Electronic Supplementary Information

Influence of the CH…N Interaction in the Self-assembly of an Oligo(isoquinolyne-ethynylyne) Molecule with Distinct Conformational States

Ajiguli Nuermaimaiti[1], *Yanxiao Ning*[1], *Jacob L. Cramer* [1,3], *Katrine Svane*[1,2], *Bjørk Hammer*[1,2], *Kurt V. Gothelf* [1,3], *and Trolle R. Linderoth* [1,2] *

[1]Interdisciplinary Nanoscience Center (iNANO), Aarhus University, 8000 Aarhus C, Denmark

[2]Department of Physics and Astronomy, Aarhus University, 8000 Aarhus C, Denmark

[3]Department of Chemistry, Aarhus University, 8000 Aarhus C, Denmark

Corresponding address:

iNANO and Department of Physics and Astronomy

Aarhus University

E-mail: trolle@inano.au.dk

1. Extra DFT results

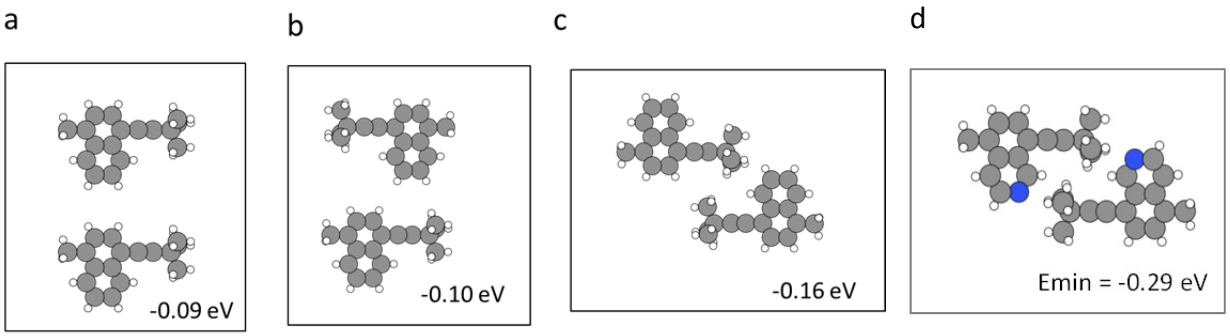
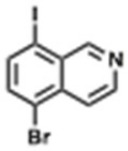


Figure 1 (a-c) DFT-based calculations of the characteristic interaction motifs with the naphthalene substituted fragments. (a) Head-to-tail naphthalene interaction. (b) Staggered head-to-tail naphthalene interaction. (c) naphthalene —tert-butyl interaction. (d) IQ to tBu interaction forming two single H-bond to the non-aromatic hydrogen.

To illuminate the significance of the C-H…N bonds deriving from the replaced nitrogen atoms in the brick-wall structure, the three characteristic interaction motives given in Fig.5 a-c are tested calculating the equivalent ones without the nitrogen atoms (see supporting information). The naphthalene substituted interaction energies are weaker in the b and c motives— the ones that are realized in the brick-wall structure, confirming again that the C-H…N bonds are important for the stabilization of the brick-wall structure.

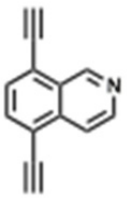
2. Synthetic Procedures



5-Bromo-8-iodoisoquinoline (3)

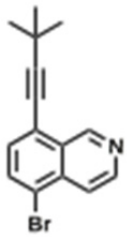
To a three-necked round-bottomed flask equipped with an addition funnel, a septum, and a reflux condenser $BF_3{\cdot}OEt_2$ (1.5 mL, 11.8 mmol) was added. The temperature was lowered to -15 °C (dry ice/acetone) and a solution of 5-bromoisoquinoline-8-amine (**2**) (1.17 g, 5.3 mmol) in THF (30 mL) was added drop wise, followed by the addition of a solution of tert-BuONO (1.4 mL, 11.8 mmol) in THF (10 mL) at the same temperature. After stirring the mixture at -15 °C for 1 h, the temperature was raised to 5 °C over a period of 20 min. Pentane (50 mL) was added and the suspended compound was filtered under suction and washed with pentane (50 mL at 0 °C and 50 mL at room temperature). The brown solid was suspended in MeCN (25 mL) and added to a solution of KI (1.66 g, 10.0 mmol) in MeCN (25 mL) and H_2O (5 mL) at room temperature. The

mixture was refluxed for 3 h and was then allowed to cool to room temperature. The aqueous layer was extracted with CH_2Cl_2 (3×40 mL) whereafter the combined organic phases were dried over $MgSO_4$, filtered, and evaporated in vacuo to yield the pure product as a yellow powder (800 mg, 48%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.37 (s, 1H), 8.69 (d, J = 5.9, 1H), 7.95 (d, J = 7.9, 1H), 7.85 (d, J = 5.9, 1H), 7.62 (d, J = 8.1, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.1, 145.6, 138.9, 136.1, 134.7, 129.3, 122.8, 119.1, 97.4. HRMS m/z calcd. for C_9H_6NBrI [M+H$^+$]: 333.7828, found 333.7828. M.p. 107-109 °C.



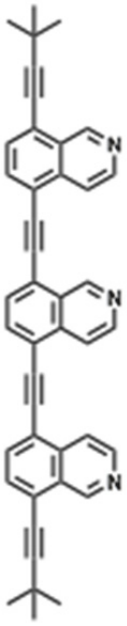
5,8-Diethynylisoquinoline (4)

To a flame-dried Schlenk flask were added **3** (406 mg, 1.22 mmol), bis-(triphenylphosphine)-palladium(II)-dichloride (85 mg, 0.12 mmol), and copper(I)-iodide (23 mg, 0.12 mmol). After three successive vacuum/argon cycles, 2-methylbut-3-yn-2-ol (1.3 mL, 6.1 mmol), DMF (15 mL), triethylamine (2 mL), and tri-tert-butylphosphine (0.24 mL, 0.24 mmol, 1 M in toluene) were introduced via syringes. The reaction was stirred at 65 °C overnight. The reaction mixture was then poured into H_2O (20 mL) and the aqueous layer was extracted with diethyl ether (3x15 mL). The combined organic phases were washed with H_2O (3x15 mL), dried over $MgSO_4$, and the solvent was evaporated in vacuo to yield a red powder. The red powder was dissolved in PhMe (10 mL) and a solution of NaOH (100 mg, 2.5 mmol) dissolved in PhMe (5 mL) was added. The reaction mixture was refluxed overnight and then allowed to cool to room temperature. The reaction mixture was poured into H_2O (20 mL) and the aqueous layer was extracted with ethyl acetate (3x15 mL). The combined organic phases were dried over $MgSO_4$, filtered, and evaporated in vacuo. Purification by flash column chromatography (ethyl acetate/pentane = 1:3, v/v) yielded the product as a red powder (151 mg, 70%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.70 (s, 1H), 8.67 (d, J = 5.9, 1H), 8.08 (d, J = 7.9, 1H), 7.80 (d, J = 5.9, 1H), 7.69 (d, J = 7.9, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.4, 144.9, 136.4, 134.2, 131.7, 128.0, 121.5, 120.3, 118.8, 85.5, 85.1, 80.1, 79.8. HRMS m/z calcd. for $C_{13}H_8N$ [M+H$^+$]: 178.0657, found 178.0664. M.p. 142-144 °C.



5-Bromo-8-(3,3-dimethylbut-1-yn-1-yl)isoquinoline (5)

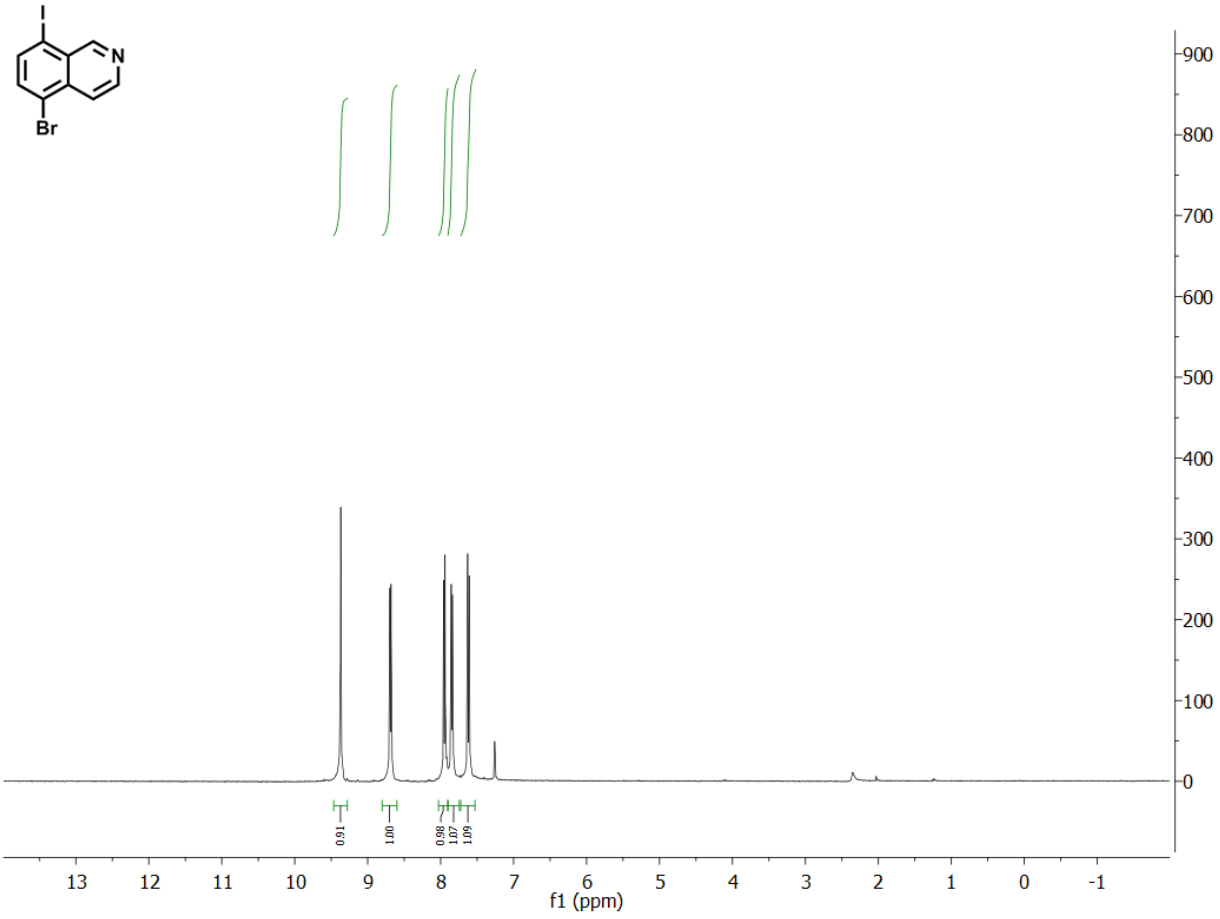
To a flame-dried Schlenk flask were added **3** (626 mg, 1.87 mmol), bis-(triphenylphosphine)-palladium(II)-dichloride (130 mg, 0.19 mmol), and copper(I)-iodide (35 mg, 0.19 mmol). After three successive vacuum/argon cycles, tert-butylacetylene (154 mg, 1.87 mmol) dissolved in DMF (10 mL) and triethylamine (2 mL) was introduced via syringes. The reaction was stirred at 25 °C overnight. The reaction mixture was then poured into H_2O (25 mL) and extracted with diethyl ether (3x15 mL). The combined organic phases were washed with H_2O (3x15 mL), dried over $MgSO_4$, filtered, and evaporated in vacuo. Purification by flash column chromatography (ethyl acetate/pentane = 1:9, v/v) yielded the product as a yellow oil (404 mg, 75%). ^{1}H NMR (400 MHz, CD_3CN) δ 9.55 (s, 1H), 8.60 (s, 1H), 7.82 (s, 1H), 7.80 (d, J = 7.7, 1H), 7.40 (d, J = 7.7, 1H), 1.44 (s, 9H). ^{13}C NMR (100 MHz, CD_3CN) δ 151.4 (d, J = 30 Hz, 1C), 145.2 (s, 1C), 134.8 (s, 1C), 133.7 (d, J = 38 Hz, 1C), 131.4 (d, J = 34 Hz, 1C), 129.0 (s, 1C), 122.4 (s, 1C), 120.5 (s, 1H), 119.0 (d, J = 39 Hz, 1C), 106.9 (s, 1C), 75.1 (s, 1C), 30.5 (q, J = 12, 3C), 28.5 (s, 1C). HRMS m/z calcd. for $C_{15}H_{15}NBr$ [M+H$^+$]: 288.0388, found 288.0388.

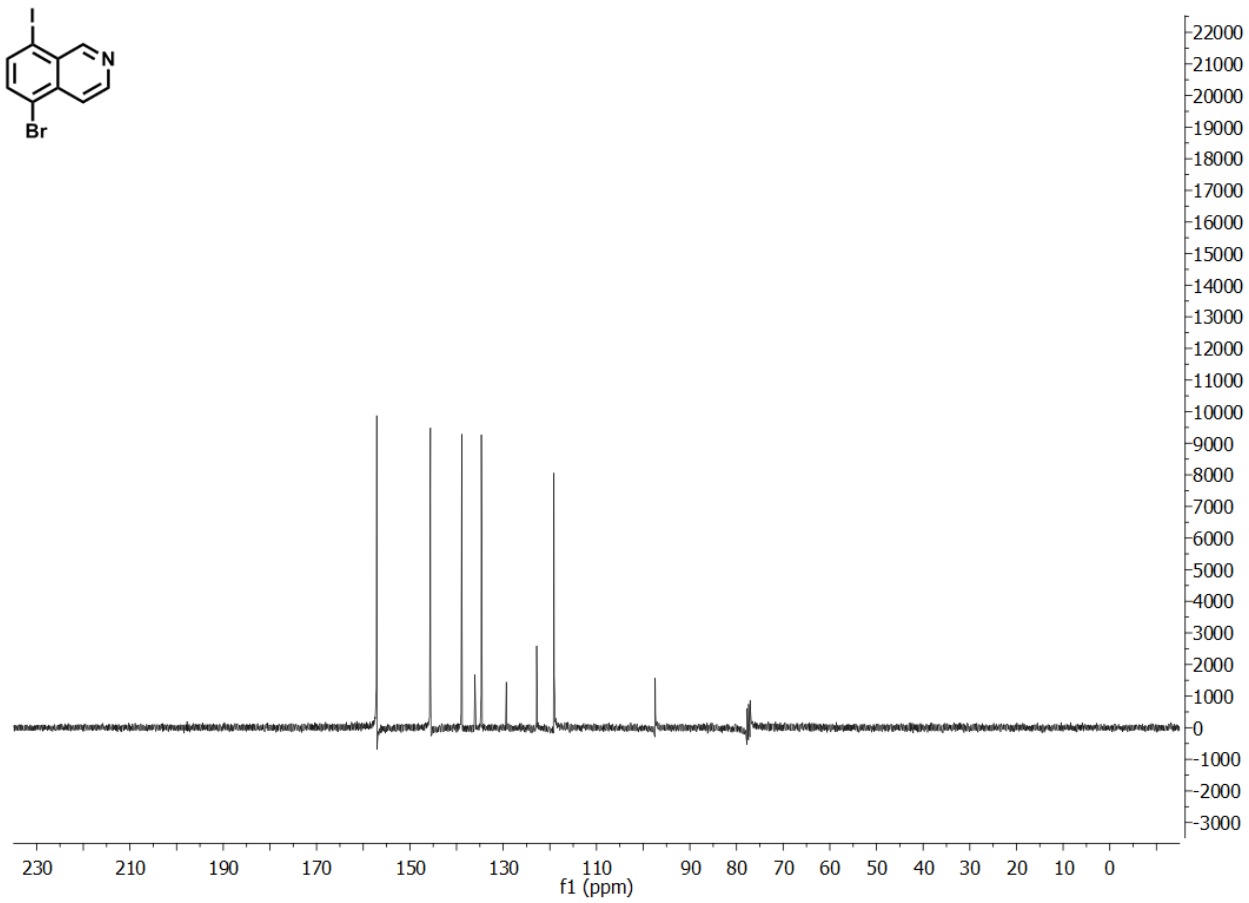


Isoquinoline trimer (1)

To a flame-dried Schlenk flask were added **4** (49 mg, 0.28 mmol), **5** (159 mg, 0.55 mmol), bis-(triphenylphosphine)-palladium(II)-dichloride (39 mg, 0.055 mmol), and copper(I)-iodide (10 mg, 0.055 mmol). After three successive vacuum/argon cycles, DMF (15 mL), triethylamine (2 mL), and tri-*tert*-butylphosphine (0.1 mL, 0.1 mmol, 1 M in toluene) were introduced via syringes. The reaction was stirred at 70 °C overnight. The reaction mixture was then poured into H_2O (30 mL) and extracted with diethyl ether (3x25 mL). The combined organic phases were washed with H_2O (3x20 mL), dried over $MgSO_4$, filtered, and evaporated in vacuo. Purification by flash column chromatography ($MeOH/CH_2Cl_2$ = 1:20, v/v) yielded the product as an orange powder (61 mg, 37%). ^1H NMR (400 MHz, $CDCl_3$) δ 9.88 (s, 1H), 9.71 (m, 2H), 8.76 (m, 3H), 8.20 (m, 3H), 7.96 – 7.84 (m, 4H), 7.65 (m, 2H), 1.43 (s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.1, 151.6, 145.2, 144.9, 144.8, 136.1, 136.0, 134.4, 134.2, 133.9, 131.4, 130.7, 128.2, 124.0, 123.9, 122.0, 120.7, 119.1, 118.9, 118.8, 108.3, 94.7, 94.3, 93.0, 92.6, 75.7, 31.1, 29.3. HRMS m/z calcd. for $C_{43}H_{34}N_3$ $[M+H^+]$: 592.2753, found 592.2755. M.p. 223-225 °C.

3. NMR spectra

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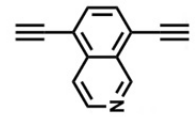

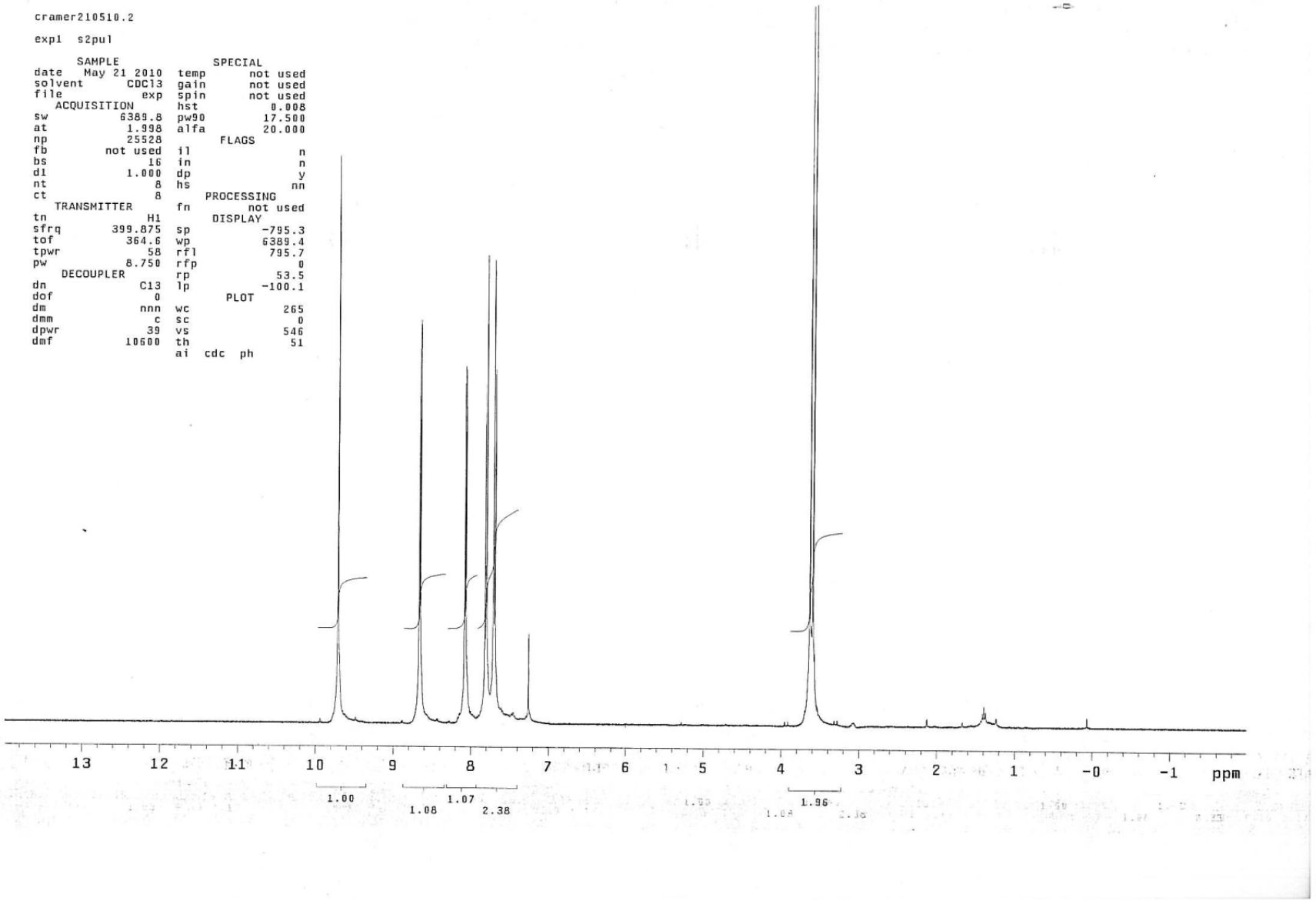
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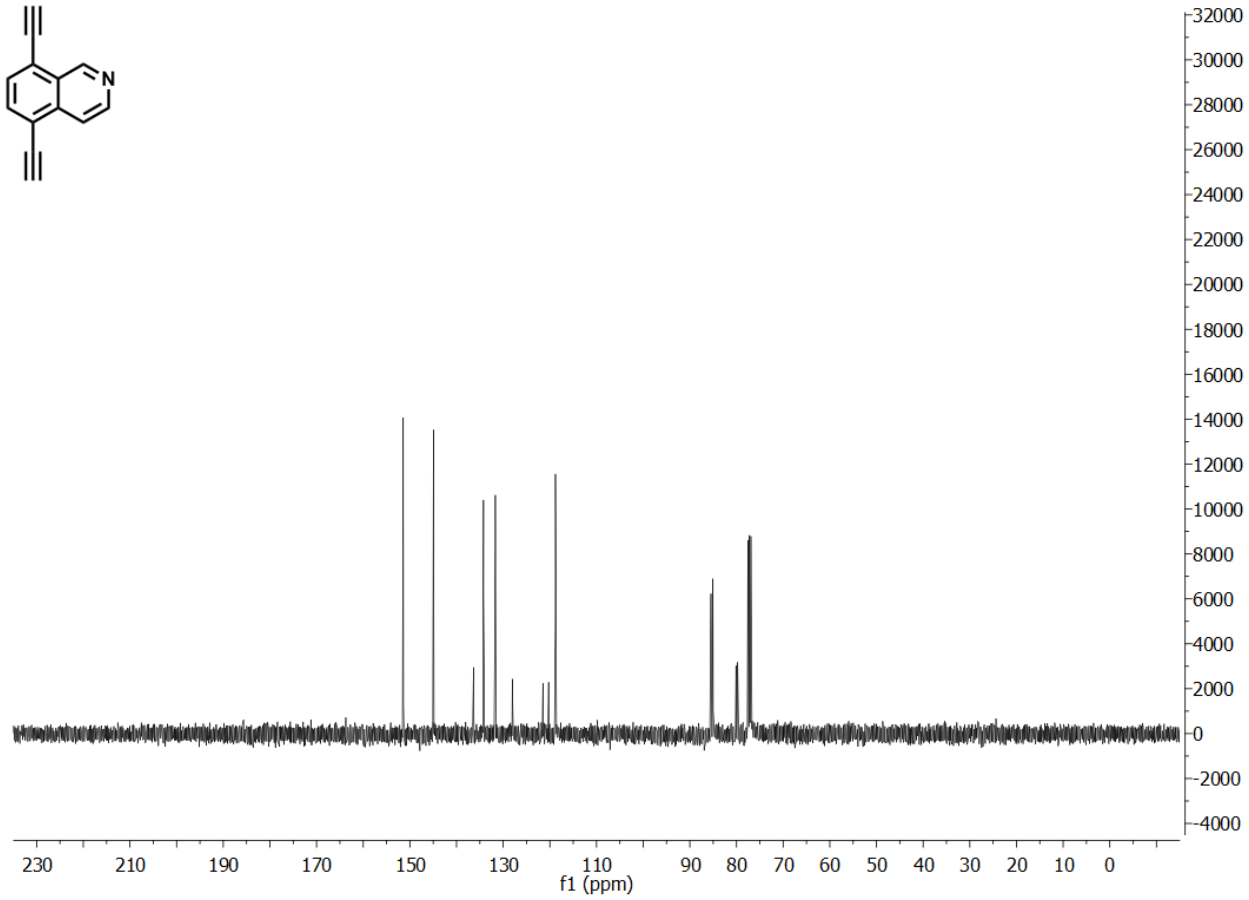
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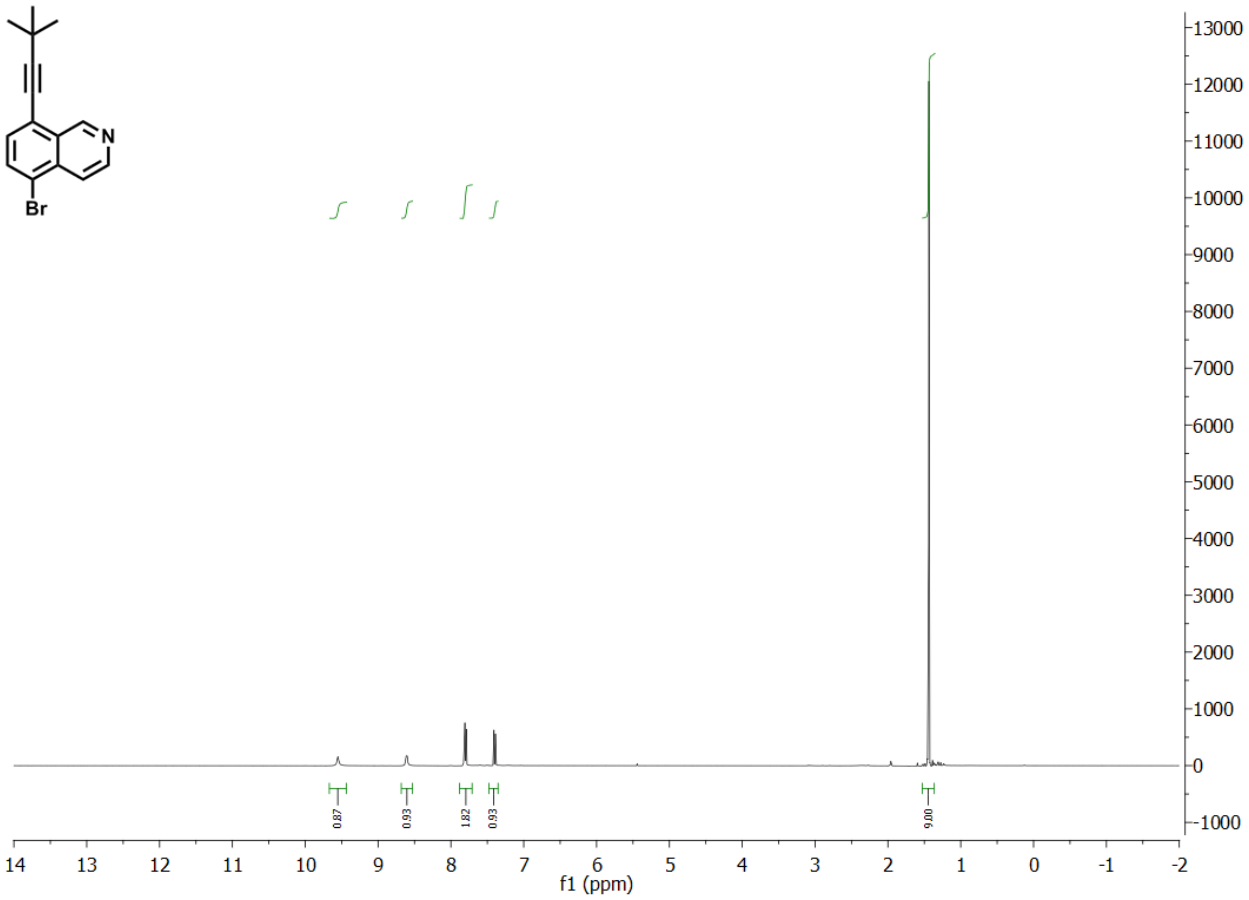
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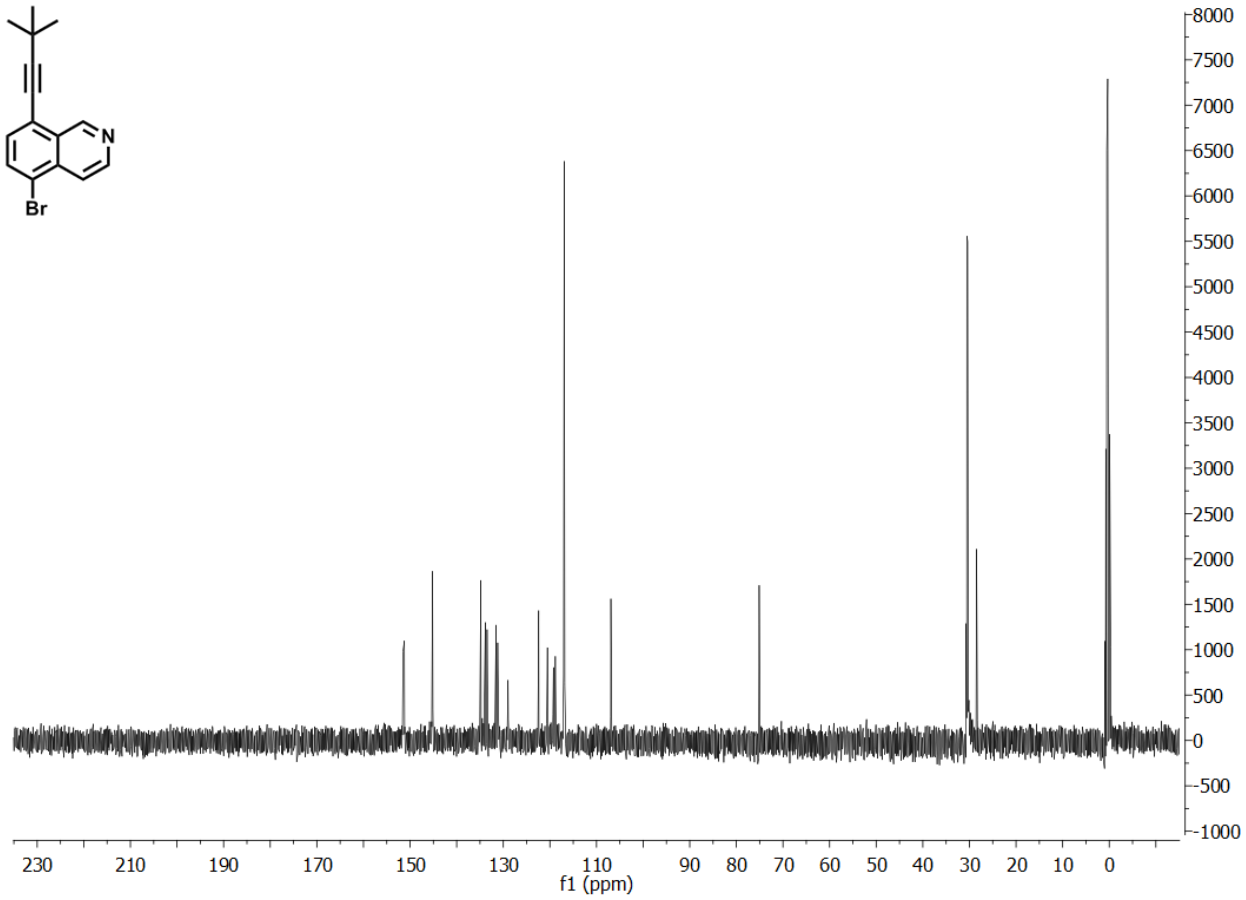
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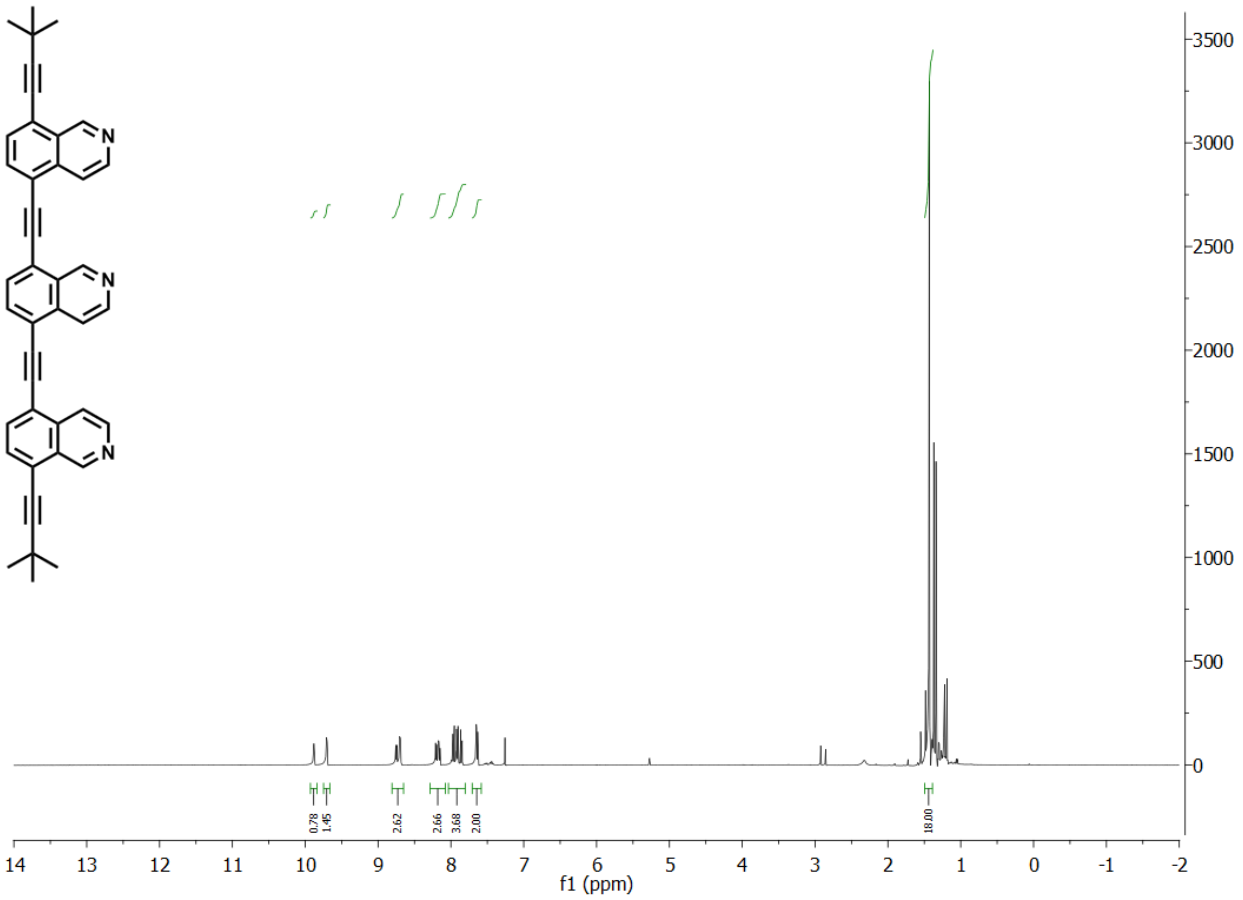
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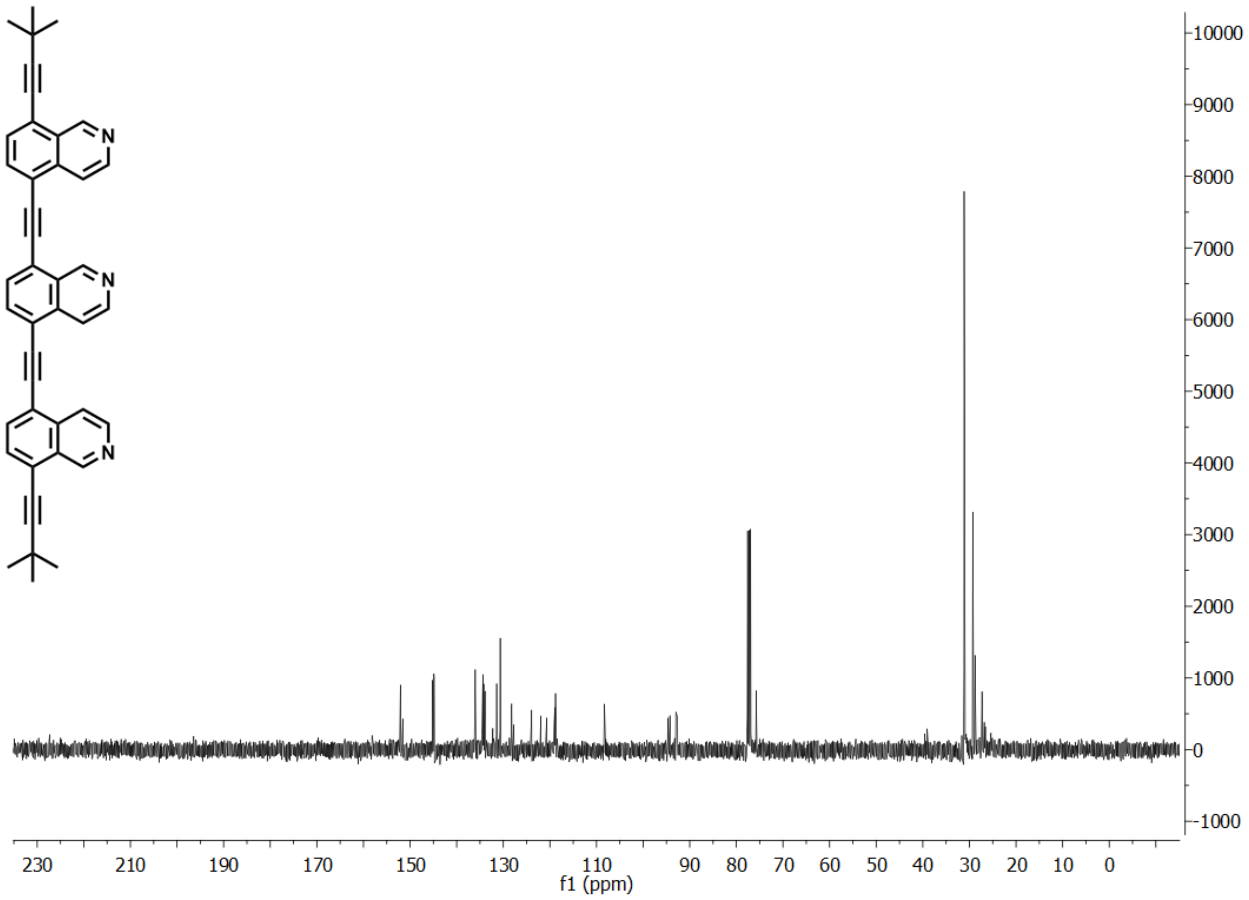
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