

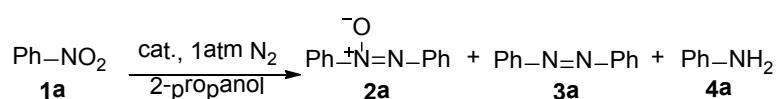
Supporting Information

Mild, Selective and Switchable Transfer Reduction of Nitroarenes Catalyzed by Supported Gold Nanoparticles

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A. Table S1. Transfer reduction of nitrobenzene using different catalysts.^a



Entry	Catalyst	Conv. (%) ^b	Sel. (%) ^b		
			2a	3a	4a
1	Au/meso-CeO ₂	100	>99	<1	-
2	Au/CeO ₂ -50	81	89	7	2
3	Au/ZrO ₂	26	74	25	1
4	Au/TiO ₂	60	65	34	<1
5	Au/Fe ₂ O ₃	21	41	59	-
6	Au/Al ₂ O ₃	36	53	46	1
7	Au/ZnO	30	58	41	<1
8	Pt/meso-CeO ₂	20	46	41	12
9	meso-CeO ₂	-	-	-	-

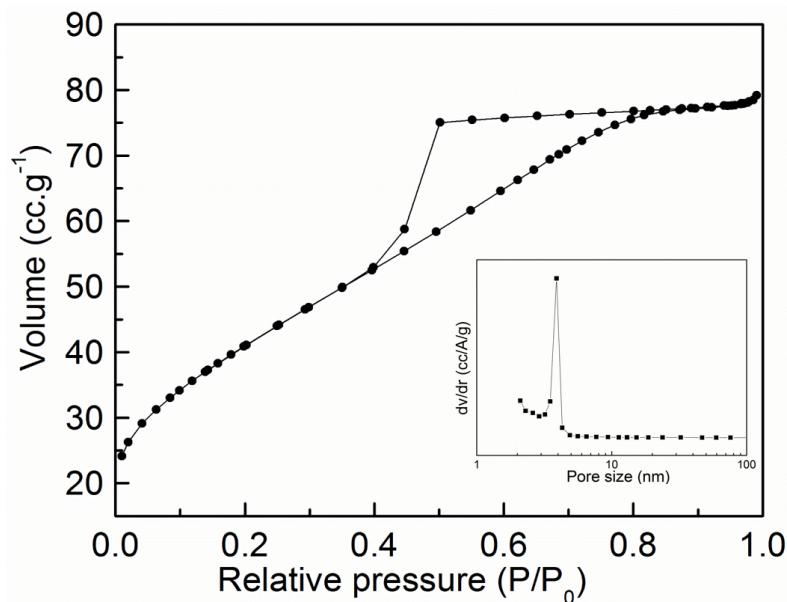
^a Reaction conditions: 1 mmol nitrobenzene, catalyst (metal: 1.0 mol%), 0.5 mmol KOH, 5.0 mL 2-propanol, 1.0 mL water, 1 atm N₂, 30 °C, 5 h. ^b Conversion and selectivity based on **1a** consumption. Determined by GC using *n*-dodecane as the internal standard.

B. Table S2. Transfer reduction of nitrobenzene in the presence of different bases.^a

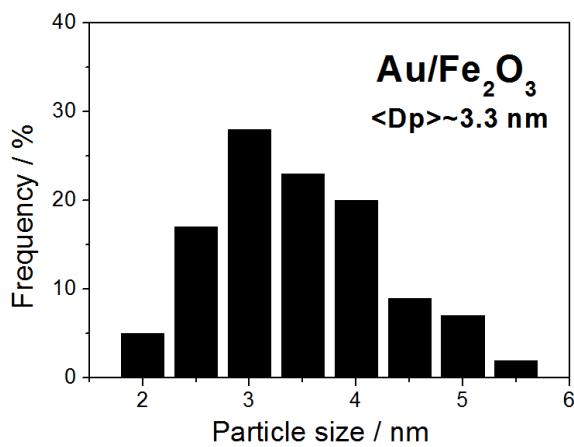
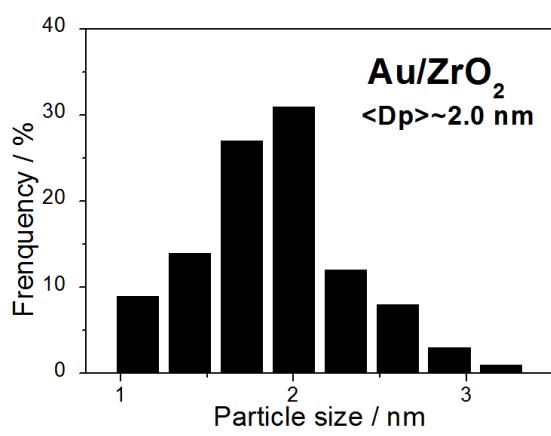
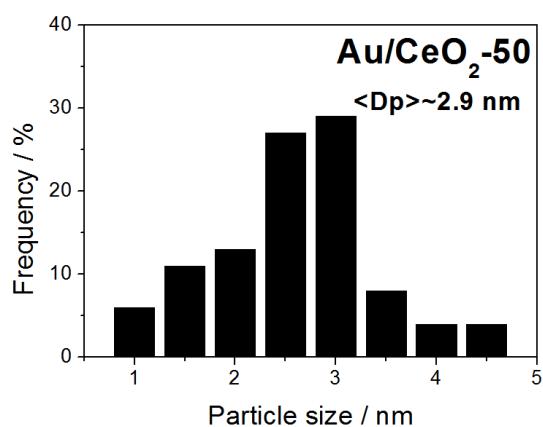
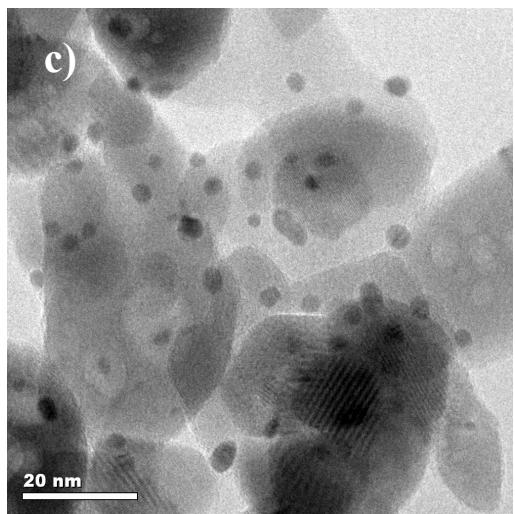
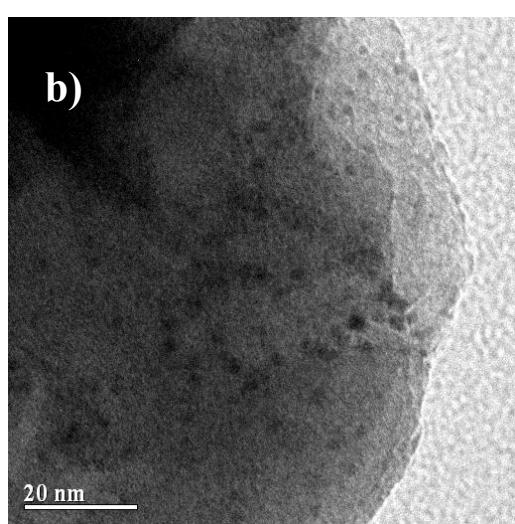
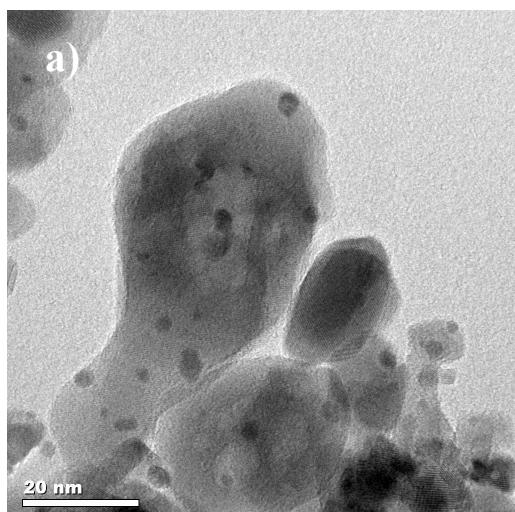
Entry	Base(equiv.)	t/h	Conv. (%) ^b	Sel. (%) ^b		
				2a	3a	4a
1	-	8	86	-	4	96
2	NaOH (0.5)	8	93	69	22	10
3	Na ₂ CO ₃ (0.5)	8	45	40	23	37
4	Cs ₂ CO ₃ (0.5)	8	89	11	81	8
5	KOH(0.25)	8	100	81	15	4
6	KOH(0.5)	5	100	>99	<1	-
7	KOH(1.0)	5	100	84	14	2
8	KOH(2.0)	5	100	69	29	2

^a Reaction conditions: 1 mmol nitrobenzene, Au/meso-CeO₂ (Au: 1.0 mol%), 5.0 mL 2-propanol, 1.0 mL water, 1 atm N₂, 30 °C. ^b Conversion and selectivity based on **1a** consumption. Determined by GC using *n*-dodecane as the internal standard.

C. Figure S1. Nitrogen adsorption-desorption isotherms of the meso-CeO₂.



D. TEM images



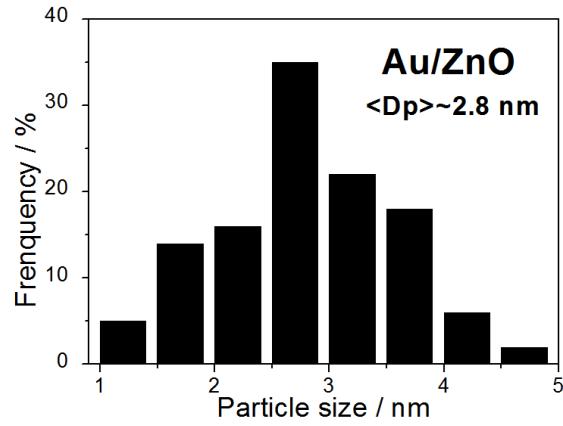
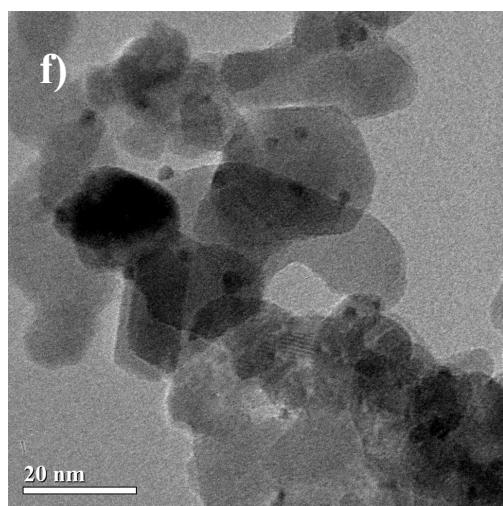
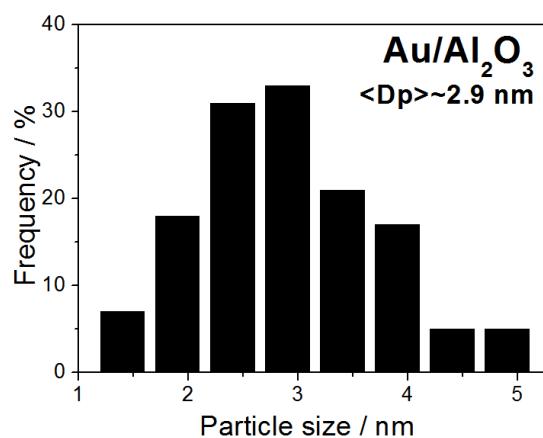
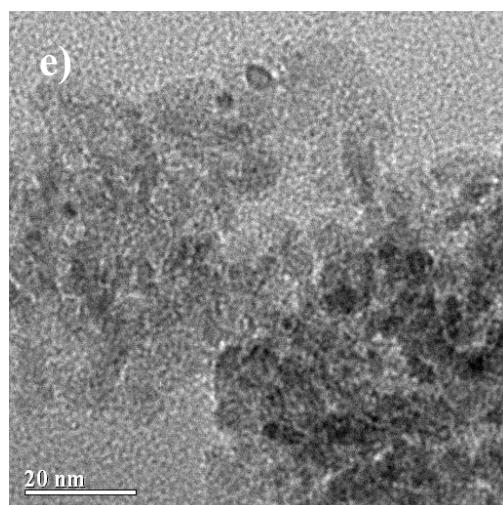
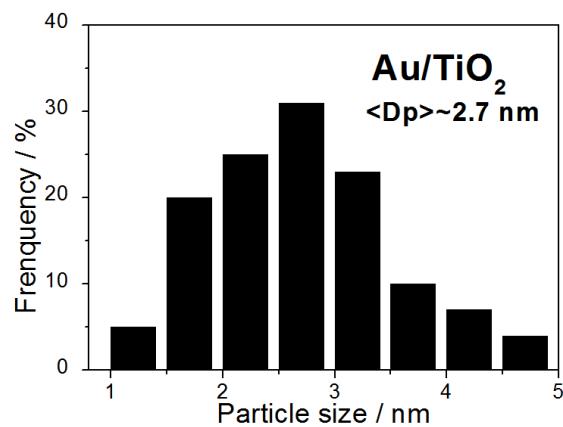
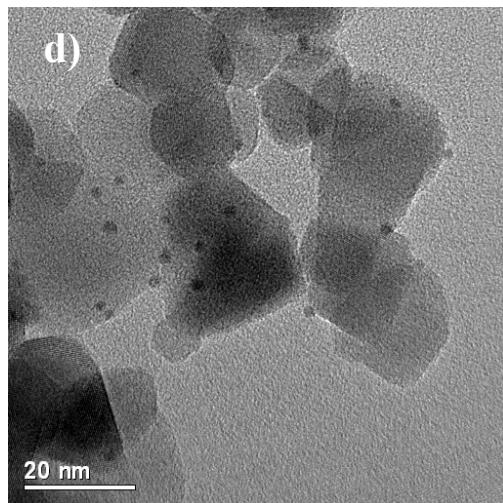


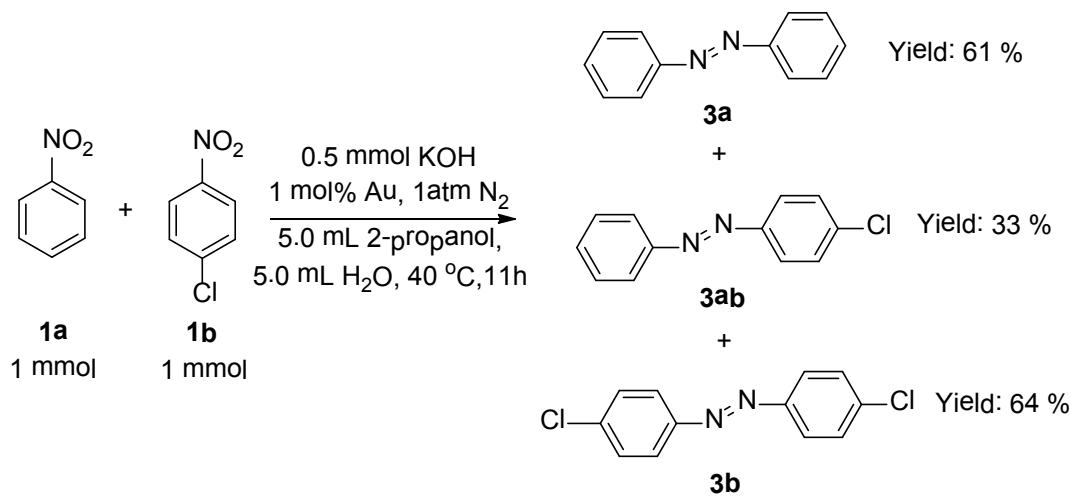
Figure S2. TEM images and gold particle size distribution of (a) 0.49 wt% Au/CeO₂-50; (b) 0.8 wt% Au/ZrO₂, (c) 4.50 wt% Au/Fe₂O₃; (d) 1.0 wt% Au/TiO₂; (e) 1.0 wt% Au/Al₂O₃; (f) 1.0 wt% Au/ZnO.

E. Table S3. Catalyst characterization by XRD, TEM, XPS, and nitrogen adsorption.

Sample	S _{BET} (m ² /g)	Crystallite size(nm) ^a	Crystallite size(nm) ^b	Surface n _{Au} /n _{Ce} ^c
meso-CeO ₂	150	7.3	n.m. ^d	-
Fresh Au/meso-CeO ₂	148	7.5	4.8	0.015
Used Au/meso-CeO ₂	147	7.5	4.8	0.014

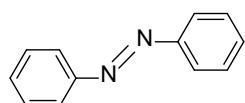
^a Determined by XRD. ^b Determined by HRTEM. ^c The XPS lines used to calculate the atomic ratios were Au (4f_{7/2}) and Ce (3d_{5/2}). Surface n_{Au}/n_{Ce} = (A_{Au}/S_{Au})/(A_{Ce}/S_{Ce}), A is peak area, atomic sensitivity factors S were taken from reference [S1]. ^d n.m. means not measured. Note that the surface Au/Ce atomic ratio unambiguously demonstrate that the gold dispersion in the Au/meso-CeO₂.

F. Cross-coupling reaction between nitrobenzene and 4-chloronitrobenzene

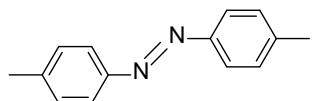


Scheme S1. Transfer reductive cross-coupling between equimolar amount of nitrobenzene and 4-chloronitrobenzene. The yield was determined by GC. The yield of **3a** and **3ab** was calculated based on **1a**, and the yield of **3b** was calculated based on **1b**. Note that aniline (5 % yield based on **1a**) and azoxybenzene (1 % yield based on **1a**) were also detected as by-products in the resultant mixture.

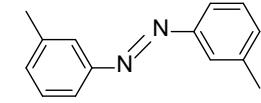
G. Characterization of Products



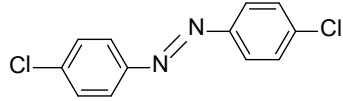
(Table 3, entry 1). ^[S2] ¹H-NMR (CDCl₃, 500 MHz): δ 7.93-7.91 (t, 4H), 7.54-7.46 (m, 6H); ¹³C NMR (CDCl₃, 125 MHz): δ 152.7, 131.0, 129.1, 122.8.



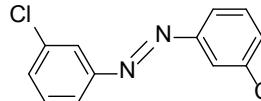
(Table 3, entry 2). ^[S2] ¹H-NMR (CDCl₃, 500 MHz): δ 7.82- 7.80 (d, 4H), 7.31-7.29 (d, 4H), 2.43 (s, 6H); ¹³C NMR (CDCl₃, 125 MHz): δ 150.9, 141.2, 129.7, 122.7, 21.5.



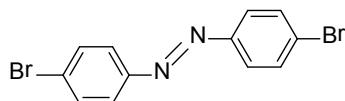
(Table 3, entry 3). ^[S2] ¹H-NMR (CDCl₃, 500 MHz): δ 7.72 (s, 4H), 7.42-7.38 (t, 2H), 7.29-7.28 (d, 2H), 2.46 (s, 6 H); ¹³C NMR (CDCl₃, 125 MHz): δ 152.8, 139.0, 131.7, 128.9, 122.9, 120.4, 21.4.



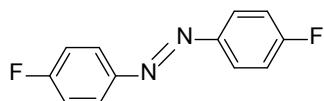
(Table 3, entry 4). ^[S2] ¹H-NMR (CDCl₃, 500 MHz): δ 7.87-7.86 (d, 4H), 7.50-7.48 (d, 4H). ¹³C NMR (CDCl₃, 125 MHz): δ 150.9, 137.3, 129.4, 124.2.



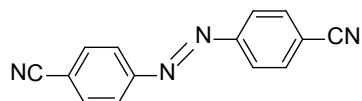
(Table 3, entry 5). ^[S3] ¹H-NMR (CDCl₃, 500 MHz): δ 7.90-7.85 (t, 2 H), 7.84-7.83 (t, 2 H), 7.50-7.47 (m, 4 H); ¹³C NMR (CDCl₃, 125 MHz): δ 153.2, 139.9, 131.2, 130.2, 122.6, 121.9.



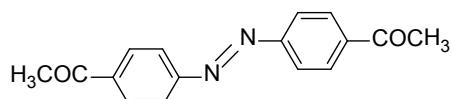
(Table 3, entry 6). ^[S2] ¹H-NMR (CDCl₃, 500 MHz): δ 7.80-7.79 (d, 4 H), 7.66-7.64 (d, 4 H); ¹³C NMR (CDCl₃, 125 MHz): δ 151.2, 139.9, 132.4, 125.7, 124.4.



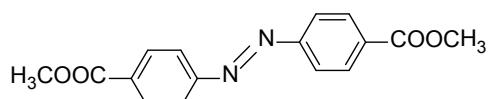
(Table 3, entry 7). ^[S4] ¹H-NMR (CDCl₃, 500 MHz): δ 7.92- 7.90 (m, 4 H), 7.24-7.16 (m, 4 H); ¹³C NMR (CDCl₃, 125 MHz): δ 165.4, 163.4, 149.0, 124.9, 124.8, 116.2, 116.0.



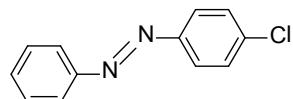
(Table 3, entry 1).^[S3] ^1H -NMR (CDCl_3 , 500 MHz): δ 8.04-8.03 (d, 4H), 7.86-7.84 (d, 4H); ^{13}C NMR (CDCl_3 , 125 MHz): δ 154.0, 133.4, 123.7, 118.1, 115.2.



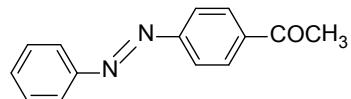
(Table 3, entry 1).^[S2] ^1H -NMR (CDCl_3 , 500 MHz): δ 8.14-8.12 (d, 4 H), 8.02-8.01 (d, 4 H), 2.68 (s, 6 H); ^{13}C NMR (CDCl_3 , 125 MHz): δ 197.3, 154.9, 139.0, 129.4, 123.2, 26.9.



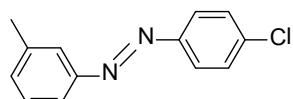
(Table 3, entry 1).^[S2] ^1H -NMR (CDCl_3 , 500 MHz): δ 8.22-8.20 (d, 4H), 8.00-7.98 (d, 4H), 3.97 (s, 6H); ^{13}C NMR (CDCl_3 , 125 MHz): δ 166.4, 155.0, 132.5, 130.7, 52.4.



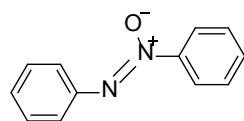
(Scheme 1).^[S4] ^1H -NMR (CDCl_3 , 500 MHz): δ 7.93-7.87 (m, 4 H), 7.53-7.48 (m, 5 H); ^{13}C NMR (CDCl_3 , 125 MHz): δ 152.5, 151.0, 136.9, 131.3, 129.3, 129.1, 124.1, 122.9.



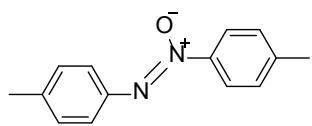
(Scheme 1).^[S5] ^1H -NMR (CDCl_3 , 500 MHz): δ 8.12-8.10 (d, 2H), 7.98-7.94 (m, 4H), 7.54-7.52 (d, 3H), 2.67 (s, 3H); ^{13}C NMR (CDCl_3 , 125 MHz): δ 197.4, 152.6, 131.8, 131.4, 129.4, 129.2, 123.2, 122.9, 29.7.



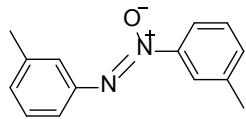
(Scheme 1).^[S4] ^1H -NMR (CDCl_3 , 500 MHz): δ 7.87-7.85 (d, 2H), 7.72-7.71 (d, 2H), 7.49-7.47 (d, 2H), 7.42-7.39 (t, 1H), 7.31-7.29 (d, 1H), 2.46 (s, 3H); ^{13}C NMR (CDCl_3 , 125 MHz): 152.6, 151.1, 139.1, 136.8, 132.1, 129.3, 129.0, 124.1, 123.0, 120.5, 21.4.



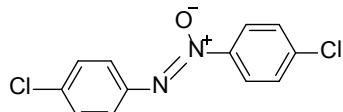
(Table 4, entry 1).^[S2] ^1H -NMR (CDCl_3 , 500 MHz): δ 8.32-8.30 (m, 2H), 8.17-8.16(d, 2H), 7.58-7.26 (m, 6H); ^{13}C NMR (CDCl_3 , 125 MHz): δ 148.4, 144.1, 131.6, 129.6, 128.8, 128.7, 125.5, 122.4.



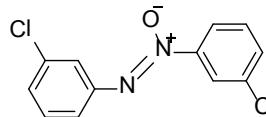
(Table 4, entry 2).^[S2] ^1H -NMR (CDCl_3 , 500 MHz): δ 8.19-8.17 (d, 2H), 8.12-8.10 (d, 2H), 7.29-7.25 (t, 4H), 2.44 (s, 3H), 2.41 (s, 3H); ^{13}C NMR (CDCl_3 , 125 MHz): δ 146.3, 141.9, 140.0, 129.3, 125.7, 122.2, 21.5, 21.3.



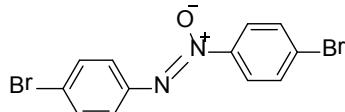
(Table 4, entry 3).^[S2] ^1H -NMR (CDCl_3 , 500 MHz): δ 8.10-8.07 (t, 2H), 7.98-7.96 (d, 2H), 7.40-7.35 (m, 3H), 7.21-7.20 (d, 1H), 2.47 (s, 3H) 2.43 (s, 3H); ^{13}C NMR (CDCl_3 , 125 MHz): δ 148.4, 144.1, 139.0, 138.4, 132.3, 130.3, 128.6, 128.5, 126.0, 122.8, 122.5, 119.5, 21.5, 21.4.



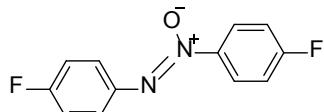
(Table 4, entry 4).^[S2] ^1H -NMR (CDCl_3 , 500 MHz): δ 8.26-8.24 (d, 2H), 8.16-8.15 (d, 2H), 7.49-7.44 (m, 4H); ^{13}C NMR (CDCl_3 , 125 MHz): δ 146.6, 144.3, 138.1, 135.3, 129.0, 129.0, 127.1, 123.7.



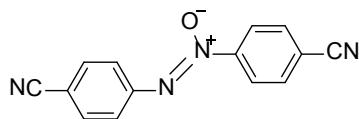
(Table 4, entry 5).^[S3] ^1H -NMR (CDCl_3 , 500 MHz): δ 8.32-8.20 (m, 3H), 8.01-8.00 (d, 1H), 7.57-7.56 (d, 1H), 7.50-7.39 (m, 4 H); ^{13}C NMR (CDCl_3 , 125 MHz): δ 144.5, 134.9, 134.5, 132.0, 129.9, 129.9, 129.7, 125.4, 124.0, 122.9, 120.6.



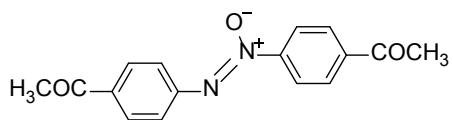
(Table 4, entry 6).^[S2] ^1H -NMR (CDCl_3 , 500 MHz): δ 8.19-8.17 (d, 2H), 8.09-8.07 (d, 2H), 7.66-7.60 (m, 4H); ^{13}C NMR (CDCl_3 , 125 MHz): δ 147.1, 142.7, 132.1, 131.9, 127.2, 126.5, 123.9, 123.6.



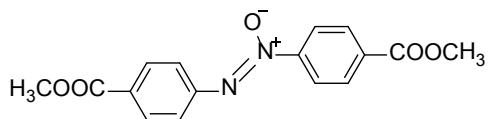
(Table 4, entry 7).^[S6] ^1H -NMR (CDCl_3 , 500 MHz): δ 8.34-8.31 (m, 2H), 8.27-8.24 (m, 2H), 7.20-7.15 (m, 4H); ^{13}C NMR (CDCl_3 , 125 MHz): δ 165.5, 163.6, 163.5, 161.6, 140.3, 128.0, 127.9, 124.6, 124.5, 115.8, 115.8, 115.6, 115.5.



(Table 4, entry 1).^[S2] ^1H -NMR (CDCl_3 , 500 MHz): δ 8.47-8.45 (d, 2H), 8.24-8.22 (d, 2H), 7.88-7.86 (d, 2H), 7.80-8.79 (d, 2H); ^{13}C NMR (CDCl_3 , 125 MHz): δ 146.3, 139.9, 139.8, 133.1, 132.8, 126.0, 123.4, 118.2, 117.3, 116.2, 113.2.



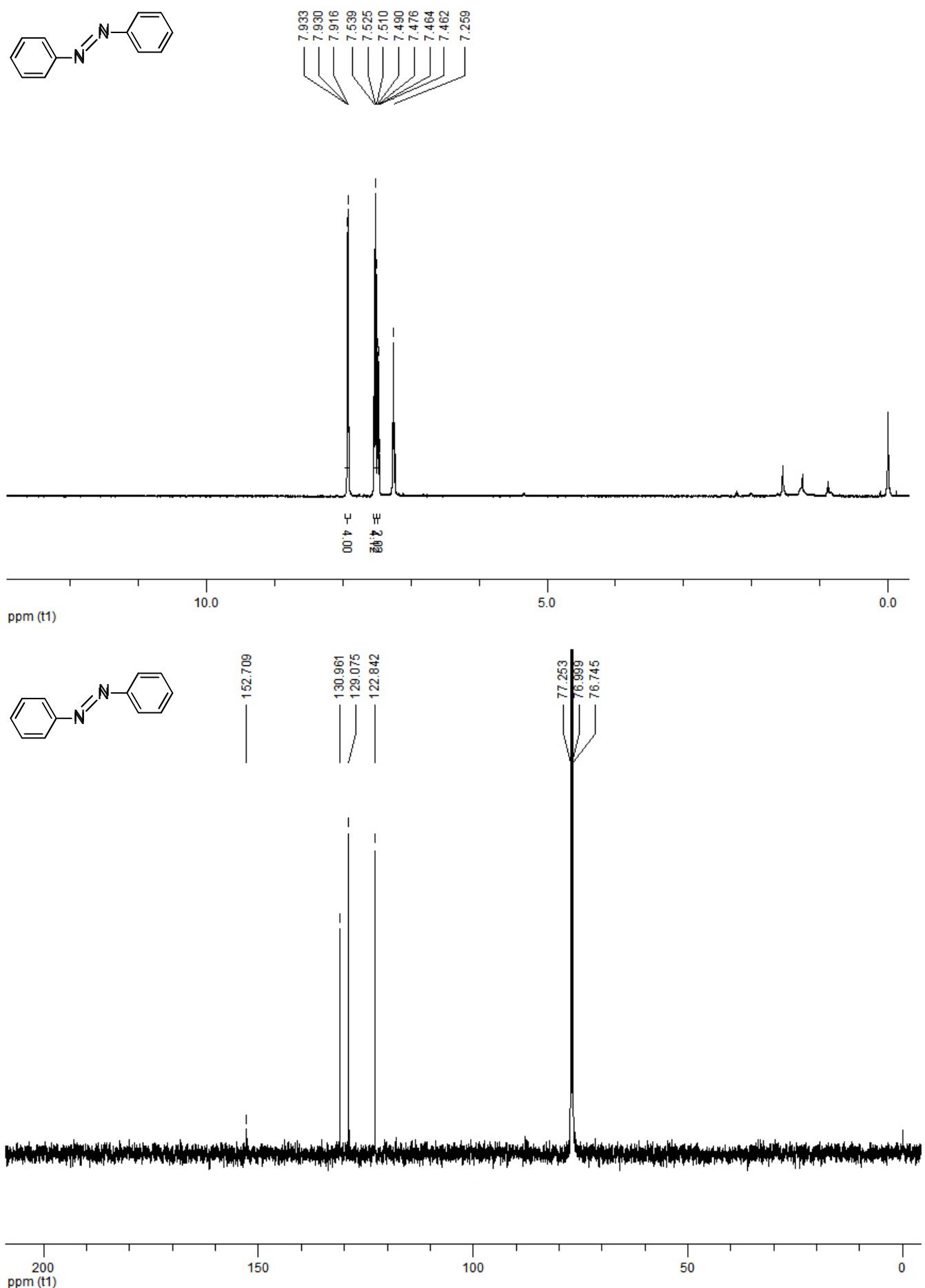
(Table 4, entry 1).^[S2] ^1H -NMR (CDCl_3 , 500 MHz): 8.41-8.40 (d, 2H), 8.22-8.20 (d, 2H), 8.11-8.07 (m, 4H), 2.68 (s, 3H), 2.65 (s, 3H); ^{13}C NMR (CDCl_3 , 125 MHz): δ 197.0, 196.7, 150.8, 147.0, 139.8, 139.6, 137.4, 129.0, 129.0, 125.5, 122.8, 26.9, 26.7.

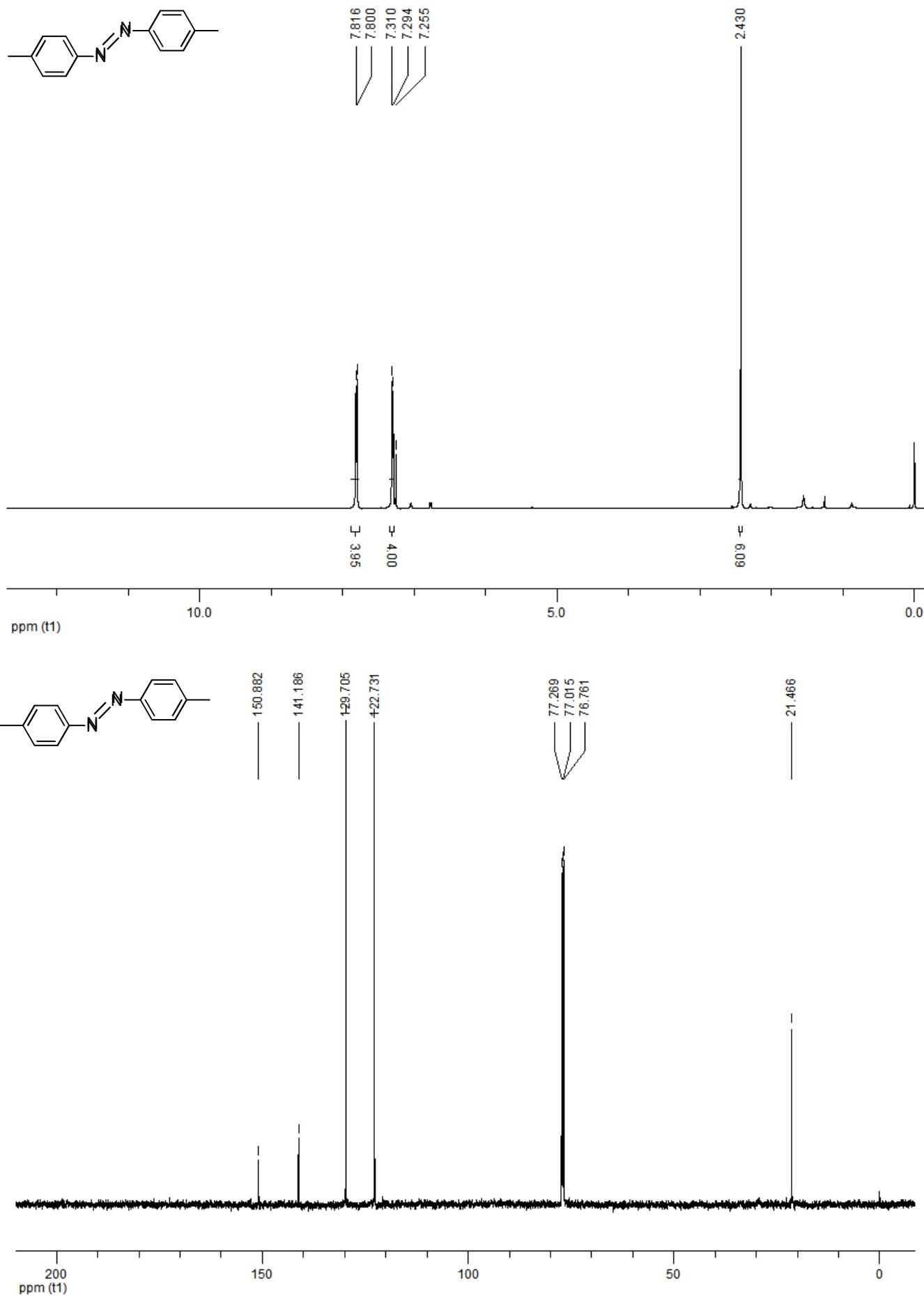


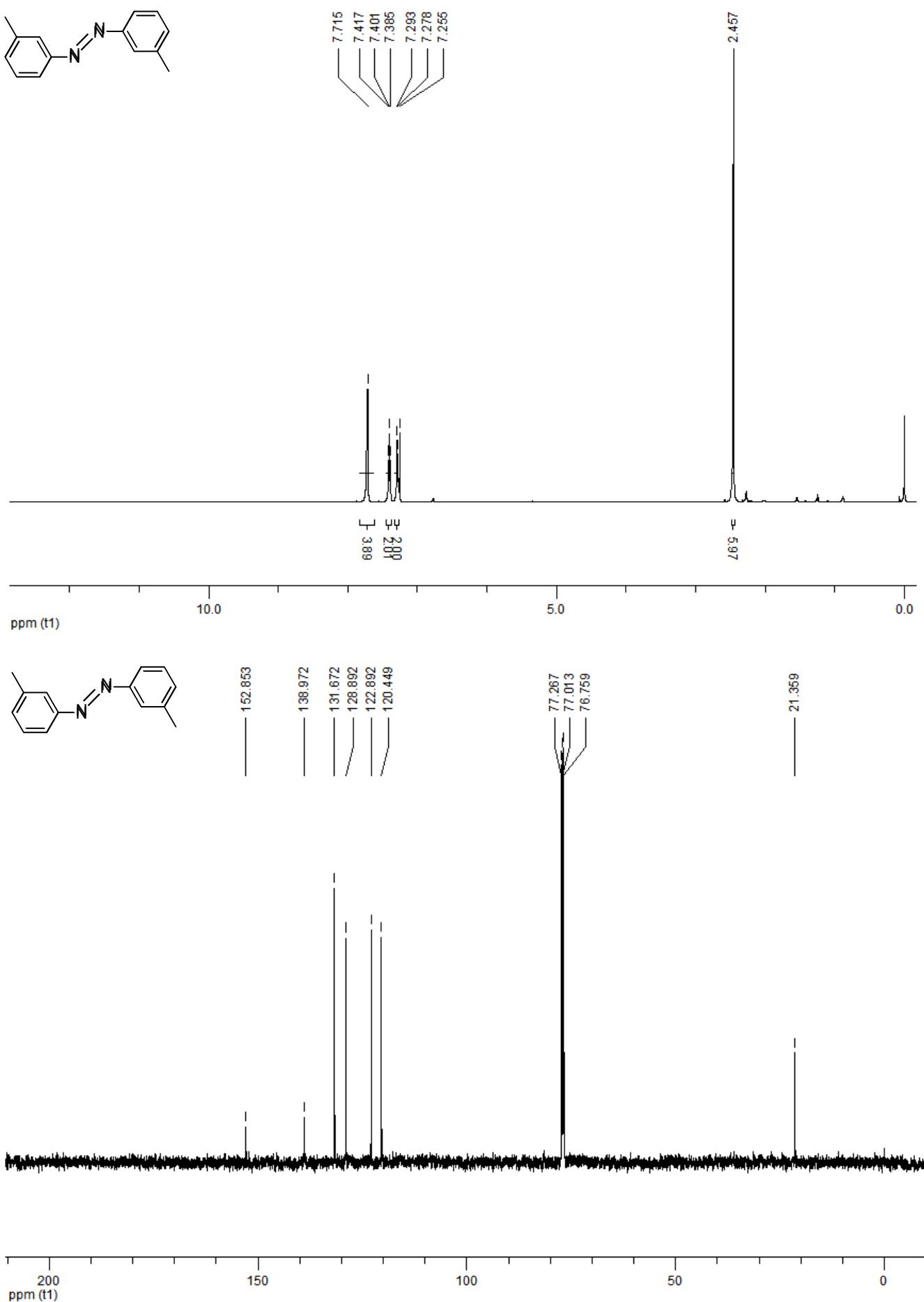
(Table 4, entry 1).^[S2] ^1H -NMR (CDCl_3 , 500 MHz): δ 8.40-8.38 (d, 2H), 8.21-8.17 (m, 6H), 3.98 (s, 3H), 3.95 (s, 3H); ^{13}C NMR (CDCl_3 , 125 MHz): δ 166.2, 165.8, 150.9, 147.0, 133.3, 130.7, 130.4, 130.2, 125.3, 122.6, 52.6, 52.3.

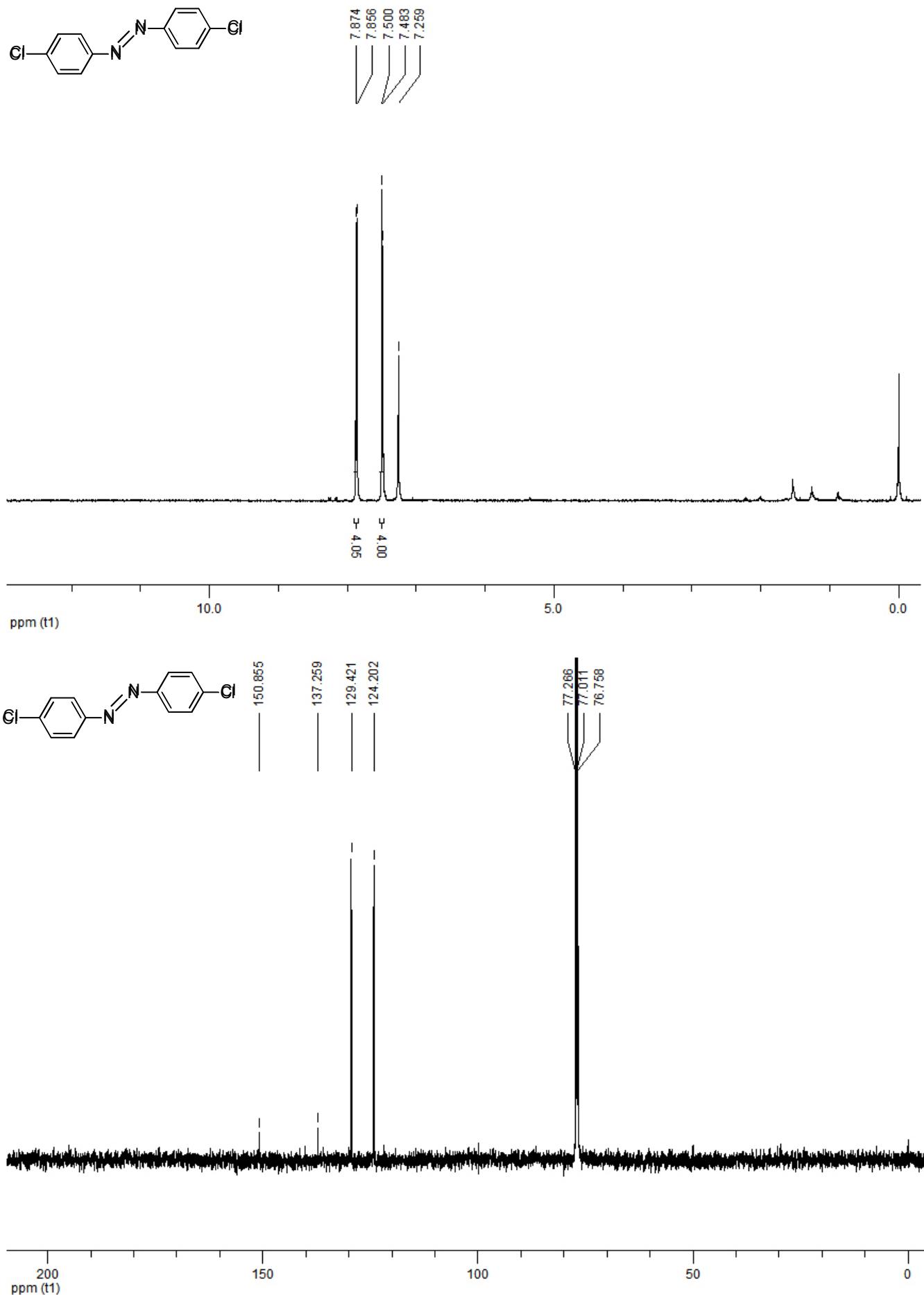
References

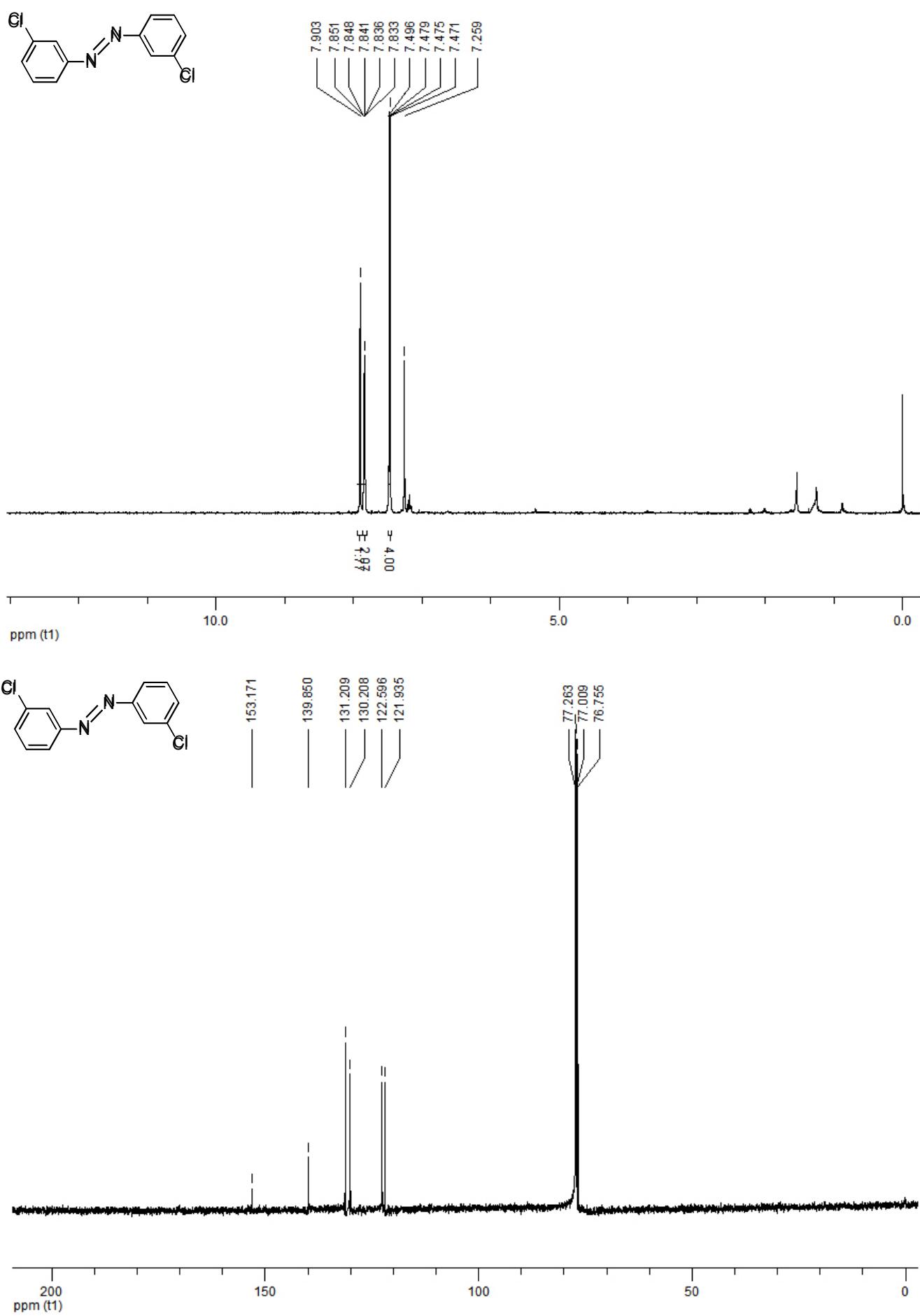
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- [S4] S. Cai, H. Rong, X. Yu, X. Liu, D. Wang, W. He, Y. Li, *ACS Catal.*, 2013, **3**, 486.
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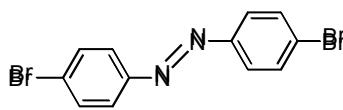




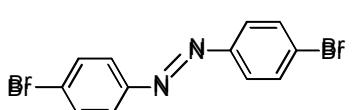
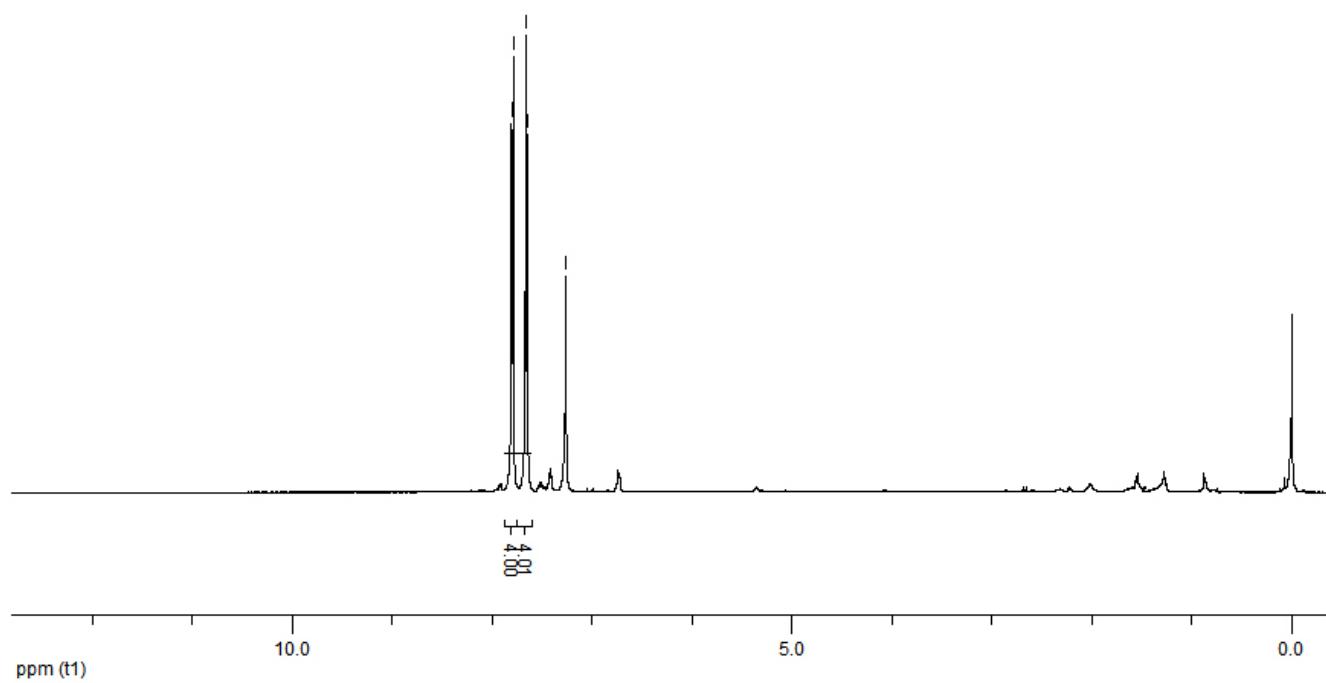








7.804
7.786
7.663
7.645
7.261



151.220
139.856
132.423
124.425

77.259
77.005
76.751

