Organocatalytic Atroposelective Fluorooxindole Addition to Coumarin Michael Acceptors

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1. General information

All commercially available reagents and solvents were used without further purification unless noted otherwise. The 3-fluorooxindoles were prepared via a three-step literature procedure.[1-5] The coumarins were prepared by a two-step procedure as described previously.[6] Catalysts were either commercially available or prepared according to literature procedures.[7-11] Solvents were stored over 4Å molecular sieves prior to use. Reaction products were purified by column chromatography on silica gel (particle size 32-63 μm) as described below. NMR spectra were obtained at 400 MHz (^{1}H NMR), 100 MHz (^{13}C NMR), and 376 MHz (^{19}F NMR) in CD_3CN or $CDCl_3$. Chemical shifts are reported in ppm relative to the deuterated solvent signal. All Michael addition reaction products were prepared in racemic form to develop a chiral HPLC method. The isolated asymmetric reaction products were then analyzed accordingly. HR-MS data were obtained using electron spray ionization time-of-flight (ESI-TOF) spectrometry. Single crystals were mounted under mineral oil on a Mitegen micromount. Data were collected on either a Bruker Apex Duo equipped with an APEXII CCD detector and Cu microfocus sealed source or Bruker D8 Quest equipped with a Photon 3 CMOS detector and Mo microfocus sealed source. Data were integrated with the Bruker SAINT program. Structure solution and refinement were performed using the SHELXTL/PC suite1 and ShelXle. Intensities were corrected for Lorentz and polarization effects and an empirical absorption correction was applied using Blessing's method as incorporated into the program SADABS. Non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were included in idealized positions.

2. Optimization studies

All optimization reactions were conducted at 0.09 mmol scale with 10 mol% of the catalyst, temperatures varying between -40 and 25 ºC, 1-5 equivalents of base and solvents typically used in organocatalysis.

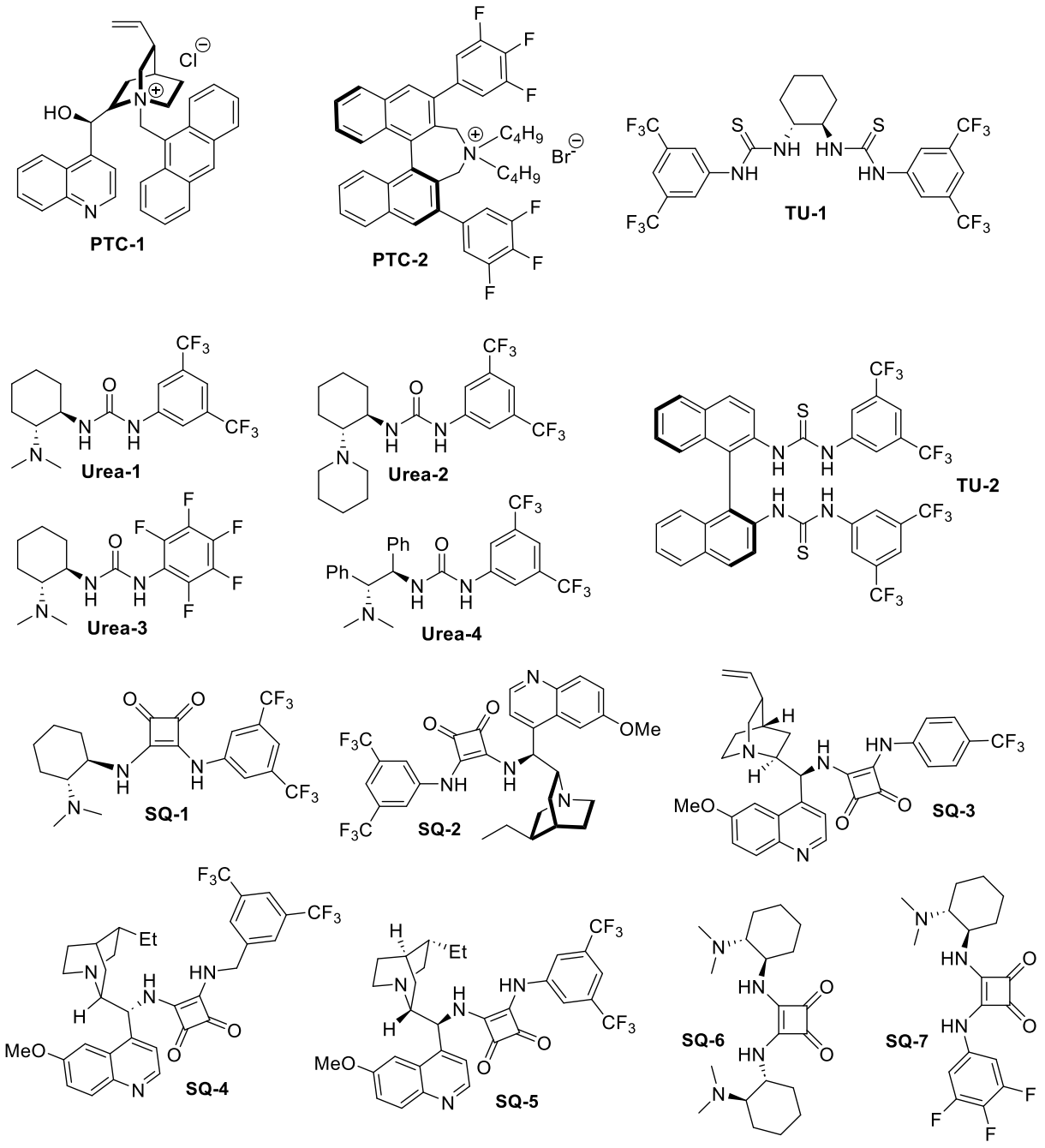
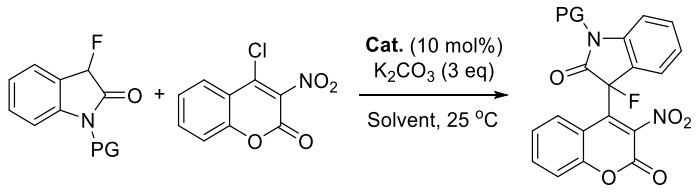


Figure S1. Catalysts used during optimization.

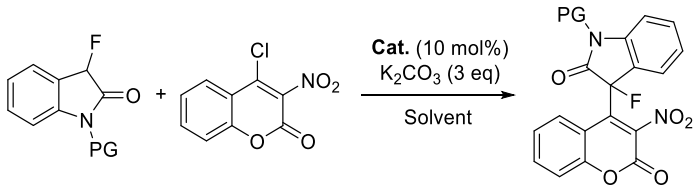
Table S1. Screening of catalysts.



Entry	PG	Time (h)	Solvent	Cat.	Conversion	*dr*	*ee*
1	Me	24	CH_2Cl_2	SQ-1	83%	20 : 1	80
2	Me	24	CH_2Cl_2	SQ-2	39%	20 : 1	83
3	Ph	48	Toluene/Ether (15:1)	SQ-3	70%	18 : 1	80
4	Ph	24	Toluene	SQ-4	99%	20 : 1	67
5	Ph	24	Toluene	SQ-5	87%	20 : 1	80
6	Ph	24	Toluene	SQ-6	30%	20 : 1	52
7	Ph	48	Toluene/Ether (15:1)	SQ-7	95%	20 : 1	0
8	Me	24	Toluene	TU-1	3%	20 : 1	n.d.
9	Me	24	Toluene	TU-2	0%	n.d.	n.d.
10	Me	24	Toluene	Urea-1	99%	20 : 1	79
11	Ph	48	Toluene/Ether (15:1)	Urea-2	73%	13 : 1	68
12	Ph	48	Toluene/Ether (15:1)	Urea-3	99%	13 : 1	22
13	Ph	48	Toluene/Ether (15:1)	Urea-4	60%	20 : 1	40
14	Me	24	Toluene	Urea-1, TBAB	48%	20 : 1	75
15	Me	24	Toluene	PTC-1, Urea-1	75%	20 : 1	70
16	Me	24	Toluene	PTC-2, Urea-1	31%	20 : 1	63
17	Me	24	Toluene	PTC-1	17%	20 : 1	0
18	Me	24	Toluene	TU-1	3%	20 : 1	n.d.
19	Me	24	CH_2Cl_2	SQ-1	83%	20 : 1	80
20	Me	24	CH_2Cl_2	SQ-2	39%	20 : 1	83
21	Me	24	CH_2Cl_2	Urea-1	83%	20 : 1	70

Reaction conditions: *N*-Methyl-3-fluoro-2-oxindole (0.09 mmol), 4-chloro-3-nitrocoumarin (0.1 mmol), potassium carbonate (3 eq) and 10 mol% of the catalyst were dissolved in 0.8 mL of the indicated solvent. Conversion determined by ^{1}H NMR spectroscopy. *dr* determined by ^{19}F NMR spectroscopy. *ee* determined by chiral HPLC. TBAB = tetrabutylammonium bromide. n.d. = not determined. PG = protecting group.

Table S2. Screening of solvents.



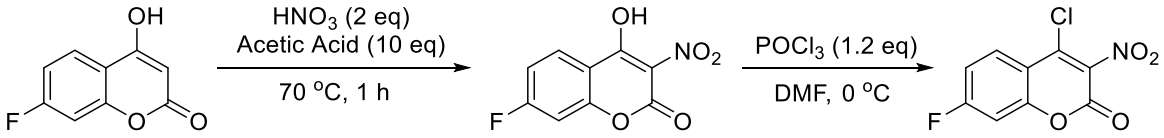
Entry	PG	Temp. (°C)	Time (h)	Solvent	Cat.	Conversion	*dr*	*ee*
1	Me	25	24	Toluene[a]	Urea-1	40%	20 : 1	71
2	Me	25	24	Toluene[b]	Urea-1	99%	20 : 1	77
3	Me	25	24	Xylenes	Urea-1	39%	20 : 1	80
4	Me	25	12	Mesitylene	SQ-2	42%	20 : 1	60
5	Me	0	24	Toluene/Ether (15:1)	Urea-1	25%	20 : 1	n.d.
6	Me	14	24	Toluene/Ether (15:1)	Urea-1	74%	20 : 1	79
7	Me	0	36	Toluene/Ether (15:1)	Urea-1	33%	20 : 1	73
8	Ph	25	24	CH_2Cl_2[c]	SQ-2	58%	20 : 1	75
9	Ph	25	24	Toluene/Ether (15:1)	Urea-1	70%	20 : 1	73
10	Ph	25	72	Toluene/Ether (1:1)[d]	Urea-1	95%	20 : 1	84
11[e]	Ph	25	24	Toluene/Ether (15:1)	Urea-1	68%	20 : 1	79
12[f]	Ph	25	24	Toluene/Ether (15:1)	Urea-1	30%	20 : 1	75
13[g]	Ph	25	18	Toluene	Urea-1	99%	20 : 1	70
14[h]	Ph	25	24	Toluene	Urea-1	75%	20 : 1	65
15	Ph	25	24	Toluene/Ether (15:1)	Urea-1	99%	20 : 1	77
16	Ph	-40	72	Toluene/Ether (15:1)	Urea-1	22%	20 : 1	79
17	Ph	25	48	Toluene/Ether (15:1)	Urea-1	72%	15 : 1	77
18	Me	0	24	Toluene/Ether (15:1)	Urea-1	38%	20 : 1	77
19	Me	25	24	Toluene/Ether (7:1)	Urea-1	77%	20 : 1	77
20	Me	25	24	Toluene/Ether (31:1)	Urea-1	56%	20 : 1	79
21	Me	25	48	Toluene/Pentane (1:1)	Urea-1	99%	20 : 1	96
22	Me	25	48	Toluene/Pentane (1:1)[d]	Urea-1	99%	20 : 1	94
23	Me	25	24	Toluene	Urea-1	99%	20 : 1	79
24	Me	25	24	Mesitylene	Urea-1	45%	20 : 1	81
25	Me	25	24	Chlorobenzene	Urea-1	79%	20 : 1	77
26	Me	-40	48	Xylene	Urea-1	73%	20 : 1	80
27	Me	25	24	Trifluorotoluene	Urea-1	37%	20 : 1	72
28	Me	25	24	Toluene/Ether (15:1)	Urea-1	99%	20 : 1	71
29	Me	-40	72	Toluene/Ether (15:1)	Urea-1	50%	20 : 1	75
30	Me	25	24	Toluene/Pentane (19:1)	Urea-1	82%	30 : 1	97
31	Me	25	48	Toluene/Pentane (19:1)	Urea-1	99%	30 : 1	97
32	Me	-40	48	CH_2Cl_2	SQ-2	38%	20 : 1	60

Reaction conditions: *N*-Methyl-3-fluoro-2-oxindole (0.09 mmol), 4-chloro-3-nitrocoumarin (0.1 mmol), potassium carbonate (3 eq) and 10 mol% of the catalyst were dissolved in 0.8 mL of the indicated solvent unless stated otherwise. [a]1.6 mL toluene used. [b]0.4 mL toluene used. [c]0.5 mL CH_2Cl_2 used. [d]0.6 mL solvent used. [e]2.0 eq potassium carbonate used. [f]1.2 eq potassium carbonate used. [g]1.0 eq potassium carbonate used. [h]3.0 eq cesium carbonate used. Conversion determined by ^{1}H NMR spectroscopy. *dr* determined by ^{19}F NMR spectroscopy. *ee* determined by chiral HPLC. Entries 7,14: molecular sieves added. n.d. = not determined. PG = protecting group.

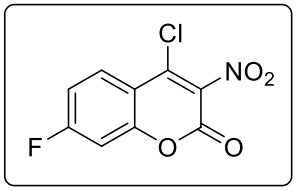
3. Synthesis procedures and compound characterization

3.1. Synthesis of coumarins

A previously unreported coumarin (4-chloro-7-fluoro-3-nitrocoumarin) was prepared as described below. All other coumarins were synthesized following literature procedures.[6]



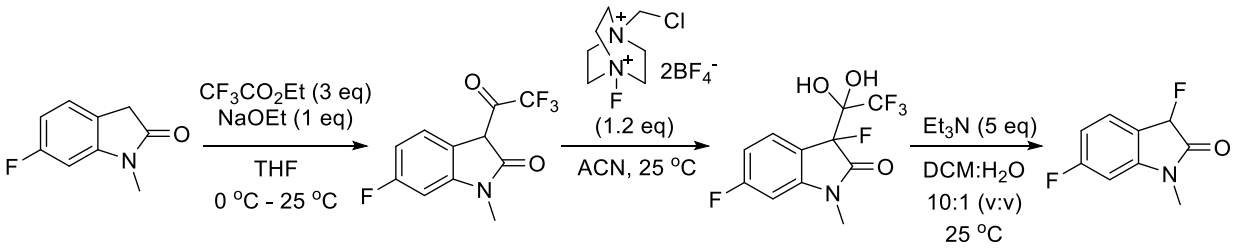
In a 3-neck flask, nitric acid (0.28 mL, 4.4 mmol) and glacial acetic acid (1.2 mL, 22.2 mmol) were combined and allowed to stir at room temperature for 10 minutes. 7-Fluoro-4-hydroxycoumarin (400.0 mg, 2.2 mmol) was then added and the resulting mixture was stirred for 1 hour. Upon completion of the reaction, the mixture was poured onto ice water and 7-fluoro-4-hydroxy-3-nitrocoumarin (425.0 mg, 1.9 mmol) was isolated in 85% yield as a yellow solid via vacuum filtration. This material was applied in the next step without further purification. Phosphorous oxychloride (0.21 mL, 2.3 mmol) was added dropwise to dimethylformamide (2.0 mL) at 0 ^{o}C under inert atmosphere and the mixture was allowed to stir for 10 minutes. 7-Fluoro-4-hydroxy-3-nitrocoumarin (425.0 mg, 1.9 mmol) was then added and the reaction was stirred at room temperature for 6 hours. Upon completion, the resulting mixture was poured onto ice water and 7-fluoro-4-chloro-3-nitrocoumarin (350 mg, 1.4 mmol) was isolated as an orange solid via vacuum filtration in 71% yield.



^{1}H NMR (400 MHz, CD_3CN) δ 8.11 (dd, *J* = 8.8, 5.8 Hz, 1H), 7.47–7.29 (m, 2H). $^{13}C\{^{1}H\}$ NMR (100 MHz, CD_3CN) δ 166.53 (d, *J* = 257.1 Hz), 161.65, 153.07 (d, *J* = 14.0 Hz), 152.45, 141.90, 129.78 (d, *J* = 11.1 Hz), 114.50 (d, *J* = 23.5 Hz), 113.31 (d, *J* = 2.7 Hz), 104.87 (d, *J* = 27.0 Hz). ^{19}F NMR (376 MHz, CD_3CN) δ -101.48 (m). HR-MS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_9H_3ClFNO_4$ 243.9807, found 243.9809.

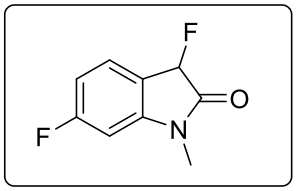
3.2. Synthesis of fluorooxindoles

Two previously unreported fluorooxindoles (*N*-methyl-6-fluoro-3-fluorooxindole, *N*-methyl-5-cyano-3-fluorooxindole) were prepared as described below. All other fluorooxindoles were synthesized following literature procedures.[1-5]

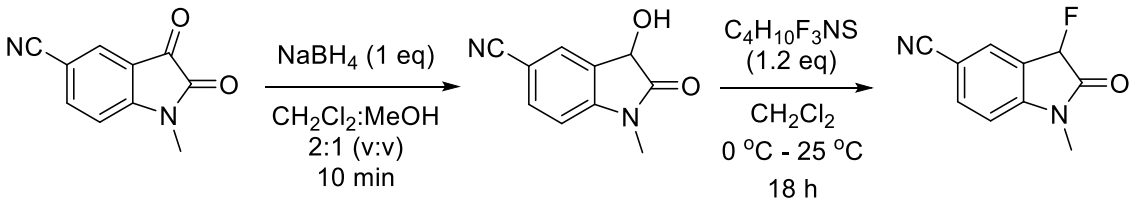


An oven-dried 3-neck flask was flushed with nitrogen before adding *N*-methyl-6-fluoro-2-oxindole (450.0 mg, 2.7 mmol) and sodium ethoxide (185.4 mg, 2.7 mmol) in dry tetrahydrofuran (3.0 mL) at room temperature. The resulting mixture was allowed to stir for 30 minutes before trifluoroethyl acetate (0.98 mL, 8.2 mmol) was added dropwise at 0 °C. The mixture was then allowed to stir at 25 °C for 18 hours before quenching with 1M HCl and extracting with ethyl acetate and water. The combined organic layers were dried over sodium

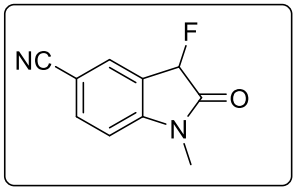
sulfate, filtered and concentrated under vacuum to isolate the crude trifluoroacetyl compound. This material was used without further purification. It was dissolved in dry acetonitrile (4.0 mL) under nitrogen atmosphere and Selectfluor (867.5 mg, 2.4 mmol) was added at 25 °C. After 18 hours, the mixture was extracted with ethyl acetate and brine. The combined organic layers were dried over sodium sulfate and the crude fluorinated compound (3,6-difluoro-*N*-methyl-3-(2,2,2-trifluoro-1,1-dihydroxyethyl)-2-oxindole) was isolated and dissolved in dichloromethane:water (5.0 mL : 0.5 mL). Triethylamine (1.14 mL, 8.17 mmol) was added and the resulting mixture was allowed to stir at room temperature for 3 hours after which it was extracted with dichloromethane and water. The combined organic layers were dried over sodium sulfate and the residue was purified by column chromatography using 2% ethyl acetate/hexane as the mobile phase.



N-Methyl-3,6-difluoro-2-oxindole was obtained as a white solid (250.0 mg, 1.4 mmol) in 50% yield over all steps from *N*-methyl-6-fluoro-2-oxindole (450.0 mg, 2.7 mmol) following the procedure described above. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (m, 1H), 6.71 (m, 1H), 6.54 (d, J = 8.7, 1H), 5.58 (d, J = 51.3 Hz, 1H), 3.13 (s, 3H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 171.37, 171.19, 164.94 (d, J = 249.9 Hz), 127.61 (d, J = 10.8 Hz), 118.18 (d, J = 17.1 Hz), 109.44 (dd, J = 22.5, 3.0 Hz), 97.82 (dd, J = 27.8, 1.6 Hz), 84.77 (d, J = 188.7 Hz), 26.34. ^{19}F NMR (376 MHz, $CDCl_3$) δ -106.68 (m), -191.58 (dd, J = 52.4, 5.5 Hz). HR-MS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_9H_7F_2NO$ 184.0568, found 184.0569.



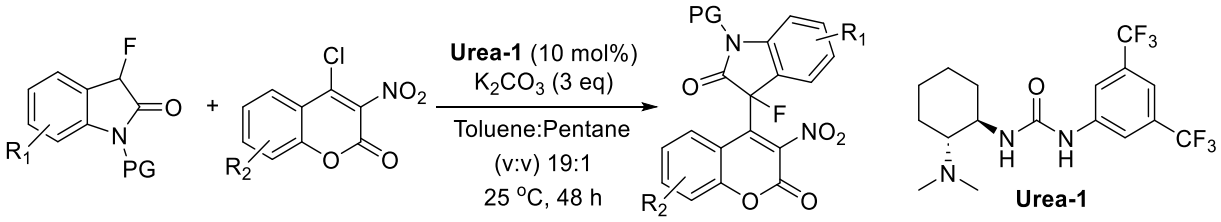
N-Methyl-5-cyanoisatin (215.0 mg, 1.1 mmol) was added to a solution of sodium borohydride (41.6 mg, 1.1 mmol) in dichloromethane:methanol (4.0 mL : 2.0 mL) at 0 °C. The resulting mixture was stirred for 10 minutes and extracted with dichloromethane and water. The combined organic layers were dried over sodium sulfate, filtered and concentrated under vacuum to give crude *N*-methyl-5-cyano-3-hydroxy-2-oxindole (206.5 mg, 1.1 mmol). To this material was added diethylaminosulfur trifluoride (0.17 mL, 1.3 mmol) in dry acetonitrile (2.0 mL) at 0 °C under nitrogen atmosphere. The resulting mixture was left to warm to room temperature overnight. After 18 hours, the reaction was extracted with dichloromethane and water. The combined organic layers were dried over sodium sulfate and the residue was purified by column chromatography using 10% ethyl acetate in hexane as the mobile phase.



N-Methyl-5-cyano-3-fluorooxindole was obtained as a white solid (50.0 mg, 0.26 mmol) in 25% yield from *N*-methyl-5-cyanoisatin (215.0 mg, 1.1 mmol) following the procedure described above. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71-7.73 (m, 2H), 6.92 (d, J = 7.5 Hz, 1H), 5.68 (d, J = 50.5 Hz, 1H), 3.22 (s, 3H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ170.52 (d, J = 18.1 Hz), 148.42 (d, J = 4.6 Hz), 136.54 (d, J = 3.0 Hz), 129.40 (d, J = 1.3 Hz), 123.65 (d, J = 16.4 Hz), 118.25, 109.34, 106.77 (d, J = 2.7 Hz), 84.07 (d, J = 191.8 Hz), 26.51. ^{19}F NMR (376 MHz, $CDCl_3$) δ -

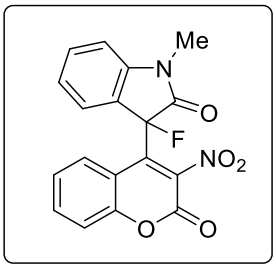
194.76 (d, *J*= 50.4 Hz). HR-MS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{10}H_7FN_2O$ 191.0615, found 191.0618.

3.3. Asymmetric organocatalytic synthesis



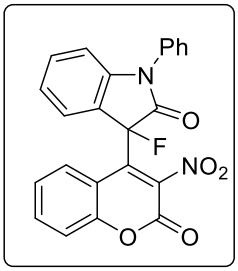
General procedure

Fluorooxindole (0.09 mmol), coumarin (1.1 eq, 0.1 mmol), potassium carbonate (3 eq, 0.27 mmol), and **Urea-1** (10 mol%) were combined in an oven-dried vial under nitrogen. Anhydrous toluene (380 μL) and anhydrous pentane (20 μL) were added and the resulting mixture was stirred at 25 ºC for 48 hours. Upon completion, the reaction mixture was placed in a centrifuge to remove any precipitates before extraction with dichloromethane and water. The combined organic layers were dried over sodium sulfate, concentrated and purified via column chromatography as described below.



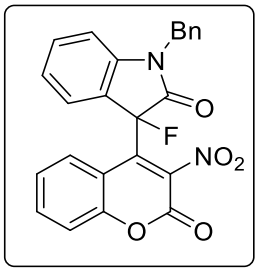
Compound **3a** was obtained as a white crystalline solid in 81% yield (26.0 mg, 0.07 mmol) from *N*-methyl-3-fluoro-2-oxindole (15.0 mg, 0.09 mmol) and 4-chloro-3-nitrocoumarin (22.6 mg, 0.1 mmol) following the general procedure described above after purification by flash chromatography using hexanes:ethyl acetate (1:1) as the mobile phase. The *dr* was determined as

30:1 using ^{19}F NMR spectroscopy. The *ee* was determined by chiral HPLC ((*S,S)*-Whelk-O 1, dichoromethane/hexanes 70:30, flow rate 1 mL/min, λ=254 nm) as 97%, t_R (major) =6.3 min, t_R (minor) =5.5 min. ^1H NMR (400 MHz, CD_3CN) δ 7.60-7.69 (m, 2H), 7.56 (m, 1H), 7.45 (d, *J*= 8.4 Hz, 1H), 7.17-7.26 (m, 3H), 6.95 (m, 1H), 3.36 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, CD_3CN) δ 168.16 (d, *J* = 21.2 Hz), 153.99, 151.97, 144.68, 138.45, 138.20, 134.41, 134.29 (d, *J* = 24.2 Hz), 126.24, 125.07, 125.03, 124.23, 123.22 (d, *J* = 17.1 Hz), 118.00, 113.54, 111.24 (d, *J* = 20.0 Hz), 92.26 (d, *J* = 186.6 Hz), 26.73 (d, *J* = 11.3 Hz). ^{19}F NMR (376 MHz, CD_3CN) δ -147.78. HR-MS (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_{18}H_{11}FN_2O_5Na$ 377.0544, found 377.0546.

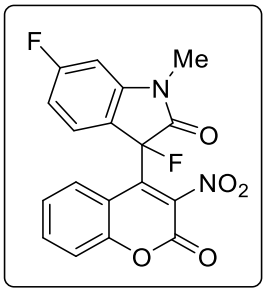


Compound **3b** was obtained as a white crystalline solid in 80% yield (30.0 mg, 0.07 mmol) from *N*-phenyl-3-fluoro-2-oxindole (20.4 mg, 0.09 mmol) and 4-chloro-3-nitrocoumarin (22.6 mg, 0.1 mmol) following the general procedure described above after purification by flash chromatography using hexanes:ethyl acetate (1:1) as the mobile phase. The *dr* was determined as 20:1 using ^{19}F NMR spectroscopy. The *ee* was determined by chiral HPLC ((*S,S)*-Whelk-O 1, dichoromethane/hexanes 70:30, flow rate 1 mL/min, λ=254 nm) as 95%, t_R (major) =6.2 min, t_R (minor) =4.8 min. ^1H NMR (400 MHz, CD_3CN) δ 7.78–7.64 (m, 4H), 7.60-7.55 (m, 4H), 7.51 (d, *J* = 8.4 Hz, 1H), 7.35 (m, 1H), 7.31–7.19 (m, 2H), 7.06 (d, *J* = 8.1 Hz, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, CD_3CN) δ 167.68 (d, *J* = 21.5 Hz), 153.94, 152.05, 144.54 (d, *J* = 5.3 Hz), 138.17, 134.44, 134.17 (d, *J* = 4.6 Hz), 132.74, 130.13, 129.41, 126.95 (d, *J* = 2.8 Hz), 126.78, 126.52, 126.26, 125.11 (d, *J* = 4.1 Hz), 124.84, 122.99, 122.82, 118.11, 113.60 (d, *J* = 5.0 Hz), 112.03 (d,

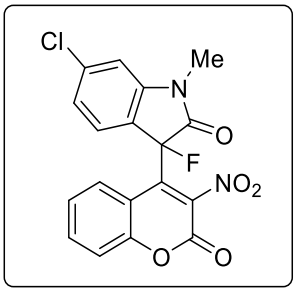
J = 2.8 Hz), 92.36 (d, J = 187.3 Hz). ^{19}F NMR (376 MHz, CD_3CN) δ -146.11. HR-MS (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_{23}H_{13}FN_2O_5Na$ 439.0701, found 439.0703.



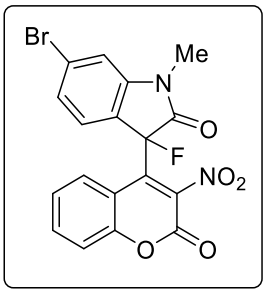
Compound **3c** was obtained as a white crystalline solid in 81% yield (31.4 mg, 0.07 mmol) from *N*-benzyl-3-fluoro-2-oxindole (21.6 mg, 0.09 mmol) and 4-chloro-3-nitrocoumarin (22.6 mg, 0.1 mmol) following the general procedure described above after purification by flash chromatography using hexanes:ethyl acetate (1:1) as the mobile phase. The *dr* was determined as 31:1 using ^{19}F NMR spectroscopy. The *ee* was determined by chiral HPLC ((*S,S)*-Whelk-O 1, dichoromethane/hexanes 70:30, flow rate 1 mL/min, λ=254 nm) as 84%, t_R (major) =4.8 min, t_R (minor) =4.3 min. ^{1}H NMR (400 MHz, CD_3CN) δ 7.54-7.65 (m, 3H), 7.38-7.48 (m, 6H), 7.29 (d, J = 7.6 Hz, 1H), 7.17 (m, 1H), 6.93 (m, 1H), 6.77 (d, J = 8.3 Hz, 1H), 5.05 (s, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, CD_3CN) δ 168.22 (d, J = 21.4 Hz), 153.94, 151.95 (d, J = 1.6 Hz), 143.61 (d, J = 5.3 Hz), 138.08 (d, J = 24.5 Hz), 134.93, 134.30, 134.02 (d, J = 4.6 Hz), 129.10, 128.37, 128.21, 126.74 (d, J = 2.7 Hz), 125.78, 125.02, 124.58 (d, J = 3.8 Hz), 123.40, 123.23, 117.93, 113.42 (d, J = 4.9 Hz), 111.70 (d, J = 2.8 Hz), 92.30 (d, J = 186.7 Hz), 44.34. ^{19}F NMR (376 MHz, CD_3CN) δ -147.21. HR-MS (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_{24}H_{15}FNO_4Na$ 453.0854, found 453.0857.



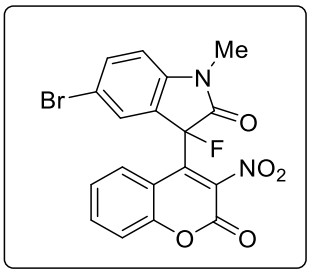
Compound **3d** was obtained as a yellow crystalline solid in 77% yield (25.8 mg, 0.07 mmol) from *N*-methyl-6-fluoro-3-fluoro-2-oxindole (16.4 mg, 0.09 mmol) and 4-chloro-3-nitrocoumarin (22.6 mg, 0.1 mmol) following the general procedure described above after purification by flash chromatography using hexanes:ethyl acetate (1:1) as the mobile phase. The *dr* was determined as 20:1 using ^{19}F NMR spectroscopy. The *ee* was determined by chiral HPLC ((*S,S)*-Whelk-O 1, dichoromethane/hexanes 60:40, flow rate 1 mL/min, λ=254 nm) as 80%, t_R (major) =8.0 min, t_R (minor) =6.6 min. ^{1}H NMR (400 MHz, CD_3CN) δ 7.68 (m, 1H), 7.58 (m, 1H), 7.47 (d, *J* = 8.4 Hz, 1H), 7.26 (m 1H), 7.08 (d, *J* = 9.1 Hz, 1H), 7.00–6.84 (m, 2H), 3.35 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, CD_3CN) δ 168.44 (d, *J* = 21.5 Hz), 166.19 (d, *J* = 246.1 Hz), 153.94, 151.97 (d, *J* = 1.6 Hz), 147.02 (d, *J* = 17.9 Hz), 137.87, 134.37, 128.53 (dd, *J* = 10.9, 2.5 Hz), 126.23, 125.02, 118.84, 117.90, 117.32, 113.43 (d, *J* = 4.9 Hz), 110.55 (dd, *J* = 23.5, 3.8 Hz), 100.33 (dd, *J* = 29.0, 2.7 Hz), 91.58 (d, *J* = 186.9 Hz), 27.02. ^{19}F NMR (376 MHz, CD_3CN) δ -104.58 (m), -146.39 (d, *J* = 8.3 Hz). HR-MS (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_{18}H_{10}F_2N_2O_5Na$ 395.0450, found 395.0449.



Compound **3e** was obtained as a yellow crystalline solid in 81% yield (28.3 mg, 0.07 mmol) from *N*-methyl-6-chloro-3-fluoro-2-oxindole (17.9 mg, 0.09 mmol) and 4-chloro-3-nitrocoumarin (22.6 mg, 0.1 mmol) following the general procedure described above after purification by flash chromatography using hexanes:ethyl acetate (1:1) as the mobile phase. The *dr* was determined as 24:1 using ^{19}F NMR spectroscopy. The *ee* was determined by chiral HPLC ((*S,S)*-Whelk-O 1, dichoromethane/hexanes 60:40, flow rate 1 mL/min, λ=254 nm) as 90%, t_R (major) =7.6 min, t_R (minor) =6.1 min. ^{1}H NMR (400 MHz, CD_3CN) δ 7.69 (m, 1H), 7.52 (d, *J* = 8.0 Hz, 1H), 7.49 (m, 1H), 7.33 (s, 1H), 7.26 (m, 1H), 7.20 (m, 1H), 6.92 (d, *J* = 8.2, 1H), 3.35 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, CD_3CN) δ 168.03, 153.91, 151.96 (d, *J* = 1.8 Hz), 146.08 (d, *J* = 5.2 Hz), 139.44 (d, *J* = 5.2 Hz), 137.79 (d, *J* = 24.4 Hz), 134.40, 127.63 (d, *J* = 2.7 Hz), 126.26, 125.00, 124.14 (d, *J* = 3.8 Hz), 121.63 (d, *J* = 17.2 Hz), 117.91, 113.38 (d, *J* = 4.9 Hz), 112.12 (d, *J* = 2.7 Hz), 110.00, 91.57 (d, *J* = 187.3 Hz), 27.00. ^{19}F NMR (376 MHz, CD_3CN) δ -147.56. HR-MS (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_{18}H_{10}ClFN_2O_5Na$ 411.0154, found 411.0154.

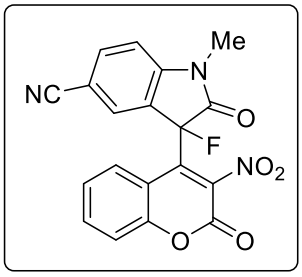


Compound **3f** was obtained as a yellow crystalline solid in 75% yield (29.2 mg, 0.07 mmol) from *N*-methyl-6-bromo-3-fluoro-2-oxindole (21.9 mg, 0.09 mmol) and 4-chloro-3-nitrocoumarin (22.6 mg, 0.1 mmol) following the general procedure described above after purification by flash chromatography using hexanes:ethyl acetate (1:1) as the mobile phase. The *dr* was determined as 26:1 using ^{19}F NMR spectroscopy. The *ee* was determined by chiral HPLC ((*S,S)*-Whelk-O 1, dichoromethane/hexanes 70:30, flow rate 1 mL/min, λ=254 nm) as 81%, t_R (major) =7.3 min, t_R (minor) =5.9 min. ^{1}H NMR (400 MHz, CD_3CN) δ 7.69 (m, 1H), 7.44-7.49 (m, 3H), 7.36 (m, 1H), 7.26 (m, 1H), 6.92 (d, *J*= 8.2 Hz, 1H), 3.35 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, CD_3CN) δ 168.03 (d, *J* = 21.4 Hz), 153.90, 151.96 (d, *J* = 1.6 Hz), 146.00 (d, *J* = 5.2 Hz), 137.75 (d, *J* = 24.6 Hz), 134.41 (d, *J* = 13.2 Hz), 127.56 (d, *J* = 5.4 Hz), 126.27 (d, *J* = 11.9 Hz), 124.99, 122.11 (d, *J* = 17.4 Hz), 117.91 (d, *J* = 15.1 Hz), 115.01, 114.85, 113.37 (d, *J* = 4.9 Hz), 91.64 (d, *J* = 187.2 Hz), 27.00 (d, *J* = 8.5 Hz). ^{19}F NMR (376 MHz, CD_3CN) δ -147.92. HR-MS (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_{18}H_{10}BrFN_2O_5Na$ 454.9649, found 454.9651.



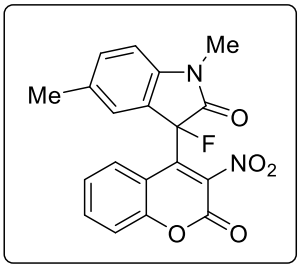
Compound **3g** was obtained as a yellow crystalline solid in 78% yield (30.4 mg, 0.07 mmol) from *N*-methyl-5-bromo-3-fluoro-2-oxindole (21.9 mg, 0.09 mmol) and 4-chloro-3-

nitrocoumarin (22.6 mg, 0.1 mmol) following the general procedure described above after purification by flash chromatography using hexanes:ethyl acetate (1:1) as the mobile phase. The *dr* was determined as 28:1 using ^{19}F NMR spectroscopy. The *ee* was determined by chiral HPLC ((*S,S)*-Whelk-O 1, dichoromethane/hexanes 70:30, flow rate 1 mL/min, λ=254 nm) as 85%, t_R (major) =6.5 min, t_R (minor) =5.5 min. ^1H NMR (400 MHz, CD_3CN) δ 7.78 (m, 1H), 7.67-7.71 (m, 2H), 7.48 (d, *J*= 8.6 Hz, 1H), 7.26 (m, 1H), 7.17 (d, *J*= 8.4 Hz, 1H), 6.88-6.97 (m, 1H), 3.35 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, CD_3CN) δ 167.66 (d, *J* = 21.3 Hz), 153.91, 151.96 (d, *J* = 1.8 Hz), 143.92 (d, *J* = 5.1 Hz), 137.64, 137.40, 134.46, 129.31 (d, *J* = 2.7 Hz), 126.30, 124.93, 117.92, 115.94 (d, *J* = 4.4 Hz), 113.32 (d, *J* = 4.9 Hz), 113.21 (d, *J* = 2.6 Hz), 91.64 (d, *J* = 187.8 Hz), 26.96. ^{19}F NMR (376 MHz, CD_3CN) δ -148.79. HR-MS (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_{18}H_{10}BrFN_2O_4Na$ 454.9649, found 454.9648.

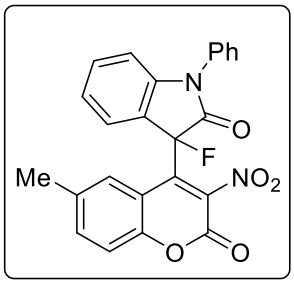


Compound **3h** was obtained as a yellow crystalline solid in 78% yield (26.6 mg, 0.07 mmol) from *N*-methyl-5-cyano-3-fluoro-2-oxindole (17.0 mg, 0.09 mmol) and 4-chloro-3-nitrocoumarin (22.6 mg, 0.1 mmol) following the general procedure described above after purification by flash chromatography using hexanes:ethyl acetate (1:1) as the mobile phase. The *dr* was determined as 16:1 using ^{19}F NMR spectroscopy. The *ee* was determined by chiral HPLC ((*S,S)*-Whelk-O 1, dichoromethane/hexanes 80:20, flow rate 1 mL/min, λ=254 nm) as 82%, t_R (major) =5.9 min, t_R (minor) =5.4 min. ^1H NMR (400 MHz, CD_3CN) δ 7.98 (m, 1H), 7.86 (dd, *J* = 3.1, 1.7 Hz, 1H), 7.70 (m 1H), 7.49 (dd, *J* = 8.5, 1.2 Hz, 1H), 7.38 (m, 1H), 7.26 (m, 1H), 6.86 (dd, *J* = 8.2, 1.3

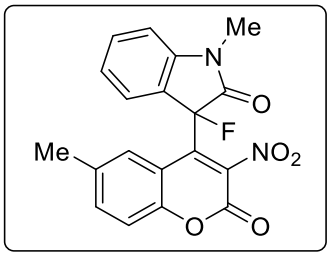
Hz, 1H), 3.40 (s, 3H). $^{13}C\{^{1}H\}$ NMR (100 MHz, CD_3CN) δ 167.95 (d, J = 21.3 Hz), 153.84, 151.95 (d, J = 1.6 Hz), 148.40 (d, J = 4.8 Hz), 138.85 (d, J = 4.1 Hz), 137.09 (d, J = 24.0 Hz), 134.54, 130.13 (d, J = 2.7 Hz), 126.36, 124.84, 123.74 (d, J = 17.3 Hz), 117.96, 113.17 (d, J = 4.9 Hz), 112.25 (d, J = 2.5 Hz), 107.27 (d, J = 3.8 Hz), 91.01 (d, J = 188.1 Hz), 78.15, 27.20. ^{19}F NMR (376 MHz, CD_3CN) δ -149.32. HR-MS (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_{19}H_{10}FN_3O_5Na$ 402.0497, found 402.0499.



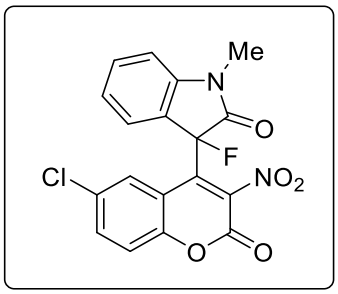
Compound **3i** was obtained as a yellow crystalline solid in 78% yield (25.9 mg, 0.07 mmol) from *N*-methyl-5-methyl-3-fluoro-2-oxindole (16.0 mg, 0.09 mmol) and 4-chloro-3-nitrocoumarin (22.6 mg, 0.1 mmol) following the general procedure described above after purification by flash chromatography using hexanes:ethyl acetate (1:1) as the mobile phase. The *dr* was determined as 27:1 using ^{1}H NMR spectroscopy. The *ee* was determined by chiral HPLC ((*S,S)*-Whelk-O 1, dichoromethane/hexanes 70:30, flow rate 1 mL/min, λ=254 nm) as 80%, t_R (major) =6.0 min, t_R (minor) =5.0 min. ^{1}H NMR (400 MHz, CD_3CN) δ 7.68 (m, 1H), 7.38-7.48 (m, 3H), 7.24 (m, 1H), 7.12 (d, J= 8.0 Hz, 1H), 6.96 (d, J= 8.3 Hz, 1H), 3.34 (s, 3H), 2.28 (s, 3H). $^{13}C\{^{1}H\}$ NMR (100 MHz, CD_3CN) δ 168.23, 168.01, 154.01, 151.95 (d, J = 1.7 Hz), 142.18 (d, J = 5.3 Hz), 138.44 (d, J = 24.4 Hz), 134.37 (d, J = 3.9 Hz), 134.31, 134.18 (d, J = 4.6 Hz), 126.96 (d, J = 2.7 Hz), 126.16, 125.11, 123.24 (d, J = 16.9 Hz), 117.87, 113.54 (d, J = 5.0 Hz), 110.99 (d, J = 2.7 Hz), 92.47 (d, J = 186.8 Hz), 26.72, 19.87. ^{19}F NMR (376 MHz, CD_3CN) δ -147.80. HR-MS (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_{19}H_{13}FN_2O_5Na$ 391.0701, found 391.0703.



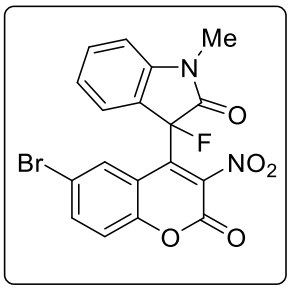
Compound **4a** was obtained as a yellow crystalline solid in 76% yield (29.4 mg, 0.07 mmol) from *N*-phenyl-3-fluoro-2-oxindole (20.4 mg, 0.09 mmol) and 4-chloro-6-methyl-3-nitrocoumarin (24.0 mg, 0.1 mmol) following the general procedure described above after purification by flash chromatography using hexanes:ethyl acetate (1:1) as the mobile phase. The *dr* was determined as 15:1 using ^{19}F NMR spectroscopy. The *ee* was determined by chiral HPLC ((*S,S)*-Whelk-O 1, dichoromethane/hexanes 70:30, flow rate 1 mL/min, λ=254 nm) as 75%, t_R (major) =5.9 min, t_R (minor) =4.5 min. ^{1}H NMR (400 MHz, CD_3CN) δ 7.70 – 7.65 (m, 3H), 7.60 – 7.56 (m, 4H), 7.52 (m, 1H), 7.40 (d, *J* = 8.6 Hz, 1H), 7.28 (m, 1H), 7.08 (d, *J* = 8.1 Hz, 1H), 6.98 (s, 1H), 2.23 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, CD_3CN) δ 167.67 (d, *J* = 21.9 Hz), 154.03, 150.28, 144.41 (d, *J* = 4.9 Hz), 138.06, 135.43, 134.27 (d, *J* = 4.5 Hz), 132.76, 130.28, 130.06, 129.44, 127.06 (d, *J* = 2.6 Hz), 126.18, 125.19 (d, *J* = 3.8 Hz), 124.29, 123.00, 122.82, 117.92, 113.32 (d, *J* = 4.9 Hz), 111.85 (d, *J* = 2.7 Hz), 92.30 (d, *J* = 187.9 Hz), 20.26. ^{19}F NMR (376 MHz, CD_3CN) δ -146.82. HR-MS (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_{24}H_{15}FN_2O_5Na$ 453.0855, found 453.0857.



Compound **4b** was obtained as a yellow crystalline solid in 77% yield (25.5 mg, 0.07 mmol) from *N*-methyl-3-fluoro-2-oxindole (15.0 mg, 0.09 mmol) and 4-chloro-6-methyl-3-nitrocoumarin (24.0 mg, 0.1 mmol) following the general procedure described above after purification by flash chromatography using hexanes:ethyl acetate (1:1) as the mobile phase. The *dr* was determined as 28:1 using ^{19}F NMR spectroscopy. The *ee* was determined by chiral HPLC ((*S,S)*-Whelk-O 1, dichoromethane/hexanes 70:30, flow rate 1 mL/min, λ=254 nm) as 72%, t_R (major) =5.8 min, t_R (minor) =4.9 min. ^{1}H NMR (400 MHz, CD_3CN) δ 7.65 (m, 1H), 7.57 (m, 1H), 7.50 (m, 1H), 7.36 (d, *J* = 8.5 Hz, 1H), 7.26 (d, *J* = 7.9 Hz, 1H), 7.21 (m, 1H), 6.65 (s, 1H), 3.37 (s, 3H), 2.17 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, CD_3CN) δ 168.19 (d, *J* = 21.4 Hz), 154.06, 150.18 (d, *J* = 1.8 Hz), 144.51 (d, *J* = 5.4 Hz), 138.26, 138.02, 135.94, 135.28, 134.18 (d, *J* = 4.4 Hz), 126.48 (d, *J* = 2.7 Hz), 124.47 (d, *J* = 3.8 Hz), 124.32, 123.25 (d, *J* = 17.5 Hz), 117.74, 113.23 (d, *J* = 4.8 Hz), 111.06 (d, *J* = 2.6 Hz), 92.19 (d, *J* = 187.3 Hz), 26.68, 20.13. ^{19}F NMR (376 MHz, CD_3CN) δ -148.48. HR-MS (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_{19}H_{13}FN_2O_5Na$ 391.0701, found 391.0699.

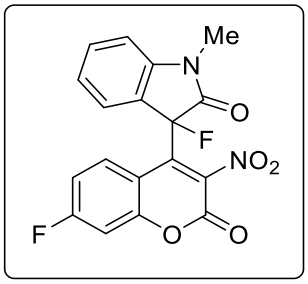


Compound **4c** was obtained as a white crystalline solid in 79% yield (27.6 mg, 0.07 mmol) from *N*-methyl-3-fluoro-2-oxindole (15.0 mg, 0.09 mmol) and 4-chloro-6-chloro-3-nitrocoumarin (26.0 mg, 0.1 mmol) following the general procedure described above after purification by flash chromatography using hexanes:ethyl acetate (1:1) as the mobile phase. The *dr* was determined as 12:1 using ^{19}F NMR spectroscopy. The *ee* was determined by chiral HPLC ((*S,S)*-Whelk-O 1, dichoromethane/hexanes 70:30, flow rate 1 mL/min, λ=254 nm) as 75%, t_R (major) =9.5 min, t_R (minor) =7.0 min. ^{1}H NMR (400 MHz, CD_3CN) δ 7.67 – 7.64 (m, 2H), 7.57 (m, 1H), 7.46 (d, *J* = 9.0 Hz, 1H), 7.29 – 7.21 (m, 2H), 6.81 (d, *J* = 2.3 Hz, 1H), 3.36 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, CD_3CN) δ 150.68, 144.40 (d, *J* = 5.1 Hz), 137.00, 134.49 (d, *J* = 4.3 Hz), 134.04, 130.46, 126.71 (d, *J* = 2.7 Hz), 124.71 (d, *J* = 3.7 Hz), 123.97, 119.80, 117.30, 114.90, 111.11 (d, *J* = 2.5 Hz), 91.95 (d, *J* = 188.8 Hz), 26.74. ^{19}F NMR (376 MHz, CD_3CN) δ -148.66. HR-MS (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_{18}H_{10}FClN_2O_5Na$ 411.0154, found 411.0154.



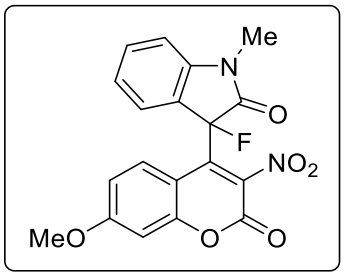
Compound **4d** was obtained as a yellow crystalline solid in 75% yield (29.2 mg, 0.07 mmol) from *N*-methyl-3-fluoro-2-oxindole (15.0 mg, 0.09 mmol) and 4-chloro-6-bromo-3-

nitrocoumarin (30.4 mg, 0.1 mmol) following the general procedure described above after purification by flash chromatography using hexanes:ethyl acetate (1:1) as the mobile phase. The *dr* was determined as 10:1 using ^{19}F NMR spectroscopy. The *ee* was determined by chiral HPLC ((*S,S)*-Whelk-O 1, dichoromethane/hexanes 50:50, flow rate 1 mL/min, λ=254 nm) as 89%, t_R (major) =9.4 min, t_R (minor) =7.7 min. ^{1}H NMR (400 MHz, CD_3CN) δ 7.78 (d, *J* = 8.9, 1H), 7.67 (m, 1H), 7.58 (m, 1H), 7.39 (d, *J* = 8.9 Hz, 1H), 7.35–7.19 (m, 2H), 6.97 (d, *J* = 2.2 Hz, 1H), 3.37 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, CD_3CN) δ 167.94, 153.51, 151.09 (d, *J* = 1.8 Hz), 144.35 (d, *J* = 5.0 Hz), 137.14, 136.86, 134.53 (d, *J* = 4.4 Hz), 127.07, 126.74 (d, *J* = 2.4 Hz), 124.74 (d, *J* = 3.8 Hz), 122.73 (d, *J* = 17.4 Hz), 119.99, 119.48, 117.68, 115.35 (d, *J* = 4.9 Hz), 111.07 (d, *J* = 2.5 Hz), 91.93 (d, *J* = 188.9 Hz), 26.73. ^{19}F NMR (376 MHz, CD_3CN) δ -149.12. HR-MS (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_{18}H_{10}BrFN_2O_5Na$ 454.9649, found 454.9648.

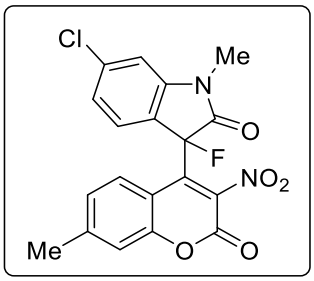


Compound **4e** was obtained as a yellow crystalline solid in 75% yield (25.1 mg, 0.07 mmol) from *N*-methyl-3-fluoro-2-oxindole (15.0 mg, 0.09 mmol) and 4-chloro-7-fluoro-3-nitrocoumarin (24.4 mg, 0.1 mmol) following the general procedure described above after purification by flash chromatography using hexanes:ethyl acetate (1:1) as the mobile phase. The *dr* was determined as 17:1 using ^{19}F NMR spectroscopy. The *ee* was determined by chiral HPLC ((*S,S)*-Whelk-O 1, dichoromethane/hexanes 70:30, flow rate 1 mL/min, λ=254 nm) as 73%, t_R (major) =5.8 min, t_R (minor) =4.9 min. ^{1}H NMR (400 MHz, CD_3CN) δ 7.67 (m, 1H), 7.57 (m, 1H), 7.53 – 7.40 (m, 2H), 7.35 – 7.15 (m, 2H), 6.56 (dd, *J* = 9.3, 2.7 Hz, 1H), 3.36 (s, 3H).

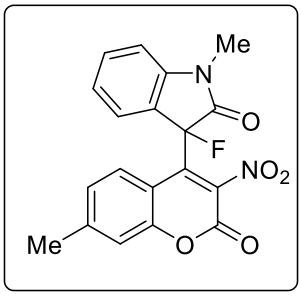
$^{13}C\{^{1}H\}$ NMR (100 MHz, CD_3CN) δ 168.02 (d, *J* = 21.3 Hz), 165.17 (d, *J* = 256.3 Hz), 153.84, 153.62 (d, *J* = 1.9 Hz), 153.48, 144.62 (d, *J* = 5.3 Hz), 137.95, 134.13 (d, *J* = 4.6 Hz), 127.43 (d, *J* = 10.8 Hz), 126.41 (d, *J* = 2.7 Hz), 124.39 (d, *J* = 3.8 Hz), 123.01 (d, *J* = 17.0 Hz), 114.33 (d, *J* = 23.2 Hz), 111.34 (d, *J* = 2.7 Hz), 110.43 (d, *J* = 1.8 Hz), 105.44 (d, *J* = 26.3 Hz), 92.17 (d, *J* = 186.9 Hz), 26.78. ^{19}F NMR (376 MHz, CD_3CN) δ -103.27 (m), 147.78. HR-MS (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_{18}H_{10}F_2N_2O_5Na$ 395.0450, found 395.0448.



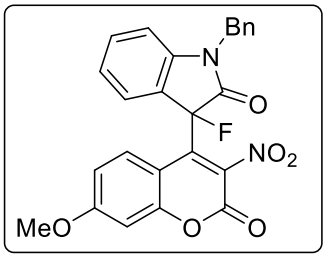
Compound **4f** was obtained as a yellow crystalline solid in 80% yield (27.7 mg, 0.07 mmol) from *N*-methyl-3-fluoro-2-oxindole (15.0 mg, 0.09 mmol) and 4-chloro-7-methoxy-3-nitrocoumarin (25.6 mg, 0.1 mmol) following the general procedure described above after purification by flash chromatography using hexanes:ethyl acetate (1:1) as the mobile phase. The *dr* was determined as 22:1 using ^{19}F NMR spectroscopy. The *ee* was determined by chiral HPLC ((*S,S)*-Whelk-O 1, dichoromethane/hexanes 70:30, flow rate 1 mL/min, λ=254 nm) as 97%, t_R (major) =7.8 min, t_R (minor) =6.4 min. ^{1}H NMR (400 MHz, CD_3CN) δ 7.54 - 7.56 (m, 2H), 7.17 - 7.24 (m, 2H), 7.00 (d, *J* = 2.5 Hz, 1H), 6.77 – 6.85 (m, 2H), 3.85 (s, 3H), 3.35 (s, 3H). $^{13}C\{^{1}H\}$ NMR (100 MHz, CD_3CN) δ 168.29 (d, *J* = 21.6 Hz), 164.38, 154.43, 154.25 (d, *J* = 1.9 Hz), 144.60 (d, *J* = 5.3 Hz), 138.76 (d, *J* = 24.5 Hz), 133.97 (d, *J* = 4.5 Hz), 126.38 (d, *J* = 2.6 Hz), 126.22, 124.32 (d, *J* = 3.8 Hz), 123.39 (d, *J* = 17.1 Hz), 114.29, 111.16 (d, *J* = 2.6 Hz), 106.31 (d, *J* = 5.0 Hz), 101.86, 92.23 (d, *J* = 186.5 Hz), 56.08, 26.71. ^{19}F NMR (376 MHz, CD_3CN) δ -148.04. HR-MS (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_{19}H_{13}FN_2O_6Na$ 407.0650, found 407.0649.



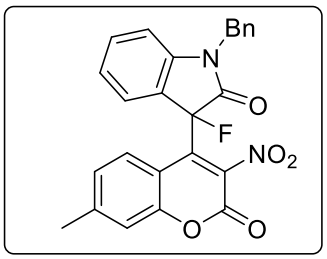
Compound **4g** was obtained as a white crystalline solid in 79% yield (28.6 mg, 0.07 mmol) from *N*-methyl-6-chloro-3-fluoro-2-oxindole (17.9 mg, 0.09 mmol) and 4-chloro-7-methyl-3-nitrocoumarin (24.0 mg, 0.1 mmol) following the general procedure described above after purification by flash chromatography using hexanes:ethyl acetate (1:1) as the mobile phase. The *dr* was determined as 19:1 using ^{19}F NMR spectroscopy. The *ee* was determined by chiral HPLC ((*S,S)*-Whelk-O 1, dichoromethane/hexanes 70:30, flow rate 1 mL/min, λ=254 nm) as 93%, t_R (major) =5.9 min, t_R (minor) =4.7 min. ^{1}H NMR (400 MHz, CD_3CN) δ 7.52 (dd, *J* = 8.0, 3.0 Hz, 1H), 7.31 (d, *J* = 8.7 Hz, 2H), 7.19 (m, 1H), 7.08 (d, *J* = 8.4, 1H), 6.78 (d, *J* = 8.4 Hz, 1H), 3.34 (s, 3H), 2.40 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, CD_3CN) δ 168.21 (d, *J* = 21.5 Hz), 154.10, 152.05 (d, *J* = 1.7 Hz), 146.63, 146.07 (d, *J* = 5.1 Hz), 139.37 (d, *J* = 5.2 Hz), 137.91 (d, *J* = 24.4 Hz), 127.62 (d, *J* = 2.7 Hz), 127.41, 124.60, 124.11 (d, *J* = 3.8 Hz), 121.73 (d, *J* = 17.2 Hz), 117.93, 112.09 (d, *J* = 2.7 Hz), 110.72 (d, *J* = 4.9 Hz), 109.99, 91.56 (d, *J* = 187.2 Hz), 26.98, 20.61. ^{19}F NMR (376 MHz, CD_3CN) δ -147.77. HR-MS (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_{19}H_{12}FClN_2O_5Na$ 425.0311, found 425.0311.



Compound **4h** was obtained as a white crystalline solid in 81% yield (26.9 mg, 0.07 mmol) from *N*-methyl-3-fluoro-2-oxindole (15.0 mg, 0.09 mmol) and 4-chloro-7-methyl-3-nitrocoumarin (24.0 mg, 0.1 mmol) following the general procedure described above after purification by flash chromatography using hexanes:ethyl acetate (1:1) as the mobile phase. The *dr* was determined as 20:1 using ^{19}F NMR spectroscopy. The *ee* was determined by chiral HPLC ((*S,S)*-Whelk-O 1, dichoromethane/hexanes 70:30, flow rate 1 mL/min, λ=254 nm) as 87%, t_R (major) =6.4 min, t_R (minor) =5.1 min. ^{1}H NMR (400 MHz, CD_3CN) δ 7.61 (m, 1H), 7.54 (m, 1H), 7.30 (s, 1H), 7.23 (d, *J* = 8.0 Hz, 1H), 7.18 (m, 1H), 7.06 (dd, *J* = 8.5, 1.7 Hz, 1H), 6.82 (d, *J* = 8.4 Hz, 1H), 3.35 (s, 3H), 2.39 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, CD_3CN) δ 168.22 (d, *J* = 21.6 Hz), 154.18, 152.04, 146.51, 144.64 (d, *J* = 5.3 Hz), 138.44 (d, *J* = 24.4 Hz), 133.99 (d, *J* = 4.4 Hz), 127.32, 126.35 (d, *J* = 2.7 Hz), 124.65, 124.30 (d, *J* = 3.8 Hz), 123.32 (d, *J* = 17.1 Hz), 117.89, 111.20 (d, *J* = 2.8 Hz), 110.83, 110.00, 92.24 (d, *J* = 186.4 Hz), 26.71, 20.59. ^{19}F NMR (376 MHz, CD_3CN) δ -147.99. HR-MS (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_{19}H_{13}FN_2O_5Na$ 391.0701, found 391.0701.



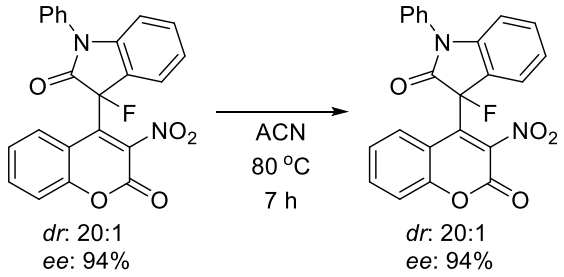
Compound **4i** was obtained as a yellow crystalline solid in 79% yield (32.7 mg, 0.07 mmol) from *N*-benzyl-3-fluoro-2-oxindole (21.7 mg, 0.09 mmol) and 4-chloro-7-methoxy-3-nitrocoumarin (25.6 mg, 0.1 mmol) following the general procedure described above after purification by flash chromatography using hexanes:ethyl acetate (1:1) as the mobile phase. The *dr* was determined as 20:1 using ^{19}F NMR spectroscopy. The *ee* was determined by chiral HPLC ((*S,S)*-Whelk-O 1, dichoromethane/hexanes 70:30, flow rate 0.5 mL/min, λ=254 nm) as 89%, t_R (major) = 9.8 min, t_R (minor) = 11.6 min. ^{1}H NMR (400 MHz, CD_3CN) δ 7.59 (s, 2H), 7.52 – 7.35 (m, 6H), 7.31 (d, *J* = 7.6 Hz, 1H), 7.19 (t, *J* = 7.2 Hz, 1H), 7.00 (s, 1H), 6.76 (m, 1H), 6.46 (d, *J* = 9.0 Hz, 1H), 5.05 (s, 2H), 3.85 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, CD_3CN) δ 164.37, 154.25, 143.56, 134.95, 133.94 (d, *J* = 4.6 Hz), 129.14, 128.38, 128.28, 126.79 (d, *J* = 2.8 Hz), 126.20, 124.58 (d, *J* = 3.7 Hz), 123.62, 113.78, 111.63 (d, *J* = 2.6 Hz), 97.60 (d, J= 182.6 Hz), 93.21, 56.11, 44.34. ^{19}F NMR (376 MHz, CD_3CN) δ -147.48. HR-MS (ESI-TOF) m/z: [M+Na]+ calcd for $C_{25}H_{17}FN_2O_6$ 483.0963, found 483.0962.



Compound **4j** was obtained as a yellow crystalline solid in 75% yield (30.1 mg, 0.07 mmol) from *N*-benzyl-3-fluoro-2-oxindole (21.7 mg, 0.09 mmol) and 4-chloro-7-methyl-3-nitrocoumarin (24.0 mg, 0.1

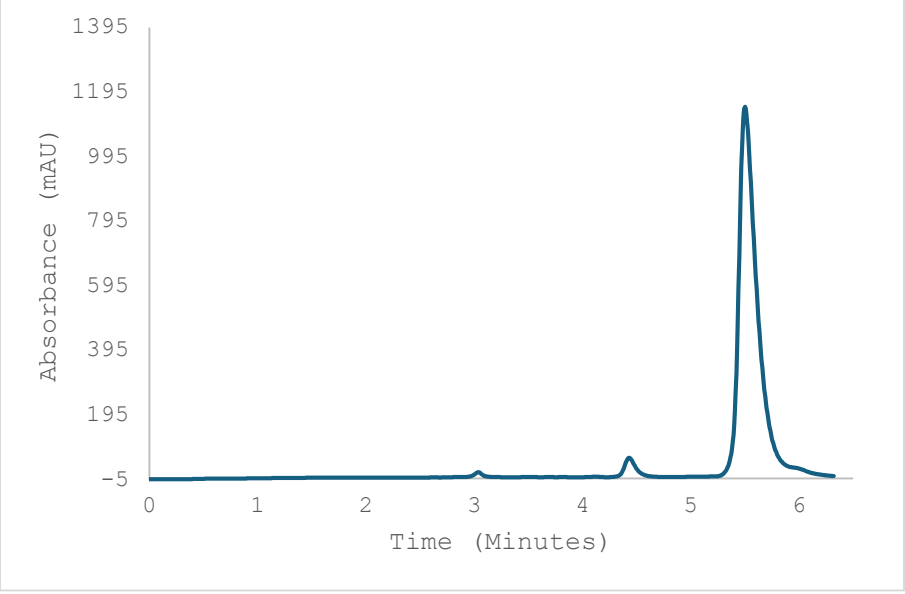
mmol) following the general procedure described above after purification by flash chromatography using hexanes:ethyl acetate (1:1) as the mobile phase. The *dr* was determined as 41:1 using ^{19}F NMR spectroscopy. The *ee* was determined by chiral HPLC ((*S,S)*-Whelk-O 1, dichoromethane/hexanes 40:60, flow rate 0.5 mL/min, λ=254 nm) as 92%, t_R (major) =42.7 min, t_R (minor) =36.1 min. ^1H NMR (400 MHz, CD_3CN) δ 7.60 – 7.55 (m, 2H), 7.52 – 7.39 (m, 5H), 7.36 – 7.26 (m, 2H), 7.19 (d, *J* = 7.9 Hz, 1H), 6.78 (d, *J* = 8.4 Hz, 1H), 6.66 (d, *J* = 8.3 Hz, 1H), 5.48 – 4.56 (m, 2H), 2.39 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, CD_3CN) δ 168.31 (d, *J* = 21.4 Hz), 154.12, 152.05 (d, *J* = 1.8 Hz), 146.55, 143.63 (d, *J* = 5.1 Hz), 138.22 (d, *J* = 24.4 Hz), 134.96, 133.96 (d, *J* = 4.6 Hz), 129.13, 128.38, 128.20, 126.96, 126.74 (d, *J* = 2.7 Hz), 124.66, 124.56 (d, *J* = 3.8 Hz), 123.54, 123.38, 117.96, 111.66 (d, *J* = 2.7 Hz), 110.79 (d, *J* = 5.0 Hz), 92.31 (d, *J* = 186.4 Hz), 44.35, 20.56. ^{19}F NMR (376 MHz, CD_3CN) δ -147.32. HR-MS (ESI-TOF) m/z: [M+Na]+ calcd for $C_{25}H_{17}FN_2O_5$ 467.1014, found 467.1013.

3.4. Stability to atropisomerization



To investigate the stability to atropisomerization of the asymmetric Michael addition product, compound **3b** (20.0 mg, 0.05 mmol) was dissolved in acetonitrile (0.5 mL) and heated to 80 ºC for 7 hours. The *ee* and *dr* before and after heating were determined by chiral HPLC ((*S,S)*-Whelk-O 1, dichoromethane/hexanes 70:30, flow rate 1 mL/min, λ=254 nm). The analysis showed that both *ee* and *dr* values remained unchanged (94% *ee* and 20:1 *dr*).

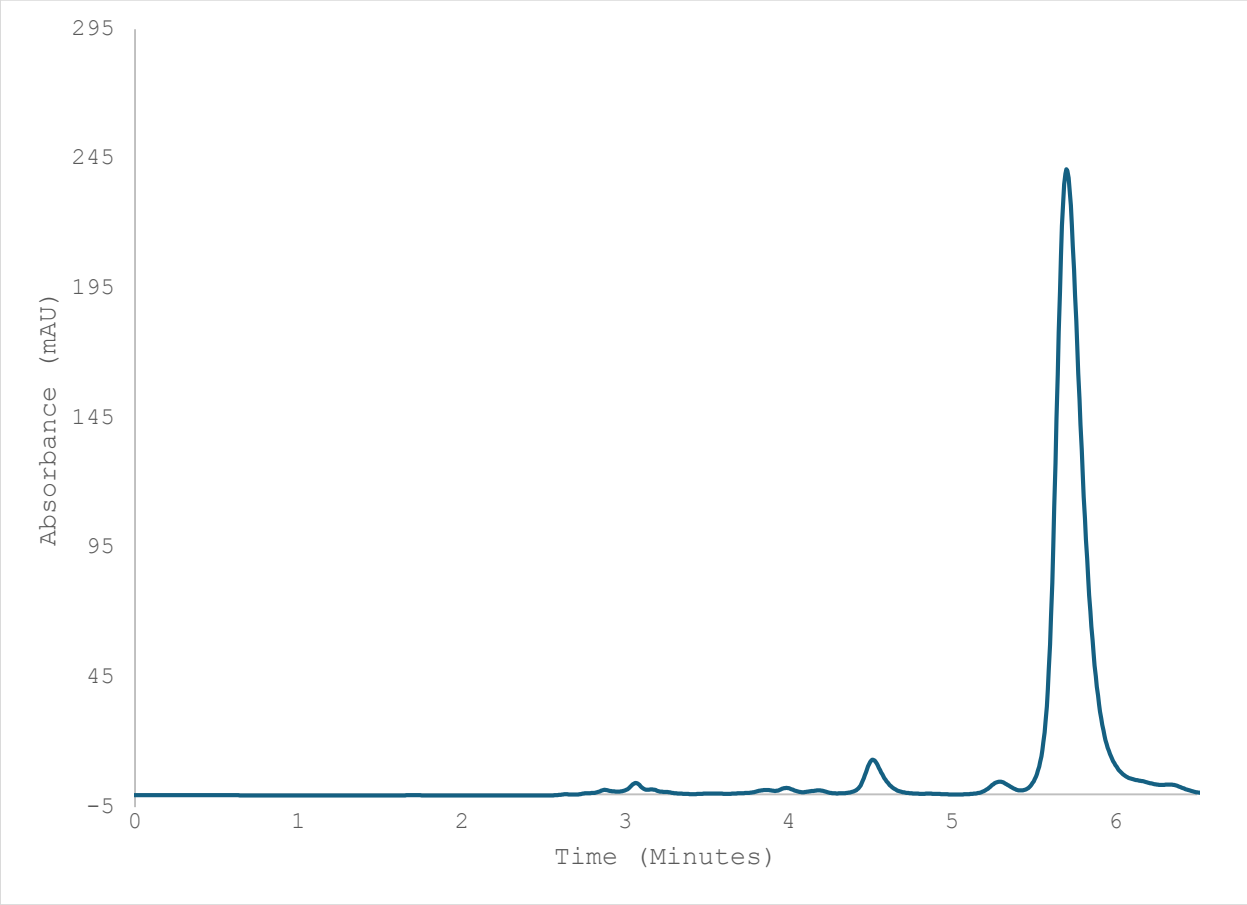
Figure S2. Chiral HPLC separation of the asymmetric reaction product, **3b**.



Conditions: (*S,S)*-Whelk-O 1, 70:30 Dichloromethane/Hexanes, flow rate 1 mL/min, λ=254 nm.

#	Time	Area	Height	Width	Area%	Symmetry
1	4.432	451.9	59.7	0.1123	2.981	0.672
2	5.502	14704.9	1163.3	0.2107	97.019	0.493

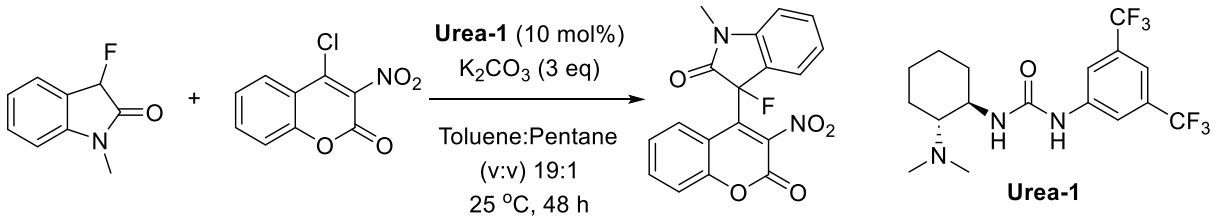
Figure S3. Chiral HPLC separation of the asymmetric reaction product, compound **3b,** after 7 hours at 80 ºC in ACN.



Conditions: (*S,S)*-Whelk-O 1, 70:30 Dichloromethane/Hexanes, flow rate 1 mL/min, λ=254 nm.

#	Time	Area	Height	Width	Area%	Symmetry
1	4.516	105	13	0.12	3.228	0.741
2	5.702	3147.5	245.7	0.2135	96.772	0.614

3.5. Upscaling of the general organocatalysis procedure

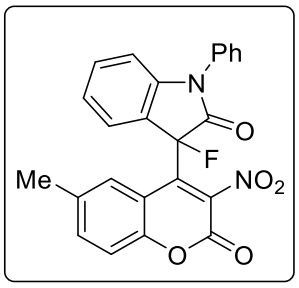


N-Methyl-3-fluoro-2-oxindole (183.0 mg, 1.1 mmol), 4-chloro-3-nitrocoumarin (250.0 mg, 1.1 mmol), potassium carbonate (456.0 mg, 3.3 mmol), and **Urea-1** (10 mol%) were added into an oven-dried vial under nitrogen. Anhydrous toluene (750 μL) and anhydrous pentane (40 μL) were added and the resulting mixture was stirred at 25 ºC for 48 hours. Upon completion, the reaction mixture was placed in a centrifuge to remove any precipitates before extraction with dichloromethane and water. The combined organic layers were dried over sodium sulfate, concentrated and purified via column chromatography using hexanes:ethyl acetate (1:1) as the mobile phase to afford compound **3a** in 82% yield (322 mg, 0.9 mmol). The *dr* was determined as 24:1 using ^{19}F NMR spectroscopy. The *ee* was determined by chiral HPLC ((*S,S*)-Whelk-O 1, 70:30 dichloromethane/hexanes, flow rate 1 mL/min, λ=254 nm) as 98%, t_R (major) = 6.0 min, t_R (minor) = 5.2 min.

4. Enantioenrichment by crystallization

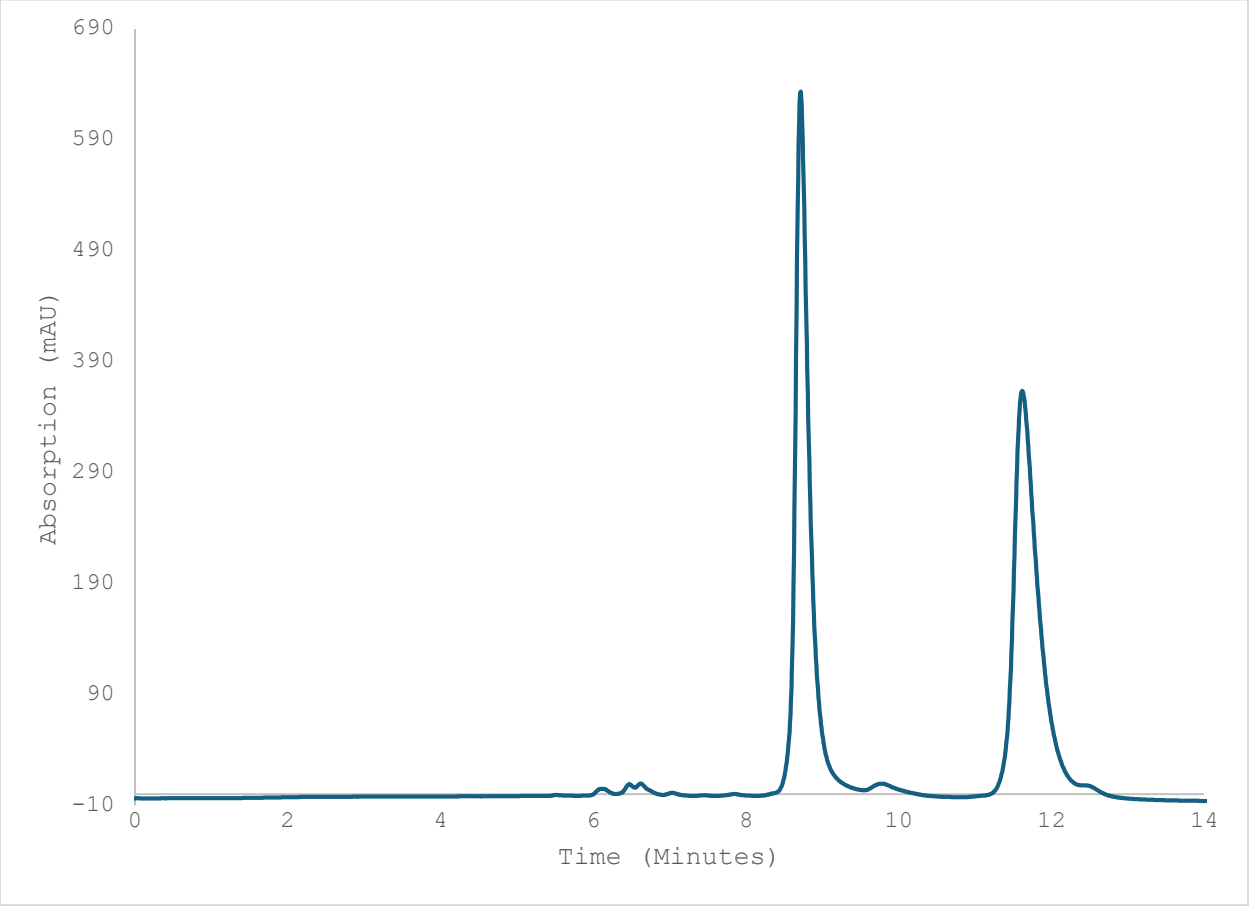
General Recrystallization Procedure

The asymmetric Michael addition products were isolated as described in the general organocatalytic procedure. The resulting products were then dissolved in dichloromethane (1.0 mL) and layered with pentane (1.0 mL) in a glass vial for 24 hours at room temperature. Racemic crystals had formed and the mother liquor was separated. The solvents were removed by vacuum evaporation prior to chiral HPLC analysis. For the increase of the *ee* of compound **3e** see Section 5.



Compound **4a** (29.4 mg, 0.07 mmol, 75% *ee*) was recrystallized according to the general procedure described above to obtain a yellow crystalline solid in 86% yield (25.6 mg, 0.06 mmol). The *ee* was determined by chiral HPLC ((*S,S)*-Whelk-O 1, dichloromethane/hexanes 70:30, flow rate 0.5 mL/min, λ=254 nm) as 80%, t_R (major) = 11.5 min, t_R (minor) = 8.7 min.

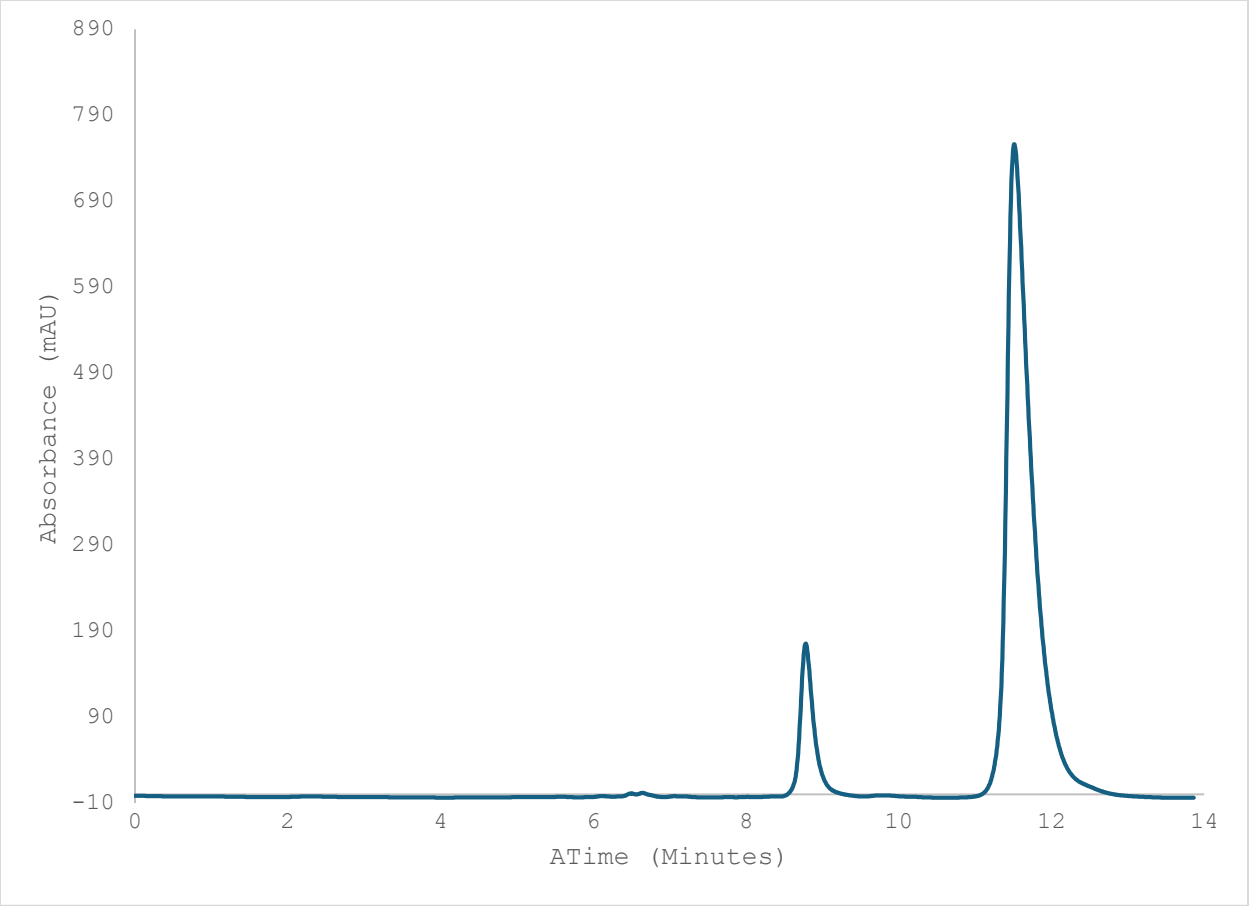
Figure S4. Chiral HPLC separation of racemic **4a**.



Conditions: (*S,S)*-Whelk-O 1, 70:30 Dichloromethane/Hexanes, flow rate 0.5 mL/min, λ=254 nm.

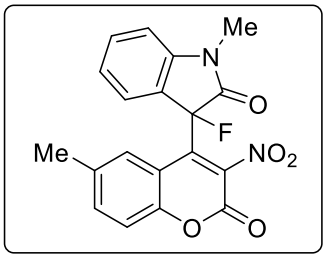
#	Time	Area	Height	Width	Area%	Symmetry
1	8.714	8421.1	635.3	0.1926	49.197	0.554
2	11.617	8696	367.5	0.3421	50.803	0.485

Figure S5. Chiral HPLC separation of purified **4a**.



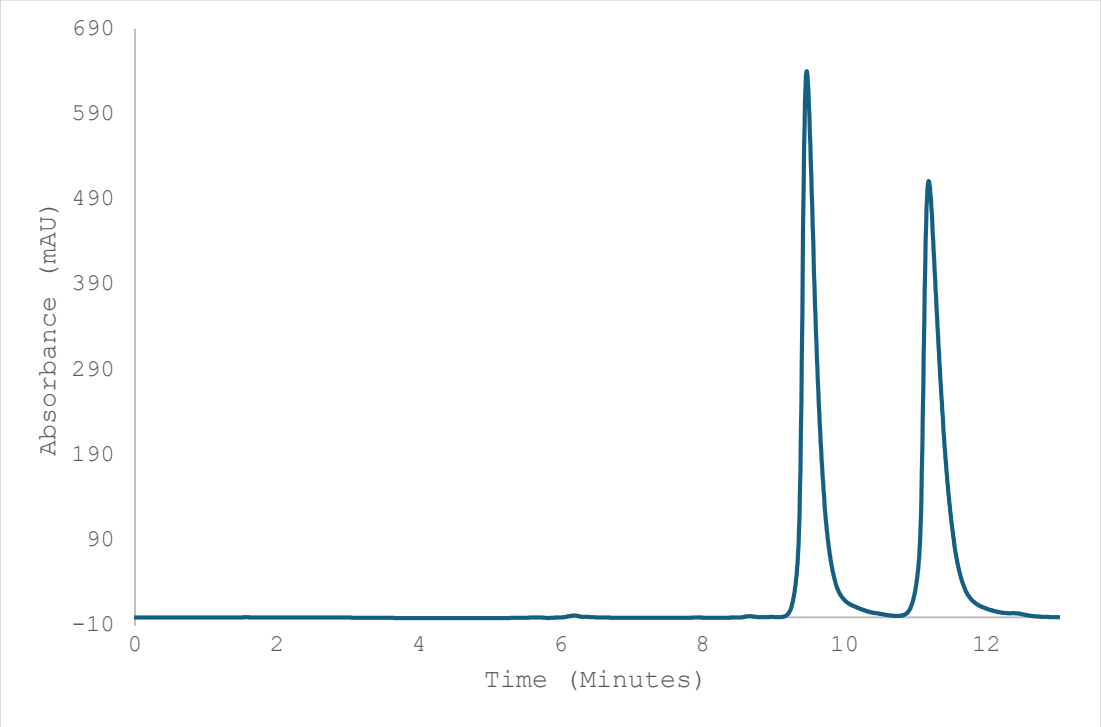
Conditions: (*S,S)*-Whelk-O 1, 70:30 Dichloromethane/Hexanes, flow rate 0.5 mL/min, λ=254 nm.

#	Time	Area	Height	Width	Area%	Symmetry
1	8.781	1884.8	169.9	0.1849	9.410	0.673
2	11.512	18145.8	760.7	0.3423	90.590	0.414



Compound **4b** (25.5 mg, 0.07 mmol, 72% *ee*) was recrystallized according to the general procedure described above to obtain a yellow crystalline solid in 88% yield (22.5 mg, 0.06 mmol). The *ee* was determined by chiral HPLC ((*S,S)*-Whelk-O 1, dichloromethane/hexanes 70:30, flow rate 0.5 mL/min, λ=254 nm) as 84%, t_R (major) = 11.2 min, t_R (minor) = 9.5 min.

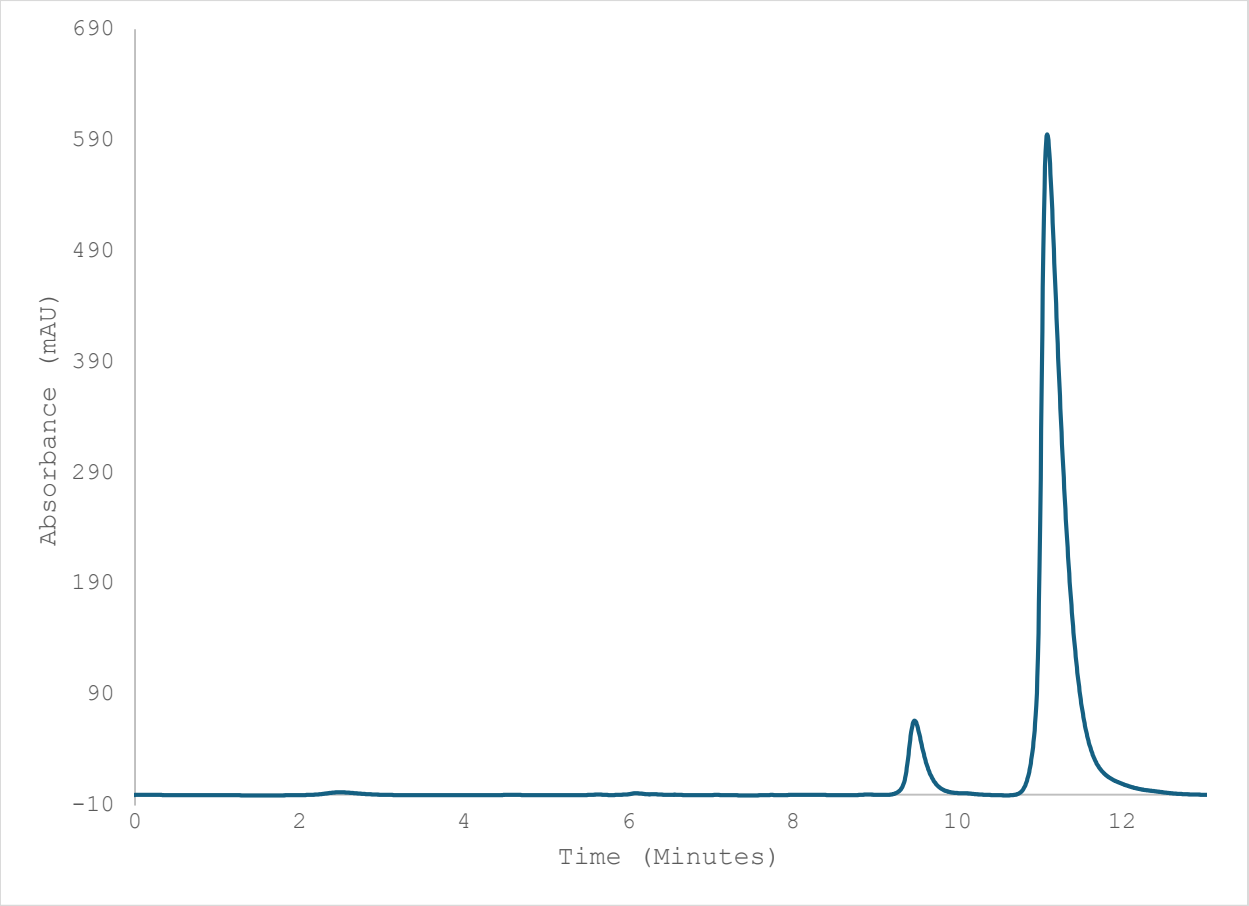
Figure S6. Chiral HPLC separation of racemic **4b**.



Conditions: (*S,S)*-Whelk-O 1, 70:30 Dichloromethane/Hexanes, flow rate 0.5 mL/min, λ=254 nm.

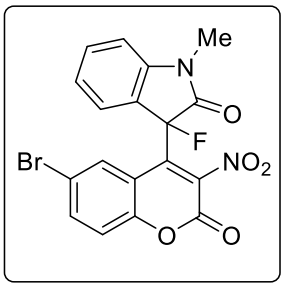
#	Time	Area	Height	Width	Area%	Symmetry
1	9.468	9663.6	640.6	0.216	50.646	0.414
2	11.186	9417	509.3	0.2637	49.354	0.387

Figure S7. Chiral HPLC separation of purified **4b**.



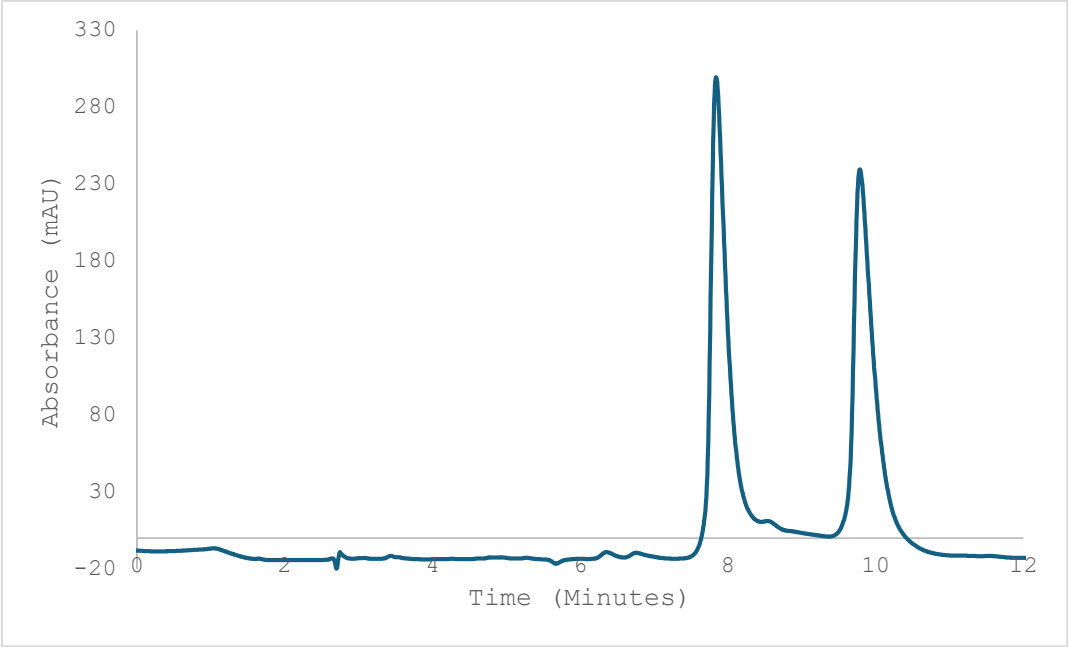
Conditions: (*S,S)*-Whelk-O 1, 70:30 Dichloromethane/Hexanes, flow rate 0.5 mL/min, λ=254 nm.

#	Time	Area	Height	Width	Area%	Symmetry
1	9.479	1003	67.1	0.2184	7.825	0.528
2	11.091	11814.7	595.9	0.2813	92.175	0.351



Compound **4d** (29.2 mg, 0.07 mmol, 68% *ee*) was recrystallized according to the general procedure described above to obtain a yellow crystalline solid in 92% yield (26.9 mg, 0.06 mmol). The *ee* was determined by chiral HPLC ((*S,S)*-Whelk-O 1, dichloromethane/hexanes 50:50, flow rate 1 mL/min, λ=254 nm) as 89%, t_R (major) = 9.4 min, t_R (minor) = 7.7 min.

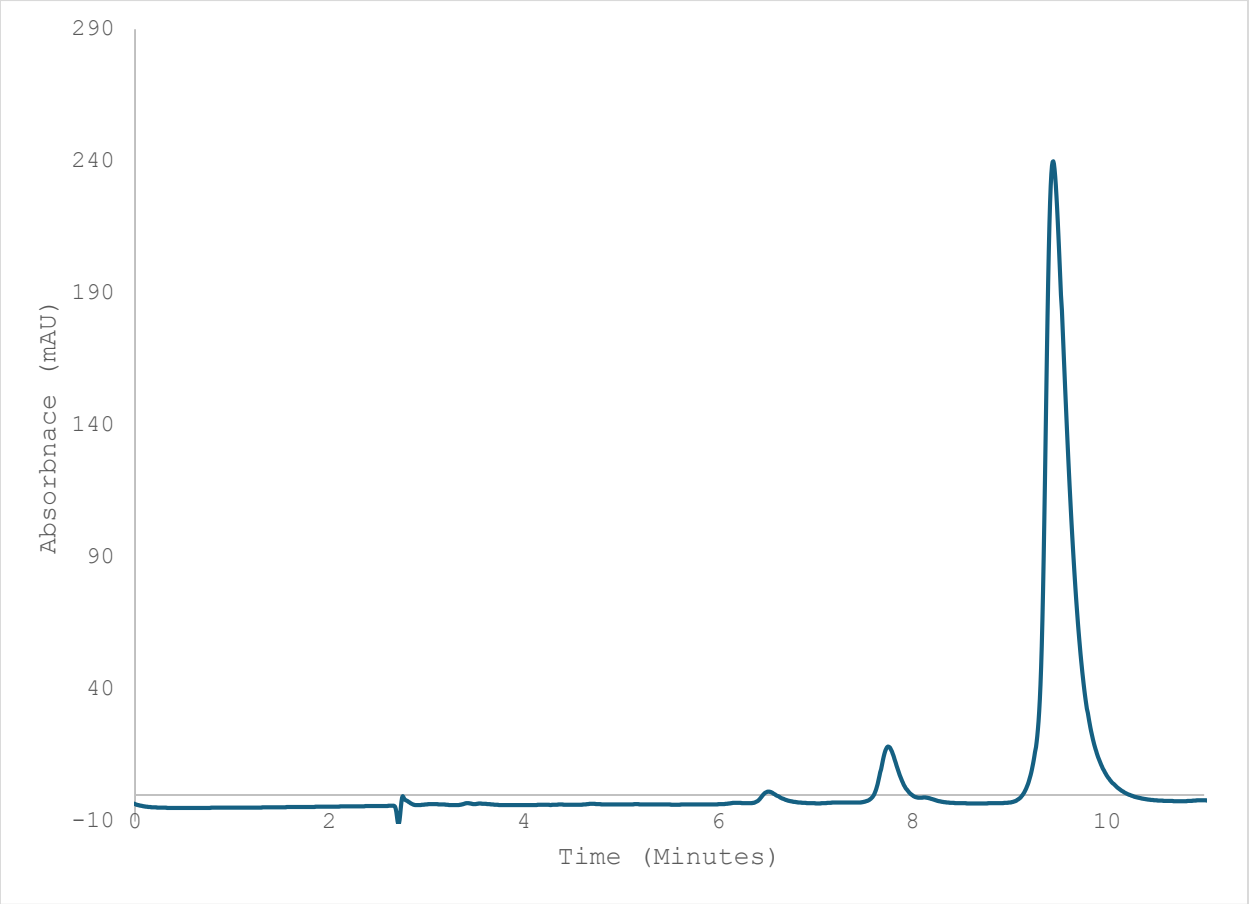
Figure S8. Chiral HPLC separation of racemic **4d**.



Conditions: (*S,S)*-Whelk-O 1, 50:50 Dichloromethane/Hexanes, flow rate 1 mL/min, λ=254 nm. Baseline adjusted by -10 mAU.

#	Time	Area	Height	Width	Area%	Symmetry
1	7.84	5320	312.6	0.2445	50.067	0.424
2	9.786	5305.7	251.7	0.2999	49.933	0.475

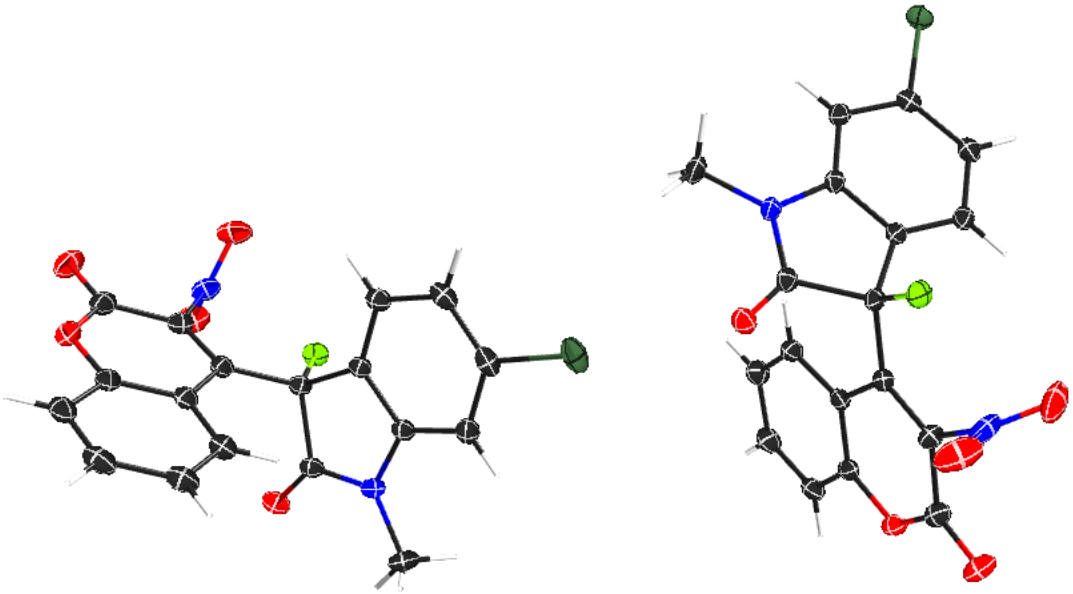
Figure S9. Chiral HPLC separation of purified **4d**.



Conditions: (*S,S)*-Whelk-O 1, 50:50 Dichloromethane/Hexanes, flow rate 1 mL/min, λ=254 nm.

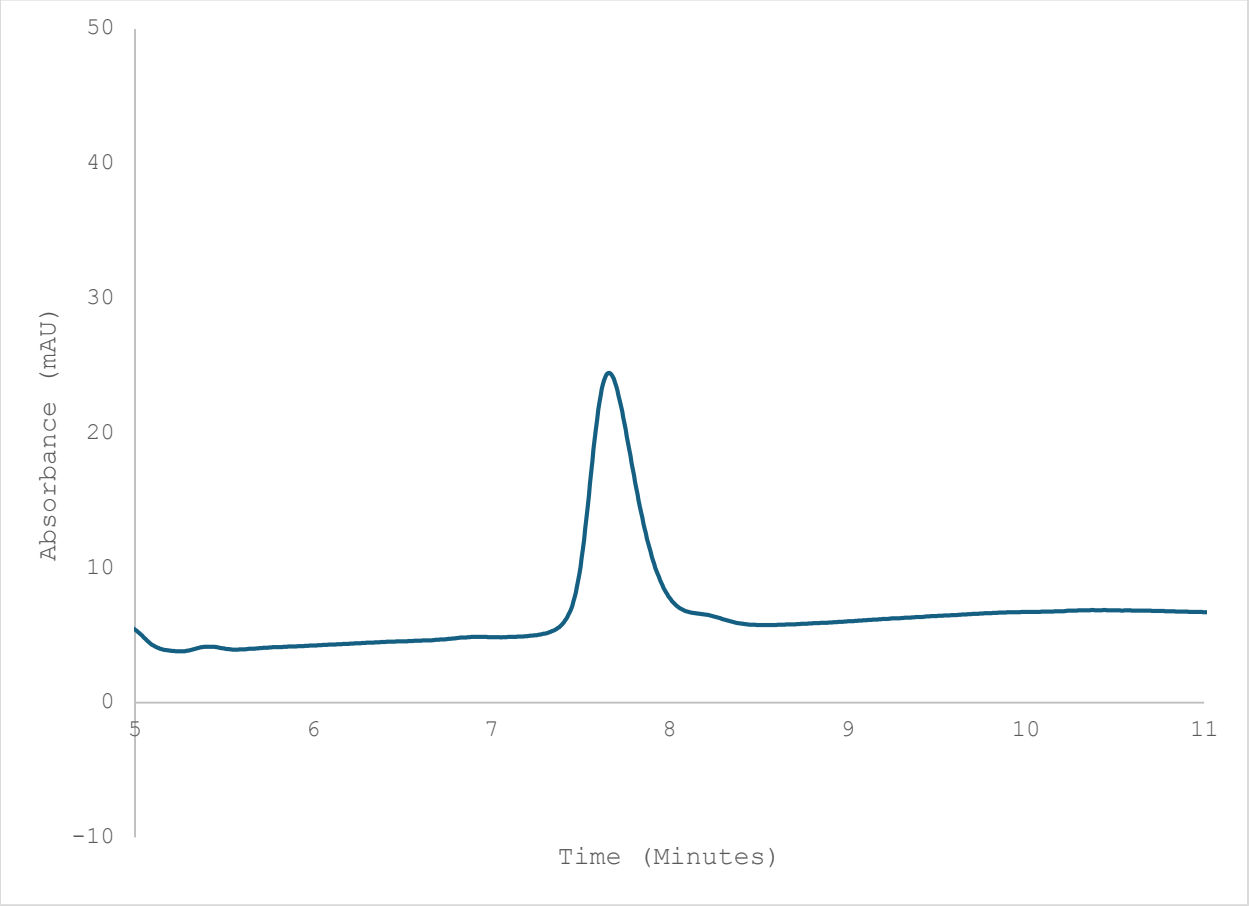
#	Time	Area	Height	Width	Area%	Symmetry
1	7.749	258.2	20.3	0.1923	5.518	0.745
2	9.445	4421	242.9	0.2623	94.482	0.453

5. Determination of absolute configuration



Single crystal analysis was performed to determine the absolute configuration of the major product formed in the general organocatalysis procedure with **Urea-1**. Despite numerous attempts including slow evaporation of dichloromethane, liquid-liquid diffusion with pentane and dichloromethane, vapor diffusion with pentane and dichloromethane, and saturation in ether at 0 ºC, compounds **3c**, **3e** and **4d** did not form enantiopure single crystals. Racemic crystals were obtained by liquid-liquid diffusion with pentane and dichloromethane as described below. To remedy this, compound **3e** (24:1 *dr*, 90% *ee*) was first subjected to recrystallization by liquid-liquid diffusion with pentane and dichloromethane to increase the *ee* of the filtrate to 95%. The filtrate (150.0 mg, 0.40 mmol, 24:1 *dr*, 95% *ee*) did not give any further crystals *via* liquid-liquid diffusion. The remaining material was therefore subjected to slow evaporation of a dichloromethane solution which gave enantiopure crystals after 3 days at room temperature. Chiral HPLC analysis of the single crystal used for X-ray crystallography showed that it was the major enantiomer formed in the catalytic asymmetric reaction.

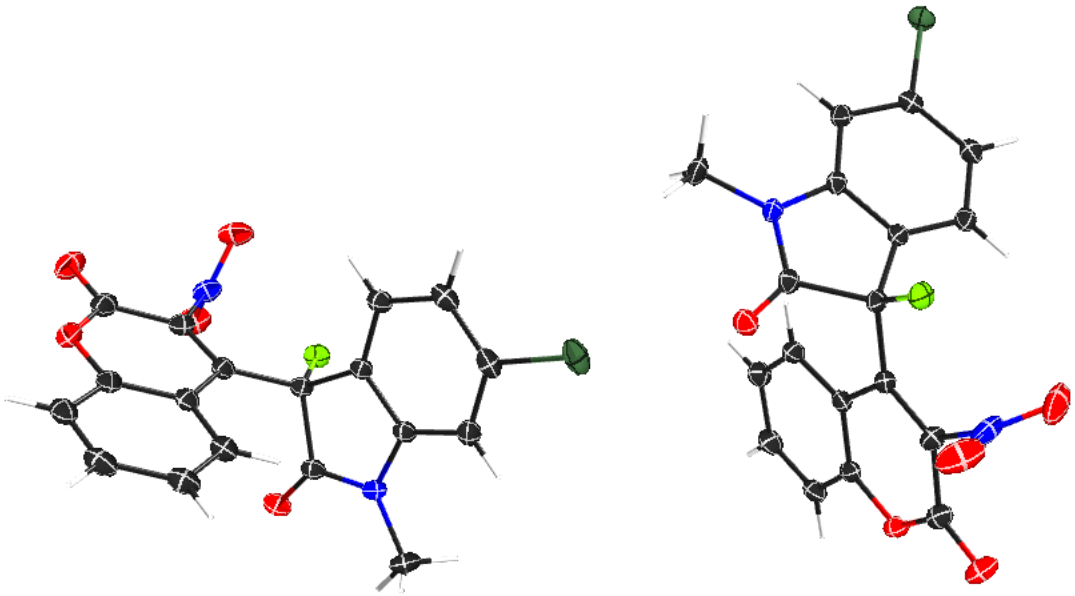
Figure S10. Chiral HPLC analysis of the single enantiopure crystal of compound **3e**.



#	Time	Area	Height	Width	Area%	Symmetry
1	7.66	380.3	19.3	0.2962	100.000	0.61

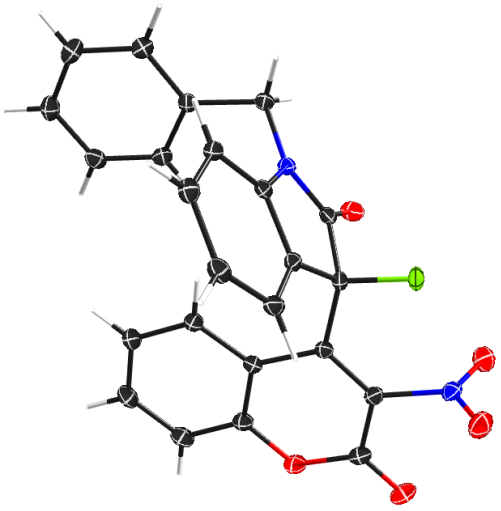
6. Crystallographic data

Figure S11. X-ray structure (50% ellipsoid probability) of compound **3e**.



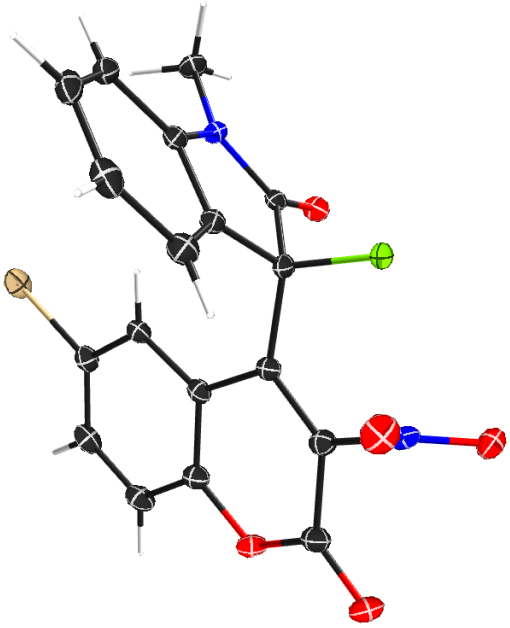
A single crystal was obtained by dissolving (*S*)-6-chloro-3-fluoro-1-methyl-3-(3-nitro-2-oxo-2H-chromen-4-yl)indolin-2-one (150.0 mg, 0.40 mmol, 24:1 *dr*, 95% *ee*) in dichloromethane (0.2 mL) and slowly evaporating at room temperature over 3 days. Single crystal X-ray analysis was performed at 100 K using a Bruker D8 Quest equipped with a Photon 3 CMOS detector and Mo microfocus sealed source (λ = 0.71073 Å). Crystal data: $C_{18}H_{10}ClFN_2O_5$, M = 388.73, colorless block, 0.314 x 0.111 x 0.107 mm^3, monoclinic, space group $P2_1$, a = 9.7610 (2), b = 10.0249 (2), c = 17.7207 (4), β = 104.6830(10), V = 1677.40(6) $Å^3$, Z = 4. Notable bond lengths: C2-C10: 1.510 (3) Å. C2-F1: 1.401 (2). Å. C10-C11: 1.349 (3) Å. Notable bond angles: N2-C11-C10: 125.04 (18)º. F1-C2-C10: 109.37 (14)º. Absolute structure parameter = -0.018 (13). The CCDC number for this compound is 2426005.

Figure S12. X-ray structure (50% ellipsoid probability) of compound **3c**.



A single crystal was obtained by dissolving racemic 1-benzyl-3-fluoro-3-(3-nitro-2-oxo-2H-chromen-4-yl)indolin-2-one (45.0 mg, 0.1 mmol) in dichloromethane (1.0 mL) and layering with pentane (1.0 mL). Single crystal X-ray analysis was performed at 100 K using a Bruker Apex DUO equipped with an APEXII CCD detector and Mo fine-focus sealed source (λ = 0.71073 Å). Crystal data: $C_{24}H_{15}FN_2O_5$, M = 430.38, colorless plate, 0.295 x 0.124 x 0.091 mm^3, triclinic, space group *P*-1, a = 8.6510(4), b = 10.0429 (4), c = 13.0902(6), α = 106.1230(10), β = 95.5930(10), γ = 112.0220(10), V = 986.56 (8) $Å^3$, Z = 2. Notable bond lengths: C2-C16: 1.5176 (15) Å. C2-F1: 1.4080 (12) Å. C16-C17: 1.3474 (15) Å. Notable bond angles: C16-C2-F1: 109.15 (8)º. C16-C17-N2: 125.64 (10)º. The CCDC number for this compound is 2426004.

Figure S13. X-ray structure (50% ellipsoid probability) of compound **4d**.



A single crystal was obtained by dissolving racemic 5-bromo-3-fluoro-1-methyl-3-(3-nitro-2-oxo-2H-chromen-4-yl)indolin-2-one (45.0 mg, 0.1 mmol) in dichloromethane (1.0 mL) and layering with pentane (1.0 mL). Single crystal X-ray analysis was performed at 100 K using a Bruker Apex DUO equipped with an APEXII CCD detector and Mo fine-focus sealed source (λ = 0.71073 Å. Crystal data: $C_{18}H_{10}BrFN_2O_5$, M = 433.19, colorless plate, 0.174 x 0.100 x 0.048 mm^3, triclinic, space group *P*-1, a = 8.0949(7), b = 8.6881(7), c = 12.6768(10), α = 74.9290(10), β = 84.954(2), γ = 73.257(2), V = 824.31(12) $Å^3$, Z = 2. Notable bond lengths: C10-C2: 1.520 (2) Å. C2-F1: 1.4029 (19) Å. C10-C11: 1.349 (2) Å. Notable bond angles: C10-C2-F1: 107.67 (13)º. C10-C11-N2: 124.30 (16)º. The CCDC number for this compound is 2426009.

7. ^{1}H, ^{13}C, and ^{19}F NMR spectra

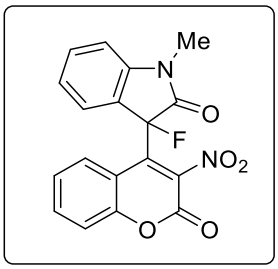


Figure S14. ^{1}H NMR (400 MHz) Spectrum of compound **3a** (*dr* = 30:1) in CD_3CN.

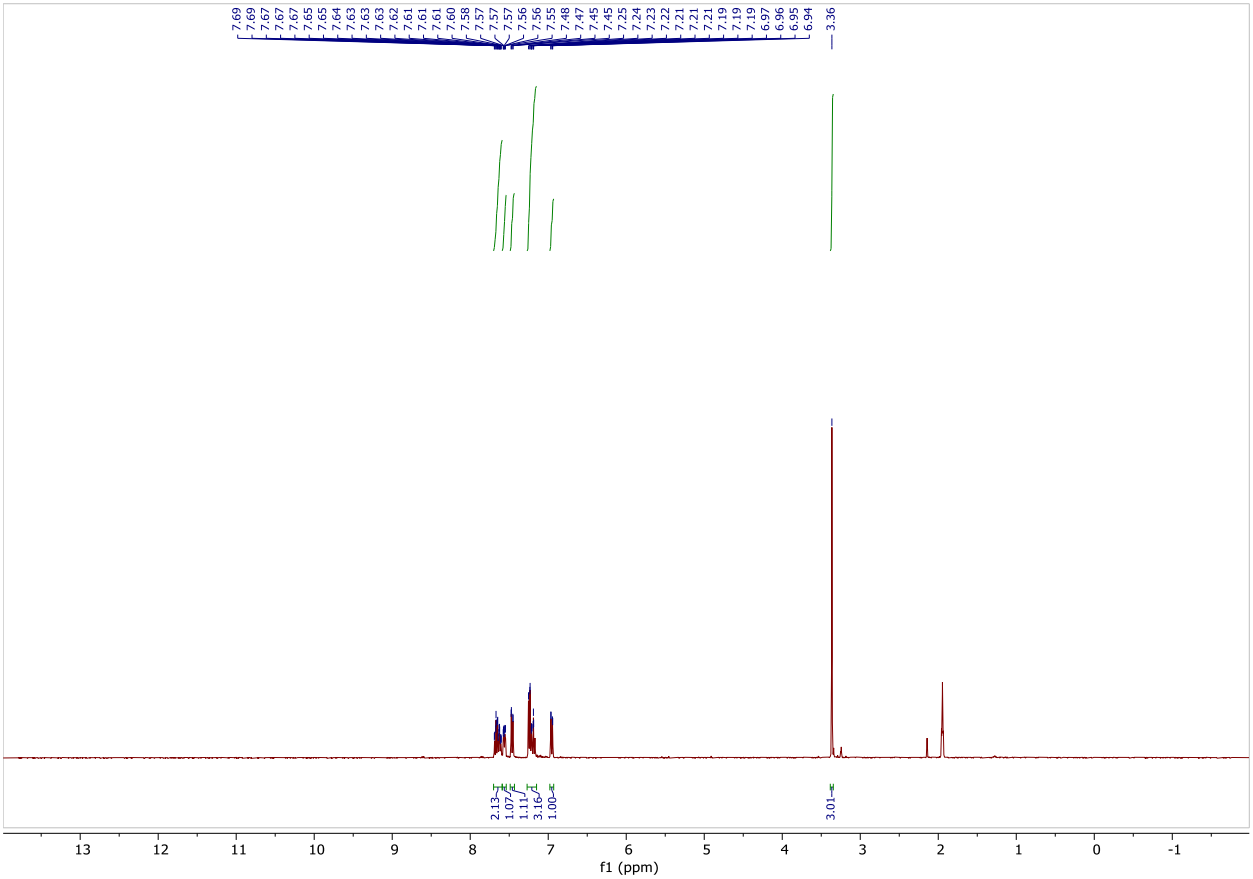


Figure S15. $^{13}C\{^{1}H\}$ NMR (100 MHz) Spectrum of compound **3a** (*dr* = 30:1) in CD_3CN.

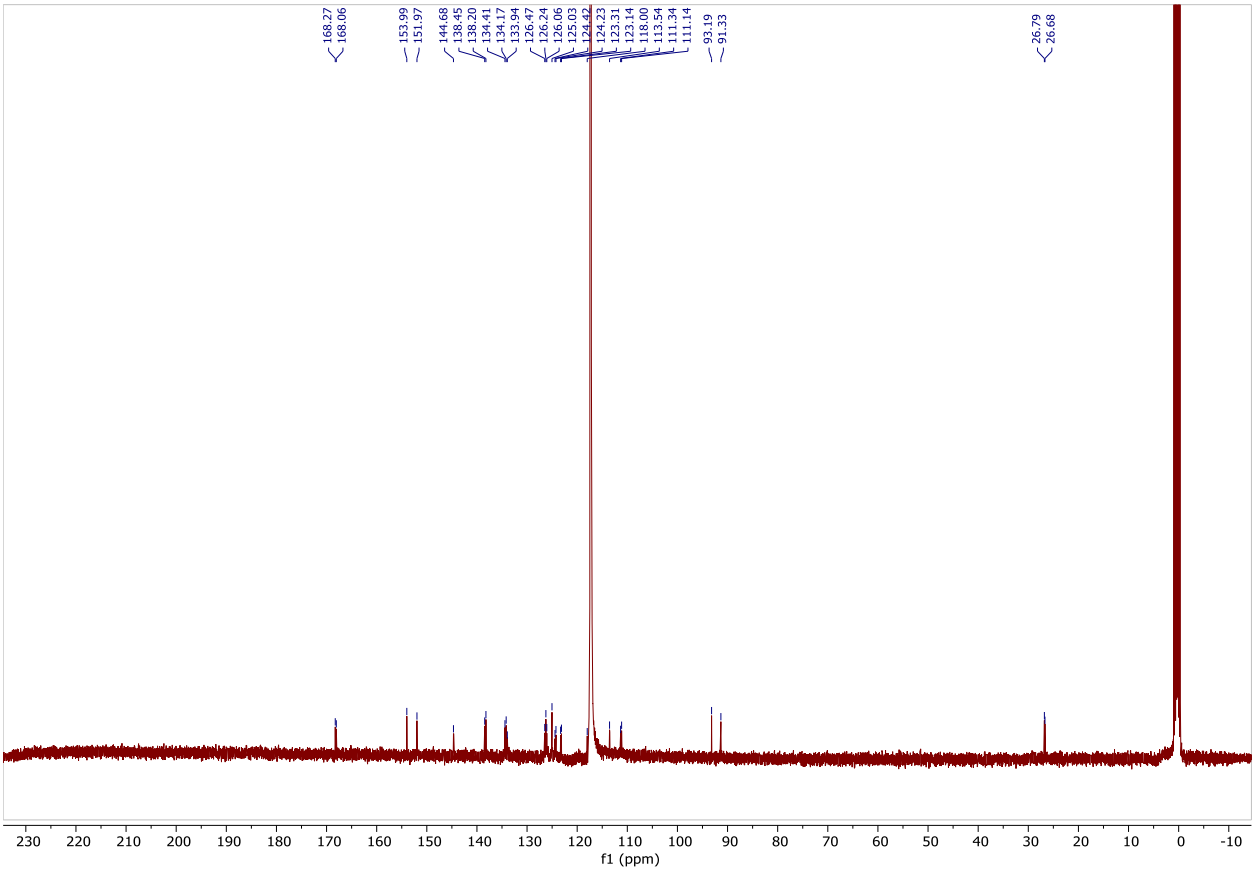
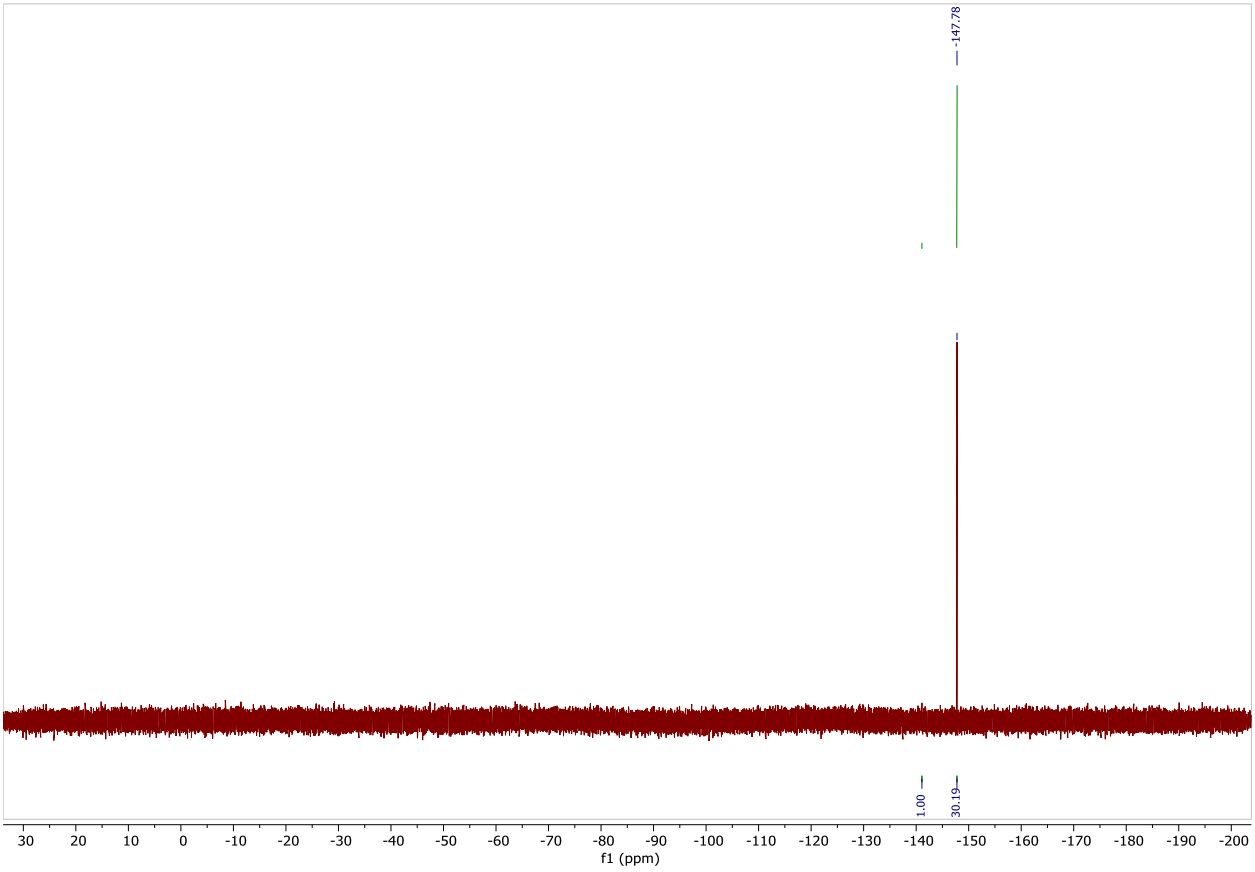


Figure S16. ^{19}F NMR (376 MHz) Spectrum of compound **3a** (*dr* = 30:1) in CD_3CN.



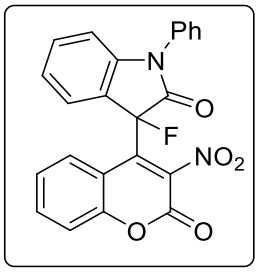


Figure 17. ^{1}H NMR (400 MHz) Spectrum of compound **3b** (*dr* = 20:1) in CD_3CN.

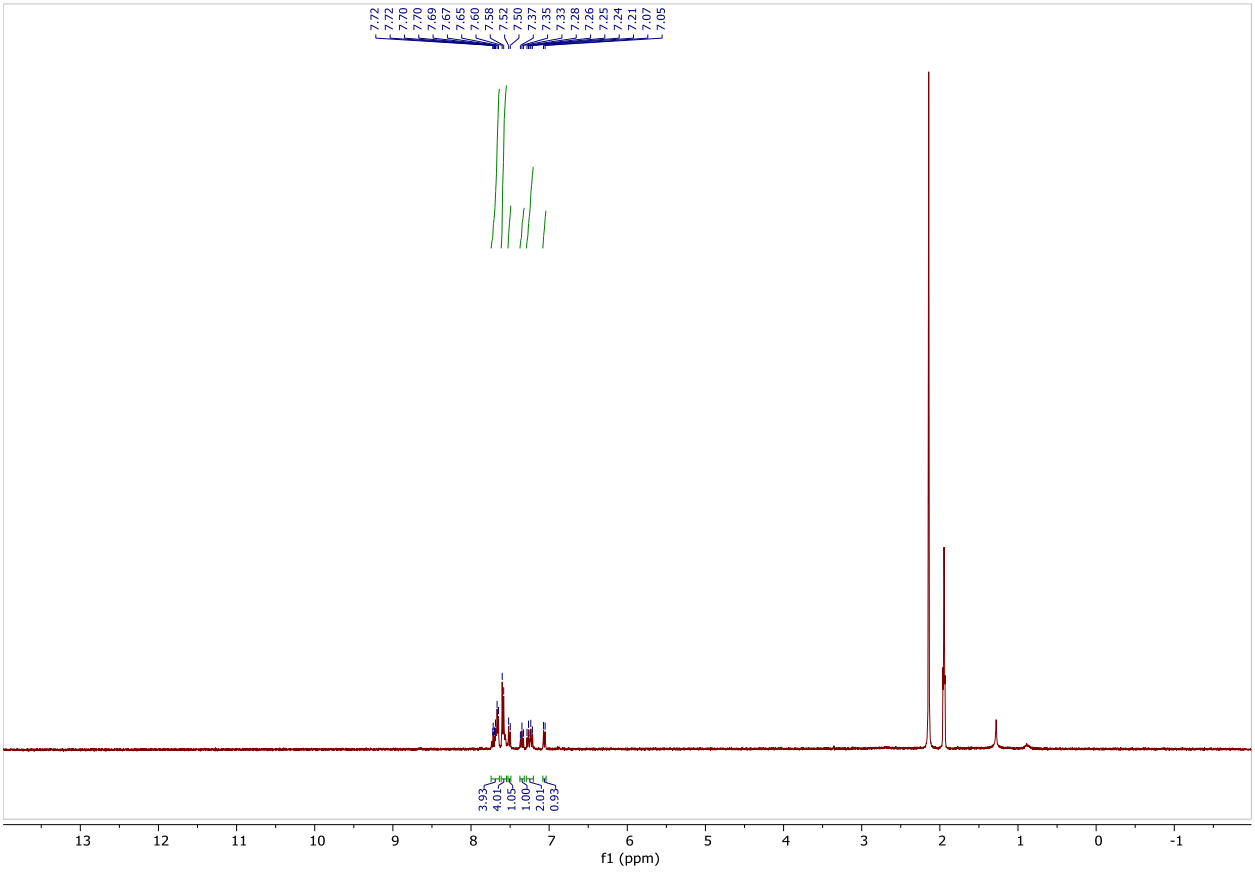


Figure S18. $^{13}C\{^{1}H\}$ NMR (100 MHz) Spectrum of compound **3b** (*dr* = 20:1) in CD_3CN.

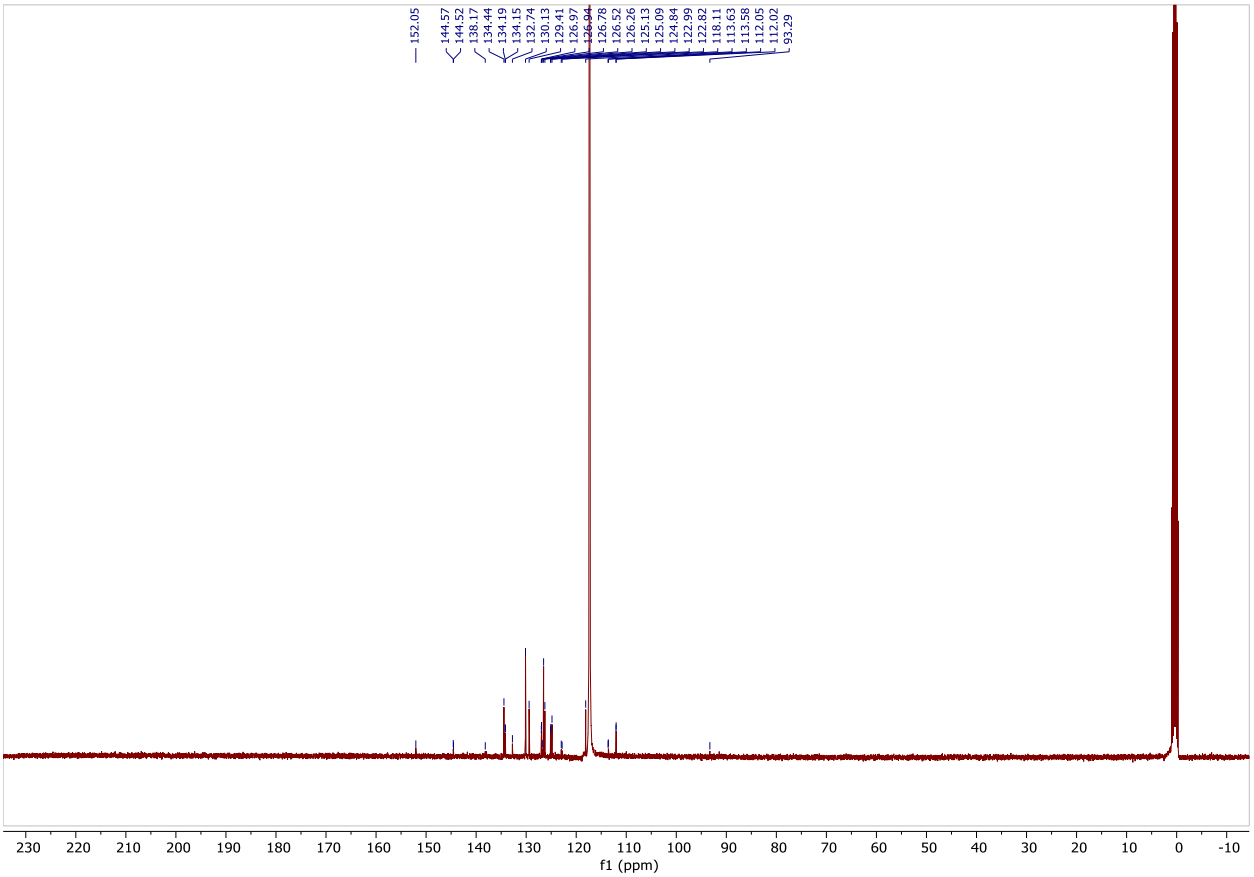
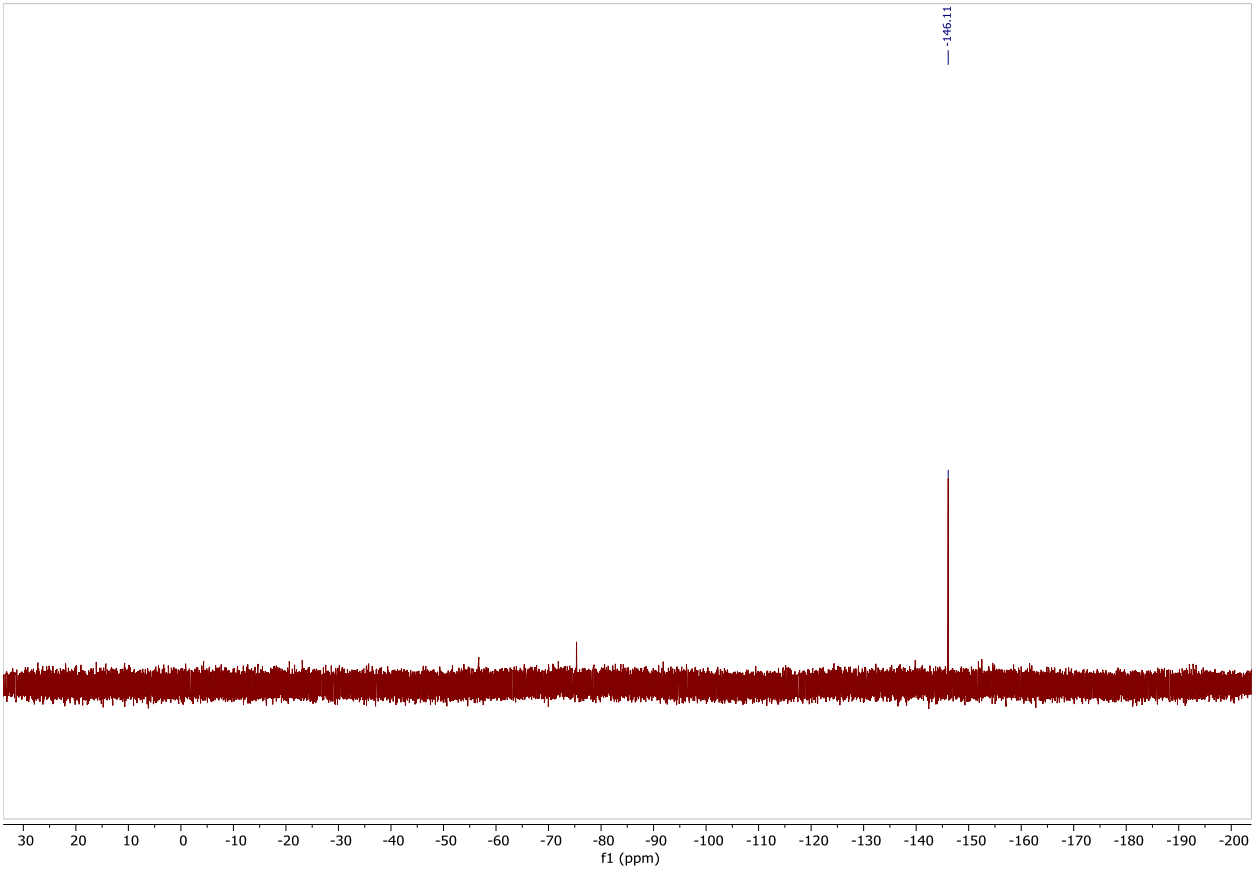


Figure S19. ^{19}F NMR (376 MHz) Spectrum of compound **3b** (*dr* = 20:1) in CD_3CN.



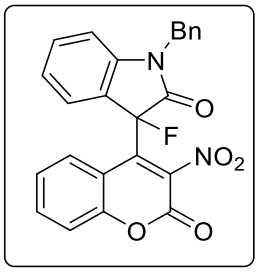


Figure S20. ^{1}H NMR (400 MHz) Spectrum of compound **3c** (*dr* = 31:1) in CD_3CN.

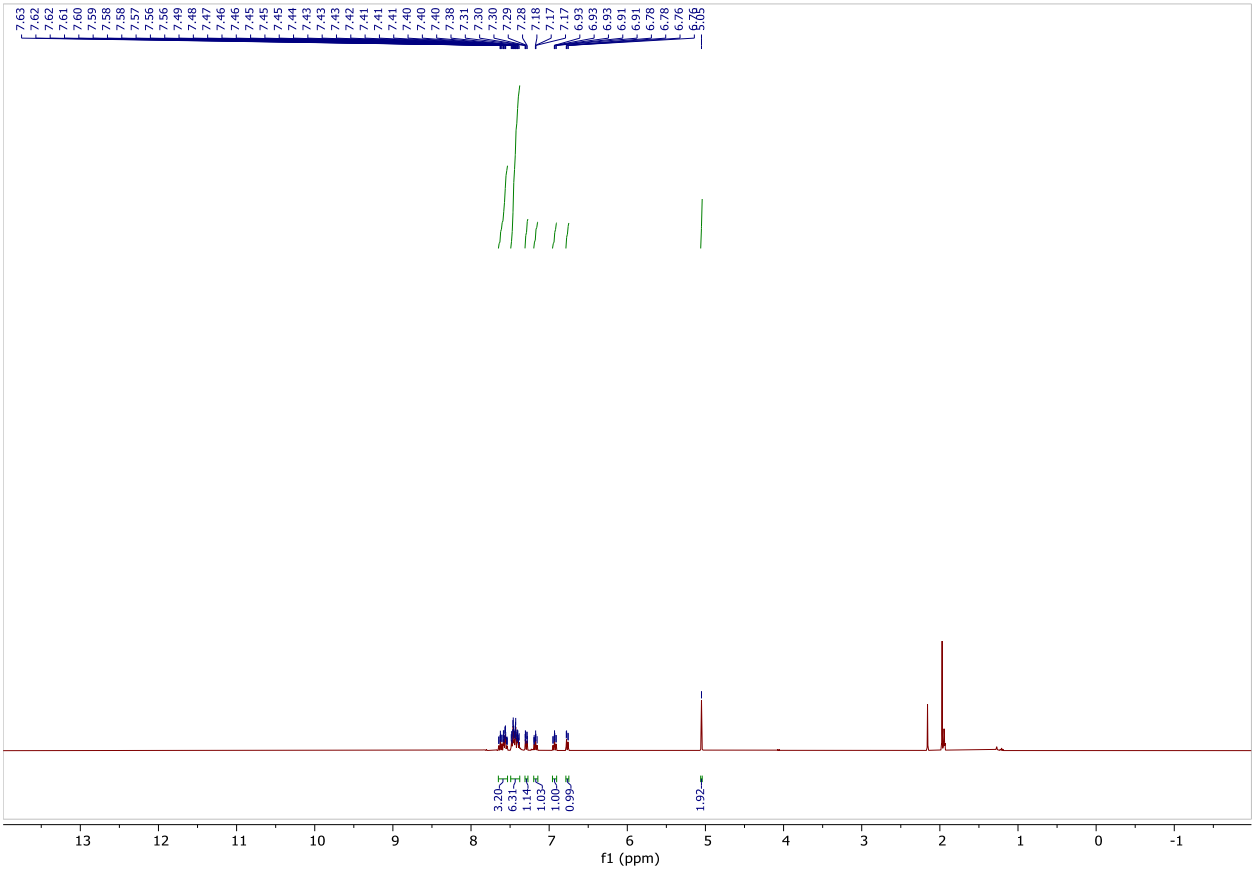


Figure S21. $^{13}C\{^{1}H\}$ NMR (100 MHz) Spectrum of compound **3c** (*dr* = 31:1) in CD_3CN.

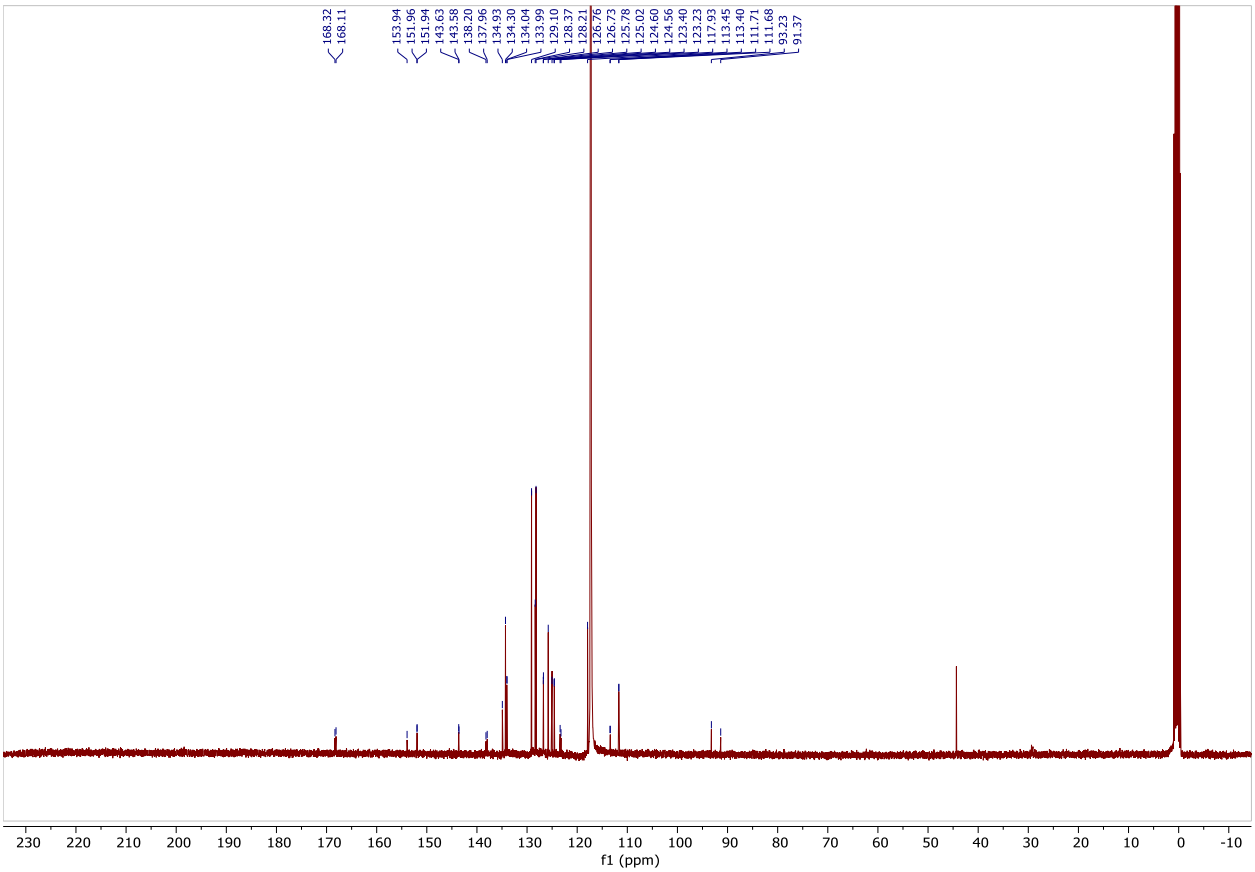
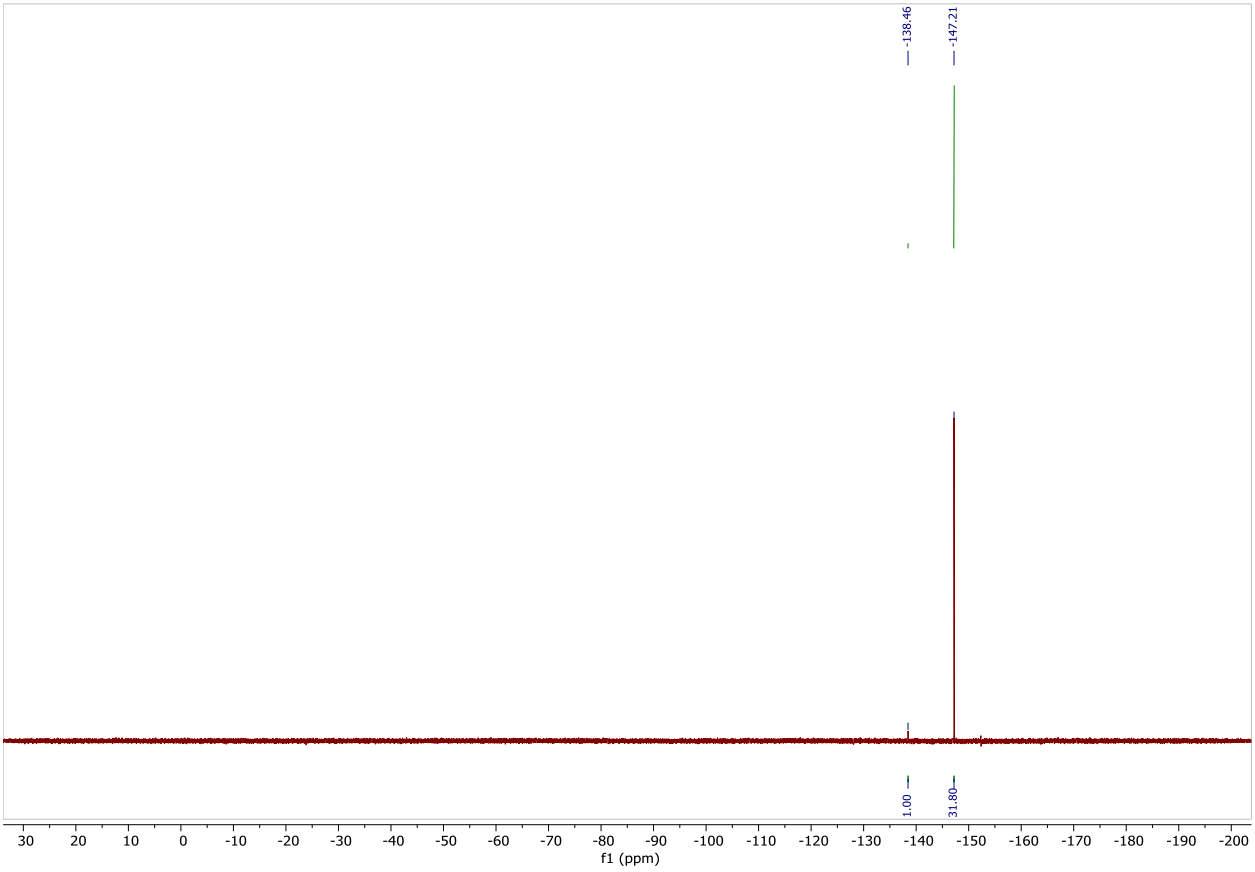


Figure S22. ^{19}F NMR (376 MHz) Spectrum of compound **3c** (*dr* = 31:1) in CD_3CN.



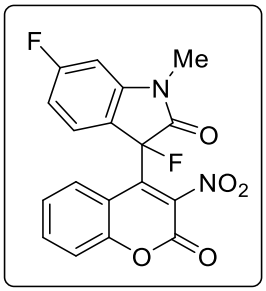


Figure S23. ^{1}H NMR (400 MHz) Spectrum of compound **3d** (*dr* = 20:1) in CD_3CN.

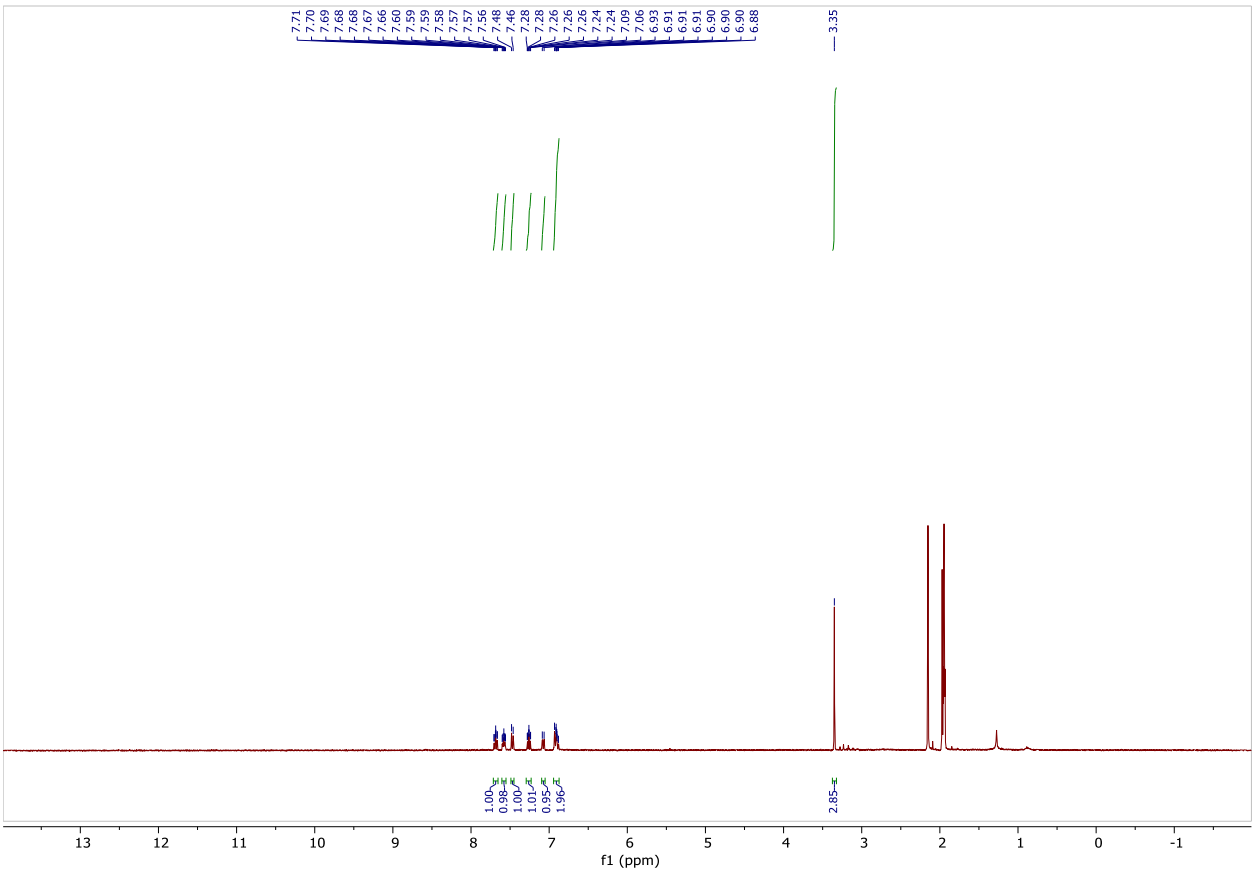


Figure S24. $^{13}C\{^{1}H\}$ NMR (100 MHz) Spectrum of compound **3d** (*dr* = 20:1) in CD_3CN.

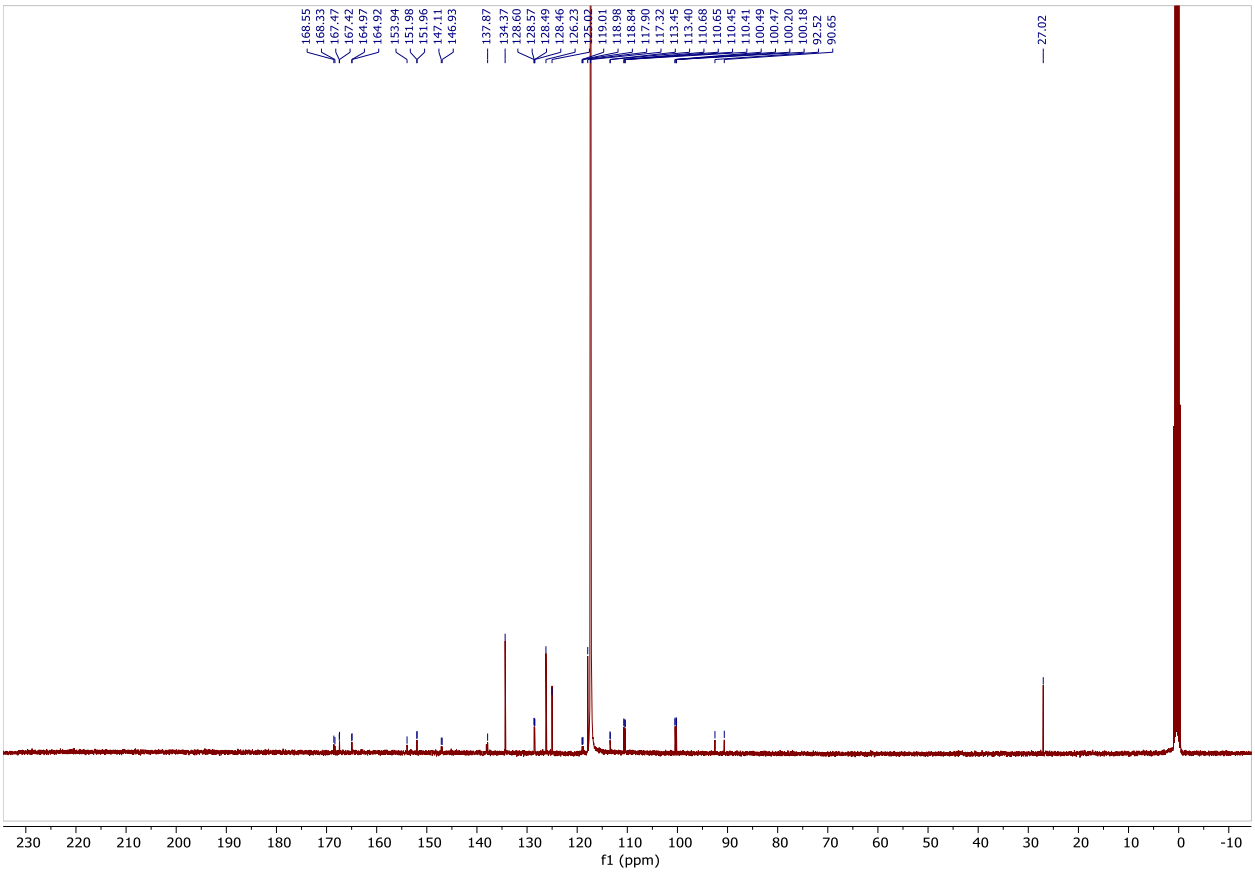
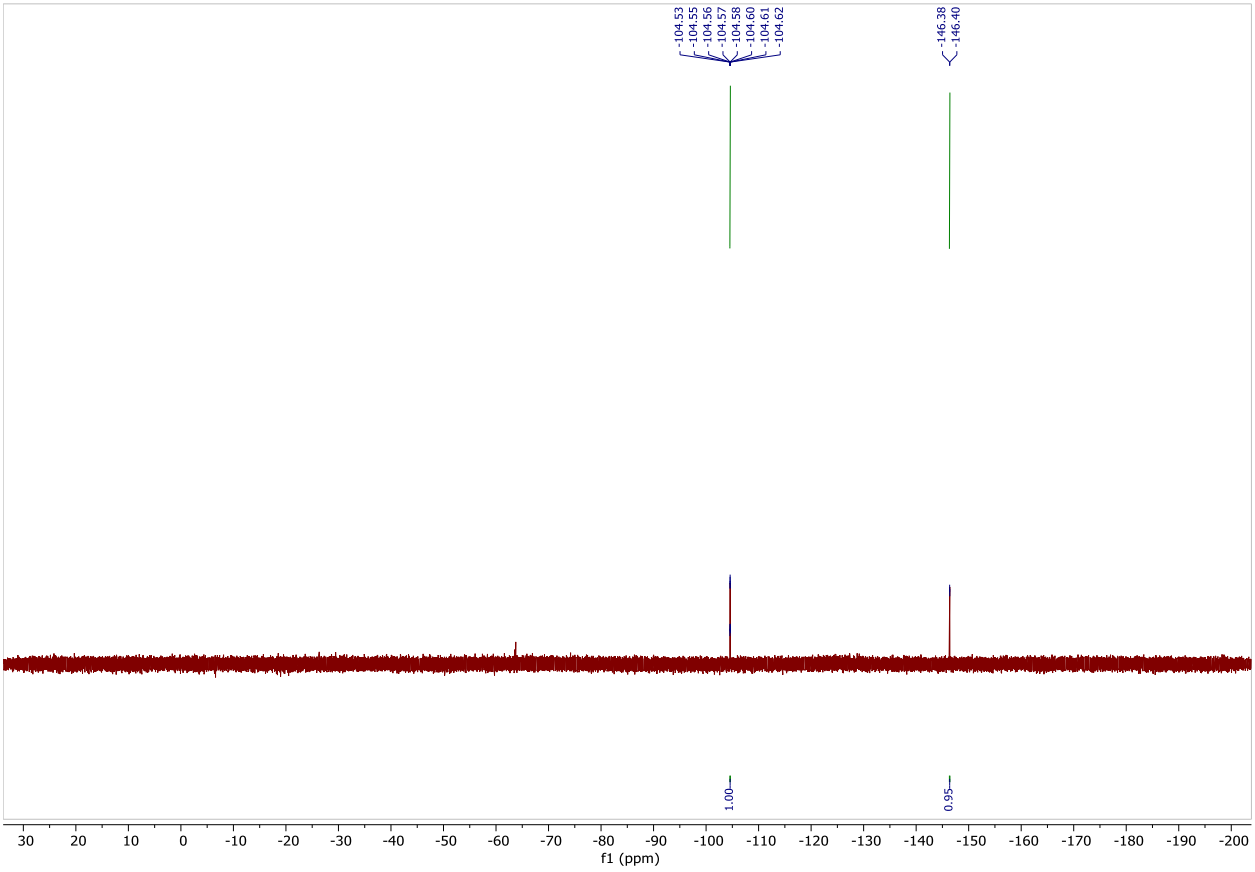


Figure S25. ^{19}F NMR (376 MHz) Spectrum of compound **3d** (*dr* = 20:1) in CD_3CN.



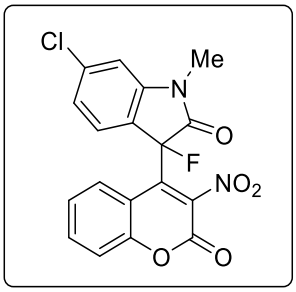


Figure S26. ^{1}H NMR (400 MHz) Spectrum of compound **3e** (*dr* = 24:1) in CD_3CN.

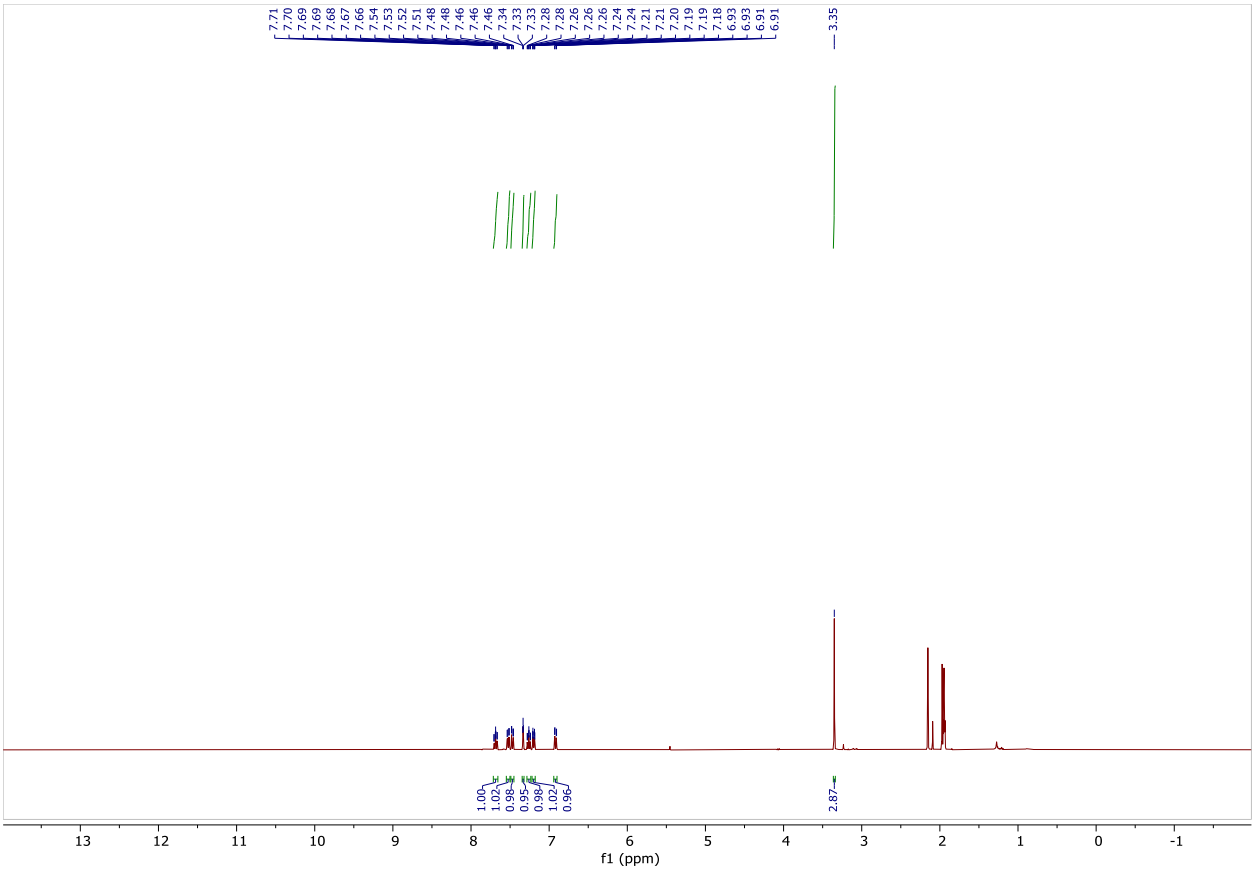


Figure S27. $^{13}C\{^{1}H\}$ NMR (100 MHz) Spectrum of compound **3e** (*dr* = 24:1) in CD_3CN.

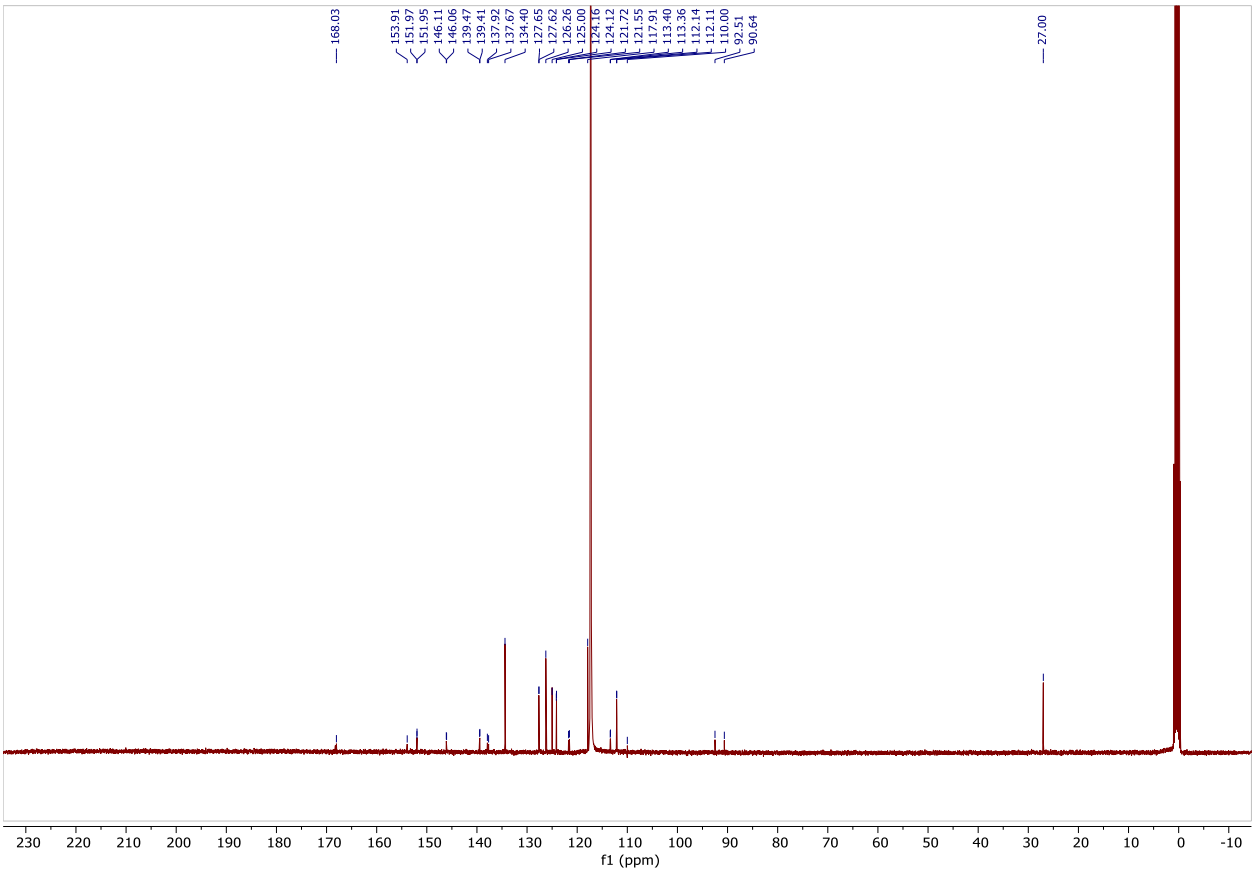
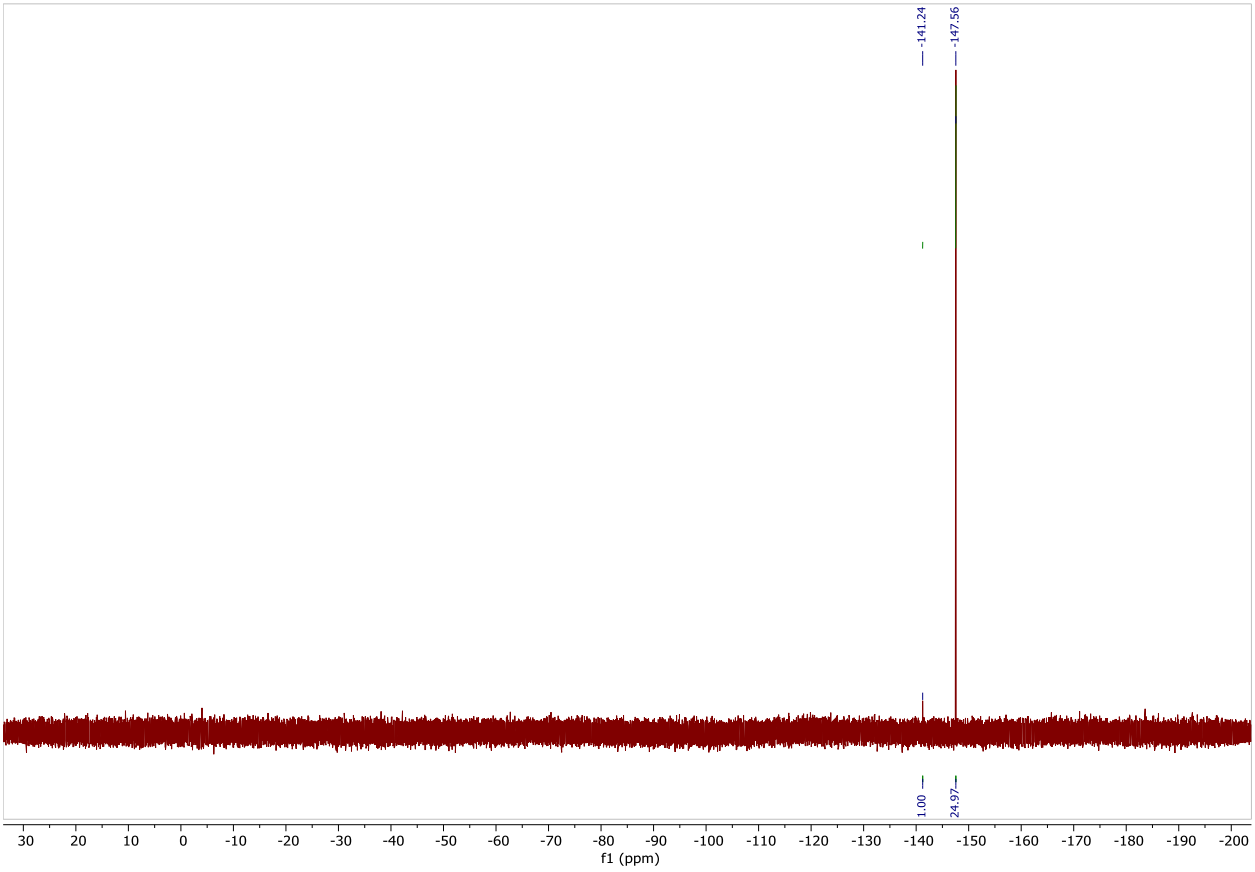


Figure S28. ^{19}F NMR (376 MHz) Spectrum of compound **3e** (*dr* = 24:1) in CD_3CN.



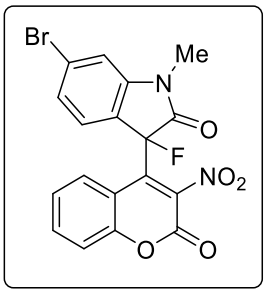


Figure S29. ^{1}H NMR (400 MHz) Spectrum of compound **3f** (*dr* = 26:1) in CD_3CN.

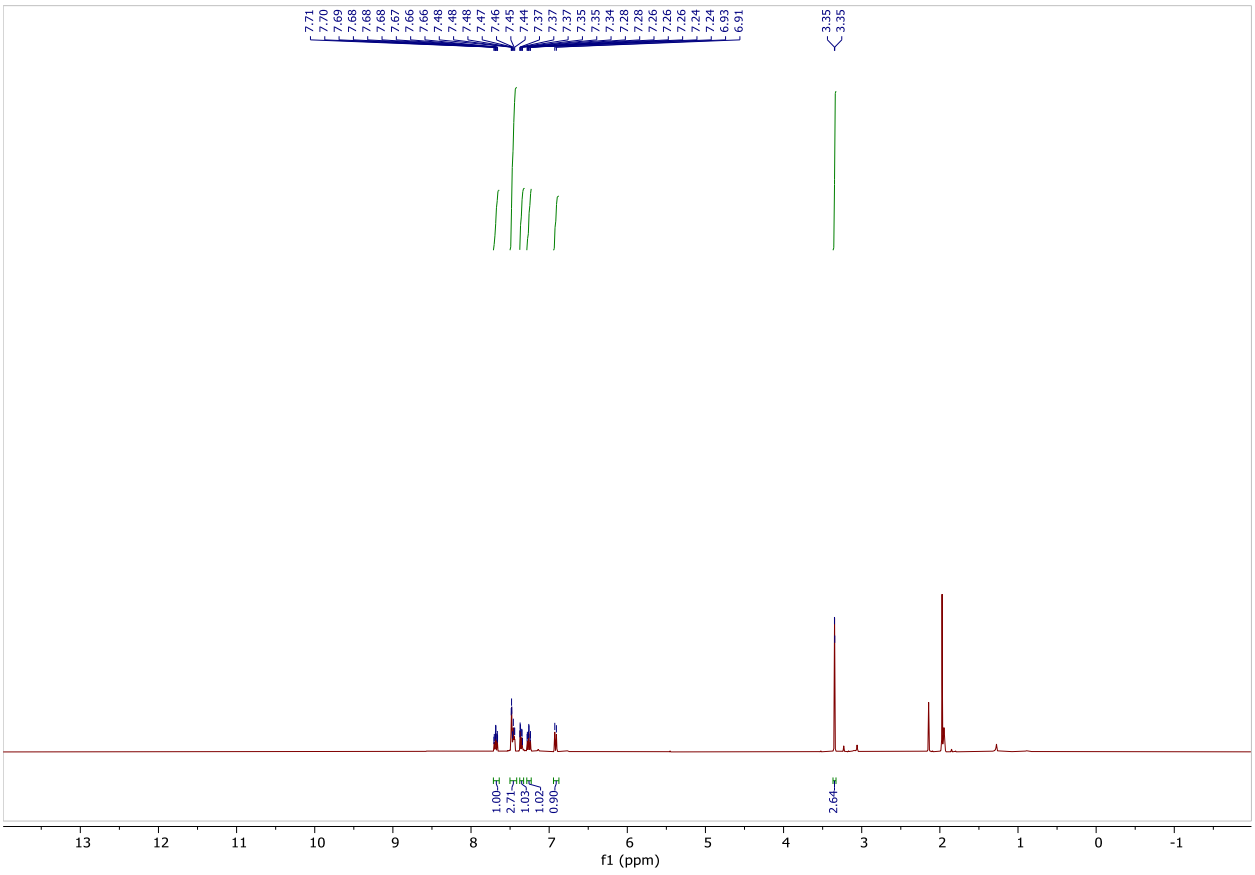


Figure S30. $^{13}C\{^{1}H\}$ NMR (100 MHz) Spectrum of compound **3f** (*dr* = 26:1) in CD_3CN.

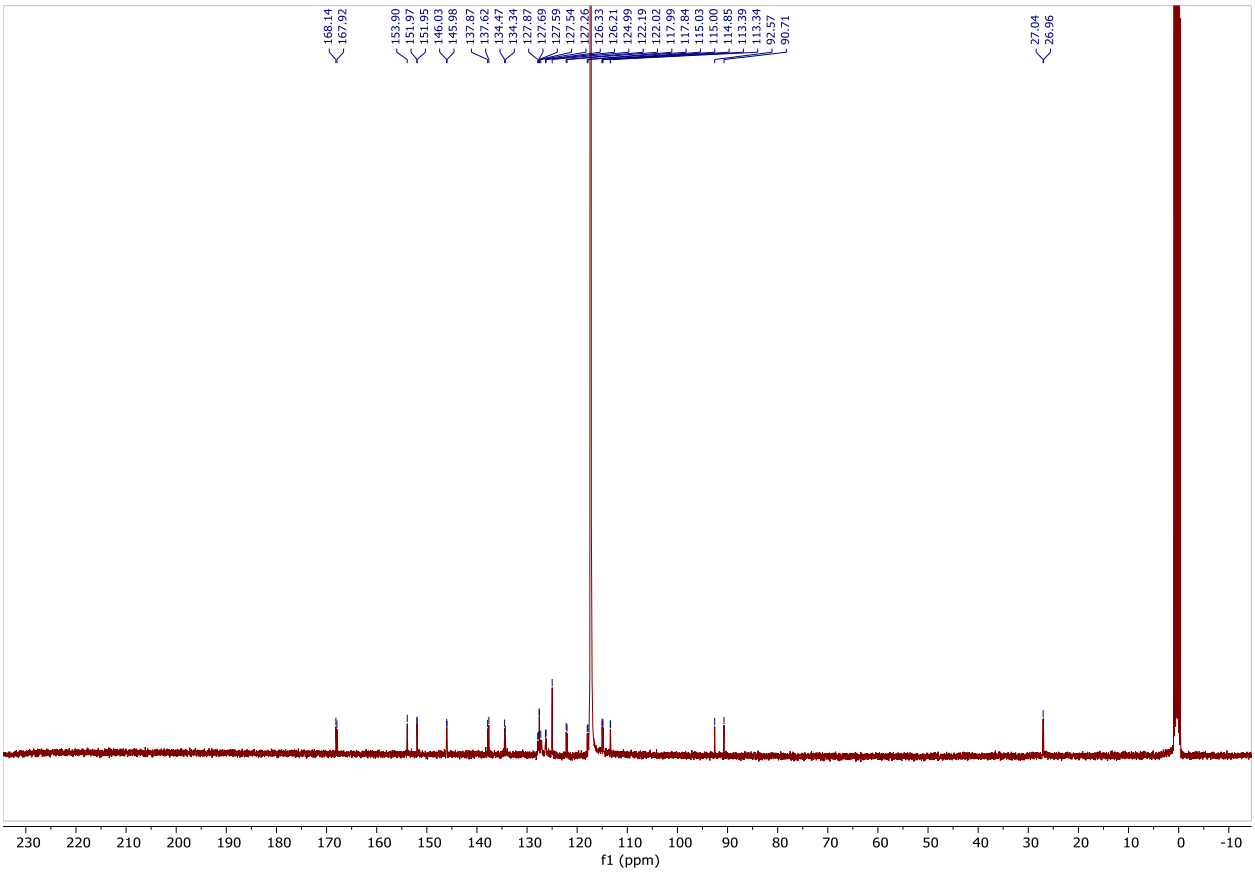
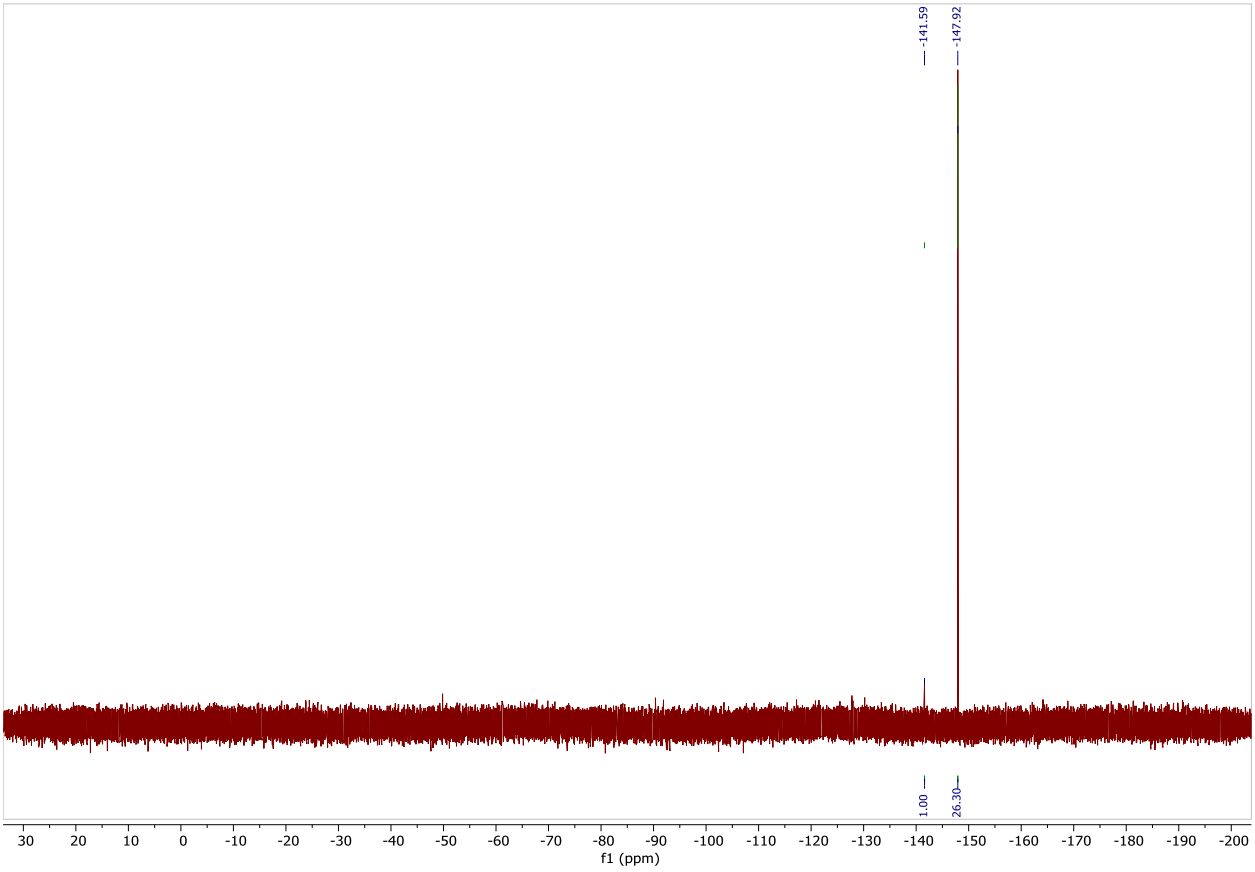


Figure S31. ^{19}F NMR (376 MHz) Spectrum of compound **3f** (*dr* = 26:1) in CD_3CN.



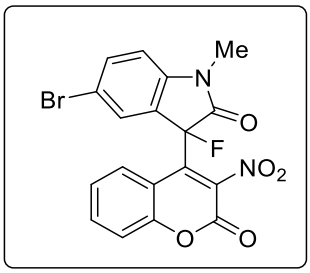


Figure S32. ^{1}H NMR (400 MHz) Spectrum of compound **3g** (*dr* = 28:1) in CD_3CN.

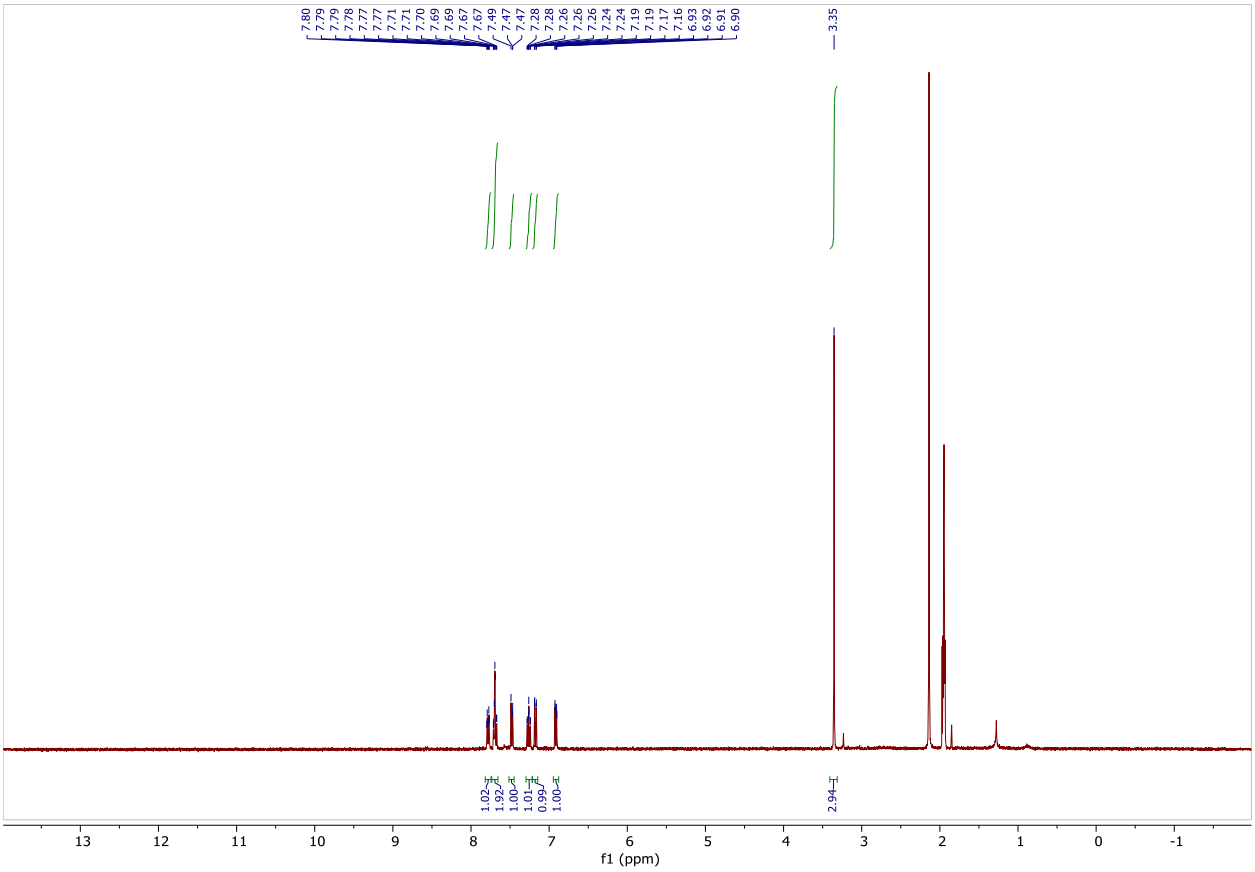


Figure S33. $^{13}C\{^{1}H\}$ NMR (100 MHz) Spectrum of compound **3g** (*dr* = 28:1) in CD_3CN.

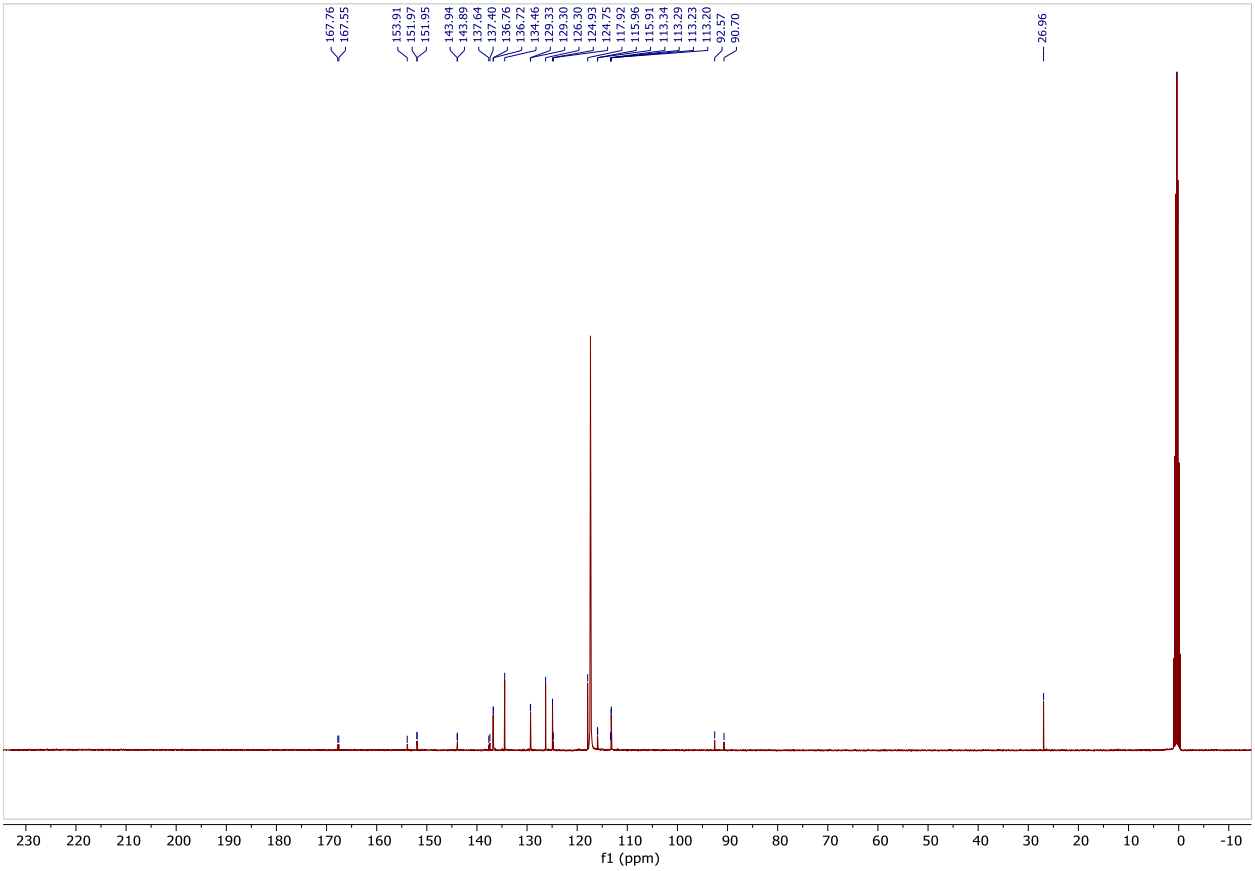
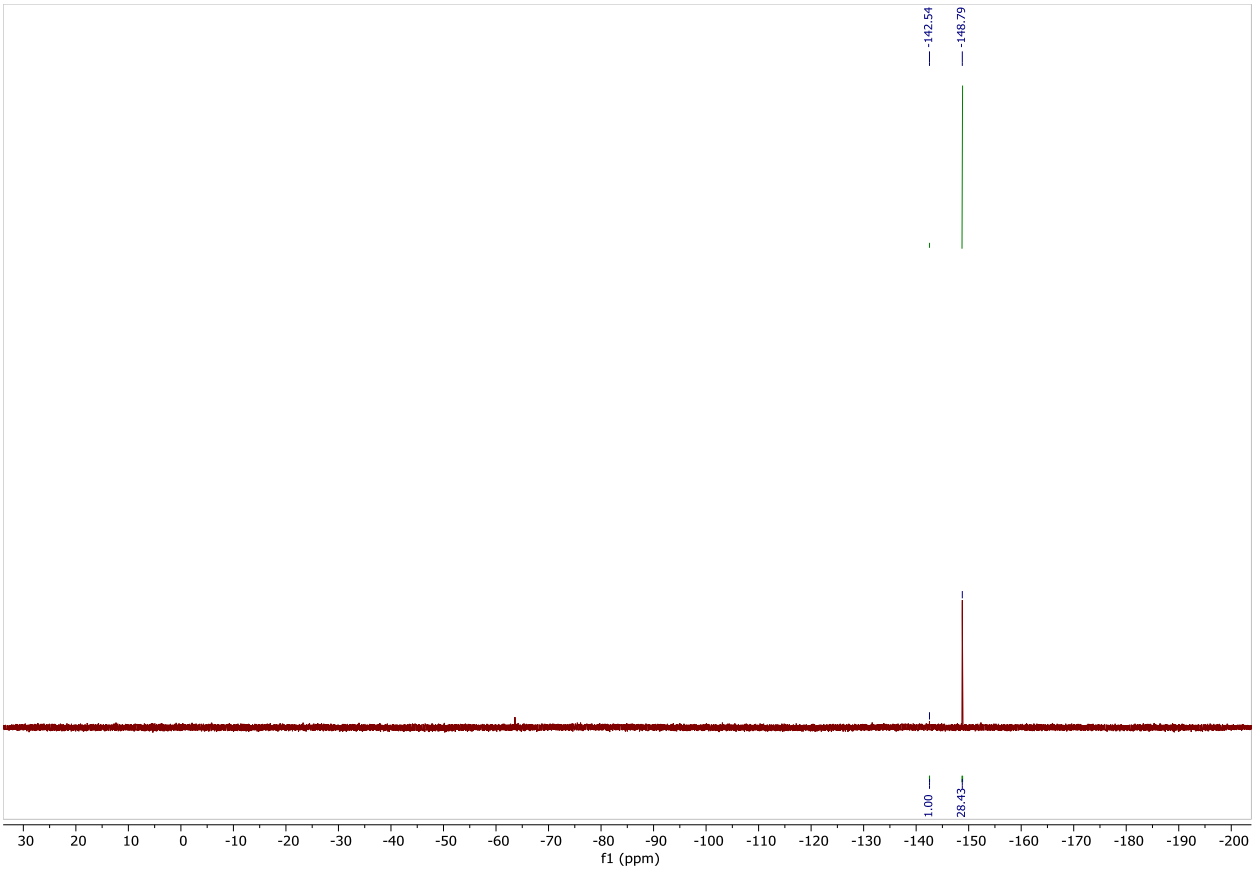


Figure S34. ^{19}F NMR (376 MHz) Spectrum of compound **3g** (*dr* = 28:1) in CD_3CN.



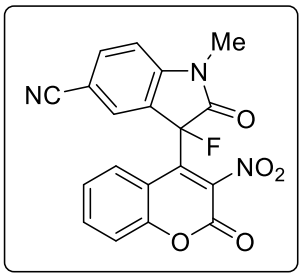


Figure S35. ^{1}H NMR (400 MHz) Spectrum of compound **3h** (*dr* = 16:1) in CD_3CN.

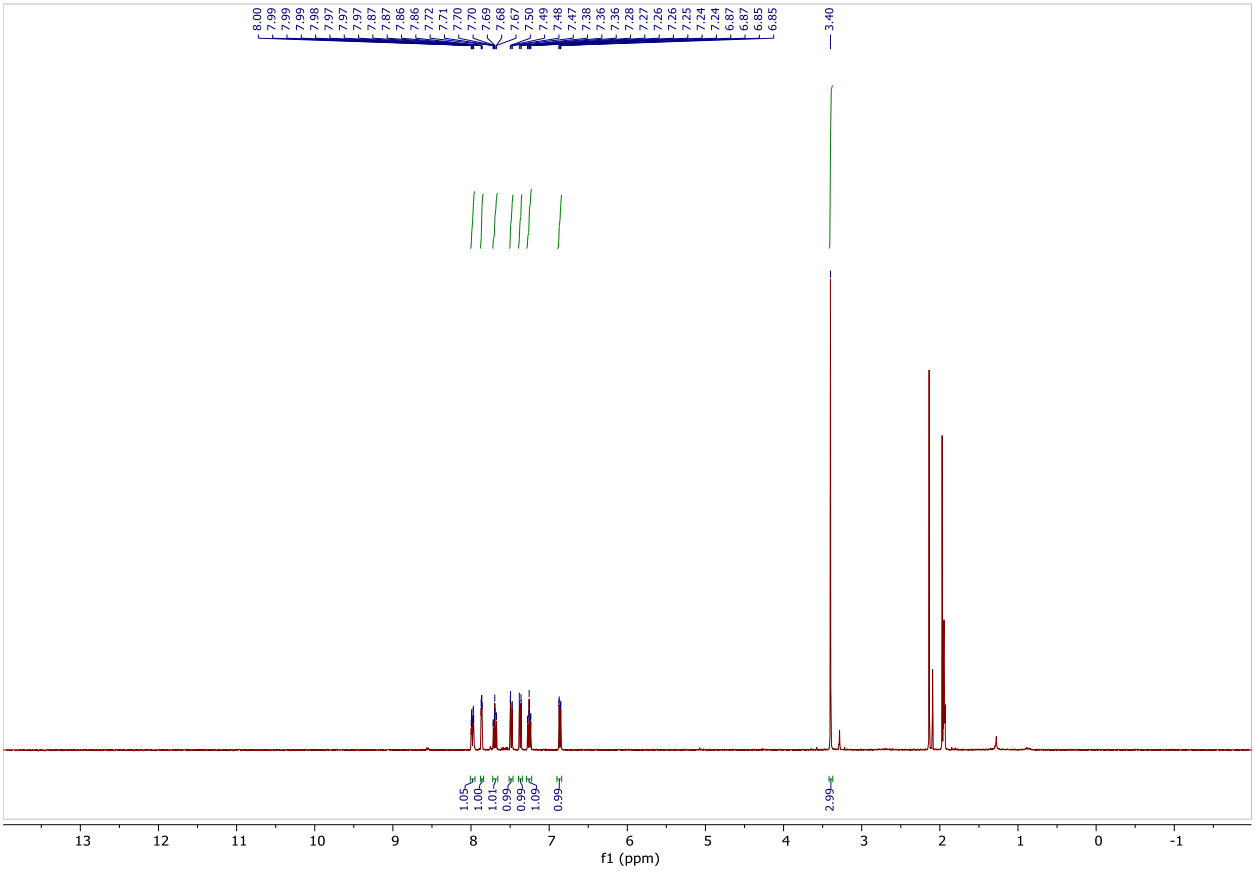


Figure S36. $^{13}C\{^{1}H\}$ NMR (100 MHz) Spectrum of compound **3h** (*dr* = 16:1) in CD_3CN.

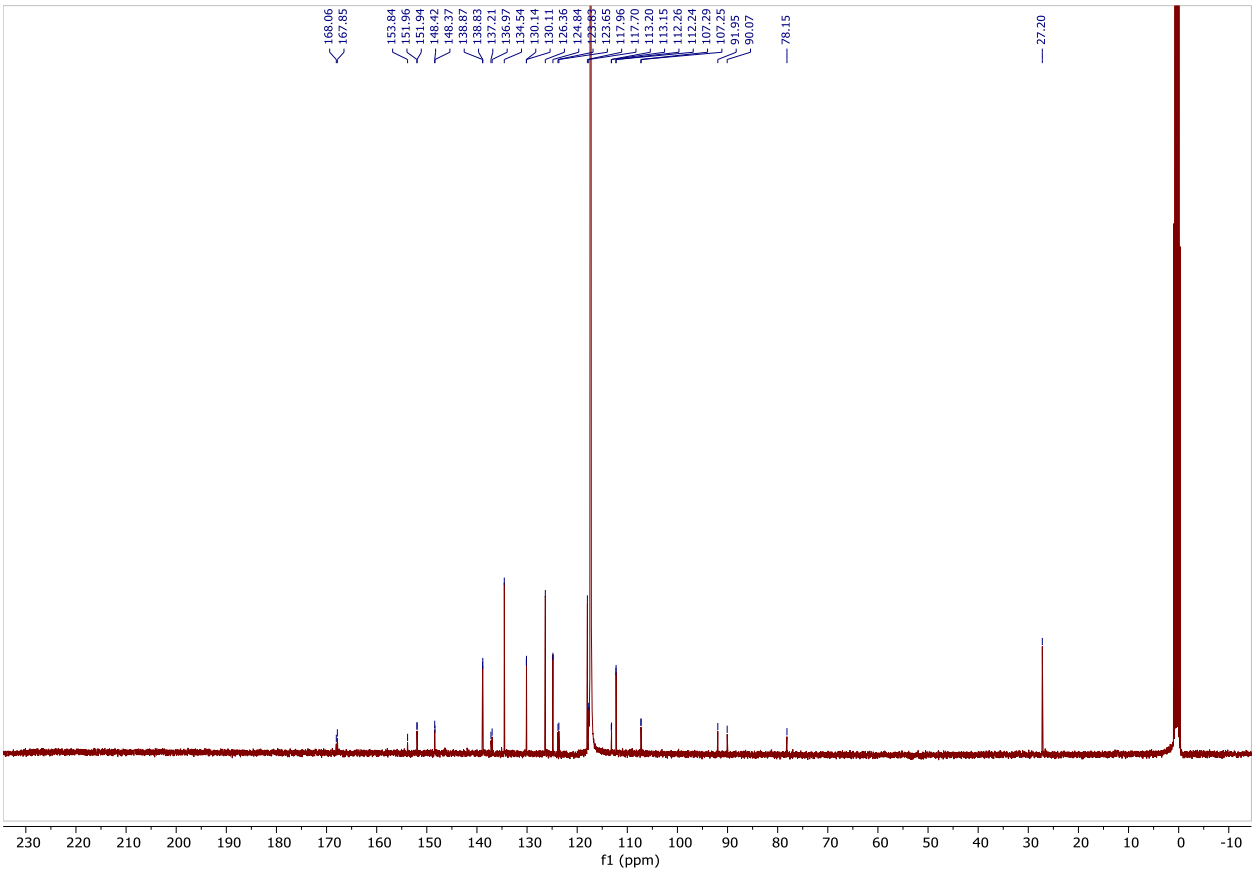
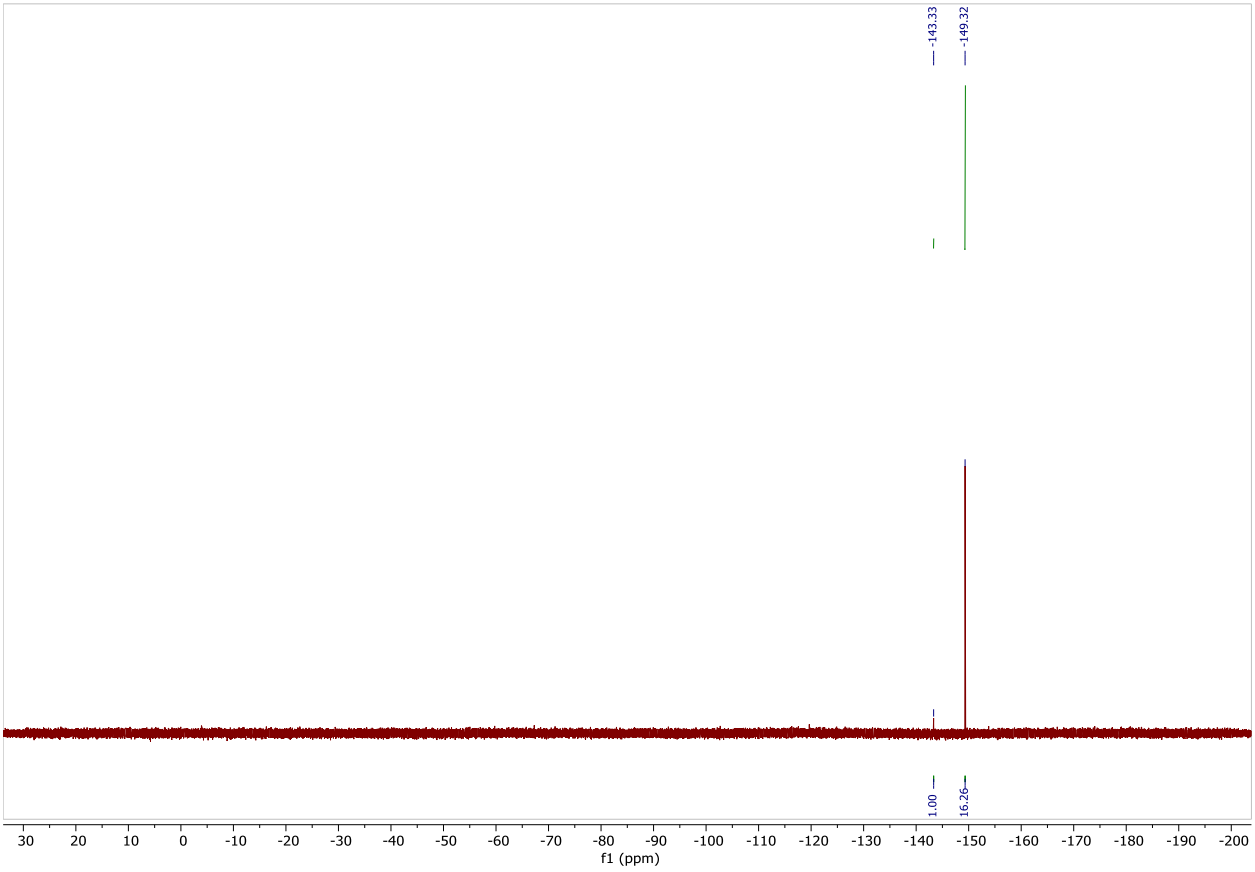


Figure S37. ^{19}F NMR (376 MHz) Spectrum of compound **3h** (*dr* = 16:1) in CD_3CN.



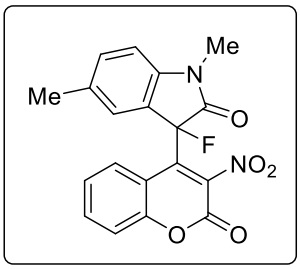


Figure S38. ^{1}H NMR (400 MHz) Spectrum of compound **3i** (*dr* = 27:1) in CD_3CN.

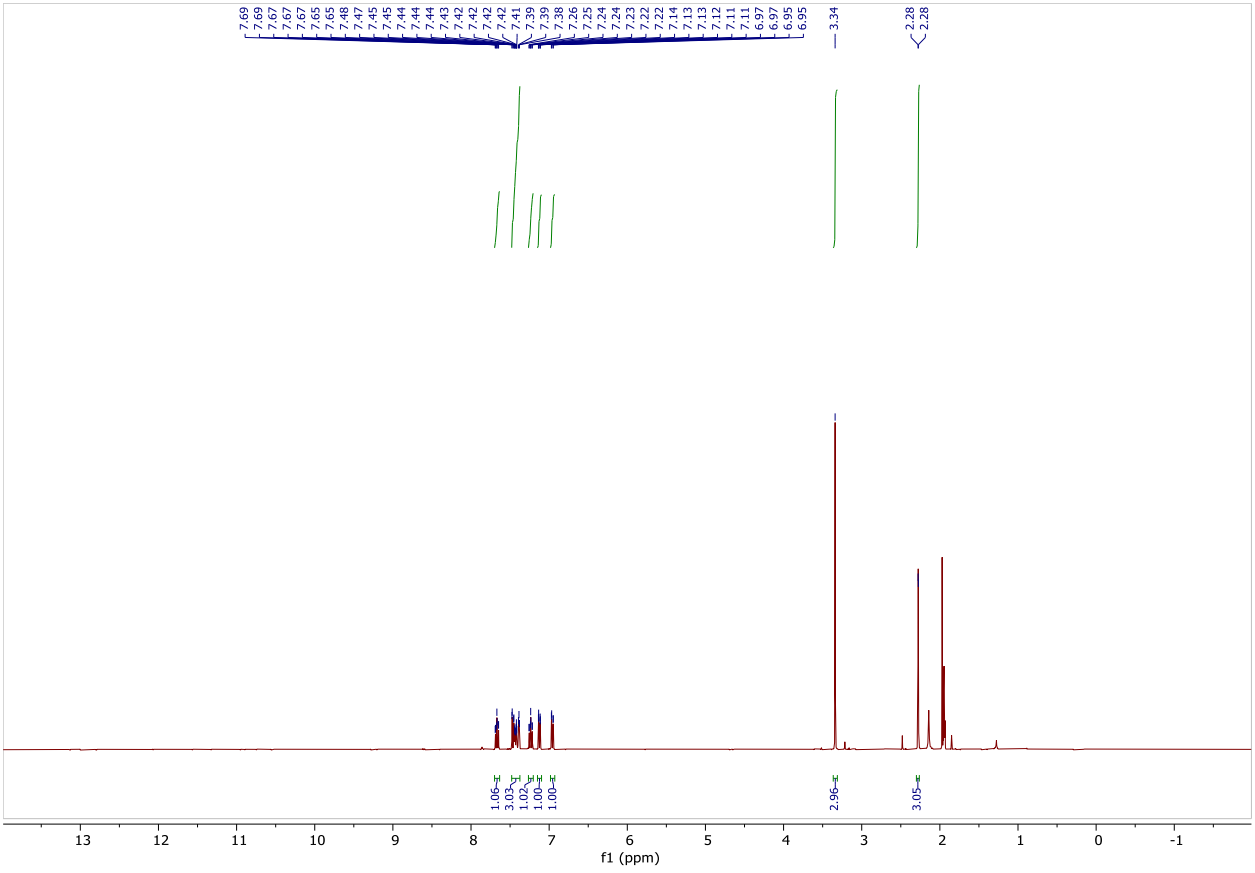


Figure S39. $^{13}C\{^{1}H\}$ NMR (100 MHz) Spectrum of compound **3i** (*dr* = 27:1) in CD_3CN.

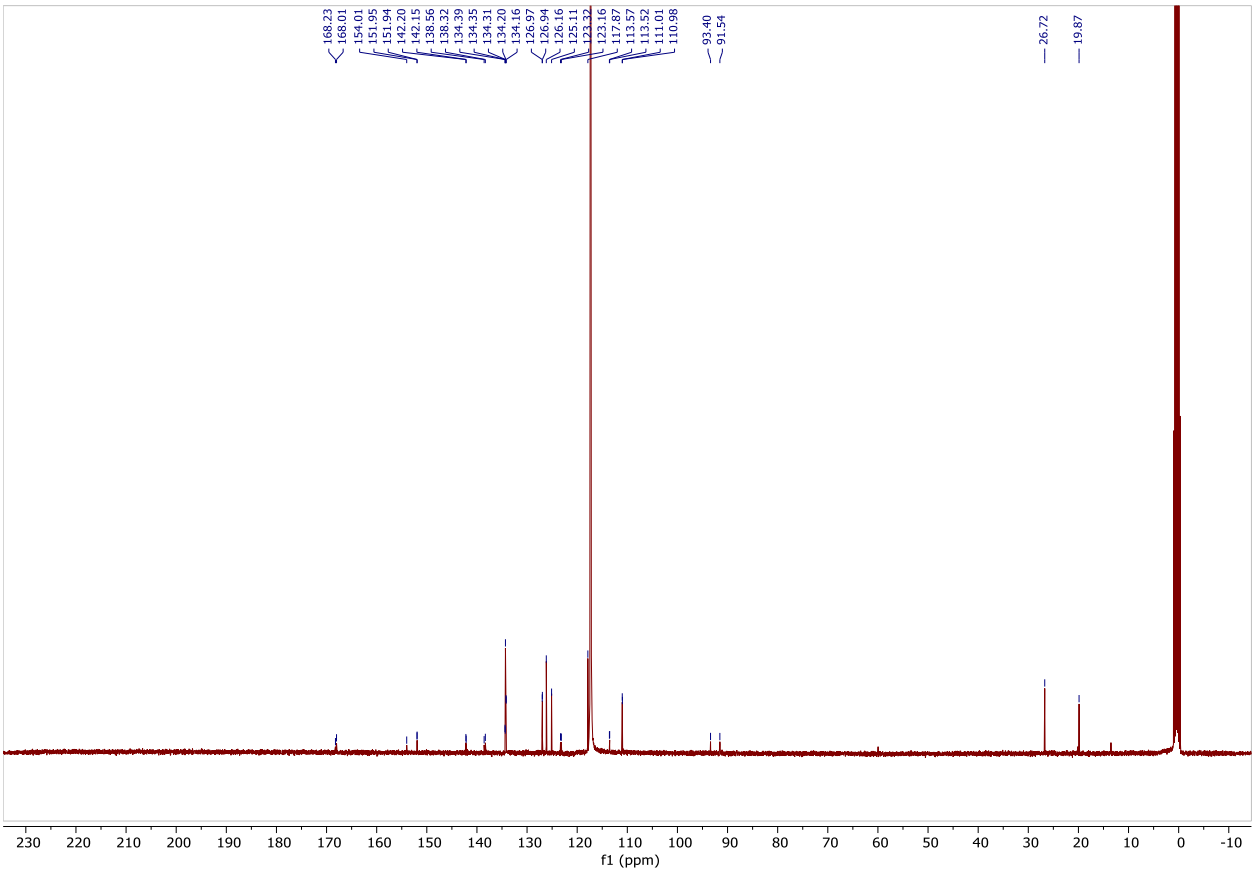
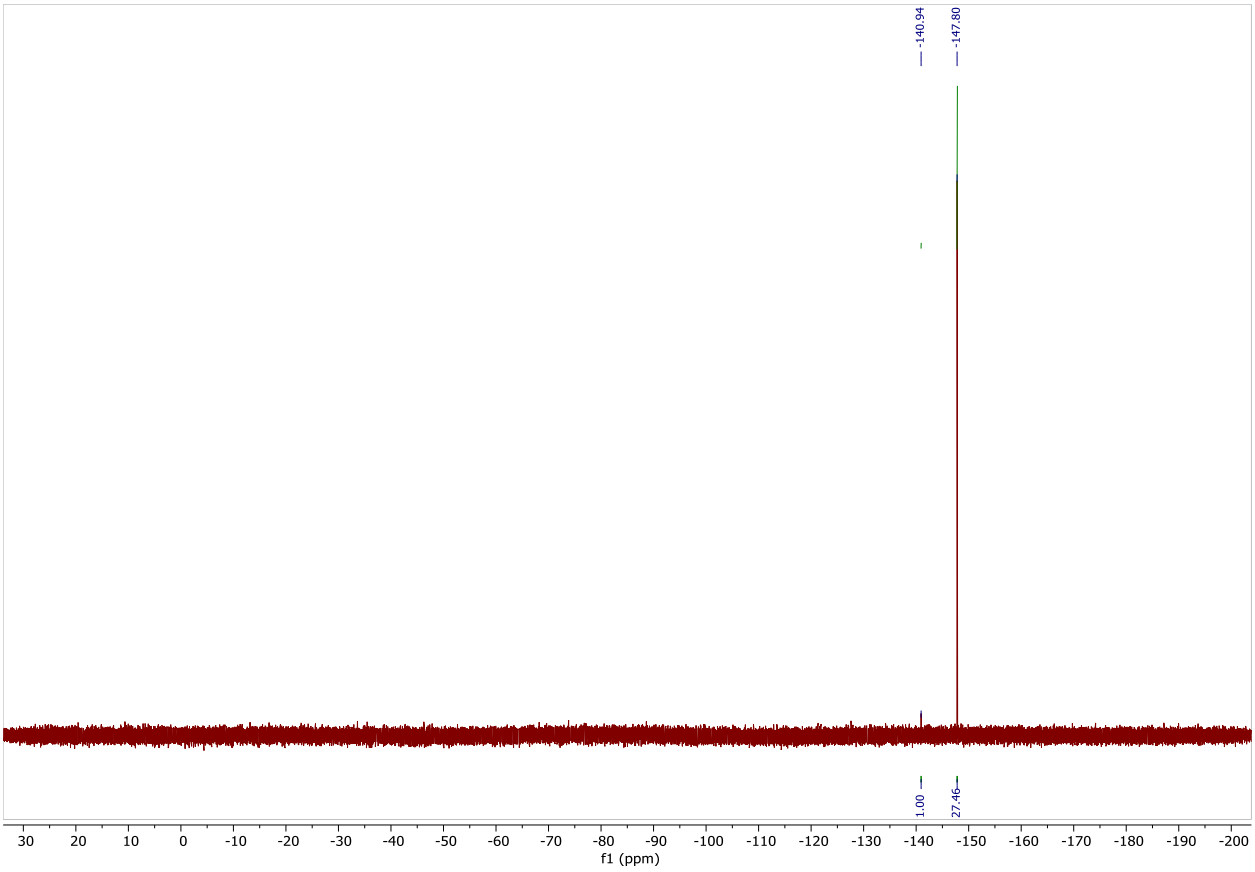


Figure S40. ^{19}F NMR (376 MHz) Spectrum of compound **3i** (*dr* = 27:1) in CD_3CN.



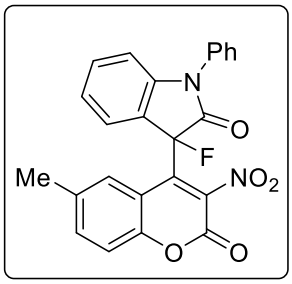


Figure S41. ^{1}H NMR (400 MHz) Spectrum of compound **4a** (*dr* = 15:1) in CD_3CN.

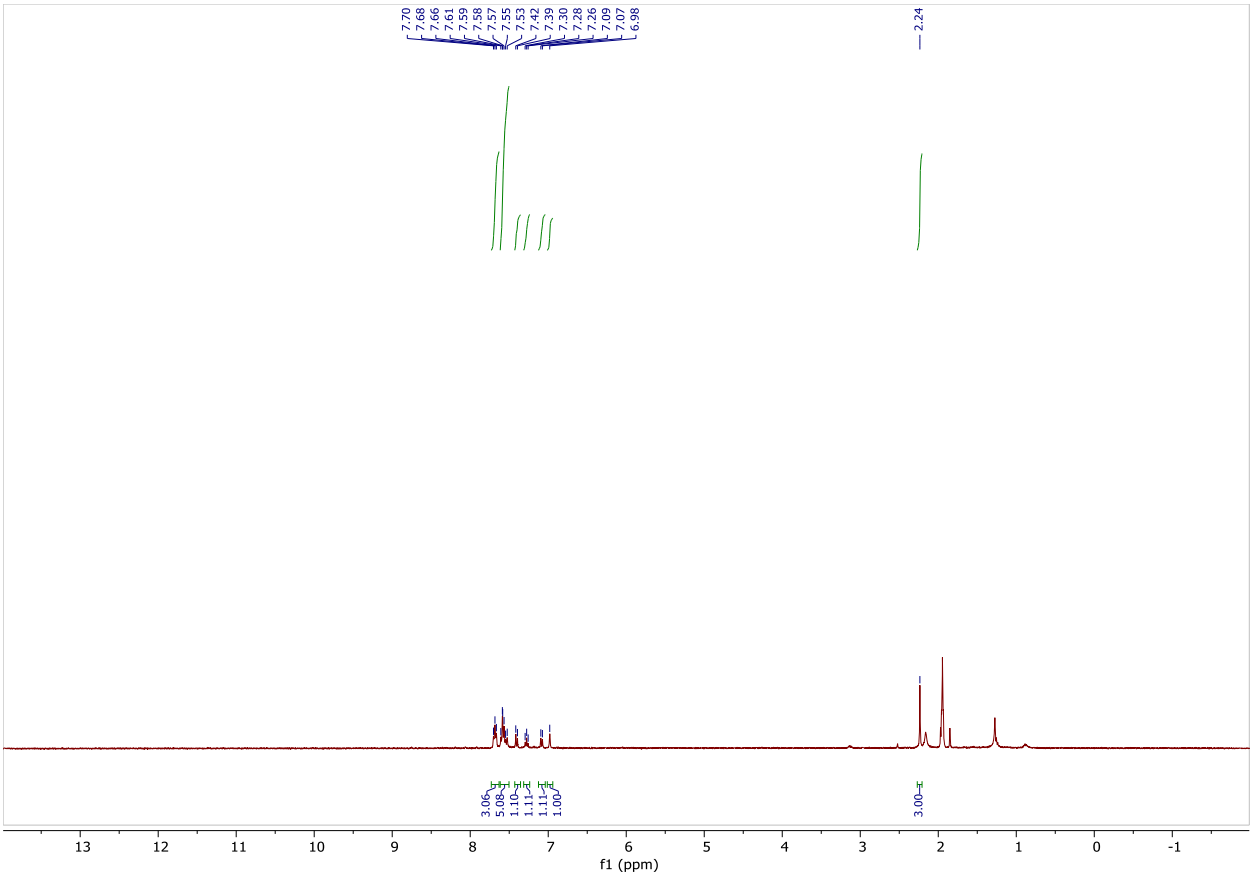


Figure S42. $^{13}C\{^{1}H\}$ NMR (100 MHz) Spectrum of compound **4a** (*dr* = 15:1) in CD_3CN.

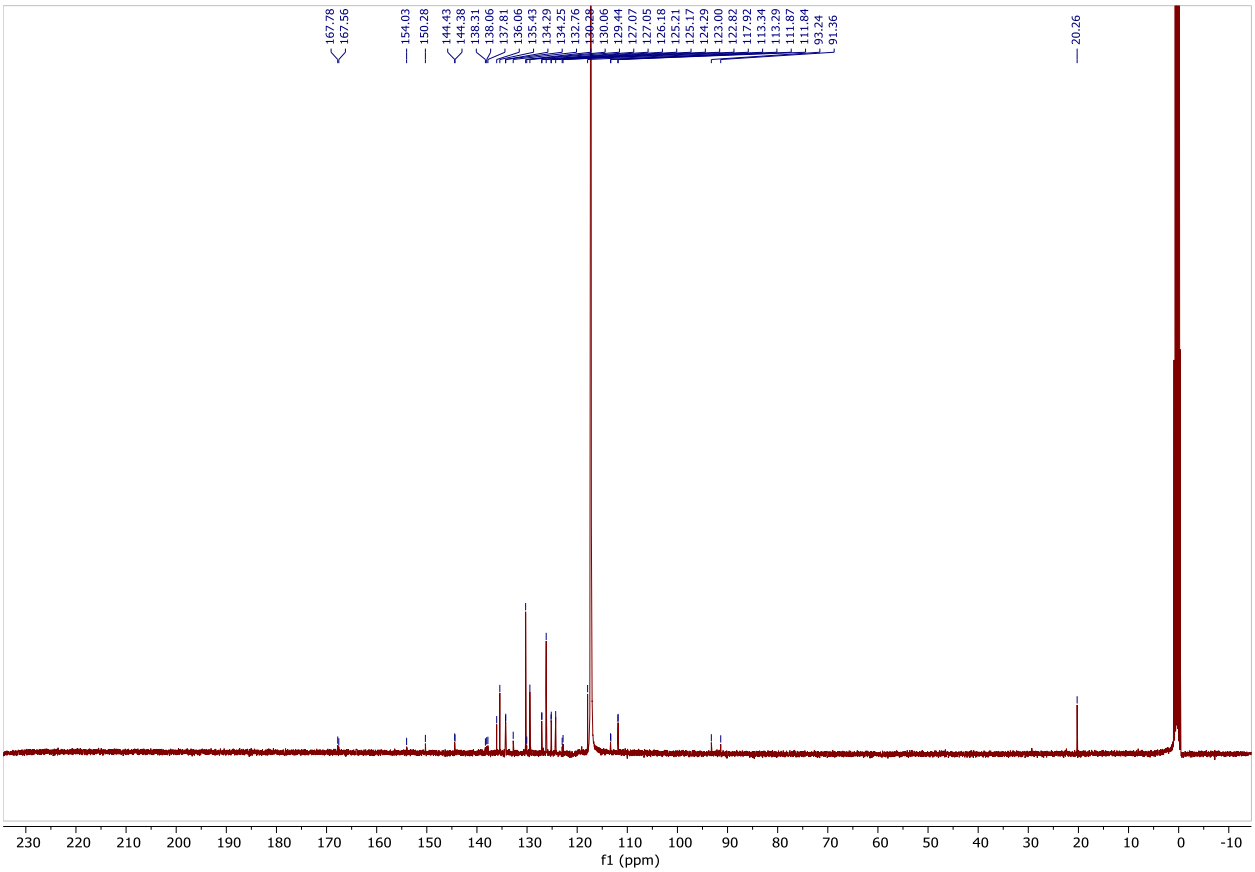
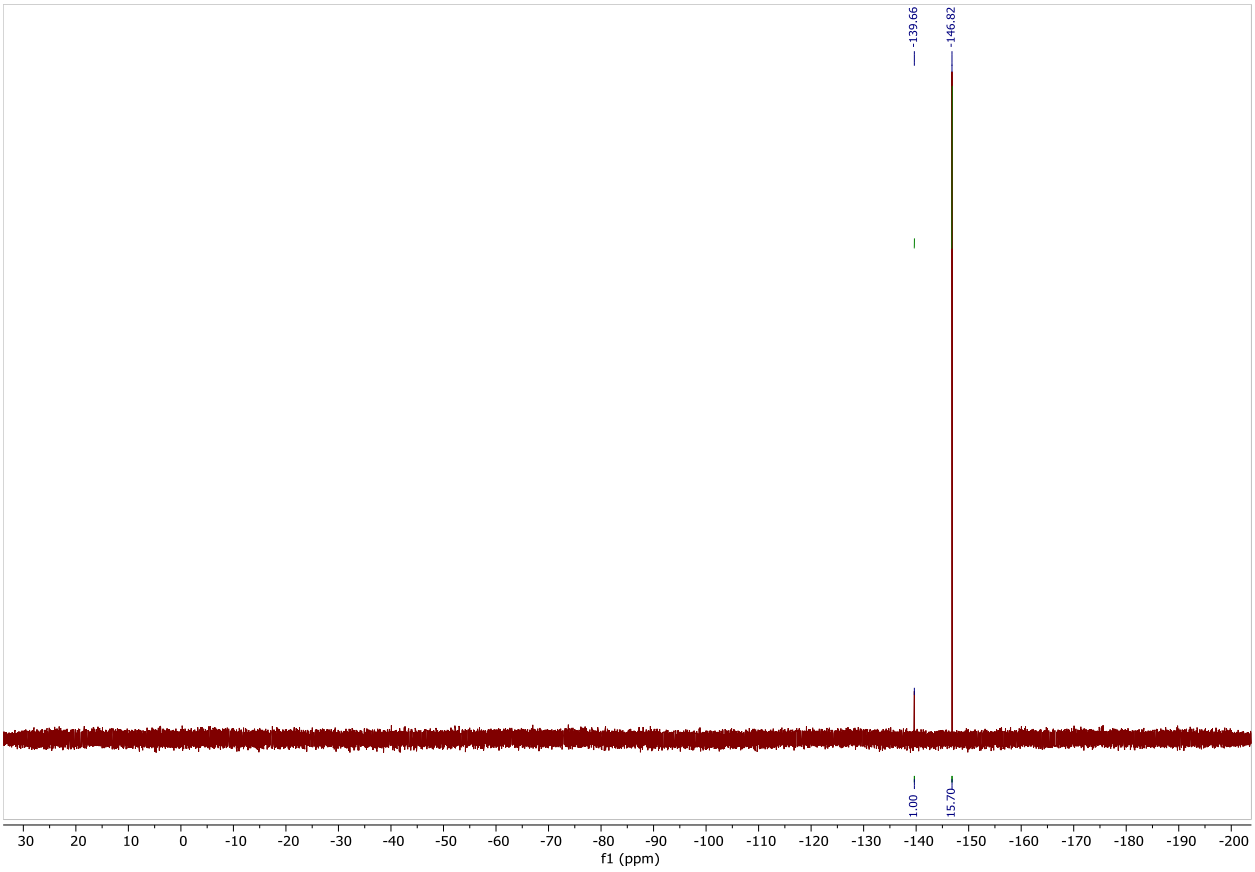


Figure S43. ^{19}F NMR (376 MHz) Spectrum of compound **4a** (*dr* = 15:1) in CD_3CN.



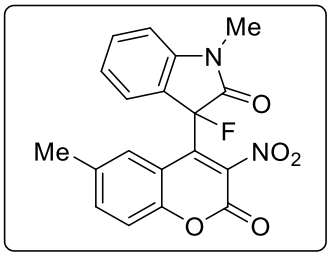


Figure S44. ^{1}H NMR (400 MHz) Spectrum of compound **4b** (*dr* = 28:1) in CD_3CN.

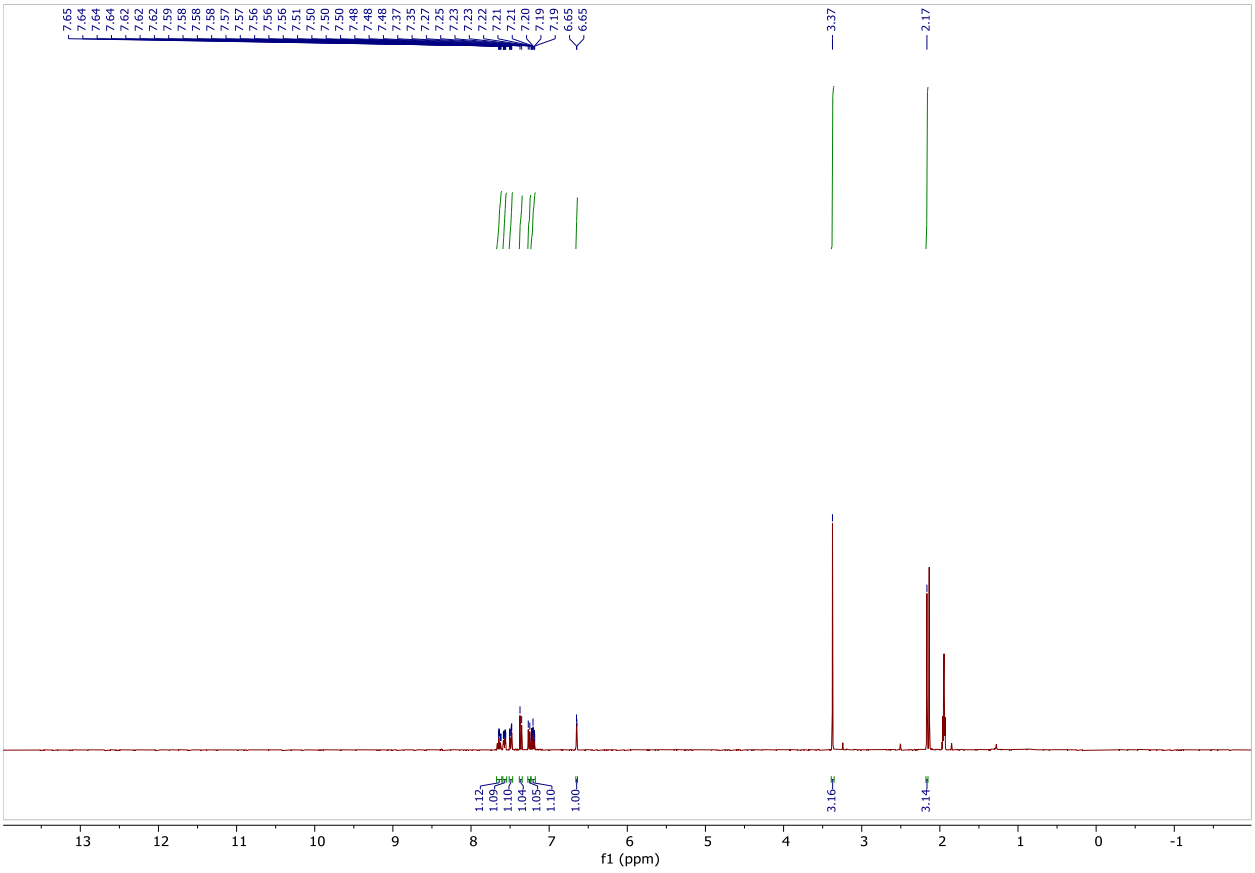


Figure S45. $^{13}C\{^{1}H\}$ NMR (100 MHz) Spectrum of compound **4b** (*dr* = 28:1) in CD_3CN.

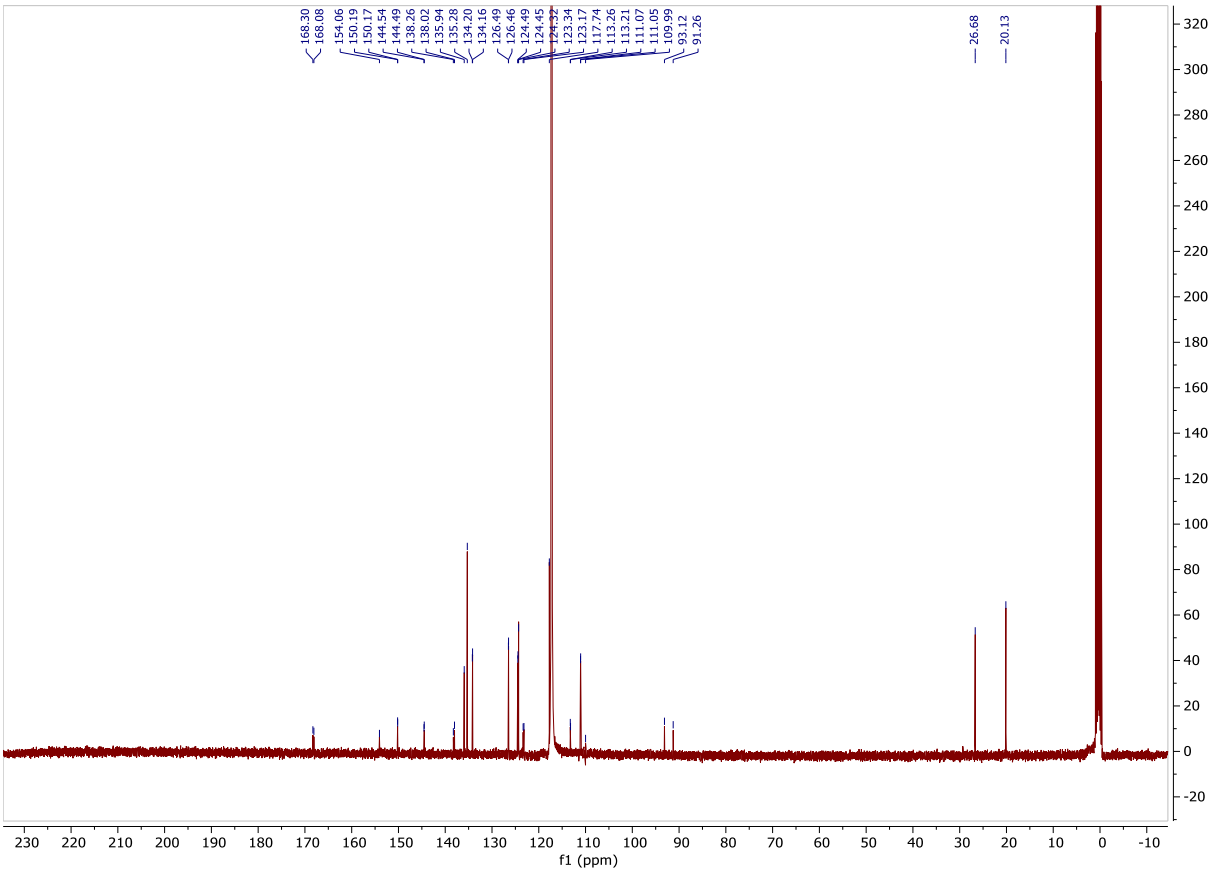
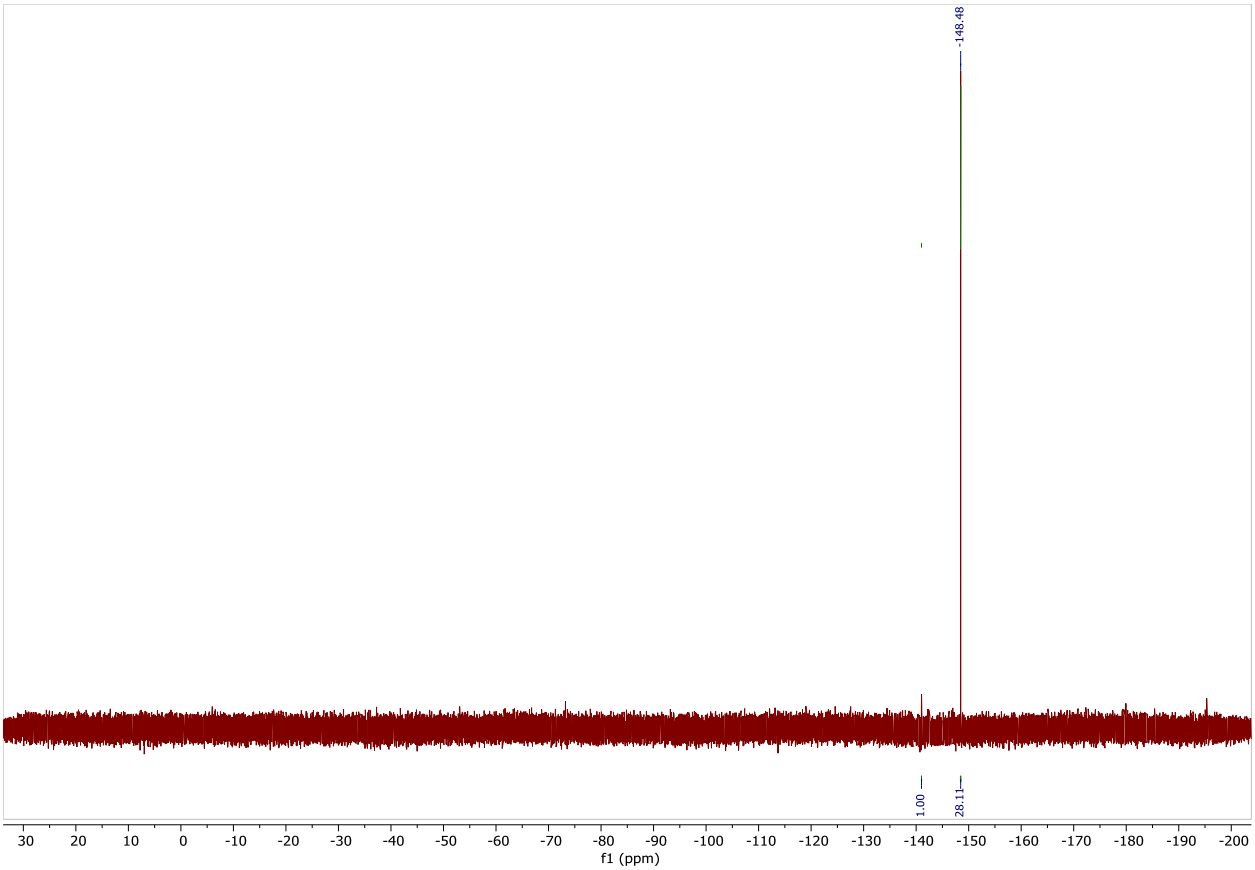


Figure S46. ^{19}F NMR (376 MHz) Spectrum of compound **4b** (*dr* = 28:1) in CD_3CN.



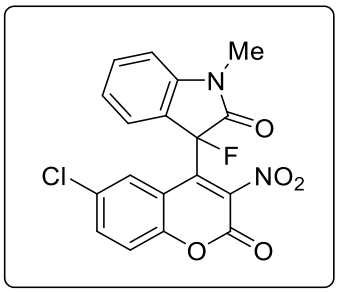


Figure S47. ^{1}H NMR (400 MHz) Spectrum of compound **4c** (*dr* = 12:1) in CD_3CN.

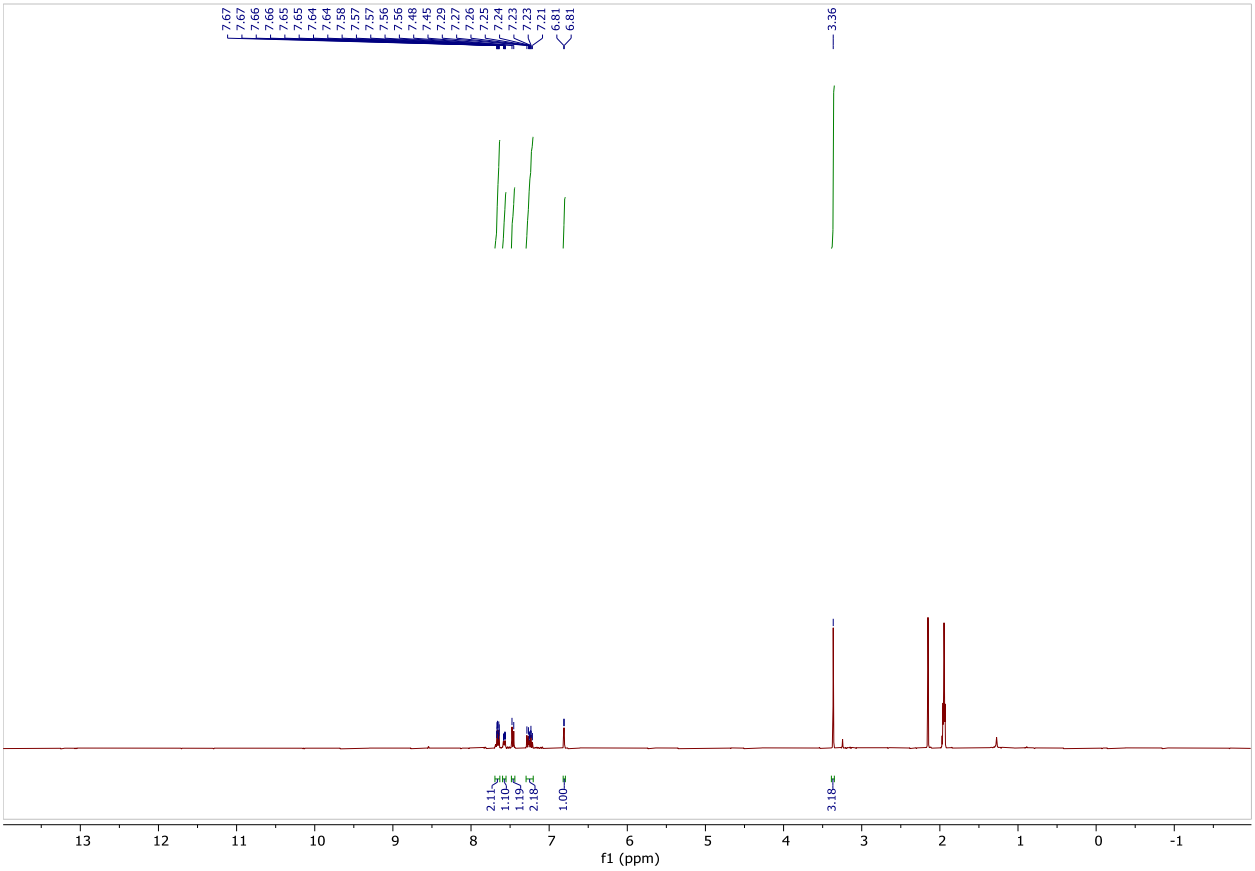


Figure S48. $^{13}C\{^{1}H\}$ NMR (100 MHz) Spectrum of compound **4c** (*dr* = 12:1) in CD_3CN.

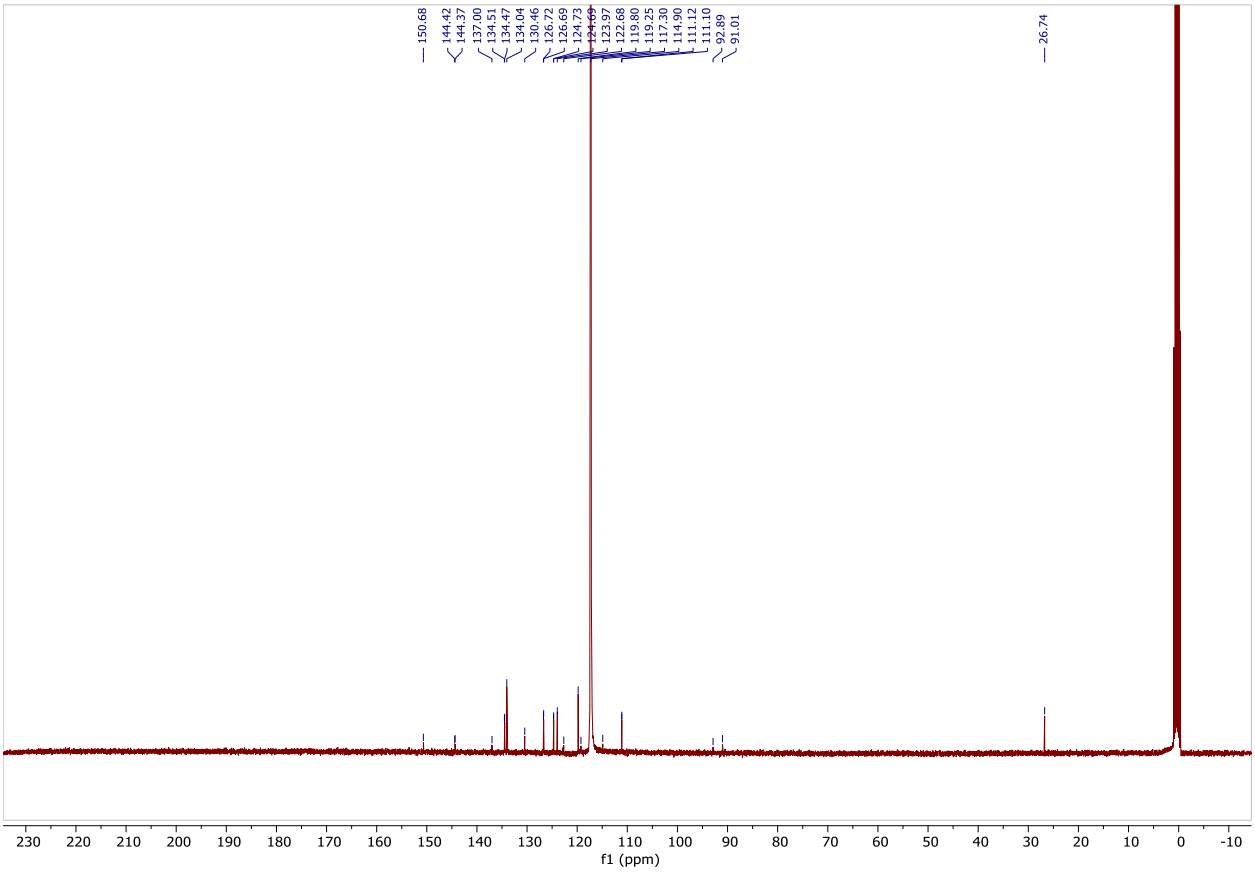
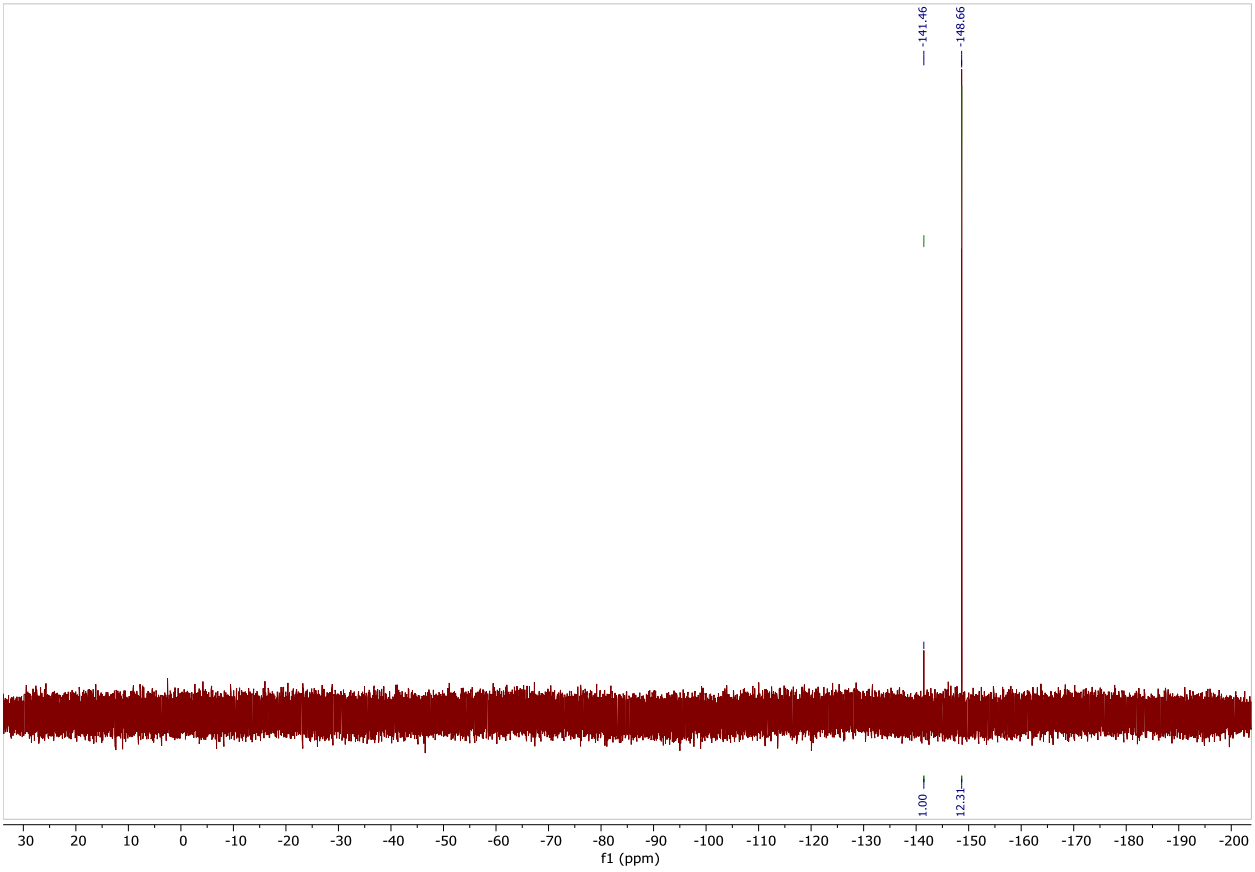


Figure S49. ^{19}F NMR (376 MHz) Spectrum of compound **4c** (*dr* = 12:1) in CD_3CN.



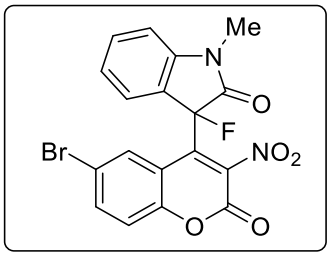


Figure S50. ^{1}H NMR (400 MHz) Spectrum of compound **4d** (*dr* = 10:1) in CD_3CN.

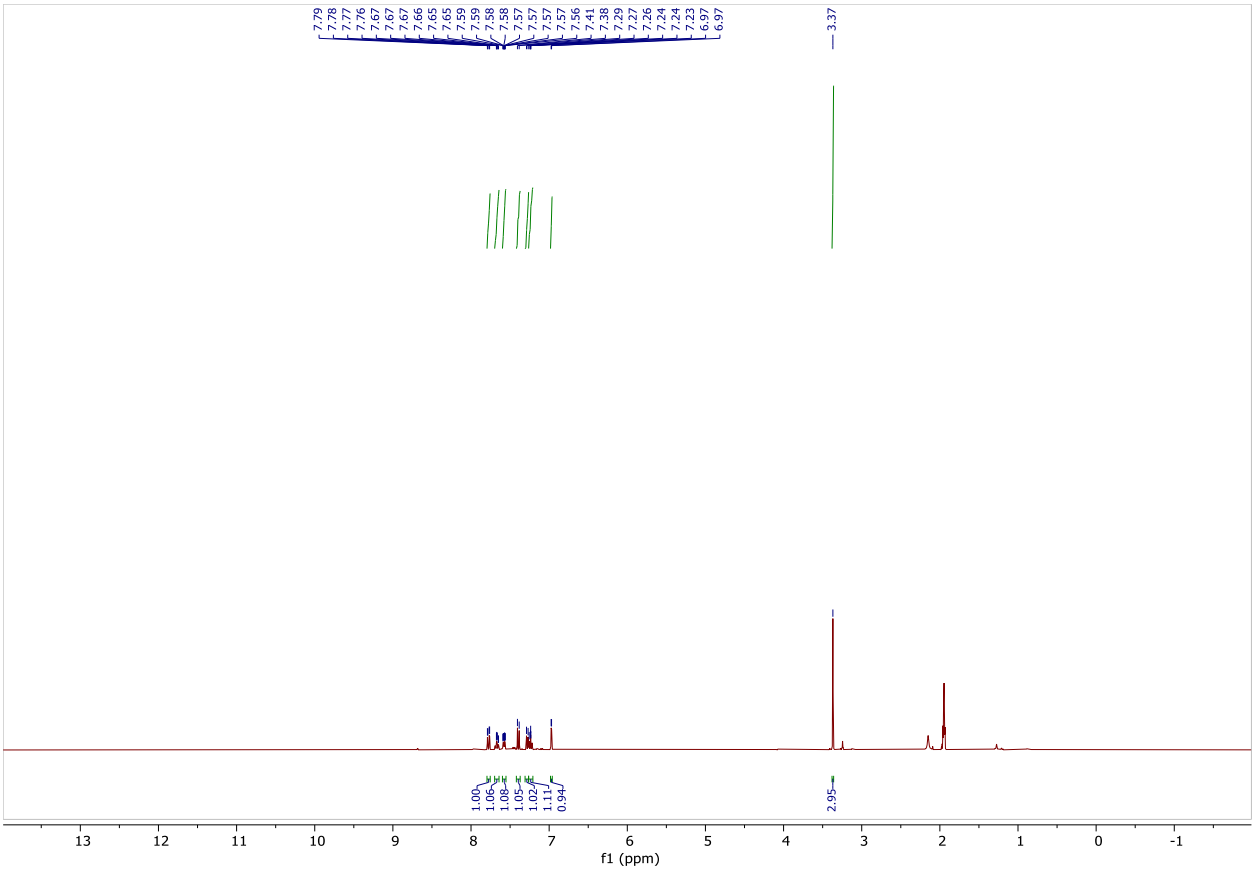


Figure S51. $^{13}C\{^{1}H\}$ NMR (100 MHz) Spectrum of compound **4d** (*dr* = 10:1) in CD_3CN.

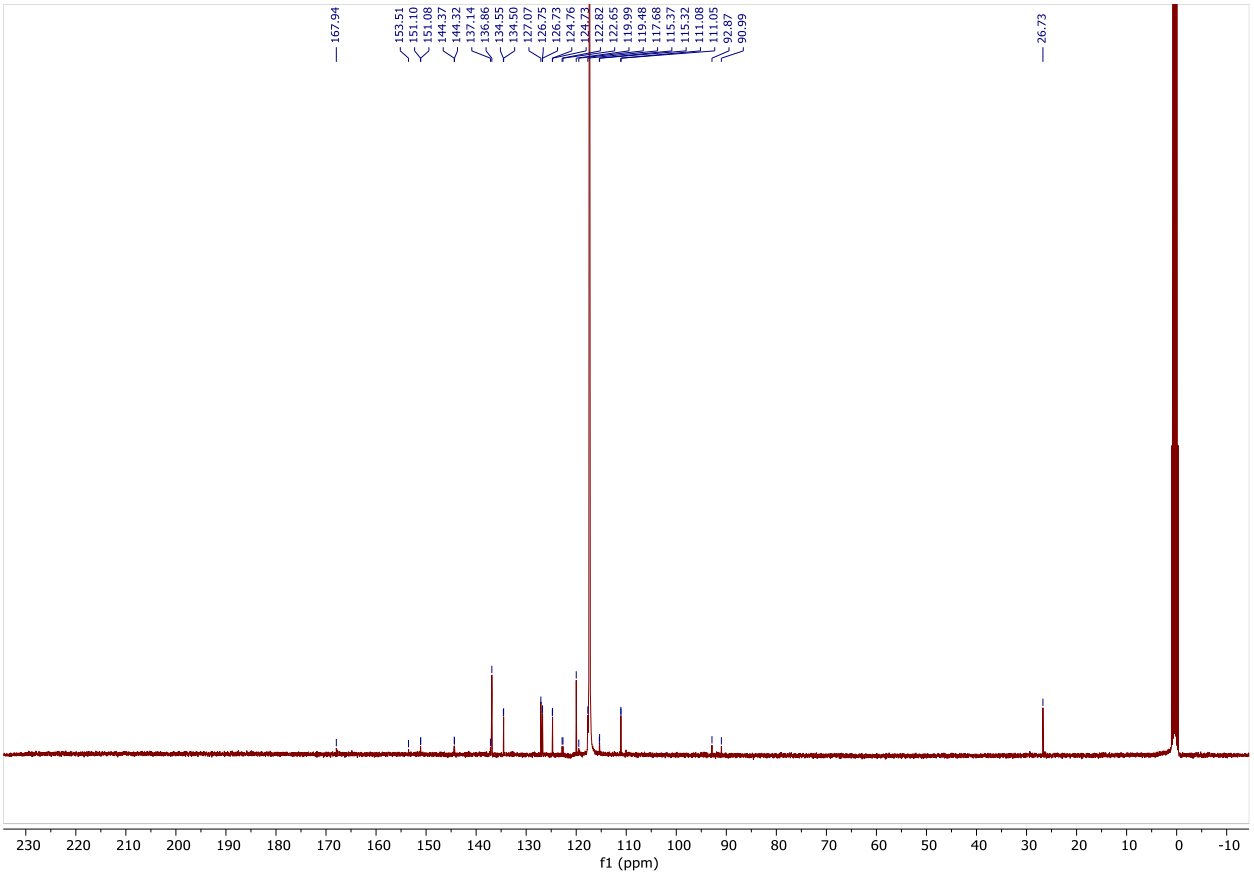
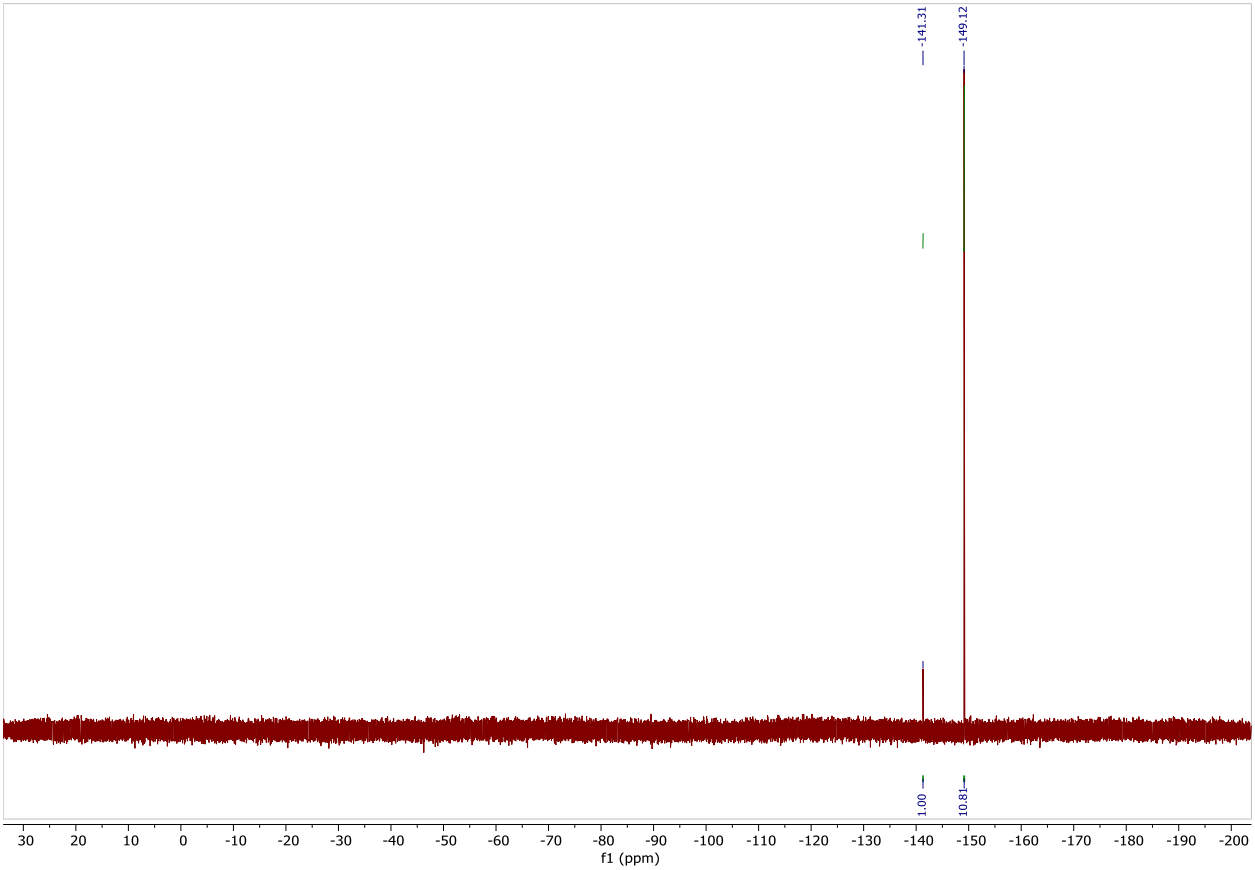


Figure S52. ^{19}F NMR (376 MHz) Spectrum of compound **4d** (*dr* = 10:1) in CD_3CN.



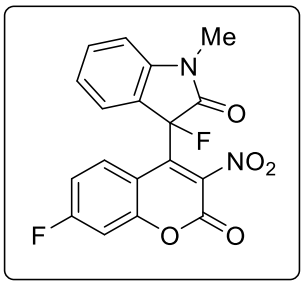


Figure S53. ^{1}H NMR (400 MHz) Spectrum of compound **4e** (*dr* = 17:1) in CD_3CN.

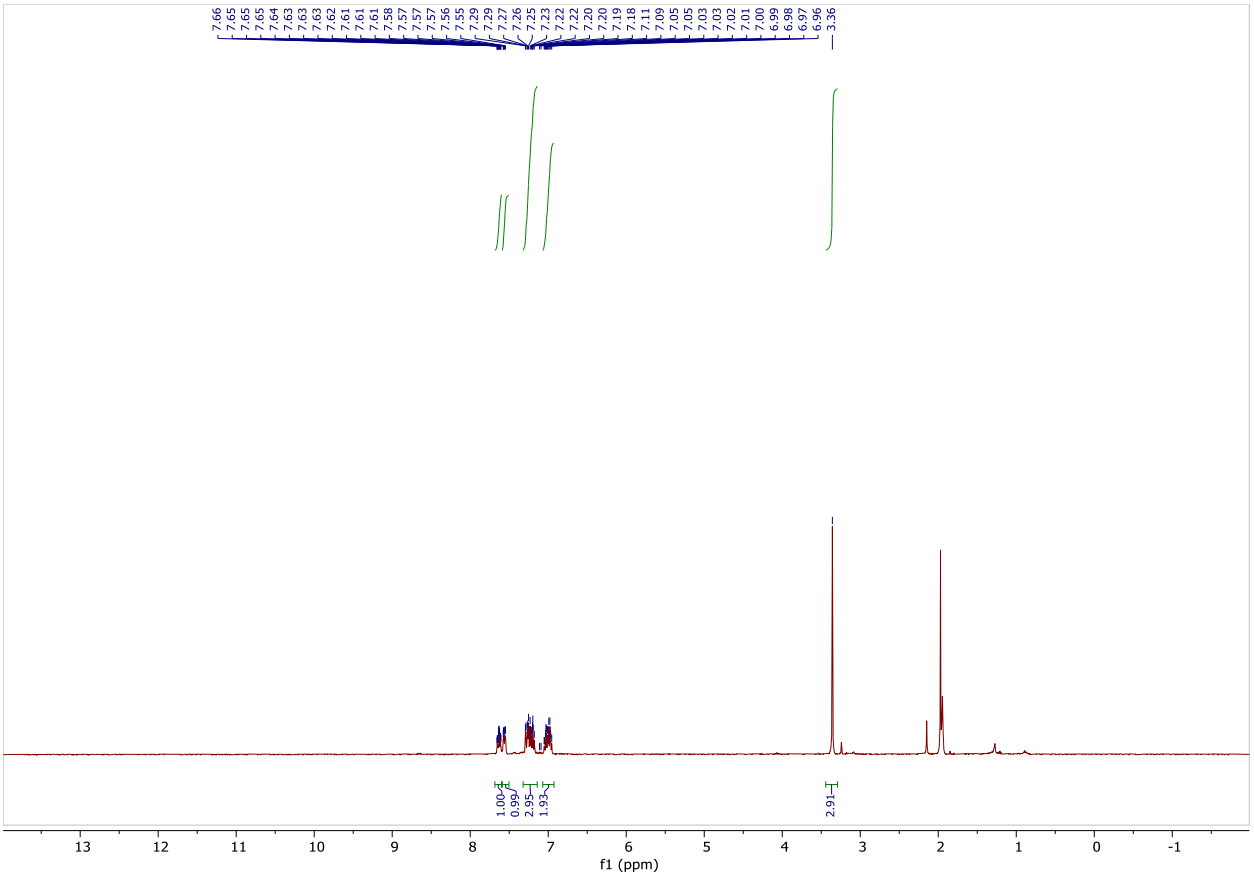


Figure S54. $^{13}C\{^{1}H\}$ NMR (100 MHz) Spectrum of compound **4e** (*dr* = 17:1) in CD_3CN.

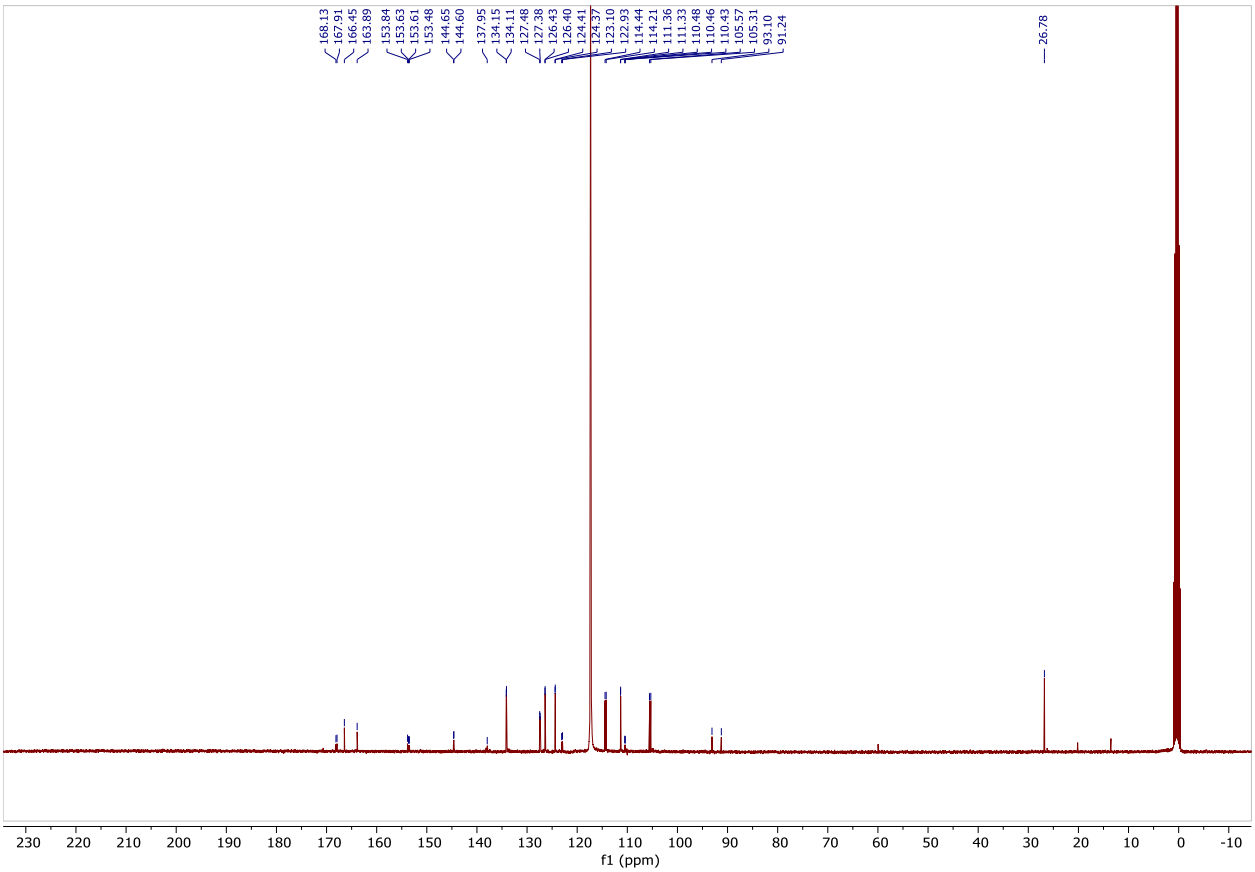
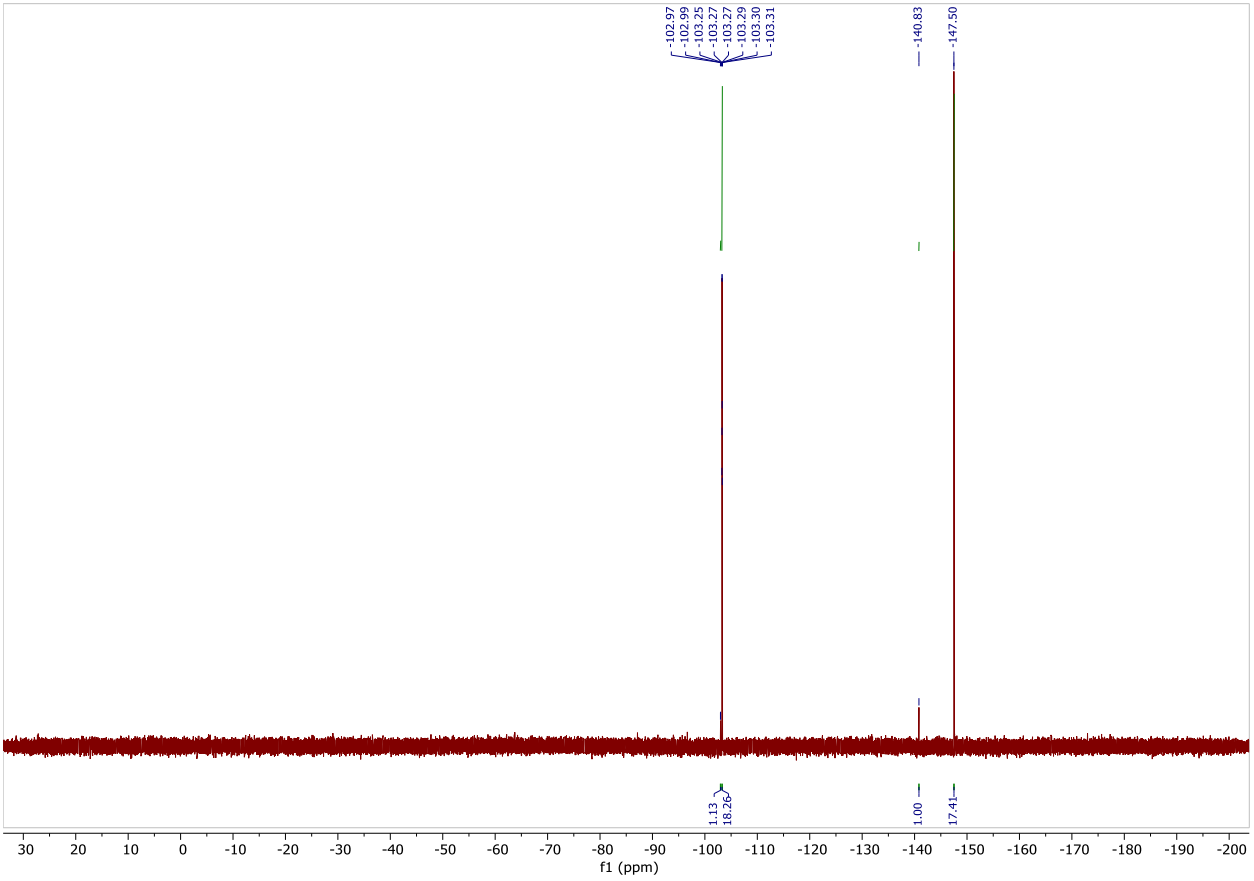


Figure S55. ^{19}F NMR (376 MHz) Spectrum of compound **4e** (*dr* = 17:1) in CD_3CN.



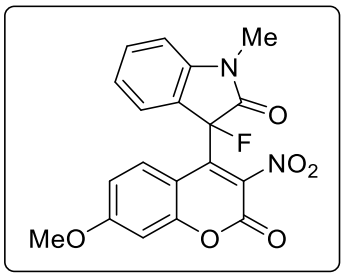


Figure S56. ^{1}H NMR (400 MHz) Spectrum of compound **4f** (*dr* = 22:1) in CD_3CN.

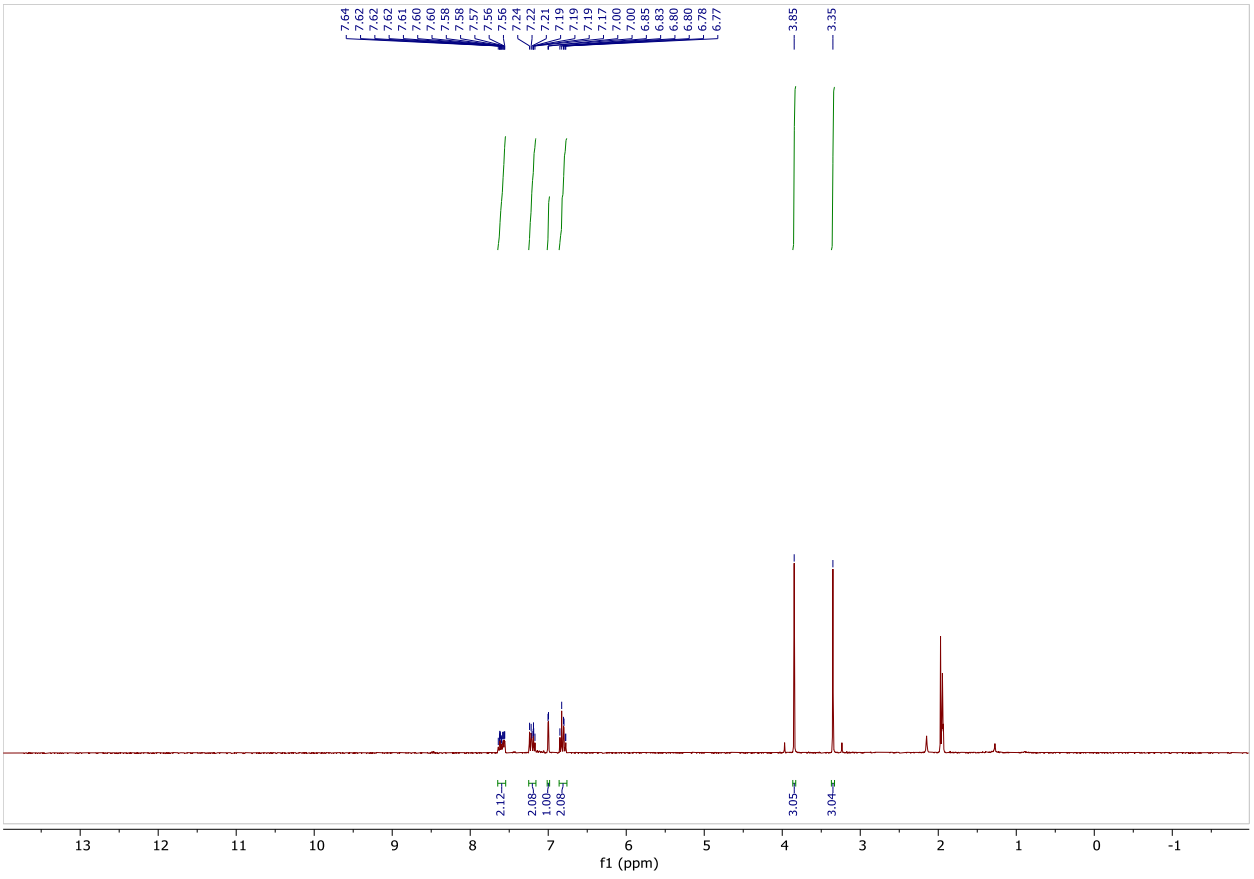


Figure S57. $^{13}C\{^{1}H\}$ NMR (100 MHz) Spectrum of compound **4f** (*dr* = 22:1) in CD_3CN.

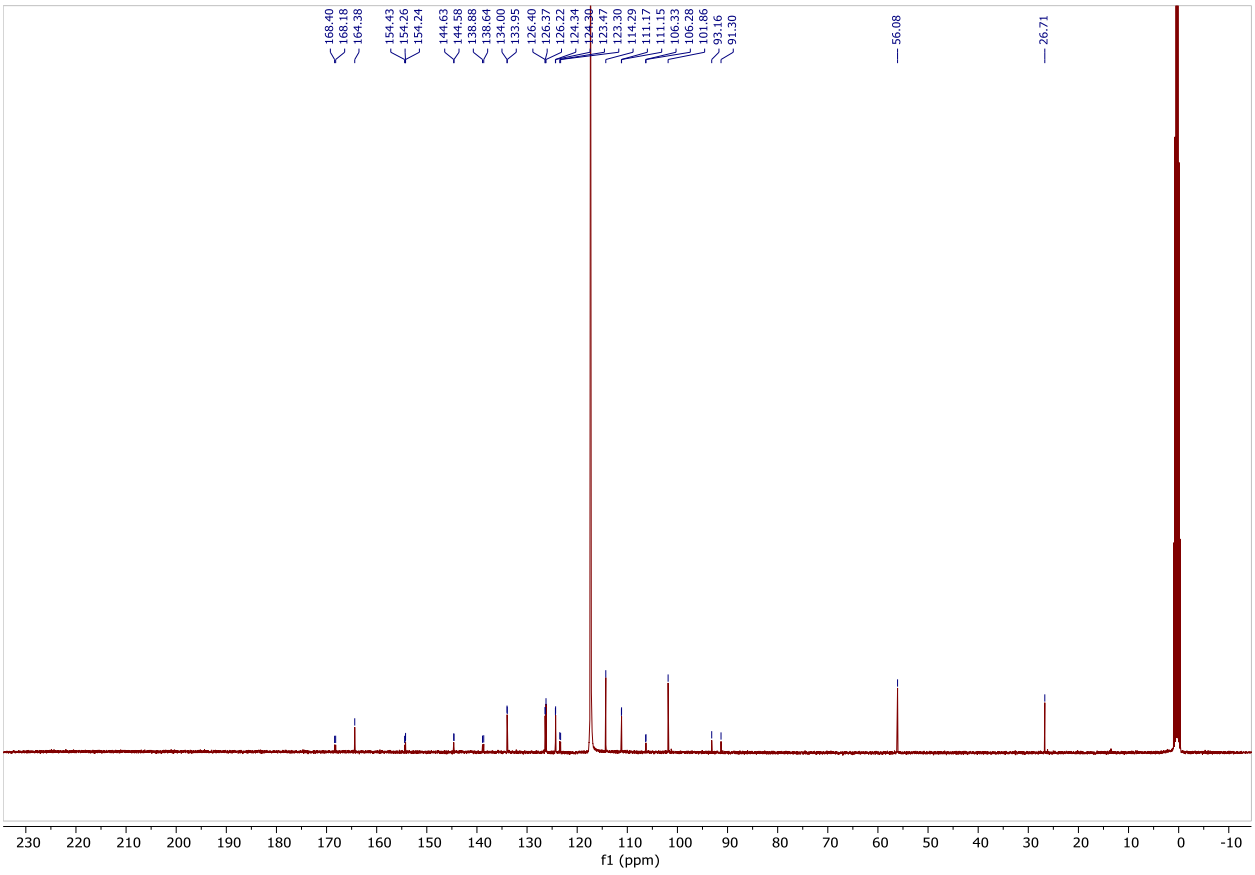
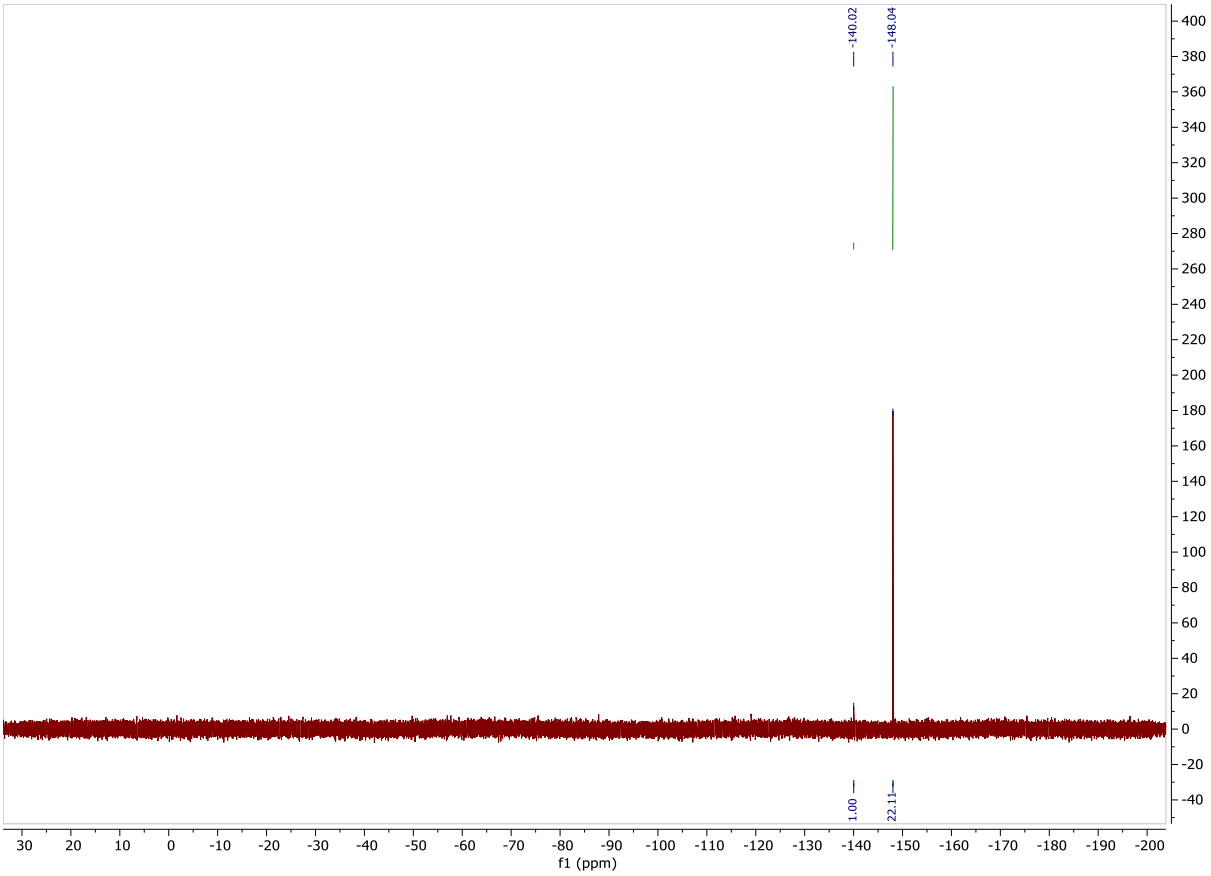


Figure S58. ^{19}F NMR (376 MHz) Spectrum of compound **4f** (*dr* = 22:1) in CD_3CN.



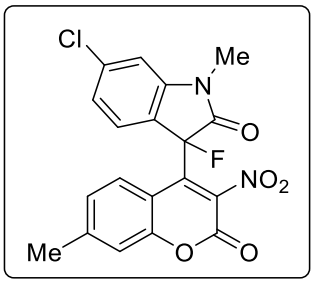


Figure S59. ^{1}H NMR (400 MHz) Spectrum of compound **4g** (*dr* = 19:1) in CD_3CN.

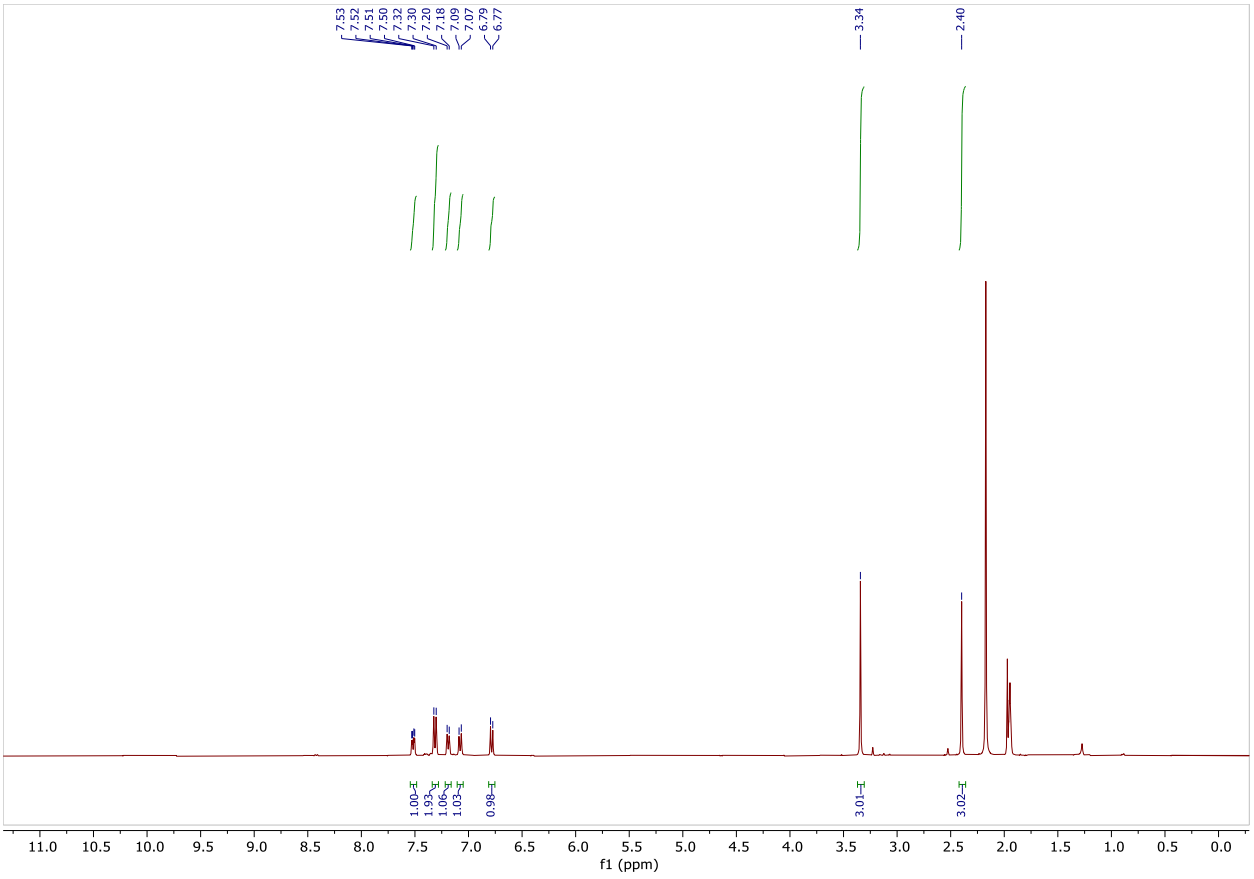


Figure S60. $^{13}C\{^{1}H\}$ NMR (100 MHz) Spectrum of compound **4g** (*dr* = 19:1) in CD_3CN.

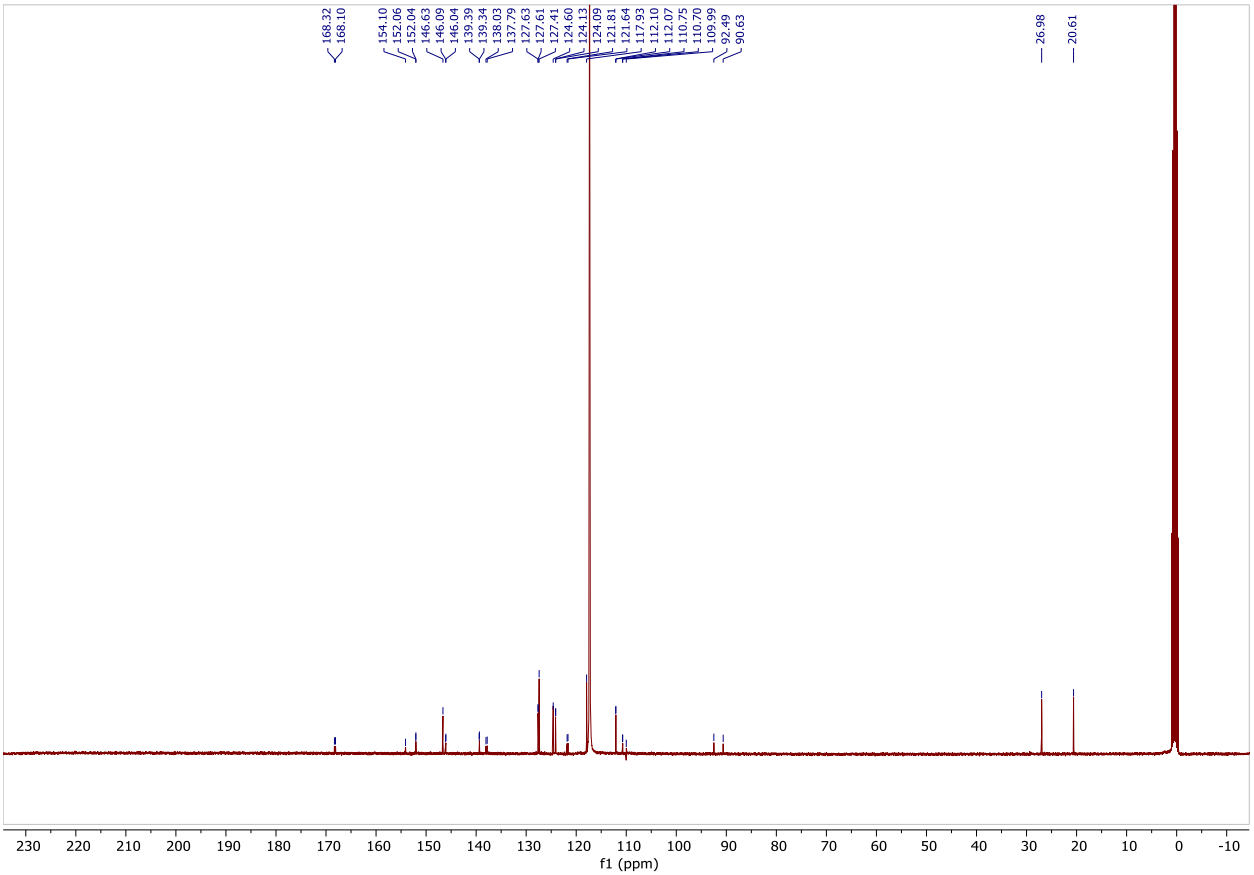
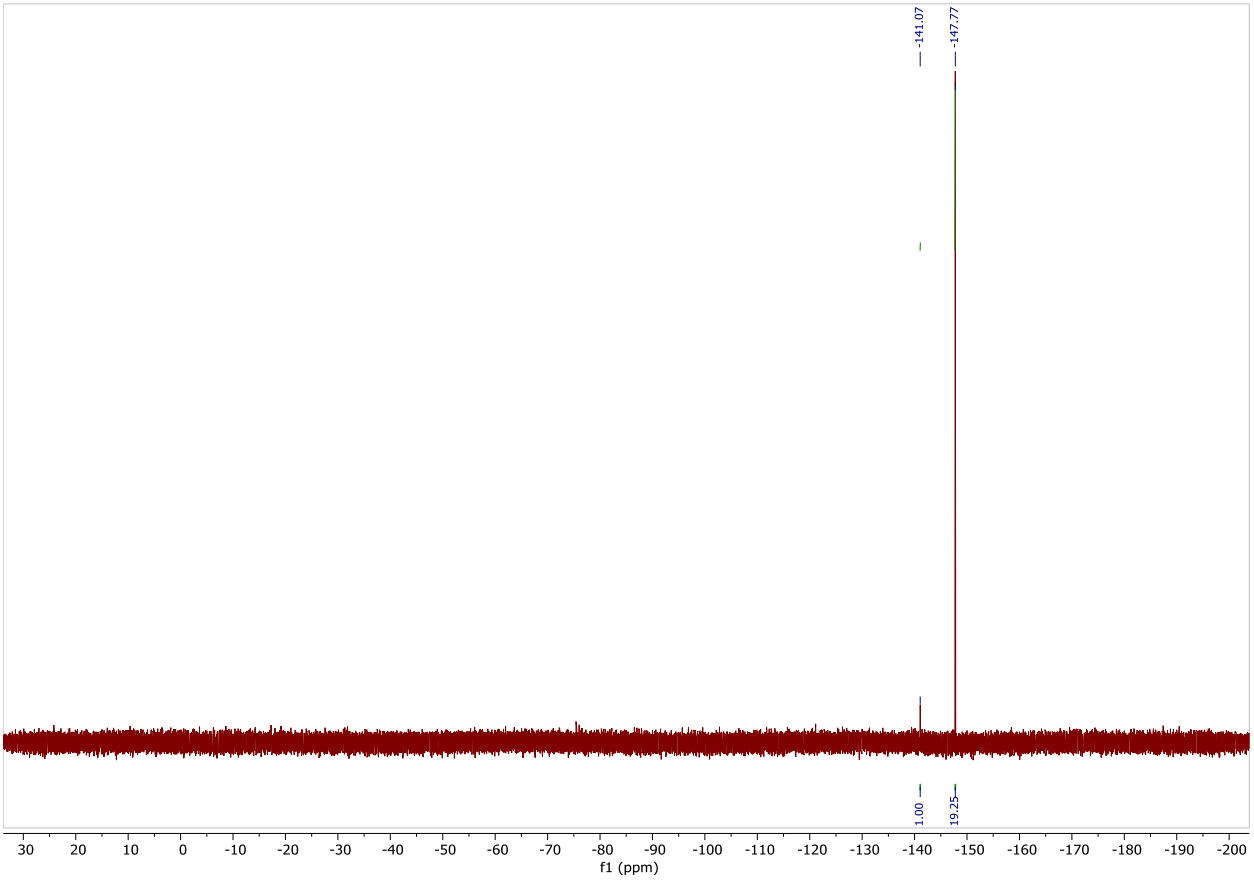


Figure S61. ^{19}F NMR (376 MHz) Spectrum of compound **4g** (*dr* = 19:1) in CD_3CN.



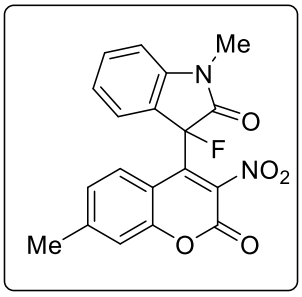


Figure S62. ^{1}H NMR (400 MHz) Spectrum of compound **4h** (*dr* = 20:1) in CD_3CN.

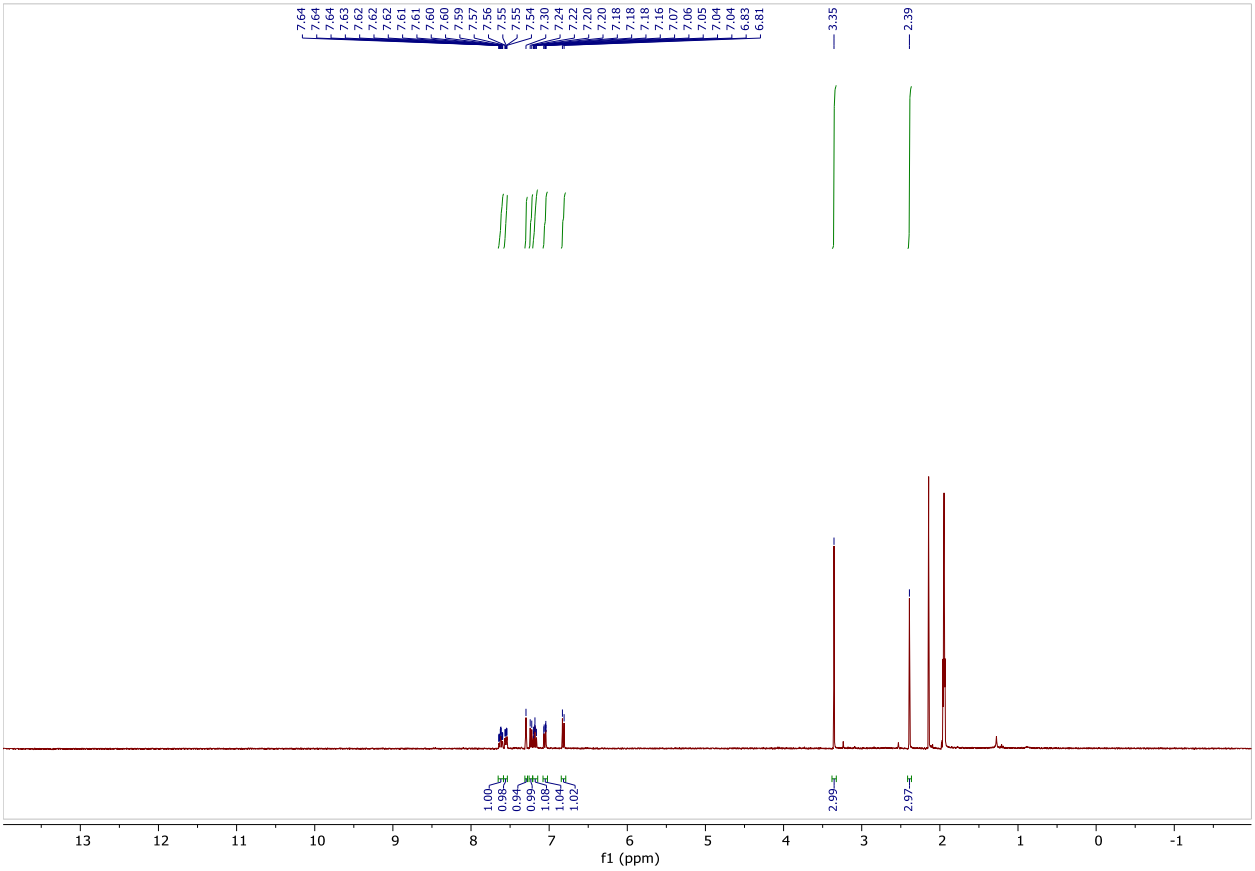


Figure S63. $^{13}C\{^{1}H\}$ NMR (100 MHz) Spectrum of compound **4h** (*dr* = 20:1) in CD_3CN.

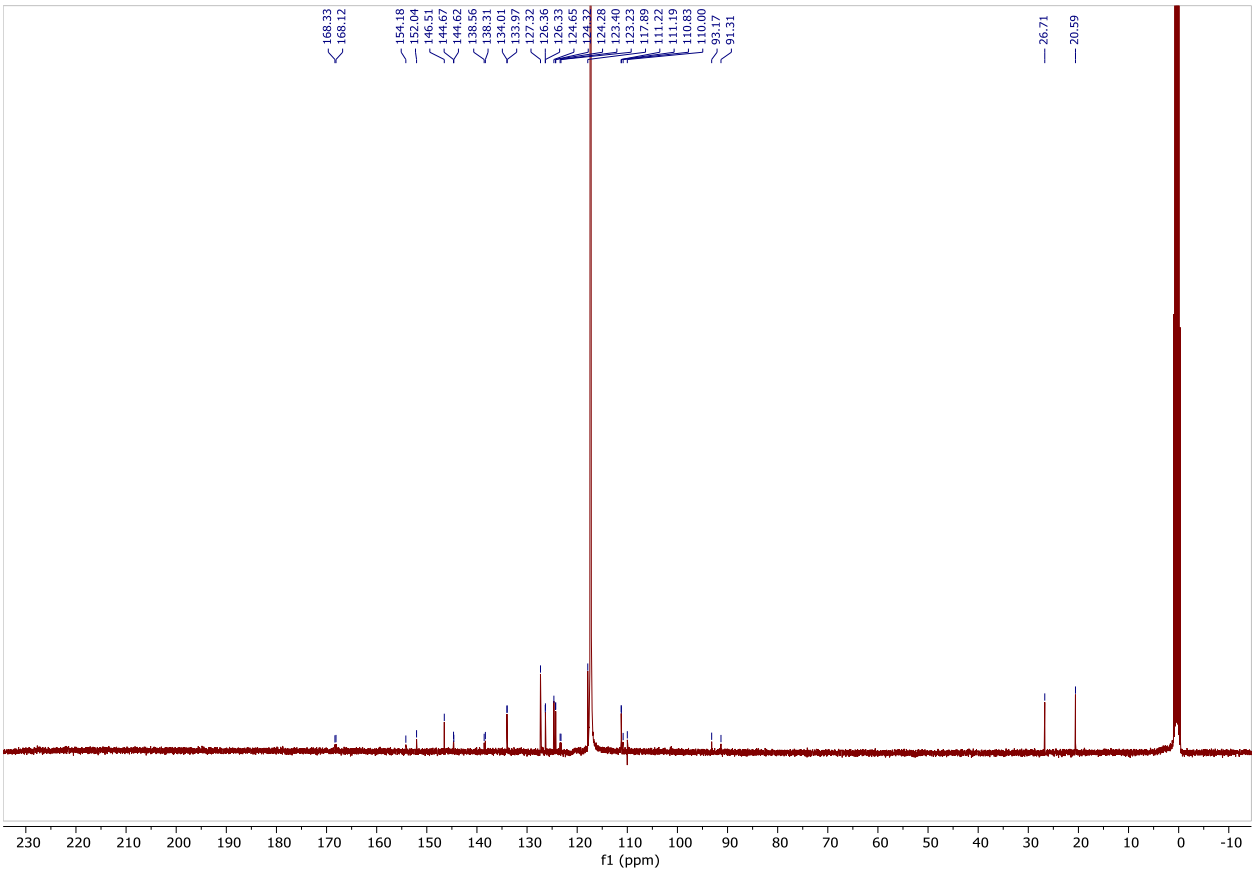
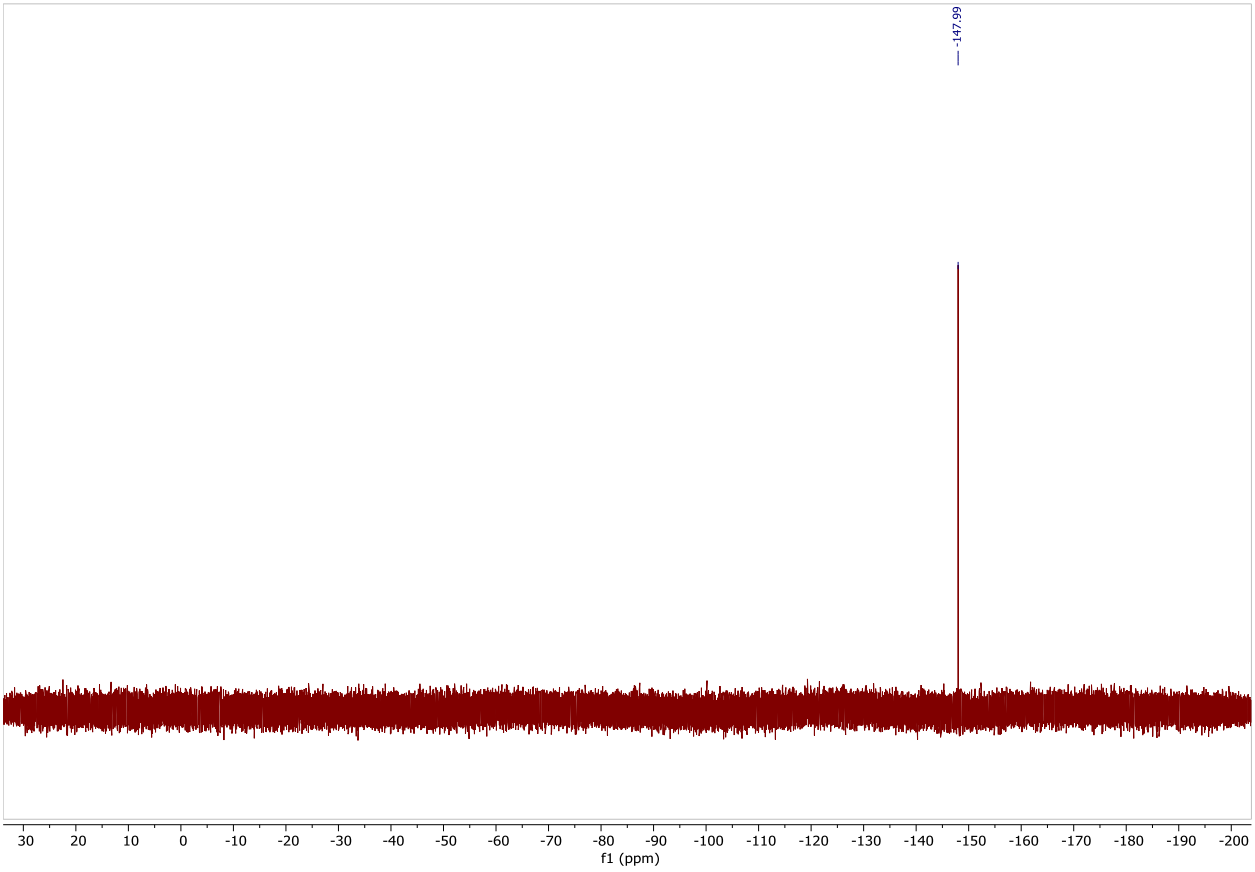


Figure S64. ^{19}F NMR (376 MHz) Spectrum of compound **4h** (*dr* = 20:1) in CD_3CN.



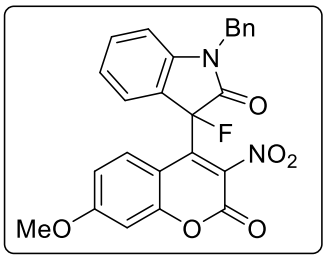


Figure S65. ^{1}H NMR (400 MHz) Spectrum of compound **4i** (*dr* = 20:1) in CD_3CN.

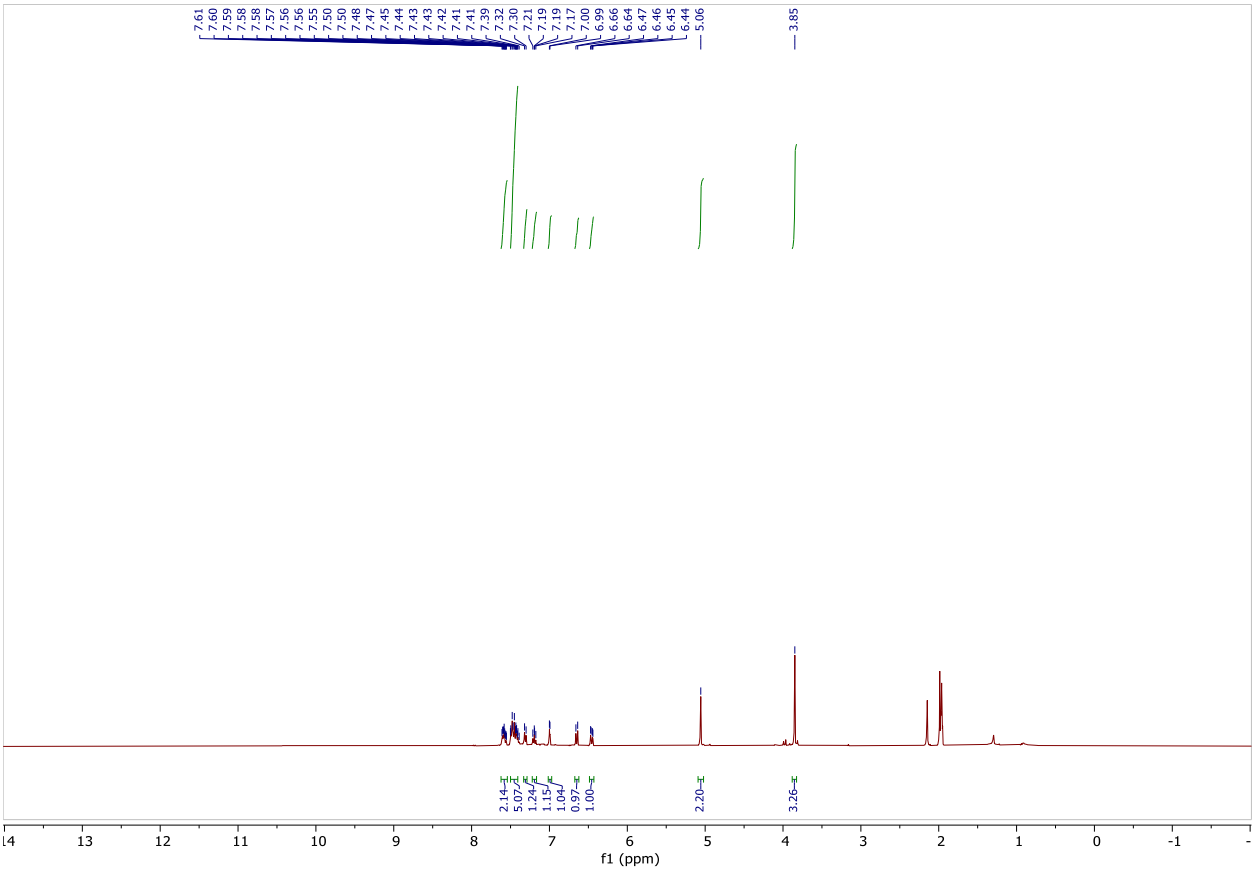


Figure S66. $^{13}C\{^{1}H\}$ NMR (100 MHz) Spectrum of compound **4i** (*dr* = 20:1) in CD_3CN.

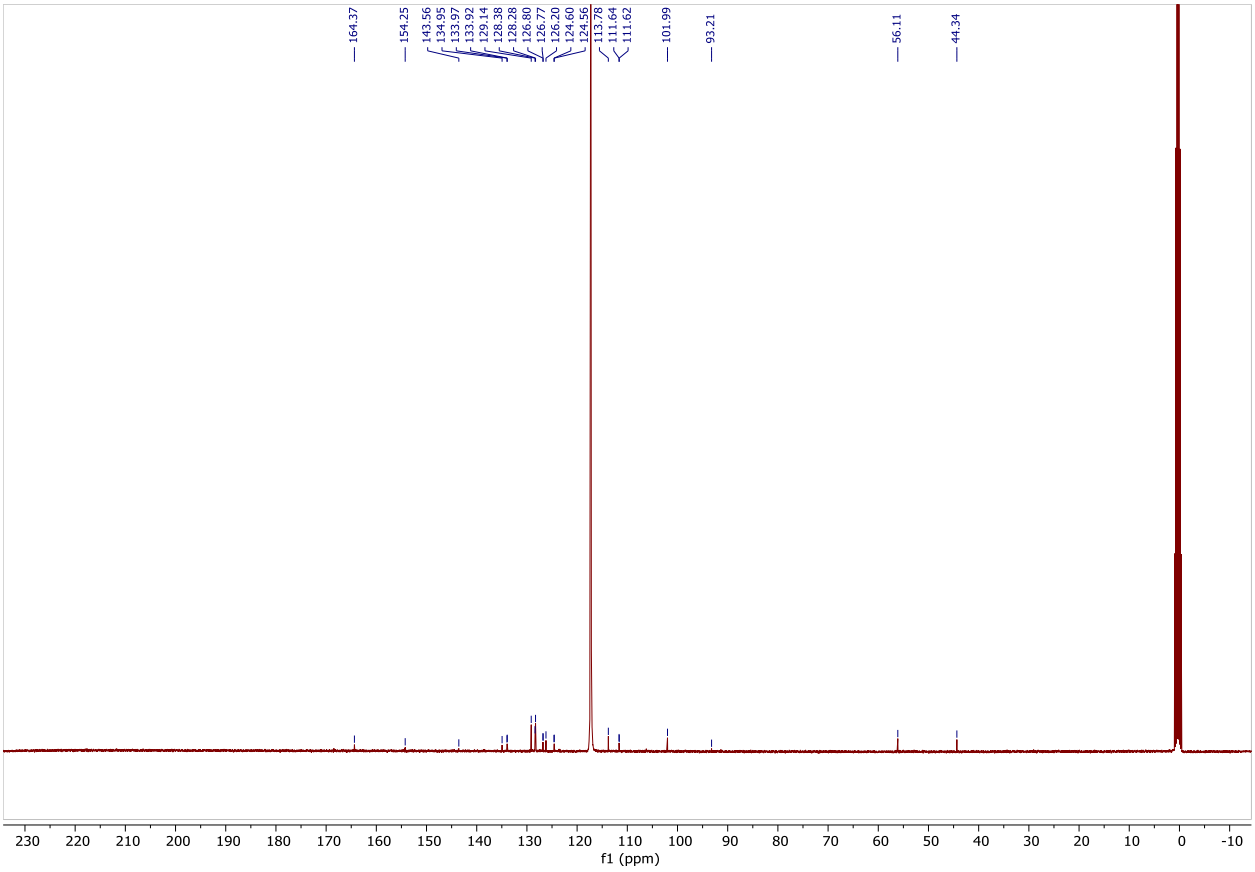
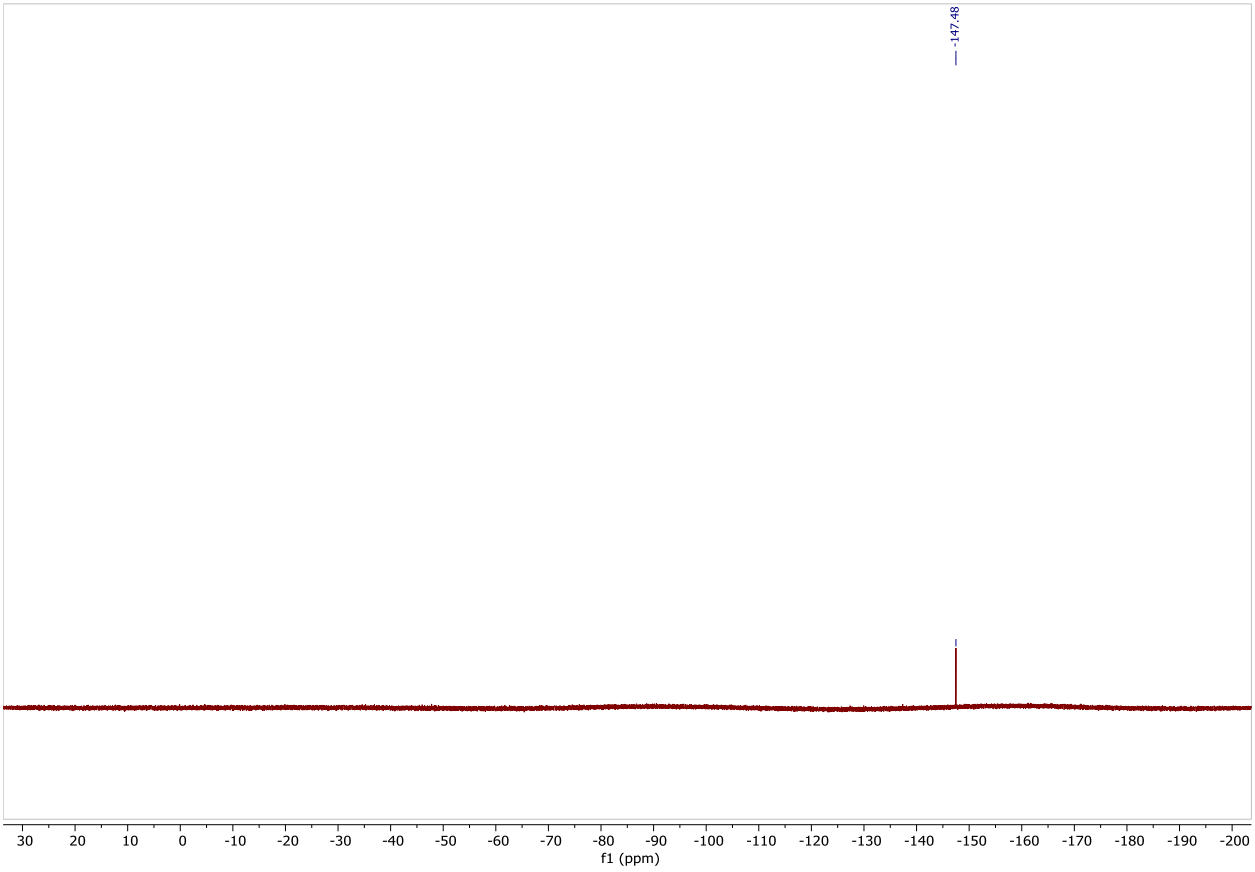


Figure S67. ^{19}F NMR (376 MHz) Spectrum of compound **4i** (*dr* = 20:1) in CD_3CN.



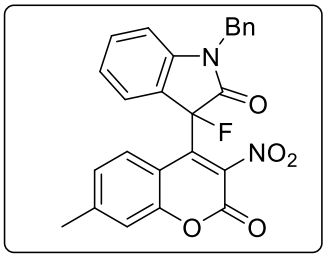


Figure S68. ^{1}H NMR (400 MHz) Spectrum of compound **4j** (*dr* = 41:1) in CD_3CN.

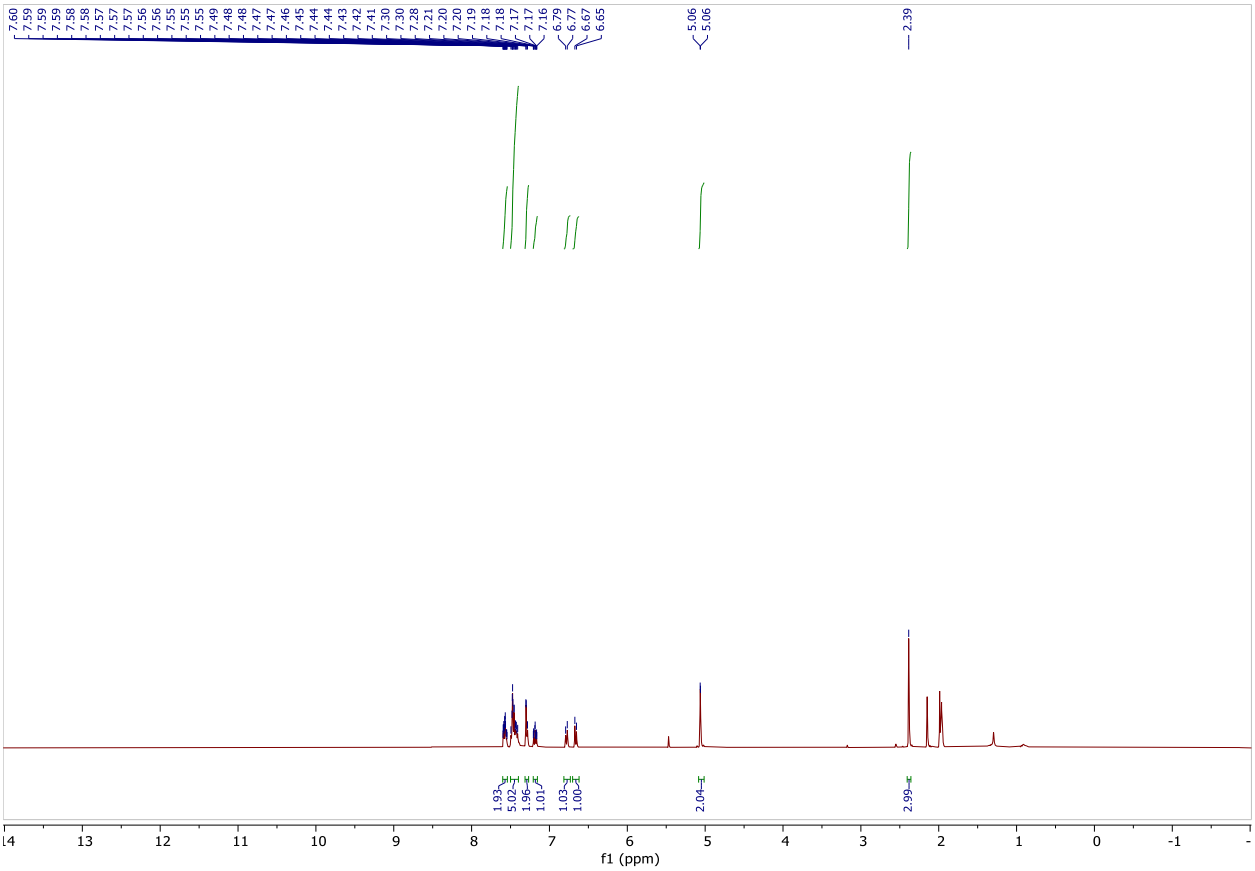


Figure S69. $^{13}C\{^{1}H\}$ NMR (100 MHz) Spectrum of compound **4j** (*dr* = 41:1) in CD_3CN.

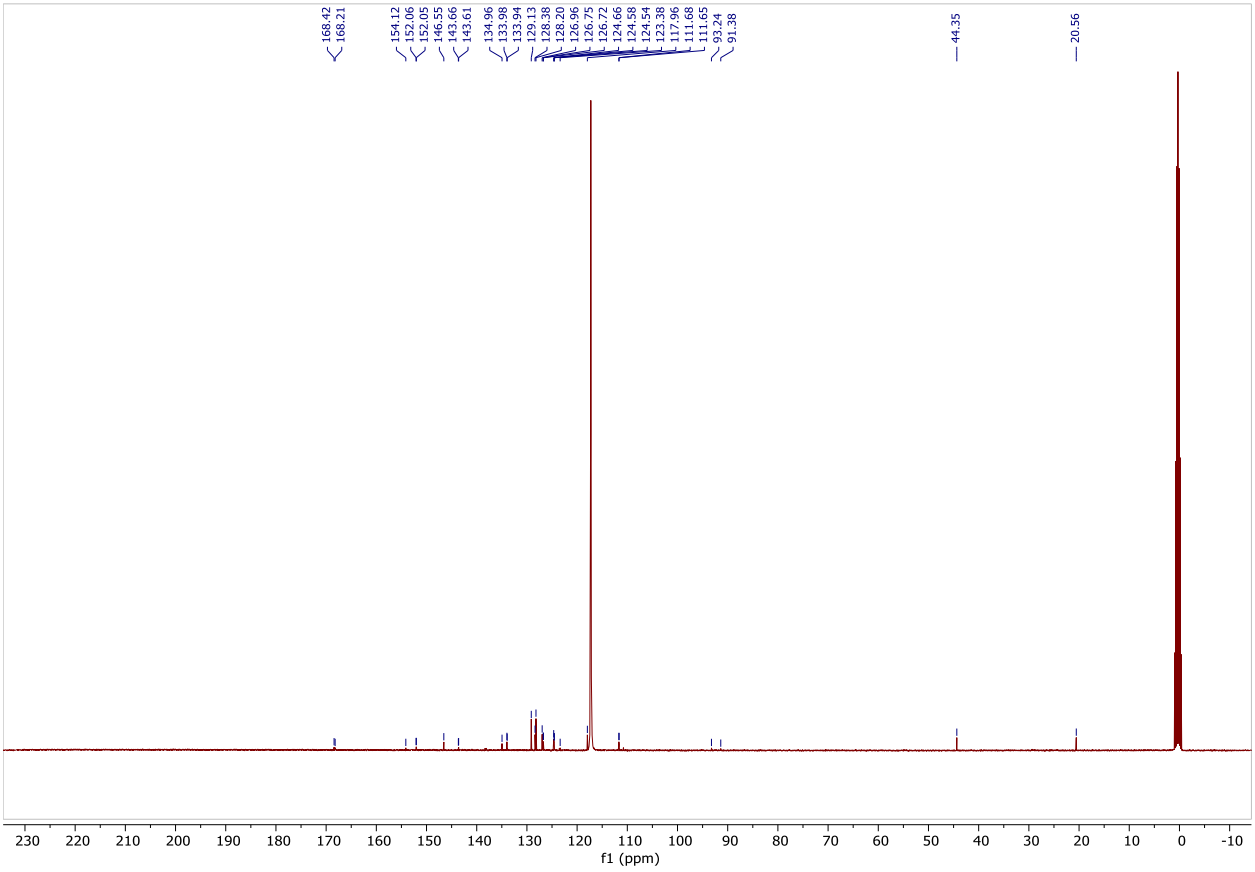
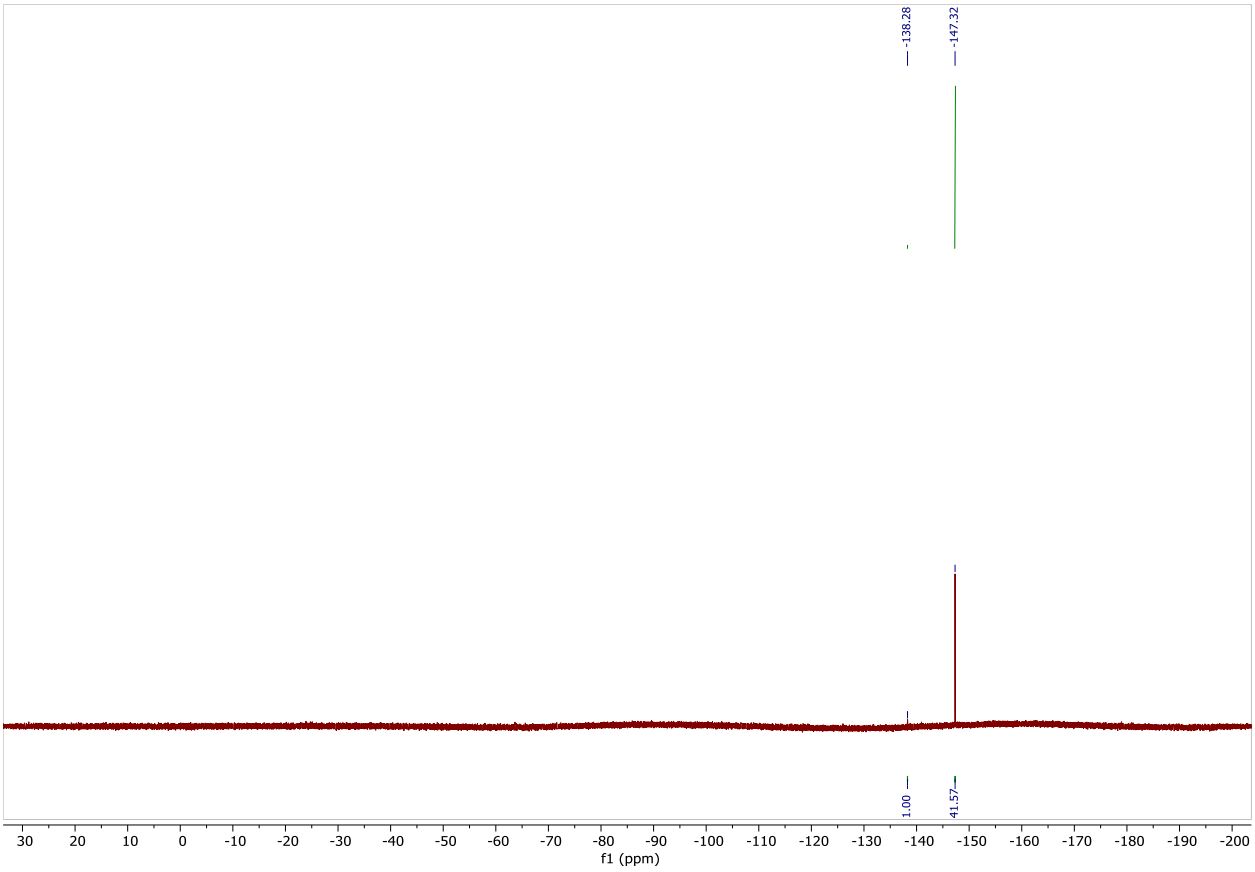


Figure S70. ^{19}F NMR (376 MHz) Spectrum of compound **4j** (*dr* = 41:1) in CD_3CN.



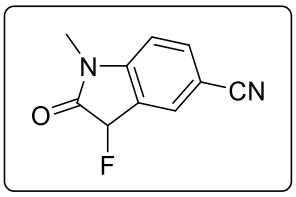


Figure S71. ^{1}H NMR (400 MHz) Spectrum of compound **1h** in $CDCl_3$.

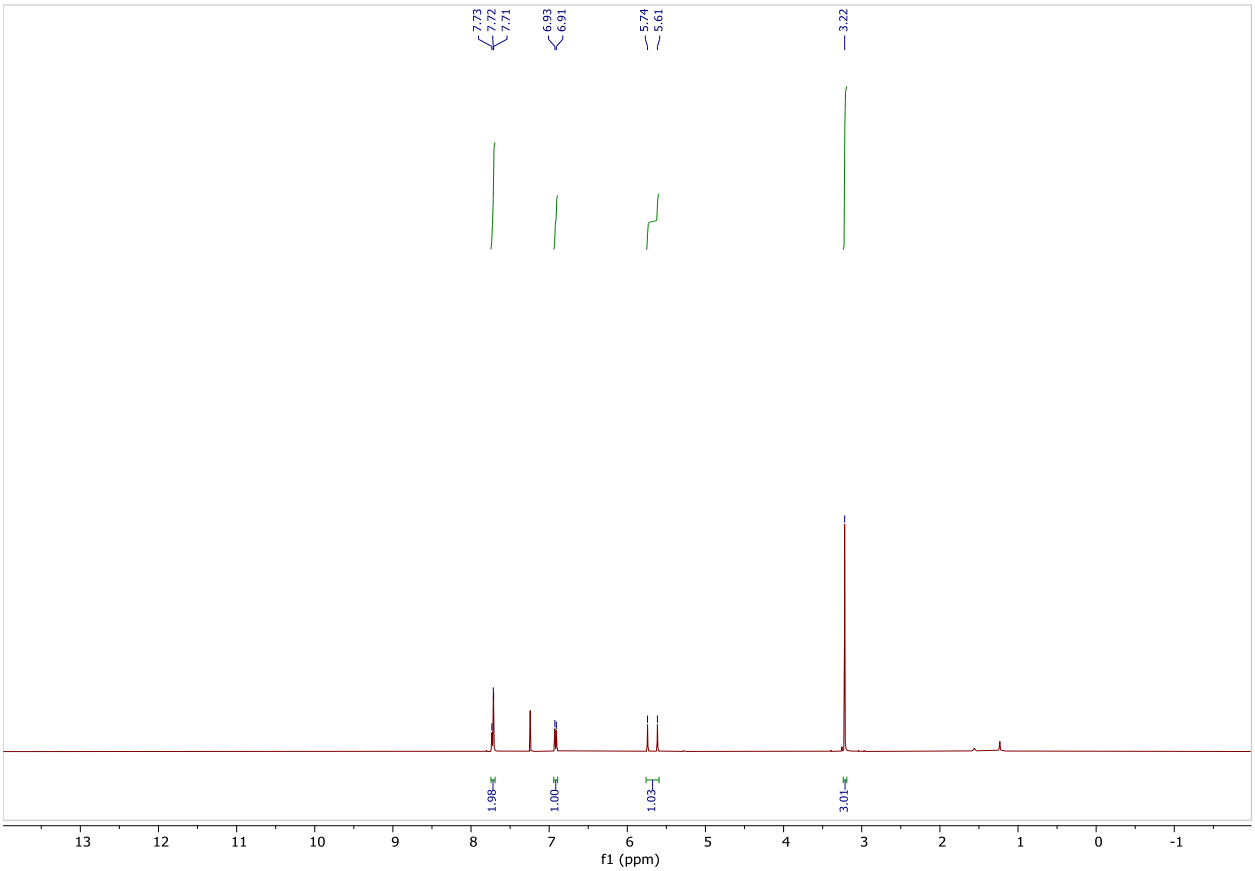


Figure S72. $^{13}C\{^{1}H\}$ NMR (100 MHz) Spectrum of compound **1h** in $CDCl_3$.

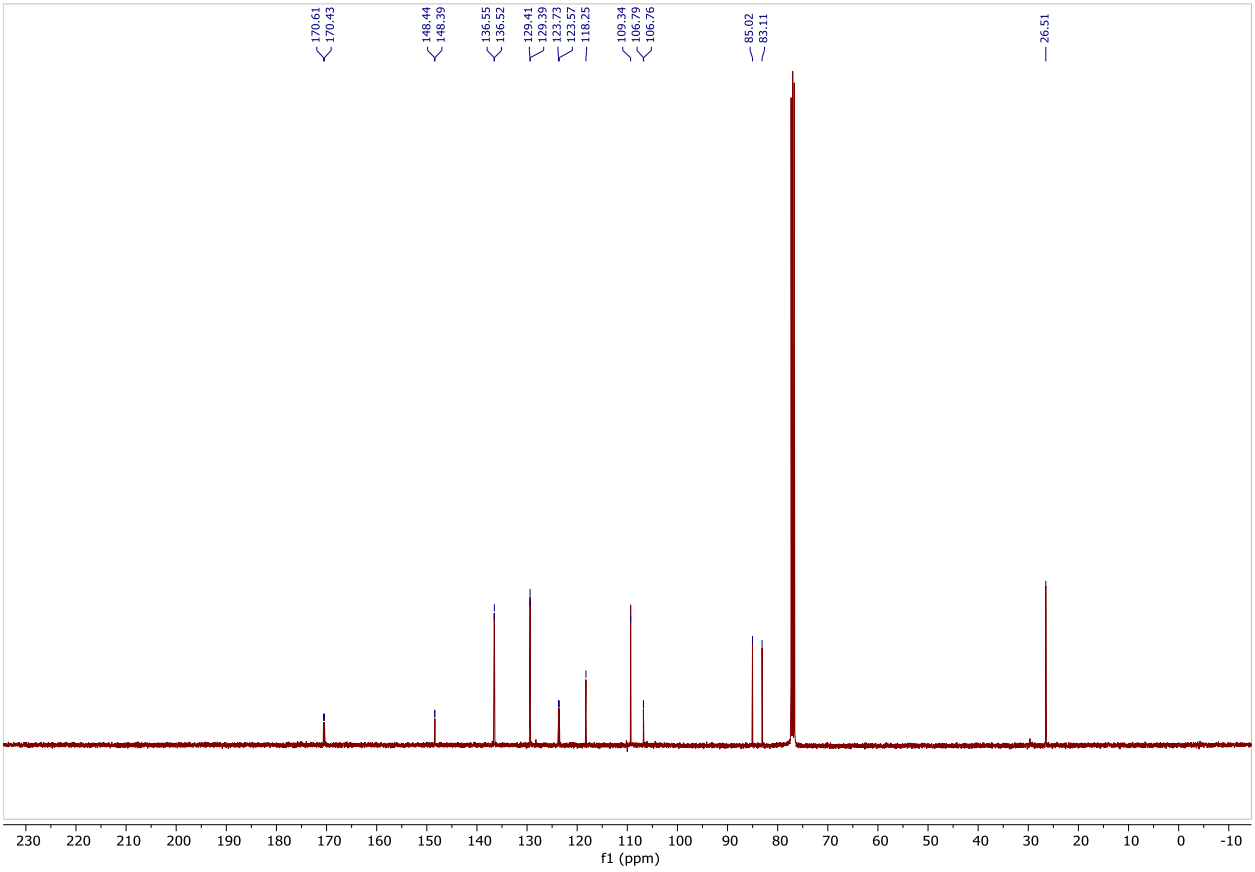
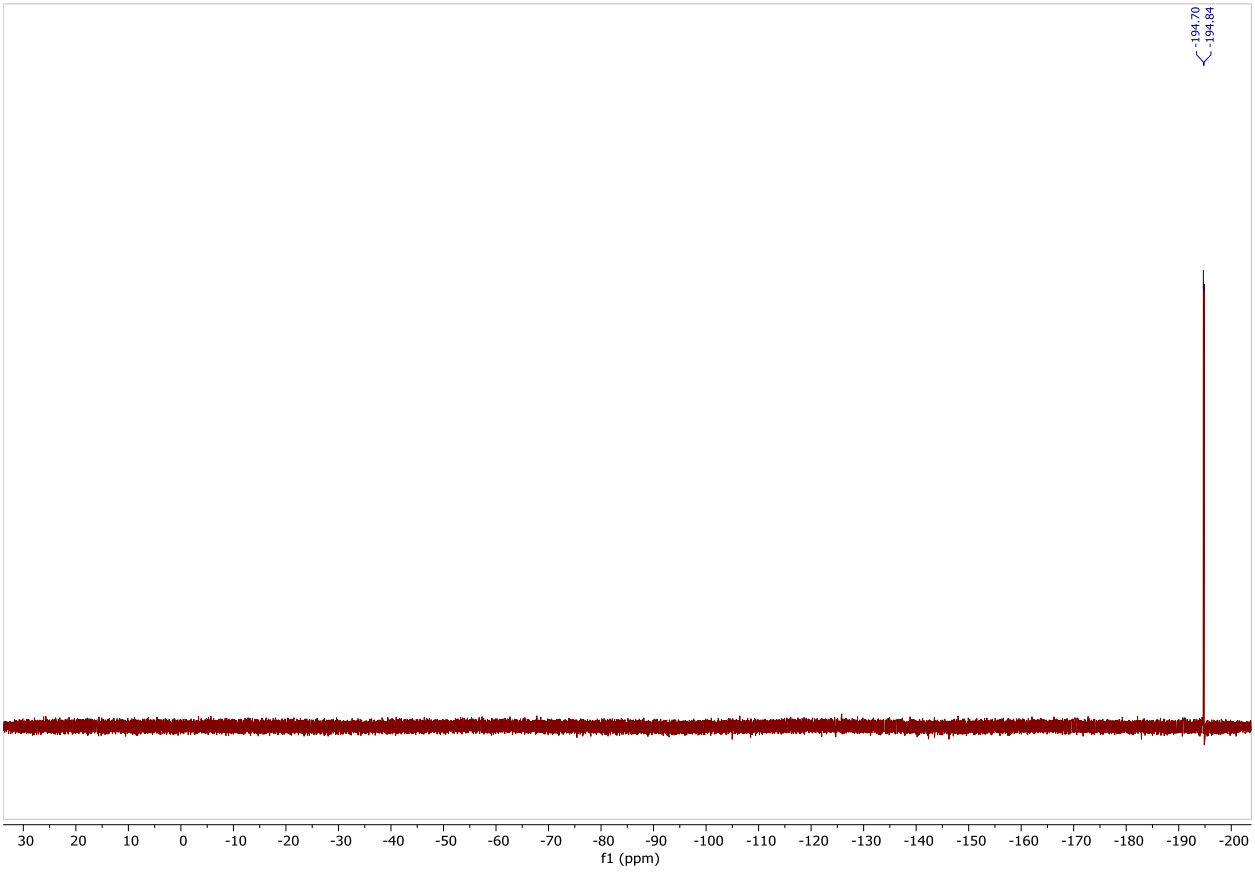


Figure S73. ^{19}F NMR (376 MHz) Spectrum of compound **1h** in $CDCl_3$.



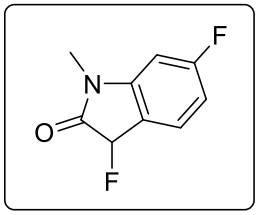


Figure S74. ^{1}H NMR (400 MHz) Spectrum of compound **1d** in $CDCl_3$.

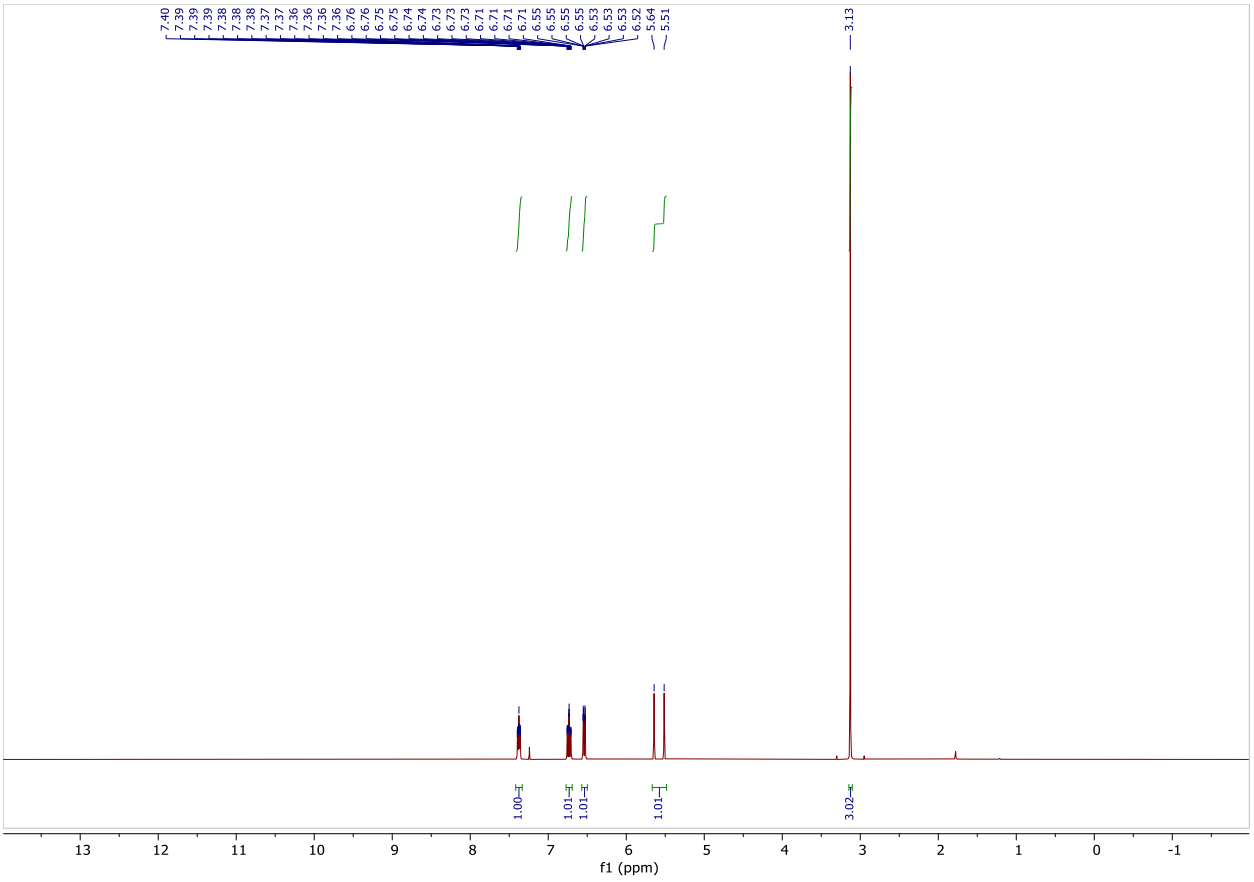


Figure S75. $^{13}C\{^{1}H\}$ NMR (100 MHz) Spectrum of compound **1d** in $CDCl_3$.

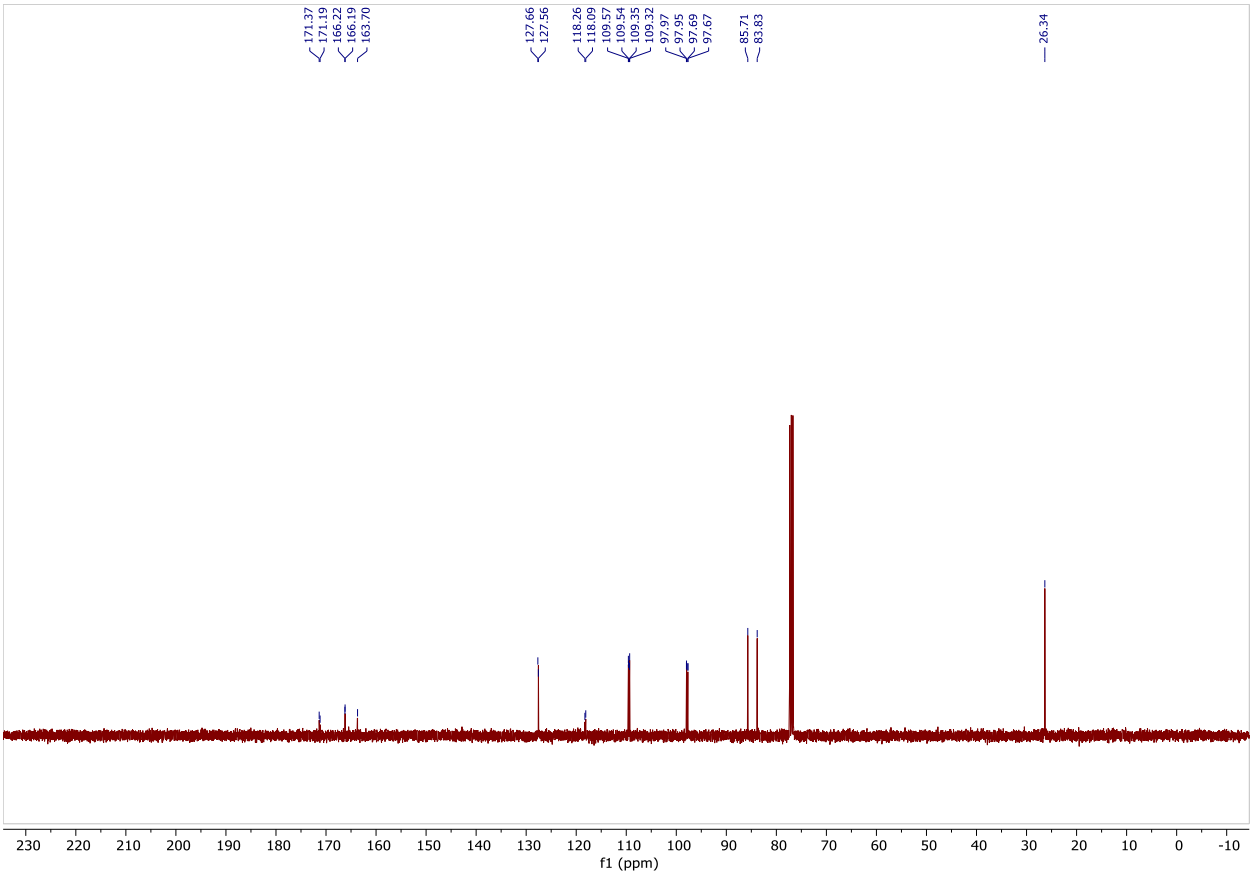
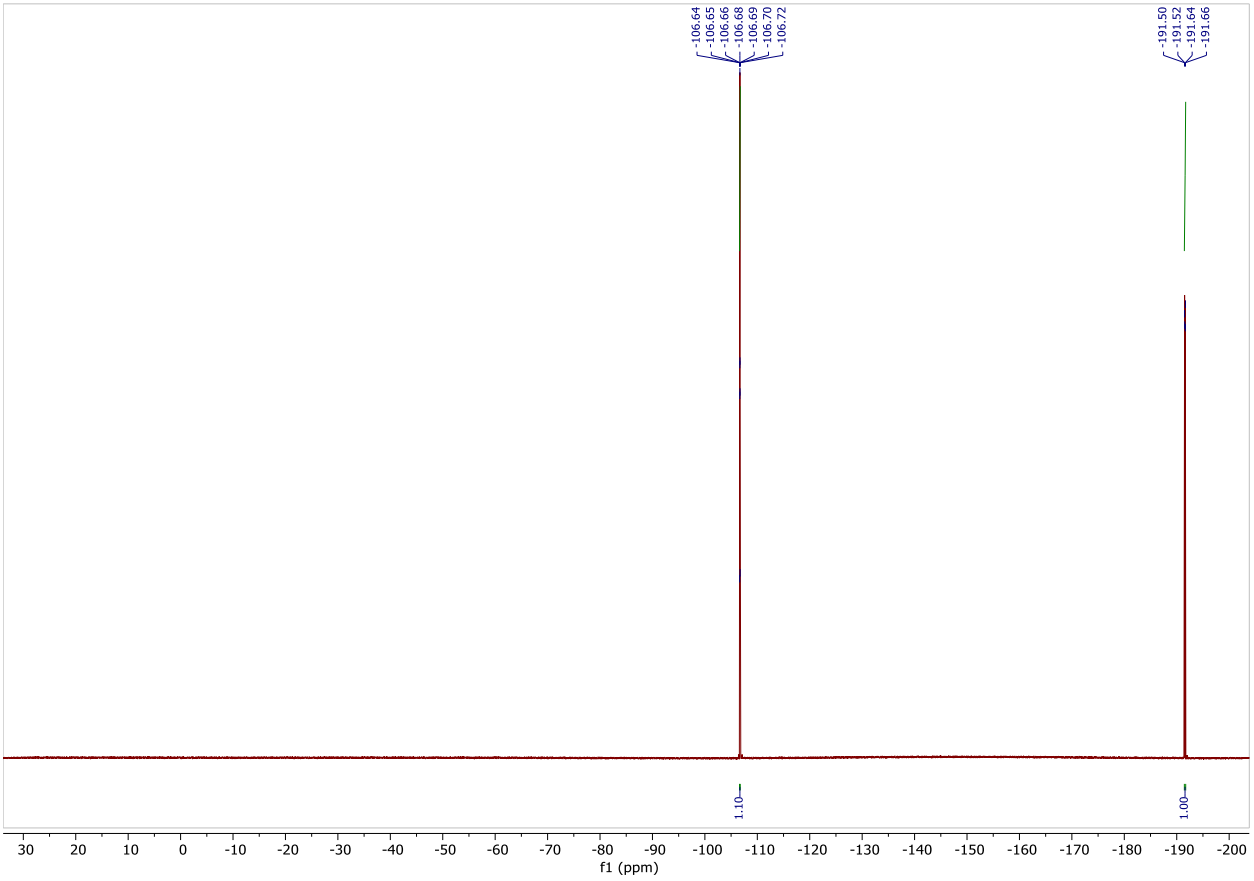


Figure S76. ^{19}F NMR (376 MHz) Spectrum of compound **1d** in $CDCl_3$.



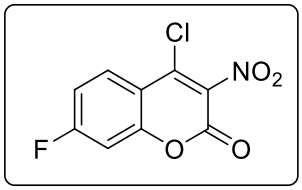


Figure S77. ^{1}H NMR (400 MHz) Spectrum of compound **2e** in CD_3CN.

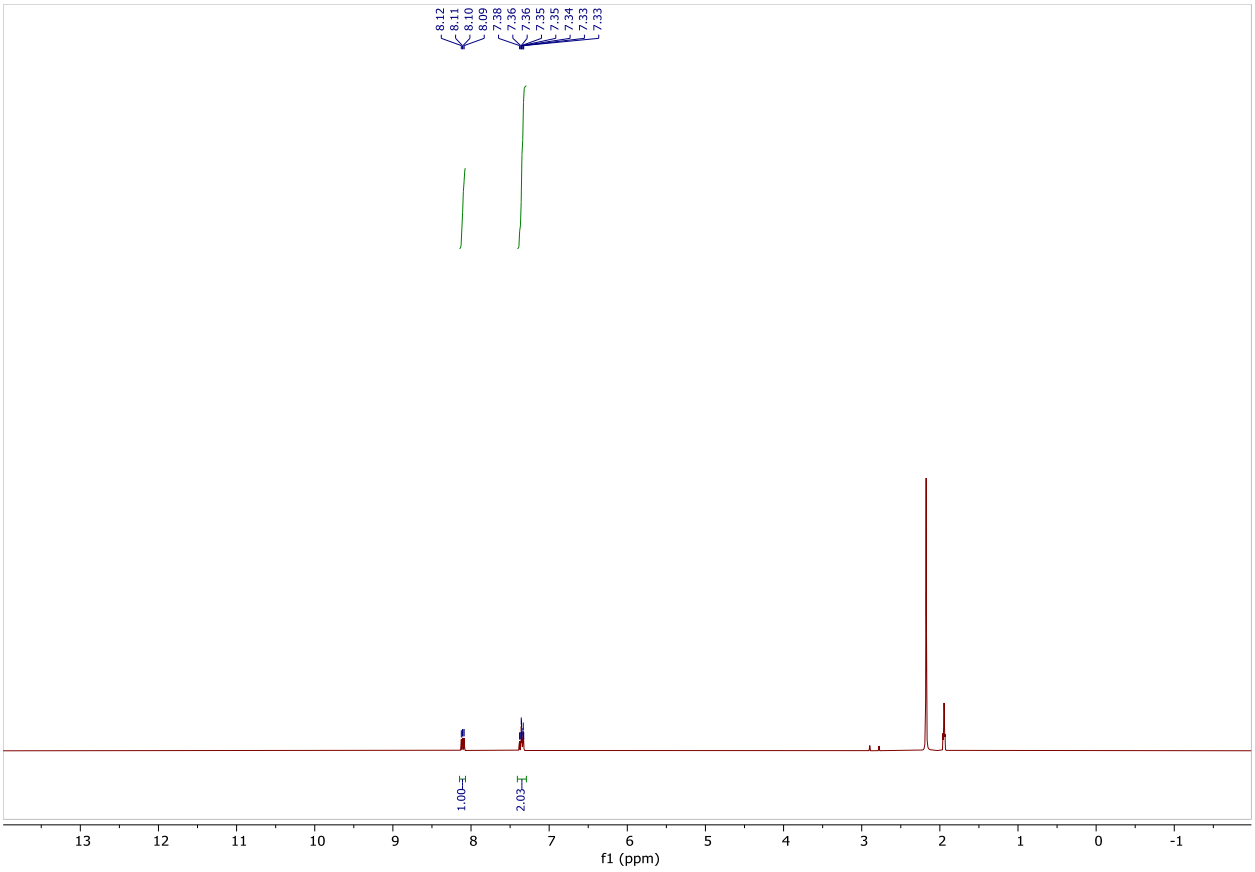


Figure S78. $^{13}C\{^{1}H\}$ NMR (100 MHz) Spectrum of compound **2e** in CD_3CN.

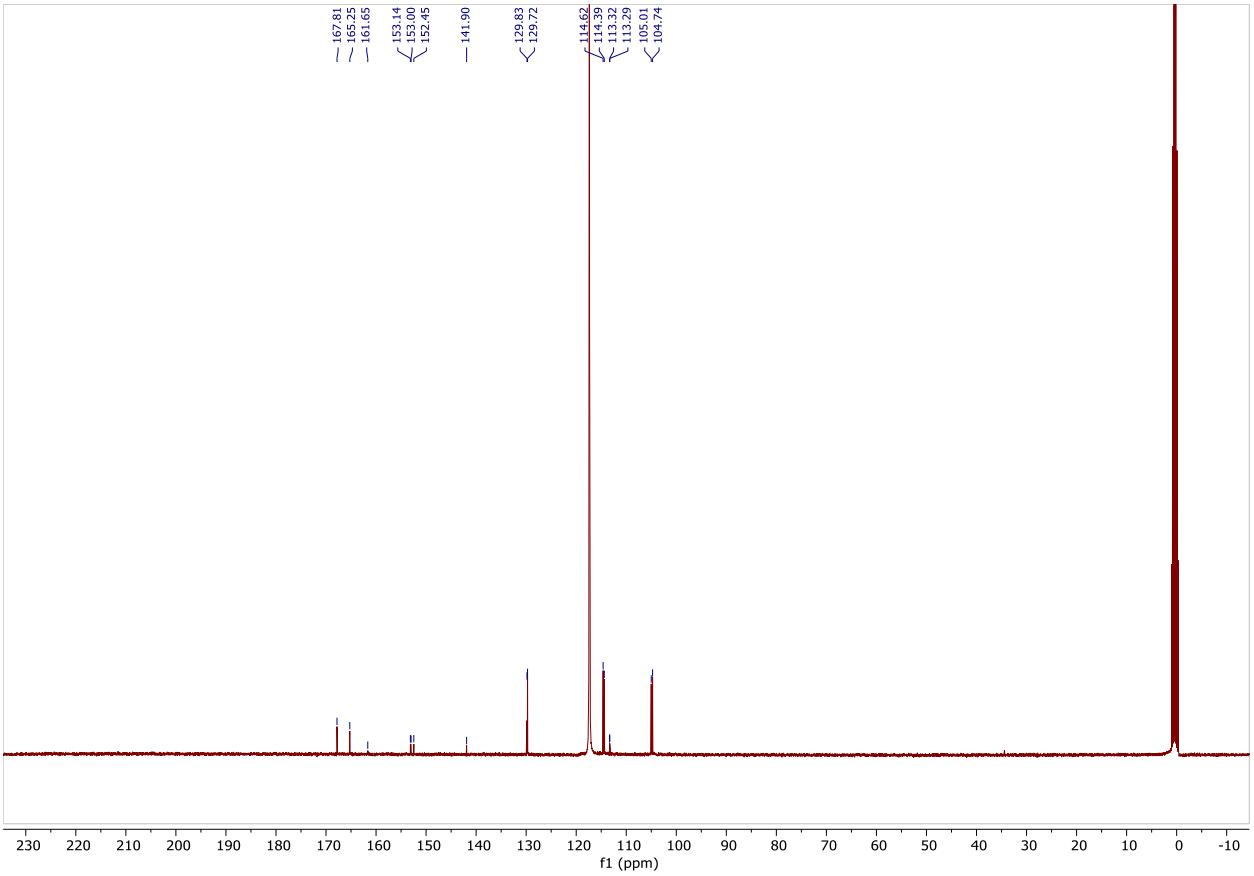
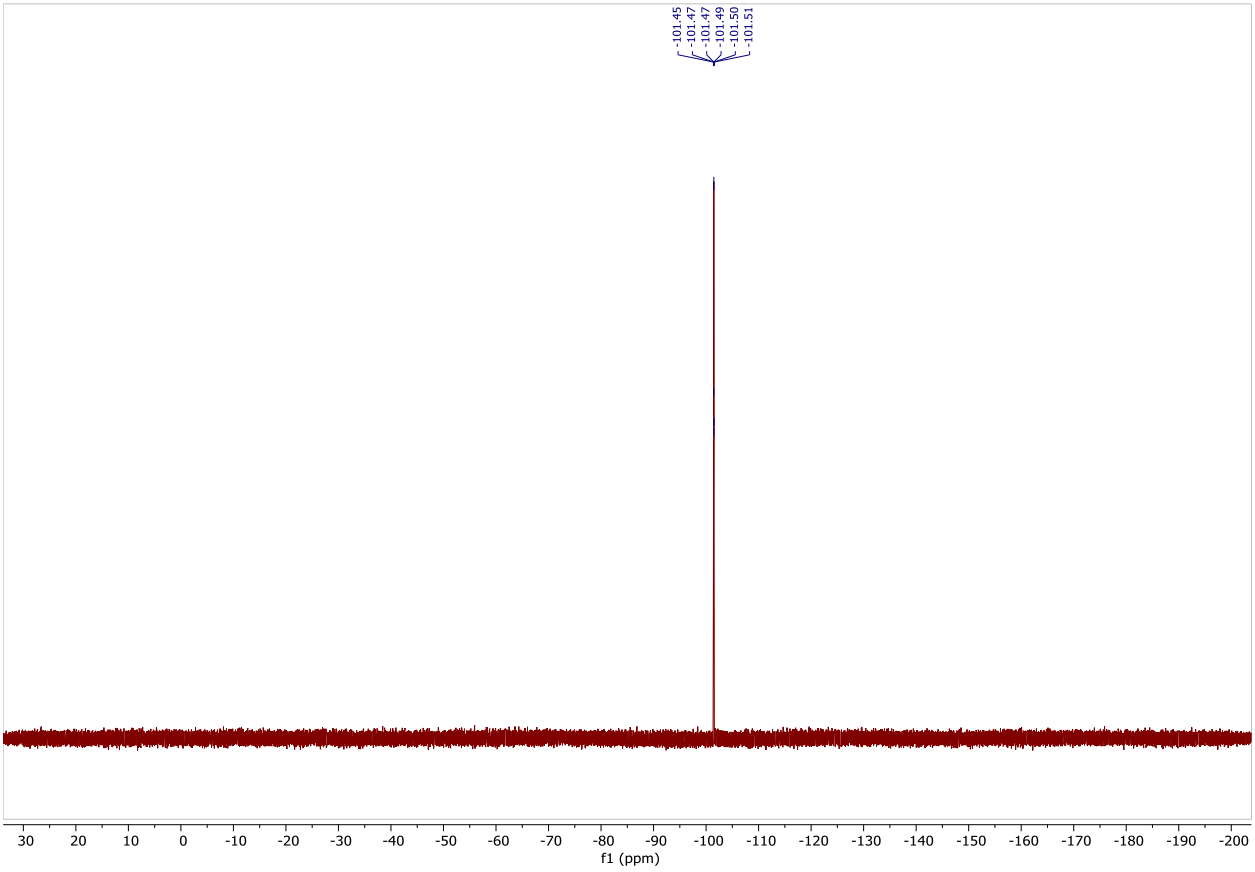


Figure S79. ^{19}F NMR (376 MHz) Spectrum of compound **2e** in CD_3CN.



8. HPLC chromatograms

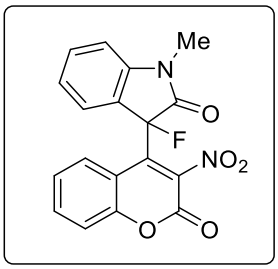
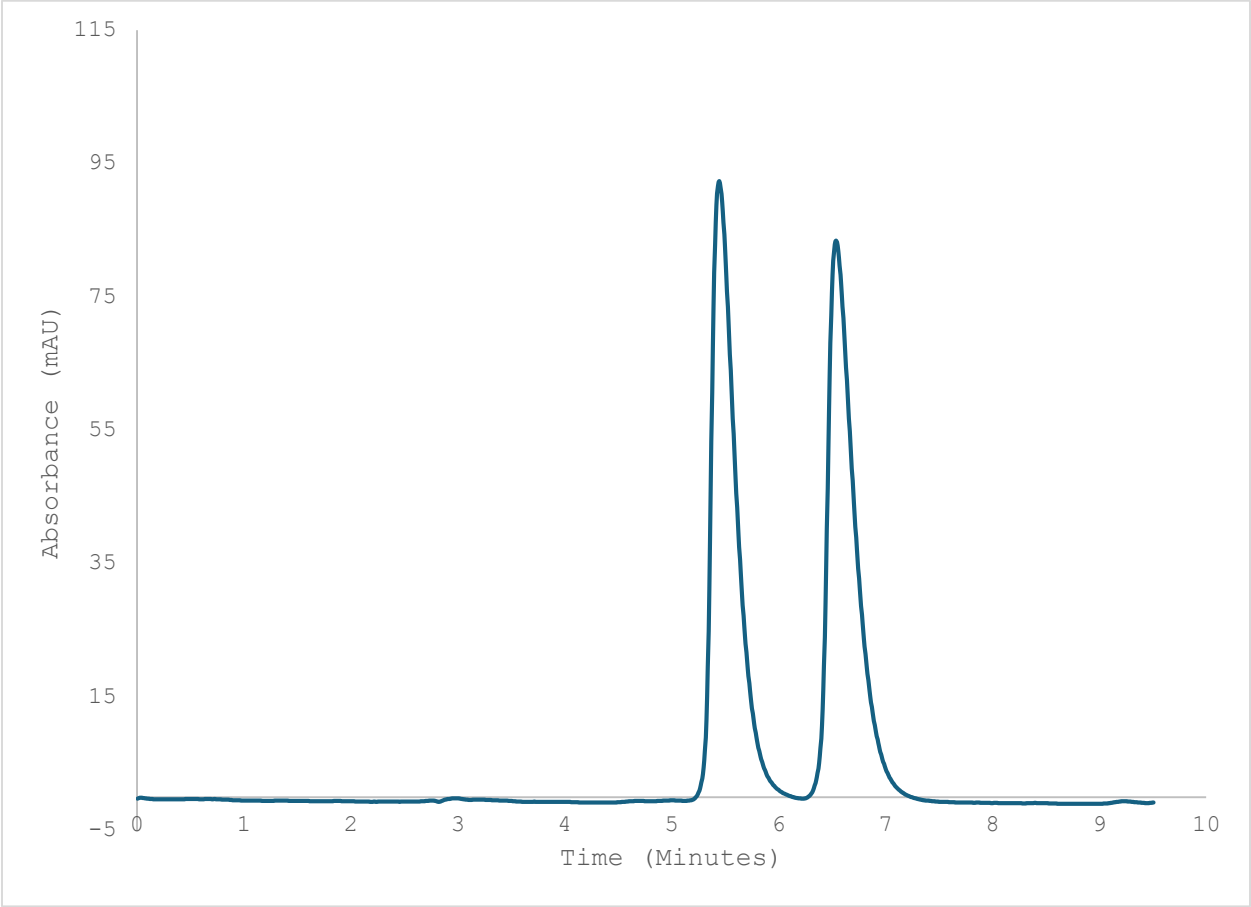


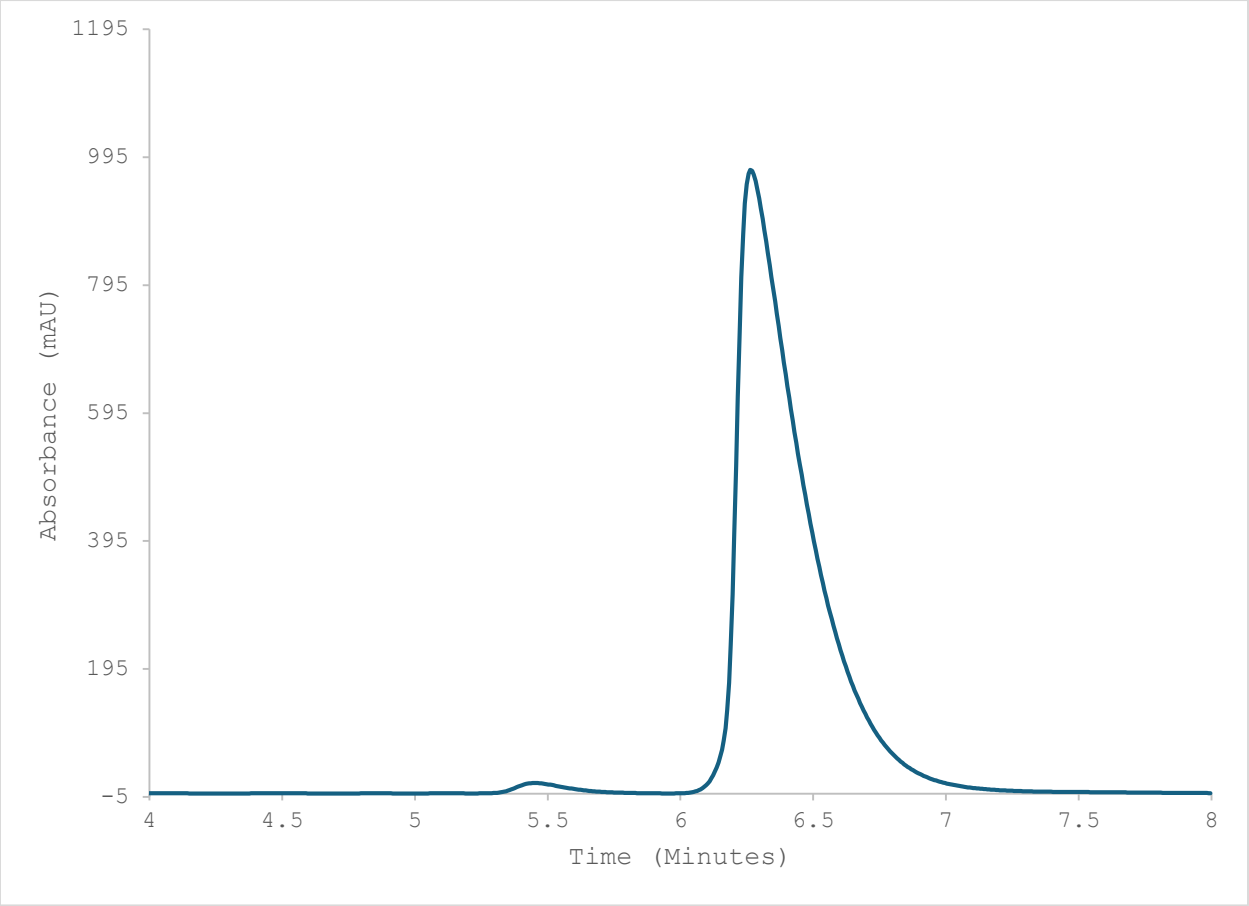
Figure S80. Chiral HPLC separation of a racemic mixture of compound **3a**.



Conditions: (*S,S)*-Whelk-O 1, 70:30 Dichloromethane/Hexanes, flow rate 1 mL/min, λ=254 nm.

#	Time	Area	Height	Width	Area%	Symmetry
1	5.444	1500.4	93	0.2423	49.820	0.416
2	6.537	1511.3	84.2	0.2675	50.180	0.411

Figure S81. Chiral HPLC separation of the asymmetric reaction product, compound **3a**.



Conditions: (*S,S)*-Whelk-O 1, 70:30 Dichloromethane/Hexanes, flow rate 1 mL/min, λ=254 nm.

#	Time	Area	Height	Width	Area%	Symmetry
1	5.45	225.3	16.2	0.2059	1.279	0.506
2	6.265	17385.1	975.1	0.254	98.721	0.246

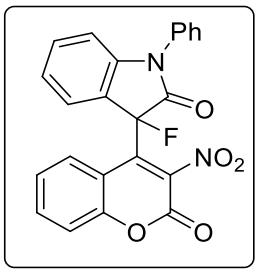
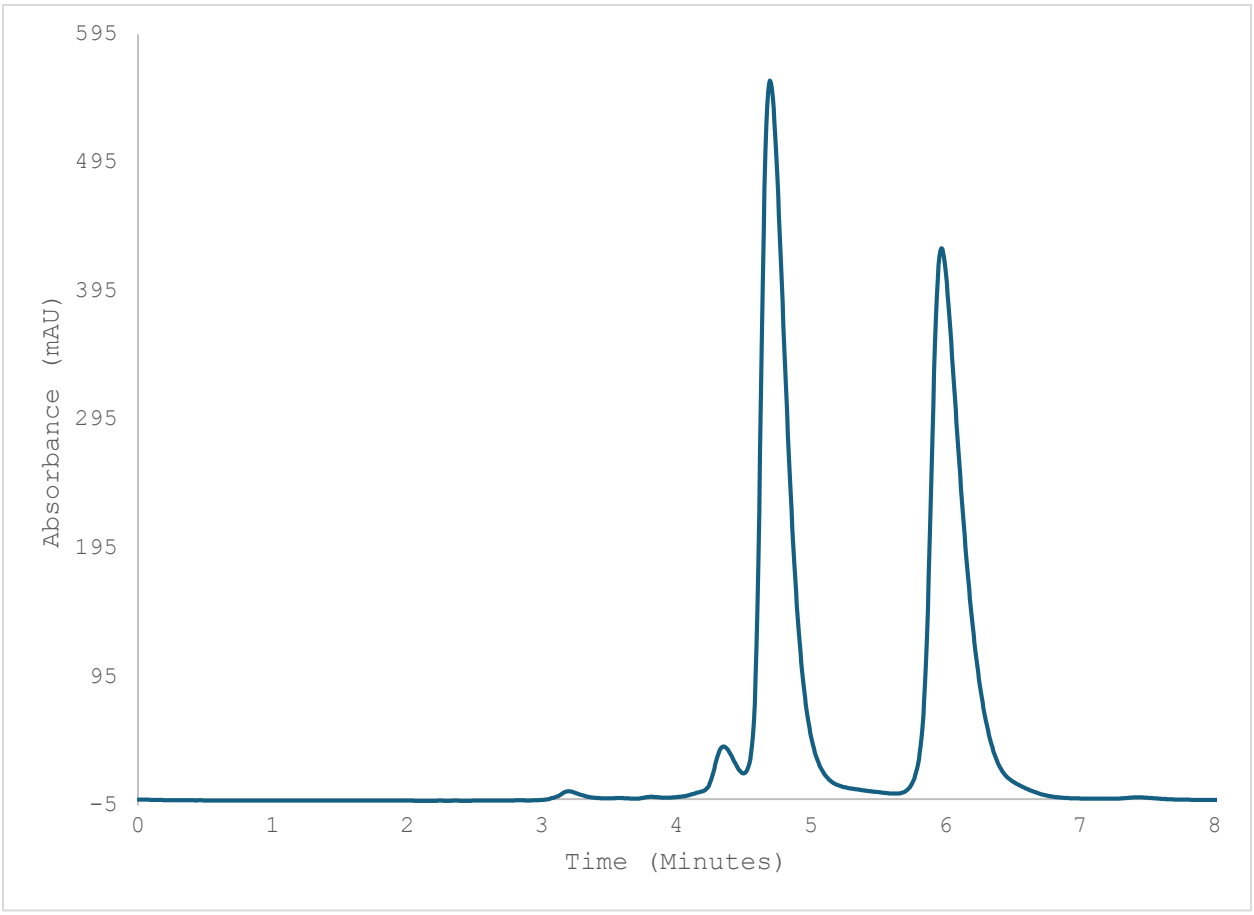


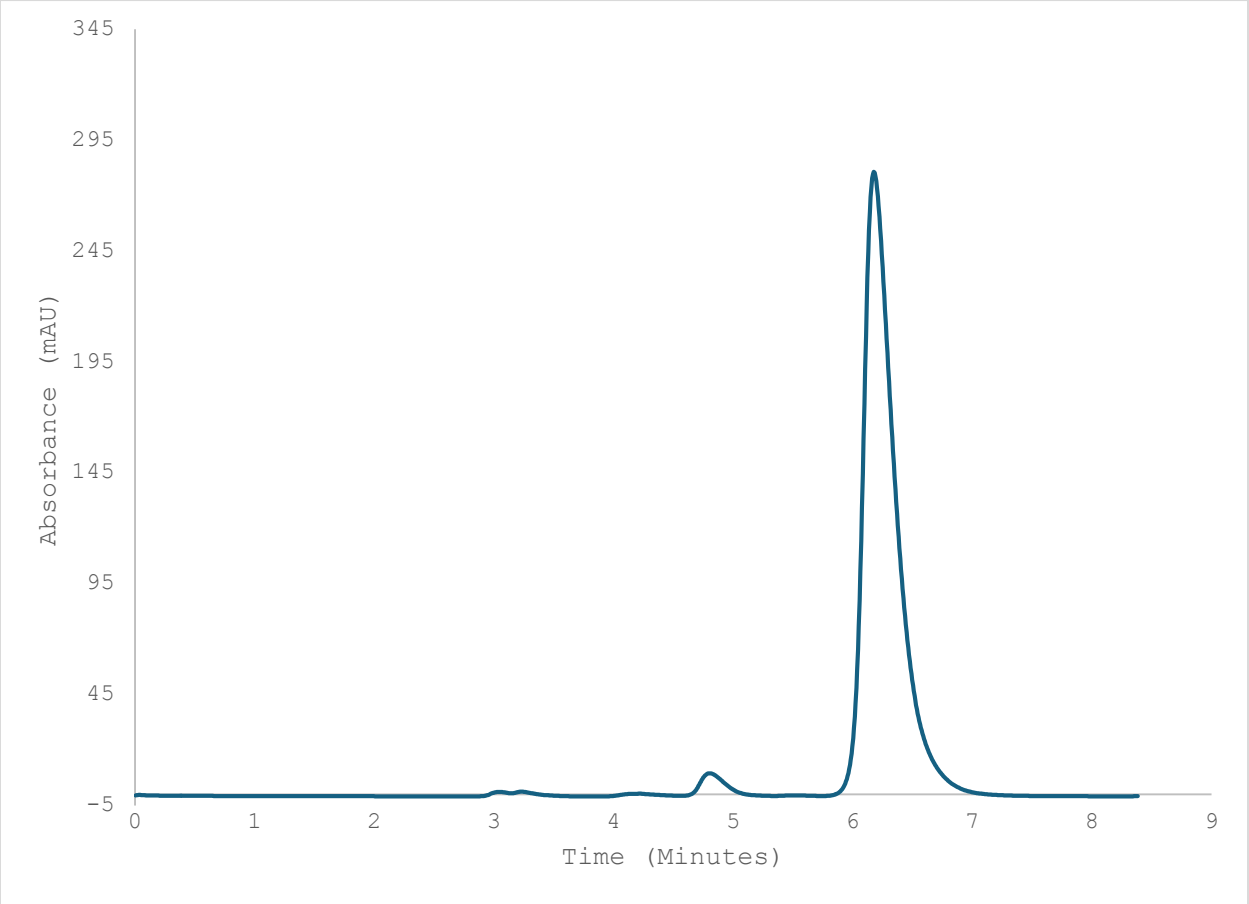
Figure S82. Chiral HPLC separation of a racemic mixture of compound **3b**.



Conditions: (*S,S)*-Whelk-O 1, 70:30 Dichloromethane/Hexanes, flow rate 1 mL/min, λ=254 nm.

#	Time	Area	Height	Width	Area%	Symmetry
1	4.697	7209.1	541.2	0.222	49.368	0.486
2	5.972	7393.7	428.4	0.2534	50.632	0.46

Figure S83. Chiral HPLC separation of the asymmetric reaction product, compound **3b**.



Conditions: (*S,S)*-Whelk-O 1, 70:30 Dichloromethane/Hexanes, flow rate 1 mL/min, λ=254 nm.

#	Time	Area	Height	Width	Area%	Symmetry
1	4.805	150	10.2	0.2274	2.749	0.567
2	6.179	5307.3	281.5	0.278	97.251	0.47

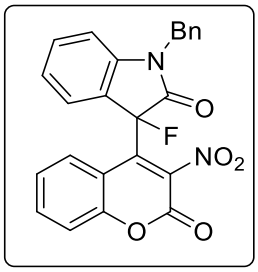
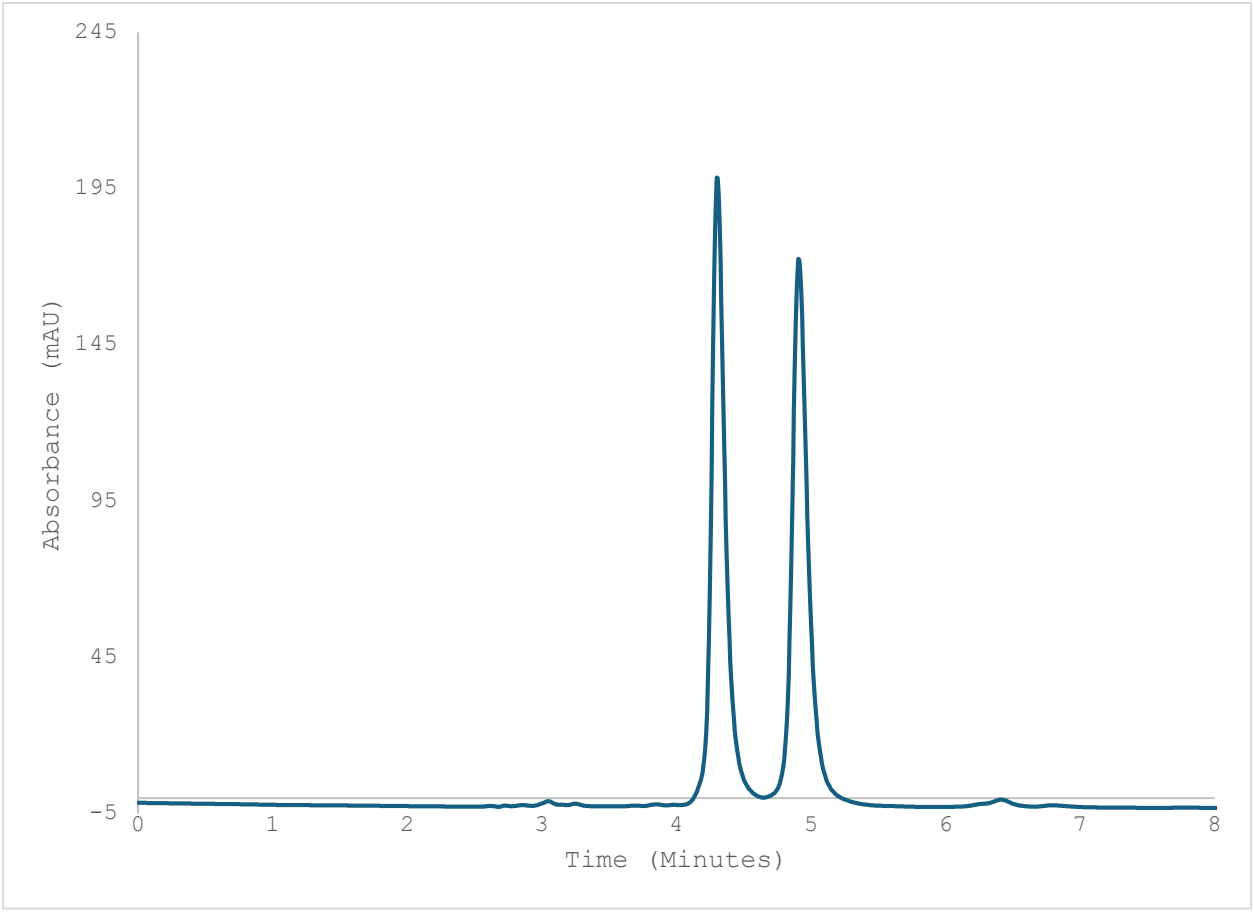


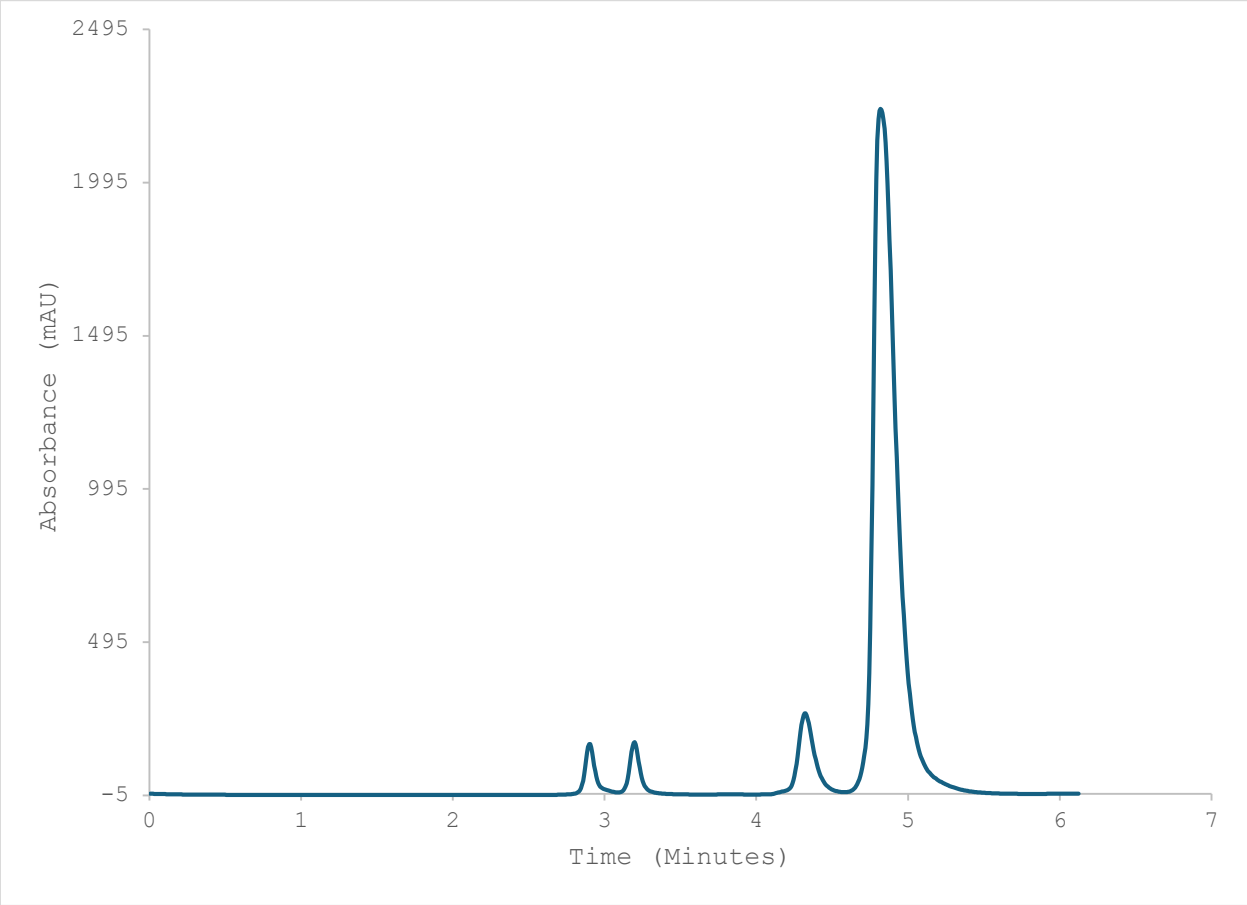
Figure S84. Chiral HPLC separation of a racemic mixture of compound **3c**.



Conditions: (*S,S)*-Whelk-O 1, 70:30 Dichloromethane/Hexanes, flow rate 1 mL/min, λ=254 nm.

#	Time	Area	Height	Width	Area%	Symmetry
1	4.305	1499.7	201.5	0.1108	49.725	0.673
2	4.911	1516.3	175.3	0.1289	50.275	0.7

Figure S85. Chiral HPLC separation of the asymmetric reaction product, compound **3c.**



Conditions: (*S,S)*-Whelk-O 1, 70:30 Dichloromethane/Hexanes, flow rate 1 mL/min, λ=254 nm.

#	Time	Area	Height	Width	Area%	Symmetry
1	4.322	2068.2	265	0.1151	7.867	0.706
2	4.819	24220.4	2237.1	0.1643	92.133	0.445

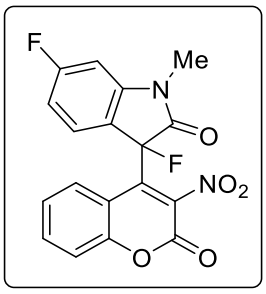
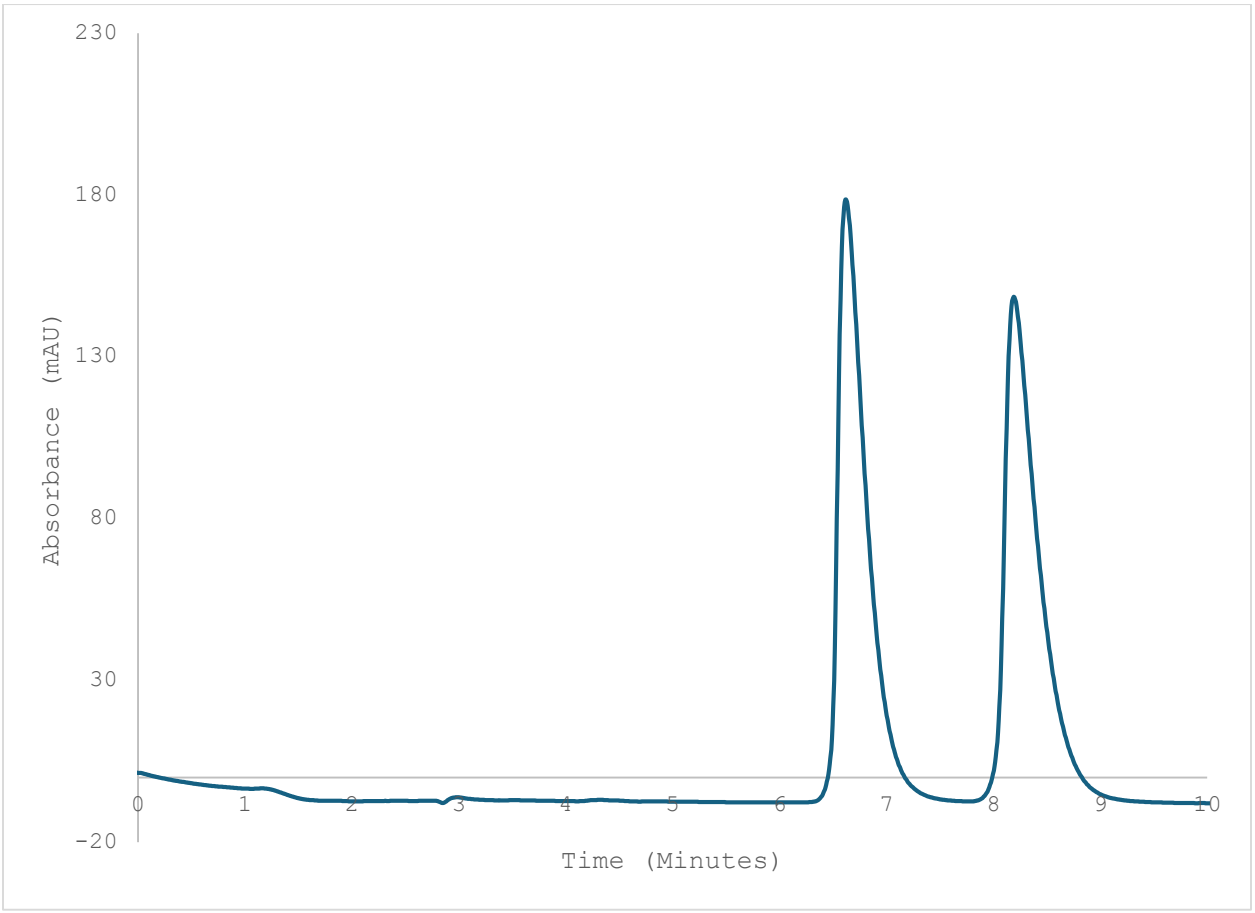


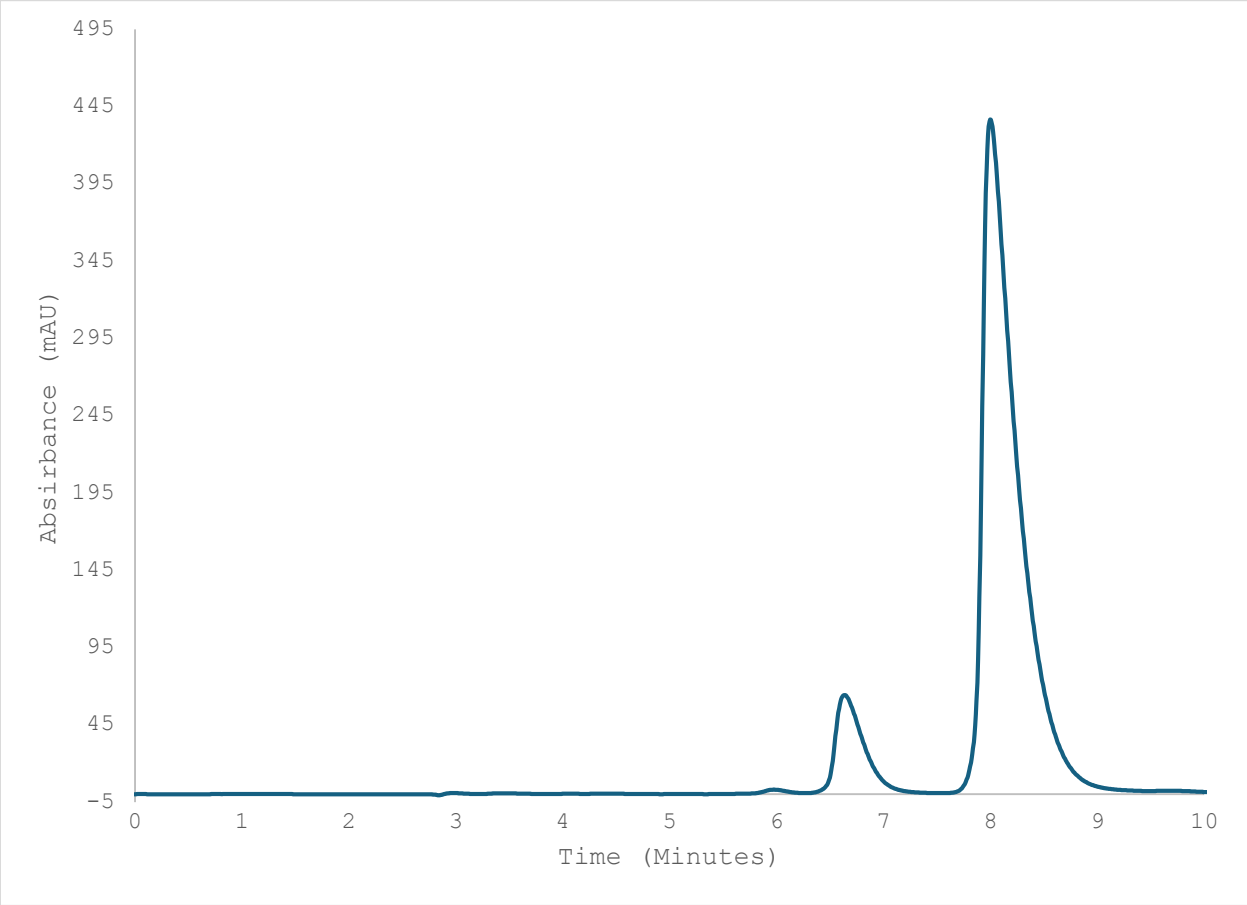
Figure S86. Chiral HPLC separation of a racemic mixture of compound **3d**.



Conditions: (*S,S)*-Whelk-O 1, 60:40 Dichloromethane/Hexanes, flow rate 1 mL/min, λ=254 nm.

#	Time	Area	Height	Width	Area%	Symmetry
1	6.62	3478.7	186.4	0.2778	50.040	0.36
2	8.191	3473.2	156.2	0.3215	49.960	0.356

Figure S87. Chiral HPLC separation of the asymmetric reaction product, compound **3d**.



Conditions: (*S,S)*-Whelk-O 1, 60:40 Dichloromethane/Hexanes, flow rate 1 mL/min, λ=254 nm.

#	Time	Area	Height	Width	Area%	Symmetry
1	6.635	1164.5	63.6	0.2777	10.515	0.456
2	8	9910.2	435.8	0.3253	89.485	0.291

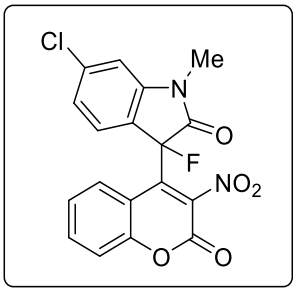
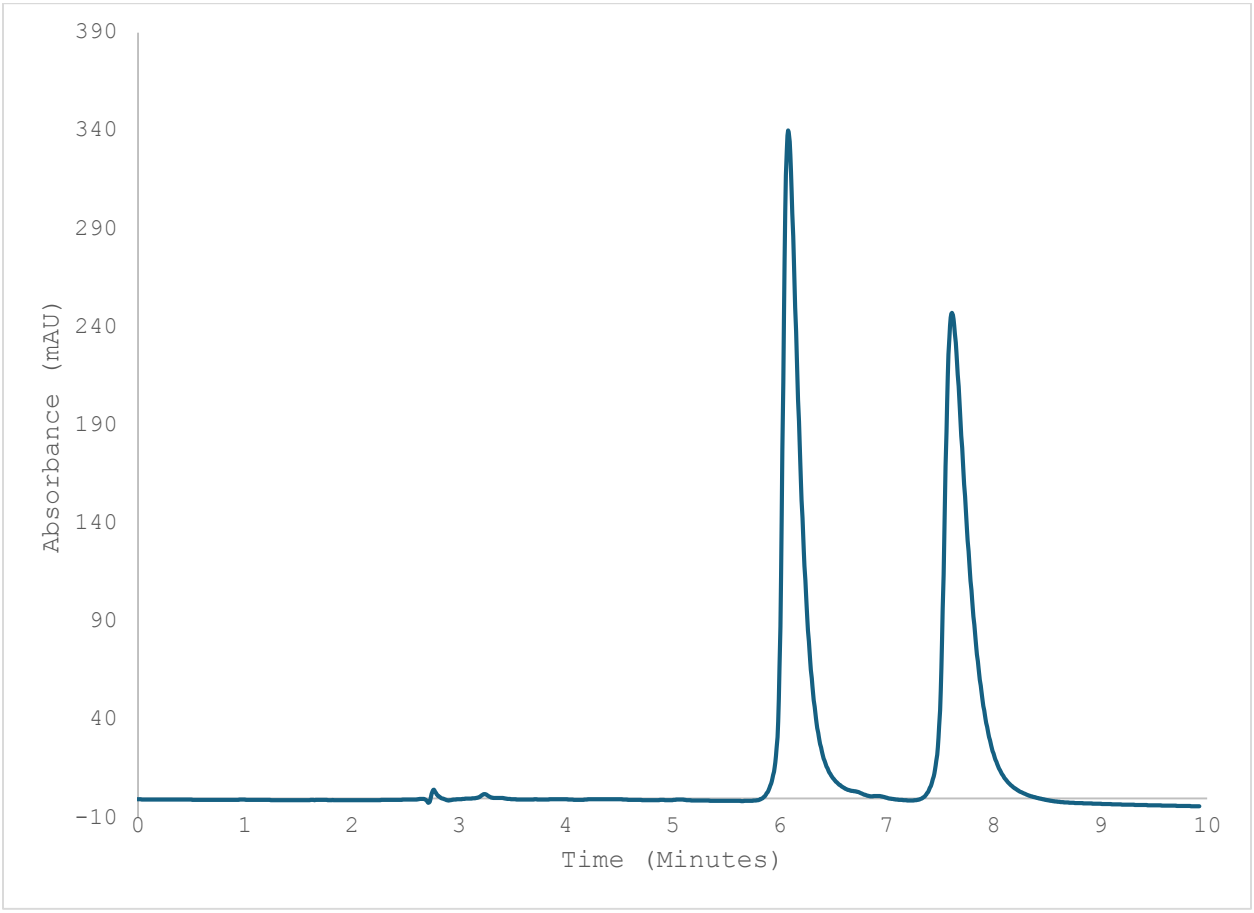


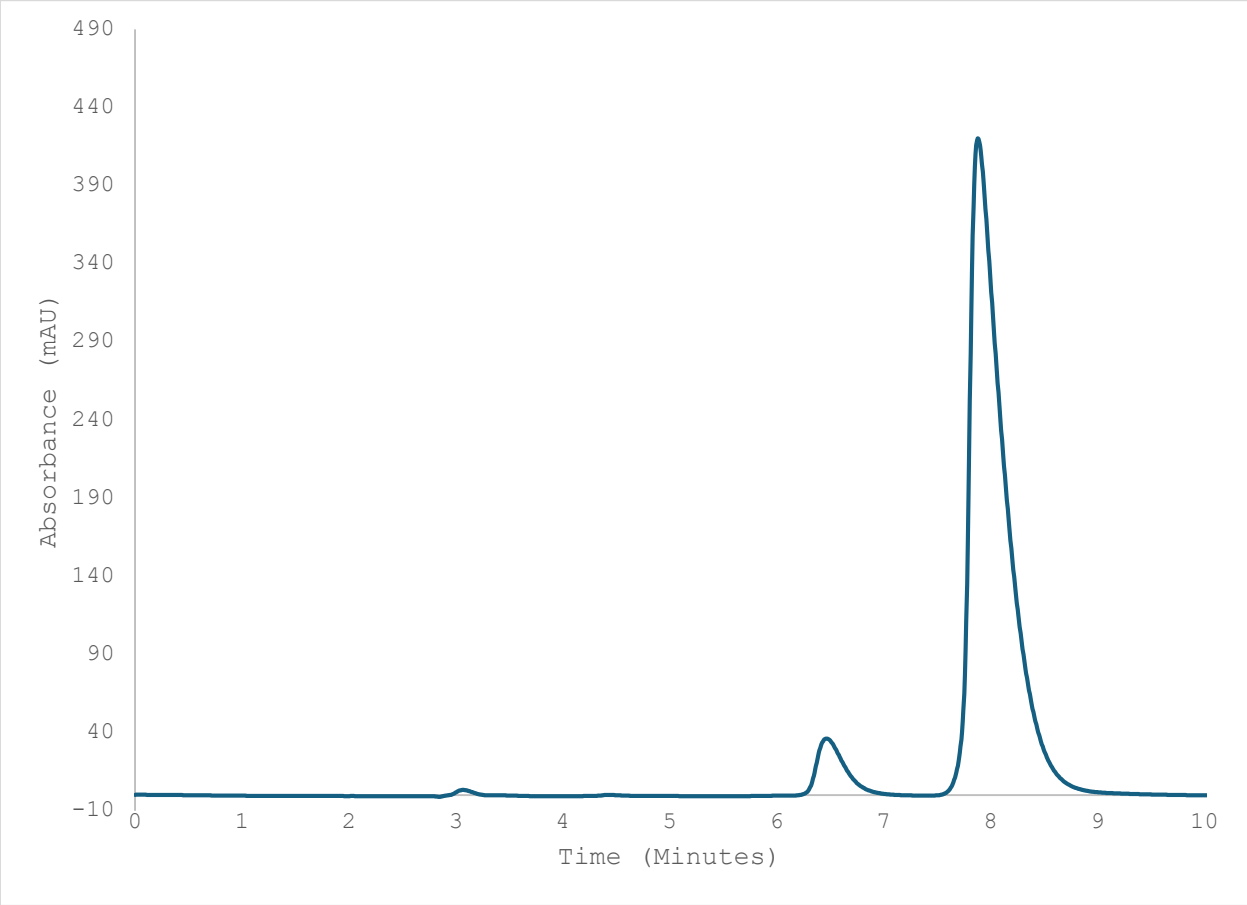
Figure S88. Chiral HPLC separation of a racemic mixture of compound **3e.**



Conditions: (*S,S)*-Whelk-O 1, 60:40 Dichloromethane/Hexanes, flow rate 1 mL/min, λ=254 nm.

#	Time	Area	Height	Width	Area%	Symmetry
1	6.081	4137.5	340.8	0.1756	49.671	0.418
2	7.612	4192.3	248.8	0.2426	50.329	0.398

Figure S89. Chiral HPLC separation of the asymmetric reaction product, compound **3e.**



Conditions: (*S,S)*-Whelk-O 1, 60:40 Dichloromethane/Hexanes, flow rate 1 mL/min, λ=254 nm.

#	Time	Area	Height	Width	Area%	Symmetry
1	6.467	504.1	32.9	0.2557	5.002	0.6
2	7.884	9574.7	420.8	0.3215	94.998	0.305

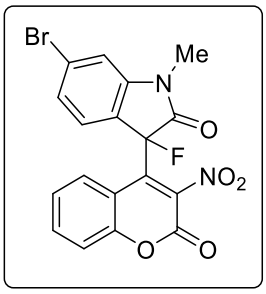
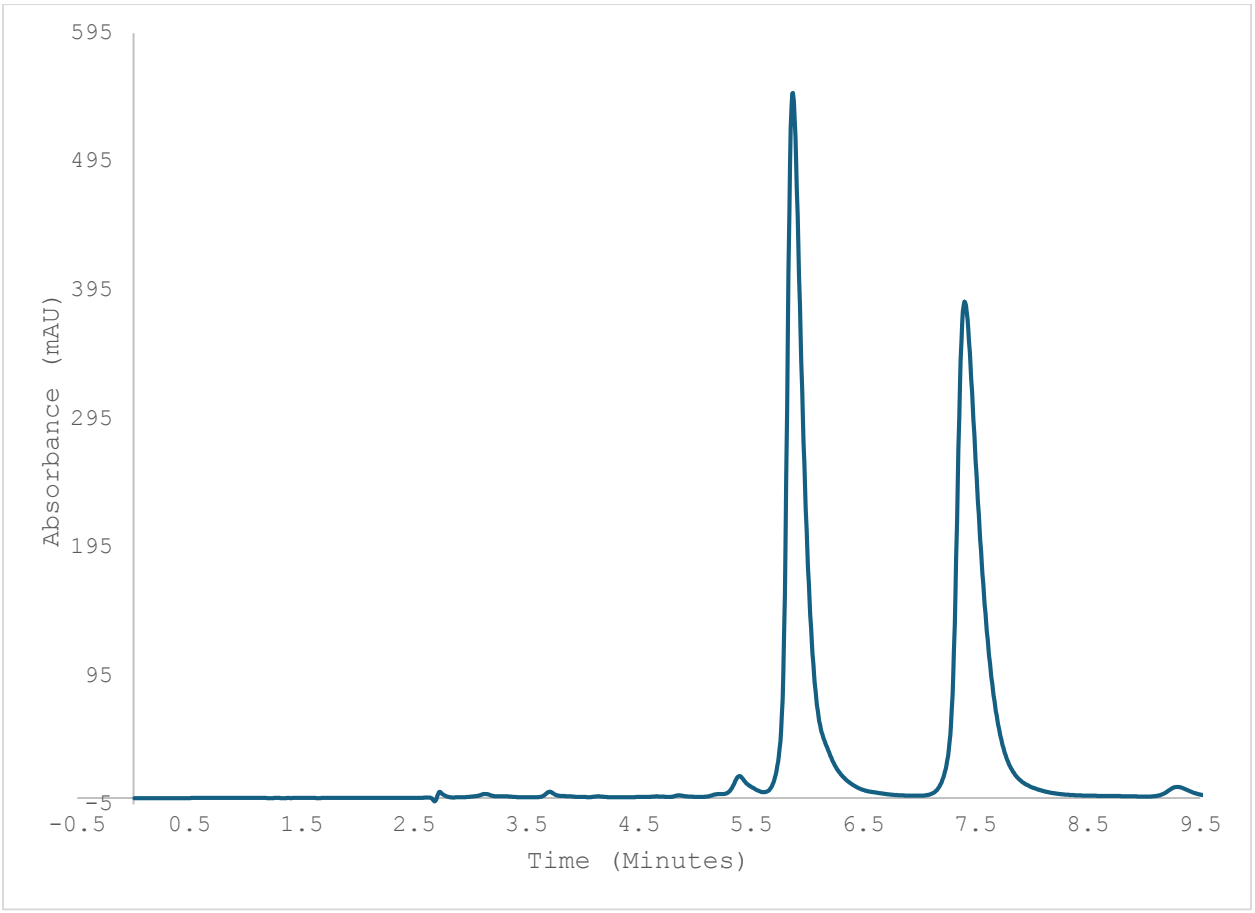


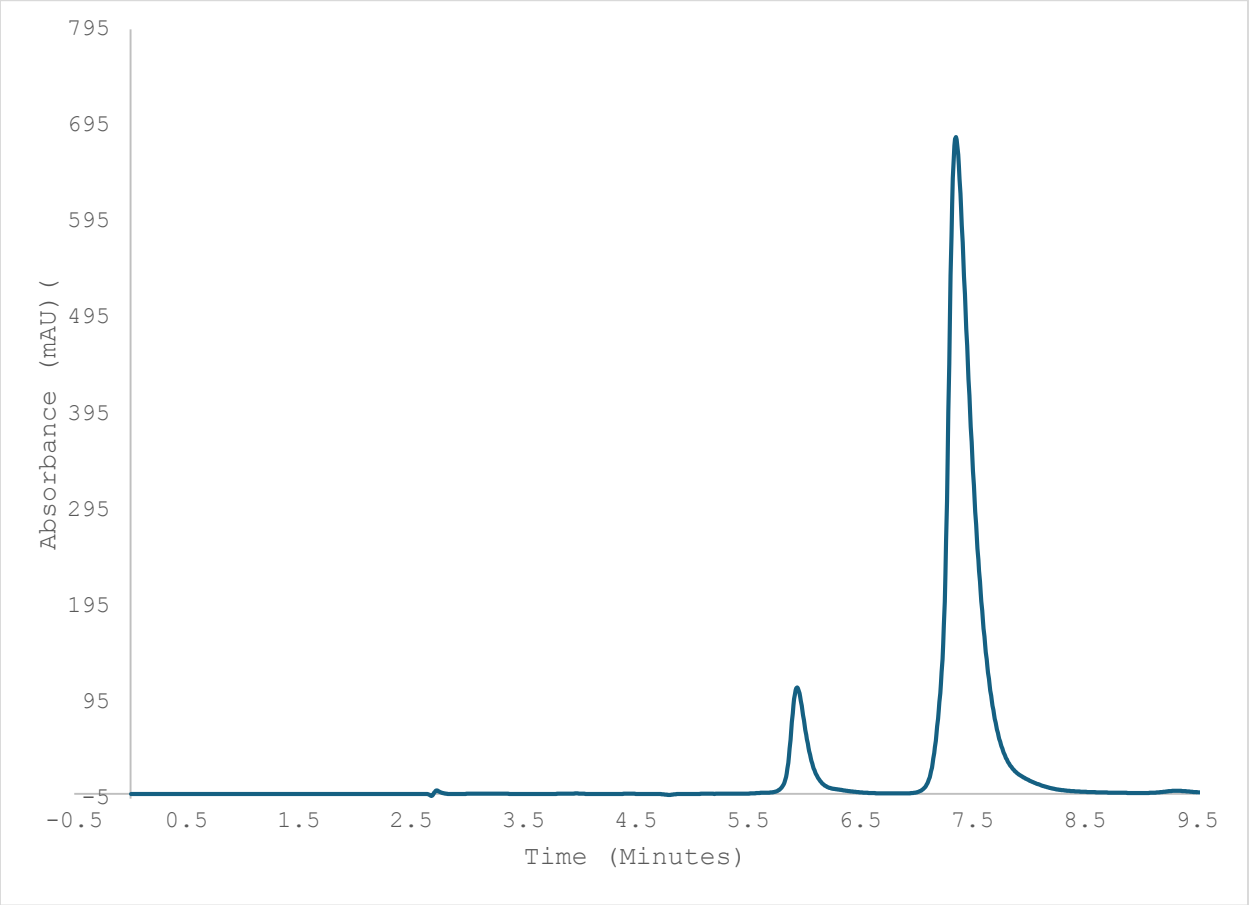
Figure S90. Chiral HPLC separation of a racemic mixture of compound **3f**.



Conditions: (*S,S)*-Whelk-O 1, 70:30 Dichloromethane/Hexanes, flow rate 1 mL/min, λ=254 nm.

#	Time	Area	Height	Width	Area%	Symmetry
1	5.872	6177.6	547.9	0.1615	50.823	0.453
2	7.404	5977.5	384.8	0.2232	49.177	0.448

Figure S91. Chiral HPLC separation of the asymmetric reaction product, compound **3f**.



Conditions: (*S,S)*-Whelk-O 1, 70:30 Dichloromethane/Hexanes, flow rate 1 mL/min, λ=254 nm.

#	Time	Area	Height	Width	Area%	Symmetry
1	5.938	1226.9	110.4	0.1617	9.809	0.564
2	7.351	11280.7	682.6	0.2348	90.191	0.451

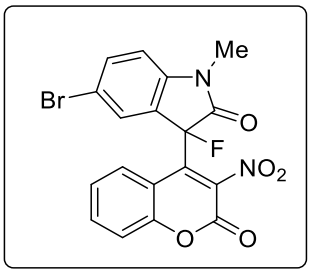
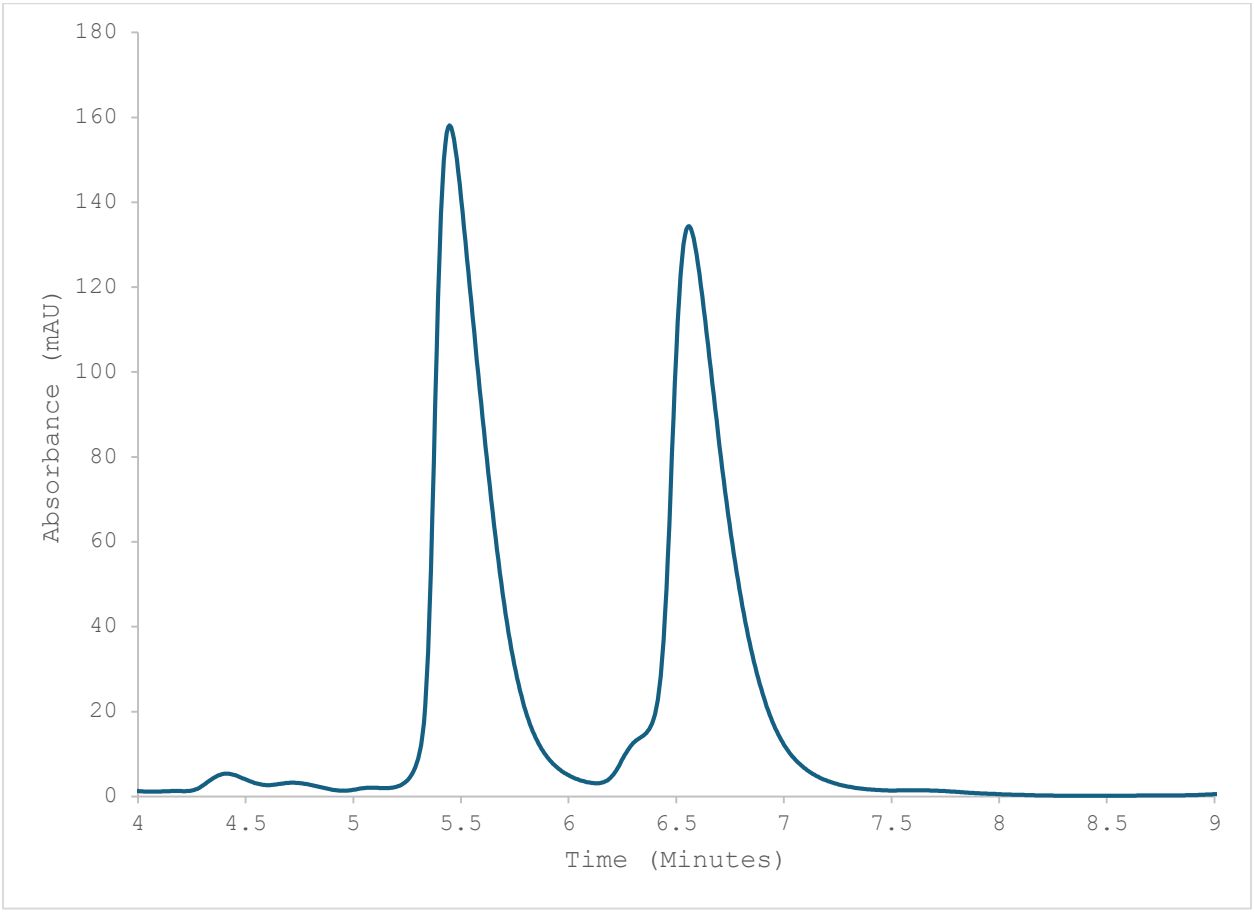


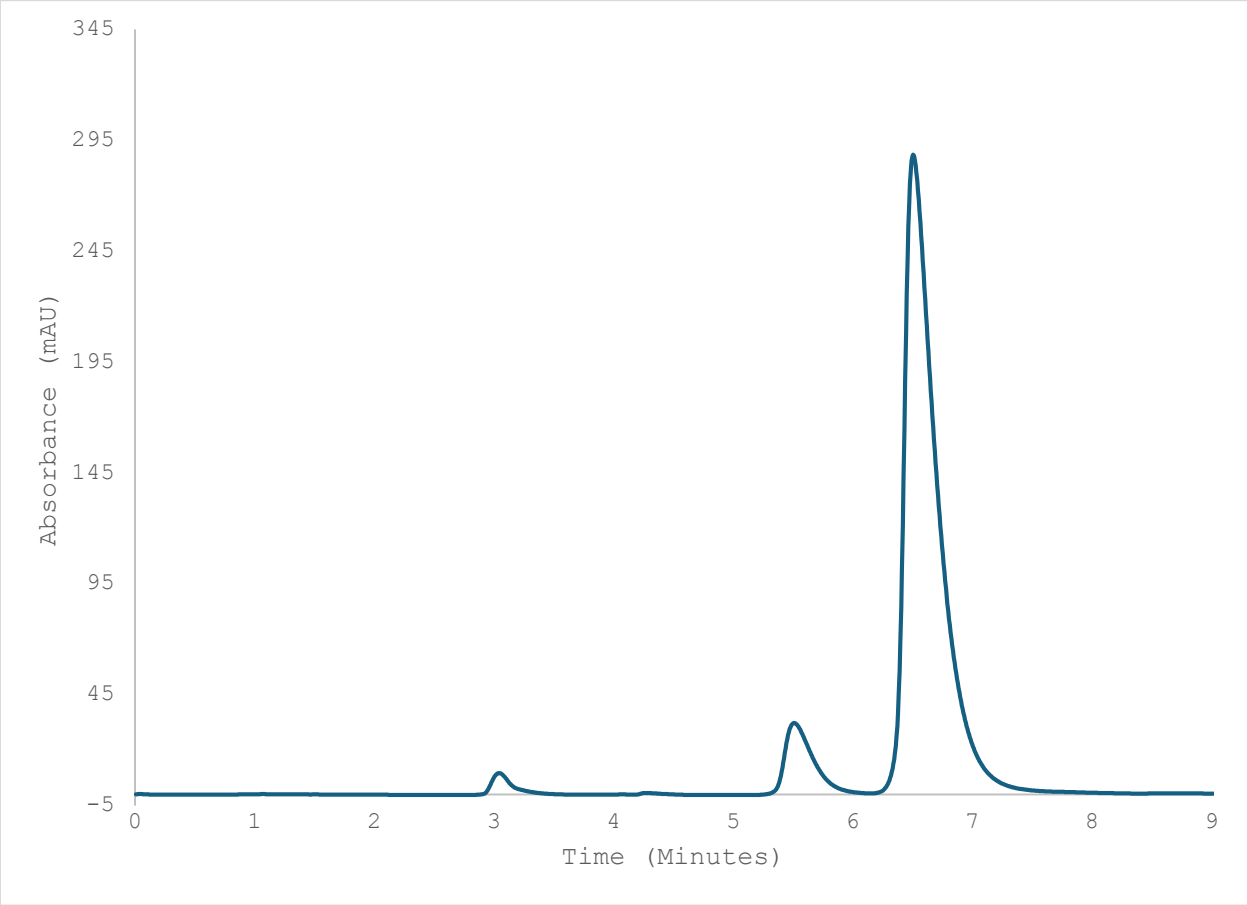
Figure S92. Chiral HPLC separation of a racemic mixture of compound **3g**.



Conditions: (*S,S)*-Whelk-O 1, 70:30 Dichloromethane/Hexanes, flow rate 1 mL/min, λ=254 nm.

#	Time	Area	Height	Width	Area%	Symmetry
1	5.447	2589.6	156.7	0.2388	50.251	0.379
2	6.558	2563.7	133	0.2789	49.749	0.501

Figure S93. Chiral HPLC separation of the asymmetric reaction product, compound **3g.**



Conditions: (*S,S)*-Whelk-O 1, 70:30 Dichloromethane/Hexanes, flow rate 1 mL/min, λ=254 nm.

#	Time	Area	Height	Width	Area%	Symmetry
1	5.51	437.7	30	0.2429	7.317	0.506
2	6.507	5544.3	288.5	0.2782	92.683	0.348

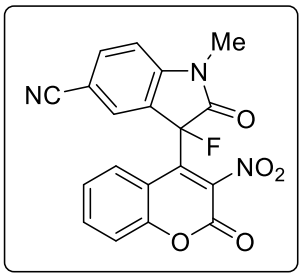
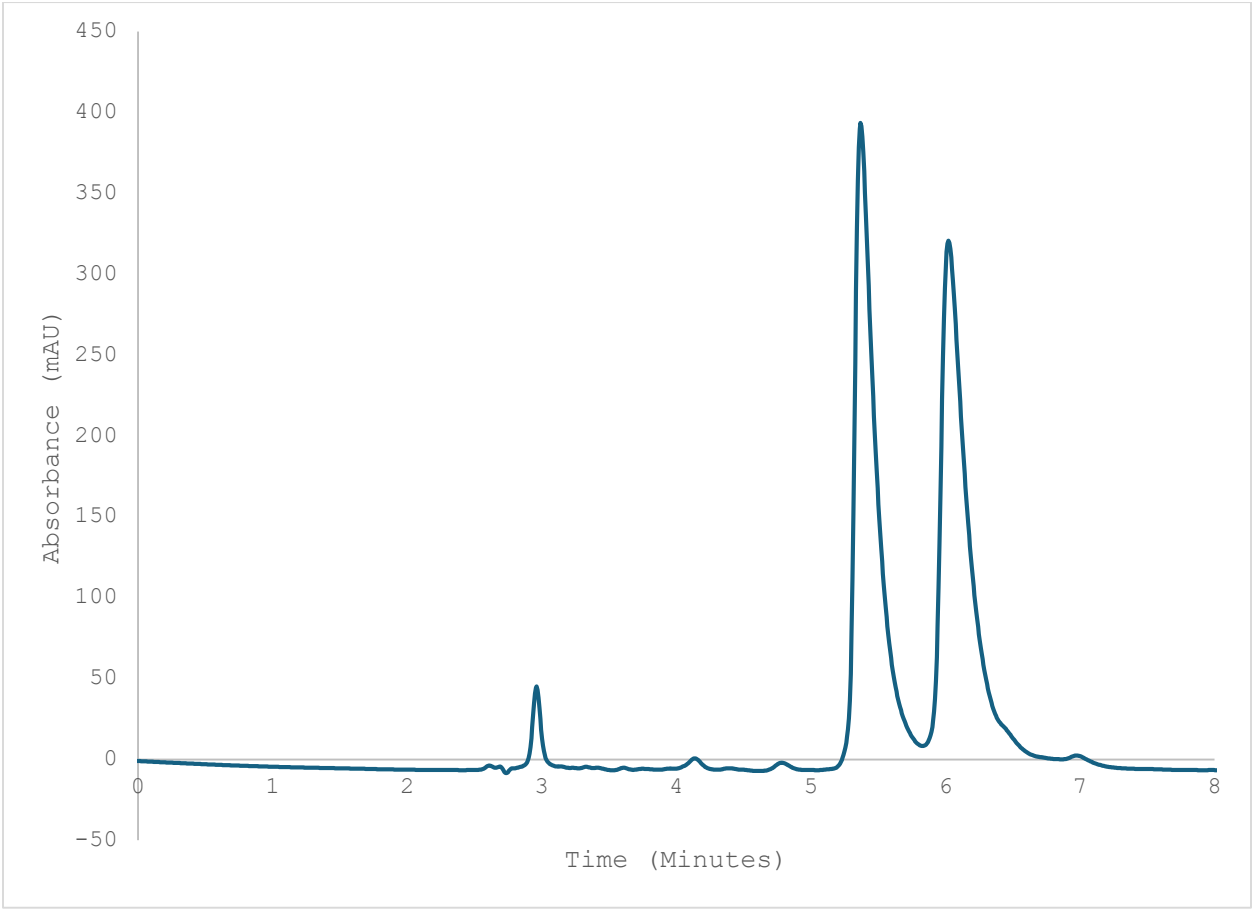


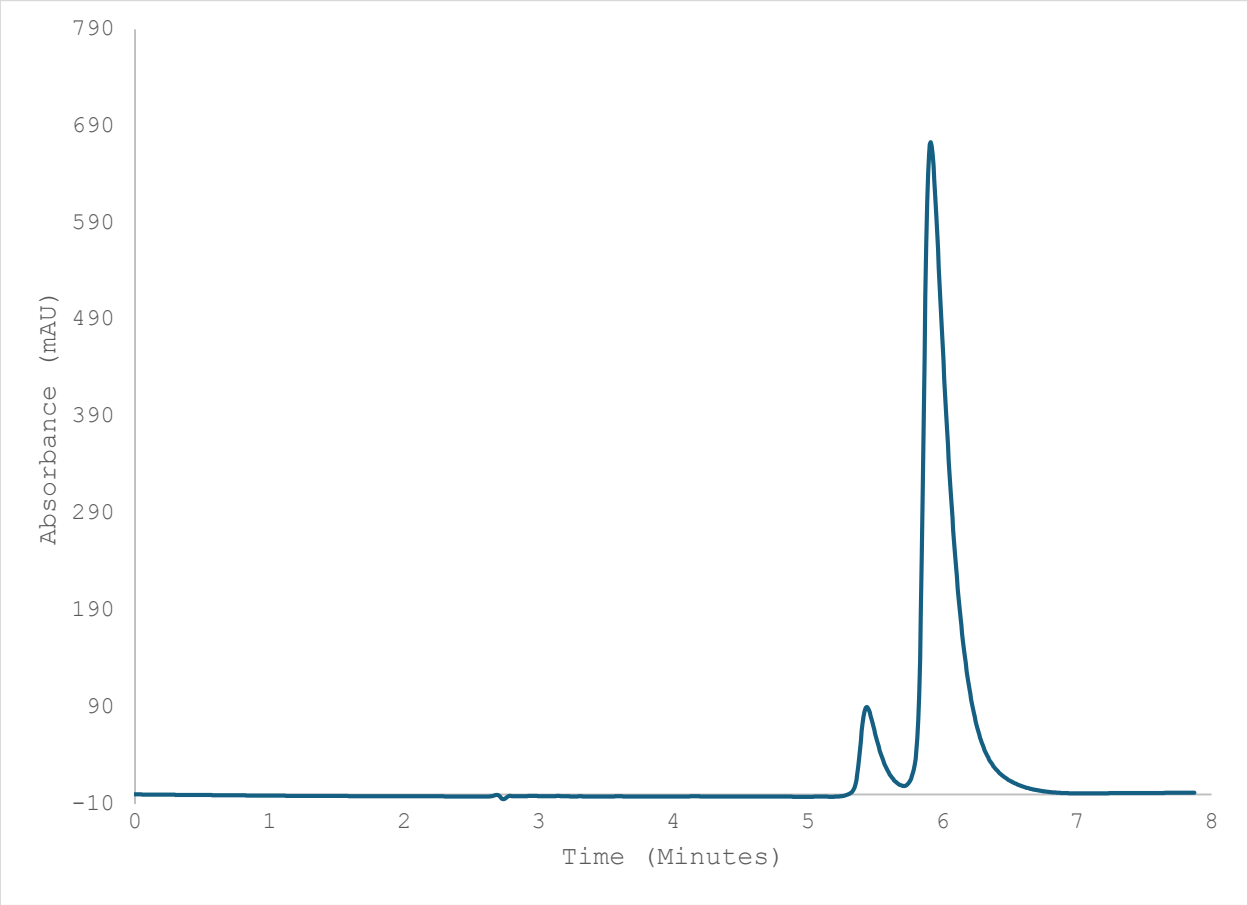
Figure S94. Chiral HPLC separation of a racemic mixture of compound **3h**.



Conditions: (*S,S)*-Whelk-O 1, 80:20 Dichloromethane/Hexanes, flow rate 1 mL/min, λ=254 nm. Baseline adjusted by +20 mAU.

#	Time	Area	Height	Width	Area%	Symmetry
1	5.371	4635.3	401.4	0.1925	50.010	0.366
2	6.024	4633.5	328.5	0.2351	49.990	0.406

Figure S95. Chiral HPLC separation of the asymmetric reaction product, compound **3h**.



Conditions: (*S,S)*-Whelk-O 1, 80:20 Dichloromethane/Hexanes, flow rate 1 mL/min, λ=254 nm.

#	Time	Area	Height	Width	Area%	Symmetry
1	5.438	966.3	92.2	0.1523	9.209	0.451
2	5.913	9526.4	674.5	0.2008	90.791	0.333

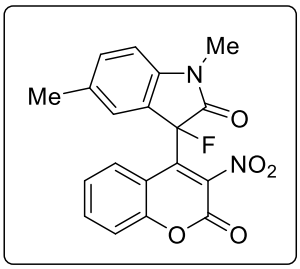
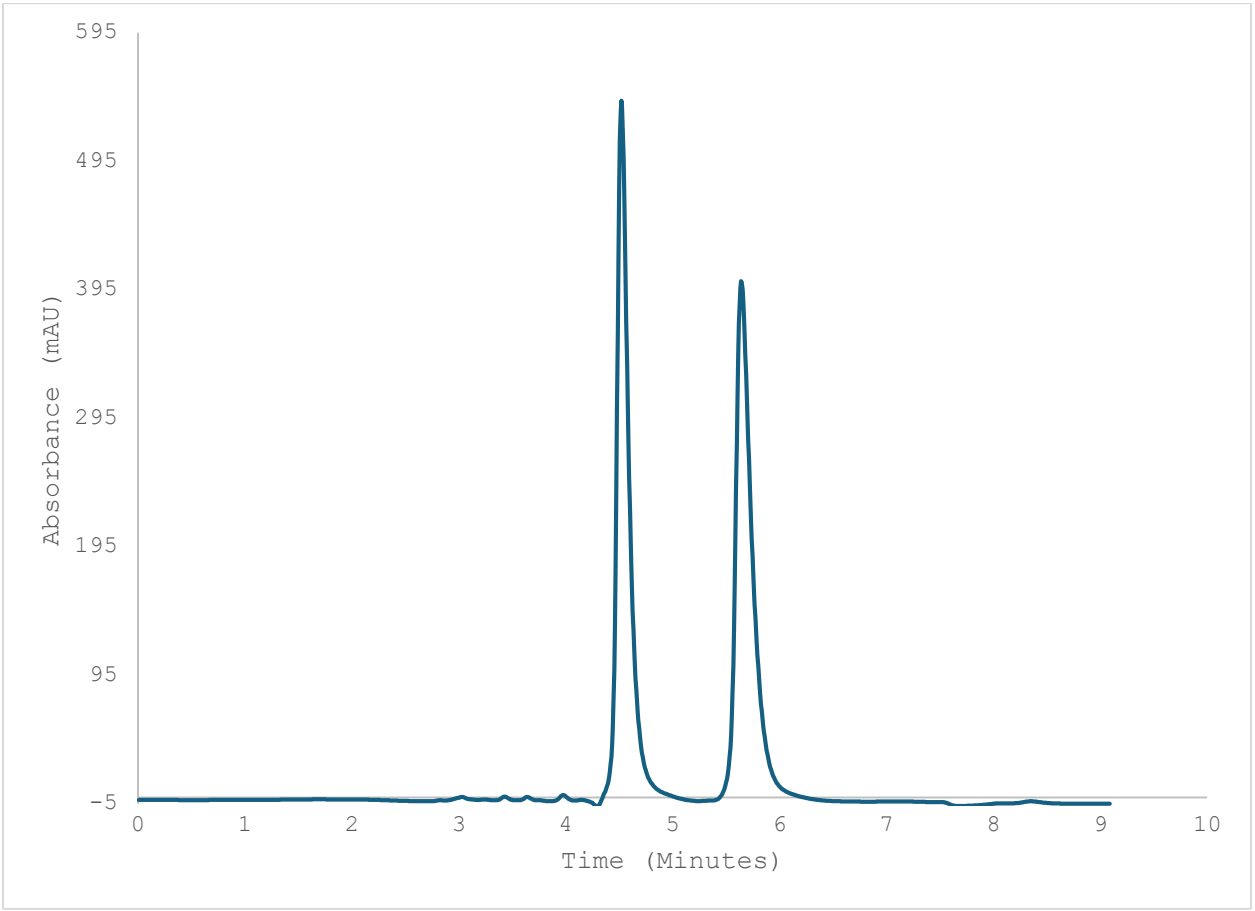


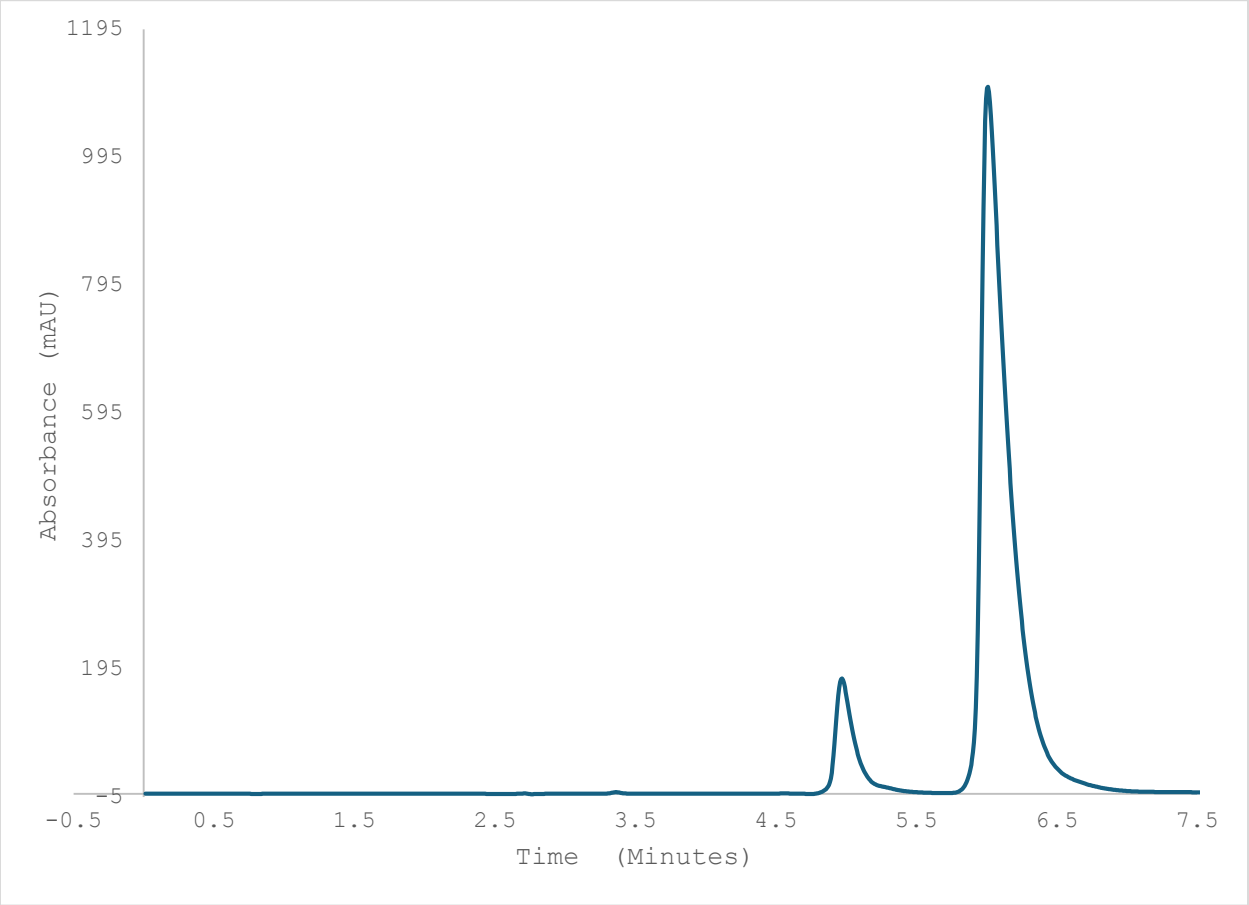
Figure S96. Chiral HPLC separation of a racemic mixture of compound **3i**.



Conditions: (*S,S)*-Whelk-O 1, 70:30 Dichloromethane/Hexanes, flow rate 1 mL/min, λ=254 nm.

#	Time	Area	Height	Width	Area%	Symmetry
1	4.521	4625.9	548.8	0.1223	50.045	0.523
2	5.643	4617.5	407.1	0.1643	49.955	0.492

Figure S97. Chiral HPLC separation of the asymmetric reaction product, compound **3i**.



Conditions: (*S,S)*-Whelk-O 1, 70:30 Dichloromethane/Hexanes, flow rate 1 mL/min, λ=254 nm.

#	Time	Area	Height	Width	Area%	Symmetry
1	4.971	1781.4	180.4	0.1412	10.292	0.438
2	6.01	15527	1105.2	0.1959	89.708	0.301

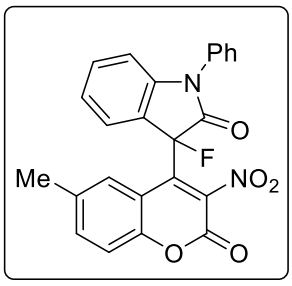
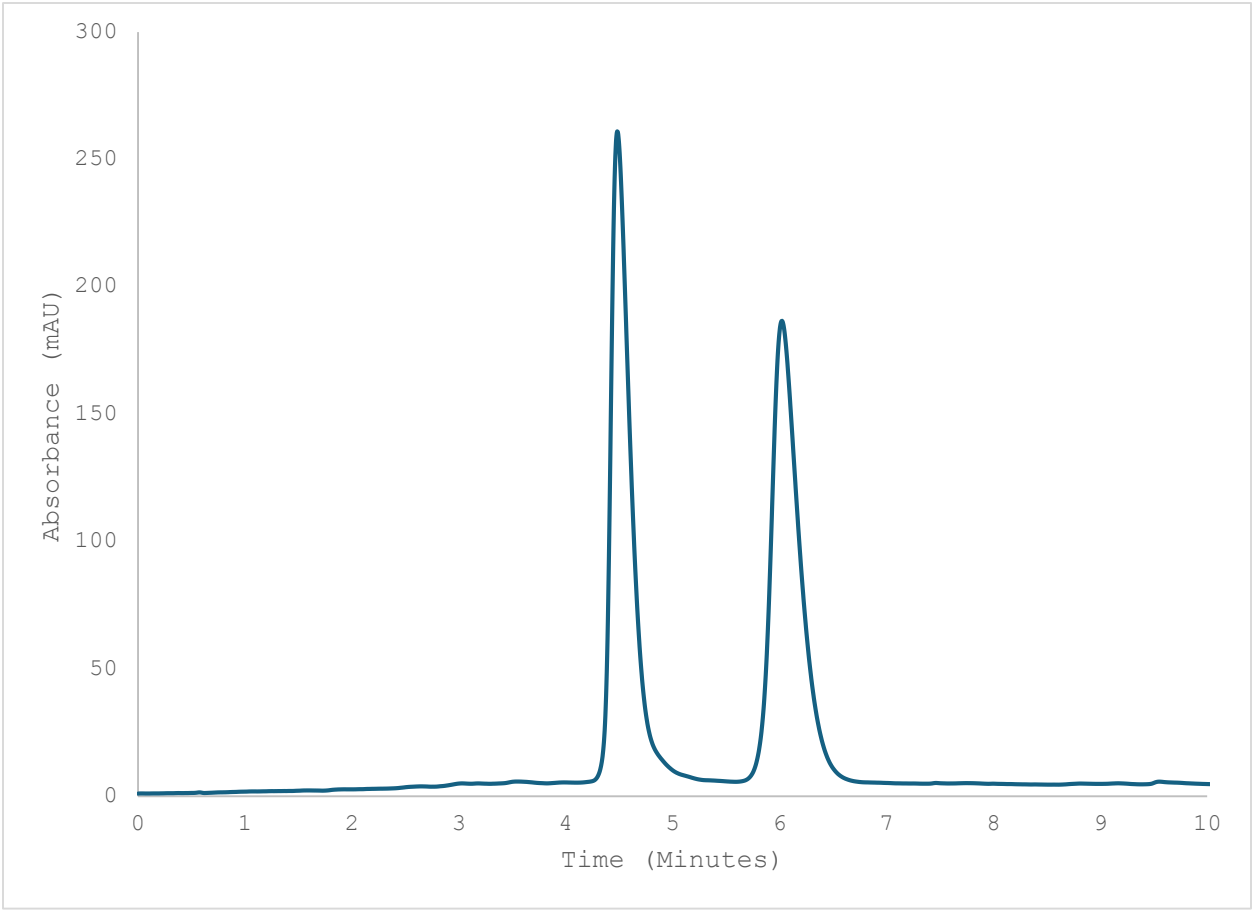


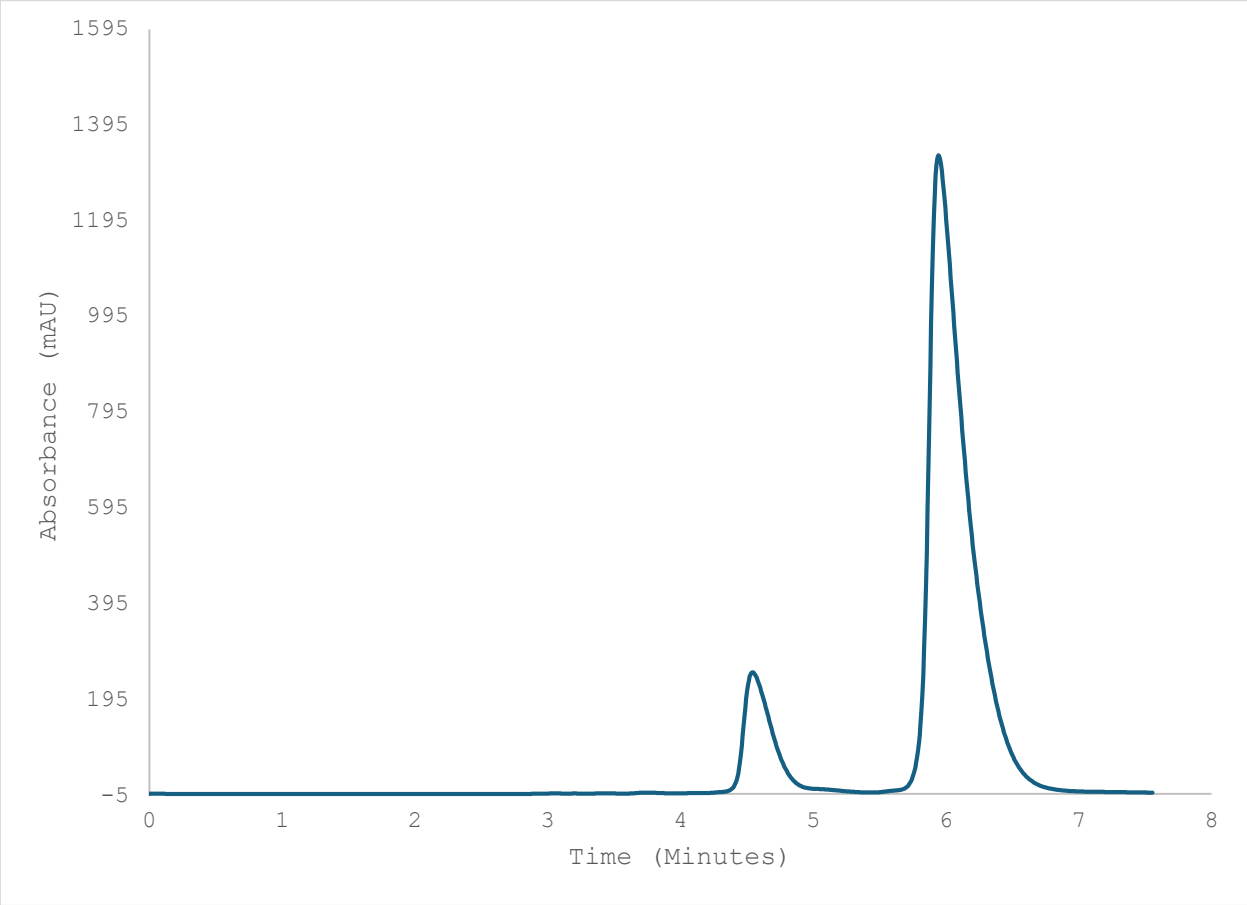
Figure S98. Chiral HPLC separation of a racemic mixture of compound **4a**.



Conditions: (*S,S)*-Whelk-O 1, 70:30 Dichloromethane/Hexanes, flow rate 1 mL/min, λ=254 nm.

#	Time	Area	Height	Width	Area%	Symmetry
1	4.483	3388.1	255.9	0.1965	50.113	0.446
2	6.022	3372.9	181.6	0.2767	49.887	0.574

Figure S99. Chiral HPLC separation of the asymmetric reaction product, compound **4a**.



Conditions: (*S,S)*-Whelk-O 1, 70:30 Dichloromethane/Hexanes, flow rate 1 mL/min, λ=254 nm.

#	Time	Area	Height	Width	Area%	Symmetry
1	4.544	3839.5	252.2	0.2336	12.710	0.423
2	5.944	26368.9	1330.8	0.2872	87.290	0.328

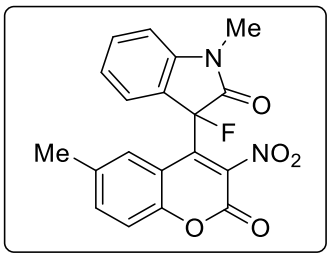
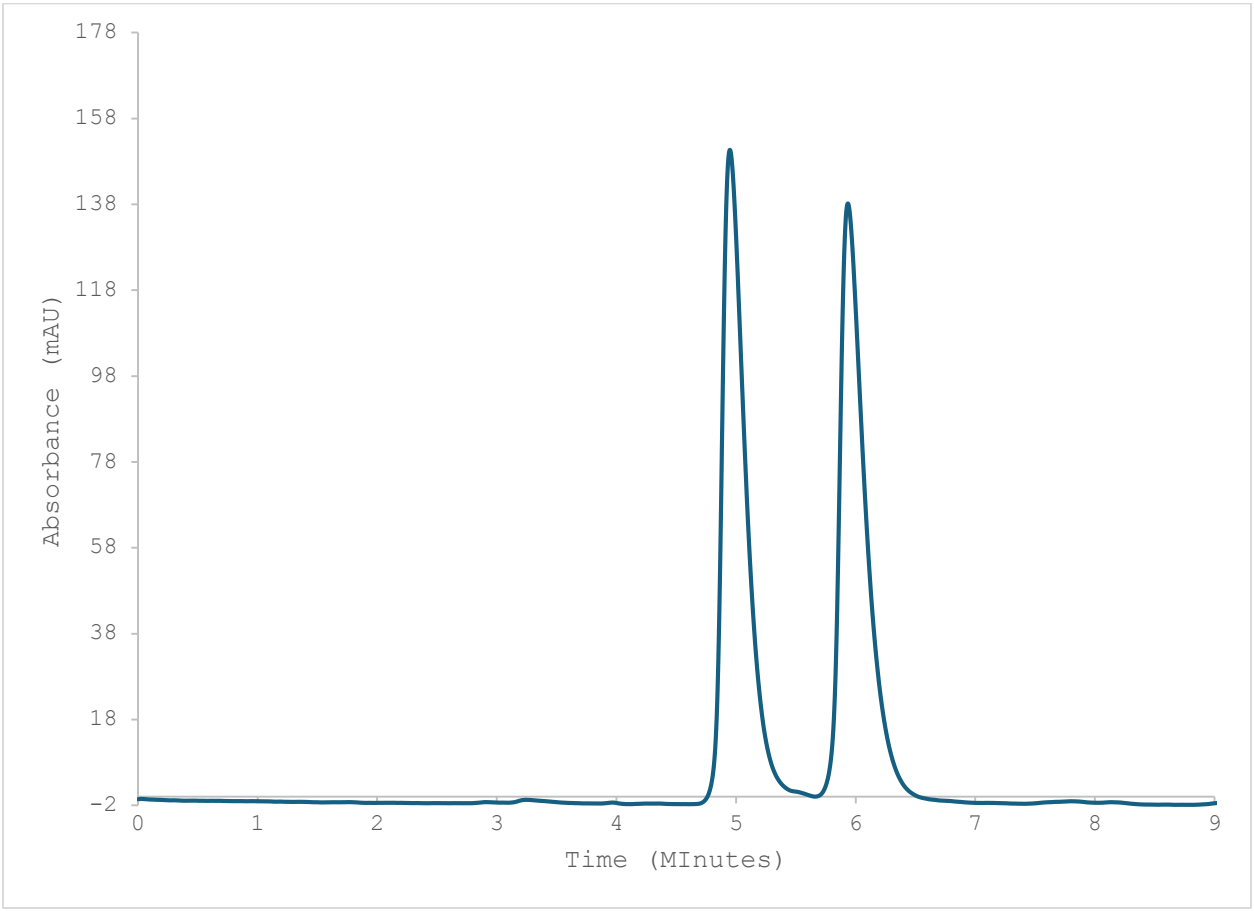


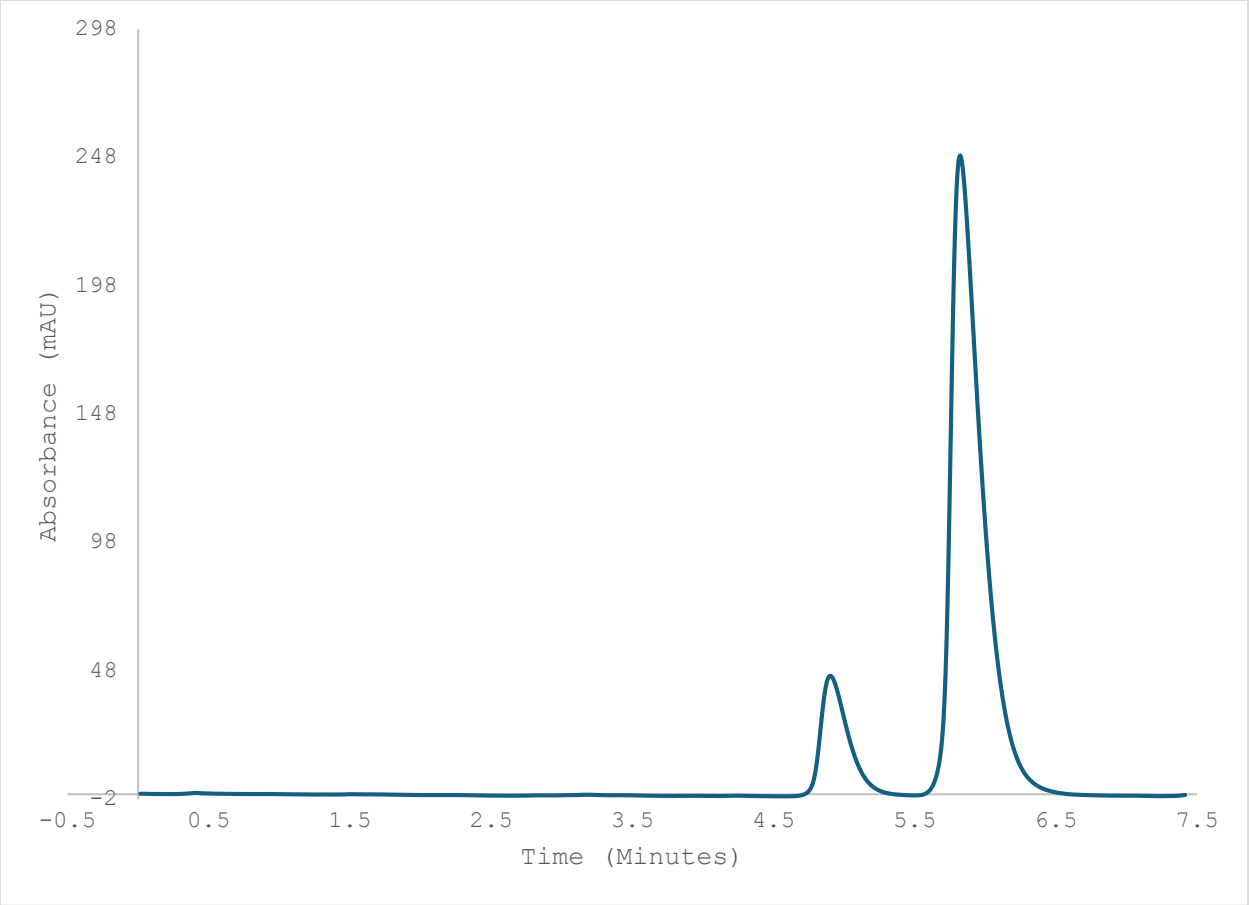
Figure S100. Chiral HPLC separation of a racemic mixture of compound **4b**.



Conditions: (*S,S)*-Whelk-O 1, 70:30 Dichloromethane/Hexanes, flow rate 1 mL/min, λ=254 nm.

#	Time	Area	Height	Width	Area%	Symmetry
1	4.948	2140.8	152.4	0.2119	50.043	0.446
2	5.934	2137.1	139.8	0.2263	49.957	0.439

Figure S101. Chiral HPLC separation of the asymmetric reaction product, compound **4b**.



Conditions: (*S,S)*-Whelk-O 1, 70:30 Dichloromethane/Hexanes, flow rate 1 mL/min, λ=254 nm.

#	Time	Area	Height	Width	Area%	Symmetry
1	4.902	636.2	46.8	0.2065	14.178	0.512
2	5.821	3851.2	249.4	0.2281	85.822	0.407

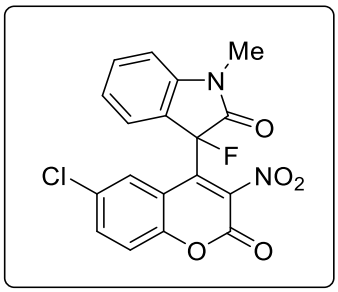
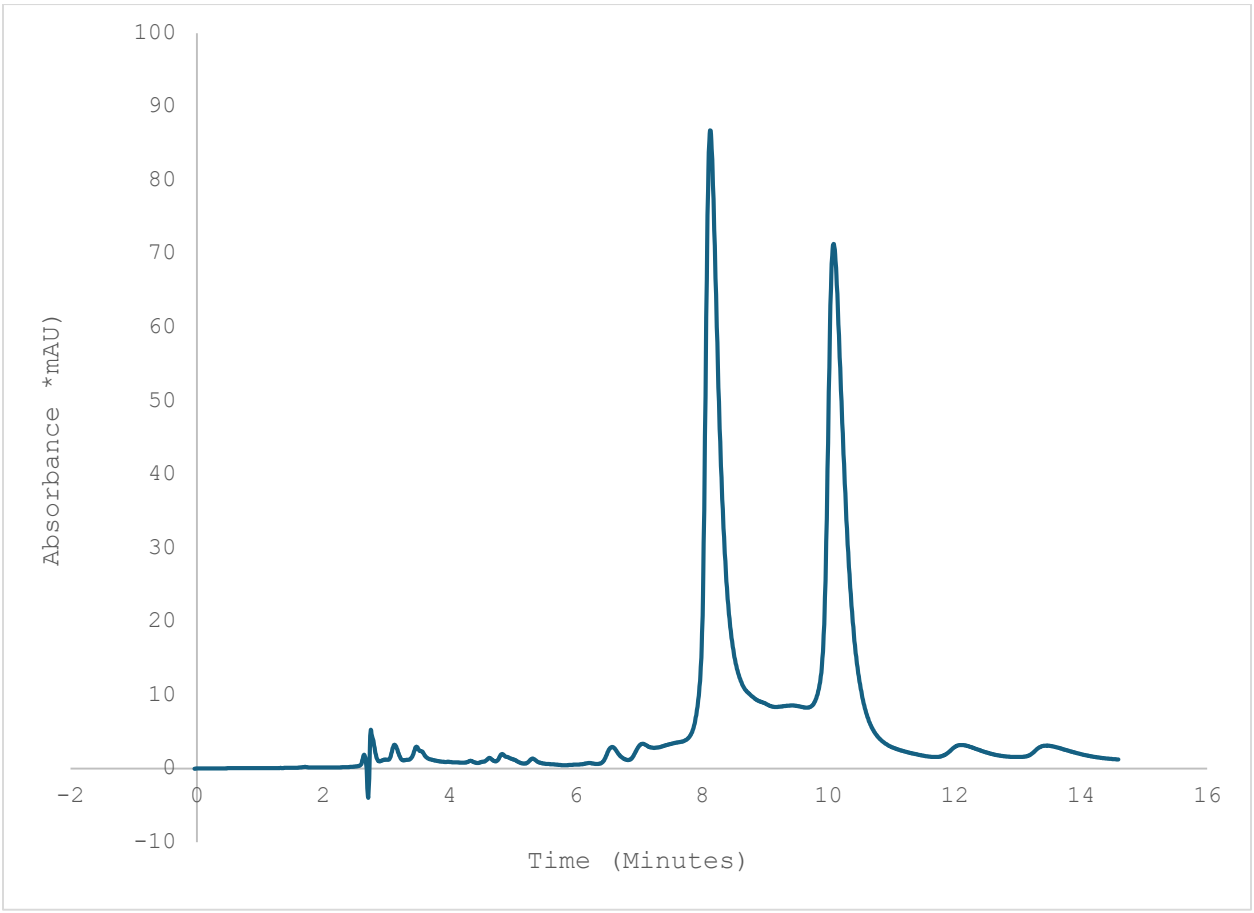


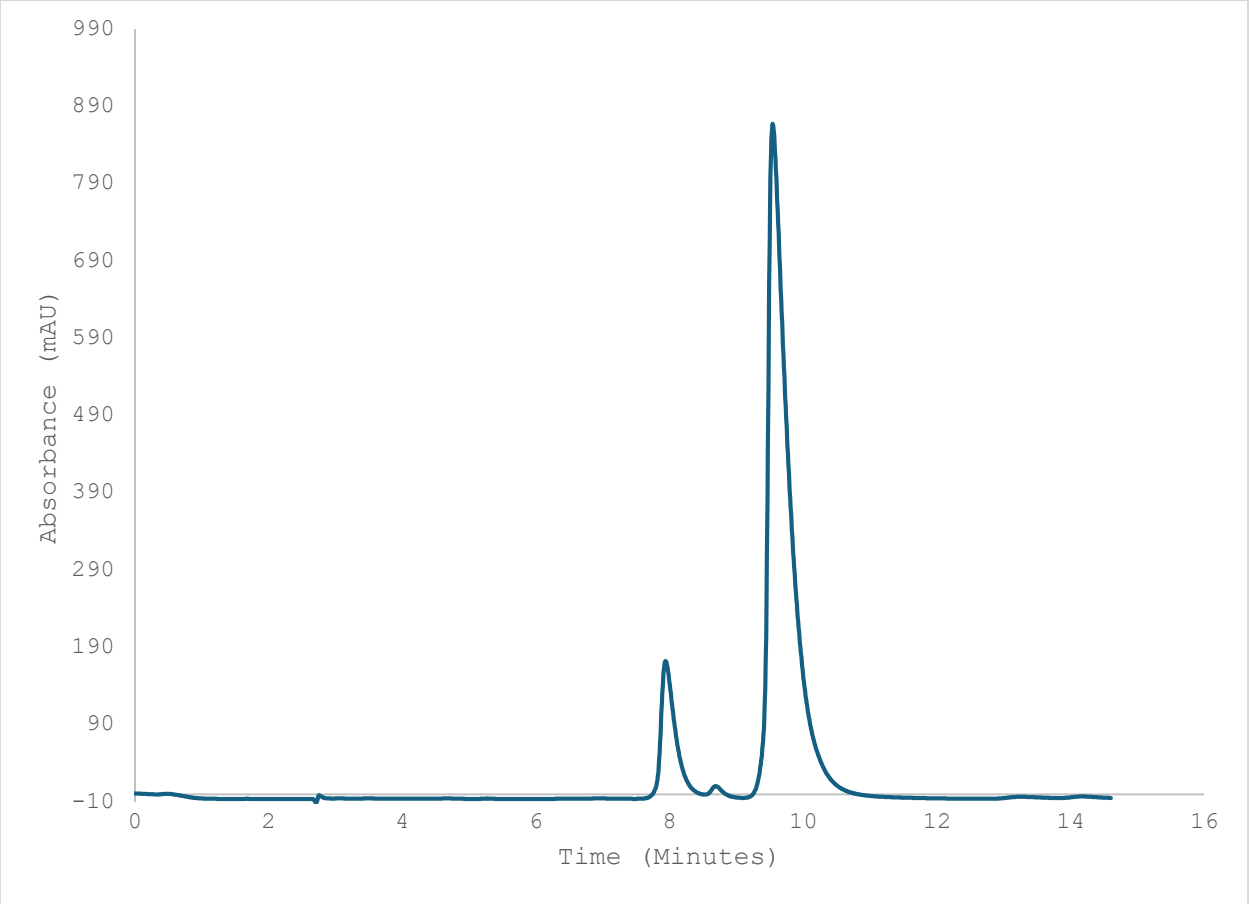
Figure S102. Chiral HPLC separation of a racemic mixture of compound **4c**.



Conditions: (*S,S)*-Whelk-O 1, 70:30 Dichloromethane/Hexanes, flow rate 1 mL/min, λ=254 nm.

#	Time	Area	Height	Width	Area%	Symmetry
1	8.13	1254.4	80.5	0.2597	49.982	0.518
2	10.083	1255.3	64.8	0.282	50.018	0.498

Figure S103. Chiral HPLC separation of the asymmetric reaction product, compound **4c.**



Conditions: (*S,S)*-Whelk-O 1, 70:30 Dichloromethane/Hexanes, flow rate 1 mL/min, λ=254 nm.

#	Time	Area	Height	Width	Area%	Symmetry
1	7.94	2766.2	178.4	0.2249	12.334	0.449
2	9.543	19660.7	873.5	0.3126	87.666	0.272

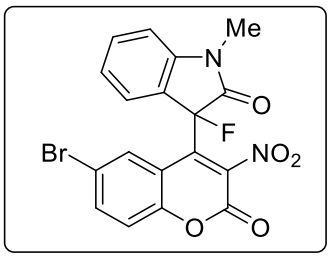
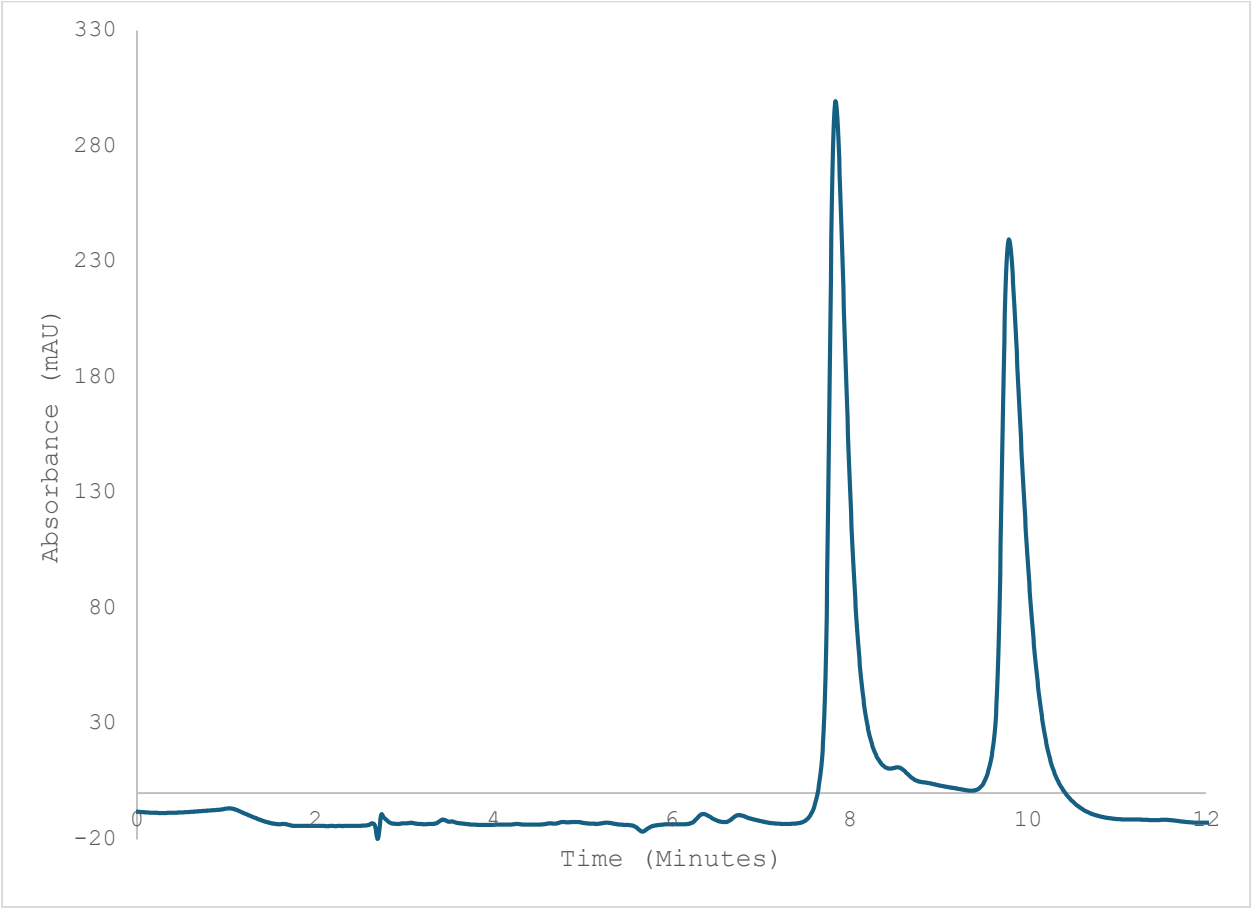


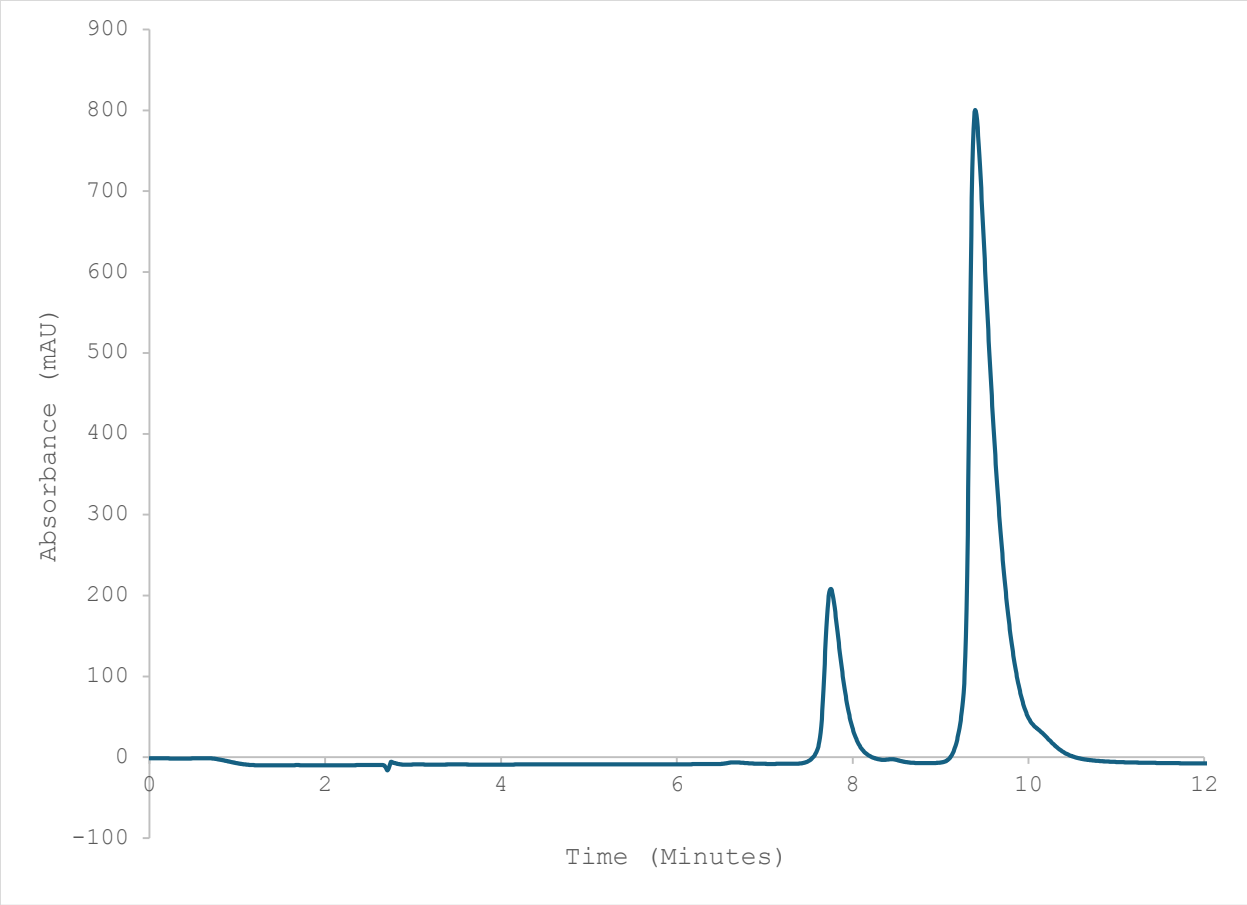
Figure S104. Chiral HPLC separation of a racemic mixture of compound **4d**.



Conditions: (*S,S)*-Whelk-O 1, 50:50 Dichloromethane/Hexanes, flow rate 1 mL/min, λ=254 nm. Baseline adjusted by -10 mAU.

#	Time	Area	Height	Width	Area%	Symmetry
1	7.84	5320	312.6	0.2445	50.067	0.424
2	9.786	5305.7	251.7	0.2999	49.933	0.475

Figure S105. Chiral HPLC separation of the asymmetric reaction product, compound **4d**.



Conditions: (*S,S)*-Whelk-O 1, 50:50 Dichloromethane/Hexanes, flow rate 1 mL/min, λ=254 nm.

#	Time	Area	Height	Width	Area%	Symmetry
1	7.751	3268.6	216.2	0.2204	16.002	0.481
2	9.396	17157.2	807.8	0.2998	83.998	0.296

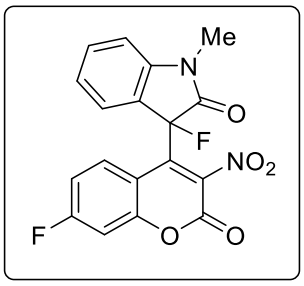
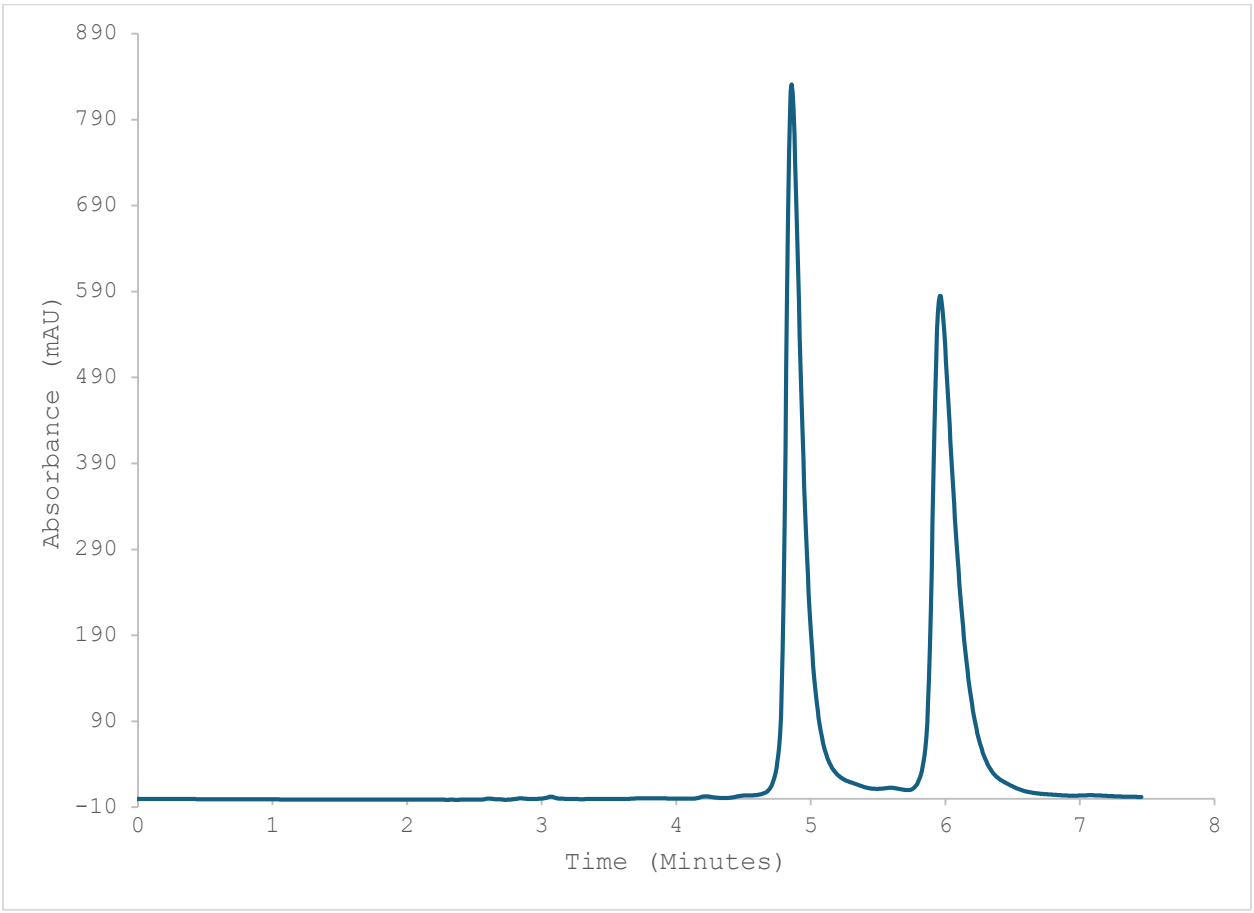


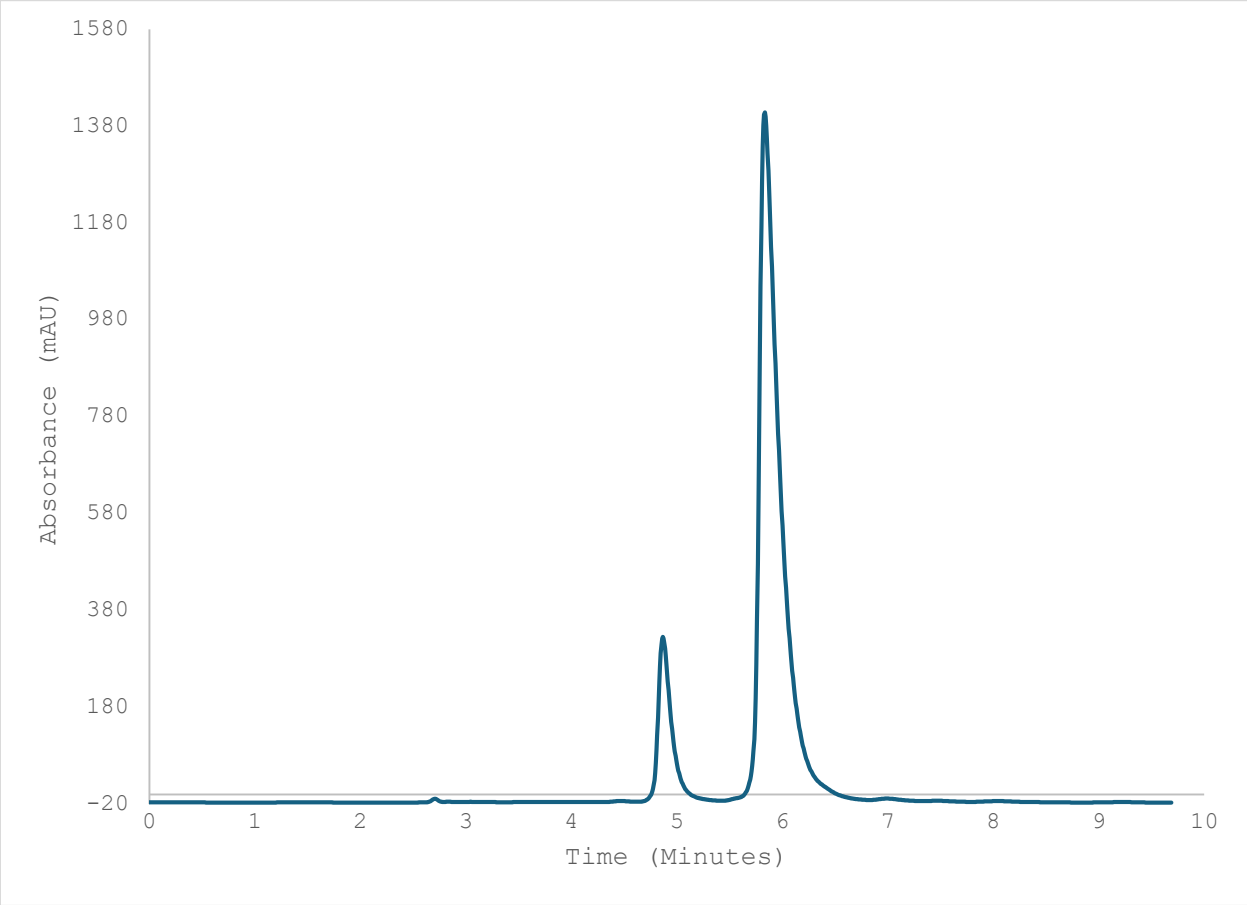
Figure S106. Chiral HPLC separation of a racemic mixture of compound **4e**.



Conditions: (*S,S)*-Whelk-O 1, 70:30 Dichloromethane/Hexanes, flow rate 1 mL/min, λ=254 nm.

#	Time	Area	Height	Width	Area%	Symmetry
1	4.858	7966.2	829.7	0.138	50.803	0.456
2	5.961	7714.4	583.3	0.1903	49.197	0.411

Figure S107. Chiral HPLC separation of the asymmetric reaction product, compound **4e**.



Conditions: (*S,S)*-Whelk-O 1, 70:30 Dichloromethane/Hexanes, flow rate 1 mL/min, λ=254 nm.

#	Time	Area	Height	Width	Area%	Symmetry
1	4.868	3089.2	340.9	0.1317	13.529	0.507
2	5.833	19744.4	1423.7	0.1958	86.471	0.338

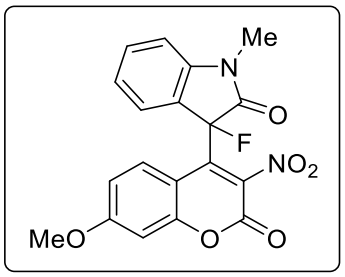
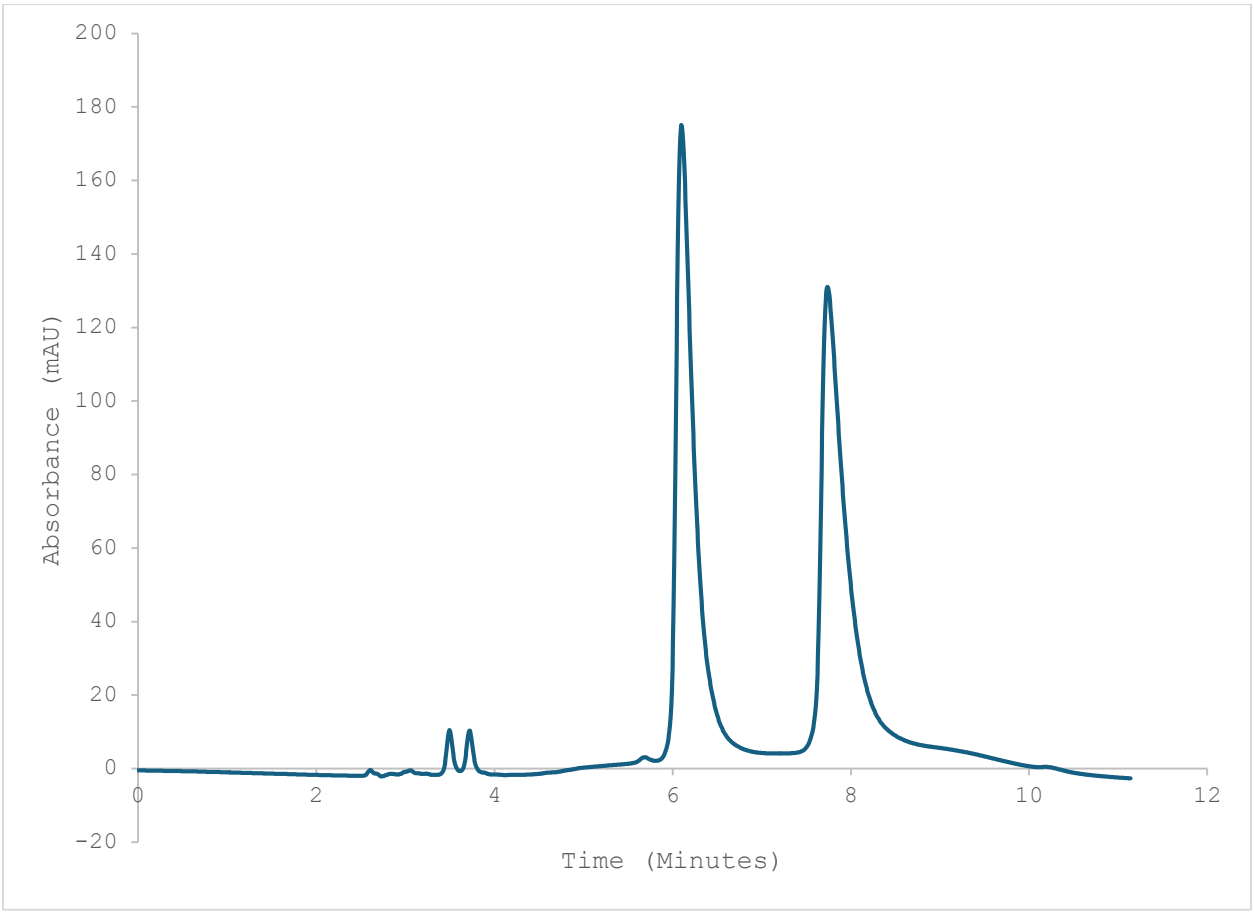


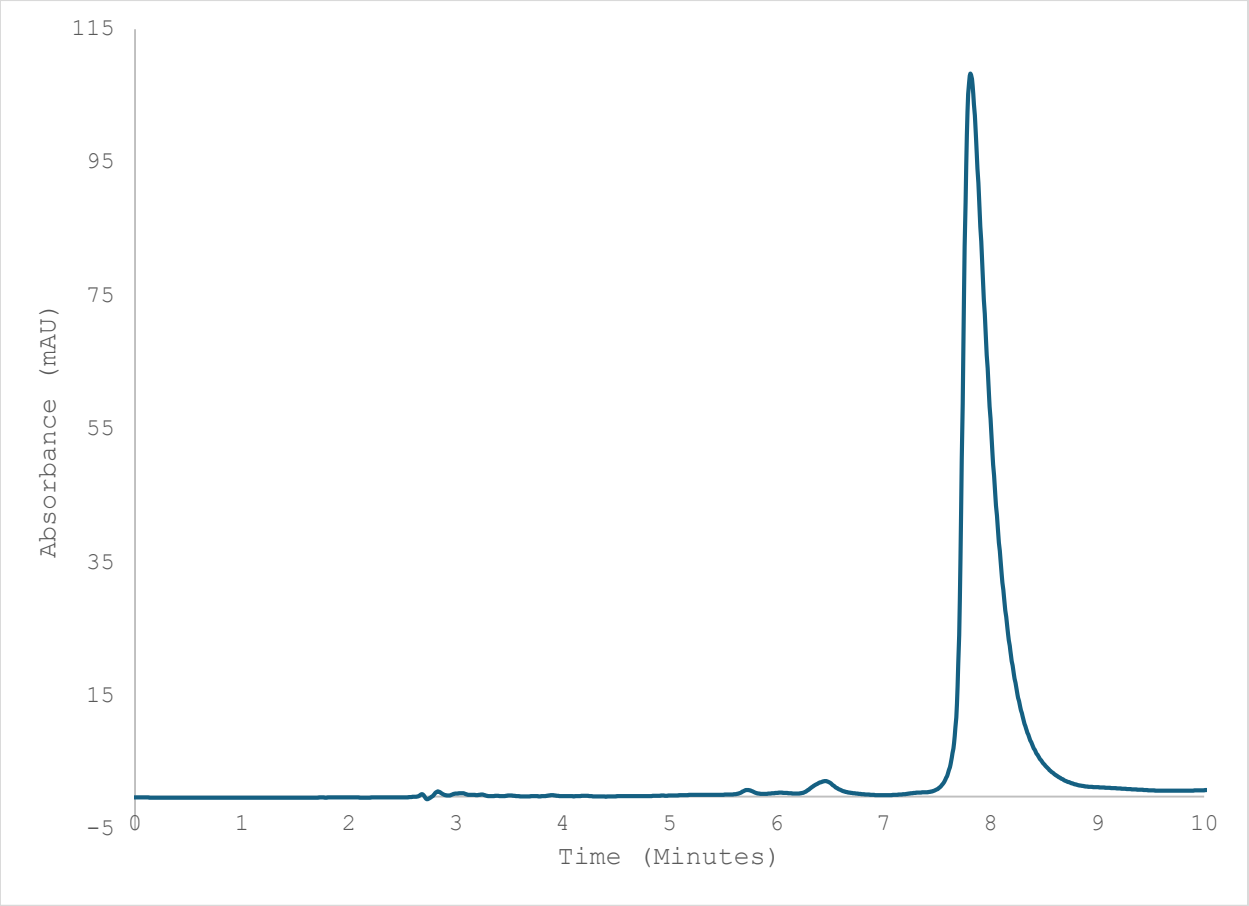
Figure S108. Chiral HPLC separation of a racemic mixture of compound **4f**.



Conditions: (*S,S)*-Whelk-O 1, 70:30 Dichloromethane/Hexanes, flow rate 1 mL/min, λ=254 nm.

#	Time	Area	Height	Width	Area%	Symmetry
1	6.1	2512.8	172.9	0.2116	50.657	0.388
2	7.739	2447.6	126.8	0.3216	49.343	0.349

Figure S109. Chiral HPLC separation of the asymmetric reaction product, compound **4f**.



Conditions: (*S,S)*-Whelk-O 1, 70:30 Dichloromethane/Hexanes, flow rate 1 mL/min, λ=254 nm.

#	Time	Area	Height	Width	Area%	Symmetry
1	6.455	30.5	2	0.2414	1.385	0.907
2	7.814	2168.5	108	0.2843	98.615	0.332

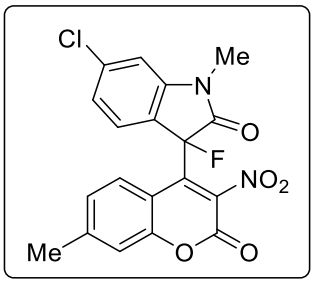
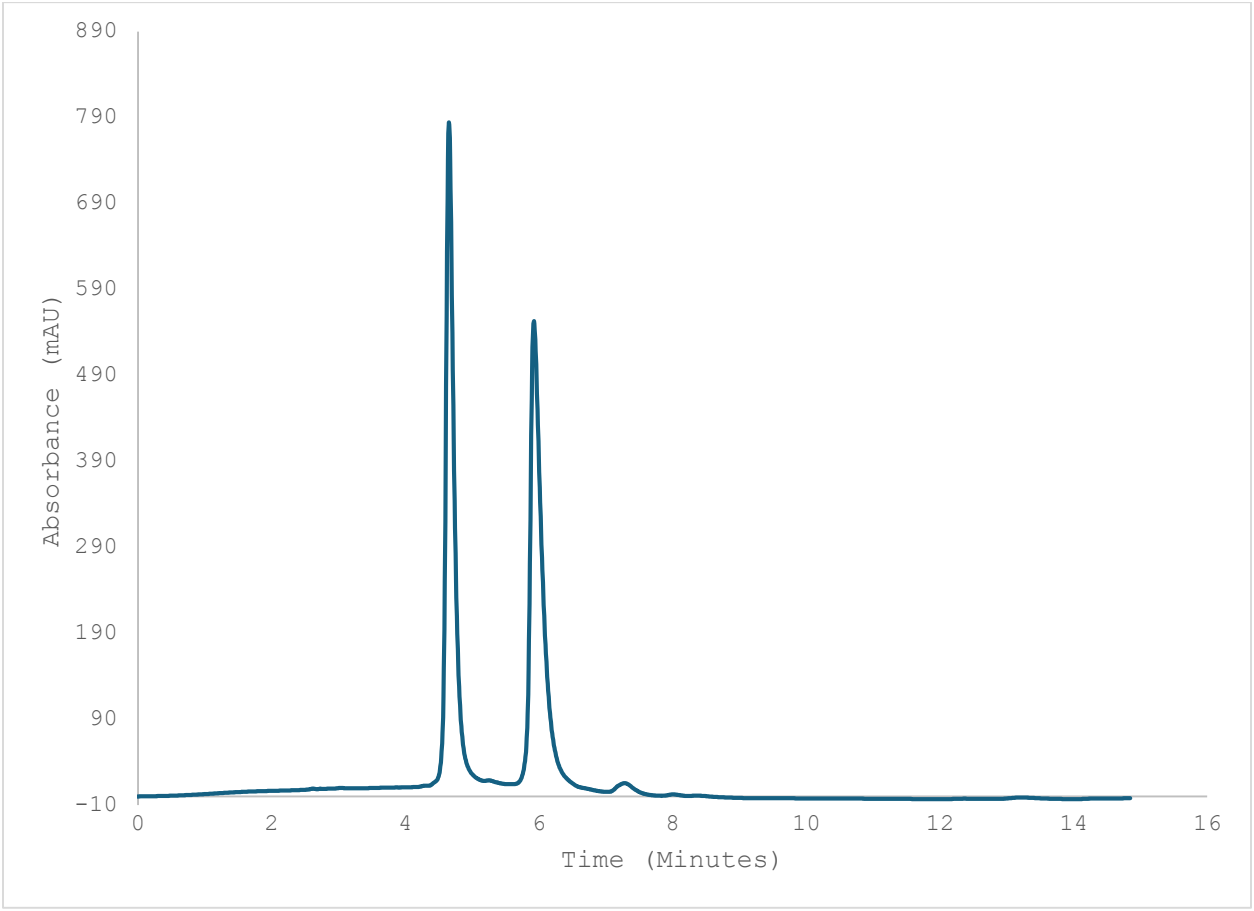


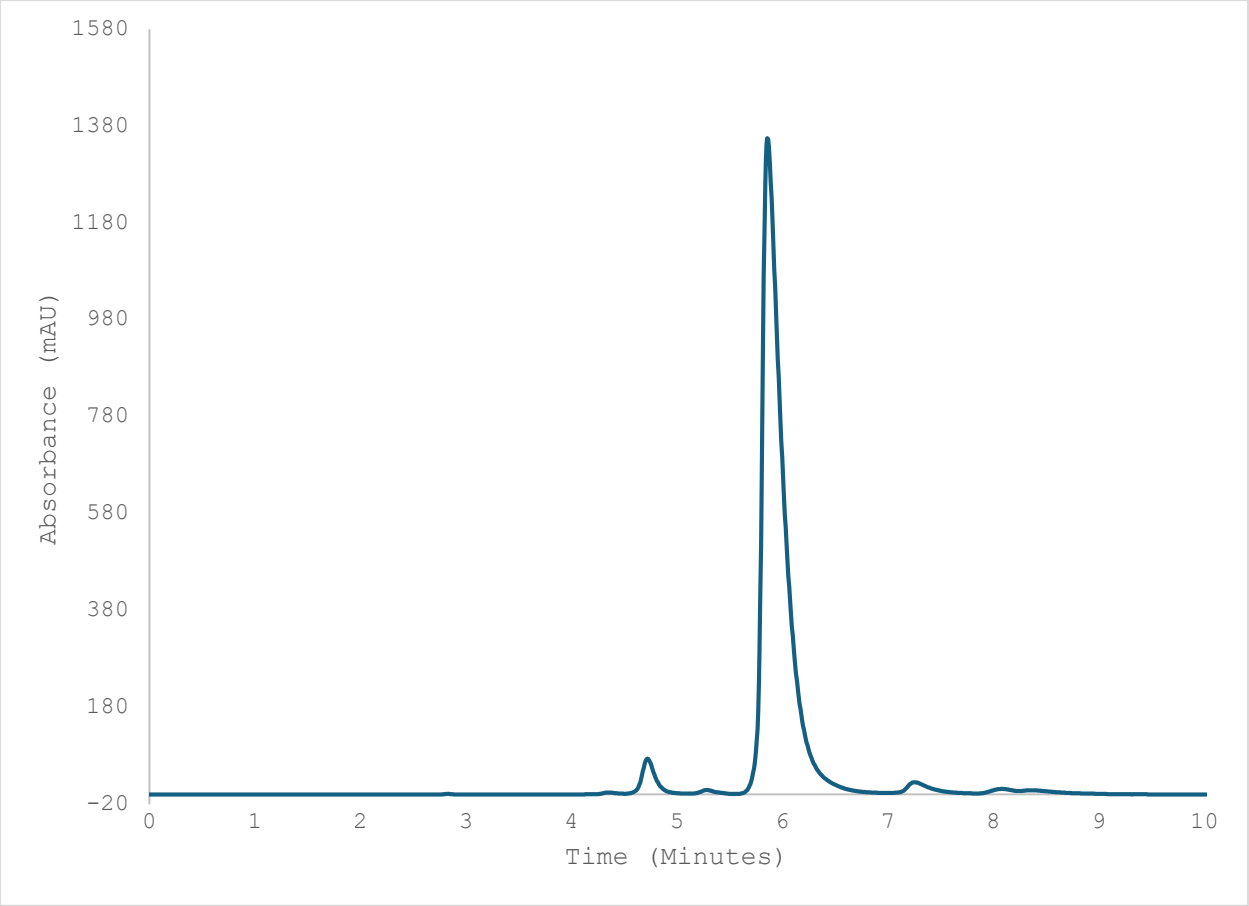
Figure S110. Chiral HPLC separation of a racemic mixture of compound **4g**.



Conditions: (*S,S)*-Whelk-O 1, 70:30 Dichloromethane/Hexanes, flow rate 1 mL/min, λ=254 nm.

#	Time	Area	Height	Width	Area%	Symmetry
1	4.653	6822.9	773.3	0.1309	49.710	0.561
2	5.924	6902.4	540.9	0.1829	50.290	0.417

Figure S111. Chiral HPLC separation of the asymmetric reaction product, compound **4g**.



Conditions: (*S,S)*-Whelk-O 1, 70:30 Dichloromethane/Hexanes, flow rate 1 mL/min, λ=254 nm.

#	Time	Area	Height	Width	Area%	Symmetry
1	4.722	673	73.7	0.1346	3.434	0.691
2	5.86	18924.6	1354.9	0.199	96.566	0.326

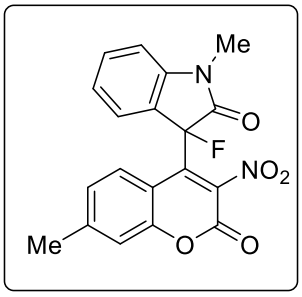
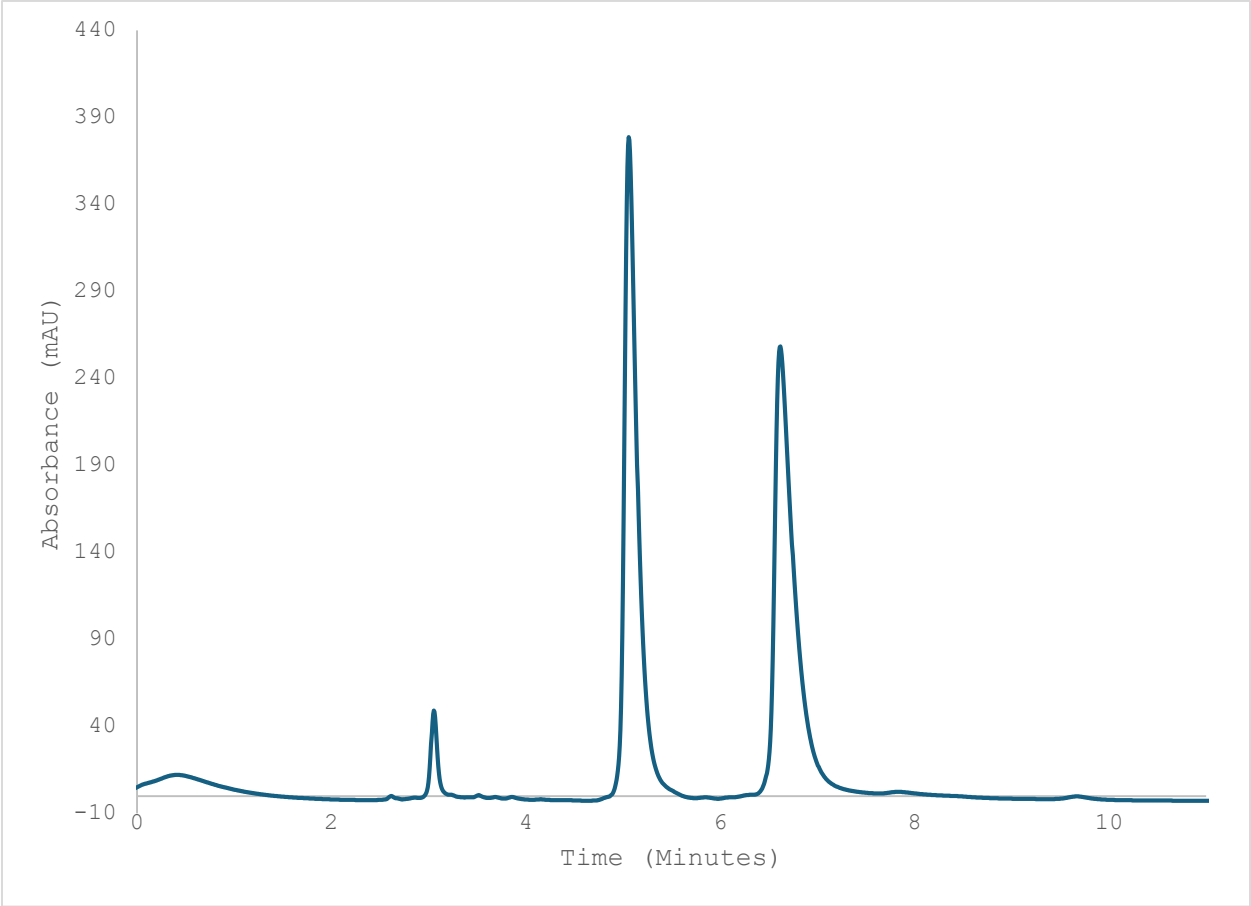


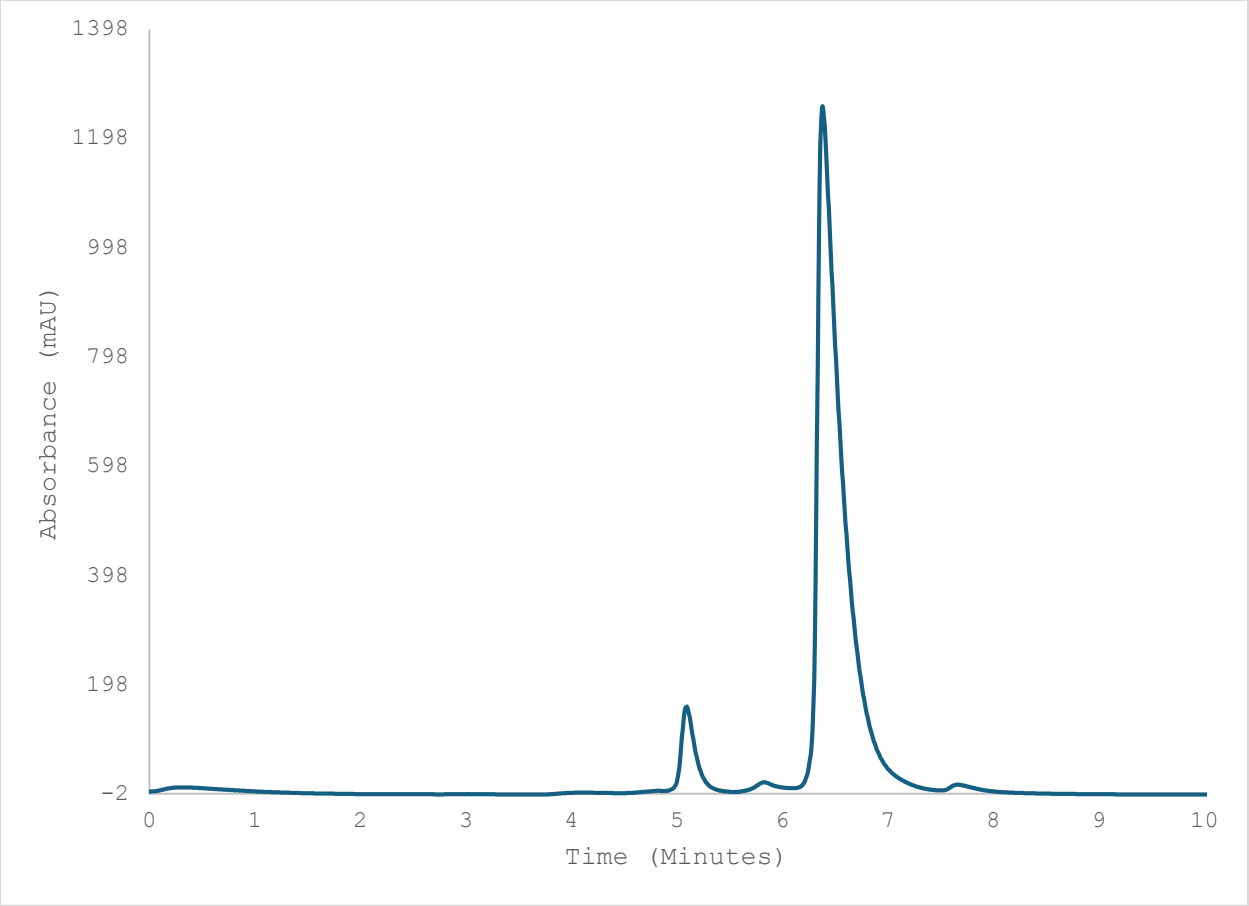
Figure S112. Chiral HPLC separation of a racemic mixture of compound **4h**.



Conditions: (*S,S)*-Whelk-O 1, 70:30 Dichloromethane/Hexanes, flow rate 1 mL/min, λ=254 nm.

#	Time	Area	Height	Width	Area%	Symmetry
1	5.061	3738.1	381.2	0.1424	49.921	0.485
2	6.617	3749.9	258.8	0.207	50.079	0.385

Figure S113. Chiral HPLC separation of the asymmetric reaction product, compound **4h**.



Conditions: (*S,S)*-Whelk-O 1, 70:30 Dichloromethane/Hexanes, flow rate 1 mL/min, λ=254 nm.

#	Time	Area	Height	Width	Area%	Symmetry
1	5.091	1495.4	157.3	0.1389	6.682	0.576
2	6.381	20883	1255.6	0.23	93.318	0.255

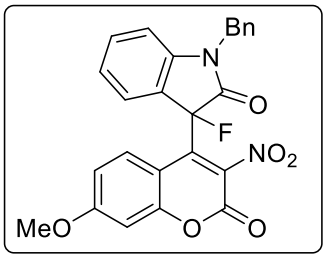
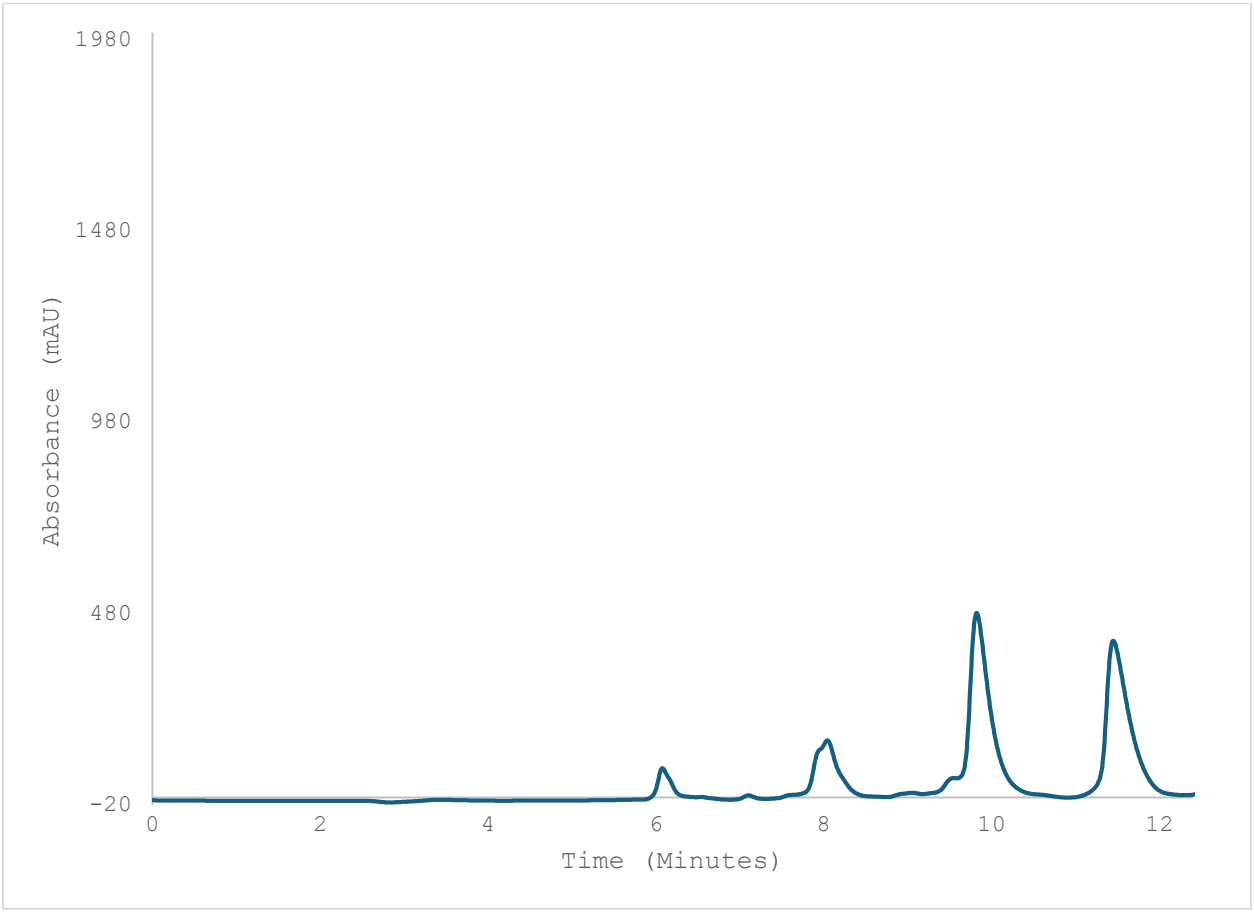
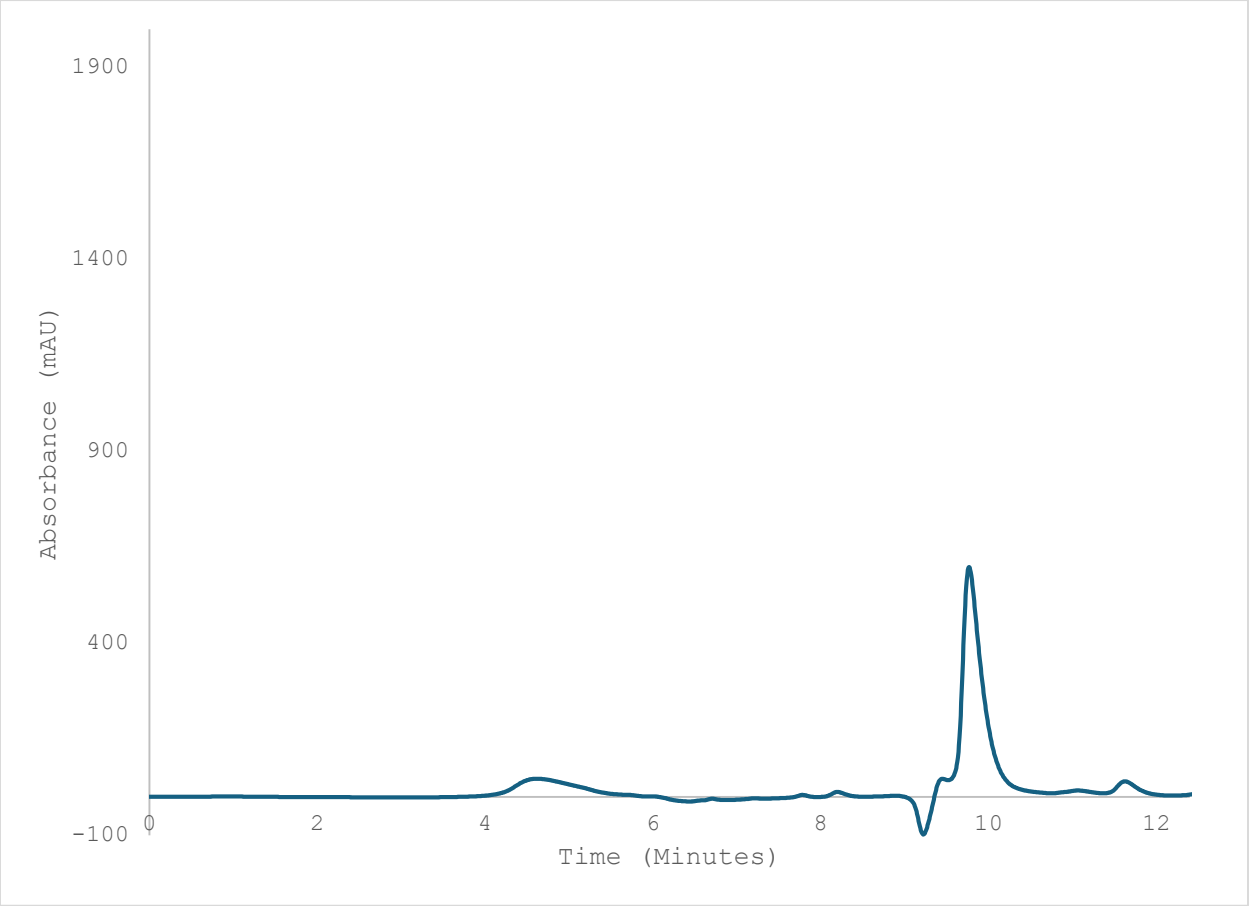


Figure S114. Chiral HPLC separation of a racemic mixture of compound **4i**.



#	Time	Area	Height	Width	Area%	Symmetry
1	9.823	7904.3	478.4	0.2753	49.851	0.47
2	11.452	7951.7	407.6	0.2856	50.149	0.448

Figure S115. Chiral HPLC separation of the asymmetric reaction product, compound **4i**.



#	Time	Area	Height	Width	Area%	Symmetry
1	9.768	10627.2	598	0.2962	94.404	0.433
2	11.625	630	38.8	0.2707	5.596	0.742

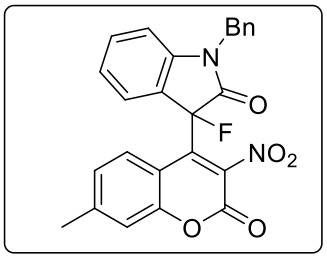
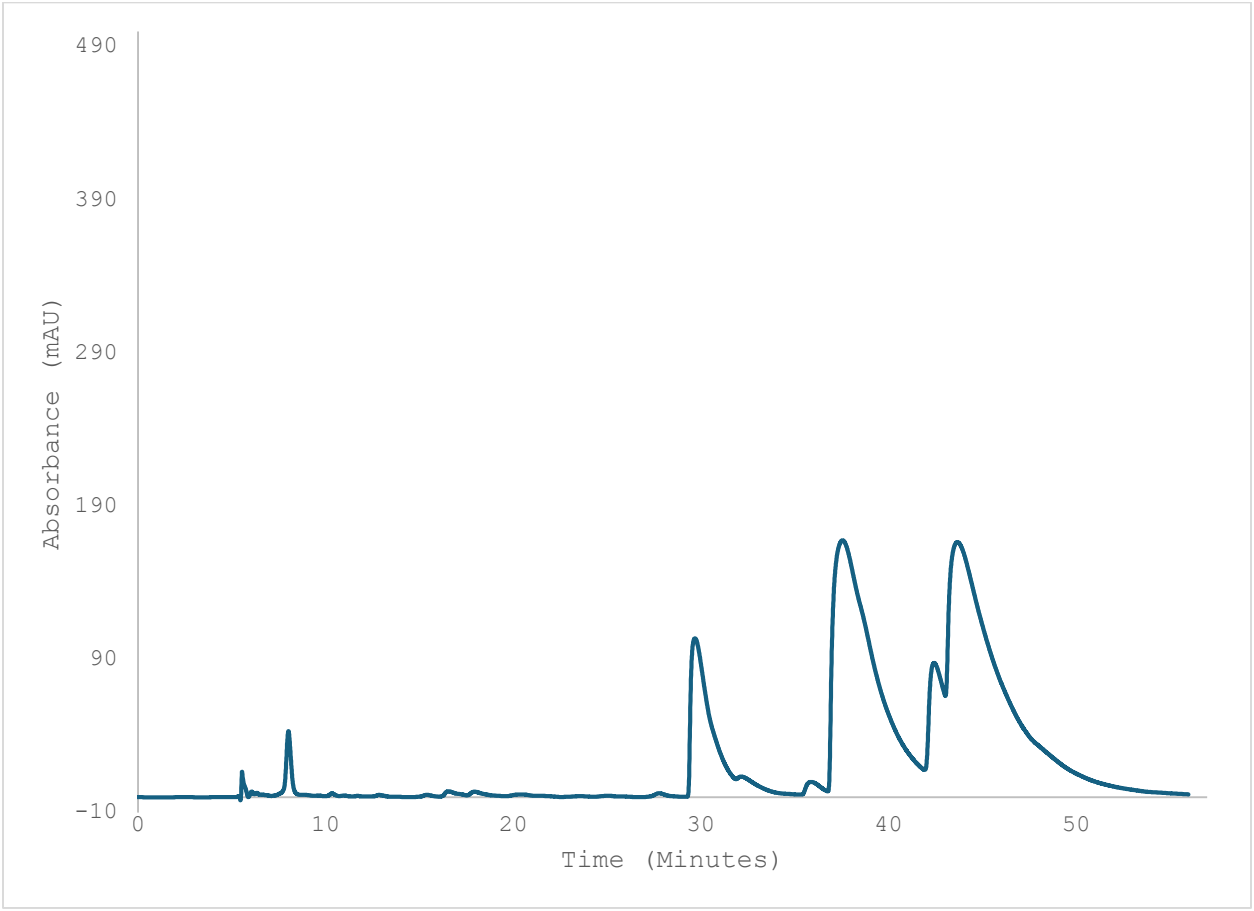
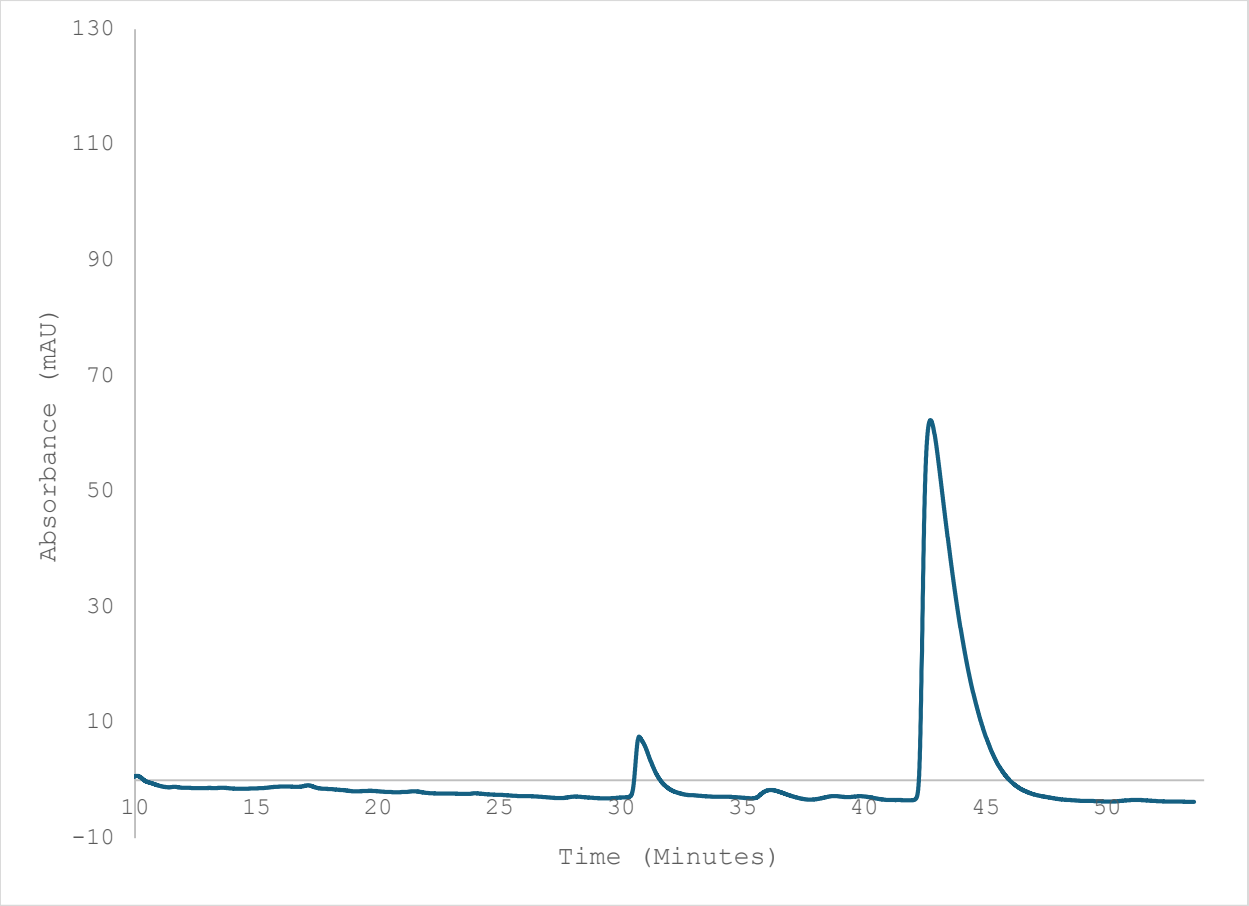


Figure S116. Chiral HPLC separation of a racemic mixture of compound **4j** (~3:1 dr).



#	Time	Area	Height	Width	Area%	Symmetry
1	29.693	7475.7	105.8	1.1775	11.043	0.246
2	37.562	24571.4	163.9	2.0791	36.297	0.277
3	42.44	4323.1	84.3	0.786	6.386	0.61
4	43.68	31325.9	163.4	2.5408	46.274	0.181

Figure S117. Chiral HPLC separation of the asymmetric reaction product, compound **4j.**



#	Time	Area	Height	Width	Area%	Symmetry
1	36.123	247.3	2.8	1.447	3.583	0.469
2	42.735	6652.9	65.8	1.3751	96.417	0.224

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