Supplementary Materials for

Article

Pyridyl-Anchored Type BODIPY Sensitizer-TiO_2 Photocatalyst for Enhanced Visible Light-Driven Photocatalytic Hydrogen Production

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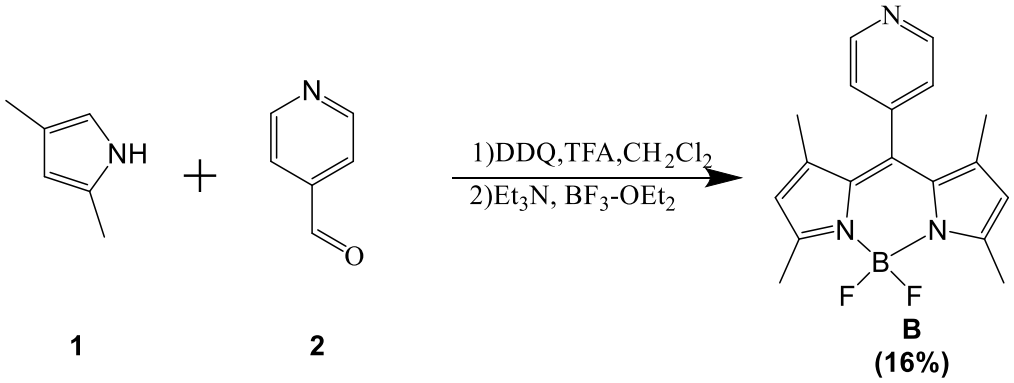
Synthesis of materials

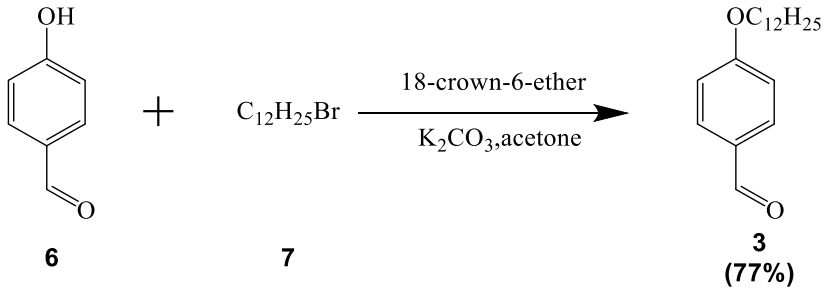
*1.1.1. Synthesis of 5,5-difluoro-1,3,7,9-tetramethyl-10-(pyridin-4-yl)-5H-4l4,5l4-dipyrrolo[1,2-c:2',1'-f][1,3,2]diazaborinine **1a***



A solution of 2,4-dimethyl-pyrrole **1** (4.9 g, 51.5 mmol) and 4-pyridinecarboxaldehyde **2** (2.3 g, 21.5 mmol) in dichloromethane (375 mL) under a nitrogen atmosphere. After added trifluoroacetic acid (8 drops), the solution was stirred at room temperature for 96 h. Then, 2,3-dichloro-5,6-dicyano-p-benzoquinone (DDQ, 3.2 g, 14.1 mmol) was added, and the mixture was stirred for 1 h in ice bath. Et_3N (20.9 mL, 150 mmol), and $BF_3{\cdot}Et_2O$ (27.8 mL, 202.3 mmol) was added at ice bath. After the reaction for 12 h at room temperature, the mixture was concentrated in vacuo. After the reaction, the mixture was concentrated in vacuo. The crude product was purified by a silica gel chromatograph eluted with CH_2Cl_2/ethyl acetate (50:1) to give

compound ***B*** (1.1 g, 16 %) as dark green solids. H (400 MHz, $CDCl_3$) 1.41 (s, 6H), 2.56 (s, 6H), 6.01 (s,2H), 7.32 (d, J = 6.0 Hz, 2H), 8.79 (d, J = 5.9 Hz, 2H). C (100 MHz, $CDCl_3$) 14.6, 121.8, 123.4, 130.4, 137.6, 142.6, 143.7, 150.5, 156.5.

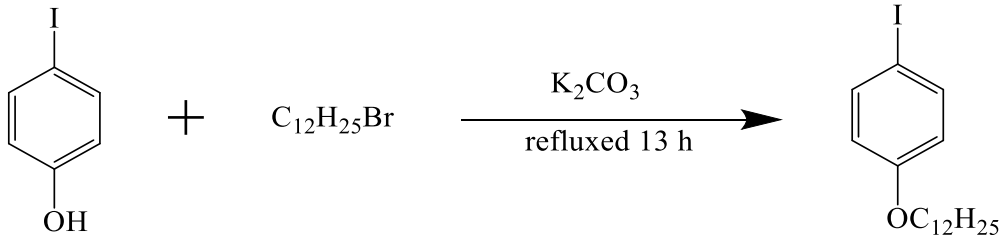
*1.1.2. Synthesis of 4-(dodecyloxy) benzaldehyde **3**.*



6 **7** **3** **(77%)**

A solution of 4-hydroxybenzaldehyde **6** (4.9 g, 40.1 mmol), 1-bromododecane **7** (10.0 g, 40.1 mmol) 18-crown-6-ether (0.2 g, 0.75 mmol) and potassium carbonate (8.6 g, 62.2 mmol) in acetone (200 mL). The solution was heated to reflux for 16 h. After the reaction, the mixture was concentrated in vacuo. The crude product was purified by a silica gel chromatograph eluted with CH_2Cl_2/hexane (1:1) to give compound ***3*** (9.0 g, 77 %) as white solids. H (400 MHz, $CDCl_3$) δ = 0.86–0.89 (m, 3H), 1.19–1.39 (m, 16H), 1.40–1.49(m, 2H), 1.76-1.85 (m, 2H), 4.04 (t, J = 6.6 Hz, 2H), 6.99 (d, J = 8.7 Hz, 2H), 7.83 (d, J = 8.7 Hz, 2H), 9.88 (s, 1H). C (100 MHz, $CDCl_3$) 14.1, 22.7, 25.9, 29.1, 29.3, 29.5, 29.6, 29.61, 29.63, 31.9, 68.4, 114.8, 130.0, 132.0, 164.3, 191.0.

*1.1.3. Synthesis of 1-(dodecyloxy)-4-iodobenzene **10***

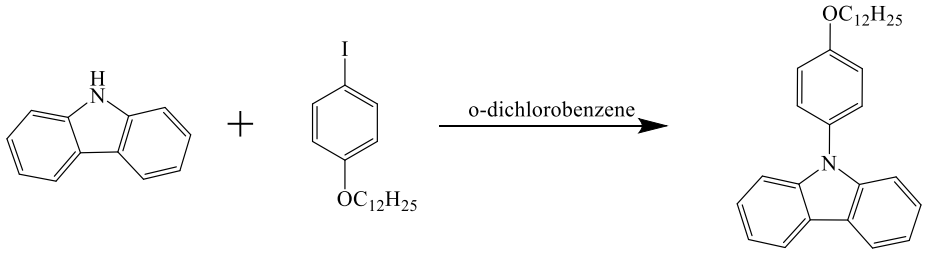


8 **9** **10** (68.3%)

A solution of 4-iodophenol **8** (13.2 g, 60.0 mmol),1-bromododecane **9** (12.5 g, 50.2 mmol) 18-crown-6-ether (0.2 g, 0.75 mmol) and potassium carbonate (14.0 g, 101.3 mmol) in acetone (100 mL). The solution was heated to reflux for 13 h. After the reaction, the mixture was concentrated in vacuo. The crude product was purified by a silica gel chromatograph eluted with hexane to give compound ***10*** (13.3 g, 68%) as white solids.

H (400 MHz, $CDCl_3$) ^{1}H NMR (400 MHz, $CDCl_3$) δ = 0.88 (t, J = 7.9 Hz, 3H), 1.20–1.35 (m, 16H), 1.38–1.47(m, 2H), 1.72–1.80 (m, 2H), 3.90 (t, J = 6.7 Hz, 2H), 6.67 (d, J = 8.9 Hz, 2H), 7.53 (d, J = 8.9 Hz, 2H). C (100 MHz, $CDCl_3$) 14.1, 22.7, 26.0, 29.2, 29.4, 29.6, 29.61, 29.66, 29.7, 31.9, 68.1, 82.4, 117.0, 138.2, 159.0.

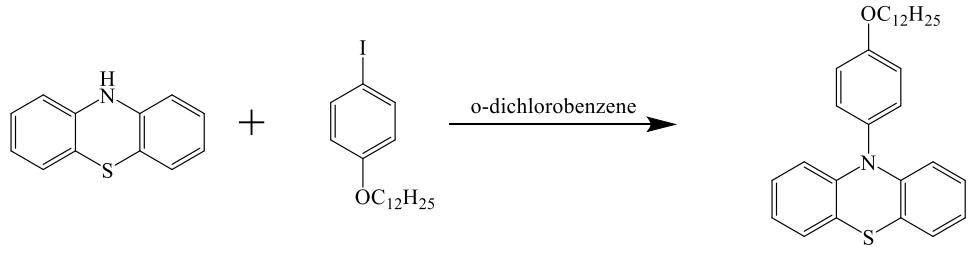
*1.1.4. Synthesis of 9-(4-(dodecyloxy)phenyl)-9H-carbazole **12***



11 **10** **12** (94 %)

A solution of precursor **10** (3.9 g,10.0 mmol), 9H-carbazole **11** (2.0 g,12 mmol), copper (1.68 g, 26 mmol), 18-crown-6-ether (0.3 g, 1.14 mmol) and potassium carbonate (12.4 g, 90 mmol) in *o*-dichlorobenzene (50 mL). The solution was heated to reflux for 24 h. After the reaction, the mixture was concentrated in vacuo. The crude product was purified by a silica gel chromatograph eluted with hexane to give compound ***12*** (4.0 g, 94 %) as white solids. H (400 MHz, $CDCl_3$) 0.86–0.90 (m, 3H), 1.22–1.47 (m, 16H), 1.46–1.55 (m, 2H), 1.80–1.89 (m, 2H), 4.04 (t, J = 6.5 Hz, 2H), 7.08 (d, J = 8.9 Hz, 2H), 7.27 (d, J = 7.8 Hz, 2H) , 7.32 (d, J = 8.1 Hz, 2H) , 7.38 (d, J = 7.0 Hz, 2H) ,7.42 (d, J = 9.6 Hz, 2H) , 8.13 (d, J = 7.7 Hz, 2H). C (100 MHz, $CDCl_3$) 14.1, 22.7, 26.1, 29.3, 29.4, 29.6, 29.66, 29.7, 31.6, 31.9, 68.4, 115.6, 119.6, 120.2, 123.1, 125.8, 128.5, 130.1, 141.4, 158.5.

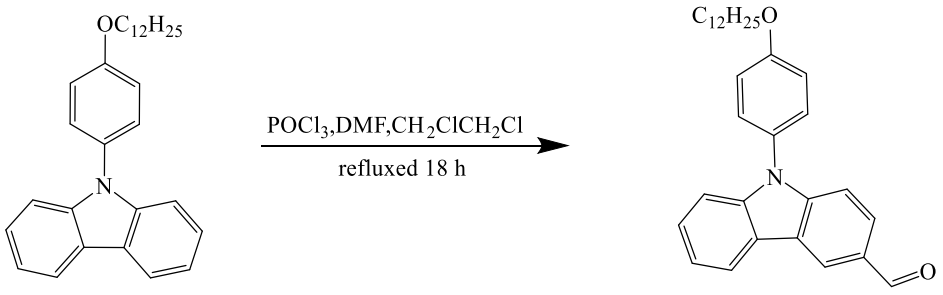
*1.1.5. Synthesis of 10-(4-(dodecyloxy)phenyl)-10H-phenothiazine **14***



13 **10** **14** (79%)

A solution of precursor **10** (3.9 g,10.0 mmol), 10H-phenothiazine **13** (6.0 g,30 mmol), copper (1.31 g, 21 mmol), 18-crown-6-ether (0.2 g, 0.8 mmol) and Potassium carbonate (12.4 g, 90 mmol) in o-dichlorobenzene (25 mL). The solution was heated to reflux for 24 h. After the reaction, the mixture was concentrated in vacuo. The crude product was purified by a silica gel chromatograph eluted with hexane to give compound ***14*** (3.6 g, 79 %) as white solids. H (400 MHz, $CDCl_3$) 0.88 (m, 3H), 1.22–1.47 (m, 18H), 1.79–1.88 (m, 2H), 4.02 (t, J = 6.5 Hz, 2H), 6.19 (d, J = 6.2 Hz, 2H), 6.71-6.82 (m, 4H), 6.98 (d, J = 7.0 Hz, 2H) , 7.09 (d, J = 7.0 Hz, 2H) , 7.28 (d, J = 8.7 Hz, 2H). C (100 MHz, $CDCl_3$)24.1, 22.7, 26.1, 29.3, 29.4, 29.44, 29.6, 29.64, 29.66, 29.7, 31.6, 32.0, 68.3, 115.6, 116.3, 126.8, 158.9.

*1.1.6. Synthesis of 9-(4-(dodecyloxy)phenyl)-9H-carbazole-3-carbaldehyde **4***

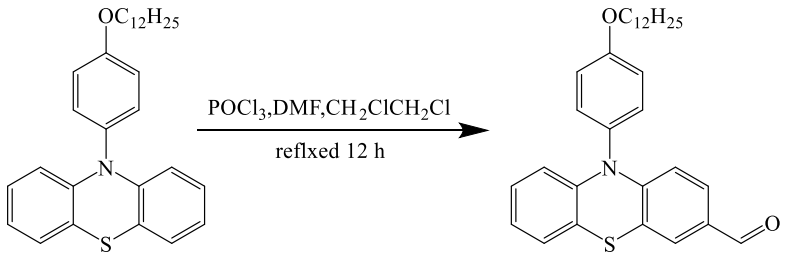


12 **4** (66 %)

A solution of DMF (1 ml) and 1,2-dichloroethane (3 ml) was stirred in ice bath under a nitrogen atmosphere. $POCl_3$ (1 ml) was added and stirred for 0.5 h at room temperature, until the color of solution changed colorless to pale yellow. Then, precursor **12** (0.3 g,1.0 mmol) was added. The solution was heated to reflux for 18 h. After the reaction, the mixture was concentrated in vacuo. The crude product was purified by a silica gel chromatograph eluted with CH_2Cl_2/hexane (2:1) to give compound ***4*** (0.3 g, 66 %) as white solids.

H (400 MHz, $CDCl_3$) 0.86–0.90 (m, 3H), 1.22–1.39 (m, 16H), 1.47–1.58 (m, 2H), 1.82–1.90 (m, 2H), 4.06 (t, J = 6.5 Hz, 2H), 7.12 (d, J = 8.8 Hz, 1H) , 7–7.50 (m, 5H) ,7.93 (dd, J = 1.5, 7.0 Hz, 1H) , 8.20 (d, J = 7.7 Hz, 1H) , 10.1 (s,1H). C (100 MHz, $CDCl_3$) 14.1, 22.7, 22.71, 29.3, 29.4, 29.7, 31.6, 31.9, 68.5, 110.1, 110.4, 115.8, 120.6, 121.0, 123.0, 126.9, 127.4, 128.5, 128.9, 129.2, 142.3, 145.0.

*1.1.7. Synthesis of 10-(4-(dodecyloxy)phenyl)-10H-phenothiazine-3-carbaldehyde **5***



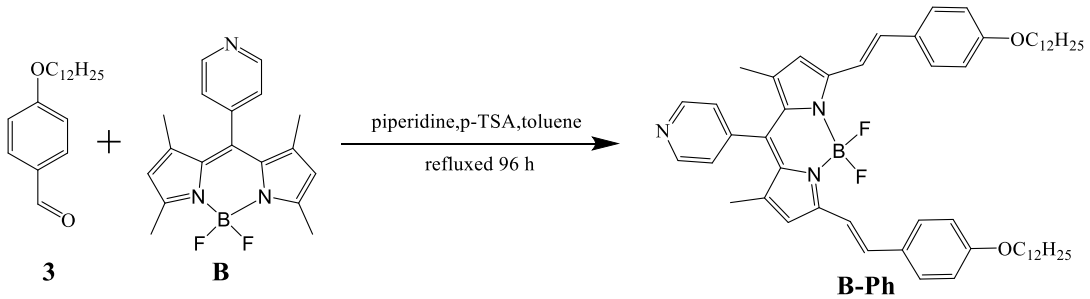
14 **5** (75%)

A solution of DMF (3 ml) and 1,2-dichloroethane (10 ml) was stirred in ice bath under a nitrogen atmosphere. $POCl_3$ (3 ml) was added and stirred for 0.5 h at room temperature, until the color of solution changed colorless to pale yellow. Then, precursor **14** (1.4 g, 3.0 mmol) was added. The solution was heated to reflux for 12 h. After the reaction, the mixture was concentrated in vacuo. The crude product was purified by a silica gel chromatograph eluted with CH_2Cl_2/hexane (2:1) to give compound ***5*** (1.1 g, 75 %) as yellow solids.

H (400 MHz, $CDCl_3$) 0.88–0.91 (m, 3H), 1.22–1.42 (m, 16H), 1.45–1.58 (m, 2H), 1.80–1.89 (m, 2H), 4.03 (t, J = 6.5 Hz, 2H), 6.15-6.1 8 (m, 1H), 6.20 (d, J = 8.6 Hz, 1H) , 6.83 (dd, J = 3.4, 6.0 Hz, 1H) , 6.90–6.97 (m, 1H) ,7.12

(d, J = 8.8 Hz, 2H) , 7.24 (s,1H), 7.26–7.29 (m,2H), 7.44–7.45 (m,1H), 9.69 (s,1H). C (100 MHz, $CDCl_3$) 14.1, 22.6, 26.1, 29.3, 29.4, 29.58, 29.6, 29.66, 31.9, 68.4, 115.0, 116.4,116.7, 119.0, 120.0, 123.5, 126.6, 127.1, 127.5, 130.0, 131.0, 131.7, 132.1, 142.9, 149.6, 159.3, 189.7.

*1.1.8. Synthesis of 3,7-bis((E)-4-(dodecyloxy)styryl)-5,5-difluoro-1,9-dimethyl-10-(pyridin-4-yl)-5H-4l4,5l4-dipyrrolo[1,2-c:2′,1′-f][1,3,2]diazaborinine **B-Ph***

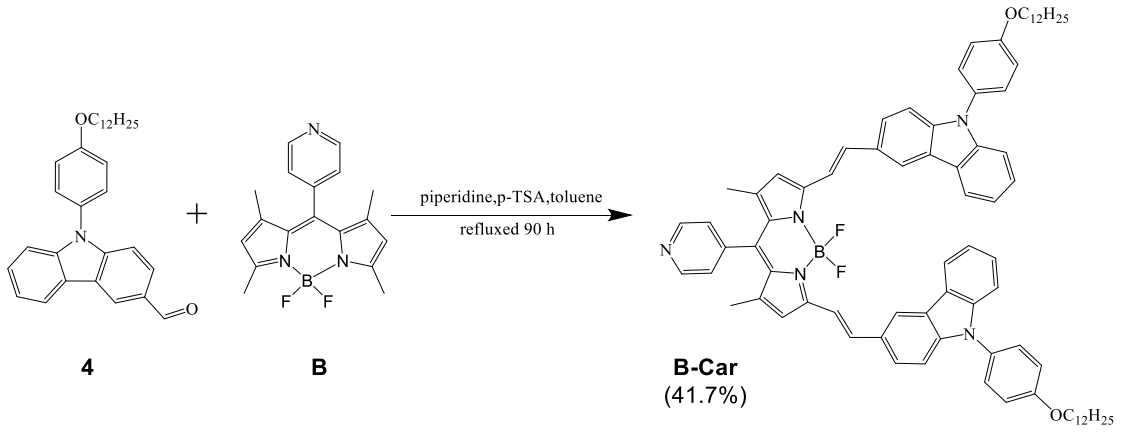


3 **B** **B-Ph** (19 %)

A solution of precursor **3** (0.7 g, 2.4 mmol) and **B** (0.2 g, 0.6 mmol) in toluene (50 mL) at room temperature. Then, p-TSA (0.1 g, 5.2 mmol) and piperidine (1.5 ml) was added. The solution was heated to reflux for 90 h. After the reaction, the mixture was concentrated in vacuo. The crude product was purified by a silica gel chromatograph eluted with CH_2Cl_2/ethanol (10:1) to give compound ***B-Ph*** (0.1 g, 19 %) as dark green solids.

H (400 MHz, CD_2Cl_2)) 0.86–0.91 (m, 6H), 1.22–1.29 (m, 34H), 1.45–1.58 (m, 8H), 1.80–1.84 (m, 4H), 4.01 (t, J = 6.6 Hz, 4H), 6.78 (s, 2H) , 6.94 (d, J=8.7 Hz, 4H) , 7.26 (s,1H), 7.30 (s, 1H), 7.38 (d, J = 5.8 Hz, 2H) , 7.53 (s,1H), 7.57-7.60 (m, 5H), 8.77 (d, J = 5.6 Hz, 2H). C (400 MHz, CD_2Cl_2)) 14.3, 15.0, 23.1, 26.4, 29.6, 29.7, 30.0, 30.03, 30.1, 32.3, 114.8, 115.3, 116.9, 118.2, 124.3, 129.4, 129.5, 129.7, 132.6, 134.7, 137.0, 142.0, 143.9, 151.0, 153.5, 160.8.

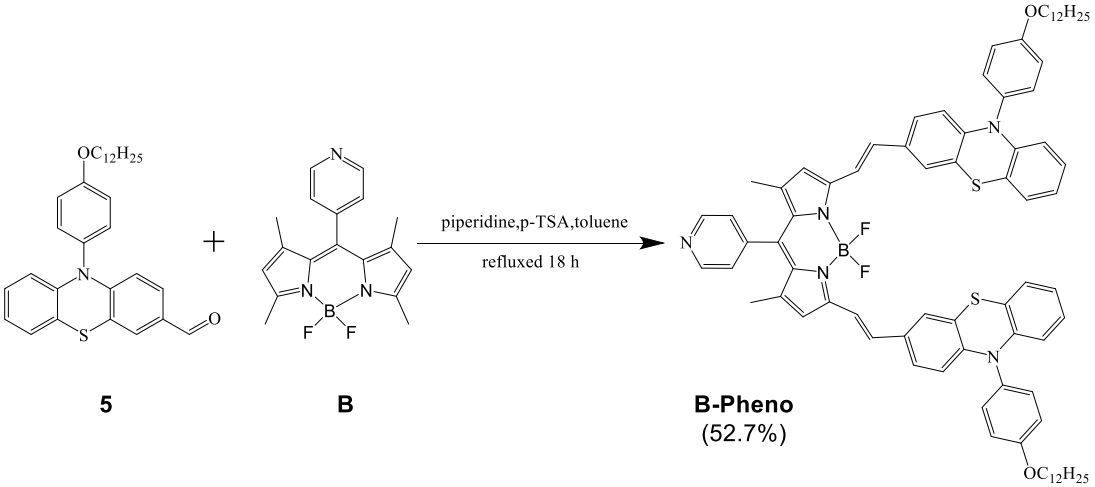
*1.1.9. Synthesis of 3,3′-((1E,1′E)-(5,5-difluoro-1,9-dimethyl-10-(pyridin-4-yl)-5H-4l4,5l4-dipyrrolo[1,2-c:2′,1′-f][1,3,2]diazaborinine-3,7-diyl)bis(ethene-2,1-diyl))bis(9-(4-(dodecyloxy)phenyl)-9H-carbazole)**B-Car***



4 **B** **B-Car** (41.7%)

A solution of precursor **4** (1.1 g, 2.4 mmol) and **B** (0.2 g, 0.6 mmol) in toluene (50 mL) at room temperature. Then, p-TSA (0.1 g, 5.2 mmol) and piperidine (1.5 ml) was added. The solution was heated to reflux for 90 h. After the reaction, the mixture was concentrated in vacuo. The crude product was purified by a silica gel chromatograph eluted with CH_2Cl_2 to give compound ***B-Car*** (0.3 g, 42 %) as dark green solids. H (400 MHz, CD_2Cl_2) δ = 0.85–0.90 (m, 6H), 1.19–1.42 (m, 34H), 1.37–1.58 (m, 8H), 1.80–1.89 (m, 4H), 4.08 (t, J = 6.5 Hz, 4H), 6.19–6.22 (m, 4H) ,6.78 (s, 2H), 6.71–6.77(m,4H), 7.33-7.49 (m, 14H), 7.55(s,1H), 7.59(s,1H), 7.75–7.79 (m, 3H), 7.81(s, 1H), 8.27 (d, J = 7.7 Hz, 2H), 8.44 (s, 2H), 8.79 (d, J = 5.1 Hz, 2H). C (400 MHz, CD_2Cl_2) 14.3, 15.0, 23.1, 26.4, 29.7, 29.74, 29.8, 30.0, 32.3, 110.4, 110.6, 116.0, 116.6, 118.3, 120.3, 120.6, 120.9, 123.4, 124.1, 124.4, 126.3, 126.7, 128.7, 128.9, 129.8, 138.4, 141.8, 142.4, 142.5, 150.9, 153.6, 159.2.

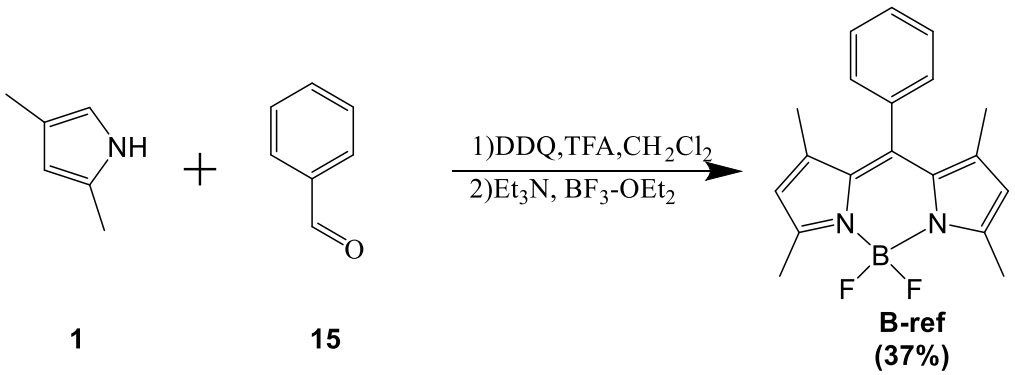
1.1.10. Synthesis of 3,3'-((1E,1'E)-(5,5-difluoro-1,9-dimethyl-10-(pyridin-4-yl)-5H-4l4,5l4-dipyrrolo[1,2-c:2',1'-f][1,3,2]diazaborinine-3,7-diyl)bis(ethene-2,1-diyl))bis(10-(4-(dodecyloxy)phenyl)-10H-phenothiazine) ***B-Pheno***



5 **B** **B-Pheno** (52.7%)

A solution of precursor **5** (1.1 g,2.3 mmol) and **B** (0.2 g,0.6 mmol) in toluene (50 mL) at room temperature. Then, p-TSA (0.1 g, 5.2 mmol) and piperidine (1.5 ml) was added. The solution was heated to reflux for 90 h. After the reaction, the mixture was concentrated in vacuo. The crude product was purified by a silica gel chromatograph eluted with CH_2Cl_2 to give compound ***B-Pheno*** (0.4 g, 53 %) as dark blue solids. H (400 MHz, CD_2Cl_2) 0.85–0.90 (m, 6H), 1.19–1.42 (m, 34H), 1.37–1.58 (m, 8H), 1.80–1.84 (m, 4H), 4.06 (t, J = 6.5 Hz, 4H), 6.19–6.22 (m, 4H), 6.64 (s, 2H), 6.78–6.88(m,4H),6.99–7.03 (m, 2H), 7.04–7.10(m,3H), 7.10–7.16 (m, 5H), 7.25–7.33 (m, 6H), 7.35 (d, J = 5.7 Hz, 2H), 7. 43(s,1H), 7.47(s,1H), 8.75 (d, J = 5.6 Hz, 2H). C (400 MHz, CD_2Cl_2) 14.3, 15.0, 23.1, 26.5, 29.7, 29.74, 29.8, 30.0, 30.1, 32.2, 116.1, 116.3, 116.9, 118.4, 119.5, 120.4, 123.0, 124.3, 125.2, 126.7, 127.3, 127.6, 131.2, 132.3, 132.7, 132.9, 135.8, 141.8, 143.9, 144.2, 145.7, 151.0, 153.2, 159.6.

*1.1.11. Synthesis of 5,5-difluoro-1,3,7,9-tetramethyl-10-phenyl-5H-4l4,5l4-dipyrrolo[1,2-c:2',1'-f][1,3,2]diazaborinine **B-ref***



1 **15** **B-ref (37%)**

A solution of 2,4-dimethyl-pyrrole **1** (1.1 g, 11 mmol) and benzaldehyde **15** (530 mg, 5.5 mmol) in dichloromethane (300 mL) under a nitrogen atmosphere. After added trifluoroacetic acid (7 drops), the solution was stirred at room temperature for 16 h. Then, 2,3-dichloro-5,6-dicyano-p-benzoquinone (DDQ, 1.15 g, 5.0 mmol) was added, and the mixture was stirred for 15 min at room temperature. Et_3N (10 mL, 72 mmol), and $BF_3{\cdot}Et_2O$ (10 mL, 73 mmol) was added at ice bath. After the reaction for 3 h at room temperature, the mixture was concentrated in vacuo. The crude product was purified by a silica gel chromatograph eluted with CH_2Cl_2/hexane (1:1) to give compound ***B-ref*** (651 mg, 37 %) as orange solids. H (400 MHz, $CDCl_3$) 1.37 (s, 6H), 2.56 (s, 6H), 5.98 (s,2H), 7.26–7.29 (m, 2H), 7.47–7.49 (m, 3H). C (100 MHz, $CDCl_3$) 14.3, 14.6, 121.2, 128.0, 128.9, 129.1, 131.4, 135.0, 141.7, 143.1, 155.4.

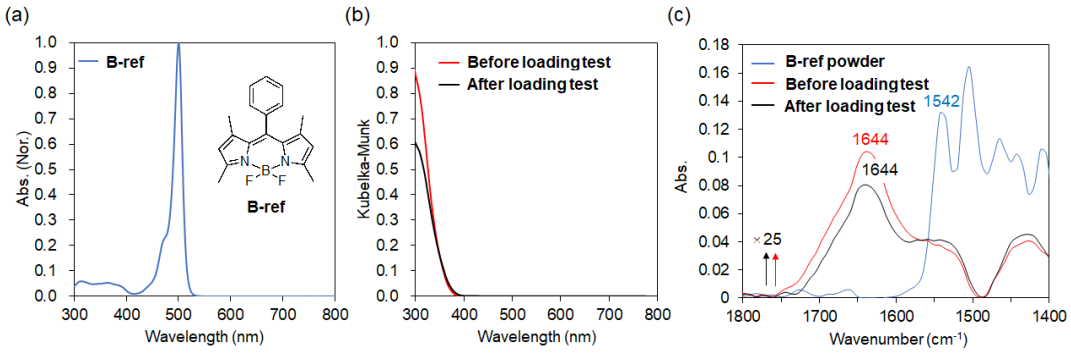


Figure S1. (**a**) Absorption spectra of **B-ref** in THF. (**b**) Diffuse reflectance spectra of **B-ref**-loading test of Pt-TiO_2. Before: red, After: black. (**c**) IR spectra of **B-ref** (blue) and **B-ref**-loading test of Pt-TiO_2. Before: red, After: black.

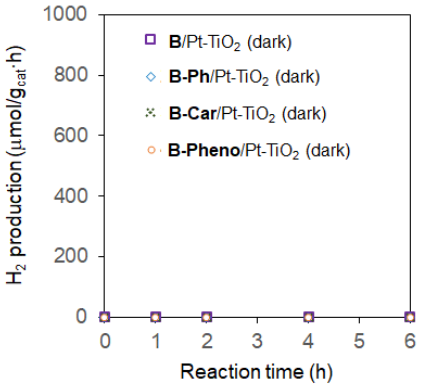


Figure S2. Hydrogen production results of **dye**/Pt-TiO_2. Conditions: Dark condition, 0.57 M ascorbic acid aq. (pH = 4.0).

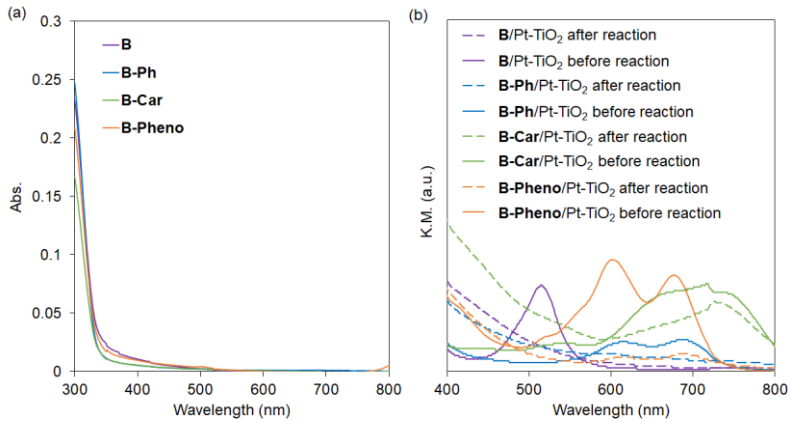


Figure S3: (**a**) Absorption spectra of **B**, **B-Ph**, **B-Car** and **B-Pheno** after photocatalytic reaction in $CHCl_3$ solution. (**b**) Diffuse reflectance spectra of **Dye**/Pt-TiO_2 before and after photocatalytic reaction.

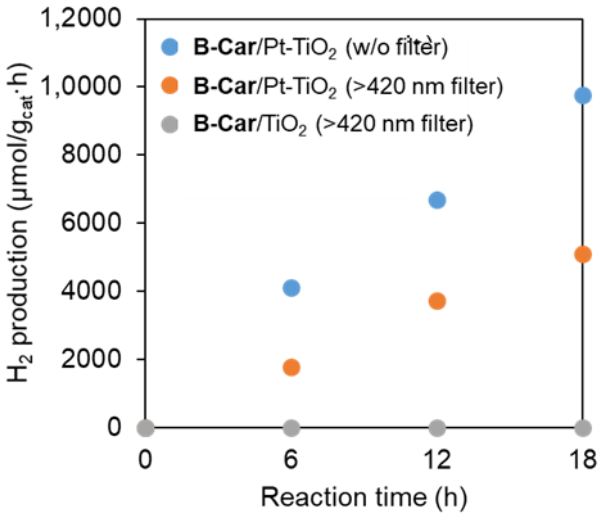


Figure S4. Photocatalytic hydrogen production results of **B-Car**/Pt-TiO_2 (> 420 nm filter, 0.15 mW/cm^2), **B-Car**/Pt-TiO_2 (Irradiated by w/o filter, 0.23 mW/cm^2), and **B-Car**/TiO_2 (> 420 nm filter, 0.15 mW/cm^2), Condition: 0.57 M ascorbic acid aq. (pH = 4.0).

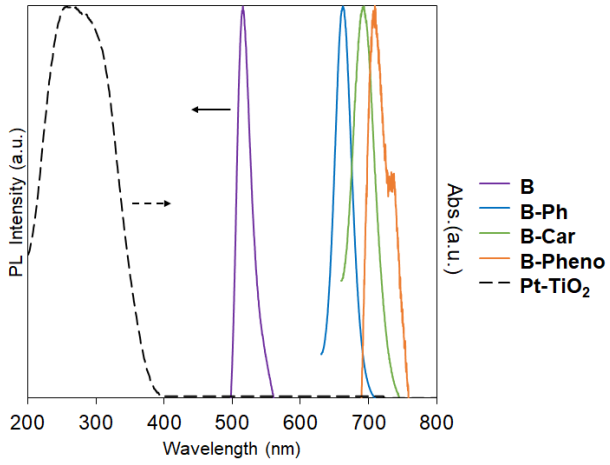


Figure S5. Diffuse reflectance spectra of Pt-TiO_2, and fluorescence spectra of **B**, **B-Ph**,**B-Car** and **B-Pheno** in THF.

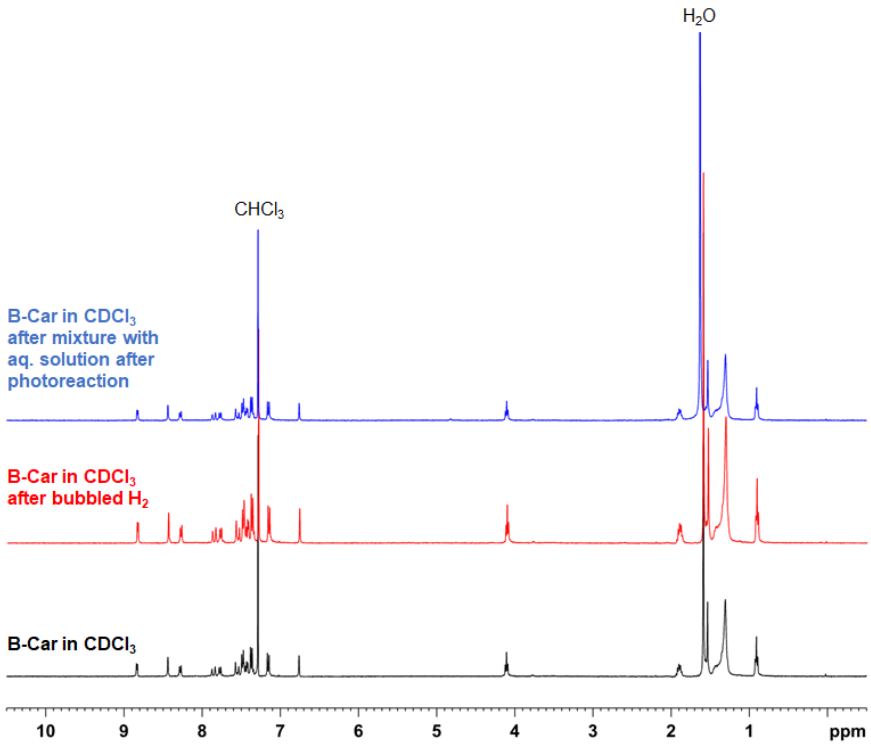


Figure S6. ^{1}HNMR spectra for reactivity test of **B-Car** with photogenerated species. Black: **B-Car** in $CDCl_3$. Red: **B-Car** in $CDCl_3$ solution after hydrogen bubbling. Blue: **B-Car** in $CDCl_3$ solution after mixed with aqueous solution after photoreaction (dehydroascorbic acid).

NMR spectra

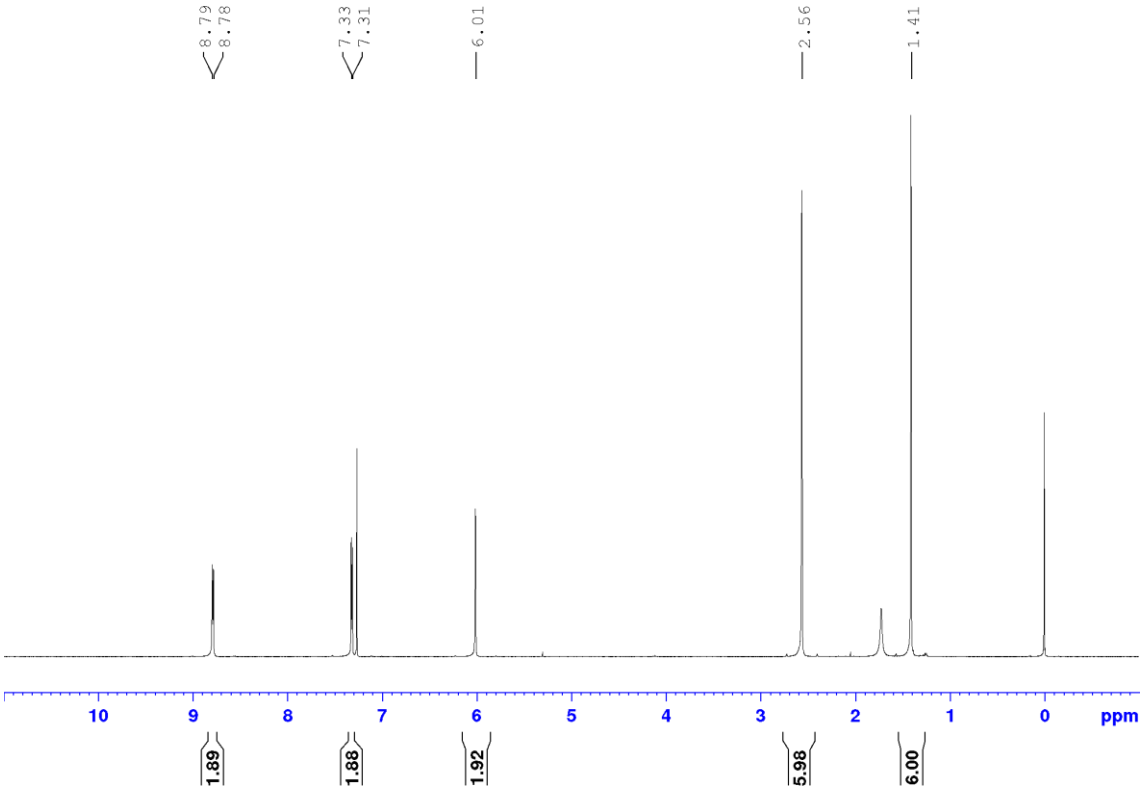


Fig S7. [1]HNMR spectra of **B** (400 MHz).

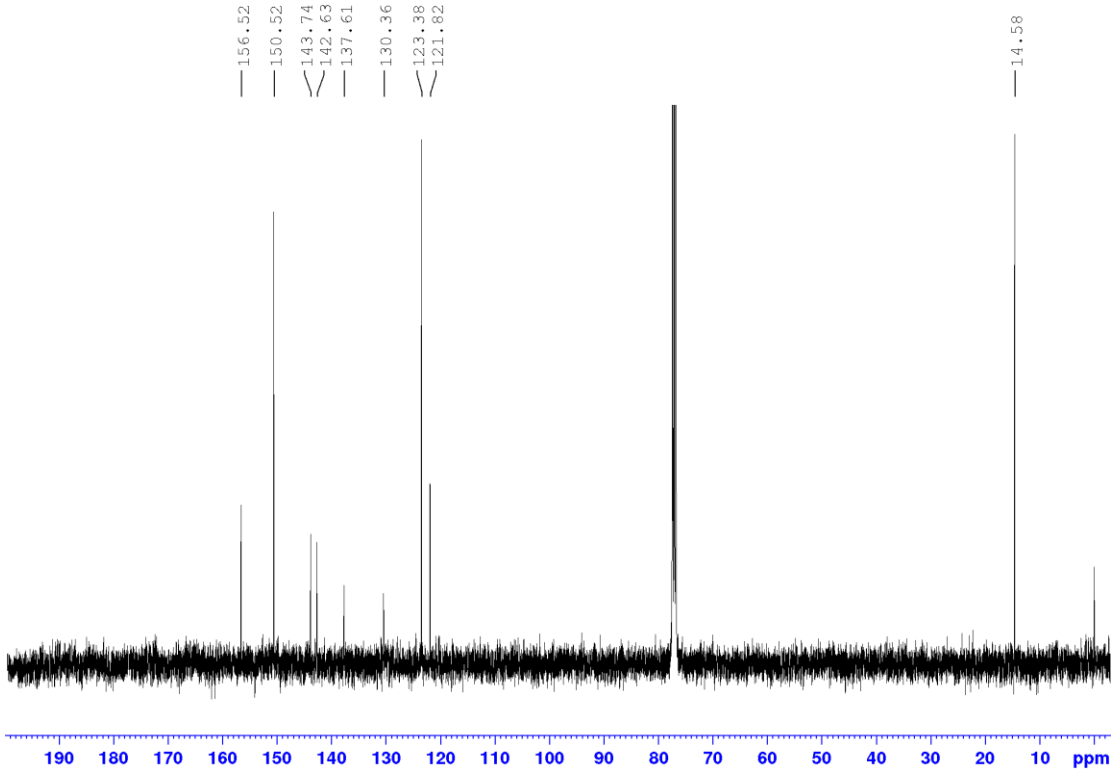


Fig S8. [13]CNMR spectra of **B** (100 MHz).

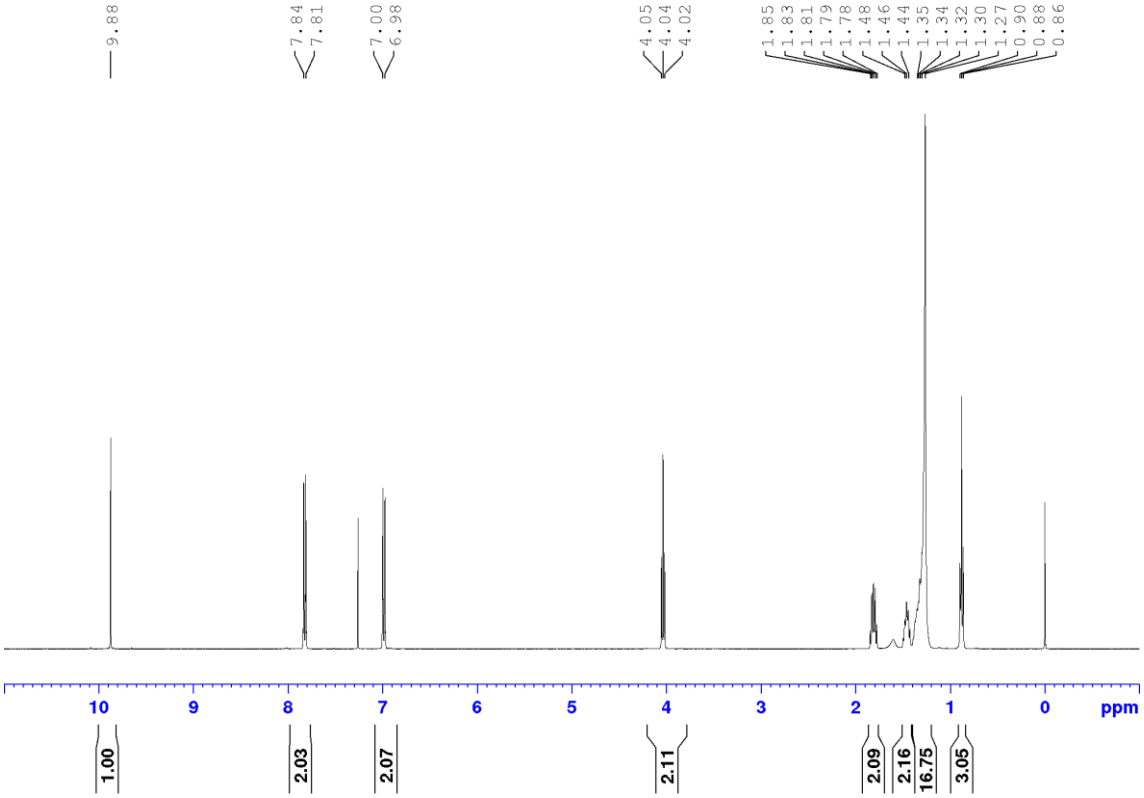


Fig S9. [1]HNMR spectra of **3** (400 MHz).

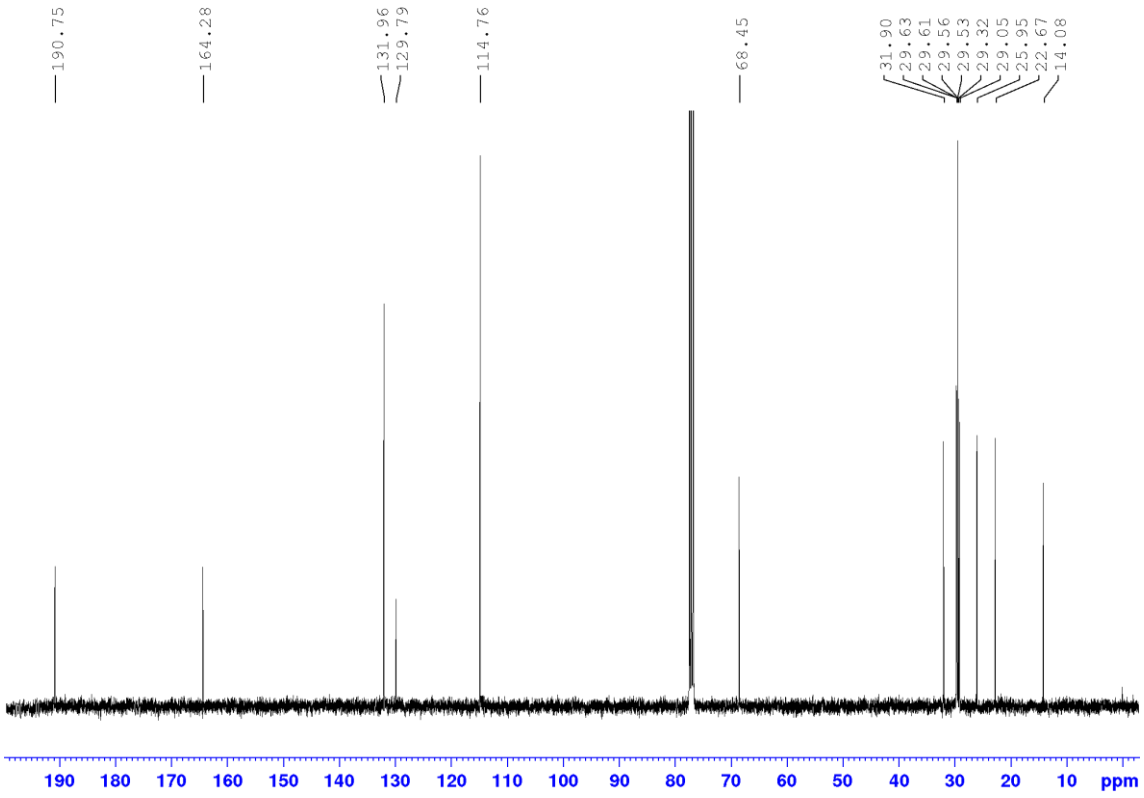


Fig S10. [13]CNMR spectra of **3** (100 MHz).

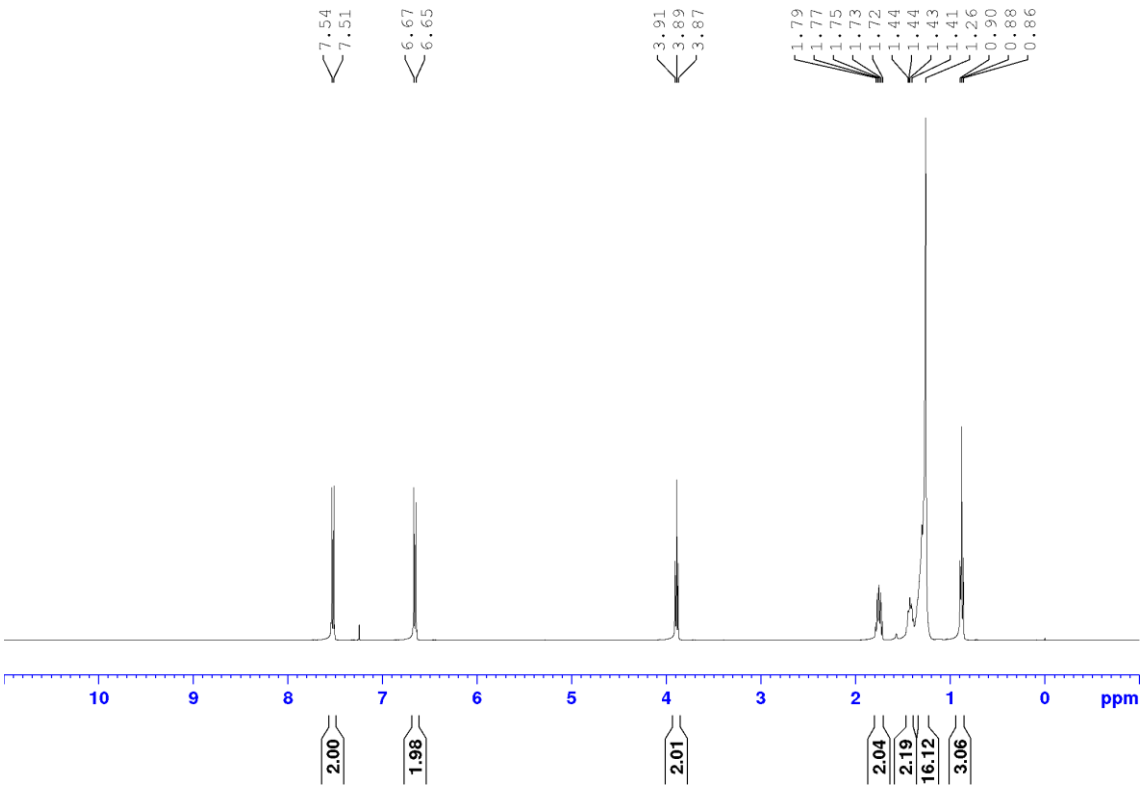


Fig S11. [1]HNMR spectra of **10** (400 MHz).

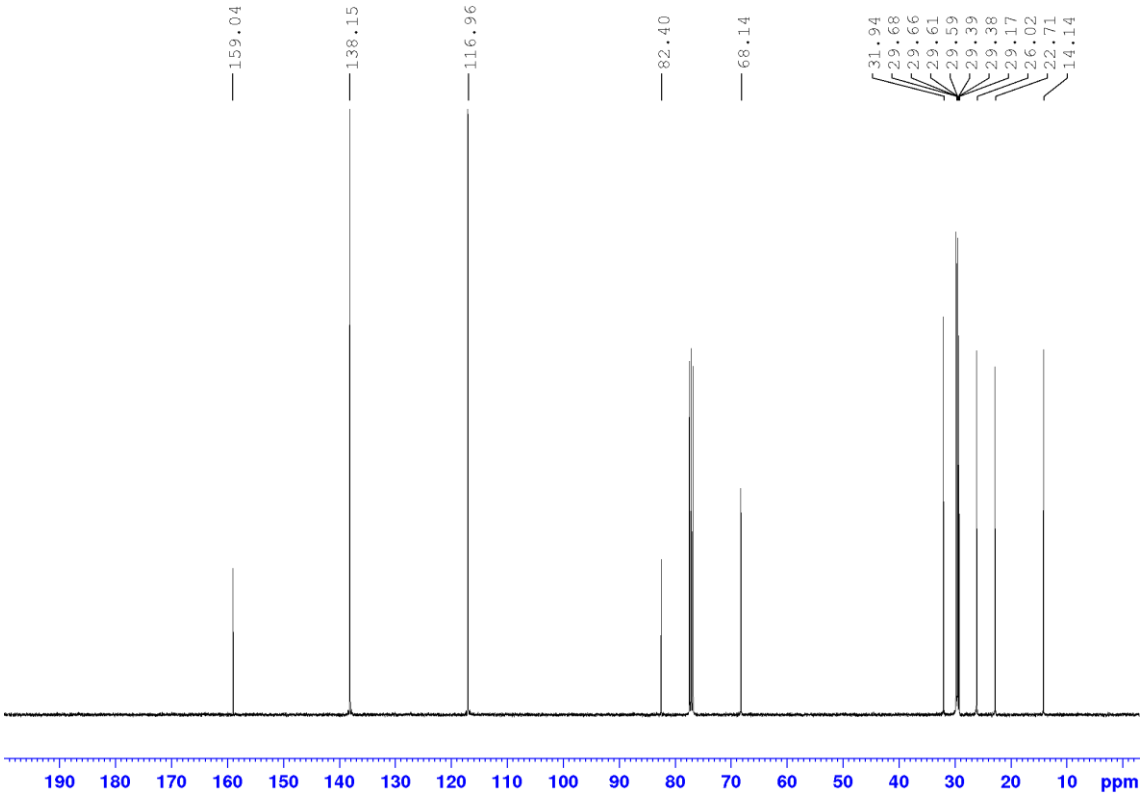


Fig S12. [13]CNMR spectra of **10** (100 MHz).

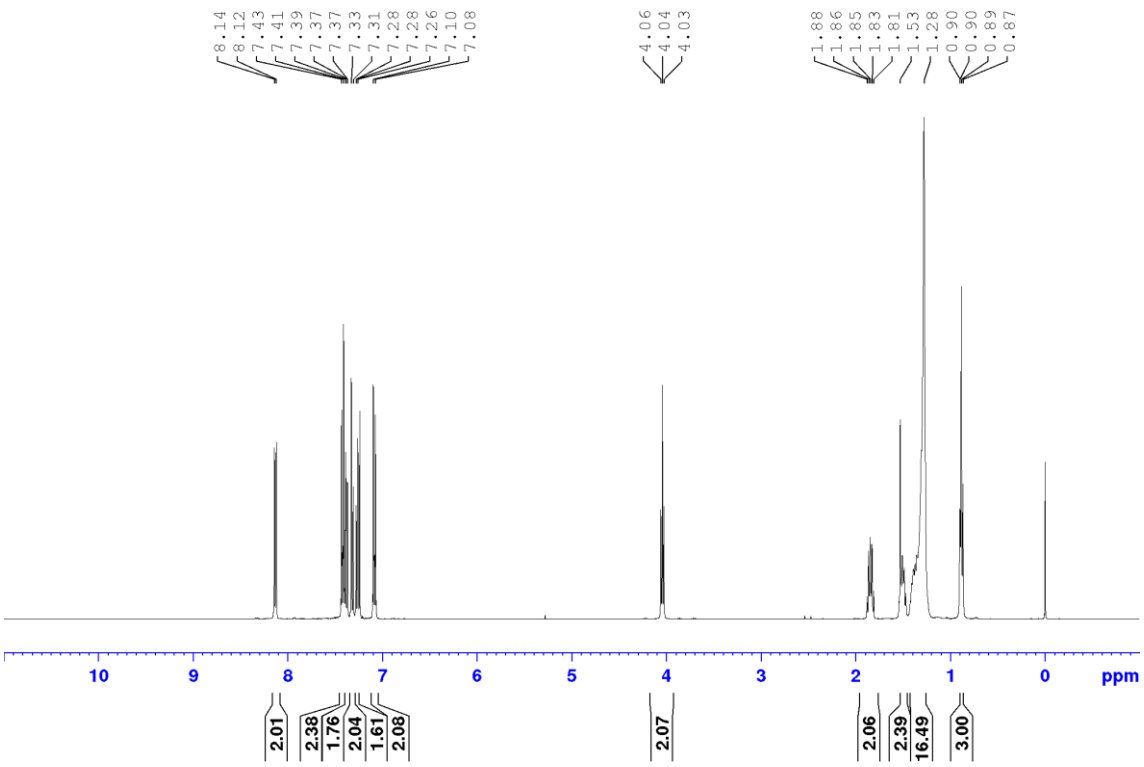


Fig S13. [1]HNMR spectra of **12** (400 MHz).

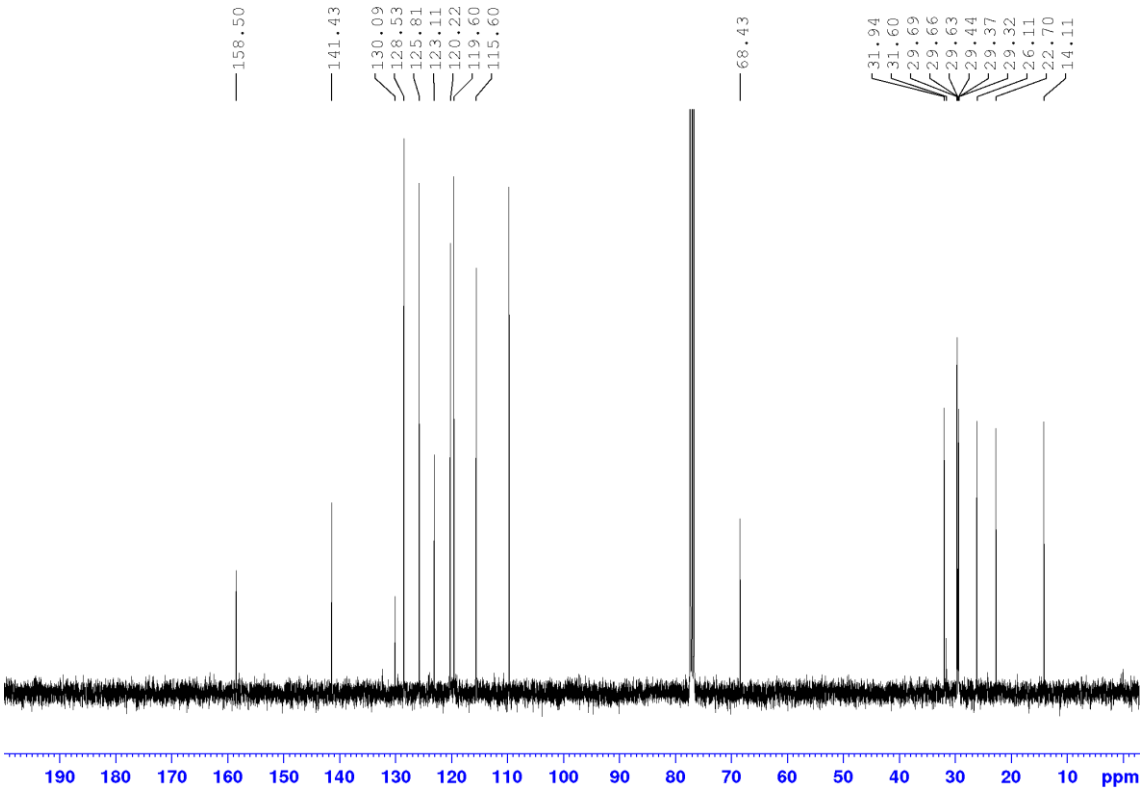


Fig S14. [13]CNMR spectra of **12** (100 MHz).

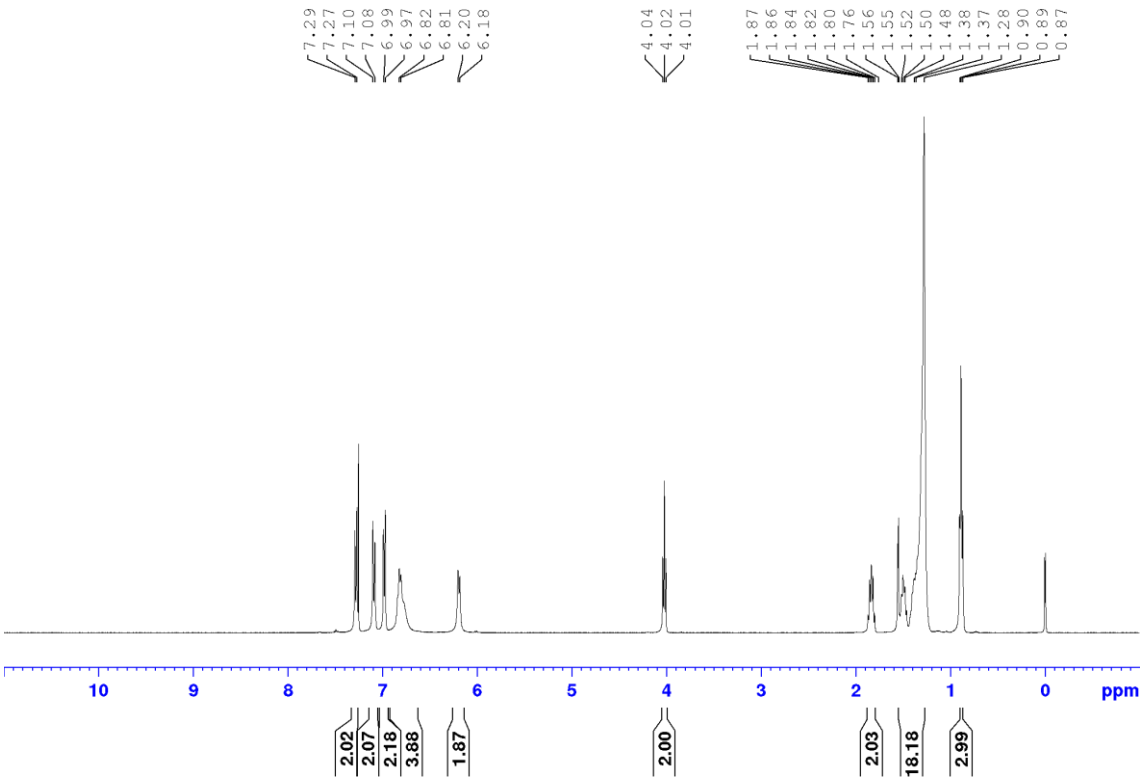


Fig S15. [1]HNMR spectra of **14** (400 MHz).

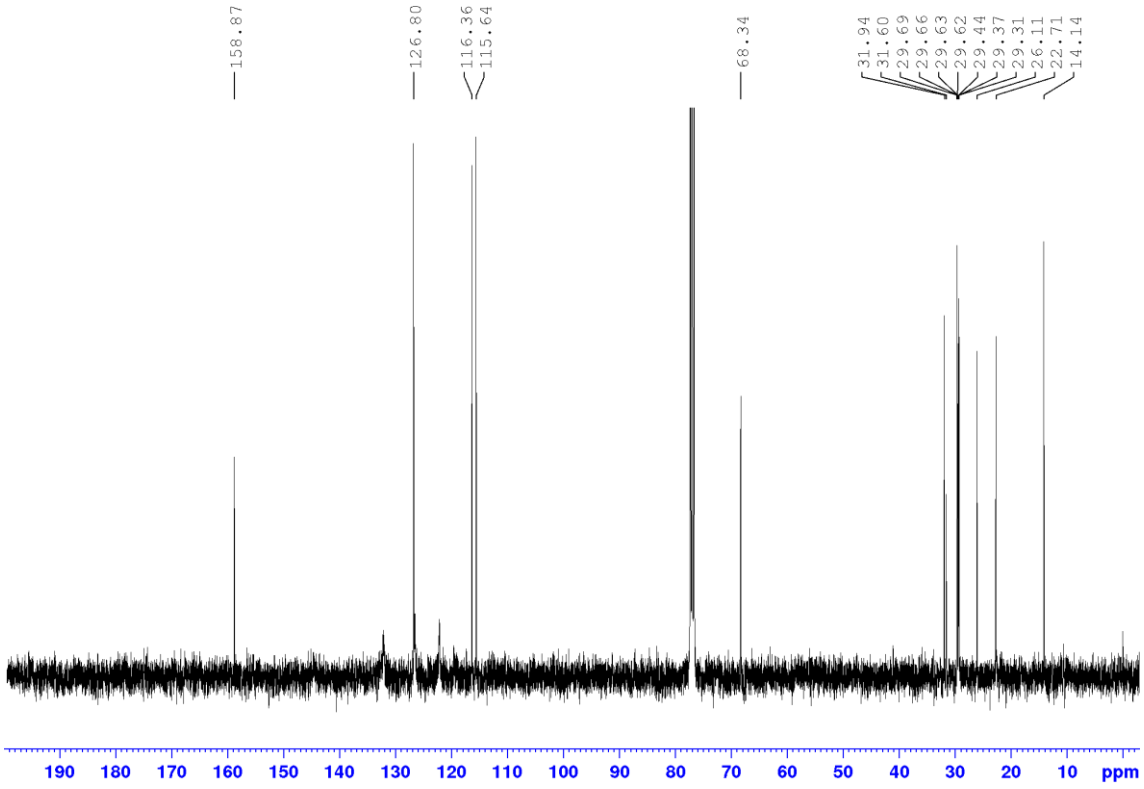


Fig S16. [13]CNMR spectra of **14** (100 MHz).

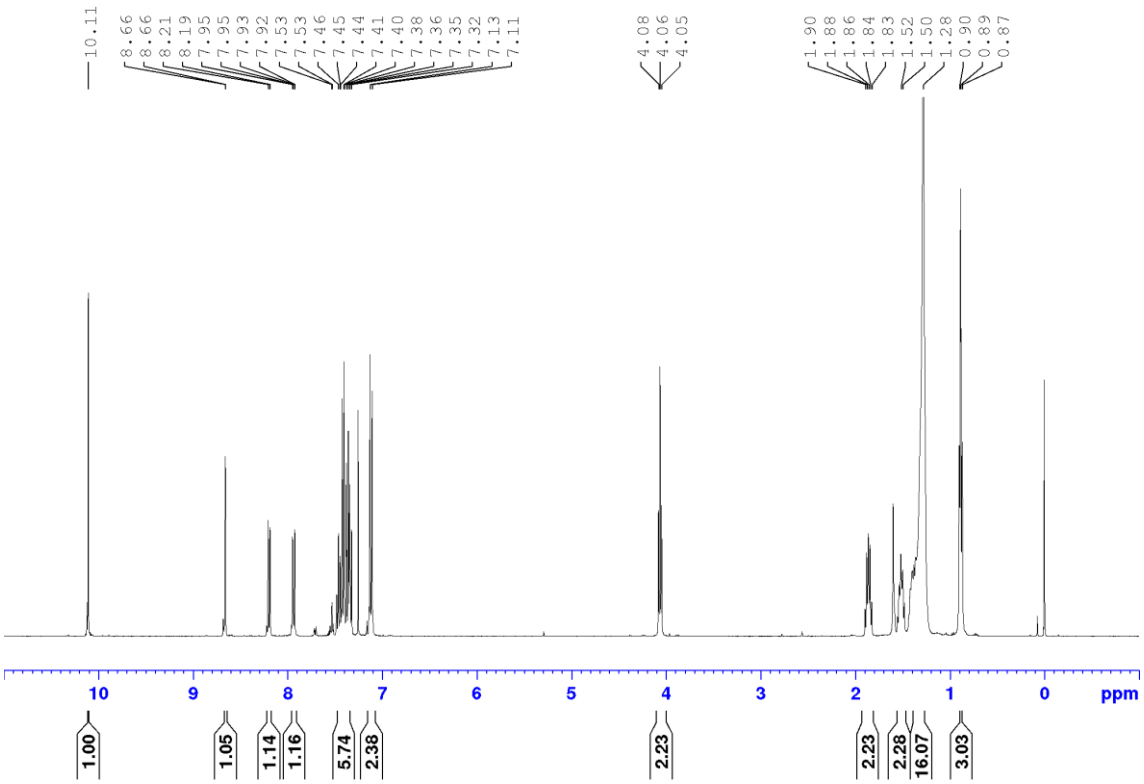


Fig S17. [1]HNMR spectra of **4** (400 MHz).

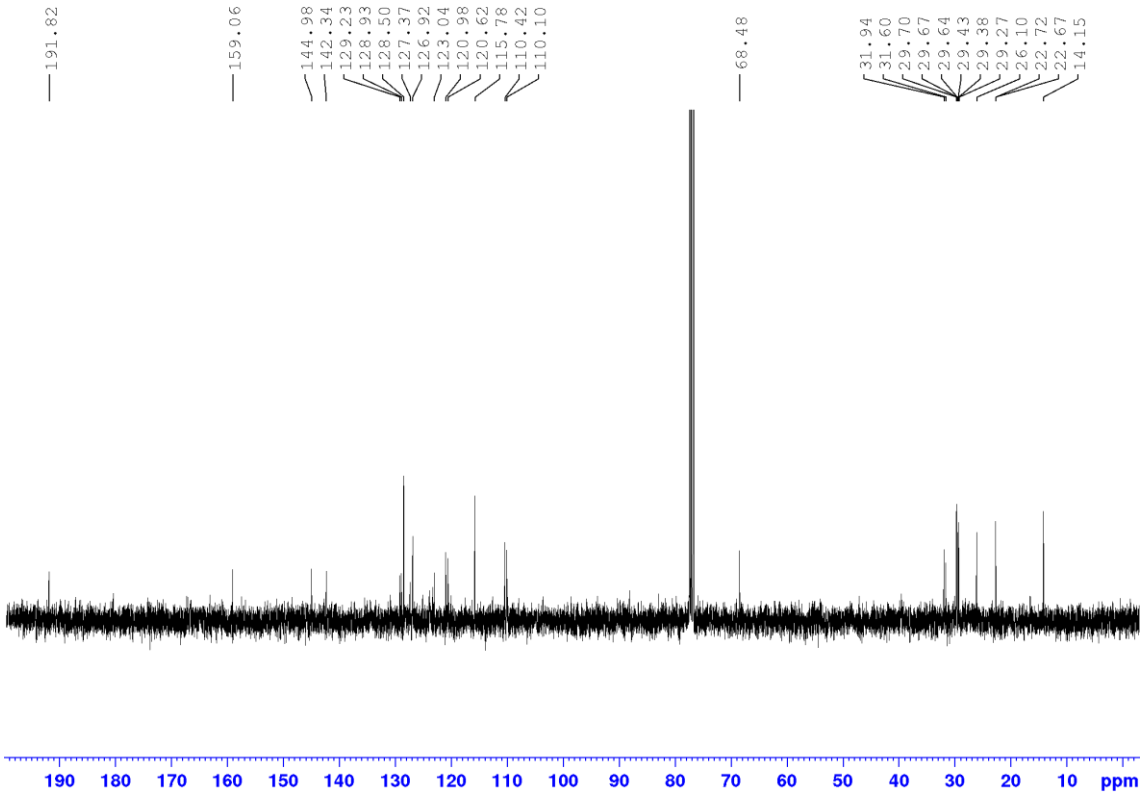


Fig S18. [13]CNMR spectra of **4** (100 MHz).

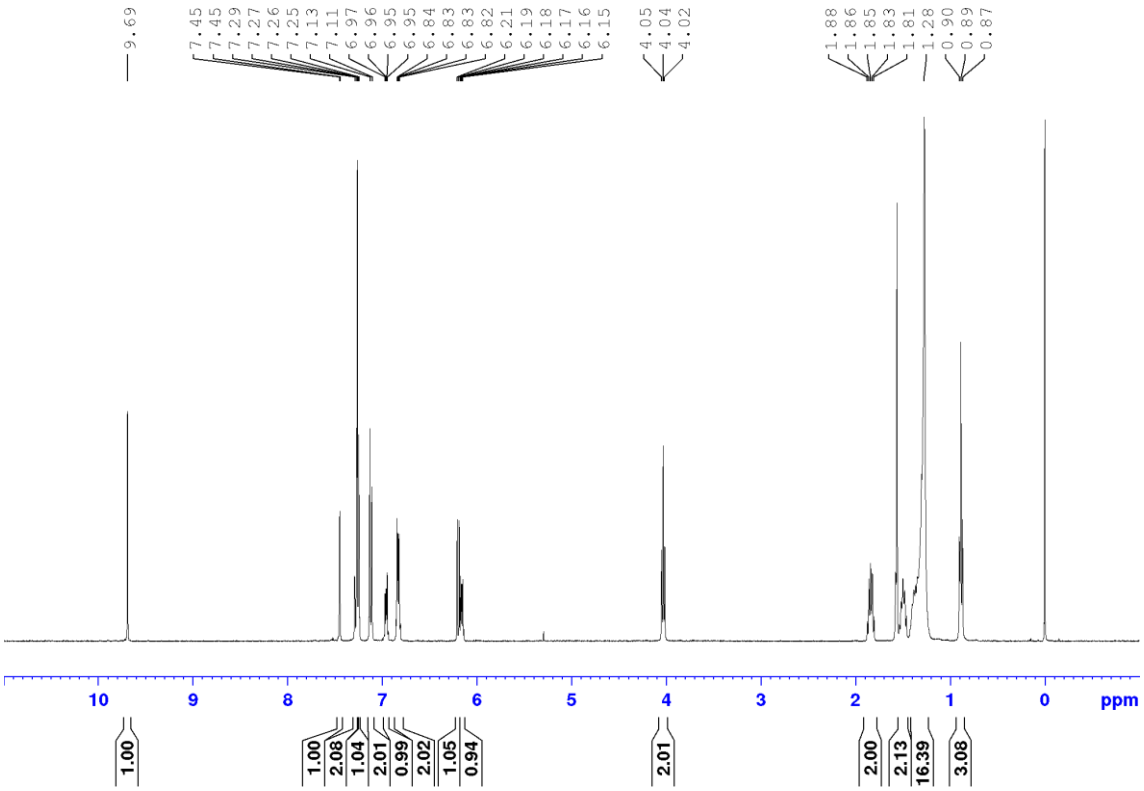


Fig S19. [1]HNMR spectra of **5** (400 MHz).

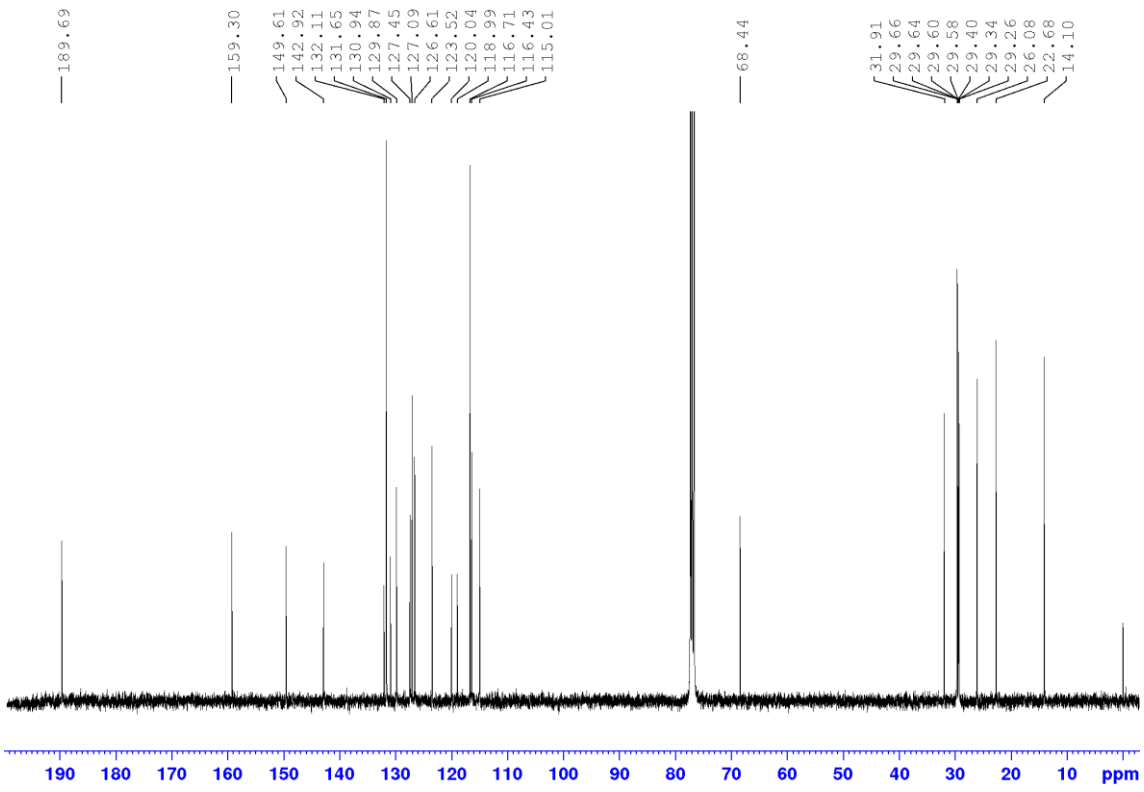


Fig S20. [13]CNMR spectra of **5** (100 MHz).

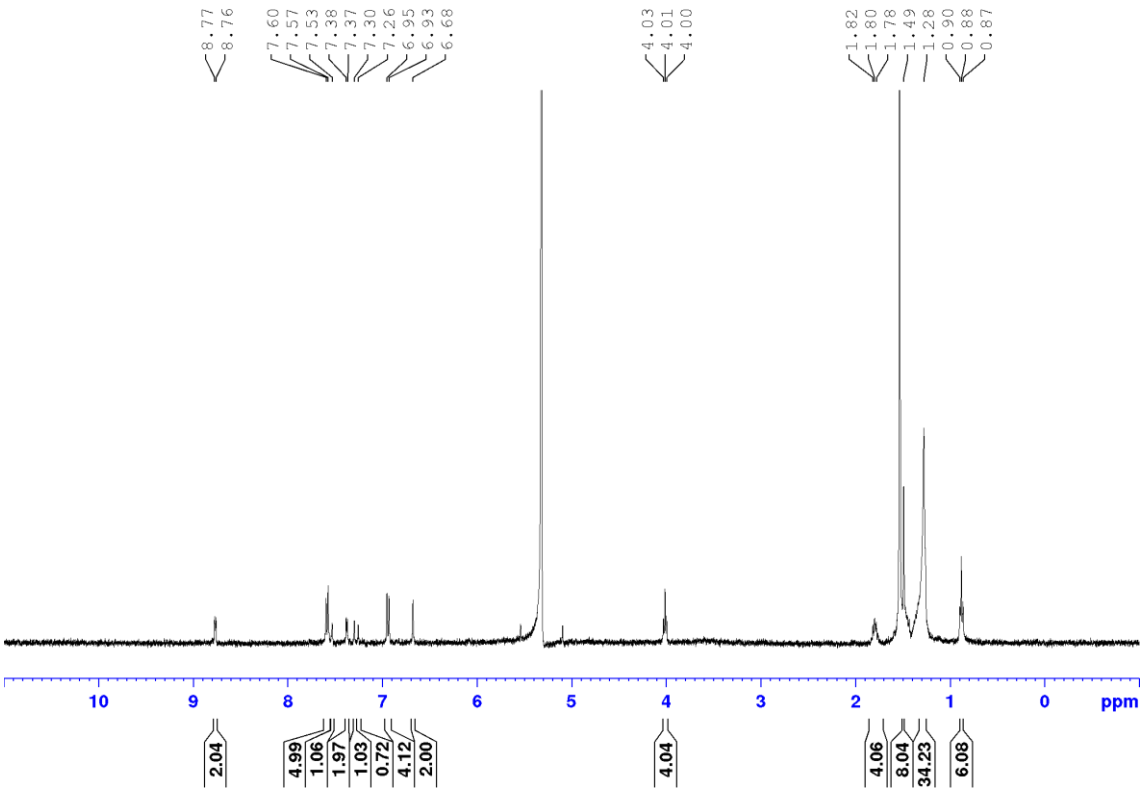


Fig S21. [1]HNMR spectra of **B-Ph** (400 MHz).

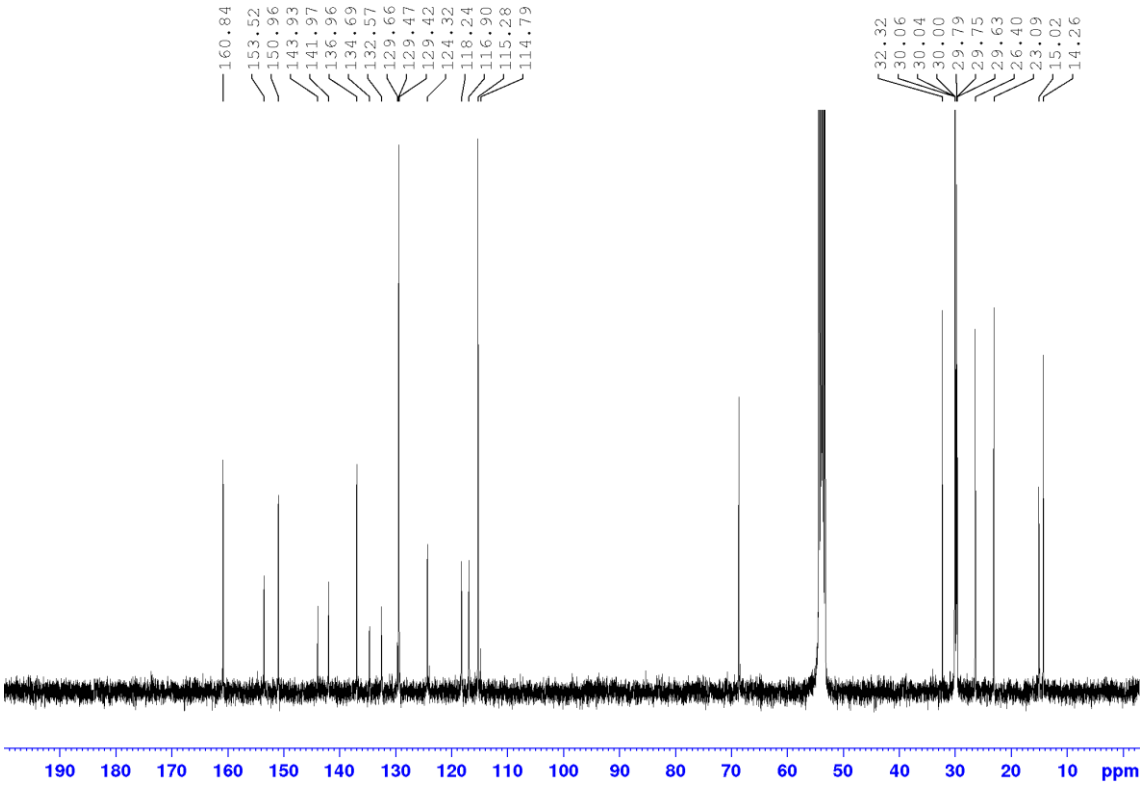


Fig S22. [13]CNMR spectra of **B-Ph** (100 MHz).

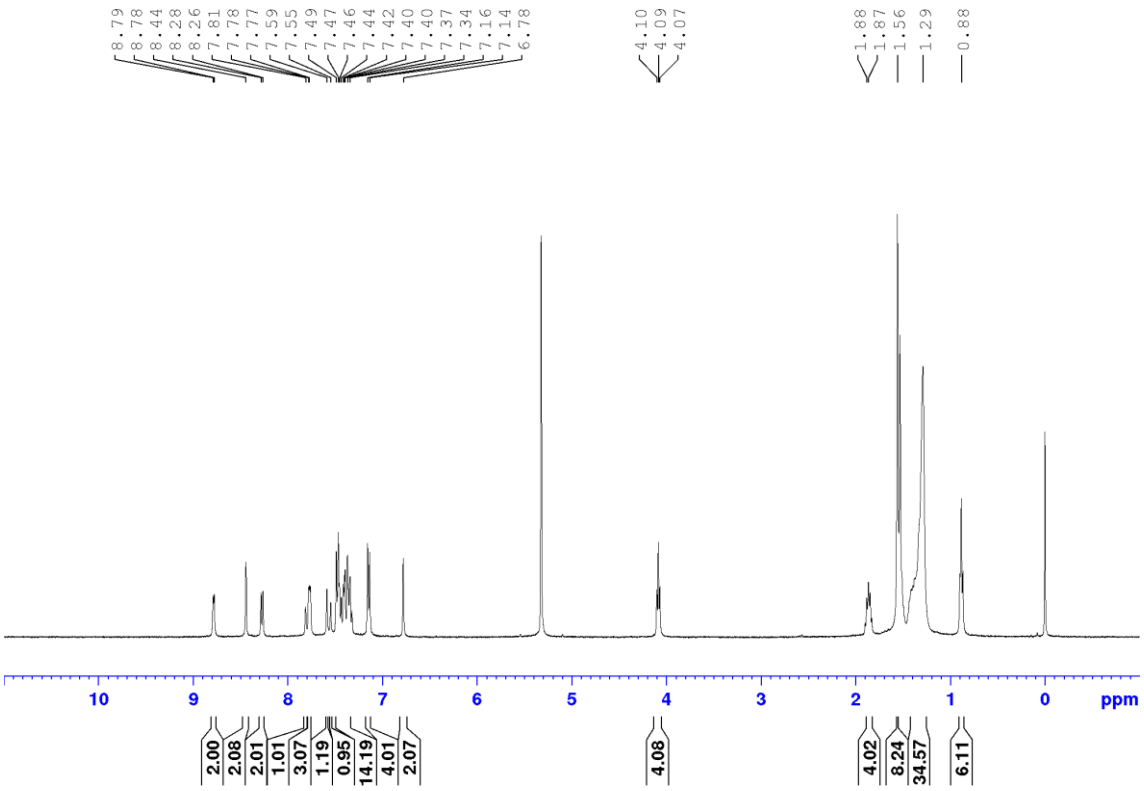


Fig S23. [1]HNMR spectra of **B-Car** (400 MHz).

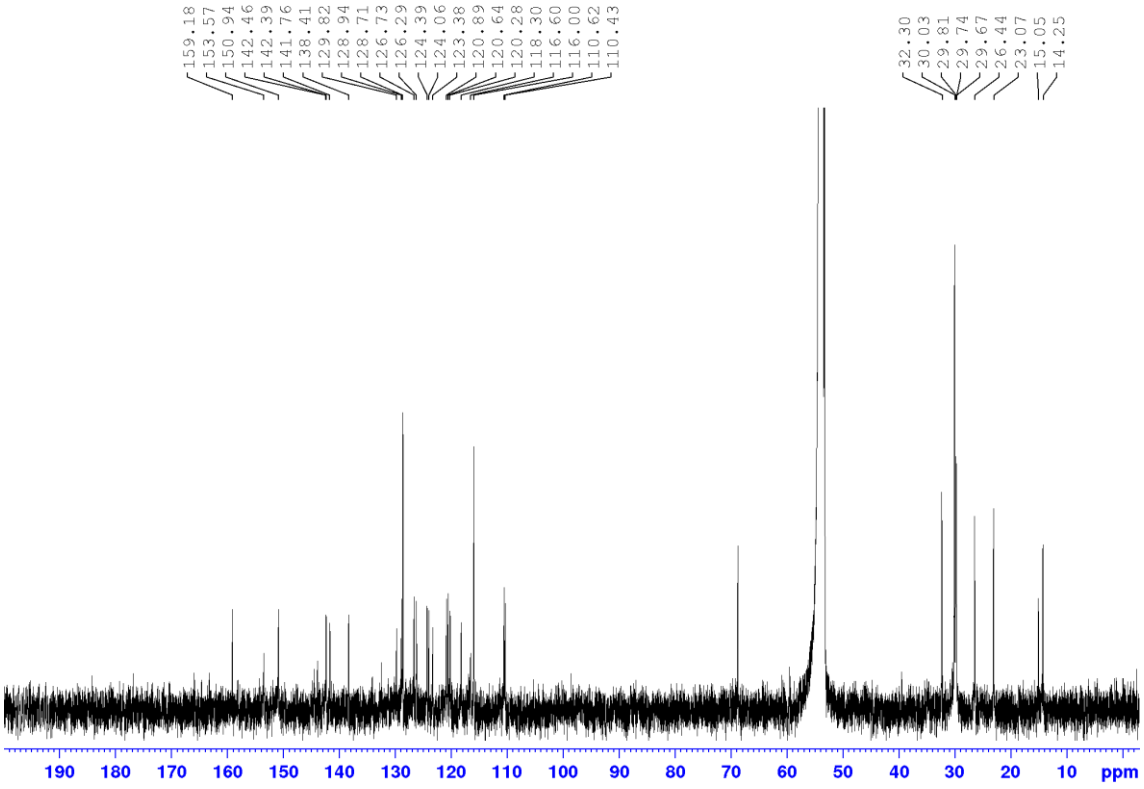


Fig S24. [13]CNMR spectra of **B-Car** (100 MHz).

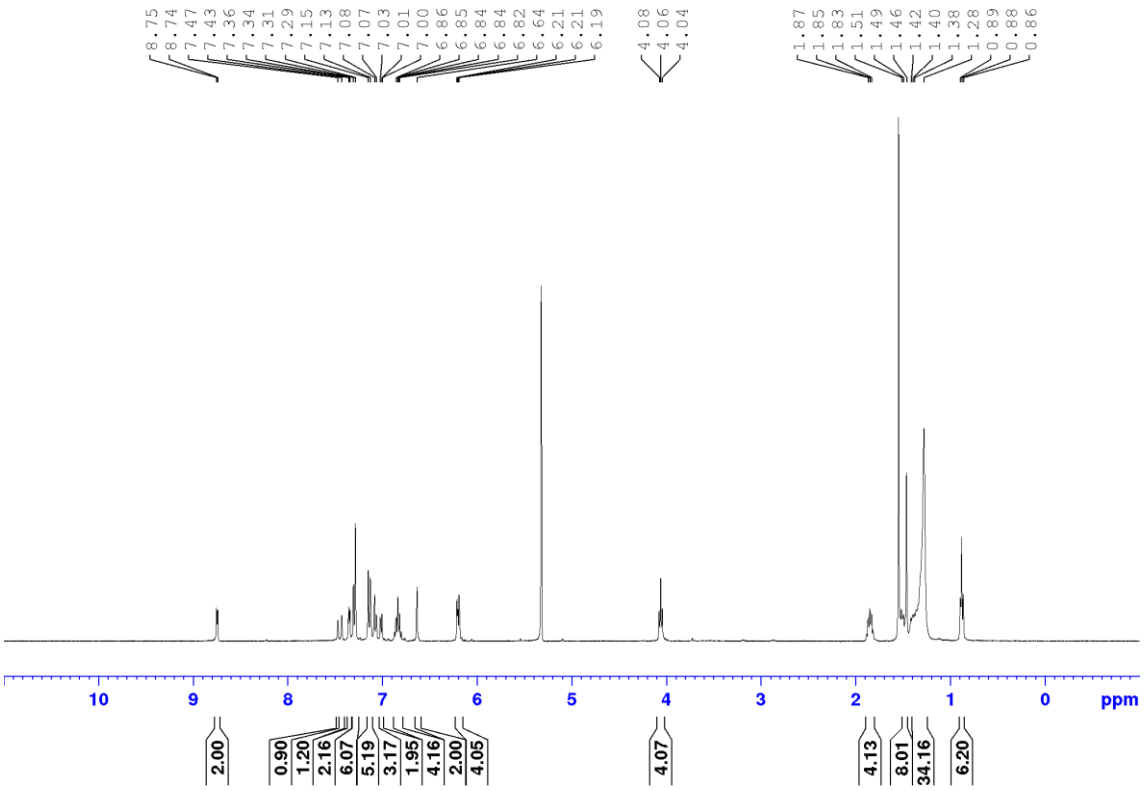


Fig S25. [1]HNMR spectra of **B-Pheno** (400 MHz).

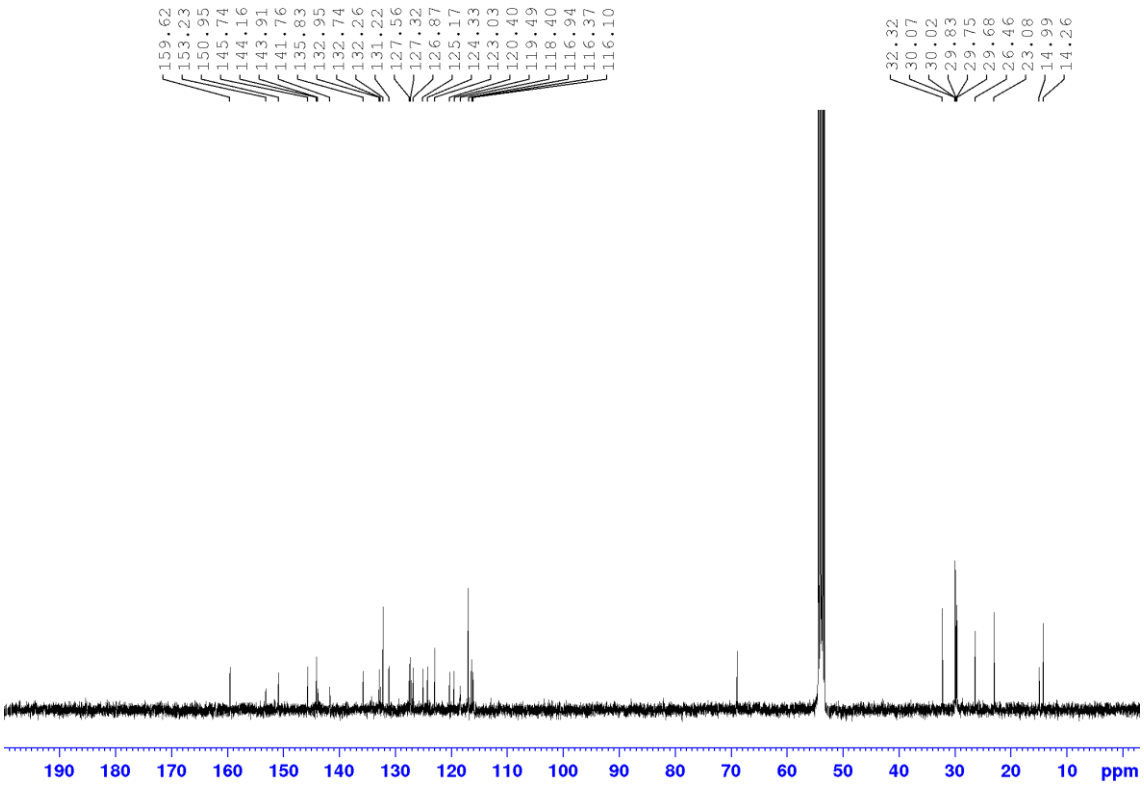


Fig S26. [13]CNMR spectra of **B-Pheno** (100 MHz).

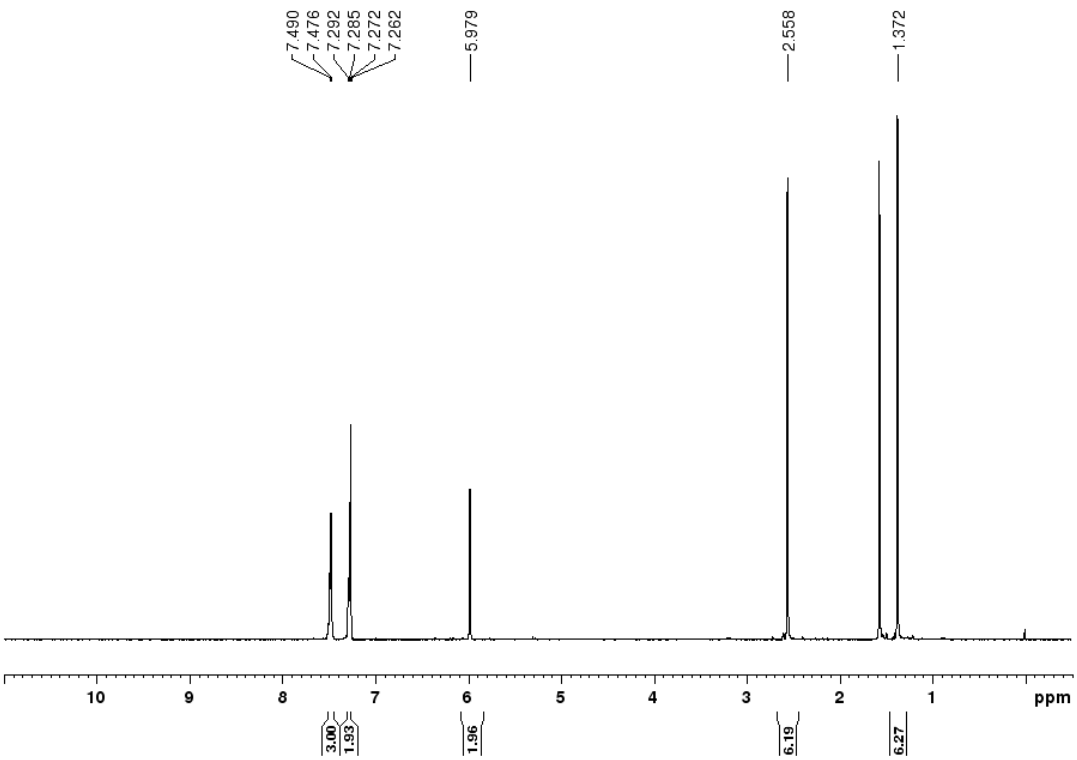


Fig S27. [1]HNMR spectra of **B-ref** (400 MHz).

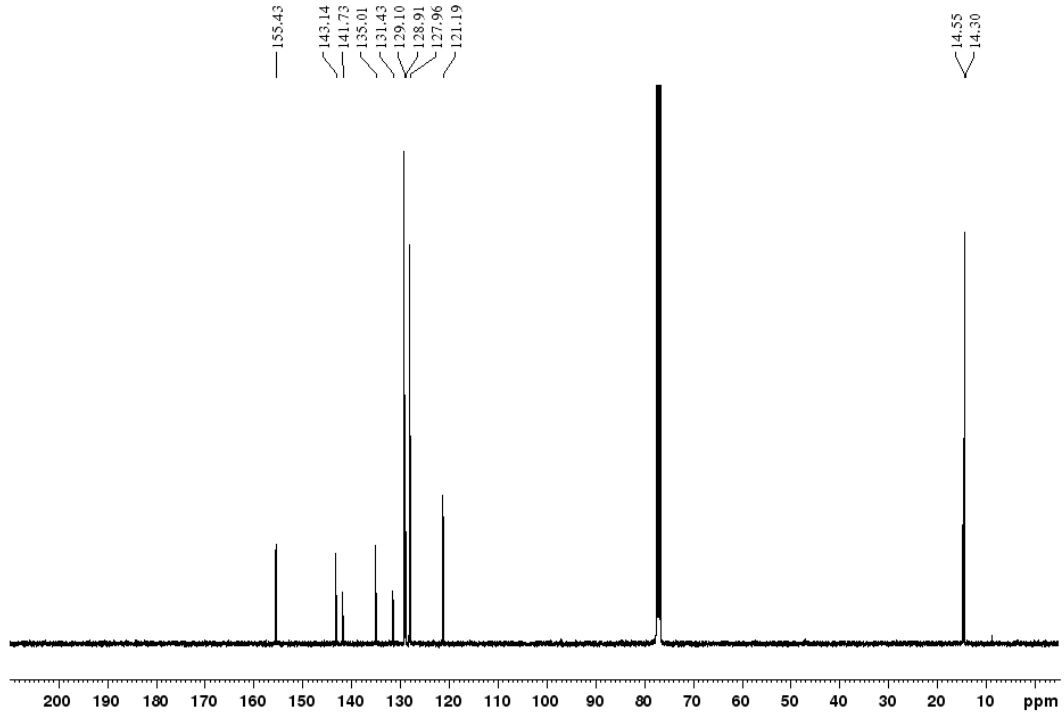


Fig S28. [13]CNMR spectra of **B-ref** (100 MHz).