Supplementary Materials

Stable non-covalent Co(Salphen) based polymeric catalyst for highly efficient and selective oxidation of 2,3,6-trimethylphenol

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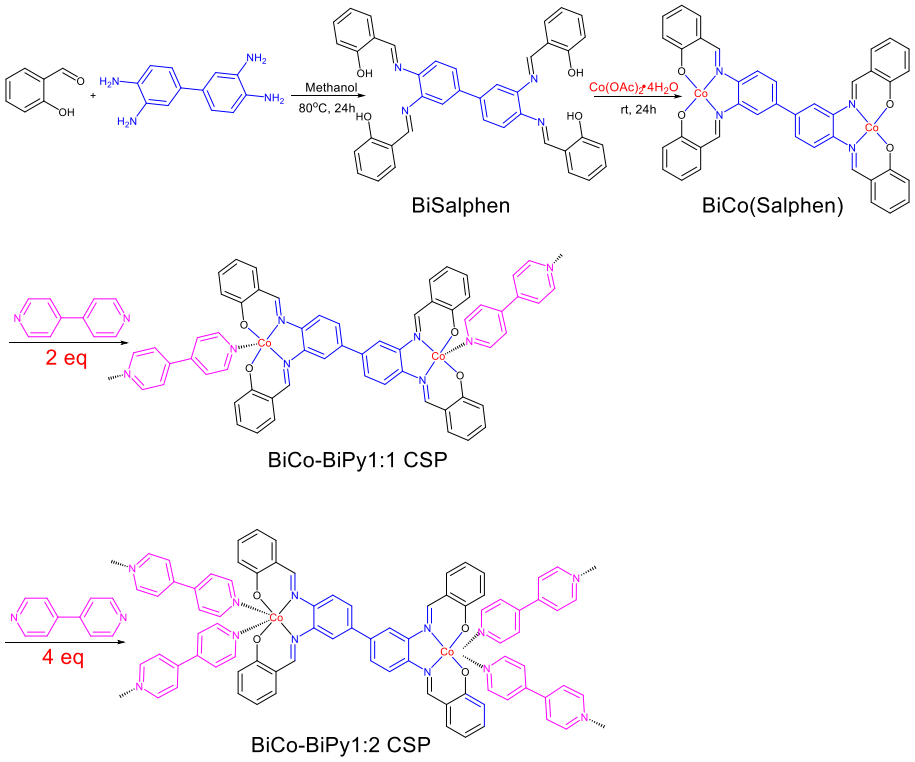
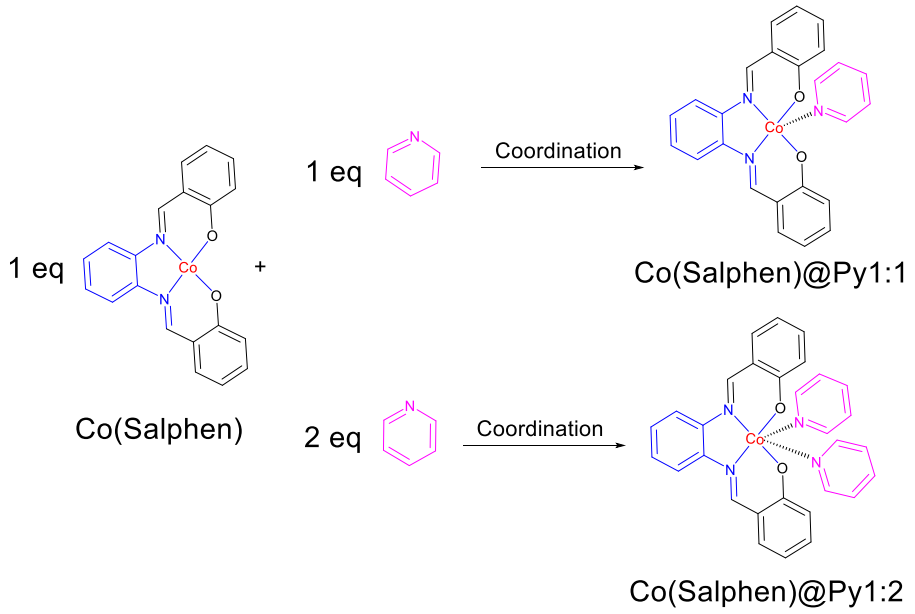


Scheme S1. Synthetic route of Bi[Co(Salphen)], BiCo-BiPy1:1 and CSP BiCo-BiPy1:1 CSP



Scheme S2. Model reactions between Co(Salphen) and pyridine

Procedure:

Preparation of ***Salphen***

In a three-necked round-bottom flask equipped with a constant pressure dropping funnel, a solution of 1,2-diaminobenzene (1.73 g, 16 mmol) in methanol (50 mL) was stirred at 80 ºC for 10 min. Subsequently, salicylaldehyde (4.1 g, 33.9 mmol) in methanol (50 mL) was dropped into the above mixture, and the reaction flask was kept stirring for 12 h at 80 ºC under N_2. After that, the mixture was cooled under 0 ºC for 12 h and the resulting precipitate was collected by filtration, washed with methanol and dried to afford the desired product as a yellow solid (5.1 g, yield 88%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 13.06 (s, 2H),8.65 (s, 2H), 7.41-7.36 (m, 6H), 7.26-7.24 (m, 2H), 7.07-7.05 (d, 2H) and 6.96-6.94 (t, 2H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ 163.7, 161.4, 142.6, 133.4, 132.3, 127.7, 119.9, 119.2, 119.0, 117.6,120.2, 119.1, 118.4 and 117.6 ppm.

Preparation of ***Co(Salphen)***

To a solution of $Co(OAc)_2 \cdot 4H_2O$ (4.8 g, 19.3 mmol) in methanol (100 mL), Salphen (5.0 g, 15.8 mmol) was added under N_2 atmosphere. The above mixture was stirred at 80 ºC for 12 h. After cooling to room temperature, the product CoSalphen was collected by filtration (7.0 g, 78%).

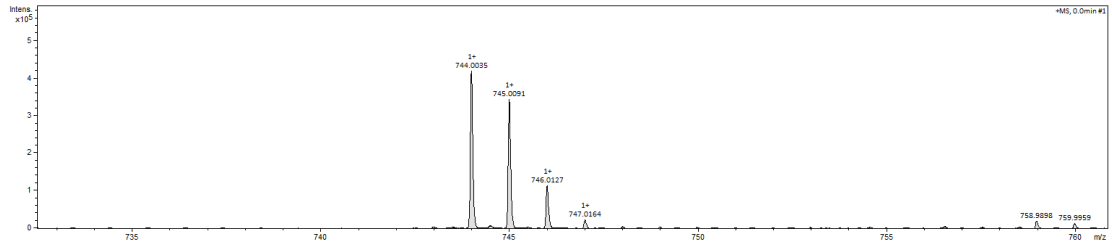


Figure. S1. HRMS of Bi[Co(Salphen)]

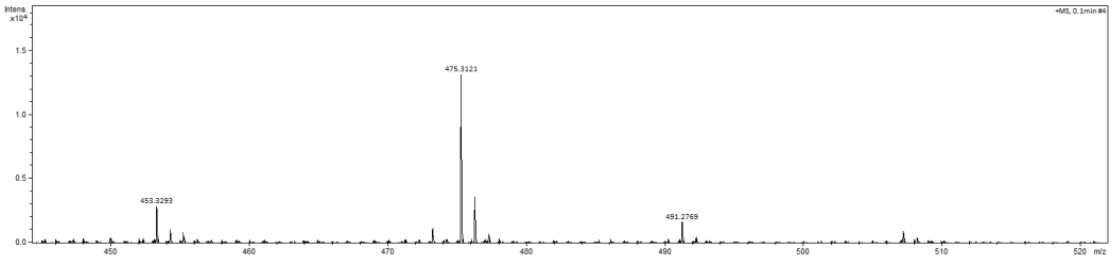


Figure. S2. HRMS of Co(Salphen)@Py 1:1

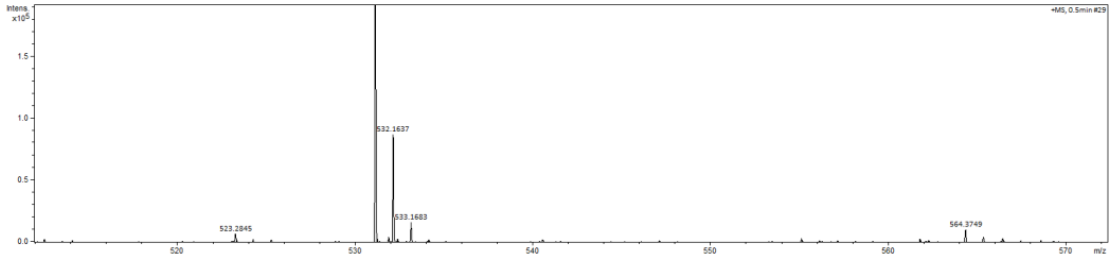


Figure. S3. HRMS of Co(Salphen)@Py 1:2

Table S1. Porosity parameters of BiCo@BiPy

Sample	S_{BET}[a]	V_{total}[b]	V_{micro}	V_{micro}/V_{total}	D_{pore}[c] nm
BiCo@BiPy 1:1	95	0.259	0.0338	0.13	8
BiCo@BiPy 1:4	58	0.116	0.0217	0.18	11

[a]Brunauer-Emmett-Teller surface area in $m^2\ g^{-1}$. [b]Pore volume determined from the N_2 isotherm at P/P_0=0.99 in $cm^3\ g^{-1}$. [c]Pore size derived from N_2 isotherm with the NLDFT approach.

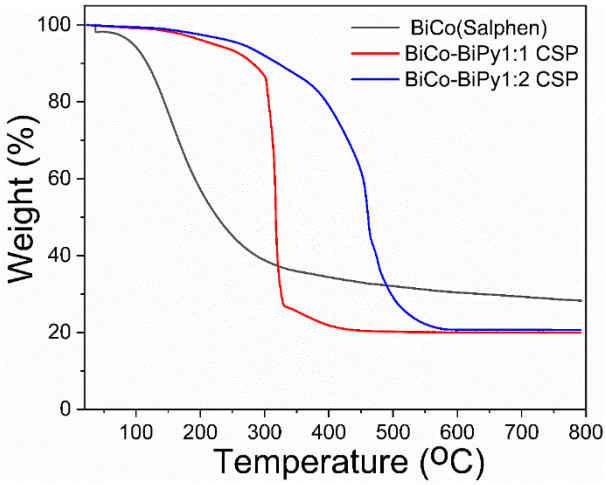
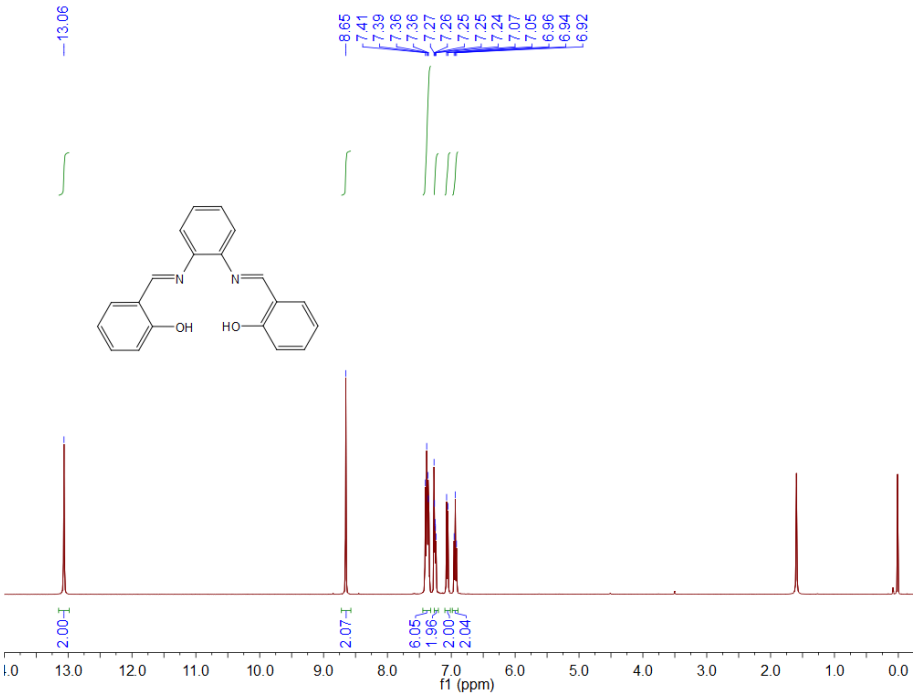


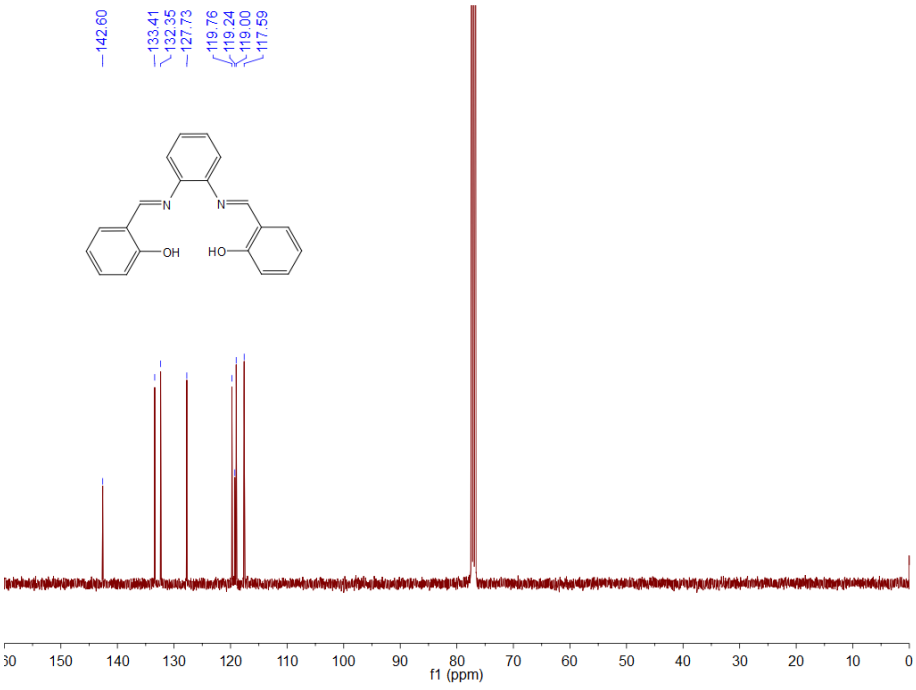
Figure. S4. TGA of BiCo(Salphen), BiCo@BiPy 1:1 and BiCo@BiPy 1:2

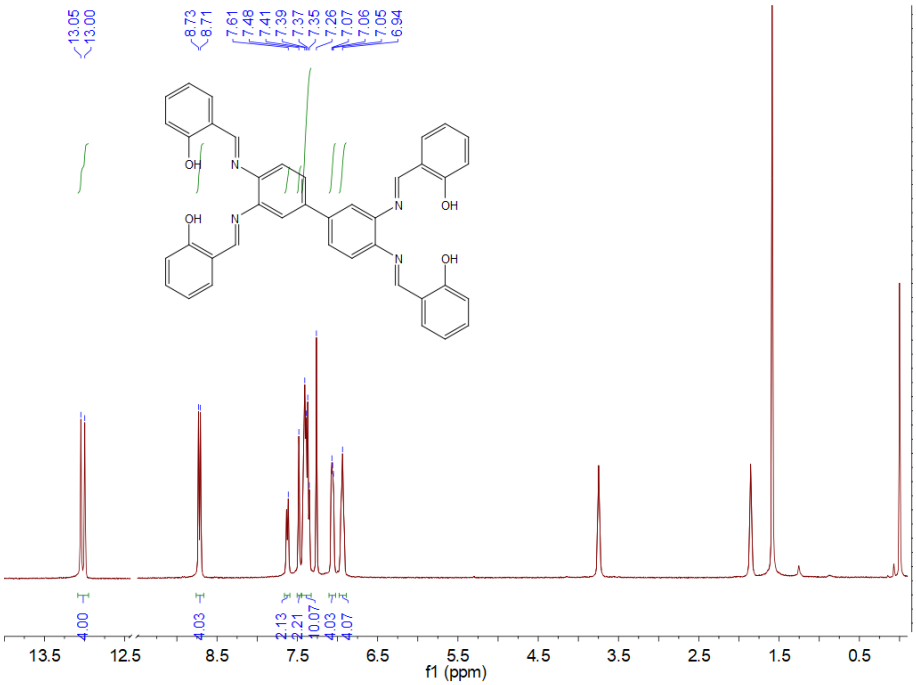
Table S2. Materials quantities and cost for the synthesis of trimethyl-1,4-benzoquinone

Chemical name	Weight of reagent (g or L)	Price (yuan/g or L)	Cost (RMB yuan)
[1,1'-biphenyl]-3,3',4,4'-tetraamine	1.0 g	2.0	2.0
THF	0.1	15	1.5
Methanol	0.25 L	4.0	0.1
Salicylaldehyde	0.1g	2.74	0.27
BiSalphen (yield: 91%)	0.25 g	1.44	0.36
Methanol	0.03 L	4.0	0.12
THF	0.1 L	15	1.5
$Co(OAc)_2 \cdot 4H_2O$	0.24 g	1.5	0.36
BiCo(Salphen) (yield: 89%)	0.1 g	2.23	0.223
THF	0.05 L	15	0.75
4,4-dipyridine	0.02 g	0.15	0.0032
DMF	0.15 L	8	1.2
Methanol	0.05 L	4.0	0.2
BiCo-BiPy1:1 CSP (yield: 51%)	0.01g	36.3	0.36
2,3,6-trimethylphenol	0.0681	2.0	0.14
Methanol	0.002	4.0	0.008
2,3,5-trimethylcyclohexa-2,5-diene-1,4-dione	N/A	2.93	N/A

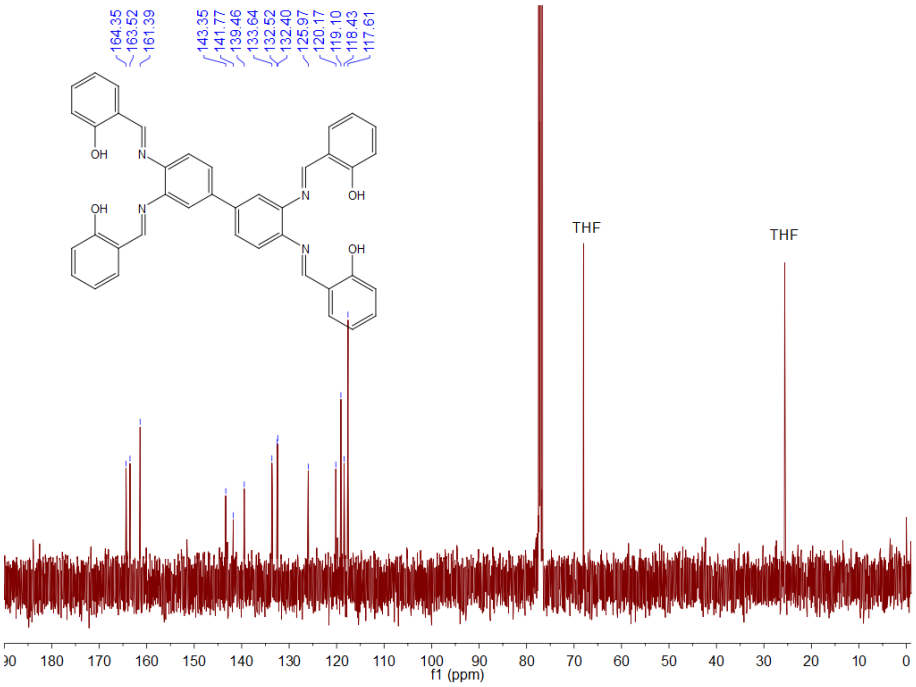


^{1}H NMR of Salphen

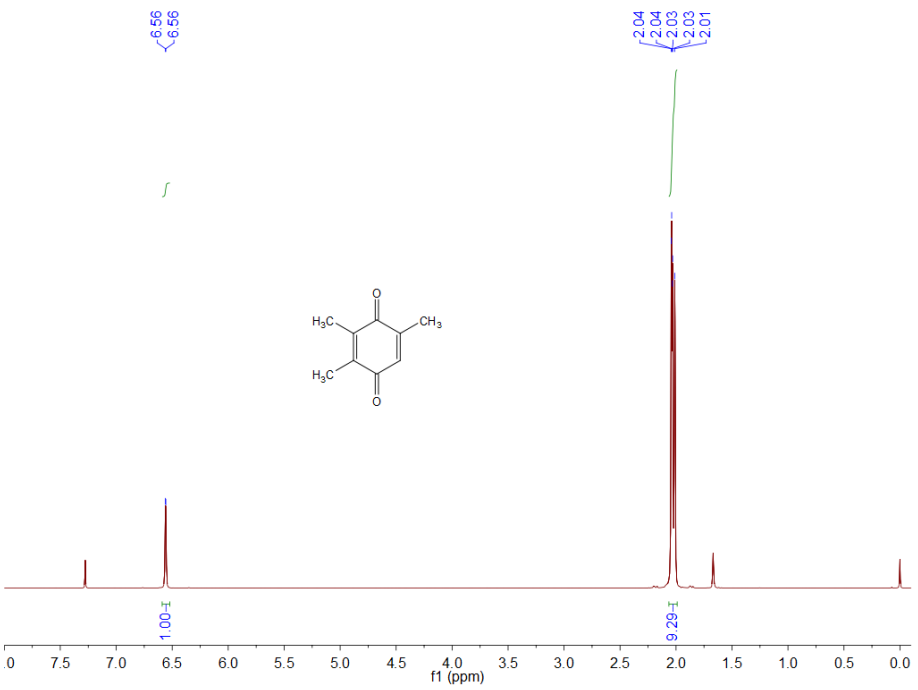




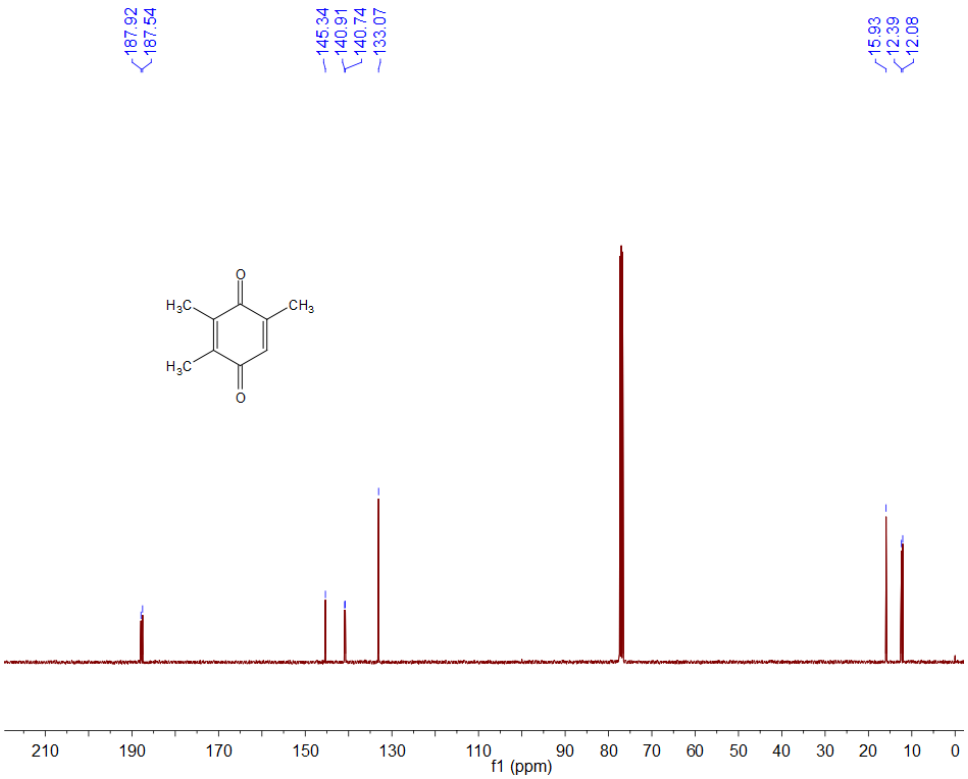
^{1}H NMR of BiSalphen



^{13}C NMR spectra of BiSalphen



^{1}H NMR of trimethyl-1,4-benzoquinone



^{13}C NMR of trimethyl-1,4-benzoquinone

Trimethyl-1,4-benzoquinone: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 6.56 (s, 1H) and 2.04-2.01 (m, 9H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ 187.9, 187.5, 145.3, 140.9, 140.7, 133.0, 15.9, 12.4 and 12.1 ppm.