Supporting Information

Ferrocenyl "Push-Pull" Chromophores with Tailorable and Switchable Second-Order Non-linear Response. Synthesis and Structure-Property Relationship

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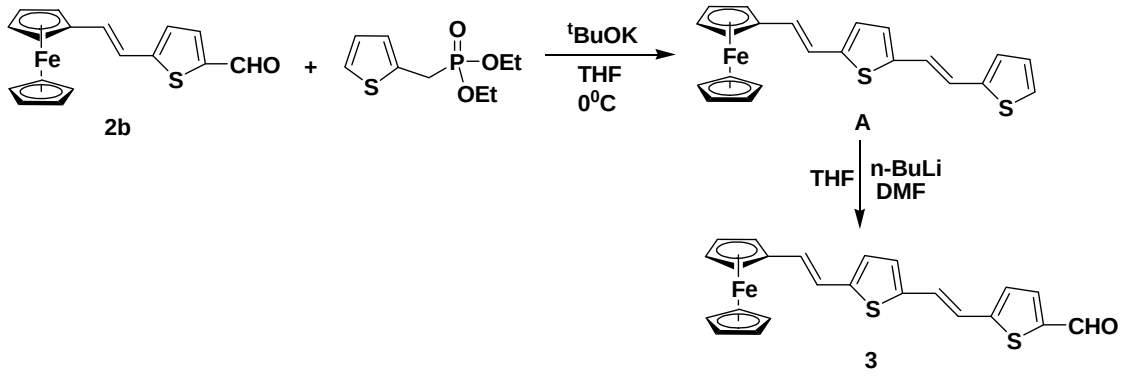
Experimental Section

Synthesis of (*E*)-5-(2-ferrocenyl vinyl)thiophene (2a): Thiophene phosphonate (3.51 g, 15 mmol) was dissolved in dry THF and cooled to 0°C. Potassium *t*-butoxide (1.68 g, 15 mmol) was added through a L-tube while stirring the solution vigorously. After stirring at 0°C for another 30 min, Ferrocene carboxaldehyde (2.14 g, 10 mmol) was added. The reaction mixture was heated to reflux for 4 h. Upon completion of reaction (TLC), it was quenched with ice water and extracted with ethyl-acetate, dried over anhydrous Na_2SO_4. After evaporation of the solvent the residue was purified by column chromatography in silica using hexane:ethylacetate as eluant. The compound was recrystallized from hot hexane to get orange solid (2.5g, 85%); mp: 125ºC. IR (KBr): ν_{max}/cm^{-1} 3095 (aromatic C-H), 1624 (C=C), 1096 (Cp). ^{1}H NMR (300 MHz): δ 4.18 (5H, s, Cp*H*), 4.36 (2H, s, Cp*H*), 4.45 (2H, s, Cp*H*), 6.67 (1H, d, *J* =15.9 Hz, C=C*H*), 6.82 (1H, d, *J* = 15.9 Hz, C=C*H*), 6.95 (2H, s, Ar*H*), 7.13 (1H, d, *J* = 4.5 Hz, Ar*H*). ^{13}C NMR (75 MHz): δ 143.56, 127.51, 126.86, 124.25, 123.06, 119.29, 82.91, 69.21, 69.03, 66.72. MS (EI): *m/z* 293.8 (M^+). Anal. Calcd. (%) for $C_{16}H_{14}FeS$: C, 65.30; H, 4.76; S, 10.88; Found: C, 65.25; H, 4.73; S, 10.73.

Synthesis of (*E*)-5-(2-ferrocenyl vinyl)thiophene-2-carboxaldehyde (2b): Vilsmeier reagent was prepared by mixing dimethyl formamide (25 ml) and phosphorus oxychloride (1.4 ml, 15 mmol) at 0°C under nitrogen atmosphere and was added drop wise over half an hour to an ice-cooled dimethyl formamide solution (20 ml) of **1** (2.94 g, 10 mmol) with vigorous stirring. The mixture was then allowed to warm to r.t. followed by heating for an hour at 60°C. The reaction was quenched with the addition of water and subsequently treated with 10% aqueous sodium hydroxide solution. The dark brown suspension formed was extracted with dichloromethane. The solvent layer was washed with brine solution and dried over anhydrous sodium sulfate. On rotary evaporation the crude aldehyde was obtained as a viscous liquid, which was purified by column chromatography in hexane:ethylacetate mixture to obtain crystalline red solid (2.4 g, 70%); mp: 120ºC. IR (KBr): ν_{max}/cm^{-1} 3087 (aromatic C-H), 1663 (-C=O), 1615 (C=C), 1098 (Cp). ^{1}H NMR (300 MHz): δ 4.16 (5H, s, Cp*H*), 4.37 (2H, s, Cp*H*), 4.48 (2H, s, Cp*H*), 6.79 (1H, d, *J* =15.9 Hz, C=C*H*), 6.97 (1H, d, *J* = 15.9 Hz, C=C*H*), 7.02 (1H, d, *J* = 3.9 Hz, Ar*H*), 7.62 (1H, d, 3.9 Hz, Ar*H*), 9.82 (1H, s, C*H*O). ^{13}C NMR (75 MHz): δ 67.43, 69.43, 70.06, 81.30, 118.01, 124.81, 132.86, 137.55, 140.38, 153.43, 182.40. MS (EI): *m/z* 322.8 (M^+). Anal. Calcd. (%) for $C_{17}H_{14}FeSO$: C, 63.30; H, 4.32; S, 9.89; Found: C, 63.38; H, 4.34; S, 9.90.

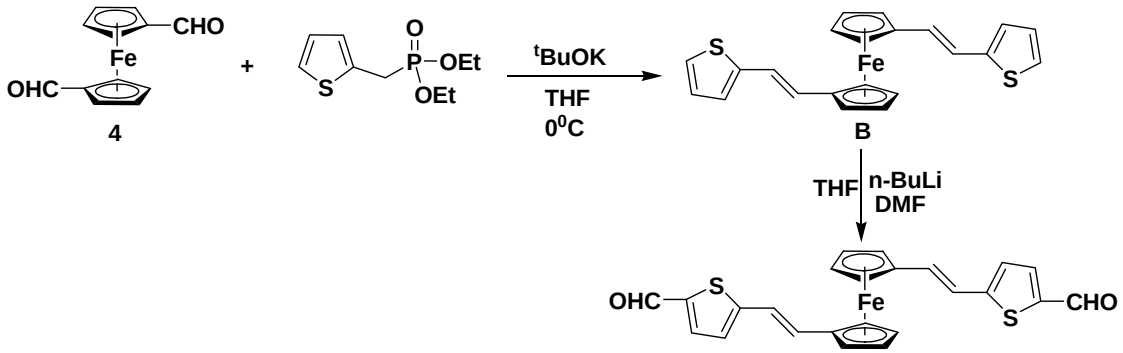
Supplemental schemes and procedures



Scheme 1

Synthesis of 2-((*E*)-2-ferrocenyl vinyl)-5-((*E*)-2-(thiophene-2-yl)vinyl)thiophene, A: Thiophene phosphonate (3.51 g, 15 mmol) was dissolved in dry THF and cooled to 0°C. Potassium *t*-butoxide (1.68 g, 15 mmol) was added through a L-tube while stirring the solution vigorously. After stirring at 0°C for another 30 min, **2b** (3.22 g, 10 mmol) was added. The reaction mixture was heated to reflux for 4 h. Monitered the reaction by tlc. On completion of reaction it was quenched with ice water and extracted with ethyl-acetate, dried over anhydrous Na_2SO_4. After evaporation of the solvent the residue was purified by column chromatography in silica using hexane:ethylacetate as eluant. The compound was recrystallized from hot hexane to get orange solid (3.41 g, 85%); mp: 152ºC. IR (KBr): ν_{max}/cm^{-1} 3080 (aromatic C-H), 1604 (C=C), 1039 (Cp). ^{1}H NMR (300 MHz): δ 4.14 (5H, s, Cp*H*), 4.29 (2H, s, Cp*H*), 4.42 (2H, s, Cp*H*), 6.65 (1H, d, *J* =15.88 Hz, C=C*H*), 6.76 (1H, d, *J* = 15.9 Hz, C=C*H*), 6.80 (1H, d, *J* = 3.6 Hz, C=C*H*), 7.00 (4H, s, Ar*H*), 7.17 (1H, d, *J* = 5.1 Hz). ^{13}C NMR (75 MHz): δ 65.70, 68.23, 69.32, 82.16, 210.78, 119.47, 124.99, 125.93, 137.12, 138.05, 140.03, 142.45, 151.24, 151.23. MS (EI): *m/z* 401.8 (M^+). Anal. Calcd. (%) for $C_{23}H_{22}FeS_2$: C, 69.34; H, 4.52; S, 8.04; Found: C, 70.04; H, 4.47; S, 7.98.

Synthesis of 2-((*E*)-2-ferrocenyl vinyl)-5-((*E*)-2-(thiophene-2-yl)vinyl)thiophene-2-carboxaldehyde (3): The compound **A** (0.500 g, 10 mmol) was taken in 30 mL of dry THF at 0^{0}C. To this *n*-BuLi (1 eq., 0.529 mL) was added under nitrogen atmosphere and the reaction mixture was allowed to stir at room temperature for another 30 min. Then DMF (0.144 mL) was added to the reaction mixture. After the completion the reaction was quenched by adding 1N HCl solution. Orangish red solid (230 mg, 50%); mp: 165ºC. IR (KBr): ν_{max}/cm^{-1} 3083 (aromatic C-H), 1655 (-C=O) 1612 (C=C), 1039 (Cp). ^{1}H NMR (300 MHz): δ 4.16 (5H, s, Cp*H*), 4.33 (2H, s, Cp*H*), 4.45 (2H, s, Cp*H*), 6.65 (1H, d, *J* = 15.84 Hz, aromatic *H*), 6.79 (1H, d, *J* = 15.88 Hz, aromatic *H*), 6.86 (1H, d, *J* = 3.72 Hz, aromatic *H*), 6.97 (1H, d, *J* = 15.72, Hz, C=C*H*), 7.003 (1H, s, *J* = 3.76 Hz, C=C*H*), 7.17 (1H, d, *J* = 5.1 Hz, C=C*H*), 7.21 (1H, d, *J* = 15.72 Hz, C=C*H*), 7.66 (1H, d, *J* = 3.92), 9.85 (1H, s, C*H*O). ^{13}C NMR (75 MHz): δ 66.98, 69.33, 69.50, 82.44, 211.96, 119.51, 125.39, 126.49, 137.30, 138.85, 141.24, 144.69, 152.34, 152.34, 182.38. MS (EI): *m/z* 429.9 (M^+). Anal. Calcd. (%) for $C_{23}H_{18}FeS_2O$ C, 64.18; H, 4.18; S, 14.88; Found: C, 64.01; H, 4.08; S, 14.76.



Synthesis of 1,2-bis((E)-2-(thiophen-2-yl)vinyl)ferrocene (B): Thiophene phosphonate (7.02 g, 30 mmol) was dissolved in dry THF and cooled to 0°C. Potassium *t*-butoxide (3.36 g, 30 mmol) was added through a L-tube while stirring the solution vigorously. After stirring at 0°C for another 30 min, **4** (2.42 g, 10 mmol) was added. The reaction mixture was heated to reflux for 4 h. Monitored the reaction by tlc. On completion of reaction it was quenched with ice water and extracted with ethyl-acetate, dried over anhydrous Na_2SO_4. After evaporation of the solvent the residue was purified by column chromatography in silica using hexane:ethylacetate as eluent. The compound was recrystallized from hot hexane to afford orange solid (3.417 g, 85%); mp: 150ºC. IR (KBr): ν_{max}/cm^{-1} 3082 (aromatic C-H), 1621 (C=C), 1032 (Cp). ^{1}H NMR (300 MHz): δ 4.25 (2H, s, Cp*H*), 4.36 (2H, s, Cp*H*), 6.56 (1H, d, *J* =15.9 Hz, C=C*H*), 6.75 (1H, d, *J* = 15.9 Hz, C=C*H*), 6.82 (1H, d, *J* =3.6 Hz, Ar*H*), 6.91 (4H, m, Ar*H*), 7.09 (1H, d, *J* = 5.1 Hz, Ar*H*). ^{13}C NMR (75 MHz): δ 66.33, 67.42, 70.01, 70.48, 117.86, 119.51, 122.63, 123.16, 124.21, 124.78, 126.98, 130.15, 136.73. MS (EI): *m/z* 401.8 (M^+). Anal. Calcd. (%) for $C_{22}H_{18}FeS_2$ C, 65.51; H, 4.32; S, 16.07; Found: C, 65.69; H, 4.47; S, 15.92.

Synthesis of 5,5'-((1E,1'E)-ferrocene-1,2-diylbis(ethene-2,1-diyl))bis(thiophene-2-carbaldehyde) 5: Compopund **B** (0.500 g, 10 mmol) was taken in 30 mL of dry THF at 0^{0}C. To this *n*-BuLi (1 eq., 0.529 mL) was added under nitrogen atmosphere and the reaction mixture was allowed to stir at room temperature for another 30 min. Then DMF (0.144 mL) was added to the reaction mixture. After the completion the reaction, it was quenched by adding 1N HCl solution. Blackish red solid (370 mg, 60%); mp: 175ºC. IR (KBr): ν_{max}/cm^{-1} 3086 (aromatic C-H), 1663 (-C=O) 1614 (C=C), 1043 (Cp).^{1}H NMR (400 MHz): δ 4.35 (4H, s, Cp*H*), 4.47 (4H, s, Cp*H*), 6.63 (4H, s, C=C*H*), 6.83 (2H, d, *J* = 3.92 Hz, C=C*H*), 7.49 (2H, d, *J* = 3.6 Hz, Ar*H*), 6.919.76 (2H, s, C*H*O). ^{13}C NMR (75 MHz): δ 67.99, 68.55, 70.15, 70.94, 118.75, 120.42, 123.21, 124.57, 124.76, 124.91, 127.46, 131.54, 137.34, 182.32. MS (EI): *m/z* 458.8 (M^+ + 1). Anal. Calcd. (%) for $C_{24}H_{18}FeS_2O_2$ C, 62.88; H, 3.93; S, 13.97; Found: C, 62.01; H, 3.98; S, 13.86.

Thermogravimetric (TGA) analysis

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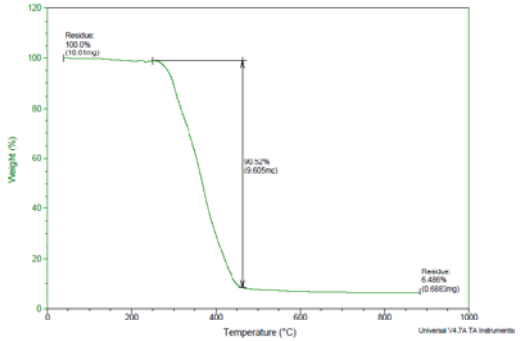

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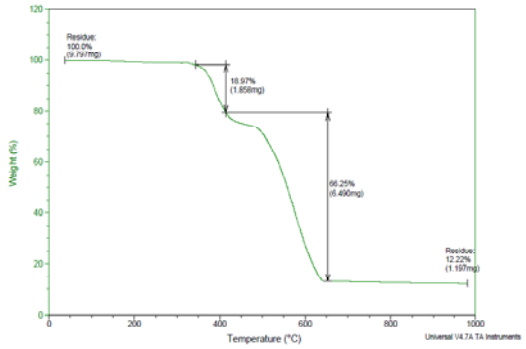

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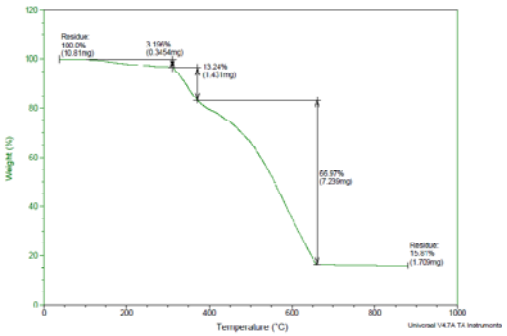

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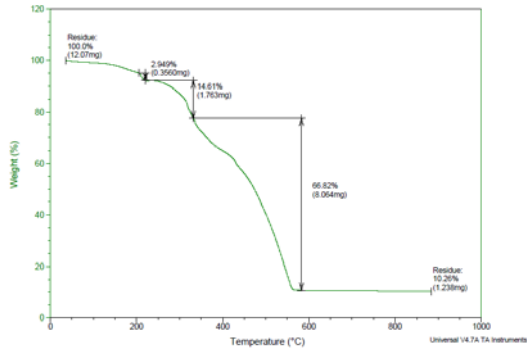

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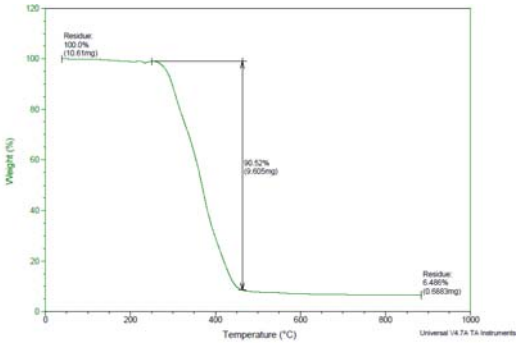


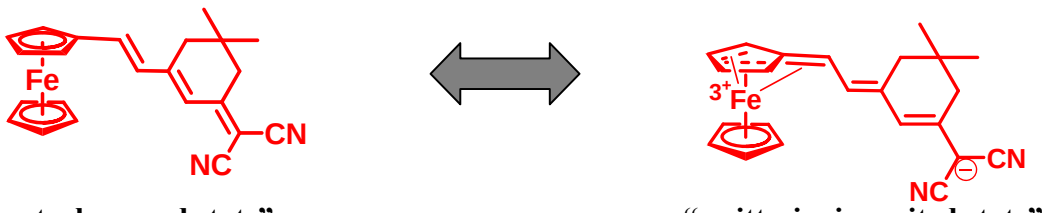
Figure S1. TGA curves of the chromophores **7**-**11**.

Solvatochromism Studies

Table S1. Solvatochromism data of the charge transfer band of the chromophores **2a-2d** and **7-11** in different solvents (2.85 X 10^{-5} M).

Solvent	π^*	2a	2b	2c	2d	7	8	9	10	11
Hexane	-0.08	450	473	480	501	536	558	562	528	insoluble
		321	341	346	344	393	468	508	364,407	
Diethylether	0.27	452	481	480	501	551	561	570	540	570
		322	343	346	346	400	470	519	375,413	465
Toluene	0.54	454	494	481	501	554	574	578	542	576
		323	364	346	347	404	476	524	380,415	472
THF	0.58	455	494	481	501	558	576	579	556	585
		323	364	346	348	405	476	525	384,416	474
Methanol	0.60	457	494	484	502	564	578	580	554	589
		324	364	346	349	406	477	525	385,417	475
Acetonitrile	0.75	457	497	484	502	565	580	583	550	597
		324	365	346	350	406	477	526	385,420	478
DCM	0.82	456	501	485	503	568	581	585	558	603
		324	371	347	351	409	478	526	385,420	479
DMF	0.88	455	501	486	503	573	585	590	569	612
		324	371	348	355	412	479	529	388,425	482
DMSO	1.00	457	504	490	503	575	590	605	576	623
		327	374	350	356	416	484	534	391,438	485

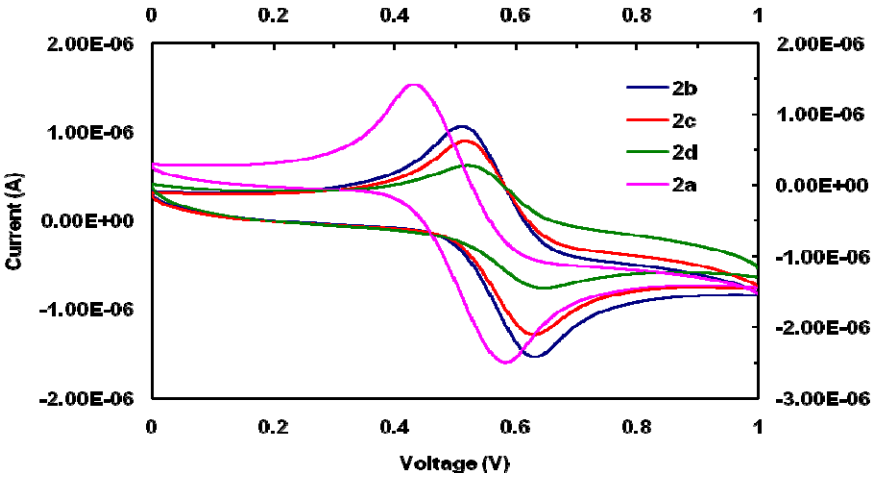
π^*: polarizability scale of solvents



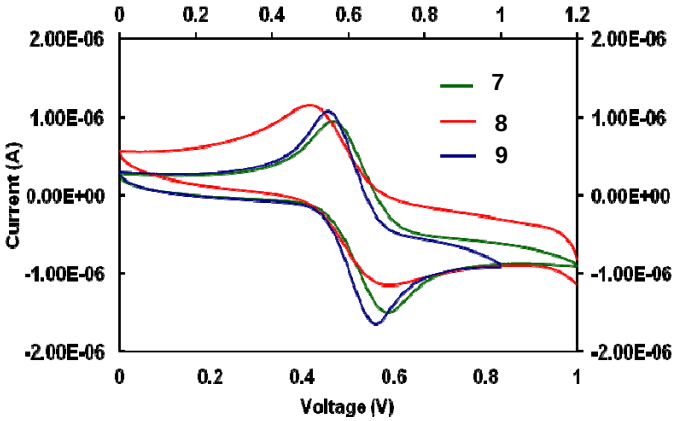
"neutral ground state" **"zwitterionic excited state"**

Figure S2. Chemical structure depiction of neutral ground and zwitterionic charge transfer state responsible for solvatochromic behavior.

Electrochemical Studies



(a)



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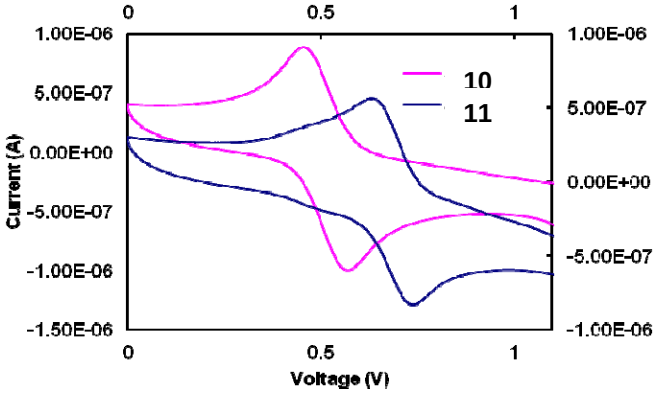


(c)

Figure S3. Cyclic voltammetry graphs of (a) **2a-2d**; (b) **7-9** and (c) **10** and **11** (1 x 10^{-4} in DCM).

Table S2. Energies of the Frontier Orbitals HOMO-n to LUMO-n (n=0, 1, 2,3,4,5 & 6) obtained from TD-DFT carried out at B3LYP/6-31G level in dichloromethane as solvent medium.

Compound	**2a**	**2b**	**2c**	**7**	**8**	**9**	**10**	**11**
HOMO-6	-7.0588	-7.1872	-7.4354	-7.4389	-7.1541	-6.9657	-7.2653	-6.6548
HOMO-5	-6.9105	-7.1453	-7.1802	-7.0740	-6.9917	-6.6434	-7.1900	-6.5209
HOMO-4	-6.9899	-7.0090	-7.0055	-7.0514	-6.4826	-6.4287	-6.7951	-6.3664
HOMO-3	-6.3641	-6.4996	-6.4922	-6.5703	-6.3797	-5.4940	-6.2508	-5.7799
HOMO-2	-5.6976	-5.9442	-5.9428	-6.0068	-5.6412	-5.4948	-6.0216	-5.7411
HOMO-1	-5.4239	-5.5627	-5.5521	-5.6391	-5.5351	-5.4918	-5.7072	-5.3609
HOMO	-5.2195	-5.4119	-5.4065	-5.4966	-5.2219	-5.0093	-5.6733	-5.2322
LUMO	-1.4700	-2.4684	-2.2224	-2.6736	-2.9380	-3.0134	-2.8333	-2.9932
LUMO+1	-0.1864	-0.7508	-0.5162	-0.7421	-1.5979	-2.0863	-2.6602	-2.9184
LUMO+2	-0.1306	-0.3135	-0.4542	-0.3802	-0.5649	-1.1358	-0.9260	-1.7178
LUMO+3	0.7340	-0.0952	-0.3050	-0.1723	-0.2876	-0.5238	-0.6974	-1.5393
LUMO+4	0.7837	0.5263	0.0433	-0.1287	-0.1567	-0.2503	-0.3701	-0.6920
LUMO+5	1.5897	1.2082	0.4708	0.8272	-0.0854	-0.1472	-0.2163	-0.5643
LUMO+6	1.6828	1.4975	1.4528	1.1824	0.2879	-0.0805	-0.2046	-0.3194

Table S3. Energies of the Frontier Orbitals HOMO-n to LUMO-n (n=0, 1, 2,3,4,5 & 6) obtained from TD-DFT carried out at B3LYP/6-31G level in gas phase.

Compound	**2a**	**2b**	**2c**	**7**	**8**	**9**	**10**	**11**
HOMO-6	-6.9532	-7.1927	-7.4354	-7.5654	-7.2144	-7.9010	-7.5790	-6.4874
HOMO-5	-6.8343	-7.0830	-7.2471	-7.2210	-7.0985	-6.6738	-7.4011	-6.6678
HOMO-4	-6.8207	-6.8523	-7.1211	-7.1377	-6.5897	-6.5280	-7.1366	-6.4874
HOMO-3	-6.2926	-6.5728	-6.6099	-6.7309	-6.4052	-5.9829	-6.4890	-6.0033
HOMO-2	-5.6028	-5.9573	-6.0052	-6.0850	-5.7299	-5.5957	-6.3255	-5.9854
HOMO-1	-5.3552	-5.6343	-5.6695	-5.7992	-5.6488	-5.5791	-6.0213	-5.5484
HOMO	-5.1272	-5.4586	-5.5019	-5.6268	-5.3005	-5.0850	-5.9448	-5.4132
LUMO	-1.3512	-2.3705	-2.2108	-2.7101	-2.9610	-3.0426	-3.0300	-3.1185
LUMO+1	-0.1135	-0.7390	-0.5722	-0.8457	-1.6549	-2.1474	-2.8511	-3.0222
LUMO+2	-0.0473	-0.3864	-0.4286	-0.5415	-0.6460	-1.2002	-1.2096	-1.8922
LUMO+3	-0.8389	-0.1341	-0.3178	-0.2718	-0.3994	-0.6079	-1.0223	-1.7085
LUMO+4	-0.8876	0.6166	-0.0215	0.1236	-0.1899	-0.3494	-0.6691	-0.8742
LUMO+5	1.5240	1.2182	0.4999	1.0157	0.1532	-0.1766	-0.4275	-0.7815
LUMO+6	1.7267	1.3444	1.2840	1.2217	0.1875	-0.0278	-0.0688	-0.5499

Table S4. Correlation between the experimentally (CV/UV) and theoretically (TD-DFT)* calculated HOMO-LUMO energies and dipole moment of chromophores **2a**-**2c** and **7**-**11**.

Chromophore	[a]HOMO	[b]LUMO	μ
	TD-DFT gas phase/solvent phase (CV/UV)		Gas-phase/solvent phase
2a	-5.127/-5.2195 (-5.125)	-1.350/-1.4700 (-1.662)	0.9048/1.1943
2b	-5.481/-5.4119 (-5.220)	-2.387/-2.4684 (-2.282)	5.9300/7.2395
2c	-5.502/-5.4065 (-5.220)	-2.211/-2.2224 (-2.251)	6.3234/8.0490
7	-5.627/-5.4966 (-5.250)	-2.710/-2.6736 (-2.639)	9.0938/11.6652
8	-5.301/-5.2219 (-5.160)	-2.961/2.9380 (-2.829)	10.6678/13.7727
9	-5.062/-5.0093 (-5.062)	-2.978/3.0134 (-3.233)	11.0444/15.2255
10	-5.945/-5.6733 (-5.320)	-3.030/-2.8333 (-2.710)	5.4407/7.3112
11	-5.413/-5.2322 (-5.130)	-3.119/-2.9932(-2.847)	6.9930/9.3026

*Calculation done at B3LYP/6-31G level.

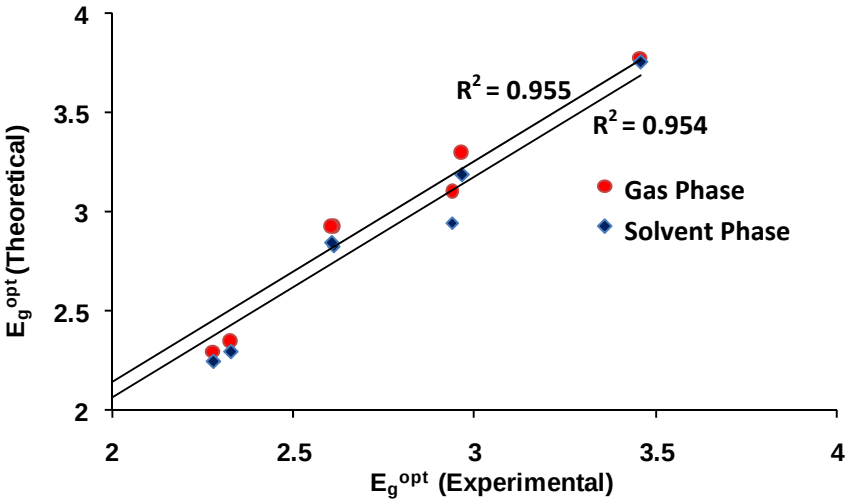


Figure S4. Linear correlation between the optical gap E_g^{opt}, determined from UV/CV and TD-DFT for **2a-c, 7-11**

Crystallographic Data

Table S5. Crystallographic data and refinement details for chromophores **2c** and **7**.

	2c	**7**
Formula	$C_{17}H_{13}FeNS$	$C_{23}H_{22}FeN_2$
M	319.19	382.28
Crystal system	Monoclinic	Triclinic
space group	P 21/n	P -1
a /Å	5.78750(10)	7.3555(4
b /Å	25.3720(5)	11.6373(7)
c/Å	9.6688(2)	11.6538(6)
α/deg	90	85.685(4)
β/deg	103.188(2)	81.702(4
γ/deg	90	75.203(5)
ρ/mg.m^{-3}	1.534	1.331
U/A^{o3}	1382.33(5)	953.60(9)
Z	4	2
T/K	120(2)	293(2)
μ/mm^{-1}	1.228	0.799
θ_{max} /deg (completeness)	25.00 (99.9 %)	25.00,(98.4 %)
Crystal size/mm	0.23 x 0.18 x 0.15	0.32 x 0.28 x 0.21
No. of reflections collected	9340	6742
No. of Independent reflections (R_{int})	2424 (0.0172)	3302 (0.0272)
Goodness-of-fit on F2	1.084	1.056
Final R1, wR2 [I>2σ(I)][a]	0.0233, 0.0552	0.0415, 0.1419
(all data)	0.0261, 0.0561	0.0477, 0.1760
peak and hole/ e.Å^{-3}	0.207, -0.356	0.442, -0.725

[a]The structures were refined on F_0^2 using all data.

Table S6. Bond lengths [A] and angles [deg] for **2c**.

Fe(1)-C(10)	2.0371(17)
Fe(1)-C(17)	2.0379(18)
Fe(1)-C(15)	2.0396(18)
Fe(1)-C(12)	2.0400(17)
Fe(1)-C(14)	2.0402(19)
Fe(1)-C(16)	2.0416(18)
Fe(1)-C(13)	2.0426(19)
Fe(1)-C(11)	2.0432(18)
Fe(1)-C(9)	2.0435(17)
Fe(1)-C(8)	2.0546(17)

S(1)-C(5)	1.7275(18)
S(1)-C(1)	1.7285(18)
N(1)-C(2)	1.146(3)
C(1)-C(3)	1.365(3)
C(1)-C(2)	1.426(3)
C(3)-C(4)	1.405(3)
C(3)-H(3)	0.9500
C(4)-C(5)	1.372(2)
C(4)-H(4)	0.9500
C(5)-C(6)	1.450(2)
C(6)-C(7)	1.333(3)
C(6)-H(6)	0.9500
C(7)-C(8)	1.458(2)
C(7)-H(7)	0.9500
C(8)-C(9)	1.431(2)
C(8)-C(12)	1.434(2)
C(9)-C(10)	1.423(2)
C(9)-H(9)	0.9500
C(10)-C(11)	1.421(3)
C(10)-H(10)	0.9500
C(11)-C(12)	1.417(3)
C(11)-H(11)	0.9500
C(12)-H(12)	0.9500
C(13)-C(14)	1.410(3)
C(13)-C(17)	1.411(3)
C(13)-H(13)	0.9500
C(14)-C(15)	1.413(3)
C(14)-H(14)	0.9500

C(15)-C(16)	1.407(3)
C(15)-H(15)	0.9500
C(16)-C(17)	1.419(3)
C(16)-H(16)	0.9500
C(17)-H(17)	0.9500

C(10)-Fe(1)-C(17)	158.31(9)
C(10)-Fe(1)-C(15)	106.49(8)
C(17)-Fe(1)-C(15)	67.97(8)
C(10)-Fe(1)-C(12)	68.58(7)
C(17)-Fe(1)-C(12)	108.38(8)
C(15)-Fe(1)-C(12)	158.38(8)
C(10)-Fe(1)-C(14)	122.33(8)
C(17)-Fe(1)-C(14)	67.99(8)
C(15)-Fe(1)-C(14)	40.53(8)
C(12)-Fe(1)-C(14)	159.85(8)
C(10)-Fe(1)-C(16)	121.57(8)
C(17)-Fe(1)-C(16)	40.70(9)
C(15)-Fe(1)-C(16)	40.33(8)
C(12)-Fe(1)-C(16)	122.95(8)
C(14)-Fe(1)-C(16)	68.15(8)
C(10)-Fe(1)-C(13)	158.94(9)
C(17)-Fe(1)-C(13)	40.47(9)
C(15)-Fe(1)-C(13)	68.03(8)
C(12)-Fe(1)-C(13)	124.00(8)
C(14)-Fe(1)-C(13)	40.40(8)
C(16)-Fe(1)-C(13)	68.29(8)
C(10)-Fe(1)-C(11)	40.77(8)

C(17)-Fe(1)-C(11)	122.96(8)
C(15)-Fe(1)-C(11)	122.04(8)
C(12)-Fe(1)-C(11)	40.61(7)
C(14)-Fe(1)-C(11)	158.22(8)
C(16)-Fe(1)-C(11)	106.86(8)
C(13)-Fe(1)-C(11)	159.47(8)
C(10)-Fe(1)-C(9)	40.82(7)
C(17)-Fe(1)-C(9)	159.97(8)
C(15)-Fe(1)-C(9)	122.08(7)
C(12)-Fe(1)-C(9)	68.82(7)
C(14)-Fe(1)-C(9)	107.40(8)
C(16)-Fe(1)-C(9)	157.63(8)
C(13)-Fe(1)-C(9)	123.47(8)
C(11)-Fe(1)-C(9)	68.69(7)
C(10)-Fe(1)-C(8)	68.71(7)
C(17)-Fe(1)-C(8)	124.03(8)
C(15)-Fe(1)-C(8)	158.77(7)
C(12)-Fe(1)-C(8)	40.99(7)
C(14)-Fe(1)-C(8)	123.29(7)
C(16)-Fe(1)-C(8)	159.85(8)
C(13)-Fe(1)-C(8)	108.61(7)
C(11)-Fe(1)-C(8)	68.67(7)
C(9)-Fe(1)-C(8)	40.89(7)
C(5)-S(1)-C(1)	91.30(9)
C(3)-C(1)-C(2)	127.37(17)
C(3)-C(1)-S(1)	111.88(14)
C(2)-C(1)-S(1)	120.74(14)
N(1)-C(2)-C(1)	179.6(2)

C(1)-C(3)-C(4)	112.37(16)
C(1)-C(3)-H(3)	123.8
C(4)-C(3)-H(3)	123.8
C(5)-C(4)-C(3)	113.47(16)
C(5)-C(4)-H(4)	123.3
C(3)-C(4)-H(4)	123.3
C(4)-C(5)-C(6)	126.96(16)
C(4)-C(5)-S(1)	110.97(13)
C(6)-C(5)-S(1)	122.08(13)
C(7)-C(6)-C(5)	126.09(16)
C(7)-C(6)-H(6)	117.0
C(5)-C(6)-H(6)	117.0
C(6)-C(7)-C(8)	124.72(16)
C(6)-C(7)-H(7)	117.6
C(8)-C(7)-H(7)	117.6
C(9)-C(8)-C(12)	107.30(15)
C(9)-C(8)-C(7)	127.18(16)
C(12)-C(8)-C(7)	125.51(15)
C(9)-C(8)-Fe(1)	69.14(10)
C(12)-C(8)-Fe(1)	68.96(10)
C(7)-C(8)-Fe(1)	126.60(12)
C(10)-C(9)-C(8)	107.97(16)
C(10)-C(9)-Fe(1)	69.35(10)
C(8)-C(9)-Fe(1)	69.97(10)
C(10)-C(9)-H(9)	126.0
C(8)-C(9)-H(9)	126.0
Fe(1)-C(9)-H(9)	126.2
C(11)-C(10)-C(9)	108.31(16)

C(11)-C(10)-Fe(1)	69.85(10)
C(9)-C(10)-Fe(1)	69.83(10)
C(11)-C(10)-H(10)	125.8
C(9)-C(10)-H(10)	125.8
Fe(1)-C(10)-H(10)	126.1
C(12)-C(11)-C(10)	108.07(16)
C(12)-C(11)-Fe(1)	69.57(10)
C(10)-C(11)-Fe(1)	69.38(10)
C(12)-C(11)-H(11)	126.0
C(10)-C(11)-H(11)	126.0
Fe(1)-C(11)-H(11)	126.6
C(11)-C(12)-C(8)	108.34(15)
C(11)-C(12)-Fe(1)	69.82(10)
C(8)-C(12)-Fe(1)	70.05(10)
C(11)-C(12)-H(12)	125.8
C(8)-C(12)-H(12)	125.8
Fe(1)-C(12)-H(12)	125.9
C(14)-C(13)-C(17)	107.87(18)
C(14)-C(13)-Fe(1)	69.71(11)
C(17)-C(13)-Fe(1)	69.59(11)
C(14)-C(13)-H(13)	126.1
C(17)-C(13)-H(13)	126.1
Fe(1)-C(13)-H(13)	126.2
C(13)-C(14)-C(15)	108.01(18)
C(13)-C(14)-Fe(1)	69.89(11)
C(15)-C(14)-Fe(1)	69.72(11)
C(13)-C(14)-H(14)	126.0
C(15)-C(14)-H(14)	126.0

Fe(1)-C(14)-H(14)	126.0
C(16)-C(15)-C(14)	108.38(17)
C(16)-C(15)-Fe(1)	69.91(11)
C(14)-C(15)-Fe(1)	69.76(10)
C(16)-C(15)-H(15)	125.8
C(14)-C(15)-H(15)	125.8
Fe(1)-C(15)-H(15)	126.1
C(15)-C(16)-C(17)	107.55(18)
C(15)-C(16)-Fe(1)	69.76(10)
C(17)-C(16)-Fe(1)	69.51(11)
C(15)-C(16)-H(16)	126.2
C(17)-C(16)-H(16)	126.2
Fe(1)-C(16)-H(16)	126.1
C(13)-C(17)-C(16)	108.20(17)
C(13)-C(17)-Fe(1)	69.94(11)
C(16)-C(17)-Fe(1)	69.79(11)
C(13)-C(17)-H(17)	125.9
C(16)-C(17)-H(17)	125.9
Fe(1)-C(17)-H(17)	125.9

Table S7. Bond lengths [A] and angles [deg] for **7**.

Fe(1)-C(18)	2.020(3)
Fe(1)-C(22)	2.021(4)
Fe(1)-C(23)	2.022(4)
Fe(1)-C(19)	2.028(4)
Fe(1)-C(20)	2.030(4)

Fe(1)-C(21)	2.031(4)
Fe(1)-C(17)	2.037(3)
Fe(1)-C(14)	2.050(3)
Fe(1)-C(15)	2.050(3)
Fe(1)-C(16)	2.059(3)
N(1)-C(1)	1.141(6)
N(2)-C(2)	1.141(6)
C(1)-C(3)	1.428(5)
C(2)-C(3)	1.432(6)
C(3)-C(4)	1.379(5)
C(4)-C(11)	1.424(4)
C(4)-C(5)	1.497(5)
C(5)-C(6)	1.531(4)
C(5)-H(5A)	0.9700
C(5)-H(5B)	0.9700
C(6)-C(7)	1.533(5)
C(6)-C(8)	1.535(5)
C(6)-C(9)	1.538(4)
C(7)-H(7A)	0.9600
C(7)-H(7B)	0.9600
C(7)-H(7C)	0.9600
C(8)-H(8A)	0.9600
C(8)-H(8B)	0.9600
C(8)-H(8C)	0.9600
C(9)-C(10)	1.512(4)
C(9)-H(9A)	0.9700
C(9)-H(9B)	0.9700
C(10)-C(11)	1.349(4)

C(10)-C(12)	1.444(4)
C(11)-H(11)	0.9300
C(12)-C(13)	1.342(4)
C(12)-H(12)	0.9300
C(13)-C(14)	1.450(4)
C(13)-H(13)	0.9300
C(14)-C(15)	1.417(5)
C(14)-C(18)	1.437(4)
C(15)-C(16)	1.421(5)
C(15)-H(15)	0.9300
C(16)-C(17)	1.420(5)
C(16)-H(16)	0.9300
C(17)-C(18)	1.416(5)
C(17)-H(17)	0.9300
C(18)-H(18)	0.9300
C(19)-C(20)	1.373(9)
C(19)-C(23)	1.413(9)
C(19)-H(19)	0.9300
C(20)-C(21)	1.353(8)
C(20)-H(20)	0.9300
C(21)-C(22)	1.329(9)
C(21)-H(21)	0.9300
C(22)-C(23)	1.386(10)
C(22)-H(22)	0.9300
C(23)-H(23)	0.9300

C(18)-Fe(1)-C(22)	127.5(2)
C(18)-Fe(1)-C(23)	166.9(3)

C(22)-Fe(1)-C(23)	40.1(3)
C(18)-Fe(1)-C(19)	147.8(3)
C(22)-Fe(1)-C(19)	67.1(2)
C(23)-Fe(1)-C(19)	40.8(3)
C(18)-Fe(1)-C(20)	114.45(19)
C(22)-Fe(1)-C(20)	65.9(2)
C(23)-Fe(1)-C(20)	67.2(2)
C(19)-Fe(1)-C(20)	39.6(3)
C(18)-Fe(1)-C(21)	106.7(2)
C(22)-Fe(1)-C(21)	38.3(3)
C(23)-Fe(1)-C(21)	65.9(2)
C(19)-Fe(1)-C(21)	65.7(2)
C(20)-Fe(1)-C(21)	38.9(2)
C(18)-Fe(1)-C(17)	40.86(14)
C(22)-Fe(1)-C(17)	108.23(19)
C(23)-Fe(1)-C(17)	130.9(3)
C(19)-Fe(1)-C(17)	171.3(2)
C(20)-Fe(1)-C(17)	146.5(2)
C(21)-Fe(1)-C(17)	115.6(2)
C(18)-Fe(1)-C(14)	41.35(13)
C(22)-Fe(1)-C(14)	165.9(3)
C(23)-Fe(1)-C(14)	151.7(3)
C(19)-Fe(1)-C(14)	117.6(2)
C(20)-Fe(1)-C(14)	108.49(16)
C(21)-Fe(1)-C(14)	129.4(2)
C(17)-Fe(1)-C(14)	68.77(13)
C(18)-Fe(1)-C(15)	68.41(14)
C(22)-Fe(1)-C(15)	152.5(2)

C(23)-Fe(1)-C(15)	120.9(2)
C(19)-Fe(1)-C(15)	112.72(18)
C(20)-Fe(1)-C(15)	132.8(2)
C(21)-Fe(1)-C(15)	168.8(2)
C(17)-Fe(1)-C(15)	67.76(14)
C(14)-Fe(1)-C(15)	40.44(13)
C(18)-Fe(1)-C(16)	68.96(14)
C(22)-Fe(1)-C(16)	118.49(18)
C(23)-Fe(1)-C(16)	111.30(18)
C(19)-Fe(1)-C(16)	134.2(2)
C(20)-Fe(1)-C(16)	171.9(2)
C(21)-Fe(1)-C(16)	148.5(2)
C(17)-Fe(1)-C(16)	40.57(15)
C(14)-Fe(1)-C(16)	68.83(13)
C(15)-Fe(1)-C(16)	40.46(14)
N(1)-C(1)-C(3)	178.1(5)
N(2)-C(2)-C(3)	178.4(5)
C(4)-C(3)-C(1)	121.6(4)
C(4)-C(3)-C(2)	122.3(3)
C(1)-C(3)-C(2)	116.0(3)
C(3)-C(4)-C(11)	121.3(3)
C(3)-C(4)-C(5)	120.3(3)
C(11)-C(4)-C(5)	118.3(3)
C(4)-C(5)-C(6)	113.4(3)
C(4)-C(5)-H(5A)	108.9
C(6)-C(5)-H(5A)	108.9
C(4)-C(5)-H(5B)	108.9
C(6)-C(5)-H(5B)	108.9

H(5A)-C(5)-H(5B)	107.7
C(5)-C(6)-C(7)	110.9(3)
C(5)-C(6)-C(8)	108.8(3)
C(7)-C(6)-C(8)	109.2(3)
C(5)-C(6)-C(9)	108.9(3)
C(7)-C(6)-C(9)	110.0(3)
C(8)-C(6)-C(9)	109.0(3)
C(6)-C(7)-H(7A)	109.5
C(6)-C(7)-H(7B)	109.5
H(7A)-C(7)-H(7B)	109.5
C(6)-C(7)-H(7C)	109.5
H(7A)-C(7)-H(7C)	109.5
H(7B)-C(7)-H(7C)	109.5
C(6)-C(8)-H(8A)	109.5
C(6)-C(8)-H(8B)	109.5
H(8A)-C(8)-H(8B)	109.5
C(6)-C(8)-H(8C)	109.5
H(8A)-C(8)-H(8C)	109.5
H(8B)-C(8)-H(8C)	109.5
C(10)-C(9)-C(6)	112.9(2)
C(10)-C(9)-H(9A)	109.0
C(6)-C(9)-H(9A)	109.0
C(10)-C(9)-H(9B)	109.0
C(6)-C(9)-H(9B)	109.0
H(9A)-C(9)-H(9B)	107.8
C(11)-C(10)-C(12)	118.8(3)
C(11)-C(10)-C(9)	120.9(3)
C(12)-C(10)-C(9)	120.3(3)

C(10)-C(11)-C(4)	123.0(3)
C(10)-C(11)-H(11)	118.5
C(4)-C(11)-H(11)	118.5
C(13)-C(12)-C(10)	126.5(3)
C(13)-C(12)-H(12)	116.8
C(10)-C(12)-H(12)	116.8
C(12)-C(13)-C(14)	125.7(3)
C(12)-C(13)-H(13)	117.1
C(14)-C(13)-H(13)	117.1
C(15)-C(14)-C(18)	106.6(3)
C(15)-C(14)-C(13)	124.5(3)
C(18)-C(14)-C(13)	128.9(3)
C(15)-C(14)-Fe(1)	69.78(18)
C(18)-C(14)-Fe(1)	68.22(18)
C(13)-C(14)-Fe(1)	127.3(2)
C(14)-C(15)-C(16)	109.8(3)
C(14)-C(15)-Fe(1)	69.78(17)
C(16)-C(15)-Fe(1)	70.11(18)
C(14)-C(15)-H(15)	125.1
C(16)-C(15)-H(15)	125.1
Fe(1)-C(15)-H(15)	126.6
C(17)-C(16)-C(15)	106.6(3)
C(17)-C(16)-Fe(1)	68.90(19)
C(15)-C(16)-Fe(1)	69.43(18)
C(17)-C(16)-H(16)	126.7
C(15)-C(16)-H(16)	126.7
Fe(1)-C(16)-H(16)	126.5
C(18)-C(17)-C(16)	109.0(3)

C(18)-C(17)-Fe(1)	68.91(19)
C(16)-C(17)-Fe(1)	70.53(19)
C(18)-C(17)-H(17)	125.5
C(16)-C(17)-H(17)	125.5
Fe(1)-C(17)-H(17)	126.6
C(17)-C(18)-C(14)	108.0(3)
C(17)-C(18)-Fe(1)	70.23(19)
C(14)-C(18)-Fe(1)	70.44(18)
C(17)-C(18)-H(18)	126.0
C(14)-C(18)-H(18)	126.0
Fe(1)-C(18)-H(18)	124.9
C(20)-C(19)-C(23)	107.2(5)
C(20)-C(19)-Fe(1)	70.3(3)
C(23)-C(19)-Fe(1)	69.4(3)
C(20)-C(19)-H(19)	126.4
C(23)-C(19)-H(19)	126.4
Fe(1)-C(19)-H(19)	125.5
C(21)-C(20)-C(19)	107.7(5)
C(21)-C(20)-Fe(1)	70.6(3)
C(19)-C(20)-Fe(1)	70.1(3)
C(21)-C(20)-H(20)	126.1
C(19)-C(20)-H(20)	126.1
Fe(1)-C(20)-H(20)	124.8
C(22)-C(21)-C(20)	110.5(5)
C(22)-C(21)-Fe(1)	70.5(3)
C(20)-C(21)-Fe(1)	70.5(3)
C(22)-C(21)-H(21)	124.8
C(20)-C(21)-H(21)	124.8

Fe(1)-C(21)-H(21)	125.9
C(21)-C(22)-C(23)	108.5(5)
C(21)-C(22)-Fe(1)	71.2(3)
C(23)-C(22)-Fe(1)	70.0(3)
C(21)-C(22)-H(22)	125.8
C(23)-C(22)-H(22)	125.8
Fe(1)-C(22)-H(22)	124.6
C(22)-C(23)-C(19)	106.2(5)
C(22)-C(23)-Fe(1)	69.9(3)
C(19)-C(23)-Fe(1)	69.8(3)
C(22)-C(23)-H(23)	126.9
C(19)-C(23)-H(23)	126.9
Fe(1)-C(23)-H(23)	125.0

Table S8. Cartesian coordinates from the optimized structure of **2a** at B3LYP/6-31G.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	26	0	2.181190	0.014711	0.004954
2	16	0	-3.901455	-0.536333	-1.123279
3	6	0	-5.515573	-0.691897	-0.335526
4	6	0	-5.513035	-0.172288	0.926398
5	1	0	-6.389012	-0.170485	1.563802
6	6	0	-4.248645	0.369234	1.327661
7	1	0	-4.076860	0.820618	2.298052
8	6	0	-3.252778	0.277747	0.380454
9	6	0	-1.888467	0.732895	0.490253
10	1	0	-1.646256	1.183951	1.451805
11	6	0	-0.929072	0.662654	-0.463779
12	1	0	-1.180565	0.236755	-1.434167
13	6	0	0.438243	1.134990	-0.325934
14	6	0	1.120793	1.571604	0.871494
15	1	0	0.706083	1.583853	1.867275
16	6	0	2.434684	2.013863	0.509474
17	1	0	3.175783	2.413942	1.183629
18	6	0	2.591594	1.835656	-0.906034
19	1	0	3.468951	2.082186	-1.483049
20	6	0	1.373370	1.285379	-1.418813
21	1	0	1.164223	1.054813	-2.452275
22	6	0	1.640912	-1.987071	0.197059
23	1	0	0.637601	-2.378783	0.135012
24	6	0	2.295007	-1.533755	1.390881

25	1	0	1.873771	-1.536665	2.383904
26	6	0	3.613323	-1.090455	1.033626
27	1	0	4.358019	-0.703991	1.711720
28	6	0	3.773083	-1.270133	-0.381446
29	1	0	4.658257	-1.040616	-0.953723
30	6	0	2.553568	-1.823121	-0.898730
31	1	0	2.361580	-2.082919	-1.927953
32	1	0	-6.321265	-1.155632	-0.882587

Table S9. Cartesian coordinates from the optimized structure of **2b** at B3LYP/6-31G.

Center Number	**Atomic Number**	**Atomic Type**	**Coordinates (Angstroms) X**	**Y**	**Z**
1	26	0	-2.783039	0.066318	-0.023279
2	16	0	3.324420	0.253098	-0.919770
3	6	0	4.927757	0.237268	-0.057529
4	6	0	4.819111	-0.391170	1.165172
5	1	0	5.675104	-0.495679	1.820254
6	6	0	3.519502	-0.869016	1.463297
7	1	0	3.269080	-1.385607	2.382339
8	6	0	2.570934	-0.629299	0.480181
9	6	0	1.180655	-0.999408	0.509486
10	1	0	0.872214	-1.510691	1.419858
11	6	0	0.267349	-0.780425	-0.470336
12	1	0	0.590275	-0.293166	-1.389563
13	6	0	-1.131968	-1.156510	-0.427053
14	6	0	-1.893381	-1.662995	0.694294
15	1	0	-1.520120	-1.823324	1.693484

16	6	0	-3.222180	-1.949117	0.245030
17	1	0	-4.019290	-2.355894	0.847231
18	6	0	-3.309683	-1.603704	-1.145378
19	1	0	-4.181710	-1.710090	-1.770990
20	6	0	-2.034188	-1.105317	-1.558201
21	1	0	-1.767549	-0.782517	-2.552971
22	6	0	-2.097769	1.975516	0.455377
23	1	0	-1.064919	2.282568	0.508740
24	6	0	-2.874031	1.442634	1.537314
25	1	0	-2.530998	1.290725	2.548613
26	6	0	-4.192934	1.165304	1.042085
27	1	0	-5.015247	0.768092	1.616158
28	6	0	-4.230233	1.526915	-0.346230
29	1	0	-5.085512	1.447944	-0.998845
30	6	0	-2.934629	2.026330	-0.709514
31	1	0	-2.645542	2.389937	-1.683028
32	6	0	6.106102	0.830516	-0.654732
33	8	0	7.224810	0.846992	-0.100915
34	1	0	5.971548	1.282794	-1.651952

Table S10. Cartesian coordinates from the optimized structure of **2c** at B3LYP/6-31G.

Center	**Atomic**	**Atomic**	**Coordinates (Angstroms)**		
Number	**Number**	**Type**	**X**	**Y**	**Z**
1	26	0	-2.691130	0.075869	-0.039591
2	16	0	3.426818	0.329302	-0.775713
3	7	0	7.124573	1.383726	-0.812896
4	6	0	5.017535	0.203010	0.103346

5	6	0	6.163916	0.845313	-0.396046
6	6	0	4.891548	-0.566255	1.238832
7	1	0	5.728118	-0.760158	1.898404
8	6	0	3.582038	-1.072103	1.456621
9	1	0	3.321781	-1.694063	2.304508
10	6	0	2.650719	-0.714752	0.499661
11	6	0	1.257436	-1.076491	0.459520
12	1	0	0.928949	-1.684439	1.300711
13	6	0	0.365139	-0.743076	-0.506511
14	1	0	0.707425	-0.160431	-1.361088
15	6	0	-1.037383	-1.110626	-0.529129
16	6	0	-1.823431	-1.721248	0.520928
17	1	0	-1.471482	-1.979976	1.507158
18	6	0	-3.144119	-1.953305	0.019122
19	1	0	-3.955209	-2.412680	0.561958
20	6	0	-3.201405	-1.471581	-1.331878
21	1	0	-4.061036	-1.509656	-1.982110
22	6	0	-1.915541	-0.942491	-1.667644
23	1	0	-1.627012	-0.524921	-2.620081
24	6	0	-2.006721	1.926976	0.630488
25	1	0	-0.974006	2.223943	0.726297
26	6	0	-2.798522	1.295212	1.646004
27	1	0	-2.468849	1.044066	2.641840
28	6	0	-4.111679	1.072741	1.109796
29	1	0	-4.942718	0.625416	1.632151
30	6	0	-4.130142	1.567595	-0.237136
31	1	0	-4.977526	1.556885	-0.904579
32	6	0	-2.828469	2.094191	-0.534344

33	1	0	-2.525655	2.549853	-1.463908

Table S11. Cartesian coordinates from the optimized structure of **7** at B3LYP/6-31G

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	26	0	-3.600241	0.065836	0.047708
2	6	0	0.267009	-1.294555	-0.516917
3	1	0	-0.056787	-2.287171	-0.209689
4	6	0	-0.658519	-0.443155	-1.036993
5	1	0	-0.329346	0.517325	-1.430394
6	6	0	-2.077510	-0.702461	-1.156854
7	6	0	-2.851376	-1.769404	-0.556849
8	1	0	-2.468274	-2.545484	0.086788
9	6	0	-4.209556	-1.636215	-0.986365
10	1	0	-5.024422	-2.289964	-0.717959
11	6	0	-4.301982	-0.481721	-1.835075
12	1	0	-5.196241	-0.121683	-2.318563
13	6	0	-3.001112	0.102369	-1.932025
14	1	0	-2.733482	0.971161	-2.513648
15	6	0	-2.746177	1.258130	1.531092
16	1	0	-1.694002	1.461476	1.654798
17	6	0	-3.468991	0.170256	2.123977
18	1	0	-3.058559	-0.580740	2.780486
19	6	0	-4.839252	0.269995	1.707140
20	1	0	-5.639949	-0.392582	1.996186
21	6	0	-4.960876	1.418234	0.855014
22	1	0	-5.868662	1.768823	0.389699

23	6	0	-3.666383	2.028338	0.744603
24	1	0	-3.429106	2.917921	0.182782
25	6	0	1.686798	-1.020441	-0.365404
26	6	0	2.595097	-2.220998	-0.169228
27	6	0	2.212296	0.247937	-0.395977
28	1	0	1.545956	1.100664	-0.473002
29	6	0	3.956943	-1.890420	0.494625
30	6	0	3.617632	0.517340	-0.294824
31	6	0	4.564707	-0.661149	-0.233993
32	6	0	4.105134	1.817791	-0.280948
33	6	0	5.500651	2.093995	-0.182147
34	7	0	6.654508	2.307946	-0.099021
35	6	0	3.229286	2.941618	-0.373354
36	7	0	2.481562	3.846411	-0.449353
37	6	0	3.766779	-1.584287	1.999260
38	6	0	4.912398	-3.092273	0.339878
39	1	0	3.078644	-0.748911	2.163800
40	1	0	3.365874	-2.462010	2.520414
41	1	0	4.726740	-1.327959	2.462667
42	1	0	5.882359	-2.880433	0.804903
43	1	0	4.496243	-3.984443	0.823273
44	1	0	5.087441	-3.329043	-0.716824
45	1	0	2.070354	-2.984146	0.422089
46	1	0	2.778407	-2.680704	-1.154734
47	1	0	5.509134	-0.373828	0.240253
48	1	0	4.813466	-0.954056	-1.266923

Table S12. Cartesian coordinates from the optimized structure of **8** at B3LYP/6-31G.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	26	0	-6.402009	0.473959	0.105325
2	16	0	-0.329975	-0.367461	-0.624876
3	6	0	1.099393	-1.378667	-0.099886
4	6	0	0.660090	-2.617553	0.338822
5	1	0	1.339495	-3.376978	0.706850
6	6	0	-0.740302	-2.808213	0.276471
7	1	0	-1.228786	-3.724958	0.585497
8	6	0	-1.461352	-1.728798	-0.212687
9	6	0	-2.884061	-1.643516	-0.389674
10	1	0	-3.429136	-2.532963	-0.077680
11	6	0	-3.572622	-0.593428	-0.908109
12	1	0	-3.019549	0.281273	-1.248020
13	6	0	-4.990745	-0.528120	-1.080048
14	6	0	-5.999685	-1.439382	-0.581649
15	1	0	-5.820421	-2.312077	0.026488
16	6	0	-7.276719	-1.004556	-1.060456
17	1	0	-8.221031	-1.490844	-0.872160
18	6	0	-7.082837	0.187369	-1.836546
19	1	0	-7.855008	0.750508	-2.336414
20	6	0	-5.684878	0.490508	-1.839674
21	1	0	-5.212101	1.312754	-2.354658
22	6	0	-5.408054	1.372199	1.702087
23	1	0	-4.345821	1.338187	1.887496
24	6	0	-6.377864	0.432816	2.186801

25	1	0	-6.174043	-0.423985	2.809525
26	6	0	-7.669274	0.844663	1.712980
27	1	0	-8.606661	0.351445	1.917118
28	6	0	-7.496080	2.038105	0.934943
29	1	0	-8.280223	2.598036	0.450025
30	6	0	-6.097976	2.363136	0.926291
31	1	0	-5.647087	3.211766	0.436425
32	6	0	2.415951	-0.823780	-0.195302
33	6	0	3.582285	-1.487866	0.069779
34	6	0	4.907168	-0.936454	-0.005039
35	6	0	5.164193	0.411475	-0.106733
36	6	0	6.055137	-1.931642	0.017620
37	6	0	6.485529	0.948944	-0.236516
38	6	0	7.414056	-1.329569	0.459187
39	6	0	7.643464	-0.019632	-0.341619
40	1	0	5.795038	-2.775963	0.670925
41	1	0	6.165002	-2.357308	-0.993679
42	1	0	8.575557	0.457190	-0.020302
43	1	0	7.778957	-0.278066	-1.404357
44	6	0	7.411111	-1.038372	1.978795
45	1	0	7.278028	-1.967469	2.546077
46	1	0	8.364384	-0.591536	2.284983
47	1	0	6.608767	-0.350024	2.262955
48	6	0	8.548703	-2.324687	0.137430
49	1	0	8.592536	-2.546463	-0.936016
50	1	0	9.520502	-1.916738	0.439358
51	1	0	8.400279	-3.269814	0.673713
52	6	0	6.707011	2.320060	-0.299147

53	6	0	5.628806	3.253638	-0.243801
54	7	0	4.721539	4.000816	-0.195954
55	6	0	8.019718	2.859912	-0.432846
56	7	0	9.108637	3.292029	-0.542484
57	1	0	3.529269	-2.541396	0.336985
58	1	0	2.469098	0.211488	-0.523984
59	1	0	4.342563	1.118930	-0.067329

Table S13. Cartesian coordinates from the optimized structure of **9** at B3LYP/6-31G

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	26	0	-9.567345	0.522413	0.191520
2	16	0	-3.481113	-0.121670	-0.644891
3	6	0	-2.057433	-1.066128	-0.2233764
4	6	0	-2.433893	-2.350779	0.137968
5	1	0	-1.722093	-3.112424	0.437418
6	6	0	-3.824315	-2.571636	0.075750
7	1	0	-4.295657	-3.517919	0.321339
8	6	0	-4.558351	-1.467740	-0.333674
9	6	0	-5.989566	-1.405666	-0.496393
10	1	0	-6.504769	-2.337172	-0.265748
11	6	0	-6.713313	-0.338187	-0.906754
12	1	0	-6.194438	0.586136	-1.161091
13	6	0	-8.156822	-0.305118	-1.077243
14	6	0	-9.129808	-1.283031	-0.669684
15	1	0	-8.922185	-2.201536	-0.136600
16	6	0	-10.418309	-0.840167	-1.086441

17	1	0	-11.351988	-1.361813	-0.920563
18	6	0	-10.266071	0.422265	-1.735417
19	1	0	-11.062596	1.024834	-2.151856
20	6	0	-8.882393	0.757484	-1.721880
21	1	0	-8.437500	1.652665	-2.138041
22	6	0	-8.597403	1.157174	1.889363
23	1	0	-7.541533	1.024394	2.086583
24	6	0	-9.634388	0.236457	2.224973
25	1	0	-9.504276	-0.709975	2.733535
26	6	0	-10.871426	0.775417	1.756962
27	1	0	-11.844216	0.310229	1.850256
28	6	0	-10.597740	2.029668	1.132476
29	1	0	-11.326529	2.681214	0.667954
30	6	0	-9.191931	2.265001	1.212589
31	1	0	-8.667754	3.126809	0.820400
32	6	0	-0.757714	-0.455513	-0.298888
33	6	0	0.423866	-1.063611	-0.006946
34	6	0	7.930463	0.999904	0.065739
35	6	0	8.633866	-0.175459	0.153750
36	6	0	8.659824	2.327402	0.130770
37	6	0	10.049000	-0.222130	0.345739
38	6	0	10.155727	2.256156	-0.245980
39	6	0	10.789489	1.080996	0.532431
40	1	0	8.147263	3.056571	-0.511139
41	1	0	8.564299	2.718611	1.156465
42	1	0	11.843582	0.965587	0.259383
43	1	0	10.777731	1.320720	1.607254
44	6	0	10.322626	2.048891	-1.764635

45	1	0	9.896432	2.894534	-2.317595
46	1	0	11.383827	1.977793	-2.030127
47	1	0	9.828299	1.136708	-2.113306
48	6	0	10.851256	3.565461	0.162057
49	1	0	10.769950	3.744570	1.241108
50	1	0	11.916752	3.539238	-0.094736
51	1	0	10.405179	4.423278	-0.355704
52	6	0	10.729400	-1.429153	0.396550
53	6	0	10.050205	-2.680219	0.269944
54	7	0	9.477406	-3.689378	0.164896
55	6	0	12.142330	-1.489727	0.591385
56	7	0	13.296245	-1.531216	0.749887
57	1	0	0.422123	-2.102077	0.320018
58	1	0	-0.738422	0.584220	-0.623274
59	1	0	8.114214	-1.123771	0.056379
60	6	0	1.728881	-0.472203	-0.087637
61	6	0	2.015358	0.832684	-0.480401
62	16	0	3.212393	-1.313004	0.309388
63	6	0	3.383347	1.150519	-0.463900
64	1	0	1.236872	1.529481	-0.773598
65	6	0	4.196536	0.099809	-0.055519
66	1	0	3.774308	2.121288	-0.748273
67	6	0	5.619905	0.027093	0.098681
68	1	0	6.014352	-0.942875	0.394713
69	6	0	6.493158	1.061386	-0.074520
70	1	0	6.087548	2.043085	-0.313136

Table S14. Cartesian coordinates from the optimized structure of **10** at B3LYP/6-31G.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	26	0	0.105193	-0.995439	0.129845
2	6	0	4.107549	-1.366111	-0.762634
3	1	0	4.018257	-2.447487	-0.668120
4	6	0	2.997631	-0.650653	-1.070722
5	1	0	3.094890	0.417357	-1.260279
6	6	0	1.655889	-1.183130	-1.220664
7	6	0	1.153308	-2.472742	-0.826146
8	1	0	1.721922	-3.252576	-0.337085
9	6	0	-0.223259	-2.547272	-1.182456
10	1	0	-0.879049	-3.390093	-1.007867
11	6	0	-0.595357	-1.307079	-1.781848
12	1	0	-1.584727	-1.043599	-2.132003
13	6	0	0.549205	-0.462844	-1.796234
14	1	0	0.597142	0.545605	-2.187249
15	6	0	0.854912	-0.108913	1.832170
16	1	0	1.890269	0.161905	1.992076
17	6	0	0.258385	-1.365479	2.148775
18	1	0	0.760212	-2.212548	2.597840
19	6	0	-1.107201	-1.322608	1.747921
20	1	0	-1.819768	-2.130146	1.850421
21	6	0	-1.378100	-0.021753	1.194710
22	6	0	-0.140679	0.713192	1.235650
23	1	0	-0.004378	1.728889	0.886233
24	6	0	5.445696	-0.823335	-0.591779

25	6	0	6.599996	-1.794789	-0.719836
26	6	0	5.678739	0.498995	-0.330726
27	1	0	4.840657	1.172078	-0.177815
28	6	0	7.911030	-1.324096	-0.051476
29	6	0	6.996722	1.049764	-0.216820
30	6	0	8.171699	0.138999	-0.479987
31	6	0	7.190002	2.383956	0.094349
32	6	0	8.495735	2.951377	0.209841
33	7	0	9.563892	3.407103	0.303439
34	6	0	6.086973	3.269213	0.306783
35	7	0	5.170230	3.967798	0.475802
36	6	0	7.801725	-1.423391	1.483275
37	6	0	9.077356	-2.204644	-0.529567
38	1	0	6.966605	-0.835382	1.877214
39	1	0	7.654434	-2.465281	1.791520
40	1	0	8.720305	-1.062350	1.960185
41	1	0	10.020298	-1.889846	-0.067524
42	1	0	8.909367	-3.254520	-0.260999
43	1	0	9.201677	-2.151407	-1.617861
44	1	0	6.301126	-2.770520	-0.312999
45	1	0	6.780492	-1.968482	-1.792991
46	1	0	9.073748	0.525223	0.005756
47	1	0	8.373509	0.160424	-1.562447
48	6	0	-2.633389	0.500498	0.683060
49	1	0	-2.567204	1.480443	0.214579
50	6	0	-3.836907	-0.119840	0.763231
51	1	0	-3.887484	-1.098992	1.237218
52	6	0	-5.092993	0.388819	0.256876

53	6	0	-6.208069	-0.401777	0.344204
54	6	0	-5.174556	1.759751	-0.379915
55	6	0	-7.490072	-0.009508	-0.163034
56	1	0	-6.127021	-1.377035	0.81747157
57	6	0	-6.596789	2.368092	-0.381719
58	1	0	-4.490643	2.449506	0.128992
59	6	0	-7.584758	1.301546	-0.905839
60	1	0	-7.360457	1.099824	-1.965094
61	6	0	-8.599265	-0.822229	-0.018490
62	6	0	-8.523321	-2.090142	0.639095
63	7	0	-8.441633	-3.120238	1.176445
64	6	0	-9.879666	-0.446170	-0.528811
65	7	0	-10.920463	-0.132319	-0.947752
66	1	0	-4.810371	1.683965	-1.416564
67	1	0	-8.610092	1.684956	-0.880694
68	6	0	-6.627810	3.586565	-1.319313
69	1	0	-7.625399	4.040388	-1.338525
70	1	0	-5.919482	4.354352	-0.985623
71	1	0	-6.364594	3.309536	-2.347386
72	6	0	-6.994154	2.815552	1.039256
73	1	0	-6.313853	3.595040	1.402041
74	1	0	-8.008663	3.230636	1.043368
75	1	0	-6.968197	1.988263	1.755622

Table S15. Cartesian coordinates from the optimized structure of **11** at B3LYP/6-31G

Center	**Atomic**	**Atomic**	**Coordinates (Angstroms)**		
Number	**Number**	**Type**	**X**	**Y**	**Z**

1	26	0	0.224790	-2.723450	0.134912
2	6	0	4.082478	-3.207778	-1.061390
3	1	0	3.882554	-4.258849	-1.047943
4	6	0	3.075726	-2.329022	-1.291511
5	1	0	3.313034	-1.271246	-1.395587
6	6	0	1.674169	-2.665405	-1.461131
7	6	0	1.052375	-3.962874	-1.425409
8	1	0	1.557703	-4.903853	-1.252647
9	6	0	-0.344161	-3.798728	-1.649445
10	1	0	-1.080451	-4.591336	-1.672633
11	6	0	-0.608540	-2.405581	-1.807724
12	1	0	-1.581645	-1.958378	-1.962514
13	6	0	0.622941	-1.705403	-1.680576
14	1	0	0.761721	-0.634089	-1.752589
15	6	0	1.152308	-2.367244	1.940111
16	1	0	2.218751	-2.253063	2.083425
17	6	0	0.426355	-3.594293	1.988956
18	1	0	0.844496	-4.573296	2.183189
19	6	0	-0.941609	-3.312536	1.712125
20	1	0	-1.739350	-4.042069	1.670104
21	6	0	-1.081736	-1.894529	1.508971
22	6	0	0.234630	-1.324731	1.633633
23	1	0	0.474030	-0.273973	1.529198
24	6	0	-2.288611	-1.134968	1.231837
25	1	0	-2.143502	-0.061229	1.130971
26	6	0	-3.536562	-1.652808	1.112831
27	1	0	-3.683766	-2.711350	1.164988
28	6	0	5.513585	-2.693025	-0.819395

29	6	0	6.605067	-3.467771	-0.578495
30	16	0	5.857838	-0.996577	-0.837164
31	6	0	7.793694	-2.666983	-0.396296
32	1	0	6.606552	-4.557958	-0.525341
33	6	0	7.523065	-1.339090	-0.510571
34	1	0	8.776511	-3.096070	-0.193050
35	6	0	8.576727	-0.225065	-0.367942
36	1	0	8.288562	0.800242	-0.470927
37	6	0	9.873501	-0.544445	-0.111087
38	1	0	10.161666	-1.569752	-0.008102
39	6	0	-4.741617	-0.717251	0.902647
40	6	0	-4.689656	0.619753	0.829704
41	16	0	-6.345246	-1.369487	0.735817
42	6	0	-6.014443	1.196677	0.624752
43	1	0	-3.782928	1.221979	0.910350
44	6	0	-6.959023	0.248402	0.560382
45	1	0	-6.190376	2.270363	0.537566
46	6	0	-8.465175	0.493339	0.352749
47	1	0	-9.141740	-0.334776	0.315542
48	6	0	-8.931893	1.752875	0.217678
49	1	0	-8.255328	2.580990	0.254886
50	6	0	-10.438046	1.997811	0.010045
51	6	0	-10.663043	3.596948	-0.114541
52	6	0	-11.279073	0.968528	-0.036322
53	6	0	-12.211075	3.601734	-0.312370
54	1	0	-10.382157	4.102781	0.785535
55	6	0	-12.715304	1.144101	-0.231294
56	1	0	-10.899118	-0.057485	0.073495

57	6	0	-13.196021	2.525831	-0.374936
58	1	0	-13.917338	2.700571	0.395822
59	6	0	-13.555983	0.114553	-0.278108
60	6	0	-15.062166	0.359168	-0.485896
61	7	0	-16.196693	0.543424	-0.642413
62	6	0	-13.023216	-1.322170	-0.124525
63	7	0	-12.621912	-2.404377	-0.008839
64	1	0	-13.697517	2.598956	-1.317302
65	1	0	-10.158301	3.997607	-0.968712
66	6	0	-12.730091	4.521301	0.808620
67	1	0	-12.137932	5.411873	0.842220
68	1	0	-13.750513	4.778574	0.615105
69	1	0	-12.662442	4.012376	1.747406
70	6	0	-12.419441	4.378476	-1.625707
71	1	0	-13.454166	4.629716	-1.731176
72	1	0	-11.834978	5.274546	-1.606697
73	1	0	-12.113953	3.770849	-2.451762
74	6	0	10.927164	0.569580	0.031543
75	6	0	12.349274	-0.128035	0.329743
76	6	0	10.566399	1.853633	-0.097518
77	6	0	13.234977	1.148202	0.434110
78	1	0	12.332594	-0.667396	1.253708
79	6	0	11.530544	2.942655	0.029196
80	1	0	9.518005	2.112083	-0.305370
81	6	0	12.913986	2.566655	0.305443
82	1	0	13.203377	3.047139	1.216644
83	1	0	13.520054	2.964776	-0.481375
84	1	0	12.656587	-0.750074	-0.484829

85	6	0	11.166334	4.215203	-0.100693
86	6	0	12.214721	5.334407	0.040256
87	7	0	13.004415	6.177444	0.146426
88	6	0	9.696229	4.569477	-0.392040
89	7	0	8.588878	4.836332	-0.611495
90	6	0	14.355228	0.917784	-0.597173
91	1	0	15.140314	1.626547	-0.435320
92	1	0	14.741935	-0.073916	-0.488136
93	1	0	13.961793	1.040627	-1.584603
94	6	0	13.902725	1.034385	1.817134
95	1	0	14.296781	0.047559	1.942814
96	1	0	14.697134	1.747540	1.889418
97	1	0	13.178216	1.228974	2.580103

Frontier Orbitals

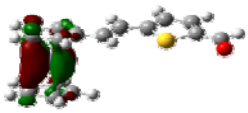
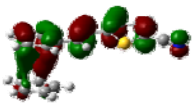
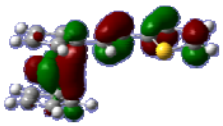
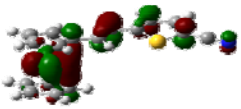
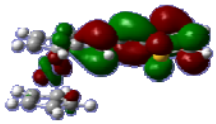
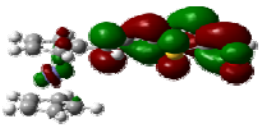
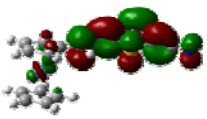
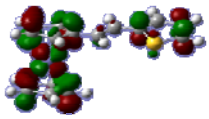
	2a	2b	2c
HOMO-2			
HOMO			
LUMO			
LUMO+2			

Figure S5. Contour surfaces of the frontier orbitals involved in the electronic transitions of the chromophores **2a**, **2b** and **2c**; derived from TD-DFT (dichloromethane as solvent medium) at isosurface value of 0.03 au.

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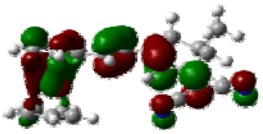
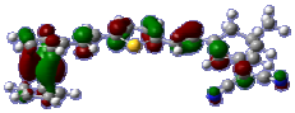
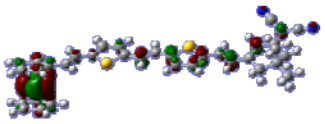
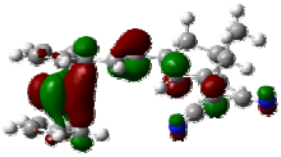
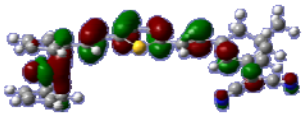
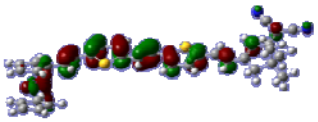
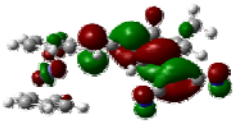
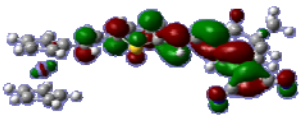
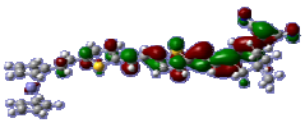
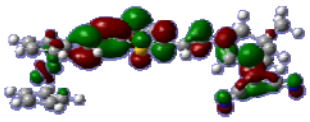
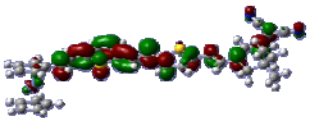
HOMO-2			
HOMO-1			
HOMO			
LUMO			
LUMO+1			

Figure S6. Contour surfaces of the frontier orbitals involved in the electronic transitions of the chromophores **7**, **8** and **9**; derived from TD-DFT (dichloromethane as solvent medium) at isosurface value of 0.03 au.

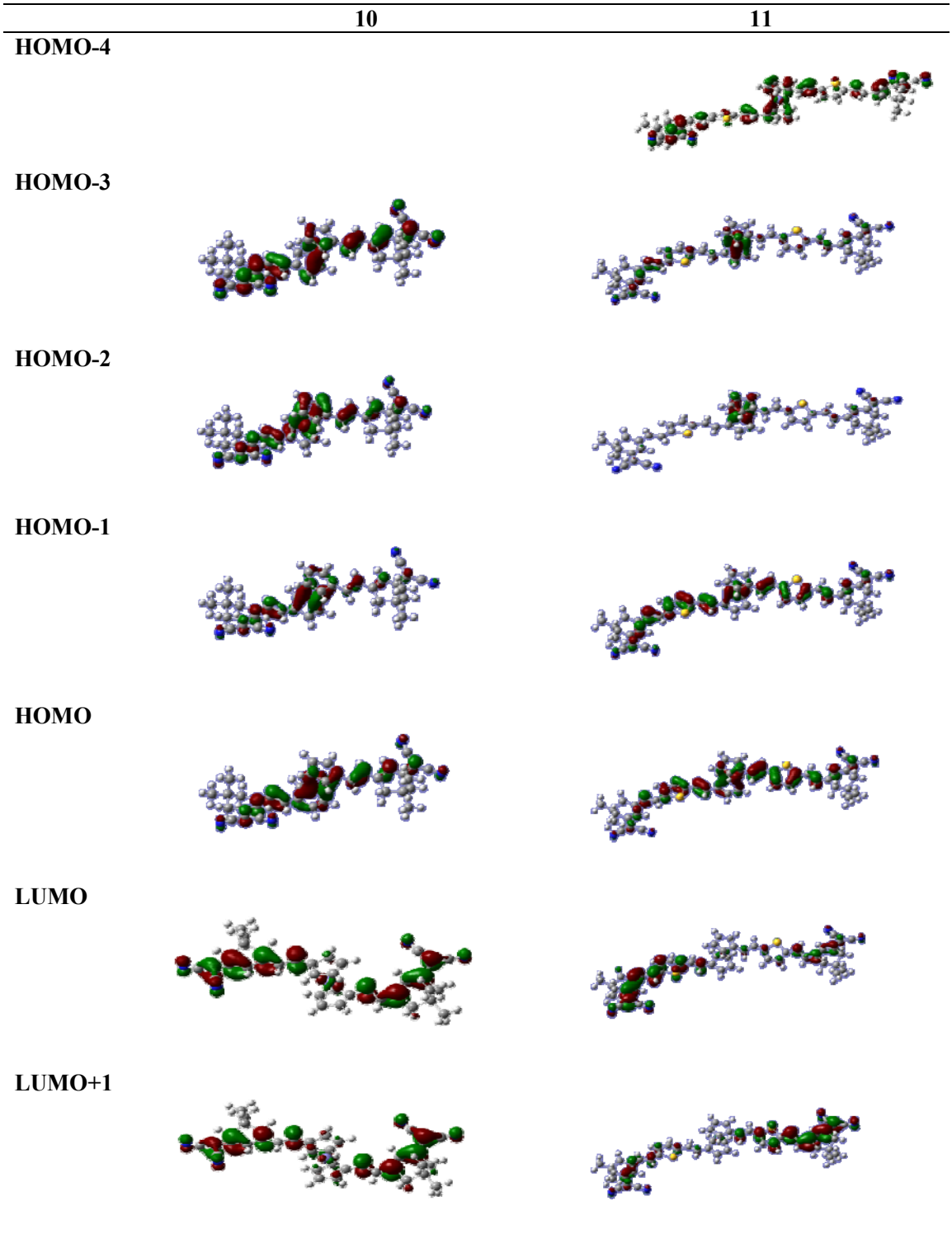
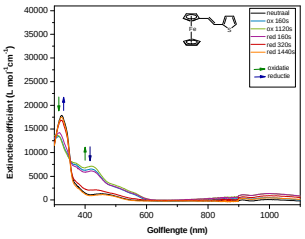


Figure S7. Contour surfaces of the frontier orbitals involved in the electronic transitions of the chromophores **10** and **11**; derived from TD-DFT (dichloromethane as solvent medium) at isosurface value of 0.03 au.

Spectro-electrochemical Studies



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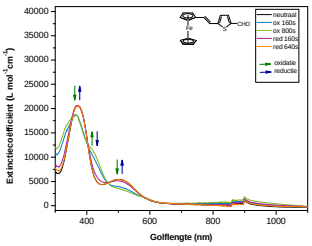

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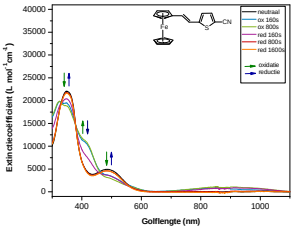
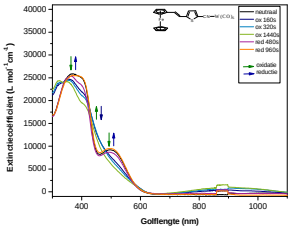


2c



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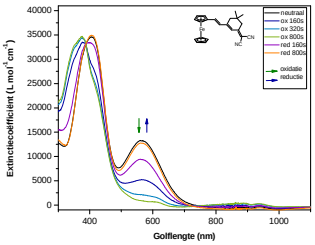

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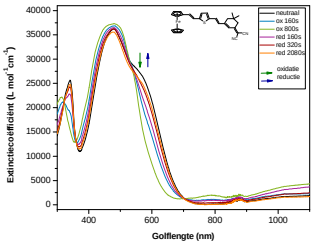

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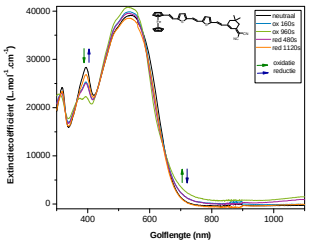

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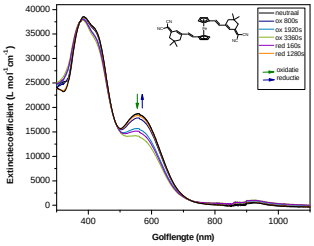

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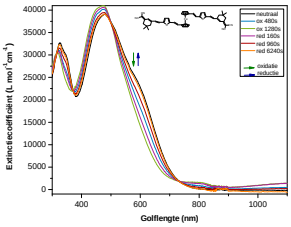
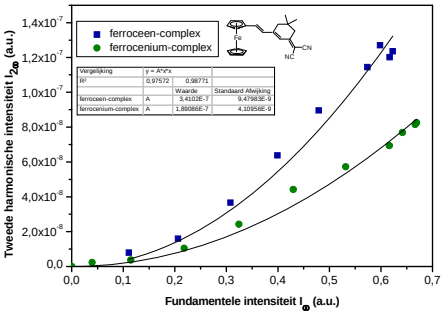


11

Figure S8. UV-Vis spectrum of oxidized compounds **2a-d**, **7-11**.

Quadratic Curves



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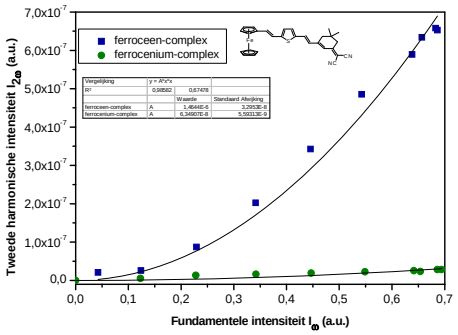

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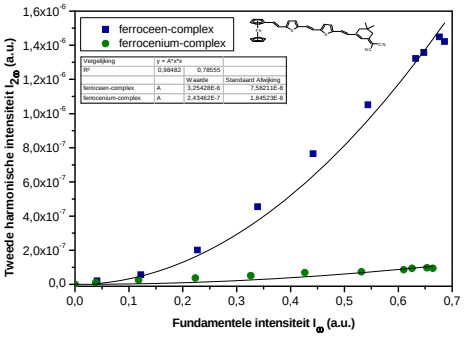

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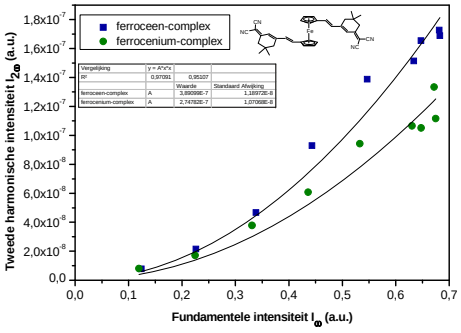

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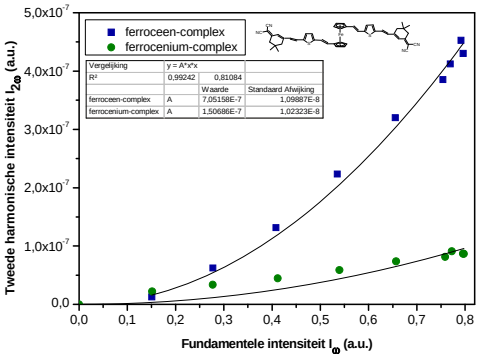

11

Figure S9. Quadratic curves of the compounds **7-11**.

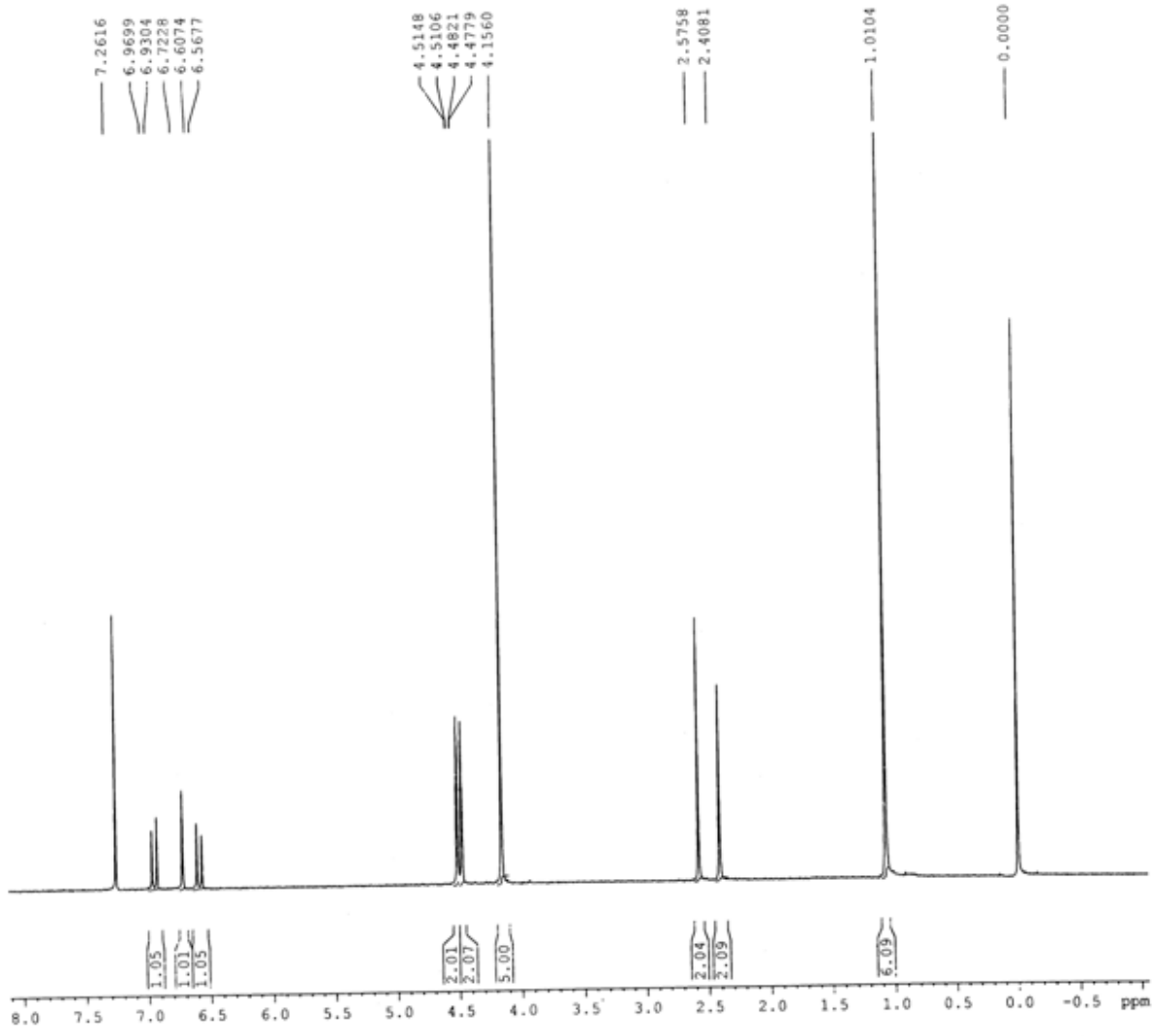

Figure S10: ^{1}H NMR spectrum of **7**.

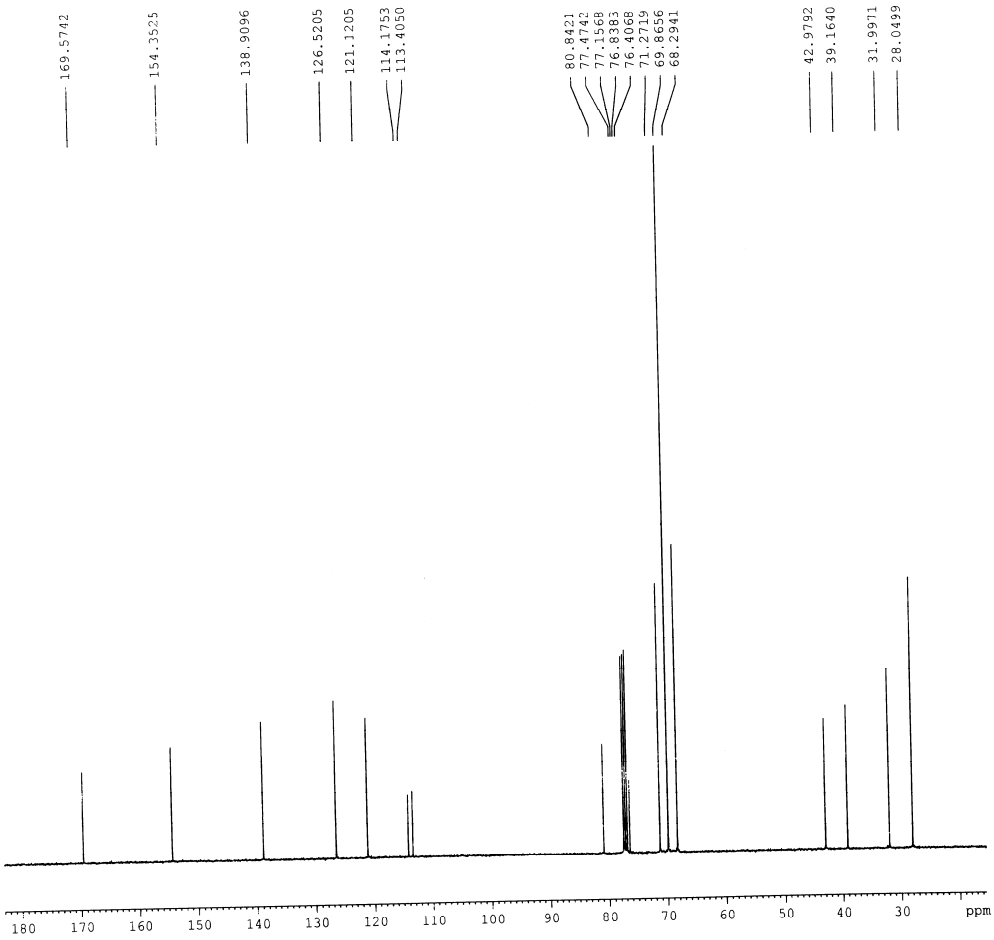

Figure S11: ^{13}C NMR spectrum of **7**.

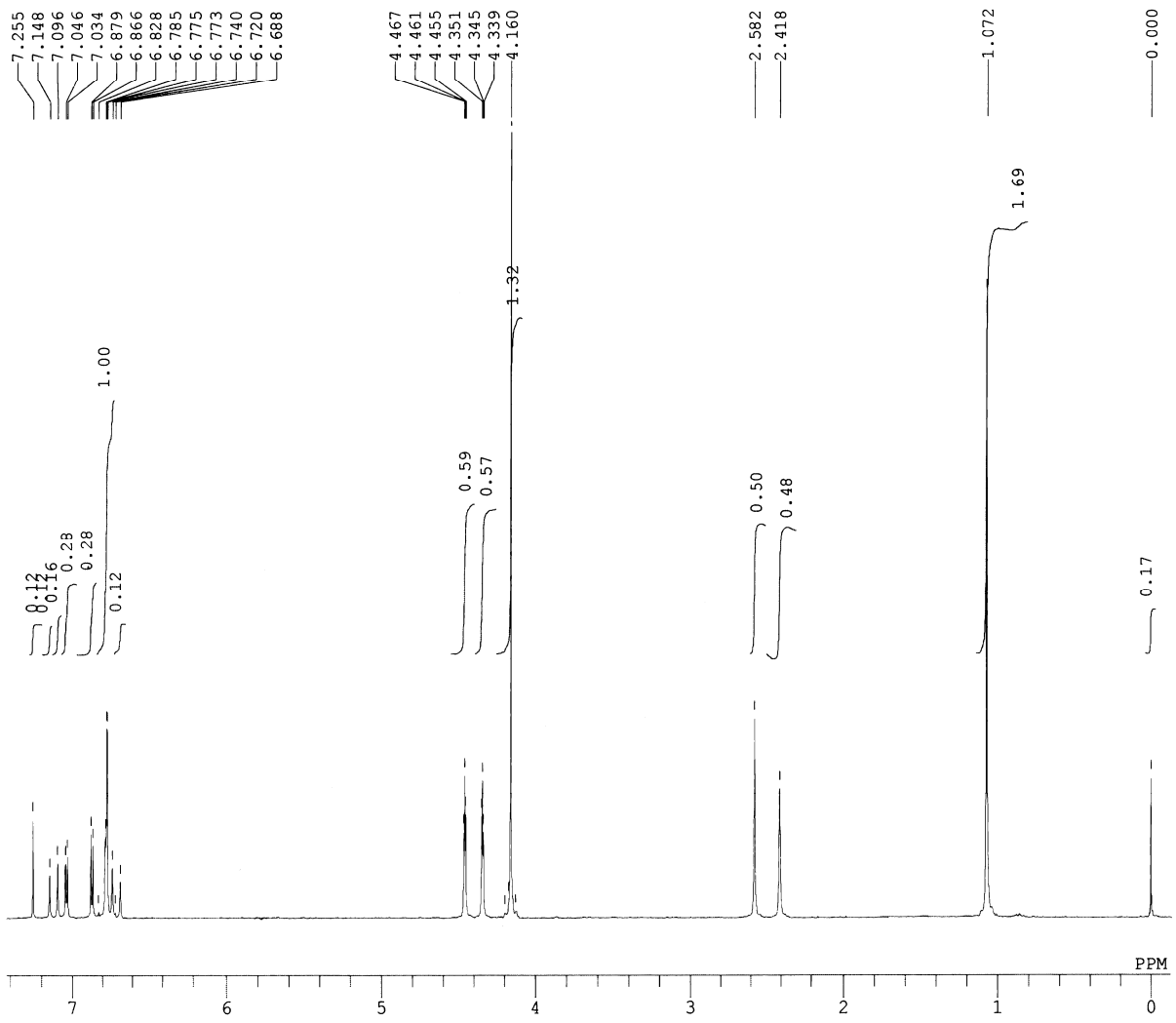

Figure S12: ^{1}H NMR spectrum of **8**.

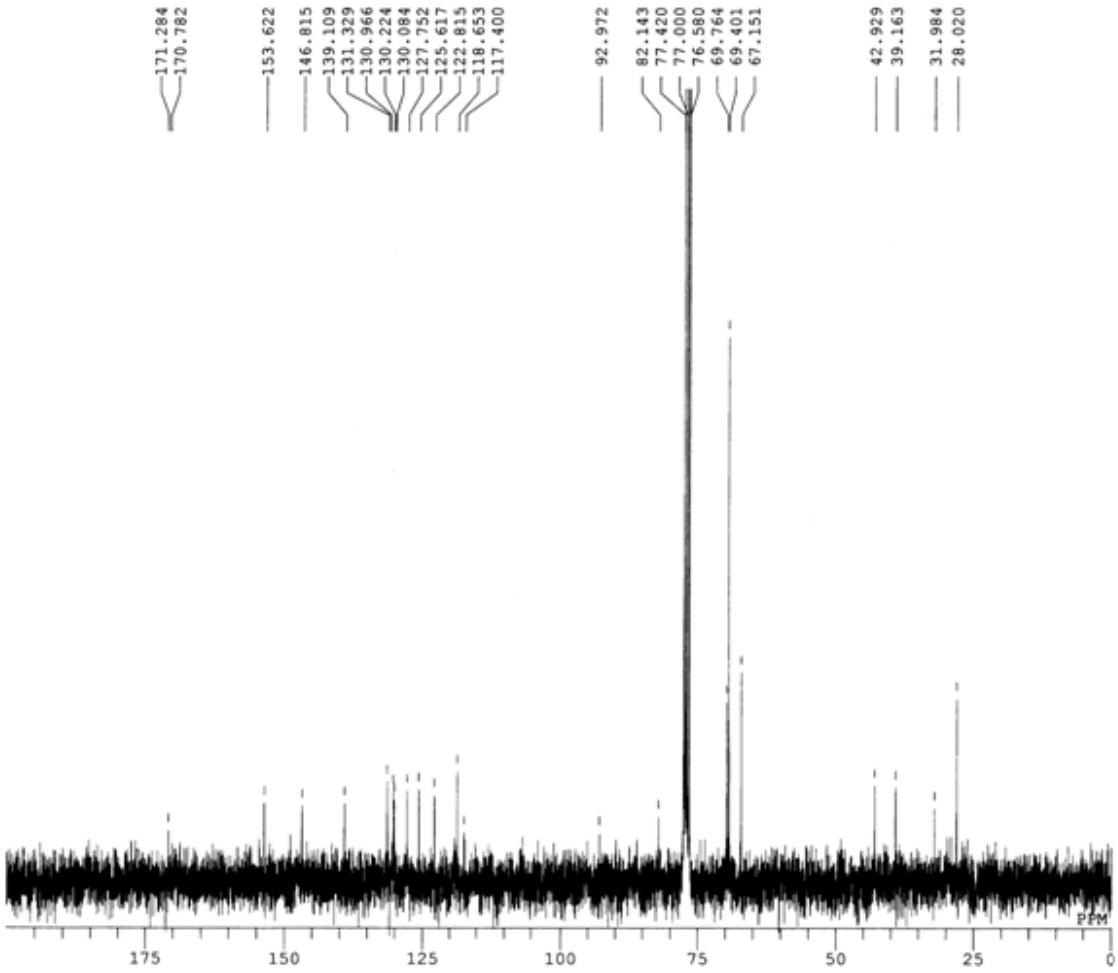

Figure S13: ^{13}C NMR spectrum of **8**.

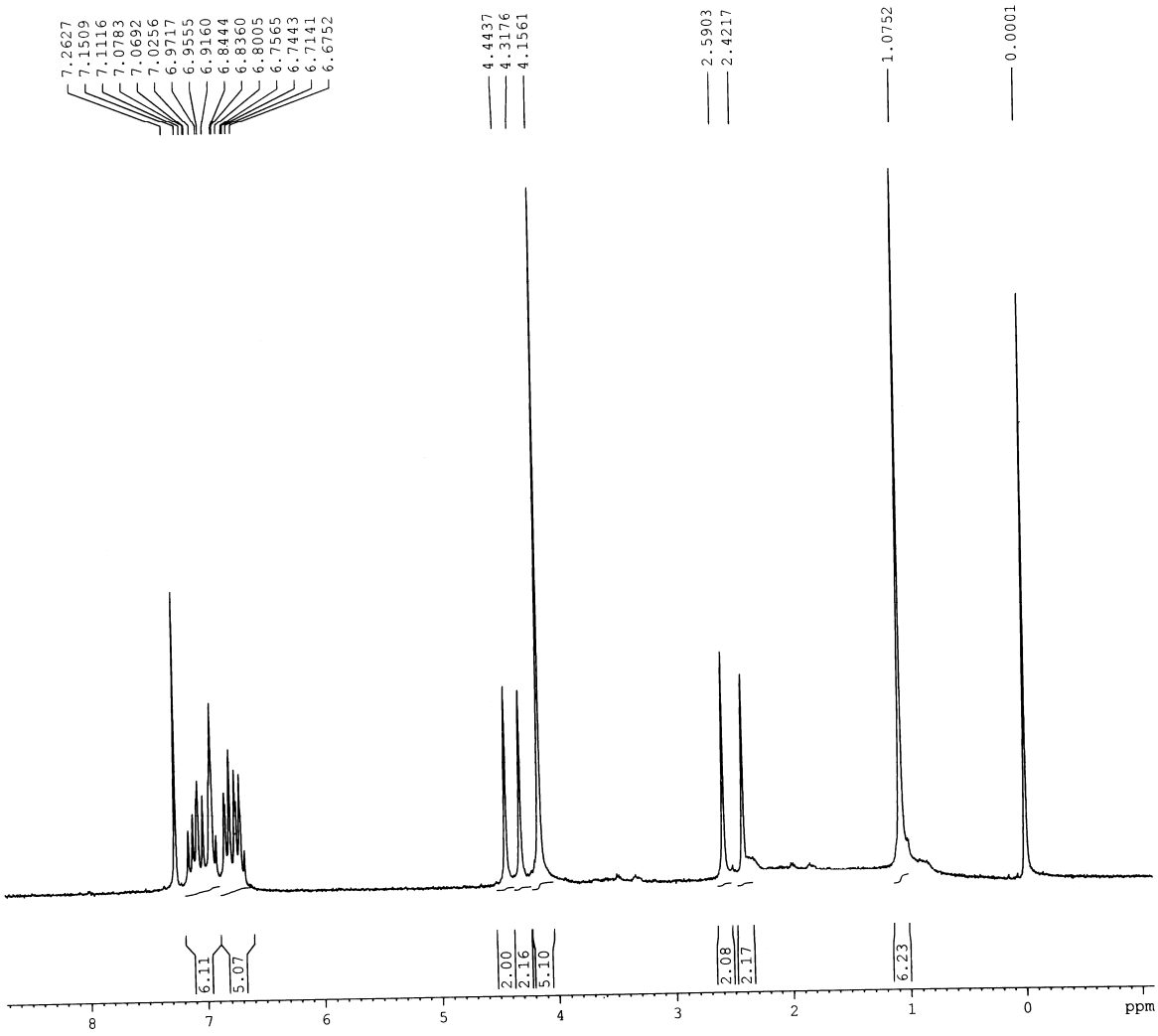

Figure S14: ^{1}H NMR spectrum of **9**.

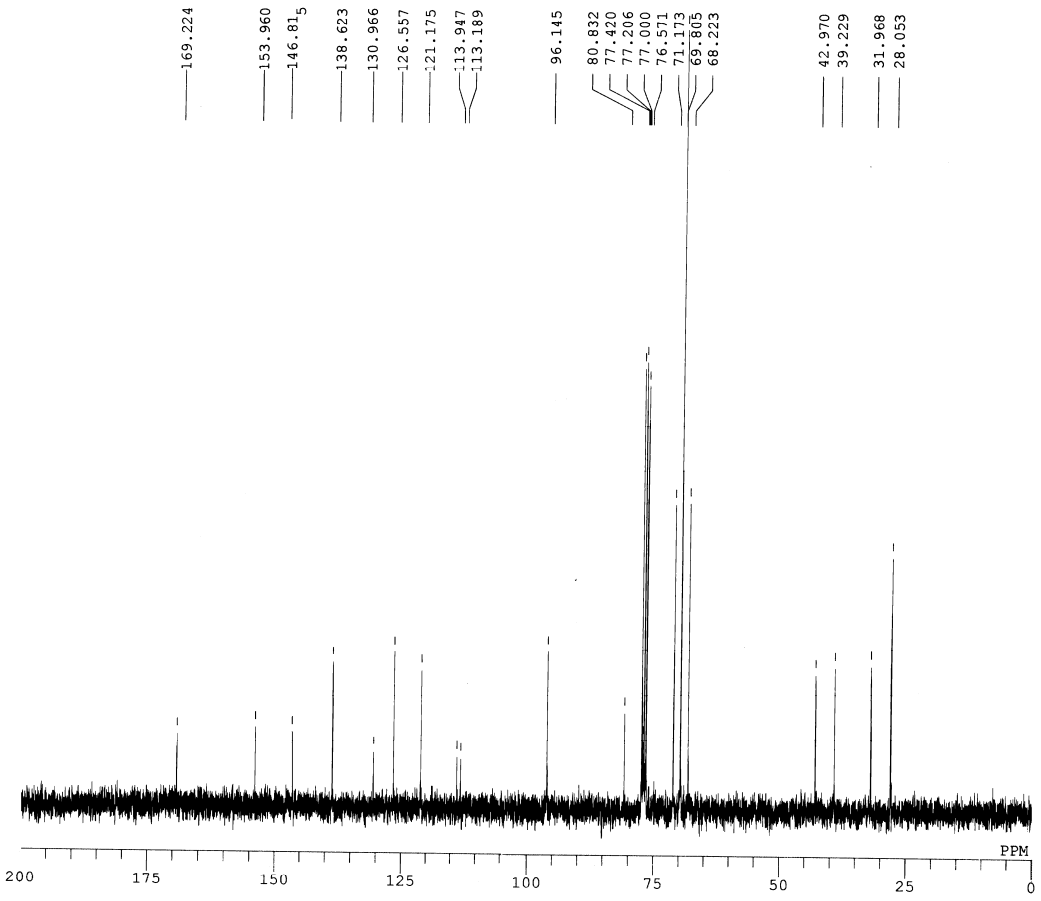

Figure S15: ^{13}C NMR spectrum of **9**.

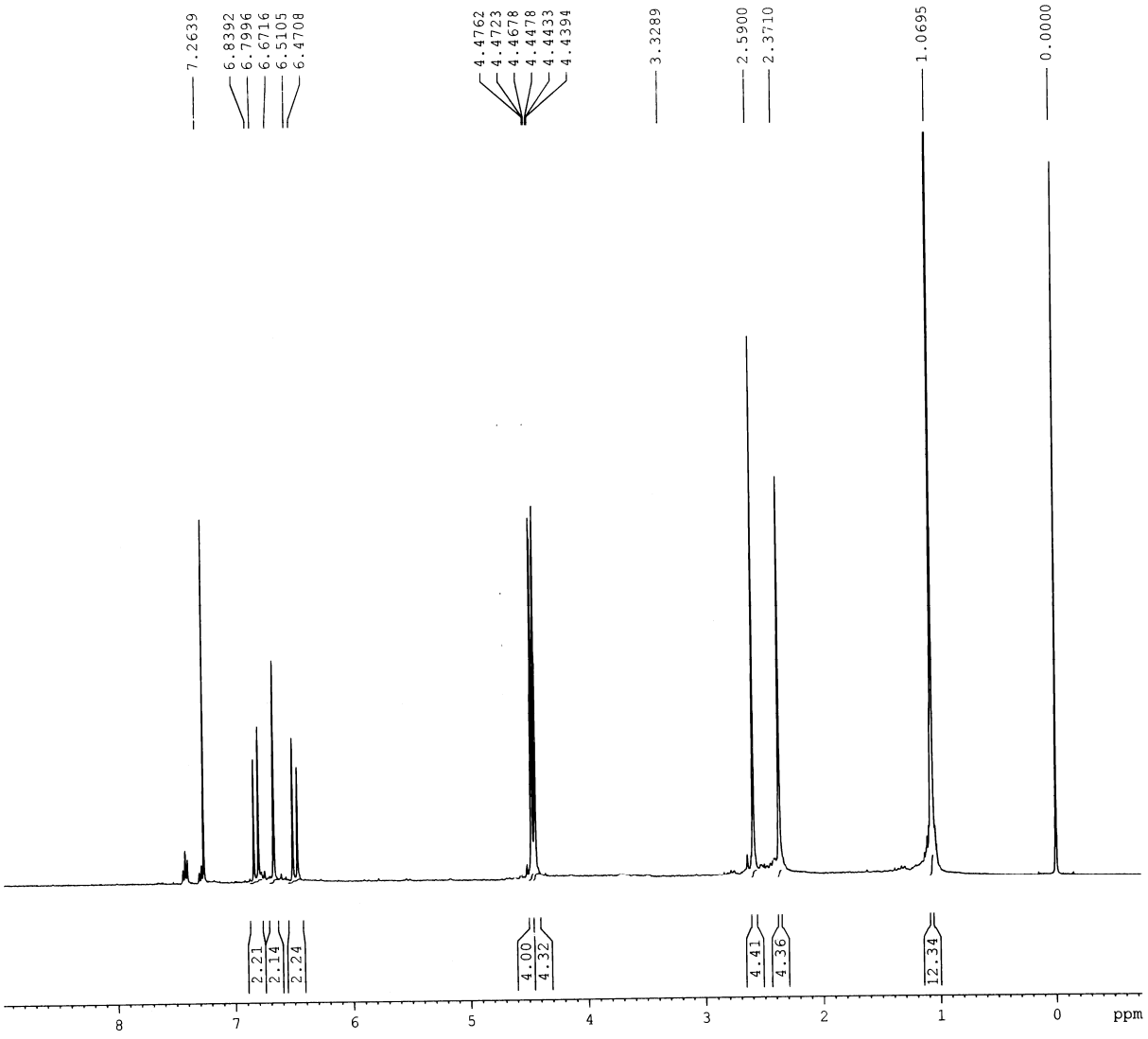

Figure S16: ^{1}H NMR spectrum of **10**.

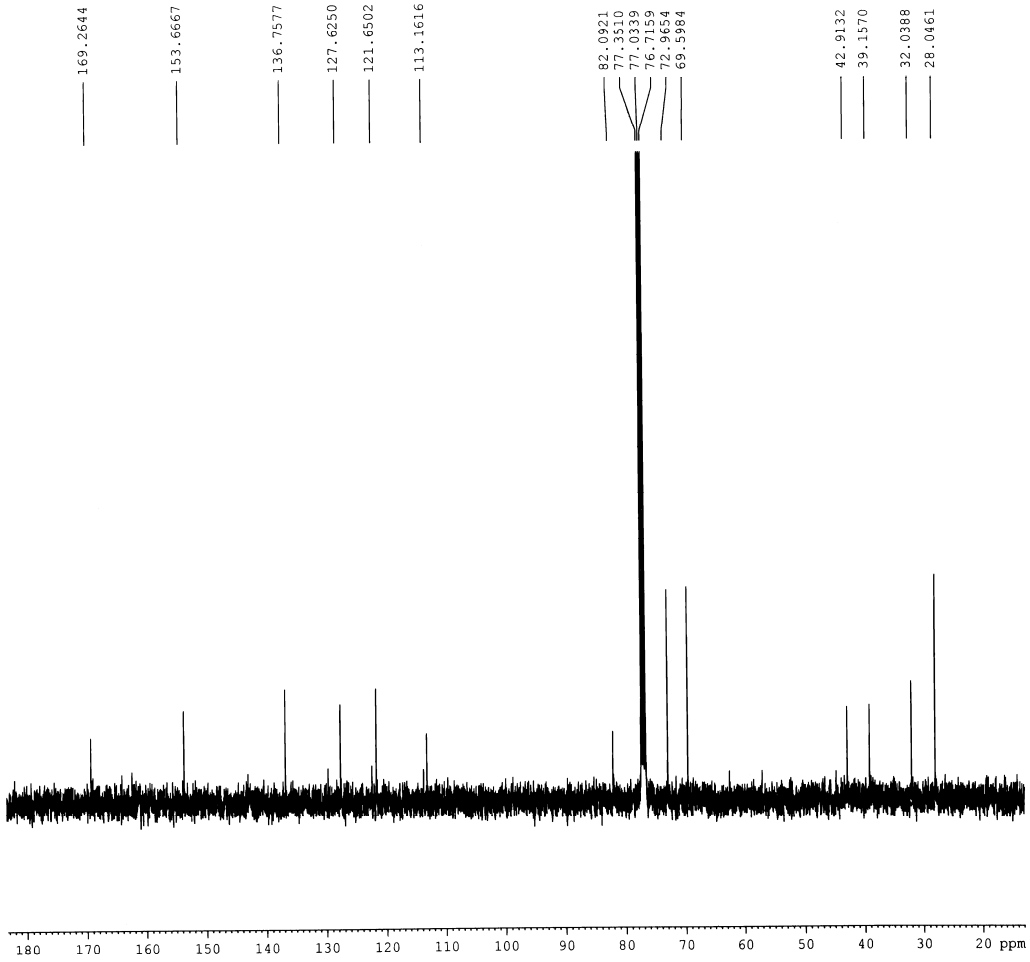

Figure S17: ^{13}C NMR spectrum of **10**.

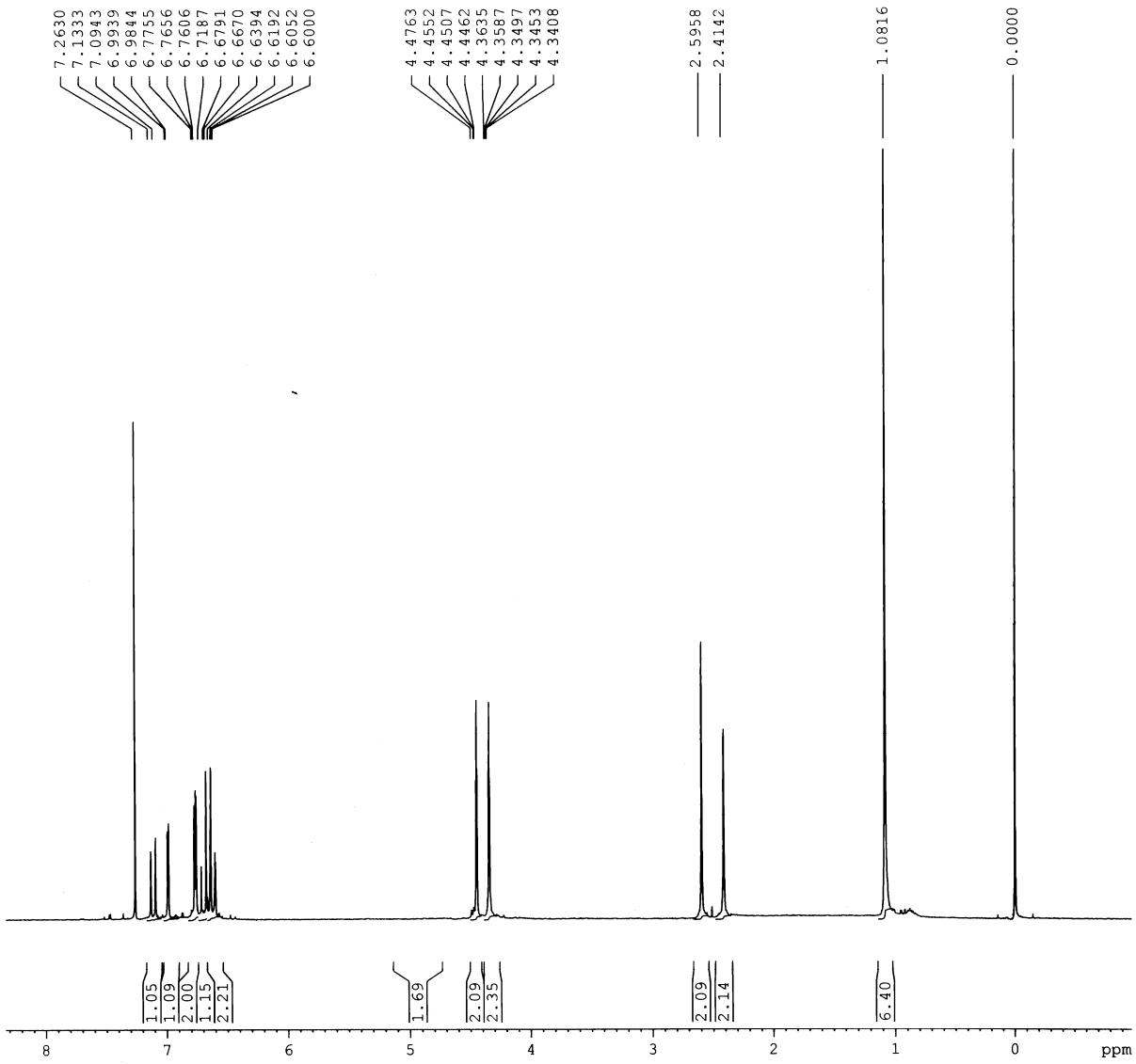

Figure S18: ^{1}H NMR spectrum of **11**.

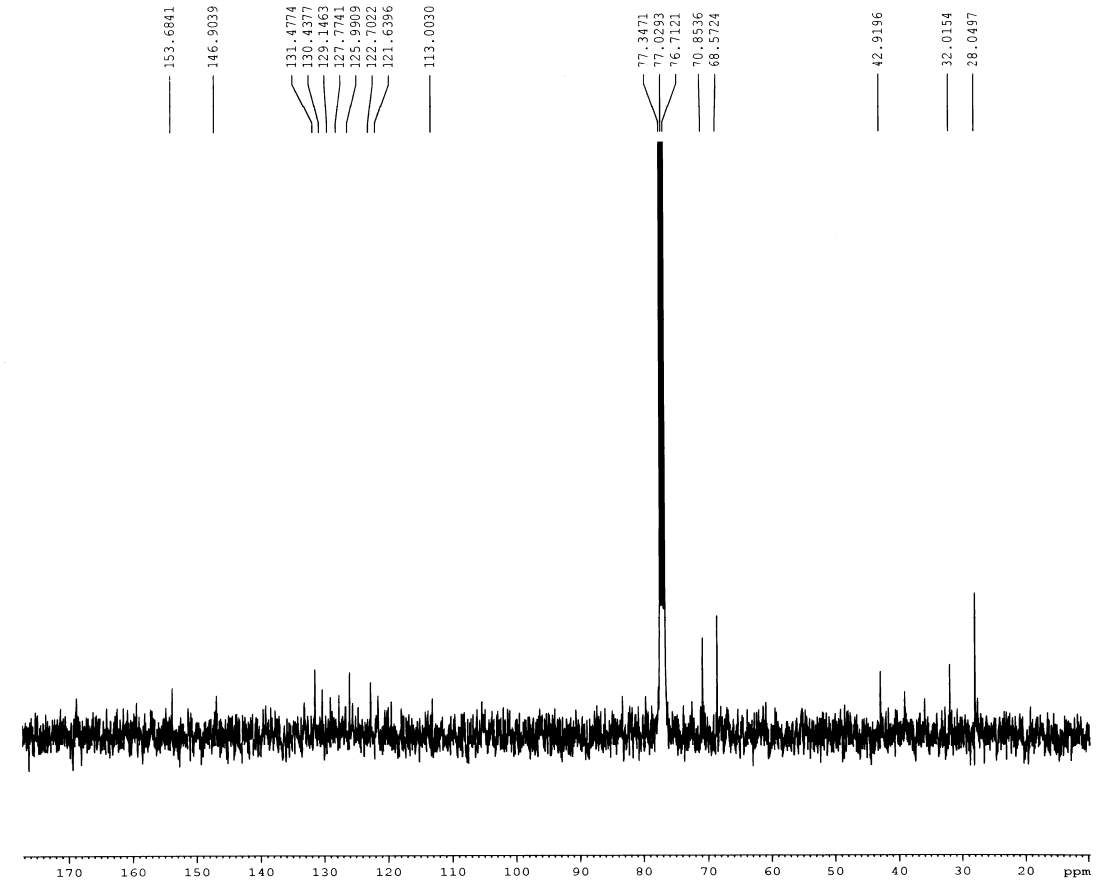

Figure S19: ^{13}C NMR spectrum of **11**.

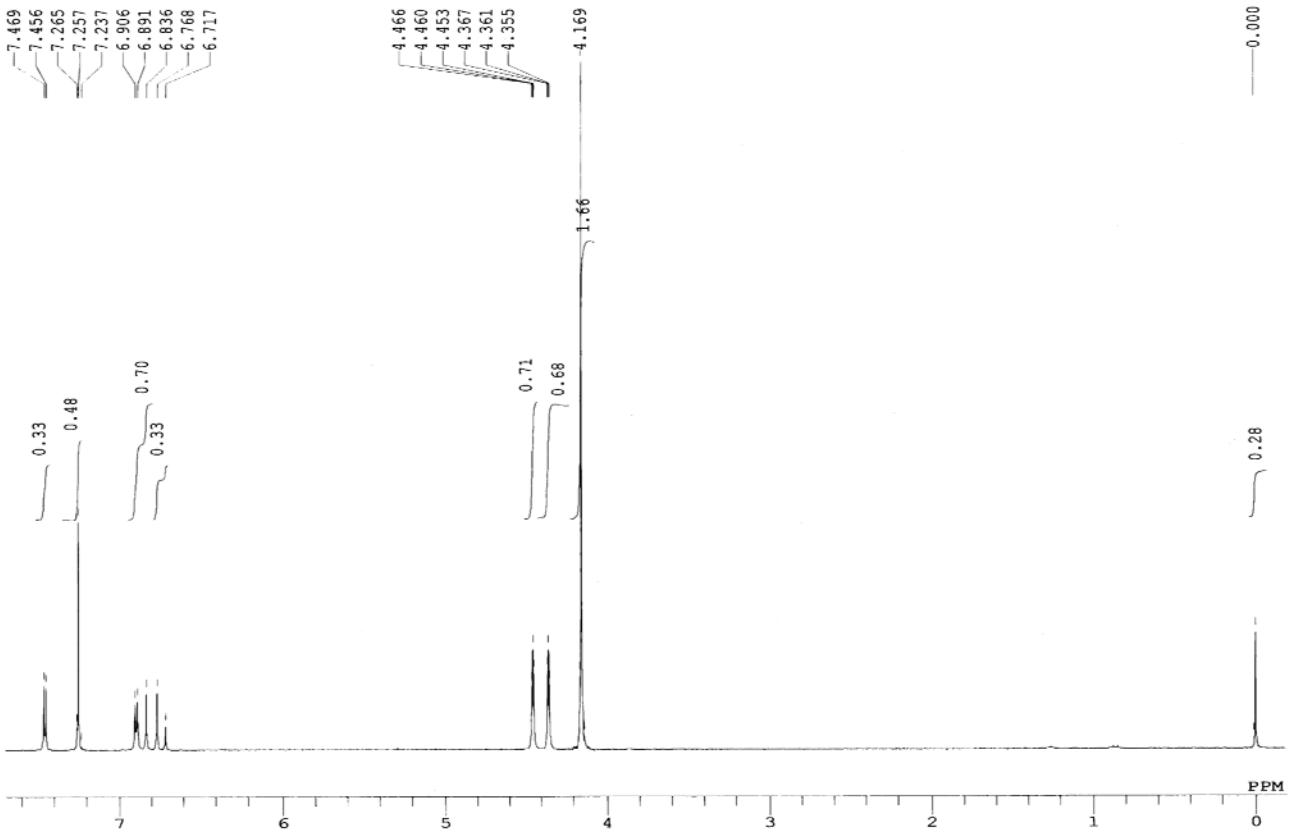

Figure S20: ^{1}H NMR spectrum of **2c**.

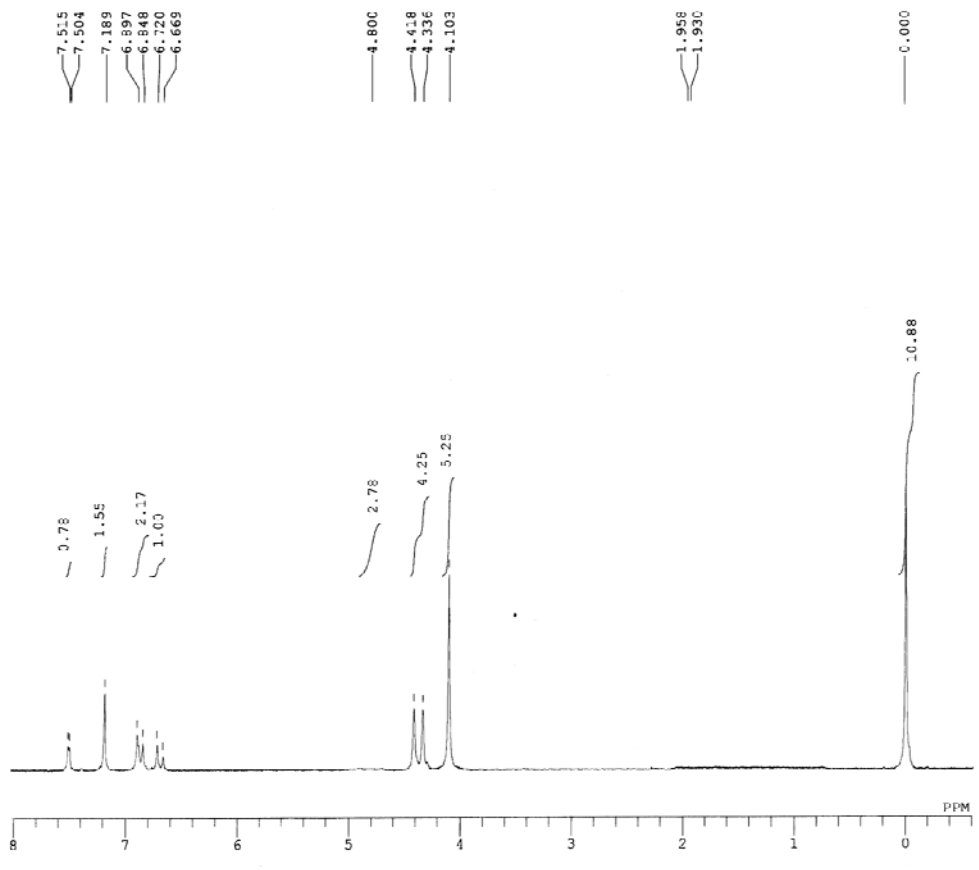

Figure S21: ^{1}H NMR spectrum of **2d**.

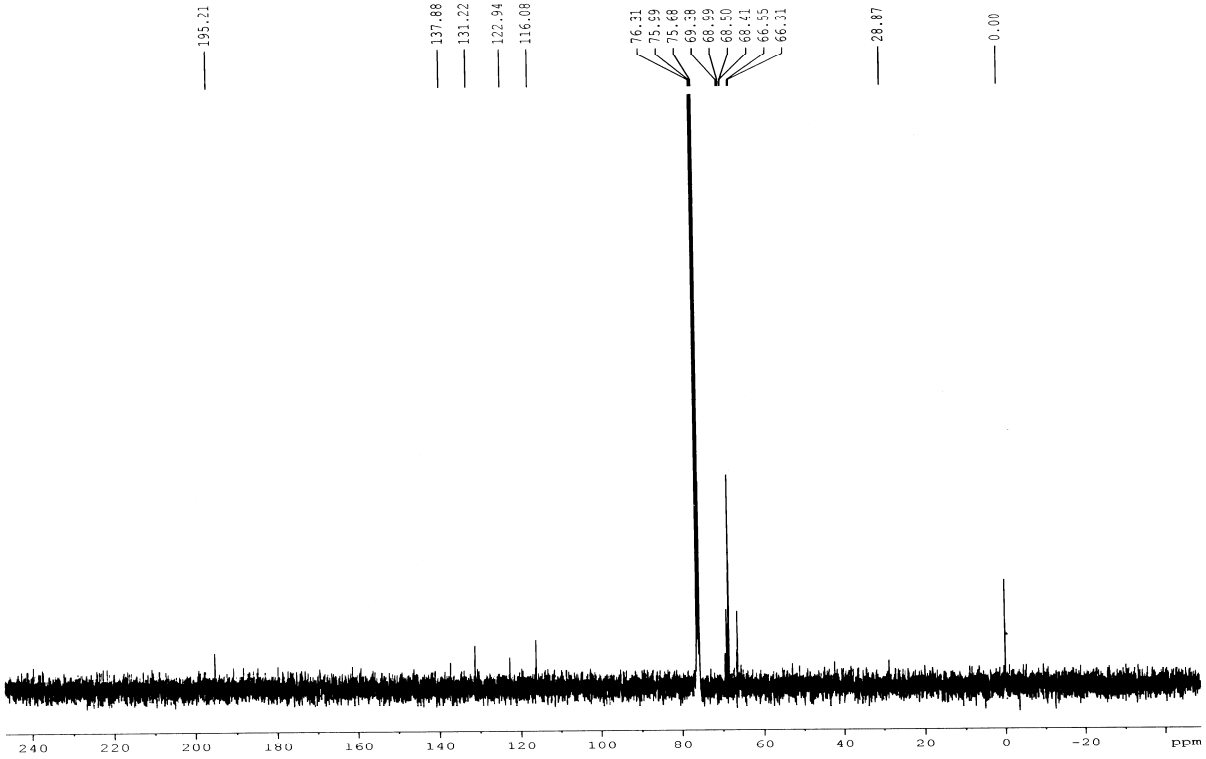

Figure S22: ^{13}C NMR spectrum of **2d**.

Complete reference 26

Gaussian 09, Revision B.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2010.

Note: Details including the references for the DFT method and basis set can be found online at the homepage of Gaussian at <http://www.gaussian.com>