Electronic Supplementary Material (ESI) for Photochemical & Photobiological Sciences.

Supporting information

Synthesis of the fused heterocyclic systems via Mallory photoreaction of arylthienoethenes

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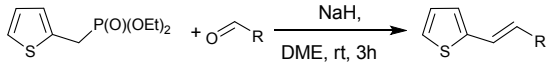
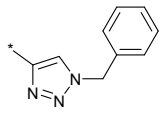
1. Synthesis of the starting stilbenes

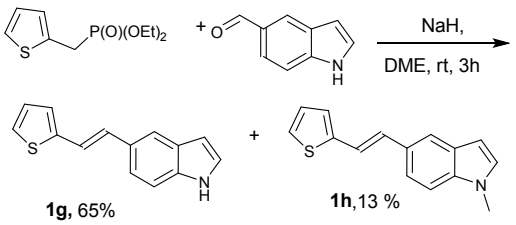
3-[(*E*)-2-(4-methoxyphenyl)vinyl]thiophene **2a** [1], 2-[(*E*)-2-(4-methoxyphenyl)vinyl]thiophene **1a** [1, 2], 3-[(*E*)-2-(3,5-dimethoxyphenyl)vinyl]thiophene **2b** [3], 2-[(*E*)-2-(3,4-dimethoxyphenyl)vinyl]thiophene **1c** [4, 5], 2-[(*E*)-2-(3,4,5-trimethoxyphenyl)vinyl]thiophene **1e** [6], are reported in the literature and were synthesized according to Horner-Wadsworth-Emmons method according to general procedure below [7].

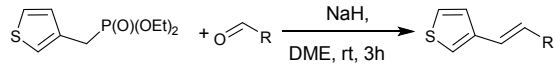
Sodium hydride (690 mg, 17.3 mmol) (60% dispersion in paraffin) washed with petroleum ether was dispersed in 70 ml of dimethoxyethane at 0 ^{0}C. Then 1 g (4.3 mmol) of diethyl 2- or 3-thienylphosphonate was added and the reaction was stirred for 15 min. Afterwards, 4.3 mmol of an aldehyde in 10 ml of DME was slowly added to the reaction mixture. The mixture is stirred at room temperature for 3 hr. Then the reaction is quenched by addition in small portions to 100 ml of cold (0-5 ^{0}C) water. The resulting precipitate was filtered and recrystallized from methanol.



1a: R = 4-(CH_3O)Ph, 87%;
1b: R = 2-(CH_3O)Ph,34%;
1c: R = 3,4-(CH_3O)$_2$Ph, 90%;
1d: R = 2,4-(CH_3O)$_2$Ph, 86%;
1e: R = 3,4,5-(CH_3O)$_2$Ph, 65%;

1f: R =  58%



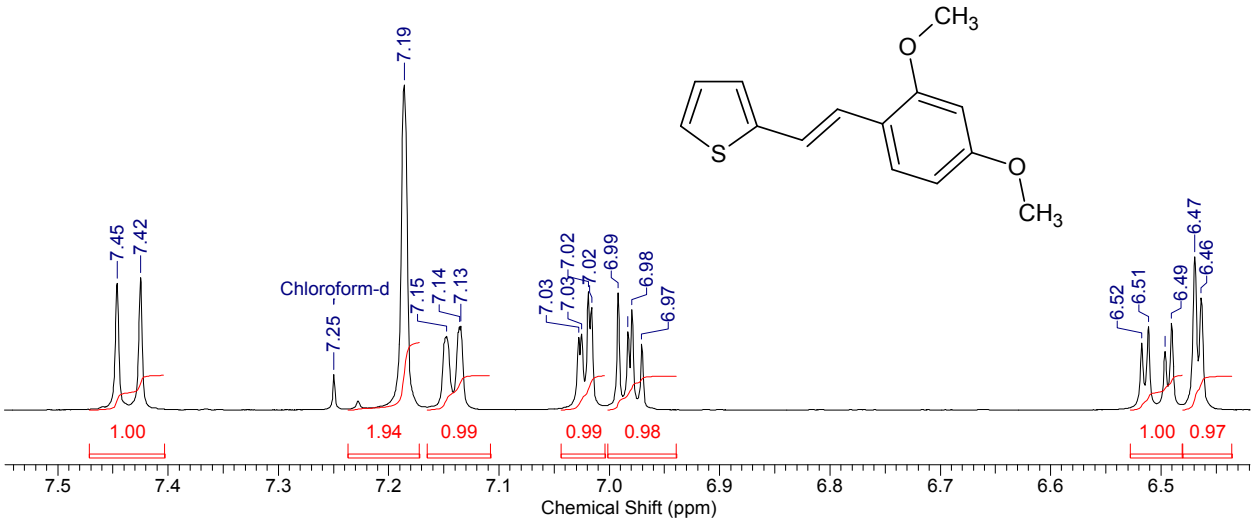


2a: R = 4-(CH_3O)Ph, 90%;
2b:R =3,5-(CH_3O)$_2$Ph, 53%;
2c: R = 4-(CH_3OCO)Ph, 55%;
2d: R = 3,4,5-(CH_3O)$_2$Ph, 93%
2e: R = 2,4-(CH_3O)$_2$Ph, 30%;
2f: R = 2,3-(CH_3O)$_2$Ph 40%;
2g:R = 2-(CH_3O)$_2$Ph, 79%;

2. NMR spectra

2.1. Starting stilbenes

a)



b)

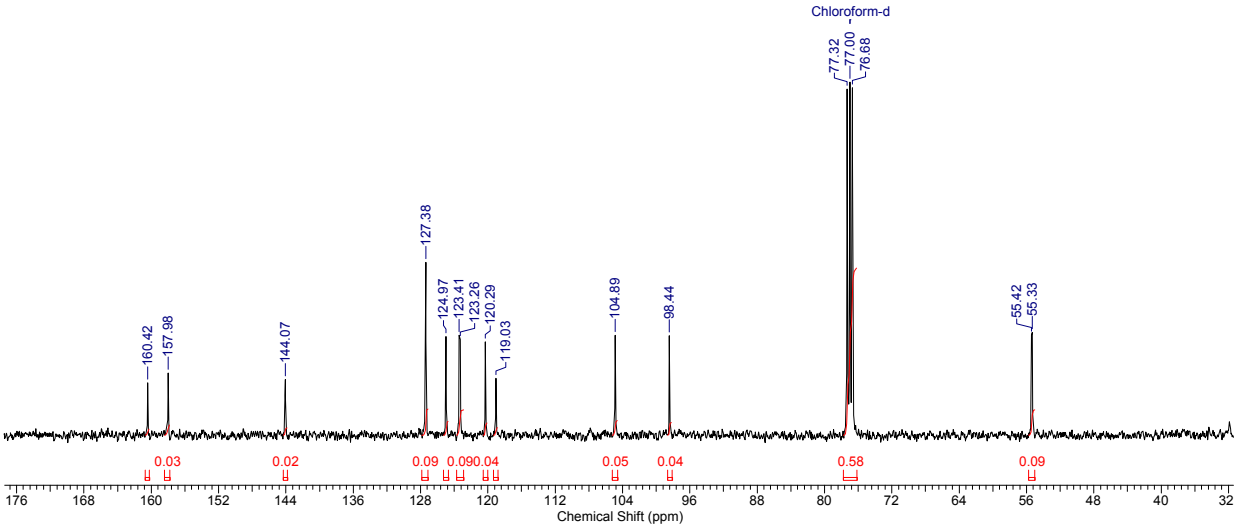


Fig. S1. ^{1}H (a) and ^{13}C (b) NMR spectra of **1d**.

a)

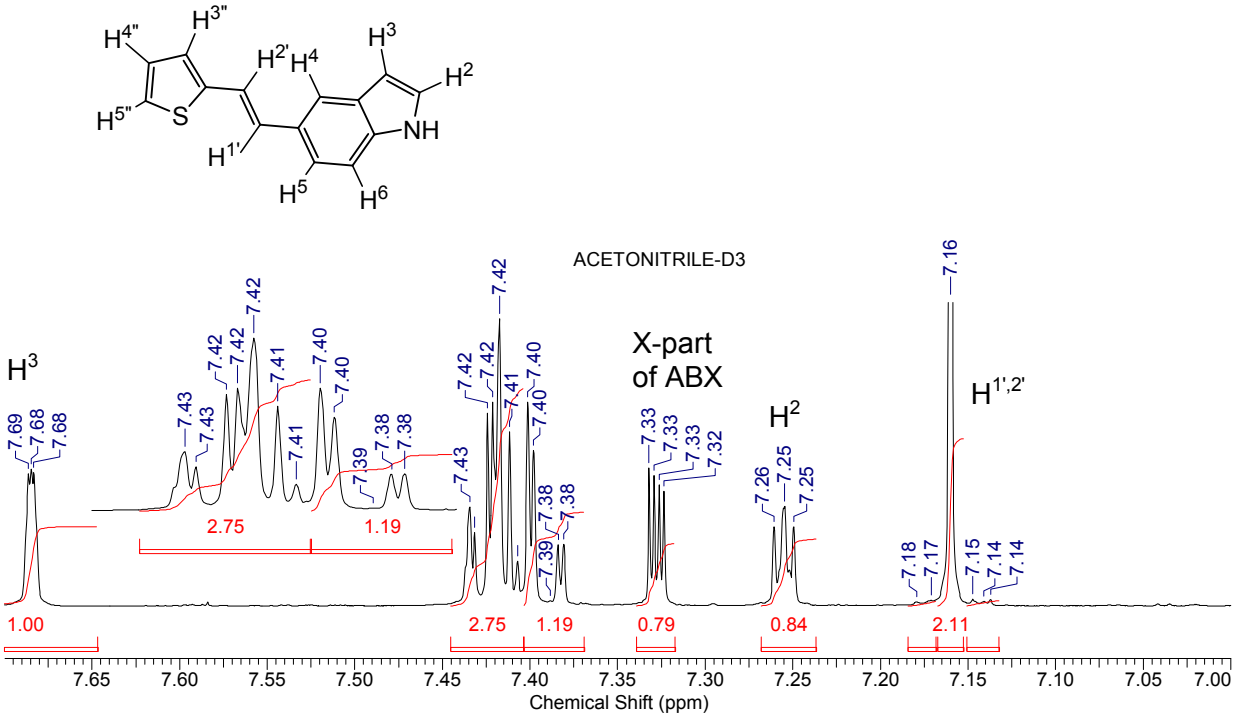
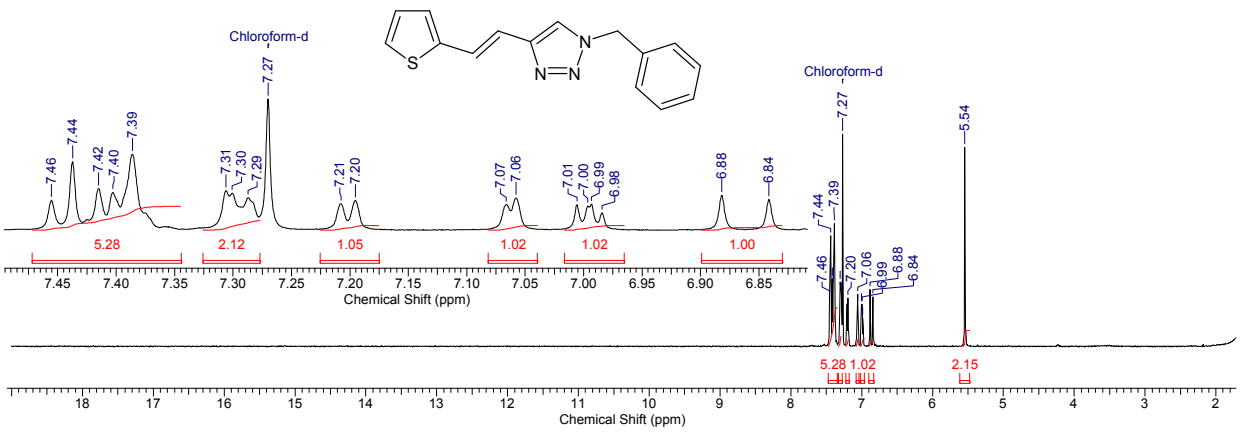


Fig. S2. ^{1}H NMR spectrum of **1f**.

a)



b)

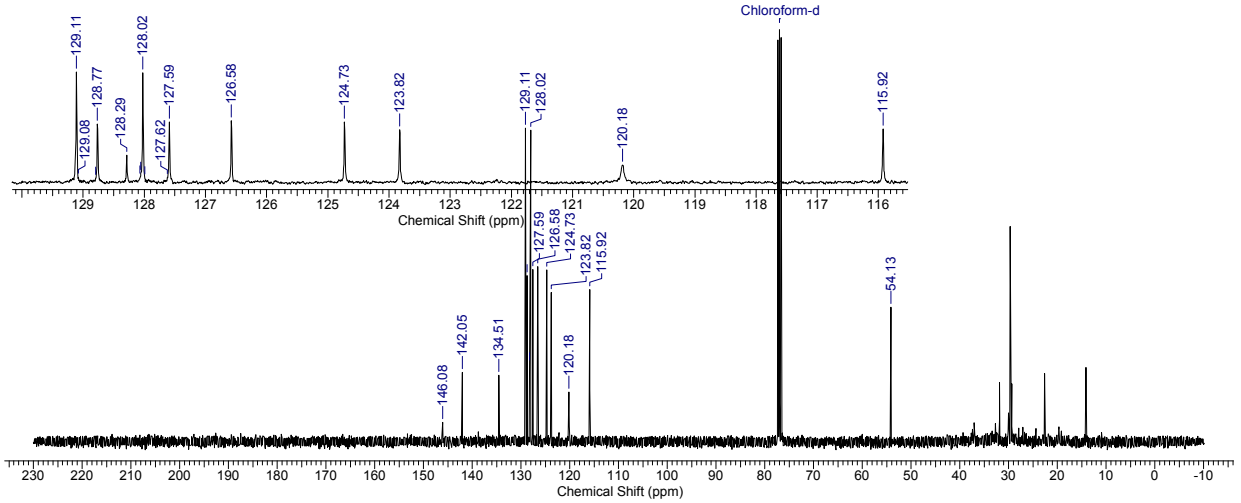


Fig. S3. ^{1}H (a) and ^{13}C (b) NMR spectra of **1g**.

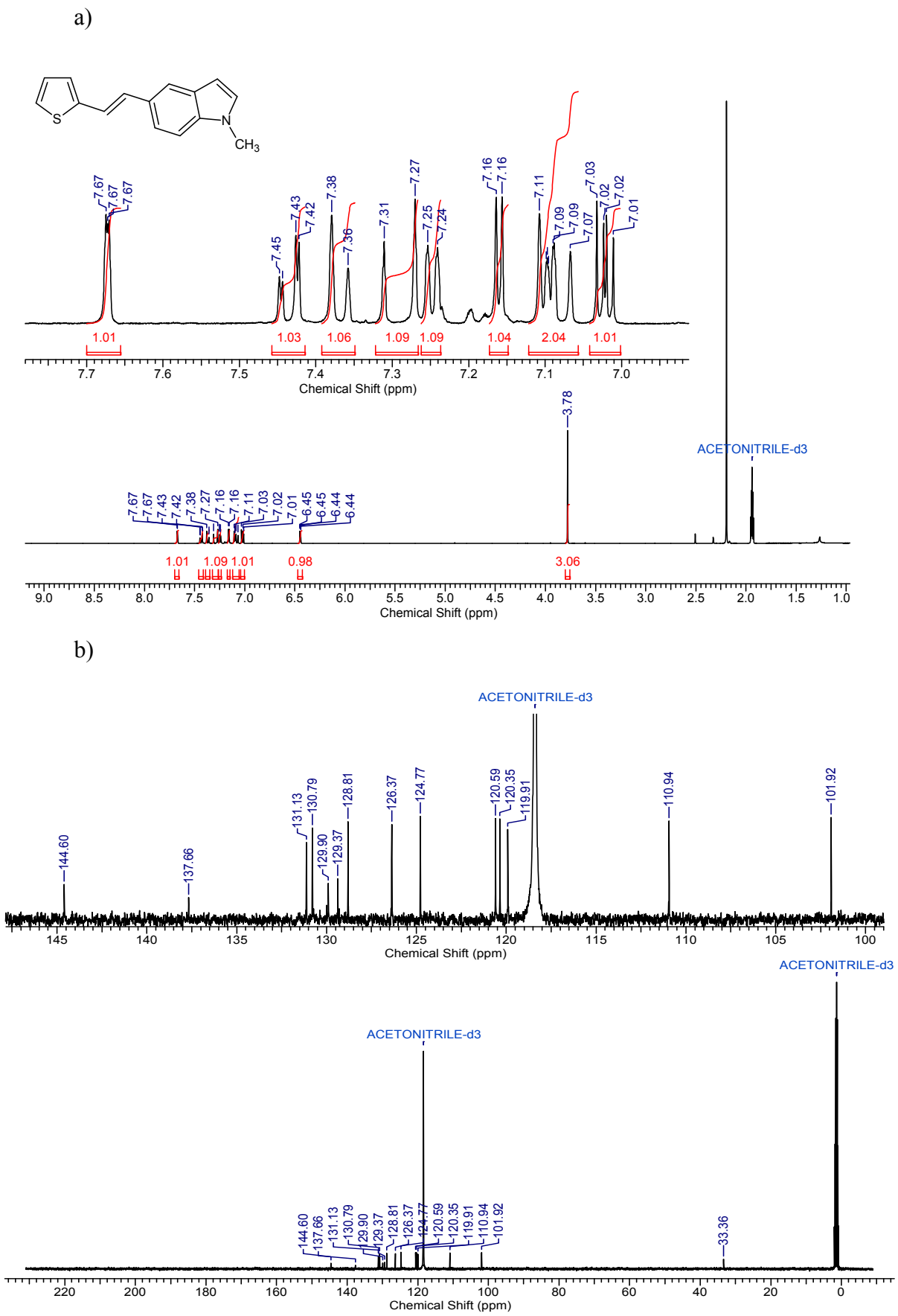
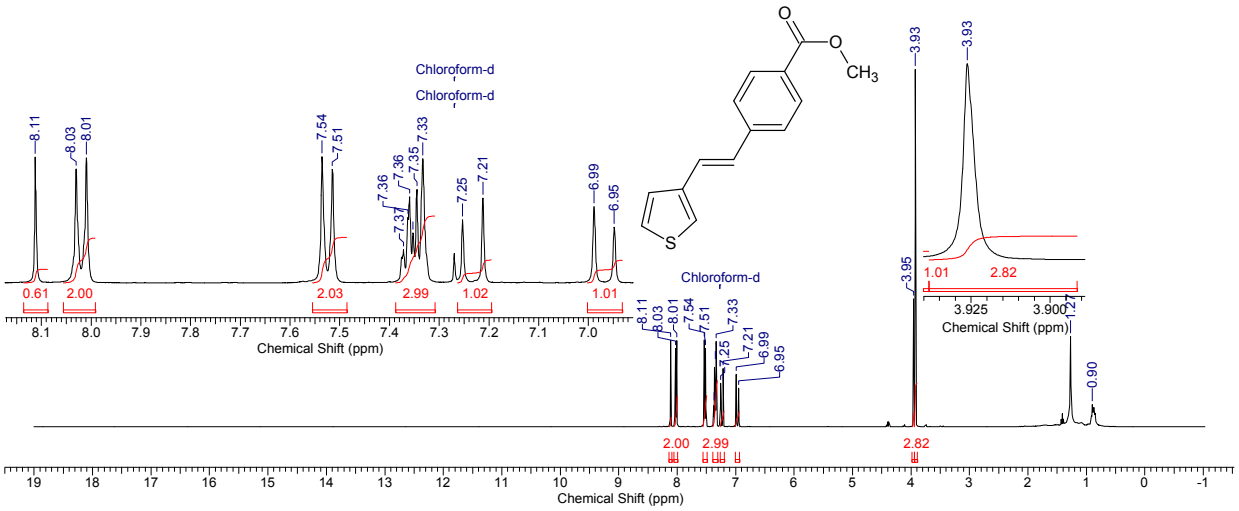


Fig. S4. ^{1}H (a) and ^{13}C (b) NMR spectra of **1h**.

a)



b)

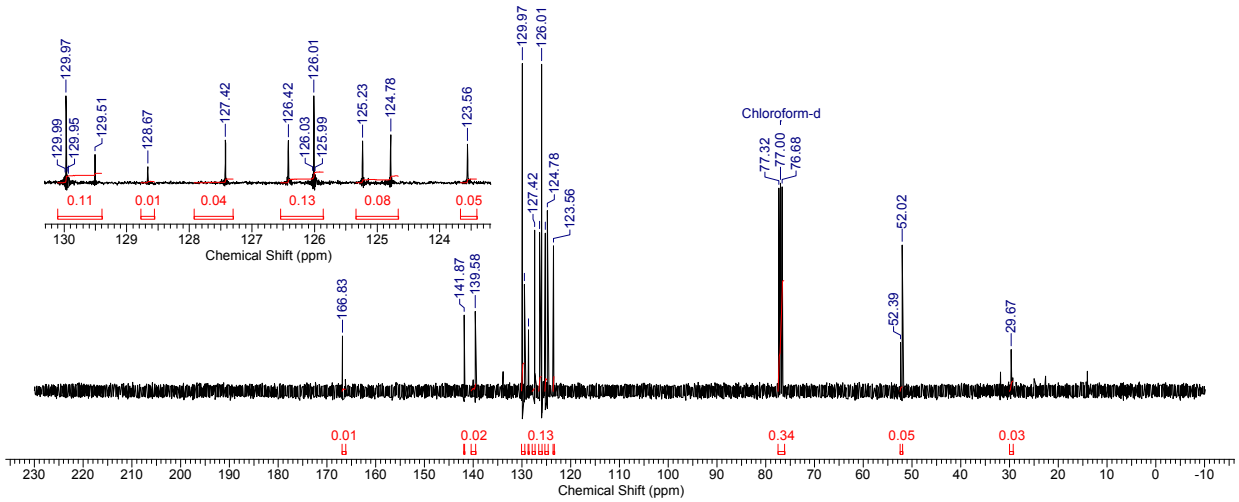
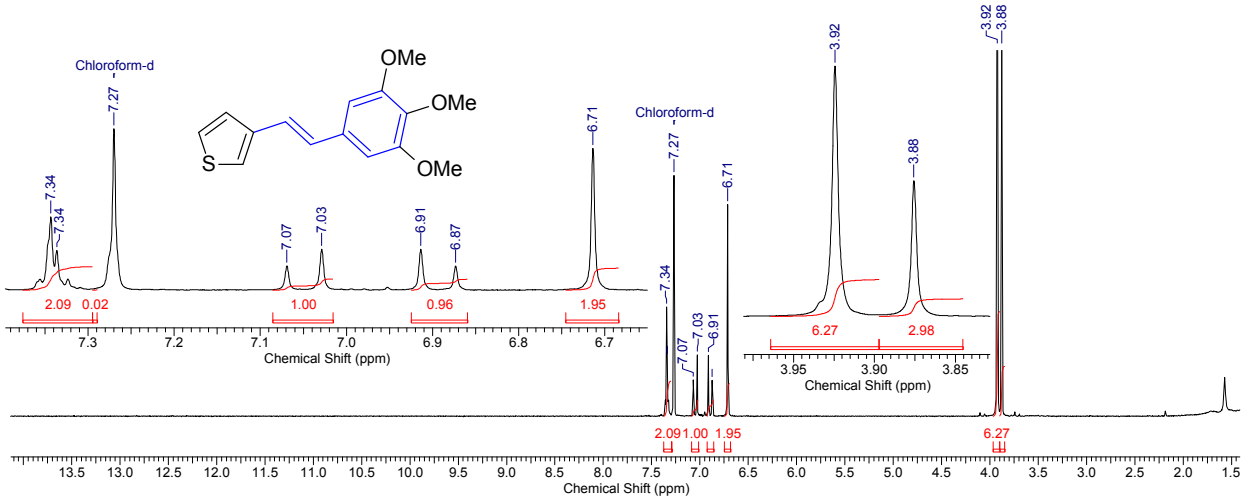


Fig. S5. ^{1}H (a) and ^{13}C (b) NMR spectra of **2c**.

a)



b)

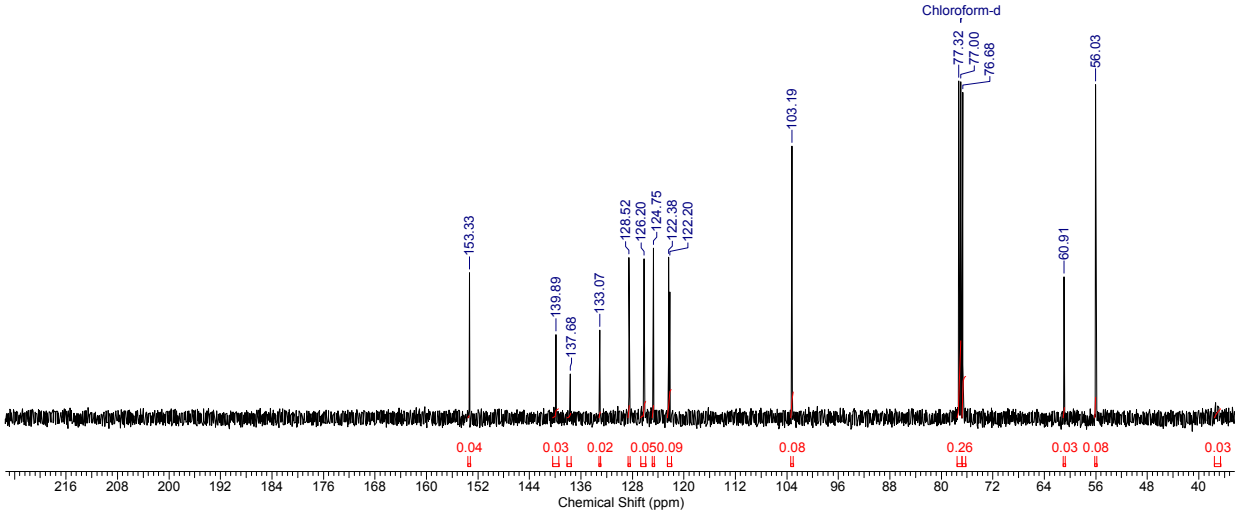
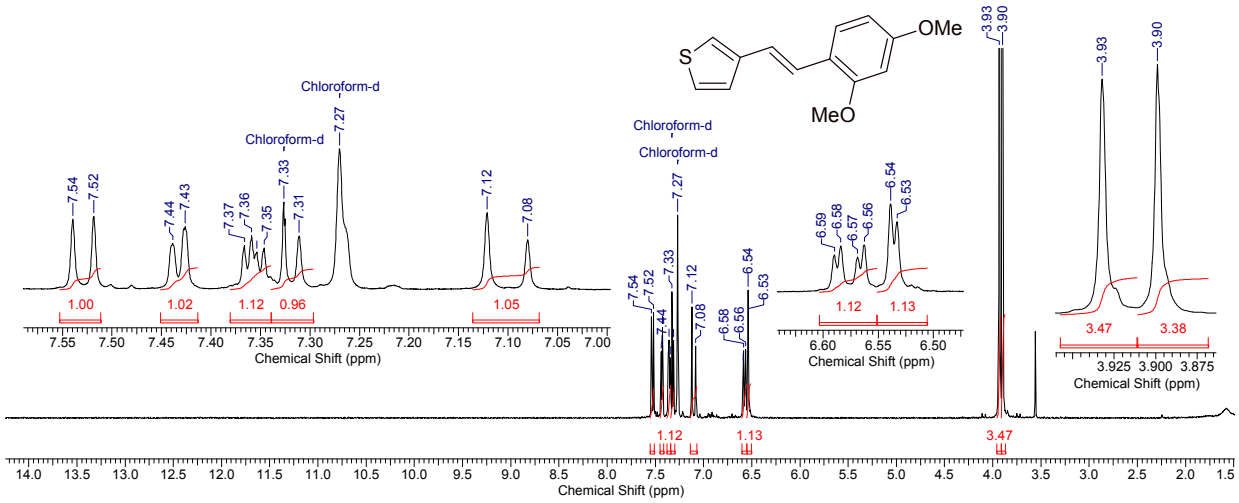


Fig. S6. ^{1}H (a) and ^{13}C (b) NMR spectra of **2d**.

a)



b)

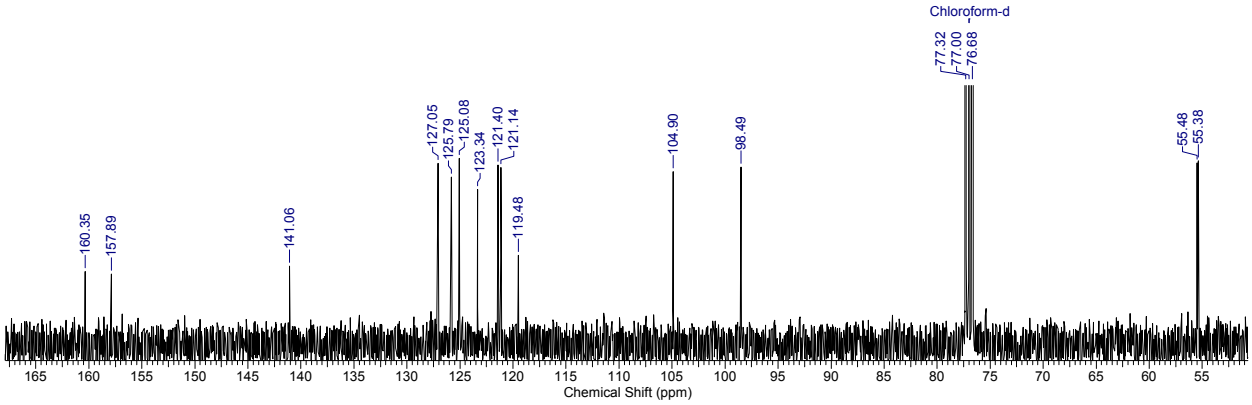


Fig. S7. ^{1}H (a) and ^{13}C (b) NMR spectra of **2e**.

a)

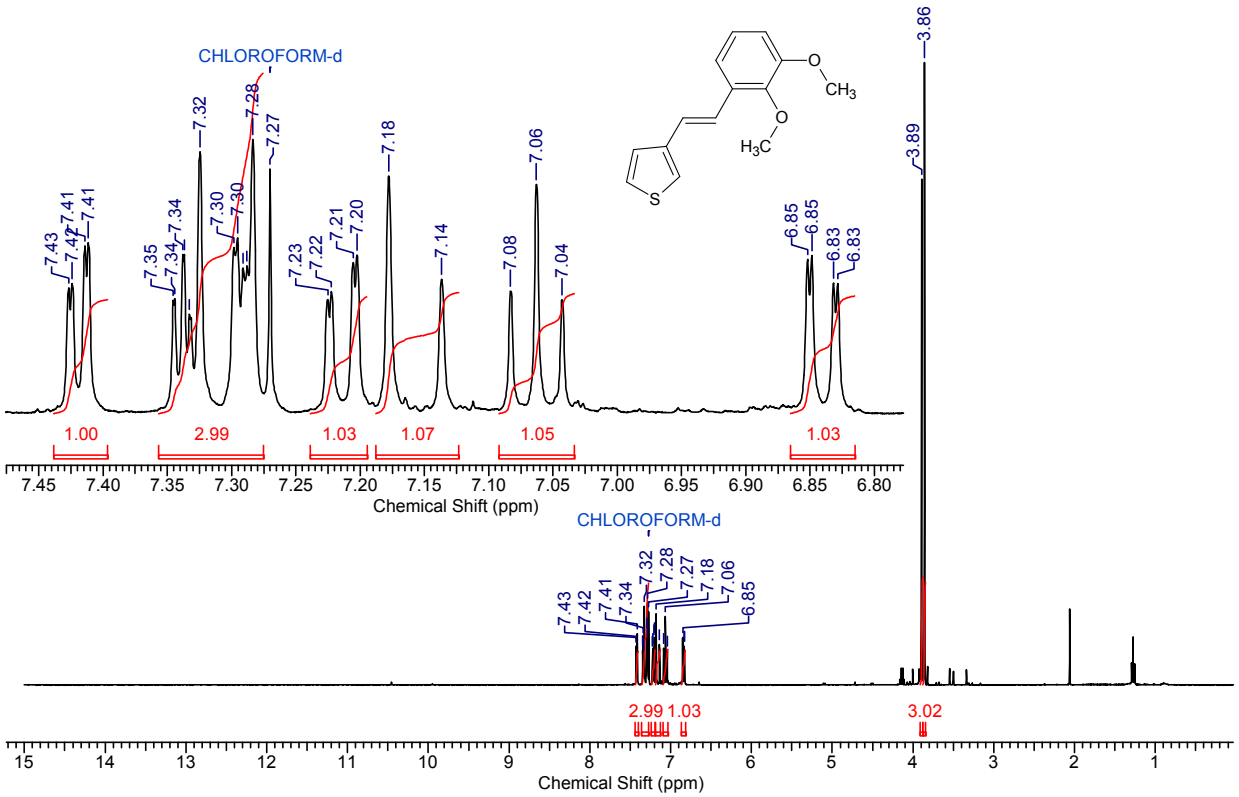


Fig. S8. (a) ^{1}H NMR spectra of **2f**.

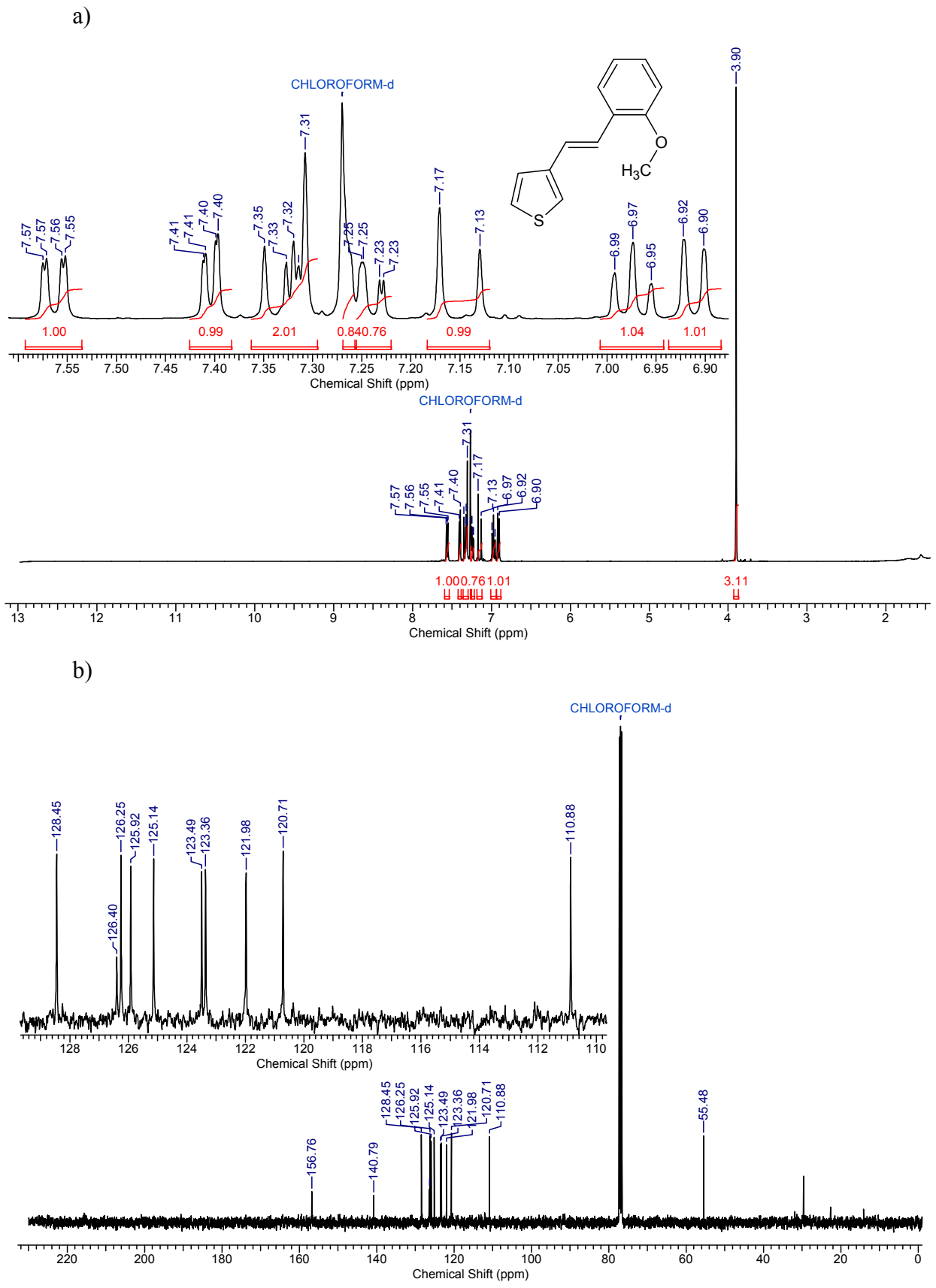
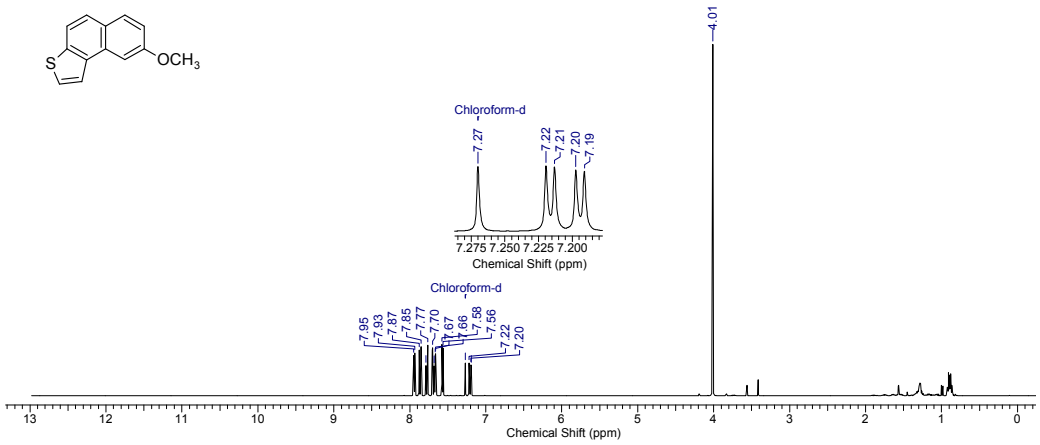


Fig. S9. ^{1}H (a) and ^{13}C (b) NMR spectra of **2g**.

2.2. Photocyclization products

a)



b)

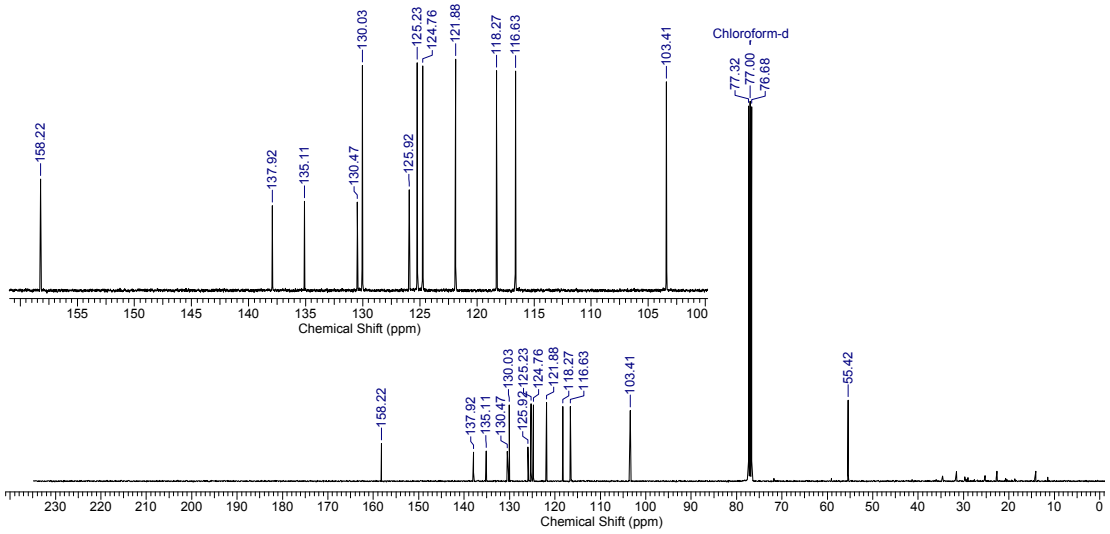


Fig. S10. ^{1}H (a) and ^{13}C (b) NMR spectra of **3a**.

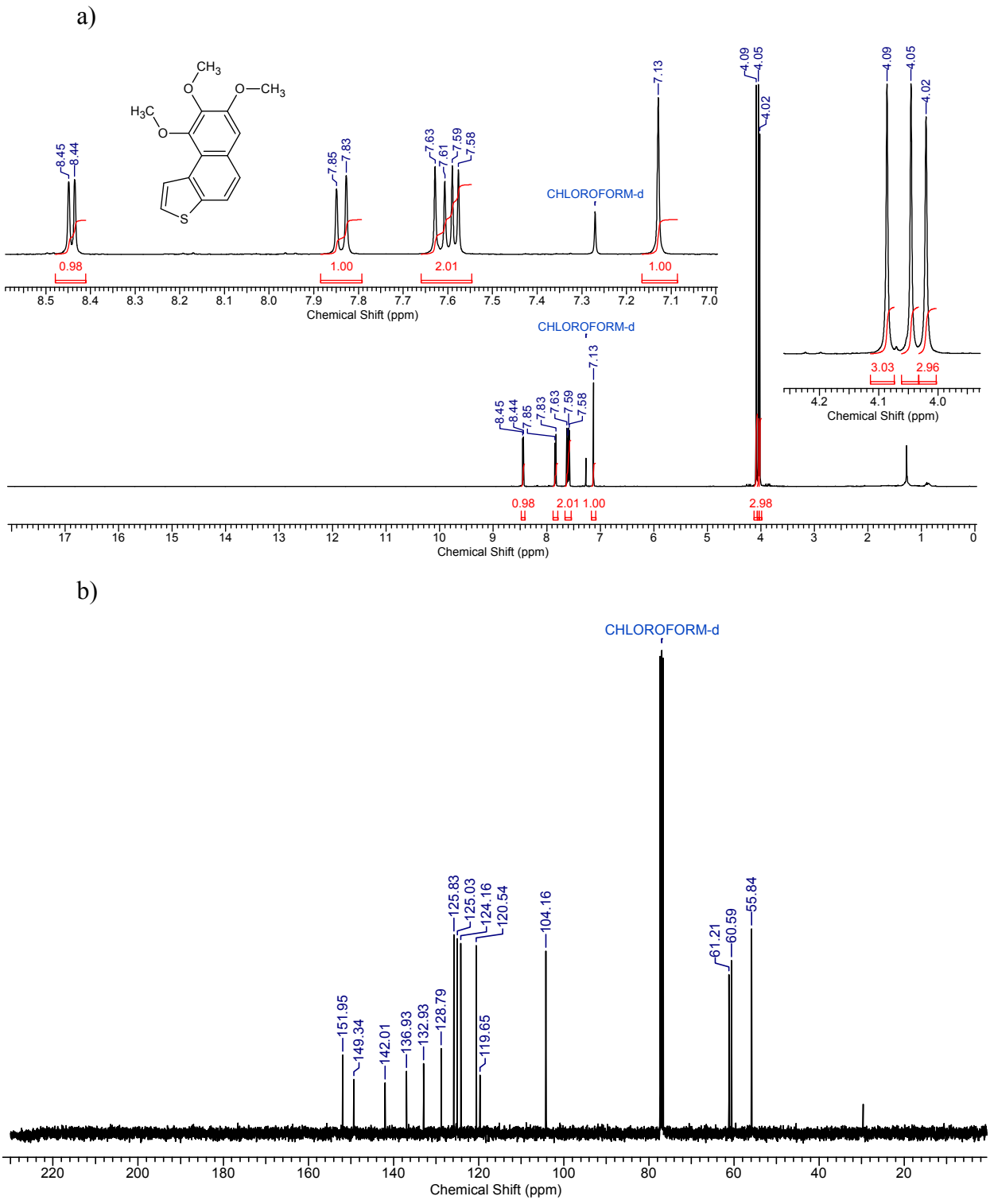


Fig. S11. ^{1}H (a) and ^{13}C (b) NMR spectra of **3e**.

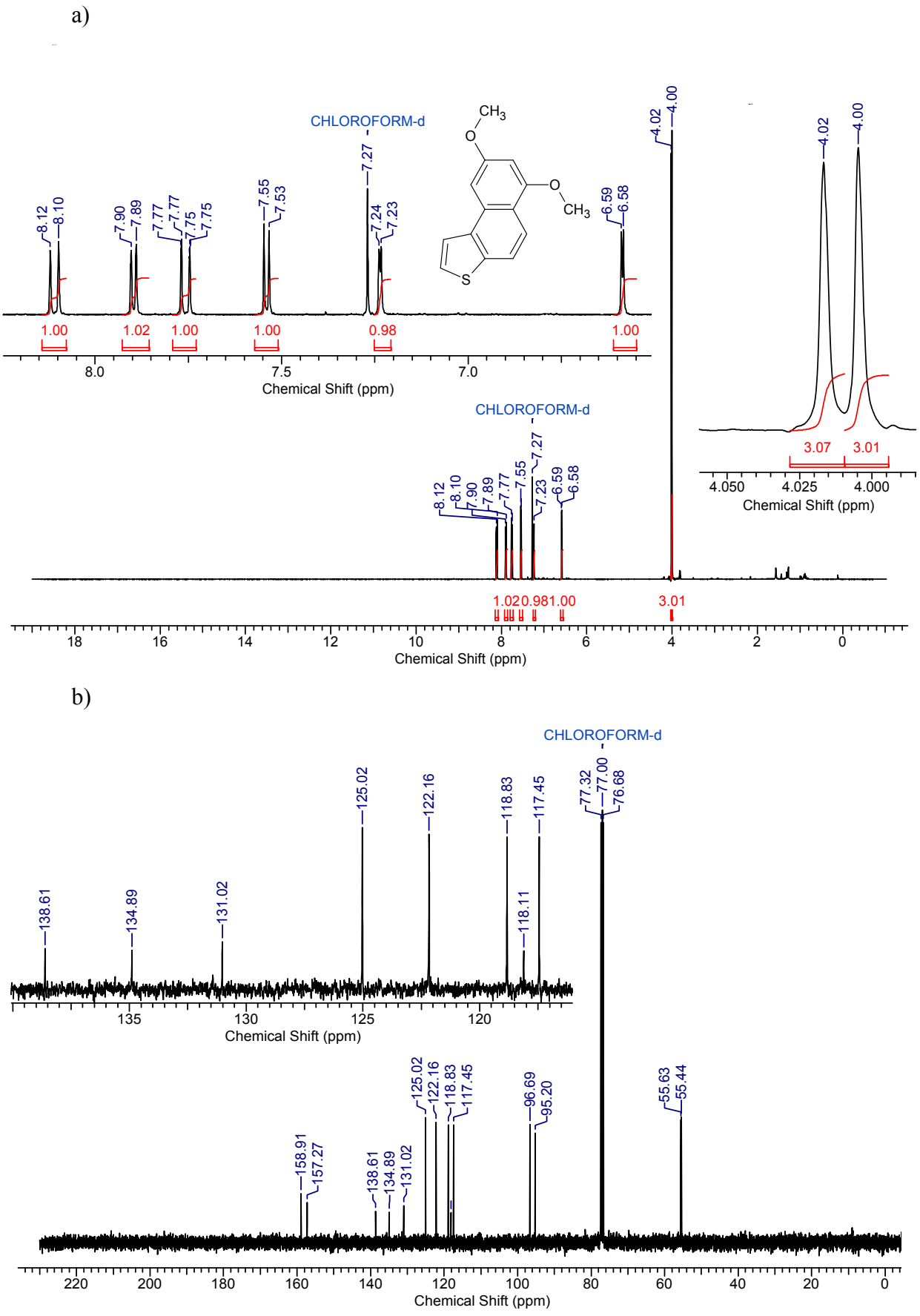
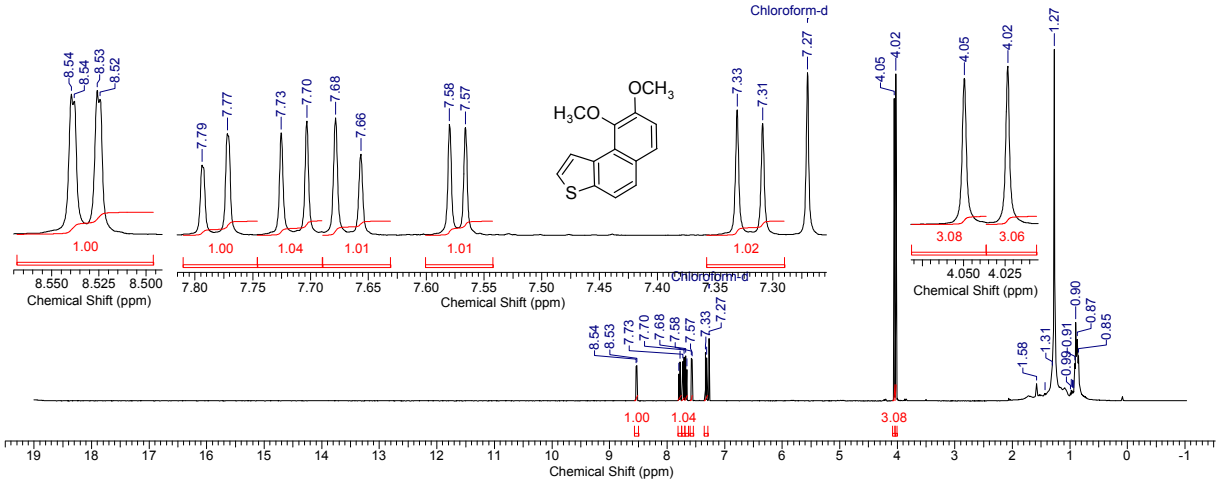


Fig. S12. ^{1}H and ^{13}C NMR spectra of **3d'**.

a)



b)

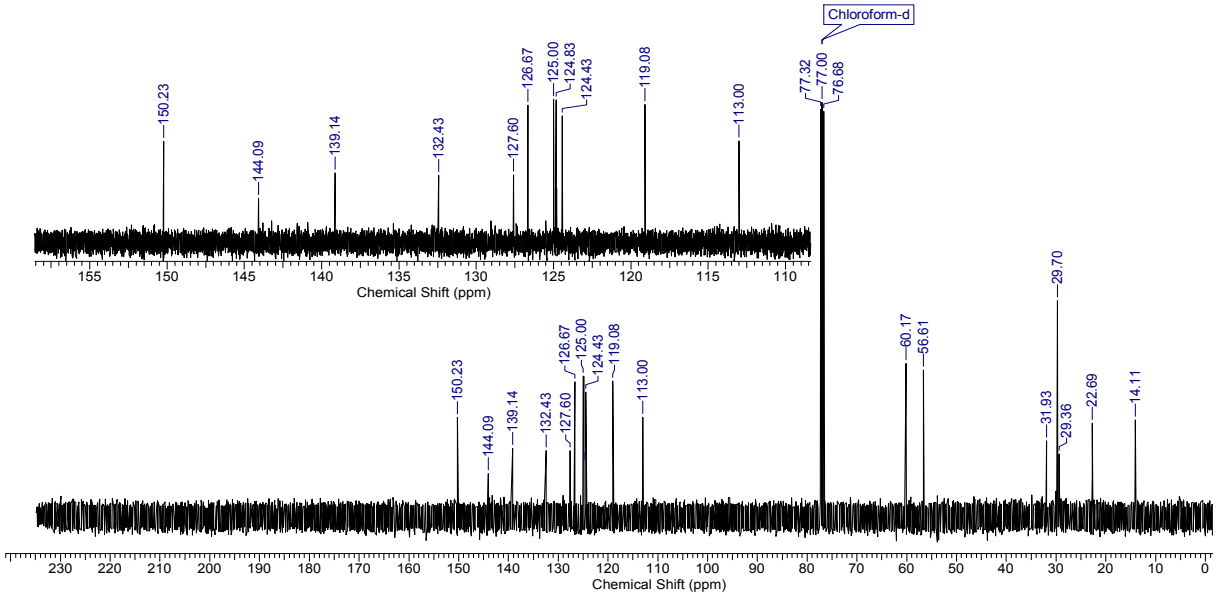
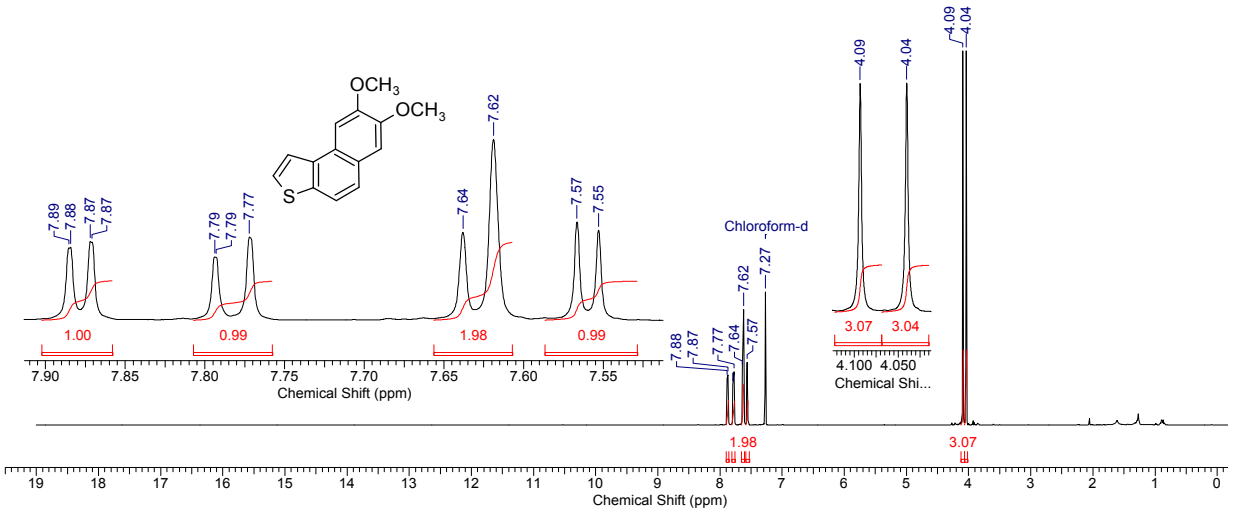


Fig. S13. ^{1}H (a) and ^{13}C (b) NMR spectra of **3c”**.

a)



b)

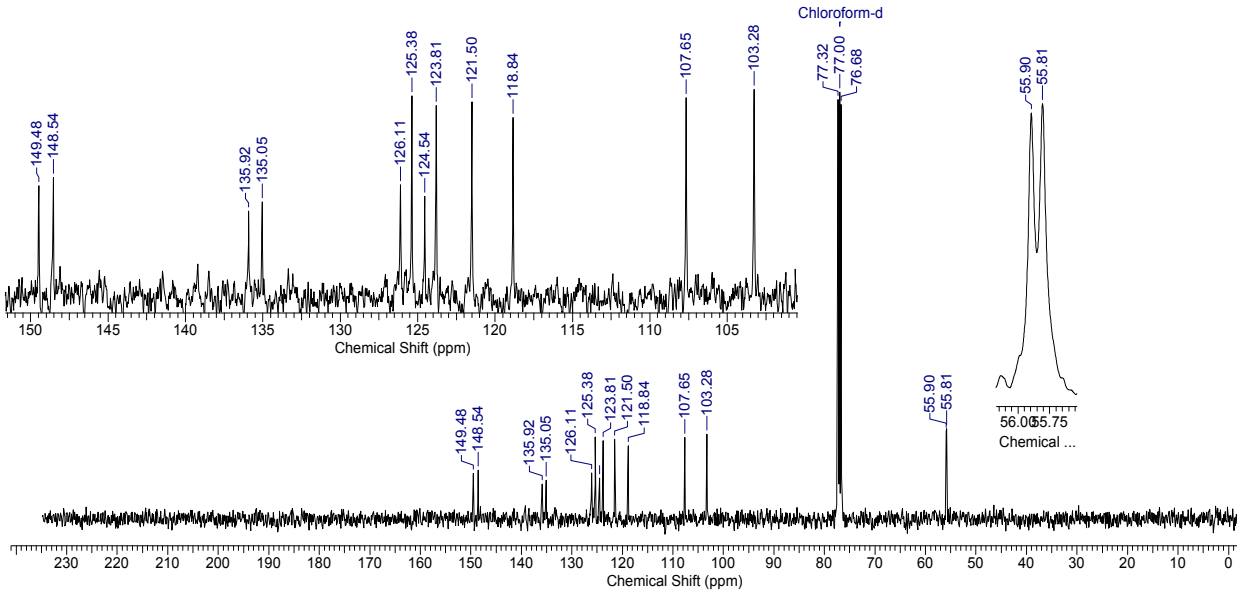


Fig. S14. ^{1}H (a) and ^{13}C (b) NMR spectra of **3c'**.

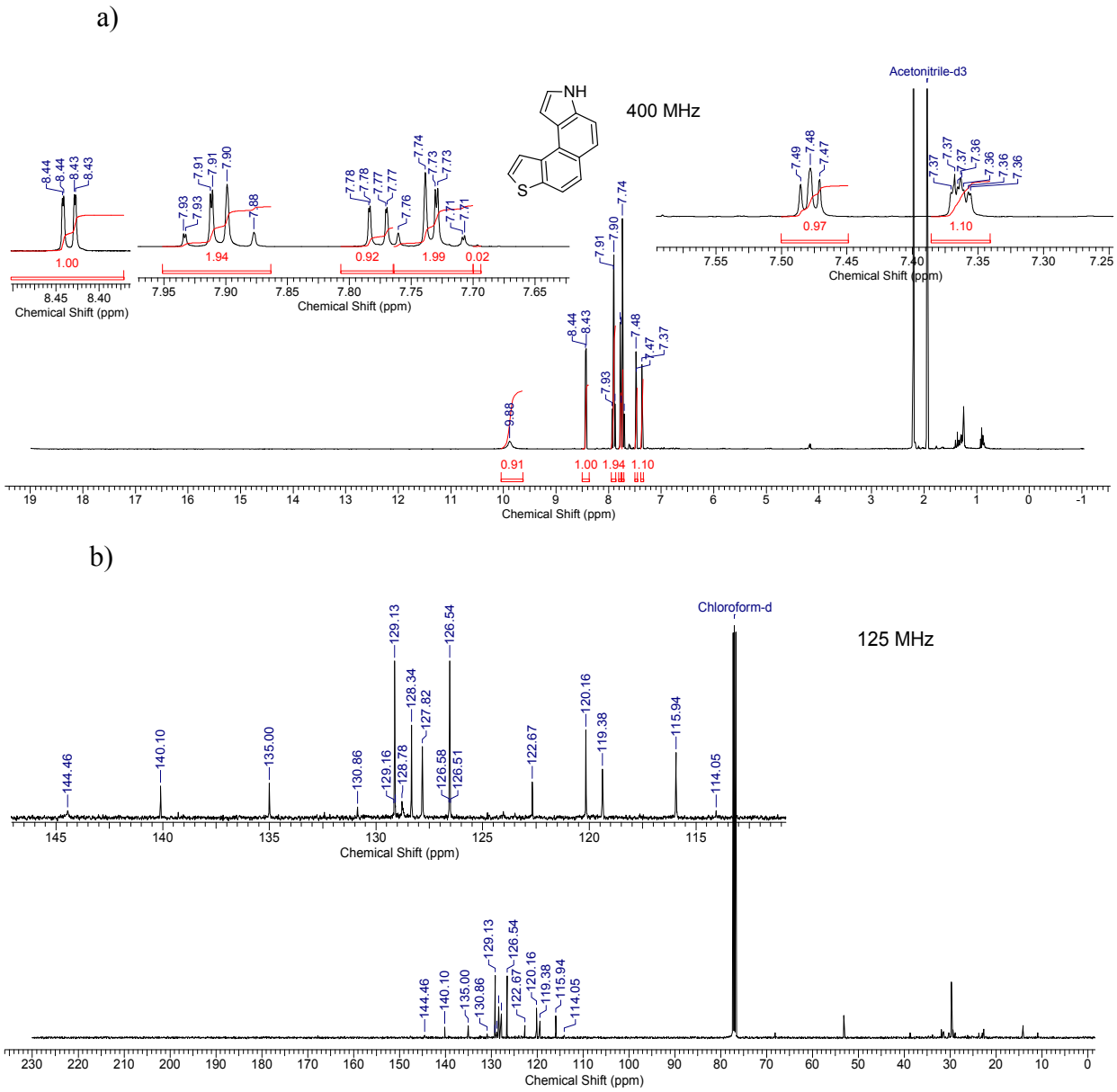


Fig. S15. ^{1}H (a) and ^{13}C (b) NMR spectra of **3f**.

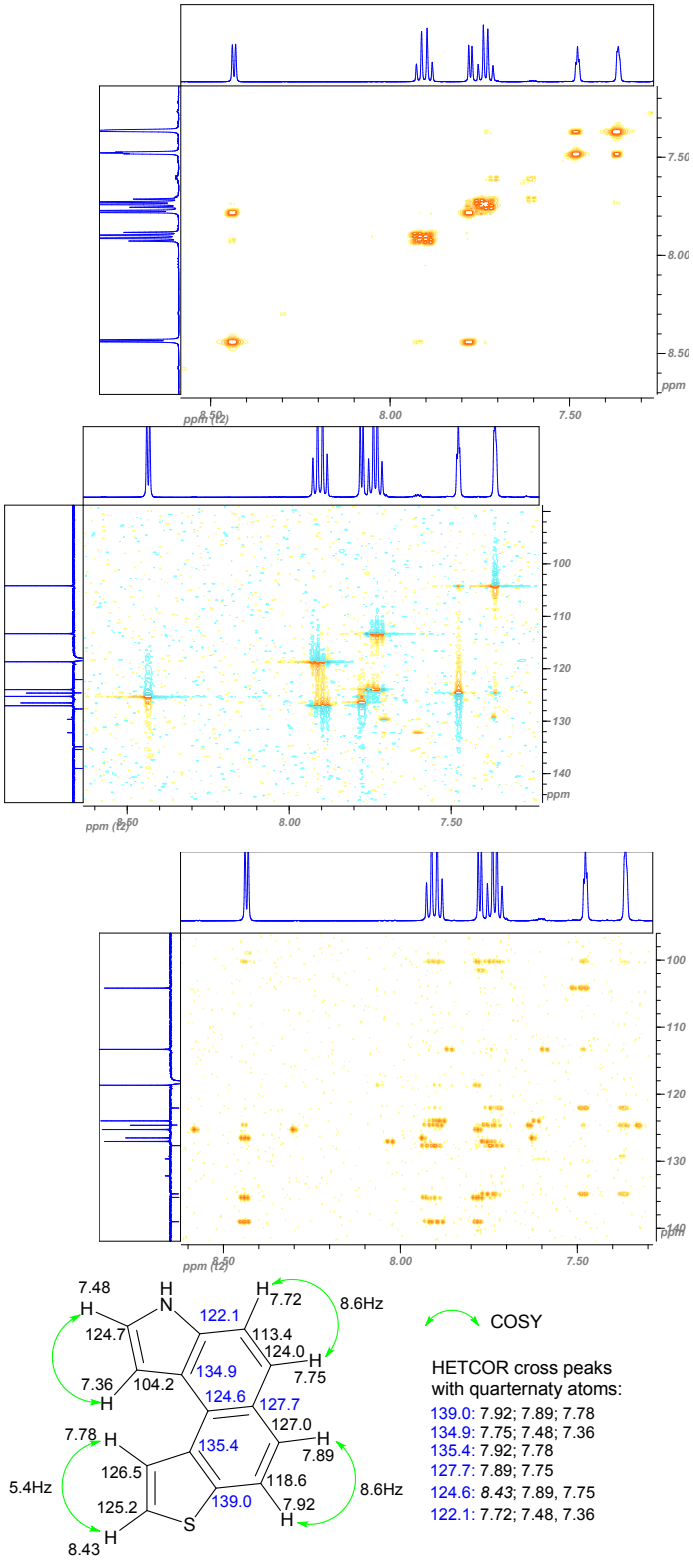
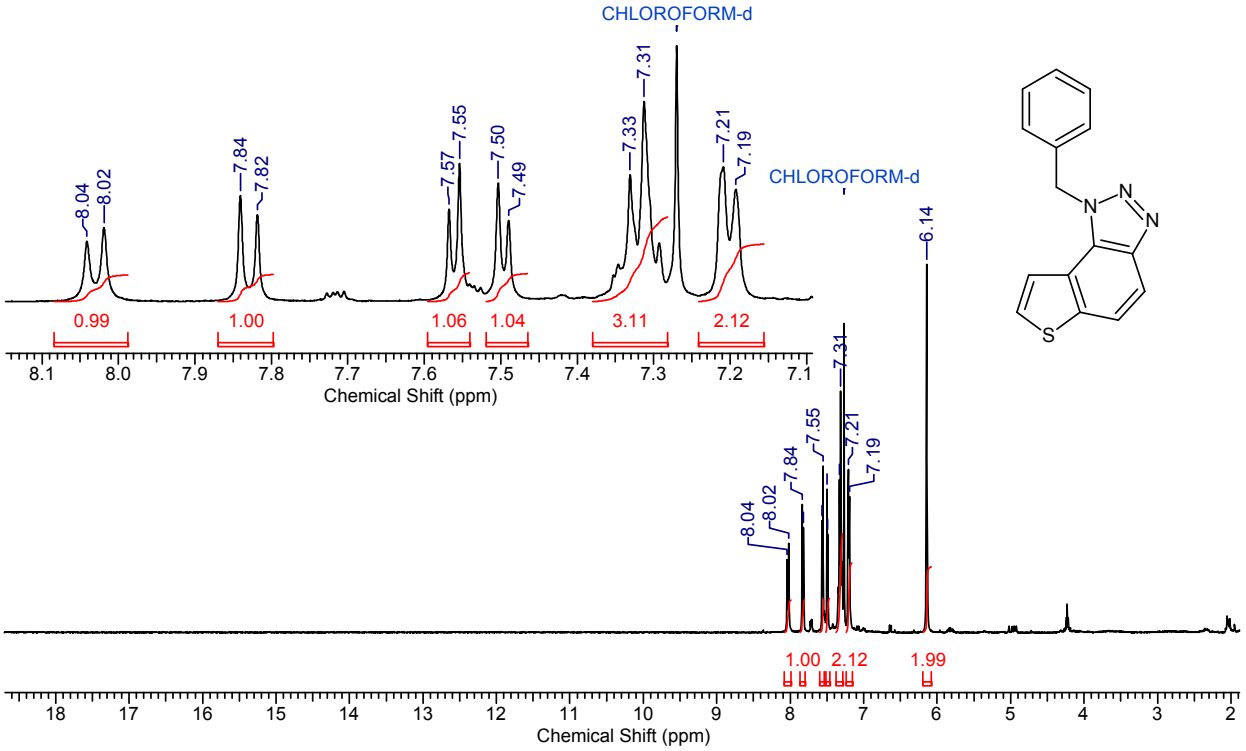


Fig. S16. COSY (500 MHz) NMR of **4i** HETCOR $^{1}H - ^{13}C$

a)



b)

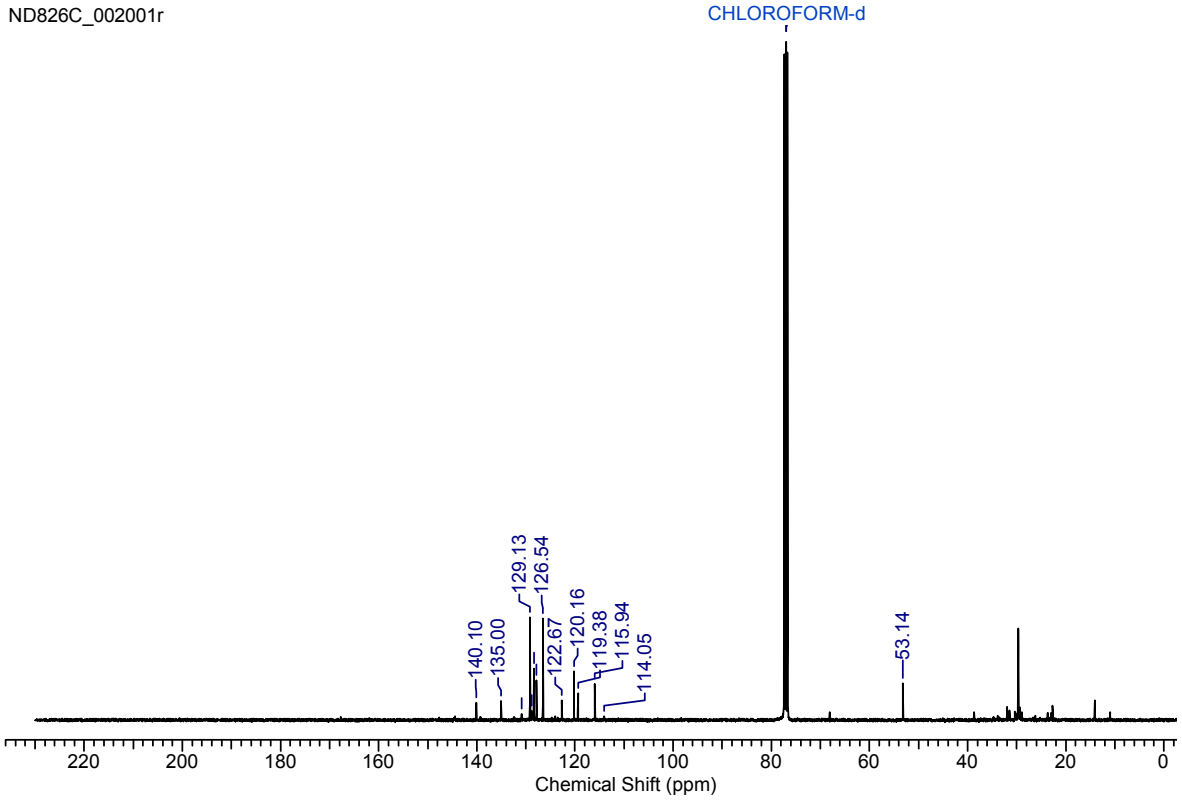


Fig. S17. ^{1}H (a) and ^{13}C (b) NMR spectra of **3g**.

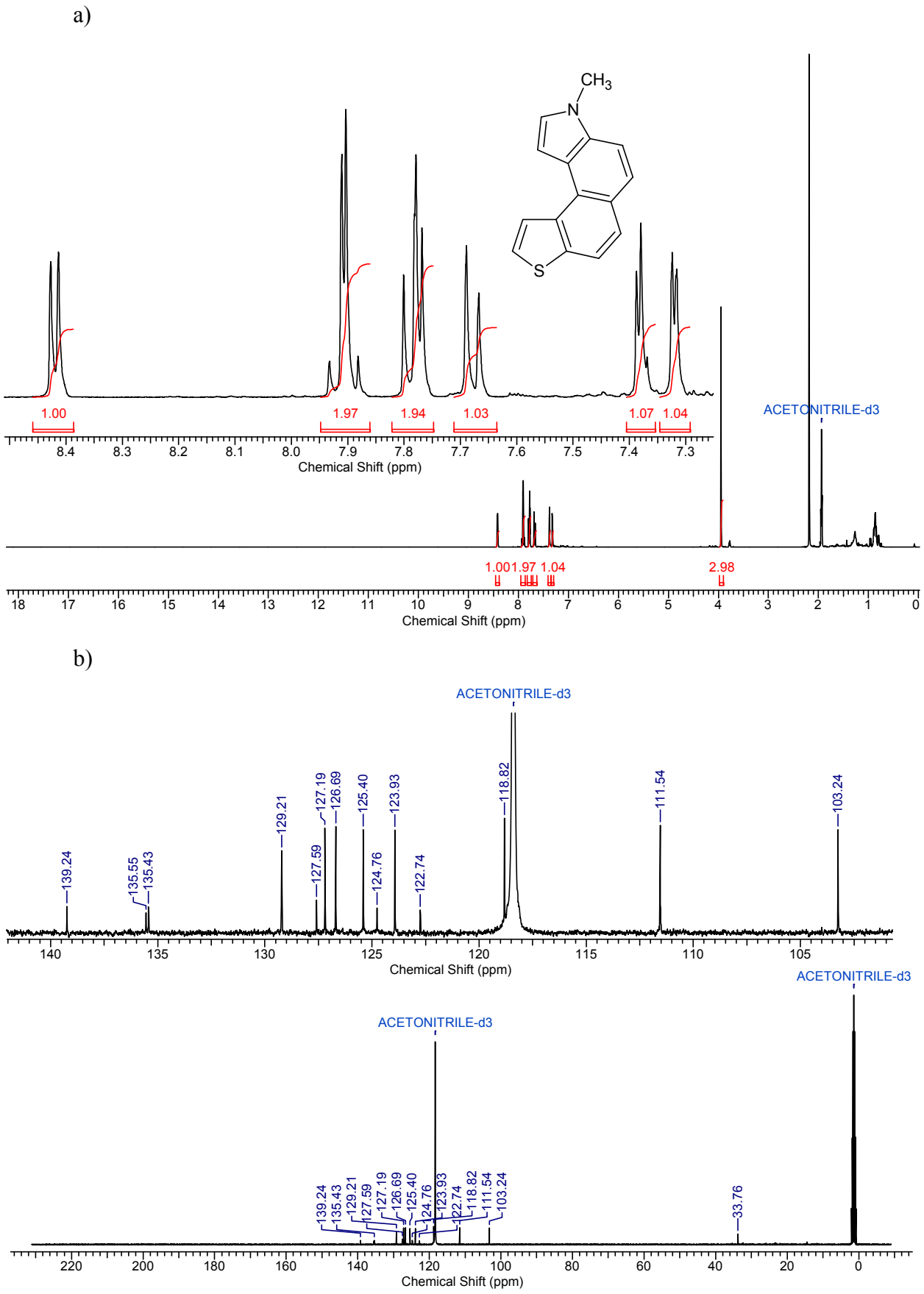


Fig. S18. ^{1}H (a) and ^{13}C (b) NMR spectra of **3h**.

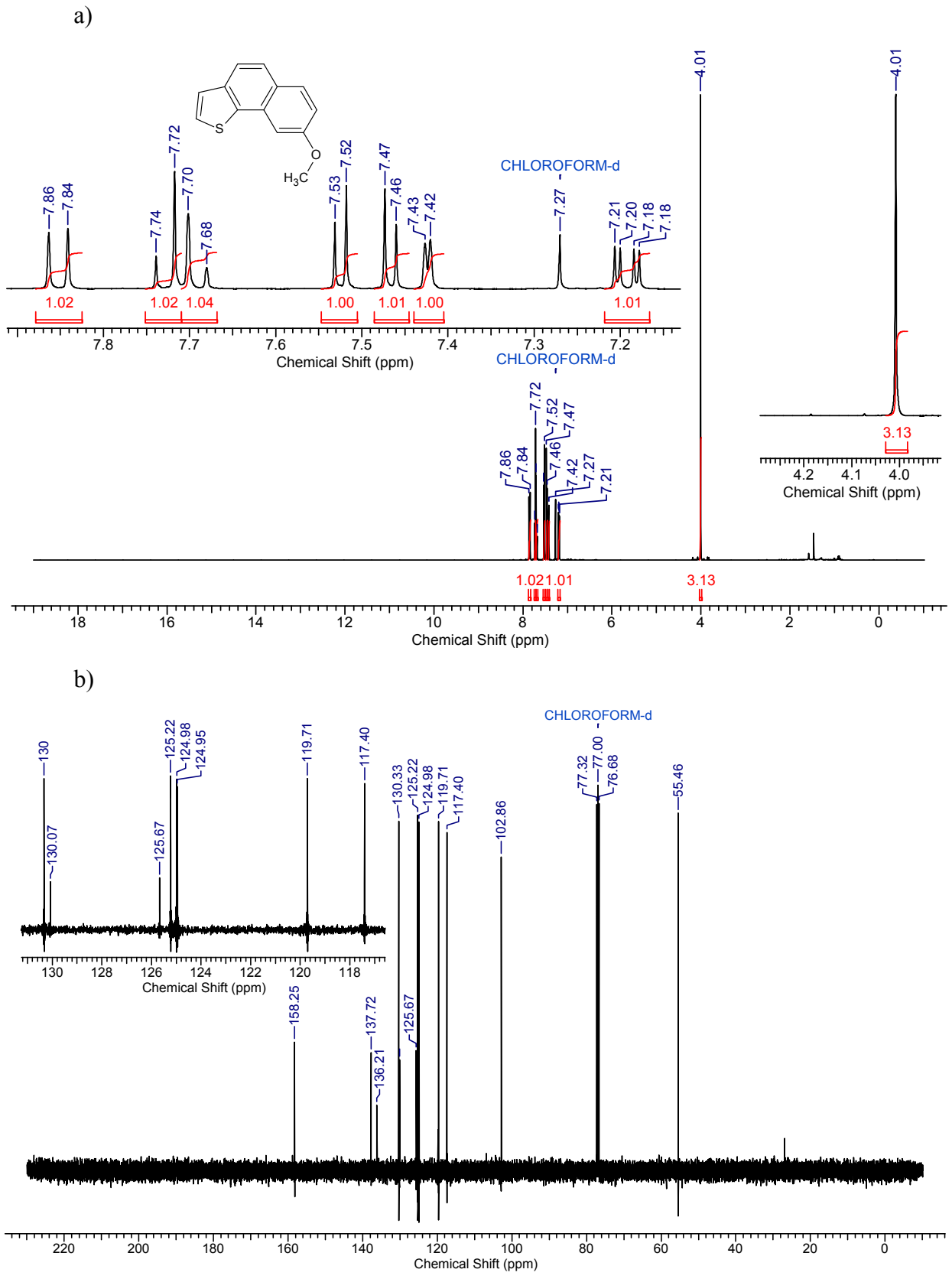


Fig. S19. ^{1}H (a) and ^{13}C (b) NMR spectra of **4a**.

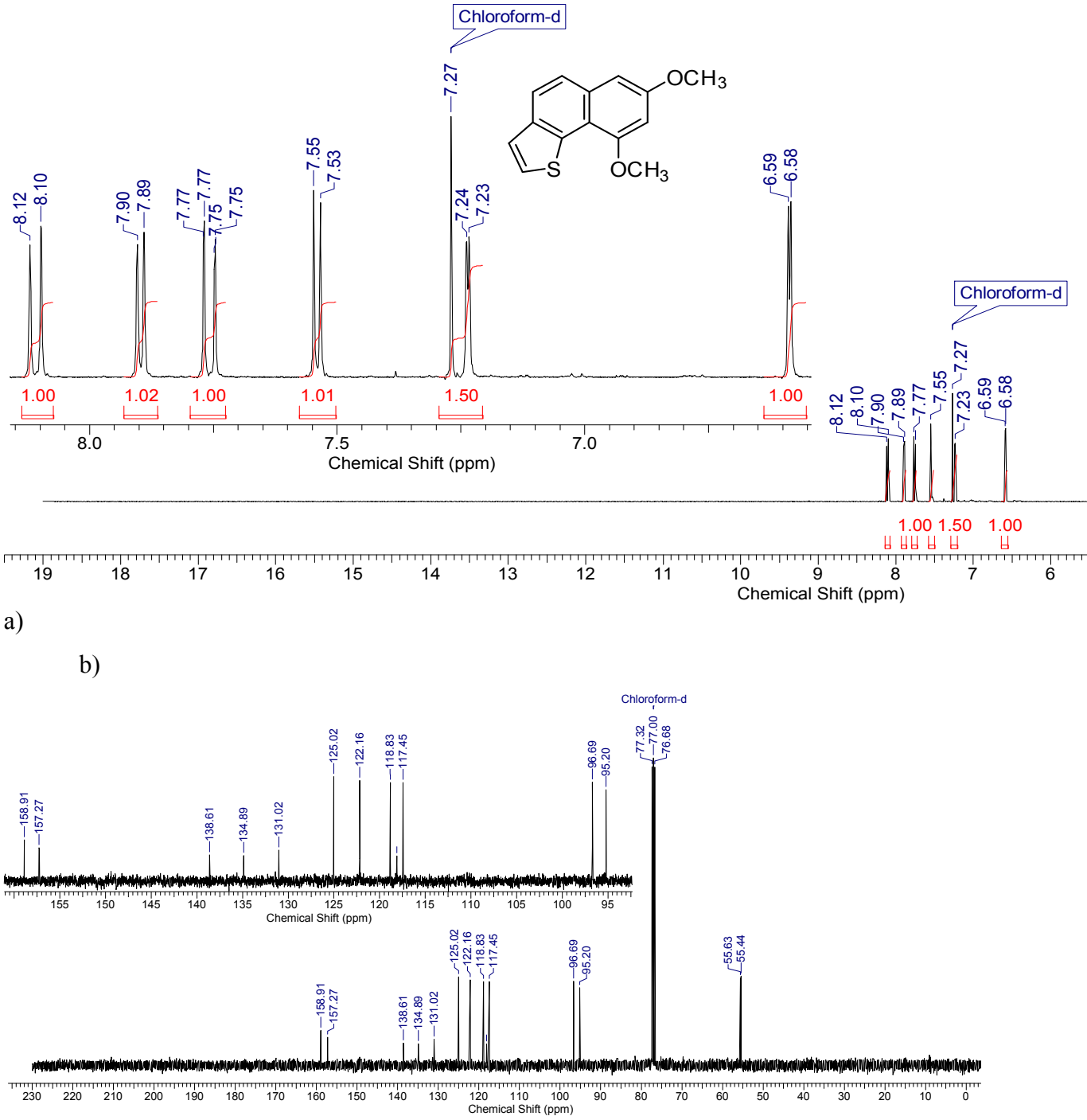


Fig. S20. ^{1}H (a) and ^{13}C (b) NMR spectra of **4b**.

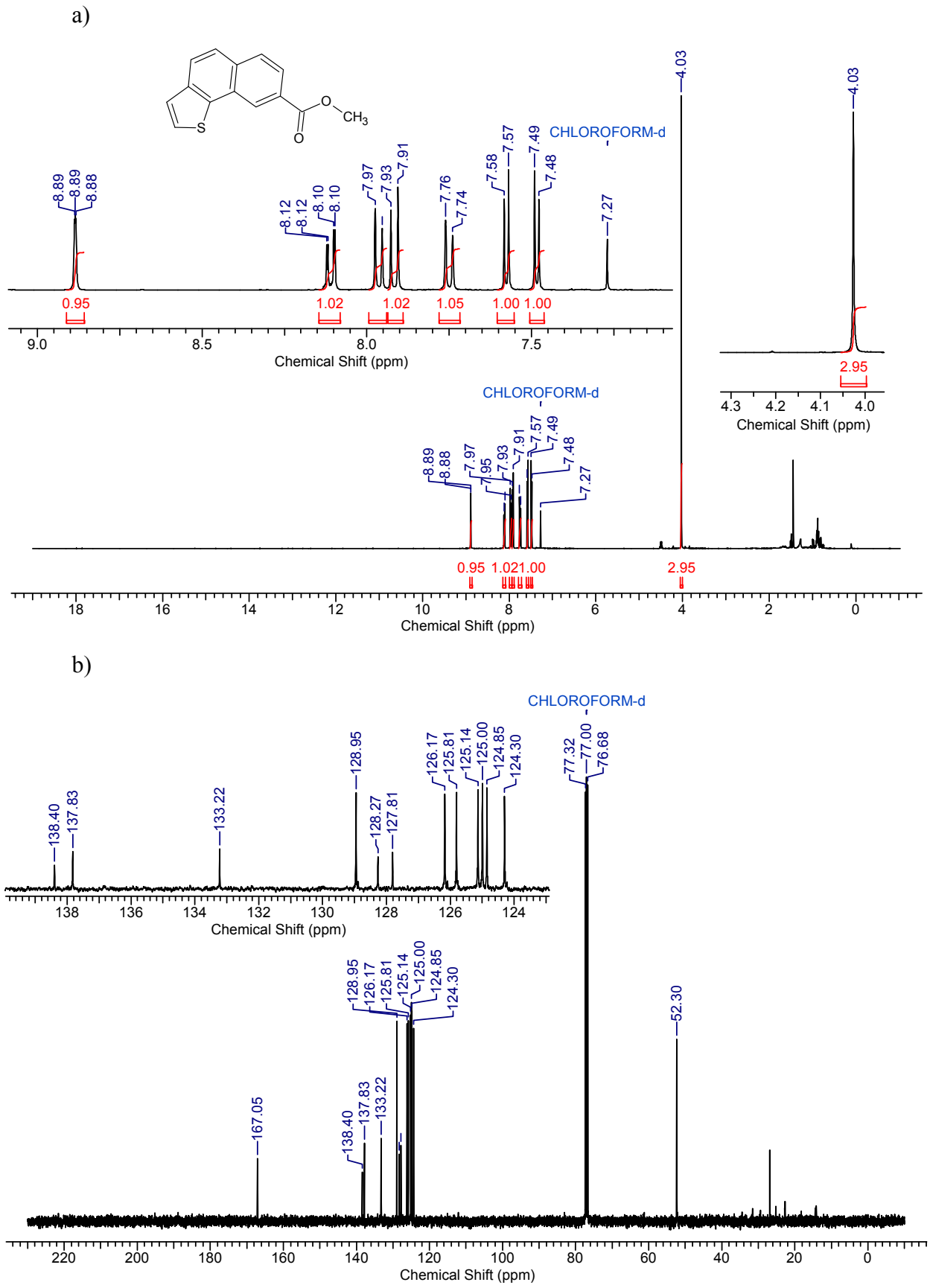
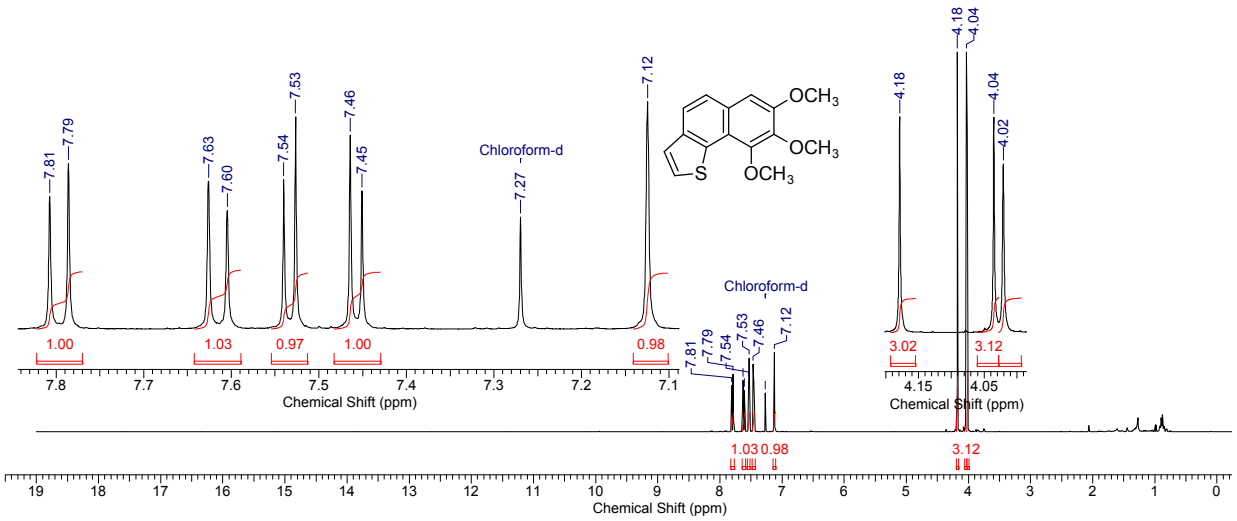


Fig. S21. ^{1}H (a) and ^{13}C (b) NMR spectra of **4c**.

a)



b)

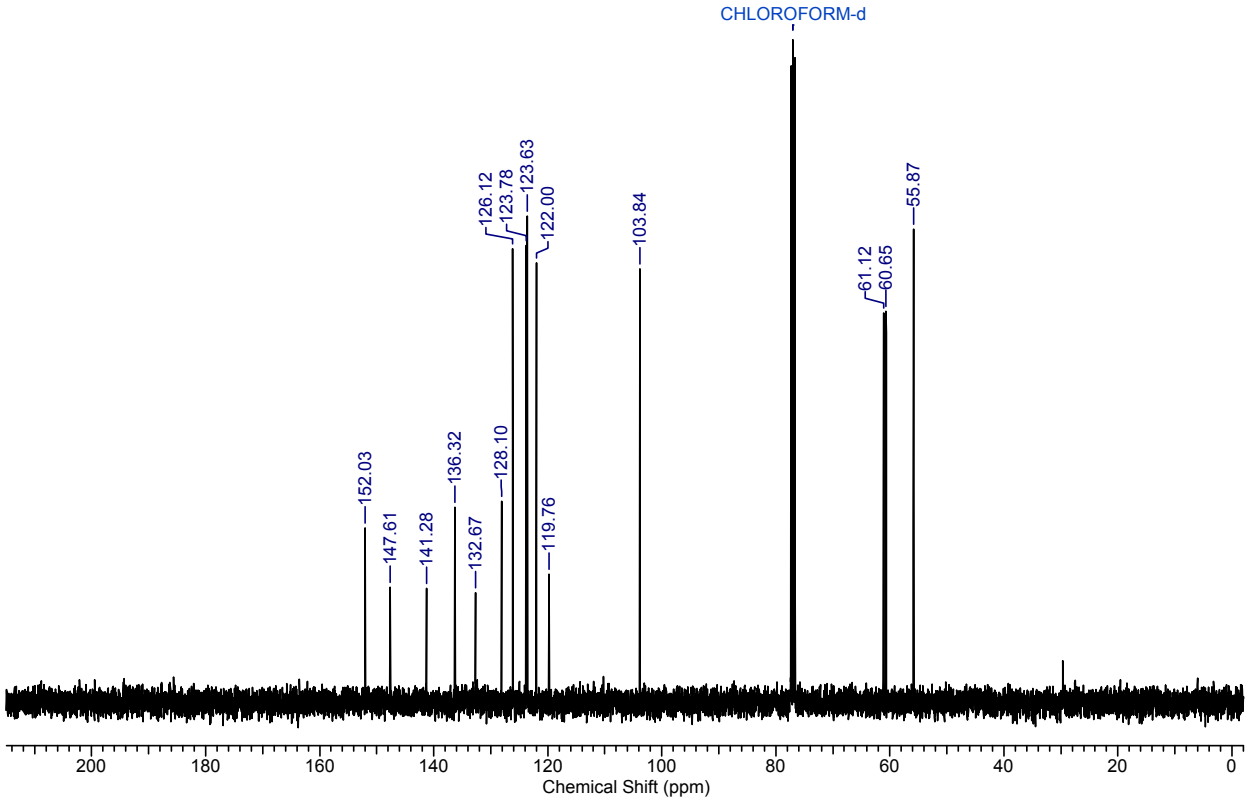


Fig. S22. ^{1}H (a) and ^{13}C (b) NMR spectra of **4d**.

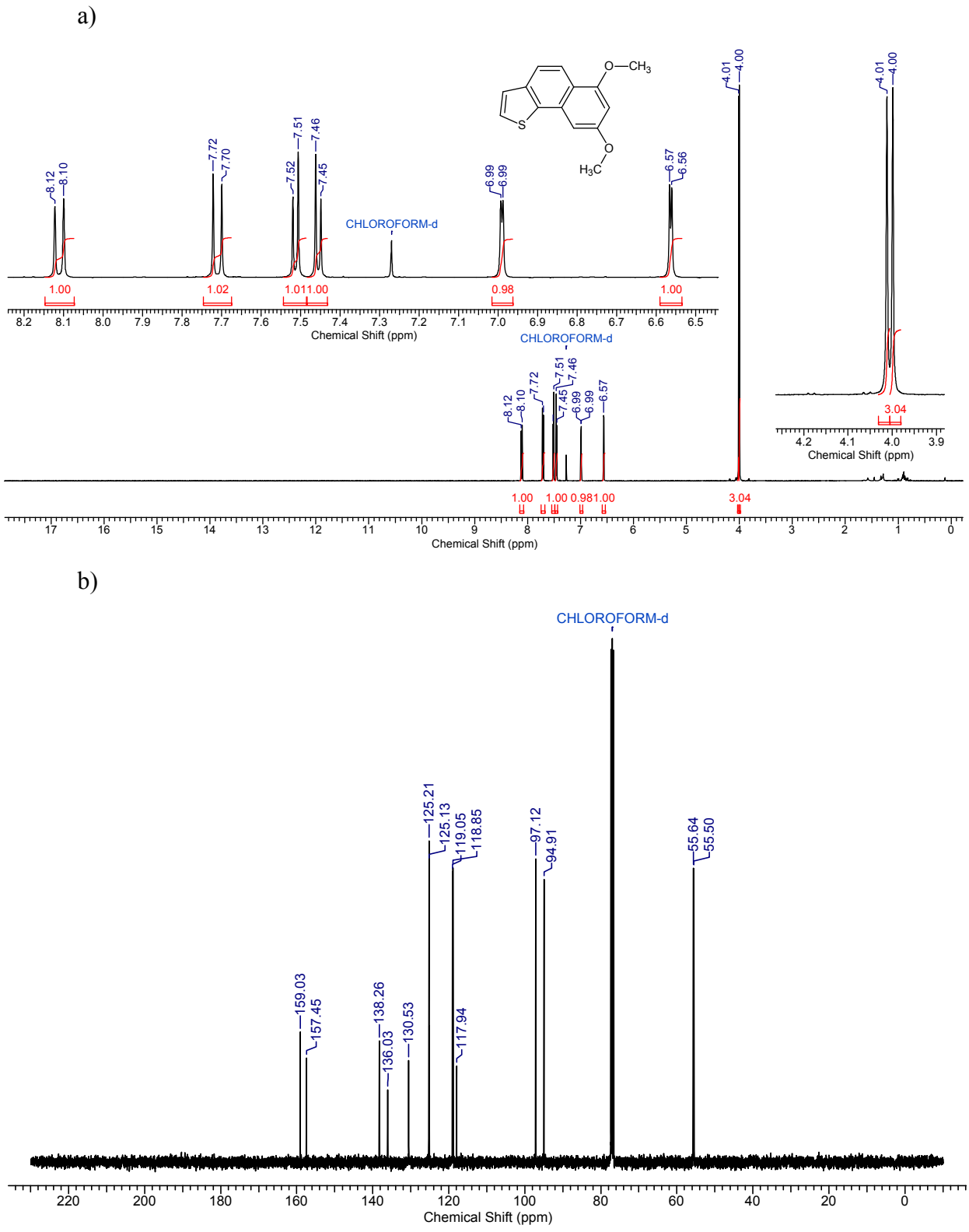


Fig. S23. ^{1}H (a) and ^{13}C (b) NMR spectra of **4e'**.

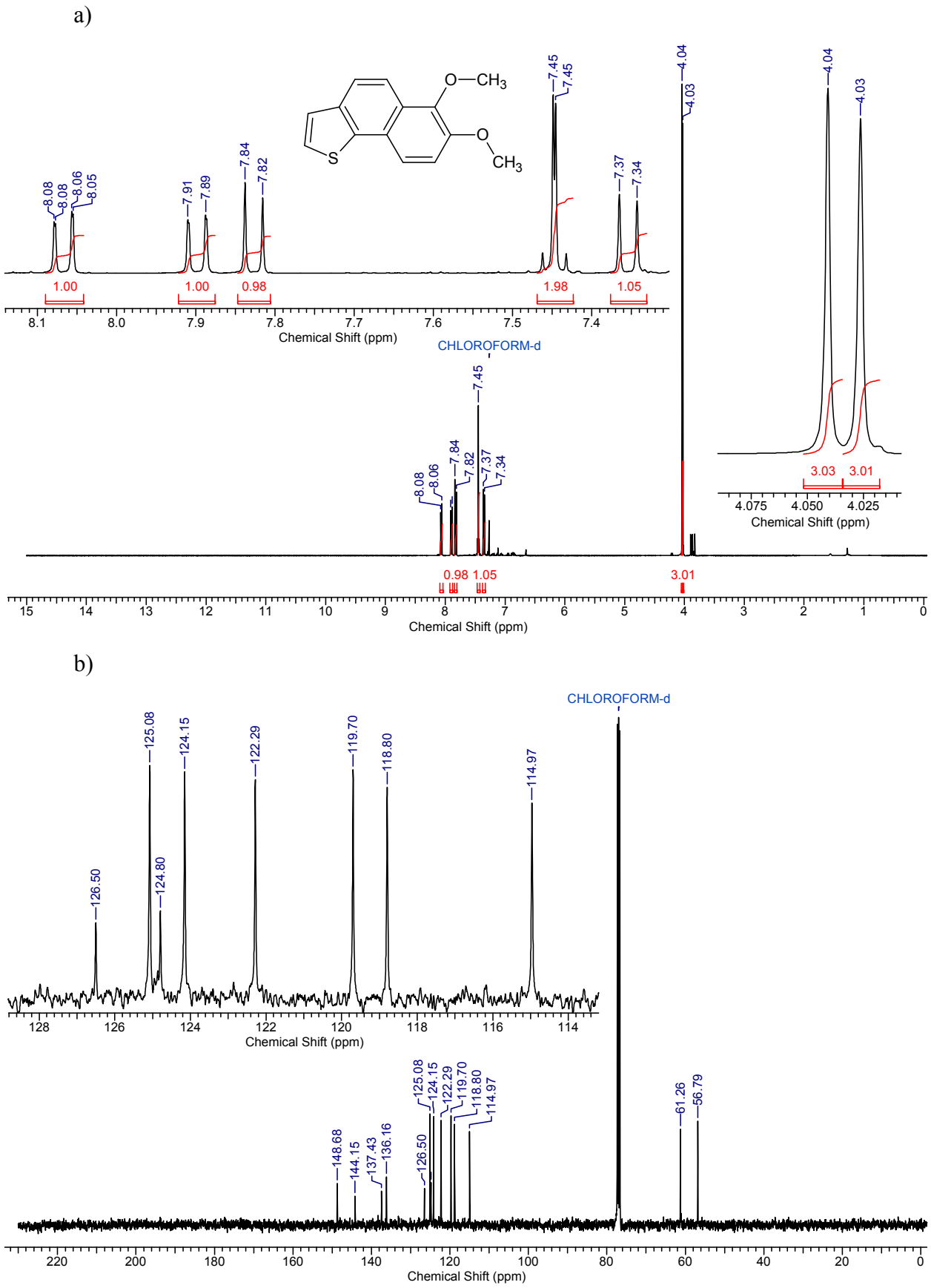


Fig. S24. ^{1}H (a) and ^{13}C (b) NMR spectra of **4f**.

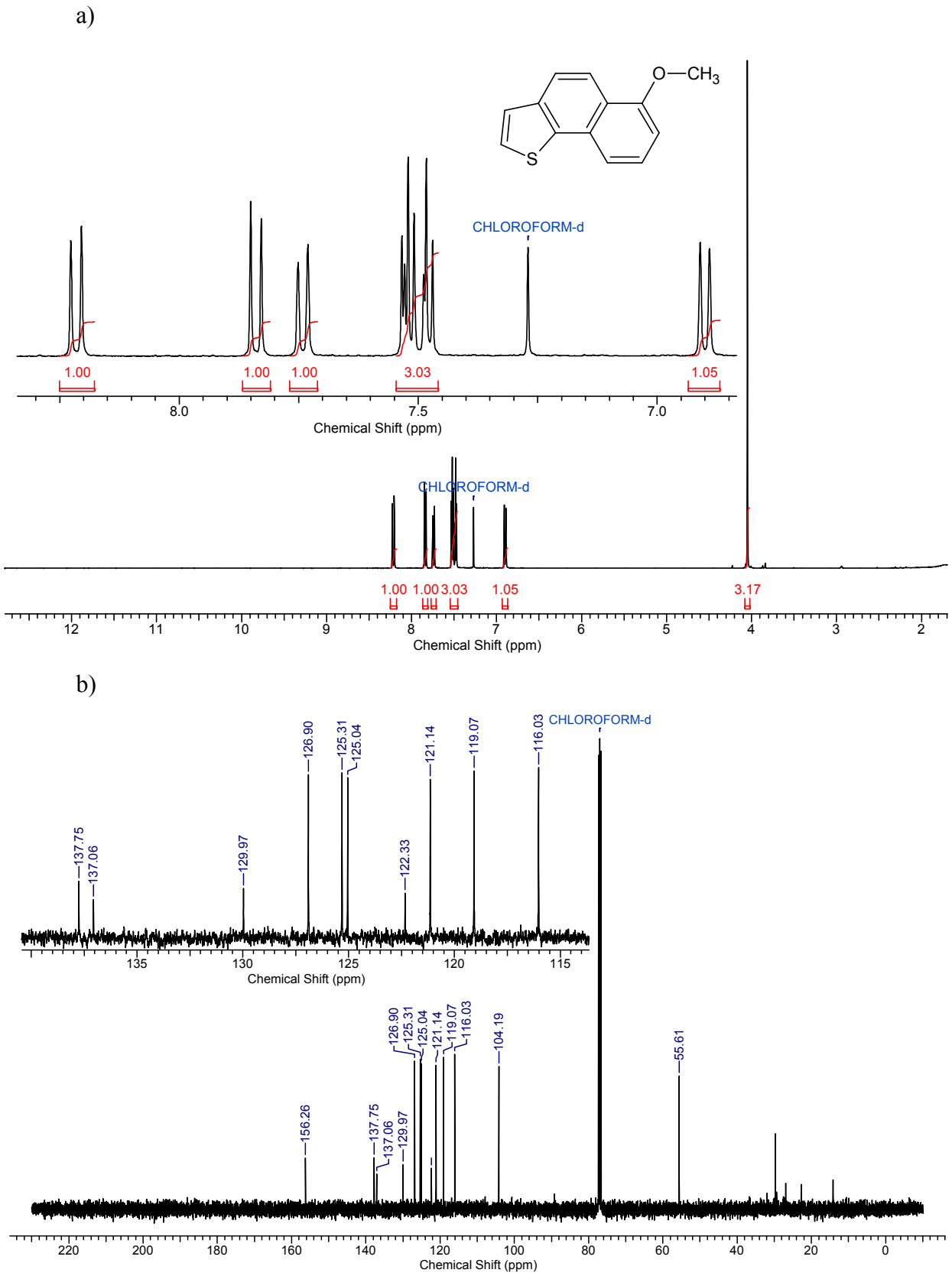


Fig. S25. ^{1}H (a) and ^{13}C (b) NMR spectra of **4g**.

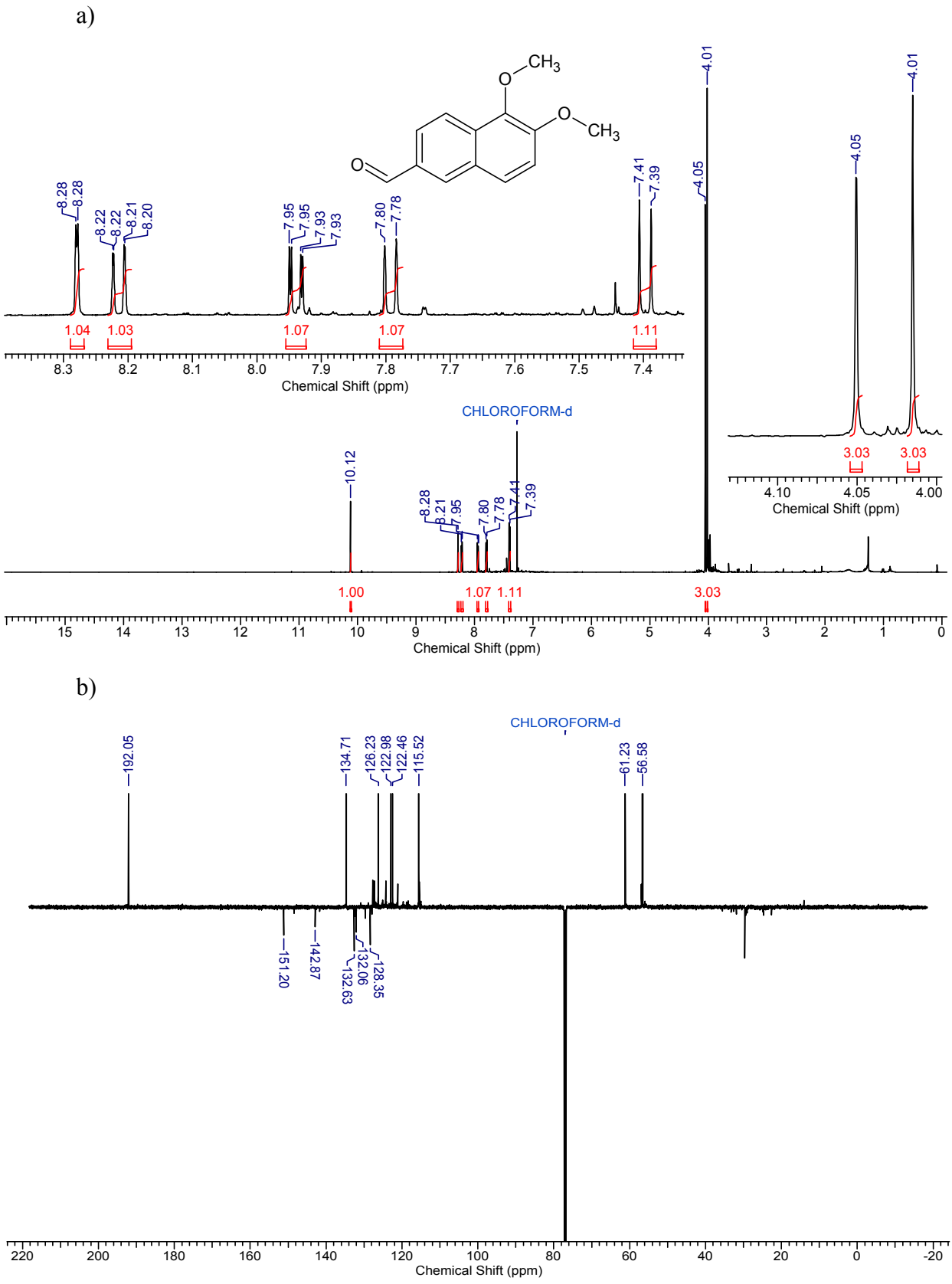


Fig. S26. ^{1}H (a) and ^{13}C (b) NMR spectra of **5**.

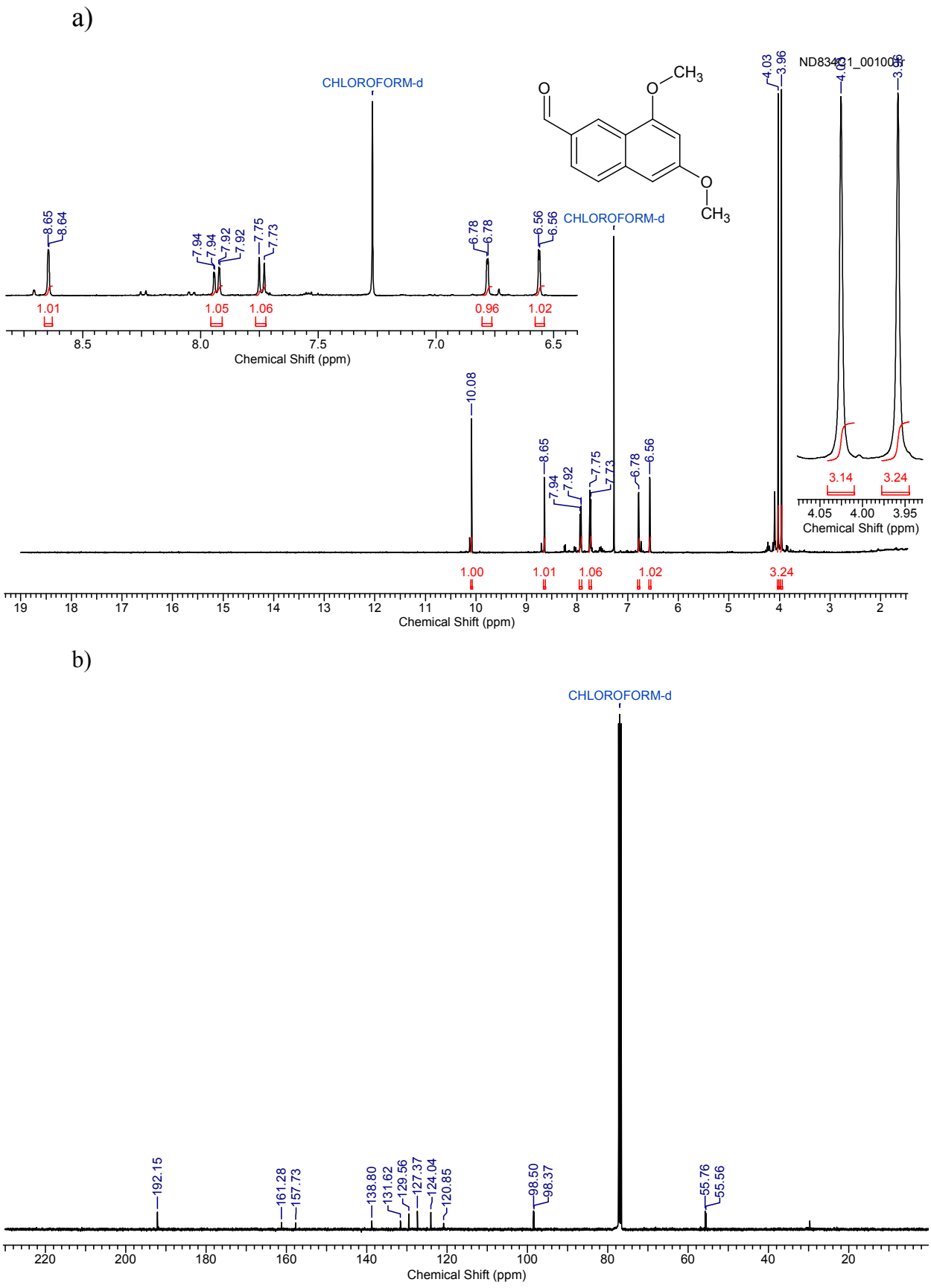


Fig. S27. ^{1}H (a) and ^{13}C (b) NMR spectra of **6**.

3. UV-Vis and fluorescence of heterostilbenes and their photoproducts

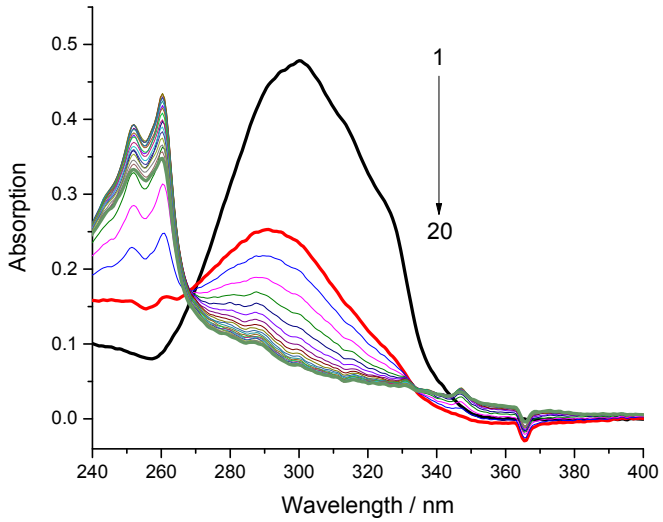


Fig S28. Variation of UV-Vis absorption spectra of 0.05 mM 3-substituted thiophene **1a** in cyclohexane with time on irradiation by full light of high pressure Hg-lamp (120W): 1 spectrum – 0 sec., 2 – 5sec. irradiation, spectra from 3 to 25 were recorded with irradiation interval of 30 seconds between adjacent spectra.

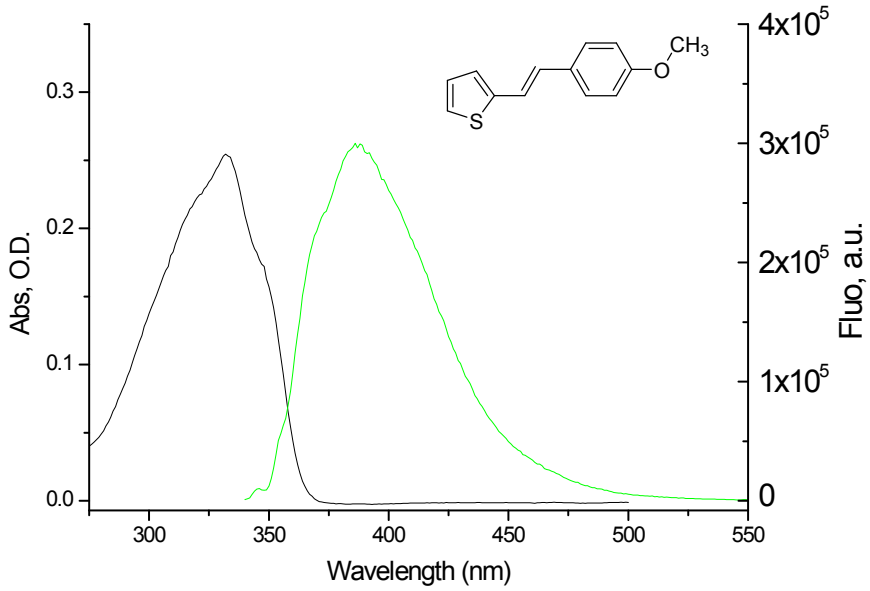


Fig S29. Absorption (solid line) and fluorescence (dotted line) spectra of **1a**, λ_{ex} = 320 nm) in MeCN, (c = $5.0 \cdot 10^{-5}$ M)

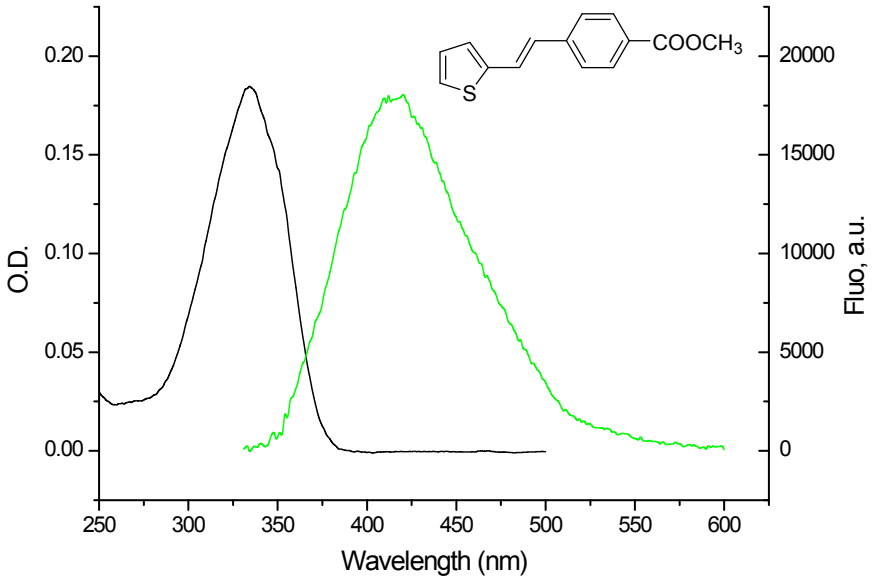


Fig S30. Absorption (solid line) and fluorescence (dotted line) spectra of **2c** (λ_{ex} = 320 nm) in MeCN, (c= $5{,}0 \cdot 10^{-5}$ M)

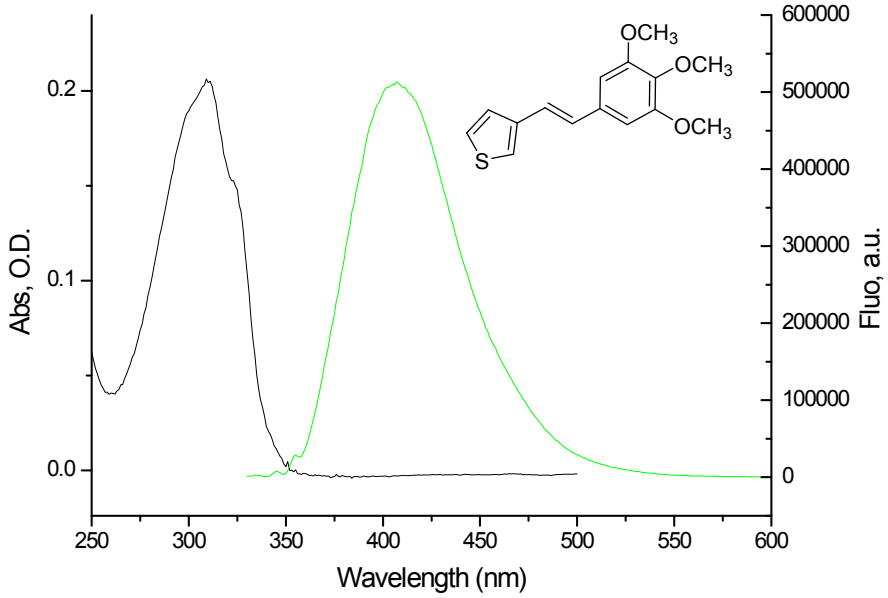


Fig S31. Absorption (solid line) and fluorescence (dotted line) spectra of **2d** (λ_{ex} = 320 nm) in MeCN (c = $5{,}0 \cdot 10^{-5}$ M)

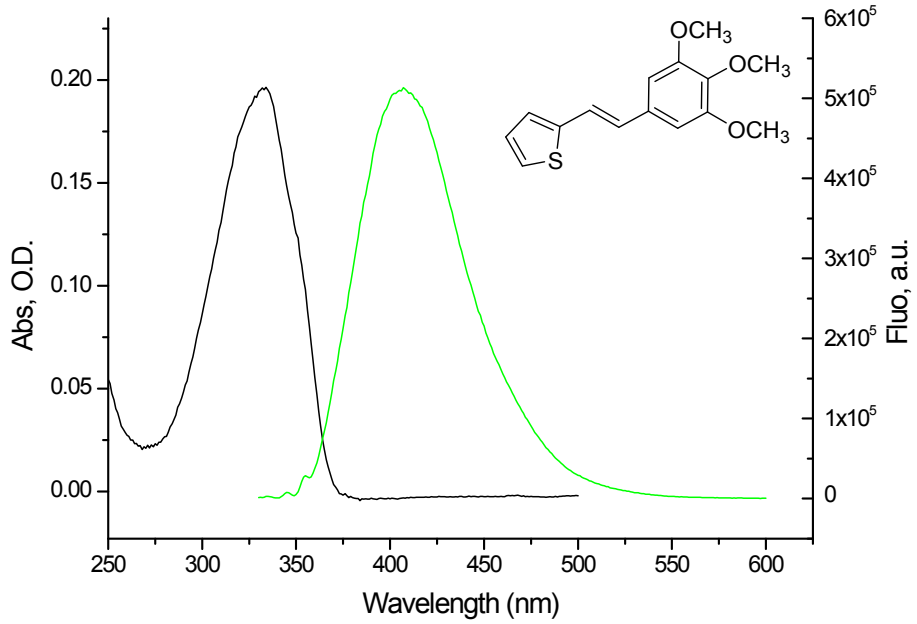


Fig S32. Absorption (sloid line) and fluorescence (dotted line) spectra of **1e** (λ_{ex} = 320 nm) in MeCN. (c = 5,0·10^{-5} M)

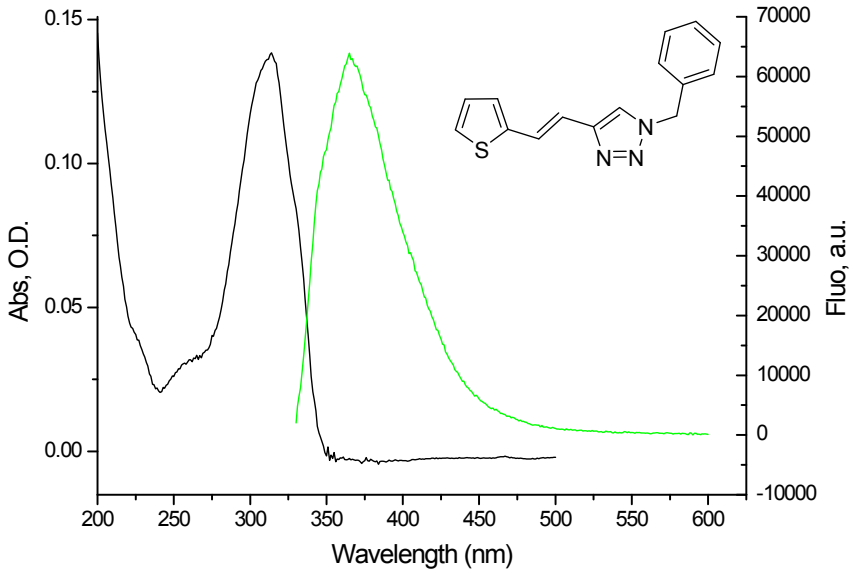


Fig S33. Absorption (solid line) and fluorescence (dotted line) spectra of **1g** (λ_{ex} = 320 nm) in MeCN (c = 5,0·10^{-5} M)

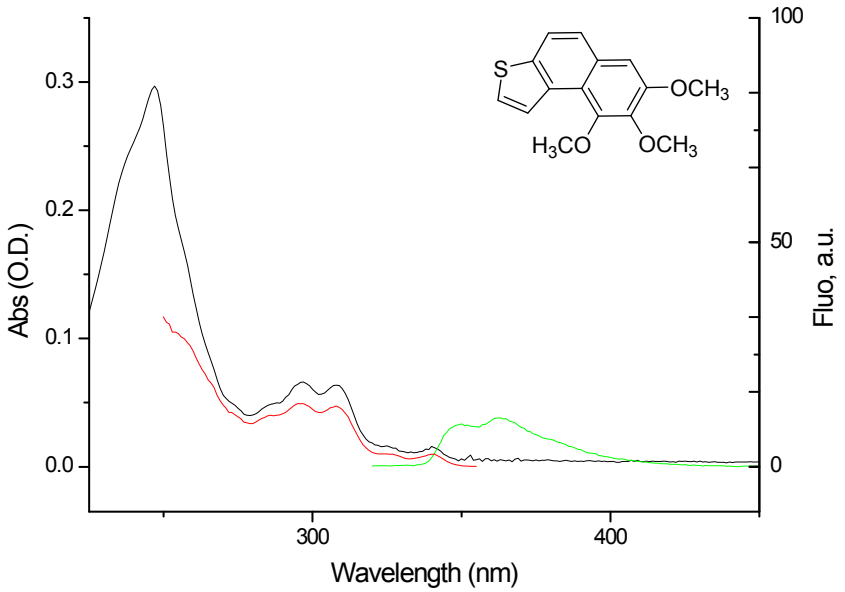


Fig S34. Absorption (black), fluorescence (green, λ_{ex} = 300 nm) and fluorescence excitation (λ_{em} = 365 nm) spectra of **3e** in MeCN (c = 5,0 × 10^{-5} M).

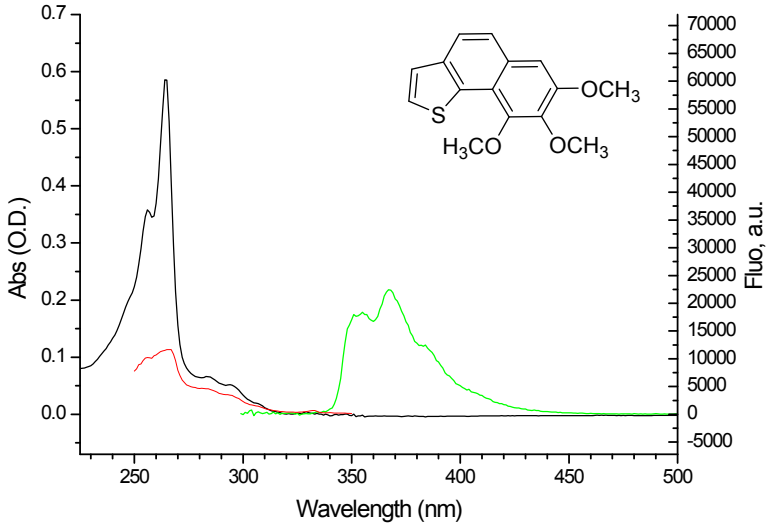


Fig S35. Absorption (black), fluorescence (green, λ_{ex} = 258 nm,) and fluorescence excitation spectra (λ_{em} = 370 nm) of **4d** in MeCN (c = 5,0×10^{-5} M)

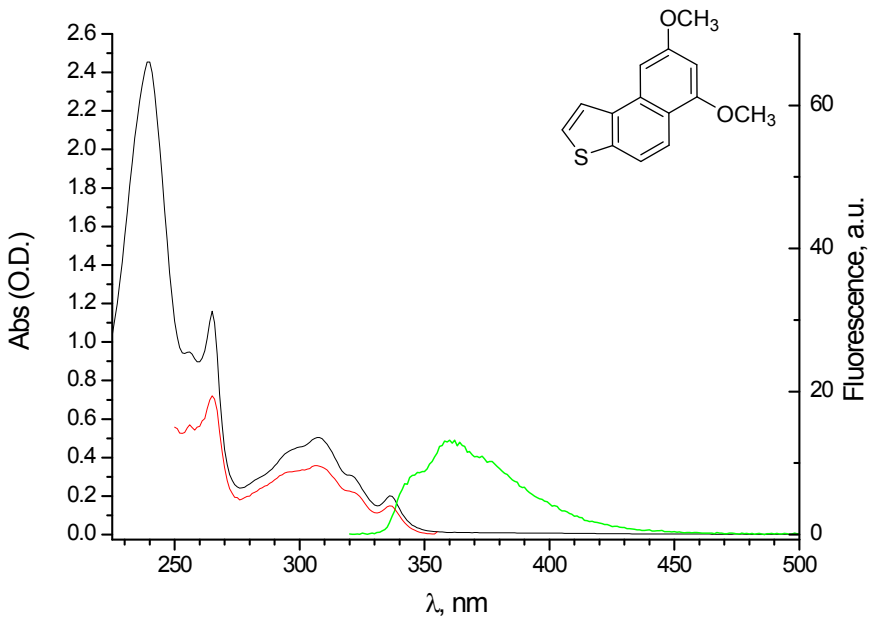


Fig S36. Absorption (black), fluorescence (green) (λ_{ex} = 307 nm, c = 3.0 × 10^{-4} M) in MeCN, c = 3,0 × 10^{-4} M) and fluorescence excitation spectra (red, c = 5.0 × 10^{-4} M, CH3CN) of **3d'**

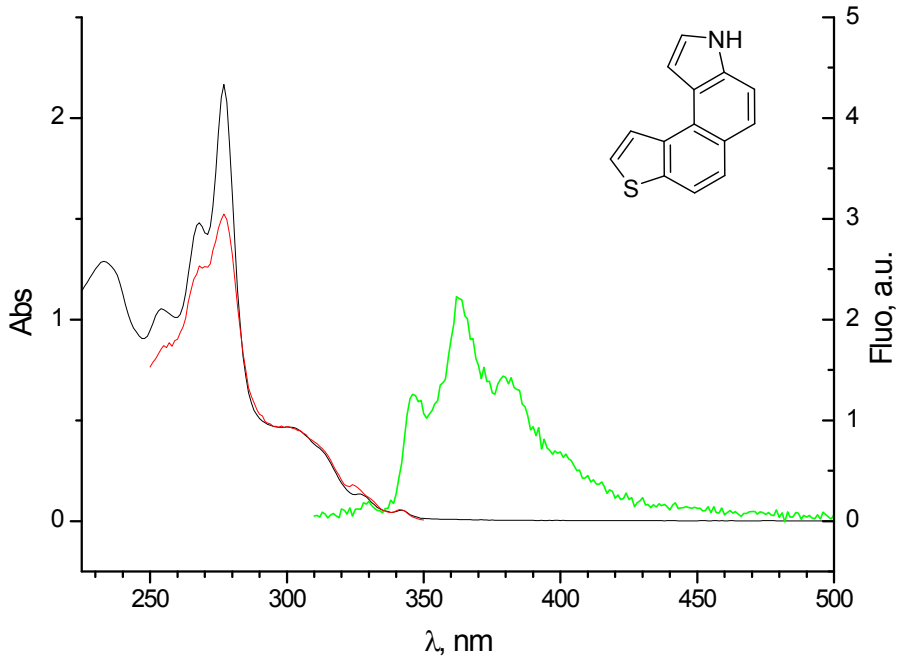


Fig S37. Absorption (black), fluorescence (green, λ_{ex} = 300 nm, c = 3,0×10^{-4} M, CH_3CN) and fluorescence excitation spectra (red, λ_{em} = 360 nm, c = 5.0×10^{-5} M, CH_3CN) of **3f**.

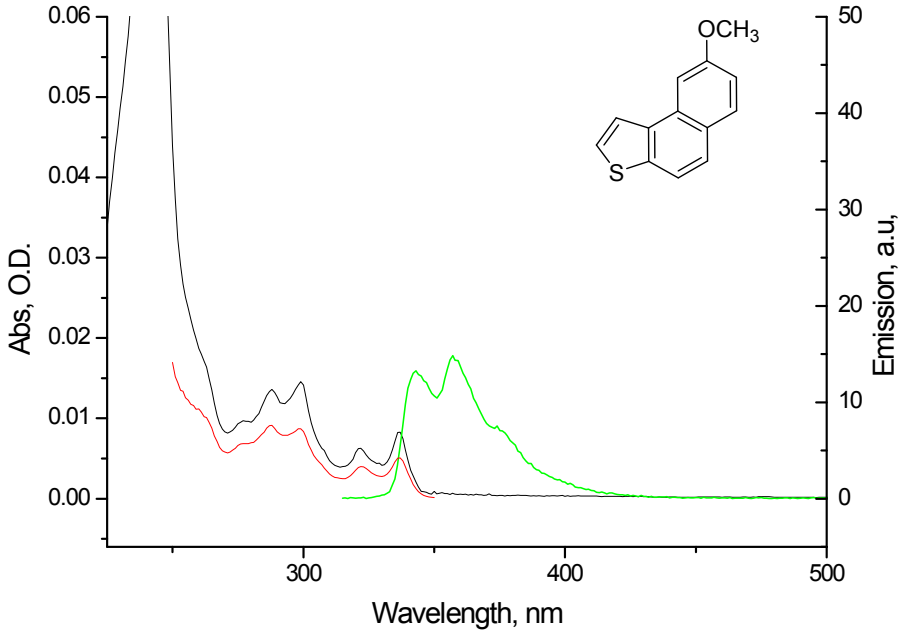


Fig S38. Absorption (black), fluorescence (green, λ_{ex} = 300 nm, c = 3,0×10^{-4} M in CH_3CN) and fluorescence excitation (red, λ_{em} = 360 nm, c = 5.0×10^{-5} M in CH_3CN) spectra of **3a**

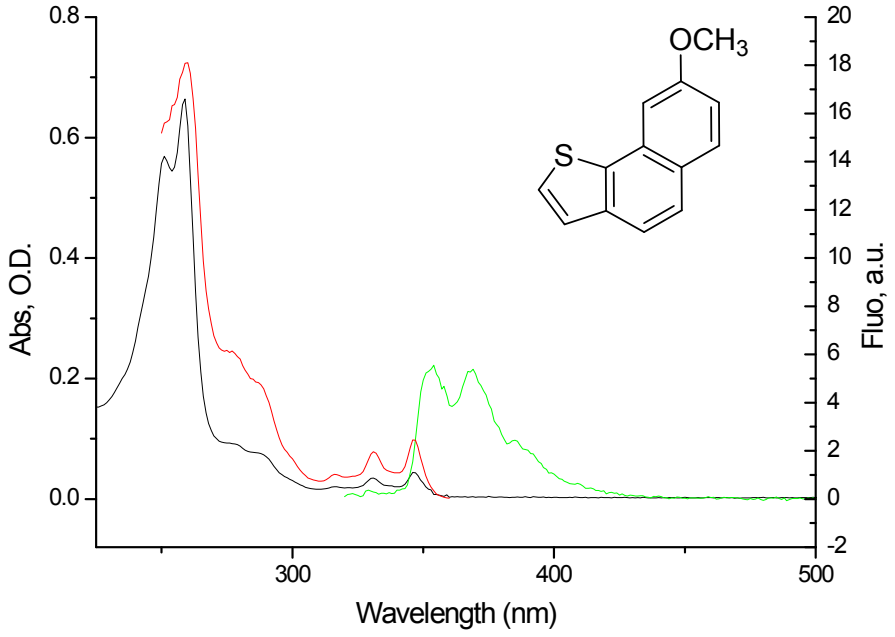


Fig S39. Absorption (black), fluorescence (green, λ_{ex} = 300 nm) and fluorescence excitation λ_{em} = 370 nm) spectra of **4a** in MeCN c = 5.0×10^{-5} M

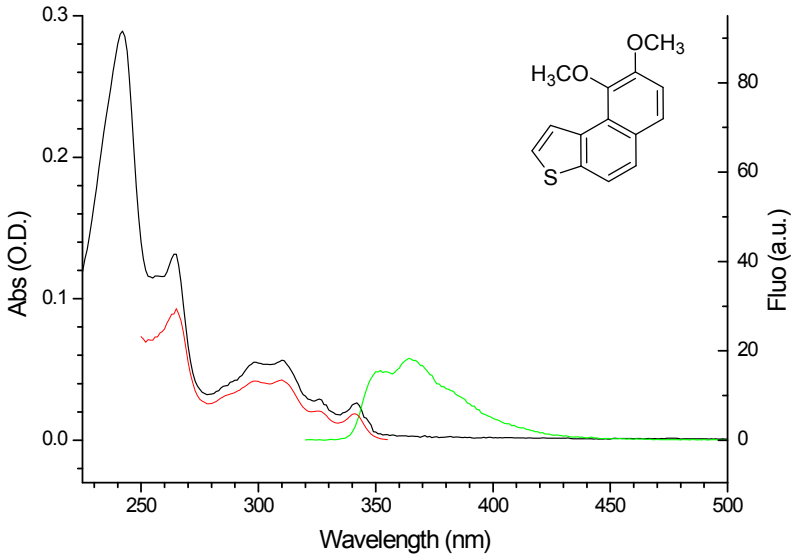


Fig S40. Absorption (black), fluorescence (green, λ_{ex} = 311 nm, c = 5,0 · 10^{-5}M, MeCN) and fluorescence excitation (red, c = 5,0×10^{-5} M) spectra of **3c"** .

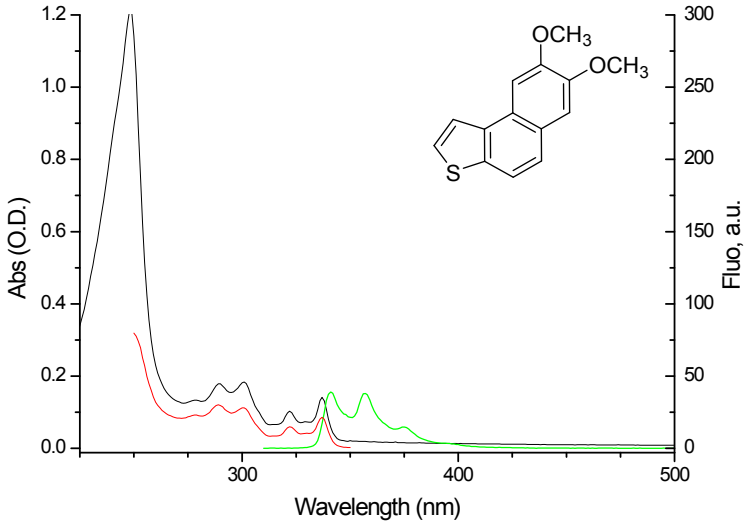


Fig S41. Absorption (black), fluorescence (green, λ_{ex} = 300 nm, c = 3,0×10^{-4} M, CH_3CN) and fluorecsence excitation (λ_{em} = 360 nm, c = 5.0×10^{-5} M, CH_3CN) spectra of **3c'**

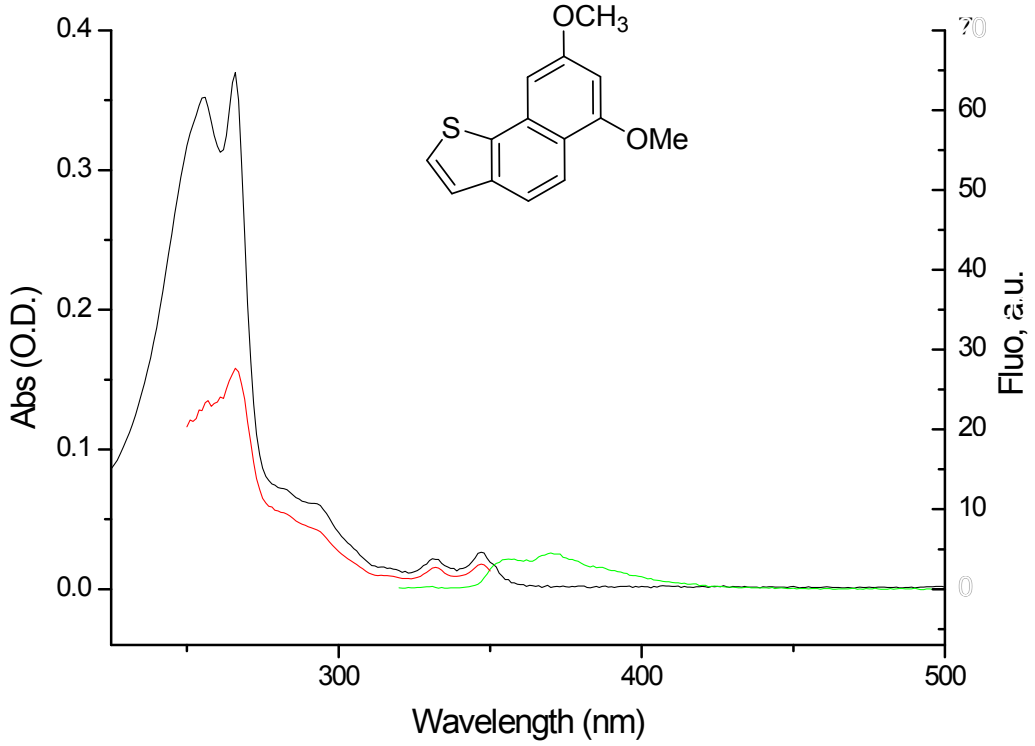


Fig S42. Absorption (black) and fluorescence (green, λ_{ex} = 300 nm, c = 5.0×10^{-5} M, CH_3CN) and fluorescence excitation spectra of **4e'** (λ_{em} = 370 nm) in MeCN (c = 5.0×10^{-5} M)

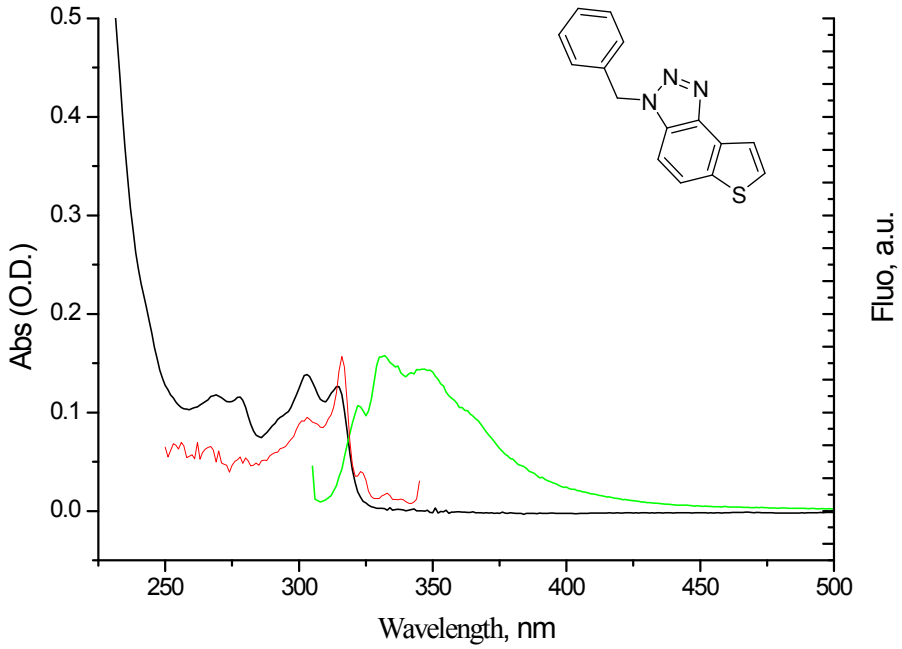


Fig S43. Absorption (black), fluorescence (green, λ_{ex} = 320 nm, c = 1,5×10^{-4} M, MeCN) and fluorescence excitation spectra (λ_{em} = 350 nm, c = 5.0×10^{-5} M, MeCN) of **3g**.

4. X-ray data

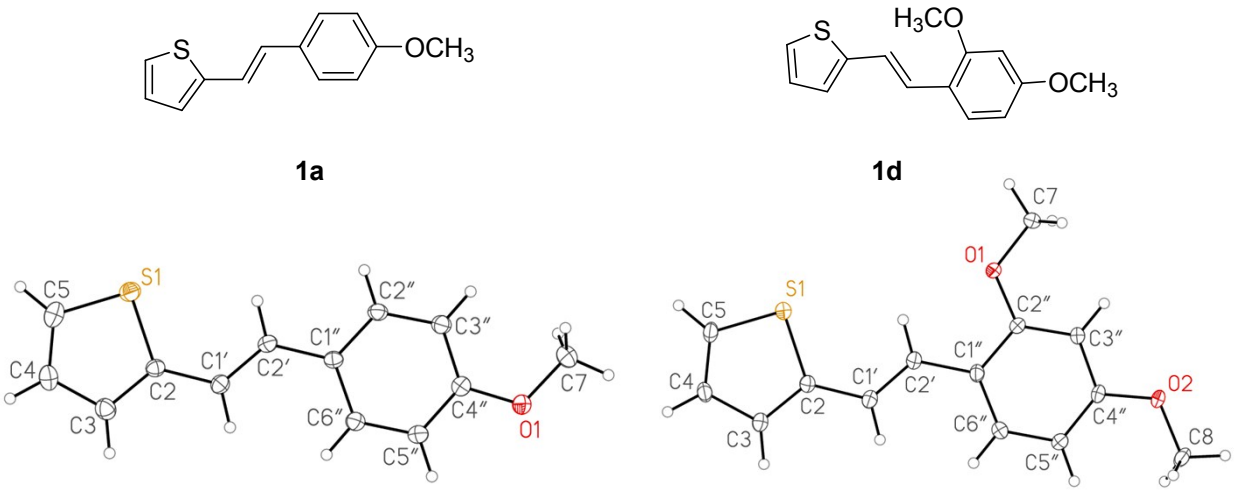


Figure S44. X-ray structures of **1a** and **1d**

Table S1. Crystal data and structure refinement for **1a**, **1d**, **3a**, **3h"**, **3g, 4a**, **4b**, **4d**, **4f'**.

	1a	**1d**	**3a**	**3c"**	**3g**	**4a**	**4b**	**4d**	**4f'**
CCDC	1903024	1903031	1903023	1903029	1903026	1903027	1903030	1903025	1903028
Empirical formula	$C_{13}H_{12}OS$	$C_{14}H_{14}O_2S$	$C_{13}H_{10}OS$	$C_{14}H_{12}O_2S$	$C_{15}H_{11}N_3S$	$C_{13}H_{10}OS$	$C_{14}H_{12}O_2S$	$C_{15}H_{14}O_3S$	$C_{14}H_{12}O_2S$
Formula weight	216.29	246.31	214.27	244.30	265.33	214.27	244.30	274.32	244.30
T (K)	120	120	120	120	120	120	120	120	120
Crystal system	Monoclinic	Monoclinic	Orthorhombic	Orthorhombic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_12_12_1$	Pbca	$P2_1/c$	$P2_1/c$	$P2_1/n$	$P2_1/c$	$P2_1/n$
Z / Z'	4 / 1	4 / 1	4 / 1	8 / 1	8 / 2	4 / 1	4 / 1	4 / 1	8 / 2
a, Å	5.9726(3)	15.2689(10)	6.0379(3)	10.3332(6)	6.9254(5)	14.7585(13)	5.1488(12)	8.7010(6)	11.3769(10)

b, Å	7.5101(4)	5.1860(3)	10.4847(5)	14.5631(9)	15.9044(11)	5.6771(5)	10.707(2)	7.6258(5)	10.1584(9)
c, Å	24.2373(13)	15.3921(10)	16.1404(8)	15.1782(9)	23.1610(16)	12.3197(11)	20.672(5)	20.3847(14)	20.2218(17)
α, °	90	90	90	90	90	90	90	90	90
β, °	92.8230(10)	96.0580(10)	90	90	92.3480(10)	97.4501(18)	91.856(4)	97.9390(10)	91.6730(19)
γ, °	90	90	90	90	90	90	90	90	90
V, Å^3	1085.84(10)	1212.01(13)	1021.78(9)	2284.1(2)	2548.9(3)	1023.50(16)	1139.0(5)	1339.60(16)	2336.1(4)
d_{calc} (g cm^{-1})	1.323	1.350	1.393	1.421	1.383	1.391	1.425	1.360	1.389
μ, cm^{-1}	2.66	2.53	2.82	2.68	2.42	2.81	2.69	2.42	2.62
F(000)	456	520	448	1024	1104	448	512	576	1024
$2\theta_{max}$, °	61.4	61.3	61.4	61.1	61.3	61.3	61.2	61.0	61.3
Refls collected	18771	15504	17850	29007	33697	13447	14960	17797	31554
Independent refls [Rint]	3364 [0.0241]	3756 [0.0328]	3162 [0.0238]	3510 [0.0327]	7848 [0.0322]	3146 [0.0295]	3476 [0.1554]	4069 [0.0309]	7191 [0.0446]
Observed reflections [$I > 2\sigma(I)$]	2917	2998	2964	3018	6416	2685	1799	3191	5544
Parameters	274	156	137	156	343	137	156	203	311
$R1$	0.0324	0.0376	0.0307	0.0322	0.0389	0.0351	0.0784	0.0381	0.0433
w$R2$	0.0880	0.1052	0.0793	0.0956	0.1064	0.0941	0.1882	0.1092	0.1183
GOF	1.024	1.014	1.021	1.024	1.008	1.019	1.025	1.016	1.023
Residual density, $\Delta\rho_{max}$/ $\Delta\rho_{min}$ (e A^{-3})	0.485/-0.253	0.445/-0.237	0.366/-0.129	0.455/-0.272	0.391/-0.278	0.480/-0.214	0.811/-0.678	0.377/-0.225	0.406/-0.299

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