Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Benzotetramisole Catalyzed Kinetic Resolution of 2*H*-Azirines

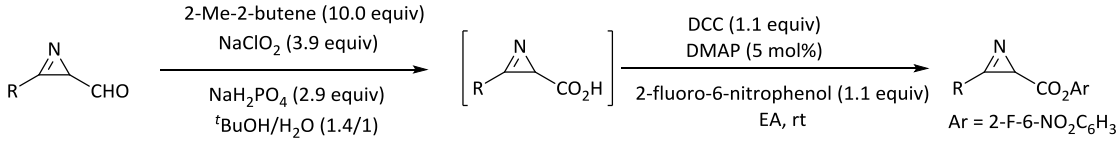
Qiupeng Peng, Donghui Guo, Bei Zhang, Lala Liu and Jian Wang*

Contents

General Information

Chemicals were purchased from commercial suppliers and used as received. Solvents were dried on alumina columns using a solvent dispensing system. Thin-layer chromatography (TLC) was conducted on plates (GF254) supplied by Yantai Chemicals (China) and visualized using a combination of UV, anisaldehyde, iodine, and potassium permanganate staining. ^{1}H NMR, ^{13}C NMR, ^{19}F NMR, spectra were recorded on a Bruker ACF400 (400 MHz) spectrometer. Chemical shifts were reported in parts per million (ppm), and the residual solvent peak was used as an internal reference: proton (chloroform δ 7.26, menthol δ 3.31), carbon (chloroform δ 77.16) or tetramethylsilane (TMS δ 0.00) was used as a reference. Multiplicity was indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (doublet of doublet), bs (broad singlet). Coupling constants were reported in Hertz (Hz). All high resolution mass spectra were obtained from the Tsinghua University Mass Spectrometry Facility. Flash chromatography separations were performed on Silica gel (300-400 mesh) supplied by Tsingdao Haiyang Chemicals (China). The enantiomeric excesses of products were determined on a Shimadzu LC-20AT Chiral HPLC. Optical rotations were recorded on SGW-1 autopolarimeter.

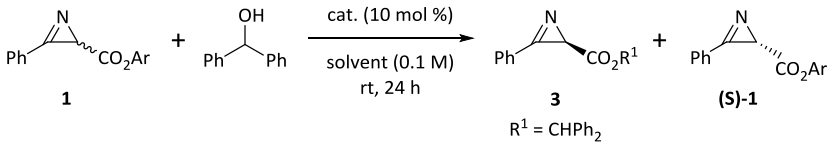
General Procedure for the Synthesis of 2*H*-Azrines[1]



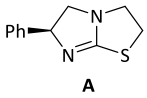
To a Schlenk reaction tube equipped with a magnetic stir bar, was added the 2*H*-azirine-2-carbaldehyde[2] (1 mmol, 1.0 equiv), 2-Me-2-butene (10 mmol, 10.0 equiv) and ^{t}BuOH (14 mL). Then $NaClO_2$ (3.9 mmol, 3.9 equiv) and NaH_2PO_4 (2.9 mmol, 2.9 equiv) were dissolved in water (10 mL) and added dropwise. The mixture was then stirred at 25 ^{o}C for about 4-6 hours. The mixture was concentrated under reduced pressure to remove ^{t}BuOH and diluted with aqueous 3*N* HCl (3 ml) and EtOAc (30 mL). The organic layers were washed with saturated brine solution, then dried over $MgSO_4$. After removal of the solvent, the intermediate was used without further

purification. To a Schlenk reaction tube equipped with a magnetic stir bar, was added the *2H*-azirine-2-carboxylic acid and EtOAc (15 mL). Then, 2-fluoro-6-nitrophenol (1.1 mmol, 1.1 equiv), DCC (1.1 mmol, 1.1 equiv) and DMAP (0.05 mmol, 5 mol %) were added successively. The mixture was then stirred at 25 ^{o}C for about 12 hours. After finished reaction, the mixture was filtered and the filtrate was concentrated under reduced pressure to remove EtOAc and the desired compound was purified by flash column chromatography.

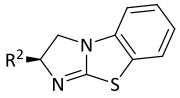
Table S-1. Optimization of the Reaction Conditions[a]



Ar^1 = 4-$NO_2C_6H_4$
Ar^2 = 2,4,6-$Br_3C_6H_2$
Ar^3 = C_6F_5
Ar^4 = 2-$NO_2C_6H_4$
Ar^5 = 2-F-6-$NO_2C_6H_3$



A

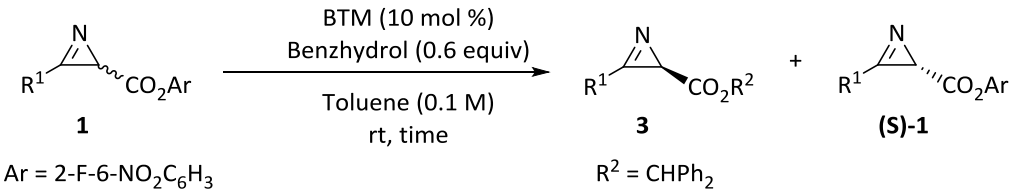


B: R^2 = Ph
C: R^2 = Bn
D: R^2 = ^{i}Pr
E: R^2 = ^{t}Bu

entry	Ar	cat.	solvent	**3:** yield, *ee* (%)[b, c]	(***S***)-**1**: yield, *ee* (%)[b, c]
1	Ar^1	**A**	DCM	38, 47	n.d.[d]
2	Ar^1	**B**	DCM	30, 49	n.d.[d]
3	Ar^1	**C**	DCM	40, 79	n.d.[d]
4	Ar^1	**D**	DCM	30, 56	n.d.[d]
5	Ar^1	**E**	DCM	n.r.[e]	n.d.[d]
6	Ar^1	**C**	THF	<5%	n.d.[d]
7	Ar^1	**C**	Toluene	34, 87	60, 30
8	Ar^1	**C**	$CHCl_3$	40, 79	55, 30
9	Ar^1	**C**	Ether	<5%	n.d.[d]
10	Ar^1	**C**	DCE	24, 81	54, 30
11	Ar^2	**C**	Toluene	<5%	n.d.[d]
12	Ar^3	**C**	Toluene	27, 87	60, 42
13	Ar^4	**C**	Toluene	30, 90	61, 41
14	Ar^5	**C**	Toluene	45, 90	55, 80
15[f]	Ar^5	**C**	Toluene	n.r.[e]	n.d.[d]
16[g]	Ar^5	**C**	Toluene	n.r.[e]	n.d.[d]
17[h]	**Ar^5**	**C**	**Toluene**	**51, 88**	**42, 91**
18[i]	Ar^5	**C**	Toluene	49, 90	50, 83

[a]Reaction conditions: **1a** (0.05 mmol), **2** (0.03 mmol), cat. (10 mol %), solvent (0.5 mL), room temperature, 24 h. [b]Yield was determined by HNMR based on the use of 1,3,5-trimethoxybenzene as internal standard. [c]*ee* was determined by HPLC analysis on a chiral stationary phase. [d]not determined. [e]no reaction. [f] Methanol was used instead of benzhydrol. [g] Cyclohexanol was used instead of benzhydrol. [h]48 h. [i]5 mol % cat was used, 72 h.

General Procedure for Benzotetramisole Catalyzed Kinetic Resolution of 2*H*-Azirines

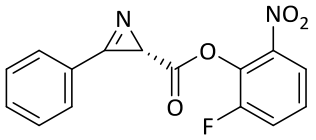


1 **3** **(S)-1**

Ar = 2-F-6-$NO_2C_6H_3$ R^2 = $CHPh_2$

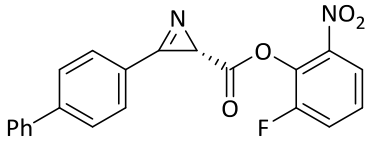
To a flame-dried Schlenk reaction tube equipped with a magnetic stir bar, was added **BTM** (2.7 mg, 0.01 mmol), **1** (0.10 mmol), and benzhydrol (11.0 mg, 0.06 mmol). The Schlenk tube was closed with a septum, evacuated and refilled with argon atmosphere, then toluene (1.0 mL) was added. The mixture was then stirred at 25 ℃ and monitored by TLC until consumed about half of **1**. The mixture was concentrated under reduced pressure and purified by column chromatography on silica gel (hexane/EtOAc = 20:1) to afford the desired product **3** and (*S*)-**1**.

Characterization Data



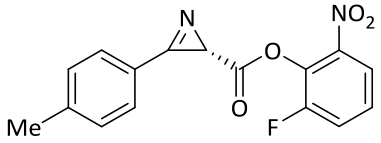
1a

13.8 mg, 46% yield, white solid, mp. : 80-82 ^{o}C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.07 (d, *J* = 7.4 Hz, 2H), 7.91 (d, *J* = 8.3 Hz, 1H), 7.73-7.60 (m, 3H), 7.50 (t, *J* = 8.6 Hz, 1H), 7.43-7.32 (m, 1H), 3.18 (s, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 168.6, 157.7, 155.3 (d, *J* = 254.1 Hz), 142.8, 134.4, 133.3 (d, *J* = 16.7 Hz), 131.0, 129.5, 126.7 (d, *J* = 8.0 Hz), 122.1 (d, *J* = 19.3 Hz), 121.4, 120.9 (d, *J* = 3.6 Hz), 29.2.^{19}F NMR (376 MHz, Chloroform-*d*) δ -124.11. HRMS (ESI): *m/z*: calculated for $C_{21}H_{10}FN_2O_4$: $[M + H]^+$ 301.0619, found: 301.0624; HPLC (Chiralpak IC, *i*-propanol/hexane = 20/80, flow rate 1.0 mL/min, 25 ^{o}C, λ = 254 nm): t_R (major) = 12.2 min, t_R (minor) = 16.9 min, *ee* = 91%; $[\alpha]^{25}_D$ = +75.4 (*c* = 1.0, DCM).



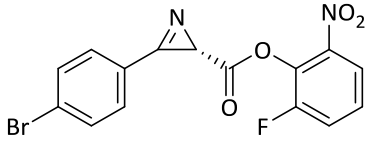
1b

16.1 mg, 43% yield, white solid, mp. : 102-105 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.12 (d, *J* = 8.4 Hz, 2H), 7.96 – 7.82 (m, 3H), 7.73 – 7.64 (m, 2H), 7.56 – 7.43 (m, 4H), 7.38 (dd, *J* = 8.4, 5.0 Hz, 1H), 3.18 (s, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 168.6, 157.4, 155.3 (d, *J* = 254.1 Hz), 147.2, 142.8, 139.5, 133.5, 131.5, 129.1, 128.7, 128.2, 127.4, 126.7 (d, *J* = 7.9 Hz), 122.1 (d, *J* = 19.4 Hz), 120.9 (d, *J* = 3.5 Hz), 120.0, 29.2. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -124.10. HRMS (ESI): *m/z*: calculated for $C_{21}H_{14}FN_2O_4$: $[M + H]^+$ 377.0932, found: 377.0930; HPLC (Chiralpak IC, *i*-propanol/hexane = 20/80, flow rate 1.0 mL/min, 25 °C, λ = 254 nm): t_R (major) = 16.9 min, t_R (minor) = 26.9 min, *ee* = 96%; $[\alpha]^{25}_D$ = +80.9 (*c* = 1.0, DCM).



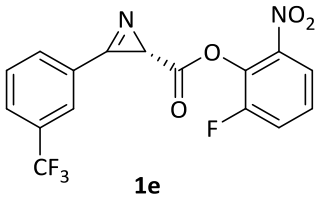
1c

18.1 mg, 58% yield, white solid, mp. : 109-111 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.95 (dd, *J* = 8.2, 2.0 Hz, 2H), 7.93 – 7.86 (m, 1H), 7.55 – 7.43 (m, 3H), 7.42 – 7.34 (m, 1H), 3.14 (s, 1H), 2.50 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 168.7, 157.2, 155.3 (d, *J* = 254.2 Hz), 145.6, 142.8, 133.4 (d, *J* = 16.6 Hz), 131.0, 130.3, 126.6 (d, *J* = 8.0 Hz), 122.1 (d, *J* = 19.4 Hz), 120.9 (d, *J* = 3.6 Hz), 118.6, 29.0, 22.1. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -124.15. HRMS (ESI): *m/z*: calculated for $C_{16}H_{12}FN_2O_4$: $[M + H]^+$ 315.0776, found: 315.0779; HPLC (Chiralpak IC, *i*-propanol/hexane = 20/80, flow rate 1.0 mL/min, 25 °C, λ = 254 nm): t_R (major) = 14.0 min, t_R (minor) = 19.5 min, *ee* = 35%; $[\alpha]^{25}_D$ = +24.8 (*c* = 1.0, DCM).



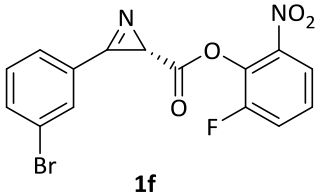
1d

19.1 mg, 50% yield, yellow solid, mp. : 136-138 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.11 – 7.87 (m, 3H), 7.81 (d, *J* = 8.4 Hz, 2H), 7.55-7.47 (m, 1H), 7.44-7.36 (m, 1H), 3.19 (s, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 168.3, 157.4, 155.3 (d, *J* = 254.2 Hz), 142.7, 133.3 (d, *J* = 16.6 Hz), 133.0, 132.1, 129.7, 126.8 (d, *J* = 8.0 Hz), 122.2 (d, *J* = 19.4 Hz), 121.0 (d, *J* = 3.6 Hz), 120.3, 29.3. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -124.19. HRMS (ESI): *m/z*: calculated for $C_{15}H_9BrFN_2O_4$: $[M + H]^+$ 378.9724, found: 378.9728; HPLC (Chiralpak IC, *i*-propanol/hexane = 20/80, flow rate 1.0 mL/min, 25 °C, λ = 254 nm): t_R (major) = 12.3 min, t_R (minor) = 18.5 min, *ee* = 86%; $[\alpha]^{25}_D$ = +68.2 (*c* = 1.0, DCM).



1e

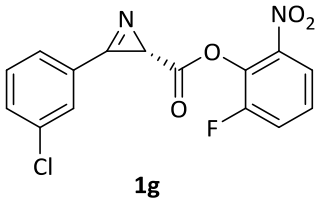
14.4 mg, 39% yield, white solid, mp. : 128-130 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.47 – 8.19 (m, 2H), 8.00 – 7.86 (m, 2H), 7.85 – 7.76 (m, 1H), 7.50 (t, *J* = 8.7 Hz, 1H), 7.39 (q, *J* = 7.2 Hz, 1H), 3.24 (s, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 168.0, 157.8, 155.2 (d, *J* = 254.2 Hz), 142.7, 134.0, 133.3, 132.5 (q, *J* = 33.3 Hz), 130.9 (d, *J* = 3.5 Hz), 130.3, 127.6 (d, *J* = 4.1 Hz), 126.8 (d, *J* = 8.1 Hz), 123.2 (q, *J* = 273.0 Hz), 122.5, 122.2 (d, *J* = 19.4 Hz), 121.0 (d, *J* = 3.7 Hz), 29.6. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -63.05, -124.31. HRMS (ESI): *m/z*: calculated for $C_{16}H_9F_4N_2O_4$: $[M + H]^+$ 369.0493, found: 369.0498; HPLC (Chiralpak IC, *i*-propanol/hexane = 20/80, flow rate 1.0 mL/min, 25 °C, λ = 254 nm): t_R (major) = 9.0 min, t_R (minor) = 12.1 min, *ee* = 97%; $[\alpha]^{25}_D$ = +44.0 (*c* = 1.0, DCM).



1f

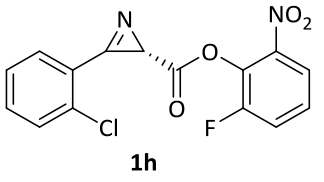
14.4 mg, 38% yield, yellow solid, mp. : 82-85 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.21 (d, *J* = 2.4 Hz, 1H), 7.97 (d, *J* = 7.7 Hz, 1H), 7.90 (d, *J* = 8.4 Hz, 1H), 7.82 (d, *J*

= 8.1 Hz, 1H), 7.57 – 7.46 (m, 2H), 7.39 (d, *J* = 5.1 Hz, 1H), 3.19 (s, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 168.1, 157.4, 155.2 (d, *J* = 254.1 Hz), 142.7, 137.3, 133.4, 133.3, 133.1, 131.1, 129.5, 126.8 (d, *J* = 8.0 Hz), 123.4 (d, *J* = 10.1 Hz), 122.2 (d, *J* = 19.3 Hz), 121.0 (d, *J* = 3.6 Hz), 29.5. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -124.16. HRMS (ESI): *m/z*: calculated for $C_{15}H_9BrFN_2O_4$: $[M + H]^+$ 378.9724, found: 378.9721; HPLC (Chiralpak IC, *i*-propanol/hexane = 20/80, flow rate 1.0 mL/min, 25 °C, λ = 254 nm): t_R (major) = 13.1 min, t_R (minor) = 19.4 min, *ee* = 96%; $[\alpha]^{25}_D$ = +75.9 (*c* = 1.0, DCM).



1g

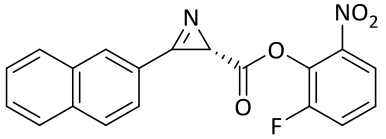
13.0 mg, 39% yield, colorless oil; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.06 (t, *J* = 1.9 Hz, 1H), 8.00 – 7.89 (m, 2H), 7.68 (d, *J* = 8.1, 1H), 7.61 (t, *J* = 7.8 Hz, 1H), 7.54-7.48 (m, 1H), 7.44-7.36 (m, 1H), 3.21 (s, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 168.1, 157.5, 155.2 (d, *J* = 254.0 Hz), 142.7, 135.7, 134.4, 133.2 (d, *J* = 16.5 Hz), 130.9, 130.4, 129.1, 126.8 (d, *J* = 8.0 Hz), 123.2, 122.1 (d, *J* = 19.3 Hz), 121.0 (d, *J* = 3.7 Hz), 29.5. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -124.19. HRMS (ESI): *m/z*: calculated for $C_{15}H_9ClFN_2O_4$: $[M + H]^+$ 335.0229, found: 335.0230; HPLC (Chiralpak IC, *i*-propanol/hexane = 20/80, flow rate 1.0 mL/min, 25 °C, λ = 254 nm): t_R (major) = 10.7 min, t_R (minor) = 15.2 min, *ee* = 97%; $[\alpha]^{25}_D$ = +75.3 (*c* = 1.0, DCM).



1h

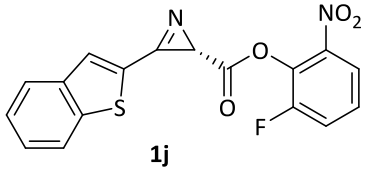
15.3 mg, 46% yield, white solid, mp. : 131-133 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.02 (d, *J* = 7.6 Hz, 1H), 7.91 (d, *J* = 8.4 Hz, 1H), 7.72 – 7.47 (m, 4H), 7.45 – 7.35 (m, 1H), 3.19 (s, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 168.2, 156.3, 155.2 (d, *J* = 253.9 Hz), 142.9, 137.2, 135.0, 133.8, 133.2 (d, *J* = 16.4 Hz), 130.9, 127.6, 126.7 (d,

J = 8.0 Hz), 122.1 (d, *J* = 19.3 Hz), 120.9 (d, *J* = 3.5 Hz), 120.4, 28.8. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -123.74. HRMS (ESI): *m/z*: calculated for $C_{15}H_9ClFN_2O_4$: [M + H]$^+$ 335.0229, found: 335.0225; HPLC (Chiralpak IC, *i*-propanol/hexane = 20/80, flow rate 1.0 mL/min, 25 ^{o}C, λ = 254 nm): t_R (major) = 15.0 min, t_R (minor) = 21.3 min, *ee* = 79%; $[\alpha]^{25}_D$ = +72.5 (*c* = 1.0, DCM).



1i

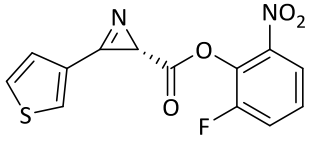
17.2 mg, 49% yield, white solid, mp. : 101-103 ^{o}C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.57 (s, 1H), 8.07 (t, *J* = 7.6 Hz, 3H), 7.99 – 7.83 (m, 2H), 7.77 – 7.61 (m, 2H), 7.57 – 7.44 (m, 1H), 7.47 – 7.32 (m, 1H), 3.27 (s, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 168.6, 157.8, 155.3 (d, *J* = 253.9 Hz), 142.8, 136.0, 133.9, 133.4 (d, *J* = 16.7 Hz), 132.8, 129.6, 129.5, 129.4, 128.1, 127.5, 126.7 (d, *J* = 8.0 Hz), 125.0, 122.1 (d, *J* = 19.4 Hz), 120.9 (d, *J* = 3.6 Hz), 118.6, 29.3. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -124.12. HRMS (ESI): *m/z*: calculated for $C_{19}H_{12}FN_2O_4$: [M + H]$^+$ 351.0776, found: 351.0777; HPLC (Chiralpak IC, *i*-propanol/hexane = 20/80, flow rate 1.0 mL/min, 25 ^{o}C, λ = 254 nm): t_R (major) = 14.9 min, t_R (minor) = 23.6 min, *ee* = 90%; $[\alpha]^{25}_D$ = +105.2 (*c* = 1.0, DCM).



1j

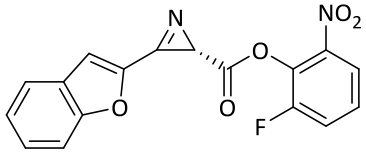
14.5 mg, 41% yield, yellow solid, mp. : 125-128 ^{o}C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.19 (s, 1H), 8.04 (d, *J* = 7.8 Hz, 1H), 7.97 (d, *J* = 8.0 Hz, 1H), 7.92 (dd, *J* = 8.4, 1.7 Hz, 1H), 7.62 – 7.47 (m, 3H), 7.43-7.34 (m, 1H), 3.30 (s, 1H).^{13}C NMR (100 MHz, Chloroform-*d*) δ 168.1, 155.3 (d, *J* = 254.3 Hz), 152.6, 143.9, 142.7, 138.3, 134.8, 133.3 (d, *J* = 16.5 Hz), 128.0, 126.8 (d, *J* = 8.0 Hz), 126.3, 125.6, 123.2, 122.9, 122.2 (d, *J* = 19.4 Hz), 121.0 (d, *J* = 3.6 Hz), 30.4. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -124.14. HRMS (ESI): *m/z*: calculated for $C_{17}H_{10}FN_2O_4S$: [M + H]$^+$ 357.0340,

found: 357.0344; HPLC (Chiralpak IC, *i*-propanol/hexane = 20/80, flow rate 1.0 mL/min, 25 ^{o}C, λ = 254 nm): t_R (major) = 13.6 min, t_R (minor) = 20.9 min, *ee* = 96%; $[\alpha]^{25}_D$ = +96.3 (*c* = 1.0, DCM).



1k

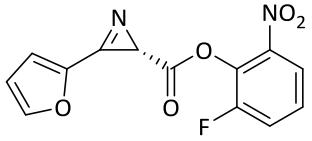
13.0 mg, 42% yield, yellow wax; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.33 (s, 1H), 7.91 (d, *J* = 8.4 Hz, 1H), 7.74 (d, *J* = 5.1 Hz, 1H), 7.66 – 7.35 (m, 3H), 3.13 (s, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 168.6, 155.3 (d, *J* = 253.8 Hz), 151.9, 142.7, 135.9, 133.4 (d, *J* = 16.3 Hz), 128.4, 127.3, 126.7 (d, *J* = 7.8 Hz), 123.3, 122.2 (d, *J* = 19.3 Hz), 121.0 (d, *J* = 3.7 Hz), 28.8. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -124.25. HRMS (ESI): *m/z*: calculated for $C_{13}H_8FN_2O_4S$: $[M + H]^+$ 307.0183, found: 307.0185; HPLC (Chiralpak IC, *i*-propanol/hexane = 20/80, flow rate 1.0 mL/min, 25 ^{o}C, λ = 254 nm): t_R (major) = 14.0 min, t_R (minor) = 19.1 min, *ee* = 86%; $[\alpha]^{25}_D$ = +20.4 (*c* = 1.0, DCM).



1l

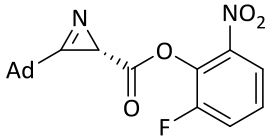
11.9 mg, 35% yield, yellow oil; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.95-9.89 (m, 1H), 7.81 (d, *J* = 7.7 Hz, 2H), 7.67 (d, *J* = 8.5 Hz, 1H), 7.58-7.47 (m, 2H), 7.43-7.34 (m, 2H), 3.26 (s, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 167.7, 157.8, 155.2 (d, *J* = 254.3 Hz), 149.3, 142.6, 139.6, 133.2 (d, *J* = 16.6 Hz), 129.0, 126.8 (d, *J* = 2.8 Hz), 126.7, 124.4, 123.4, 122.2 (d, *J* = 19.3 Hz), 121.0 (d, *J* = 3.5 Hz), 119.6, 112.5, 29.4. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -124.11. HRMS (ESI): *m/z*: calculated for $C_{17}H_{10}FN_2O_5$: $[M + H]^+$ 341.0568, found: 341.0561; HPLC (Chiralpak IC, *i*-propanol/hexane = 20/80, flow rate 1.0 mL/min, 25 ^{o}C, λ = 254 nm): t_R (major) = 13.8

min, t_R (minor) = 23.2 min, *ee* = 96%; $[\alpha]^{25}_D$ = +70.3 (*c* = 1.0, DCM).



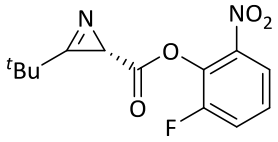
1m

12.4 mg, 43% yield, yellow solid, mp. : 90-92 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.95-7.87 (m, 2H), 7.55 – 7.47 (m, 2H), 7.45-7.36 (m, 1H), 6.76 (dd, *J* = 3.6, 1.8 Hz, 1H), 3.17 (s, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 167.9, 155.3 (d, *J* = 254.5 Hz), 150.1, 147.4, 142.7, 138.6, 133.2 (d, *J* = 16.6 Hz), 126.7 (d, *J* = 8.0 Hz), 123.4, 122.1 (d, *J* = 19.4 Hz), 120.9 (d, *J* = 3.6 Hz), 113.2, 28.9. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -124.13. HRMS (ESI): *m/z*: calculated for $C_{13}H_8FN_2O_5$: $[M + H]^+$ 291.0412, found: 291.0411; HPLC (Chiralpak IC, *i*-propanol/hexane = 20/80, flow rate 1.0 mL/min, 25 °C, λ = 254 nm): t_R (major) = 14.6 min, t_R (minor) = 22.4 min, *ee* = 83%; $[\alpha]^{25}_D$ = +90.2 (*c* = 1.0, DCM).



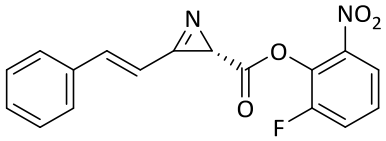
1n

19.5 mg, 54% yield, colorless oil; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.90 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.52-7.46 (m, 1H), 7.43-7.36 (m, 1H), 2.77 (s, 1H), 2.15 (t, *J* = 3.2 Hz, 3H), 2.10 – 1.99 (m, 6H), 1.83 (t, *J* = 3.4 Hz, 6H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 169.2, 165.0, 155.3 (d, *J* = 254.0 Hz), 143.1, 133.3 (d, *J* = 16.5 Hz), 126.6 (d, *J* = 7.9 Hz), 121.9 (d, *J* = 19.4 Hz), 120.8 (d, *J* = 3.6 Hz), 37.9, 36.3, 35.6, 27.8, 27.4. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -123.99. HRMS (ESI): *m/z*: calculated for $C_{19}H_{20}FN_2O_4$: $[M + H]^+$ 359.1402, found: 359.1402; HPLC (Chiralpak IC, *i*-propanol/hexane = 20/80, flow rate 1.0 mL/min, 25 °C, λ = 254 nm): t_R (major) = 10.8 min, t_R (minor) = 18.8 min, *ee* = 46%; $[\alpha]^{25}_D$ = +47.1 (*c* = 1.0, DCM).



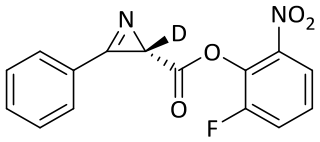
1o

5.1 mg, 18% yield, pale yellow oil; 1H NMR (400 MHz, Chloroform-d) δ 7.90 – 7.85 (m, 1H), 7.52 – 7.46 (m, 1H), 7.42 – 7.35 (m, 1H). 2.81 (s, 1H), 1.37 (s, 9H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 169.0, 166.2, 155.1 (d, *J* = 253.5 Hz), 142.9, 133.1 (d, *J* = 16.7 Hz), 126.8 (d, *J* = 7.9 Hz), 122.0 (d, *J* = 19.4 Hz), 120.8 (d, *J* = 3.5 Hz), 33.4, 29.0, 25.7. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -124.33. HRMS (ESI): *m/z*: calculated for $C_{13}H_{14}FN_2O_4$: $[M + H]^+$ 281.0932, found: 281.0936; HPLC (Chiralpak IC, *i*-propanol/hexane = 20/80, flow rate 1.0 mL/min, 25 °C, λ = 254 nm): t_R (major) = 7.5 min, t_R (minor) = 13.8 min, *ee* = 96%; $[\alpha]^{25}_D$ = +89.4 (*c* = 1.0, DCM).



1p

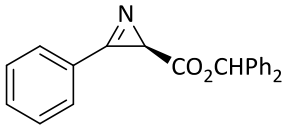
12.7 mg, 37% yield, yellow solid, mp. : 96-99 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.91 (d, *J* = 8.4 Hz, 1H), 7.74 – 7.65 (m, 3H), 7.54 – 7.45 (m, 4H), 7.40 (m, 1H), 7.22 (d, *J* = 15.8 Hz, 1H), 3.04 (s, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 168.6, 156.3, 155.3 (d, *J* = 254.2 Hz). 151.5, 142.9, 134.0, 133.3 (d, *J* = 16.6 Hz), 131.5, 129.2, 128.8, 126.7 (d, *J* = 8.0 Hz), 122.1 (d, *J* = 19.3 Hz), 120.9 (d, *J* = 3.6 Hz), 108.2, 28.2. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -124.08. HRMS (ESI): *m/z*: calculated for $C_{17}H_{12}FN_2O_4$: $[M + H]^+$ 327.0776, found: 327.0778; HPLC (Chiralpak IC, *i*-propanol/hexane = 20/80, flow rate 1.0 mL/min, 25 °C, λ = 254 nm): t_R (major) = 20.3 min, t_R (minor) = 27.7 min, *ee* = 88%; $[\alpha]^{25}_D$ = +87.1 (*c* = 1.0, DCM).



1q

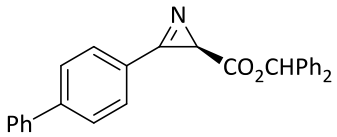
11.7 mg, 39% yield, white solid, mp. : 81-84 °C, H/D = 4:96; ^{1}H NMR (400 MHz,

Chloroform-*d*) δ 8.07 (d, *J* = 7.4 Hz, 2H), 7.91 (d, *J* = 8.3 Hz, 1H), 7.76-7.62 (m, 3H), 7.50 (t, *J* = 8.6 Hz, 1H), 7.43-7.36 (m, 1H), 3.19 (s, 0.04H). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -124.17. ^{13}C NMR (100 MHz, Chloroform-*d*) δ 168.5, 157.7, 155.3 (d, *J* = 254.2 Hz), 142.8, 134.4, 133.3 (d, *J* = 16.6 Hz), 131.0, 129.5, 126.7 (d, *J* = 8.0 Hz), 122.1 (d, *J* = 19.3 Hz), 121.4, 120.9 (d, *J* = 3.4 Hz), 29.2(CH), 28.9 (t, *J* = 29.7 Hz, CD). HRMS (ESI): *m/z*: calculated for $C_{15}H_9DFN_2O_4$: $[M + H]^+$ 302.0682, found: 302.0685; HPLC (Chiralpak IC, *i*-propanol/hexane = 20/80, flow rate 1.0 mL/min, 25 ^oC, λ = 254 nm): t_R (major) = 12.2 min, t_R (minor) = 17.0 min, *ee* = 99%.



3a

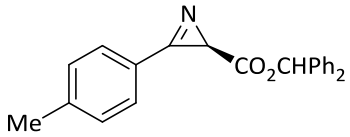
14.1 mg, 45% yield, white solid, mp. : 98-101 ^oC; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.91 – 7.81 (m, 2H), 7.65 – 7.58 (m, 1H), 7.57-7.51 (m, 2H), 7.36 – 7.31 (m, 4H), 7.31 – 7.25 (m, 6H), 6.95 (s, 1H), 2.96 (s, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 170.8, 158.5, 139.9, 139.9, 134.2, 134.0, 130.5, 129.4, 128.5, 128.5, 128.0, 127.1, 127.0, 122.2, 77.5, 29.9. HRMS (ESI): *m/z*: calculated for $C_{22}H_{18}NO_2$: $[M + H]^+$ 328.1332, found: 328.1337; HPLC (Chiralpak IC, *i*-propanol/hexane = 20/80, flow rate 1.0 mL/min, 25 ^oC, λ = 254 nm): t_R (major) = 13.9 min, t_R (minor) = 10.2 min, *ee* = 91%; $[\alpha]^{25}_D$ = -43.0 (*c* = 1.0, DCM).



3b

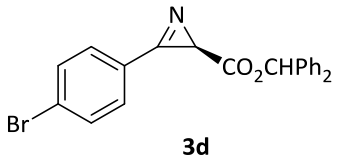
15.3 mg, 38% yield, white solid, mp. : 116-118 ^oC; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.96 (d, *J* = 8.4 Hz, 2H), 7.82 (d, *J* = 8.3 Hz, 2H), 7.72 – 7.64 (m, 2H), 7.54 (t, *J* = 7.4 Hz, 2H), 7.47 (t, *J* = 7.3 Hz, 1H), 7.43 – 7.36 (m, 4H), 7.37 – 7.28 (m, 6H), 7.02 (s, 1H), 3.03 (s, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 170.8, 158.2, 146.8, 140.0, 139.9, 139.5, 131.0, 129.1, 128.6, 128.6, 128.5, 128.0, 128.0, 127.4, 127.1, 127.1, 120.9, 77.6, 29.9, miss one carbon. HRMS (ESI): *m/z*: calculated for $C_{28}H_{22}NO_2$: [M

+ H]$^+$ 404.1645, found: 404.1655; HPLC (Chiralpak IC, *i*-propanol/hexane = 20/80, flow rate 1.0 mL/min, 25 ^{o}C, λ = 254 nm): t_R (major) = 21.5 min, t_R (minor) = 16.3 min, *ee* = 91%; $[\alpha]^{25}_D$ = -64.1 (*c* = 1.0, DCM).



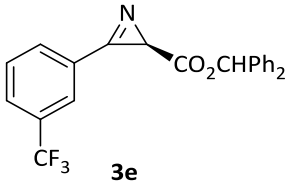
3c

7.9 mg, 23% yield, yellow oil; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.77 (d, *J* = 7.8 Hz, 2H), 7.43 – 7.36 (m, 6H), 7.34 – 7.27 (m, 6H), 6.98 (s, 1H), 2.96 (s, 1H), 2.49 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.9, 158.0, 145.0, 140.0, 140.0, 130.5, 130.1, 128.5, 128.5, 127.9, 127.1, 127.0, 119.4, 77.4, 29.7, 22.0, miss one carbon. HRMS (ESI): *m/z*: calculated for $C_{23}H_{20}NO_2$: [M + H]$^+$ 342.1489, found: 342.1490; HPLC (Chiralpak IC, *i*-propanol/hexane = 20/80, flow rate 1.0 mL/min, 25 ^{o}C, λ = 254 nm): t_R (major) = 16.7 min, t_R (minor) = 13.2 min, *ee* = 92%; $[\alpha]^{25}_D$ = -55.3 (*c* = 1.0, DCM).



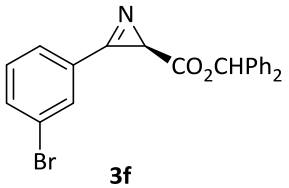
3d

18.6 mg, 46% yield, yellow wax; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.74 (s, 4H), 7.41 – 7.29 (m, 10H), 6.97 (s, 1H), 3.00 (s, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 170.4, 158.2, 139.8, 139.8, 132.8, 131.7, 129.1, 128.6, 128.5, 128.0, 128.0, 127.1, 127.0, 121.2, 77.7, 30.1. HRMS (ESI): *m/z*: calculated for $C_{22}H_{17}BrNO_2$: [M + H]$^+$ 406.0437, found: 406.0433; HPLC (Chiralpak IC, *i*-propanol/hexane = 20/80, flow rate 1.0 mL/min, 25 ^{o}C, λ = 254 nm): t_R (major) = 13.9 min, t_R (minor) = 10.2 min, *ee* = 91%; $[\alpha]^{25}_D$ = -52.7 (*c* = 1.0, DCM).



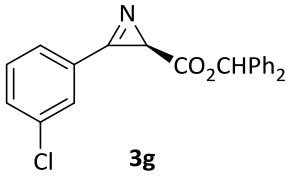
3e

17.4 mg, 44% yield, yellow oil; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.13 – 8.01 (m, 2H), 7.91-7.84 (m, 1H), 7.71 (t, *J* = 7.8 Hz, 1H), 7.38 – 7.31 (m, 4H), 7.30 – 7.22 (m, 6H), 6.96 (s, 1H), 3.04 (s, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 170.2, 158.5, 139.7, 139.7, 133.3, 132.2 (q, *J* = 33.5 Hz), 130.4 (q, *J* = 3.5 Hz), 130.1, 128.6, 128.5, 128.1, 128.1, 127.2 (q, *J* = 3.9 Hz), 127.1, 127.0, 123.3, 123.3 (q, *J* = 272.7 Hz), 77.9, 30.4. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -62.96. HRMS (ESI): *m/z*: calculated for $C_{23}H_{17}F_3NO_2$: $[M + H]^+$ 396.1206, found: 396.1209; HPLC (Chiralpak IC, *i*-propanol/hexane = 20/80, flow rate 1.0 mL/min, 25 °C, λ = 254 nm): t_R (major) = 10.5 min, t_R (minor) = 7.5 min, *ee* = 87%; $[\alpha]^{25}_D$ = -32.3 (*c* = 1.0, DCM).



3f

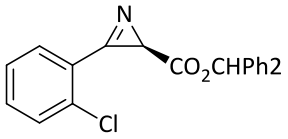
21.6 mg, 53% yield, white solid, mp. : 91-94 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.97 (t, *J* = 1.8 Hz, 1H), 7.80 – 7.71 (m, 2H), 7.42 (t, *J* = 7.9 Hz, 1H), 7.34 – 7.31 (m, 4H), 7.30 – 7.25 (m, 6H), 6.95 (s, 1H), 2.98 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.3, 158.2, 139.8, 139.7, 136.9, 133.1, 130.9, 128.8, 128.6, 128.5, 128.1, 128.1, 127.1, 127.0, 124.2, 123.3, 77.8, 30.3. HRMS (ESI): *m/z*: calculated for $C_{23}H_{17}BrNO_2$: $[M + H]^+$ 406.0437, found: 406.0435; HPLC (Chiralpak IC, *i*-propanol/hexane = 20/80, flow rate 1.0 mL/min, 25 °C, λ = 254 nm): t_R (major) = 15.9 min, t_R (minor) = 10.4 min, *ee* = 87%; $[\alpha]^{25}_D$ = -49.2 (*c* = 1.0, DCM).



3g

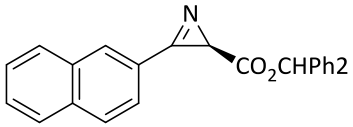
17.1 mg, 47% yield, yellow oil; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.86 (t, *J* = 1.8 Hz, 1H), 7.78 m, 1H), 7.64 (m, 1H), 7.53 (t, *J* = 7.9 Hz, 1H), 7.43 – 7.35 (m, 4H), 7.35 – 7.29 (m, 6H), 6.99 (s, 1H), 3.02 (s, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 170.3, 158.3, 139.8, 139.7, 135.5, 134.0, 130.7, 130.2, 128.6, 128.5, 128.4, 128.1,

128.1, 127.1, 127.0, 124.0, 77.8, 30.3. HRMS (ESI): *m/z*: calculated for $C_{23}H_{17}ClNO_2$: $[M + H]^+$ 362.0942, found: 362.0940; HPLC (Chiralpak IC, *i*-propanol/hexane = 20/80, flow rate 1.0 mL/min, 25 ^oC, λ = 254 nm): t_R (major) = 12.5 min, t_R (minor) = 8.7 min, *ee* = 85%; $[\alpha]^{25}_D$ = -21.8 (*c* = 1.0, DCM).



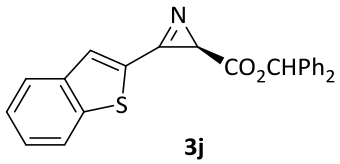
3h

16.7 mg, 46% yield, yellow oil; ^1H NMR (400 MHz, Chloroform-*d*) δ 7.82 (d, *J* = 7.6 Hz, 1H), 7.54 (dd, *J* = 6.0, 1.8 Hz, 2H), 7.43 (s, 1H), 7.39 – 7.32 (m, 4H), 7.32 – 7.26 (m, 6H), 6.97 (s, 1H), 3.02 (s, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 170.6, 157.5, 139.9, 139.8, 136.8, 134.6, 132.7, 130.8, 128.5, 128.5, 128.0, 128.0, 127.4, 127.2, 127.1, 121.0, 77.7, 30.5. HRMS (ESI): *m/z*: calculated for $C_{22}H_{17}ClNO_2$: $[M + H]^+$ 362.0942, found: 362.0943; HPLC (Chiralpak IC, *i*-propanol/hexane = 20/80, flow rate 1.0 mL/min, 25 ^oC, λ = 254 nm): t_R (major) = 21.7 min, t_R (minor) = 13.2 min, *ee* = 92%; $[\alpha]^{25}_D$ = -40.2 (*c* = 1.0, DCM).



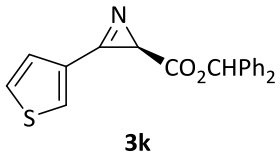
3i

19.5 mg, 51% yield, white solid, mp. : 107-109 ^oC; ^1H NMR (400 MHz, Chloroform-*d*) δ 8.28 (d, *J* = 1.4 Hz, 1H), 8.15 – 8.00 (m, 2H), 7.96 (dd, *J* = 7.9, 1.5 Hz, 2H), 7.67 (dddd, *J* = 23.1, 8.3, 7.0, 1.3 Hz, 2H), 7.48 – 7.36 (m, 4H), 7.36 – 7.24 (m, 6H), 7.03 (s, 1H), 3.09 (s, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 170.9, 158.7, 140.0, 139.9, 135.9, 133.0, 132.7, 129.5, 129.2, 129.2, 128.6, 128.5, 128.2, 128.0, 128.0, 127.4, 127.1, 127.1, 124.8, 119.5, 77.6, 30.1. HRMS (ESI): *m/z*: calculated for $C_{26}H_{20}NO_2$: $[M + H]^+$ 378.1489, found: 378.1493; HPLC (Chiralpak IC, *i*-propanol/hexane = 20/80, flow rate 1.0 mL/min, 25 ^oC, λ = 254 nm): t_R (major) = 18.4 min, t_R (minor) = 13.2 min, *ee* = 90%; $[\alpha]^{25}_D$ = -57.9 (*c* = 1.0, DCM).



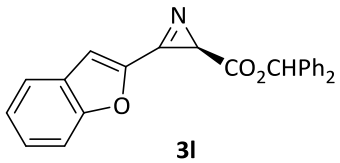
3j

15.7 mg, 39% yield, white solid, mp. : 117-121 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.01 – 7.91 (m, 2H), 7.87 (s, 1H), 7.61 – 7.45 (m, 2H), 7.43 – 7.37 (m, 4H), 7.35 – 7.26 (m, 6H), 7.01 (s, 1H), 3.11 (s, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 170.2, 153.4, 143.5, 139.8, 139.8, 138.3, 133.5, 128.6, 128.5, 128.1, 128.0, 127.8, 127.1, 127.0, 125.9, 125.6, 124.2, 122.9, 77.8, 31.2. HRMS (ESI): *m/z*: calculated for $C_{24}H_{18}NO_2S$: $[M + H]^+$ 384.1053, found: 384.1056; HPLC (Chiralpak IC, *i*-propanol/hexane = 20/80, flow rate 1.0 mL/min, 25 °C, λ = 254 nm): t_R (major) = 23.2 min, t_R (minor) = 13.6 min, *ee* = 76%; $[\alpha]^{25}_D$ = -72.0 (*c* = 1.0, DCM).



3k

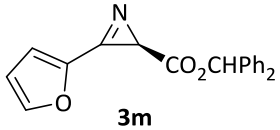
12.6 mg, 38% yield, yellow wax; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.01 (d, *J* = 2.8 Hz, 1H), 7.73 – 7.61 (m, 1H), 7.55 (dd, *J* = 5.1, 2.9 Hz, 1H), 7.37 (d, *J* = 4.3 Hz, 4H), 7.35 – 7.29 (m, 6H), 6.98 (s, 1H), 2.94 (s, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 170.7, 152.8, 139.9, 139.9, 134.4, 128.5, 128.5, 128.2, 128.0, 128.0, 127.1, 127.1, 127.0, 124.2, 77.5, 29.5. HRMS (ESI): *m/z*: calculated for $C_{20}H_{16}NO_2S$: $[M + H]^+$ 334.0896, found: 334.0899; HPLC (Chiralpak IC, *i*-propanol/hexane = 20/80, flow rate 1.0 mL/min, 25 °C, λ = 254 nm): t_R (major) = 17.4 min, t_R (minor) = 12.7 min, *ee* = 89%; $[\alpha]^{25}_D$ = -60.8 (*c* = 1.0, DCM).



3l

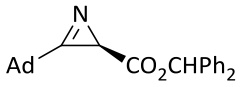
18.4 mg, 50% yield, yellow solid, mp. : 97-100 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.78-7.74 (m, 1H), 7.67 (dd, *J* = 8.5, 1.0 Hz, 1H), 7.61 – 7.51 (m, 2H), 7.43 – 7.36 (m, 5H), 7.36 – 7.28 (m, 6H), 7.00 (s, 1H), 3.09 (s, 1H). ^{13}C NMR (100 MHz,

Chloroform-*d*) δ 169.9, 157.3, 150.3, 140.4, 139.8, 139.7, 128.7, 128.6, 128.5, 128.0, 127.1, 127.1, 126.9, 126.6, 124.3, 123.1, 118.0, 112.5, 77.8, 30.2. HRMS (ESI): *m/z*: calculated for $C_{24}H_{18}NO_3$: $[M + H]^+$ 368.1281, found: 368.1288; HPLC (Chiralpak IC, *i*-propanol/hexane = 20/80, flow rate 1.0 mL/min, 25 °C, λ = 254 nm): t_R (major) = 20.4 min, t_R (minor) = 13.4 min, *ee* = 80%; $[\alpha]^{25}_D$ = -51.8 (*c* = 1.0, DCM).



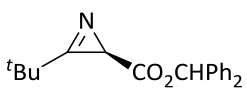
3m

13.6 mg, 43% yield, yellow oil; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.81 (d, *J* = 1.7 Hz, 1H), 7.34 – 7.31 (m, 4H), 7.31 – 7.24 (m, 6H), 7.20 (d, *J* = 3.6 Hz, 1H), 6.94 (s, 1H), 6.65 (dd, *J* = 3.6, 1.8 Hz, 1H), 2.95 (s, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 170.2, 149.3, 148.4, 139.8, 139.8, 139.3, 128.6, 128.5, 128.0, 127.1, 127.0, 121.9, 113.0, 77.7, 29.6, miss one carbon. HRMS (ESI): *m/z*: calculated for $C_{20}H_{16}NO_3$: $[M + H]^+$ 318.1125, found: 318.1128; HPLC (Chiralpak IC, *i*-propanol/hexane = 20/80, flow rate 1.0 mL/min, 25 °C, λ = 254 nm): t_R (major) = 18.8 min, t_R (minor) = 14.4 min, *ee* = 84%; $[\alpha]^{25}_D$ = -109.5 (*c* = 1.0, DCM).



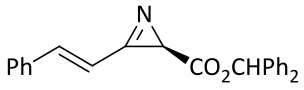
3n

12.2 mg, 32% yield, colorless oil; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.53 – 7.24 (m, 10H), 6.95 (s, 1H), 2.58 (s, 1H), 2.07 (t, *J* = 3.2 Hz, 3H), 1.98 – 1.72 (m, 12H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 171.5, 166.0, 139.9, 139.9, 128.5, 128.5, 128.1, 127.8, 127.6, 126.8, 77.4, 37.9, 36.3, 35.2, 28.6, 27.4. HRMS (ESI): *m/z*: calculated for $C_{26}H_{28}NO_2$: $[M + H]^+$ 386.2115, found: 386.2114; HPLC (Chiralpak IC, *i*-propanol/hexane = 20/80, flow rate 1.0 mL/min, 25 °C, λ = 204 nm): t_R (major) = 16.0 min, t_R (minor) = 11.3 min, *ee* = 91%; $[\alpha]^{25}_D$ = -98.2 (*c* = 1.0, DCM).



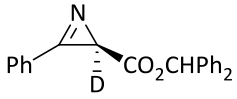
3o

14.6 mg, 48% yield, colorless oil; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.39 – 7.28 (m, 10H), 6.95 (s, 1H), 2.65 (s, 1H), 1.28 (s, 9H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 171.2, 167.1, 139.9, 139.8, 128.5, 128.1, 127.8, 127.5, 126.8, 77.5, 33.1, 30.0, 25.8, miss one carbon. HRMS (ESI): *m/z*: calculated for $C_{20}H_{22}NO_2$: $[M + H]^+$ 308.1645, found: 308.1641; HPLC (Chiralpak IC, *i*-propanol/hexane = 20/80, flow rate 1.0 mL/min, 25 °C, λ = 204 nm): t_R (major) = 14.2 min, t_R (minor) = 11.4 min, *ee* = 76%; $[\alpha]^{25}_D$ = -49.7 (*c* = 1.0, DCM).



3p

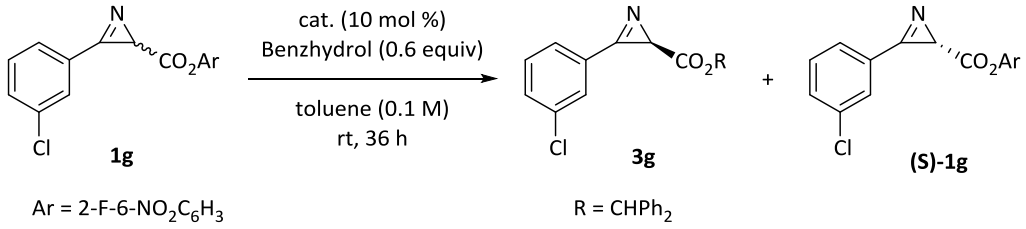
16.3 mg, 46% yield, white solid, mp. : 100-102 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.57 (dd, *J* = 6.8, 3.0 Hz, 2H), 7.52 – 7.45 (m, 3H), 7.40 – 7.36 (m, 4H), 7.36 – 7.27 (m, 7H), 7.21 (d, *J* = 15.8 Hz, 1H), 6.98 (s, 1H), 2.84 (s, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 170.8, 157.0, 149.8, 140.0, 139.9, 133.9, 131.3, 129.2, 128.6, 128.5, 128.5, 128.0, 127.1, 127.0, 109.3, 77.5, 29.1, miss one carbon. HRMS (ESI): *m/z*: calculated for $C_{24}H_{20}NO_2$: $[M + H]^+$ 354.1489, found: 354.1486; HPLC (Chiralpak IC, *i*-propanol/hexane = 20/80, flow rate 1.0 mL/min, 25 °C, λ = 254 nm): t_R (major) = 22.3 min, t_R (minor) = 20.8 min, *ee* = 92%; $[\alpha]^{25}_D$ = -68.2 (*c* = 1.0, DCM).



3q

17.4 mg, 58% yield, white solid, mp. : 96-99 °C, H/D = 5:95; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.85 (d, *J* = 7.5 Hz, 2H), 7.64 (t, *J* = 7.4 Hz, 1H), 7.55 (t, *J* = 7.6 Hz, 2H), 7.37 – 7.32 (m, 4H), 7.32 – 7.24 (m, 6H), 6.95 (s, 1H), 2.96 (s, 0.05H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 170.7, 158.5, 139.9, 139.9, 134.0, 130.5, 129.4, 128.5, 128.5, 128.0, 127.1, 127.0, 122.2, 77.5, 29.9, miss one carbon. HRMS (ESI): *m/z*: calculated for $C_{22}H_{17}DNO_2$: $[M + H]^+$ 329.1395, found: 329.1390; HPLC (Chiralpak IC, *i*-propanol/hexane = 20/80, flow rate 1.0 mL/min, 25 °C, λ = 254 nm): t_R (major) = 14.6 min, t_R (minor) = 11.2 min, *ee* = 86%.

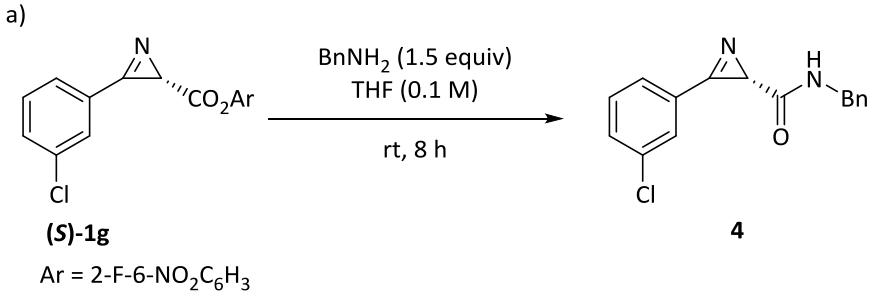
1.0 mmol Scale Synthesis



Ar = 2-F-6-$NO_2C_6H_3$ R = $CHPh_2$

To a flame-dried Schlenk reaction tube equipped with a magnetic stir bar, was added **BTM** (26.6 mg, 0.1 mmol), **1g** (334.7 mg, 1.0 mmol), and benzhydrol (110.4 mg, 0.6 mmol). The Schlenk tube was closed with a septum, evacuated and refilled with argon atmosphere, then toluene (10 mL) was added. The mixture was then stirred at 25 ℃ for 36 h**.** The mixture was concentrated under reduced pressure and purified by column chromatography on silica gel (hexane/EtOAc = 20:1) to afford the desired product **3g** as yellow oil, 177 mg, 49% yield, 85% ee and (***S***)**-1g** as colorless oil, 176 mg, 52% yield, 92% ee.

Synthetic Transformation

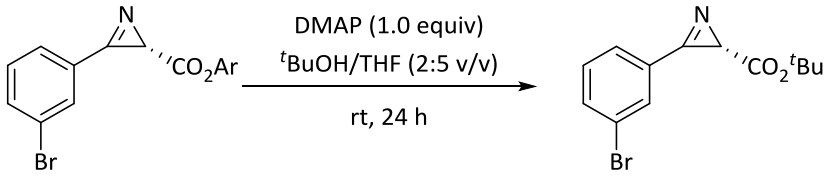


Ar = 2-F-6-$NO_2C_6H_3$

To a flame-dried Schlenk reaction tube equipped with a magnetic stir bar, was added **(*S*)-1g** (33.4 mg, 0.1 mmol) and toluene (1.0 mL). Then $BnNH_2$ (16.0 mg, 0.15 mmol) was added then the mixture was then stirred at rt for 8 h. The mixture was concentrated under reduced pressure and purified by column chromatography on silica gel (hexane/EtOAc = 10:1) to afford the **4** as a yellow solid, 27.0 mg, 95% yield, m.p. 156-160 ^{o}C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.89 (s, 1H), 7.80 (d, *J* = 7.6 Hz, 1H), 7.62 (d, *J* = 8.1 Hz, 1H), 7.53 (t, *J* = 7.9 Hz, 1H), 7.39 – 7.26 (m, 3H), 7.22 (d, *J* = 7.4 Hz, 2H), 5.91 (s, 1H), 4.51 – 4.36 (m, 2H), 2.83 (s, 1H). ^{13}C NMR (100 MHz,

$CDCl_3$) δ 170.0, 161.6, 137.7, 135.6, 134.2, 130.8, 130.2, 128.8, 128.5, 127.8, 127.7, 124.2, 43.6, 31.8. HRMS (ESI): *m/z*: calculated for $C_{16}H_{14}ClNO_2$: $[M + H]^+$ 285.0789, found: 285.0790; HPLC (Chiralpak IC, *i*-propanol/hexane = 20/80, flow rate 1.0 mL/min, 25 °C, λ = 254 nm): t_R (major) = 25.4 min, t_R (minor) = 28.7 min, *ee* = 99%; $[\alpha]^{25}_D$ = +36.3 (*c* = 1.0, DCM).

b)

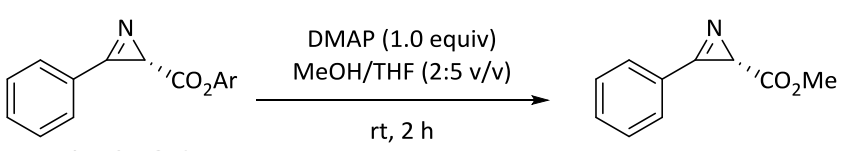


(*R*)-1f
Ar = 2-F-6-$NO_2C_6H_3$

5
68%, 91% ee

To a flame-dried Schlenk reaction tube equipped with a magnetic stir bar, was added **(*S*)-1f** (18.9 mg, 0.05 mmol), DMAP (6.1 mg, 0.05 mmol). Then ^{t}BuOH/THF (2:5, v/v, 0.5 mL) was added and the mixture was then stirred at rt for 24 h. The mixture was concentrated under reduced pressure and purified by column chromatography on silica gel (hexane/EtOAc = 20:1) to afford the product **5** as a yellow wax[3], 10.1 mg, 68% yield; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.01 (t, *J* = 1.7 Hz, 1H), 7.82 (d, *J* = 7.7 Hz, 1H), 7.76 (d, *J* = 9.2 Hz, 1H), 7.46 (t, *J* = 7.9 Hz, 1H), 2.78 (s, 1H), 1.47 (s, 9H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 170.4, 158.5, 136.6, 132.9, 130.8, 128.7, 124.7, 123.3, 82.0, 31.0, 28.1. HPLC (Chiralpak IC, *i*-propanol/hexane = 20/80, flow rate 1.0 mL/min, 25 °C, λ = 254 nm): t_R (major) = 6.1 min, t_R (minor) = 8.4 min, *ee* = 91%; $[\alpha]^{25}_D$ = +51.2 (*c* = 1.0, DCM).

c)



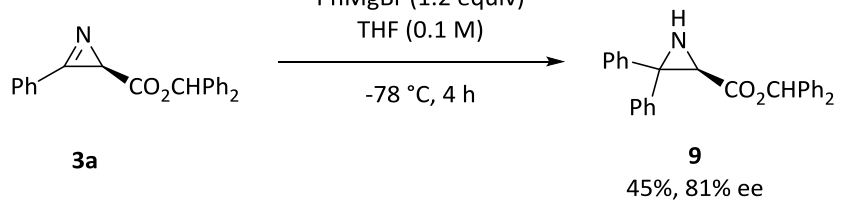
Ar = 2-F-6-$NO_2C_6H_3$
(*S*)-1a

7
89%, 85% ee

To a flame-dried Schlenk reaction tube equipped with a magnetic stir bar, was added **(*S*)-1a** (15.0 mg, 0.05 mmol), DMAP (6.1 mg, 0.05 mmol). Then MeOH/THF (2:5, v/v, 0.5 mL) was added and the mixture was then stirred at rt for 2 h. The mixture was

concentrated under reduced pressure and purified by column chromatography on silica gel (hexane/EtOAc = 20:1) to afford the product **7** as yellow oil[4], 7.8 mg, 89% yield; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.93 – 7.86 (m, 2H), 7.70 – 7.63 (m, 1H), 7.61 – 7.56 (m, 2H), 3.75 (s, 3H), 2.86 (s, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 172.1, 158.5, 134.0, 130.5, 129.4, 122.2, 52.3, 29.5. HPLC (Chiralpak IC, *i*-propanol/hexane = 20/80, flow rate 1.0 mL/min, 25 ^{o}C, λ = 254 nm): t_R (major) = 18.4 min, t_R (minor) = 20.6 min, *ee* = 85%; $[\alpha]^{25}_D$ = 26.8 (*c* = 1.0, DCM).

d)

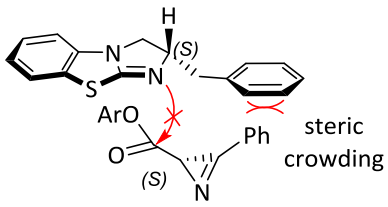


3a **9**

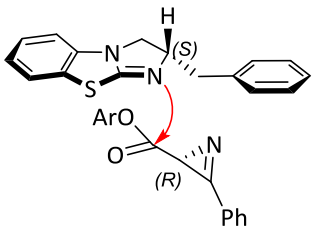
45%, 81% ee

To a flame-dried Schlenk reaction tube equipped with a magnetic stir bar, was added **3a** (32.7 mg, 0.1 mmol). The Schlenk tube was closed with a septum, evacuated and refilled with argon atmosphere and toluene (1.0 mL) was added at -78 ℃. Then PhMgBr (0.12 mL, 0.1 M) was added dropwised and the mixture was reacted at the same temperature for 4 hours. Then saturated aqueous NH_4Cl and EtOAc were added and the organic layers were wash with saturated aqueous brine, then dried over $MgSO_4$. The organic phase was concentrated under reduced pressure and purified by column chromatography on silica gel (hexane/EtOAc = 10:1) to afford the product **9** as a white wax, 18.4 mg, 45% yield; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.40 – 7.26 (m, 13H), 7.24 – 7.19 (m, 3H), 7.16 – 7.06 (m, 4H), 6.81 (s, 1H), 3.13 (d, *J* = 8.2Hz, 1H), 2.29 (d, *J* = 8.2 Hz, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 168.4, 141.7, 139.5, 139.4, 139.4, 137.7, 128.7, 128.6, 128.5, 128.5, 128.3, 128.0, 127.9, 127.3, 126.9, 126.8, 78.2, 51.2, 45.4, miss one carbon. HRMS (ESI): *m/z*: calculated for $C_{28}H_{24}NO_2$: $[M + H]^+$ 406.1802, found: 406.1811; HPLC (Chiralpak IC, *i*-propanol/hexane = 20/80, flow rate 1.0 mL/min, 25 ^{o}C, λ = 254 nm): t_R (major) = 18.5 min, t_R (minor) = 19.9 min, *ee* = 81%; $[\alpha]^{25}_D$ = -32.9 (*c* = 1.0, DCM).

Proposed Transition State Mode of Enantiodiscrimination



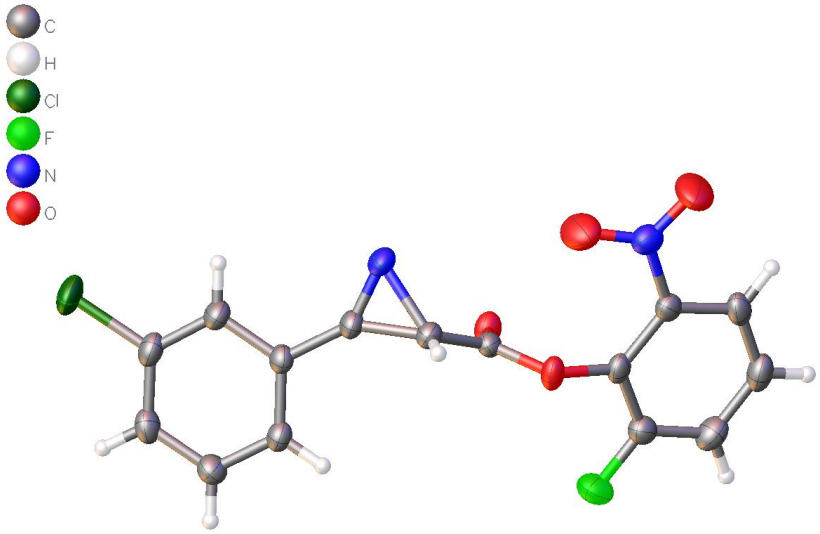
Ar = 2-F-6-$NO_2C_6H_3$
disfavor



Ar = 2-F-6-$NO_2C_6H_3$
favor

We hypothesize that the catalyst **C** approaches the 3-phenyl-2*H*-azirine-2-carboxylate carbonyl preferentially from the unsubstituted face first. In this orientation, the benzyl of catalyst **C** will be repelled by the phenyl group of ***S***-configuration substrate leading to the disfavored transition state. In contrast, catalyst **C** attacks to the ***R***-configuration substrate faster and delivers ***R***-configuration product.

Crystal Structure of *S*-1g



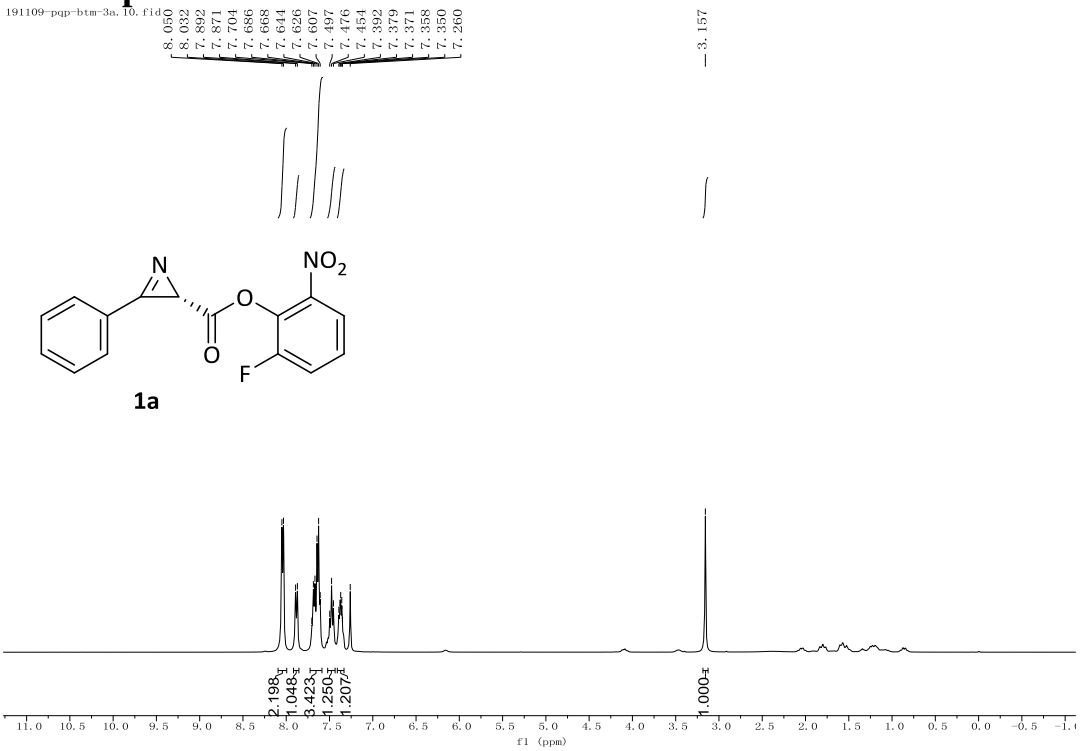
Identification code	20191128pengqiupeng
Empirical formula	$C_{15}H_8ClFN_2O_4$
Formula weight	334.68
Temperature/K	173.00(10)
Crystal system	monoclinic
Space group	$P2_1$
a/Å	4.32650(10)
b/Å	13.4831(2)
c/Å	12.3293(3)
α/°	90
β/°	93.614(2)
γ/°	90
Volume/Å^3	717.79(3)
Z	2
ρ_{calc}g/cm^3	1.549
μ/mm^{-1}	2.690
F(000)	340.0
Crystal size/mm^3	0.4 × 0.2 × 0.02
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	7.184 to 149.842
Index ranges	$-5 \le h \le 4$, $-16 \le k \le 16$, $-15 \le l \le 15$
Reflections collected	10108
Independent reflections	2903 [R_{int} = 0.0348, R_{sigma} = 0.0309]
Data/restraints/parameters	2903/1/208
Goodness-of-fit on F^2	1.026
Final R indexes [I>=2σ (I)]	R_1 = 0.0359, wR_2 = 0.0937
Final R indexes [all data]	R_1 = 0.0377, wR_2 = 0.0962

Largest diff. peak/hole / e $Å^{-3}$	0.53/-0.34
Flack parameter	-0.001(9)

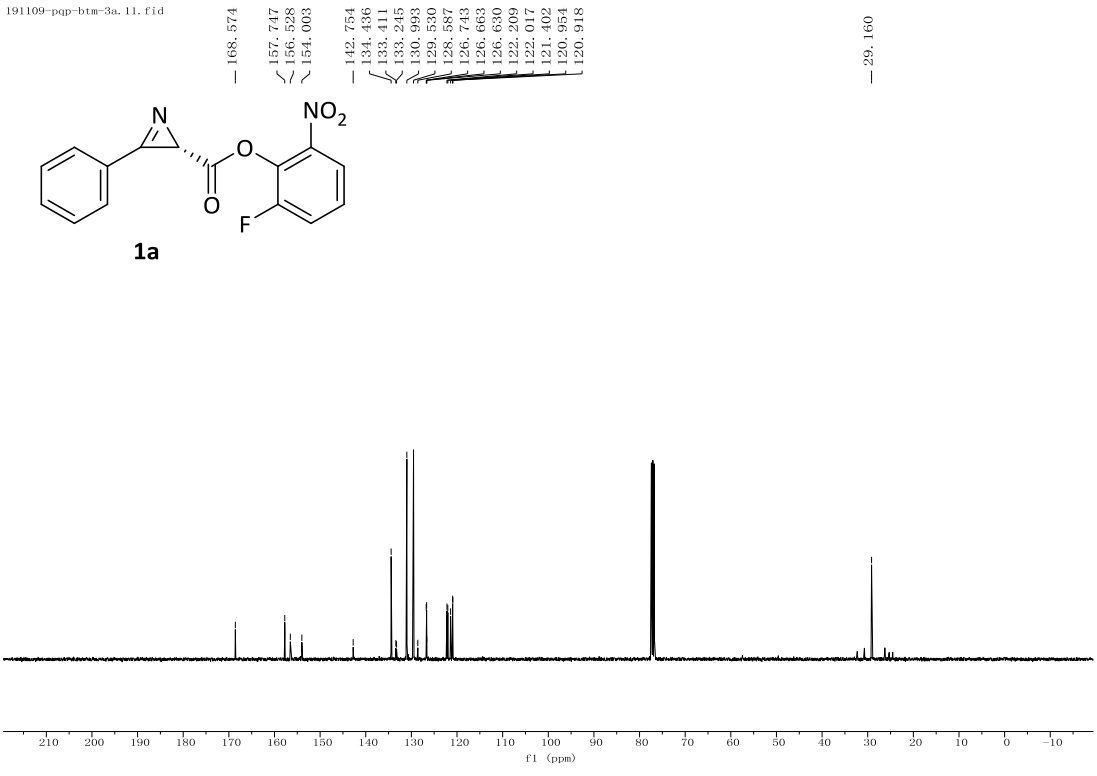
References

1. B. S. Bal, W. E. Childers Jr and H. W. Pinnick, *Tetrahedron*, 1981, **37**, 2091-2096.
2. (a) M. S. Novikov, N. V. Rostovskii, A. N. Koronatov, K. V. Zavyalov, G. V. Zubakin, A. F. Khlebnikov and G. L. Starova, *J. Org. Chem.*, 2017, **82**, 13396-13404; (b) Q. Peng, B. Zhang, Y. Xie and J. Wang, *Org. Lett.*, 2018, **20**, 7641-7644.
3. A. Dupas, P.-A. Lhotellier, G. Guillamot, C. Meyer and J. Cossy, *Org. Lett.*, 2019, **21**, 3589-3593.
4. K. Okuda, A. C. Seila and S. A. Strobel, *Biochemistry*, 2005, **44**, 6675-6684.

NMR Spectra

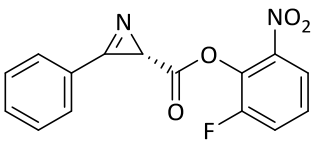


1a



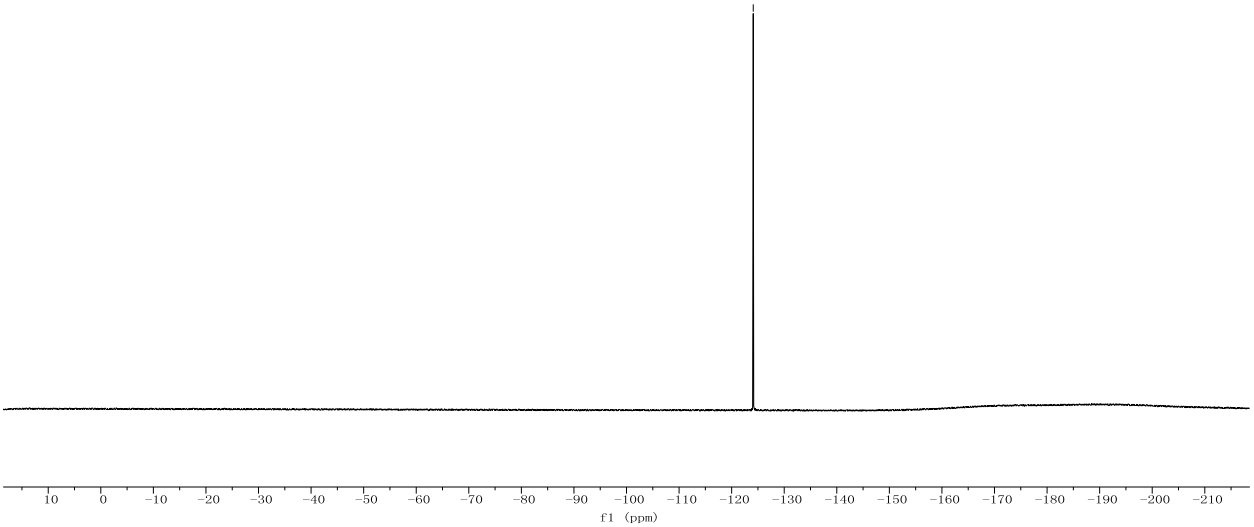
1a

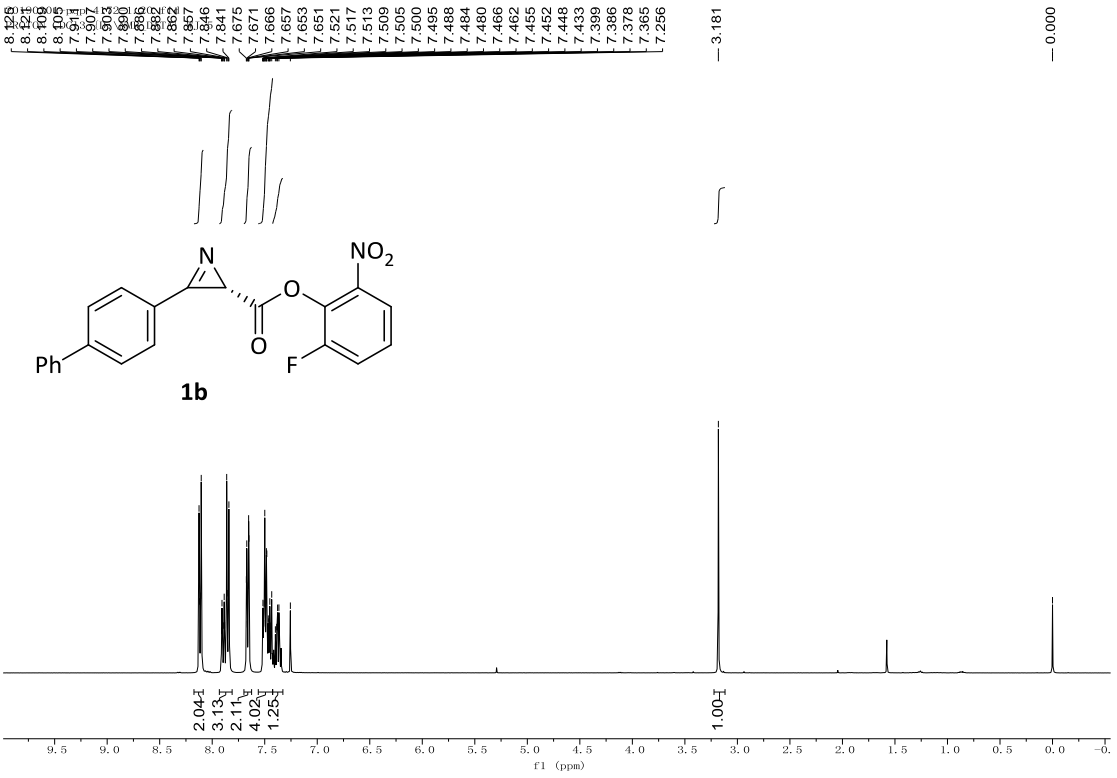
20190214-pqp-416-3.11.fid
F19CPD CDCl3 {D:\NMR_DATA} WJ 50

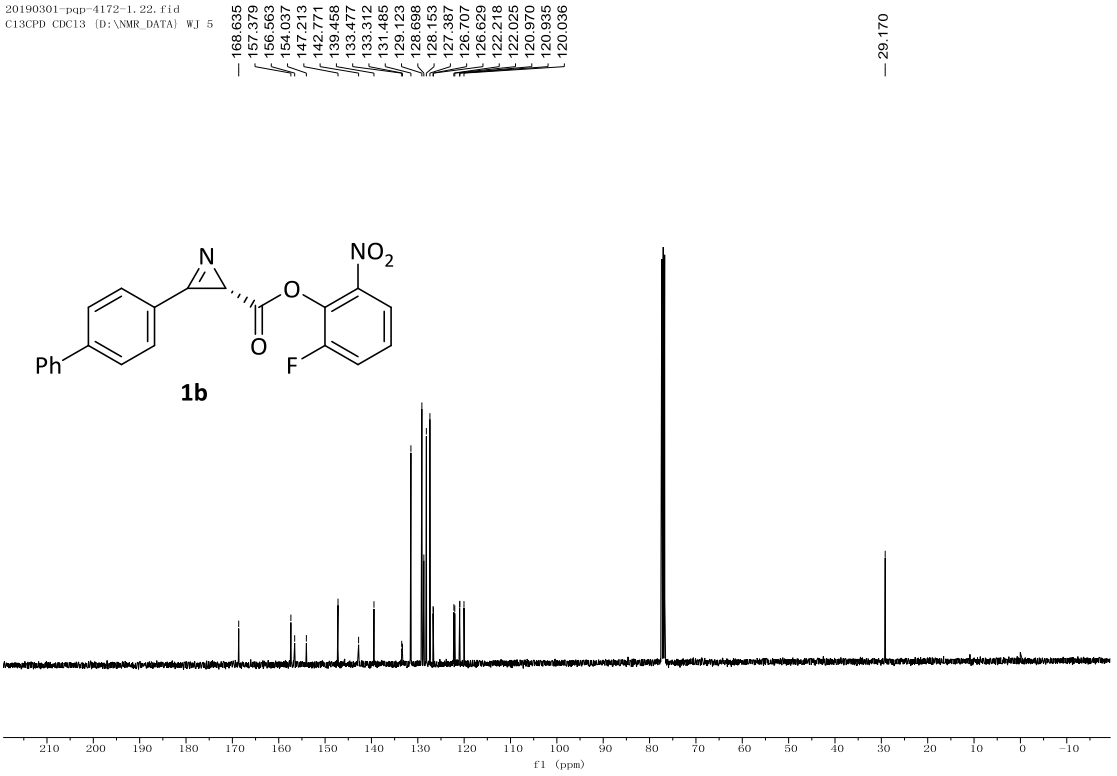


1a

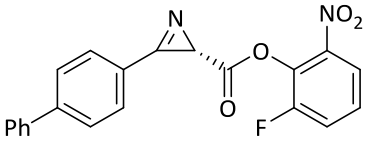
−124.109




8.125
8.121
8.109
8.105
7.911
7.907
7.903
7.890
7.886
7.882
7.862
7.857
7.846
7.841
7.675
7.671
7.666
7.657
7.653
7.651
7.521
7.517
7.513
7.509
7.505
7.500
7.495
7.488
7.484
7.480
7.466
7.462
7.455
7.452
7.448
7.433
7.399
7.386
7.378
7.365
7.256
3.181
0.000
N
O
NO2
O
F
Ph
1b
2.04
3.13
2.11
4.02
1.25
1.00
f1 (ppm)

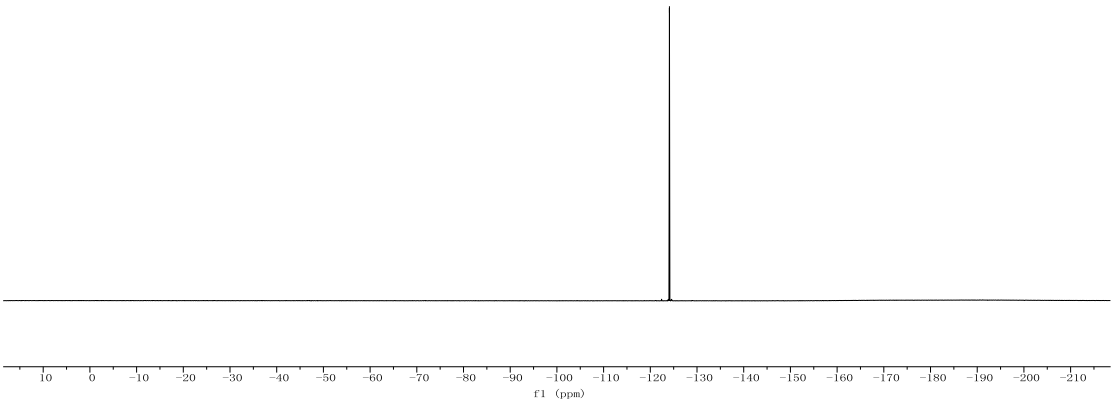

20190301-pqp-4172-1.22.fid
C13CPD CDCl3 (D:\NMR_DATA) WJ 5
168.635
157.379
156.563
154.037
147.213
142.771
139.458
133.477
133.312
131.485
129.123
128.698
128.153
127.387
126.707
126.629
122.218
122.025
120.970
120.935
120.036
29.170
N
O
NO2
O
F
Ph
1b
f1 (ppm)

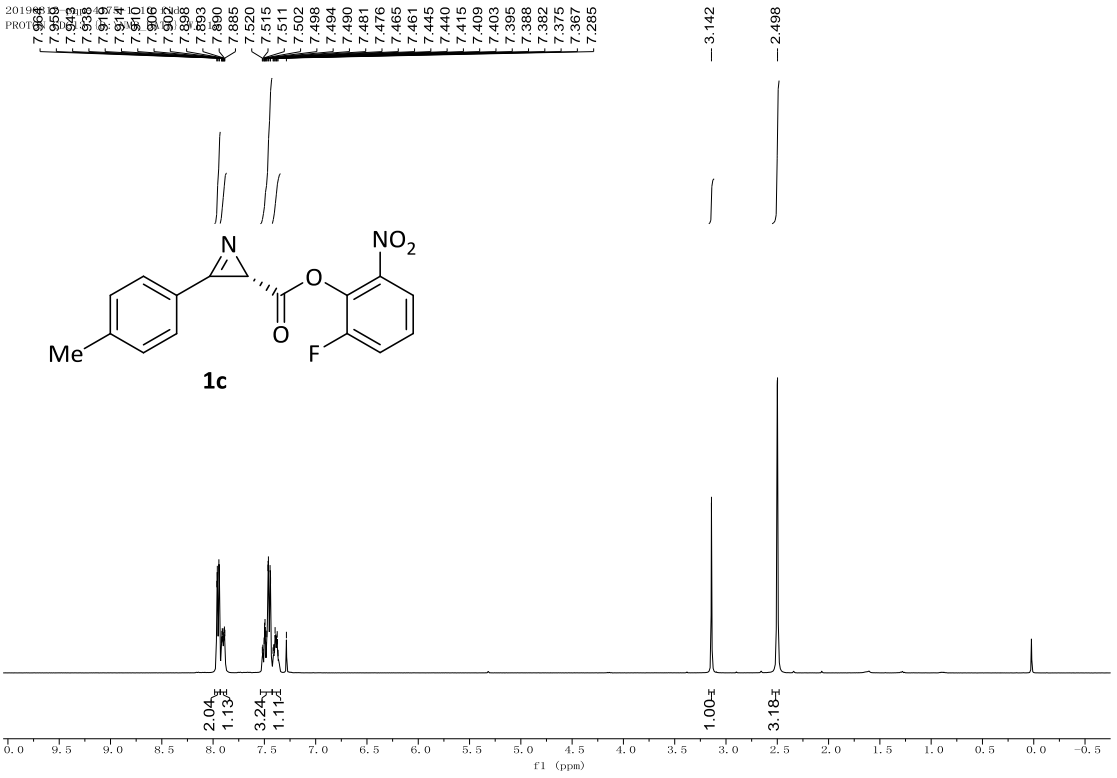
20190301-pqp-4172-1.21.fid
F19CPD CDCl3 (D:\NMR_DATA) WJ 5

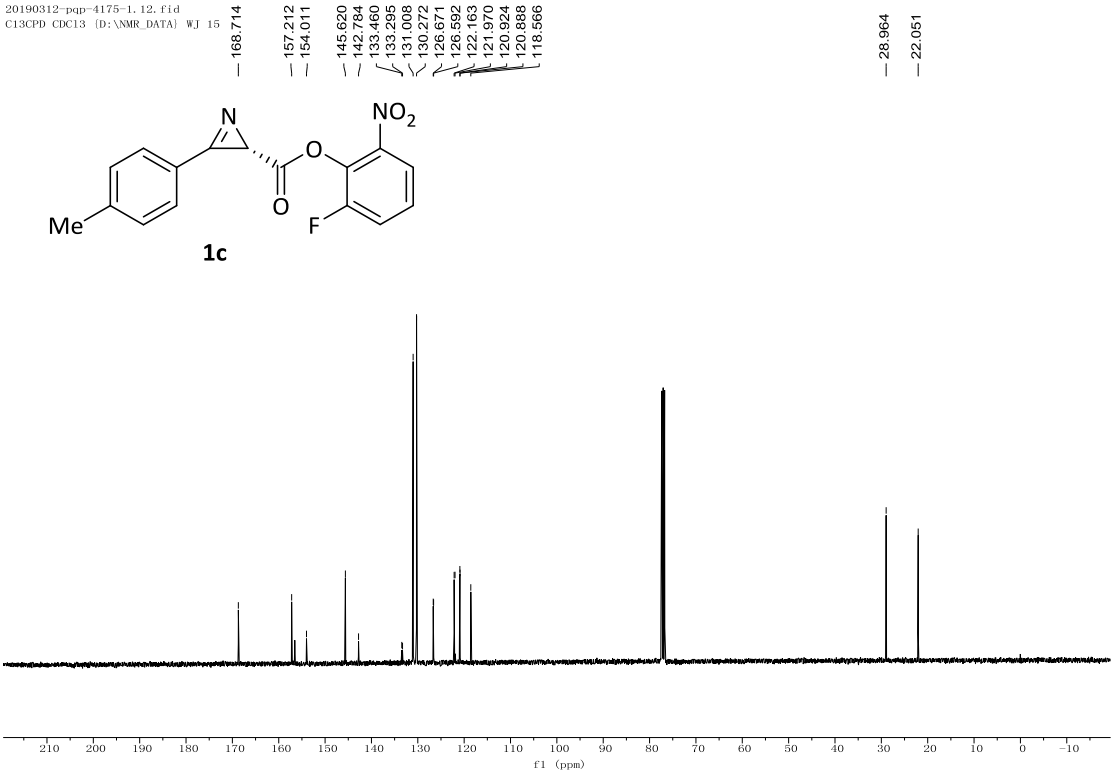


1b

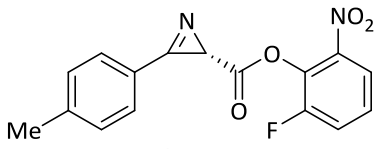
-124.098




7.964
7.959
7.943
7.938
7.914
7.910
7.906
7.902
7.896
7.893
7.890
7.885
7.520
7.515
7.511
7.502
7.498
7.494
7.490
7.481
7.476
7.465
7.461
7.445
7.440
7.415
7.409
7.403
7.395
7.388
7.382
7.375
7.367
7.285
3.142
2.498
N
O
O
NO2
Me
F
1c
2.04
1.13
3.24
1.11
1.00
3.18
f1 (ppm)

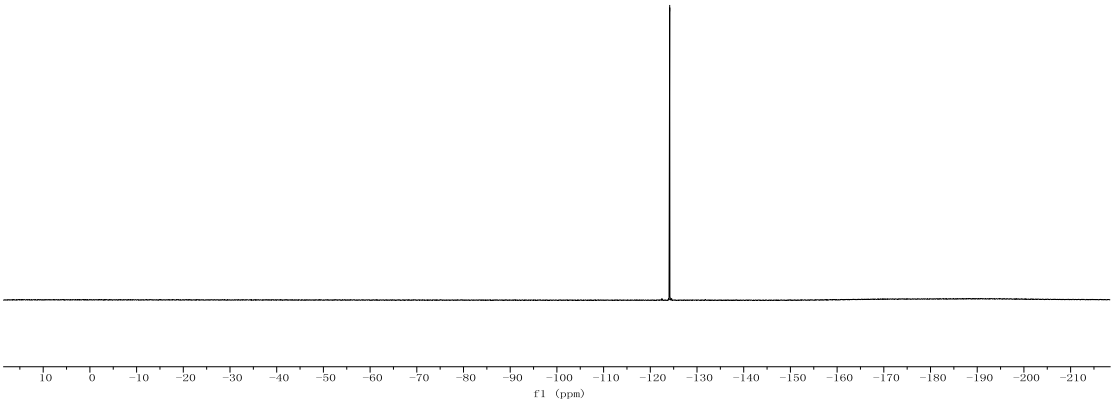

20190312-pqp-4175-1.12.fid
C13CPD CDCl3 (D:\NMR_DATA) WJ 15
168.714
157.212
154.011
145.620
142.784
133.460
133.295
131.008
130.272
126.671
126.592
122.163
121.970
120.924
120.888
118.566
28.964
22.051
N
O
O
NO2
Me
F
1c
f1 (ppm)

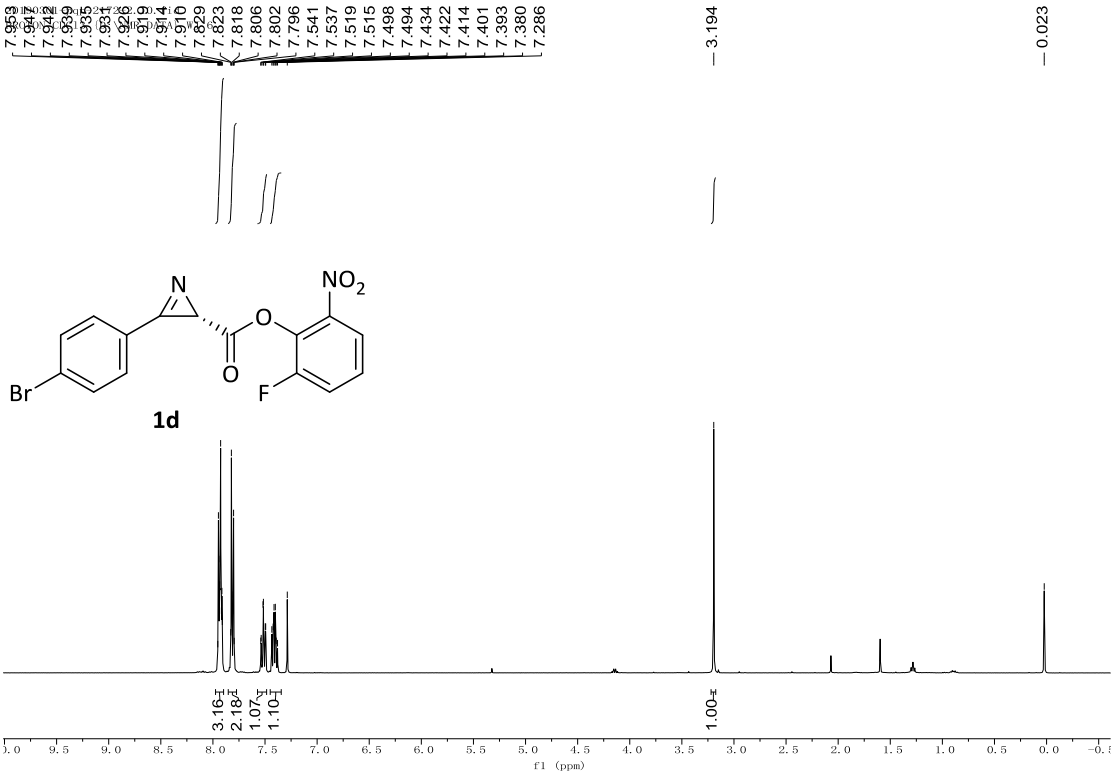
20190312-pqp-4175-1.11.fid
F19CPD CDCl3 (D:\NMR_DATA) WJ 15

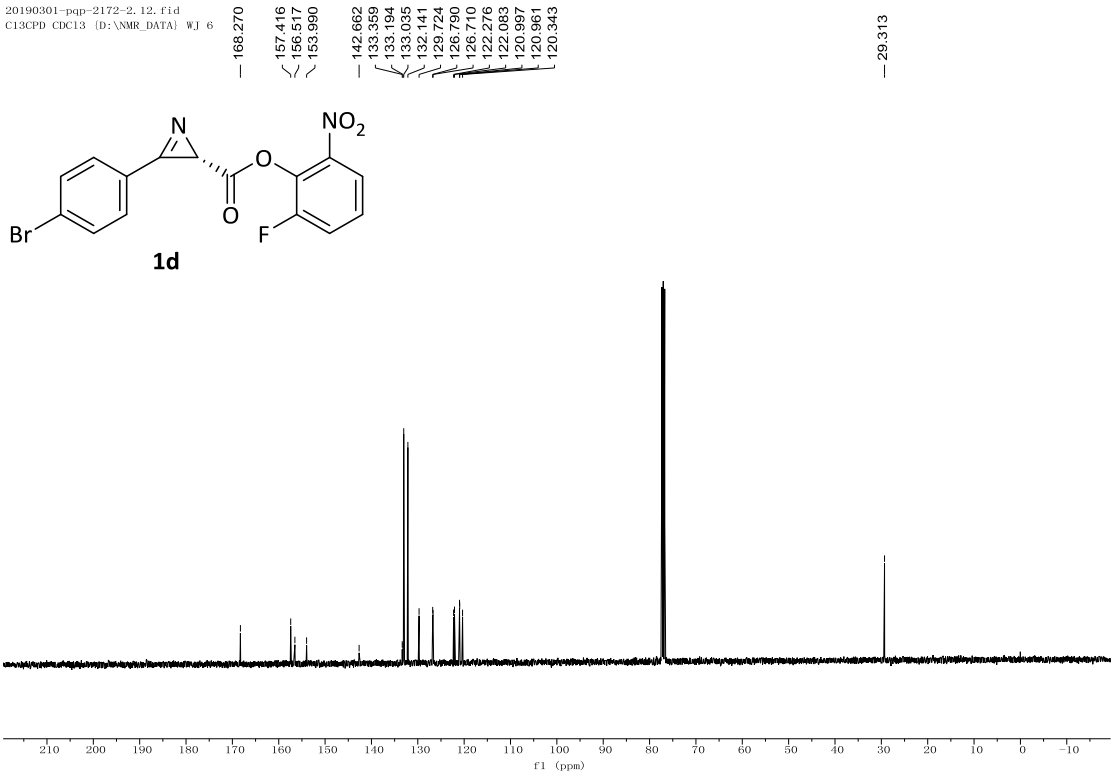


1c

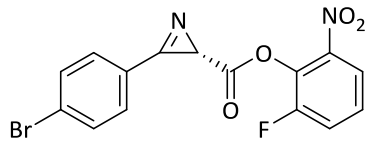
-124.153




7.953
7.947
7.942
7.939
7.935
7.933
7.926
7.919
7.914
7.916
7.829
7.823
7.818
7.806
7.802
7.796
7.541
7.537
7.519
7.515
7.498
7.494
7.434
7.422
7.414
7.401
7.393
7.380
7.286
3.194
0.023
N
O
O
NO2
Br
F
1d
3.16
2.18
1.07
1.10
1.00
f1 (ppm)

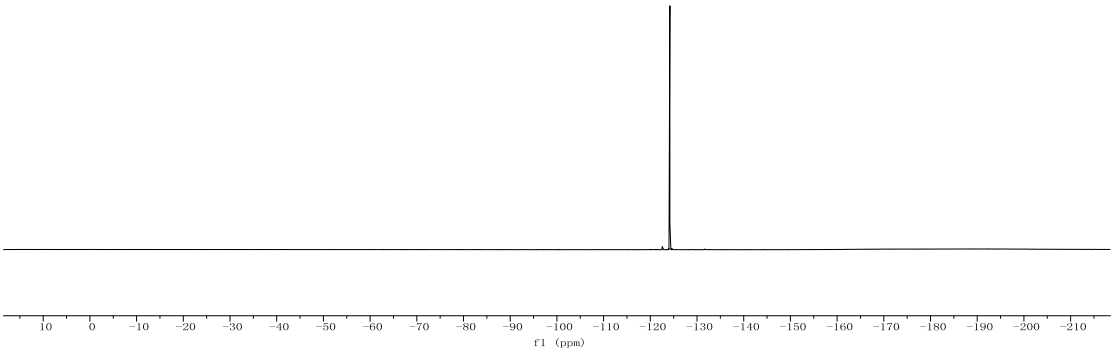

20190301-pqp-2172-2.12.fid
C13CPD CDCl3 (D:\NMR_DATA) WJ 6
168.270
157.416
156.517
153.990
142.662
133.359
133.194
133.035
132.141
129.724
126.790
126.710
122.276
122.083
120.997
120.961
120.343
29.313
N
O
O
NO2
Br
F
1d
f1 (ppm)

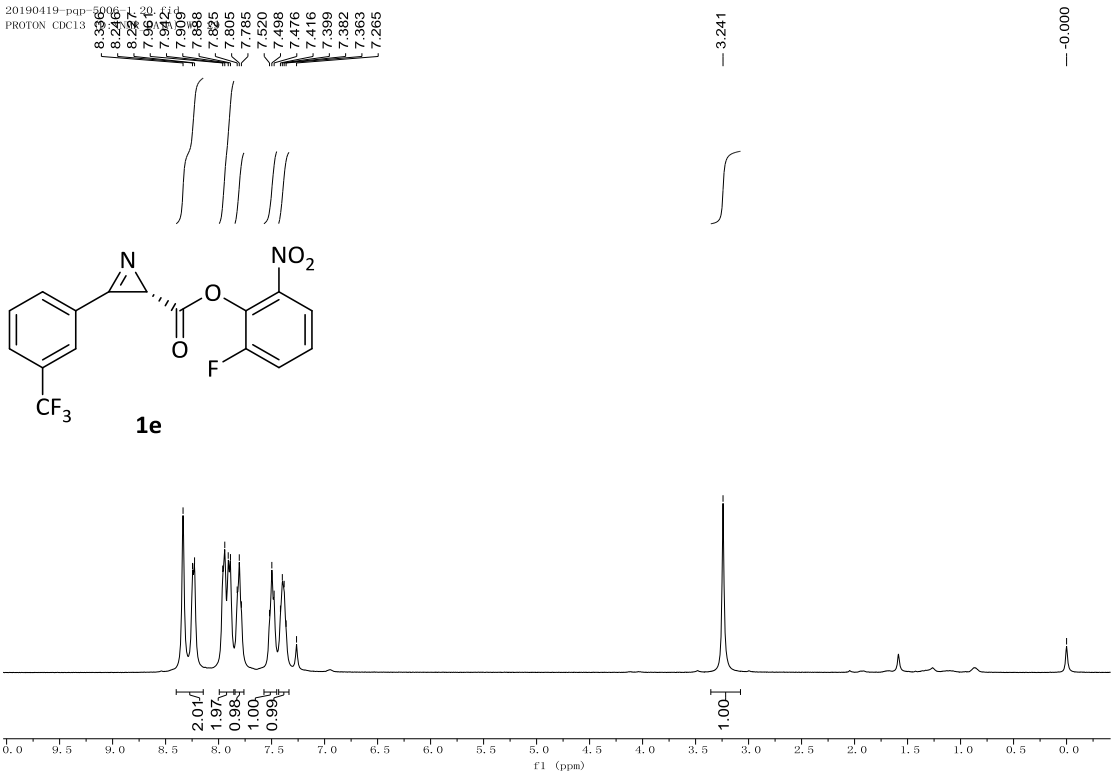
20190301-pqp-2172-2.11.fid
F19CPD CDCl3 (D:\NMR_DATA) WJ 6



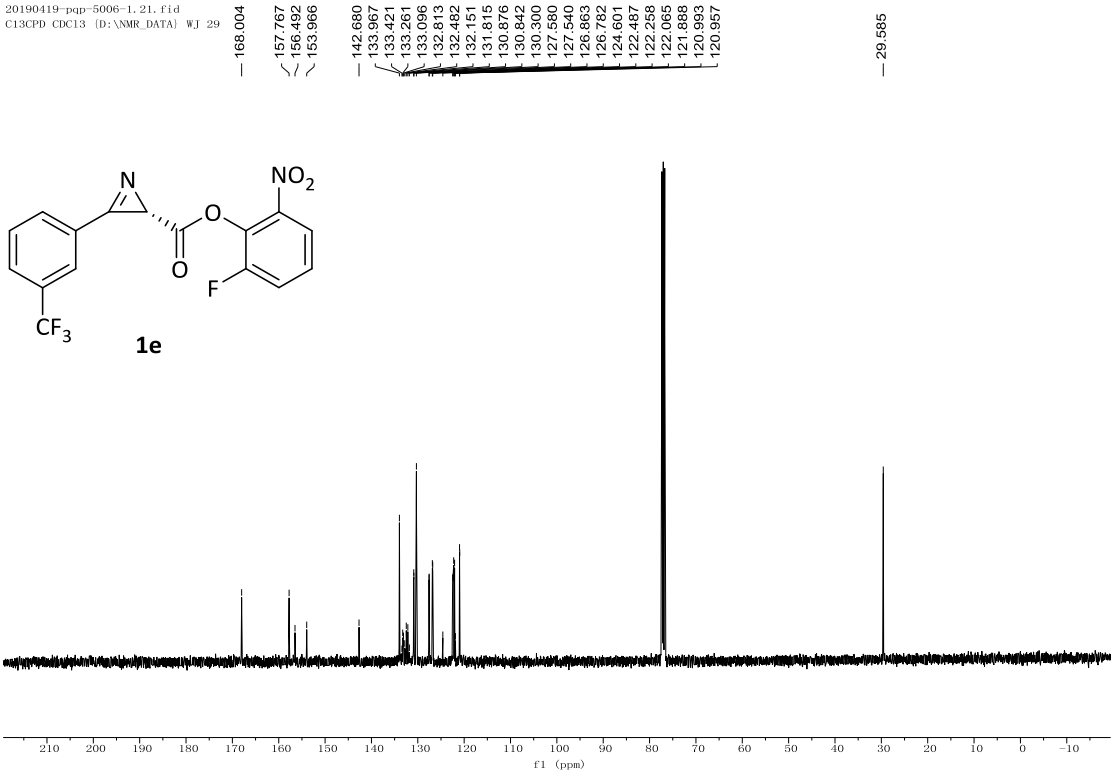
1d

-124.187

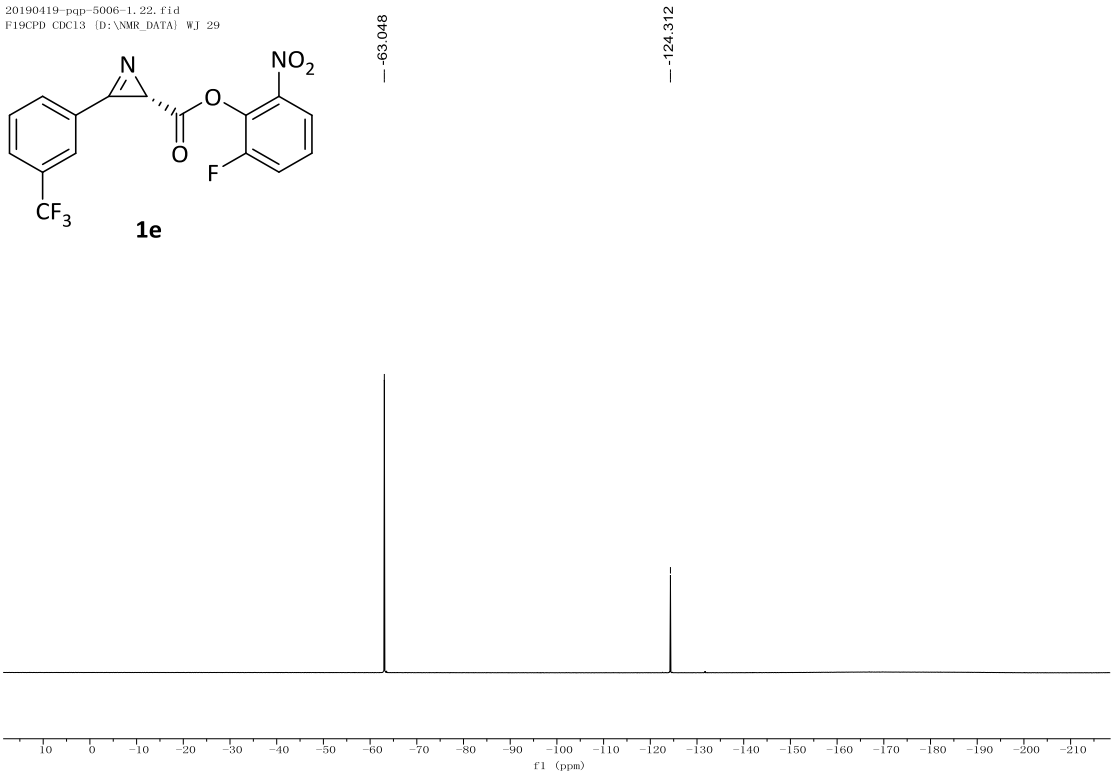


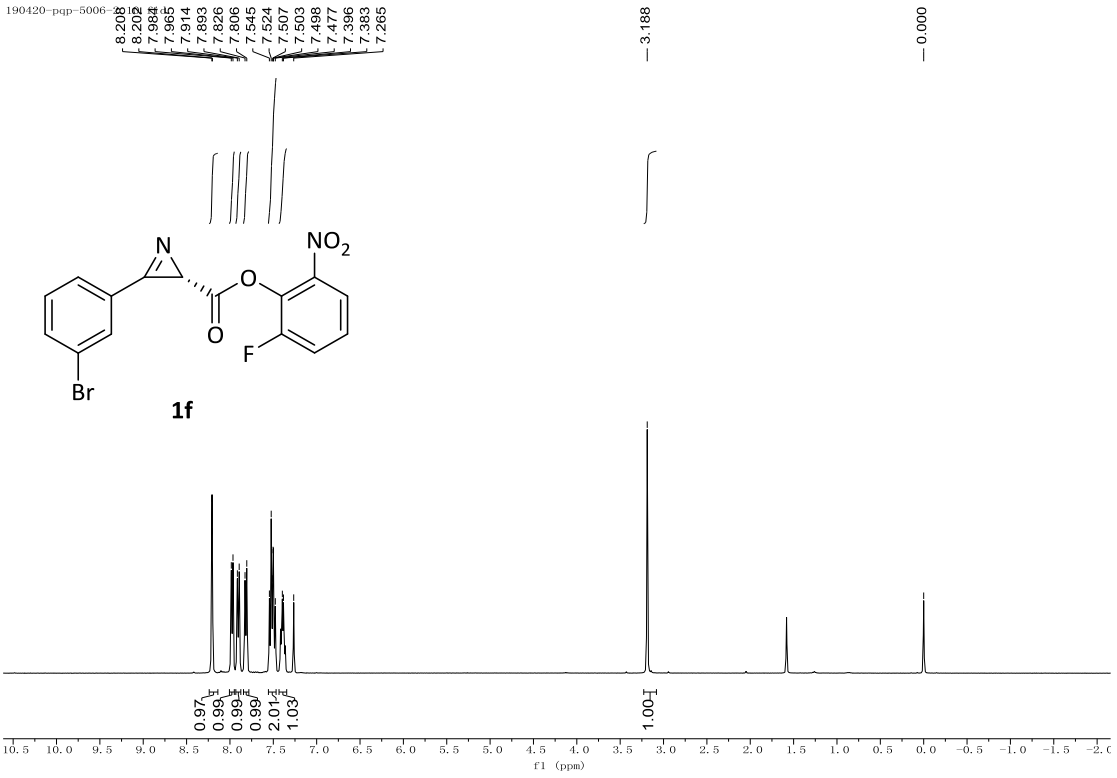

20190419-pqp-5006-1.20.fid
PROTON CDC13
8.336
8.246
8.227
7.961
7.942
7.909
7.888
7.825
7.805
7.785
7.520
7.498
7.476
7.416
7.399
7.382
7.363
7.265
3.241
-0.000
N
O
O
NO2
F
CF3
2.01
1.97
0.98
1.00
0.99
1.00
f1 (ppm)

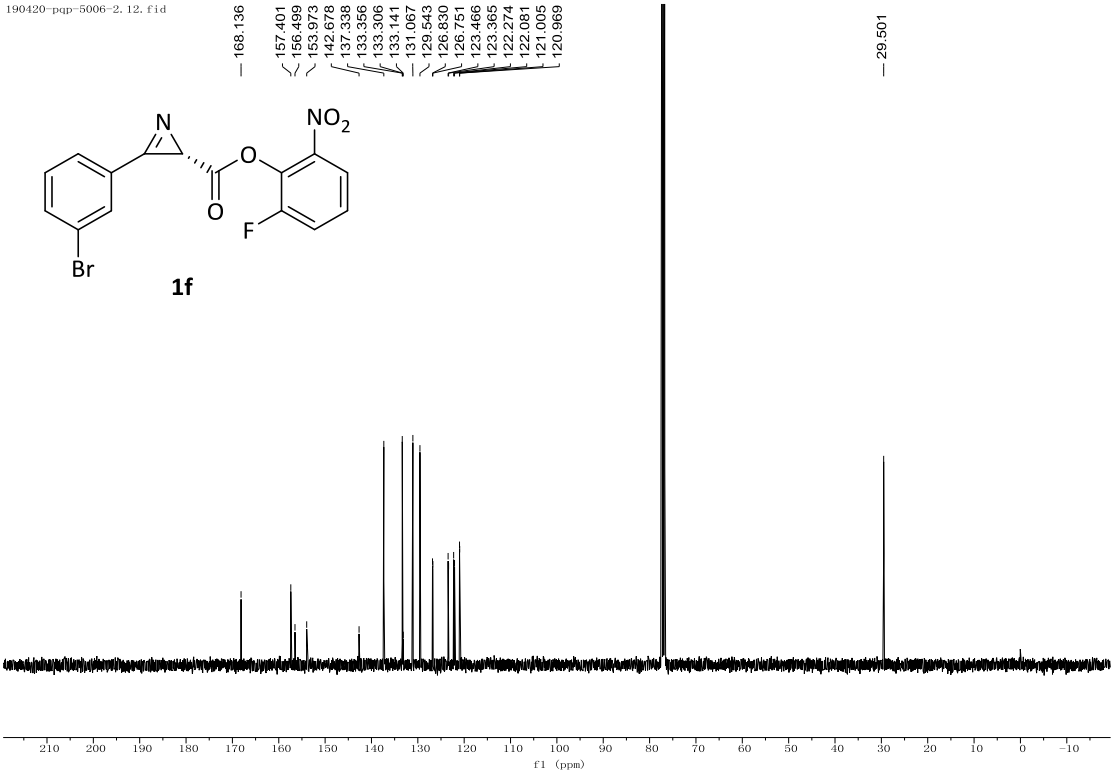
1e


20190419-pqp-5006-1.21.fid
C13CPD CDC13 (D:\NMR_DATA) WJ 29
168.004
157.767
156.492
153.966
142.680
133.967
133.421
133.261
133.096
132.813
132.482
132.151
131.815
130.876
130.842
130.300
127.580
127.540
126.863
126.782
124.601
122.487
122.258
122.065
121.888
120.993
120.957
29.585
N
O
O
NO2
F
CF3
f1 (ppm)

1e

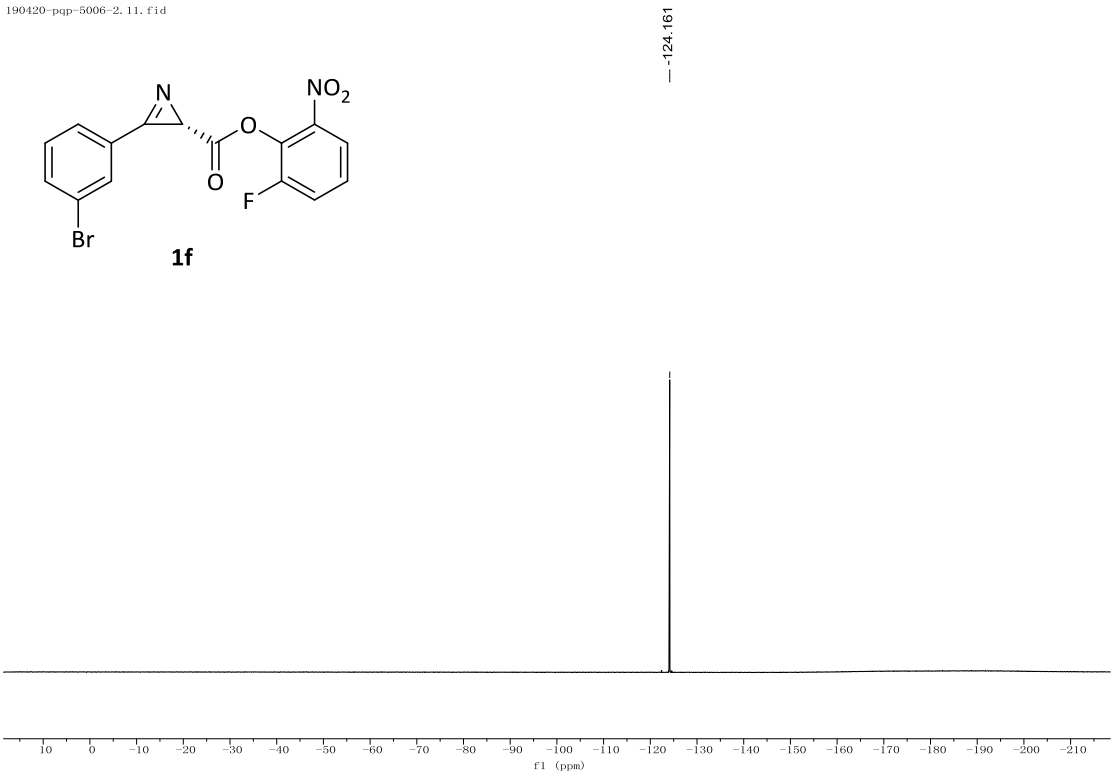

20190419-pqp-5006-1.22.fid
F19CPD CDCl3 (D:\NMR_DATA) WJ 29
-63.048
-124.312
N
O
O
F
NO2
CF3
1e
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

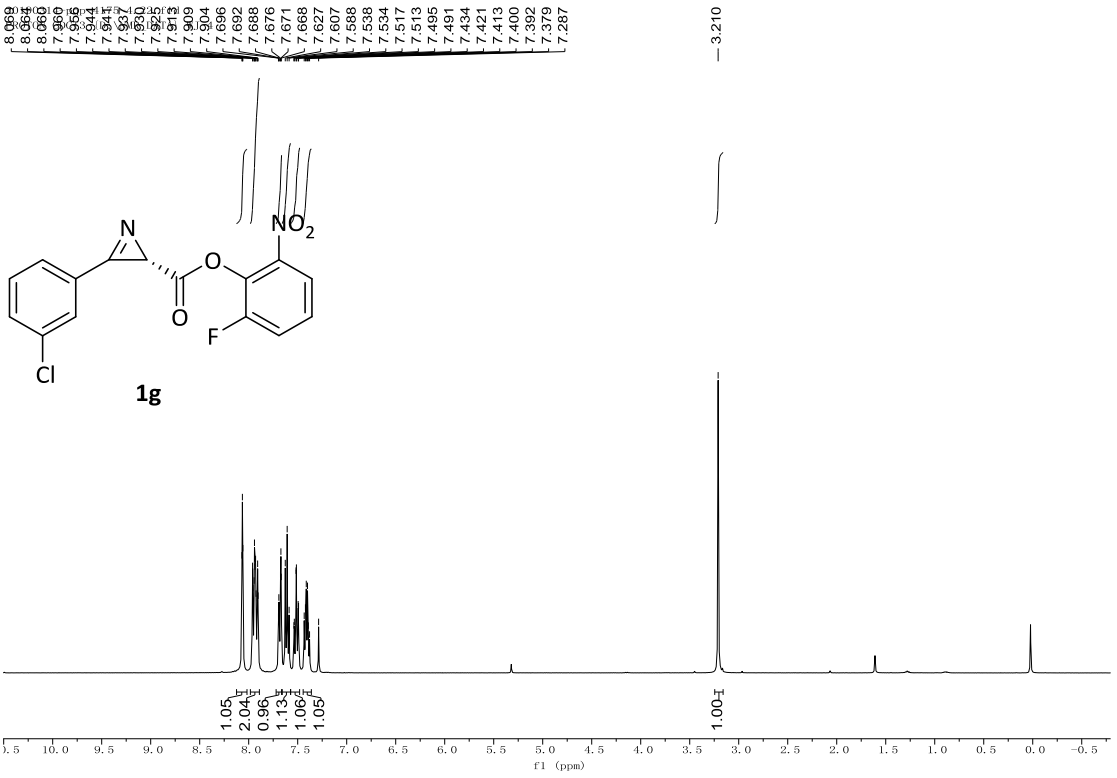

8.208
8.202
7.984
7.965
7.914
7.893
7.826
7.806
7.545
7.524
7.507
7.503
7.498
7.477
7.396
7.383
7.265
3.188
0.000
N
O
O
NO2
F
Br
1f
0.97
0.99
0.99
0.99
2.01
1.03
1.00
f1 (ppm)

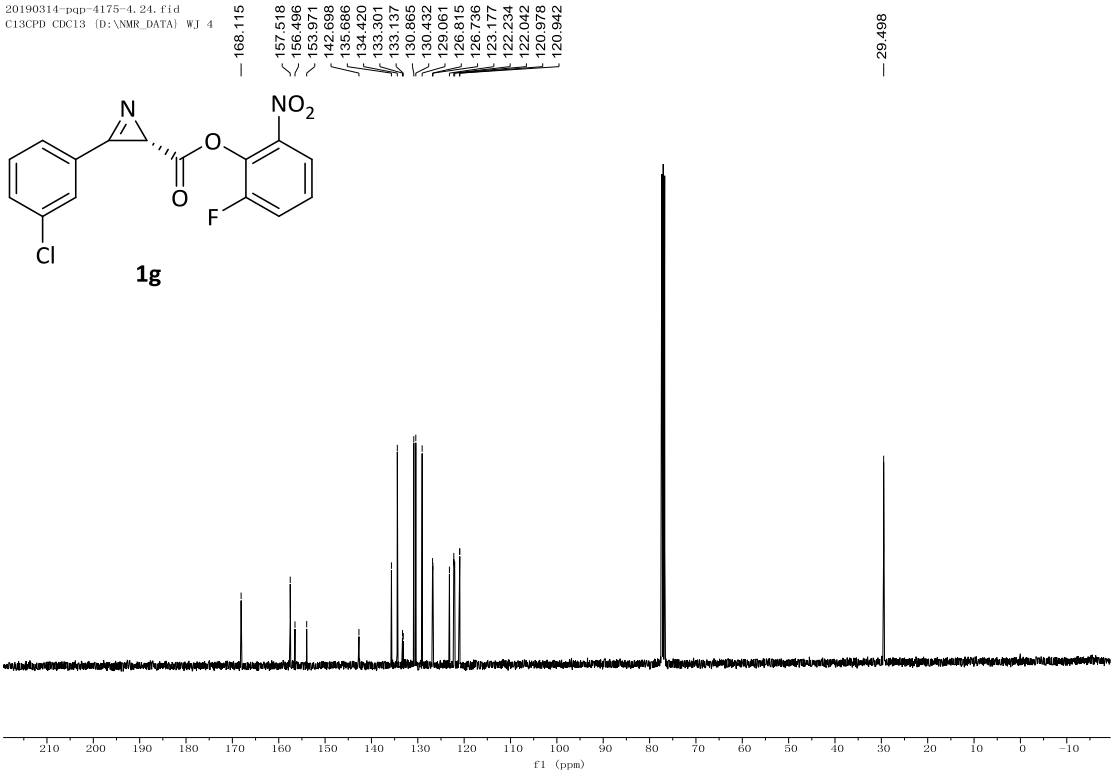

190420-pqp-5006-2.12.fid
168.136
157.401
156.499
153.973
142.678
137.338
133.356
133.306
133.141
131.067
129.543
126.830
126.751
123.466
123.365
122.274
122.081
121.005
120.969
29.501
N
O
O
NO2
F
Br
1f
f1 (ppm)

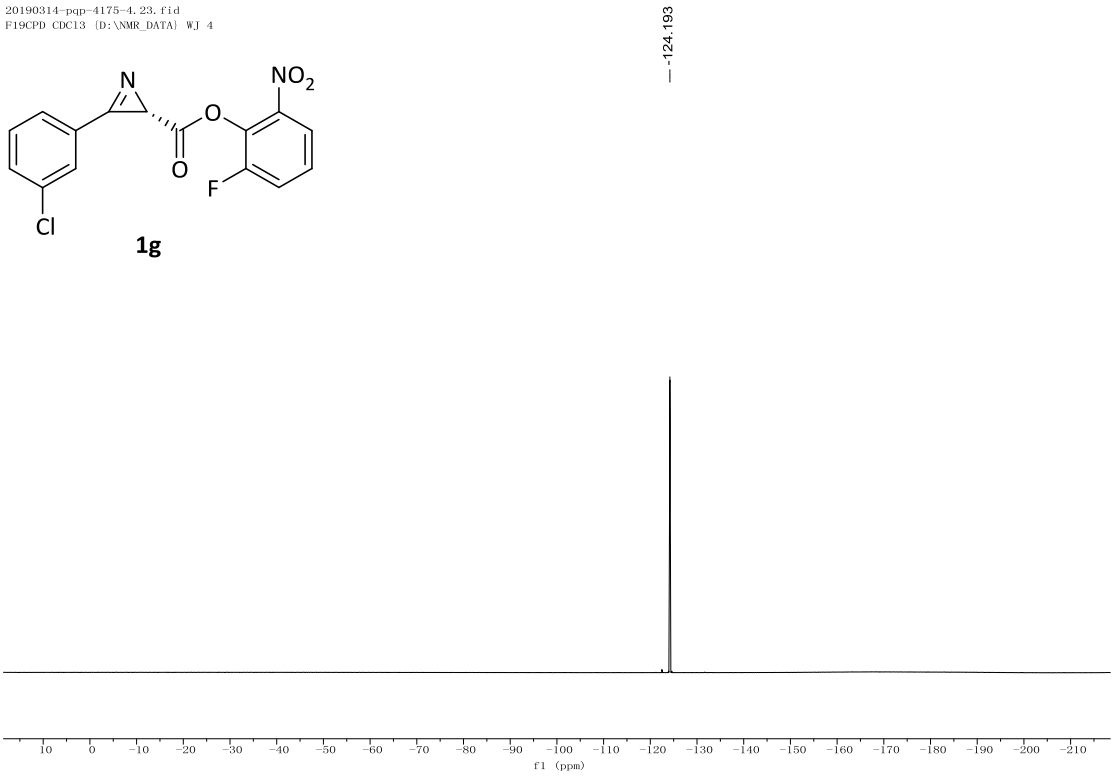
190420-pqp-5006-2.11.fid

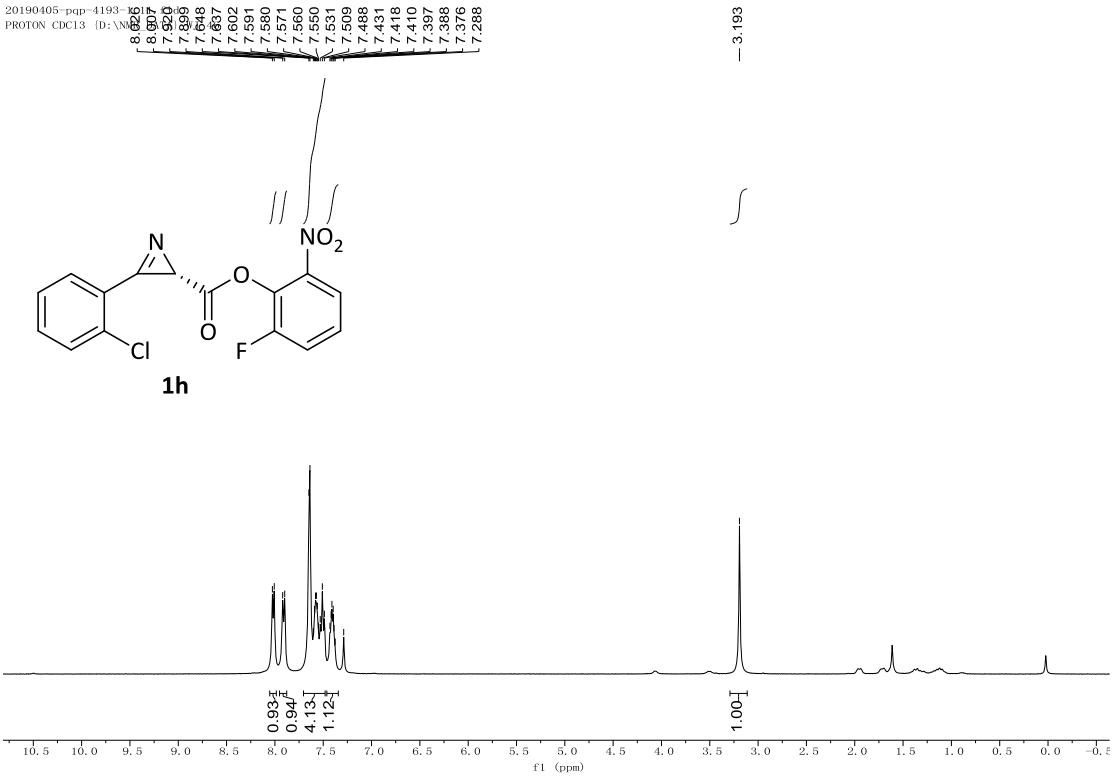
1f

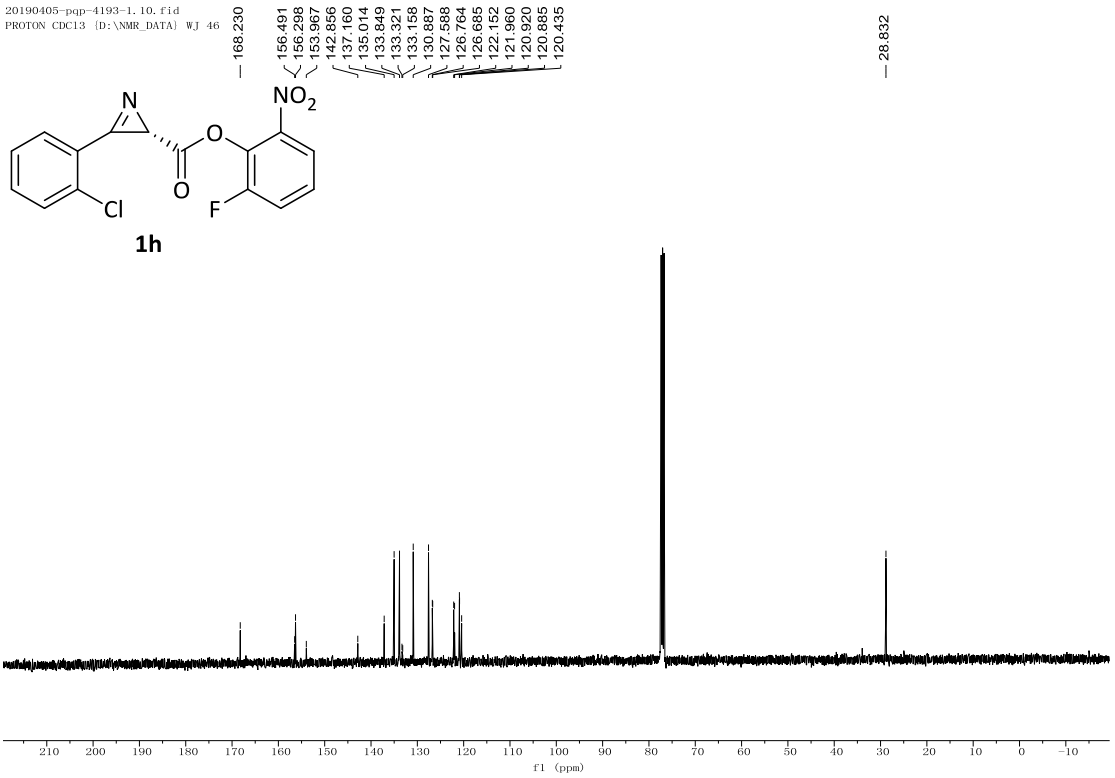



8.069
8.064
8.060
7.966
7.955
7.944
7.937
7.930
7.925
7.913
7.909
7.904
7.696
7.692
7.688
7.676
7.671
7.668
7.627
7.607
7.588
7.538
7.534
7.517
7.513
7.495
7.491
7.434
7.421
7.413
7.400
7.392
7.379
7.287
3.210
N
O
O
NO2
F
Cl
1g
1.05
2.04
0.96
1.13
1.06
1.05
1.00
f1 (ppm)


20190314-pqp-4175-4.24.fid
C13CPD CDC13 (D:\NMR_DATA) WJ 4
168.115
157.518
156.496
153.971
142.698
135.686
134.420
133.301
133.137
130.865
130.432
129.061
126.815
126.736
123.177
122.234
122.042
120.978
120.942
29.498
N
O
O
NO2
F
Cl
1g
f1 (ppm)

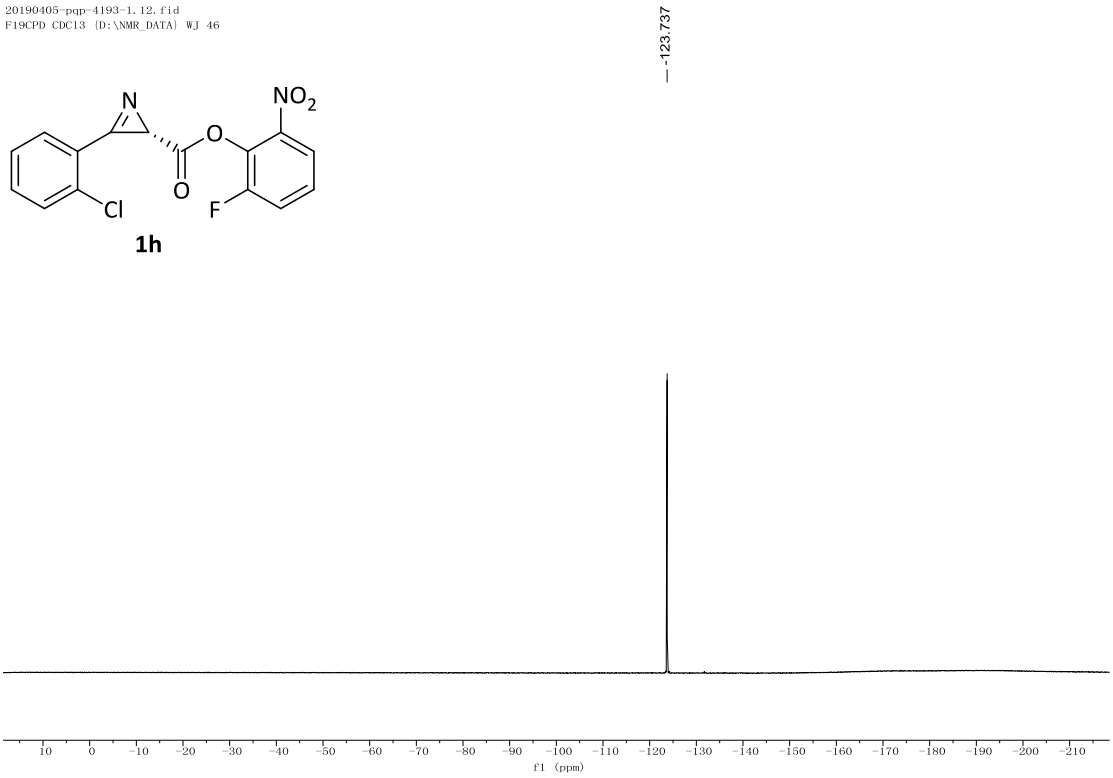

20190314-pqp-4175-4.23.fid
F19CPD CDCl3 (D:\NMR_DATA) WJ 4
N
O
O
NO2
F
Cl
1g
-124.193
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

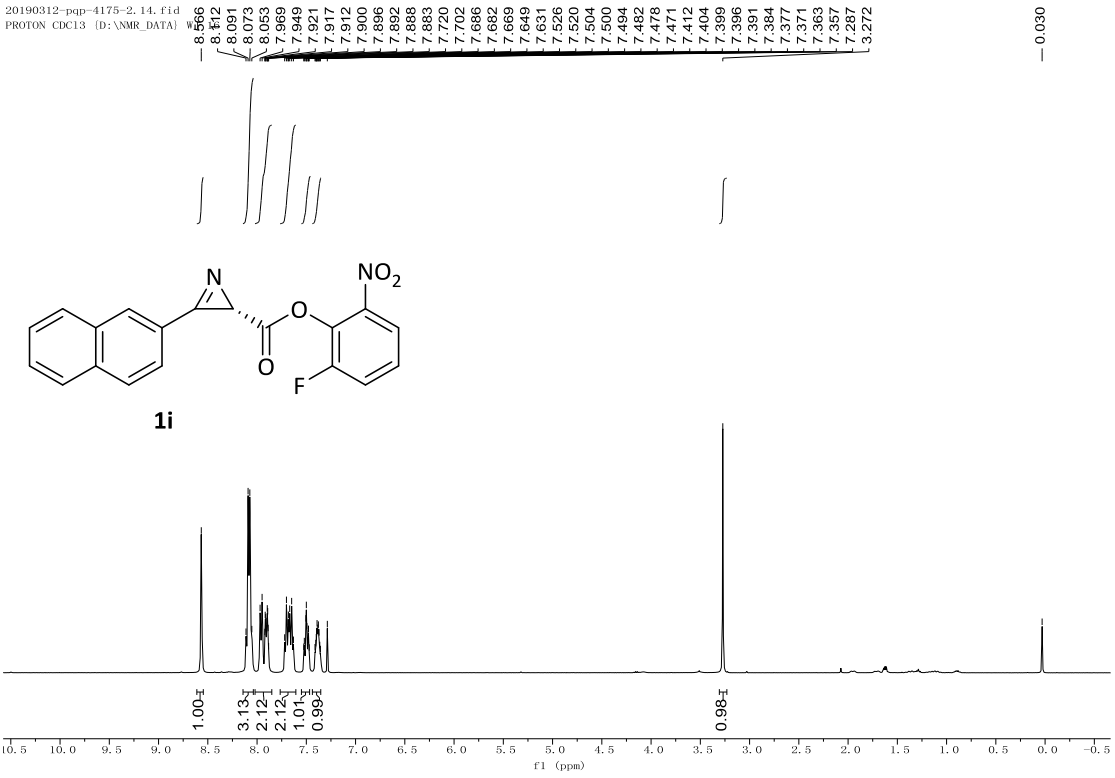

20190405-pqp-4193-K
PROTON CDC13 {D:\NMR_DATA} WJ 46
8.026
8.007
7.926
7.899
7.648
7.637
7.602
7.591
7.580
7.571
7.560
7.550
7.531
7.509
7.488
7.431
7.418
7.410
7.397
7.388
7.376
7.288
3.193
N
O
O
NO2
Cl
F
1h
0.93
0.94
4.13
1.12
1.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

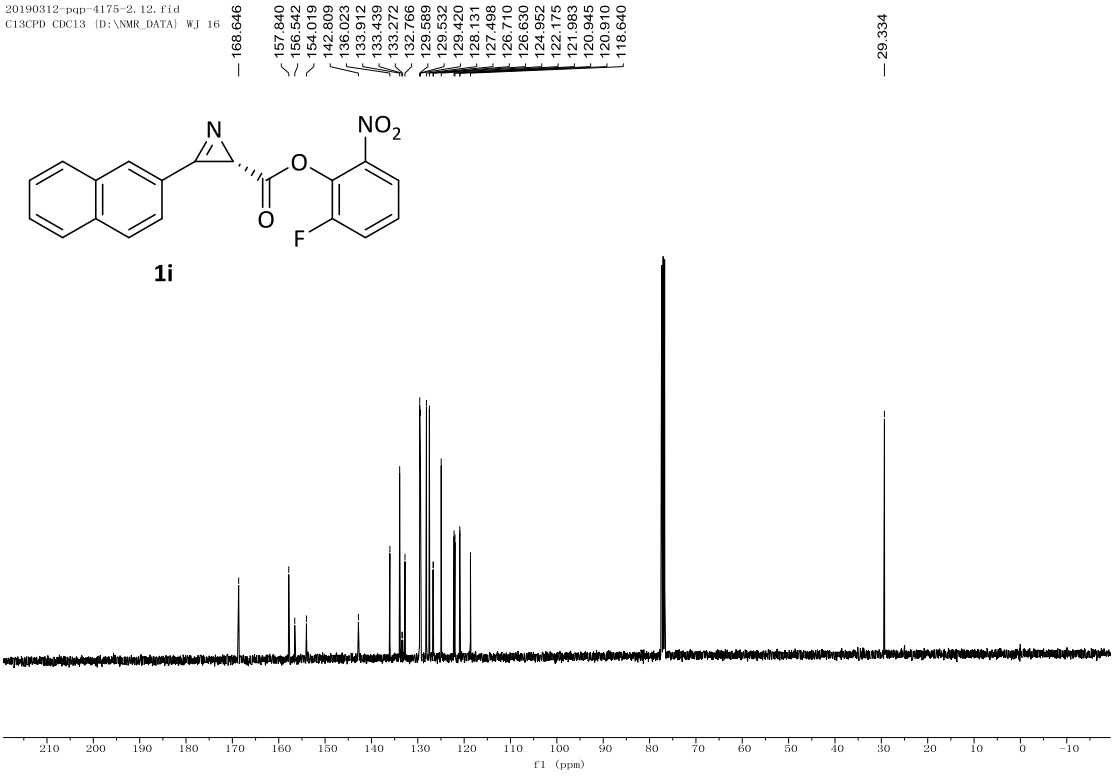

20190405-pqp-4193-1.10.fid
PROTON CDC13 {D:\NMR_DATA} WJ 46
168.230
156.491
156.298
153.967
142.856
137.160
135.014
133.849
133.321
133.158
130.887
127.588
126.764
126.685
122.152
121.960
120.920
120.885
120.435
28.832
N
O
O
NO2
Cl
F
1h
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

20190405-pqp-4193-1.12.fid
F19CPD CDCl3 (D:\NMR_DATA) WJ 46

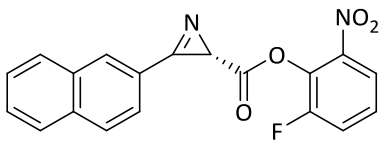
1h




20190312-pqp-4175-2.14.fid
PROTON CDC13 (D:\NMR_DATA) WJ 16
8.566
8.112
8.091
8.073
8.053
7.969
7.949
7.921
7.917
7.912
7.900
7.896
7.892
7.888
7.883
7.720
7.702
7.686
7.682
7.669
7.649
7.631
7.526
7.520
7.504
7.500
7.494
7.482
7.478
7.471
7.412
7.404
7.399
7.396
7.391
7.384
7.377
7.371
7.363
7.357
7.287
3.272
0.030
N
O
O
NO2
F
1i
1.00
3.13
2.12
2.12
1.01
0.99
0.98
f1 (ppm)

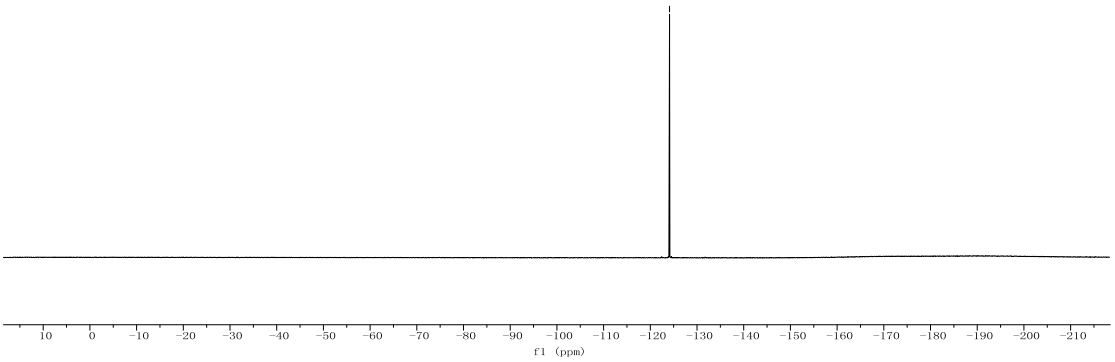

20190312-pqp-4175-2.12.fid
C13CPD CDC13 (D:\NMR_DATA) WJ 16
168.646
157.840
156.542
154.019
142.809
136.023
133.912
133.439
133.272
132.766
129.589
129.532
129.420
128.131
127.498
126.710
126.630
124.952
122.175
121.983
120.945
120.910
118.640
29.334
N
O
O
NO2
F
1i
f1 (ppm)

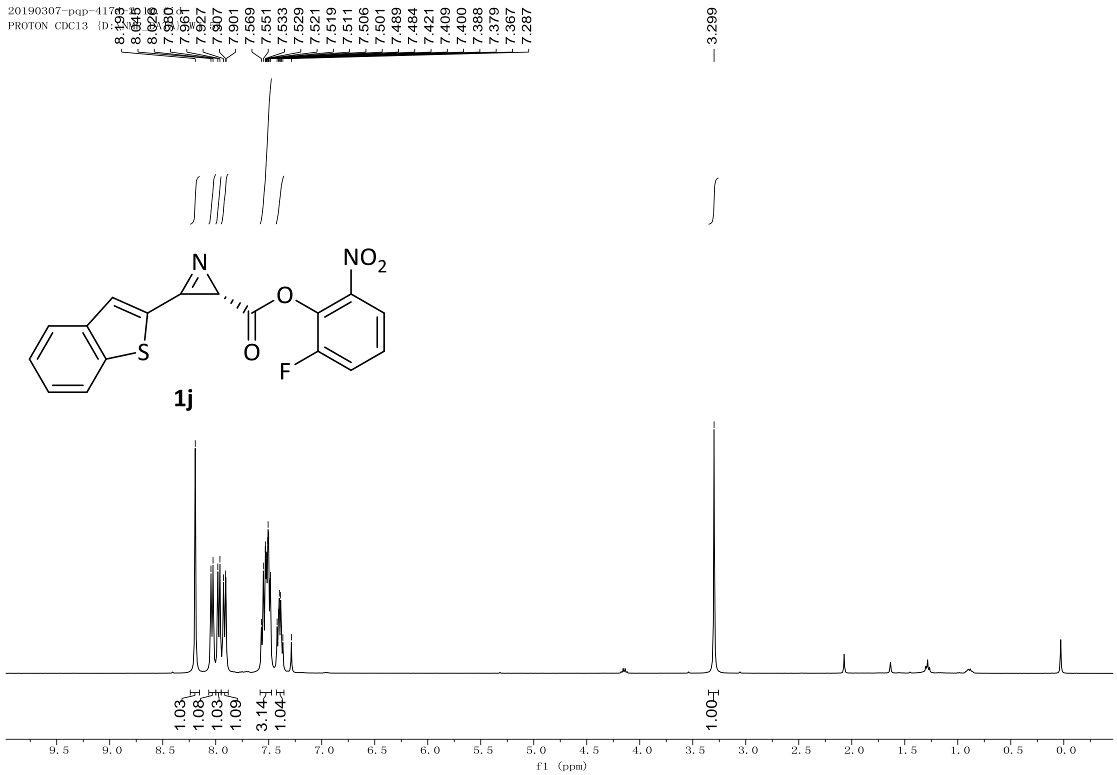
20190312-pqp-4175-2.13.fid
F19CPD CDCl3 (D:\NMR_DATA) WJ 16

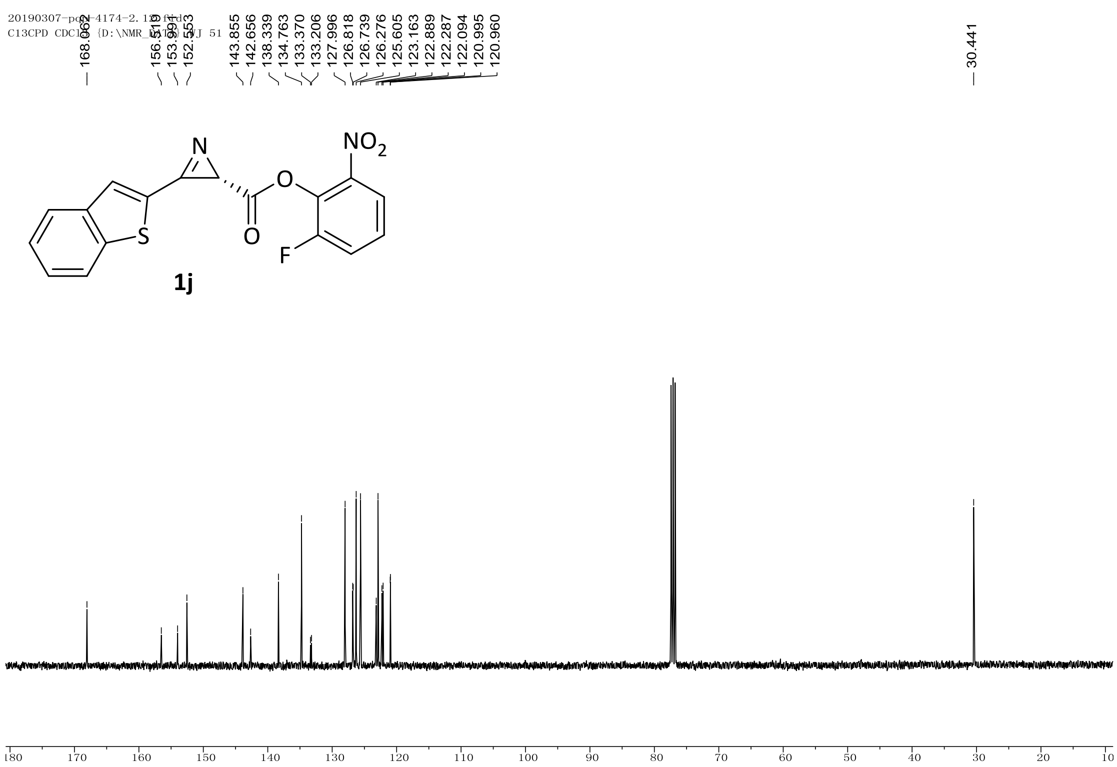


1i

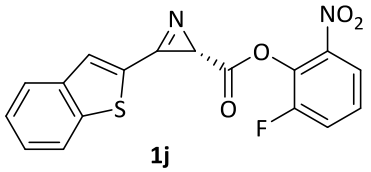
-124.119




20190307-pqp-4174
PROTON CDCl3
8.193
8.045
8.026
7.980
7.961
7.927
7.907
7.901
7.569
7.551
7.533
7.529
7.521
7.519
7.511
7.506
7.501
7.489
7.484
7.421
7.409
7.400
7.388
7.379
7.367
7.287
3.299
NO2
N
O
S
O
F
1j
1.03
1.08
1.03
1.09
3.14
1.04
1.00
f1 (ppm)

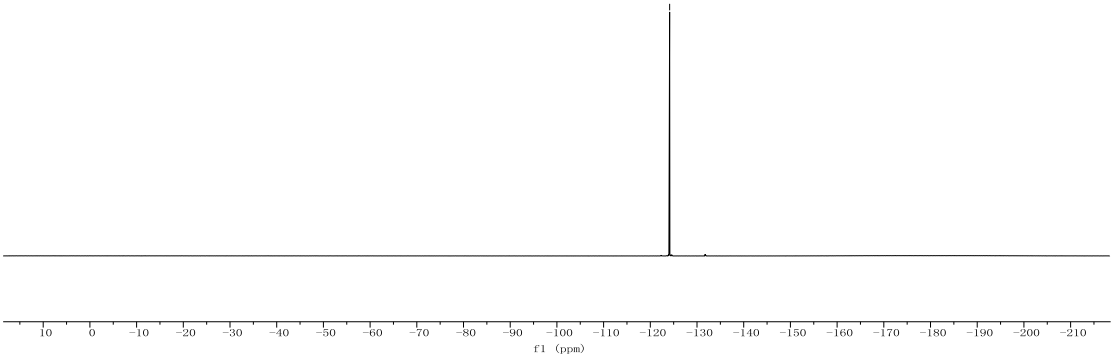

20190307-pqp-4174-2.
C13CPD CDCl3
168.062
156.519
153.991
152.553
143.855
142.656
138.339
134.763
133.370
133.206
127.996
126.818
126.739
126.276
125.605
123.163
122.889
122.287
122.094
120.995
120.960
30.441
NO2
N
O
S
O
F
1j
f1 (ppm)

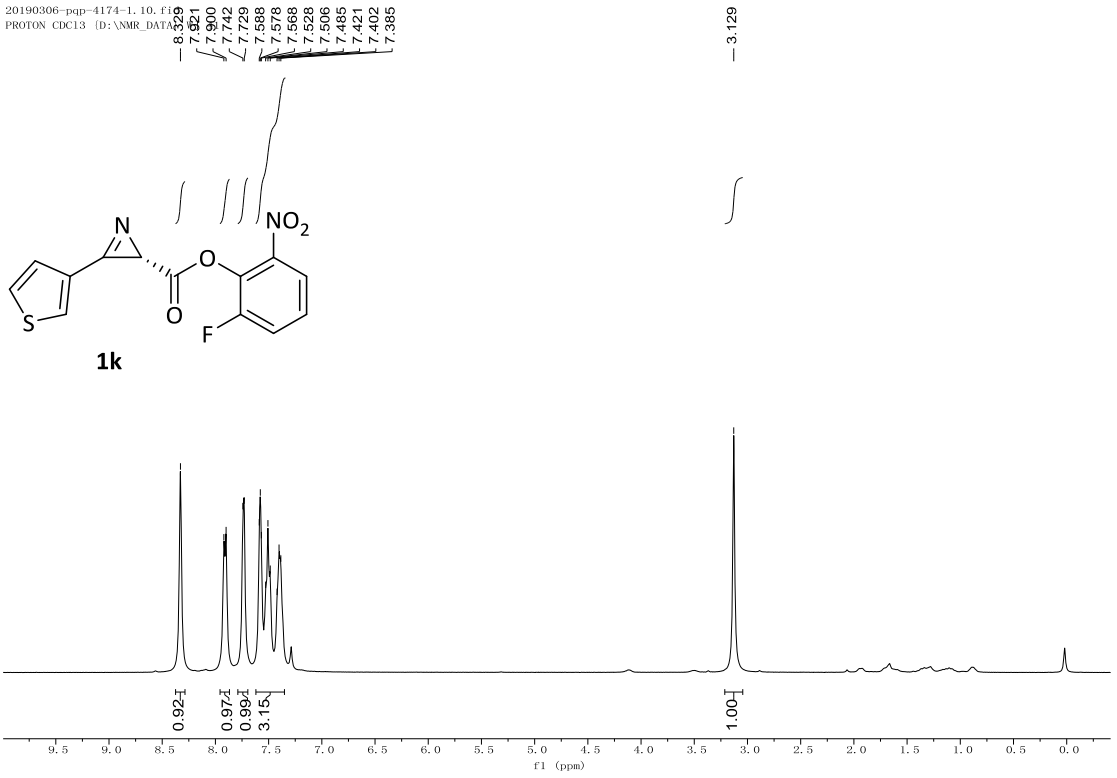
20190308-pqp-4074-2.10.fid
F19CPD CDCl3 (D:\NMR_DATA) WJ 8



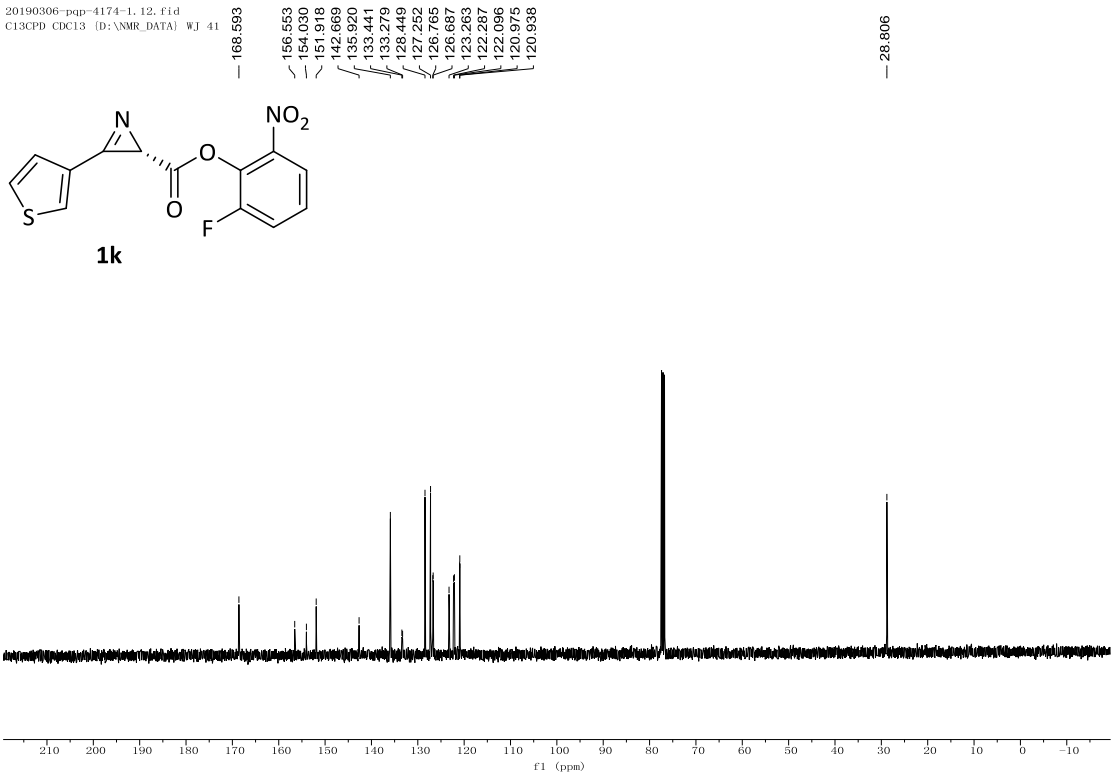
1j

-124.141



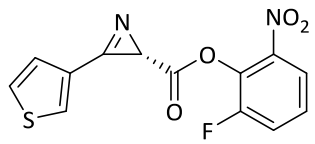

20190306-pqp-4174-1.10.fid
PROTON CDC13 (D:\NMR_DATA)
8.329
7.921
7.900
7.742
7.729
7.588
7.578
7.568
7.528
7.506
7.485
7.421
7.402
7.385
3.129
N
O
NO2
O
S
O
F
0.92
0.97
0.99
3.15
1.00
f1 (ppm)

1k


20190306-pqp-4174-1.12.fid
C13CPD CDC13 (D:\NMR_DATA) WJ 41
168.593
156.553
154.030
151.918
142.669
135.920
133.441
133.279
128.449
127.252
126.765
126.687
123.263
122.287
122.096
120.975
120.938
28.806
N
O
NO2
O
S
O
F
f1 (ppm)

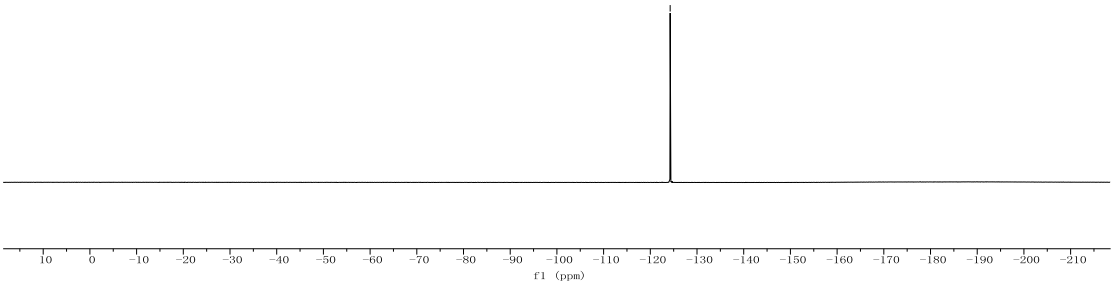
1k

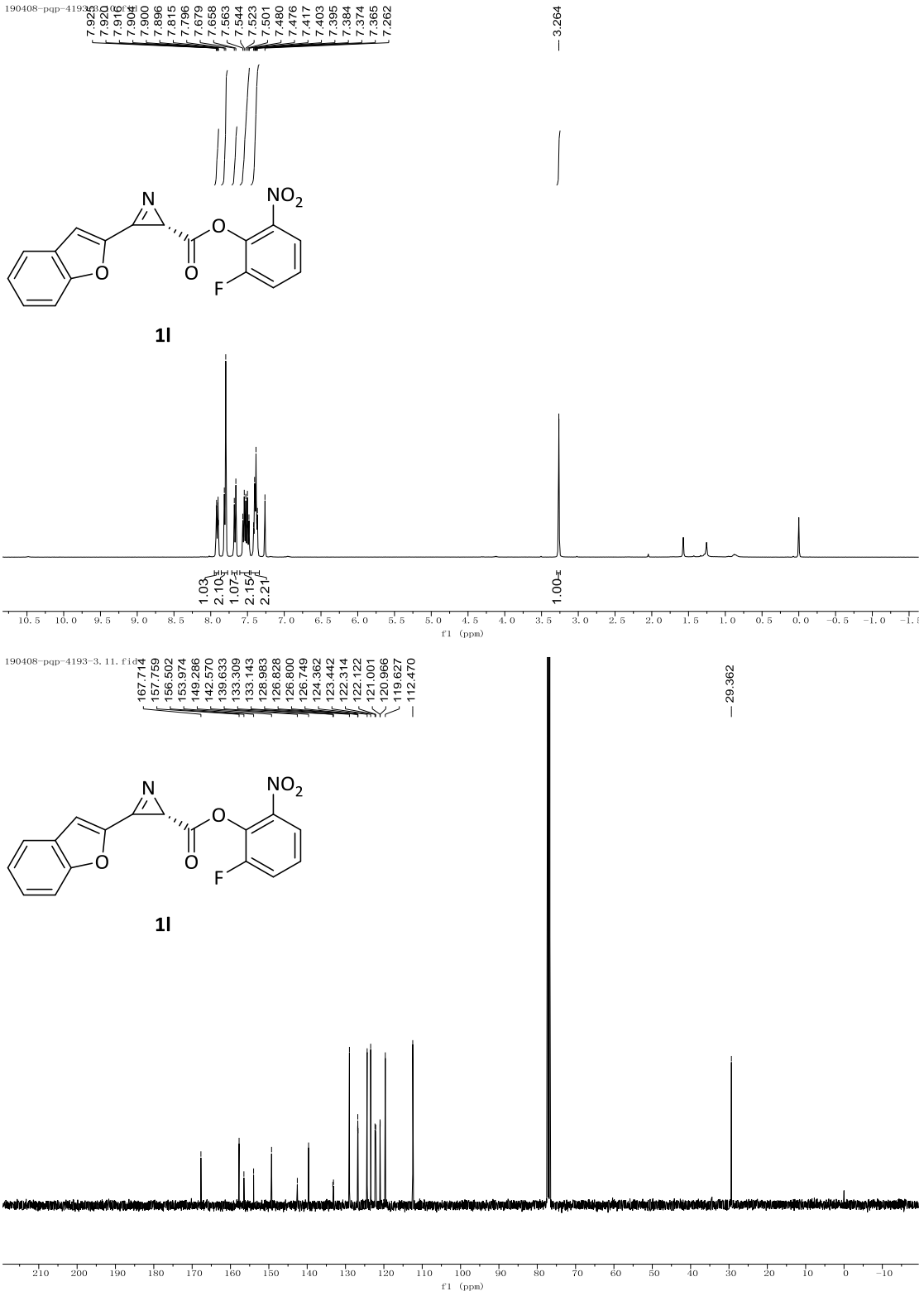
20190306-pqp-4174-1.11.fid
F19CPD CDC13 (D:\NMR_DATA) WJ 41



1k

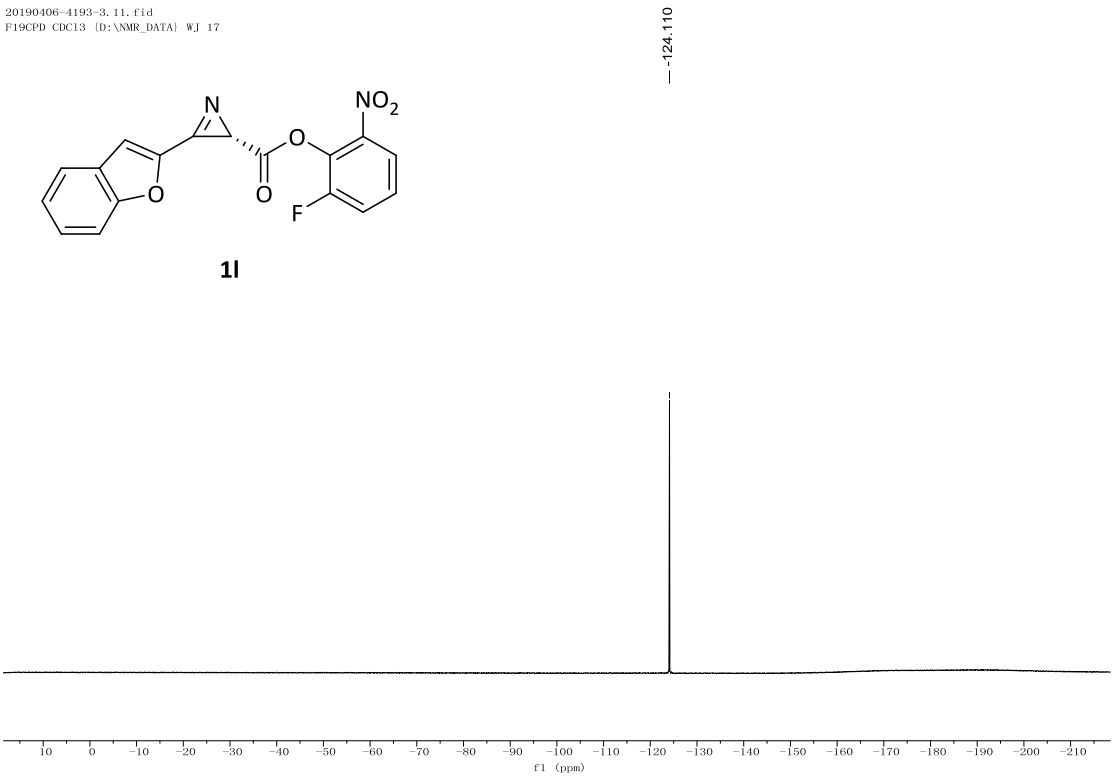
-124.250

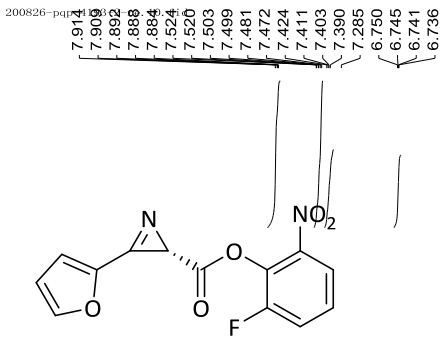



190408-pqp-4193-3.11.fid
7.925
7.920
7.916
7.904
7.900
7.896
7.815
7.796
7.679
7.658
7.563
7.544
7.523
7.501
7.480
7.476
7.417
7.403
7.395
7.384
7.374
7.365
7.262
3.264
N
O
O
O
NO2
F
1l
1.03
2.10
1.07
2.15
2.21
1.00
f1 (ppm)
190408-pqp-4193-3.11.fid
167.714
157.759
156.502
153.974
149.286
142.570
139.633
133.309
133.143
128.983
126.828
126.800
126.749
124.362
123.442
122.314
122.122
121.001
120.966
119.627
112.470
29.362
N
O
O
O
NO2
F
1l
f1 (ppm)

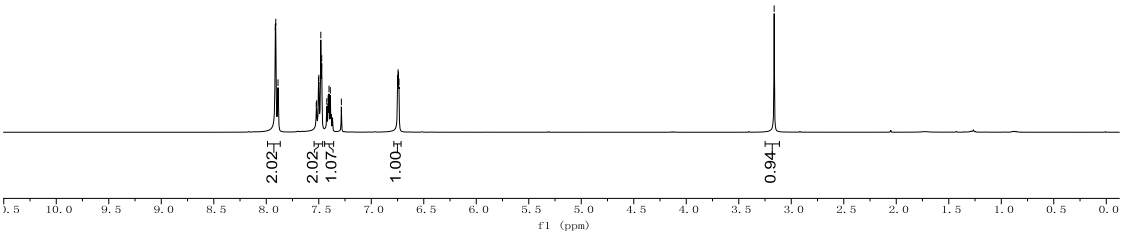
20190406-4193-3.11.fid
F19CPD CDCl3 (D:\NMR_DATA) WJ 17

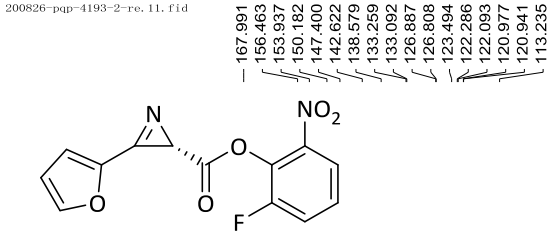
1l



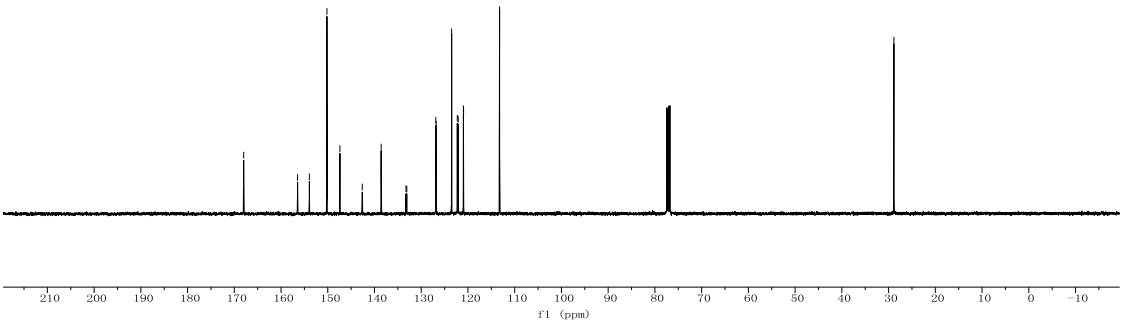

7.914
7.909
7.892
7.888
7.884
7.524
7.520
7.503
7.499
7.481
7.472
7.424
7.411
7.403
7.390
7.285
6.750
6.745
6.741
6.736
3.163
N
O
O
NO2
O
F

1m

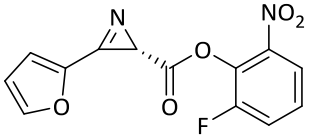

2.02
2.02
1.07
1.00
0.94
f1 (ppm)


200826-pqp-4193-2-re.11.fid
167.991
156.463
153.937
150.182
147.400
142.622
138.579
133.259
133.092
126.887
126.808
123.494
122.286
122.093
120.977
120.941
113.235
28.858
N
O
O
NO2
O
F

1m

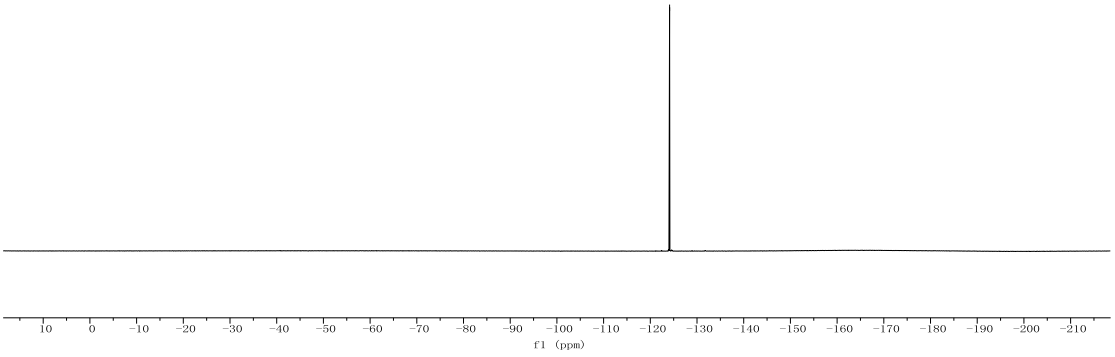

f1 (ppm)

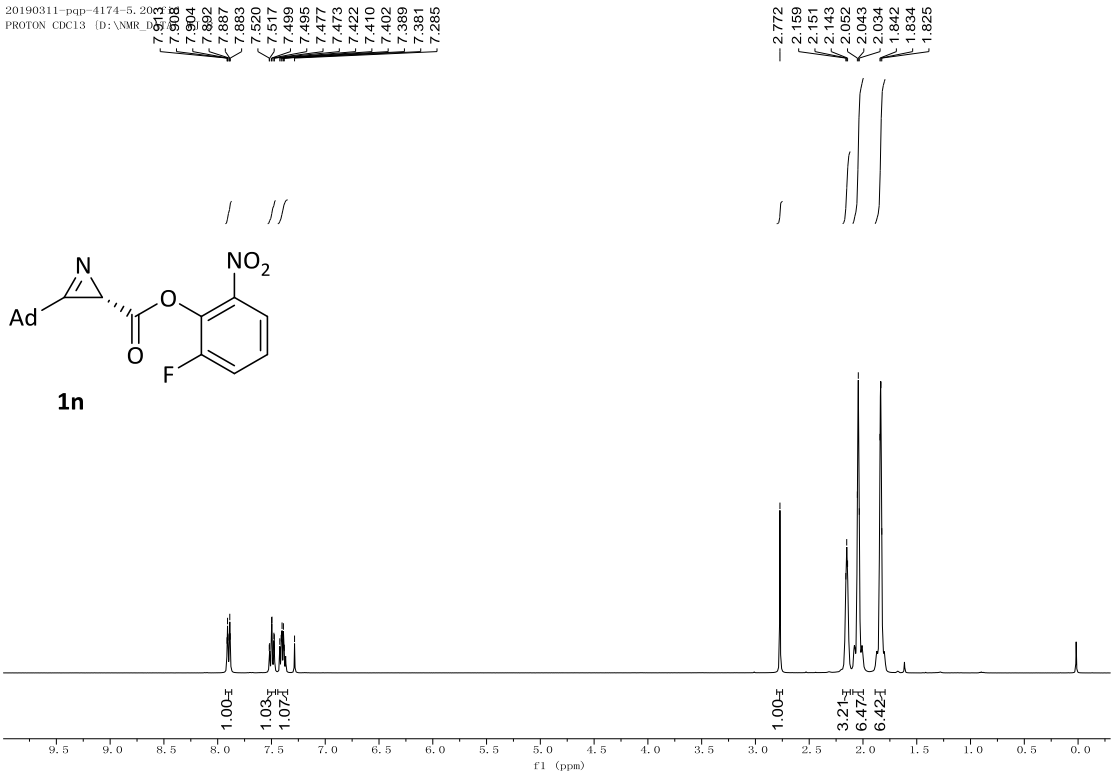
20190405-pqp-4193-2.11.fid
F19CPD CDCl3 (D:\NMR_DATA) WJ 47

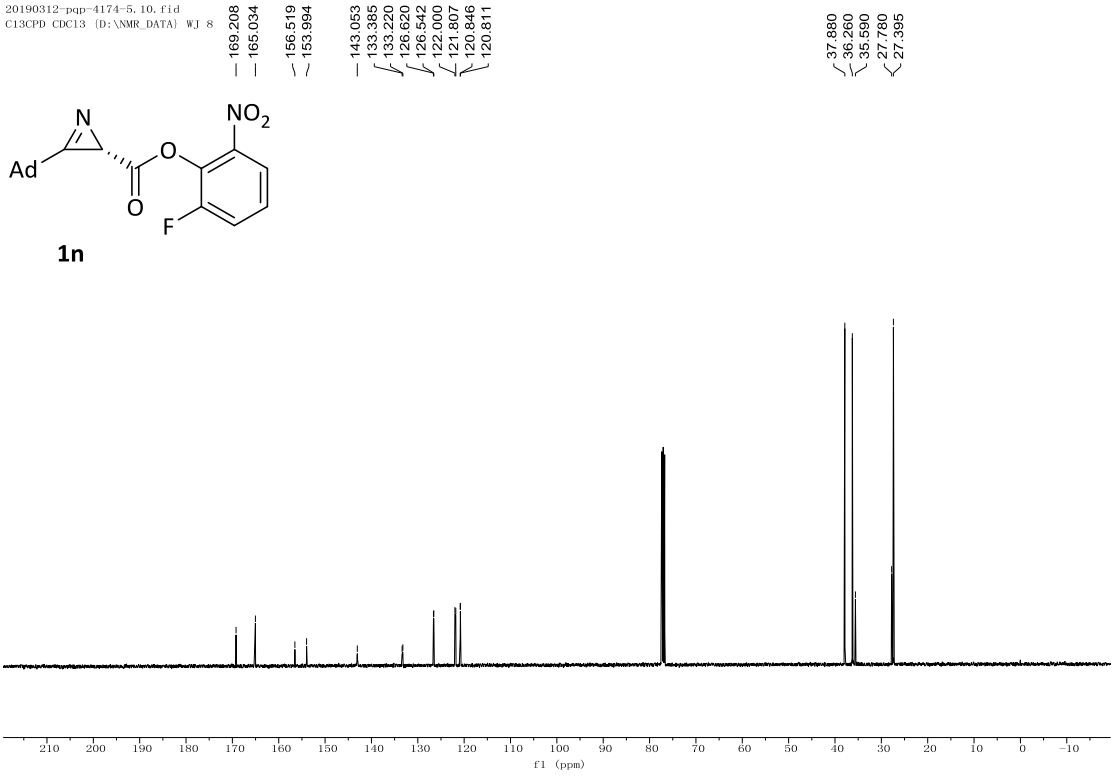


1m

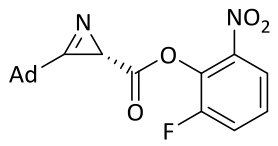
-124.128




PROTON CDC13 [D:\NMR_DATA] WJ 8
7.913
7.908
7.904
7.892
7.887
7.883
7.520
7.517
7.499
7.495
7.477
7.473
7.422
7.410
7.402
7.389
7.381
7.285
2.772
2.159
2.151
2.143
2.052
2.043
2.034
1.842
1.834
1.825
N
Ad
O
O
NO2
F
1n
1.00
1.03
1.07
1.00
3.21
6.47
6.42
f1 (ppm)

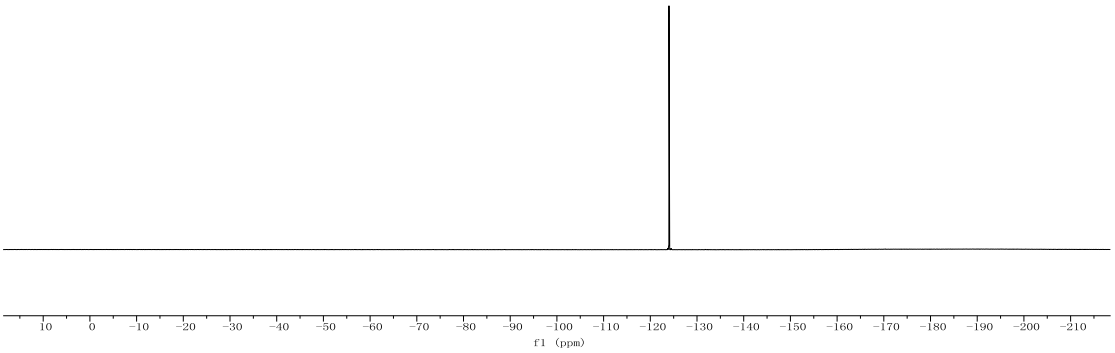

20190312-pqp-4174-5.10.fid
C13CPD CDC13 [D:\NMR_DATA] WJ 8
169.208
165.034
156.519
153.994
143.053
133.385
133.220
126.620
126.542
122.000
121.807
120.846
120.811
37.880
36.260
35.590
27.780
27.395
N
Ad
O
O
NO2
F
1n
f1 (ppm)

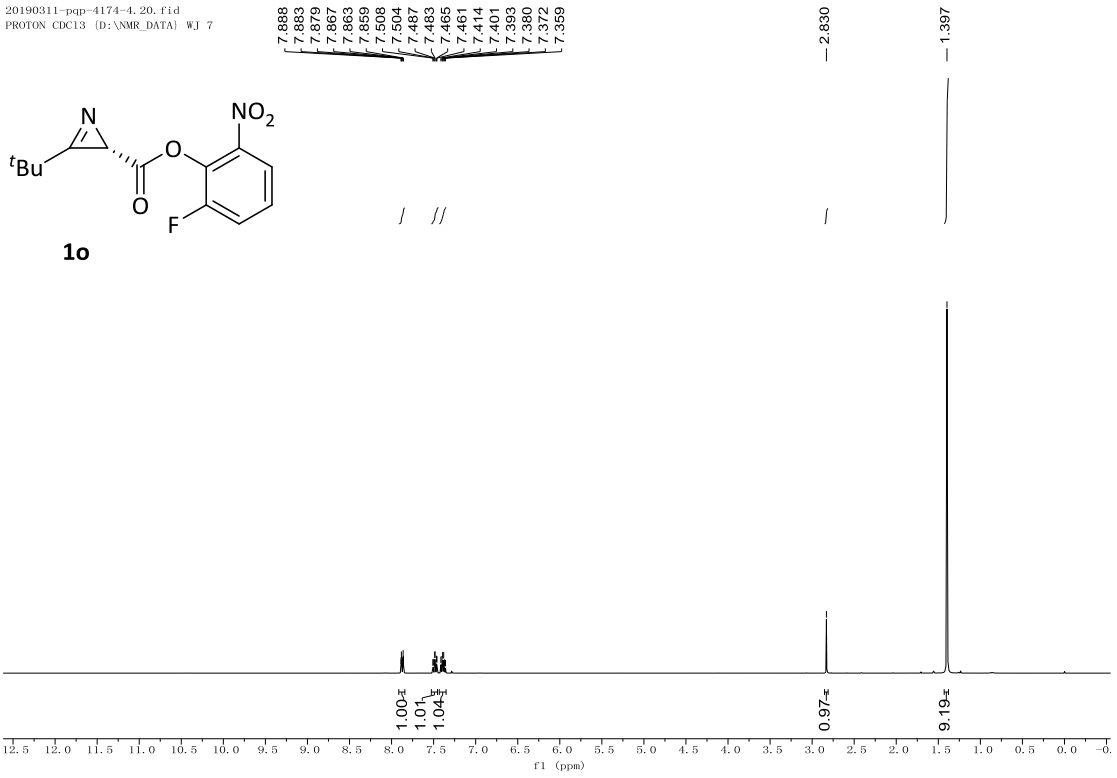
20190311-pqp-4174-5.21.fid
F19CPD CDCl3 (D:\NMR_DATA) WJ 8



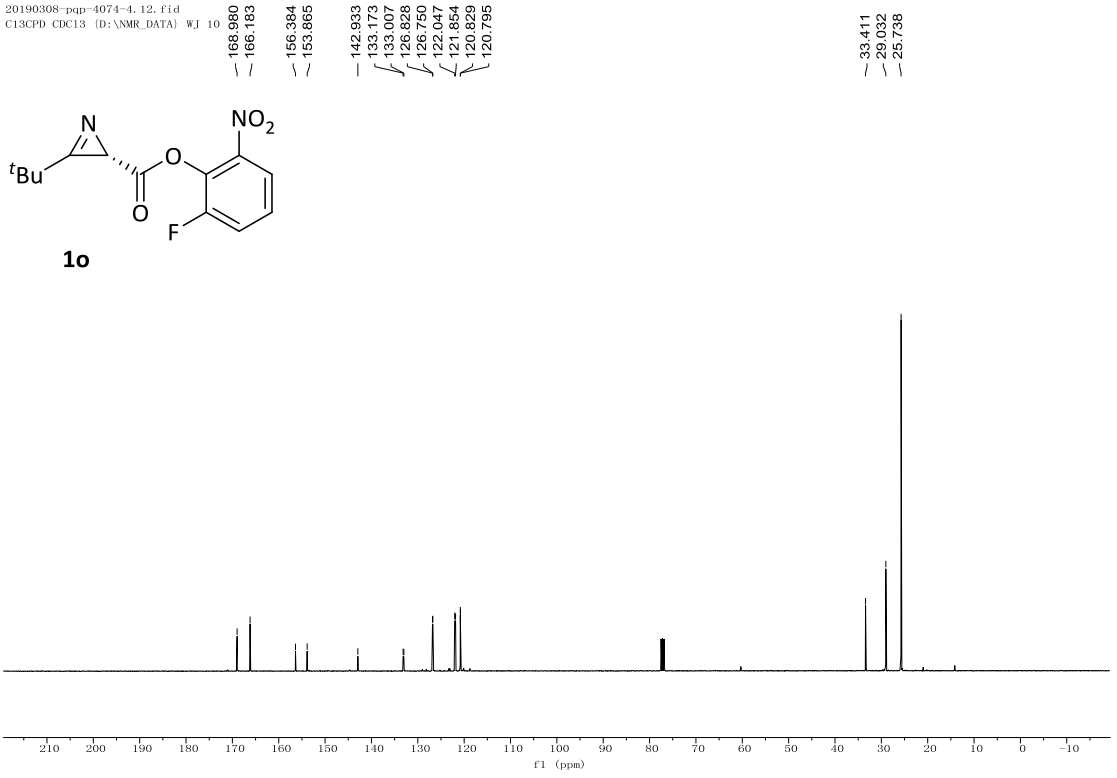
1n

-123.994



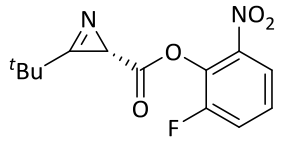

20190311-pqp-4174-4.20.fid
PROTON CDCl3 (D:\NMR_DATA) WJ 7
7.888
7.883
7.879
7.867
7.863
7.859
7.508
7.504
7.487
7.483
7.465
7.461
7.414
7.401
7.393
7.380
7.372
7.359
2.830
1.397
N
tBu
O
O
NO2
F
1.00
1.01
1.04
0.97
9.19
f1 (ppm)

1o


20190308-pqp-4074-4.12.fid
C13CPD CDCl3 (D:\NMR_DATA) WJ 10
168.980
166.183
156.384
153.865
142.933
133.173
133.007
126.828
126.750
122.047
121.854
120.829
120.795
33.411
29.032
25.738
N
tBu
O
O
NO2
F
f1 (ppm)

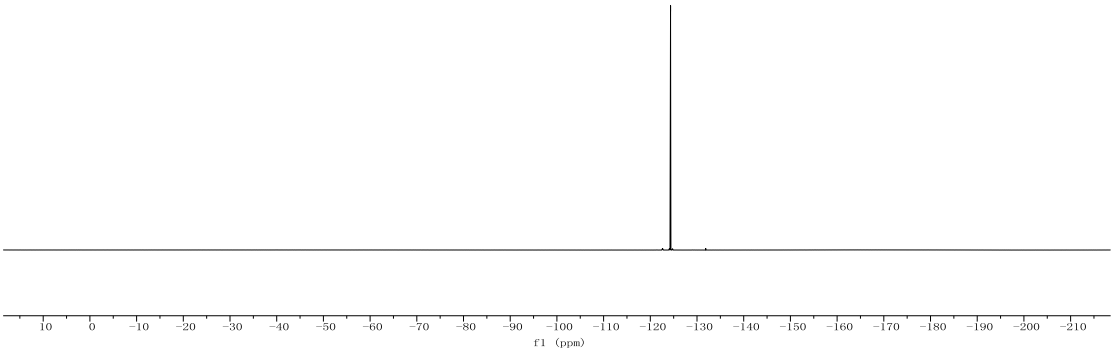
1o

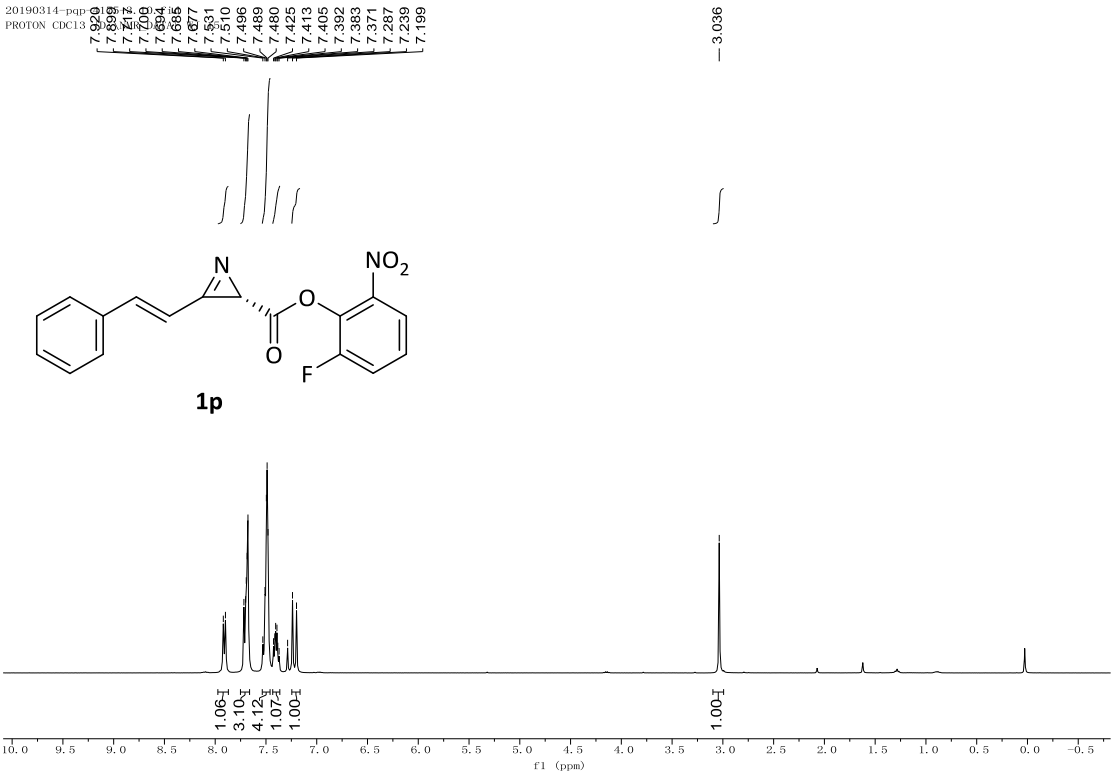
20190311-pqp-4174-4.21.fid
F19CPD CDCl3 (D:\NMR_DATA) WJ 7

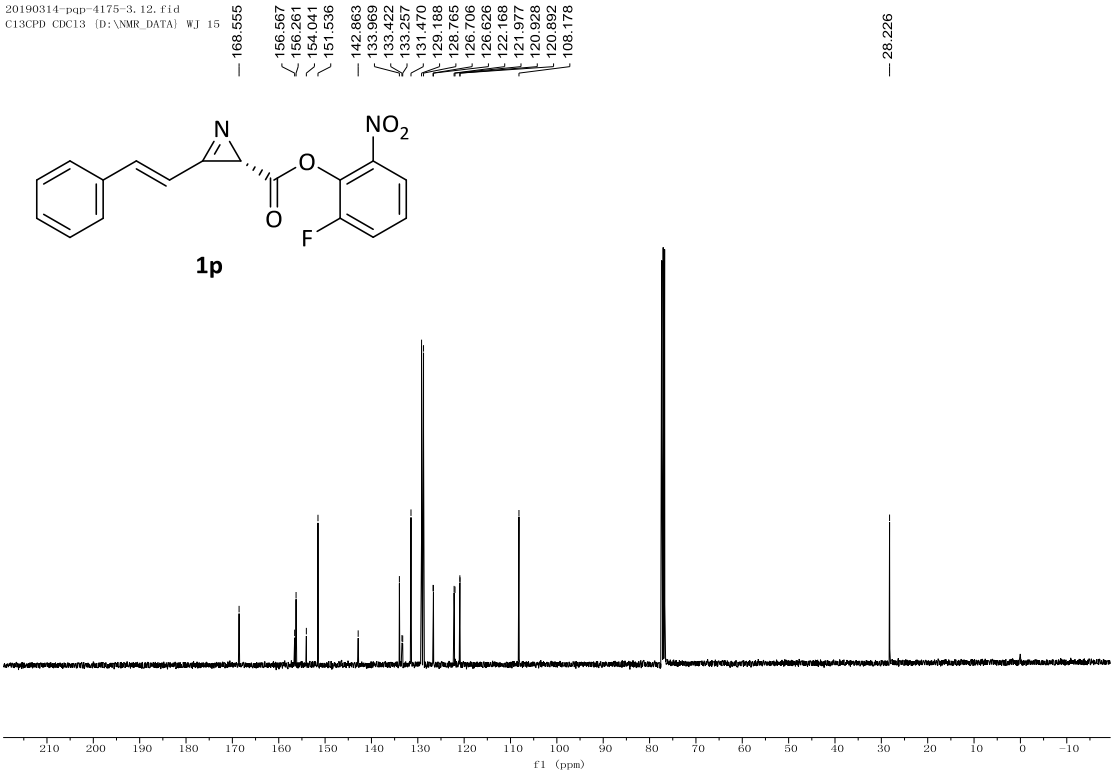


1o

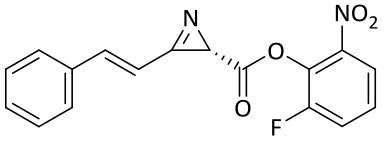
-124.331




20190314-pqp-4175-3.12.fid
PROTON CDC13 {D:\NMR_DATA} WJ 15
7.920
7.899
7.717
7.709
7.694
7.685
7.677
7.531
7.510
7.496
7.489
7.480
7.425
7.413
7.405
7.392
7.383
7.371
7.287
7.239
7.199
3.036
N
O
O
NO2
F
1p
1.06
3.10
4.12
1.07
1.00
1.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

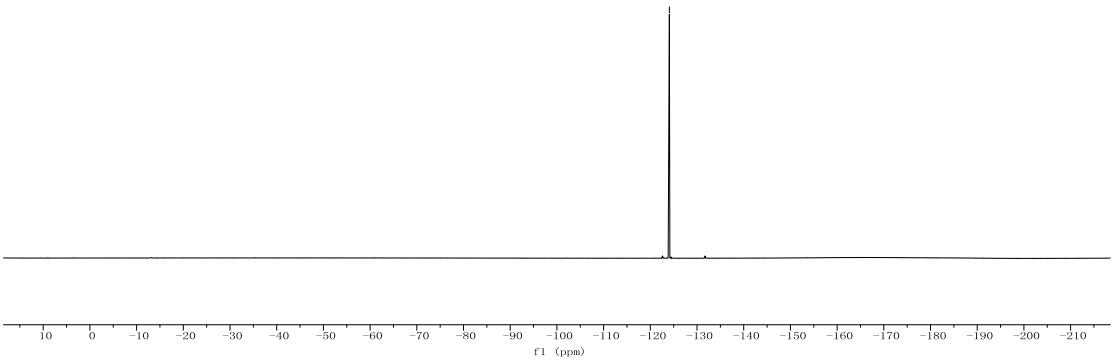

20190314-pqp-4175-3.12.fid
C13CPD CDC13 {D:\NMR_DATA} WJ 15
168.555
156.567
156.261
154.041
151.536
142.863
133.969
133.422
133.257
131.470
129.188
128.765
126.706
126.626
122.168
121.977
120.928
120.892
108.178
28.226
N
O
O
NO2
F
1p
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

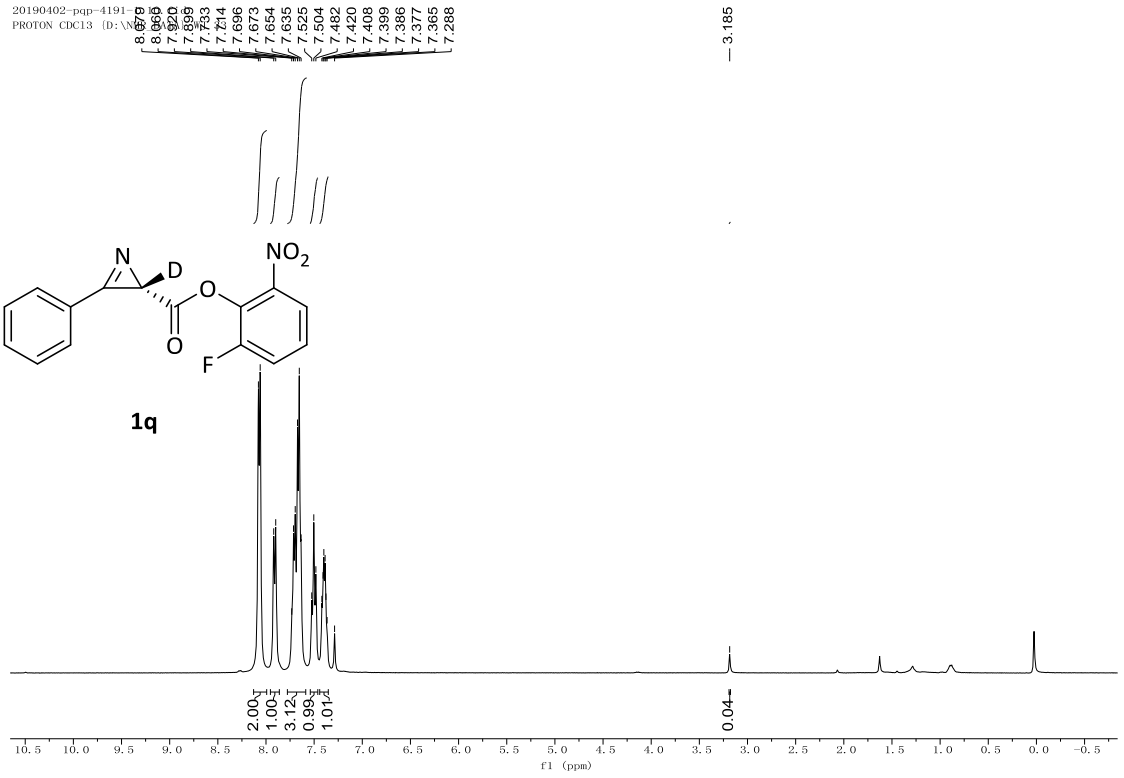
20190314-pqp-4175-3.13.fid
F19CPD CDCl3 (D:\NMR_DATA) WJ 15



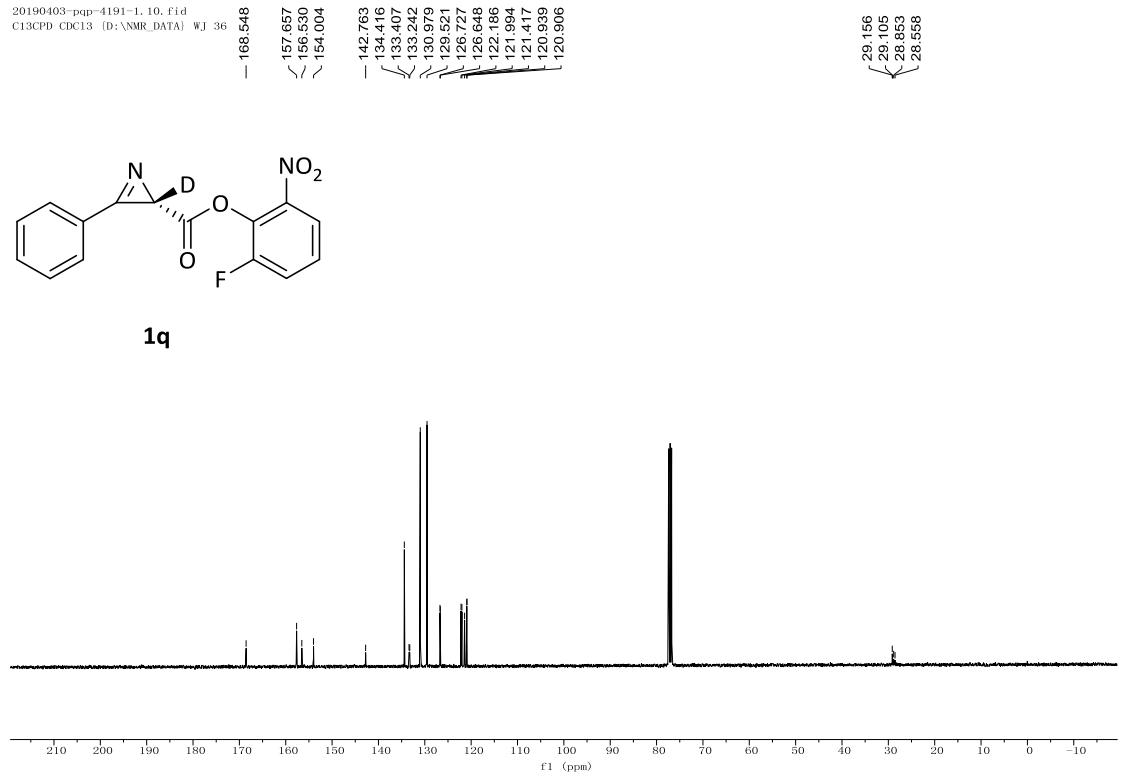
1p

-124.079



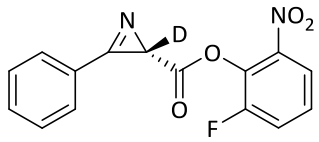

20190402-pqp-4191-
PROTON CDC13 {D:\
8.677
8.666
7.920
7.899
7.733
7.714
7.696
7.673
7.654
7.635
7.525
7.504
7.482
7.420
7.408
7.399
7.386
7.377
7.365
7.288
3.185
N
D
O
O
NO2
O
F
2.00
1.00
3.12
0.99
1.01
0.04
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

1q


20190403-pqp-4191-1.10.fid
C13CPD CDC13 {D:\NMR_DATA} WJ 36
168.548
157.657
156.530
154.004
142.763
134.416
133.407
133.242
130.979
129.521
126.727
126.648
122.186
121.994
121.417
120.939
120.906
29.156
29.105
28.853
28.558
N
D
O
O
NO2
O
F
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

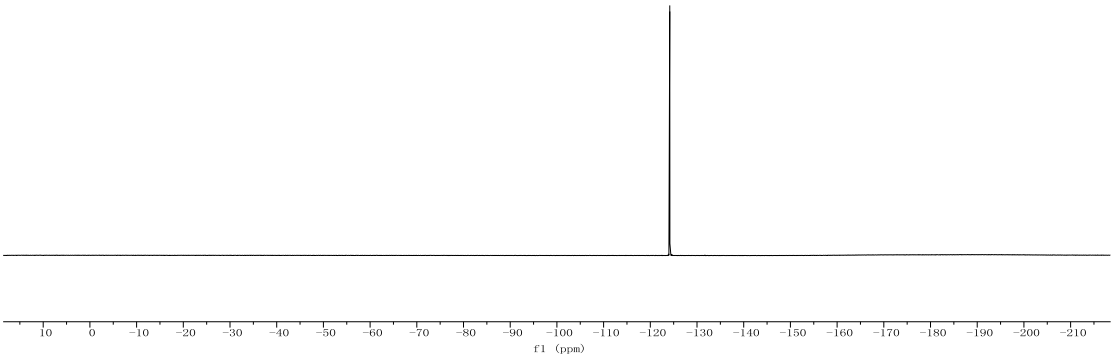
1q

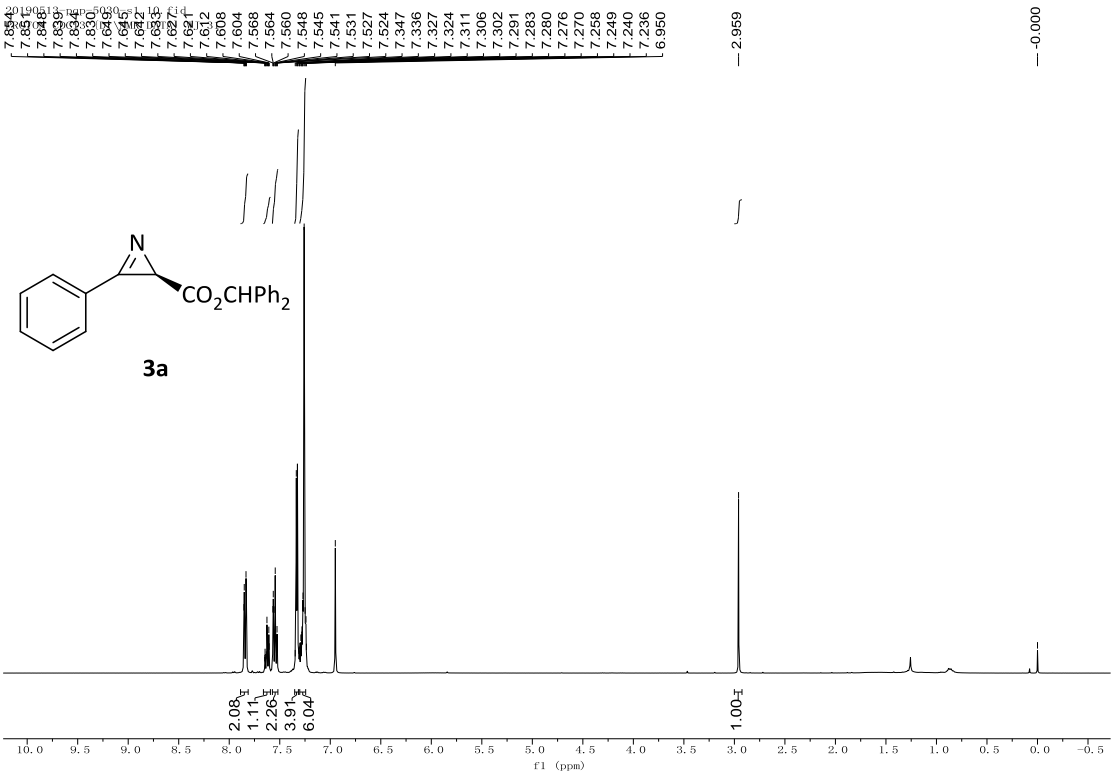
20190402-pqp-4191-1.11.fid
F19CPD CDCl3 (D:\NMR_DATA) WJ 33

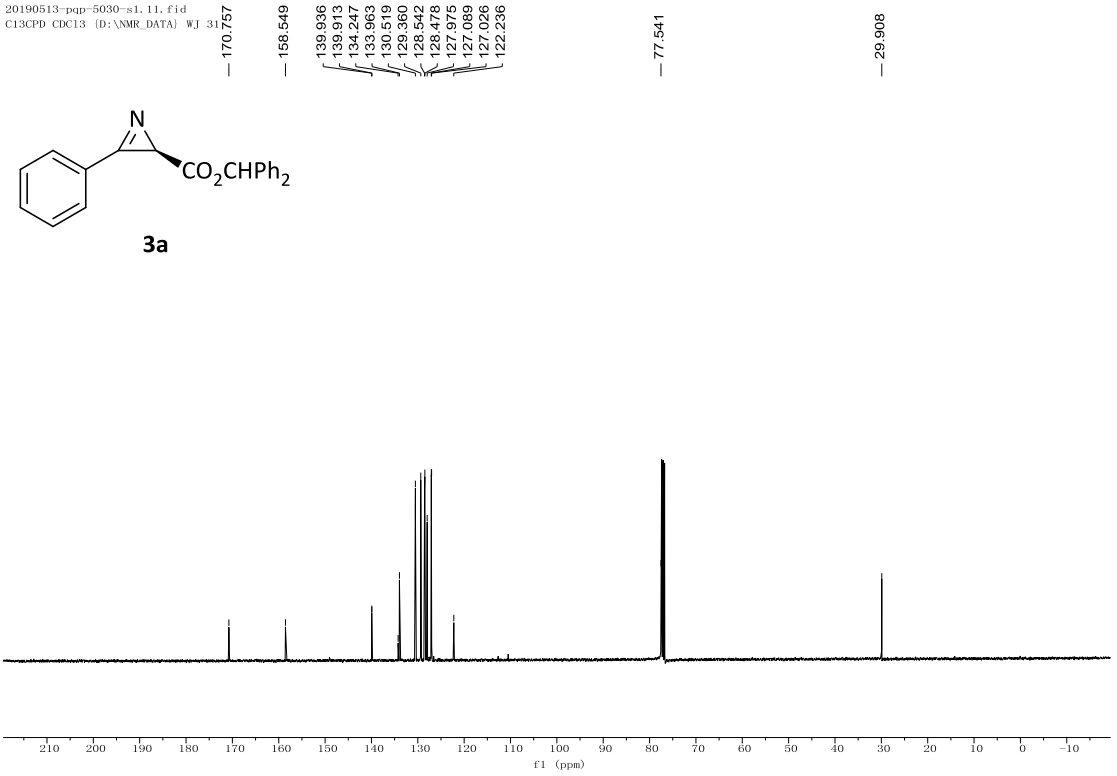


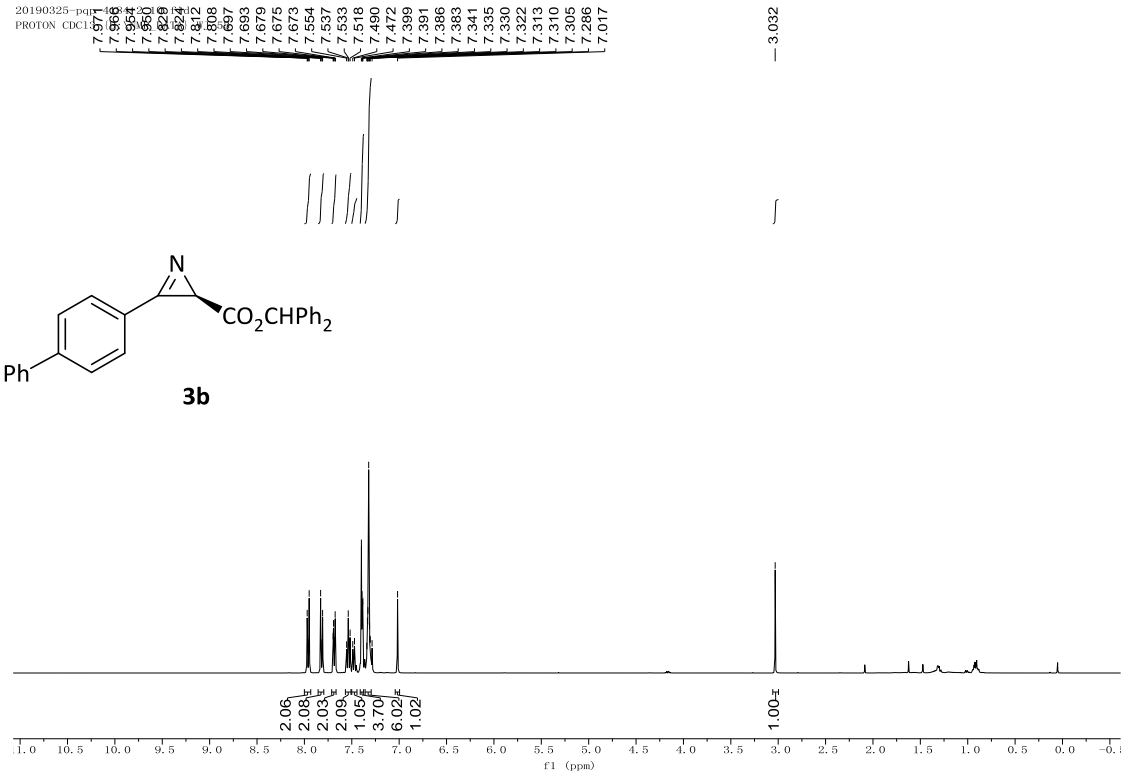
1q

-124.166

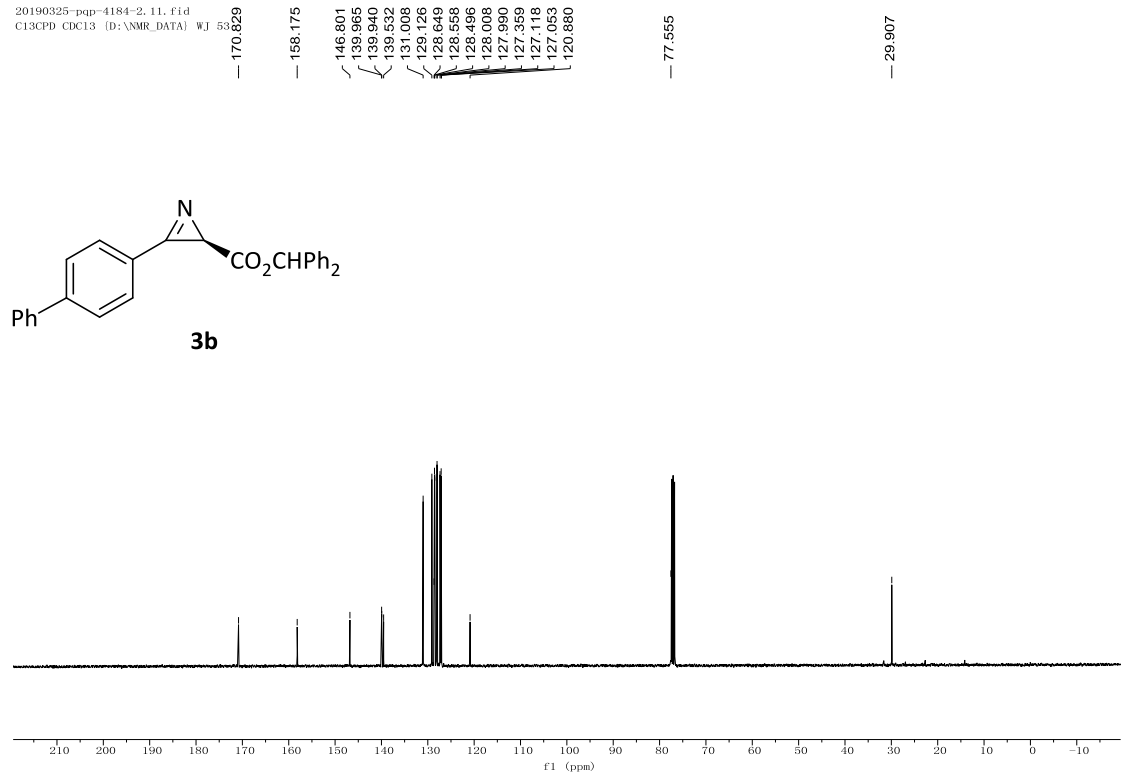



7.954
7.851
7.848
7.839
7.836
7.830
7.649
7.645
7.642
7.633
7.627
7.621
7.612
7.608
7.604
7.568
7.564
7.560
7.548
7.545
7.541
7.531
7.527
7.524
7.347
7.336
7.327
7.324
7.311
7.306
7.302
7.291
7.283
7.280
7.276
7.270
7.258
7.249
7.240
7.236
6.950
2.959
-0.000
N
CO2CHPh2
3a
2.08
1.11
2.26
3.91
6.04
1.00
f1 (ppm)

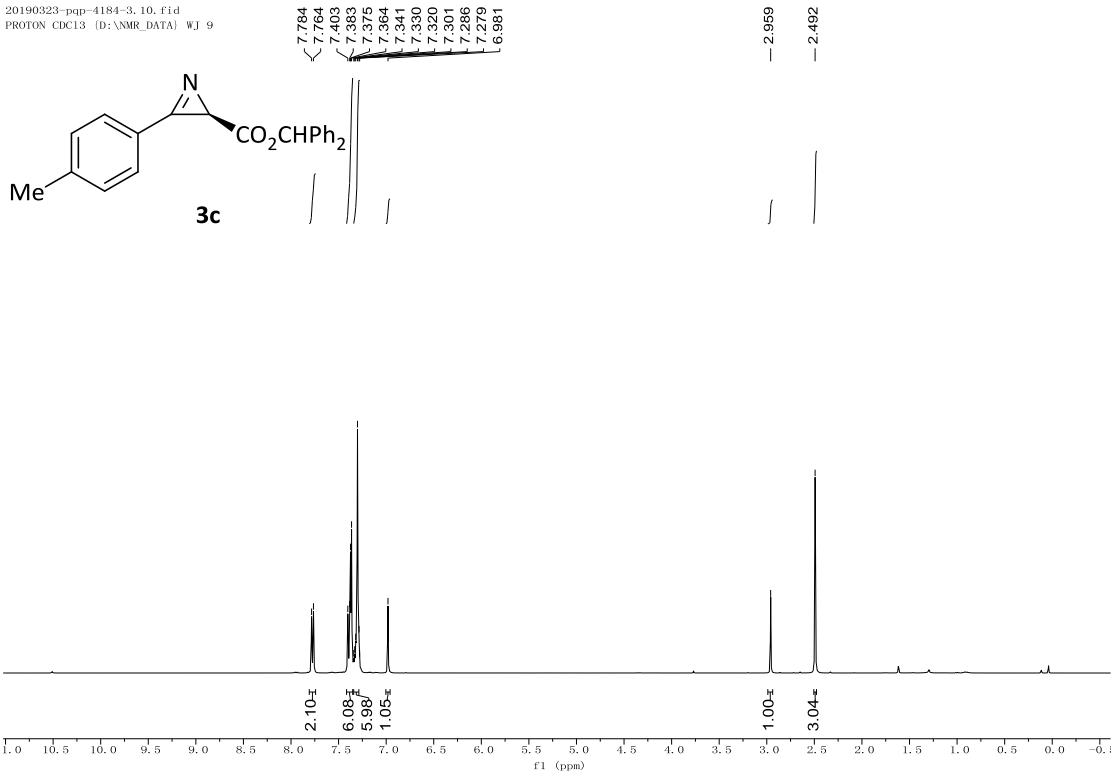

20190513-pqp-5030-s1.11.fid
C13CPD CDCl3 (D:\NMR_DATA) WJ 31
170.757
158.549
139.936
139.913
134.247
133.963
130.519
129.360
128.542
128.478
127.975
127.089
127.026
122.236
77.541
29.908
N
CO2CHPh2
3a
f1 (ppm)

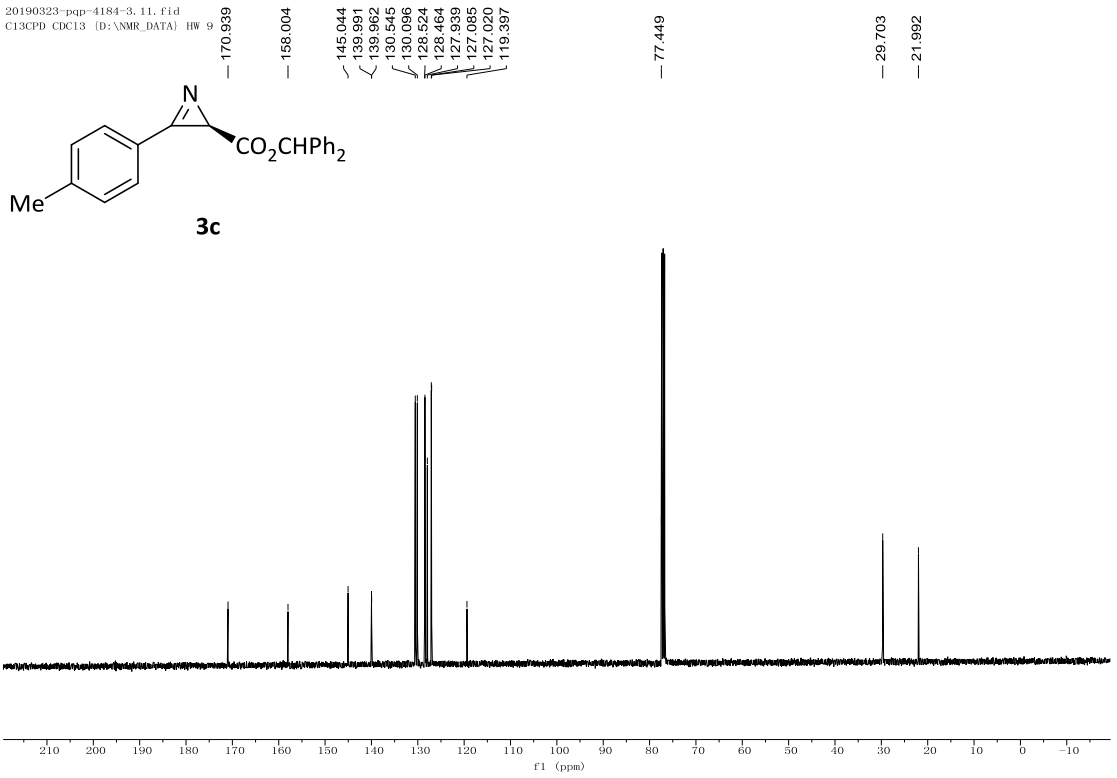

20190325-pqp-4184-2.10.fid
PROTON CDCl3 {D:\NMR_DATA} WJ 53
7.977
7.966
7.954
7.950
7.826
7.824
7.812
7.808
7.697
7.693
7.679
7.675
7.673
7.554
7.537
7.533
7.518
7.490
7.472
7.399
7.391
7.386
7.383
7.341
7.335
7.330
7.322
7.313
7.310
7.305
7.286
7.017
3.032
N
CO2CHPh2
Ph
2.06
2.08
2.03
2.09
1.05
3.70
6.02
1.02
1.00
f1 (ppm)

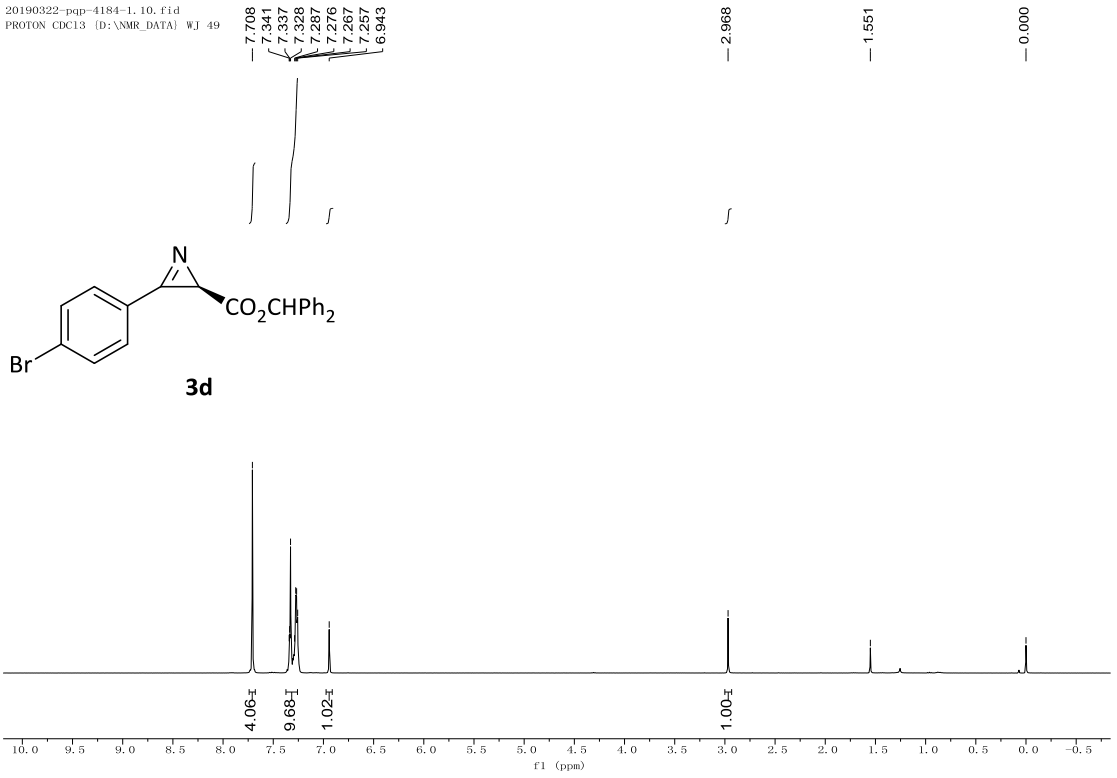
3b

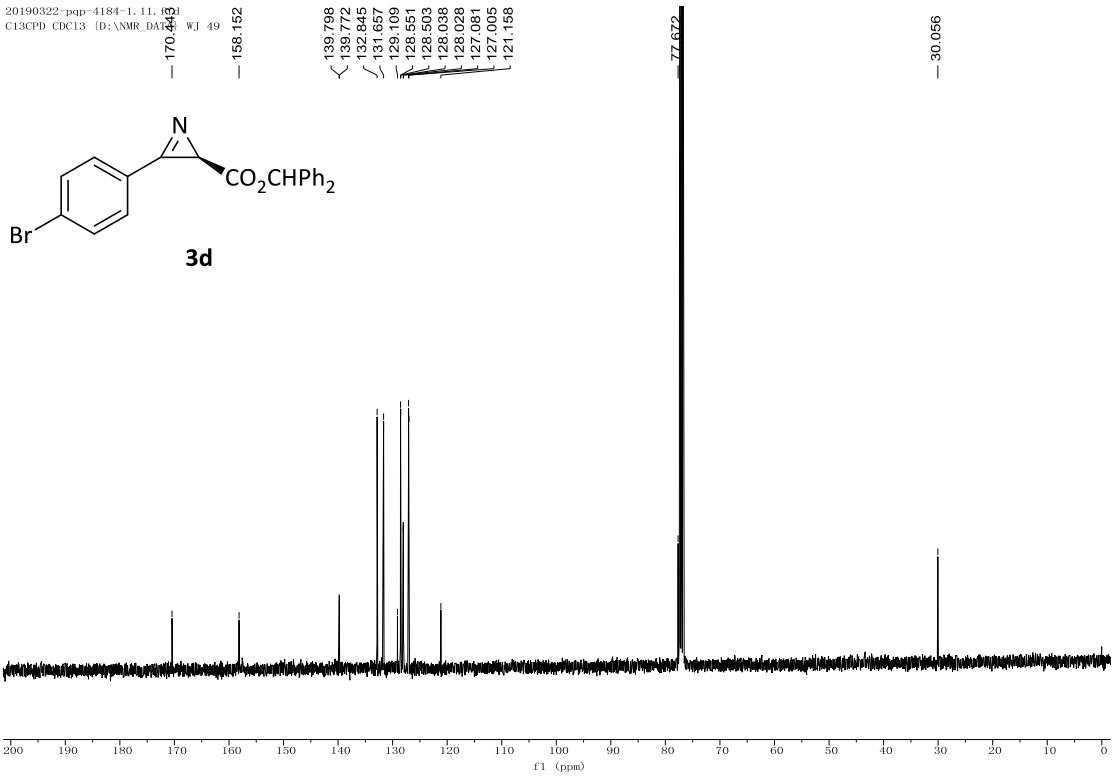

20190325-pqp-4184-2.11.fid
C13CPD CDCl3 {D:\NMR_DATA} WJ 53
170.829
158.175
146.801
139.965
139.940
139.532
131.008
129.126
128.649
128.558
128.496
128.008
127.990
127.359
127.118
127.053
120.880
77.555
29.907
N
CO2CHPh2
Ph
f1 (ppm)

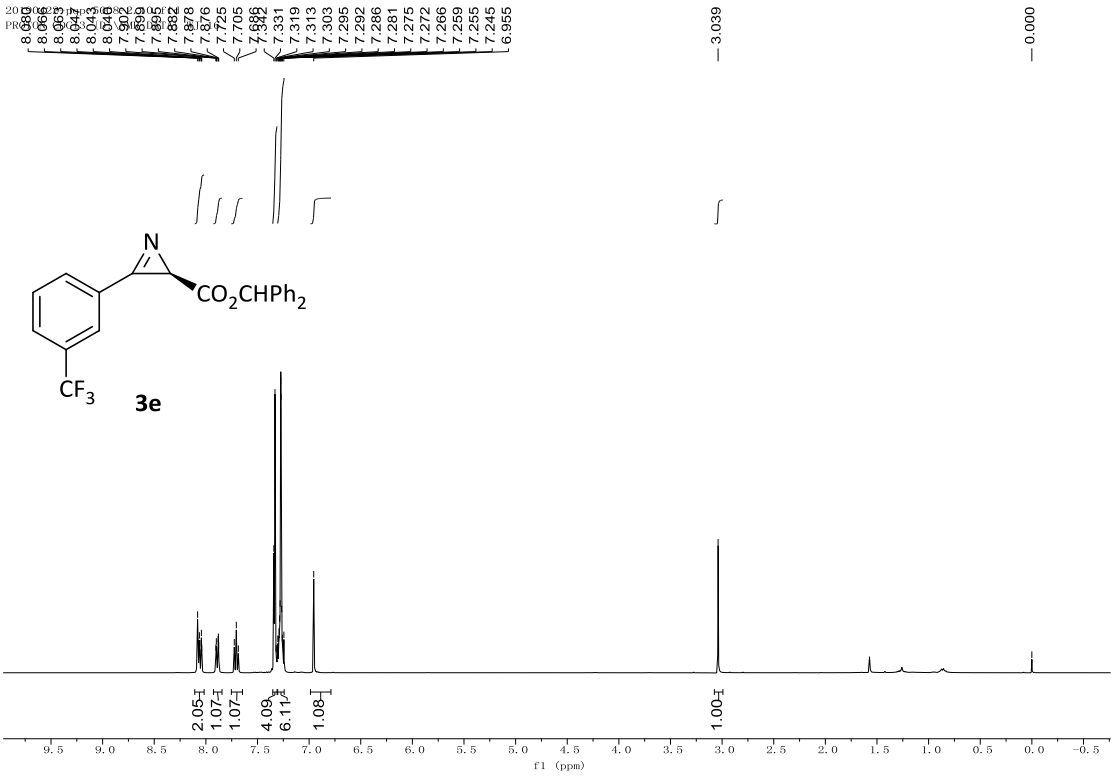
3b

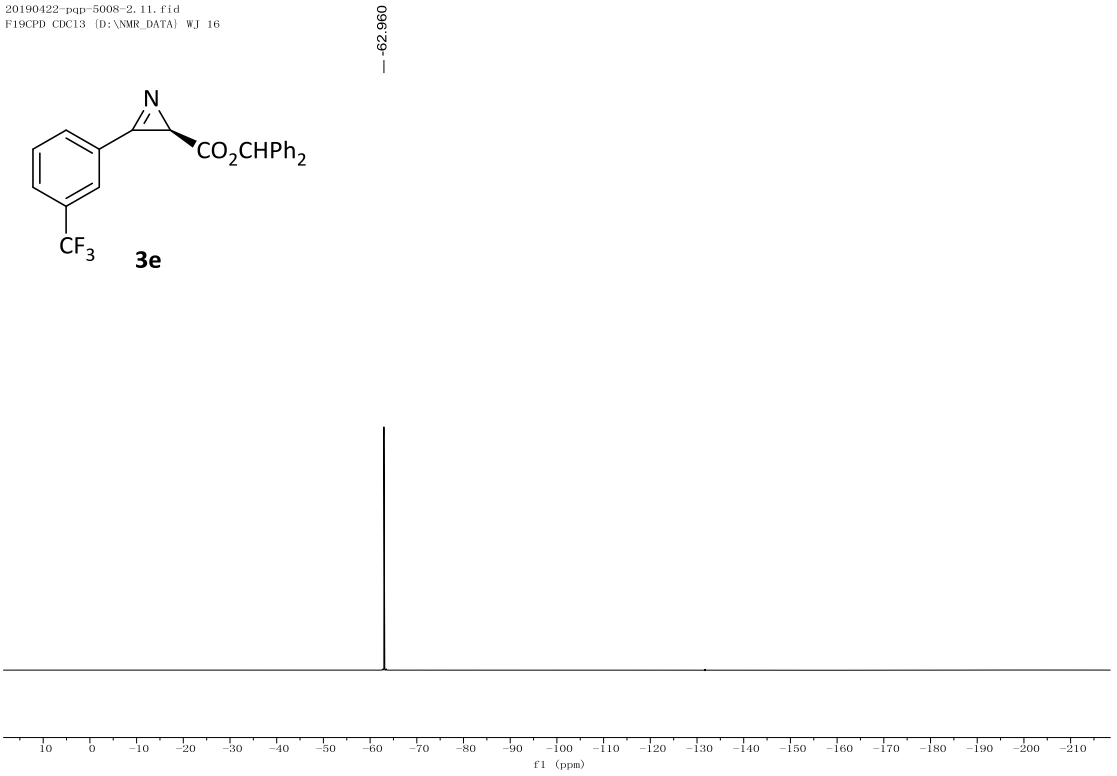

20190323-pqp-4184-3.10.fid
PROTON CDC13 (D:\NMR_DATA) WJ 9
7.784
7.764
7.403
7.383
7.375
7.364
7.341
7.330
7.320
7.301
7.286
7.279
6.981
2.959
2.492
N
CO2CHPh2
Me
3c
2.10
6.08
5.98
1.05
1.00
3.04
f1 (ppm)

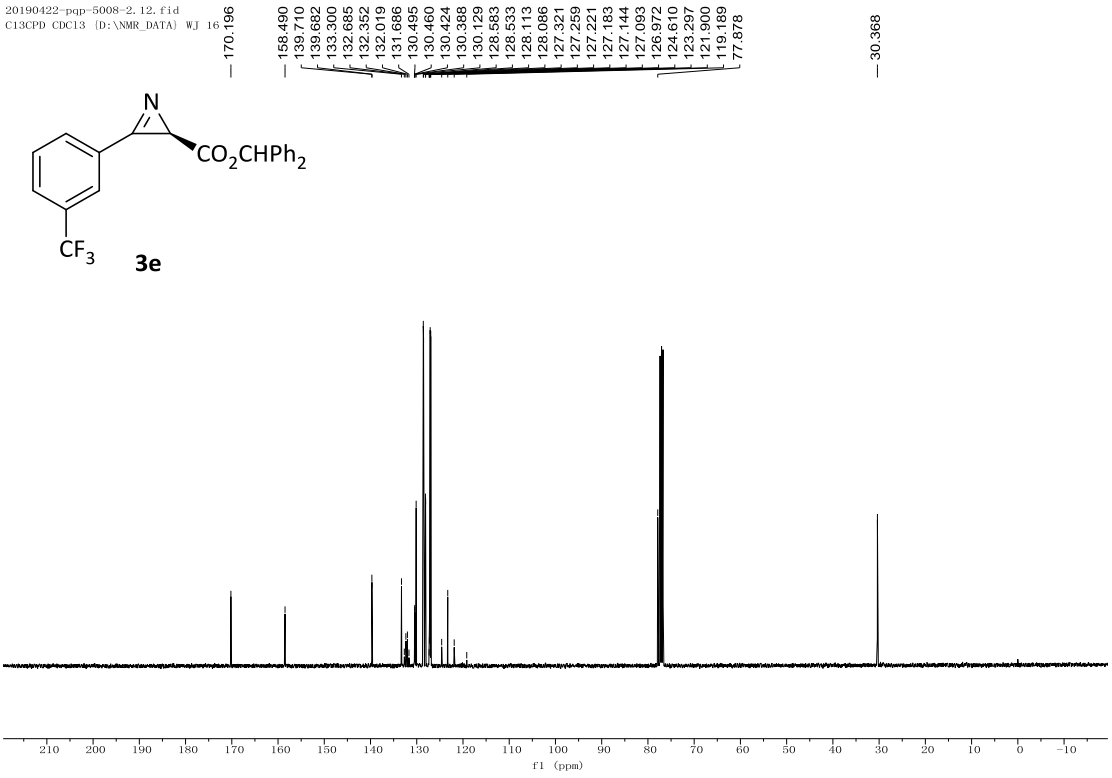

20190323-pqp-4184-3.11.fid
C13CPD CDC13 (D:\NMR_DATA) HW 9
170.939
158.004
145.044
139.991
139.962
130.545
130.096
128.524
128.464
127.939
127.085
127.020
119.397
77.449
29.703
21.992
N
CO2CHPh2
Me
3c
f1 (ppm)

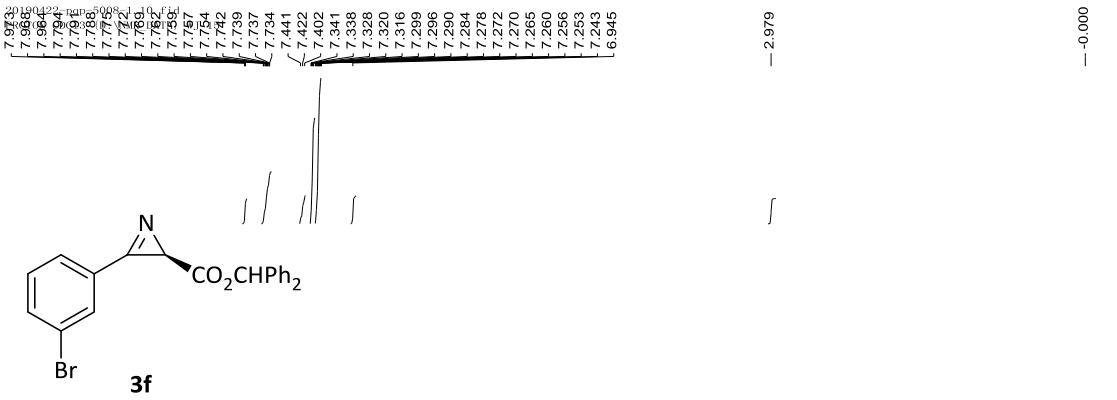

20190322-pqp-4184-1.10.fid
PROTON CDC13 (D:\NMR_DATA) WJ 49
7.708
7.341
7.337
7.328
7.287
7.276
7.267
7.257
6.943
2.968
1.551
0.000
N
CO2CHPh2
Br
3d
4.06
9.68
1.02
1.00
f1 (ppm)

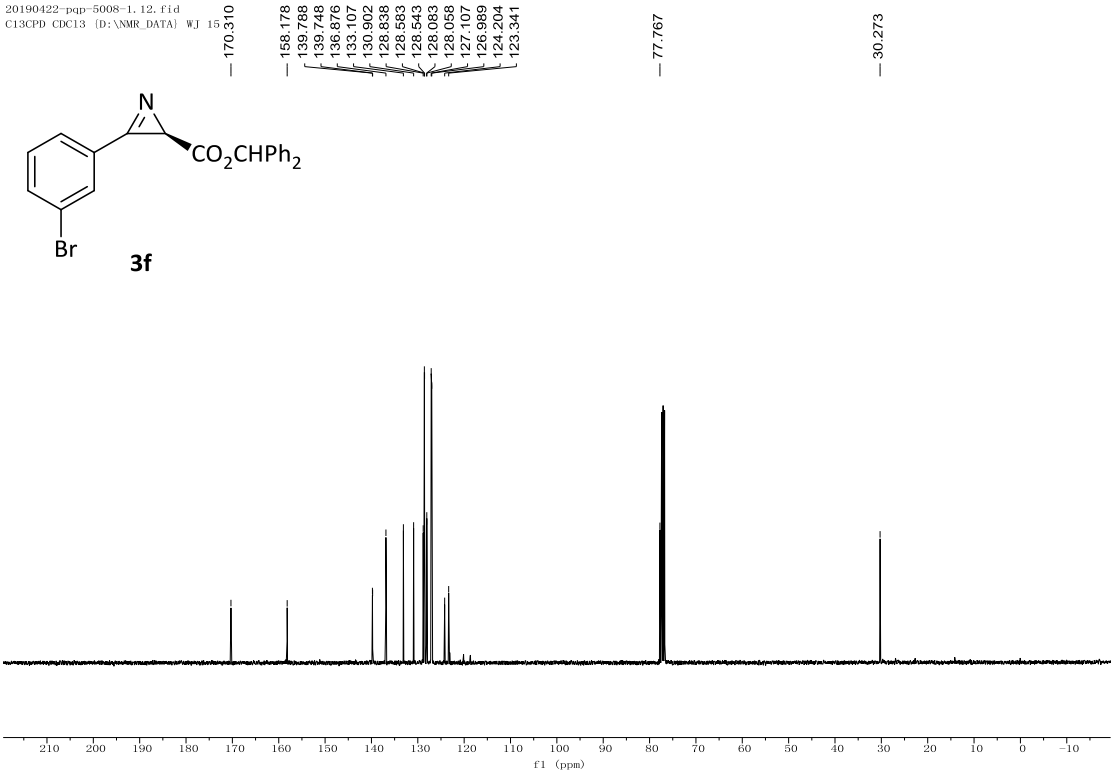

20190322-pqp-4184-1.11.fid
C13CPD CDC13 (D:\NMR_DATA) WJ 49
170.443
158.152
139.798
139.772
132.845
131.657
129.109
128.551
128.503
128.038
128.028
127.081
127.005
121.158
77.672
30.056
N
CO2CHPh2
Br
3d
f1 (ppm)

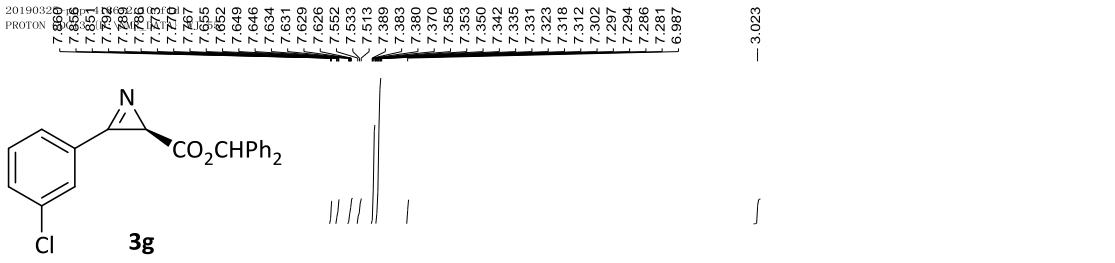

8.080
8.066
8.063
8.047
8.043
8.040
8.036
7.902
7.899
7.895
7.882
7.878
7.876
7.725
7.705
7.686
7.342
7.331
7.319
7.313
7.303
7.295
7.292
7.286
7.281
7.275
7.272
7.266
7.259
7.255
7.245
6.955
3.039
0.000
N
CO2CHPh2
CF3
3e
2.05
1.07
1.07
4.09
6.11
1.08
1.00
f1 (ppm)


20190422-pqp-5008-2.11.fid
F19CPD CDC13 (D:\NMR_DATA) WJ 16
-62.960
N
CO2CHPh2
CF3
3e
f1 (ppm)

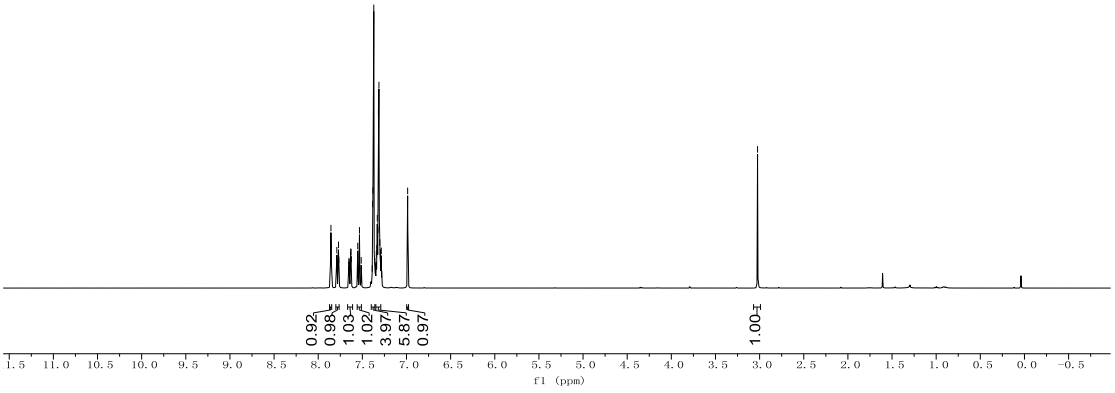

20190422-pqp-5008-2.12.fid
C13CPD CDCl3 (D:\NMR_DATA) WJ 16
170.196
158.490
139.710
139.682
133.300
132.685
132.352
132.019
131.686
130.495
130.460
130.424
130.388
130.129
128.583
128.533
128.113
128.086
127.321
127.259
127.221
127.183
127.144
127.093
126.972
124.610
123.297
121.900
119.189
77.878
30.368
N
CO2CHPh2
CF3
3e
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

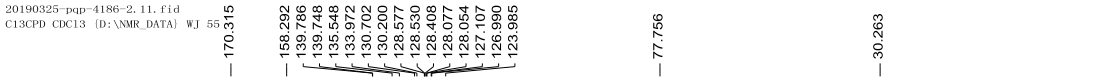

7.973
7.968
7.964
7.794
7.791
7.785
7.781
7.775
7.772
7.769
7.762
7.759
7.757
7.754
7.742
7.739
7.737
7.734
7.441
7.422
7.402
7.341
7.338
7.328
7.320
7.316
7.299
7.296
7.290
7.284
7.278
7.272
7.270
7.265
7.260
7.256
7.253
7.243
6.945
2.979
-0.000
N
CO2CHPh2
Br
3f
0.99
2.06
1.12
4.19
5.76
1.11
1.00
f1 (ppm)


20190422-pqp-5008-1.12.fid
C13CPD CDCl3 (D:\NMR_DATA) WJ 15
170.310
158.178
139.788
139.748
136.876
133.107
130.902
128.838
128.583
128.543
128.083
128.058
127.107
126.989
124.204
123.341
77.767
30.273
N
CO2CHPh2
Br
3f
f1 (ppm)


20190325
PROTON
7.660
7.655
7.651
7.792
7.789
7.786
7.773
7.770
7.767
7.655
7.652
7.649
7.646
7.634
7.631
7.629
7.626
7.552
7.533
7.513
7.389
7.383
7.380
7.370
7.358
7.353
7.350
7.342
7.335
7.331
7.323
7.318
7.312
7.302
7.297
7.294
7.286
7.281
6.987
3.023
N
CO2CHPh2
Cl

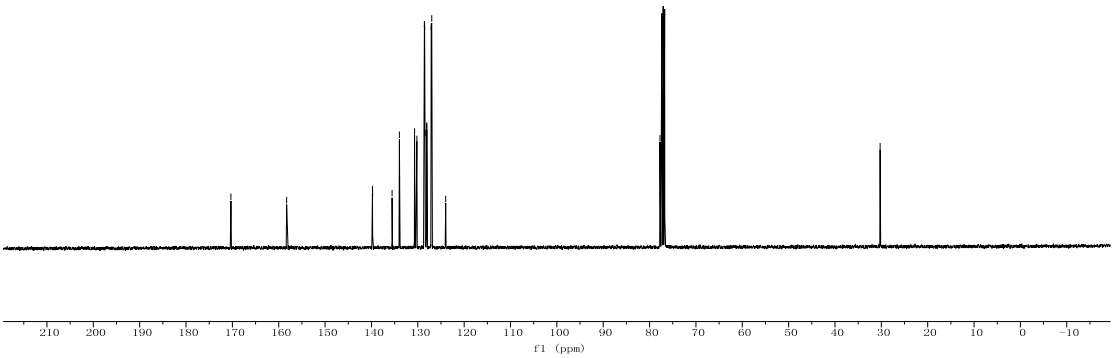
3g

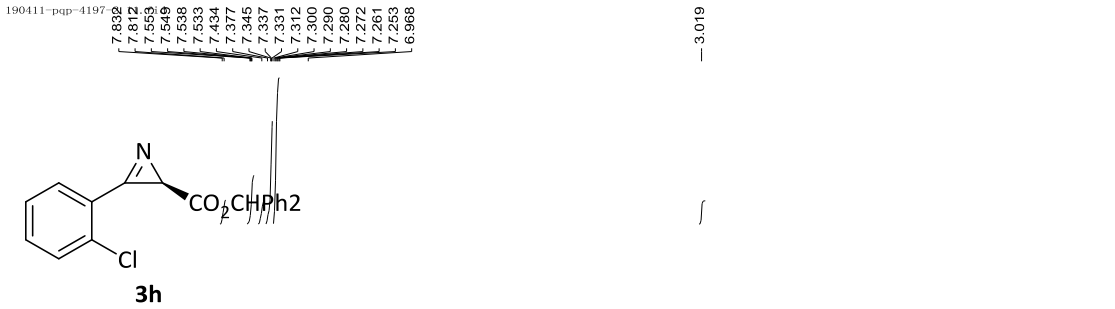

0.92
0.98
1.03
1.02
3.97
5.87
0.97
1.00
f1 (ppm)


20190325-pqp-4186-2.11.fid
C13CPD CDC13 (D:\NMR_DATA) WJ 55
170.315
158.292
139.786
139.748
135.548
133.972
130.702
130.200
128.577
128.530
128.408
128.077
128.054
127.107
126.990
123.985
77.756
30.263

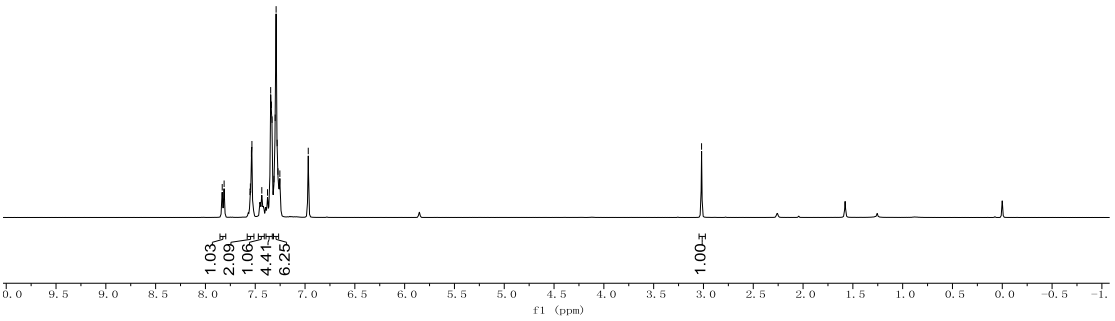

N
CO2CHPh2
Cl

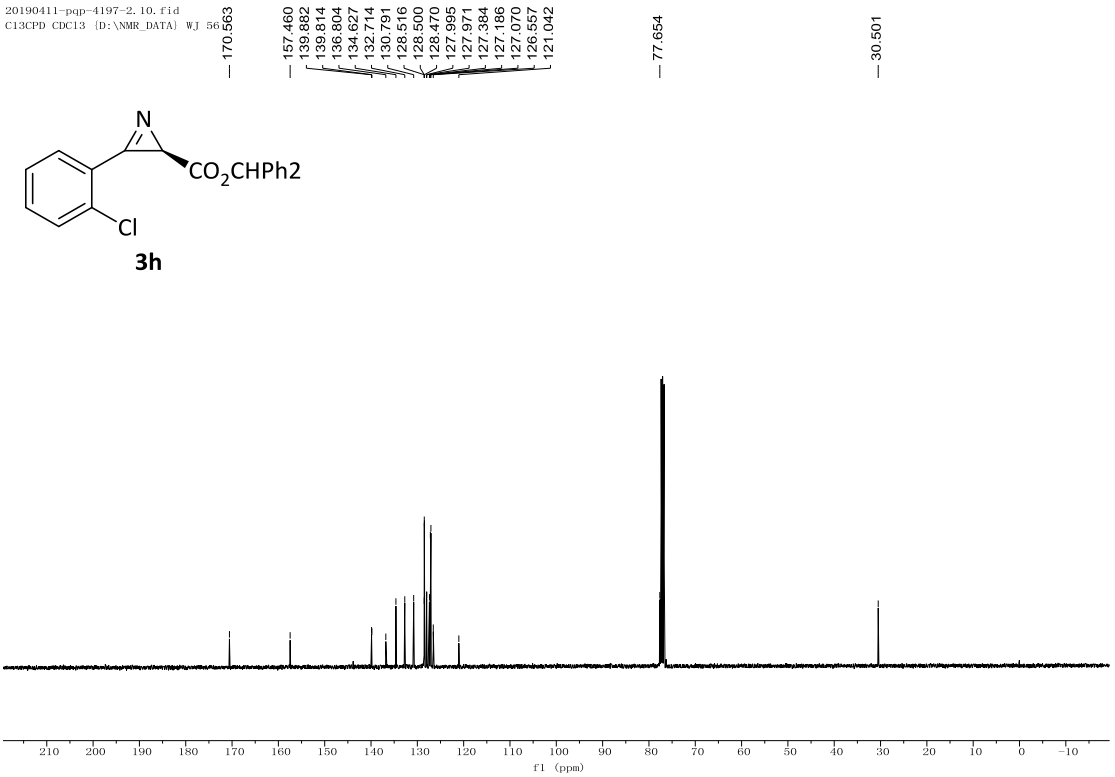
3g


f1 (ppm)

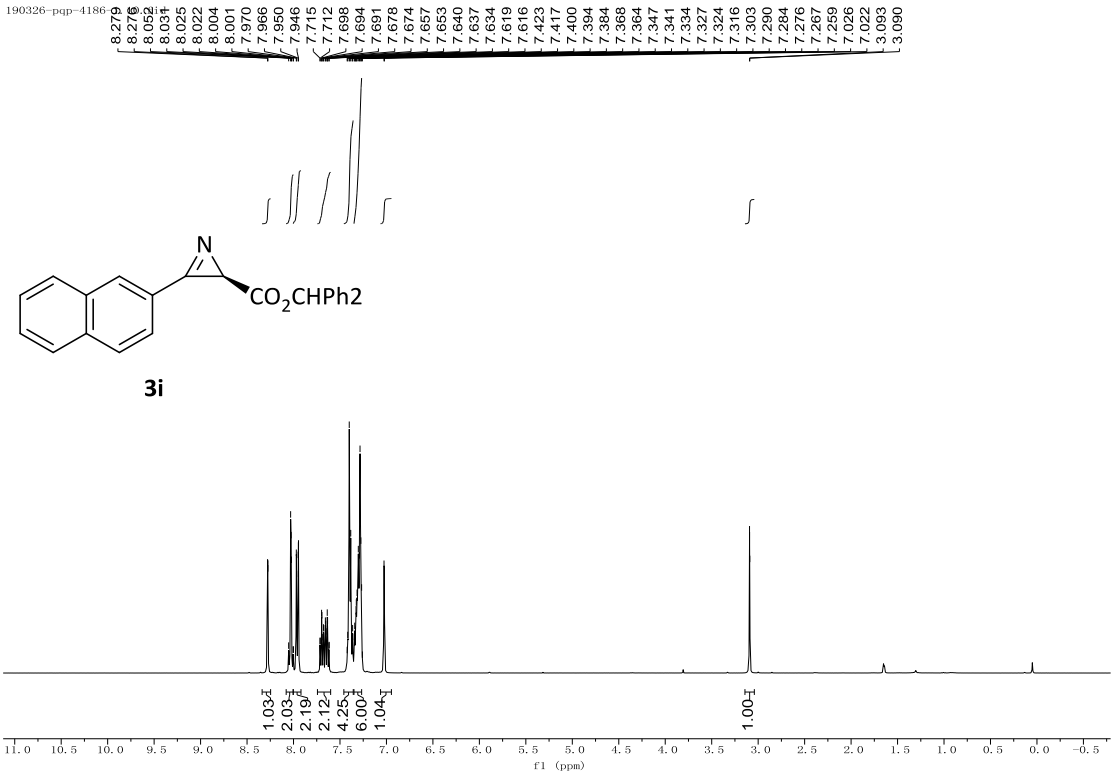

190411-pqp-4197
7.832
7.812
7.555
7.549
7.538
7.533
7.434
7.377
7.345
7.337
7.331
7.312
7.300
7.290
7.280
7.272
7.261
7.253
6.968
3.019
N
CO2CHPh2
Cl

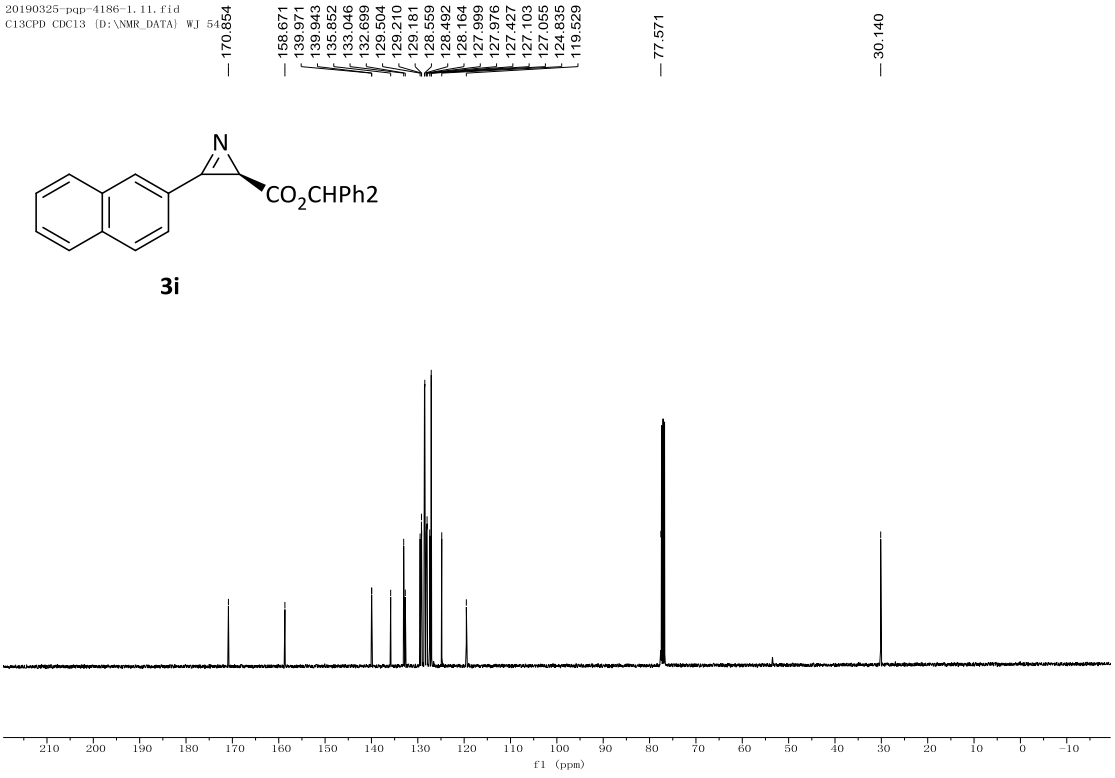
3h

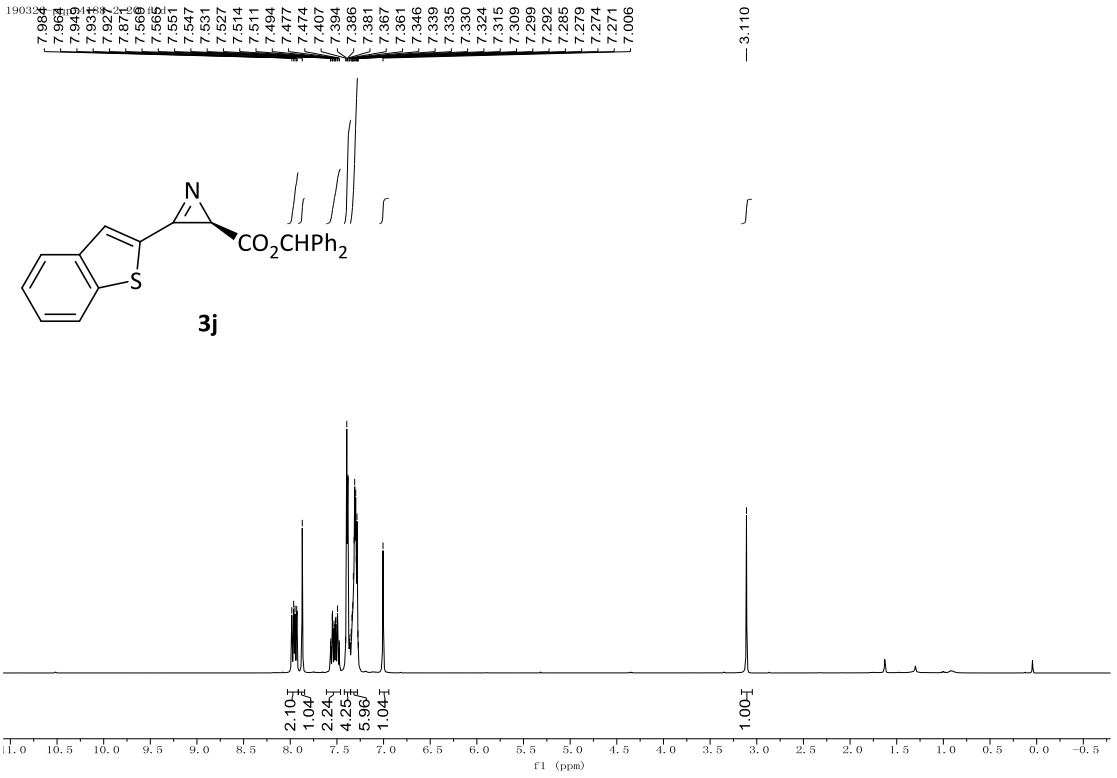

1.03
2.09
1.06
4.41
6.25
1.00
f1 (ppm)


20190411-pqp-4197-2.10.fid
C13CPD CDC13 (D:\NMR_DATA) WJ 56
170.563
157.460
139.882
139.814
136.804
134.627
132.714
130.791
128.516
128.500
128.470
127.995
127.971
127.384
127.186
127.070
126.557
121.042
77.654
30.501
N
CO2CHPh2
Cl
f1 (ppm)

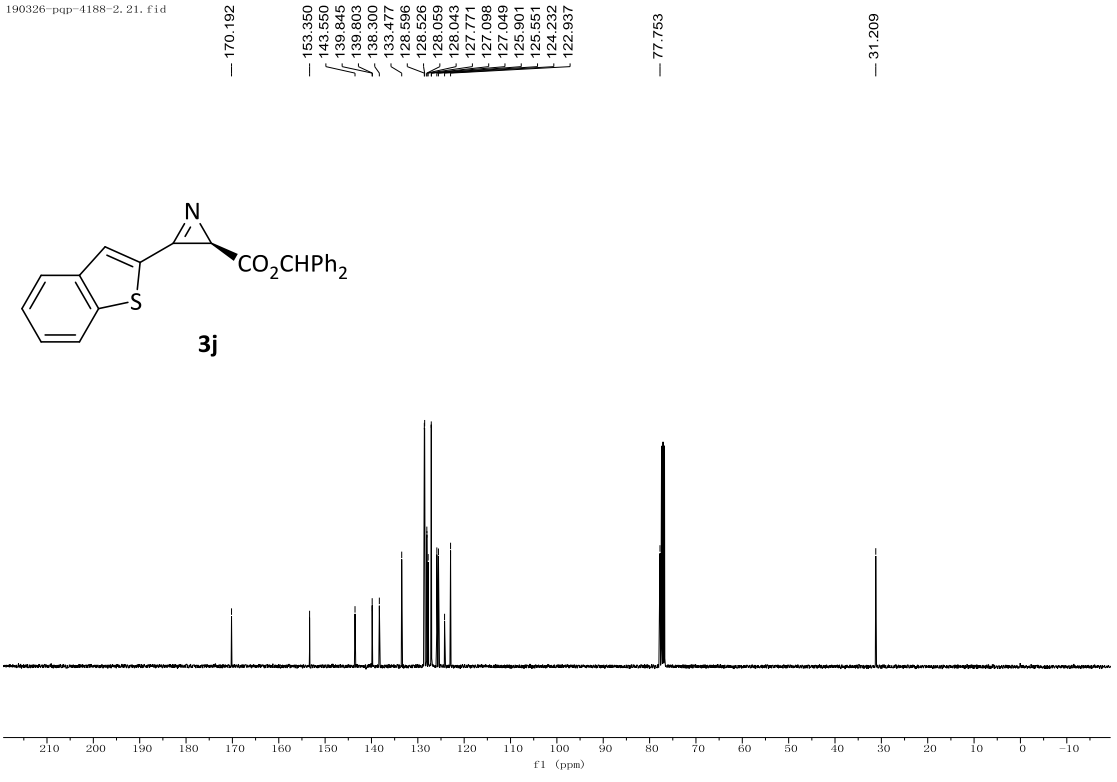
3h


190326-pqp-4186
8.279
8.276
8.052
8.031
8.025
8.022
8.004
8.001
7.970
7.966
7.950
7.946
7.715
7.712
7.698
7.694
7.691
7.678
7.674
7.657
7.653
7.640
7.637
7.634
7.619
7.616
7.423
7.417
7.400
7.394
7.384
7.368
7.364
7.347
7.341
7.334
7.327
7.324
7.316
7.303
7.290
7.284
7.276
7.267
7.259
7.026
7.022
3.093
3.090
N
CO2CHPh2
3i
1.03
2.03
2.19
2.12
4.25
6.00
1.04
1.00
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

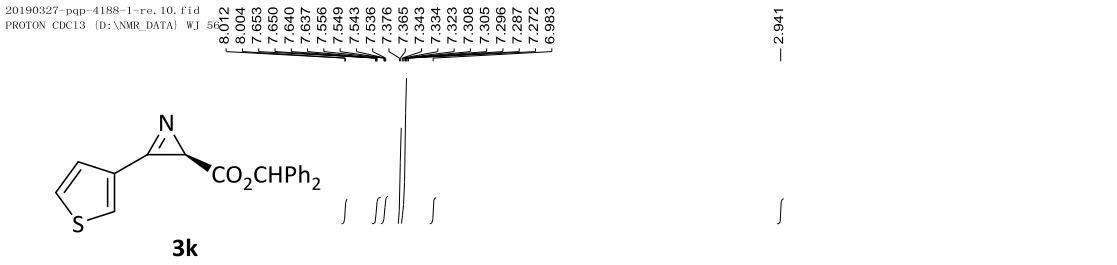

20190325-pqp-4186-1.11.fid
C13CPD CDCl3 (D:\NMR_DATA) WJ 54
170.854
158.671
139.971
139.943
135.852
133.046
132.699
129.504
129.210
129.181
128.559
128.492
128.164
127.999
127.976
127.427
127.103
127.055
124.835
119.529
77.571
30.140
N
CO2CHPh2
3i
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.984
7.964
7.945
7.927
7.875
7.566
7.565
7.551
7.547
7.531
7.527
7.514
7.511
7.494
7.477
7.474
7.407
7.394
7.386
7.381
7.367
7.361
7.346
7.339
7.335
7.330
7.324
7.315
7.309
7.299
7.292
7.285
7.279
7.274
7.271
7.006
3.110
N
CO2CHPh2
S
2.10
1.04
2.24
4.25
5.96
1.04
1.00
f1 (ppm)

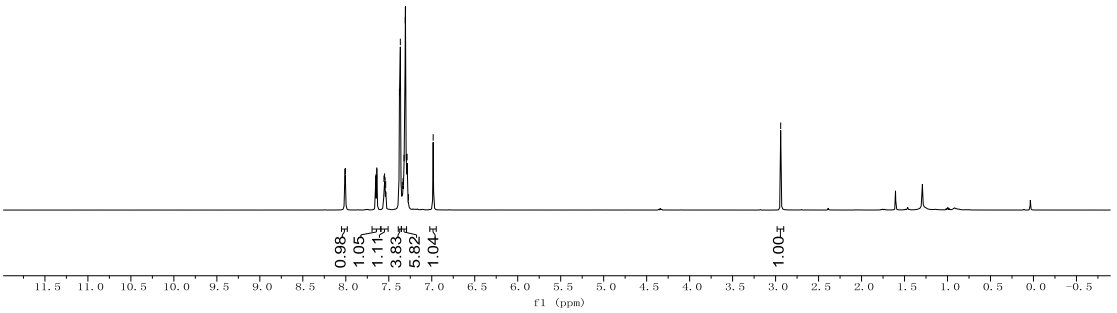
3j


190326-pqp-4188-2.21.fid
170.192
153.350
143.550
139.845
139.803
138.300
133.477
128.596
128.526
128.059
128.043
127.771
127.098
127.049
125.901
125.551
124.232
122.937
77.753
31.209
N
CO2CHPh2
S
f1 (ppm)

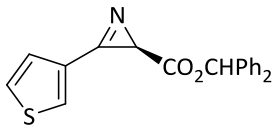
3j


20190327-pqp-4188-1-re.10.fid
PROTON CDC13 (D:\NMR_DATA) WJ 56
8.012
8.004
7.653
7.650
7.640
7.637
7.556
7.549
7.543
7.536
7.376
7.365
7.343
7.334
7.323
7.308
7.305
7.296
7.287
7.272
6.983
2.941
N
CO2CHPh2
S

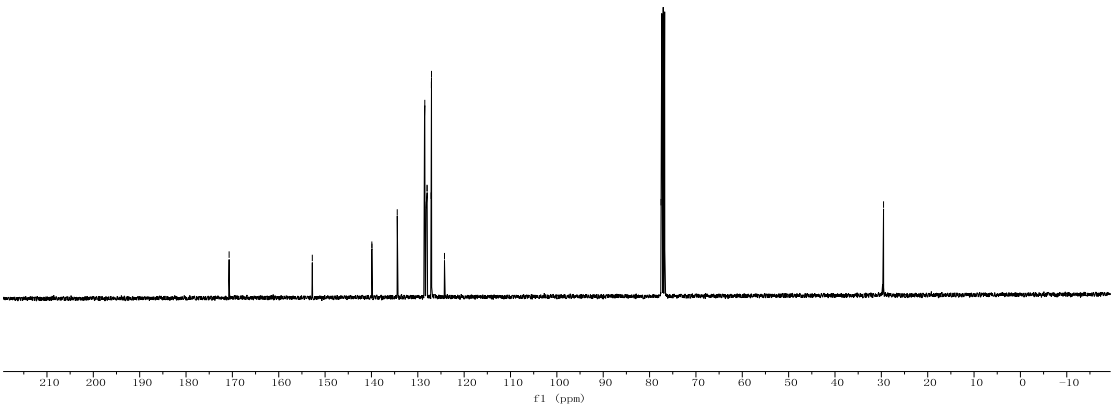
3k

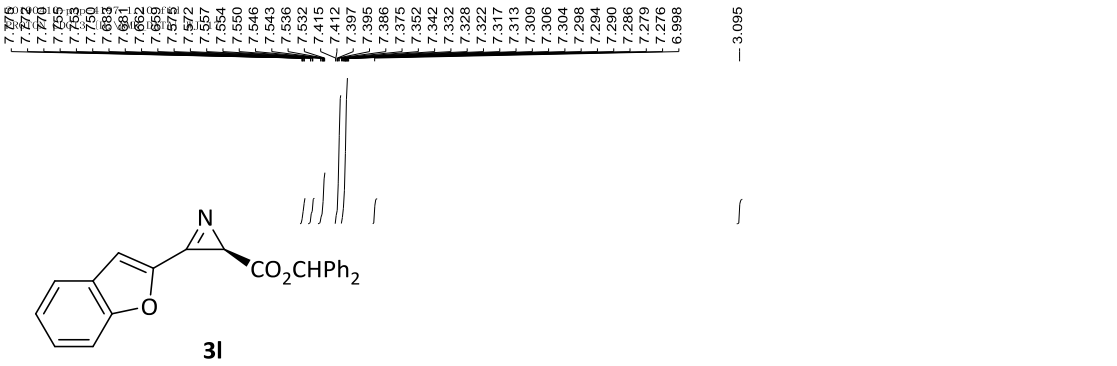

0.98
1.05
1.11
3.83
5.82
1.04
1.00
f1 (ppm)


20190327-pqp-4188-1-re.11.fid
C13CPD CDC13 (D:\NMR_DATA) WJ 56
170.705
152.757
139.918
139.889
134.433
128.549
128.492
128.203
128.004
127.985
127.131
127.063
127.045
124.242
77.527
29.528

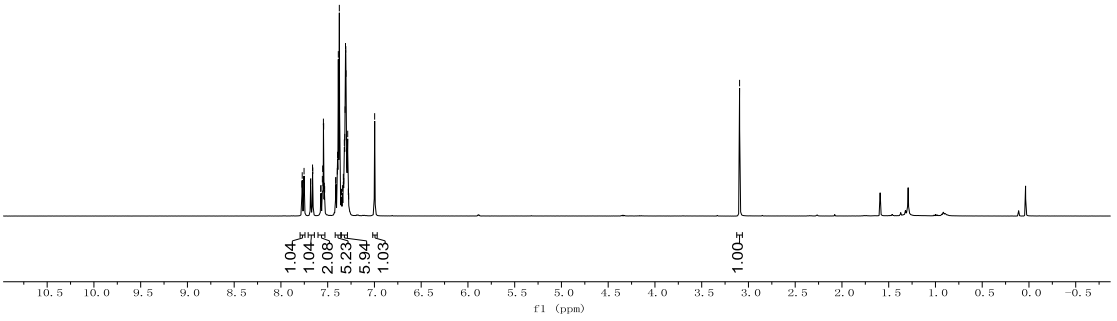

N
CO2CHPh2
S

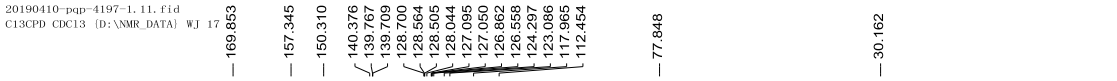
3k


f1 (ppm)

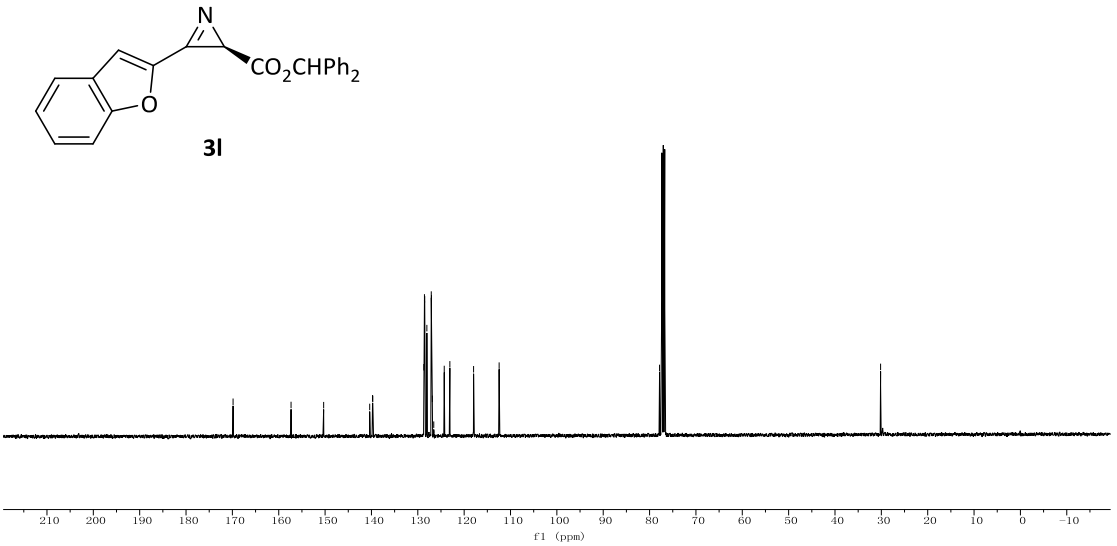

7.778
7.772
7.770
7.755
7.753
7.750
7.683
7.681
7.662
7.659
7.575
7.572
7.557
7.554
7.550
7.546
7.543
7.536
7.532
7.415
7.412
7.397
7.395
7.386
7.375
7.352
7.342
7.332
7.328
7.322
7.317
7.313
7.309
7.306
7.304
7.298
7.294
7.290
7.286
7.279
7.276
6.998
3.095
N
CO2CHPh2
O

3l

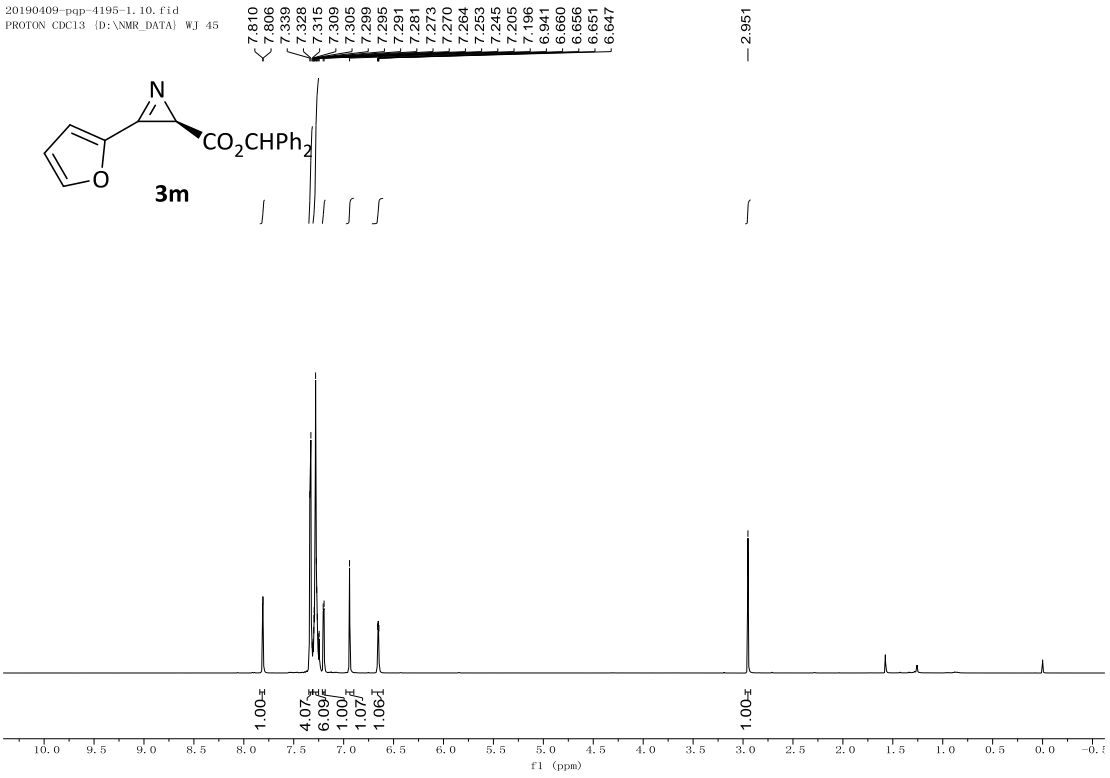

1.04
1.04
2.08
5.23
5.94
1.03
1.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

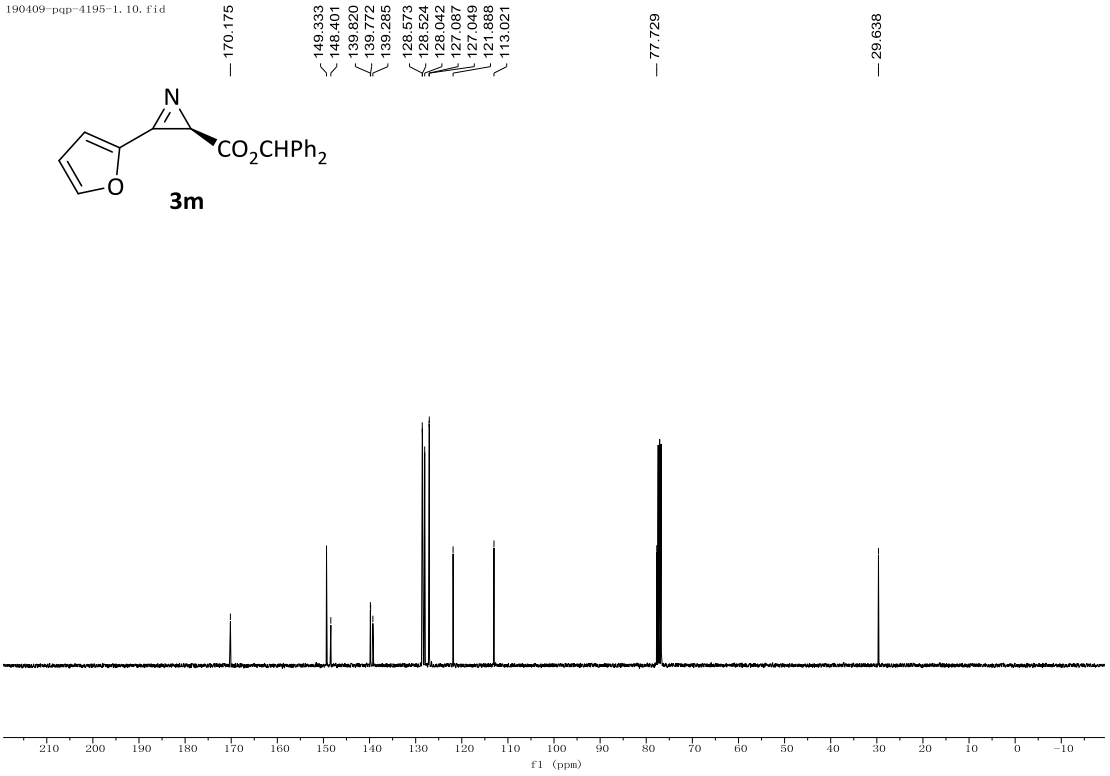

20190410-pqp-4197-1.11.fid
C13CPD CDC13 (D:\NMR_DATA) WJ 17

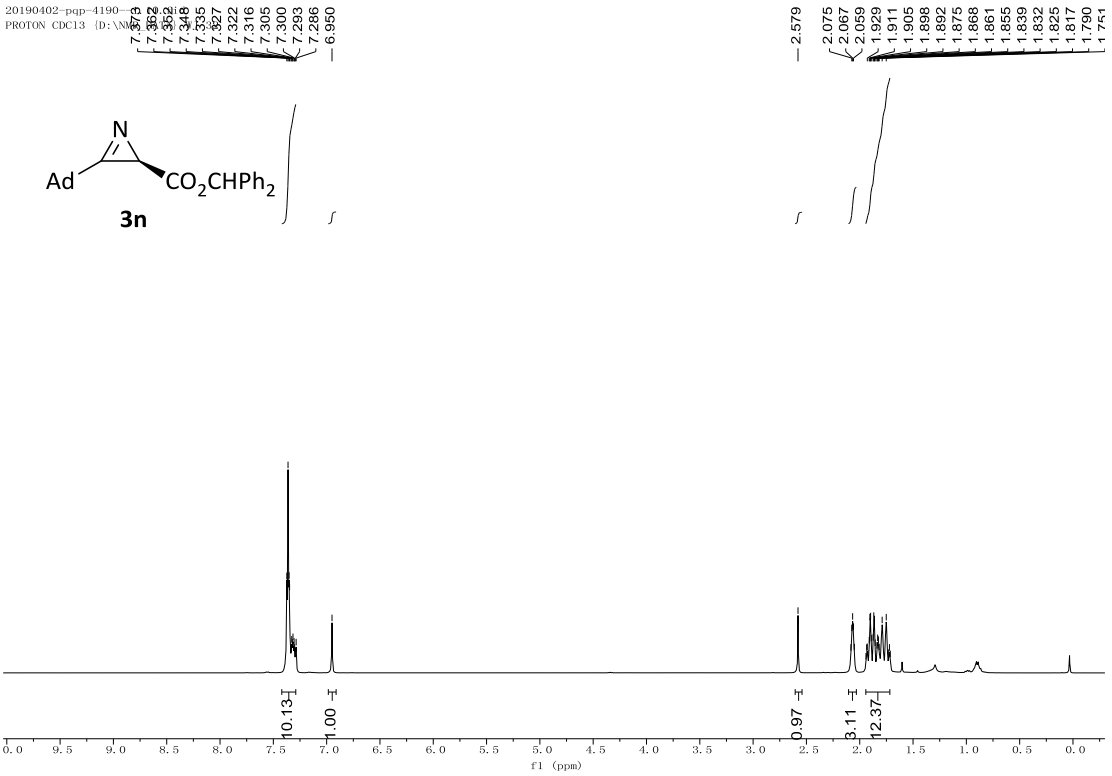
169.853
157.345
150.310
140.376
139.767
139.709
128.700
128.564
128.505
128.044
127.095
127.050
126.862
126.558
124.297
123.086
117.965
112.454
77.848
30.162

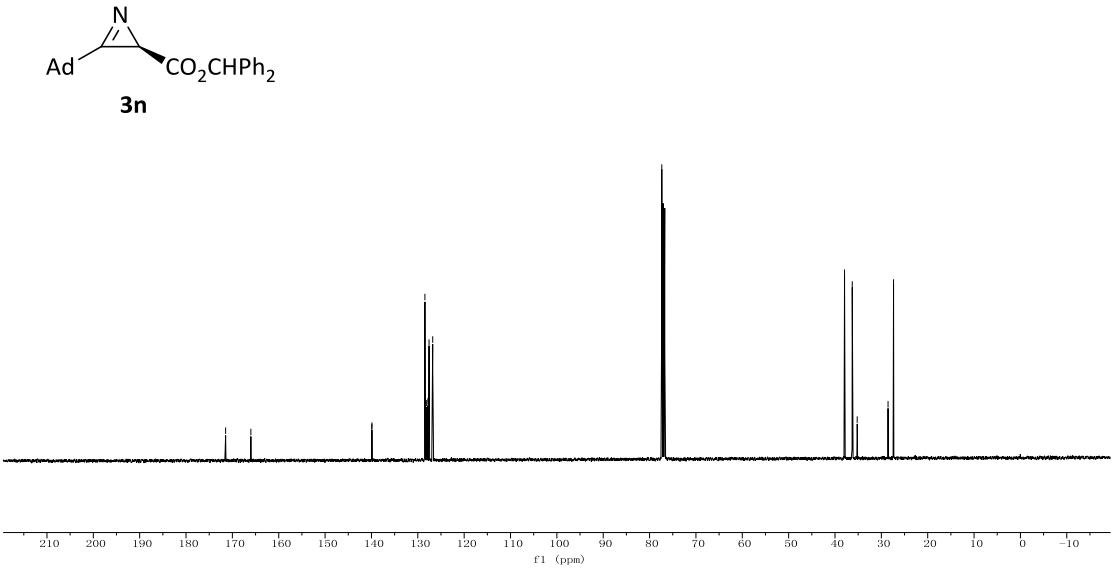

N
CO2CHPh2
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

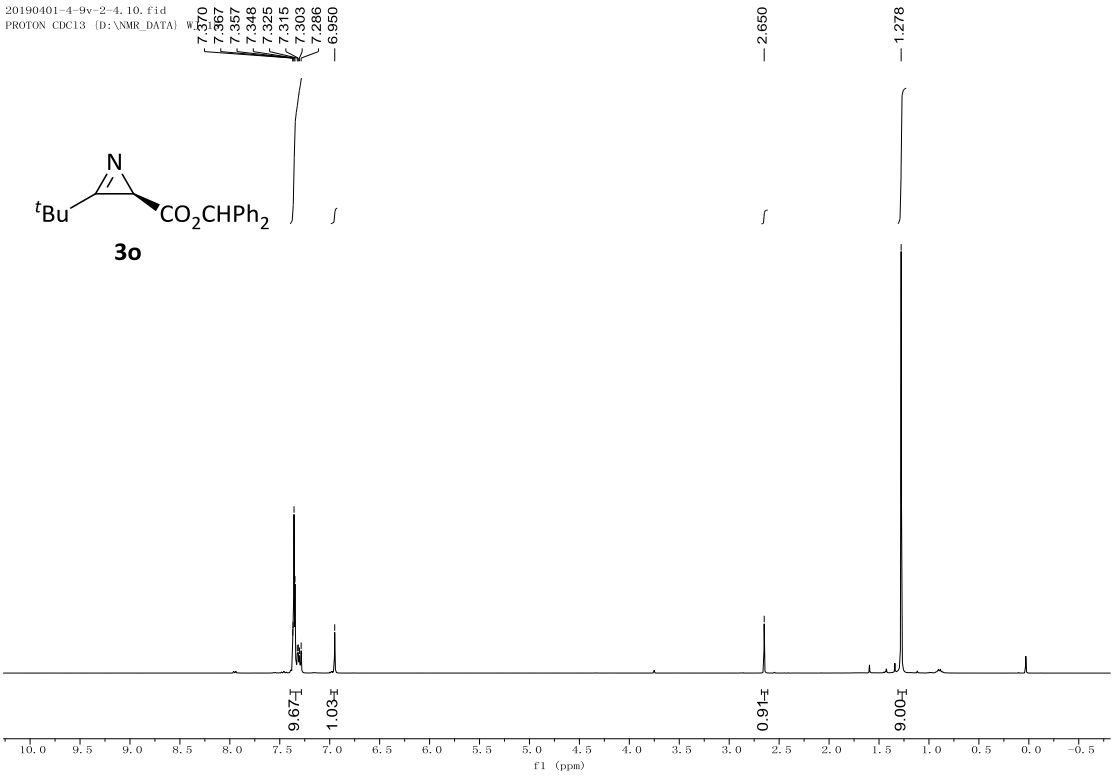
3l

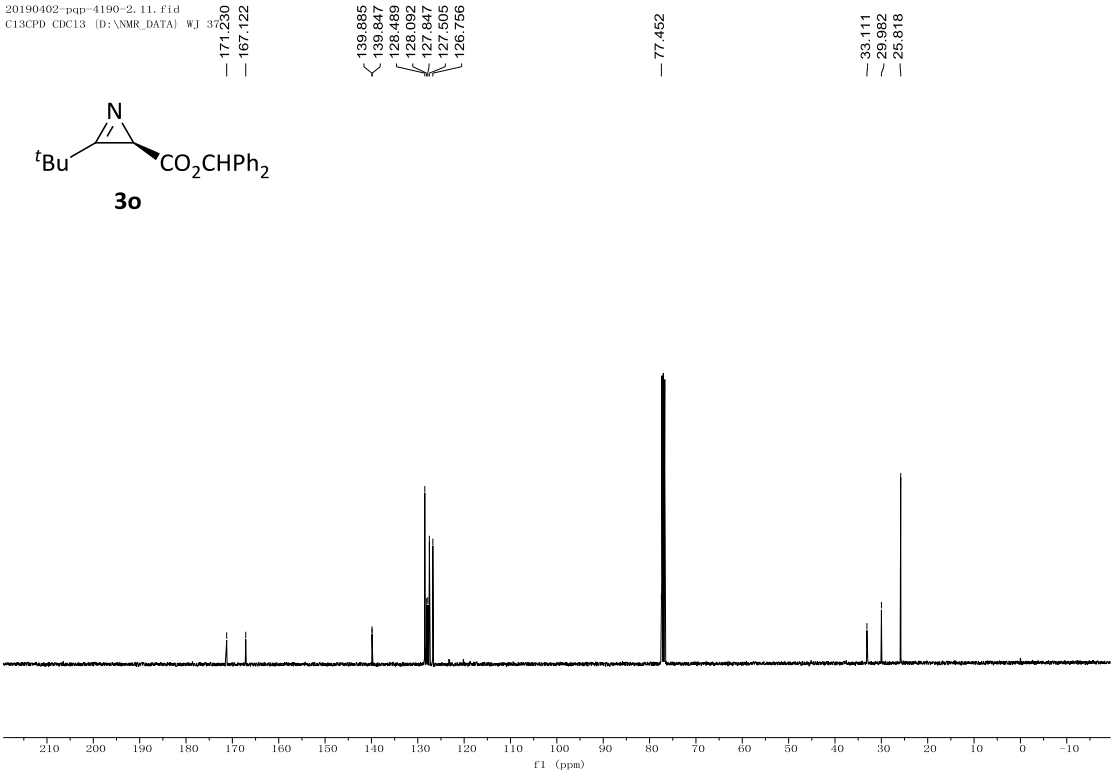

20190409-pqp-4195-1.10.fid
PROTON CDC13 {D:\NMR_DATA} WJ 45
7.810
7.806
7.339
7.328
7.315
7.309
7.305
7.299
7.295
7.291
7.281
7.273
7.270
7.264
7.253
7.245
7.205
7.196
6.941
6.660
6.656
6.651
6.647
2.951
N
O
CO2CHPh2
3m
1.00
4.07
6.09
1.00
1.07
1.06
1.00
f1 (ppm)

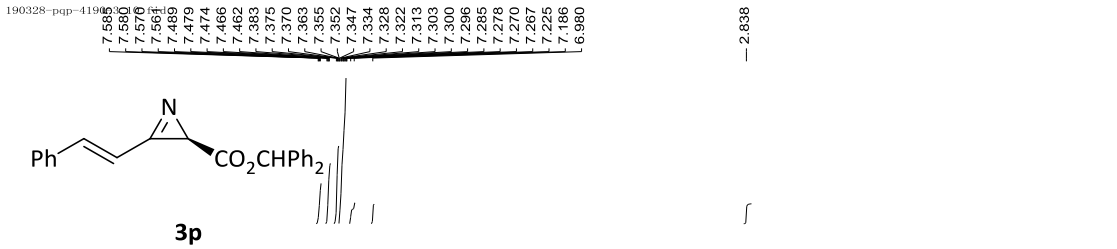

190409-pqp-4195-1.10.fid
170.175
149.333
148.401
139.820
139.772
139.285
128.573
128.524
128.042
127.087
127.049
121.888
113.021
77.729
29.638
N
O
CO2CHPh2
3m
f1 (ppm)


20190402-pqp-4190--1
PROTON CDC13 {D:\NMR_DATA} WJ 32
7.373
7.362
7.352
7.348
7.335
7.327
7.322
7.316
7.305
7.300
7.293
7.286
6.950
2.579
2.075
2.067
2.059
2.029
1.911
1.905
1.898
1.892
1.875
1.868
1.861
1.855
1.839
1.832
1.825
1.817
1.790
N
Ad
CO2CHPh2
3n
10.13
1.00
0.97
3.11
12.37
f1 (ppm)

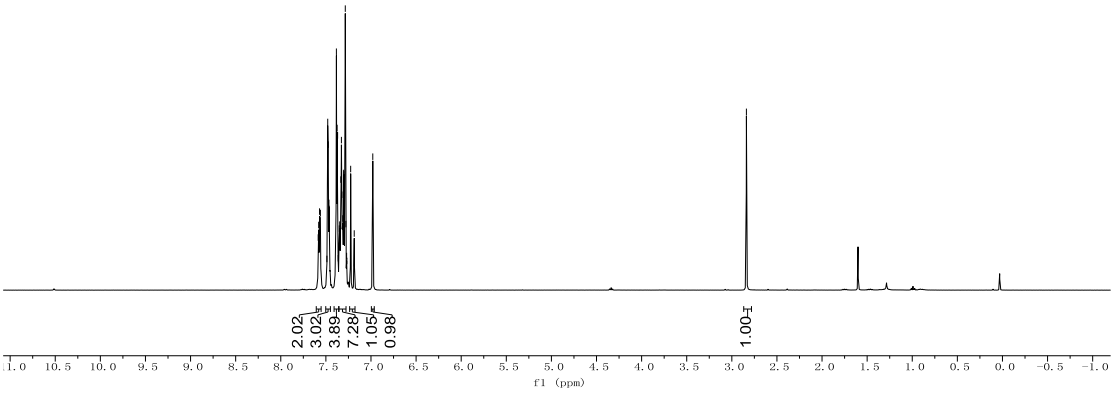

20190402-pqp-4190--1.11.fid
C13CPD CDC13 {D:\NMR_DATA} WJ 32
171.460
166.014
139.926
139.895
128.467
128.086
127.821
127.578
126.786
77.364
37.942
36.279
35.208
28.555
27.371
N
Ad
CO2CHPh2
3n
f1 (ppm)

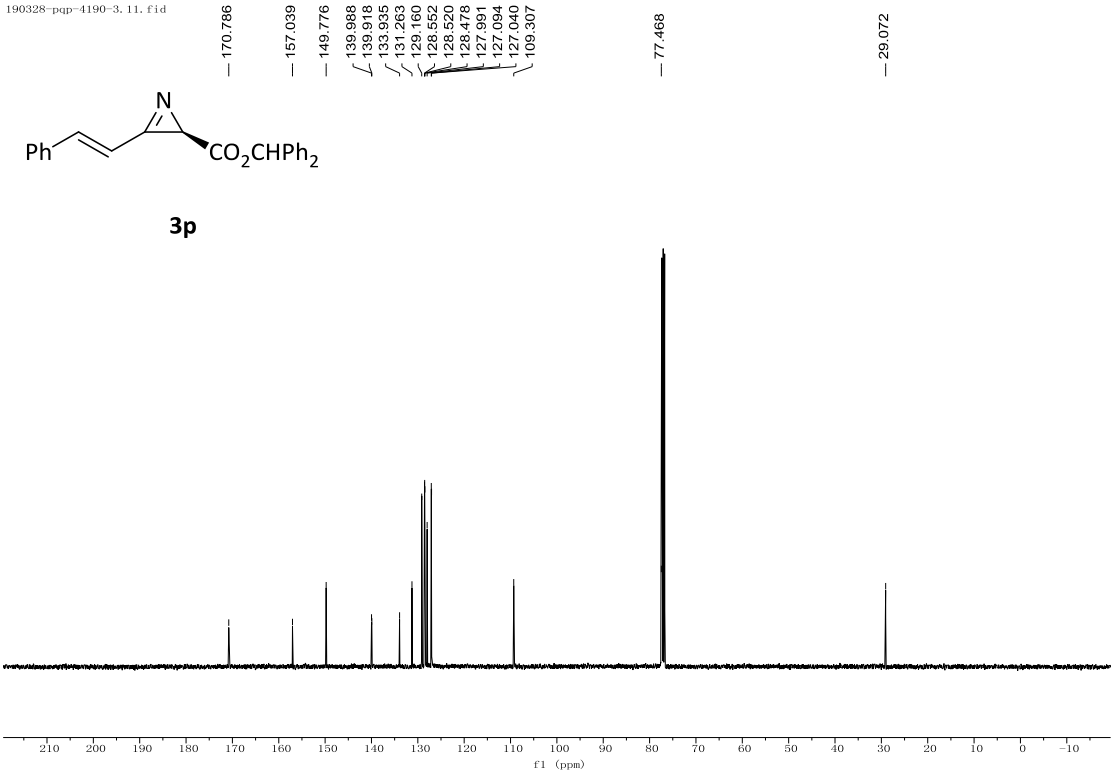

20190401-4-9v-2-4.10.fid
PROTON CDC13 (D:\NMR_DATA) WJ
7.370
7.367
7.357
7.348
7.325
7.315
7.303
7.286
6.950
2.650
1.278
N
tBu
CO2CHPh2
3o
9.67
1.03
0.91
9.00
f1 (ppm)


20190402-pqp-4190-2.11.fid
C13CPD CDC13 (D:\NMR_DATA) WJ
171.230
167.122
139.885
139.847
128.489
128.092
127.847
127.505
126.756
77.452
33.111
29.982
25.818
N
tBu
CO2CHPh2
3o
f1 (ppm)

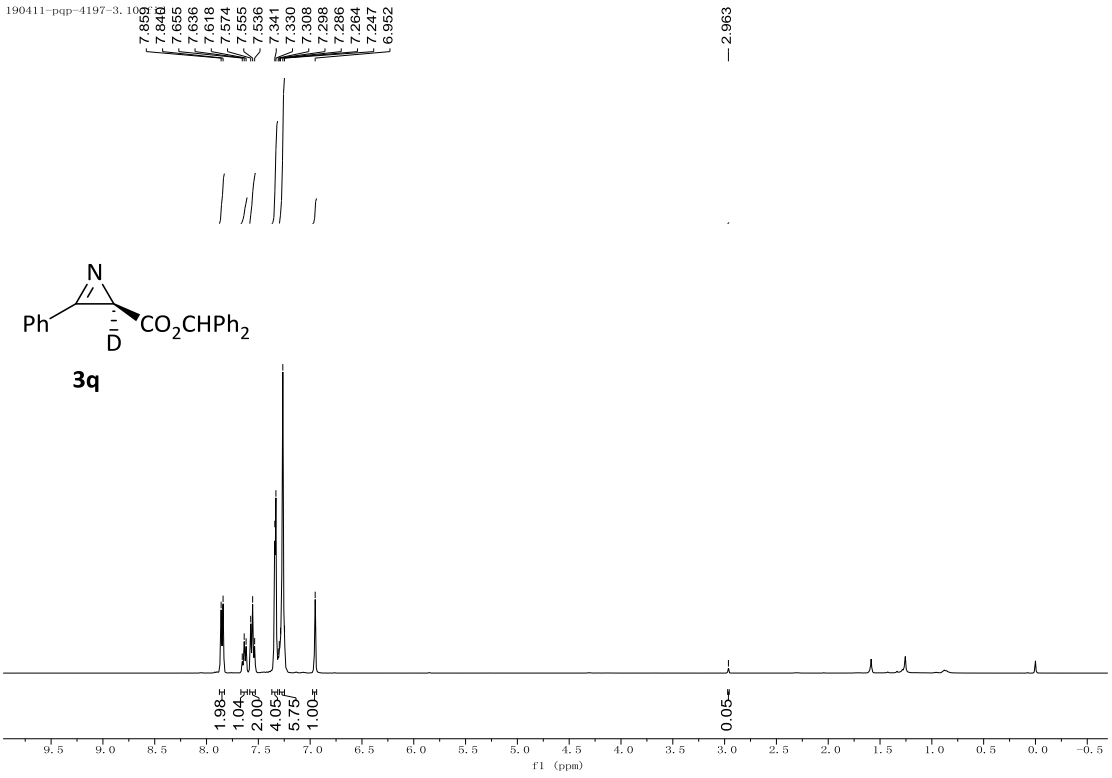

7.589
7.580
7.576
7.561
7.489
7.479
7.474
7.466
7.462
7.383
7.375
7.370
7.363
7.355
7.352
7.347
7.334
7.328
7.322
7.313
7.303
7.300
7.296
7.285
7.278
7.270
7.267
7.225
7.186
6.980
2.838
N
Ph
CO2CHPh2

3p

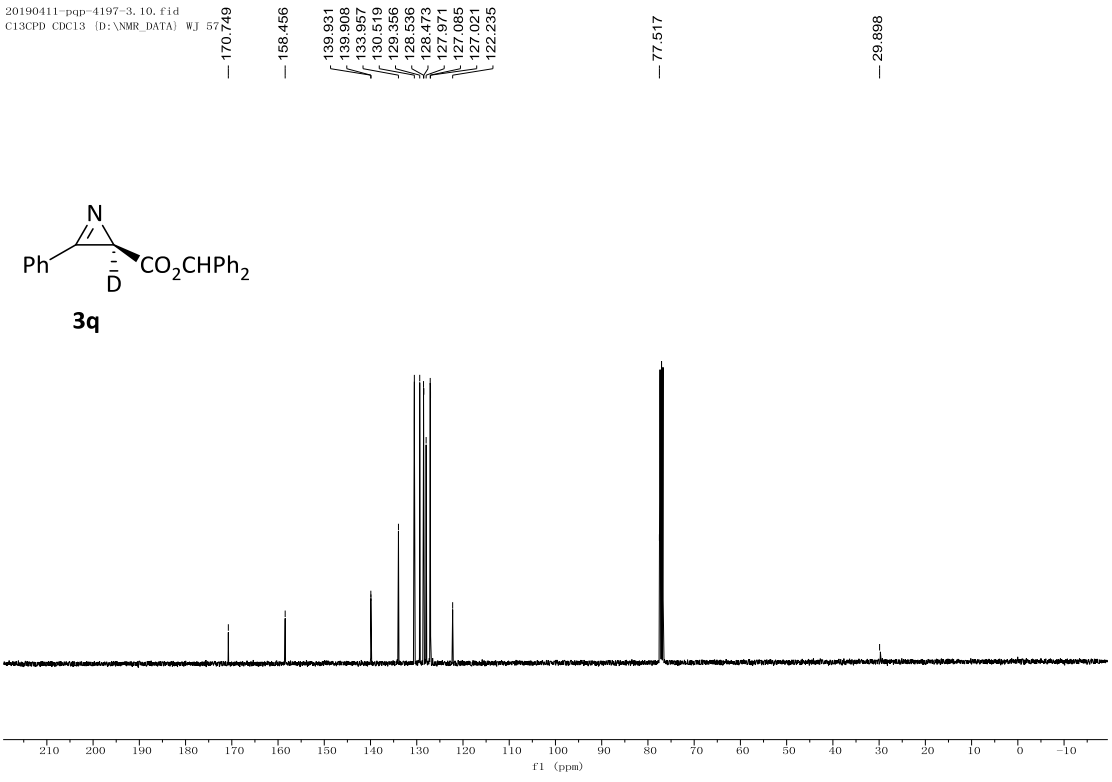

2.02
3.02
3.89
7.28
1.05
0.98
1.00
f1 (ppm)


190328-pqp-4190-3.11.fid
170.786
157.039
149.776
139.988
139.918
133.935
131.263
129.160
128.552
128.520
128.478
127.991
127.094
127.040
109.307
77.468
29.072
N
Ph
CO2CHPh2
f1 (ppm)

3p

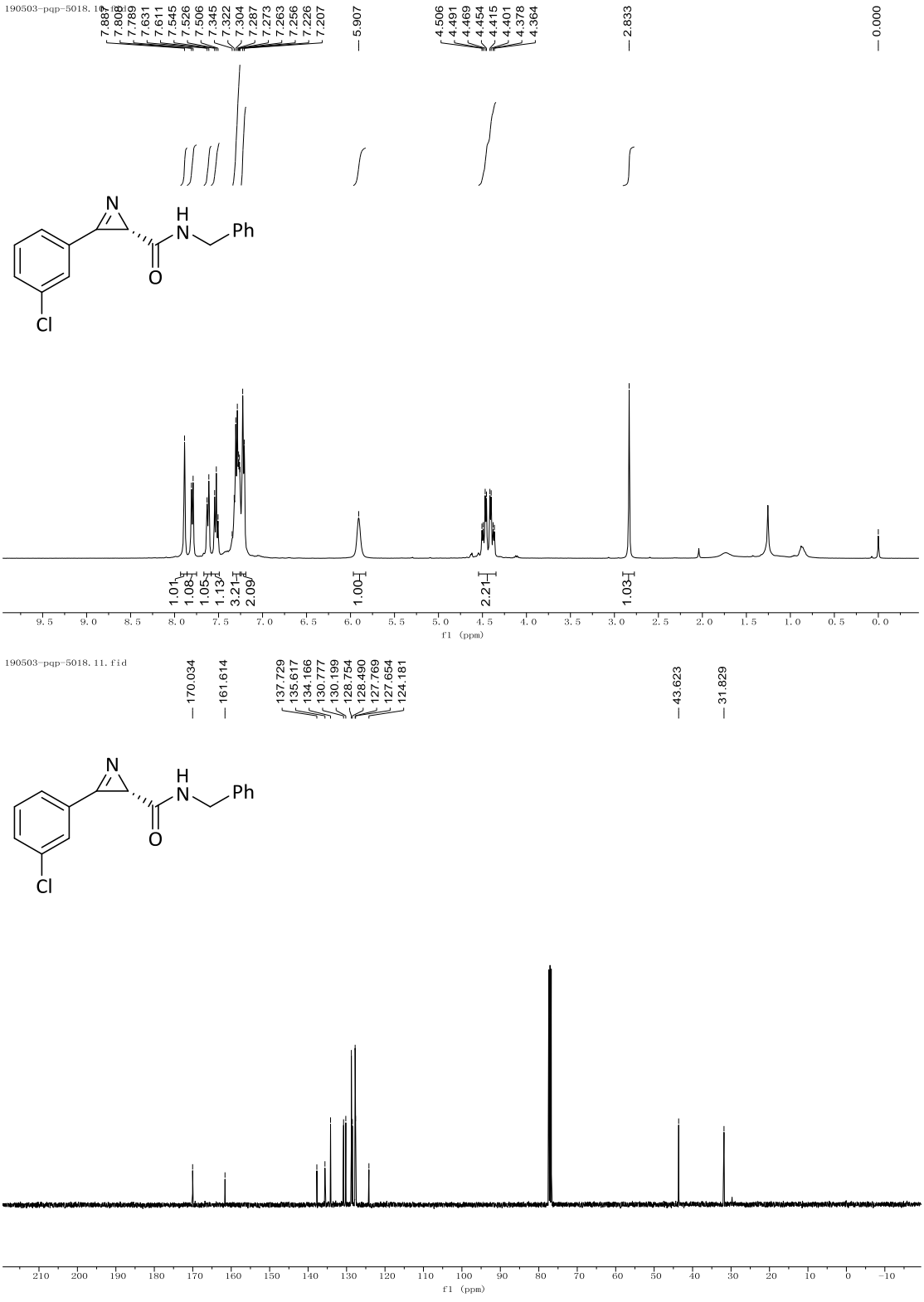

190411-pqp-4197-3.10.fid
7.859
7.840
7.655
7.636
7.618
7.574
7.555
7.536
7.341
7.330
7.308
7.298
7.286
7.264
7.247
6.952
2.963
N
Ph
CO2CHPh2
D
1.98
1.04
2.00
4.05
5.75
1.00
0.05
f1 (ppm)

3q

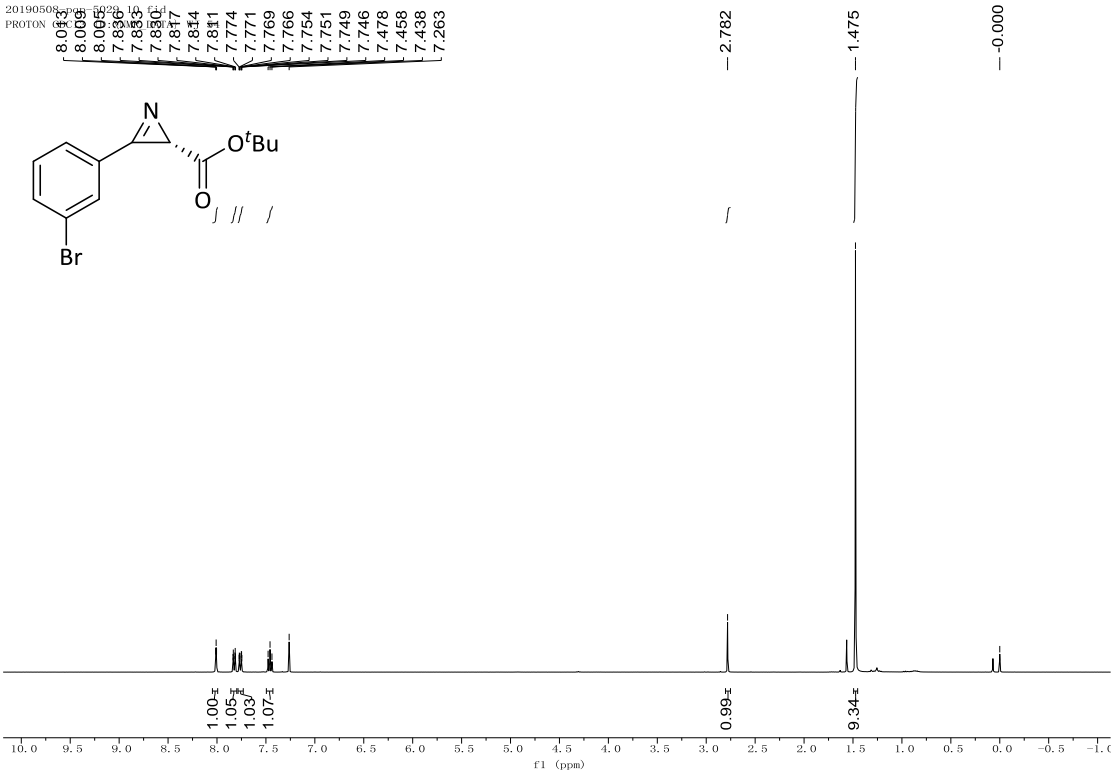

20190411-pqp-4197-3.10.fid
C13CPD CDC13 (D:\NMR_DATA) WJ 57
170.749
158.456
139.931
139.908
133.957
130.519
129.356
128.536
128.473
127.971
127.085
127.021
122.235
77.517
29.898
N
Ph
CO2CHPh2
D
f1 (ppm)

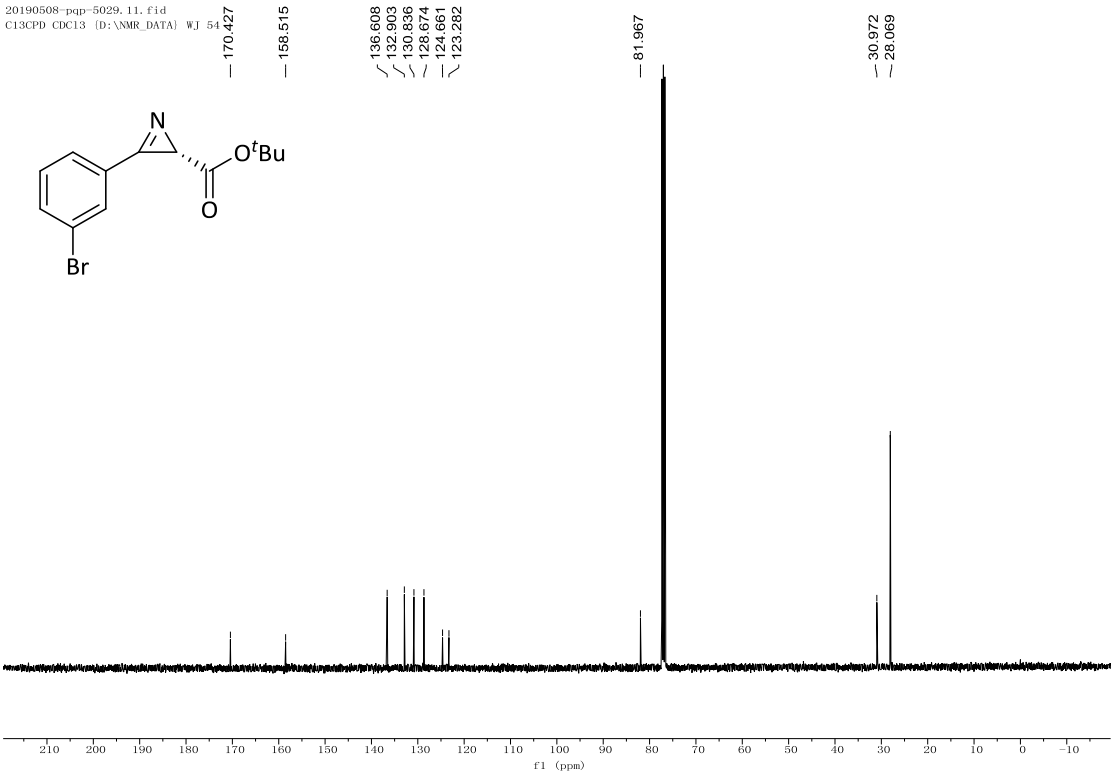
3q

4

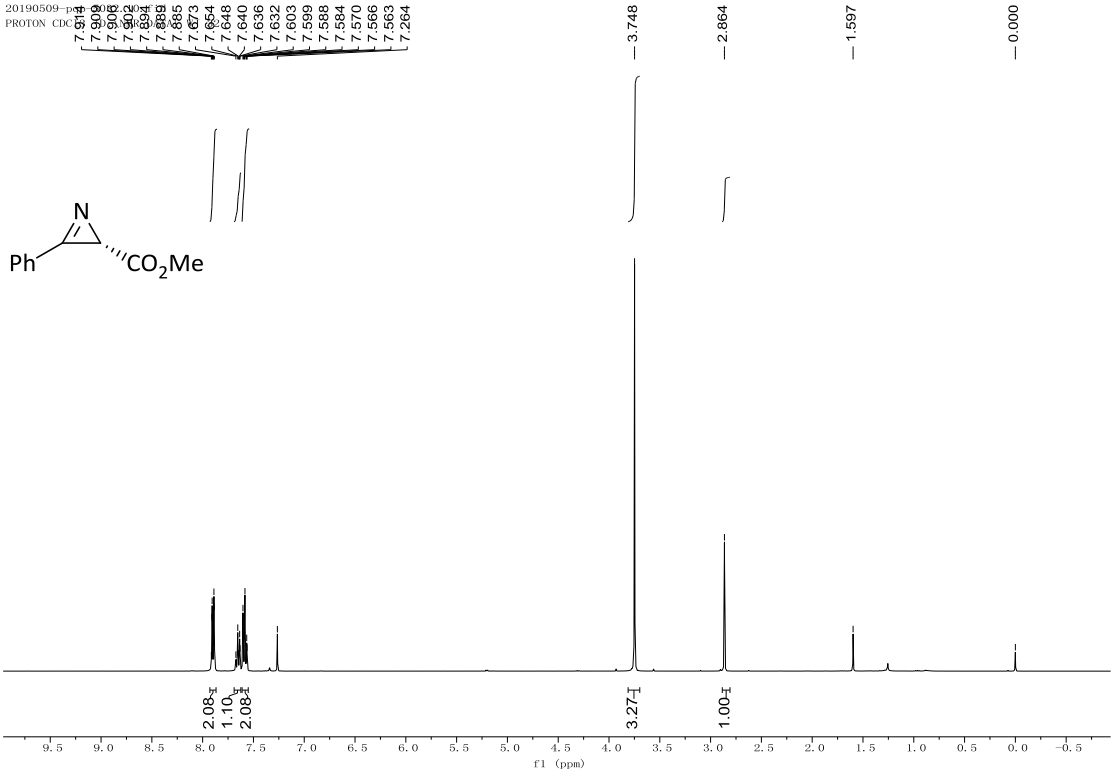

190503-pqp-5018.11.fid
7.887
7.808
7.789
7.631
7.611
7.545
7.526
7.506
7.345
7.322
7.304
7.287
7.273
7.263
7.256
7.226
7.207
5.907
4.506
4.491
4.469
4.454
4.415
4.401
4.378
4.364
2.833
0.000
N
H
N
Ph
O
Cl
1.01
1.08
1.05
1.13
3.21
2.09
1.00
2.21
1.03
f1 (ppm)
190503-pqp-5018.11.fid
170.034
161.614
137.729
135.617
134.166
130.777
130.199
128.754
128.490
127.769
127.654
124.181
43.623
31.829
f1 (ppm)

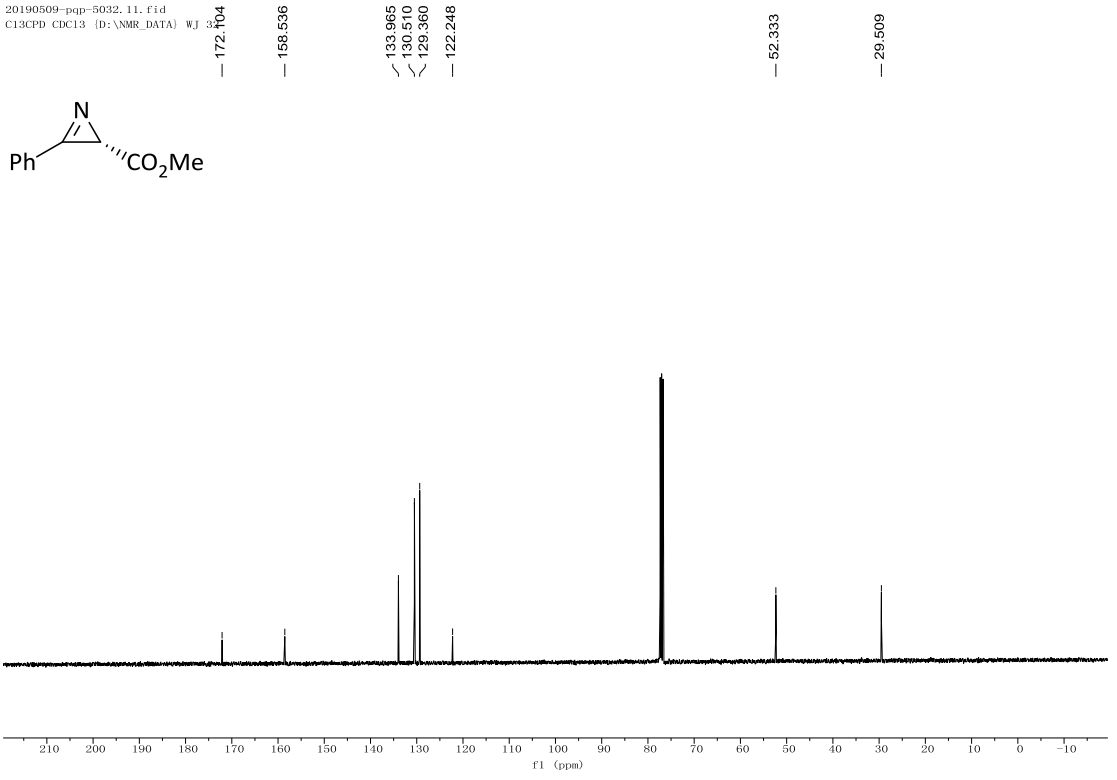
5


8.013
8.009
8.005
7.836
7.833
7.830
7.817
7.814
7.811
7.774
7.771
7.769
7.766
7.754
7.751
7.749
7.746
7.478
7.458
7.438
7.263
2.782
1.475
-0.000
N
O^{t}Bu
O
Br
1.00
1.05
1.03
1.07
0.99
9.34
f1 (ppm)

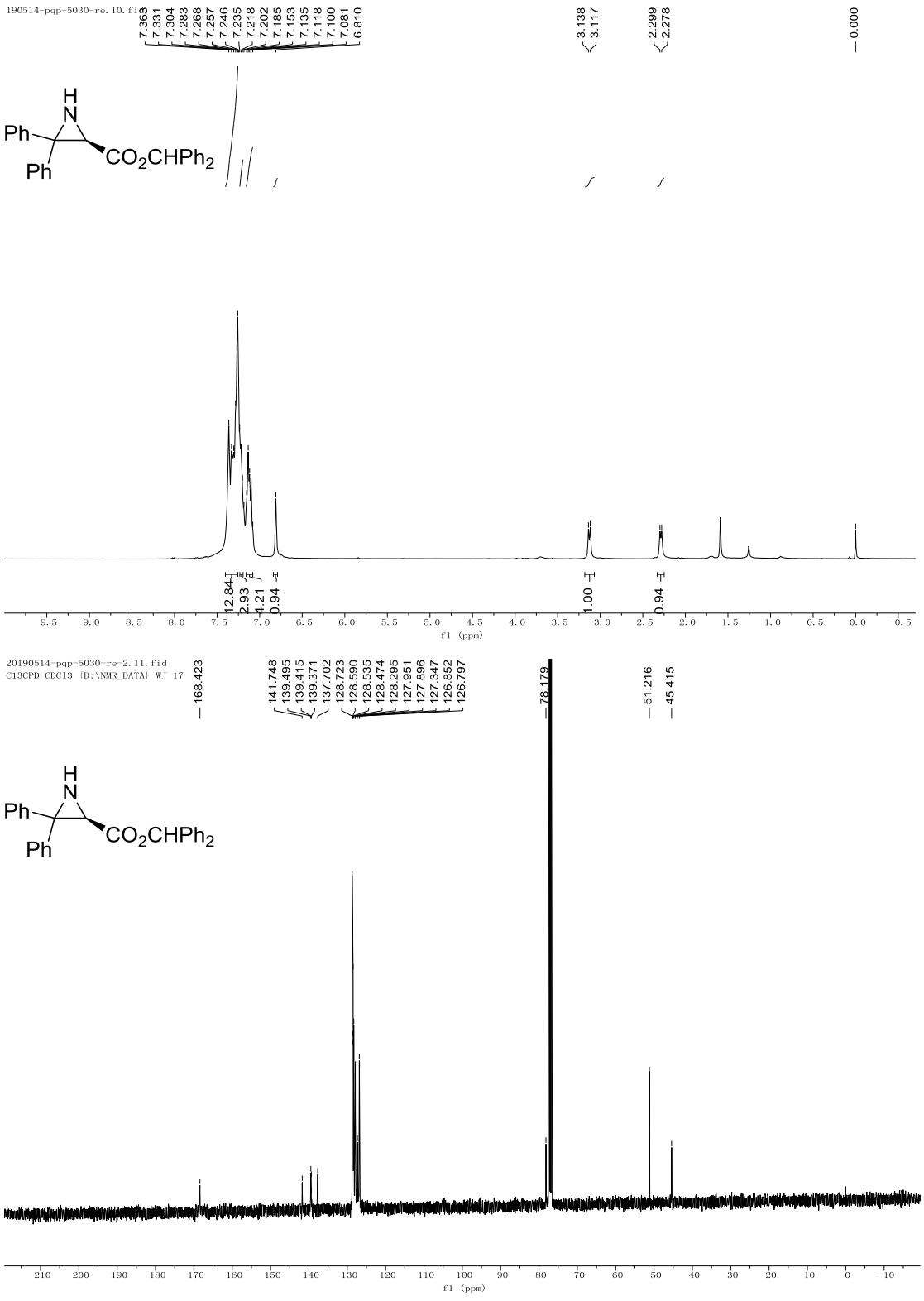

170.427
158.515
136.608
132.903
130.836
128.674
124.661
123.282
81.967
30.972
28.069
N
O^{t}Bu
O
Br
f1 (ppm)

7

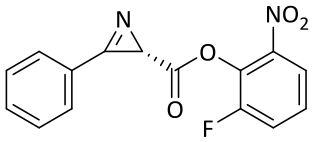

PROTON CDCl3
7.914
7.908
7.906
7.902
7.894
7.889
7.885
7.673
7.654
7.648
7.640
7.636
7.632
7.603
7.599
7.588
7.584
7.570
7.566
7.563
7.264
3.748
2.864
1.597
0.000
N
Ph
CO2Me
2.08
1.10
2.08
3.27
1.00
f1 (ppm)


C13CPD CDCl3
172.104
158.536
133.965
130.510
129.360
122.248
52.333
29.509
N
Ph
CO2Me
f1 (ppm)

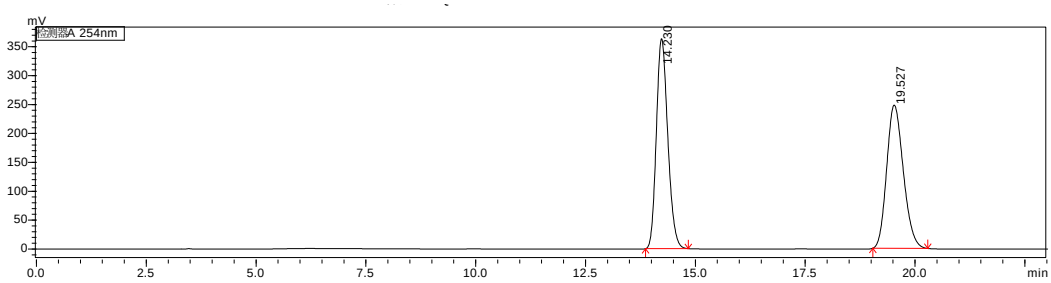
9


190514-pqp-5030-re.10.fid
7.365
7.331
7.304
7.283
7.268
7.257
7.246
7.235
7.218
7.202
7.185
7.153
7.135
7.118
7.100
7.081
6.810
3.138
3.117
2.299
2.278
0.000
Ph
Ph
CO2CHPh2
12.84
2.93
4.21
0.94
1.00
0.94
f1 (ppm)
20190514-pqp-5030-re-2.11.fid
C13CPD CDCl3 (D:\NMR_DATA) WJ 17
168.423
141.748
139.495
139.415
139.371
137.702
128.723
128.590
128.535
128.474
128.295
127.951
127.896
127.347
126.852
126.797
78.179
51.216
45.415
f1 (ppm)

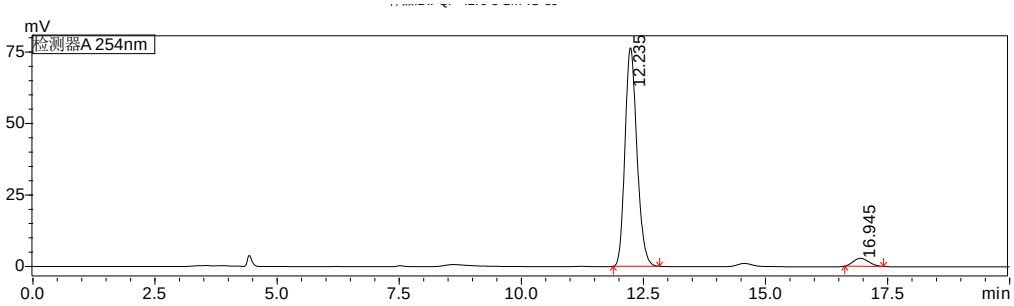
HPLC Spectra



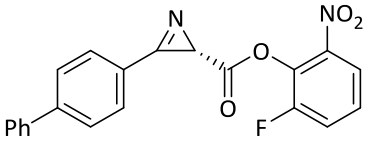
1a



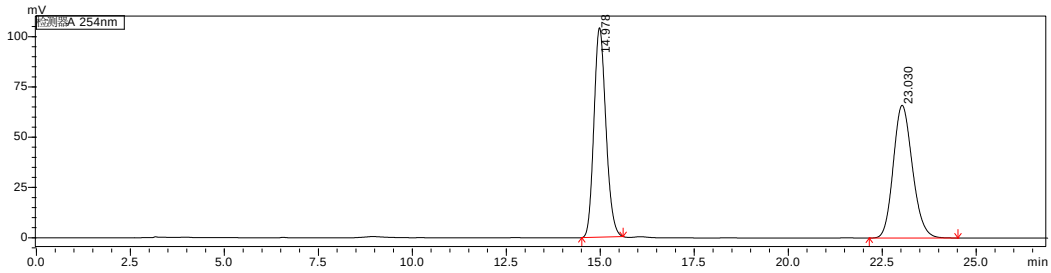
Peak	Ret. time	Area	height	Area%	height%
1	14.230	6582532	363452	50.172	59.450
2	19.527	6537275	247904	49.828	40.550
Total		13119807	611356	100.000	100.000



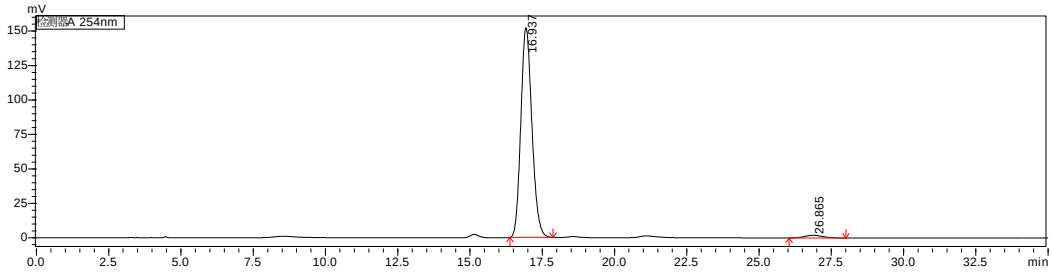
Peak	Ret. time	Area	height	Area%	height%
1	12.235	1305626	76453	95.528	96.487
2	16.945	61115	2783	4.472	3.513
Total		1366742	79236	100.000	100.000



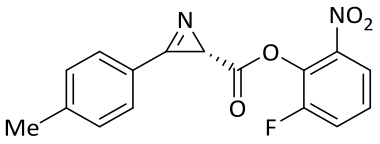
1b



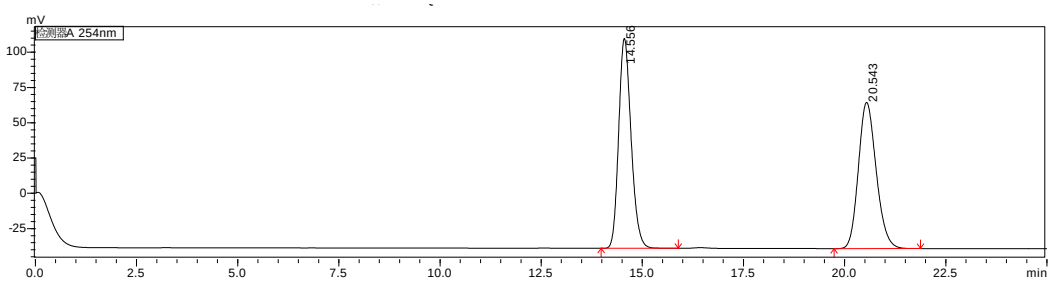
Peak	Ret. time	Area	height	Area%	height%
1	14.978	2305185	104183	49.658	61.219
2	23.030	2336909	65997	50.342	38.781
Total		4642095	170179	100.000	100.000



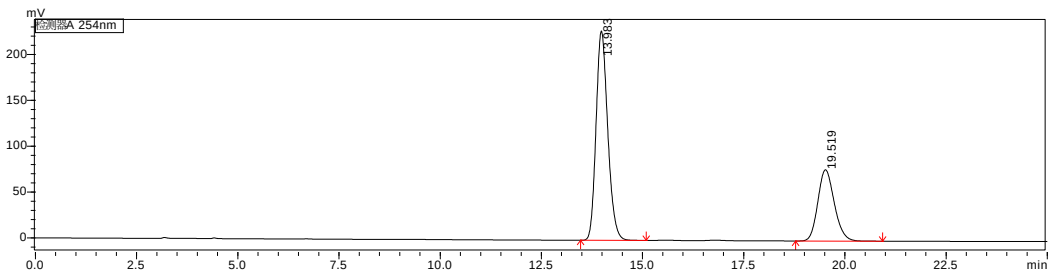
Peak	Ret. time	Area	height	Area%	height%
1	16.937	4061358	152199	97.985	98.742
2	26.865	83527	1939	2.015	1.258
Total		4144885	154138	100.000	100.000



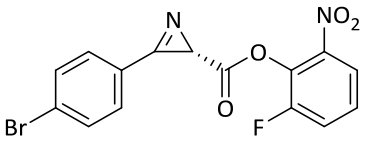
1c



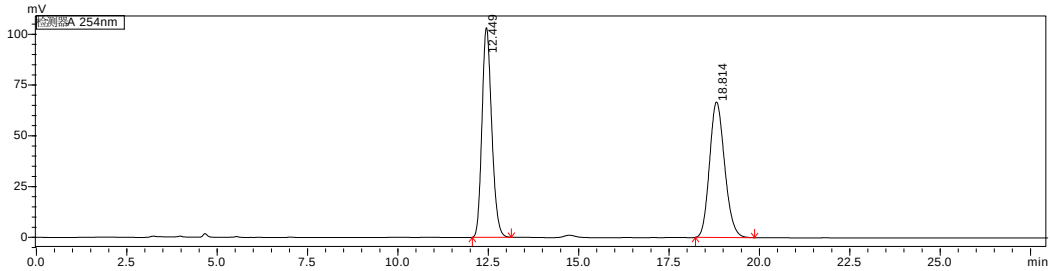
Peak	Ret. time	Area	height	Area%	height%
1	14.556	3178153	148842	50.017	58.955
2	20.543	3176015	103624	49.983	41.045
Total		6354168	252466	100.000	100.000



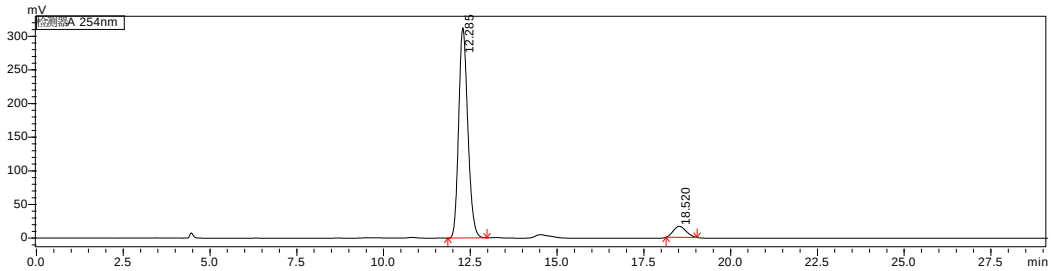
Peak	Ret. time	Area	height	Area%	height%
1	13.983	4583600	228177	67.578	74.599
2	19.519	2199099	77695	32.422	25.401
Total		6782698	305872	100.000	100.000



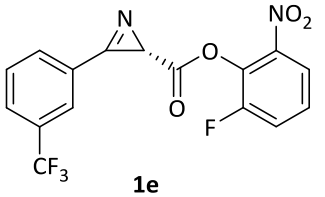
1d



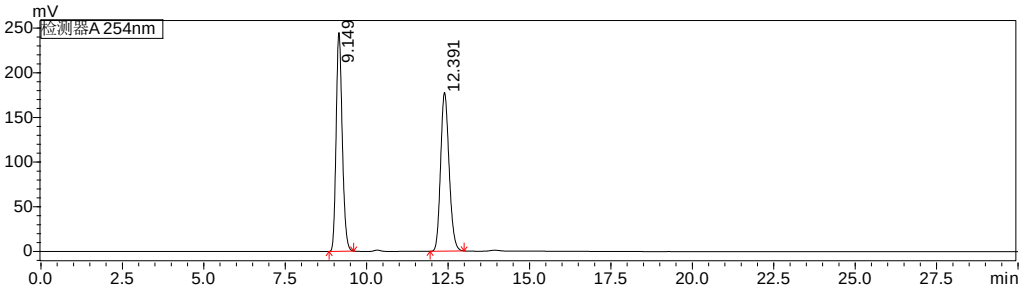
Peak	Ret. time	Area	height	Area%	height%
1	12.449	1937378	103221	50.036	60.752
2	18.814	1934593	66683	49.964	39.248
Total		3871971	169903	100.000	100.000



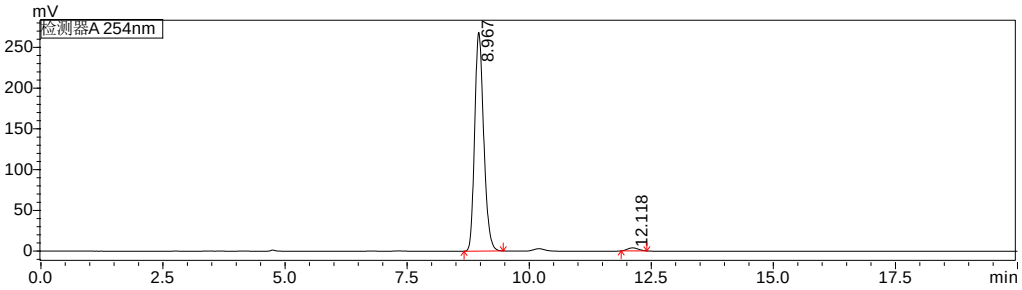
Peak	Ret. time	Area	height	Area%	height%
1	12.285	5736473	312360	93.184	95.034
2	18.520	419597	16321	6.816	4.966
Total		6156070	328682	100.000	100.000



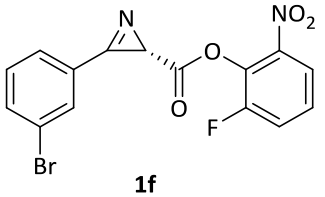
1e



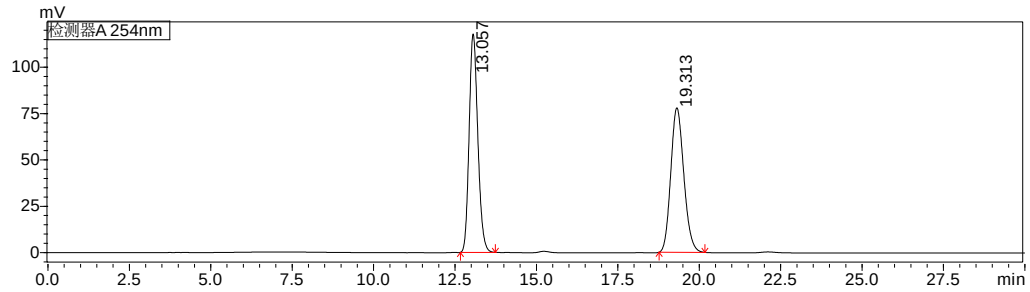
Peak	Ret. time	Area	height	Area%	height%
1	9.149	3203292	244865	49.924	57.964
2	12.391	3213071	177580	50.076	42.036
Total		6416364	422445	100.000	100.000



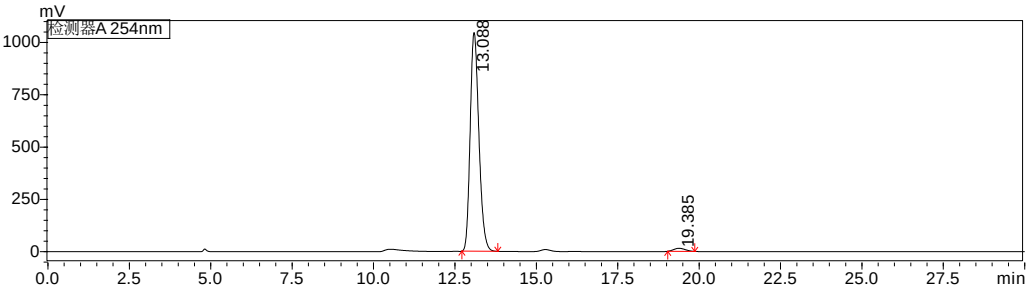
Peak	Ret. time	Area	height	Area%	height%
1	8.967	3453972	268555	98.340	98.627
2	12.118	58296	3738	1.660	1.373
Total		3512268	272292	100.000	100.000



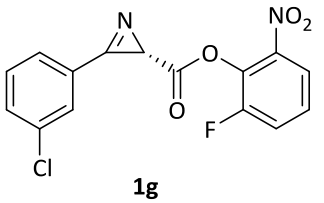
1f



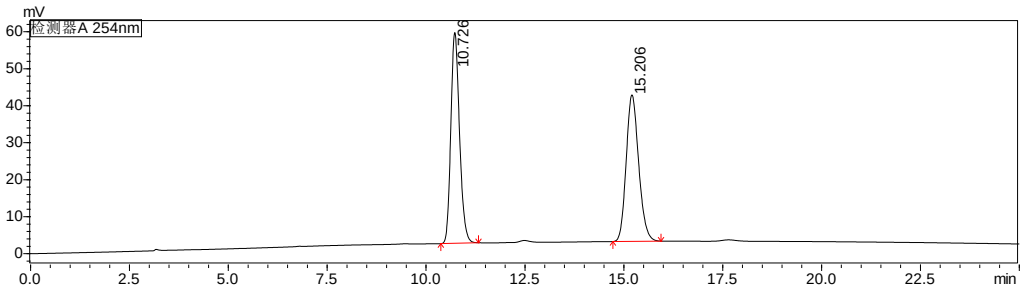
Peak	Ret. time	Area	height	Area%	height%
1	13.057	2184617	117894	50.171	60.195
2	19.313	2169710	77960	49.829	39.805
Total		4354327	195854	100.000	100.000



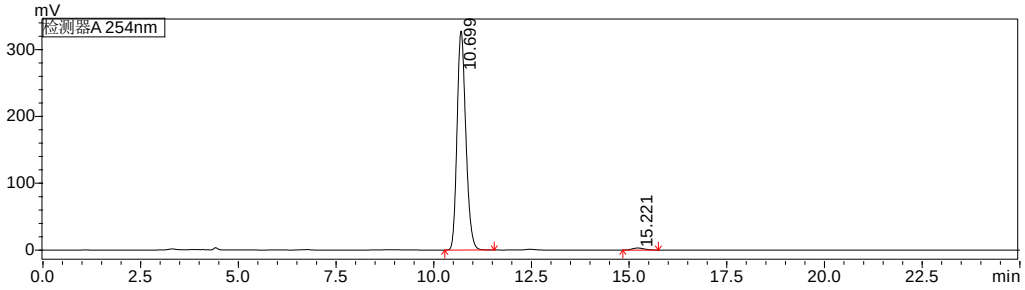
Peak	Ret. time	Area	height	Area%	height%
1	13.088	19486529	1045529	98.183	98.614
2	19.385	360578	14693	1.817	1.386
Total		19847107	1060222	100.000	100.000



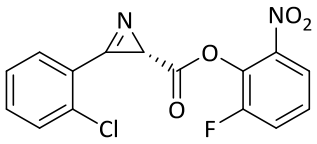
1g



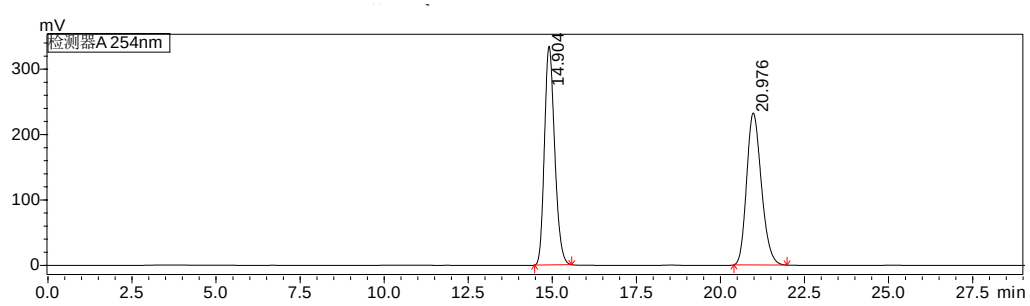
Peak	Ret. time	Area	height	Area%	height%
1	10.726	869749	56984	50.033	59.015
2	15.206	868613	39574	49.967	40.985
Total		1738362	96558	100.000	100.000



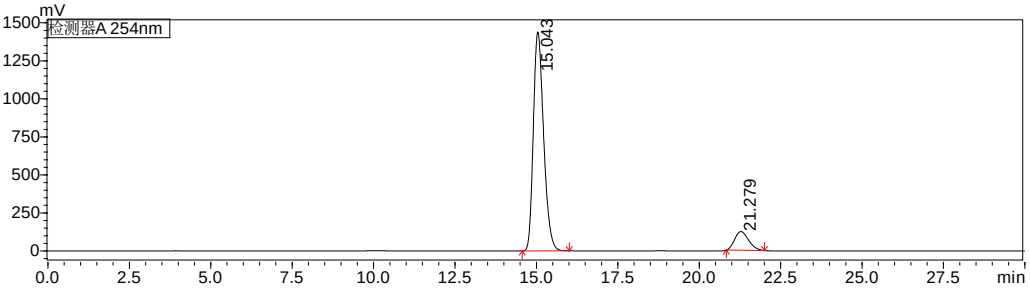
Peak	Ret. time	Area	height	Area%	height%
1	10.699	4448088	268548	98.796	99.111
2	15.221	54229	2408	1.204	0.889
Total		4502317	270957	100.000	100.000



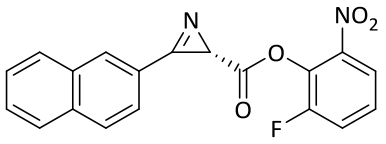
1h



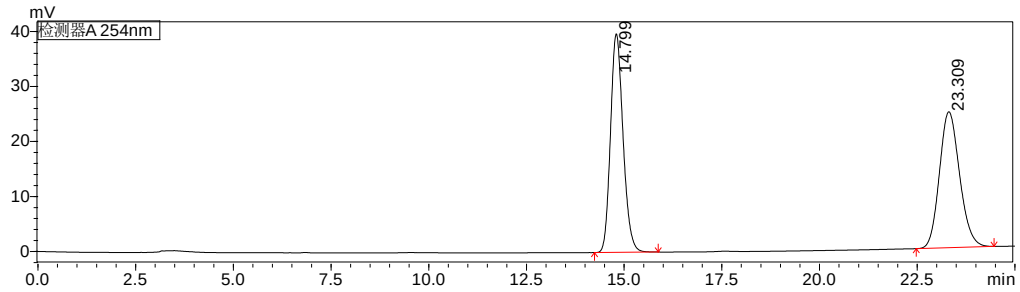
Peak	Ret. time	Area	height	Area%	height%
1	14.904	7073567	334425	49.997	59.010
2	20.976	7074315	232300	50.003	40.990
Total		14147882	566725	100.000	100.000



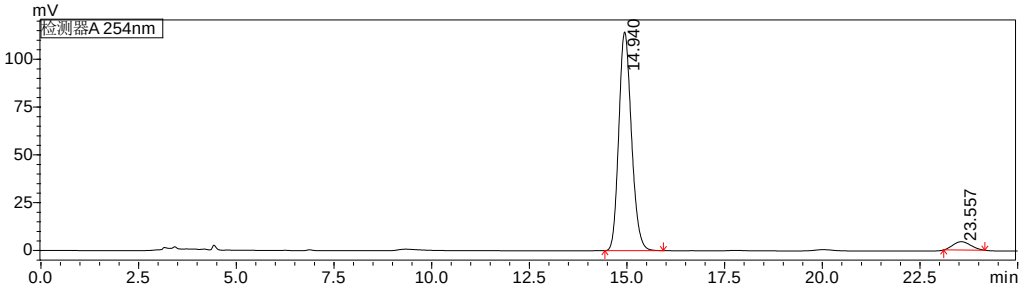
Peak	Ret. time	Area	height	Area%	height%
1	15.043	31579421	1440614	89.595	92.130
2	21.279	3667574	123054	10.405	7.870
Total		35246995	1563668	100.000	100.000



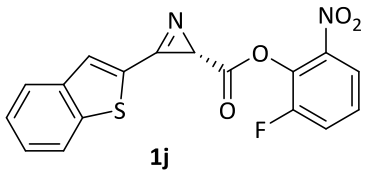
1i



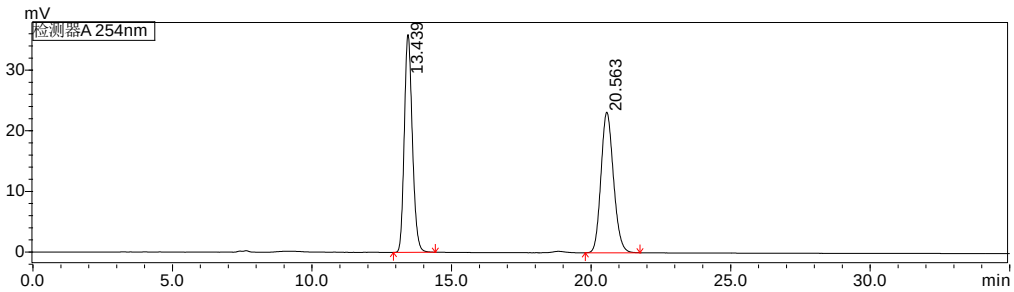
Peak	Ret. time	Area	height	Area%	height%
1	14.799	887802	39729	50.053	61.653
2	23.309	885932	24711	49.947	38.347
Total		1773733	64440	100.000	100.000



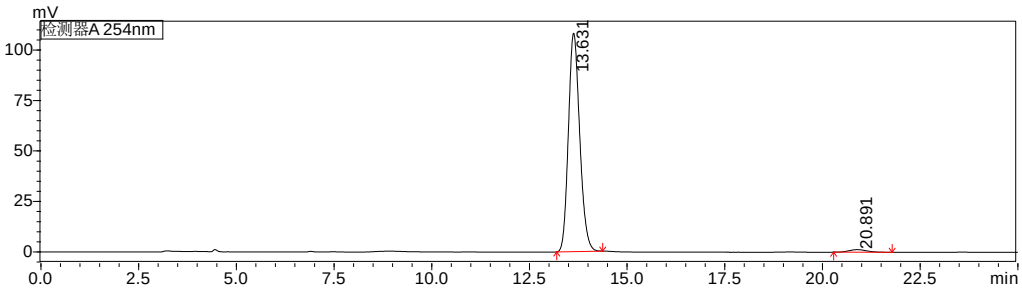
Peak	Ret. time	Area	height	Area%	height%
1	14.940	2574246	114402	94.933	96.334
2	23.557	137389	4353	5.067	3.666
Total		2711636	118756	100.000	100.000



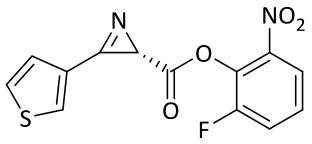
1j



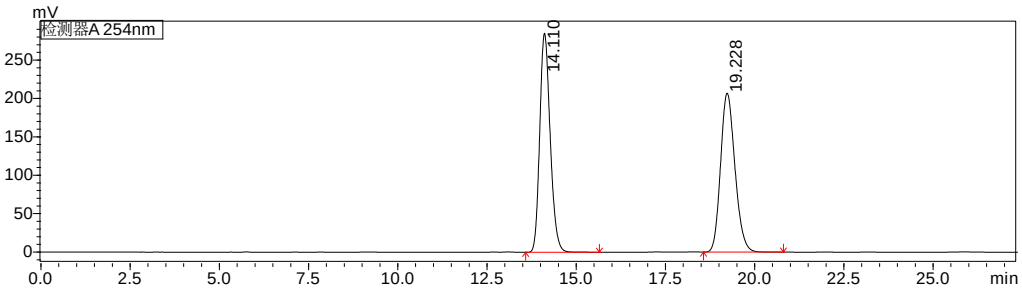
Peak	Ret. time	Area	height	Area%	height%
1	13.439	719853	35944	49.929	60.792
2	20.563	721895	23183	50.071	39.208
Total		1441748	59127	100.000	100.000



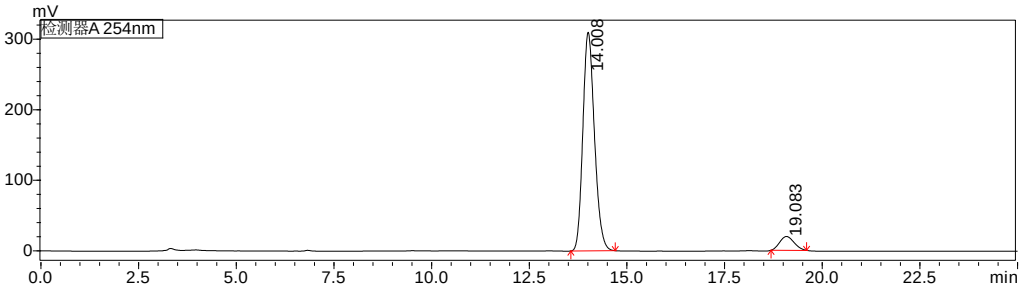
Peak	Ret. time	Area	height	Area%	height%
1	13.631	2179996	108184	98.154	98.831
2	20.891	40997	1279	1.846	1.169
Total		2220993	109463	100.000	100.000



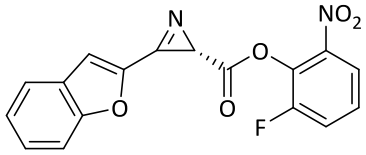
1k



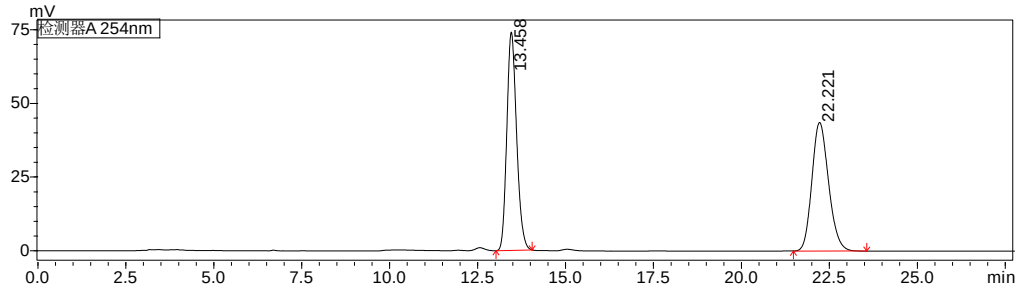
Peak	Ret. time	Area	height	Area%	height%
1	14.110	5808775	285431	50.015	57.961
2	19.228	5805286	207020	49.985	42.039
Total		11614062	492451	100.000	100.000



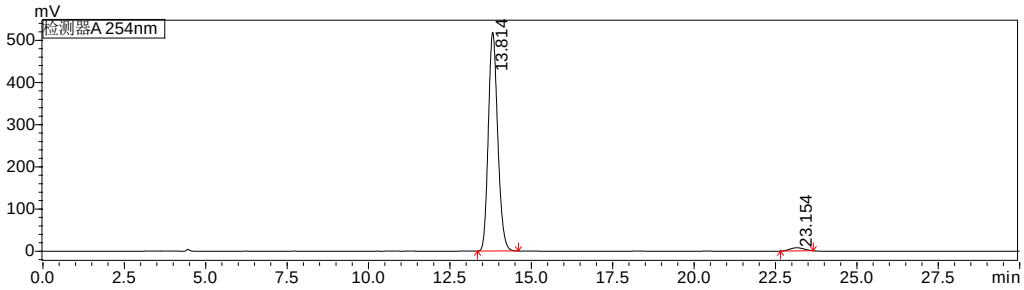
Peak	Ret. time	Area	height	Area%	height%
1	14.008	6394432	309818	92.738	94.050
2	19.083	500739	19599	7.262	5.950
Total		6895171	329417	100.000	100.000



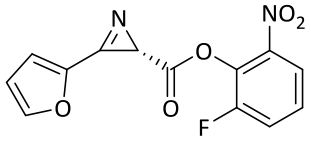
1l



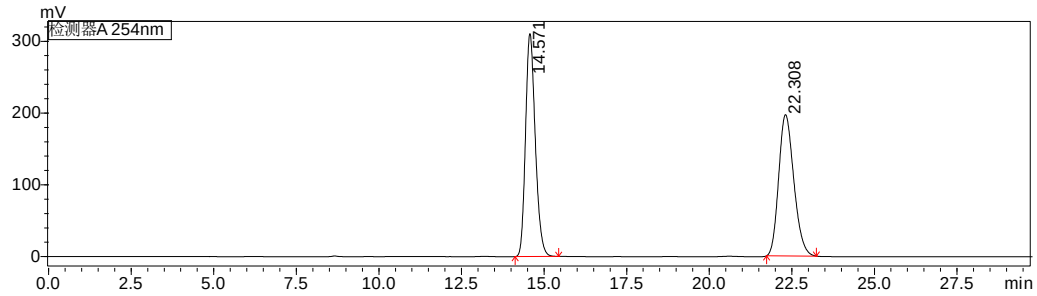
Peak	Ret. time	Area	height	Area%	height%
1	13.458	1432587	74093	49.819	62.930
2	22.221	1442970	43646	50.181	37.070
Total		2875557	117739	100.000	100.000



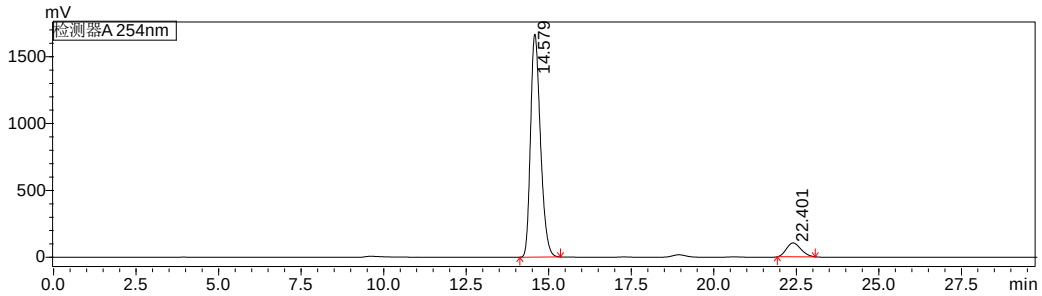
Peak	Ret. time	Area	height	Area%	height%
1	13.814	10416535	518820	97.848	98.566
2	23.154	229047	7549	2.152	1.434
Total		10645582	526369	100.000	100.000



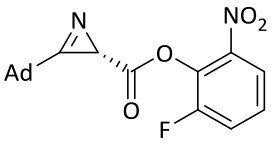
1m



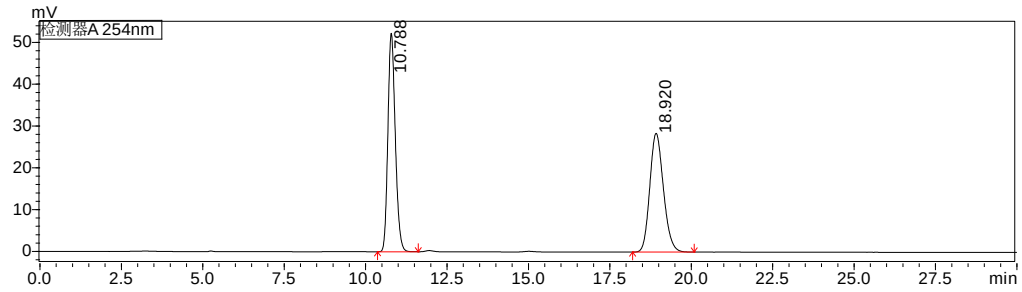
Peak	Ret. time	Area	height	Area%	height%
1	14.571	6352465	310501	50.354	61.206
2	22.308	6263059	196805	49.646	38.794
Total		12615524	507306	100.000	100.000



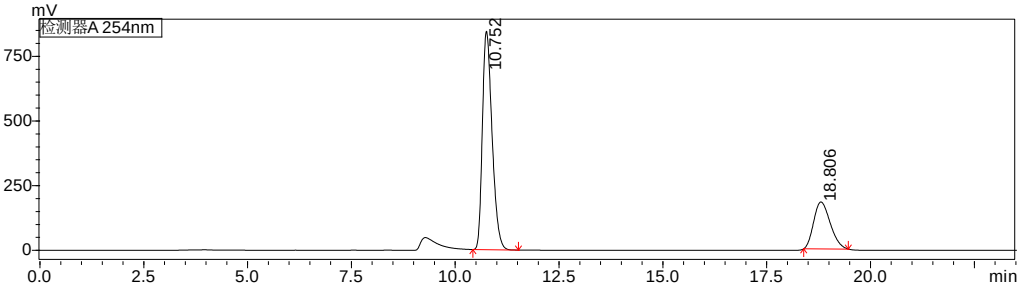
Peak	Ret. time	Area	height	Area%	height%
1	14.579	34848620	1666949	91.715	94.160
2	22.401	3148094	103392	8.285	5.840
Total		37996714	1770341	100.000	100.000



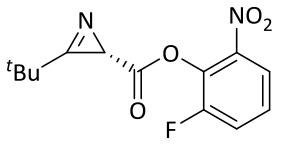
1n



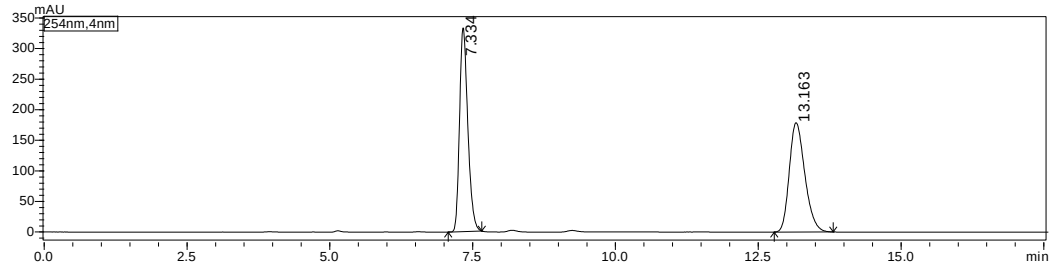
Peak	Ret. time	Area	height	Area%	height%
1	10.788	826290	52271	49.993	64.786
2	18.920	826536	28411	50.007	35.214
Total		1652826	80682	100.000	100.000



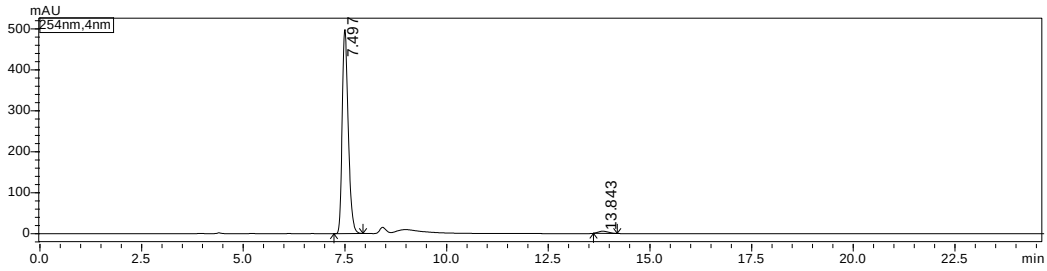
Peak	Ret. time	Area	height	Area%	height%
1	10.752	13698020	844786	73.141	82.323
2	18.806	5030305	181401	26.859	17.677
Total		18728325	1026187	100.000	100.000



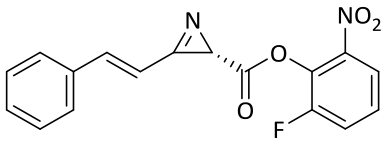
1o



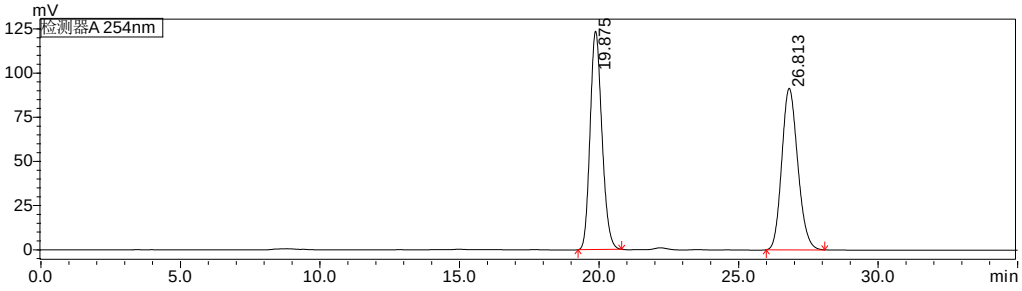
Peak	Ret. time	Area	height	Area%	height%
1	7.334	3348706	332801	49.753	65.035
2	13.163	3381958	178924	50.247	34.965
Total		6730664	511725	100.000	100.000



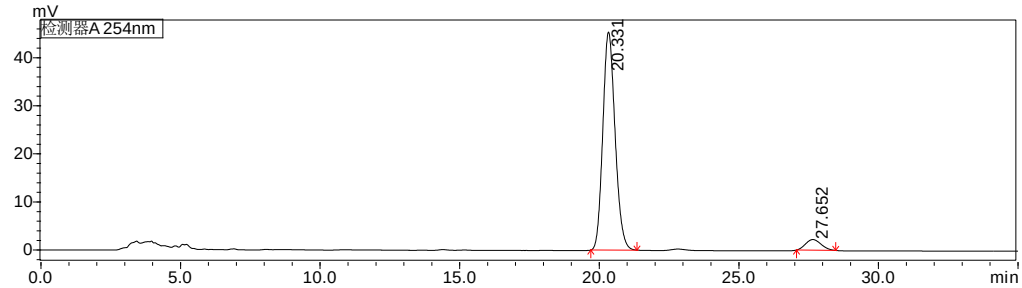
Peak	Ret. time	Area	height	Area%	height%
1	7.497	5158193	498429	98.237	98.930
2	13.843	92575	5392	1.763	1.070
Total		5250767	503821	100.000	100.000



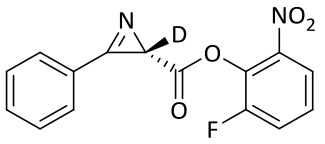
1p



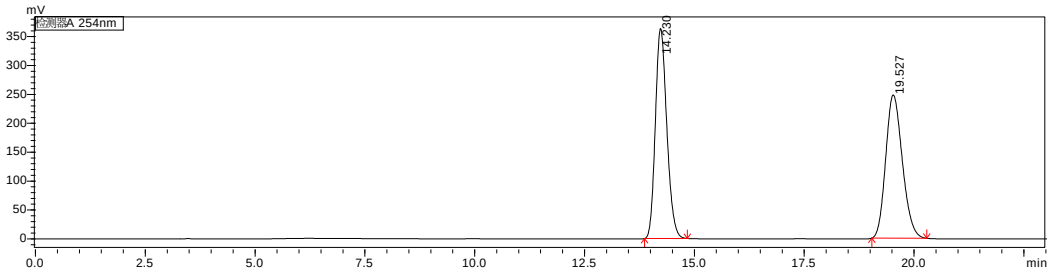
Peak	Ret. time	Area	height	Area%	height%
1	19.875	3640321	123657	50.000	57.497
2	26.813	3640376	91411	50.000	42.503
Total		7280697	215068	100.000	100.000



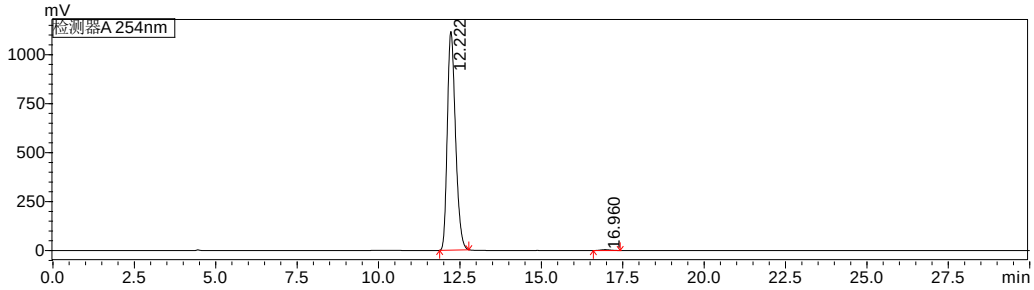
Peak	Ret. time	Area	height	Area%	height%
1	20.331	1386450	45352	94.186	95.334
2	27.652	85586	2219	5.814	4.666
Total		1472035	47572	100.000	100.000



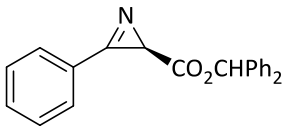
1q



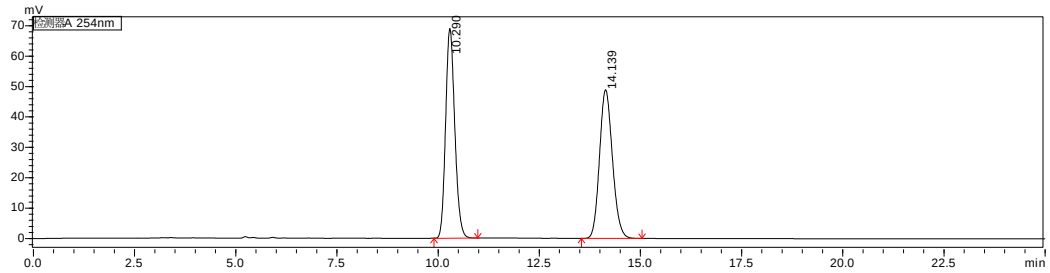
Peak	Ret. time	Area	height	Area%	height%
1	14.230	6582532	363452	50.172	59.450
2	19.527	6537275	247904	49.828	40.550
Total		13119807	611356	100.000	100.000



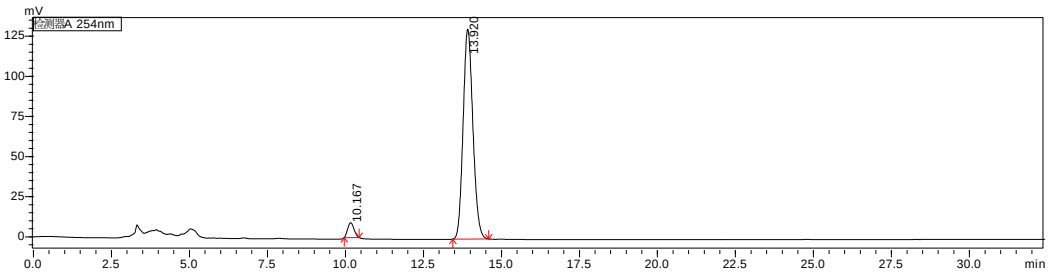
Peak	Ret. time	Area	height	Area%	height%
1	12.222	19517770	1116211	99.489	99.602
2	16.960	100246	4463	0.511	0.398
Total		19618016	1120674	100.000	100.000



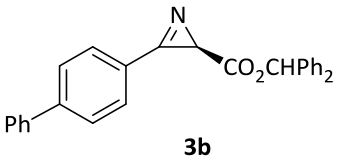
3a



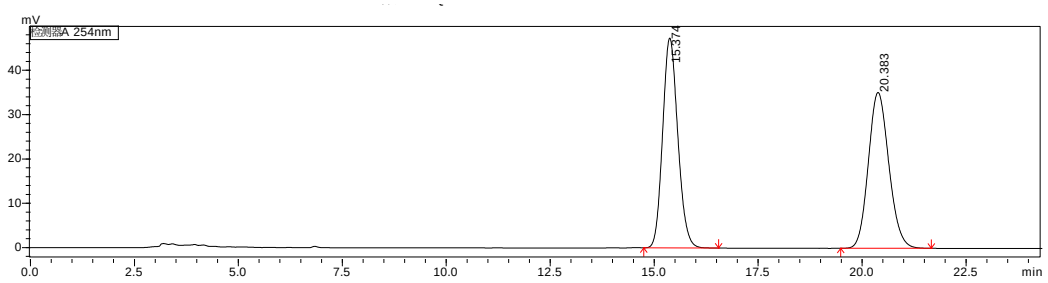
Peak	Ret. time	Area	height	Area%	height%
1	10.290	1085983	68994	49.996	58.521
2	14.139	1086173	48902	50.004	41.479
Total		2172157	117896	100.000	100.000



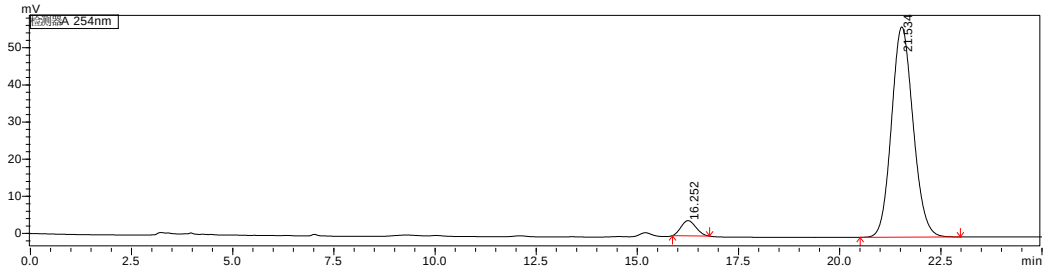
Peak	Ret. time	Area	height	Area%	height%
1	10.167	131663	9351	4.416	6.673
2	13.920	2849740	130783	95.584	93.327
Total		2981403	140134	100.000	100.000



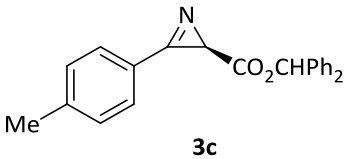
3b



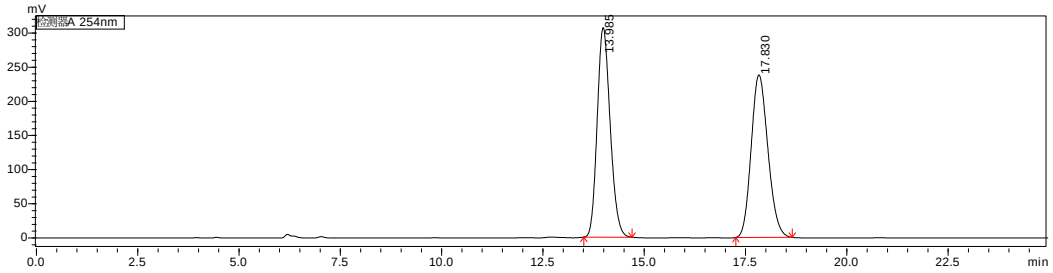
Peak	Ret. time	Area	height	Area%	height%
1	15.374	1201867	47367	49.912	57.383
2	20.383	1206094	35178	50.088	42.617
Total		2407961	82545	100.000	100.000



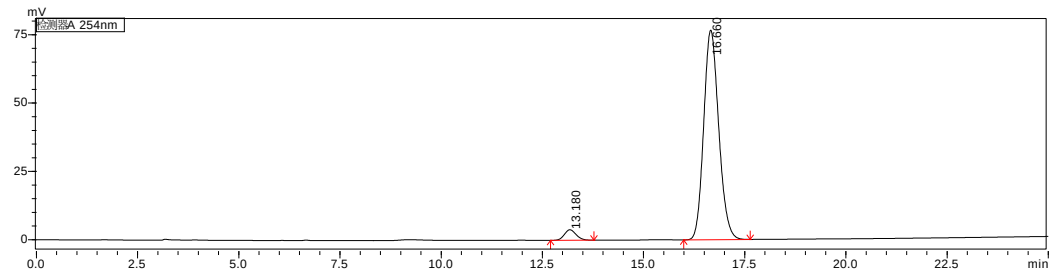
Peak	Ret. time	Area	height	Area%	height%
1	16.252	104461	4092	4.729	6.742
2	21.534	2104608	56597	95.271	93.258
Total		2209069	60689	100.000	100.000



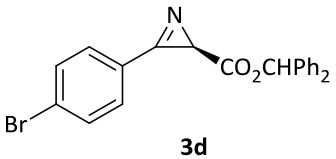
3c



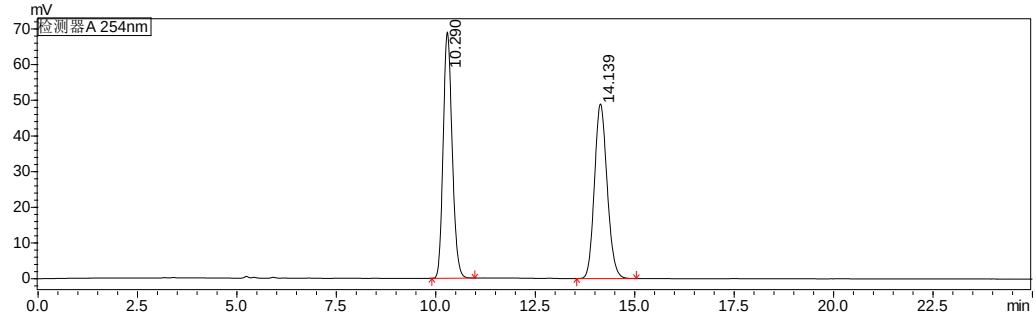
Peak	Ret. time	Area	height	Area%	height%
1	13.985	6843506	306819	50.058	56.345
2	17.830	6827732	237719	49.942	43.655
Total		13671239	544539	100.000	100.000



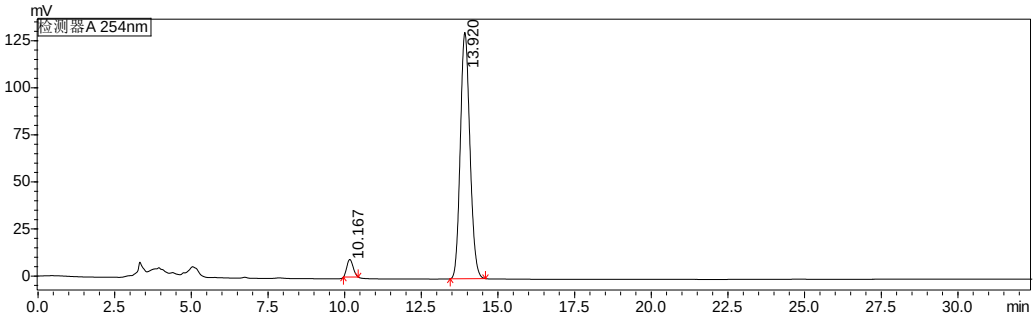
Peak	Ret. time	Area	height	Area%	height%
1	13.180	77999	3863	3.794	4.796
2	16.660	1978106	76685	96.206	95.204
Total		2056105	80549	100.000	100.000



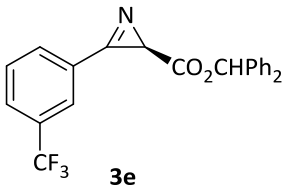
3d



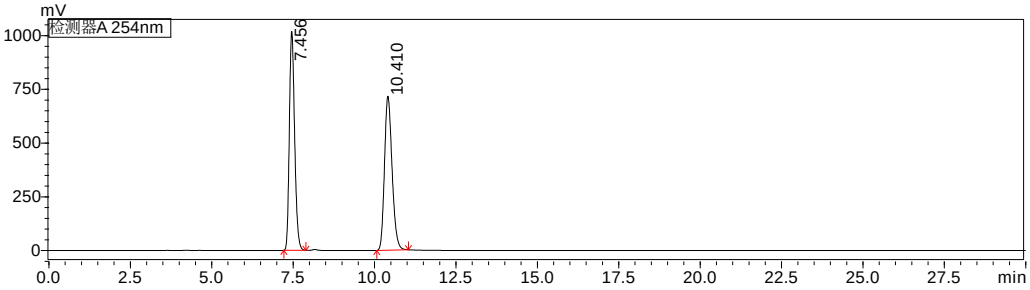
Peak	Ret. time	Area	height	Area%	height%
1	10.290	1085983	68994	49.996	58.521
2	14.139	1086173	48902	50.004	41.479
Total		2172157	117896	100.000	100.000



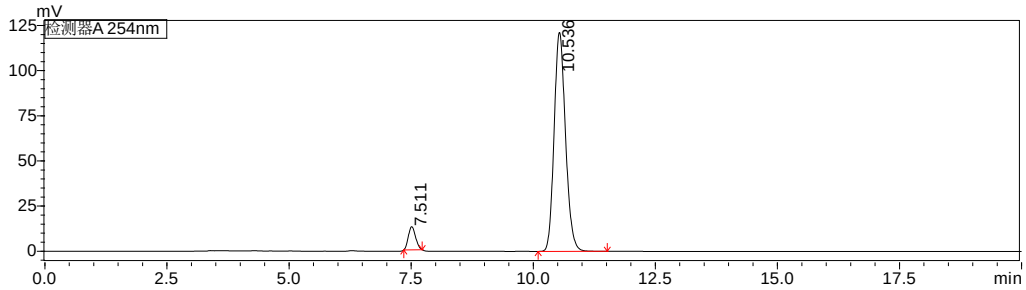
Peak	Ret. time	Area	height	Area%	height%
1	10.167	131663	9351	4.416	6.673
2	13.920	2849740	130783	95.584	93.327
Total		2981403	140134	100.000	100.000



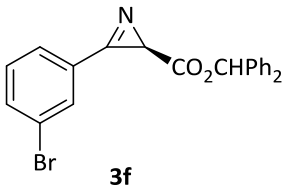
3e



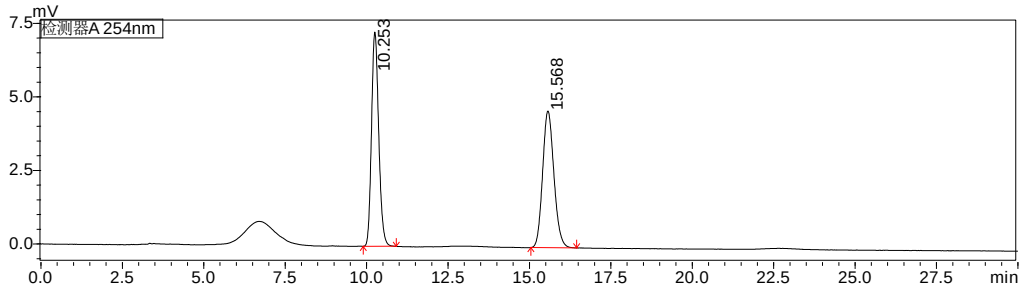
Peak	Ret. time	Area	height	Area%	height%
1	7.456	11452480	1018882	49.682	58.711
2	10.410	11598878	716532	50.318	41.289
Total		23051358	1735414	100.000	100.000



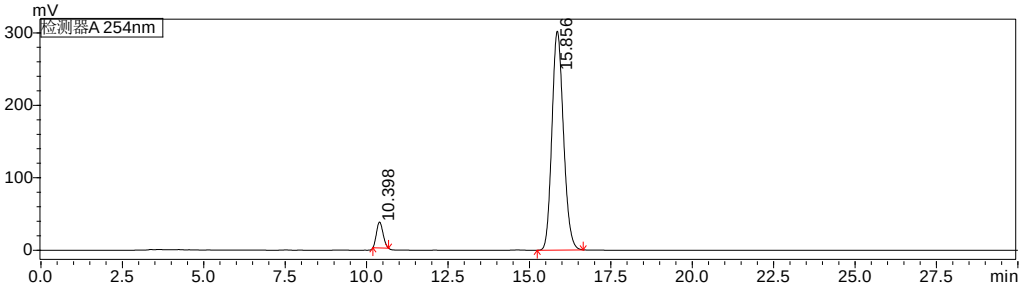
Peak	Ret. time	Area	height	Area%	height%
1	7.511	132060	12819	6.293	9.561
2	10.536	1966363	121257	93.707	90.439
Total		2098423	134076	100.000	100.000



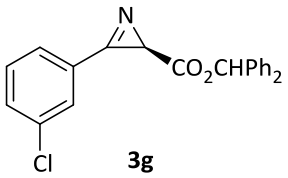
3f



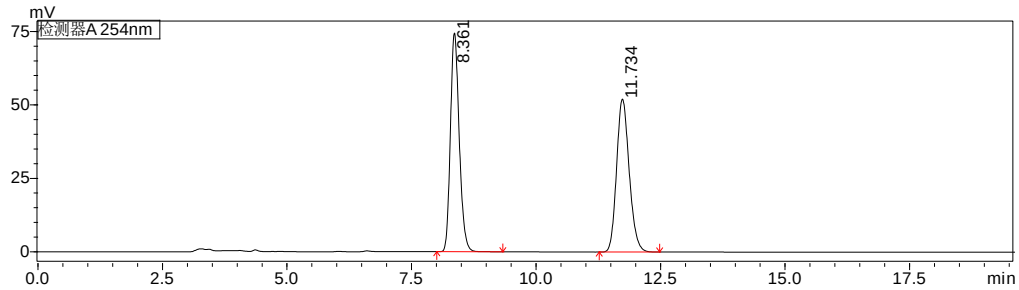
Peak	Ret. time	Area	height	Area%	height%
1	10.253	111857	7284	49.936	61.053
2	15.568	112146	4647	50.064	38.947
Total		224003	11931	100.000	100.000



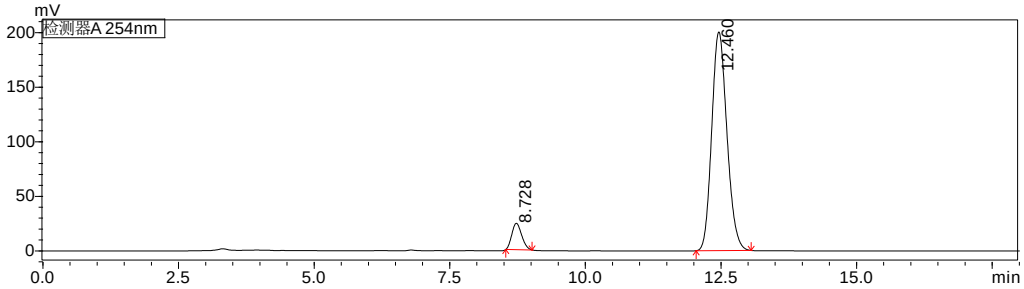
Peak	Ret. time	Area	height	Area%	height%
1	10.398	498175	35896	6.276	10.618
2	15.856	7439936	302182	93.724	89.382
Total		7938110	338078	100.000	100.000



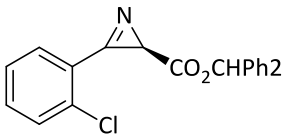
3g



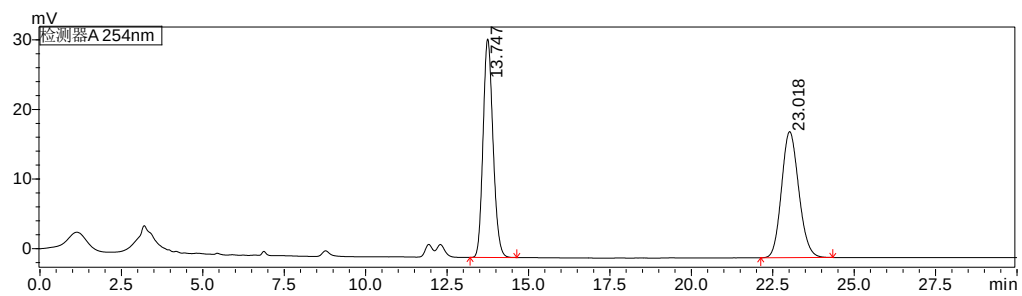
Peak	Ret. time	Area	height	Area%	height%
1	8.361	919941	74464	50.039	58.827
2	11.734	918494	52116	49.961	41.173
Total		1838435	126581	100.000	100.000



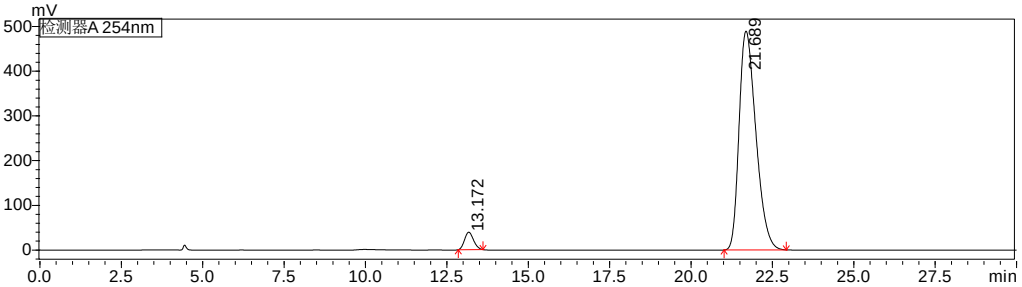
Peak	Ret. time	Area	height	Area%	height%
1	8.728	305674	24197	7.261	10.769
2	12.460	3903993	200496	92.739	89.231
Total		4209667	224693	100.000	100.000



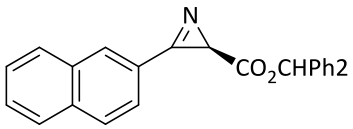
3h



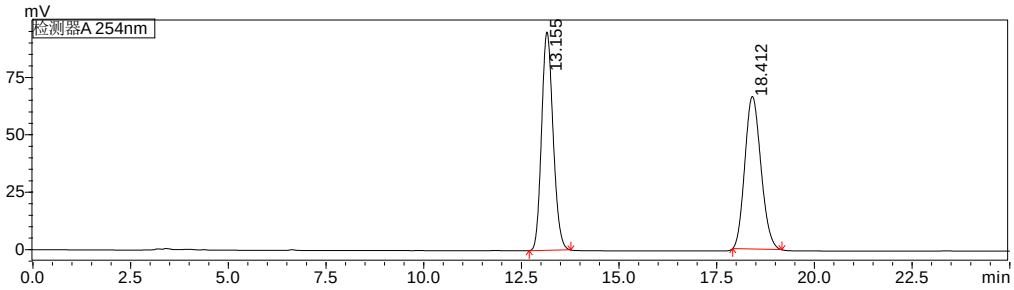
Peak	Ret. time	Area	height	Area%	height%
1	13.747	666473	31394	49.978	63.417
2	23.018	667049	18110	50.022	36.583
Total		1333522	49505	100.000	100.000



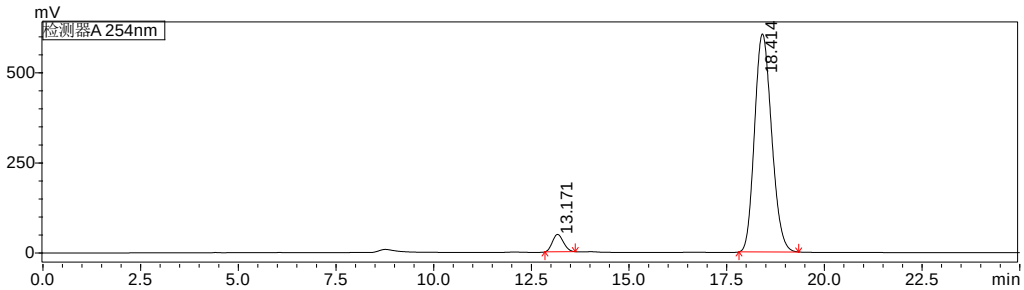
Peak	Ret. time	Area	height	Area%	height%
1	13.172	751891	39087	4.108	7.393
2	21.689	17553015	489650	95.892	92.607
Total		18304907	528737	100.000	100.000



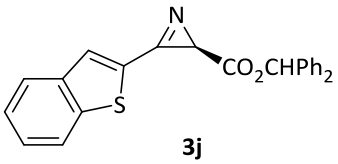
3i



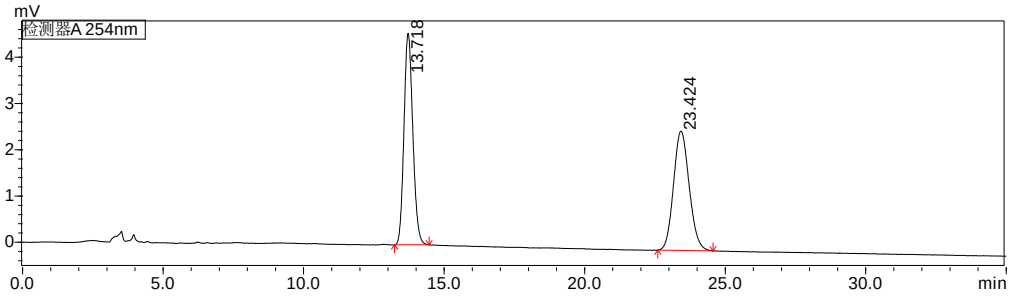
Peak	Ret. time	Area	height	Area%	height%
1	13.155	1949304	95112	50.557	58.872
2	18.412	1906333	66445	49.443	41.128
Total		3855637	161558	100.000	100.000



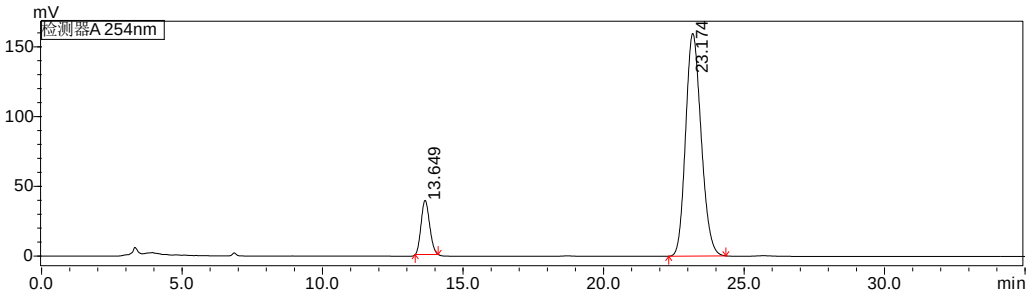
Peak	Ret. time	Area	height	Area%	height%
1	13.171	943585	48242	4.881	7.386
2	18.414	18387108	604913	95.119	92.614
Total		19330692	653155	100.000	100.000



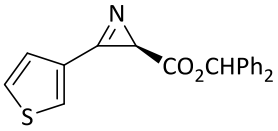
3j



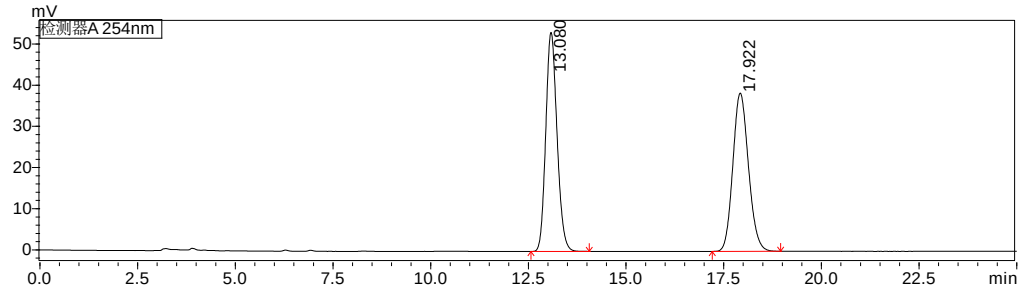
Peak	Ret. time	Area	height	Area%	height%
1	13.718	100068	4577	50.036	63.947
2	23.424	99924	2580	49.964	36.053
Total		199992	7157	100.000	100.000



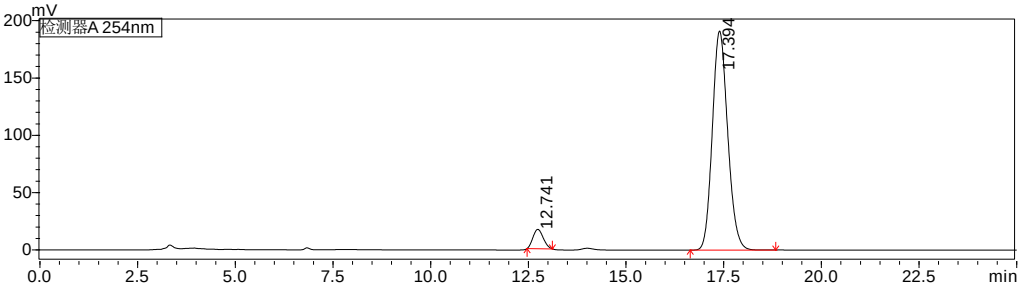
Peak	Ret. time	Area	height	Area%	height%
1	13.649	816033	38817	11.756	19.564
2	23.174	6125415	159596	88.244	80.436
Total		6941448	198413	100.000	100.000



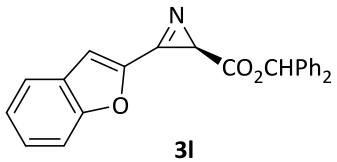
3k



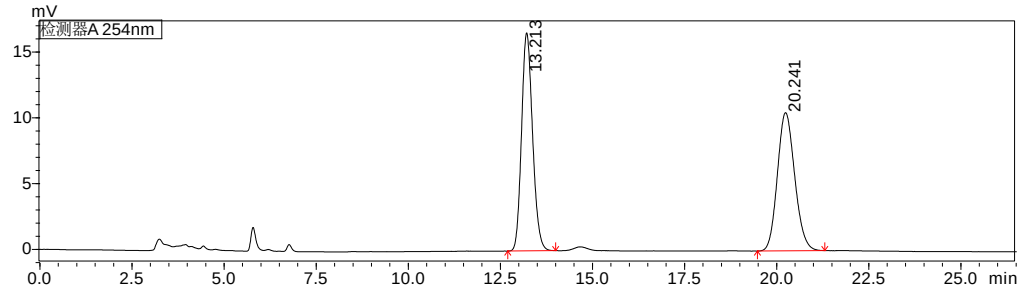
Peak	Ret. time	Area	height	Area%	height%
1	13.080	1066480	53209	49.985	58.060
2	17.922	1067123	38435	50.015	41.940
Total		2133603	91643	100.000	100.000



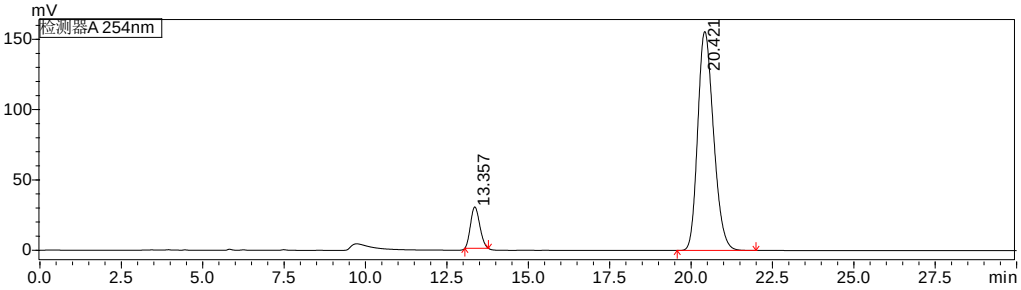
Peak	Ret. time	Area	height	Area%	height%
1	12.741	308497	16913	5.571	8.130
2	17.394	5228642	191125	94.429	91.870
Total		5537139	208038	100.000	100.000



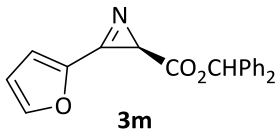
3l



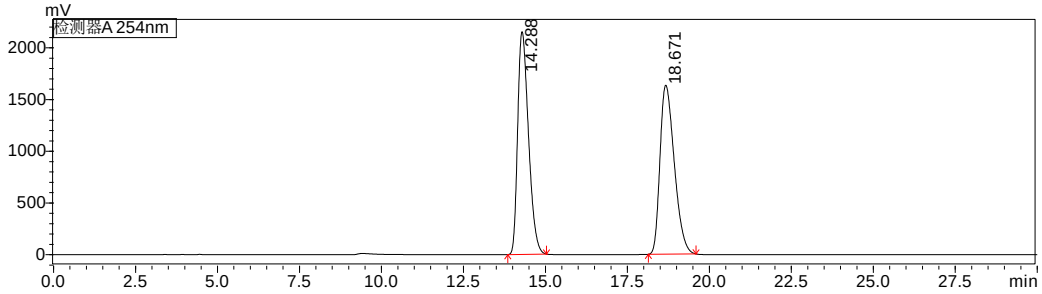
Peak	Ret. time	Area	height	Area%	height%
1	13.213	344632	16572	50.060	61.193
2	20.241	343802	10510	49.940	38.807
Total		688433	27082	100.000	100.000



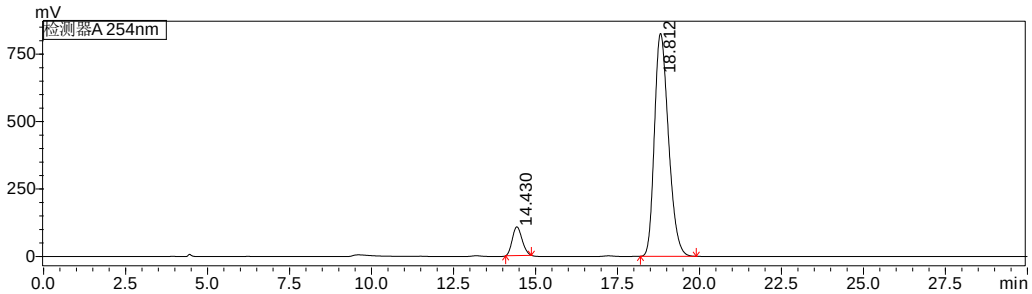
Peak	Ret. time	Area	height	Area%	height%
1	13.357	578768	29447	9.909	15.897
2	20.421	5262348	155793	90.091	84.103
Total		5841117	185240	100.000	100.000



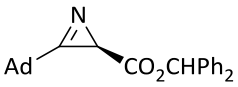
3m



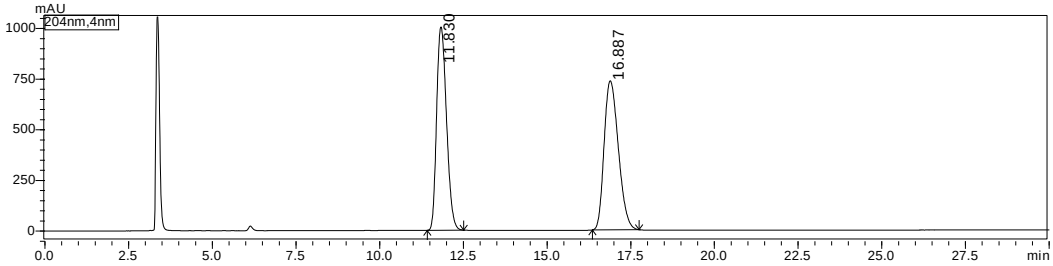
Peak	Ret. time	Area	height	Area%	height%
1	14.288	49367584	2154573	49.887	56.868
2	18.671	49591908	1634163	50.113	43.132
Total		98959492	3788736	100.000	100.000



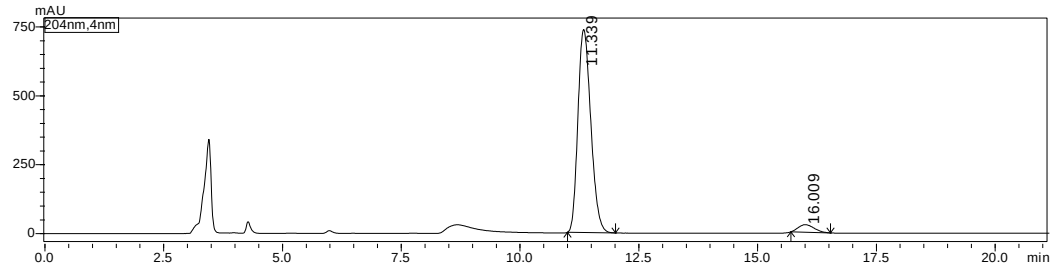
Peak	Ret. time	Area	height	Area%	height%
1	14.430	2202383	106240	8.209	11.389
2	18.812	24625912	826586	91.791	88.611
Total		26828295	932826	100.000	100.000



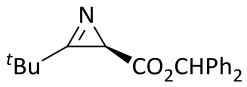
3n



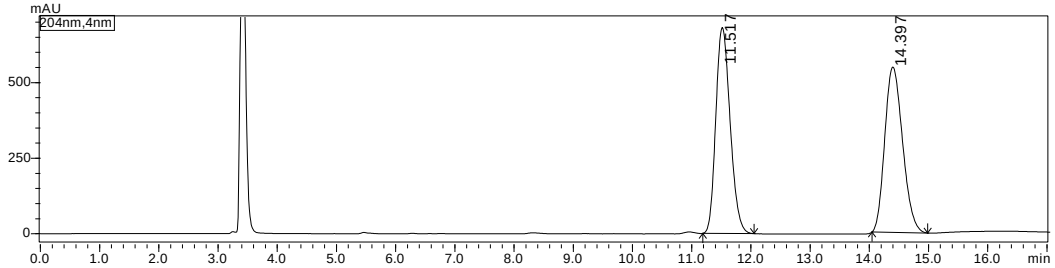
Peak	Ret. time	Area	height	Area%	height%
1	11.830	20626359	1004433	48.629	57.696
2	16.887	21789227	736472	51.371	42.304
Total		42415586	1740905	100.000	100.000



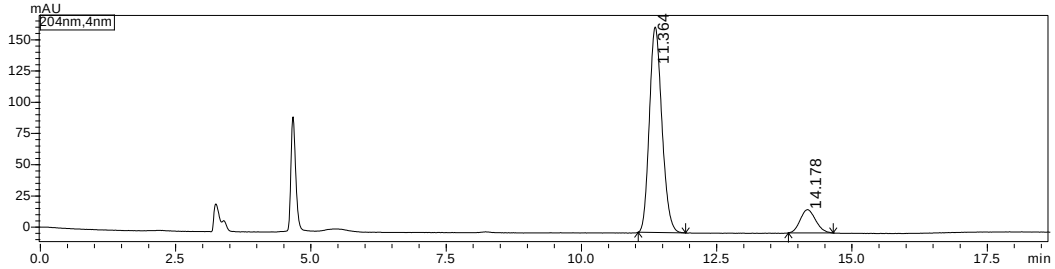
Peak	Ret. time	Area	height	Area%	height%
1	11.339	13919236	736971	95.648	96.416
2	16.009	633261	27395	4.352	3.584
Total		14552496	764366	100.000	100.000



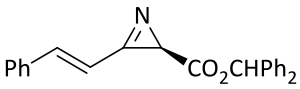
3o



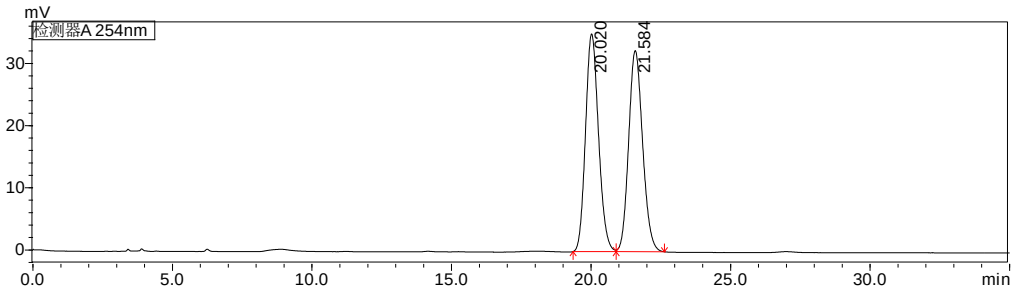
Peak	Ret. time	Area	height	Area%	height%
1	11.517	11450529	681293	50.012	55.487
2	14.397	11444889	546561	49.988	44.513
Total		22895418	1227854	100.000	100.000



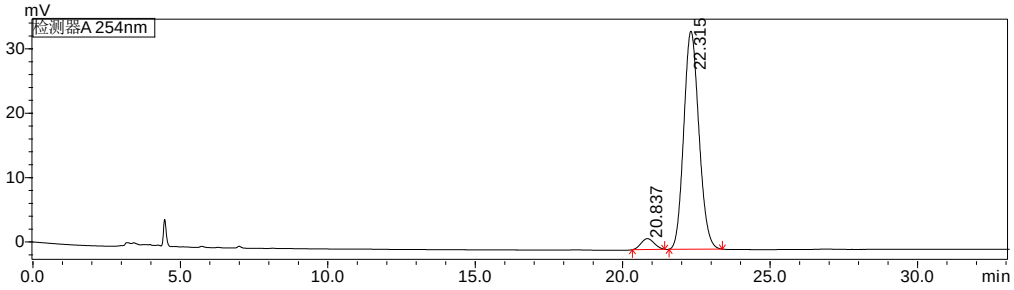
Peak	Ret. time	Area	height	Area%	height%
1	11.364	2655745	164555	87.798	89.845
2	14.178	369099	18600	12.202	10.155
Total		3024844	183154	100.000	100.000



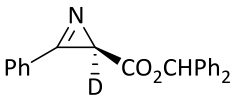
3p



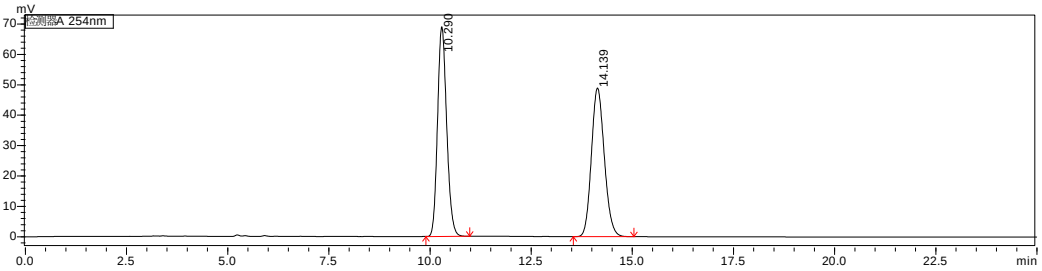
Peak	Ret. time	Area	height	Area%	height%
1	20.020	1134040	35018	50.178	51.983
2	21.584	1125990	32346	49.822	48.017
Total		2260029	67364	100.000	100.000



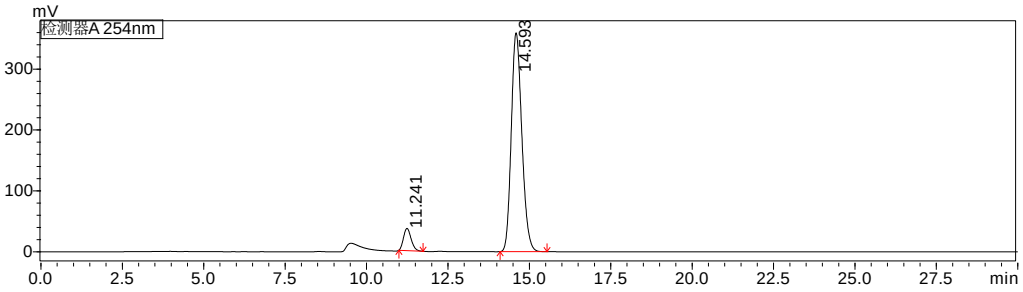
Peak	Ret. time	Area	height	Area%	height%
1	20.837	52008	1682	4.120	4.732
2	22.315	1210232	33875	95.880	95.268
Total		1262240	35558	100.000	100.000



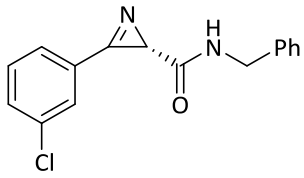
3q



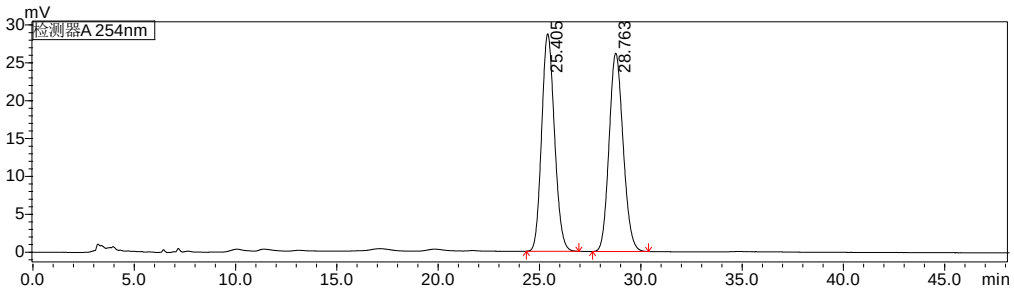
Peak	Ret. time	Area	height	Area%	height%
1	10.290	1085983	68994	49.996	58.521
2	14.139	1086173	48902	50.004	41.479
Total		2172157	117896	100.000	100.000



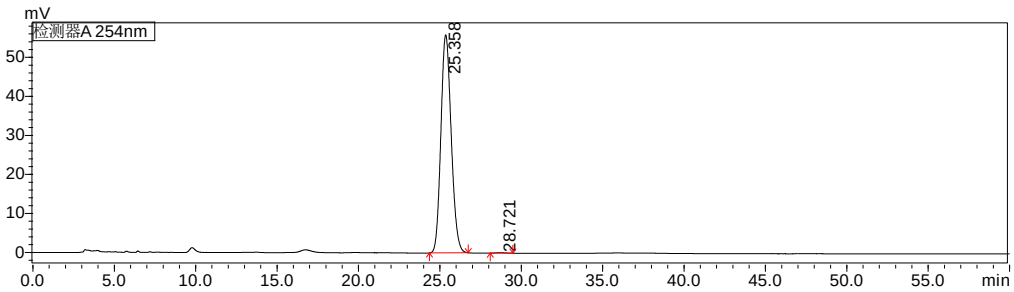
Peak	Ret. time	Area	height	Area%	height%
1	11.241	593764	36585	6.822	9.233
2	14.593	8110060	359669	93.178	90.767
Total		8703824	396254	100.000	100.000



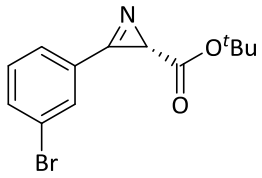
4



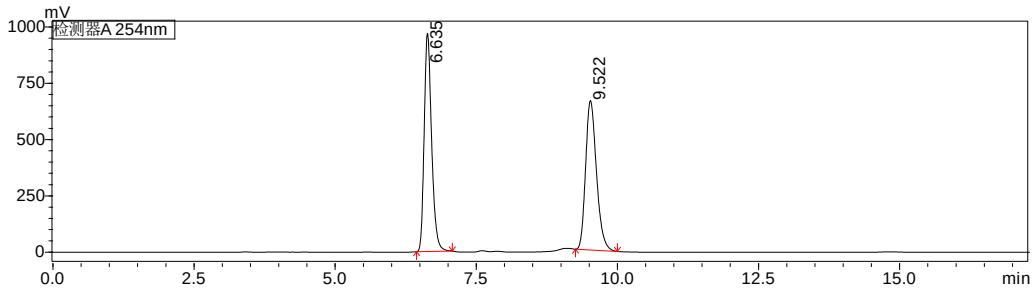
Peak	Ret. time	Area	height	Area%	height%
1	25.405	1264964	28727	50.022	52.318
2	28.763	1263845	26181	49.978	47.682
Total		2528809	54908	100.000	100.000



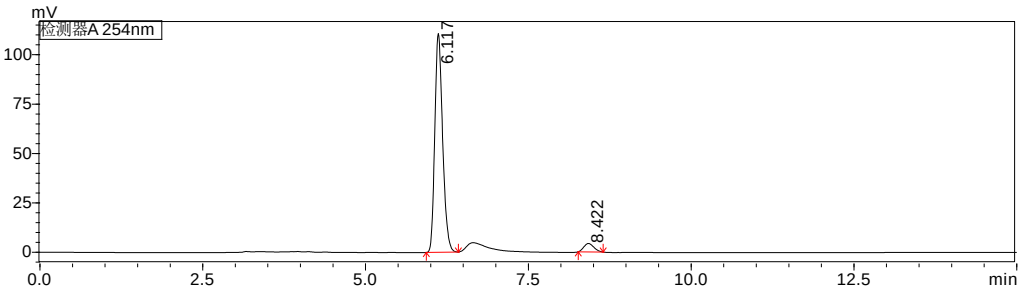
Peak	Ret. time	Area	height	Area%	height%
1	25.358	2459207	55894	99.811	99.802
2	28.721	4647	111	0.189	0.198
Total		2463854	56005	100.000	100.000



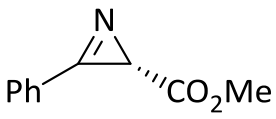
5



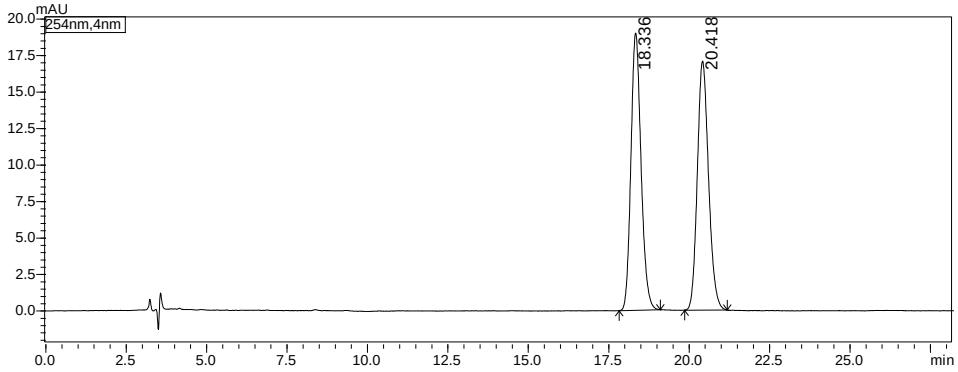
Peak	Ret. time	Area	height	Area%	height%
1	6.635	8872424	969698	50.031	59.356
2	9.522	8861302	663992	49.969	40.644
Total		17733726	1633690	100.000	100.000



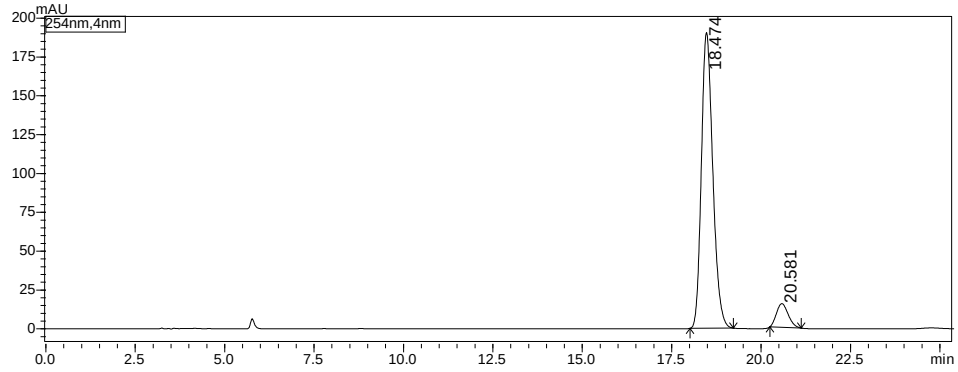
Peak	Ret. time	Area	height	Area%	height%
1	6.117	924119	110757	95.314	96.298
2	8.422	45433	4257	4.686	3.702
Total		969551	115014	100.000	100.000



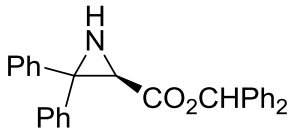
7



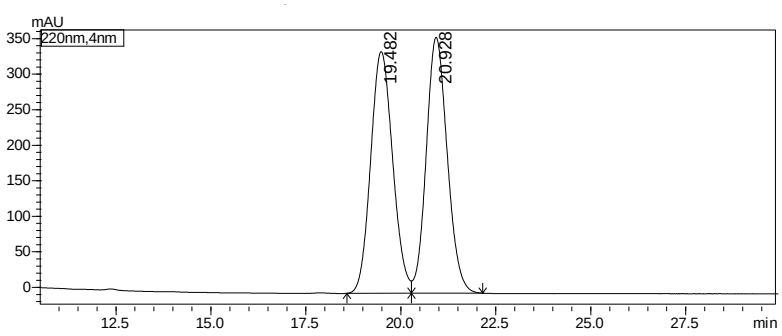
Peak	Ret. time	Area	height	Area%	height%
1	18.336	416508	19004	50.108	52.693
2	20.418	414711	17062	49.892	47.307
Total		831219	36065	100.000	100.000



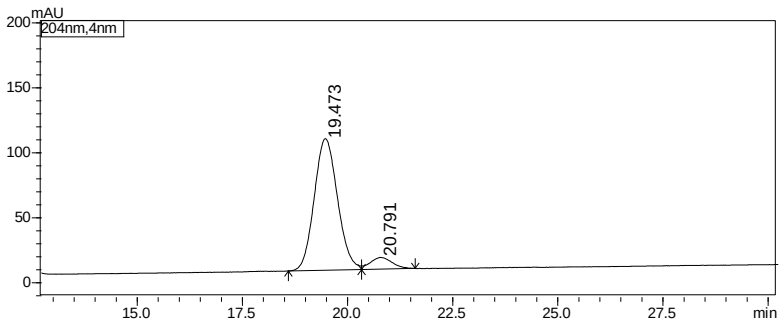
Peak	Ret. time	Area	height	Area%	height%
1	18.474	4234380	190384	92.417	92.583
2	20.581	347462	15252	7.583	7.417
Total		4581842	205636	100.000	100.000



9



Peak	Ret. time	Area	height	Area%	height%
1	19.483	24247646	594773	49.347	48.581
2	20.926	24889505	629513	50.653	51.419
Total		49137151	1224286	100.000	100.000



Peak	Ret. time	Area	height	Area%	height%
1	19.473	3896811	101263	92.273	91.816
2	20.791	326303	9026	7.727	8.184
Total		4223114	110288	100.000	100.000