Supporting information

•Thestructures of cyclic aminals from aldehydes and "roofed" mono-*N*-sulfonyl *cis*-diamines

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•Schemes, tables, and figures, and Spectral data

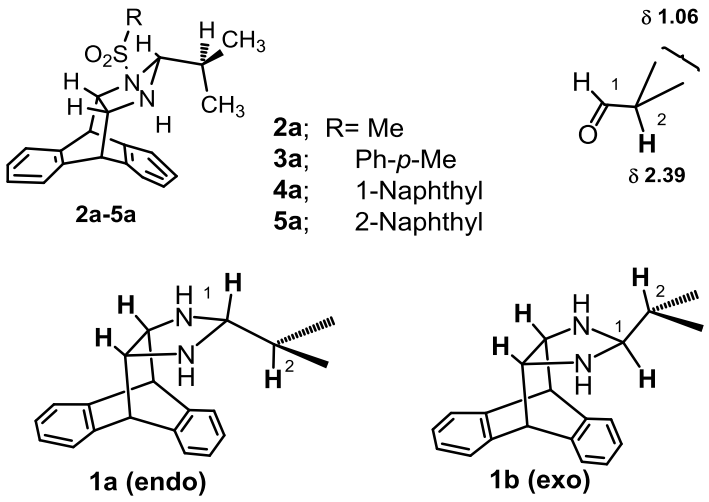
Table S1 (A) Selected chemical shifts, Δδ of geminal methyl protons, and coupling constants for "roofed" aminals (**1a**, **1b** and **2a-5a**), and their structures. (B) Stable conformations for **1a** and **1b**. (C) Structure of **2a**.

(A)

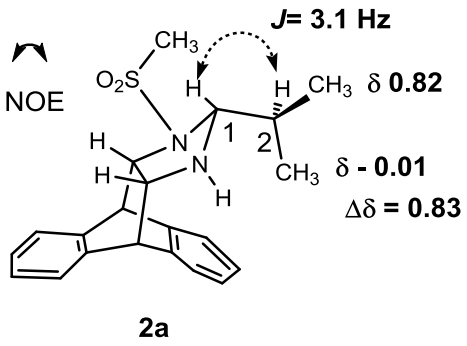
	1a	**1b**	**2a**	**3a**	**4a**	**5a**
^{1}H NMR						
geminal Me	0.64	0.75	0.82	0.79	0.82	0.81
			-0.01	0.03	0.02	0.05
Δδ	0	0	**0.83**	**0.76**	**0.80**	**0.76**
methine	1.34	1.31	2.22	2.39	2.58	2.50
$^{3}J_{HH}$ (Hz)	5.2	7.5	**3.1**	**3.5**	**2.7**	**3.1**
^{13}C NMR						
geminal Me	17.88	19.12	19.44	19.50	19.60	19.53
			11.18	11.37	11.29	11.41
Δδ	0	0	**8.26**	**8.13**	**8.31**	**8.21**
methine	30.81	33.19	28.21	28.31	28.74	28.36

[270 MHz/67.5 MHz or 500 MHz/126 MHz (^{1}H/^{13}C)] in $CDCl_3$

(B)



(C)



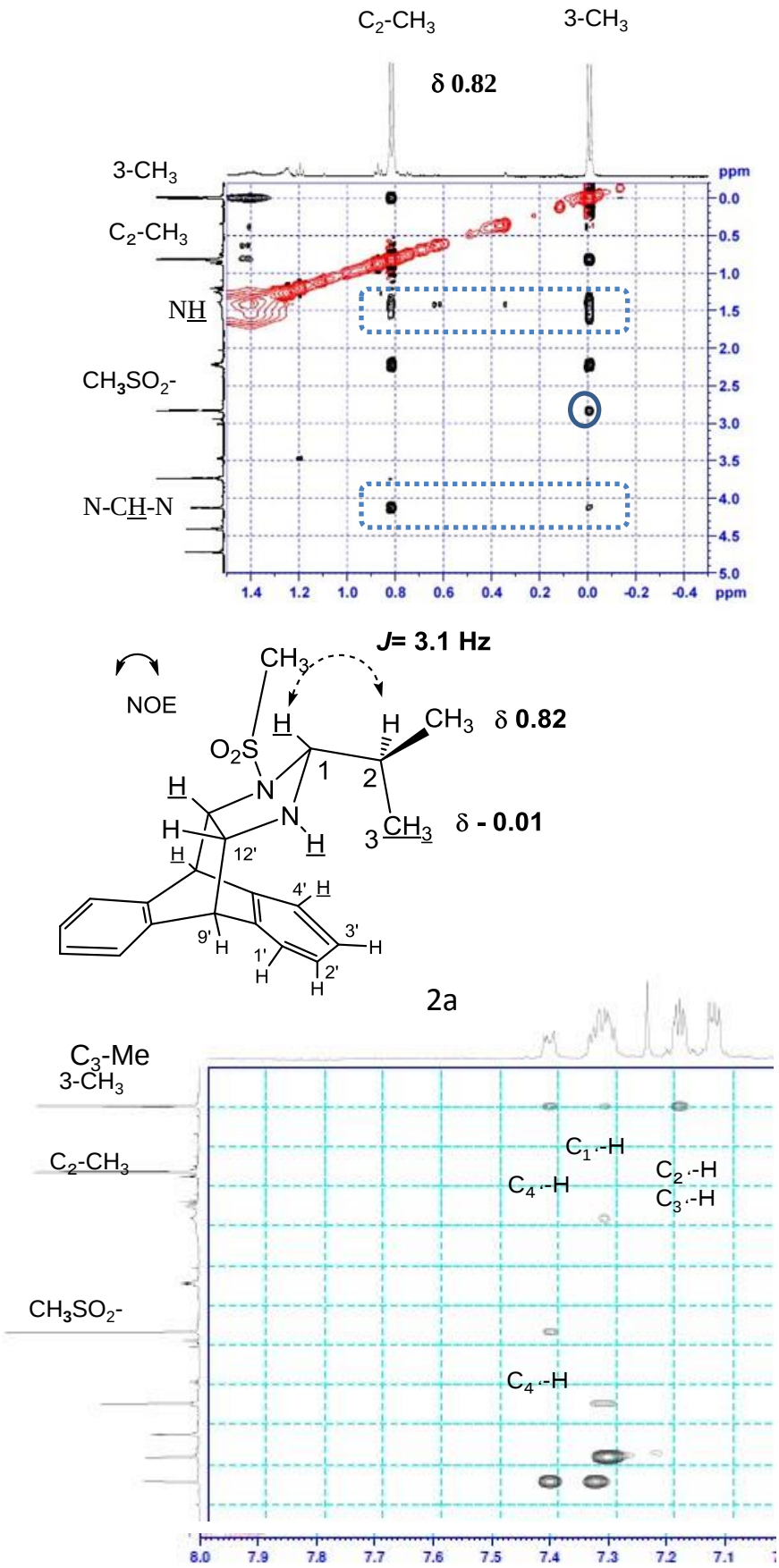
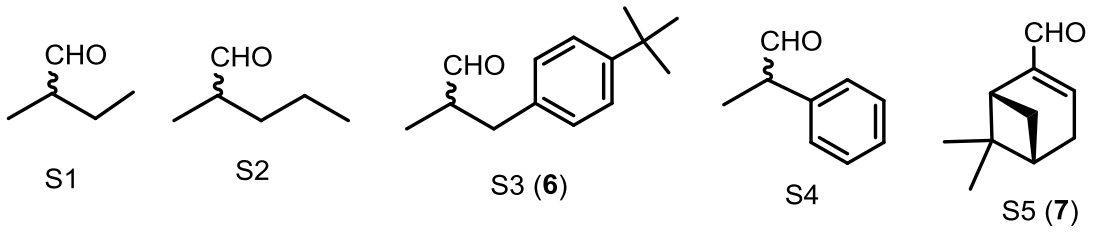


Fig. S2 Partial NOESY spectrum (500 MHz; $CDCl_3$) for **7a** and the conformation of **7a**.

Table S3 R_f values of diastereomeric aminals form racemic reagent (**2**-**5**) and aldehydes (**S1**-**S5**).

Reagents/aldehydes	**S1**	**S2**	**S3** (6)	**S4**	**S5** (7)
2; RDA-Ms	B 0.45/0.49	B 0.57/0.68	B 0.63/0.73	B 0.61/0.72	B 0.55/0.63
	C 0.44/0.47	C 0.58/0.60	C 0.59/0.65	C 0.59/0.66	C 0.57/0.68
3; RDA-Ts	A 0.30/0.36	A 0.35/0.45	A 0.39/0.53	A 0.33/0.46	A 0.33/0.36
	E 0.56/0.62	E 0.43/0.58	D 0.40/0.57	D 0.49/0.53	E 0.41/0.43
4; RDA-1Nps	A 0.34/0.41	A 0.39/0.47	A 0.41/0.54	A 0.36/0.46	A 0.34/0.41
	E 0.56/0.62	E 0.42/0.58	D 0.41/0.56	D 0.51/0.57	E 0.39/0.52
5; RDA-2Nps	A 0.39/0.45	A 0.44/0.53	A 0.49/0.63	A 0.43/0.52	A 0.41/0.45
	E 0.61/0.69	E 0.51/0.66	D 0.50/0.67	D 0.43/0.57	E 0.50/0.57

Silica-gel TLC plate: Merck $60F_{254}$ 5715
Solvent combinations: A: Hexane/EtOAc (2:1), B: EtOAc, C: $CHCl_3$/MeOH (10:1), D: Toluene/EtOAc (20:1), E: Toluene/EtOAc (10:1).



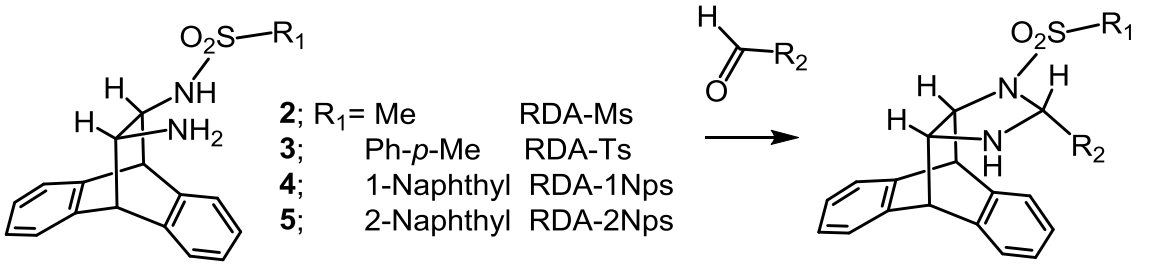
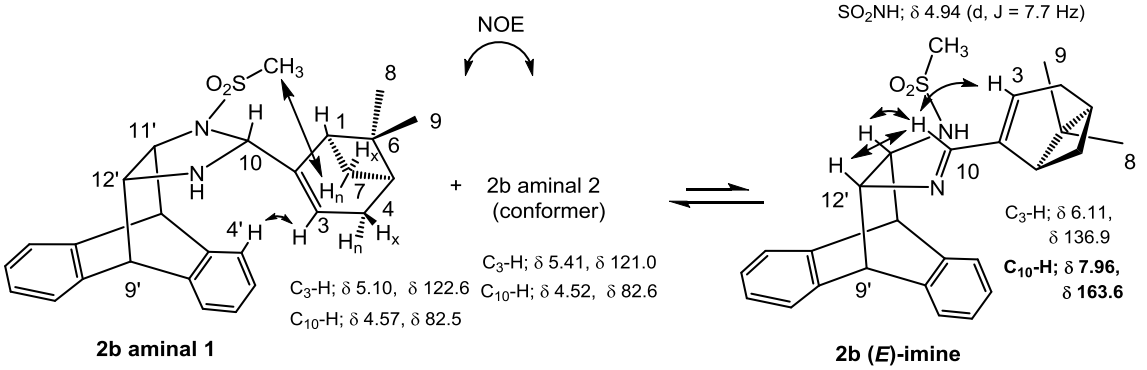


Table S4. Proton and carbon chemical shifts (d in ppm) for myrtenal moieties and selected mother skeleton of **2b (aminal)**, **2b** (**imine**), **2c** and myrtenal **7**.

Proton	2b (aminal)	2b (imine)	2c	Myrtenal
H-1	1.13	2.59	0.72	2.85
H-3	5.10	6.11	5.60	6.70
H-4n	2.13	2.49	2.26	2.52
H-4x	2.05	2.39	2.09	2.58
H-5	1.94	2.12	1.95	2.18
H-7n	0.85	1.07	1.06	1.04
H-7x	2.13	2.40	2.19	2.48
8-CH_3	1.14	1.24	1.04	1.33
9-CH_3	0.67	0.68	0.58	0.73
H-10	4.57	7.96	4.64	9.43
SO_2Me	2.85	2.68	2.84	-
-NH-	1.2-1.8		1.17	-
SO_2-NH-	-	4.94	-	-
N-Me	-	-	-	-
$C_{9'}$-H	4.37	4.04	4.39	-
$C_{10'}$-H	4.68	4.50	4.73	-
$C_{11'}$-H	3.89	3.93	3.86	-
C_{12}'-H	3.76	3.74	3.77	-

Carbon	2b (aminal)	2b (imine)	2c	Myrtenal
1	41.7	39.8	38.9	38.18
2	144.6	148.3	142.7	151.36
3	122.6	136.9	125.2	147.66
4	31.07	32.5	31.3	33.04
5	40.6	40.8	40.5	40.74
6	37.5	37.8	37.0	37.42
7	32.3	31.11	31.7	31.12
8	25.85	25.80	25.7	25.70
9	21.4	21.2	21.3	20.92
10	82.5	163.6	82.7	191.21
SO_2Me	37.7	40.9	37.7	-
N-Me	-	-	-	-
9'	48.0	51.5	47.8	-
10'	49.3	53.0	49.3	-
11'	64.2	54.5	63.8	-
12'	60.5	67.9	60.3	-



2b aminal 1 :2b aminal 2 : 2b (*E*)-imine= 71 : 8 : 21

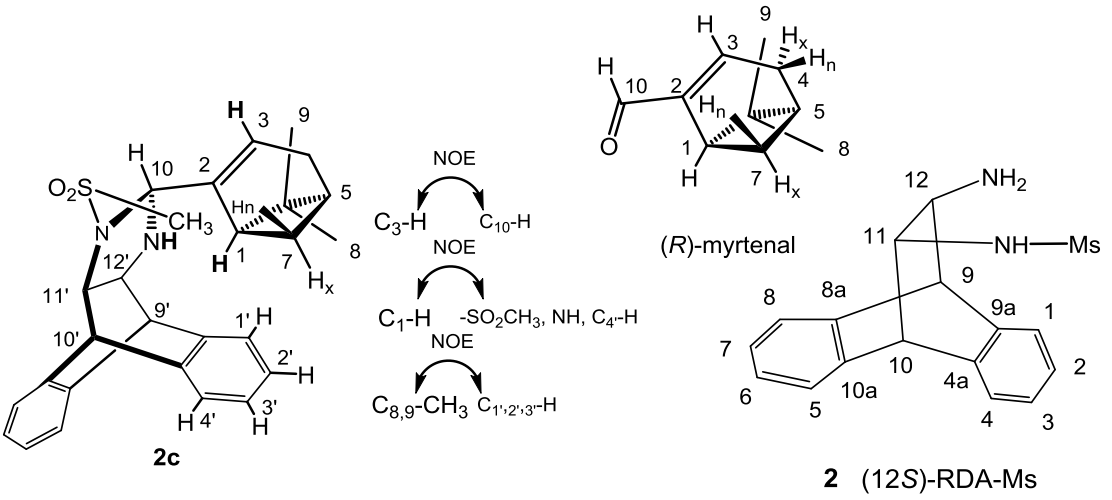


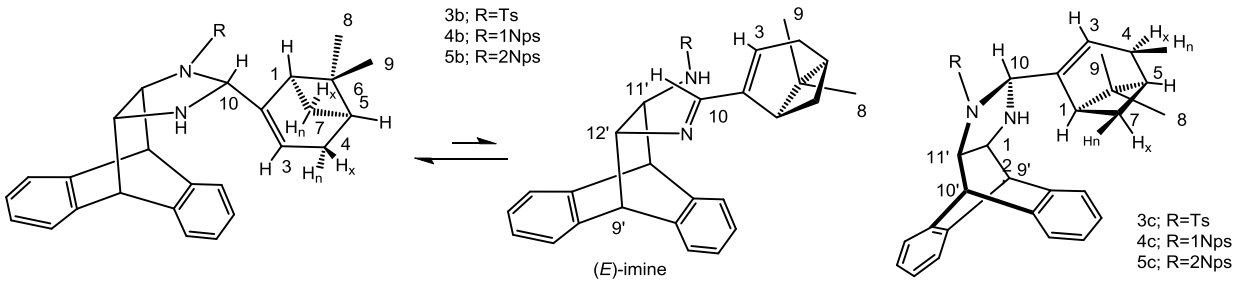
Table S5. Proton and carbon chemical shifts (δ in ppm) for myrtenal moieties and selected mother skeleton of **3b**, **3c**, **4b**, **4c**, **5b**, and **5c**.

Proton	**3b** (aminal)	**3b** (imine)	**3c**	**4b** (aminal)	**4b** (imine)	**4c**	**5b** (aminal)	**5b** (imine)	**5c**
H-1	0.98	2.58	0.87	1.24	2.61	0.82	1.02	2.58	0.88
H-3	5.22	6.01	5.50	5.07	6.05	5.53	5.24	5.85	5.56
H-4n	2.13	2.45	2.29	2.02*	2.38*	2.20	2.15	2.24	2.32
H-4x	2.13	2.45	2.07	1.95*	2.47*	2.05	2.09	2.37	2.09
H-5	1.95	2.14	1.93	1.91	2.22	1.88	1.95	2.12	1.94
H-7n	0.85	1.04	1.19	0.72	1.04	0.78	0.86	1.02	1.16
H-7x	2.08	2.39	2.19	2.08	2.39	2.01	2.09	2.38	2.18
8-CH_3	1.15	1.27	1.03	1.18	1.27	0.99	1.16	1.27	1.04
9-CH_3	0.77	0.78	0.56	0.73	0.71	0.53	0.792	0.787	0.56
H-10	4.25	7.58	4.13	4.66	7.83	4.69	4.36	4.51	4.23
-NH-	1.25		1.07	1.0-1.5		1.06	1.28		1.10
SO_2NH	-	5.42	-	-	5.54	-	-	5.52	-
SO_2Me	-	-	-	-	-	-	-	-	-
Me (Ts)	2.40	2.36	2.39	-	-	-	-	-	-
$C_{9'}$-H	4.28	3.93	4.30	4.26	3.98	4.25	4.27	3.92	4.29
$C_{10'}$-H	4.76	4.49	4.89	4.12	4.14	4.30	4.79	4.51	4.94
$C_{11'}$-H	3.55	3.66	3.47	3.77	3.80	3.77	3.66	3.72	3.59
C_{12}'-H	3.42	3.39	3.44	3.51	3.58	3.56	3.40	3.36	3.43

* exchangeable

Table S5
(continued)

Carbon	**3b** (aminal)	**3b** (imine)	**3c**	**4b** (aminal)	**4b** (imine)	**4c**	**5b** (aminal)	**5b** (imine)	**5c**
1	40.7	39.9	39.3	41.8	40.0	39.3	40.8	39.9	39.4
2	144.4	148.4	143.6	144.4	148.4	143.3	144.3	148.3	143.5
3	122.3	136.4	123.7	122.2	136.4	123.4	122.5	136.5	124.0
4	31.1	32.5	31.2	41.0	32.5	31.2	31.1	32.4	31.3
5	40.8	41.7	40.4	40.7	40.5	40.3	40.75	40.8	40.4
6	37.9	37.5	36.8	37.9	37.6	36.8	37.9	37.5	36.8
7	32.3	31.2	31.5	32.1	31.1	31.1	32.3	31.2	31.5
8	25.9	25.8	25.7	26.0	26.0	25.7	25.9	25.8	25.7
9	21.5	21.5	21.3	21.3	20.9	21.2	21.5	21.1	21.3
10	82.8	163.4	82.8	82.2	163.7	82.5	82.9	163.5	82.9
SO_2Me	-	-	-	-	-	-	-	-	-
Me (Ts)	21.5	21.1	21.5	-	-	-	-	-	-
$C_{9'}$	47.9	53.0	47.6	47.9	52.8	48.9	47.9	52.9	47.6
$C_{10'}$	49.7	51.1	49.6	49.0	50.0	47.6	49.6	51.1	49.7
$C_{11'}$	64.3	54.0	63.8	64.3	66.9	63.8	64.3	54.1	63.9
$C_{12'}$	60.2	67.0	60.3	60.6	54.3	60.5	60.2	67.0	60.4

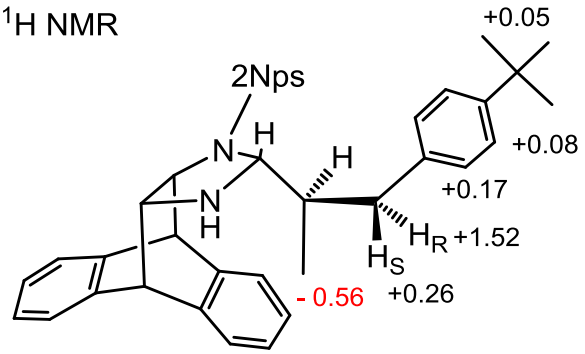


3b (aminal 1) : **3b** (aminal 2, data not shown) : **3b** (*E*)-imine = 80 : 5 : 15
4b (aminal 1) : **4b (**aminal 2, data not shown) : **4b** (*E*)-imine = 67 : 10 : 23
5b (aminal 1) : **5b** (aminal 2, data not shown) : **5b** (*E*)-imine = 75 : 7 : 18

Table S6 Proton and carbon chemical shifts (δ in ppm) for lilial (**S3**) moieties of **5d**, **5e**, and lilial **6**.

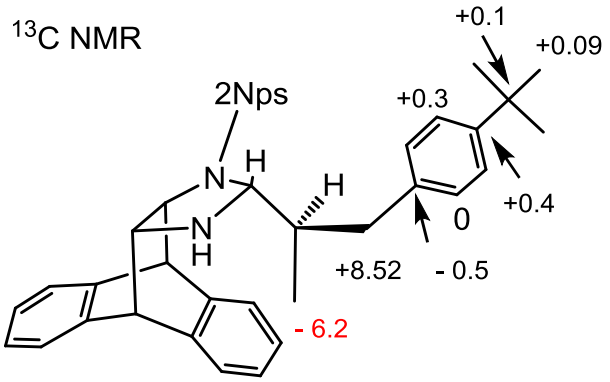
	5d	5e	Dd = d_{5d}-d_{5e}	lilial (6)
Proton				
C_1-H	3.76	3.92	-0.16	9.71
C_2-H	2.81	2.59	0.22	2.66
C_2-CH_3	0.15	0.71	-0.56	1.09
C_3-H_R	2.39*	0.88	1.51	3.06*
C_3-H_S	2.42*	2.16	0.26	2.57*
$C_{2',6'}$-H	7.11	6.94	0.17	7.10
$C_{3',5'}$-H	7.28	7.20	0.08	7.30
$C_{4'}$-t-Bu	1.34	1.29	0.05	1.30
Carbon				
C_1	81.9	84.5	-2.6	204.5
C_2	35.5	35.9	-0.4	48.0
C_2-CH_3	10.2	16.4	-6.2	13.3
C_3	39.9	31.38	8.52	36.1
$C_{1'}$	137.1	137.6	-0.5	135.7
$C_{2',6'}$	128.7	128.7	0.0	125.4
$C_{3',5'}$	125.2	124.9	0.3	126.8
$C_{4'}$	148.7	148.3	0.4	149.2
t-Bu (Me)	31.5	31.41	0.09	31.3
t-Bu (C)	34.4	34.3	0.1	34.4
* exchangeable				

^{1}H NMR



$\Delta\delta = \delta_{\mathbf{5d}} - \delta_{\mathbf{5e}}$

^{13}C NMR



$\Delta\delta = \delta_{\mathbf{5d}} - \delta_{\mathbf{5e}}$

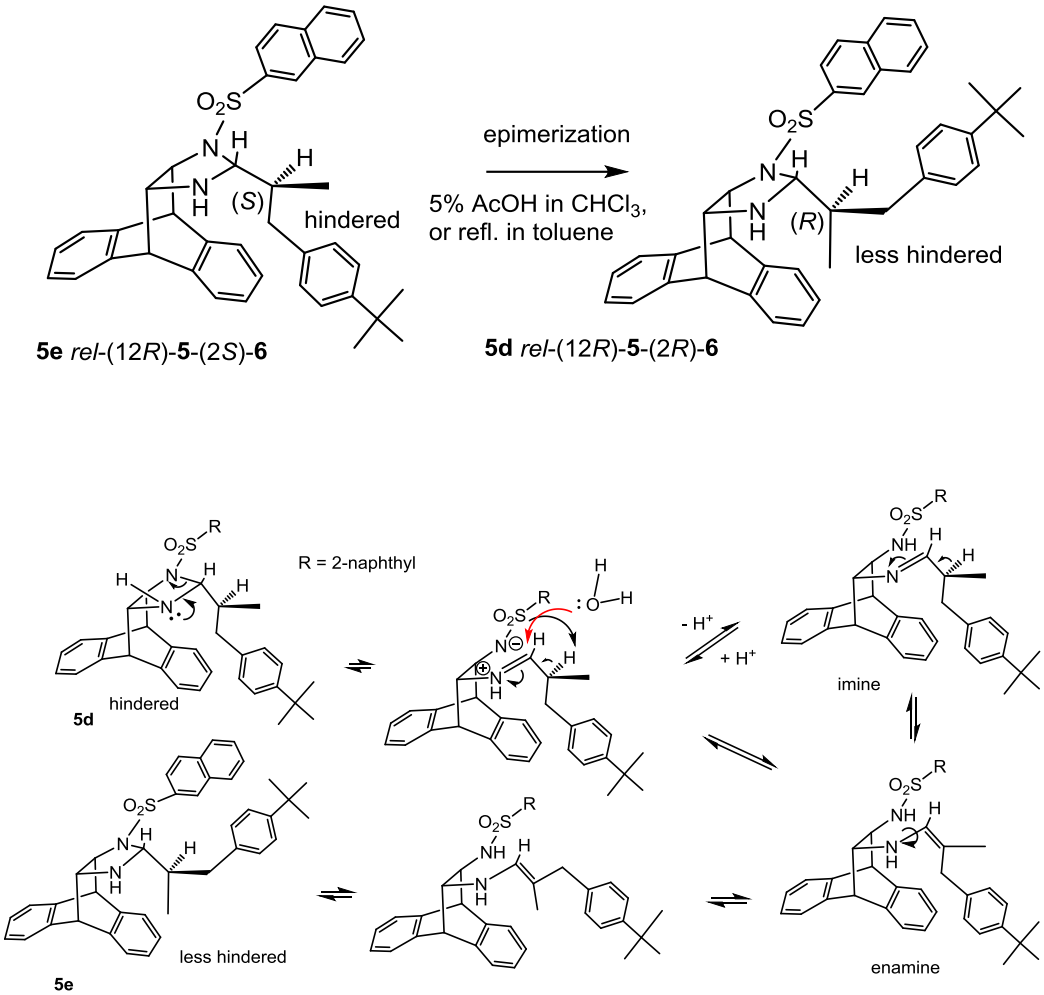


Fig. S7 Possible epimerization mechanism from **5e** to **5d**.

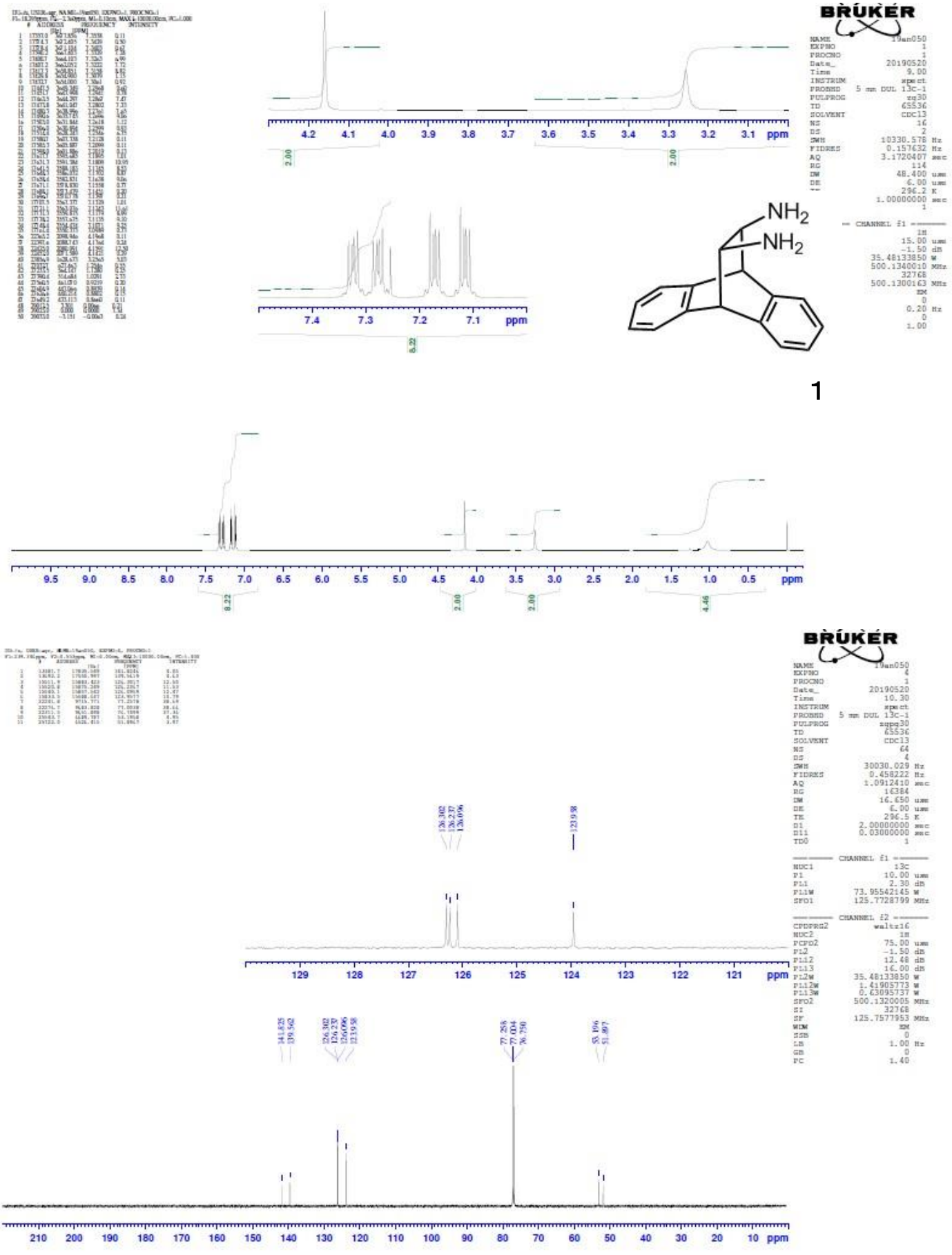
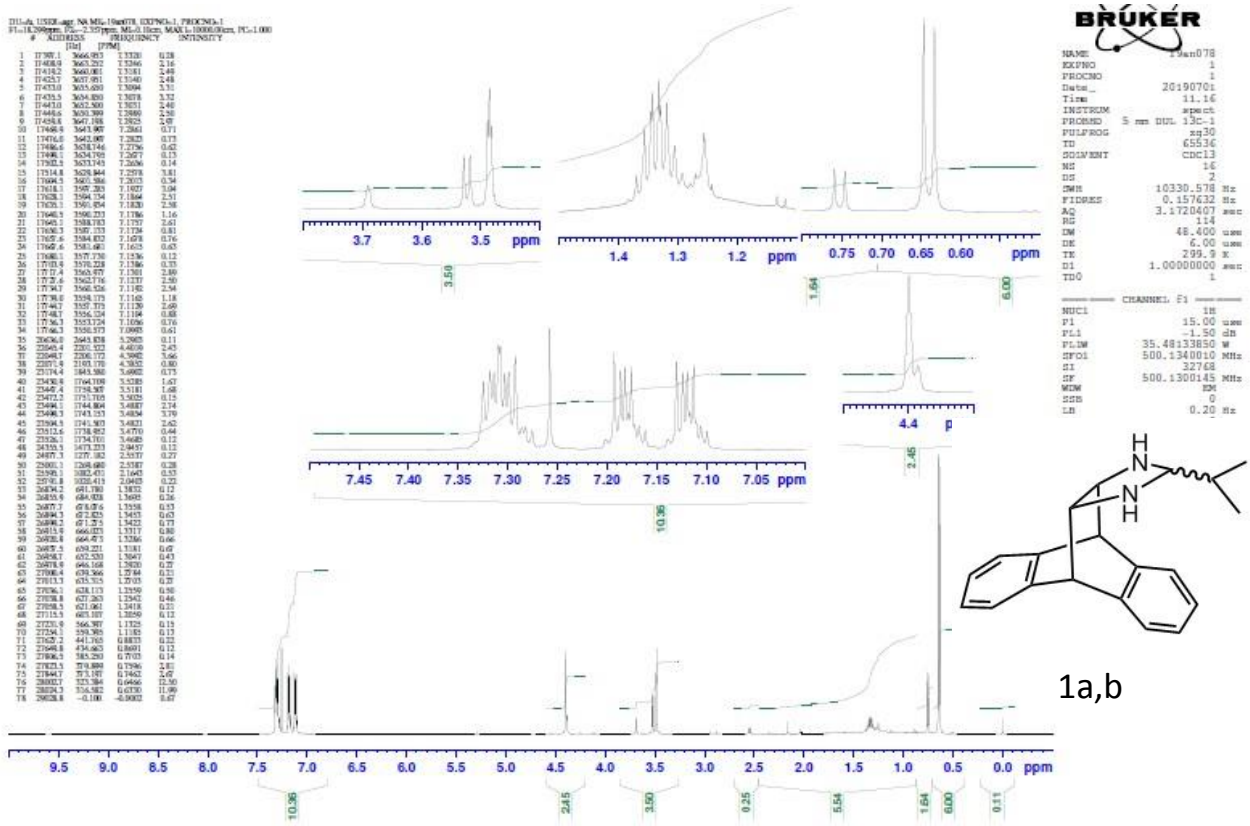


Fig. S8 ^{1}H NMR and ^{13}C spectra for **1**. (500 MHz/126MHz, $CDCl_3$)



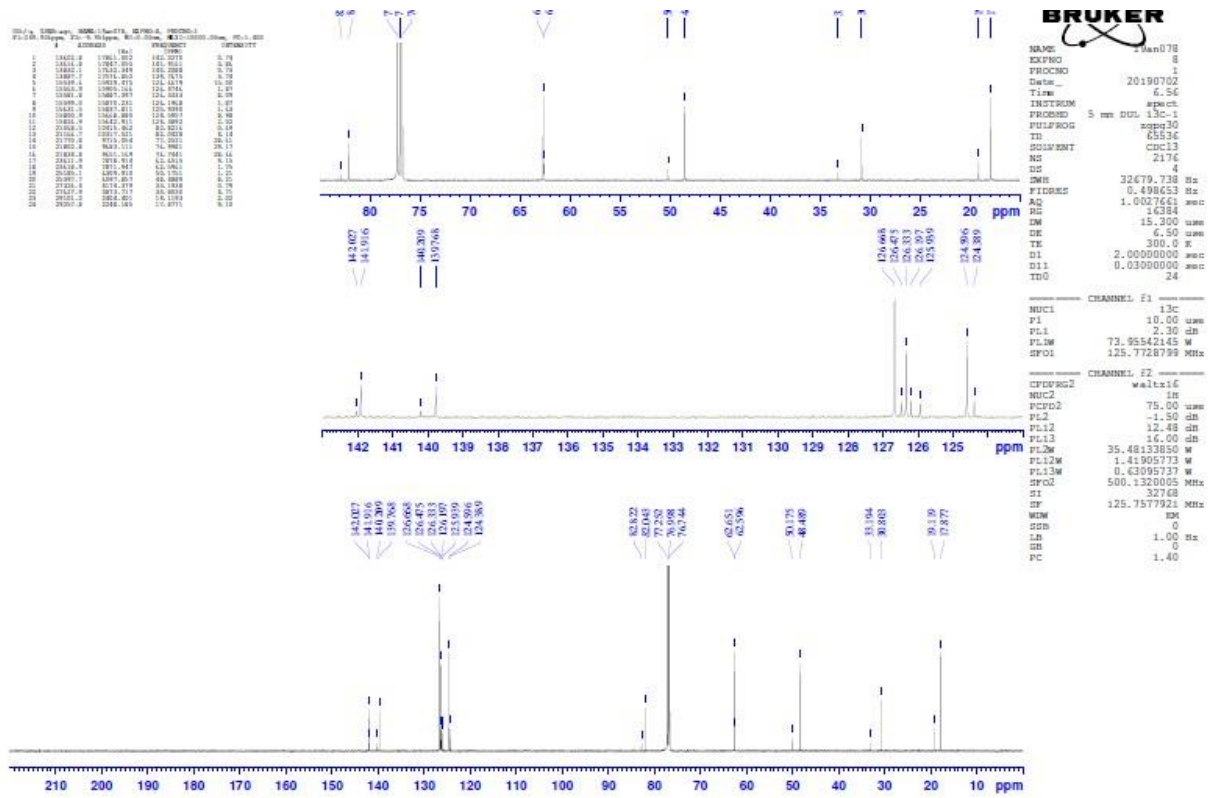
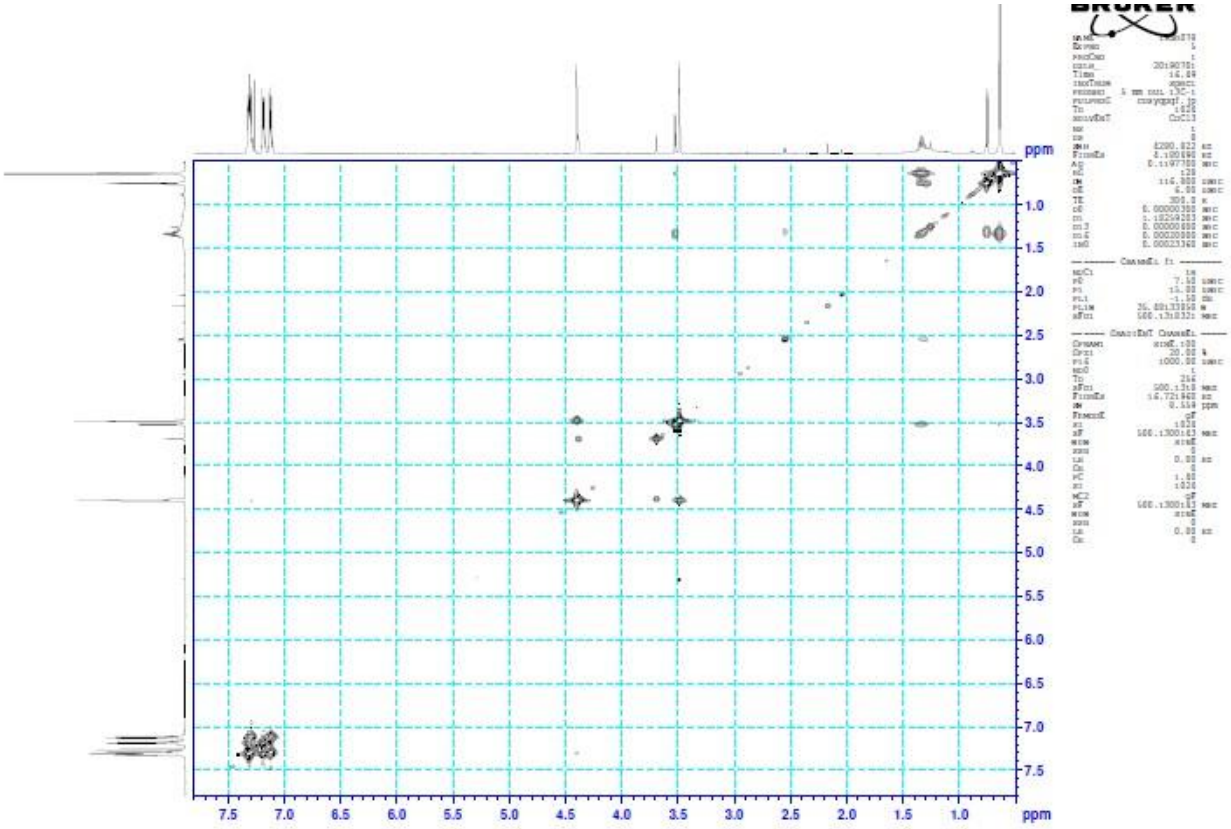


Fig. S9 ^{1}H and ^{13}C NMR spectra for **1a**,**b**.(500 MHz/126MHz, $CDCl_3$)



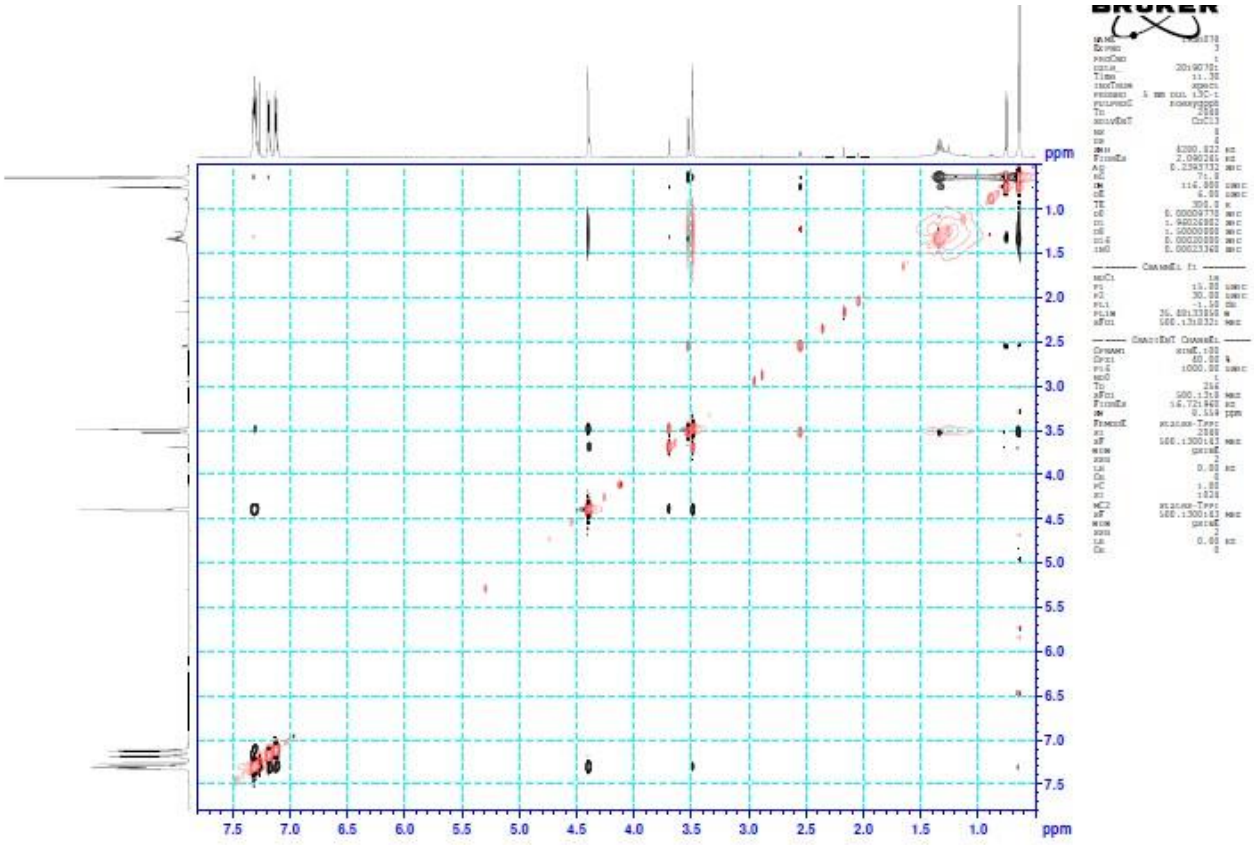


Fig. S10 COSY (above) and NOESY (below) spectra for **1a,b** (500 MHz, $CDCl_3$)

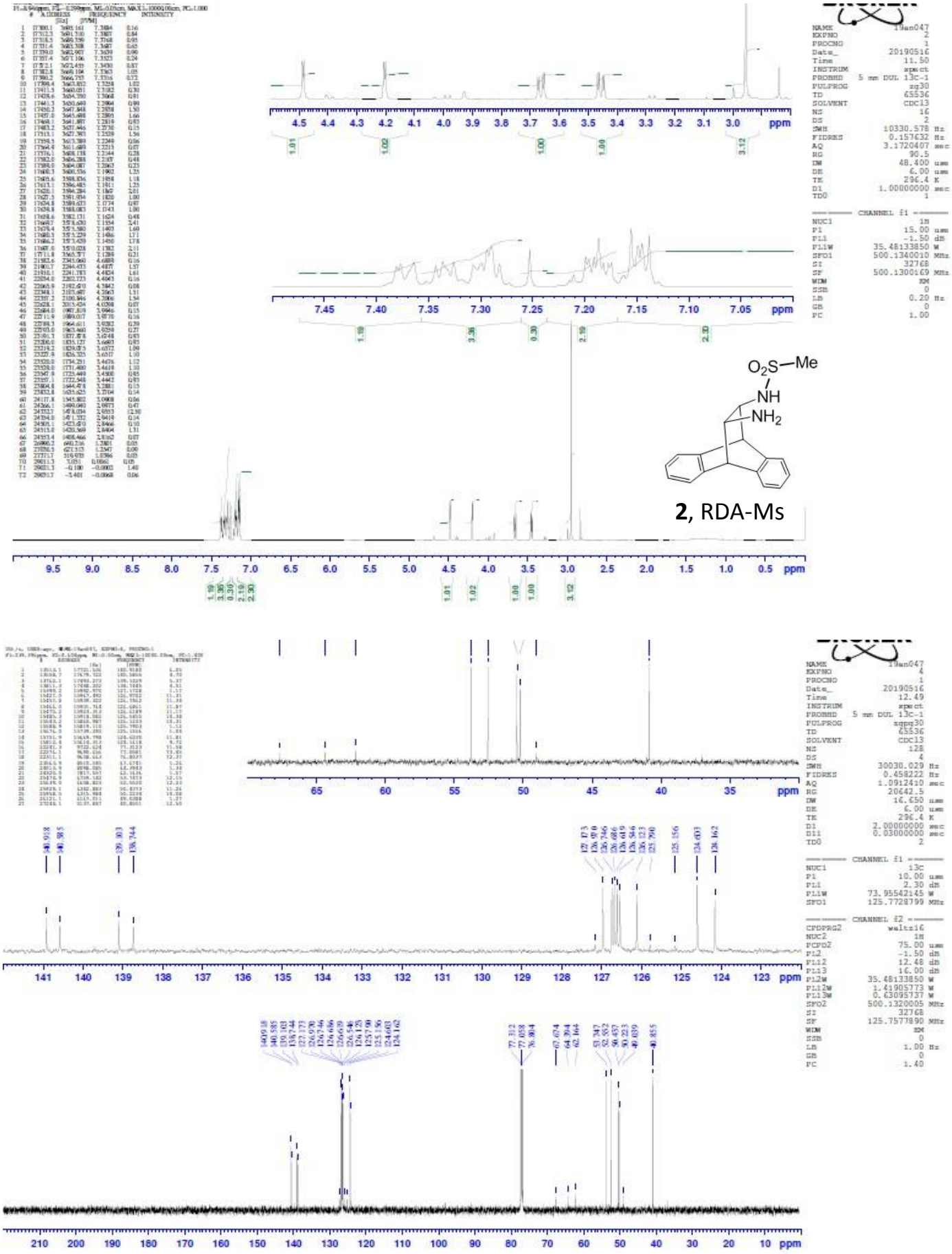
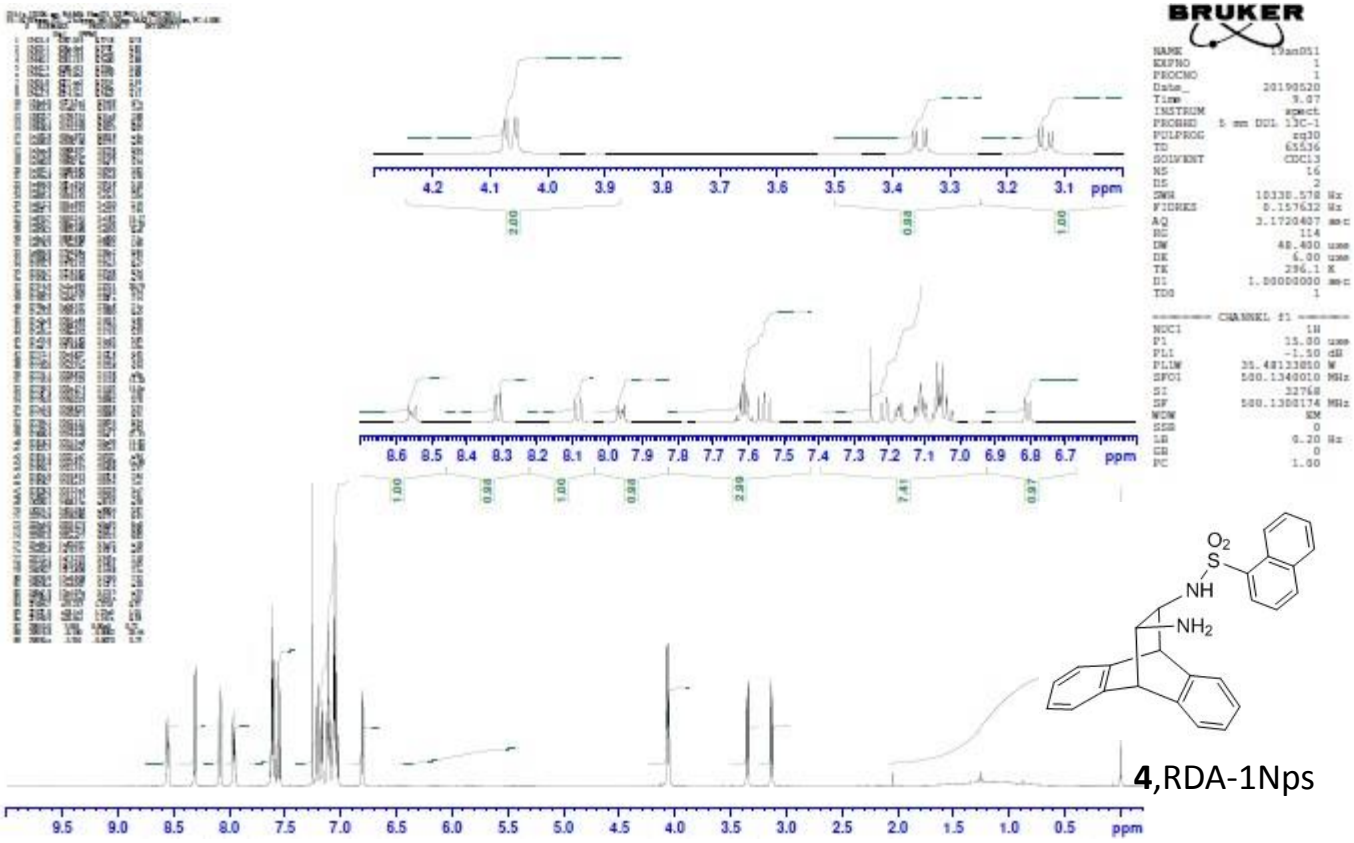


Fig. S11 ^{1}H NMR and ^{13}C spectra for **2**; **RDA-Ms**. (500 MHz/126MHz, $CDCl_3$)



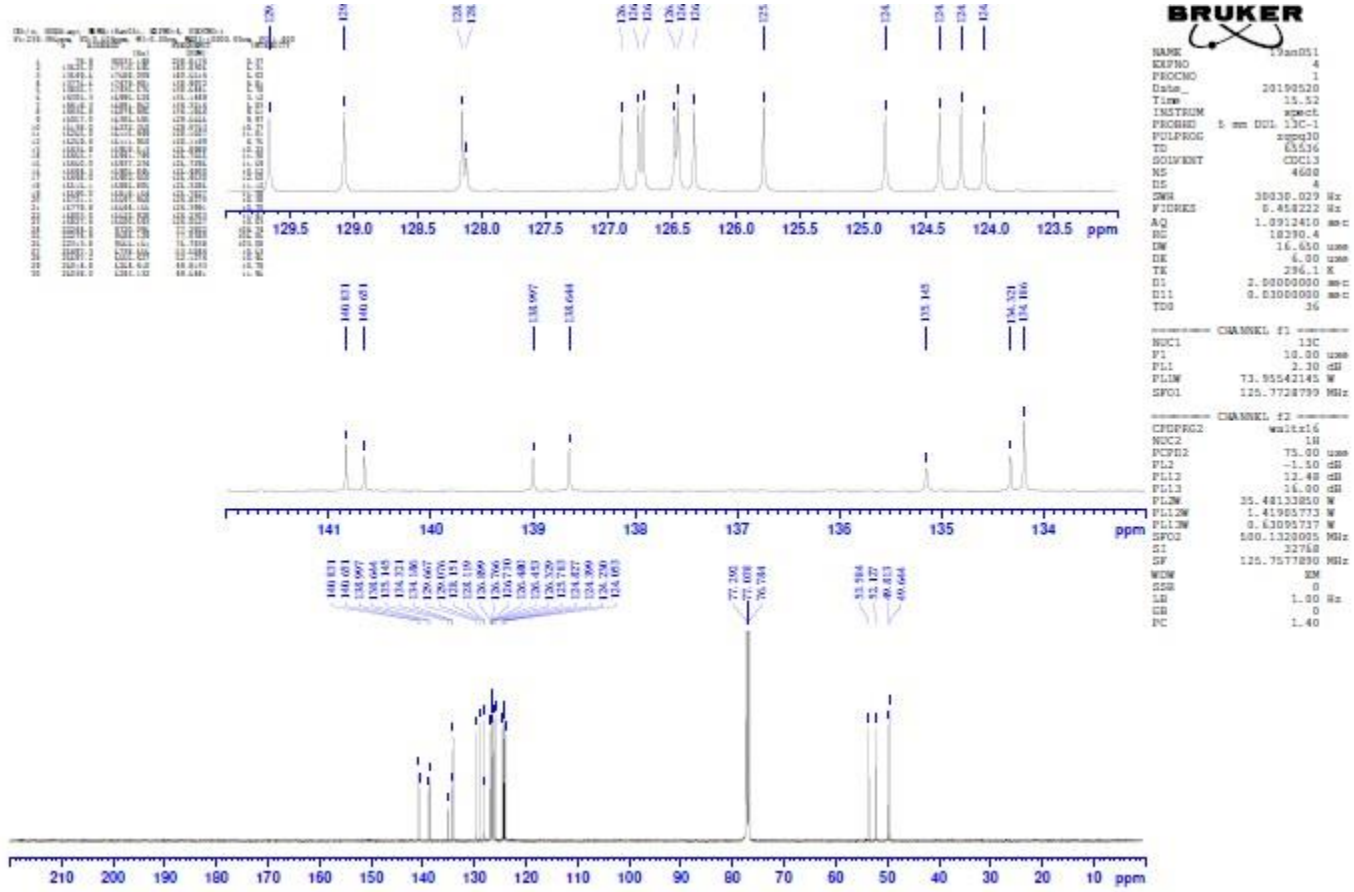
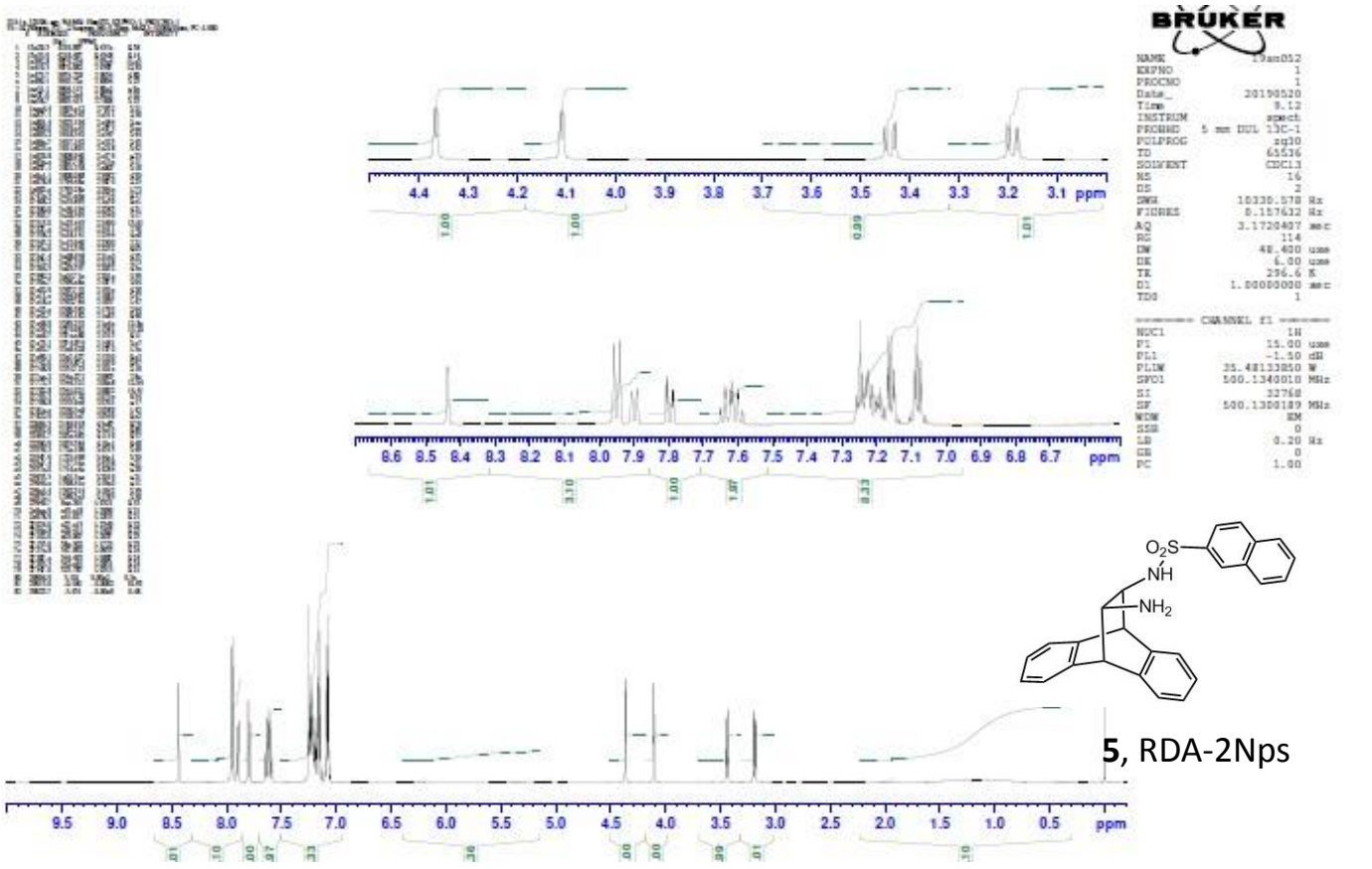


Fig. S12 ^{1}H NMR and ^{13}C spectra for **4**; **RDA-1Nps**. (500 MHz/126MHz, $CDCl_3$)



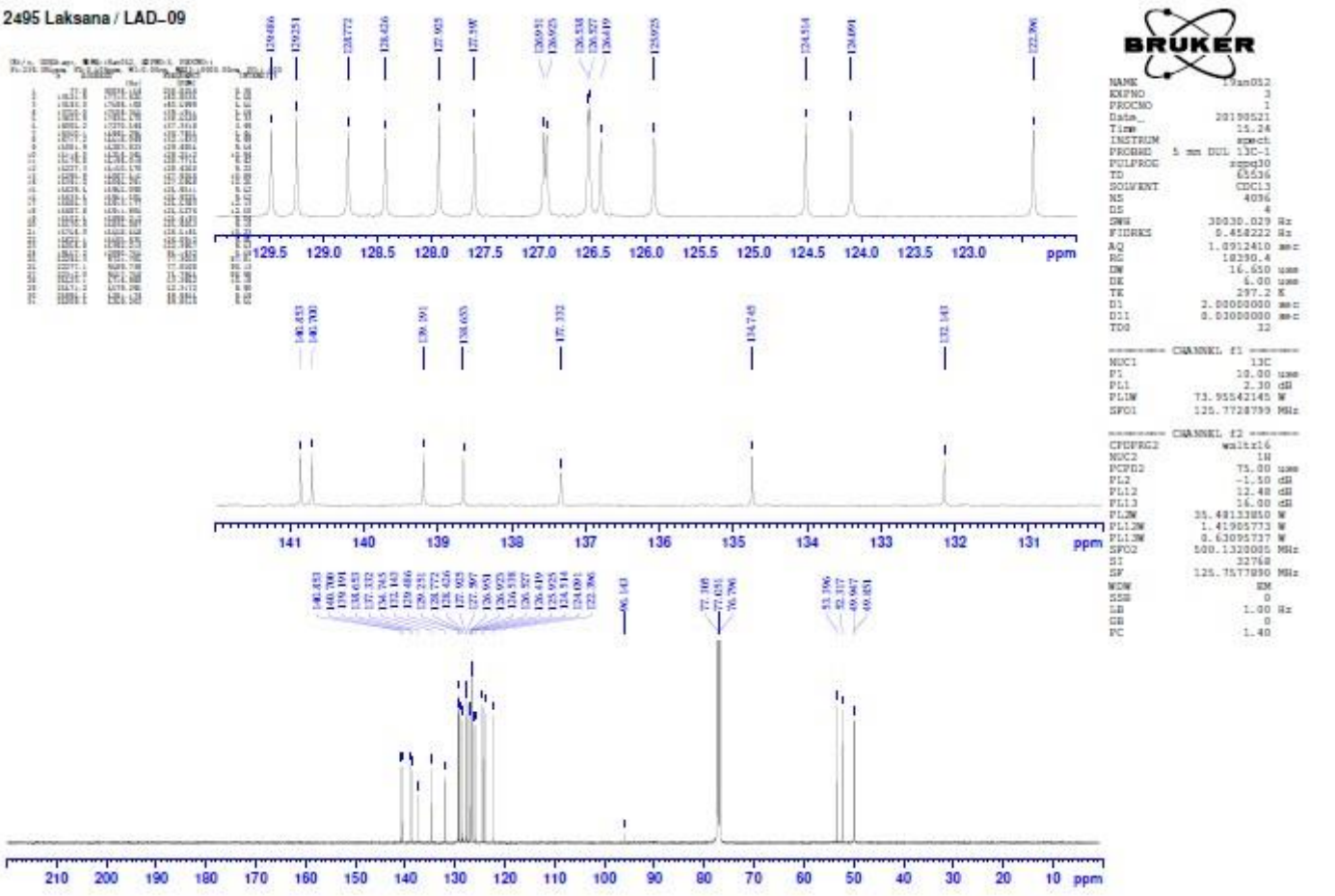
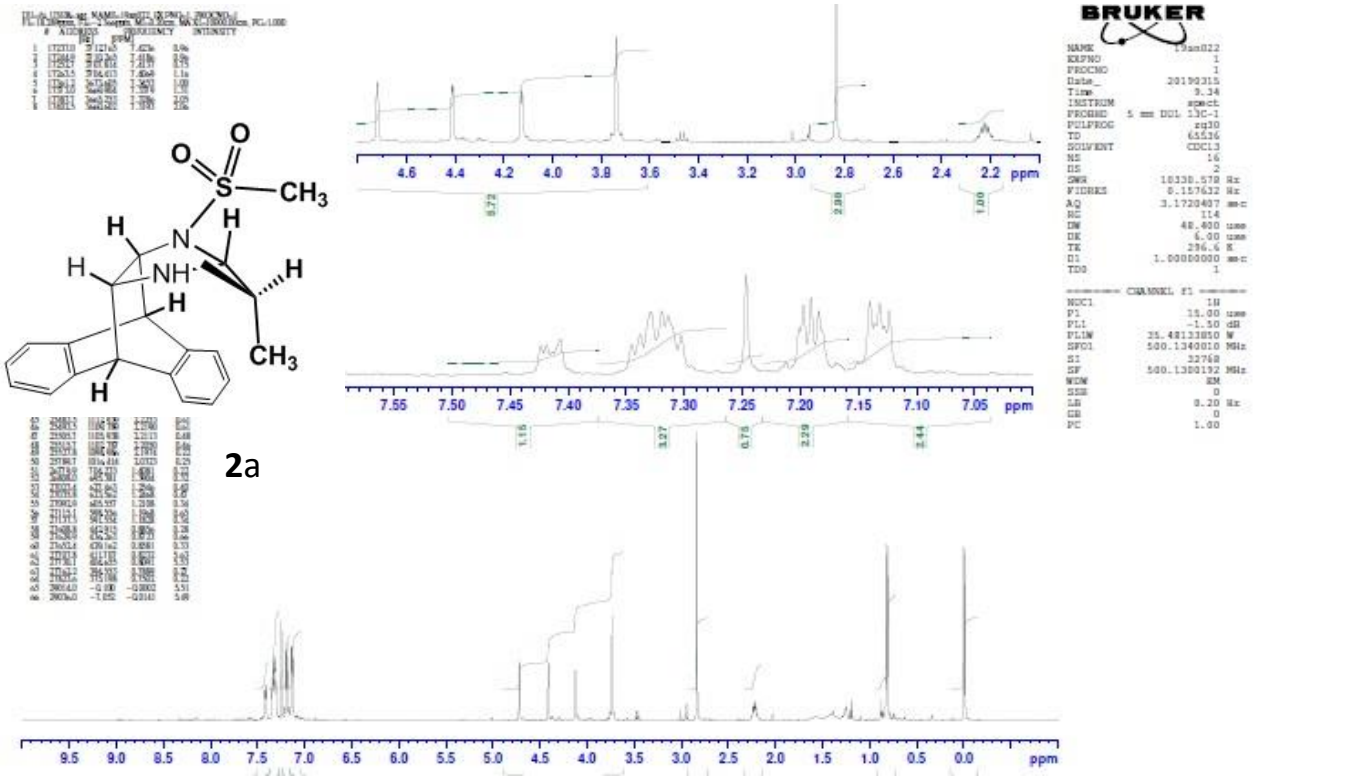


Fig. S13 ^{1}H NMR and ^{13}C spectra for **5**; **RDA-2Nps**. (500 MHz/126MHz, $CDCl_3$)



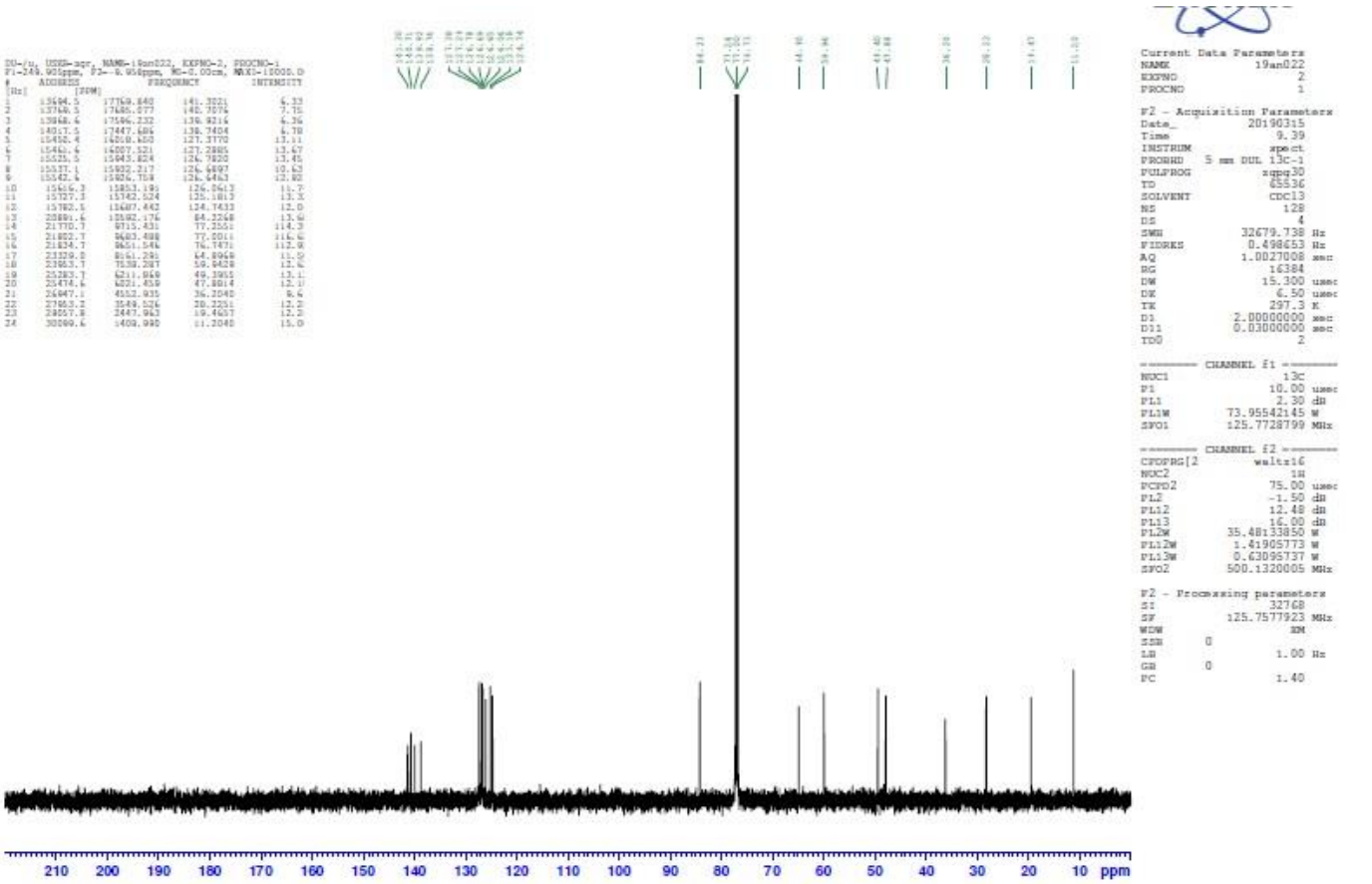


Fig. S14 ^{1}H and ^{13}C NMR spectra for **2a** (500 MHz/126MHz, $CDCl_3$)

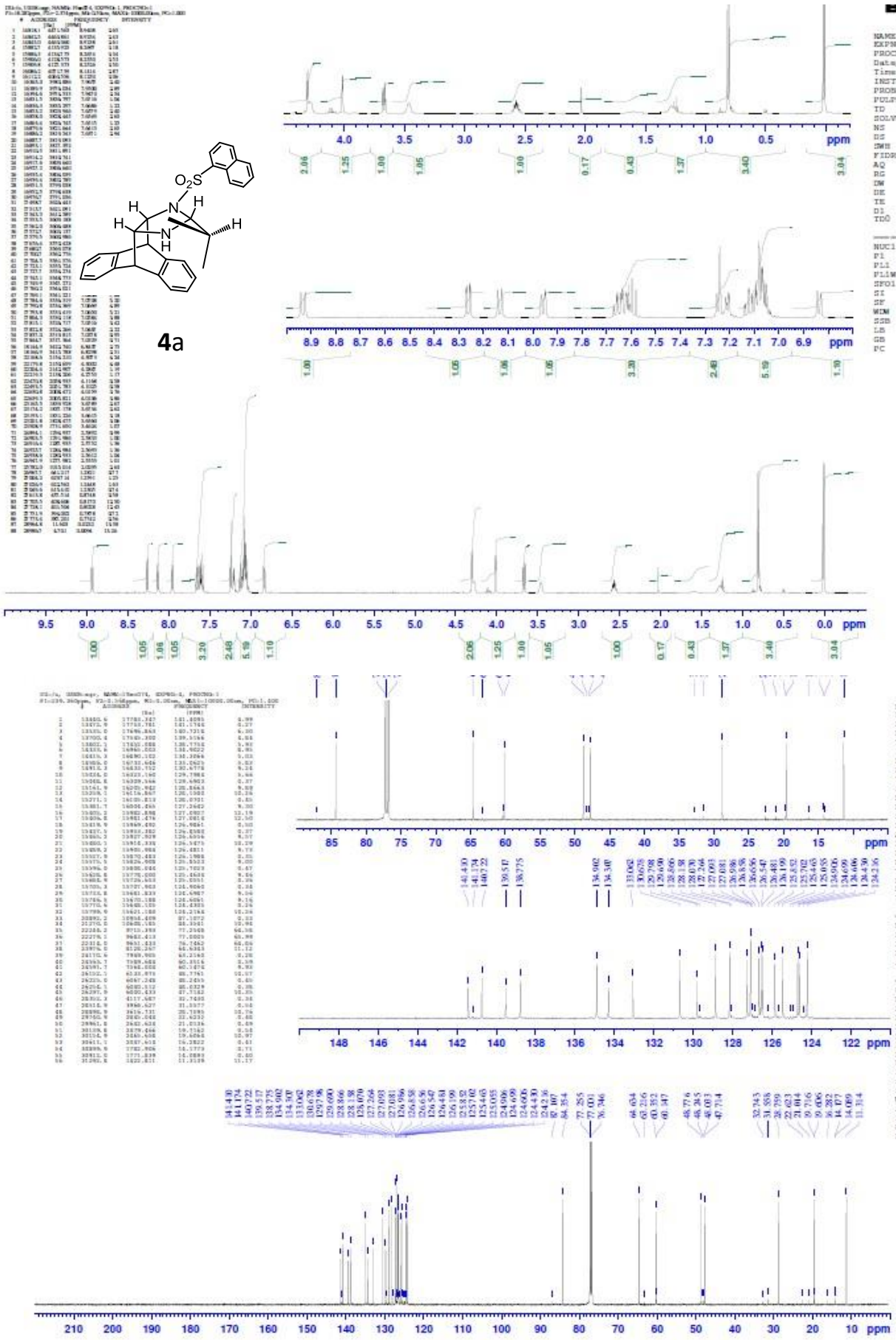


Fig. S15 ^{1}H NMR and ^{13}C spectra for compound **4a**. (500 MHz/126MHz, $CDCl_3$)

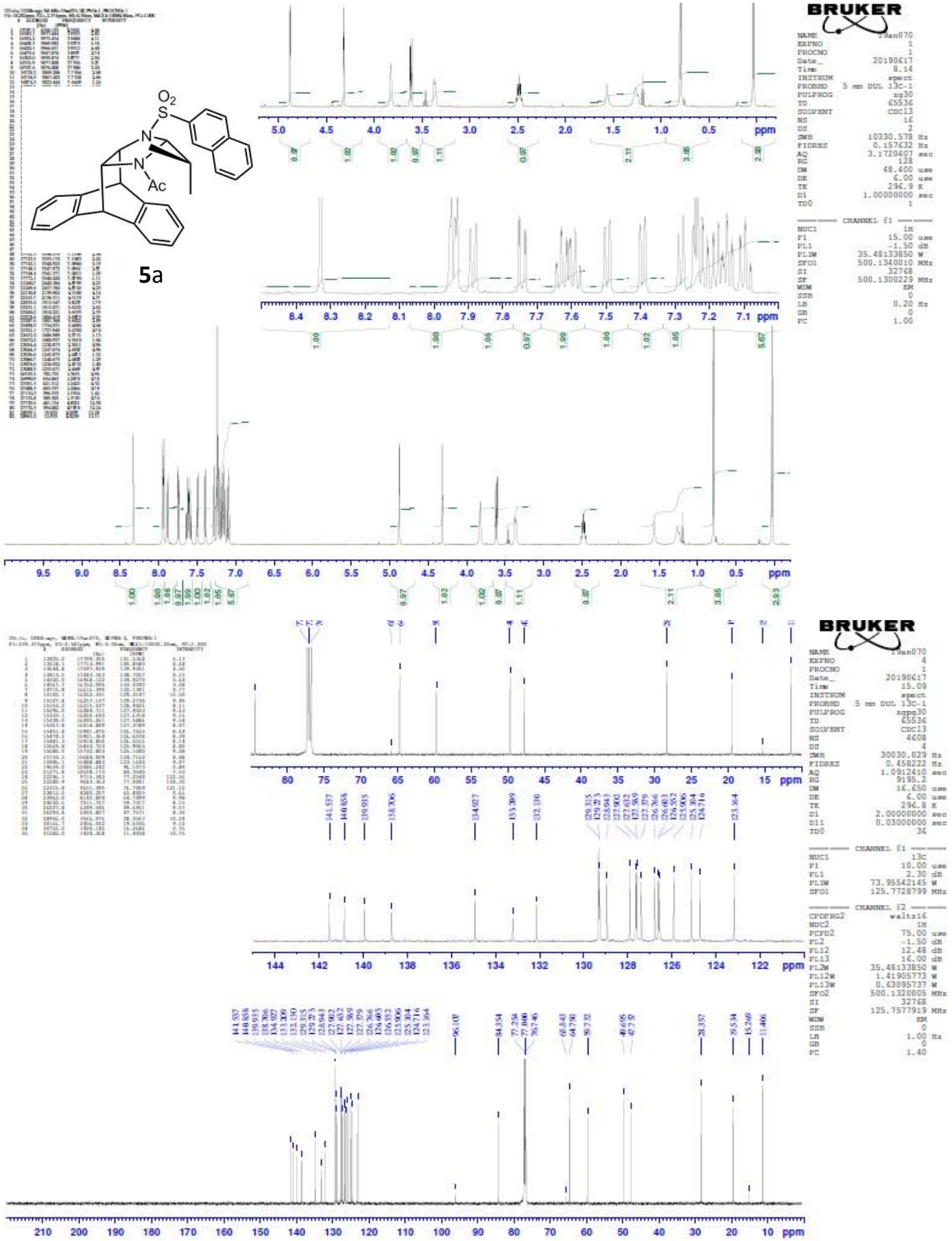
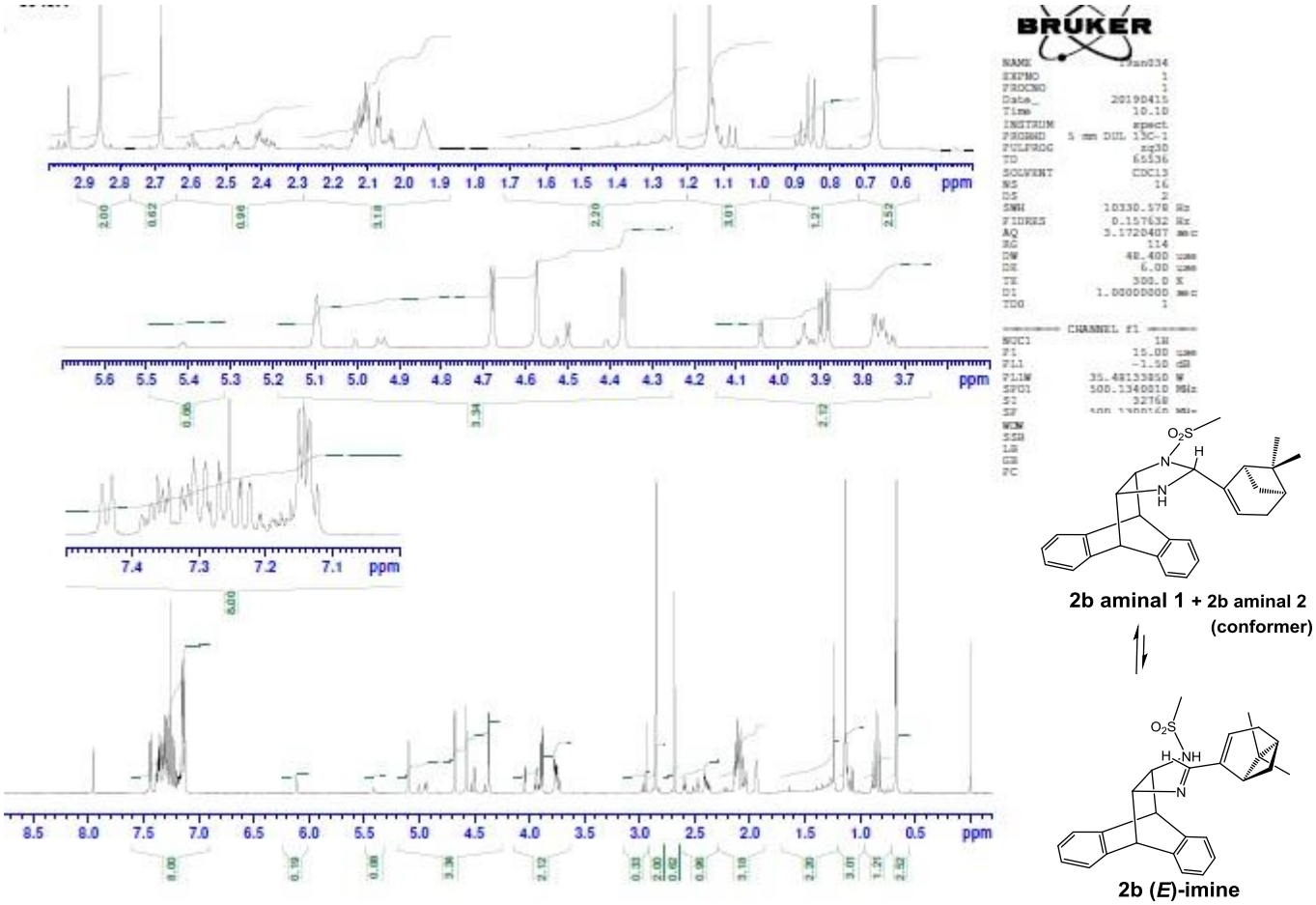


Fig. S16 ^{1}H NMR and ^{13}C spectra for **5a**. (500 MHz/126MHz, $CDCl_3$)



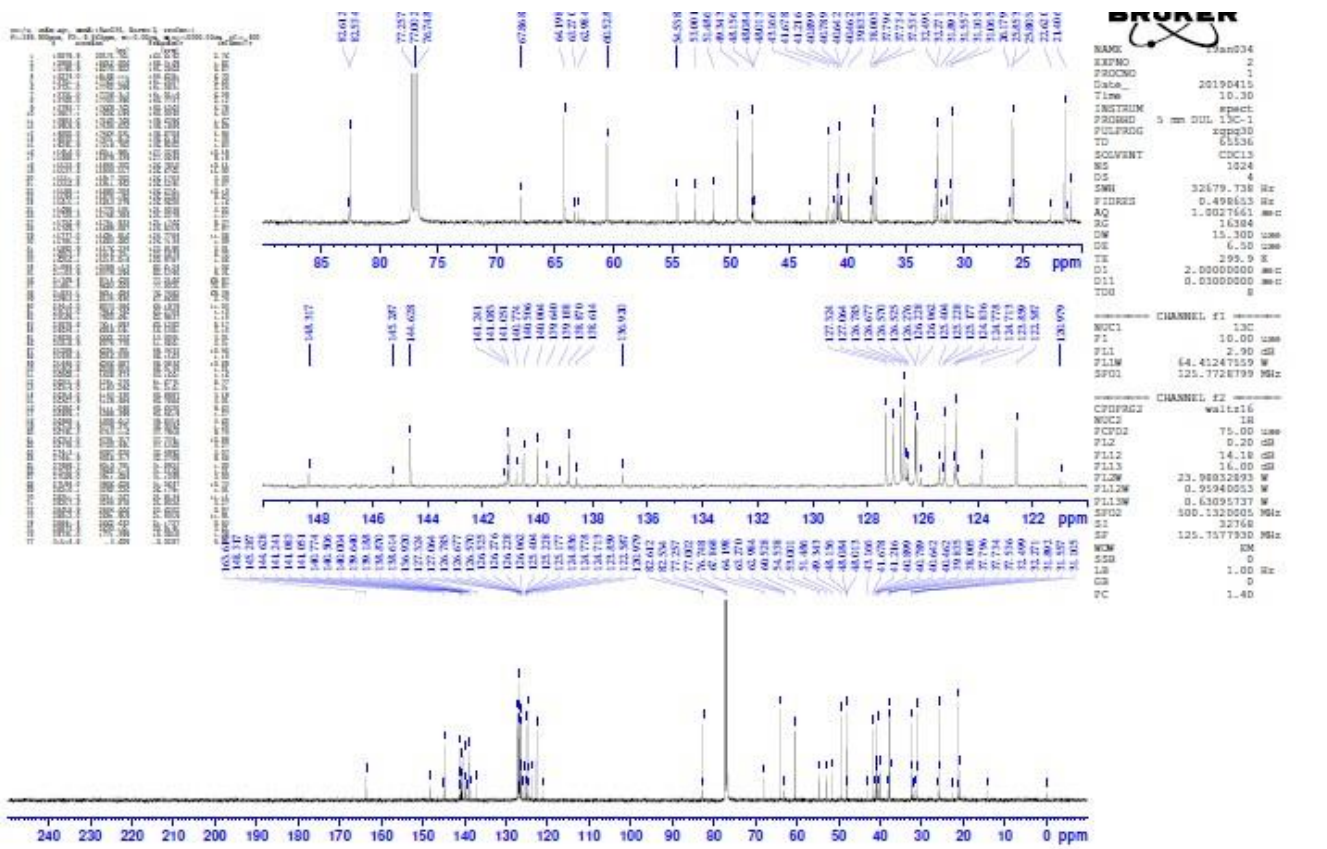
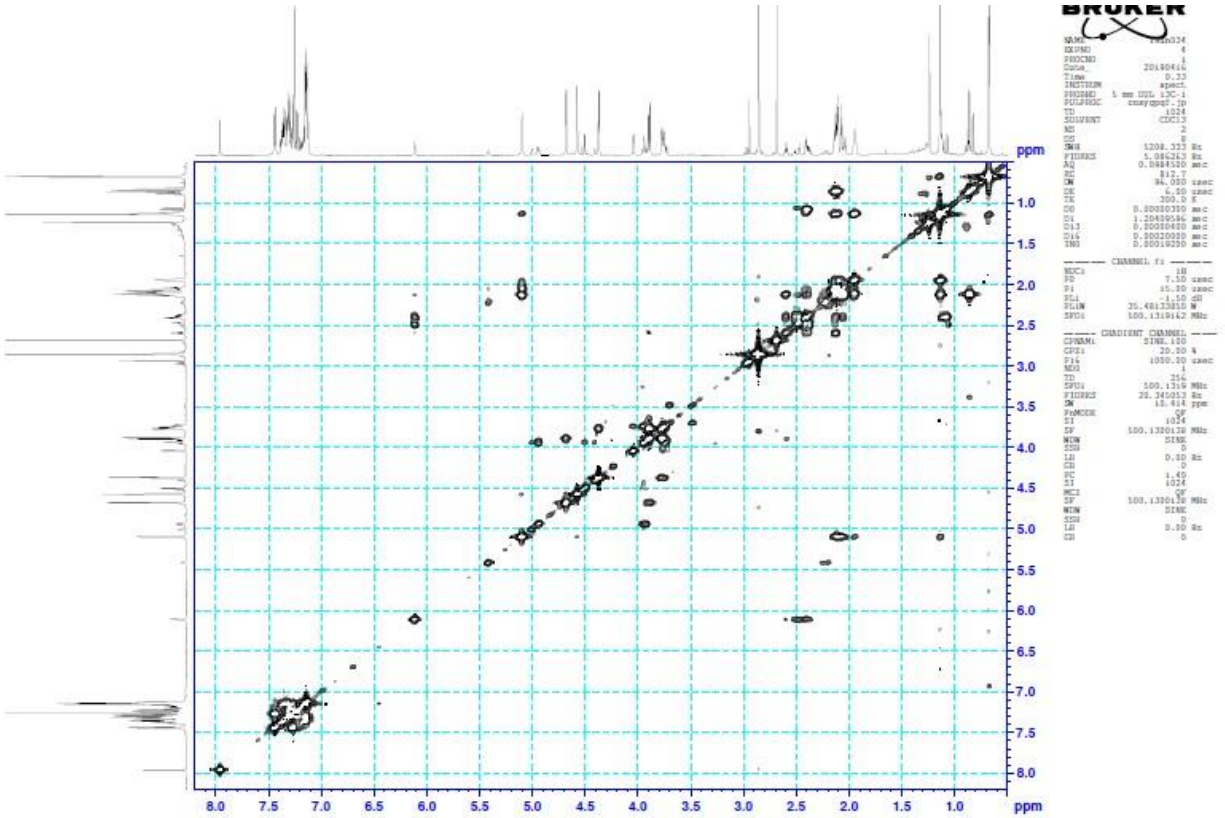


Fig. S17 ^{1}H NMR and ^{13}C spectra for **2b**. (500 MHz/126MHz, $CDCl_3$)



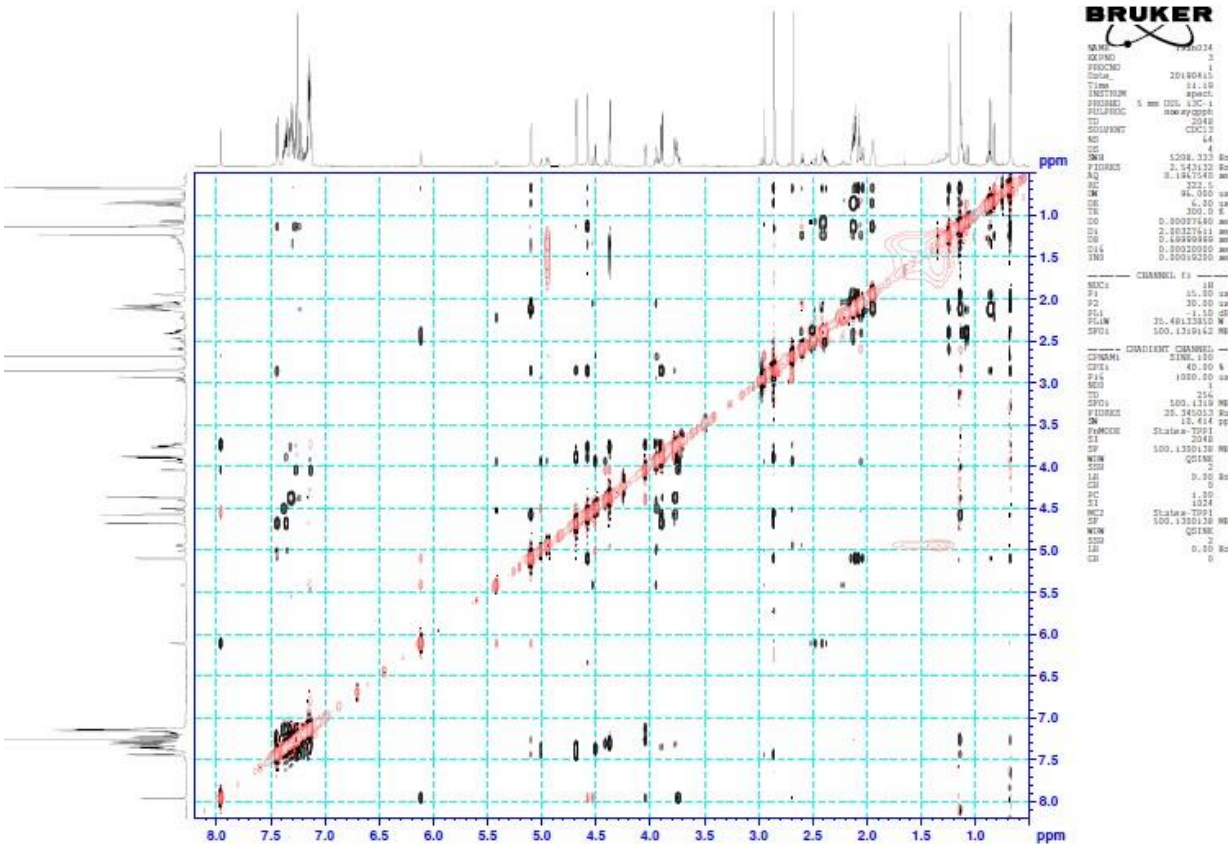
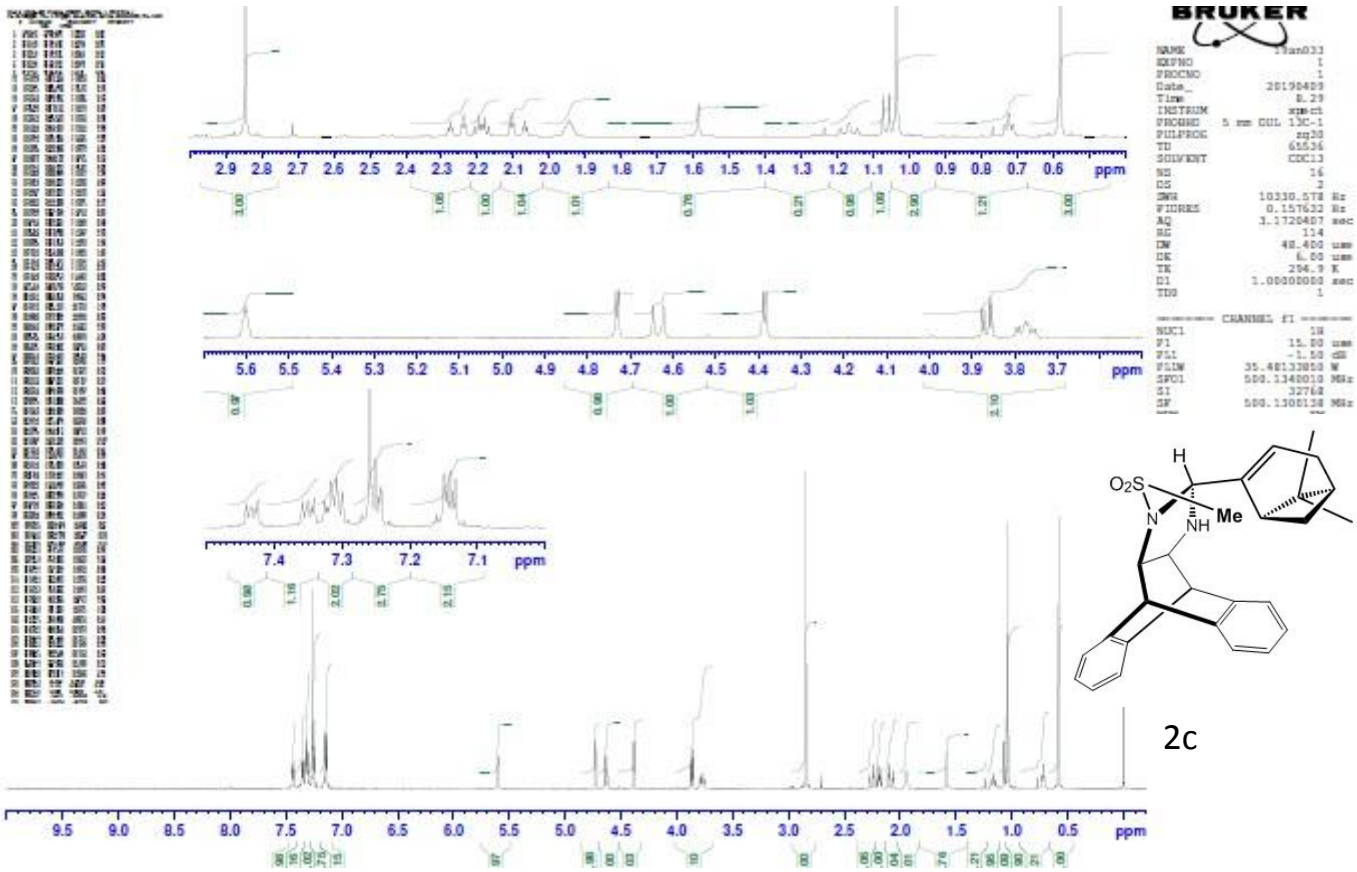


Fig. S18 COSY (above) and NOESY (below) spectra for **2b** (500 MHz, $CDCl_3$)



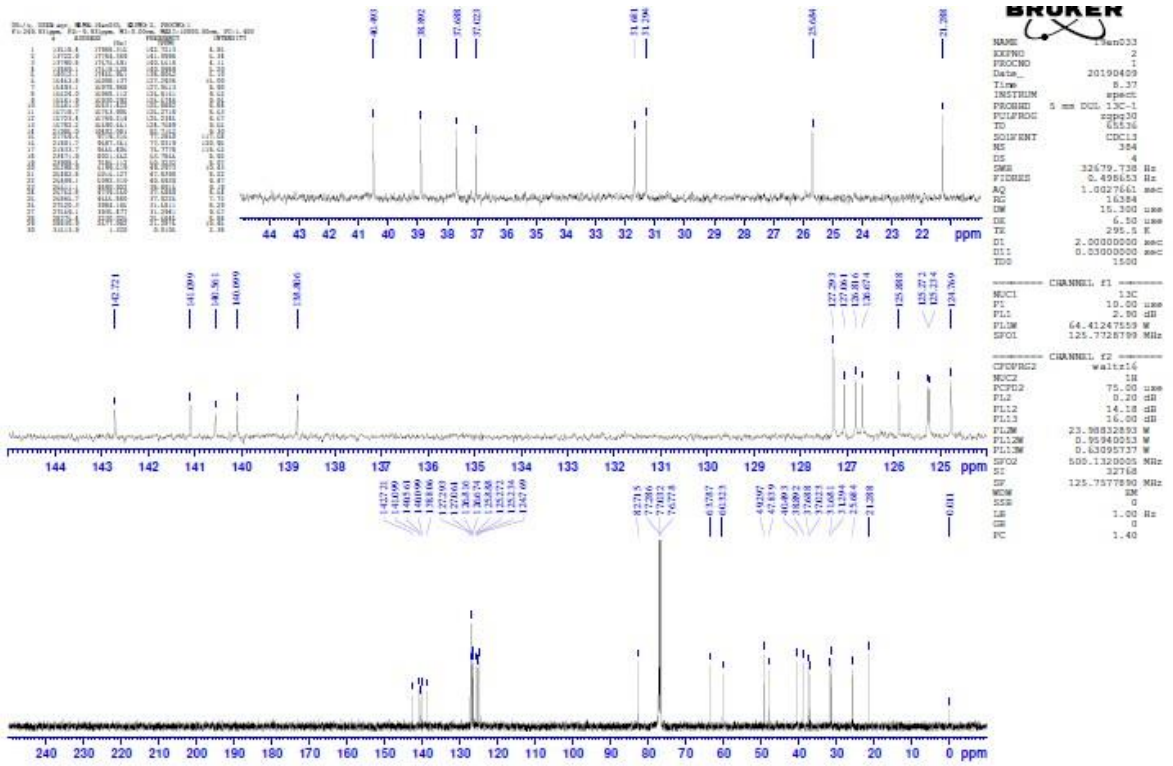
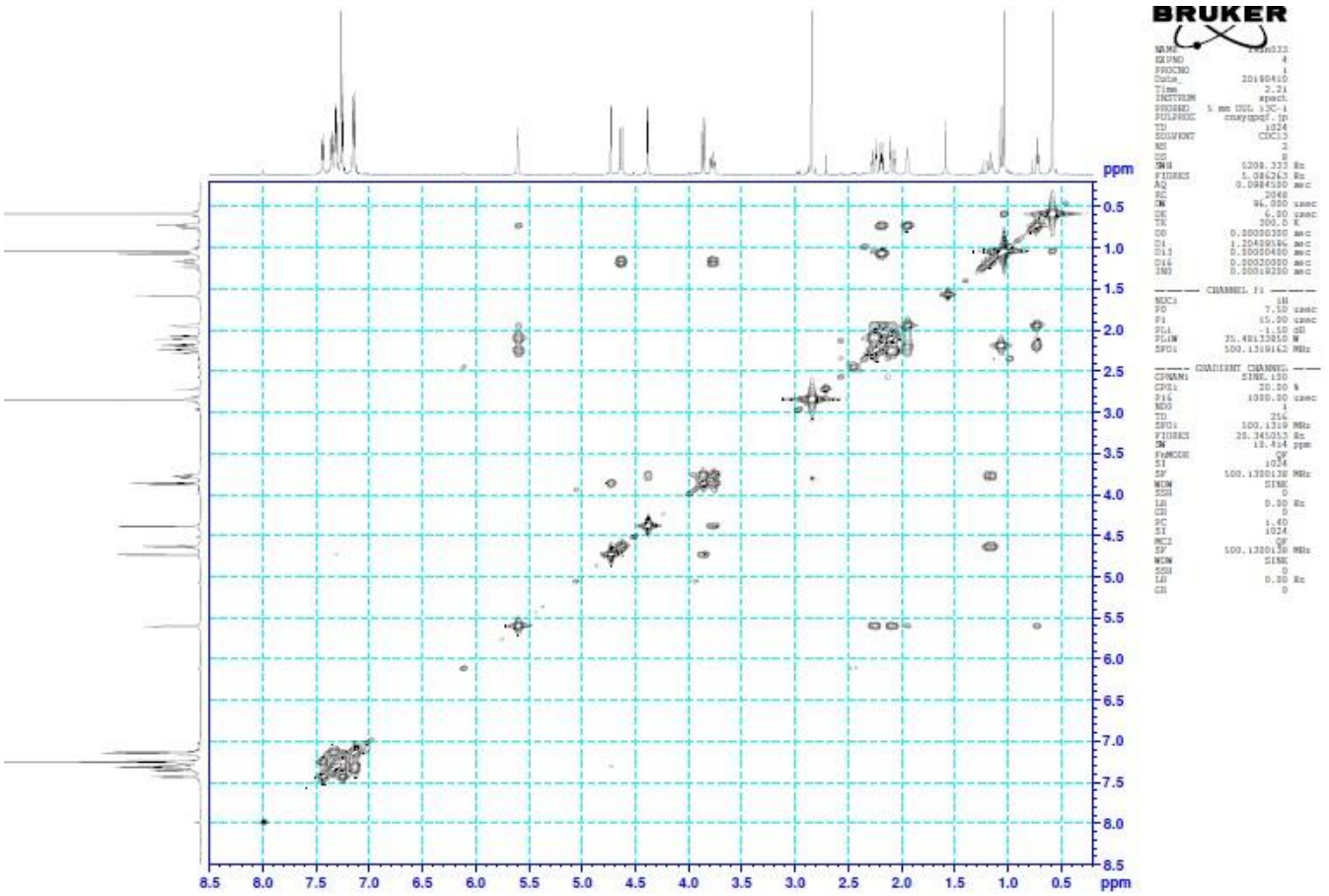


Fig. S19 ^{1}H and ^{13}C NMR spectra for **2c**. (500 MHz/126MHz, $CDCl_3$)



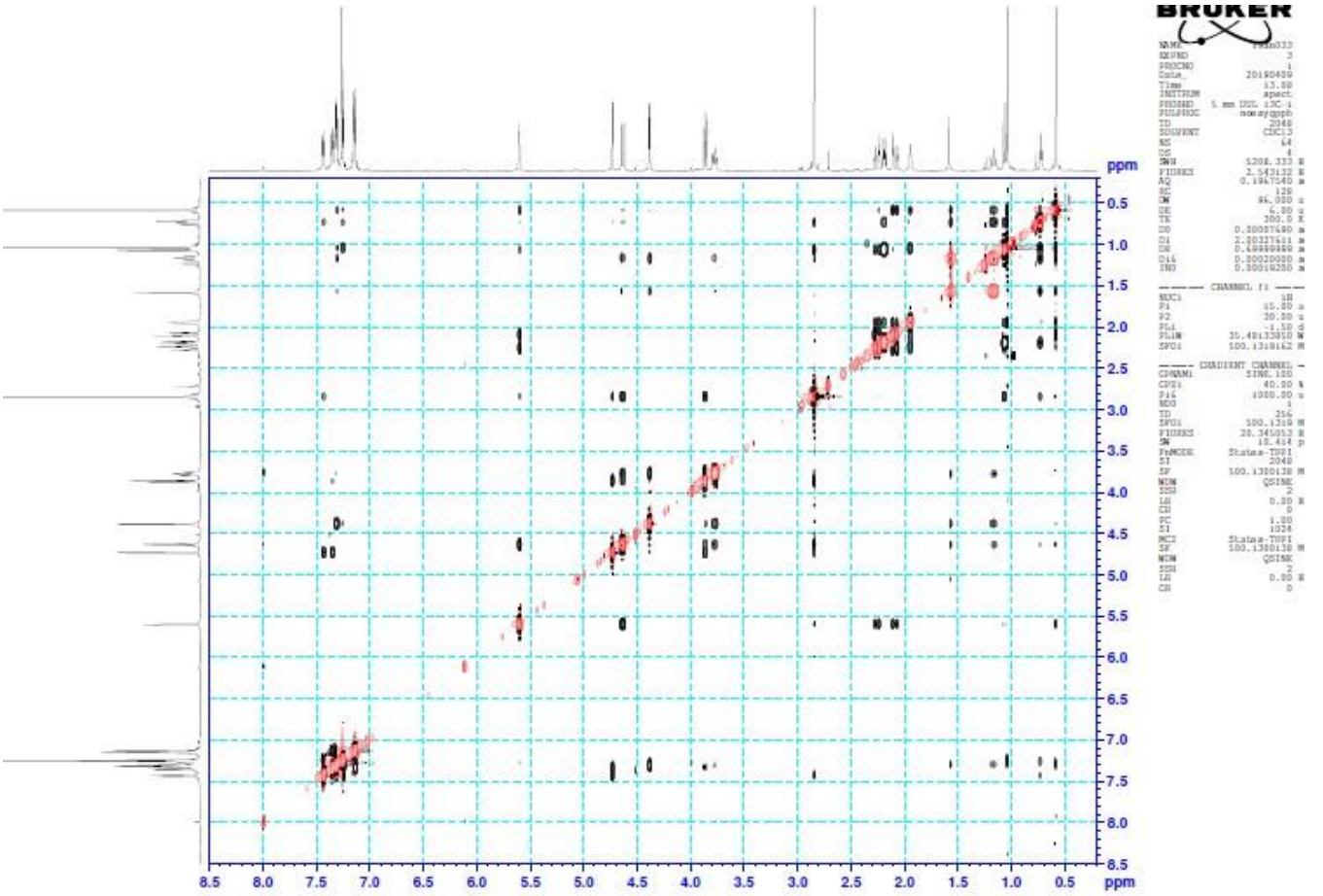
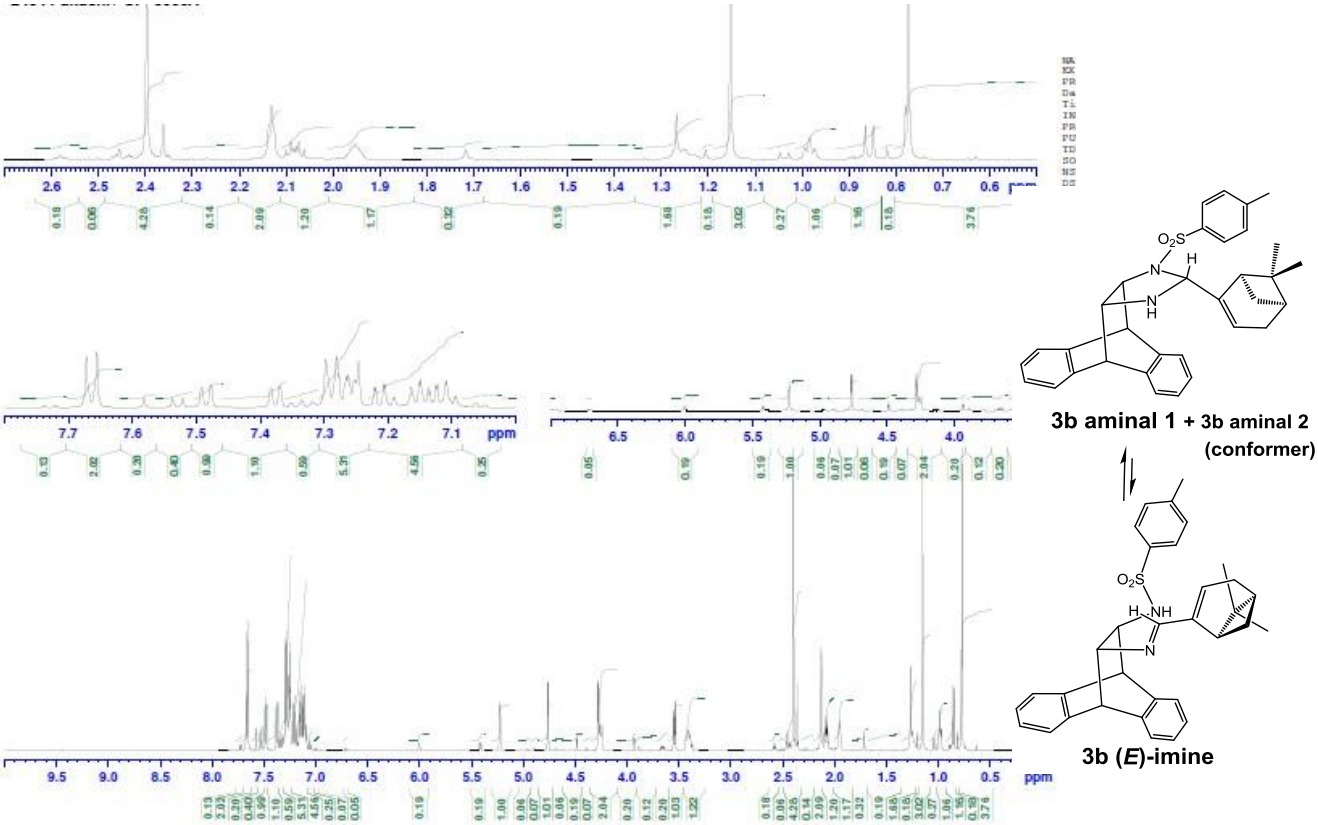


Fig. S20 COSY (above) and NOESY (below) spectra for **2c**. (500 MHz, $CDCl_3$)



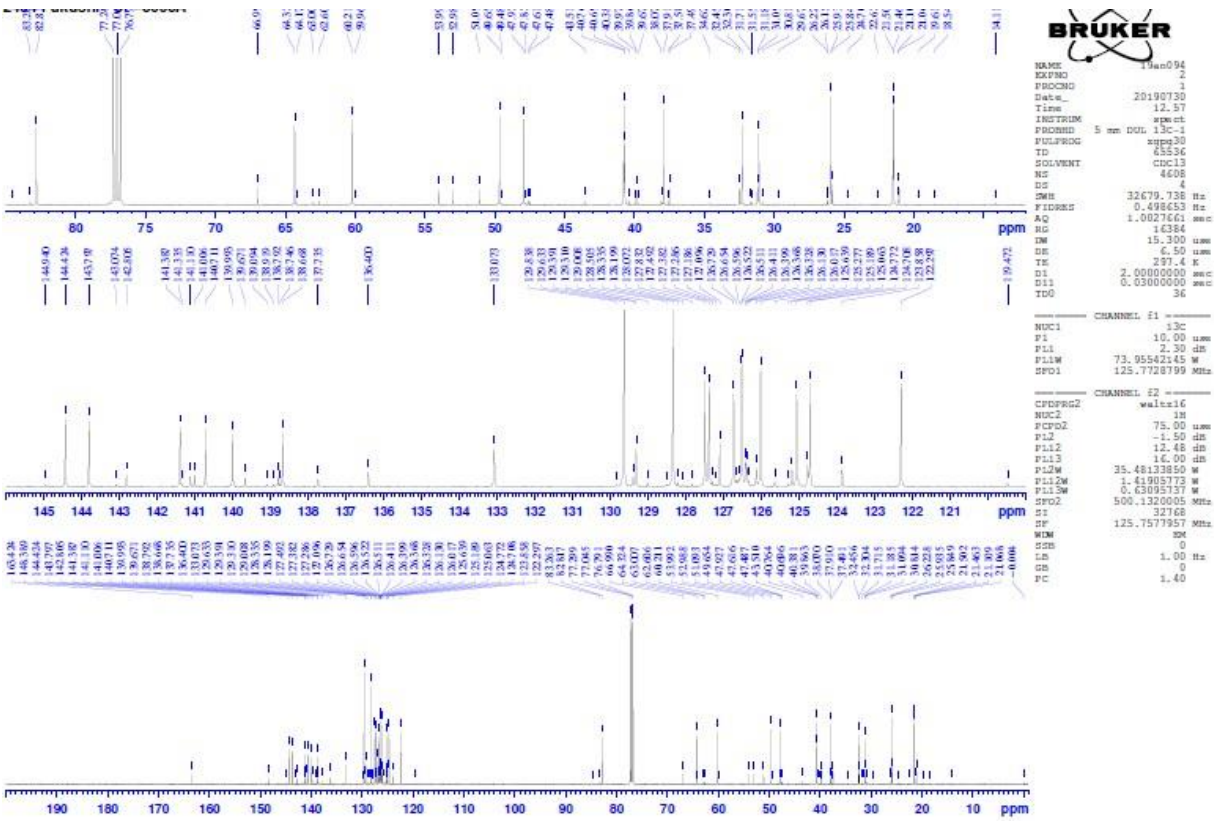
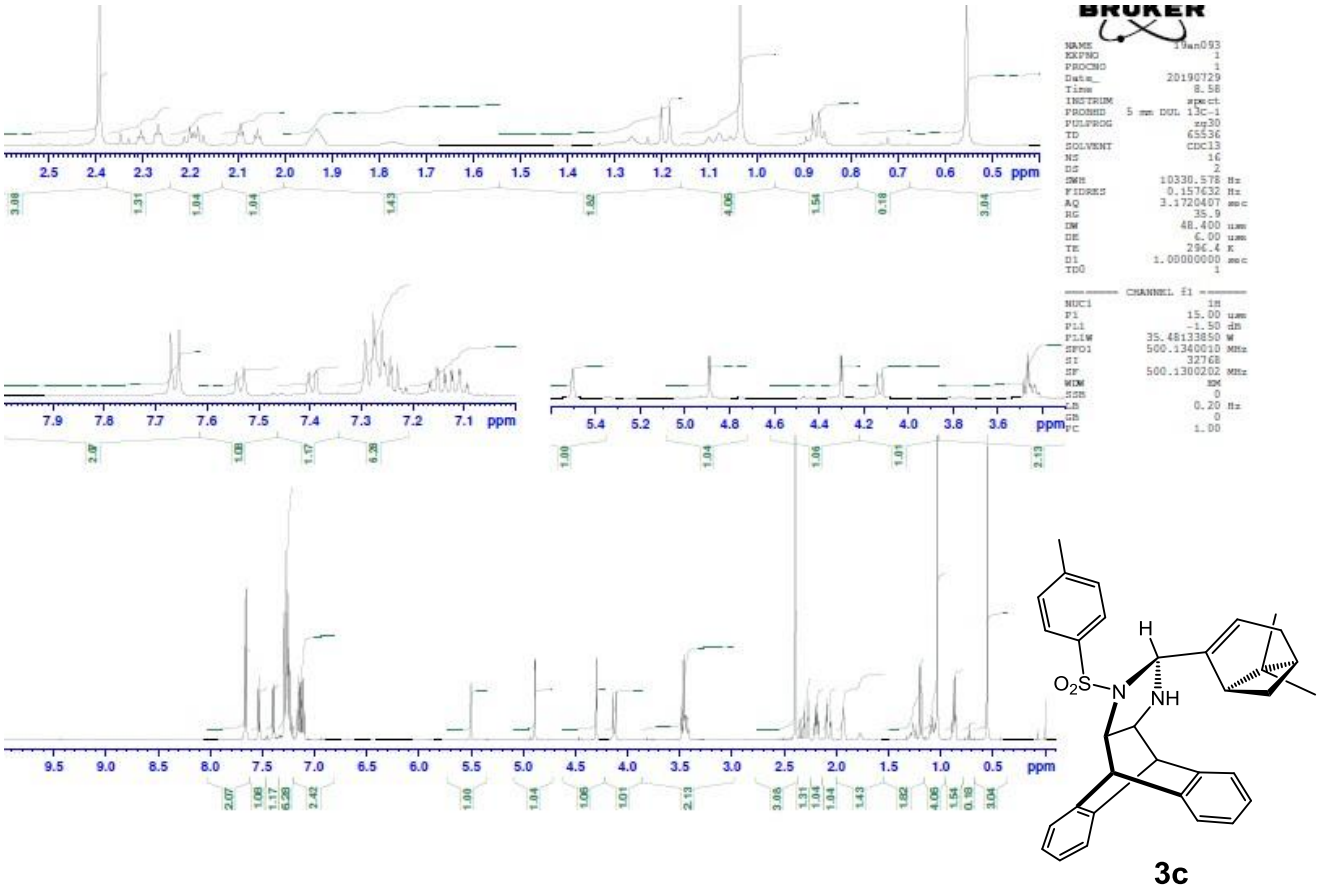


Fig. S21 ^{1}H NMR and ^{13}C spectra for **3b**. (500 MHz/126MHz, $CDCl_3$)



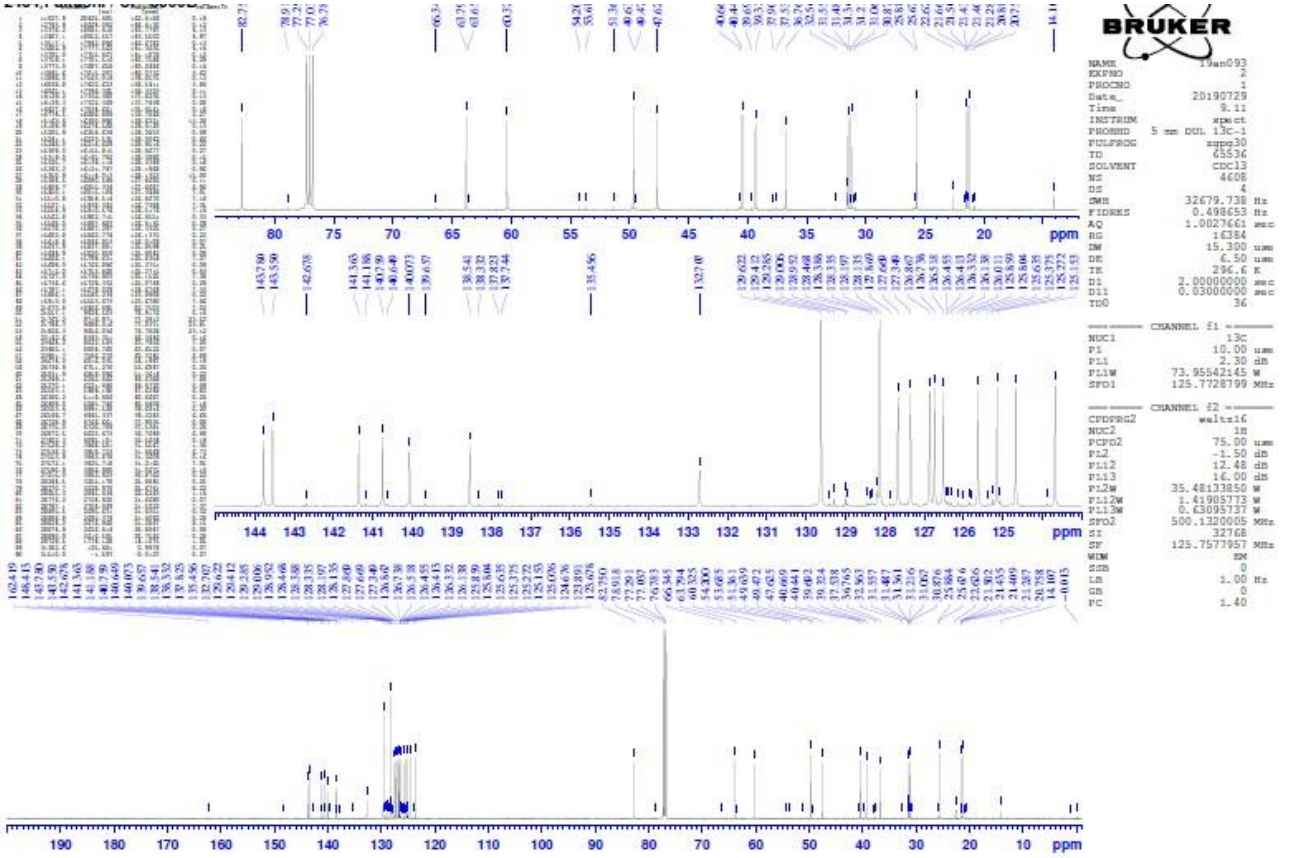
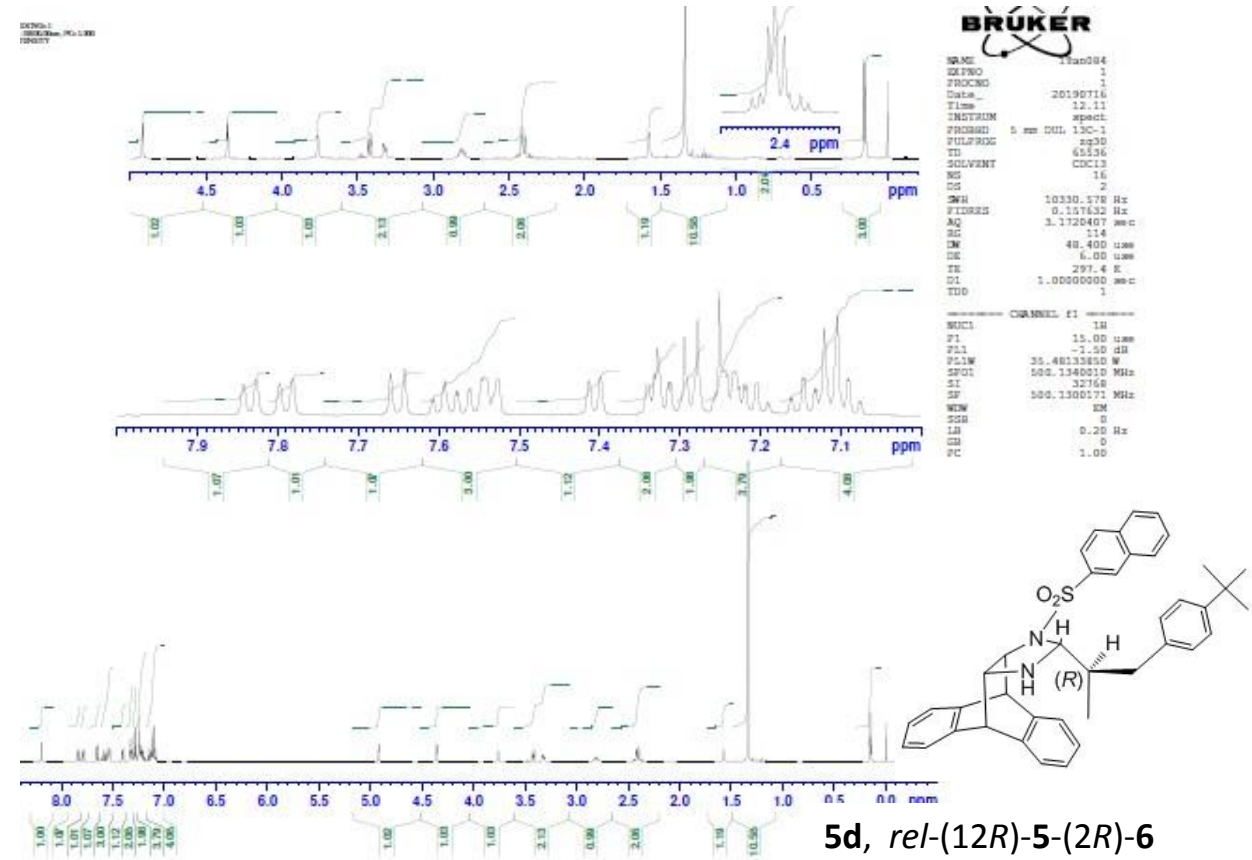


Fig. S22 ^{1}H NMR and ^{13}C spectra for **3c** (500 MHz/126MHz, $CDCl_3$)



5d, *rel*-(12*R*)-**5**-(2*R*)-**6**

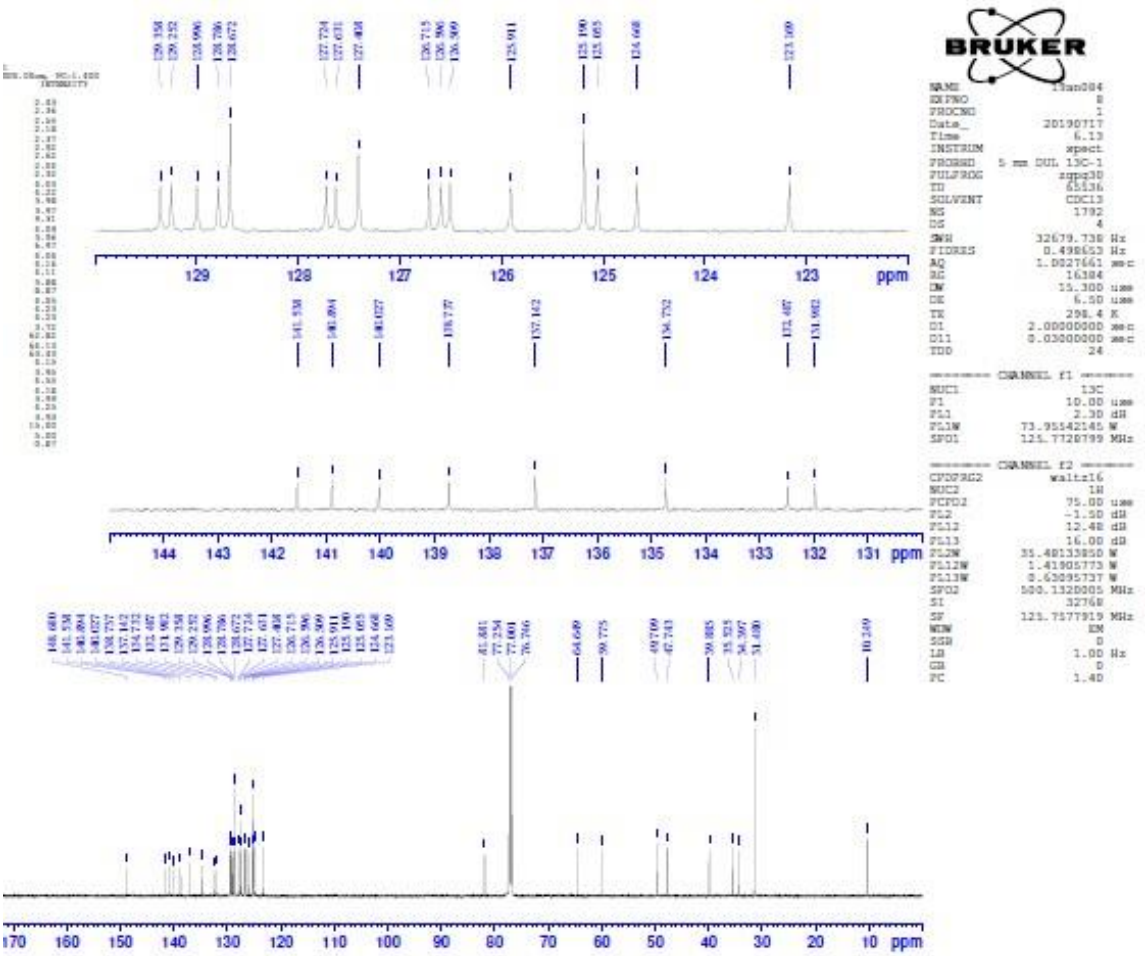
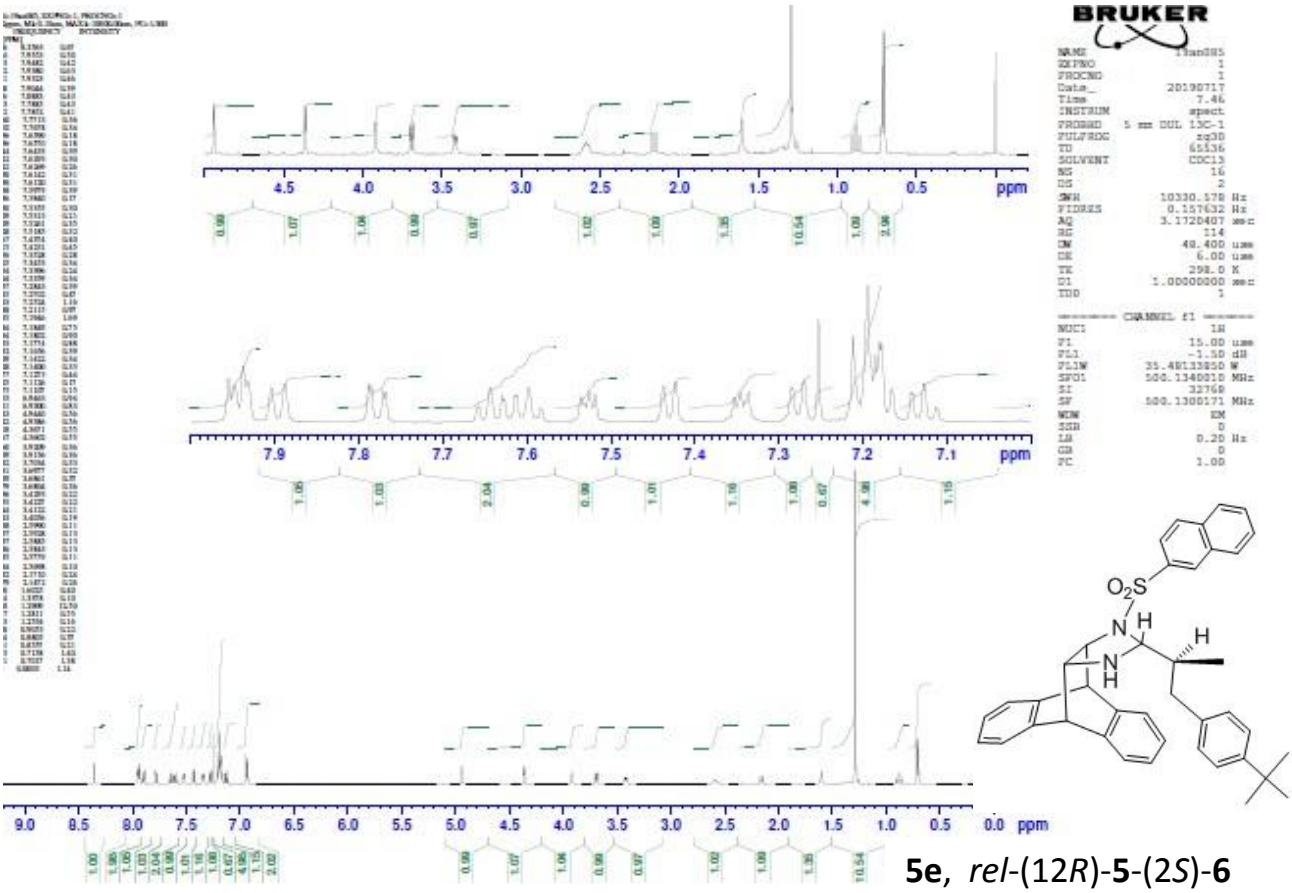


Fig. S23 ^{1}H NMR and ^{13}C spectra for **5d**. (500 MHz/126MHz, $CDCl_3$)



5e, *rel*-(12*R*)-**5**-(2*S*)-**6**

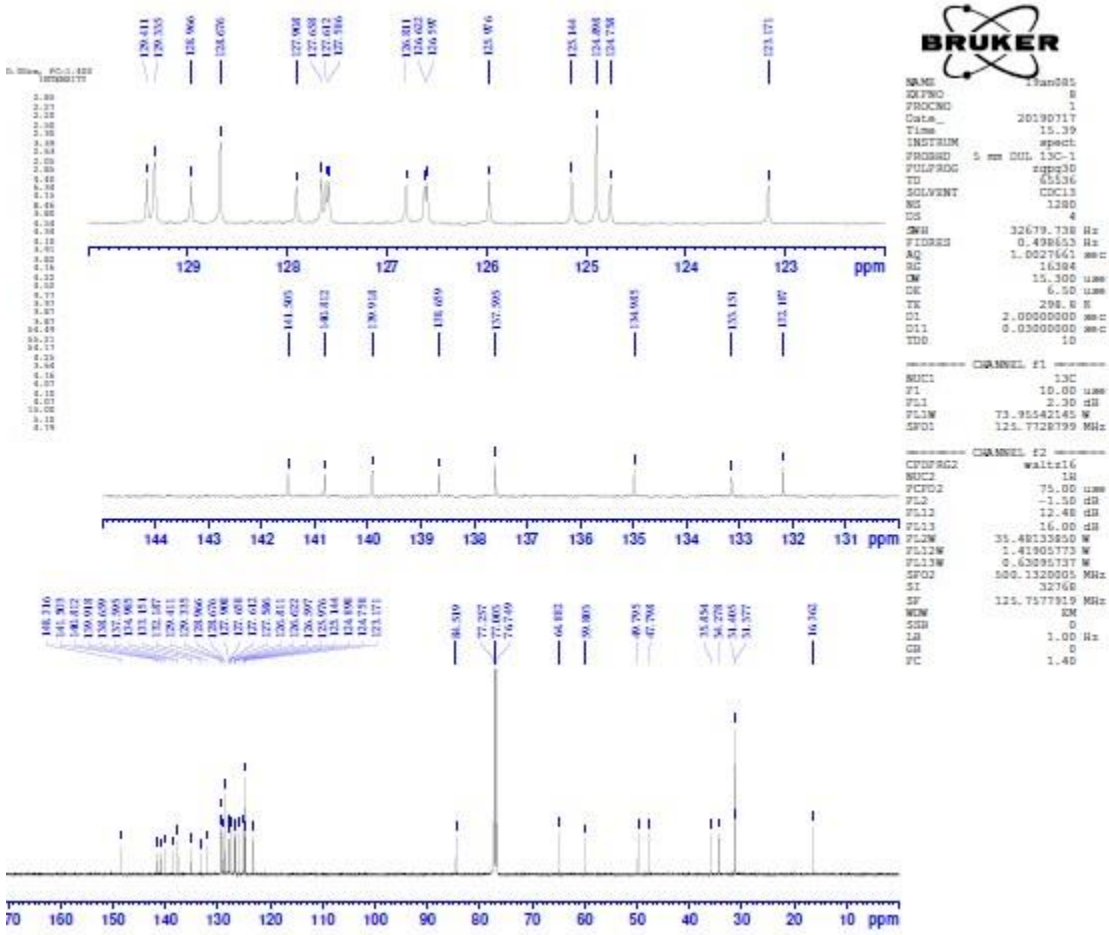


Fig. S24 ^{1}H NMR and ^{13}C spectra for **5e**. (500 MHz/126MHz, $CDCl_3$)