Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Cover Page for Supporting Information

Manuscript Title:

Combining Pd(π-allyl)Cp and PPh_3 as a unique Catalyst for Efficient Synthesis of Alkyliodo Indoles via C(sp3)-I Reductive Elimination

Authors:

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1) Experimental Details and Characterization Data

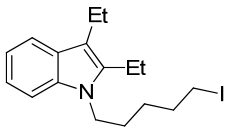
General Information

Unless otherwise noted, all starting materials were commercially available and were used without further purification. Solvents were purified by a Mbraun SPS-800 Solvent Purification System. *n*BuLi, palladium catalyst and phosphine ligand was obtained from Aldrich, TCI, Alfa, Acros, Adamas-beta, J&K and others. All reactions were carried out under a dry and oxygen-free nitrogen atmosphere in slight positive pressure by using Schlenk techniques, unless otherwise noted.

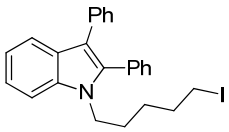
^{1}H and ^{13}C NMR spectra were recorded on a Bruker ARX400 spectrometer (FT, 400 MHz for ^{1}H; 100 MHz for ^{13}C) or Bruker ARX500 spectrometer (FT, 500 MHz for ^{1}H, 125 MHz for ^{13}C, 202 MHz for ^{31}P) at room temperature, unless otherwise noted. For ^{31}P NMR, chemical shifts are referenced to 85% H_3PO_4 as an external standard. High-resolution mass spectra (HRMS) were recorded on a Bruker Apex IV FTMS mass spectrometer using ESI (electrospray ionization). GC analyses were recorded on SHIMADZU GC-2010 spectrometer using FID.

Procedures and Characterization Data

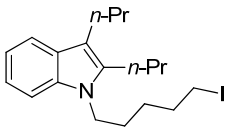
Typical procedure for the preparation of 2: Under an atmosphere of nitrogen, Pd(π-allyl)(Cp) (5 mol %), PPh_3 (10 mol %) and LiO^tBu (0.36 mmol), were added in 2 mL cyclohexane. The reaction mixture was then stirred at room temperature for 5 min and **1** (0.3 mmol) and alkyne (0.36 mmol) were added under nitrogen. The reaction mixture was stirred at 130 °C for 12 h (aliphatic alkynes) or 48 h (aromatic alkynes). The reaction mixture was cooled to room temperature, quenched with water and extracted with Et_2O. The combined organic layer was washed with brine and dried over $MgSO_4$. The solvent was then evaporated in vacuo and the residue was purified by silica gel column chromatography with petroleum ether and ethyl acetate (10:1) as eluent to afford the final products. Products **2a-c** and **2e-f** are known compounds and their NMR spectra are in consistence with those in the literature.[1]



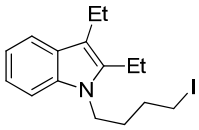
2a[1]**:** Yellow oil, isolated yield 90% (100 mg). ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si): δ 1.19-1.25 (m, 6H, CH_3), 1.44-1.52 (m, 2H, CH_2), 1.73-1.87 (m, 4H, CH_2), 2.70-2.79 (m, 4H, CH_2), 3.16 (t, J = 6.9, 2H, CH_2), 4.05 (t, J = 7.6 Hz, 2H, CH_2), 7.06 (t, J = 7.4 Hz, 1H, CH), 7.13 (t, J = 7.5 Hz, 1H, CH), 7.24 (d, J = 8.8 Hz, 1H, CH), 7.54 (d, J = 7.8 Hz, 1H, CH).



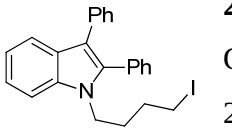
2b[1]**:** Yellow oil, isolated yield 72% (100 mg). ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si): δ 1.21-1.28 (m, 2H, CH_2), 1.60-1.71 (m, 4H, CH_2), 3.02 (t, J = 7.0 Hz 2H, CH_2), 4.10 (t, J = 7.5 Hz, 2H, CH_2), 7.23-7.33 (m, 9H, CH), 7.38-7.40 (m, 4H, CH), 7.80 (d, J = 7.9 Hz , 1H, CH).



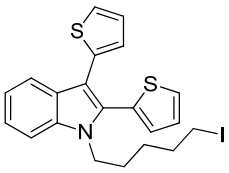
2c[1]**:** Yellow oil, isolated yield 88% (105 mg). ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si): δ 0.95-1.03 (m, 6H, CH_3), 1.43-1.50 (m, 2H, CH_2), 1.56-1.68 (m, 4H, CH_2), 1.71-1.77 (m, 2H, CH_2), 1.79-1.86 (m, 2H, CH_2), 2.65-2.71 (m, 4H, CH_2)， 3.16 (t, J = 6.9 Hz, 2H, CH_2), 4.04 (t, J = 7.6 Hz, 2H, CH_2), 7.03-7.07 (m, 1H, CH), 7.10-7.14 (m, 1H, CH), 7.23 (d, J = 8.6 Hz, 1H, CH), 7.52 (d, J = 7.7 Hz, 1H, CH).



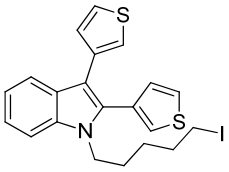
2d[1]**:** Yellow oil, isolated yield 82% (87 mg). ^{1}H NMR (500 MHz, $CDCl_3$, Me_4Si): δ 1.20-1.25 (m, 6H, CH_3), 1.87-1.89 (m, 4H, CH_2), 2.71-2.79 (m, 4H, CH_2), 3.17 (t, J = 6.5 Hz, 2H, CH_2), 4.08 (t, J = 7.0 Hz, 2H, CH_2), 7.04-7.08 (m, 1H, CH), 7.12-7.15 (m, 1H, CH), 7.25 (s, 1H, CH), 7.54 (d, J = 7.5 Hz, 1H, CH).



2e: Yellow oil, isolated yield 66% (89 mg). ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si): δ 1.60-1.67 (m, 2H, CH_2), 1.75-1.82 (m, 2H, CH_2), 2.96 (t, J = 6.8 Hz, 2H, CH_2), 4.12 (t, J = 7.2 Hz, 2H, CH_2), 7.14-7.20 (m, 2H, CH), 7.23-7.34 (m, 7H, CH), 7.37-7.43 (m, 4H, CH), 7.80 (d, J = 7.9 Hz, 1H, CH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 5.6 (CH_2), 30.6 (CH_2), 30.7 (CH_2), 42.6 (CH_2), 109.8 (CH), 115.6 (quat. C), 119.9 (CH), 120.2 (CH), 122.2 (CH), 125.5 (CH), 127.3 (quat. C), 128.1 (2 CH), 128.2 (CH), 128.5 (2 CH), 129.8 (2 CH), 131.2 (2 CH), 132.1 (quat. C), 135.0 (quat. C), 136.3 (quat. C), 137.4 (quat. C). HRMS calcd. for $C_{24}H_{23}IN$ $[M+H]^+$: 452.0870, found 452.0876.

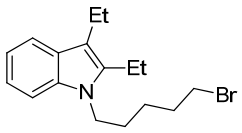


2f[1]**:** Yellow oil, isolated yield 75% (107 mg). ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si): δ 1.32-1.40 (m, 2H, CH_2), 1.70-1.80 (m, 4H, CH_2), 3.10 (t, J = 6.9 Hz, 2H, CH_2), 4.10 (t, J = 7.6 Hz, 2H, CH_2), 6.99-7.03 (m, 2H, CH), 7.15-7.23 (m, 4H, CH), 7.29-7.33 (m, 1H, CH), 7.38 (d, J = 8.2 Hz, 1H, CH), 7.52-7.54 (m, 1H, CH), 7.93 (d, J = 8.0 Hz, 1H, CH).



2g: Yellow oil, isolated yield 62% (89 mg). ^{1}H NMR (400 MHz, C_6D_6, Me_4Si): δ 0.68-0.76 (m, 2H, CH_2), 1.04-1.11 (m, 2H, CH_2), 1.12-1.19 (m, 2H, CH_2), 2.43 (t, J = 7.1 Hz, 2H, CH_2), 3.58 (t, J = 7.4 Hz, 2H, CH_2), 6.75-6.77 (m, 1H, CH), 6.84-6.86 (m, 2H, CH), 6.90-6.92 (m, 1H, CH), 6.99-7.00 (m, 1H, CH), 7.09-7.11 (m, 1H, CH), 7.17 (s, 1H, CH), 7.23-7.34 (m, 2H, CH), 7.95 (d, J = 7.7 Hz, 1H, CH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 6.3 (CH_2), 27.7 (CH_2), 28.9 (CH_2), 32.7 (CH_2), 43.6 (CH_2), 109.7 (CH), 111.2 (quat. C), 119.9 (CH), 120.2 (CH), 120.8 (CH), 122.2 (CH), 124.5 (CH), 126.0 (CH), 126.1 (CH), 126.9 (quat. C), 128.5 (CH), 129.5 (CH), 132.2 (quat. C), 132.3 (quat. C), 135.2 (quat. C), 136.2 (quat. C). HRMS calcd. for $C_{21}H_{21}INS_2$ $[M+H]^+$: 478.0155, found 478.0152.

Procedure for the preparation of 4: Under an atmosphere of nitrogen, Pd(-allyl)(Cp) (5 mol %), PPh_3 (10 mol %) and LiO^tBu (0.36 mmol), were added to 2 mL cyclohexane After this reaction mixture was stirred at room temperature for 5 min, **3** (0.3 mmol) and 3-hexyne (0.36 mmol) were added and the reaction mixture was stirred at 130 °C for 12 h. The reaction mixture was quenched with water and extracted with Et_2O. The combined organic layer was washed with brine and dried over $MgSO_4$. The solvent was then evaporated in vacuo and the residue was purified by silica gel column chromatography with petroleum ether and ethyl acetate as eluent to afford the final product **4**.



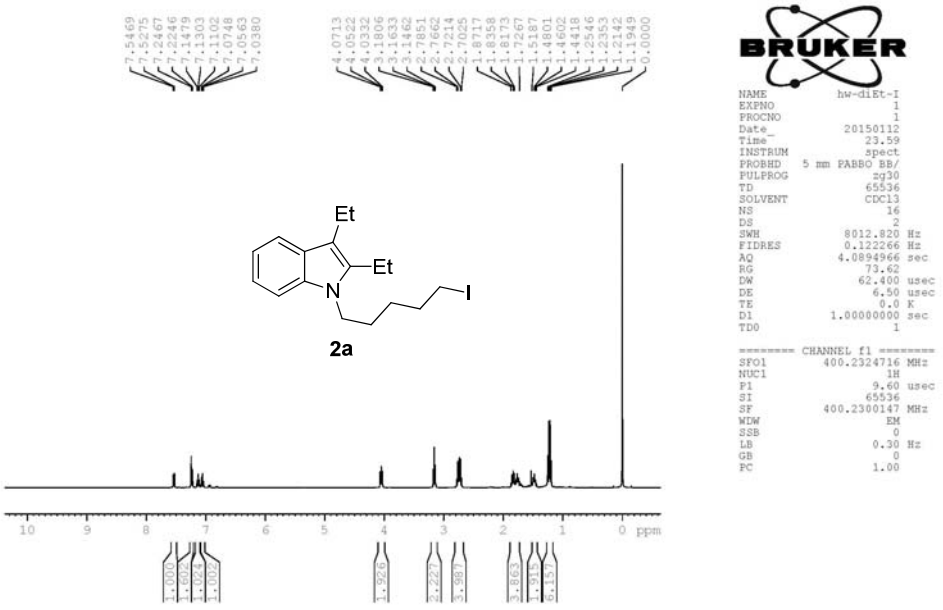
4: Yellow oil, isolated yield 32% (31 mg). ^{1}H NMR (400 MHz, C_6D_6): δ 0.91-0.99 (m, 2H, CH2), 1.03 (t, J = 7.6 Hz, 3H, CH_3), 1.20-1.29 (m, 7H, CH_3+2CH_2), 2.48 (q, J = 7.5 Hz, 2H, CH_2), 2.70-2.78 (m, 4H, CH_2), 3.53 (t, J = 7.5 Hz, 2H, CH_2), 7.09-7.12 (m, 1H, CH), 7.21-7.29 (m, 2H, CH), 7.65-7.67 (m, 1H, CH); ^{13}C NMR (100 MHz, C_6D_6): 15.5 (CH_3), 16.5 (CH_3), 17.8 (CH_2), 18.1 (CH_2), 25.7 (CH_2), 29.6 (CH_2), 32.4 (CH_2), 33.2 (CH_2), 42.8

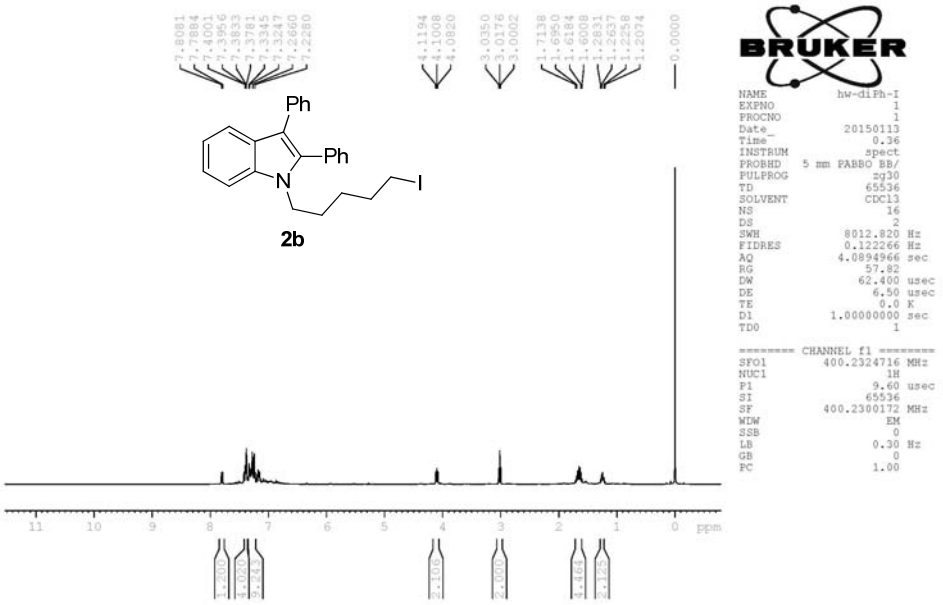
(CH_2), 109.4 (CH), 113.3 (quat. C), 118.9 (CH), 119.2 (CH), 121.0 (CH), 128.6 (quat. C), 136.6 (quat. C), 137.0 (quat. C). HRMS calcd. for $C_{17}H_{25}BrN$ [M+H]+: 322.1165, found 322.1174.

2) Reference:

1. Hao, W.; Wei, J.; Zhang, W.-X.; Xi, Z. *Angew. Chem. Int. Ed.* **2014**, *53*, 14533.

3) Scanned ^{1}H NMR and ^{13}C NMR Spectra of All Compounds





BRUKER

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NS	16
DS	2
SWH	8012.820 Hz
FIDRES	0.122266 Hz
AQ	4.0894966 sec
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DE	6.50 usec
TE	0.0 K
D1	1.00000000 sec
TD0	1
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P1	9.60 usec
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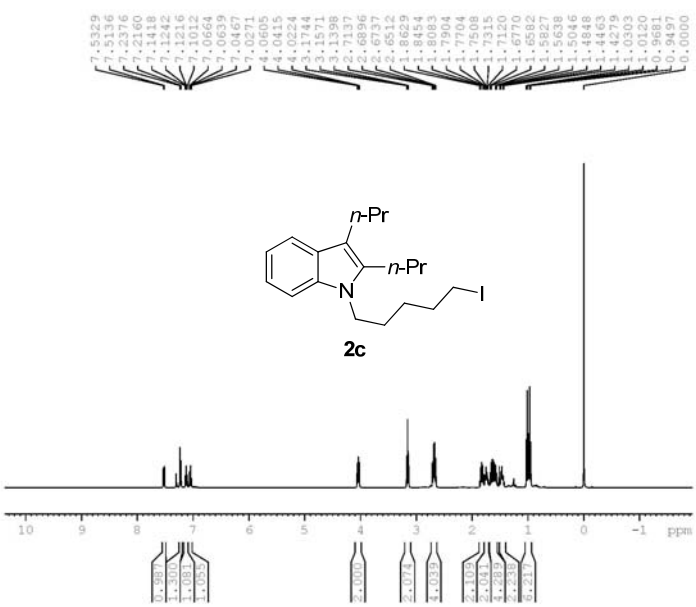
SSB	0
LB	0.30 Hz
GB	0
PC	1.00



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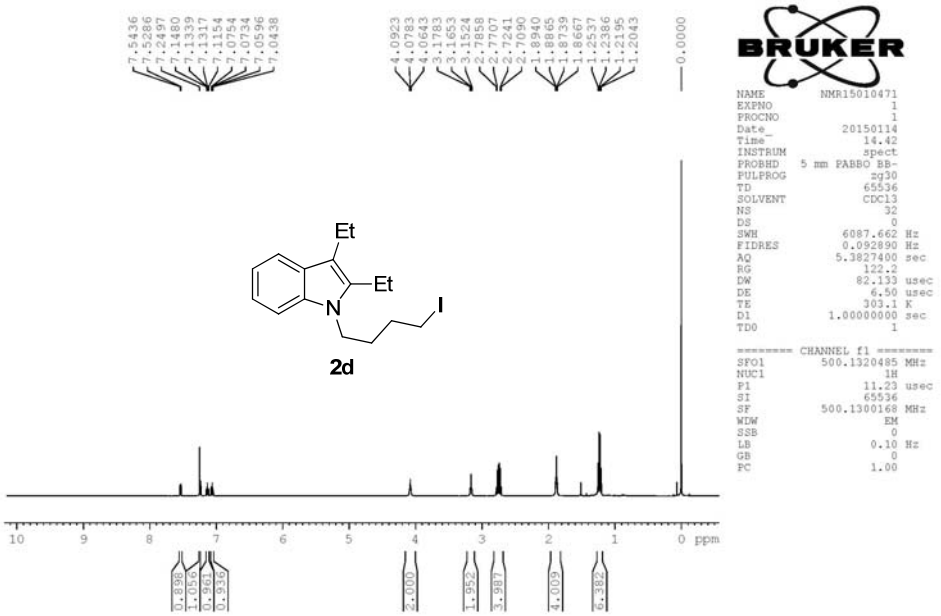
GB	0
PC	1.00



BRUKER

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FIDRES	0.092890 Hz
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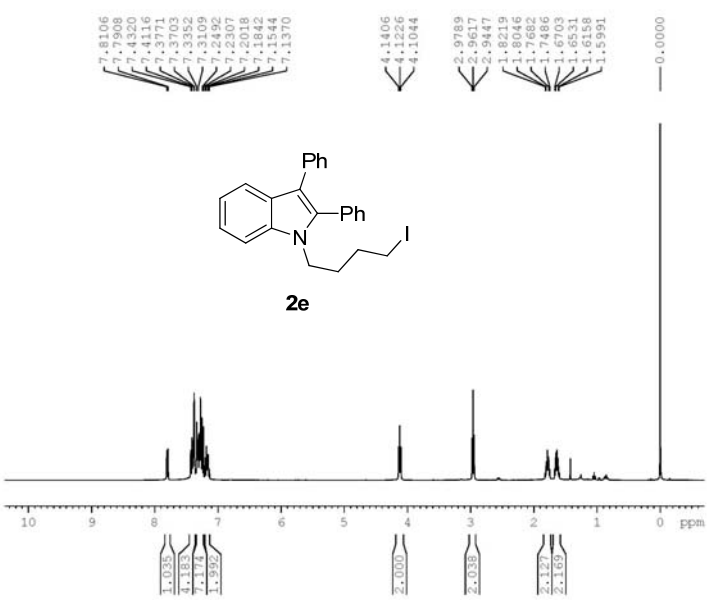
GB	0
PC	1.00



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NS                       16
DS                        2
SWH                8223.685 Hz
FIDRES             0.125483 Hz
AQ                 3.9846387 sec
RG                      80.6
DW                    60.800 usec
DE                     6.50 usec
TE                    294.8 K
D1                 1.00000000 sec
TD0                       1

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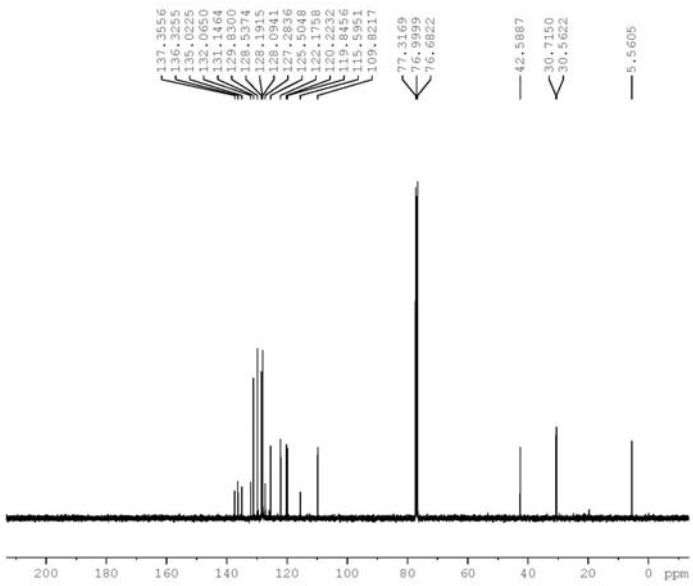

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NS                      256
DS                        4
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DE                     6.50 usec
TE                    303.0 K
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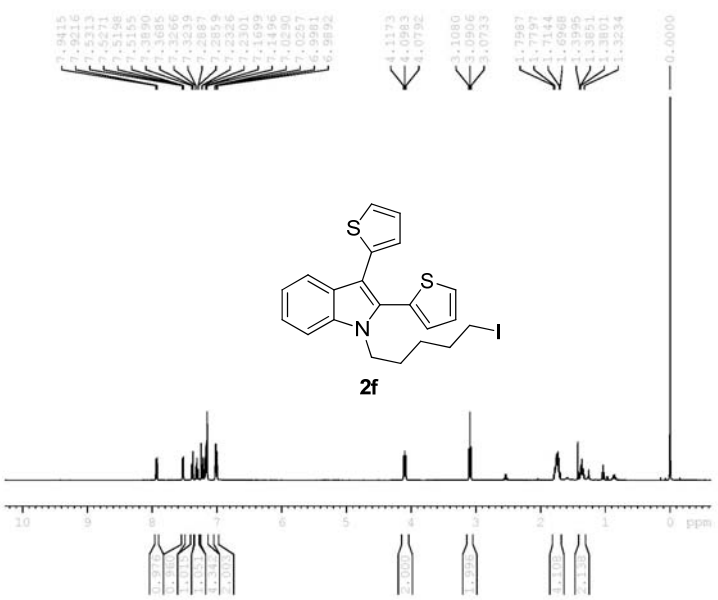

BRUKER

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PROCNO	1
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FIDRES	0.122266 Hz
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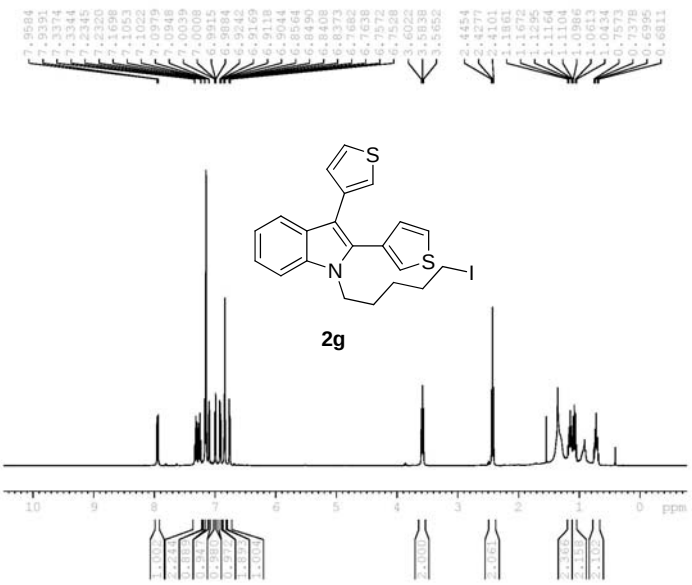


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NS                       16
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FIDRES            0.125483 Hz
AQ                3.9846387 sec
RG                     71.8
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DE                    6.50 usec
TE                   297.0 K
D1                1.00000000 sec
TD0                        1

======== CHANNEL f1 ========
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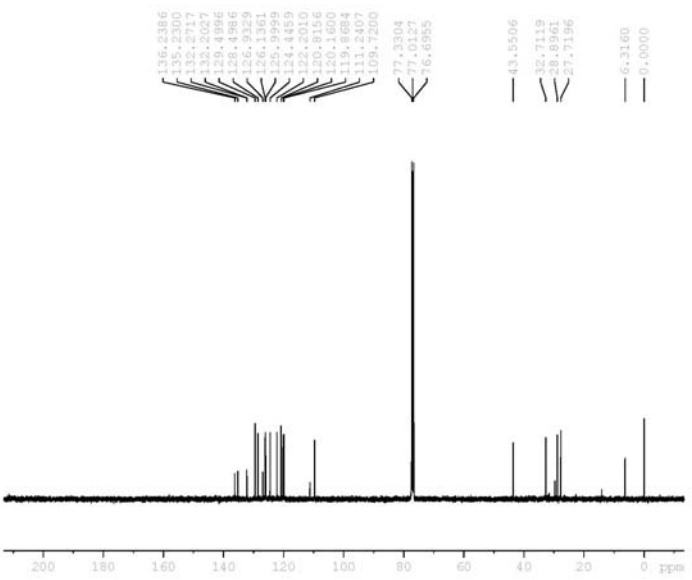

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PROCNO                     1
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FIDRES            0.366798 Hz
AQ                1.3631988 sec
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DE                    6.50 usec
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======== CHANNEL f1 ========
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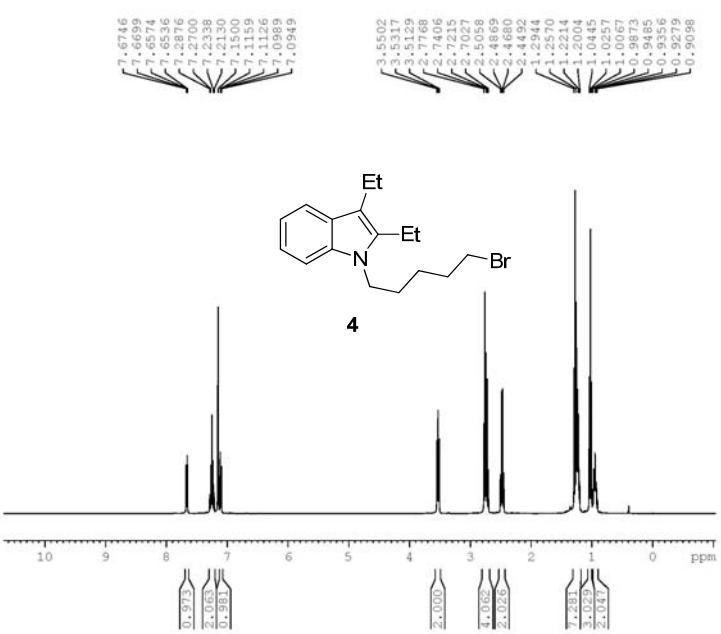

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TE                    296.4 K
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TD0                        1

======== CHANNEL f1 ========
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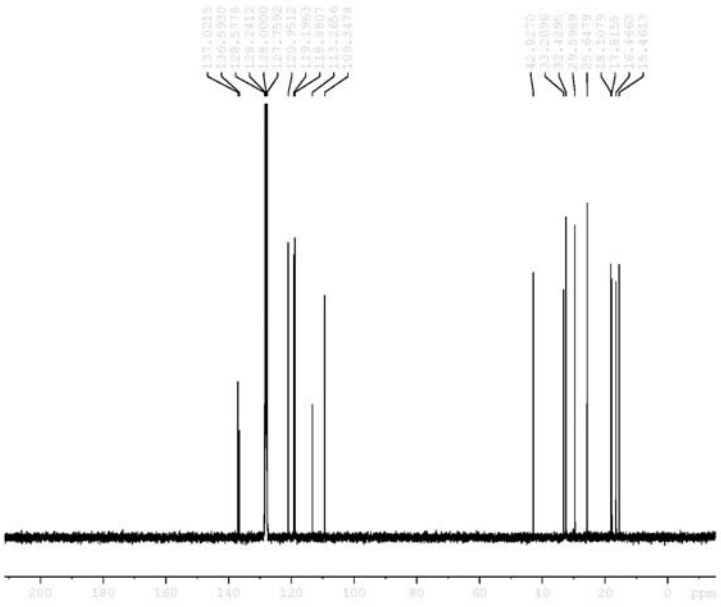

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PROCNO                     1
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TD                    65536
SOLVENT                C6D6
NS                       480
DS                         4
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FIDRES             0.366798 Hz
AQ                 1.3631988 sec
RG                       203
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DE                     6.50 usec
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D1                 2.00000000 sec
D11                0.03000000 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                      13C
P1                      9.80 usec
SI                     32768
SF               100.6127372 MHz
WDW                       EM
SSB                        0
LB                      1.00 Hz
GB                         0
PC                      1.40
```