Electronic Supplementary Material (ESI) for RSC Advances.

Organocatalytic Construction of Spirooxindole Naphthoquinones through Michael/hemiketalization using L-Proline derived Bifunctional Thiourea

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Supporting information

List of content

General remarks

All reactions were carried out in an oven dried flask. Solvents used for reactions and column chromatography were commercial grade and distilled prior to use. Toluene and THF were dried over sodium/benzophenone, CH_2Cl_2 and $CHCl_3$ over CaH_2. Solvents for HPLC

bought as analytical grade and used without further purification. TLC was performed on pre-coated silica gel aluminium plates with 60_F254 indicator, visualised by irradiation with UV light. Column chromatography was performed using silica gel 60-100 mesh. ^{1}H-NMR and ^{13}C-NMR were recorded on a 500 MHz instrument using DMSO-d_6 and $CDCl_3$ as solvent and multiplicity as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (doublet of doublet), dt (doublet of triplet) bs (broad singlet). Coupling constants *J* were reported in Hertz. High resolution mass spectra were obtained by ESI using Q-TOF mass spectrometer. IR spectra were reported in terms of frequency of absorption (cm^{-1}). The enantiomeric excess is obtained by HPLC analysis using a chiral stationary phase column (CHIRALPAK AD-H, AS-H and OD-H). Optical rotation was recorded using polarimeter at a wavelength of 589 nm.

1. X-ray Crystallographic data for compound (5b)

CCDC 985882 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

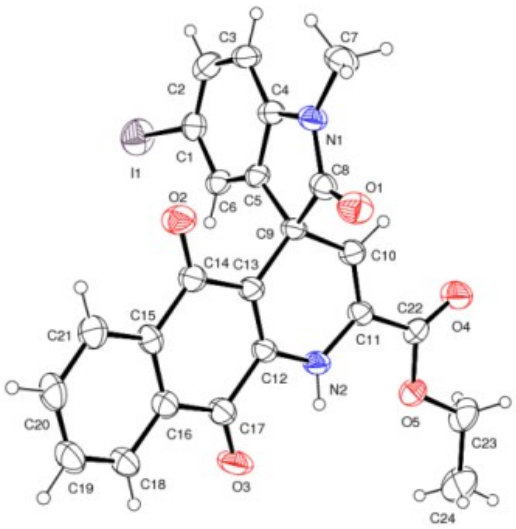
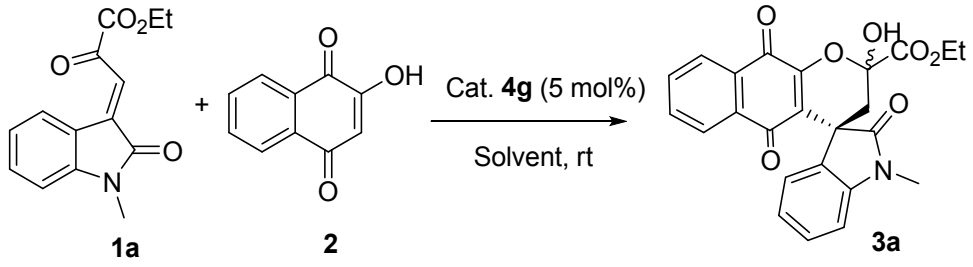


Table 1. Crystal data and structure refinement for 5b

Identification code	shelxl
Empirical formula	C_{25} H_{21} I N_2 O_6
Formula weight	572.34
Temperature	296(2) K
Wavelength	0.71073 A
Crystal system, space group	Orthorhombic, C222(1)
Unit cell dimensions	a = 14.6769(8) A alpha = 90 deg. b = 25.2457(8) A beta = 90 deg. c = 13.0633(6) A gamma = 90 deg.
Volume	4840.3(4) A^3
Z, Calculated density	8, 1.571 Mg/m^3
Absorption coefficient	1.366 mm^-1
F(000)	2288
Crystal size	0.35 x 0.32 x 0.30 mm
Theta range for data collection	2.24 to 25.00 deg.
Limiting indices	-17<=h<=17, -30<=k<=30, -15<=l<=15
Reflections collected / unique	29859 / 4280 [R(int) = 0.0526]
Completeness to theta	= 25.00 99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.6897 and 0.6425
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4280 / 57 / 326
Goodness-of-fit on F^2	1.042
Final R indices [I>2sigma(I)]	R1 = 0.0391, wR2 = 0.0934
R indices (all data)	R1 = 0.0756, wR2 = 0.1169
Absolute structure parameter	-0.05(3)
Largest diff. peak and hole	0.433 and -0.549 e.A^-3

Optimization studies:

Table . Solvent optimization studies of reaction conditions using organocatalyst **4g**[a]

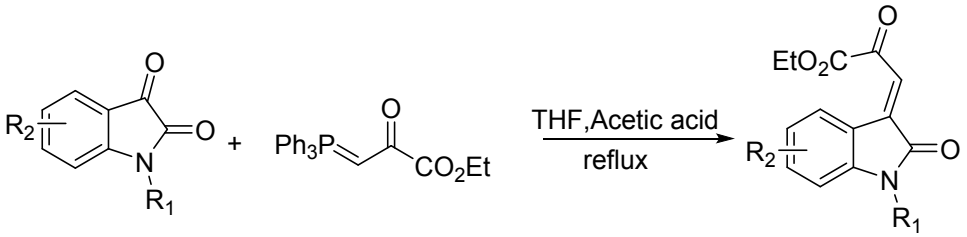


S.No	Solvent	Yield (%)[b]	ee (%)[c]
1	DCM	84	98
2	$CHCl_3$	85	94
3	DCE	85	97
4	Acetone	80	96
5	Toluene	81	94
6	CF_3-C_6H_5	82	98
7	THF	81	95
8	Diethylether	80	98
9	MTBE	82	97
10	Acetonitrile	86	96

[a] The reactions were carried out with **1** (0.1 mmol), **2** (0.1 mmol), and catalyst **4g** (5 mol%) in 1 ml of appropriate solvent at mentioned temperature. [b] Isolated yield. [c] Determined using chiral stationary phase.

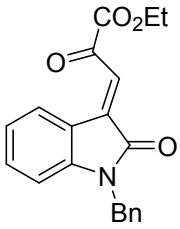
Subsequently, optimization of other parameters of the reaction conditions for the purpose of obtaining better yield was undertaken. Increasing the catalyst loading to 10 mol% or 20 mol%, did not have any significant improvement in the yield of the product **3a**. Prolonged reaction duration was observed, when only 2 mol% of organocatalyst **4g** was used. Instead of 5h, the completion of reaction was ascertained only after 3 days. Hence 5 mol% of catalyst loading was chosen for the identification of suitable reaction medium.. Since, protic solvents such as methanol and isopropanol are not suitable for H-bonding catalysis, they were not explored in solvent screening. The results suggest that there was little influence of solvents in this transformation. The expected product **3a** was isolated in 80% yield and 90% ee irrespective of the reaction medium.

I.General procedure for the preparation of oxindole ketoesters 1.



Isatin (1.0 equiv) and phosphorus ylide (3.0 equiv) are stirred in THF under reflux for 2h. The solvent was removed under reduced pressure and the residue was purified by a flash column chromatography (silica gel, ethyl acetate: hexane = 1:10) to give the corresponding oxindole ketoesters **1**

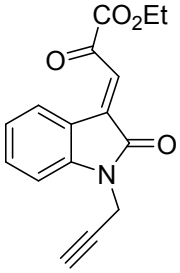
ethyl (E)-3-(1-benzyl-2-oxoindolin-3-ylidene)-2-oxopropanoate 1b



General experimental procedure **I** was followed to prepare the product **1b .** The desired product was obtained as reddish brown solid Yield: 0.5 g, 36%; ^{1}H NMR (500MHz, CHLOROFORM-d): δ = 8.69 (d, *J*=7.6 Hz, 1H), 7.92 (s, 1H), 7.27 - 7.38 (m, 6H), 7.05 (t, *J*=7.7 Hz, 1H), 6.72 (d, *J*=7.9 Hz, 1H), 4.96 (s, 2H), 4.45 (q, *J*=7.0 Hz, 2H), 1.45 (t, *J*=7.1 Hz, 3H); ^{13}C NMR (125MHz, CHLOROFORM-d): δ = 182.93, 167.64, 161.01, 146.31, 140.26, 135.21, 134.42, 129.17, 128.90, 127.86, 127.27, 123.11, 121.94, 120.26, 109.44, 63.00, 44.0, 14.07; IR (ν, cm^{-1}): 2982, 2933, 2360, 1722, 1689, 1594, 1463, 1350, 1268, 1186, 1096, 1047, 1012, 959, 902, 859, 834, 782, 750 ; HRMS (ESI) Calcd. for $C_{20}H_{17}NO_4$+Na^{+}: 358.1050, Found: 358.1045.

ethyl (E)-2-oxo-3-(2-oxo-1-(prop-2-yn-1-yl)indolin-3-ylidene)propanoate1c

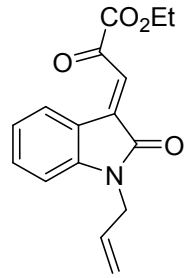
General experimental procedure **I** was followed to prepare the product **1c.** The desired product



was obtained as reddish brown solid, Yield: 0.54 g, 35%. ^{1}H NMR (500MHz, CHLOROFORM-d): δ = 8.71 (d, *J*=7.6 Hz, 1H), 7.87 (s, 1H), 7.49 (t, *J*=7.7 Hz, 1H), 7.13 (t, *J*=7.7 Hz, 1H), 7.05 (d, *J*=7.9 Hz, 1H), 4.56 (d, *J*=2.5 Hz, 2H), 4.44 (q, *J*=7.3 Hz, 2H), 2.28 (t, *J*=2.5 Hz, 1H), 1.45 (t, *J*=7.1 Hz, 3H). ^{13}C NMR (125MHz, CHLOROFORM-d): δ = 182.83, 166.61, 160.93, 145.1, 139.91, 134.46, 129.19, 123.44, 122.12, 120.20, 109.42, 76.31, 72.70, 63.03, 29.43, 14.05; IR (ν, cm^{-1}): 3255, 2922, 2857, 1728, 1604, 1462, 1343, 1273, 1183, 1093, 1038, 924, 860, 814, 794, 753; HRMS (ESI) Calcd. for $C_{16}H_{13}NO_4$+Na^{+}: 306.0737, Found: 306.0735.

Ethyl (E)-3-(1-allyl-2-oxoindolin-3-ylidene)-2-oxopropanoate 1d

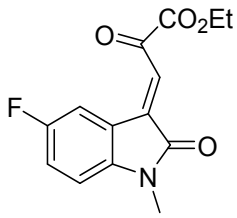
General experimental procedure **I** was followed to prepare the product **1d.** The desired product



was obtained as reddish brown solid, Yield: 0.56 g, 38%; ^{1}H NMR (500MHz, CHLOROFORM-d): δ = 8.68 (d, *J*=7.6 Hz, 1H), 7.85 (s, 1H), 7.41 (t, *J*=7.7 Hz, 1H), 7.06 (t, *J*=7.7 Hz, 1H), 6.80 (d, *J*=7.6 Hz, 1H), 5.79 - 5.90 (m, 1H), 5.19 - 5.30 (m, 2H), 4.43 (q, *J*=7.1 Hz, 2H), 4.38 (d, *J*=4.7 Hz, 2H), 1.44 (t, *J*=7.1 Hz, 3H); ^{13}C NMR (125MHz, CHLOROFORM-d): δ = 182.92, 167.19, 161.00, 146.4, 140.25, 134.4, 130.87, 129.13, 123.01, 121.76, 120.17, 117.92, 109.29, 62.96, 42.48, 14.05; IR (ν, cm^{-1}): 3059, 2986, 1736, 1689, 1611, 1467, 1435, 1349, 1265, 1189, 1154, 1093, 1046, 989, 929, 854, 783, 729, 699; HRMS (ESI) Calcd. for $C_{16}H_{15}NO_4$+Na^{+}: 308.0893, Found: 308.0890.

ethyl (E)-3-(5-fluoro-1-methyl-2-oxoindolin-3-ylidene)-2-oxopropanoate 1e

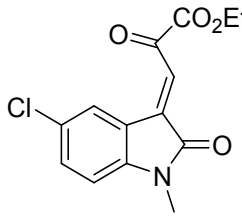
General experimental procedure **I** was followed to prepare the product **1e.** The desired product



was obtained as reddish brown solid, Yield: 0.6 g, 40%. ^{1}H NMR (500MHz, CHLOROFORM-d): δ = 8.43 (dd, *J*=9.1, 2.8 Hz, 1H), 7.85 (s, 1H), 7.14 (td, *J*=8.5, 2.5 Hz, 1H), 6.72 (dd, *J*=8.7, 4.3 Hz, 1H), 4.43 (q, *J*=7.3 Hz, 2H), 3.22 (s, 3H), 1.44 (t, *J*=7.1 Hz, 3H); ^{13}C NMR (125MHz, CHLOROFORM-d): δ = 182.87, 167.09, 160.73, 159.79, 157.88, 143.27, 143.26, 139.95, 139.93, 122.72, 120.75, 120.70, 120.69, 120.51, 116.60, 116.39, 108.81, 108.75, 63.10, 26.42, 14.03; IR (ν, cm^{-1}): 3111, 3062, 2927, 2856, 1717, 1683, 1597, 1459, 1364, 1326, 1265, 1200, 1141, 1110, 1075, 1032, 998, 900, 838, 805, 723, 701; HRMS (ESI) Calcd. for $C_{14}H_{12}NO_4F$+Na^{+}: 300.0643, Found: 300.0640

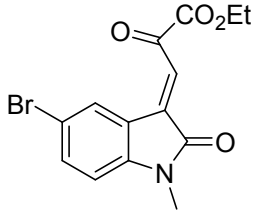
ethyl (E)-3-(5-chloro-1-methyl-2-oxoindolin-3-ylidene)-2-oxopropanoate 1f

General experimental procedure **I** was followed to prepare the product **1f.** The desired product



was obtained as reddish brown solid. 0.45 g, 38%. ^{1}H NMR (500MHz, CHLOROFORM-d): δ= 8.68 (s, 1H), 7.87 (d, *J*=1.6 Hz, 1H), 7.40 (d, *J*=8.2 Hz, 1H), 6.73 (d, *J*=8.2 Hz, 1H), 4.44 (q, *J*=7.3 Hz, 2H), 3.23 (s, 3H), 1.44 - 1.48 m, 3 H). ^{13}C NMR (125MHz, CHLOROFORM-d): δ = 181.76, 165.88, 159.64, 144.44, 13.36, 132.83, 127.90, 127.42, 121.80, 119.98, 108.22, 62.07, 28.65, 12.98; IR (ν, cm^{-1}): 3744, 3240, 3064, 2922, 2855, 2326, 1723, 1599, 1453, 1353, 1313, 1254, 1170, 1101, 1025, 897, 820, 714 ; HRMS (ESI) Calcd. for $C_{14}H_{12}NO_4Cl$+Na^{+}: 316.0347, Found: 316.0345.

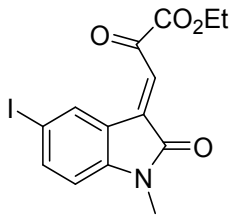
ethyl (E)-3-(5-bromo-1-methyl-2-oxoindolin-3-ylidene)-2-oxopropanoate 1g



General experimental procedure **I** was followed to prepare the product **1g.** The desired product was obtained as reddish brown solid.Yield: 0.42 g, 40%. ^{1}H NMR (400MHz, CHLOROFORM-d): δ = 8.67 (d, *J*=2.2 Hz, 1H), 7.86 (s, 1H), 7.39 (dd, *J*=8.4, 2.1 Hz, 1H), 6.72 (d, *J*=8.3 Hz, 1H), 4.43 (q,

J=7.1 Hz, 2H), 3.22 (s, 3H), 1.44 (t, *J*=7.2 Hz, 3H). ^{13}C NMR (100MHz, CHLOROFORM-d): δ = 182.89, 166.99, 160.76, 145.55, 139.45, 133.90, 128.98, 128.51, 122.92, 121.09, 109.29, 63.13, 26.45, 14.05; IR (ν, cm^{-1}): 3739, 3111, 3065, 2928, 2379, 2322, 1741, 1714, 1677, 1584, 1447, 1357, 1319, 1237, 1098, 998, 895, 833, 768, 708; HRMS (ESI) Calcd. for $C_{14}H_{12}NO_4Br+Na^+$: 359.9842, Found: 359.9840.

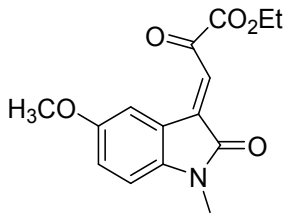
ethyl (E)-3-(5-iodo-1-methyl-2-oxoindolin-3-ylidene)-2-oxopropanoate 1h



General experimental procedure **I** was followed to prepare the product **1h.** The desired product was obtained as reddish brown solid. Yield: 0.61g, 40%; ^{1}H NMR (500MHz, CHLOROFORM-d) δ = 9.03 (d, *J* = 1.6 Hz, 1 H), 7.89 (s, 1 H), 7.77 (dd, *J* = 1.6, 8.2 Hz, 1 H), 6.62 (d, *J* = 8.2 Hz, 1 H), 4.45 (q, *J* = 7.1 Hz, 2 H), 3.24 (s, 3 H), 1.46 (t, *J* = 7.3 Hz, 3 H);^{13}C NMR (125MHz, CHLOROFORM-d) δ = 182.8, 166.7, 160.7, 146.6, 142.8, 139.2, 137.3, 122.8, 121.9, 110.3, 85.4, 63.2, 26.4, 14.1; IR (ν, cm^{-1}): 3671, 2929, 2871, 2355, 1721, 1685, 1589, 1460, 1425, 1357, 1292, 1259, 1100, 1072, 1040, 1005, 906, 850, 803, 776, 707 HRMS (ESI) Calcd. for $C_{14}H_{12}NO_4I+Na^+$: 407.9703, Found: 407.9702.

ethyl (E)-3-(5-methoxy-1-methyl-2-oxoindolin-3-ylidene)-2-oxopropanoate 1i

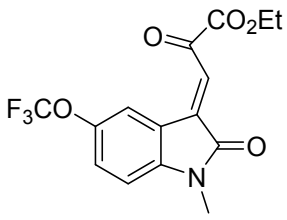
General experimental procedure **I** was followed to prepare the product **1i.** The desired product



was obtained as reddish brown solid. Yield: 0.32 g, 25%; ^{1}H NMR (400MHz, CHLOROFORM-d): δ = 8.67 (d, *J* = 2.0Hz, 1H) 8.36 (d, *J*=2.7 Hz, 1H), 7.82 (s, 1H), 7.00 (dd, *J*=8.6, 2.7 Hz, 1H), 6.68 (d, *J*=8.4 Hz, 1H), 4.43 (q, *J*=7.1 Hz, 2H), 3.85 (s, 3H), 3.20 (s, 3H), 1.43 (t, *J*=7.2 Hz, 3H). ^{13}C NMR (100MHz, CHLOROFORM-d): δ = 182.99, 167.35, 161.00, 155.91, 141.26, 141.19, 121.61, 121.13, 120.65, 114.09, 108.93, 63.04, 55.96, 26.37, 14.08. IR (ν, cm^{-1}): 3062, 2931, 1742, 1711, 1675, 1587, 1475, 1360, 1273, 1228, 1133, 1087, 1027, 869, 814, 704; HRMS (ESI) Calcd. for $C_{15}H_{15}NO_5+Na^+$: 312.0842, Found: 312.0839.

ethyl (E)-3-(1-methyl-2-oxo-5-(trifluoromethoxy)indolin-3-ylidene)-2-oxopropanoate 1j

General experimental procedure **I** was followed to prepare the product **1j.** The desired product was obtained as reddish brown solid. Yield: 0.2g, 22%. ^{1}H NMR (500MHz, CHLOROFORM-d):

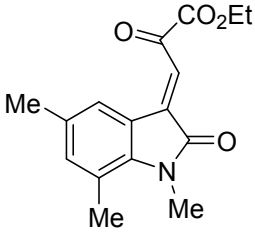


δ = 7.87 (d, *J*=8.8 Hz, 1H), 7.80 (d, *J*=7.9 Hz, 1H), 7.45 (d, *J*=8.8 Hz, 1H), 7.29 (s, 1H), 4.30 - 4.40 (m, 2H), 3.47 (s, 3H), 1.38 (t, J = 3H). ^{13}C NMR (125MHz, CHLOROFORM-d): δ = 177.06, 161.00, 150.07, 145.69, 136.37, 131.61, 131.35, 130.81, 129.1, 127.52, 124.81, 122.25, 122.19, 119.05, 109.35, 62.01, 27.17, 14.16. IR (ν, cm^{-1}): 3435, 3056, 2926, 2855, 2362, 1723, 1692, 1603, 1472, 1366, 1255, 1213, 1165, 1142, 1113, 1083, 1042,

1007, 907, 861, 825, 733. HRMS (ESI) Calcd. for $C_{15}H_{12}NO_5F_3$+Na^+: 366.0560, Found: 366.0558

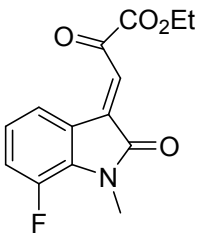
ethyl (E)-2-oxo-3-(1,5,7-trimethyl-2-oxoindolin-3-ylidene)propanoate 1k

General experimental procedure **I** was followed to prepare the product **1k.** The desired product was obtained as reddish brown solid: Yield: 0.18 g, 19%. ^{1}H NMR (500MHz, CHLOROFORM-d): δ = 8.41 (s, 1H), 7.79 (s, 1H), 6.98 (s, 1H), 4.43 (q, *J*=7.1 Hz, 2H), 3.49 (s, 3H), 2.50 (s, 3H), 2.29 (s, 3H), 1.44 (t, *J*=7.1 Hz, 3H) .^{13}C NMR (125MHz, CHLOROFORM-d): δ = 182.89, 168.35, 161.10, 142.62, 140.67, 139.14, 132.37, 127.55, 120.98, 120.91, 119.59, 62.89, 29.87, 20.67, 18.87, 14.06. IR (ν, cm^{-1}): 3057, 2926, 2863, 1739, 1707, 1683, 1589, 1444, 1349, 1237, 1124, 1077, 1014, 893, 858, 817, 774, 729 ; HRMS (ESI) Calcd. for $C_{16}H_{17}NO_4$+Na^+: 310.1050, Found: 310.1046.



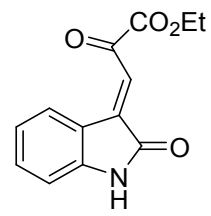
ethyl (E)-3-(7-fluoro-1-methyl-2-oxoindolin-3-ylidene)-2-oxopropanoate 1l

General experimental procedure **I** was followed to prepare the product **1l.** The desired product was obtained as reddish brown solid: Yield: 0.25 g, 22%. ^{1}H NMR (500MHz, CHLOROFORM-d): δ = 8.49 (d, *J*=7.6 Hz, 1H), 7.88 (s, 1H), 7.15 - 7.22 (m, 1H), 7.01 (td, *J*=8.1, 4.6 Hz, 1H), 4.44 (q, *J*=7.1 Hz, 2H), 3.48 (d, *J*=2.8 Hz, 3H), 1.45 (t, *J*=7.1 Hz, 3H). ^{13}C NMR (125MHz, CHLOROFORM-d): δ = 182.84, 167.09, 160.81, 148.58, 146.64, 139.50, 139.47, 133.46, 133.39, 124.94, 124.91, 123.45, 123.40, 123.0, 122.67, 122.64, 122.31, 122.16, 63.09, 29.04, 28.99, 14.04; IR (ν, cm^{-1}): 3076, 2956, 2923, 2854, 2359, 1750, 1719, 1682, 1625, 1593, 1460, 1352, 1236, 1125, 1087, 1012, 932, 890, 859, 795, 752, 712 ; HRMS (ESI) Calcd. for $C_{14}H_{12}NO_4F$+Na^+: 300.0643, Found: 300.0641.

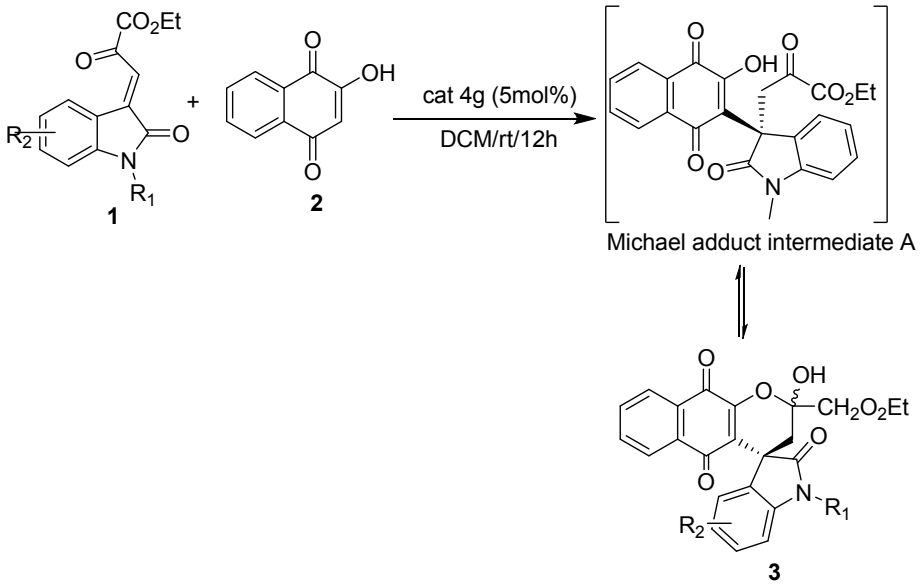


ethyl (E)-2-oxo-3-(2-oxoindolin-3-ylidene)propanoate 1m

General experimental procedure **I** was followed to prepare the product **1m.** The desired product was obtained as reddish brown solid. Yield: 0.2g, 20%. ^{1}H NMR (500MHz, CHLOROFORM-d): δ = 8.68 (s, 1H), 7.82 (s, 1H), 7.70 (dd, *J*=11.8, 7.7 Hz, 1H), 7.53 - 7.62 (m, 1H), 7.46 - 7.53 (m, 1H), 7.40 (t, *J*=7.6 Hz, 1H), 7.06 (t, *J*=7.7 Hz, 1H), 6.85 - 6.94 (m, 1H), 4.44 (q, *J*=6.9 Hz, 2H), 1.45. ^{13}C NMR (125MHz, CHLOROFORM-d)): δ = 182.85, 169.04, 161.02, 144.69, 140.70, 134.64, 129.39, 123.10, 121.59, 120.67, 110.45, 63.01, 14.05 (t, *J*=7.1 Hz, 3H). IR (ν, cm^{-1}): 31881, 3078, 2924, 2855, 1721, 1677, 1591, 1457, 1407, 1335, 1280, 1217, 1156, 1072, 900, 863, 776, 713 ; HRMS (ESI) Calcd. for $C_{13}H_{11}NO_4$+Na^+: 267.9689, Found: 267.9689.



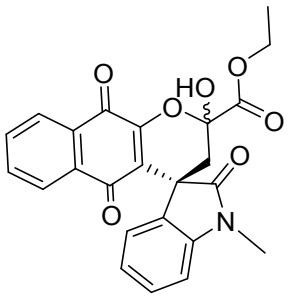
II. Typical procedure for spirooxindole napthaquinones:



To the solution of oxindole ketoester **1** (0.2 mmol) and 2-hydroxynaphthaquinone **2** (0.2 mmol), and thiourea catalyst **4g** (0.02 mmol) were stirred in 1 mL of dichloromethane at room temperature. After TLC showed that oxindole ketoester was completely consumed, the solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel (hexane / acetate = 4:1) to give the corresponding products **3**.

The Michael addition product was found to exist in rapid equilibrium with a hemiketal form in solution. These anomers equilibrate slowly enough that they show up as separate compounds by 1H and 13C NMR but quickly enough that they do not resolve by chromatography.

ethyl (4R)-2-hydroxy-1'-methyl-2',5,10-trioxo-2,3,5,10-tetrahydrospiro[benzo[g]chromene-4,3'-indoline]-2-carboxylate 3a

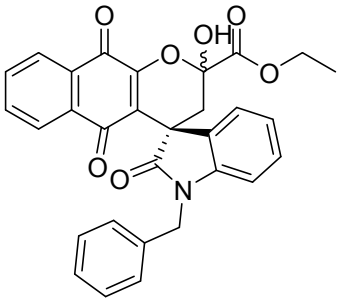


General experimental procedure **II** was followed to prepare the product **3a.** The desired product was obtained as foamy solid. Yield: 42 mg, 84%. ^{1}H NMR (500MHz, DMSO-d_6): δ = 8.76 (s, 1H), 8.02 - 8.09 (m, 1H), 7.71 - 7.92 (m, 4H), 7.51 (d, *J*=6.9 Hz, 1H), 7.29 (t, *J*=7.7 Hz, 1H), 7.09 (d, *J*=7.9 Hz, 1H), 6.87 - 6.98 (m, 1H), 4.25 (q, *J*=7.3 Hz, 2H), 3.24 (s, 3H), 2.48 (s, 1H), 2.25 (d, *J*=14.2 Hz, 1H), 1.25 (t, *J*=7.3 Hz, 3H). ^{13}C NMR (125MHz, DMSO-d_6): δ = 182.20, 178.86, 178.10, 166.89, 154.65, 144.29, 135.31, 134.57, 132.35, 131.16, 130.77, 128.68, 126.64, 126.44, 126.40, 122.08, 121.52, 109.05, 96.70, 62.65, 45.90, 38.4127.14, 14.32 ; IR (ν, cm^{-1}): 3655, 3417, 2925, 2858, 2358, 1727, 1649, 1606, 1461, 1374, 1346, 1274, 1127, 1024, 817, 732 ; HRMS (ESI) Calcd. for $C_{24}H_{19}NO_7$+Na^+: 582.0020, Found: 582.0014 The ee was determined

to be 98 % by chiral HPLC analysis (Chiralcel AD-H, hexane/isopropanol 70/30, 1.0mL/min, λ= 254 nm): t_R (minor) = 15.8 min, t_R (major) = 23.1 min. $[\alpha]^{25}_D$ = -38.2 (c = 1.0, $CHCl_3$).

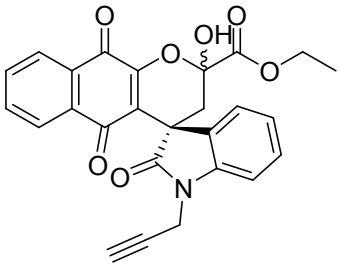
ethyl (4R)-1'-benzyl-2-hydroxy-2',5,10-trioxo-2,3,5,10-tetrahydrospiro[benzo[g]chromene-4,3'-indoline]-2-carboxylate 3b

General experimental procedure **II** was followed to prepare the product **3b.** The desired product was obtained as foamy solid. Yield: 39 mg, 85%. ^{1}H NMR (400MHz, DMSO-d_6): δ = 8.82 (s, 1H), 8.03 - 8.11 (m, 1H), 7.81 - 7.89 (m, 4H), 7.47 - 7.56 (m, 4H), 7.35 - 7.42 (m, 2H), 7.26 - 7.35 (m, 1H), 7.19 (td, *J*=7.7, 1.2 Hz, 1H), 6.87 - 6.98 (m, 3H), 4.95 - 5.08 (m, 2H), 4.26 (q, *J*=7.1 Hz, 2H), 2.58 (d, *J*=14.3 Hz, 1H), 2.34 (d, *J*=14.2 Hz, 1H), 1.26 (t, *J*=7.2 Hz, 3H). ^{13}C NMR (100MHz, DMSO-d_6): δ = 181.73, 178.34, 178.03, 177.75, 167.34, 154.46, 142.68, 136.23, 134.82, 134.10, 131.91, 130.66, 130.31, 128.60, 128.56, 128.06, 127.29, 127.17, 127.10, 126.17, 126.01, 125.95, 121.73, 120.72, 109.22, 96.96, 96.34, 62.19, 45.63, 38.33, 13.82. IR (ν, cm^{-1}): 3451, 3051, 2982, 1710, 1671, 1489, 1435, 1406, 1388, 1362, 1308, 1267, 1223, 1201, 1093, 1048, 1028, 950, 896, 822, 728; HRMS (ESI) Calcd. for $C_{30}H_{23}NO_7$+Na^+: 532.1367, Found: 532.1347 The ee was determined to be 97 % by chiral HPLC analysis (Chiralcel OD-H, hexane/isopropanol 70/30, 1.0mL/min, λ= 254 nm): t_R (minor) = 19.4 min, t_R (major) = 6.6 min. $[\alpha]^{25}_D$ = -56.2 (c = 1.0, $CHCl_3$).



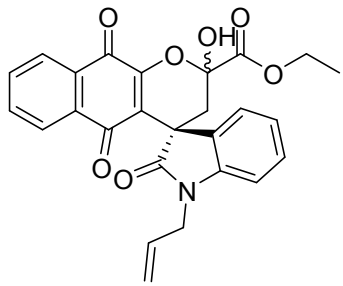
ethyl (4R)-2-hydroxy-2',5,10-trioxo-1'-(prop-2-yn-1-yl)-2,3,5,10-tetrahydrospiro[benzo[g]chromene-4,3'-indoline]-2-carboxylate 3c

General experimental procedure **II** was followed to prepare the product **3c.** The desired product was obtained as foamy solid. Yield: 38 mg, 81%. ^{1}H NMR (400MHz, DMSO-d_6): δ = 8.75 - 8.86 (m, 1H), 7.99 - 8.08 (m, 1H), 7.74 - 7.89 (m, 3H), 7.49 - 7.58 (m, 1H), 7.33 (td, *J*=7.7, 1.1 Hz, 1H), 7.20 (d, *J*=7.7 Hz, 1H), 6.93 - 7.03 (m, 1H), 4.54 - 4.73 (m, 2H), 4.26 (q, *J*=7.1 Hz, 2H), 2.43 - 2.49 (m, 1H), 2.25 (d, *J*=14.1 Hz, 1H), 1.26 (t, *J*=7.1 Hz, 4H). ^{13}C NMR (100MHz, DMSO-d_6): δ = 181.61, 178.30, 177.99, 176.81, 167.26, 154.27, 141.83, 134.81, 134.09, 131.69, 130.59, 130.2, 128.62, 128.15, 126.17, 126.11, 125.92, 121.98, 120.58, 96.18, 77.80, 74.63, 62.20, 45.45, 38.02, 29.42, 13.81. IR (ν, cm^{-1}): 3300, 3053, 1718, 1682, 1654, 1617, 1487, 1466, 1427, 1359, 1335, 1301, 1265, 1198, 1049, 1027, 1005, 968, 898, 82, 728, 700; HRMS (ESI) Calcd. for $C_{26}H_{19}NO_7$+Na^+: 480.1054, Found: 480.1050. The ee was determined to be 94 % by chiral HPLC analysis (Chiralcel OD-H, hexane/isopropanol 70/30, 1.0mL/min, λ= 254 nm): t_R (minor) = 11.3 min, t_R (major) = 6.1 min. $[\alpha]^{25}_D$ = -45.5 (c = 1.0, $CHCl_3$).



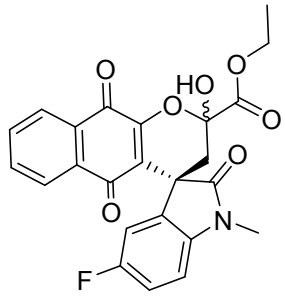
ethyl (4R)-1'-allyl-2-hydroxy-2',5,10-trioxo-2,3,5,10-tetrahydrospiro[benzo[g]chromene-4,3'-indoline]-2-carboxylate 3d

General experimental procedure **II** was followed to prepare the product **3d.** The desired product was obtained as foamy solid**.** Yield: 35 mg, 86%. ^{1}H NMR (400MHz, DMSO-d_6): δ = 8.76 (s, 1H), 8.02 - 8.08 (m, 1H), 7.77 - 7.87 (m, 4H), 7.52 (dd, *J*=7.6, 0.9 Hz, 1H), 7.26 (td, *J*=7.7, 1.2 Hz, 1H), 6.98 - 7.08 (m, 1H), 6.93 (td, *J*=7.6, 0.9 Hz, 1H), 5.94 (ddt, *J*=17.2, 10.2, 4.9 Hz, 1H), 5.38 - 5.49 (m, 1H), 5.14 - 5.31 (m, 1H), 4.40 (dd, *J*=4.6, 1.8 Hz, 2H), 4.25 (q, *J*=7.1 Hz, 2H), 2.54 (s, 1H), 2.29 (d, *J*=14.2 Hz, 1H), 1.24 - 1.28 (m, 3H). ^{13}C NMR (100MHz, DMSO-d_6): δ = 181.70, 178.34, 177.37, 167.34, 154.33, 142.74, 134.79, 134.06, 131.91, 131.85, 131.64, 130.67, 130.29, 128.03, 126.14, 125.94, 121.58, 120.88, 116.84, 109.18, 96.28, 62.15, 59.70, 45.53, 42.06, 38.27, 20.70, 14.04, 13.56. IR (ν, cm^{-1}): 3302, 2959,2582, 1727, 1618, 1465, 1421,1402, 1365, 1264, 1222, 1186, 1035, 1025, 922, 802, 731, 702 ;HRMS (ESI) Calcd. for $C_{26}H_{21}NO_7$+Na^+: 482.1210, Found: 482.1203. The ee was determined to be 97 % by chiral HPLC analysis (Chiralcel OD-H, hexane/isopropanol 70/30, 1.0mL/min, λ= 254 nm): t_R (minor) = 13.7 min, t_R (major) = 5.8 min. $[\alpha]^{25}_D$ = -71.2 (c = 1.0, $CHCl_3$).



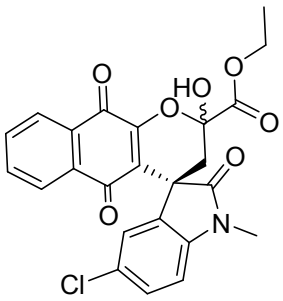
ethyl (4R)-5'-fluoro-2-hydroxy-1'-methyl-2',5,10-trioxo-2,3,5,10-tetrahydrospiro[benzo[g]chromene-4,3'-indoline]-2-carboxylate 3e

General experimental procedure **II** was followed to prepare the product **3e.** The desired product was obtained as foamy solid**.** Yield: 43 mg, 91%. ^{1}H NMR (500MHz, DMSO-d_6) δ 8.86 (s, 1H), 8.02 - 8.09 (m, 1H), 7.77 - 7.88 (m, 3H), 7.36 (dd, *J*=8.8, 2.5 Hz, 1H), 7.08 - 7.22 (m, 2H), 4.26 (q, *J*=6.9 Hz, 2H), 3.24 (s, 3H), 2.47 (s, 1H), 2.29 (d, *J*=14.2 Hz, 1H), 1.26 (t, *J*=7.1 Hz, 3H). ^{13}C NMR (125MHz, DMSO-d_6) δ 182.26, 178.78, 177.88, 167.77, 159.26, 156.04 (d, *J* = 234 Hz, C-F) , 140.65, 135.25, 133.82 (d, *J* = 8.8 Hz, C-F) , 133.79, 131.16, 130.86, 126.52 (d, *J* = 28.3 Hz, C-F), 120.92, 114.93, 114.74, 114.71, 114.51, 109.75, 109.69, 97.32, 96.60, 62.72, 60.21, 46.19, 38.04, 27.34, 14.32. IR (ν, cm^{-1}): 3058, 2926, 1750, 1713, 1683, 1656, 1619, 1494, 1466, 1356, 1301, 1265, 1201, 1152, 1120, 1023, 958, 878, 814, 728 ; HRMS (ESI) Calcd. for $C_{24}H_{18}NO_7F$+Na^+: 474.0960, Found: 474.0957. The ee was determined to be 96 % by chiral HPLC analysis (Chiralcel AD-H, hexane/isopropanol 80/20, 1.0mL/min, λ= 254 nm): t_R (minor) = 21.9 min, t_R (major) = 32.0 min. $[\alpha]^{25}_D$ = -53.2 (c = 1.0, $CHCl_3$).



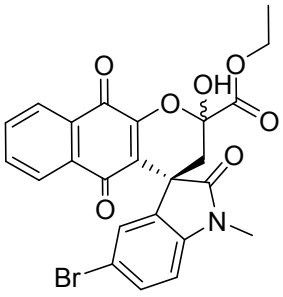
ethyl (4R)-5'-chloro-2-hydroxy-1'-methyl-2',5,10-trioxo-2,3,5,10-tetrahydrospiro[benzo[g]chromene-4,3'-indoline]-2-carboxylate 3f

General experimental procedure **II** was followed to prepare the product **3f.** The desired product was obtained as foamy solid**.** Yield: 41 mg, 88%. ^{1}H NMR (500MHz, DMSO-d_6): δ = 8.80 - 8.88 (m, 1H), 8.01 - 8.10 (m, 1H), 7.78 - 7.87 (m, 4H), 7.57 (d, *J*=2.2 Hz, 1H), 7.36 (dd, *J*=8.2, 2.2 Hz, 1H), 7.14 (d, *J*=8.2 Hz, 1H), 4.26 (q, *J*=6.9 Hz, 2H), 3.25 (s, 3H), 2.48 (d, *J*=14.5 Hz, 1H), 2.30 (d, *J*=14.2 Hz, 1H), 1.25 - 1.28 (m, 3H). ^{13}C NMR (125MHz, DMSO-d_6): δ = 182.31, 178.75, 177.79, 167.75, 154.77, 143.33, 135.22, 134.56, 134.03, 131.17, 130.91, 128.48, 126.83, 126.64, 126.46, 126.42, 126.12, 120.82, 110.48, 96.56, 62.72, 60.21, 45.99, 38.03, 27.32, 14.32. IR (ν, cm^{-1}): 3844, 3743, 3054, 2312, 1707, 1682, 1626, 1515, 1425, 1325, 1301, 1264, 1147, 1120, 1056, 945, 896, 729; HRMS (ESI) Calcd. for $C_{24}H_{18}NO_7Cl$+Na^+: 490.0664, Found: 490.0667. The ee was determined to be 98 % by chiral HPLC analysis (Chiralcel AD-H, hexane/isopropanol 80/20, 1.0mL/min, λ= 254 nm): t_R (minor) = 19.7 min, t_R (major) = 28.8 min. $[\alpha]^{25}_D$ = -94.0 (c = 1.0, $CHCl_3$).



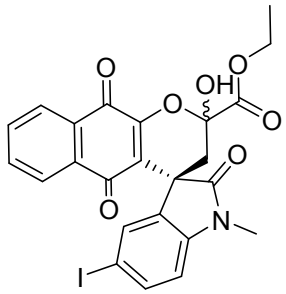
ethyl (4R)-5'-bromo-2-hydroxy-1'-methyl-2',5,10-trioxo-2,3,5,10-tetrahydrospiro[benzo[g]chromene-4,3'-indoline]-2-carboxylate 3g

General experimental procedure **II** was followed to prepare the product **3g.** The desired product was obtained as foamy solid**.** Yield: 42 mg, 91%. ^{1}H NMR (500MHz, DMSO-d_6): δ = 8.76 (s, 1H), 8.00 - 8.12 (m, 1H), 7.75 - 7.90 (m, 4H), 7.51 (d, *J*=6.9 Hz, 1H), 7.24 - 7.39 (m, 1H), 7.06 - 7.19 (m, 1H), 6.86 - 7.00 (m, 2H), 4.25 (q, *J*=7.3 Hz, 2H), 3.24 (s, 3H), 2.42 - 2.49 (m, 1H), 2.25 (d, *J*=14.2 Hz, 1H), 1.25 (t, *J*=7.3 Hz, 3H); ^{13}C NMR (125MHz, DMSO-d_6): δ = 182.33, 178.74, 177.70, 167.75, 154.78, 143.72, 135.23, 134.57, 134.39, 131.33, 131.16, 130.91, 129.49, 126.64, 126.42, 120.80,113.94, 111.05, 96.55, 62.73, 45.93, 38.03, 27.29, 27.32, 14.32; IR (ν, cm^{-1}): 3837, 3726, 3051, 2357, 1703, 1682, 1626, 1517, 1428, 1348, 1301, 1267, 1139, 1107, 1075, 959, 886, 731; HRMS (ESI) Calcd. for $C_{24}H_{18}BrNO_7$+Na^+: 534.0159, Found: 534.0167. The ee was determined to be 96 % by chiral HPLC analysis (Chiralcel AD-H, hexane/isopropanol 80/20, 1.0mL/min, λ= 254 nm): t_R (minor) = 15.5 min, t_R (major) = 22.0 min. $[\alpha]^{25}_D$ = -47.2 (c = 1.0, $CHCl_3$).



ethyl (4R)-2-hydroxy-5'-iodo-1'-methyl-2',5,10-trioxo-2,3,5,10-tetrahydrospiro[benzo[g]chromene-4,3'-indoline]-2-carboxylate 3h

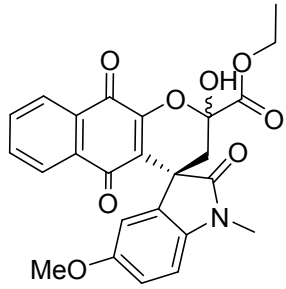
General experimental procedure **II** was followed to prepare the product **3h.** The desired product was obtained as foamy solid**.** Yield: 41 mg, 90%. ^{1}H NMR (400MHz, DMSO-d_6) δ = 8.85 (s, 1H), 8.02 - 8.06 (m, 1H), 7.83 - 7.86 (m, 2H), 7.77 - 7.83 (m, 2H), 7.61 - 7.69 (m, 1H), 6.98 (d, *J*=8.2 Hz, 1H), 4.26 (q, *J*=7.1 Hz, 2H), 3.22 (s, 3H), 2.48 (d, *J*=4.9 Hz, 1H), 2.29 (d, *J*=14.2 Hz,



1H), 1.26 (t, *J*=7.1 Hz, 3H);^{13}C NMR (100MHz, DMSO-d_6): δ = 181.84, 178.25, 177.06, 167.27, 154.29, 143.67, 136.63, 134.74, 134.40, 134.16, 134.09, 130.65, 130.41, 126.15, 125.93, 120.35, 111.11, 96.05, 84.83, 62.23, 45.25, 37.58, 26.72, 13.83; IR (ν, cm^{-1}): 3671, 2929, 2871, 2355, 1721, 1685, 1589, 1460, 1425, 1357, 1292, 1259, 1100, 1072, 1040, 1005, 906, 850, 803, 776, 707; HRMS (ESI) Calcd. for $C_{24}H_{18}NO_7I+Na^+$: 582.0020, Found: 582.0014. The ee was determined to be 98 % by chiral HPLC analysis (Chiralcel AD-H, hexane/isopropanol 80/20, 1.0mL/min, λ= 254 nm): t_R (minor) =35.2 min, t_R (major) = 52 min. $[\alpha]^{25}_D$ = -102.5 (c = 1.0, $CHCl_3$).

ethyl (4R)-2-hydroxy-5'-methoxy-1'-methyl-2',5,10-trioxo-2,3,5,10-tetrahydrospiro[benzo[g]chromene-4,3'-indoline]-2-carboxylate 3i

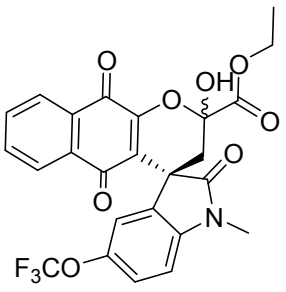
General experimental procedure **II** was followed to prepare the product **3i.** The desired product



was obtained as foamy solid**.** Yield: 38 mg, 82%. ^{1}H NMR (500MHz, DMSO-d_6): δ = 8.77 (s, 1H), 8.04 (dd, *J*=6.0, 2.5 Hz, 1H), 7.78 - 7.86 (m, 4H), 7.18 (d, *J*=2.5 Hz, 1H), 7.00 (d, *J*=8.5 Hz, 1H), 6.86 (dd, *J*=8.5, 2.8 Hz, 1H), 4.25 (q, *J*=7.3 Hz, 2H), 3.63 - 3.67 (m, 4H), 3.21 (s, 3H), 2.48 (s, 1H), 2.24 (d, *J*=14.2 Hz, 1H), 1.25 (t, *J*=7.1 Hz, 3H); ^{13}C NMR (125MHz, DMSO-d_6): δ = 182.19, 178.88, 179.69, 167.87, 155.27, 154.63, 137.74, 135.27, 134.52, 133.63, 131.20, 130.80, 126.61, 126.40, 121.49, 114.28, 112.60, 109.18, 96.69, 62.65, 55.78, 46.26, 38.35, 27.21, 14.32; IR (ν, cm^{-1}): 3844, 3742, 3056, 1749, 1679, 1616, 1499, 1465, 1427, 1358, 1264, 1202, 1162, 1026, 952, 895, 729, 701; HRMS (ESI) Calcd. for $C_{25}H_{21}NO_8+Na^+$: 486.1159, Found: 486.1151. The ee was determined to be 95 % by chiral HPLC analysis (Chiralcel AD-H, hexane/isopropanol 80/20, 0.8 mL/min, λ= 254 nm): t_R (minor) = 22.5 min, t_R (major) = 29.9 min. $[\alpha]^{25}_D$ = -89.5 (c = 1.0, $CHCl_3$).

ethyl (4R)-2-hydroxy-1'-methyl-2',5,10-trioxo-5'-(trifluoromethoxy)-2,3,5,10-tetrahydrospiro[benzo[g]chromene-4,3'-indoline]-2-carboxylate 3j

General experimental procedure **II** was followed to prepare the product **3i.** The desired product

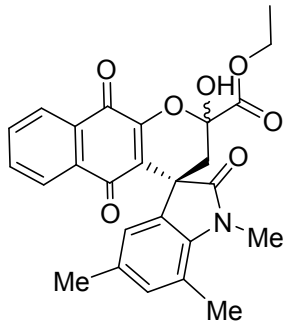


was obtained as foamy solid. Yield: 38 mg, 86%. ^{1}H NMR (500MHz, DMSO-d_6): δ = 8.88 (s, 1H), 8.05 (dd, *J*=6.3, 1.9 Hz, 1H), 7.79 - 7.88 (m, 3H), 7.54 (s, 1H), 7.30 - 7.35 (m, 1H), 7.20 (d, *J*=8.5 Hz, 1H), 4.26 (q, *J*=6.9 Hz, 2H), 3.26 (s, 3H), 2.46 (s, 1H), 2.33 (d, *J*=14.2 Hz, 1H), 1.26 (t, *J*=7.1 Hz, 3H) ppm. ^{13}C NMR (125MHz, DMSO-d_6): δ = 182.28, 178.73, 178.03, 167.74, 154.82, 143.50, 143.48, 135.26, 134.59, 133.60, 131.13, 130.91, 126.67, 126.41, 123.68, 121.77, 121.65, 120.66, 120.47, 119.62, 110.82, 109.8, 96.62, 62.74, 46.05, 37.93, 27.36, 14.31 ppm. IR (ν, cm^{-1}): 3744, 3672,

3054, 1718, 1685, 1653, 1620, 1499, 1422, 1358, 1263, 1220, 1161, 1054, 1029, 969, 896, 819, 729, 701; HRMS (ESI) Calcd. for $C_{25}H_{18}NO_8F_3$+Na^+: 540.0877, Found: 540.0877. The ee was determined to be 94 % by chiral HPLC analysis (Chiralcel AD-H, hexane/isopropanol 90/10, 1.0mL/min, λ= 254 nm): t_R (minor) = 25.4 min, t_R (major) = 37.9 min. $[\alpha]^{25}_D$ = -61.4 (c = 1.0, $CHCl_3$).

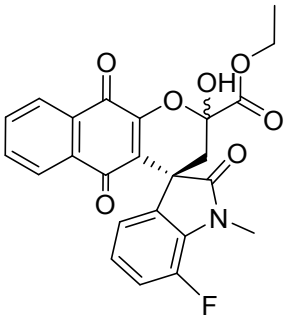
ethyl (4R)-2-hydroxy-1',5',7'-trimethyl-2',5,10-trioxo-2,3,5,10-tetrahydrospiro[benzo[g]chromene-4,3'-indoline]-2-carboxylate 3k

General experimental procedure **II** was followed to prepare the product **3k.** The desired product was obtained as foamy solid. Yield: 37 mg, 81%. ^{1}H NMR (400MHz, DMSO-d_6): δ = 8.66 (s, 1H), 7.80 (m, 4H), 7.16 (s, 1H), 7.15(s, 1H), 6.83 (s, 1H), 4.23 (q, *J*=7.1 Hz, 2H), 3.46 (s, 3H), 2.56 (s, 3H), 2.46 (s, 1H), 2.19 (d, *J*=14.2 Hz, 1H), 2.13 (s, 3H), 1.22 - 1.26 (m, 3H). ^{13}C NMR (100MHz, DMSO-d_6): δ = 181.65, 178.38, 178.10, 167.30, 154.24, 138.98, 134.77, 134.01, 132.83, 132.11, 130.73, 130.25, 126.09, 125.90, 124.06, 121.35, 119.11, 96.78, 96.30, 62.04, 46.16, 45.16, 29.74, 20.43, 18.48, 13.79; IR (ν, cm^{-1}): 3457, 2856, 2874, 1839, 1745, 1683, 1514, 1466, 1444, 1349, 1237, 1125, 1142, 1025, 956, 817, 782, 752; HRMS (ESI) Calcd. for $C_{26}H_{23}NO_7$+Na^+: 484.1367, Found: 484.1365. The ee was determined to be 89 % by chiral HPLC analysis (Chiralcel AD-H, hexane/isopropanol 80/20, 1.0mL/min, λ= 254 nm): t_R (minor) = 14.7 min, t_R (major) = 26.2 min. $[\alpha]^{25}_D$ = -65.5 (c = 1.0, $CHCl_3$).



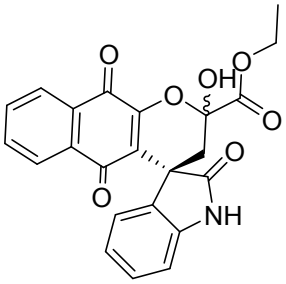
ethyl (4R)-7'-fluoro-2-hydroxy-1'-methyl-2',5,10-trioxo-2,3,5,10-tetrahydrospiro[benzo[g]chromene-4,3'-indoline]-2-carboxylate 3l

General experimental procedure **II** was followed to prepare the product **3k.** The desired product was obtained as foamy solid. Yield: 41 mg, 81%. ^{1}H NMR (400MHz, DMSO-d_6): δ = 8.82 (s, 1H), 8.01 - 8.07 (m, 1H), 7.78 - 7.86 (m, 4H), 7.37 (dd, *J*=7.6, 1.0 Hz, 1H), 7.17 (ddd, *J*=11.9, 8.4, 0.7 Hz, 1H), 6.93 (td, *J*=8.0, 4.7 Hz, 1H), 4.25 (q, *J*=7.2 Hz, 2H), 3.41 (d, *J*=2.8 Hz, 4H), 2.47 (s, 1H), 2.33 (d, *J*=14.3 Hz, 1H), 1.23 - 1.27 (m, 3H) ppm. ^{13}C NMR (100MHz, DMSO-d_6): δ = 187.06, 183.53, 182.50, 172.50, 172.19, 159.80, 152.29 (d, *J* = 239 Hz, C-F) , 140.10, 139.93, 139.40, 135.84, 135.64, 131.55, 131.45, 127.56 (d, *J* = 5.6 Hz, C-F) , 125.78, 121.31 (d, *J* = 23.3 Hz, C-F) , 101.45, 67.44, 50.85, 43.30, 43.07, 34.30, 34.24, 19.06; IR (ν, cm^{-1}): 3402, 3050, 2925, 2855, 2362, 1719, 1683, 1655, 1623, 1463, 1363, 1266, 1202, 1119, 1055, 1029, 819, 730, 702; HRMS (ESI) Calcd. for $C_{24}H_{18}NO_7F$+Na^+: 474.0960, Found: 474.0957. The ee was determined to be 94 % by chiral HPLC analysis (Chiralcel AD-H, hexane/isopropanol 80/20, 1.0mL/min, λ= 254 nm): t_R (minor) = 23.4 min, t_R (major) = 34.6 min. $[\alpha]^{25}_D$ = -114.0 (c = 1.0, $CHCl_3$).



ethyl (4R)-2-hydroxy-2',5,10-trioxo-2,3,5,10-tetrahydrospiro[benzo[g]chromene-4,3'-indoline]-2-carboxylate 3m

General experimental procedure **II** was followed to prepare the product **3k.** The desired product was obtained as foamy solid. Yield: 39mg,78%. ^{1}H NMR (400MHz, DMSO-d_6): δ = 10.72 (s, 1H), 8.68 (d, *J*=1.8 Hz, 1H), 8.02 - 8.11 (m, 1H), 7.78 - 7.89 (m, 4H), 7.44 (d, *J*=7.5 Hz, 1H), 7.18 (td, *J*=7.7, 1.3 Hz, 1H), 6.89 - 7.02 (m, 1H), 6.82 - 6.88 (m, 2H), 4.25 (q, *J*=7.2 Hz, 2H), 2.46 (d, *J*=2.0 Hz, 1H), 2.24 (d, *J*=14.2 Hz, 1H), 1.25 - 1.27 (m, 3H). ^{13}C NMR (100MHz, DMSO-d_6): δ= 181.70, 179.24, 178.41, 167.43, 154.13, 142.28, 134.79, 134.02, 132.85, 130.73, 130.26, 128.0, 126.15, 126.10, 125.87, 123.06, 121.22, 120.9, 109.57, 96.22, 62.10, 45.94, 38.16, 13.82; IR (ν, cm^{-1}): 3429, 3025, 2251, 2124, 1719, 1656, 1612, 1205, 1201, 1145, 1051, 1023, 1002, 821, 758; HRMS (ESI) Calcd. for $C_{23}H_{17}NO_7$+Na^+: 442.0897, Found: 442.0895 The ee was determined to be 60 % by chiral HPLC analysis (Chiralcel OD-H, hexane/isopropanol 80/20, 1.0mL/min, λ= 254 nm): t_R (minor) = 15.4 min, t_R (major) = 22.4 min. $[\alpha]^{25}_D$ = -72.5 (c = 1.0, $CHCl_3$).

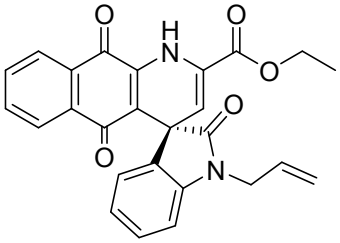


III. Typical procedure for the synthesis of spirooxindole dihydropyridine napthaquinones

A solution of compound **3**(1equiv) and ammonium acetate (1.5 equiv) in dichloromethane was stirred for 4h. The solvent was evaporated and the mixture was purified by column chromatography on silica gel, eluted by hexane/EtOAc= 15:1 to affords products **5**

ethyl (R)-1'-allyl-2',5,10-trioxo-5,10-dihydro-1H-spiro[benzo[g]quinoline-4,3'-indoline]-2-carboxylate 5a

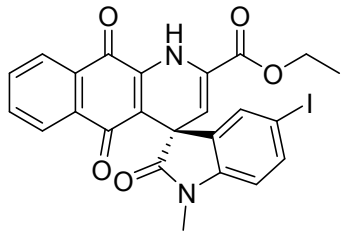
General experimental procedure **III** was followed to prepare the product **5a.** The desired product was obtained as foamy solid**.** Yield: 35 mg, 89%. ^{1}H NMR (400MHz, CHLOROFORM-d): δ = 8.00 - 8.05 (m, 1H), 7.81 - 7.85 (m, 2H), 7.55 - 7.60 (m, 2H), 7.20 - 7.25 (m, 1H), 7.19 - 7.20 (m, 1H), 7.11 (dd, *J*=7.4, 0.9 Hz, 1H), 6.95 (td, *J*=7.5, 0.9 Hz, 1H), 6.84 (d, *J*=7.8 Hz, 1H), 5.94 (ddt, *J*=17.2, 10.4, 5.2 Hz, 1H), 5.59 (d, *J*=1.8 Hz, 1H), 5.44 (dd, *J*=17.2, 1.1 Hz, 1H), 5.26 (dd, *J*=10.4, 1.2 Hz, 1H), 4.34 - 4.49 (m, 3H), 4.19 - 4.28 (m, 2H), 1.23 - 1.27 (m, 3H) ppm. ^{13}C NMR (100MHz, CHLOROFORM-d) δ = 181.29, 179.46, 177.95, 161.52, 141.30, 140.16, 136.17, 135.0, 132.75, 132.65, 131.37, 130.05, 129.11, 127.5, 126.67, 126.36, 124.81, 123.10, 117.97, 112.57, 109.18, 62.39, 50.88, 43.03, 29.70, 14.11; IR (ν, cm^{-1}): 3625, 3428, 3152, 2259, 2623, 2210, 1697, 1651, 1610, 1615, 1414, 1245, 1220, 1165, 1092, 1034, 952, 802, 731, 702; HRMS (ESI) Calcd. for $C_{26}H_{20}N_2O_5$+Na^+: 463.1511, Found: 463.1512. The ee was determined to be 89 % by chiral HPLC analysis (Chiralcel AD-H, hexane/isopropanol 70/30,



1.0mL/min, λ= 254 nm): t_R (minor) = 12.7 min, t_R (major) = 17.3 min. $[\alpha]^{25}_D$ = -59.5 (c = 1.0, $CHCl_3$).

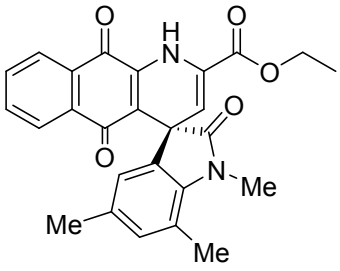
ethyl (R)-5'-iodo-1'-methyl-2',5,10-trioxo-5,10-dihydro-1H-spiro[benzo[g]quinoline-4,3'-indoline]-2-carboxylate 5b

General experimental procedure **III** was followed to prepare the product **5b.** The desired product was obtained as foamy solid**.** Yield: 32 mg, 80%. ^{1}H NMR (500MHz, DMSO-d_6): δ = 8.05 - 8.07 (m, 1H), 8.01 - 8.05 (m, 1H), 7.82 - 7.86 (m, 1H), 7.77 - 7.82 (m, 1H), 7.66 (dd, *J*=8.2, 1.6 Hz, 1H), 7.60 (d, *J*=1.9 Hz, 1H), 6.93 (d, *J*=8.2 Hz, 1H), 5.62 (d, *J*=1.6 Hz, 1H), 4.23 - 4.31 (m, 2H), 3.21 (s, 3H), 1.27 (t, *J*=7.3 Hz, 3H) ppm. ^{13}C NMR (125MHz DMSO-d_6): δ = 181.18, 179.16, 177.19, 161.63, 142.39, 140.98, 138.66, 137.87, 135.69, 133.81, 133.38, 132.29, 130.45, 127.76, 126.61, 126.24, 112.38, 111.36, 111.16, 85.98, 62.69, 50.64, 27.01, 14.31 ppm. IR (ν, cm^{-1}): 3396, 3066, 2962, 1716, 1679, 1652, 1600, 1575, 1484, 1405, 1337, 1278, 1215, 1143, 1088, 1049, 1021, 931, 861, 804, 765, 725; HRMS (ESI) Calcd. for $C_{24}H_{17}N2O_5I+Na^+$: 563.0074, Found: 563.0068 .The ee was determined to be 95 % by chiral HPLC analysis (Chiralcel AD-H, hexane/isopropanol 90/10, 1.0mL/min, λ= 254 nm): t_R (minor) = 34.6 min, t_R (major) = 48.0 min. $[\alpha]^{25}_D$ = -95.5 (c = 1.0, $CHCl_3$).



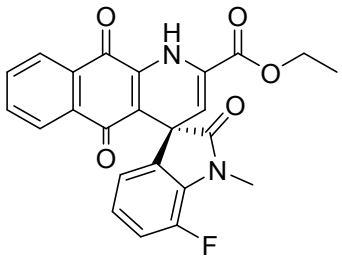
ethyl (R)-1',5',7'-trimethyl-2',5,10-trioxo-5,10-dihydro-1H-spiro[benzo[g]quinoline-4,3'-indoline]-2-carboxylate 5c

General experimental procedure **III** was followed to prepare the product **5c.** The desired product was obtained as foamy solid. Yield: 36 mg, 85%. ^{1}H NMR (400MHz, CHLOROFORM-d): δ = 7.99 - 8.03 (m, 1H), 7.82 - 7.85 (m, 1H), 7.79 (s, 1H), 7.53-7.61 (m,, 2H), 7.19 (s, 1H), 6.72 - 6.79 (m, 2H), 5.58 (d, *J*=1.8 Hz, 1H), 4.22 (m, 4.12-4.26, 2H), 3.54 (s, 3H), 2.53 (s, 3H), 2.13 (s, 3H), 1.24 (t, 3H) ppm. ^{13}C NMR (100MHz, CHLOROFORM-d): δ = 181.43, 179.49, 179.06, 161.61, 140.02, 137.34, 137.06, 134.89, 133.48, 132.70, 132.57, 130.10, 127.12, 126.59, 126.33, 123.72, 119.45, 113.16, 112.42, 62.28, 50.45, 30.24, 29.70, 20.69, 18.89, 14.08; IR (ν, cm^{-1}): 3396, 3057, 2922, 2853, 2358, 1720, 1605, 1467, 1343, 1267, 1175, 1101, 1048, 944, 859, 732 ;HRMS (ESI) Calcd. for $C_{26}H_{22}N_2O_5+Na^+$: 465.1421, Found: 465.1425. The ee was determined to be 82 % by chiral HPLC analysis (Chiralcel AD-H, hexane/isopropanol 70/30, 1.0mL/min, λ= 254 nm): t_R (minor) = 11.1 min, t_R (major) = 14.3 min. $[\alpha]^{25}_D$ = -24.5 (c = 1.0, $CHCl_3$).



ethyl (R)-7'-fluoro-1'-methyl-2',5,10-trioxo-5,10-dihydro-1H-spiro[benzo[g]quinoline-4,3'-indoline]-2-carboxylate 5d

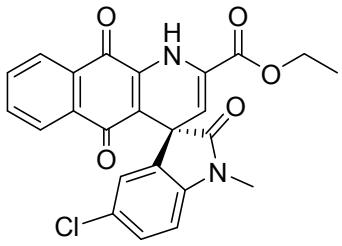
General experimental procedure **III** was followed to prepare the product **5d.** The desired product



was obtained as foamy solid. Yield: 39 mg, 90%. ^{1}H NMR (400MHz, CHLOROFORM-d): δ = 8.01 - 8.03 (m, 1H), 7.81 - 7.83 (m, 2H), 7.55 - 7.63 (m, 2H), 7.19 (s, 1H), 6.93 - 7.01 (m, 1H), 6.86 - 6.89 (m, 2H), 5.59 (d, *J*=1.8 Hz, 1H), 3.48 - 3.51 (m, 3H), 1.23 - 1.26 (t, 3H) ppm. ^{13}C NMR (100MHz, CHLOROFORM-d): δ= 181.3, 179.28, 178.00, 161.38, 147.5 (d, *J* = 243 Hz, C-F) , 140.06, 135.04, 132.87, 132.56, 130.04, 129.61, 126.55, 126.45, 123.58 (d, *J* = 7.8 Hz, C-F) , 120.65, 120.62, 117.11 (d, *J* = 24 Hz, C-F) , 112.05, 111.88, 62.45, 29.42, 29.37, 14.07; IR (ν, cm^{-1}): 3395, 2927, 2862, 1720, 1683, 1651, 1633, 1602, 1483, 1339, 1276, 1239, 1171, 1119, 1070, 1011, 943, 866, 786, 728 ; HRMS (ESI) Calcd. for $C_{24}H_{17}FN_2O_5$+Na^+: 455.1014, Found: 455.1023. The ee was determined to be 97 % by chiral HPLC analysis (Chiralcel AD-H, hexane/isopropanol 80/20, 1.0mL/min, λ= 254 nm): t_R (minor) = 14.3 min, t_R (major) = 17.9 min. $[\alpha]^{25}_D$ = -58.5 (c = 1.0, $CHCl_3$).

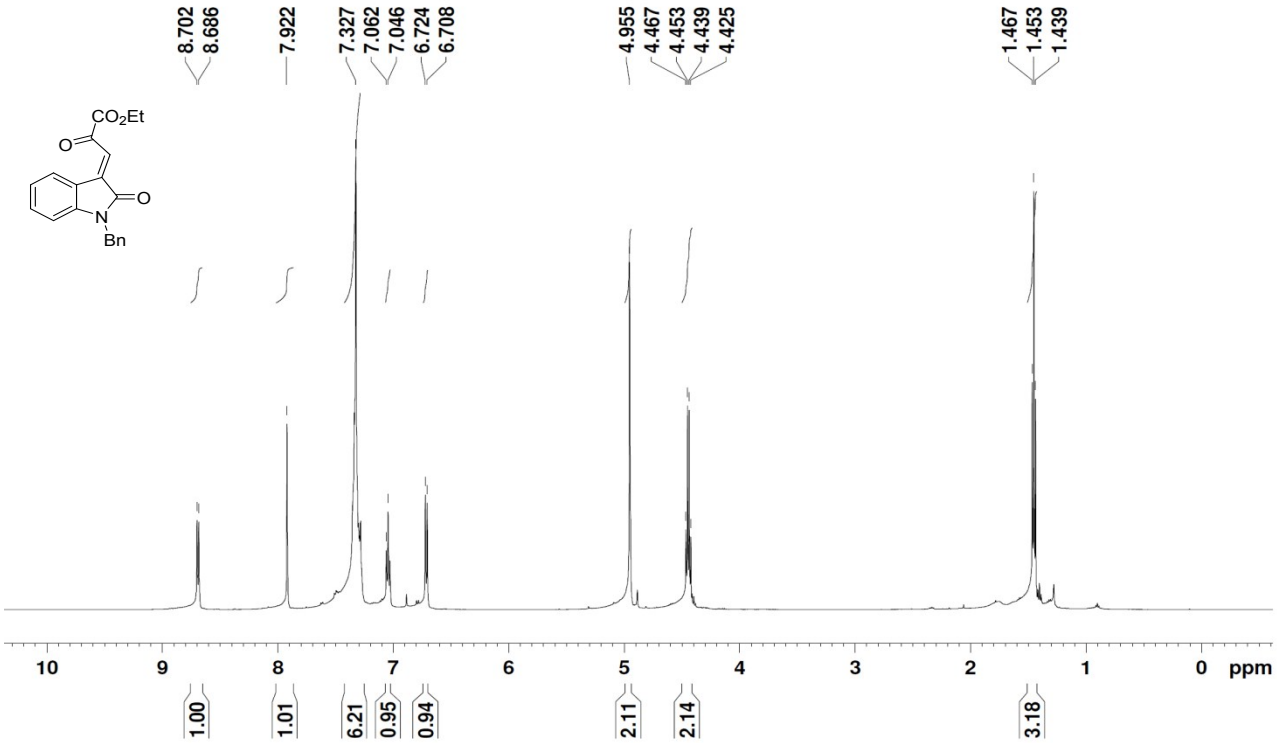
ethyl (R)-5'-chloro-1'-methyl-2',5,10-trioxo-5,10-dihydro-1H-spiro[benzo[g]quinoline-4,3'-indoline]-2-carboxylate 5e

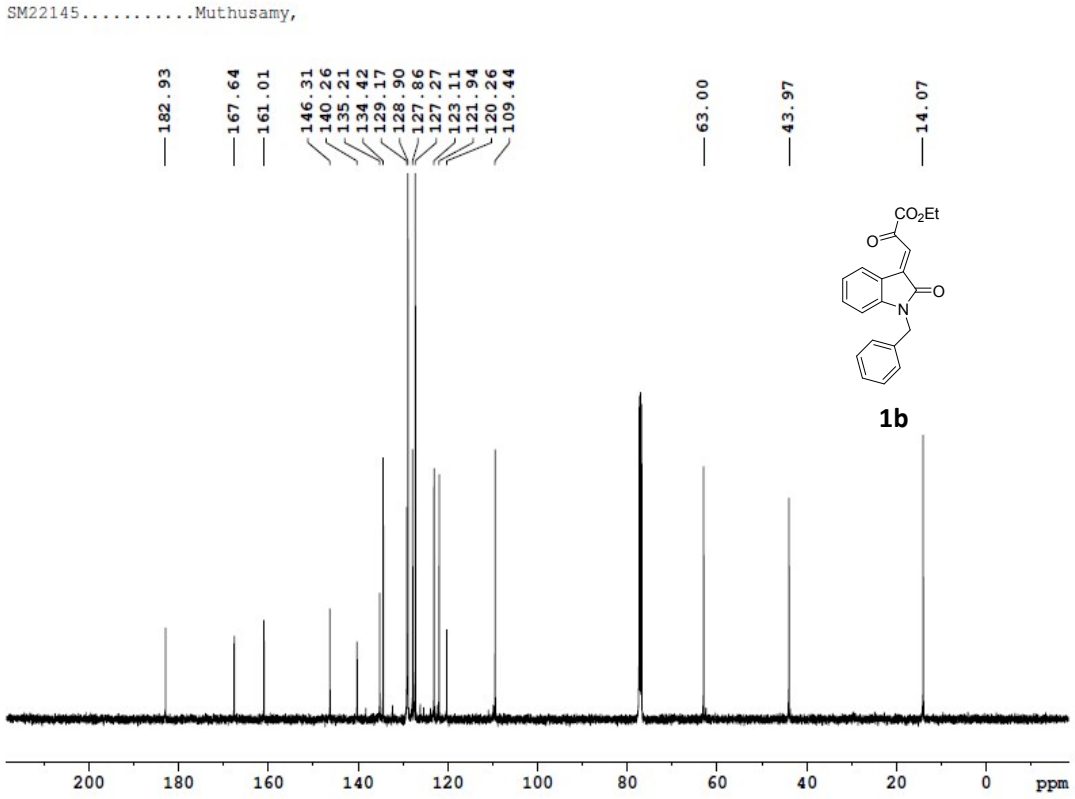
General experimental procedure **III** was followed to prepare the product **5e.** The desired product



was obtained as foamy solid. Yield: 31 mg, 82%. ^{1}H NMR (500MHz, DMSO-d_6): δ = 8.04 - 8.06 (m, 2H), 7.78 - 7.85 (m, 3H), 7.38 (s, 1H), 7.35 - 7.37 (m, 1H), 7.07 - 7.12 (m, 1H), 5.62 (d, *J*=1.6 Hz, 1H), 4.24 - 4.31 (m, 2H), 3.23 (s, 3H), 1.26 (s, 3H) ppm. ^{13}C NMR (125MHz, DMSO-d_6): δ = 181.18, 179.17, 177.48, 161.61, 141.50, 141.0, 138.05, 135.71, 133.83, 132.29, 130.43, 129.17, 127.84, 127.03, 126.61, 126.24, 125.42, 112.27, 111.12, 110.29, 62.69, 50.87, 27.11, 14.30 ppm. IR (ν, cm^{-1}): 3672, 3398, 3052, 2926, 2857, 2359, 1720, 1651, 1605, 1488, 1464, 1345, 1270, 1221, 1129, 1055, 1030, 902, 817, 731, 701; HRMS (ESI) Calcd. for $C_{24}H_{17}ClN2O_5$+Na^+: 471.0718, Found: 471.0709. The ee was determined to be 97 % by chiral HPLC analysis (Chiralcel AD-H, hexane/isopropanol 80/20, 1.0mL/min, λ= 254 nm): t_R (minor) = 22.8 min, t_R (major) = 29.9 min. $[\alpha]^{25}_D$ = -33.5 (c = 1.0, $CHCl_3$).

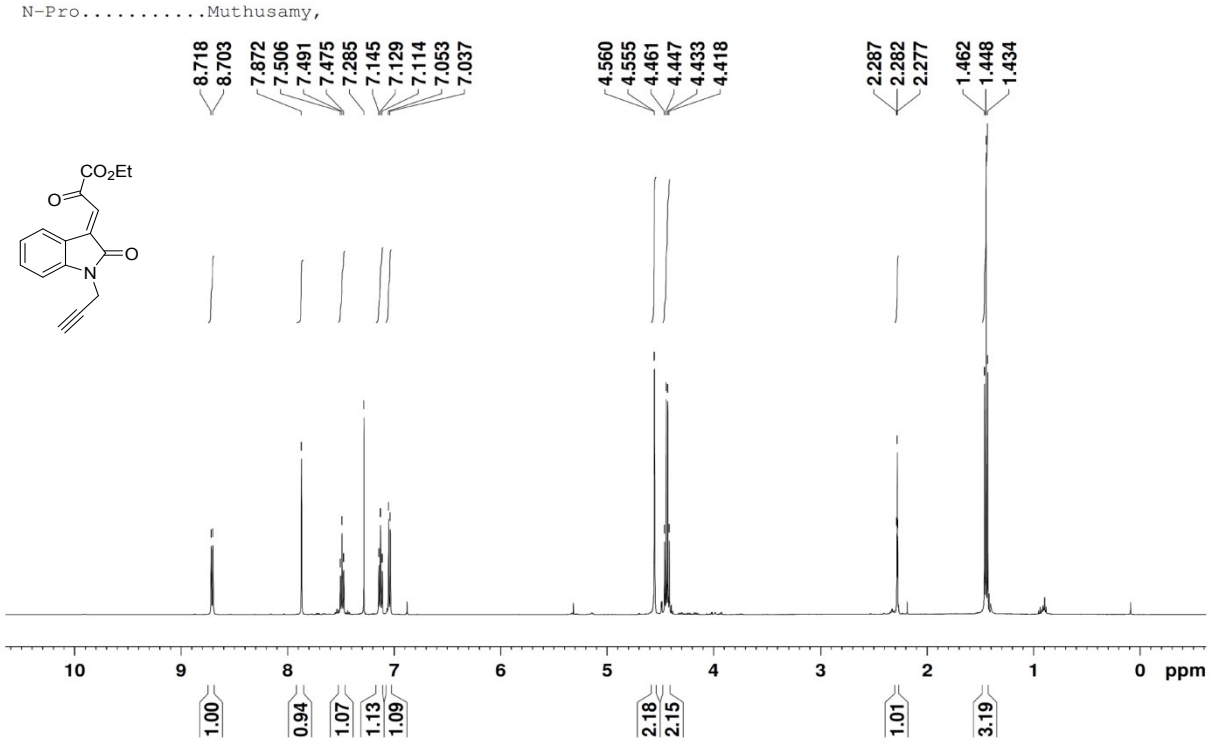
2. ^{1}H NMR and ^{13}C NMR spectra for new compounds compound 1b

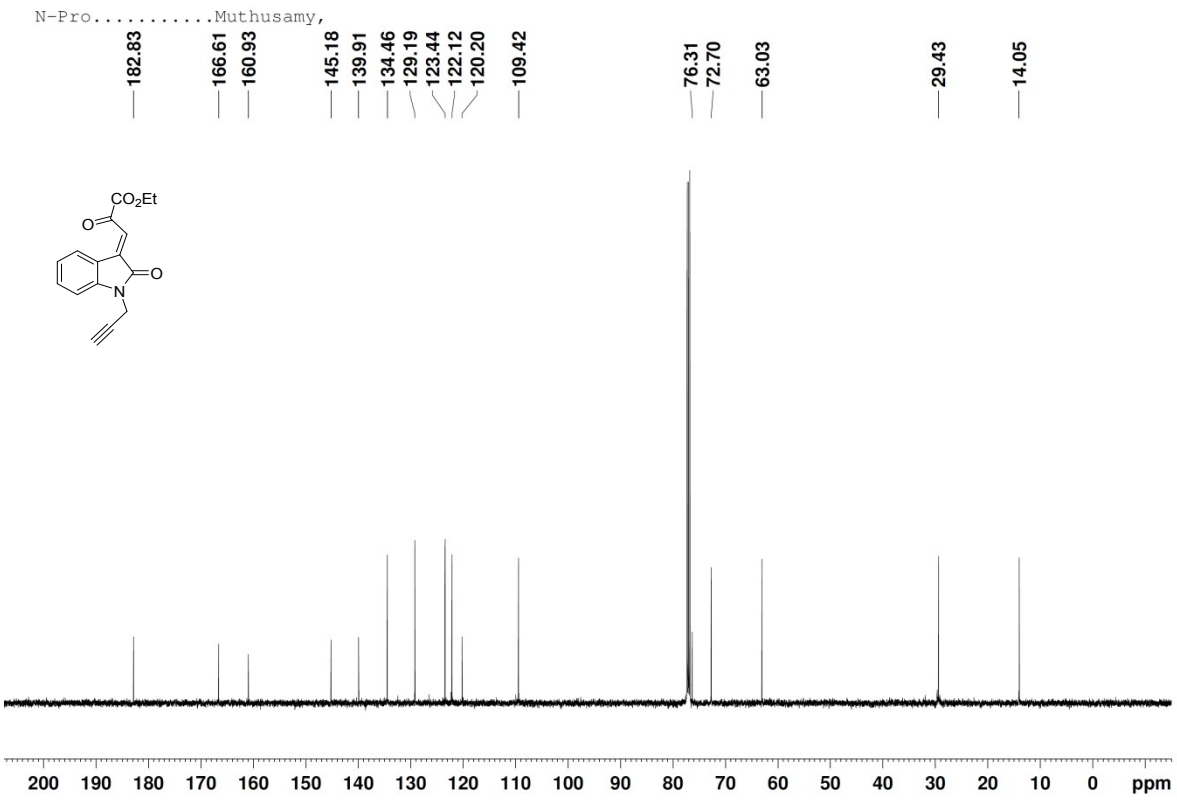




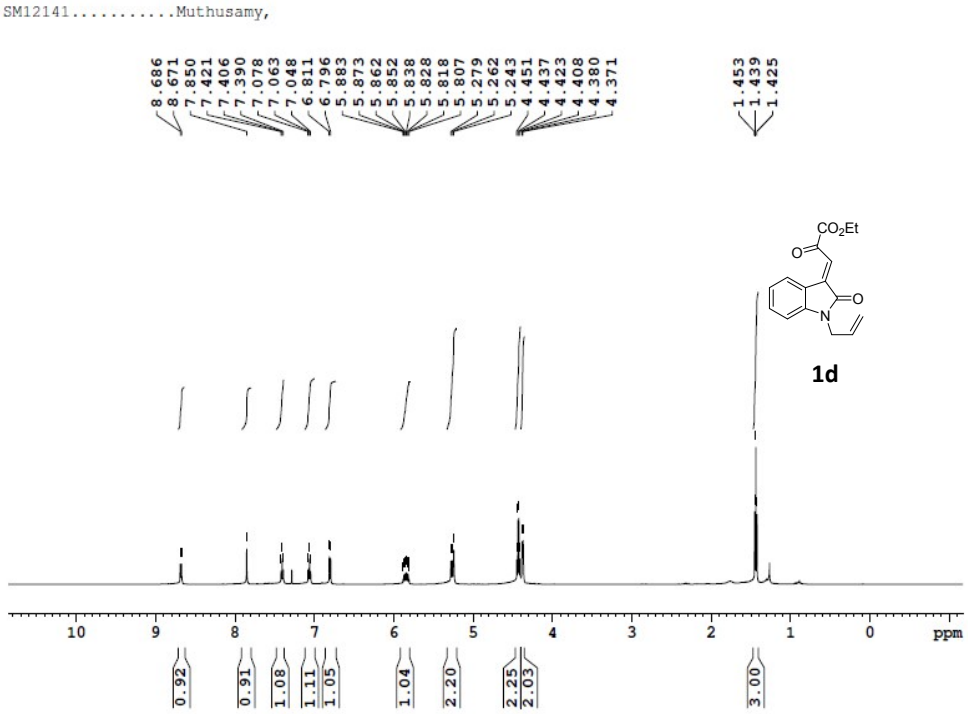
1b

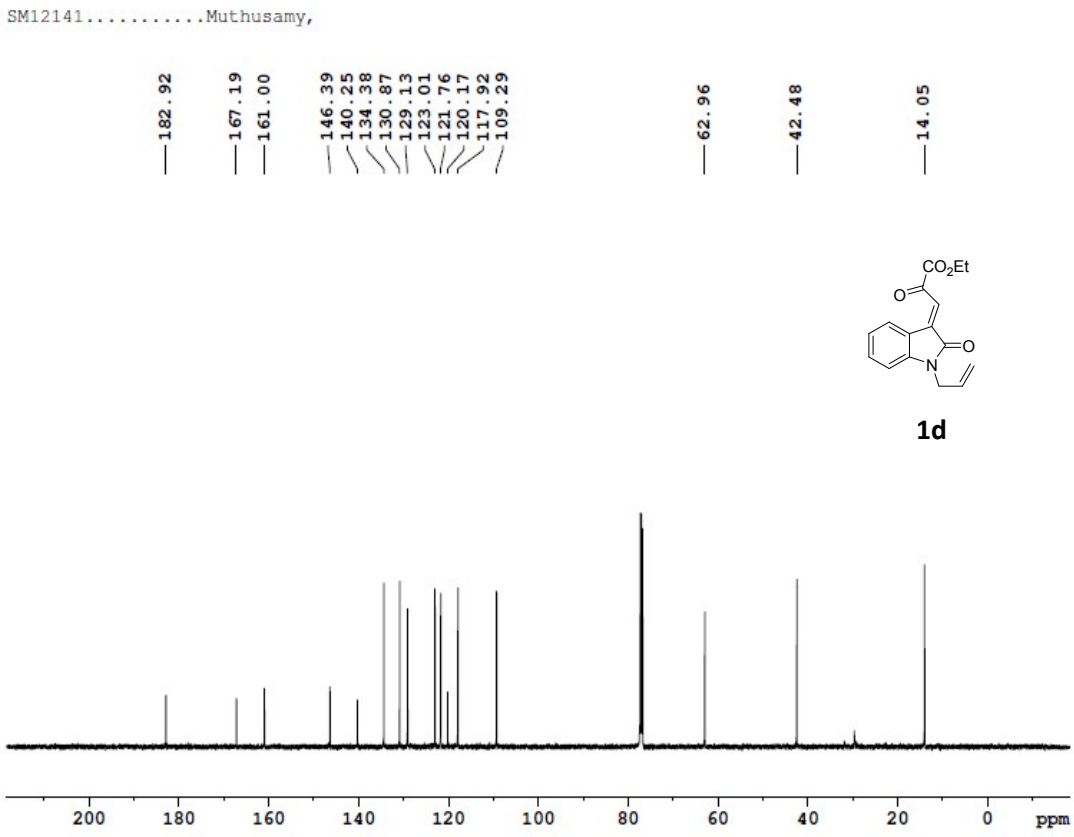
^{1}H and ^{13}C NMR of compound 1c



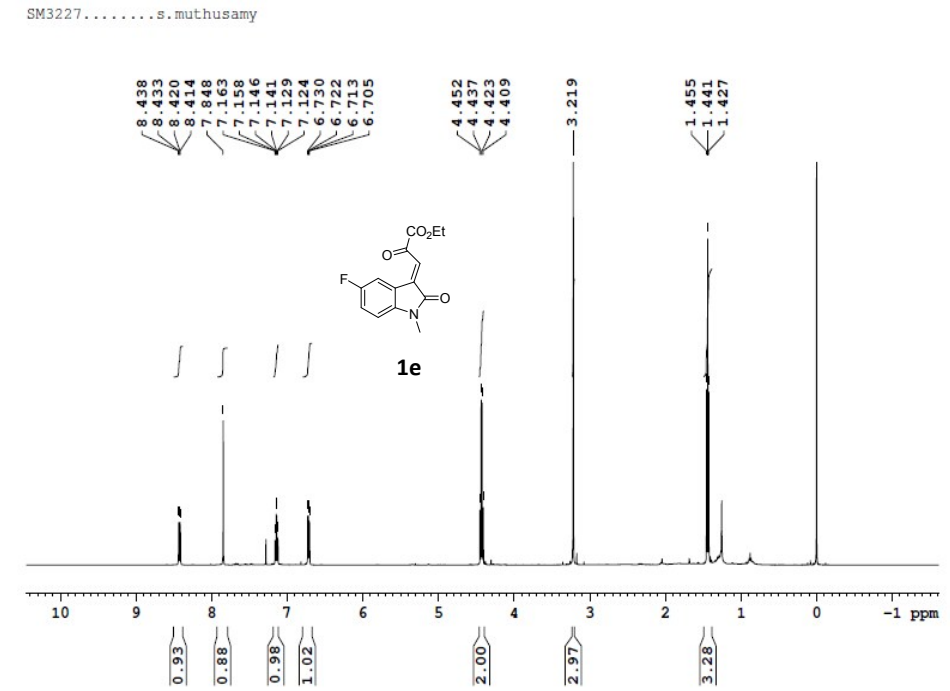


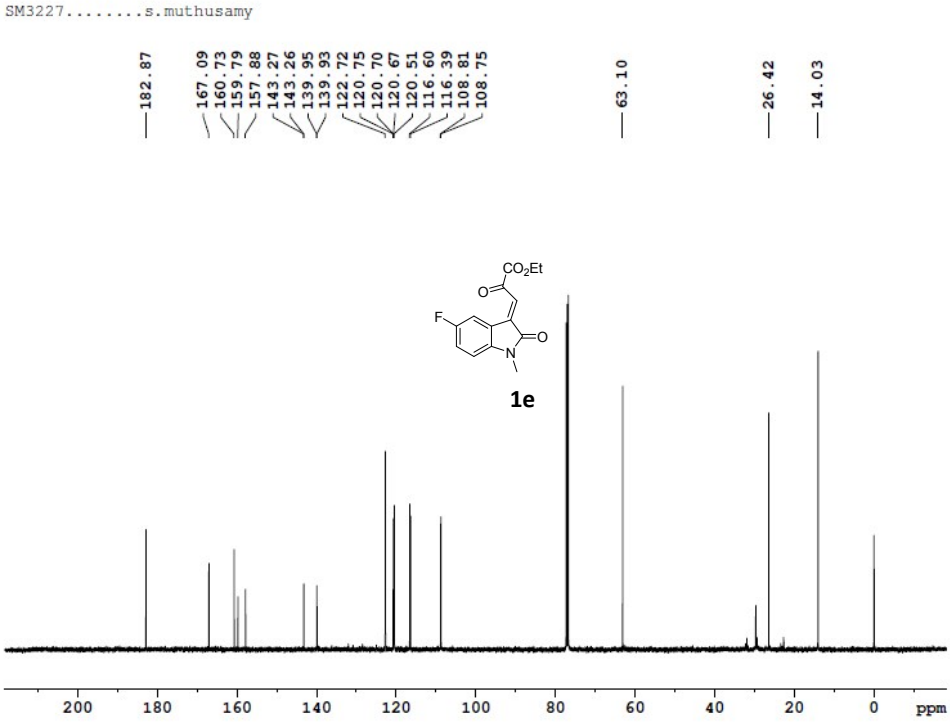
^{1}H and ^{13}C NMR of compound 1d



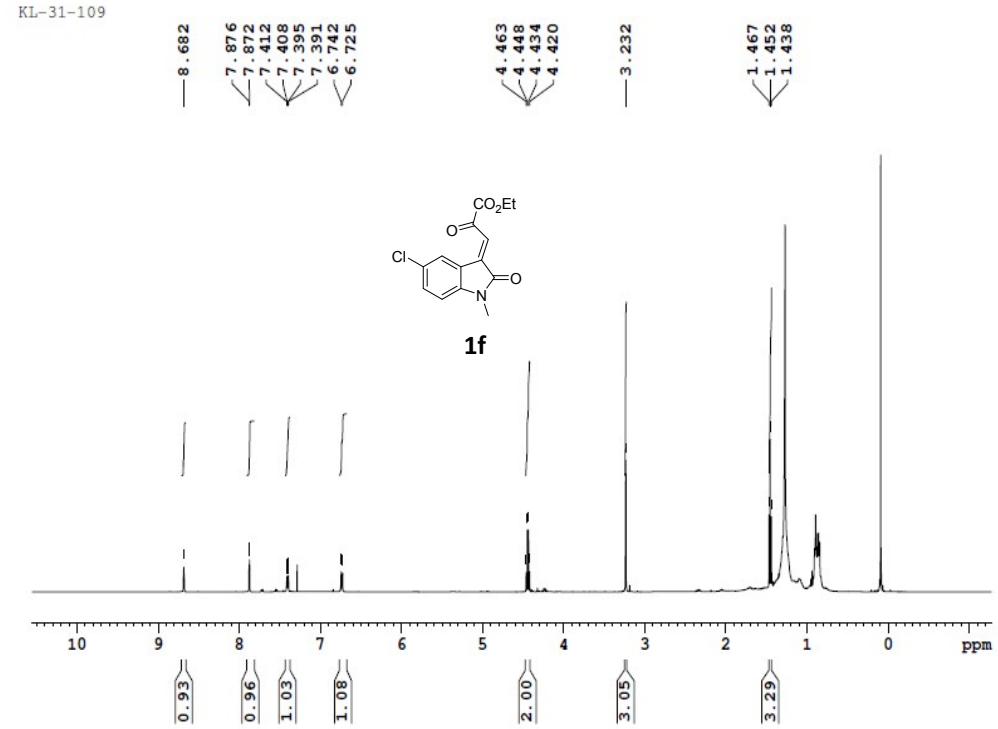


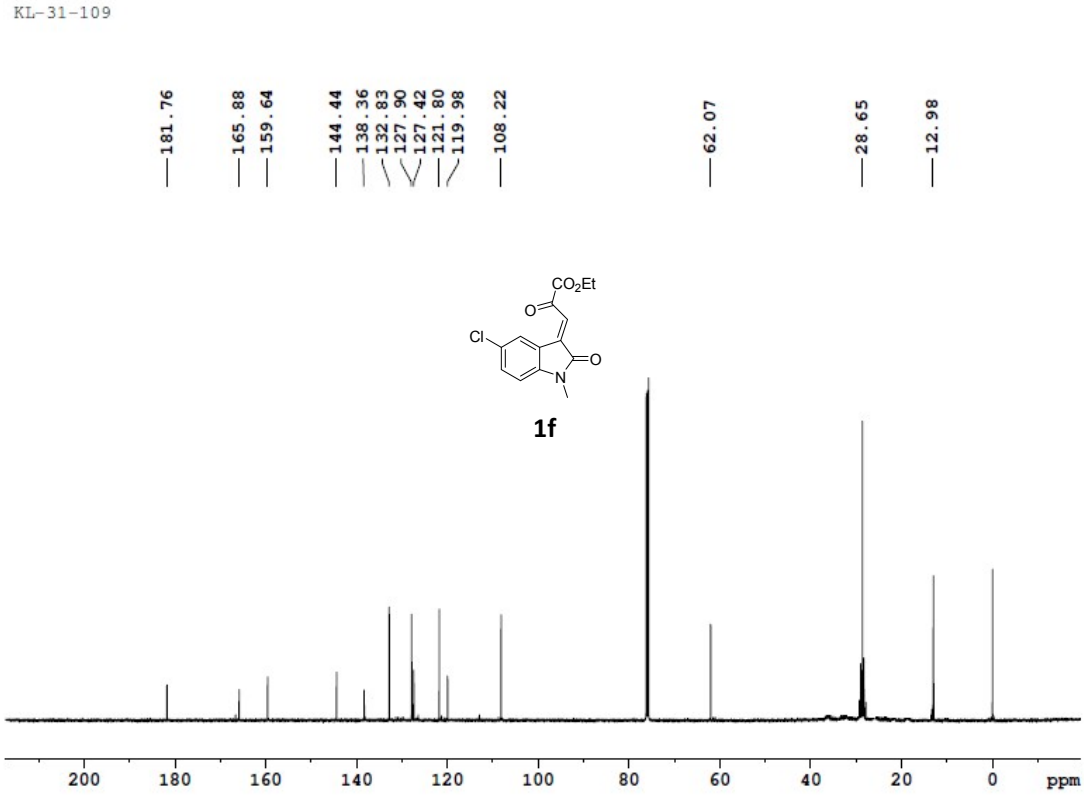
^{1}H and ^{13}C NMR of compound 1e



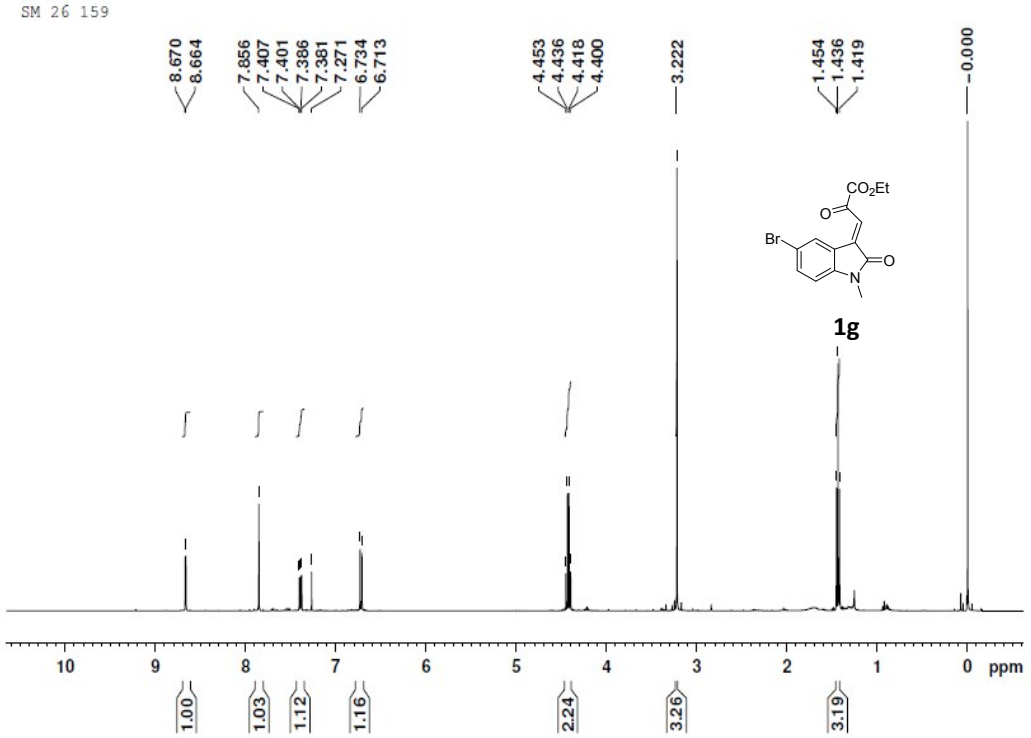


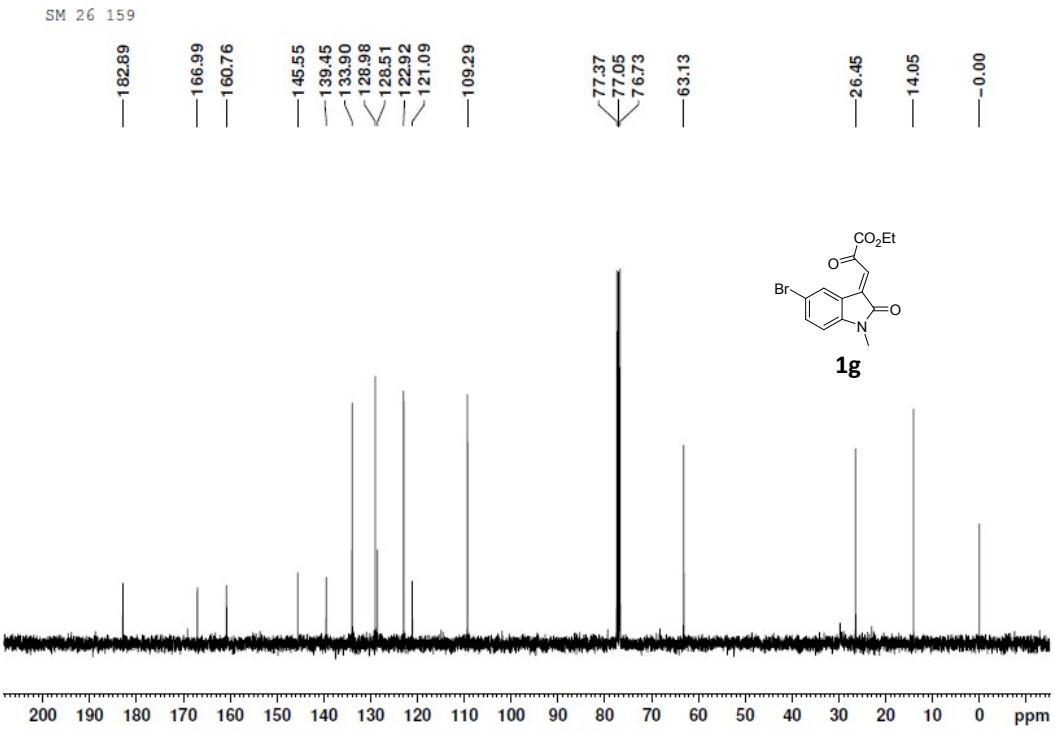
^{1}H and ^{13}C NMR of compound 1f



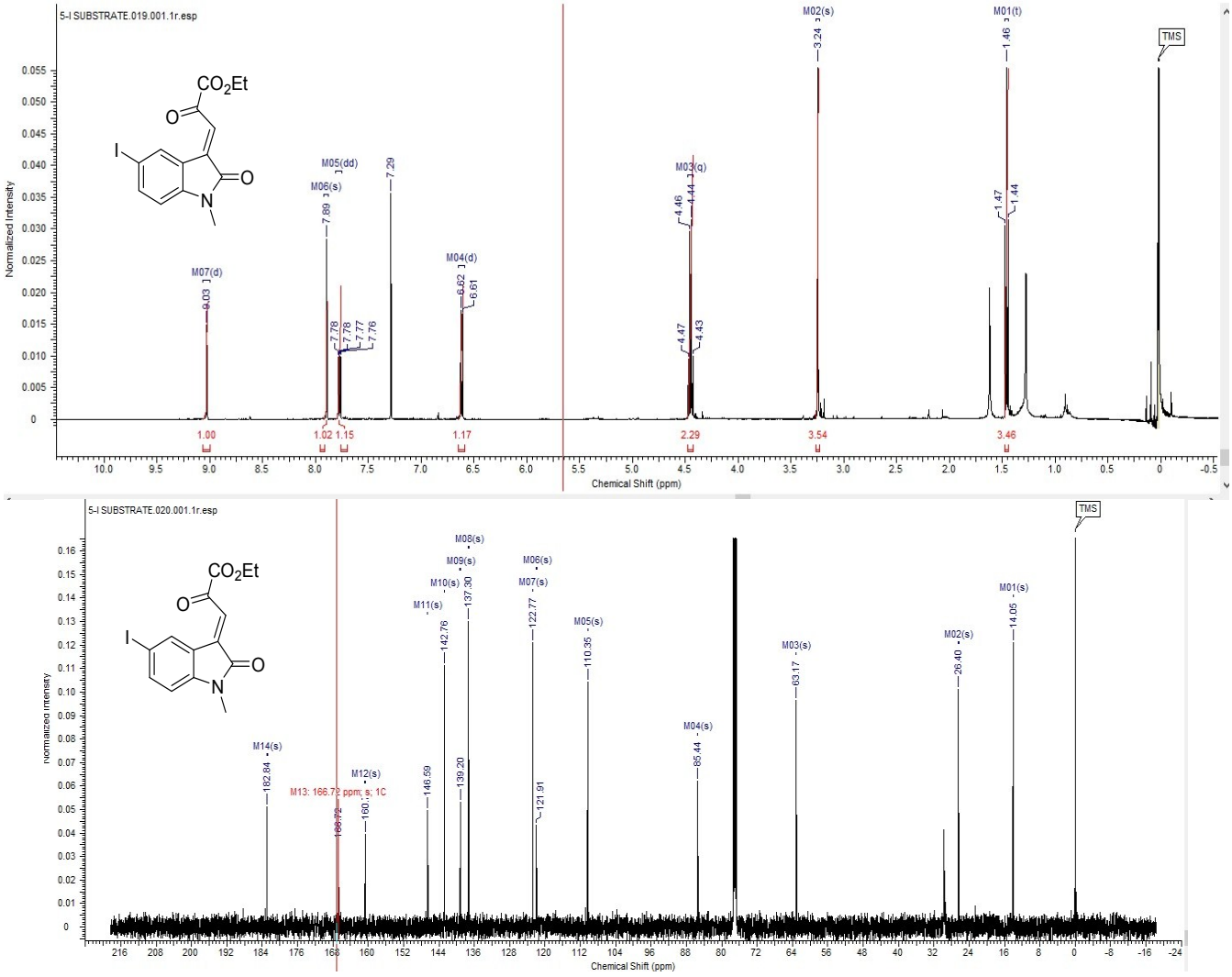


^{1}H and ^{13}C NMR of compound 1g

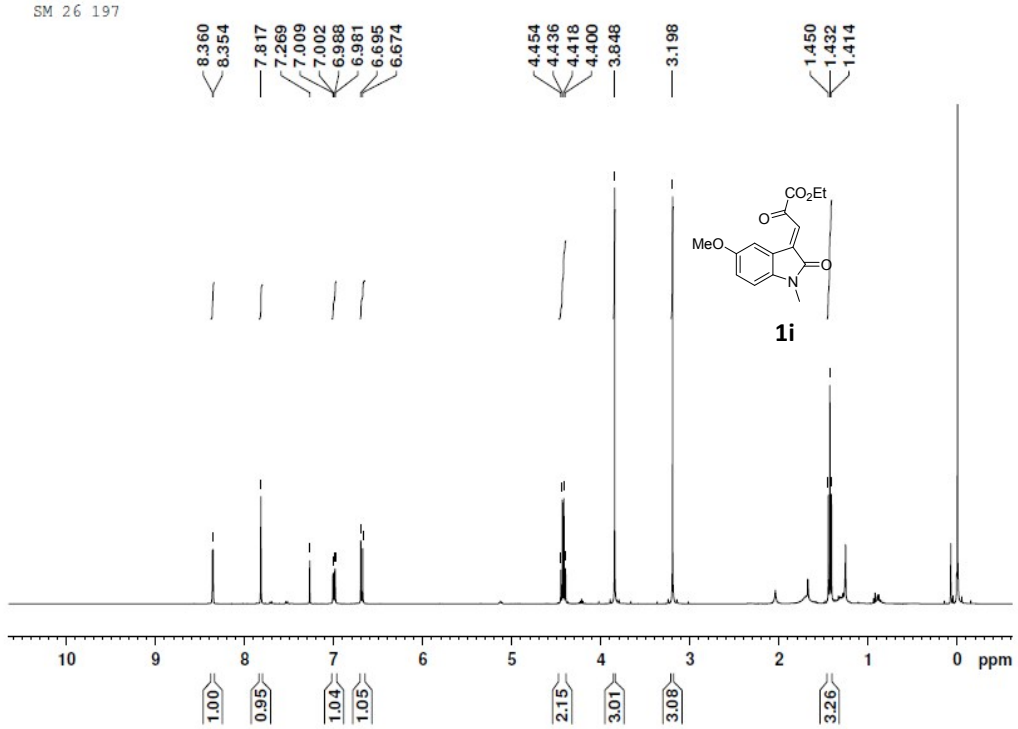


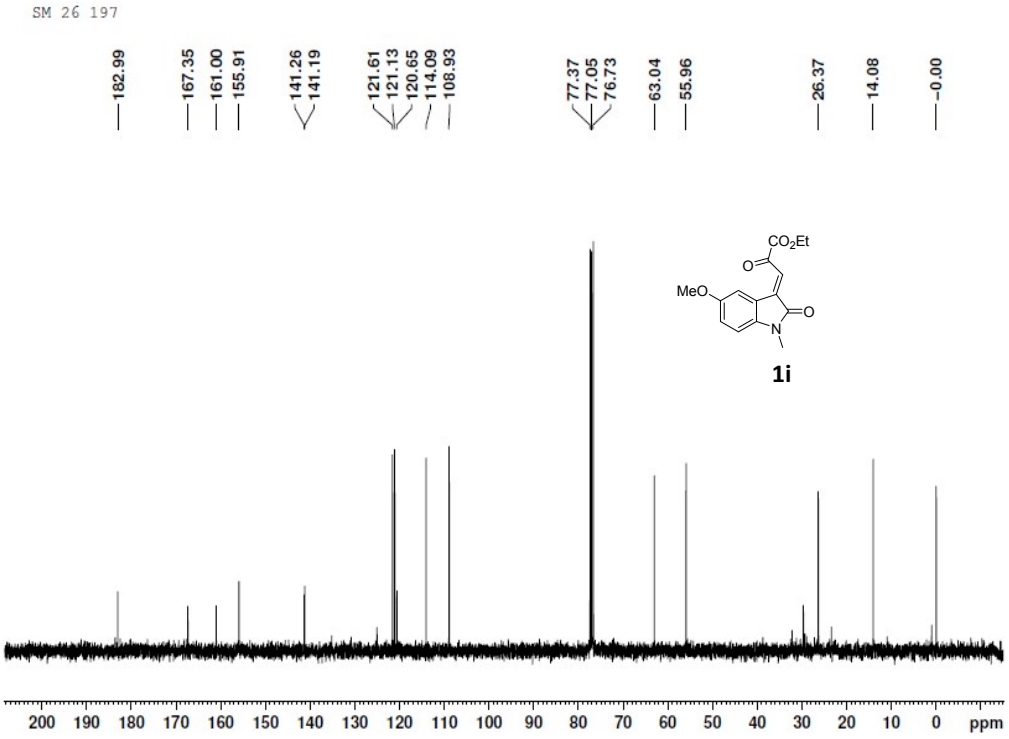


^{1}H and ^{13}C NMR of compound 1h

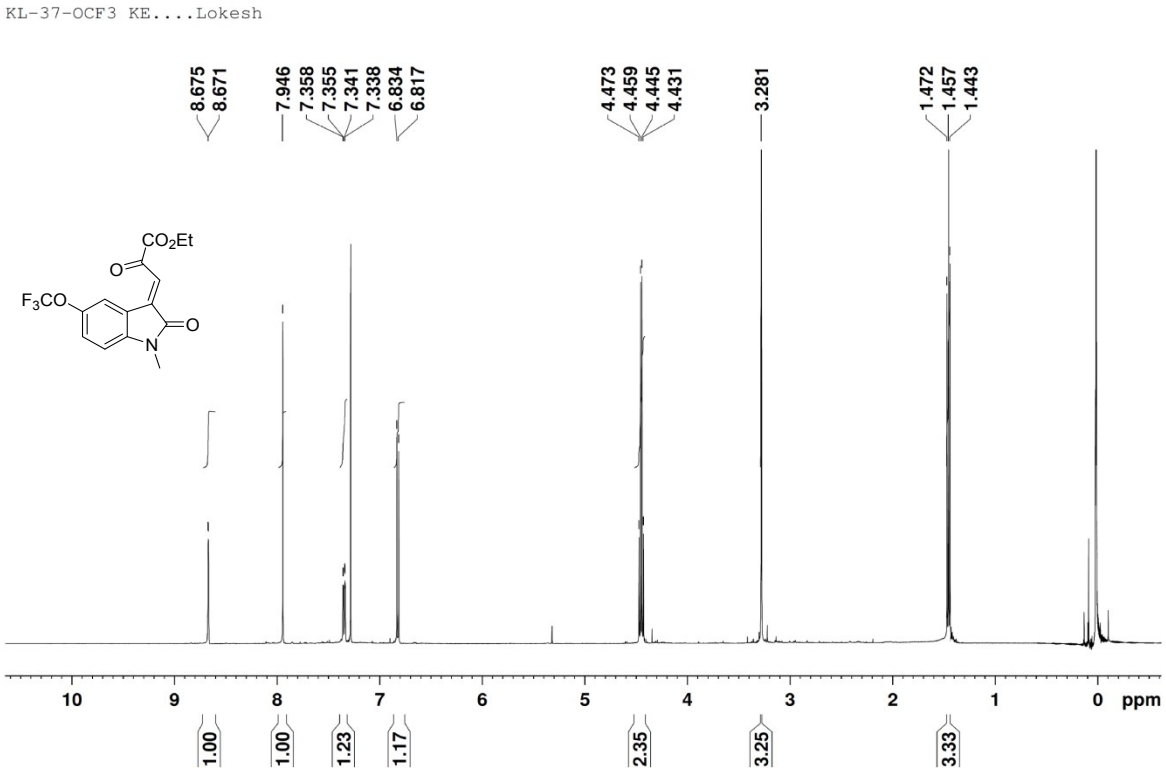


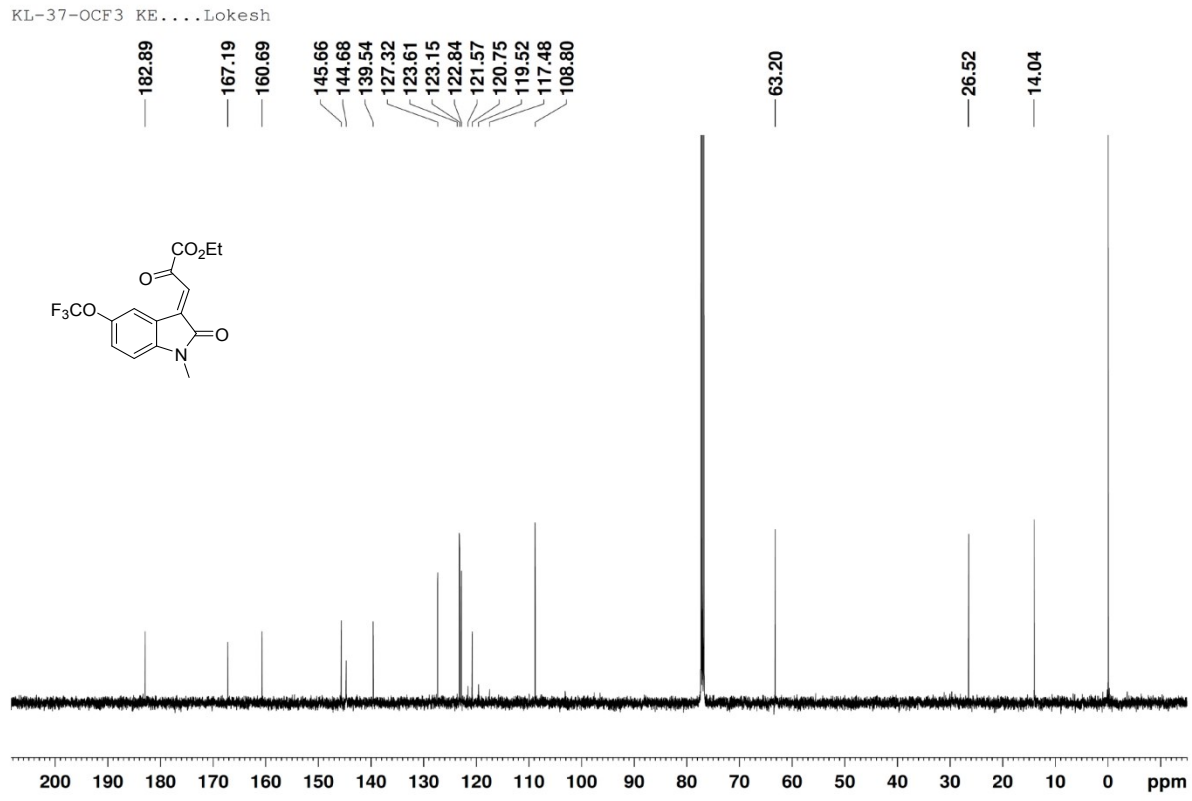
^{1}H and ^{13}C NMR of compound 1i



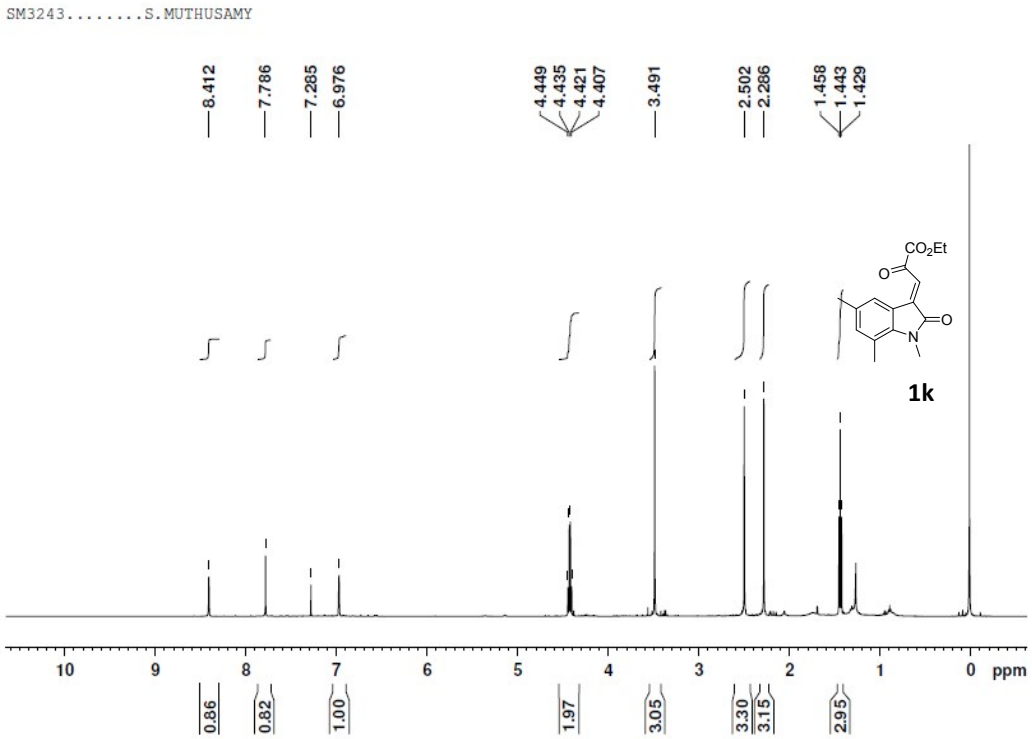


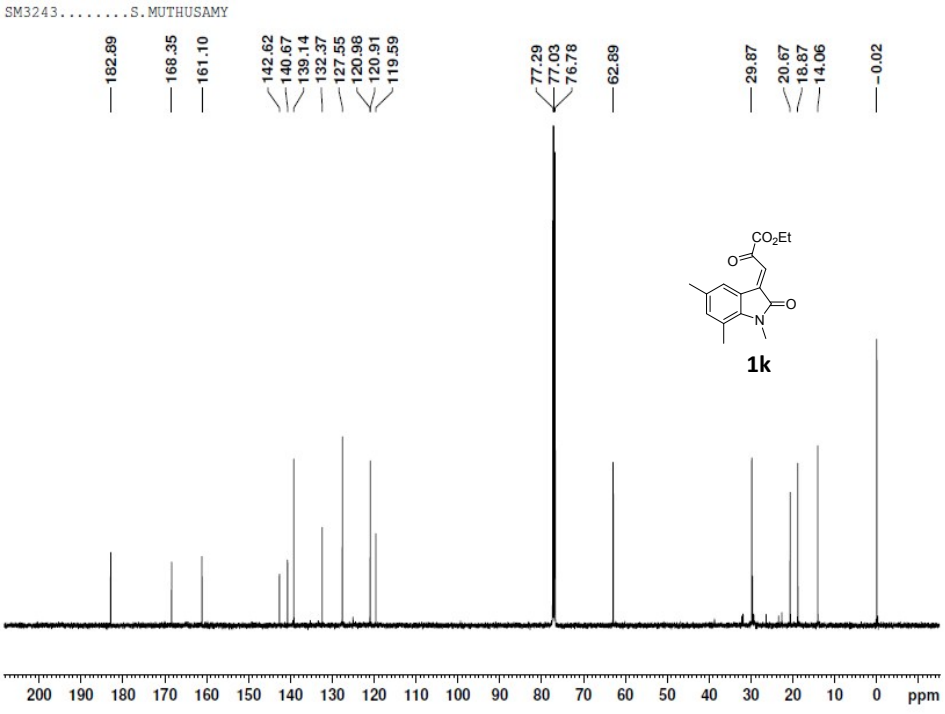
^{1}H and ^{13}C NMR of compound 1j



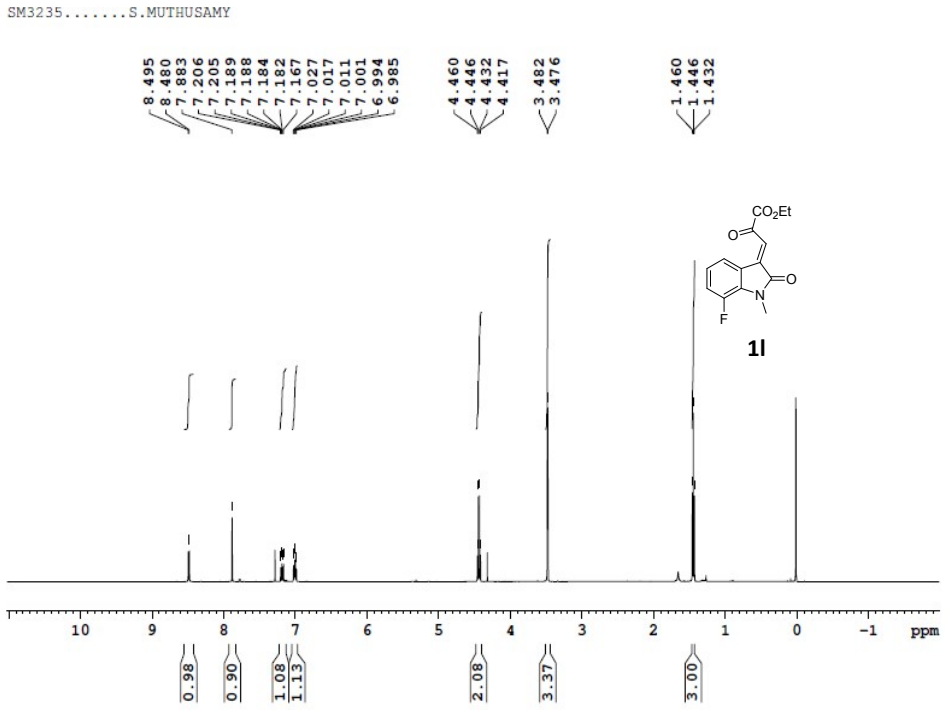


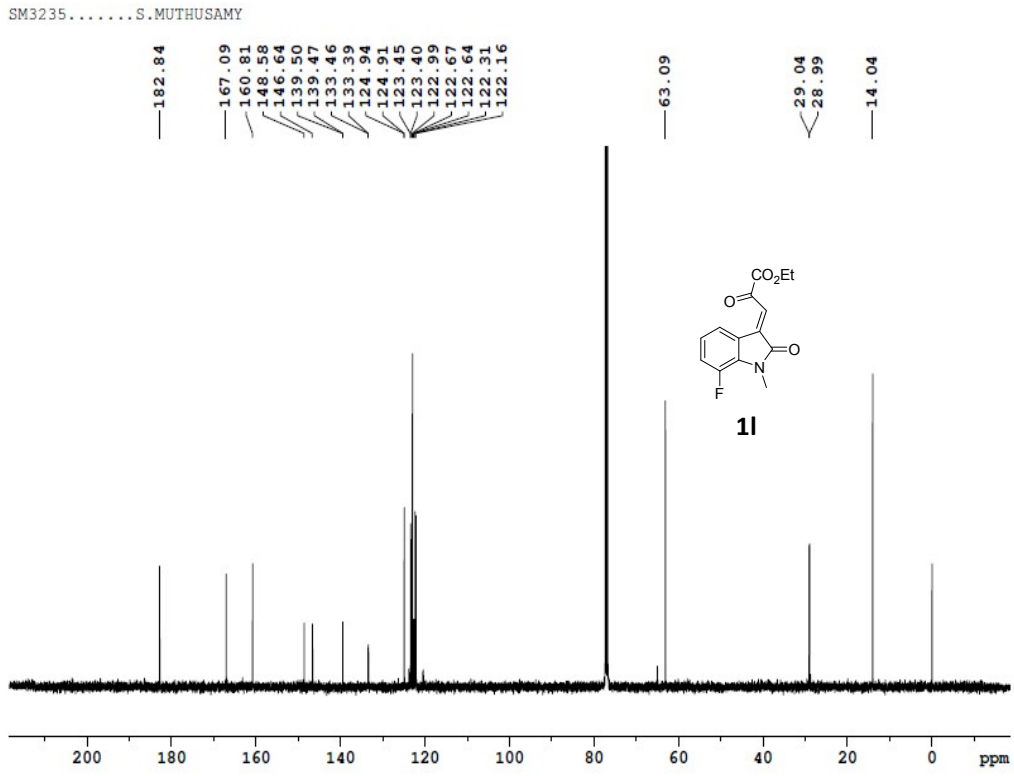
^{1}H and ^{13}C NMR of 1k



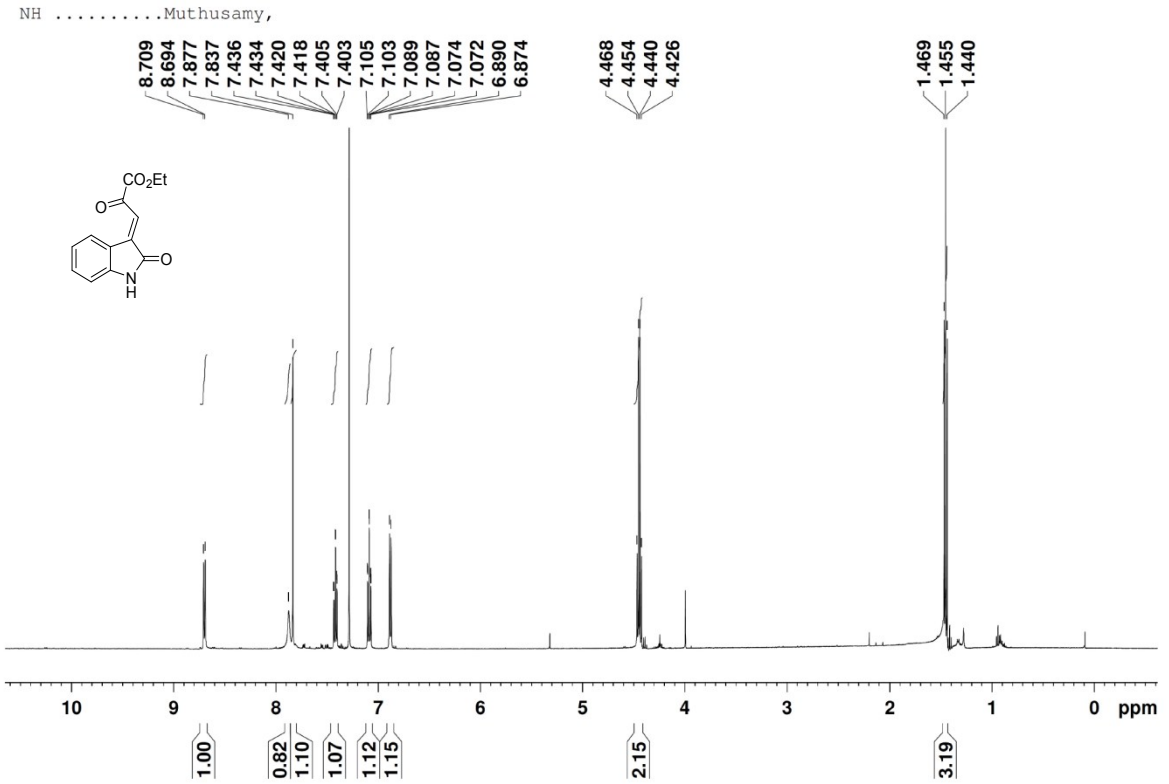


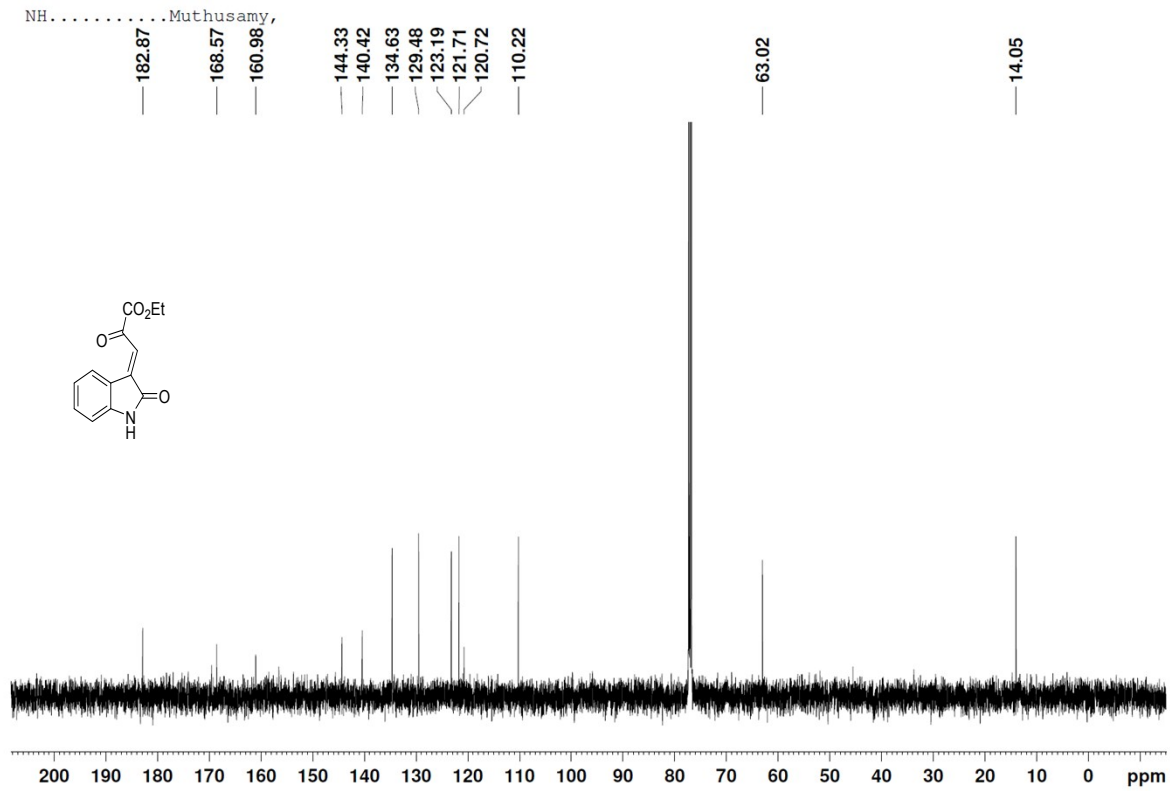
^{1}H and ^{13}C NMR of compound 1l



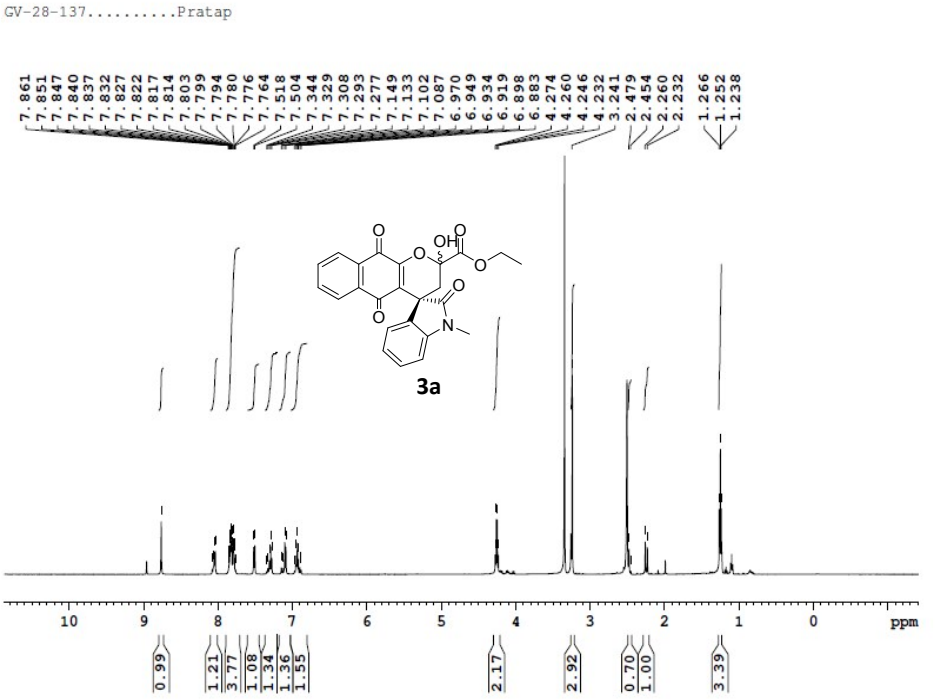


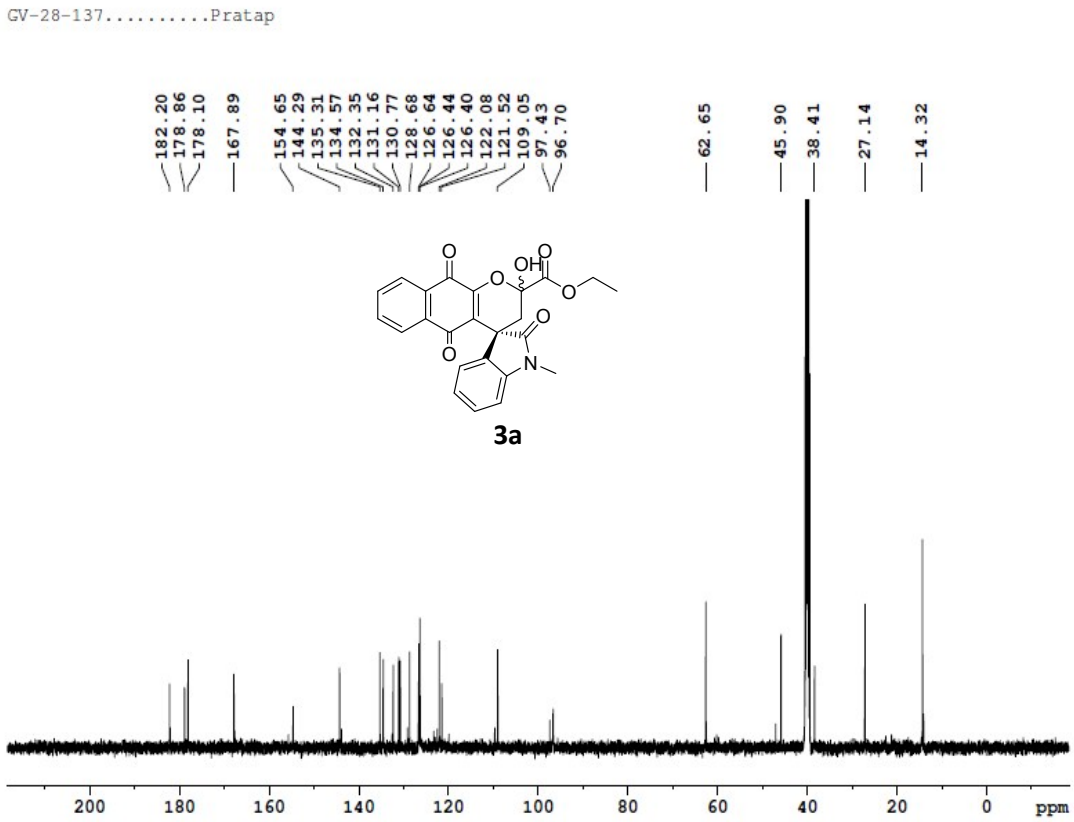
^{1}H and ^{13}C NMR of compound 1m



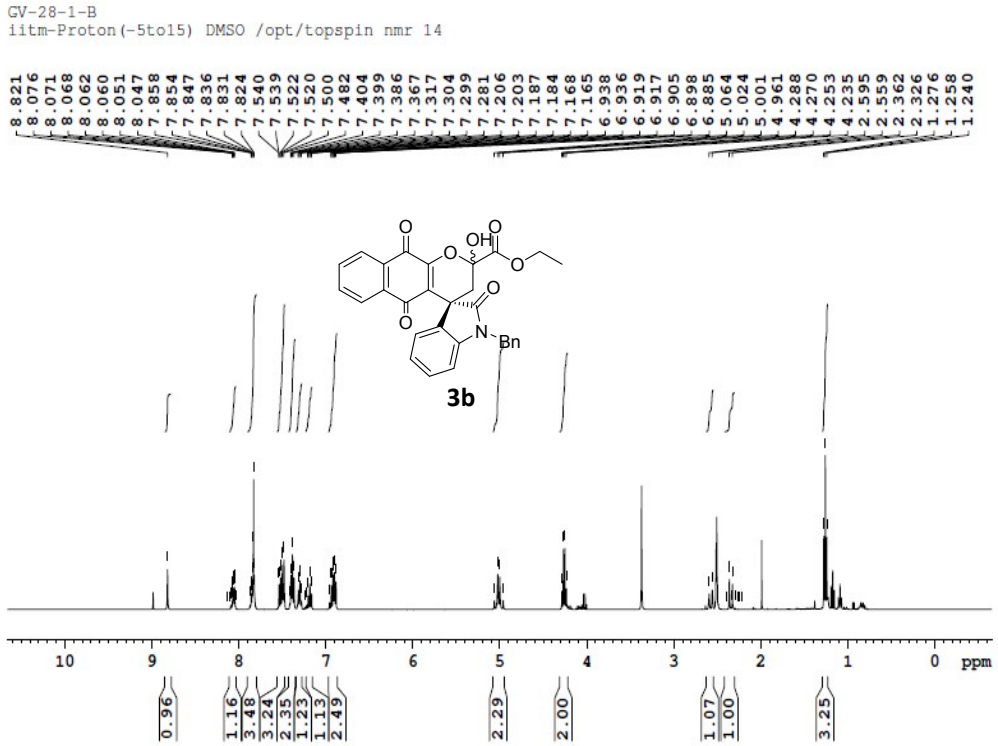


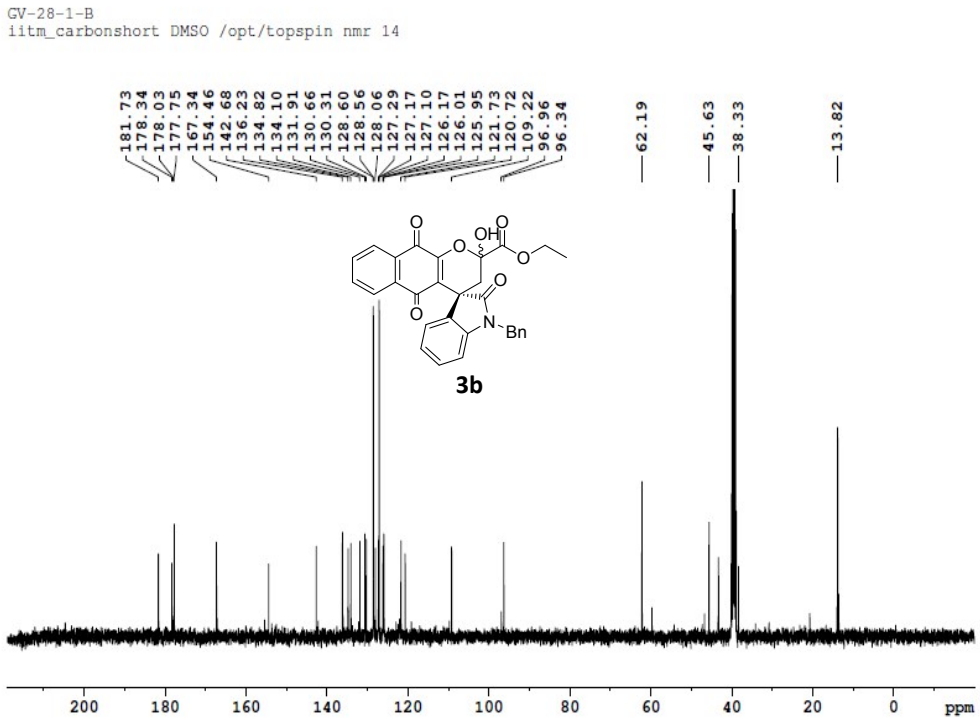
^{1}H and ^{13}C NMR of compound 3a



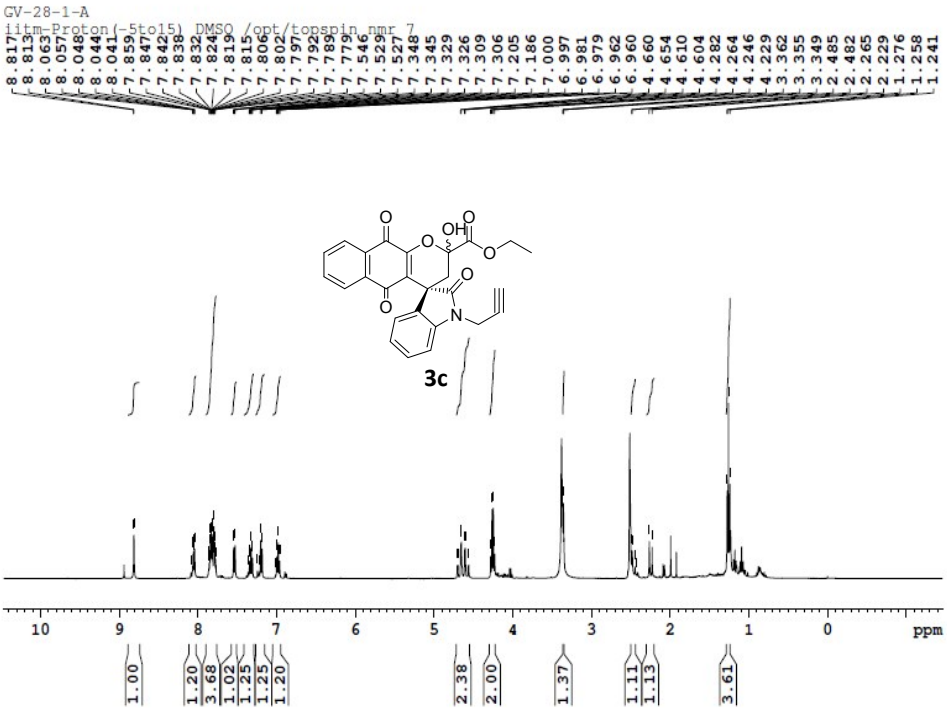


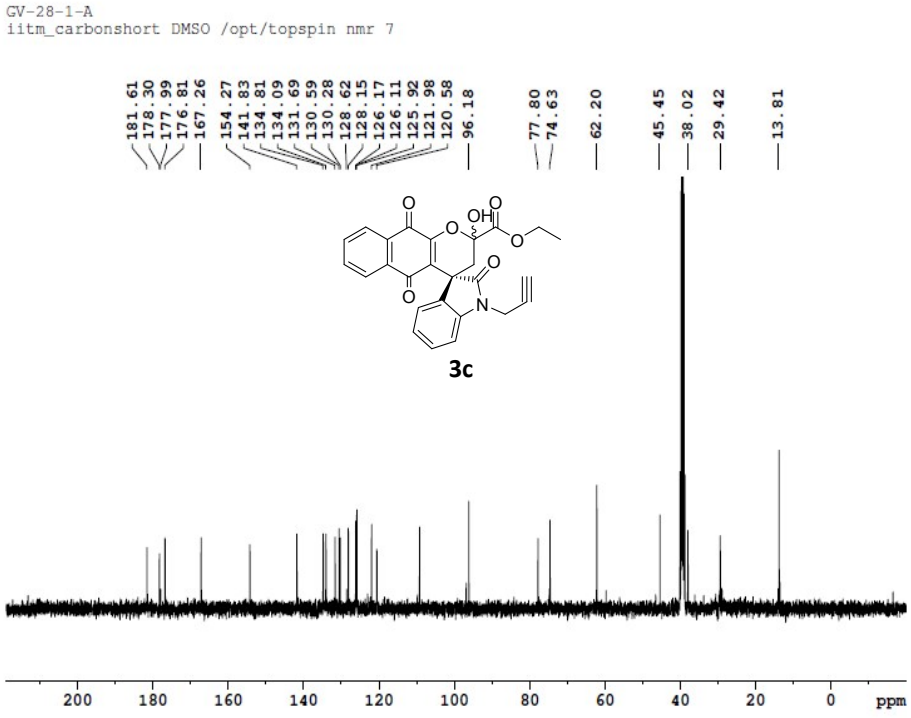
^{1}H and ^{13}C NMR of compound 3b



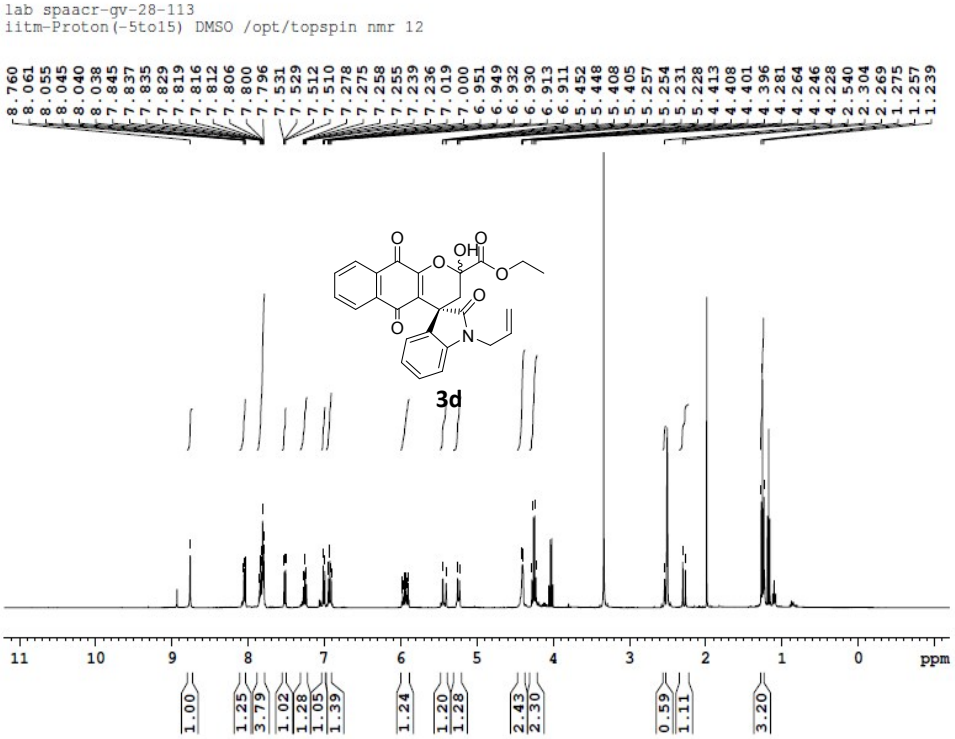


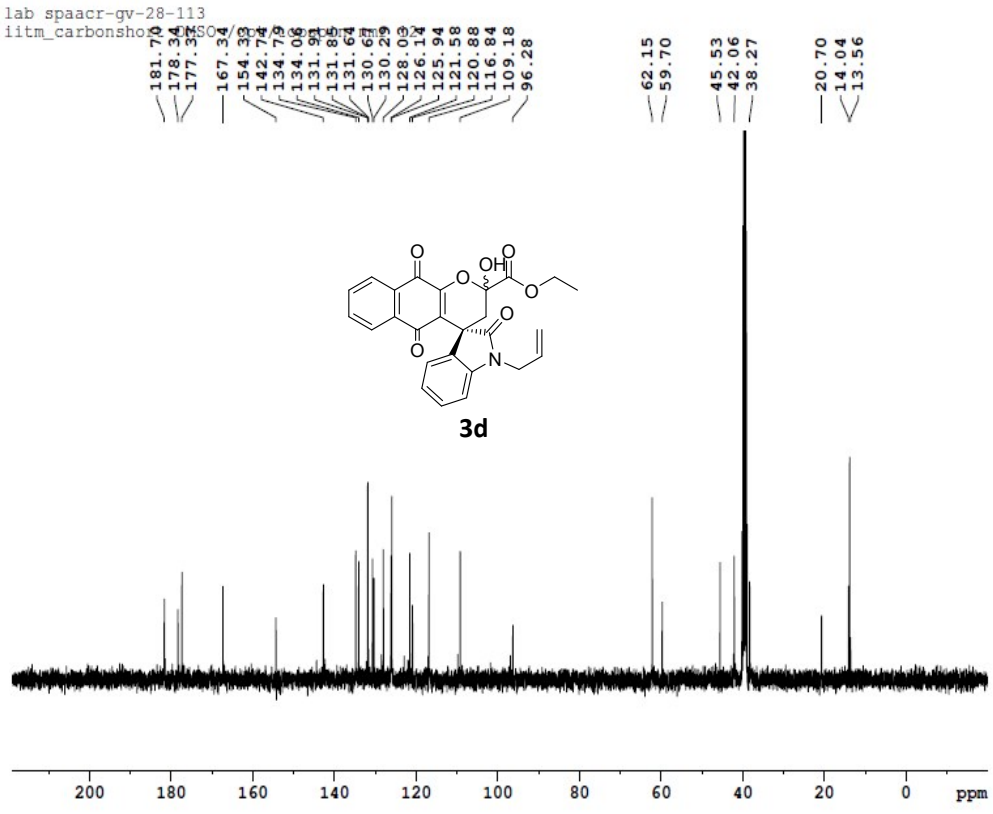
^{1}H and ^{13}C NMR of compound 3c



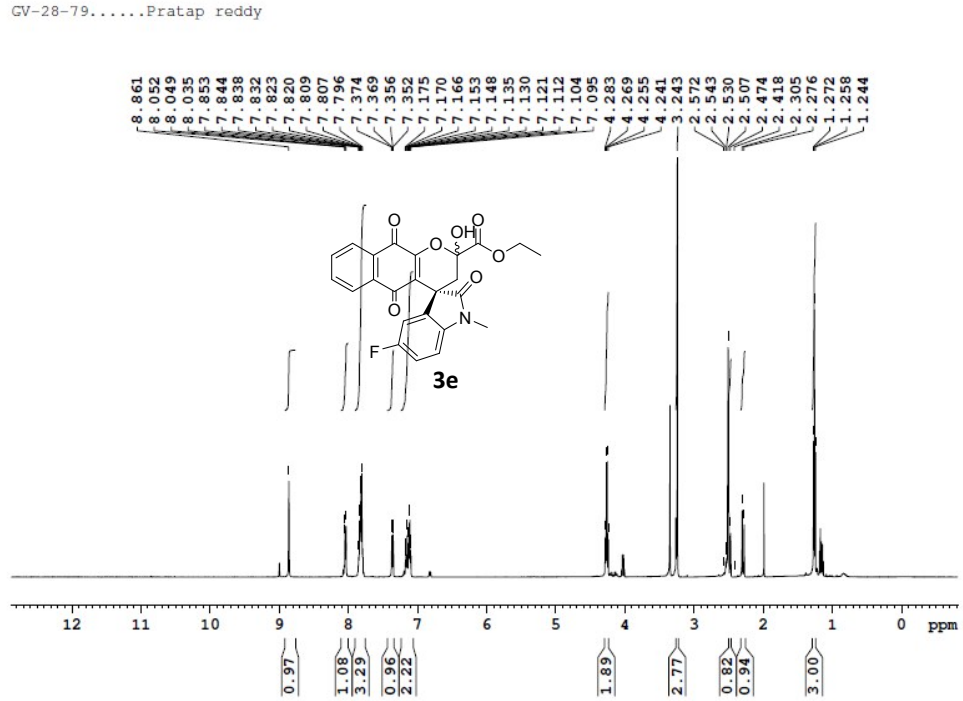


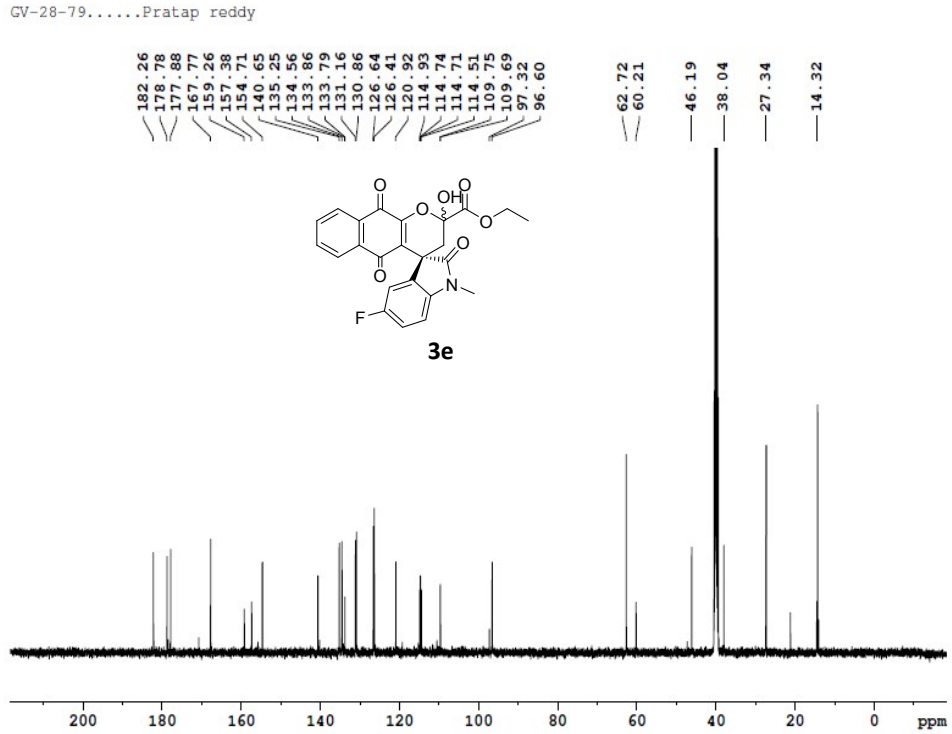
^{1}H and ^{13}C NMR of compound 3d



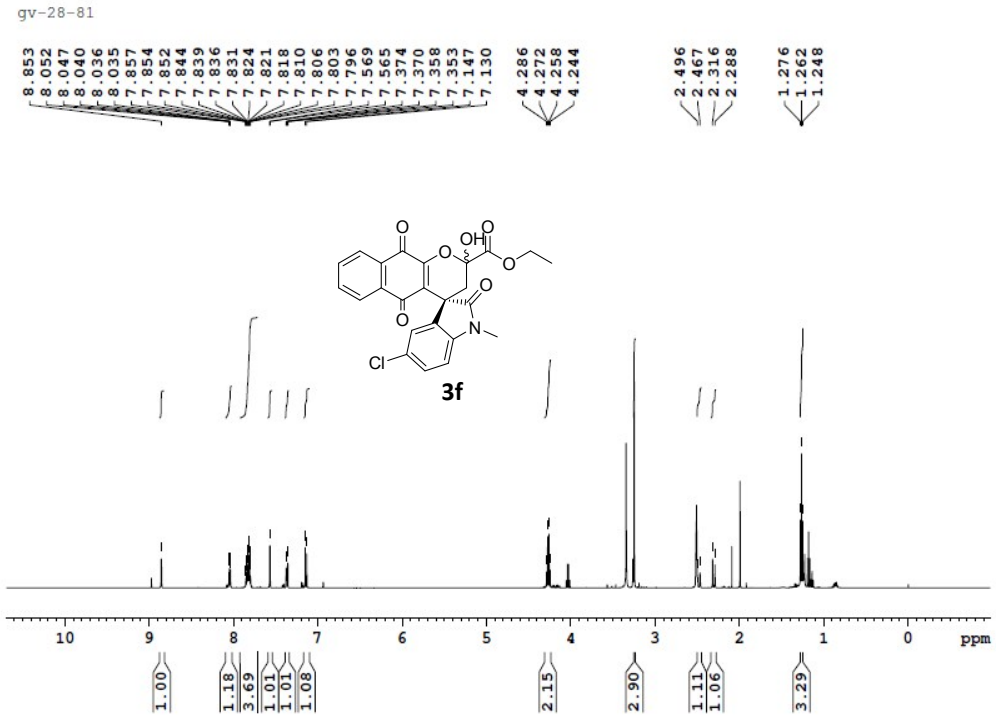


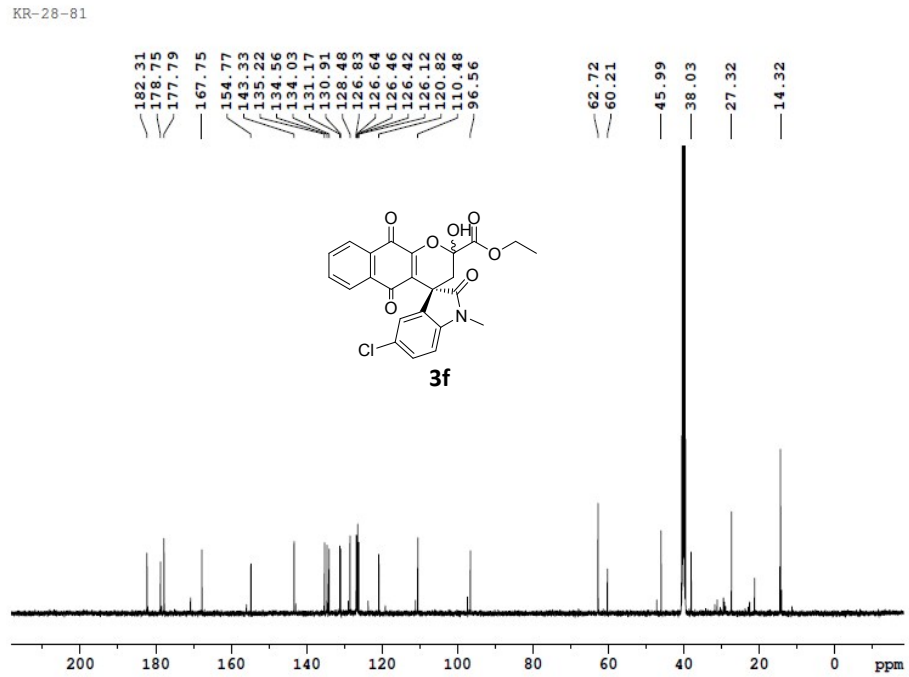
^{1}H and ^{13}C NMR of compound 3e



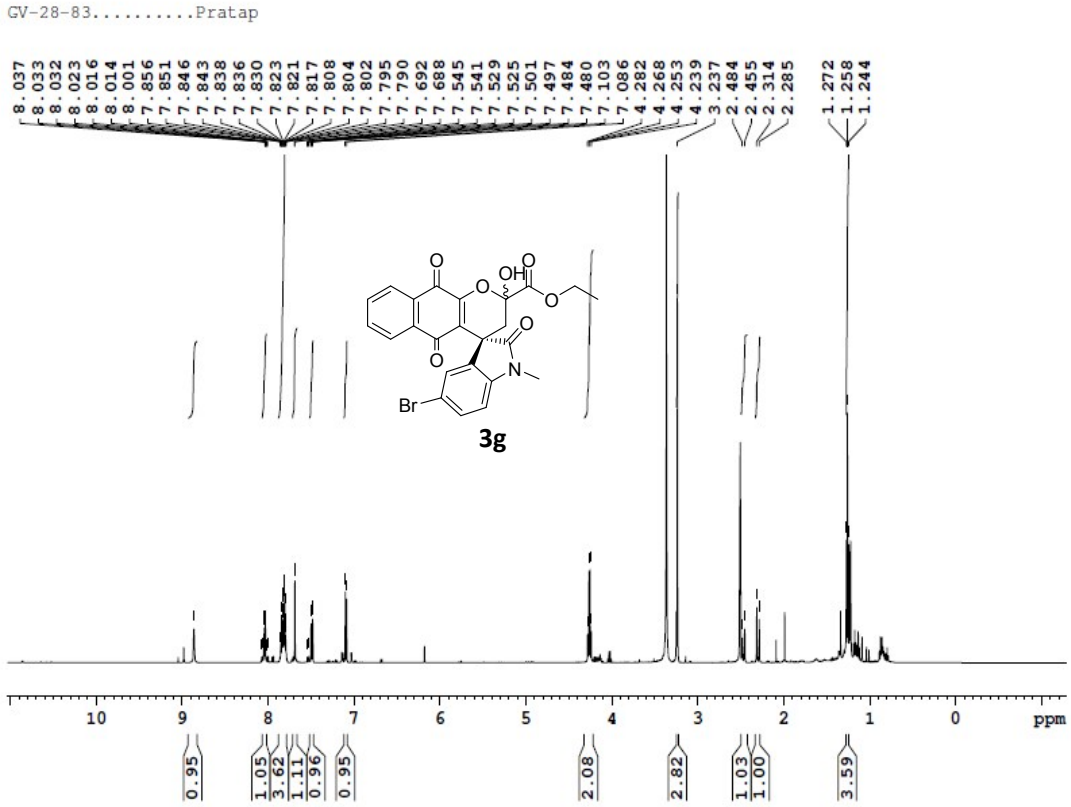


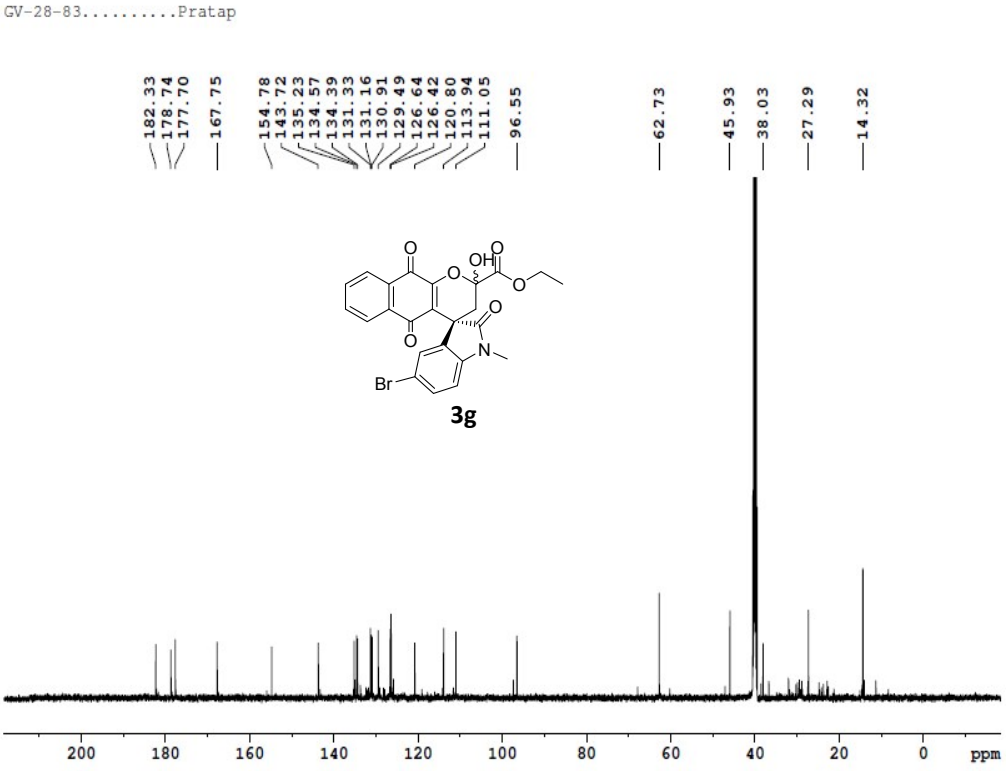
^{1}H and ^{13}C NMR of compound 3f



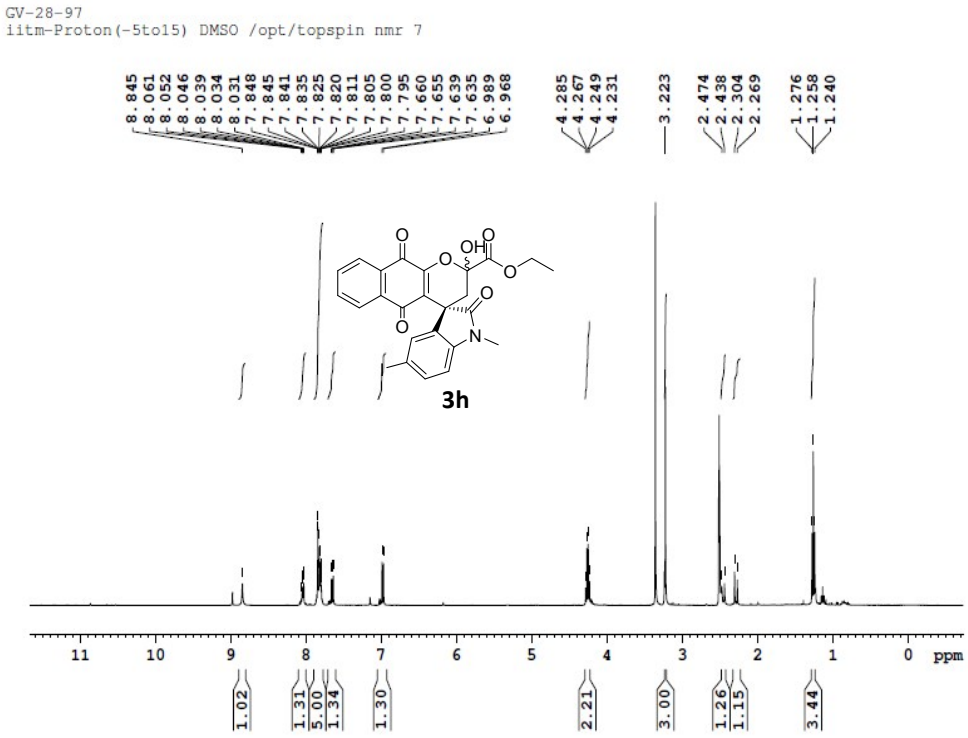


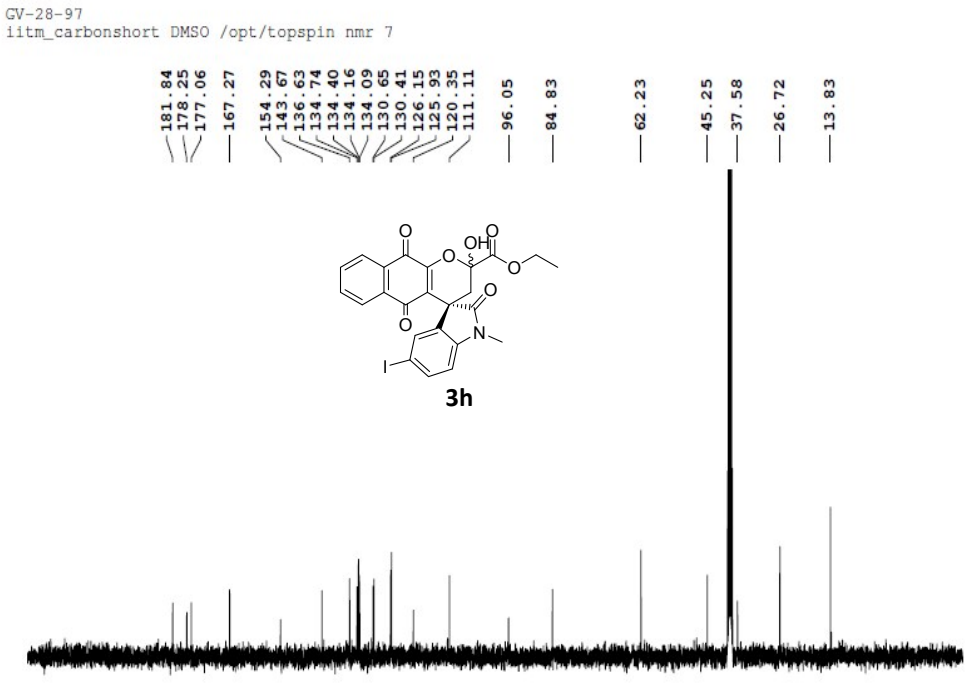
^{1}H and ^{13}C NMR of compound 3g



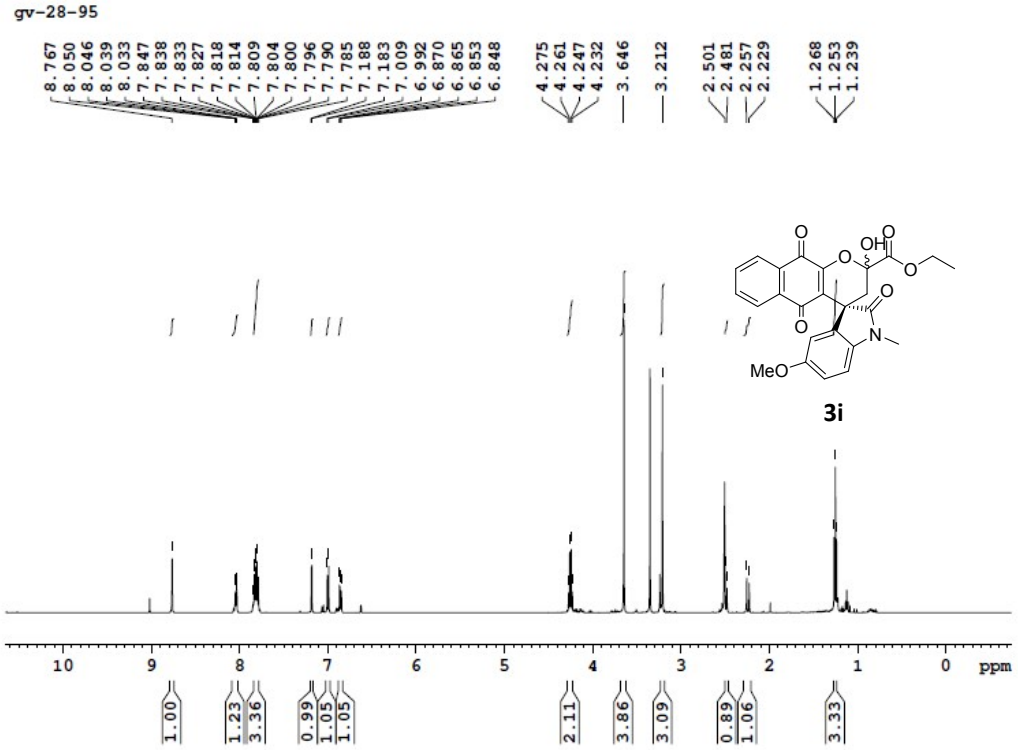


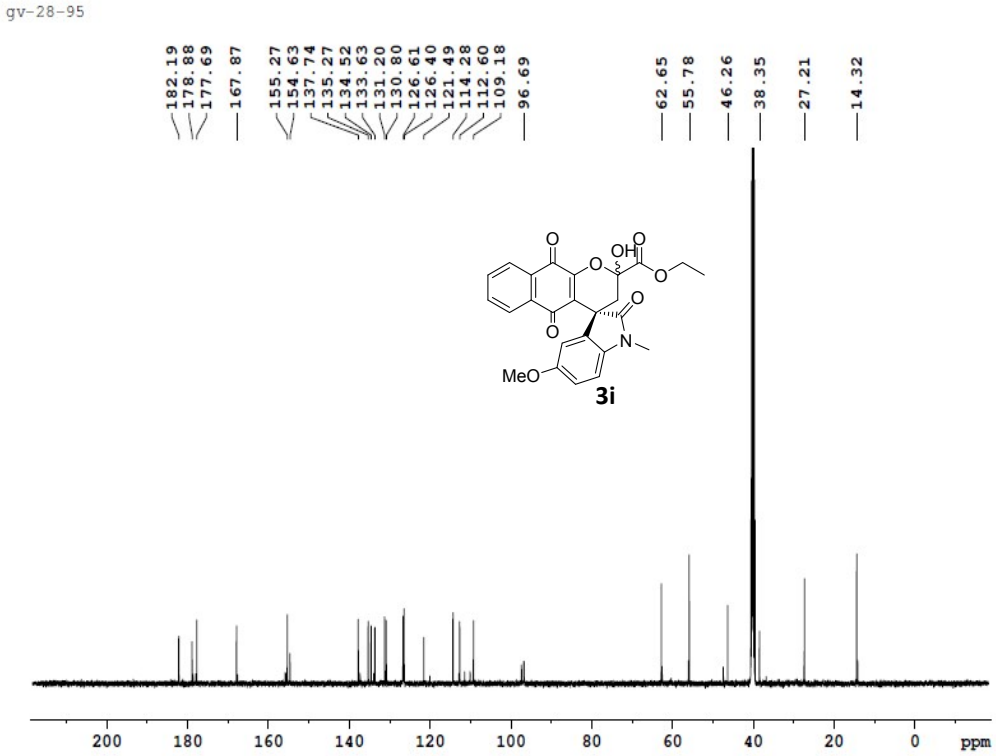
^{1}H and ^{13}C NMR of compound 3h



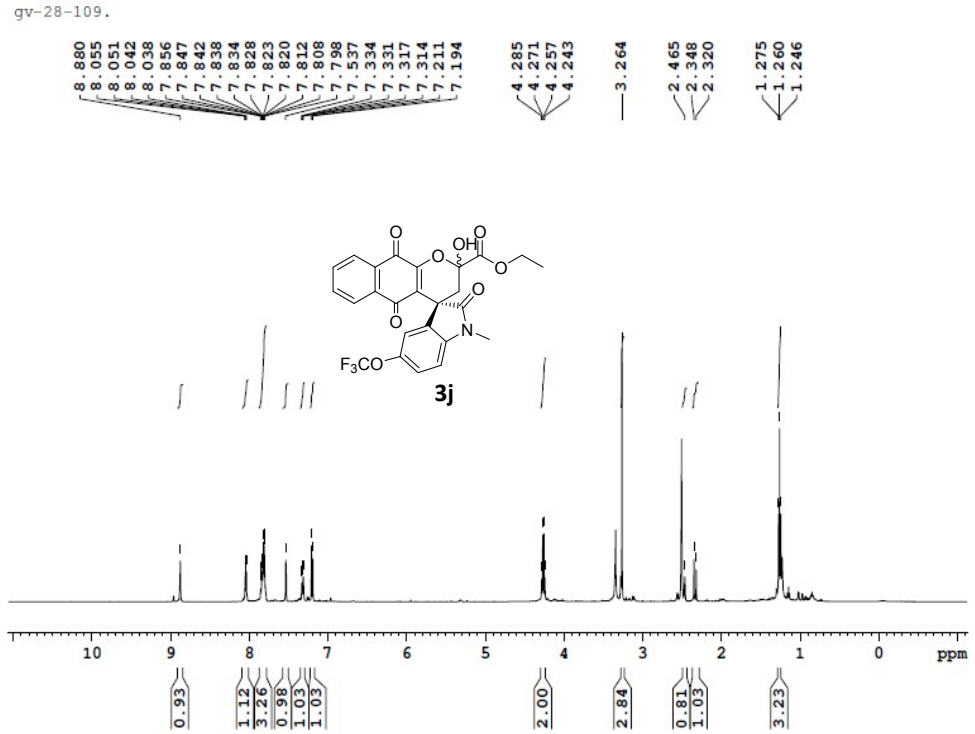


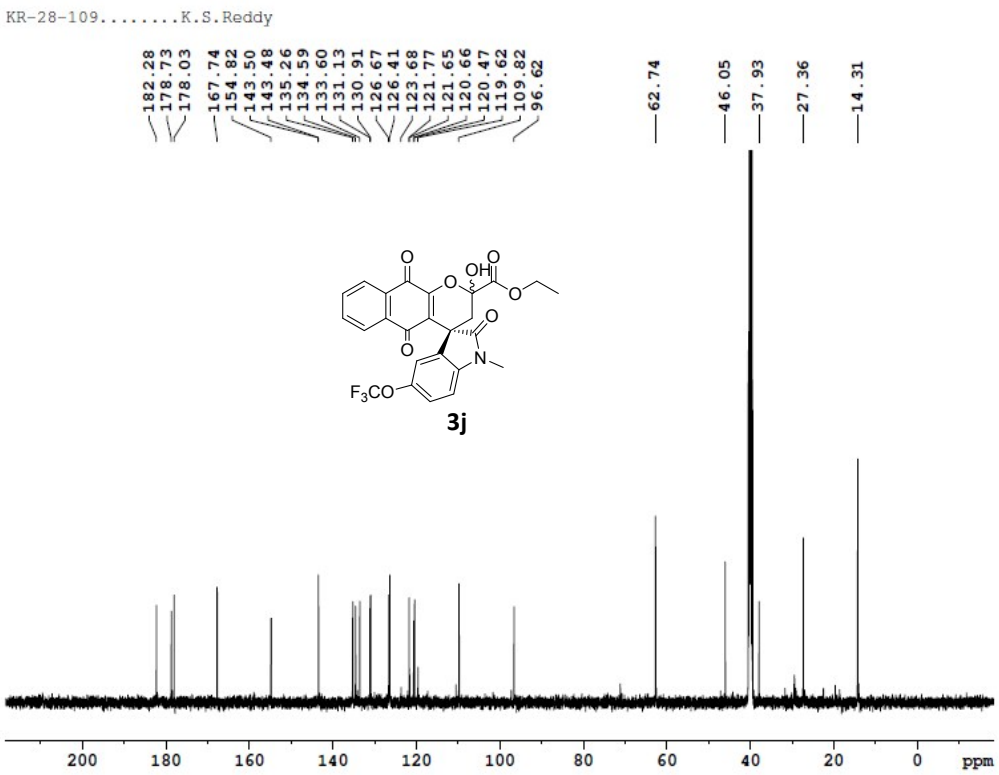
^{1}H and ^{13}C NMR of compound 3i



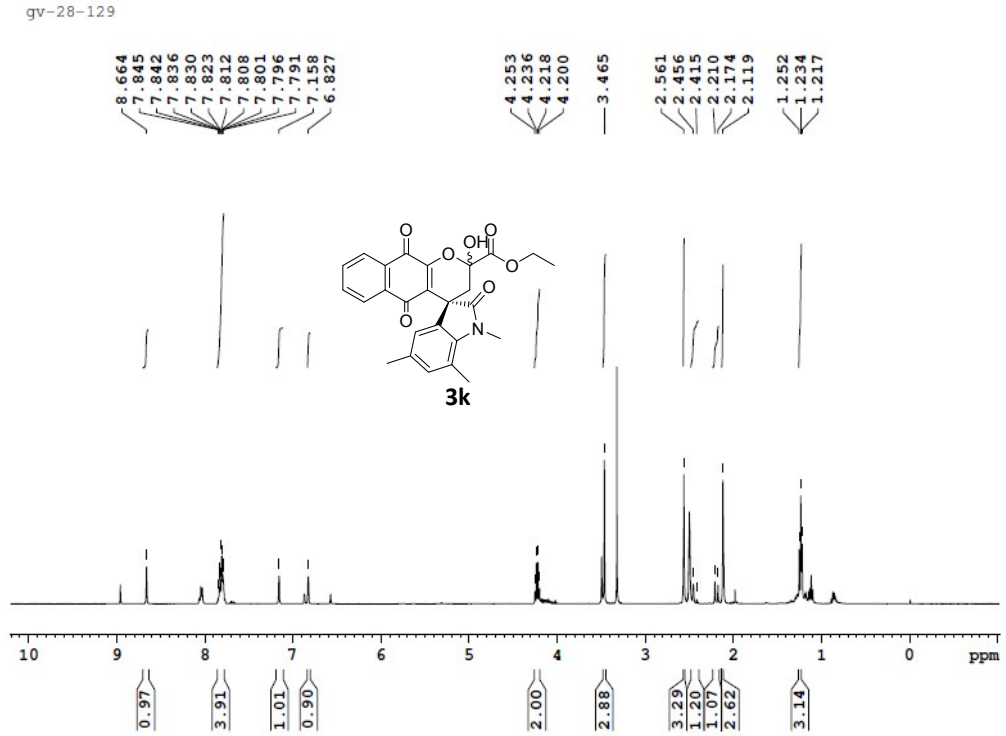


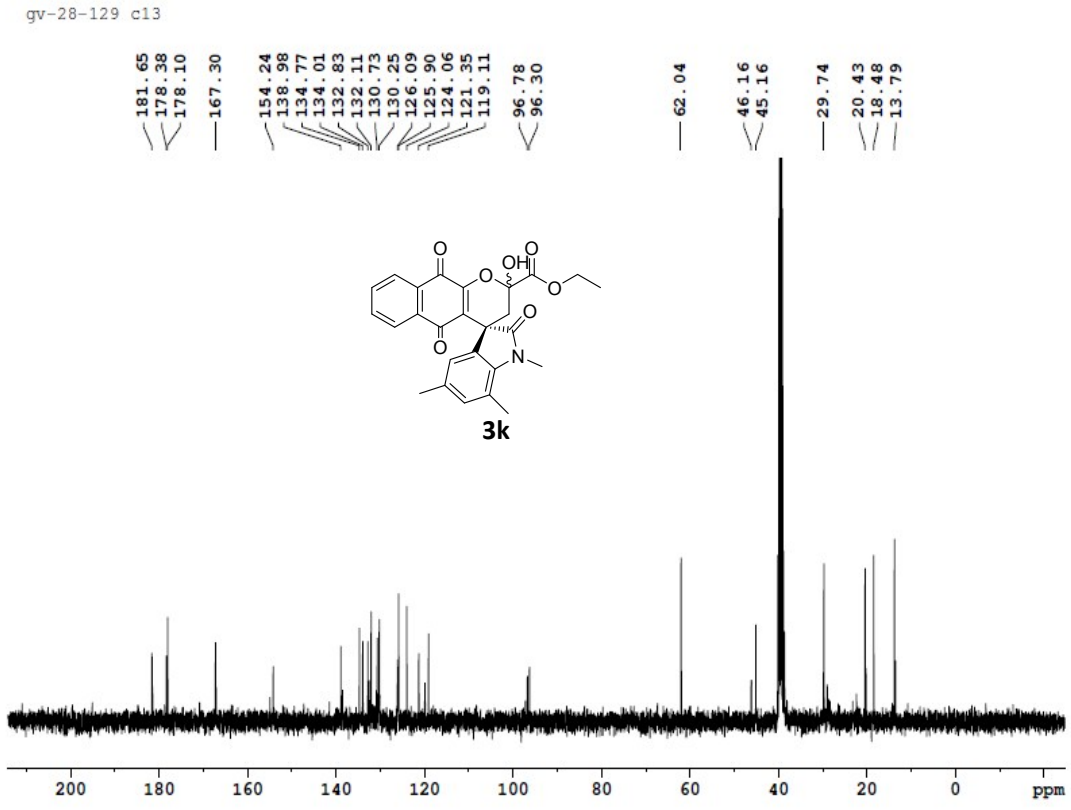
^{1}H and ^{13}C NMR of compound 3j



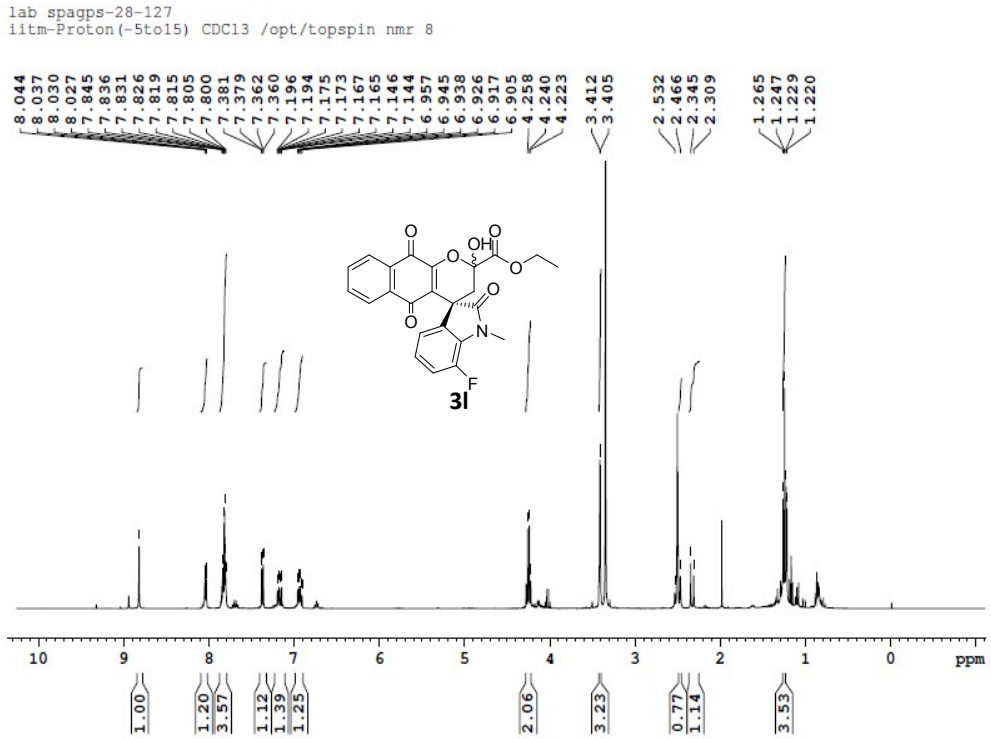


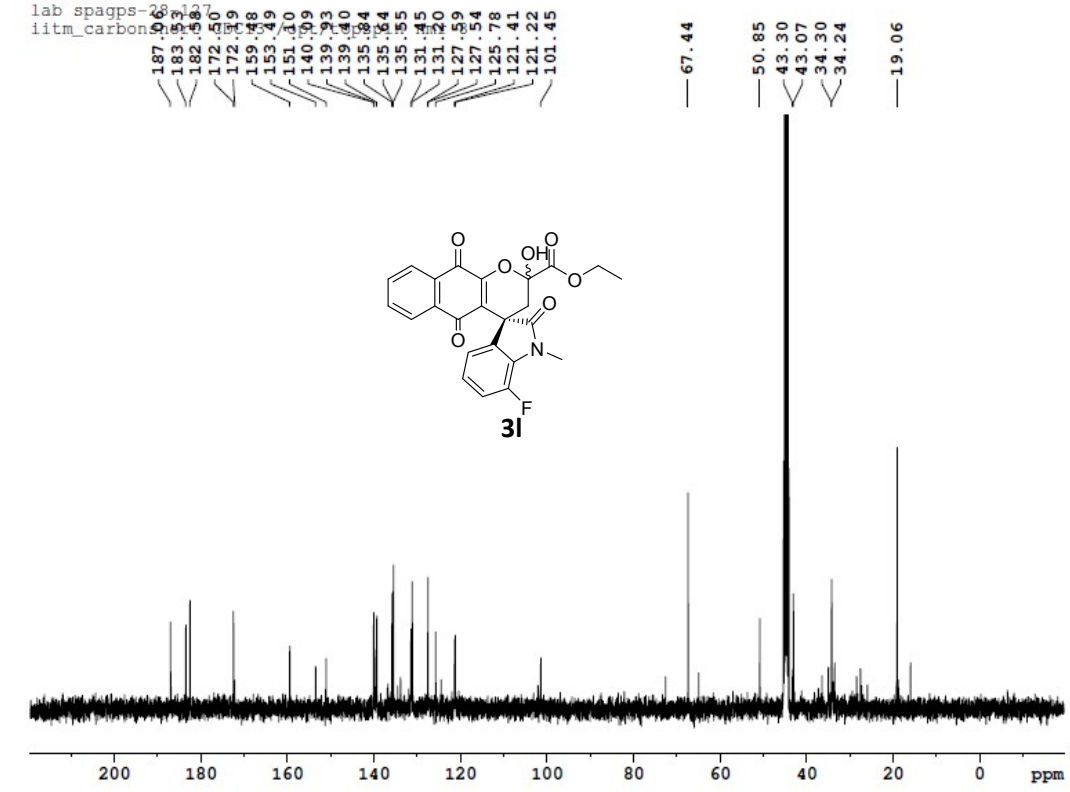
^{1}H and ^{13}C NMR of compound 3k



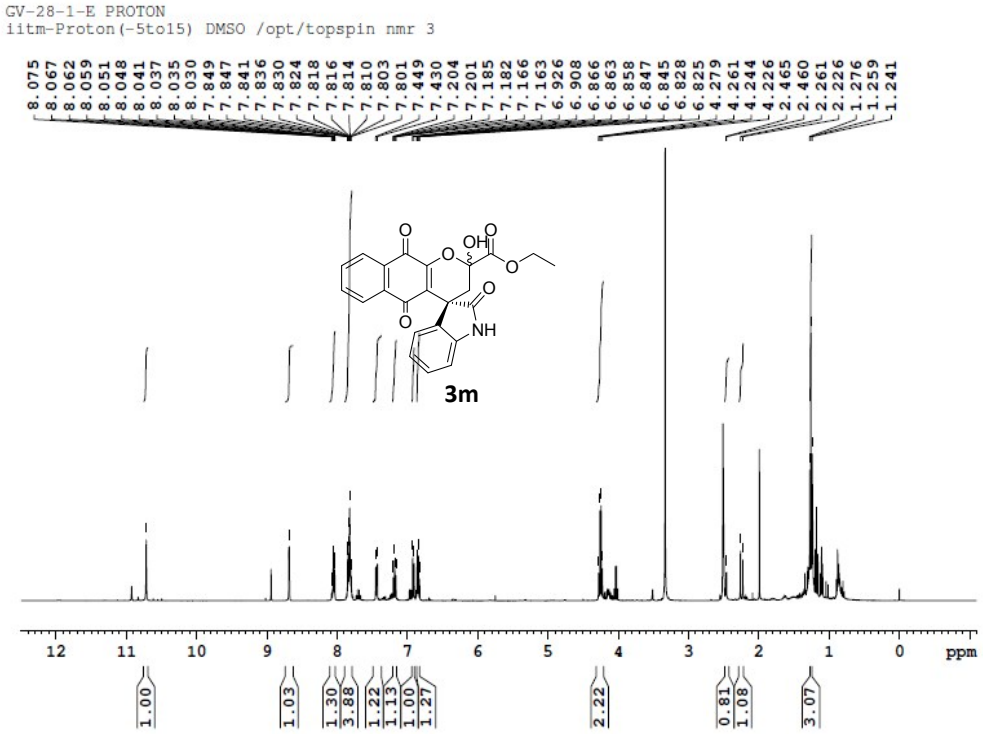


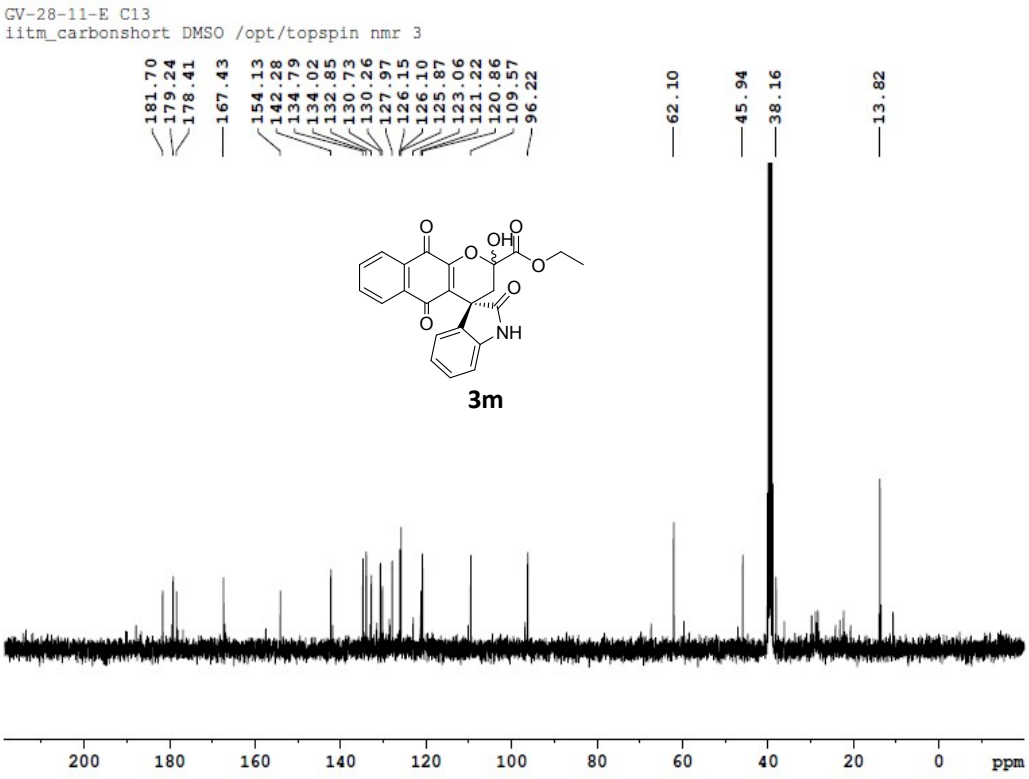
^{1}H and ^{13}C NMR of compound 3l



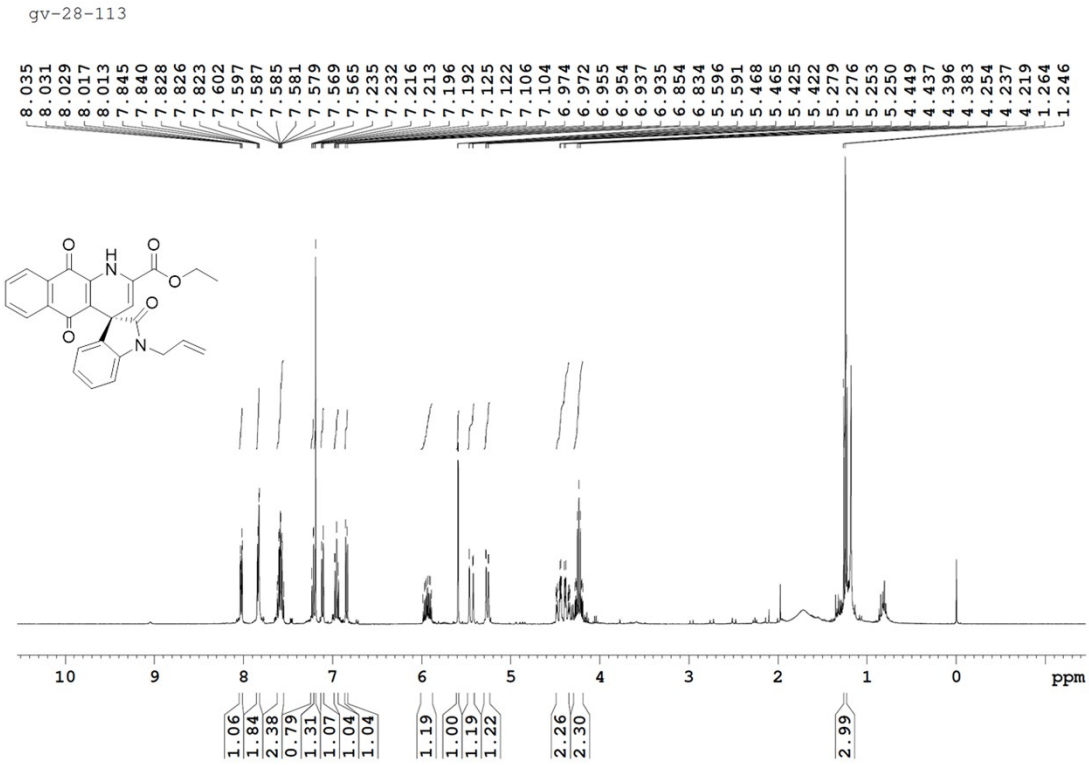


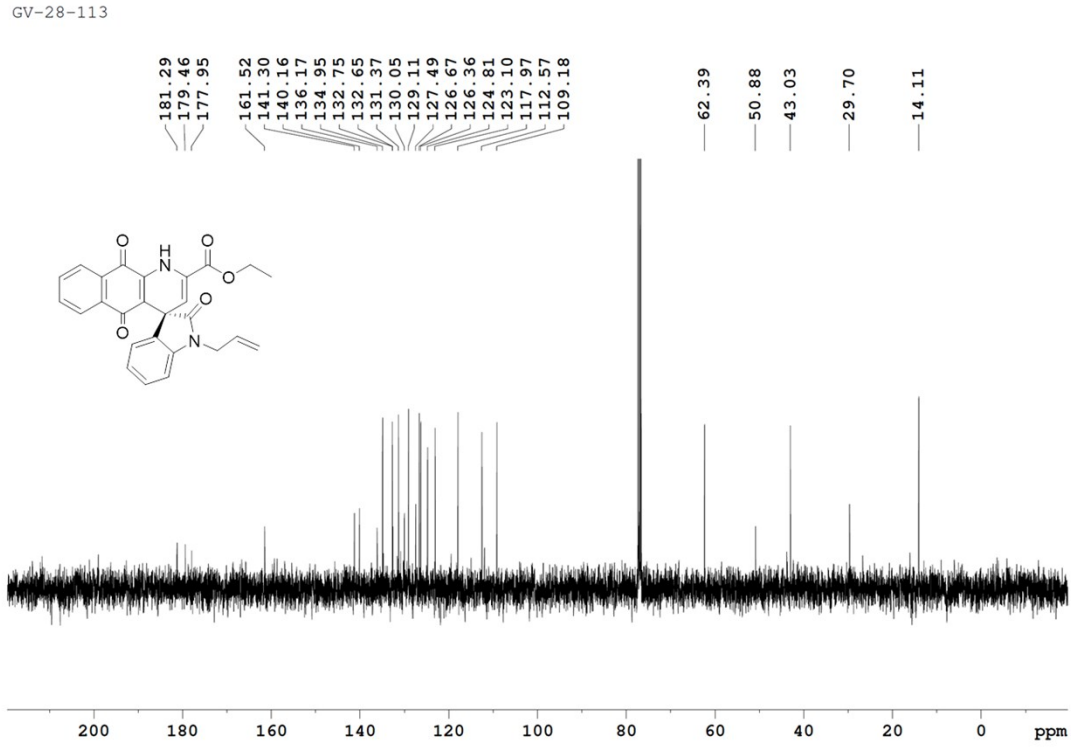
^{1}H and ^{13}C NMR of compound 3m



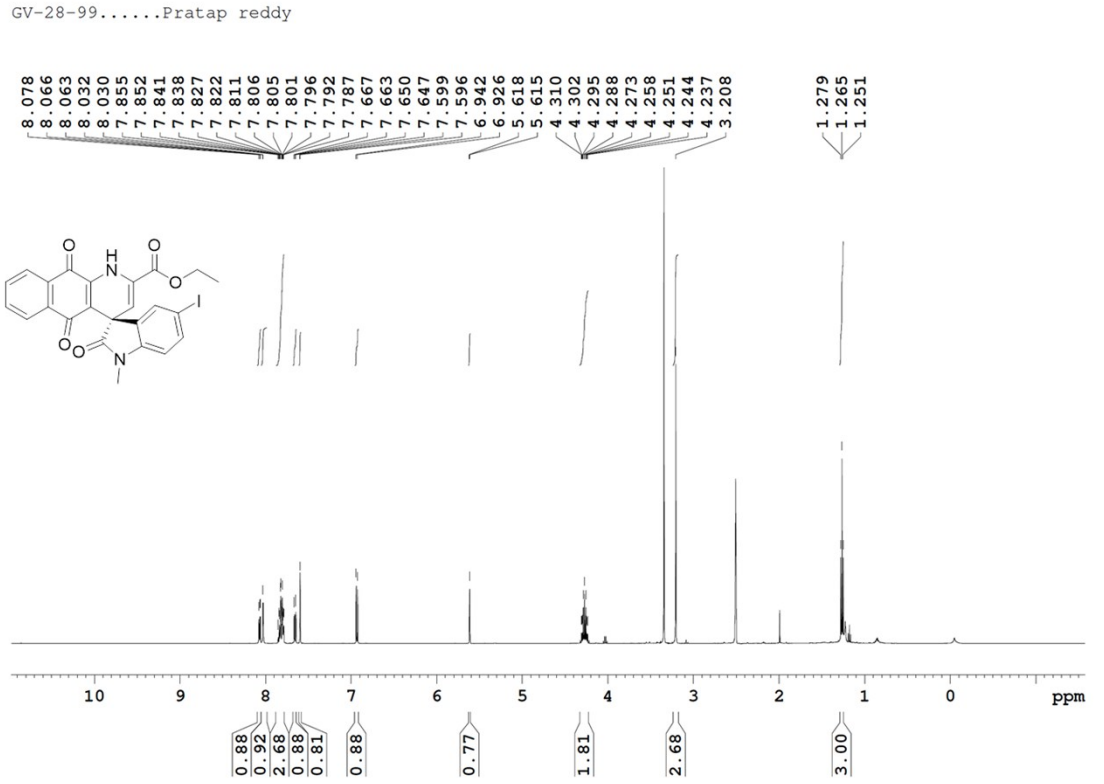


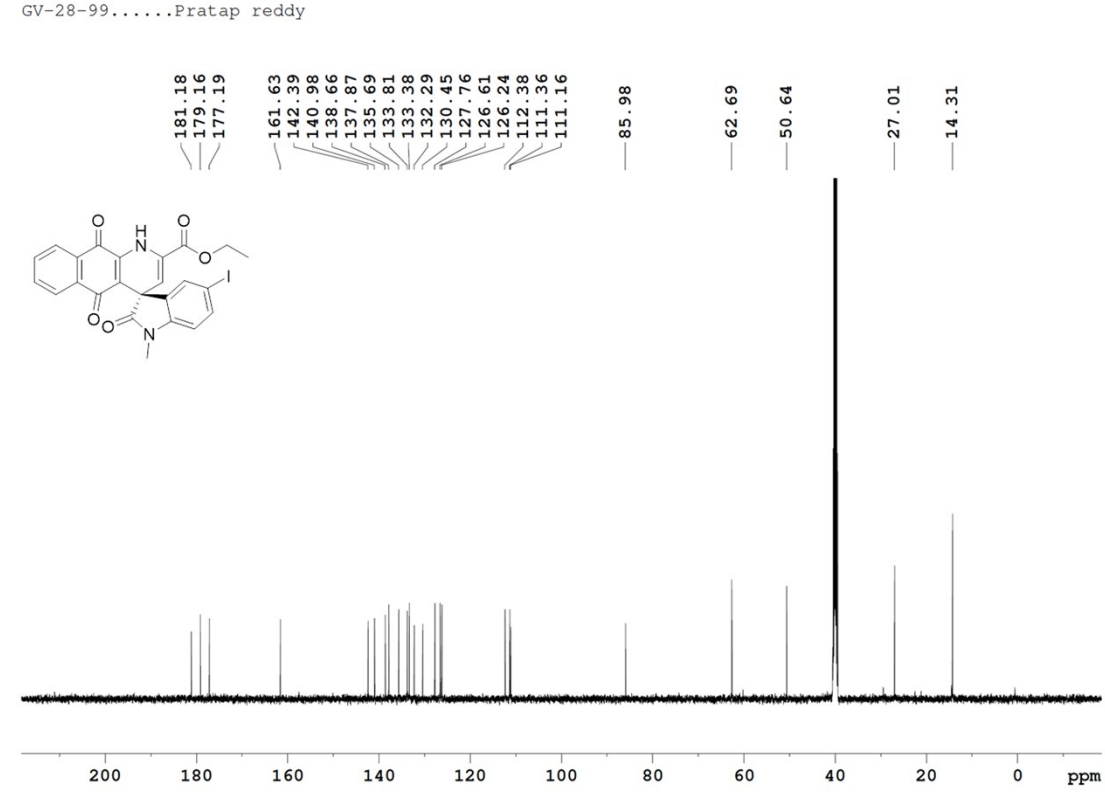
^{1}H and ^{13}C NMR of compound 5a



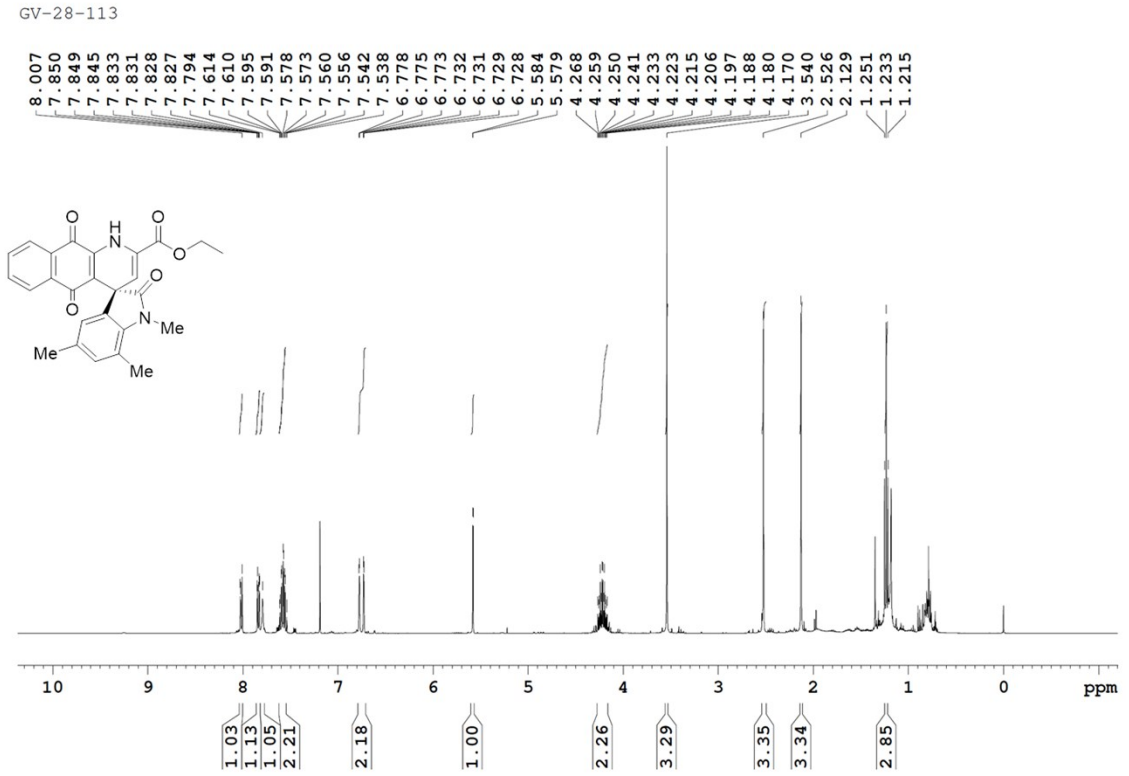


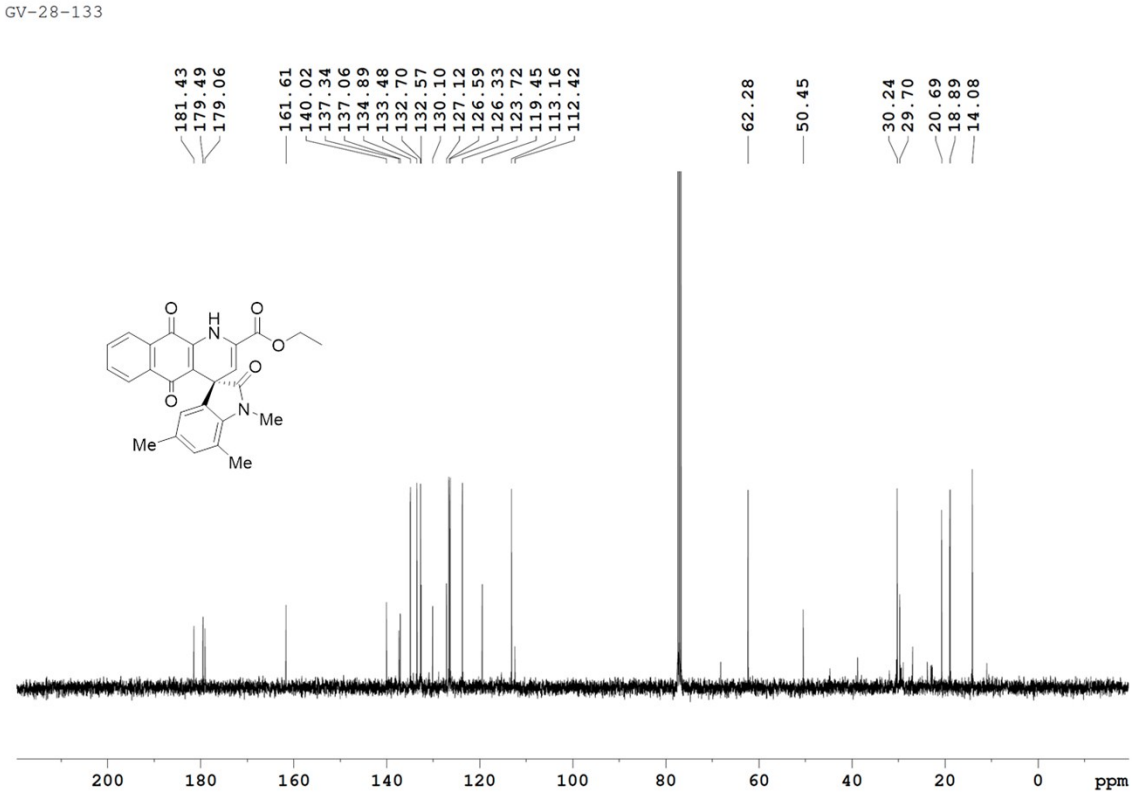
^{1}H and ^{13}C NMR of Compound 5b



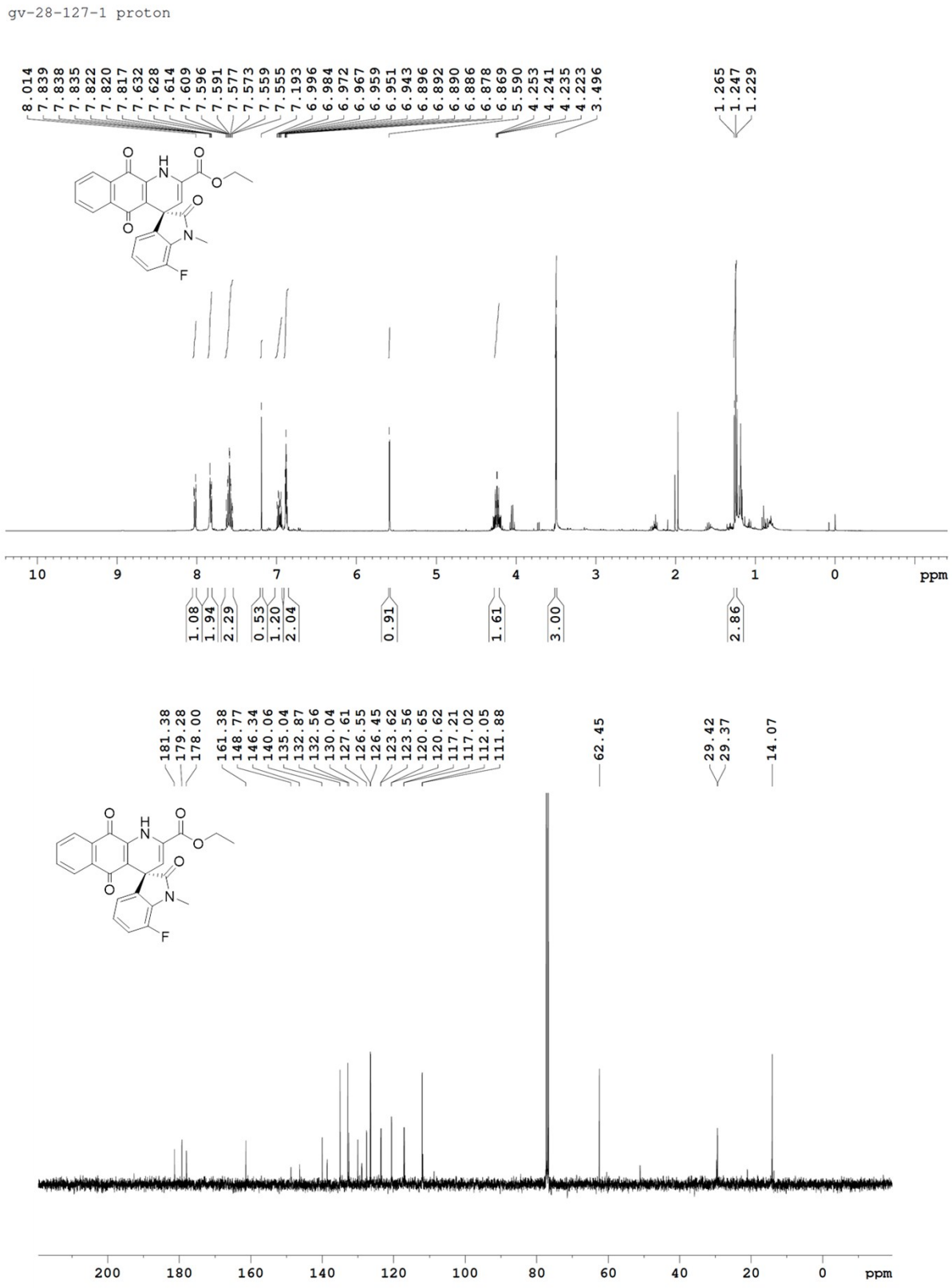


^{1}H and ^{13}C NMR of compound 5c

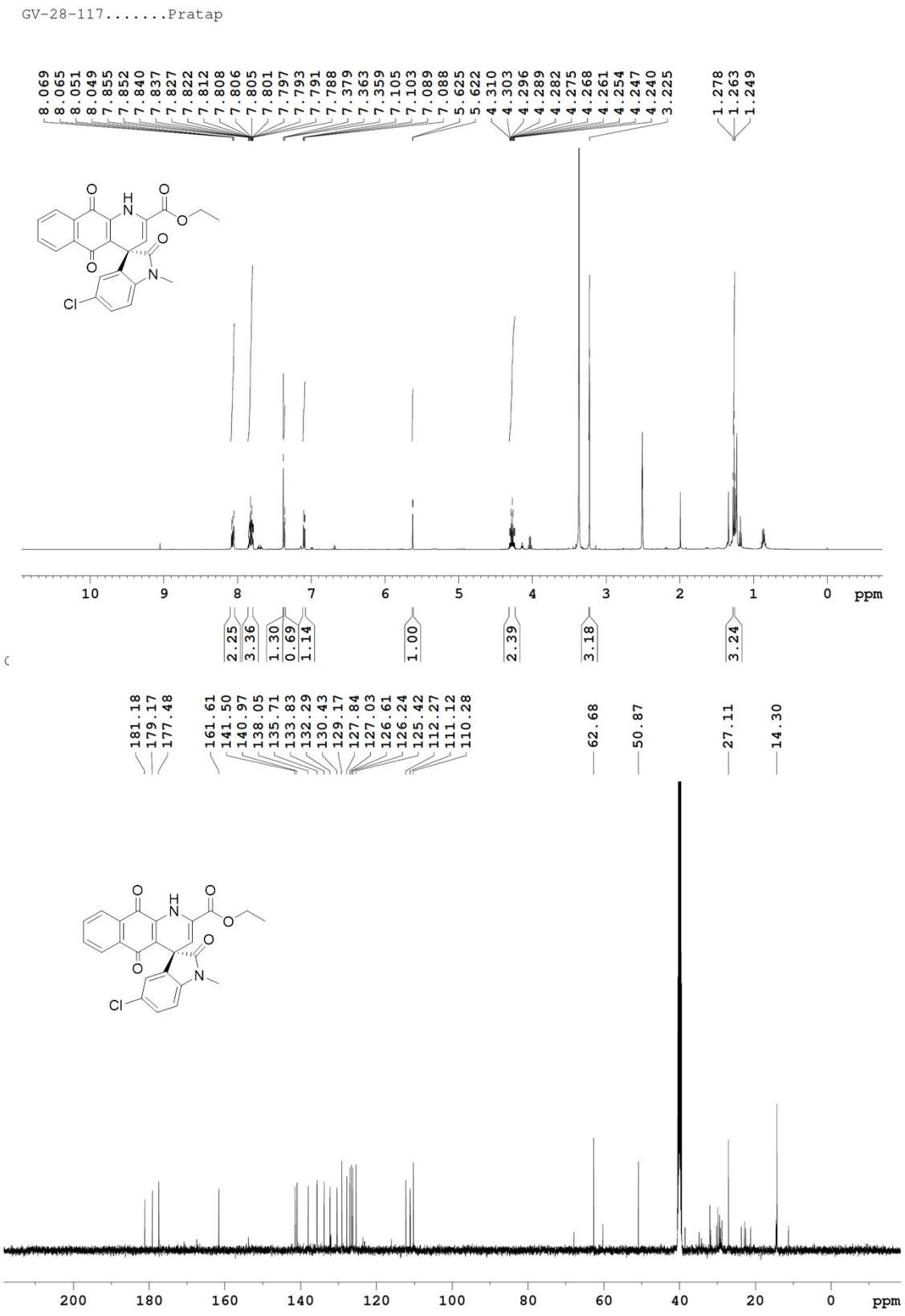




^{1}H and ^{13}C NMR of compound 5d



^{1}H and ^{13}C NMR of compound 5e



3. HPLC profile for catalyst screening

HPLC profile for racemic compound 3a

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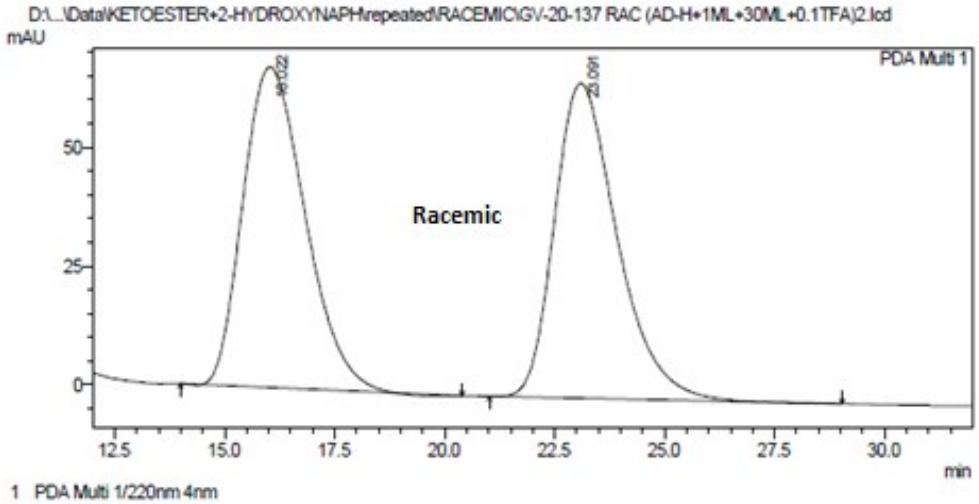


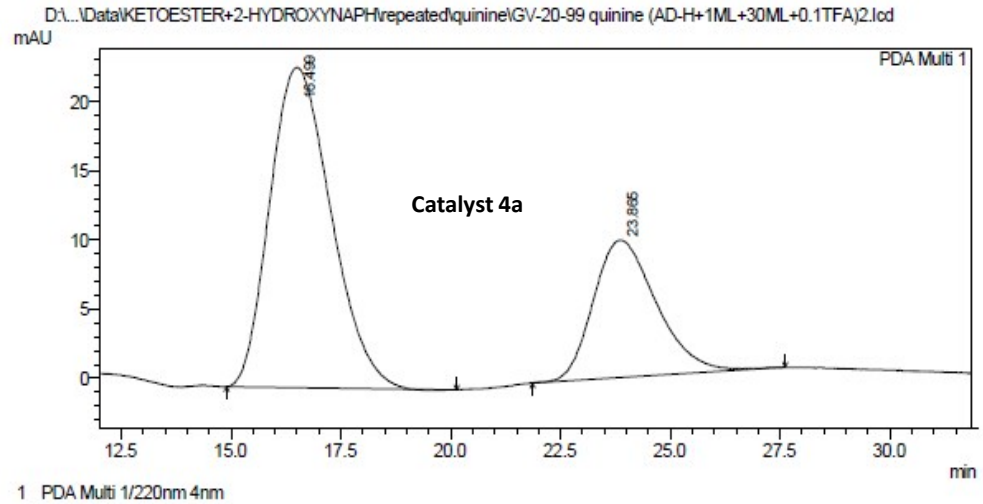
PeakTable

PDA Ch1 220nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	16.022	6620327	67443	50.202	50.451
2	23.091	6567057	66238	49.798	49.549
Total		13187384	133682	100.000	100.000

HPLC profile for table 1, entry 1

<Chromatogram>



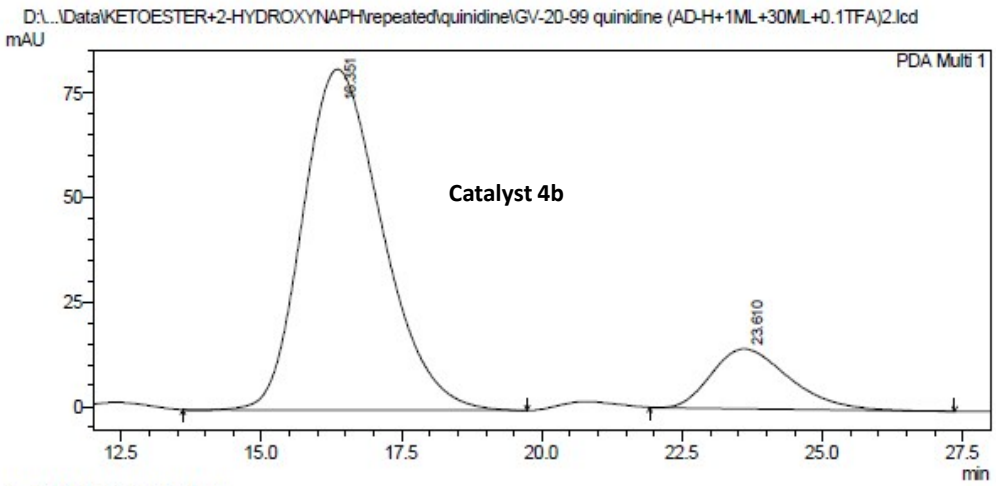
PeakTable

PDA Ch1 220nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	16.499	2242164	23134	69.366	69.969
2	23.865	990196	9929	30.634	30.031
Total		3232360	33063	100.000	100.000

HPLC profile for table 1, entry 2

<Chromatogram>



1 PDA Multi 1/254nm 4nm

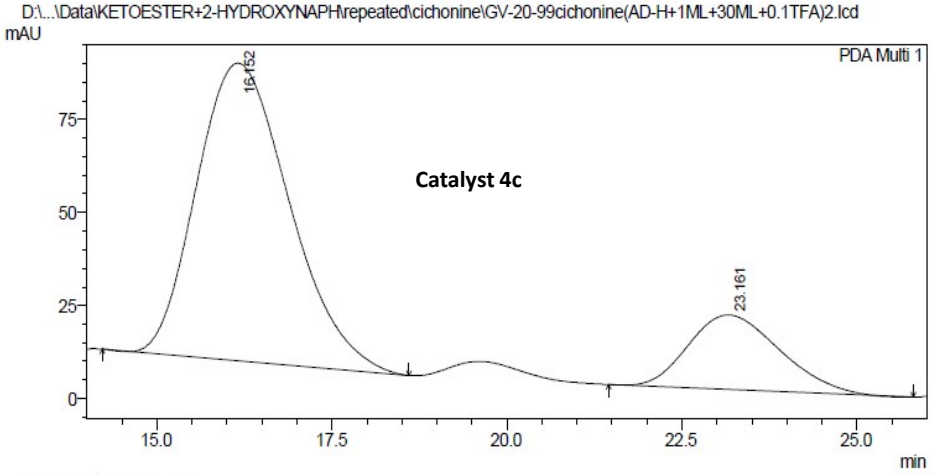
PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	16.351	8033811	81560	85.461	85.128
2	23.610	1366721	14249	14.539	14.872
Total		9400532	95809	100.000	100.000

HPLC profile for table 1, entry 3

<Chromatogram>



1 PDA Multi 1/220nm 4nm

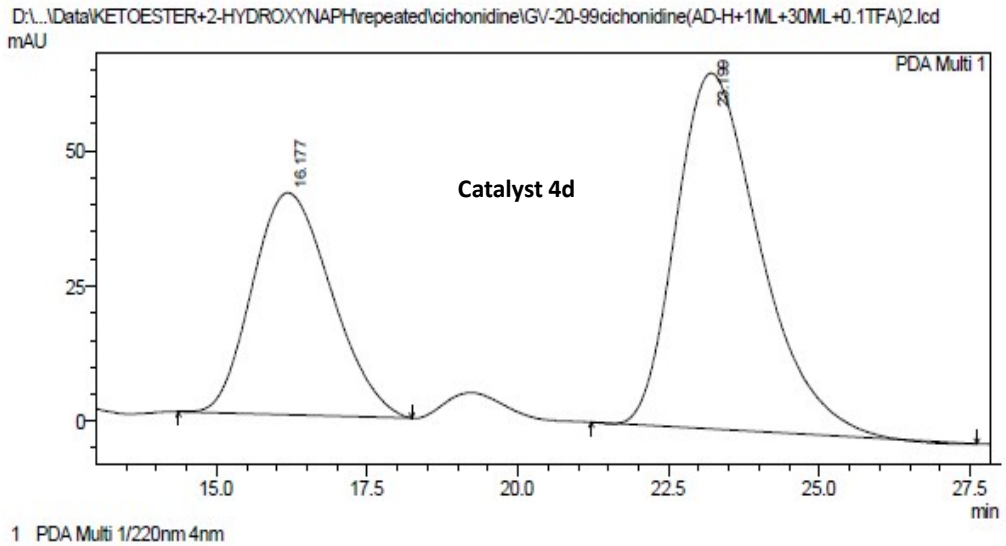
PeakTable

PDA Ch1 220nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	16.152	7381994	80017	80.348	80.011
2	23.161	1805526	19991	19.652	19.989
Total		9187520	100008	100.000	100.000

HPLC profile for table 1, entry 4

<Chromatogram>



1 PDA Multi 1/220nm 4nm

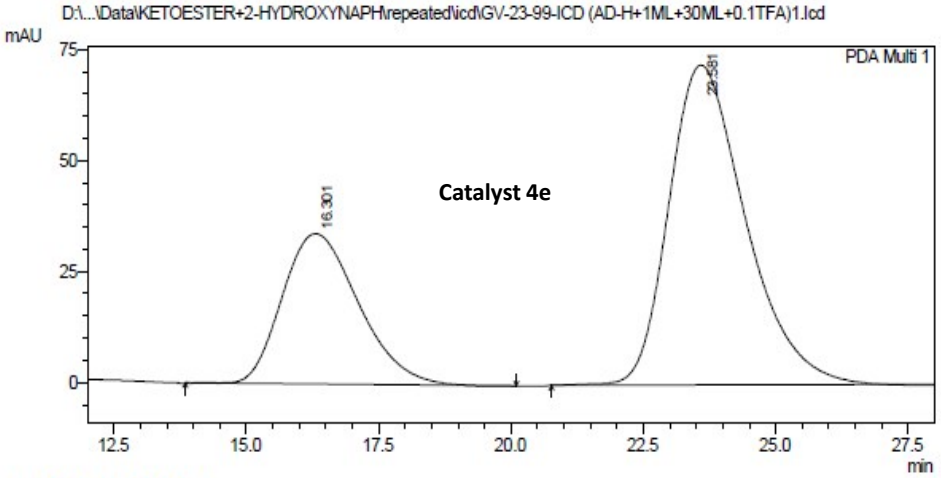
PeakTable

PDA Ch1 220nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	16.177	3745378	41022	36.917	38.388
2	23.199	6399887	65840	63.083	61.612
Total		10145265	106862	100.000	100.000

HPLC profile for table 1, entry 5

<Chromatogram>



1 PDA Multi 1/220nm 4nm

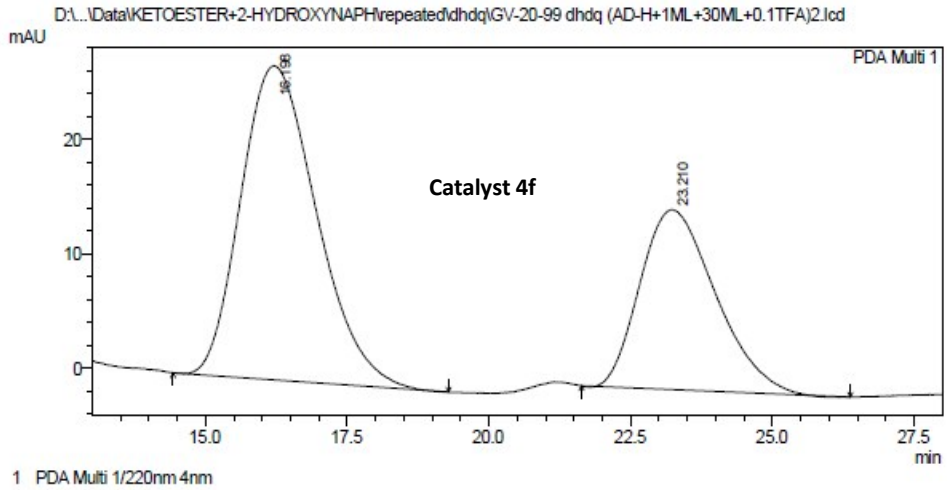
PeakTable

PDA Ch1 220nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	16.301	3397507	33862	31.995	31.978
2	23.581	7221231	72029	68.005	68.022
Total		10618739	105891	100.000	100.000

HPLC profile for table 1, entry 6

<Chromatogram>



1 PDA Multi 1/220nm 4nm

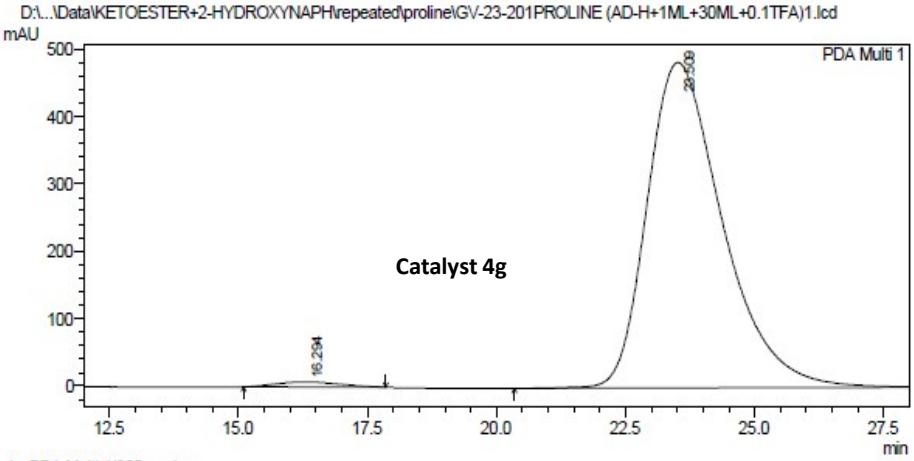
PeakTable

PDA Ch1 220nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	16.198	2550071	27460	63.653	63.604
2	23.210	1456131	15713	36.347	36.396
Total		4006202	43173	100.000	100.000

HPLC profile for table 1, entry 7

<Chromatogram>



1 PDA Multi 1/220nm 4nm

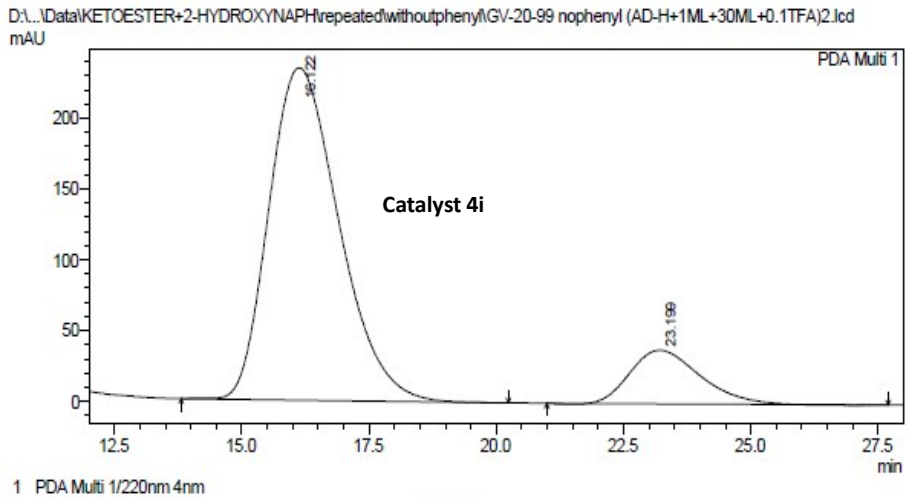
PeakTable

PDA Ch1 220nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	16.294	648338	7513	1.301	1.531
2	23.509	49193147	483143	98.699	98.469
Total		49841485	490655	100.000	100.000

HPLC profile for table 1, entry 9

<Chromatogram>



1 PDA Multi 1/220nm 4nm

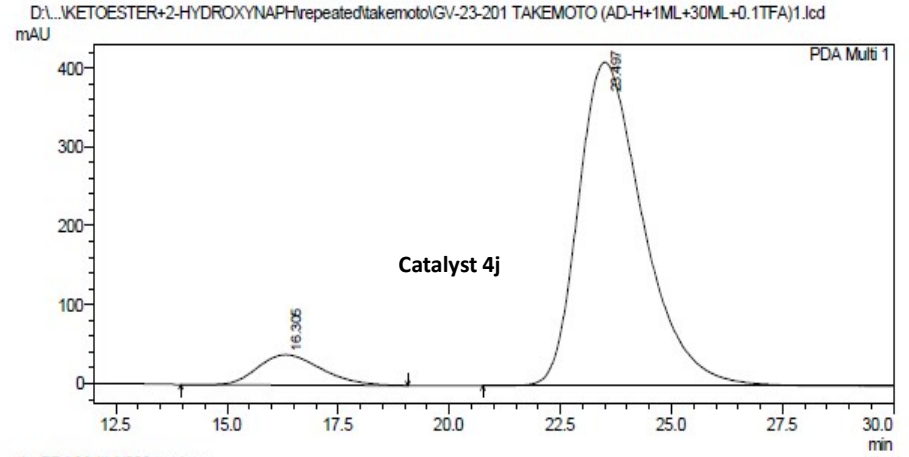
PeakTable

PDA Ch1 220nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	16.122	22467881	234644	86.101	86.087
2	23.199	3626947	37921	13.899	13.913
Total		26094827	272564	100.000	100.000

HPLC profile for table 1, entry 10

<Chromatogram>



1 PDA Multi 1/220nm 4nm

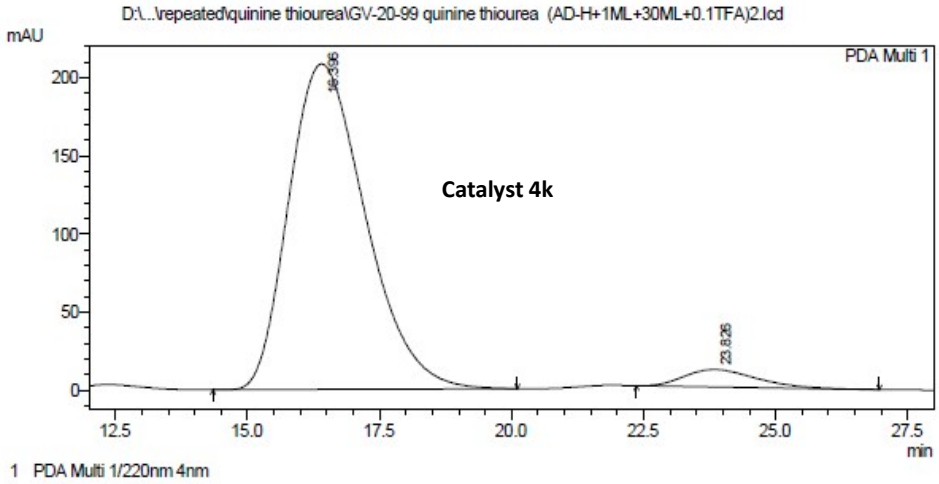
PeakTable

PDA Ch1 220nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	16.305	3776143	38094	8.352	8.503
2	23.497	41433947	409921	91.648	91.497
Total		45210090	448014	100.000	100.000

HPLC profile for table 1, entry 11

<Chromatogram>



1 PDA Multi 1/220nm 4nm

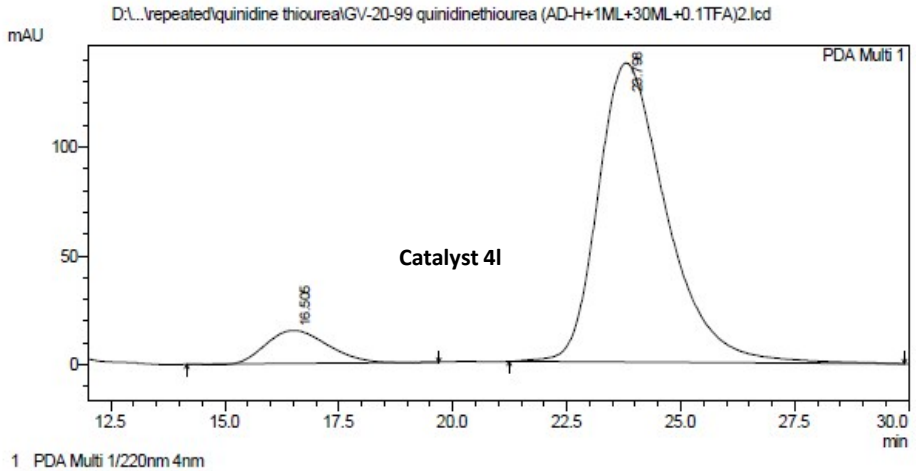
PeakTable

PDA Ch1 220nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	16.396	21047206	208265	95.227	94.919
2	23.826	1054908	11149	4.773	5.081
Total		22102114	219414	100.000	100.000

HPLC profile for table 1, entry 12

<Chromatogram>



1 PDA Multi 1/220nm 4nm

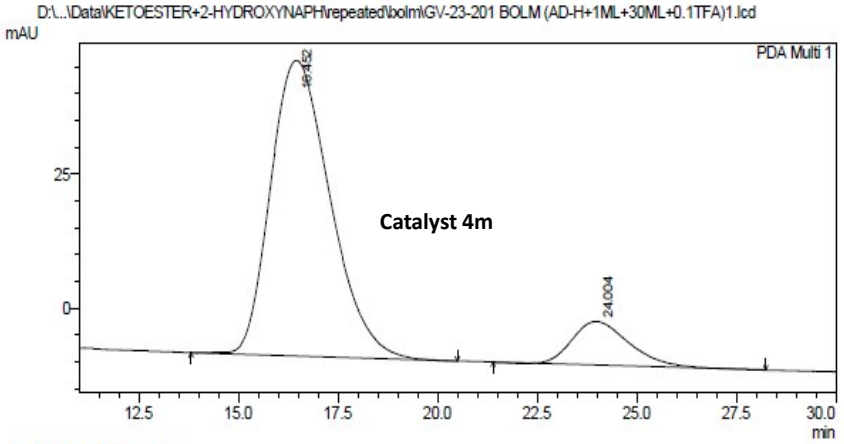
PeakTable

PDA Ch1 220nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	16.505	1403337	15178	8.890	9.950
2	23.798	14381748	137359	91.110	90.050
Total		15785085	152537	100.000	100.000

HPLC profile for table 1, entry 13

<Chromatogram>



1 PDA Multi 1/220nm 4nm

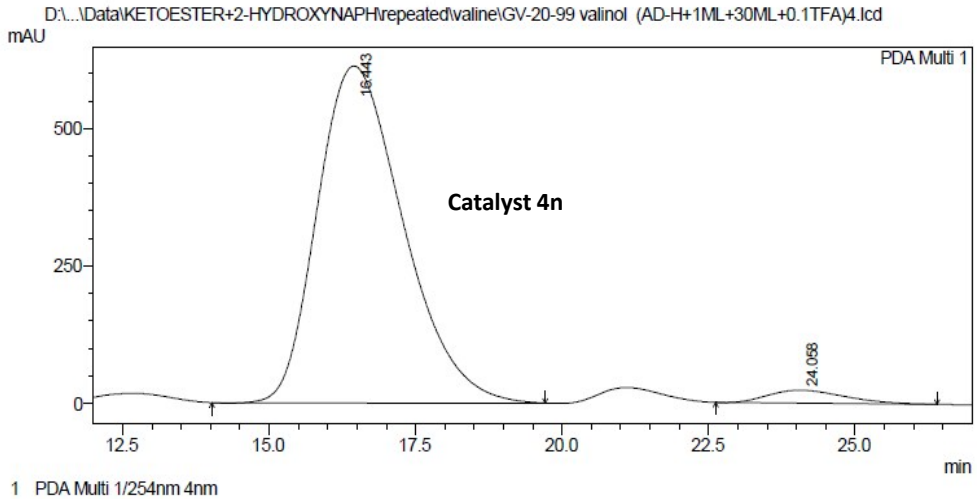
PeakTable

PDA Ch1 220nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	16.452	5749177	55186	87.713	87.159
2	24.004	805370	8131	12.287	12.841
Total		6554548	63317	100.000	100.000

HPLC profile for table 1, entry 14

<Chromatogram>



1 PDA Multi 1/254nm 4nm

PeakTable

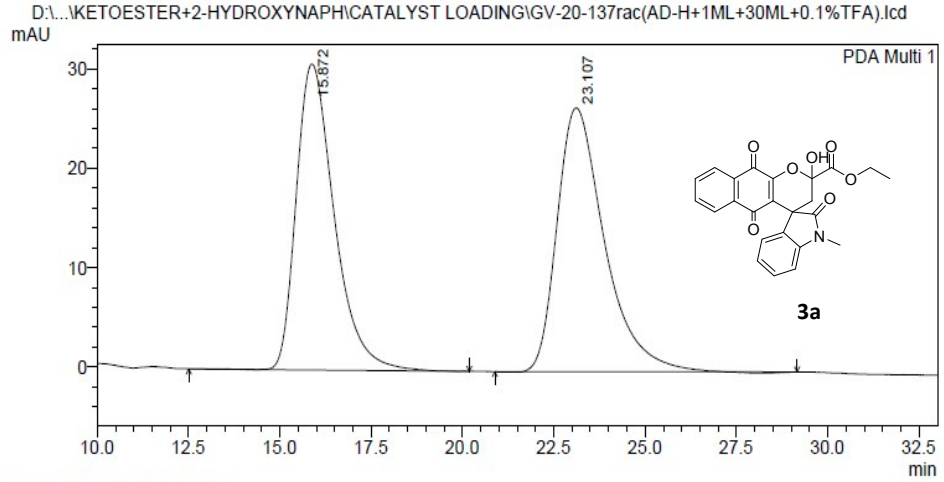
PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	16.443	62636435	613728	96.656	96.271
2	24.058	2166780	23771	3.344	3.729
Total		64803216	637499	100.000	100.000

4. HPLC profile for the substrates

HPLC profile for table 3, entry 1

<Chromatogram>



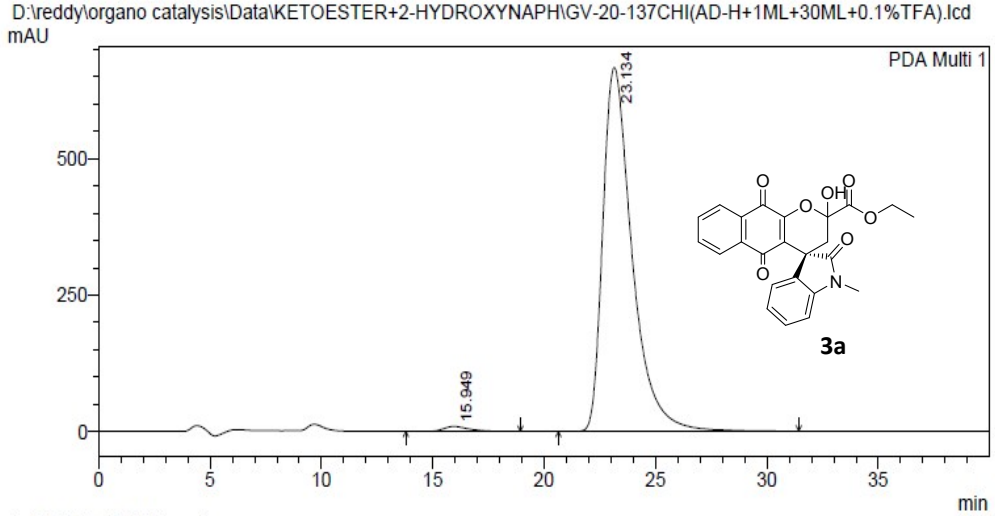
1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	15.872	2231116	30794	48.245	53.694
2	23.107	2393407	26557	51.755	46.306
Total		4624524	57351	100.000	100.000

<Chromatogram>



1 PDA Multi 1/254nm 4nm

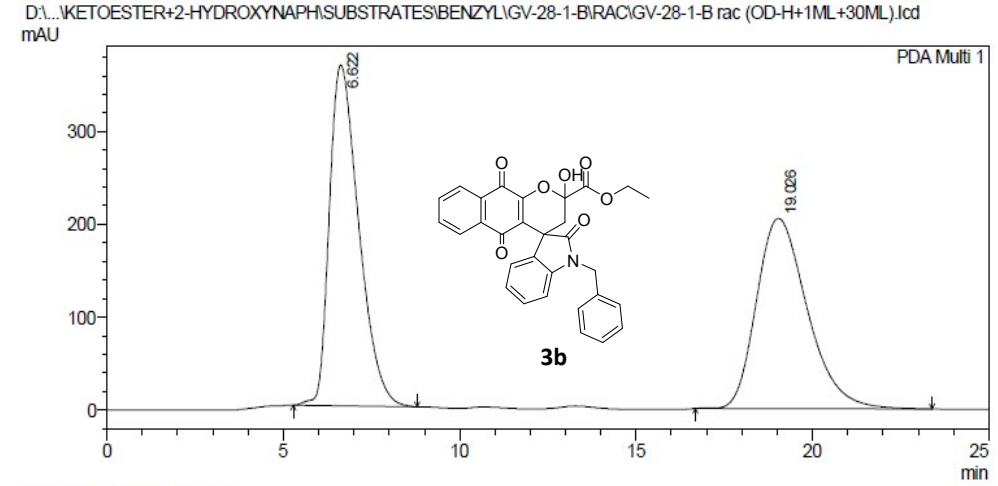
PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	15.949	673358	8872	1.092	1.312
2	23.134	60991857	667158	98.908	98.688
Total		61665214	676030	100.000	100.000

HPLC profile for table 3, entry 2

<Chromatogram>



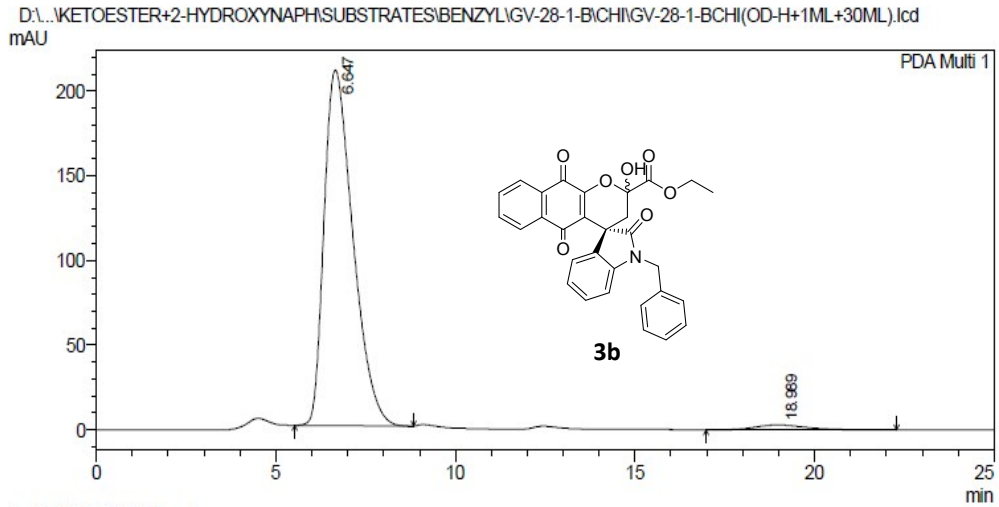
1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.622	21368073	367318	50.913	64.167
2	19.026	20601819	205123	49.087	35.833
Total		41969893	572441	100.000	100.000

<Chromatogram>



1 PDA Multi 1/254nm 4nm

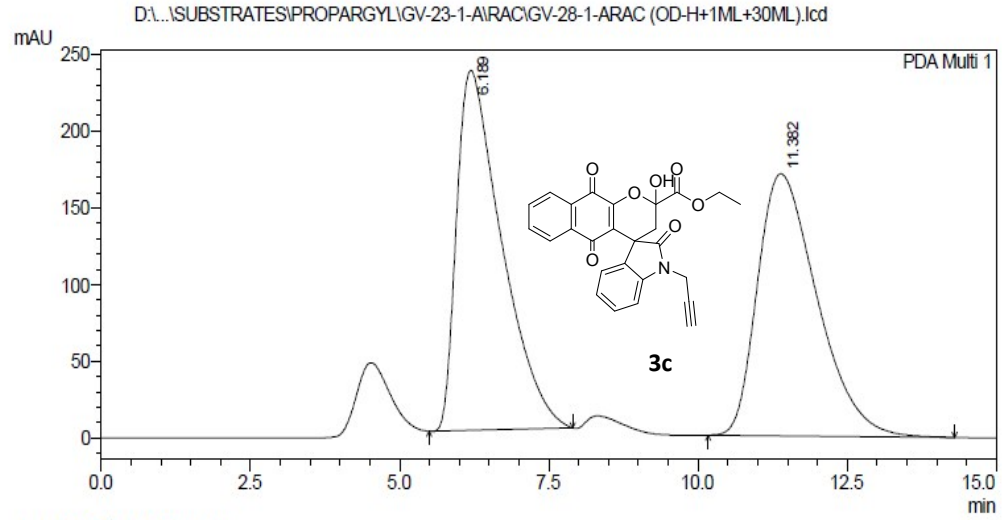
PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.647	11773278	210076	97.611	98.607
2	18.989	288111	2968	2.389	1.393
Total		12061389	213043	100.000	100.000

HPLC profile for table 3, entry 3

<Chromatogram>



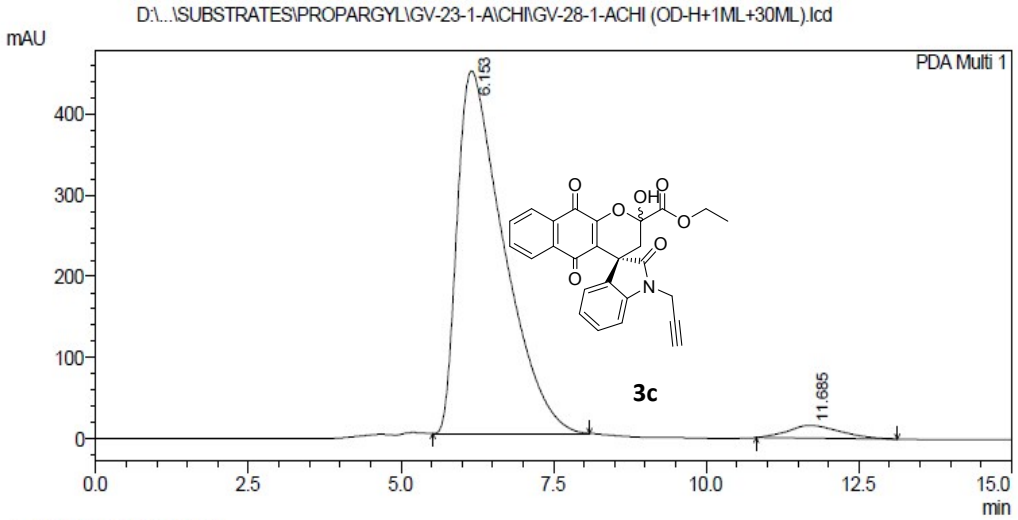
1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.189	12292571	234317	50.896	57.881
2	11.382	11859664	170506	49.104	42.119
Total		24152235	404822	100.000	100.000

<Chromatogram>



1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.153	23682127	447319	96.179	96.606
2	11.685	940951	15716	3.821	3.394
Total		24623078	463035	100.000	100.000

HPLC profile for table 3, entry 4

<Chromatogram>

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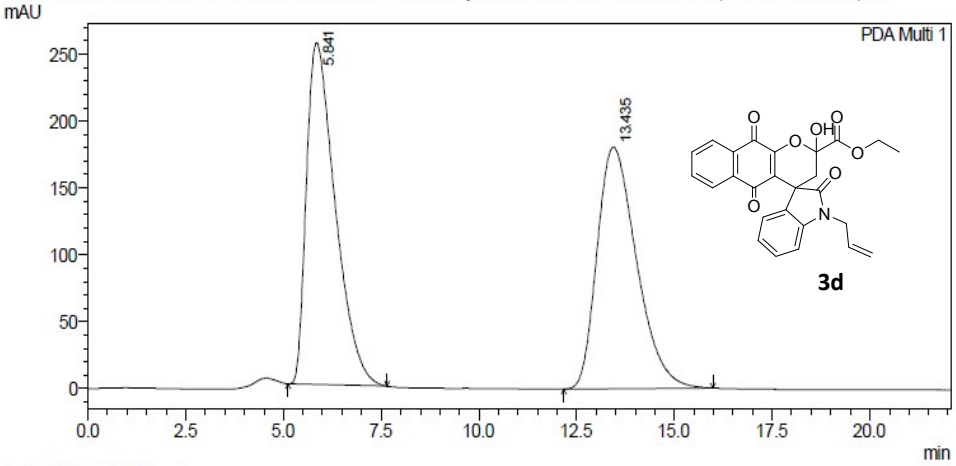

1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.841	13107367	255671	50.771	58.599
2	13.435	12709246	180637	49.229	41.401
Total		25816613	436307	100.000	100.000

<Chromatogram>

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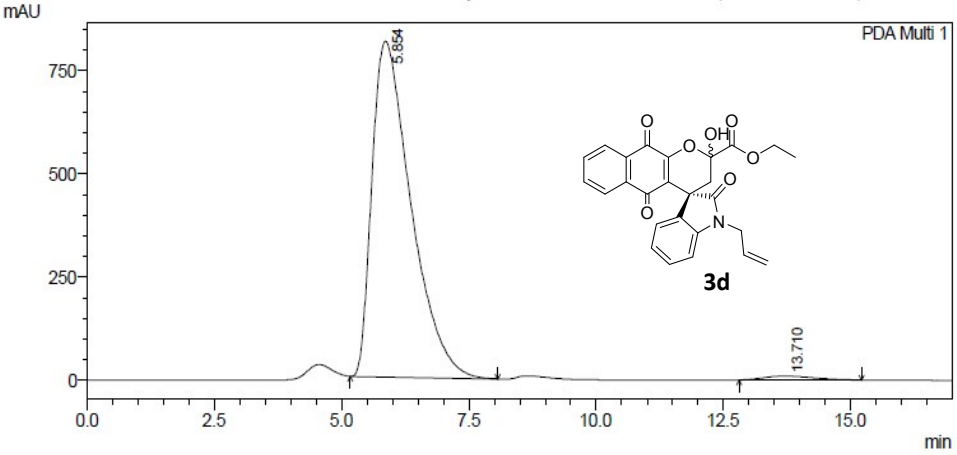


1 PDA Multi 1/254nm 4nm

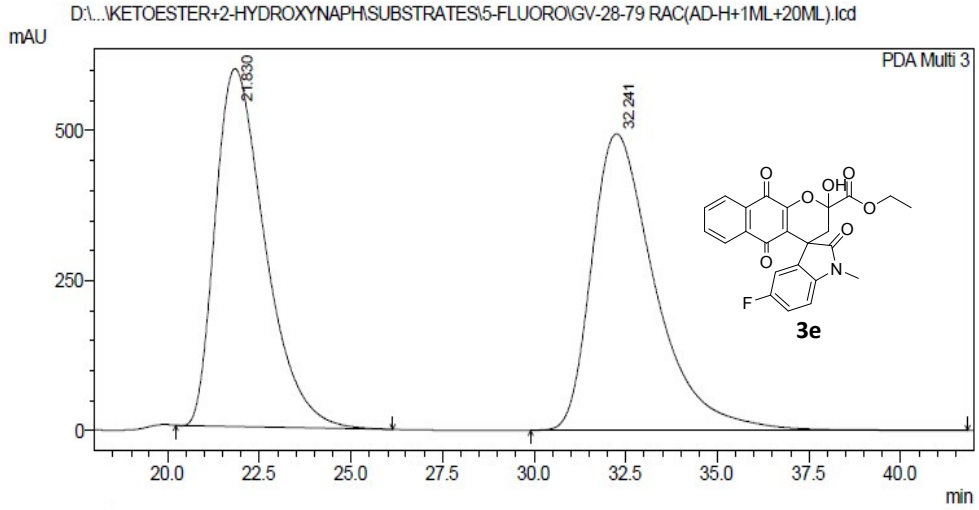
PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.854	43317617	812407	98.494	98.807
2	13.710	662515	9806	1.506	1.193
Total		43980132	822213	100.000	100.000

HPLC profile for table 3, entry 5

<Chromatogram>



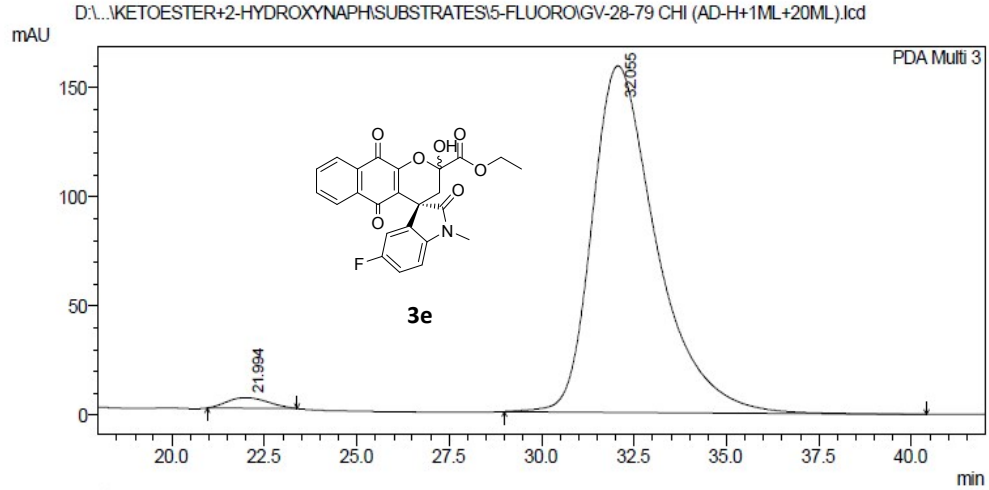
1 PDA Multi 3/254nm 4nm

PeakTable

PDA Ch3 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	21.830	56303012	596272	48.603	54.672
2	32.241	59540687	494367	51.397	45.328
Total		115843699	1090639	100.000	100.000

<Chromatogram>



1 PDA Multi 3/254nm 4nm

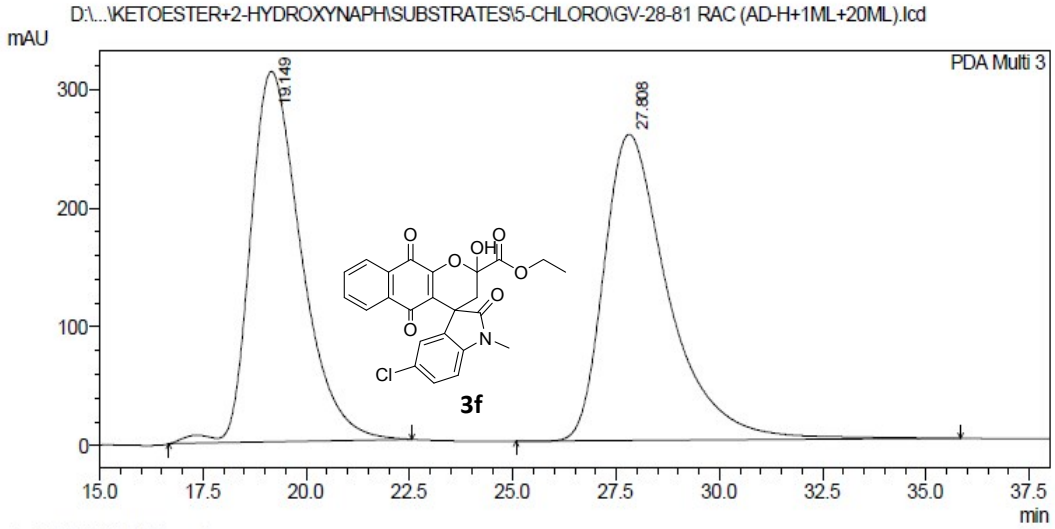
PeakTable

PDA Ch3 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	21.994	373979	4914	1.905	3.000
2	32.055	19259073	158865	98.095	97.000
Total		19633052	163779	100.000	100.000

HPLC profile for table 3, entry 6

<Chromatogram>



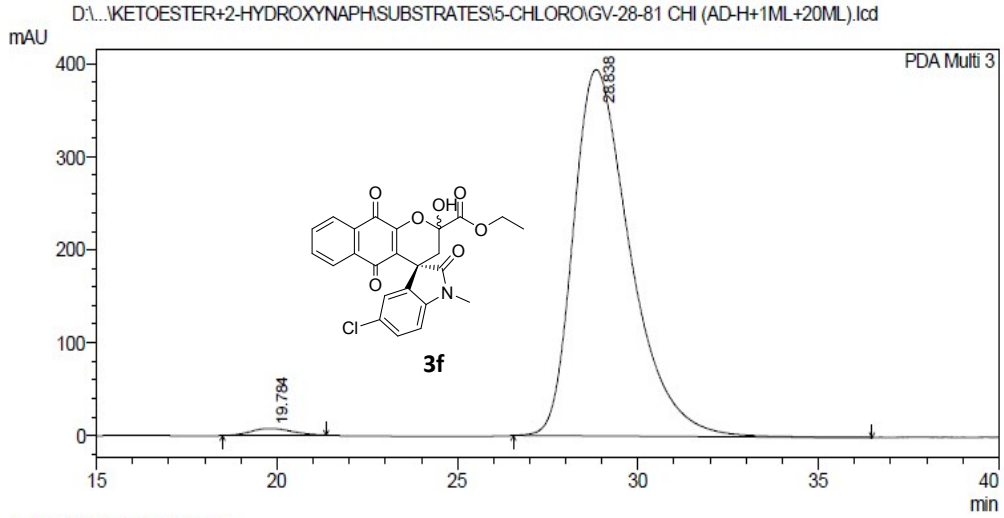
1 PDA Multi 3/254nm 4nm

PeakTable

PDA Ch3 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	19.149	26636057	311582	48.621	54.736
2	27.808	28146634	257666	51.379	45.264
Total		54782691	569247	100.000	100.000

<Chromatogram>



1 PDA Multi 3/254nm 4nm

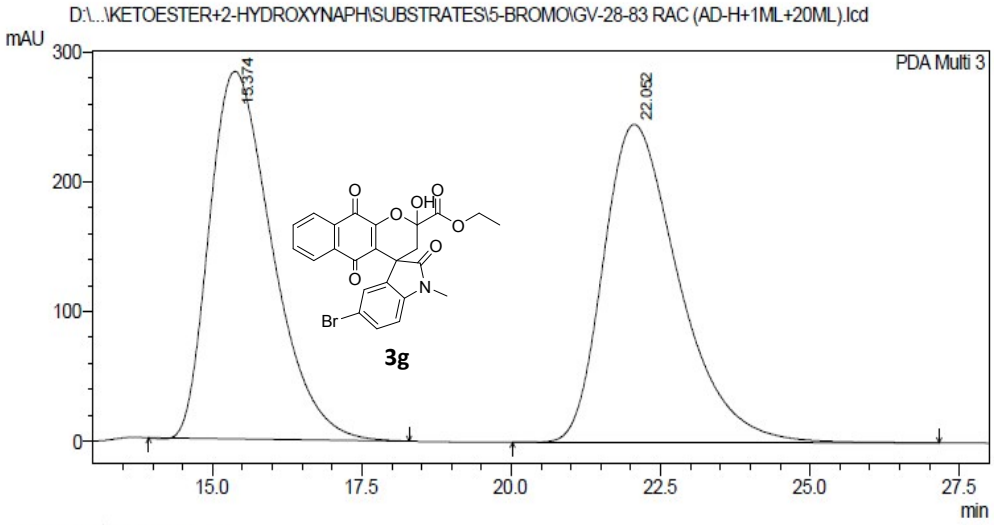
PeakTable

PDA Ch3 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	19.784	600277	7543	1.372	1.879
2	28.838	43139848	393934	98.628	98.121
Total		43740125	401476	100.000	100.000

HPLC profile for table 3, entry 7

<Chromatogram>



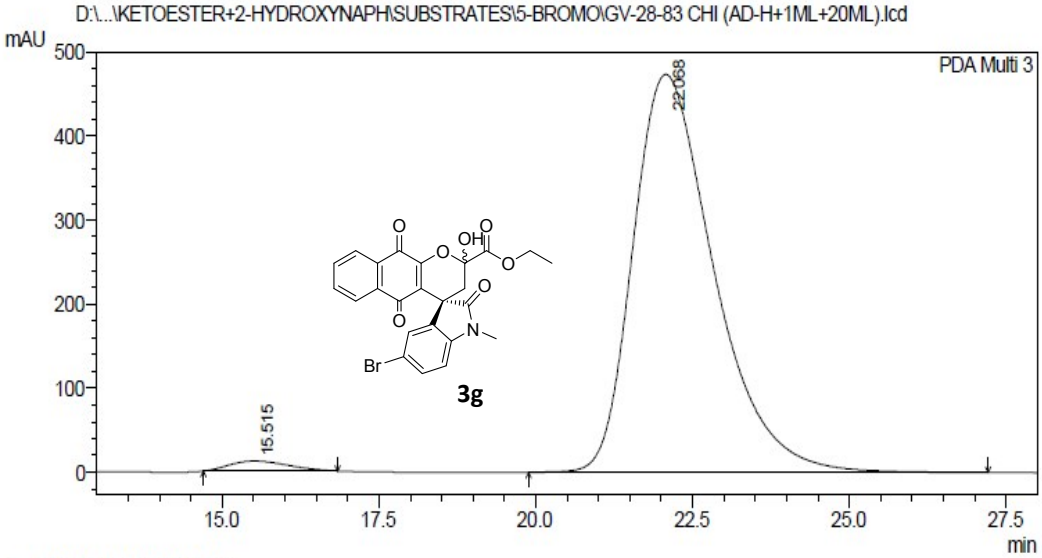
1 PDA Multi 3/254nm 4nm

PeakTable

PDA Ch3 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	15.374	20668300	283346	48.888	53.616
2	22.052	21608327	245124	51.112	46.384
Total		42276627	528470	100.000	100.000

<Chromatogram>



1 PDA Multi 3/254nm 4nm

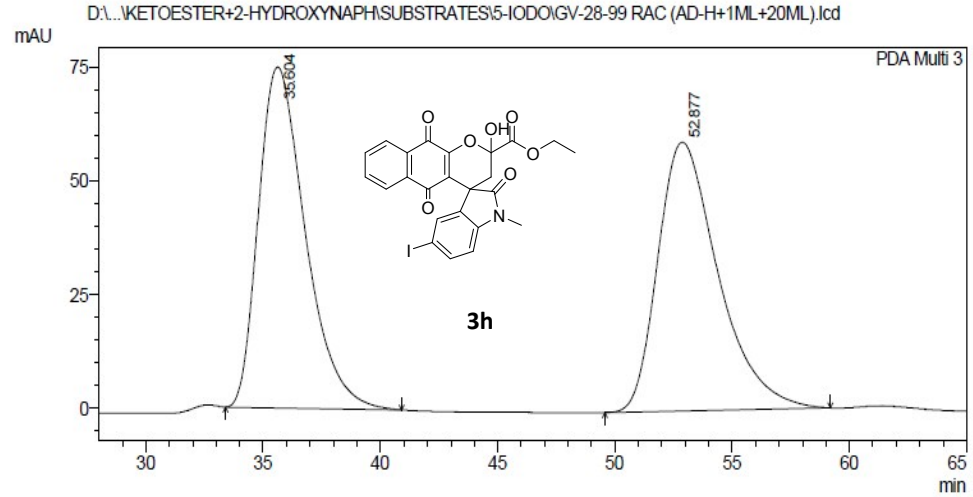
PeakTable

PDA Ch3 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	15.515	778261	11974	1.801	2.468
2	22.068	42433819	473190	98.199	97.532
Total		43212080	485164	100.000	100.000

HPLC profile for table 3, entry 8

<Chromatogram>



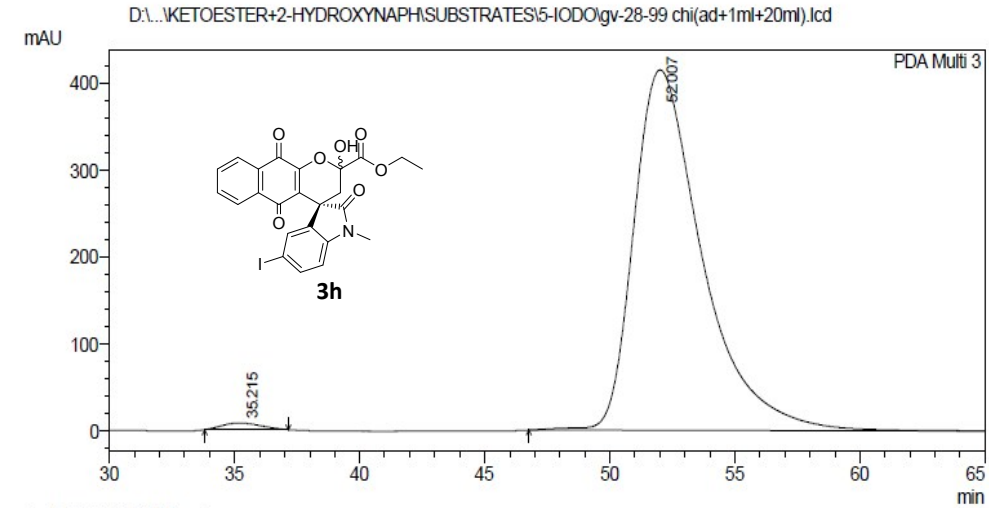
1 PDA Multi 3/254nm 4nm

PeakTable

PDA Ch3 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	35.604	10395700	74850	49.585	55.918
2	52.877	10569521	59007	50.415	44.082
Total		20965221	133857	100.000	100.000

<Chromatogram>



1 PDA Multi 3/254nm 4nm

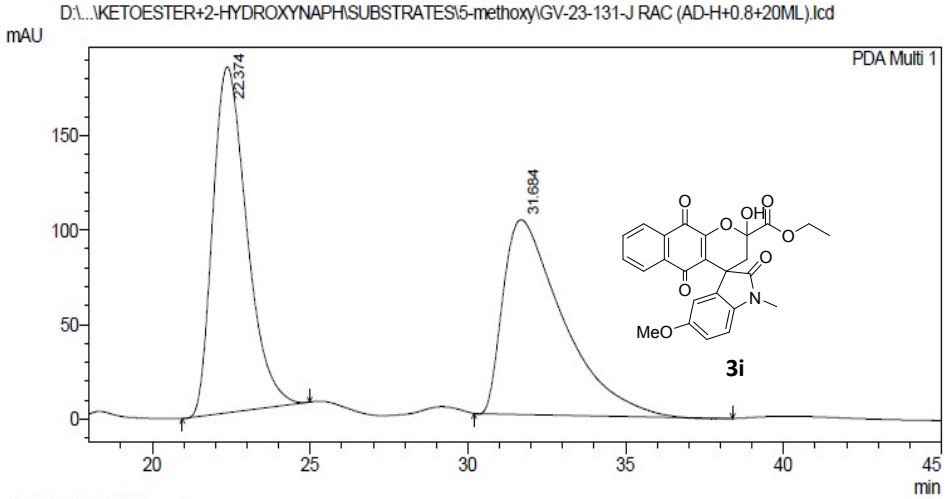
PeakTable

PDA Ch3 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	35.215	830428	7627	1.042	1.807
2	52.007	78834983	414375	98.958	98.193
Total		79665411	422001	100.000	100.000

HPLC profile for table 3, entry 9

<Chromatogram>



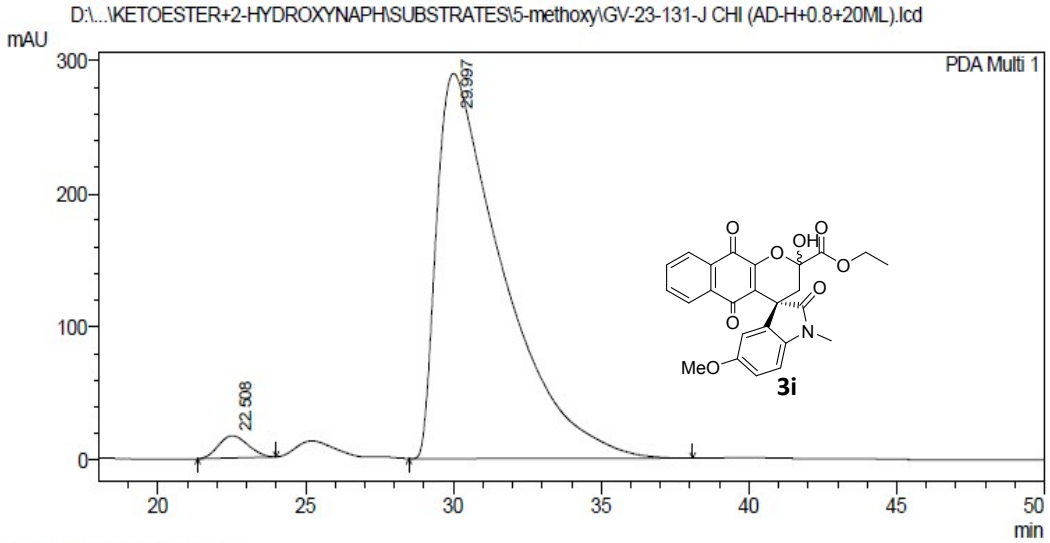
1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	22.374	13716680	182908	50.261	63.992
2	31.684	13574218	102923	49.739	36.008
Total		27290898	285831	100.000	100.000

<Chromatogram>



1 PDA Multi 1/254nm 4nm

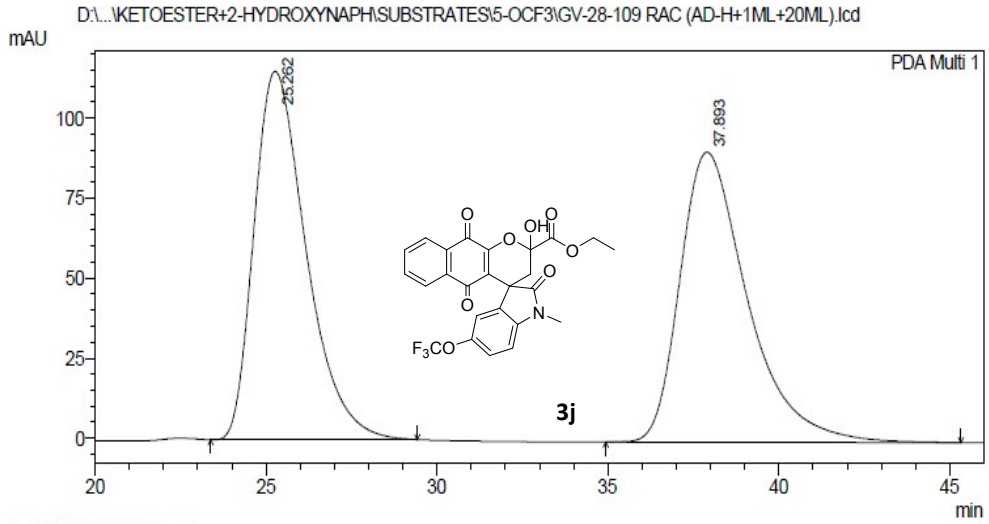
PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	22.508	1163157	16741	2.509	5.465
2	29.997	45193905	289567	97.491	94.535
Total		46357063	306308	100.000	100.000

HPLC profile for table 3, entry 10

<Chromatogram>



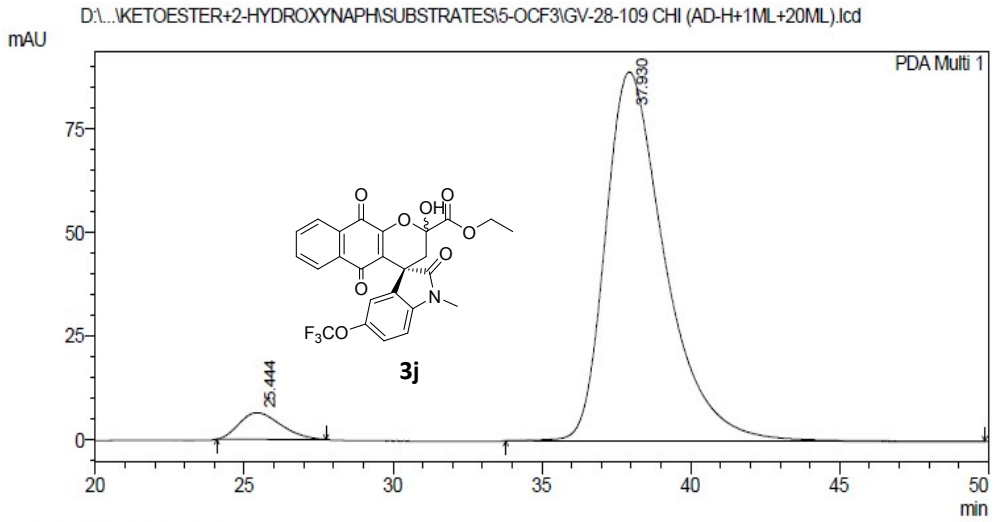
1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	25.262	12214424	115252	49.458	55.965
2	37.893	12481996	90685	50.542	44.035
Total		24696420	205937	100.000	100.000

<Chromatogram>



1 PDA Multi 1/254nm 4nm

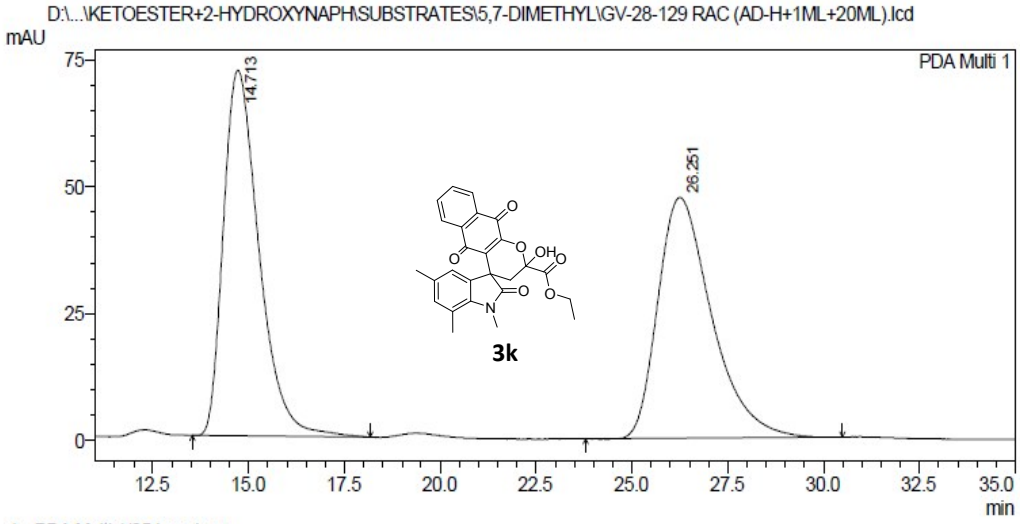
PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	25.444	629427	6449	4.819	6.743
2	37.930	12432201	89191	95.181	93.257
Total		13061628	95641	100.000	100.000

HPLC profile for table 3, entry 11

<Chromatogram>



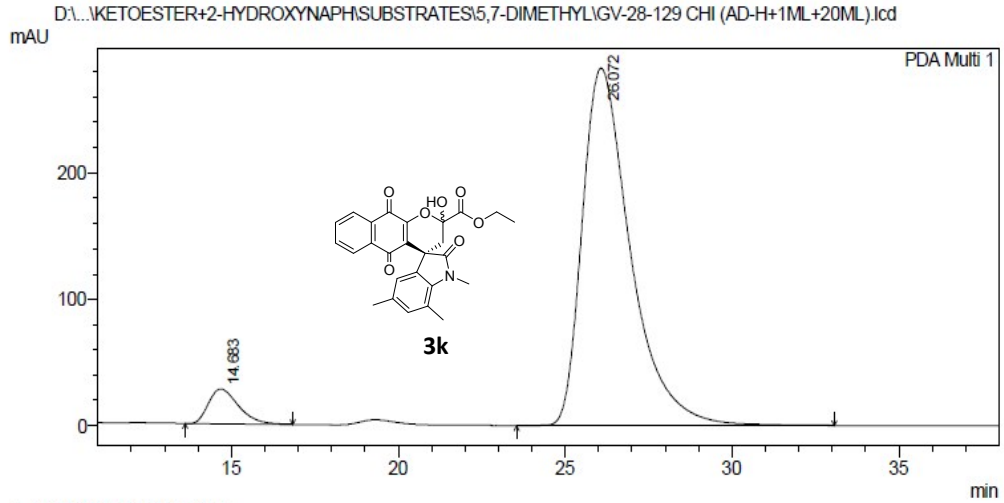
1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.713	4653664	71993	50.136	60.288
2	26.251	4628331	47422	49.864	39.712
Total		9281995	119415	100.000	100.000

<Chromatogram>



1 PDA Multi 1/254nm 4nm

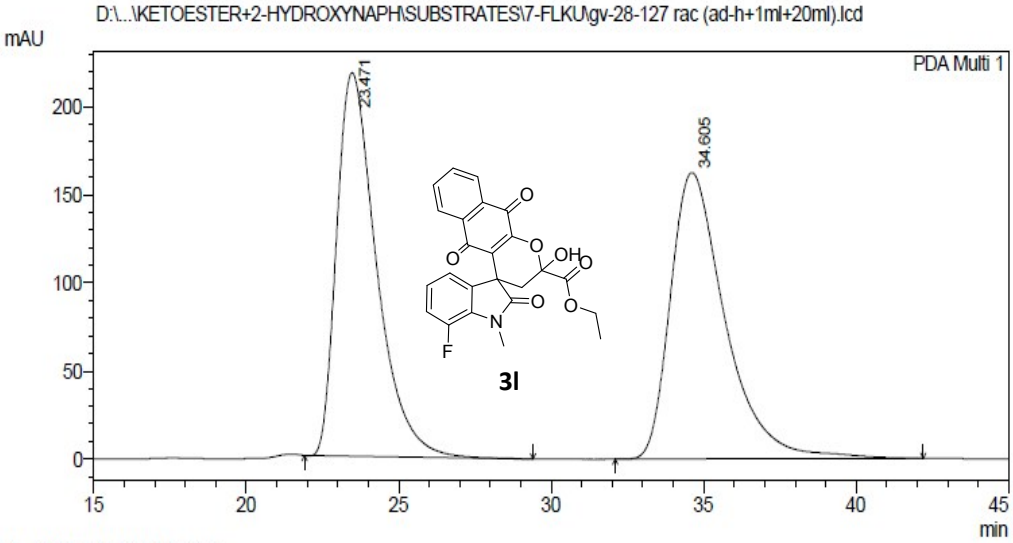
PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.683	1728479	27516	5.757	8.883
2	26.072	28295127	282253	94.243	91.117
Total		30023606	309768	100.000	100.000

HPLC profile for table 3, entry 12

<Chromatogram>



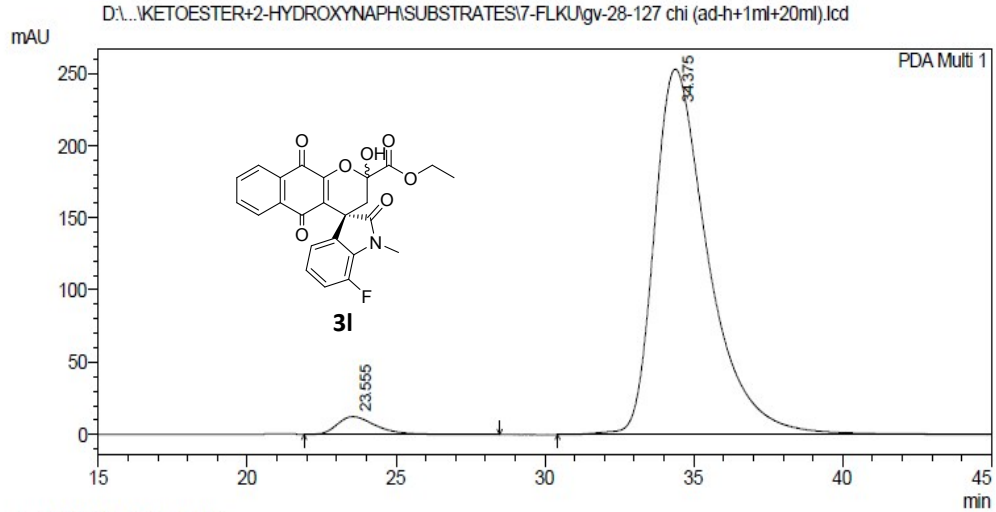
1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	23.471	19750844	217651	49.278	57.240
2	34.605	20329375	162590	50.722	42.760
Total		40080219	380241	100.000	100.000

<Chromatogram>



1 PDA Multi 1/254nm 4nm

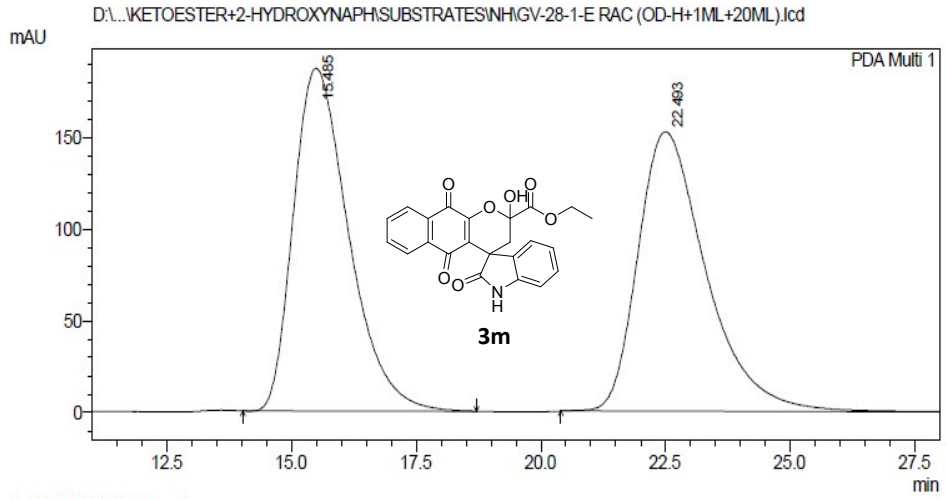
PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	23.555	1103281	12309	3.346	4.636
2	34.375	31874459	253175	96.654	95.364
Total		32977739	265484	100.000	100.000

HPLC profile for table 3, entry 13

<Chromatogram>



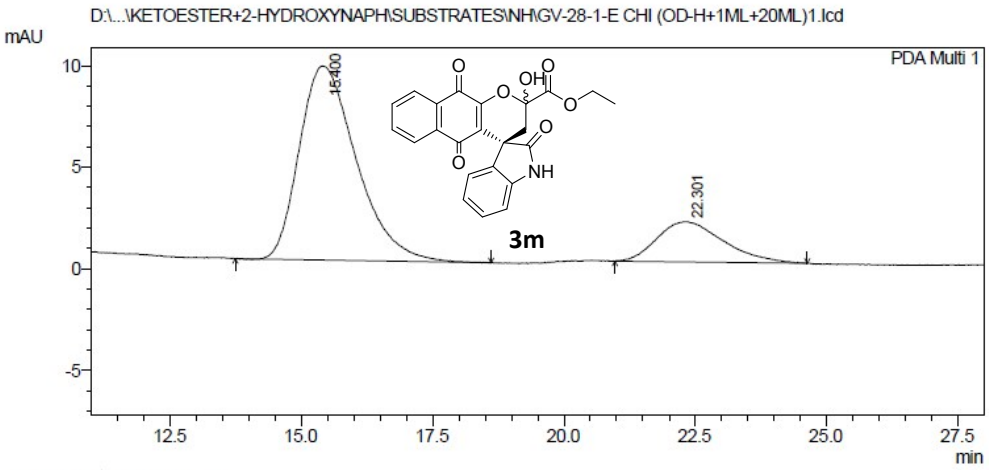
1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	15.485	14426583	187313	49.778	55.081
2	22.493	14555210	152753	50.222	44.919
Total		28981793	340066	100.000	100.000

<Chromatogram>



1 PDA Multi 1/254nm 4nm

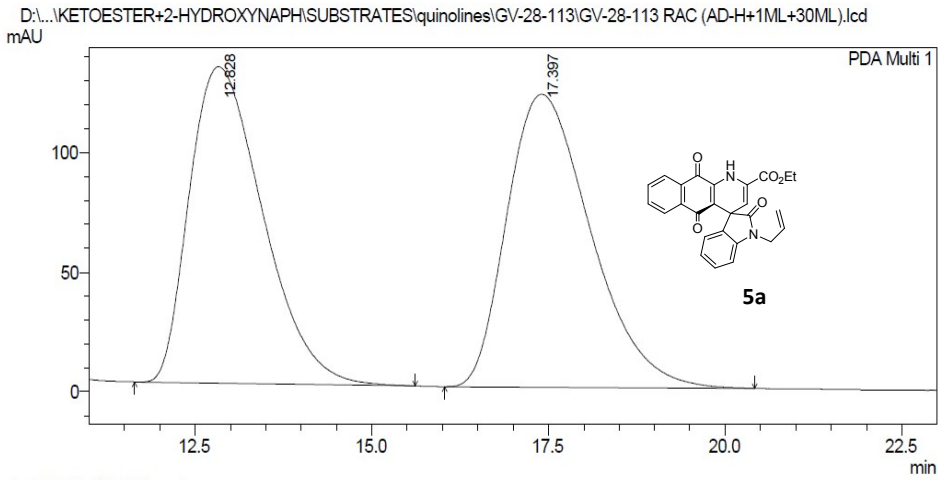
PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	15.400	719538	9548	80.494	82.795
2	22.301	174367	1984	19.506	17.205
Total		893905	11532	100.000	100.000

HPLC profile for table 4, entry 1

<Chromatogram>



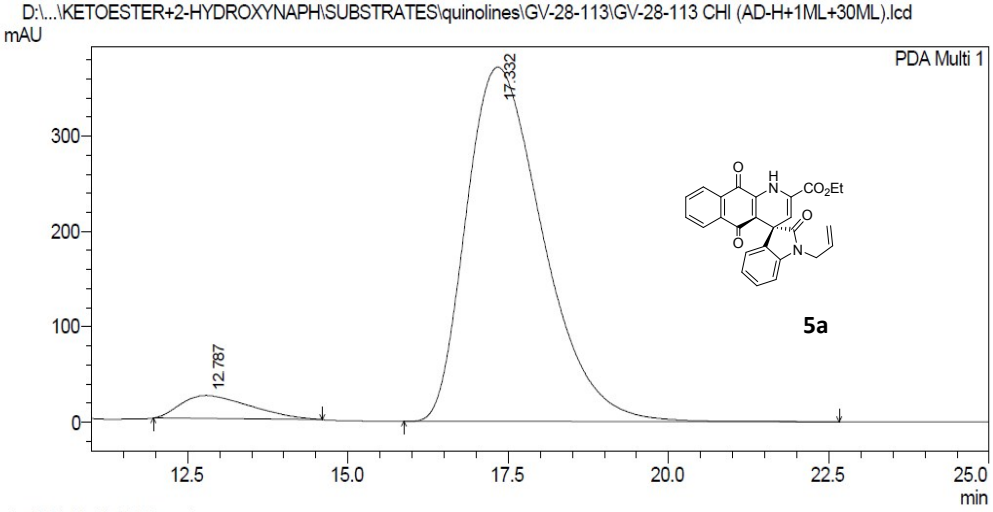
1 PDA Multi 1/220nm 4nm

PeakTable

PDA Ch1 220nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.828	9581504	132431	48.640	51.927
2	17.397	10117316	122600	51.360	48.073
Total		19698820	255031	100.000	100.000

<Chromatogram>



1 PDA Multi 1/220nm 4nm

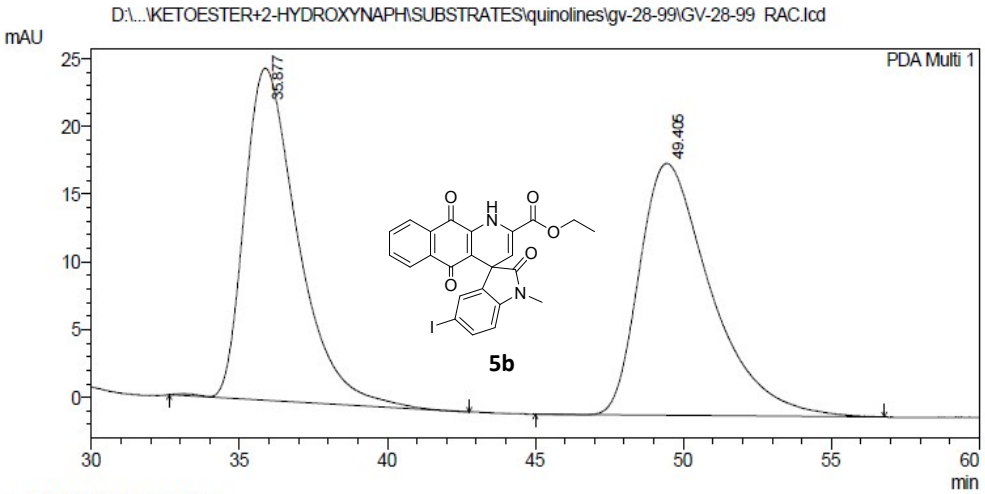
PeakTable

PDA Ch1 220nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.787	1829096	24085	5.587	6.088
2	17.332	30910891	371491	94.413	93.912
Total		32739986	395576	100.000	100.000

HPLC profile for table 4, entry 2

<Chromatogram>



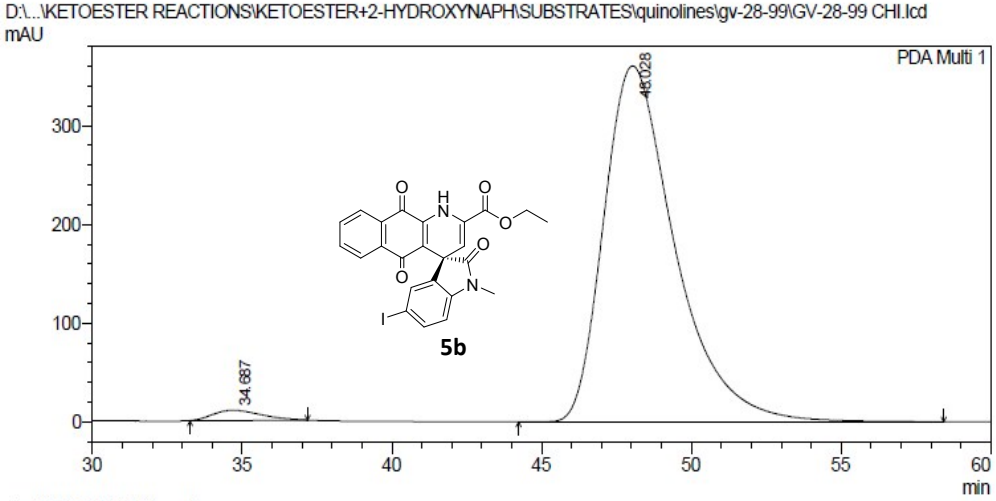
1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	35.877	3069642	24509	49.553	56.879
2	49.405	3125049	18580	50.447	43.121
Total		6194691	43089	100.000	100.000

<Chromatogram>



1 PDA Multi 1/254nm 4nm

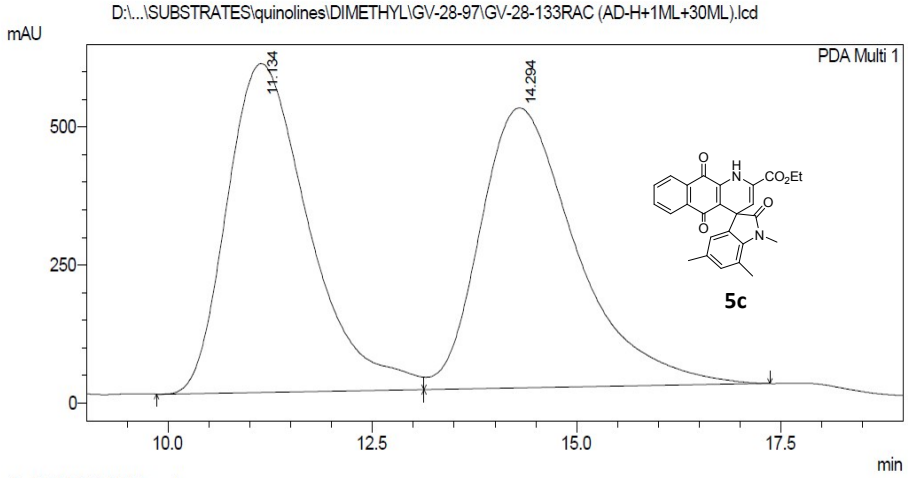
PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	34.687	1146058	10302	1.890	2.779
2	48.028	59499974	360364	98.110	97.221
Total		60646031	370666	100.000	100.000

HPLC profile for table 4, entry 3

<Chromatogram>



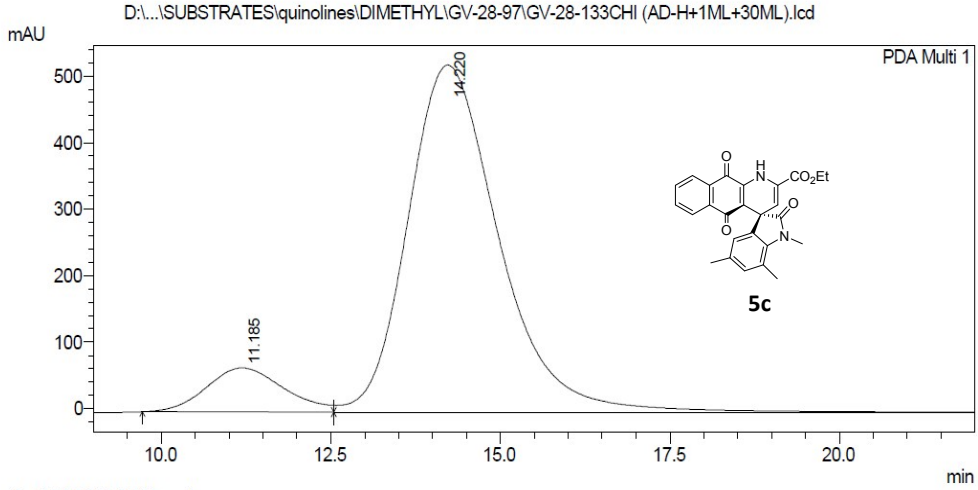
1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.134	41555352	595401	49.910	54.004
2	14.294	41706012	507107	50.090	45.996
Total		83261365	1102507	100.000	100.000

<Chromatogram>



1 PDA Multi 1/254nm 4nm

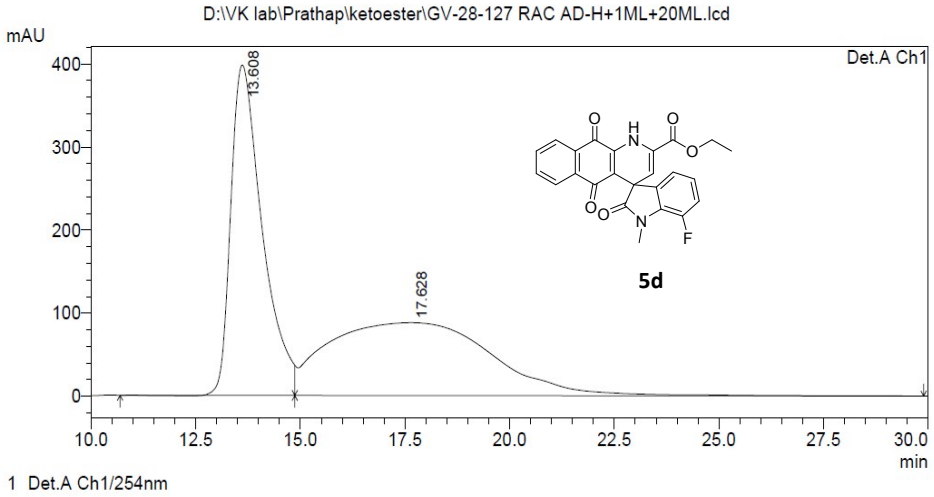
PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.185	5227677	66026	9.710	11.235
2	14.220	48612015	521677	90.290	88.765
Total		53839691	587703	100.000	100.000

HPLC profile for table 4, entry 4

<Chromatogram>

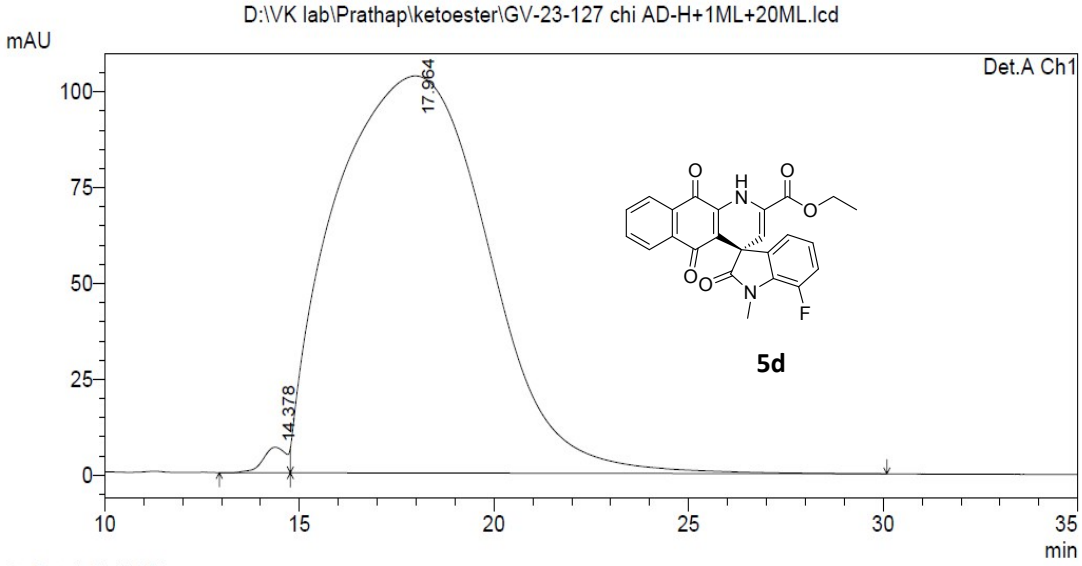


PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.608	20740691	397729	46.396	81.925
2	17.628	23962736	87750	53.604	18.075
Total		44703427	485479	100.000	100.000

<Chromatogram>



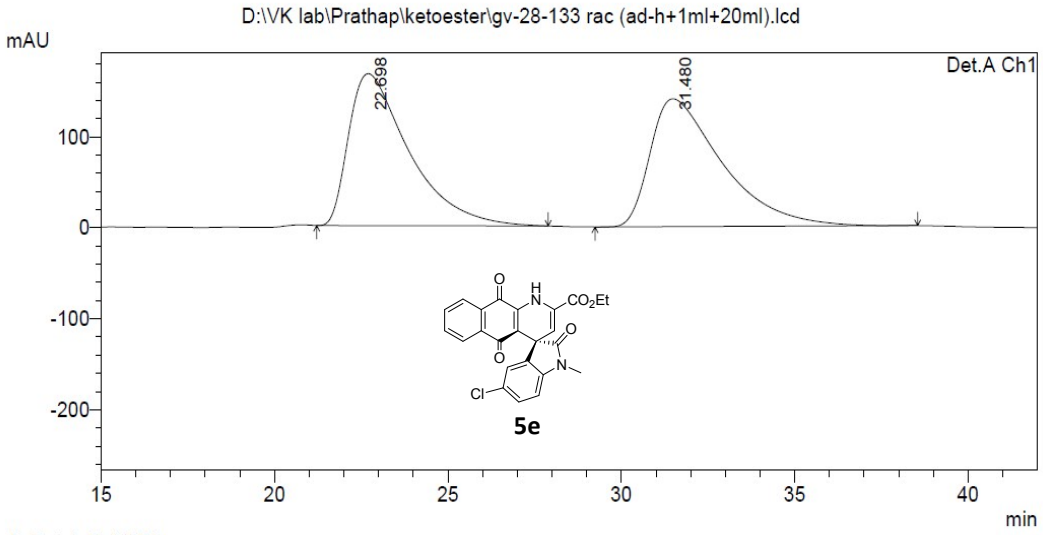
PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.378	280626	6667	0.979	6.048
2	17.964	28377583	103564	99.021	93.952
Total		28658209	110231	100.000	100.000

HPLC profile for table 4, entry 5

<Chromatogram>



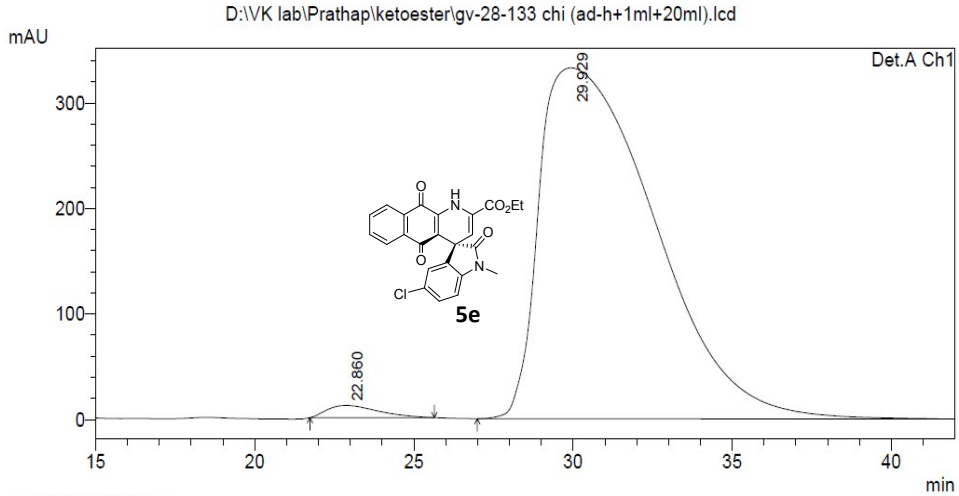
1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	22.698	20214599	167116	49.966	54.325
2	31.480	20241830	140508	50.034	45.675
Total		40456429	307624	100.000	100.000

<Chromatogram>



1 Det.A Ch1/254nm

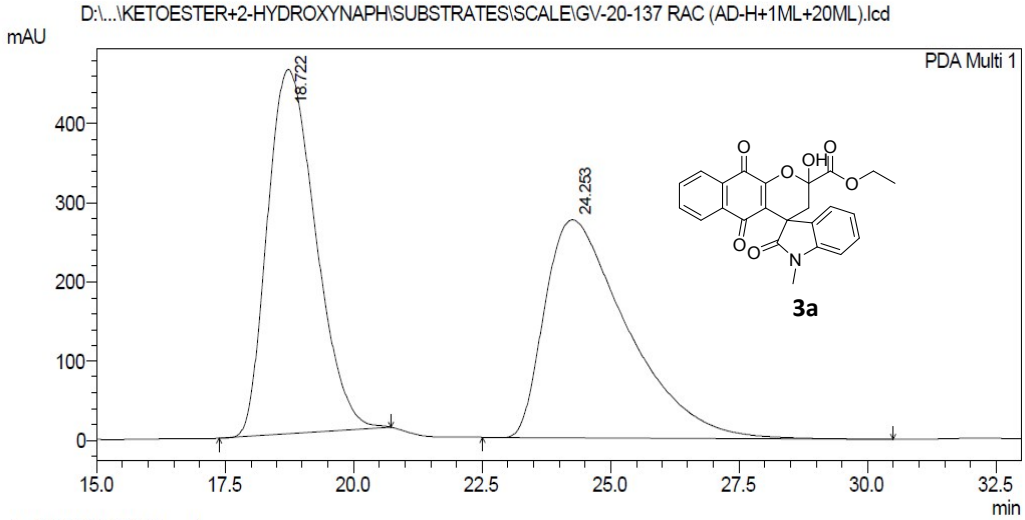
PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	22.860	1291064	11558	1.513	3.359
2	29.929	84013683	332524	98.487	96.641
Total		85304747	344082	100.000	100.000

HPLC profile for large scale: compound 3a

<Chromatogram>



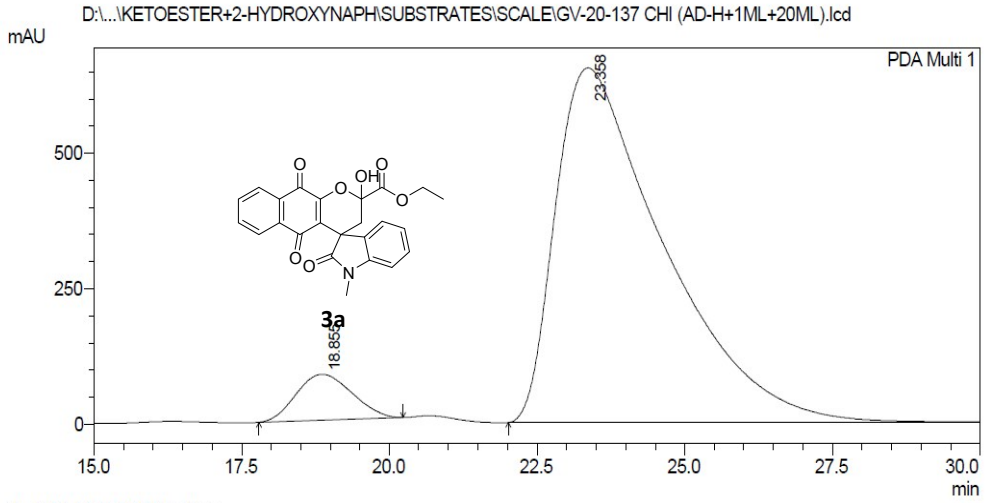
1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	18.722	30096299	460401	49.475	62.569
2	24.253	30735184	275430	50.525	37.431
Total		60831483	735830	100.000	100.000

<Chromatogram>



1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	18.855	5564547	84792	6.247	11.474
2	23.358	83512769	654191	93.753	88.526
Total		89077316	738982	100.000	100.000