Electronic Supplementary Material (ESI) for Green Chemistry

Supporting Information

One-by-One Hydrogenation, Cross-Coupling Reaction, and Knoevenagel Condensations Catalyzed by $PdCl_2$ and Downstream Palladium Residue

Hu Wang[a], Li Li[a], Xing-Feng Bai[a], Wen-Hui Deng[a], Zhan-Jiang Zheng[a], Ke-Fang Yang[a]*,
Li-Wen Xu[a,b]*

[a] *Key Laboratory of Organosilicon Chemistry and Material Technology of Ministry of Education*
Hangzhou Normal University, Hangzhou 310012, China
E-mail: licpxulw@yahoo.com, liwenxu@hznu.edu.cn
[b] *State Key Laboratory for Oxo Synthesis and Selective Oxidation, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou, 730000, P. R. China*

Table of Contents

1. General remarks

AP-grade methyl acrylate, butyl acrylate, methyl methacrylate, ethyl acrylate, 2,2,2-trifluorethyl methacrylate, acrylic acid 2-hydroxyethyl ester, 2-hydroxyethyl methacrylate, 2-hydroxypropyl methylacrylate, allyl methylacrylate, $Co(OAc)_2$, TsOH, and chlorofrom were used as received. The molecular weight of PMHS was about 8684 g/mol. ^{1}H NMR spectra were recorded on a Bruker AM-400 instrument in $CDCl_3$ without TMS. Attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy was performed on VERTEX70 IR (Bruker). The data were collected over 32 scans with a resolution of 4 cm^{-1} at room temperature. The glass transition temperature (T_g) of the polymers were determined by differential scanning calorimetry (DSC) using Q100 (TA) at a heating rate of 10°C min^{-1} under nitrogen atmosphere. Data were collected from the second scan curves. Thermogravimetric analysis (TGA) was performed on a TG209C instrument (Netzsch) under nitrogen atmosphere in a temperature range of 50-700°C at a heating rate of 10°C min^{-1}. The morphology of the polymer fracture surface was characterized by scanning electron micrograph (SEM, Hitachi S3000N). The samples were frozen in liquid nitrogen and snapped immediately. Transmission electron microscopy (TEM) was carried out with the phosphotungstic acid staining method on a Hitachi H-7650 transmission electron microscope.

2. Synthesis of PMHS/PA semi-IPN material

In a typical reaction, a PMHS/PEA semi-IPN was prepared as follows: ethyl acrylate (1.07 g), PMHS (2.01 g), TsOH (0.0184 g) and $Co(OAc)_2$ (0.026 g) were mixed in a reactor and stirred for 24 h at 70 °C. The resulting mixture was washed with the distilled water and dried for 24 h at 60 °C under vacuum. The PMHS-based semi-interpenetrating networks (PMHSIPN) is a novel organosilicon material and *the research work about the synthesis of PMHSIPN will be reported elsewhere in the future.*

3. A typical procedure for the reduction of ketones and benzylic alcohols to corresponding alkanes

Under nitrogen atmosphere, aromatic ketones (1mmol) was added to a dry tube containing $PdCl_2$ (5mol% or 10mol%), SPINs of PMHS/PEA (0.2mL: 5eq, calculated on the Si-H hydrogen content) and methanol 2 mL. the mixture was stirring at 40 ^{o}C for 24 hours. After the completion of the reaction, the product was dissolve in *n*-hexane, the reaction course was monitored by GC-MS or TLC. The combined organic layers were dried (Na_2SO_4), concentrated in vacuo, and purified by column chromatography on silica gel to gain the pure product.

The preparation of Pd@silicone-based SIPN catalysts after every reaction is simple: After the certain reaction was completed, the palladium catalyst embedded in the silicone-based SIPN was filtered through a Büchner funnel and the cake washed with methanol and hexane.

All the products are known compounds and confirmed by GC-MS, NMR, and IR. [1]

4.General Procedure of the palladium-catalyzed Suzuki reaction with aryl bromides and arylboronic acids

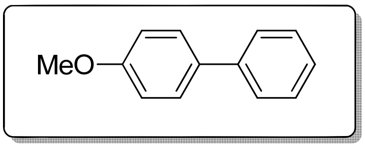
A mixture of aryl bromide (0.5 mmol), arylboronic acid (0.75 mmol), recovery palladium catalyst residue (A) of the C-O Hydrogenolysis reaction (0.1544g, $PdCl_2$: 5mol%), K_2CO_3 (1 mmol) was stirred in ethanol (2 mL) at room temperature in air for the indicated time (18h). The reaction course was monitored by GC-MS or TLC. After the completion of the reaction, the mixture was quenched by brine, and extracted with *n*-hexane (4×10 mL). The combined organic phase was dried by anhydrous $MgSO_4$, concentrated under vacuum. The product was purified by column chromatography on silica gel.

The preparation of Pd@silicone-based SIPN catalysts after every reaction is simple:

After the certain reaction was completed, the palladium catalyst embedded in the silicone-based SIPN was filtered through a Büchner funnel and the cake washed with methanol, water, and hexane.

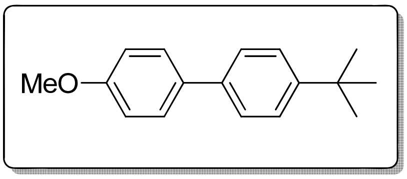
All the products are known compounds and confirmed by GC-MS, NMR, and IR. For example:

6a



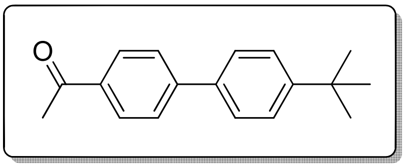
^{1}H-NMR (400 MHz, $CDCl_3$) : δ = 7.60 (d, J = 1.6 Hz, 1H) ; 7.57 (d, J = 2.0 Hz, 2H) ; 7.55 (t, J = 3.2 Hz, 1H); 7.44 (m, 2H); 7.33 (t, J = 7.2 Hz, 1H); 7.01 (d, J = 8.8 Hz, 2H), 3.87 (s, 3H); ^{13}C-NMR ($CDCl_3$, 100 MHz) : 159.21, 140.88, 132.28, 128.76, 128.19, 126.78, 115.78, 114.27, 55.38.

6b



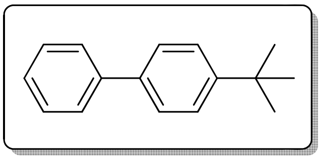
^{1}H-NMR (400 MHz, $CDCl_3$) : δ = 7.51 (m, 4H) ; 7.39 (d, J = 9.2 Hz, 1H) ; 6.98 (d, J = 8.8 Hz, 2H) ; 6.80 (d, J = 9.2 Hz, 1H) ; 3.86 (s, 3H) ; 1.38 (s, 9H) ; ^{13}C-NMR ($CDCl_3$, 100 MHz) : 158.97, 149.63, 137.96, 133.66, 132.26, 128.02, 126.39, 125.68, 115.76, 114.18, 55.35, 34.51, 31.98, 29.75, 22.74, 14.16.

6c



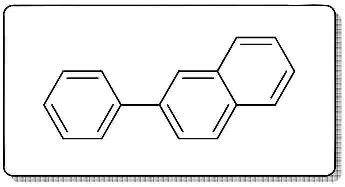
^{1}H-NMR (400 MHz, $CDCl_3$) : δ = 8.03 (d, J = 8.4 Hz, 2H) ; 7.69 (d, J = 8.4 Hz, 2H) ; 7.59 (d, J = 8.4 Hz, 2H); 7.51 (d, J = 8.4 Hz, 2H); 2.64 (s, 3H); 1.38 (s, 9H); ^{13}C-NMR ($CDCl_3$, 100 MHz) : 197.76, 151.48, 145.65, 136.94, 135.66, 128.93, 127.08, 126.95, 125.96, 34.67, 31.35, 26.66.

6d



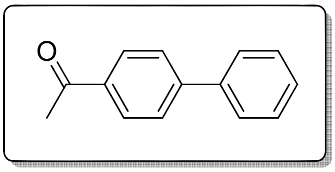
^{1}H-NMR (400 MHz, $CDCl_3$) : δ = 7.71 (d, J = 8.0 Hz, 2H) ; 7.66 (t, J = 6.8 Hz, 2H) ; 7.59 (d, J = 8.0 Hz, 2H); 7.54 (t, J = 7.6Hz, 2H); 7.43 (t, J = 7.6 Hz, 1H); 1.49 (d, J = 1.6 Hz, 9H) ; ^{13}C-NMR ($CDCl_3$, 100 MHz) : 150.34, 141.10, 138.45, 128.81, 127.14, 127.09, 126.91, 125.82, 125.75, 34.64, 31.52.

6e



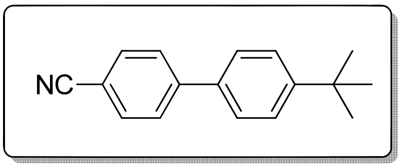
^{1}H-NMR (400 MHz, $CDCl_3$) : δ = 7.96 (m, 2H); 7.91 (d, J = 8.0 Hz, 1H) ; 7.62 (m, 6H), 7.48 (d, J = 6.8 Hz, 3H) ; ^{13}C-NMR ($CDCl_3$, 100 MHz): 140.85, 140.35, 130.15, 128.33, 127.70, 127.30, 127.0, 126.10, 125.83, 125.45.

6f



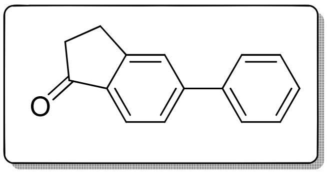
^{1}H-NMR (400 MHz, $CDCl_3$) : δ = 8.04 (d, J = 8.4 Hz, 2H); 7.69 (d, J = 8.4 Hz, 2H); 7.63 (d, J = 7.2 Hz, 2H); 7.48 (t, J = 7.6 Hz, 2H); 7.41 (t, J = 6.8 Hz, 1H); 2.64 (s, 3H); ^{13}C-NMR ($CDCl_3$, 100 MHz) : 197.74, 145.79, 139.89, 135.90, 128.99, 128.95, 128.27, 127.29, 127.24, 26.68.

6g



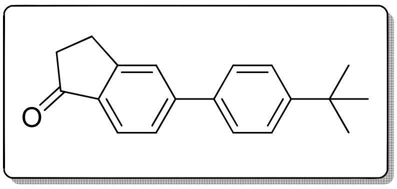
^{1}H-NMR (400 MHz, $CDCl_3$) : δ = 7.70 (m, 4H) ; 7.54 (m, 4H) ; 1.38 (s, 9H) ; ^{13}C-NMR ($CDCl_3$, 100 MHz) : 151.99, 145.52, 136.23, 132.58, 127.57, 126.92, 126.13, 119.06, 110.61, 34.72, 31.32.

6h



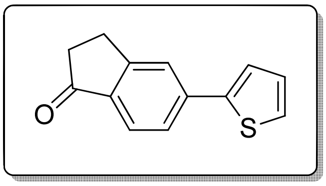
^{1}H-NMR (400 MHz, $CDCl_3$) : δ = 7.81 (d, J = 8.0 Hz, 1H) ; 7.63 (m, 5H) ; 7.47 (m, 2H); 3.17 (m, 2H); 2.69 (m, 2H); ^{13}C-NMR ($CDCl_3$, 100 MHz) : 206.63, 155.88, 147.71, 140.23, 128.98, 128.35, 127.50, 126.79, 125.17, 124.09, 36.56, 25.91.

6i



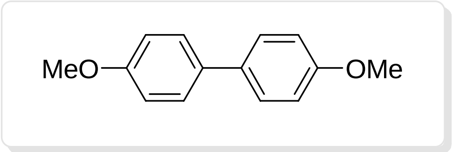
^{1}H-NMR (400 MHz, $CDCl_3$) : δ = 7.81 (d, J = 8.0 Hz, 1H) ; 7.67 (s, 1H) ; 7.59 (t, J = 8.4 Hz, 3H); 7.50 (d, J = 8.0 Hz, 2H) ; 3.19 (t, J = 6.4 Hz, 2H) ; 2.73 (q, J = 6.0 Hz, 2H); 1.37 (s, 9H); ^{13}C-NMR ($CDCl_3$, 100 MHz) : 206.65, 155.89, 151.61, 147.58, 137.26, 135.79, 127.16, 126.62, 125.96, 124.89, 124.07, 36.56, 34.69, 31.34, 25.92.

6j



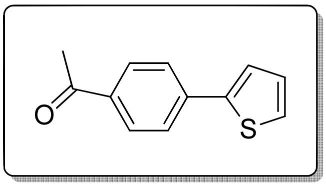
^{1}H-NMR (400 MHz, $CDCl_3$) : δ = 7.76 (d, J = 8.0 Hz, 1H) ; 7.70 (s, 1H) ; 7.63 (d, J = 8.0 Hz, 1H) ; 7.45 (dd, J = 2.4 Hz, 1H) ; 7.39 (dd, J = 4.0 Hz, 1H) ; 7.13 (m, 1H) ; 3.17 (t, J = 6.8 Hz, 2H) ; 2.73 (m, 2H) ; ^{13}C-NMR ($CDCl_3$, 100 MHz) : 206.18, 156.07, 143.16, 140.38, 135.98, 128.45, 126.71, 125.22, 124.95, 124.32, 123.33, 36.49, 25.83.

6k



^{1}H-NMR (400 MHz, $CDCl_3$) : δ = 7.39 (m, 4H) ; 6.80 (m, 4H) ; 3.80 (s, 6H) ; ^{13}C-NMR ($CDCl_3$, 100 MHz) : 158.71, 132.26, 115.74, 112.83, 55.46.

6l



^{1}H-NMR (400 MHz, $CDCl_3$) : δ = 7.98 (d, J = 8.4 Hz, 2H) ; 7.71 (dd, J = 5.2 Hz, 2H) ; 7.45 (dd, J = 2.8 Hz, 1H) ; 7.38 (dd, J = 4.0 Hz, 1H); 7.13 (q, J = 4.0 Hz, 1H) ; 2.62 (s, 3H); ^{13}C-NMR ($CDCl_3$, 100 MHz) : 197.36, 142.96, 138.80, 135.76, 131.92, 129.87, 129.15, 128.40, 126.50, 125.69, 124.64, 26.63.

5. General Procedure of the Palladium-catalyzed Sonogashira reaction of aryl iodide with aryl alkyne

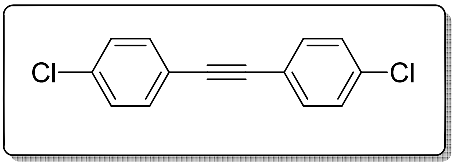
A mixture of aryl iodide (0.5 mmol), aryl alkyne (0.55 mmol), recovery palladium catalyst residue (**B** catalyst) of the C-O Hydrogenolysis reaction (0.1544g, $PdCl_2$: 5 mol%), K_2CO_3 (1 mmol), PhCl (10mol%) was stirred in ethanol (2 mL) at room temperature in air for the indicated time (18h). And the reaction course was monitored by GC-MS or TLC. After the completion of the reaction, the mixture was quenched by brine, extracted with *n*-hexane (4×10 mL). The combined organic phase was dried by anhydrous $MgSO_4$, concentrated under vacuum. The product was purified by column chromatography on silica gel.

The preparation of Pd@silicone-based SIPN catalysts after every reaction is simple:

After the certain reaction was completed, the palladium catalyst embedded in the silicone-based SIPN was filtered through a Büchner funnel and the cake washed with methanol, water, and hexane.

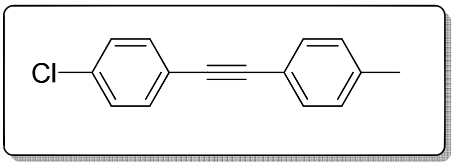
All the products **9** are known compounds and confirmed by GC-MS, NMR, and IR. For example:

9a



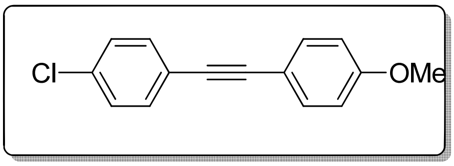
^{1}H-NMR (400 MHz, $CDCl_3$) : δ = 7.46 (d, J = 8.4 Hz, 4H) ; 7.23 (d, J = 8.4 Hz, 4H).

9b



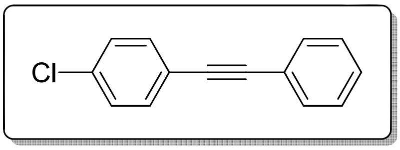
^{1}H-NMR (400 MHz, $CDCl_3$) : δ = 7.43 (t, J = 8.4 Hz, 4H) ; 7.31 (d, J = 8.4 Hz, 2H) ; 7.16(d, J = 7.6 Hz, 2H) ; 2.37 (s, 3H) ; ^{13}C-NMR ($CDCl_3$, 100 MHz) : 134.54, 132.82, 131.74, 130.74, 129.18, 128.89, 128.78, 128.55, 128.40, 127.71, 121.45, 89.20, 29.75.

9c



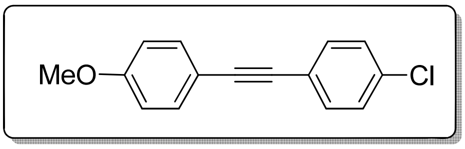
^{1}H-NMR (400 MHz, $CDCl_3$) : δ = 7.44 (q, J = 8.4 Hz, 4H) ; 7.31 (d, J = 7.6 Hz, 2H) ; 6.88 (d, J = 8.4 Hz, 2H) ; 3.83 (s, 2H) ; ^{13}C-NMR ($CDCl_3$, 100 MHz) : 159.81, 133.89, 133.10, 132.67, 128.67, 122.16, 115.04, 114.08, 90.40, 87.03, 55.34.

9d



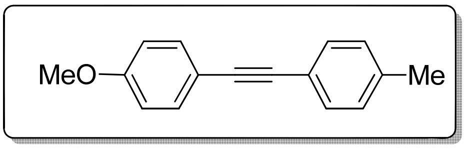
^{1}H-NMR (400 MHz, $CDCl_3$) : δ = 7.52 (q, J = 3.6 Hz, 2H) ; 7.45 (d, J = 8.4 Hz, 2H) ; 7.33 (q, J = 4.0Hz, 4H) ; 7.30 (s 1H).

9e



^{1}H-NMR (400 MHz, $CDCl_3$) : δ = 7.44 (q, J = 8.4 Hz, 4H) ; 7.31 (d, J = 7.6 Hz, 2H) ; 6.878 (d, J = 8.4 Hz, 2H) ; 3.83 (s, 2H) ; ^{13}C-NMR ($CDCl_3$, 100 MHz) : 159.81, 133.89, 133.10, 132.67, 128.67, 122.16, 115.04, 114.08, 90.40, 87.03, 55.34.

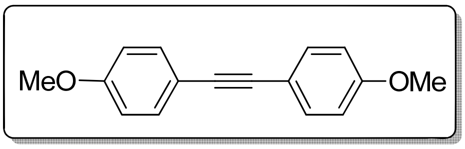
9f



^{1}H-NMR (400 MHz, $CDCl_3$) : δ = 7.49 (q, J = 8.0 Hz, 4H) ; 7.32 (d, J = 7.2 Hz, 2H) ; 6.874 (d, J = 8.8 Hz, 2H) ; 3.82 (s, 3H) ; 1.26 (s, 3H) ; ^{13}C-NMR ($CDCl_3$, 100 MHz) :

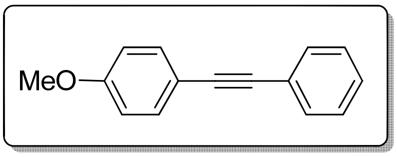
159.64, 133.07, 131.48, 128.34, 123.62, 115.41, 114.03, 89.40, 88.10, 77.06, 70.75, 55.34.

9g



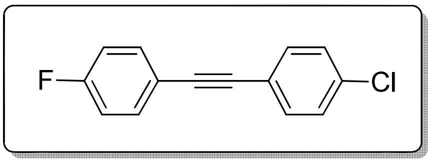
^{1}H-NMR (400 MHz, $CDCl_3$) : δ = 7.45 (d, J = 9.2 Hz, 4H) ; 6.87 (d, J = 8.4 Hz, 4H) ; 3.82 (s, 6H) ; ^{13}C-NMR ($CDCl_3$, 100 MHz) : 159.42, 132.91, 115.75, 114.0, 88.0, 55.31, 29.77.

9h



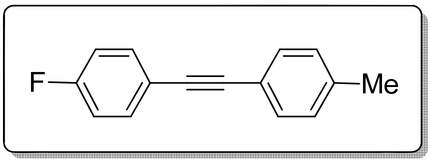
^{1}H-NMR (400 MHz, $CDCl_3$) : δ = 7.51 (dd, J = 8.0 Hz, 2H) ; δ = 7.47 (d, J = 8.8Hz, 2H) ; δ = 7.32 (m, 3H) ; δ = 6.87 (d, J = 8.8 Hz, 2H) ; 3.820 (s, 3H) ; ^{13}C-NMR ($CDCl_3$, 100 MHz) : 159.65, 133.70, 131.49, 128.76, 128.21, 127.98, 127.76, 127.44, 114.04, 55.34.

9i



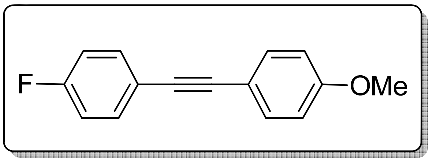
^{1}H-NMR (400 MHz, $CDCl_3$) : δ = 7.53 (s, 2H) ; 7.48 (d, J = 6.0 Hz, 2H) ; 7.36 (d, J = 6.0Hz, 2H) ; 7.09 (t, J = 8.4 Hz, 2H) ; ^{13}C-NMR ($CDCl_3$, 100 MHz) : 134.37, 133.57, 133.48, 132.78, 128.76, 121.62, 115.86, 115.64.

9j



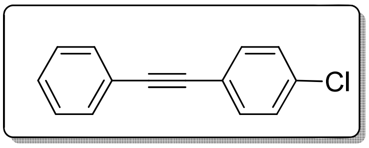
^{1}H-NMR (400 MHz, $CDCl_3$) : δ = 7.49 (m, 2H) ; 7.41 (d, J = 8.0 Hz, 2H) ; 7.15 (d, J = 8.0 Hz, 2H) ; 7.027 (d, J = 8.4 Hz, 2H) ; 2.36 (s, 2H) ; ^{13}C-NMR ($CDCl_3$, 100 MHz) : 138.51, 133.46, 133.38, 131.47, 129.17, 120.02, 115.73, 115.51, 21.55.

9k



^{1}H-NMR (400 MHz, $CDCl_3$) : δ = 7.47 (m, 4H) ; 7.02 (t, J = 8.4 Hz, 2H) ; 6.87 (d, J = 7.2 Hz, 2H) ; 3.81(s, 3H) ; ^{13}C-NMR ($CDCl_3$, 100 MHz) : 159.70, 133.35, 133.27, 133.04, 115.72, 115.50, 114.06, 55.32.

9l



^{1}H-NMR (400 MHz, $CDCl_3$) : δ = 7.52 (q, J = 3.6 Hz, 2H) ; 7.45 (d, J = 8.4 Hz, 2H) ; 7.33 (q, J=4.0Hz, 4H) ; 7.30 (s 1H).

6. General Procedure of the Knoevenagel condensation reaction of aldehyde with Ethyl cyanoacetate

A mixture of aldehyde (0.5 mmol), ethyl cyanoacetate (0.55 mmol), recovery palladium catalyst residue (**C** catalyst) of the Suzuki or Sonogashira cross-coupling reaction was stirred in ethanol (2 mL) at room temperature in air for the indicated time (18h). The reaction course was monitored by GC-MS or TLC. The combined organic layers were dried (Na_2SO_4), concentrated in vacuo, and purified by column chromatography on silica gel to gain the pure product.

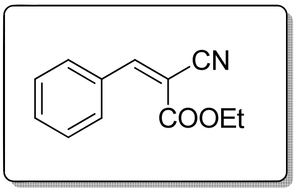
The preparation of Pd@silicone-based SIPN catalysts after every reaction is simple:

After the certain reaction was completed, the palladium catalyst embedded in the silicone-based SIPN was filtered through a Büchner funnel and the cake washed with methanol, water, and hexane.

All the products **11** are known compounds and confirmed by GC-MS, NMR, and IR.

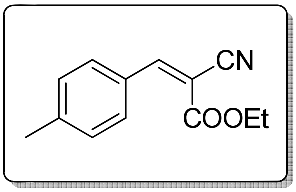
For example:

11a



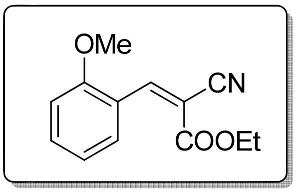
^{1}H-NMR (400 MHz, $CDCl_3$) : δ = 8.25 (s, 1H) ; 7.99 (d, J = 7.6 Hz, 2H) ; 7.53 (m, 3H) ; 4.39 (q, J = 7.6 Hz, 2H) ; 1.40 (t, J = 7.2Hz, 3H) ; ^{13}C-NMR ($CDCl_3$, 100 MHz): 162.50, 155.06, 133.32, 131.50, 131.09, 129.30, 115.50, 103.06, 62.76, 29.72, 14.19.

11b



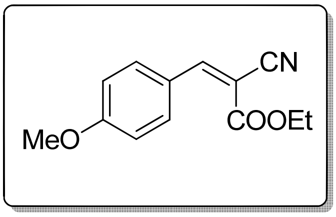
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.21 (s, 1H) ; 7.90 (d, J = 8.0 Hz, 2H); 7.30 (d, J = 7.6 Hz, 2H); 4.37 (q, J = 7.2 Hz, 3H); 2.43 (s 3H); 1.39 (t, J = 7.2 Hz, 3H) ; ^{13}C-NMR ($CDCl_3$, 100 MHz) : 162.79, 154.99, 144.65, 131.27, 130.05, 128.92, 115.78, 101.66, 62.61, 21.88, 14.20.

11c



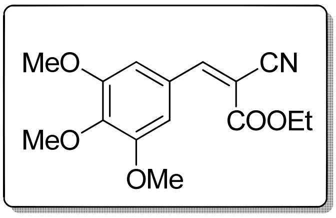
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.76 (s, 1H) ; 8.29 (d, J = 8.0 Hz, 1H) ; 7.52 (t, J = 8.0 Hz, 1H) ; 7.06 (t, J = 7.6 Hz, 1H) ; 6.96 (d, J = 7.6 Hz, 1H) ; 4.38 (q J = 7.6 Hz, 2H); 3.91 (s 3H) ; 1.40 (t, J = 6.8 Hz, 3H); ^{13}C-NMR ($CDCl_3$, 100 MHz) : 159.23, 149.79, 135.02, 129.34, 120.96, 120.70, 115.94, 111.19, 102.34, 62.52, 55.79, 14.22.

11d



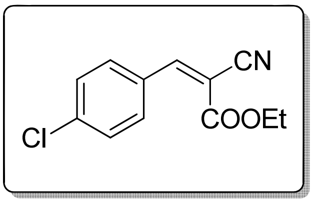
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.16 (s, 1H) ; 7.99 (d, J = 7.2 Hz, 2H) ; 6.98 (d, J = 8.8 Hz, 2H) ; 4.36 (q, J = 7.2 Hz, 2H) ; 3.88 (s 3H) ; 1.38 (t, J = 7.2Hz, 3H) ; ^{13}C-NMR ($CDCl_3$, 100 MHz): 163.80, 163.12, 154.37, 133.64, 124.41, 116.21, 114.79, 99.44, 62.43, 55.63, 14.22.

11e

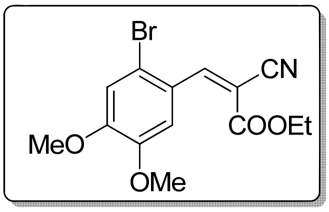


^{1}H-NMR (400 MHz, CDCl$_3$): δ = 8.14 (s, 1H) ; 7.29 (s 2H) ; 4.38 (q, J = 7.2 Hz, 2H) ; 3.95 (s, 3H) ; 3.95 (s 6H) ; 1.40 (t, J = 6.8 Hz, 3H) ; ^{13}C-NMR (CDCl$_3$, 100 MHz): 162.75, 154.81, 153.31, 126.58, 115.98, 108.67, 101.35, 62.65, 61.12, 56.341, 14.21.

11f



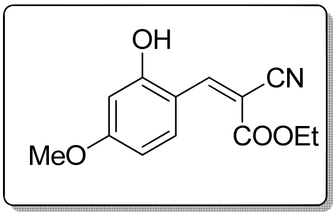
^{1}H-NMR (400 MHz, CDCl$_3$) : δ = 8.20 (s, 1H) ; 7.94 (d, J = 8.4 Hz, 2H) ; 7.48 (d, J = 8.4 Hz, 2H) ; 7.39 (q, J = 7.2 Hz, 2H) ; 1.40 (t, J = 7.2 Hz, 3H) ; ^{13}C-NMR (CDCl$_3$, 100 MHz) : 162.24, 153.41, 139.60, 132.23, 129.89, 129.69, 115.29, 103.504, 62.90, 14.18.



11g

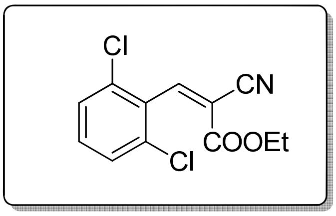
^{1}H-NMR (400 MHz, CDCl$_3$) : δ = 8.62 (s, 1H) ; 7.99 (s, 1H) ; 7.14 (s, 1H) ; 4.40 (q, J = 7.2 Hz, 2H) ; 3.95 (s, 6H) ; 1.41 (t, J = 7.2 Hz, 3H) ; ^{13}C-NMR (CDCl$_3$, 100 MHz) : 162.50, 153.41, 153.08, 148.55, 132.41, 120.79, 115.88, 115.83, 102.33, 62.73, 56.49, 56.35, 14.22.

11h



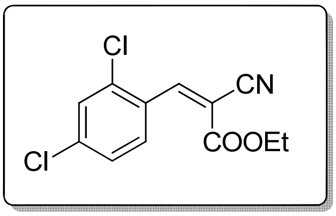
^{1}H-NMR (400 MHz, CDCl$_3$) : δ = 8.18 (s, 1H) ; 7.49 (d, J = 8.8 Hz, 1H) ; 6.95 (d, J = 8.8 Hz, 1H) ; 6.85 (s, 1H) ; 3.94 (s 3H) ; 3.91 (m 2H) ; 1.27 (s, 3H) ; ^{13}C-NMR (CDCl$_3$, 100 MHz) : 165.98, 165.18, 157.60, 149.02, 130.73, 113.72, 100.38, 61.75, 56.04, 29.73, 14.31.

11i



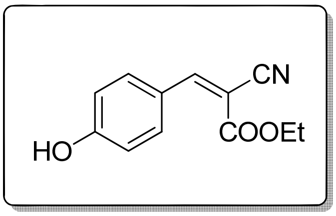
^{1}H-NMR (400 MHz, $CDCl_3$) : δ = 8.29 (s, 1H) ; 7.43 (s, 1H) ; 7.41 (s, 1H) ; 7.35 (t, J = 6.8 Hz, 1H) ; 4.435 (q, J = 7.2 Hz, 2H) ; 1.43 (t, J = 7.2 Hz, 3H) ; ^{13}C-NMR ($CDCl_3$, 100 MHz) : 160.65, 151.17, 134.11, 131.70, 130.33, 128.55, 113.98, 113.35, 63.22, 14.11.

11j



^{1}H-NMR (400 MHz, $CDCl_3$) : δ = 8.61 (s, 1H) ; 8.21 (d, J = 8.4 Hz, 1H) ; 7.54 (d, J = 6.4 Hz, 1H) ; 7.40 (dd, J = 6.4 Hz, 1H) ; 4.41 (q, J = 7.2 Hz, 2H) ; 1.41 (q, J = 7.2 Hz, 3H) ; ^{13}C-NMR ($CDCl_3$, 100 MHz) : 161.62, 149.70, 139.41, 137.25, 130.53, 130.35, 128.37, 128.02, 114.68, 106.68, 106.45, 63.11, 14.16.

11k



^{1}H-NMR (400 MHz, $CDCl_3$) : δ = 8.22 (s, 1H) ; 8.05 (d, J = 8.8 Hz, 2H) ; 7.04 (d, J = 8.8 Hz, 2H) ; 4.33 (q, J = 7.2 Hz, 2H) ; 1.344 (t, J = 7.2 Hz, 3H) ; ^{13}C-NMR ($CDCl_3$, 100 MHz) : 205.33, 162.69, 162.46, 154.16, 133.99, 123.59, 116.00, 98.55, 61.89, 13.59.

Selected Recent References, and references cited therein:

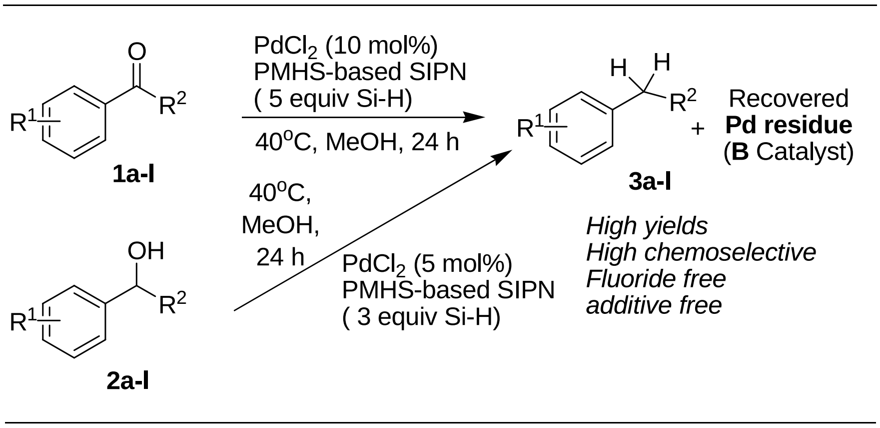
[1] For reductions: a) **3a**: L. Xing, X. Wang, C. Cheng, R. Zhu, B. Liu, Y. Hu, *Tetrahedron*, **2007**, *63*, 9382-9386; b) **3b**: V. Pandarus, G. Gingras, F. Beland, R. Ciriminna, *Org. Proc. Res. Dev.* **2012**, *16*, 1230-1234; c) **3d**: B. Punji , J. T. Mague M. S. Balakrishna, *Dalton Trans.*, **2006**, 1322-1330; d) **3e**: M. Mirza-Aghayana, R. Boukherroubb, M. Rahimifarda, R. Zadmard, *J. Iran, Chem. Soc.* **2011**, 570-573; e) **3f**: C. Mapelli, S. I. Natarajan, Jean-Philippe Meyer, W. R. Ewing, *J. Med. Chem.* **2009**,

52, 7788-7799; f) **3g**: S. Banerjee, V, Balasanthiran, R. T. Koodali, G. A. Sereda, *Org. Biomol. Chem.*, **2010**, *8*, 4316-4321; g) **3h**: K. Karami.,C. Rizzoli, M. M. Salah, *J. Organomet. Chem.* **2011**, *696*, 940-945; h) **3i**: N. Barbero, R. Martin, *Org. Lett.*, **2012**, *14*, 796-799; i) **3j**: L. H. Klemm, R. Zel1, J. S. Shabtai, *J. Org. Chem.*, **1974**, *39*, 5; j) **3k**: F. B. Mallory, M. Jonathan Rudolph, Soon M. Oh, *J. Org. Chem.* **1989**, *54*, 4619-4626; k) **3l**: M. Barbero, S. Bazzi, S. Cadamuro, S. Dughera, G. Ghigo, *Eur. J. Org. Chem.* **2009**, 4346-4351; m) R. J. Rahaim, R. E. Maleczka, *Org. Lett.* **2011**, *13*, 584-587; n) H. Wang, L. Li, X. F. Bai, J. Y. Shang, K. F. Yang, L. W. Xu, *Adv. Synth. Catal.* **2013**, *355*, 341-347.

[2] For Suzuki reaction: a) A. B. Patil, D. S. Patil, B. M. Bhanage, *J. Mol. Catal. A. Chem.* **2012**, *365*, 146-153; b) J. F. Hu, Y. P. Wang, M. Han, Y. M. Zhou, X. Q. Jiang, P. P. Sun, *Catal. Sci. Tech.* **2012**, *2*, 2332-2340; c) C. Amatore, A. Jutand, G. Le Duc, *Angew. Chem. Int. Ed.* **2012**, *51*, 1379-1382 ; d) H. Nowothnik, J. Blum, R. Schomacker, *Angew. Chem. Int. Ed.* **2011**, *50*, 1918-1921; e) T. Noel, S. Kuhn, A. J. Musacchio, K. F. Jensen, S. L. Buchwald, *Angew. Chem. Int. Ed.* **2011**, *50*, 5943-5946; f) P. P. Fang, A. Jutand, Z. Q. Tian, C. Amatore, *Angew. Hem. Int. Ed.* **2011**, *50*, 12184-12188; g) M. J. Jin, D. H. Lee, *Angew. Chem. Int. Ed.* **2010**, *49*, 1119-1122; h) B. Z. Yuan, Y. Y. Pan, Y. W. Li, B. L. Yin, H. F. Jiang, *Angew. Chem. Int. Ed.* **2010**, *49*, 4054-4058.

[3] For Sonogashi reaction: a) Z. Peng, W. Fen, H. Keli, X. W. Li. *Org. Lett.* **2012**, *14*, 5506-5509; b) M. Carril, A. Correa, C. Bolm, *Angew. Chem. Int. Ed.* **2008**, *47*, 4862-4865; c) H. Doucet, J. C. Hierso, *Angew. Chem. Int. Ed.* **2007**, *46*, 834-871; d) C. Gonzalez-Arellano, A. Abad, A. Corma, H. Garcia, M. Iglesias, F. Sanchez, *Angew. Chem. Int. Ed.* **2007**, *46*, 1536-1538.

[4] For Knoevenagel condensation: M. Holan, R. Pohl, I. Císarova, U. Jahn, *Eur. J. Org. Chem.* **2012**, 3459-3475.



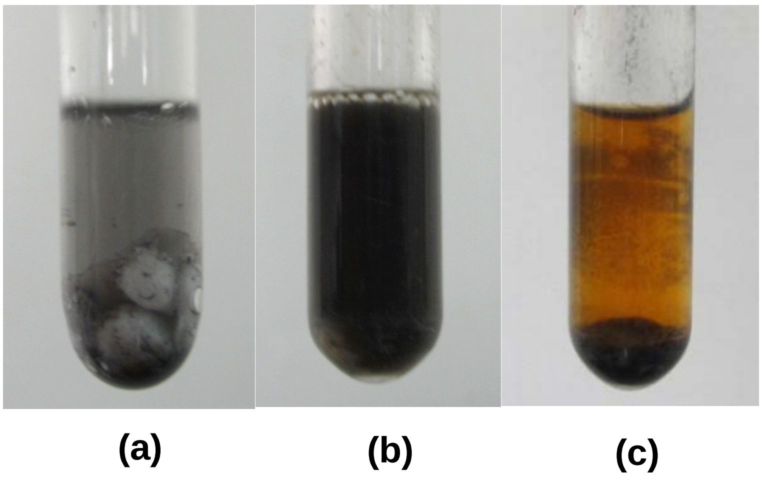
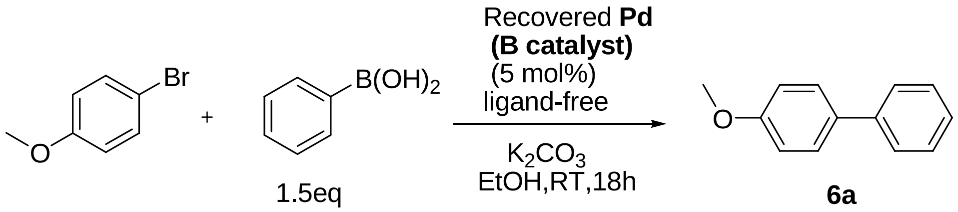


Figure S1. The picture of $PdCl_2$-catalyzed deoxygenated reduction of aromatic ketone and the desired supported palladium residue formed at the end of the deoxygenated reduction: (a) 1 min; (b) after 1 h; (c) at the last.

Table S1. Recovered palladium (A) catalyzed Suzuki reaction: Optimization of reaction conditions

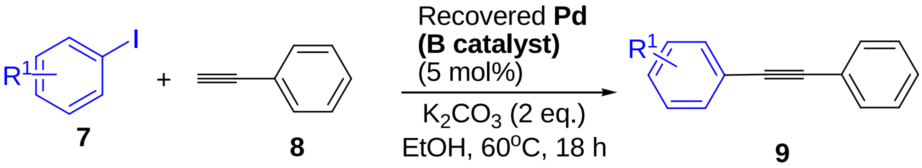


6a

Entry[a]	Cat	Solvent	Base	Time / h	Yield(%)-**6a**[b]
1	Pd-A	EtOH	K_2CO_3	18	81
2	Pd-A	MeOH	K_3PO_4	18	18
3	Pd-A	DMF-H_2O/(V:9:1)	K_3PO_4	18	33
4	Pd-A	DMF	CS_2CO_3	18	trace
5	Pd-A	MeOH	KOH	18	10
6	Pd-A	H_2O	Na_2CO_3	18	trace
7	Pd-A	H_2O	CS_2CO_3	18	trace

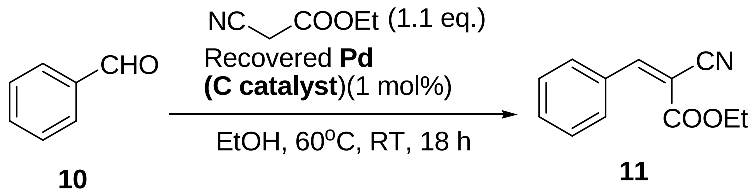
[a] Reaction conditions : aryl bromide (0.5 mmol), arylboronic acid (0.75 mmol), the Recovered palladium catalyst residue (A) (0.1544g, $PdCl_2$:5mol%), K_2CO_3 (1 mmol) was stirred in ethanol (2 mL) at room temperature in air. [b] Isolated yields.

Table S2. Recovered palladium (B) catalyzed Sonogashira reaction: Optimization of reaction conditions



Entry	SM1	Solvent	Base	Additive (10mol%)	Yield(%)-**9** [a]
1	4-Iodoanisole	H_2O	K_2CO_3	None	trace
2	4-Iodoanisole	EtOH	K_2CO_3	None	trace
3	1-Chloro-4-iodobenzene	EtOH	K_2CO_3	None	92
4	1-Chloro-4-iodobenzene	EtOH	K_2CO_3	None	77[b]
5	1-Chloro-4-iodobenzene	EtOH	K_2CO_3	None	49[c]
6	1-Fluoro-4-iodobenzene	EtOH	K_2CO_3	None	trace
7	Iodobenzene	EtOH	K_2CO_3	None	trace
8	1-Fluoro-4-iodobenzene	EtOH	K_2CO_3	PhCl	87
9	4-Iodoanisole	EtOH	K_2CO_3	PhCl	92
10	Iodobenzene	EtOH	K_2CO_3	PhCl	88
11	1-iodo-4-methylbenzene	EtOH	K_2CO_3	None	trace

[a] Isolated yield. [b] The recovered Pd (B) catalyst was recycled for reusing in the second cycle. [c] The recovered Pd (B) catalyst was recycled for reusing in the third cycle.



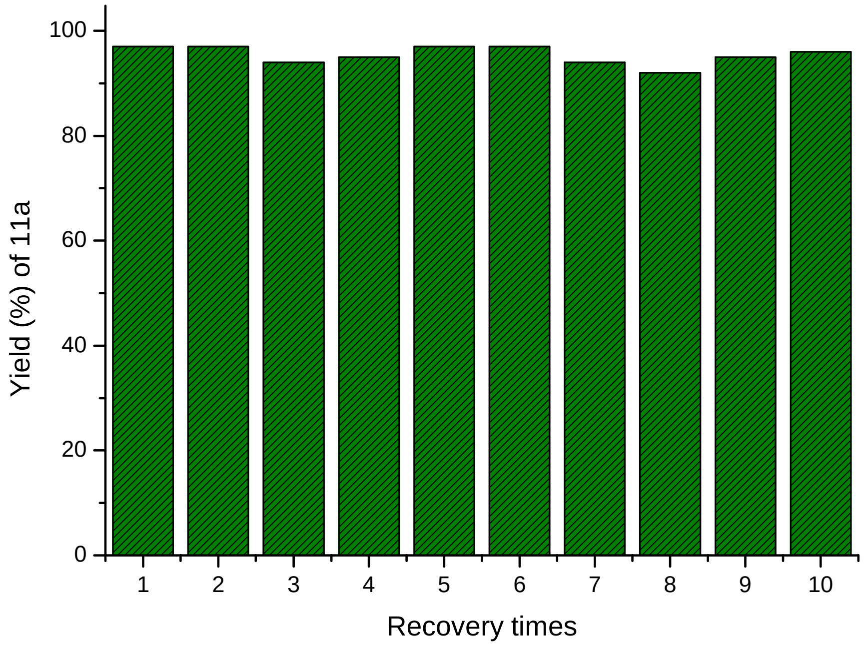
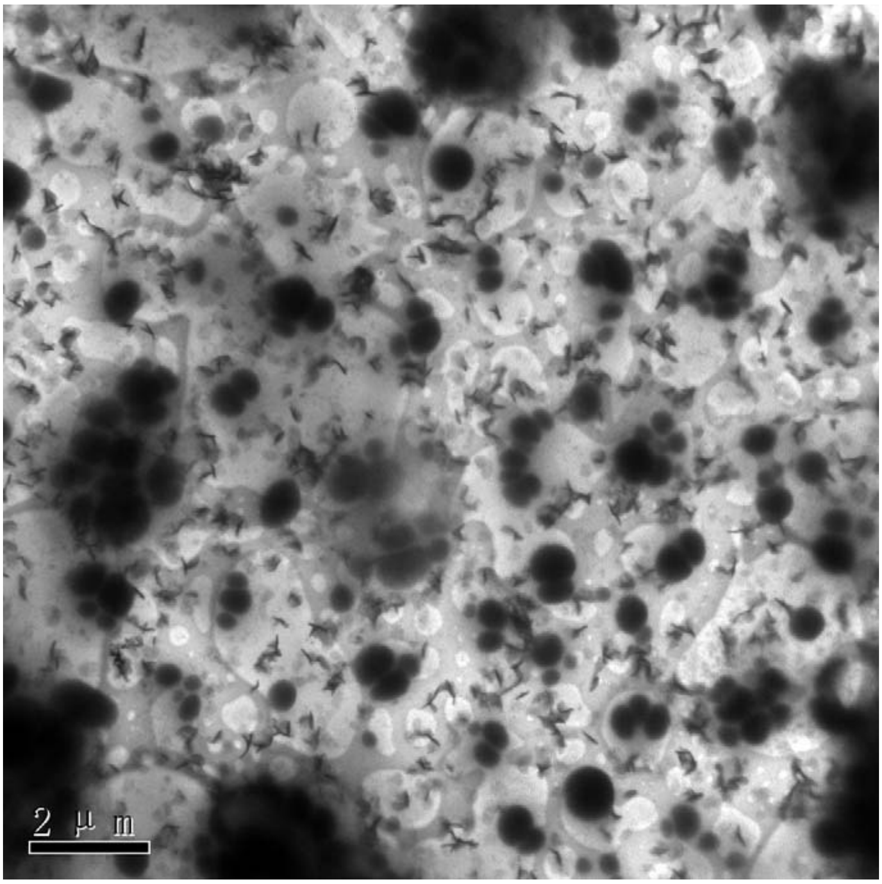


Figure S2. Catalyst recycling in the recovered palladium (**B**)-catalyzed Knoevenagel condensation

Figure 3 of Text. TEM images (**larger size**) of the recovered palladium catalyst embedded in the silicone-based SIPN (B catalyst) at the end of the deoxygenated reduction



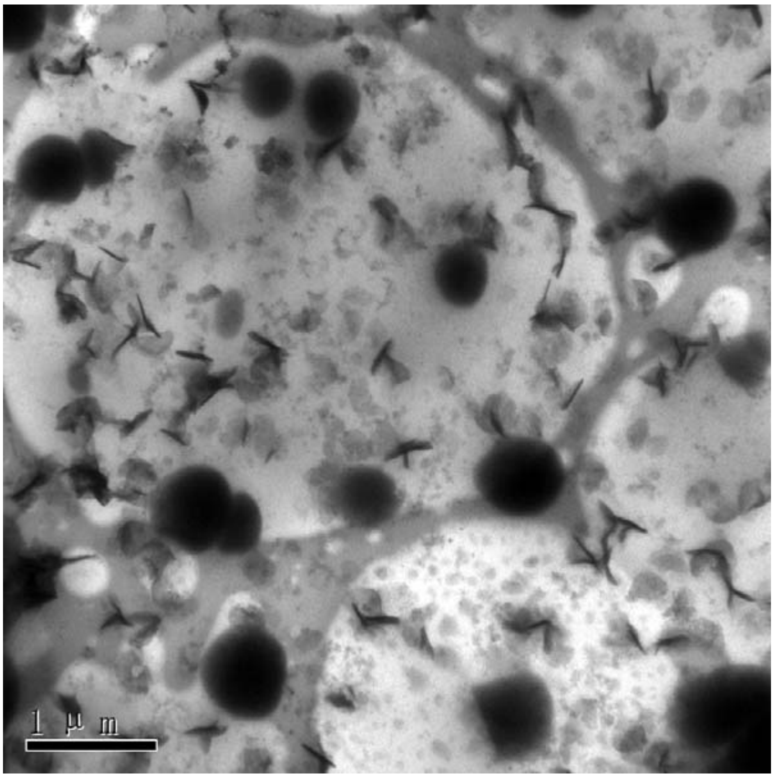
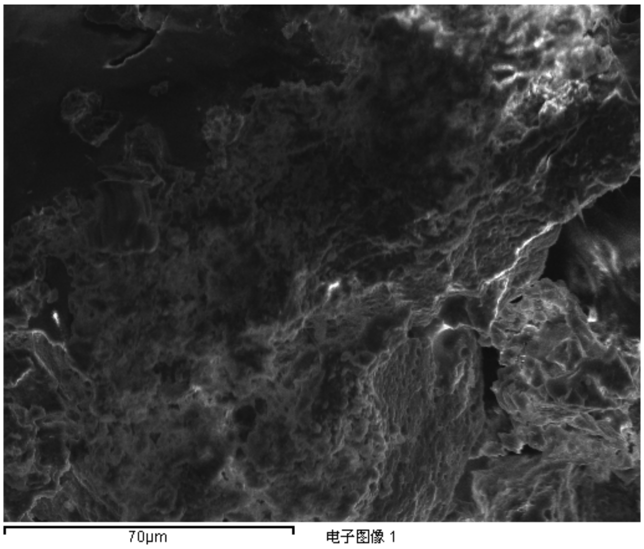
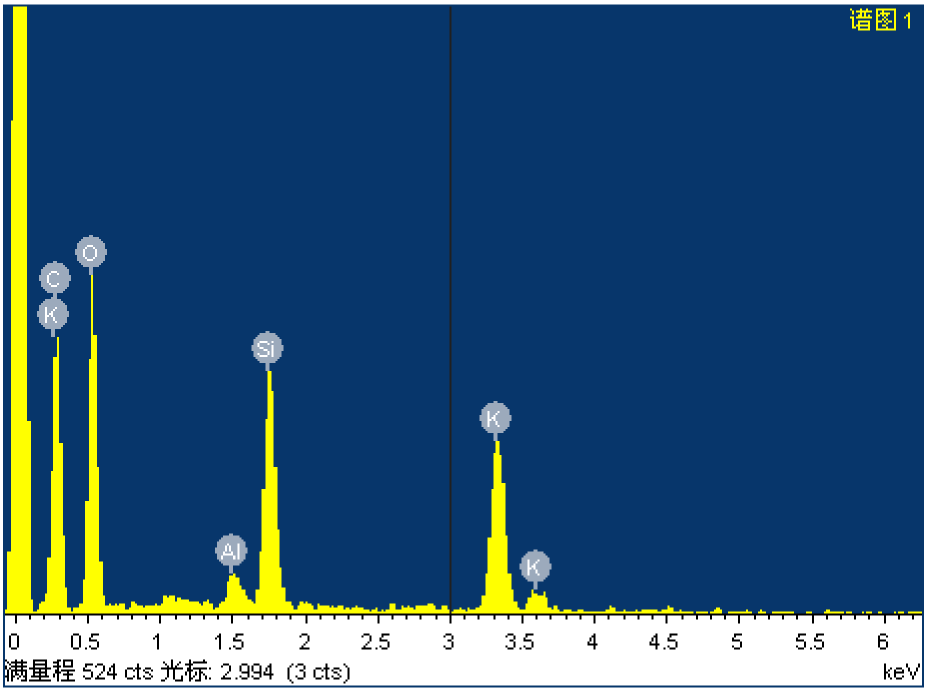


Figure S6. The SEM picture and EDS spectra of palladium/silicone-based PN material

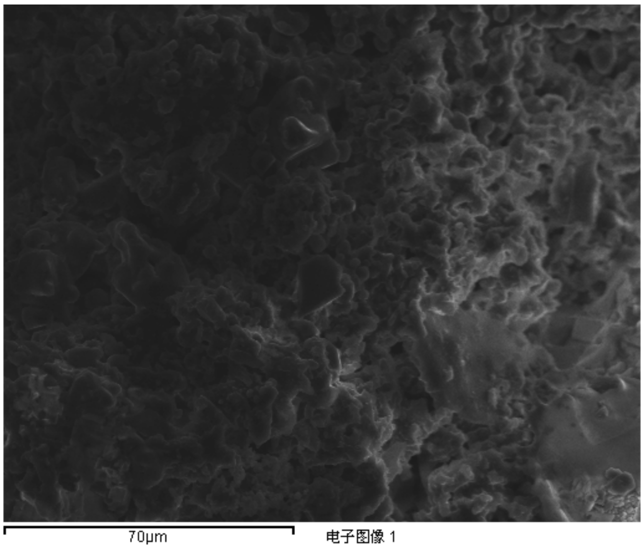
(a) Before reduction (the mixture of $PdCl_2$ + PA semi-IPN material):

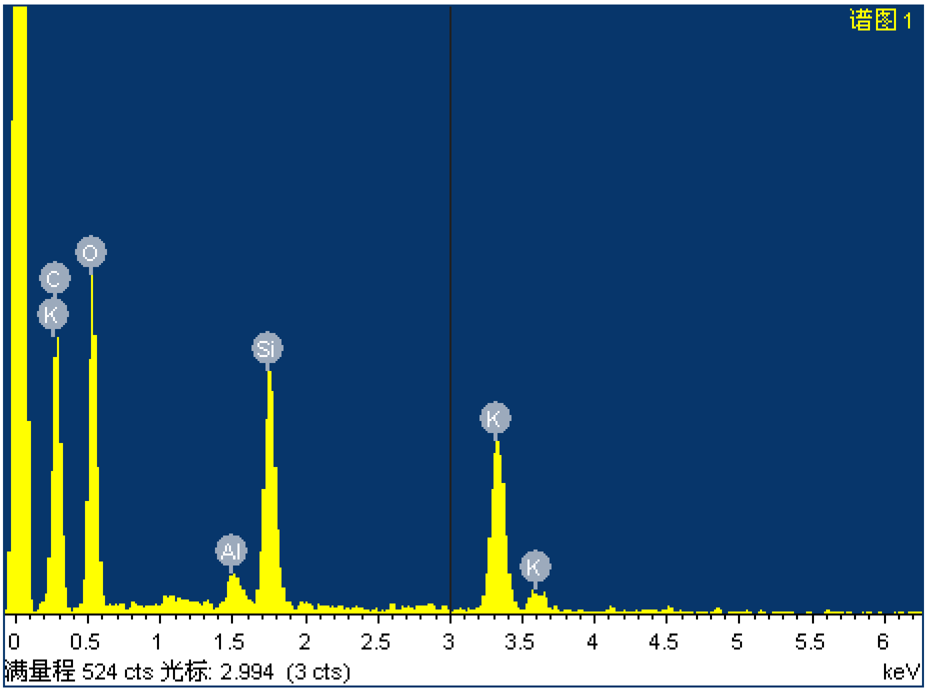
The palladium catalyst embedded in the silicone-based SIPN (**A** catalyst)



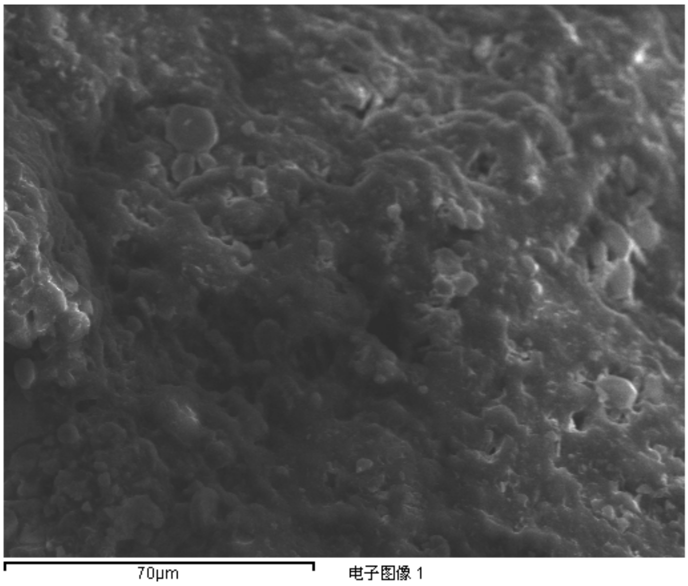


(b) After deoxygenated reduction of aromatic ketones or benzylic alcohols: The palladium catalyst embedded in the silicone-based SIPN (**B** catalyst)





(c) After Suzuki cross-coupling reaction: The palladium catalyst embedded in the silicone-based SIPN (**C** catalyst)



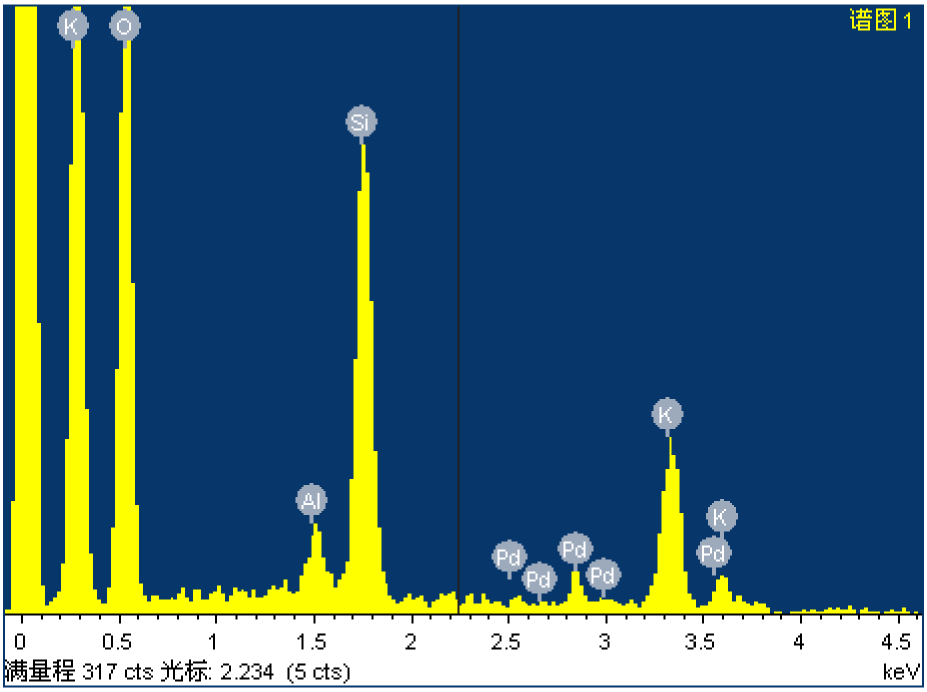
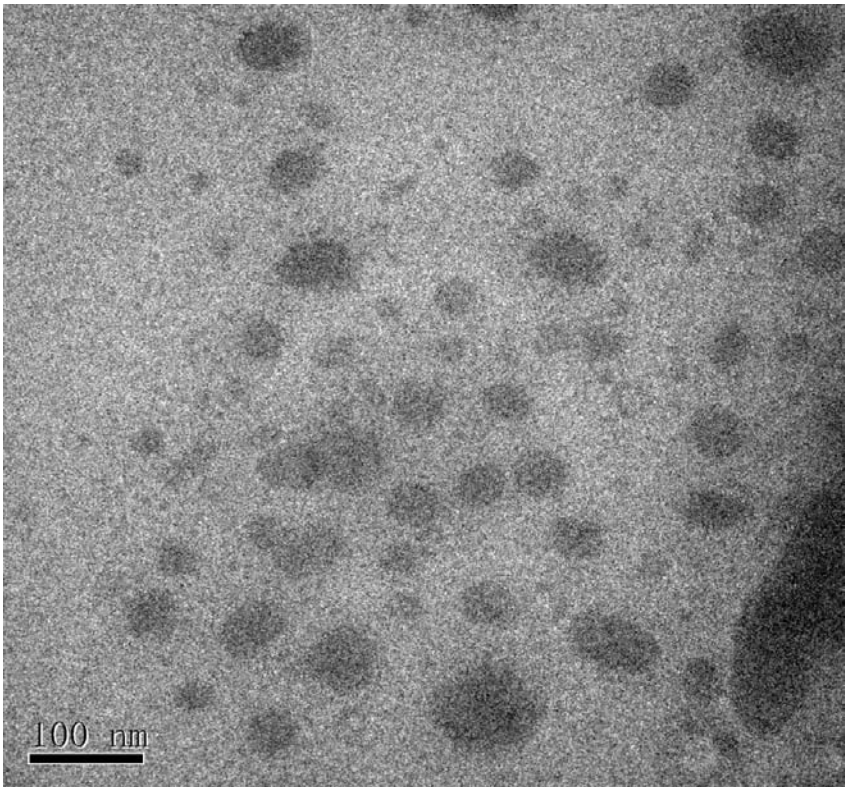
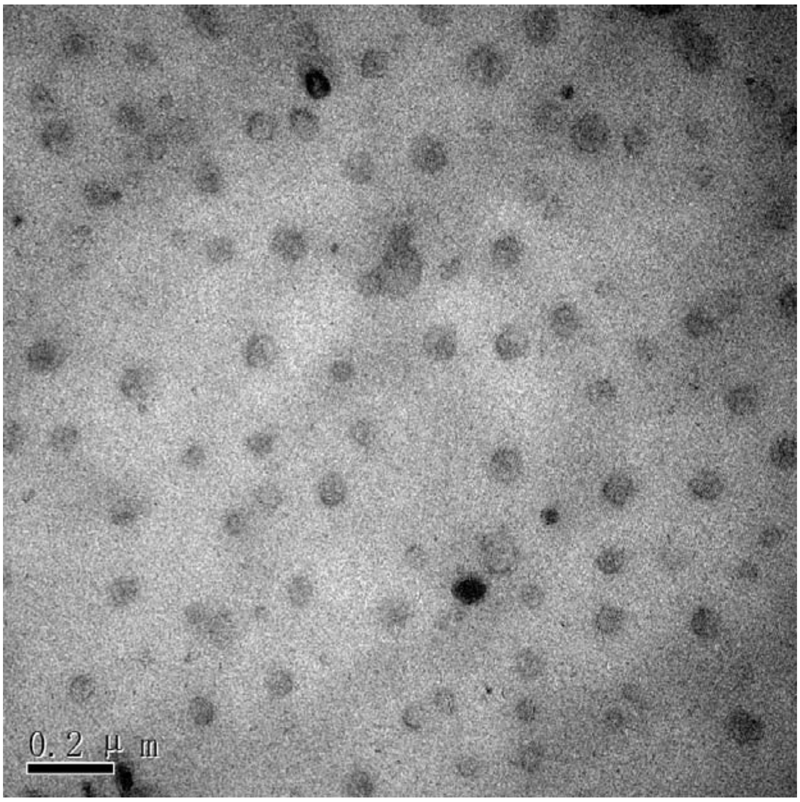
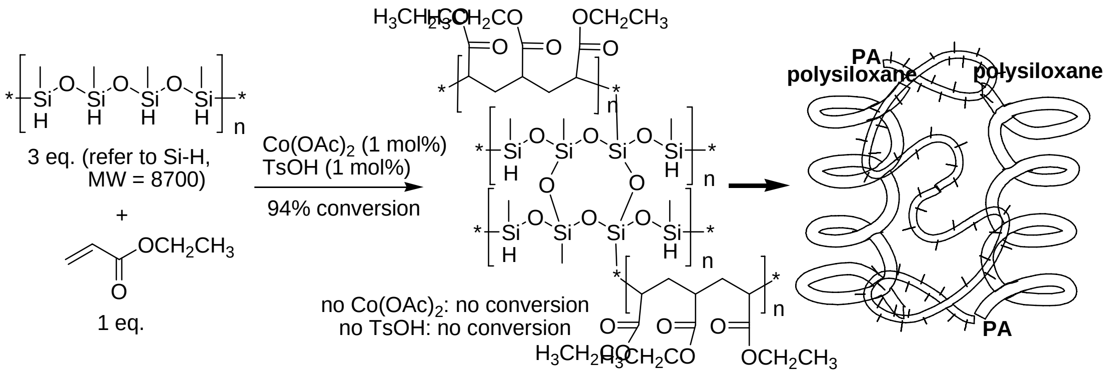


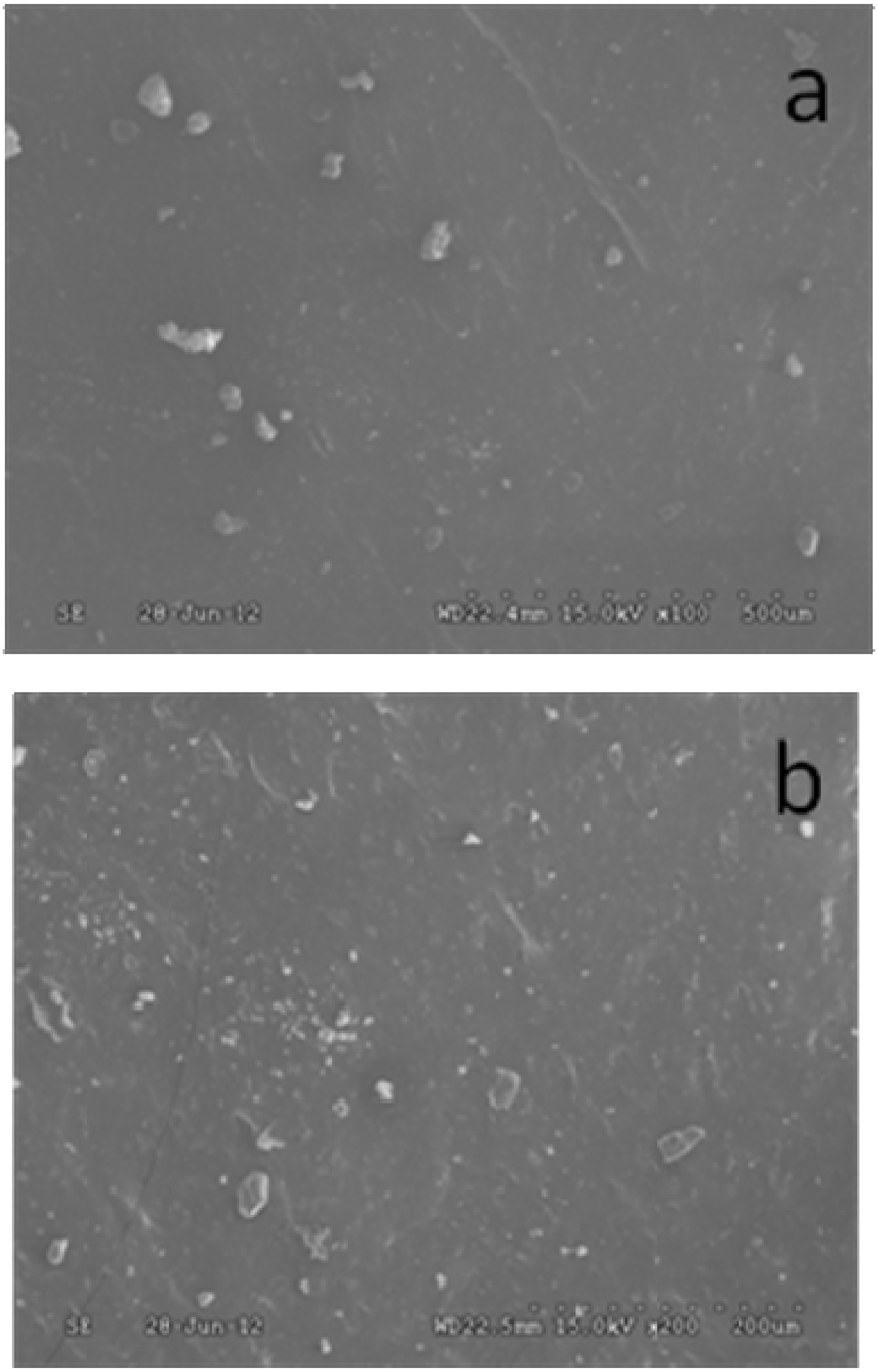
Figure S7. TEM images of the recovered palladium catalyst embedded in the silicone-based SIPN (C catalyst) at the end of the cross-coupling reactions



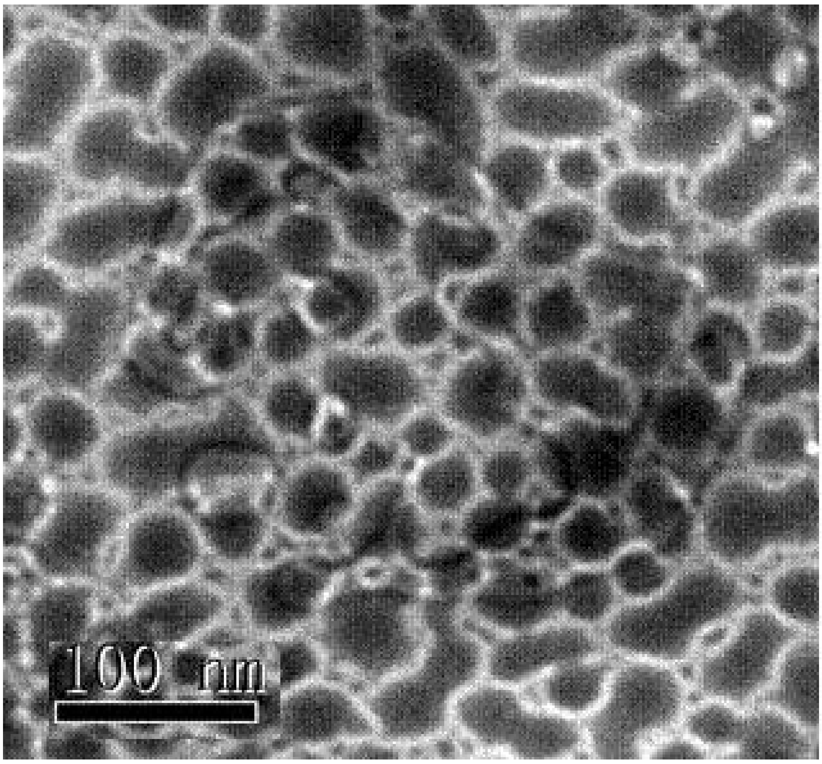


7. The characterization of PMHS/PA-semi-IPN material

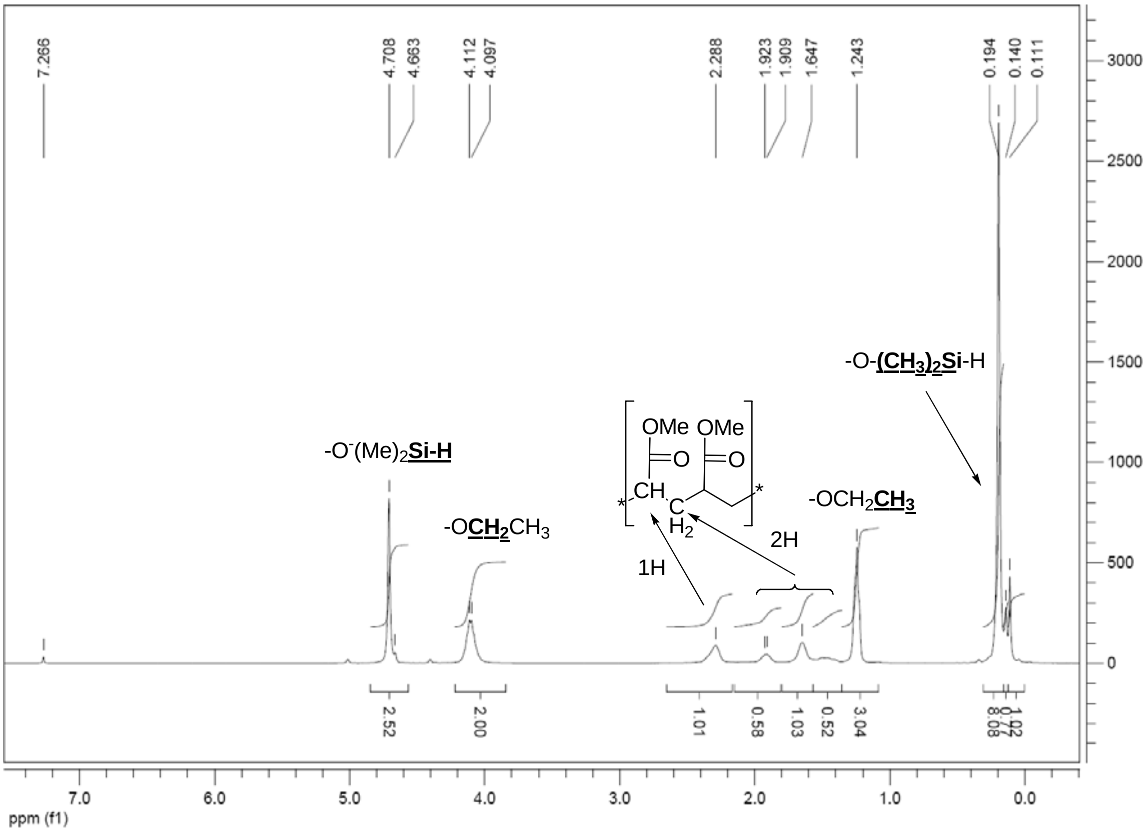




SEM images of the fracture surface of PMHS/PEA SIPN a) ×100 times, b) ×200 times

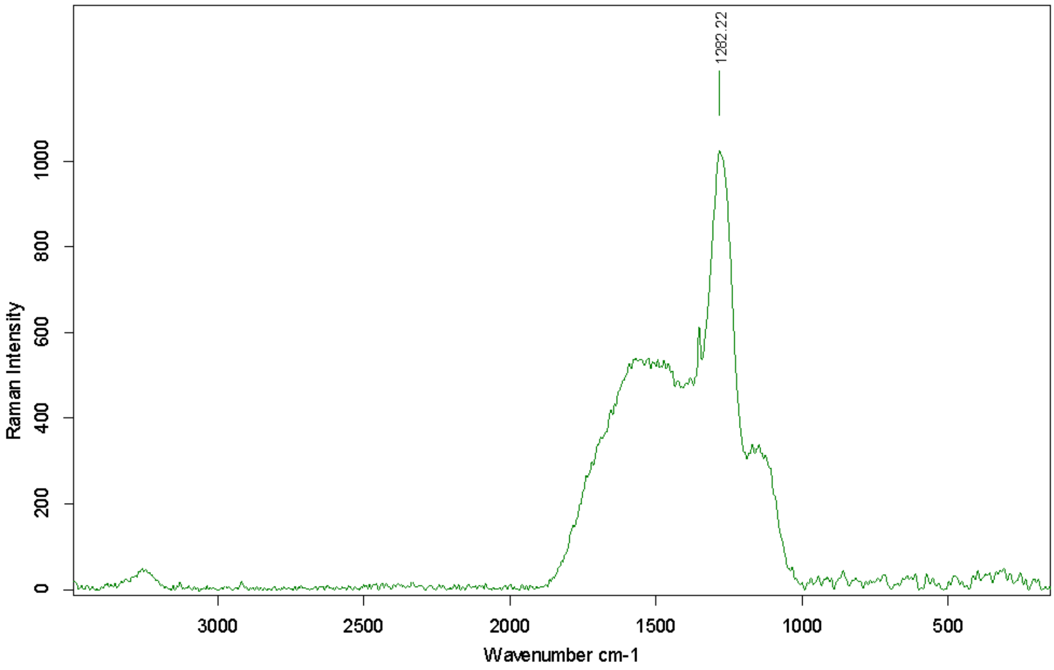


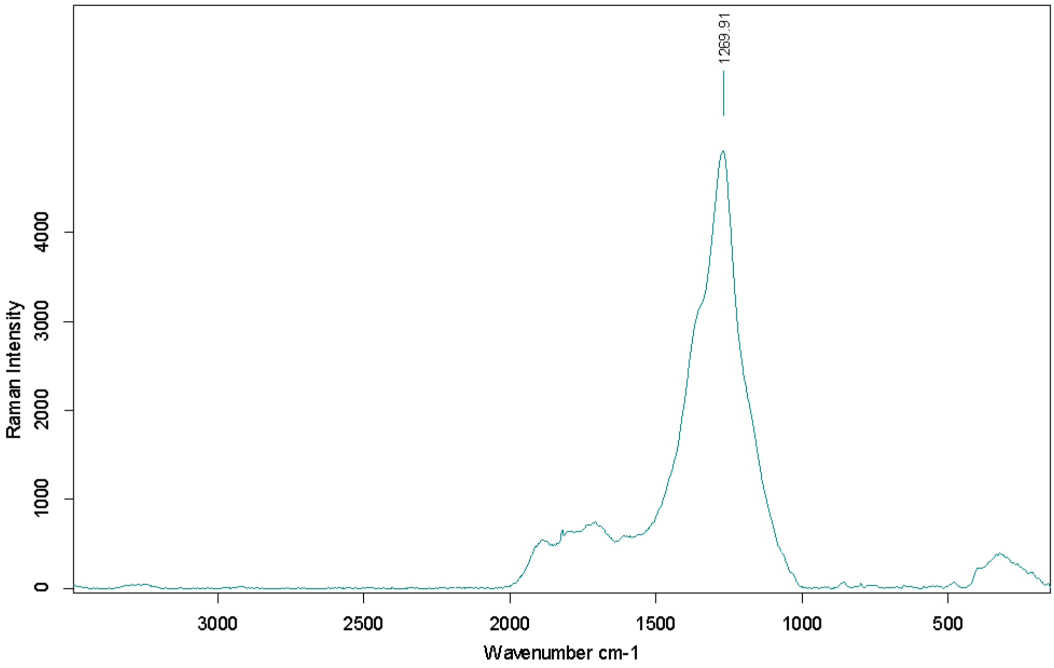
TEM images of PMHS/PEA SIPN



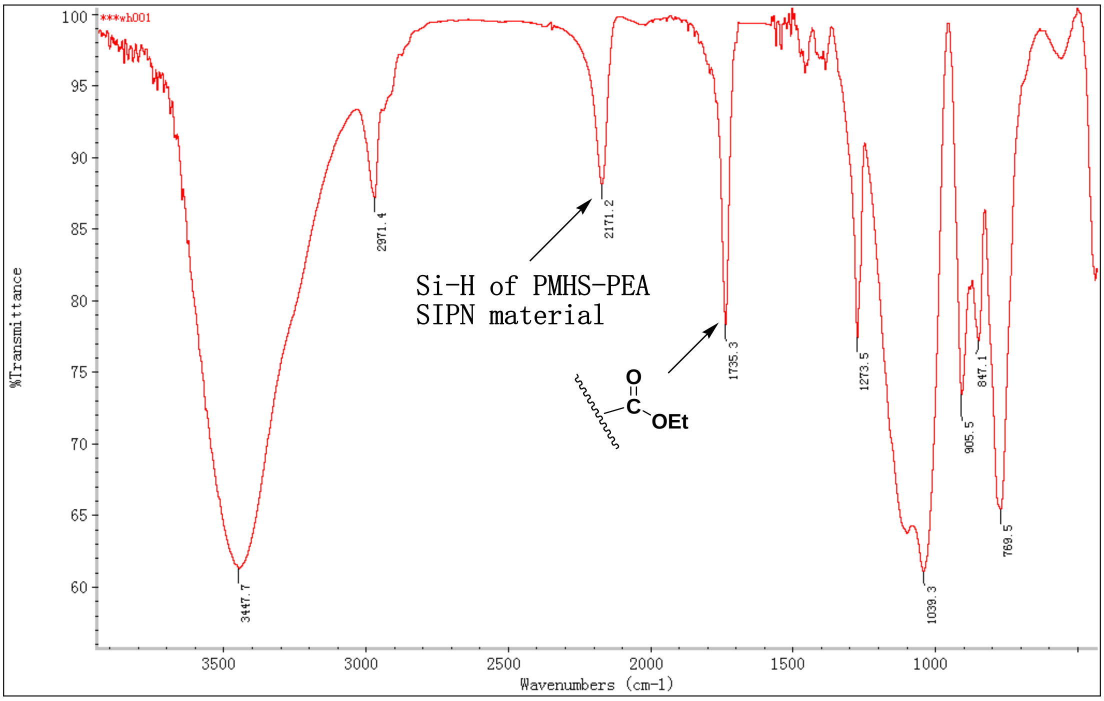
^{1}H NMR spectra of the PHMS/PEA SIPN

8. **The Raman spectra of the palladium@silicone-based SIPNs: The Raman spectrum of the residue of palladium@silicone-based SIPN after the Knoevenagel condensation (down) was similarly to that of palladium catalyst B (up), which revealed there are no obvious changes for the structure of silicone-based SIPNs during these reactions in this work.**

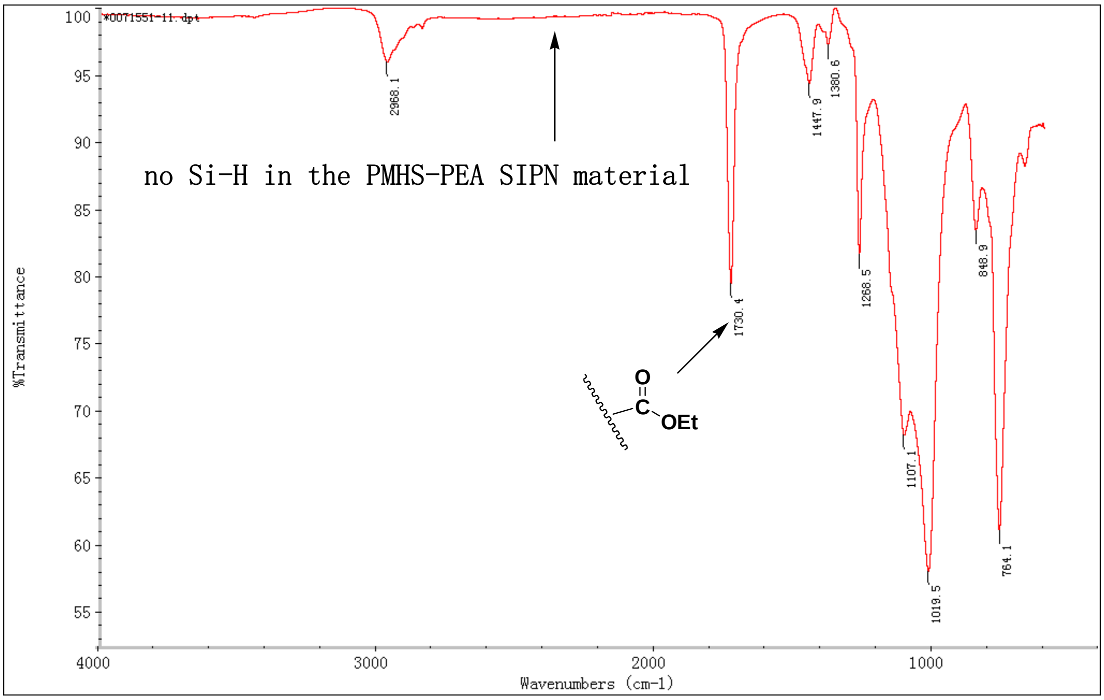




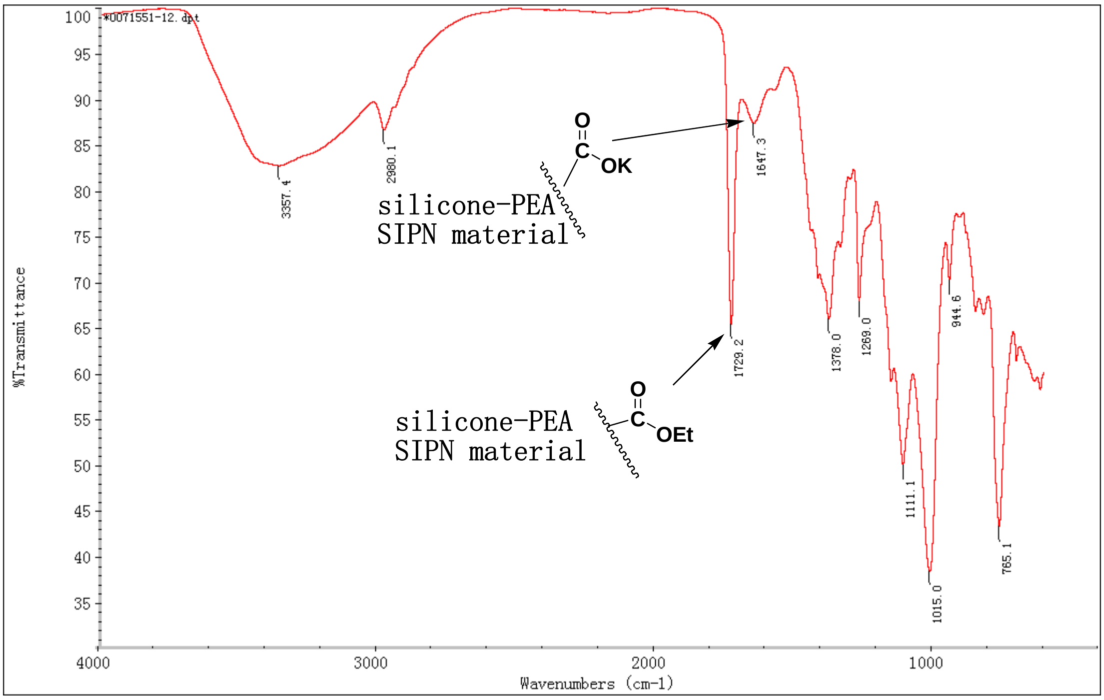
IR spectra of Palladium@silicon-based SIPN material



Pd@silicone-based SIPN before reduction: the solid sample was obtained from mixture of $PdCl_2$ and silicone-based SPIN in MeOH

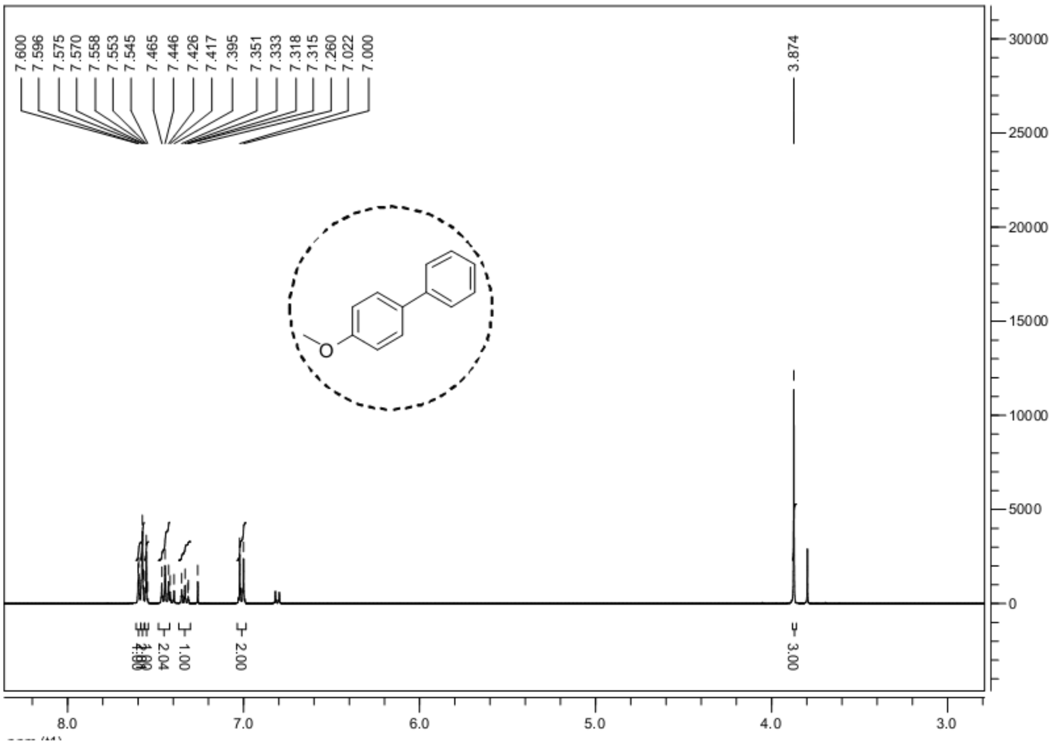


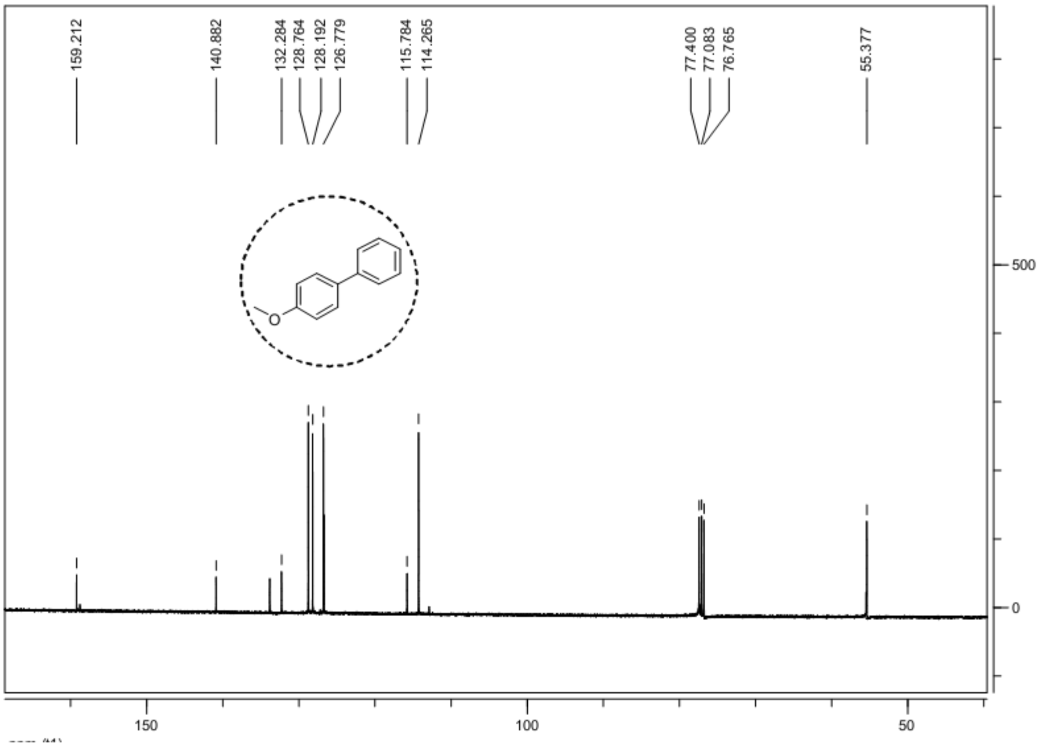
Pd@silicone-based SIPN after reduction or before cross-coupling reaction

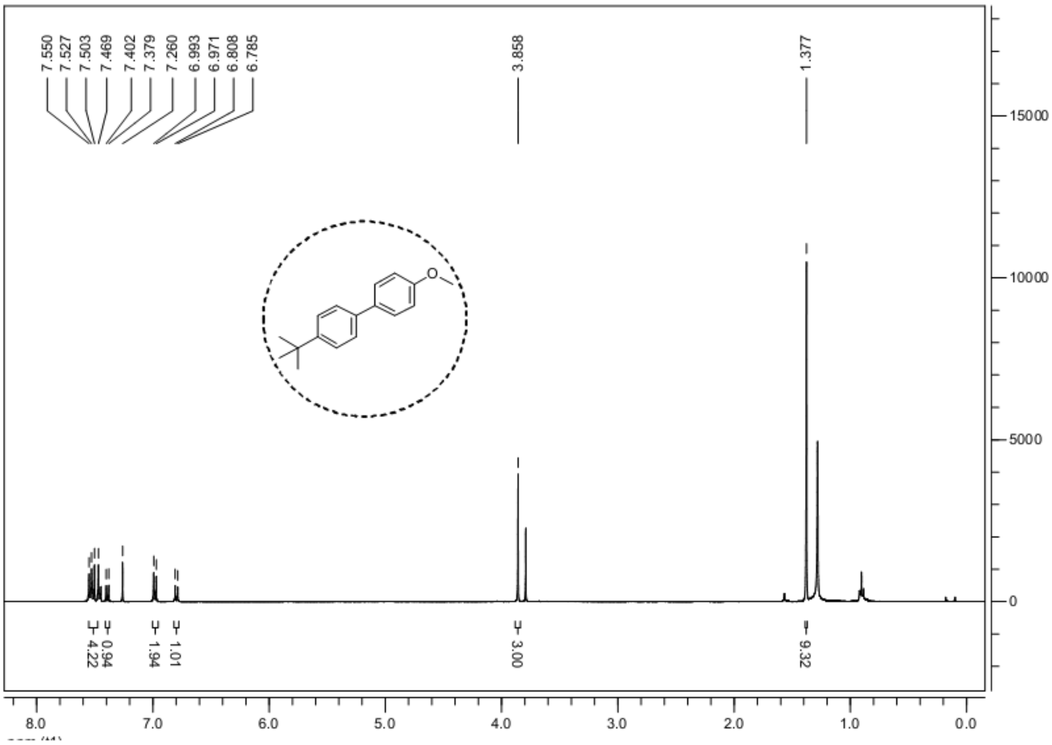


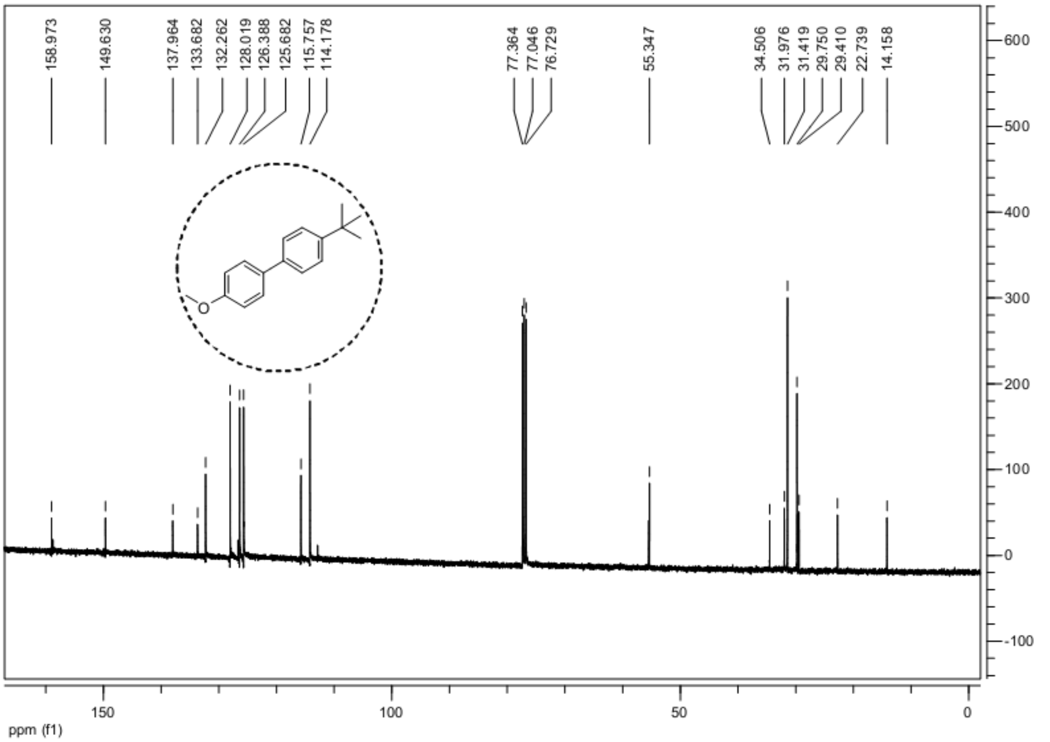
Pd@silicone-based SIPN after cross-coupling reaction

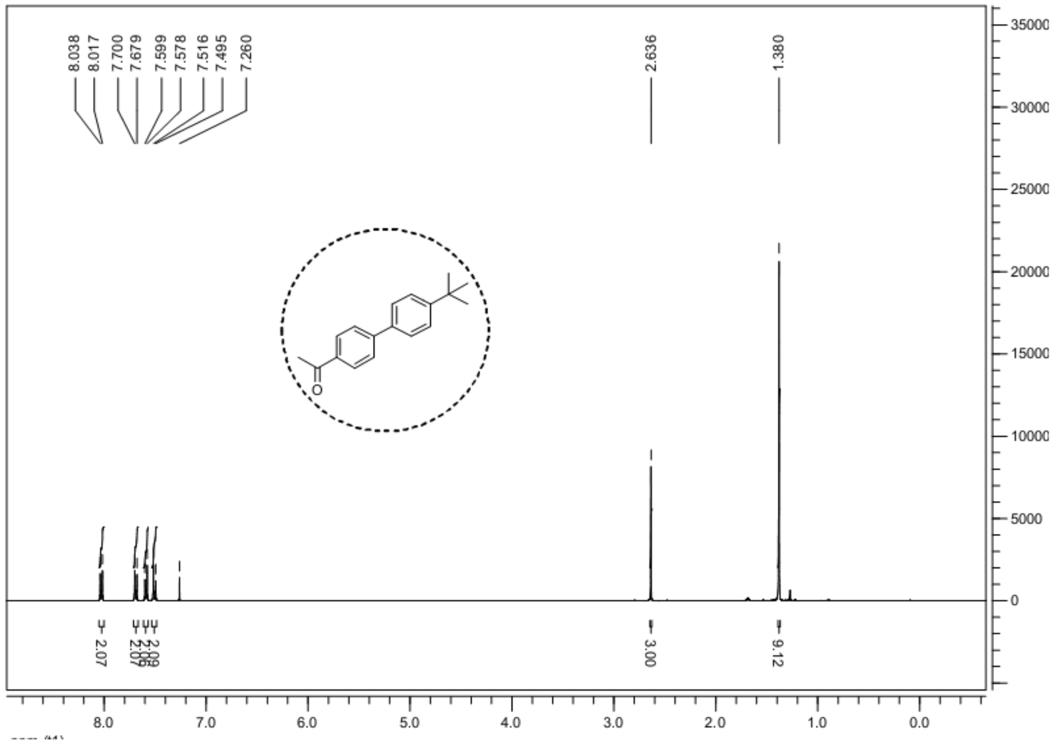
9. ^{1}H-NMR and ^{13}C-NMR spectra

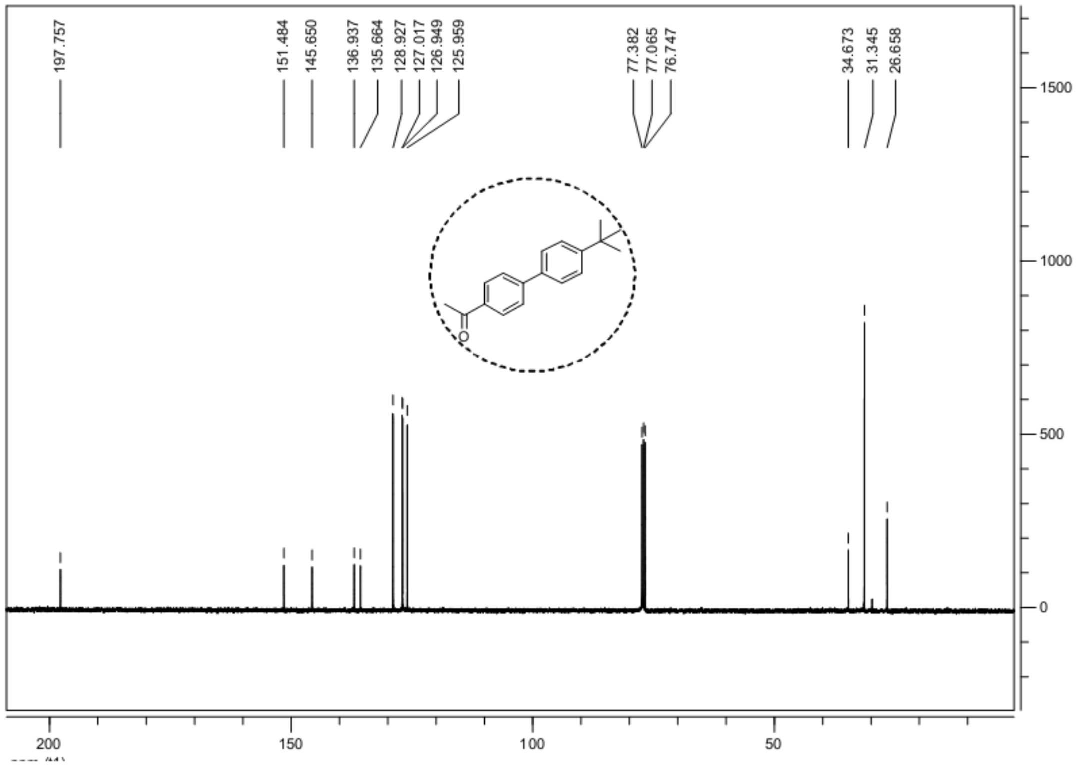


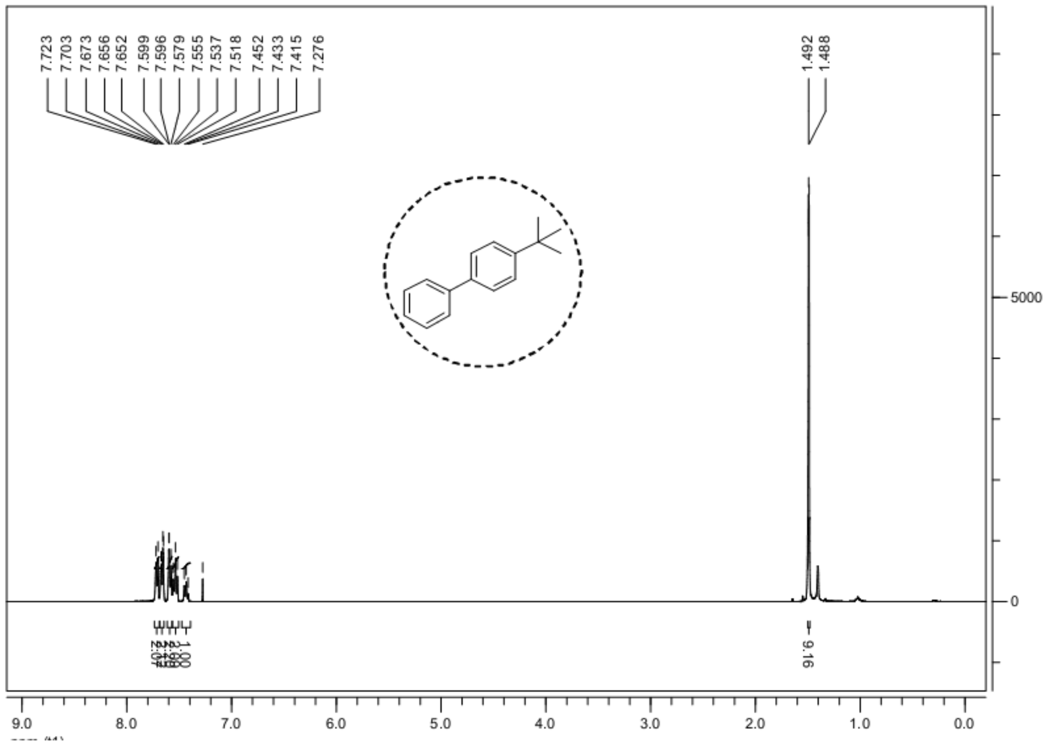


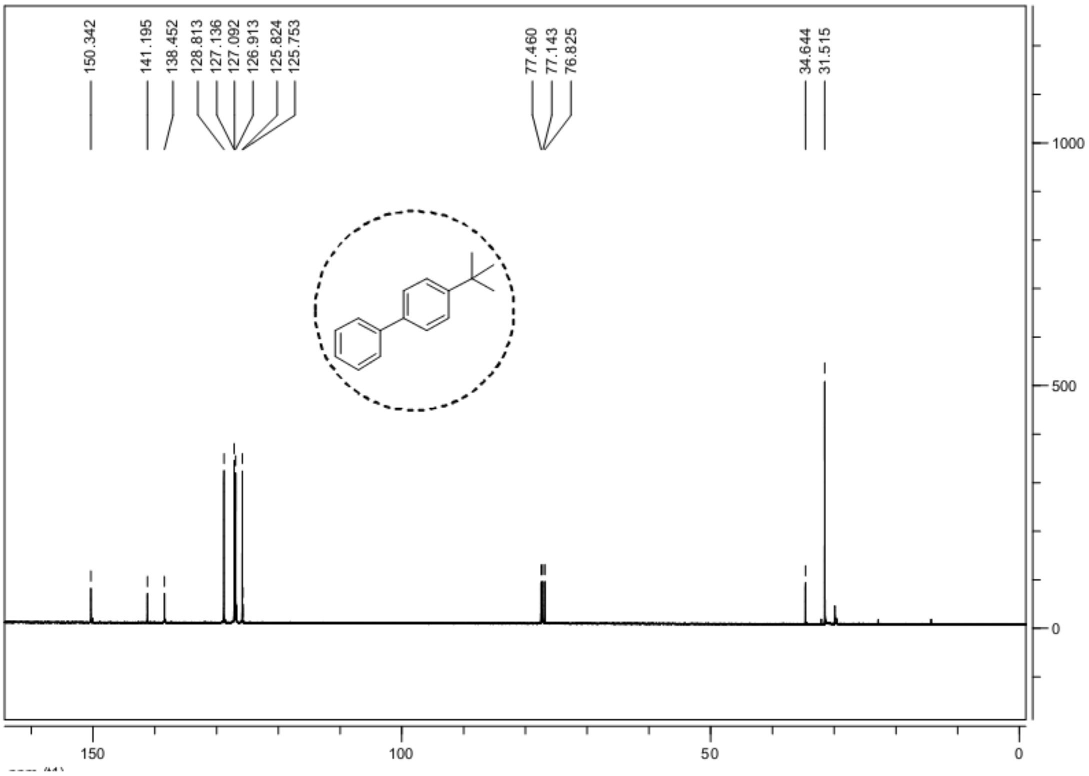

7.550
7.527
7.503
7.469
7.402
7.379
7.260
6.993
6.971
6.808
6.785
3.858
1.377
O
4.22
0.94
1.94
1.01
3.00
9.32
15000
10000
5000
0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0

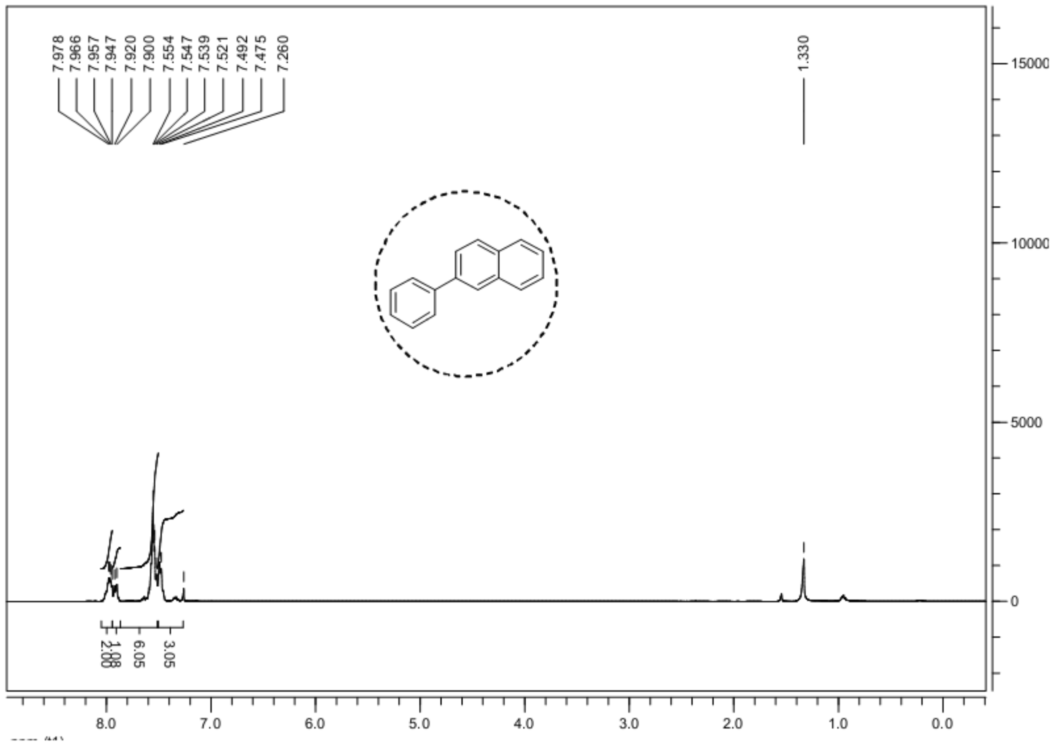

158.973
149.630
137.964
133.682
132.262
128.019
126.388
125.682
115.757
114.178
77.364
77.046
76.729
55.347
34.506
31.976
31.419
29.750
29.410
22.739
14.158
O
600
500
400
300
200
100
0
-100
150
100
50
0
ppm (f1)

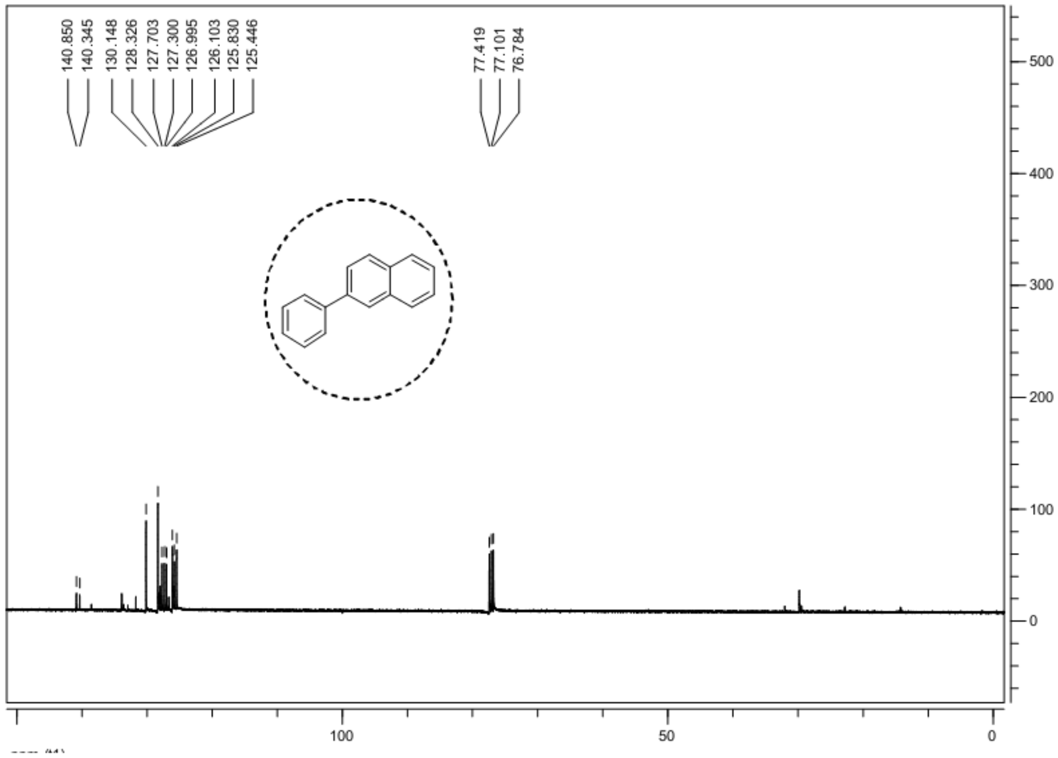

8.038
8.017
7.700
7.679
7.599
7.578
7.516
7.495
7.260
2.636
1.380
2.07
2.07
2.06
2.09
3.00
9.12
O
35000
30000
25000
20000
15000
10000
5000
0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0

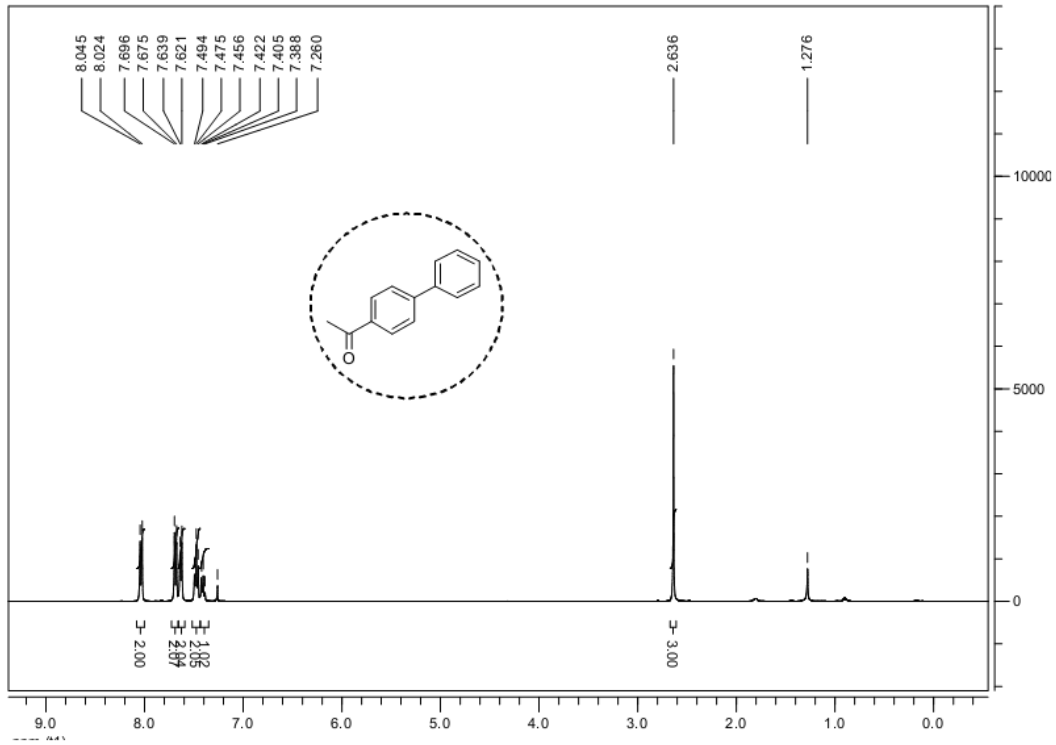

197.757
151.484
145.650
136.937
135.664
128.927
127.017
126.949
125.959
77.382
77.065
76.747
34.673
31.345
26.658
O
1500
1000
500
0
200
150
100
50

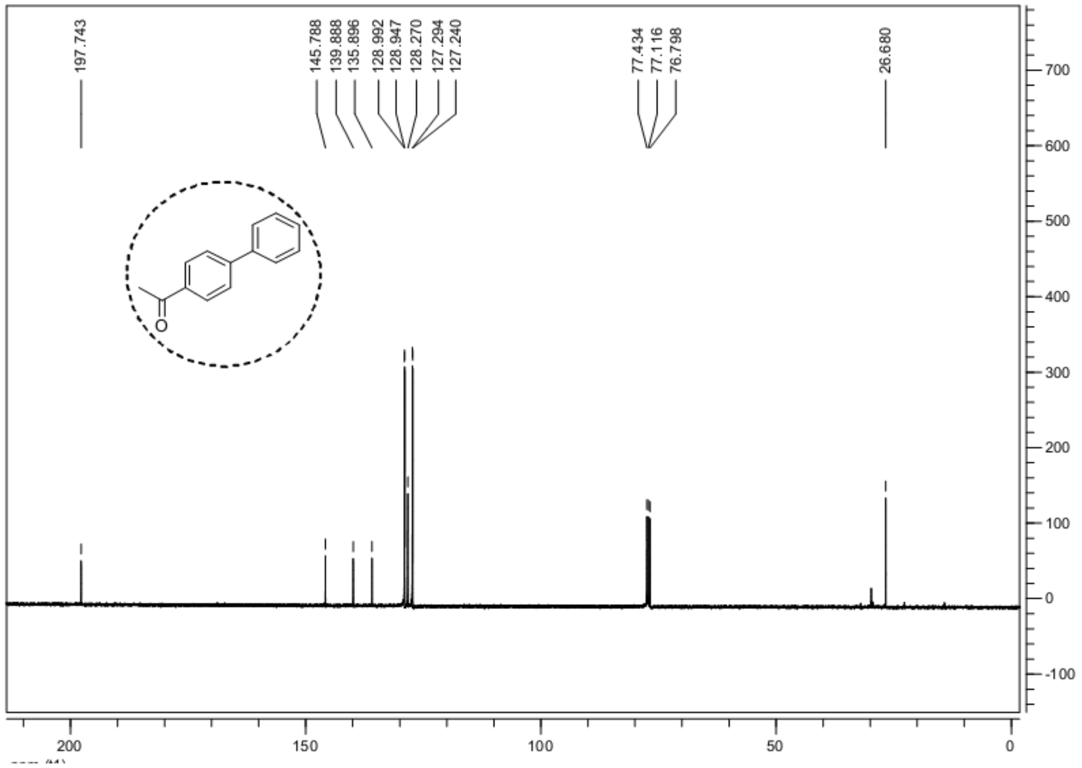

7.723
7.703
7.673
7.656
7.652
7.599
7.596
7.579
7.555
7.537
7.518
7.452
7.433
7.415
7.276
1.492
1.488
2.07
1.00
9.16
5000
0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0

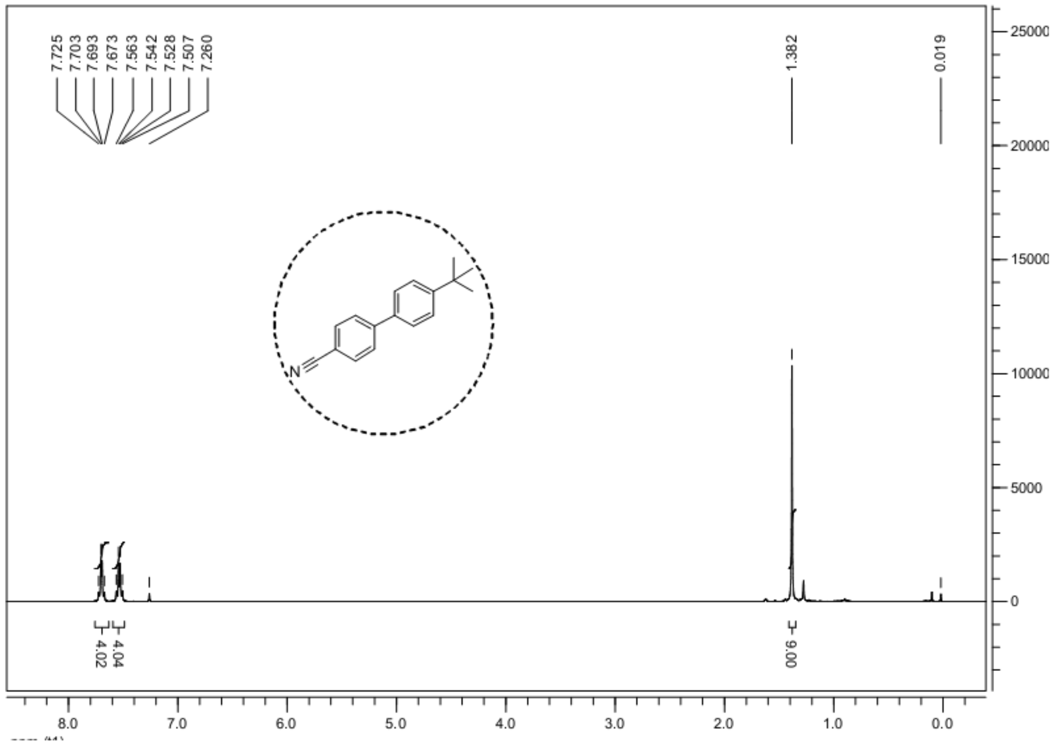

150.342
141.195
138.452
128.813
127.136
127.092
126.913
125.824
125.753
77.460
77.143
76.825
34.644
31.515
1000
500
0
150
100
50
0

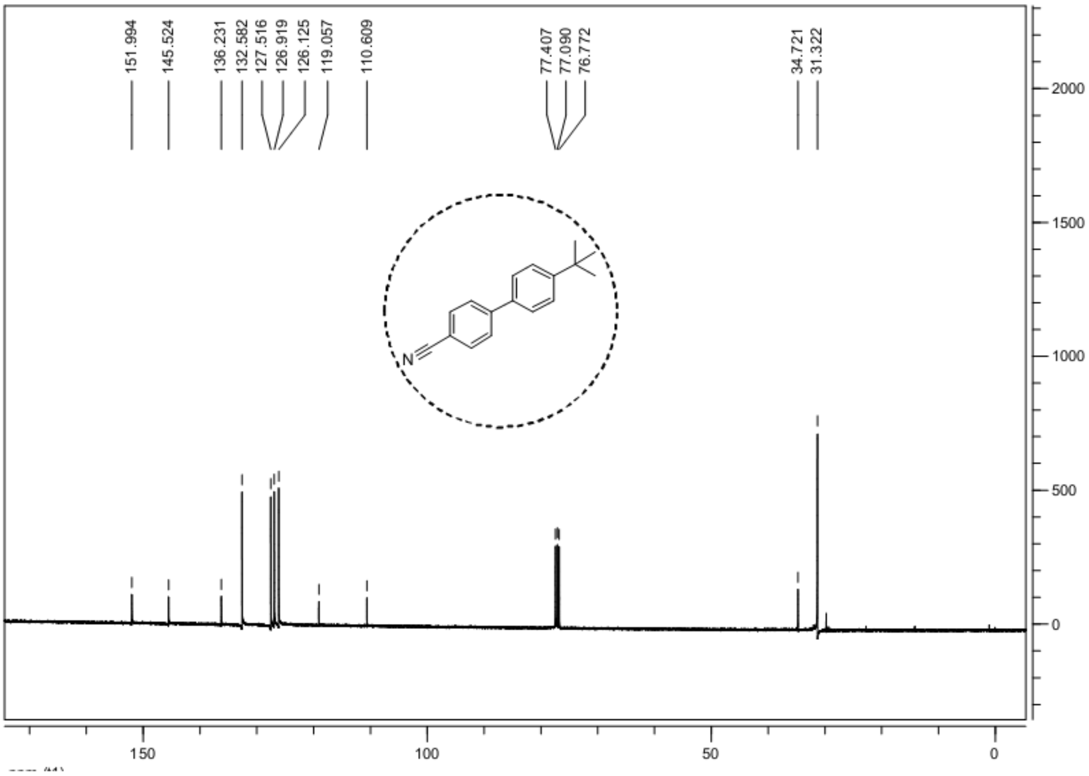

7.978
7.966
7.957
7.947
7.920
7.900
7.554
7.547
7.539
7.521
7.492
7.475
7.260
1.330
15000
10000
5000
0
2.00
1.08
6.05
3.05
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0

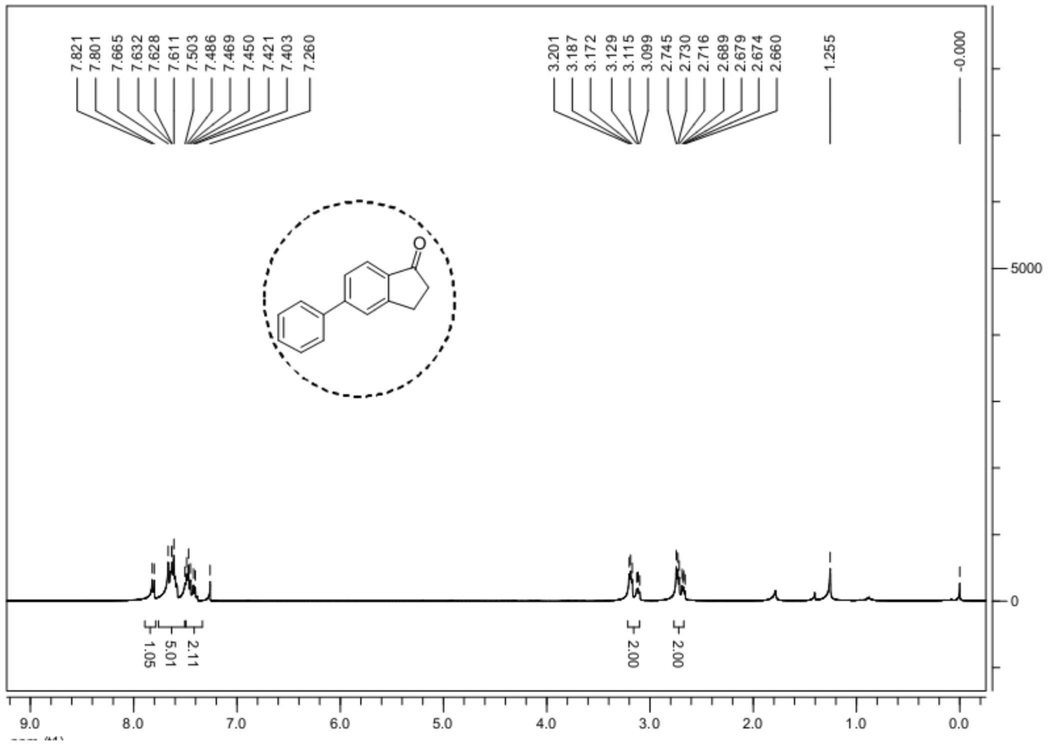

140.850
140.345
130.148
128.326
127.703
127.300
126.995
126.103
125.830
125.446
77.419
77.101
76.784
500
400
300
200
100
0
100
50
0

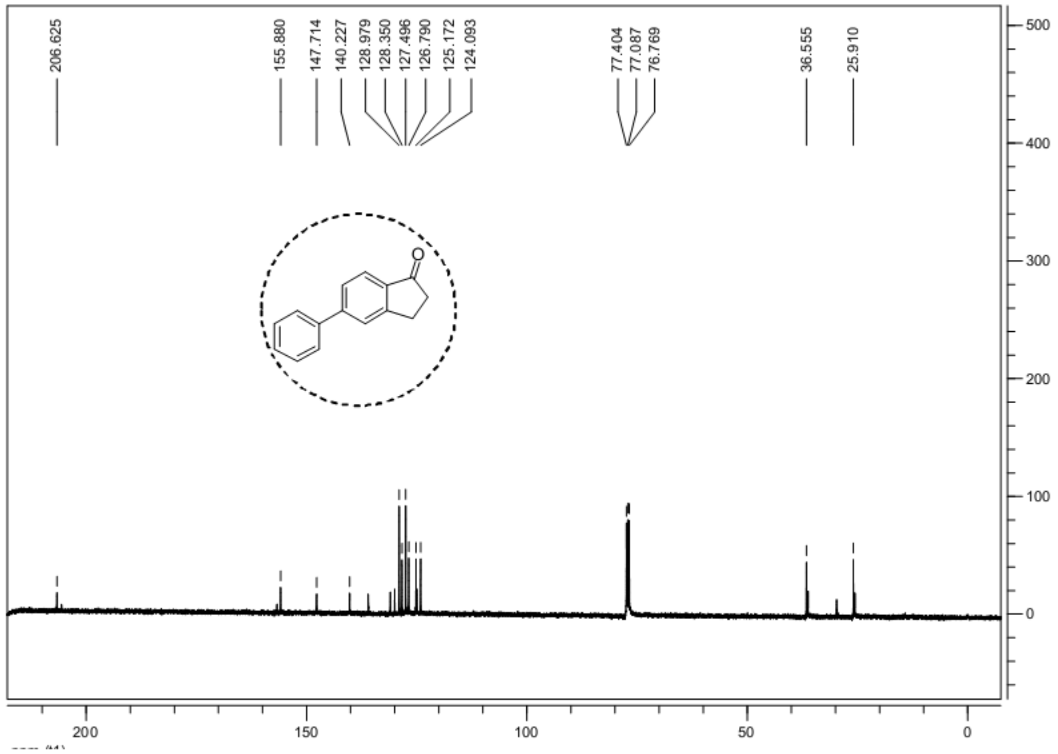

8.045
8.024
7.696
7.675
7.639
7.621
7.494
7.475
7.456
7.422
7.405
7.388
7.260
2.636
1.276
O
2.00
2.07
2.04
2.05
1.02
3.00
10000
5000
0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0

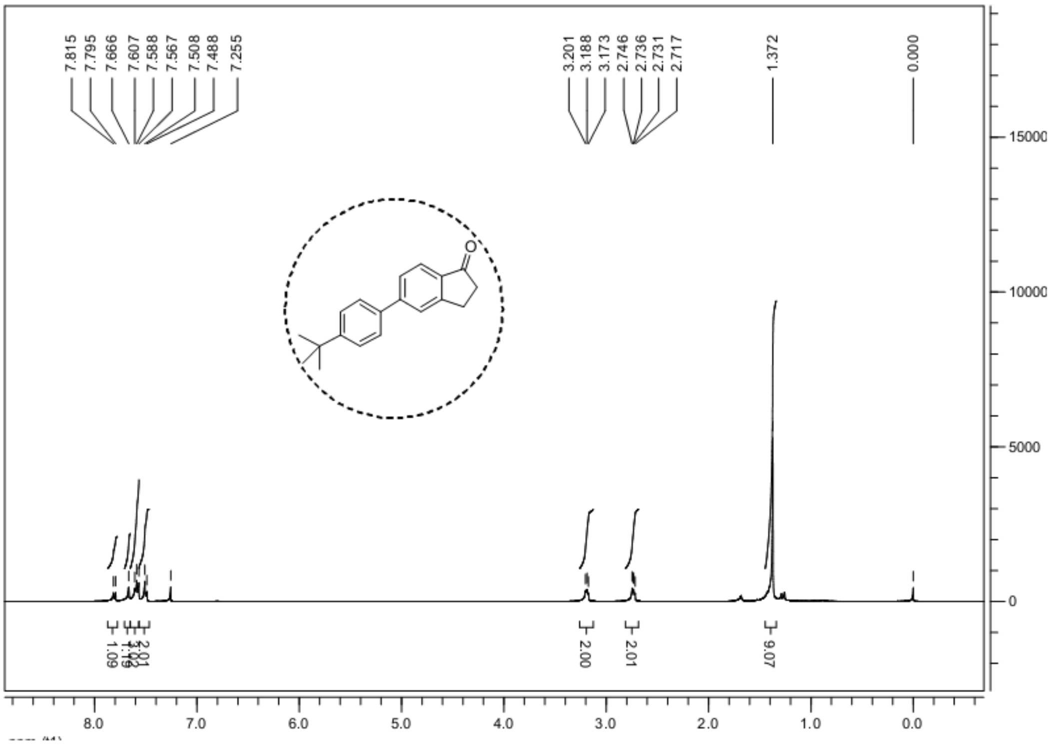

197.743
145.788
139.888
135.896
128.992
128.947
128.270
127.294
127.240
77.434
77.116
76.798
26.680
O
700
600
500
400
300
200
100
0
-100
200
150
100
50
0

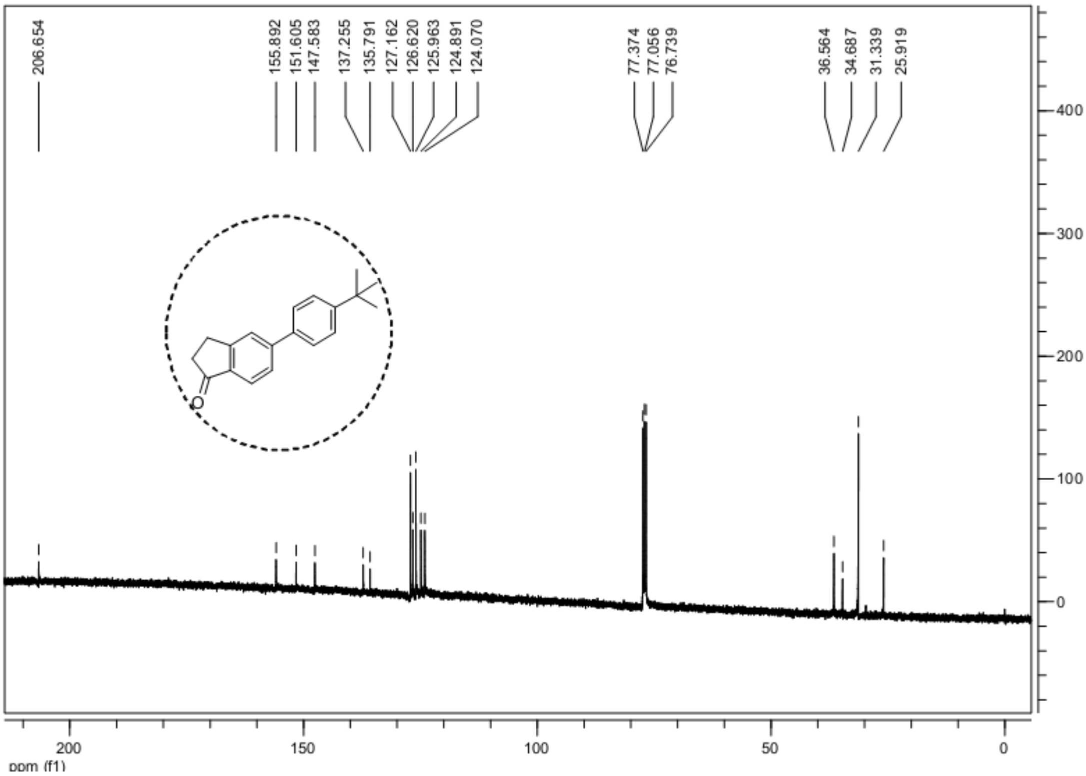

7.725
7.703
7.693
7.673
7.563
7.542
7.528
7.507
7.260
1.382
0.019
N
4.02
4.04
9.00
25000
20000
15000
10000
5000
0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0

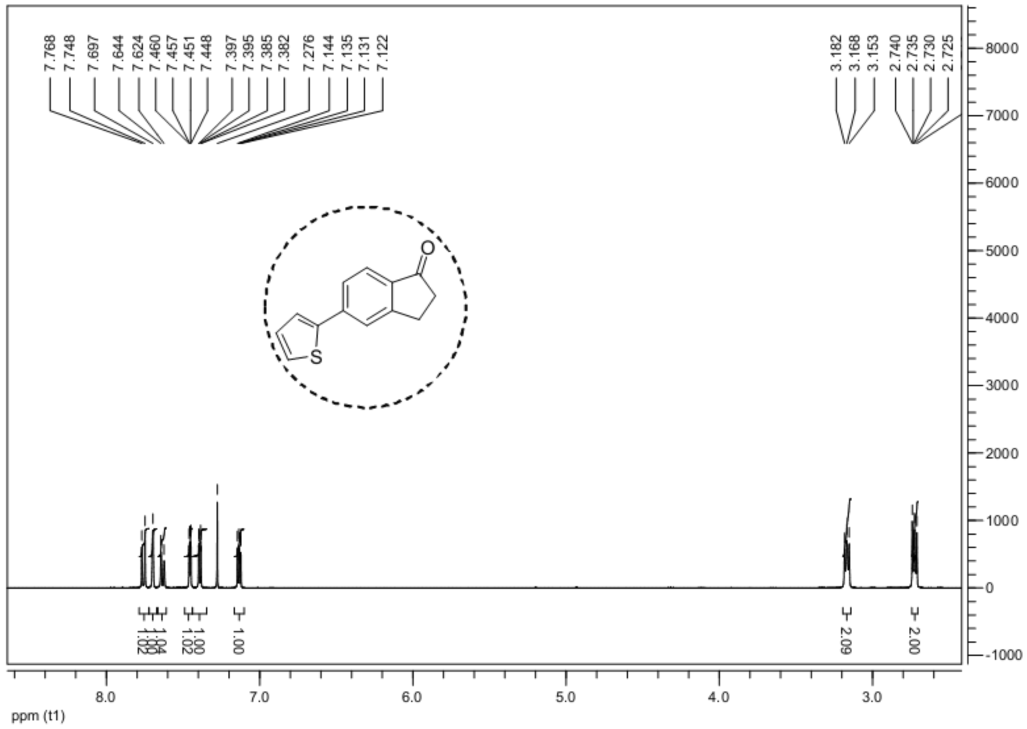

151.994
145.524
136.231
132.582
127.516
126.919
126.125
119.057
110.609
77.407
77.090
76.772
34.721
31.322
N
2000
1500
1000
500
0
150
100
50
0

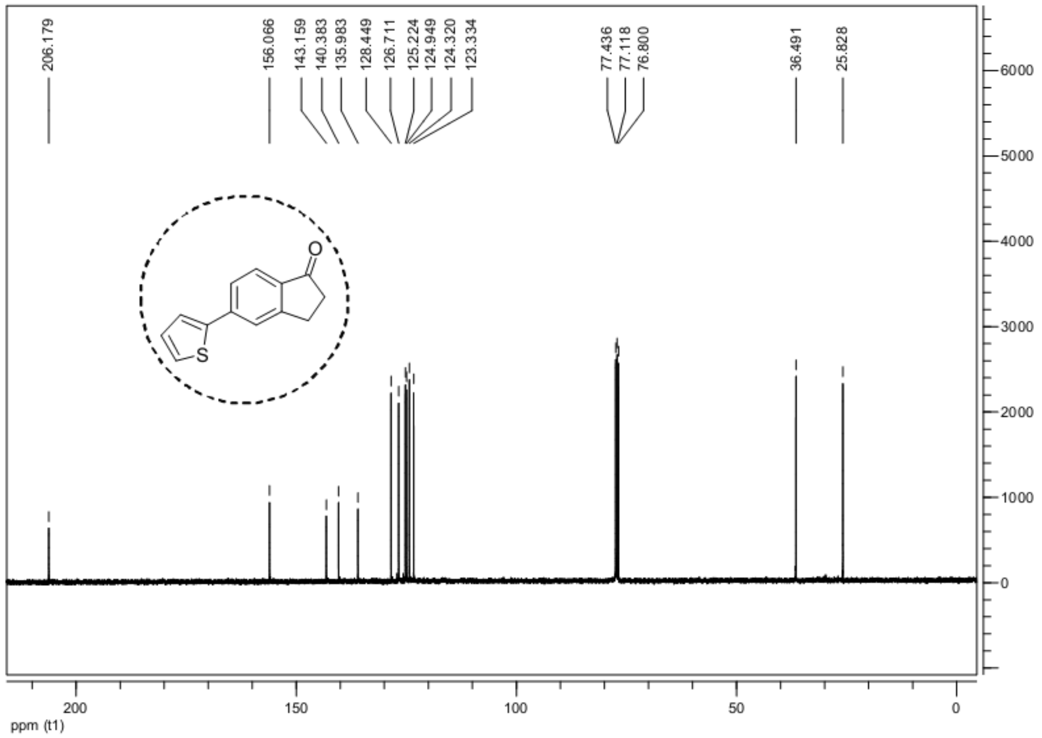

7.821
7.801
7.665
7.632
7.628
7.611
7.503
7.486
7.469
7.450
7.421
7.403
7.260
3.201
3.187
3.172
3.129
3.115
3.099
2.745
2.730
2.716
2.689
2.679
2.674
2.660
1.255
-0.000
O
5000
0
1.05
5.01
2.11
2.00
2.00
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0

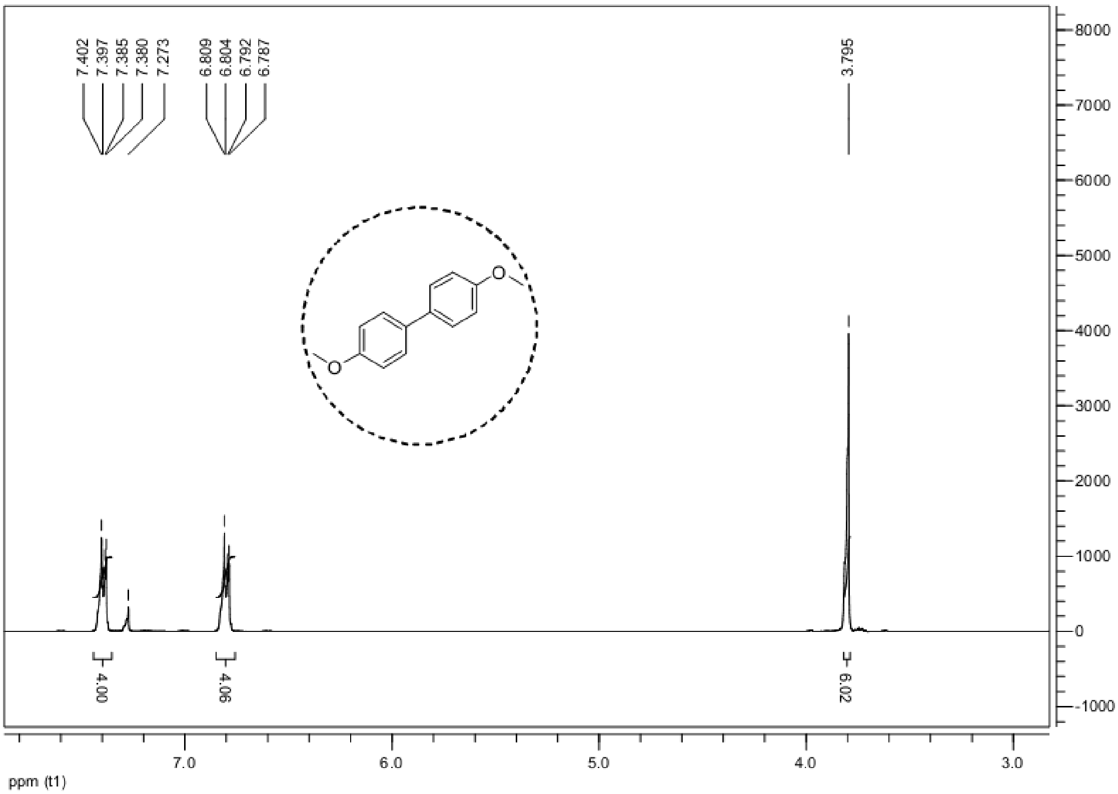

206.625
155.880
147.714
140.227
128.979
128.350
127.496
126.790
125.172
124.093
77.404
77.087
76.769
36.555
25.910
O
500
400
300
200
100
0
200
150
100
50
0

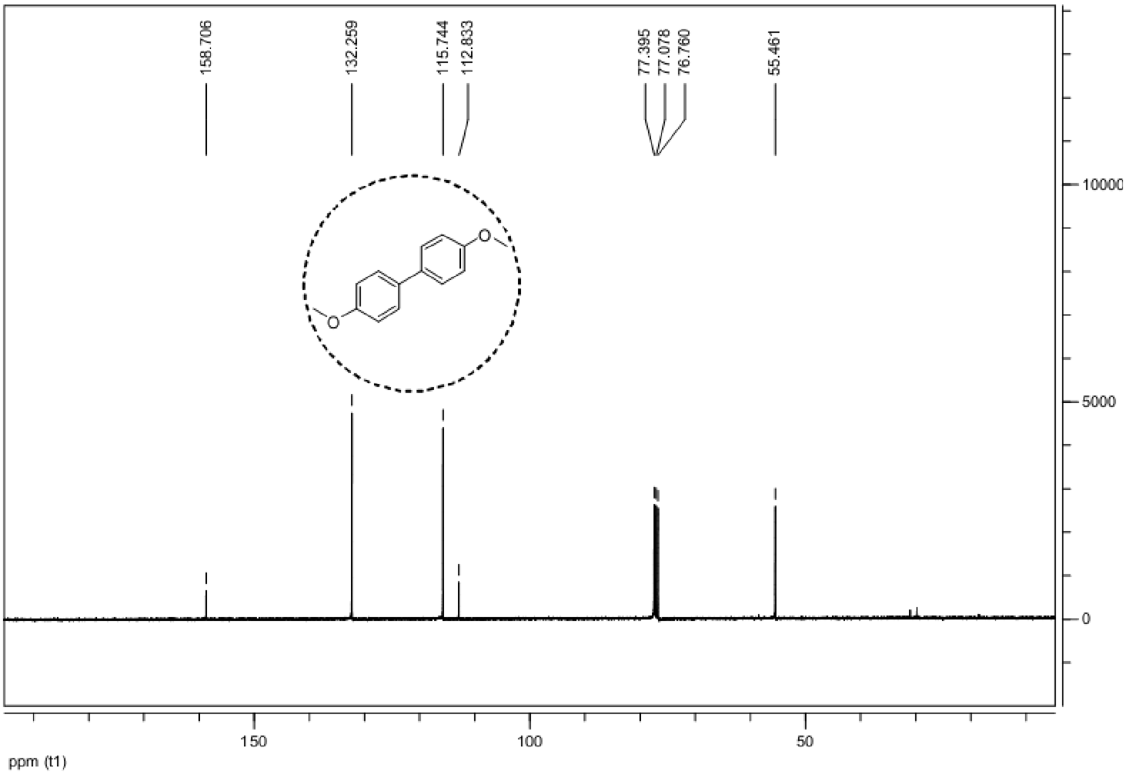

7.815
7.795
7.666
7.607
7.588
7.567
7.508
7.488
7.255
3.201
3.188
3.173
2.746
2.736
2.731
2.717
1.372
0.000
15000
10000
5000
0
O
1.09
3.02
2.01
2.00
2.01
9.07
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0

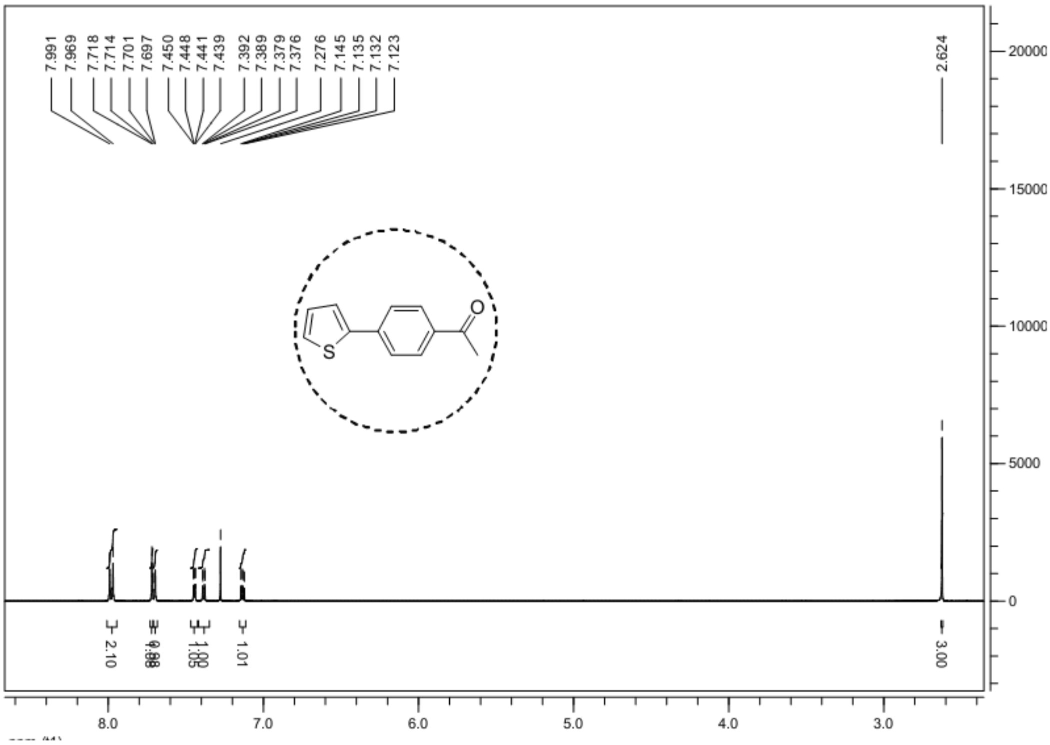

206.654
155.892
151.605
147.583
137.255
135.791
127.162
126.620
125.963
124.891
124.070
77.374
77.056
76.739
36.564
34.687
31.339
25.919
400
300
200
100
0
O
200
150
100
50
0
ppm (f1)

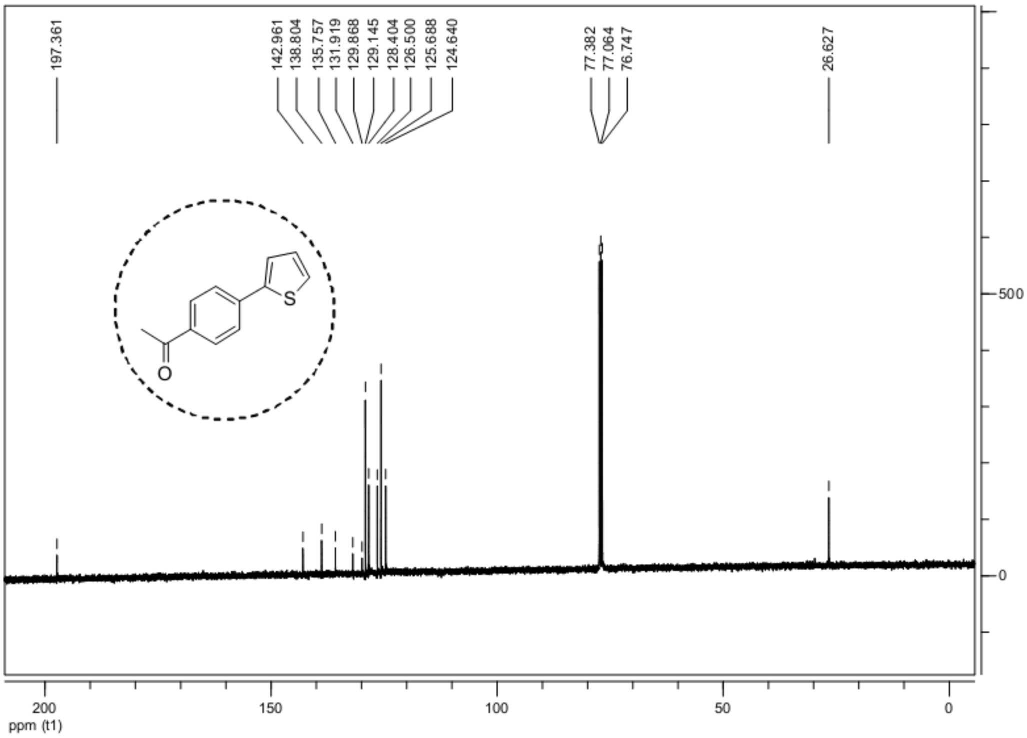

7.768
7.748
7.697
7.644
7.624
7.460
7.457
7.451
7.448
7.397
7.395
7.385
7.382
7.276
7.144
7.135
7.131
7.122
3.182
3.168
3.153
2.740
2.735
2.730
2.725
O
S
1.02
1.04
1.00
1.02
1.00
2.09
2.00
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
8.0
7.0
6.0
5.0
4.0
3.0
ppm (t1)

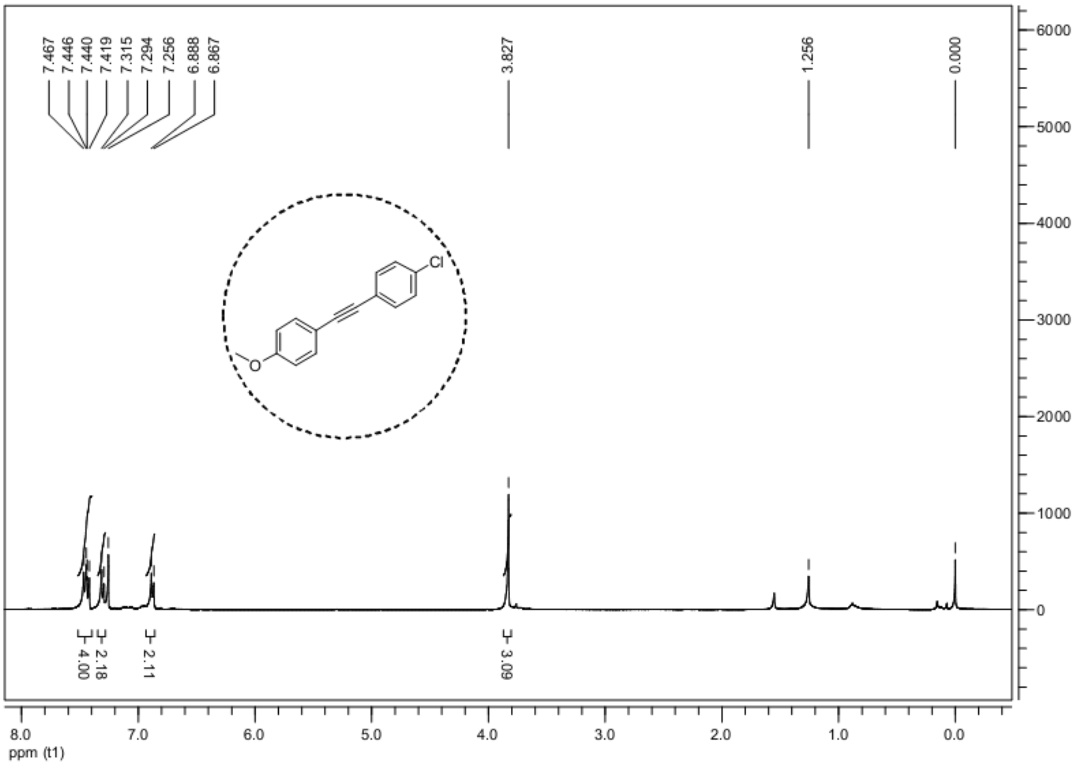

206.179
156.066
143.159
140.383
135.983
128.449
126.711
125.224
124.949
124.320
123.334
77.436
77.118
76.800
36.491
25.828
O
S
6000
5000
4000
3000
2000
1000
0
200
150
100
50
0
ppm (t1)

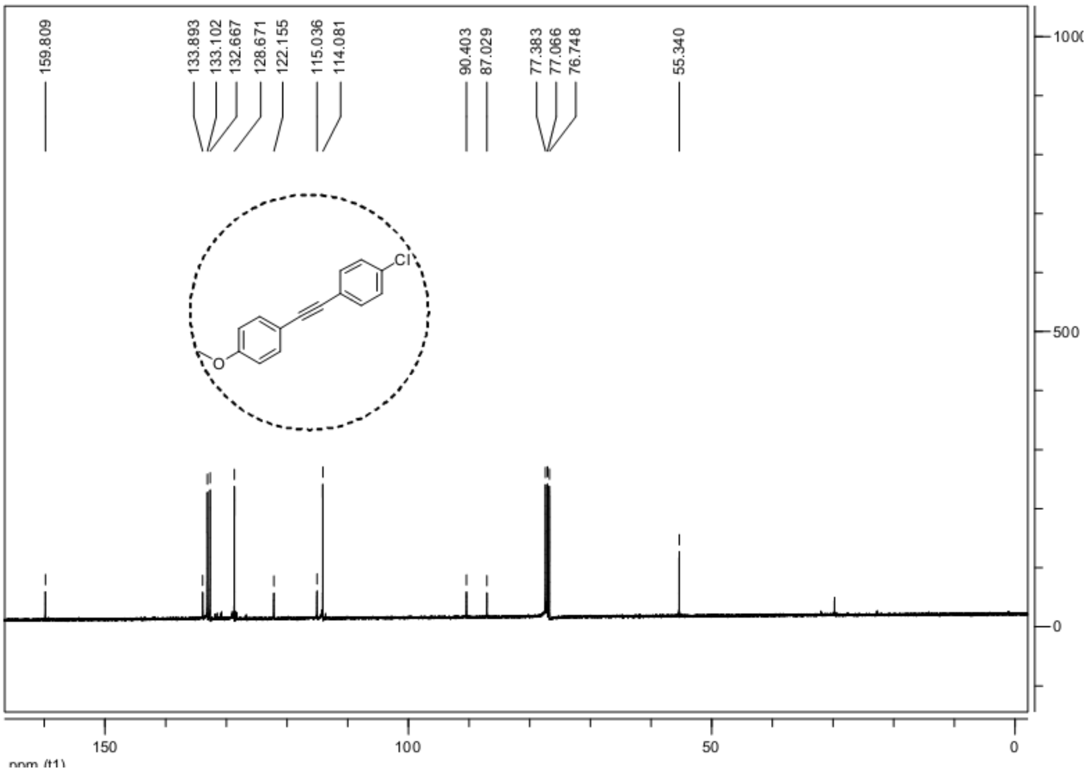

7.402
7.397
7.385
7.380
7.273
6.809
6.804
6.792
6.787
3.795
4.00
4.06
6.02
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
7.0
6.0
5.0
4.0
3.0
ppm (t1)
O
O

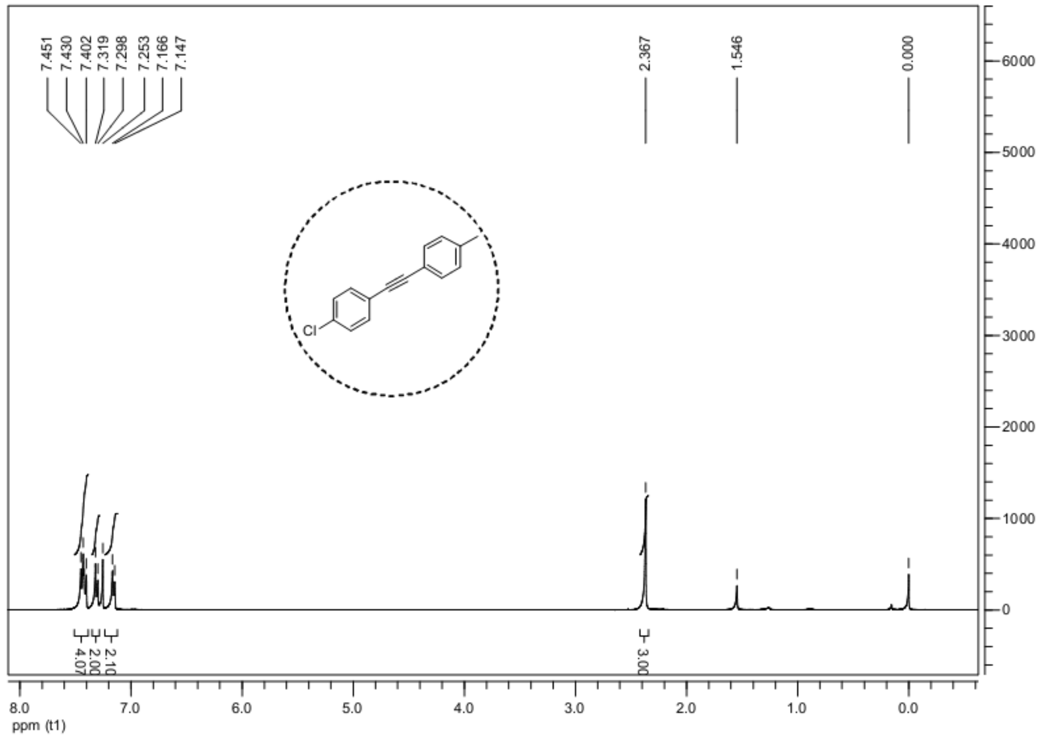

158.706
132.259
115.744
112.833
77.395
77.078
76.760
55.461
10000
5000
0
150
100
50
ppm (t1)
O
O

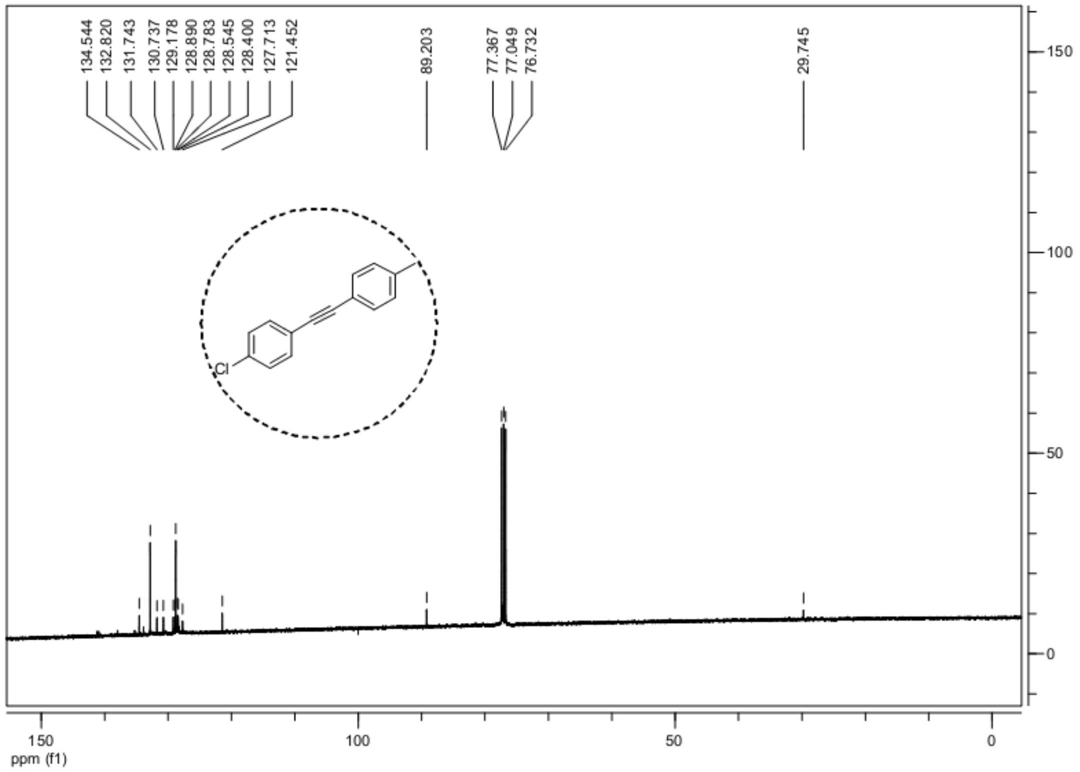

7.991
7.969
7.718
7.714
7.701
7.697
7.450
7.448
7.441
7.439
7.392
7.389
7.379
7.376
7.276
7.145
7.135
7.132
7.123
2.624
S
O
2.10
1.98
1.05
1.00
1.01
3.00
20000
15000
10000
5000
0
8.0
7.0
6.0
5.0
4.0
3.0

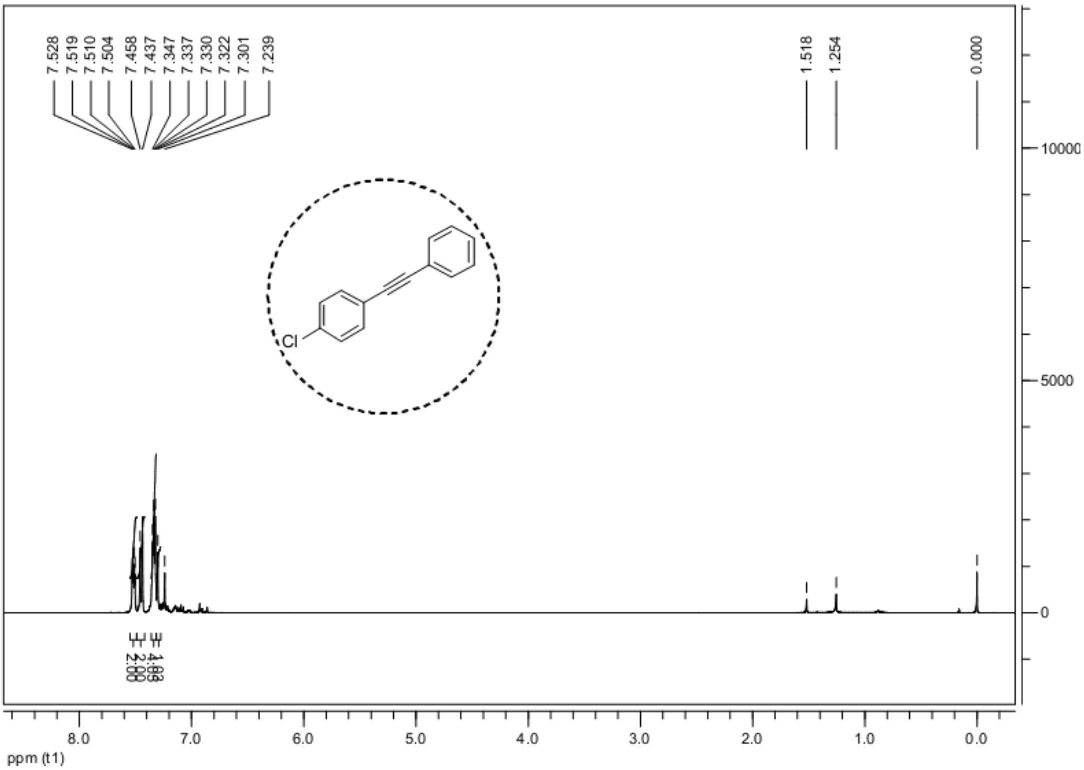

197.361
142.961
138.804
135.757
131.919
129.868
129.145
128.404
126.500
125.688
124.640
77.382
77.064
76.747
26.627
S
O
500
0
200
150
100
50
0
ppm (t1)

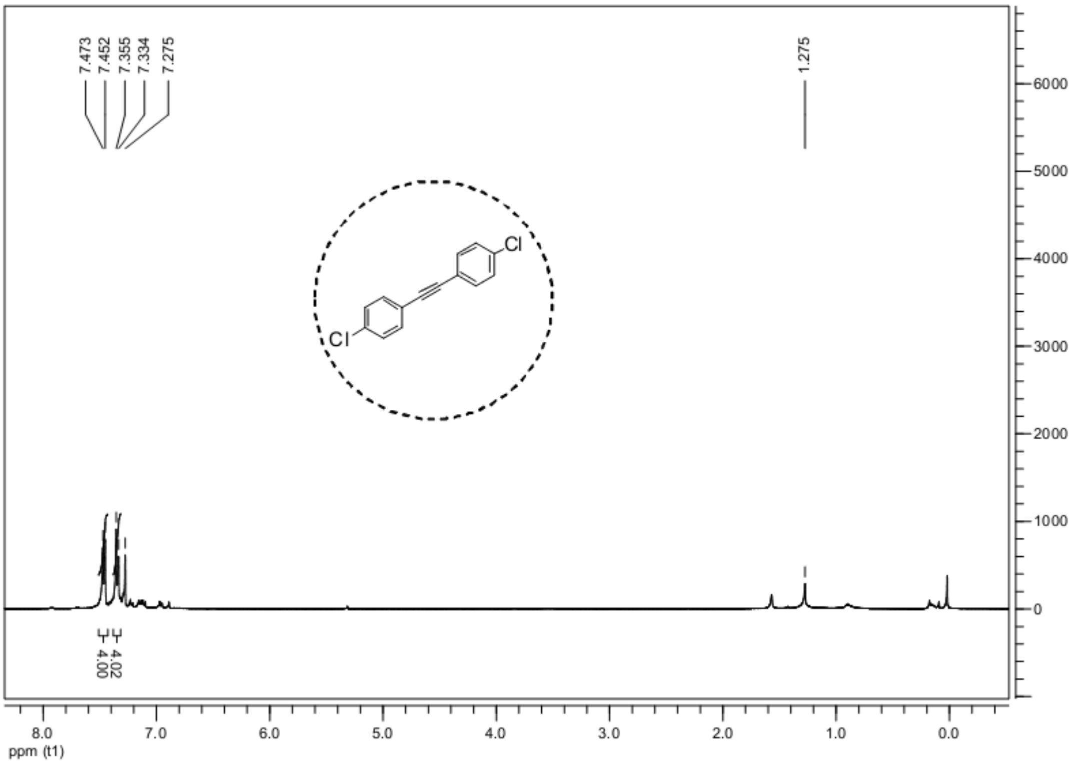

7.467
7.446
7.440
7.419
7.315
7.294
7.256
6.888
6.867
3.827
1.256
0.000
Cl
O
4.00
2.18
2.11
3.09
6000
5000
4000
3000
2000
1000
0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

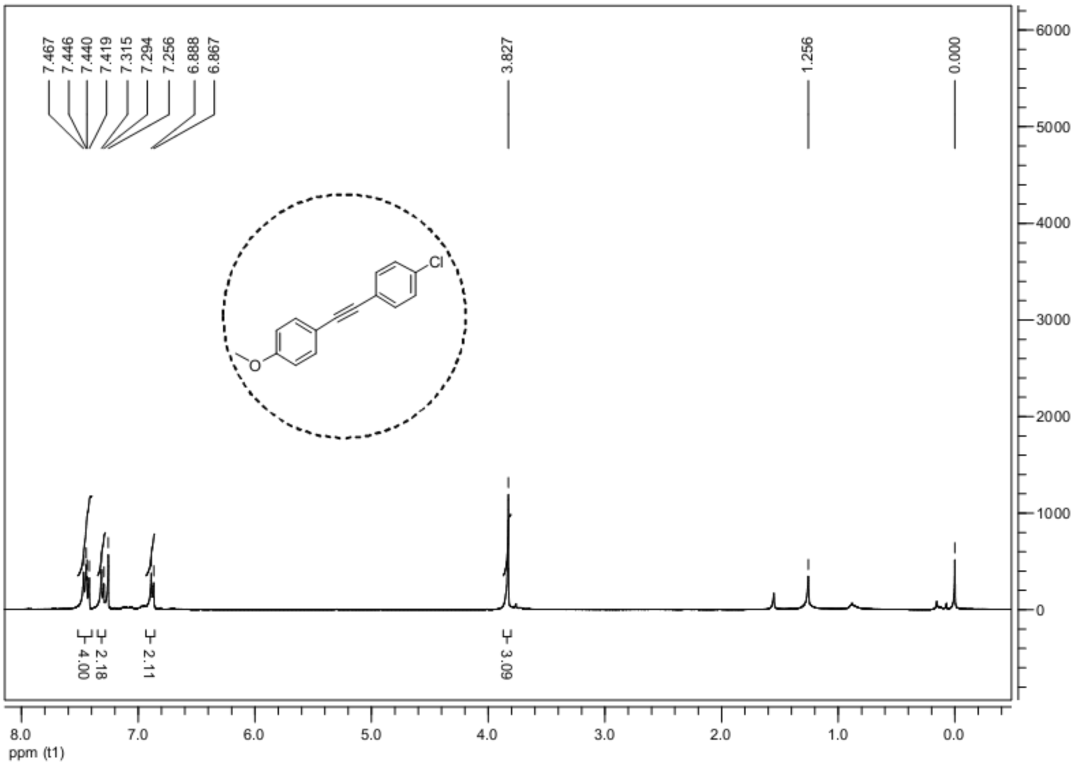

159.809
133.893
133.102
132.667
128.671
122.155
115.036
114.081
90.403
87.029
77.383
77.066
76.748
55.340
Cl
O
1000
500
0
150
100
50
0
ppm (t1)

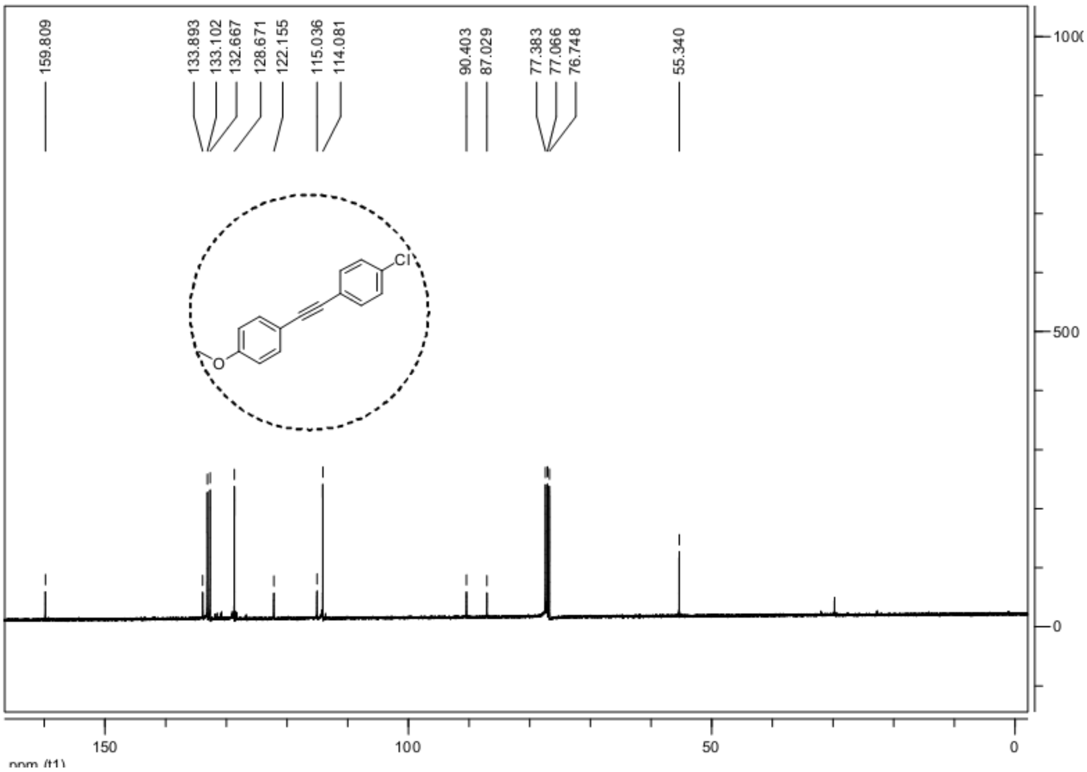

7.451
7.430
7.402
7.319
7.298
7.253
7.166
7.147
2.367
1.546
0.000
Cl
4.07
2.00
2.10
3.00
6000
5000
4000
3000
2000
1000
0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

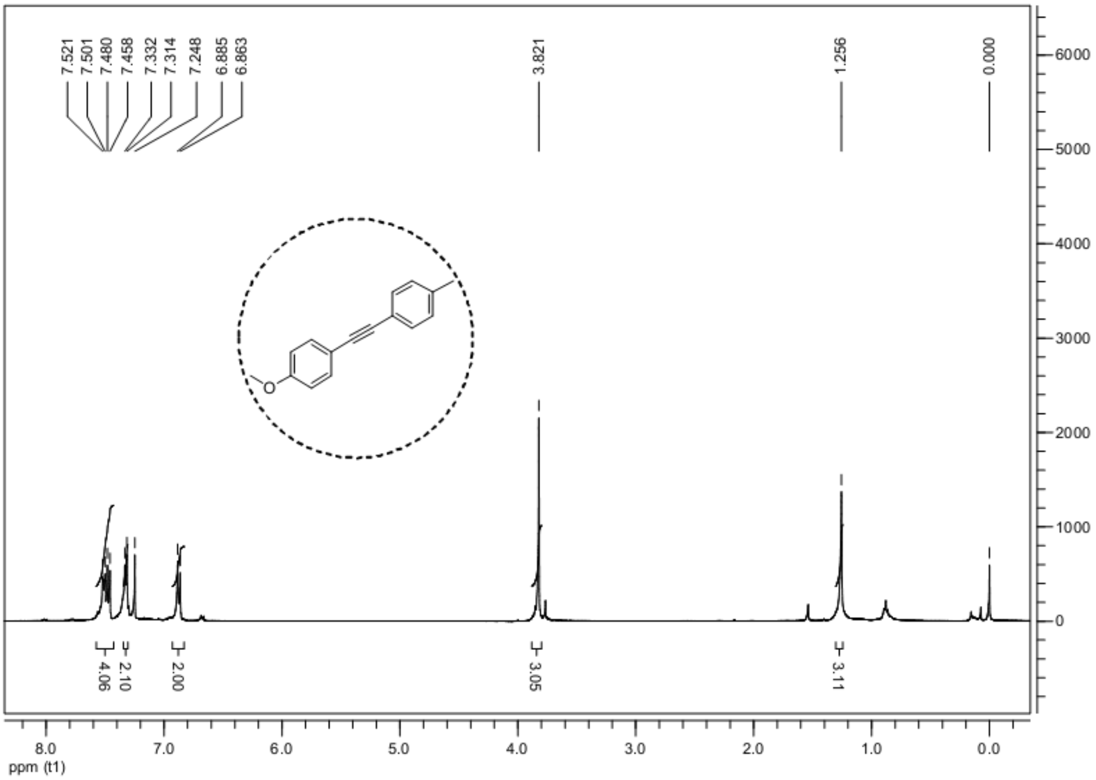

134.544
132.820
131.743
130.737
129.178
128.890
128.783
128.545
128.400
127.713
121.452
89.203
77.367
77.049
76.732
29.745
Cl
150
100
50
0
150
100
50
0
ppm (f1)

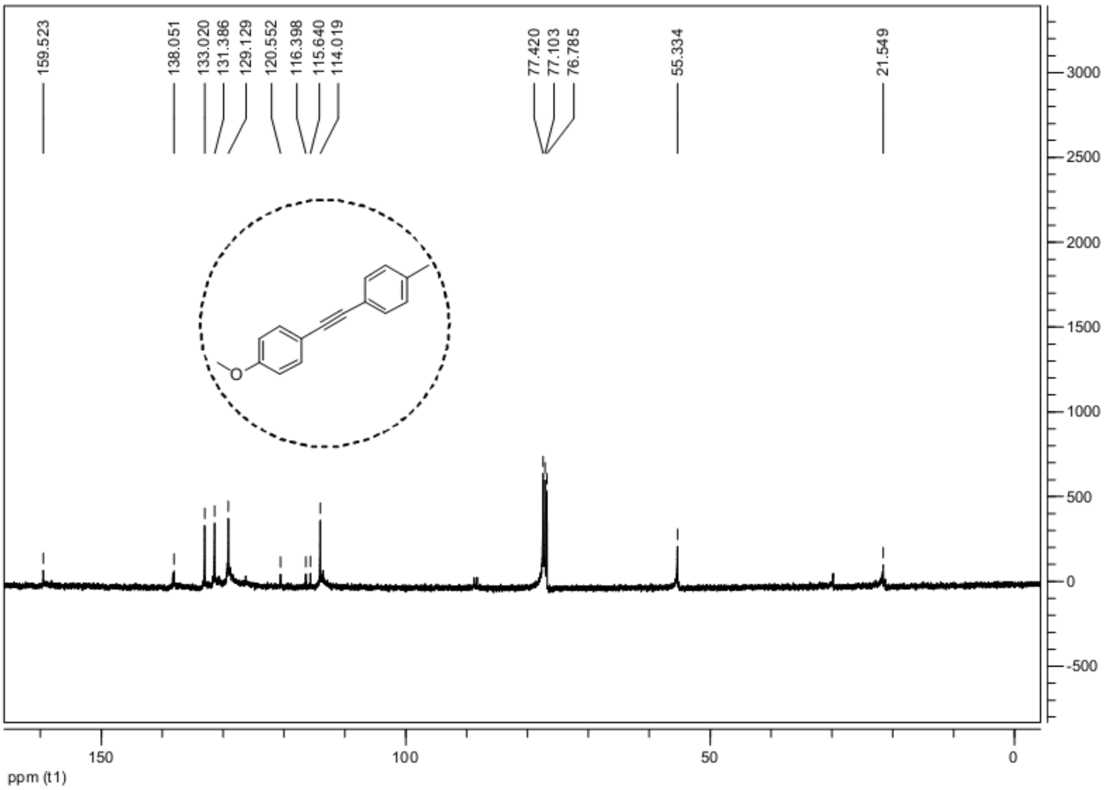

7.528
7.519
7.510
7.504
7.458
7.437
7.347
7.337
7.330
7.322
7.301
7.239
1.518
1.254
0.000
Cl
10000
5000
0
2.00
2.00
4.06
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

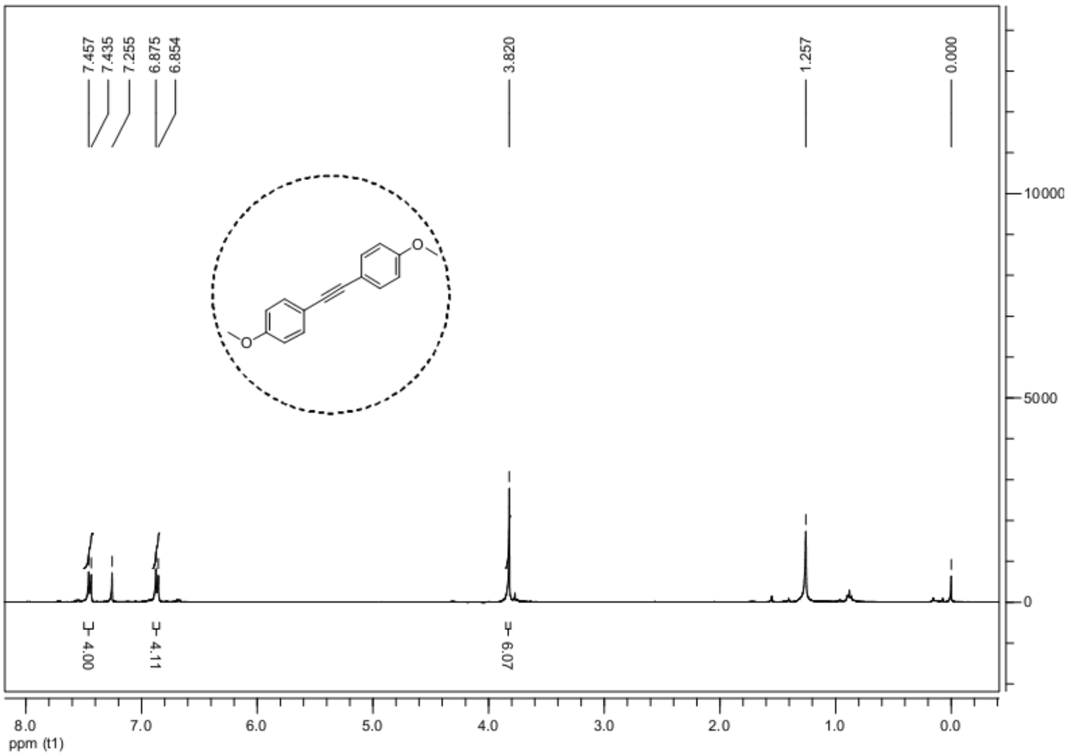

7.473
7.452
7.355
7.334
7.275
1.275
Cl
Cl
6000
5000
4000
3000
2000
1000
0
4.00
4.02
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

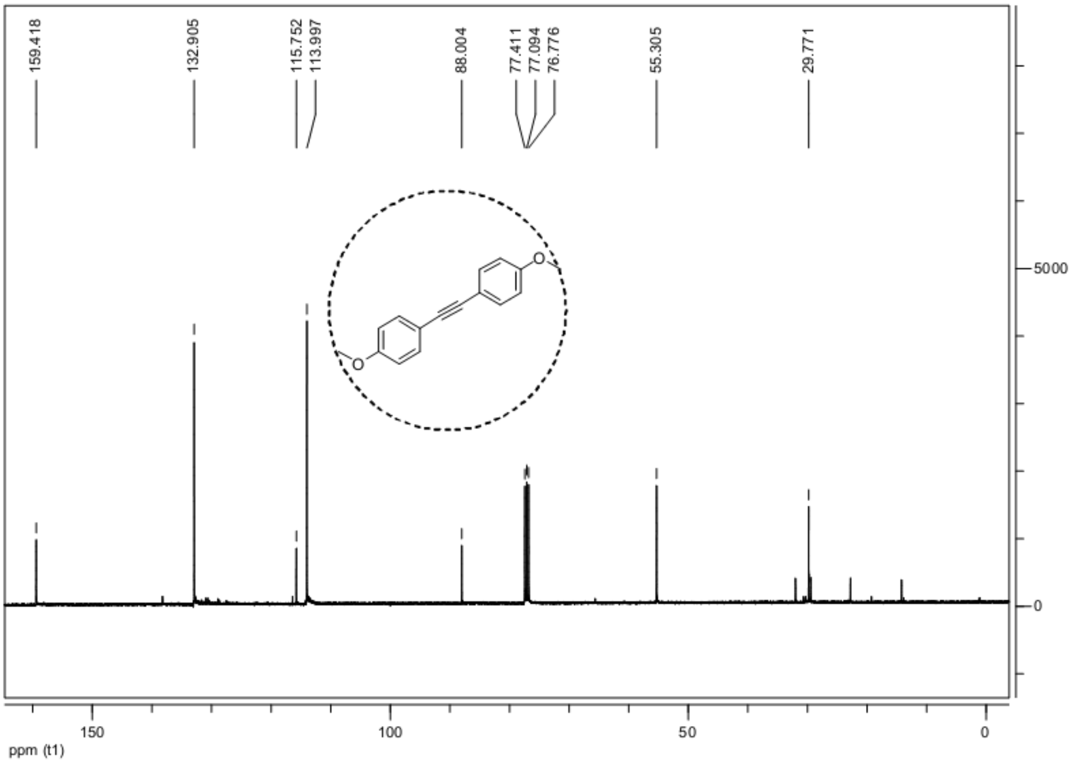

7.467
7.446
7.440
7.419
7.315
7.294
7.256
6.888
6.867
3.827
1.256
0.000
Cl
O
4.00
2.18
2.11
3.09
6000
5000
4000
3000
2000
1000
0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

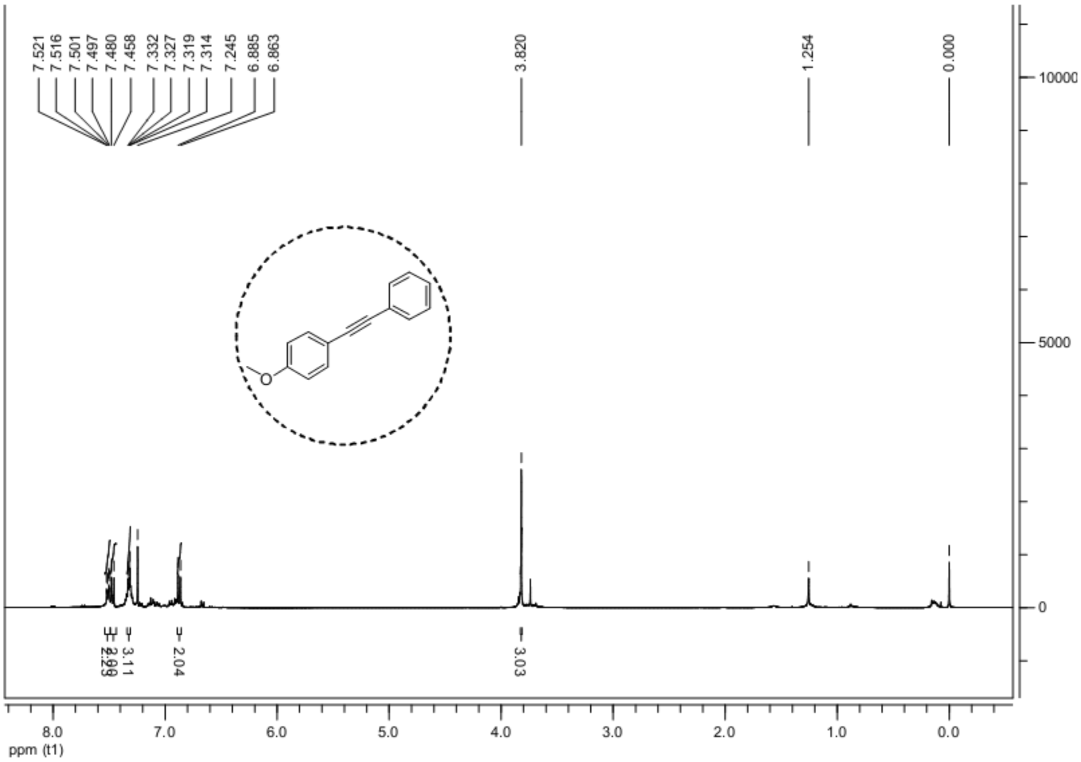

159.809
133.893
133.102
132.667
128.671
122.155
115.036
114.081
90.403
87.029
77.383
77.066
76.748
55.340
Cl
O
1000
500
0
150
100
50
0
ppm (t1)

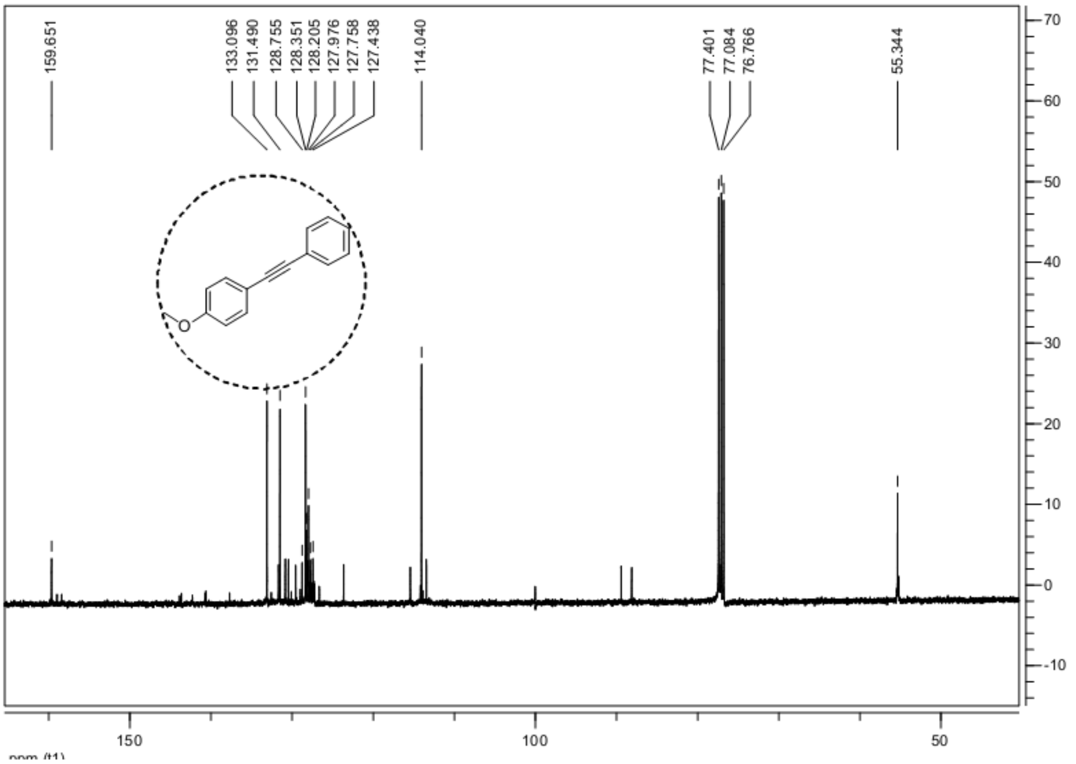

7.521
7.501
7.480
7.458
7.332
7.314
7.248
6.885
6.863
3.821
1.256
0.000
O
4.06
2.10
2.00
3.05
3.11
6000
5000
4000
3000
2000
1000
0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

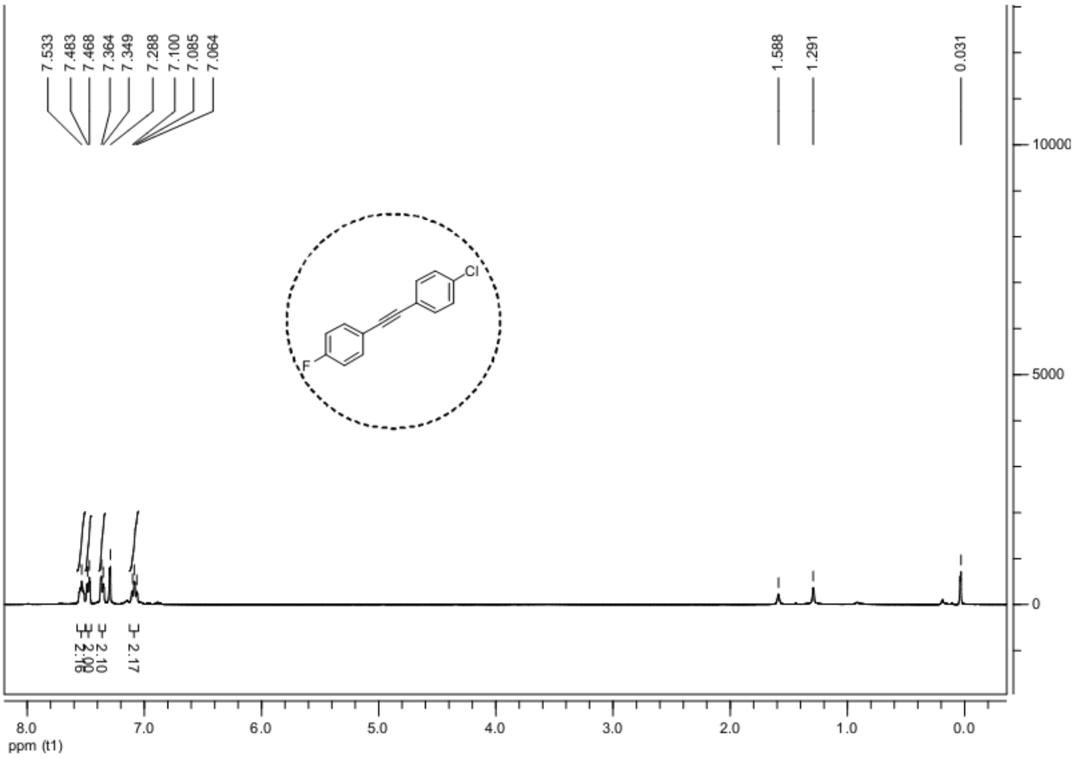

159.523
138.051
133.020
131.386
129.129
120.552
116.398
115.640
114.019
77.420
77.103
76.785
55.334
21.549
O
3000
2500
2000
1500
1000
500
0
-500
150
100
50
0
ppm (t1)

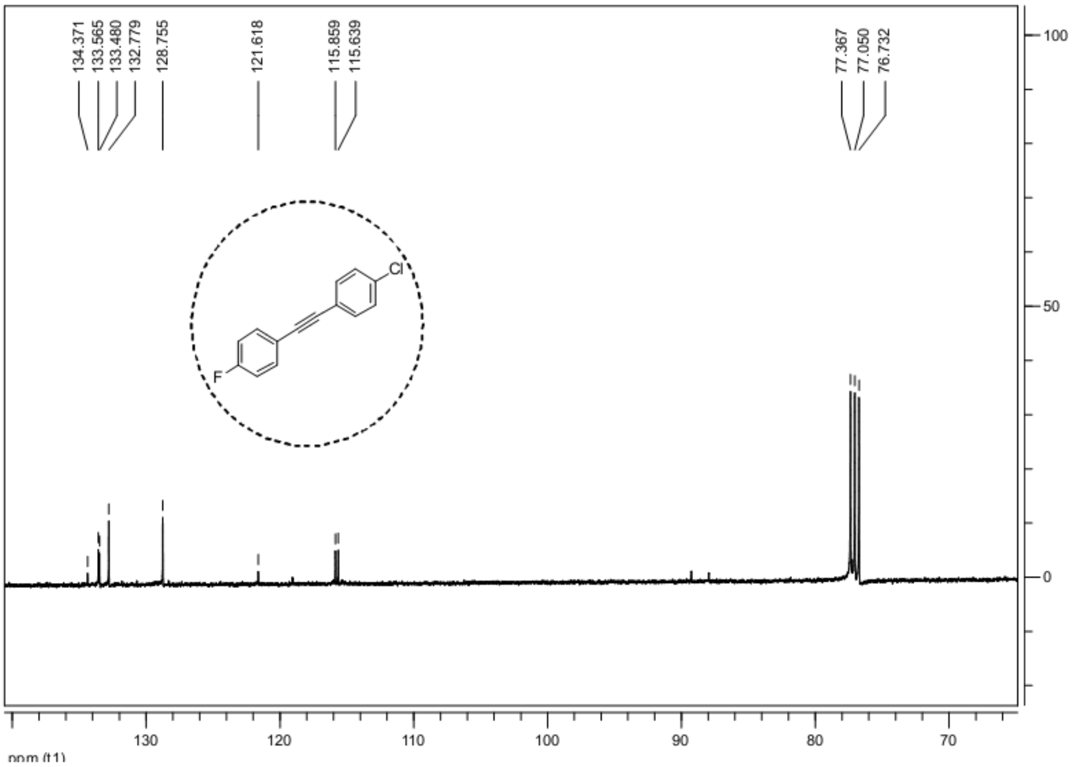

7.457
7.435
7.255
6.875
6.854
3.820
1.257
0.000
O
O
10000
5000
0
4.00
4.11
6.07
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

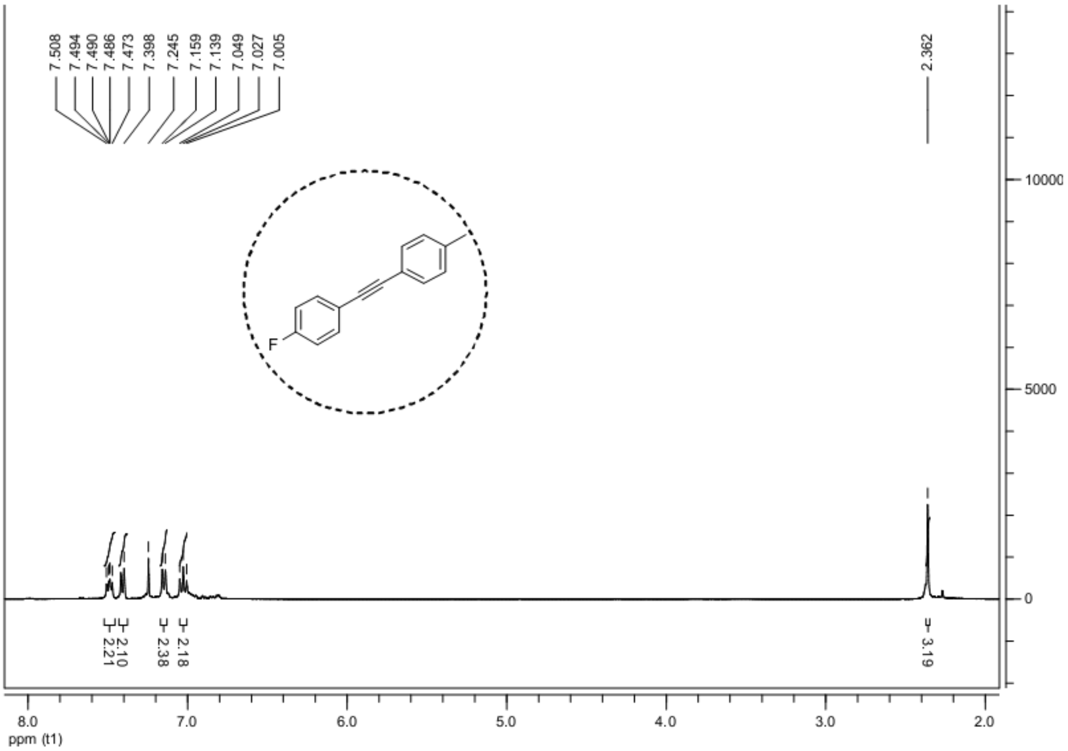

159.418
132.905
115.752
113.997
88.004
77.411
77.094
76.776
55.305
29.771
O
O
5000
0
150
100
50
0
ppm (t1)

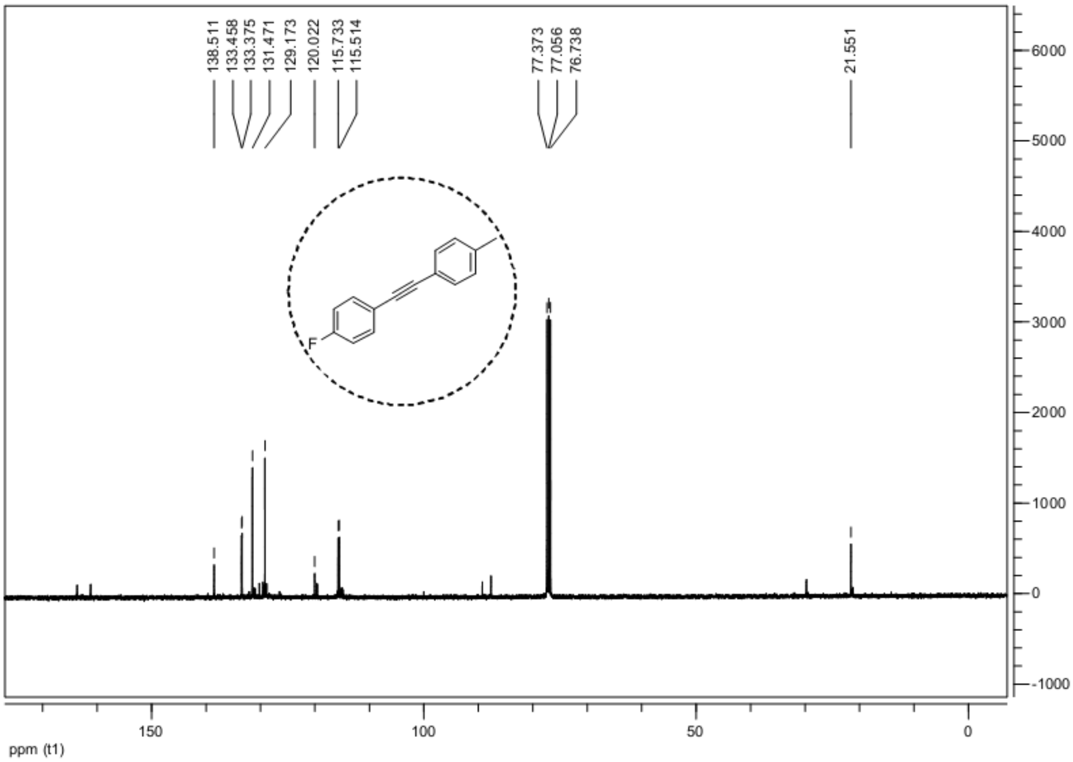

7.521
7.516
7.501
7.497
7.480
7.458
7.332
7.327
7.319
7.314
7.245
6.885
6.863
3.820
1.254
0.000
O
2.29
2.00
3.11
2.04
3.03
10000
5000
0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

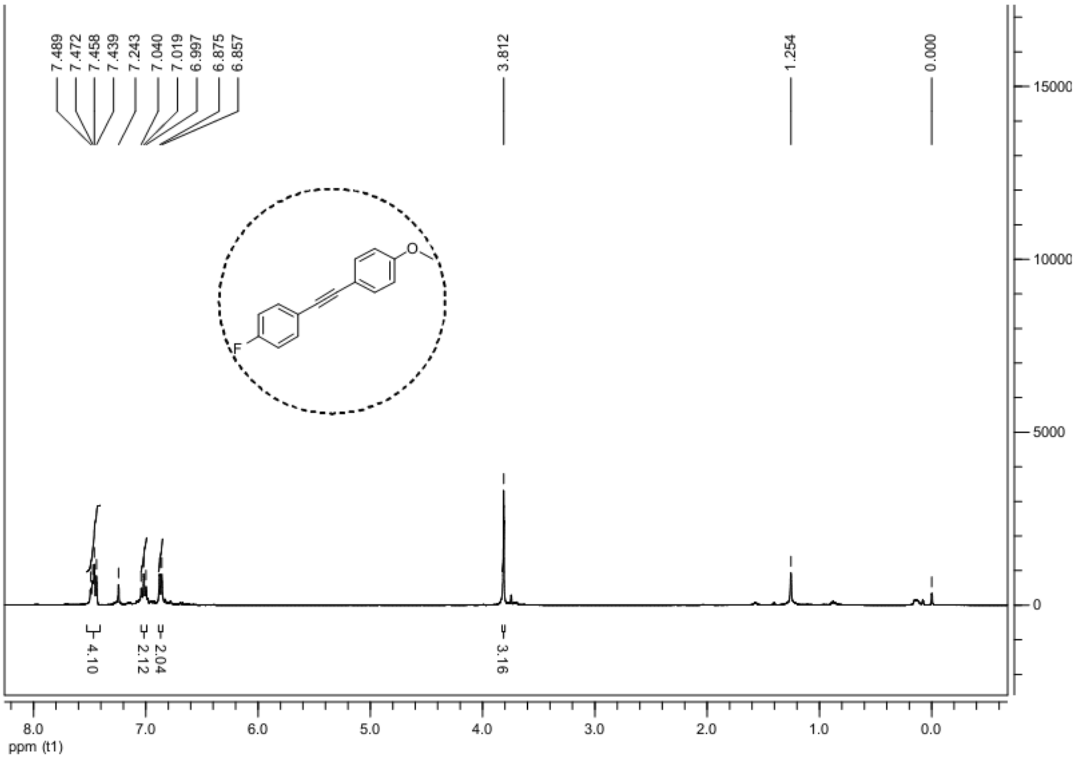

159.651
133.096
131.490
128.755
128.351
128.205
127.976
127.758
127.438
114.040
77.401
77.084
76.766
55.344
O
70
60
50
40
30
20
10
0
-10
150
100
50
ppm (t1)

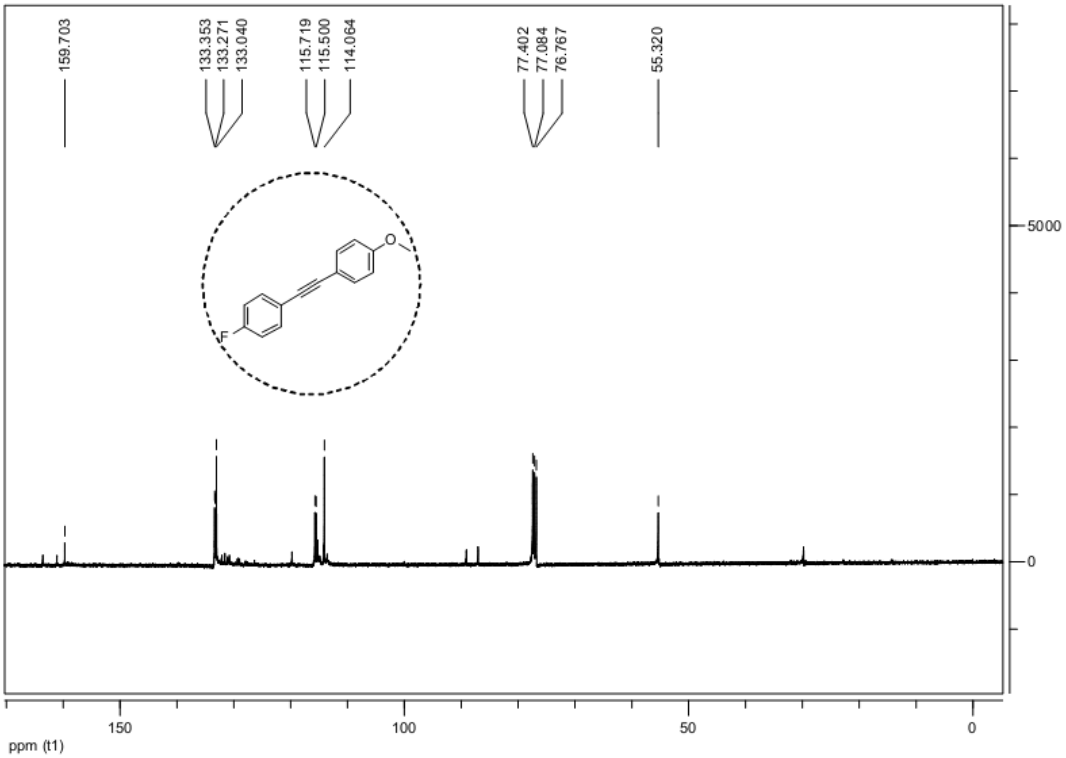

7.533
7.483
7.468
7.364
7.349
7.288
7.100
7.085
7.064
1.588
1.291
0.031
Cl
F
10000
5000
0
2.16
2.00
2.10
2.17
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

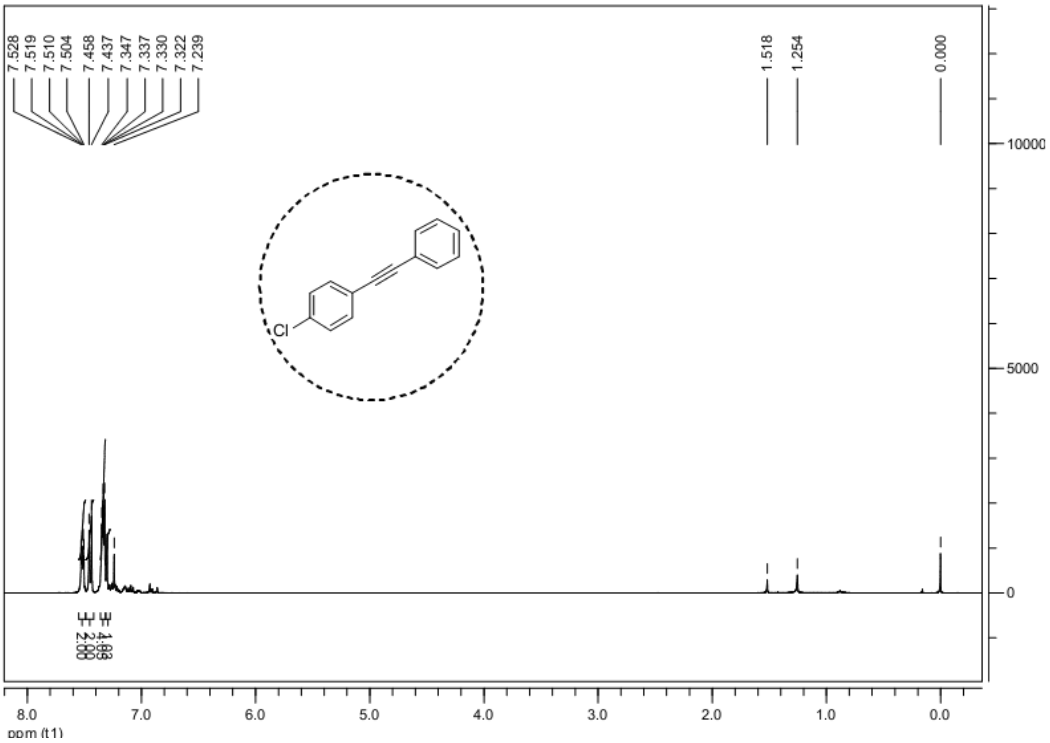

134.371
133.565
133.480
132.779
128.755
121.618
115.859
115.639
77.367
77.050
76.732
Cl
F
100
50
0
130
120
110
100
90
80
70
ppm (t1)

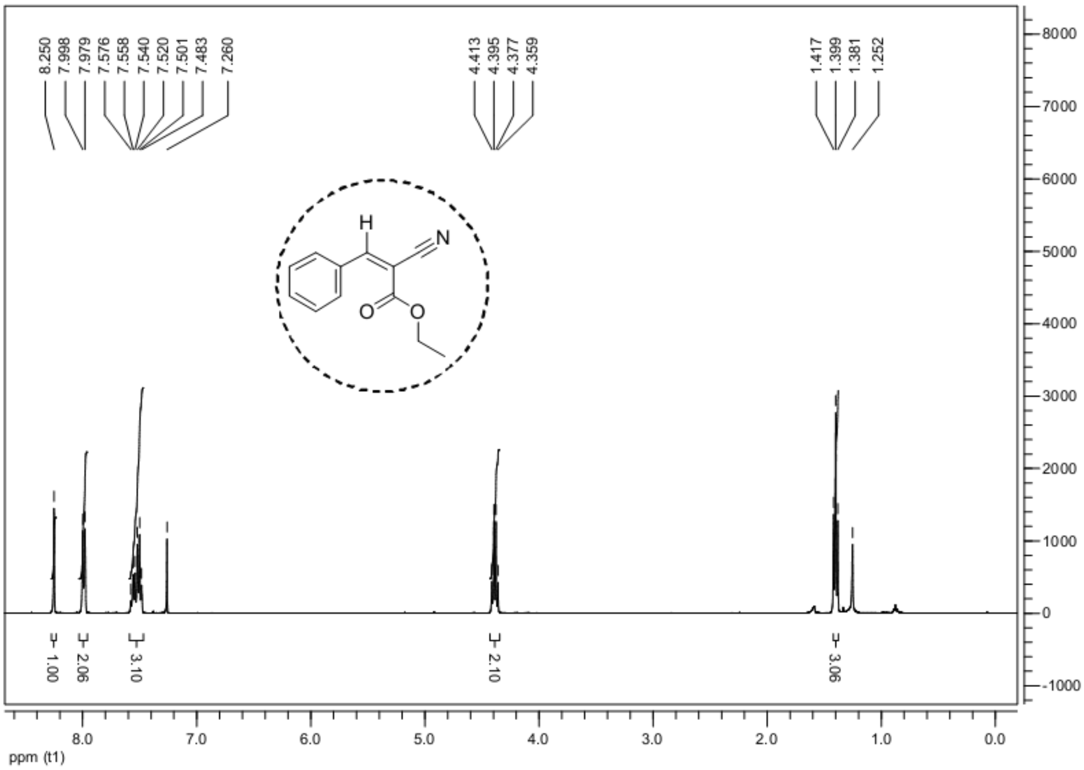

7.508
7.494
7.490
7.486
7.473
7.398
7.245
7.159
7.139
7.049
7.027
7.005
2.362
F
2.21
2.10
2.38
2.18
3.19
10000
5000
0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
ppm (t1)

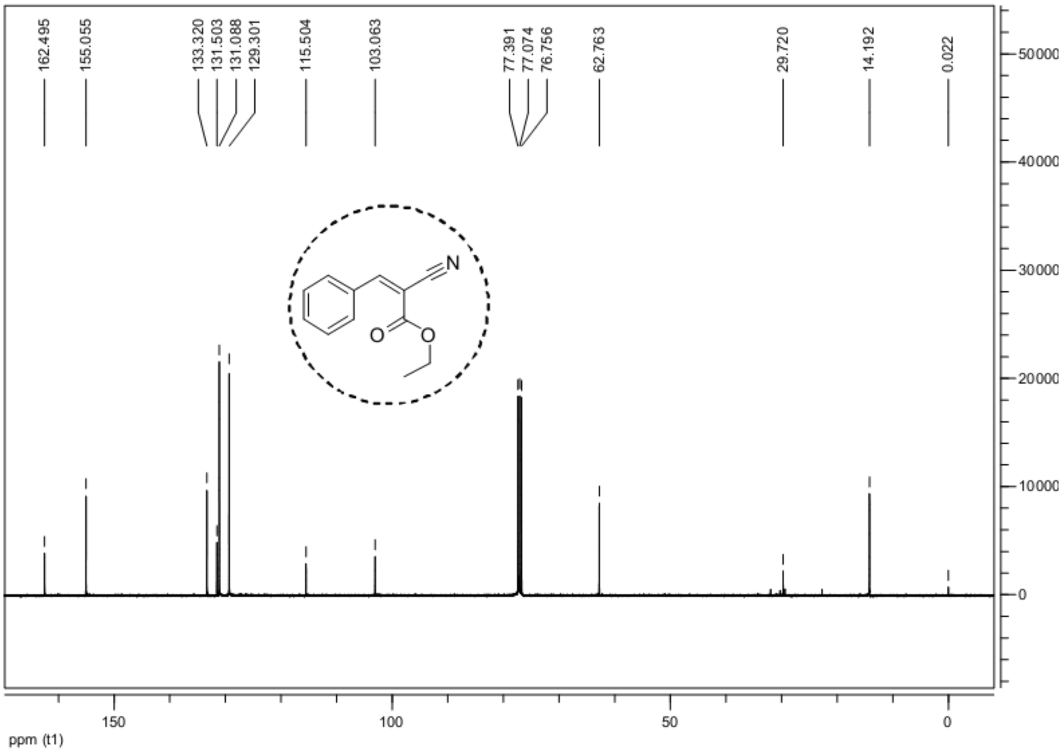

138.511
133.458
133.375
131.471
129.173
120.022
115.733
115.514
77.373
77.056
76.738
21.551
F
6000
5000
4000
3000
2000
1000
0
-1000
150
100
50
0
ppm (t1)

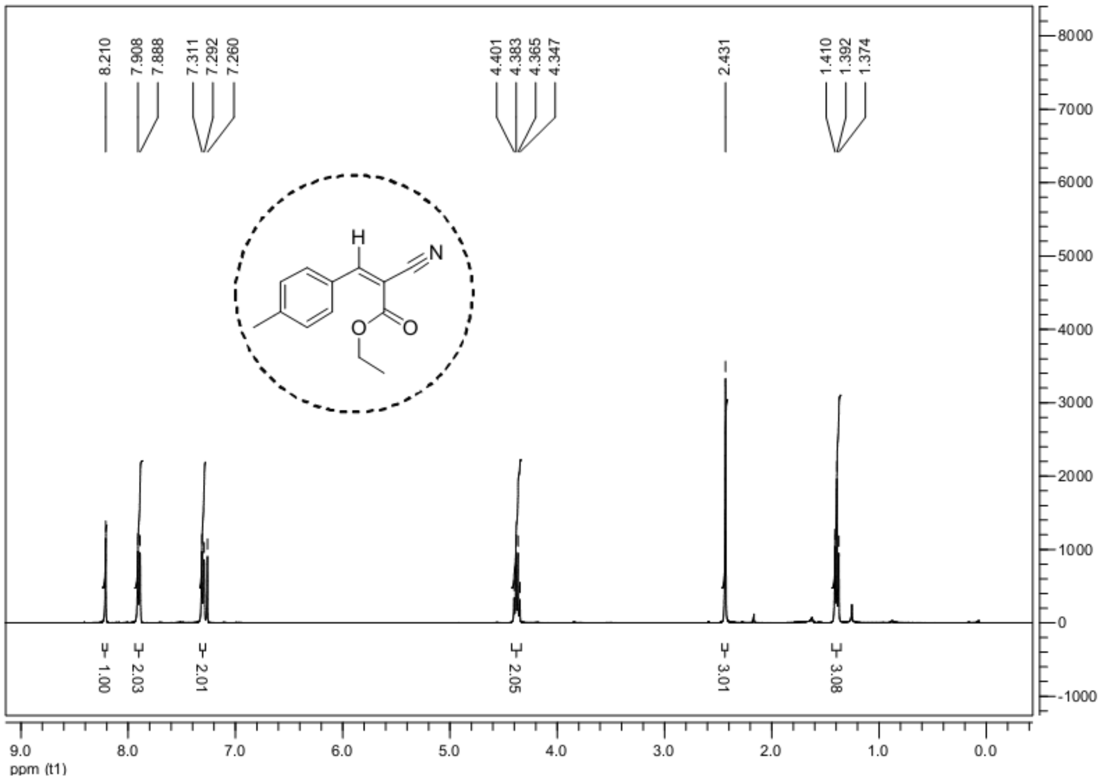

7.489
7.472
7.458
7.439
7.243
7.040
7.019
6.997
6.875
6.857
3.812
1.254
0.000
F
O
4.10
2.12
2.04
3.16
15000
10000
5000
0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

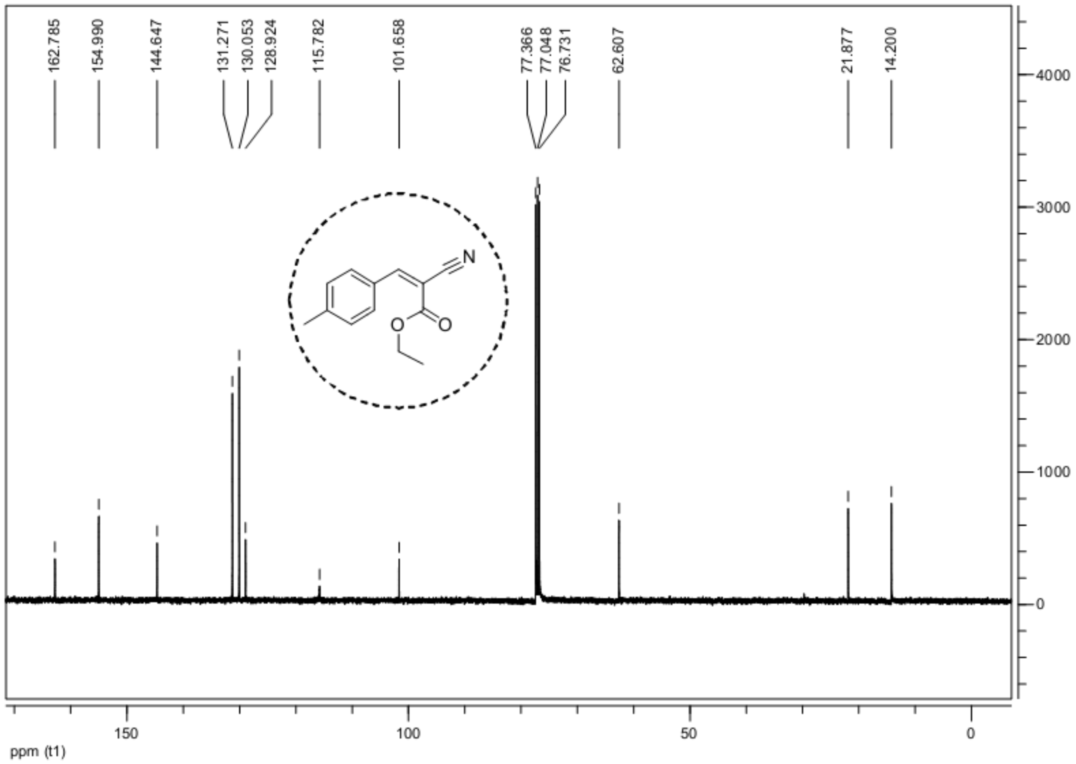

159.703
133.353
133.271
133.040
115.719
115.500
114.064
77.402
77.084
76.767
55.320
F
O
5000
0
150
100
50
0
ppm (t1)

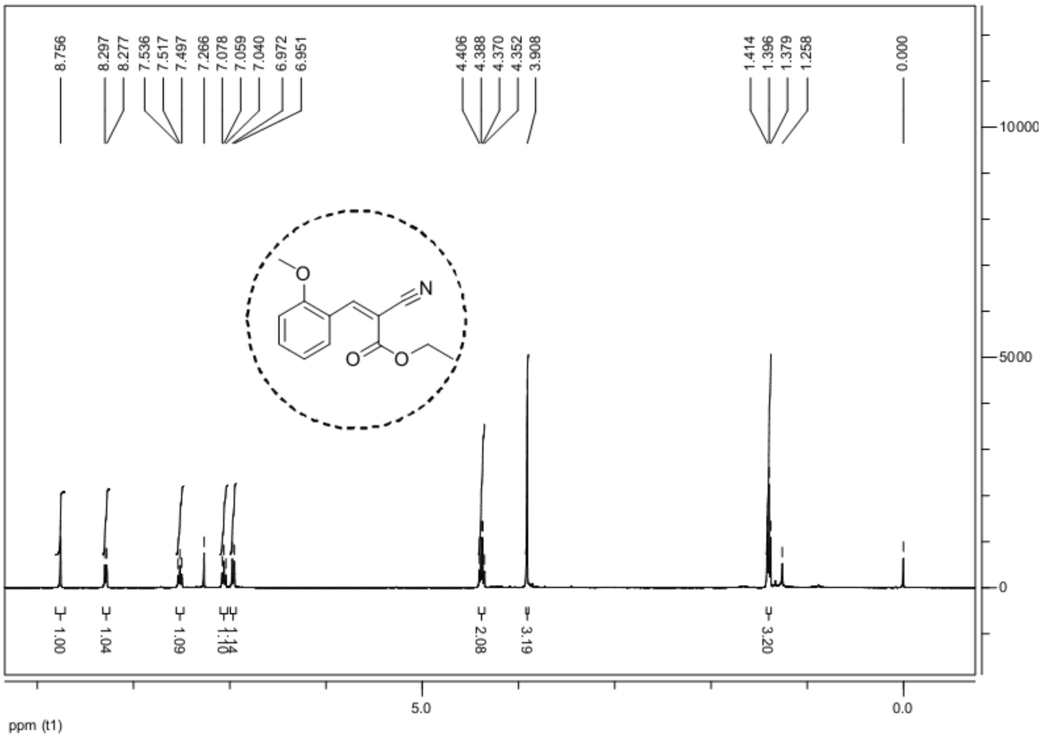

7.528
7.519
7.510
7.504
7.458
7.437
7.347
7.337
7.330
7.322
7.239
1.518
1.254
0.000
Cl
10000
5000
0
2.00
2.00
4.03
1.06
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

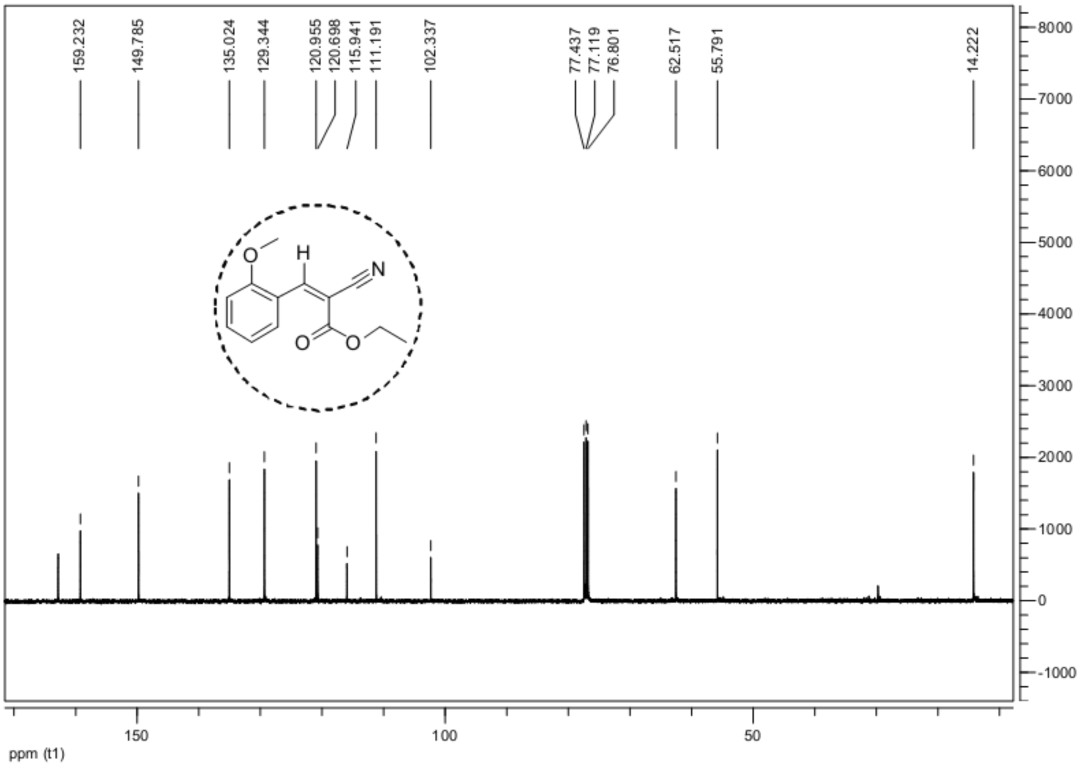

8.250
7.998
7.979
7.576
7.558
7.540
7.520
7.501
7.483
7.260
4.413
4.395
4.377
4.359
1.417
1.399
1.381
1.252
H
N
O
O
1.00
2.06
3.10
2.10
3.06
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

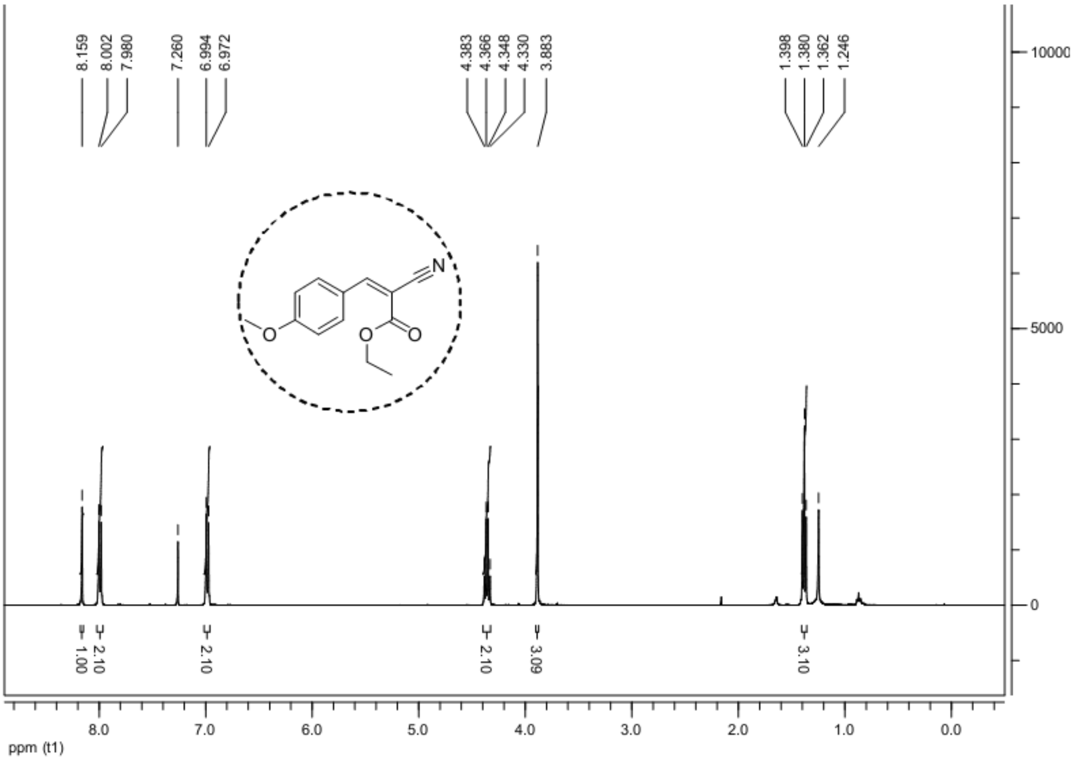

162.495
155.055
133.320
131.503
131.088
129.301
115.504
103.063
77.391
77.074
76.756
62.763
29.720
14.192
0.022
N
O
O
50000
40000
30000
20000
10000
0
150
100
50
0
ppm (t1)

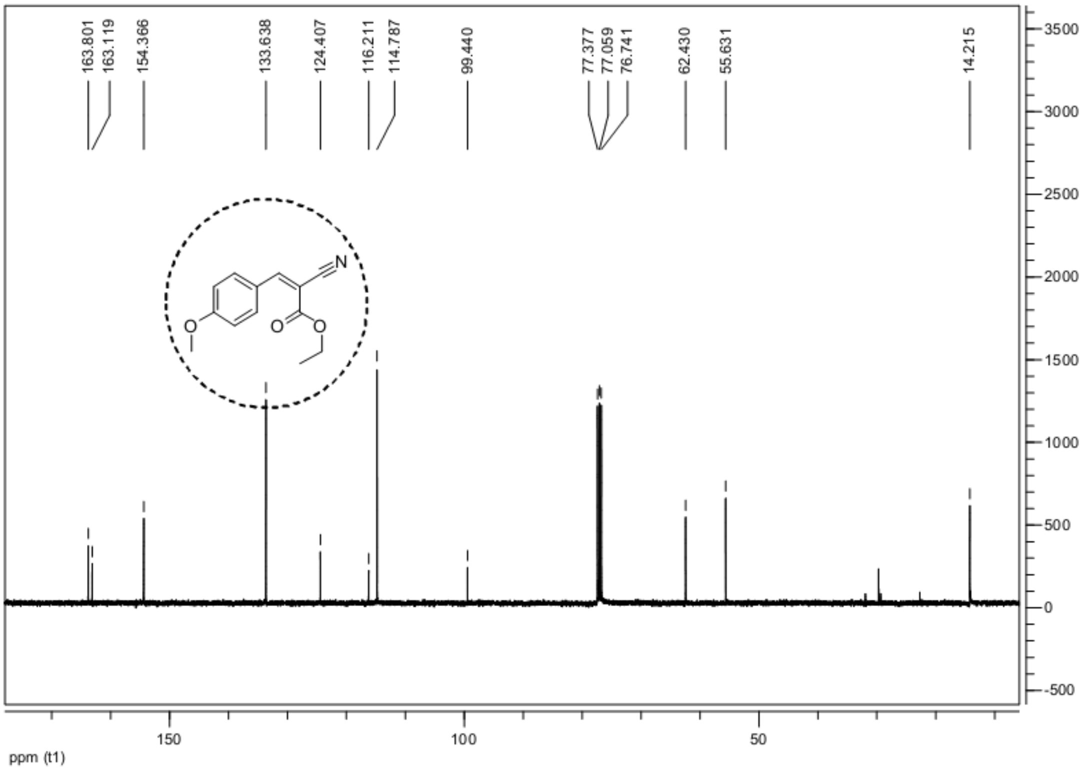

8.210
7.908
7.888
7.311
7.292
7.260
4.401
4.383
4.365
4.347
2.431
1.410
1.392
1.374
H
N
O
O
1.00
2.03
2.01
2.05
3.01
3.08
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

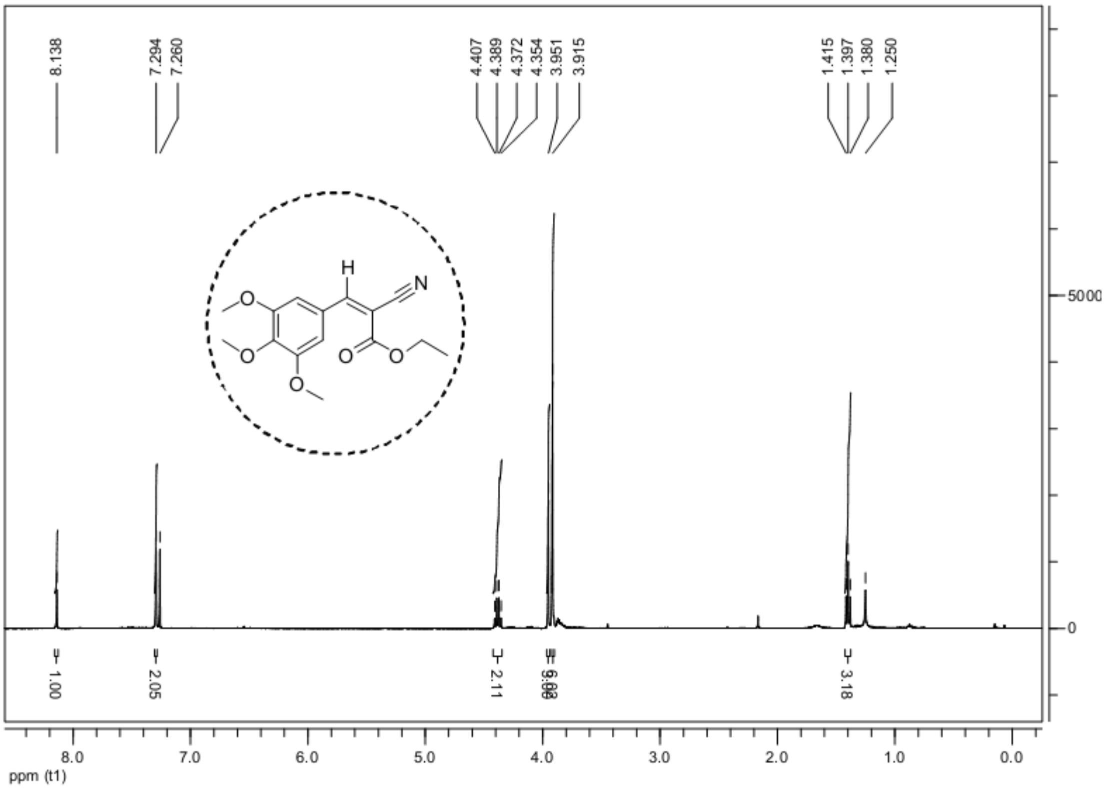

162.785
154.990
144.647
131.271
130.053
128.924
115.782
101.658
77.366
77.048
76.731
62.607
21.877
14.200
N
O
O
4000
3000
2000
1000
0
150
100
50
0
ppm (t1)

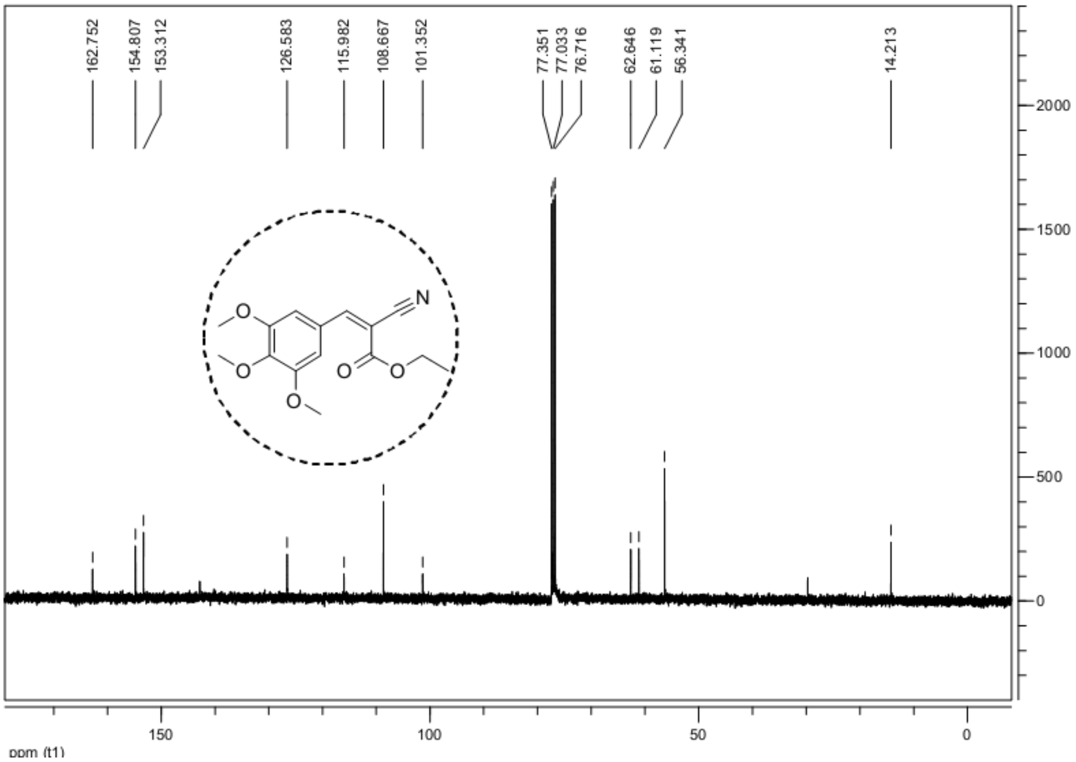

8.756
8.297
8.277
7.536
7.517
7.497
7.266
7.078
7.059
7.040
6.972
6.951
4.406
4.388
4.370
4.352
3.908
1.414
1.396
1.379
1.258
0.000
O
N
O
O
10000
5000
0
1.00
1.04
1.09
1.14
1.10
2.08
3.19
3.20
5.0
0.0
ppm (t1)

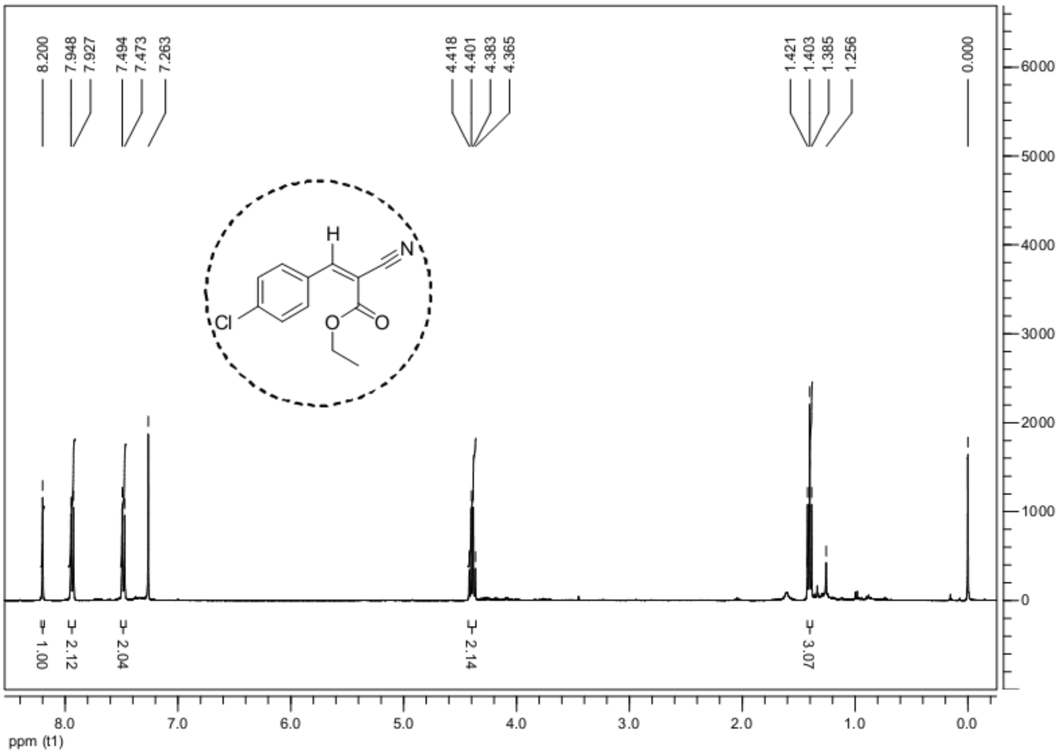

159.232
149.785
135.024
129.344
120.955
120.698
115.941
111.191
102.337
77.437
77.119
76.801
62.517
55.791
14.222
O
H
N
O
O
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
150
100
50
ppm (t1)

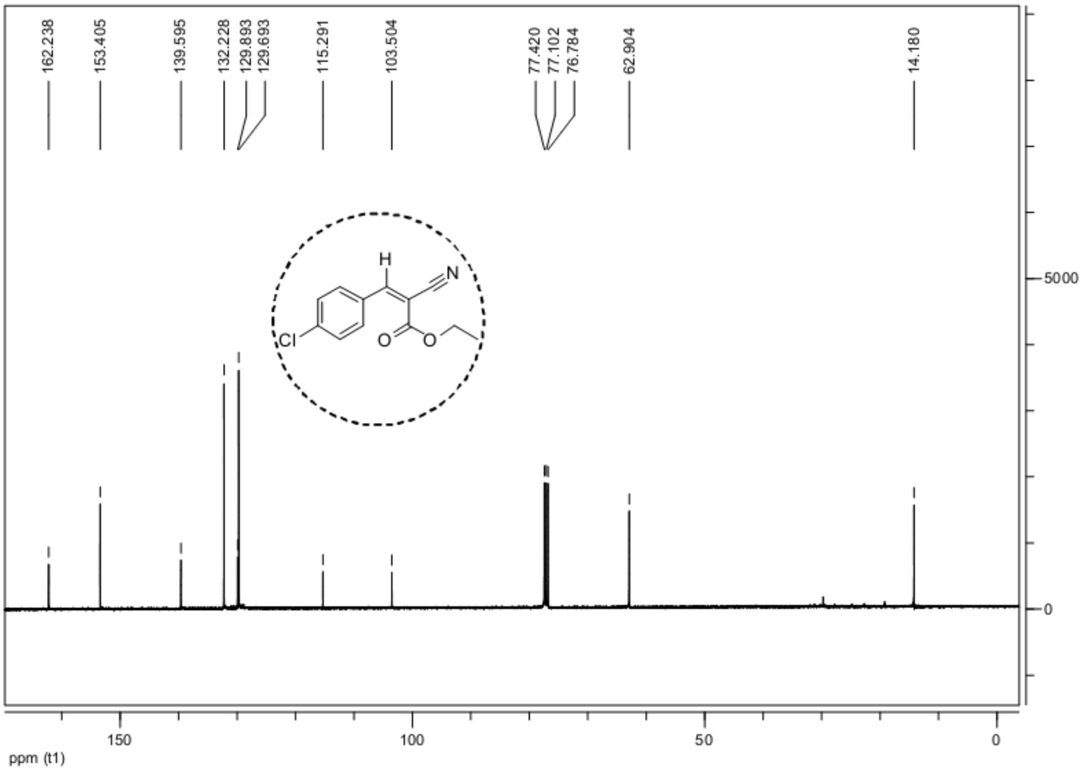

8.159
8.002
7.980
7.260
6.994
6.972
4.383
4.366
4.348
4.330
3.883
1.398
1.380
1.362
1.246
N
O
O
O
1.00
2.10
2.10
2.10
3.09
3.10
10000
5000
0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

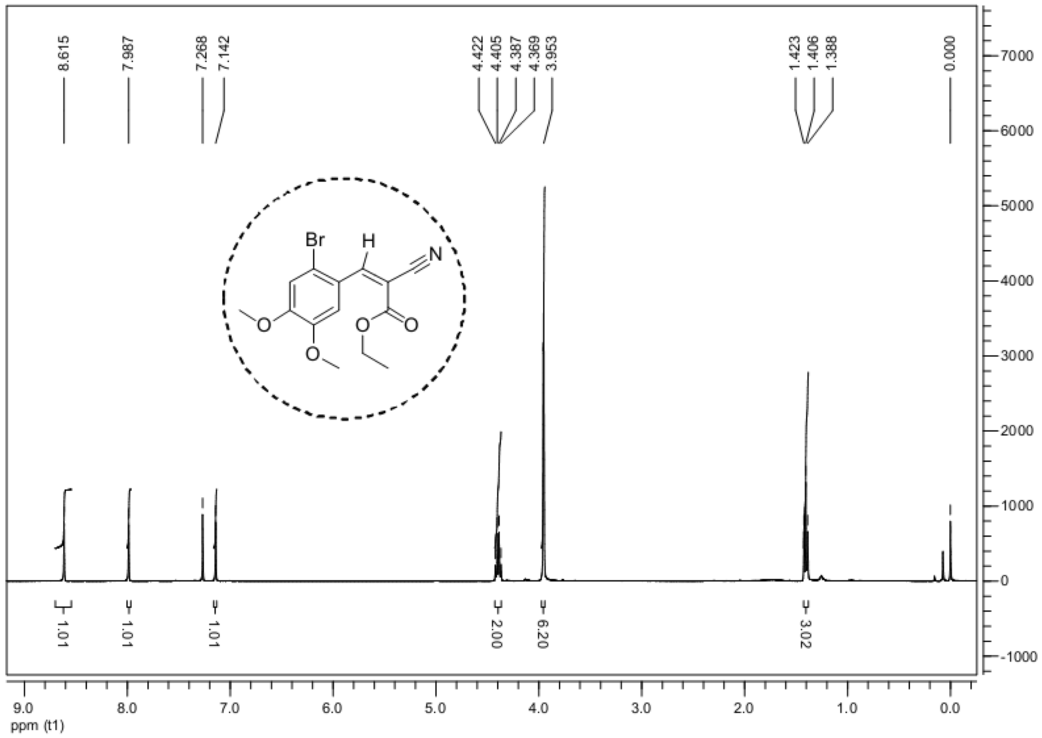

163.801
163.119
154.366
133.638
124.407
116.211
114.787
99.440
77.377
77.059
76.741
62.430
55.631
14.215
N
O
O
O
3500
3000
2500
2000
1500
1000
500
0
-500
150
100
50
ppm (t1)

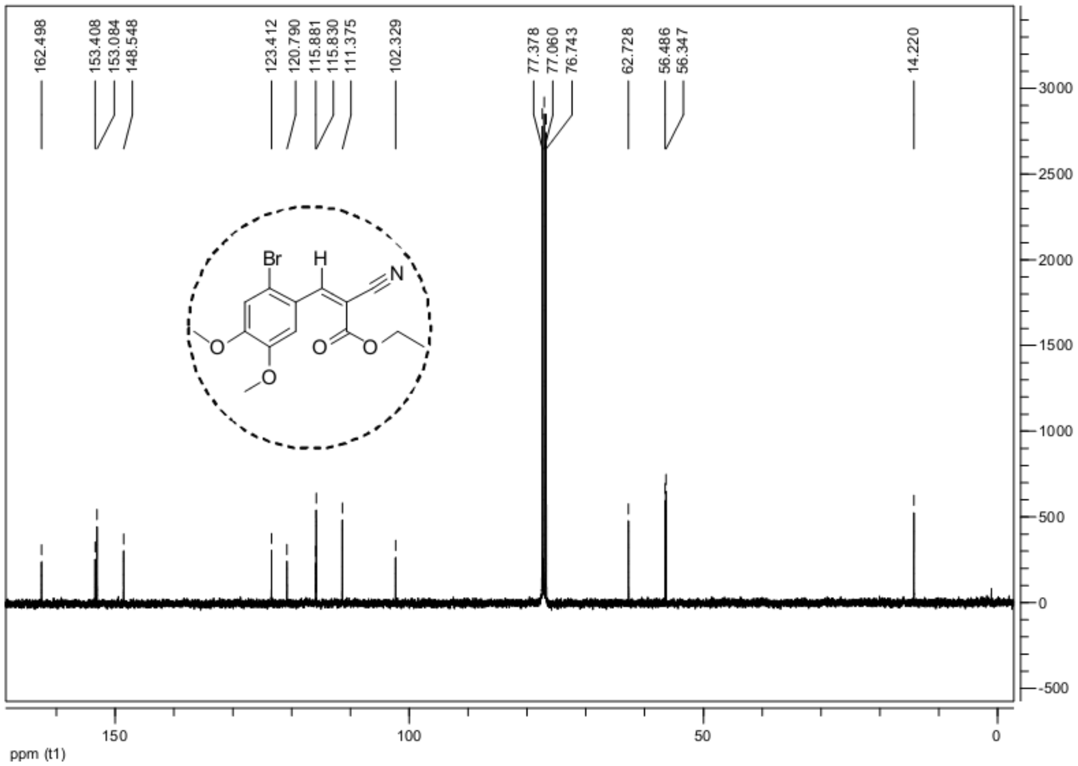

8.138
7.294
7.260
4.407
4.389
4.372
4.354
3.951
3.915
1.415
1.397
1.380
1.250
H
N
O
O
O
O
O
5000
0
1.00
2.05
2.11
9.08
3.18
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

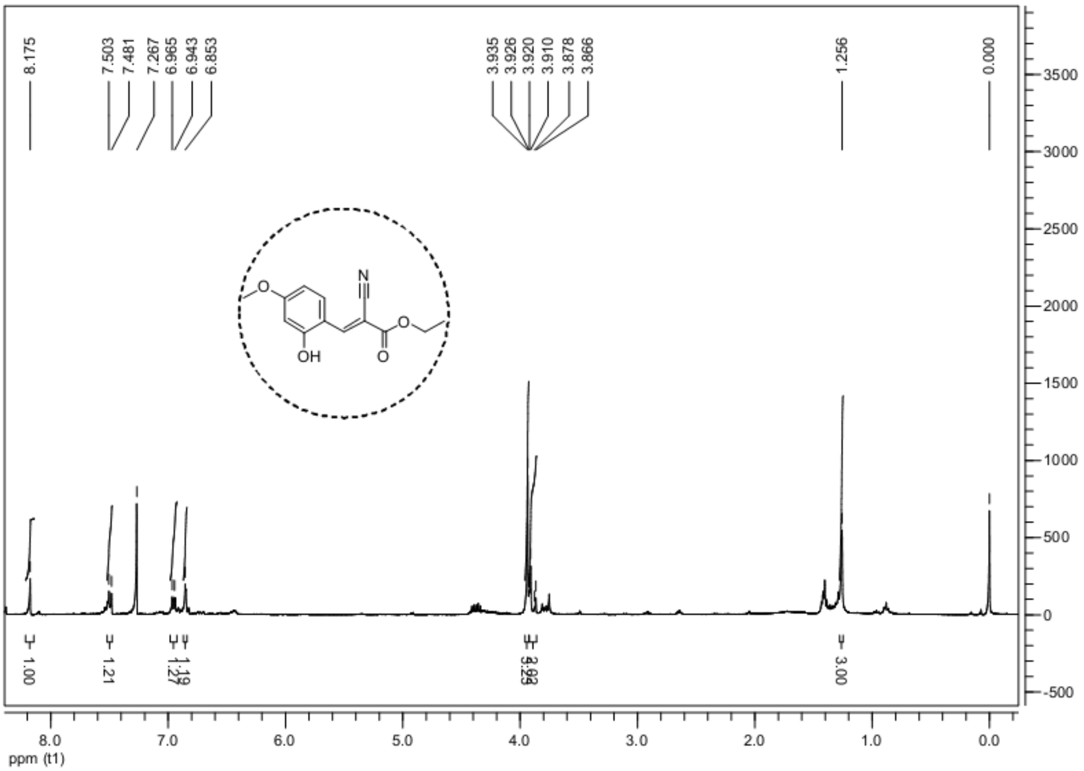

162.752
154.807
153.312
126.583
115.982
108.667
101.352
77.351
77.033
76.716
62.646
61.119
56.341
14.213
N
O
O
O
O
O
2000
1500
1000
500
0
150
100
50
0
ppm (t1)

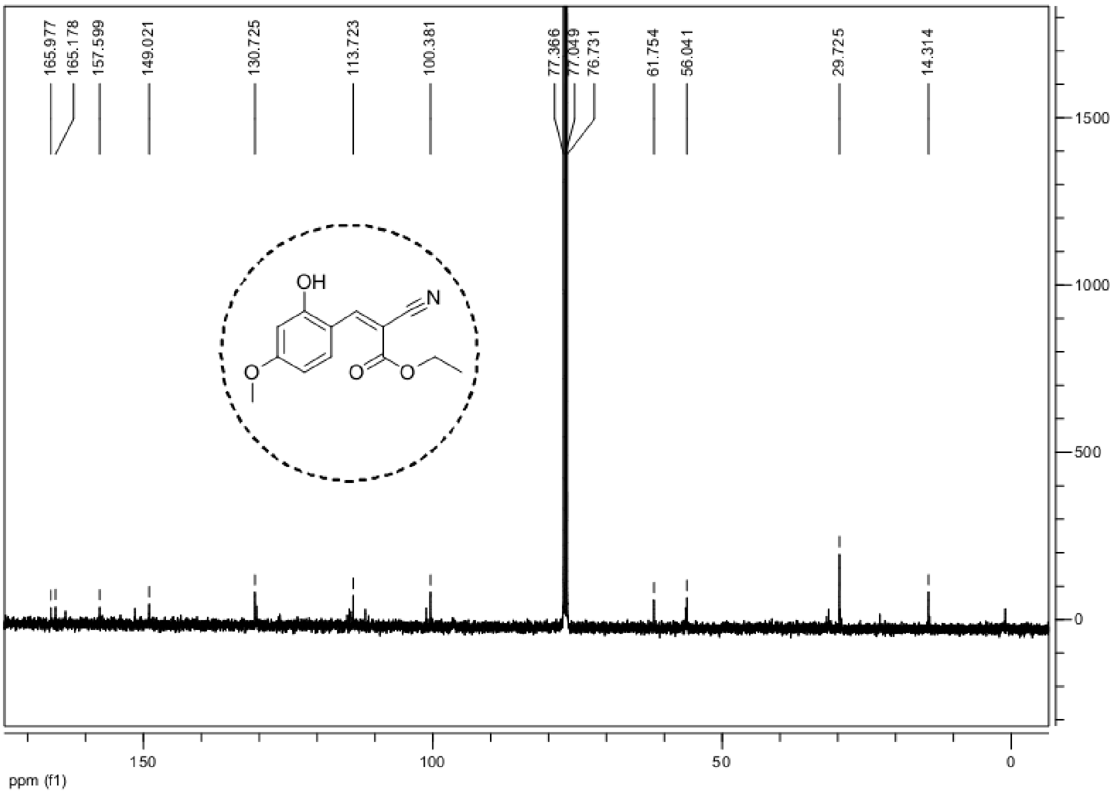

8.200
7.948
7.927
7.494
7.473
7.263
4.418
4.401
4.383
4.365
1.421
1.403
1.385
1.256
0.000
H
N
Cl
O
O
1.00
2.12
2.04
2.14
3.07
6000
5000
4000
3000
2000
1000
0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

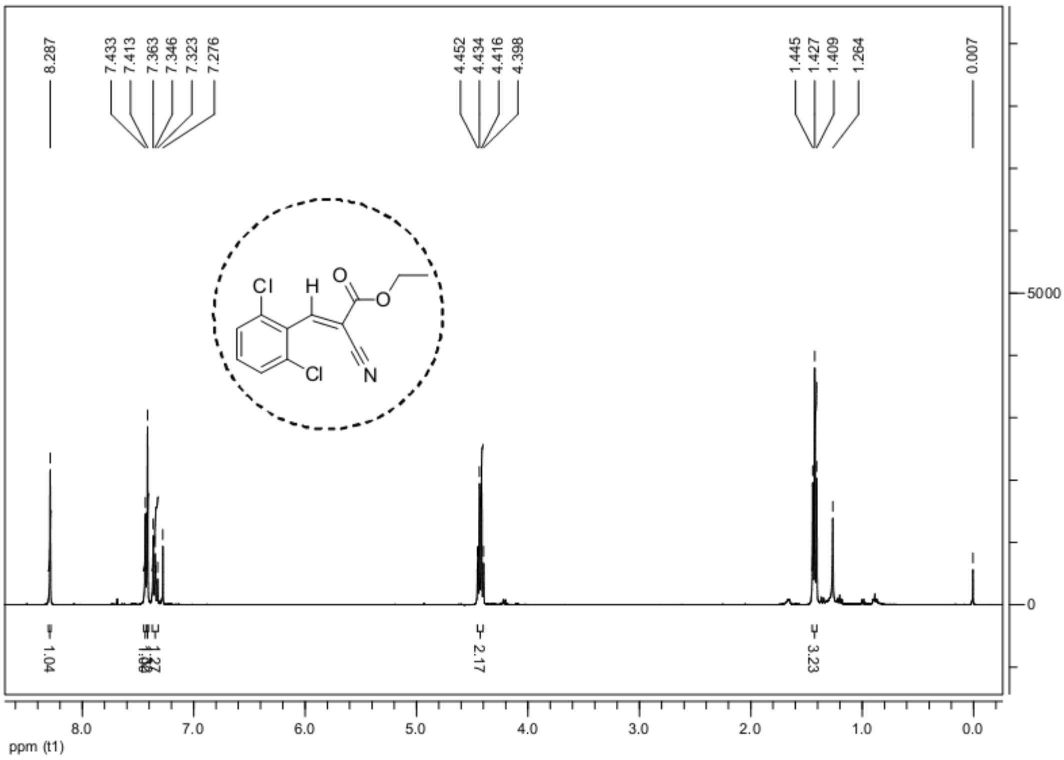

162.238
153.405
139.595
132.228
129.893
129.693
115.291
103.504
77.420
77.102
76.784
62.904
14.180
H
N
Cl
O
O
5000
0
150
100
50
0
ppm (t1)

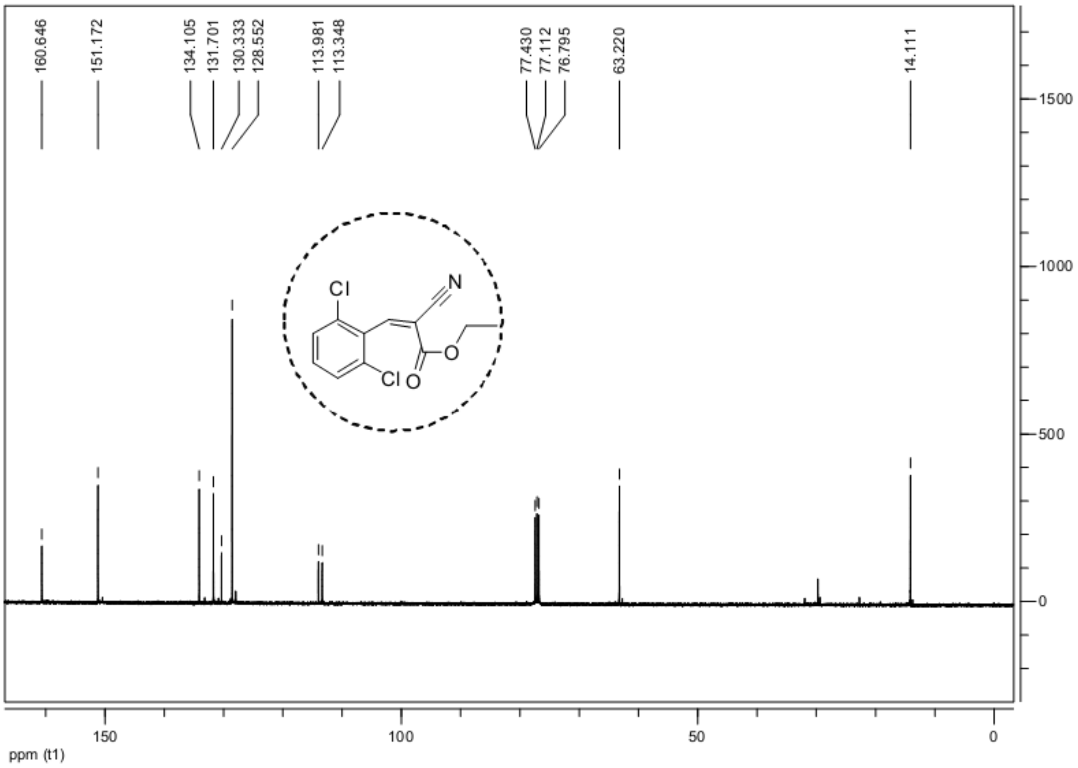

8.615
7.987
7.268
7.142
4.422
4.405
4.387
4.369
3.953
1.423
1.406
1.388
0.000
Br
H
N
O
O
O
O
1.01
1.01
1.01
2.00
6.20
3.02
7000
6000
5000
4000
3000
2000
1000
0
-1000
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

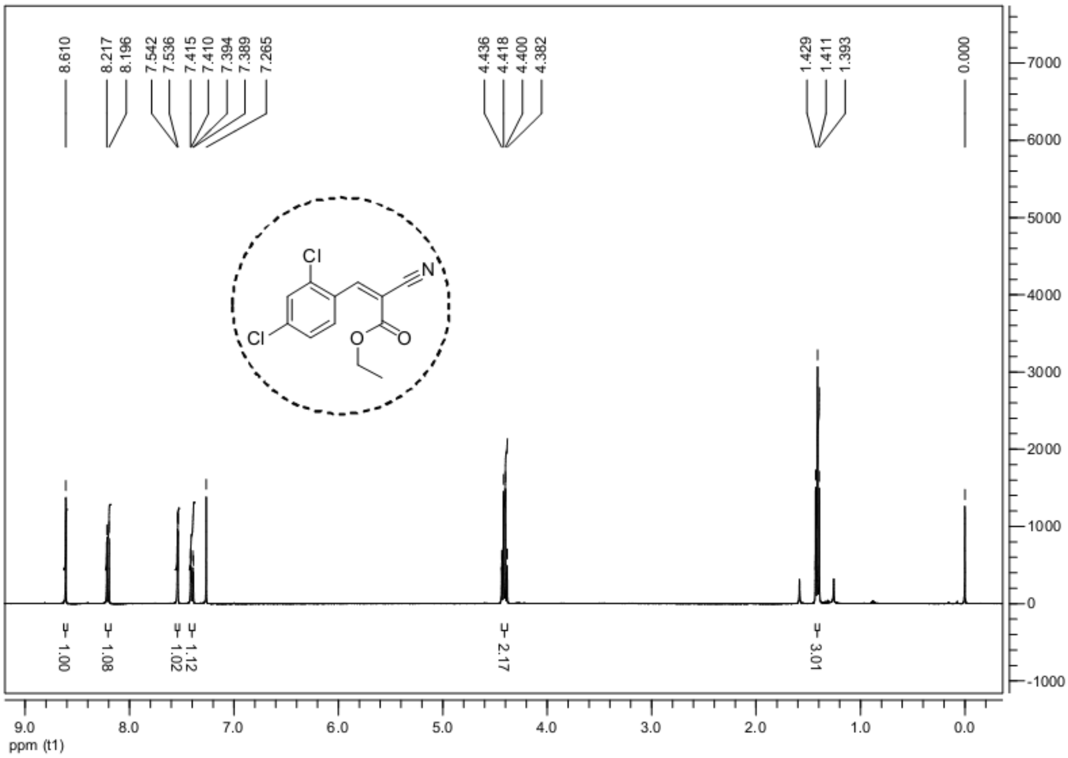

162.498
153.408
153.084
148.548
123.412
120.790
115.881
115.830
111.375
102.329
77.378
77.060
76.743
62.728
56.486
56.347
14.220
Br
H
N
O
O
O
O
3000
2500
2000
1500
1000
500
0
-500
150
100
50
0
ppm (t1)

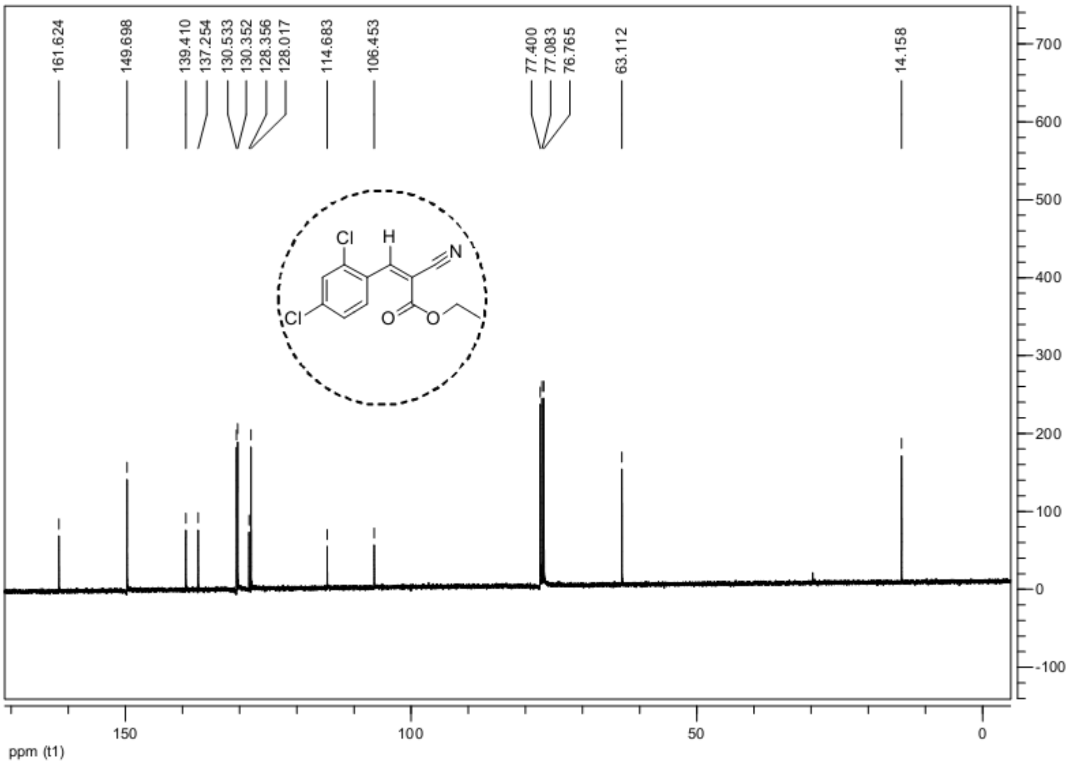

8.175
7.503
7.481
7.267
6.965
6.943
6.853
3.935
3.926
3.920
3.910
3.878
3.866
1.256
0.000
O
N
OH
O
O
1.00
1.21
1.27
1.19
3.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)
3500
3000
2500
2000
1500
1000
500
0
-500

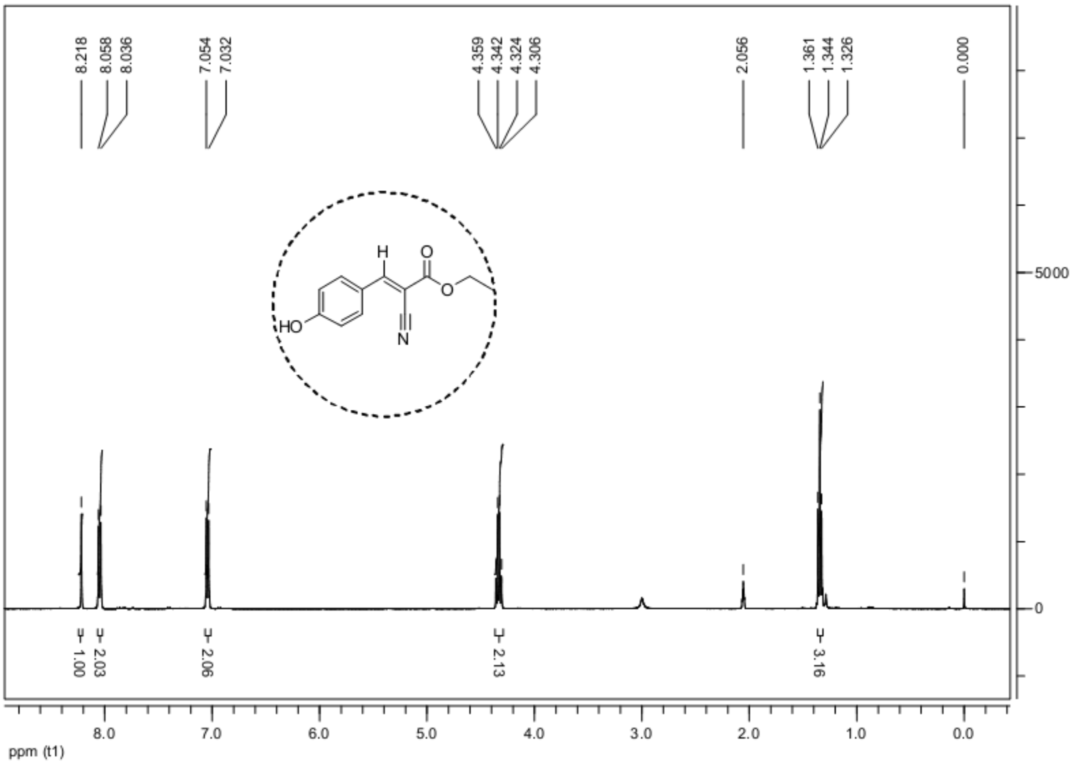

165.977
165.178
157.599
149.021
130.725
113.723
100.381
77.366
77.049
76.731
61.754
56.041
29.725
14.314
OH
N
O
O
O
150
100
50
0
ppm (f1)
1500
1000
500
0

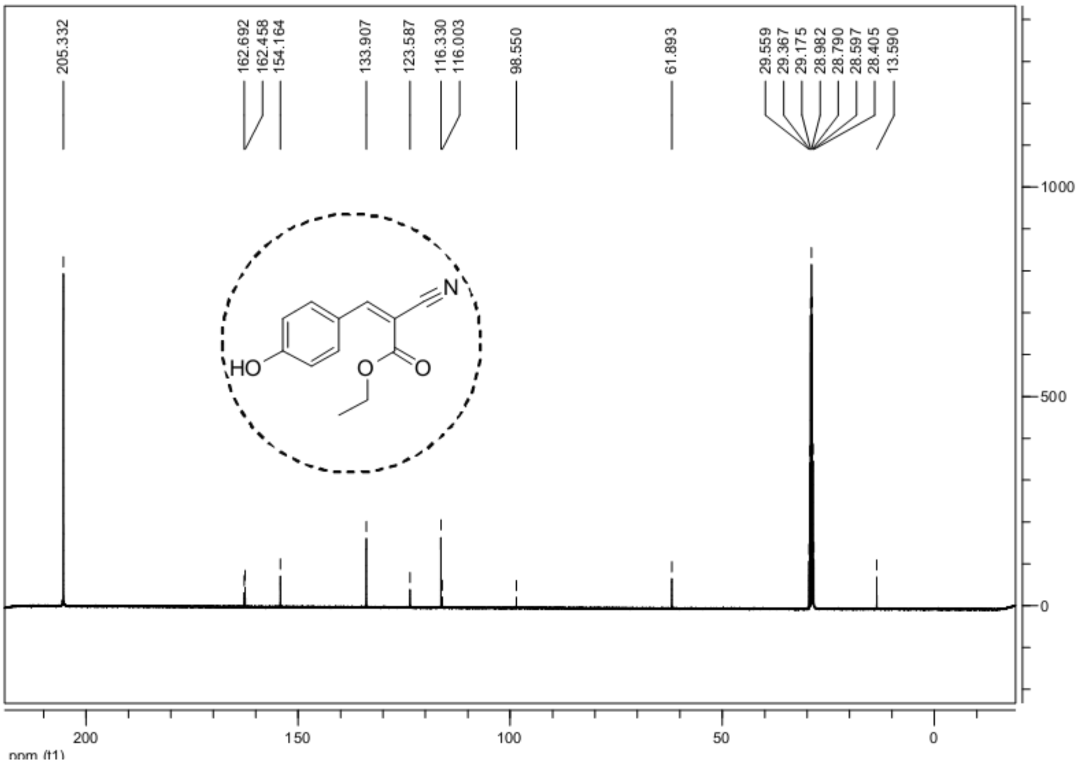

8.287
7.433
7.413
7.363
7.346
7.323
7.276
4.452
4.434
4.416
4.398
1.445
1.427
1.409
1.264
0.007
Cl
H
O
O
Cl
N
5000
0
1.04
1.27
2.17
3.23
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)


160.646
151.172
134.105
131.701
130.333
128.552
113.981
113.348
77.430
77.112
76.795
63.220
14.111
Cl
N
O
Cl
O
1500
1000
500
0
150
100
50
0
ppm (t1)


8.610
8.217
8.196
7.542
7.536
7.415
7.410
7.394
7.389
7.265
4.436
4.418
4.400
4.382
1.429
1.411
1.393
0.000
Cl
Cl
N
O
O
1.00
1.08
1.02
1.12
2.17
3.01
7000
6000
5000
4000
3000
2000
1000
0
-1000
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)


161.624
149.698
139.410
137.254
130.533
130.352
128.356
128.017
114.683
106.453
77.400
77.083
76.765
63.112
14.158
Cl
H
N
Cl
O
O
700
600
500
400
300
200
100
0
-100
150
100
50
0
ppm (t1)


8.218
8.058
8.036
7.054
7.032
4.359
4.342
4.324
4.306
2.056
1.361
1.344
1.326
0.000
H
O
O
HO
N
5000
0
1.00
2.03
2.06
2.13
3.16
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)


205.332
162.692
162.458
154.164
133.907
123.587
116.330
116.003
98.550
61.893
29.559
29.367
29.175
28.982
28.790
28.597
28.405
13.590
N
HO
O
O
1000
500
0
200
150
100
50
0
ppm (t1)