Electron rich porous extended framework as heterogeneous catalyst for Diels-Alder reaction

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1. Materials and Methods:

All the reagents and solvents were obtained from different commercial sources and used without further purification, unless otherwise mentioned. All NMR spectra were recorded on a Bruker 400 MHz spectrometer. The chemical shifts (δ) in the ¹H NMR spectra are reported in ppm relative to tetramethylsilane (TMS) as internal standard (0.0 ppm). IR spectra were recorded on a Bruker ALPHA FT-IR spectrometer used in the 4000–400 cm⁻¹range. The elemental analyses were carried out on a PerkinElmer 240C element analyzer.Powder X-ray diffractions (XRD) were recorded on a *Philips X'pert Pro* using Cu-K α radiation ($\lambda = 1.5406$ Å).Thermogravimetric (TG) analysis of **MOF-1** andits activated sample were carried out on the *Metler-Toledo* thermal gravimetric analyser under nitrogen flow.Nitrogen, hydrogen and carbon dioxide adsorption experiments were performed on Quantachrome Quadrasorb automatic volumetric instrument. ESI-HRMS measurements were done on an Agilent 6538 UHD accurate-mass Q-TOF LC/MS instrument.

2. Synthesis and general characterization:

2.1. dimethyl 5'-bromo-[1,1':3',1''-terphenyl]-4,4''-dicarboxylate (1): Compound 1 was prepared according to the modified literature procedure.¹ In a two neck flask 1,3,5tribromobenzene (2.518 g, 8 mmol), methyl 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2yl)benzoate (4.613 g, 17.6 mmol), Na₂CO₃(4.240 g, 40 mmol), Pd(PPh₃)₄(200 mg) were taken under nitrogen atmosphere. To this 60 mL of degased solvent mixture of toluene-methanolwater (2:1:1) was added. The reaction mixture was stirred under nitrogen with reflux for 36 h. The solution was concentrated and extracted with ethyl acetate. The organic phase was washed for three times with brine solution and dried with anhydrous Na₂SO₄. The filtered solutions finally dried under reduce pressure. The crude product distinctly contain three products correspond to mono-, di- and tri-substituted products. Each spot was separated by column chromatography using silica gel as stationary phase (60-120 mesh) and 10% ethyl acetate hexane mixture as an elutant to obtain compound **1** (39% yield). ¹H NMR (CDCl3): δ (ppm) 8.15 (d, 4 H), 7.78 (s, 2 H), 7.75 (s, 1 H), 7.69 (d, 4 H, *J*= 8.0 Hz), 3.96 (s, 6 H).¹³C NMR (CDCl₃): δ (ppm) 167.183, 144.239, 143.121, 130.720, 130.648, 130.268, 127.719, 127.629, 125.468, 52.687.



Scheme 1. Synthetic route of preparation of H₄ADBTD.

2.2. Dimethyl-5'-pinacolatoborontel-[1,1':3',1''-terphenyl]- 4,4''-dicarboxylate (2):Compound 1 (850.5 mg, 2 mmol),bis(pinacolato)diboron (558.7 mg, 2.2 mmol), KOAC (1.570 g, 16 mmol), Pd(dppf)Cl₂ (45 mg) were charged with degased 30 mL 1,2-dimethoxyethane (DME) in a two neck flask under nitrogen atmosphere. The reaction mixture was refluxed with stirring under 2.3.

nitrogen atmosphere for 3 h. The reaction was cooled to room temperature and extracted with ethyl acetate (20 mL ×3). The combined organic phase was washed with brine solution (30 mL ×3) and dried with anhydrous Na₂SO₄. The filtered organic solvent dried over reduced pressure and the residue was purified by the column chromatography using silica gel and 10% ethyl acetate hexane mixture to obtain compound **2** (yield 78%). ¹H NMR (CDCl₃): δ (ppm)8.13 (d, 4 H), 8.09 (s, 2 H), 7.94 (s, 1 H),7.76 (d, 4 H), 3.95 (s, 6 H), 1.39 (s,12 H); ¹³C NMR (CDCl₃): δ (ppm) 166.953,145.225, 140.147, 133.320, 130.066, 129.077, 128.956, 127.253, 84.162, 52.125,24.877.

Tetramethyl-5',5''''-(anthracene-9,10-diyl)bis([1,1':3',1''-terphenyl]-4,4''-dicarboxylate)

(3): 9,10-dibromoanthracene (201.6 mg, 0.6 mmol), compound **2** (708.5 mg, 1.50 mmol), Na₂CO₃ (318 mg, 3 mmol) and Pd(PPh₃)₄(100 mg) were added to 40 mL degassed solvent mixture of toluene-methanol-water (2:1:1) in a two neck flask under nitrogen atmosphere. The solution was refluxed with stirring under nitrogen for 60 h. After the reaction was completed, mixture was concentrated under high vacuum and extracted with ethyl acetate. The organic phase was washed by brine solution (30 mL × 3) and finally dried in anhydrous Na₂SO₄. The filtered organic phase was dried under reduced pressure. The crude product was purified by small filtration column using silica gel as stationary phase and chloroform as elutant to get a bright white powder of **3** (yield 84%). ¹H NMR (CDCl₃): δ (ppm) 8.16 (d, 8H), 8.09 (s, 2H), 7.84 (q, 4H), 7.83 (s, 4H), 7.82 (d, 8H), 7.42 (q, 4H), 3.95 (s, 12H);¹³C NMR (CDCl₃): δ (ppm) 167.365,

145.370, 141.538, 141.026, 137.054, 130.849, 130.770, 130.421, 129.910, 127.780, 127.358, 126.093, 125.925, 52.706.

2.4.5',5''''-(anthracene-9,10-diyl)bis(([1,1':3',1''-terphenyl]-4,4''-dicarboxylicacid))

(H4ADBTD) (4): Compound 3 (475 mg, 0.55 mmol) was taken in 50 mL of mixed solvents

THF/MeOH/H₂O (v/v = 1:1:1) in a round bottom flask, NaOH (440 mg, 20mmol) was added to that solution and heated to reflux for 15 h. The blue solution was cooled to room temperature and organic solvent was removed using rotary evaporator. The aqueous phase was acidified using dilute hydrochloric acid to obtain pale yellow solid, which was filtered and washed several time by distilled water. Yield: 95%. IR spectra: v/cm^{-1} 3055, 1684, 1602, 1565, 1513, 1385, 1228, 1176, 1103, 1015, 847, 787, 701, 667, 515.¹H NMR (DMSO-d⁶): δ (ppm) 8.35 (s, 2H), 8.06 (s, 16H), 7.89 (s, 4H), 7.78 (q, 4H), 7.49 (q, 4H).¹³C NMR (DMSO-d⁶): δ (ppm) 168.022, 144.459, 141.271, 140.783, 137.104, 130.939, 130.276, 130.153, 128.304, 127.368, 126.904, 126.088.



Figure S1: ¹H-NMR of **3** in CDCl₃.



Figure S2: ¹³C-NMR of 3 in CDCl₃.



Figure S3: ¹H-NMR of H₄ADBTD recorded in DMSO-D₆.



Figure S4: ¹³C-NMR of H₄ADBTD recorded in DMSO-D₆.

3. Synthesis of MOF-1:

Cu(NO₃)₂·3H₂O (2.4 mg, 0.01mmol) and H₄ADBTD(4.1 mg, 0.005 mmol) were taken in a 5 mL scintillation vial. 3 mL dimethylformamide (DMF) was added and stirred at room temperature until complete dissolution. 5 drops of HBF₄were added to that solution and stirred for another 2 min. Then the reaction vial was placed in a programmable oven and heated at 90 °C for 1 day and cooled at a rate of 0.15°C/min. Green block shaped crystals (4 mg, 82%) of **MOF-1**were collected by filtration and washed with DMF (3 ×5 mL). IR spectra: $\nu/cm^{-1}1708$, 1592, 1513,1399, 1187, 1103, 1015, 848, 810, 776, 708, 673, 612, 528, 508, 406. Elemental analysis: Anal. Calcd for C₅₄H₃₀O₈Cu₂ (The sample was heated upto 200°C to remove all the coordinated and non-coordinated solvent molecules); C, 66.87; H, 3.53. Found: C, 66.55; H, 3.29.



Figure S5: IR spectra of H₄ADBTD and MOF-1.

3.1. Activation of MOF-1:

An as-synthesized **MOF-1** sample (about 150 mg) was soaked in methanol and the supernatant methanol discarded in every 6h (3 times) and fresh methanol was added subsequently each time. After methanol exchange, the sample was treated further in same way with acetone and dichloromethane to remove methanol and acetone respectively. Finally, the dichloromethane was decanted and the sample was dried under a dynamic vacuum at 120 °C for 6 h. Interestingly, the colour of the sample was changed from green to blue during the solvent exchange from DMF to DCM. This may be due to charge transfer interaction with the MOF and the solvents.



Figure S6: Visual colour change of **MOF-1** in different solvents. The initial green colour of the **MOF-1** changed towards blue as the polarity of the solvents shifted from polar to non-polar.

4. Powder X-ray diffraction and thermogravimetric analysis:

Powder X-ray diffraction (PXRD) patterns of both the as-made **MOF-1** and activated**MOF-1** asamples were recorded on a *Philips X'pert Pro* using Cu-K α radiation ($\lambda = 1.5406$ Å). The spectra were collected between the 2 θ of 5° and 40° at a scan speed of 5 deg/min. Graphite monochromator was used and the generator power settings are at 40kV and 40 mA. As indicated by the sharp peaks after removal of the guest molecules, **MOF-1a**was highly crystalline and maintains the framework stability. Thermogravimetric (TG) analyses of **MOF-1** and **MOF-1** awere carried out on the *Metler-Toledo* thermal gravimetric analyser with nitrogen flow (purge rate at 40ml/min, Figure S8). The heating rate was ramped from room temperature to 850 °C at 10 °C/min. The weight loss was due to the removal of guest molecules (DMF and non-coordinated water) and the coordinated water molecules. The framework was stable up to 300°C, before it collapsed. Moreover, the **MOF-1** is stable after removal of guest molecules.



Figure S7: PXRD of simulated, as-synthesized and activated MOF-1.



Figure S8: Thermo-gravimetric analysis (TGA) of MOF-1 and activated MOF-1a.



Figure S9: Schematic representation of combination of tetraacid with metal ion connectors to form three-dimensional porous network. The structure of **MOF-1** showing (a) hexagonal channel like pores along *b*-axis, (b) channels along *c*-axis and (c) pores along *a*-axis.

5. Single crystal X-ray diffraction analysis:

A crystal of MOF-1was coated with paratone oil, and the diffraction data were collected at 90 K on a Bruker SMART APEX CCD diffractometer using SMART/SAINT software. Intensity data were collected using graphite-monochromatized Mo-K α radiation (0.71073 Å^o) at 90 K. The

structure was solved by direct methods using the SHELX-97program incorporated into WinGX. Empirical absorption corrections were applied with SADABS. All nonhydrogen atoms were refined with anisotropic displacement coefficients. The hydrogen atoms bonded to carbon were included in geometric positions and given thermal parameters equivalent to 1.2 times those of the atom to which they were attached. The hydrogen atoms of the solvent water molecule were not included in the least-squares refinement. Structure refinement after modification of the data for the solvent molecules with the SQUEEZE routine of PLATON led to better refinement and data convergence. One ring of the anthracene moiety is not planer due to high thermal vibration of the C33 atoms. Several attempts to collect better data were failed because of the instability of the crystals. The crystallographic refinement parameters are given in Table 1.

Compound	$[Cu_2(ADBTD) \cdot (H_2O)_2] (MOF-1)$		
Formula	$C_{54}H_{34}O_{10}Cu_2$		
Μ	969.93		
Crystal system	Orthorhombic		
Space group	Ima2		
a/Å	37.755(2)		
b/Å	13.781(7)		
c/Å	29.867(1)		
α/°	90		
β/°	90		
$\gamma/^{o}$	90		

Table S1. Crystal data and structure refinement parameters for MOF-1:

$V/Å^3$	15540(1)
Z	8
Temperature (K)	90(2)
μ (Mo K α)mm ⁻¹	0.298
D, g/cm^3	0.468
Reflections collected	12323
$R1^{a}[I > 2\sigma(I)]$	0.0718
$wR2^{b} [I > 2\sigma(I)]$	0.2558
Goodness-of-fit	0.453

 ${}^{a}R1 = \Sigma \left[F_{o} - F_{c} \right] / \Sigma \left[F_{o} \right] {}^{b}wR2 = \Sigma \left[w (F_{o}^{2} - F_{c}^{2})^{2} \right] / w (F_{o}^{2})^{2} \right]^{1/2}$



Figure S10: Space filling structure of **MOF-1;** (a) hexagonal channel like pores along *b*-axis, (b) channels along *c*-axis and (c) pores along *a*-axis.

6. Gas Adsorption

All gas adsorption experiments (up to 1 bar) were performed on a Quantachrome Quadrasorb automatic volumetric instrument. N₂and H₂adsorptions study was carried out at 77 K whereas CO_2 adsorption was carried out at 273 K on the activated sample of **MOF-1**.150 mg of the sample was used, which had been degased at 493 K under a high vacuum (10-1 Pa) for 12 h prior to measurement of the isotherms. Theadsorbate was charged into the sample tube, and then the change of the pressure was monitored and the degree of adsorption was determined by the decrease of the pressure at the equilibrium state.



Figure S11: Pore size distribution of **MOF-1a** revealed that the compound possesses three different pores, which are 7.1 Å, 8.5 Å and 20.7 Å.

7. Typical procedure for 9-hydroxymethylanthracene adsorption experiment:

The initial absorption of 9-hydroxymethylanthracene was recorded using 2 mL (0.1 mM in ethanol) solution of it in a capped UV-Vis cuvette. To that 10 mg of activated **MOF-1a** was

added and the cuvette was capped properly. The absorption of the solution was recorded after several time intervals. The decrease of the absorbance with respect to the initial one indicates encapsulation of 9-hydroxymethylanthracene within the pore of the MOF-1. MOF-1 was recovered by filtration and PXRD was recorded. Similar PXRD with activated MOF-1a indicates that MOF-1 is stable in presence of 9-hydroxymethylanthracene.



FigureS12:(a)UV-vis spectra of 9-hydroxymethylanthracene before and after addition of MOF-1a at different time intervals.(b)PXRD of MOF-1a and after 9-hydroxymethylanthracene adsorption experiment.

8. Typical procedure for catalytic Diels-Alder reactions:

9-hydroxymethylanthracene (0.05 mmol) and the appropriate dienophile (0.05 mmol) were taken in 4 mL ethanol. To that 5 mg (11 mol %) of **MOF-1a** was added. The final mixture was stirred at mentioned temperature for one day along with blank reaction (without **MOF-1a**). The course of the reaction was monitored by TLC. The reaction mixture was cooled to room temperature, filtered to remove MOF, concentrated under vacuum. The NMR was recorder of the crude product and the yield was calculated from the ratio of unreacted 9-hydroxymethylanthracene and product formed. Yield of the non-catalyzed reaction was also measured in same way. Finally, the products were purified by preparative TLC using silica gel as stationary phase and hexane/ethyl acetate mixture was used as eluent. The PXRD of the recovered **MOF-1a** was recorded to ensure the stability of it under catalytic conditions. The PXRD of the **MOF-1a** after first run of catalysis (even after three different runs) indicated that it is quite stable under catalytic conditions and can be used for further catalytic process.



Figure S13: PXRDs of the MOF-1a (black), after first (red) and third runs (blue).

Diels-Alder reactions are known to be catalyzed (homogeneous catalysis) by Lewis acid like Cu(II).² In the present case, we have used MOF as a heterogeneous catalyst. A few similar reactions were carried out in the presence of $Cu(OAc)_2 \cdot 2H_2O$. The yields of the product are much less compared to the same reactions in presence of MOF (see the table below).

Diene	Dienophile	Temp.	Time	Yield without	Yield with
				catalyst	Cu(OAc) ₂ ·2H ₂ O
9-hydroxymethylanthracene	N-phenylmaleimide	40 °C	24 h	22%	42%
9-hydroxymethylanthracene	N-(1-pyrenyl)maleimide	50 °C	24 h	8%	23%

9. Characterization of Diels-Alder Products:

¹H-NMR (CDCl₃);δ (ppm): 8.206-8.157 (m, 3H), 8.110 (d, 1H), 8.088-7.997 (m, 2H), 7.730-7.650 (m, 4H), 7.593 (d, 1H), 7.573-7.461 (m, 4H), 7.367-7.239 (m, 2), 5.595 (d, 1H), 5.245 (m, 1H), 5.086 (m, 1H), 5.027 (d, 1H), 3.788 (d, 1H), 3.709 (m, 1H), 2.875 (t, 1H).

¹³C-NMR (CDCl₃); δ (ppm): 177.279, 177.059, 176.893, 142.854, 142.786, 142.364, 140.637, 140.266, 132.555, 131.296,

131.029, 129.099, 129.027, 127.872, 127.798, 127.692, 127.420, 127.348, 127.247, 127.143, 126.773, 126.568, 126.293, 126.124, 125.703, 125.499, 125.423, 125.309, 124.617, 123.953, 123.847, 123.644, 123.053, 121.234, 61.158, 50.133, 48.945, 48.819, 47.390, 46.550, 46.108.

HRMS (ESI): C₃₅H₂₄NO₃, [M+H]⁺ (506.1711) found: 506.1748;



¹H-NMR (CDCl₃); δ (ppm): 7.675 (d, 1H), 7.393 (m, 1H), 7.306 (m, 1H), 7.275-7.204 (m, 8H), 6.527 (m, 2H), 5.200 (m, 1H), 5.003 (m, 1H), 4.879 (d, 1H), 3.564 (d, 1H), 3.490 (m, 1H), 2.685 (t, 1H).



¹³C-NMR (CDCl₃); δ (ppm): 176.507, 176.473, 142.300, 139.761, 139.382, 131.669, 129.571, 129.324, 127.545, 127.510, 127.222, 127.121, 126.844, 125.883, 124.616, 123.838, 122.851,

60.708, 50.218, 48.404, 46.659, 46.372.

HRMS (ESI): C₂₅H₁₉NaNO₃, [M+Na]⁺ (404.1263) found: 404.1272;





¹H-NMR (CDCl₃); δ (ppm): 7.683 (d, 1H), 7.435 (m, 1H), 7.375 (m, 1H), 7.290-OMe 7.218 (m, 3H), 6.823 (d, 2H), 6.429 (d, 2H), 5.195 (q, 1H), 5.025 (q, 1H), 4.867 (d, 1H), 3.753 (s, 3H), 3.543 (d, 1H), 3.466 (m, 1H), 2.917 (t, 1H).

¹³C-NMR (CDCl₃); δ (ppm): 176.734, 160.124, 142.327, 139.859, 139.446, 128.025, 127.459, 127.103, 125.877,

124.587, 124.251, 123.817, 122.869, 114.904, 60.740, 55.861, 50.206, 48.347, 46.620, 46.353.

HRMS (ESI): C₂₆H₂₂NO₄, [M+H]⁺ (412.1504) found: 412.1532;



¹H-NMR (CDCl₃); δ (ppm): 7.672 (d, 1H), 7.587 (d, 2H), 7.441 (m, 1H), 7.389 (m, 1H), 7.282-7.216 (m, 5H), 6.715 (d, 2H), 5.197 (q, 1H), 5.046 (q, 1H), 4.877 (d, 1H), 3.598 (d, 1H), 3.511 (m, 1H), 2.561 (t, 1H).

¹³C-NMR (CDCl₃); δ (ppm): 175.925, 175.881, 142.110, 139.685, 139.346, 134.798, 131.425, 131.098, 127.605,

127.563, 127.307, 127.184, 126.662, 125.868, 124.617, 123.938, 122.770, 60.534, 50.314, 48.443, 46.612, 46.430.

HRMS (ESI): C₂₆H₁₉F₃NO₃, [M+H]⁺ (450.1272) found: 450.1302;





¹H-NMR (CDCl₃); δ (ppm): 7.676 (d, 1H), 7.435 (m, 1H), 7.378 (m, 1H), 7.289-^{Cl} 7.197 (m, 7H), 6.489 (d, 2H), 5.188 (q, 1H), 5.032 (q, 1H), 4.861 (d, 1H), 3.559 (d, 1H), 3.478 (m, 1H), 2.624 (t, 1H).

¹³C-NMR (CDCl₃); δ (ppm): 176.217, 176.182, 142.153, 139.693, 139.342, 135.210, 130.086, 129.801, 128.101, 127.571, 127.533, 127.280, 127.178, 125.867, 124.632, 123.908, 122.781, 60.571, 50.246, 48.372, 46.550, 46.373.

HRMS (ESI): C₂₅H₁₉ClNO₃, [M+H]⁺(417.0946) found: 416.1036;



¹H-NMR (CDCl₃); δ (ppm): 7.861 (d, 1H), 7.793 (d, 1H), 7.655 (d, 1H), 7.513-7.378 (m, 8H), 7.321-7.173 (m, 2H), 7.109 (t, 1H), 5.345 (d, 1H), 5.226 (m, 1H), 5.061 (m, 1H), 4.962 (s, 1H), 3.708 (d, 1H), 3.631 (m, 1H), 2.858 (t, 1H).

¹³C-NMR (CDCl₃); δ (ppm): 177.033, 176.630, 142.841, 140.561, 140.185, 134.495, 130.469, 129.465, 128.937, 128.547, 127.787, 127.576, 127.453, 127.211, 126.837, 126.477, 126.293,

126.047, 125.725, 125.561, 124.582, 123.787, 123.578, 122.980, 122.075, 61.159, 50.038, 48.859, 47.350, 46.926, 46.484, 46.004.

HRMS (ESI): C₂₉H₂₁NaNO₃, [M+Na]⁺ (454.1419) found: 454.1435;





Two distinct isomeric products were formed (54% and 46%) which are not separable by chromatographic method. ¹H-NMR (CDCl₃); δ (ppm): 7.672 and



7.608 (d, 1H), 7.413 (m, 2H), 7.356-7.056 (m, 9H), 6.927 and 5.518 (d, 1H), 5.195 (m, 1H), 5.023 (m, 1H), 4.891 (m, 1H), 3.592 (d, 1H), 3.523 (m, 1H), 2.968 and 2.710 (t, 1H).

OH OH ¹³C-NMR (CDCl₃); δ (ppm): 176.758, 176.369, 176.269, 142.887, 142.329, 142.276, 140.317, 139.927, 139.854, 139.514, 136.341, 135.886, 131.424, 131.226, 130.963, 129.976, 128.087, 127.688, 127.552, 127.514, 127,327, 127,207, 127.116, 127.083, 127.029, 126.144, 125.984, 124.584, 124.506, 123.851, 123.500, 123.447, 122.944, 61.246, 60.721, 50.228, 49.845, 48.576, 47.139, 46.784, 46.391, 45.856, 18.013, 16.725.

HRMS (ESI): C₂₆H₂₂NO₃, [M+H]⁺ (396.1555) found: 396.1589;

$\sum_{i=1}^{n} \sum_{j=2}^{n} \sum_{i=1}^{n} \sum_{j=2}^{n} \sum_{i=1}^{n} \sum_{j=1}^{n} \sum_{j=1}^{n} \sum_{i=1}^{n} \sum_{i=1}^{n} \sum_{j=1}^{n} \sum_{i=1}^{n} \sum_{$





Two distinct isomeric products formed (74% and 26%) which are not



formed (74% and 26%) which are not separable by chromatographic method. ¹H-NMR (CDCl₃); δ (ppm): 7.654 and 7.591 (d, 1H), 7.423-7.365 (m, 2H), 7.287-7.185 (m, 6H), 6.875 and 5.617 (d, 1H), 6.444 (d, 1H), 6.319 (m, 1H), 5.172 (m, 1H), 5.003 (m, 1H), 4.849 (d, 1H), 3.752 and

3.741 (s, 3H), 3.699 and 3.378 (s, 3H), 3.545 (d, 1H), 3.502 (m, 1H), 3.009 and 2.769 (t, 1H).

¹³C-NMR (CDCl₃); δ (ppm):176.814, 176.682, 176.603, 176.300, 162.054, 161.963, 156.062, 155.942, 143.167, 143.125, 142.408, 142.350, 140.218, 139.999, 139.805, 139.629, 129.618, 129.433, 127.381, 127.321, 127.137, 127.040, 126.996, 126.895, 125.904, 124.558, 124.460, 123.758, 123.321, 123.270, 122.973, 113.293, 113.221, 105.215, 104.915, 99.938, 61.394, 60.872, 56.192, 55.944, 50.155, 49.751, 48.585, 47.252, 46.880, 46.399, 45.835.

HRMS (ESI): C₂₇H₂₃NaNO₅, [M+Na]⁺ (464.1474) found: 464.1482;



OH



¹H-NMR (CDCl₃); δ (ppm): 7.587 (d, 1H), 7.378 (m, 1H), 7.243-7.105 (m, 7H), 7.088 (m, 2H), 6.619 (d, 2H), 5.104 (m, 1H), 4.972 (m, 1H), 4.317 (s, 2H), 3.406 (d, 1H), 3.341 (m, 1H), 2.873 (t, 1H).

 $^{13}\text{C-NMR}$ (CDCl₃); δ (ppm): 177.189, 176.899, 142.718, 139.621, 139.263, 135.172, 128.869, 127.844, 127.752,

127.438, 127.056, 126.958, 125.621, 124.480, 123.537, 122.834, 61.016, 49.707, 48.298, 46.719, 45.874, 42.554.

HRMS (ESI): C₂₆H₂₂NO₃, [M+H]⁺ (396.1555) found: 396.1590;





¹³C-NMR (CDCl₃); δ (ppm): 176.023, 175.963, 175.896, 142.245, 139.620, 139.279, 131.929,

129.651, 127.564, 127.488, 127.209, 127.076, 126.430, 125.747, 124.552, 124.311, 123.970, 122.663, 60.474, 51.324, 50.221, 48.298, 46.365.

HRMS (ESI): C₄₄H₃₃N₂O₆, [M+H]⁺ (685.2294) found: 685.2325;





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