

Supplementary Information for:

Rigid Dendritic Gelators Based on Oligocarbazoles

*Xinchun Yang, Ran Lu, * Fangyuan Gai, Pengchong Xue, and Yong Zhan*

State Key Laboratory of Supramolecular Structure and Materials, College of Chemistry,
Jilin University, Changchun 130012, P. R. China

E-Mail: luran@jlu.edu.cn

General information: ^1H NMR and ^{13}C NMR spectra were recorded on Mercury plus 500 MHz using CDCl_3 as solvent. Mass spectra were performed on Agilent 1100 MS series and AXIMA CFR MALDI/TOF (Matrix assisted laser desorption ionization/Time-of-flight) MS (COMPACT). C, H, and N elemental analyses were performed on a Perkin-Elmer 240C elemental analyzer. UV-vis absorption spectra were determined on a Shimadzu UV-1601PC Spectrophotometer. Fluorescence spectra were carried out on a Shimadzu RF-5301 Luminescence Spectrometer. Fluorescence microscopy images were taken on Fluorescence Microscope (Olympus Reflected Fluorescence System BX51, Olympus, Japan). FT-IR spectra were measured using a Nicolet-360 FT-IR spectrometer by incorporating samples in KBr pellet. X-Ray diffraction (XRD) patterns were carried out on a Japan Rigaku D/max- γ A instrument. XRD was equipped with graphite monochromatized Cu-K α radiation ($\lambda = 1.5418\text{\AA}$), employing a scanning rate of 0.02 s^{-1} in the 2θ range from 0.7 to 10. Scanning electron microscopy (SEM) observations were carried out on a Japan Hitachi model X-650 Scanning electron microscope. The samples for these measurements were prepared by casting the organogel on silicon wafers and dried at room temperature, and then were coated by gold. Transmission electron microscopy (TEM) was taken with a Hitachi mode H600A-2 apparatus by wiping the samples onto a 200-mesh copper grid followed by naturally evaporating the solvent.

Synthesis and Characterizations:

The synthetic routes for the dendrons 1-3 were shown in Scheme S1, and 3,6-diiodo-9-tosyl-9H-carbazole (**6**) was prepared according to the literatures.¹⁻³

3, 6-di-tert-butyl-9H-carbazole (4):

Carbazole (5.0 g, 0.03 mol) and anhydrous AlCl_3 (4.0 g, 0.03 mol) were dissolved in CH_2Cl_2 (100 mL). When the mixture was cooled to $0\text{ }^\circ\text{C}$, a solution of $^t\text{BuCl}$ (6.6 mL, 0.06 mol) in CH_2Cl_2 (20 mL) was added slowly. After that, the ice-bath was removed and the resulting mixture was stirred for 24 h at room temperature. Then, the mixture was poured into water, extracted with CH_2Cl_2 , and dried with anhydrous MgSO_4 . Solvent was evaporated to afford the crude products, which were recrystallized from petroleum ether twice to give 4.5 g (54%) of a white solid, mp: $233.0\text{-}235.0\text{ }^\circ\text{C}$. $^1\text{H-NMR}$ (CDCl_3 , 500

MHz, ppm): δ = 8.08 (2 H, s, Ar-H), 7.86 (1 H, s, N-H), 7.48 (2 H, d, Ar-H), 7.33 (2 H, d, Ar-H), 1.46 (18 H, s, -CH₃). MS, m/z: cal.: 279.2, found: 280.0 [M⁺ + H].

3,6-di-tert-butyl-9-(4-methoxycarbonyl)-9H-carbazole (5):

3,6-Di-tert-butyl-9H-carbazole **4** (2.8 g, 0.01 mol), 1-iodo-4-methbenzoate (3.0 g, 0.012 mol), Cu₂O (3.0 g, 0.021 mol), and DMAc (15 mL) were filled sequentially into a seal-tube under nitrogen atmosphere and heated to 160 °C in oil bath for 24 h. Then, the mixture was cooled to room temperature and filtrated. The filtrate was poured into 300 mL H₂O and stirred for 20 min. The crude products were collected by filtration, and purified by chromatography (silica gel, petroleum ether/ethyl acetate, v:v = 10:1) to give 3.3 g (80%) of a white solid, mp: 172.0-174.0 °C. ¹H-NMR (CDCl₃, 500 MHz, ppm): δ = 8.25 (2 H, d, Ar-H), 8.14 (2 H, s, Ar-H), 7.67 (2 H, d, Ar-H), 7.47 (2 H, d, Ar-H), 7.42 (2 H, d, Ar-H) 3.98 (3 H, s, -COOMe), 1.47 (18 H, s, -CH₃). MS, m/z: cal.: 413.5, found: 414.3 [M⁺ + H].

4-(3,6-di-tert-butyl-9H-carbazol-9-yl) benzoic acid (1):

A mixture of 3,6-di-tert-butyl-9-(4-methoxycarbonyl)-9H-carbazole **5** (2.5g, 6.0 mmol), 20 mL of methanol and 20 mL of 1 M aqueous NaOH was stirred and refluxed for 10 h. After cooling to room temperature, the mixture was poured into 100 mL H₂O and acidified by addition of 40 mL of 1M aqueous HCl. The crude products were collected by filtration, and purified by chromatography (silica gel, petroleum ether/ethyl acetate, v:v = 1:1) to give 2.2 g (92%) of a white solid, mp: 202.0-204.0 °C. ¹H-NMR (CDCl₃, 500 MHz, ppm): δ = 8.34 (2 H, d, Ar-H), 8.14 (2 H, s, Ar-H), 7.67 (2 H, d, Ar-H), 7.73 (2 H, d, Ar-H), 7.50-7.47 (4 H, m, Ar-H), 1.47 (18 H, s, -CH₃) (See Fig. S4 and S5). ¹³C NMR (CDCl₃, 125 MHz) [ppm]: δ = 171.6, 144.2, 138.9, 132.4, 127.4, 126.3, 124.4, 124.3, 116.8, 109.7, 35.2, 32.4 (See Fig. S10). Elemental analysis calcd (%) for C₂₇H₂₉NO₂ : C, 81.17; H, 7.32; N, 3.51; found: C, 81.28; H, 7.22; N, 3.48. MS, m/z: cal.: 399.2, found: 399.4 [M⁺] (See Fig. S13).

3,6-di-tert-butyl-9-(3-(3,6-di-tert-butyl-9H-carbazol-9-yl)-9H-carbazol-6-yl)-9H-carbazole (7):

3,6-Ditert-butyl-9H-carbazole **4** (7.6 g, 0.028 mol), 3,6-diiodo-9-tosyl-9H-carbazole **6**

(7.2 g, 0.012 mol), Cu₂O (6.0 g, 0.042 mol), and DMAc (25 mL) were filled sequentially into a seal-tube under nitrogen atmosphere and heated to 180 °C in oil bath for 24 h. Then, the mixture was cooled to room temperature and filtrated. The filtrate was poured into 500 mL H₂O and stirred for 20 min. The crude products were collected by filtration, and recrystallized from EtOH:THF (v:v = 1:1,) to give 8.4 g (76 %) of a white solid. The obtained products (8.4 g, 9.6 mmol) were dissolved in THF (24 mL), DMSO (12 mL) and H₂O (4.8 mL), then KOH (10.8 g, 0.19 mol) was added. The mixture was refluxed for 4 h (monitored by TLC), cooled to room temperature, neutralized by HCl, and then poured into water to give the white solid, which was recrystallized from EtOH:THF (v:v = 4:1,) to give 6.2 g (90%) of a white solid, mp: >250 °C. ¹H-NMR (CDCl₃, 500 MHz, ppm): δ = 8.41 (1 H, s, N-H), 8.15 (6 H, d, Ar-H), 7.67 (2 H, d, Ar-H), 7.60 (2 H, d, Ar-H), 7.45 (4 H, d, Ar-H), 7.30 (4 H, d, Ar-H), 1.46 (36 H, s). MS, m/z: cal.: 721.4, found: 722.0 [M⁺+H].

3,6-bis(3,6-di-tert-butyl-9H-carbazol-9-yl)-9-(4-methoxycarbonyl)-9H-carbazole (8):

By following the synthetic procedure for compound **5** and using compound **7** (3.6 g

5.0 mmol), 1-iodo-4-methbenzoate (1.7 g, 6.4 mmol), Cu₂O (2.0 g, 14.9 mmol), and DMAc (15 mL) as reagents, 3.1 g (76%) of **8** was obtained after chromatography (silica gel, petroleum ether/ethyl acetate, v:v = 10:1,) as a white solid, mp: >250 °C. ¹H-NMR (CDCl₃, 500 MHz, ppm): δ = 8.41 (2 H, d, Ar-H), 8.26 (2 H, s, Ar-H), 8.18 (4 H, s, Ar-H), 7.86 (2 H, d, Ar-H), 7.71 (2 H, d, Ar-H), 7.64 (2 H, d, Ar-H), 7.47 (4 H, d, Ar-H), 7.35 (4 H, d, Ar-H), 4.04 (3 H, s, -COOMe), 1.48 (36 H, s, -CH₃). MS, m/z: cal.: 855.5, found: 856.2 [M⁺+H].

4-(3,6-bis(3,6-di-tert-butyl-9H-carbazol-9-yl)-9H-carbazol-9-yl) benzoic acid (2):

By following the synthetic procedure for compound **1**, compound **8** (2.6 g 3.0 mmol) was hydrolyzed in 20 mL of methanol and 20 mL of 1 M aqueous NaOH. The crude product was purified by chromatography (silica gel, petroleum ether/ethyl acetate, v:v = 1:1) to give 2.3 g (90%) of a white solid, mp: >250 °C. ¹H-NMR (CDCl₃, 125 MHz) [ppm]: δ = 143.1, 140.4, 132.8, 132.0, 127.0, 126.6, 125.0, 124.0, 123.6, 119.8, 116.7, 111.5, 109.4, 35.2, 32.4 (See Fig. S11). Elemental analysis calcd (%) found: C, 85.21; H, 7.12;

N,4.90. MS, m/z: cal.: 841.5, found: 842.1[M⁺ + H] (See Fig. S14).

4-(9H-Carbazol-9-yl)benzaldehyde (9):

Carbazole (3.34 g, 20 mmol), 4-iodobenzaldehyde (5.0 g, 21.6 mmol), Cu₂O (4.0 g, 27.8 mmol), and DMAc (15 mL) were added sequentially to a sealed tube under nitrogen and heated at 160 °C in an oil bath for 20 h. Then the mixture was cooled to room temperature and filtered. The filtrate was poured into H₂O (300 mL) and stirred for 20 min. The solid was collected by filtration and recrystallized from EtOH to give 4.1 g (76%) of a light-yellow solid, mp. 156.0–158.0 °C. ¹H NMR (CDCl₃, 500 MHz, ppm): δ = 10.14 (1 H, s, -CHO), 8.29 (2 H, d, Ar-H), 8.22 (2 H, d, Ar-H), 7.92 (2 H, d, Ar-H), 7.54 (2 H, d, Ar-H), 7.49 (2 H, t, Ar-H), 7.36 (2 H, t, Ar-H). MS: cal: 271.3; found 272.5 [M + H].

4-(3,6-Diiodo-9H-carbazol-9-yl)benzaldehyde (10):

Compound **9** (3.0 g, 11.1 mmol) was dissolved in refluxing acetic acid (75 mL). The solution was cooled to 80 °C, KI (2.48 g, 14.9 mmol) and KIO₃ (1.8 g, 8.4 mmol) were added, and the system was maintained at 80 °C for another 5 h. After that, the mixture was cooled to room temperature, filtered, and then the collected solid was poured into 5% NaHSO₃ (200 mL) to remove I₂ and KIO₃. The solid was collected by filtration and recrystallized from THF to give 4.8 g (82%) of a light-yellow solid, mp: > 250 °C. ¹H NMR (CDCl₃, 500 MHz, ppm): δ = 10.14 (1 H, s, -CHO), 8.76 (2 H, s, Ar-H), 8.21 (2 H, d, Ar-H), 7.90 (2 H, d, Ar-H), 7.77 (2 H, d, Ar-H), 7.35 (2 H, d, Ar-H). MS: cal: 523.1; found 523.8 [M + H].

4-{3,6-Bis[3,6-bis(3,6-di-tert-butyl-9H-carbazol-9-yl)-9H-carbazol-9-yl]-9H-carbazol-9-yl}benzaldehyde (11):

3,6-Di-*tert*-butyl-9-[3-(3,6-di-*tert*-butyl-9H-carbazol-9-yl)-9H-carbazol-6-yl]-9H-carbazole (**7**) (5.0 g, 6.9 mmol), 4-(3,6-diiodo-9H-carbazol-9-yl)benzaldehyde (**10**) (1.5 g, 2.9 mmol), Cu₂O (2.1 g, 14.6 mmol), and DMAc (20 mL) were added sequentially to a sealed tube under nitrogen and heated at 190 °C in oil bath for 24 h. Then the

mixture was cooled to room temperature and filtered. The filtrate was poured into H₂O (400 mL) and stirred for 20 min. The solid was collected by filtration and was purified by chromatography (silica gel, petroleum ether/CH₂Cl₂, v:v = 1:2) to give 1.9 g of a white solid which was further recrystallized three times from EtOH/THF (v:v = 2:1) to give 0.5 g (10%) of a white solid, mp: > 250 °C. ¹H NMR (CDCl₃, 500 MHz, ppm): δ = 10.23 (1 H, s, -CHO), 8.56 (2 H, s, Ar-H), 8.32–8.27 (6 H, m, Ar-H), 8.15 (8 H, s, Ar-H), 8.04 (2 H, d, Ar-H), 7.87 (4 H, s, Ar-H), 7.65–7.60 (8 H, m, Ar-H), 7.44 (8 H, d, Ar-H), 7.33 (8 H, d, Ar-H), 1.45 (72 H, s, -CH₃). MS: cal: 1711.3; found 1712.3 [M⁺ + H].

4-{3,6-Bis[3,6-bis(3,6-di-tert-butyl-9H-carbazol-9-yl)-9H-carbazol-9-yl]-9H-carbazol-9-yl}benzoic acid (3):

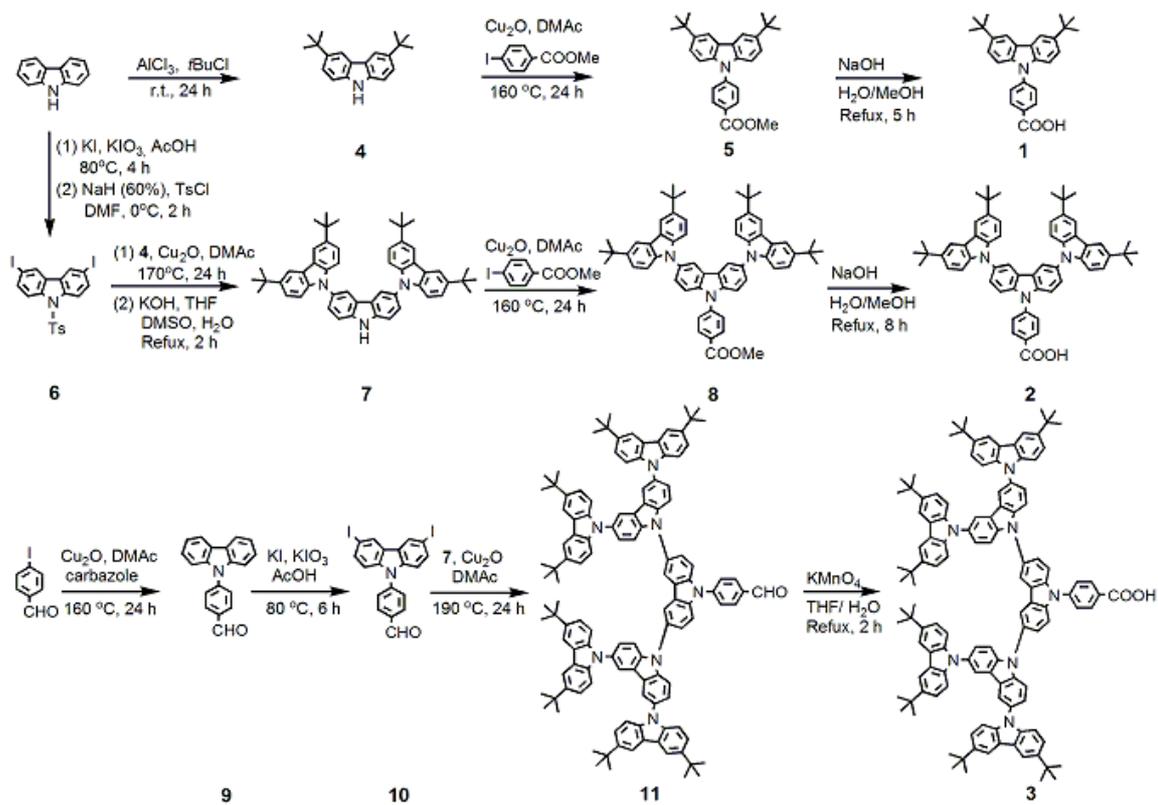
The solution of 4-{3,6-Bis[3,6-bis(3,6-di-tert-butyl-9H-carbazol-9-yl)-9H-carbazol-9-yl]-9H-carbazol-9-yl}benzaldehyde (**11**) (0.4 g, 0.23 mmol) in 80 mL THF was stirred and refluxed. Then, the saturated aqueous solution of KMnO₄ was added dropwise until the color of purple was maintained. The mixture was filtered and washed with THF for several times. The filtrate was poured into H₂O (300 mL) and stirred for 20 min. The solid was collected by filtration and was purified by chromatography (silica gel, methanol/CH₂Cl₂, v:v = 1:15) to give 0.3 g (76 %) of a white solid, mp 120-122 °C. ¹H NMR (CDCl₃, 500 MHz): δ = 8.49 (4 H, d Ar-H), 8.35 (4 H, s, Ar-H), 8.24 (8H, s, Ar-H), 8.05 (2 H, d, Ar-H), 7.96 (4 H, s, Ar-H), 7.40-7.69 (8 H, m, Ar-H), 7.54(8 H, d, Ar-H), 7.43 (8 H, d, Ar-H), 1.54 (72 H, s, -CH₃) (See Fig. S8 and S9). ¹³C NMR (CDCl₃, 125 MHz) [ppm]: δ = 143.0, 141.7, 140.6, 131.2, 127.2, 126.5, 125.0, 124.2, 124.0, 123.5, 120.0, 116.6, 112.2, 111.4, 109.5, 35.1, 32.5 (See Fig. S12). Elemental analysis calcd (%) for C₁₂₃H₁₁₉N₇O₂ : C, 85.53; H, 6.94; N, 5.68; found: C, 85.45; H, 7.01; N, 5.60. MS, m/z: cal.: 1726.0, found: 1727.5[M⁺+H] (See Fig. S15).

Table S1 Gelation properties of dendrons **1**, **2** and **3** in various solvents.

Solvent	1	2	3
hexane	P	P	P
cyclohexane	P	P	p
petroleum ether	I	P	p
toluene	G ^a	S	S
THF	S	S	S
chloroform	S	S	S
acetonitrile	P	P	I
ethyl acetate	S	S	S
ethanol	S	S	I
DMF	S	S	S
chloroform/hexane (v/v = 1/10)	P	G ^b	S
chloroform/cyclohexane (v/v = 1/12)	P	G	S

G: gel, S: soluble, I: insoluble, P: precipitate. a: two-component gel based on **1** and

1,6-diaminohexane, cgc = 5.5×10^{-4} M, b: cgc = 3.5×10^{-4} M.



Scheme S1 Syntheses of dendrons 1, 2 and 3.

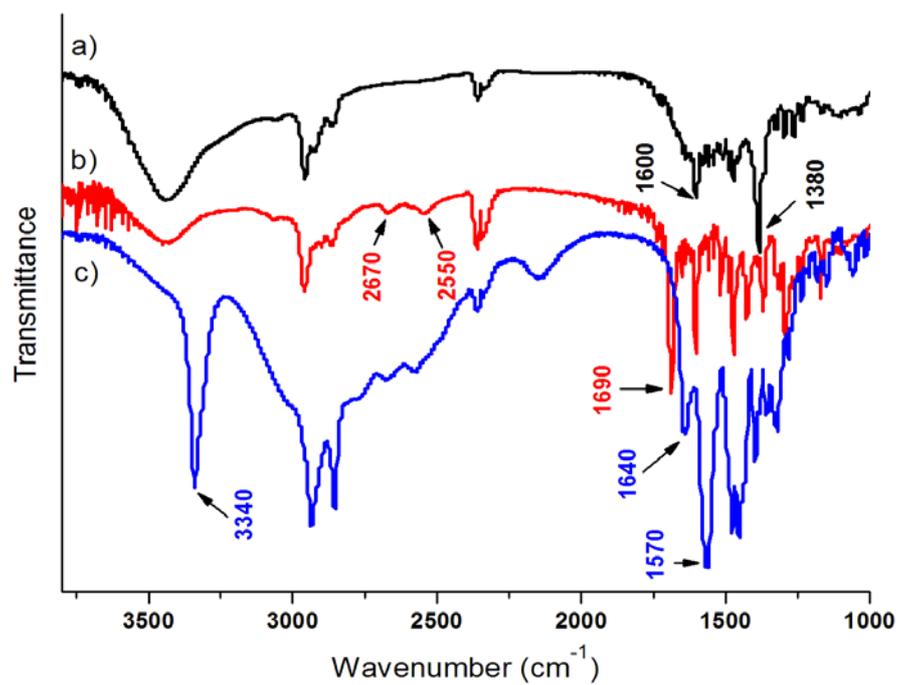


Fig. S1 FT-IR spectra of a) two-component gel based on **1** and 1,6-diaminohexane (the molar ratio is 2:1), b) the powder of **1** and c) 1,6-diaminohexane.

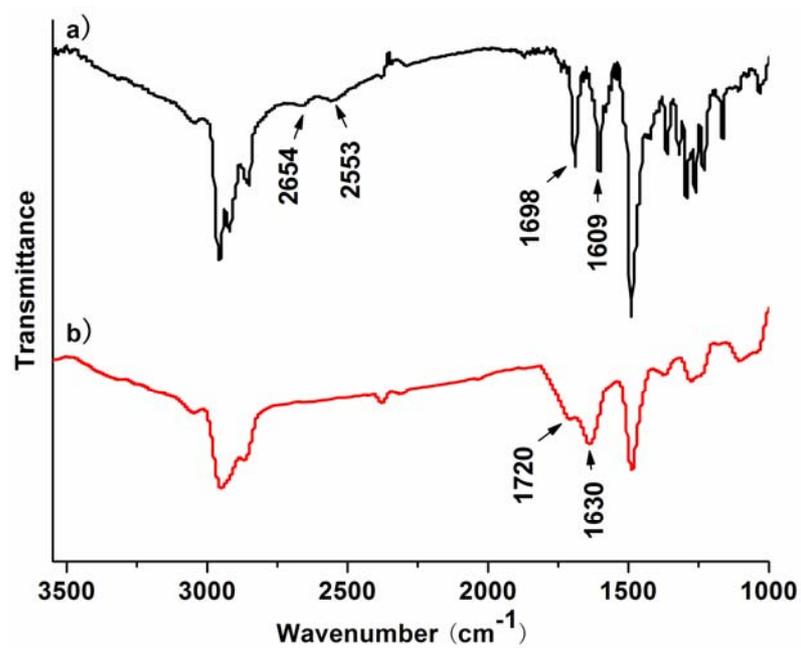


Fig. S2 FT-IR spectra of dried gel **2** (a) and the powder of **3** (b).

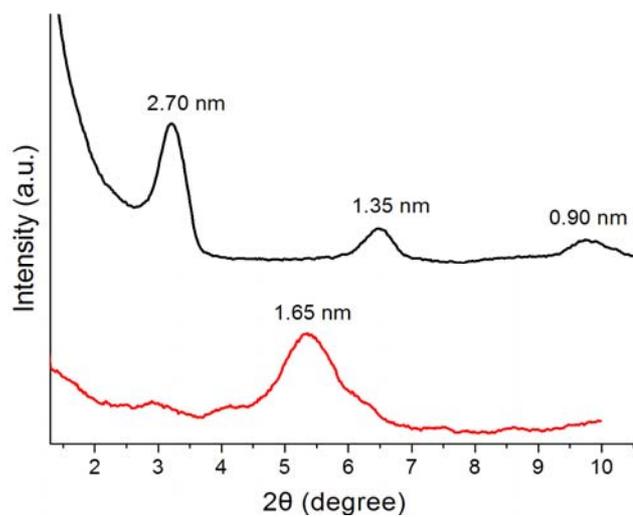


Fig. S3 XRD patterns of dried two-component gel based on **1** and 1,6-diaminohexane (—, the molar ratio is 2:1), and dried gel **2** (—).

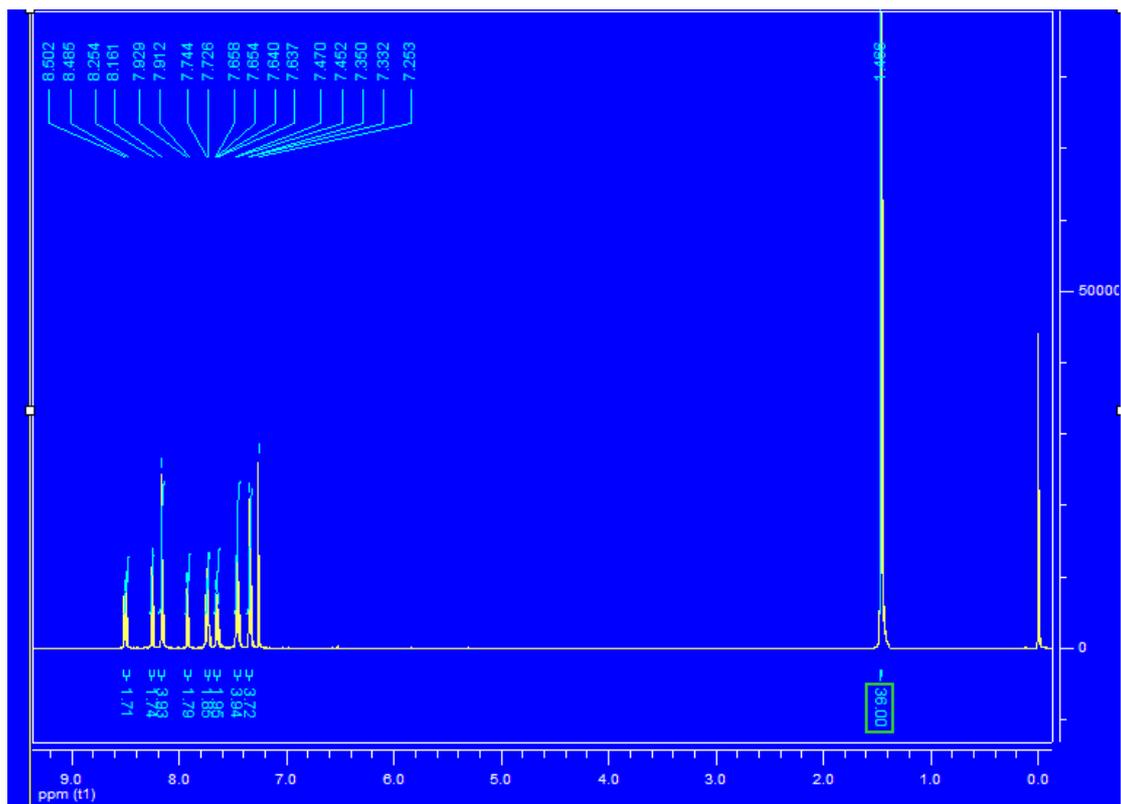


Fig. S4. ^1H NMR spectrum (500 MHz) of **1**.

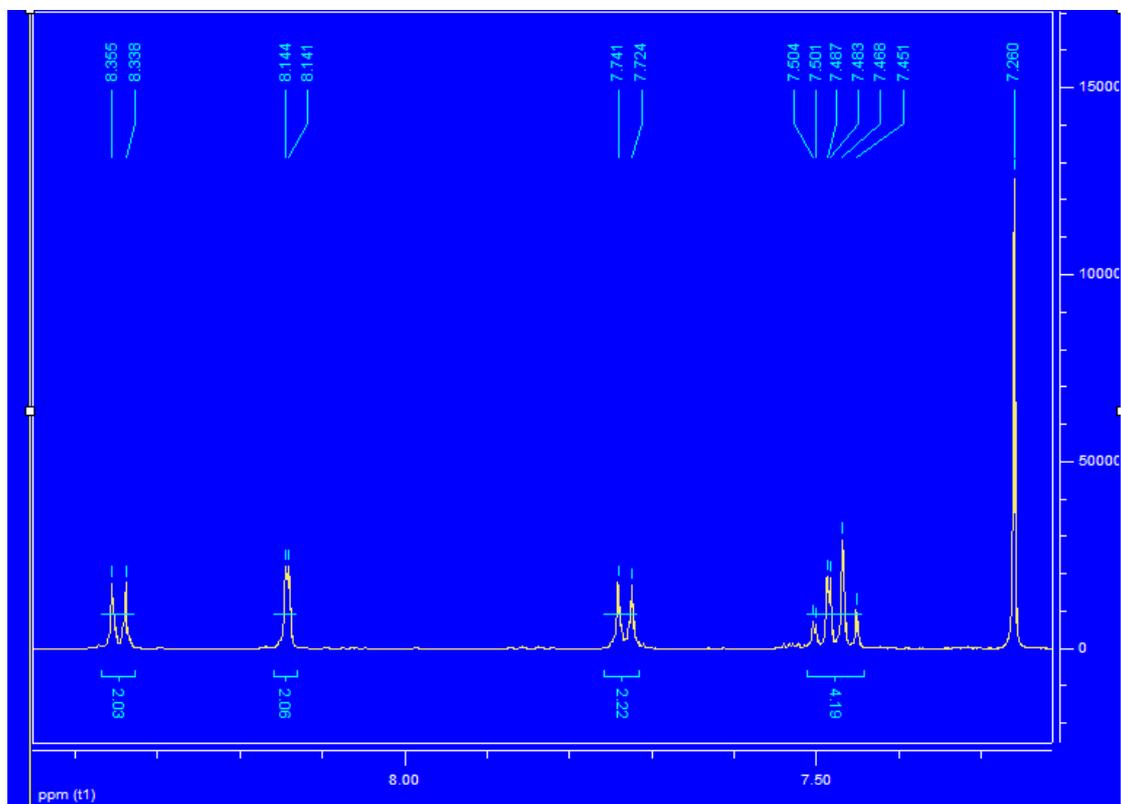


Fig. S5. ^1H NMR spectrum (500 MHz) of **1**.

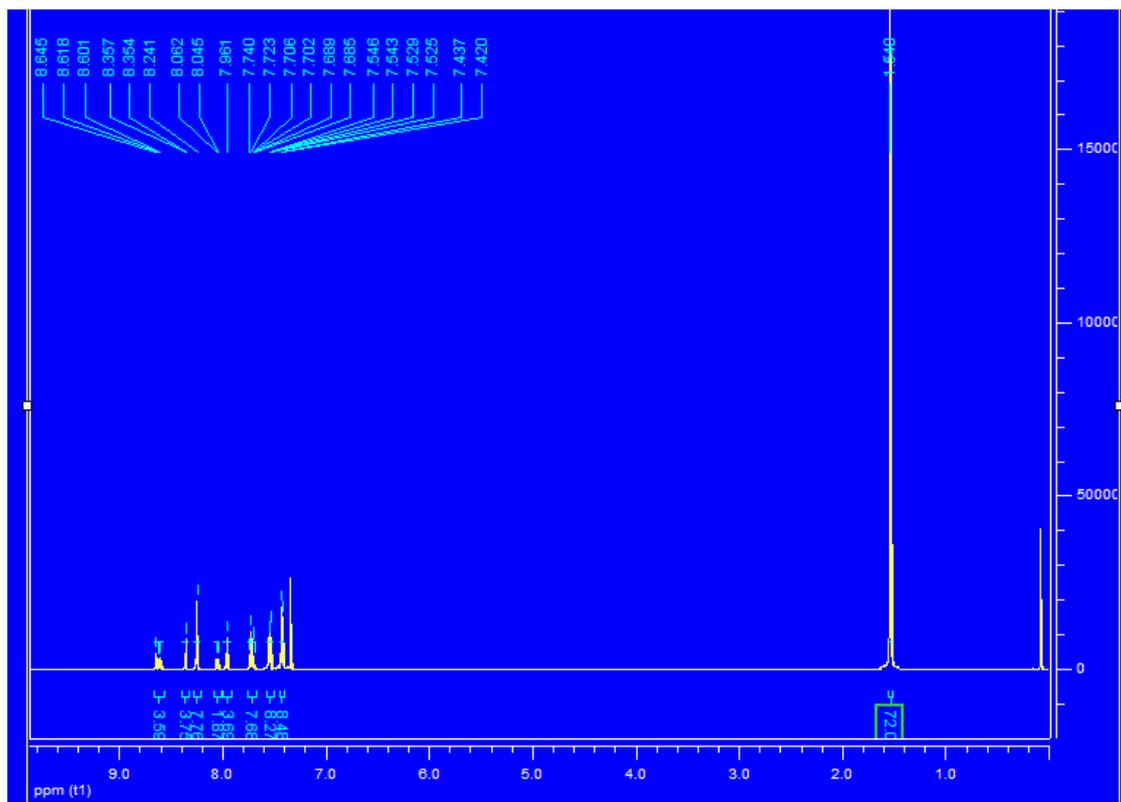


Fig. S8. ^1H NMR spectrum (500 MHz) of **3**.

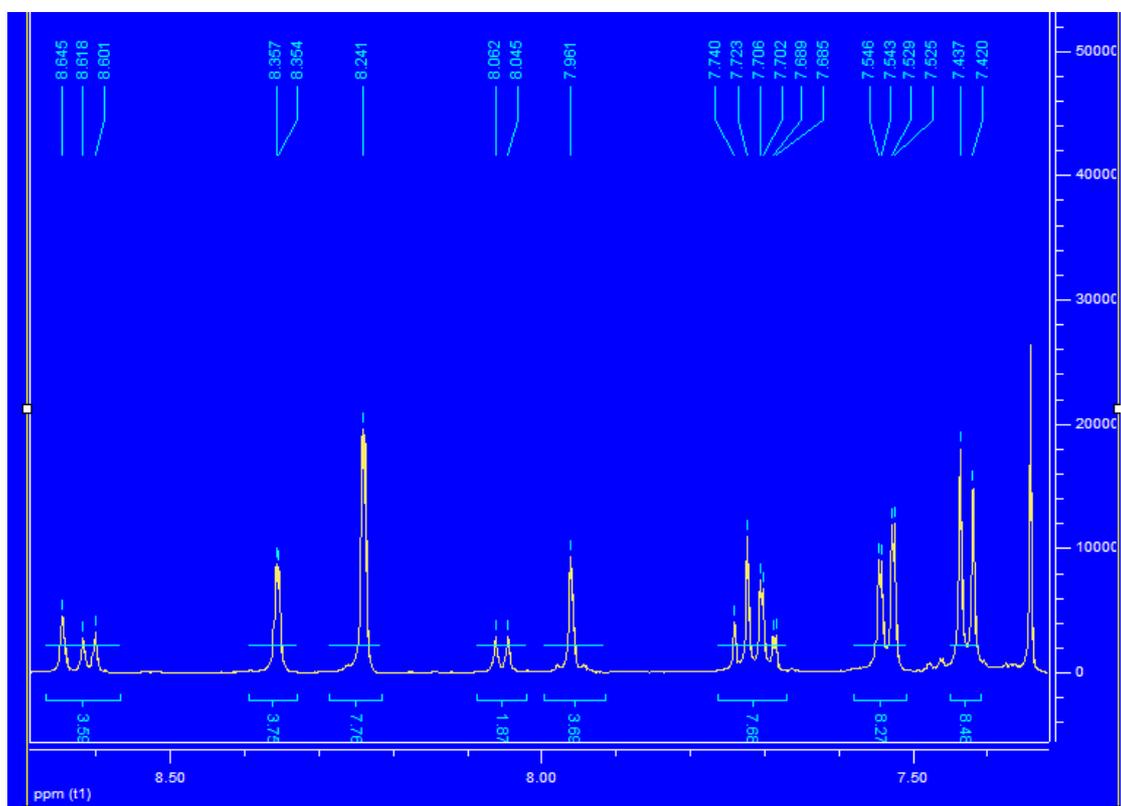


Fig. S9. ^1H NMR spectrum (500 MHz) of **3**.

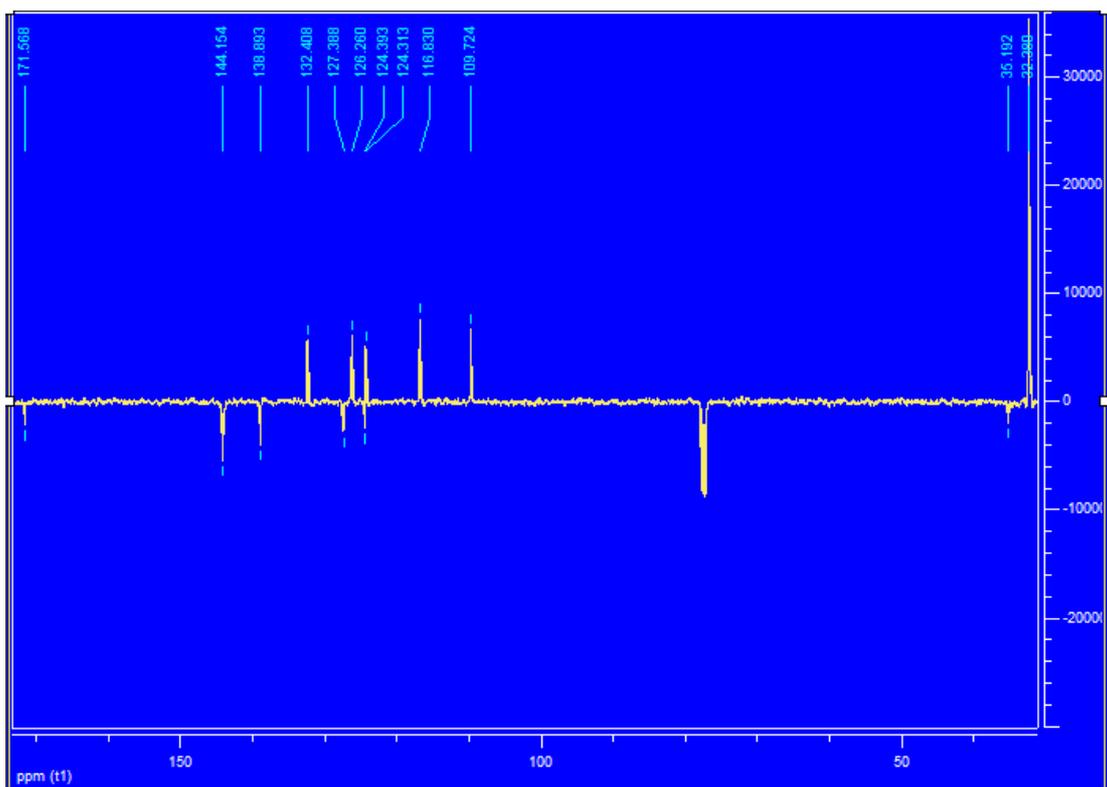


Fig. S10 ^{13}C NMR spectrum (125 MHz) of **1**.

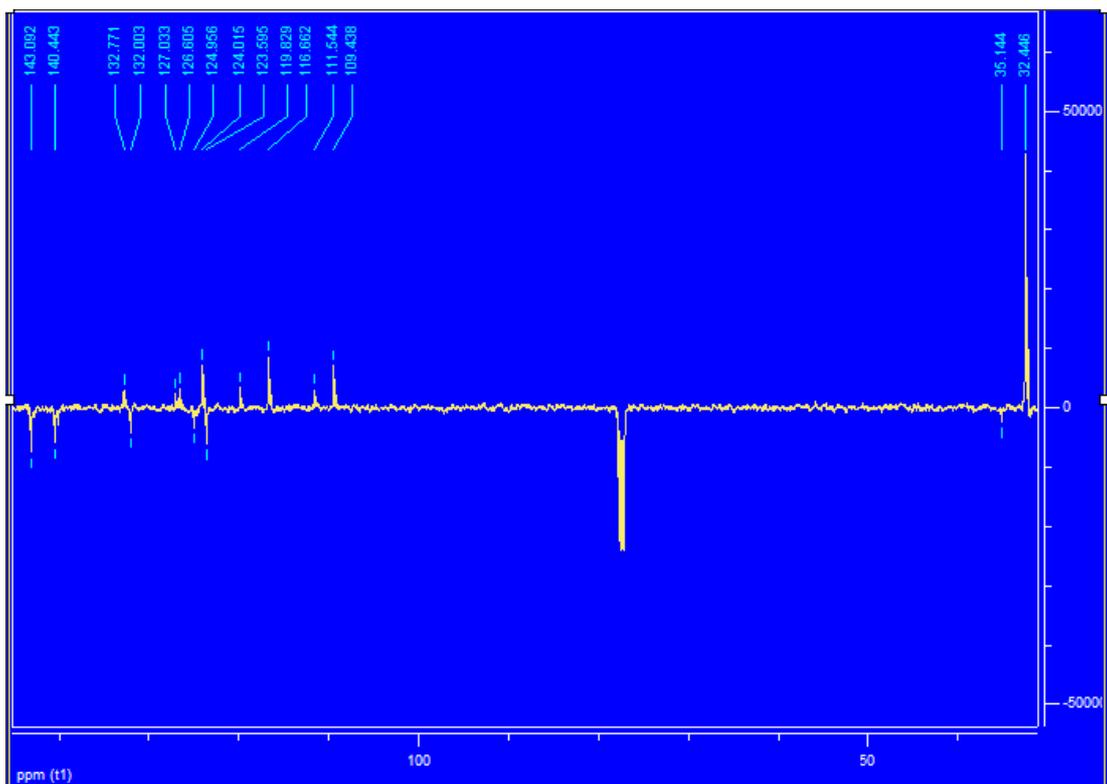


Fig. S11 ^{13}C NMR spectrum (125 MHz) of **2**.

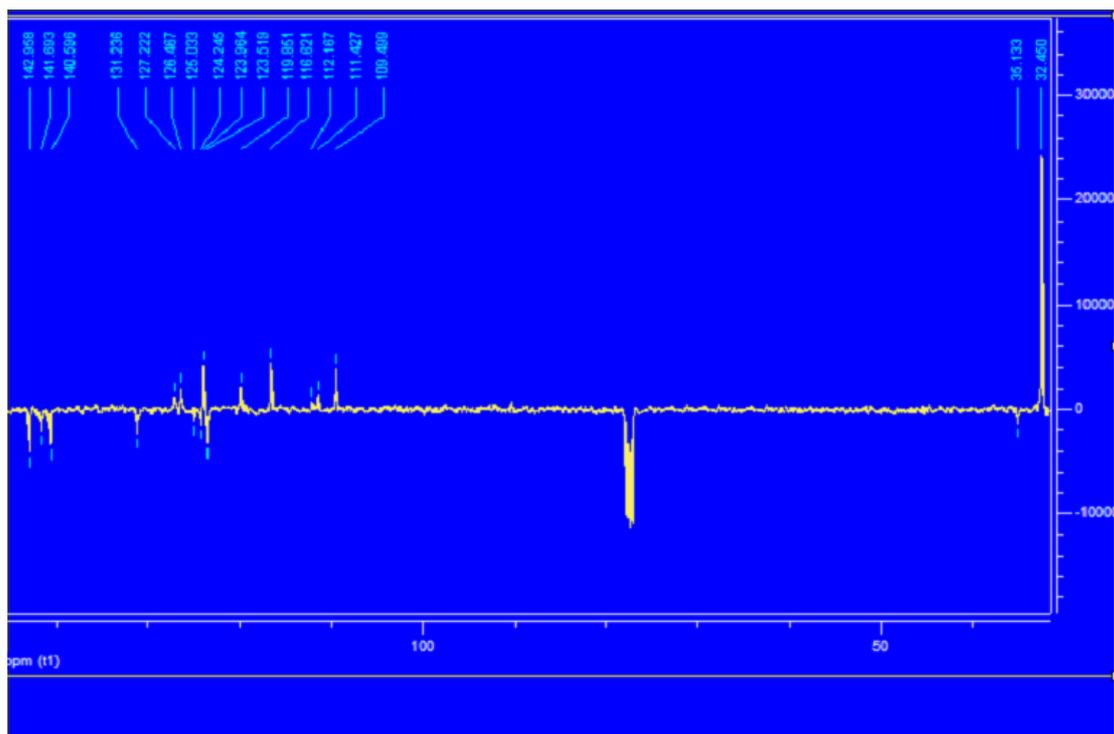


Fig. S12 ^{13}C NMR spectrum (125 MHz) of **3**.

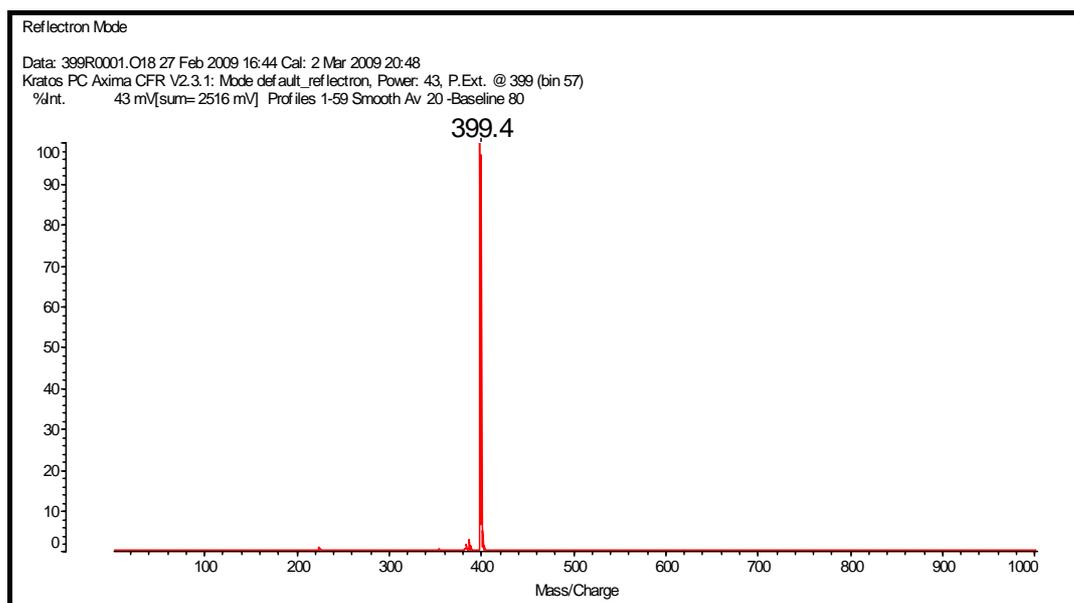


Fig. S13 MS spectrum of **1**.

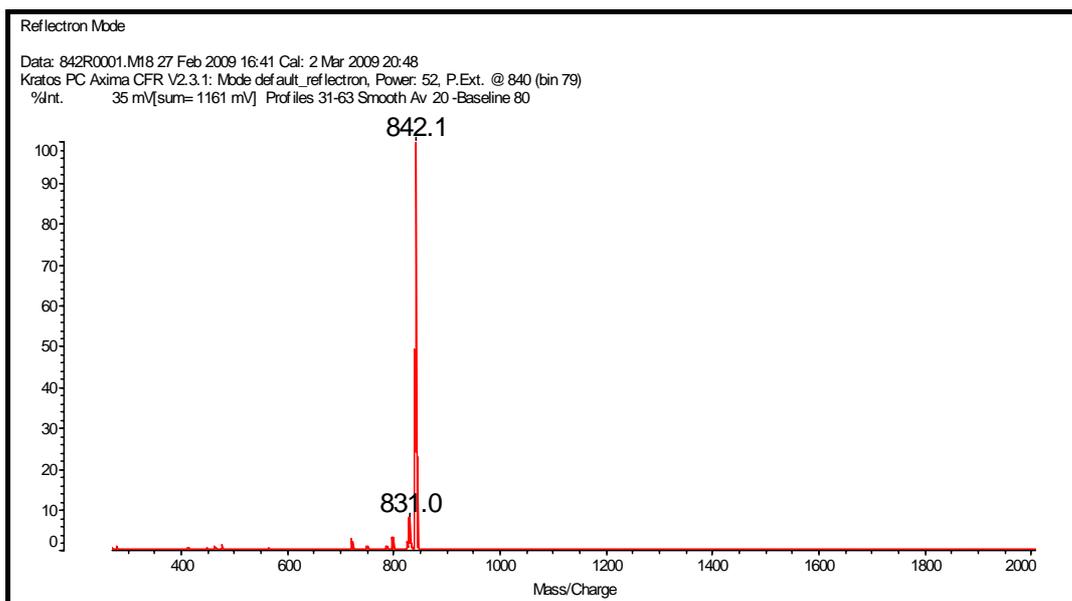


Fig. S14 MS spectrum of **2**.

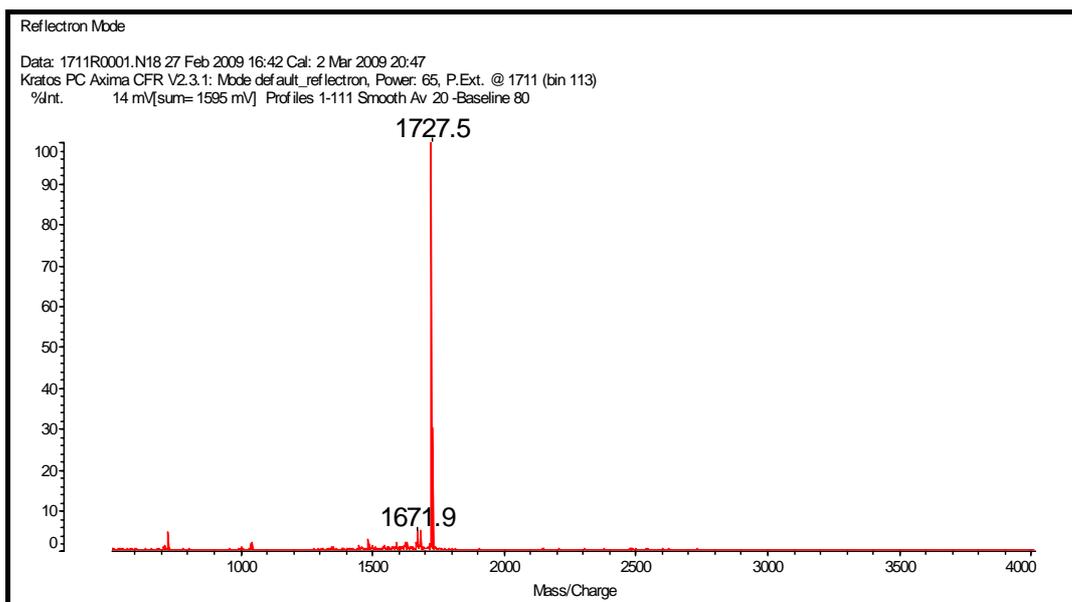


Fig. S15 MS spectrum of **3**.

References:

- 1 T. Xu, R. Lu, X. Liu, X. Zheng, X. Qiu and Y. Zhao, *Org. Lett.*, 2007, **9**, 797.
- 2 T. Xu, R. Lu, X. Liu, X. P. Chen, X. Qiu and Y. Zhao, *J. Org. Chem.*, 2008, **73**, 1809.
- 3 T. Xu, R. Lu, X. Liu, X. P. Chen, X. Qiu and Y. Zhao, *Eur. J. Org. Chem.*, 2008, **6**, 1065.