

Supporting Information

Imidazolium Ionic Liquid-tagged Palladium Complex: An Efficient Catalyst for the Heck and Suzuki Reaction in Aqueous Medium

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1.1 IR spectra of 4 and 5

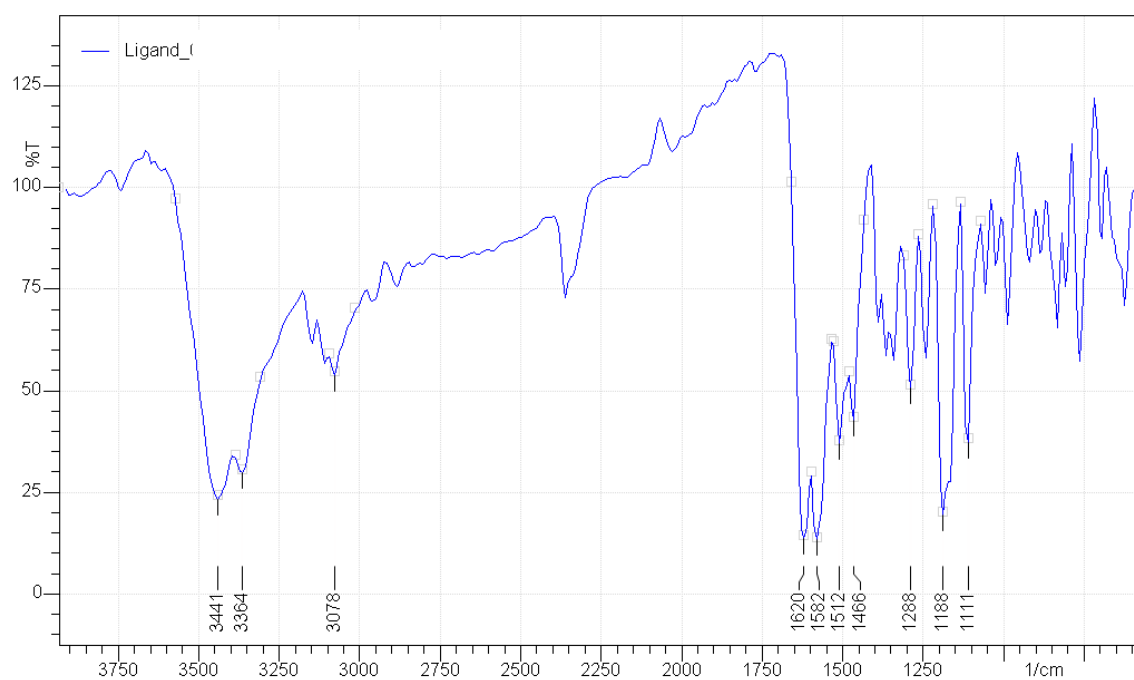


Fig. 1: IR spectra of 4

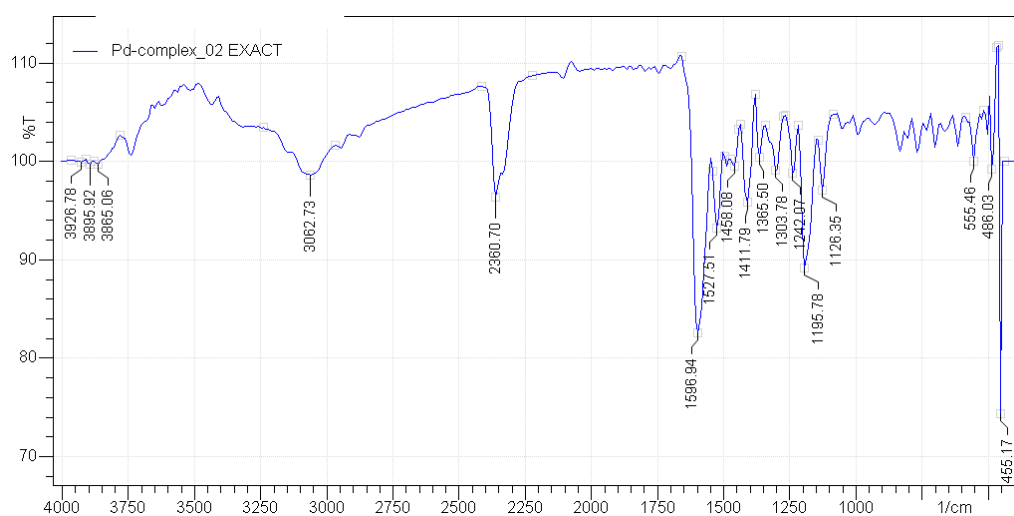


Fig. 2: IR spectra of 5

1.2 UV-visible spectra of 4 and 5

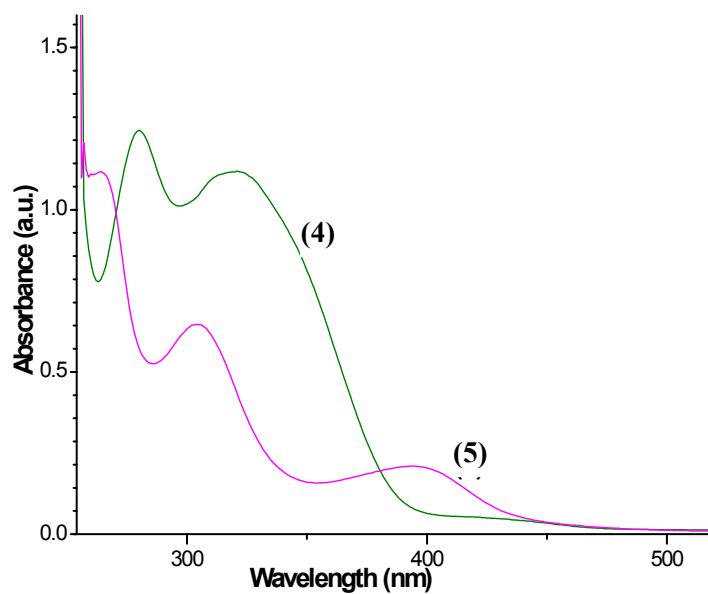


Fig. 3: UV-visible spectra of 4 and 5

1.3 Powdered XRD spectra of 4 and 5

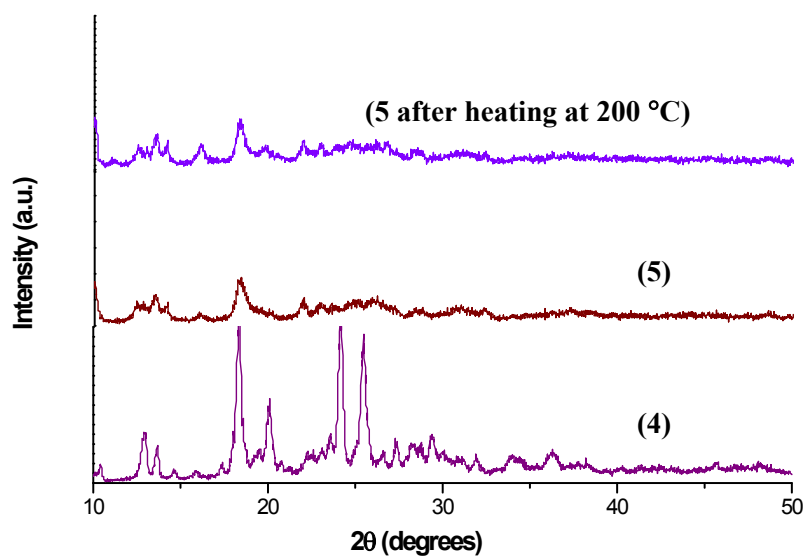


Fig. 4: Powdered XRD spectra of 4 and 5

1.4 ¹H NMR spectra of 2-5 and ¹³C NMR spectra of 4 & 5.

Compound 2: ¹H NMR (400 MHz, DMSO-*d*₆) δ 11.00 (s, 1H), 10.02 (s, 1H), 7.63 (d, *J* = 8.72 Hz, 1H), 6.58 (dd, *J* = 8.72, 2.16 Hz, 1H), 6.50 (d, *J* = 2.16 Hz, 1H), 4.14 (t, *J* = 6.0 Hz, 2H), 3.66 (t, *J* = 6.52 Hz, 2H), 2.29–2.22 (m, 2H). ESI-MS: 259.0 [M + H]⁺ and 261.01 [M + H + 2]⁺ ion.

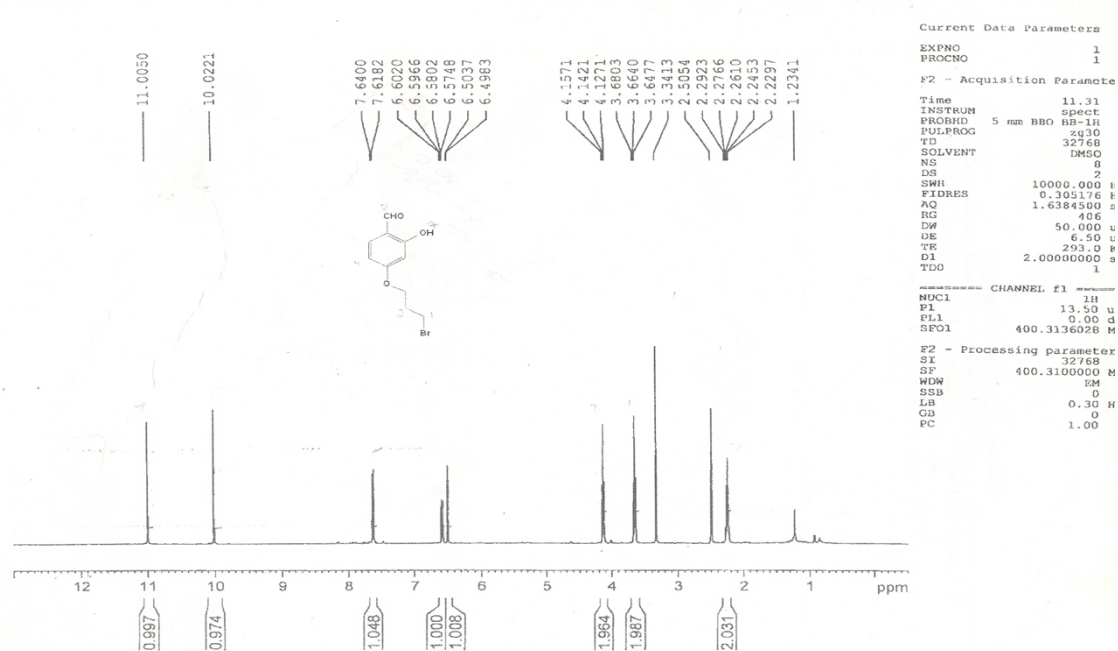


Fig. 5 (a): ¹H NMR spectra of 2

Compound 3:

¹H NMR (400 MHz, DMSO-*d*₆) δ 10.02 (s, 1H), 9.25 (s, 1H), 7.84 (s, 1H), 7.74 (s, 1H), 7.62 (d, *J* = 8.64 Hz, 1H), 6.52 – 6.42 (m, 2H), 4.36 (t, *J* = 6.88 Hz, 2H), 4.10 (t, *J* = 5.88 Hz, 2H), 3.86 (s, 3H), 2.32–2.26 (m, 2H). ESI-MS: 261.2 [M - Br]⁺.

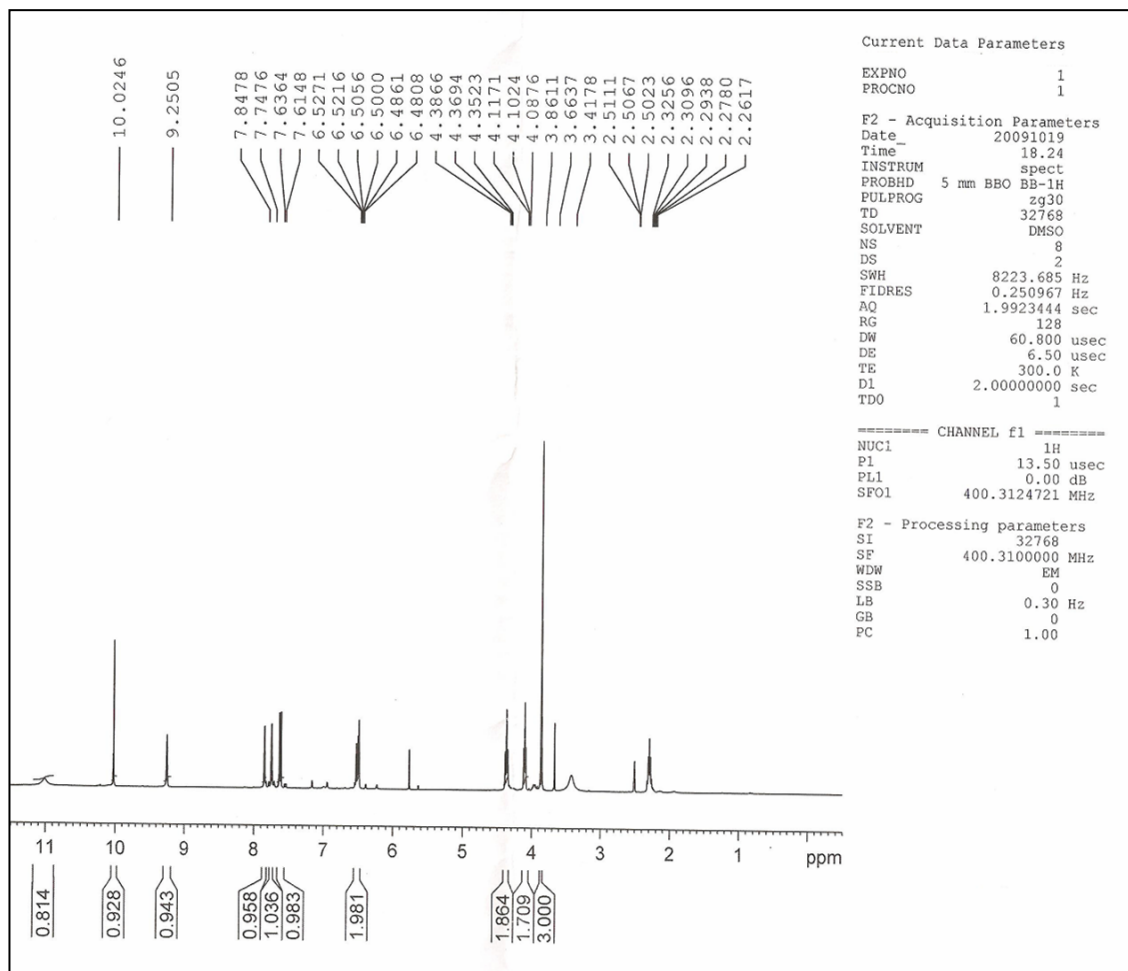


Fig. 5 (b): ^1H NMR spectra of **3**

Compound 4: Yellow apparent solid; yield 90%; mp 81- 83 °C;

^1H NMR (400 MHz, $\text{DMSO-}d_6$) δ 13.77 (s, 1H), 9.48 (s, 1H), 8.79 (s, 1H), 8.20 (t, $J = 1.8$, 1H), 7.90 (t, $J = 1.8$ Hz, 1H), 7.79–7.78 (m, 1H), 7.69 (s, 1H), 7.57–7.48 (m, 3H), 7.29 (d, $J = 7.2$ Hz, 1H), 6.58–6.47 (m, 2H), 4.50 (t, $J = 6.5$ Hz, 2H), 4.15 (t, $J = 5.1$ Hz, 2H), 3.97 (s, 3H), 2.50–2.31 (m, 2H); ^{13}C NMR (126 MHz, $\text{DMSO-}d_6$) δ 163.6, 163.0, 162.9, 148.2, 137.3, 134.7, 129.9, 129.3, 127.0, 124.0, 122.9, 121.6, 114.5, 113.6, 107.5, 101.8, 65.4, 46.7, 36.2, 29.4.

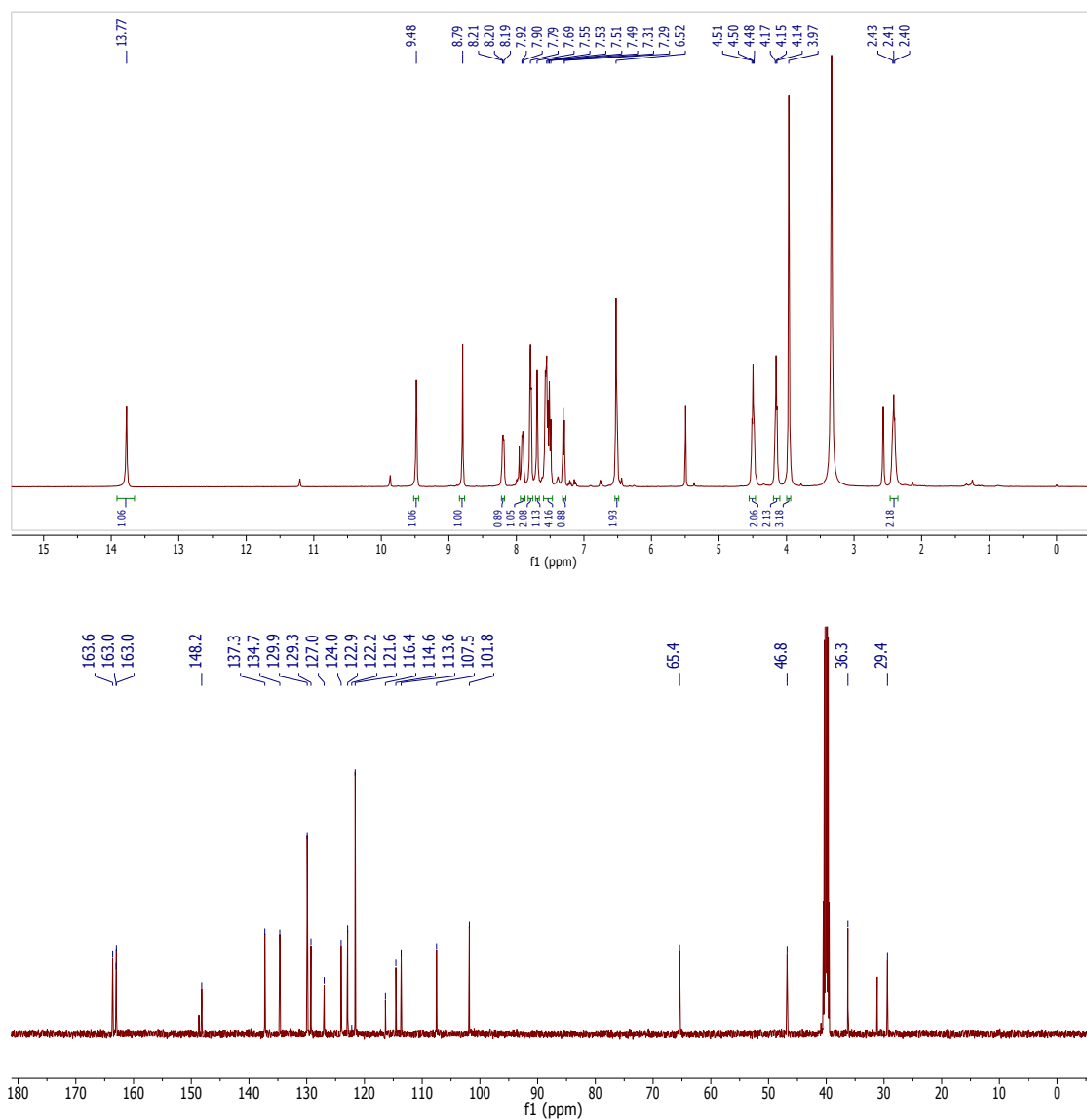


Fig. 5 (c): ¹H and ¹³C NMR spectra of **4**

Compound 5: Orange apparent solid; yield 91%; mp 209-211 °C.

¹H NMR (300 MHz, DMSO-*d*₆) δ 9.16 (s, 2H), 7.93 (s, 2H), 7.80 (t, *J* = 1.8, 2H), 7.73 (t, *J* = 1.8 Hz, 2H), 7.46–7.41 (m, 4H), 7.39–7.36 (m, 3H), 7.35 (s, 2H), 7.32 (d, *J* = 1.4 Hz, 3H), 7.30 (s, 2H), 6.12 (dd, *J* = 8.8, 2.3 Hz, 2H), 4.32 (t, *J* = 6.9 Hz, 4H), 3.89 – 3.84 (m, 10H), 2.29–2.19 (m, 4H). ¹³C NMR (75 MHz, DMSO) δ 166.1, 164.3, 162.5, 149.5, 137.3, 128.8, 128.3, 126.4, 125.3, 124.0, 122.9, 115.4, 111.3, 105.5, 102.2, 98.2, 64.9, 46.9, 36.2, 29.3.

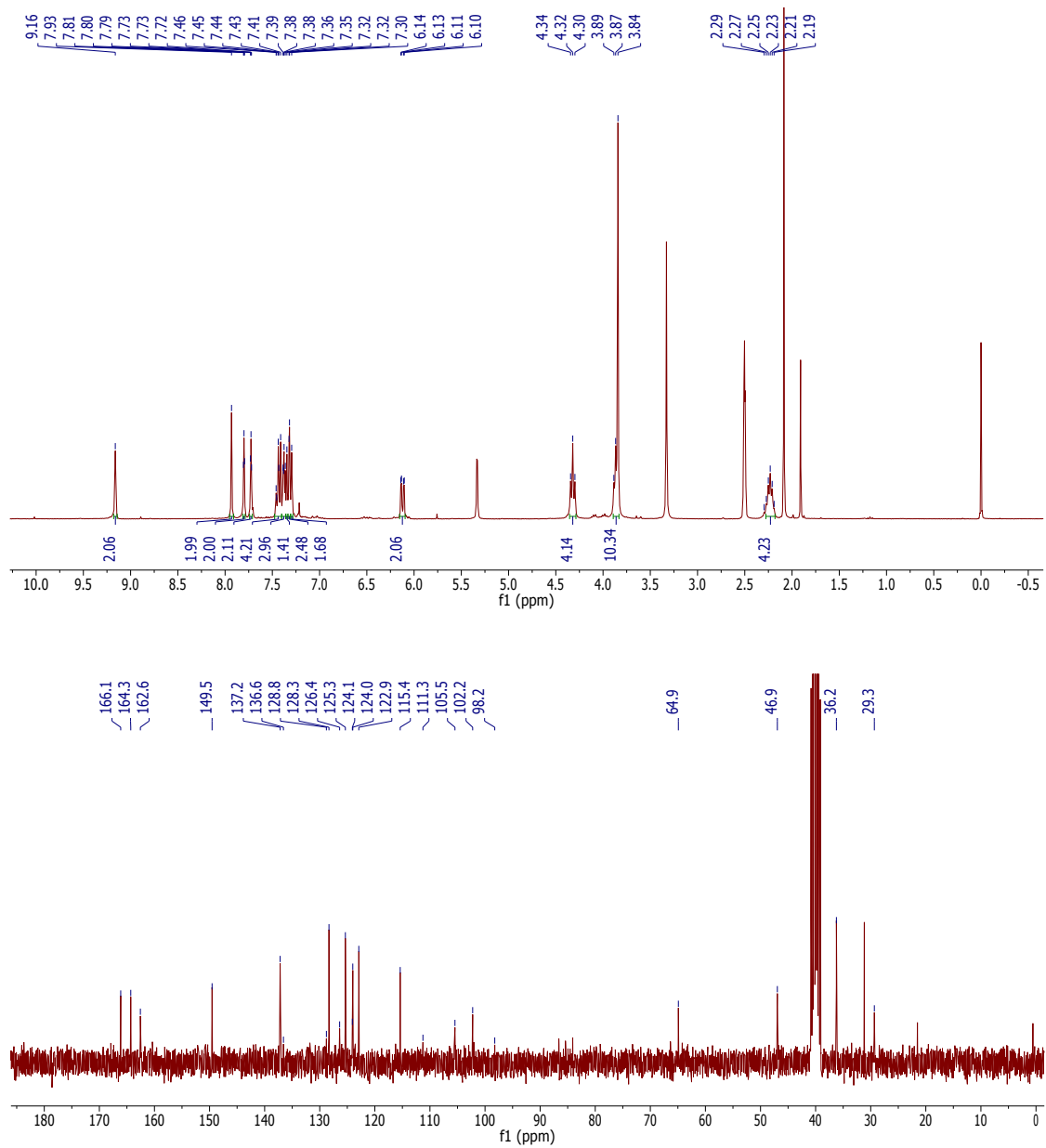


Fig. 6: ^1H and ^{13}C NMR spectra of **5**

1.5 ESI Mass spectra of 2-4 and MALDI-Mass spectra of 5

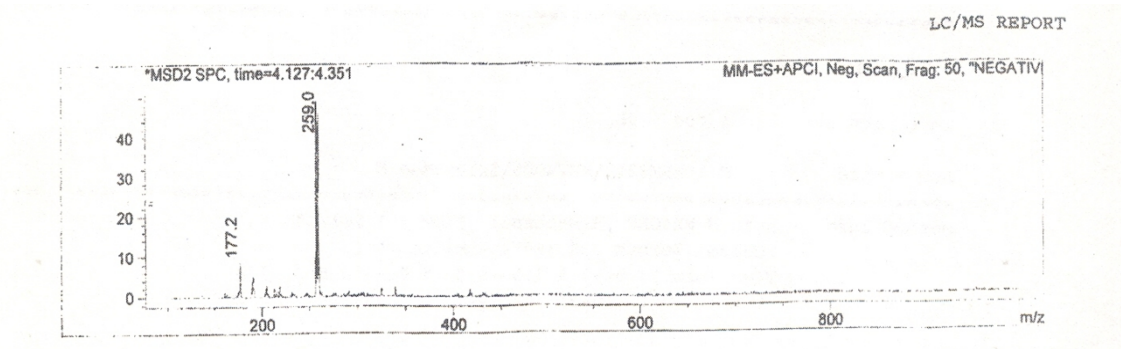


Fig 7 (a): ESI MS of 2

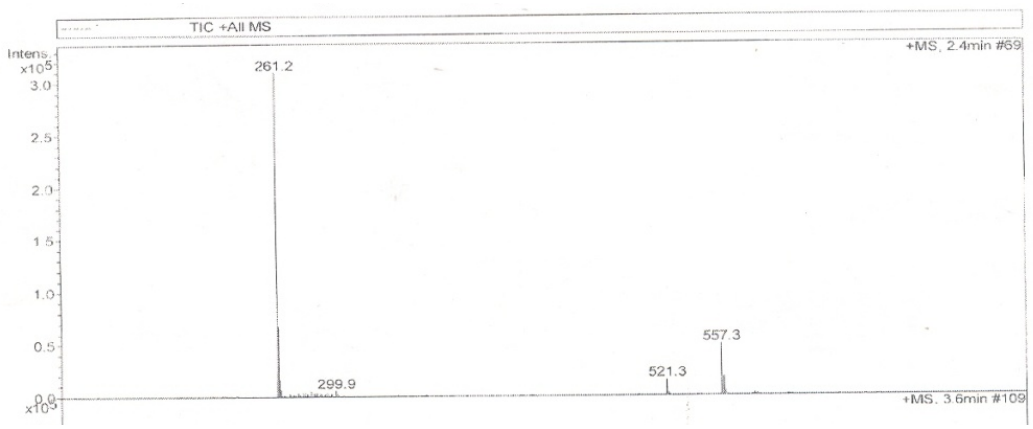
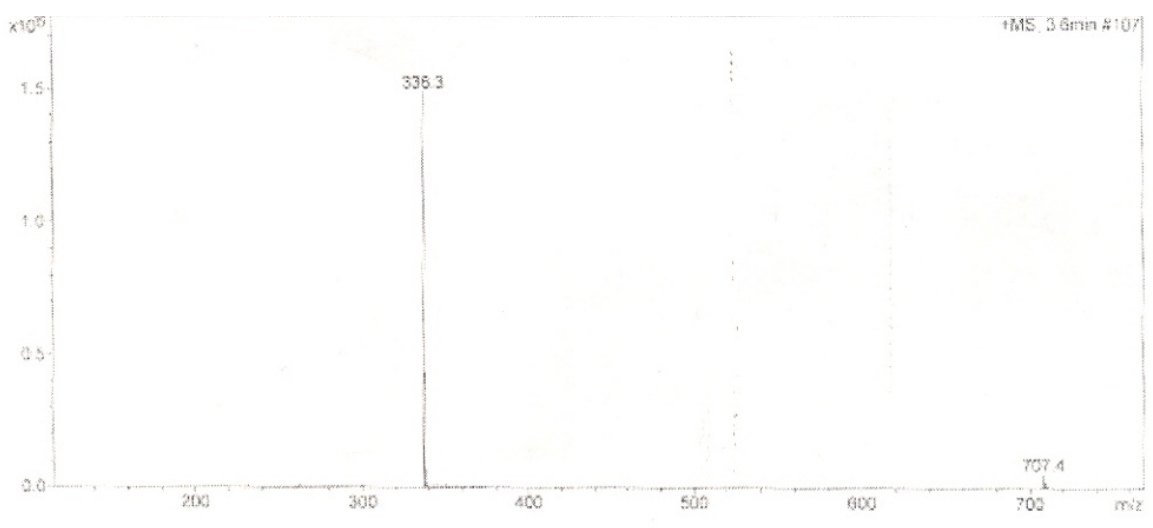


Fig. 7 (b): ESI-MS of 3



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Fig. 7 (c): ESI-MS of 4

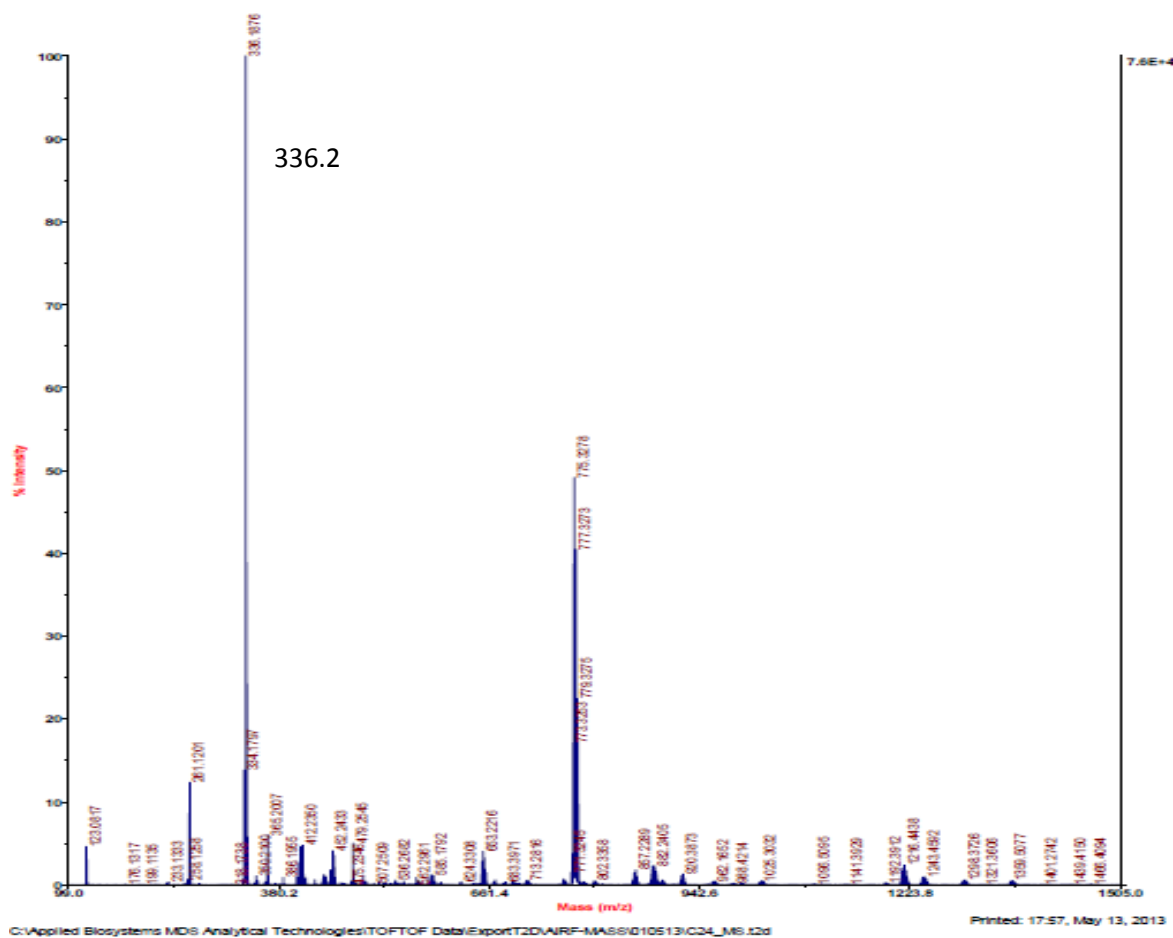


Fig. 8: MALDI-Mass of 5

2. Analysis of reaction products 8 and 10

2.1 ^1H and ^{13}C NMR analysis of the Heck coupling products

(E)-Benzyl cinnamate (8aa'): Colorless liquid; ^1H NMR (400 MHz, CDCl_3) δ 7.78 (d, $J = 16.0$ Hz, 1H), 7.59 – 7.53 (m, 2H), 7.49 – 7.33 (m, 8H), 6.53 (d, $J = 16.0$ Hz, 1H), 5.30 (s, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 166.8, 145.2, 136.10, 134.4, 130.4, 128.9, 128.6, 128.3, 128.3, 128.1, 117.9, 66.4.

(E)-Methyl cinnamate (8ab'): Colorless liquid²; ^1H NMR (400 MHz, CDCl_3) δ 7.72 (d, $J = 16.0$ Hz, 1H), 7.59 – 7.52 (m, 2H), 7.45 – 7.37 (m, 3H), 6.47 (d, $J = 16.0$ Hz, 1H), 3.83 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 167.4, 144.9, 134.4, 130.3, 128.9, 128.1, 117.8, 51.7.

(E)-1,2-Diphenylethene (8ac'): Colorless solid; mp 122 – 123 $^\circ\text{C}$ (Lit. mp 120 – 122 $^\circ\text{C}$)¹; ^1H NMR (300 MHz, CDCl_3) δ 7.55 (dd, $J = 8.2, 1.2$ Hz, 4H), 7.39 – 7.34 (m, 4H), 7.28 – 7.23 (m, 2H), 7.11 (s, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 137.4, 128.7, 128.7, 127.7, 126.5.

(E)-1-Methyl-4-styrylbenzene (8ad'): Colorless solid, mp 114 – 116 °C (Lit. mp 119 – 122 °C)²; ¹H NMR (400 MHz, CDCl₃) δ 7.59 – 7.54 (m, 2H), 7.48 (d, *J* = 8.1 Hz, 2H), 7.44 – 7.38 (m, 2H), 7.34 – 7.28 (m, 1H), 7.23 (d, *J* = 7.9 Hz, 2H), 7.14 (d, *J* = 2.6 Hz, 2H), 2.42 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 137.6, 134.6, 129.5, 128.7, 128.7, 127.7, 127.5, 126.5, 126.5, 21.3.

(E)-1-Chloro-4-styrylbenzene (8ae'): Colorless solid, mp 128 – 129 °C (Lit. mp 126 – 128 °C)³; ¹H NMR (300 MHz, CDCl₃) δ 7.52 (dd, *J* = 8.2, 1.1 Hz, 2H), 7.44 (d, *J* = 8.2 Hz, 2H), 7.39 – 7.29 (m, 4H) 7.26 (d, *J* = 4.5 Hz, 1H), 7.07 (d, *J* = 2.8 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 137.0, 135.9, 133.2, 129.3, 128.9, 128.8, 127.9, 127.8, 127.4, 126.6.

(E)-1-Bromo-4-styrylbenzene (8af'): Colorless solid, mp 136 – 138 °C (Lit. mp 136.5 – 139)³; ¹H NMR (400 MHz, CDCl₃) δ 7.56 – 7.48 (m, 4H), 7.43 – 7.36 (m, 4H), 7.31 (dt, *J* = 4.1, 1.7 Hz, 1H), 7.13 (d, *J* = 16.3 Hz, 1H), 7.06 (d, *J* = 16.3 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 136.9, 136.3, 131.8, 129.4, 128.7, 128.0, 127.9, 127.3, 126.6, 121.3.

(E)-Benzyl 3-(4-methylphenyl)acrylate (8ba'): Yellow crystalline solid, mp 87 – 88 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.73 (d, *J* = 16.0 Hz, 1H), 7.46 – 7.35 (m, 7H), 7.21 (d, *J* = 8.0 Hz, 2H), 6.47 (d, *J* = 16.0 Hz, 1H), 2.40 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 167.0, 145.2, 140.8, 136.2, 131.7, 129.6, 128.6, 128.3, 128.2, 128.1, 116.8, 66.3, 21.5.

(E)-Benzyl 3-(4-nitrophenyl)acrylate (8ca'): Pale yellow solid, mp 110 – 112 °C; ¹H NMR (500 MHz, CDCl₃) δ 8.26 (d, *J* = 8.6 Hz, 2H), 7.77 (d, *J* = 16.0 Hz, 1H), 7.69 (d, *J* = 8.6 Hz, 2H), 7.49 – 7.27 (m, 5H), 6.63 (d, *J* = 16.0 Hz, 1H), 5.30 (s, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 165.8, 148.5, 142.2, 140.5, 135.6, 128.7, 128.5, 128.4, 124.4, 124.2, 122.2, 66.9.

1-(4-Nitrostyryl)benzene (8cc'): Yellow solid, mp 151 – 152 °C (Lit. mp 155 °C)¹; ¹H NMR (500 MHz, CDCl₃) δ 8.23 (d, *J* = 8.6 Hz, 2H), 7.64 (d, *J* = 8.5 Hz, 2H), 7.58 (d, *J* = 7.5 Hz, 2H), 7.43 (t, *J* = 7.4 Hz, 2H), 7.37 (t, *J* = 7.2 Hz, 1H), 7.32 – 7.24 (m, 1H), 7.16 (d, *J* = 16.3 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 146.8, 143.9, 136.2, 133.3, 128.9, 128.9, 127.0, 126.9, 126.3, 124.2.

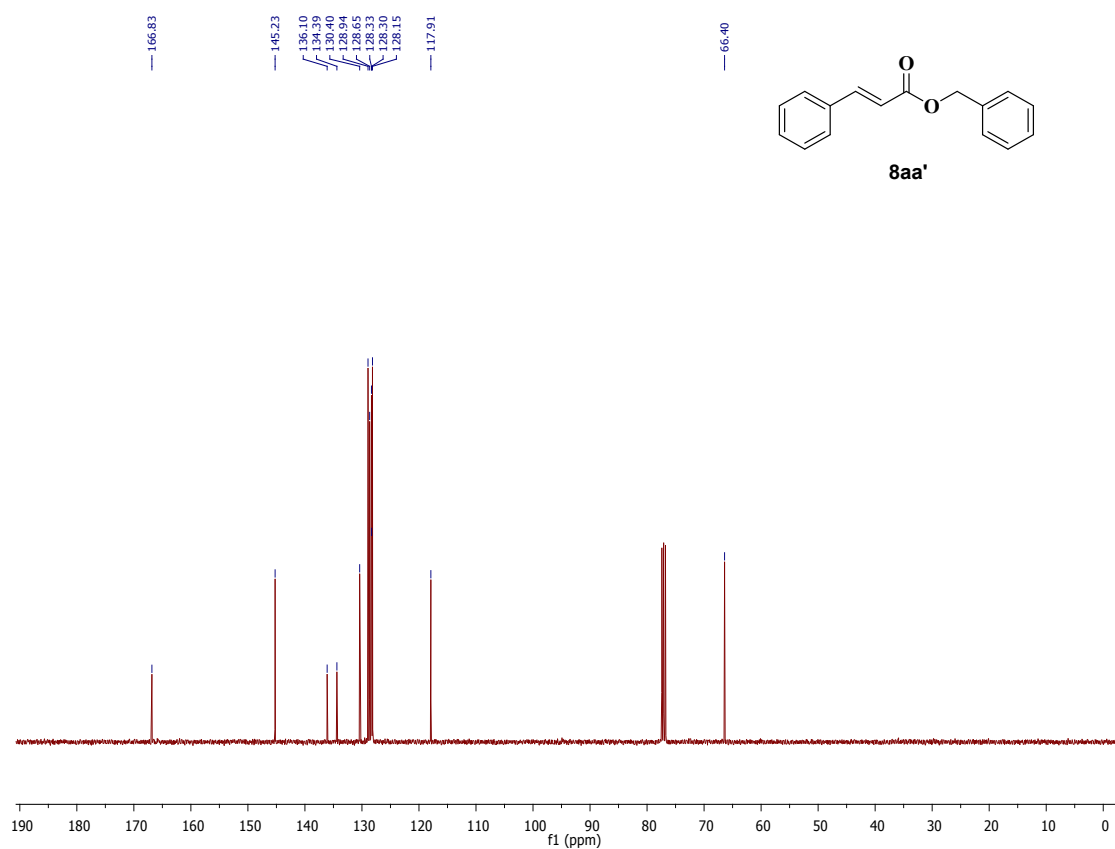
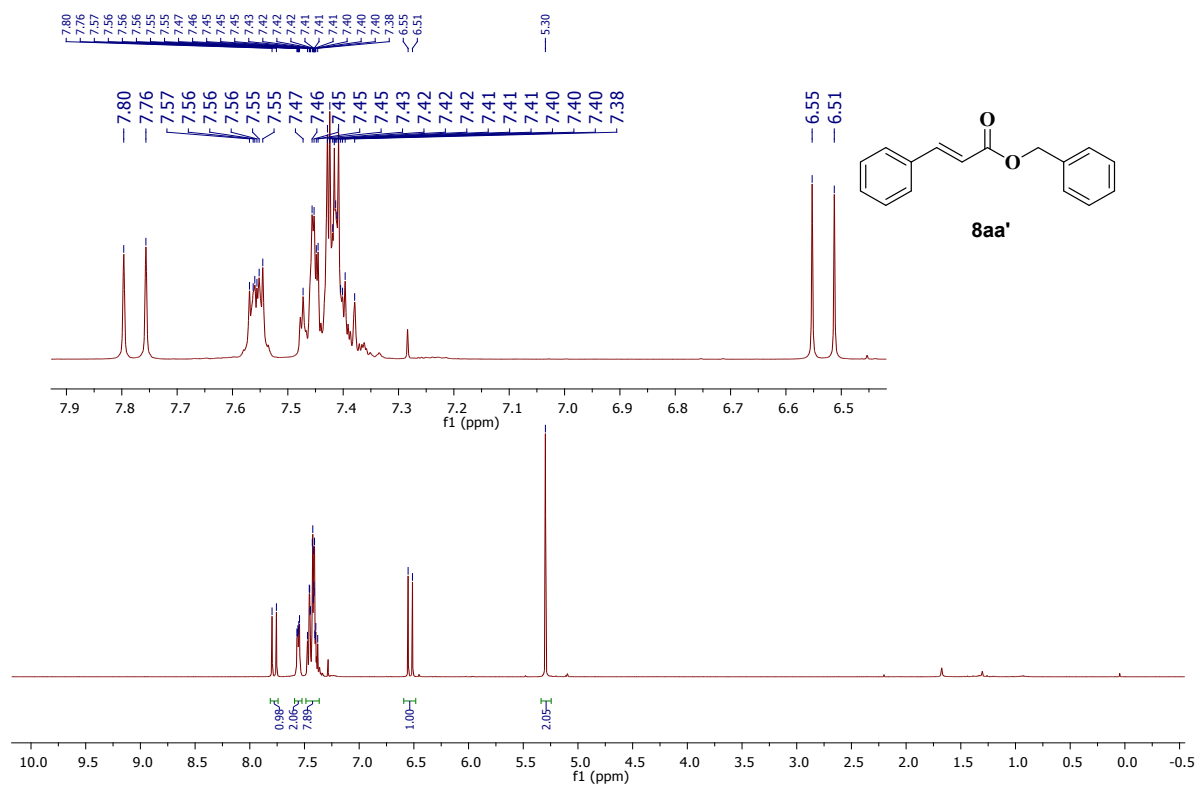
1-(4-Nitrostyryl)-4-methylbenzene (8cd'): Yellow solid, mp 144 – 146 °C; ¹H NMR (500 MHz, CDCl₃) δ 8.23 (d, *J* = 8.5 Hz, 2H), 7.63 (d, *J* = 8.5 Hz, 2H), 7.48 (d, *J* = 7.6 Hz, 2H), 7.29 – 7.23 (m, 3H), 7.12 (d, *J* = 16.3 Hz, 1H), 2.41 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 146.6, 144.1, 139.0, 133.4, 133.3, 129.6, 127.0, 126.7, 125.3, 124.1, 21.4.

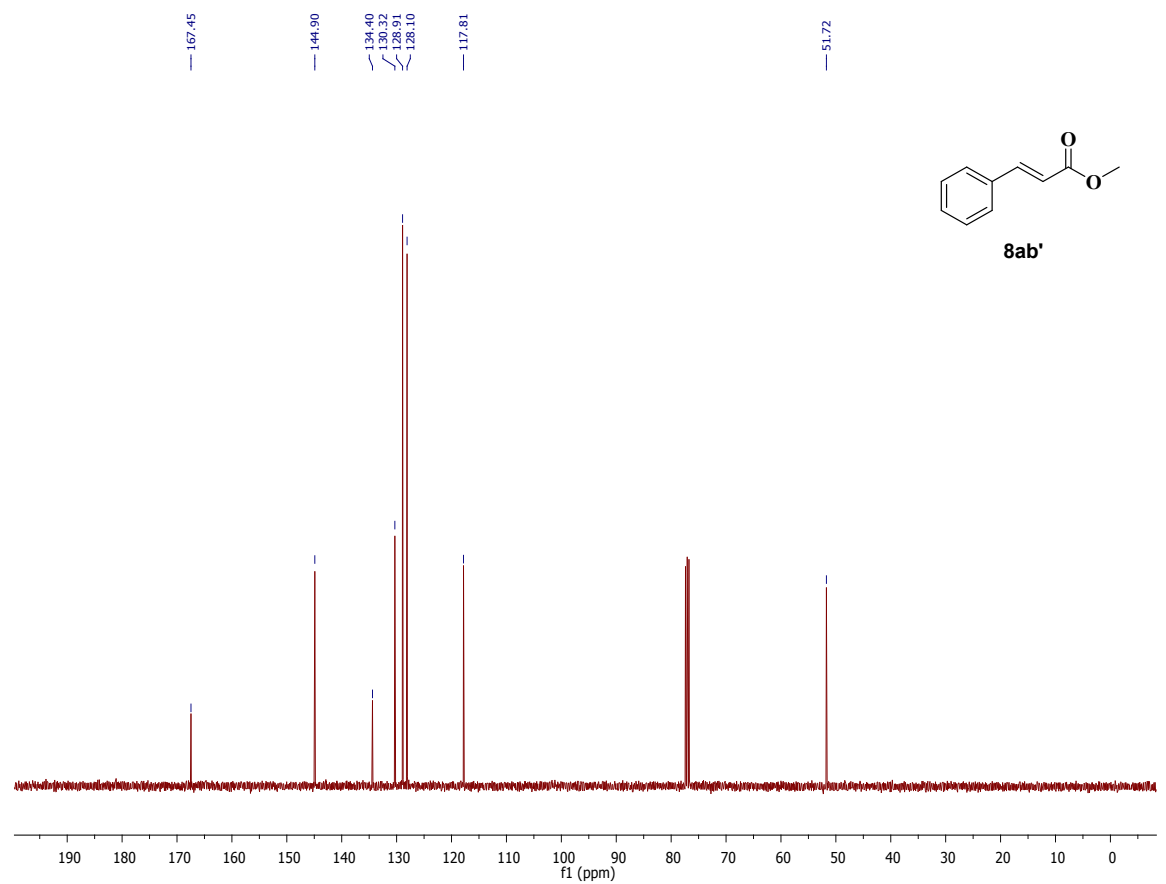
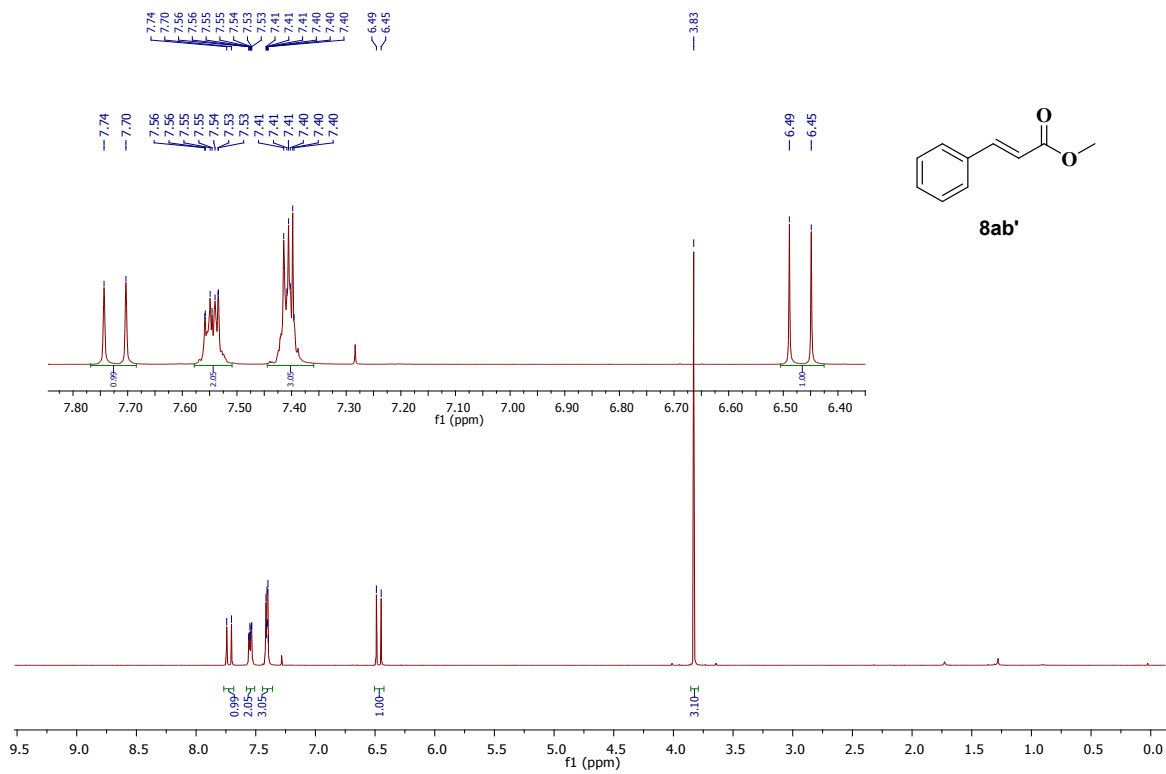
1-(4-Nitrostyryl)-4-chlorobenzene (8ce'): Yellow solid, mp 187 – 188 °C; ¹H NMR (500 MHz, CDCl₃) δ 8.25 (d, *J* = 8.6 Hz, 2H), 7.65 (d, *J* = 8.6 Hz, 2H), 7.50 (d, *J* = 8.3 Hz, 2H), 7.39 (d, *J* = 8.3 Hz, 2H), 7.30 – 7.21 (m, 1H), 7.14 (d, *J* = 16.3 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 146.9, 143.5, 134.7, 134.6, 131.9, 129.1, 128.2, 126.9, 126.9, 124.2.

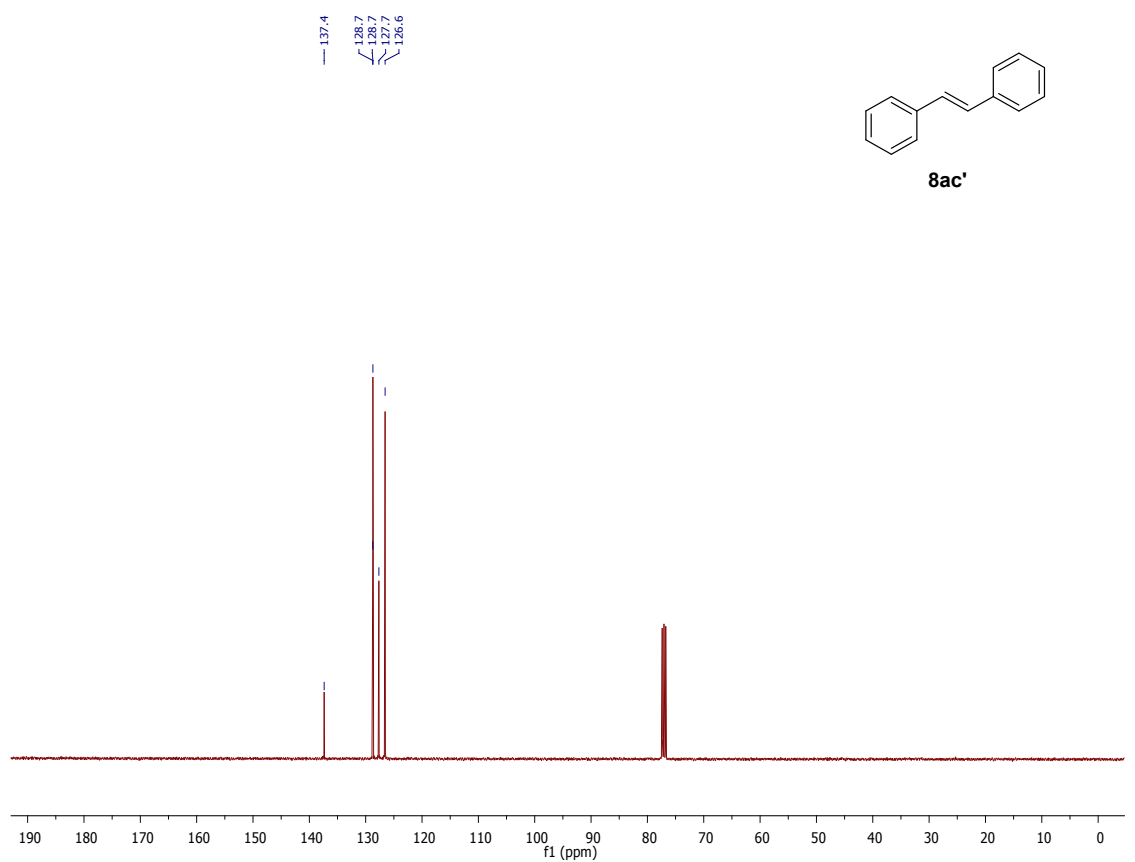
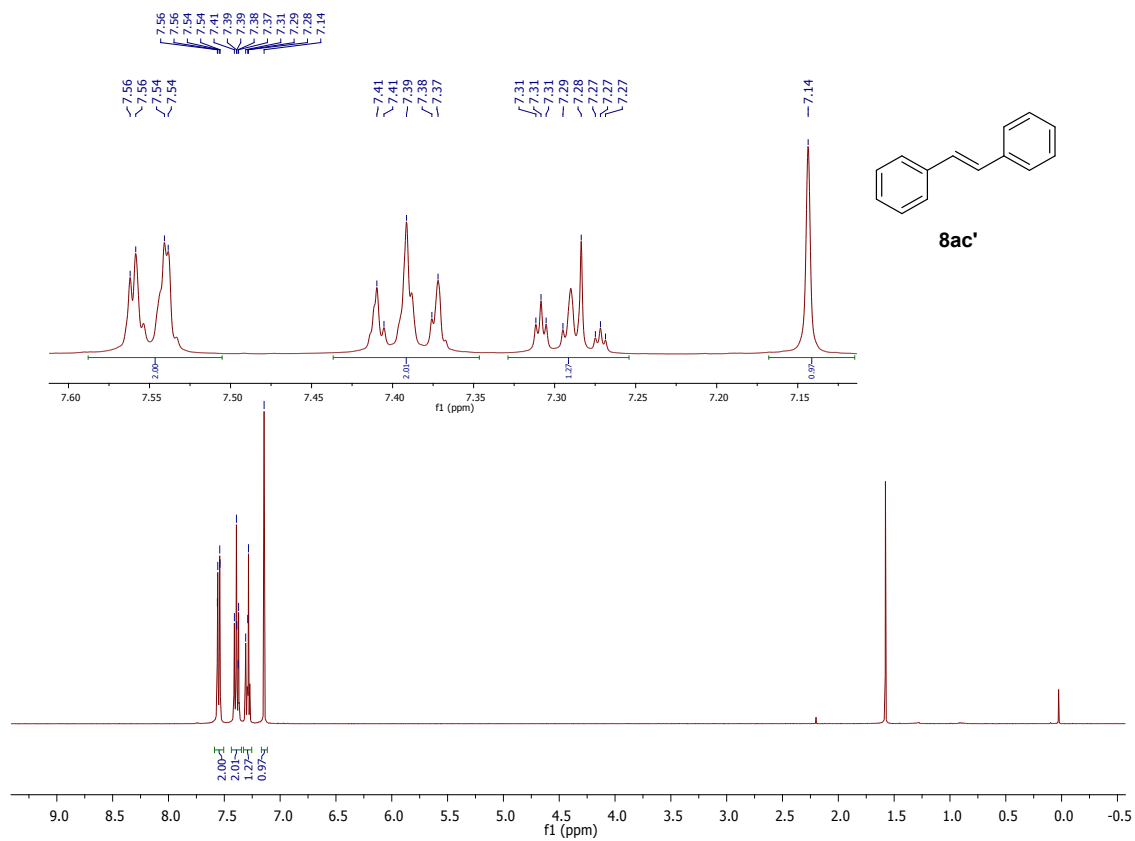
(E)-Benzyl 3-(4-methoxyphenyl)acrylate (8da'): Colorless liquid; ¹H NMR (400 MHz, CDCl₃) δ 7.73 (d, *J* = 16.0 Hz, 1H), 7.53 – 7.47 (m, 2H), 7.47 – 7.36 (m, 5H), 6.93 (d, *J* = 8.8 Hz, 2H), 6.40 (d, *J* = 16.0 Hz, 1H), 5.28 (s, 2H), 3.86 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 167.1, 161.4, 144.9, 136.2, 129.8, 128.6, 128.3, 128.2, 127.1, 115.3, 114.3, 66.2, 55.4.

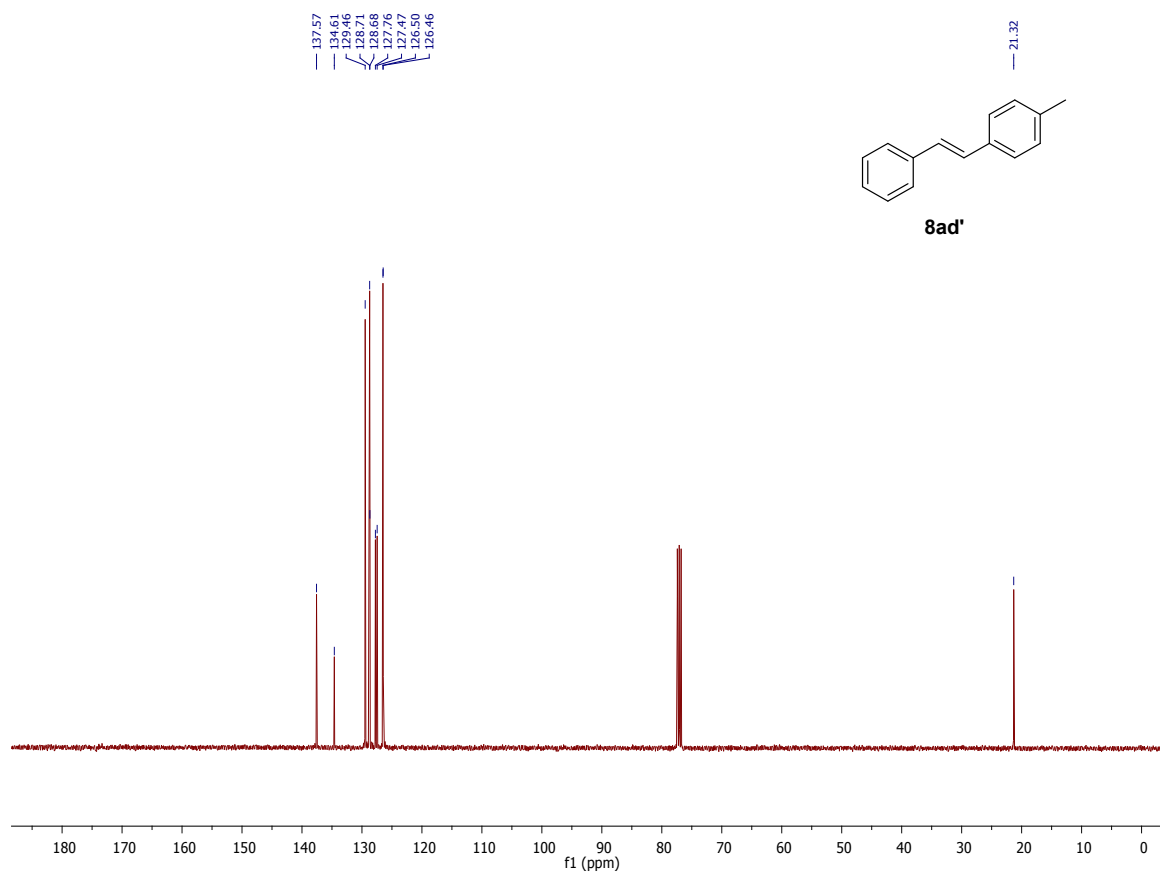
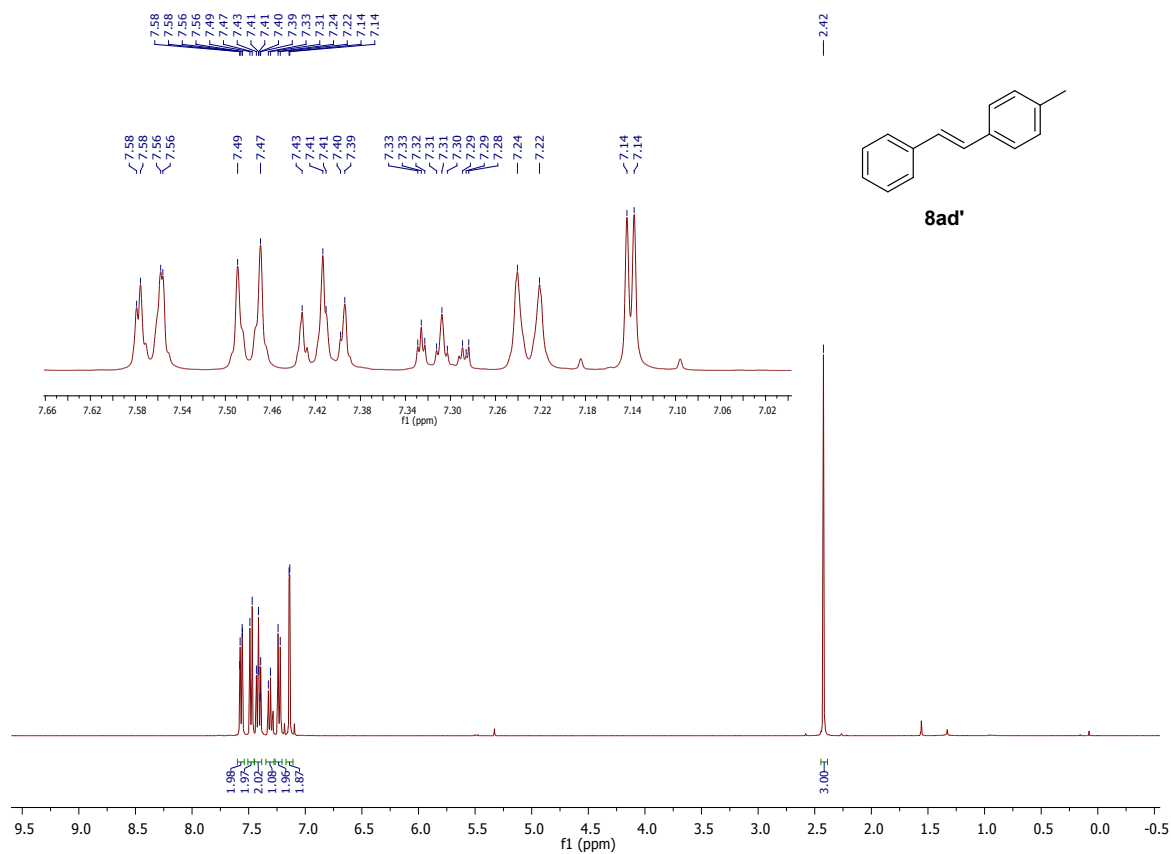
(E)-Benzyl 3-(thiophen-2-yl)acrylate (8ea'): Yellow solid, mp 46 – 47 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.86 (d, *J* = 15.7 Hz, 1H), 7.47 – 7.35 (m, 6H), 7.30 – 7.24 (m, 1H), 7.08 (dd, *J* = 5.1, 3.6 Hz, 1H), 6.32 (d, *J* = 15.7 Hz, 1H), 5.27 (s, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 166.6, 139.5, 137.6, 136.1, 131.1, 128.6, 128.6, 128.3, 128.3, 128.1, 116.6, 66.4.

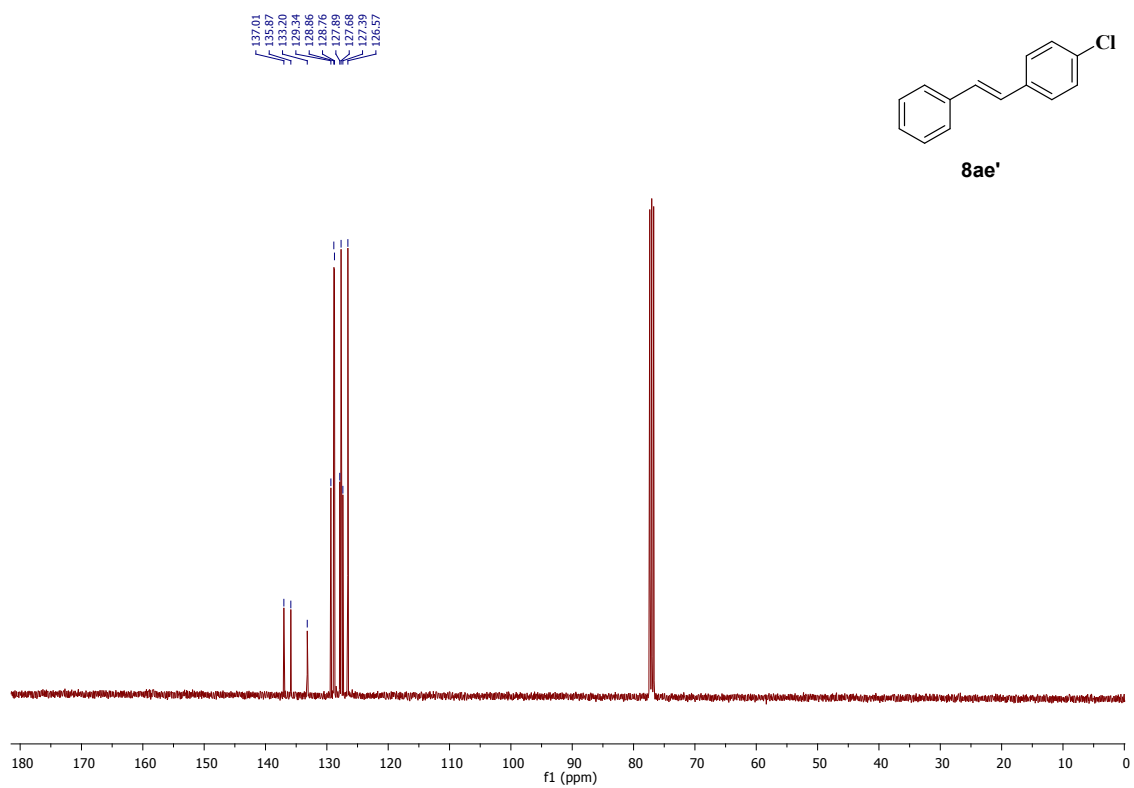
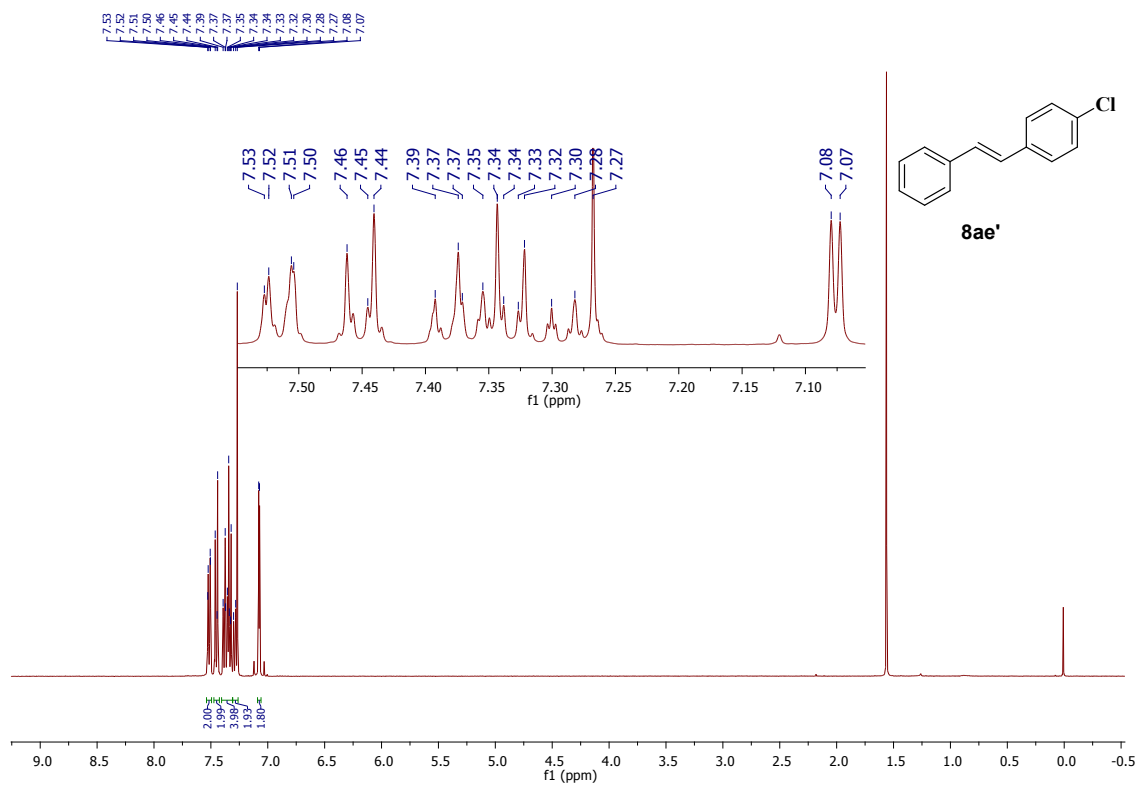
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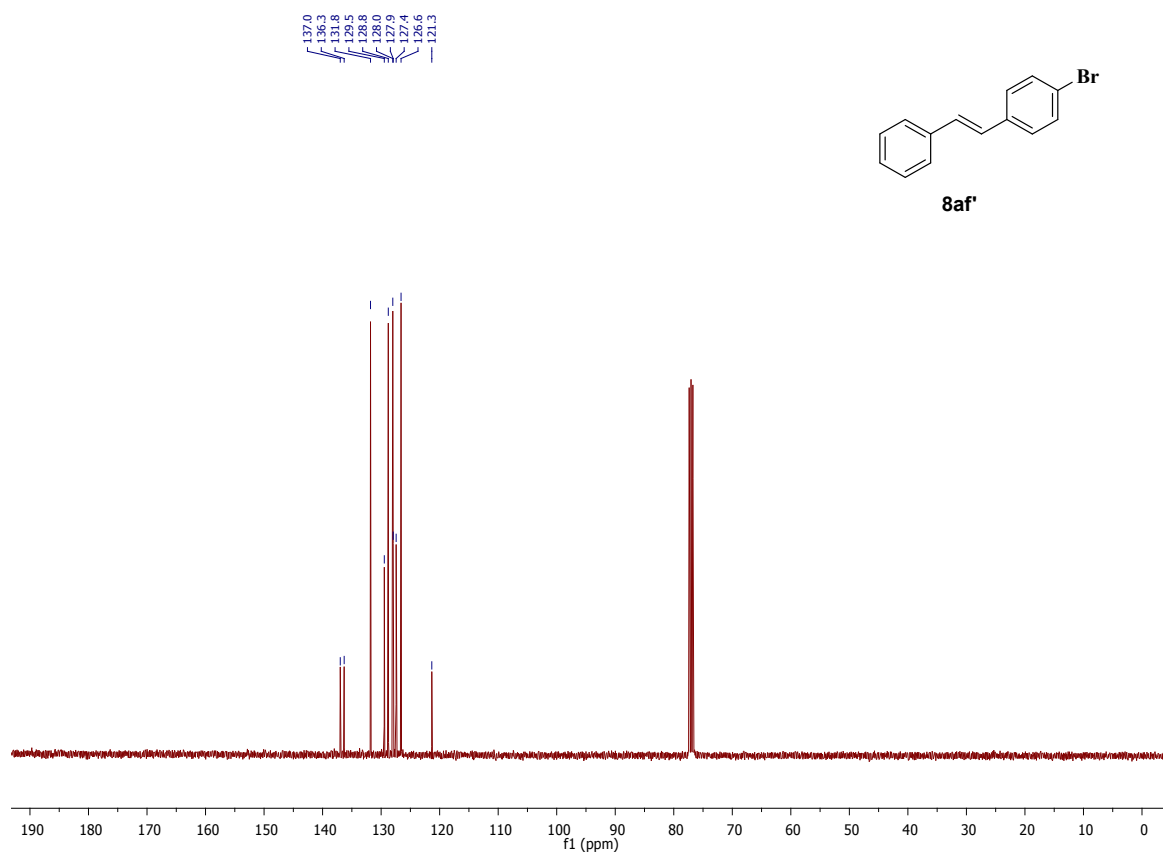
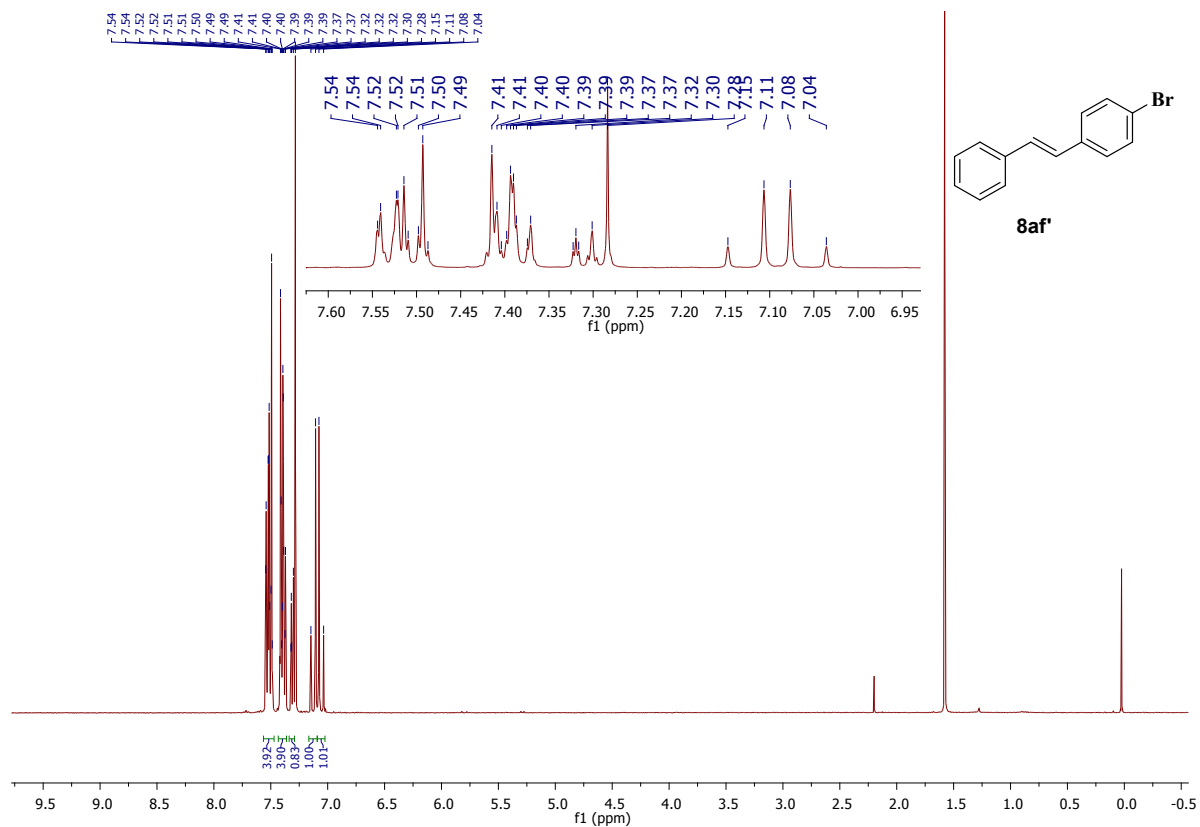


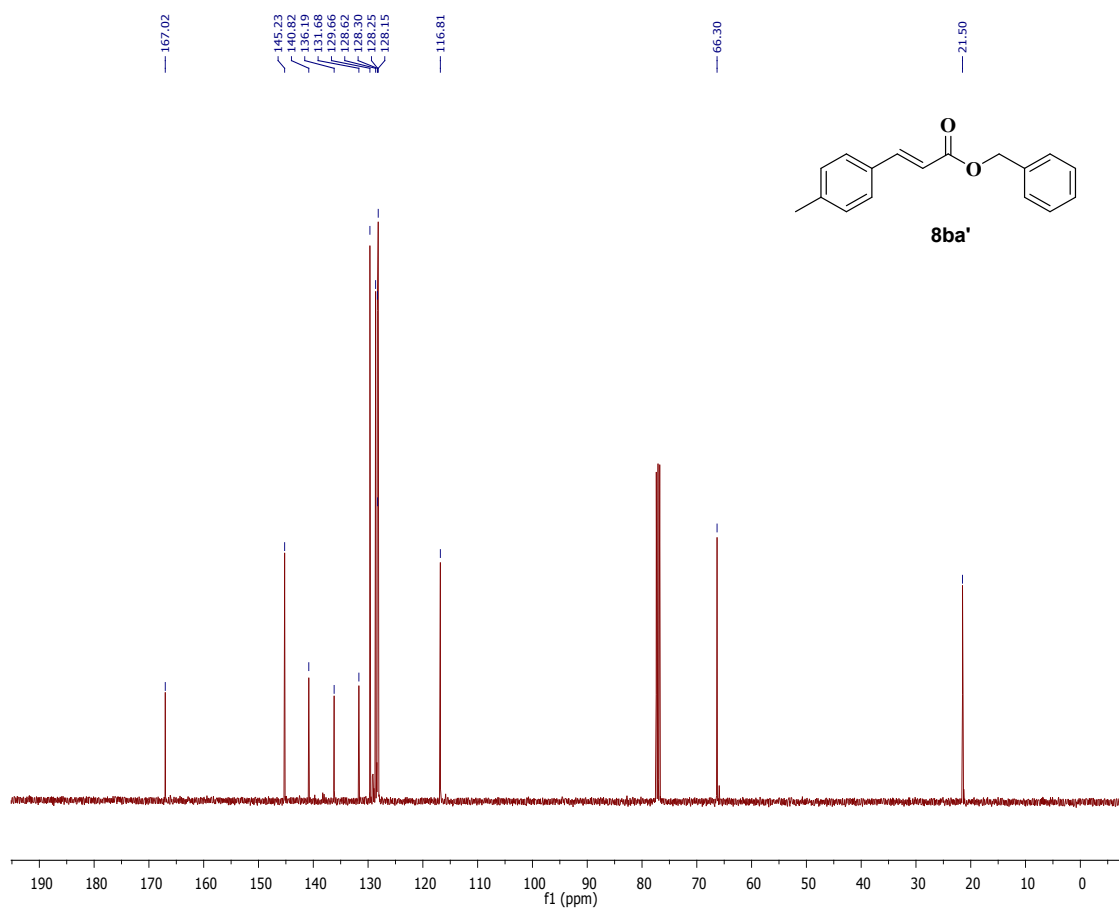
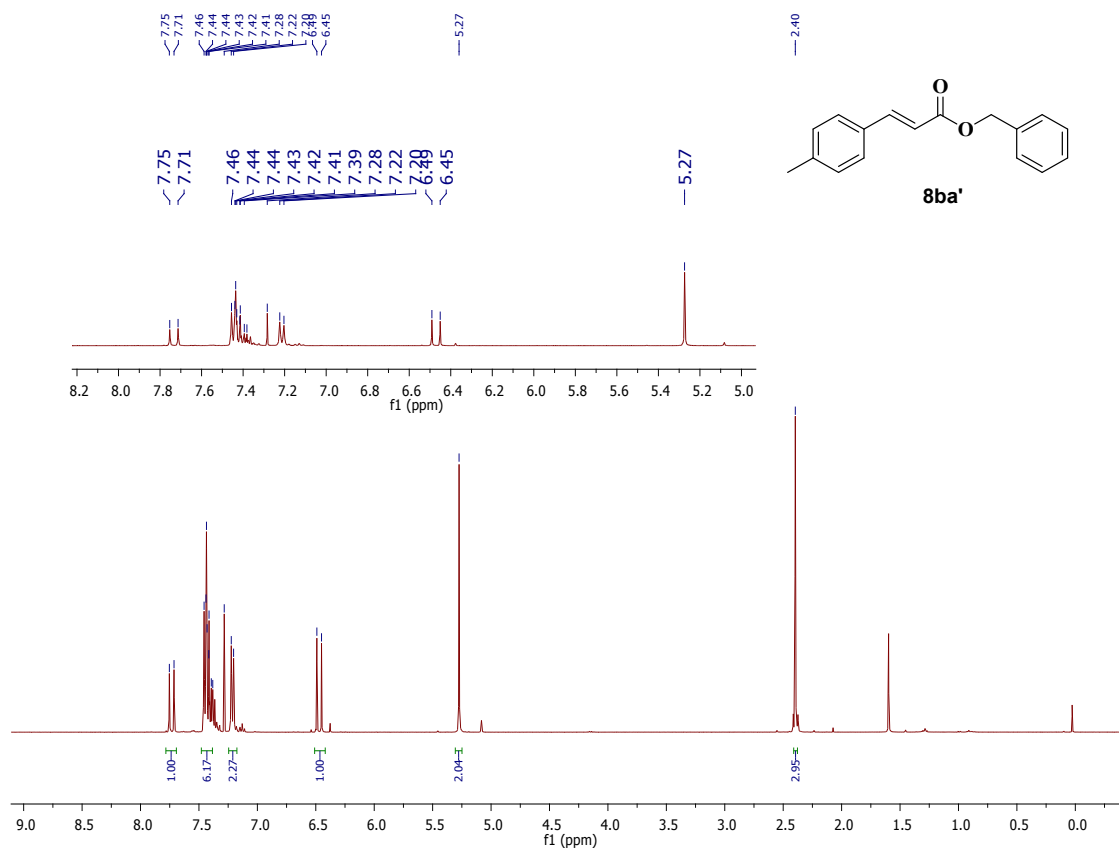


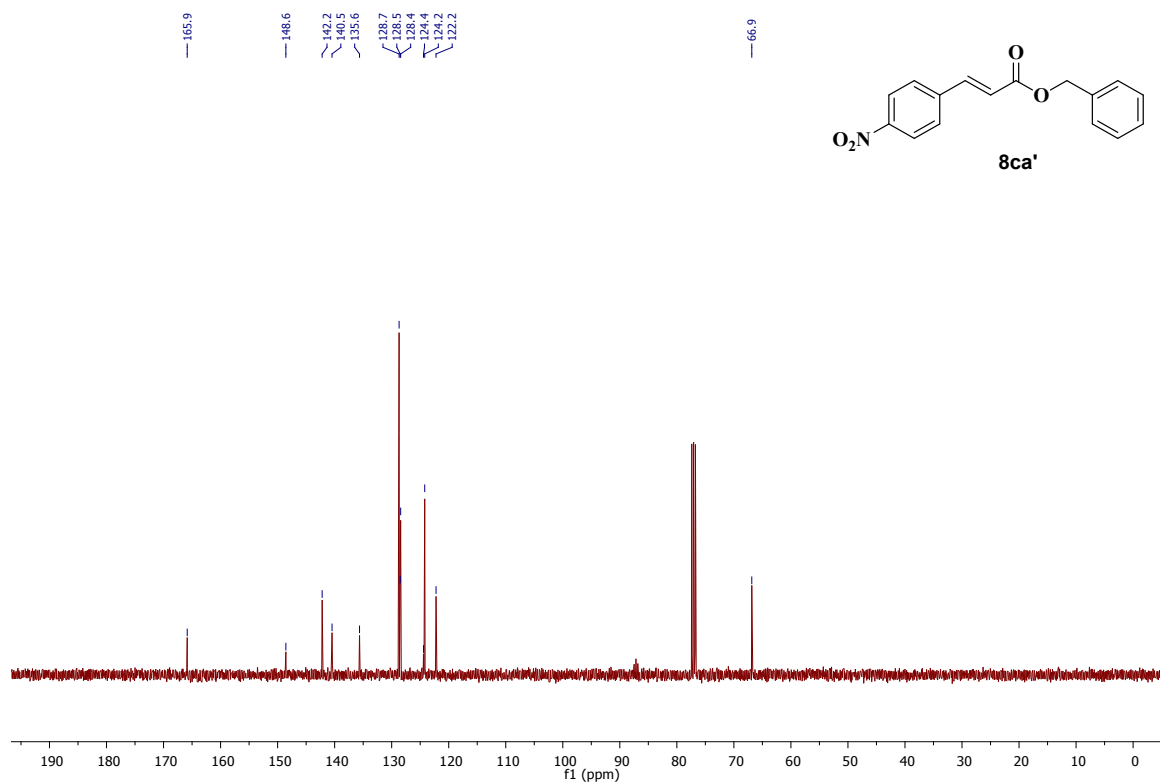
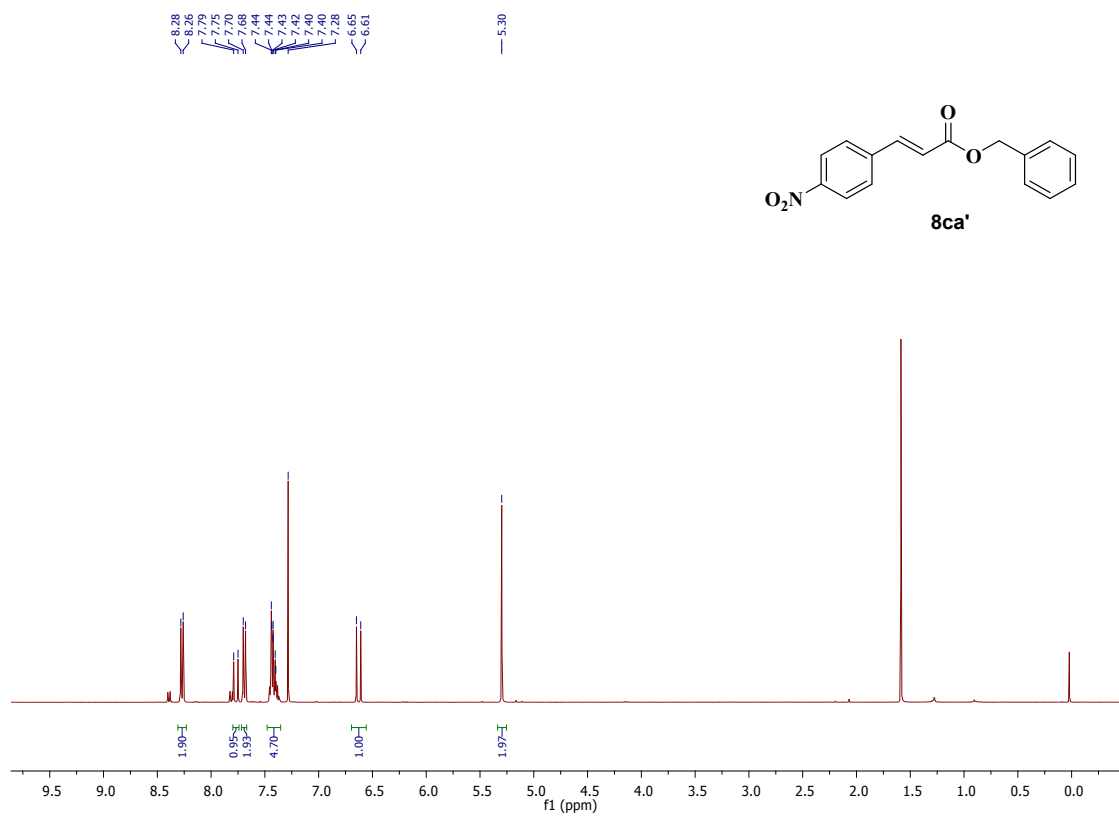


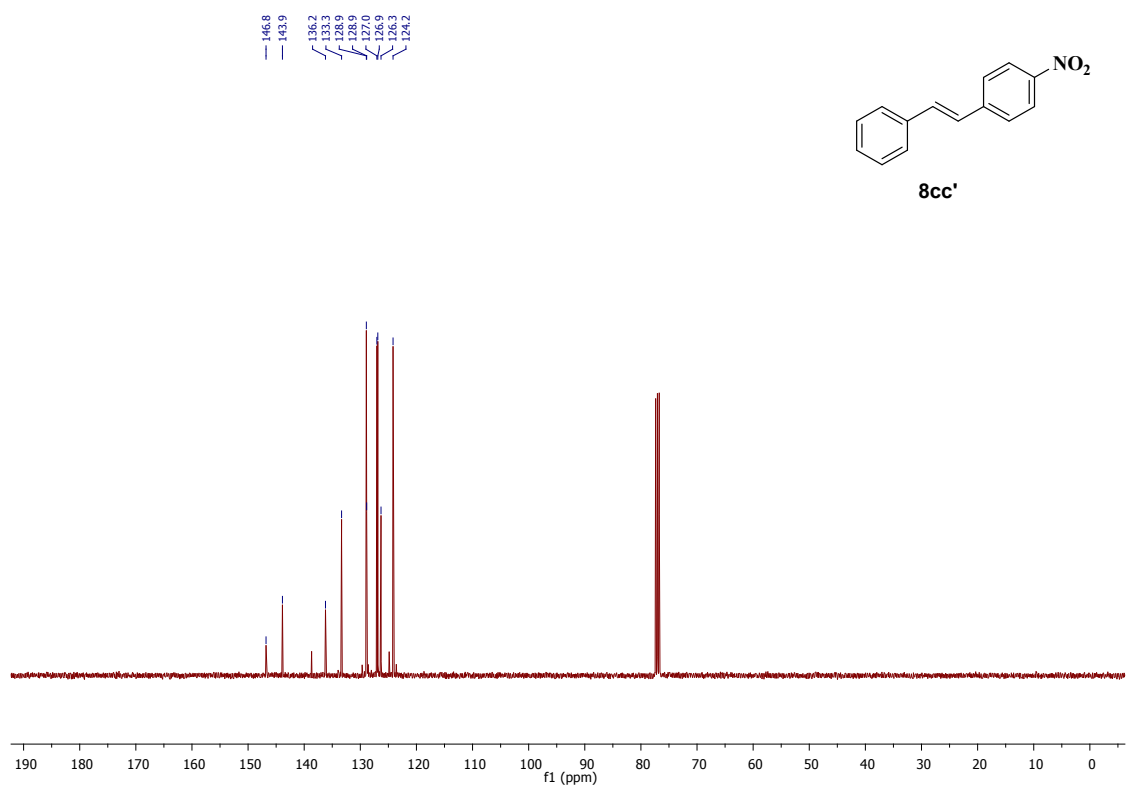
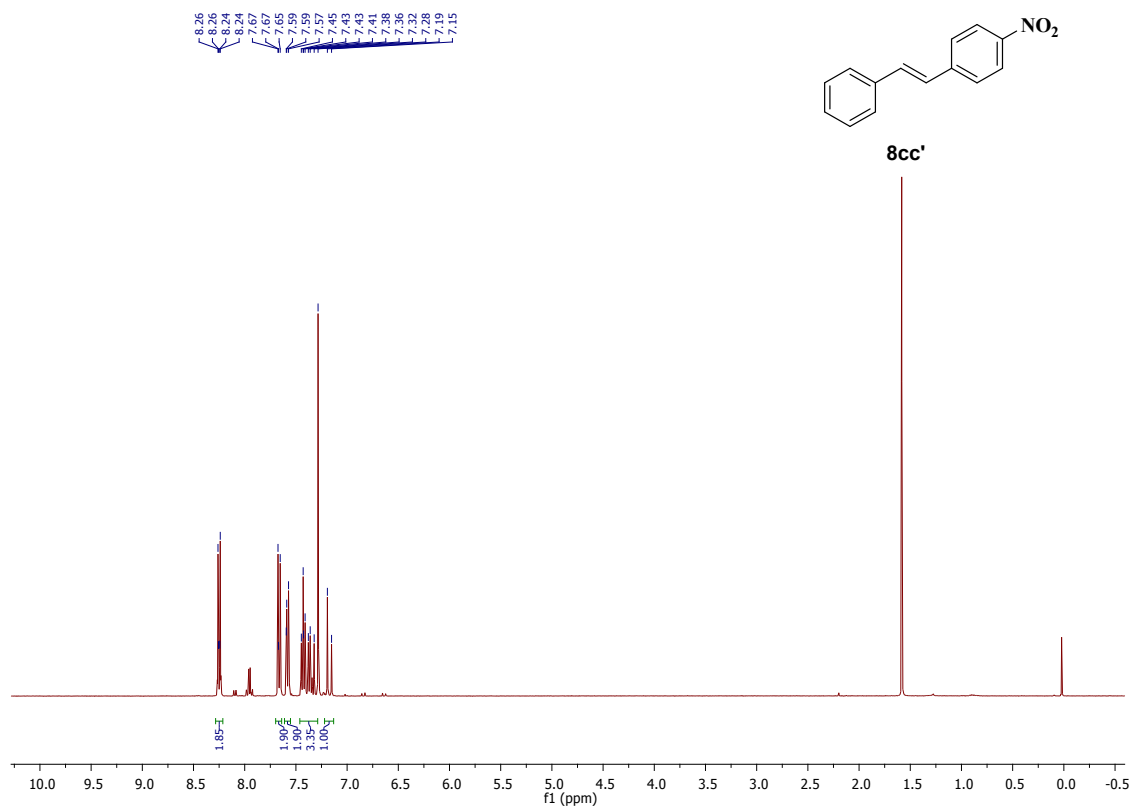


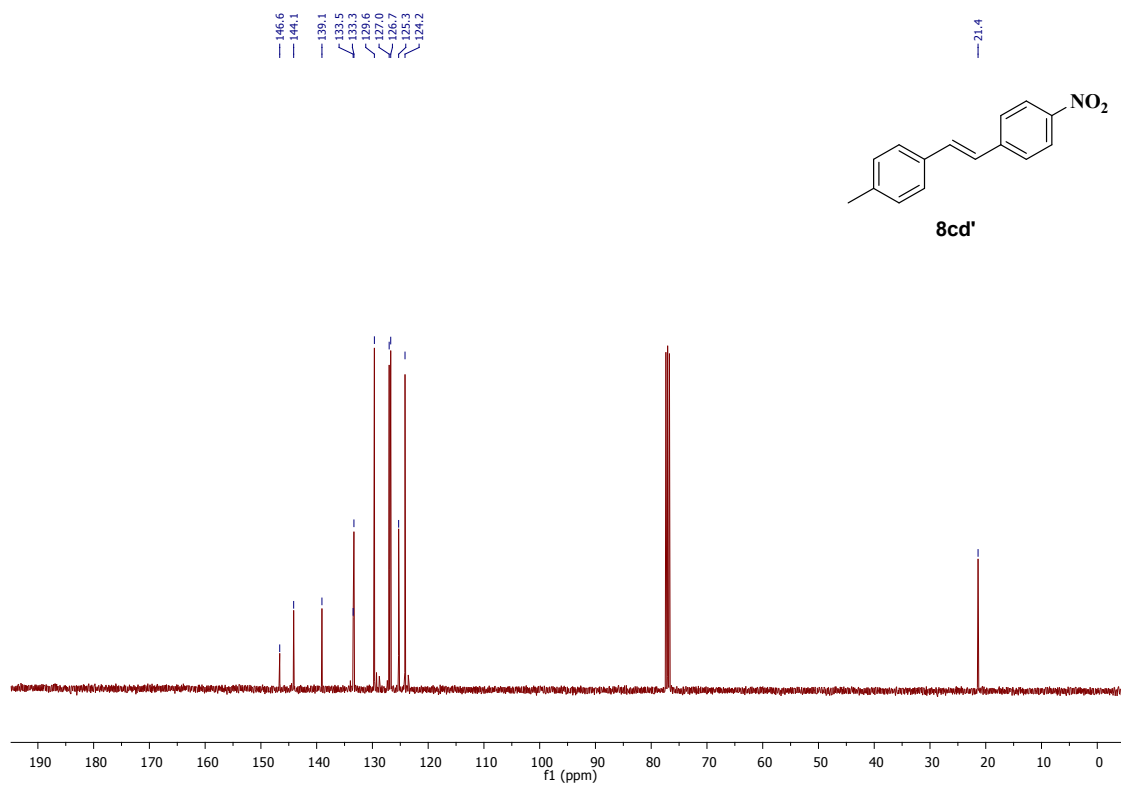
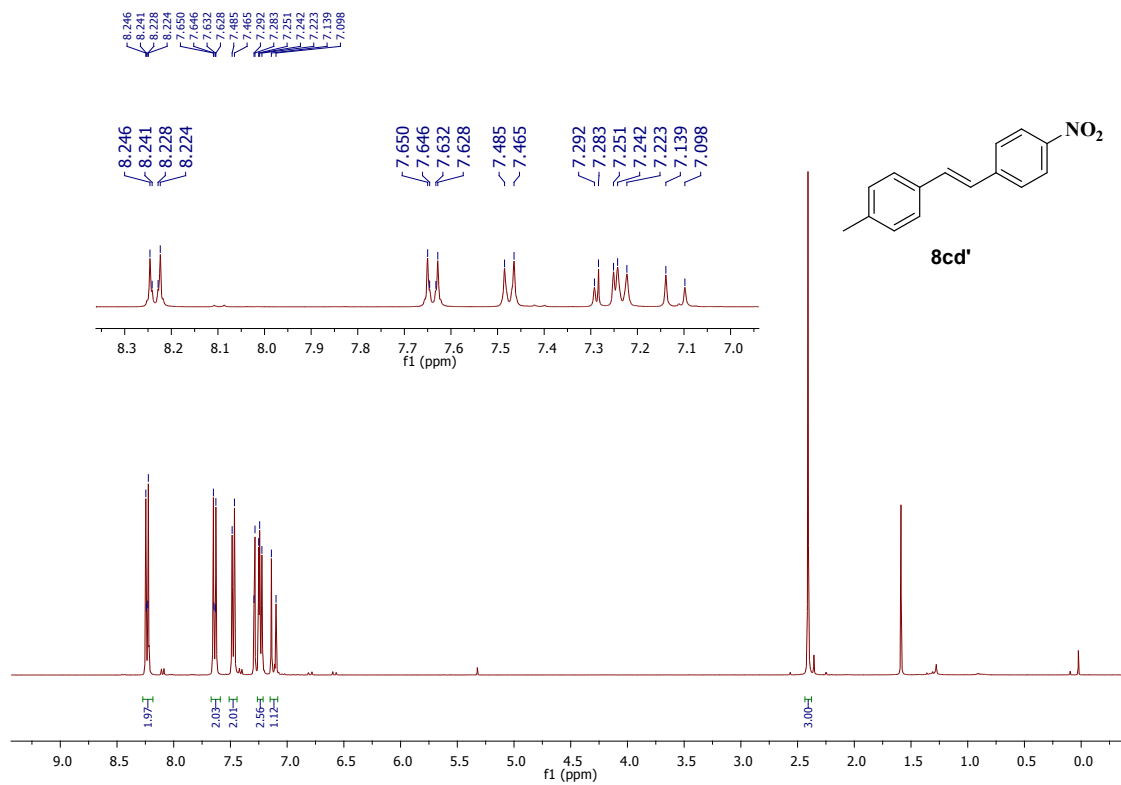


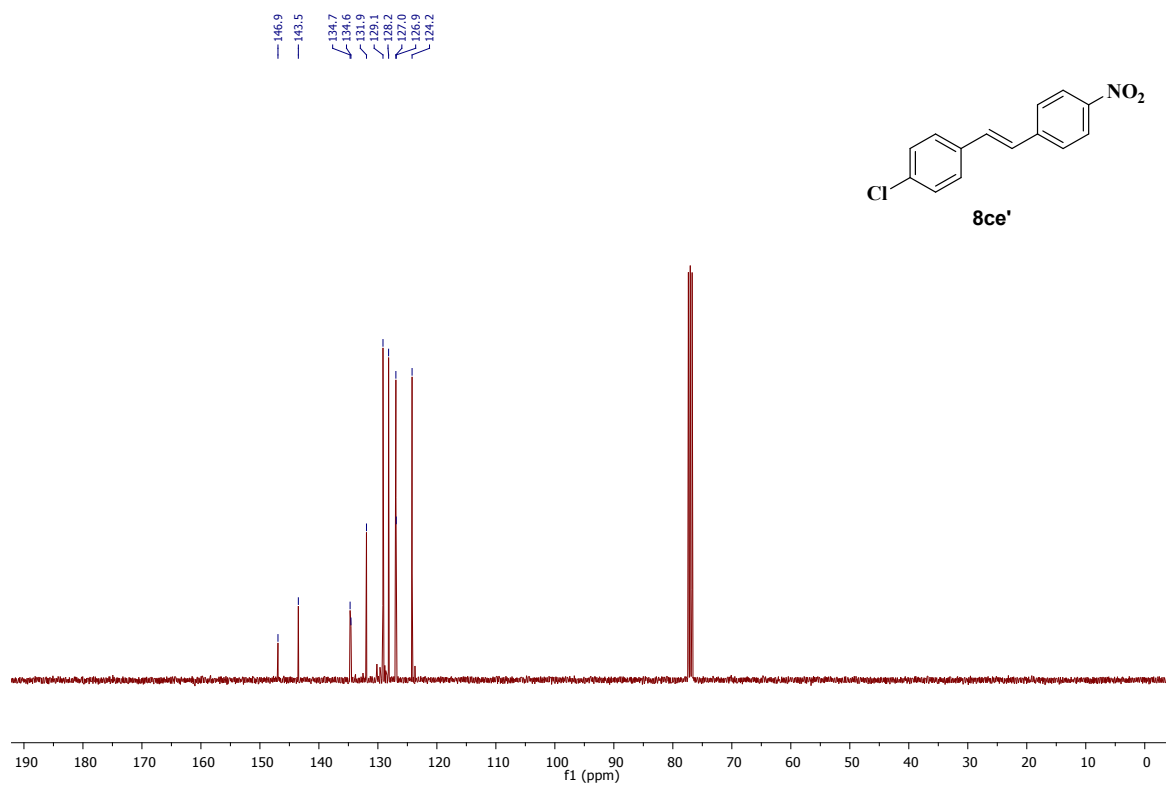
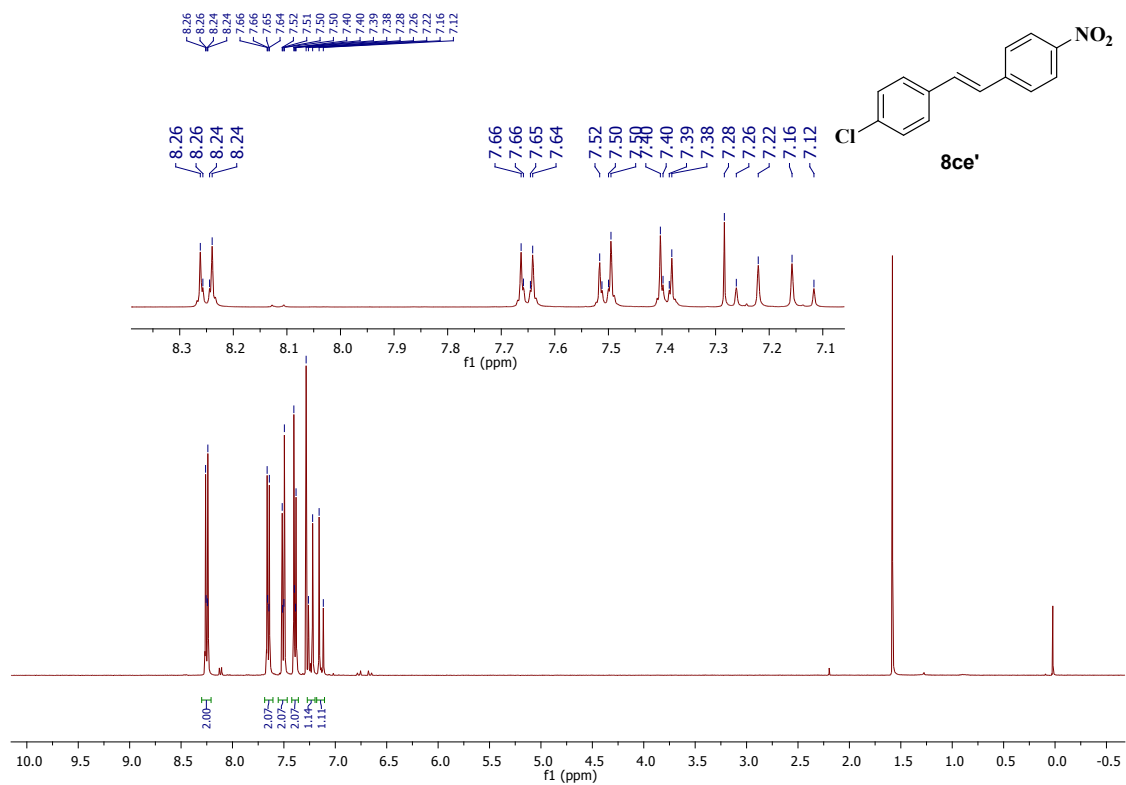


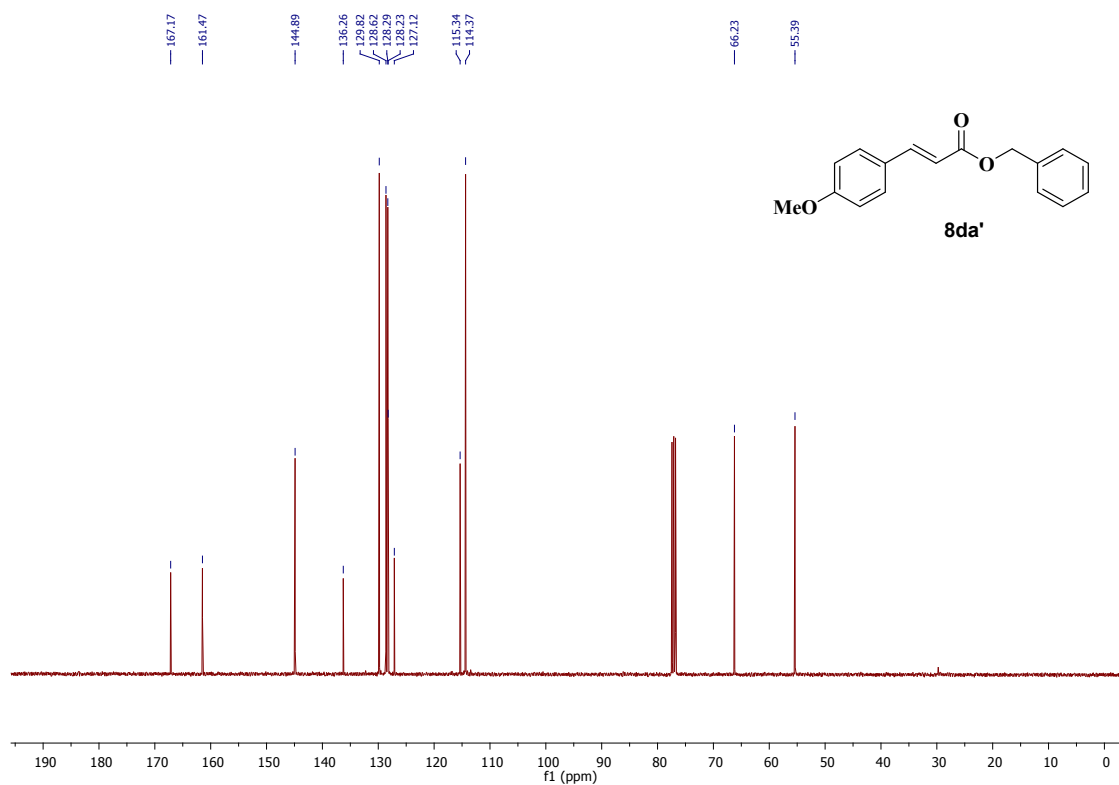
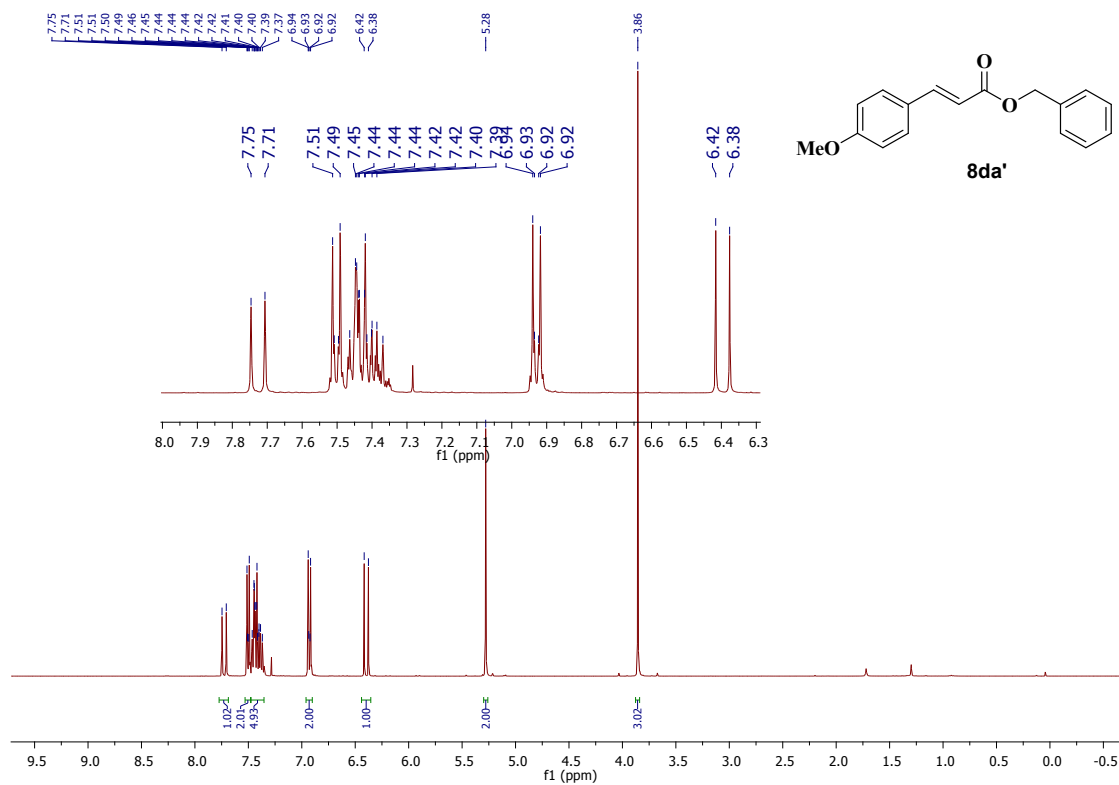


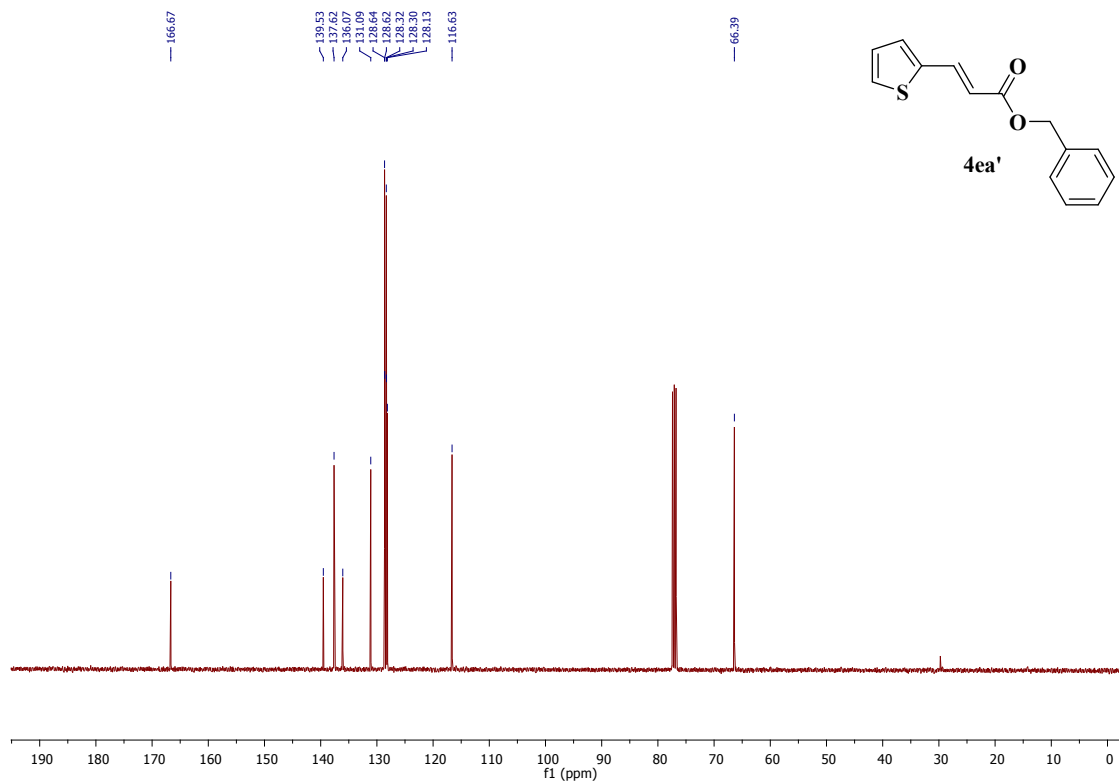
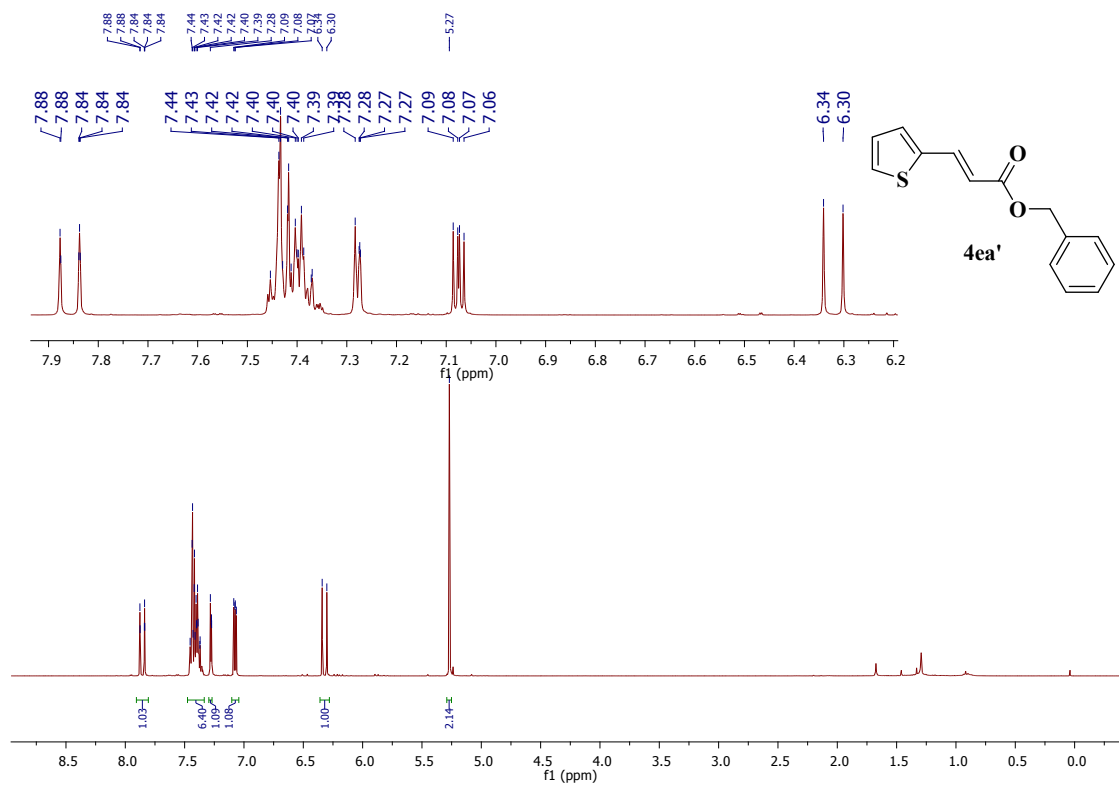












2.3 ¹H and ¹³C NMR analysis of the Suzuki coupling products

1,1'-Biphenyl (10aa'): Colorless solid; mp 68 – 70 °C (Lit. mp 71 – 72 °C)⁴; ¹H NMR (400 MHz, CDCl₃) δ 7.66 – 7.61 (m, 2H), 7.52 – 7.45 (m, 2H), 7.41 – 7.36 (m, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 141.4, 128.9, 127.4, 127.3.

3,4,5-Trimethoxy-1,1'-biphenyl (10ab'): Colorless solid, mp 141 – 141.5 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.63 – 7.56 (m, 2H), 7.50 – 7.43 (m, 2H), 7.41 – 7.34 (m, 1H), 6.81 (s, 2H), 3.95 (s, 6H), 3.92 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 153.5, 141.4, 137.6, 137.3, 128.8, 127.3, 127.1, 104.5, 61.0, 56.2.

4-Methyl-1,1'-biphenyl (10ba'): Colorless solid, mp 49–50 °C (Lit. mp 49 – 51 °C)¹; ¹H NMR (400 MHz, CDCl₃) δ 7.64 – 7.60 (m, 2H), 7.57 – 7.52 (m, 2H), 7.50 – 7.44 (m, 2H), 7.40 – 7.34 (m, 1H), 7.29 (d, *J* = 7.3 Hz, 2H), 2.44 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 141.2, 138.4, 137.1, 129.5, 128.8, 128.8, 127.1, 127.0, 21.2.

4-Nitro-1,1'-biphenyl (10ca'): Pale yellow coloured solid, mp 113–114 °C (Lit. mp 113 – 115)¹; ¹H NMR (300 MHz, CDCl₃) δ ¹H NMR (400 MHz, CDCl₃) δ 8.33 (dt, *J* = 8.8, 2.4 Hz, 2H), 7.77 (dt, *J* = 8.8, 2.4 Hz, 2H), 7.66 – 7.63 (m, 2H), 7.55 – 7.45 (m, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 147.7, 147.1, 138.8, 129.2, 128.9, 127.8, 127.4, 124.1.

2-Methyl-1,1'-biphenyl (10ha'): Colorless liquid⁵; ¹H NMR (400 MHz, CDCl₃) δ 7.70 – 7.63 (m, 1H), 7.54 – 7.44 (m, 3H), 7.44 – 7.40 (m, 1H), 7.40 – 7.36 (m, 1H), 7.35 – 7.28 (m, 3H), 2.34 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 141.98, 135.39, 130.35, 129.84, 129.24, 128.80, 128.11, 127.29, 127.22, 126.81, 125.81, 20.52.

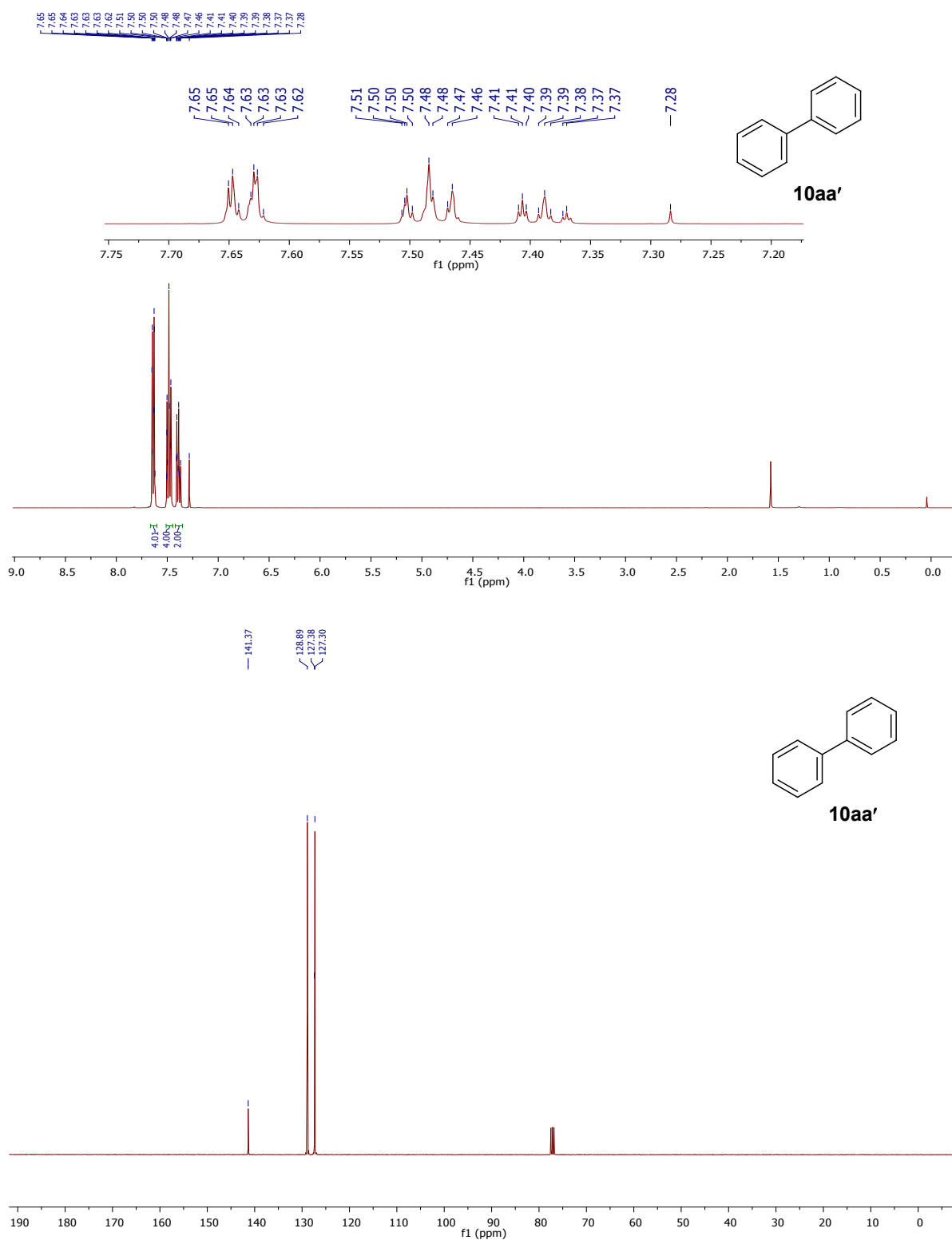
4-Methoxy-1,1'-biphenyl (10da'): Colorless solid, mp 87 – 90 °C (Lit. mp 88 – 92 °C)¹; ¹H NMR (400 MHz, CDCl₃) δ 7.62 – 7.52 (m, 4H), 7.47 – 7.42 (m, 2H), 7.37 – 7.30 (m, 1H), 7.01 (dt, *J* = 8.8, 2.4 Hz, 2H), 3.88 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 159.2, 140.9, 133.8, 128.8, 128.2, 126.8, 126.7, 114.2, 55.4.

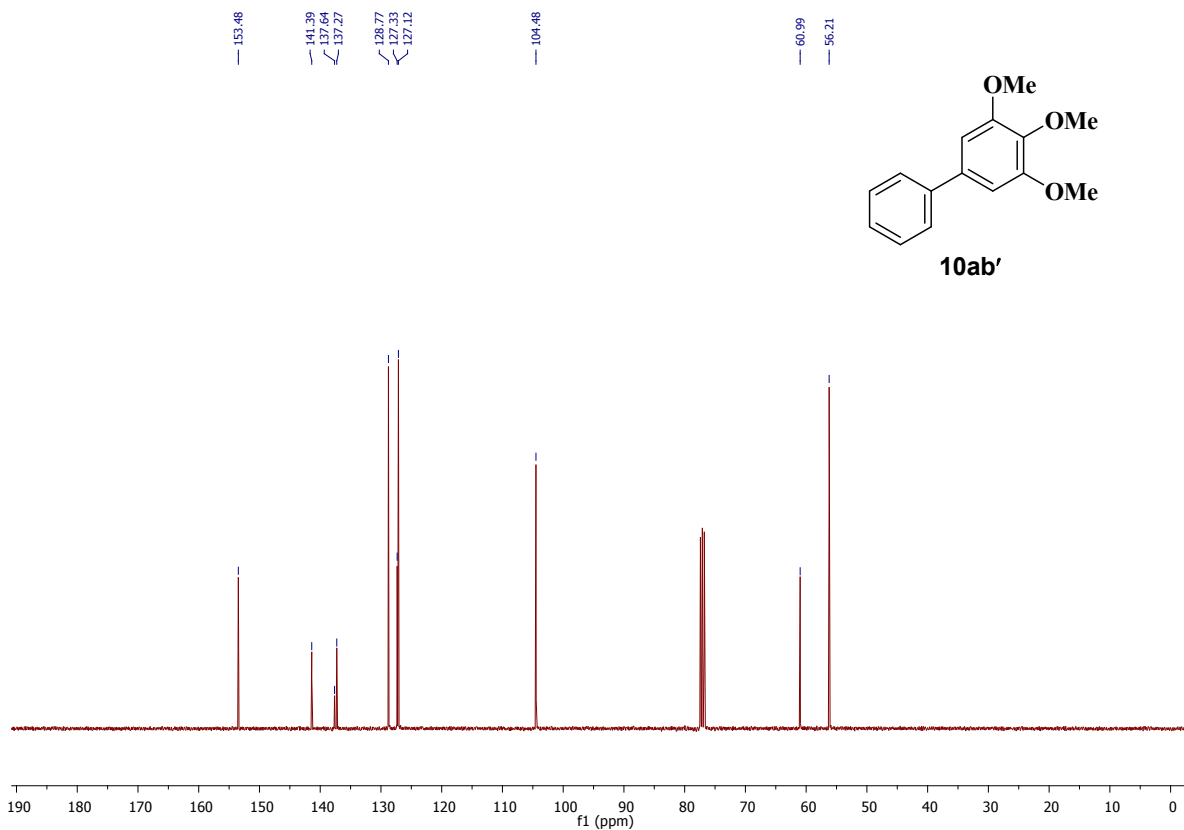
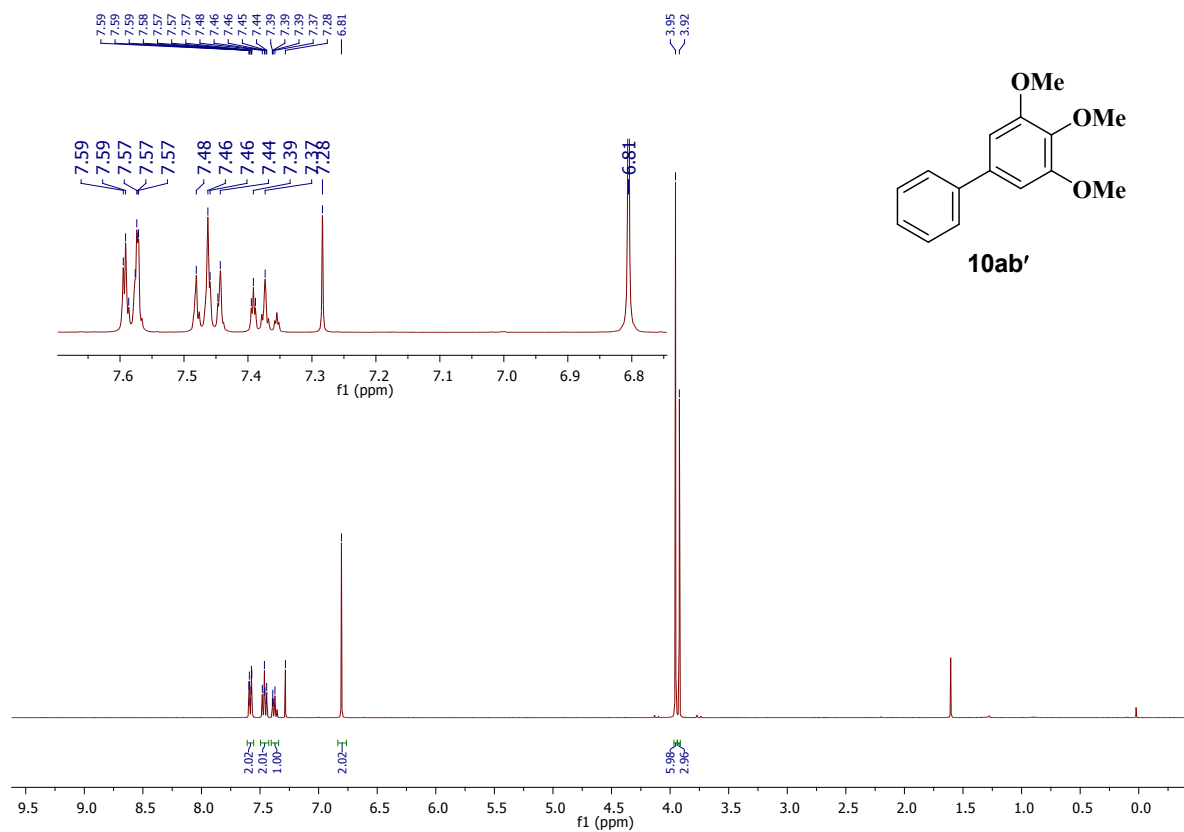
2-Amino-1,1'-biphenyl (10ia'): Colorless solid, mp 47–50 °C (Lit. mp 50 – 53 °C)⁴; ¹H NMR (400 MHz, CDCl₃) δ 7.56 – 7.45 (m, 4H), 7.44 – 7.35 (m, 1H), 7.26 – 7.15 (m, 2H), 6.88 (dt, *J* = 7.5, 3.8 Hz, 1H), 6.84 – 6.79 (m, 1H), 3.77 (br s, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 143.5, 139.6, 130.5, 129.1, 128.9, 128.5, 127.7, 127.2, 118.7, 115.6.

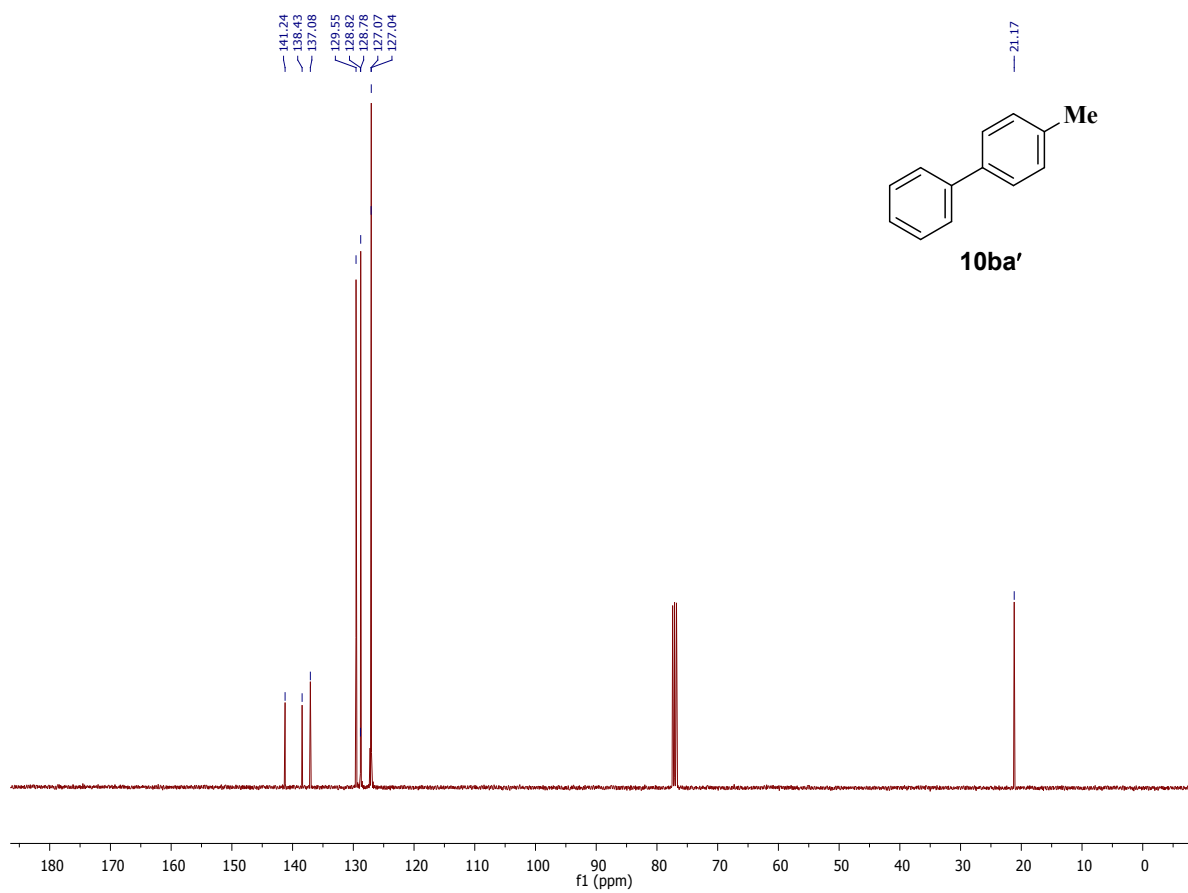
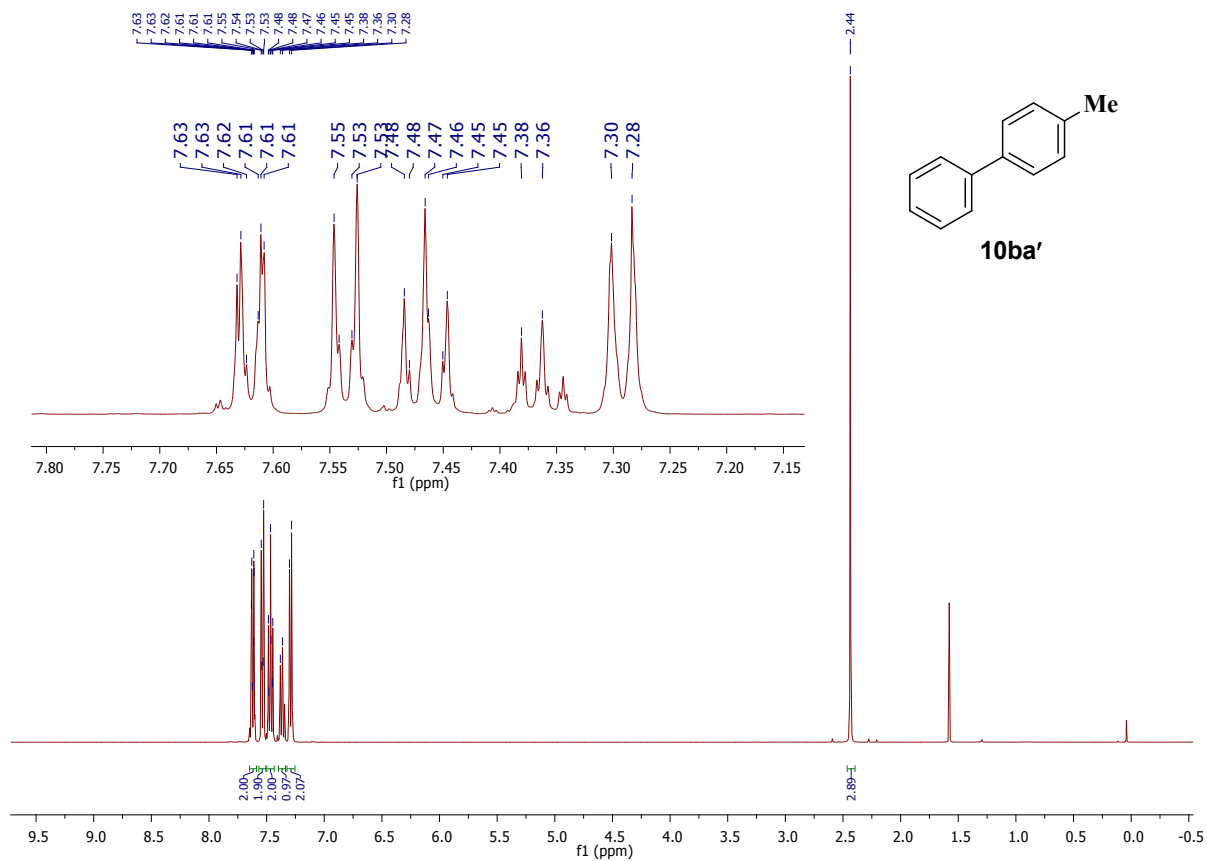
4-Naphthyl-1,1'-biphenyl (10ja'): Colorless liquid; ¹H NMR (300 MHz, CDCl₃) δ 8.17–8.04(m, 3H), 7.73 – 7.59 (m, 9H). ¹H NMR (400 MHz, CDCl₃) δ 8.14 (d, *J* = 7.8 Hz, 1H), 8.09 (d, *J* = 8.8 Hz, 1H), 8.04 (d, *J* = 8.2 Hz, 1H), 7.72 – 7.65 (m, 5H), 7.66 – 7.58 (m, 4H). ¹³C NMR (101 MHz, CDCl₃) δ 141.0, 140.5, 134.0, 131.9, 130.3, 129.0, 128.5, 128.4, 127.9, 127.4, 127.2, 126.2, 125.9, 125.6.

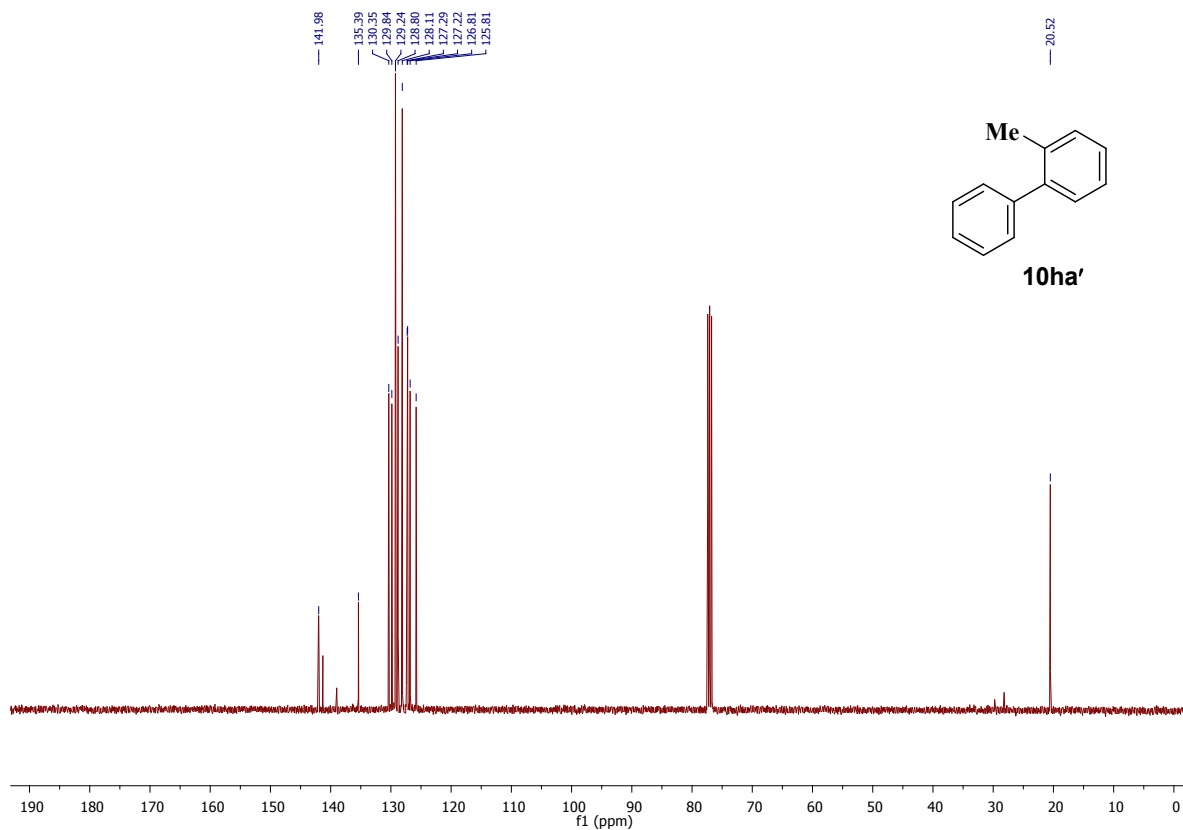
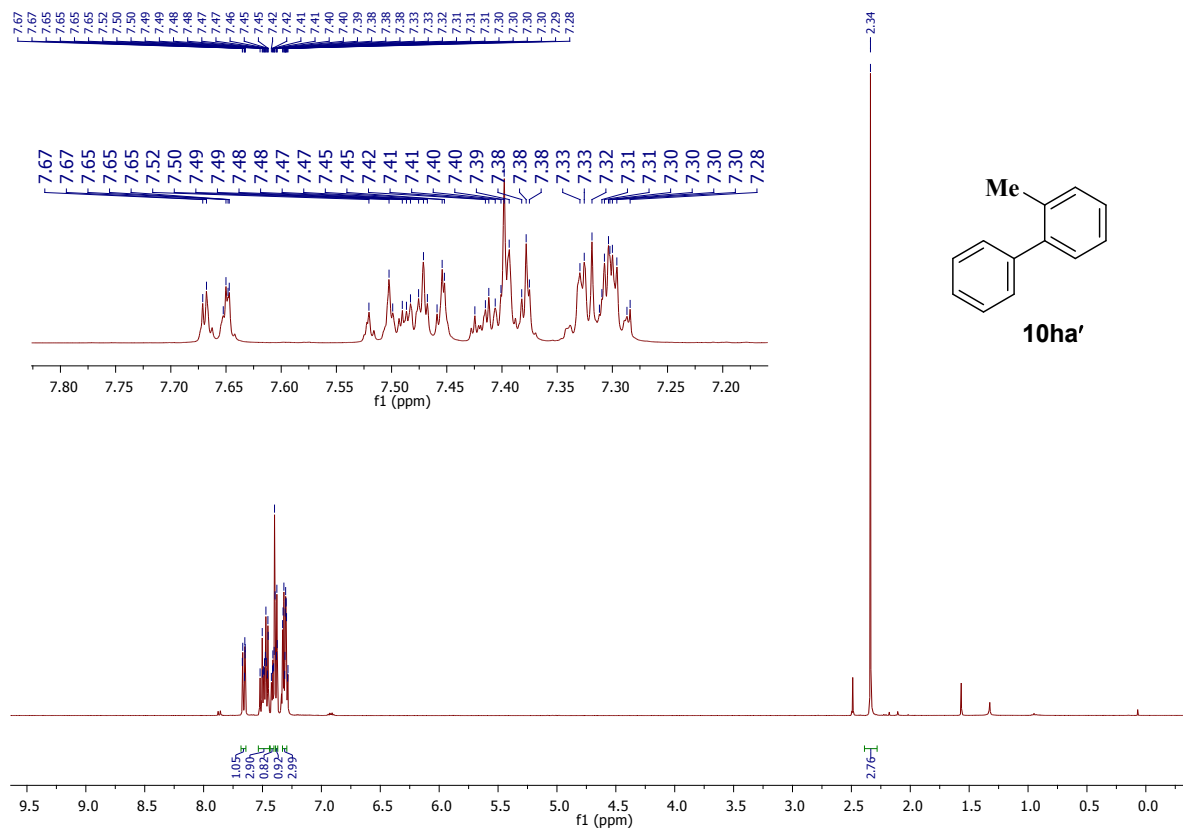
2-phenylthiophene (10ea'): Low melting colorless solid (Lit. mp 34 – 36 °C)⁵; ¹H NMR (400 MHz, CDCl₃) δ 7.71 – 7.65 (m, 2H), 7.47 – 7.40 (m, 2H), 7.37 (dd, *J* = 3.6, 1.2 Hz, 1H), 7.36 – 7.31 (m, 2H), 7.13 (dd, *J* = 5.1, 3.6 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 144.5, 134.5, 128.9, 128.1, 127.5, 126.0, 124.9, 123.1.

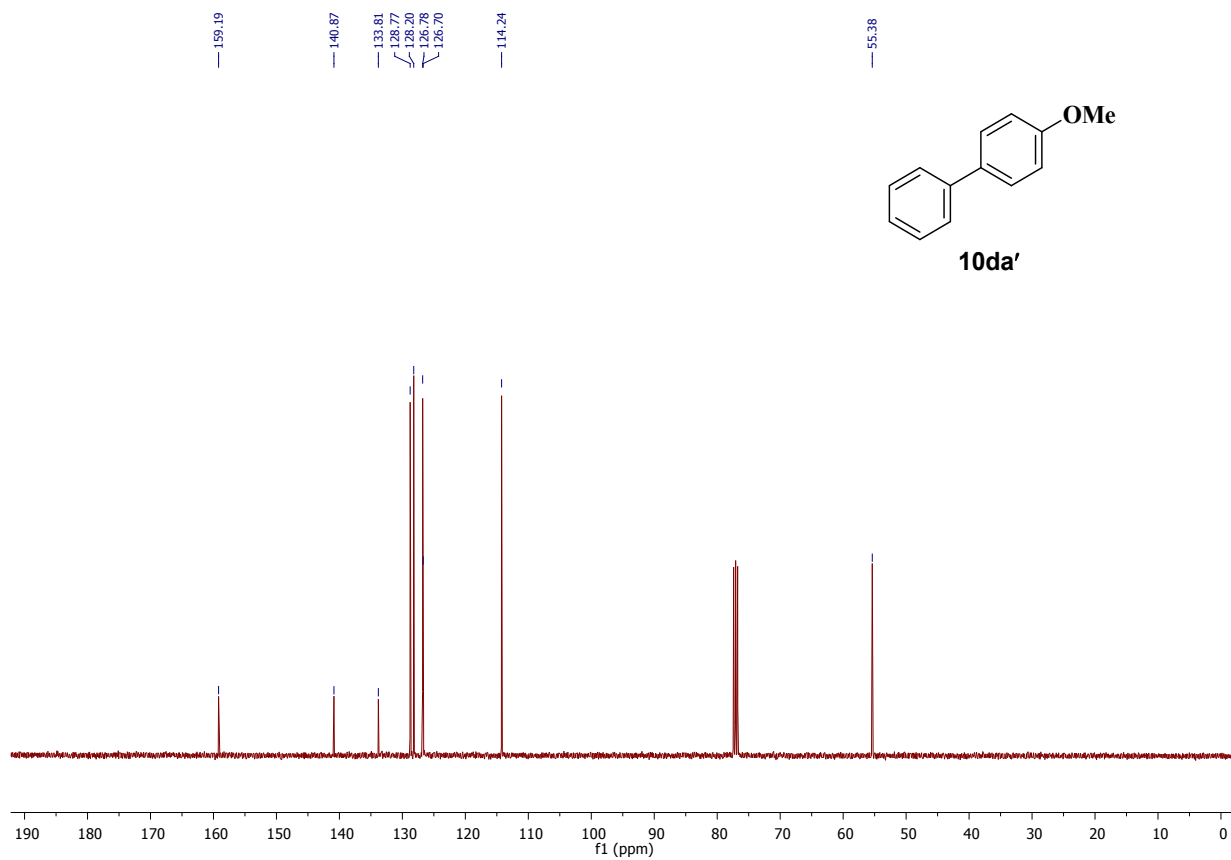
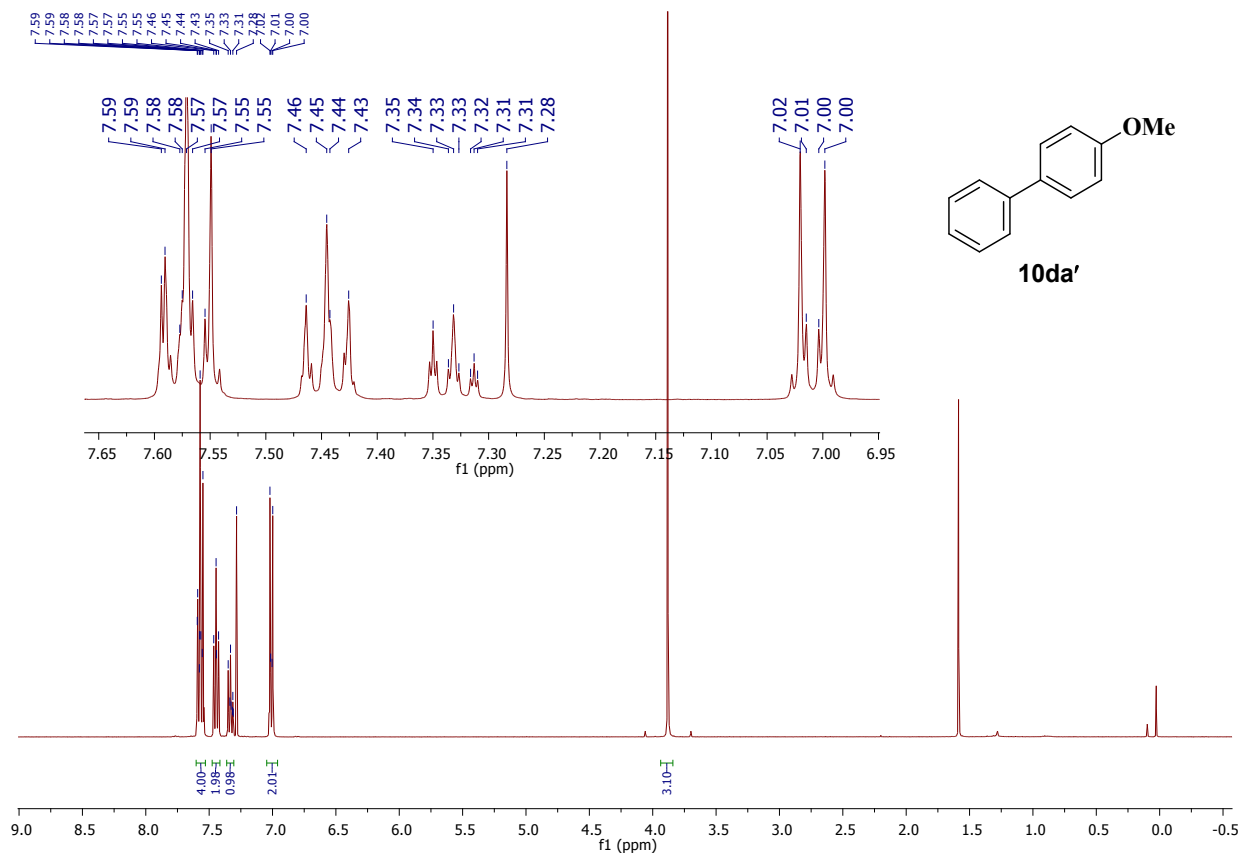
2.4 Copies of ¹H and ¹³C NMR spectra of Suzuki coupling products 10

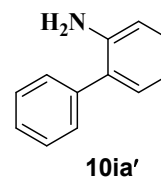
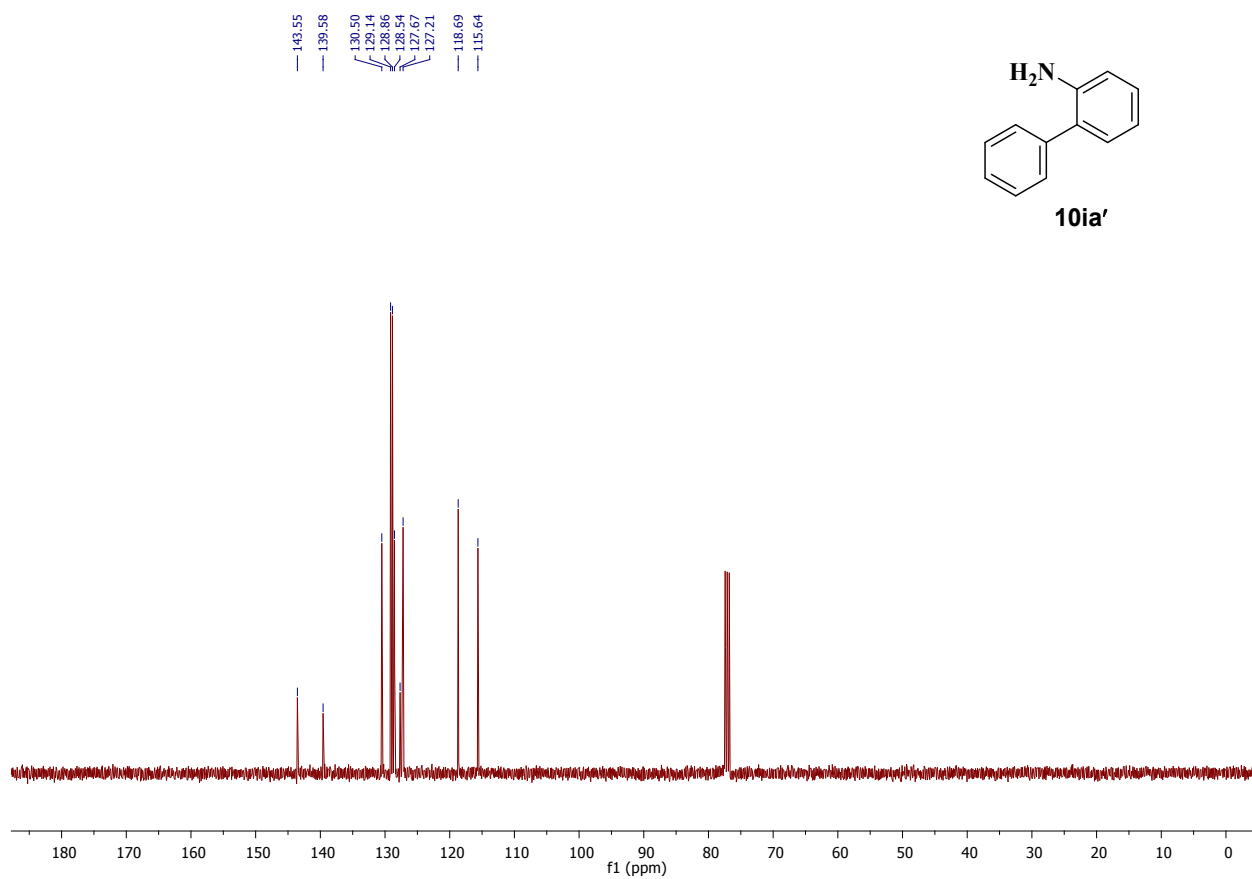
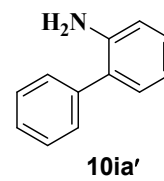
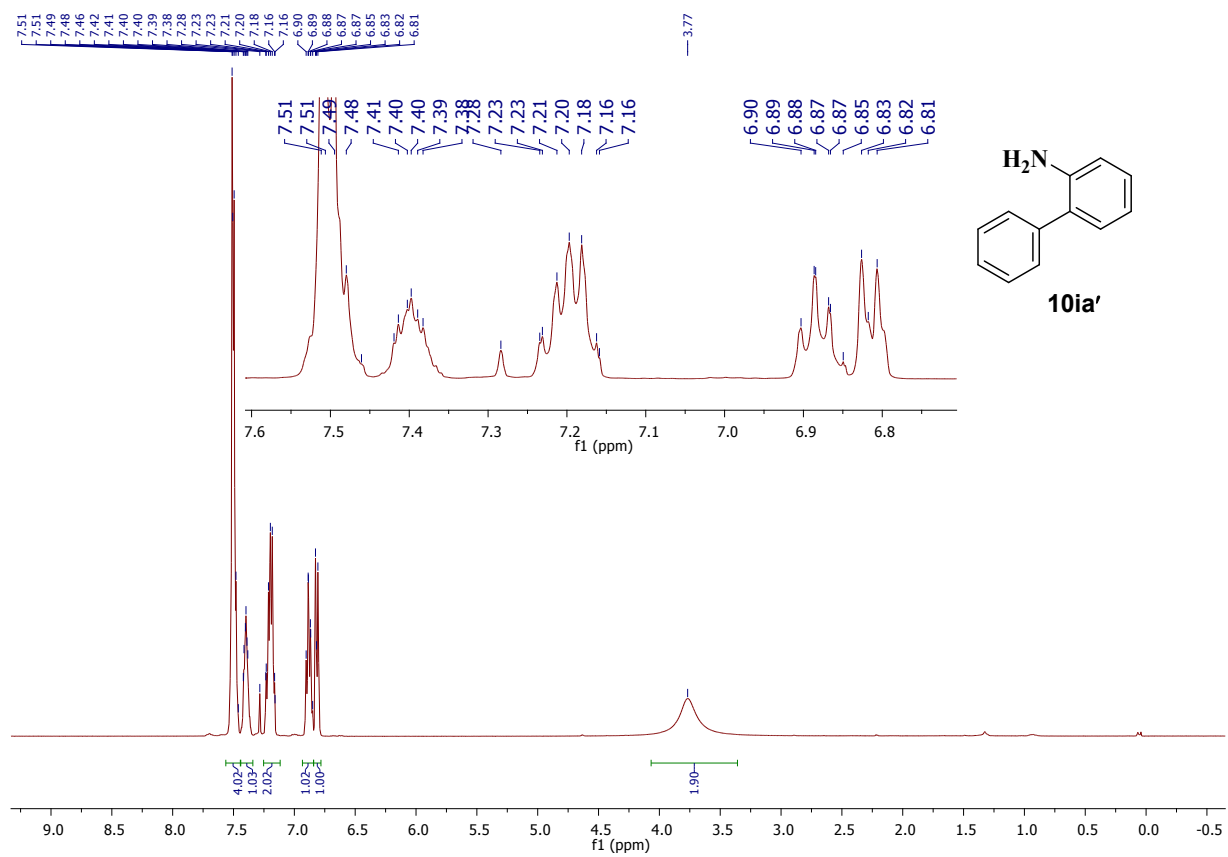


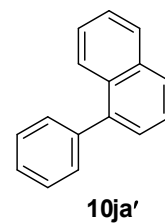
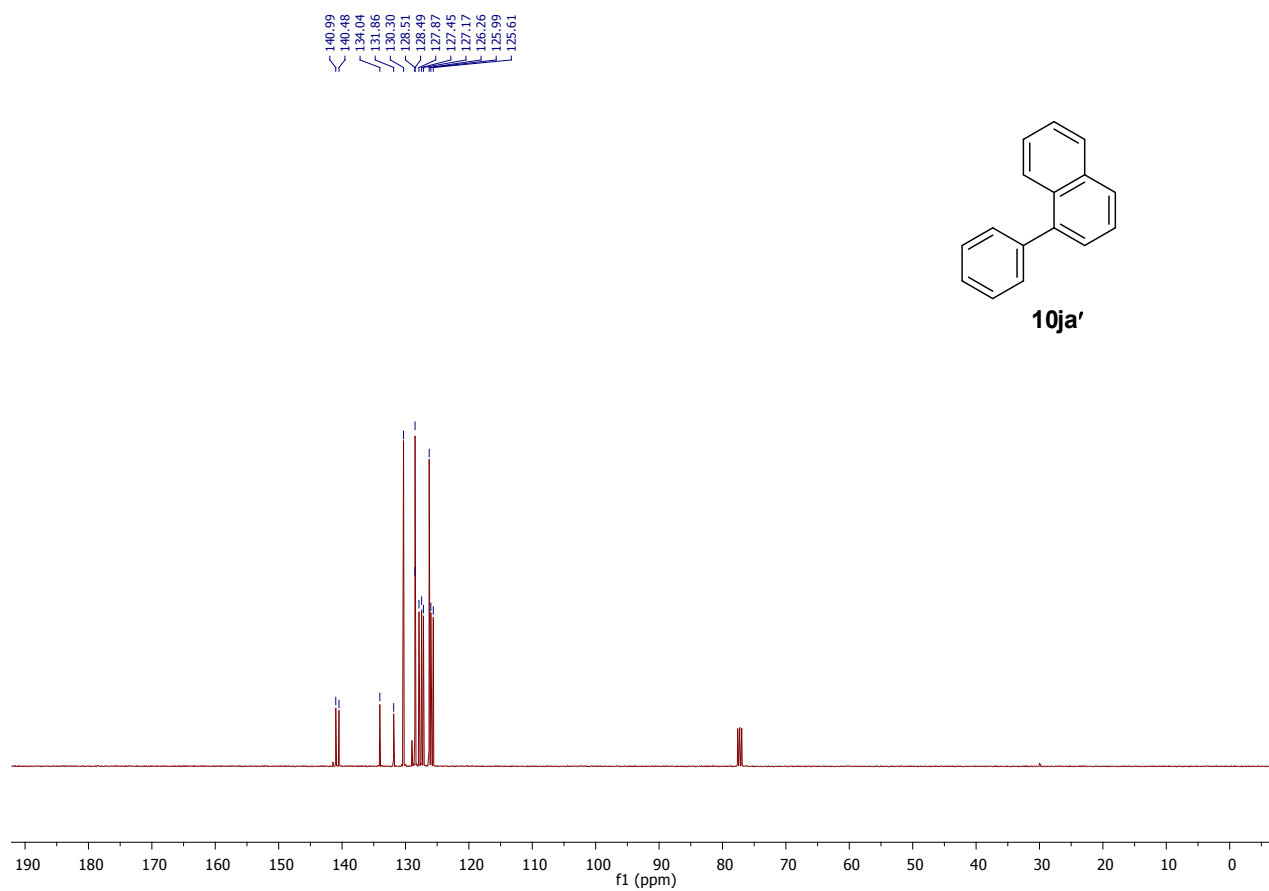
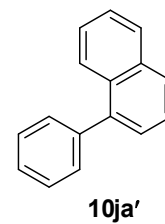
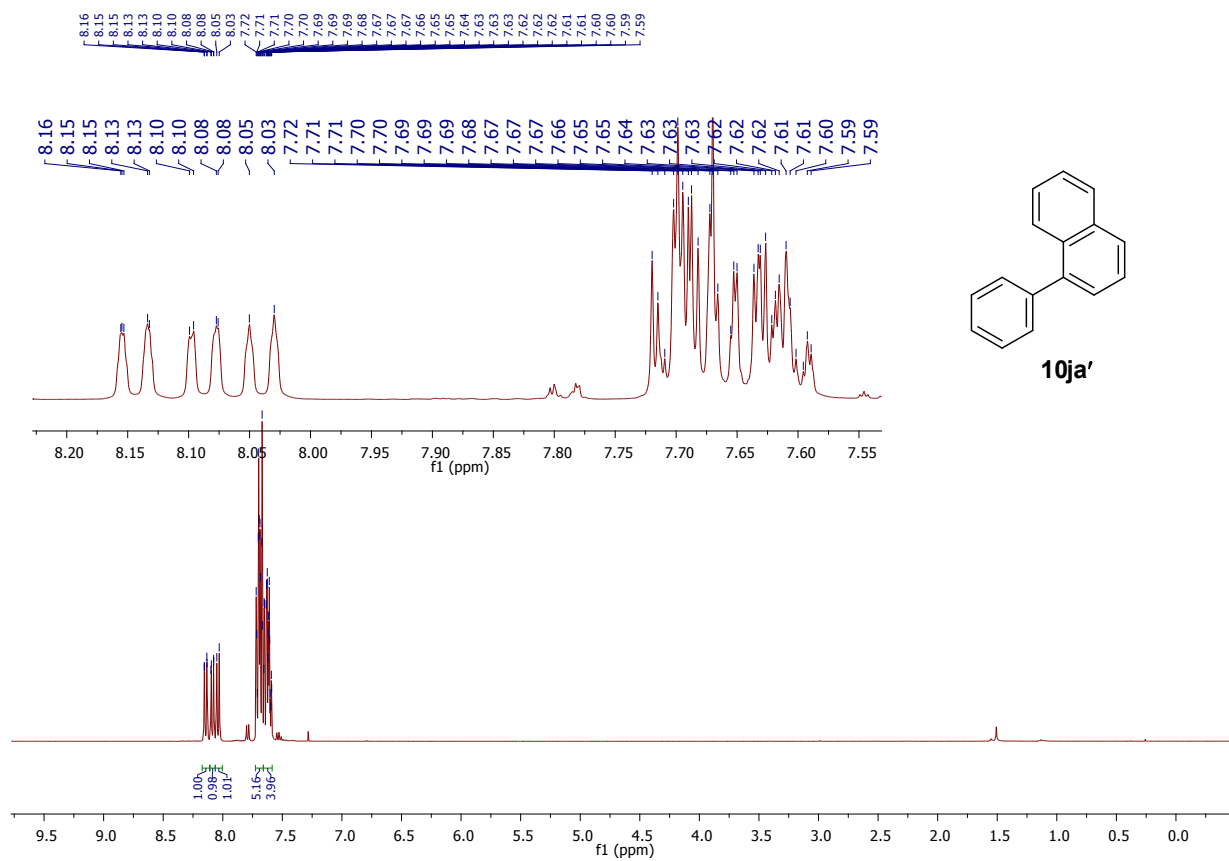


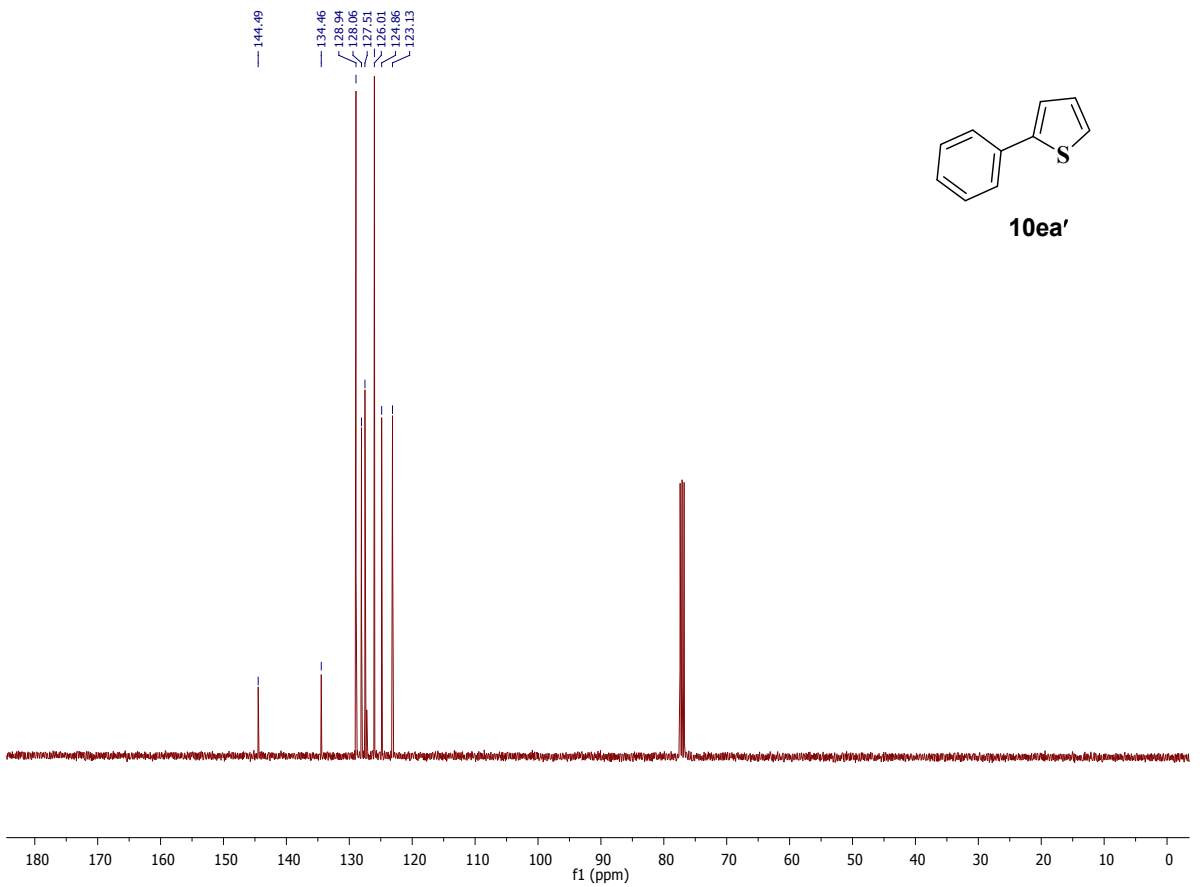
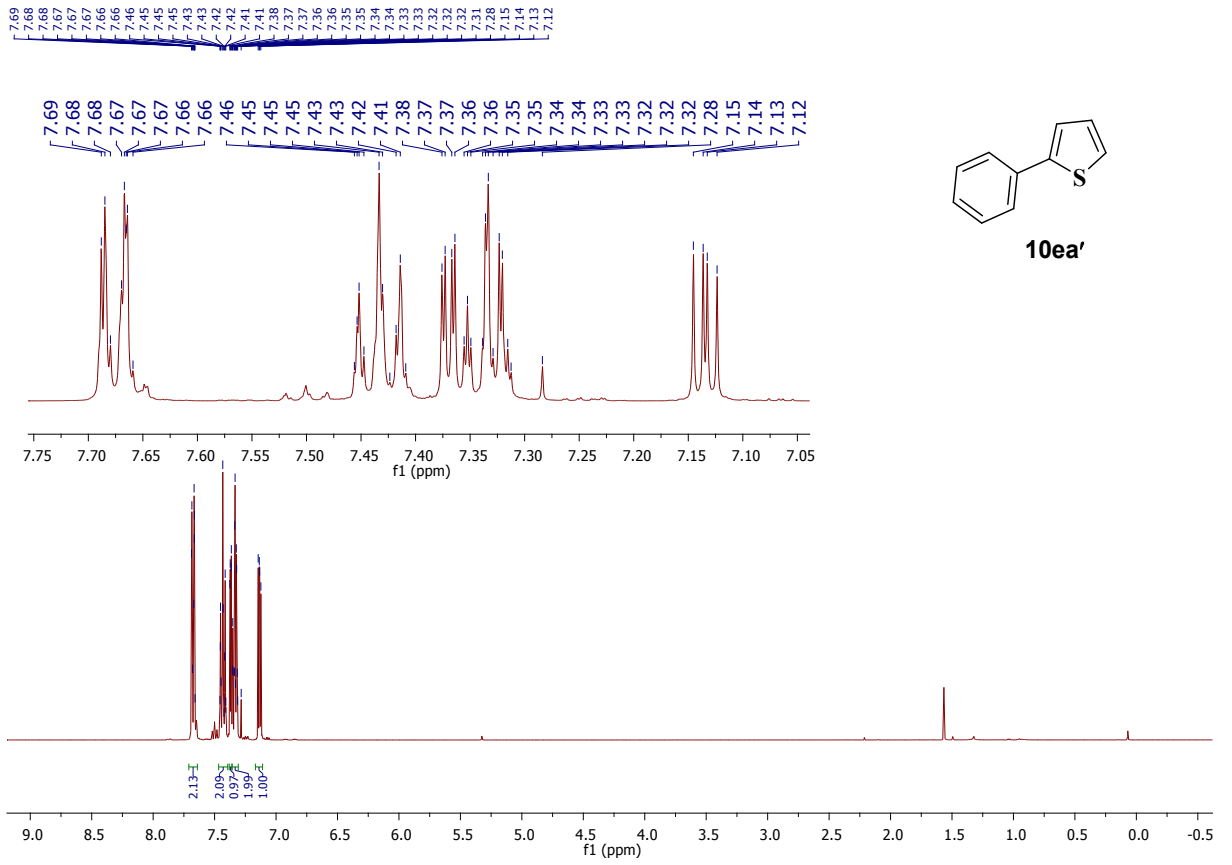












3. References

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