

## Supplementary Information

For

### **Polymer immobilized Tantalum(V)-amino acid complexes as selective and recyclable heterogeneous catalysts for oxidation of olefins and sulfides with aqueous H<sub>2</sub>O<sub>2</sub>**

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Table S1: Analytical data of the complexes **1** and **2**

Compound	% found from element analysis (% obtained from EDX spectra)							% O <sub>2</sub> <sup>2-</sup>	Ta:O <sub>2</sub> <sup>2-</sup>	Metal loading <sup>a</sup> (mmolg <sup>-1</sup> )
	C	H	N	O	Na	Cl	Ta			
<b>MRAsn</b>	77.96 (77.31)	7.18	6.98 (7.02)	(15.67)						
<b>Catalyst 1</b>	67.27 (67.01)	6.33	6.37 (6.28)	(19.25)	(0.80)		(6.66)	2.4	1:2	0.37
<b>MRArg</b>	76.59 (76.80)	7.0	9.67 (9.88)	(12.04)			(1.28)			
<b>Catalyst 2</b>	65.90 (65.51)	6.16	8.89 (8.71)	(18.51)	(1.09)	(0.30)	(5.88)	2.3	1:2	0.32

$${}^a \text{Metal loading} = \frac{\text{Observed metal \%} \times 10}{\text{Atomic weight of metal}}$$

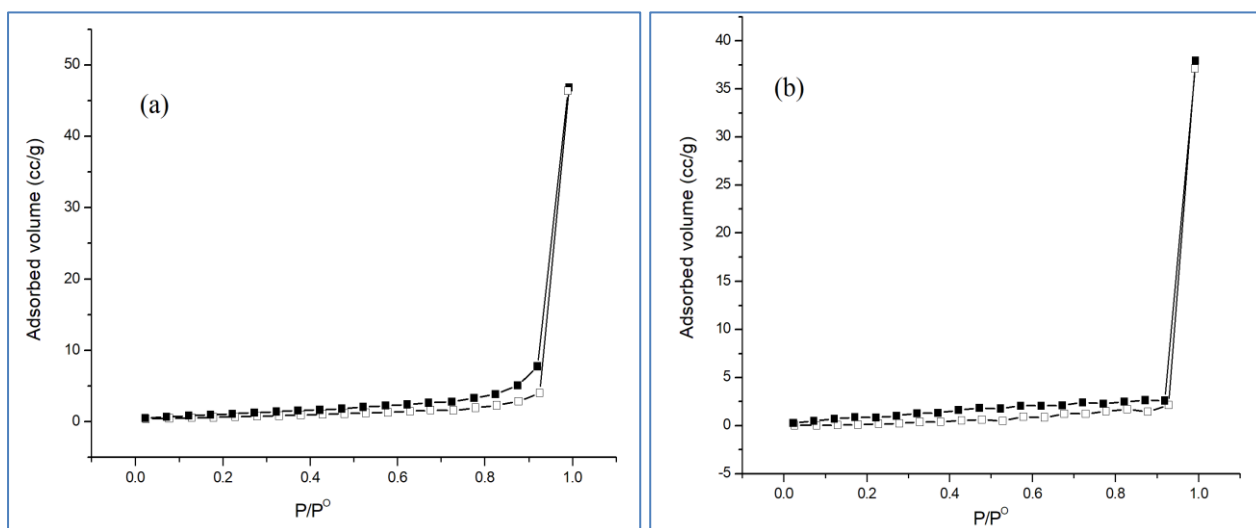


Fig. S1 Adsorption/desorption isotherm of complexes (a) **1** and (b) **2**

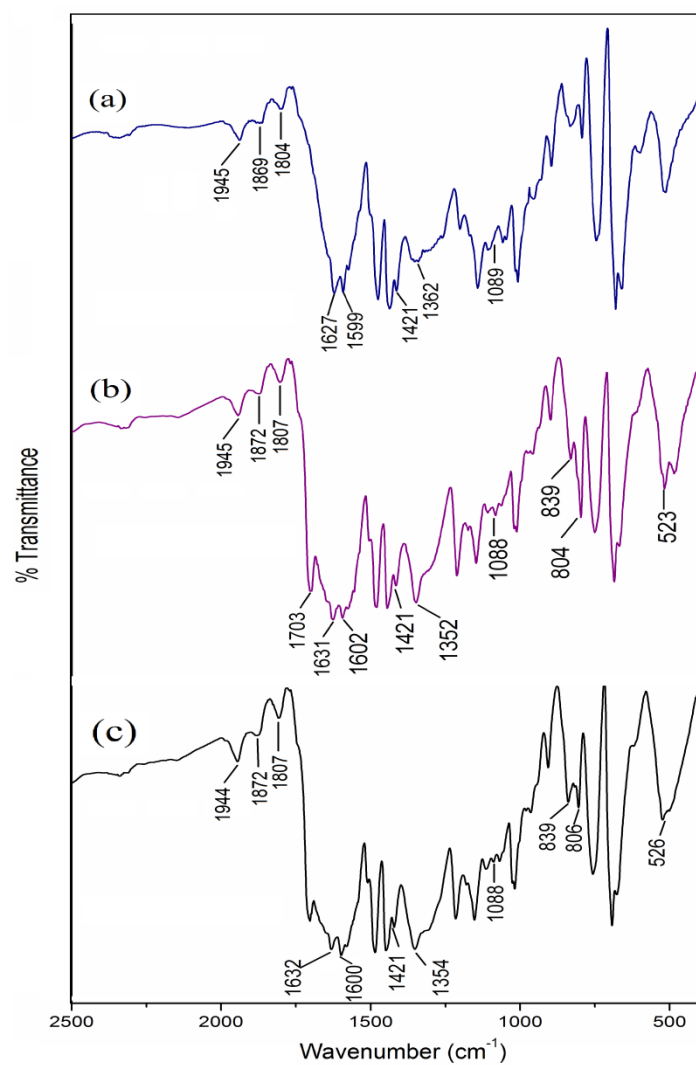


Fig. S2 IR spectra of (a) **MRArg**, (b) **catalyst 2** and (c) **catalyst 2** after 5<sup>th</sup> cycle of reaction.

Table S2: Infrared (IR) and Raman (R) spectral data for the polymer support, amino acid linked Merrifield resin and polymer immobilized peroxotantalates<sup>a</sup>

Assignments		MR	MRAsn	Catalyst 1	MRArg	Catalyst 2
v(C-Cl)	(IR)	1264(m)	-	-	-	-
	(R)	1263(m)				
v(C=O, amide I)	(IR)		1629(s)	1630(s)		
	(R)		1621(m)	1624(m)		
v <sub>s</sub> (CN <sub>3</sub> H <sub>5</sub> <sup>+</sup> )	(IR)				1627(s)	1631(s)
	(R)				1622(m)	1624(m)
v <sub>as</sub> (COO)	(IR)		1598(s)	1601(s)	1599(s)	1602(s)
	(R)		1597(sh)	1599(sh)	1596(sh)	1600(sh)
v <sub>s</sub> (COO)	(IR)		1422(sh)	1353(s)	1421(sh)	1352(s)
	(R)		1461(m)	1362(m)	1466(m)	1385(s)
v(C-N)	(IR)		1085(vw)	1088(vw)	1089(vw)	1088(vw)
	(R)		1091(vw)	1090(vw)	1091(vw)	1088(vw)
v(O-O)	(IR)			805(s),839(m)		804(s),839(m)
	(R)			819(m),855(m)		821(m),858(m)
v <sub>as</sub> (M-O <sub>2</sub> )	(IR)			526(m)		523(m)
	(R)			571(m)		575(m)
v <sub>s</sub> (M-O <sub>2</sub> )	(IR)			-		-
	(R)			550(sh)		550(sh)

<sup>a</sup>s, strong; m, medium; vw, very weak; sh, shoulder.

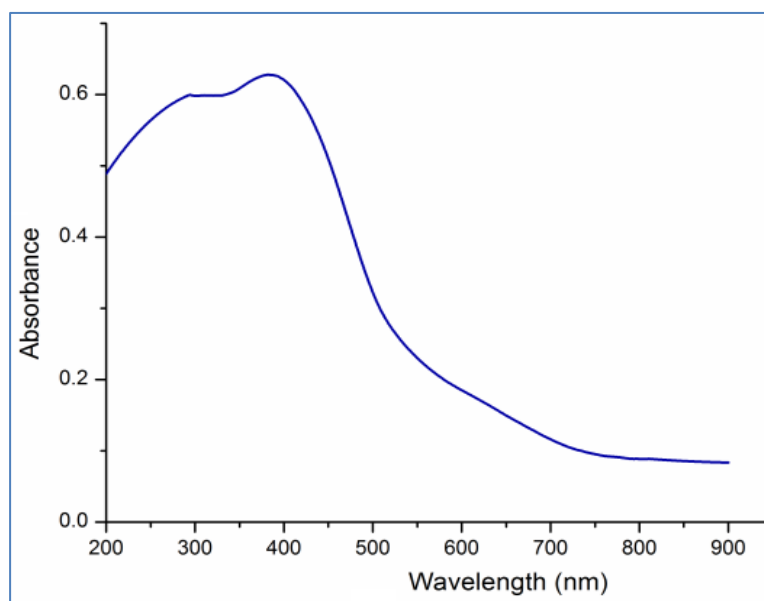


Fig. S3 Diffuse reflectance UV-visible spectra of Catalyst **1**.

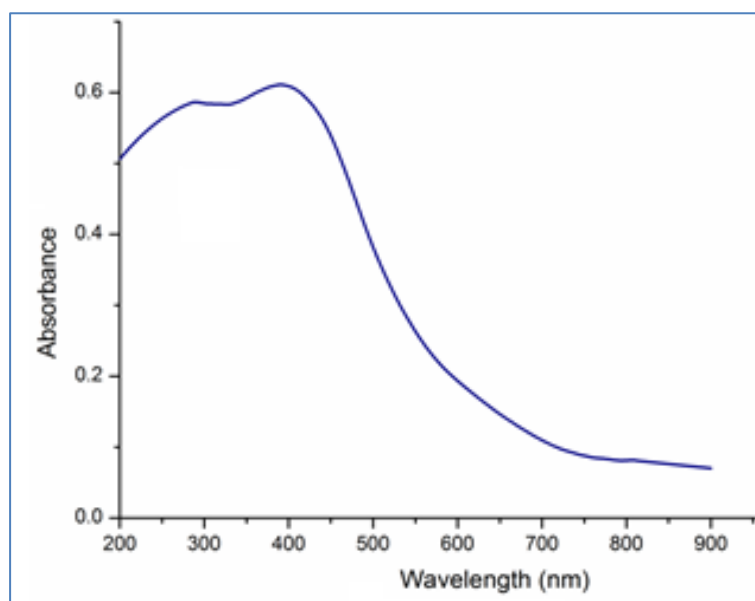


Fig. S4 Diffuse reflectance UV-visible spectra of Catalyst **2**.

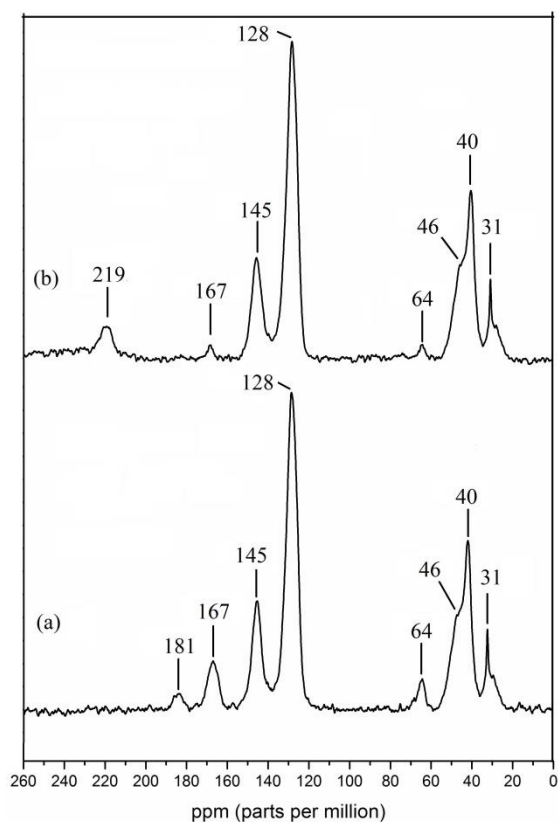


Fig. S5 Solid state  $^{13}\text{C}$  NMR spectra of (a) **MRArg** and (b) **Catalyst 2**

Table S3  $^{13}\text{C}$  NMR chemical shifts for **MR**, amino acid linked **MR** and polymer bound catalysts **1** and **2**

Compound	Chemical shift (ppm)							
	Merrifield resin				Amino acid			
	Quaternary Aromatic Carbons	Protonated Aromatic Carbons	Aliphatic Methine Carbons	$\text{CH}_2\text{Cl}$	C-NH	C=NH/ CONH <sub>2</sub>	Carboxylate Free	Complexed
<b>MR</b>	145.18	128.36	41.04	46.17	--	--	--	--
<b>MRA<sub>sn</sub></b>	145.16	128.96	40.45	--	64.44	179.89	181.59	--
<b>Catalyst 1</b>	145.52	128.14	40.81	--	64.57	179.94	-	219.89
<b>MRArg</b>	145.82	128.35	40.35	46.24	64.79	167.59	181.03	--
<b>Catalyst 2</b>	145.52	128.59	40.55	46.44	64.57	167.46	--	219.96

Table S4: TGA data for amino acid functionalized MR and polymer bound pTa catalysts.

Compound	Temperature range (°C)	Observed weight loss (%)	Final residue(%)
<b>MRAsn</b>	35-95	3.5	13.1
	148-257	12.5	
	263-698	70.9	
<b>Catalyst 1</b>	35-92	2.8	26.1
	104-146	2.5	
	147-299	8.7	
	302-699	59.9	
<b>MRArg</b>	40-95	1.7	13.9
	155-239	9.4	
	264-698	75.0	
<b>Catalyst 2</b>	35-98	2.7	24.9
	104-145	2.4	
	150-291	8.4	
	293-699	61.6	

Table S5: Optimization of reaction conditions for catalyst **1** catalyzed selective oxidation of methyl phenyl sulfide (MPS) to sulfoxide by 30% H<sub>2</sub>O<sub>2</sub><sup>a</sup>

Cc1ccccc1S  $\xrightarrow[\text{Solvent}]{\text{Catalyst 1, 30\% H}_2\text{O}_2}$  Cc1ccccc1S(=O) + Cc1ccccc1S(=O)(=O)

1
1a
1b

Entry	Molar ratio (Ta:MPS)	H <sub>2</sub> O <sub>2</sub> (equiv.)	Solvent	Time (min)	Isolated yield	1a:1b	TON <sup>b</sup>	TOF <sup>c</sup> (h <sup>-1</sup> )
1	1:1000	2	-	95	95	78:22	950	601
2	1:1000	2	H <sub>2</sub> O	180	56	54:46	560	187
3	1:1000	2	CH <sub>3</sub> CN	180	82	92:8	820	273
4	1:1000	2	EtOH	180	89	96:4	890	297
5	1:1000	2	MeOH	160	98	100:0	980	367
6	1:1000	1	MeOH	180	87	100:0	870	290
7	1:1000	3	MeOH	100	97	100:0	970	581
<b>8</b>	<b>1:1000</b>	<b>4</b>	<b>MeOH</b>	<b>40</b>	<b>97</b>	<b>100:0</b>	<b>970</b>	<b>1447</b>
9	1:1500	4	MeOH	140	98	100:0	1484	637
10	1:2000	4	MeOH	180	96	100:0	1920	640
11	1:500	4	MeOH	25	95	61:39	475	1130
12 <sup>d</sup>	-	4	MeOH	40	14	59:41	-	-
13 <sup>e</sup>	1:1000	4	MeOH	40	38	68:32	380	567
14 <sup>f</sup>	1:1000	4	MeOH	20	98	69:31	980	2969

<sup>a</sup>Reactions were carried out with 5 mmol of substrate, 30 % H<sub>2</sub>O<sub>2</sub> in 5 mL of solvent at room temperature. Catalyst (13.5 mg for 0.005 Ta). <sup>b</sup>TON (turn over number)= mmol of product per mmol of catalyst. <sup>c</sup>TOF(turn over frequency)= mmol of product per mmol of catalyst per hour. <sup>d</sup>Blank experiment without any catalyst. <sup>e</sup>Using Na<sub>3</sub>[Ta(O<sub>2</sub>)<sub>4</sub>]·H<sub>2</sub>O as catalyst (2.0 mg, 0.005 mmol Ta). <sup>f</sup>Reaction conducted at 60 °C under optimum condition. Values in bold signify optimized reaction condition.



Table S6: Comparison of catalytic performance between complexes **1** and **2**(this work) and literature reported Ta-based catalysts for sulfide oxidation using H<sub>2</sub>O<sub>2</sub> as oxidant

Entry	Catalyst	Catalyst amount	Conditions [Time, Temperature, Solvent]	Conversion /Sulfoxide Selectivity (%)	TON/ TOF(h <sup>-1</sup> )	Reusability	Ref.
1	[Ta(O <sub>2</sub> ) <sub>2</sub> (Asn) <sub>2</sub> ] <sup>-</sup> -MR	0.002 mmol	40 min, RT, MeOH	100/100	970/1447	5 <sup>th</sup> cycle	This work
2	[Ta(O <sub>2</sub> ) <sub>2</sub> (Arg) <sub>2</sub> ] <sup>-</sup> -MR	0.002 mmol	70 min, RT, MeOH	100/100	950/812	5 <sup>th</sup> cycle	This work
3	TaCl <sub>5</sub>	0.02 equiv.	2.5 h, RT, CH <sub>3</sub> CN	100/95	--	--	14a
4	TaC	0.02 equiv.	1.25 h, 45 °C, CH <sub>3</sub> OH	100/99	--	4 <sup>th</sup> cycle	54
5	Modified Ta-MCM with DET or DIPT	0.012 mmol	24 h, RT, CH <sub>3</sub> OH	60-80/>80	--/1-2.5	2 <sup>nd</sup> cycle	6b

**Text S1:** Calculations of efficiency of hydrogen peroxide in the sulfoxidation reaction systems

The calculations are shown with oxidation of styrene and methyl phenyl sulfide (MPS) to styrene oxide and methyl phenyl sulfoxide, respectively with catalyst **1** as a representative example.

**H<sub>2</sub>O<sub>2</sub> efficiency (%) = 100 × [mole of H<sub>2</sub>O<sub>2</sub> consumed in the formation of oxyfunctionalized products / mole of H<sub>2</sub>O<sub>2</sub> converted]**

(a) Assuming that one mole of oxidant reacts with one mole of substrate.

(b) The spent catalyst was separated from the reaction mixture simply by centrifugation. The H<sub>2</sub>O<sub>2</sub> left was estimated by titration with standard cerium (IV) solution.

### **1. In styrene oxidation**

H<sub>2</sub>O<sub>2</sub> (mole) consumed in the formation of styrene oxide (yield: 99.4 %) from 5 mmol styrene = **4.97 mmol**.

The titrated value was found to be: **4.34 mmol**

Since 10 mmol H<sub>2</sub>O<sub>2</sub> has been originally used for the reaction.

Therefore, total mole of H<sub>2</sub>O<sub>2</sub> converted = (10-4.34) mmol = 5.66 mmol

Thus, **H<sub>2</sub>O<sub>2</sub> efficiency = 100 × [4.97/5.66]**

**= 87.8%**

### **2. In sulfide oxidation**

H<sub>2</sub>O<sub>2</sub> (mole) consumed in the formation of sulfoxide (yield: 97%) from 5 mmol sulfides = **4.85 mmol**.

The titrated value was found to be: **14.98 mmol**

Since 20 mmol H<sub>2</sub>O<sub>2</sub> has been originally used for the reaction.

Therefore, total mole of H<sub>2</sub>O<sub>2</sub> converted = (20-14.98) mmol = 5.02 mmol

Thus, **H<sub>2</sub>O<sub>2</sub> efficiency = 100 × [4.85/5.02]**

**= 96.6%**

## Text S2: Characterization of Sulfoxides:

- (1) **Methylphenylsulfoxide:** Isolated as light yellow solid; mp 28-29°C;  $\nu$  (KBr)/cm<sup>-1</sup> 1048;  
<sup>1</sup>H NMR (400MHz; CDCl<sub>3</sub>,  $\delta$ ): 2.75(s, 3H); 7.31-7.36(m, 1H); 7.42-7.47(m, 2H); 7.61-7.68(m, 2H)  
<sup>13</sup>C NMR (100.5MHz; CDCl<sub>3</sub>,  $\delta$ ): 43.87; 123.54; 129.12; 131.02; 145.42
- (2) **Dimethylsulfoxide:** Isolated as liquid;  $\nu$  (KBr)/cm<sup>-1</sup> 1055;  
<sup>1</sup>H NMR (400MHz; CDCl<sub>3</sub>,  $\delta$ ): 2.65(s, 6H)  
<sup>13</sup>C NMR (100.5MHz; CDCl<sub>3</sub>,  $\delta$ ): 40.54
- (3) **Dibutylsulfoxide:** Isolated as white solid; mp 32-33°C;  $\nu$  (KBr)/cm<sup>-1</sup> 1063;  
<sup>1</sup>H NMR (400MHz; CDCl<sub>3</sub>,  $\delta$ ): 0.98(t, 6H, J=7.41Hz); 1.39-1.50(m, 4H); 1.66-1.78(m, 4H);  
2.62-2.69(m, 4H)  
<sup>13</sup>C NMR (100.5MHz; CDCl<sub>3</sub>,  $\delta$ ): 13.44; 22.17; 24.54; 51.91
- (4) **Ethylphenylsulfoxide:** Isolated as pale yellow liquid;  $\nu$  (KBr)/cm<sup>-1</sup> 1055;  
<sup>1</sup>H NMR (400MHz; CDCl<sub>3</sub>,  $\delta$ ): 1.25(t, 3H, J=6.61Hz); 2.70-2.79(q, 1H, J=6.58Hz); 2.93(q, 1H,  
J=6.61Hz) 7.13-7.48(m, 3H); 7.50-7.84(m, 2H)  
<sup>13</sup>C NMR (100.5MHz; CDCl<sub>3</sub>,  $\delta$ ): 10.41, 47.19, 125.44, 129.88, 131.47, 145.69
- (5) **Methyl-p-tolylsulfoxide:** Isolated as pale yellow liquid; mp 42-45 °C;  $\nu$  (KBr)/cm<sup>-1</sup> 1036  
<sup>1</sup>H NMR (400MHz; CDCl<sub>3</sub>,  $\delta$ ): 7.55 (d, 2H), 7.36 (d, 2H), 2.71 (s, 3H), 2.42 (s, 3H)  
<sup>13</sup>C NMR (100.5MHz; CDCl<sub>3</sub>,  $\delta$ ): 142.60, 141.57, 129.93, 123.59, 44.11, 21.41
- (6) **2-Phenylthio ethanol:** Isolated as light brown solid; mp 42-43°C;  $\nu$  (KBr)/cm<sup>-1</sup> 1041;  
<sup>1</sup>H NMR (400MHz; CDCl<sub>3</sub>,  $\delta$ ): 2.47(s, 1H); 3.13(t, 2H, J=5.31Hz); 3.77(t, 2H, J=5.26Hz);  
7.29-7.39(m, 1H); 7.48-7.57(m, 2H); 7.64-7.68(m, 2H)  
<sup>13</sup>C NMR (100.5MHz; CDCl<sub>3</sub>,  $\delta$ ): 56.18; 61.06; 125.47; 129.98; 131.53; 144.55
- (7) **Allylphenylsulfoxide:** Isolated as pale yellow liquid;  $\nu$  (KBr)/cm<sup>-1</sup> 1045;  
<sup>1</sup>H NMR (400MHz; CDCl<sub>3</sub>,  $\delta$ ): 3.33(dt, 2H, J=7.11, 1.12Hz); 5.06(dq, 1H, J=1.43, 17.10Hz);  
5.18(dq, 1H, J=1.12, 10.22Hz); 5.44(ddt, 1H, J=7.11, 10.22, 17.10 Hz); 7.26-7.31(m, 1H);  
7.36-7.39(m, 2H); 7.61-7.64(m, 2H)  
<sup>13</sup>C NMR (100.5MHz; CDCl<sub>3</sub>,  $\delta$ ): 60.38; 117.83; 124.71; 125.13; 129.06; 131.24; 145.13
- (8) **Diphenyl sulfoxide:** Isolated as white solid; mp 70 °C;  $\nu$  (KBr)/cm<sup>-1</sup> 1043;  
<sup>1</sup>H NMR(400MHz; CDCl<sub>3</sub>,  $\delta$ ): 7.61-7.68(m, 4H), 7.42-7.53(m, 6H)  
<sup>13</sup>C NMR (100.5MHz; CDCl<sub>3</sub>,  $\delta$ ): 144.84, 129.78, 128.13, 123.72  
Splitting patterns are designated as s (singlet), d (doublet), t (triplet), dt (double triplet), ddt (double-double triplet), q (quartet), dq (double quartet), m (multiplet).