Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Stereoselective Synthesis of 2-Trifluoromethylated and 2-Difluoromethylated Dihydrofurans via Organocatalytic Cascade Michael/Alkylation Reaction

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1. General methods

^{1}H and ^{13}C NMR spectra were recorded on Varian 400 MHz spectrometers. Chemical shifts (δ) were reported in ppm downfield from $CDCl_3$ (δ = 7.26 ppm) for ^{1}H NMR and relative to the central $CDCl_3$ resonance (δ = 77.0 ppm) for ^{13}C NMR spectroscopy. Coupling constants (*J*) were given in Hz. An ESI-HRMS spectrometer was measured with a Thermo Scientific LTQ Orbitrap XL mass spectrometer. Enantiomeric excess was determined by HPLC analysis on Chiralpak AD-H, AS-H and OD-H columns in comparison with the authentic racemates. Optical rotation data were recorded on a Rudolph Autopol I automatic polarimeter. Commercially available compounds were used without further purification. Solvents were dried according to standard procedures. Column chromatography was performed with silica gel (300-400 mesh).

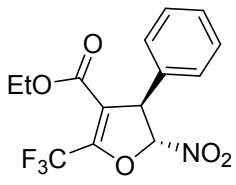
Bifunctional squaramides **C1** and **C2**,[1] thioureas **C3-C6** were prepared according to the literature procedures.[2] *β,β*-Bromonitrostyrenes **2a-2n** were obtained via Knoevenagel condensations and the following brominations of the resulting nitrostyrenes.[3] Compound **2o** was prepared via a modified process according to Soengas's procedure.[4] When 0.5 equiv of NaI was utilized under otherwise identical conditions, the desired product **2o** was obtained as a yellow solid in 47% overall yield.

((1*E*,3*Z*)-4-bromo-4-nitrobuta-1,3-dien-1-yl)benzene (2o).[5] ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 8.23 (d, *J* = 11.2 Hz, 1H), 7.59-7.57 (m, 2H), 7.45-7.41 (m, 4H), 7.27 (d, *J* = 15.6 Hz, 1H), 6.99 (dd, *J* = 15.6, 10.8 Hz, 1H); IR (KBr): 1612, 1581, 1521, 1131, 1288, 974, 758, 691 cm^{-1}.

2. General procedure for the asymmetric Michael reaction

Squaramide **C2** based on quinine (12.8 mg, 0.02 mmol), *β,β*-bromonitrostyrene **1** (0.1 mmol), 4,4,4-trifluoroacetoacetate **2** (0.12 mmol) and TMDEA (2.9 μL, 0.02 mmol) were stirred in redistilled chloroform (1 mL) at rt. After due reaction time, the reaction mixture was concentrated *in vacuo*. The residue was purified by flash chromatography on silica gel (CH_2Cl_2/petroleum ether = 1/8, v/v) to afford the desired adduct **3**.

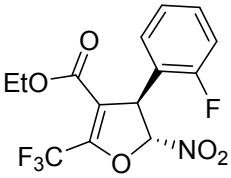
Ethyl 5-nitro-4-phenyl-2-(trifluoromethyl)-4,5-dihydrofuran-3-carboxylate (3aa). The



product **3aa** was obtained as a yellow oil (31.7 mg, 96% yield). 96% ee was determined by HPLC on AS-H column, hexane/*i*-propanol (90/10), 1.0 mL/min, UV 254 nm, t_{minor} = 5.293 min, t_{major} = 8.370 min; $[\alpha]_D^{25}$ = -179.7°

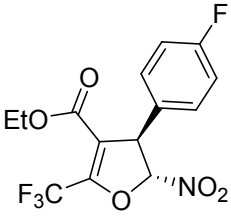
(c = 0.938, $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.44-7.39 (m, 3H), 7.24 (d, J = 6.4 Hz, 2H), 5.91 (d, J = 1.6 Hz, 1H), 4.81 (app s,1H), 4.21-4.08 (m, 2H), 1.18 (t, J = 7.0 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm): 159.5, 149.6 (q, $^2J_{CF}$ = 41.8 Hz), 135.1, 129.6, 129.2, 127.0, 117.4 (q, $^1J_{CF}$ = 271.7 Hz), 115.0 (q, $^3J_{CF}$ = 2.6 Hz), 108.4, 61.9, 56.9, 13.6; ^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm): -64.5 (d, J = 1.9 Hz); IR (KBr): 3036, 3006, 1734, 1689, 1571, 1380, 1327, 1169, 1107, 1024, 986, 731, 698 cm^{-1}; HRMS (ESI) m/z: $[M+H]^+$ calcd. for $C_{14}H_{13}F_3NO_5$ 332.0740, found 332.0731.

Ethyl 4-(2-fluorophenyl)-5-nitro-2-(trifluoromethyl)-4,5-dihydrofuran-3-carboxylate (3ab).



The product **3ab** was obtained as a colorless oil (32.8 mg, 94% yield). 89% ee was determined by HPLC on AS-H column, hexane/*i*-propanol (90/10), 1.0 mL/min, UV 254 nm, t_{minor} = 5.553 min, t_{major} = 7.310 min; $[\alpha]_D^{25}$ = -169.4° (c = 0.534, $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.42-7.37 (m, 1H), 7.22-7.14 (m, 3H), 5.99 (d, J = 2.4 Hz, 1H), 5.07 (quint, J = 2.2 Hz, 1H), 4.21-4.08 (m, 2H), 1.18 (t, J = 7.0 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm): 160.4 (d, $^1J_{C\text{-}F}$ = 247.8 Hz), 159.4, 150.2 (q, $^2J_{C\text{-}F}$ = 42.5 Hz), 131.1 (d, $^3J_{C\text{-}F}$ = 8.3 Hz), 128.8 (d, $^4J_{C\text{-}F}$ = 3.1 Hz), 125.0 (q, $^4J_{C\text{-}F}$ = 3.7 Hz), 122.4 (d, $^2J_{C\text{-}F}$ = 13.6 Hz), 117.3 (q, $^1J_{C\text{-}F}$ = 271.9 Hz), 116.4 (q, $^2J_{C\text{-}F}$ = 21.1 Hz), 113.5 (q, $^4J_{C\text{-}F}$ = 2.9 Hz), 107.8, 61.9, 51.0 (q, $^3J_{C\text{-}F}$ = 3.0 Hz), 13.6; ^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm): -64.8 (d, J = 3.0 Hz), -117.0; IR (KBr): 3003, 1738, 1687, 1586, 1501, 1372, 1325, 1211, 1108, 1024, 765 cm^{-1}; HRMS (ESI) m/z: $[M+Na]^+$ calcd. for $C_{14}H_{11}F_4NNaO_5^+$ 372.0466, found 372.0462.

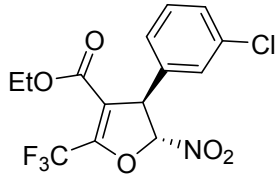
Ethyl 4-(4-fluorophenyl)-5-nitro-2-(trifluoromethyl)-4,5-dihydrofuran-3-carboxylate (3ac).



The product **3ac** was obtained as a yellow oil (34.5 mg, 99% yield). 95% ee was determined by HPLC on AS-H column, hexane/*i*-propanol (90/10), 1.0 mL/min, UV 254 nm, t_{minor} = 5.993 min, t_{major} = 7.717 min; $[\alpha]_D^{25}$ = -80.1° (c = 0.166, $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.23 (dd, J = 8.4, 5.2 Hz, 2H), 7.12 (t, J = 8.4 Hz, 2H), 5.88 (d, J = 2.0 Hz, 1H), 4.80 (app s, 1H), 4.20-4.10 (m, 2H), 1.19 (t, J = 7.2 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm): 163.0 (d, $^1J_{CF}$ = 247.6 Hz), 159.4, 149.7 (q, $^2J_{CF}$ = 41.8 Hz), 131.0 (d, $^4J_{CF}$ = 3.4 Hz), 128.9 (d, $^3J_{CF}$ = 8.5 Hz), 117.3 (q, $^1J_{CF}$ = 271.9 Hz), 116.6 (d, $^2J_{CF}$ = 21.9 Hz), 114.9 (q, $^3J_{CF}$ = 2.9 Hz), 108.2, 62.0, 56.2, 13.6; ^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm): -64.6 (d, J = 2.3 Hz), -111.9; IR (KBr): 3040, 2996,

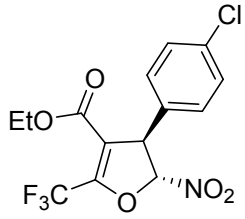
1739, 1688, 1583, 1520, 1377, 1326, 1209, 1107, 1075, 845 cm^{-1}; HRMS (ESI) m/z: $[M+H]^+$ calcd. for $C_{14}H_{12}F_4NO_5$ 350.0646, found 350.0649.

Ethyl 4-(3-chlorophenyl)-5-nitro-2-(trifluoromethyl)-4,5-dihydrofuran-3-carboxylate (3ad).



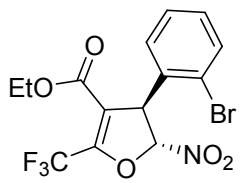
The product **3ad** was obtained as a yellow oil (28.8 mg, 79% yield). 91% ee was determined by HPLC on AS-H column, hexane/*i*-propanol (95/5), 1.0 mL/min, UV 254 nm, t_{minor} = 6.297 min, t_{major} = 11.110 min; $[\alpha]_D^{25}$ = -137.9° (*c* = 0.488, $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.39-7.37 (m, 2H), 7.24 (dd, *J* = 2.0, 1.2 Hz, 1H), 7.15-7.12 (m, 1H), 5.90 (d, *J* = 2.0 Hz, 1H), 4.78 (quint, *J* = 2.0 Hz, 1H), 4.23-4.10 (m, 2H), 1.20 (t, *J* = 7.2 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm): 159.4, 149.7 (q, $^2J_{C-F}$ = 41.6 Hz), 137.0, 135.5, 130.9, 129.5, 127.4, 125.2, 117.3 (q, $^1J_{C-F}$ = 272.0 Hz), 114.5 (q, $^3J_{C-F}$ = 2.7 Hz), 107.9, 62.1, 56.4, 13.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm): -64.5 (d, *J* = 1.9 Hz); IR (KBr): 3032, 3007, 1718, 1678, 1583, 1368, 1323, 1235, 1204, 1182, 1117, 769, 693 cm^{-1}; HRMS (ESI) m/z: $[M+Na]^+$ calcd. for $C_{14}H_{11}ClF_3NNaO_5^+$ 388.0170, found 388.0169.

Ethyl 4-(4-chlorophenyl)-5-nitro-2-(trifluoromethyl)-4,5-dihydrofuran-3-carboxylate (3ae).



The product **3ae** was obtained as a yellow oil (35.0 mg, 96% yield). 95% ee was determined by HPLC on AS-H column, hexane/*i*-propanol (90/10), 1.0 mL/min, UV 254 nm, t_{minor} = 5.800 min, t_{major} = 8.433 min; $[\alpha]_D^{25}$ = -135.7° (*c* = 0.218, $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.41 (d, *J* = 8.4 Hz, 2H), 7.19 (d, *J* = 8.4 Hz, 2H), 5.87 (d, *J* = 2.0 Hz, 1H), 4.79 (app s, 1H), 4.20-4.11 (m, 2H), 1.20 (t, *J* = 7.2 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm): 159.4, 149.9 (q, $^2J_{CF}$ = 42.0 Hz), 135.3, 133.6, 129.8, 128.4, 117.3 (q, $^1J_{CF}$ = 271.4 Hz), 114.7 (q, $^3J_{CF}$ = 2.6 Hz), 108.0, 62.0, 56.2, 13.6; ^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm): -64.5 (d, *J* = 1.9 Hz); IR (KBr): 3001, 1735, 1685, 1585, 1499, 1371, 1324, 1213, 1175, 1107, 766 cm^{-1}; HRMS (ESI) m/z: $[M+Na]^+$ calcd. for $C_{14}H_{11}ClF_3NNaO_5$ 388.0170, found 388.0170.

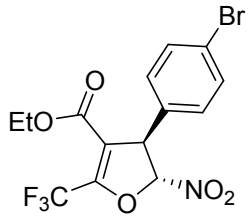
Ethyl 4-(2-bromophenyl)-5-nitro-2-(trifluoromethyl)-4,5-dihydrofuran-3-carboxylate (3af).



The product **3af** was obtained as a yellow oil (34.7 mg, 85% yield). 96% ee was determined by HPLC on AS-H column, hexane/*i*-propanol (95/5), 1.0 mL/min, UV 254 nm, t_{minor} = 7.233 min, t_{major} = 12.170 min; $[\alpha]_D^{25}$ = -55.8° (*c* = 0.768, $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.69 (dd, *J* = 8.0, 1.2 Hz, 1H),

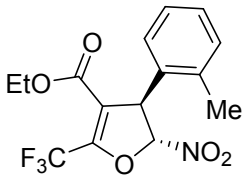
7.37 (td, J = 7.6, 1.2 Hz, 1H), 7.28-7.24 (m, 1H), 7.06 (dd, J = 8.0, 1.6 Hz, 1H), 5.89 (d, J = 2.0 Hz, 1H), 5.43 (quint, J = 1.8 Hz, 1H), 4.18-4.10 (m, 2H), 1.17 (t, J = 7.0 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm): 159.3, 150.6 (q, $^3J_{C\text{-}F}$ = 42.1 Hz), 133.9, 130.7, 128.5, 124.2, 117.3 (q, $^3J_{C\text{-}F}$ = 272.0 Hz), 114.6 (q, $^3J_{C\text{-}F}$ = 2.1 Hz), 108.0, 61.9, 55.5, 13.6; ^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm): -64.6 (d, J = 1.5 Hz); IR (KBr): 3046, 1725, 1679, 1577, 1367, 1330, 1204, 1114, 1072, 1001, 761 cm^{-1}; HRMS (ESI) m/z: $[M+Na]^+$ calcd. for $C_{14}H_{11}BrF_3NNaO_5^+$ 431.9665, found 431.9665.

Ethyl 4-(4-bromophenyl)-5-nitro-2-(trifluoromethyl)-4,5-dihydrofuran-3-carboxylate (3ag).



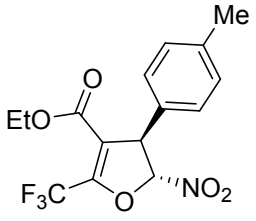
The product **3ag** was obtained as a yellow oil (39.6 mg, 97% yield). 95% ee was determined by HPLC on AS-H column, hexane/*i*-propanol (90/10), 1.0 mL/min, UV 254 nm, t_{minor} = 6.207 min, t_{major} = 8.663 min; $[\alpha]_D^{25}$ = -130.2° (c = 0.350, $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.56 (d, J = 8.4 Hz, 2H), 7.13 (d, J = 8.4 Hz, 2H), 5.87 (d, J = 2.0 Hz, 1H), 4.77 (app s, 1H), 4.20-4.11 (m, 2H), 1.20 (t, J = 7.2 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm): 159.4, 150.0 (q, $^2J_{CF}$ = 42.0 Hz), 134.1, 132.8, 128.7, 123.4, 117.3 (q, $^1J_{CF}$ = 271.9 Hz), 114.6 (q, $^3J_{CF}$ = 2.6 Hz), 107.9, 62.1, 56.3, 13.6; ^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm): -64.5 (d, J = 2.3 Hz); IR (KBr): 3000, 1736, 1684, 1585, 1496, 1370, 1325, 1213, 1107, 1077, 765, 743 cm^{-1}; HRMS (ESI) m/z: $[M+H]^+$ calcd. for $C_{14}H_{12}BrF_3NO_5$ 409.9846, found 409.9846.

Ethyl 5-nitro-4-(*o*-tolyl)-2-(trifluoromethyl)-4,5-dihydrofuran-3-carboxylate (3ah). The



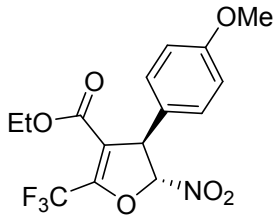
product **3ah** was obtained as a colorless oil (28.6 mg, 83% yield). 95% ee was determined by HPLC on AS-H column, hexane/*i*-propanol (95/5), 1.0 mL/min, UV 254 nm, t_{minor} = 5.717 min, t_{major} = 7.963 min; $[\alpha]_D^{25}$ = -145.4° (c = 0.350, $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.30-7.27 (m, 2H), 7.26-7.22 (m, 1H), 6.97 (q, J = 2.8 Hz , 1H), 5.83 (d, J = 2.4 Hz, 1H), 5.09 (quint, J = 2.2 Hz, 1H), 4.20-4.07 (m, 2H), 2.54 (s, 3H), 1.17 (t, J = 7.0 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm): 159.6, 149.7 (q, $^2J_{C\text{-}F}$ = 41.5 Hz), 136.4, 133.2, 131.4, 129.0, 127.2，125.5，117.4 (q, $^1J_{C\text{-}F}$ = 271.8 Hz), 115.5 (q, $^3J_{C\text{-}F}$ = 2.6 Hz), 108.5, 61.8, 52.8, 19.6, 13.6; ^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm): -64.5 (d, J = 2.3 Hz); IR (KBr): 3041, 3000, 1728, 1690, 1582, 1376, 1329, 1209, 1157, 1107, 1074, 754 cm^{-1}; HRMS (ESI) m/z: $[M+Na]^+$ calcd. for $C_{15}H_{14}F_3NNaO_5^+$ 368.0716, found 368.0712.

Ethyl 5-nitro-4-(*p*-tolyl)-2-(trifluoromethyl)-4,5-dihydrofuran-3-carboxylate (3ai). The



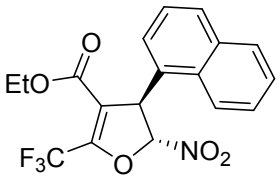
product **3ai** was obtained as a yellow oil (32.7 mg, 95% yield). 93% ee was determined by HPLC on AS-H column, hexane/*i*-propanol (95/5), 1.0 mL/min, UV 254 nm, t_{minor} = 7.420 min, t_{major} = 10.527 min; $[\alpha]_D^{25}$ = -126.1° (*c* = 0.470, $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.22 (d, *J* = 8.0 Hz, 2H), 7.12 (d, *J* = 8.0 Hz, 2H), 5.88 (d, *J* = 2.0 Hz, 1H), 4.76 (app s, 1H), 4.19-4.10 (m, 2H), 2.37 (s, 3H), 1.19 (t, *J* = 7.2 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm): 159.6, 149.4 (q, $^2J_{CF}$ = 41.7 Hz), 139.2, 132.1, 130.2, 126.9, 117.4 (q, $^1J_{CF}$ = 271.7 Hz), 115.1 (q, $^3J_{CF}$ = 2.8 Hz), 108.6, 61.8, 56.6, 21.1, 13.6; ^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm): -64.5 (d, *J* = 2.6 Hz); IR (KBr): 3001, 2948, 1735, 1687, 1587, 1508, 1372, 1326, 1209, 1108, 1023, 795 cm^{-1}; HRMS (ESI) m/z: $[M+H]^+$ calcd. for $C_{15}H_{15}F_3NO_5$ 346.0897, found 346.0894.

Ethyl 4-(4-methoxyphenyl)-5-nitro-2-(trifluoromethyl)-4,5-dihydrofuran-3-carboxylate (3aj).



The product **3aj** was obtained as a yellow oil (32.1 mg, 89% yield). 94% ee was determined by HPLC on AS-H column, hexane/*i*-propanol (95/5), 1.0 mL/min, UV 254 nm, t_{minor} = 8.173 min, t_{major} = 12.947 min; $[\alpha]_D^{25}$ = -170.7° (*c* = 0.476, $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.16 (d, *J* = 8.8 Hz, 2H), 6.93 (d, *J* = 8.8 Hz, 2H), 5.87 (d, *J* = 2.0 Hz, 1H), 4.75 (pseudo t, *J* = 1.8 Hz, 1H), 4.19-4.10 (m, 2H), 3.82 (s, 3H), 1.19 (t, *J* = 7.2 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm): 160.2, 159.6, 149.3 (q, $^1J_{CF}$ = 41.7 Hz), 132.0, 128.2, 127.0, 117.4 (q, $^1J_{CF}$= 271.5 Hz), 115.2 (q, $^3J_{CF}$ = 2.7 Hz), 114.9, 108.6, 61.9, 56.4, 55.3, 13.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm): -64.6 (d, *J* = 2.3 Hz); IR (KBr): 3001, 2940, 1736, 1684, 1584, 1372, 1323, 1211, 1173, 1107, 766 cm^{-1}; HRMS (ESI) m/z: $[M+H]^+$ calcd. for $C_{15}H_{15}F_3NO_6$ 362.0846, found 362.0847.

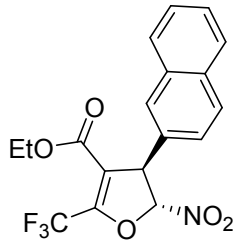
Ethyl 4-(naphthalen-1-yl)-5-nitro-2-(trifluoromethyl)-4,5-dihydrofuran-3-carboxylate (3ak).



The product **3ak** was obtained as a yellow oil (33.9 mg, 89% yield). 94% ee was determined by HPLC on AS-H column, hexane/*i*-propanol (90/10), 1.0 mL/min, UV 254 nm, t_{minor} = 5.530 min, t_{major} = 7.817 min; $[\alpha]_D^{25}$ = -78.0° (*c* = 0.292, $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz) δ (ppm): 8.36 (d, *J* = 8.0 Hz, 1H), 7.96 (d, *J* = 8.0 Hz, 1H), 7.91 (d, *J* = 8.0 Hz, 1H), 7.71 (t, *J* = 7.6 Hz, 1H), 7.61 (t, *J* = 7.4 Hz, 1H),

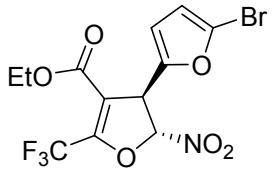
7.48 (t, J = 7.8 Hz, 1H), 7.24 (d, J = 7.2 Hz, 1H), 5.88 (app s, 1H), 5.69 (app s, 1H), 4.16-4.11 (m, 2H), 1.12 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 159.7, 150.1, 134.3, 130.7, 130.3, 130.0, 129.3, 127.6, 126.6, 125.4, 124.0, 121.5, 117.4 (q, $^1J_{C\text{-}F}$ = 271.7 Hz), 114.7 (q, $^3J_{C\text{-}F}$ = 2.6 Hz), 108.2, 62.0, 52.3, 13.6; ^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm): -64.5 (d, J = 1.1 Hz); IR (KBr): 3046, 1721, 1677, 1574, 1367, 1330, 1176, 1114, 1074, 809, 786 cm^{-1}; ESI-HRMS: $[M+H]^+$ calcd. for $C_{18}H_{14}F_3NNaO_5^+$ 404.0716, found 404.0714.

Ethyl 4-(naphthalen-2-yl)-5-nitro-2-(trifluoromethyl)-4,5-dihydrofuran-3-carboxylate (3al).



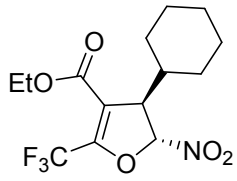
The product **3al** was obtained as a yellow oil (37.7 mg, 99% yield). 91% ee was determined by HPLC on AS-H column, hexane/*i*-propanol (90/10), 1.0 mL/min, UV 254 nm, t_{minor} = 6.187 min, t_{major} = 8.570 min; $[\alpha]_D^{25}$ = -202.0° (c = 0.638, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.92 (d, J = 8.4 Hz, 1H), 7.88-7.86 (m, 2H), 7.72 (s, 1H), 7.56-7.54 (m, 2H), 7.33 (d, J = 8.8 Hz, 1H), 5.98 (app s 1H), 4.98 (app s, 1H), 4.19-4.08 (m, 1H), 1.17 (t, J = 7.2 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ (ppm): 159.6, 149.7 (q, $^2J_{CF}$ = 41.8 Hz), 133.34, 133.32, 132.3, 129.8, 128.0, 126.98, 126.96, 126.6, 124.0, 117.4 (q, $^1J_{CF}$ = 271.8 Hz), 115.0 (q, $^3J_{CF}$ = 2.9 Hz), 108.4, 61.9, 57.0, 13.6; ^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm): -64.5 (d, J = 1.9 Hz); IR (KBr): 2998, 1734, 1683, 1583, 1369, 1323, 1209, 1172, 1107, 823, 756 cm^{-1}; HRMS (ESI) m/z: $[M+H]^+$ calcd. for $C_{18}H_{15}F_3NO_5$ 382.0897, found 382.0895.

Ethyl 2'-nitro-5'-(trifluoromethyl)-2',3'-dihydro-[2,3'-bifuran]-4'-carboxylate (3am). The



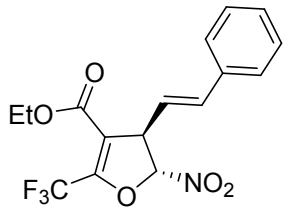
product **3am** was obtained as a yellow oil (33.9 mg, 85% yield). 93% ee was determined by HPLC on AS-H column, hexane/*i*-propanol (80/20), 1.0 mL/min, UV 254 nm, t_{minor} = 4.773 min, t_{major} = 6.073 min; $[\alpha]_D^{25}$ = -208.5° (c = 0.576, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 6.33 (s, 2H), 6.06 (d, J = 2.0 Hz, 1H), 4.92 (pseudo t, J = 1.8 Hz, 1H), 4.29-4.16 (m, 2H), 1.26 (t, J = 7.2 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ (ppm): 159.3, 150.7 (q, $^1J_{CF}$ = 41.9 Hz), 148.7, 123.4, 117.1 (q, $^1J_{CF}$ = 272.1 Hz), 112.9, 112.0, 111.6 (q, $^3J_{CF}$ = 2.4 Hz), 105.5, 62.1, 50.5, 13.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm): -64.7 (d, J = 1.9 Hz); IR (KBr): 2995, 1739, 1586, 1373, 1325, 1176, 1109, 1023, 799 cm^{-1}; HRMS (ESI) m/z: $[M+Na]^+$ calcd. for $C_{12}H_9BrF_3NNaO_6$ 421.9458, found 421.9457.

Ethyl 4-cyclohexyl-5-nitro-2-(trifluoromethyl)-4,5-dihydrofuran-3-carboxylate (3an). The



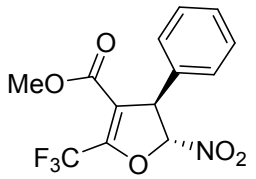
product **3an** was obtained as a colorless oil (19.8 mg, 59% yield). 92% ee was determined by HPLC on AS-H column, hexane/*i*-propanol (95/5), 1.0 mL/min, UV 254 nm, t_{minor} = 5.430 min, t_{major} = 6.180 min; $[\alpha]_D^{25}$ = -111.0° (*c* = 0.100, $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz) δ (ppm): 5.84 (d, *J* = 2.0 Hz, 1H), 4.31-4.21 (m, 2H), 3.57 (quint, *J* = 2.0 Hz, 1H), 1.86-1.60 (m, 6H), 1.31 (t, *J* = 7.2 Hz, 3H), 1.28-1.12 (m, 4H), 0.94-0.84 (m, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm): 160.5, 148.5 (q, $^2J_{C\text{-}F}$ = 40.6 Hz), 117.3 (q, $^1J_{C\text{-}F}$ = 271.4 Hz), 113.2 (q, $^3J_{C\text{-}F}$ = 2.8 Hz), 105.2, 61.9, 57.7, 38.4, 30.7, 27.1, 26.0, 25.9, 25.8, 13.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm): -64.6 (d, *J* = 2.3 Hz); IR (KBr): 2946, 1734, 1584, 1457, 1374, 1324, 1208, 1173, 1116, 774 cm^{-1}; HRMS (ESI) m/z: HRMS (ESI) m/z: $[M+Na]^+$ calcd. for $C_{14}H_{18}F_3NNaO_5^+$ 360.1029, found 360.1034.

Ethyl (*E*)-5-nitro-4-styryl-2-(trifluoromethyl)-4,5-dihydrofuran-3-carboxylate (3ao). The



product **3ao** was obtained as a colorless oil (23.9 mg, 67% yield). 82% ee was determined by HPLC on AS-H column, hexane/*i*-propanol (90/10), 1.0 mL/min, UV 254 nm, t_{minor} = 7.093 min, t_{major} = 8.667 min; $[\alpha]_D^{25}$ = -168.3° (*c* = 0.294, $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.41-7.29 (m, 5H), 6.71 (d, *J* = 16.0 Hz, 1H), 6.14 (dd, *J* = 16.0, 8.4 Hz, 1H), 5.91 (d, *J* = 2.0 Hz, 1H), 4.45 (d, *J* = 8.4 Hz, 1H), 4.27-4.18 (m, 2H), 1.28 (t, *J* = 7.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 159.7, 149.3 (q, $^2J_{C\text{-}F}$ = 41.8 Hz), 135.9, 135.1, 128.9, 128.8, 126.7, 121.5, 117.3 (q, $^1J_{C\text{-}F}$ = 271.8 Hz), 114.0 (q, $^3J_{C\text{-}F}$ = 2.6 Hz), 107.1, 62.0, 54.4, 13.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm): -64.7 (d, *J* = 1.8 Hz); IR (KBr): 2939, 1735, 1683, 1583, 1374, 1322, 1208, 1172, 1109, 758, 697 cm^{-1}; ESI-HRMS: $[M+H]^+$ calcd. for $C_{16}H_{15}F_3NO_5^+$ 358.0897, found 358.0893.

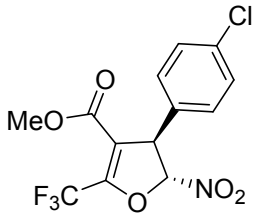
Methyl 5-nitro-4-phenyl-2-(trifluoromethyl)-4,5-dihydrofuran-3-carboxylate (3ba). The



product **3ba** was obtained as a yellow oil (29.1 mg, 92% yield). 95% ee was determined by HPLC on AS-H column, hexane/*i*-propanol (95/5), 0.7 mL/min, UV 254 nm, t_{minor} = 7.923 min, t_{major} = 13.153 min; $[\alpha]_D^{25}$ = -173.4° (*c* = 0.520, $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.46-7.40 (m, 3H), 7.26-7.24 (m, 2H), 5.90 (d, *J* = 2.0 Hz, 1H), 4.82 (pseudo quint, *J* = 2.0 Hz, 1H), 3.70 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm): 160.1, 150.0 (q, $^2J_{CF}$ = 41.9 Hz), 135.0, 129.7, 129.3, 127.0, 117.3 (q, $^1J_{CF}$ = 271.9 Hz), 114.6 (q, $^3J_{CF}$ = 2.6 Hz), 108.4, 56.8, 52.6; ^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm):

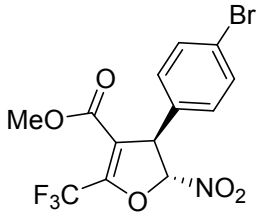
-64.7 (d, J = 1.9 Hz); IR (KBr): 2972, 1743, 1684, 1584, 1448, 1372, 1331, 1214, 1110, 733, 702 cm^{-1}; HRMS (ESI) m/z: $[M+H]^+$ calcd. for $C_{13}H_{11}F_3NO_5$ 318.0584, found 318.0583.

Methyl 4-(4-chlorophenyl)-5-nitro-2-(trifluoromethyl)-4,5-dihydrofuran-3-carboxylate (3be).



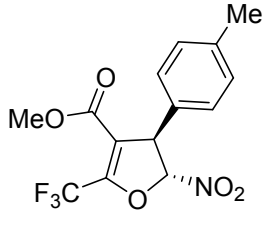
The product **3be** was obtained as a yellow oil (34.4 mg, 98% yield). 93% ee was determined by HPLC on AS-H column, hexane/*i*-propanol (95/5), 1.0 mL/min, UV 254 nm, t_{minor} = 7.420 min, t_{major} = 10.527 min; $[\alpha]_D^{25}$ = -166.6° (c = 0.834, $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.41 (d, J = 8.4 Hz, 2H), 7.19 (d, J = 8.4 Hz, 2H), 5.86 (d, J = 2.0 Hz, 1H), 4.79 (pseudo quint, J = 2.0 Hz, 1H), 3.71 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm): 159.9, 150.2 (q, $^2J_{CF}$ = 41.9 Hz), 135.4, 133.5, 129.9, 128.4, 117.2 (q, $^1J_{CF}$ = 272.0 Hz), 114.3 (q, $^3J_{CF}$ = 2.6 Hz), 108.0, 56.2, 52.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm): -64.7 (d, J = 2.3 Hz); IR (KBr): 3031, 3005, 1719, 1680, 1585, 1499, 1369, 1321, 1235, 1210, 1183, 1116, 836, 765 cm^{-1}; HRMS (ESI) m/z: $[M+Na]^+$ calcd. for $C_{13}H_9ClF_3NNaO_5$ 374.0014, found 374.0008.

Methyl 4-(4-bromophenyl)-5-nitro-2-(trifluoromethyl)-4,5-dihydrofuran-3-carboxylate (3bg).



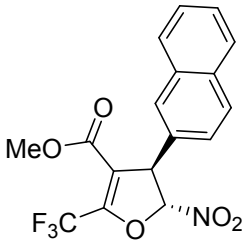
The product **3bg** was obtained as a yellow oil (35.1 mg, 89% yield). 95% ee was determined by HPLC on AS-H column, hexane/*i*-propanol (95/5), 1.0 mL/min, UV 254 nm, t_{minor} = 8.097 min, t_{major} = 10.977 min; $[\alpha]_D^{25}$ = -125.5° (c = 1.02, $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.56 (d, J = 8.0 Hz, 2H), 7.13 (d, J = 8.0 Hz, 2H), 5.87 (d, J = 2.0 Hz, 1H), 4.78 (app s, 1H), 3.71 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm): 159.9, 150.2 (q, $^2J_{CF}$ = 42.2 Hz), 134.0, 132.8, 128.7, 123.5, 117.2 (q, $^1J_{CF}$ = 272.0 Hz), 114.2 (q, $^3J_{CF}$ = 2.6 Hz), 108.0, 56.2, 52.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm): -64.7 (d, J = 1.9 Hz); IR (KBr): 2972, 1742, 1684, 1585, 1370, 1331, 1213, 1174, 1110, 765 cm^{-1}; HRMS (ESI) m/z: $[M+Na]^+$ calcd. for $C_{13}H_9BrF_3NNaO_5$ 417.9508, found 417.9507.

Methyl 5-nitro-4-(*p*-tolyl)-2-(trifluoromethyl)-4,5-dihydrofuran-3-carboxylate (3bi). The product **3bi** was obtained as a yellow oil (31.1 mg, 94% yield). 96% ee was determined by HPLC on AS-H column, hexane/*i*-propanol (95/5), 1.0 mL/min, UV 254 nm, t_{minor} = 5.750 min, t_{major} = 7.370 min; $[\alpha]_D^{25}$ = -178.3° (c = 0.328, $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.23



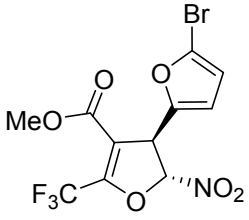
(d, J = 8.0 Hz, 2H), 7.12 (d, J = 7.6 Hz, 2H), 5.88 (app s, 1H), 4.78 (app s, 1H), 3.70 (s, 3H), 2.37 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm): 160.1, 149.7 (q, $^2J_{CF}$ = 41.8 Hz), 139.2, 132.0, 130.3, 126.8, 117.6 (q, $^1J_{CF}$ = 271.8 Hz), 114.7 (q, $^3J_{CF}$ = 2.6 Hz), 108.6, 56.5, 52.6, 21.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm): -64.8 (d, J = 1.9 Hz); IR (KBr): 2972, 2939, 1741, 1685, 1584, 1448, 1371, 1330, 1210, 1109, 819, 765 cm^{-1}; HRMS (ESI) m/z: $[M+H]^+$ calcd. for $C_{14}H_{13}F_3NO_5$ 332.0740, found 332.0743.

Methyl 4-(naphthalen-2-yl)-5-nitro-2-(trifluoromethyl)-4,5-dihydrofuran-3-carboxylate (3bl).



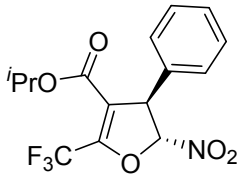
The product **3bl** was obtained as a yellow oil (34.1 mg, 93% yield). 95% ee was determined by HPLC on AS-H column, hexane/*i*-propanol (95/5), 1.0 mL/min, UV 254 nm, t_{minor} = 9.687 min, t_{major} = 13.467 min; $[\alpha]_D^{25}$ = -185.5° (c = 0.152, $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.92 (d, J = 8.4 Hz, 1H), 7.88-7.86 (m, 2H), 7.70 (d, J = 1.2 Hz, 1H), 7.58-7.53 (m, 2H), 7.33 (dd, J = 8.4, 2.0 Hz, 1H), 5.97 (d, J = 2.0 Hz, 1H), 4.99 (pseudo quint, J = 2.0 Hz, 1H), 3.69 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm): 160.1, 150.0 (q, $^2J_{C\text{-}F}$ = 42.2 Hz), 133.4, 133.3, 132.2, 129.9, 128.0, 127.8, 127.0, 126.5, 123.9, 117.4 (q, $^1J_{C\text{-}F}$ = 271.9 Hz), 114.5 (q, $^3J_{C\text{-}F}$ = 2.7 Hz), 108.4, 57.0, 52.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm): -64.7 (d, J = 2.3 Hz); IR (KBr): 3046, 1721, 1677, 1574, 1367, 1330, 1223, 1204, 1177, 1114, 809, 786 cm^{-1}; HRMS (ESI) m/z: $[M+H]^+$ calcd. for $C_{17}H_{13}F_3NO_5$ 368.0740, found 368.0740.

Methyl 5-bromo-2'-nitro-5'-(trifluoromethyl)-2',3'-dihydro-[2,3'-bifuran]-4'-carboxylate (3bm).



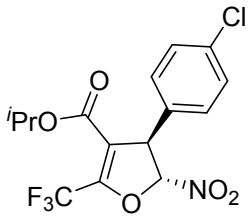
The product **3bm** was obtained as a yellow oil (32.3 mg, 84% yield). 90% ee was determined by HPLC on AS-H column, hexane/*i*-propanol (90/10), 1.0 mL/min, UV 254 nm, t_{minor} = 6.350 min, t_{major} =14.563 min; $[\alpha]_D^{25}$ = -46.9° (c = 0.230, $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz) δ (ppm): 6.34 (t, J = 3.6 Hz, 1H), 6.33 (t, J = 3.6 Hz, 1H), 6.06 (d, J = 2.0 Hz, 1H), 4.92 (pseudo quint, J = 2.0 Hz, 1H), 3.77 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm): 159.7, 150.9 (q, $^2J_{C\text{-}F}$ = 42.2 Hz), 148.6, 123.5, 117.1 (q, $^1J_{C\text{-}F}$ = 272.1 Hz), 112.9, 112.0, 111.3 (q, $^3J_{C\text{-}F}$ = 2.5 Hz), 105.5, 52.8, 50.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm): -64.9 (d, J = 1.9 Hz); IR (KBr): 2974, 1743, 1686, 1587, 1449, 1371, 1332, 1210, 1110, 796, 768 cm^{-1}; HRMS (ESI) m/z: $[M+Na]^+$ calcd. for $C_{11}H_7BrF_3NNaO_6^+$ 407.9301, found 407.9304.

Isopropyl 5-nitro-4-phenyl-2-(trifluoromethyl)-4,5-dihydrofuran-3-carboxylate (3ca). The



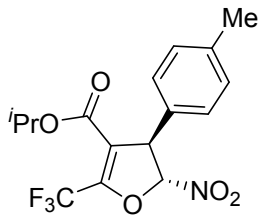
product **3ca** was obtained as a colorless oil (28.3 mg, 82% yield). 85% ee was determined by HPLC on AS-H column, hexane/*i*-propanol (95/5), 1.0 mL/min, UV 254 nm, t_{minor} = 5.077 min, t_{major} = 7.500 min; $[\alpha]_D^{25}$ = -165.0° (*c* = 0.550, $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.45-7.39 (m, 3H), 7.24 (dd, *J* = 7.6, 1.6 Hz, 2H), 5.91 (d, *J* = 2.0 Hz, 1H), 4.97 (hept, *J* = 6.2 Hz, 1H), 4.79 (pseudo quint, *J* = 2.2 Hz, 1H), 1.20 (d, *J* = 6.0 Hz, 3H), 1.09 (d, *J* = 6.4 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm): 159.1, 149.4 (q, $^2J_{C\text{-}F}$ = 42.0 Hz), 135.2, 129.5, 129.1, 127.0, 117.4 (q, $^1J_{C\text{-}F}$ = 271.7 Hz), 115.4 (q, $^3J_{C\text{-}F}$ = 2.6 Hz), 108.4, 69.9, 56.9, 21.4, 21.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm): -64.5 (d, *J* = 1.5 Hz); IR (KBr): 3001, 1730, 1689, 1578, 1376, 1322, 1172, 1106, 757, 701 cm^{-1}; HRMS (ESI) m/z: $[M+H]^+$ calcd. for $C_{15}H_{15}F_3NO_5^+$ 346.0897, found 346.0900.

Isopropyl 4-(4-chlorophenyl)-5-nitro-2-(trifluoromethyl)-4,5-dihydrofuran-3-carboxylate



(3ce). The product **3ce** was obtained as a colorless oil (34.5 mg, 91% yield). 92% ee was determined by HPLC on AS-H column, hexane/*i*-propanol (95/5), 1.0 mL/min, UV 254 nm, t_{minor} = 5.617 min, t_{major} = 7.957 min; $[\alpha]_D^{25}$ = -172.2° (*c* = 0.584, $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.40 (d, *J* = 8.4 Hz, 2H), 7.19 (d, *J* = 8.8 Hz, 2H), 5.87 (d, *J* = 2.0 Hz, 1H), 4.98 (hept, *J* = 6.2 Hz, 1H), 4.77 (pseudo quint, *J* = 2.0 Hz, 1H), 1.20 (d, *J* = 6.0 Hz, 3H), 1.11 (d, *J* = 6.0 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm): 158.9, 149.6 (q, $^2J_{C\text{-}F}$ = 41.8 Hz), 135.3, 133.7, 129.8, 128.4, 117.3 (q, $^1J_{C\text{-}F}$ = 271.8 Hz), 115.1 (q, $^3J_{C\text{-}F}$ = 2.6 Hz), 108.0, 70.2, 56.3, 21.4, 21.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm): -64.4 (d, *J* = 1.9 Hz); IR (KBr): 3031, 3001, 1732, 1690, 1580, 1499, 1375, 1328, 1218, 1171, 1102, 765 cm^{-1}; HRMS (ESI) m/z: $[M+Na]^+$ calcd. for $C_{15}H_{13}ClF_3NNaO_5^+$ 402.0327, found 402.0328.

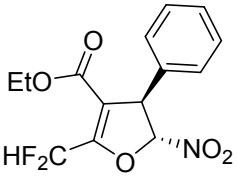
Isopropyl 5-nitro-4-(*p*-tolyl)-2-(trifluoromethyl)-4,5-dihydrofuran-3-carboxylate (3ci). The



product **3ci** was obtained as a colorless oil (28.7 mg, 80% yield). 87% ee was determined by HPLC on AS-H column, hexane/*i*-propanol (95/5), 1.0 mL/min, UV 254 nm, t_{minor} = 4.890 min, t_{major} = 6.127 min; $[\alpha]_D^{25}$ = -157.6° (*c* = 0.170, $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.22 (d, *J* = 8.0 Hz, 2H), 7.12 (d, *J* = 8.4 Hz, 2H), 5.88 (d, *J* = 2.4 Hz, 1H), 4.98 (hept, *J* = 6.2 Hz, 1H),

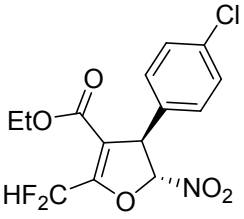
4.75 (pseudo quint, J = 2.2 Hz, 1H), 2.37 (s, 3H), 1.20 (d, J = 6.4 Hz, 3H), 1.11 (d, J = 6.4 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm): 159.1, 149.2 (q, $^2J_{C\text{-}F}$ = 41.6 Hz), 139.1, 132.2, 130.2, 126.9, 117.4 (q, $^1J_{C\text{-}F}$ = 271.7 Hz), 115.5 (q, $^3J_{C\text{-}F}$ = 2.6 Hz), 108.6, 69.9, 56.7, 21.4, 21.2, 21.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm): -64.4 (d, J = 2.3 Hz); IR (KBr): 3029, 3001, 1730, 1689, 1579, 1374, 1328, 1216, 1173, 1102, 766 cm^{-1}; HRMS (ESI) m/z: $[M+H]^+$ calcd. for $C_{16}H_{16}F_3NNaO_5^+$ 382.0873, found 382.0873.

Ethyl 2-(difluoromethyl)-5-nitro-4-phenyl-4,5-dihydrofuran-3-carboxylate (3da). The product



3da was obtained as a colorless oil (28.8 mg, 92% yield). 93% ee was determined by HPLC on AS-H column, hexane/*i*-propanol (95/5), 1.0 mL/min, UV 254 nm, t_{minor} = 8.373 min, t_{major} = 13.033 min; $[\alpha]_D^{25}$ = -177.6° (c = 0.250, $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.43-7.37 (m, 3H), 7.22 (d, J = 6.4 Hz, 2H), 7.21 (t, J = 52.2 Hz, 1H), 5.95 (d, J = 2.0 Hz, 1H), 4.70 (app t, J = 1.8 Hz, 1H), 4.17-4.09 (m, 2H), 1.15 (t, J = 7.0 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm): 160.9, 156.1 (t, $^2J_{CF}$ = 23.5 Hz), 135.7, 129.5, 128.9, 127.0, 114.8 (t, $^3J_{CF}$ = 6.4 Hz), 109.2, 106.0 (dd, $^1J_{C\text{-}F}$ = 239.4, 237.1 Hz), 61.6, 55.7, 13.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm): -125.0 (dd, J = 51.9, 2.3 Hz), -125.3 (dd, J = 52.1, 4.7 Hz); IR (KBr): 3046, 3003, 1721, 1586, 1383, 1316, 1224, 1192, 1143, 1054, 998, 851, 808, 781, 735, 700 cm^{-1}; HRMS (ESI) m/z: $[M+Na]^+$ calcd. for $C_{14}H_{13}F_2NNaO_5^+$ 336.0654, found 336.0649.

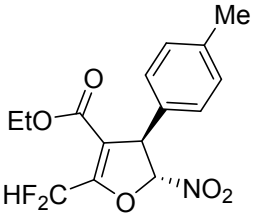
Ethyl 4-(4-chlorophenyl)-2-(difluoromethyl)-5-nitro-4,5-dihydrofuran-3-carboxylate (3de).



The product **3de** was obtained as a colorless oil (31.9 mg, 92% yield). 93% ee was determined by HPLC on AS-H column, hexane/*i*-propanol (90/10), 1.0 mL/min, UV 254 nm, t_{minor} = 7.250 min, t_{major} = 9.673 min; $[\alpha]_D^{25}$ = -212.5° (c = 0.574, $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.39 (d, J = 8.4 Hz, 2H), 7.19 (t, J = 52.2 Hz, 1H), 7.17 (d, J = 8.4 Hz, 2H), 5.91 (d, J = 2.0 Hz, 1H), 4.69 (pseudo quint, J = 2.0 Hz, 1H), 4.14 (q, J = 7.2 Hz, 2H), 1.17 (t, J = 7.2 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm): 160.7, 156.3 (t, $^2J_{CF}$ = 23.5 Hz), 135.1, 134.2, 129.7, 128.4, 114.5 (t, $^3J_{CF}$ = 6.2 Hz), 108.8, 105.9 (dd, $^1J_{CF}$ = 239.7, 237.1 Hz), 61.8, 55.1, 13.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm): -124.9 (dd, J = 52.1, 2.4 Hz), -125.3 (dd, J = 52.5, 4.3 Hz); IR (KBr): 2998, 1726, 1692, 1583, 1500, 1381, 1319, 1221, 1136, 1071, 1029, 853, 810, 757 cm^{-1}; HRMS (ESI) m/z:

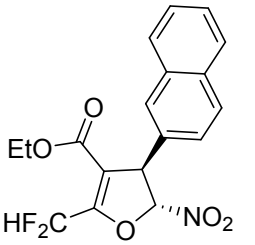
$[M+Na]^+$ calcd. for $C_{14}H_{12}ClF_2NNaO_5^+$ 370.0264, found 370.0260.

Ethyl 2-(difluoromethyl)-5-nitro-4-(*p*-tolyl)-4,5-dihydrofuran-3-carboxylate (3di). The

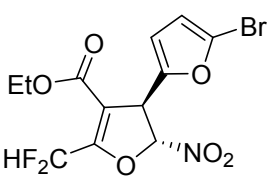


product **3di** was obtained as a colorless oil (30.7 mg, 94% yield). 87% ee was determined by HPLC on AS-H column, hexane/*i*-propanol (90/10), 1.0 mL/min, UV 254 nm, t_{minor} = 5.760 min, t_{major} = 7.350 min; $[\alpha]_D^{25}$ = -200.6° (*c* = 0.622, $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.21 (d, *J* = 7.6 Hz, 2H), 7.19 (t, *J* = 52.0 Hz, 1H), 7.10 (d, *J* = 7.6 Hz, 2H), 5.92 (d, *J* = 2.0 Hz, 1H), 4.67 (app s, 1H), 4.13 (q, *J* = 7.2 Hz, 2H), 2.36 (s, 3H), 1.17 (t, *J* = 7.2 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm): 160.9, 155.9 (t, $^2J_{CF}$ = 28.5 Hz), 138.9, 132.8, 130.1, 126.9, 114.9 (t, $^3J_{CF}$ = 6.3 Hz), 109.4, 106.0 (dd, $^1J_{CF}$ = 239.1, 237.2 Hz), 61.6, 55.4, 21.1, 13.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm): -125.0 (dd, *J* = 51.9, 2.6 Hz), -125.2 (dd, *J* = 52.5, 4.3 Hz); IR (KBr): 3043, 3009, 1726, 1679, 1571, 1381, 1324, 1225, 1133, 1062, 1014, 853, 803, 763 cm^{-1}; HRMS (ESI) m/z: $[M+Na]^+$ calcd. for $C_{15}H_{15}F_2NNaO_5^+$ 350.0810, found 350.0806.

Ethyl 2-(difluoromethyl)-4-(naphthalen-2-yl)-5-nitro-4,5-dihydrofuran-3-carboxylate (3dl).



The product **3dl** was obtained as a colorless oil (33.7 mg, 93% yield). 92% ee was determined by HPLC on AS-H column, hexane/*i*-propanol (90/10), 1.0 mL/min, UV 254 nm, t_{minor} = 7.203 min, t_{major} = 9.953 min; $[\alpha]_D^{25}$ = -247.7° (*c* = 0.672, $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.89 (d, *J* = 8.4 Hz, 1H), 7.86-7.84 (m, 2H), 7.69 (s, 1H), 7.54-7.52 (m, 2H), 7.30 (d, *J* = 8.4 Hz, 1H), 7.26 (t, *J* = 52.0 Hz, 1H), 6.00 (app s, 1H), 4.89 (app s, 1H), 4.11 (q, *J* = 6.8 Hz, 2H), 1.13 (t, *J* = 7.0 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm): 160.9, 156.2 (t, $^2J_{CF}$ = 23.5 Hz), 133.31, 133.26, 132.9, 129.6, 127.9, 127.8, 126.9, 126.8, 126.5, 124.1, 114.8 (t, $^3J_{CF}$ = 6.3 Hz), 109.2, 106.1 (dd, $^1J_{CF}$ = 239.2, 237.4 Hz), 61.7, 55.9, 13.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm): -124.9 (dd, *J* = 51.5, 2.6 Hz), -125.1 (dd, *J* = 52.3, 4.5 Hz); IR (KBr): 3007, 1725, 1695, 1585, 1382, 1313, 1213, 1136, 1084, 1052, 769 cm^{-1}; HRMS (ESI) m/z: $[M+Na]^+$ calcd. for $CH_{15}F_2NNaO_5^+$ 386.0811, found 386.0809.



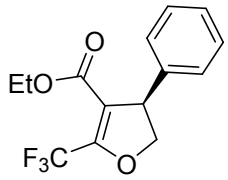
Ethyl 5'-(difluoromethyl)-2'-nitro-2',3'-dihydro-[2,3'-bifuran]-4'-carboxylate (3dm). The product **3dm** was obtained as a yellow oil (34.2 mg, 90% yield). 96% ee was determined by HPLC on AS-H

column, hexane/*i*-propanol (90/10), 1.0 mL/min, UV 254 nm, t_{minor} = 8.613 min, t_{major} = 20.260 min; $[\alpha]_D^{25}$ = -46.9° (*c* = 0.230, $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.14 (t, *J* = 52.0 Hz, 1H), 6.31 (d, *J* = 3.2 Hz, 1H), 6.29 (d, *J* = 3.2 Hz, 1H), 6.09 (d, *J* = 1.6 Hz, 1H), 4.83 (d, *J* = 1.6 Hz, 1H), 4.28-4.14 (m, 2H), 1.25 (t, *J* = 7.2 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm): 160.5, 157.0 (t, $^2J_{C\text{-}F}$ = 23.8 Hz), 149.4, 123.1, 112.8, 111.6, 111.3 (t, $^3J_{C\text{-}F}$ = 6.3 Hz), 106.4, 105.8 (dd, $^1J_{C\text{-}F}$ = 239.5, 238.1 Hz), 61.9, 49.3, 13.9; ^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm): -125.3 (dd, *J* = 52.1, 4.3 Hz), -125.7 (dd, *J* = 51.9, 2.3 Hz); IR (KBr): 3000, 1727, 1585, 1381, 1319, 1204, 1130, 1068, 1029, 851, 796, 766 cm^{-1}; HRMS (ESI) m/z: $[M+Na]^+$ calcd. for $C_{12}H_{10}BrF_2NNaO_6^+$ 403.9552, found 403.9558.

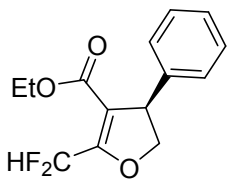
3. Procedure for the reductive denitration

$^nBu_3SnH$ (80.7 μL, 0.3 mmol) was added to a solution of the compound **3aa** (33.1 mg, 0.1 mmol) in benzene (1 mL) followed by AIBN (6.6 mg, 0.04 mmol). The reaction mixture was stirred at 80 °C for 12 h and concentrated. The residue was purified by flash column chromatography on a silica gel (EtOAc/hexane = 1:40, v/v), giving the product **4a**.

Ethyl 4-phenyl-2-(trifluoromethyl)-4,5-dihydrofuran-3-carboxylate (4a). The product **4a** was



obtained as a pale yellow oil (12.8 mg, 45% yield). 94% ee was determined by HPLC on OD-H column, hexane/*i*-propanol (80/20), 1.0 mL/min, UV 254 nm, t_{minor} = 4.697 min; t_{major} = 5.840 min; $[\alpha]_D^{25}$ = -14.5° (c = 0.096, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.34 (t, *J* = 7.2 Hz, 2H), 7.29-7.23 (m, 3H), 4.90 (t, *J* = 12.2 Hz, 1H), 4.55-4.50 (m, 2H), 4.16-4.02 (m, 2H), 1.12 (t, *J* = 7.2 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm): 161.9, 152.2 (t, $^2J_{C\text{-}F}$ = 39.4 Hz), 141.1, 128.9, 127.6 , 127.2, 118.3 (t, $^1J_{C\text{-}F}$ = 271.9 Hz), 113.6 (t, $^3J_{C\text{-}F}$ = 2.6 Hz), 79.2, 60.8, 49.8, 13.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm): -64.8; IR (KBr): 3439, 2986, 2941, 1727, 1666, 1385, 1339, 1316, 1199, 1161, 1116, 1041, 703 cm^{-1}; HRMS (ESI) m/z: $[M+H]^+$ calcd. for $C_{14}H_{14}F_3O_3^+$ 287.0890, found 287.0895.



Ethyl 2-(difluoromethyl)-4-phenyl-4,5-dihydrofuran-3-carboxylate (4b). The product **4b** was obtained as a pale yellow oil (15.0 mg, 56% yield) after 6 h. 91% ee was determined by HPLC on OD-H column, hexane/*i*-propanol (80/20), 1.0 mL/min, UV 254 nm, t_{minor} = 4.890 min, t_{major} = 5.717 min; $[\alpha]_D^{25}$ =

-10.7° (c = 0.056, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.35-7.31 (m, 2H), 7.28-7.26 (m, 1H), 7.24-7.22 (m, 2H), 7.15 (t, J = 52.8 Hz, 1H), 4.91 (t, J = 10.2 Hz, 1H), 4.56 (dd, J = 9.6, 5.6 Hz, 1H), 4.34-4.38 (m, 1H), 4.11-4.01 (m, 2H), 1.10 (t, J = 7.2 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm): 163.2, 158.5 (t, $^2J_{C\text{-}F}$ = 22.6 Hz), 141.9, 128.7, 127.4, 127.2, 113.9 (t, $^3J_{C\text{-}F}$ = 6.3 Hz), 107.0 (t, $^1J_{C\text{-}F}$ = 236.9 Hz), 79.8, 60.5, 48.3, 13.9; ^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm): -125.1 (dd, J = 53.0, 4.5 Hz), -125.3 (dd, J = 52.8, 2.8 Hz); IR (KBr): 3413, 2973, 2937, 2865, 1716, 1653, 1471, 1384, 1267, 1102, 1033, 806 cm^{-1}; HRMS (ESI) m/z: $[M+H]^+$ calcd. for $C_{14}H_{15}F_2O_3^+$ 269.0984, found 269.0984.

4. Procedure for the reduction of the ester group

To a solution of **3aa** (33.1 mg, 0.1 mmol) in dry CH_2Cl_2 (1 mL) was added DIBAL-H (1.0 M solution in hexanes, 220 μL, 0.22 mmol) dropwise at 0 °C. The reaction mixture was allowed to stir at 0 °C for 30 min, and then it was quenched with 1 mL CH_3OH at 0 °C. The solution was treated with 1N HCl (10 mL) and extracted with CH_2Cl_2 (10 mL×3). The combined organic layers were washed with brine, dried over Na_2SO_4 and concentrated. The residue was purified by flash column chromatography on silica gel, eluting with (EtOAc/petroleum ether = 1/5, v/v) to give **5a**.

(5-nitro-4-phenyl-2-(trifluoromethyl)-4,5-dihydrofuran-3-yl)methanol (5a). The product **5a** was obtained as a colorless oil (25.1 mg, 87% yield). 96% ee was determined by HPLC on AD-H column, hexane/*i*-propanol (90/10), 1.0 mL/min, UV 210 nm, t_{major} = 5.587 min，t_{minor} = 6.993 min; $[\alpha]_D^{25}$ = -218.3° (c = 0.448, $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.46-7.38 (m, 3H), 7.23 (dd, J = 7.8, 1.6 Hz, 2H), 5.87 (d, J = 1.6 Hz, 1H), 4.70 (app s, 1H), 4.54 (d, J = 13.6 Hz, 1H), 3.96 (d, J = 13.6 Hz, 1H) , 1.73 (br s, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm): 139.0 (q, $^2J_{C\text{-}F}$ = 40.1 Hz), 134.9, 129.7, 129.2, 127.3, 122.8 (q, $^3J_{C\text{-}F}$ = 2.4 Hz), 118.5 (q, $^1J_{C\text{-}F}$ = 269.5 Hz), 108.9, 57.5, 53.7 (q, $^4J_{C\text{-}F}$ = 2.0 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm): -66.1; IR (KBr): 3337, 2937, 1582, 1379, 1193, 1151, 1116, 1008, 727, 704 cm^{-1}; ESI-HRMS: $[M+H]^+$ calcd. for $C_{12}H_{11}F_3NO_4^+$ 290.0635, found 290.0637.

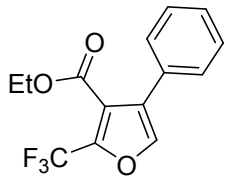
(2-(difluoromethyl)-5-nitro-4-phenyl-4,5-dihydrofuran-3-yl)methanol (5b). The product **5b** was obtained as a colorless oil (21.9 mg, 81% yield) after 1 h. 91% ee was

determined by HPLC on AD-H column, hexane/*i*-propanol (95/5), 1.0 mL/min, UV 210 nm, t_{minor} = 19.630 min，t_{major} = 23.047 min; $[\alpha]_D^{25}$ = -218.7° (*c* = 0.342, $CHCl_3$). ^1H NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.44-7.36 (m, 3H), 7.22 (dd, *J* = 8.0, 1.2 Hz, 2H), 6.66 (t, *J* = 52.8 Hz, 1H), 5.82 (d, *J* = 2.0 Hz, 1H), 4.54 (app s, 1H), 4.36 (d, *J* = 14.4 Hz, 1H), 4.02 (d, *J* = 14.0 Hz, 1H), 2.09 (br s, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm): 143.9 (t, $^2J_{C\text{-}F}$ = 25.3 Hz), 135.3, 129.6, 129.0, 127.3, 121.4 (t, $^3J_{C\text{-}F}$ = 5.0 Hz), 109.4, 107.7 (dd, $^1J_{C\text{-}F}$ = 236.7, 235.3 Hz), 57.4, 54.7 (t, $^4J_{C\text{-}F}$ = 1.0 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm): -120.7 (dd, *J* = 319.4, 53.2 Hz), -122.8 (dd, *J* = 318.6, 52.4 Hz); IR (KBr): 3334, 1578, 1402, 1377, 1257, 1229, 1091, 1053, 1006, 824, 733, 705 cm^{-1}; ESI-HRMS: $[M+H]^+$ calcd. for $C_{12}H_{12}F_2NO_4^+$ 272.0729 found 272.0731.

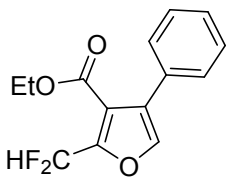
5. Procedure for the elimination of HNO_2

3aa (33.1 mg, 0.1 mmol) and KO^{t}Bu (12.3 mg, 0.11 mmol) were stirred in DMF (2 mL) at rt for 30 min. After this period, the reaction mixture was partitioned between ethyl acetate and water. The combined organic phases were dried over Na_2SO_4, filtered and concentrated *in vacuo* to afford the crude product. The following purification by flash column chromatography (EtOAc/petroleum ether = 1/40, v/v) furnished desired product **6a**.

Ethyl 4-phenyl-2-(trifluoromethyl)furan-3-carboxylate (6a). The product **6a** was obtained as a



yellow oil (19.6 mg, 69% yield). ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.55 (s, 1H), 7.42-7.37 (m, 5H), 4.29 (q, *J* = 7.2 Hz, 2H), 1.24 (t, *J* = 7.2 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm): 161.5, 143.0 (q, $^2J_{C\text{-}F}$ = 42.2 Hz), 140.8 (q, $^4J_{C\text{-}F}$ = 1.3 Hz), 129.5, 128.7, 128.4, 128.31, 128.28, 119.2 (q, $^3J_{C\text{-}F}$ = 2.3 Hz), 118.6 (q, $^1J_{C\text{-}F}$ = 267.9 Hz), 61.7, 13.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm): -62.2; IR (KBr): 3005, 1736, 1352, 1286, 1195, 1144, 1105, 759, 704 cm^{-1}; HRMS (ESI) m/z: $[M+H]^+$ calcd. for $C_{14}H_{12}F_3O_3^+$ 285.0733, found 285.0736.



Ethyl 2-(difluoromethyl)-4-phenylfuran-3-carboxylate (6b). The product **6b** was obtained as a yellow oil (20.7 mg, 78% yield). ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.52 (t, *J* = 1.8 Hz, 1H), 7.39-7.36 (m, 5H), 7.19 (t, *J* = 52.6 Hz, 1H), 4.24 (q, *J* = 7.0 Hz, 2H), 1.20 (t, *J* = 7.0 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm): 161.9, 150.3 (t, $^2J_{C\text{-}F}$ = 23.9 Hz), 141.6, 130.1, 129.4, 128.0, 127.9, 126.3,

118.5 (t, $^{3}J_{C\text{-}F}$ = 5.6 Hz), 107.0 (t, $^{1}J_{C\text{-}F}$ = 235.2 Hz), 61.2, 13.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm): -117.3 (d, J = 52.7 Hz); IR (KBr): 2939, 1722, 1287, 1153, 1123, 1047, 764, 702 cm^{-1}; HRMS (ESI) m/z: $[M+H]^+$ calcd. for $C_{14}H_{13}F_2O_3^+$ 267.0827, found 267.0828.

6. X-ray crystallographic analysis of 3al (CCDC 2061710)

Single crystals of $C_{17}H_{12}F_3NO_5$ [lq-w1] were obtained via slow diffusion of petroleum ether into their chloroform solution. A suitable crystal was selected and determined on a New Gemini, Dual, Cu at home/near, EosS2 diffractometer. The crystal was kept at 297.41(14) K during data collection. Using Olex2, the structure was solved with the ShelXT structure solution program using Direct Methods and refined with the ShelXL refinement package using Least Squares minimisation.

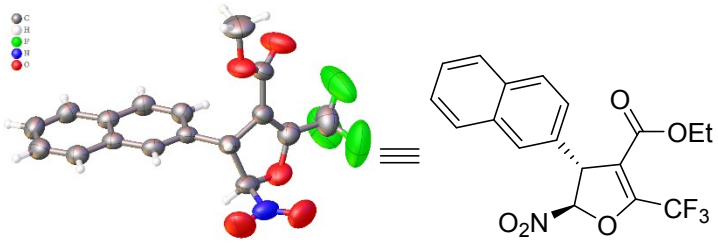


Table 1 Crystal data and structure refinement for lq-w1.

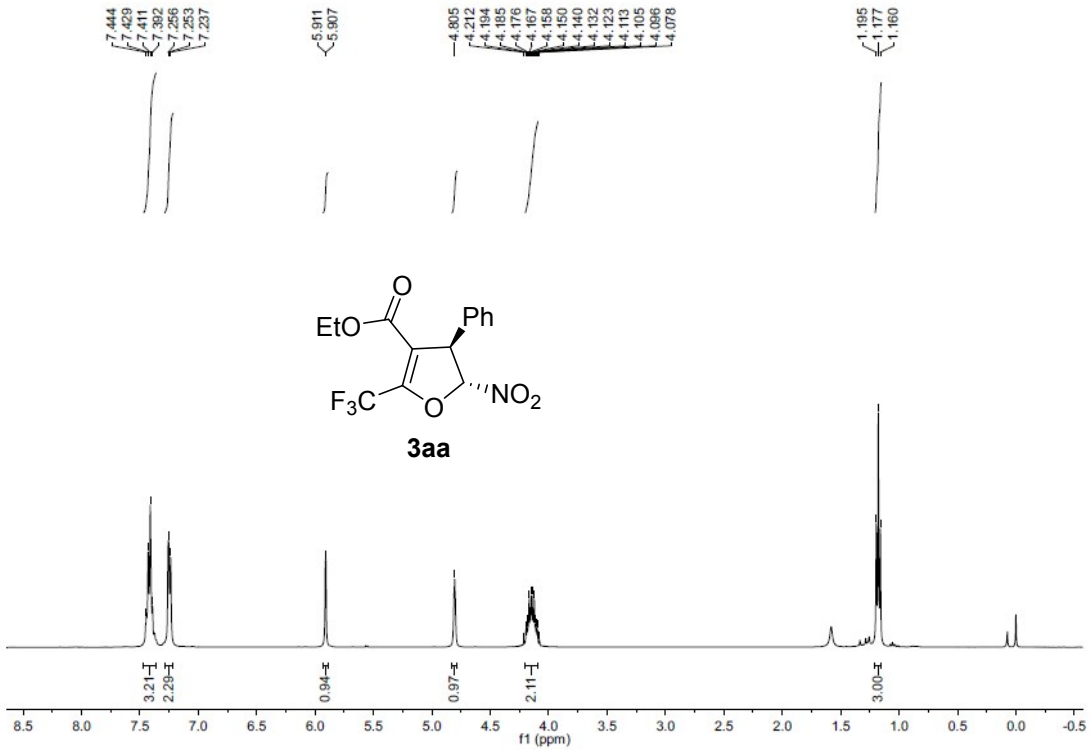
Identification code	lq-w1
Empirical formula	$C_{17}H_{12}F_3NO_5$
Formula weight	367.28
Temperature/K	297.41(14)
Crystal system	monoclinic
Space group	$P2_1$
a/Å	7.8743(3)
b/Å	5.7621(3)
c/Å	18.0567(7)
α/°	90
β/°	93.984(3)
γ/°	90

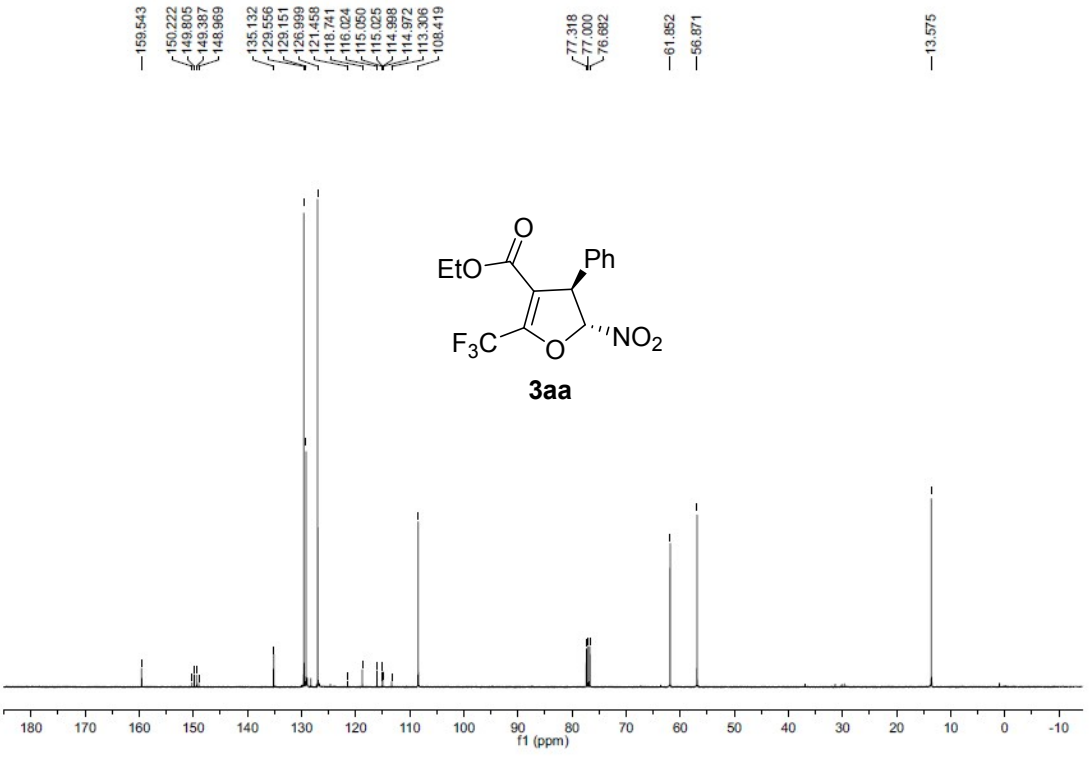
Volume/Å^3	817.31(6)
Z	2
ρ_{calc}g/cm^3	1.492
μ/mm^{-1}	1.156
F(000)	376.0
Crystal size/mm^3	0.7 × 0.4 × 0.2
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	9.82 to 145.244
Index ranges	$-9 \leq h \leq 9$, $-6 \leq k \leq 7$, $-22 \leq l \leq 17$
Reflections collected	7559
Independent reflections	2913 [R_{int} = 0.0264, R_{sigma} = 0.0264]
Data/restraints/parameters	2913/1/236
Goodness-of-fit on F^2	1.060
Final R indexes [I>=2σ (I)]	R_1 = 0.0544, wR_2 = 0.1560
Final R indexes [all data]	R_1 = 0.0576, wR_2 = 0.1620
Largest diff. peak/hole / e Å^{-3}	0.37/-0.23
Flack parameter	0.03(12)

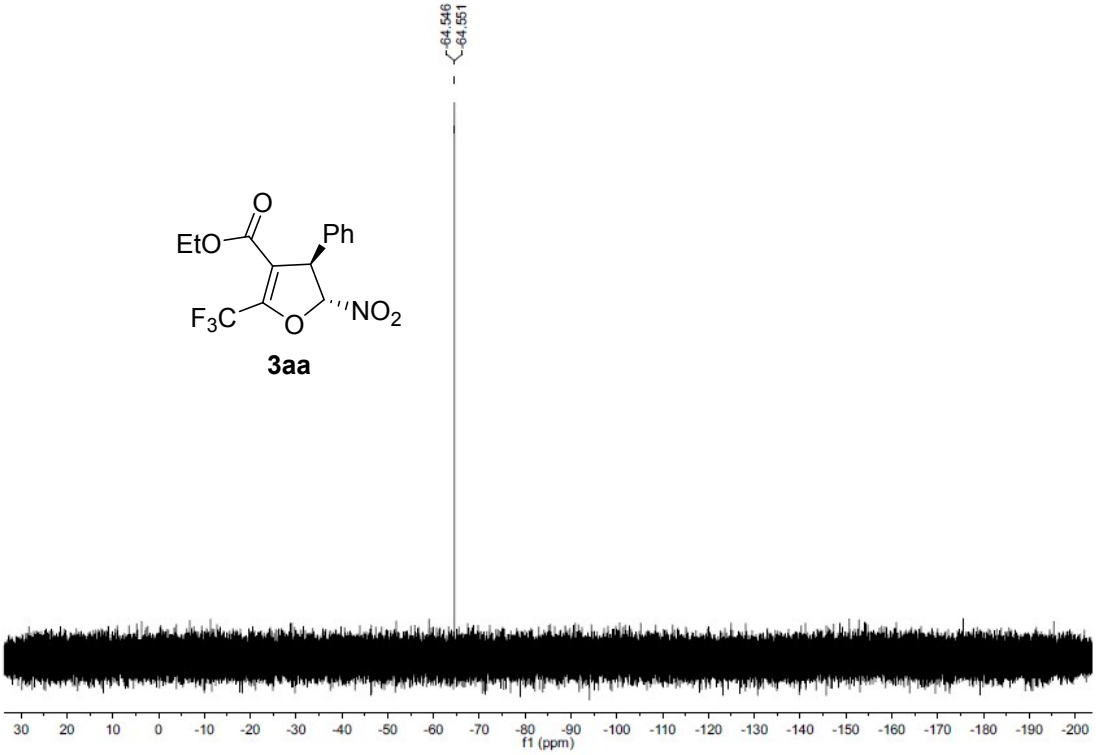
7. Reference

1. (a) J. P. Malerich, K. Hagihara and V. H. Rawal, *J. Am. Chem. Soc.*, 2008, **130**, 14416; (b) H. Konishi, T. Y. Lam, J. P. Malerich and V. H. Rawal, *Org. Lett.*, 2010, **12**, 2028.
2. B. Vakulya, S. Varga, A. Csámpai and T. Soós, *Org. Lett.*, 2005, **7**, 1967.
3. (a) J. G. Greger, S. J. P. Yoon-Miller, N. R. Bechtold, S. A. Flewelling, J. P. MacDonald, C. R. Downey, E. A. Cohen and E. T. Pelkey, *J. Org. Chem.*, 2011, **76**, 8203; (b) M. Ganesh and I. N. N. Namboothiri, *Tetrahedron*, 2007, **63**, 11973; (c) G. Bharathiraja, S. Sakthivel, M. Sengoden and T. Punniyamurthy, *Org. Lett.*, 2013, **15**, 4996.
4. R. G. Soengas, H. Rodríguez-Solla, A. M. S. Silva, R. Llavona and F. A. A. Paz, *J. Org. Chem.*, 2013, **78**, 12831.
5. J. J. A. Durden, D. L. Heywood, A. A. Sousa and H. W. Spurr, *J. Agric. Food. Chem.*, 1970, **18**, 50.

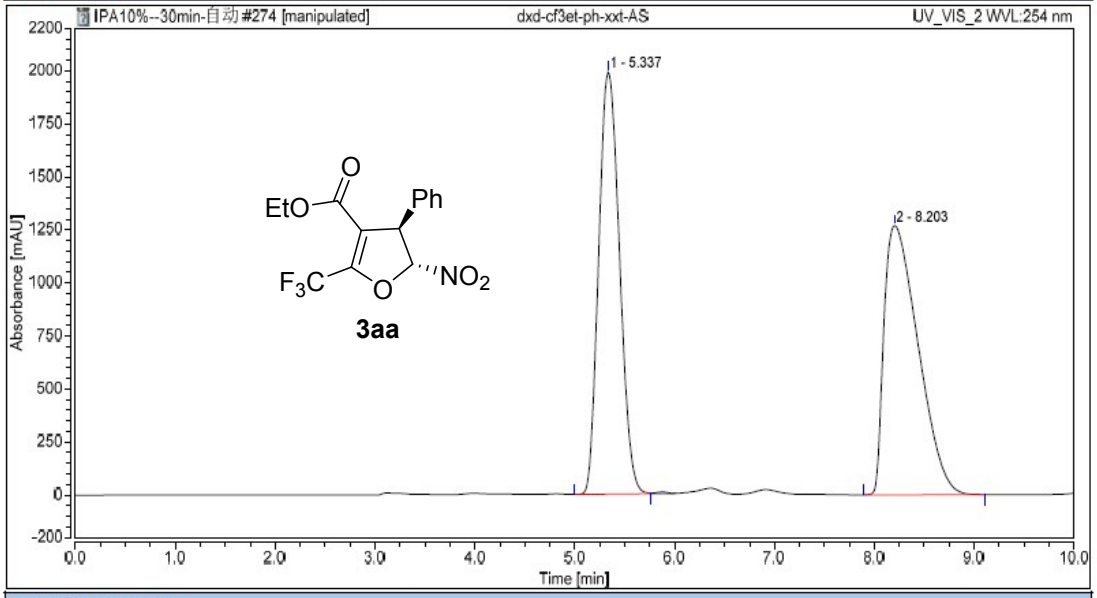
8. NMR spectra and HPLC chromatograms of products







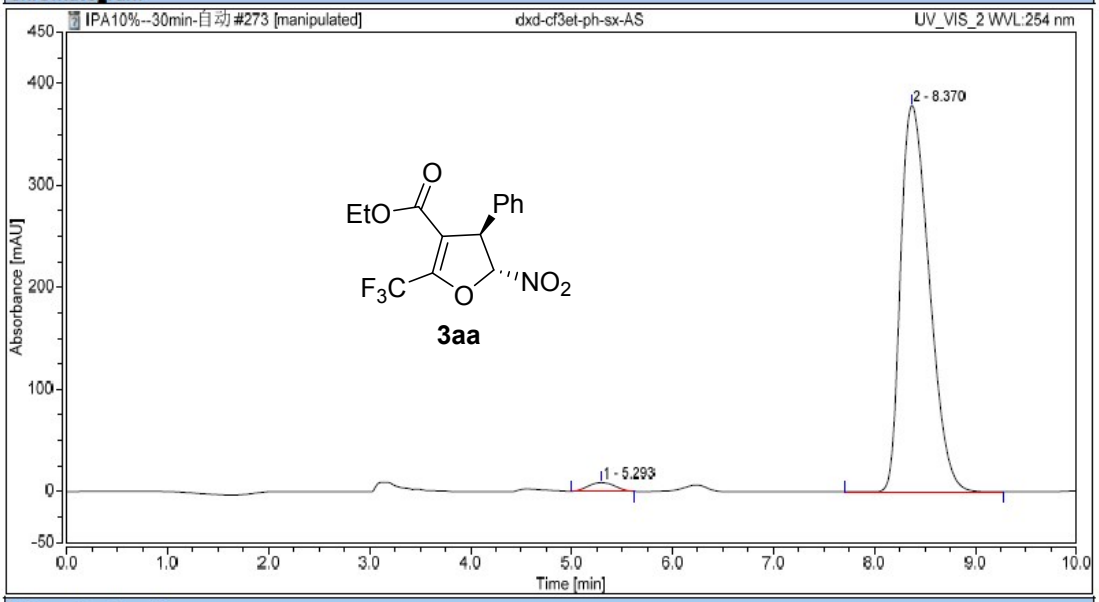
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.337	481.195	1990.838	48.99	61.05	n.a.
2		8.203	500.944	1269.973	51.01	38.95	n.a.
Total:			**982.138**	**3260.811**	**100.00**	**100.00**	

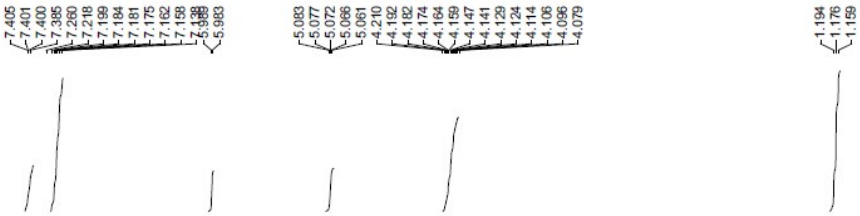
Chromatogram

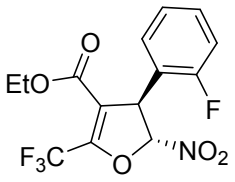


3aa

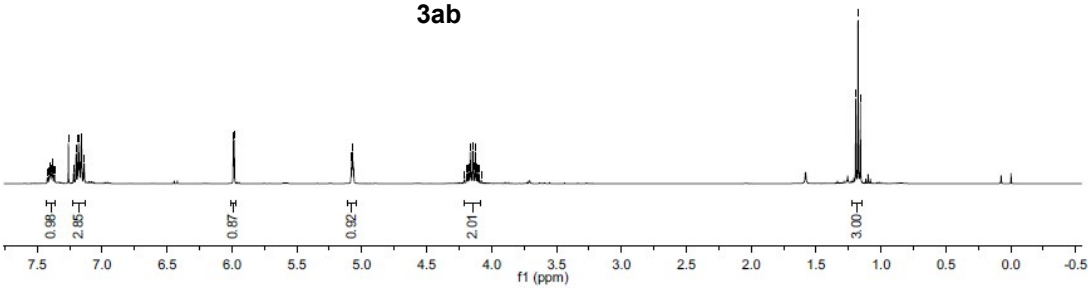
Integration Results

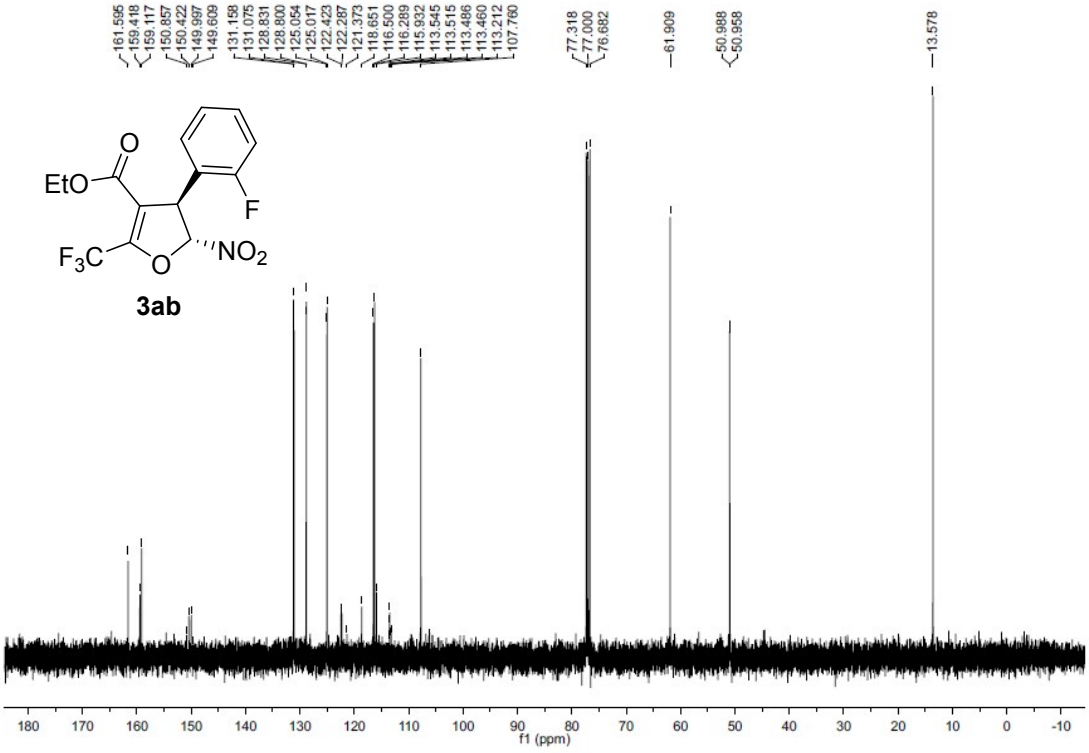
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.293	2.625	8.561	2.07	2.21	n.a.
2		8.370	124.208	378.611	97.93	97.79	n.a.
Total:			**126.832**	**387.172**	**100.00**	**100.00**	





3ab

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125.017
122.423
122.287
121.373
118.651
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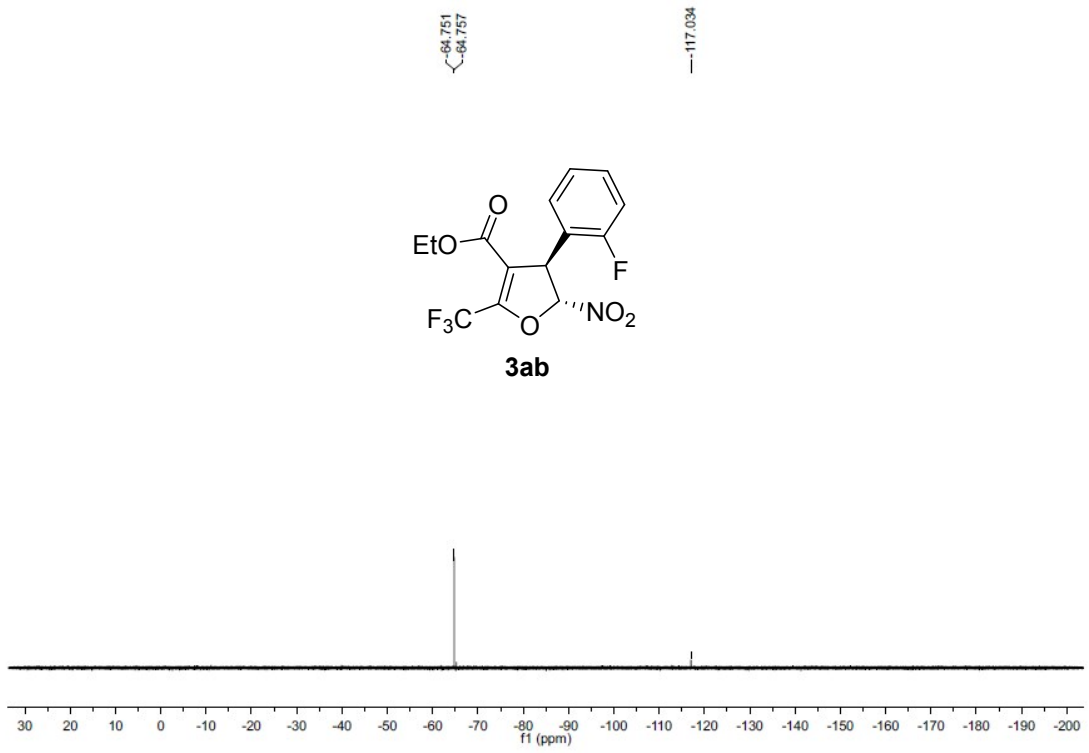
116.289
115.932
113.545
113.515
113.486
113.460
113.212
107.760
77.318
77.000
76.682
61.909
50.988
50.958
13.578
O
EtO
F
F3C
O
NO2
3ab
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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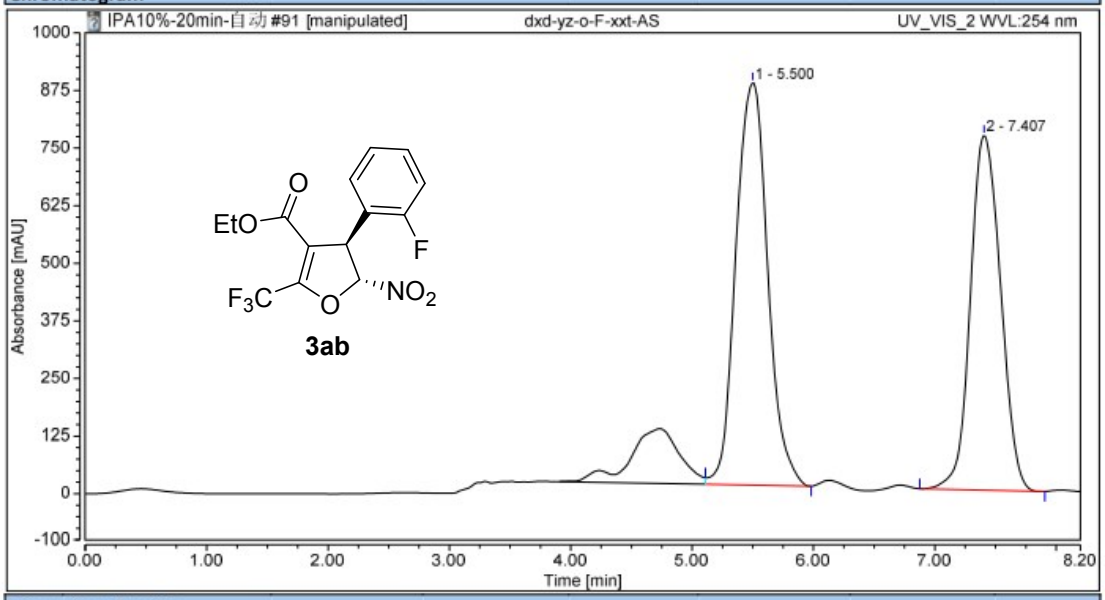
EtO
F
F3C
O
NO2
3ab
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)

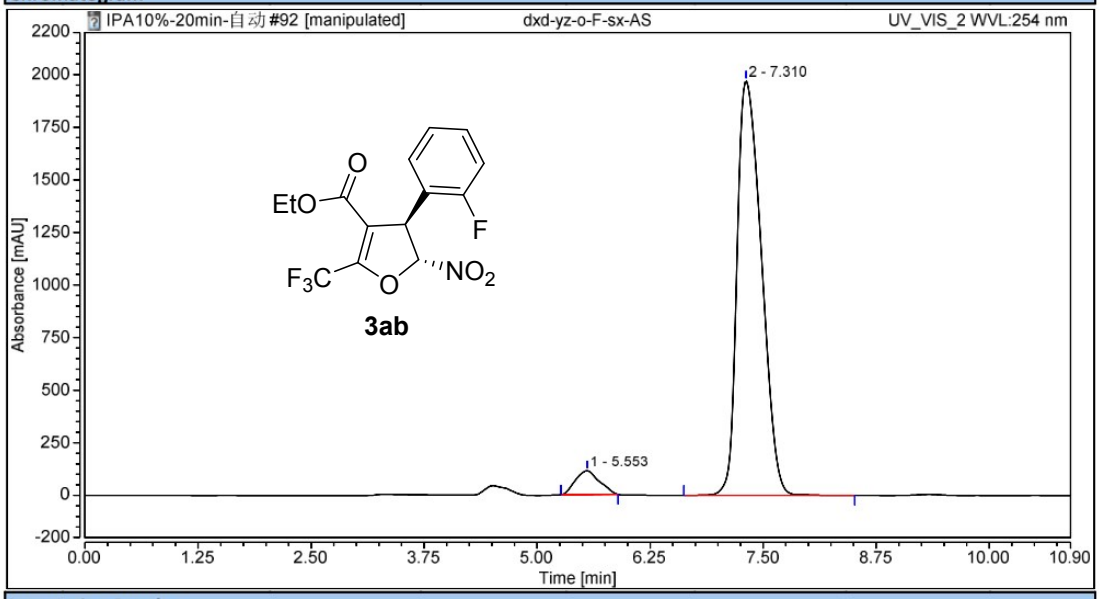
Chromatogram



Integration Results

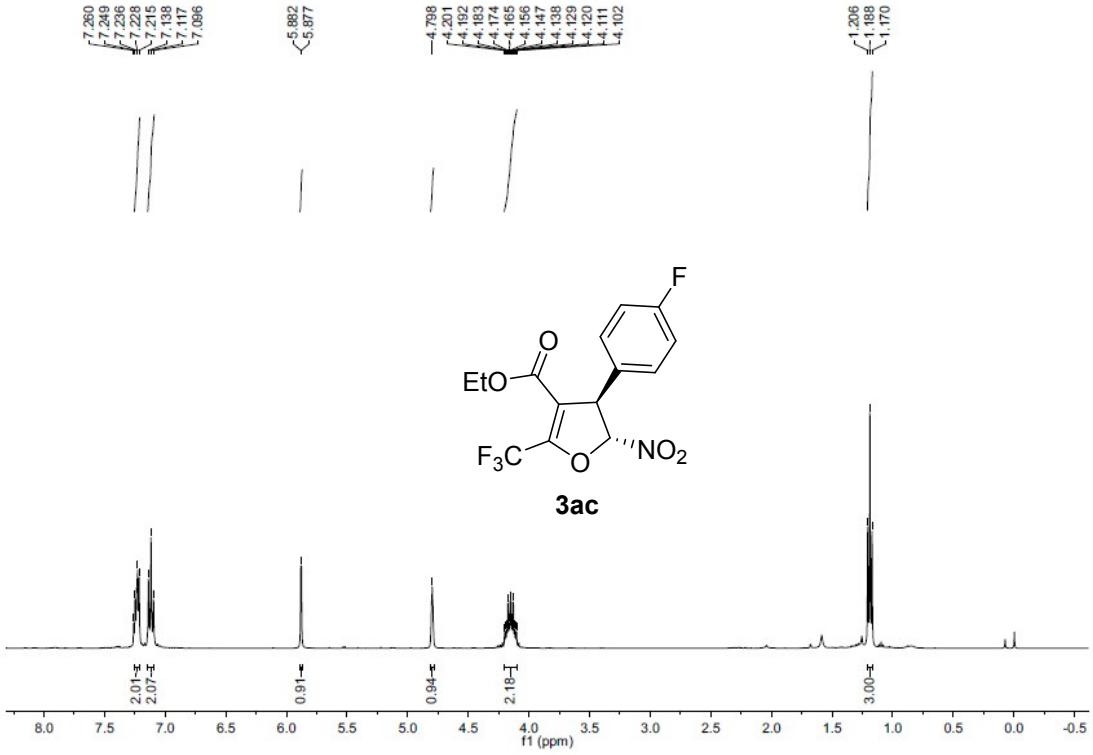
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.500	265.561	873.459	54.43	53.16	n.a.
2		7.407	222.376	769.600	45.57	46.84	n.a.
Total:			**487.937**	**1643.060**	**100.00**	**100.00**	

Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.553	35.002	113.444	5.37	5.44	n.a.
2		7.310	616.705	1970.697	94.63	94.56	n.a.
Total:			**651.708**	**2084.141**	**100.00**	**100.00**	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4.165
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4.147
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4.129
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4.111
4.102
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1.188
1.170
F
O
EtO
F3C
O
NO2
3ac
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2.07
0.91
0.94
2.18
3.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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4.0
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3.0
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2.0
1.5
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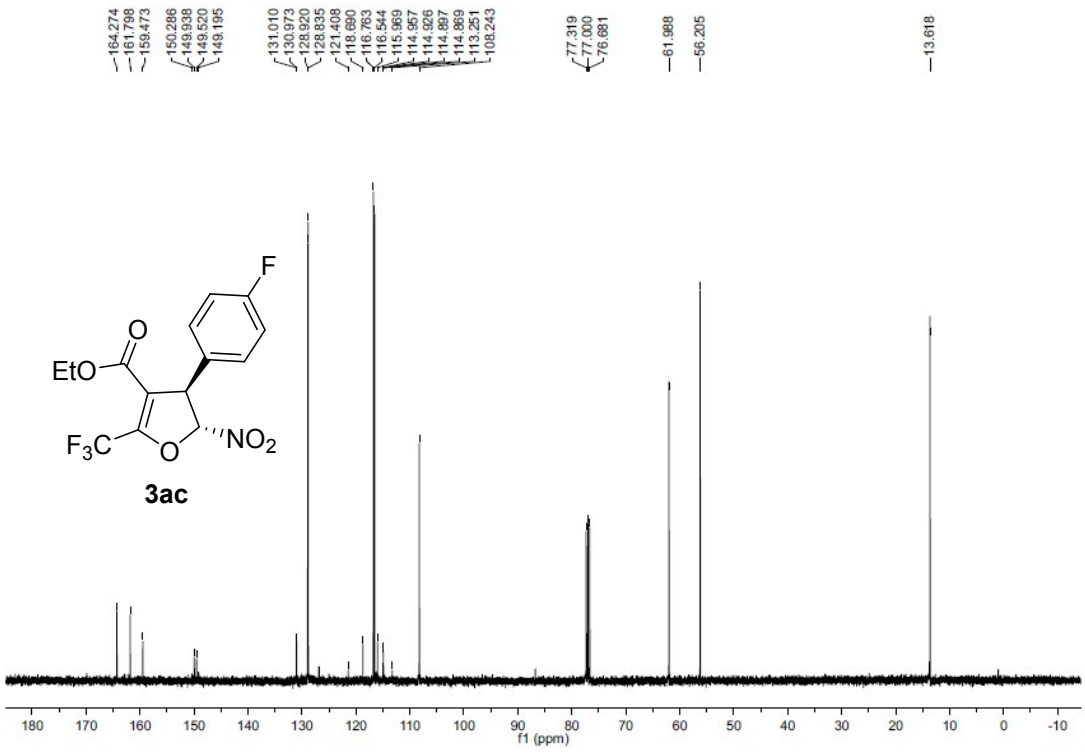
0.5
0.0
-0.5
f1 (ppm)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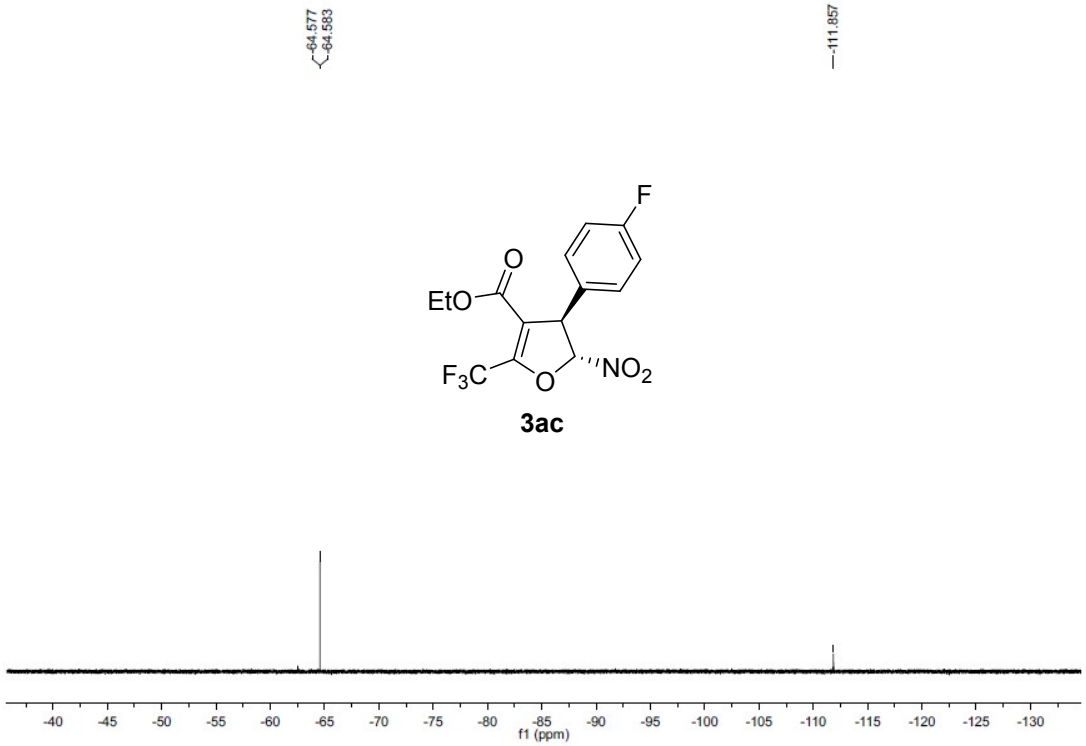
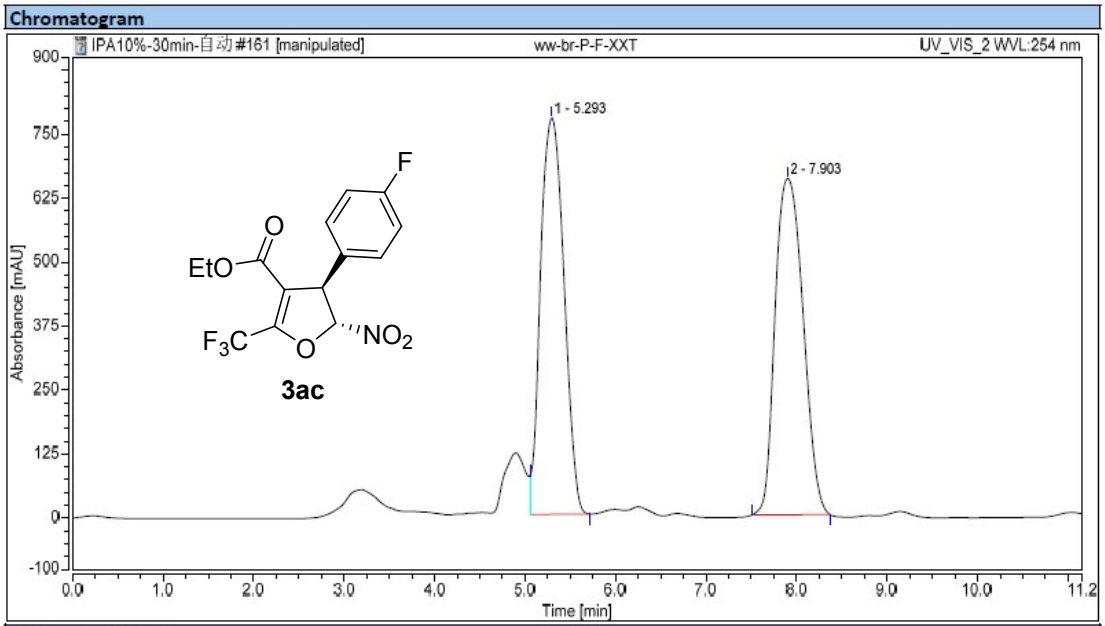
f1 (ppm)

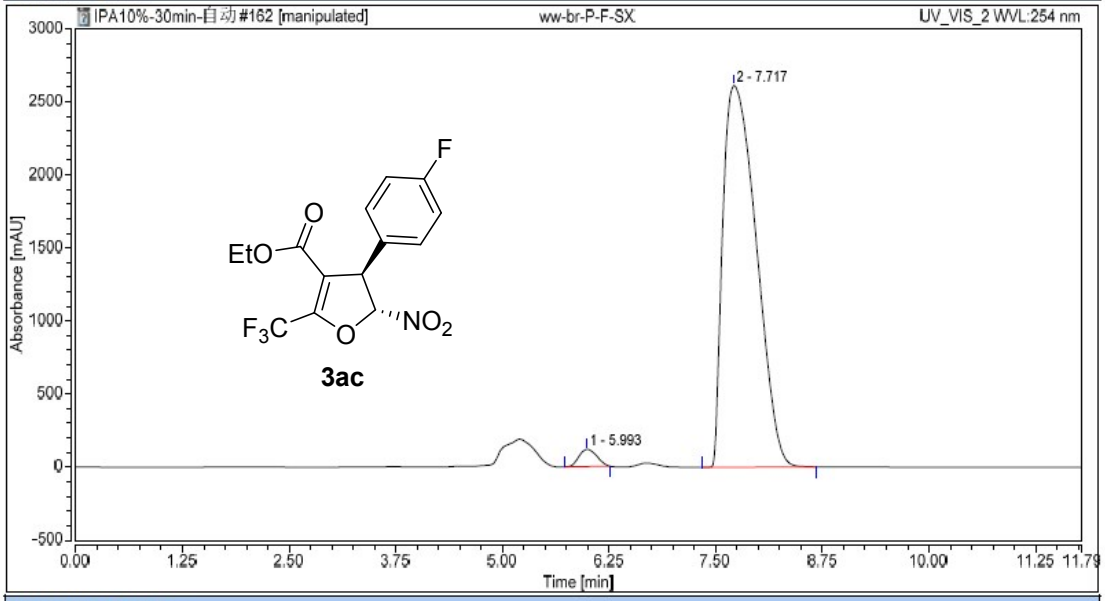




Integration Results

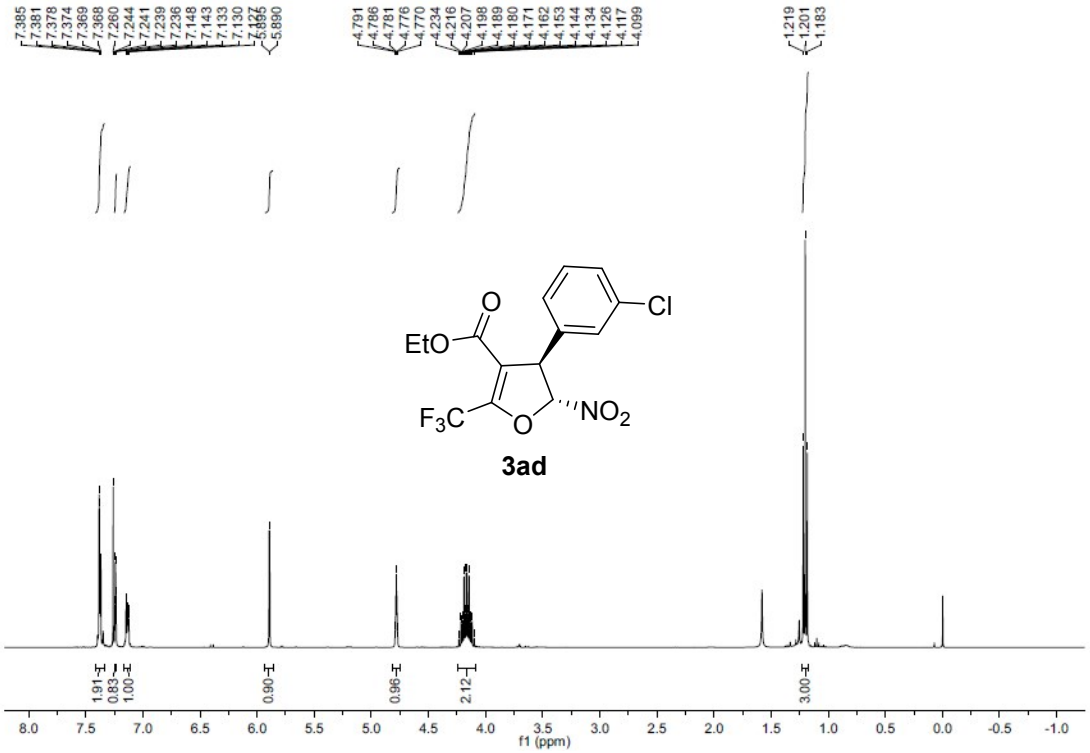
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.293	232.119	774.644	49.69	54.09	n.a.
2		7.903	234.992	657.390	50.31	45.91	n.a.
Total:			**467.110**	**1432.034**	**100.00**	**100.00**	

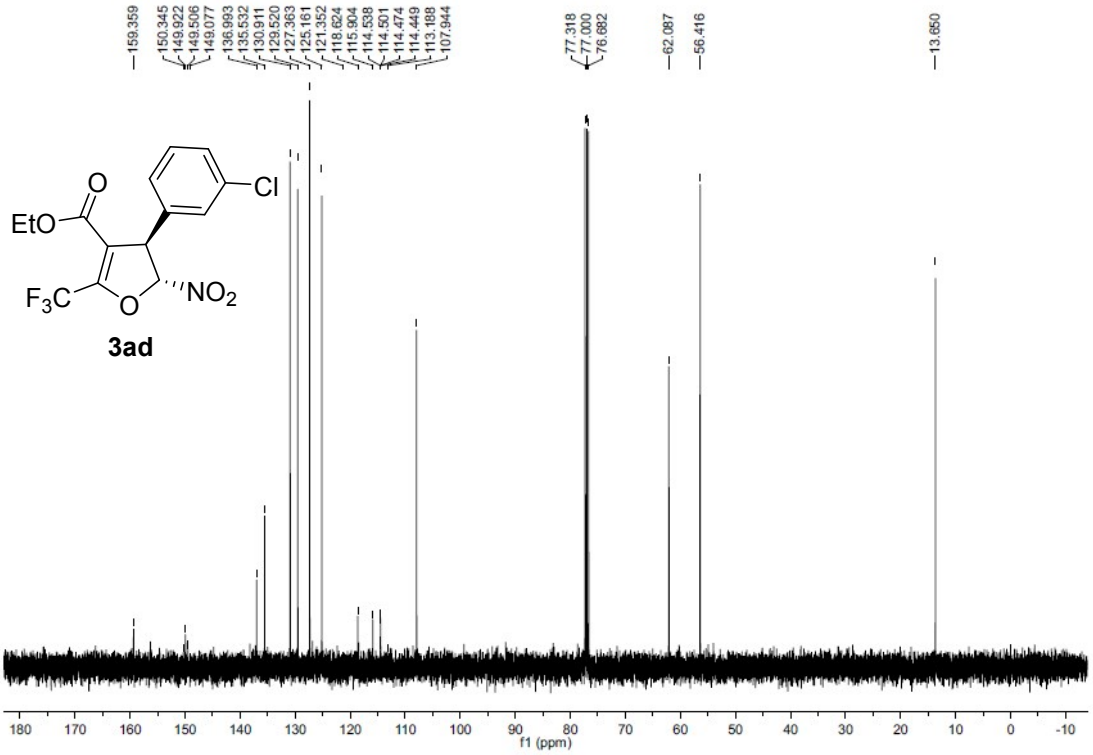
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.993	28.150	115.985	2.33	4.25	n.a.
2		7.717	1182.336	2610.816	97.67	95.75	n.a.
Total:			**1210.486**	**2726.801**	**100.00**	**100.00**	

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114.538
114.501
114.474
114.449
113.188
107.944
77.318
77.000
76.682
62.087
56.416
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Cl
F3C
O
NO2
3ad
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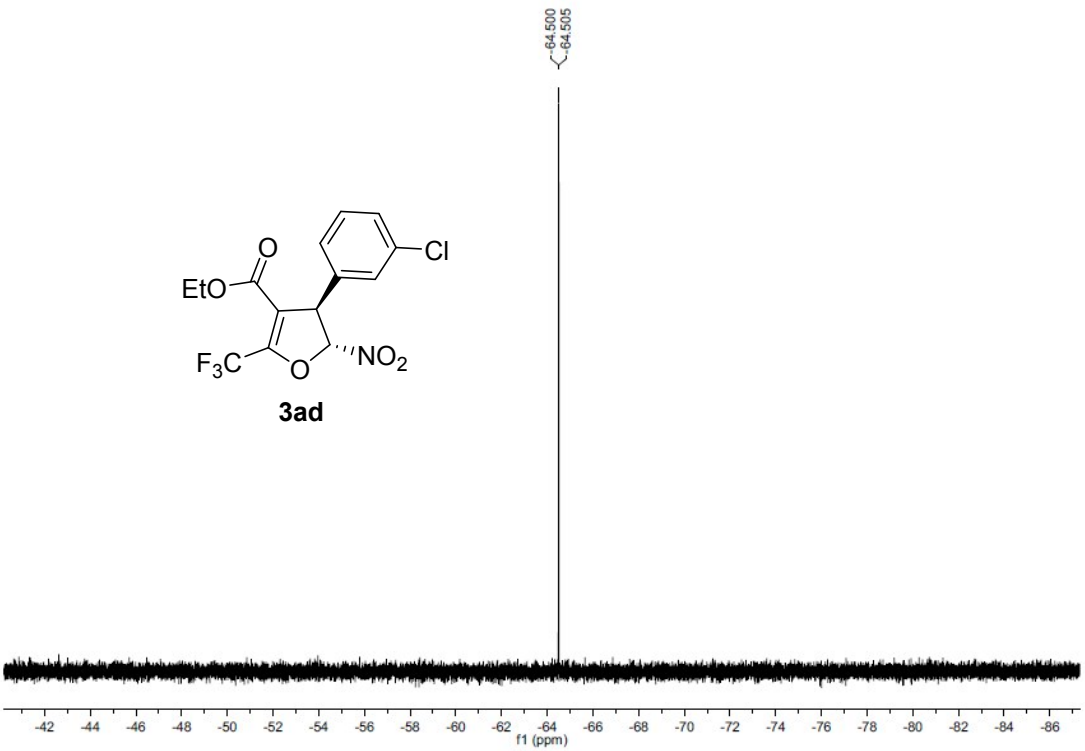
f1 (ppm)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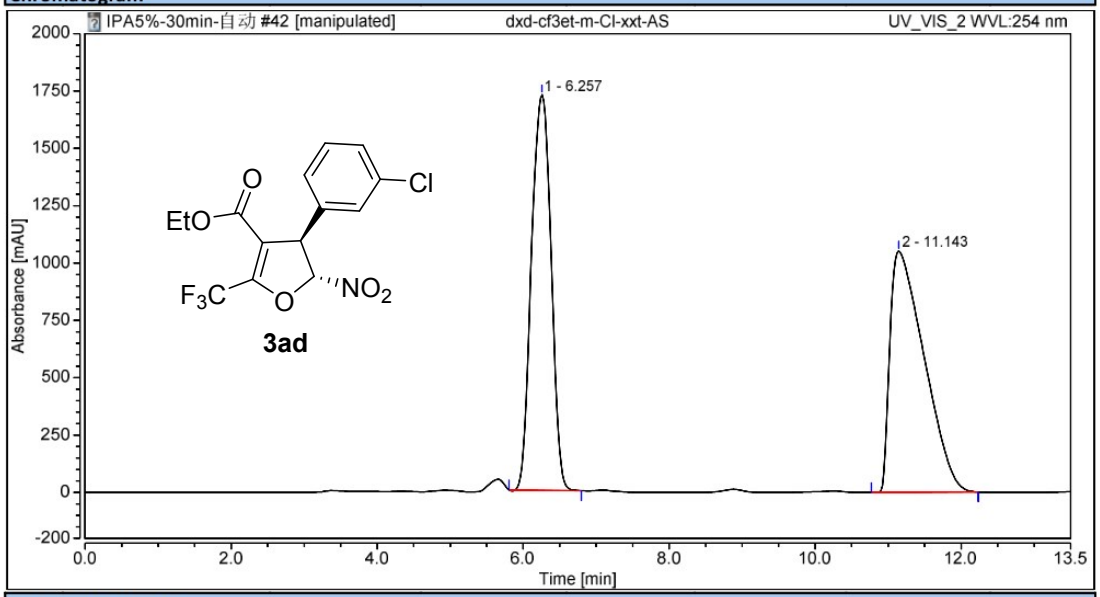
f1 (ppm)

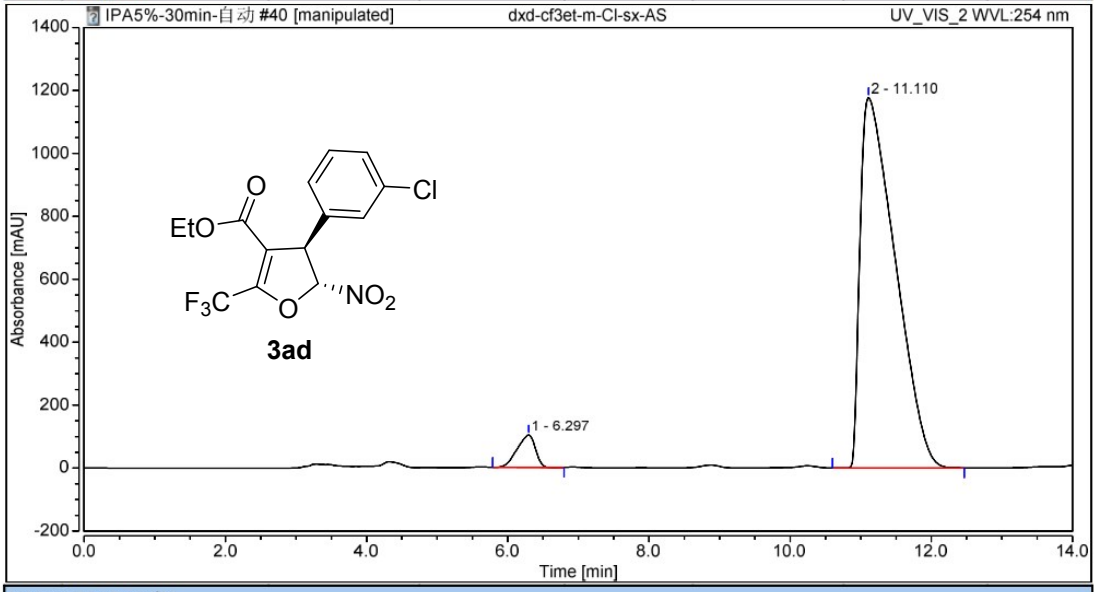
Chromatogram



Integration Results

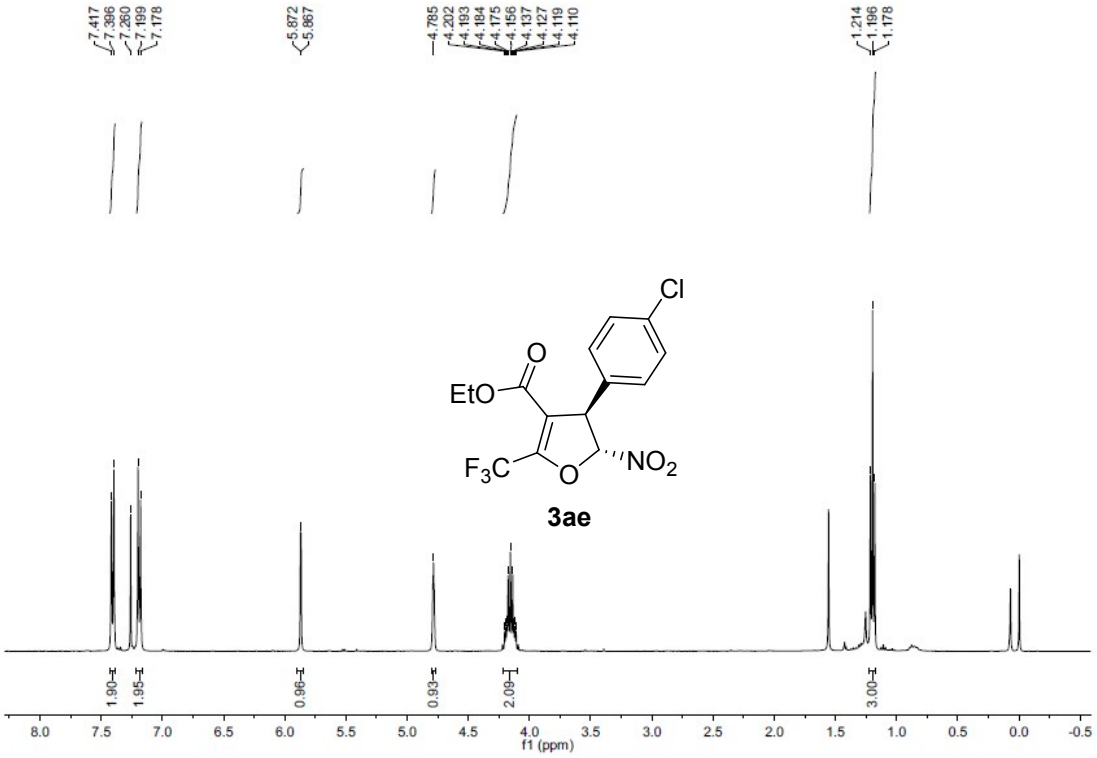
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		6.257	536.486	1723.988	48.52	62.09	n.a.
2		11.143	569.130	1052.427	51.48	37.91	n.a.
Total:			**1105.616**	**2776.415**	**100.00**	**100.00**	

Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		6.297	30.655	102.824	4.33	8.03	n.a.
2		11.110	676.813	1177.368	95.67	91.97	n.a.
Total:			**707.467**	**1280.192**	**100.00**	**100.00**	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4.110
1.214
1.196
1.178
Cl
O
EtO
F3C
O
NO2
3ae
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1.95
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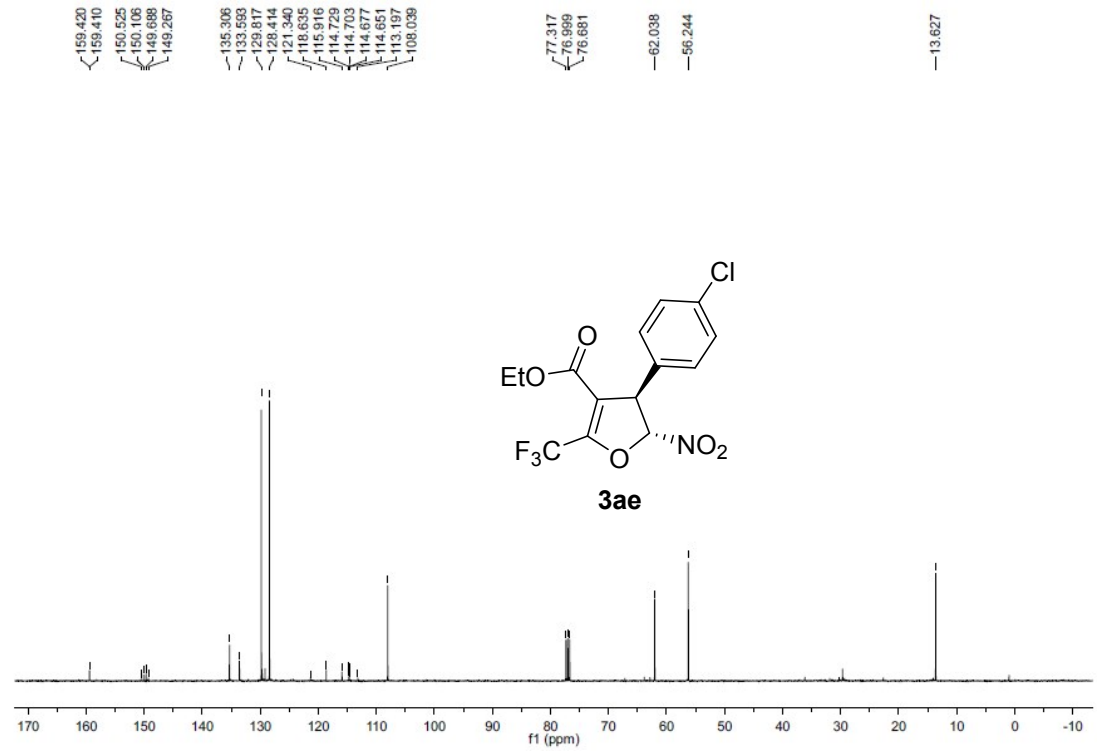
0.93
2.09
3.00
f1 (ppm)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114.703
114.677
114.651
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108.039
77.317
76.999
76.681
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13.627
Cl
O
EtO
F3C
O
NO2
3ae
f1 (ppm)

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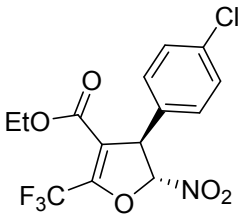
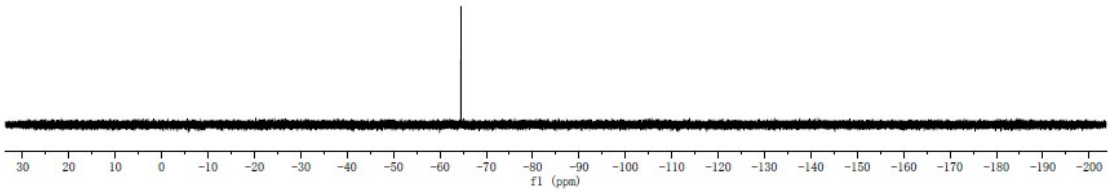
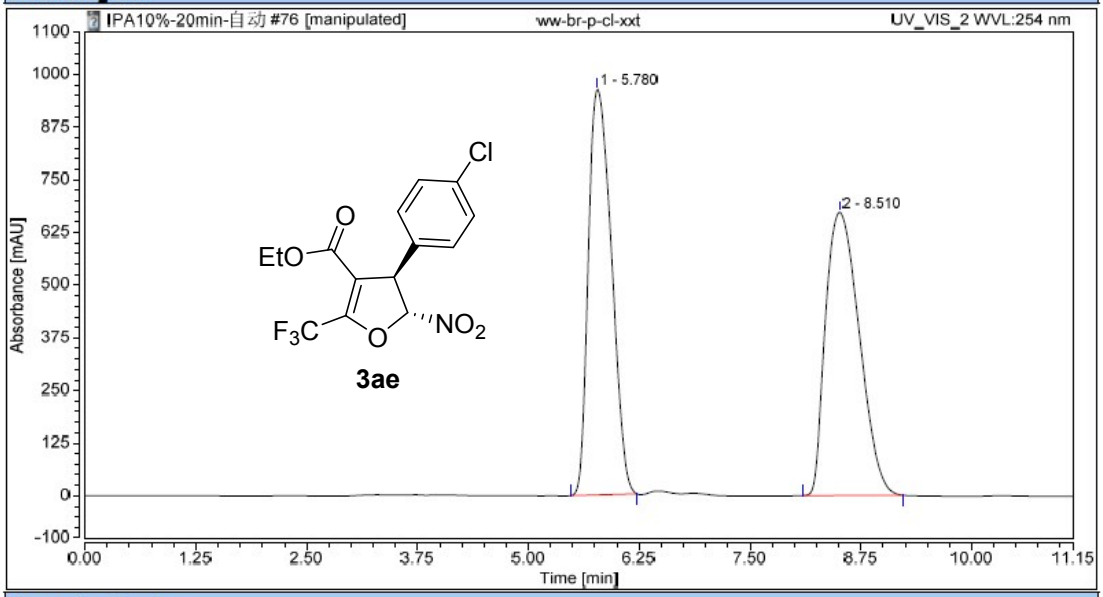
-64.544



3ae

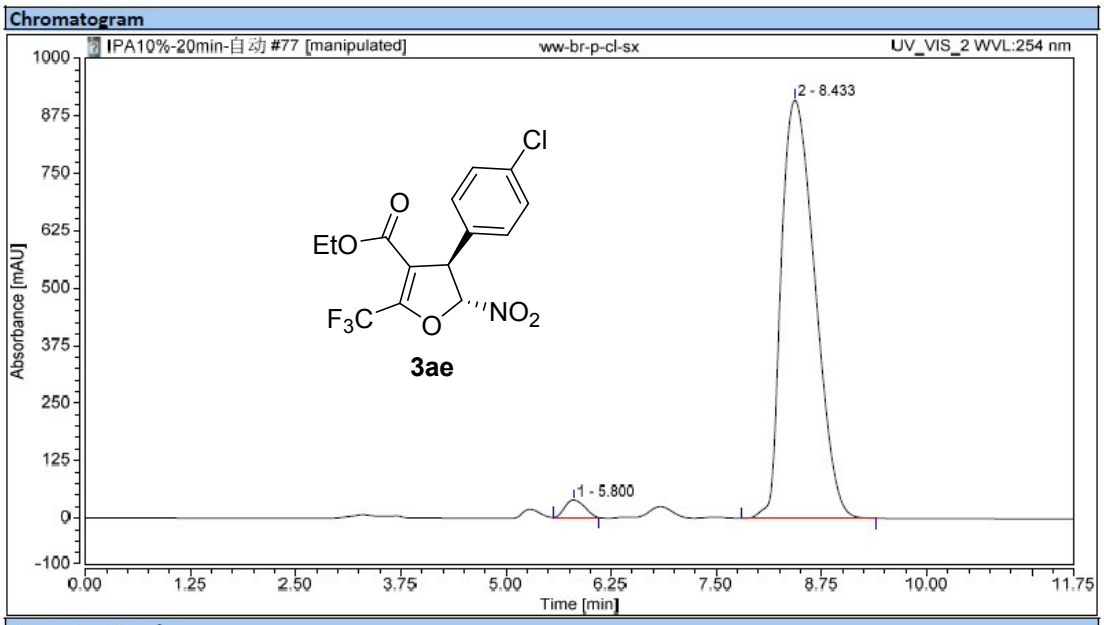


Chromatogram



Integration Results

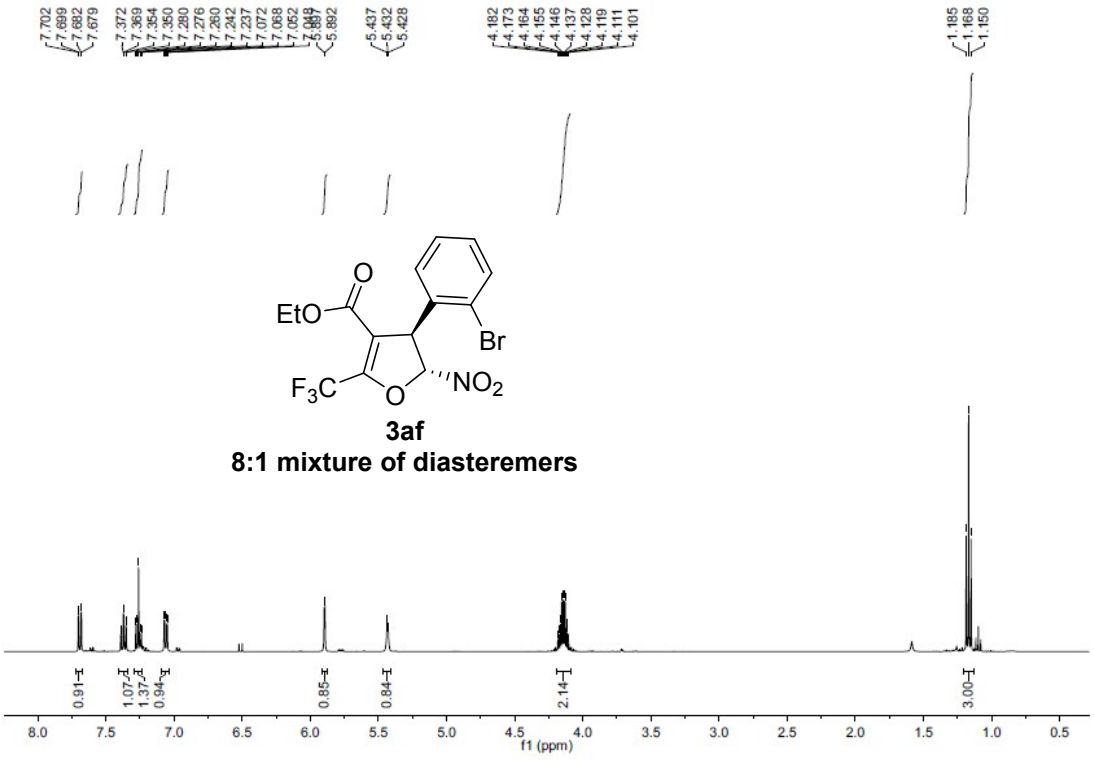
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.780	290.328	962.822	49.46	58.88	n.a.
2		8.510	296.645	672.317	50.54	41.12	n.a.
Total:			**586.973**	**1635.140**	**100.00**	**100.00**	



3ae

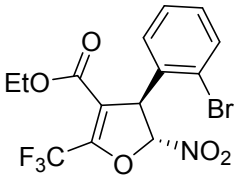
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.800	10.212	37.582	2.37	3.97	n.a.
2		8.433	421.053	910.049	97.63	96.03	n.a.
Total:			**431.264**	**947.631**	**100.00**	**100.00**	

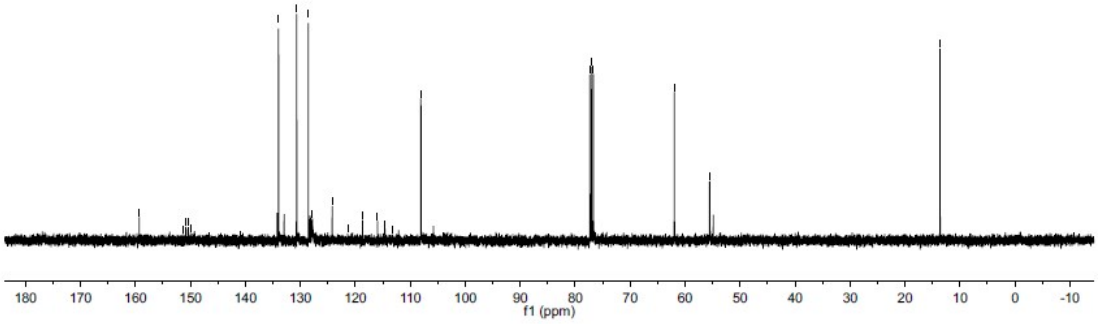


3af

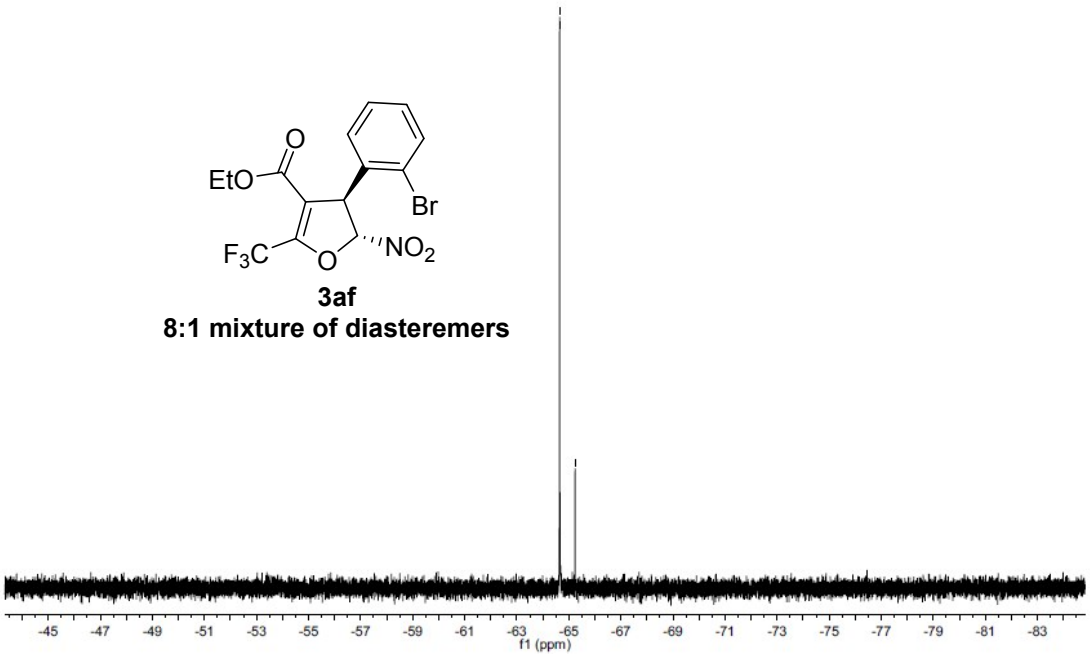
8:1 mixture of diasteremers



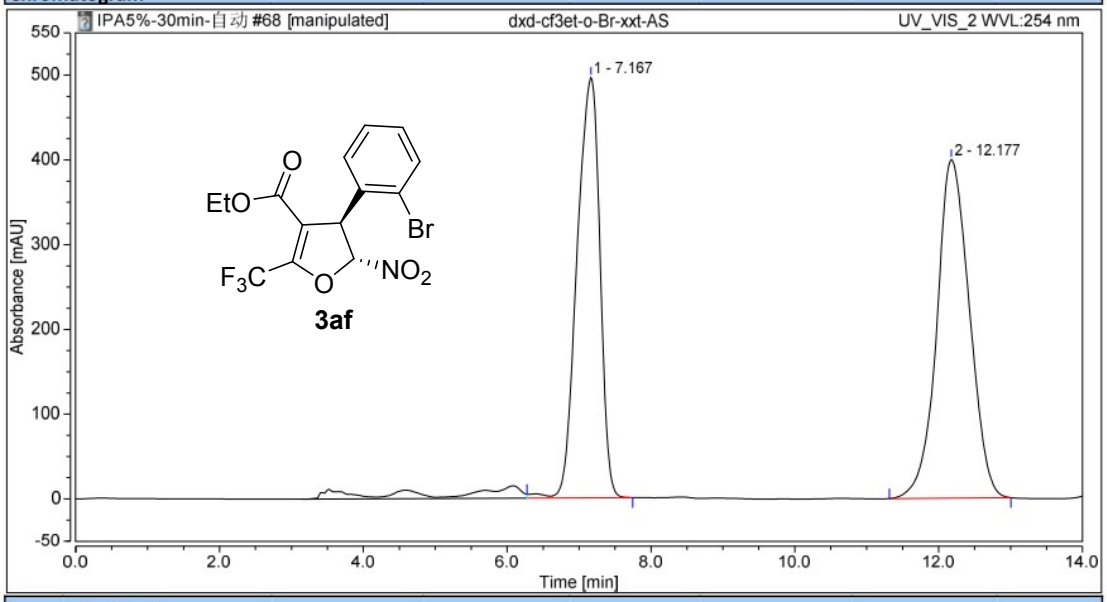
3af
8:1 mixture of diasteremers



3af
8:1 mixture of diasteremers



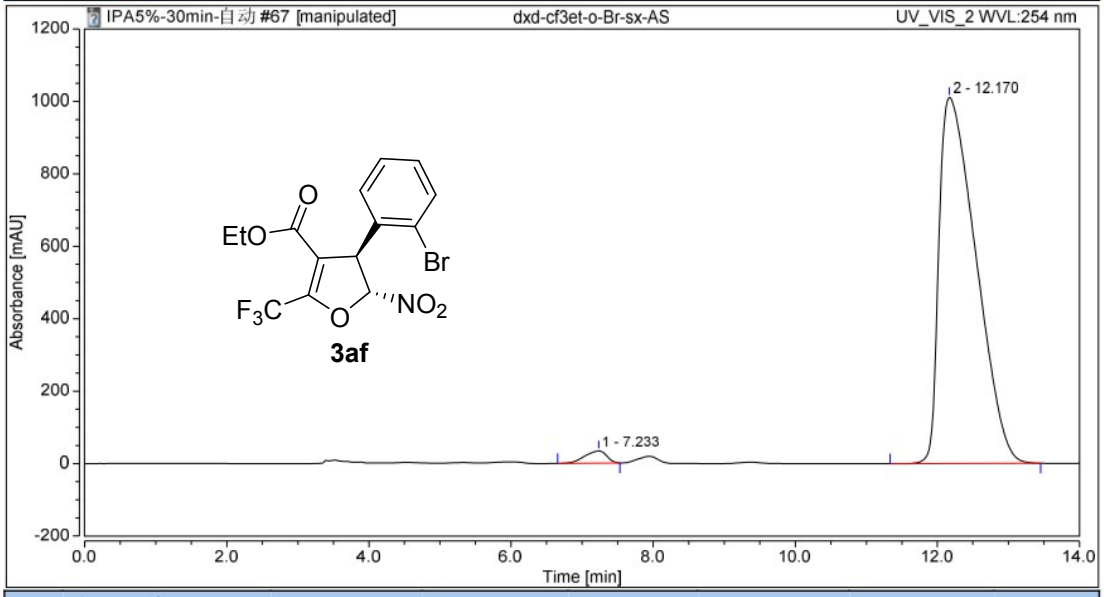
Chromatogram



Integration Results

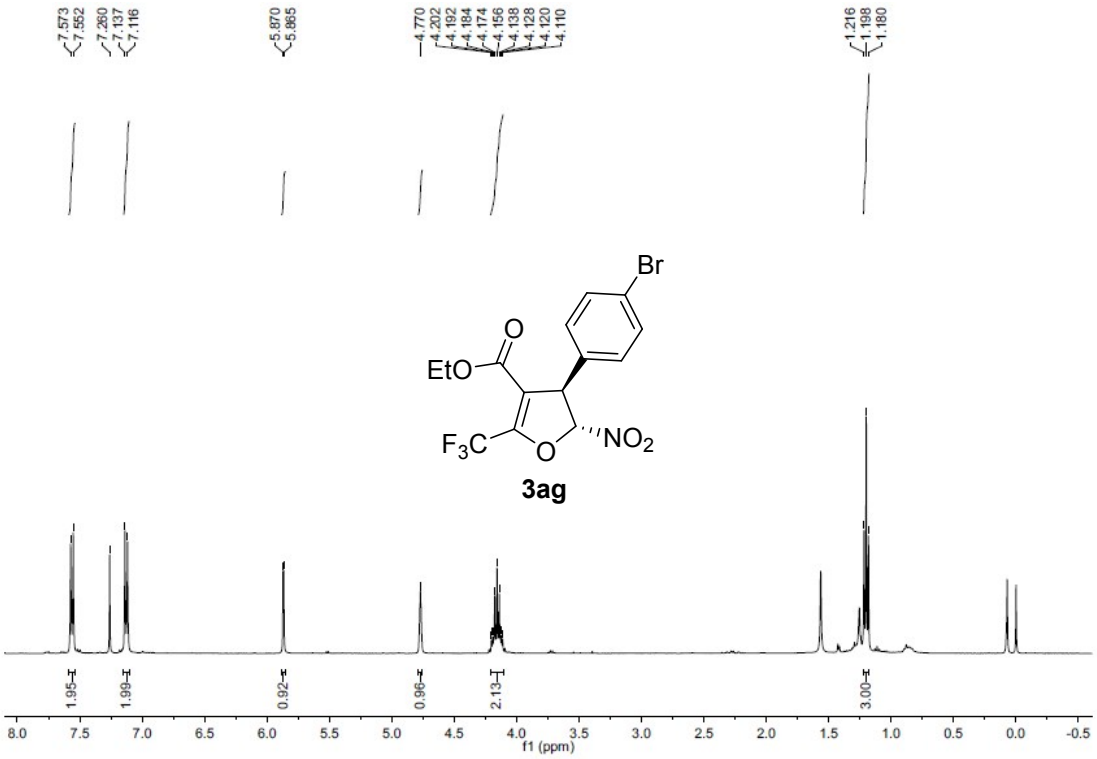
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		7.167	182.909	496.496	46.53	55.41	n.a.
2		12.177	210.151	399.605	53.47	44.59	n.a.
Total:			**393.060**	**896.101**	**100.00**	**100.00**	

Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		7.233	12.087	33.857	1.95	3.24	n.a.
2		12.170	607.572	1010.941	98.05	96.76	n.a.
Total:			**619.659**	**1044.797**	**100.00**	**100.00**	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4.770
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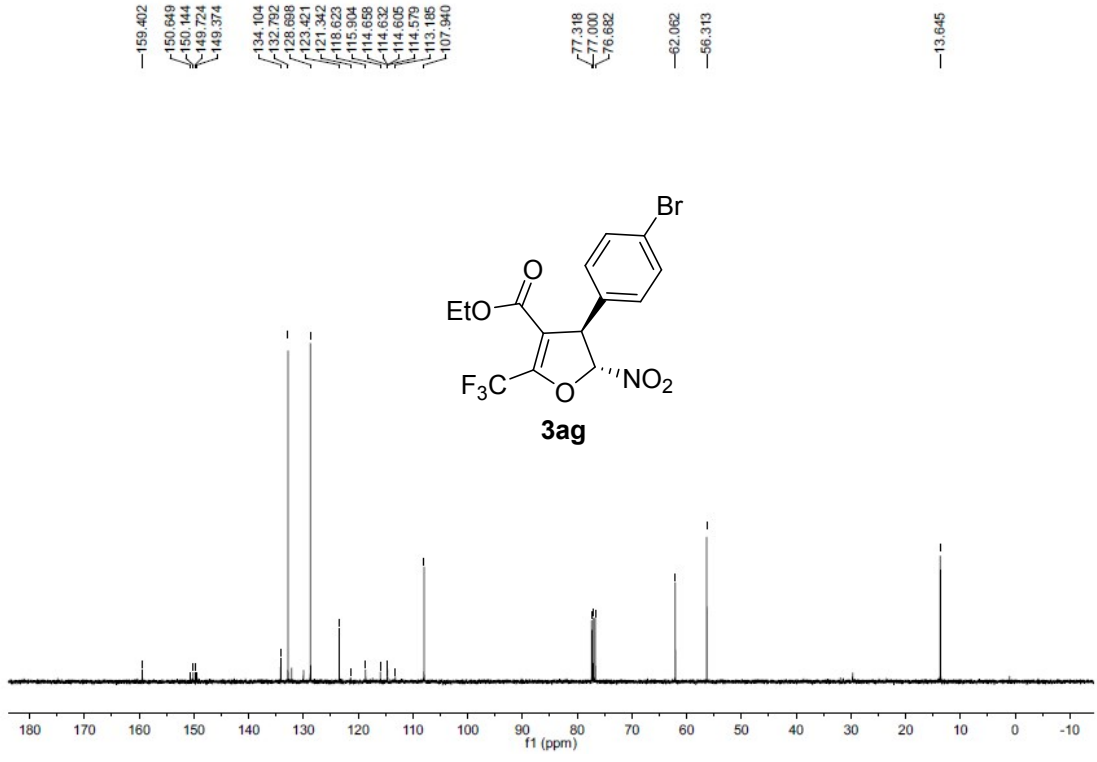
4.184
4.174
4.156
4.138
4.128
4.120
4.110
1.216
1.198
1.180
Br
O
EtO
F3C
O
NO2
3ag
1.95
1.99
0.92
0.96
2.13
3.00
f1 (ppm)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114.632
114.605
114.579
113.185
107.940
77.318
77.000
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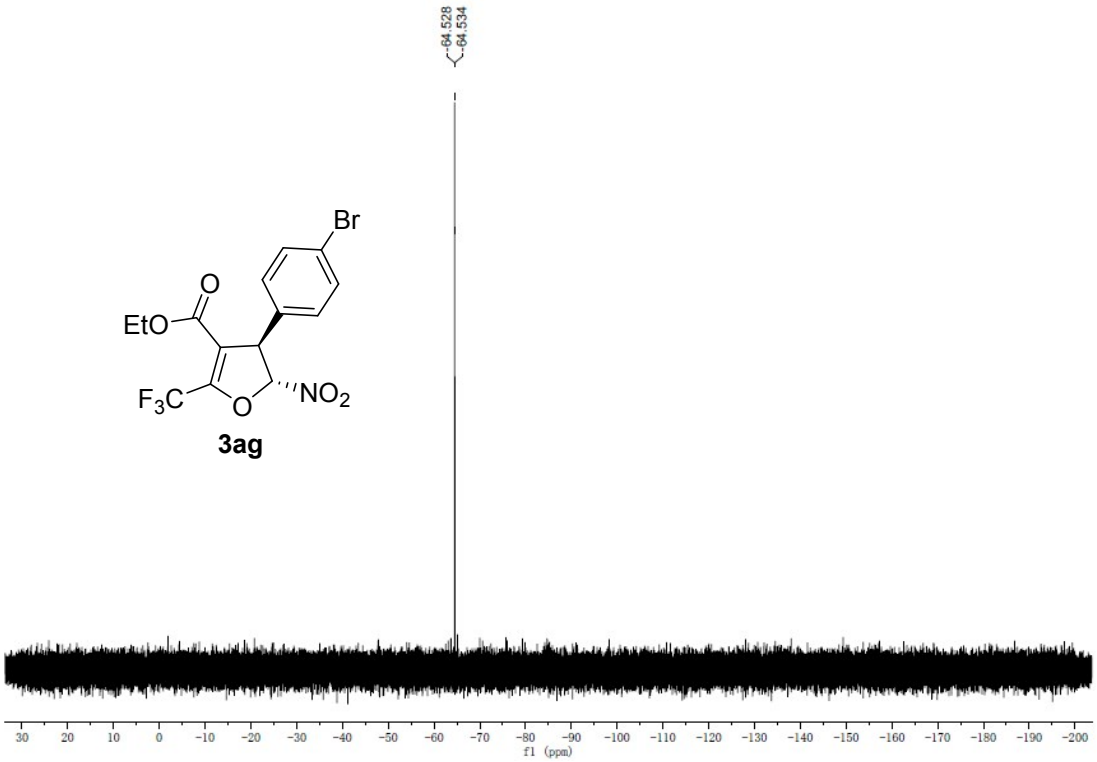
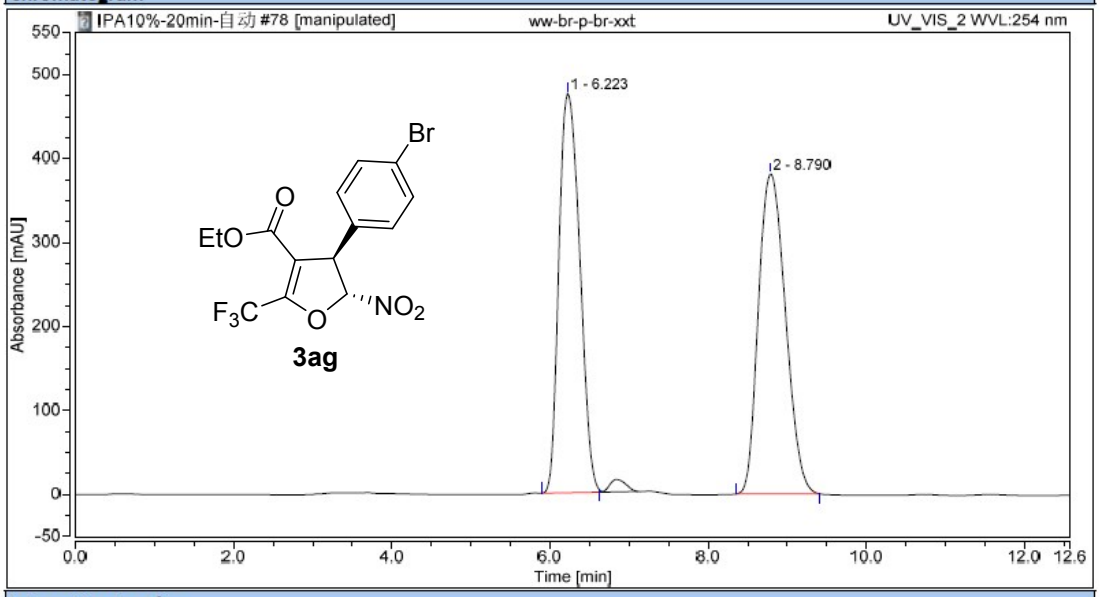
62.062
56.313
13.645
Br
O
EtO
F3C
O
NO2
3ag
f1 (ppm)



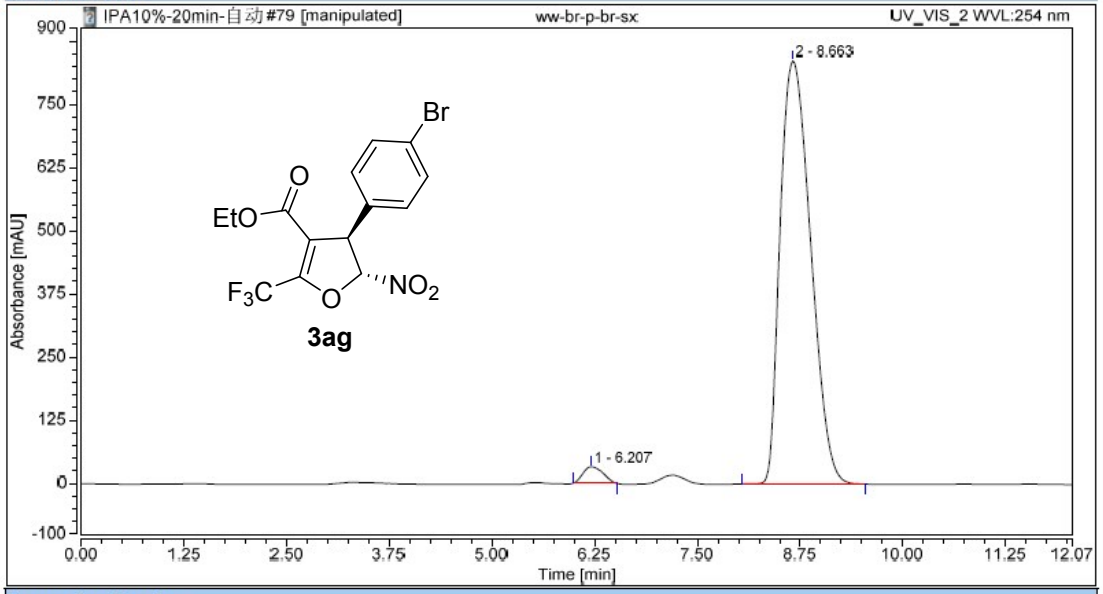
Chromatogram



Integration Results

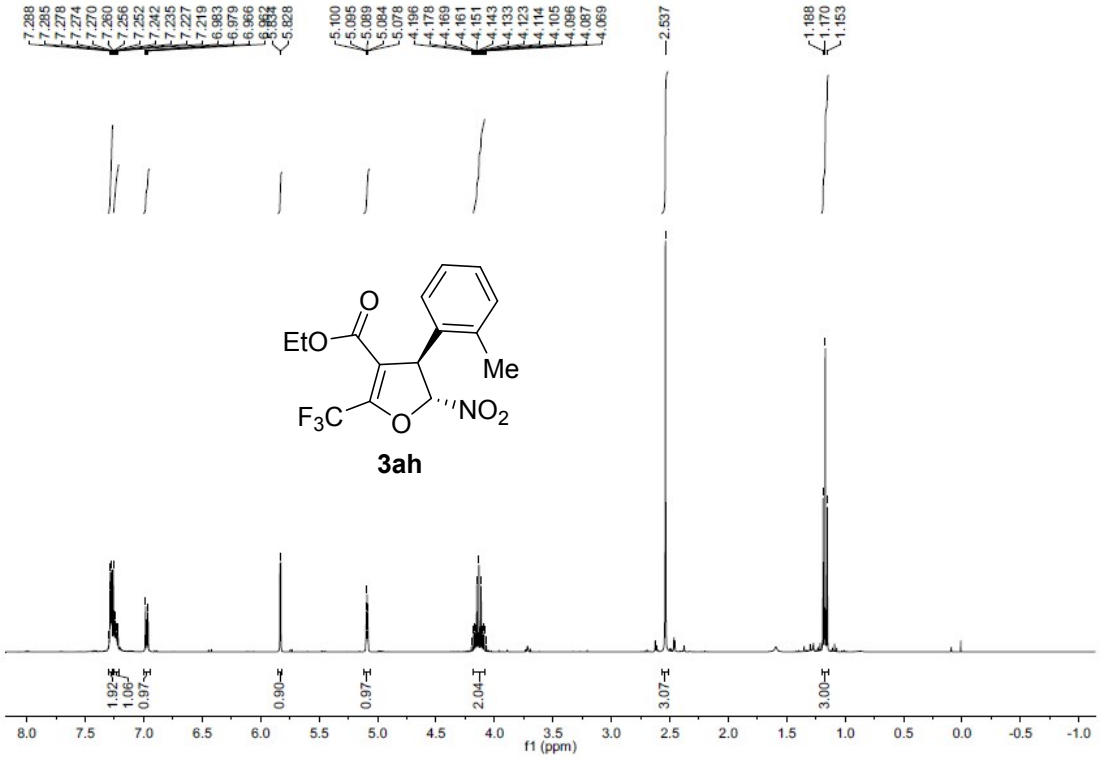
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		6.223	145.052	475.808	49.03	55.51	n.a.
2		8.790	150.805	381.345	50.97	44.49	n.a.
Total:			**295.857**	**857.153**	**100.00**	**100.00**	

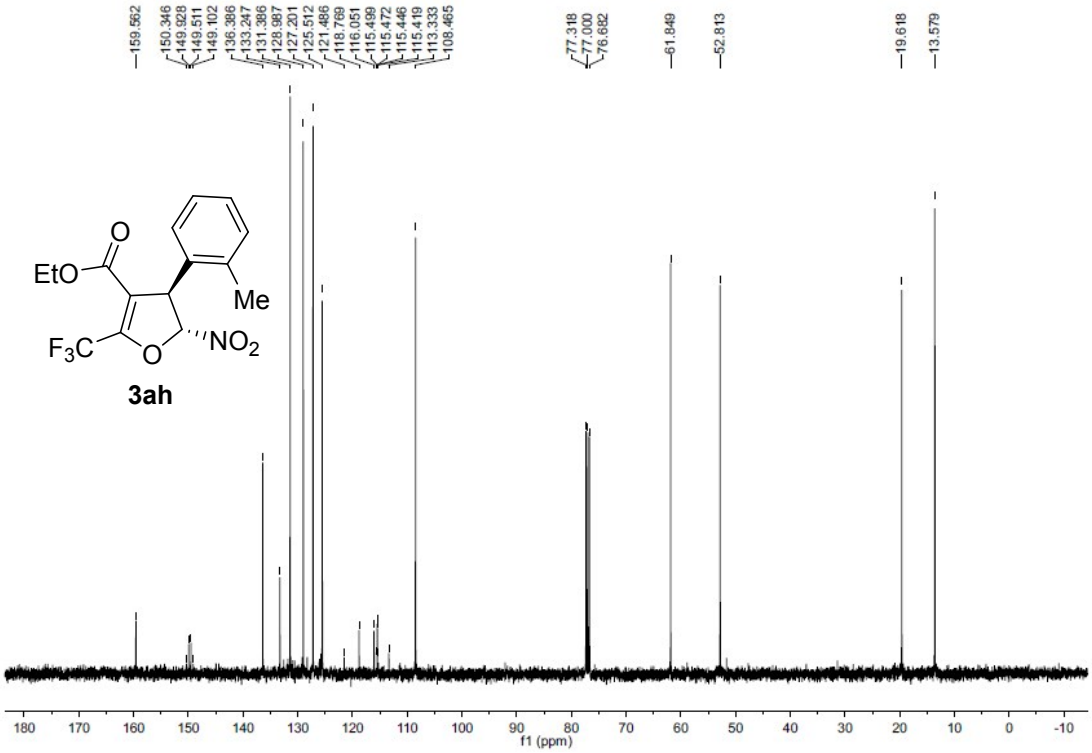
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		6.207	9.220	32.688	2.50	3.76	n.a.
2		8.663	359.910	836.465	97.50	96.24	n.a.
Total:			**369.130**	**869.153**	**100.00**	**100.00**	

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115.472
115.446
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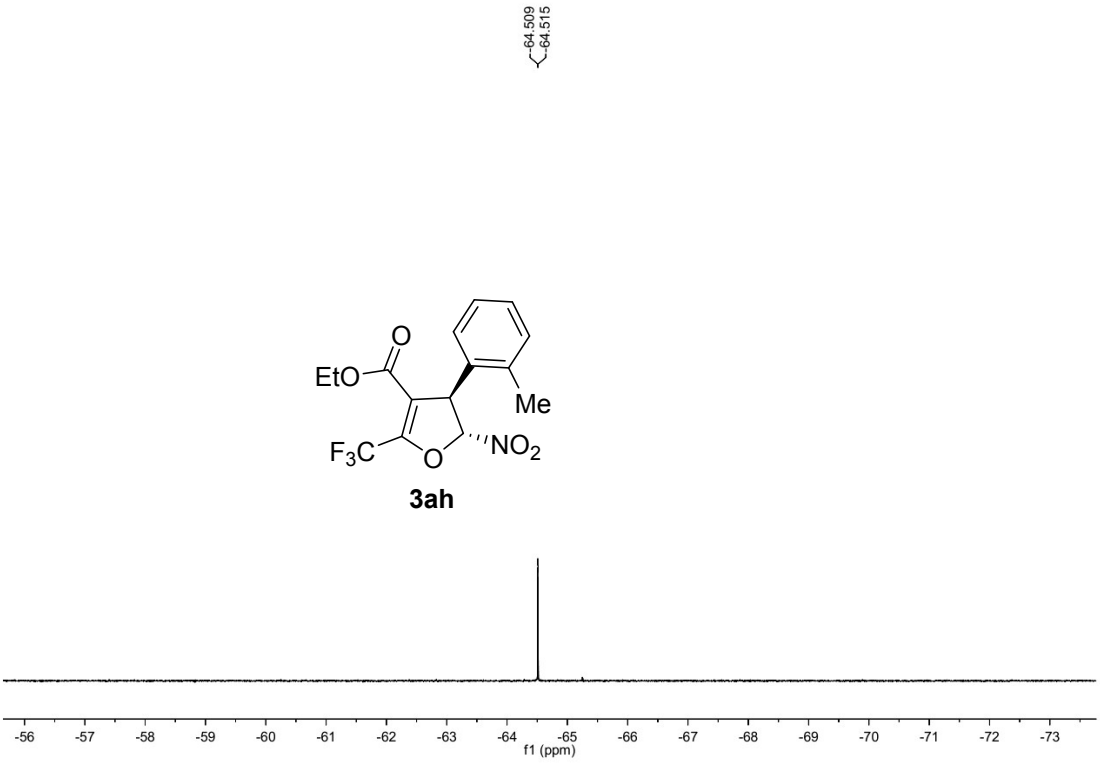
113.333
108.465
77.318
77.000
76.682
61.849
52.813
19.618
13.579
O
EtO
Me
F3C
O
NO2
3ah
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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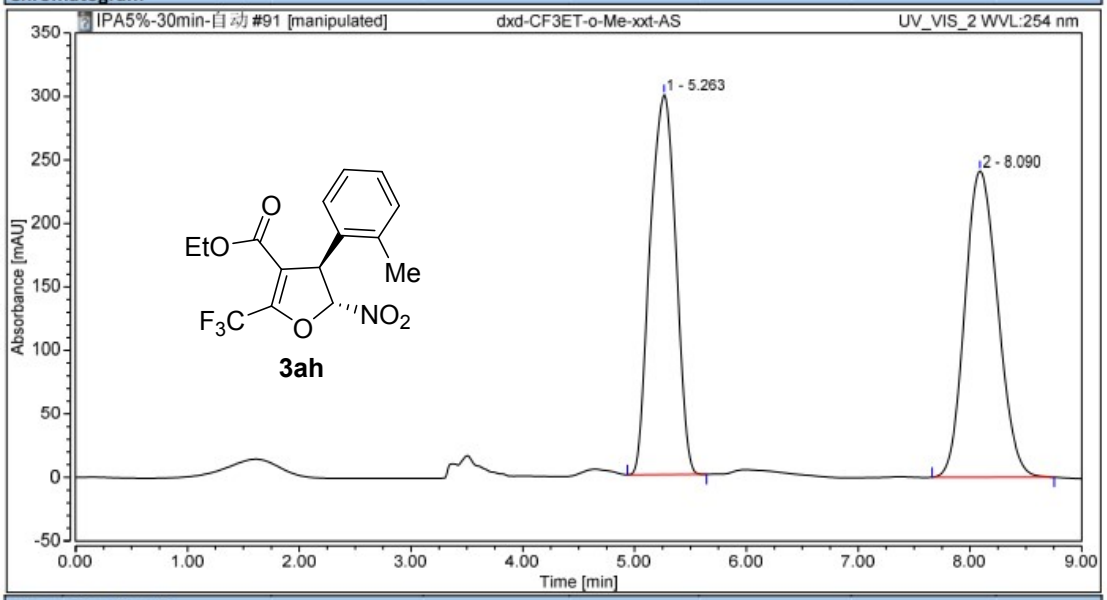
O
EtO
Me
F3C
O
NO2
3ah
-56 -57 -58 -59 -60 -61 -62 -63 -64 -65 -66 -67 -68 -69 -70 -71 -72 -73
f1 (ppm)

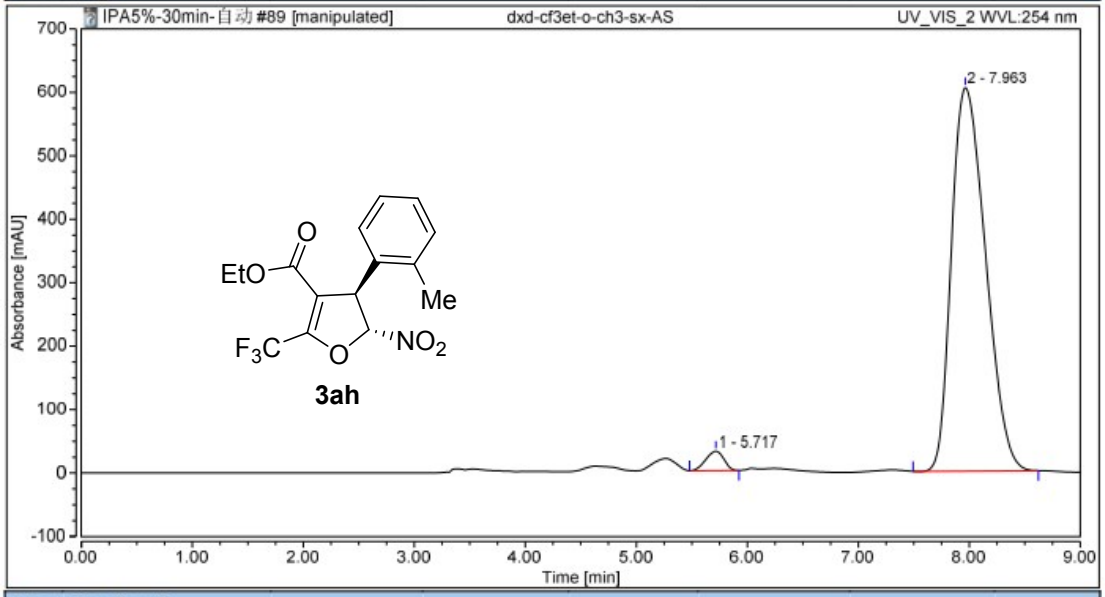
Chromatogram



Integration Results

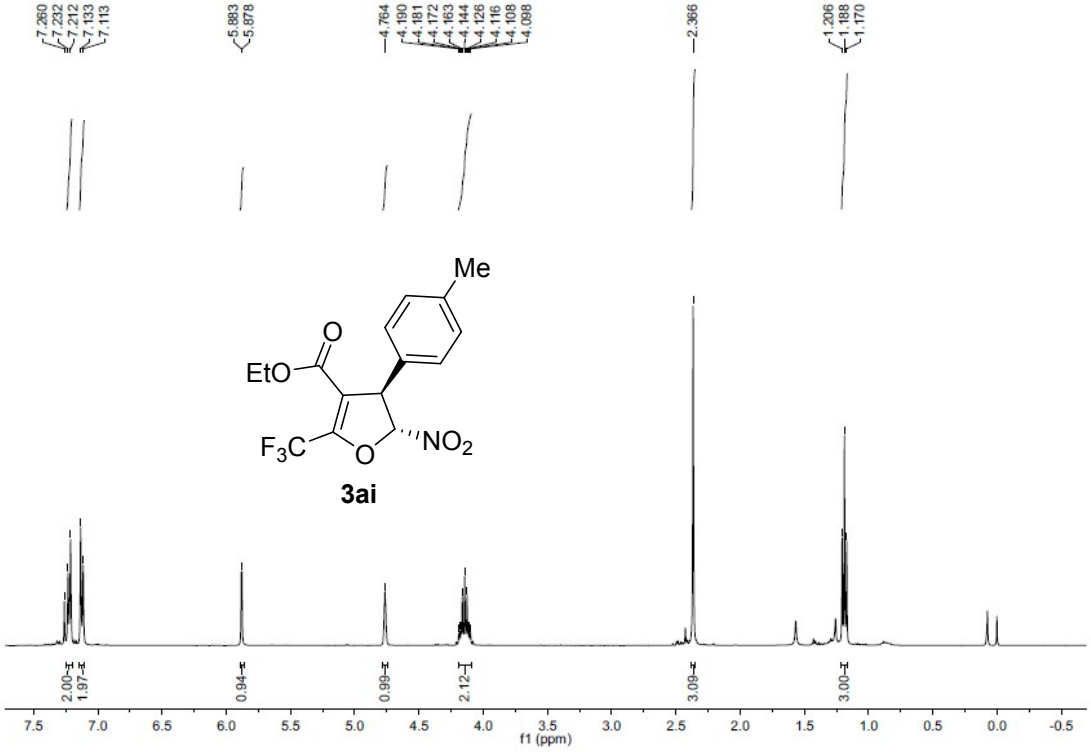
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.263	79.647	299.103	49.18	55.36	n.a.
2		8.090	82.287	241.211	50.82	44.64	n.a.
Total:			**161.933**	**540.314**	**100.00**	**100.00**	

Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.717	5.737	30.660	2.60	4.83	n.a.
2		7.963	214.950	604.320	97.40	95.17	n.a.
Total:			**220.687**	**634.980**	**100.00**	**100.00**	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2.366
1.206
1.188
1.170
Me
O
EtO
F3C
O
NO2
3ai
2.00
1.97
0.94
0.99
2.12
3.09
3.00
7.5
7.0
6.5
6.0
5.5
5.0
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3.0
2.5
2.0
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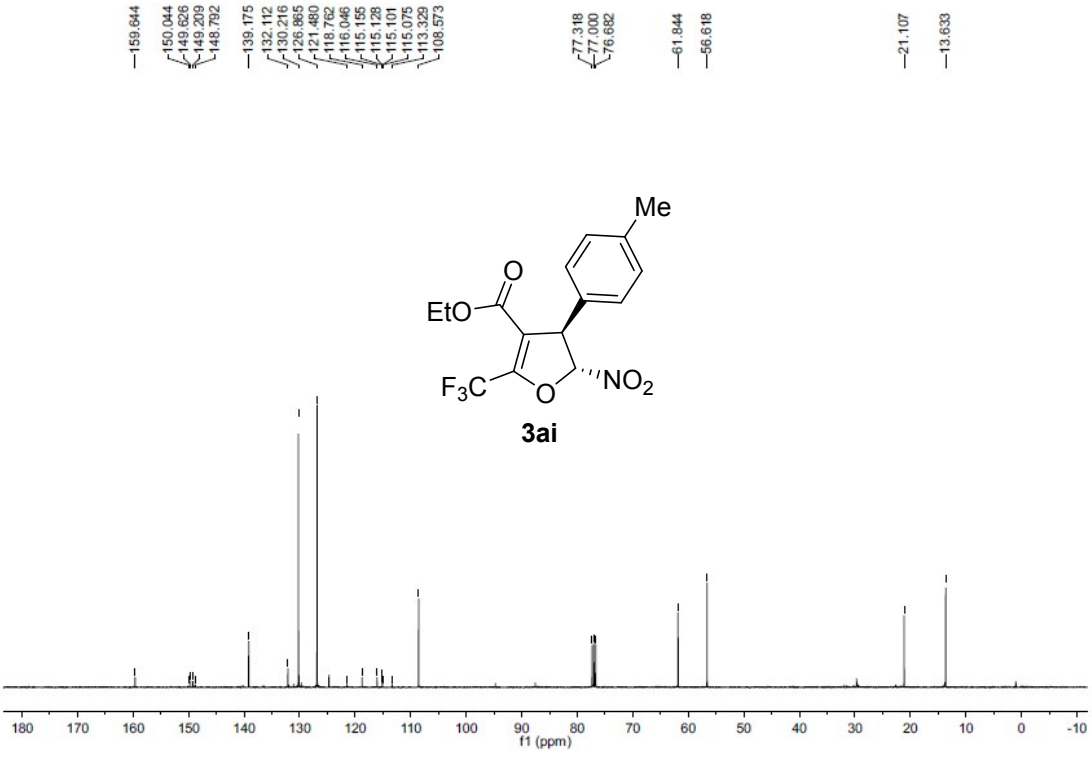
f1 (ppm)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115.128
115.101
115.075
113.329
108.573
77.318
77.000
76.682
61.844
56.618
21.107
13.633
Me
O
EtO
F3C
O
NO2
3ai
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
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20
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-10
f1 (ppm)

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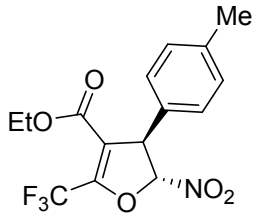
-64.555



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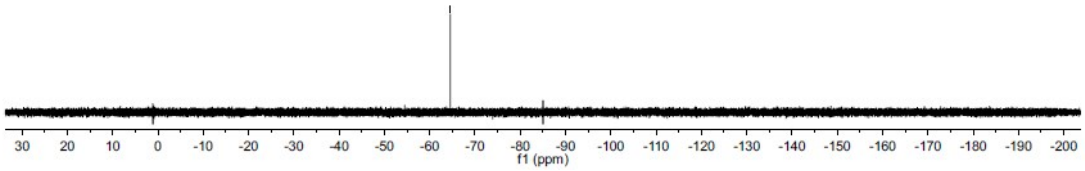
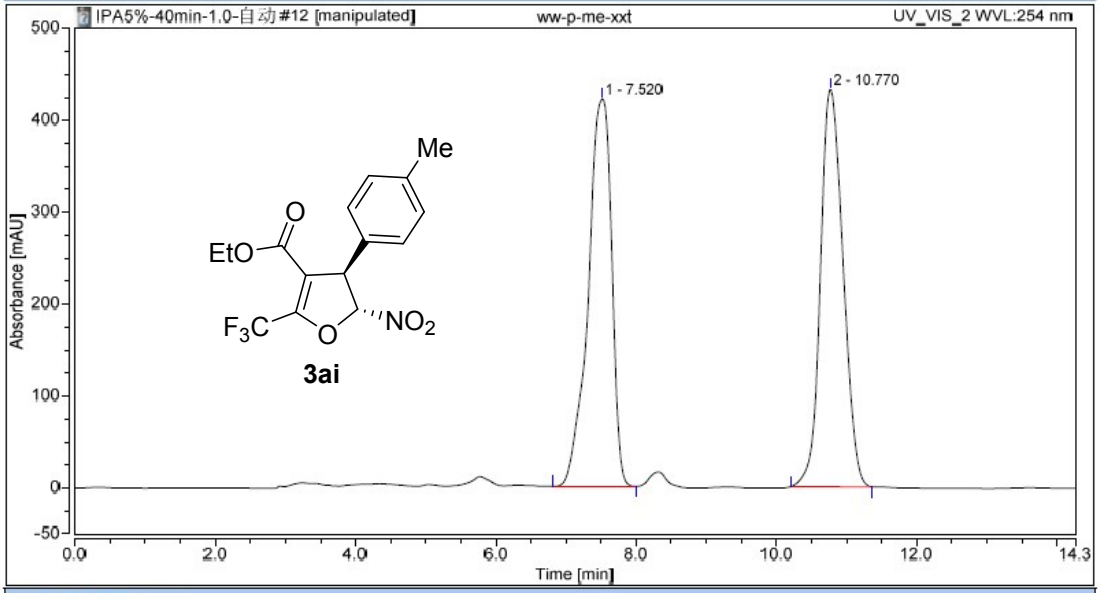
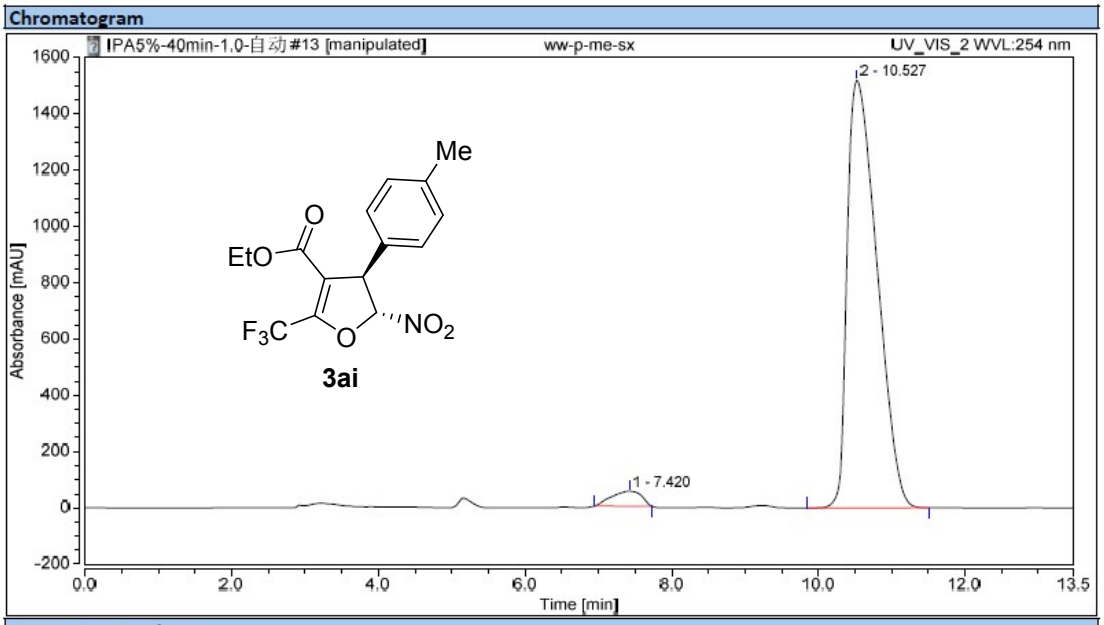


Chromatogram



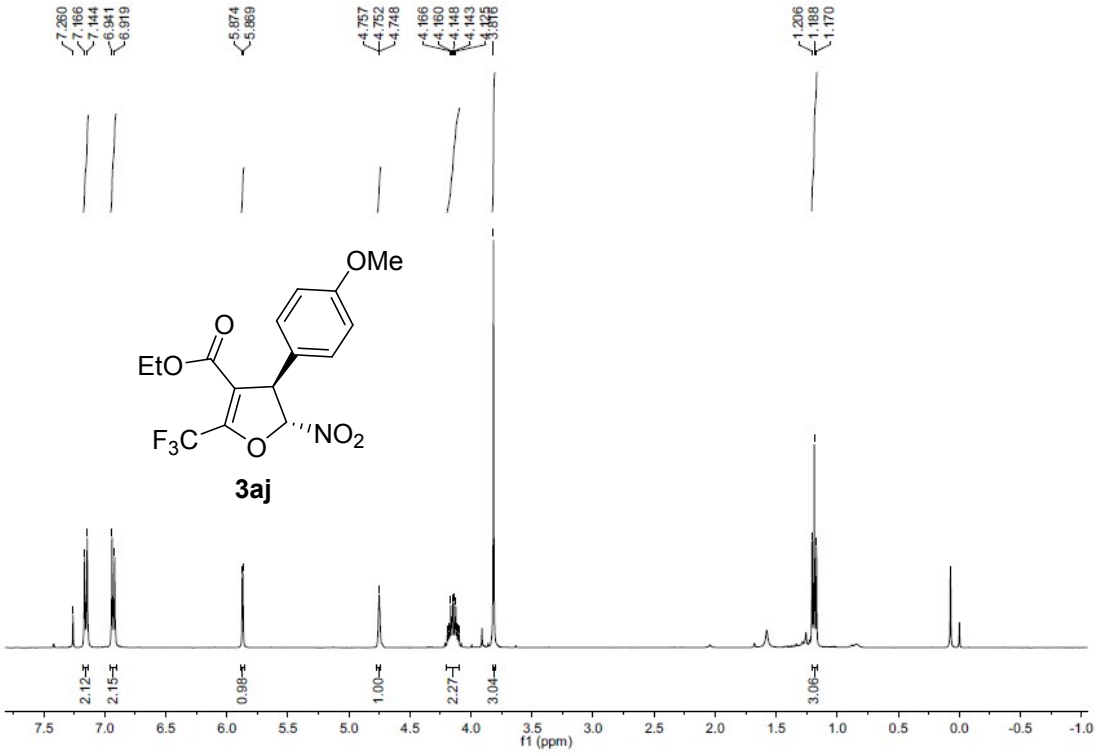
Integration Results

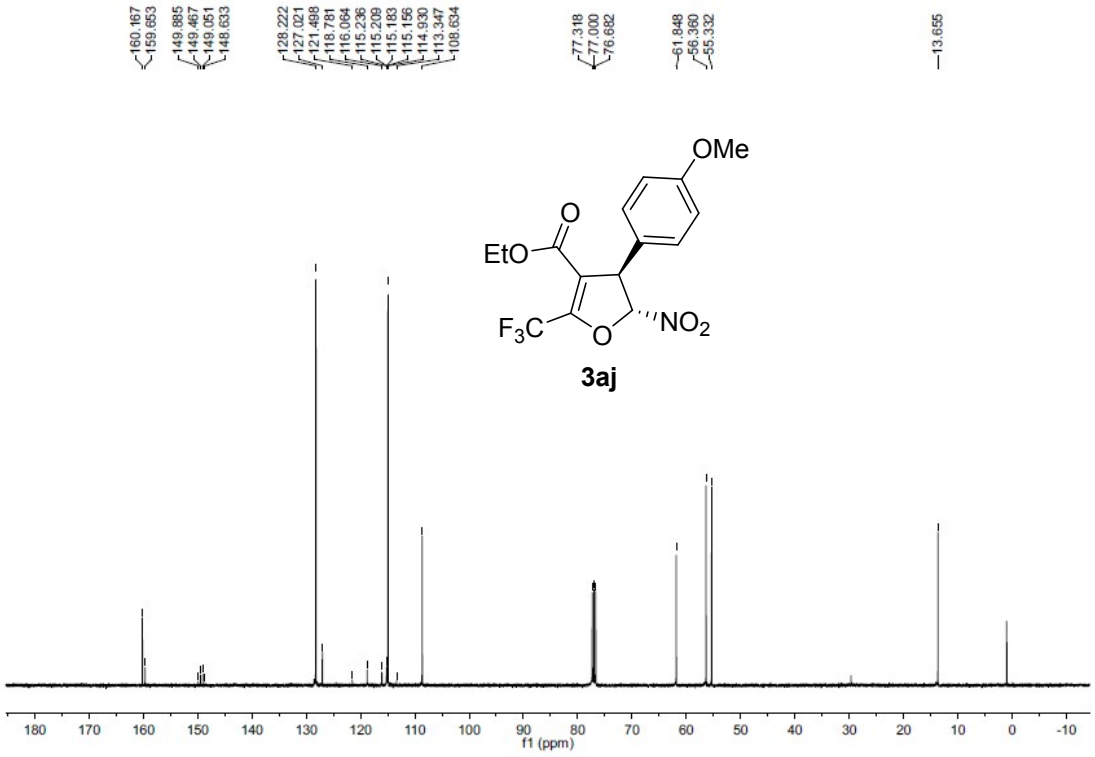
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		7.520	163.440	421.595	50.32	49.35	n.a.
2		10.770	161.392	432.773	49.68	50.65	n.a.
Total:			**324.832**	**854.368**	**100.00**	**100.00**	



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		7.420	25.267	53.460	3.42	3.40	n.a.
2		10.527	713.875	1519.272	96.58	96.60	n.a.
Total:			**739.142**	**1572.733**	**100.00**	**100.00**	

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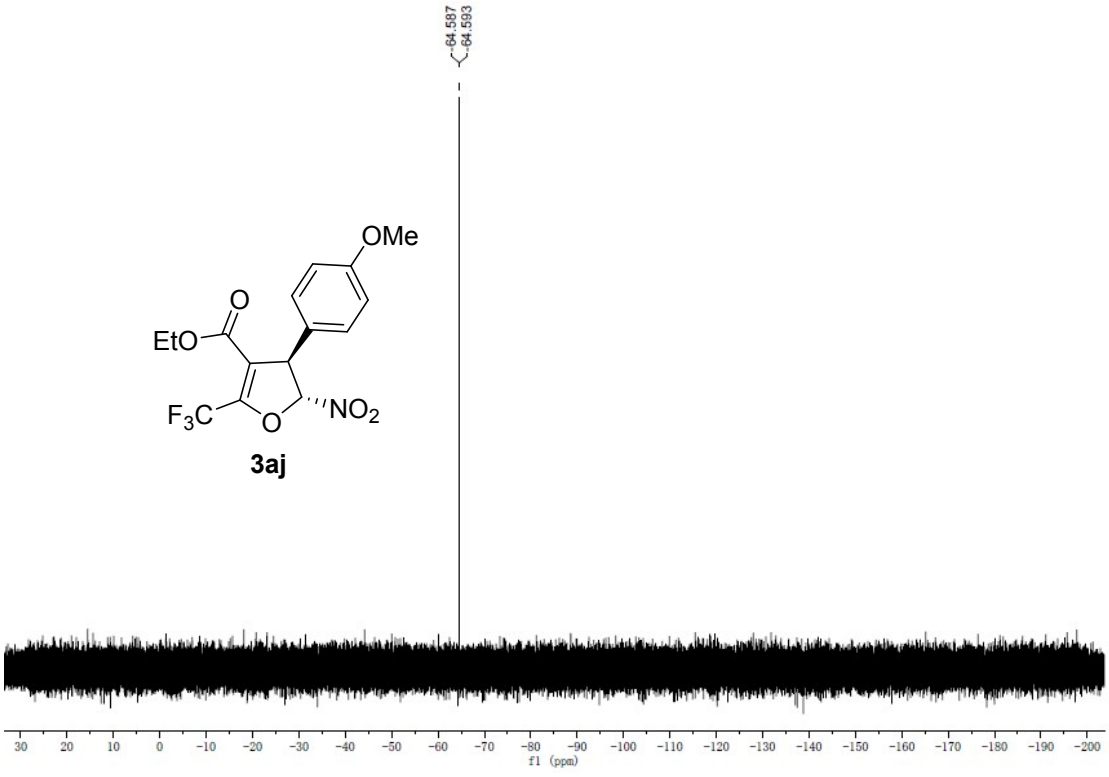
115.156
114.930
113.347
108.634
77.318
77.000
76.682
61.848
56.360
55.332
13.655
OMe
O
EtO
F3C
O
NO2
3aj
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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64.593
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EtO
F3C
O
NO2
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30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
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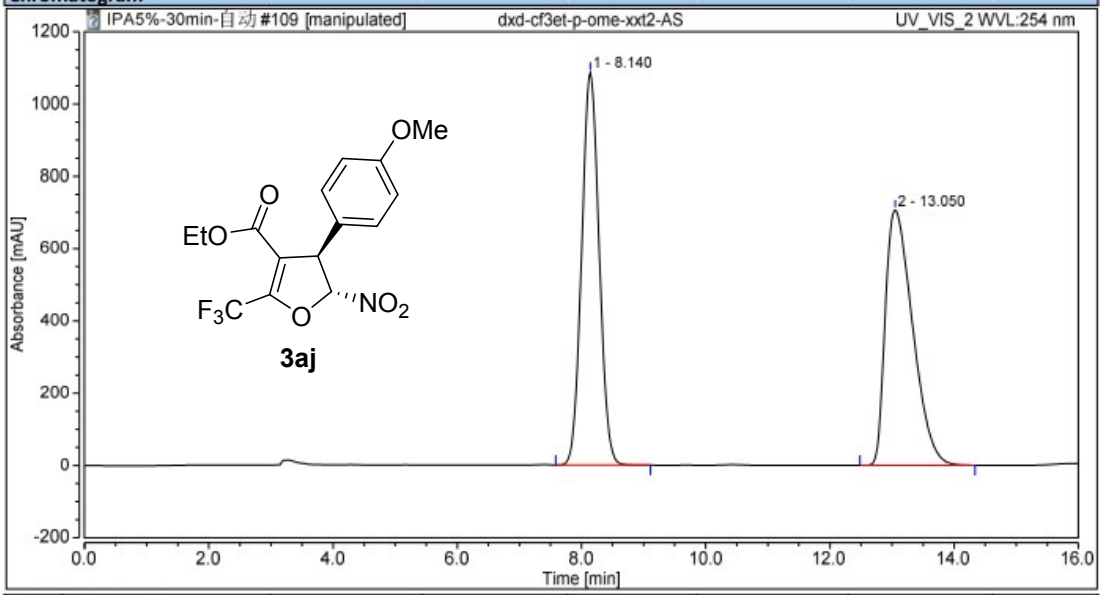
-120
-130
-140
-150
-160
-170
-180
-190
-200
f1 (ppm)

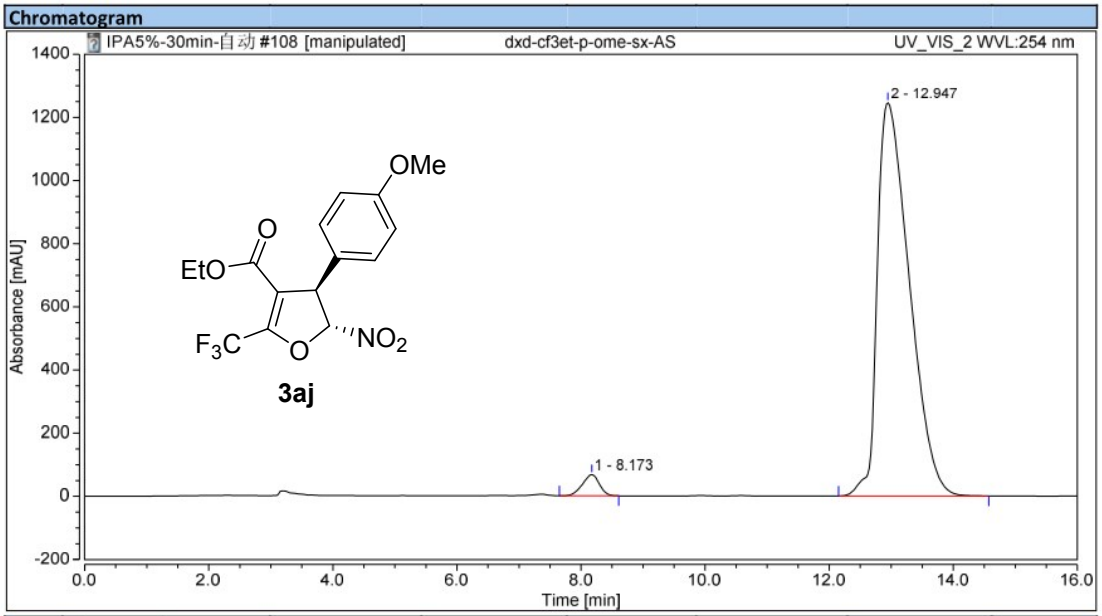
Chromatogram



Integration Results

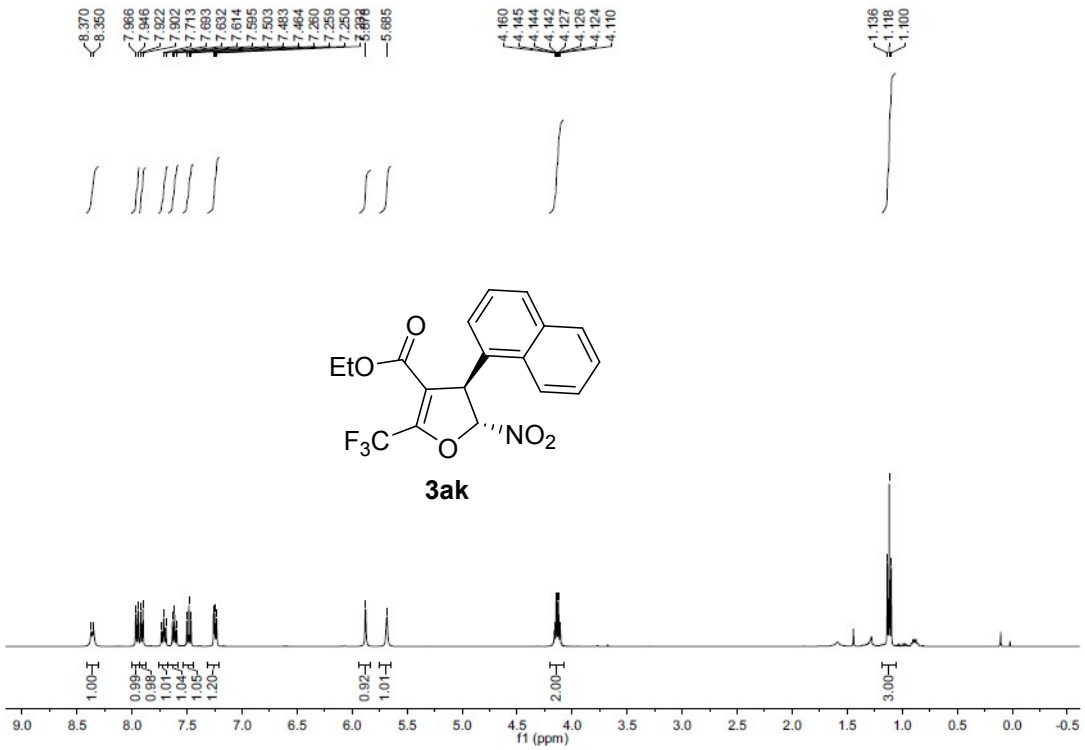
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		8.140	352.557	1086.882	49.52	60.60	n.a.
2		13.050	359.427	706.517	50.48	39.40	n.a.
Total:			**711.984**	**1793.400**	**100.00**	**100.00**	

Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		8.173	21.382	67.325	2.79	5.13	n.a.
2		12.947	744.331	1245.408	97.21	94.87	n.a.
Total:			**765.713**	**1312.734**	**100.00**	**100.00**	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4.126
4.124
4.110
1.136
1.118
1.100
EtO
O
F3C
O
NO2
3ak
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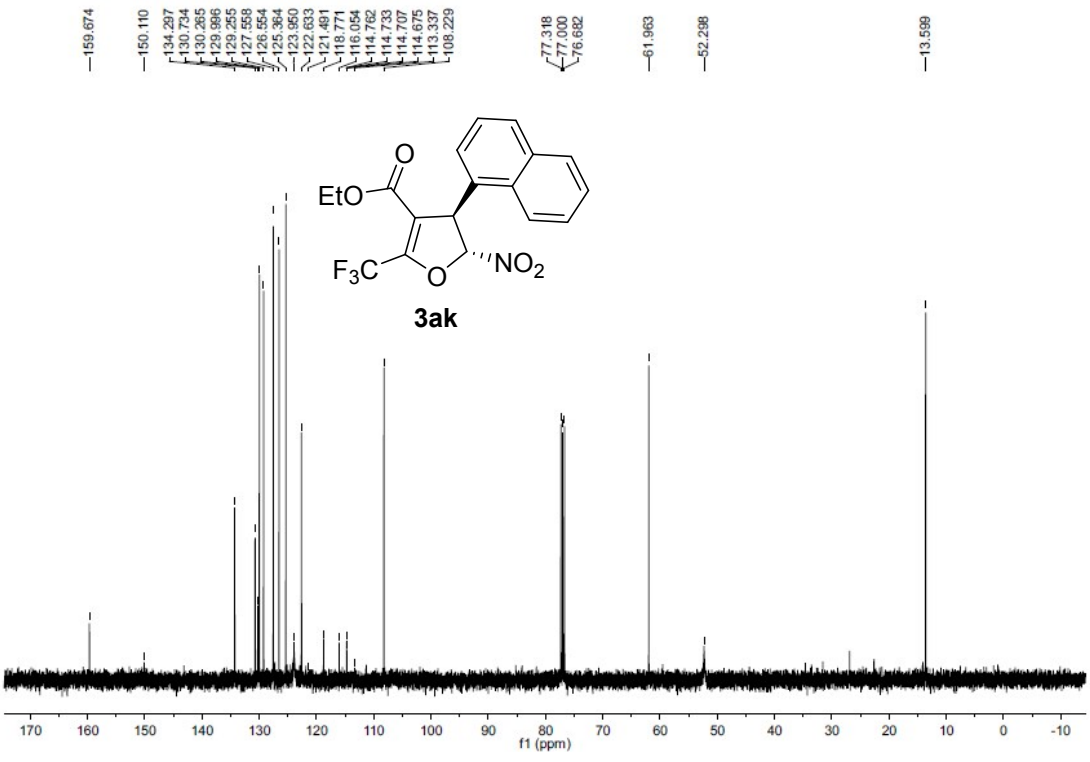
1.01
1.04
1.05
1.20
0.92
1.01
2.00
3.00
f1 (ppm)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116.054
114.762
114.733
114.707
114.675
113.337
108.229
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61.963
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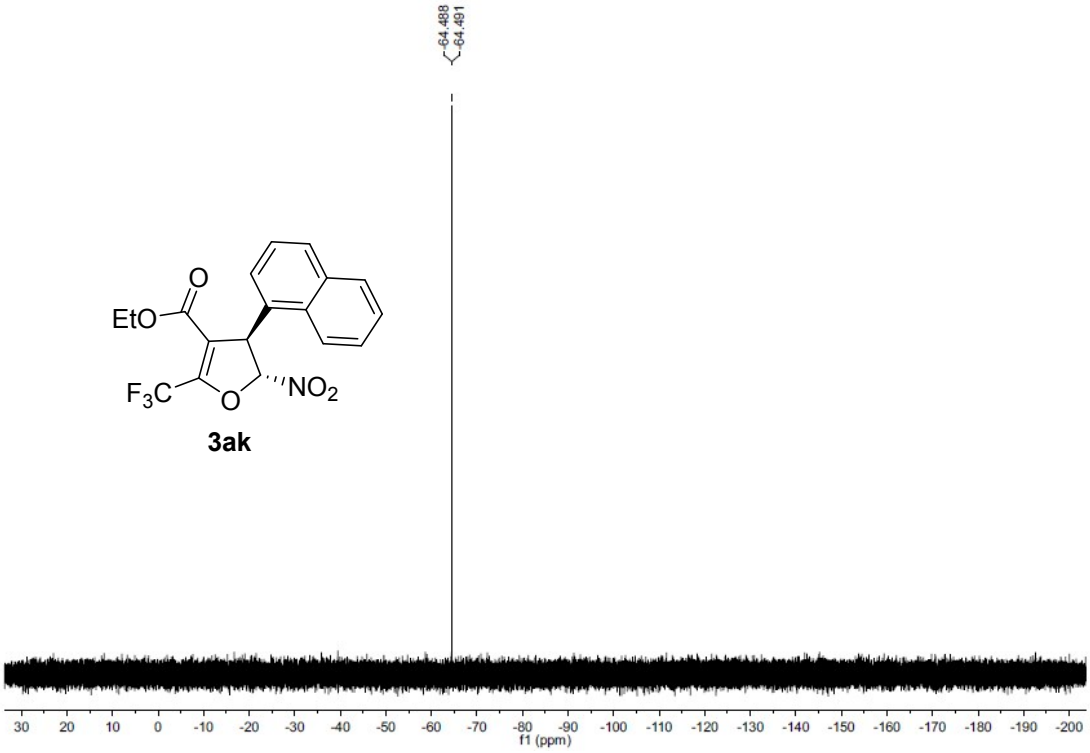
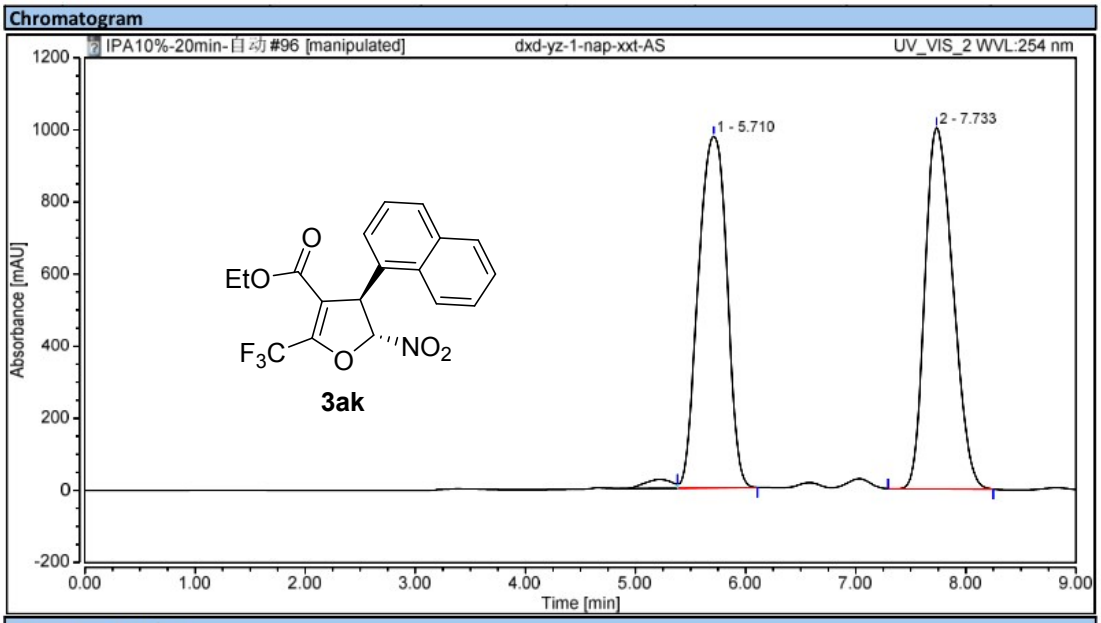
O
F3C
O
NO2
3ak
f1 (ppm)

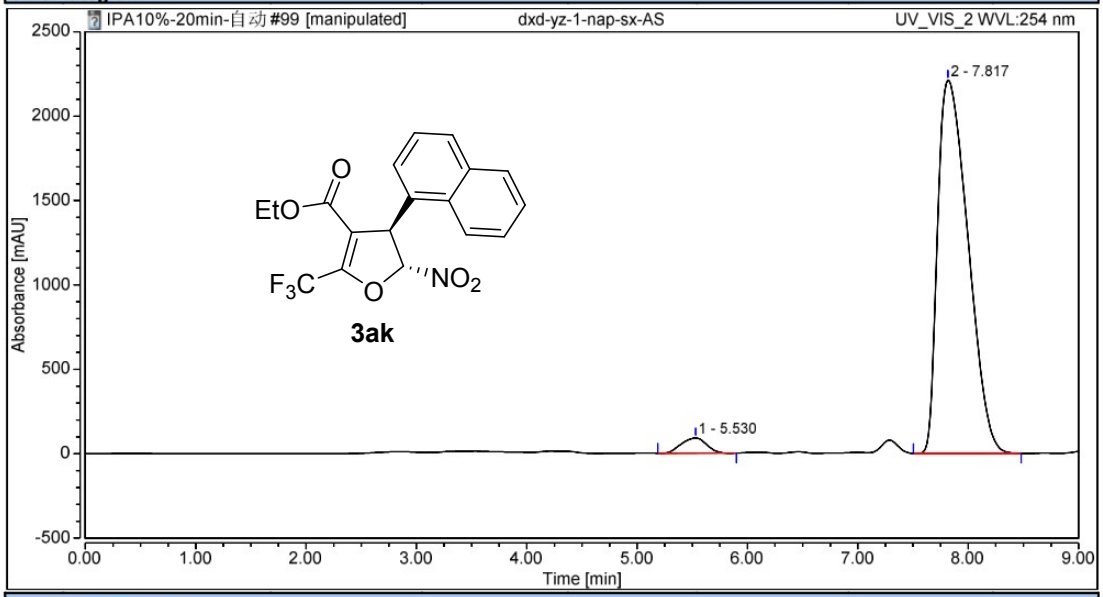




Integration Results

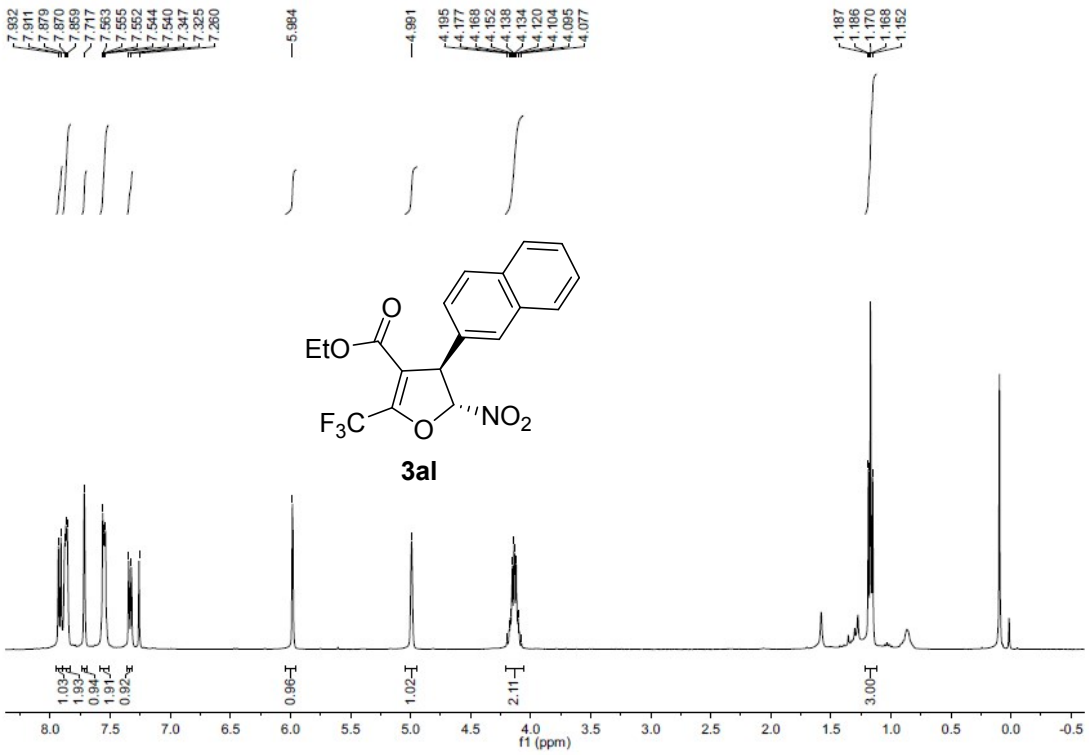
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.710	293.150	974.611	49.73	49.32	n.a.
2		7.733	296.280	1001.660	50.27	50.68	n.a.
Total:			**589.430**	**1976.271**	**100.00**	**100.00**	

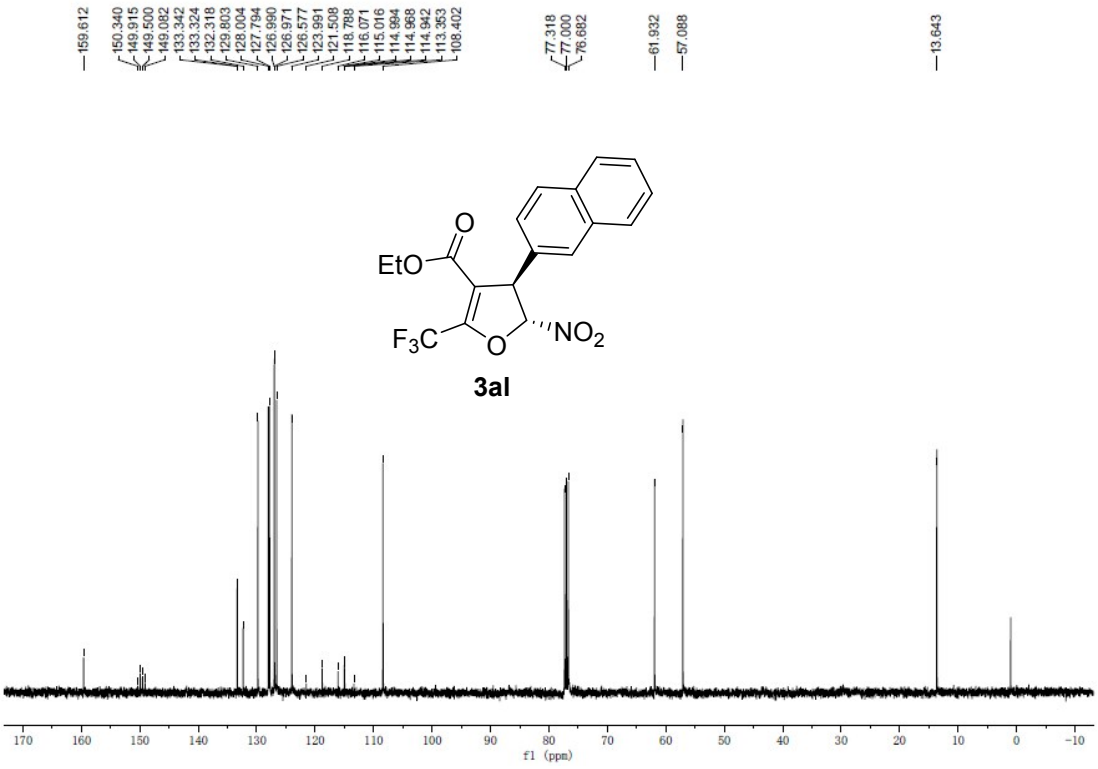
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.530	23.536	89.870	3.23	3.90	n.a.
2		7.817	705.537	2211.868	96.77	96.10	n.a.
Total:			**729.073**	**2301.738**	**100.00**	**100.00**	

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149.500
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133.342
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129.803
128.004
127.794
126.990
126.971
126.577
123.991
121.508
118.788
116.071
115.016
114.984
114.968
114.942
113.353
108.402
77.318
77.000
76.682
61.932
57.088
13.643
O
EtO
F3C
O
NO2
3aI
170
160
150
140
130
120
110
100
90
80
70
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50
40
30
20
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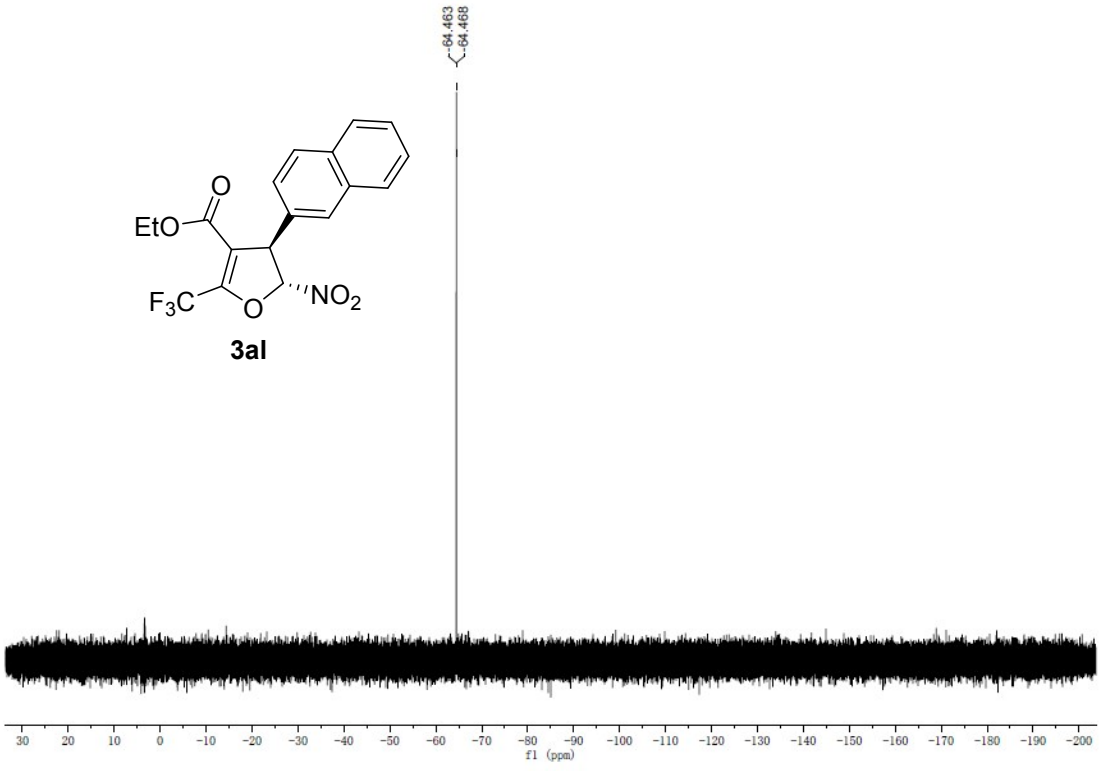
0
-10
f1 (ppm)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O
EtO
F3C
O
NO2
3aI
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20
10
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-10
-20
-30
-40
-50
-60
-70
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-150
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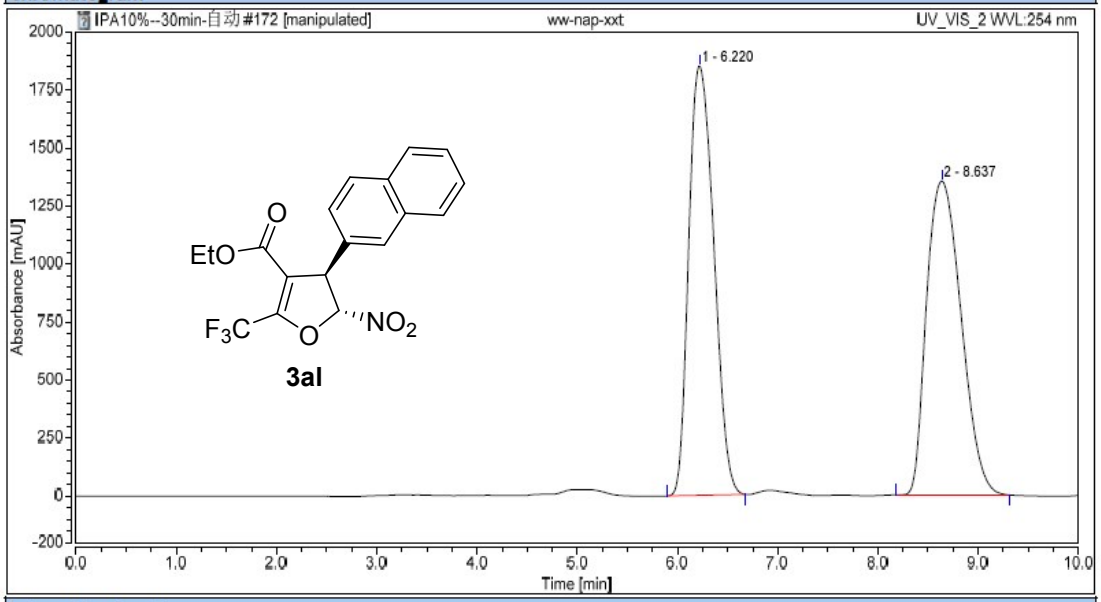
-170
-180
-190
-200
f1 (ppm)

Chromatogram

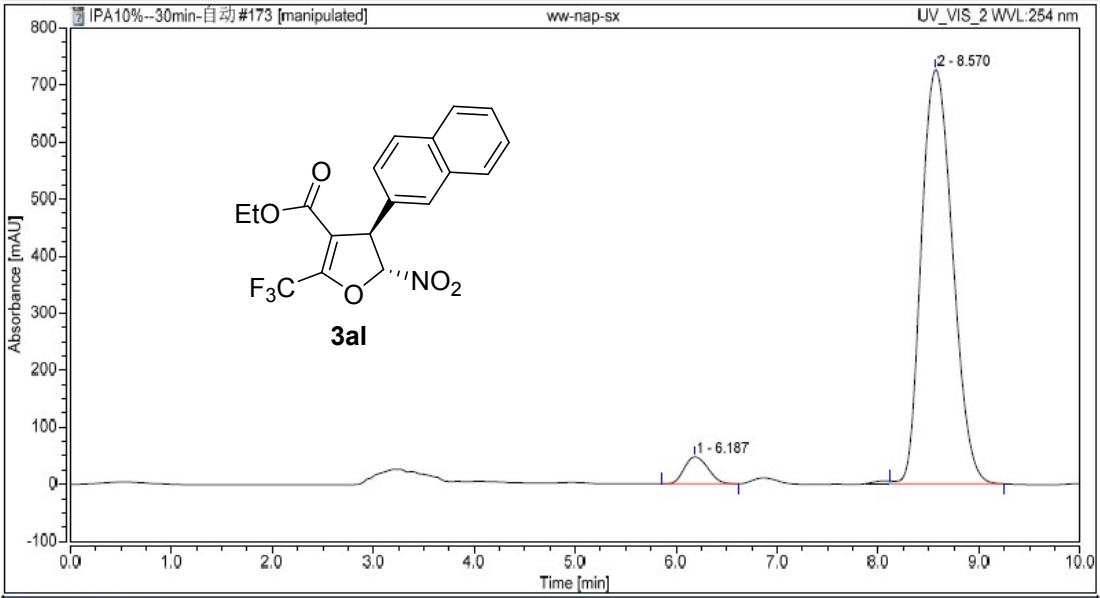


3al

Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		6.220	535.764	1850.582	49.75	57.76	n.a.
2		8.637	541.149	1353.365	50.25	42.24	n.a.
Total:			**1076.912**	**3203.947**	**100.00**	**100.00**	

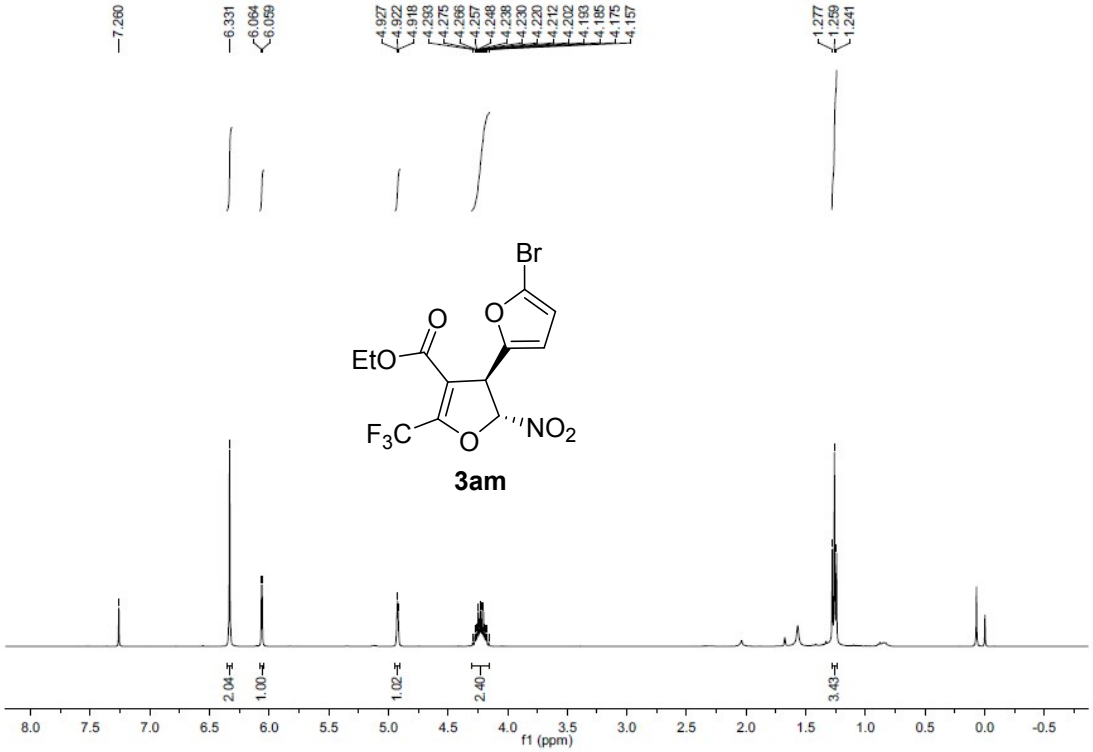
Chromatogram



3al

Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		6.187	12.776	47.120	4.68	6.09	n.a.
2		8.570	260.197	726.061	95.32	93.91	n.a.
Total:			**272.973**	**773.181**	**100.00**	**100.00**	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4.293
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4.266
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4.248
4.238
4.230
4.220
4.212
4.202
4.193
4.185
4.175
4.157
1.277
1.259
1.241
Br
O
O
EtO
F3C
O
NO2
2.04
1.00
1.02
2.40
3.43
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
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2.5
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1.5
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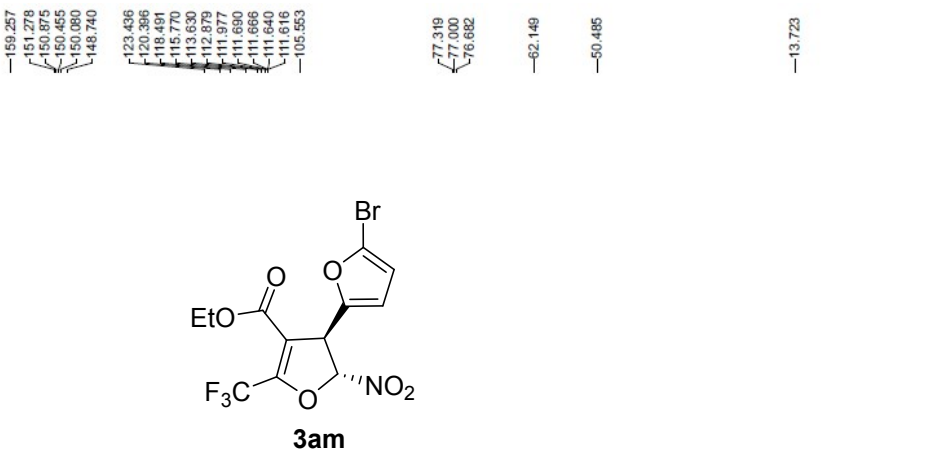
0.0
-0.5
f1 (ppm)

3am


159.257
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150.875
150.455
150.080
148.740
123.436
120.396
118.491
115.770
113.630
112.879
111.977
111.690
111.666
111.640
111.616
105.553
77.319
77.000
76.682
62.149
50.485
13.723
Br
O
O
EtO
F3C
O
NO2
180
170
160
150
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120
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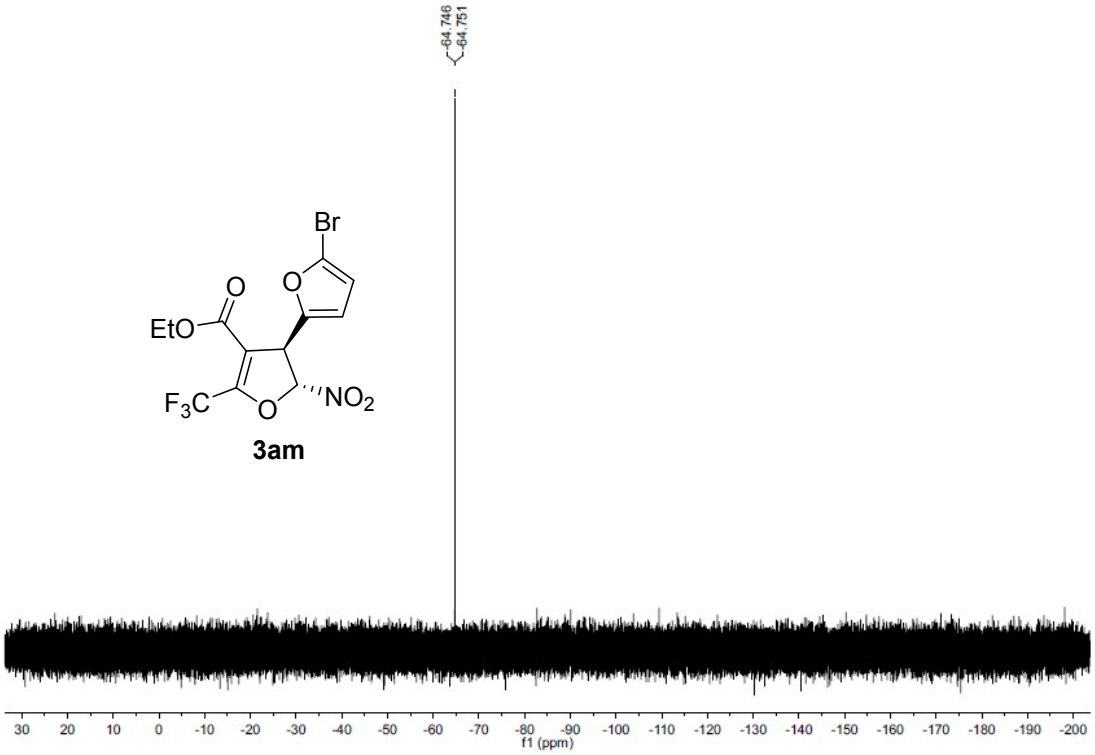
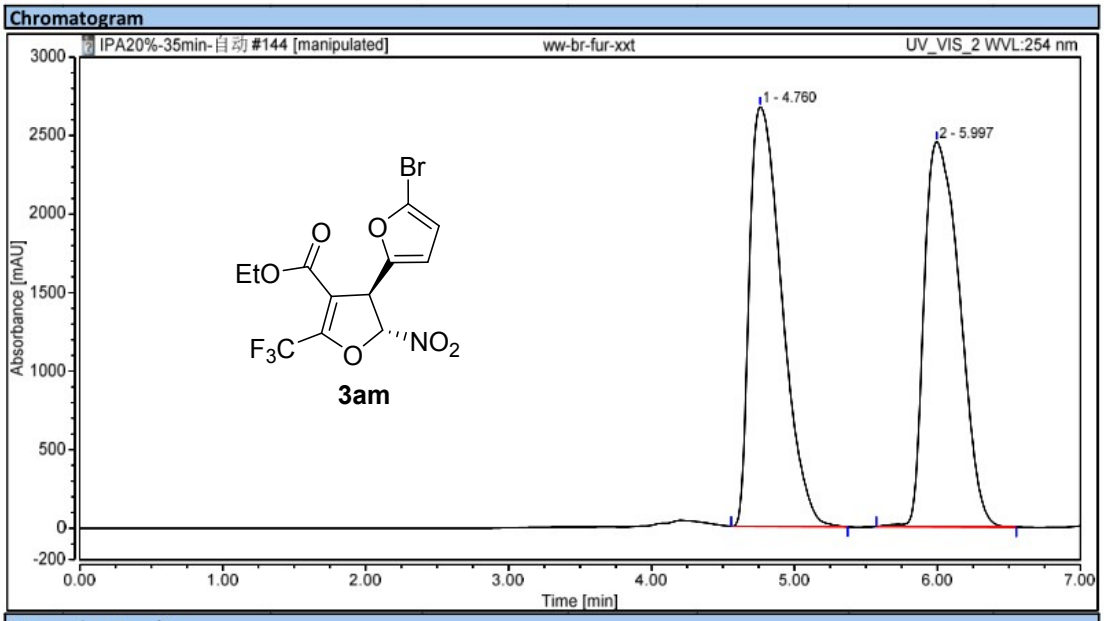
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

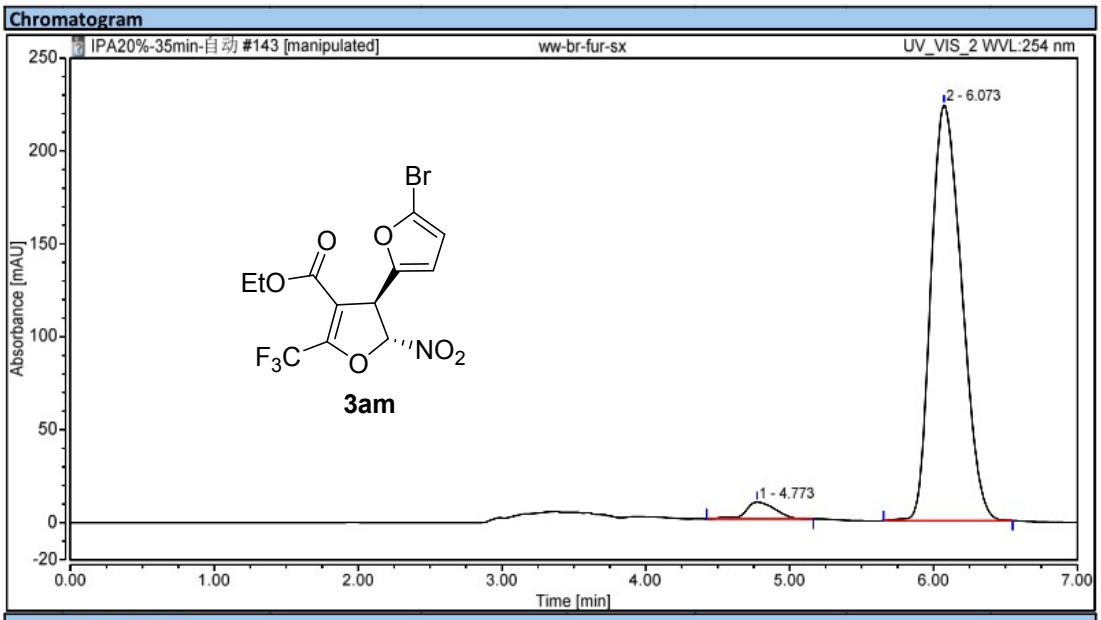
3am





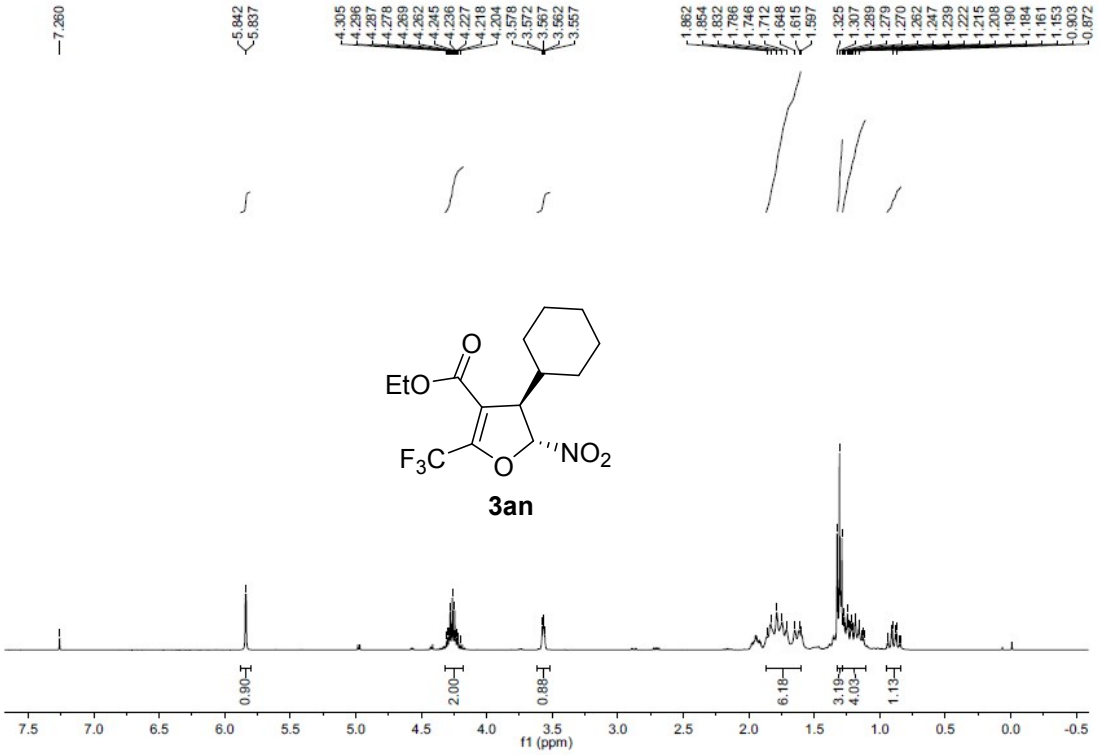
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		4.760	704.732	2670.969	49.99	52.15	n.a.
2		5.997	705.001	2451.124	50.01	47.85	n.a.
Total:			**1409.734**	**5122.093**	**100.00**	**100.00**	



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		4.773	2.150	9.025	3.73	3.88	n.a.
2		6.073	55.444	223.710	96.27	96.12	n.a.
Total:			**57.593**	**232.735**	**100.00**	**100.00**	




160.464
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148.654
148.248
147.827
121.407
118.693
115.979
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113.241
113.213
113.187
105.171
77.318
77.000
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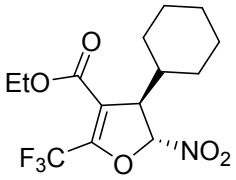
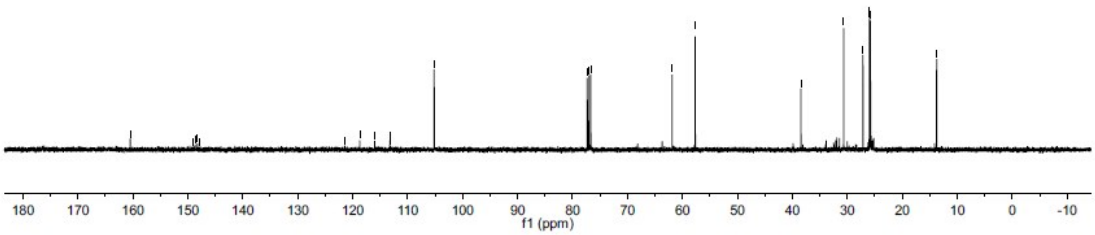
27.148
25.994
25.938
25.793
13.746


O
EtO
F3C
O
NO2

3an


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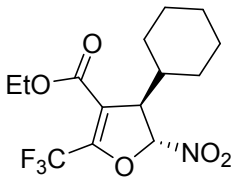
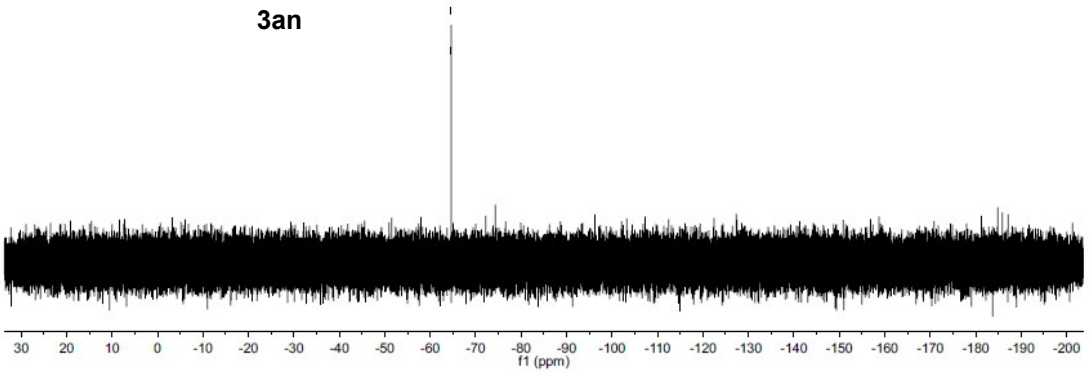
40
30
20
10
0
-10
f1 (ppm)


64.613
64.619


O
EtO
F3C
O
NO2

3an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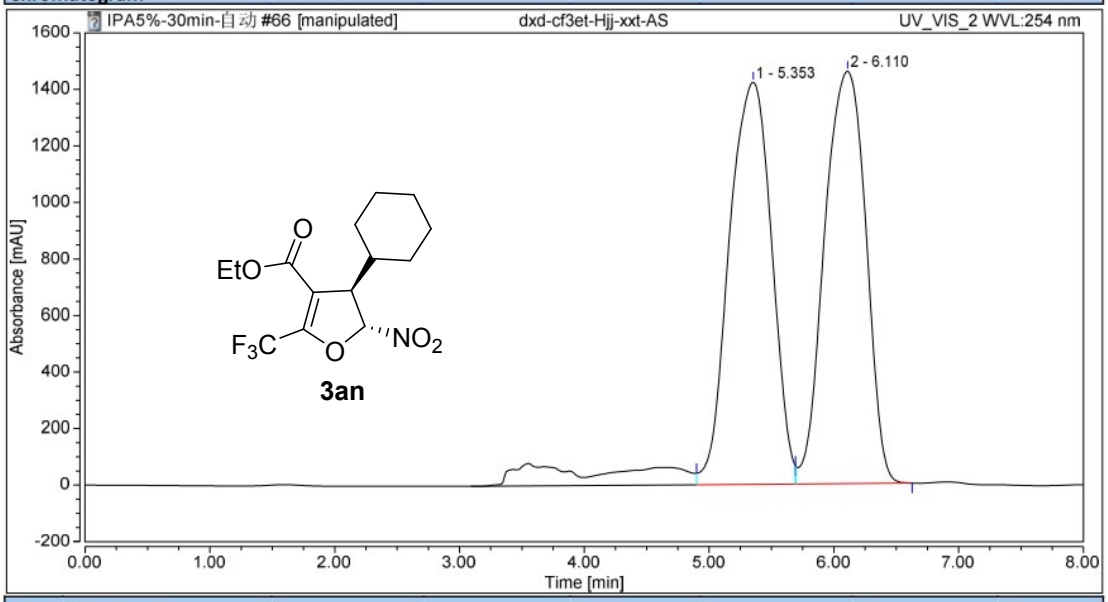
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
f1 (ppm)

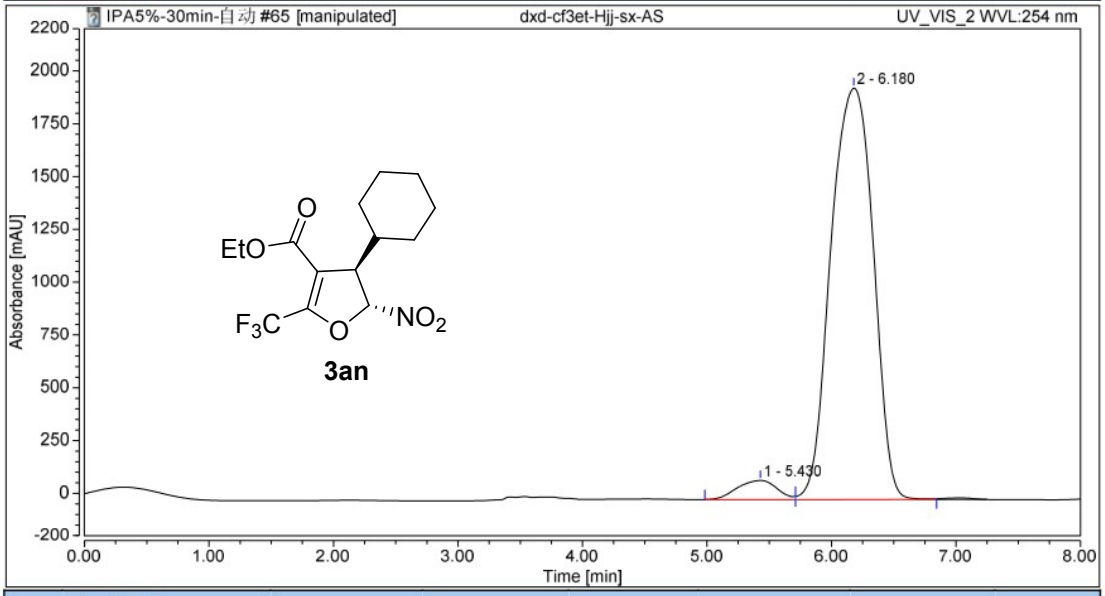
Chromatogram



Integration Results

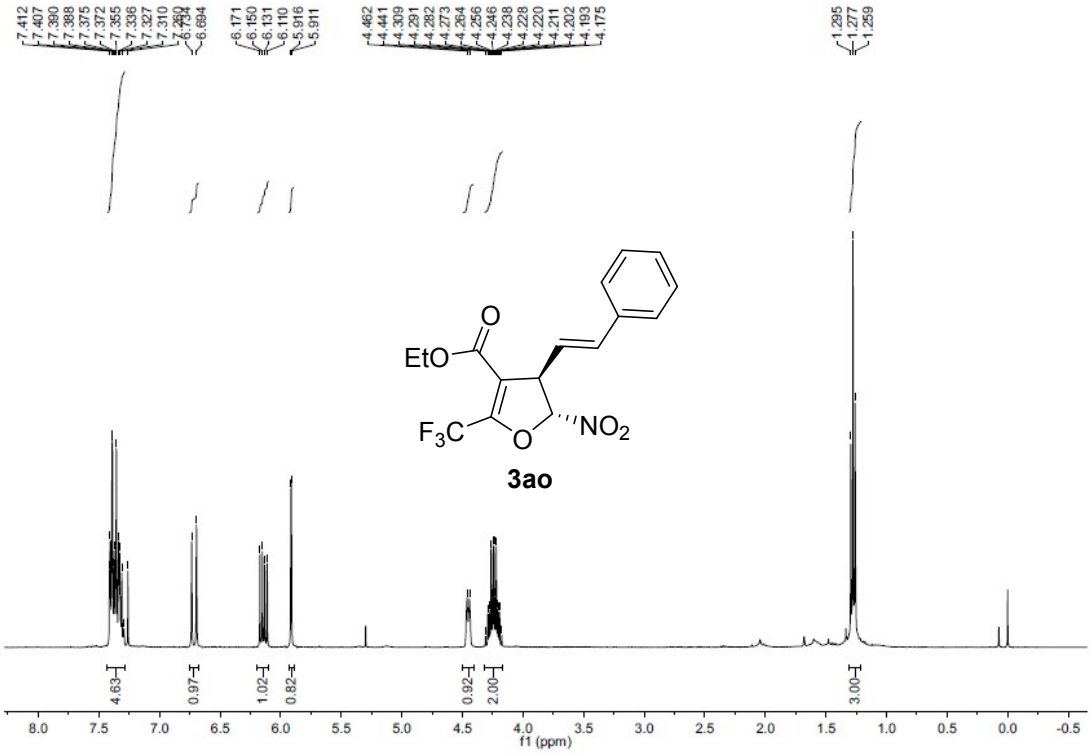
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.353	560.664	1423.042	49.99	49.37	n.a.
2		6.110	560.788	1459.422	50.01	50.63	n.a.
Total:			**1121.452**	**2882.464**	**100.00**	**100.00**	

Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.430	33.375	90.232	4.15	4.43	n.a.
2		6.180	769.953	1948.637	95.85	95.57	n.a.
Total:			**803.329**	**2038.868**	**100.00**	**100.00**	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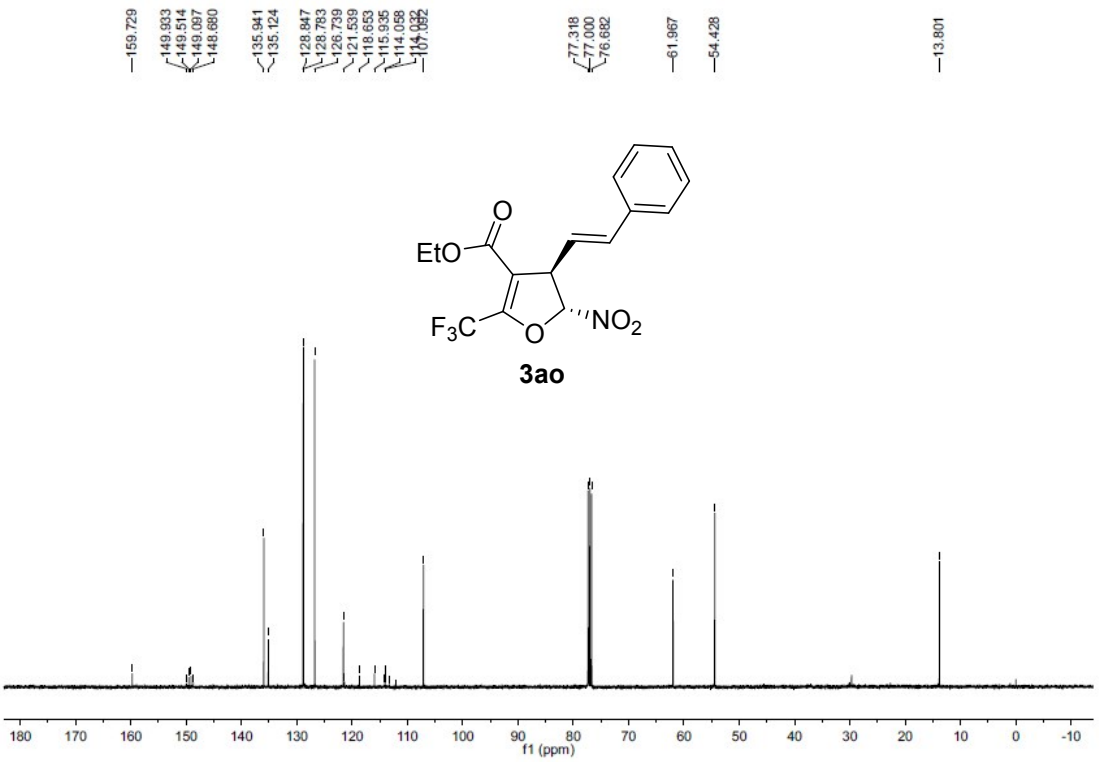
6.150
6.131
6.110
5.916
5.911
4.462
4.441
4.309
4.291
4.282
4.273
4.264
4.256
4.246
4.238
4.228
4.220
4.211
4.202
4.193
4.175
1.295
1.277
1.259
EtO
O
F3C
O
NO2
3ao
4.63
0.97
1.02
0.82
0.92
2.00
3.00
f1 (ppm)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149.097
148.680
135.941
135.124
128.847
128.783
126.739
121.539
118.653
115.935
114.058
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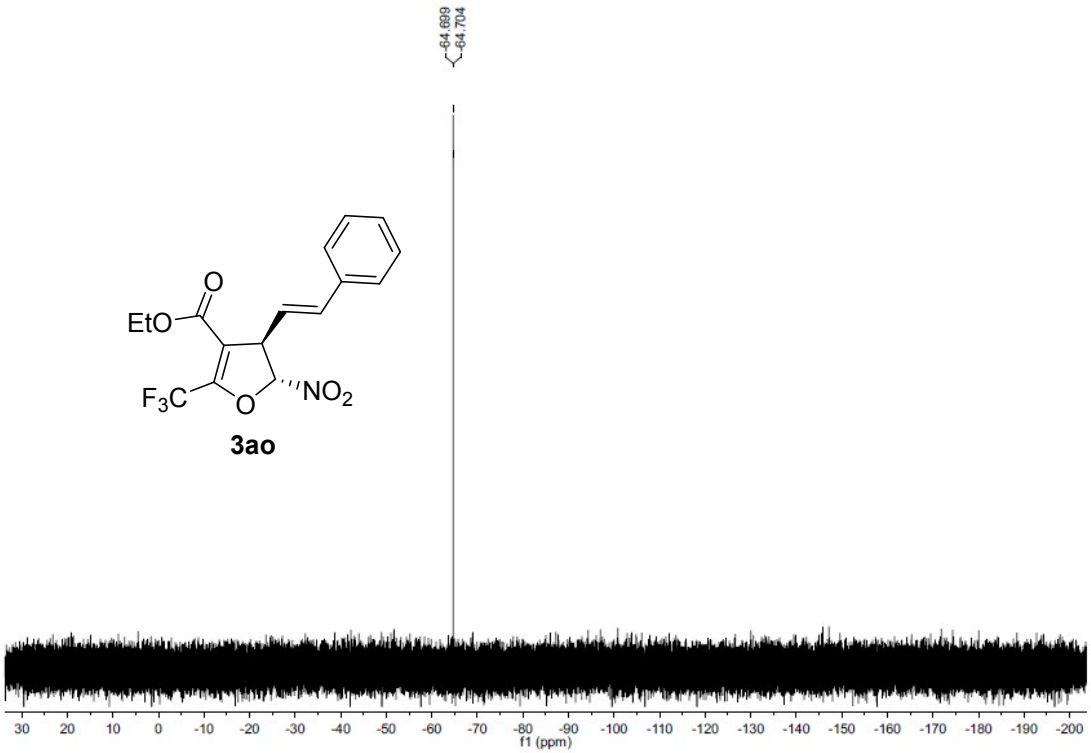
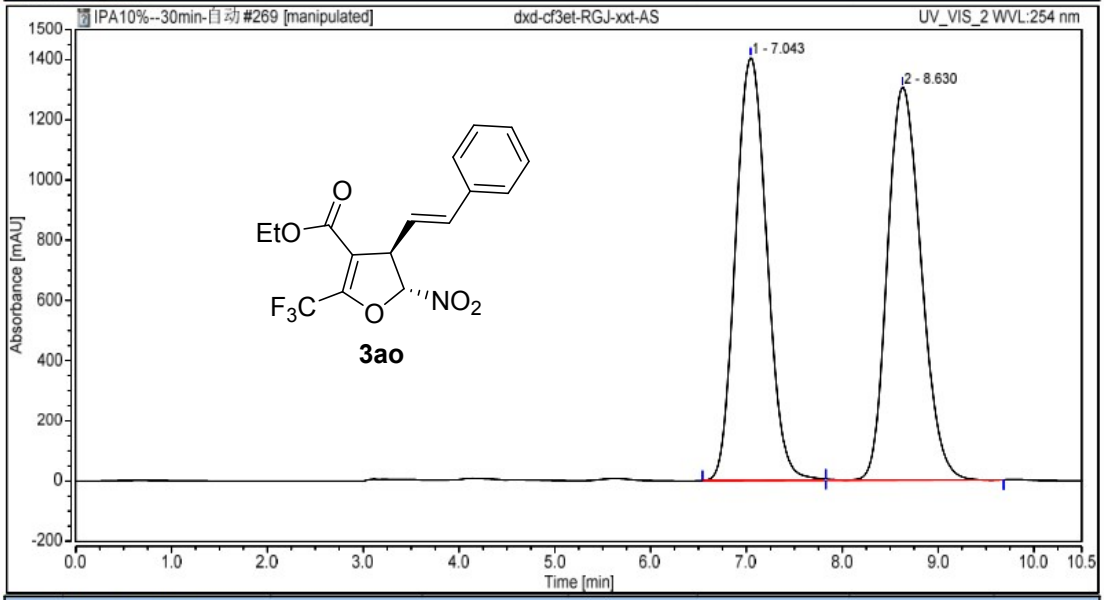
77.000
76.682
61.967
54.428
13.801
EtO
O
F3C
O
NO2
3ao
f1 (ppm)



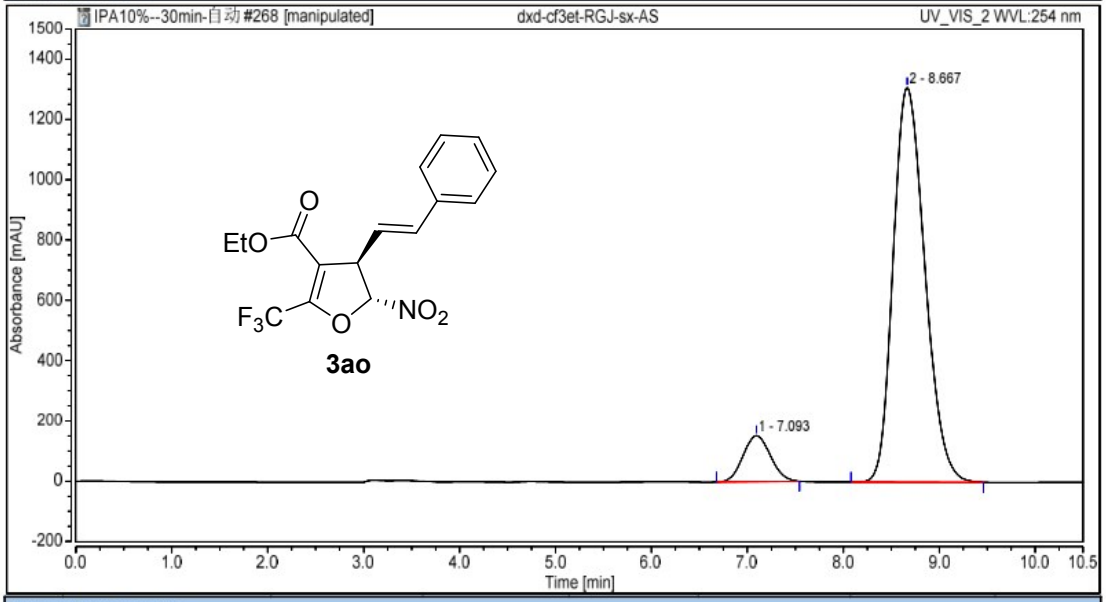
Chromatogram



Integration Results

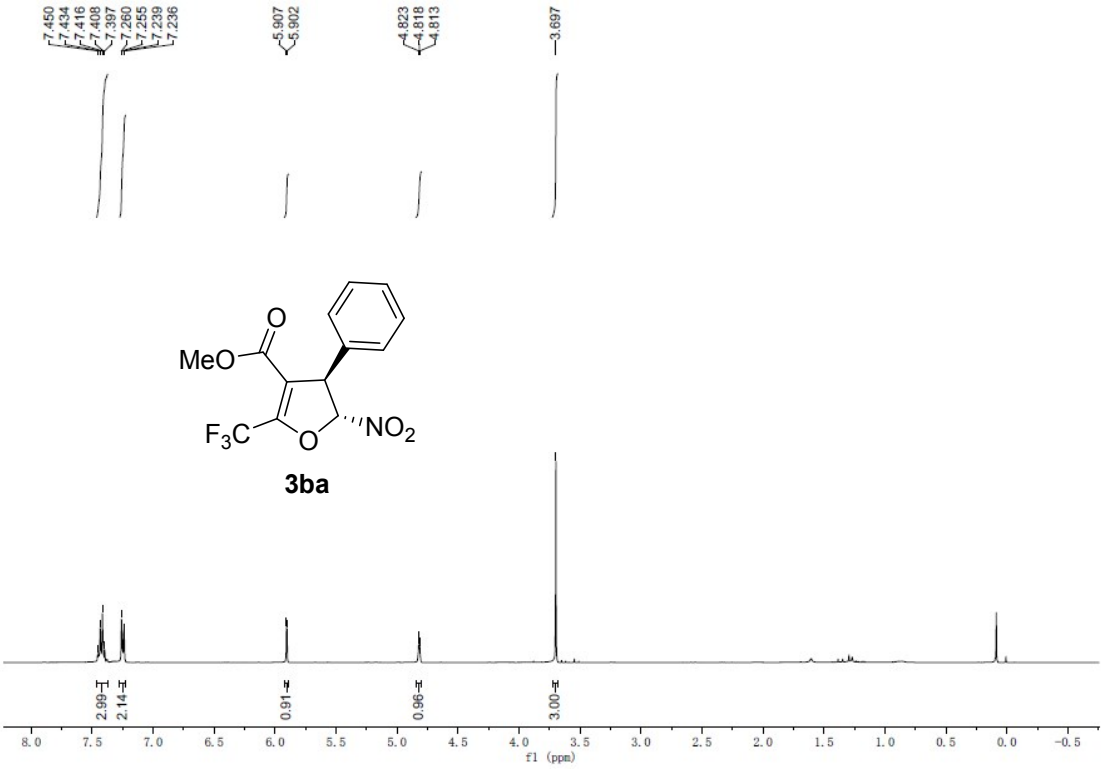
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		7.043	530.657	1404.457	49.88	51.83	n.a.
2		8.630	533.153	1305.106	50.12	48.17	n.a.
Total:			**1063.810**	**2709.563**	**100.00**	**100.00**	

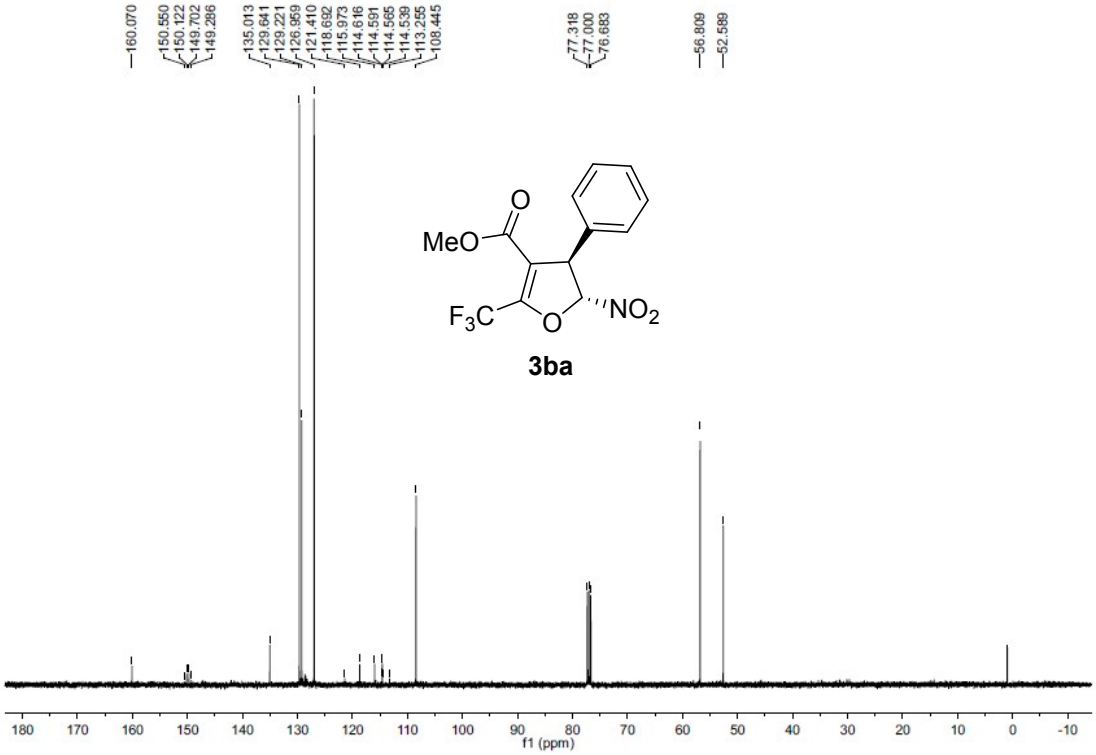
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		7.093	50.583	152.365	9.17	10.43	n.a.
2		8.667	500.933	1309.065	90.83	89.57	n.a.
Total:			**551.516**	**1461.430**	**100.00**	**100.00**	

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129.221
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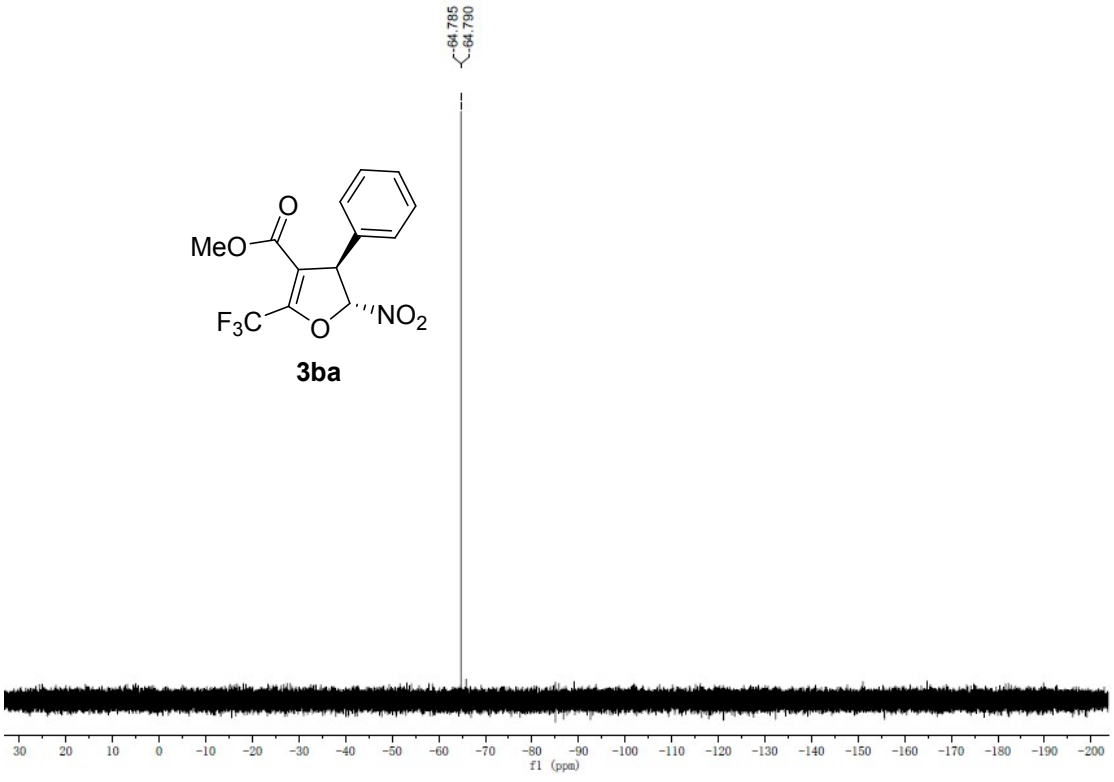
121.410
118.692
115.973
114.616
114.591
114.565
114.539
113.255
108.445
77.318
77.000
76.683
56.809
52.589
MeO
O
F3C
O
NO2
3ba
f1 (ppm)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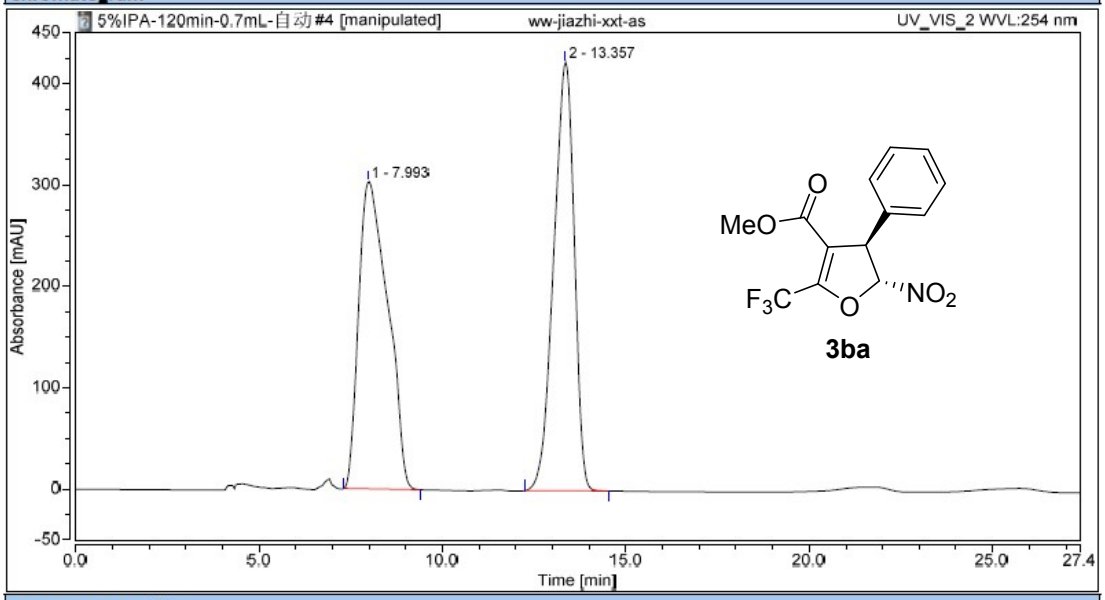
O
NO2
3ba
f1 (ppm)

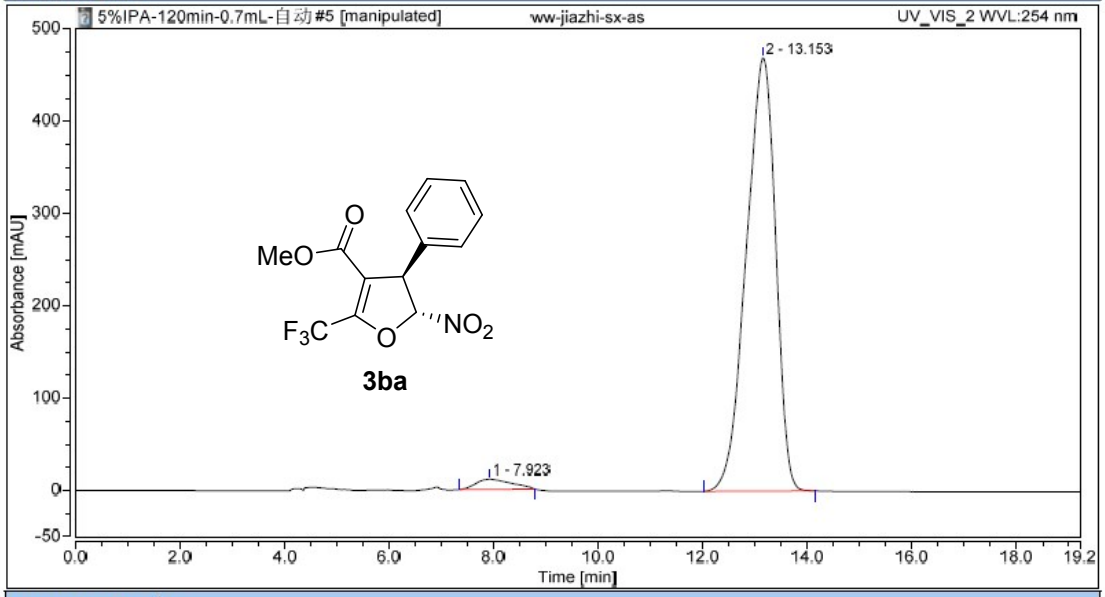
Chromatogram



Integration Results

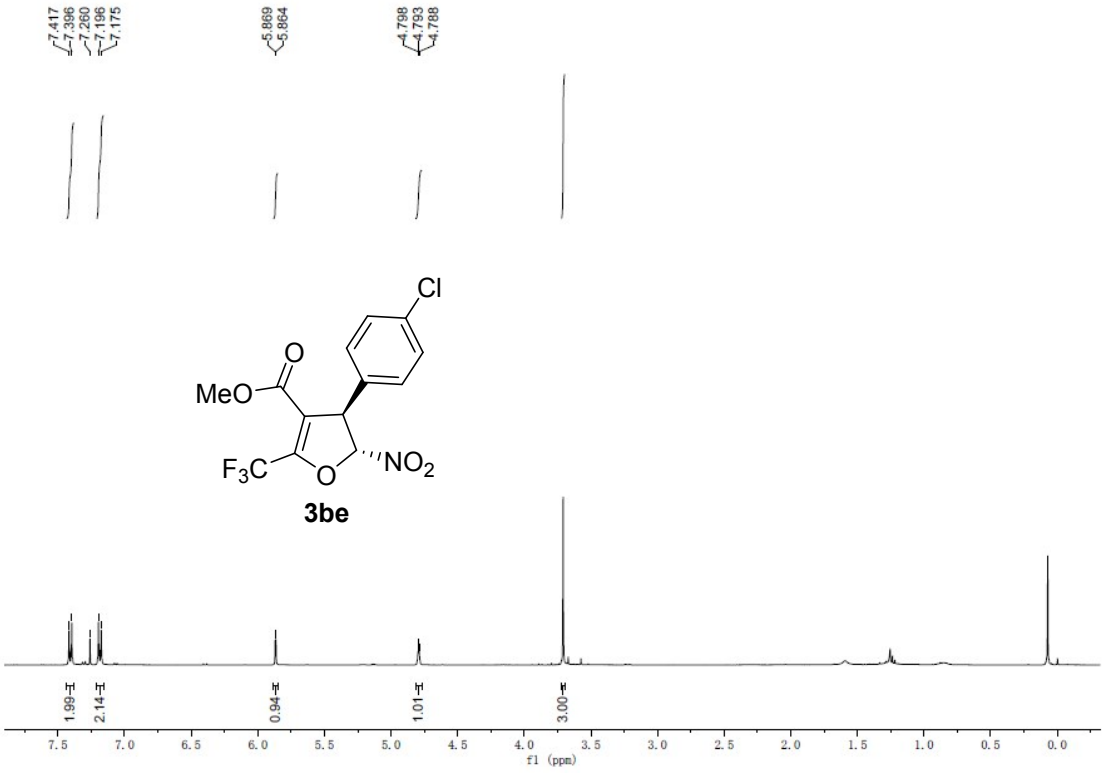
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		7.993	278.103	302.919	50.34	41.74	n.a.
2		13.357	274.293	422.808	49.66	58.26	n.a.
Total:			**552.396**	**725.727**	**100.00**	**100.00**	

Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		7.923	8.596	10.813	2.74	2.25	n.a.
2		13.153	305.646	469.551	97.26	97.75	n.a.
Total:			**314.242**	**480.363**	**100.00**	**100.00**	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4.793
4.788
Cl
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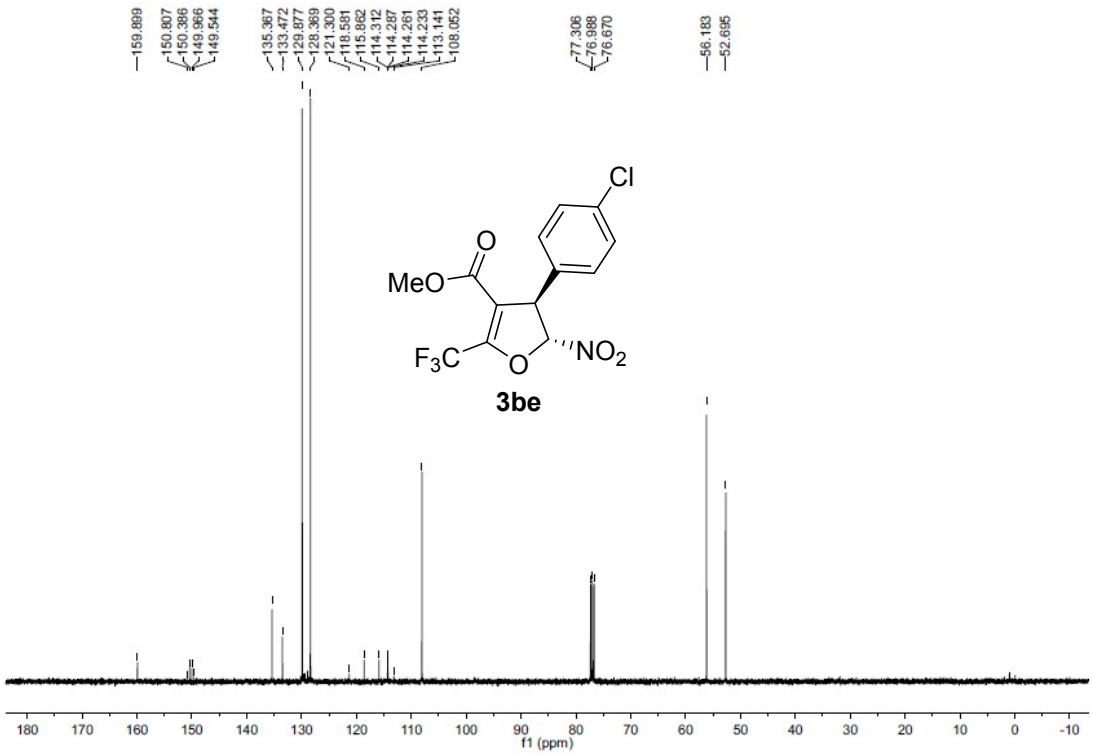
MeO
F3C
O
NO2
3be
1.99
2.14
0.94
1.01
3.00
f1 (ppm)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114.287
114.261
114.233
113.141
108.052
77.306
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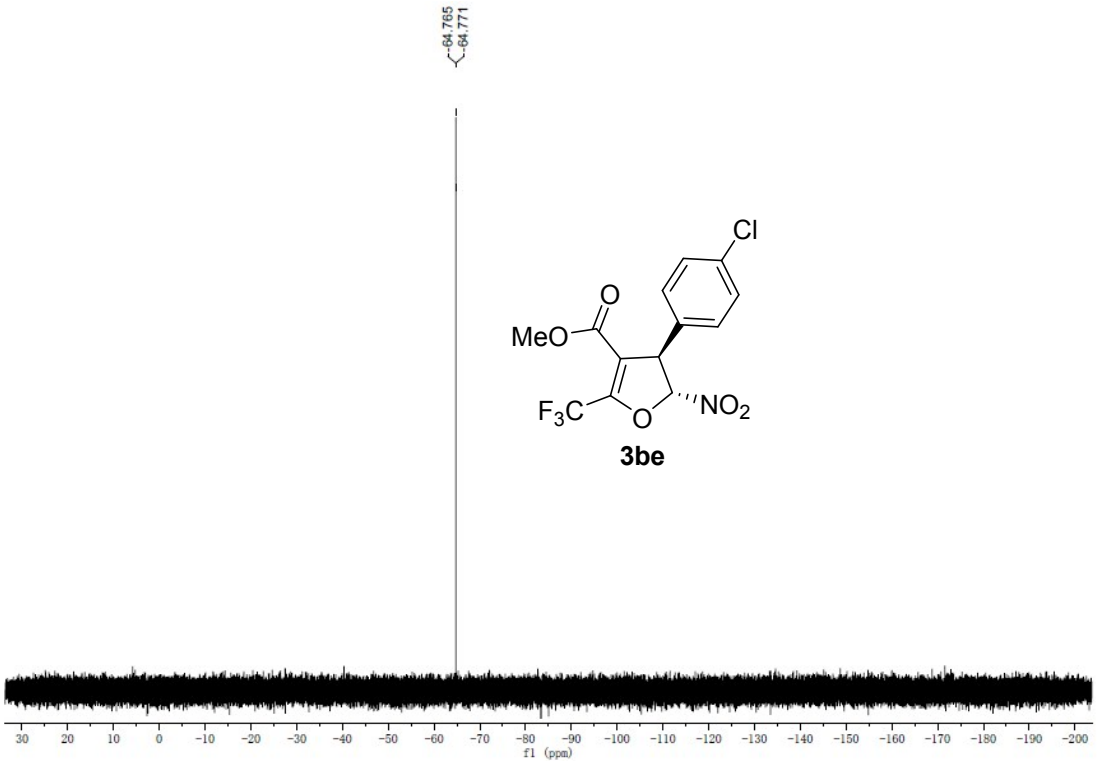
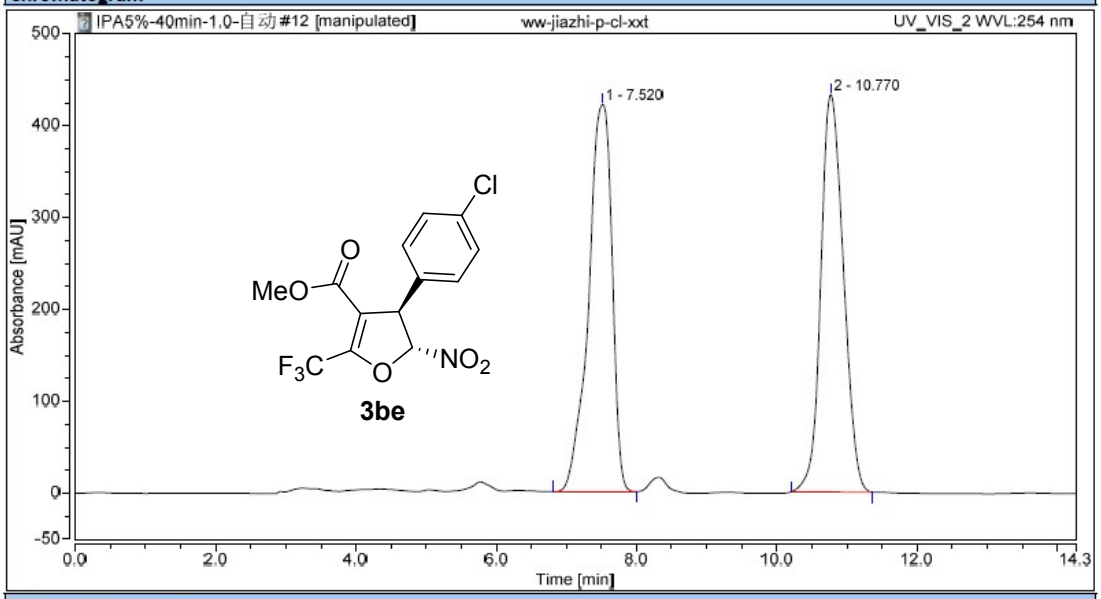
76.670
56.183
52.695
Cl
O
MeO
F3C
O
NO2
3be
f1 (ppm)



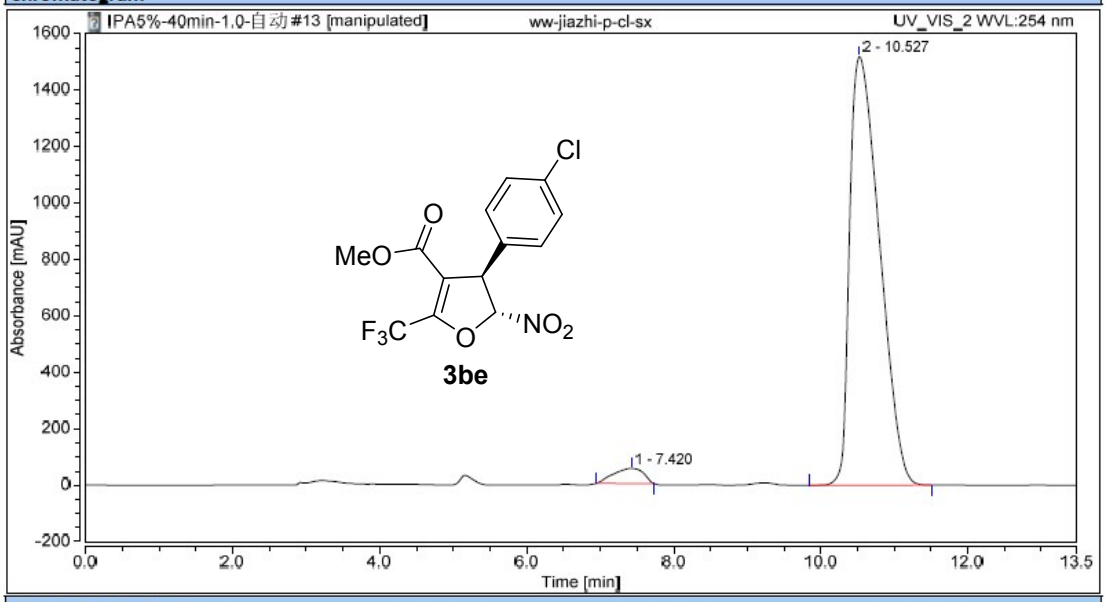
Chromatogram



Integration Results

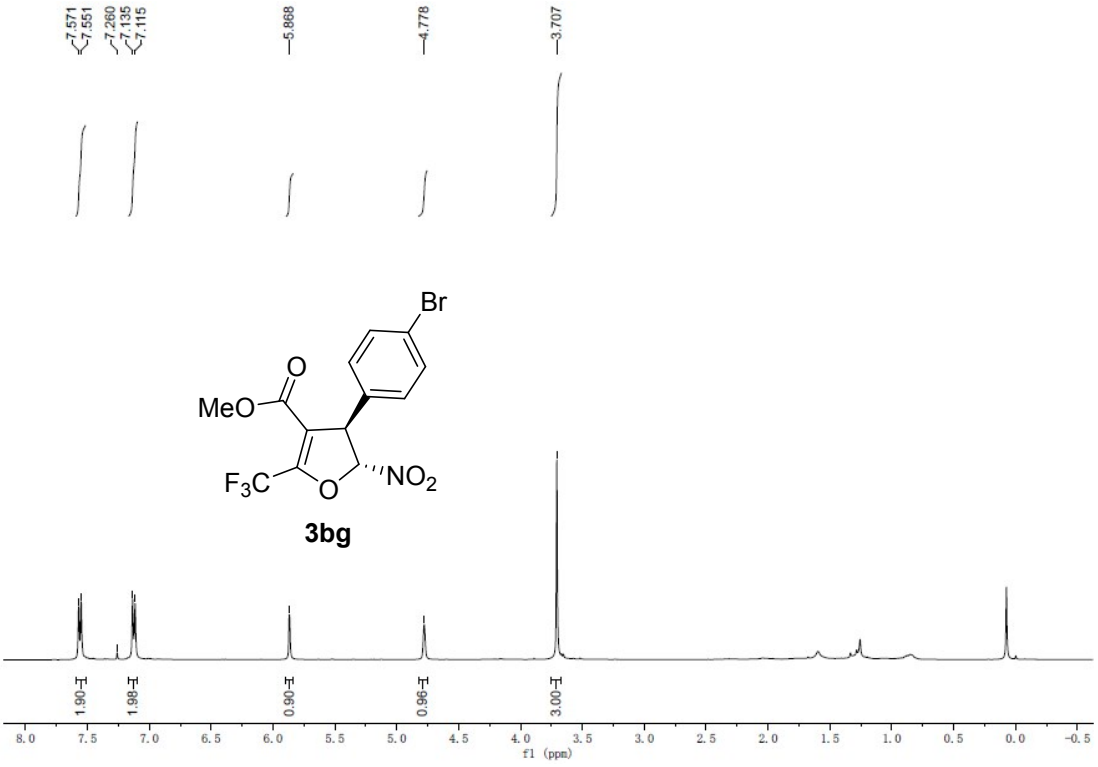
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		7.520	163.440	421.595	50.32	49.35	n.a.
2		10.770	161.392	432.773	49.68	50.65	n.a.
Total:			**324.832**	**854.368**	**100.00**	**100.00**	

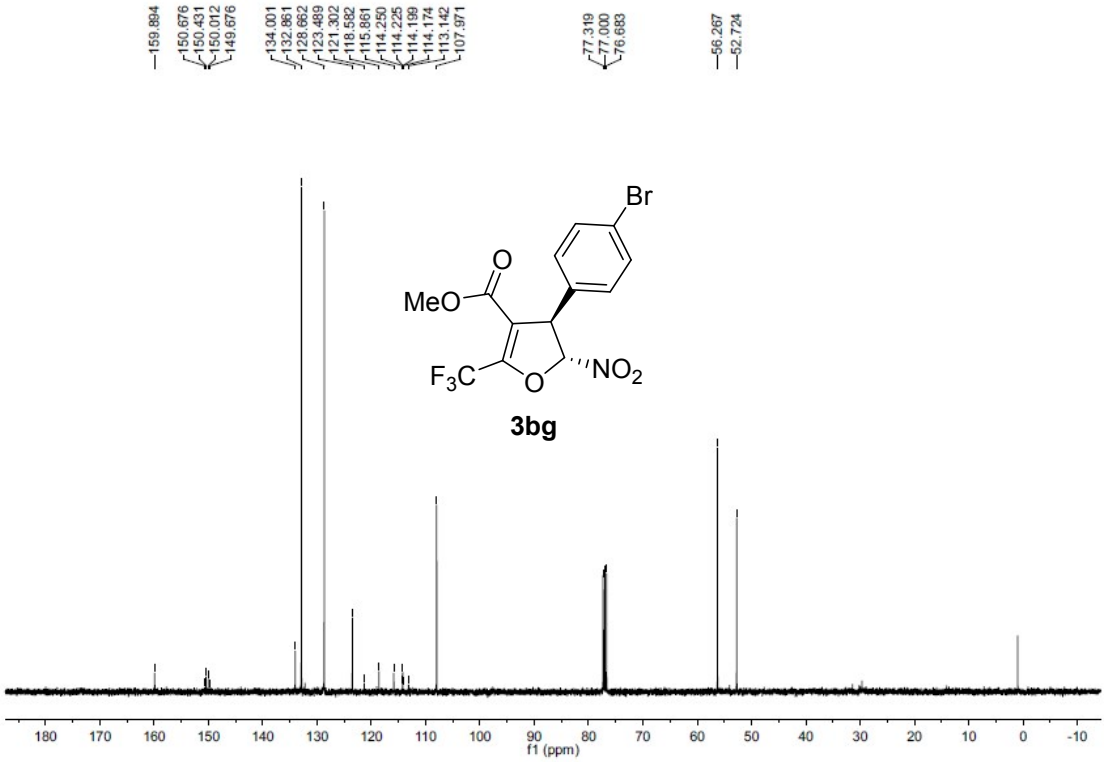
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		7.420	25.267	53.460	3.42	3.40	n.a.
2		10.527	713.875	1519.272	96.58	96.60	n.a.
Total:			**739.142**	**1572.733**	**100.00**	**100.00**	

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121.302
118.582
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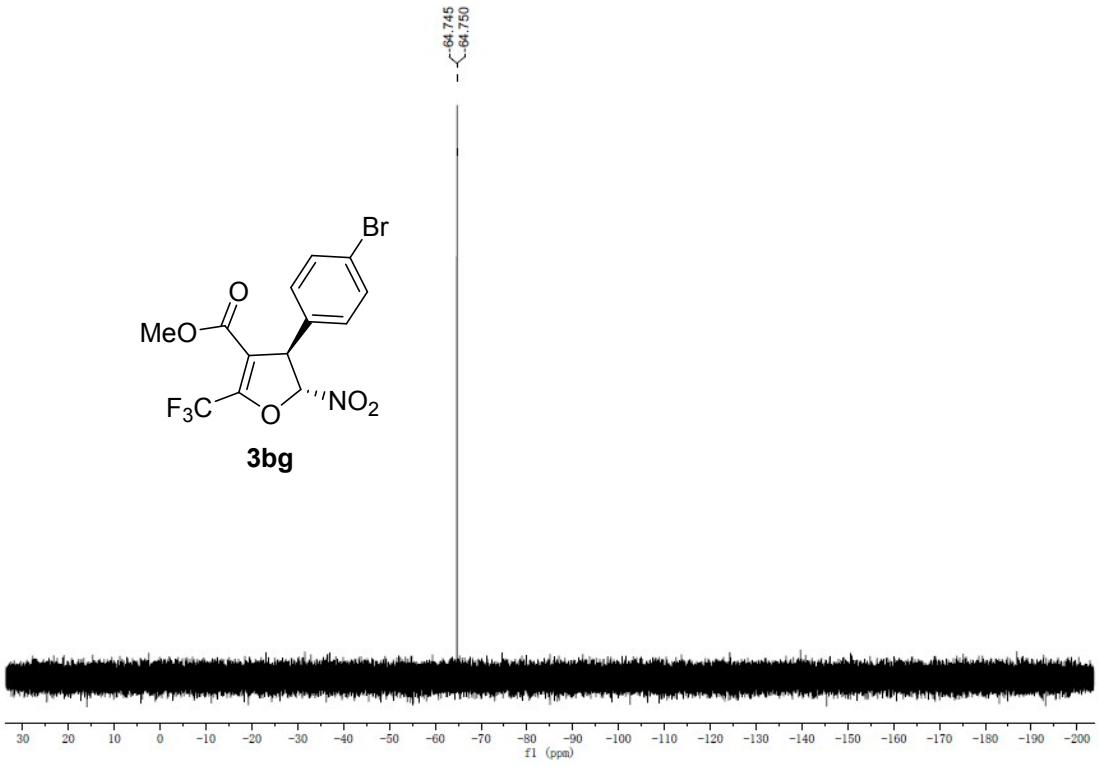
114.250
114.225
114.199
114.174
113.142
107.971
77.319
77.000
76.683
56.267
52.724
Br
O
MeO
F3C
O
NO2
3bg
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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O
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F3C
O
NO2
3bg
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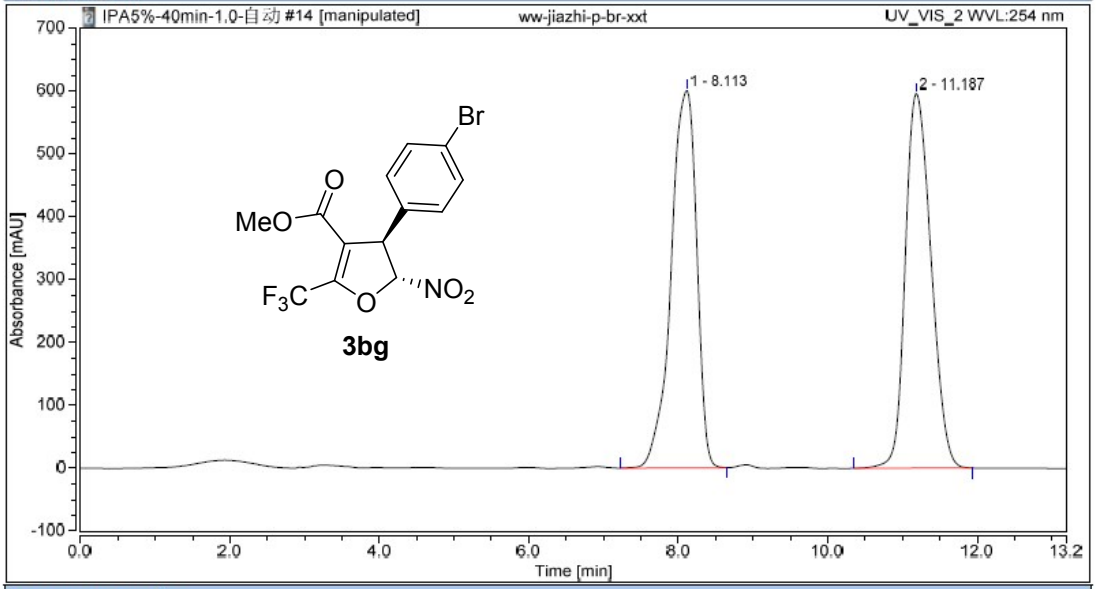
f1 (ppm)

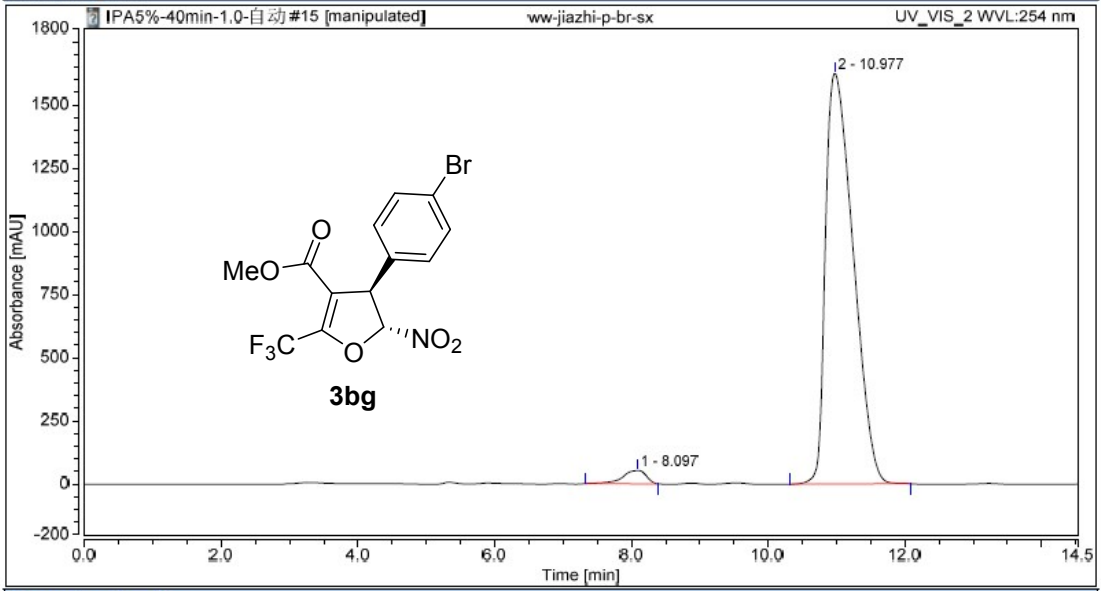
Chromatogram



Integration Results

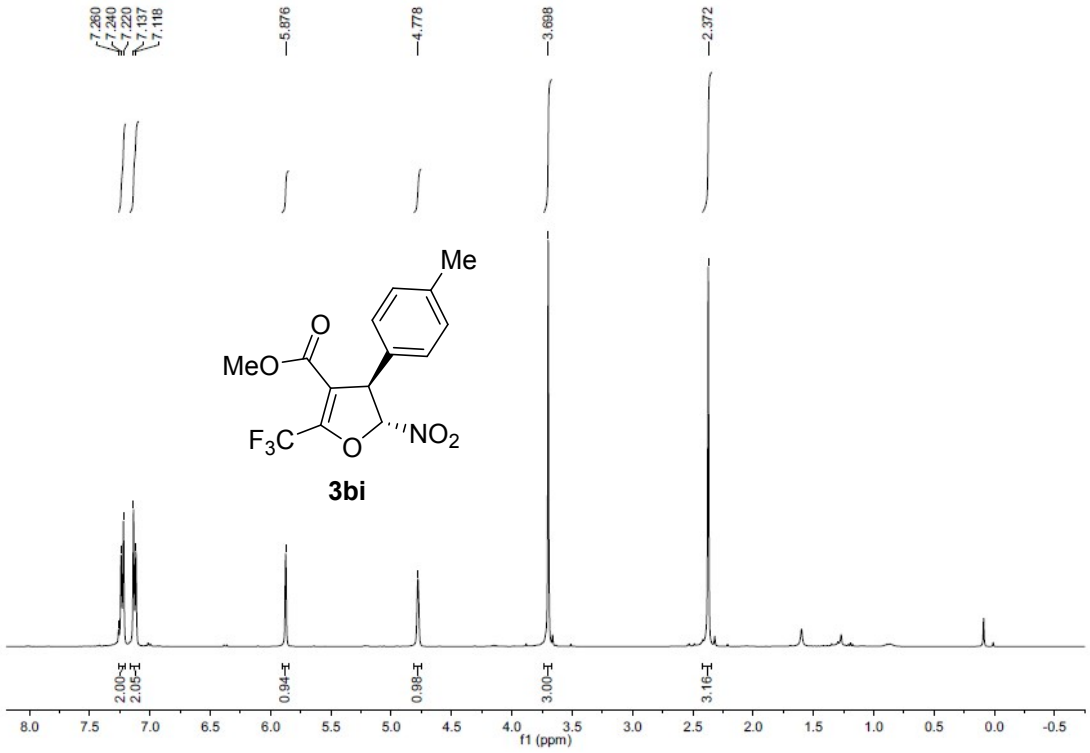
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		8.113	237.491	600.662	49.93	50.18	n.a.
2		11.187	238.135	596.347	50.07	49.82	n.a.
Total:			**475.625**	**1197.009**	**100.00**	**100.00**	

Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		8.097	21.034	52.401	2.69	3.12	n.a.
2		10.977	761.626	1624.592	97.31	96.88	n.a.
Total:			**782.660**	**1676.993**	**100.00**	**100.00**	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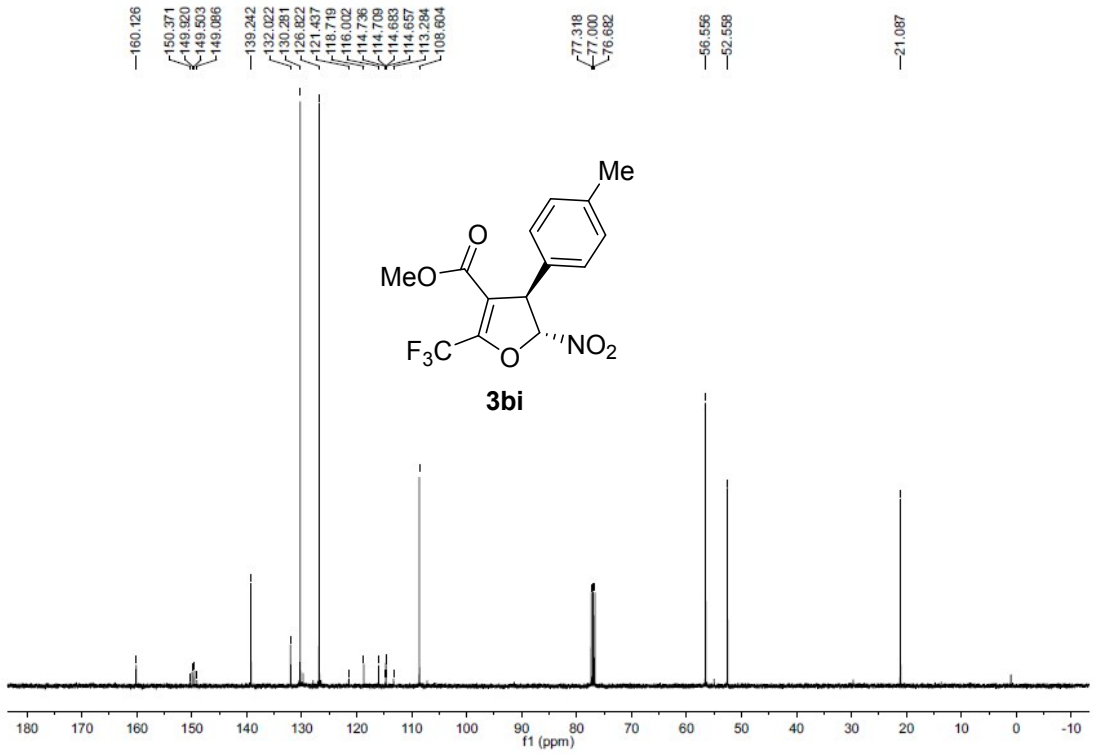
7.240
7.220
7.137
7.118
5.876
4.778
3.698
2.372
Me
O
MeO
F3C
O
NO2
3bi
2.00
2.05
0.94
0.98
3.00
3.16
f1 (ppm)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149.503
149.086
139.242
132.022
130.281
126.822
121.437
118.719
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114.736
114.709
114.683
114.657
113.284
108.604
77.318
77.000
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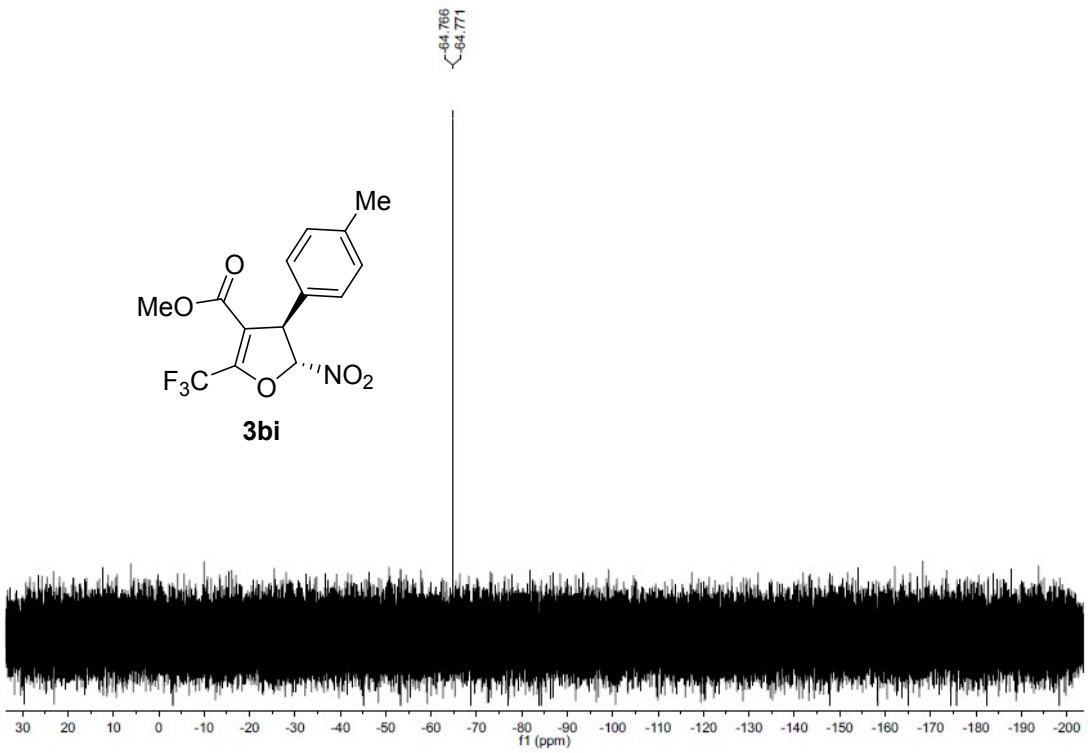
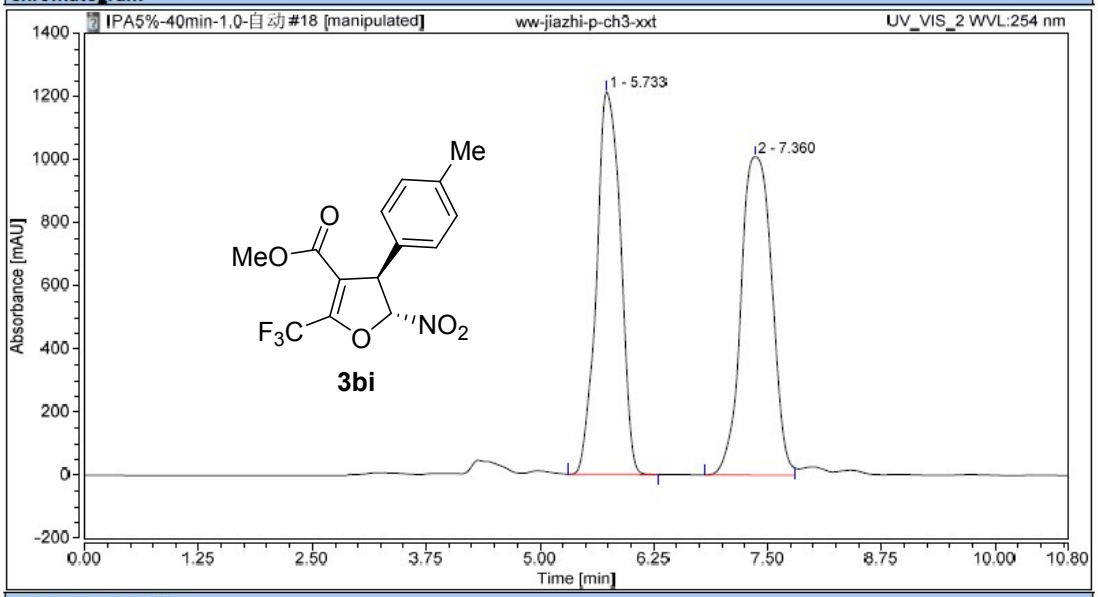
56.556
52.558
21.087
Me
O
MeO
F3C
O
NO2
3bi
f1 (ppm)



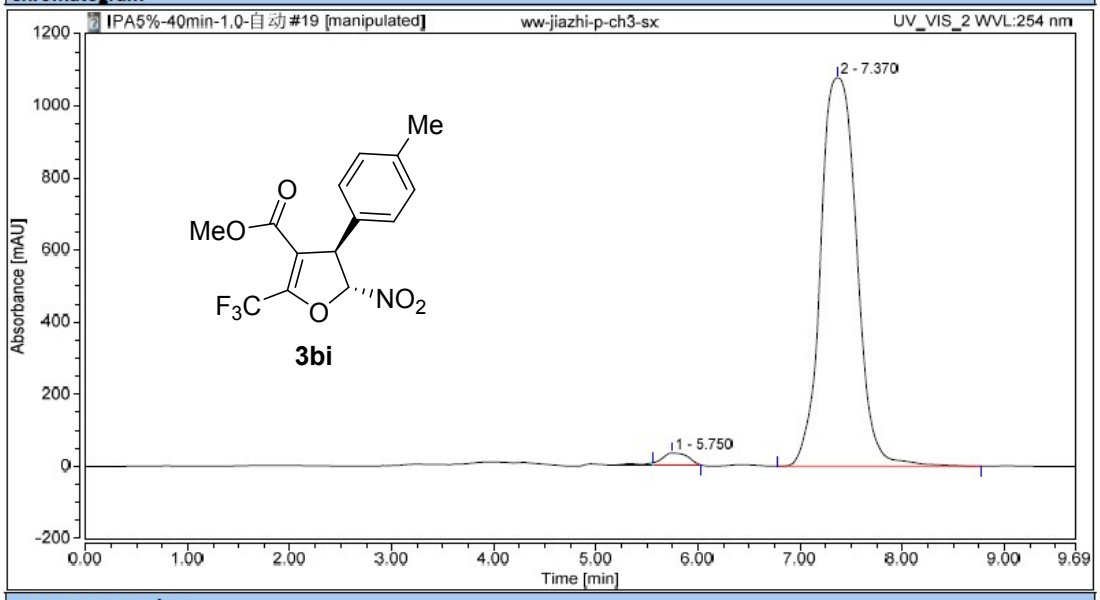
Chromatogram



Integration Results

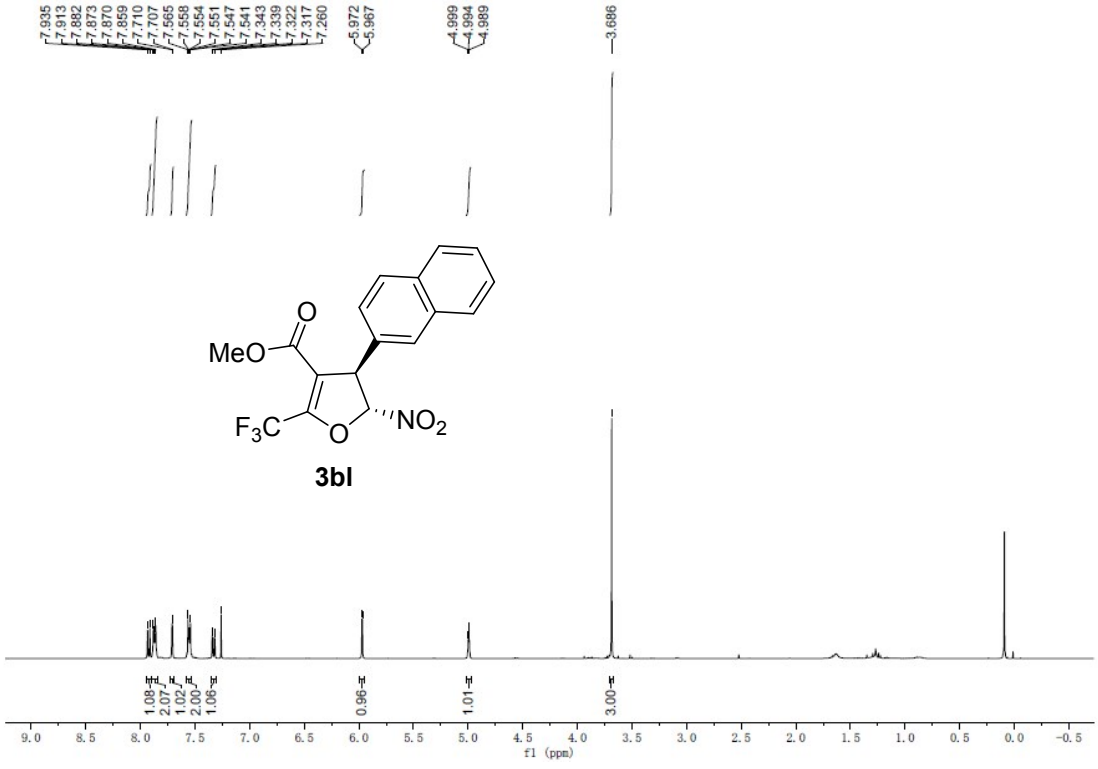
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.733	371.444	1212.667	48.36	54.58	n.a.
2		7.360	396.699	1009.200	51.64	45.42	n.a.
Total:			**768.143**	**2221.867**	**100.00**	**100.00**	

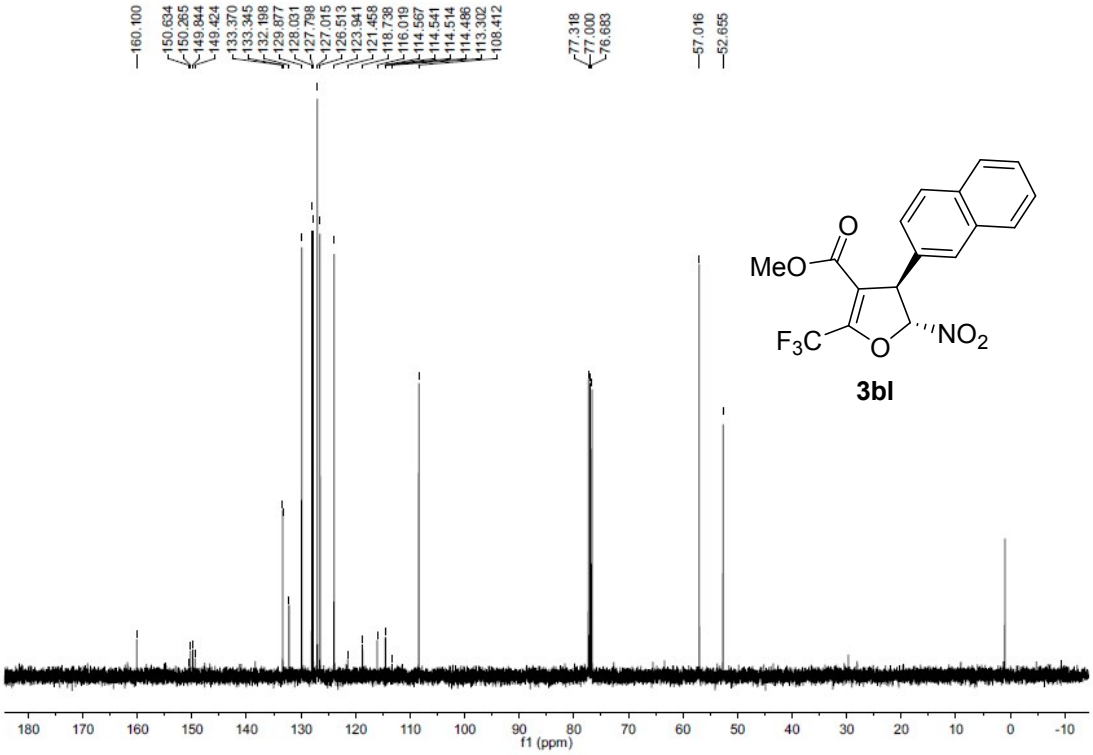
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.750	9.799	33.821	2.18	3.04	n.a.
2		7.370	439.531	1077.424	97.82	96.96	n.a.
Total:			**449.329**	**1111.245**	**100.00**	**100.00**	




160.100
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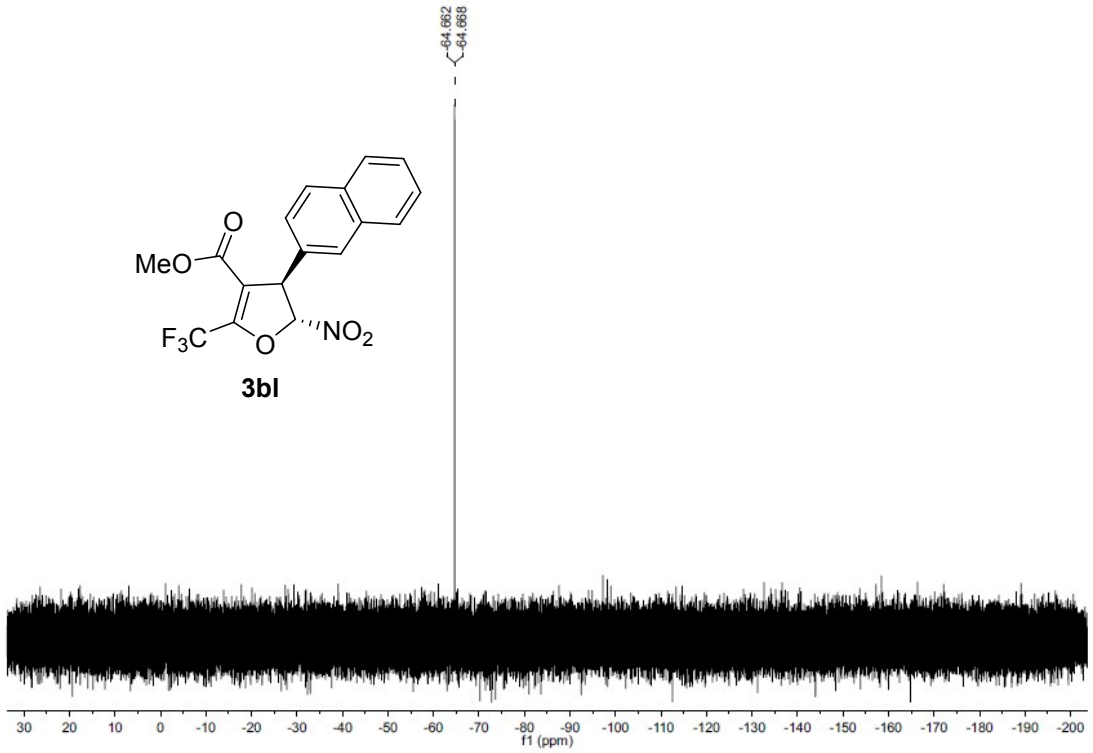
150.265
149.844
149.424
133.370
133.345
132.198
129.877
128.031
127.798
127.015
126.513
123.941
121.458
118.738
116.019
114.567
114.541
114.514
114.486
113.302
108.412
77.318
77.000
76.683
57.016
52.655
MeO
O
F3C
O
NO2
3bl
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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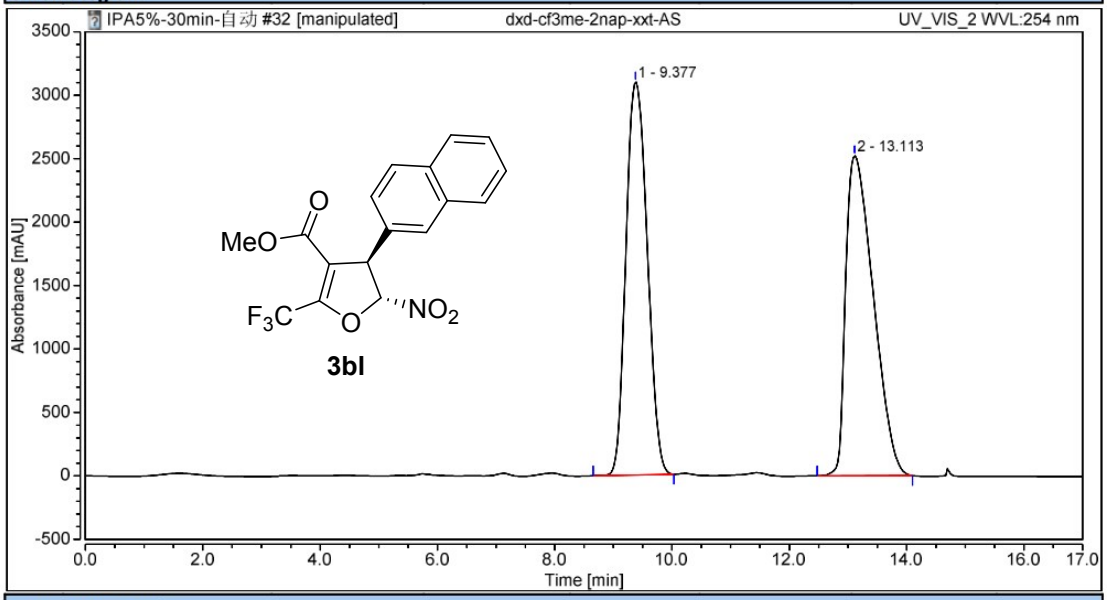
64.668
MeO
O
F3C
O
NO2
3bl
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)

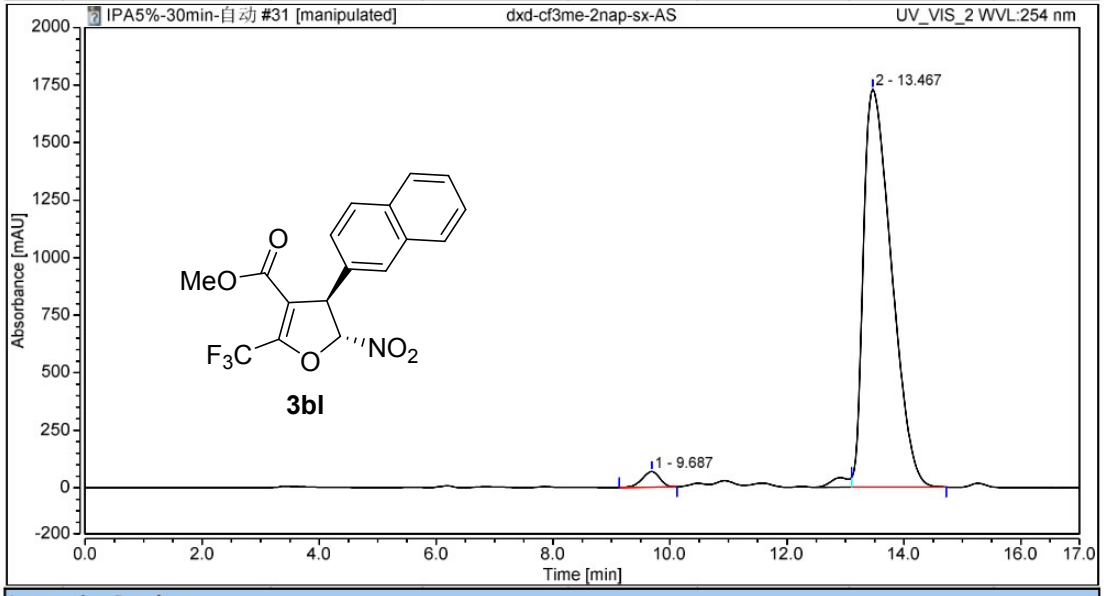
Chromatogram



Integration Results

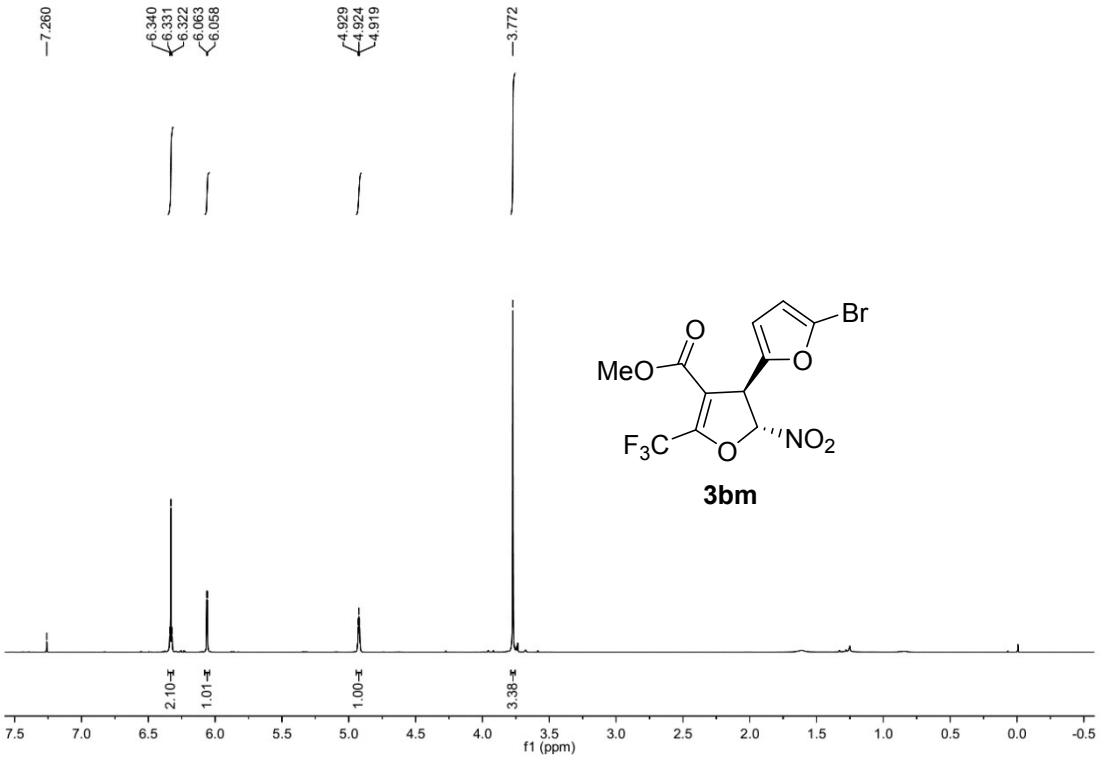
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		9.377	1305.755	3098.795	48.70	55.13	n.a.
2		13.113	1375.333	2522.337	51.30	44.87	n.a.
Total:			**2681.088**	**5621.133**	**100.00**	**100.00**	

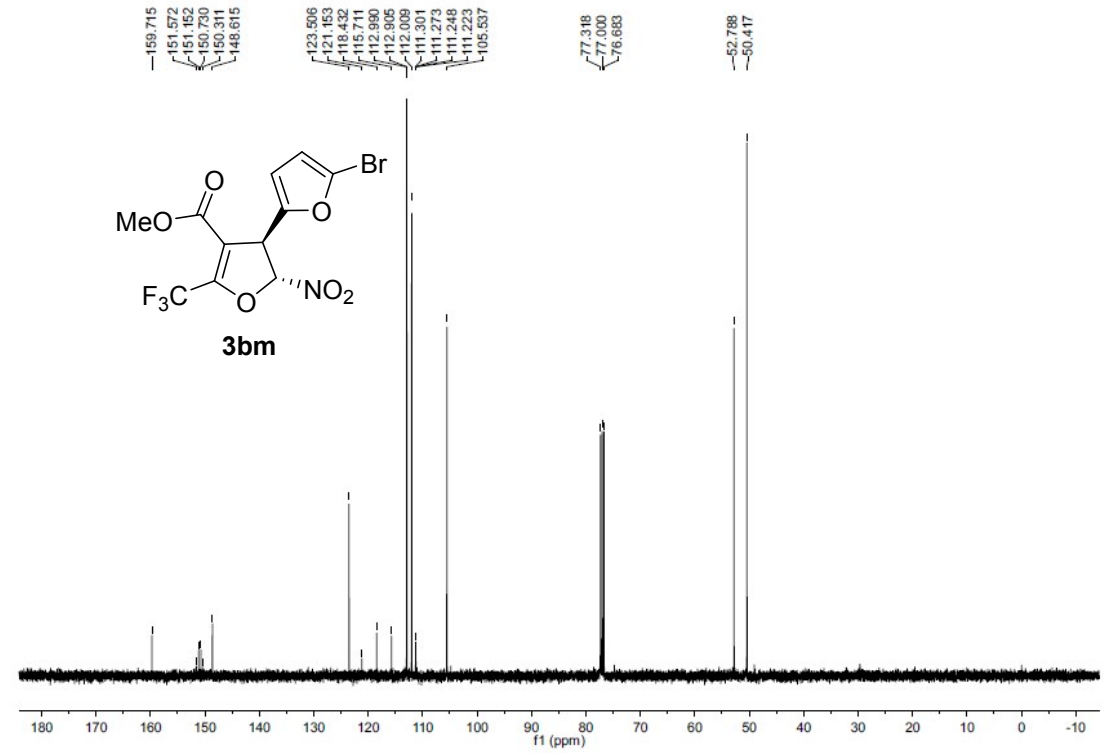
Chromatogram

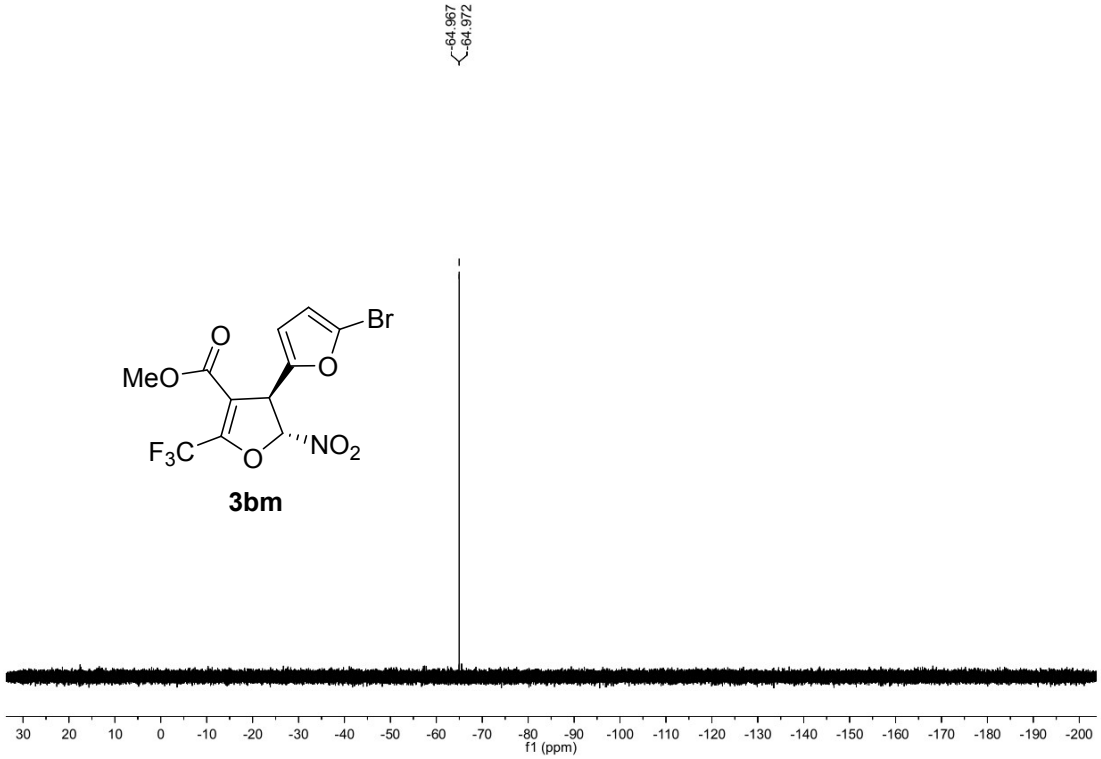


Integration Results

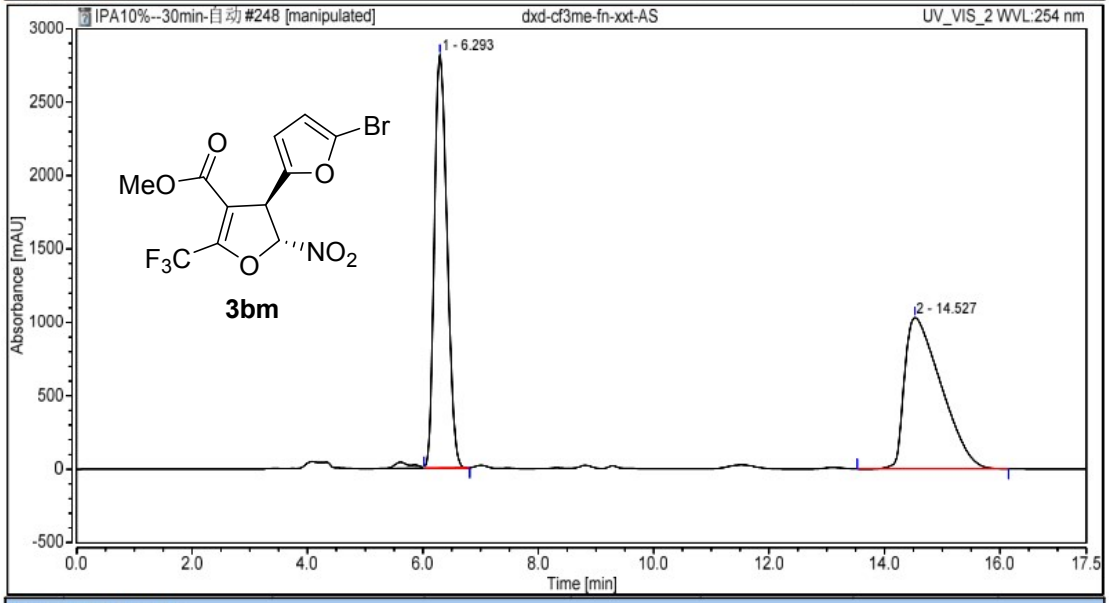
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		9.687	23.593	67.823	2.39	3.77	n.a.
2		13.467	962.592	1729.328	97.61	96.23	n.a.
Total:			**986.185**	**1797.151**	**100.00**	**100.00**	


7.260
6.340
6.331
6.322
6.063
6.058
4.929
4.924
4.919
3.772
Br
O
MeO
O
F3C
O
NO2
3bm
2.10
1.01
1.00
3.38
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
-0.5
f1 (ppm)


159.715
151.572
151.152
150.730
150.311
148.615
123.506
121.153
118.432
115.711
112.990
112.905
112.009
111.301
111.273
111.248
111.223
105.537
77.318
77.000
76.683
52.788
50.417
Br
O
MeO
O
F3C
O
NO2
3bm
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



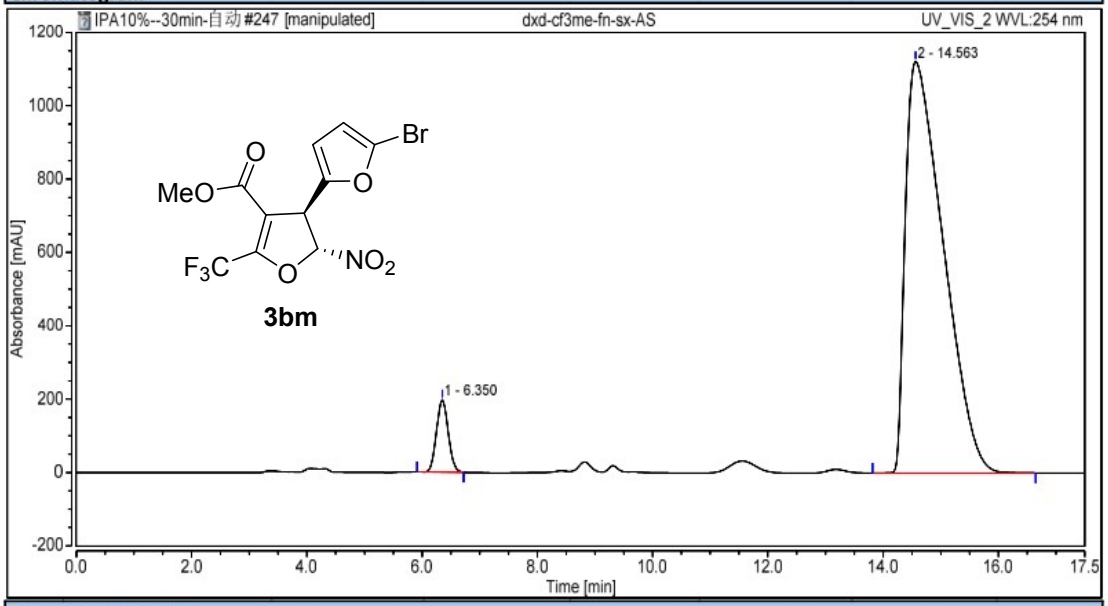
Chromatogram



Integration Results

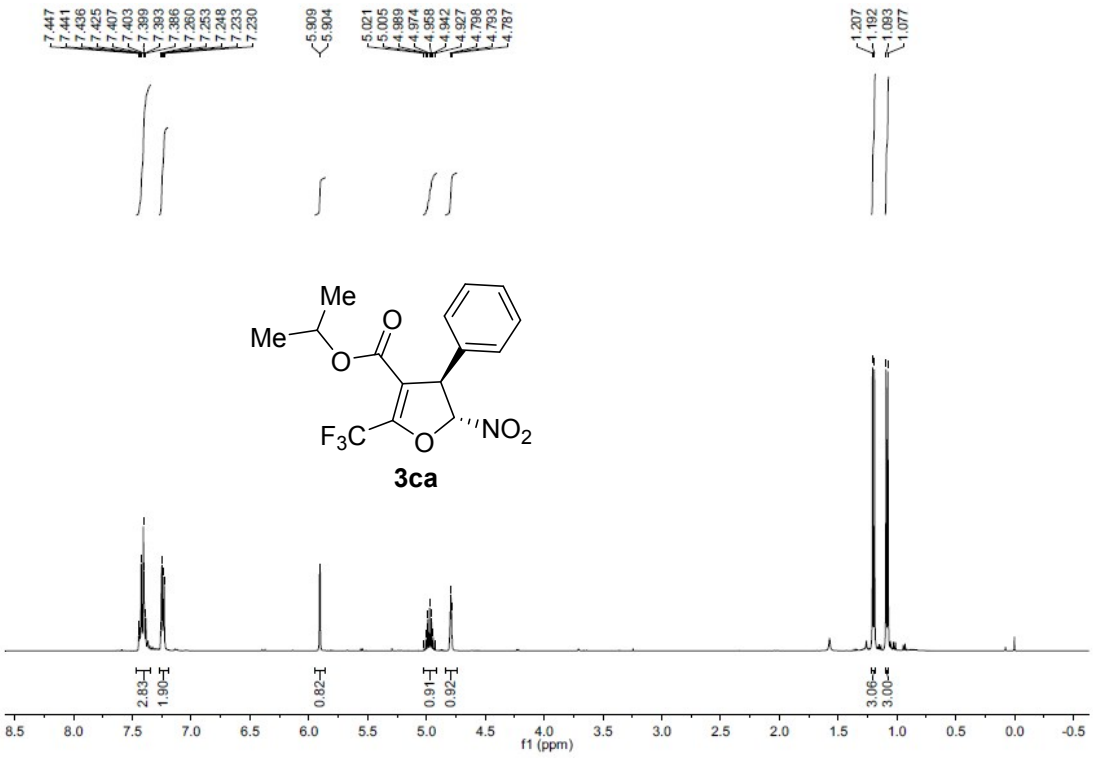
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		6.293	720.821	2815.334	48.81	73.21	n.a.
2		14.527	755.823	1030.213	51.19	26.79	n.a.
Total:			**1476.644**	**3845.547**	**100.00**	**100.00**	

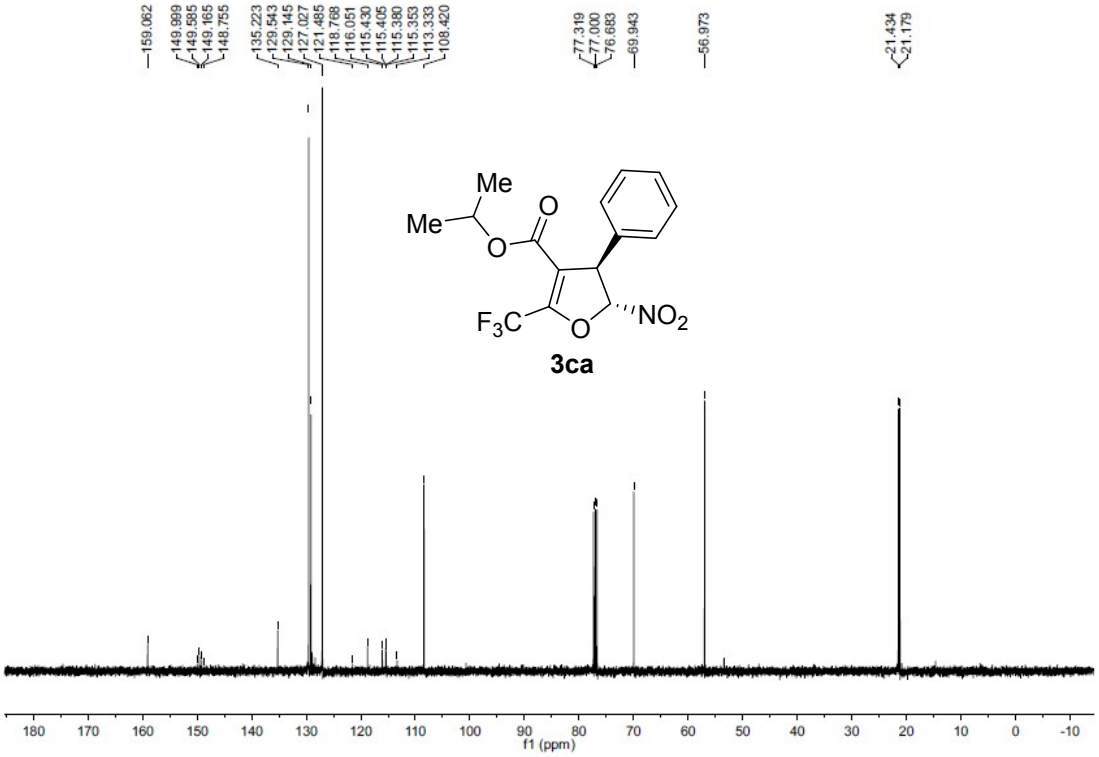
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		6.350	46.449	196.478	5.16	14.90	n.a.
2		14.563	854.129	1122.423	94.84	85.10	n.a.
Total:			**900.578**	**1318.901**	**100.00**	**100.00**	

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149.165
148.755
135.223
129.543
129.145
127.027
121.485
118.768
116.051
115.430
115.405
115.380
115.353
113.333
108.420
77.319
77.000
76.683
69.943
56.973
21.434
21.179
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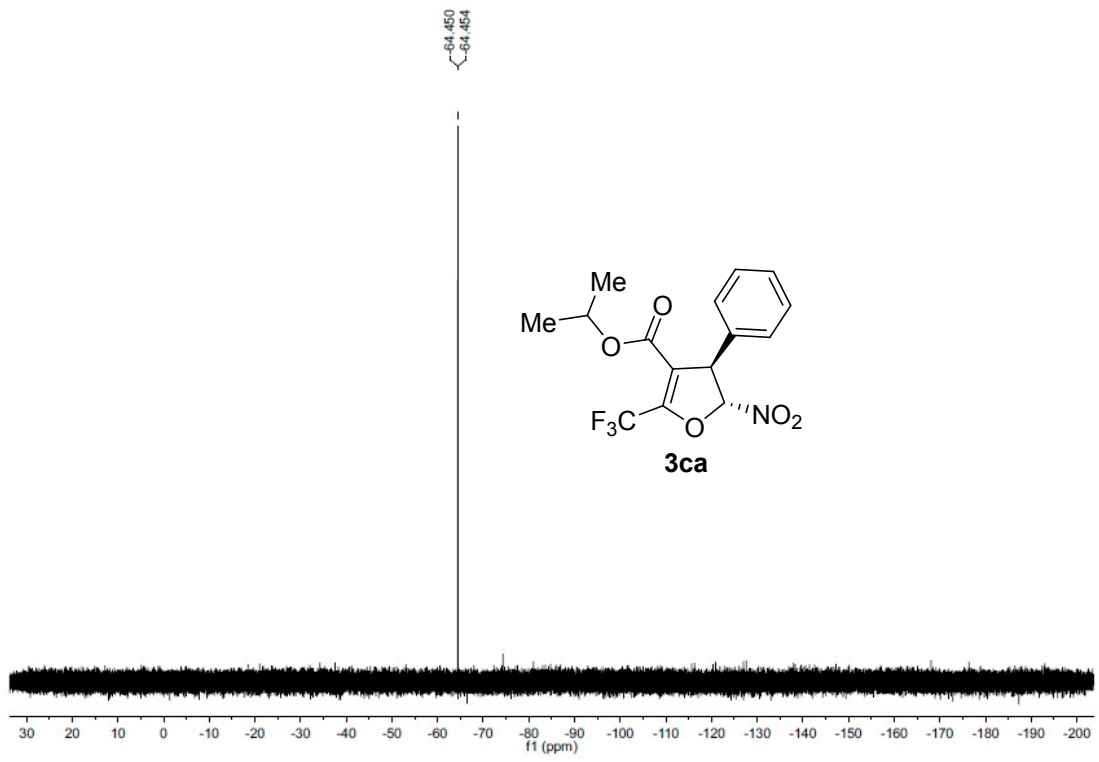
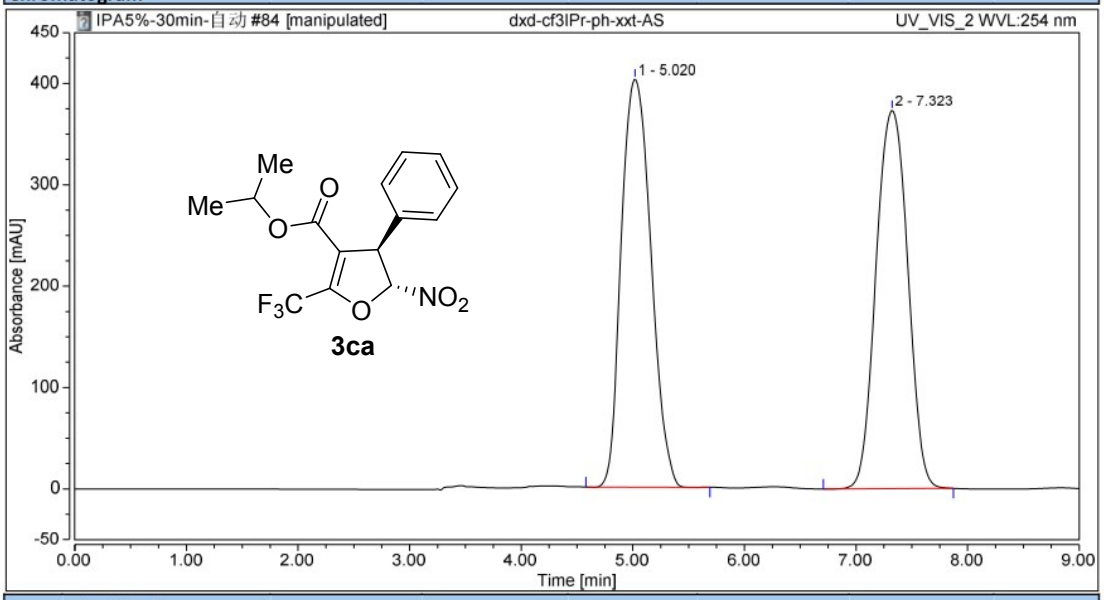
F3C
O
NO2
3ca
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


64.450
64.454
Me
Me
O
O
F3C
O
NO2
3ca
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)

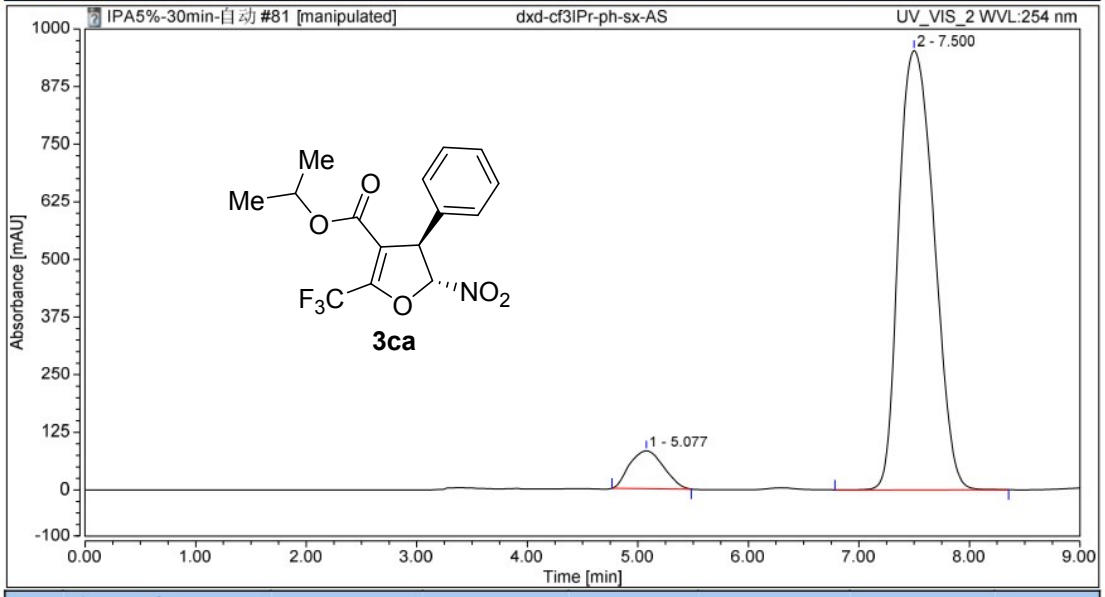
Chromatogram



Integration Results

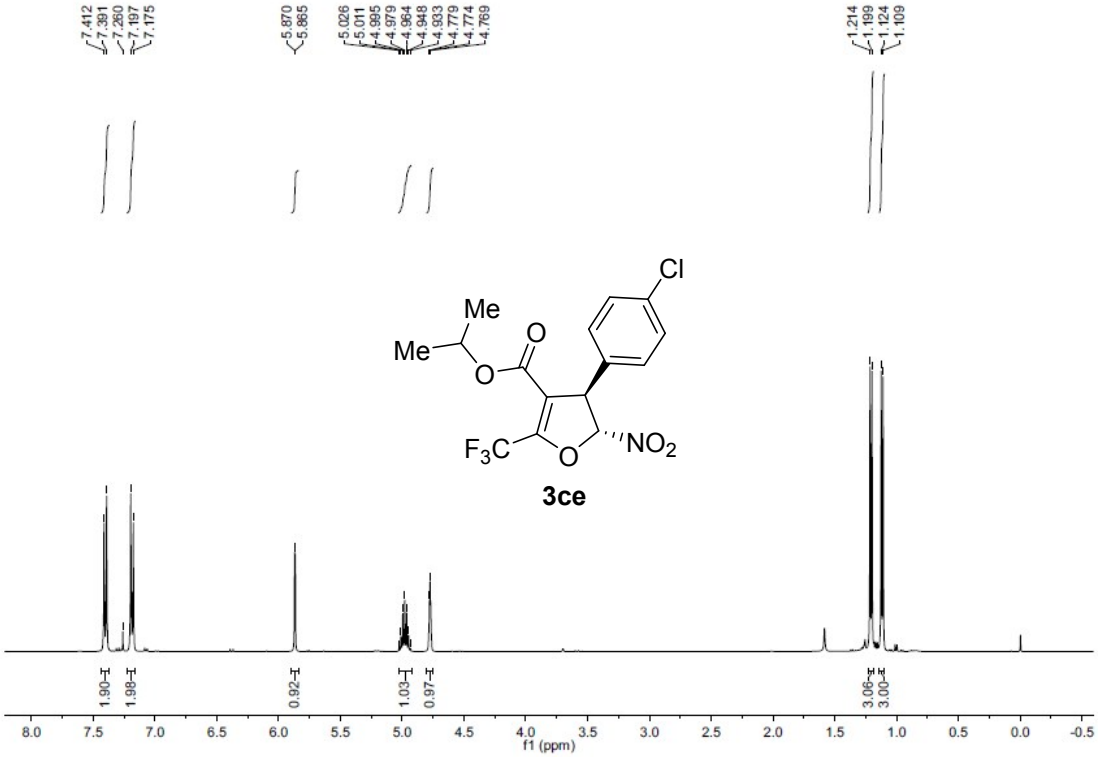
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.020	123.970	402.367	50.20	51.89	n.a.
2		7.323	122.981	373.084	49.80	48.11	n.a.
Total:			**246.951**	**775.451**	**100.00**	**100.00**	

Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.077	29.211	81.841	7.64	7.91	n.a.
2		7.500	353.100	953.400	92.36	92.09	n.a.
Total:			**382.310**	**1035.241**	**100.00**	**100.00**	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5.026
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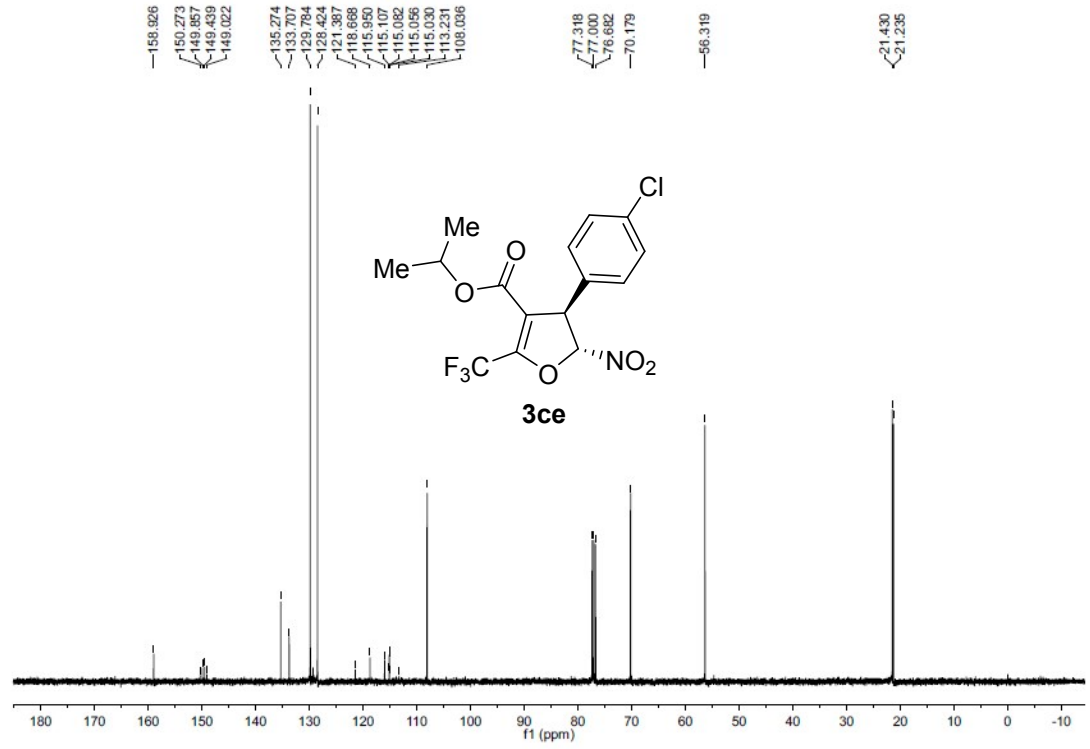
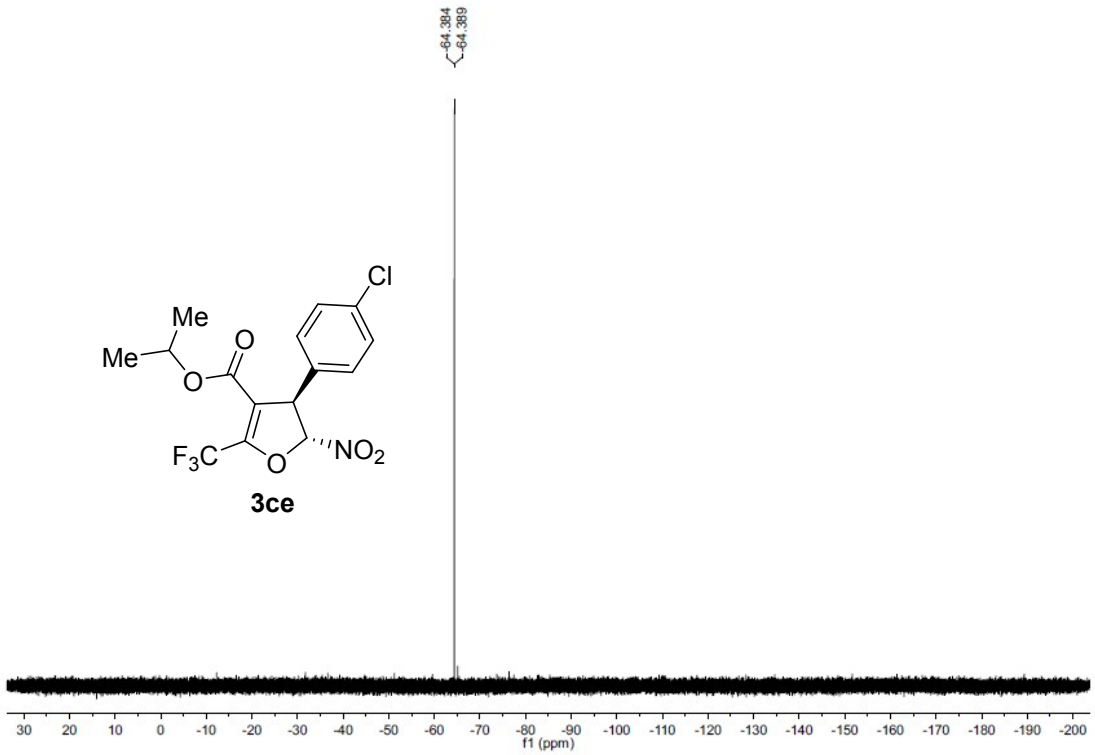
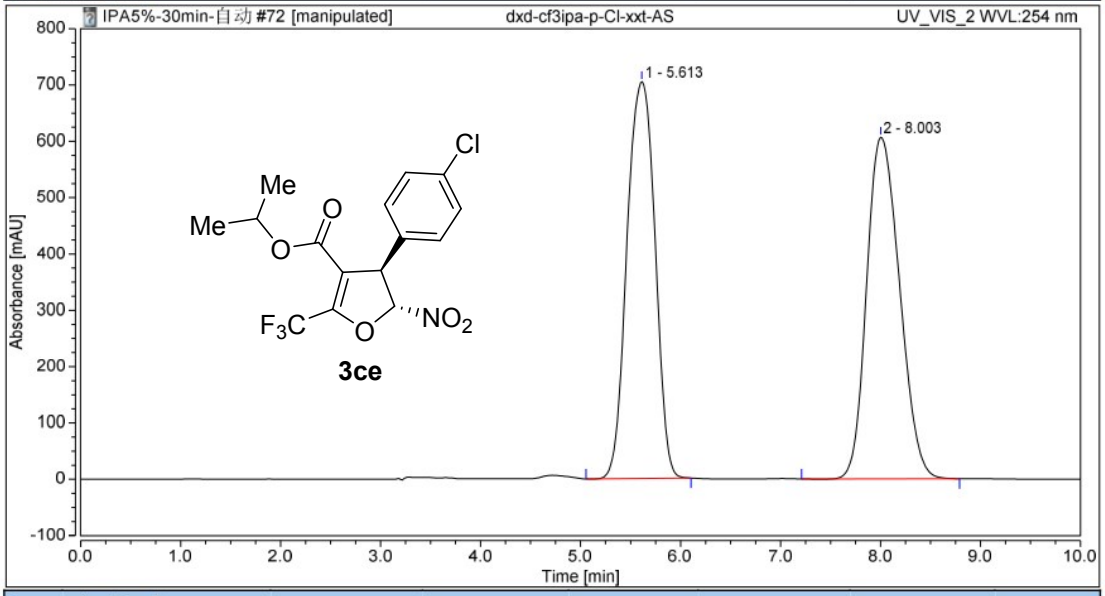
4.979
4.964
4.948
4.933
4.779
4.774
4.769
1.214
1.199
1.124
1.109
Cl
Me
Me
O
O
F3C
O
NO2
3ce
1.90
1.98
0.92
1.03
0.97
3.06
3.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


158.926
150.273
149.857
149.439
149.022
135.274
133.707
129.784
128.424
121.387
116.668
115.950
115.107
115.082
115.056
115.030
113.231
108.036
77.318
77.000
76.682
70.179
56.319
21.430
21.235
Cl
Me
Me
O
O
F3C
O
NO2
3ce
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

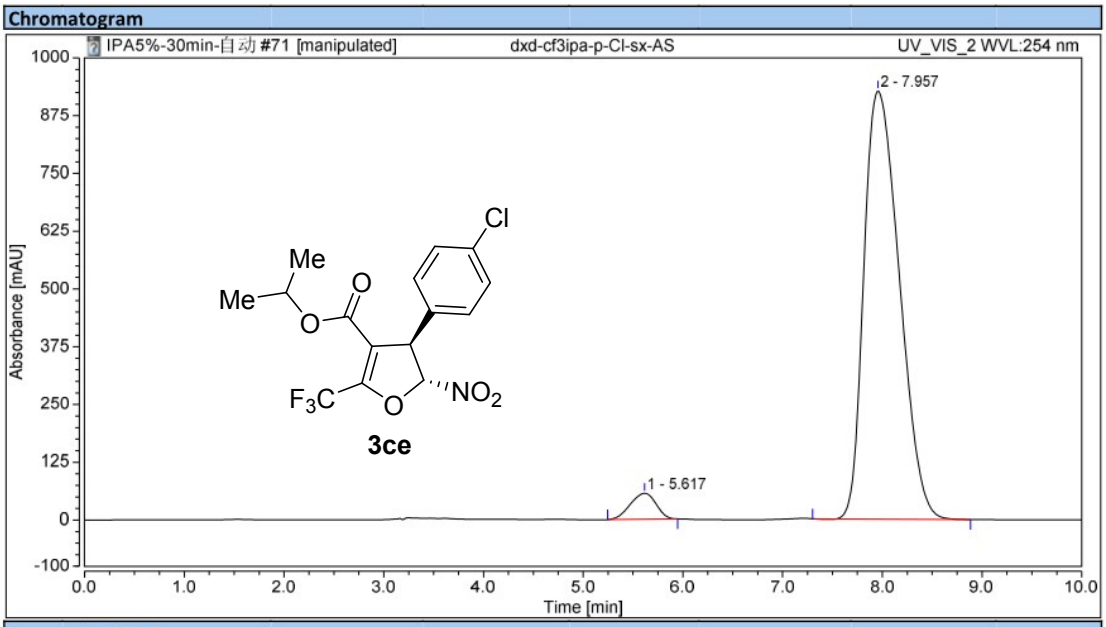


Chromatogram



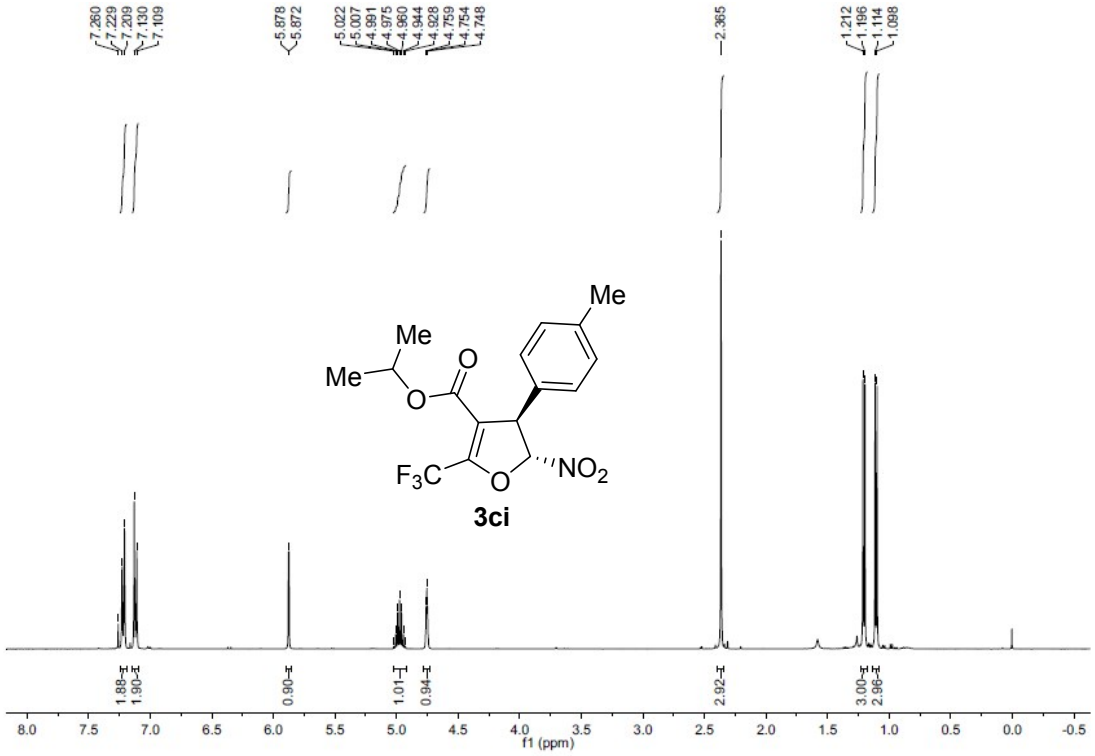
Integration Results

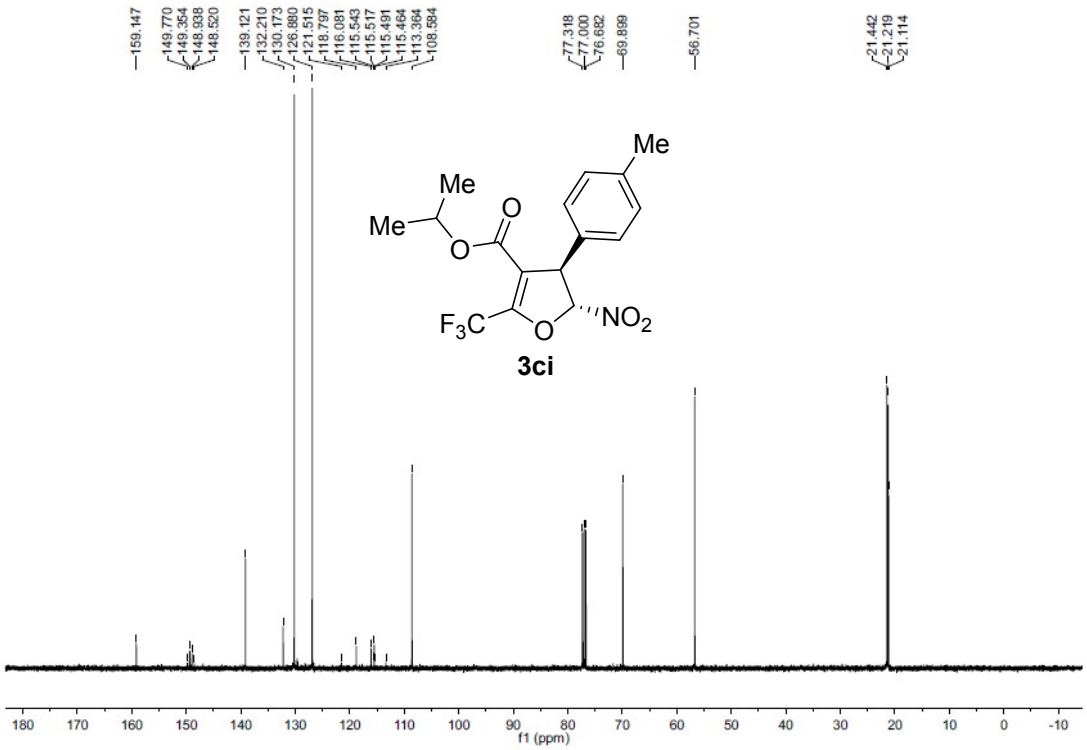
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.613	229.012	704.780	49.70	53.74	n.a.
2		8.003	231.771	606.787	50.30	46.26	n.a.
Total:			**460.783**	**1311.567**	**100.00**	**100.00**	



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.617	16.841	56.100	4.24	5.71	n.a.
2		7.957	380.663	926.472	95.76	94.29	n.a.
Total:			**397.504**	**982.572**	**100.00**	**100.00**	

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139.121
132.210
130.173
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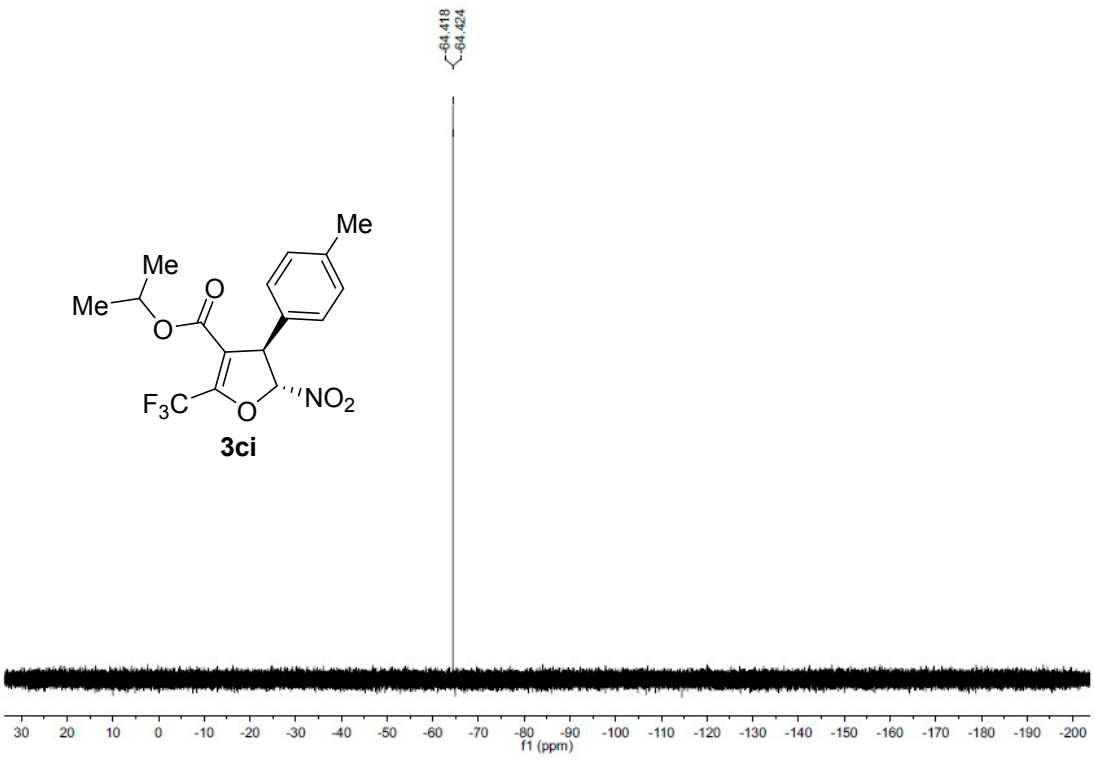
121.515
118.797
116.081
115.543
115.517
115.491
115.464
113.364
108.584
77.318
77.000
76.682
69.899
56.701
21.442
21.219
21.114
Me
Me
Me
O
O
F3C
O
NO2
3ci
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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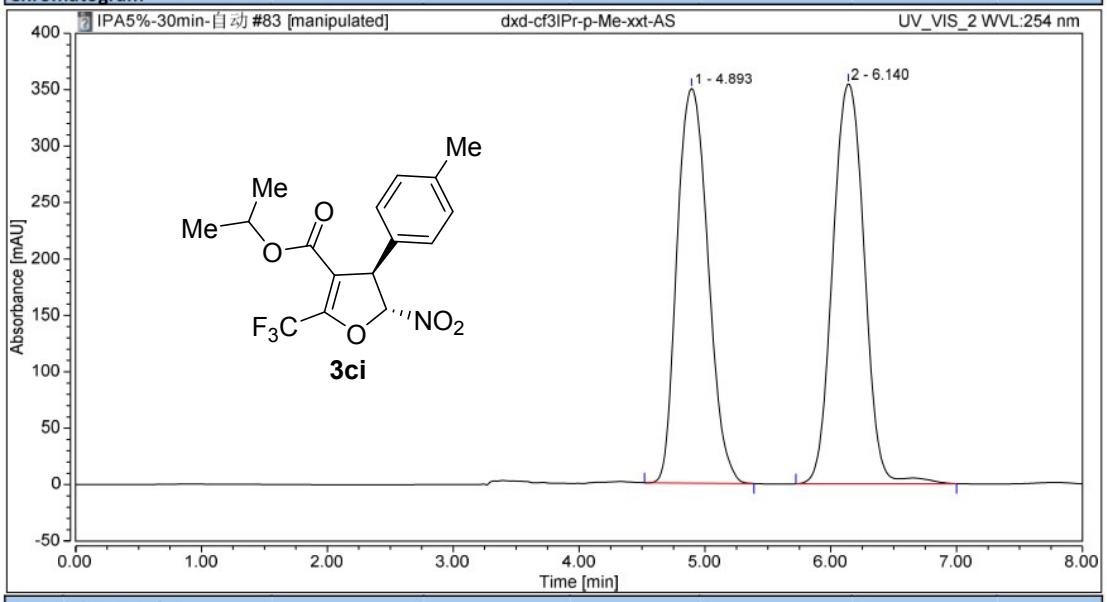
64.424
Me
Me
Me
O
O
F3C
O
NO2
3ci
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)

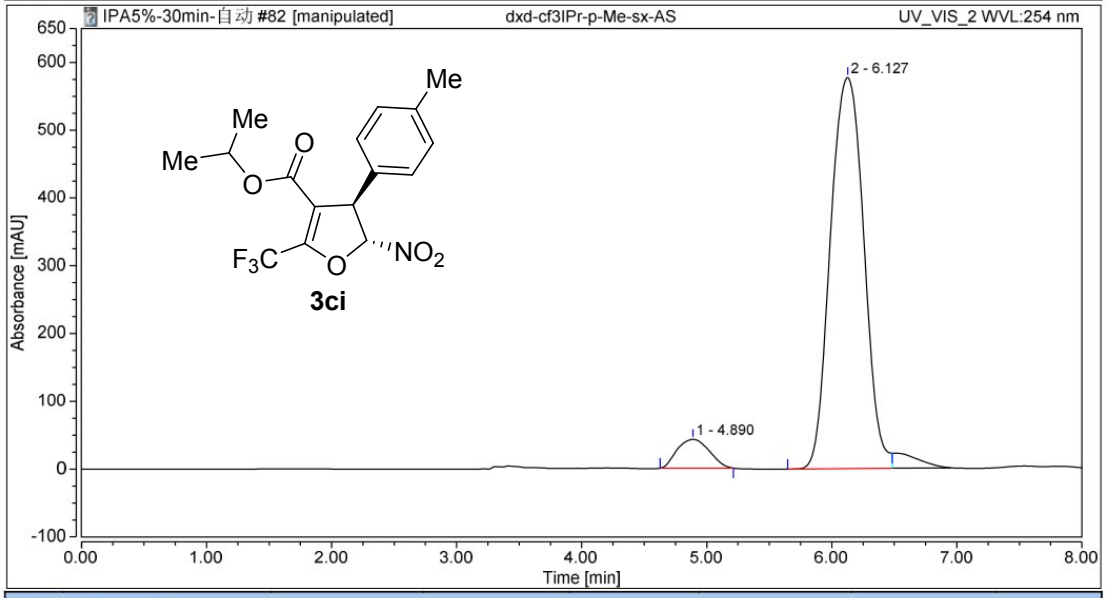
Chromatogram



Integration Results

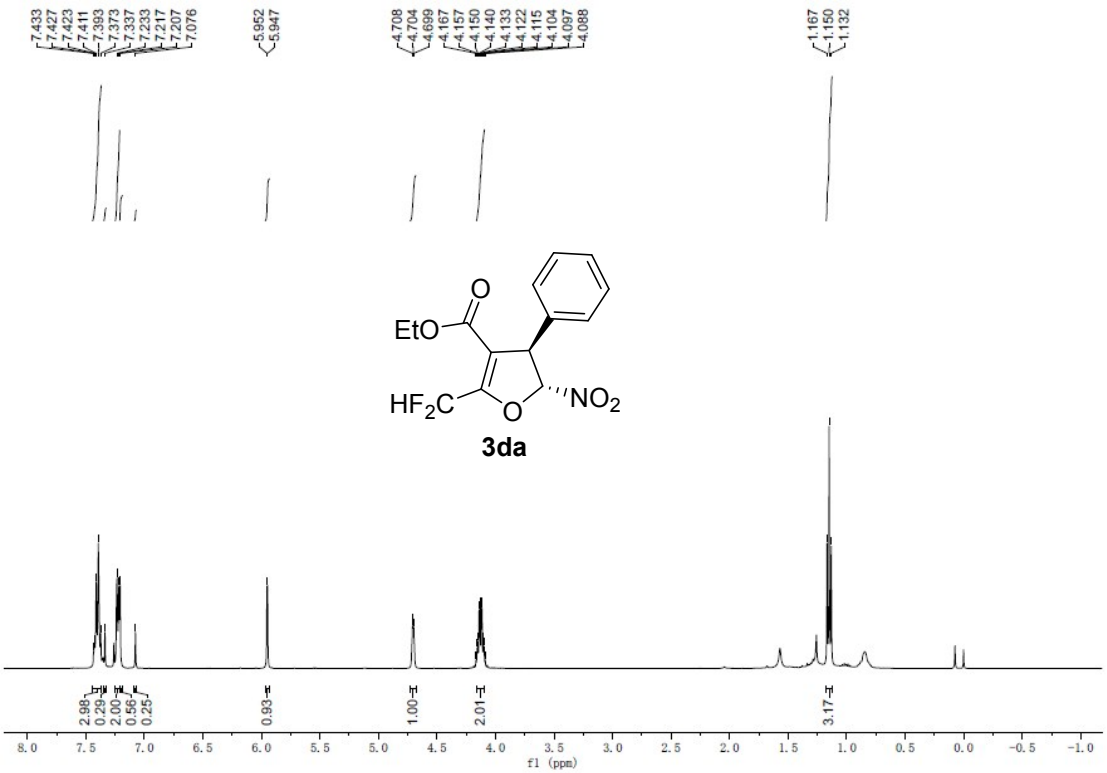
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		4.893	99.868	349.787	49.20	49.66	n.a.
2		6.140	103.105	354.541	50.80	50.34	n.a.
Total:			**202.973**	**704.328**	**100.00**	**100.00**	

Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		4.890	12.690	42.617	6.62	6.88	n.a.
2		6.127	178.949	577.255	93.38	93.12	n.a.
Total:			**191.639**	**619.872**	**100.00**	**100.00**	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4.704
4.699
4.167
4.157
4.150
4.140
4.133
4.122
4.115
4.104
4.097
4.088
1.167
1.150
1.132
O
EtO
HF2C
O
NO2
3da
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0.29
2.00
0.56
0.25
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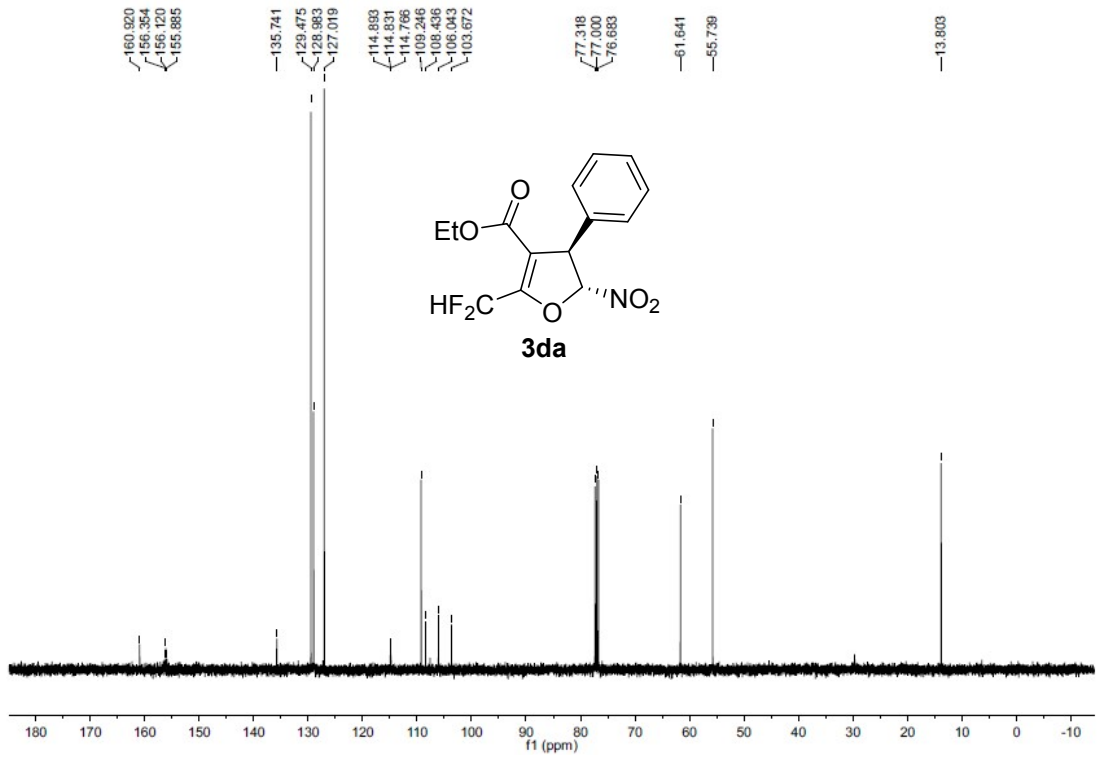
1.00
2.01
3.17
f1 (ppm)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127.019
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114.831
114.766
109.246
108.436
106.043
103.672
77.318
77.000
76.683
61.641
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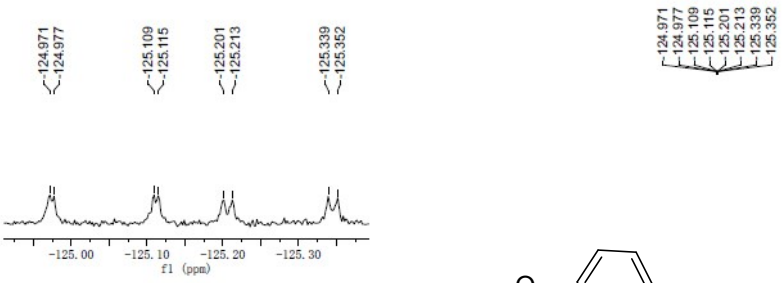
O
EtO
HF2C
O
NO2
3da
f1 (ppm)



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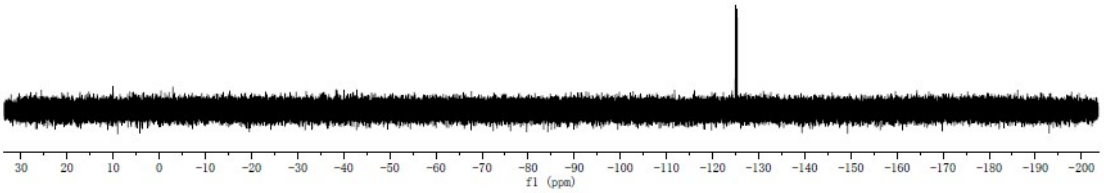
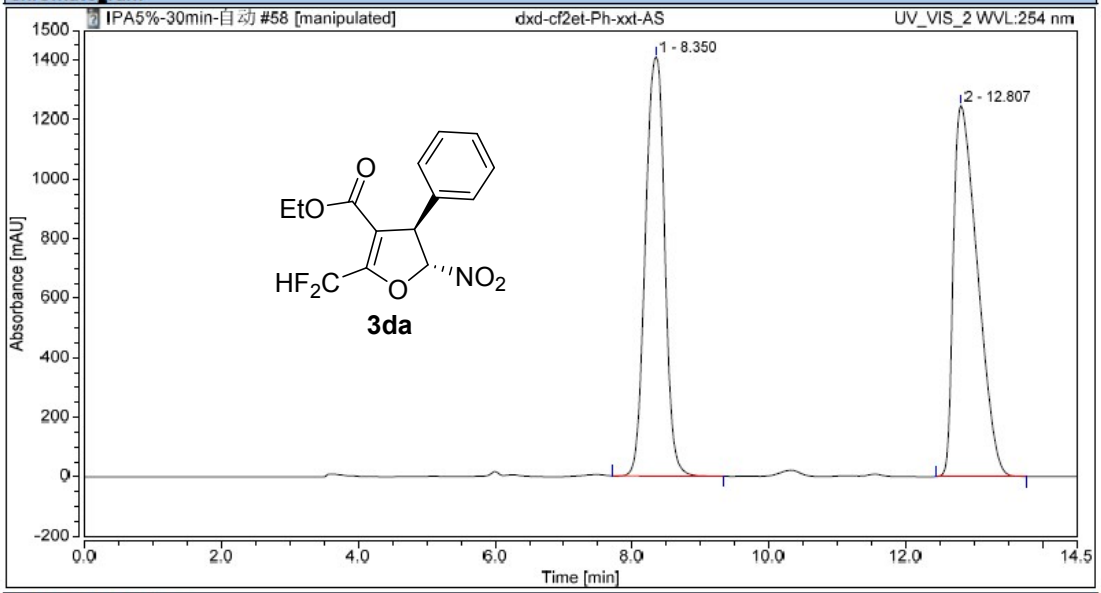


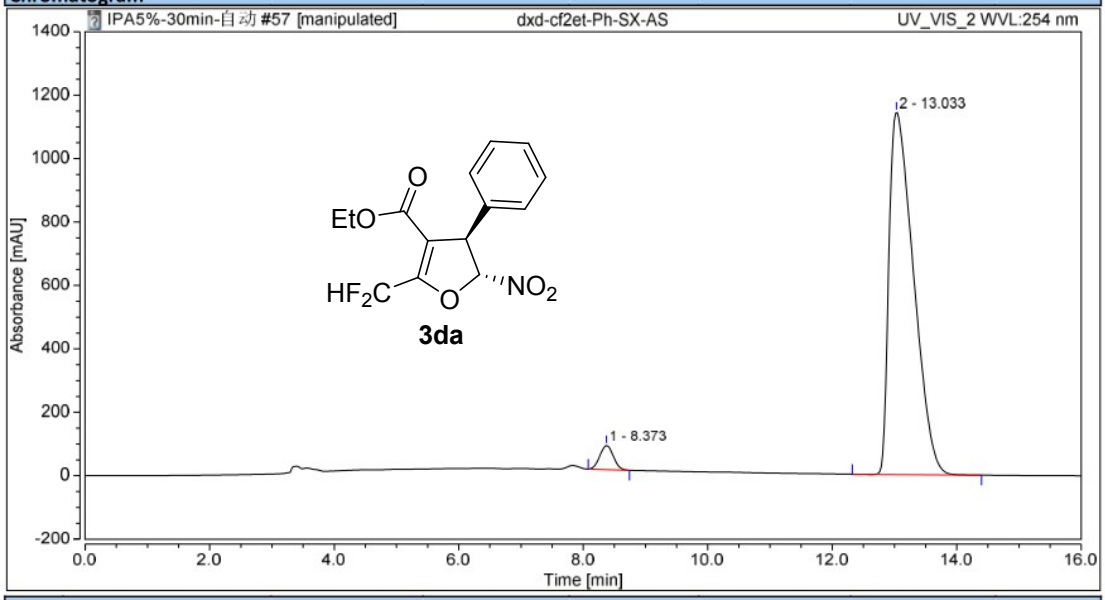
Chromatogram



Integration Results

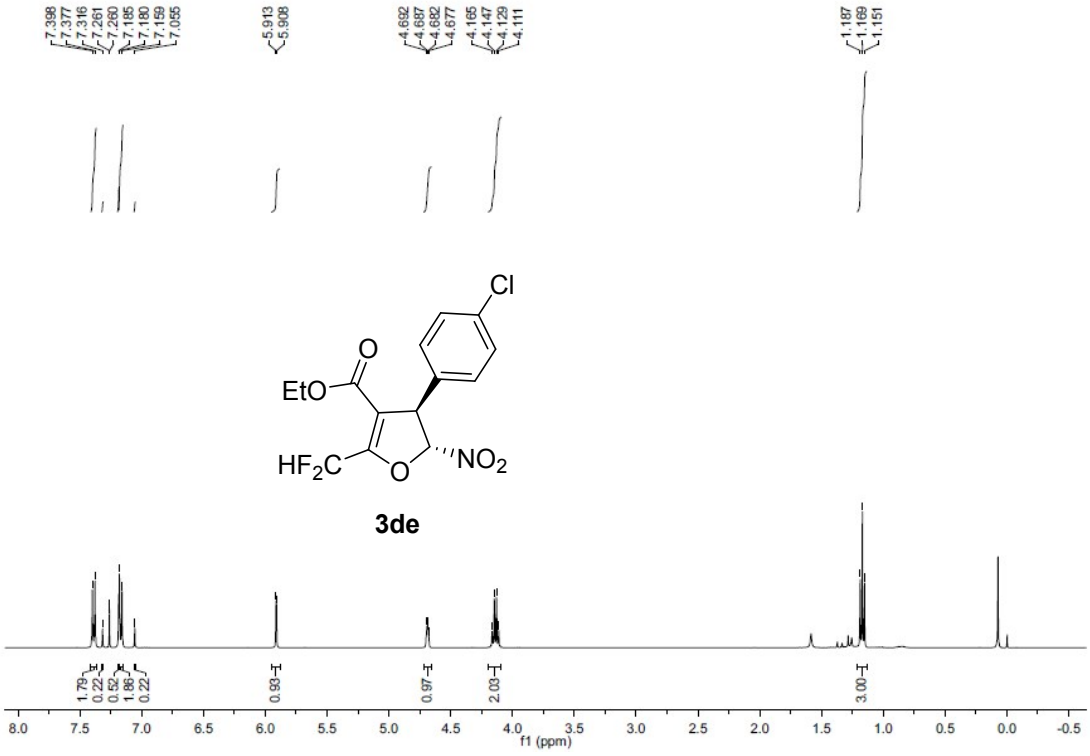
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		8.350	460.635	1408.359	47.62	53.05	n.a.
2		12.807	506.638	1246.258	52.38	46.95	n.a.
Total:			**967.274**	**2654.617**	**100.00**	**100.00**	

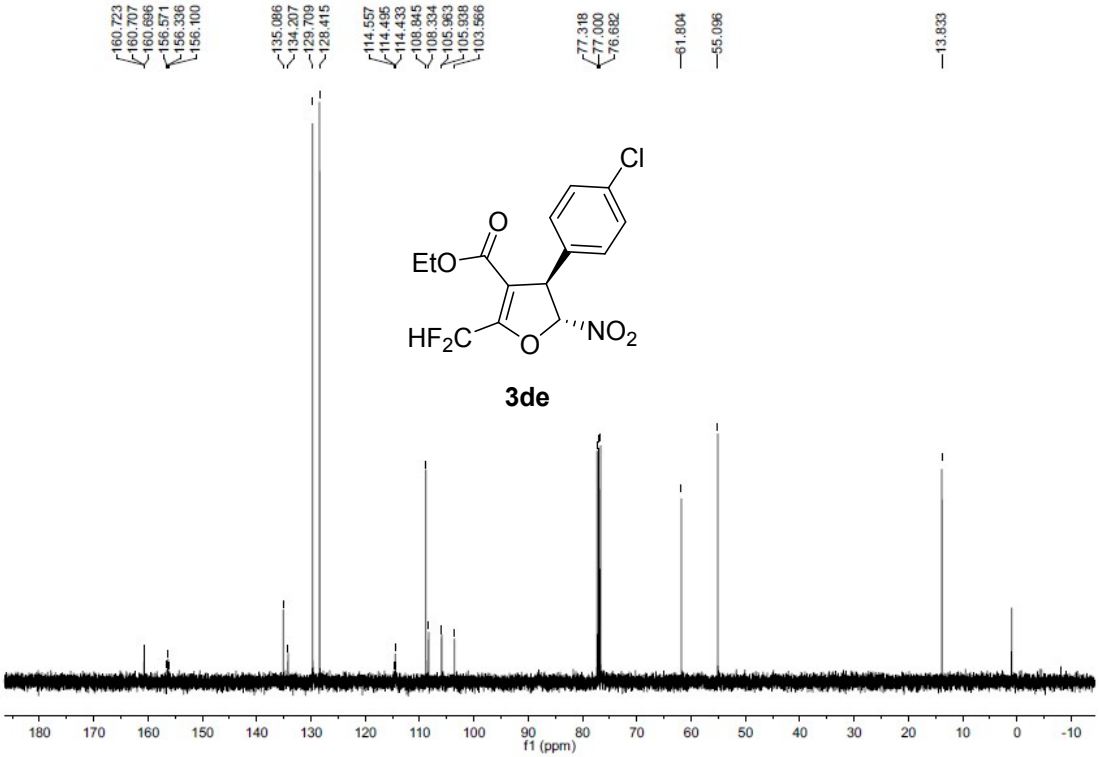
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		8.373	19.102	75.855	3.55	6.22	n.a.
2		13.033	519.487	1142.844	96.45	93.78	n.a.
Total:			**538.589**	**1218.698**	**100.00**	**100.00**	

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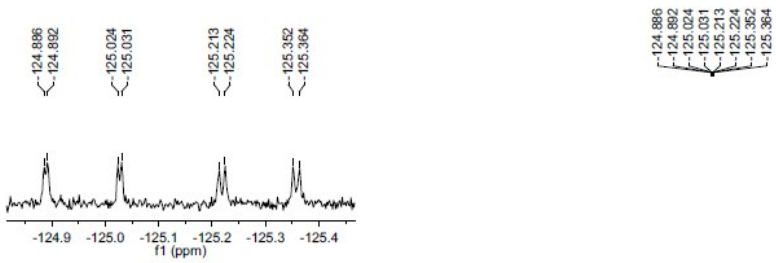
108.845
108.334
105.963
105.938
103.566
77.318
77.000
76.682
61.804
55.096
13.833
Cl
O
EtO
HF2C
O
NO2
3de
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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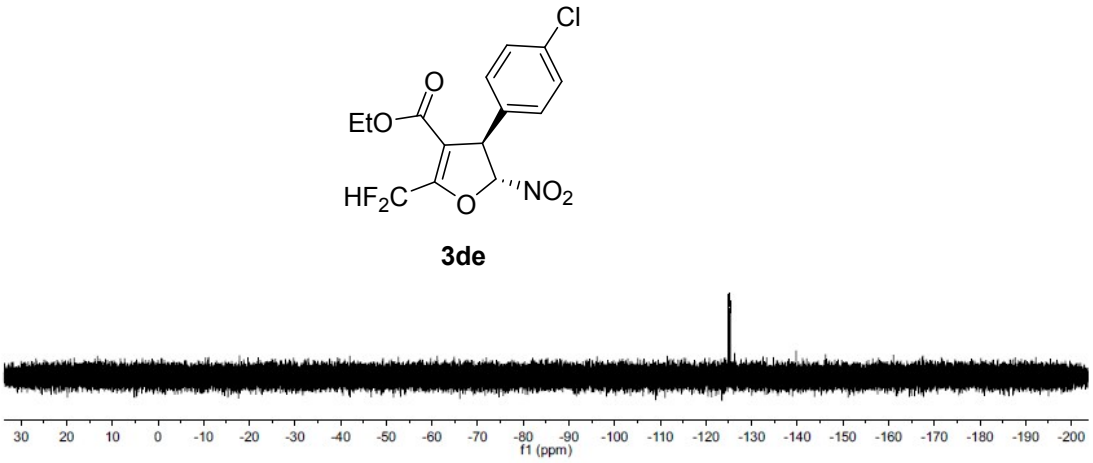
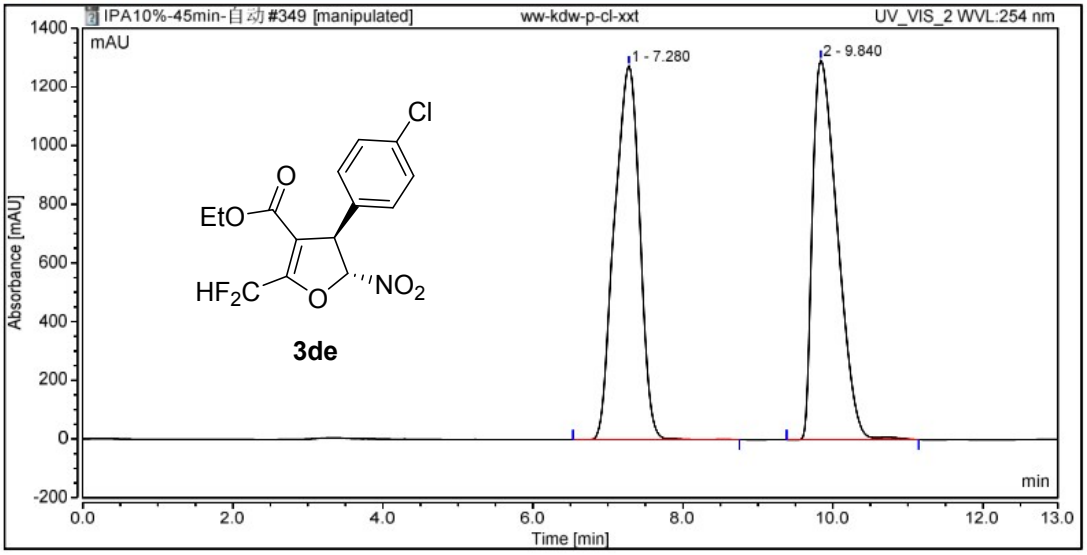
125.224
125.352
125.364
-124.9 -125.0 -125.1 -125.2 -125.3 -125.4
f1 (ppm)


Cl
O
EtO
HF2C
O
NO2
3de
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)

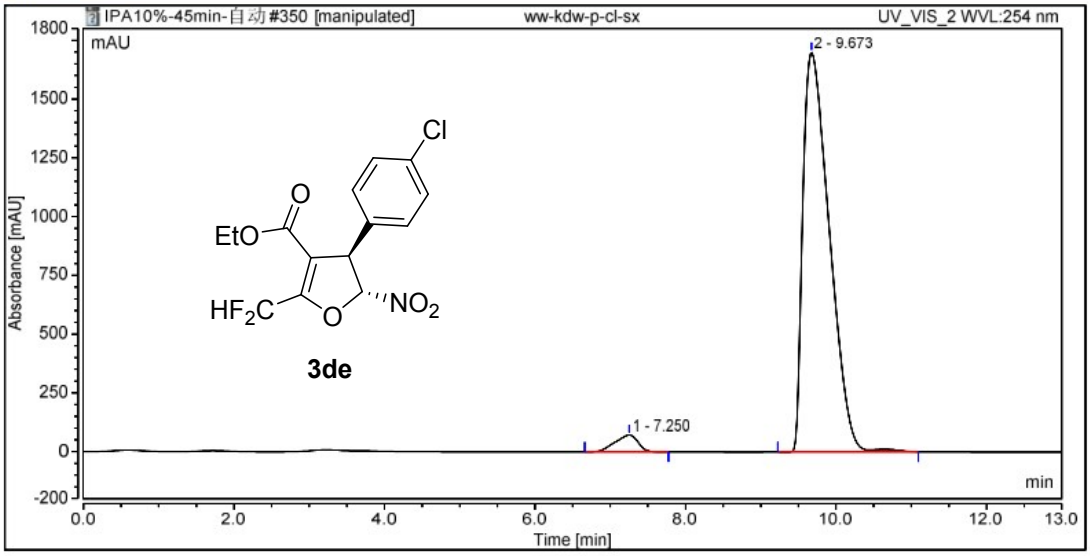
Chromatogram



Integration Results

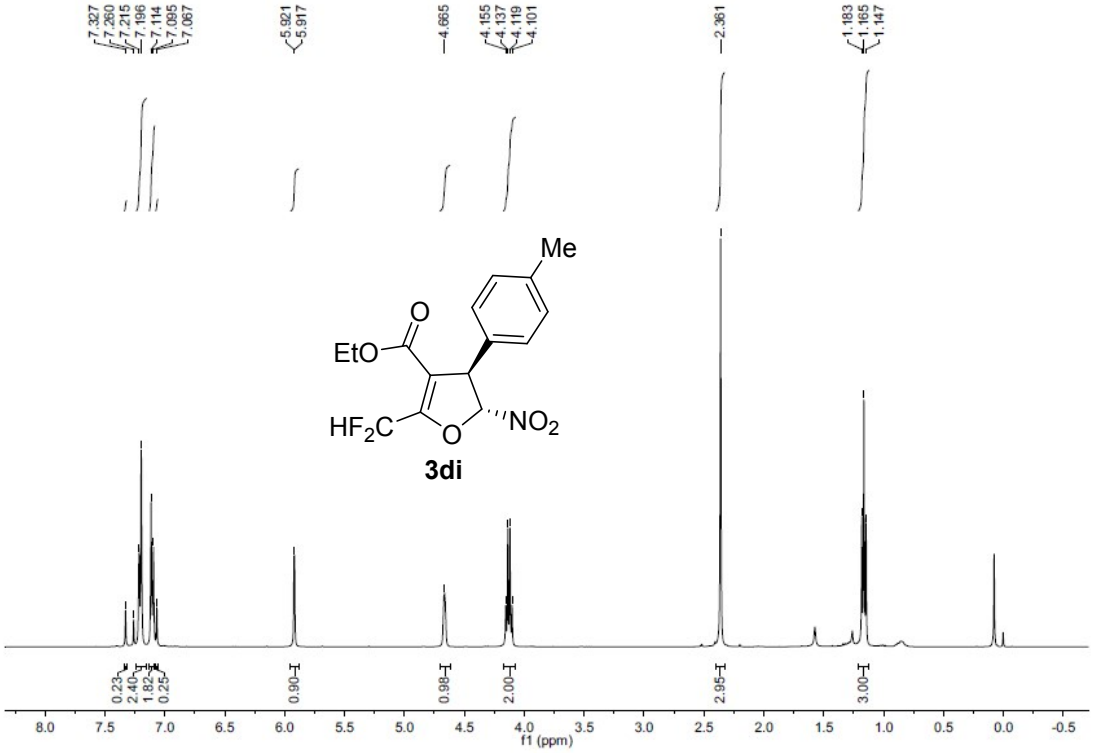
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		7.280	496.506	1274.018	49.85	49.63	n.a.
2		9.840	499.560	1293.008	50.15	50.37	n.a.
Total:			**996.066**	**2567.027**	**100.00**	**100.00**	

Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		7.250	25.567	72.175	3.55	4.07	n.a.
2		9.673	694.051	1699.741	96.45	95.93	n.a.
Total:			**719.618**	**1771.916**	**100.00**	**100.00**	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7.067
5.921
5.917
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4.101
2.361
1.183
1.165
1.147
Me
O
EtO
HF2C
O
NO2
3di
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2.40
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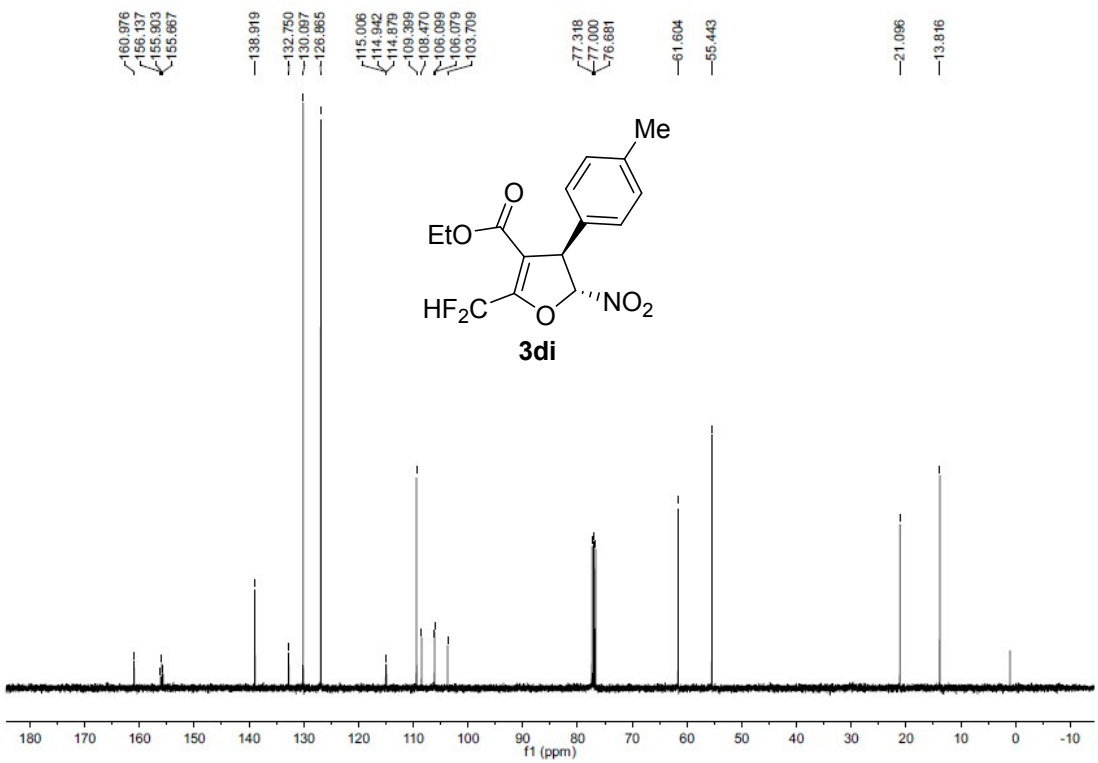
0.25
0.90
0.98
2.00
2.95
3.00
f1 (ppm)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106.079
103.709
77.318
77.000
76.681
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55.443
21.096
13.816
Me
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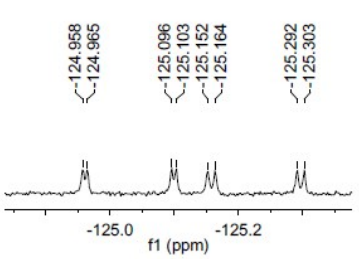
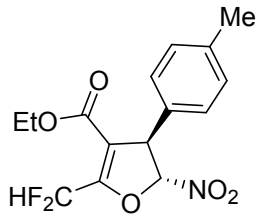
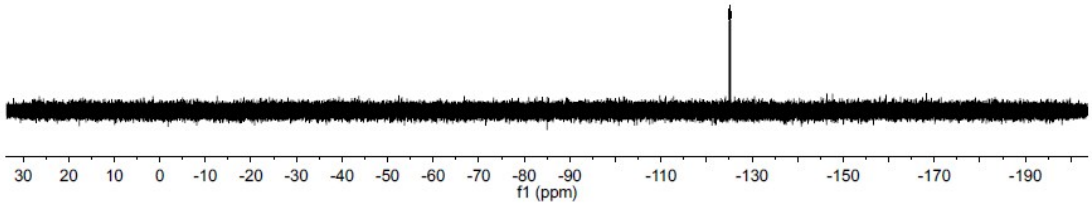
EtO
HF2C
O
NO2
3di
f1 (ppm)

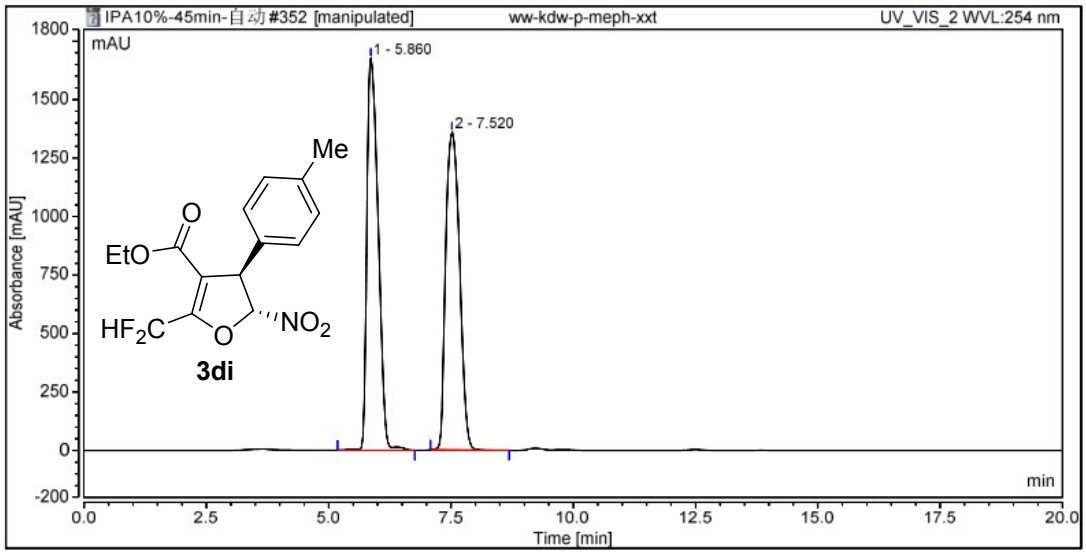




3di



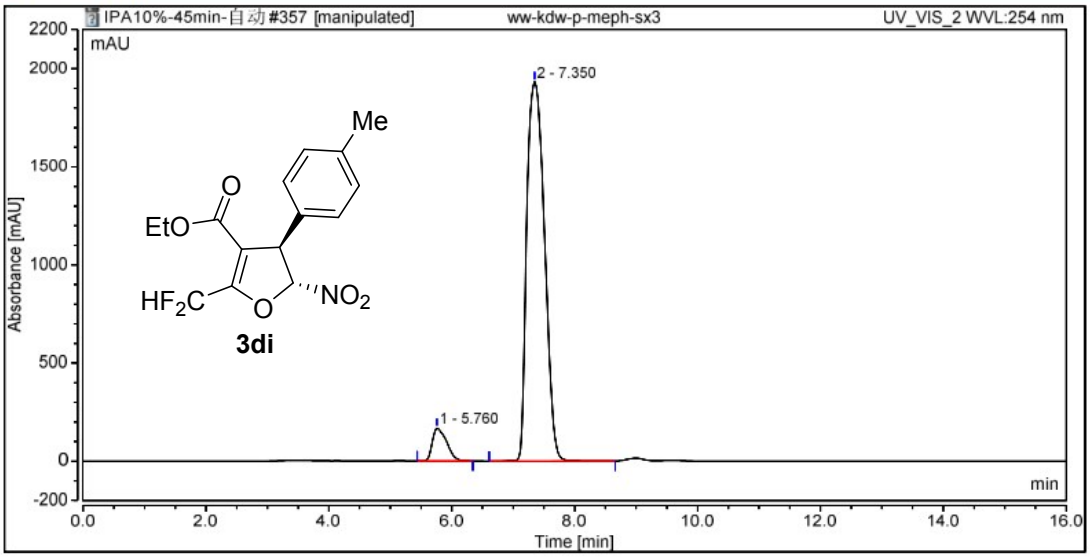
Chromatogram



Integration Results

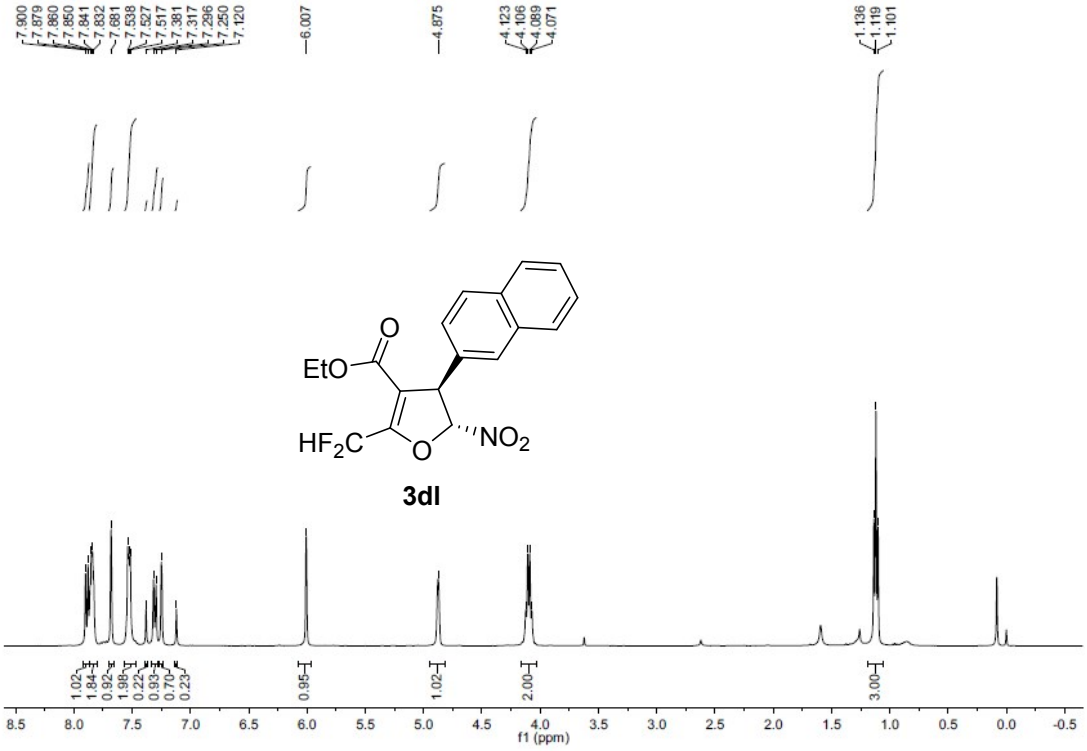
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.860	446.065	1675.747	50.01	55.23	n.a.
2		7.520	445.863	1358.231	49.99	44.77	n.a.
Total:			**891.928**	**3033.978**	**100.00**	**100.00**	

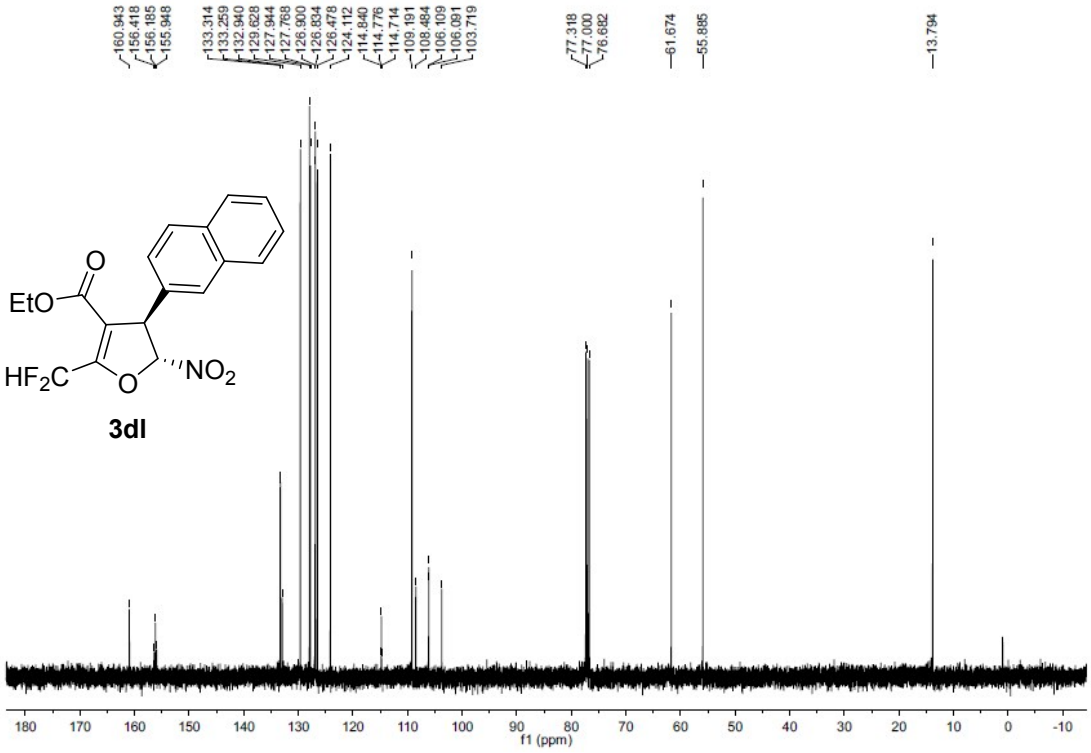
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.760	44.819	166.675	6.50	7.94	n.a.
2		7.350	644.673	1932.370	93.50	92.06	n.a.
Total:			**689.493**	**2099.045**	**100.00**	**100.00**	

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124.112
114.840
114.776
114.714
109.191
108.484
106.109
106.091
103.719
77.318
77.000
76.682
61.674
55.885
13.794
O
EtO
HF2C
O
NO2
3dl
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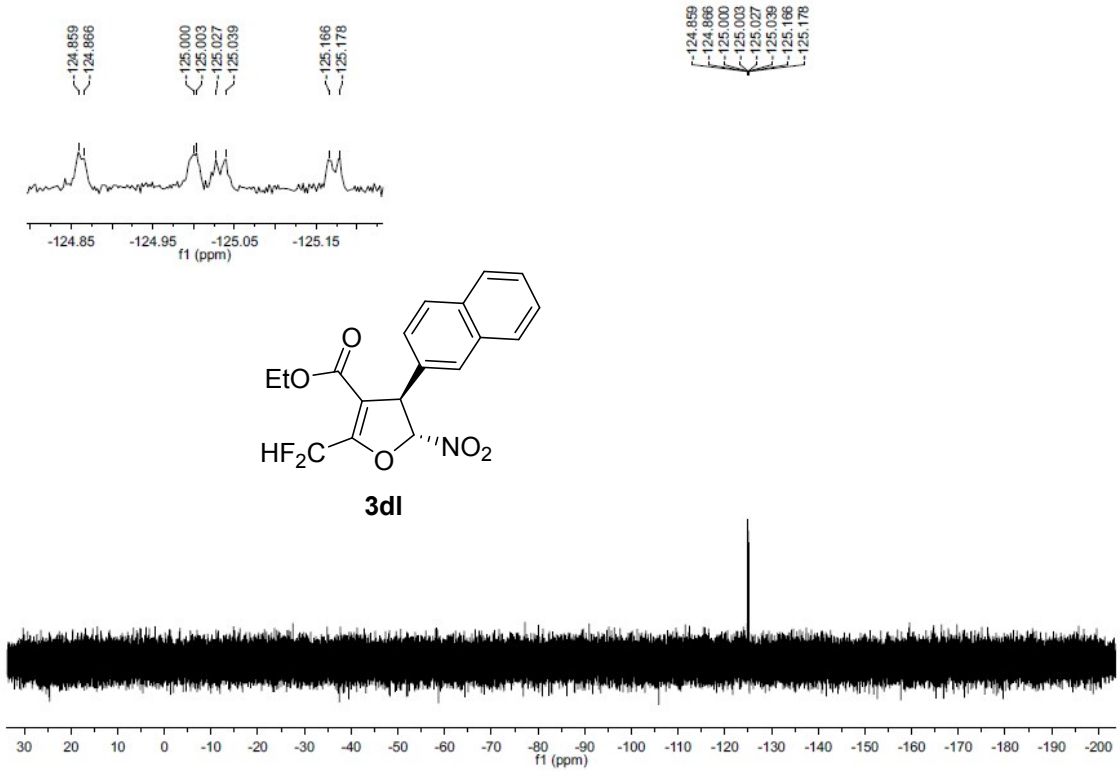
f1 (ppm)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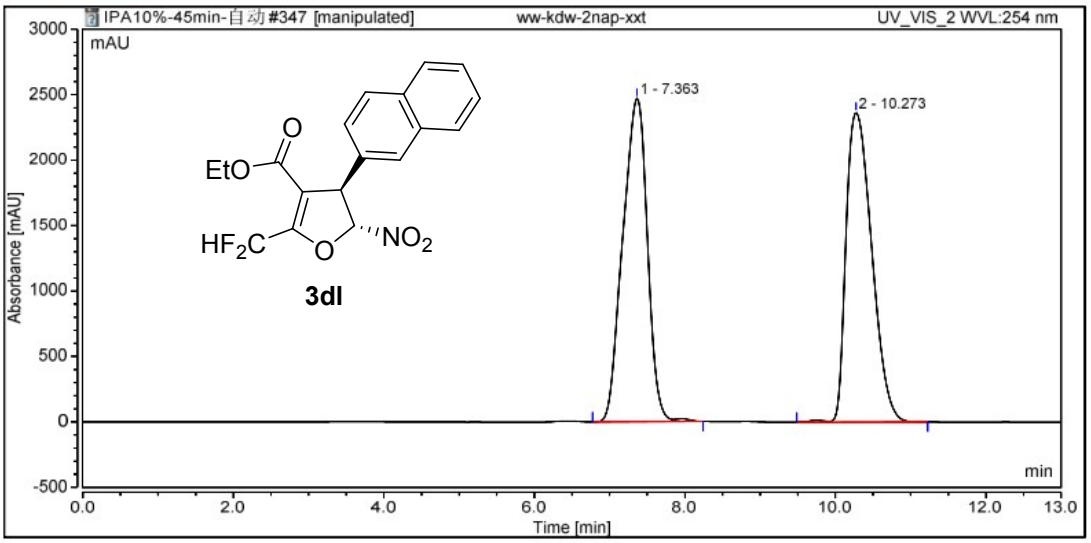
-124.95
-125.05
-125.15
f1 (ppm)
O
EtO
HF2C
O
NO2
3dl
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)

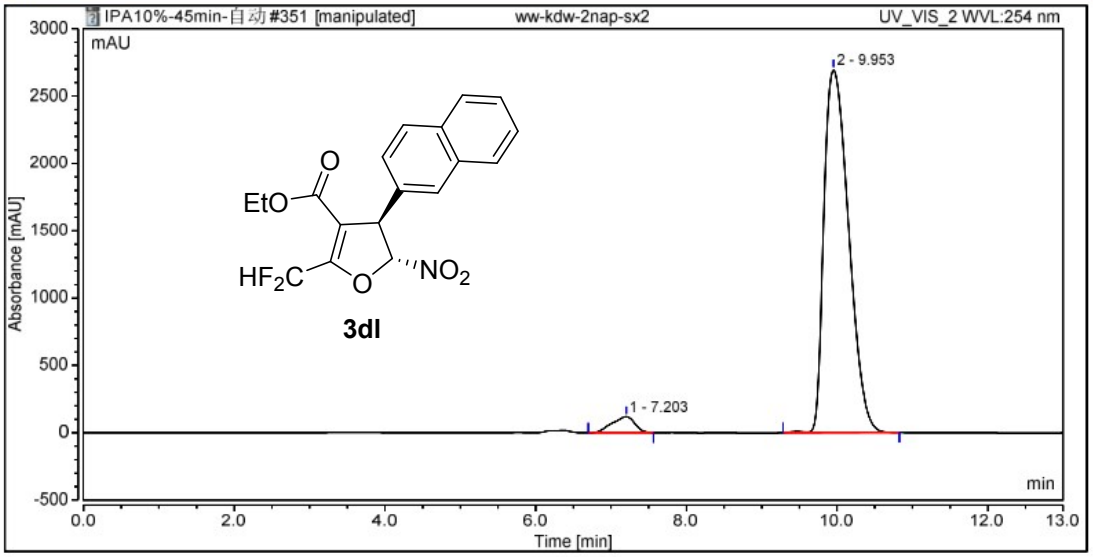
Chromatogram



Integration Results

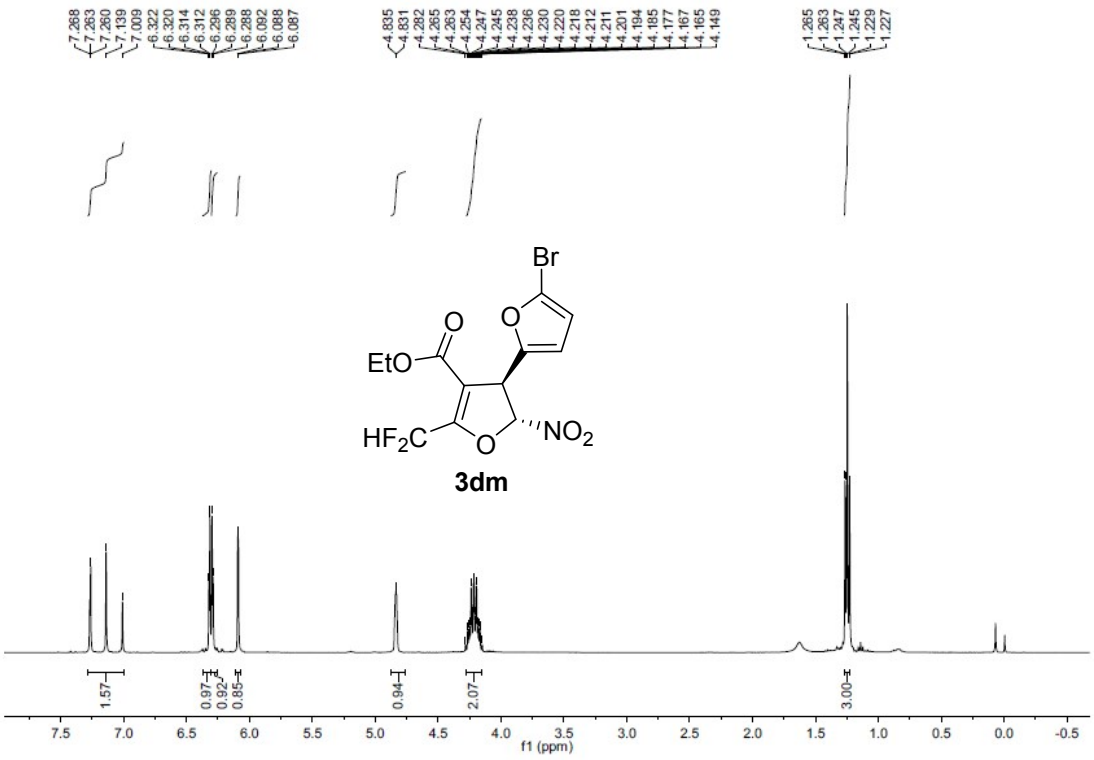
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		7.363	937.879	2471.038	50.02	51.10	n.a.
2		10.273	937.174	2364.267	49.98	48.90	n.a.
Total:			**1875.053**	**4835.305**	**100.00**	**100.00**	

Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		7.203	42.058	119.616	3.95	4.25	n.a.
2		9.953	1021.684	2695.077	96.05	95.75	n.a.
Total:			**1063.742**	**2814.694**	**100.00**	**100.00**	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6.088
6.087
4.835
4.831
4.282
4.265
4.263
4.254
4.247
4.245
4.238
4.236
4.230
4.220
4.218
4.212
4.211
4.201
4.194
4.185
4.177
4.167
4.165
4.149
1.265
1.263
1.247
1.245
1.229
1.227
Br
O
O
EtO
HF2C
O
NO2
3dm
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0.97
0.92
0.85
0.94
2.07
3.00
7.5
7.0
6.5
6.0
5.5
5.0
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4.0
3.5
3.0
2.5
2.0
1.5
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0.5
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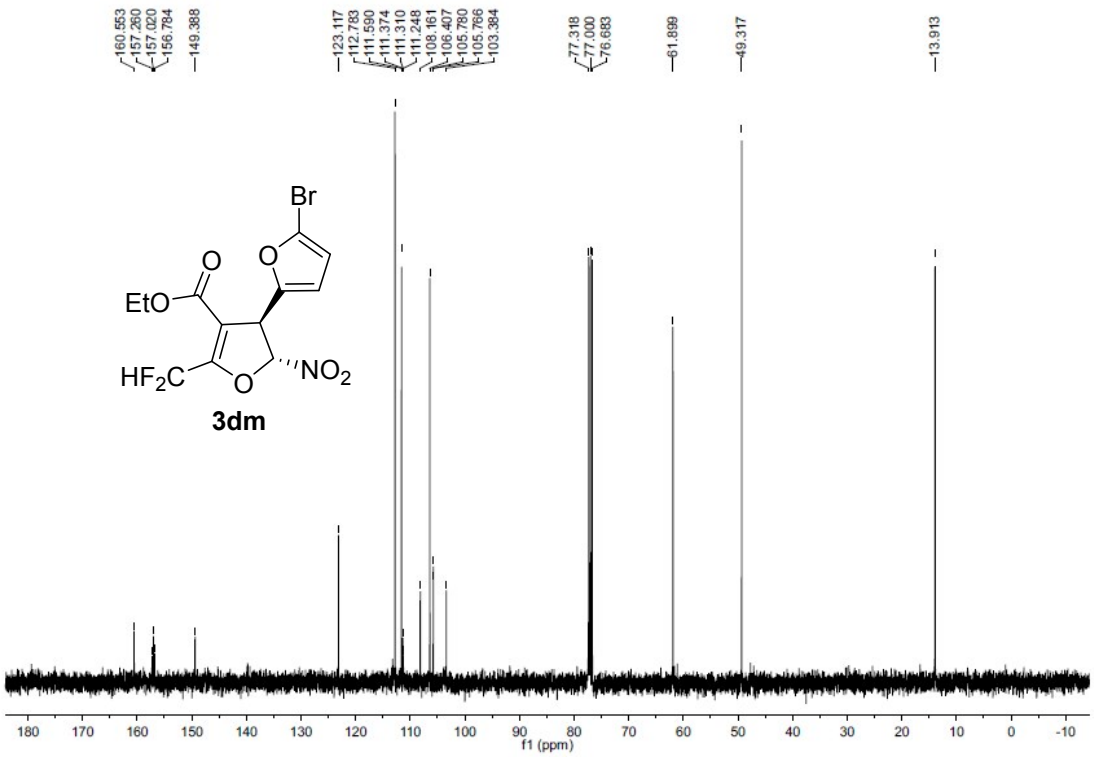
-0.5
f1 (ppm)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111.248
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106.407
105.780
105.766
103.384
77.318
77.000
76.683
61.899
49.317
13.913
Br
O
O
EtO
HF2C
O
NO2
3dm
180
170
160
150
140
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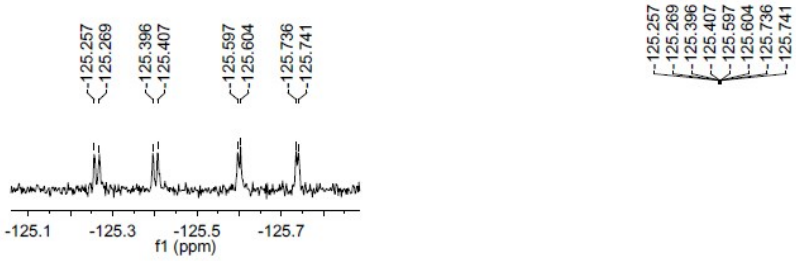
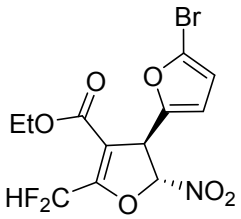
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)





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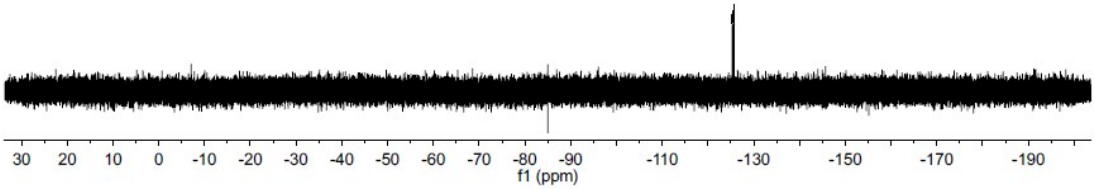
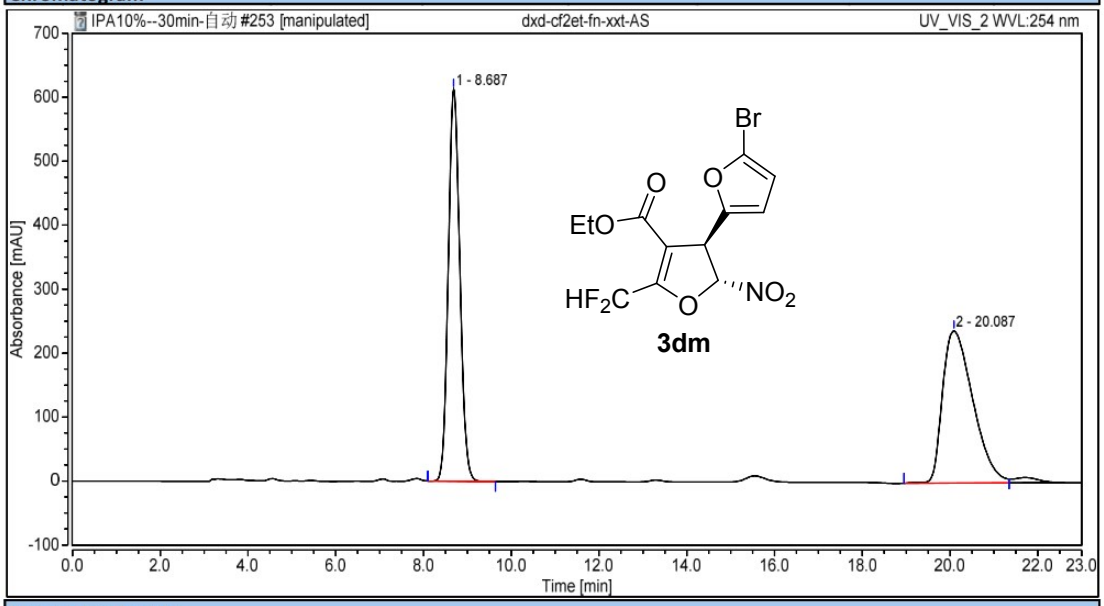


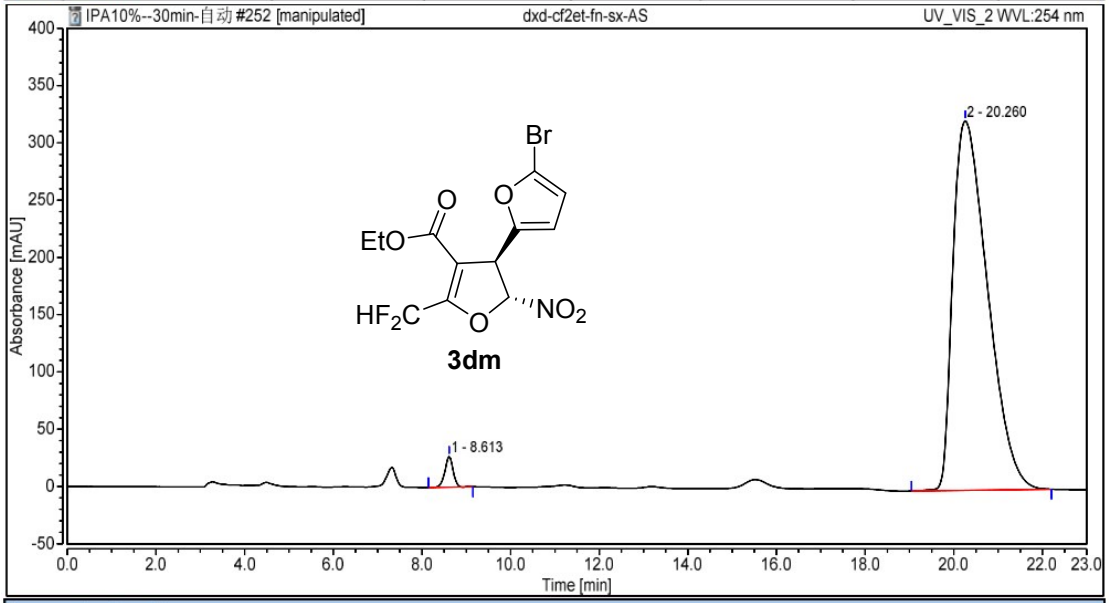
Chromatogram



Integration Results

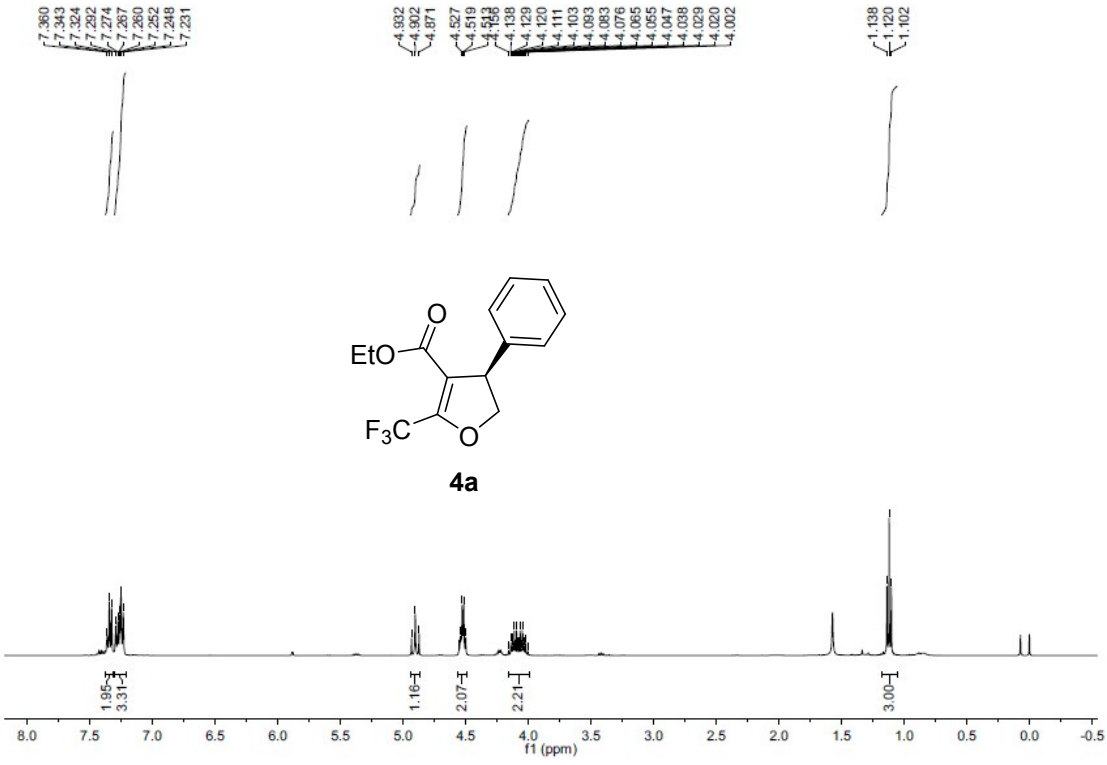
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		8.687	186.061	612.814	49.42	72.04	n.a.
2		20.087	190.392	237.885	50.58	27.96	n.a.
Total:			**376.453**	**850.699**	**100.00**	**100.00**	

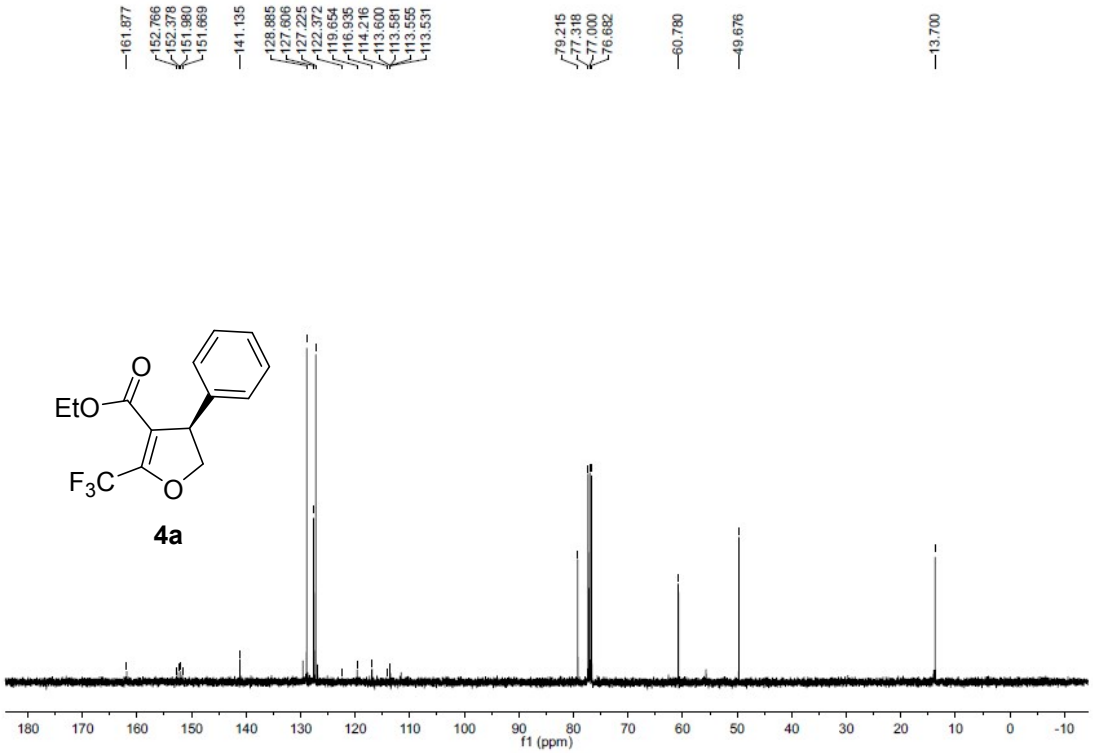
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		8.613	5.751	26.827	1.93	7.67	n.a.
2		20.260	292.106	322.781	98.07	92.33	n.a.
Total:			**297.856**	**349.608**	**100.00**	**100.00**	

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77.318
77.000
76.682
60.780
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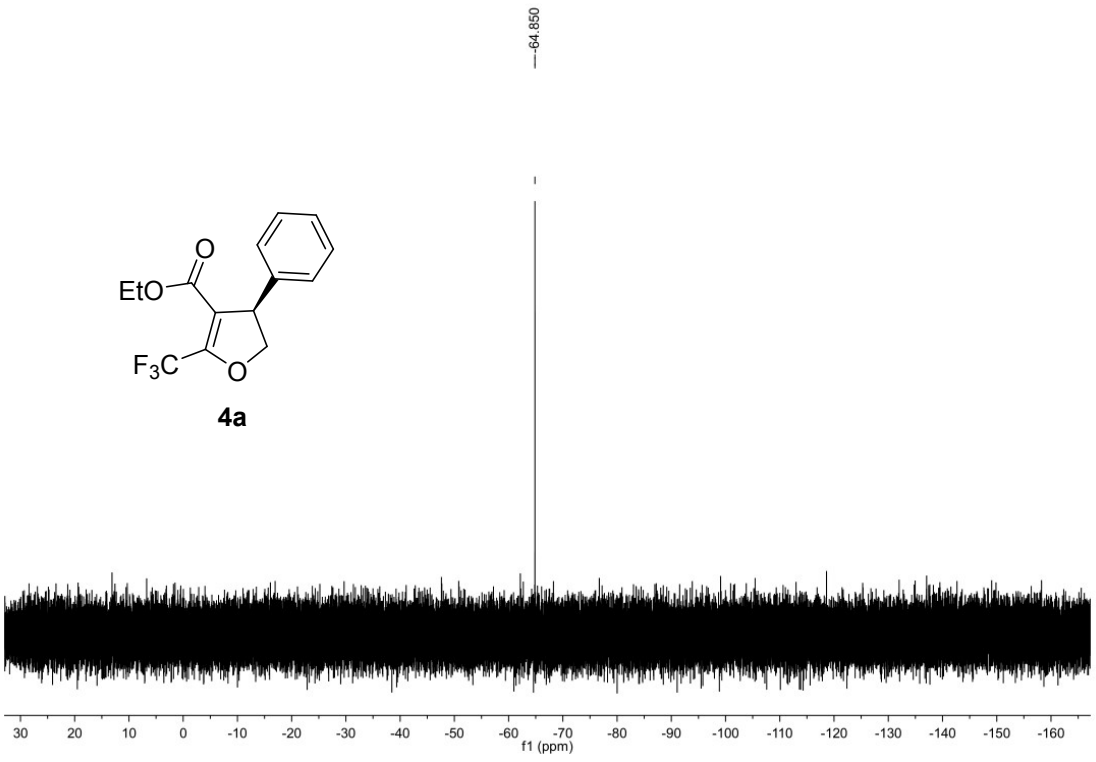
EtO
O
F3C
O
4a
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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F3C
O
4a
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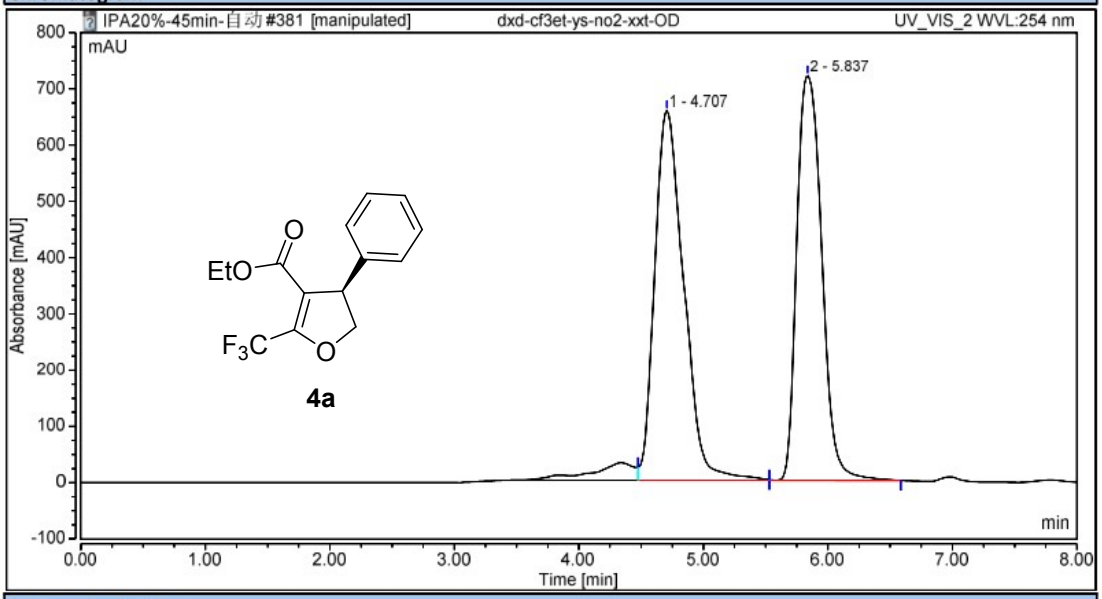
f1 (ppm)

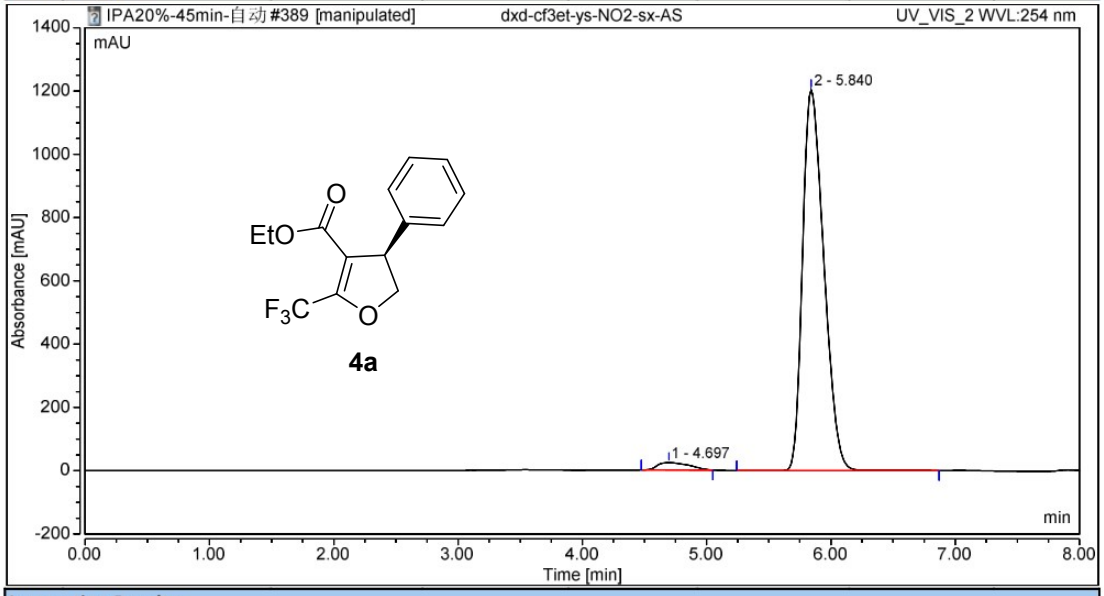
Chromatogram



Integration Results

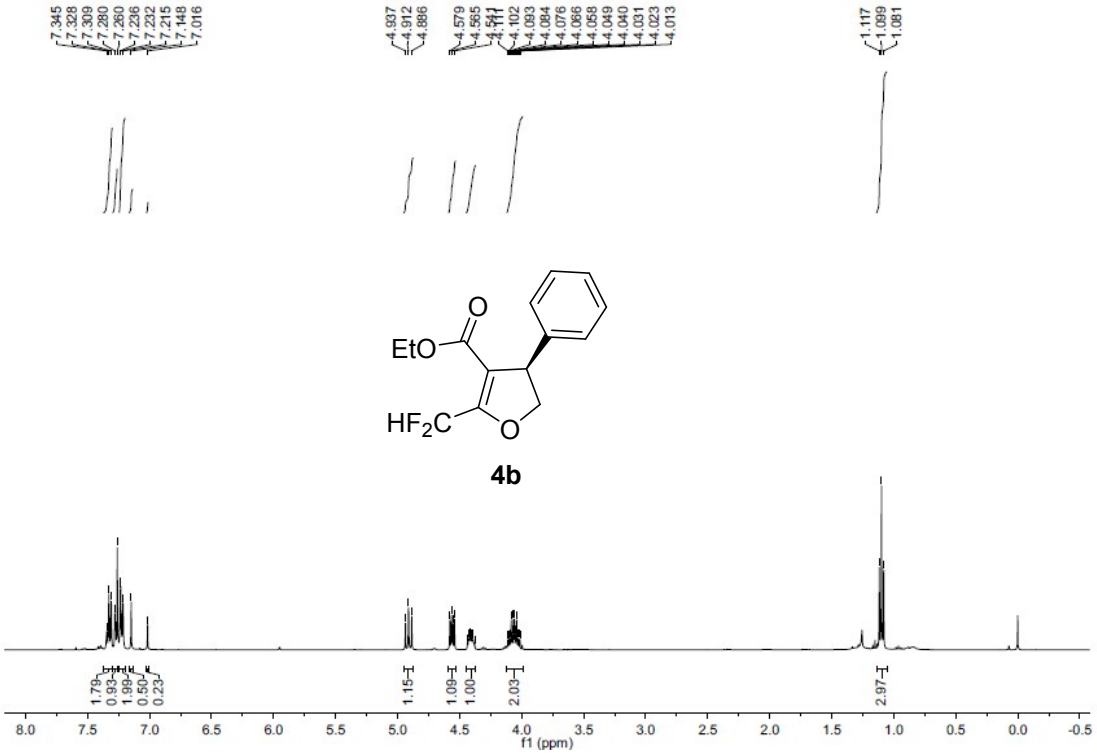
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		4.707	177.790	657.515	51.50	47.75	n.a.
2		5.837	167.405	719.517	48.50	52.25	n.a.
Total:			**345.195**	**1377.033**	**100.00**	**100.00**	

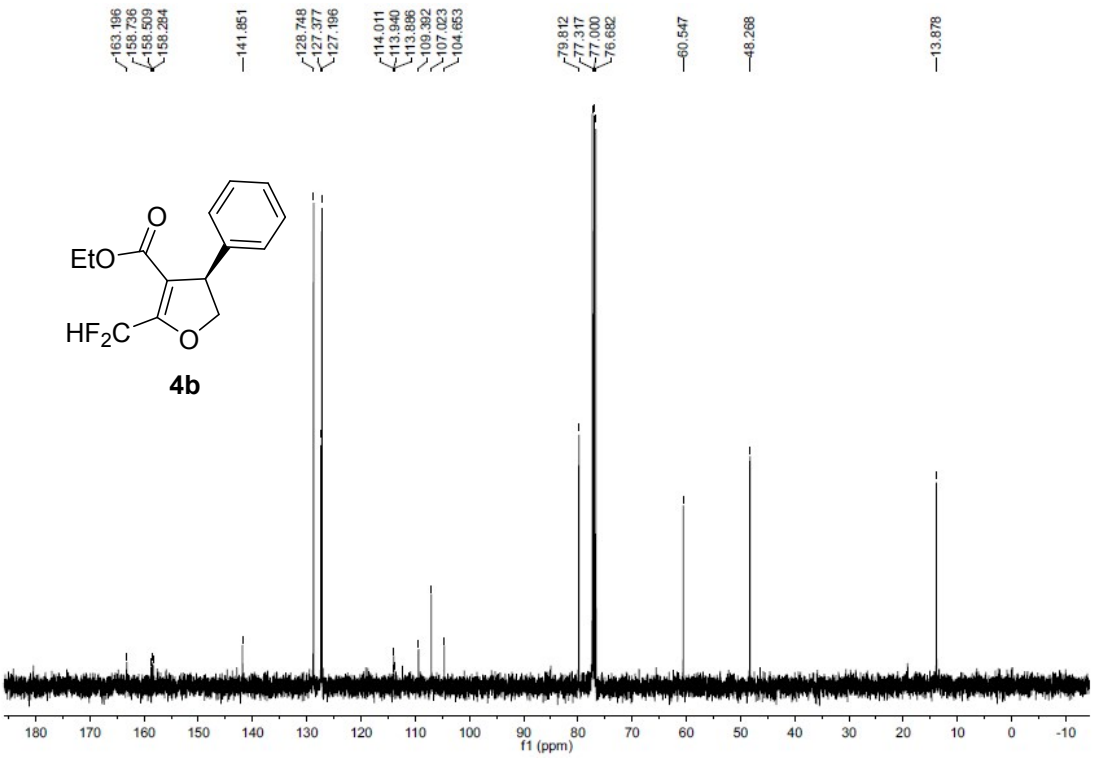
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		4.697	6.819	23.245	2.78	1.89	n.a.
2		5.840	238.738	1204.008	97.22	98.11	n.a.
Total:			**245.558**	**1227.253**	**100.00**	**100.00**	


7.345
7.328
7.309
7.280
7.260
7.236
7.232
7.215
7.148
7.016
4.937
4.912
4.886
4.579
4.565
4.111
4.102
4.093
4.084
4.076
4.066
4.058
4.049
4.040
4.031
4.023
4.013
1.117
1.099
1.081
EtO
O
HF2C
O
4b
1.79
0.93
1.99
0.50
0.23
1.15
1.09
1.00
2.03
2.97
f1 (ppm)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158.284
141.851
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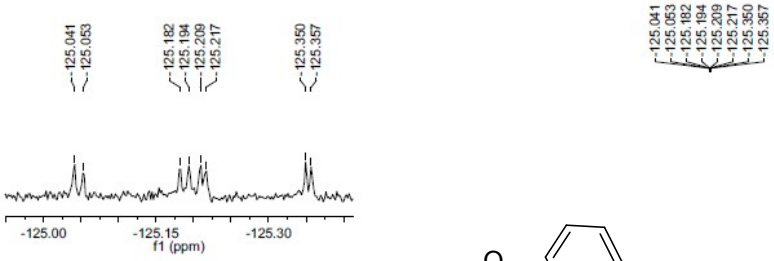
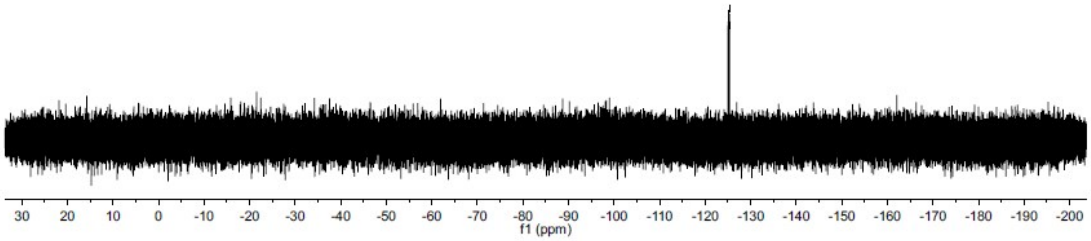
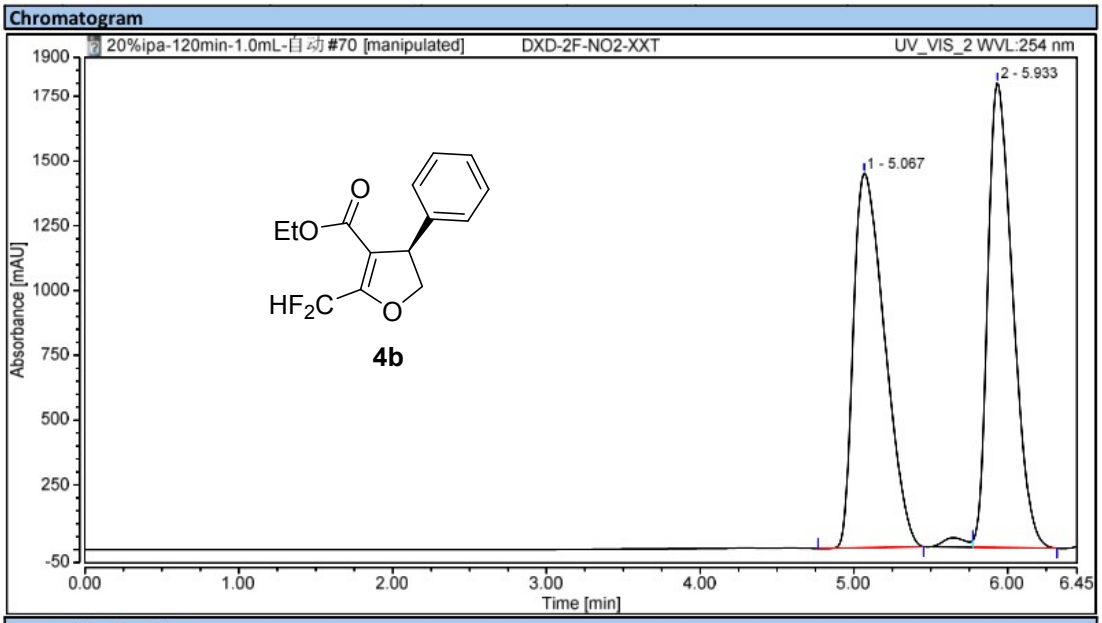
127.377
127.196
114.011
113.940
113.886
109.392
107.023
104.653
79.812
77.317
77.000
76.682
60.547
48.268
13.878
EtO
O
HF2C
O
4b
f1 (ppm)



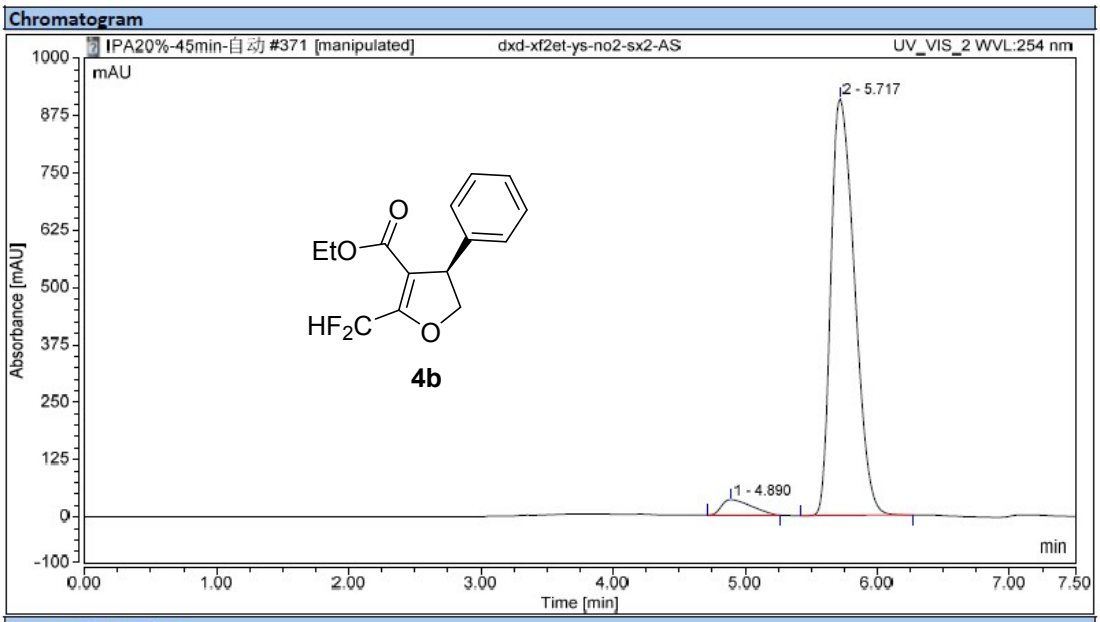
4b





Integration Results

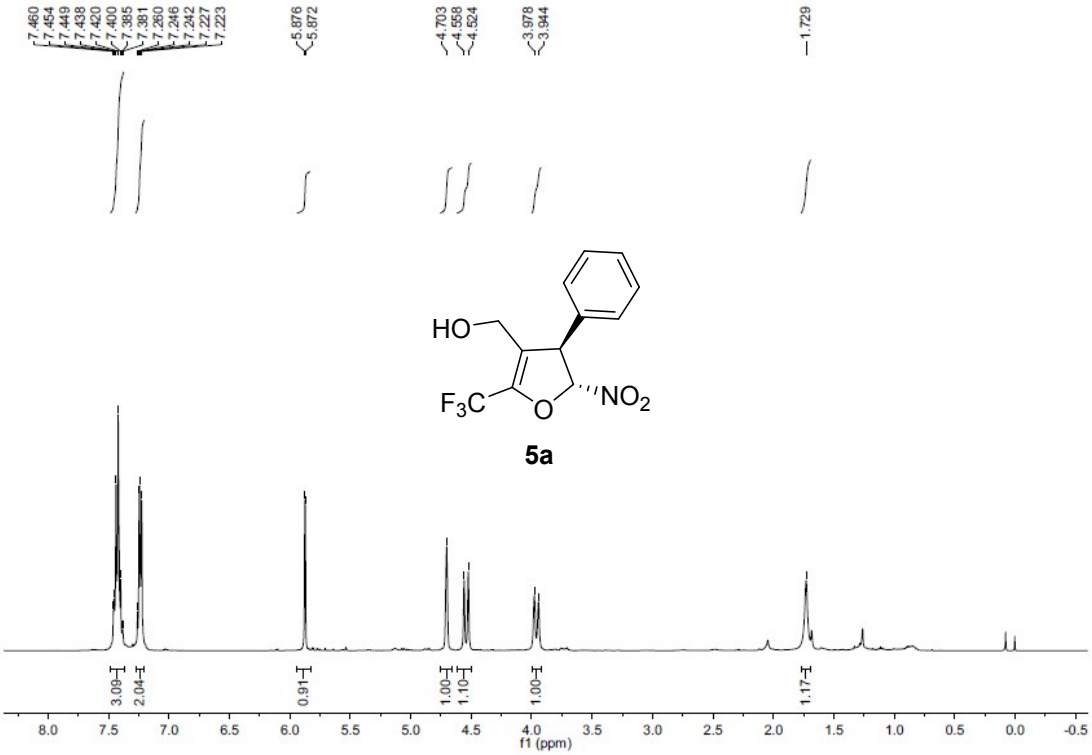
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.067	339.420	1445.197	50.14	44.62	n.a.
2		5.933	337.496	1793.401	49.86	55.38	n.a.
Total:			**676.917**	**3238.597**	**100.00**	**100.00**	



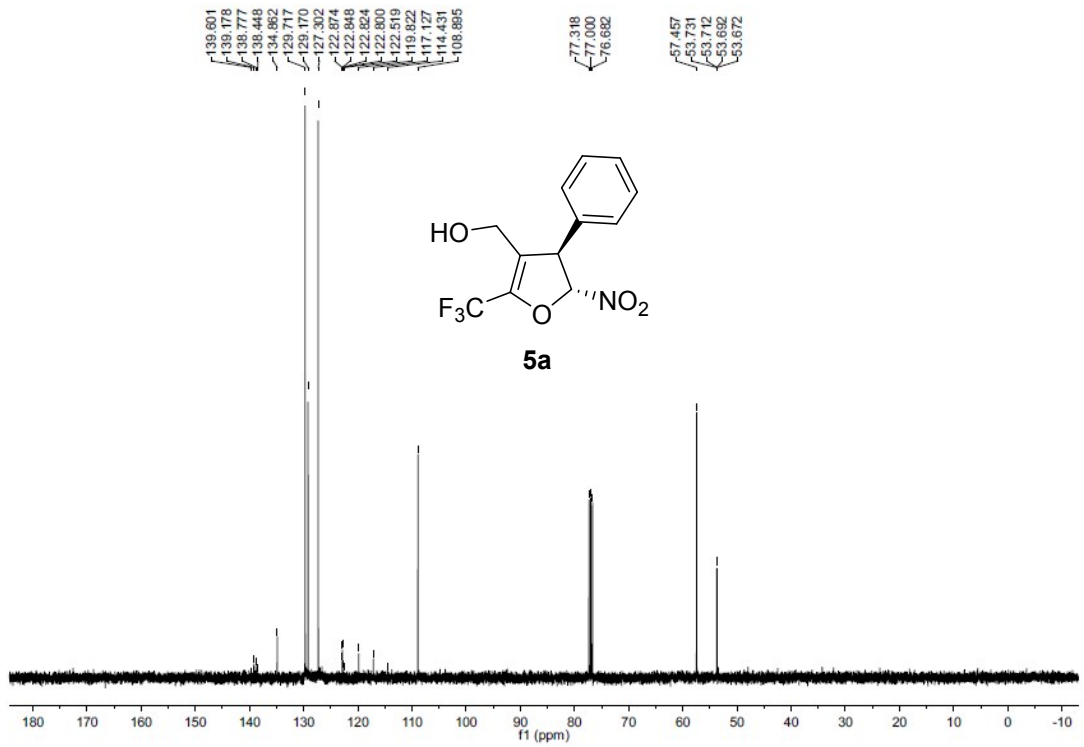
4b

Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		4.890	8.750	33.723	4.43	3.58	n.a.
2		5.717	188.567	909.008	95.57	96.42	n.a.
Total:			**197.318**	**942.730**	**100.00**	**100.00**	



5a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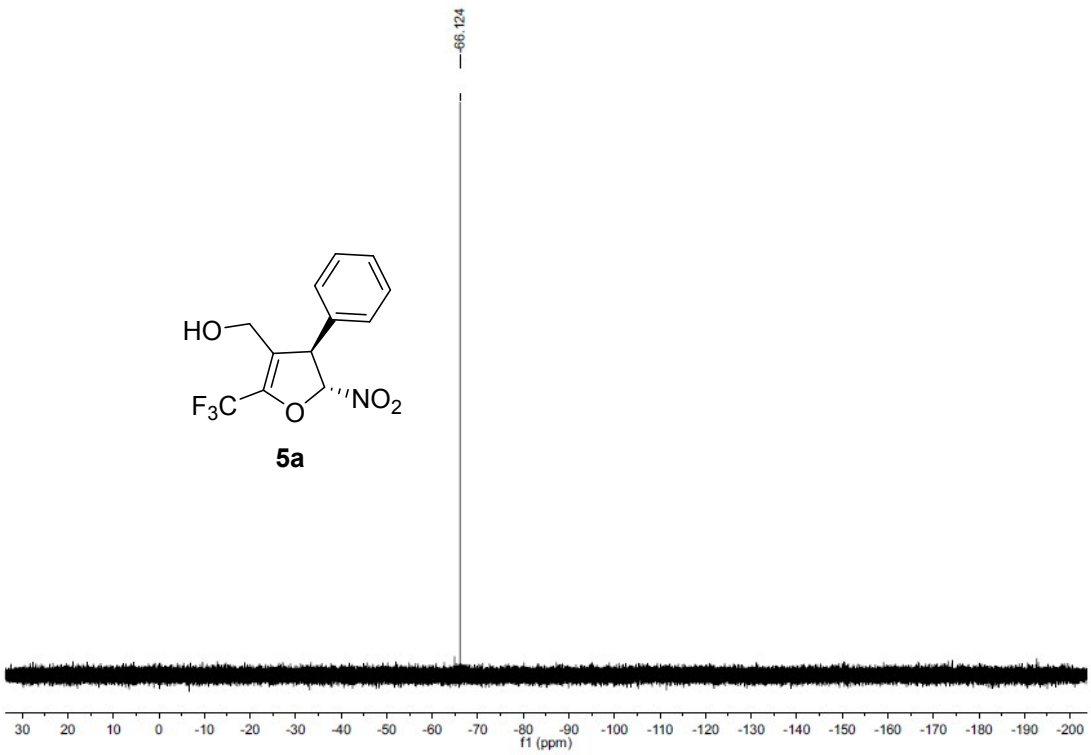
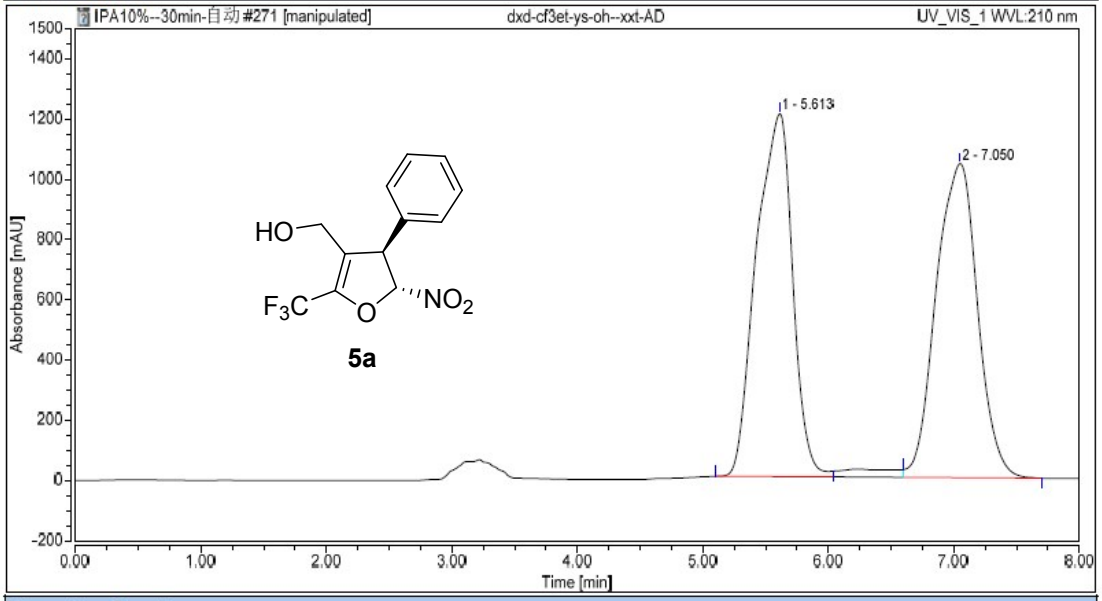
138.448
134.862
129.717
129.170
127.302
122.874
122.848
122.824
122.800
122.519
119.822
117.127
114.431
108.895
77.318
77.000
76.682
57.457
53.731
53.712
53.692
53.672
HO
F3C
O
NO2
5a
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


66.124
HO
F3C
O
NO2
5a
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)

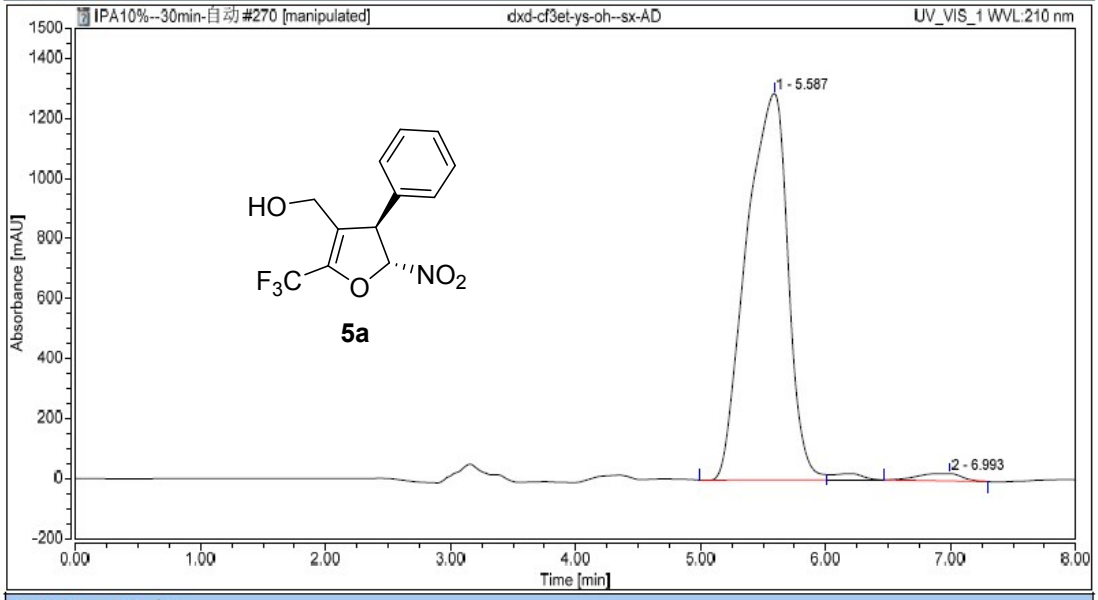
Chromatogram



Integration Results

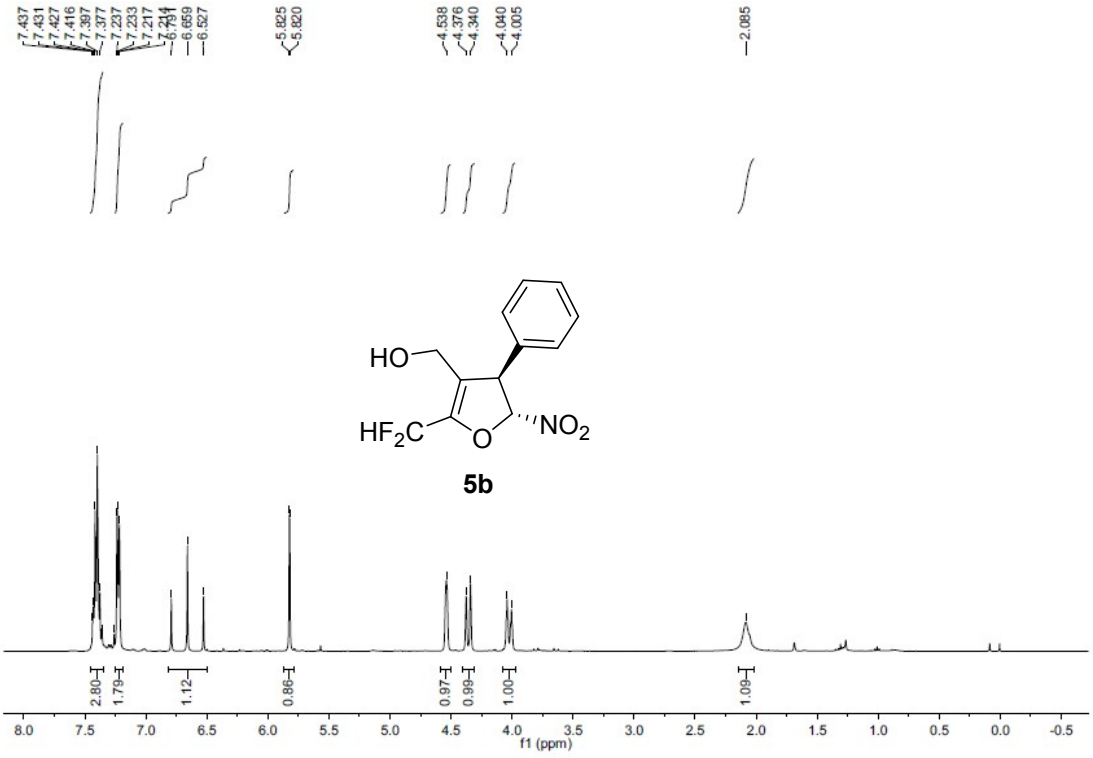
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.613	406.114	1204.776	50.50	53.60	n.a.
2		7.050	398.142	1042.855	49.50	46.40	n.a.
Total:			**804.256**	**2247.631**	**100.00**	**100.00**	

Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.587	496.478	1287.904	98.06	98.15	n.a.
2		6.993	9.836	24.339	1.94	1.85	n.a.
Total:			**506.314**	**1312.243**	**100.00**	**100.00**	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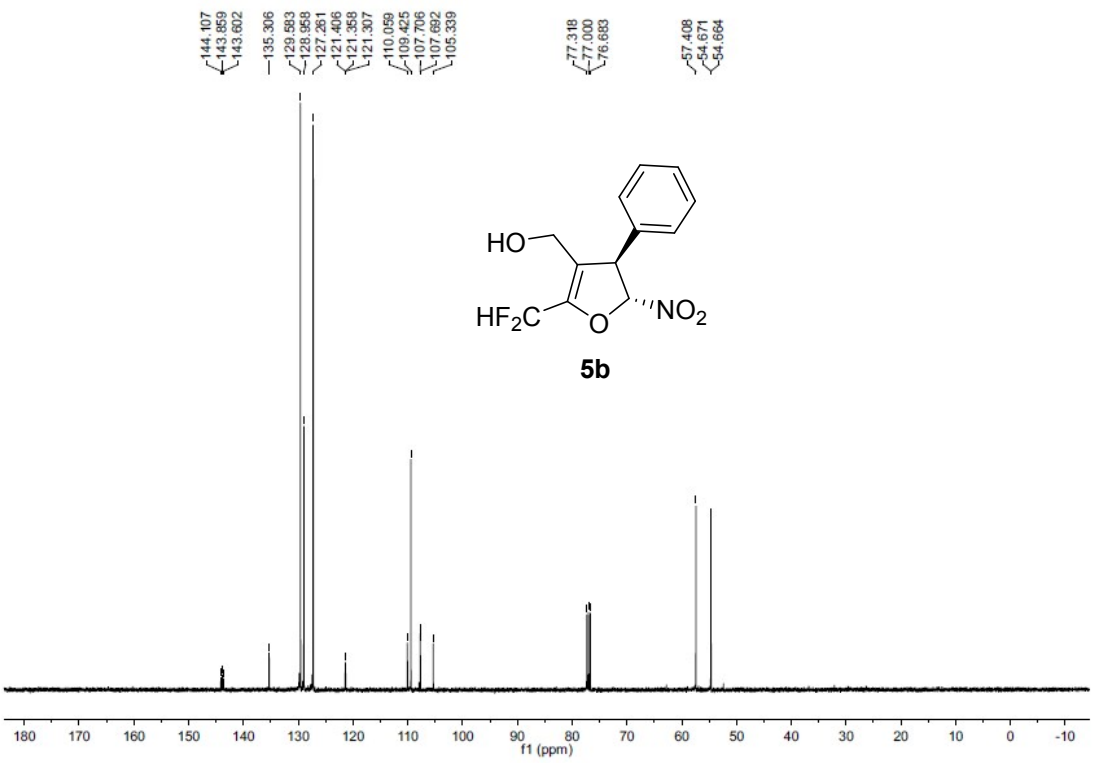
7.377
7.237
7.233
7.217
6.659
6.527
5.825
5.820
4.538
4.376
4.340
4.040
4.005
2.085
HO
HF2C
O
NO2
5b
2.80
1.79
1.12
0.86
0.97
0.99
1.00
1.09
f1 (ppm)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135.306
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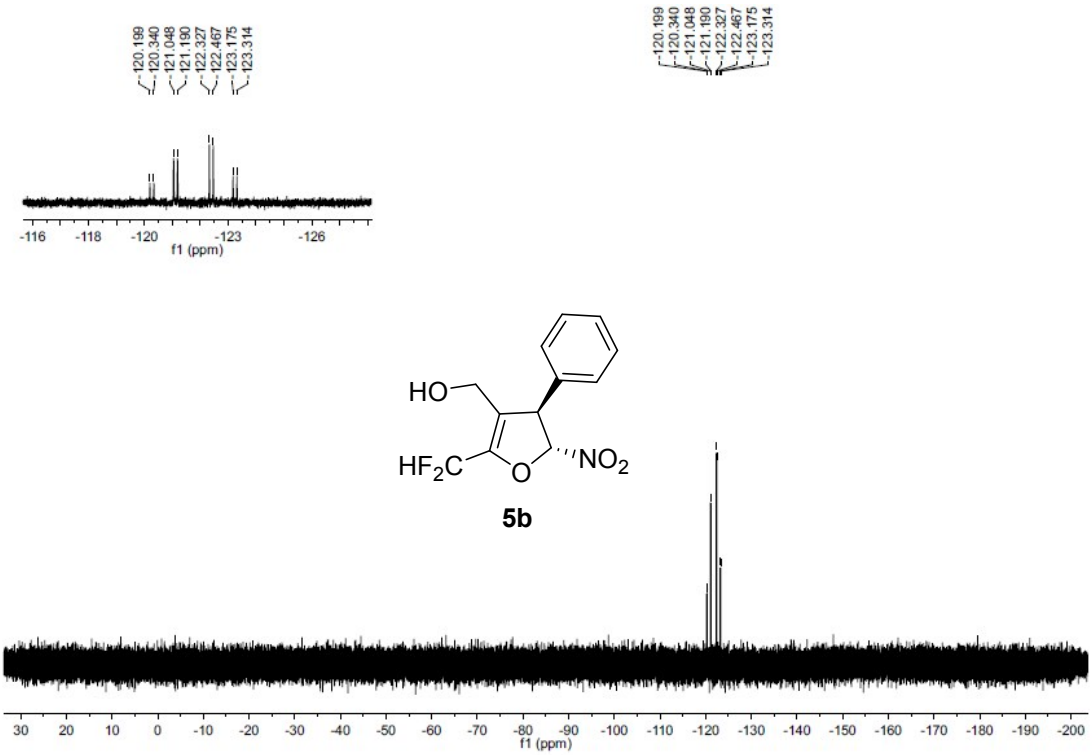
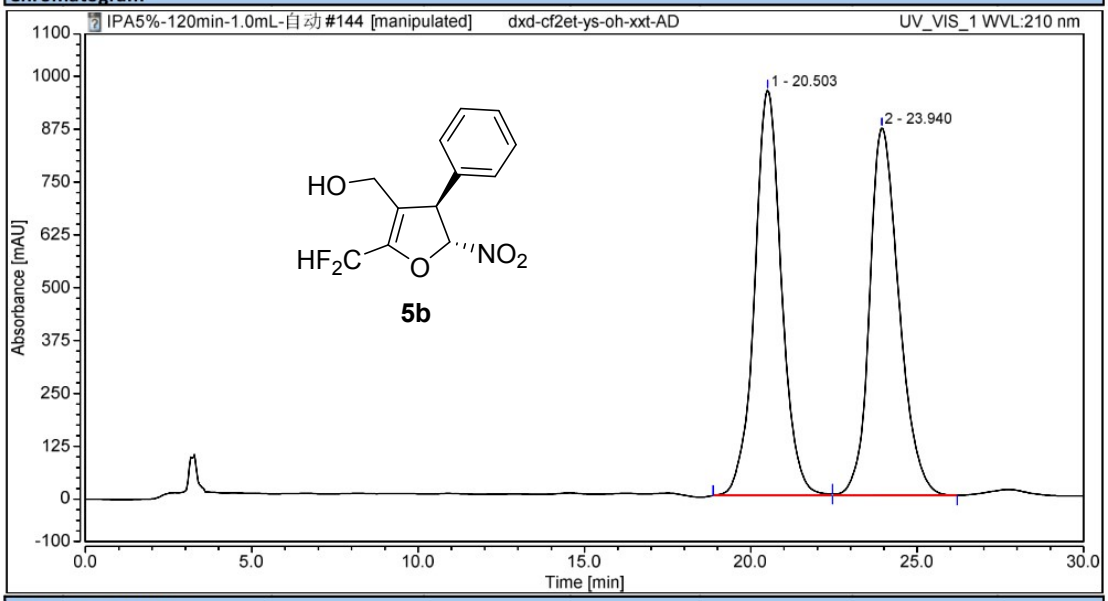
128.958
127.261
121.406
121.358
121.307
110.059
109.425
107.706
107.692
105.339
77.318
77.000
76.683
57.408
54.671
54.664
HO
HF2C
O
NO2
5b
f1 (ppm)

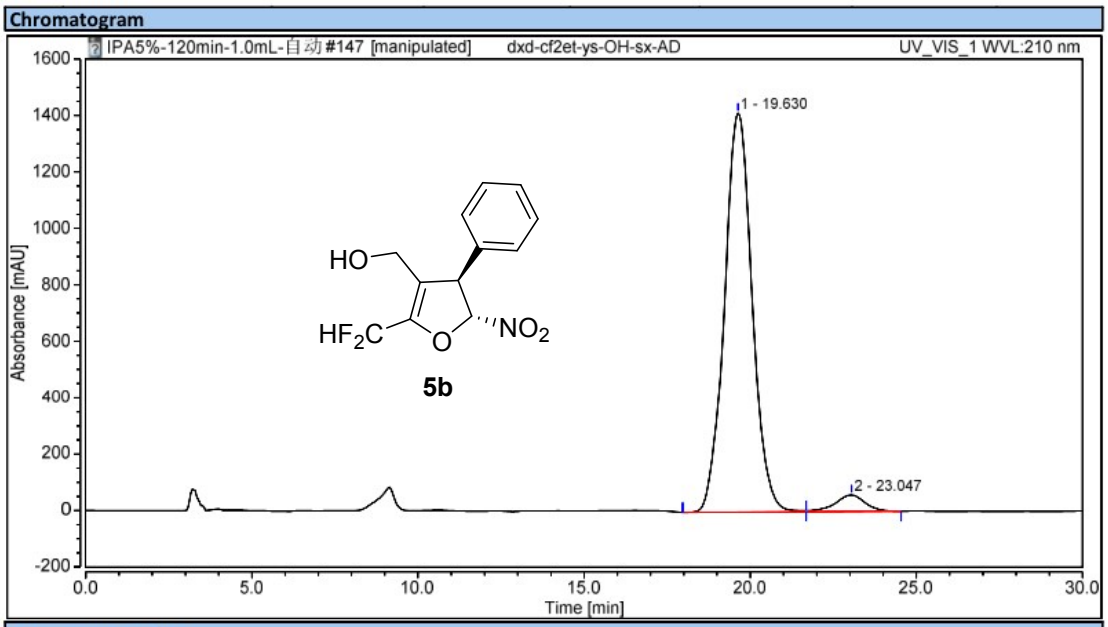


Chromatogram



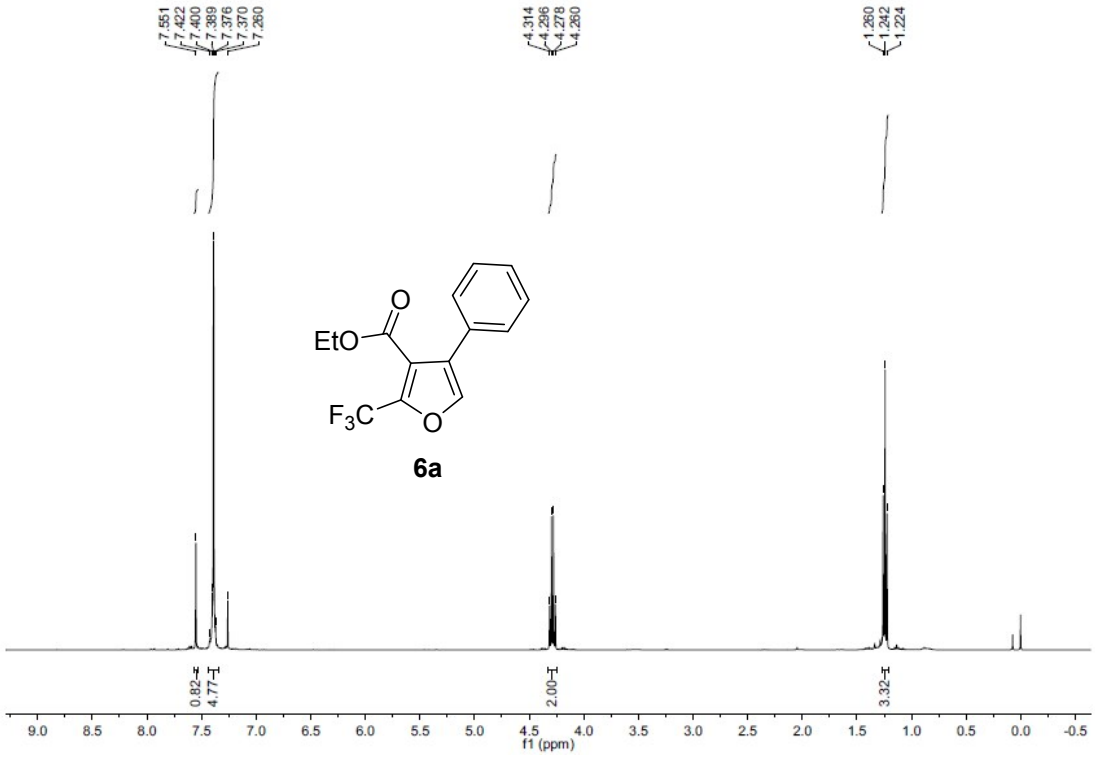
Integration Results

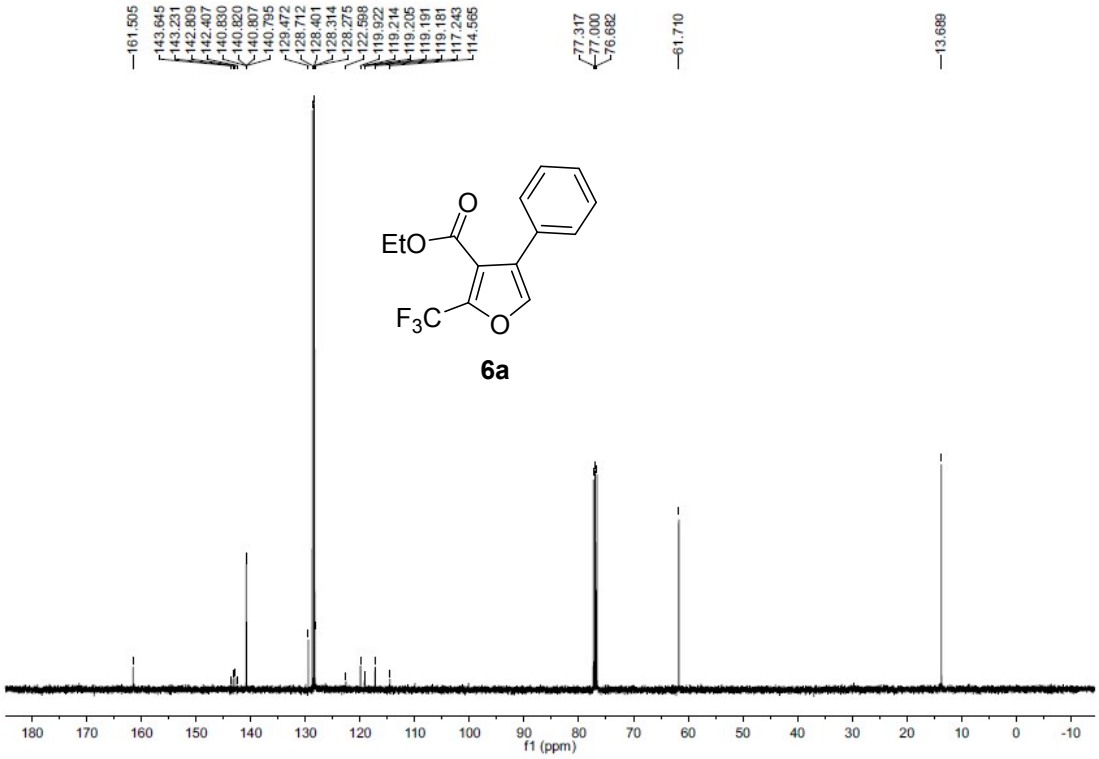
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		20.503	899.197	957.839	50.18	52.44	n.a.
2		23.940	892.767	868.743	49.82	47.56	n.a.
Total:			**1791.964**	**1826.582**	**100.00**	**100.00**	



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		19.630	1364.531	1413.408	95.70	96.02	n.a.
2		23.047	61.335	58.523	4.30	3.98	n.a.
Total:			**1425.866**	**1471.931**	**100.00**	**100.00**	

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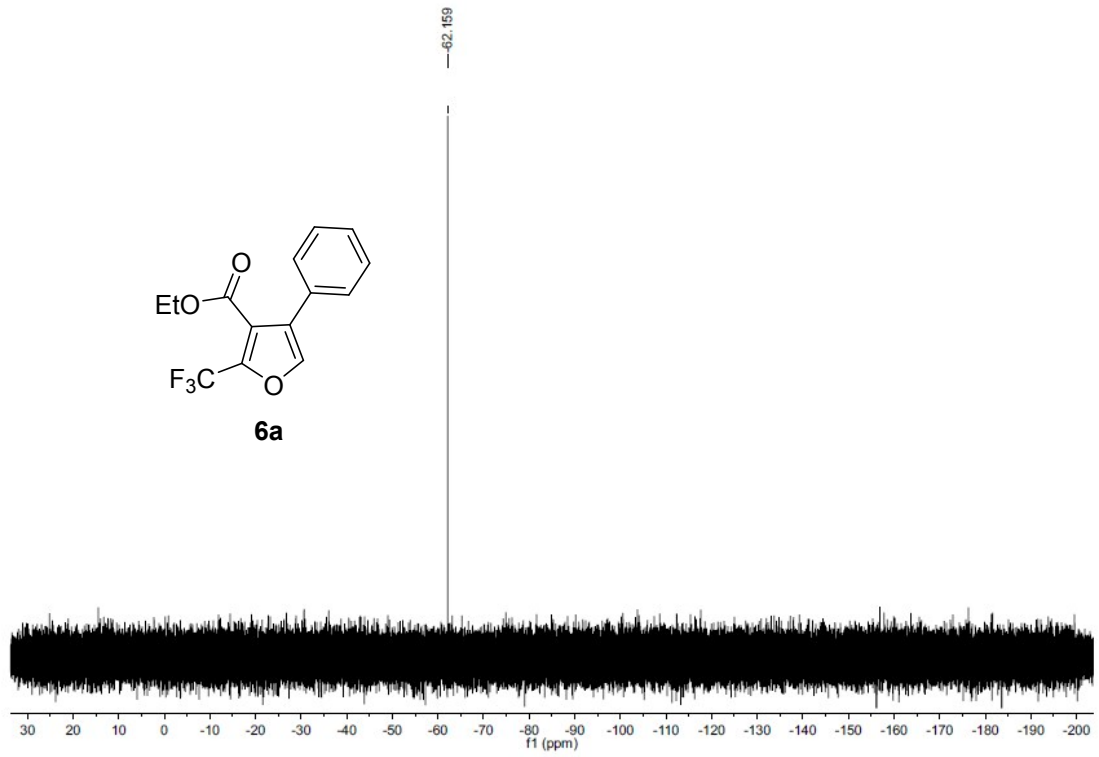
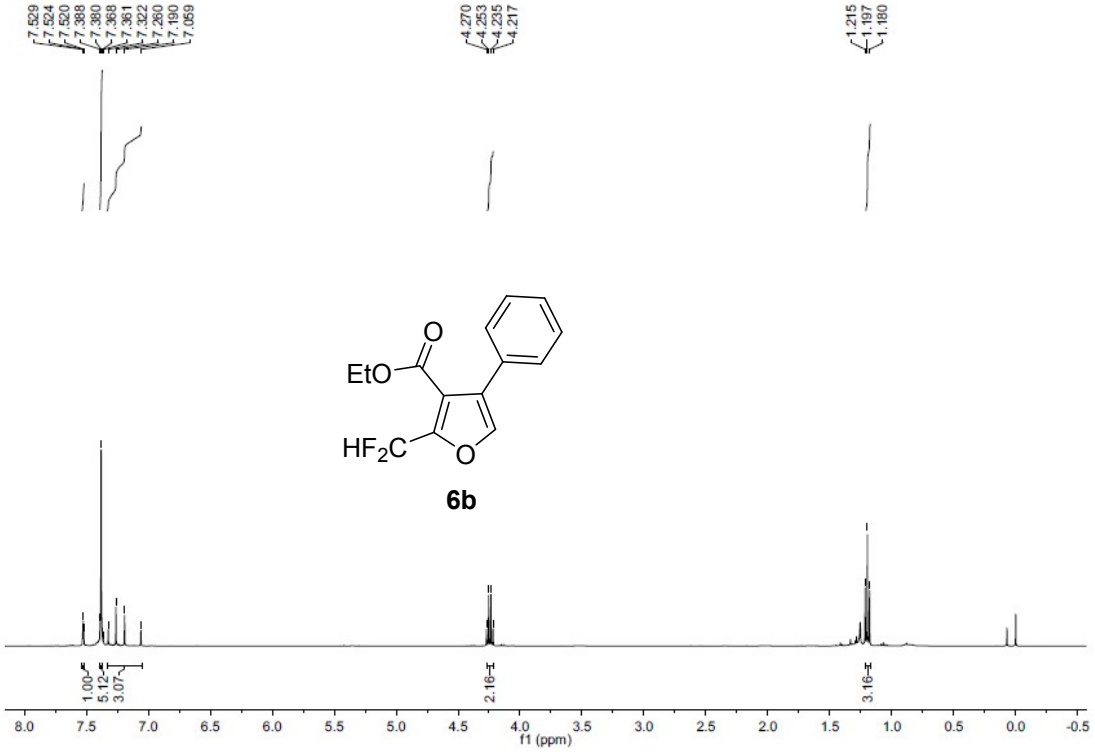
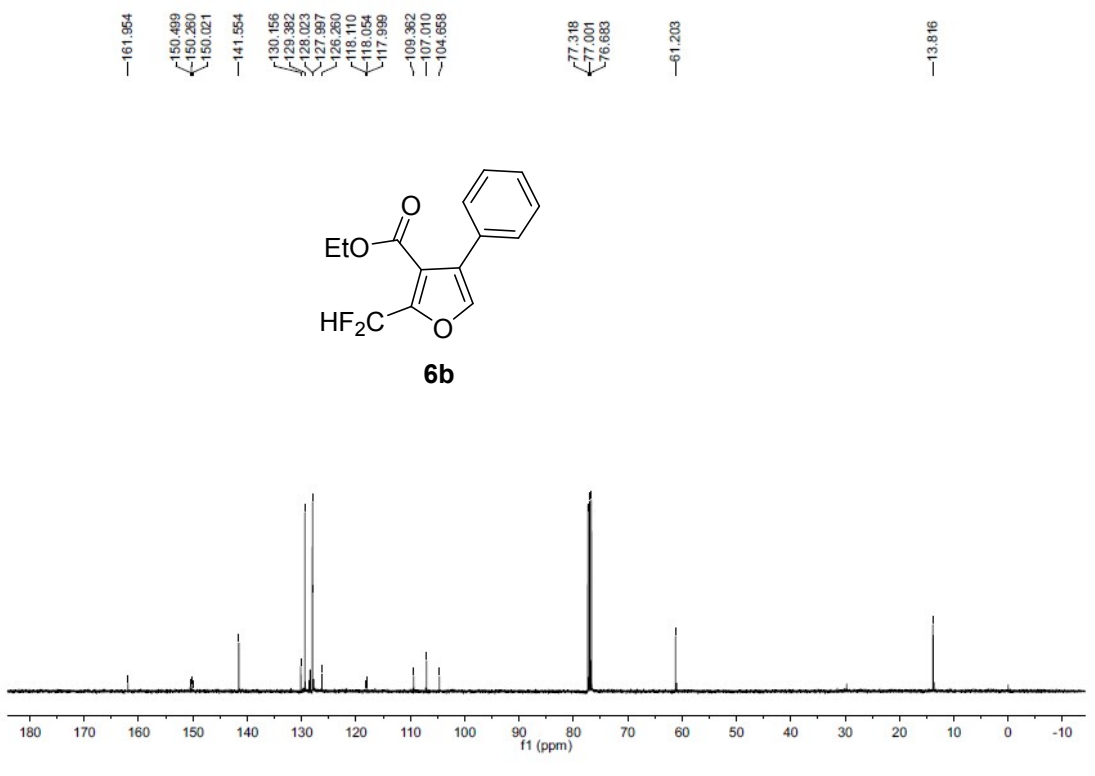
142.407
140.830
140.820
140.807
140.795
129.472
128.712
128.401
128.314
128.275
122.598
119.922
119.214
119.205
119.191
119.181
117.243
114.565
77.317
77.000
76.682
61.710
13.689
EtO
O
F3C
O
6a
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


62.159
EtO
O
F3C
O
6a
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)


7.529
7.524
7.520
7.388
7.380
7.368
7.361
7.322
7.260
7.190
7.059
4.270
4.253
4.235
4.217
1.215
1.197
1.180
EtO
O
HF2C
O
1.00
5.12
3.07
2.16
3.16
f1 (ppm)

6b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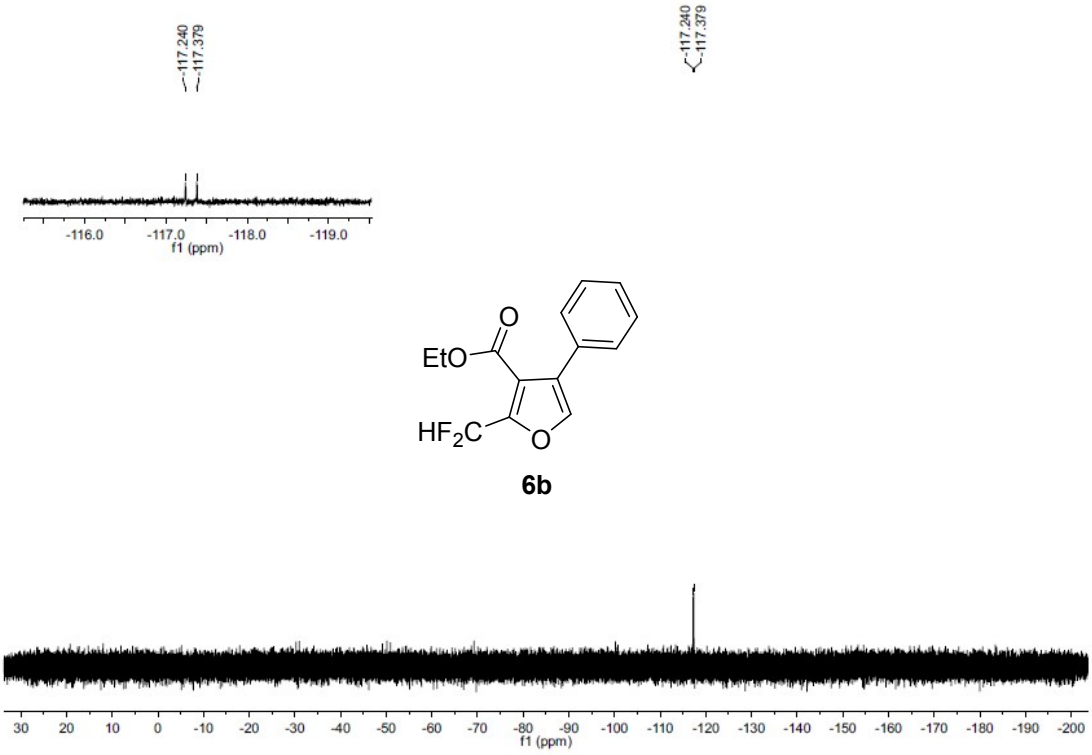
141.554
130.156
129.382
128.023
127.997
126.260
118.110
118.054
117.999
109.362
107.010
104.658
77.318
77.001
76.683
61.203
13.816
EtO
O
HF2C
O
f1 (ppm)

6b


-117.240
-117.379
-116.0
-117.0
-118.0
-119.0
f1 (ppm)
-117.240
-117.379
O
EtO
HF2C
O
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)

6b