Heck Couplings at Room Temperature in Nanometer Aqueous Micelles

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Supporting Information

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General. Reactions were performed in non-oven-dried glassware under an Argon atmosphere containing a Teflon coated stir bar and septum. Water (HPLC grade) was purchased from ACROS and degassed prior to use. All commercially available reagents were used without further purification. (dtbpf)PdCl$_2$ (**7**) was generously supplied by Johnson Matthey, PTS and PSS where supplied by Zymes, and TPGS was supplied by Eastman. SDS and PEG-400 were purchased from Aldrich. Triton X-100 was purchased from ACROS. TLC analyses were performed on commercial Kieselgel 60 F254 silica gel plates. GC analyses were performed on an HP-5 capillary column (0.25 μ x 30 m; cross-linked 5% PHME siloxane) and a time program beginning with 5 min at 50 ^{o}C followed by 20 ^{o}C/min ramp to 280 ^{o}C, then 20 min at this temp. Column chromatography was performed using Davisil Grade 633 Type 60Å silica gel. NMR spectra were obtained on a Varian Inova system using CDCl$_3$ as solvent, with proton and carbon resonances at 400 MHz and 100 MHz, respectively. Mass spectral data were acquired on a VF Autospec or an analytical VG-70-250 HF instrument. Dynamic light scattering (DLS) was performed on a Brookhaven Instruments particle size analyzer equipped with an Avalanche photodiode detector and a MG Vertically polarized 35 mW He-Ne 633 nm laser. Cryo-TEM images were obtained using a JEOL JEM#8209;1210, 120kv, (tungsten filament) instrument.

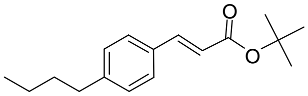
Preparation of 15 wt.% PTS aqueous solution: PTS (3.0 g, ~3.0 mL) was added to a 60 mL serum bottle along with a “large” Teflon coated stir bar. The bottle was purged with argon before addition of degassed water (17.0 mL) and sealed under a positive flow of argon. The mixture was stirred vigorously overnight at room temperature to give a clear, homogeneous, “soapy” solution. The solution was stored under argon on the bench-top for weeks without noticeable decomposition.

General Procedure for Heck Coupling: (dtbpf)PdCl$_2$ (**7**) (6.5 mg, 0.01 mmol) and aryl iodide (0.50 mmol) were added under argon to a 5.0 mL microwave vial equipped with a large stir bar and Teflon lined septum. PTS solution (1.0 mL, 15 wt.%), triethylamine (208 μL, 1.50 mmol), and acrylate/styrene (1.0 mmol) were added by syringe. The heterogeneous mixture was stirred vigorously at rt, becoming pseudo-homogeneous after 20-40 min. Reaction progress was monitored by TLC (5-10% EtOAc/hexane) and/or GC. Upon consumption of aryl iodide (2-24 h), the dark brown mixture was diluted with EtOAc (~1.5 mL) and filtered through a pad of silica gel using EtOAc as the eluent. The volatiles were removed on a rotary evaporator and the crude product was purified by silica gel chromatography or crystallization from warm EtOH. (Alternatively, the crude reaction mixture can be partitioned between hexane/EtOAc (3/1) and H$_2$O/brine (3/1) and washed to remove the catalyst and surfactant).

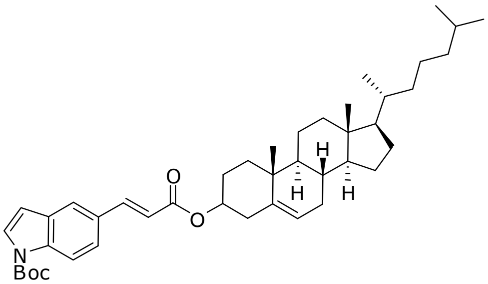
Notes:

- Reactions were conducted in 5.0 mL microwave tubes with large Teflon coated stir bars and Teflon lined septum under 1.0 atm of Ar.
- Oversize stir bars were used, without which solutions can be viscous and difficult to mix.
- Solutions generally become a dark brown as reaction progresses, and oftentimes the product will precipitate out of solution.
- Generally, cinnamate products were purified via silica gel chromatography, while stilbene derivatives were purified via crystallization from warm EtOH.

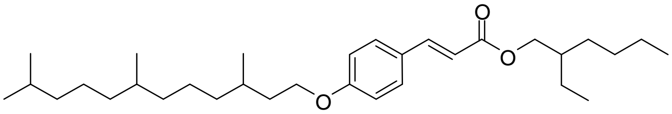
Compound Characterization Data. Compounds not listed are known compounds; spectral data correspond to that in the literature.[1]



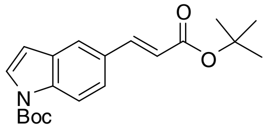
***(E)-tert*-Butyl 3-(4-butylphenyl)acrylate.** Following the general procedure using 4-*n*-butyliodobenzene (130 mg, 0.5 mmol) and *t*-butyl acrylate (145 µL, 1.0 mmol), the reaction was stirred for 5 h at rt. Following the standard workup, chromatography of the crude material on silica gel (1:20, EtOAc/hexanes) gave 101 mg (77%) of a tan waxy semi-solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 15.8 Hz, 1H), 7.42 (d, *J* = 8.1 Hz, 2H), 7.19 (d, *J* = 8.1 Hz, 2H), 6.34 (d, *J* = 15.8 Hz, 1H), 2.62 (t, *J* = 7.8 Hz, 2H), 1.60 (m, 2H), 1.54 (s, 9H), 1.37 (m, 2H), 0.94 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.7, 145.4, 143.7, 132.2, 129.0, 128.1, 119.2, 80.4, 35.7, 33.6, 28.4, 22.5, 14.1. HREIMS calcd for $C_{17}H_{24}O_2$ [M^+] = 260.1776, found 260.1767.



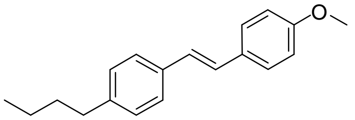
***(E)-tert*-Butyl 5-(3-*cholesteryl*oxy-3-oxoprop-1-enyl)-indole-1-carboxylate (8).** Following the general procedure using (dtbpf)$PdCl_2$ (3.5 mg, 0.005 mmol), *t*-butyl 5-iodoindole-1-carboxylate (142 mg, 0.5 mmol), and cholesteryl acrylate (111 mg, 0.25 mmol), the reaction was stirred for 8 h at rt. Following the standard workup, chromatography of the crude material on silica gel (1:10, EtOAc/hexanes) gave 138 mg (84%) of a colorless solid, mp = 172-174 °C (decomposition). [Additionally 10 mg of the (*Z*)-isomer was obtained (6%).] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, *J* = 8.4 Hz, 1H), 7.79 (d, *J* = 16.0 Hz, 1H), 7.72 (s, 1H), 7.61 (d, *J* = 3.6 Hz, 1H), 7.52 (dd, *J* = 7.7, 1.5 Hz, 1H), 6.59 (d, *J* = 3.6 Hz, 1H), 6.44 (d, *J* = 16.0 Hz, 1H), 5.42 (d, *J* = 4.7 Hz, 1H), 4.77 (m, 1H), 2.42 (d, *J* = 7.2 Hz, 2H), 2.05-1.80 (m, 6H), 1.69 (s, 9H), 1.78-0.96 (m, 26H), 0.94 (d, *J* = 6.1 Hz, 2H), 0.88 (dd, *J* = 6.6, 1.5 Hz, 4H), 0.70 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.2, 149.9, 145.6, 140.2, 131.4, 129.7, 127.4, 124.4, 123.2, 122.0, 117.7, 116.0, 107.9, 94.9, 84.6, 74.4, 57.2, 56.6, 50.5, 42.8, 40.2, 40.0, 38.8, 37.5, 37.1, 36.7, 36.3, 32.4, 32.3, 28.8, 28.7, 28.5, 28.4, 24.8, 24.3, 23.4, 23.1, 21.5, 19.9, 19.2, 12.4. HREIMS calcd for $C_{43}H_{61}NO_4Na$ [M+Na] = 678.4498, found 678.4521.



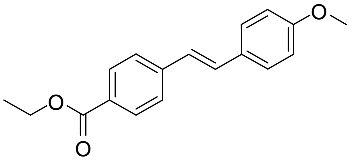
***(E)*-2-Ethylhexyl 3-(4-(3,7,11-trimethyldodecyloxy)phenyl)acrylate.** Following the general procedure using 1-iodo-4-(3,7,11-trimethyldodecyloxy)benzene (215 mg, 0.5 mmol) and 2-ethylhexyl acrylate (208 µL, 1.0 mmol), the reaction was stirred for 8 h at 50 °C. Following the standard workup, chromatography of the crude material on silica gel (1:20, EtOAc/hexanes) gave 229 mg (94%) of a colorless oil. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.58 (d, *J* = 15.8 Hz, 1H), 7.61 (d, *J* = 16.0 Hz, 1H), 7.46 (d, *J* = 8.0 Hz, 2H), 6.88 (d, *J* = 8.0 Hz, 2H), 6.30 (d, *J* = 16.0 Hz, 1H), 4.09 (m, 2H), 4.01 (m, 2H), 1.83 (m, 1H), 1.70-1.01 (m, 27H), 0.94-0.82 (m, 18H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 167.5, 160.9, 144.2, 129.6, 126.9, 115.5, 114.7, 66.7, 66.4, 39.3, 38.8, 37.3, 37.2, 36.1, 36.0, 32.7, 30.4, 29.7, 28.9, 27.9, 24.3, 23.8, 23.0, 22.7, 22.6, 19.7, 19.6, 19.5, 14.1, 11.0. HREIMS calcd for $C_{32}H_{54}O_3$ [M$^+$] = 486.4073, found 486.4064.



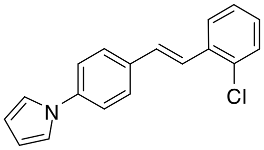
***(E)-tert*-Butyl 5-(3-*tert*-butoxy-3-oxoprop-1-enyl)-indole-1-carboxylate.** Following the general procedure using *t*-butyl 5-iodoindole-1-carboxylate (142 mg, 0.5 mmol), and *t*-butyl acrylate (145 μL, 1.0 mmol), the reaction was stirred for 6 h at rt. Following the standard workup, chromatography of the crude material on silica gel (1:10, EtOAc/hexanes) gave 164 mg (96%) of a light yellow oil. ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.13 (d, *J* = 8.5 Hz, 1H), 7.70 (m, 2H), 7.61 (d, *J* = 3.5 Hz, 1H), 7.51 (dd, *J* = 8.7, 2.0 Hz, 1H), 6.59 (d, *J* = 3.8 Hz, 1H), 6.40 (d, *J* = 16.0 Hz, 1H), 1.68 (s, 9H), 1.56 (s, 9H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 166.8, 149.6, 144.4, 136.3, 131.1, 129.5, 127.0, 124.0, 121.5, 118.9, 115.6, 107.6, 84.3, 80.5, 28.5, 28.4. HREIMS calcd for $C_{20}H_{25}NO_4$ [M+Na] = 366.1681, found 366.1667.



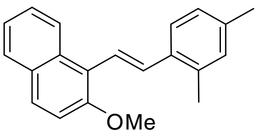
***(E)*-1-Butyl-4-(4-methoxystyryl)benzene.** Following the general procedure using 4-*n*-butyliodobenzene (130 mg, 0.5 mmol) and 4-methoxystyrene (133 μL, 1.0 mmol), the reaction was stirred for 1.5 h at rt. Following the standard workup, recrystallization of the crude product from warm EtOH gave 115 mg (86%,) of a tan solid, mp = 116-118 °C. [Additionally 12 mg (*Z*)-isomer was isolated (10%).] ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.46 (d, *J* = 8.6 Hz, 2H), 7.43 (d, *J* = 8.6 Hz, 2H), 7.18 (d, *J* = 8.2 Hz, 2H), 7.05 (d, *J* = 16.3 Hz, 1H), 6.97 (d, *J* = 16.3 Hz, 1H), 6.91 (d, *J* = 8.6 Hz, 2H), 3.84 (s, 3H), 2.62 (t, *J* = 7.4 Hz, 2H), 1.61 (m, 2H), 1.39 (m, 2H), 0.95 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 159.3, 142.3, 135.2, 130.5, 128.9, 127.8, 127.4, 126.7, 126.4, 114.3, 55.4, 35.6, 33.8, 22.6, 14.2. HREIMS calcd for $C_{19}H_{22}O$ [M$^+$] = 266.1671, found 266.1661.



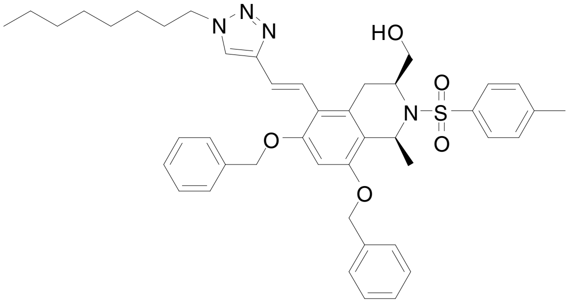
***(E)*-Ethyl 4-(4-methoxystyryl)benzoate.** Following the general procedure using ethyl 4-iodobenzoate (84 μL, 0.5 mmol) and 4-methoxystyrene (133 μL, 1.0 mmol), the reaction was stirred for 4 h at rt. Following the standard workup, recrystallization of the crude product from warm EtOH gave 127 mg (90%,) of a colorless solid, mp = 142-144 °C . [Additionally 10 mg (*Z*)-isomer was isolated (7%).] ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.03 (d, *J* = 8.3 Hz, 2H), 7.55 (d, *J* = 8.3 Hz, 2H), 7.49 (d, *J* = 8.6 Hz, 2H), 7.18 (d, *J* = 16.2 Hz, 1H), 7.02 (d, *J* = 16.2 Hz, 1H), 6.93 (d, *J* = 8.7 Hz, 2H), 4.39 (q, *J* = 7.1 Hz, 2H), 3.85 (s, 3H), 1.41 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.5, 159.8, 142.2, 130.7, 130.0, 129.6, 128.9, 128.2, 126.1, 125.5, 114.3, 61.0, 55.4, 14.5. HREIMS calcd for $C_{18}H_{18}O_3$ [M^+] = 282.1256, found 282.1266.



***(E)*-1-(4-(2-Chlorostyryl)phenyl)pyrrole.** Following the general procedure using 1-(4-iodophenyl)-pyrrole (135 mg, 0.5 mmol) and 2-chlorostyrene (128 μL, 1.0 mmol), the reaction was stirred for 18 h at rt. Following the standard workup, recrystallization of the crude product from warm EtOH gave 117 mg (84%,) of a light brown solid, mp = 130-132 °C. [Additionally 15 mg (*Z*)-isomer was isolated (11%).] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 7.8 Hz, 1H), 7.62 (d, *J* = 8.6 Hz, 2H), 7.51 (d, *J* = 16.3 Hz, 1H), 7.42 (m, 3H), 7.29 (m, *J* = 6.7 Hz, 1H), 7.22 (m, *J* = 7.4, 1.4 Hz, 1H), 7.14 (m, *J* = 2.0 Hz, 2H), 7.09 (d, *J* = 16.3 Hz, 1H), 6.38 (m, *J* = 2.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.4, 135.5, 134.6, 133.6, 130.3, 130.1, 128.8, 128.2, 127.1, 126.6, 124.8, 120.6, 119.3, 110.8. HREIMS calcd for $C_{18}H_{14}ClN$ [M^+] = 279.0815, found 279.0819.

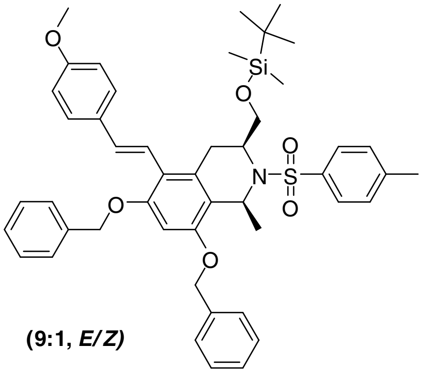


(E)-1-(2,4-Dimethylstyryl)-2-methoxynaphthalene. Following the general procedure using 1-iodo-2-methoxynaphthalene (142 mg, 0.5 mmol) and 2,4-dimethylstyrene (132 μL, 1.0 mmol), the reaction was stirred for 24 h at rt. Following the standard workup, chromatography of the crude material on silica gel (1:20, EtOAc/hexanes) gave 129 mg (89%,) of a tan semi-solid. [Additionally 8 mg (*Z*)-isomer was isolated (6%).] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (d, *J* = 8.7 Hz, 1H), 7.81 (t, *J* = 7.8 Hz, 2H), 7.68 (d, *J* = 7.8 Hz, 1H), 7.47 (t, *J* = 7.2 Hz, 1H), 7.40-7.30 (m, 4H), 7.10 (d, *J* = 8.2 Hz, 1H), 7.05 (s, 1H), 3.98 (s, 3H), 2.40 (s, 3H), 2.37 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.8, 137.4, 135.7, 134.6, 133.0, 132.8, 131.3, 129.5, 128.8, 128.5, 127.1, 126.6, 125.5, 124.6, 123.7, 122.5, 121.3, 113.5, 56.7, 21.3, 20.1. HREIMS calcd for $C_{21}H_{20}O$ [M^+] = 288.1514, found 288.1510.



***((1S,3S)*-6,8-Bis(benzyloxy)-1-methyl-5-((E)-2-(1-octyl-1,2,3-triazol-4-yl)vinyl)-2-tosyl-1,2,3,4-tetrahydroisoquinolin-3-yl)methanol.** Following the general procedure using (dtbpf)$PdCl_2$ (2.6 mg, 0.004 mmol), aryl iodide **11** (134 mg, 0.20 mmol), 1-octyl-4-vinyl-1,2,3-triazole (**12**; 83 mg, 0.40 mmol), triethylamine (84 μL, 0.6

mmol), and 15 wt.% PTS/H_2O (400 μL) the reaction was stirred for 8 h at 50 °C. Following the standard workup, chromatography of the crude material on silica gel (1:1, EtOAc/hexanes) gave 132 mg (92%,) of a light brown oil. [Additionally 5 mg (*Z*)-isomer was isolated (3%).] ^{1}H NMR (400 MHz, $(CD_3)_2CO$) δ 7.96 (s, 1H), 7.54 (d, *J* = 7.2 Hz, 2H), 7.46 (m, 6H), 7.41-7.29 (m, 4H), 7.08 (d, *J* = 8.0 Hz, 2H), 6.88 (d, *J* = 16.5 Hz, 1H), 6.64 (s, 1H), 5.44 (q, *J* = 7.0 Hz, 1H), 5.18-5.07 (m, 4H), 4.38 (t, *J* = 7.0 Hz, 1H), 4.14 (t, *J* = 6.7 Hz, 1H), 3.84 (m, 1H), 3.82 (m, 2H), 3.36 (dd, *J* = 16.1, 6.5 Hz, 1H), 2.88 (m, 2H), 2.26 (s, 3H), 1.89 (m, 2H), 1.45 (d, *J* = 7.0 Hz, 3H), 1.38-1.24 (m, 10H), 0.87 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.8, 153.4, 146.8, 143.0, 137.1, 136.7, 135.6, 133.4, 129.2, 129.0, 128.8, 128.3, 128.1, 127.4, 127.2, 127.1, 123.6, 121.7, 120.2, 117.9, 96.3, 71.0, 70.1, 67.4, 56.3, 50.5, 47.9, 31.9, 30.5, 29.2, 29.1, 26.6, 26.5, 23.0, 22.8, 21.6, 14.2. HREIMS calcd for $C_{44}H_{52}N_4O_5S$ [M+Na] = 771.3556, found 771.3515.



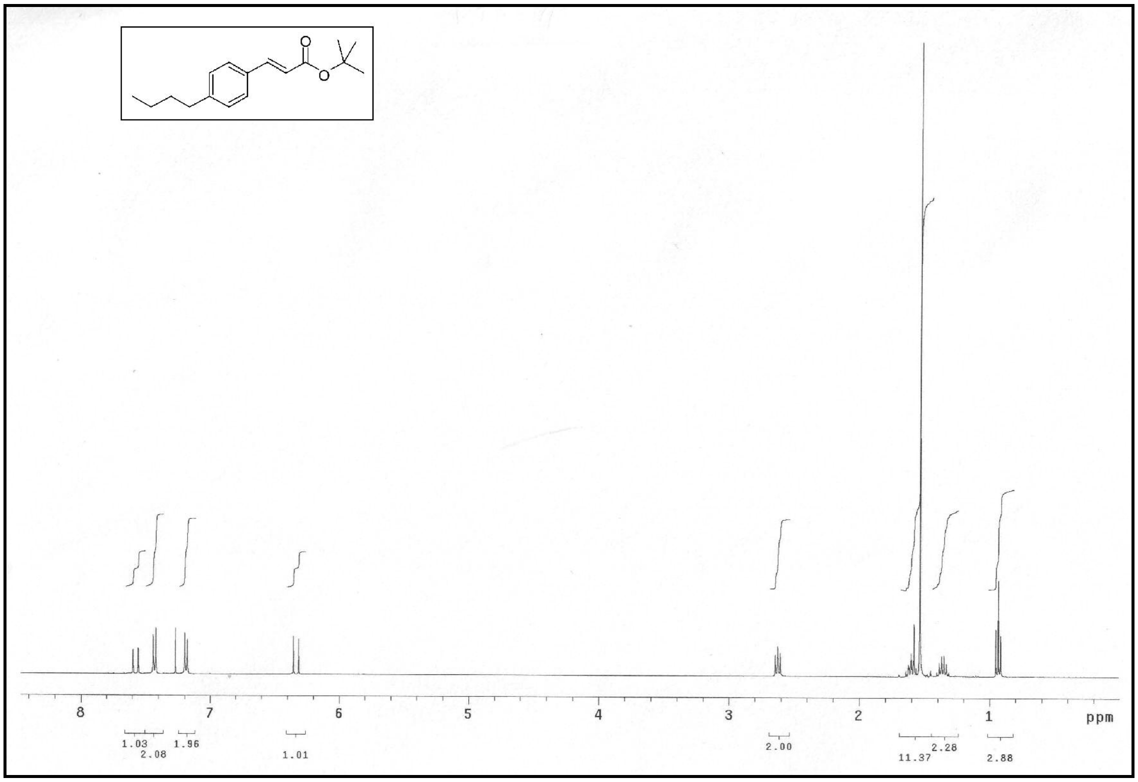
(9:1, *E/Z*)

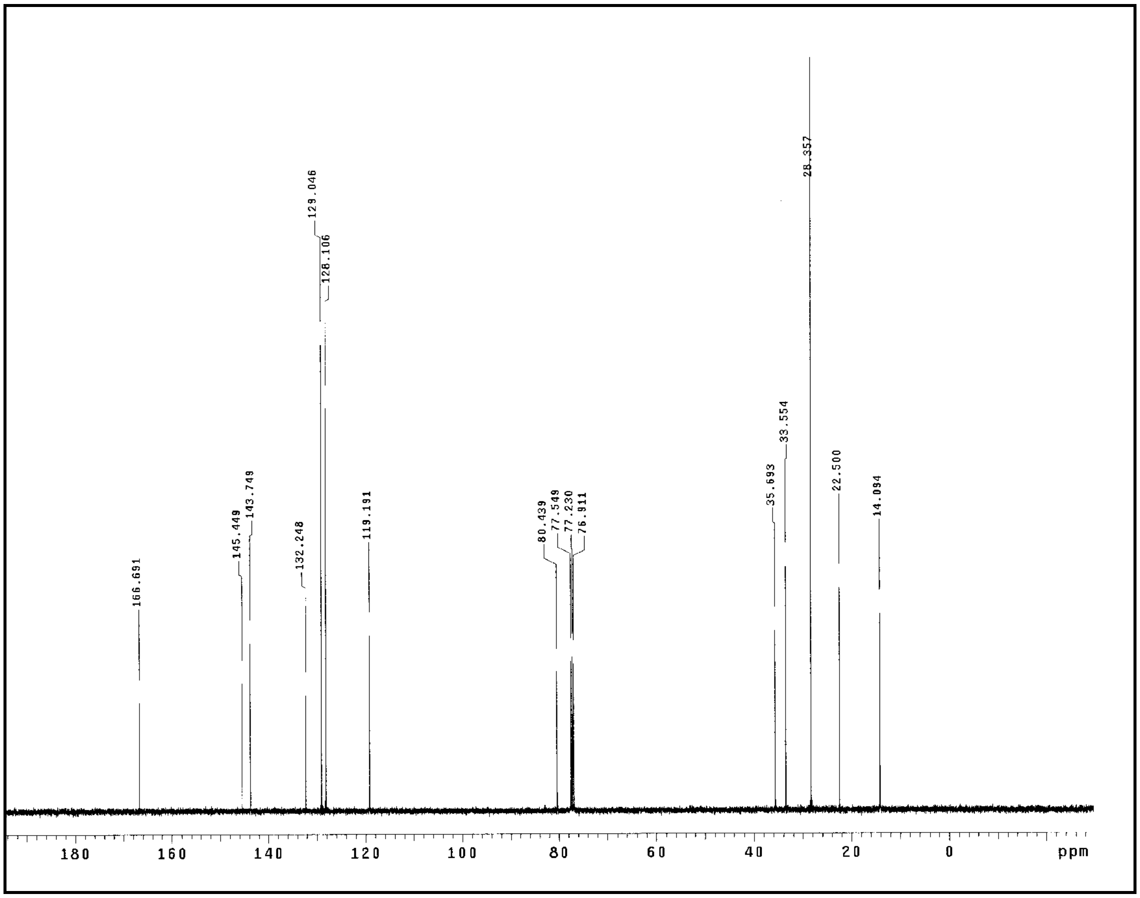
Table 3, entry 7. Following the general procedure using (dtbpf)$PdCl_2$ (1.0 mg, 0.0015 mmol), aryl iodide **13** (50 mg, 0.063 mmol), 4-methoxystyrene (20 μL, 0.127 mmol), triethylamine (27 μL, 0.189 mmol), and 15 wt.% PTS/H_2O (200 μL) the reaction was stirred for 8 h at rt. Following the standard workup, chromatography of the crude material on silica gel (1:10, EtOAc/hexanes) gave 45 mg (90%,) of a colorless semi-solid (9:1 isomeric mixture, inseparable). ^{1}H NMR (400 MHz, $CDCl_3$) 'see below'. HREIMS calcd for $C_{47}H_{55}NO_6SSi$ [M+Na] = 812.3417, found 812.3431.

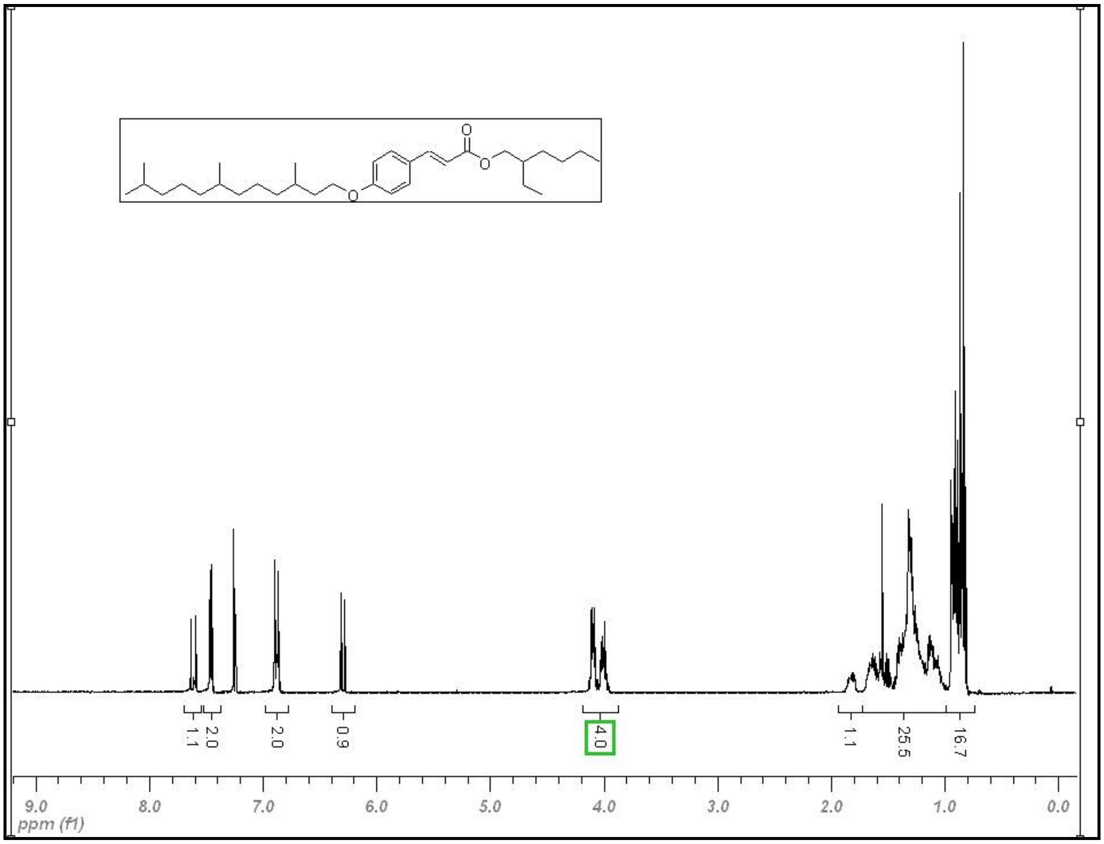
References

[1] (a) Tang, Y.; Yu, Y.; Xia, W.; Song, Y. Huang, Z.; *J. Org. Chem.* **2002**, *67*, 3096-3103. (b) List, B.; Doehring, A.; Fonseca, M.; Job, A.; Torres, R. *Tetrahedron*, **2006**, *62*, 476-482. (c) Herrmann, W.; Bohm, V. *J. Organomet. Chem.* **1999**, *572*, 141-145. (d) Vazquez, E.; Caron, S.; Stevens, R.; Nakao, K.; Koike, H.; Yoshinori. M.; *J. Org. Chem.* **2003**, *68*, 4104-4107. (e) Shi, M.; Xu, B. *J. Org. Chem.* **2002**, *67*, 294-297.

^{1}H and ^{13}C NMR spectra.



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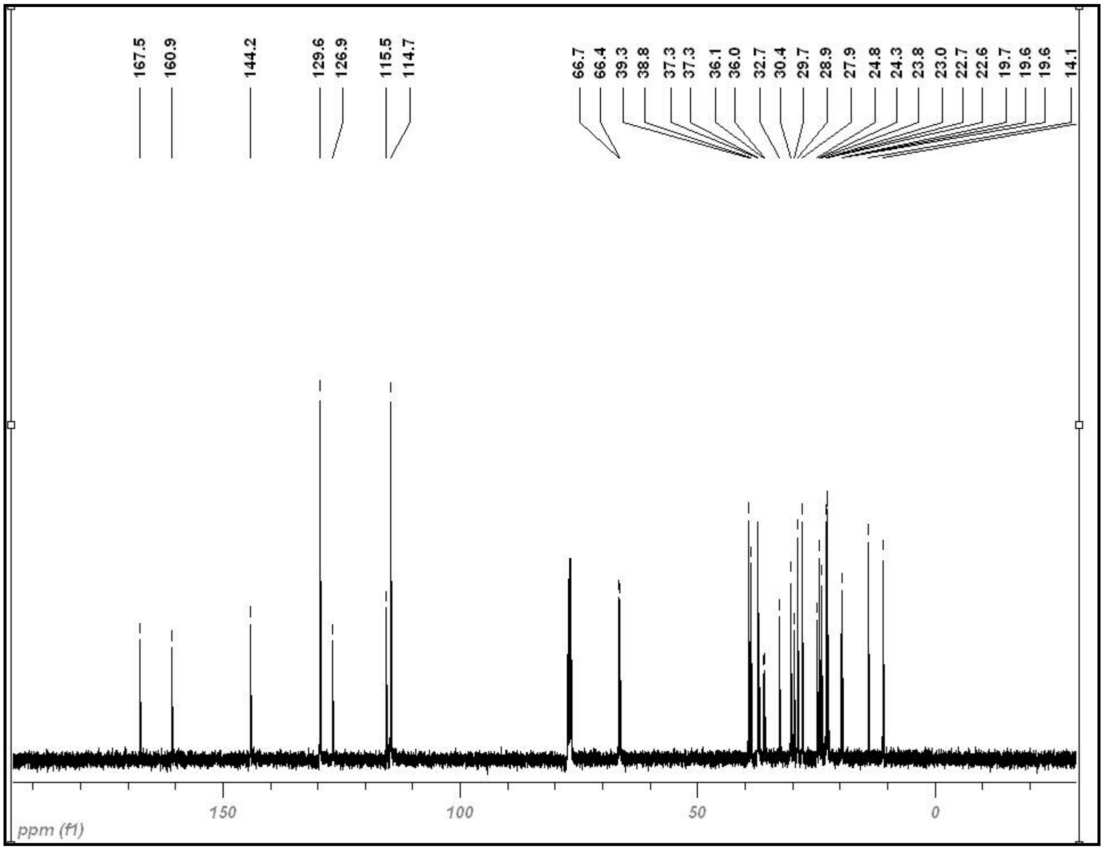
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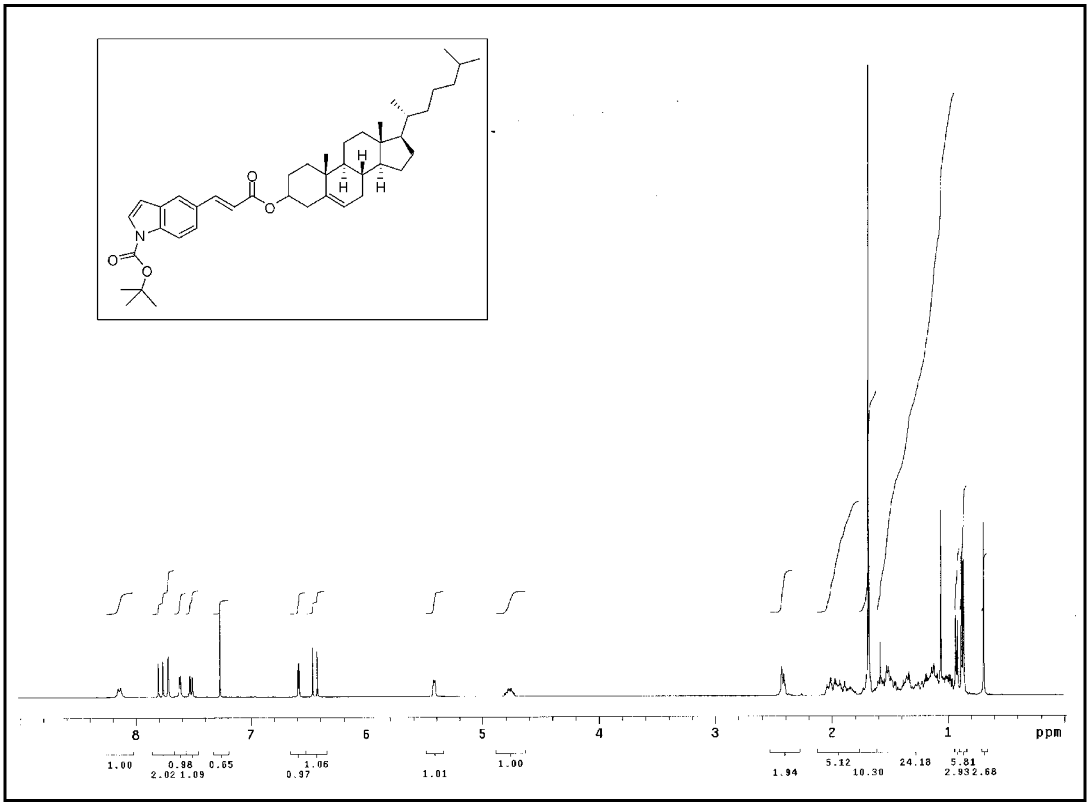

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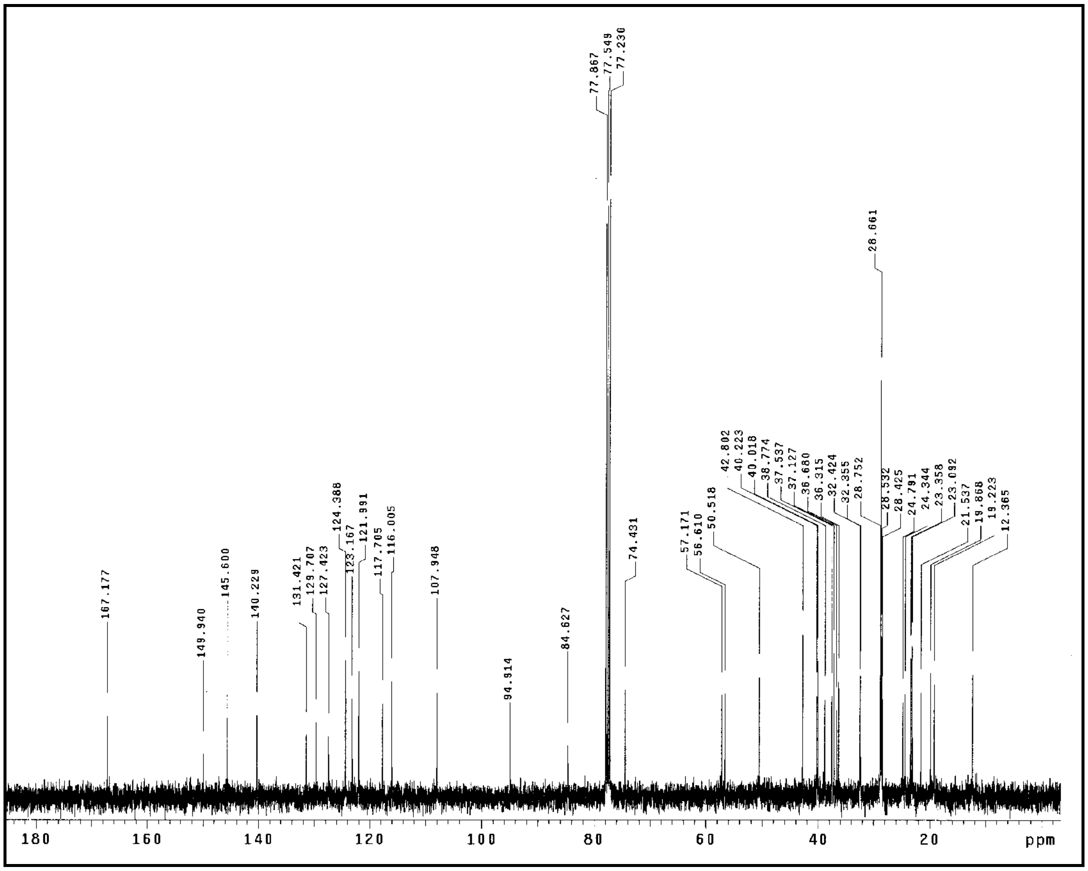

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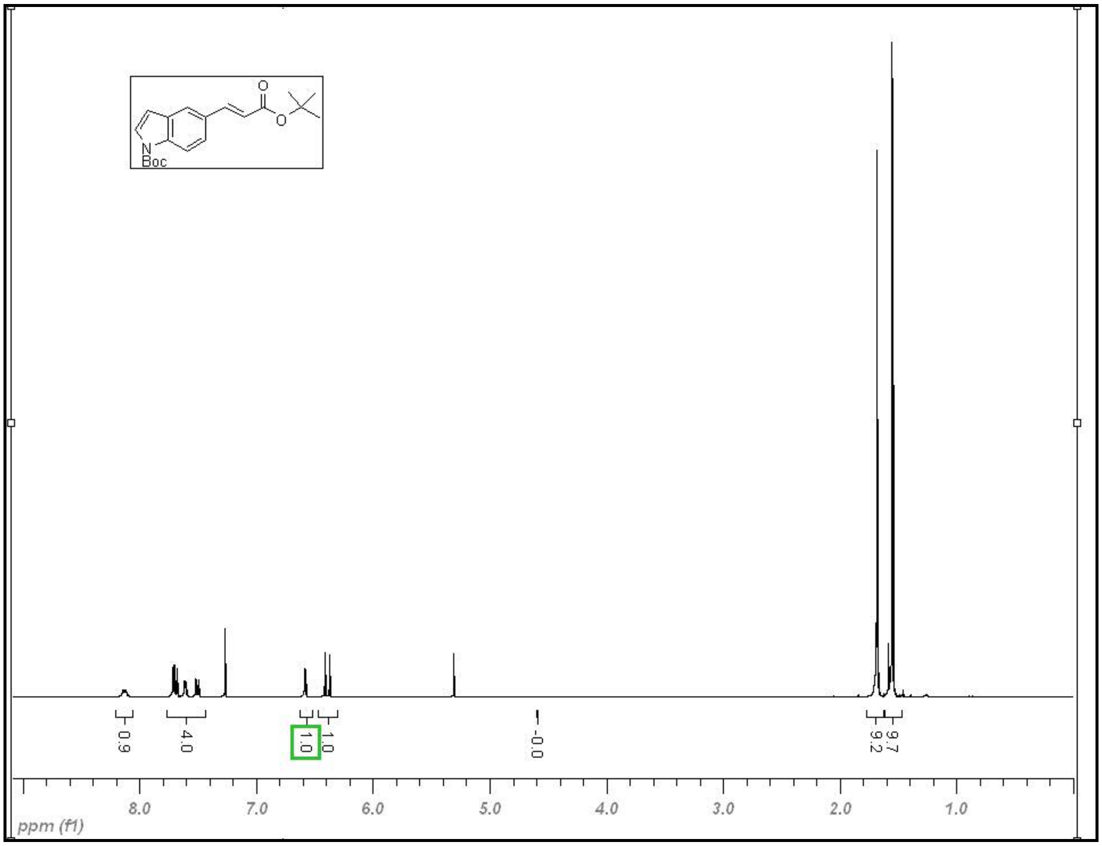
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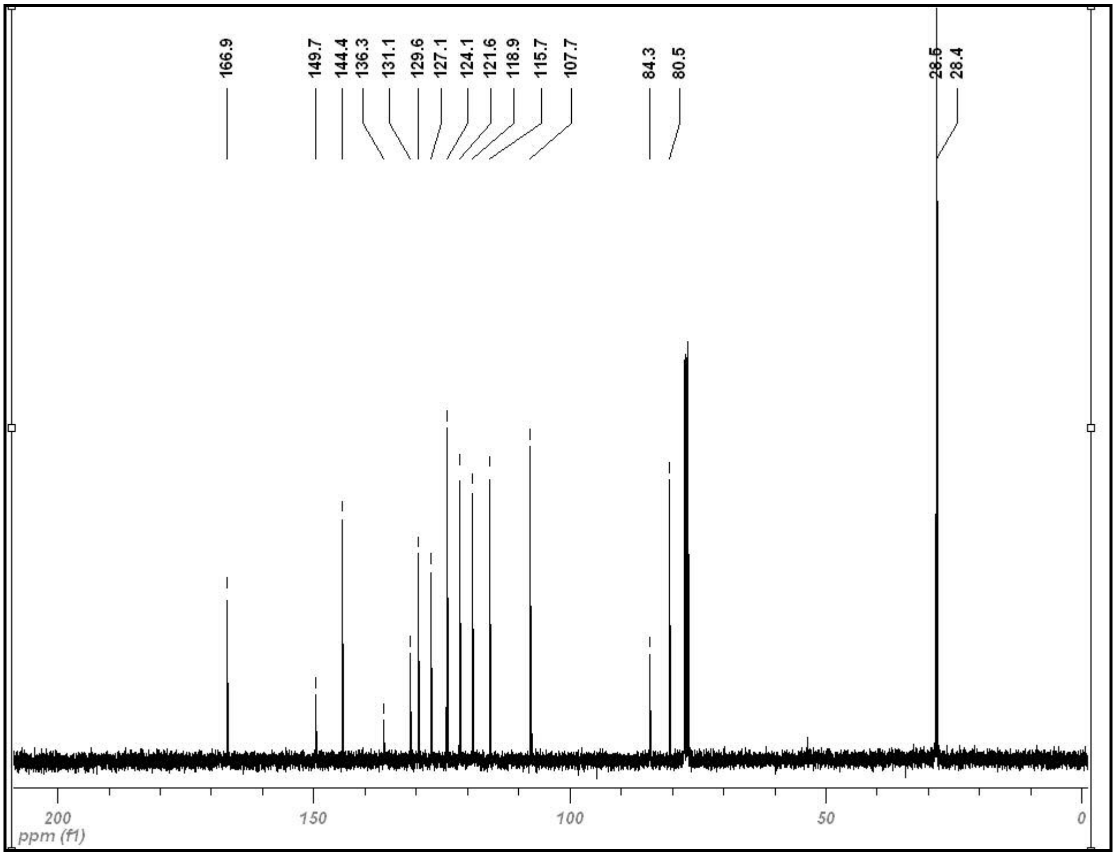
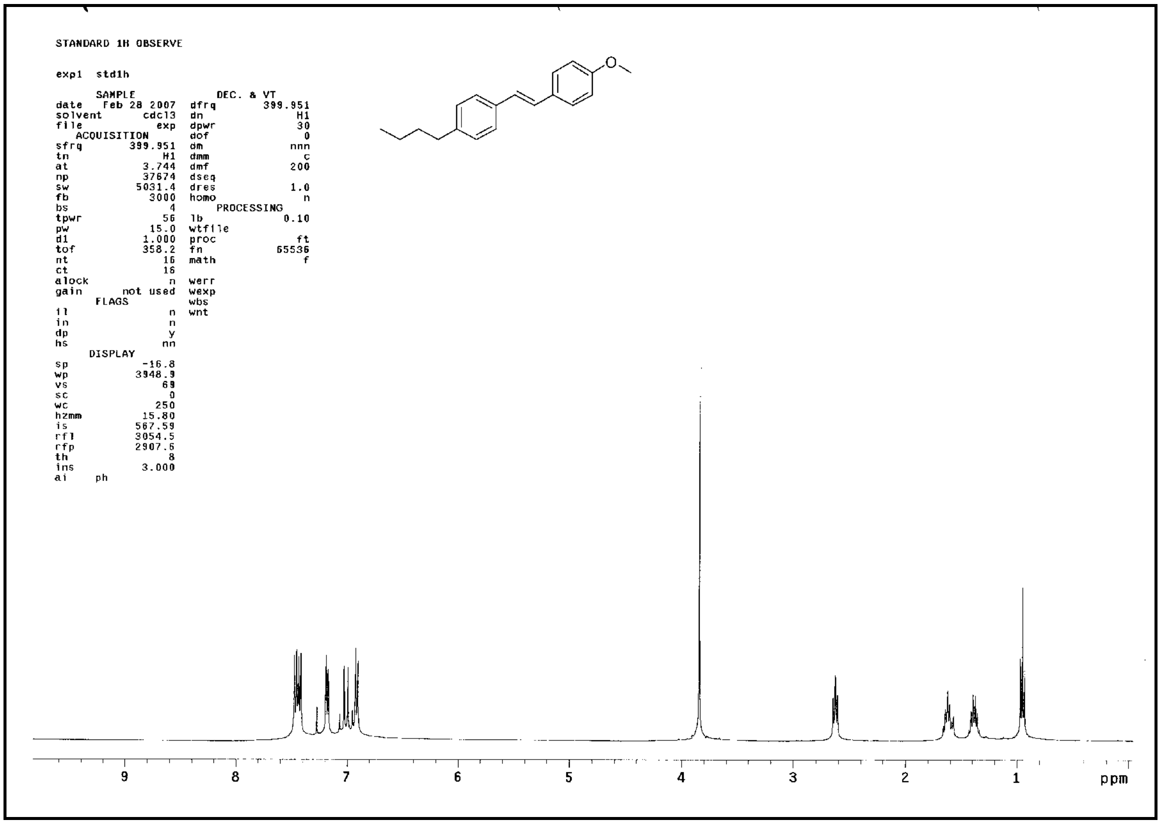
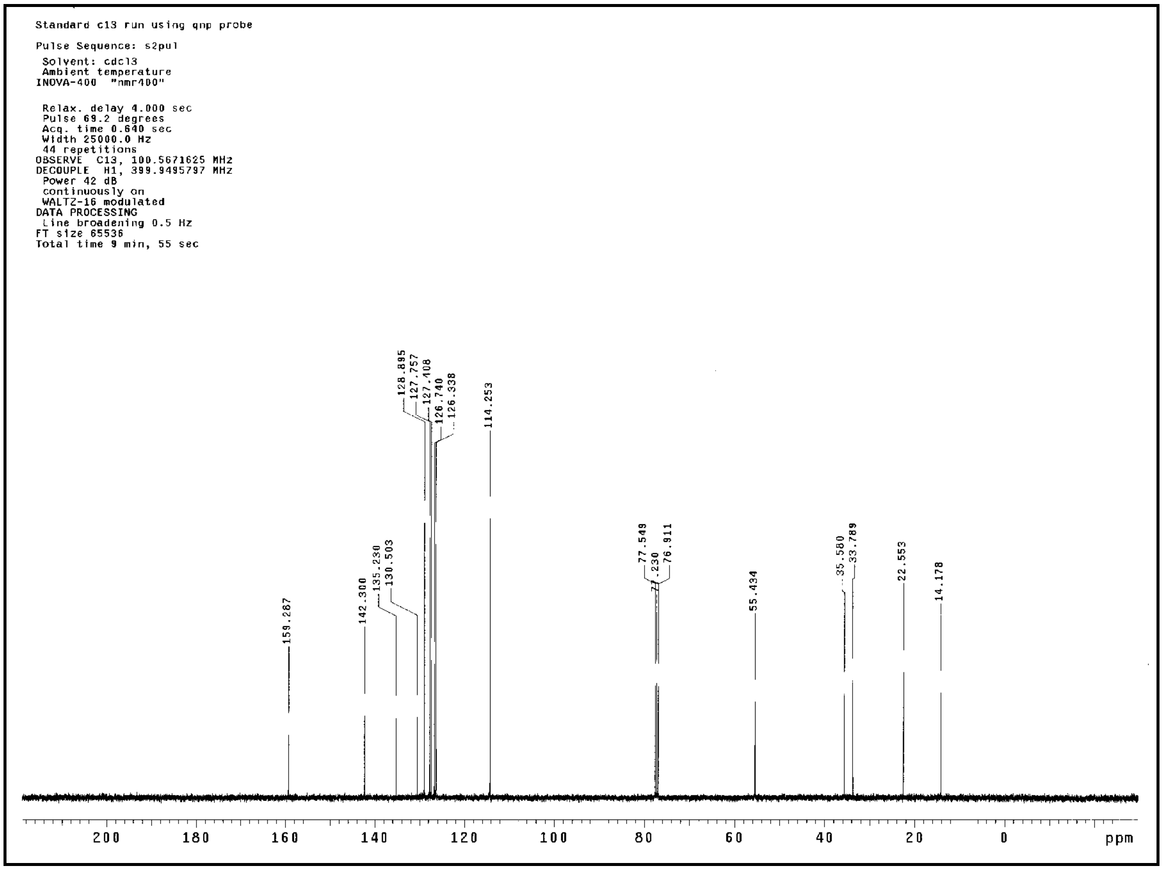
Boc
O
O
0.9
4.0
1.0
1.0
-0.0
9.2
9.7
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (f1)

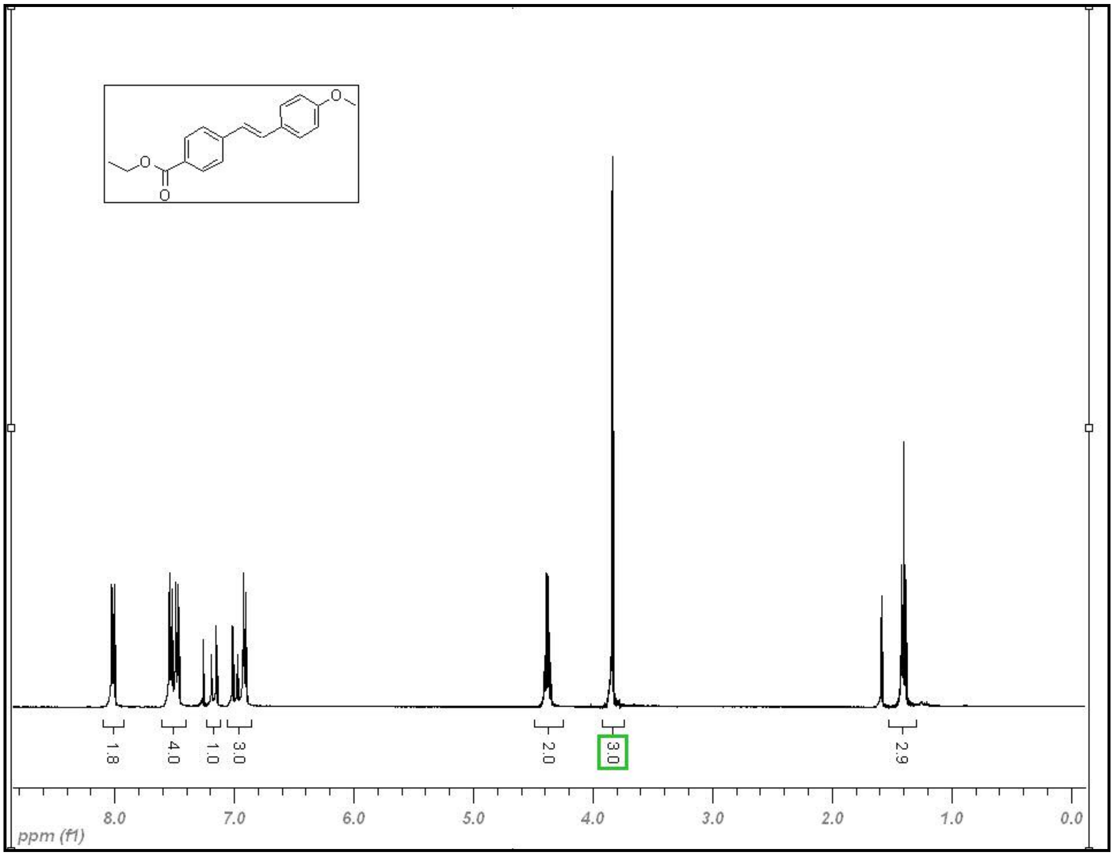

166.9
149.7
144.4
136.3
131.1
129.6
127.1
124.1
121.6
118.9
115.7
107.7
84.3
80.5
28.5
28.4
200
150
100
50
0
ppm (f1)

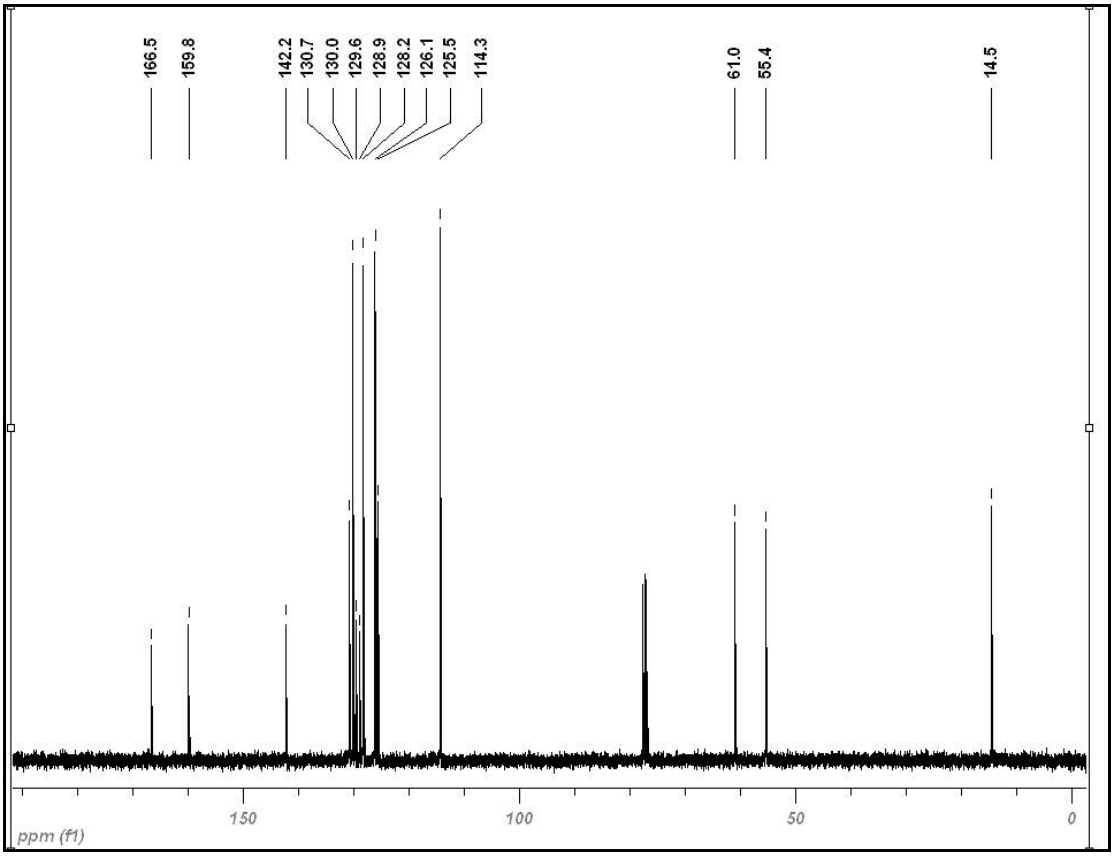


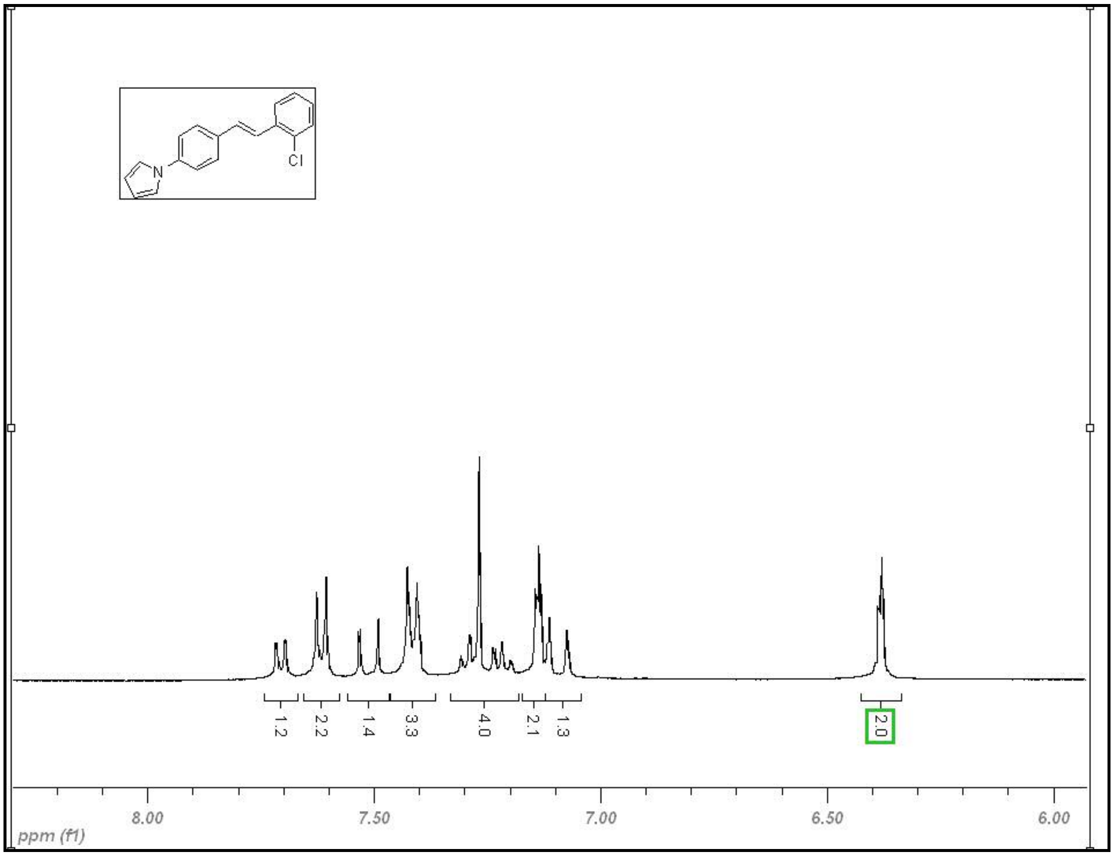
```
STANDARD 1H OBSERVE

exp1  std1h

      SAMPLE              DEC. & VT
date   Feb 28 2007  dfrq        399.951
solvent      cdcl3  dn               H1
file           exp  dpwr             30
   ACQUISITION      dof               0
sfrq       399.951  dm              nnn
tn              H1  dmm               c
at           3.744  dmf             200
np           37674  dseq
sw          5031.4  dres            1.0
fb            3000  homo              n
bs               4      PROCESSING
tpwr            56  lb             0.10
pw            15.0  wtfile
d1           1.000  proc             ft
tof          358.2  fn            65536
nt              16  math              f
ct              16
alock            n  werr
gain      not used  wexp
      FLAGS         wbs
il               n  wnt
in               n
dp               y
hs              nn
     DISPLAY
sp           -16.8
wp          3948.9
vs              69
sc               0
wc             250
hzmm         15.80
is          567.59
rfl         3054.5
rfp         2907.6
th               8
ins          3.000
ai    ph
```



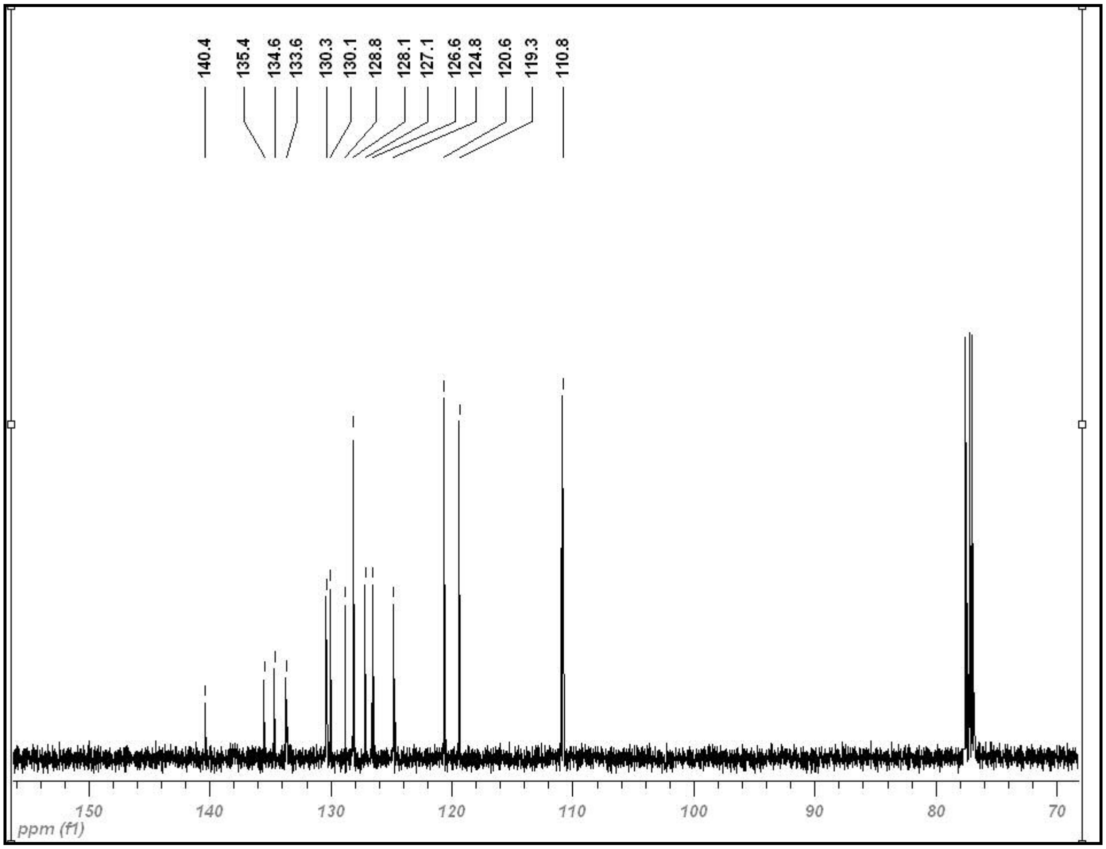
```
Standard c13 run using qnp probe

Pulse Sequence: s2pul
 Solvent: cdcl3
 Ambient temperature
INOVA-400  "nmr400"

 Relax. delay 4.000 sec
 Pulse 69.2 degrees
 Acq. time 0.640 sec
 Width 25000.0 Hz
 44 repetitions
OBSERVE  C13, 100.5671625 MHz
DECOUPLE  H1, 399.9495797 MHz
 Power 42 dB
 continuously on
 WALTZ-16 modulated
DATA PROCESSING
 Line broadening 0.5 Hz
FT size 65536
Total time 9 min, 55 sec
```


1.8
4.0
1.0
3.0
2.0
3.0
2.9
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)

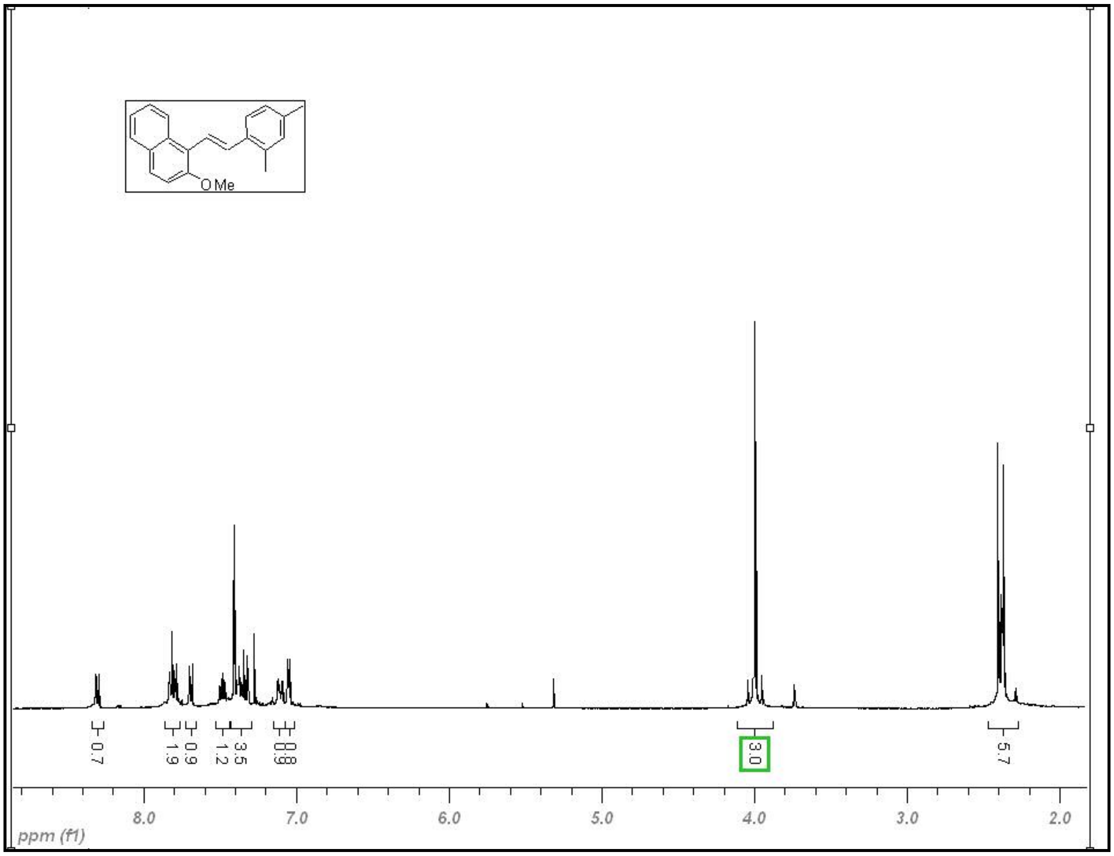

166.5
159.8
142.2
130.7
130.0
129.6
128.9
128.2
126.1
125.5
114.3
61.0
55.4
14.5
150
100
50
0
ppm (f1)

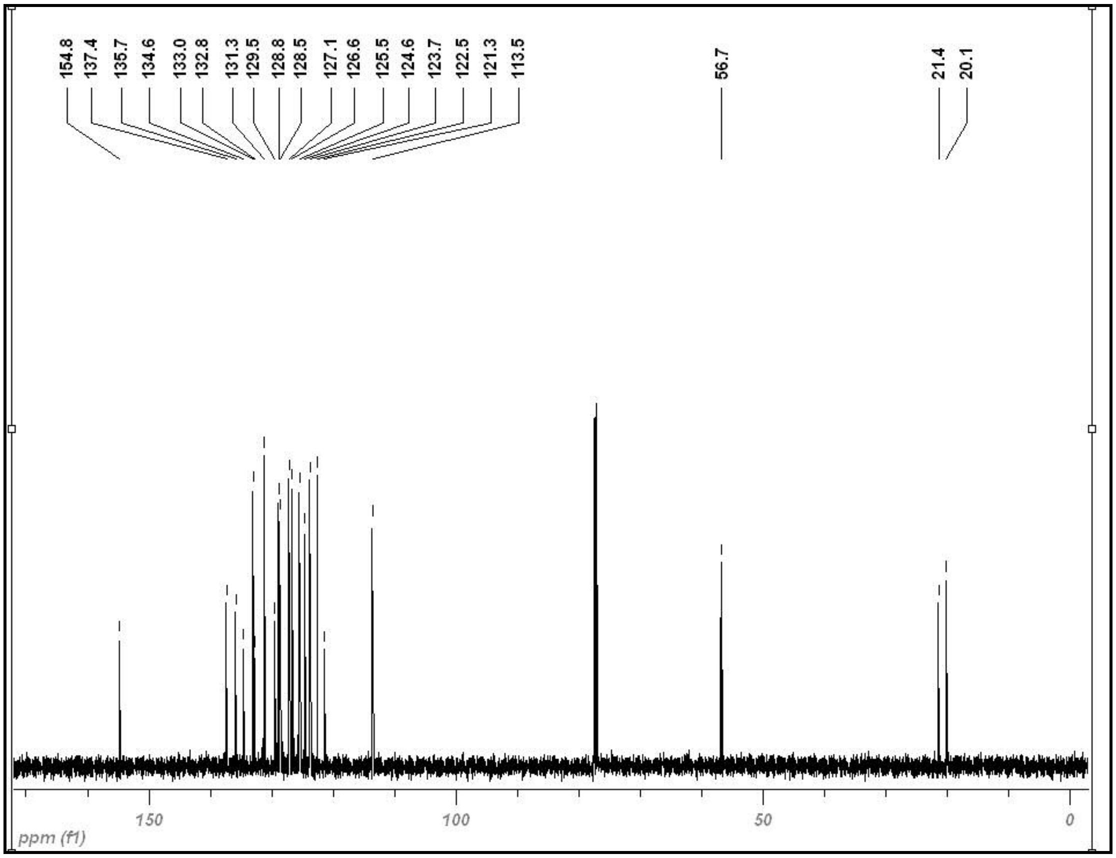


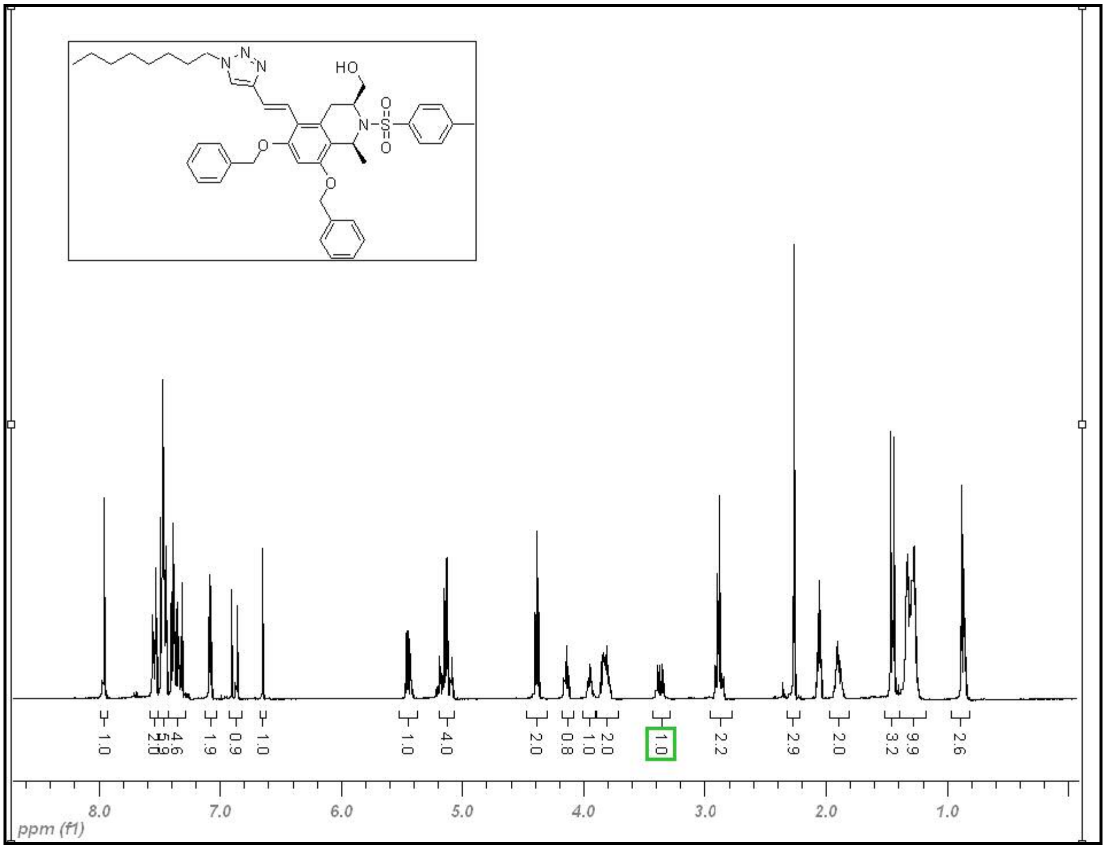
N
Cl
1.2
2.2
1.4
3.3
4.0
2.1
1.3
2.0
8.00
7.50
7.00
6.50
6.00
ppm (f1)

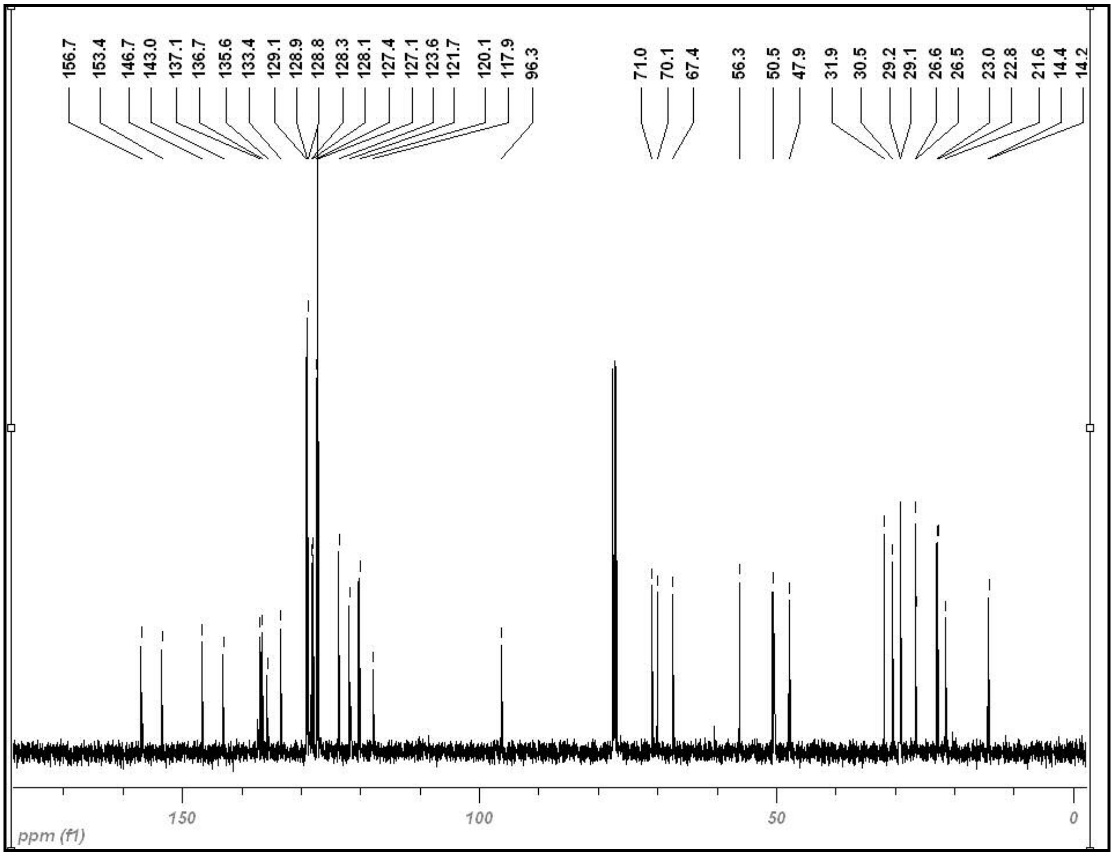


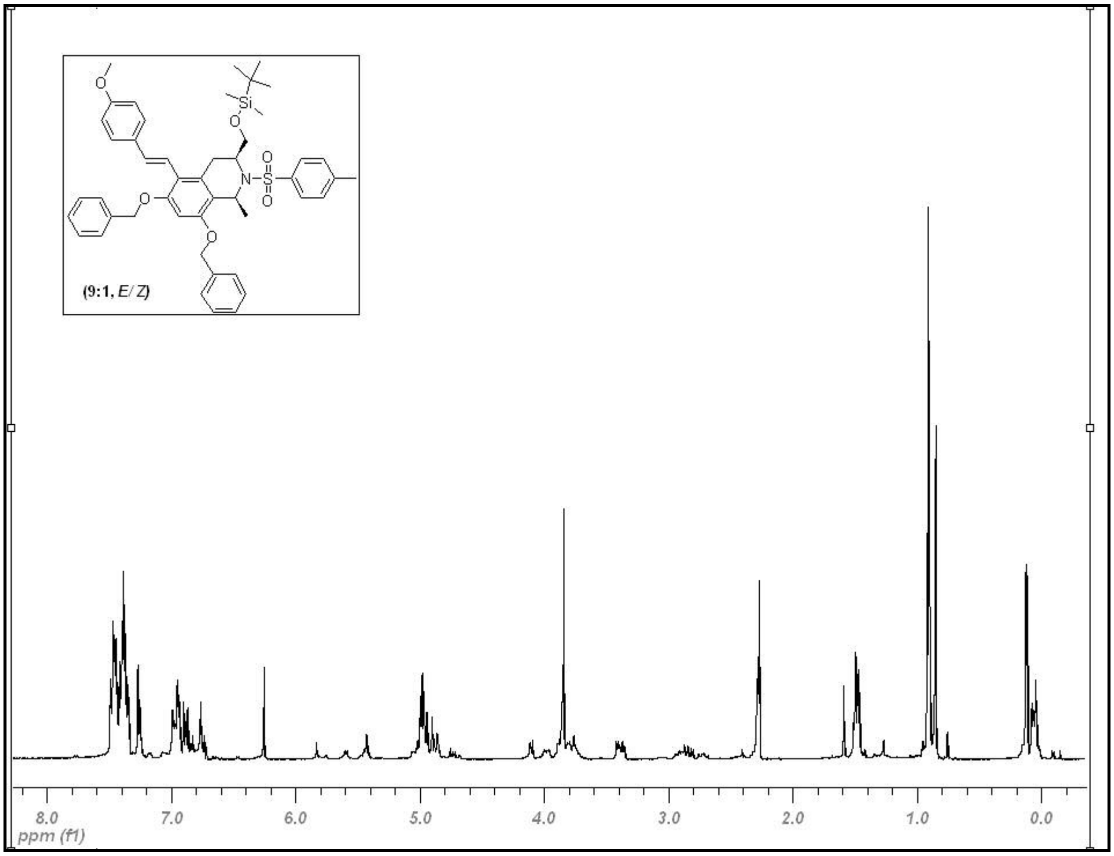
140.4
135.4
134.6
133.6
130.3
130.1
128.8
128.1
127.1
126.6
124.8
120.6
119.3
110.8
150
140
130
120
110
100
90
80
70
ppm (f1)


OMe
0.7
1.9
0.9
1.2
3.5
0.9
0.8
3.0
5.7
8.0
7.0
6.0
5.0
4.0
3.0
2.0
ppm (f1)


154.8
137.4
135.7
134.6
133.0
132.8
131.3
129.5
128.8
128.5
127.1
126.6
125.5
124.6
123.7
122.5
121.3
113.5
56.7
21.4
20.1
150
100
50
0
ppm (f1)


HO
N
N
N
N
S
O
O
O
O
1.0
2.0
5.9
4.6
1.9
0.9
1.0
1.0
4.0
2.0
0.8
1.0
2.0
1.0
2.2
2.9
2.0
3.2
9.9
2.6
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (f1)


156.7
153.4
146.7
143.0
137.1
136.7
135.6
133.4
129.1
128.9
128.8
128.3
128.1
127.4
127.1
123.6
121.7
120.1
117.9
96.3
71.0
70.1
67.4
56.3
50.5
47.9
31.9
30.5
29.2
29.1
26.6
26.5
23.0
22.8
21.6
14.4
14.2
150
100
50
0
ppm (f1)


(9:1, *E*/*Z*)
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)