Supplementary Material (ESI) for Green Chemistry

Supporting Information for:

Practical, environment-benign and atom economic KOAc–catalysed deprotection of aryl TIPS ethers under mild fluoride-free conditions.

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General Information. All ^{1}H NMR spectra were recorded at ambient temperature in $CDCl_3$ (500 MHz) unless otherwise stated. All ^{13}C NMR spectra were recorded at ambient temperature in $CDCl_3$ (125 MHz). Chemical shifts are reported in parts per million as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), integration, and coupling constant. Melting points were uncorrected.

Procedure for large-scale reaction without chromatography (unoptimized):

To a solution of ethyl 4-(triisopropylsilyoxy)benzoate (15.3 g, 47.5 mmol) in DMF–H_2O (20:1, 50 mL) was added KOAc (466 mg, 4.8 mmol) and water (0.9 mL, 1 equiv to substrate), and stirring was continued for 7 h at 25 °C. The mixture was concentrated on a rotavap (bath temp 50 °C) to remove DMF (~90% recovery). The remaining oil was bulb-to-bulb distilled (bath temp 75 °C/1–2 mmHg) to recover TIPSOH (6.5 g, 79% yield), the cooled residue was taken up in EtOAc–Et_2O (1:1, 30 mL) and filtered to remove KOAc (reusable); the filtrate was concentrated. The crude product was triturated with hexane to afford ethyl 4-hydroxybenzoate (7.0 g, 89%) as white crystals (m.p.: 113–118 °C, lit. 115–118 °C). The recovered KOAc gave negative results for $FeCl_3$-test of phenols.

Optimal purification procedure for an individual product should take into consideration of the physical property and stability of the compound concerned. The above procedure is a proof-of-concept and does not recommend recovering the cheap catalyst.

Characterization data of new compounds.

Compound **1c**:

^{1}H NMR ($CDCl_3$) δ 6.70 (d, 2H, J = 8.5 Hz), 6.56 (d, 2H, J = 8.5 Hz), 3.39 (s br, 2H), 1.20 (septet, 3H, J = 7.0 Hz), 1.08 (d, 18H, J = 7.0 Hz).

^{13}C NMR ($CDCl_3$) δ 148.7, 140.0, 120.4, 116.3, 17.9, 12.6.

HR-ESI-MS m/z Calcd for $C_{15}H_{28}NOSi$ ($M + H^+$) 266.1940, Found 266.1935.

Compound **1d**:

M.p.: 54.5–55.0 °C.

^{1}H NMR ($CDCl_3$) δ 7.18 (d br, 2H, J = 8.5 Hz), 6.80 (d, 2H, J = 8.5 Hz), 6.32 (s br, 1H), 1.50 (s, 9H), 1.22 (septet, 3H, J = 7.0 Hz), 1.08 (d, 18H, J = 7.0 Hz).

^{13}C NMR ($CDCl_3$) δ 153.1, 151.9, 131.6, 120.0 (2C), 80.1, 28.4, 17.9, 12.6

HR-ESI-MS m/z Calcd for $C_{20}H_{36}NO_3Si$ ($M + H^+$) 366.2464, Found 366.2438.

Compound **1e**:

^{1}H NMR ($CDCl_3$) δ 6.74 (s, 2H), 2.21 (s, 6H), 2.20 (s, 3H), 1.30 (septet, 3H, J = 8.0 Hz), 1.11 (d, 18H, J = 8.0 Hz).

^{13}C NMR ($CDCl_3$) δ 151.1, 129.9, 129.3, 127.6, 20.4, 18.1, 17.8, 14.2.

HR-ESI-MS m/z Calcd for $C_{18}H_{33}OSi$ ($M + H^+$) 293.2301, Found 293.2335.

Compound **1h**:

^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.80–7.76 (m, 1H), 7.46–7.39 (m, 1H), 7.05–6.95 (m, 2H), 1.34

(septet, 3H, J = 7.5 Hz), 1.12 (d, 18H, J = 7.2 Hz).
^{13}C NMR ($CDCl_3$) δ 149.5, 133.5, 125.4, 121.4, 120.5, 17.8, 12.9.
HR-ESI-MS m/z Calcd for $C_{15}H_{26}NO_3Si$ ($M + H^+$) 296.1682, Found 296.1672.

Compound **1o**:
^{1}H NMR ($CDCl_3$) δ 7.58 (d, 1H, J = 5.6 Hz), 6.30 (d, 1H, J = 5.5 Hz), 2.34 (s, 3H), 1.36 (septet, 3H, J = 7.5 Hz), 1.07 (d, 18H, J = 7.5 Hz).
^{13}C NMR ($CDCl_3$) δ 173.8, 153.9, 152.6, 143.4, 115.4, 18.2, 14.8, 14.2.
HR-ESI-MS m/z Calcd for $C_{15}H_{27}O_3Si$ ($M + H^+$) 283.1729, Found 283.1732.

Compound **1p**:
^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.16 (d, 2H, J = 8.1 Hz), 6.84 (d, 2H, J = 8.4 Hz), 4.67 (s, 2H), 1.24 (septet, 3H, J = 7.5 Hz), 1.10 (d, 18H, J = 6.9 Hz), 0.92 (s, 9H), 0.08 (s, 6H).
^{13}C NMR ($CDCl_3$) δ 155.0, 133.8, 127.4, 119.6, 64.8, 26.0, 18.4, 17.9, 12.7, –5.2.
HR-ESI-MS m/z Calcd for $C_{22}H_{42}O_2Si_2Na$ ($M + Na^+$) 417.2621, Found 417.2656.

Compound **1q**:
^{1}H NMR ($CDCl_3$) δ 7.23 (d, 2H, J = 8.6 Hz), 6.81 (d, 2H, J = 8.6 Hz), 6.50 (d, 1H, J = 15.8 Hz), 6.13 (dt, 1H, J = 15.8, 5.4 Hz), 4.32 (d, 2H, J = 5.4 Hz), 1.25 (septet, 3H, J = 7.0 Hz), 1.09 (d, 18H, J = 7.0 Hz), 0.93 (s, 9H), 0.10 (s, 6H).
^{13}C NMR ($CDCl_3$) δ 155.6, 130.2, 129.3, 127.5, 126.9, 119.9, 64.1, 26.0, 18.5, 17.9, 12.7, –5.1.
HR-ESI-MS m/z Calcd for $C_{24}H_{45}O_2Si_2$ ($M + H^+$) 421.2958, Found 421.2945.

Compound **1r**:
^{1}H NMR ($CDCl_3$) δ 7.71 (m, 4H), 7.41 (m, 2H), 7.35 (m, 4H), 6.96 (t, 1H, J = 8.2 Hz), 6.47 (ddd, 1H, J = 8.0, 2.0, 1.0 Hz), 6.41 (ddd, 1H, J = 8.0, 2.5, 1.0 Hz), 6.20 (t, 1H, J = 2.5 Hz), 1.08 (s, 9H), 0.94–0.88 (m, 21H).
^{13}C NMR ($CDCl_3$) δ 156.7, 156.5, 135.5, 133.0, 129.8, 129.4, 127.7, 113.2, 112.8, 111.5, 26.5, 19.4, 17.8, 12.4.

Compound **1t**:
^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.21 (t, 1H, J = 7.5 Hz), 6.95–6.80 (m, 3H), 5.05 (s, 2H), 2.11 (s, 3H), 1.26 (septet, 3H, J = 7.2 Hz), 1.10 (d, 18H, J = 7.2 Hz).
^{13}C NMR ($CDCl_3$) δ 170.7, 156.2, 137.3, 129.4, 120.6, 119.5, 66.0, 20.9, 17.8, 12.6.
HR-ESI-MS m/z Calcd for $C_{18}H_{30}O_3SiNa$ ($M + Na^+$) 345.1862, Found 345.1876.

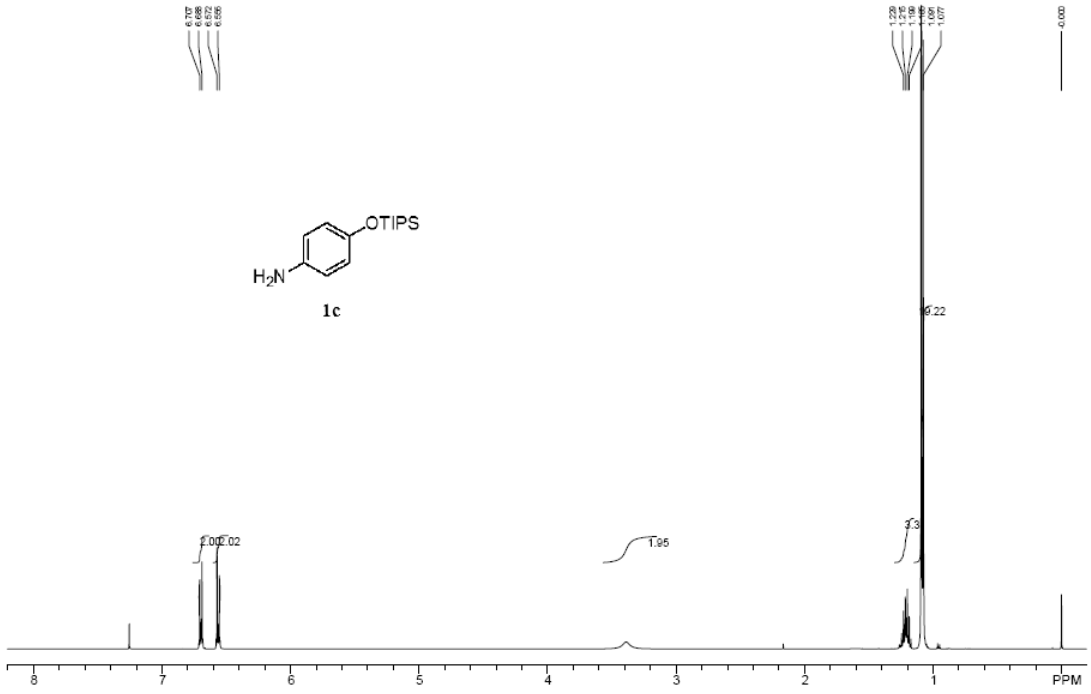
Compound **1u**:
^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.18 (t, 1H, J = 8.1 Hz), 6.95–6.87 (m, 2H), 6.80 (m, 1H), 4.76–4.46 (AB, 2H, J_{AB} = 12.3 Hz), 4.69 (t-like, 1H, J = 3.3 Hz), 3.92 (m, 1H), 3.54 (m, 1H), 1.95–1.40 (m, 6H), 1.24 (septet, 3H, J = 7.2 Hz), 1.10 (d, 18H, J = 6.9 Hz).
^{13}C NMR ($CDCl_3$) δ 156.1, 139.9, 129.2, 120.2, 119.1, 118.9, 97.5, 68.4, 62.1, 30.6, 25.5, 19.3, 17.9, 12.7.
HR-ESI-MS m/z Calcd for $C_{21}H_{36}O_3SiNa$ ($M + Na^+$) 387.2331, Found 387.2346.

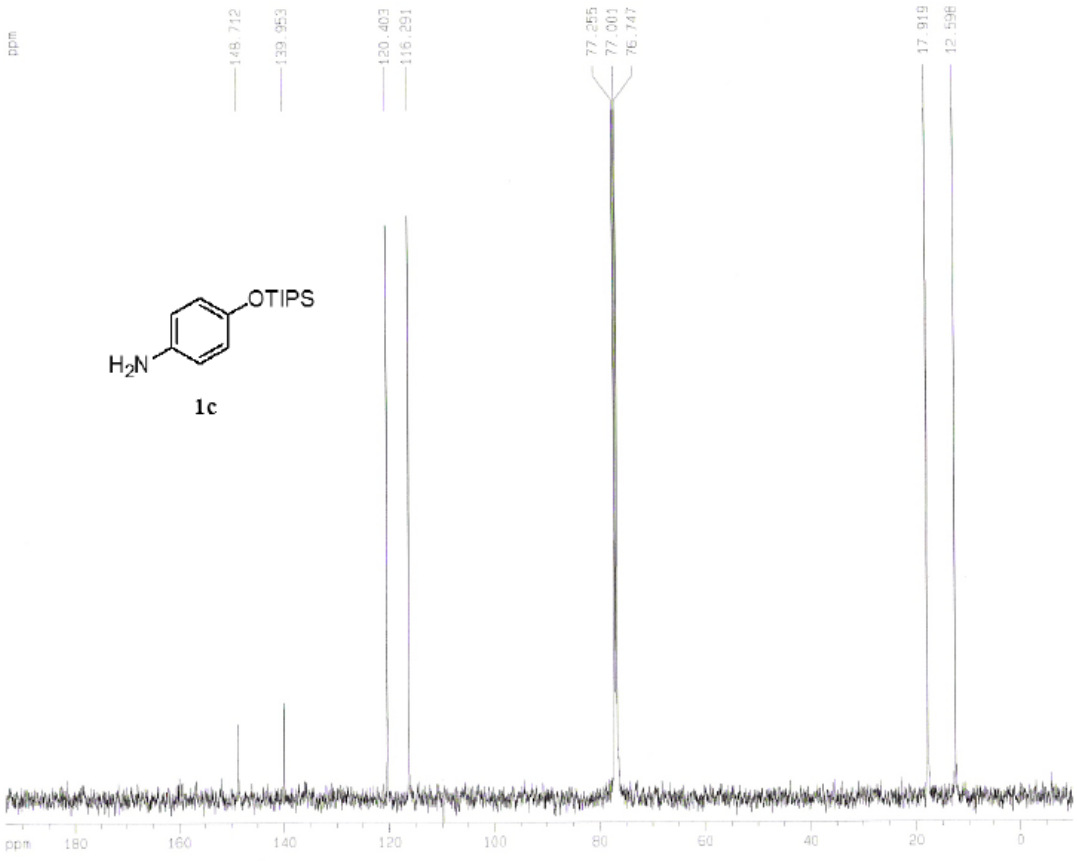
Compound **1v**:
^{1}H NMR ($CDCl_3$) δ 7.22 (t, 1H, J = 7.8 Hz), 7.04 (d, 1H, J = 7.6 Hz), 6.99 (m, 1H), 6.87 (m, 1H), 5.78 (s, 1H), 4.12–4.06 (m, 2H), 4.05–3.98 (m, 2H), 1.26 (septet, 3H, J = 7.0 Hz), 1.09 (d, 18H, J = 7.0 Hz).
^{13}C NMR ($CDCl_3$) δ 156.0, 139.5, 129.3, 120.4, 118.9, 117.9, 103.5, 65.2, 17.9, 12.7.
HR-ESI-MS m/z Calcd for $C_{18}H_{31}O_3Si$ ($M + H^+$) 323.2042, Found 323.2063.

Compound **1w**:
^{1}H NMR ($CDCl_3$) δ 7.10 (t, 1H, J = 8.2 Hz), 6.51 (dd, 2H, J = 8.5, 2.2 Hz), 6.47 (m, 1H), 4.16 (dd, 1H, J = 10.9, 3.3 Hz), 3.93 (dd, 1H, J = 10.9, 5.6 Hz), 3.34 (m, 1H), 2.90 (dd, 1H, J = 5.0, 4.3 Hz), 2.75 (dd, 1H, J = 5.0, 2.7 Hz), 1.26 (septet, 3H, J = 7.3 Hz), 1.10 (d, 18H, J = 7.3 Hz).
^{13}C NMR ($CDCl_3$) δ 159.6, 157.2, 129.7, 113.0, 107.1, 106.9, 68.7, 50.0, 44.8, 17.9, 12.6.
HR-ESI-MS m/z Calcd for $C_{18}H_{31}O_3Si$ ($M + H^+$) 323.2042, Found 323.2032.

Compound **1x**:
^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.01 (d, 2H, J = 8.7 Hz), 6.79 (d, 2H, J = 8.4 Hz), 3.61 (quintet, 1H, J = 5.7 Hz), 2.69–2.46 (m, 2H), 1.80–1.62 (m, 2H), 1.57–1.45 (m, 2H), 1.22 (septet, 3H, J = 6.9 Hz), 1.08 (d, 18H, J = 7.2 Hz), 0.96 (t, 9H, J = 7.5 Hz), 0.88 (t, 3H, J = 7.2 Hz), 0.60 (q, 6H, J = 7.8 Hz).
^{13}C NMR ($CDCl_3$) δ 153.9, 135.0, 129.0, 119.6, 73.1, 38.6, 31.0, 29.8, 17.9, 12.7, 9.6, 7.0, 5.1.
HR-ESI-MS m/z Calcd for $C_{26}H_{51}O_2Si_2$ ($M + H^+$) 451.3428, Found 451.3461.

Compound **2x**:
^{1}H NMR ($CDCl_3$) δ 7.04 (d, 2H, J = 8.4 Hz), 6.75 (d, 2H, J = 8.4 Hz), 4.75 (s br, 1H), 3.64 (quintet, 1H, J = 5.8 Hz), 2.63 (ddd, 1H, J = 14.0, 10.0, 6.0 Hz), 2.52 (ddd, 1H, J = 14.0, 10.5, 6.0 Hz), 1.77–1.64 (m, 2H), 1.56–1.45 (m, 2H), 0.97 (t, 9H, J = 8.0 Hz), 0.89 (t, 3H, J = 7.5 Hz), 0.61 (q, 6H, J = 8.0 Hz).
^{13}C NMR ($CDCl_3$) δ 153.6, 134.7, 129.3, 115.2, 73.3, 38.7, 30.9, 29.8, 9.7, 6.9, 5.1.
HR-ESI-MS m/z Calcd for $C_{17}H_{29}O_2Si$ ($M - H^+$, negative ion) 293.1937, Found 293.1899.

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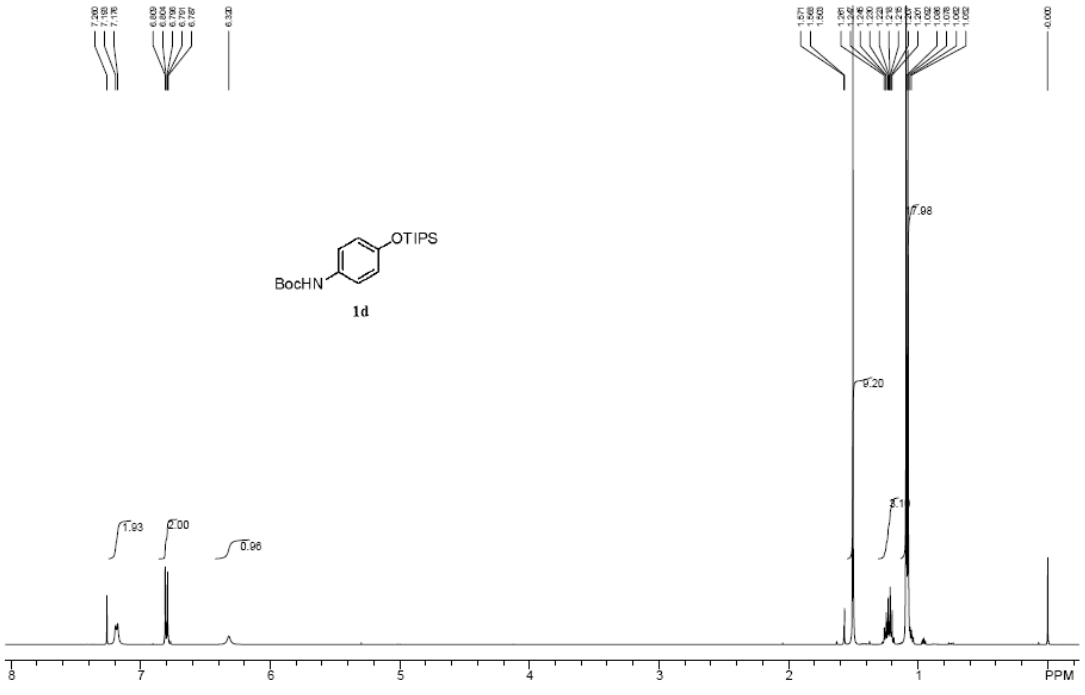
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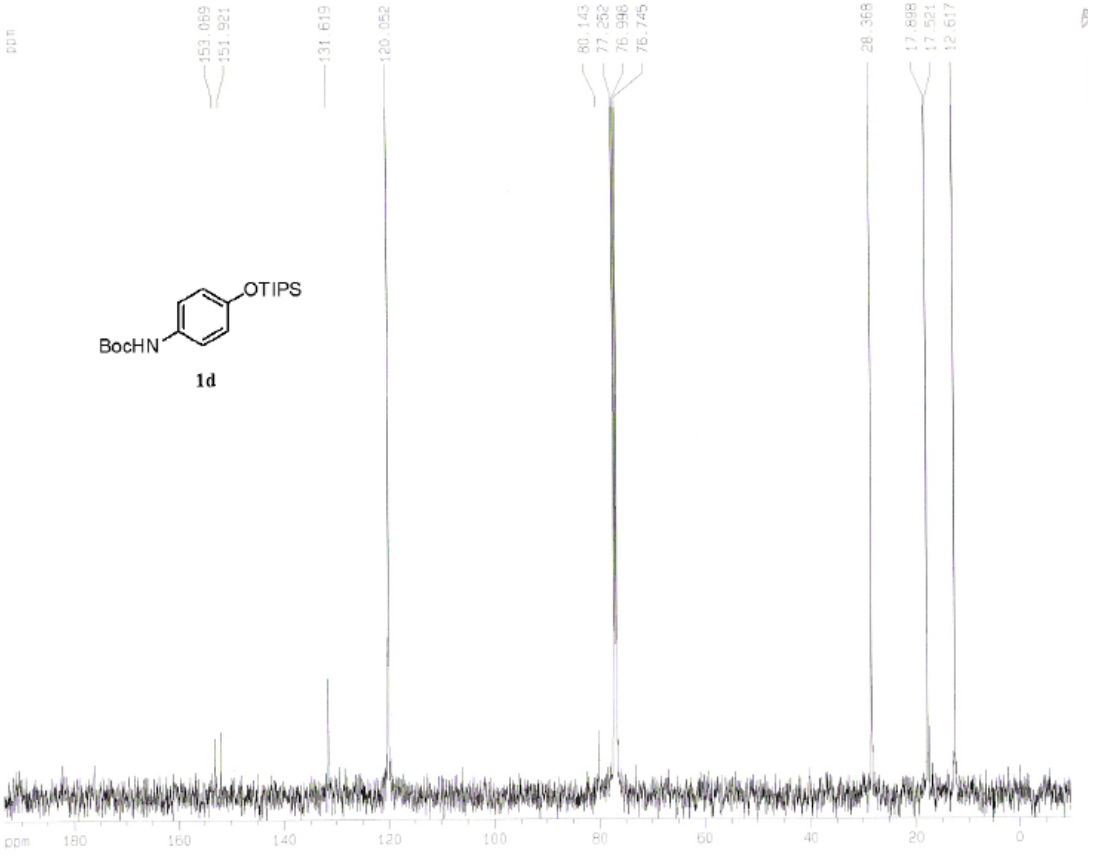
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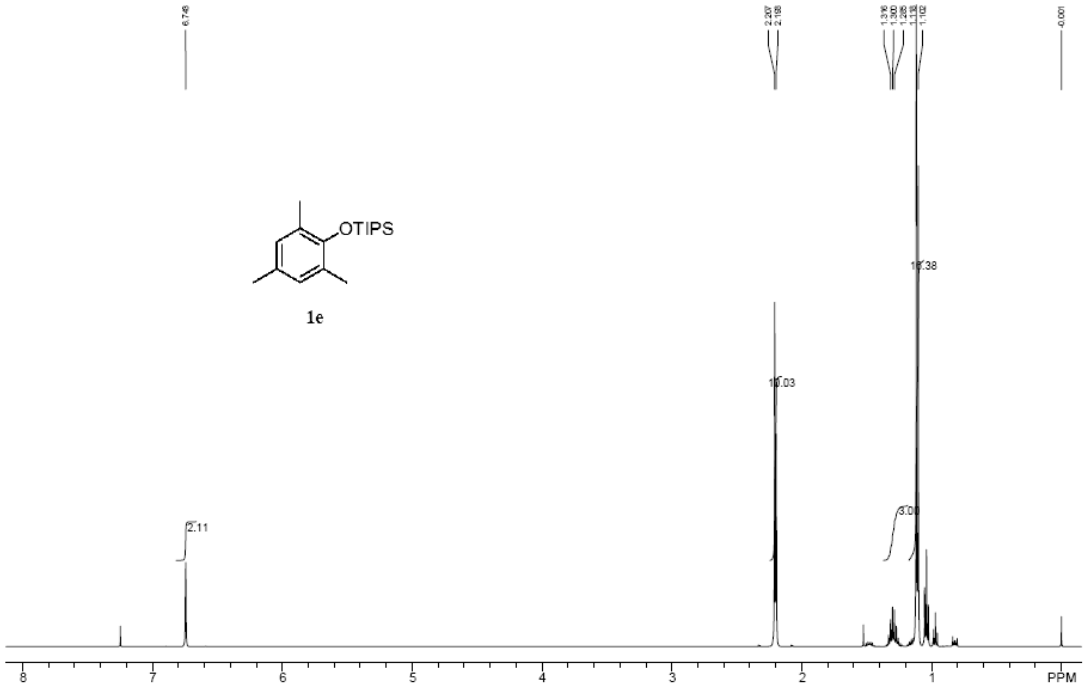
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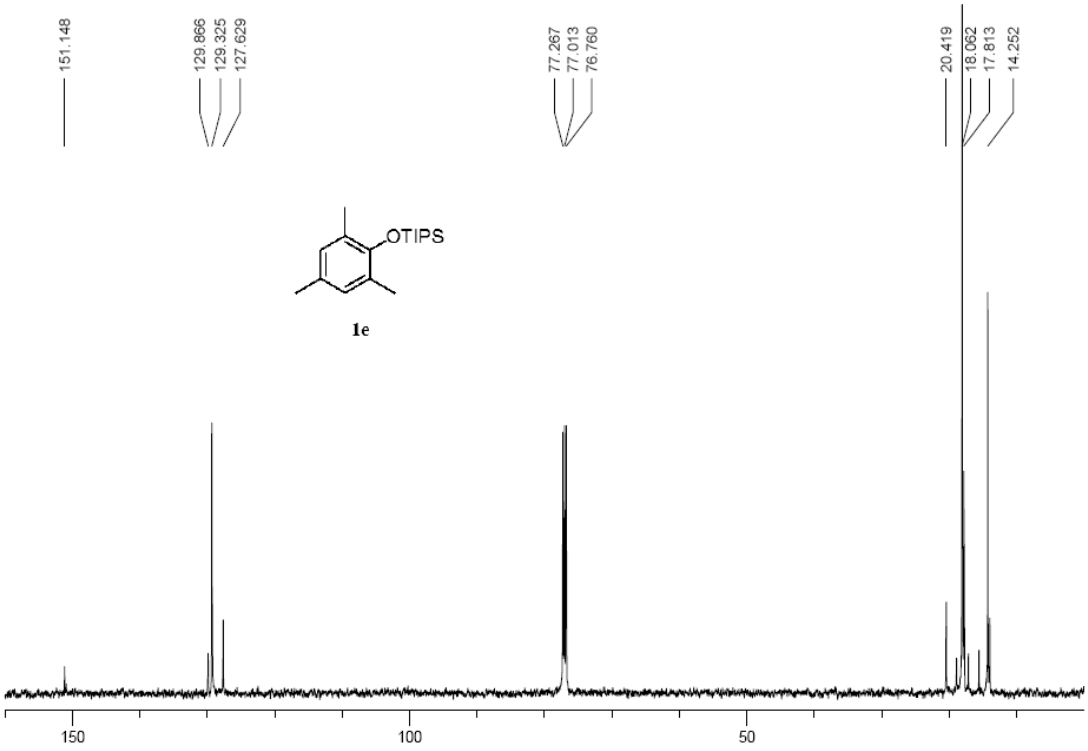
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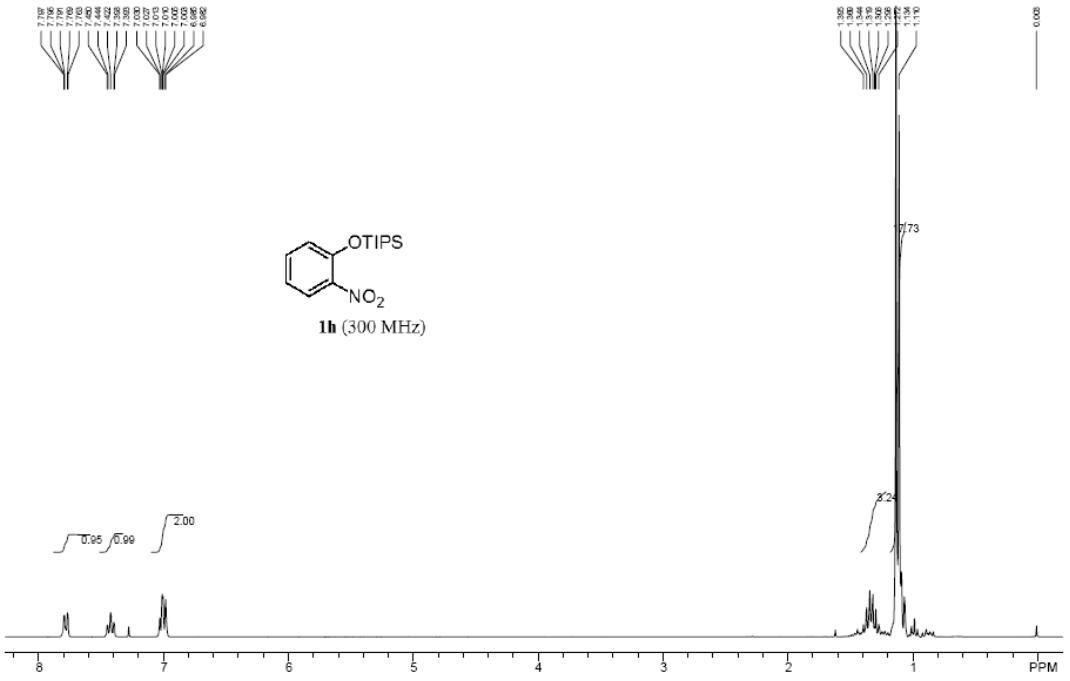
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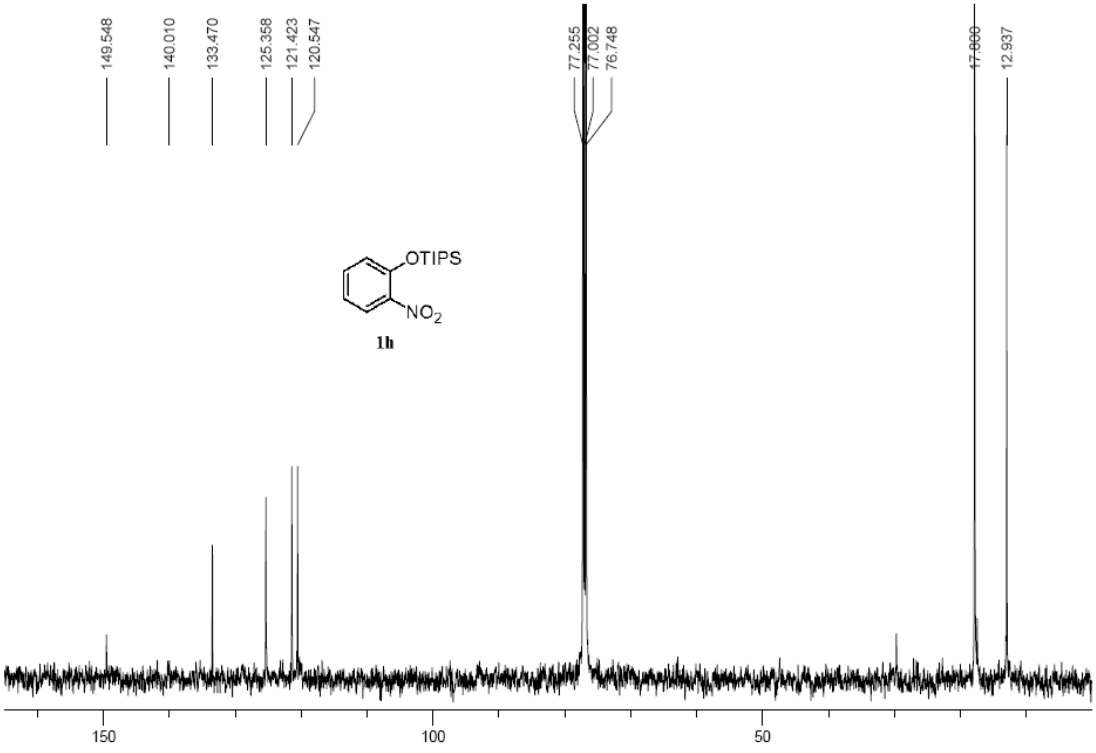
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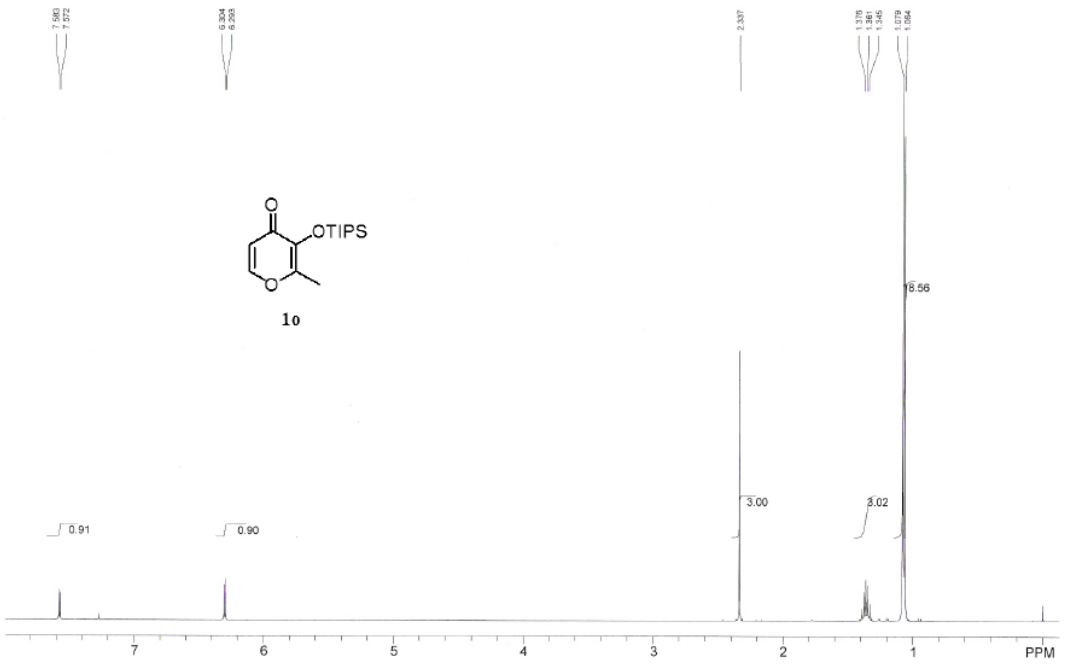
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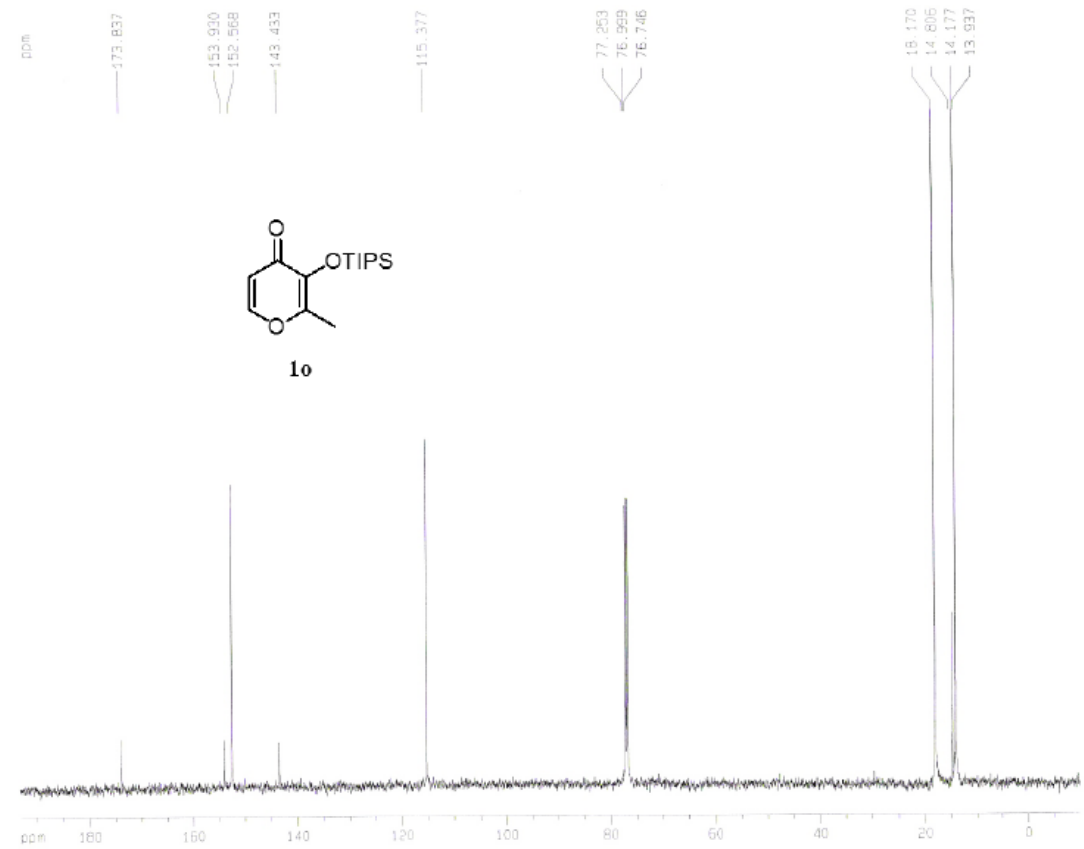
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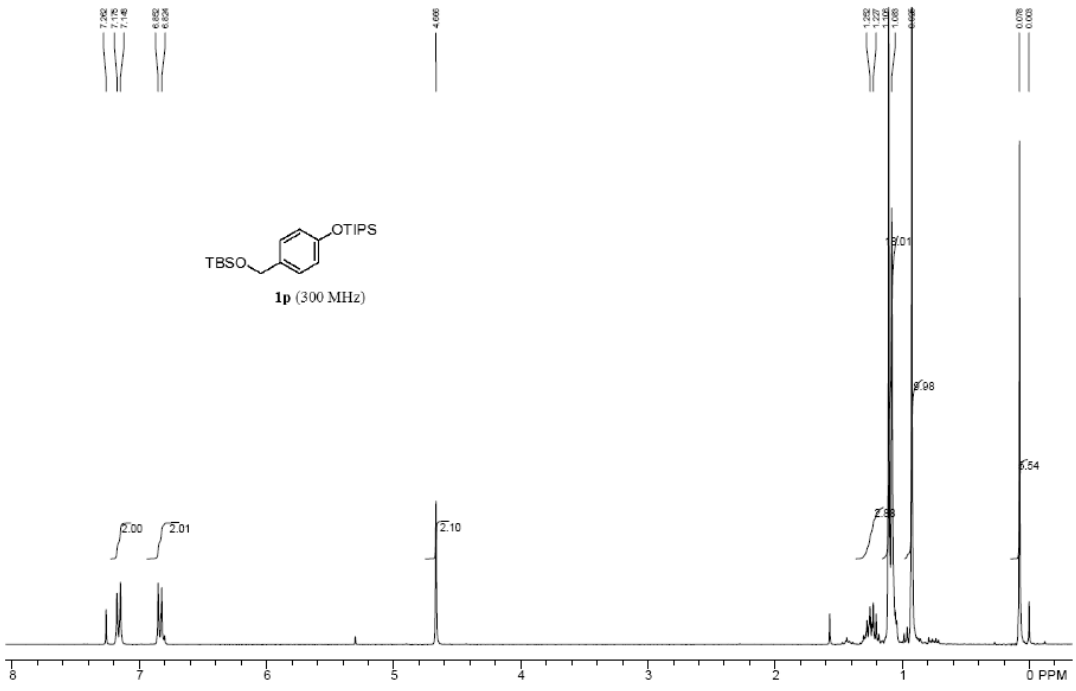
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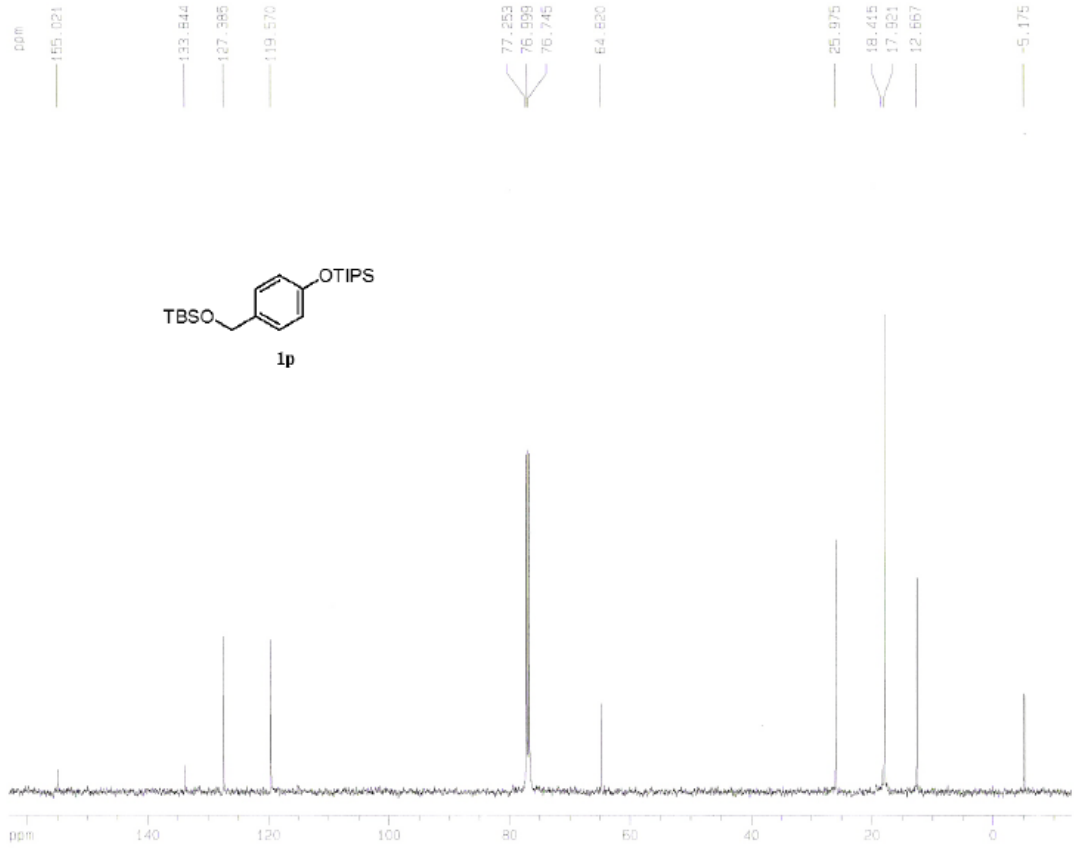
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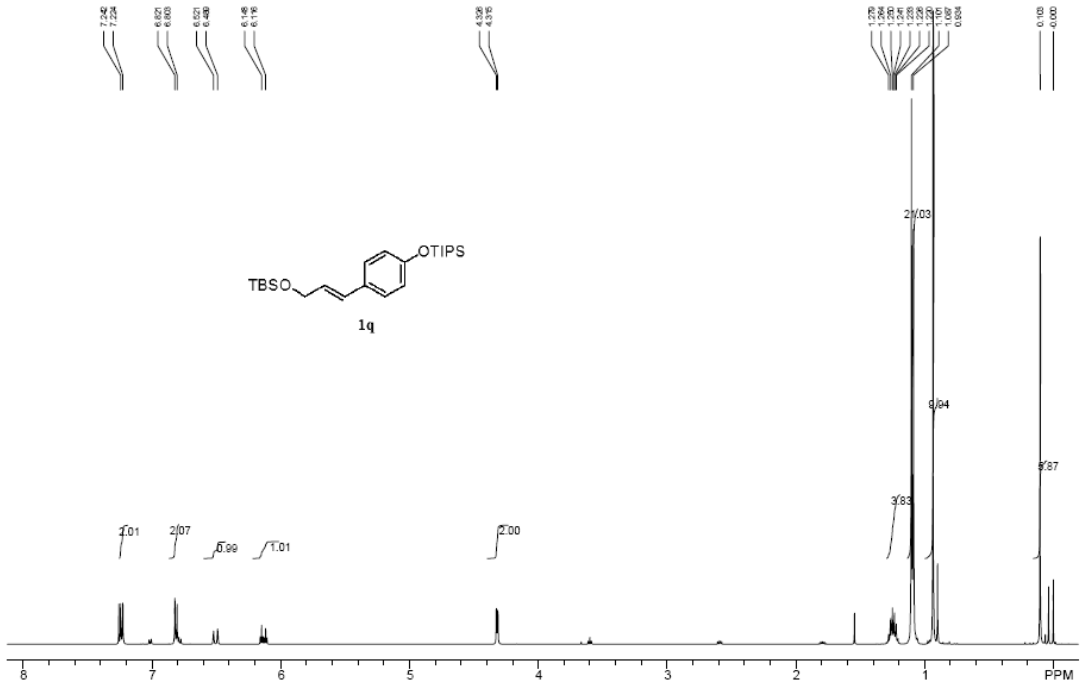
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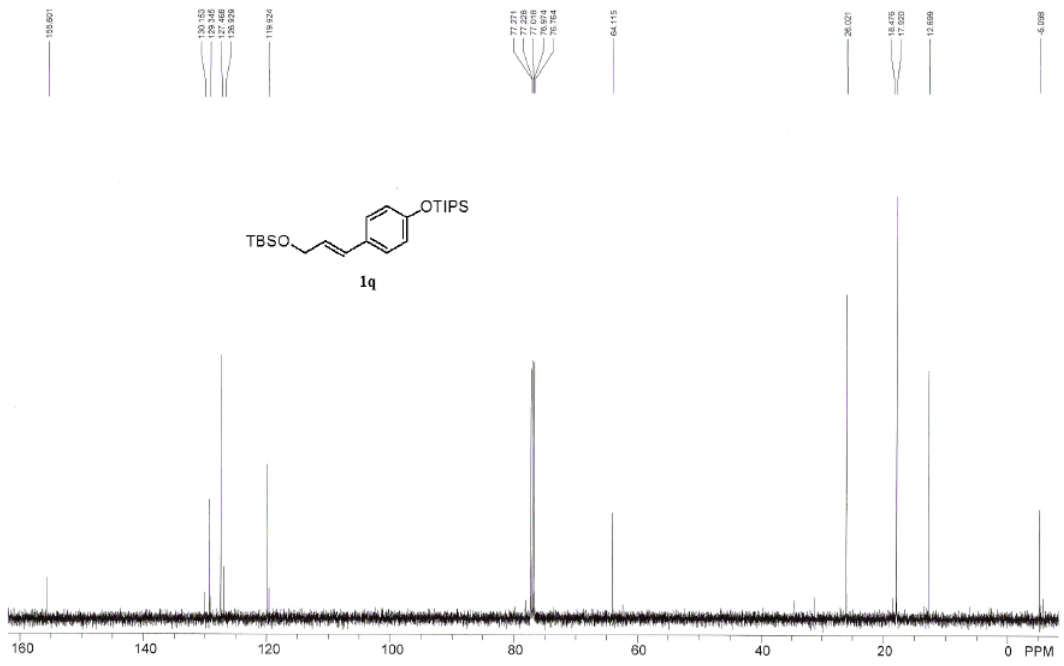
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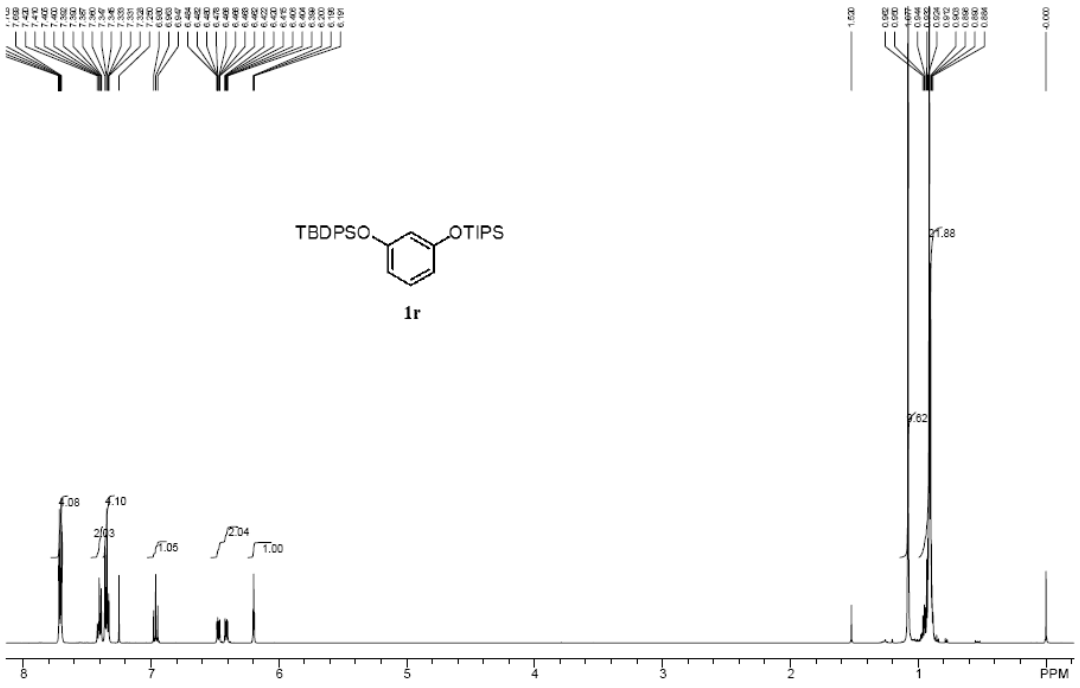
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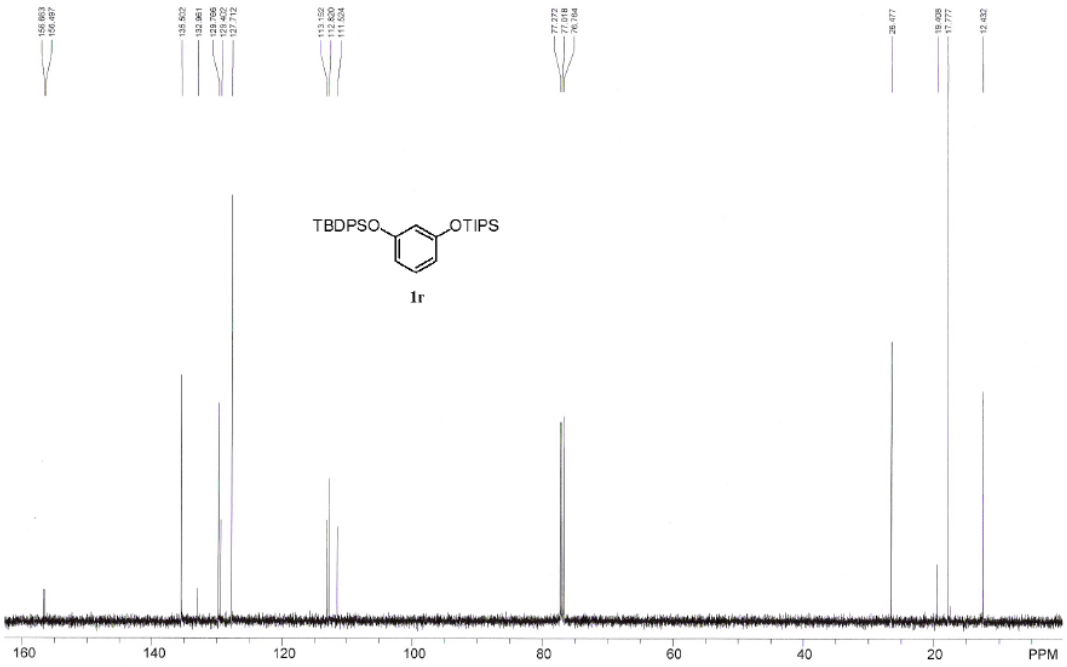
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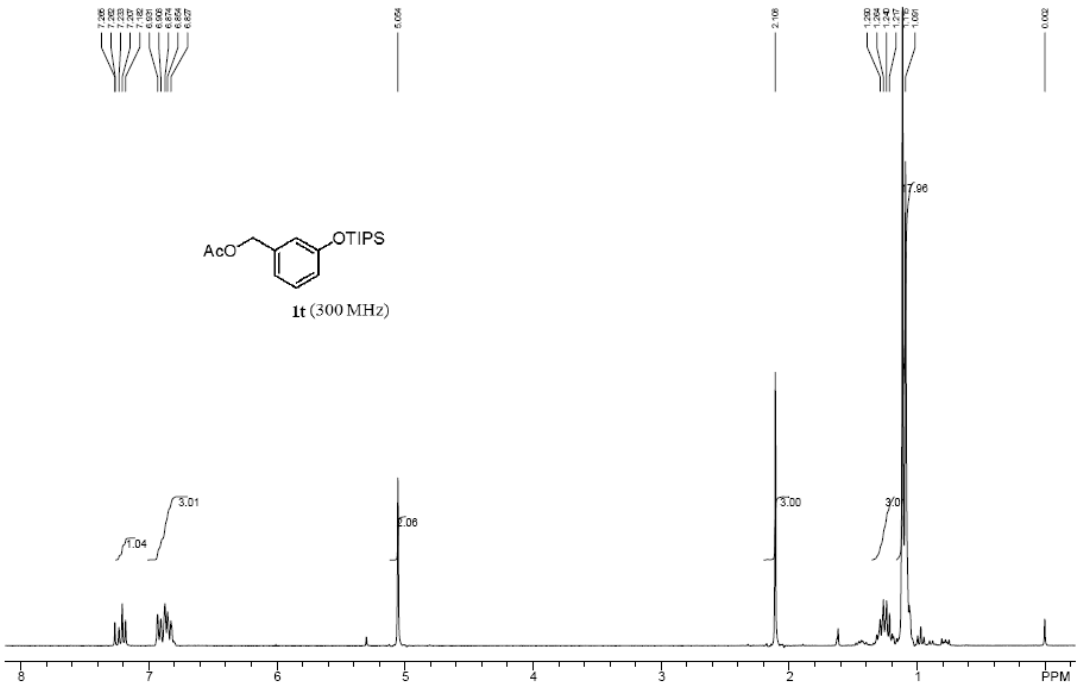
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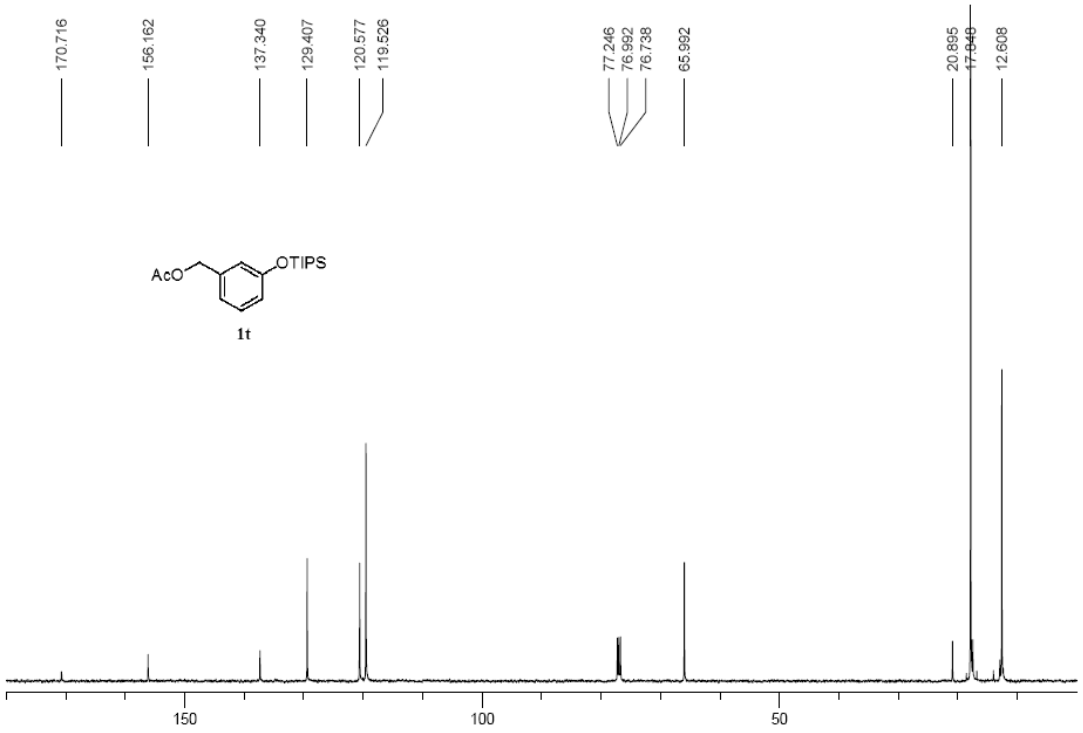
1t (300 MHz)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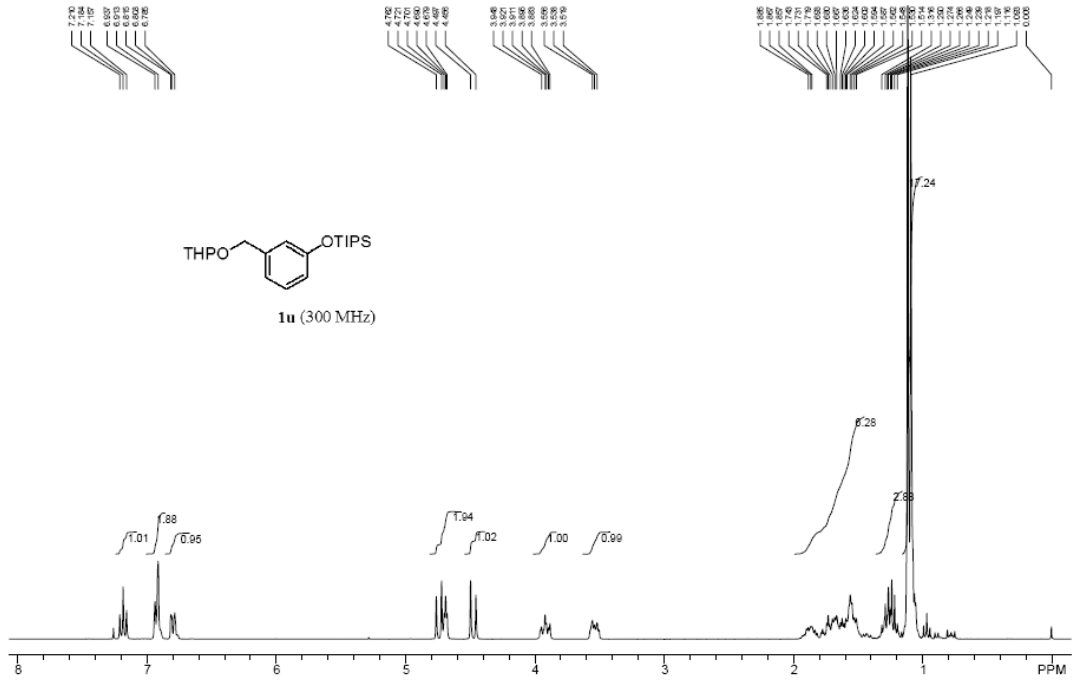
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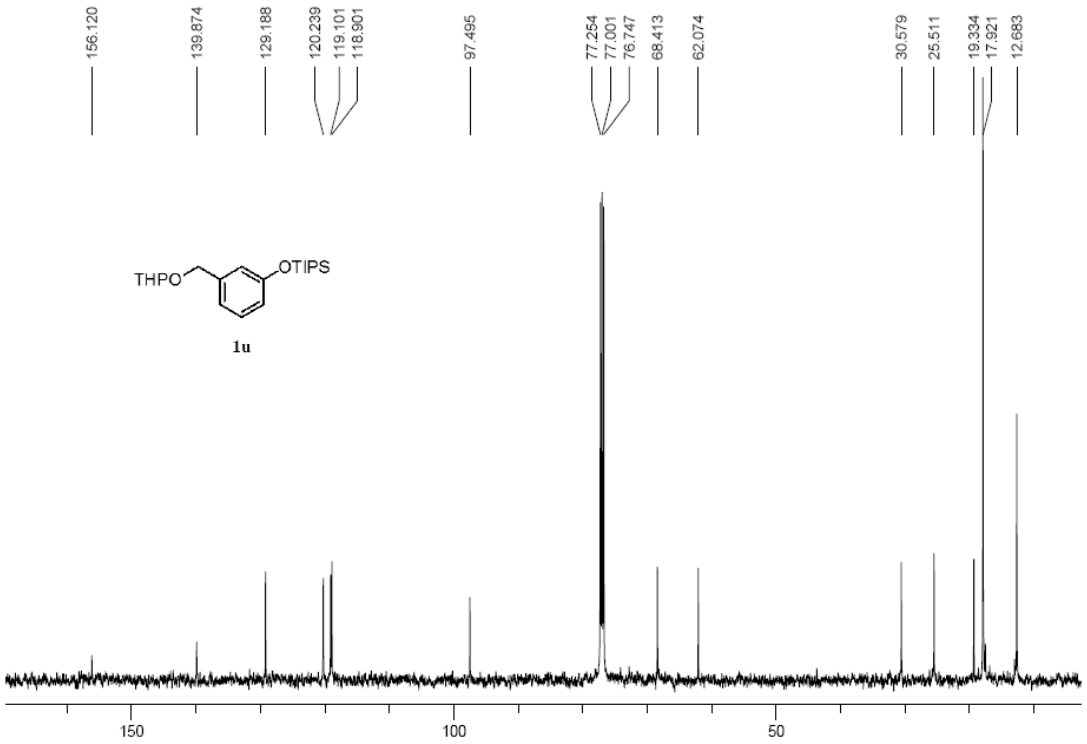
1u (300 MHz)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THPO
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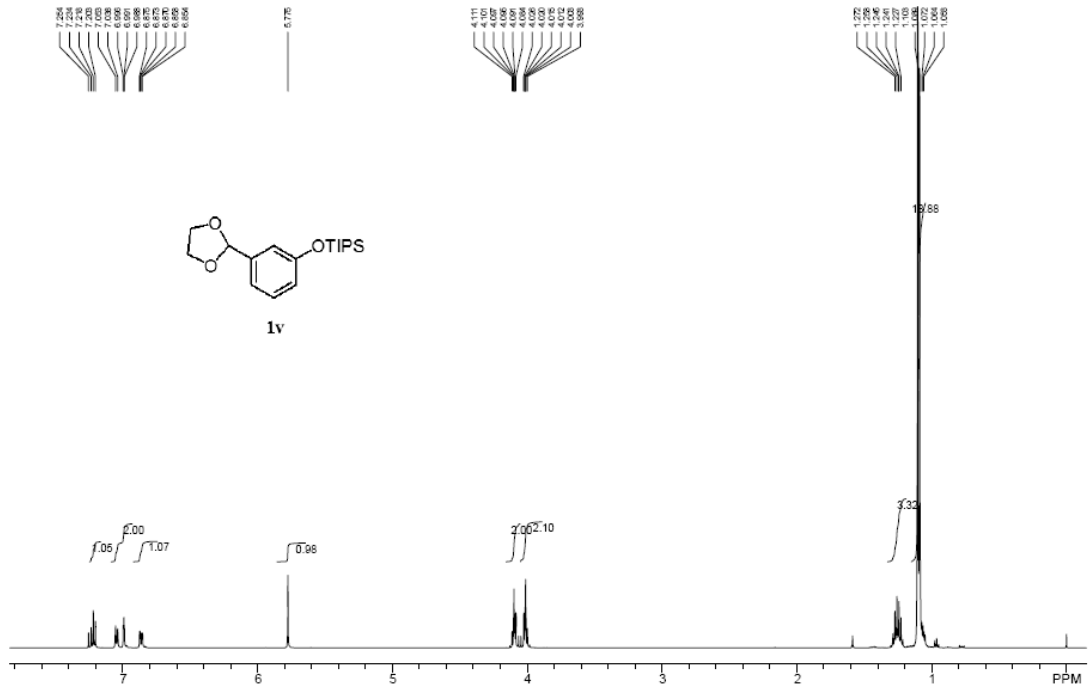
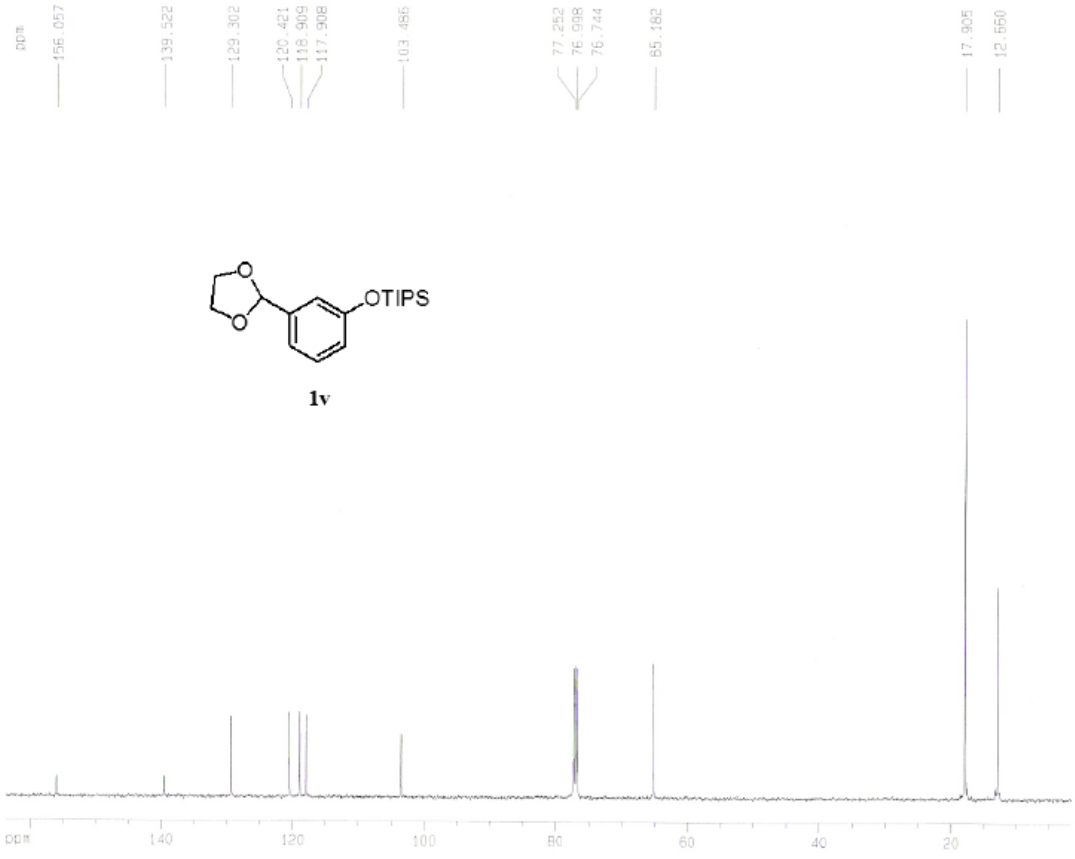
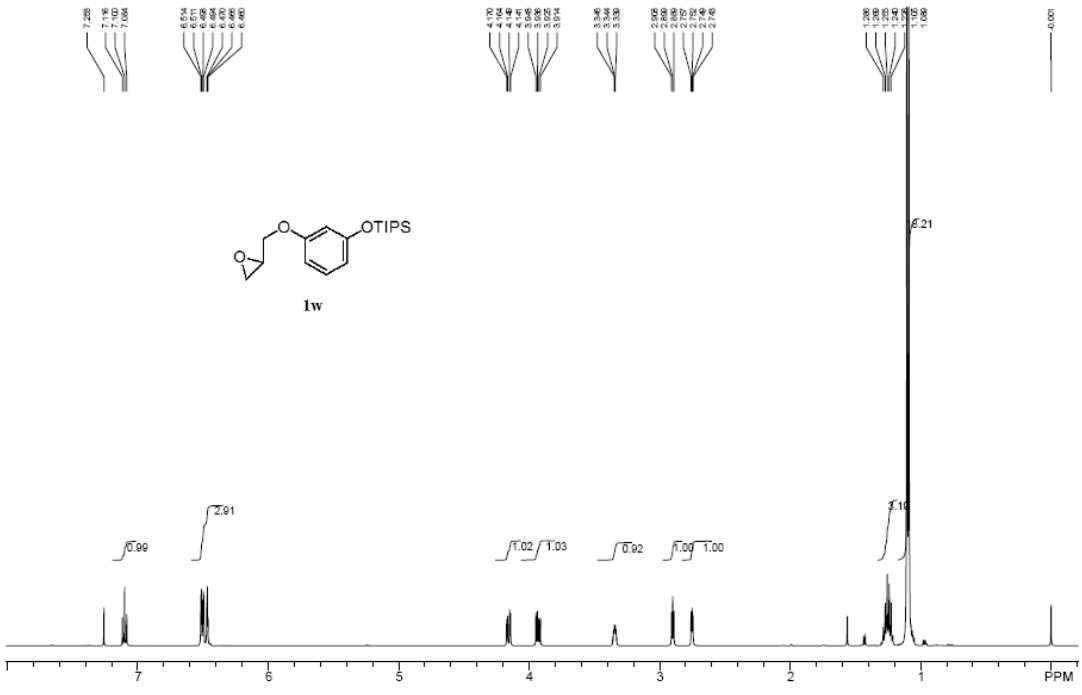
150
100
50

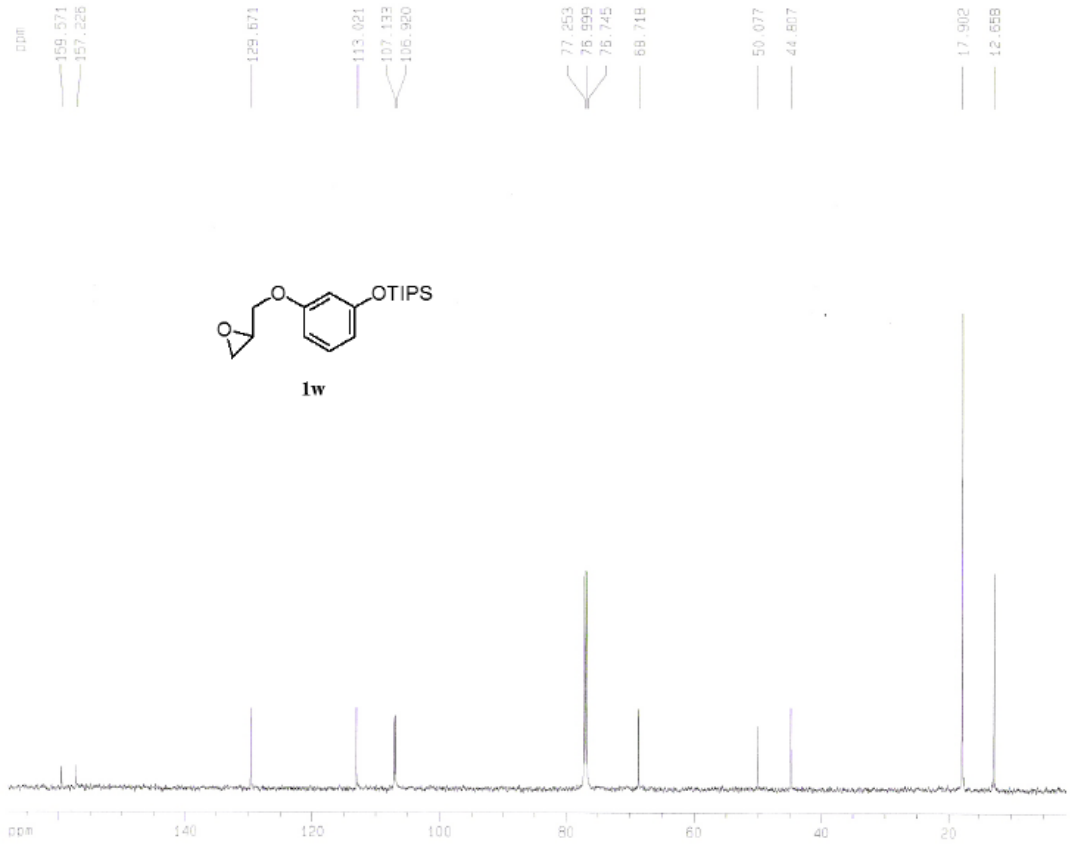
1u

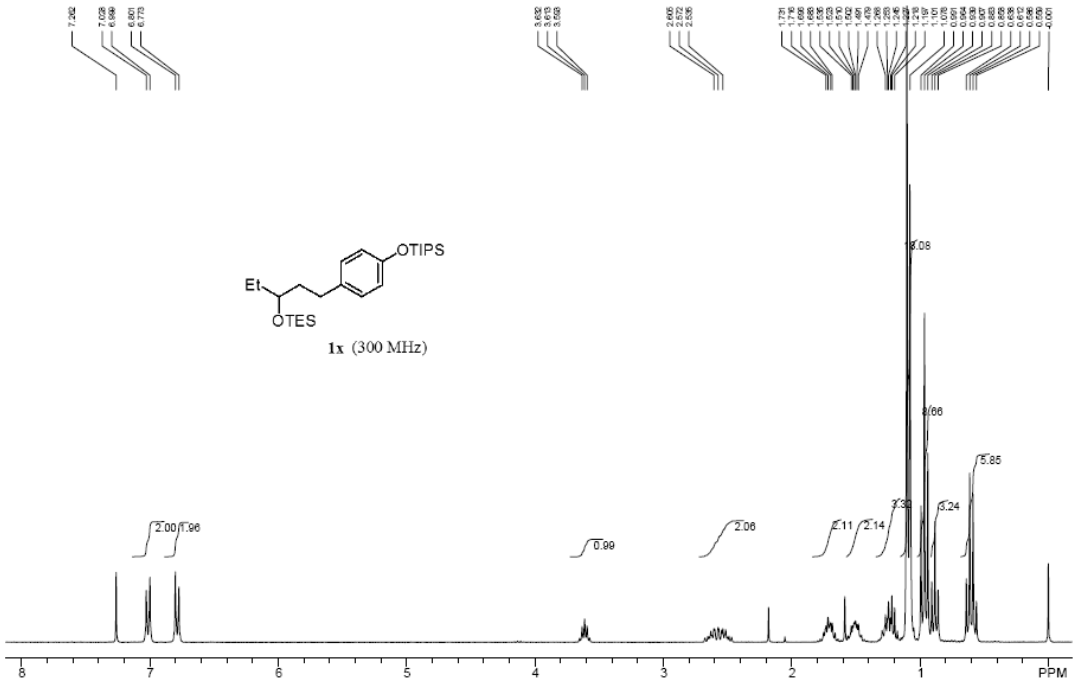

OTIPS
1.05
2.00
1.07
0.98
2.02
2.10
18.88
3.32
7
6
5
4
3
2
1
PPM

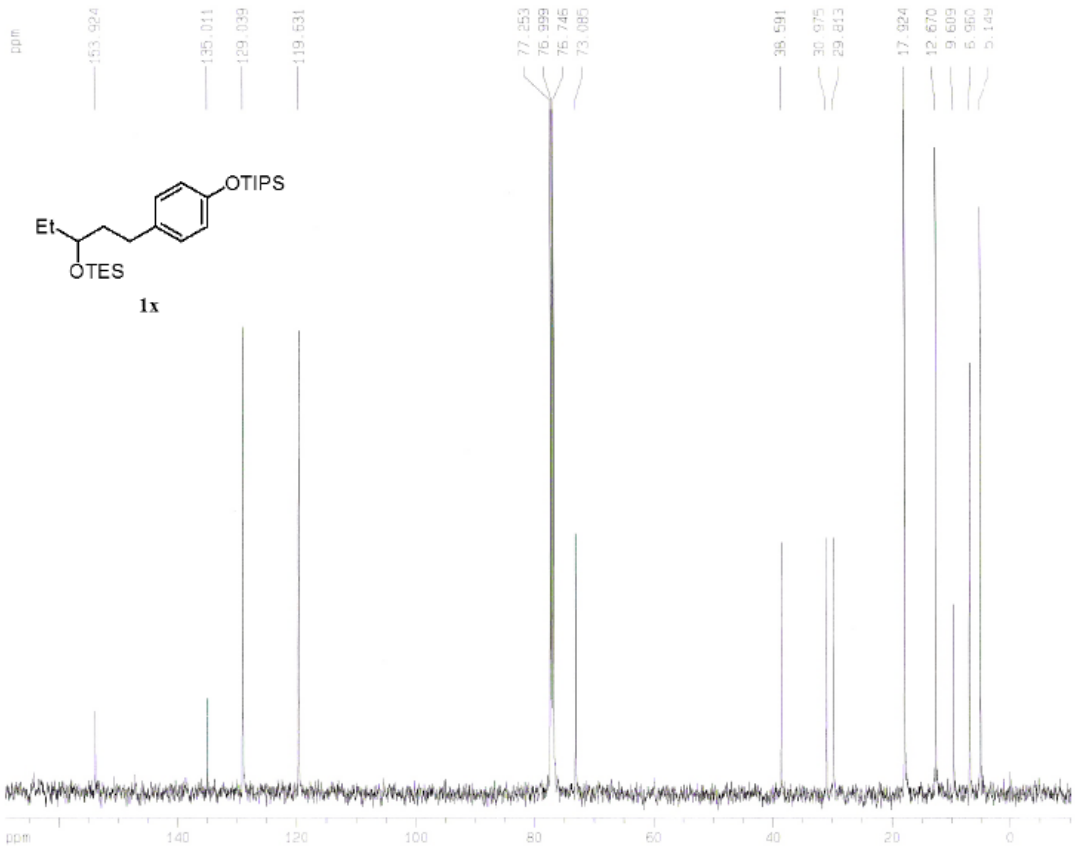
1v

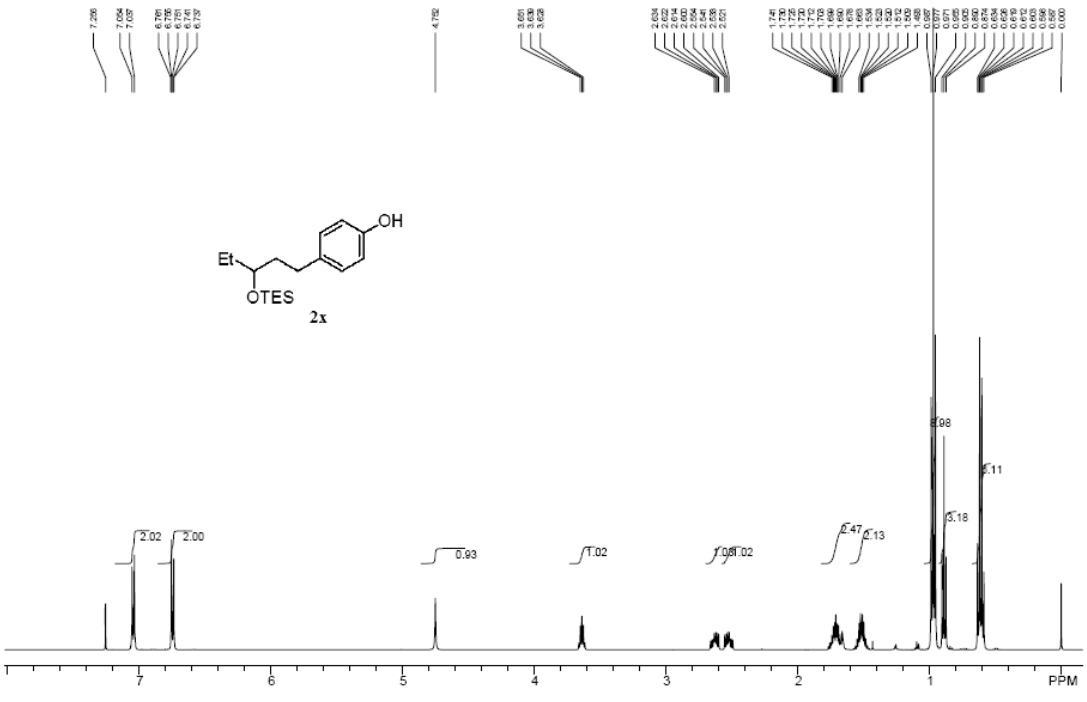

OTIPS
1v
ppm
156.057
139.522
129.302
120.421
118.909
117.908
103.486
77.252
76.998
76.744
65.182
17.905
12.660
140
120
100
80
60
40
20

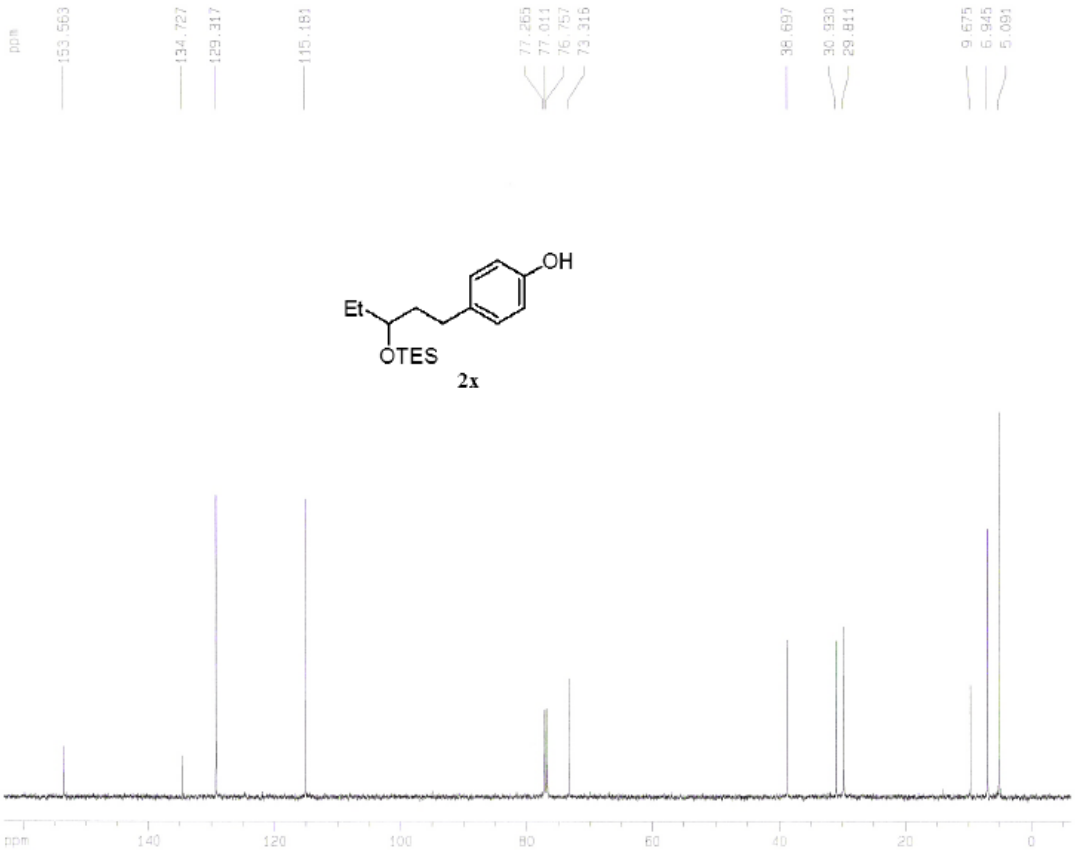

OTIPS
1w
6.21
2.91
0.99
1.02
1.03
0.92
1.00
1.00
3.19
PPM


OTIPS
O
O
1w
ppm
159.571
157.226
129.671
113.021
107.133
106.920
77.253
76.999
76.745
68.718
50.077
44.867
17.902
12.658
140
120
100
80
60
40
20


OTIPS
Et
OTES
1x (300 MHz)
2.00
1.96
0.99
2.06
2.11
2.14
3.24
5.85
8
7
6
5
4
3
2
1
PPM


ppm
153.924
135.011
129.039
119.631
77.253
76.999
76.745
73.085
36.591
30.975
29.613
17.924
12.670
9.609
6.960
5.149
OTIPS
Et
OTES
1x
ppm
140
120
100
80
60
40
20
0


OH
Et
OTES
2x
2.02
2.00
0.93
1.02
1.02
2.47
2.13
3.08
3.11
3.18
7
6
5
4
3
2
1
PPM


ppm
153.563
134.727
129.317
115.181
77.265
77.011
76.757
73.316
38.697
30.930
29.811
9.675
6.945
5.091
OH
Et
OTES
2x
ppm
140
120
100
80
60
40
20
0