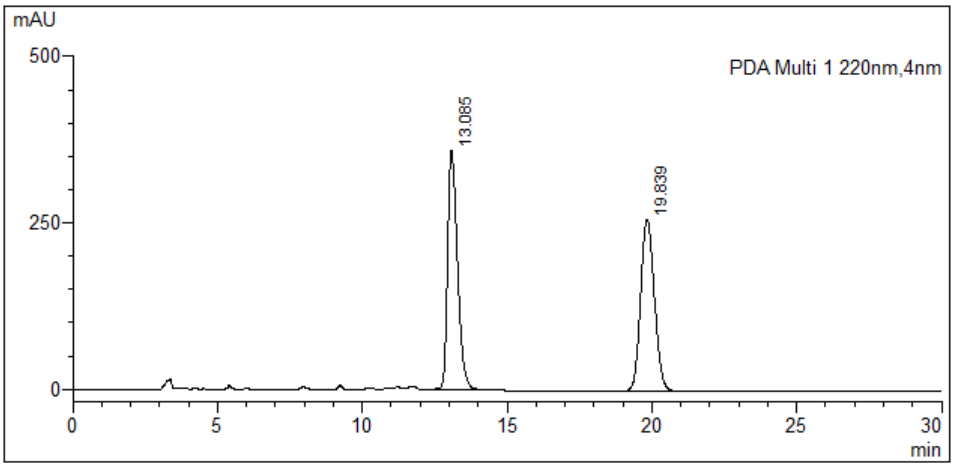
PDA Ch1 220nm

Peak No.	Ret Time	Height	Area	Conc.(%)
1	6.656	432298	4784035	70.209
2	7.021	178505	2029920	29.791



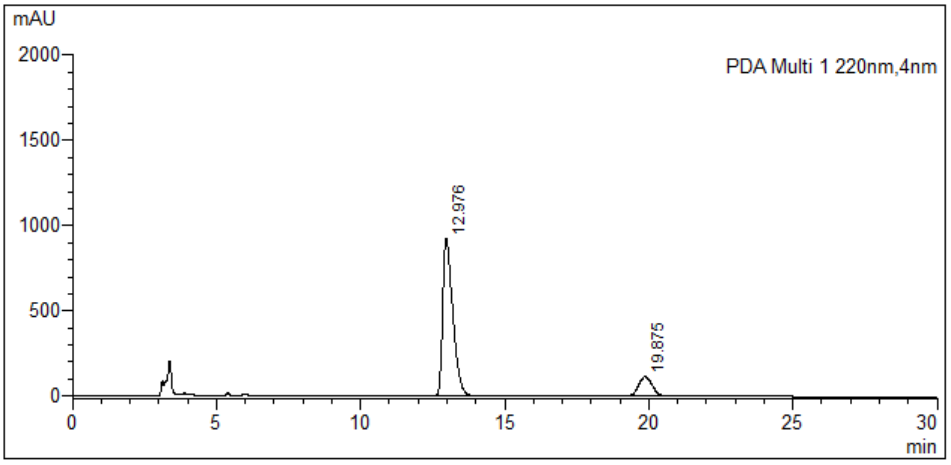
phenyl (*S*)-2-(*tert*-butylthio)-2-(3,4-dimethoxyphenyl)acetate (**3j**).

HPLC: Chiralpak IC column (250 mm); detected at 220 nm; hexane/*i*-propanol = 80/20; flow = 1.0 mL/min; Retention time: 13.0 min (major), 19.9 min, 71% ee.



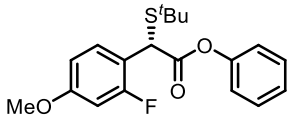
PDA Ch1 220nm

Peak No.	Ret Time	Height	Area	Conc.(%)
1	13.085	360093	8605829	50.272
2	19.839	258458	8512552	49.728



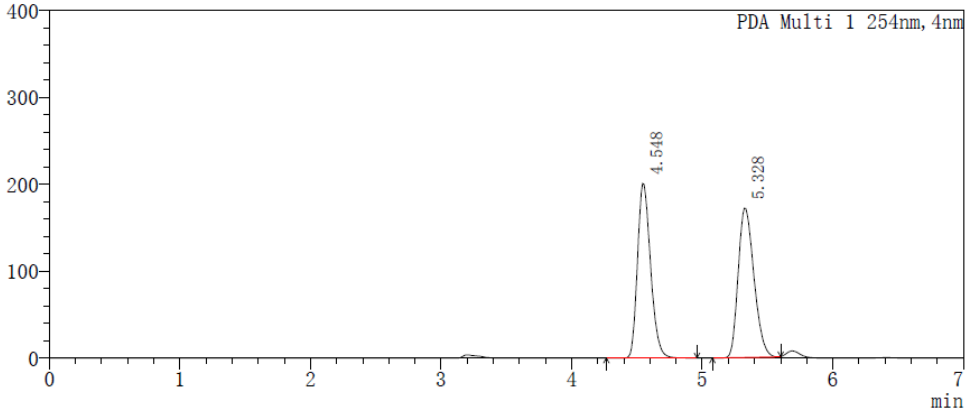
PDA Ch1 220nm

Peak No.	Ret Time	Height	Area	Conc.(%)
1	12.976	928663	22641858	85.601
2	19.875	116126	3808534	14.399



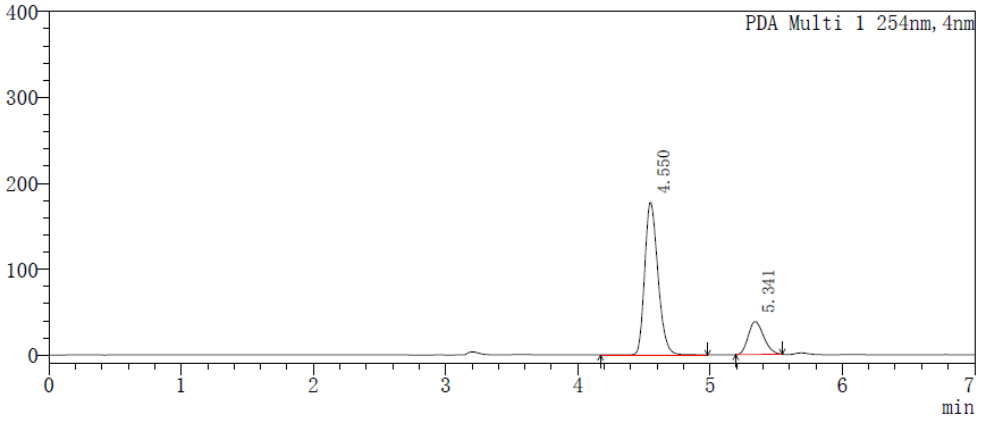
phenyl (*S*)-2-(tert-butylthio)-2-(2-fluoro-4-methoxyphenyl)acetate (**3k**)

HPLC: Chiralpak OZ-H column (250 mm); detected at 254 nm; hexane/*i*-propanol = 95/5; flow = 1.0 mL/min; Retention time: 4.5 min (major), 5.3 min, 60% ee.



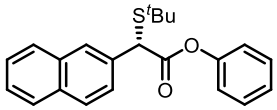
PDA Ch1 254nm

Number	Retention	Area	Height	Area%
1	4.548	1397028	201078	49.302
2	5.328	1436587	171696	50.698



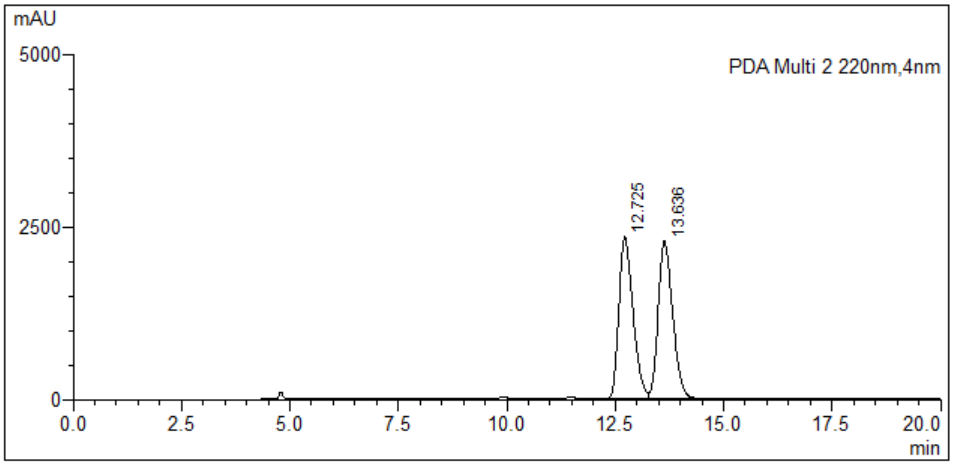
PDA Ch1 254nm

Number	Retention	Area	Height	Area%
1	4.550	1254726	177836	80.080
2	5.341	312119	38344	19.920



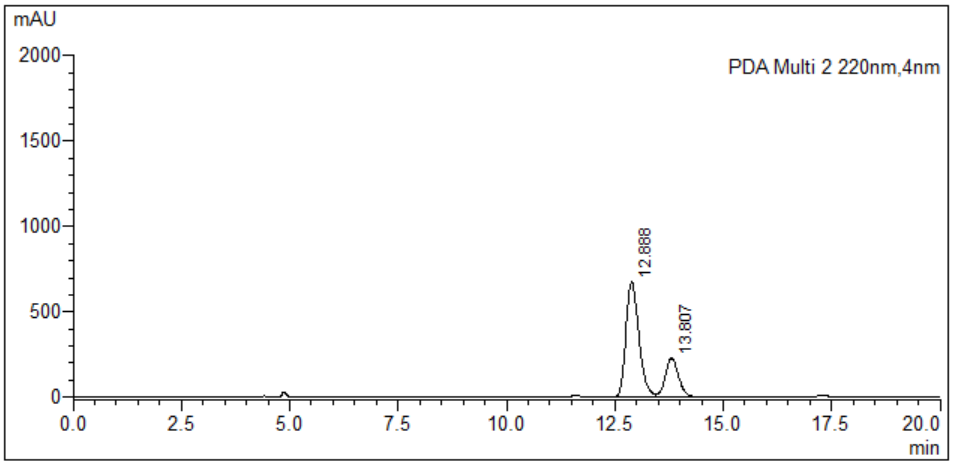
phenyl (*S*)-2-(*tert*-butylthio)-2-(naphthalen-2-yl)acetate (**3l**).

HPLC: Chiralpak OZ-H column (250 mm); detected at 220 nm; hexane/*i*-propanol = 99.5/0.5; flow = 0.7 mL/min; Retention time: 12.9 min (major), 13.8 min, 50% ee.



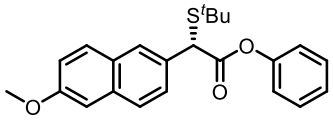
PDA Ch2 220nm

Peak No.	Ret Time	Height	Area	Conc.(%)
1	12.725	2364011	53519722	49.741
2	13.636	2298965	54076043	50.259



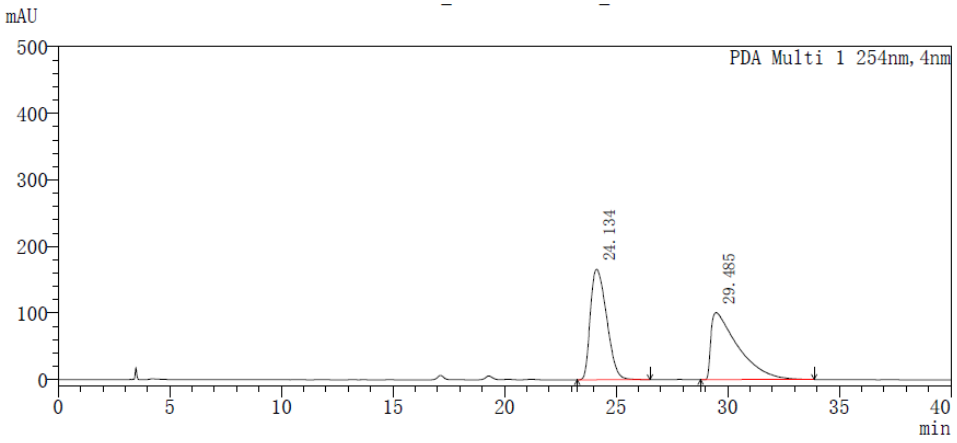
PDA Ch2 220nm

Peak No.	Ret Time	Height	Area	Conc.(%)
1	12.888	672500	13977272	74.843
2	13.807	225140	4698176	25.157



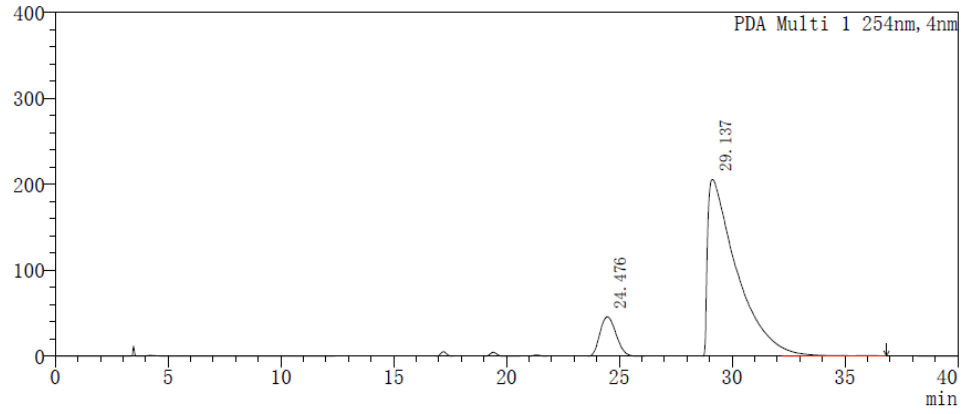
phenyl (*S*)-2-(tert-butylthio)-2-(6-methoxynaphthalen-2-yl)acetate (**3m**)

HPLC: Chiralpak IC-3 column (250 mm); detected at 254 nm; hexane/*i*-propanol = 99/1; flow = 1.0 mL/min; Retention time: 24.1 min, 29.4 min (major), 50% ee.



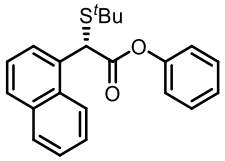
PDA Ch1 254nm

Number	Retention	Area	Height	Area%
1	24.134	8411555	165764	49.878
2	29.485	8452654	100744	50.122



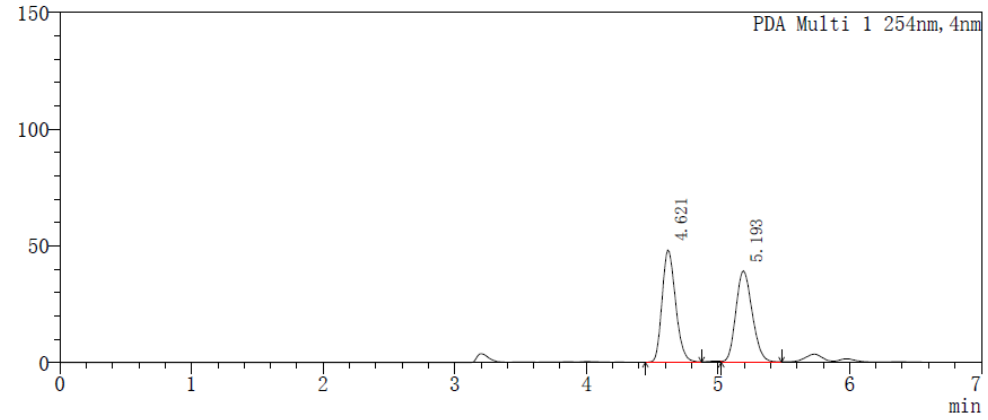
PDA Ch1 254nm

Number	Retention	Area	Height	Area%
1	24.476	2326036	46097	11.093
2	29.137	18642880	206045	88.907



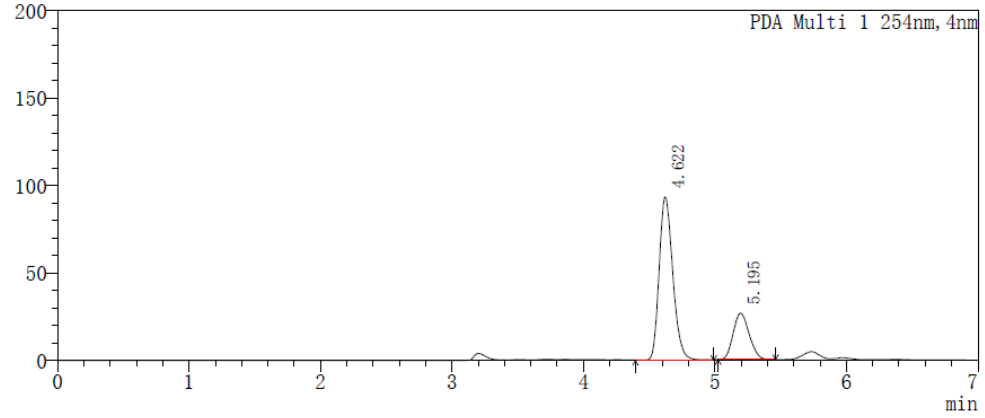
phenyl (*S*)-2-(tert-butylthio)-2-(naphthalen-1-yl)acetate (**3n**)

HPLC: Chiralpak OZ-H column (250 mm); detected at 254 nm; hexane/*i*-propanol = 95/5; flow = 1.0 mL/min; Retention time: 4.6 min (major), 5.1 min, 54% ee.



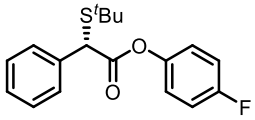
PDA Ch1 254nm

Number	Retention	Area	Height	Area%
1	4.621	342952	48042	50.285
2	5.193	339064	39125	49.715



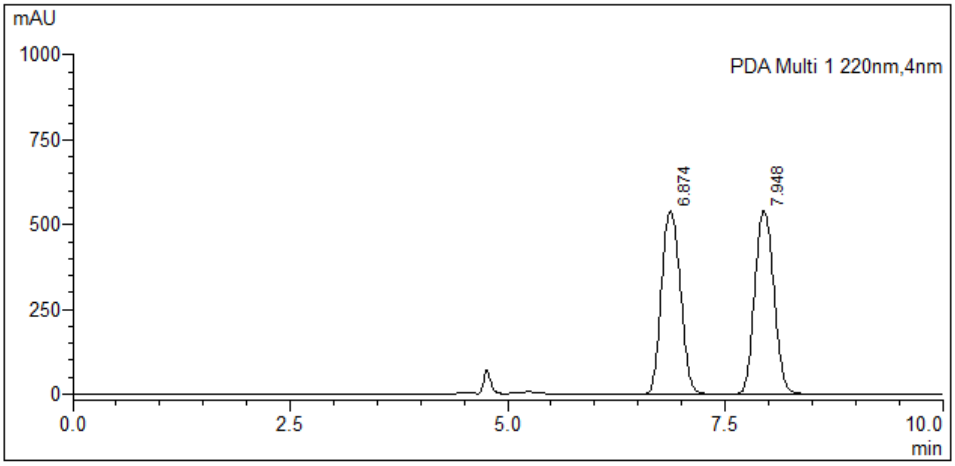
PDA Ch1 254nm

Number	Retention	Area	Height	Area%
1	4.622	687829	93761	75.352
2	5.195	224996	26612	24.648



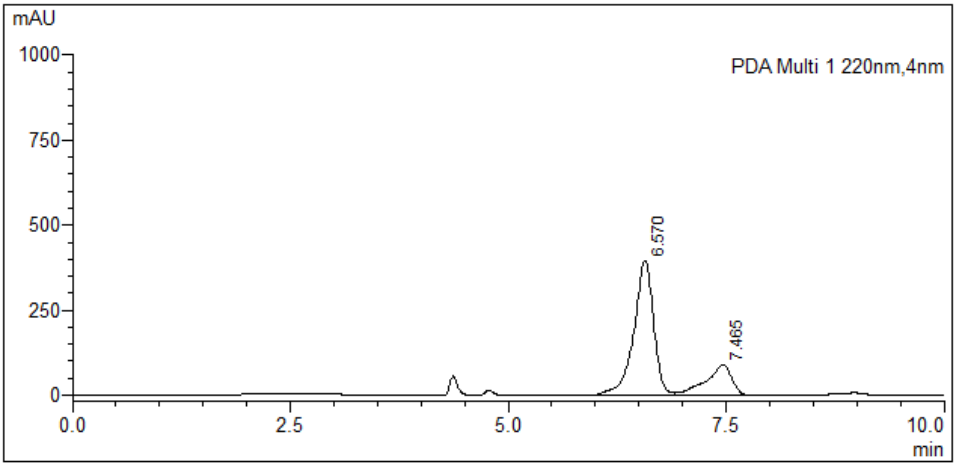
4-fluorophenyl (*S*)-2-(*tert*-butylthio)-2-phenylacetate (**3o**).

HPLC: Chiralpak OZ-H column (250 mm); detected at 220 nm; hexane/*i*-propanol = 99/1; flow = 0.7 mL/min; Retention time: 6.6 min (major), 7.5 min, 54% ee.



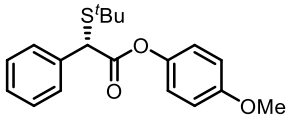
PDA Ch1 220nm

Peak No.	Ret Time	Height	Area	Conc.(%)
1	6.874	538625	8205871	49.846
2	7.948	541598	8256533	50.154



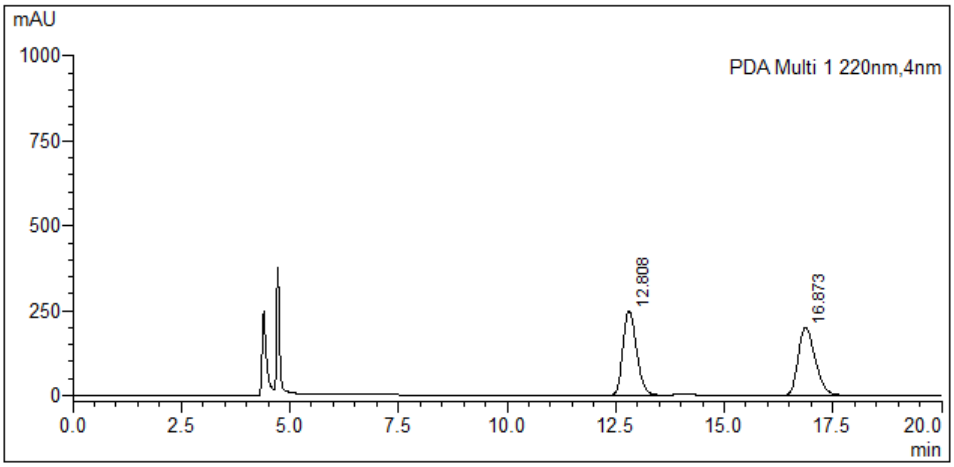
PDA Ch1 220nm

Peak No.	Ret Time	Height	Area	Conc.(%)
1	6.570	397526	6308279	77.066
2	7.465	90642	1877310	22.934



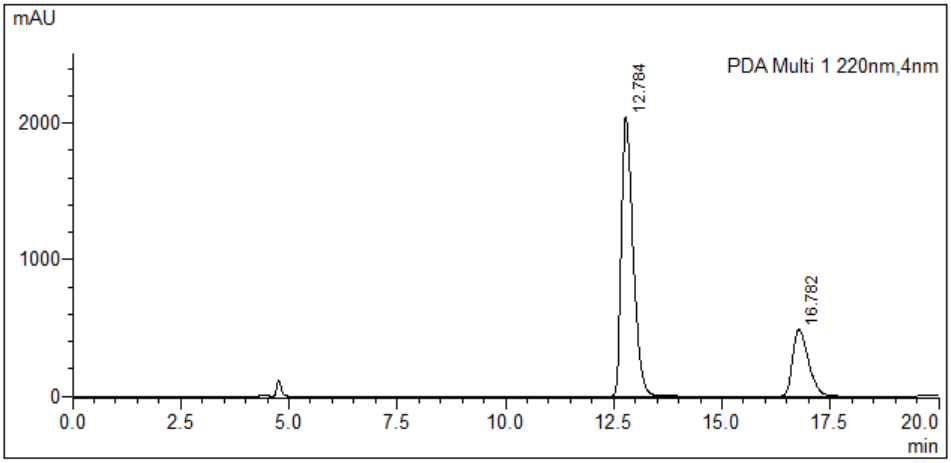
4-methoxyphenyl (*S*)-2-(*tert*-butylthio)-2-phenylacetate (**3p**).

HPLC: Chiralpak OZ-H column (250 mm); detected at 220 nm; hexane/*i*-propanol = 99/1; flow = 0.7 mL/min; Retention time: 12.8 min (major), 16.8 min, 51% ee.



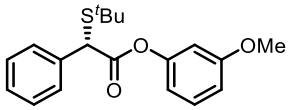
PDA Ch1 220nm

Peak No.	Ret Time	Height	Area	Conc.(%)
1	12.808	248102	5442884	50.160
2	16.873	200261	5408063	49.840



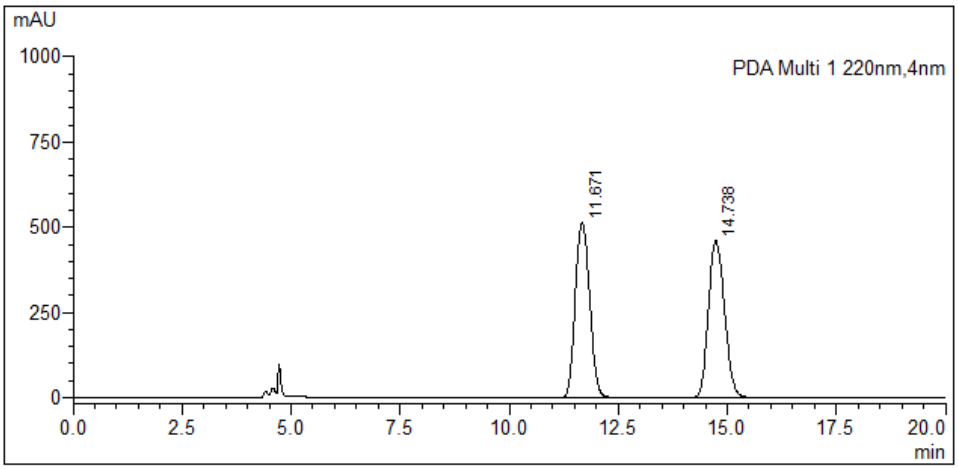
PDA Ch1 220nm

Peak No.	Ret Time	Height	Area	Conc.(%)
1	12.784	2044296	38477012	75.694
2	16.782	485760	12355487	24.306



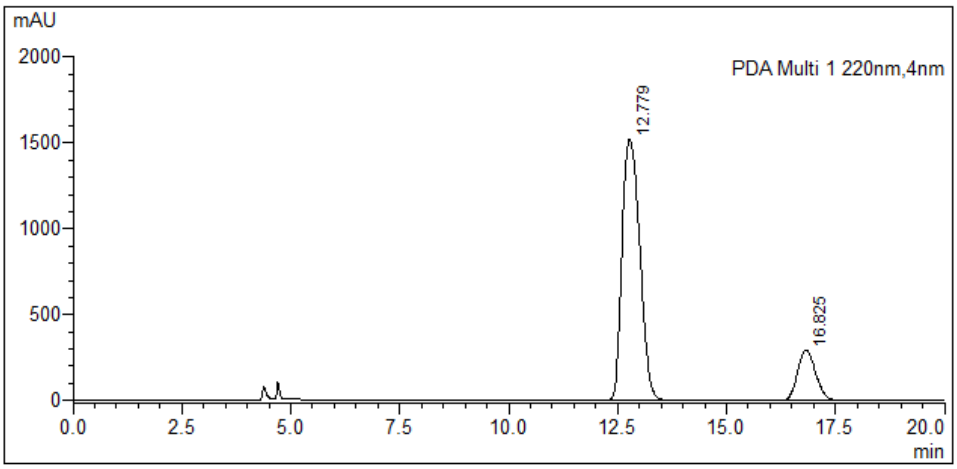
3-methoxyphenyl (*S*)-2-(*tert*-butylthio)-2-phenylacetate (**3q**).

HPLC: Chiralpak OZ-H column (250 mm); detected at 220 nm; hexane/*i*-propanol = 99/1; flow = 0.7 mL/min; Retention time: 12.8 min (major), 16.8 min, 68% ee.



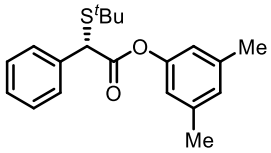
PDA Ch1 220nm

Peak No.	Ret Time	Height	Area	Conc.(%)
1	11.671	512891	11841098	49.916
2	14.738	459981	11881107	50.084



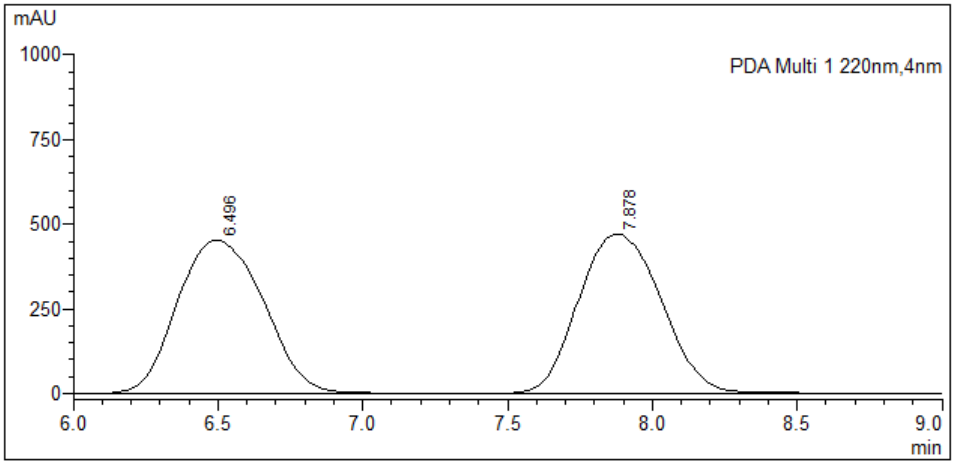
PDA Ch1 220nm

Peak No.	Ret Time	Height	Area	Conc.(%)
1	12.779	1522286	42953021	83.795
2	16.825	291864	8306897	16.205



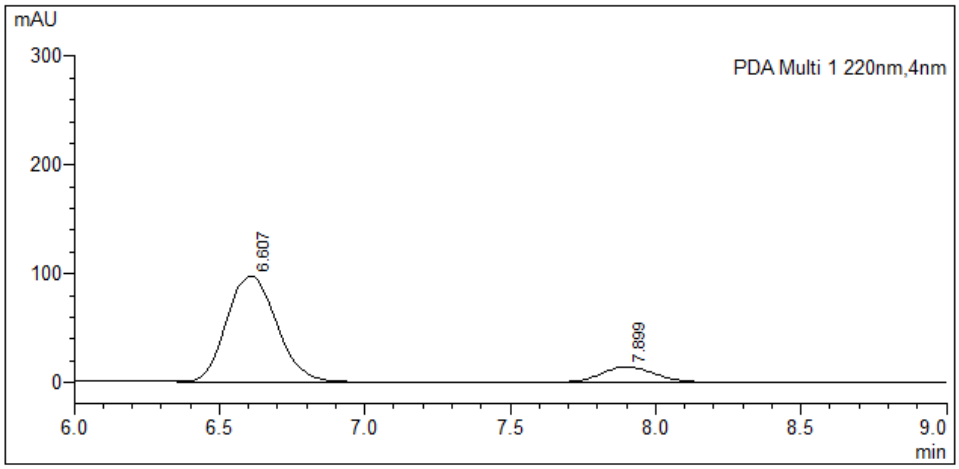
phenyl (*S*)-2-(4-bromophenyl)-2-(*tert*-butylthio)acetate (**3r**).

HPLC: Chiralpak OZ-H column (250 mm); detected at 220 nm; hexane/*i*-propanol = 99/1; flow = 0.7 mL/min; Retention time: 6.6 min, 7.9 min (major), 74% ee.



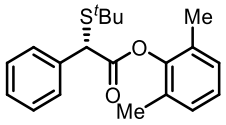
PDA Ch1 220nm

Peak No.	Ret Time	Height	Area	Conc.(%)
1	6.496	451604	9409210	49.923
2	7.878	470424	9438154	50.077



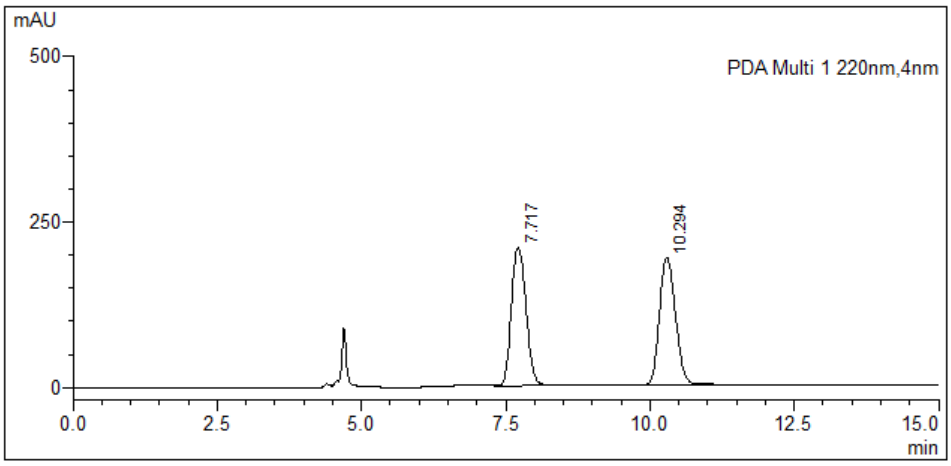
PDA Ch1 220nm

Peak No.	Ret Time	Height	Area	Conc.(%)
1	6.607	97949	1185538	86.928
2	7.899	14010	178285	13.072



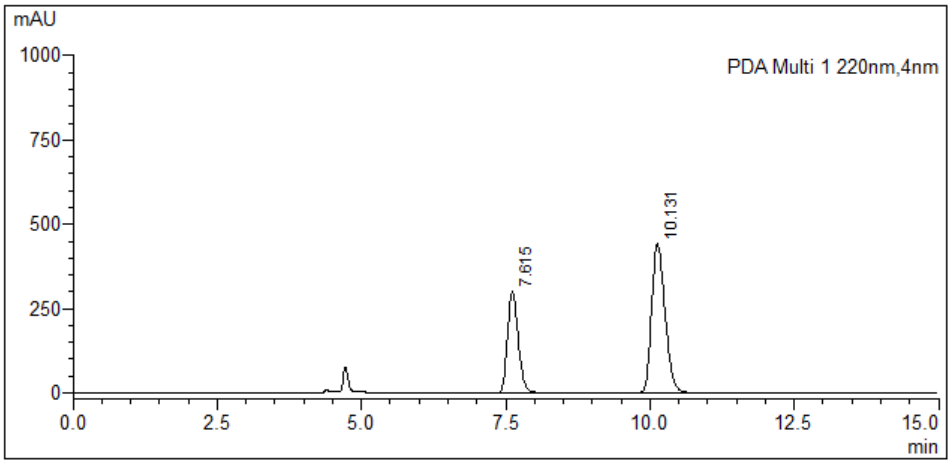
2,6-dimethylphenyl (*S*)-2-(*tert*-butylthio)-2-phenylacetate (**3s**).

HPLC: Chiralpak OZ-H column (250 mm); detected at 220 nm; hexane/*i*-propanol = 99/1; flow = 0.7 mL/min; Retention time: 7.6 min, 10.1 min (major), 30% ee.



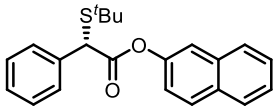
PDA Ch1 220nm

Peak No.	Ret Time	Height	Area	Conc.(%)
1	7.717	208799	3713548	49.737
2	10.294	192408	3752839	50.263



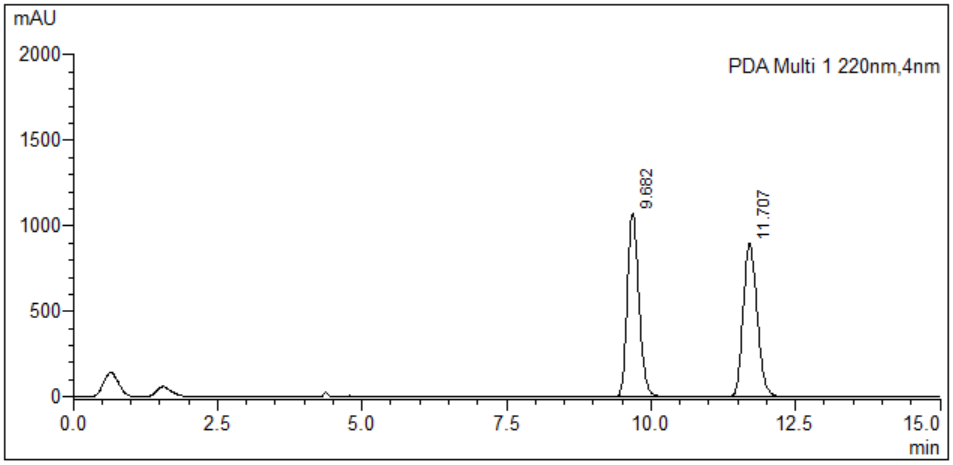
PDA Ch1 220nm

Peak No.	Ret Time	Height	Area	Conc.(%)
1	7.615	300027	3924112	35.315
2	10.131	442232	7187755	64.685



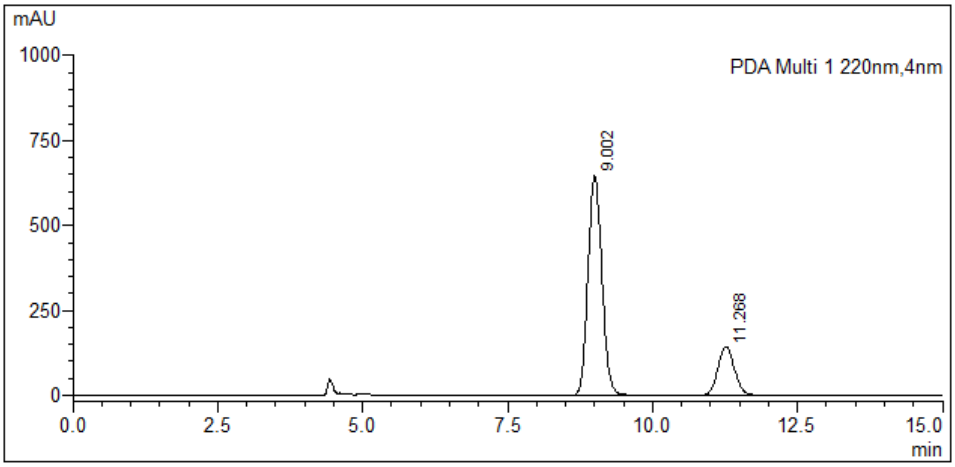
naphthalen-2-yl (*S*)-2-(*tert*-butylthio)-2-phenylacetate (**3t**).

HPLC: Chiralpak OZ-H column (250 mm); detected at 220 nm; hexane/*i*-propanol = 99/1; flow = 0.7 mL/min; Retention time: 9.0 min (major), 11.3 min, 59% ee.



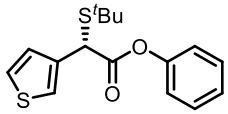
PDA Ch1 220nm

Peak No.	Ret Time	Height	Area	Conc.(%)
1	9.682	1073278	15134277	49.800
2	11.707	898825	15255727	50.200



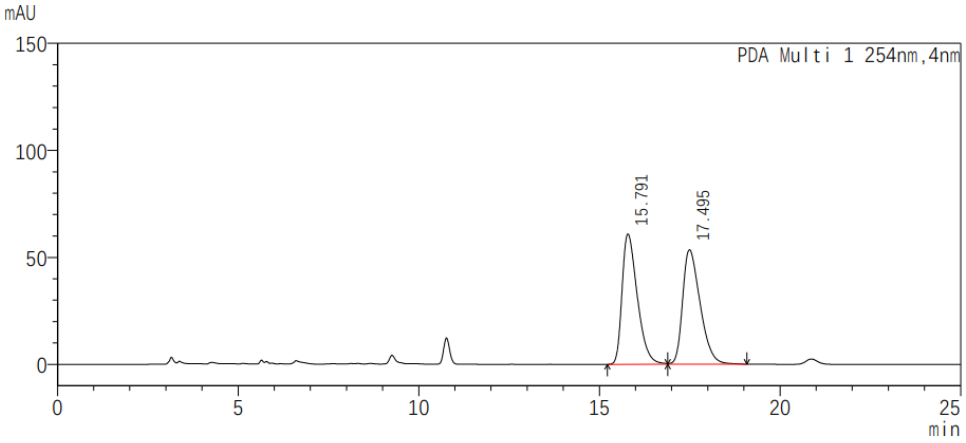
PDA Ch1 220nm

Peak No.	Ret Time	Height	Area	Conc.(%)
1	9.002	645494	10798097	79.184
2	11.268	143613	2838631	20.816



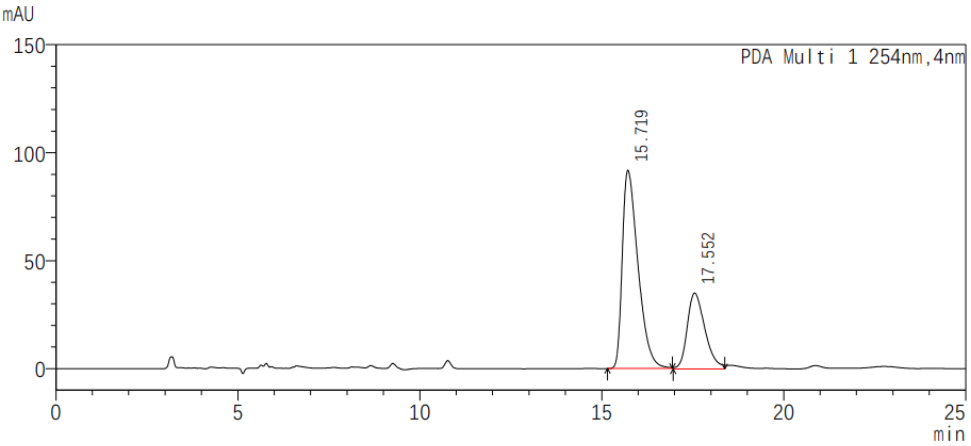
phenyl (*S*)-2-(tert-butylthio)-2-(thiophen-3-yl)acetate (**3u**)

HPLC: Chiralpak OJ-H column (250 mm); detected at 254 nm; hexane/*i*-propanol = 90/10; flow = 1.0 mL/min; Retention time: 15.7 min (major), 17.4 min, 40% ee.



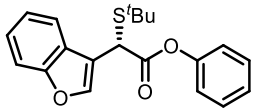
PDA Ch1 254nm

Number	Retention	Area	Height	Area%
1	15.791	1790853	60937	49.789
2	17.495	1806003	53537	50.211



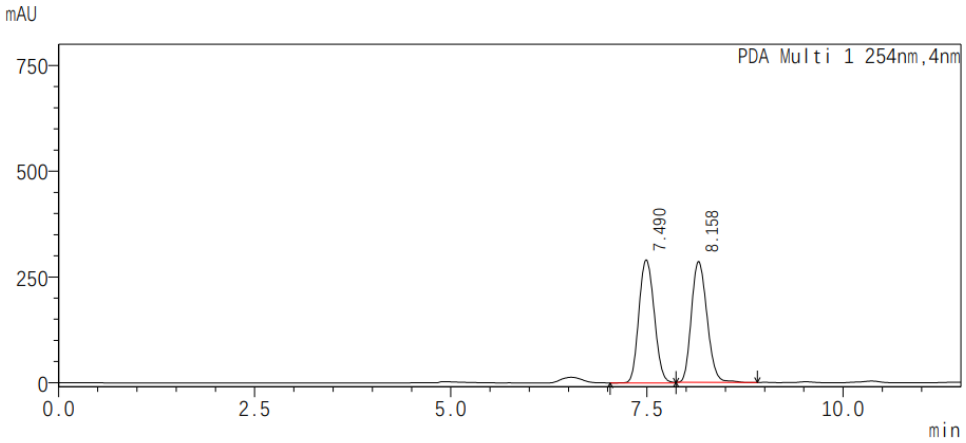
PDA Ch1 254nm

Number	Retention	Area	Height	Area%
1	15.719	2763096	91857	69.885
2	17.552	1190656	35175	30.115



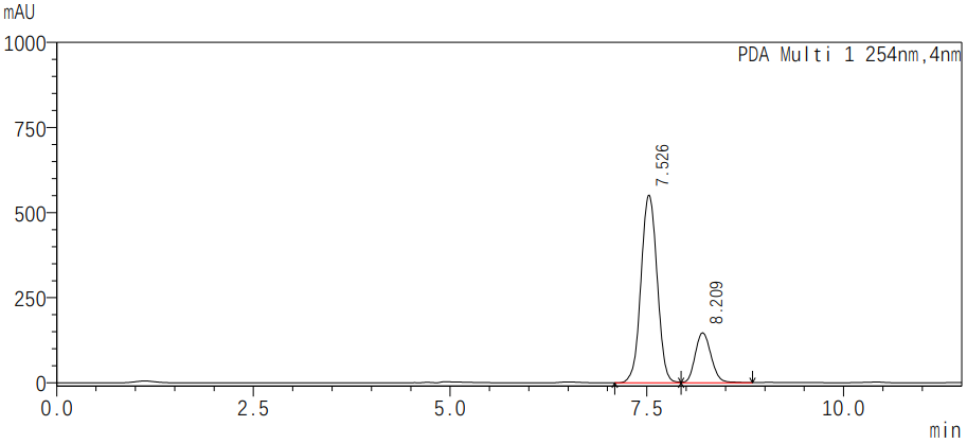
phenyl (*S*)-2-(benzofuran-3-yl)-2-(tert-butylthio)acetate (**3v**)

HPLC: Chiralpak OZ-H column (250 mm); detected at 254 nm; hexane/*i*-propanol = 99/1; flow = 0.7 mL/min; Retention time: 7.5 min (major), 8.2 min, 58% ee.



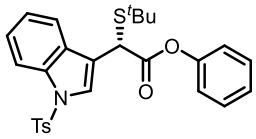
PDA Ch1 254nm

Number	Retention	Area	Height	Area%
1	7.490	3977338	291336	50.041
2	8.158	3970863	285908	49.959



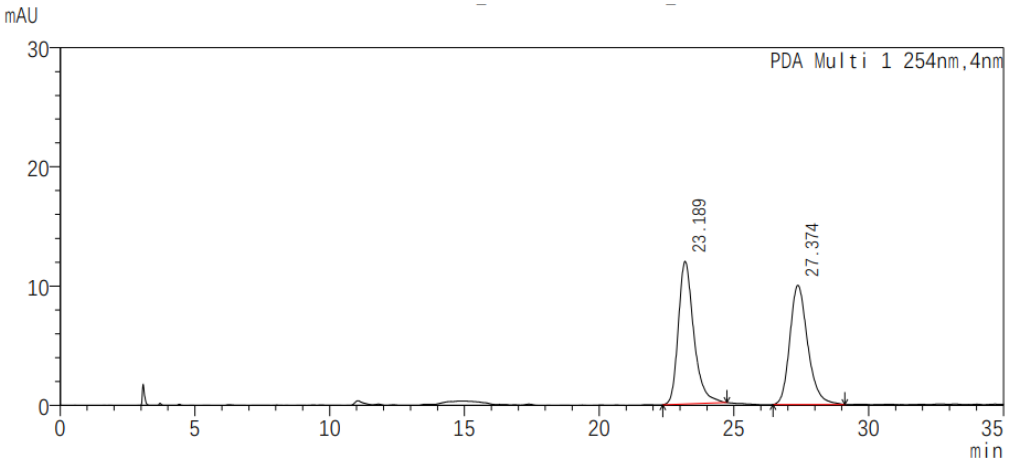
PDA Ch1 254nm

Number	Retention	Area	Height	Area%
1	7.526	7881602	551420	79.148
2	8.209	2076456	146852	20.852



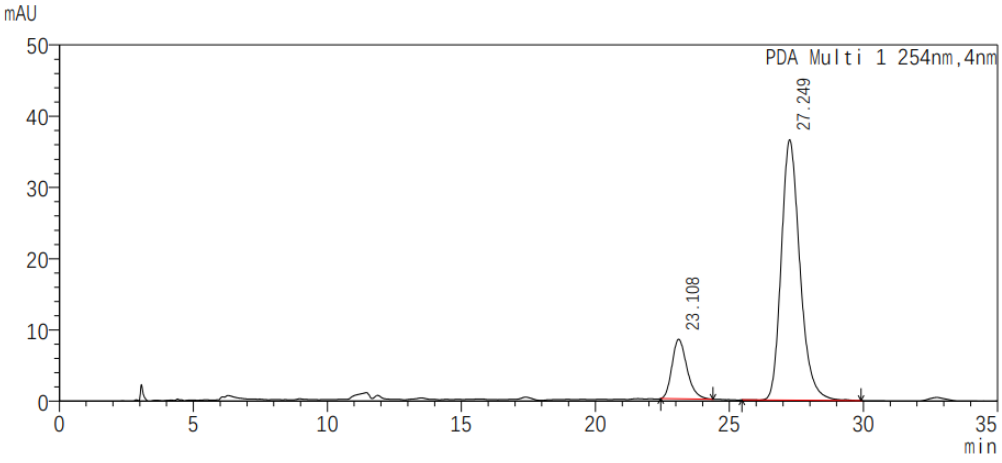
phenyl (S)-2-(tert-butylthio)-2-(1-tosyl-1H-indol-3-yl)acetate (**3w**)

HPLC: Chiralpak AD-H column (250 mm); detected at 254 nm; hexane/*i*-propanol = 95/5; flow = 1.0 mL/min; Retention time: 23.1 min, 27.2 min (major), 69% ee.



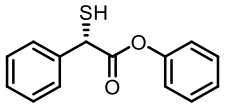
PDA Ch1 254nm

Number	Retention	Area	Height	Area%
1	23.189	477401	11958	50.794
2	27.374	462473	9991	49.206



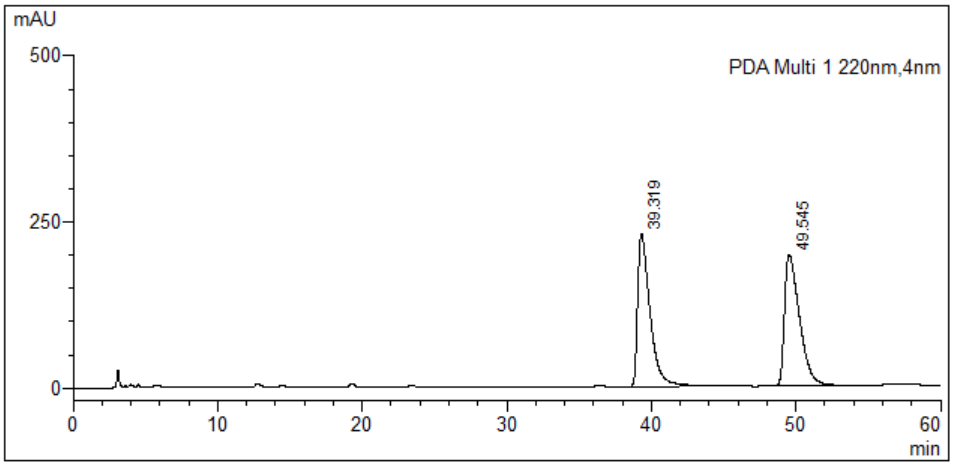
PDA Ch1 254nm

Number	Retention	Area	Height	Area%
1	23.108	323477	8346	15.448
2	27.249	1770519	36535	84.552



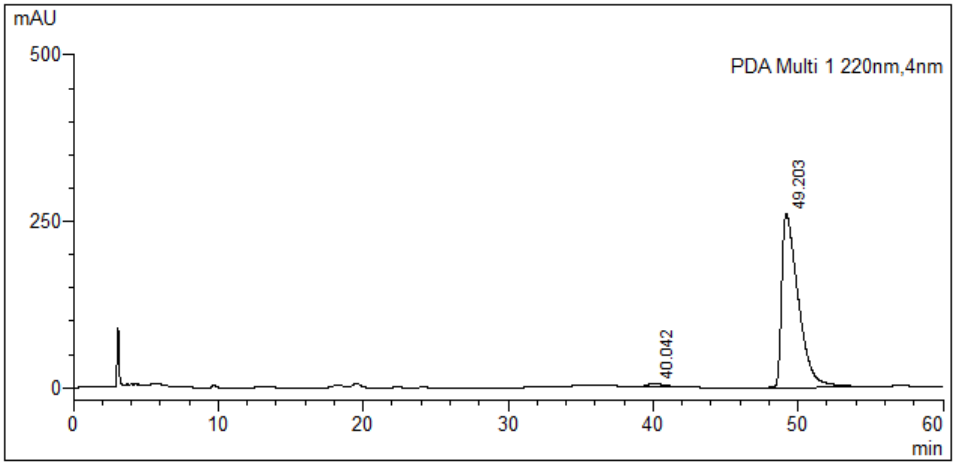
phenyl (*S*)-2-mercapto-2-phenylacetate (**4a**).

HPLC: Chiralpak OZ-H column (250 mm); detected at 220 nm; hexane/*i*-propanol = 80/20; flow = 0.7 mL/min; Retention time: 40.0 min, 49.2 min (major), 95% ee.



PDA Ch1 220nm

Peak No.	Ret Time	Height	Area	Conc.(%)
1	39.319	230310	13963063	49.334
2	49.545	197840	14340250	50.666



PDA Ch1 220nm

Peak No.	Ret Time	Height	Area	Conc.(%)
1	40.042	5847	553159	2.604
2	49.203	259823	20693317	97.396