Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry
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Supporting Information

Asymmetric synthesis of *ethano*-Tröger bases using CuTC-catalyzed diazo decomposition reactions

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General Remarks:

All Copper and $Rh_2(OAc)_4$ catalysts were purchased from commercial sources and used as received. *Methano*-Tröger base and its enantiomers were initially purchased from a commercial source and then prepared internally in the laboratory. 2,8-Dimethoxy Tröger base was prepared and resolved by a method previously reported.[1,2] ^{1}H-NMR spectroscopy (400 or 500 MHz): Chemical shifts are given in ppm relative to Me_4Si with solvent resonances used as internal standards (7.26 ppm for $CDCl_3$). Data were reported as follows: chemical shift (δ) in ppm on the δ scale, multiplicity (s = singlet, d = doublet, t = triplet, dd = doublet of doublet, dt = doublet of triplet, and m = multiplet, td = two doublets, b = broad peak), coupling constant (Hz) and integration. ^{13}C-NMR spectroscopy (100 or 125 MHz): Chemicals shifts were given in ppm relative to Me_4Si with solvent resonances used as internal standards (77.36 ppm for $CDCl_3$). FT-IR spectra were recorded with a spectrometer using an ATR accessory. Melting points (mp) were measured in open capillary tubes and are uncorrected. Electrospray mass spectra were obtained by the Sciences Mass Spectrometry (SMS) platform at the Faculty of Sciences (University of Geneva).

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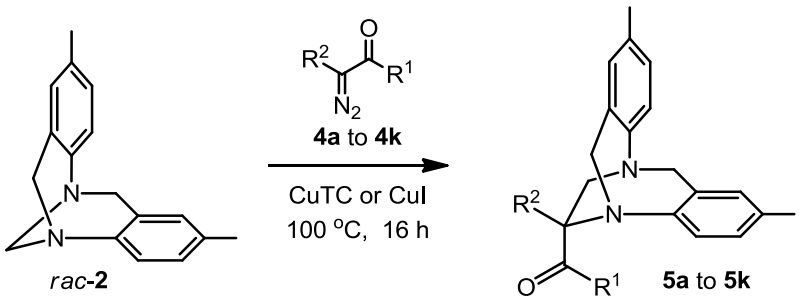
Table S1: Comparison of CuTC and CuI



Entry	Diazo	R^1	R^2	Product	CuTC		CuI	
					Yield [b]	*dr* [c]	Yield [b]	*dr* [c]
1	**4a**	Me	Ph	**5a**	80	11:1	81	10:1
2	**4b**	Me	COMe	**5b**	70	-	40	-
3	**4c**	Me	CO_2Me	**5c**	80	4.3:1	78	3.8:1
4	**4d**	Me	CO_2Et	**5d**	82	5.5:1	70 [d]	3.4:1
5	**4e**	Et	CO_2Et	**5e**	91	5.0:1	87	4.3:1
6	**4f**	*n*Pr	CO_2Et	**5f**	80	5.0:1	83	3.7:1
7	**4g**	*i*Pr	CO_2Et	**5g**	78	6.0:1	46	4.8:1
8	**4h**	Ph	CO_2Et	**5h**	80	4.3:1	65	4.2:1
9	**4i**	Me	CO_2*i*Pr	**5i**	85	3.9:1	78	3.3:1
10	**4j**	Me	CO_2*t*Bu	**5j**	87	4.0:1	81	2.6:1
11	**4k**	OEt	CO_2Et	**5k**	40	-	13	-

[a] Conditions: *rac*-**2** 0.4 mmol, diazo reagents **4** 0.8 mmol, CuTC (5 mol%) or CuI (5 mol%), 1.0 mL of toluene, 100 °C, 16 h; reported results are the average of at least two experiments. The relative configuration displayed is that of the major diastereoisomers of compounds **5**. [b] Isolated yield (%, both diastereoisomers). [c] *dr* ratios determined by ^{1}H-NMR analysis (400 MHz) of the crude reactions mixtures. [d] 25% *ee* obtained by using (+)-(*S*,*S*)-**2** 0.1 mmol, **4d** 0.2 mmol , 5 mol% of CuI, 0.25 mL of toluene, 90 °C, 6 h while 50% *ee* was reached with CuTC as catalyst.

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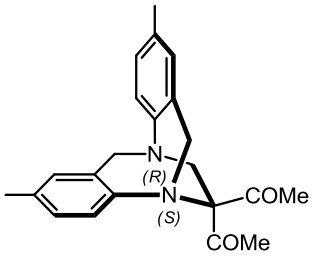
General procedure I: Synthesis of racemic *ethano*-bridged Tröger base (5)

In a 10 mL 2 neck round bottom flask equipped with a magnetic stirring bar, 100.0 mg of Tröger base **2** (0.399 mmol) were introduced along with 1 ml of dry toluene and 3.8 mg CuTC (0.02 mmol, 5 mol%) under dinitrogen atmosphere. To this solution, diazo compound **4** (0.4 mmol) was added in one portion. The reaction mixture was placed in an already heated oil bath (100 ^{o}C). The reaction was stirred for 30 min at that temperature. Then, 0.4 mmol of the same diazo compound **4** was added in one portion to the reaction mixture at 100 °C. The reaction was monitored by ESI-MS. The solution was then allowed to cool to 25 °C and the solvent was removed under reduced pressure. The desired product **5** was purified by column chromatography.

General procedure II: Enantiospecific transformation

Same as above using enantiopure (+)-(*S*,*S*)-**2** (0.1 mmol) as substrate in place of *rac*-**2**. Reactions were kept at 90 °C as indicated in Table 3.

1,1'-(2,8-dimethyl-6,12-dihydro-5,11-ethanodibenzo[b,f][1,5]diazocine-13,13-diyl)diethanone (5b):



Following procedure **I**, 97.4 mg (70%) of **5b** was obtained from 100 mg of *rac*-**2**. **M.P.**: 170-173 ^{o}C. **IR**: (neat): ν = 2961, 2920, 1707, 1701, 1492, 1432, 1349, 1219 cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.25 (d, *J* = 8.1 Hz, 1H), 6.97 (d, J = 8.0 Hz, 1H), 6.93 (d, J = 8.1 Hz, 1H), 6.86 (d, J = 8.1 Hz, 1H), 6.69 (s, J = 9.0 Hz, 1H), 6.57 (s, J = 12.4 Hz, 1H), 4.94 (d, J = 14.8 Hz, 1H), 4.58 (d, J = 17.9 Hz, 1H), 4.48 (d, *J* = 17.9 Hz, 1H), 4.36 (d, *J* = 17.5 Hz, 1H), 4.23 (d, *J* = 17.5 Hz, 1H), 3.55 (d, *J* = 14.8 Hz, 1H), 2.18 (s, 6H), 2.17 (s, 3H), 2.16 (s, 3H), 1.87 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 203.3, 201.6, 146.6, 143.7, 136.1, 135.8, 135.0, 134.8, 130.2, 129.5, 128.9, 128.6, 128.3, 128.0, 93.4, 59.3, 57.5, 56.7, 26.8, 26.0, 20.9, 20.8. **HRMS** (**ESI**) calculated for $C_{22}H_{26}N_2O_2$ (M+1): 349.191. Found: 349.1907.

Following procedure **II**, using (+)-(*S*,*S*)-**2** as substrate at 100 ^{o}C, **(5*R*,11*S*)-5b** (70%, *ee* 64%), $[\alpha]_D^{20}$ = +80 (c 0.02, CH_2Cl_2).

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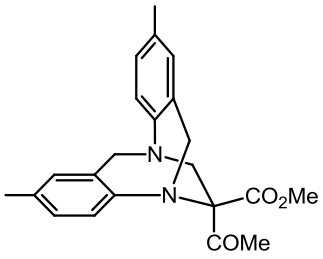
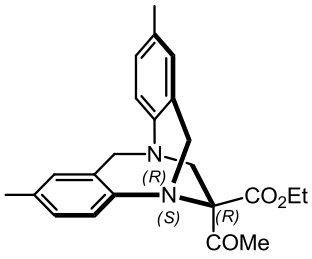
Ethyl 14-acetyl-2,8-dimethyl-6,12-dihydro-5,11-ethanodibenzo[b,f][1,5] diazocine -14-carboxylate (5c):



Following procedure **I**, 116.4 mg (80%, both diastereoisomers) of **5c** was obtained from 100 mg of *rac*-***2***. Separation of the diastereoisomers was done by column chromatography (SiO_2, 3 x 30 cm, acetone/pentane 3/97).

Major diastereoisomer {(5*R*,11*S*,14*S*) and (5*S*,11*R*,14*R*)}: 99 mg (68%). **IR**: (neat): ν =2921, 1737, 1720, 1495, 1433, 1351, 1233, 1182 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.24 (d, *J* = 8.1 Hz, 1H), 6.98 (d, *J* = 8.0 Hz, 1H), 6.91 (d, *J* = 8.1 Hz, 1H), 6.86 (d, *J* = 8.0 Hz, 1H), 6.70 (s, 1H), 6.56 (s, 1H), 4.96 (d, *J* = 18.1 Hz, 1H), 4.78 (d, *J* = 15.2 Hz, 1H), 4.49 (d, *J* = 5.7 Hz, 1H), 4.44 (d, *J* = 5.0 Hz, 1H), 4.21 (d, *J* = 17.5 Hz, 1H), 3.72 (s, 3H), 3.55 (d, *J* = 15.2 Hz, 1H), 2.17 (s, 3H), 2.15 (s, 3H), 1.93 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 200.5, 169.7, 147.0, 143.3, 136.4, 136.3, 136.1, 135.0, 130.6, 129.5, 128.9, 128.8, 128.4, 128.3, 85.0, 59.6, 57.7, 56.6, 53.3, 26.3, 21.2, 21.1. **HRMS** (**ESI**) calculated for $C_{22}H_{25}N_2O_3$(M+1): 365.1859. Found: 365.1855.

Ethyl 14-acetyl-2,8-dimethyl-6,12-dihydro-5,11-ethanodibenzo[b,f][1,5] diazocine-14-carboxylate (5d):



Following procedure **I**, 124 mg (82%, both diastereoisomers) of **5d** was obtained from 100 mg of *rac*-***2***. Separation of the diastereoisomers was done by column chromatography (SiO_2, 3 x 30 cm, acetone/pentane 3/97).

Major diastereoisomer {(5*R*,11*S*,14*S*) and (5*S*,11*R*,14*R*)}: 105.8 mg (70%). **IR**: (neat): ν =2921, 1720, 1496, 1434, 1352, 1217, 1183 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.24 (d, *J* = 8.0 Hz, 1H), 6.98 (d, *J* = 8.0 Hz, 1H), 6.91 (d, *J* = 8.0 Hz, 1H), 6.87 (d, *J* = 8.0 Hz, 1H), 6.71 (s, 1H), 6.56 (s, 1H), 4.98 (d, *J* = 18.2 Hz, 1H), 4.78 (d, *J* = 15.2 Hz, 1H), 4.47 (td, *J* = 18.2 Hz, 2H), 4.27 – 4.08 (m, 3H), 3.55 (d, *J* = 15.2 Hz, 1H), 2.17 (s, 3H), 2.16 (d, *J* = 9.7 Hz, 6H), 2.15 (s, 3H), 1.94 (s, 3H), 1.94 (s, 3H), 1.22 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 200.6, 169.2, 147.1, 143.3, 136.4, 136.4, 136.1, 135.0, 130.6, 129.5, 128.9, 128.8, 128.4, 128.3, 84.9, 62.3, 59.6, 57.7, 56.6, 26.2, 21.14, 21.10, 14.4. **HRMS** (**ESI**) calculated for $C_{23}H_{27}N_2O_3$(M+1): 379.2016. Found: 379.2015.

Following procedure **II**, using (+)-(*S*,*S*)-**2** as substrate at 90 °C, **(5*S*,11*R*,14*R*)-5d** (67%, *ee* 50%), $[\alpha]_D^{20}$ = +135 (c 0.02, CH_2Cl_2).

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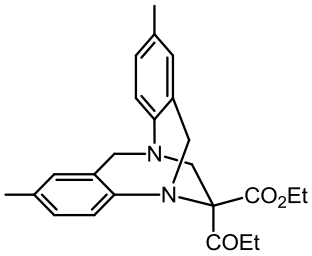
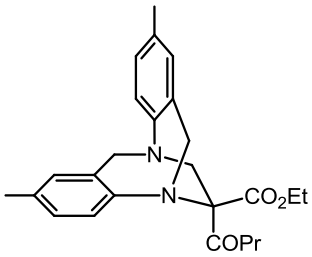
Ethyl 2,8-dimethyl-14-propionyl-6,12-dihydro-5,11-ethanodibenzo[b,f][1,5] diazocine-14-carboxylate (5e):



Following procedure **I**, 142.6 mg (91%, both diastereoisomers) of **5e** was obtained from 100 mg of *rac*-***2***. Separation of the diastereoisomers was done by column chromatography (SiO_2, 3 x 30 cm, acetone/pentane 3/97).

Major diastereoisomer {(5*R*,11*S*,14*S*) and (5*S*,11*R*,14*R*)}: 117.5 mg (75%). **M.P.**: 170-173°C. **IR**: (neat): ν = 2976, 1719, 1496, 1434, 1336, 1256, 1216 cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.23 (d, *J* = 8.1 Hz, 1H), 6.98 (d, *J* = 8.0 Hz, 1H), 6.90 (dd, *J* = 8.1, 1.6 Hz, 1H), 6.86 (dd, *J* = 8.0, 1.6 Hz, 1H), 6.70 (d, *J* = 0.8 Hz, 1H), 6.56 (d, *J* = 0.9 Hz, 1H), 5.00 (d, *J* = 18.1 Hz, 1H), 4.80 (d, *J* = 15.2 Hz, 1H), 4.48 (t, *J* = 16.9 Hz, 2H), 4.27 – 4.09 (m, 3H), 3.53 (dd, *J* = 15.2, 1.1 Hz, 1H), 2.53 – 2.27 (m, 2H), 2.17 (s, 3H), 2.14 (s, 3H), 1.22 (t, *J* = 7.1 Hz, 3H), 0.57 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 204.2, 169.3, 147.1, 143.4, 136.5, 136.4, 136.3, 134.9, 130.7, 129.5, 128.9, 128.8, 128.4, 128.3, 84.4, 62.1, 59.7, 57.7, 56.7, 31.7, 21.12, 21.09, 14.4, 8.8. **HRMS** (**ESI**) calculated for $C_{24}H_{29}N_2O_3$(M+1): 393.2172. Found: 393.2171.

Ethyl 14-butyryl-2,8-dimethyl-6,12-dihydro-5,11-ethanodibenzo[b,f][1,5] diazocine-14-carboxylate (5f):



Following procedure **I**, 129.8 mg (80%, both diastereoisomers) of **5f** was obtained from 100 mg of *rac*-***2***. Separation of the diastereoisomers was done by column chromatography (SiO_2, 3 x 30 cm, acetone/pentane 3/97).

Major diastereoisomer {(5*R*,11*S*,14*S*) and (5*S*,11*R*,14*R*)}: 107.1 mg (66%). **M.P.**: 168-170 °C. **IR**: (neat): ν = 2962, 1718, 1496, 1434, 1260, 1216 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.25 (d, *J* = 8.1 Hz, 1H), 7.00 (d, *J* = 7.8 Hz, 1H), 6.89 (td, *J* = 8.1, 7.8 Hz, 2H), 6.72 (s, 1H), 6.56 (s, 1H), 4.99 (d, *J* = 18.2 Hz, 1H), 4.82 (d, *J* = 15.2 Hz, 1H), 4.49 (td, *J* = 18.2 Hz, 2H), 4.28 – 4.07 (m, 3H), 3.55 (d, *J* = 15.2 Hz, 1H), 2.46 – 2.24 (m, 2H), 2.18 (s, 3H), 2.15 (s, 3H), 1.37 – 1.18 (m, 4H), 1.10 – 0.81 (m, 1H), 0.59 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 203.2, 169.3, 147.1, 143.4, 136.5, 136.3, 135.0, 134.3, 130.7, 129.5, 128.8, 128.7, 128.4, 128.3, 84.6, 62.2, 59.6, 57.8, 56.8, 40.2, 21.1, 21.0, 17.9, 14.4, 13.5. **HRMS** (**ESI**) calculated for $C_{25}H_{31}N_2O_3$(M+1): 407.2329. Found: 407.2334.

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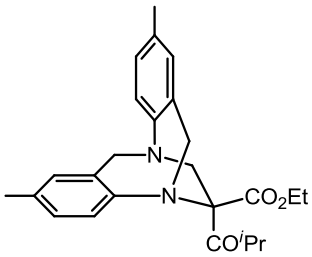
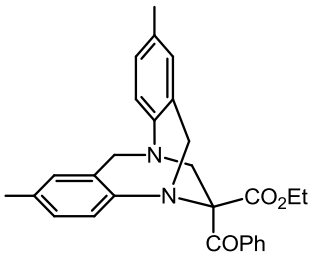
Ethyl 14-isobutyryl-2,8-dimethyl-6,12-dihydro-5,11-ethanodibenzo[b,f][1,5] diazocine-14-carboxylate (5g):



Following procedure **I**, 126.6 mg (78%, both diastereoisomers) of **5g** was obtained from 100 mg of *rac*-***2***. Separation of the diastereoisomers was done by column chromatography (SiO_2, 3 x 30 cm, acetone/pentane 4/96).

Major diastereoisomer {(5*R*,11*S*,14*S*) and (5*S*,11*R*,14*R*)}: 90.7 mg (56%). **IR**: (neat): ν = 2962, 1718, 1607, 1495, 1434, 1260, 1216 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.27 (d, *J* = 8.1 Hz, 1H), 6.97 (d, *J* = 8.0 Hz, 1H), 6.90 (d, *J* = 8.1 Hz, 1H), 6.86 (d, *J* = 8.0 Hz, 1H), 6.70 (s, 1H), 6.56 (s, 1H), 4.92 (d, *J* = 18.1 Hz, 1H), 4.84 (d, *J* = 15.2 Hz, 1H), 4.51 – 4.39 (m, 2H), 4.27 – 4.16 (m, Hz, 2H), 4.08 (dq, *J* = 10.8, 7.1 Hz, 2H), 3.49 (d, *J* = 16.1 Hz, 1H), 3.43 (dt, *J* = 13.4, 6.7 Hz, 2H), 2.17 (s, 3H), 2.14 (s, 3H), 1.23 (t, *J* = 7.1 Hz, 3H), 0.85 (d, *J* = 6.8 Hz, 3H), 0.03 (d, *J* = 6.6 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 208.8, 169.3, 147.1, 143.6, 136.4, 136.3, 134.9, 131.0, 129.5, 129.0, 128.8, 128.4, 128.3, 84.2, 62.1, 59.5, 57.8, 57.1, 36.5, 23.1, 21.1, 21.1, 18.0, 14.5. **HRMS** (**ESI**) calculated for $C_{25}H_{31}N_2O_3$(M+1): 407.2329. Found: 407.2334.

Ethyl 14-benzoyl-2,8-dimethyl-6,12-dihydro-5,11-ethanodibenzo[b,f][1,5] diazocine-14-carboxylate (5h):



Following procedure **I**, 140.8 mg (80%, both diastereoisomers) of **5h** was obtained from 100 mg of *rac*-***2***. Separation of the diastereoisomers was done by column chromatography (SiO_2, 3 x 30 cm, acetone/pentane 3/97).

Major diastereoisomer {(5*R*,11*S*,14*S*) and (5*S*,11*R*,14*R*)}: 112.6 mg (64%). **M.P.**: 143-145 °C. **IR**: (neat): ν = 2922, 1737, 1686, 1495, 1446, 1242, 1211 cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 8.17-8.14 (m, 2H), 7.46 – 7.34 (m, 1H), 7.28 – 7.23 (m, 2H), 7.02 (d, *J* = 8.0 Hz, 1H), 6.87 (d, *J* = 8 Hz, 1H), 6.75 – 6.67 (m, 2H), 6.56 – 6.43 (m, 2H), 5.54 (t, *J* = 18.7 Hz, 1H), 5.03 (d, *J* = 15.1 Hz, 1H), 4.71 (d, *J* = 17.4 Hz, 1H), 4.47 (d, *J* = 18.3 Hz, 1H), 4.24 (d, *J* = 17.4 Hz, 1H), 4.18 – 4.02 (m, 2H), 3.61 (d, *J* = 15.1, 1H), 2.18 (s, 3H), 1.99 (s, 3H), 1.05 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 191.50, 169.99, 147.24, 143.07, 137.07, 136.73, 136.10, 135.64, 134.95, 132.99, 131.30, 129.95,

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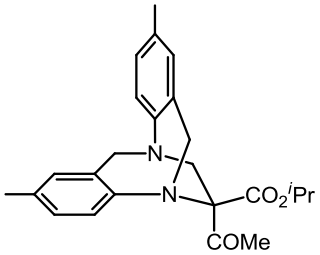
128.81, 128.64, 128.35, 128.21, 128.19, 128.05, 82.35, 62.02, 59.84, 58.91, 57.39, 21.09, 21.01, 14.26. **HRMS** (**ESI**) calculated for $C_{28}H_{29}N_2O_3$(M+1): 441.2172. Found: 441.2170.

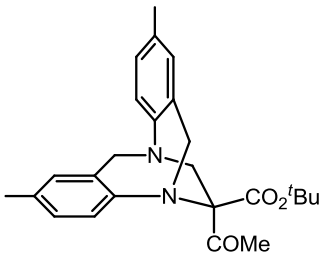
Isopropyl 14-acetyl-2,8-dimethyl-6,12-dihydro-5,11-ethanodibenzo[b,f][1,5] diazocine-14-carboxylate (5i):



Following procedure **I**, 133.2 mg (85%, both diastereoisomers) of **5i** was obtained from 100 mg of *rac-**2***. Separation of the diastereoisomers was done by column chromatography (SiO_2, 3 x 30 cm, acetone/pentane 3/97).

Major diastereoisomer {(5*R*,11*S*,14*S*) and (5*S*,11*R*,14*R*)}: 106.6 mg (68%). **M.P.**: 172-175 °C. **IR**: (neat): ν = 2980, 1720, 1496, 1434, 1370, 1234 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.24 (d, *J* = 8.0 Hz, 1H), 6.99 (d, *J* = 8.0 Hz, 1H), 6.91 (d, *J* = 8.0 Hz, 1H), 6.86 (d, *J* = 8.0 Hz, 1H), 6.71 (s, 1H), 6.56 (s, 1H), 5.08 – 4.96 (m, 2H), 4.76 (d, *J* = 15.2 Hz, 1H), 4.54 – 4.42 (td, *J* = 17.4 Hz, 2H), 4.21 (d, *J* = 17.4 Hz, 1H), 3.52 (d, *J* = 15.2 Hz, 1H), 2.17 (s, 3H), 2.15 (s, 3H), 1.93 (s, 3H), 1.28 – 1.11 (m, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 200.6, 168.6, 147.1, 143.4, 136.5, 136.3, 136.3, 134.9, 130.6, 129.5, 128.9, 128.8, 128.5, 128.3, 84.8, 69.9, 59.6, 57.6, 56.6, 26.1, 21.9, 21.6, 21.1, 21.0. **HRMS** (**ESI**) calculated for $C_{24}H_{29}N_2O_3$(M+1): 393.2172. Found: 393.2171.

tert-Butyl 14-acetyl-2,8-dimethyl-6,12-dihydro-5,11-ethanodibenzo[b,f][1,5] diazocine-14-carboxylate (5j):



Following procedure **I**, 141.2 mg (87%, both diastereoisomers) of **5j** was obtained from 100 mg of *rac-**2***. Separation of the diastereoisomers was done by column chromatography (SiO_2, 3 x 30 cm, acetone/pentane 3/97).

Major diastereoisomer {(5*R*,11*S*,14*S*) and (5*S*,11*R*,14*R*)}: 112 mg (69%). **M.P.**: 179-181 °C. **IR**: (neat): ν = 2980, 1718, 1495, 1456, 1368, 1245 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.22 (d, *J* = 8 Hz, 1H), 6.99 (d, *J* = 7.6 Hz, 1H), 6.89 (td, *J* = 8, 7.6 Hz, 2H), 6.71 (s, 1H), 6.56 (s, 1H), 5.02 (d, *J* = 18.1 Hz, 1H), 4.73 (d, *J* = 15.2 Hz, 1H), 4.47 (td, *J* = 18.1, 17.5 Hz, 2H), 4.20 (d, *J* = 17.5 Hz, 1H), 3.52 (d, *J* = 15.2 Hz, 1H), 2.18 (s, 3H), 2.13 (d, *J* = 10.2 Hz, 3H), 1.94 (s, 3H), 1.42 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 200.8, 168.2, 147.1, 143.5, 136.6, 136.2, 134.9, 130.6, 129.5, 128.8, 128.4, 128.3, 85.1, 83.1, 59.6,

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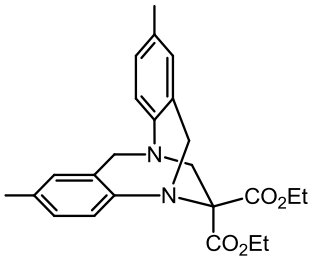
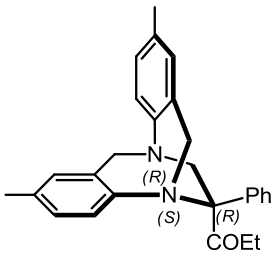
57.5, 56.6, 28.1, 26.1, 21.1, 21.1. **HRMS** (**ESI**) calculated for $C_{25}H_{31}N_2O_3$(M+1): 407.2329. Found: 407.2323.

Diethyl 2,8-dimethyl-6,12-dihydro-5,11-ethanodibenzo[b,f][1,5]diazocine-13,13-dicarboxylate (5k):



Following procedure **I**, 1.65 mg (40%) of **5k** was obtained from 100 mg of *rac*-***2***. **M.P.**: 190-193 °C. **IR**: (neat): ν = 2980, 2925, 1735, 1497, 1444 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.22 (d, *J* = 8.0 Hz, 1H), 7.00 (d, *J* = 8.0 Hz, 1H), 6.88-6.86 (m, 2H), 6.70 (s, 1H), 6.59 (s, 1H), 5.14 (d, *J* = 18.4 Hz, 1H), 4.86 (d, *J* = 17.4 Hz, 1H), 4.68 (d, *J* = 15.2 Hz, 1H), 4.46 (d, *J* = 18.4 Hz, 1H), 4.33 – 4.13 (m, 3H), 3.96 (dq, *J* = 10.7, 7.1 Hz, 1H), 3.84 (dq, *J* = 10.7, 7.1 Hz, 1H), 3.68 (d, *J* = 15.2 Hz, 1H), 2.17 (s, 3H), 2.15(s, 3H), 1.22 (t, *J* = 7.1 Hz, 3H), 0.77 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 169.1, 168.7, 147.0, 143.8, 137.4, 137.0, 135.9, 135.1, 130.8, 128.8, 128.7, 128.3, 128.2, 78.3, 62.3, 62.1, 59.7, 59.3, 57.3, 21.1, 21.08, 14.5, 13.6. **HRMS** (**ESI**) calculated for $C_{24}H_{29}N_2O_4$ (M+1): 409.2121. Found: 409.2116.

1-(2,8-dimethyl-14-phenyl-6,12-dihydro-5,11-ethanodibenzo[b,f][1,5]diazocin-14-yl)propan-1-one (5l):



Following procedure **I**, 131.5 mg (83%, major diastereoisomer) of **5l** was obtained from 100 mg of *rac*-***2***. Separation of the diastereoisomers was done by column chromatography (SiO_2, 3 x 30 cm, acetone/pentane 5/95).

Major diastereoisomer {(5*R*,11*S*,14*S*) and (5*S*,11*R*,14*R*)}: White solid 131.5 mg (60%). **M.P.**: 196-198 °C. **IR:** (neat): ν = 2964, 1706, 1495, 1259, 1015 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = δ 7.58 (b, 2H), 7.35 (t, *J* = 7.7 Hz, 2H), 7.32 – 7.27 (m, 12H), 6.99 (d, *J* = 8.0 Hz, 1H), 6.95 (d, *J* = 7.7 Hz, 1H), 6.84 (d, *J* = 8.0 Hz, 1H), 6.63 (s, 1H), 6.62 (s, 1H), 5.28 (d, *J* = 14.6 Hz, 1H), 4.73 (d, *J* = 17.6 Hz, 1H), 4.60 (d, *J* = 17.5 Hz, 1H), 4.41 (d, *J* = 17.6 Hz, 1H), 4.29 (d, *J* = 17.4 Hz, 1H), 3.49 (d, *J* = 14.6 Hz, 1H), 2.25 – 1.96 (m, 8H), 0.26 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 209.37, 147.66, 144.74, 141.61, 136.28, 136.21, 135.90, 134.47, 130.67, 129.78, 129.03, 128.78, 128.76, 128.28, 128.09, 127.72, 127.33, 82.13, 59.70, 59.35, 56.41, 30.68, 21.16, 21.09, 9.47. **HRMS** (**ESI**) calculated for $C_{27}H_{29}N_2O$(M+1): 397.2274. Found: 397.2293.

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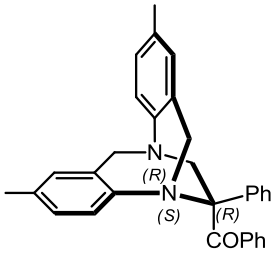
Following procedure **II**, using (+)-(*S*,*S*)-**2** as substrate, **(5*S*,11*R*,14*R*)-5l**: *major diastereoisomer* (83%, *ee* 90%), $[\alpha]_D^{20}$ = +217 (c 0.02, CH_2Cl_2).

(2,8-dimethyl-14-phenyl-6,12-dihydro-5,11-ethanodibenzo[b,f][1,5]diazocin-14-yl)(phenyl)methanone (5m):



Following procedure **I**, 152 mg (85%, major diastereoisomer) of **5m** was obtained from 100 mg of *rac*-***2***. Separation of the diastereoisomers was done by precipitation in acetone/hexane solution.

Major diastereoisomer {(5*R*,11*S*,14*S*) and (5*S*,11*R*,14*R*)}: White solid 152 mg (85%). **M.P.**: 255-257 °C. **IR:** (neat): ν = 2921, 1671, 1596, 1495, 1259 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.72 (d, *J* = 7.5 Hz, 2H), 7.68 – 7.61 (m, 2H), 7.39 (t, *J* = 7.8 Hz, 2H), 7.22 (t, *J* = 7.4 Hz, 1H), 7.15 (t, *J* = 7.4 Hz, 1H), 7.06 – 6.95 (m, 3H), 6.84 (d, *J* = 7.9 Hz, 1H), 6.71 (d, *J* = 8.0 Hz, 1H), 6.66 (s, 1H), 6.48 (s, 1H), 6.44 (d, *J* = 8.1 Hz, 1H), 5.41 (d, *J* = 14.7 Hz, 1H), 5.12 (d, *J* = 17.4 Hz, 1H), 4.70 (d, *J* = 17.4 Hz, 1H), 4.50 (d, *J* = 17.5 Hz, 1H), 4.27 (d, *J* = 17.5 Hz, 1H), 3.48 (d, *J* = 13.9 Hz, 1H), 2.14 (s, 3H), 2.00 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 198.4, 147.7, 144.7, 141.0, 138.0, 136.5, 135.7, 135.2, 134.4, 131.5, 131.3, 129.4, 129.2, 129.0, 128.7, 128.4, 128.2, 127.8, 127.6, 127.4, 127.3, 82.5, 62.2, 59.7, 56.9, 21.1, 21.0. **HRMS** (**ESI**) calculated for $C_{31}H_{29}N_2O$(M+1): 445.2274. Found: 445.2272.

Following procedure **II**, using (+)-(*S*,*S*)-**2** as substrate, **(5*S*,11*R*,14*R*)-5m**: *major diastereoisomer before crystallization* (85%, *ee* 90%) and *after crystallization* (80%, *ee* 95%), $[\alpha]_D^{20}$ = +245 (c 0.02, CH_2Cl_2).

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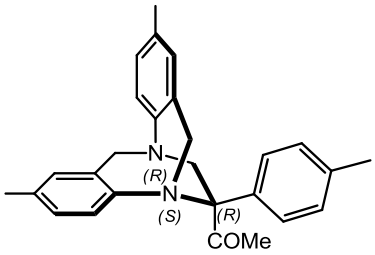
1-(2,8-dimethyl-14-(*p*-tolyl)-6,12-dihydro-5,11-ethanodibenzo[b,f][1,5] diazocin-14-yl)ethanone (5n):

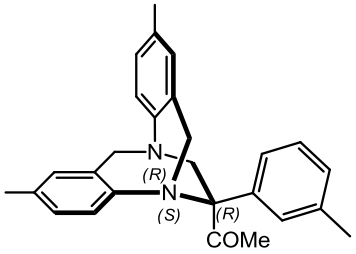


Following procedure **I**, 181 mg (80%, major diastereoisomer) of **5n** was obtained from 100 mg of *rac*-***2***. Separation of the diastereoisomers was done by column chromatography (SiO_2, 3 x 30 cm, acetone/pentane 5/95).

Major diastereoisomer {(5*R*,11*S*,14*S*) and (5*S*,11*R*,14*R*)}: White solid 181 mg (80%). **M.P.**: 174-175 °C. **IR**: (neat): ν = 2922, 1705, 1679, 1496, 1432, 1260, 1220 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.47 (b, 2H), 7.28 (d, *J* = 8.0 Hz, 1H), 7.17 (d, *J* = 8.3 Hz, 2H), 6.98 (d, *J* = 8.0 Hz, 1H), 6.94 (d, *J* = 8.1 Hz, 1H), 6.84 (d, *J* = 8.8 Hz, 1H), 6.62 (s, 2H), 5.24 (d, *J* = 14.6 Hz, 1H), 4.72 (d, *J* = 17.5 Hz, 1H), 4.58 (d, *J* = 17.5 Hz, 1H), 4.38 (d, *J* = 17.6 Hz, 1H), 4.28 (d, *J* = 17.6 Hz, 1H), 3.49 (d, *J* = 14.2 Hz, 1H), 2.34 (s, 3H), 2.17 (s, 3H), 2.13 (s, 3H), 1.64 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 205.59, 147.63, 144.88, 137.57, 136.31, 135.89, 135.88, 134.43, 130.56, 129.82, 129.78, 128.80, 128.72, 128.24, 128.07, 127.32, 82.12, 59.64, 59.46, 56.33, 25.23, 21.37, 21.16, 21.09. **HRMS** (**ESI**) calculated for $C_{27}H_{29}N_2O$(M+1): 397.2274. Found: 397.2271.

Following procedure **II**, using (+)-(*S*,*S*)-**2** as substrate, **(5*S*,11*R*,14*R*)-5n**: *major diastereoisomer* (80%, *ee* 82%), $[\alpha]_D^{20}$ = +138 (c 0.02, CH_2Cl_2).

1-(2,8-dimethyl-14-(*m*-tolyl)-6,12-dihydro-5,11-ethanodibenzo[b,f][1,5] diazocin-14-yl)ethanone (5o):



Following procedure **I**, 187.8 mg (83%, major diastereoisomer) of **5o** was obtained from 100 mg of *rac*-***2***. Separation of the diastereoisomers was done by column chromatography (SiO_2, 3 x 30 cm, acetone/pentane 5/95).

Major diastereoisomer {(5*R*,11*S*,14*S*) and (5*S*,11*R*,14*R*)}: White solid 187.8 mg (83%). **M.P.**: 174-175 °C. **IR:** (neat): ν = 2922, 1705, 1679,1496, 1432, 1260, 1220 cm^{-1}. 7.45 (b, 1H), 7.36 – 7.22 (m, 3H), 7.07 (d, *J* = 7.5 Hz, 1H), 7.01 – 6.92 (m, 2H), 6.83 (d, *J* = 8.1 Hz, 1H), 6.62 (s, 2H), 5.24 (d, *J* = 14.6 Hz, 1H), 4.73 (d, *J* = 17.6 Hz, 1H), 4.58 (d, *J* = 17.4 Hz, 1H), 4.39 (d, *J* = 17.6 Hz, 1H), 4.28 (d, *J* = 17.4 Hz, 1H), 3.50 (d, *J* = 14.6 Hz, 1H), 2.36 (s, 4H), 2.17 (s, 3H), 2.14 (s, 3H), 1.64 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 205.6, 147.6, 144.8, 141.5, 138.7, 136.3, 135.9, 135.8, 134.4, 130.6,

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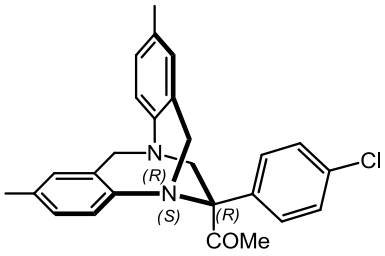
129.8, 128.9, 128.8, 128.7, 128.5, 128.2, 128.1, 128.0, 124.5, 82.3, 59.6, 59.5, 56.4, 25.3, 22.0, 21.2, 21.1 **HRMS** (**ESI**) calculated for $C_{27}H_{29}N_2O$(M+1): 397.2274. Found: 397.2263.

Following procedure **II**, using (+)-(*S*,*S*)-**2** as substrate, **(5*S*,11*R*,14*R*)-5o**: *major diastereoisomer* (83%, *ee* 84 %), $[\alpha]_D^{20}$ = +153 (c 0.02, CH_2Cl_2).

1-(14-(4-chlorophenyl)-2,8-dimethyl-6,12-dihydro-5,11-ethanodibenzo[b,f] [1,5]diazocin-14-yl)ethanone (5p):



Following procedure **I**, 138.3 mg (83%, both diastereoisomers) of **5p** was obtained from 100 mg of *rac-**2***. Separation of the diastereoisomers was performed by column chromatography (SiO_2, 3 x 30 cm, acetone/pentane 5/95).

Major diastereoisomer {(5*R*,11*S*,14*S*) and (5*S*,11*R*,14*R*)}: White solid 138.3 mg (83%). **M.P.**: 168-170 °C. **IR:** (neat): ν = 2922, 1707, 1493, 1349, 1220 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.53 (b, 2H), 7.34 (d, *J* = 8.9 Hz, 2H), 7.27 (d, *J* = 8.1 Hz, 1H), 7.02 – 6.93 (m, 2H), 6.85 (d, *J* = 8.0 Hz, 1H), 6.63 (s, 1H), 6.62 (s, 1H), 5.23 (d, *J* = 14.5 Hz, 1H), 4.65 (d, *J* = 17.5 Hz, 1H), 4.55 (d, *J* = 17.5 Hz, 1H), 4.39 (d, *J* = 17.6 Hz, 1H), 4.28 (d, *J* = 17.5 Hz, 1H), 3.46 (d, *J* = 14.2 Hz, 1H), 2.17 (s, 3H), 2.14 (s, 3H), 1.63 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 205.01, 147.44, 144.47, 140.02, 136.15, 135.93, 135.72, 134.61, 133.86, 130.48, 129.86, 129.27, 128.85, 128.80, 128.39, 128.09, 82.03, 59.58, 59.32, 56.29, 25.22, 21.17, 21.08. **HRMS** (**ESI**) calculated for $C_{26}H_{26}N_2OCl$ (M+1): 417.1728. Found: 417.1730.

Following procedure **II**, using (+)-(*S*,*S*)-**2** as substrate, **(5*S*,11*R*,14*R*)-5p**: *major diastereoisomer before crystallization* (83%, *ee* 93%) and *after crystallization* (75%, *ee* 99%), $[\alpha]_D^{20}$ = +226 (c 0.02, CH_2Cl_2).

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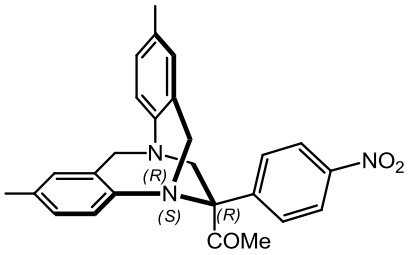
1-(2,8-dimethyl-14-(4-nitrophenyl)-6,12-dihydro-5,11-ethanodibenzo[b,f][1,5] diazocin-14-yl)ethanone (5q):

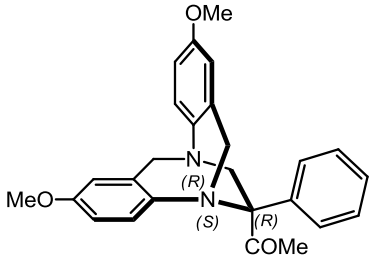


Following procedure **I**, 145.2 mg (85 %, major diastereoisomer) of **5q** was obtained from 100 mg of *rac-**2***. Separation of the diastereoisomers was done by column chromatography (SiO_2, 3 x 30 cm, acetone/pentane 5/95).

Major diastereoisomer {(5*R*,11*S*,14*S*) and (5*S*,11*R*,14*R*)}: White solid 145.2 mg (85%). **M.P.**: 174-175 °C. **IR:** (neat): ν = 2916, 1711, 1601, 1520, 1496,1346 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.24 (d, *J* = 9.1 Hz, 2H), 7.92 – 7.64 (m, 2H), 7.30 (d, *J* = 8.0 Hz, 1H), 7.01 – 6.95 (m, 2H), 6.86 (d, *J* = 8.0 Hz, 1H), 6.64 (s, 2H), 5.30 (d, *J* = 14.5 Hz, 1H), 4.59 (d, *J* = 17.5 Hz, 1H), 4.54 (d, *J* = 17.5 Hz, 1H), 4.44 (d, *J* = 17.6 Hz, 1H), 4.30 (d, *J* = 17.6 Hz, 1H), 3.48 (d, *J* = 14.5 Hz, 1H), 2.19 (s, 3H), 2.15 (s, 3H), 1.64 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 204.0, 148.8, 147.5, 147.2, 144.0, 136.5, 135.5, 134.9, 130.4, 130.0, 129.1, 128.8, 128.6, 128.3(2C), 128.1, 124.3(2C), 82.93, 59.57, 59.40, 56.47, 25.43, 21.18, 21.09. **HRMS** (**ESI**) calculated for $C_{26}H_{26}N_3O_3$(M+1): 428.1968. Found: 428.1951.

Following procedure **II**, using (+)-(*S*,*S*)-**2** as substrate, **(5*S*,11*R*,14*R*)-5q**: *major diastereoisomer* (85%, *ee* 95%), $[\alpha]_D^{20}$ = +197 (c 0.02, CH_2Cl_2).

1-(2,8-dimethoxy-14-phenyl-6,12-dihydro-5,11-ethanodibenzo[b,f][1,5] diazocin-14-yl)ethanone(5r):



Following procedure **I,** 132.5 mg (80%, major diastereoisomer) of **5r** was obtained from 100 mg of *rac-**2***. Separation of the diastereoisomers was done by column chromatography (SiO_2, 3 x 30 cm, acetone/pentane 5/95).

Major diastereoisomer {(5*R*,11*S*,14*S*) and (5*S*,11*R*,14*R*)}: White solid 132.5 mg (80%). **M.P.**: 213-215 °C. **IR:** (neat): ν = 2928, 1705, 1608, 1493, 1462 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.60 (b, 2H), 7.43 – 7.32 (m, 3H), 7.31 – 7.24 (m, 1H), 7.04 (d, *J* = 8.7 Hz, 1H), 6.73 (dd, *J* = 8.7, 2.9 Hz, 1H), 6.61 (dd, *J* = 8.7, 2.9 Hz, 1H), 6.37 (d, *J* = 2.9 Hz, 1H), 6.33 (d, *J* = 2.9 Hz, 1H), 5.28 (d, *J* = 14.6 Hz, 1H), 4.74 (d, *J* = 17.6 Hz, 1H), 4.60 (d, *J* = 17.4 Hz, 1H), 4.40 (d, *J* = 17.6 Hz, 1H), 4.29 (d, *J* = 17.4 Hz, 1H), 3.69 (s, 3H), 3.66 (s, 3H), 3.51 (d, *J* = 14.5 Hz, 1H), 1.67 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 205.4, 157.8, 156.8, 143.1, 141.4, 140.1, 137.8, 137.5, 131.9, 129.3, 129.1, 127.8,

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127.4, 114.5, 113.1, 112.8, 112.6, 82.5, 59.9, 59.6, 56.6, 55.6, 55.5, 25.3. **HRMS** (**ESI**) calculated for $C_{26}H_{27}N_2O_3$(M+1): 415.2016. Found: 415.2014.

Following procedure **II**, using (+)-(*S*,*S*) enantiomer of dimethoxy Tröger base as substrate, **(5*S*,11*R*,14*R*)-5r**: *major diastereoisomer* (80%, *ee* 92%), $[\alpha]_D^{20}$ = +210 (c 0.02, CH_2Cl_2).

References:

(1) Satishkumar, S.; Periasamy, M. *Tetrahedron: Asymmetry* **2009**, *20*, 2257.
(2) Satishkumar, S.; Periasamy, M. *Tetrahedron: Asymmetry* **2006**, *17*, 1116.

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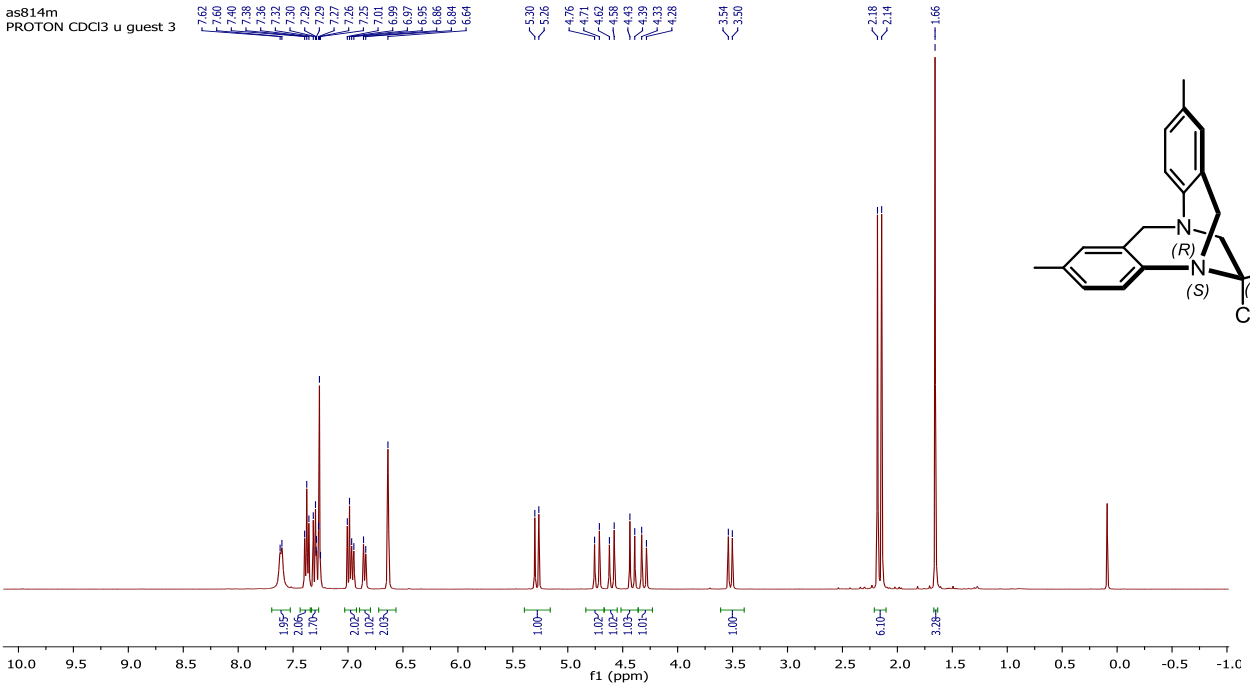
Table 1x: Crystal data and structure refinement for **5a**, **5c**, **5i**

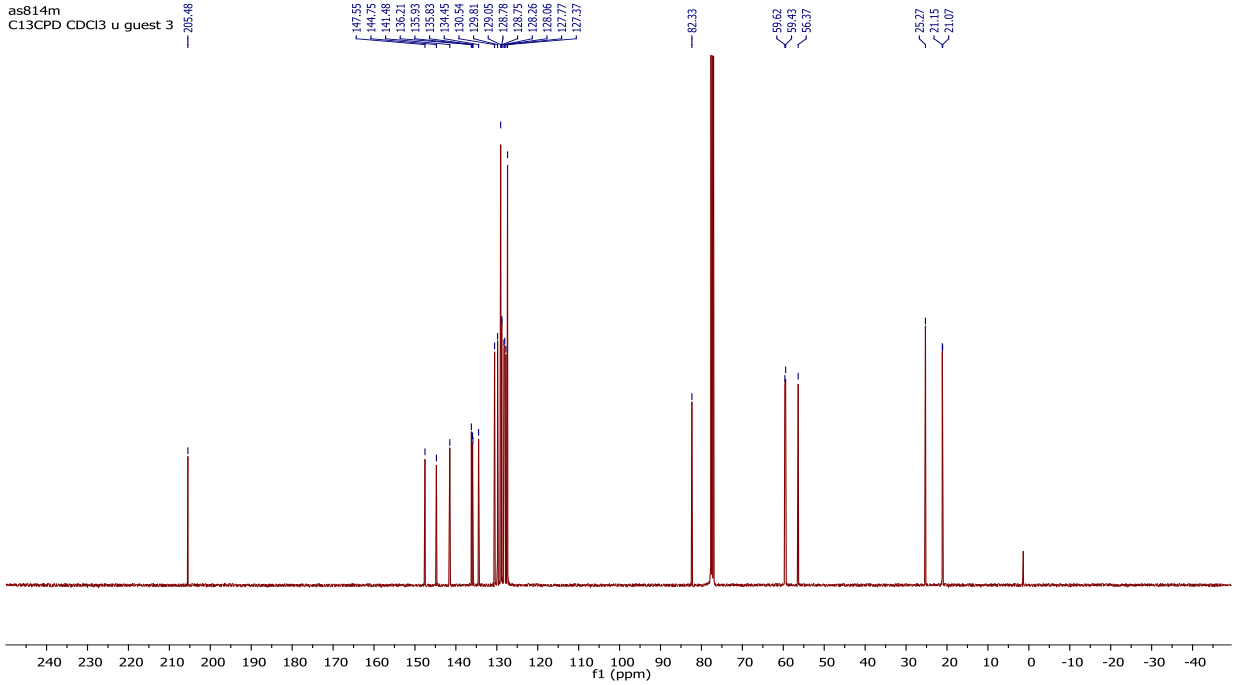
	5a	**5c**	**5i**
Empirical formula	$C_{26}H_{26}N_2O$	$C_{22}H_{24}N_2O_3$	$C_{24}H_{28}N_2O_3$
Formula weight	382.49	364.44	392.50
Temperature / K	180(2)	220(2)	200(2)
Wavelength	1.54184 Å	0.71073 Å	0.71073 Å
Diffractometer	Supernova CCD (Agilent)	Stoe IPDS	Stoe IPDS
Crystal system	monoclinic	monoclinic	orthorhombic
Space group	*C*2/*c*	*C*2/*c*	*Pbca*
a / Å, *b* / Å, *c* / Å	17.0172(3), 8.60512(13), 28.3901(5)	17.051(2), 7.5405(6), 28.226(4)	14.113(6), 14.919(5), 19.801(5)
α/°, *β*/°, *γ*/°	90, 91.4359(17), 90	90, 93.201(10), 90	90, 90, 90
Volume / Å^3	4156.01(12)	3623.3(7)	4169(2)
Z	8	8	8
ρ_{calc} / mg mm^{-3}	1.223	1.336	1.251
μ / mm^{-1}	0.578	0.089	0.083
F(000)	1632	1552	1680
Crystal size / mm^3	0.2416 × 0.1364 × 0.1012	0.500 × 0.400 × 0.050	0.400 × 0.400 × 0.100
2Θ range for data collection	6.22 to 148.52°	2.89 to 51.314°	9.886 to 52.76°
Index ranges	$-17 \le h \le 21$, $-10 \le k \le 10$, $-35 \le l \le 35$	$-20 \le h \le 20$, $-9 \le k \le 9$, $-34 \le l \le 34$	$-17 \le h \le 17$, $-18 \le k \le 18$, $-24 \le l \le 24$
Reflections collected	22460	11824	29403
Independent reflections	4161 [*R*(int) = 0.0242]	3385 [*R*(int) = 0.051]	4240 [*R*(int) = 0.031]
Data/restraints/parameters	4161/0/264	3385/0/244	4240/0/262
Goodness-of-fit on F^2	1.025	1.1573	0.9975
Final *R* indexes [$I>2\sigma(I)$]	R_1 = 0.0406, wR_2 = 0.1118	R_1 = 0.0667, wR_2 = 0.1011	R_1 = 0.0561, wR_2 = 0.1189
Final *R* indexes [all data]	R_1 = 0.0457, wR_2 = 0.1174	R_1 = 0.0721, wR_2 = 0.1015	R_1 = 0.0576, wR_2 = 0.1193
Largest diff. peak/hole / e Å^{-3}	0.197/-0.183	0.34/-0.28	0.31/-0.26

Spectrums

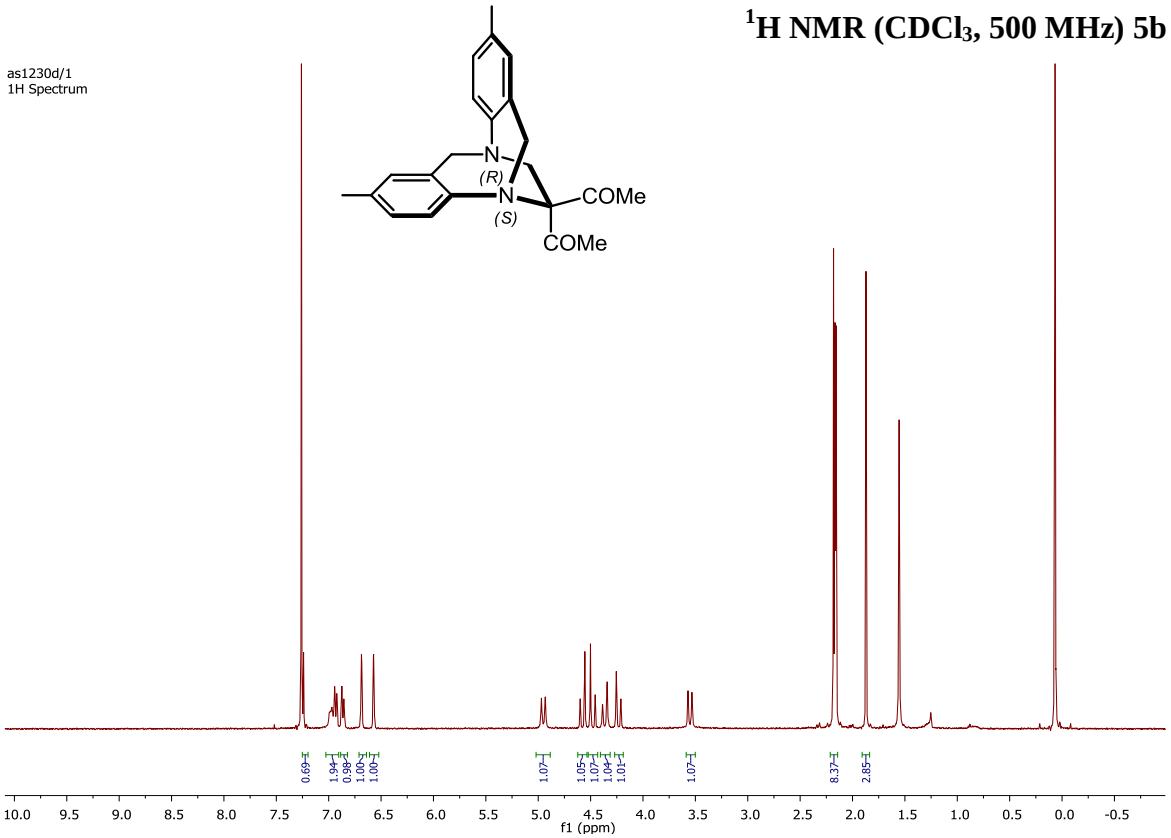
^{1}H NMR ($CDCl_3$, 400 MHz) 5a



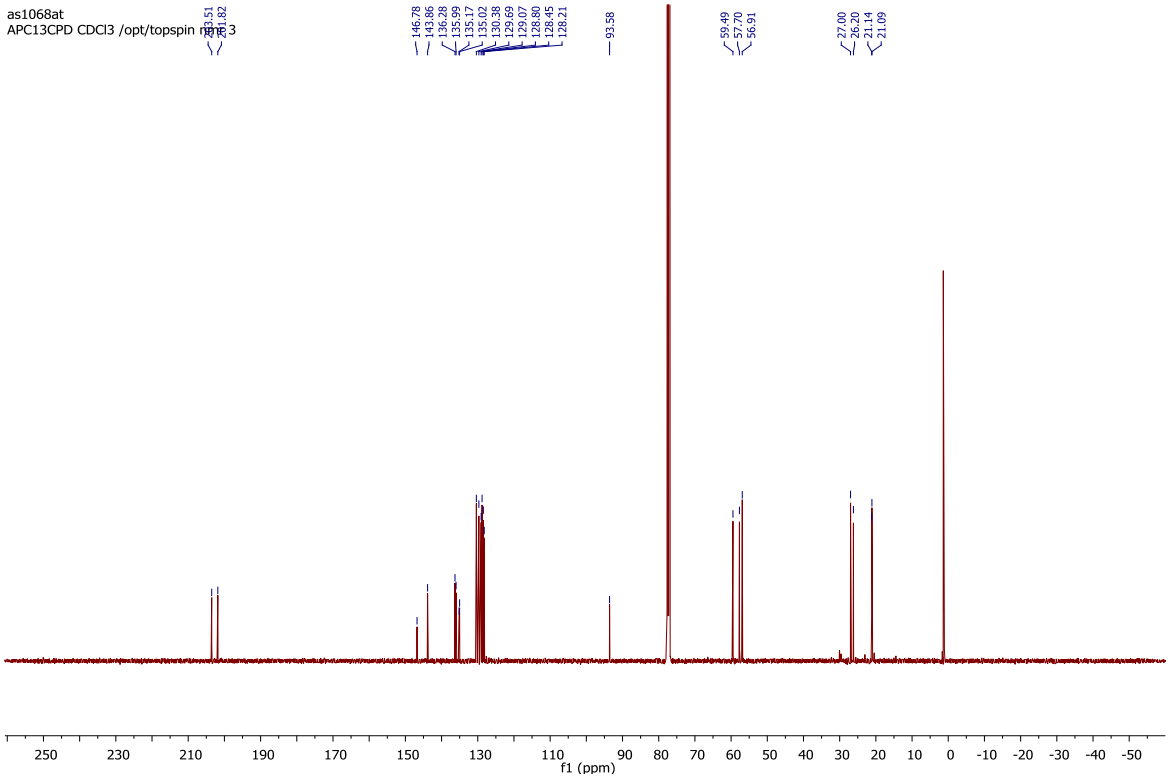
^{13}C NMR ($CDCl_3$, 100 MHz) 5a



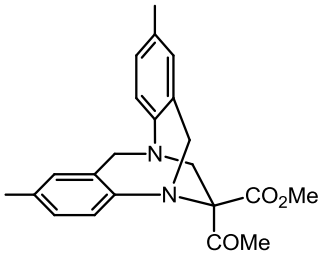
^{1}H NMR ($CDCl_3$, 500 MHz) 5b



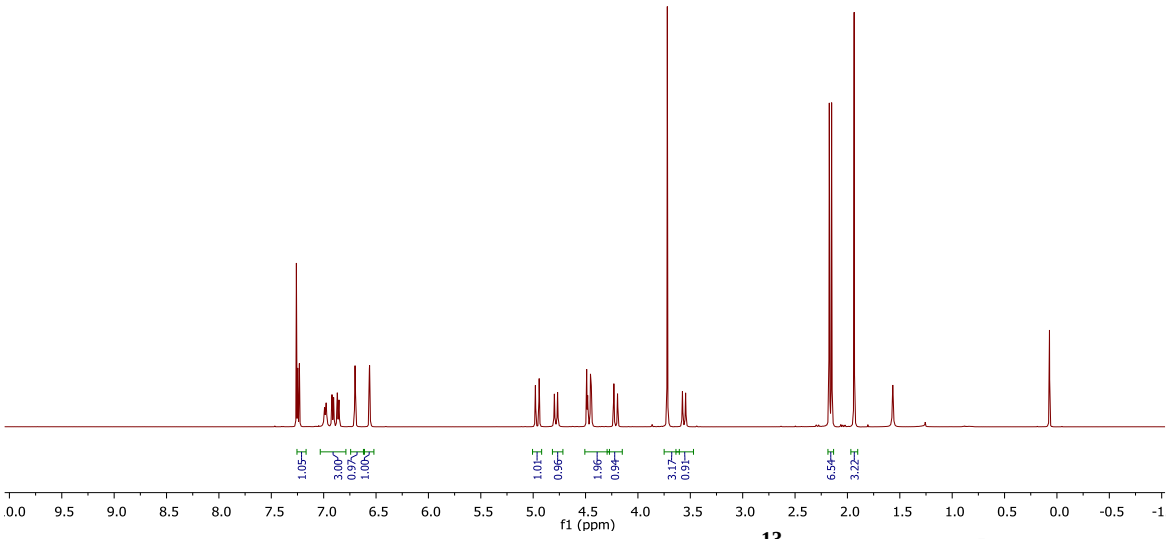
^{13}C NMR ($CDCl_3$, 125 MHz) 5b



as1230at
PROTON CDCl3 /opt/topspin nmr 18

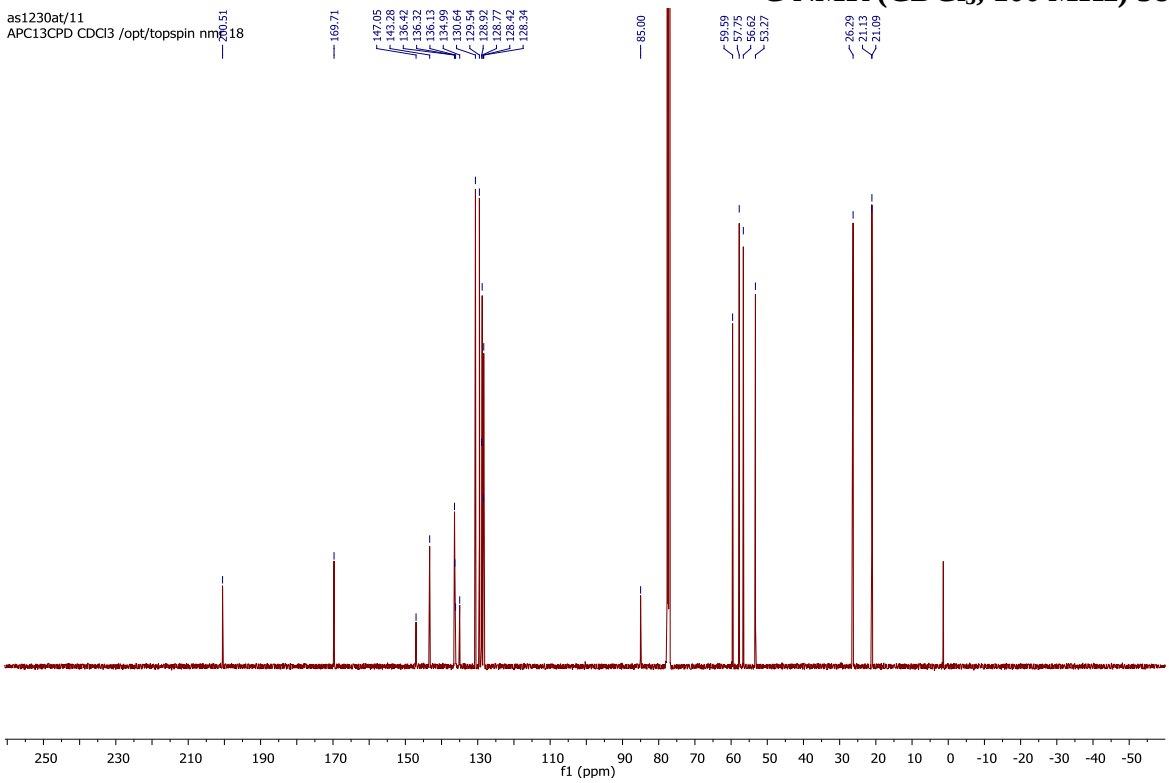


^{1}H NMR ($CDCl_3$, 400 MHz) 5c



^{13}C NMR ($CDCl_3$, 100 MHz) 5c

as1230at/11
APC13CPD CDCl3 /opt/topspin nmr 18



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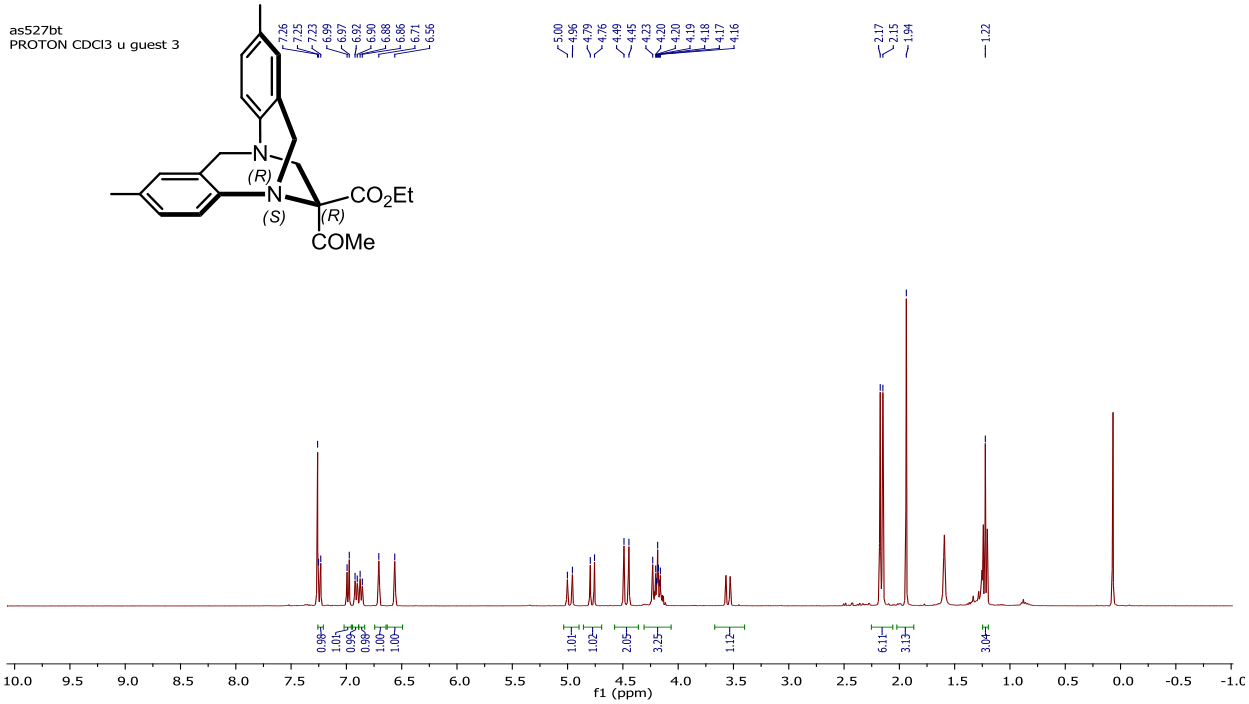
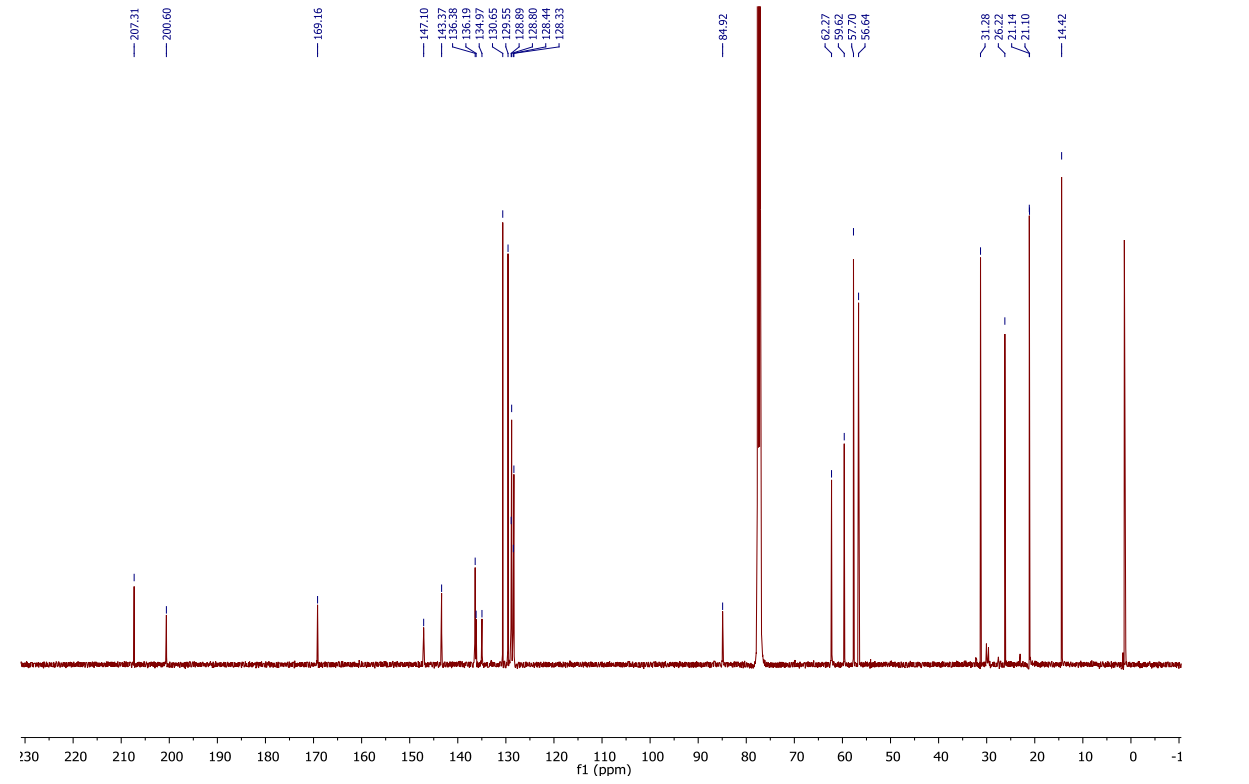
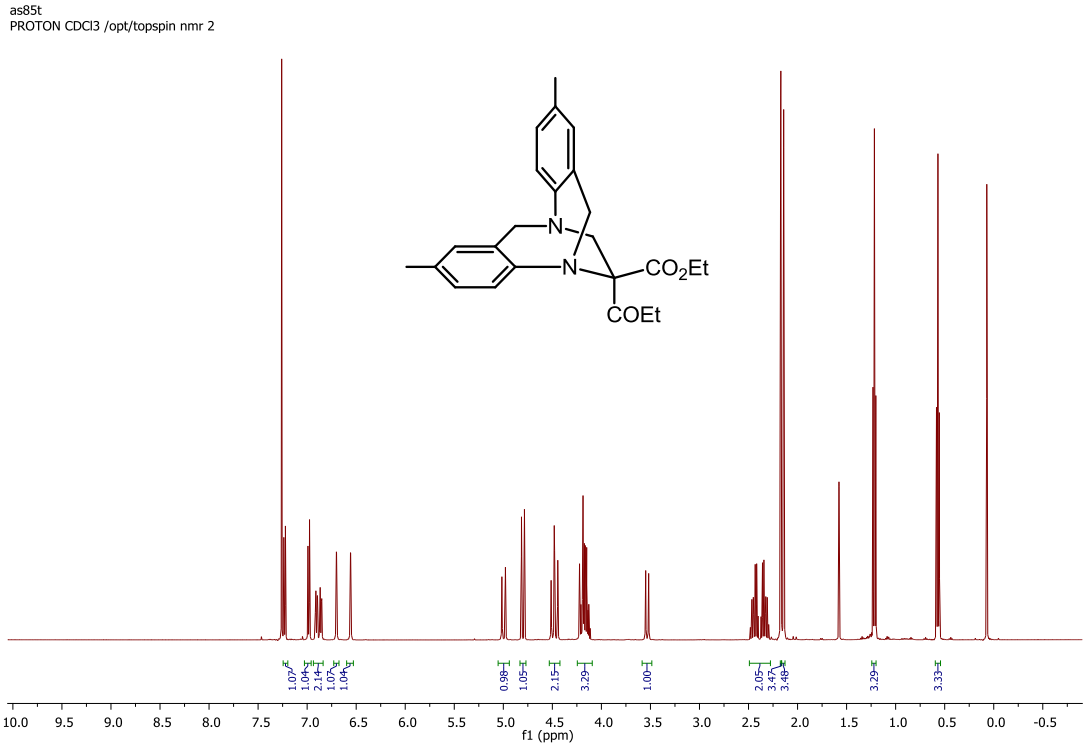
^{1}H NMR ($CDCl_3$, 400 MHz) 5d (Major)



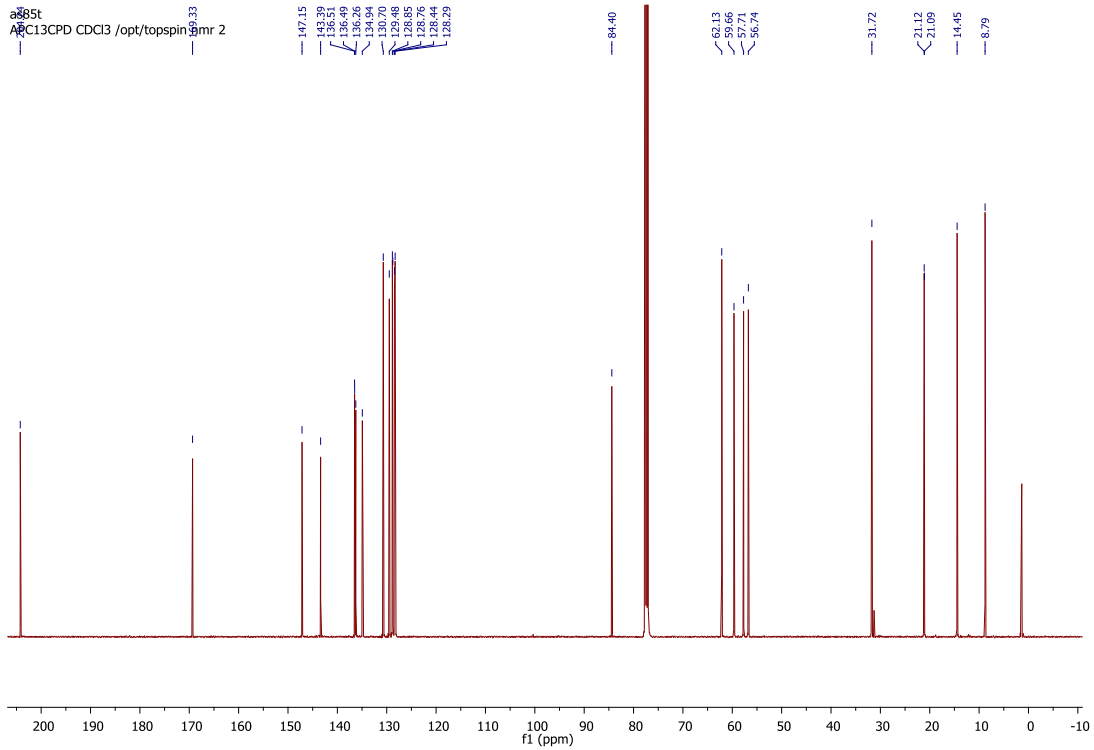
^{13}C NMR ($CDCl_3$, 100 MHz) 5d



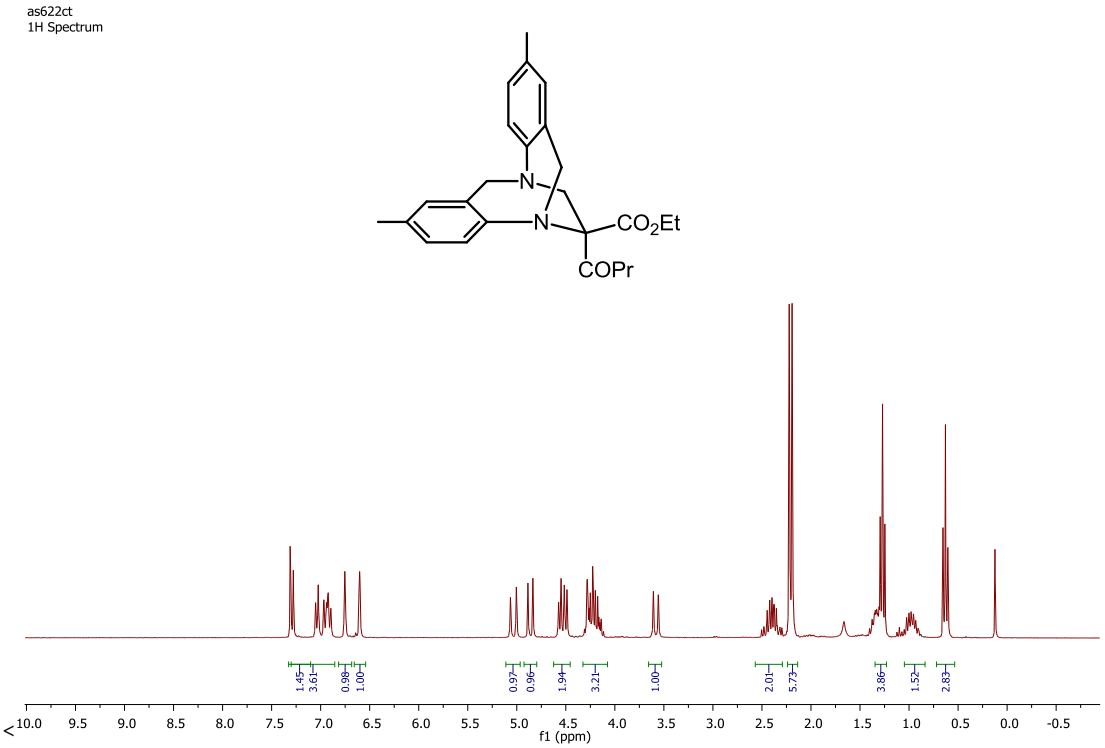
^{1}H NMR ($CDCl_3$, 400 MHz) 5e



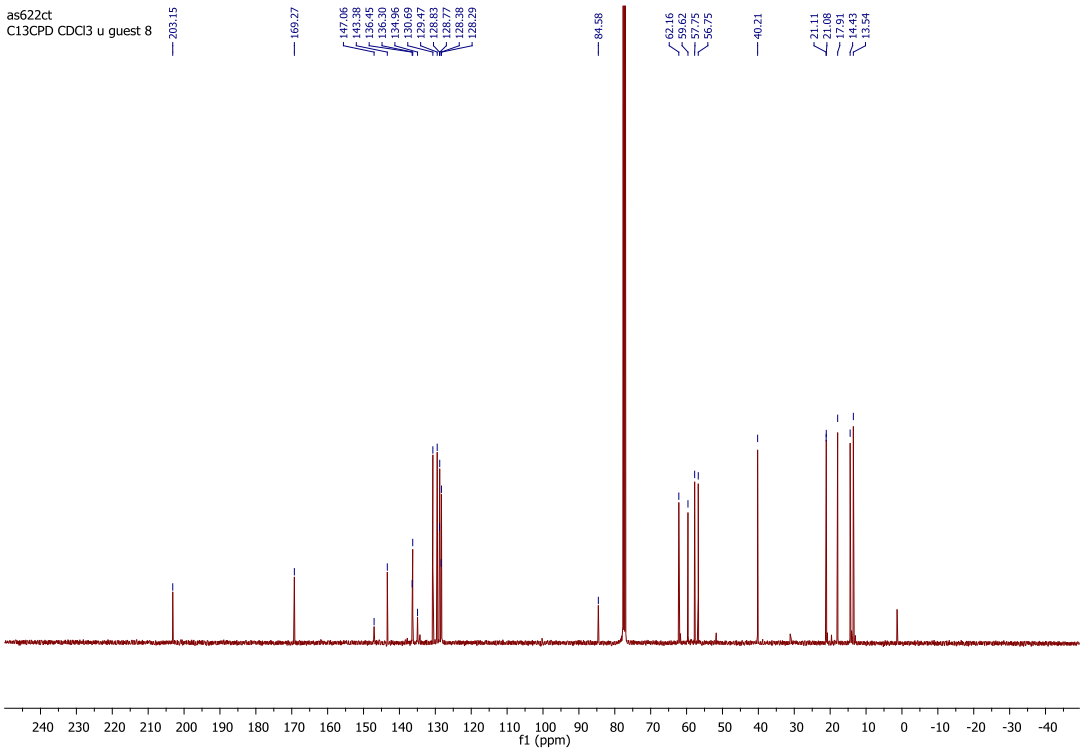
^{13}C NMR ($CDCl_3$, 125 MHz) 5e



^{1}H NMR ($CDCl_3$, 400 MHz) 5f (Major)



^{13}C NMR ($CDCl_3$, 100 MHz) 5f



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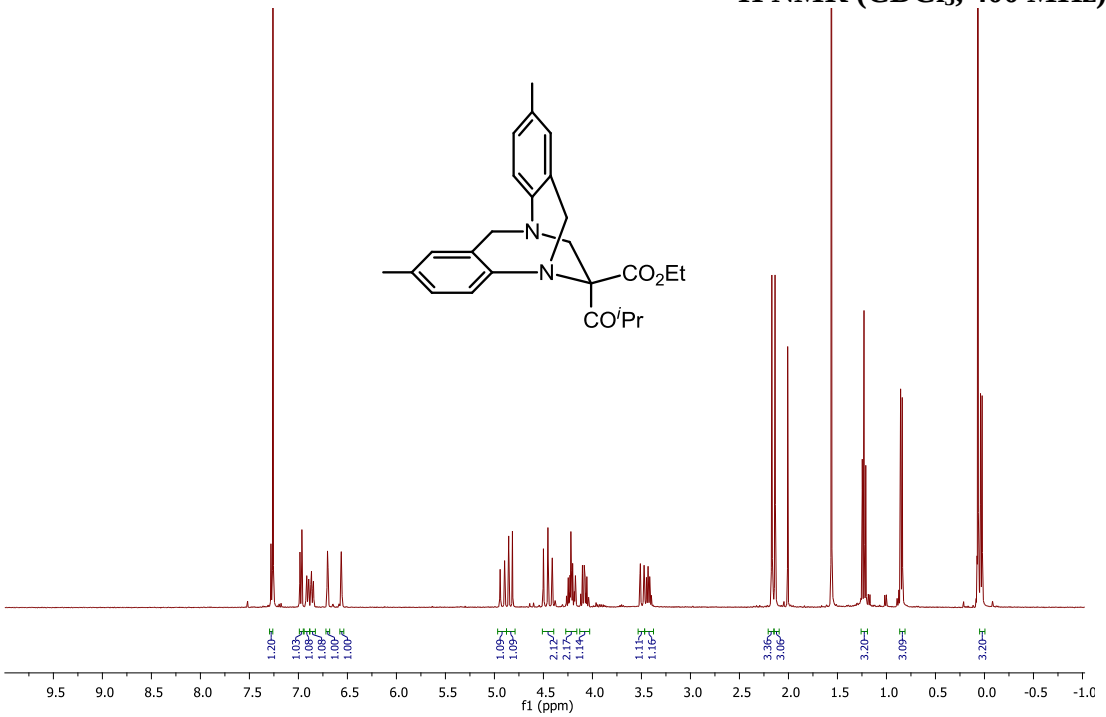
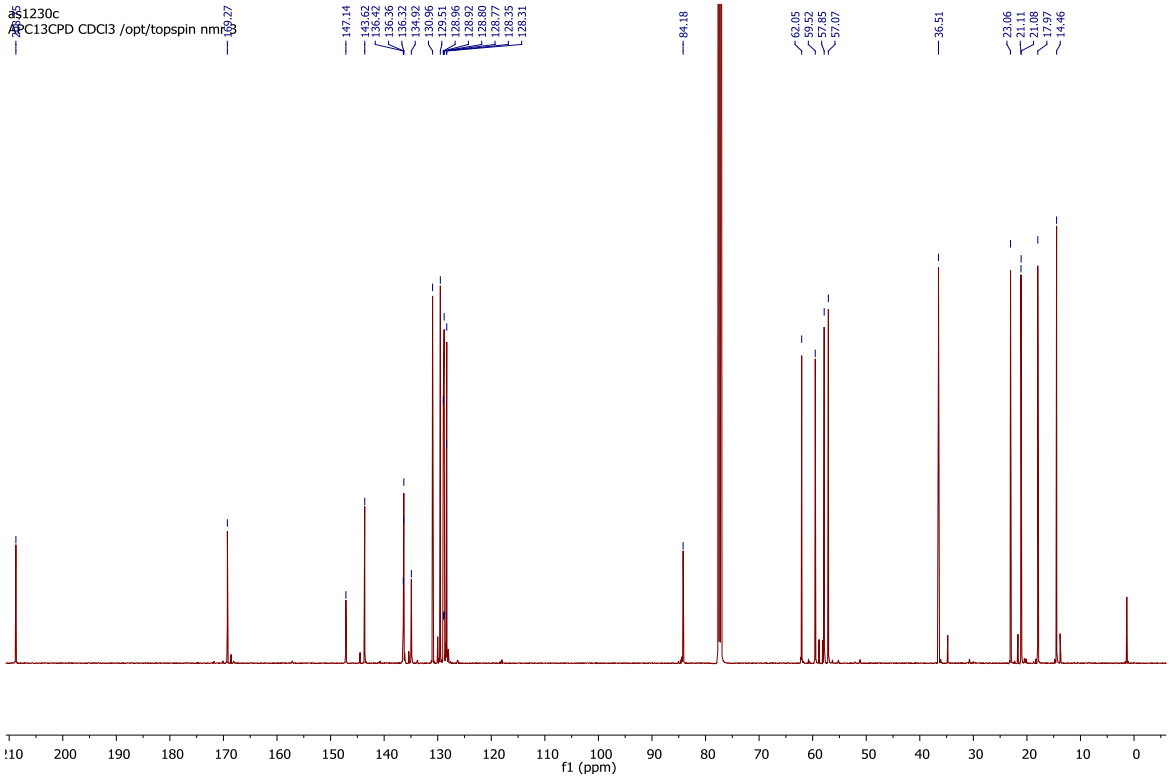
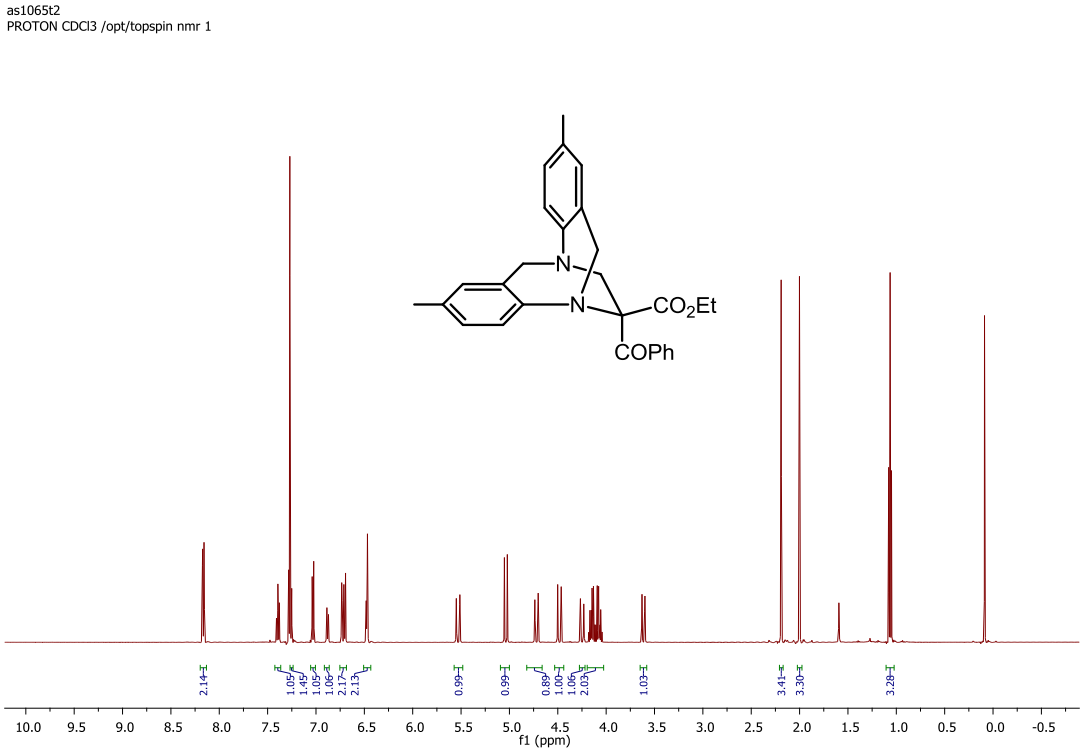
^{1}H NMR ($CDCl_3$, 400 MHz) 5g



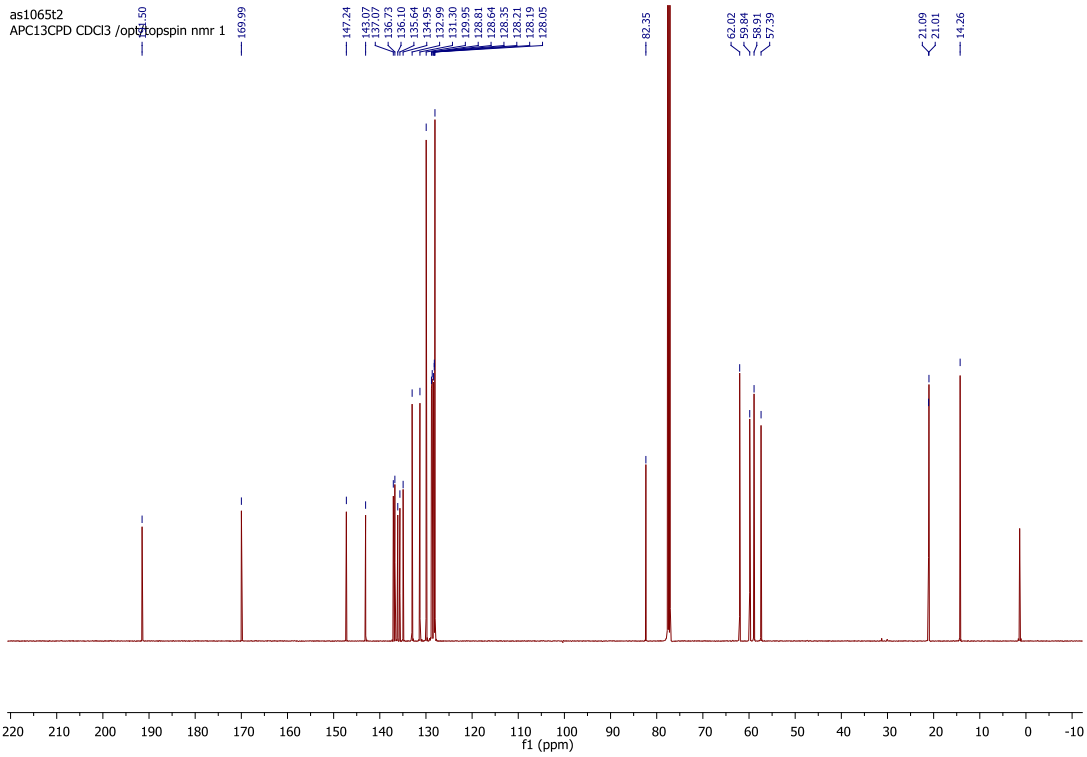
^{13}C NMR ($CDCl_3$, 100 MHz) 5g



^{1}H NMR ($CDCl_3$, 500 MHz) 5h



^{13}C NMR ($CDCl_3$, 125 MHz) 5h



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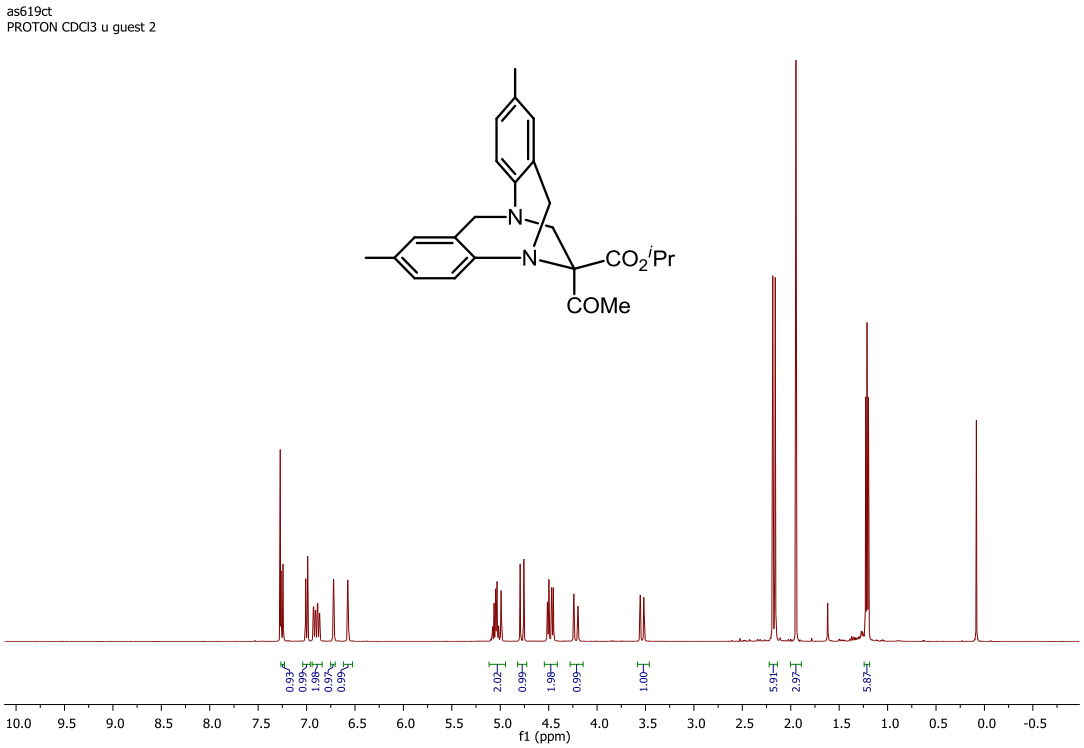
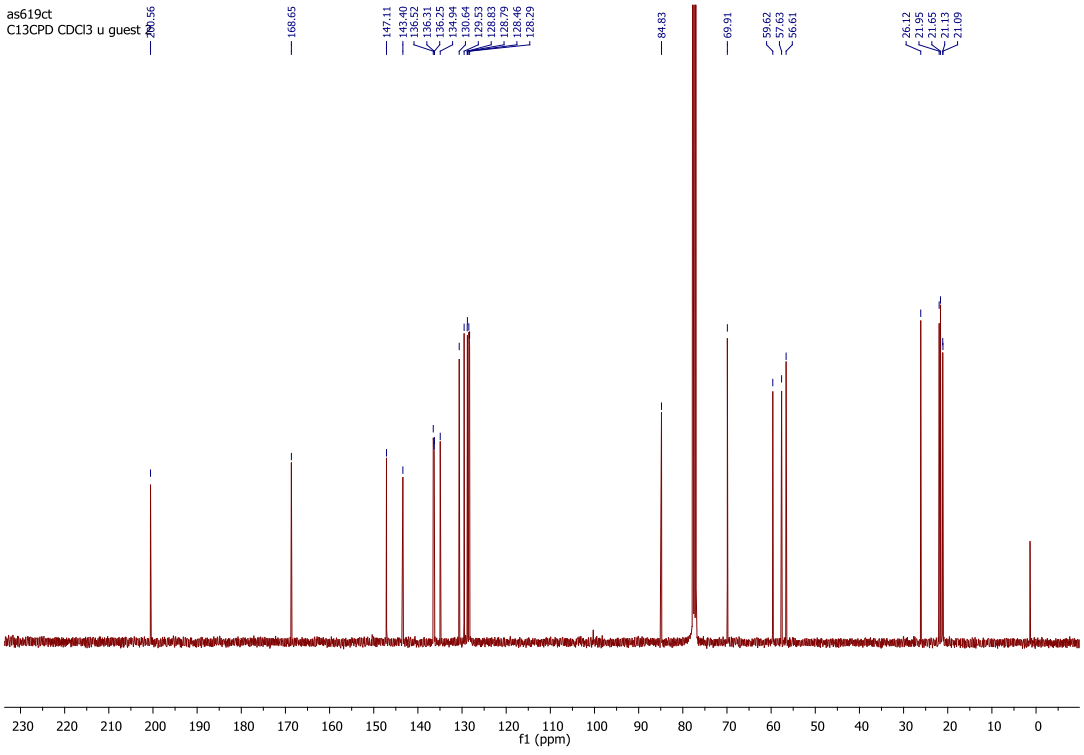
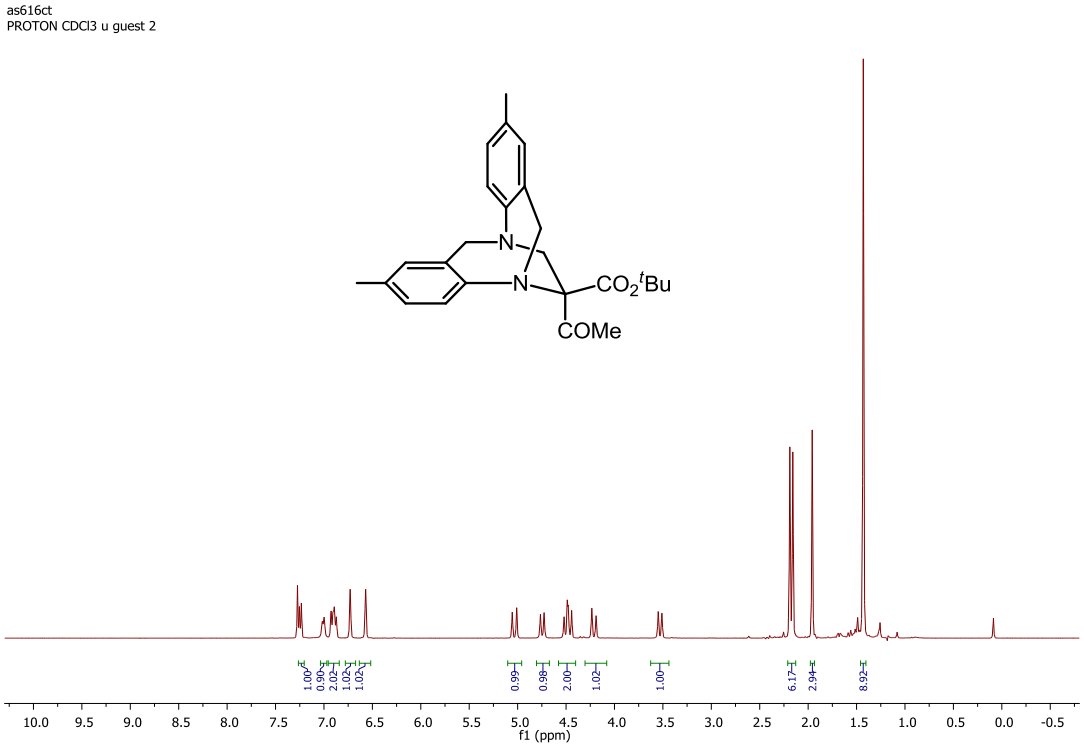
^{1}H NMR ($CDCl_3$, 400 MHz) 5i



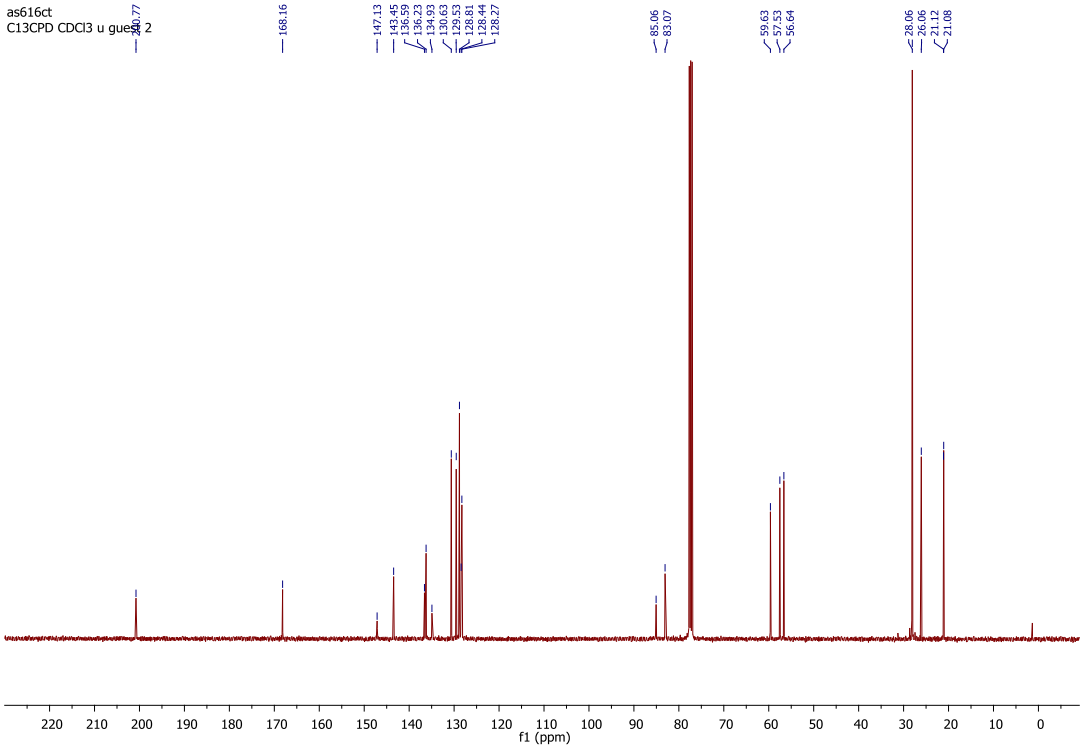
^{13}C NMR ($CDCl_3$, 100 MHz) 5i



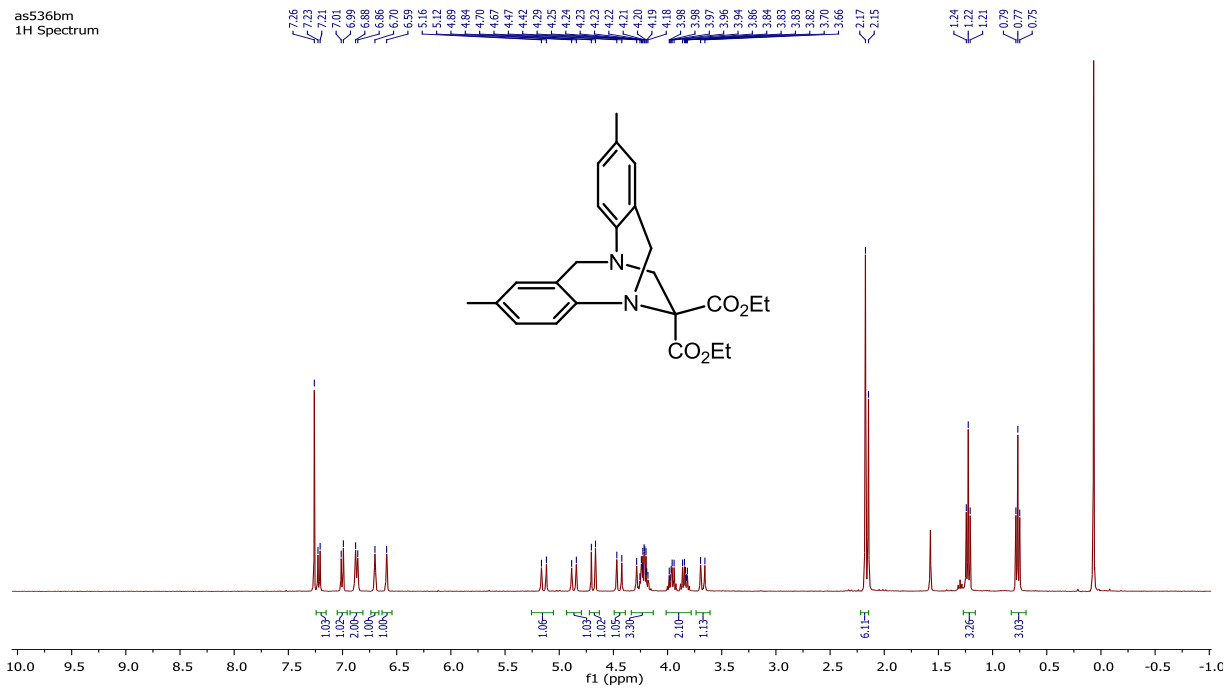
^{1}H NMR ($CDCl_3$, 400 MHz) 5j



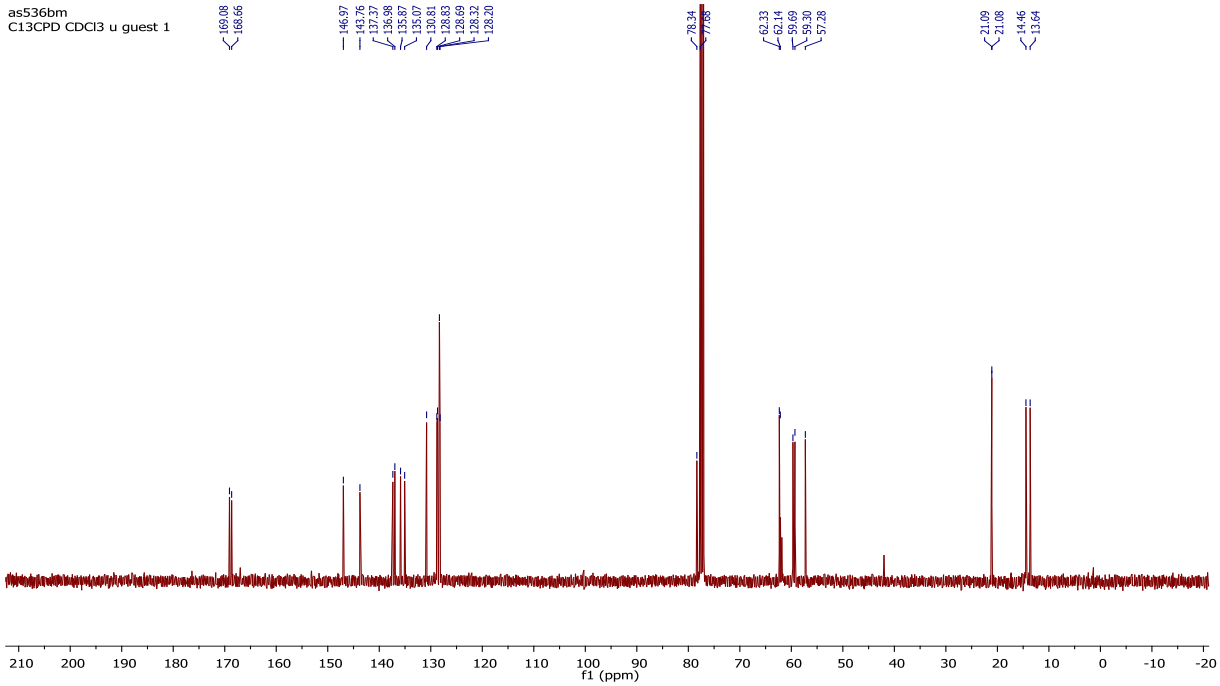
^{13}C NMR ($CDCl_3$, 100 MHz) 5j



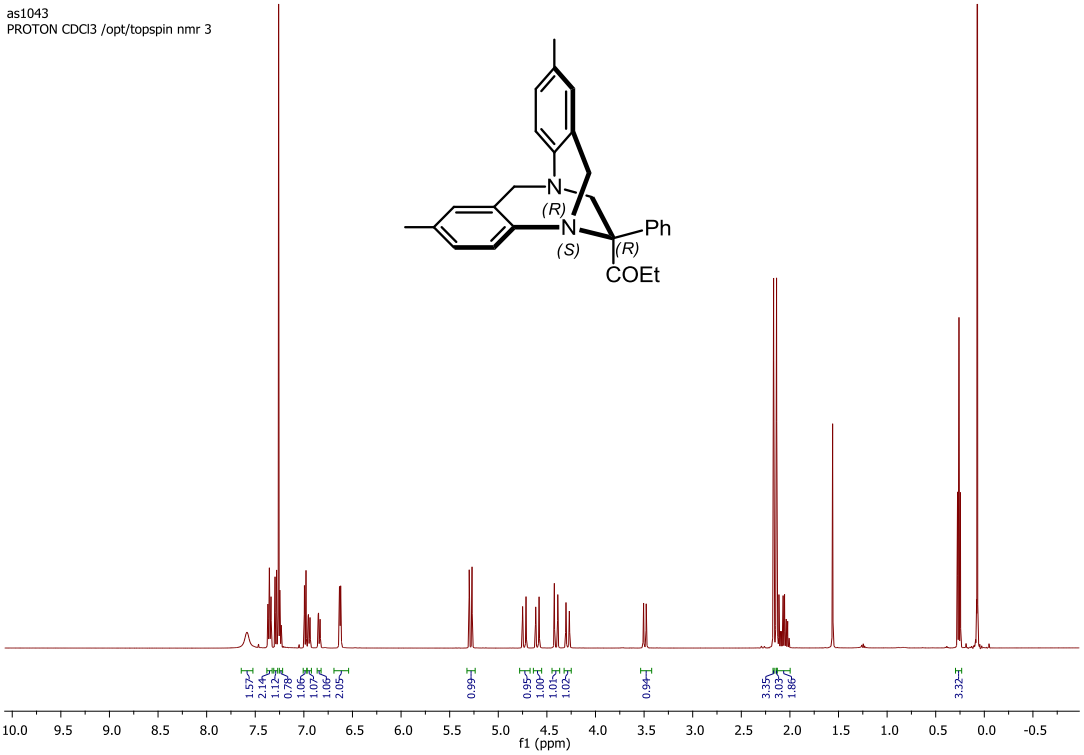
^{1}H NMR ($CDCl_3$, 400 MHz) 5k



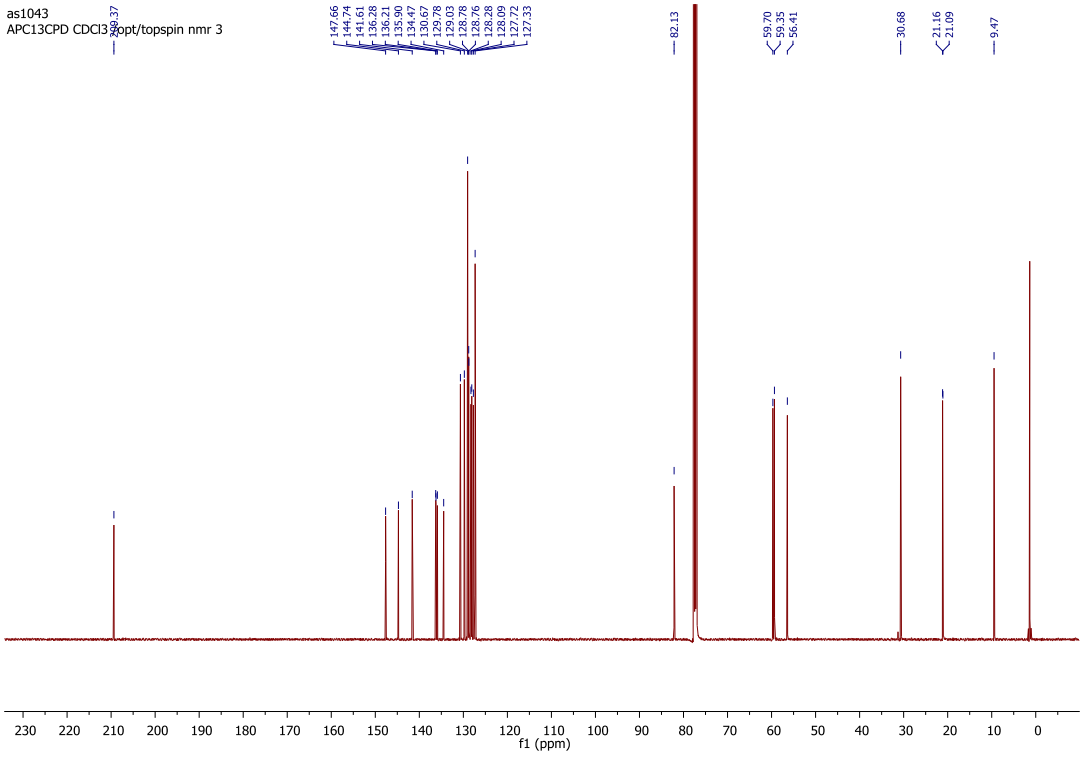
^{13}C NMR ($CDCl_3$, 100 MHz) 5k



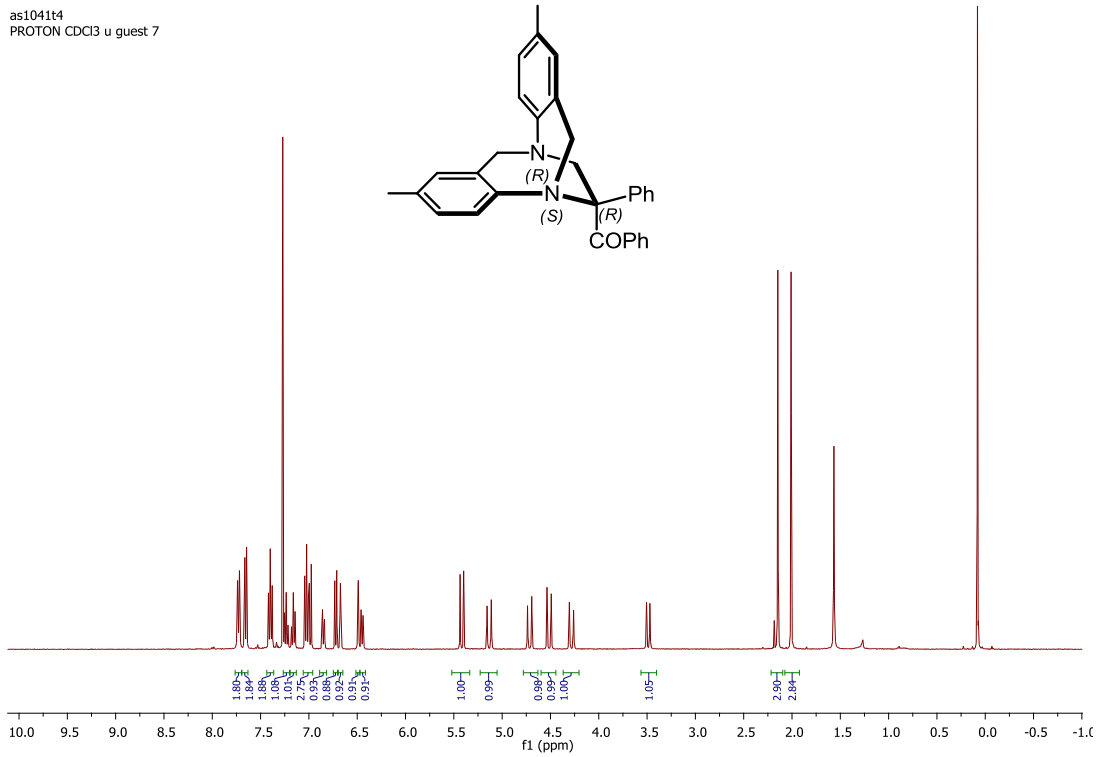
^{1}H NMR ($CDCl_3$, 500 MHz) 5l



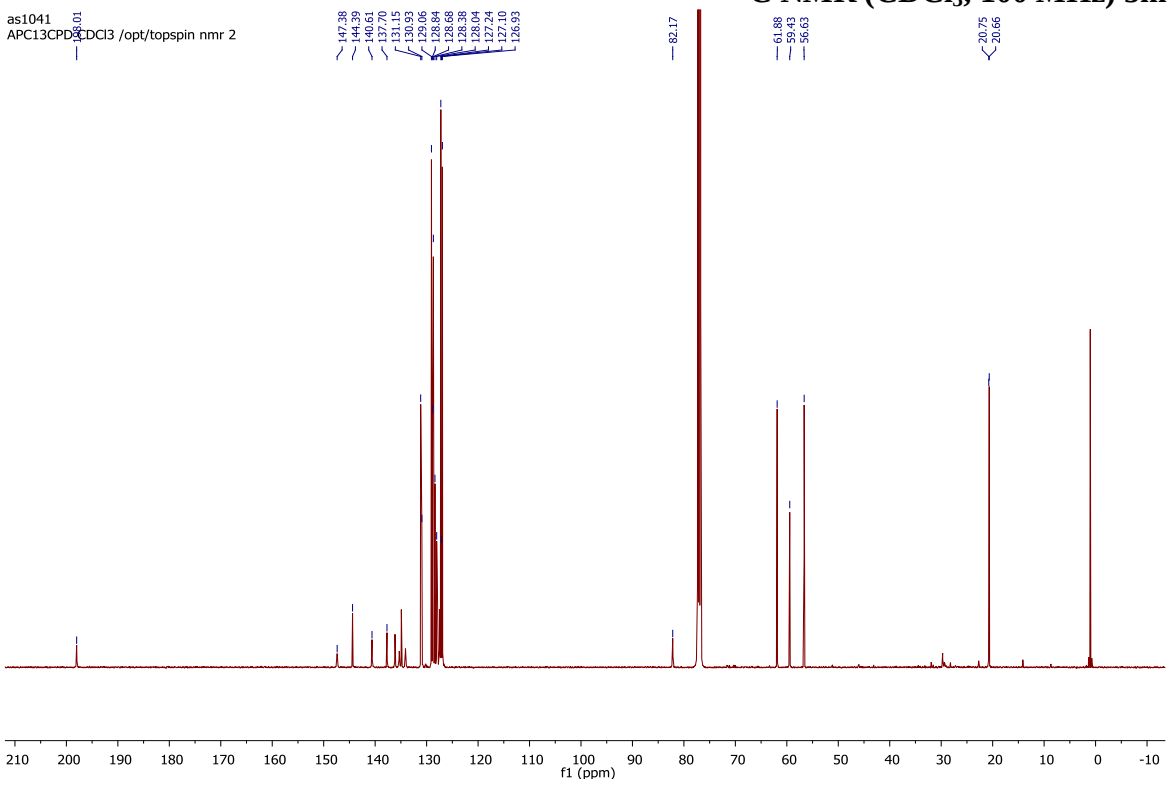
^{13}C NMR ($CDCl_3$, 125 MHz) 5l



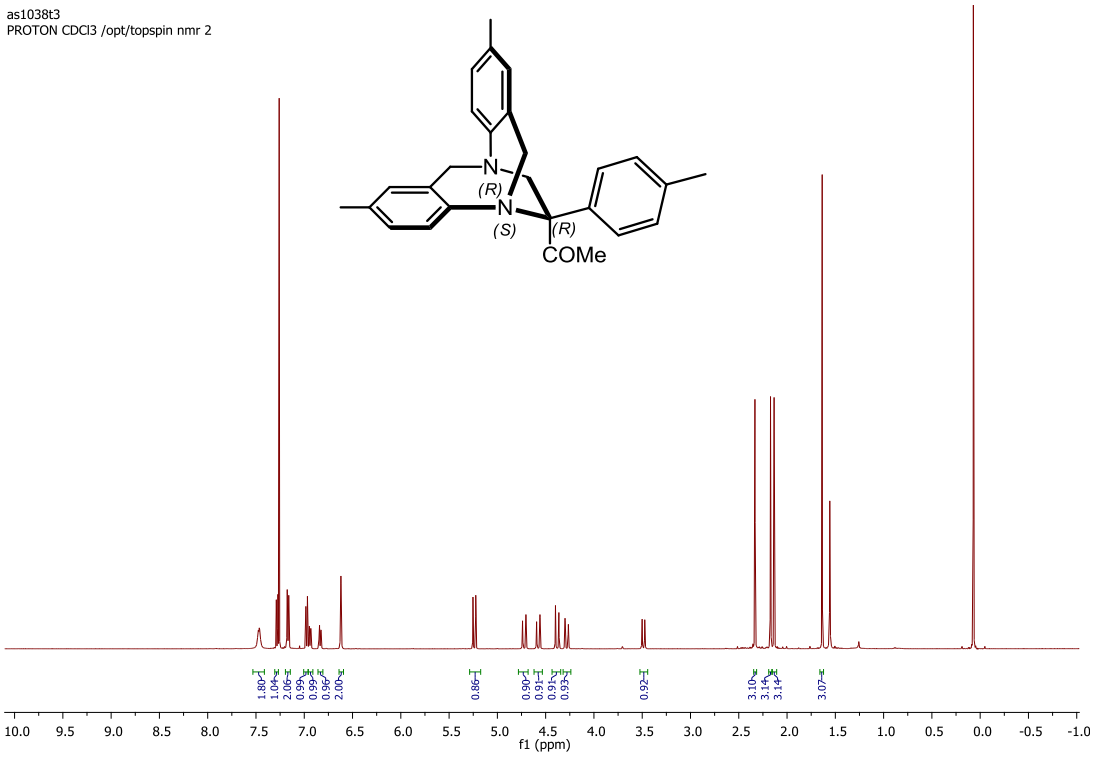
^{1}H NMR ($CDCl_3$, 400 MHz) 5m



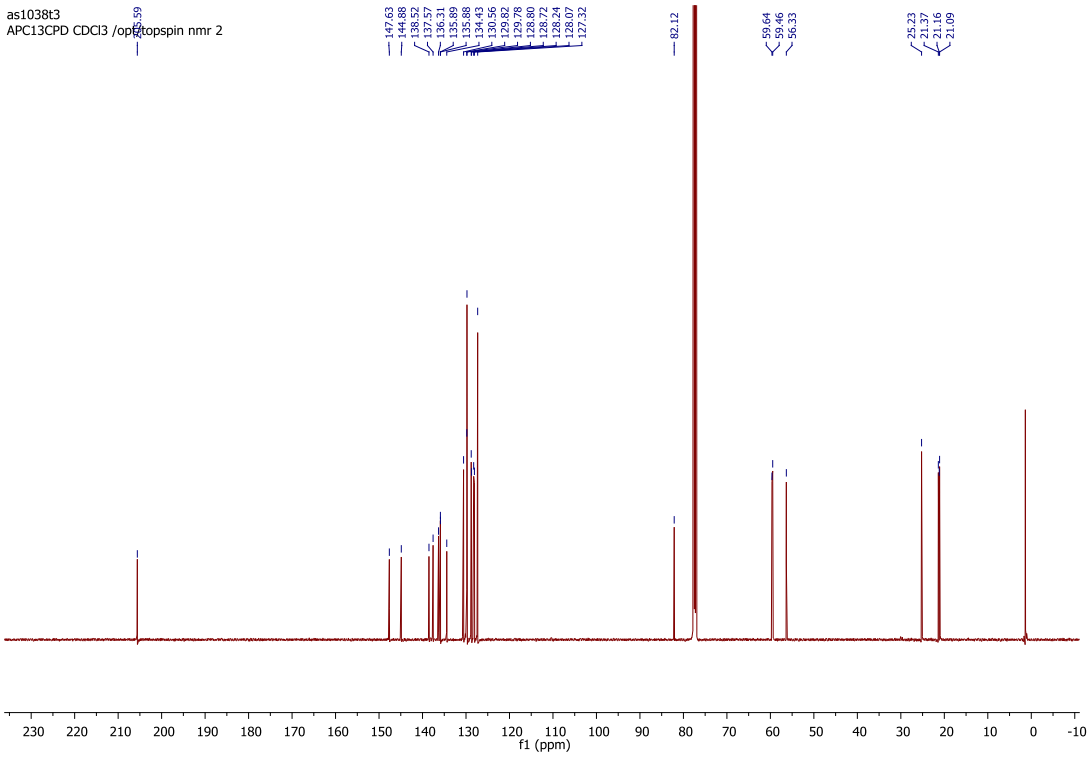
^{13}C NMR ($CDCl_3$, 100 MHz) 5m



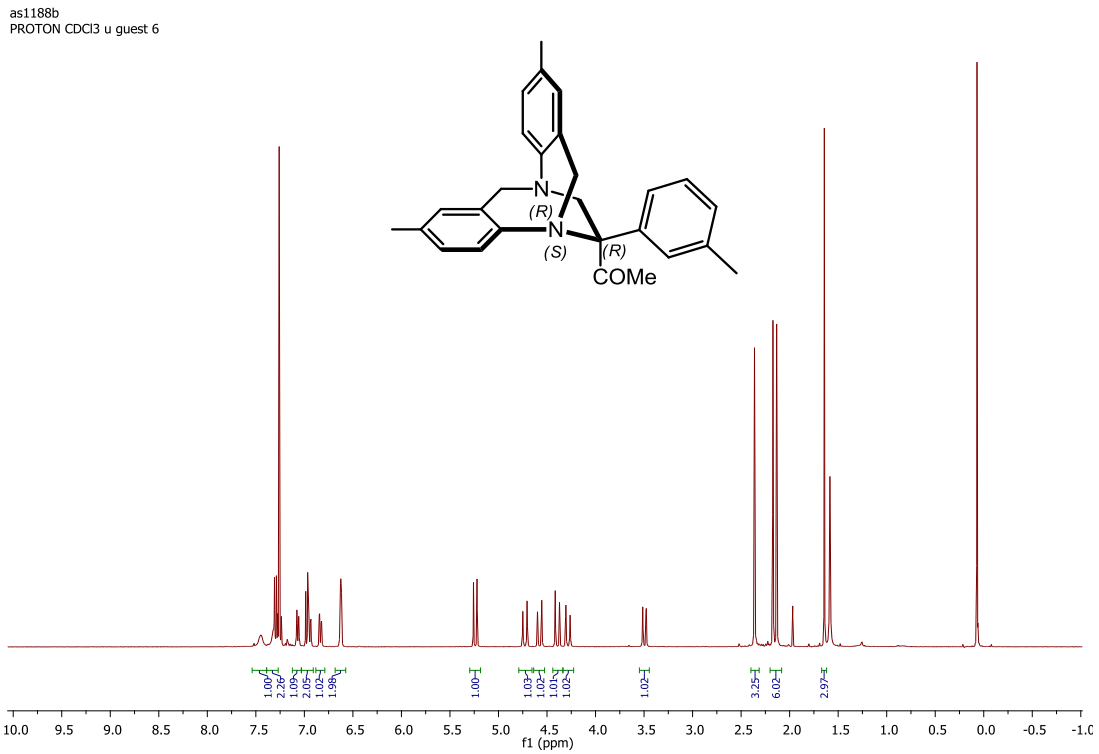
^{1}H NMR ($CDCl_3$, 500 MHz) 5n



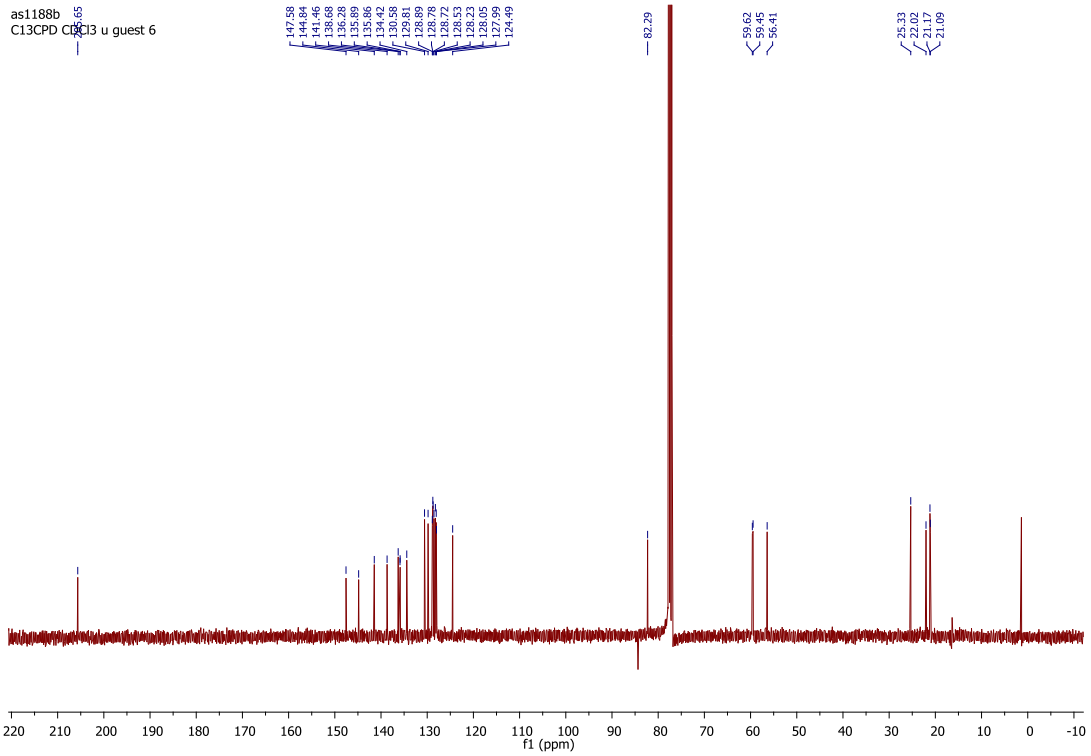
^{13}C NMR ($CDCl_3$, 125 MHz) 5n



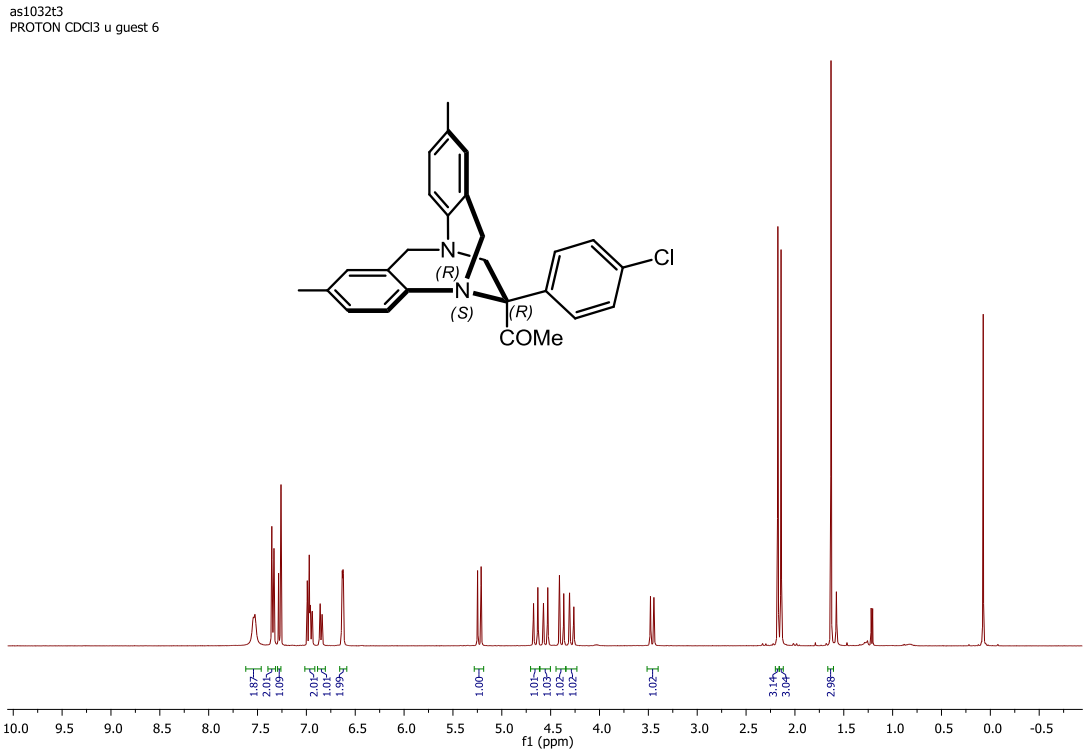
^{1}H NMR ($CDCl_3$, 400 MHz) 5o



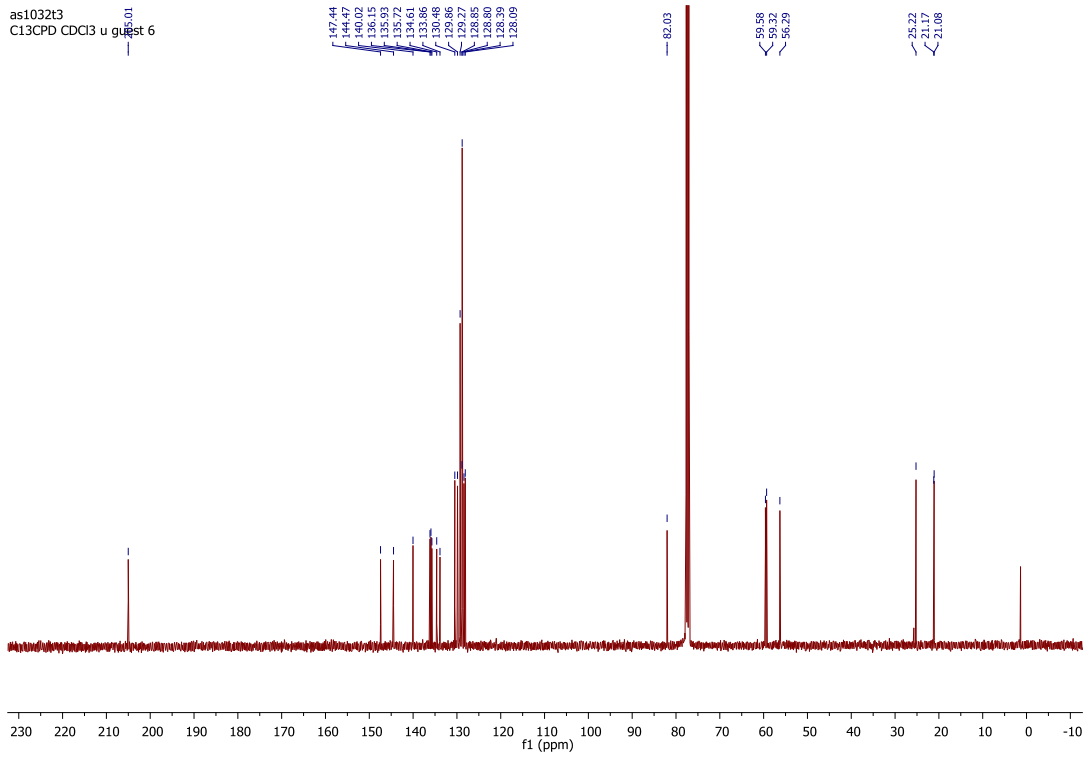
^{13}C NMR ($CDCl_3$, 100 MHz) 5o



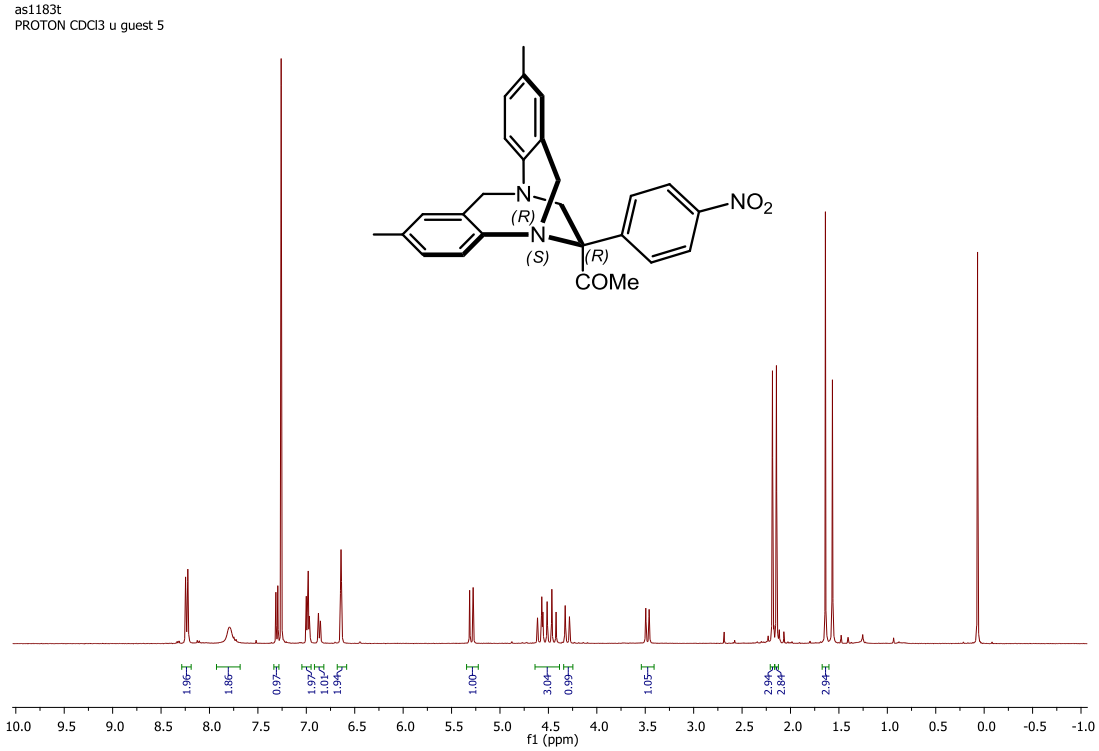
^{1}H NMR ($CDCl_3$, 400 MHz) 5p



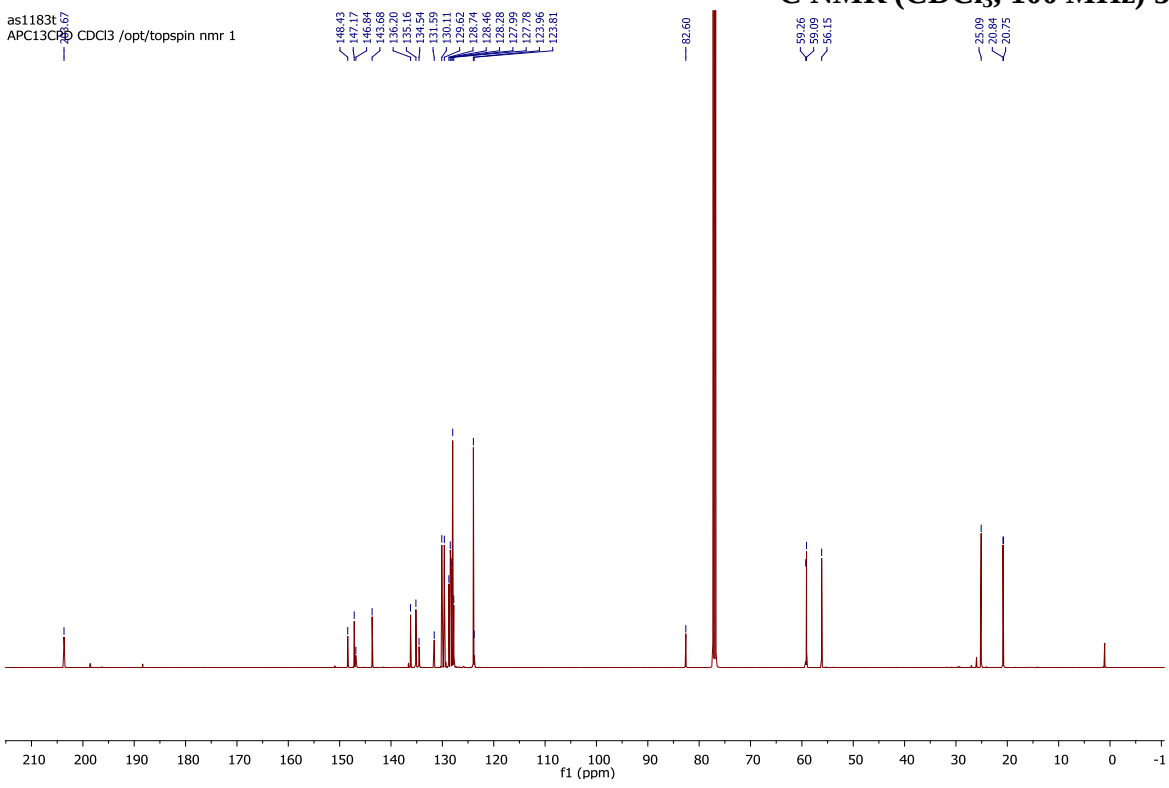
^{13}C NMR ($CDCl_3$, 100 MHz) 5p



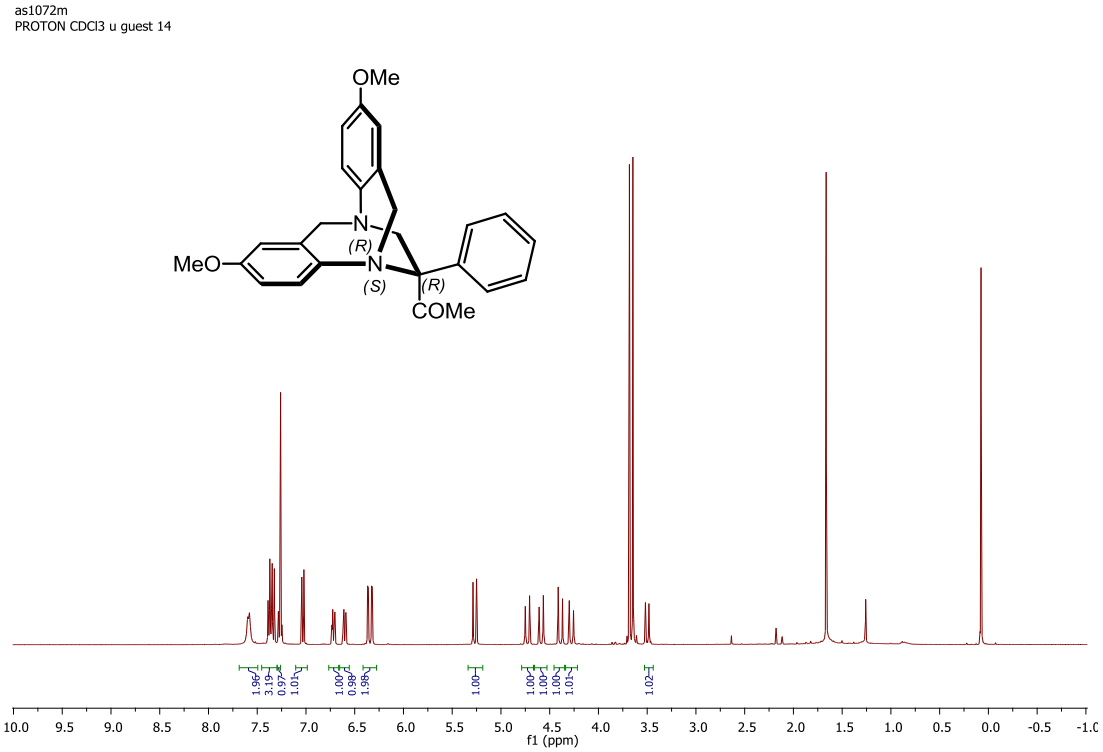
^{1}H NMR ($CDCl_3$, 400 MHz) 5q



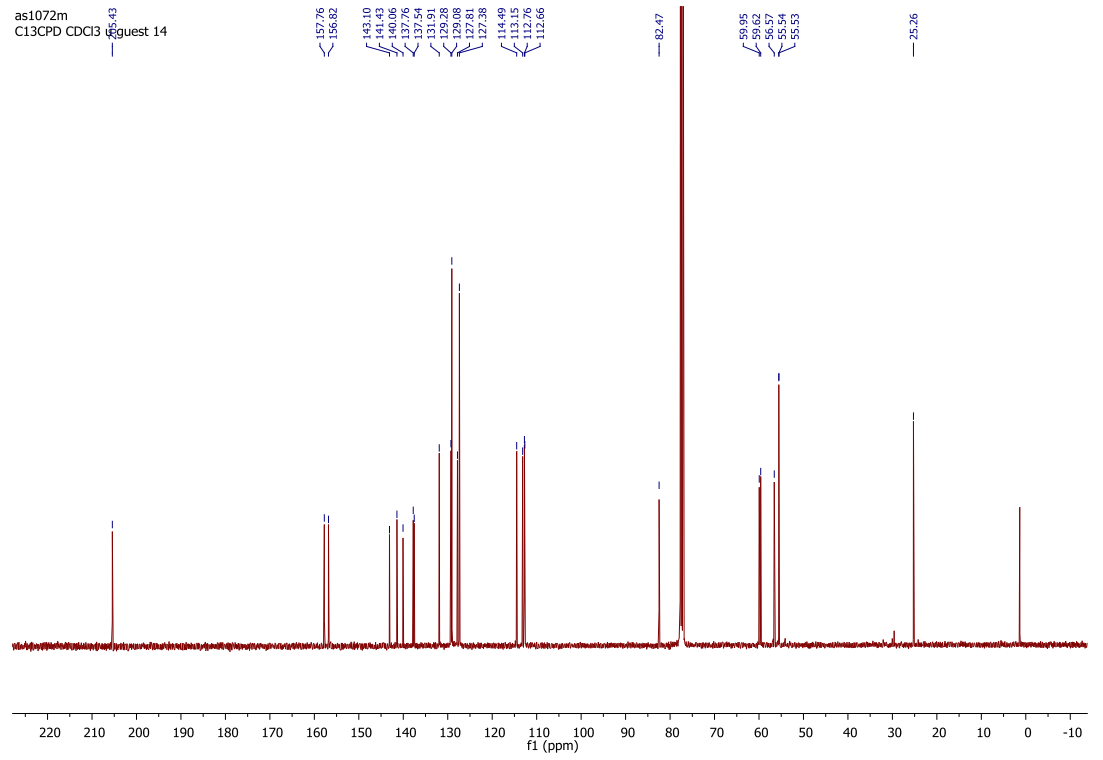
^{13}C NMR ($CDCl_3$, 100 MHz) 5q



^{1}H NMR ($CDCl_3$, 400 MHz) 5r



^{13}C NMR ($CDCl_3$, 100 MHz) 5r



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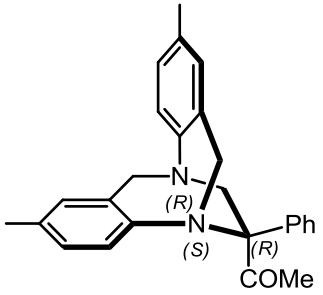
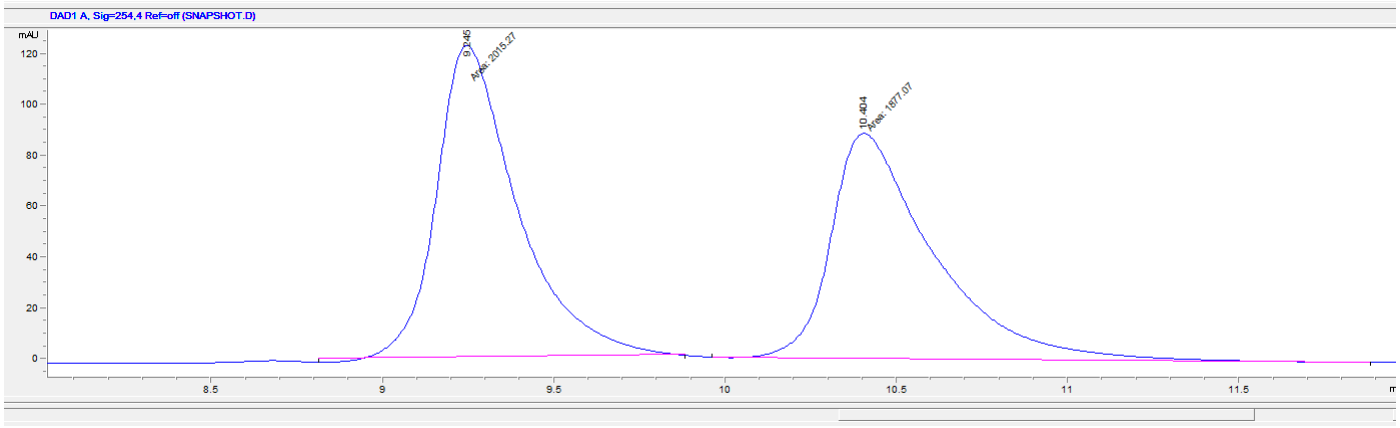
CSP-HPLC: Whelk *O1* column, n-Hexane/i-PrOH 99/1%, 0.7 ml/min, 23 °C, λ = 254 nm



5a



#	Time	Area	Height	Width	Area%	Symmetry
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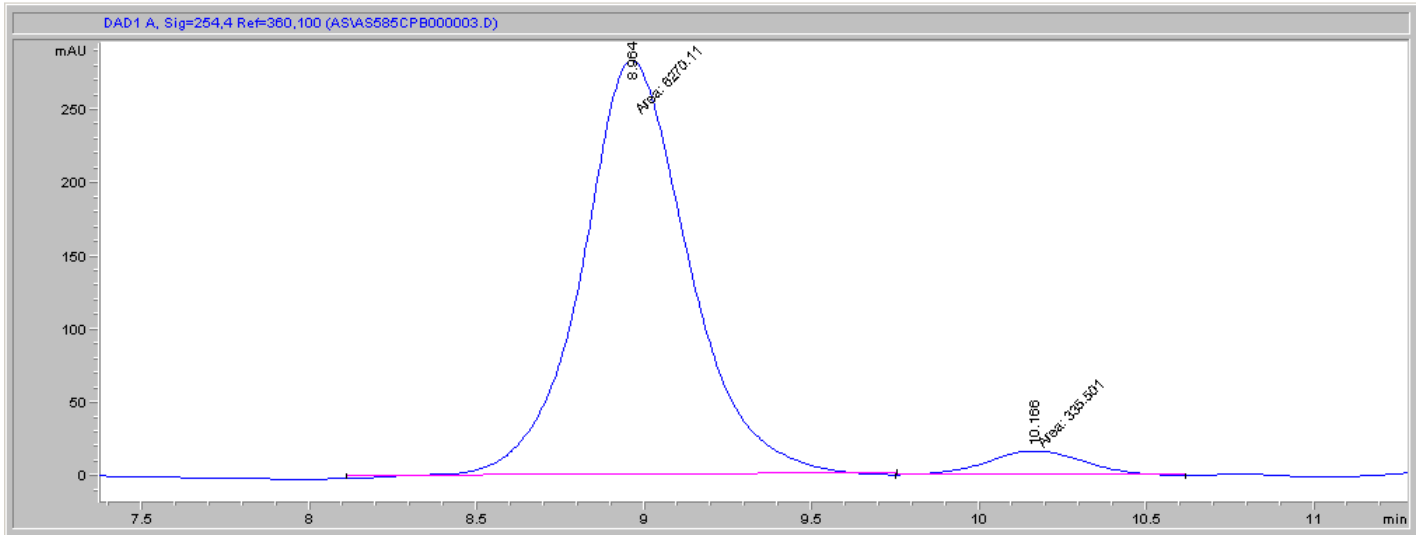
2	10.404	1877.1	88.8	0.3524	48.225	0.46



#	Time	Area	Height	Width	Area%	Symmetry
1	8.964	6270.1	283	0.3693	94.921	0.856
2	10.166	335.5	16.6	0.3364	5.079	0.956

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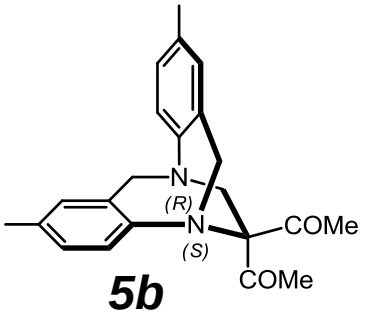
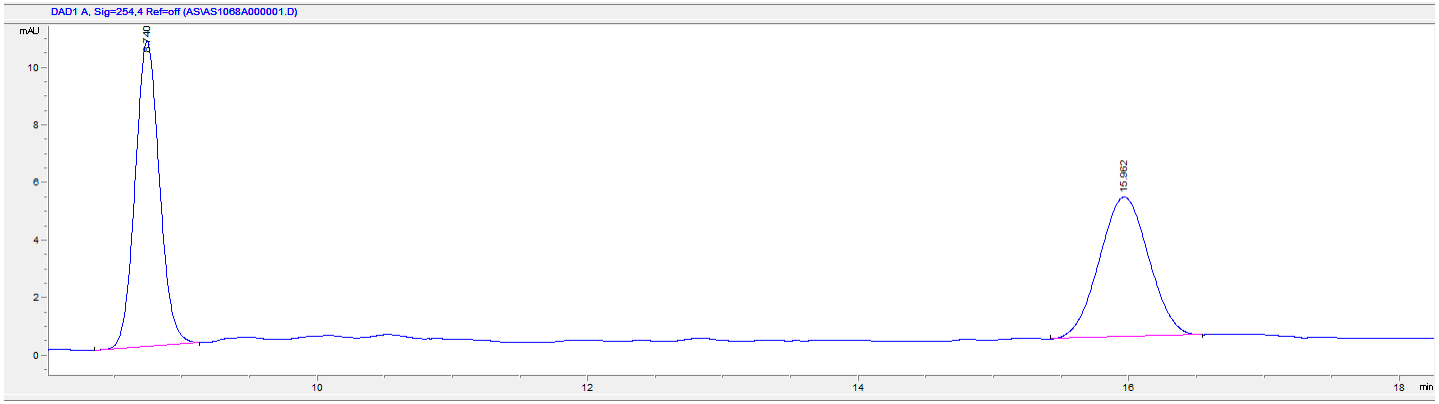
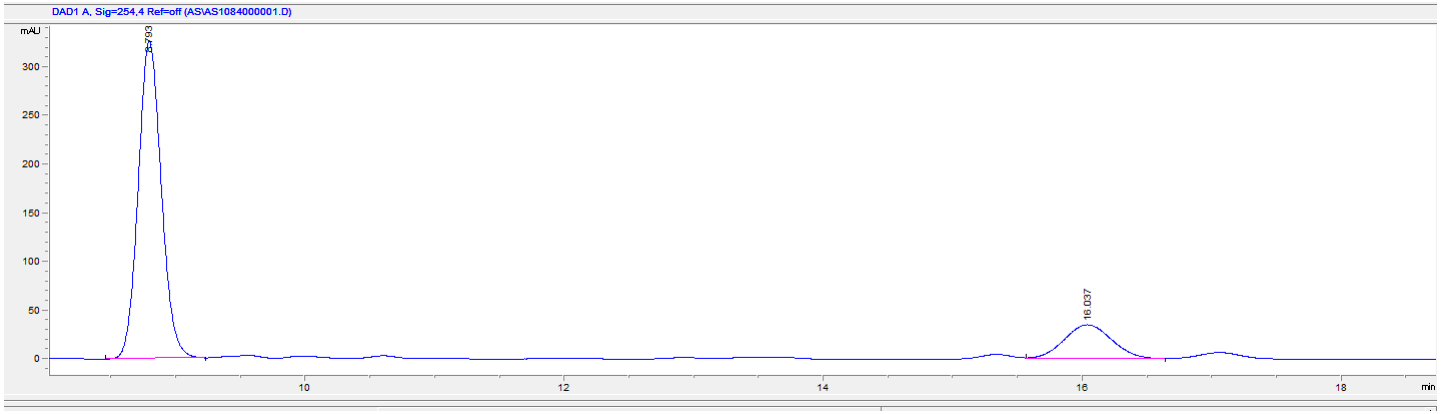
CSP-HPLC: IC column, *n-Hexane/i-PrOH 80/20%, 1 ml/min, 23 °C, λ = 254 nm*



5b



#	Time	Area	Height	Width	Area%	Symmetry
1	8.74	132.6	10.6	0.1928	51.797	0.917
2	15.962	123.4	4.9	0.3726	48.203	0.982



#	Time	Area	Height	Width	Area%	Symmetry
1	8.793	4038.7	325.8	0.1916	81.877	0.883
2	16.037	893.9	34.9	0.4008	18.123	0.943

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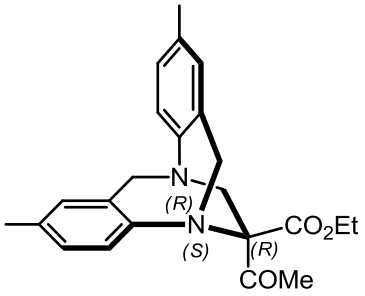
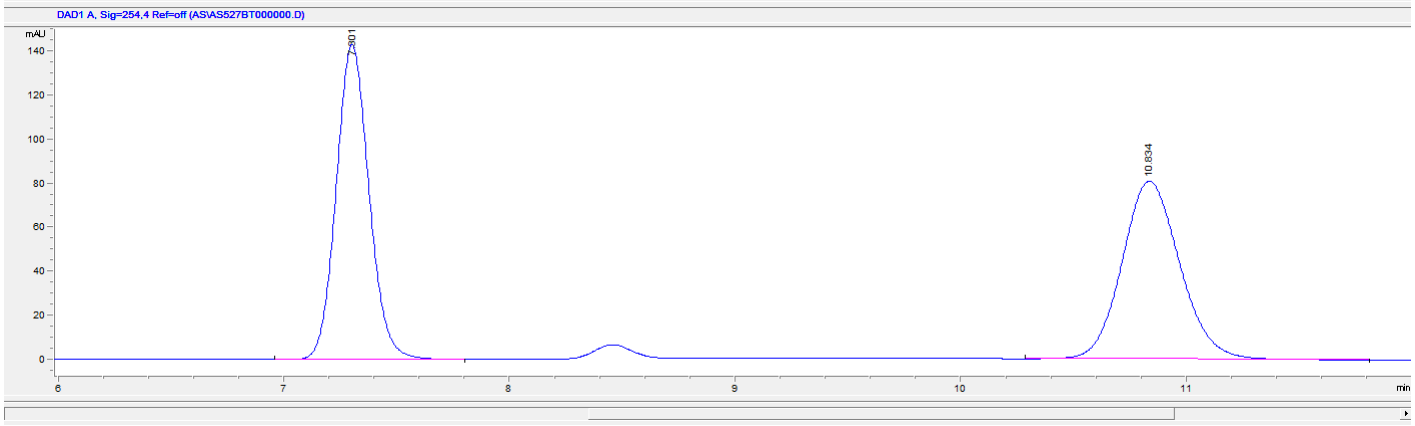
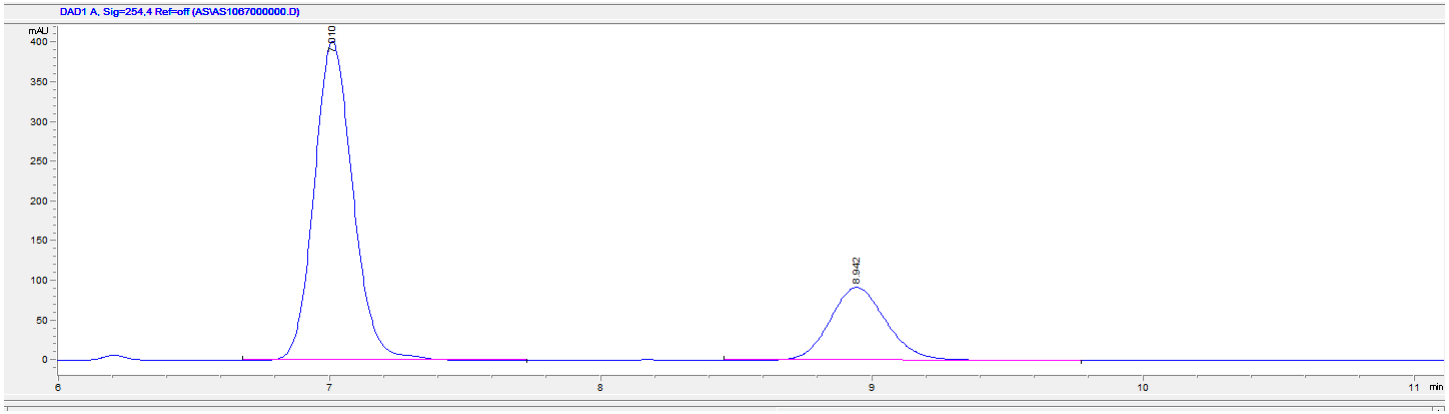
CSP-HPLC: IC column, *n-Hexane/i-PrOH 80/20%, 1 ml/min, 23 °C, λ = 254 nm*



5d



#	Time	Area	Height	Width	Area%	Symmetry
1	7.301	1450.9	143.1	0.1573	50.149	0.885
2	10.834	1442.3	80.8	0.2762	49.851	0.859



#	Time	Area	Height	Width	Area%	Symmetry
1	7.01	3986.6	401.4	0.1529	75.071	0.847
2	8.942	1323.8	91.7	0.2224	24.929	0.858

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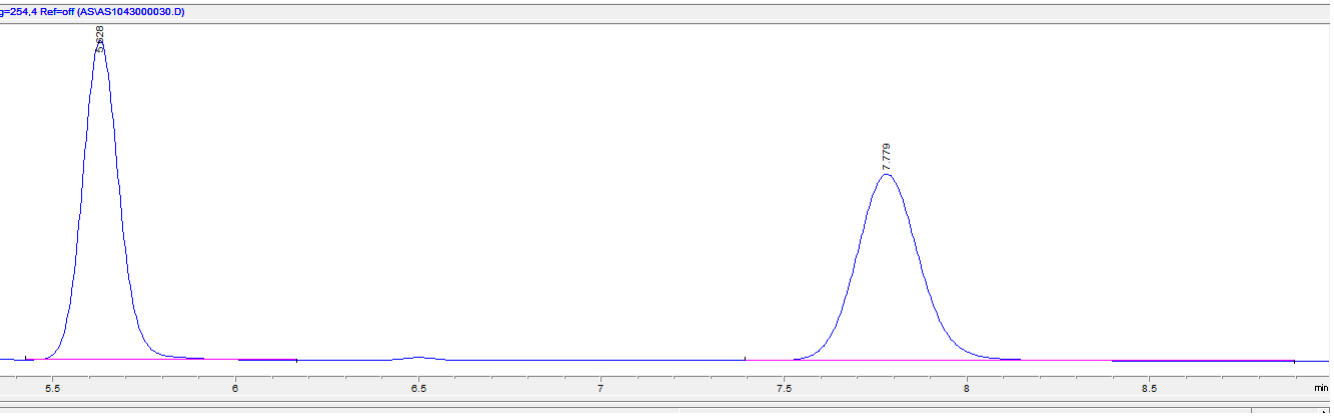
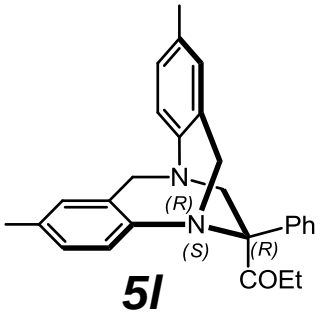
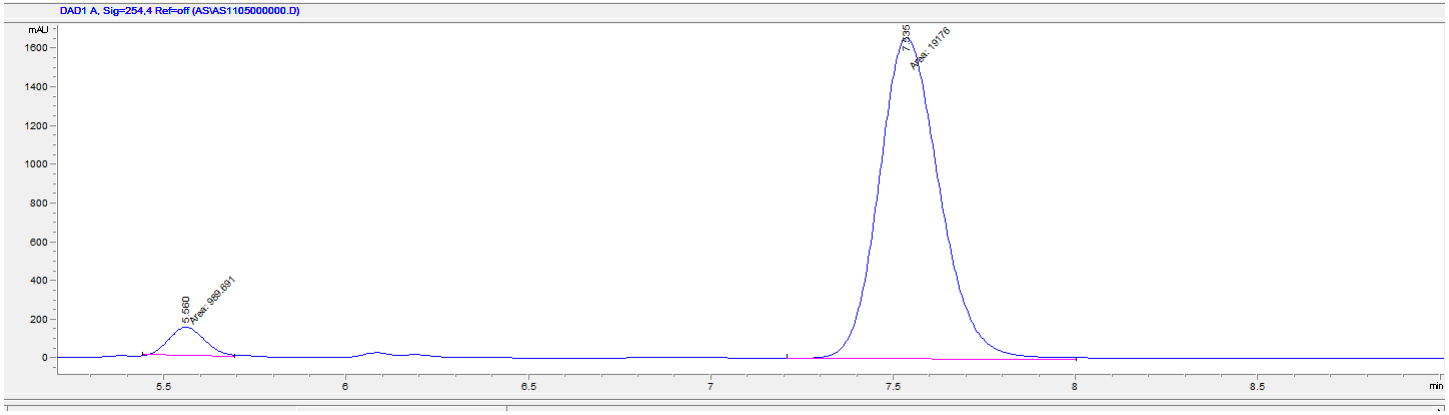
CSP-HPLC: IC column, *n-Hexane/i-PrOH 80/20%, 1 ml/min, 23 °C, λ = 254 nm*





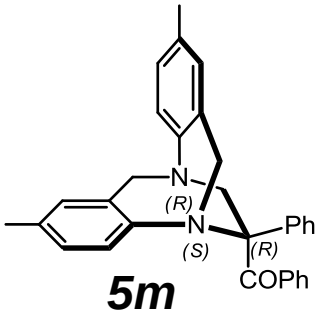
5l

#	Time	Area	Height	Width	Area%	Symmetry
1	5.628	713.9	101.3	0.1092	49.850	0.893
2	7.779	718.2	59.2	0.1875	50.150	0.902

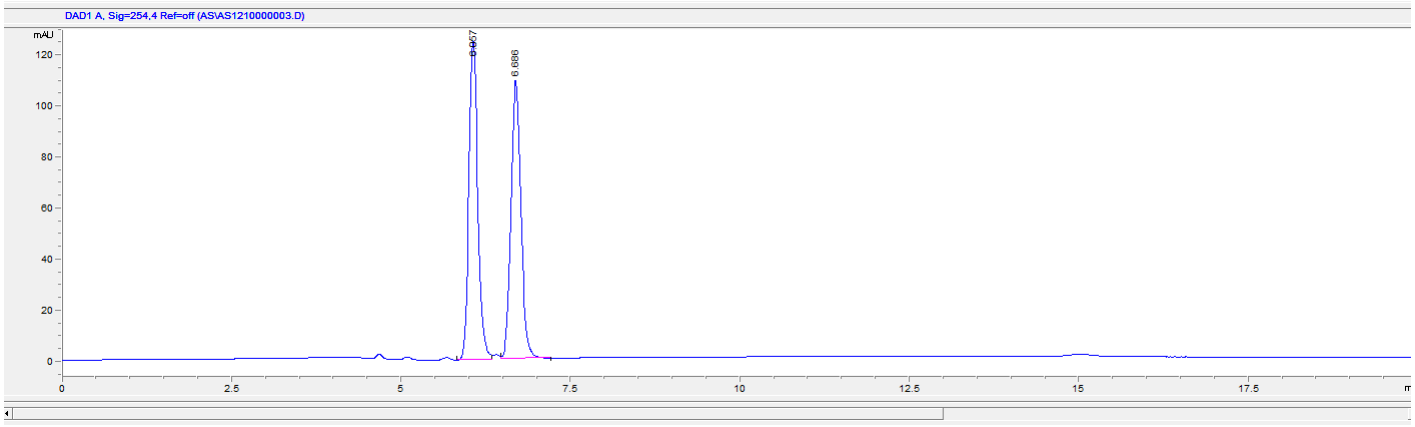


#	Time	Area	Height	Width	Area%	Symmetry
1	5.56	989.7	146	0.113	4.908	0.85
2	7.535	19176	1660	0.1925	95.092	0.817

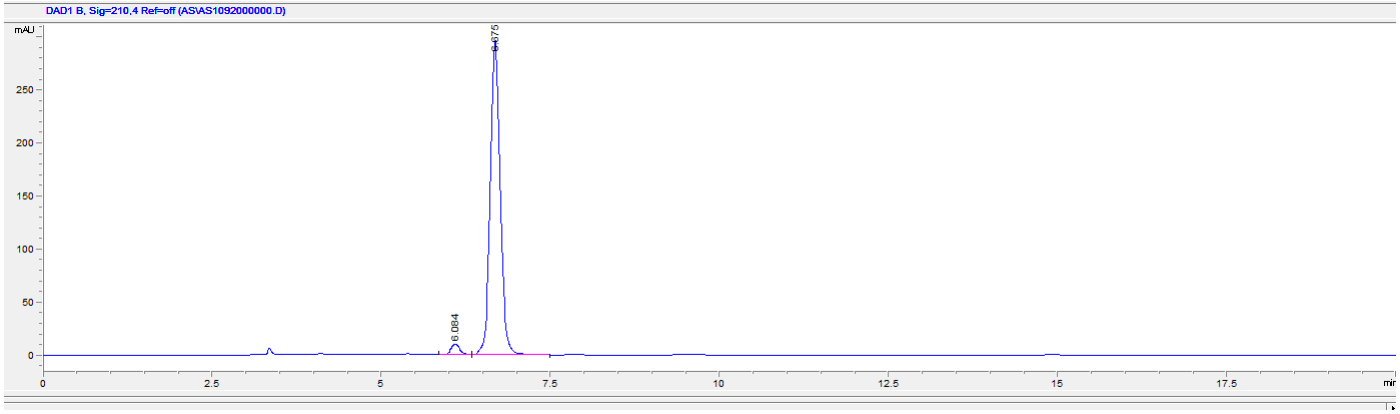
CSP-HPLC: IC column, *n-Hexane/i-PrOH 80/20%, 1 ml/min, 23 °C, λ = 254 nm*



5m



#	Time	Area	Height	Width	Area%	Symmetry
1	6.057	1144.2	124.6	0.1411	50.578	0.843
2	6.686	1118.1	109	0.1577	49.422	0.875



#	Time	Area	Height	Width	Area%	Symmetry
1	6.084	86.1	9.6	0.1389	2.741	0.86
2	6.675	3056.8	296.5	0.1583	97.259	0.9

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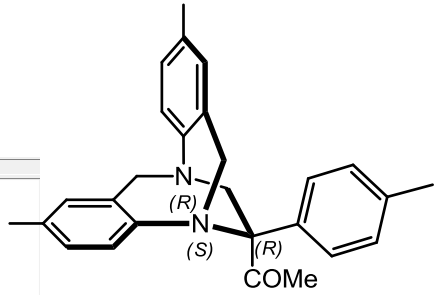
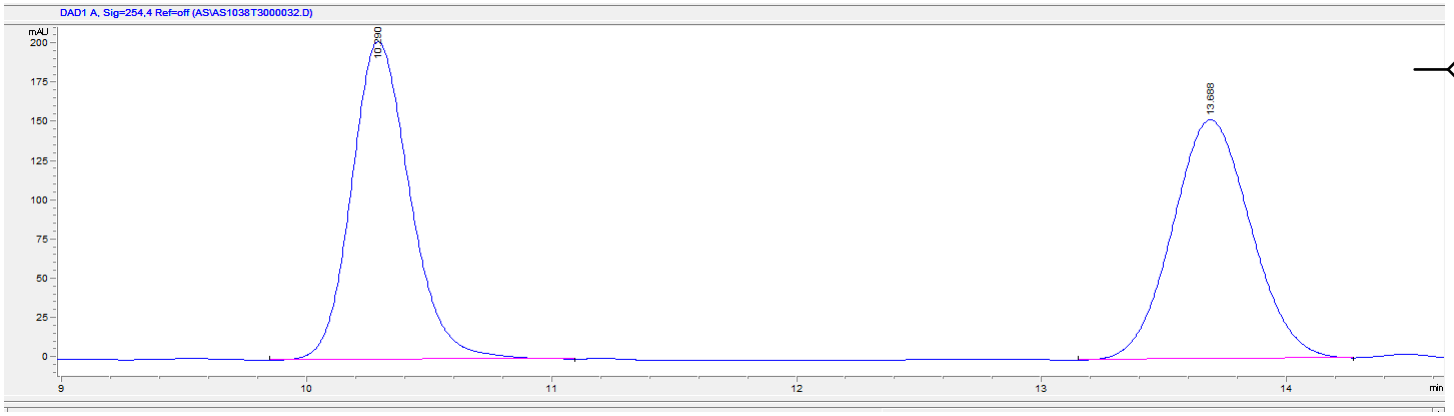
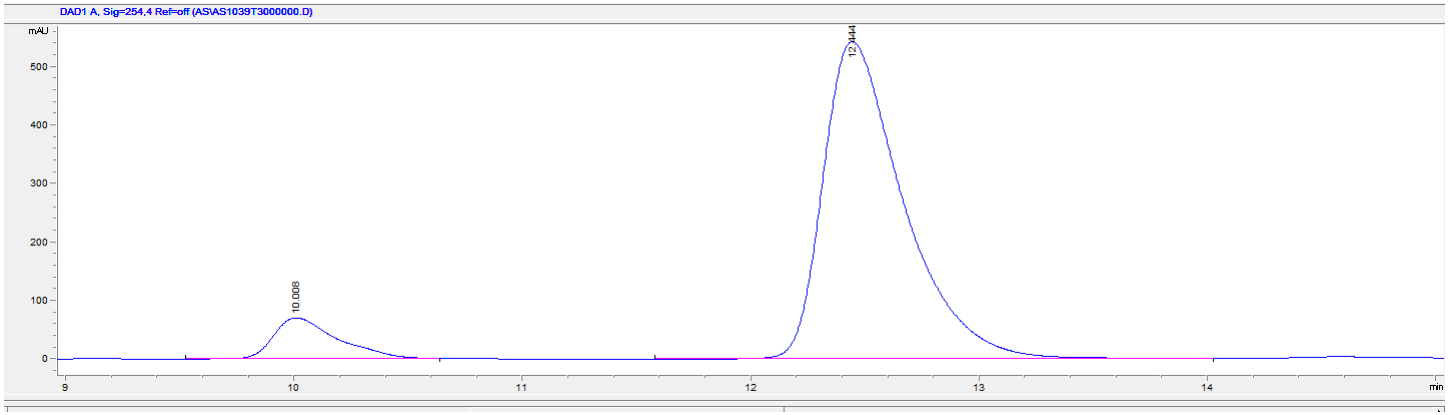
CSP-HPLC: IC column, *n-Hexane/i-PrOH 95/5%, 1 ml/min, 23 °C, λ = 254 nm*



5n



#	Time	Area	Height	Width	Area%	Symmetry
1	10.29	3364.2	202.9	0.2554	49.816	0.801
2	13.688	3389.1	152.6	0.3462	50.184	0.915



#	Time	Area	Height	Width	Area%	Symmetry
1	10.008	1348.1	70	0.2847	9.235	0.524
2	12.444	13250.1	543.1	0.3656	90.765	0.54

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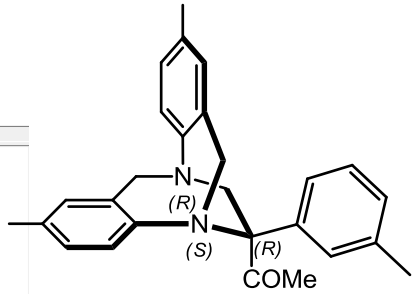
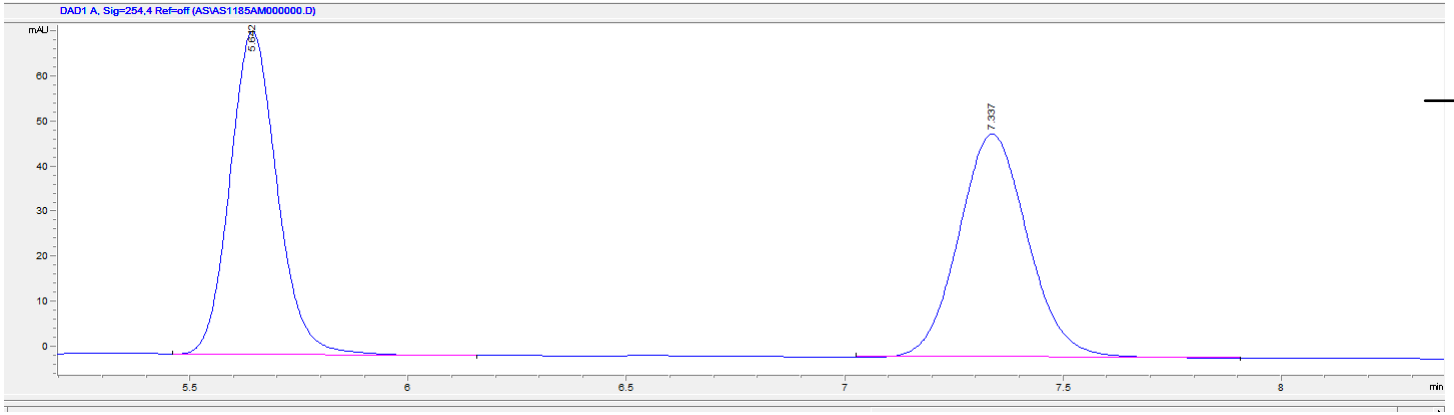
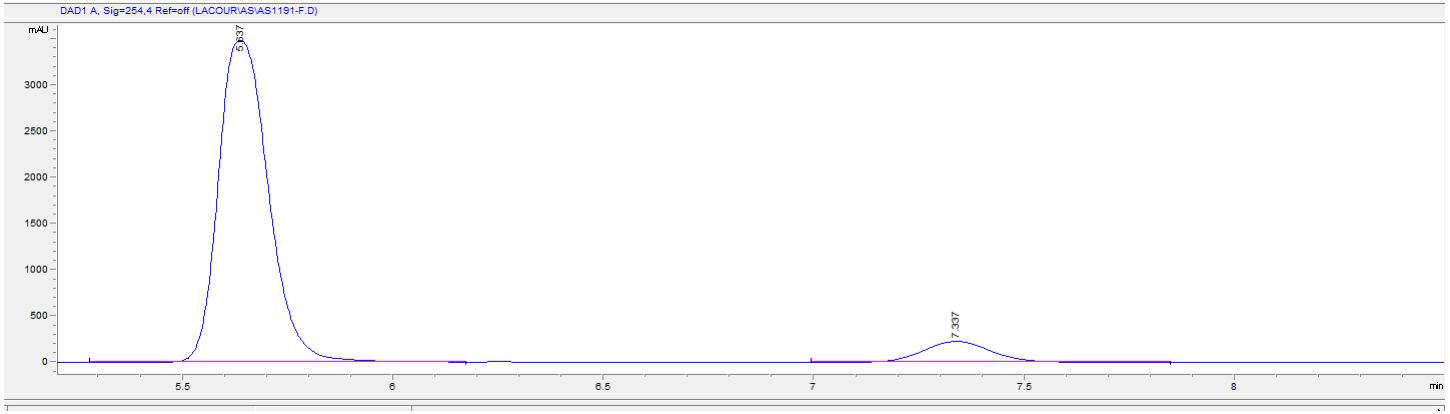
CSP-HPLC: IC column, *n-Hexane/i-PrOH 80/20%, 1 ml/min, 23 °C, λ = 254 nm*



5o



#	Time	Area	Height	Width	Area%	Symmetry
1	5.642	539.2	71.8	0.1156	49.662	0.853
2	7.337	546.6	49.7	0.1704	50.338	0.904



#	Time	Area	Height	Width	Area%	Symmetry
1	5.637	28700.8	3481.4	0.1282	91.871	0.72
2	7.337	2539.5	225.7	0.1743	8.129	0.902

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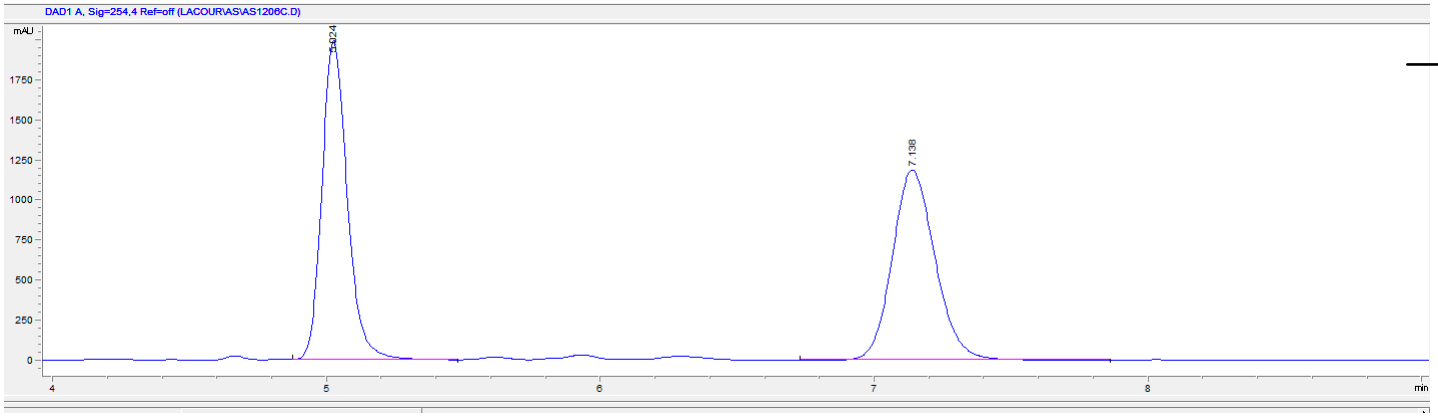
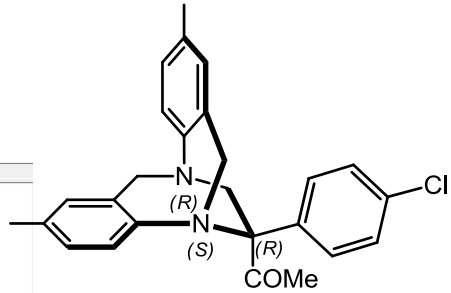
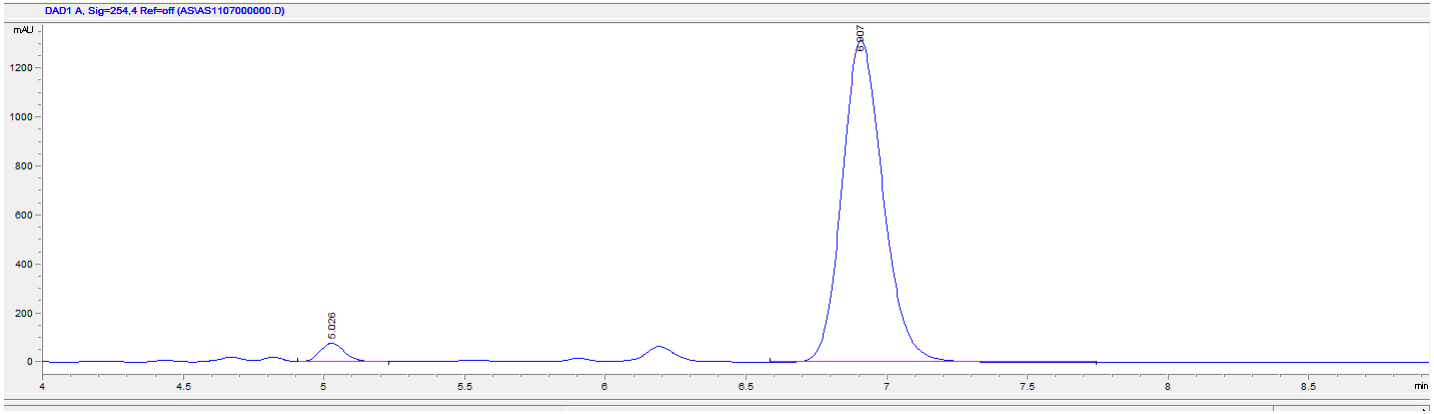
CSP-HPLC: IC column, *n-Hexane/i-PrOH 80/20%, 1 ml/min, 23 °C, λ = 254 nm*





5p

#	Time	Area	Height	Width	Area%	Symmetry
1	5.024	12858.2	1995.7	0.0992	49.884	0.786
2	7.138	12918.2	1188.3	0.1678	50.116	0.83



#	Time	Area	Height	Width	Area%	Symmetry
1	5.026	465.6	76	0.0955	3.386	0.852
2	6.907	13283.1	1312.8	0.156	96.614	0.814

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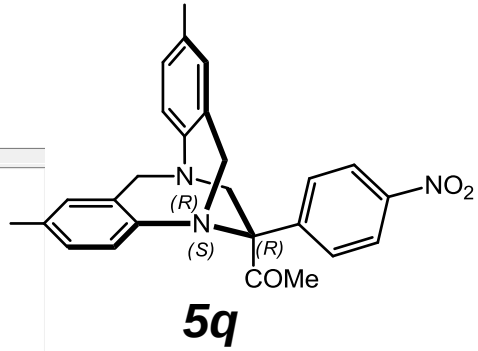
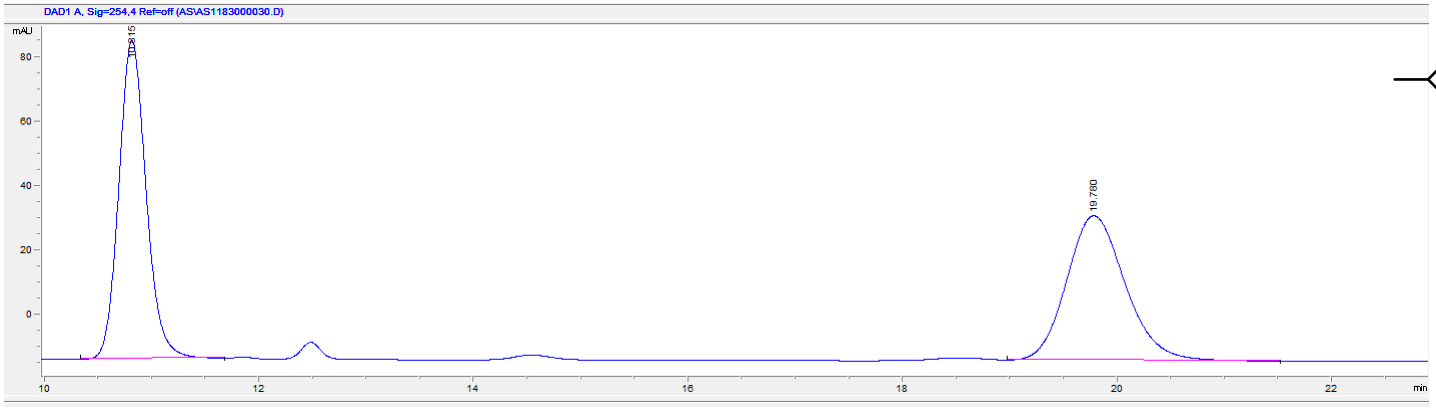
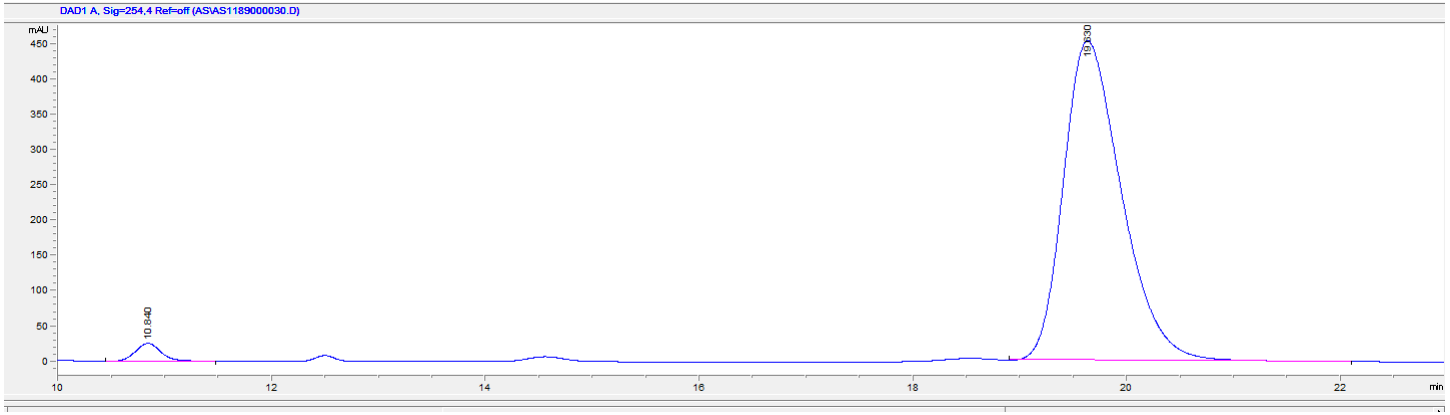
CSP-HPLC: IC column, *n-Hexane/i-PrOH 80/20%, 1 ml/min, 23 °C, λ = 254 nm*



5q



#	Time	Area	Height	Width	Area%	Symmetry
1	10.815	1747.8	98.7	0.2725	50.631	0.859
2	19.78	1704.2	44.9	0.585	49.369	0.822



#	Time	Area	Height	Width	Area%	Symmetry
1	10.84	429.4	25.5	0.2561	2.442	0.917
2	19.63	17154.9	453.5	0.5804	97.558	0.664

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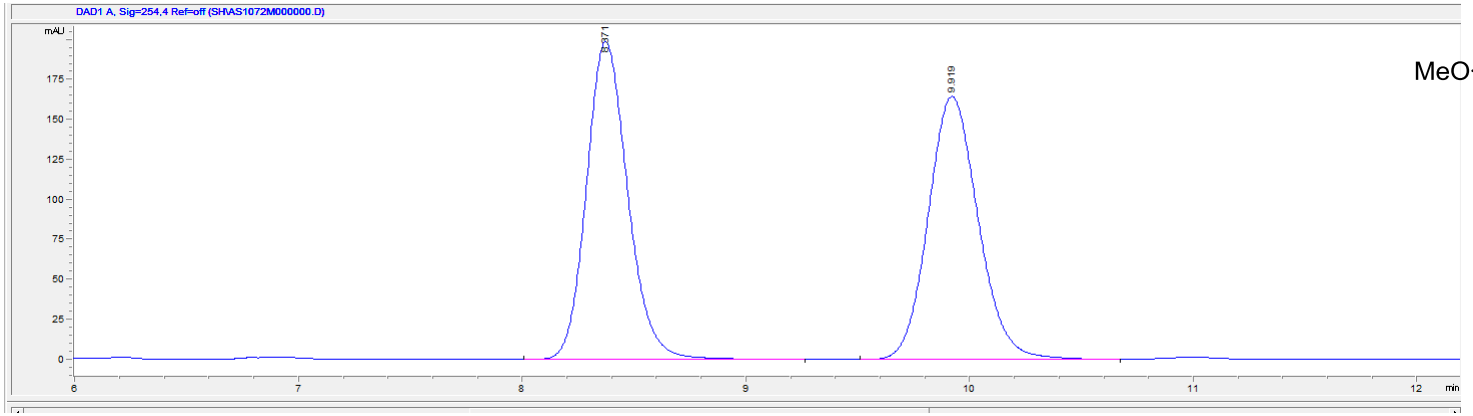
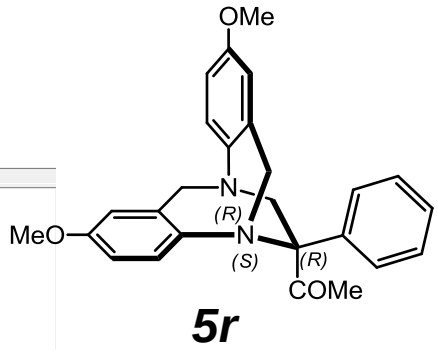
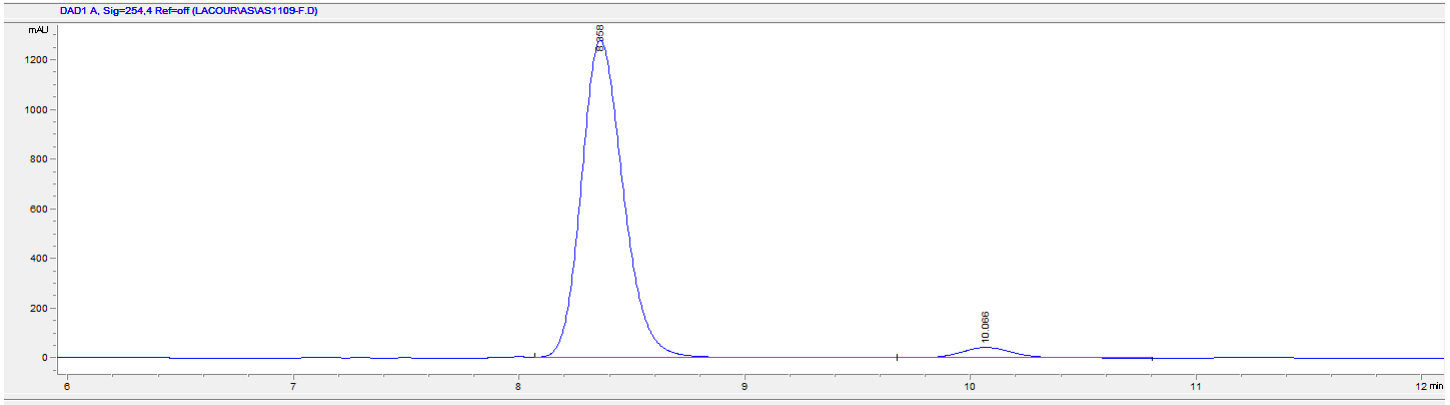
CSP-HPLC: IC column, *n-Hexane/i-PrOH 80/20%, 1 ml/min, 23 °C, λ = 254 nm*





5r

#	Time	Area	Height	Width	Area%	Symmetry
1	8.371	2551.4	199	0.1976	49.963	0.818
2	9.919	2555.2	164.6	0.2401	50.037	0.857



#	Time	Area	Height	Width	Area%	Symmetry
1	8.358	16445.6	1278.1	0.1981	96.141	0.787
2	10.066	660.2	41.8	0.2452	3.859	0.9