Supporting Information

Novel glycosyl pyridyl-triazole@palladium nanoparticles: efficient and recoverable catalysts for C-C cross-couplings

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1. General Information

The starting materials were commercially available and were used without further purification except solvents. The products were isolated by column chromatography on silica gel (200-300 mesh) using petroleum ether (60-90^{o}C) and ethyl acetate. Melting points were determined on an X-5 Data microscopic melting point apparatus. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker Advance 400 spectrometer at ambient temperature with $CDCl_3$ or DMSO-d_6 as solvent unless otherwise noted and tetramethylsilane (TMS) as the internal standard. Mass spectra (EI-MS) were acquired on an Agilent 5975 spectrometer. Mass spectra (GC-MS) were acquired on an Agilent 5975 spectrometer. Transmission electron microscopy (TEM) images were taken on FEI T20 microscope. ICP-AES metal determinations were carried out on a Perkin-Elmer Optima 3100 XL inductively coupled plasma atomic emission spectrometer equipped with an axial torch, segmented array charge-coupled device detector, and Babington-type nebulizer with cyclonic spray chamber for sample introduction. The small-angle X-ray diffraction (SAXRD) data were taken on a German Bruker D4 X-ray diffractometer with Niltered Cu Ka radiation (40 kV, 40 mA). Thermogravimetric analyses were performed with a SII Nano Technology EXTAR TG/DTA7220 thermal analyzer at 10 °C/min in nitrogen atmosphere (10 ml/min). 5 mg of each sample in an alumina pan was analyzed in the 40-900 °C temperature range. Analytical thin layer chromatography (TLC) was performed on Merk precoated TLC (silica gel 60 F254) plates. The sugar substrates were prepared according to our previous reports.[1] All compounds were characterized by ^{1}H NMR and mass spectroscopy, which are consistent with those reported in the literature.[2-5] The quinolone bromides was prepared according to a similar reference.[6]

2. Experimental Section

General Procedure for synthesis of glycosyl pyridyl-triazole@palladium nanoparticle catalysts 5a-e

Synthesis of GPT-Pd catalyst **5c**: PdX_2(X = OAc, Cl, Br) (0.50 mmol) was dissolved in anhydrous toluene (20.0 mL) and **4a-c** (0.60 mmol) was added. The solid-liquid mixture was stirred for 6 h at room temperature, during this course, the yellow precipitate slowly appeared and after which the solid was filtered, washed thoroughly with large volume of

acetone in order to remove any adsorbed palladium and finally dried at 30 ^{o}C under vacuum. The nanoparticle catalysts was obtained as light yellow powder.

General procedure for Suzuki-Miyaura coupling reaction between aryl halides and arylboronic acids .

The Suzuki reaction was performed in a 10 mL round- bottomed flask, aryl halide (1.0 mmol), arylboronic acid (1.5 mmol), GPT-Pd catalysts **5** (0.025 mol% respect to aryl halides), K_2CO_3 (1.5 mmol) and water (3 mL) were charged and stirred at 80 to100 ^{o}C under air. The reaction progress was monitored by TLC. After completion of the reaction, the mixture was allowed to cool to room temperature. Then the aqueous phase was extracted with CH_2Cl_2 for 3 times (3 × 2 mL). Then the combined organic layers were dried over anhydrous Na_2SO_4, concentrated under vacuum and purified by column chromatography (n-hexane/ethyl acetate 10:1) to afford the desired product.

General procedure for Heck reaction between aryl halides and olefins.

The Heck reaction was performed in a 10 mL round- bottomed flask, aryl halide (0.5 mmol), olefins (0.6 mmol), GPT-Pd catalysts **5** (0.025 mol% respect to aryl halides), Et_3N (1.5 mmol) and a mixture of water and DMSO (1:1, 3 mL) were charged and stirred at 80 to100 ^{o}C under air. Monitoring of the reaction, workup procedure, and purification of the Heck-coupled products were performed as described for the Suzuki-Miyaura coupling reactions.

General procedure for Sonogashira coupling reaction between aryl halides and terminal alkynes.

The Sonogashira coupling reaction was performed in a 10 mL round- bottomed flask, aryl halide (1.0 mmol), terminal alkynes (1.5 mmol), GPT-Pd catalysts **5** (0.025 mol% respect to aryl halides), Et_3N (1.5 mmol) and a mixture of water and DMSO (1:1, 3 mL) were charged and stirred at 80 to100 ^{o}C under air. Monitoring of the reaction, workup procedure, and purification of the Sonogashira-coupled products were performed as described for the Suzuki-Miyaura coupling reactions.

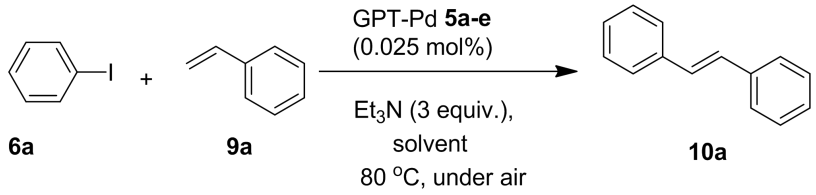
General procedure for the catalyst recycling experiment.

4-iodoanisole **6a** (1 mmol), phenylboronic acid **7a** (1.5 mmol), GPT-Pd catalyst **5c** (0.025 mol%), K_2CO_3 (1.5 mmol) and in water (3 mL) was added to 3 mL water and ether was heated under air in an oil bath at 80 ^oC. After the completion of the reaction, the product was separated using ethyl acetate extraction and the catalyst by centrifugation (5000 rpm, 5 min). The products were purified by column chromatography. The catalyst was washed with ethyl acetate twice and was dried for 12 h at 50 °C. Then the separated catalyst was recharged with fresh substrate for the next run under the same reaction conditions.

General procedure for the Hg poisoning experiments.[7]

4-iodoanisole **6a** (1 mmol), phenylboronic acid **7a** (1.5 mmol), GPT-Pd catalyst **5c** (0.025 mol%) and K_2CO_3 (1.5 mmol) was added to 3 mL water and was heated under air in an oil bath at 80 ^oC. After 20 min, a mercury droplet was added to the reaction mixture. an immediate suppression of activity was noted, pointing to the heterogeneous nature of the present system.

Table S1. Mizoroki-Heck Reaction with GPT-Pd **5** in various solvents[a]

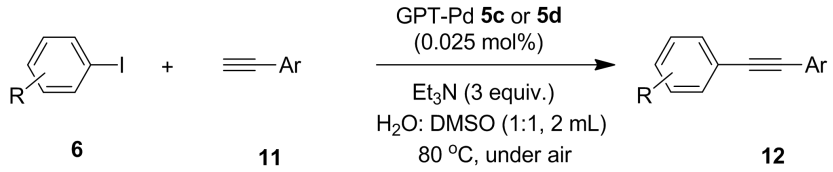


entry	catalyst	solvent	yield[b](%)
1	**5a**	H_2O	53
2	**5b**	H_2O	46
3	**5c**	H_2O	60
4	**5d**	H_2O	55
5	**5e**	H_2O	32
6	**5c**	DMF	92
7	**5c**	DMSO	96
8	**5c**	DMSO-H_2O(1:2)	91
9	**5c**	DMSO-H_2O(1:1)	95

10	**5c**	DMSO-H_2O(3:1)	95

[a] Reaction conditions: **6**a (0.5 mmol), **9a** (0.6 mmol), Et_3N (1.5 mmol), 0.025 mol% of **5a-e,** 3 mL of solvent at 80 °C under air. [b] Yields of isolated products are the average of at least two experiments.

Table S2. Sonogashira reaction with GPT-Pd **5c** and **5d**.[a]



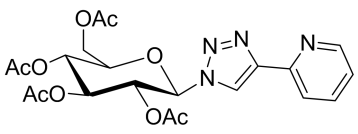
6 **11** **12**

Entry	Catalyst	R	Ar	Yield[b] (%)
1	**5c**	4-CH_3	Ph	93(**12a**)
2	**5d**	4-CH_3	Ph	88(**12a**)
3	**5c**	4-OCH_3	Ph	95(**12b**)
4	**5d**	4-OCH_3	Ph	92(**12b**)
5	**5c**	4-Cl	Ph	87(**12c**)
6	**5d**	4-Cl	Ph	83(**12c**)
7	**5c**	4-NO_2	Ph	95(**12d**)
8	**5d**	4-NO_2	Ph	89(**12d**)
9	**5c**	3-NO_2	Ph	96(**12e**)
10	**5d**	3-NO_2	Ph	91(**12e**)
11	**5c**	H	pyridine	92(**12f**)
12	**5d**	H	pyridine	90(**12f**)

[a]Reaction conditions: aryl iodides **6** (0.5 mmol), terminal alkynes **11** (0.75 mmol), 0.025 mol% of **5c** and **5d**, Et_3N (1.5 mmol), 3 mL of H_2O: DMSO (1:1) at 80 °C under air. [b]Isolated yield.

3. Characterization of the Products:

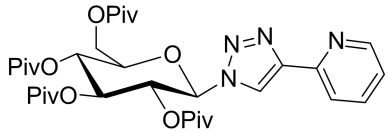
4-Pyridyl-1-(2,3,4,6-tetra-*O*-acetyl-1-D-glucopyranosyl)-1,2,3-triazole 4a[1]**:**



white solid, 93% yield, mp. 214-218°C. ^{1}H NMR (500 MHz, DMSO): δ 9.00 (s, 1H), 8.64 (d, *J* = 4 Hz, 1H), 8.05 (d, *J* = 8 Hz, 1H), 7.93 (td, *J* = 7.8,

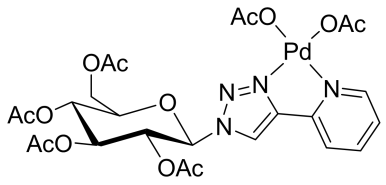
1.5 Hz, 1H), 7.39 (dd, *J* = 6.9, 5.3 Hz, 1H), 6.44 (d, *J* = 9.2 Hz, 1H), 5.80 (t, *J* = 9.4 Hz, 1H), 5.62 (t, *J* = 9.5 Hz, 1H), 5.25 (t, *J* = 9.8 Hz, 1H), 4.41 (ddd, *J* = 10.0, 5.5, 2.4 Hz, 1H), 4.13 (qd, *J* = 12.5, 3.9 Hz, 2H), 2.05 (s, 3H), 2.01 (s, 3H), 1.99 (s, 3H), 1.82 (s, 3H). ^{13}C NMR (126 MHz, DMSO)：δ 170.55, 170.08, 169.90, 169.14, 150.24, 149.73, 148.31, 137.82, 123.87, 122.76, 120.10, 84.52, 73.70, 72.45, 70.66, 67.95, 62.35, 20.99, 20.89, 20.74, 20.40.

4-Pyridyl-1-(2,3,4,6-tetra-*O*-pivaloyl-1-D-glucopyranosyl)-1,2,3-triazole 4b:



white solid, 95% yield, mp. 227-231°C. ^{1}H NMR (500 MHz, DMSO): δ 9.02 (s, 1H), 8.64 (d, *J* = 4.3 Hz, 1H), 8.02 (d, *J* = 7.8 Hz, 1H), 7.92 (d, *J* = 7.4 Hz, 1H), 7.48 – 7.22 (m, 1H), 6.46 (d, *J* = 9.2 Hz, 1H), 5.83 (t, *J* = 9.3 Hz, 1H), 5.68 (t, *J* = 9.5 Hz, 1H), 5.36 (t, *J* = 9.8 Hz, 1H), 4.50 (d, *J* = 10.0 Hz, 1H), 4.14 (d, *J* = 2.0 Hz, 2H), 1.15 (s, 8H), 1.13 (s, 9H), 1.07 (s, 9H), 0.84 (s, 9H). ^{13}C NMR (126 MHz, DMSO)： δ 177.52, 176.85, 176.21, 176.01, 150.23, 148.29, 137.75, 123.79, 122.87, 120.14, 84.92, 74.20, 72.52, 70.71, 67.38, 61.67, 38.79, 38.76, 38.71, 38.56, 27.23, 27.11, 26.77.

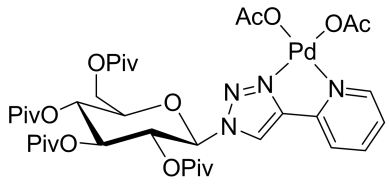
GPT-Pd catalyst **5a:**



yellow solid 90% yield, ^{1}H NMR (500 MHz, DMSO): δ 9.57 (s, 1H), 8.33 (td, *J* = 7.8, 1.1 Hz, 1H), 8.20 (d, *J* = 7.6 Hz, 1H), 8.09 (d, *J* = 5.5 Hz, 1H), 7.72 – 7.67 (m, 1H), 6.64 – 6.61 (m, 1H), 5.66 – 5.61 (m, 1H), 5.57 (t, *J* = 9.2 Hz, 1H), 5.23 (dd, *J* = 13.1, 6.4 Hz, 1H), 4.45 (ddd, *J* = 10.0, 5.6, 2.2 Hz, 2H), 4.21 (dd, *J* = 12.6, 5.6 Hz, 1H), 4.13 (d, *J* = 12.4 Hz, 2H), 2.05 (s, 3H), 2.03 (s, 3H), 2.00 (s, 3H), 1.95 (s, 3H), 1.92 (s, 3H), 1.83 (s, 3H). ^{13}C NMR (126 MHz, DMSO)： δ 176.10, 175.95, 170.47, 169.94, 169.82, 169.53, 149.95, 148.01, 147.71, 141.91, 126.62, 124.68, 122.78, 85.98, 74.32, 71.97, 70.75, 67.78, 62.15, 40.58, 40.41, 40.25, 40.08, 39.91, 39.75, 39.58,

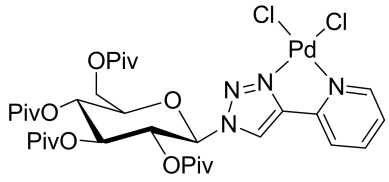
23.77, 23.29, 20.96, 20.82, 20.68, 20.41. Anal. calcd. for $C_{25}H_{30}N_4O_{13}Pd$: C, 42.84; H, 4.31; N, 7.99; found: C, 42.80; H, 4.41; N, 782.

GPT-Pd catalyst **5b:**



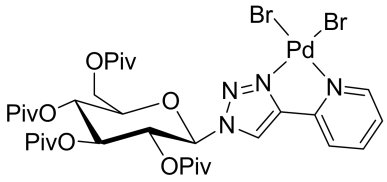
yellow solid 92% yield, ^{1}H NMR (500 MHz, DMSO): δ 9.63 (s, 1H), 8.33 (s, 1H), 8.18 (d, *J* = 7.8 Hz, 1H), 8.10 (d, *J* = 5.6 Hz, 1H), 7.70 (s, 1H), 6.63 (d, J = 9.0 Hz, 1H), 5.72 (t, J = 9.6 Hz, 1H), 5.55 (d, J = 9.2 Hz, 1H), 5.34 (d, *J* = 9.9 Hz, 1H), 4.58 (s, 1H), 4.18 (d, *J* = 3.5 Hz, 3H), 1.92 (s, 3H), 1.81 (s, 3H), 1.17 (d, *J* = 2.5 Hz, 11H), 1.12 (s, 11H), 1.07 (s, 11H), 0.99 (d, *J* = 5.1 Hz, 11H). ^{13}C NMR (126 MHz, DMSO)： δ 177.53, 176.86, 176.20, 176.02, 150.25, 149.80, 148.30, 137.78, 123.82, 122.86, 120.14, 84.89, 74.15, 72.49, 70.68, 67.31, 61.65, 27.23, 27.11, 26.77. Anal. calcd. for $C_{37}H_{54}N_4O_{13}Pd$: C, 51.12; H, 6.26; N, 6.45; found: C, 51.18; H, 6.20; N, 6.451.

GPT-Pd catalyst **5c:**



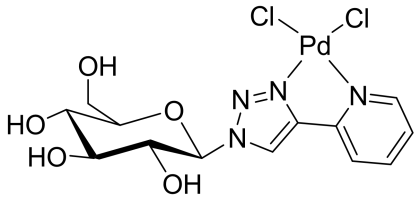
yellow solid 97% yield, ^{1}H NMR (500 MHz, DMSO): δ 9.69 (s, 1H), 9.01 (d, *J* = 5.4 Hz, 1H), 8.34 (d, *J* = 1.1 Hz, 1H), 8.18 (d, *J* = 7.7 Hz, 1H), 7.76 (s, 1H), 6.66 (d, *J* = 9.0 Hz, 1H), 5.76 (t, *J* = 9.5 Hz, 1H), 5.55 (s, 1H), 5.34 (t, *J* = 9.8 Hz, 1H), 4.61 (s, 1H), 4.19 (d, *J* = 2.7 Hz, 2H), 1.18 (s, 9H), 1.13 (s, 10H), 1.07 (s, 10H), 0.98 (s, 9H). ^{13}C NMR (126 MHz, DMSO)： δ 177.50, 176.79, 176.48, 176.16, 151.33, 149.25, 148.10, 142.06, 126.87, 124.82, 123.00, 86.36, 74.58, 71.80, 71.07, 67.09, 61.66, 27.27, 27.19, 27.09, 27.04. Anal. calcd. for $C_{33}H_{48}Cl_2N_4O_9Pd$: C, 48.21; H, 5.89; N, 6.82; found: C, 48.13; H, 5.77; N, 6.80.

GPT-Pd catalyst **5d:**



yellow solid 81% yield. ^{1}H NMR (500 MHz, DMSO): δ 9.70 (s, 1H), 9.24 (s, 1H), 8.35 (t, *J* = 7.3 Hz, 1H), 8.18 (d, *J* = 7.4 Hz, 1H), 7.76 (s, 1H), 6.67 (d, *J* = 8.8 Hz, 1H), 5.75 (t, *J* = 9.3 Hz, 1H), 5.56 (t, *J* = 9.0 Hz, 1H), 5.35 (t, *J* = 9.7 Hz, 1H), 4.60 (d, *J* = 9.6 Hz, 1H), 4.19 (s, 2H), 1.18 (s, 9H), 1.13 (s, 9H), 1.07 (s, 9H), 0.98 (s, 9H). ^{13}C NMR (126 MHz, DMSO)：δ 177.50, 176.79, 176.48, 176.16, 151.33, 149.25, 148.10, 142.06, 126.87, 124.82, 123.00, 86.36, 74.58, 71.80, 71.07, 67.09, 61.66, 27.27, 27.19, 27.09, 27.04. Anal. calcd. for $C_{33}H_{48}Br_2N_4O_9Pd$: C, 43.51; H, 5.31; N, 6.15; found: C, 43.56; H, 5.27; N, 6.07.

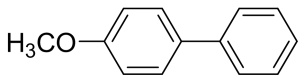
GPT-Pd catalyst **5e:**



yellow solid 78% yield. ^{1}H NMR (500 MHz, DMSO): δ 9.54 (s, 1H), 9.02 (d, *J* = 5.6 Hz, 1H), 8.34 (t, *J* = 7.7 Hz, 1H), 8.19 (d, *J* = 7.7 Hz, 1H), 7.74 (t, *J* = 6.6 Hz, 1H), 5.84 (d, *J* = 9.2 Hz, 1H), 5.66 (d, *J* = 5.6 Hz, 1H), 5.40 (d, *J* = 5.1 Hz, 1H), 5.24 (d, *J* = 5.5 Hz, 1H), 4.68 (t, *J* = 5.7 Hz, 1H), 3.73 (ddd, *J* = 15.0, 10.0, 5.9 Hz, 2H), 3.64 – 3.57 (m, 1H), 3.56 – 3.44 (m, 3H). ^{13}C NMR (126 MHz, DMSO)：δ 150.27, 148.47, 141.92, 126.18, 125.19, 122.54, 89.75, 80.71, 76.64, 73.16, 69.69, 61.08, 60.55. Anal. calcd. for $C_{13}H_{16}Cl_2N_4O_5Pd$: C, 32.15; H, 3.32; N, 11.54; found: C, 32.19; H, 3.28; N, 11.48.

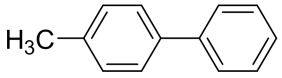
Products of Suzuki-Miyaura reactions:[3]

4-methoxybiphenyl 8a:



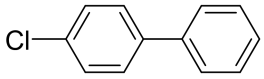
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.60 (dd, *J* = 11.4, 8.2 Hz, 4H), 7.47 (t, *J* = 7.7 Hz, 2H), 7.36 (t, *J* = 7.4 Hz, 1H), 7.03 (d, *J* = 8.7 Hz, 2H), 3.90 (s, 3H). GC-MS (EI) [M]+: m/z calcd. for $C_{13}H_{12}O$: 184.0, found: 184.

4-methylbiphenyl 8b:



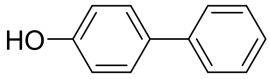
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.69 (dt, *J* = 8.2, 4.2 Hz, 2H), 7.59 (d, *J* = 8.1 Hz, 1H), 7.54 (q, *J* = 7.9 Hz, 2H), 7.37 – 7.31 (m, 1H), 7.34 (d, *J* = 7.9 Hz, 2H), 2.48 (s, 3H). GC-MS (EI) [M]+: m/z calcd. for $C_{13}H_{12}$: 168.0, found: 168.

4-chlorobiphenyl 8c:



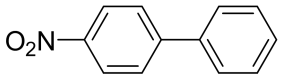
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.59 – 7.50 (m, 4H), 7.42 (m, *J* = 10.9, 8.5, 4.6 Hz, 4H), 7.35 (t, *J* = 7.4 Hz, 1H). GC-MS (EI) [M]+: m/z calcd. For $C_{12}H_9Cl$: 188.0, found: 188.

biphenyl-4-ol 8d:



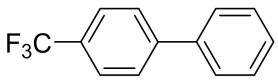
^{1}H NMR (500 MHz, DMSO): δ 9.51 (s, 1H), 7.58 (dd, *J* = 8.2, 1.1 Hz, 2H), 7.52 – 7.47 (m, 2H), 7.41 (t, *J* = 7.7 Hz, 2H), 7.28 (t, *J* = 7.4 Hz, 1H). GC-MS (EI) [M]+: m/z calcd. for $C_{12}H_{10}O$: 170.0, found: 170.

4-nitrobiphenyl 8e:



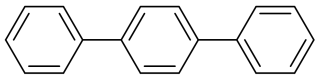
^{1}H NMR (500 MHz, $CDCl_3$): δ 8.39 – 8.34 (m, 1H), 7.83 – 7.78 (m, 1H), 7.70 (dd, *J* = 5.3, 3.3 Hz, 1H), 7.60 – 7.54 (m, 0.5H), 7.52 (dt, *J* = 9.6, 4.3 Hz, 0.5H). GC-MS (EI) [M]+: m/z calcd. for $C_{12}H_9NO_2$: 199.0, found: 199.

4-(trifluoromethyl)biphenyl 8f:

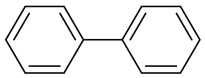


^{1}H NMR (500 MHz, $CDCl_3$): δ 7.73 (s, 1H), 7.65 (dd, *J* = 8.2, 1.0 Hz, 3H), 7.56 – 7.44 (m, 3H), 7.42 – 7.38 (m, 1H). GC-MS (EI) [M]+: m/z calcd. for $C_{13}H_9F_3$: 222.0, found: 222.

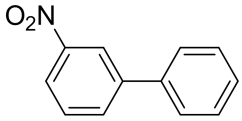
1,1':4',1''-Terphenyl 8g:


^{1}H NMR (500 MHz, $CDCl_3$): δ 7.71 (s, 4H), 7.69 – 7.68 (m, 4H), 7.46 (t, *J* = 7.7 Hz, 4H), 7.36 (t, *J* = 7.4 Hz, 2H). GC-MS (EI) [M]+: m/z calcd. for $C_{14}H_{12}O$: 196.0, found: 196.

biphenyl 8h:

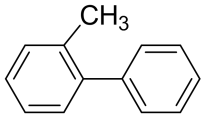

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.74 – 7.71 (m, 4H), 7.56 (dd, *J* = 10.5, 4.8 Hz, 4H), 7.48 – 7.46 (m, 2H). GC-MS (EI) [M]+: m/z calcd. for $C_{12}H_{10}$: 154.0, found: 154.

3-nitrobiphenyl 8i:



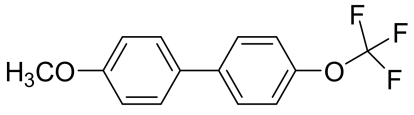
^{1}H NMR (500 MHz, $CDCl_3$): δ 8.48 (t, *J* = 1.9 Hz, 1H), 8.22 (dd, *J* = 8.2, 1.4 Hz, 1H), 7.94 (d, *J* = 7.8 Hz, 1H), 7.65 (dt, *J* = 13.9, 4.7 Hz, 3H), 7.53 (dd, *J* = 10.3, 4.8 Hz, 2H), 7.50 – 7.44 (m, 1H). GC-MS (EI) [M]+: m/z calcd. for $C_{12}H_9NO_2$: 199.0, found: 199.

2-methylbiphenyl 8j:



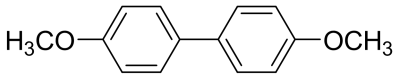
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.60 (dd, *J* = 8.2, 1.1 Hz, 1H), 7.46 – 7.38 (m, 3H), 7.37 – 7.31 (m, 3H), 7.29 – 7.22 (m, 2H), 2.27 (s, 3H).GC-MS (EI) [M]+: m/z calcd. for $C_{13}H_{12}$: 168.0, found: 168.

4-methoxy-4'-(trifluoromethoxy)biphenyl 8k:



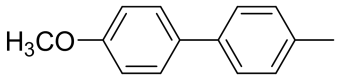
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.68 (dd, *J* = 9.1, 2.4 Hz, 2H), 7.29 – 7.27 (m, 2H), 7.02 – 7.00 (m, 2H), 3.88 (s, 3H). GC-MS (EI) [M]+: m/z calcd. for $C_{14}H_{11}F_3O_2$: 268.0, found: 268.

4,4'-dimethoxybiphenyl 8l:



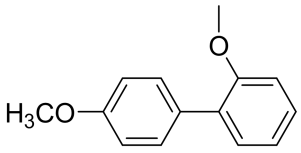
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.51 – 7.49 (m, 4H), 6.99 – 6.97 (m, 4H), 3.87 (s, 6H). GC-MS (EI) [M]+: m/z calcd. for $C_{14}H_{14}O_2$: 214.0, found: 214.

4-methoxy-4'-methylbiphenyl 8m:



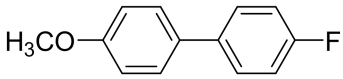
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.55 (dd, *J* = 9.3, 2.5 Hz, 2H), 7.49 (d, *J* = 8.1 Hz, 2H), 7.26 (d, *J* = 7.9 Hz, 2H), 7.00 (dd, *J* = 9.3, 2.5 Hz, 2H), 3.87 (s, 3H), 2.41 (s, 3H). GC-MS (EI) [M]+: m/z calcd. for $C_{14}H_{14}O$: 198.0, found: 198.

2,4'-dimethoxybiphenyl 8n:



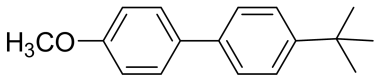
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.55 – 7.53 (m, 2H), 7.38 – 7.36 (m, 2H), 7.10 (td, *J* = 7.5, 0.9 Hz, 1H), 7.07 – 7.00 (m, 3H), 3.90 (s, 3H), 3.87 (s, 3H) GC-MS (EI) [M]+: m/z calcd. for $C_{14}H_{14}O_2$: 214.0, found: 214.

14-fluoro-4'-methoxybipheny 8o:



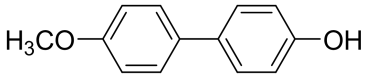
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.53 – 7.49 (m, 4H), 7.14 – 7.10 (m, 2H), 7.02 – 6.99 (m, 2H), 3.87 (s, 3H). GC-MS (EI) [M]+: m/z calcd. for $C_{13}H_{11}FO$: 202.0, found: 202.

4-tert-butyl-4'-methoxybiphenyl 8p:



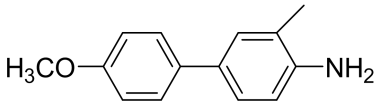
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.56 – 7.52 (m, 4H), 7.48 – 7.46 (m, 2H), 7.00 – 6.99 (m, 2H), 3.89 (s, 3H), 1.40 (s, 9H). GC-MS (EI) [M]+: m/z calcd. for $C_{17}H_{20}O$: 240.0, found: 240.

4'-methoxybiphenyl-4-ol 8q:



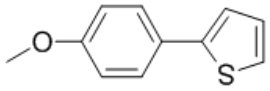
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.49 – 7.48 (m, 2H), 7.46 – 7.44 (m, 2H), 6.99 – 6.97 (m, 2H), 6.91 – 6.89 (m, 2H), 3.87 (s, 3H). GC-MS (EI) [M]+: m/z calcd. for $C_{13}H_{12}O_2$: 200.0, found: 200.

4'-methoxy-3-methylbiphenyl-4-amine 8r:



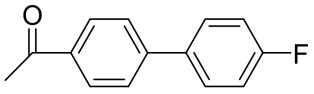
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.41 – 7.39 (m, 2H), 7.00 (dd, *J* = 6.7, 2.1 Hz, 4H), 6.79 (d, *J* = 7.9 Hz, 1H), 4.01 (dd, *J* = 61.2, 43.2 Hz, 2H), 3.90 – 3.83 (m, 3H), 2.32 (s, 3H). GC-MS (EI) [M]+: m/z calcd. for $C_{14}H_{12}O$: 196.0, found: 196

2-(4-methoxyphenyl)thiophene 8s:



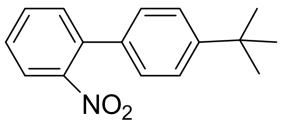
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.57 – 7.55 (m, 2H), 7.24 – 7.22 (m, 2H), 7.15 (dd, *J* = 5.1, 3.6 Hz, 1H), 7.05 – 7.00 (m, 2H), 3.86 (s, 3H).GC-MS (EI) [M]+: m/z calcd. for $C_{11}H_{10}OS$: 190.0, found: 190.

1-(4'-fluorobiphenyl-4-yl)ethanone 8t:



^{1}H NMR (500 MHz, $CDCl_3$): δ 8.05 – 8.04 (m, 2H), 7.67 – 7.60 (m, 2H), 7.29 (2H), 7.20 – 7.19 (m, 2H), 2.66 (s, 3H). GC-MS (EI) [M]+: m/z calcd. for $C_{14}H_{12}O$: 196.0, found: 196

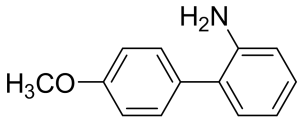
4'-tert-butyl-2-nitrobiphenyl 8u:



^{1}H NMR (500 MHz, $CDCl_3$): δ 8.55 (t, *J* = 1.9 Hz, 1H), 8.30 – 8.25 (m, 1H), 8.02 – 7.99 (m, 1H), 7.71 – 7.66 (m, 3H), 7.64 – 7.60 (m, 2H), 1.48 (s, 9H).

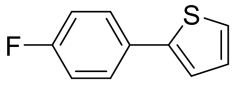
GC-MS (EI) [M]+: m/z calcd. for $C_{14}H_{12}O$: 196.0, found: 196.

4'-methoxybiphenyl-2-amine 8v:



^{1}H NMR (500 MHz, $CDCl_3$): δ 7.42 (dd, *J* = 6.7, 4.8 Hz, 2H), 7.23 – 7.16 (m, 2H), 7.01 – 6.91 (m, 4H), 5.04 (br, 2H), 3.84 (d, *J* = 4.3 Hz, 3H). GC-MS (EI) [M]+: m/z calcd. for $C_{13}H_{13}NO$: 199.0, found: 199.

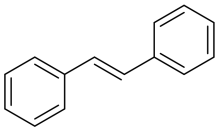
2-(4-fluorophenyl)thiophene 8w:



^{1}H NMR (500 MHz, $CDCl_3$): δ 7.65 – 7.58 (m, 2H), 7.31 (dd, J = 5.1, 1.0 Hz, 1H), 7.28 – 7.27 (m, 1H), 7.17 – 7.03 (m, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 163.33, 161.37, 143.30, 130.63, 127.97, 127.67, 124.64, 122.97, 115.74, 115.61.

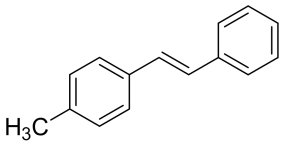
Products of Mizoroki-Heck reaction reactions:[4]

(*E*)-1,2-diphenylethene 10a:



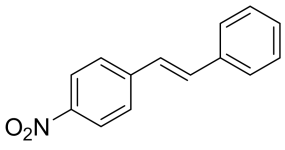
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.58 (d, *J* = 7.5 Hz, 4H), 7.43 (dd, *J* = 9.8, 5.5 Hz, 4H), 7.36 – 7.29 (m, 2H), 7.18 (d, *J* = 1.3 Hz, 2H).GC-MS (EI) [M]+: m/z calcd. for $C_{14}H_{12}$: 180.0, found: 180.

(*E*)-1-methyl-4-styrylbenzene 10b:



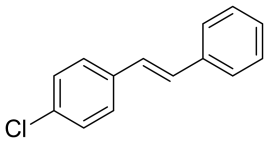
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.60 – 7.54 (m, 2H), 7.51 – 7.45 (m, 2H), 7.45 – 7.38 (m, 2H), 7.32 (dd, *J* = 8.3, 5.4 Hz, 1H), 7.26 – 7.20 (m, 2H), 7.17 – 7.11 (m, 2H), 2.49 – 2.37 (m, 3H).GC-MS (EI) [M]+: m/z calcd. for $C_{15}H_{14}$: 194.0, found: 194.

(*E*)-1-nitro-4-styrylbenzene 10c:



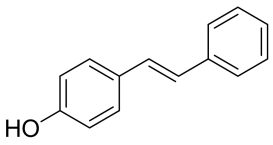
^{1}H NMR (500 MHz, $CDCl_3$): δ 8.24 (d, *J* = 8.8 Hz, 2H), 7.65 (d, J = 8.7 Hz, 2H), 7.58 (d, *J* = 7.3 Hz, 2H), 7.43 (t, *J* = 7.5 Hz, 2H), 7.39 – 7.34 (m, 1H), 7.29 (t, *J* = 4.4 Hz, 1H), 7.17 (d, *J* = 16.3 Hz, 1H). GC-MS (EI) [M]+: m/z calcd. for $C_{14}H_{11}NO_2$: 225.0, found: 225.

(*E*)-1-chloro-4-styrylbenzene 10d:



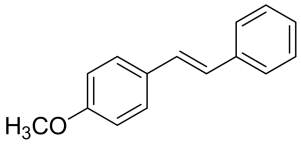
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.55 (d, *J* = 7.4 Hz, 2H), 7.46 (t, *J* = 9.4 Hz, 2H), 7.41 (t, *J* = 7.6 Hz, 2H), 7.37 (d, *J* = 8.5 Hz, 2H), 7.33 (t, *J* = 7.3 Hz, 1H), 7.15 – 7.06 (m, 2H).GC-MS (EI) [M]+: m/z calcd. for $C_{14}H_{11}Cl$: 214.0, found: 214.

(*E*)-4-styrylphenol 10e:



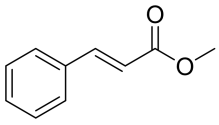
^{1}H NMR (500 MHz, DMSO): δ 9.55 (d, *J* = 12.0 Hz, 1H), 7.54 (d, *J* = 7.3 Hz, 2H), 7.46 – 7.38 (m, 2H), 7.35 (t, *J* = 7.7 Hz, 2H), 7.26 – 7.18 (m, 1H), 7.18 – 7.09 (m, 1H), 7.02 (d, *J* = 16.4 Hz, 1H), 6.83 – 6.72 (m, 2H). GC-MS (EI) [M]+: m/z calcd. for $C_{14}H_{12}O$: 196.0, found: 196.

(*E*)-1-methoxyl-4-styrylbenzene 10f:



^{1}H NMR (500 MHz, $CDCl_3$): δ 7.50 – 7.40 (m, 4H), 7.33 (dd, *J* = 10.6, 4.7 Hz, 2H), 7.21 (t, *J* = 3.7 Hz, 1H), 7.05 (d, *J* = 16.3 Hz, 1H), 6.96 (d, *J* = 16.3 Hz, 1H), 6.90 – 6.85 (m, 2H), 3.80 (s, 3H). GC-MS (EI) [M]+: m/z calcd. for $C_{15}H_{14}O$: 210.0, found: 210.

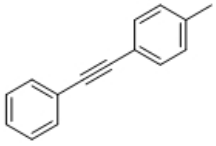
Methyl cinnamate 10g:



^{1}H NMR (500 MHz, $CDCl_3$): δ 7.72 (d, *J* = 16.0 Hz, 1H), 7.57 – 7.49 (m, 2H), 7.44 – 7.35 (m, 3H), 6.47 (d, *J* = 16.0 Hz, 1H), 3.83 (s, 3H).GC-MS (EI) [M]+: m/z calcd. for $C_{10}H_{10}O_2$: 162.0, found: 162.

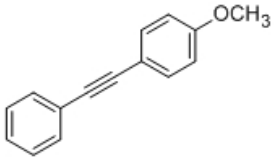
Products of Sonogashira reaction reactions:[5]

1-methyl-4-(phenylethynyl)benzene 12a:



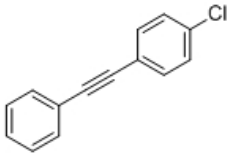
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.58 (dd, *J* = 7.8, 1.7 Hz, 2H), 7.48 (d, *J* = 8.1 Hz, 2H), 7.38 (dd, *J* = 5.6, 3.8 Hz, 3H), 7.20 (d, *J* = 7.9 Hz, 2H), 2.42 (s, 3H). GC-MS (EI) [M]+: m/z calcd. for $C_{15}H_{12}$: 192.0, found: 192.

1-methoxy-4-(phenylethynyl)benzene 12b:



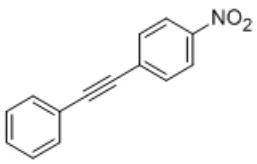
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.55 (dd, *J* = 7.8, 1.4 Hz, 2H), 7.52 – 7.49 (m, 2H), 7.39 – 7.33 (m, 3H), 6.92 (t, *J* = 5.7 Hz, 2H), 3.86 (s, 3H). GC-MS (EI) [M]+: m/z calcd. for $C_{15}H_{12}O$: 208.0, found: 208.

1-chloro-4-(phenylethynyl)benzene 12c:



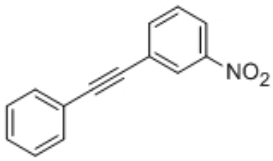
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.57 (dd, *J* = 6.5, 3.1 Hz, 2H), 7.49 (d, *J* = 8.4 Hz, 2H), 7.39 (dd, *J* = 5.0, 1.8 Hz, 3H), 7.36 (d, *J* = 8.4 Hz, 2H). GC-MS (EI) [M]+: m/z calcd. for $C_{14}H_9Cl$: 212.0, found: 212.

1-nitro-4-(phenylethynyl)benzene 12d:



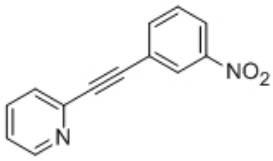
^{1}H NMR (500 MHz, $CDCl_3$): δ 8.27 – 8.22 (m, 2H), 7.72 – 7.67 (m, 2H), 7.61 – 7.56 (m, 2H), 7.44 – 7.38 (m, 3H). GC-MS (EI) [M]+: m/z calcd. for $C_{14}H_9NO_2$: 223.0, found:223.

1-nitro-3-(phenylethynyl)benzene 12e:



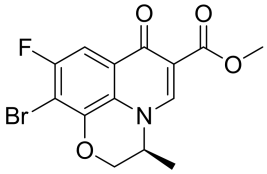
^{1}H NMR (500 MHz, $CDCl_3$): δ 8.42 – 8.38 (m, 1H), 8.20 (ddd, *J* = 8.3, 2.3, 1.0 Hz, 1H), 7.88 – 7.82 (m, 1H), 7.57 (ddd, *J* = 17.5, 11.1, 5.2 Hz, 3H), 7.44 – 7.38 (m, 3H). GC-MS (EI) [M]+: m/z calcd. for $C_{14}H_9NO_2$: 223.0, found: 223.

2-((3-nitrophenyl)ethynyl)pyridine 12f:



^{1}H NMR (500 MHz, $CDCl_3$): δ 8.67 (d, *J* = 4.8 Hz, 1H), 8.45 (d, *J* = 1.6 Hz, 1H), 8.25 – 8.19 (m, 1H), 7.92 (d, *J* = 7.7 Hz, 1H), 7.77 (td, *J* = 7.7, 1.7 Hz, 1H), 7.58 (dd, *J* = 16.8, 8.5 Hz, 2H), 7.36 – 7.31 (m, 1H). GC-MS (EI) [M]+: m/z calcd. for $C_{13}H_8N_2O_2$: 224.0, found: 224.

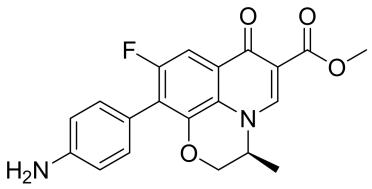
Quinolone bromides：



^{1}HNMR (500 MHz, $CDCl_3$) δ 8.68 (s, 1H), 7.57 (d, *J* = 8.9 Hz, 1H), 4.85 – 4.72 (m, 1H), 4.64 (d, *J* = 1.9 Hz, 1H), 4.49 (d, *J* = 2.3 Hz, 1H), 4.24 (dd, *J* = 7.1, 4.0 Hz, 2H), 1.42 (d, *J* = 6.8 Hz, 3H), 1.30 (t, *J* = 7.1 Hz, 3H).^{13}C NMR (126 MHz,

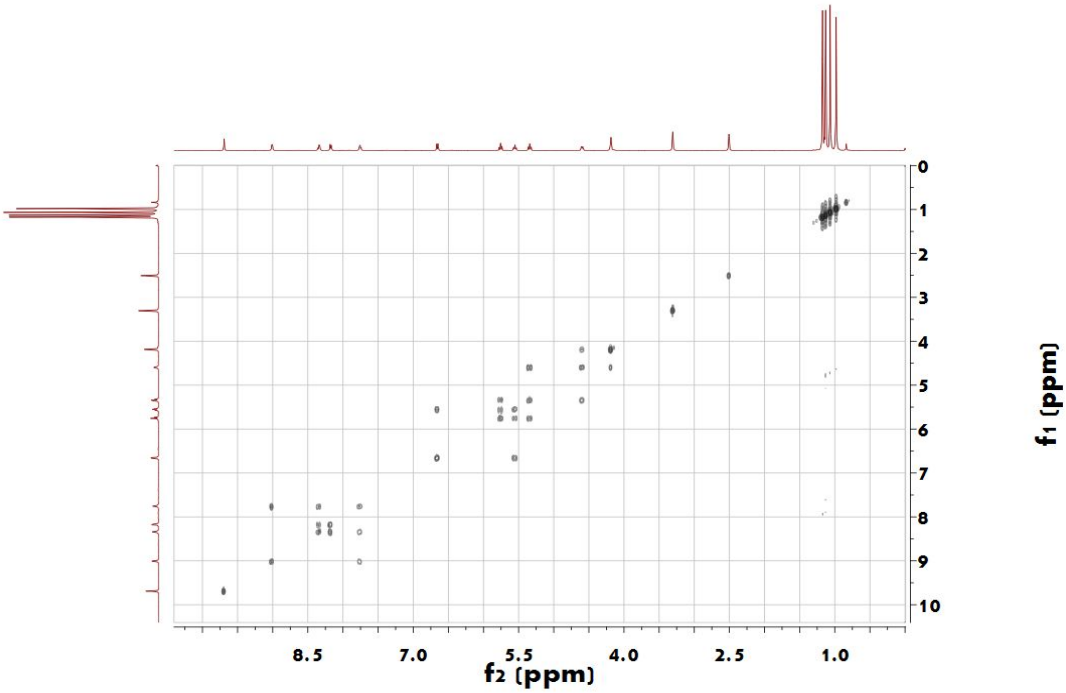
DMSO) δ 172.51, 165.04, 155.39, 146.47, 145.03, 128.65, 123.48, 110.08, 103.41, 101.56, 68.86, 60.34, 53.25, 18.39, 14.61.

Novel fluoroquinolone derivatives:



^{1}H NMR (500 MHz, $CDCl_3$) δ 8.40 (s, 1H), 7.80 (dd, *J* = 15.0, 7.0 Hz, 1H), 7.69 (dd, *J* = 7.8, 4.2 Hz, 1H), 7.55 (ddd, *J* = 25.2, 15.6, 6.5 Hz, 1H), 7.47 (dd, *J* = 7.2, 2.8 Hz, 1H), 7.30 – 7.25 (m, 2H), 6.80 (t, *J* = 21.2 Hz, 2H), 4.46 – 4.37 (m, 3H), 4.36 (s, 2H), 1.60 (d, *J* = 6.7 Hz, 3H), 1.44 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.81, 165.86, 156.77, 144.98, 132.29, 130.45, 129.28, 128.34, 123.68, 115.08, 114.99, 110.80, 105.07, 68.13, 60.87, 54.85, 34.56, 29.38, 23.22, 17.93, 14.01.

3.Copies of NMR and GC-MS Spectra



4.

Figure S1. 2D ROESY NMR spectrum of Pd catalyst **5c**.

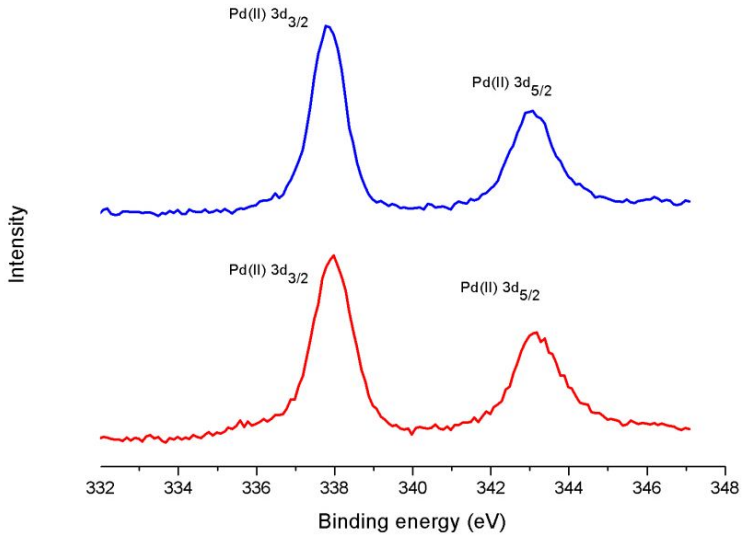
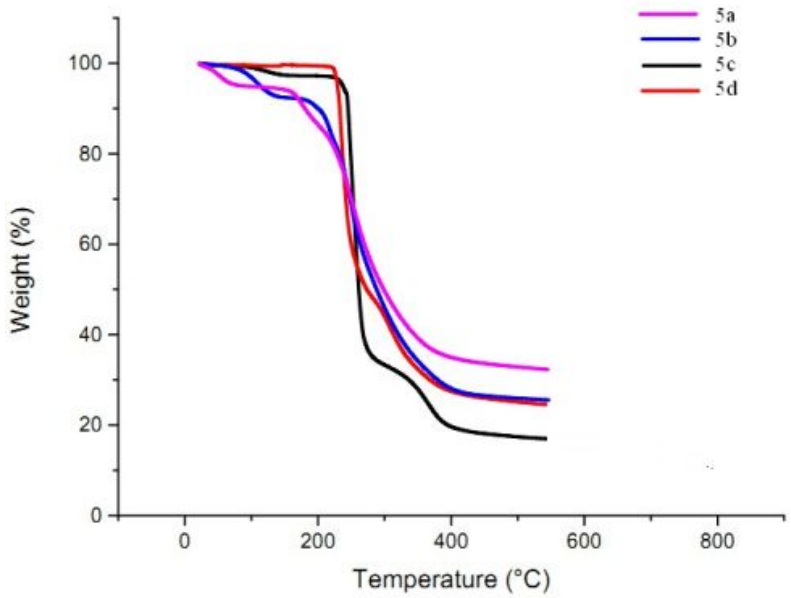
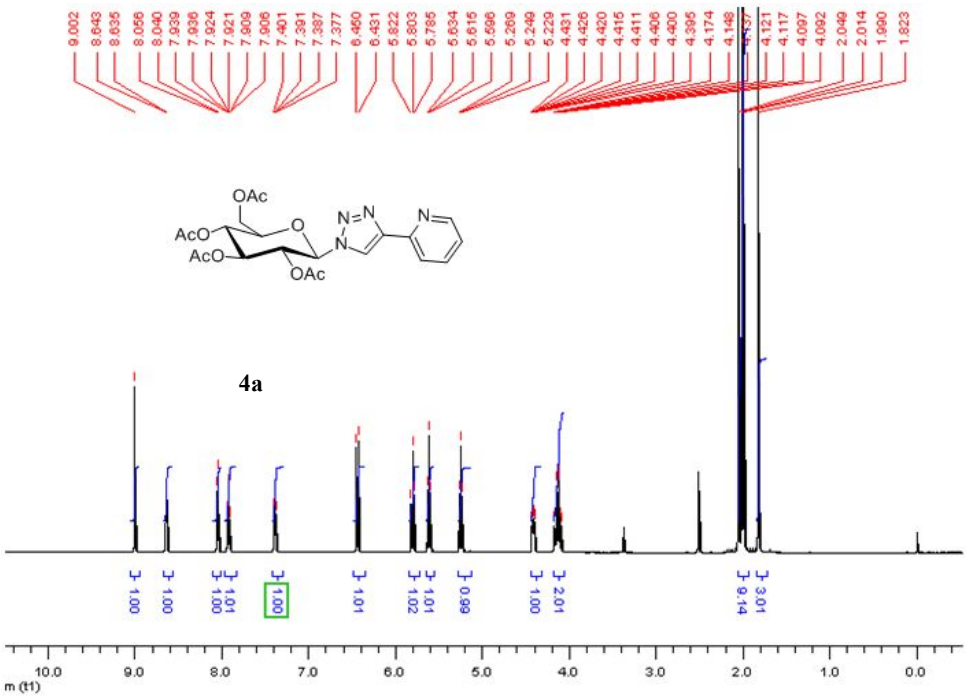


Figure S2. XPS analysis of GPT-Pd catalyst **5c** (blue for before and red for after the reaction.)

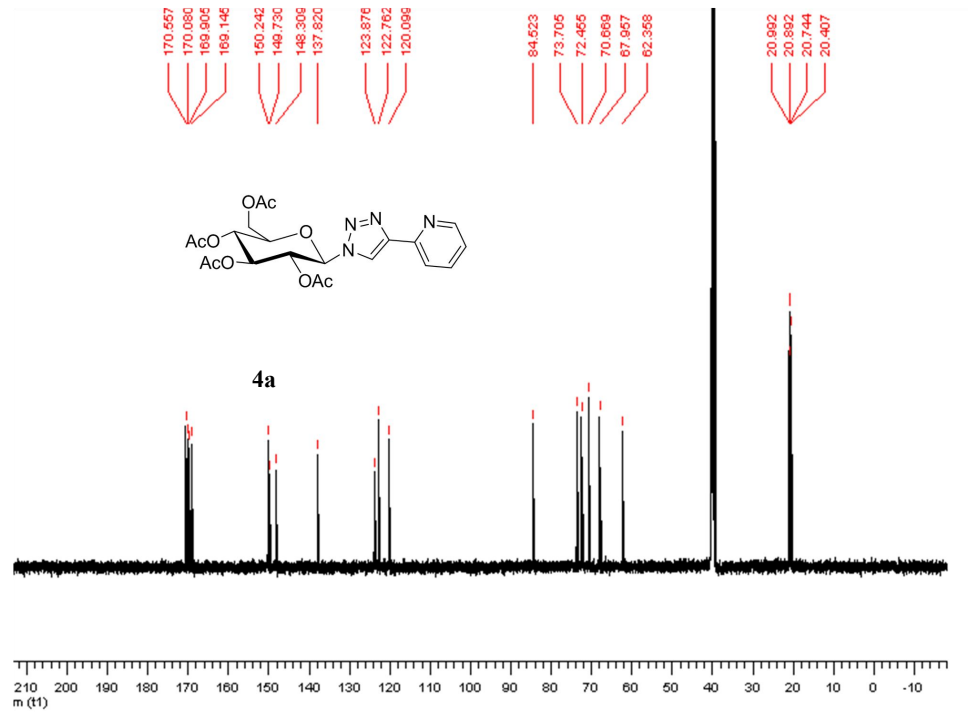
Figure S3. Thermo-gravimetric analysis graphs of GPT-Pd catalysts **5a-d**



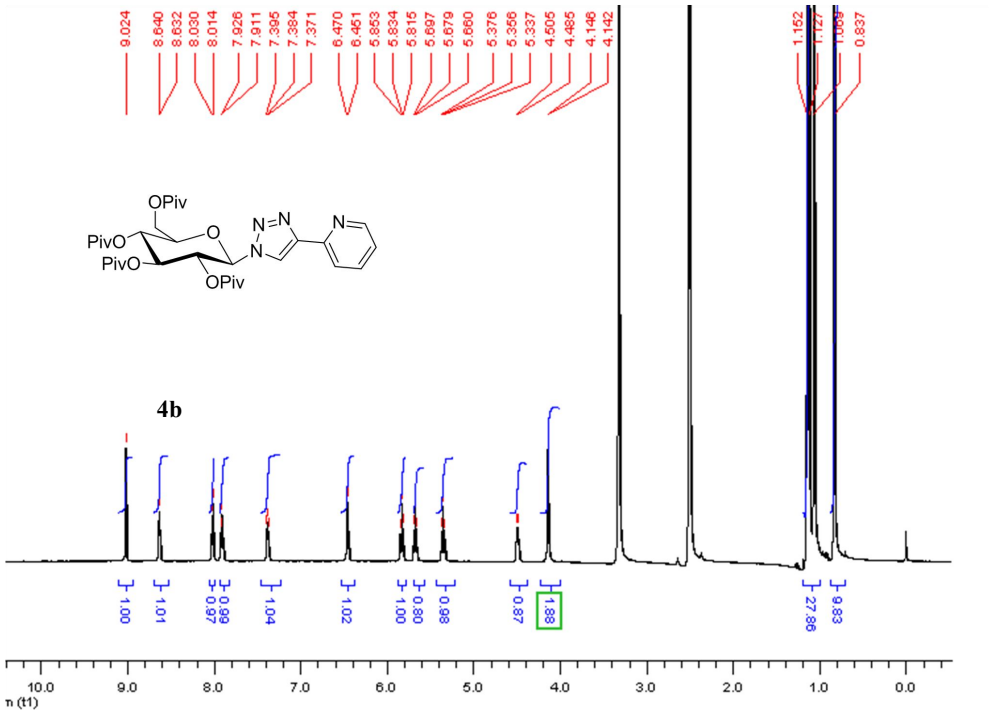
^{1}H NMR



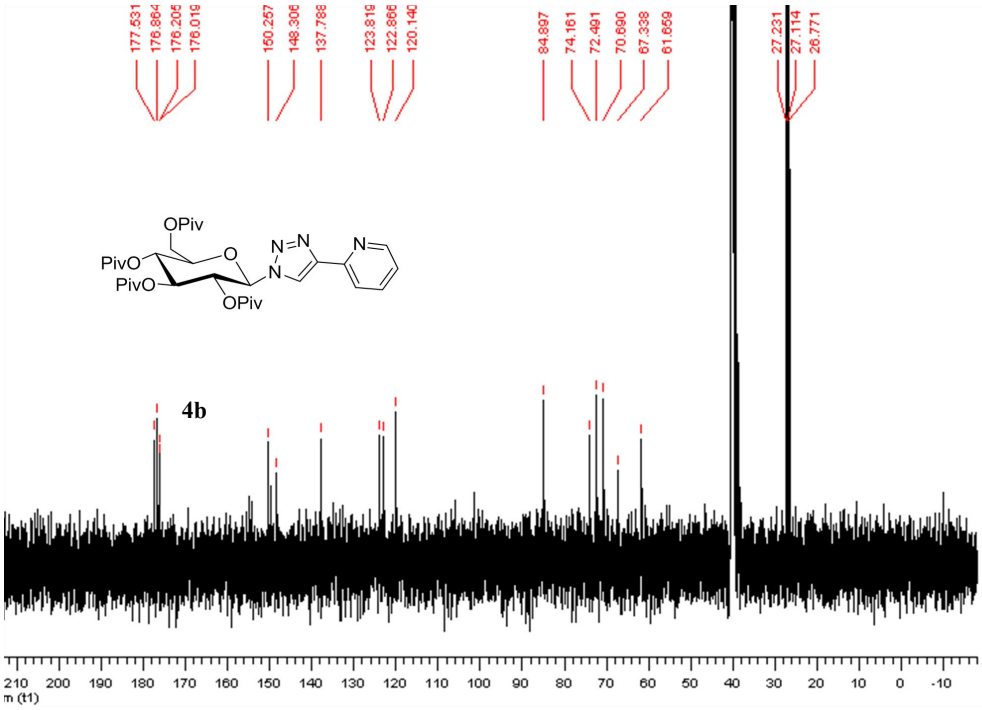
^{13}C NMR



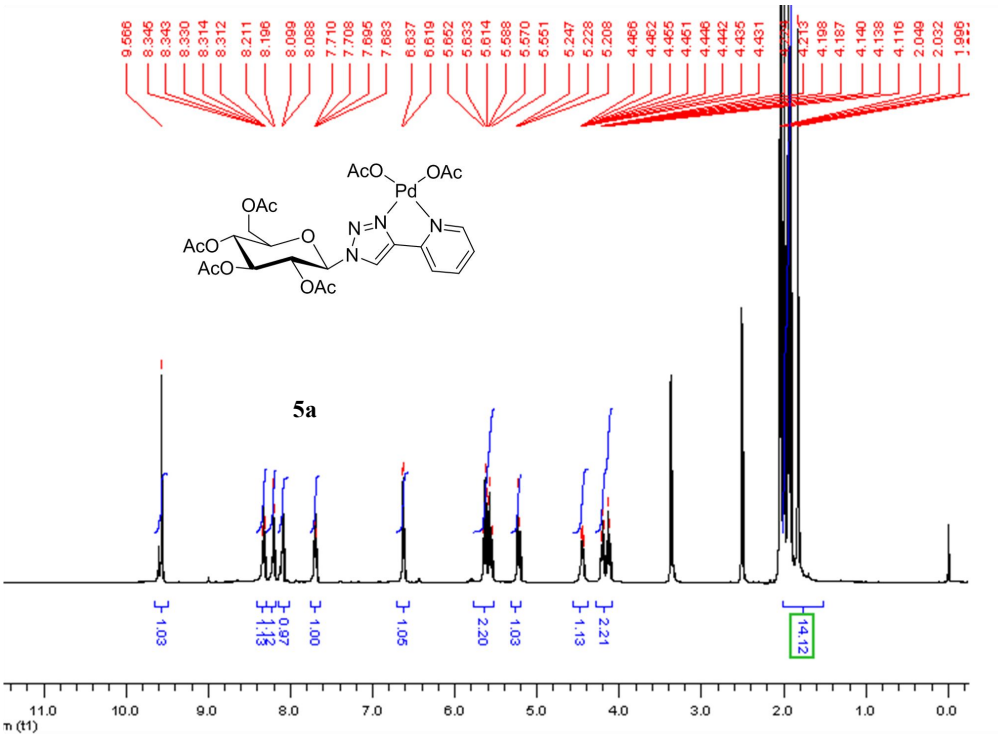
^{1}H NMR



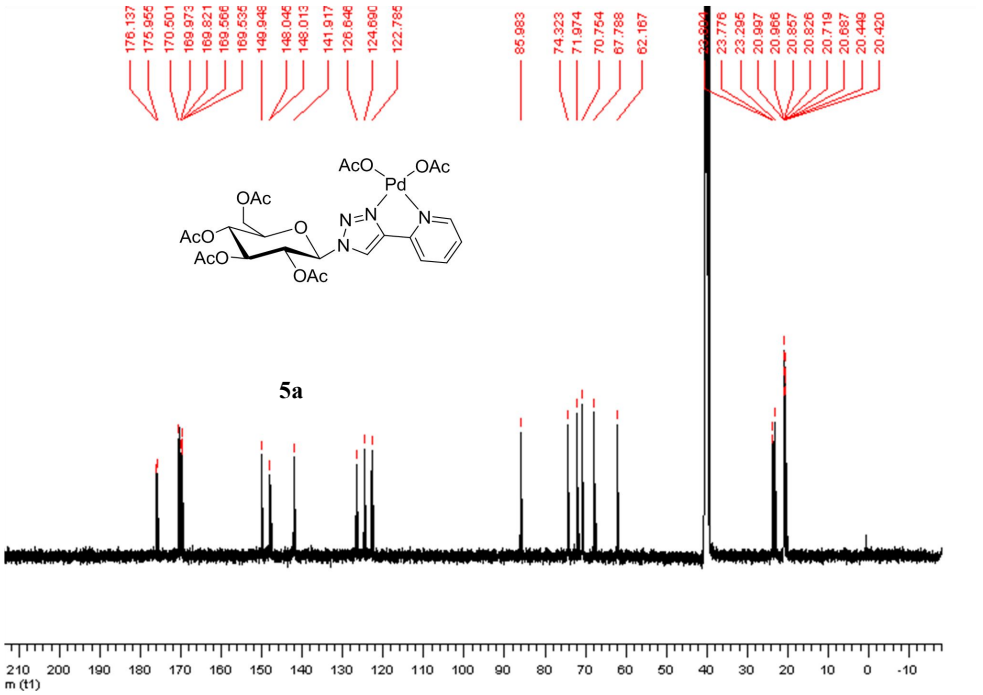
^{13}C NMR



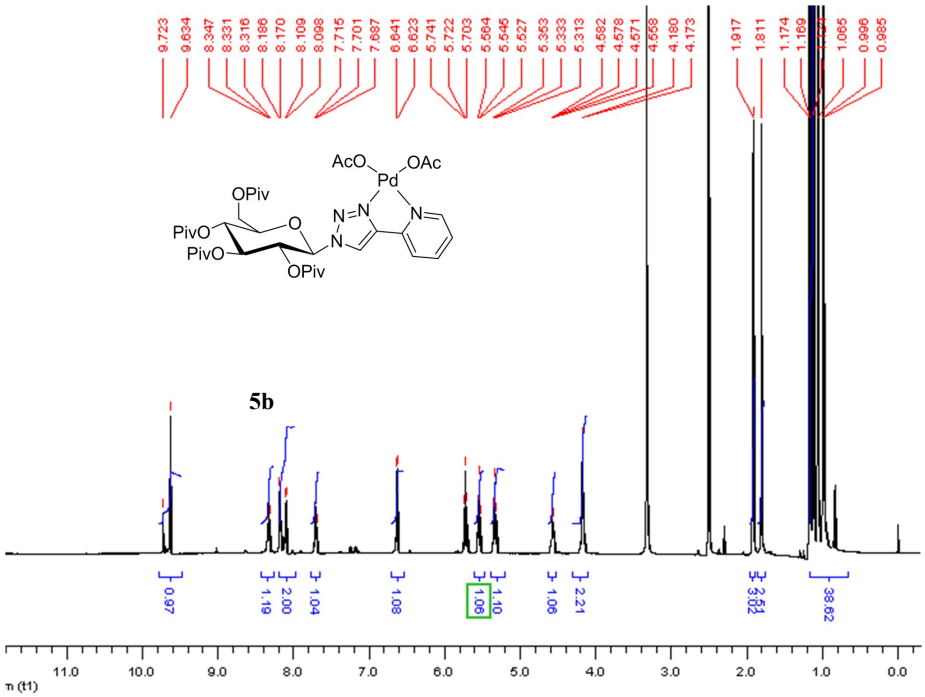
^{1}H NMR



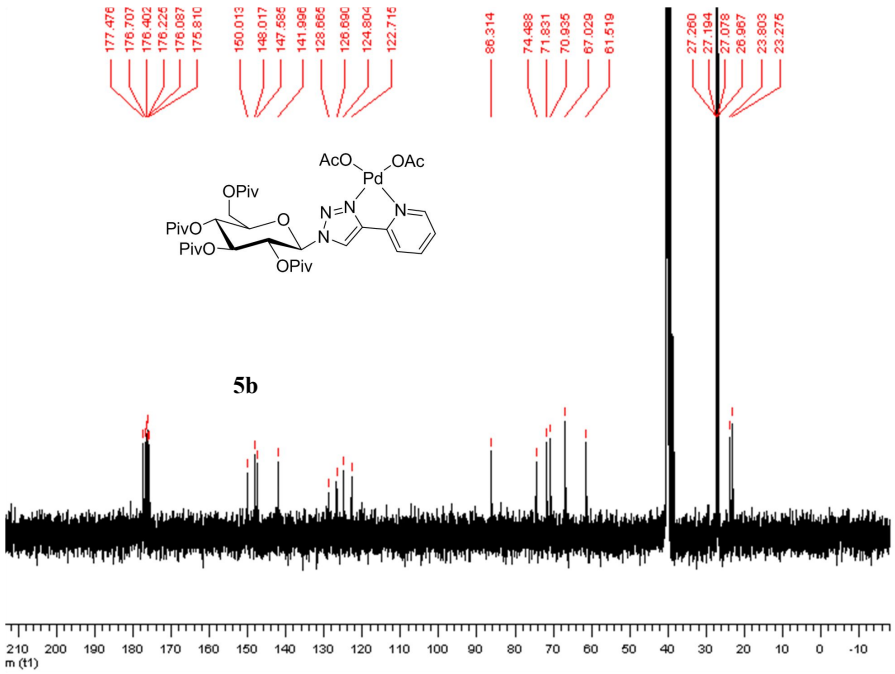
^{13}C NMR



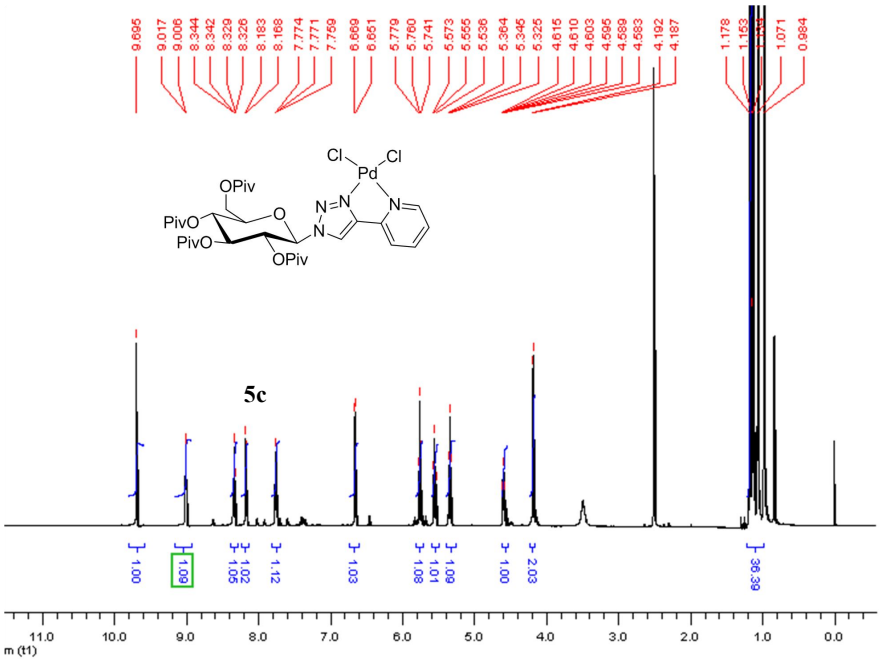
^{1}H NMR



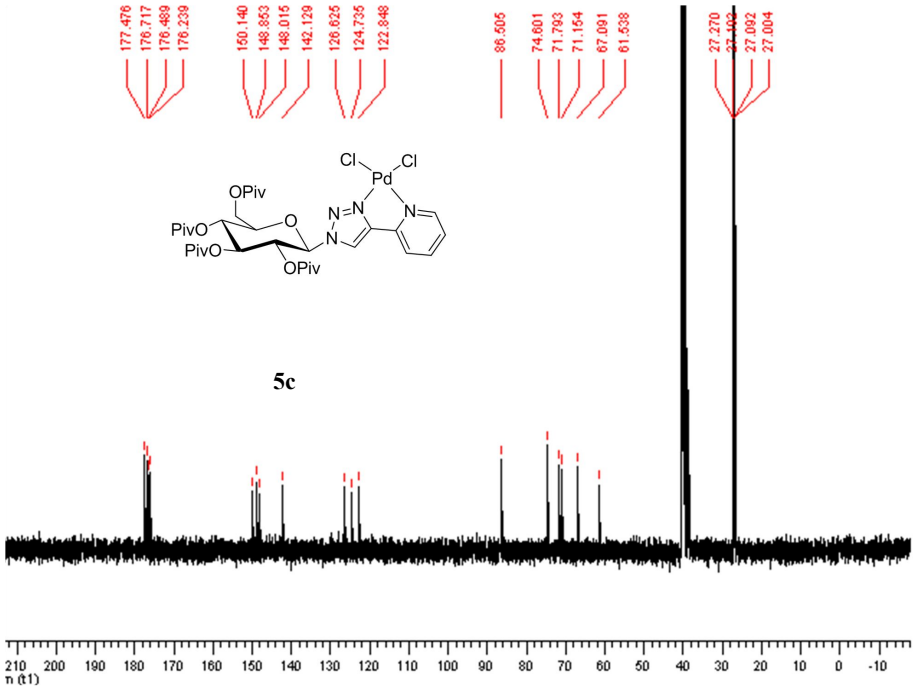
^{13}C NMR



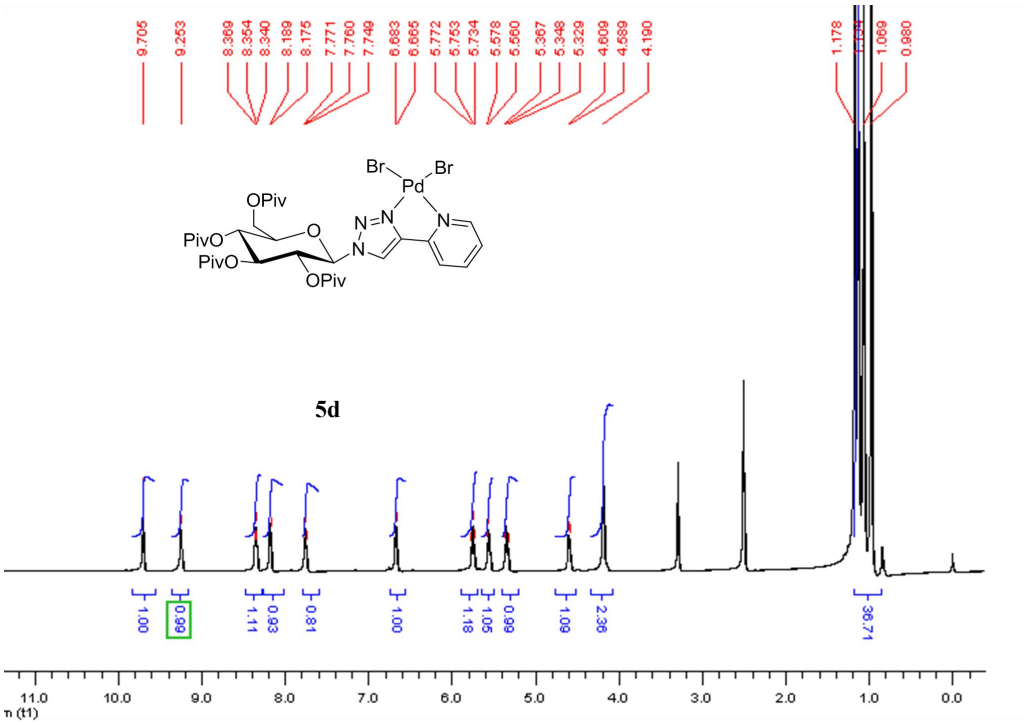
^{1}H NMR



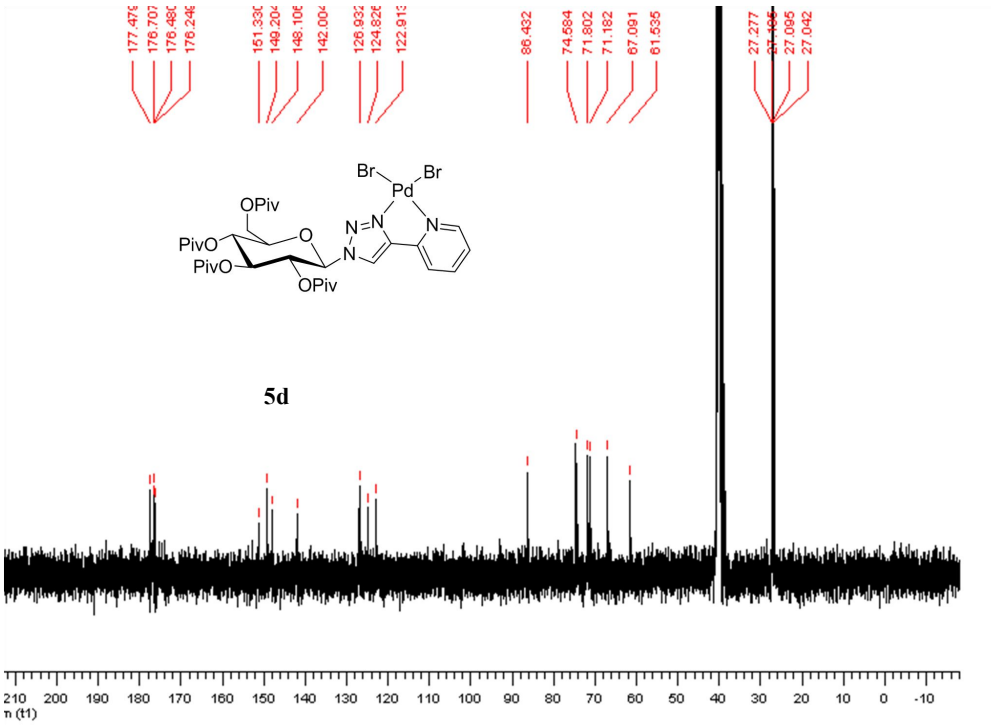
^{13}C NMR



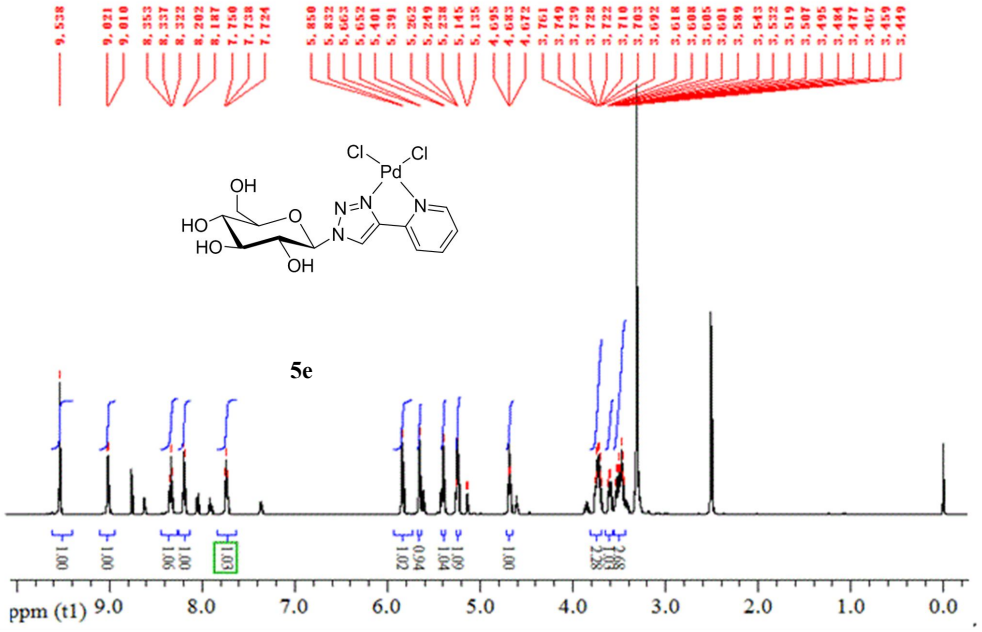
^{1}HNMR



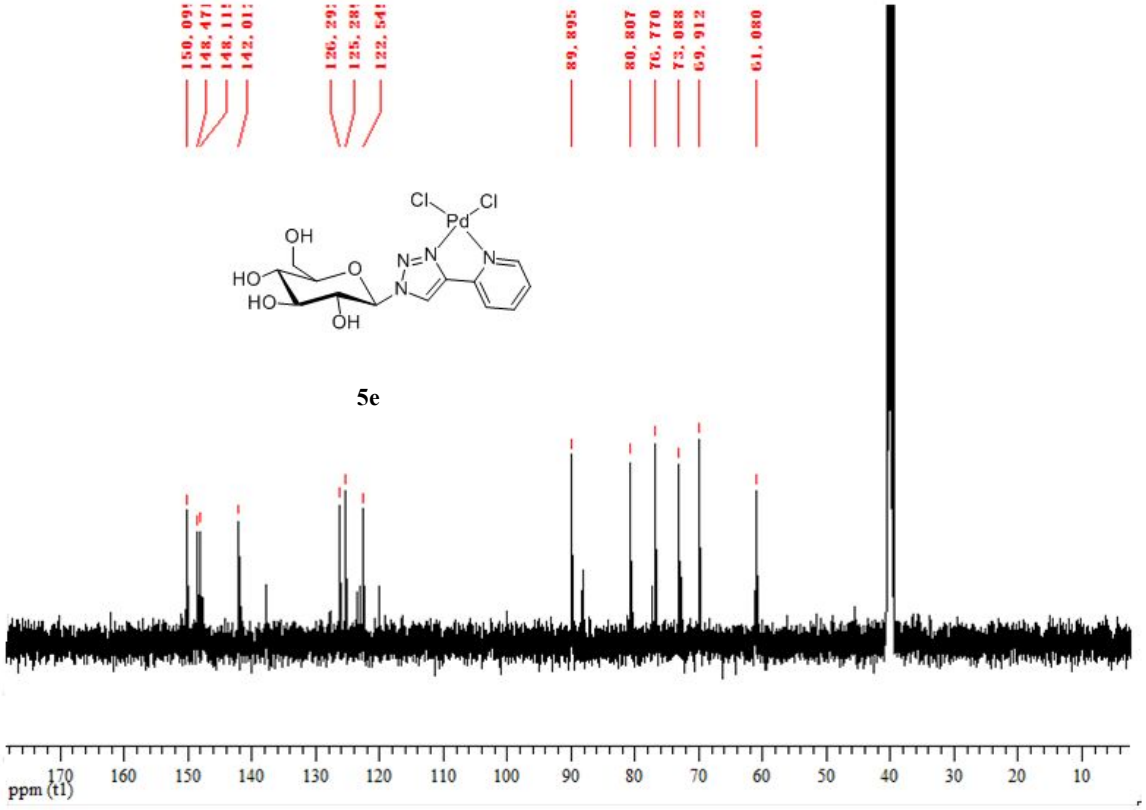
^{13}C NMR



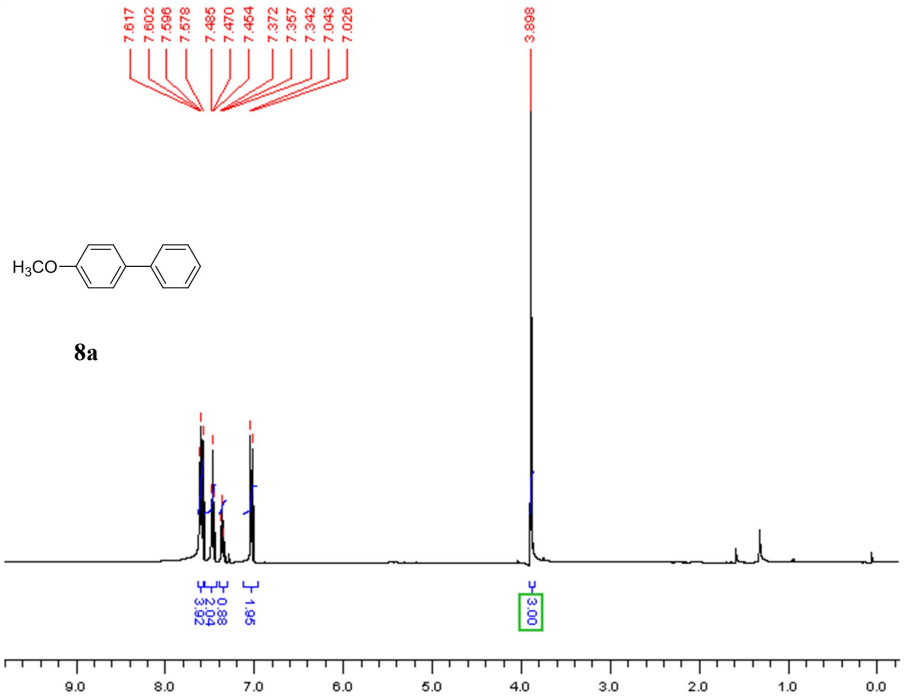
^{1}H NMR



^{13}C NMR

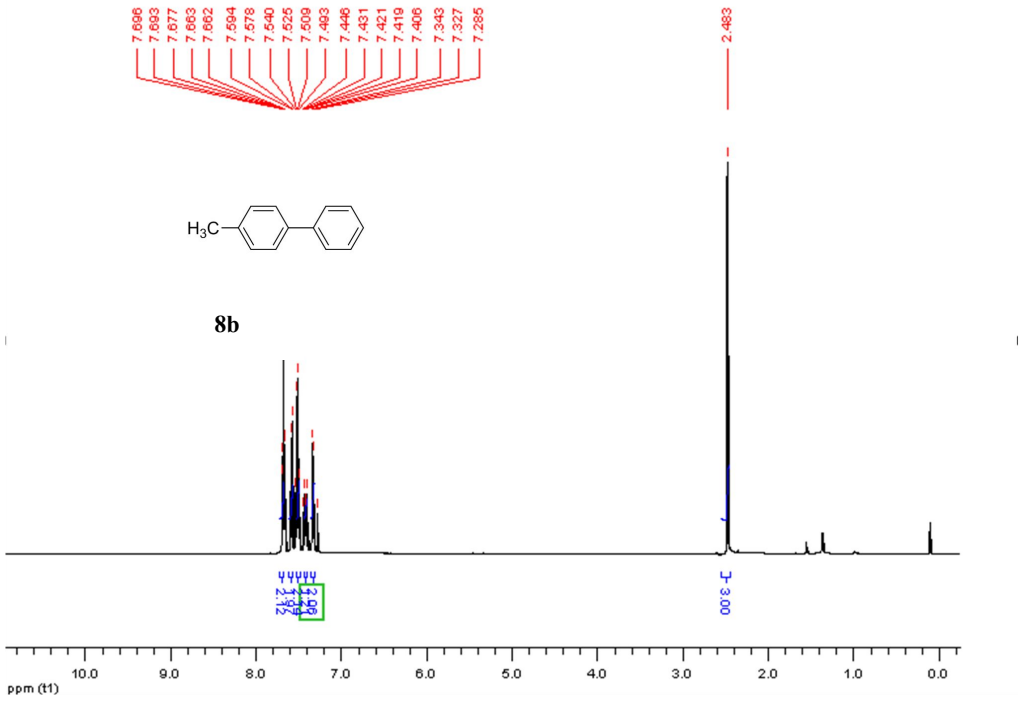


^{1}H NMR



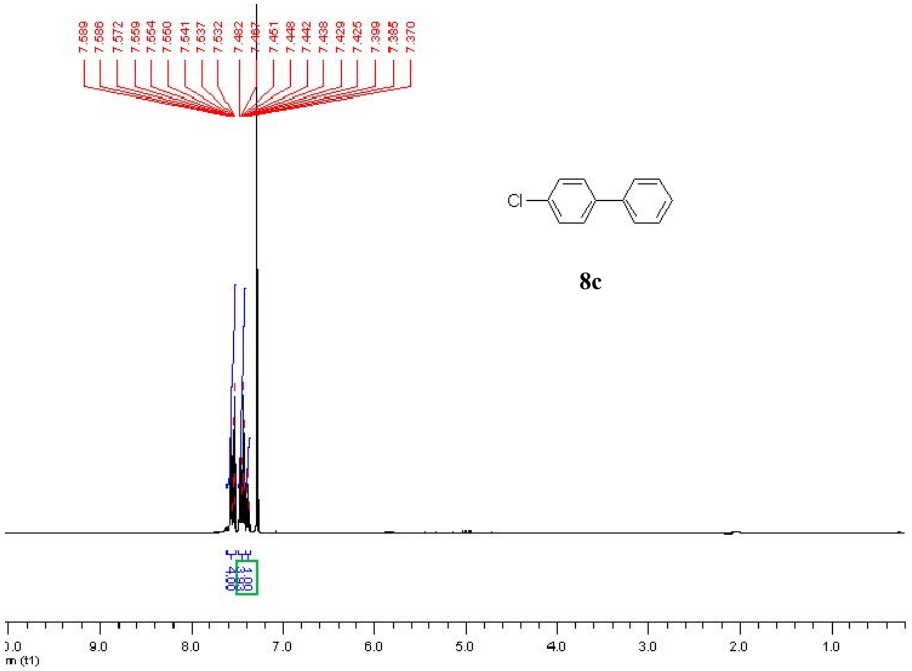
8a

^{1}H NMR



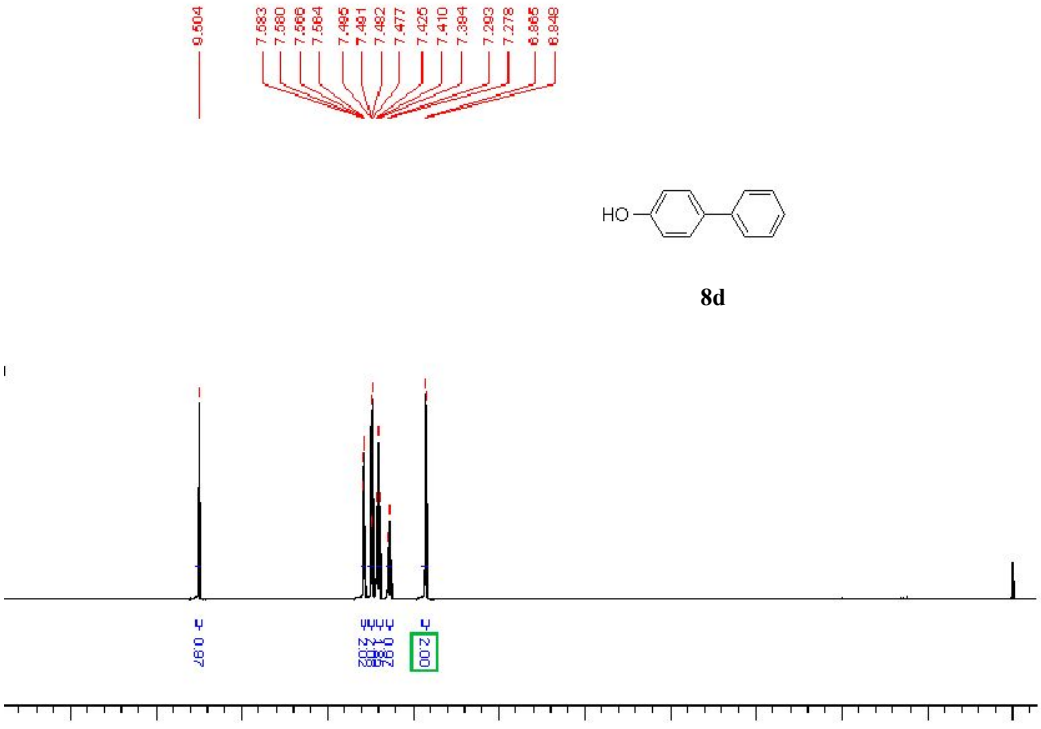
8b

^{1}H NMR



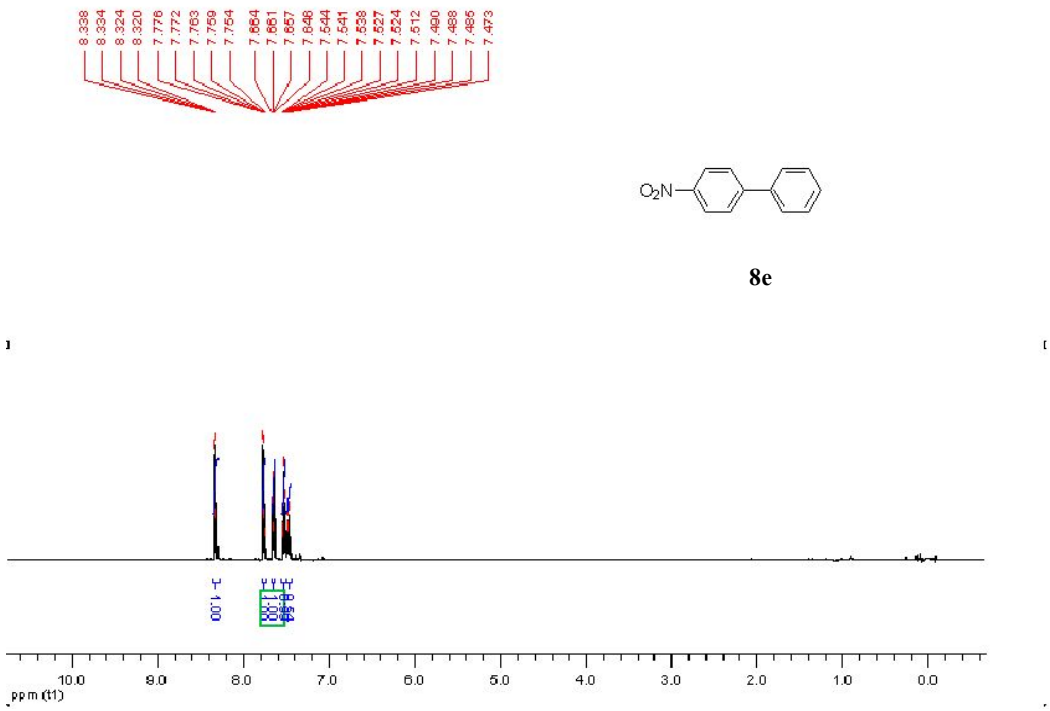
8c

^{1}H NMR



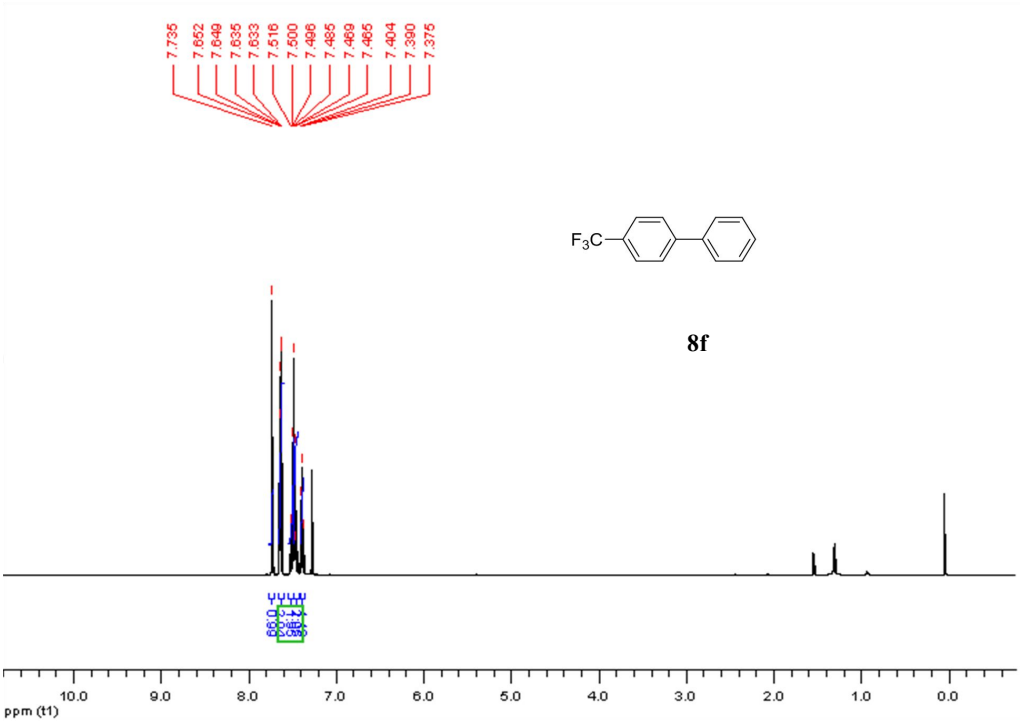
8d

^{1}H NMR



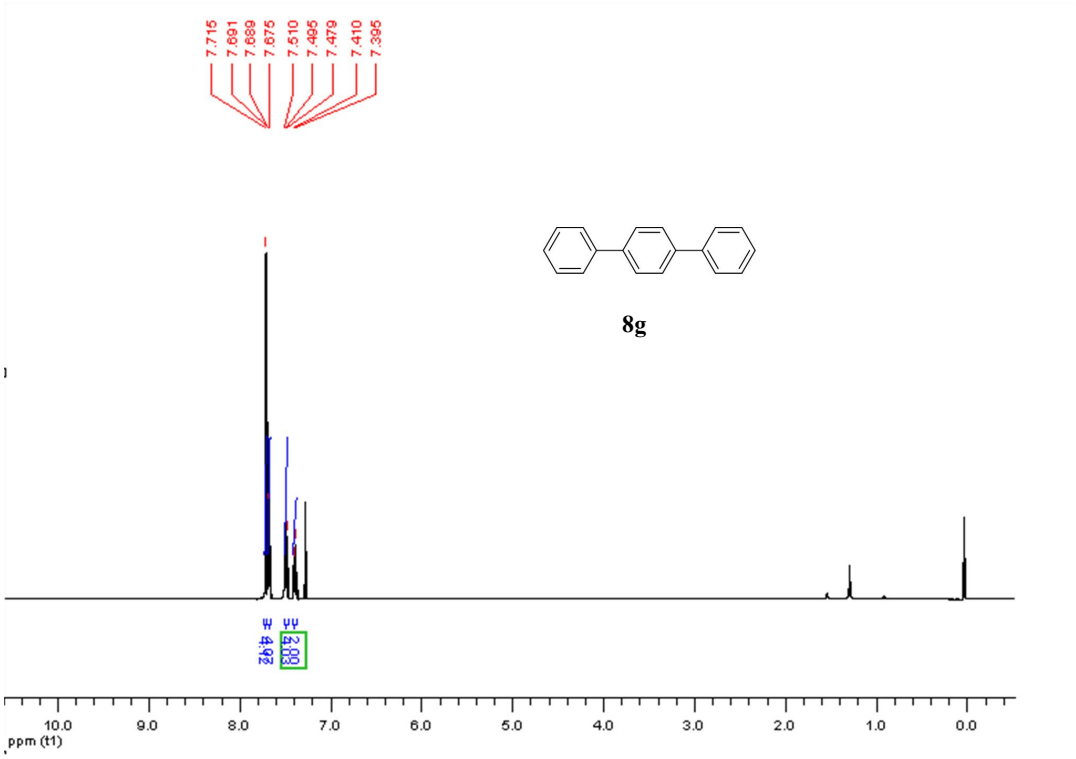
8e

^{1}H NMR



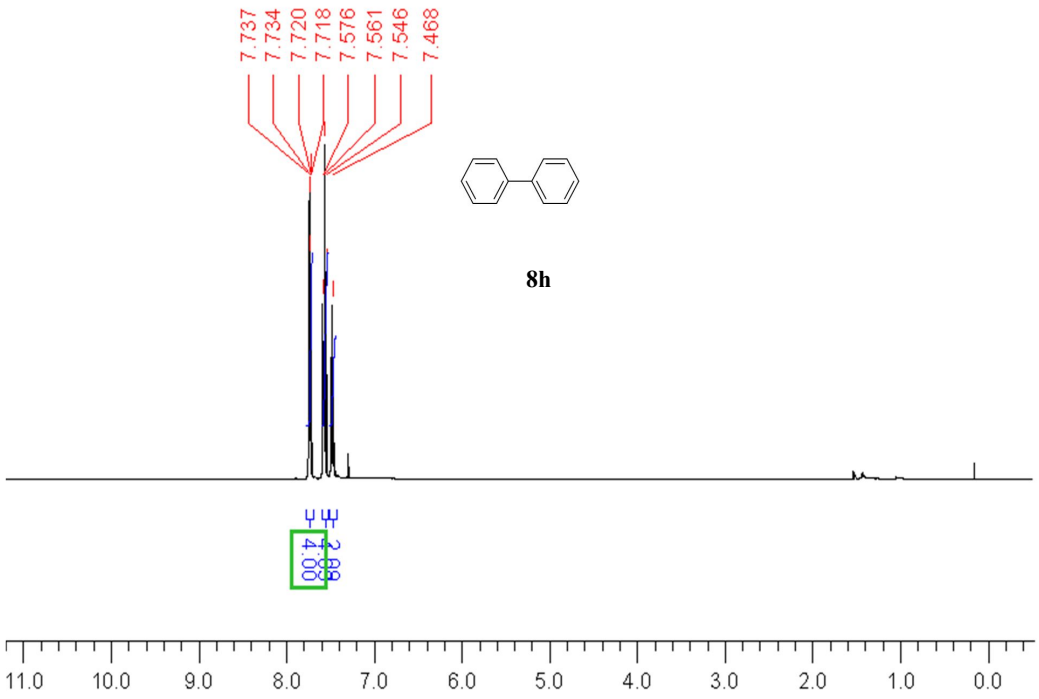
8f

^{1}H NMR



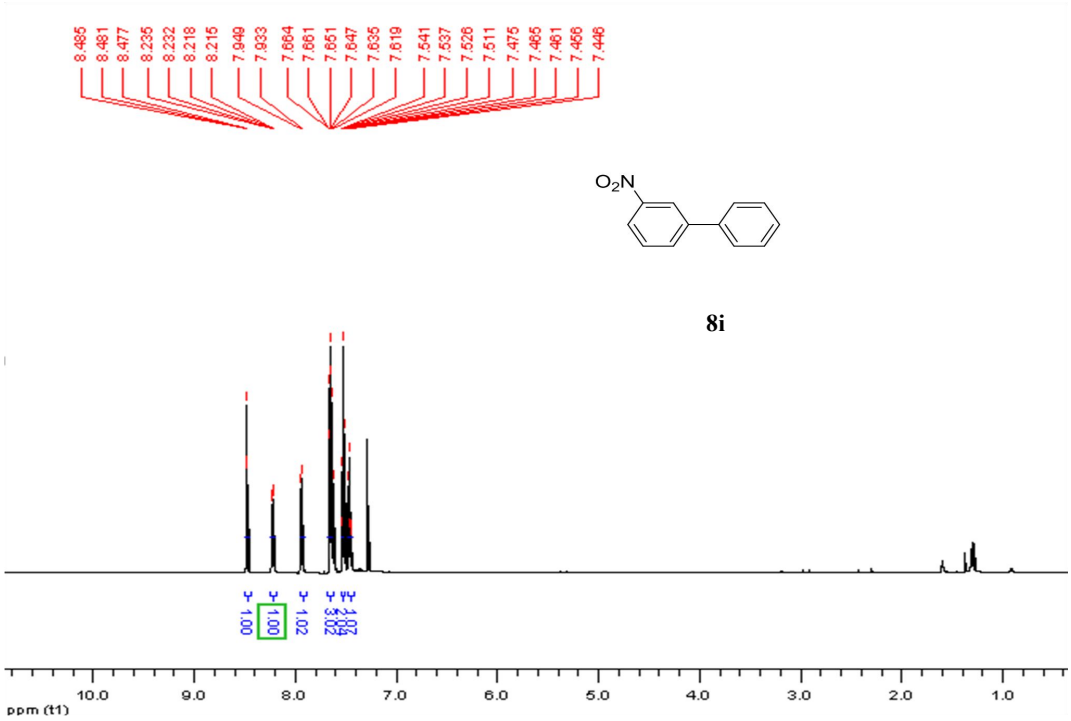
8g

^{1}H NMR

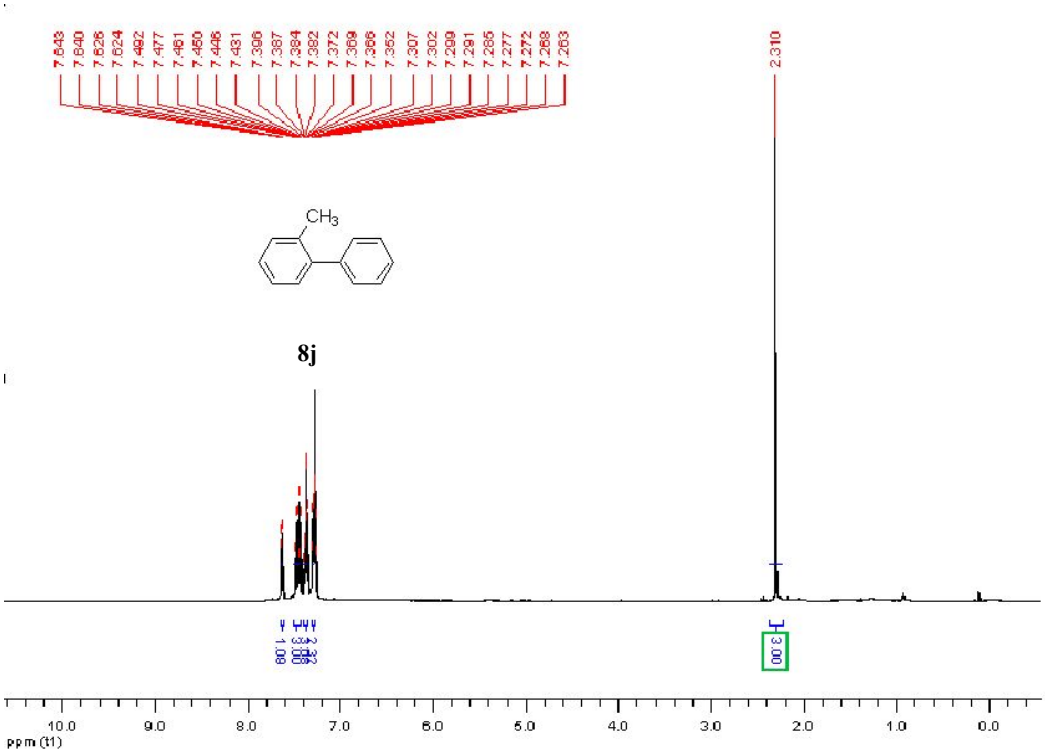


8h

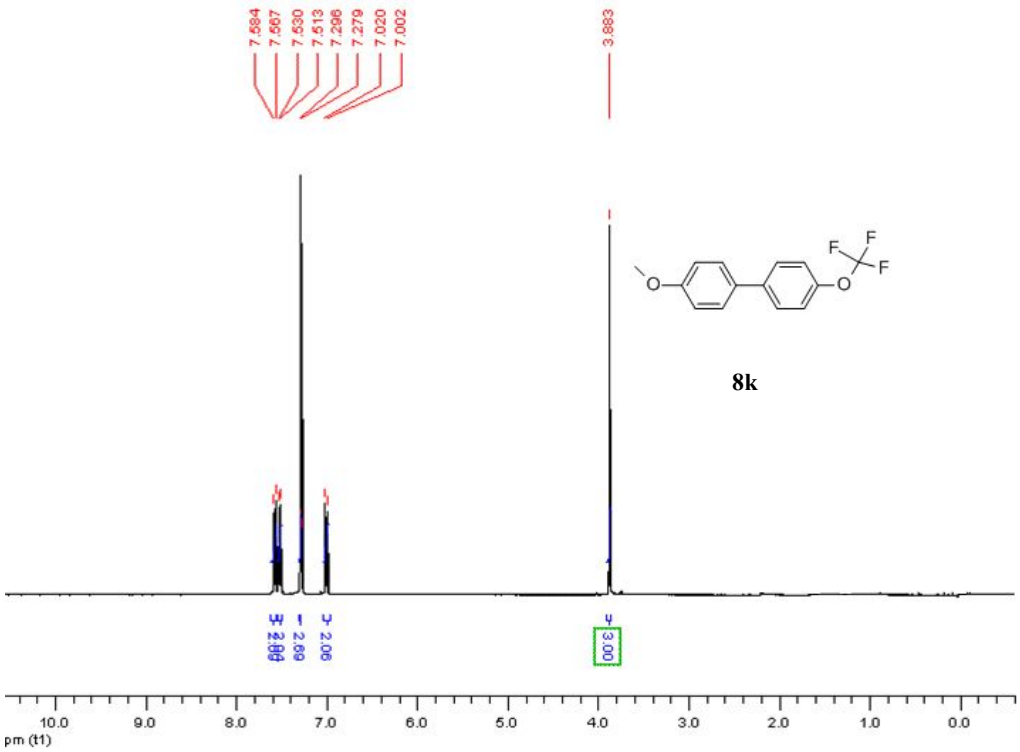
^{1}H NMR



^{1}H NMR



^{1}H NMR


7.584
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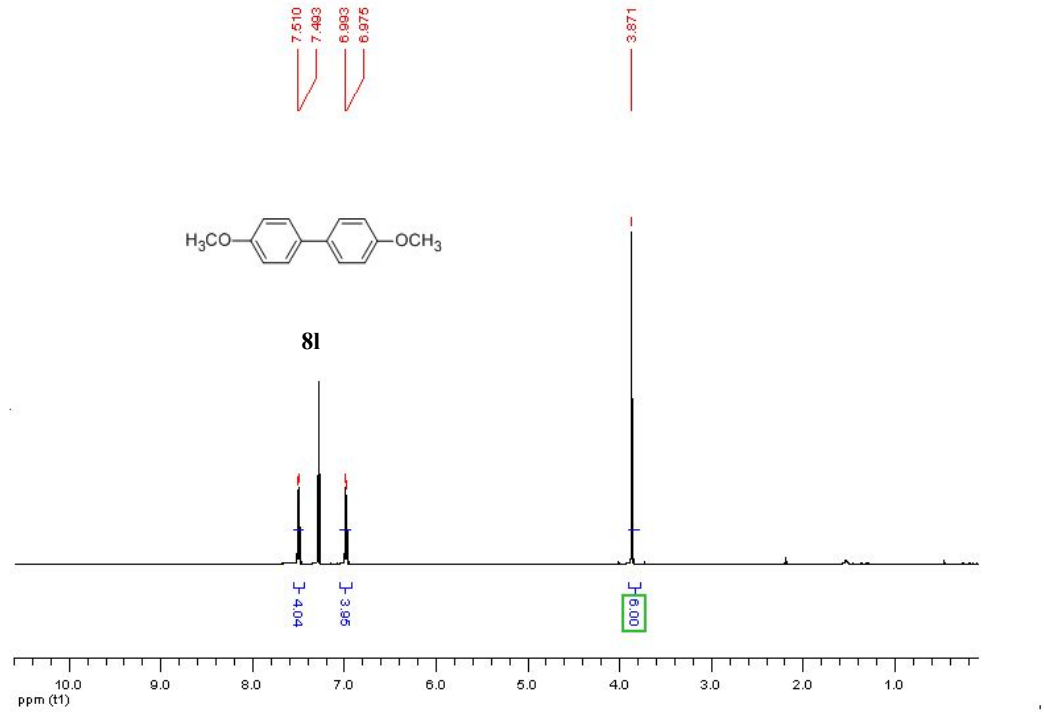
7.530
7.513
7.296
7.279
7.020
7.002
3.883
8k
2.23
1.29
2.06
3.00
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

^{1}H NMR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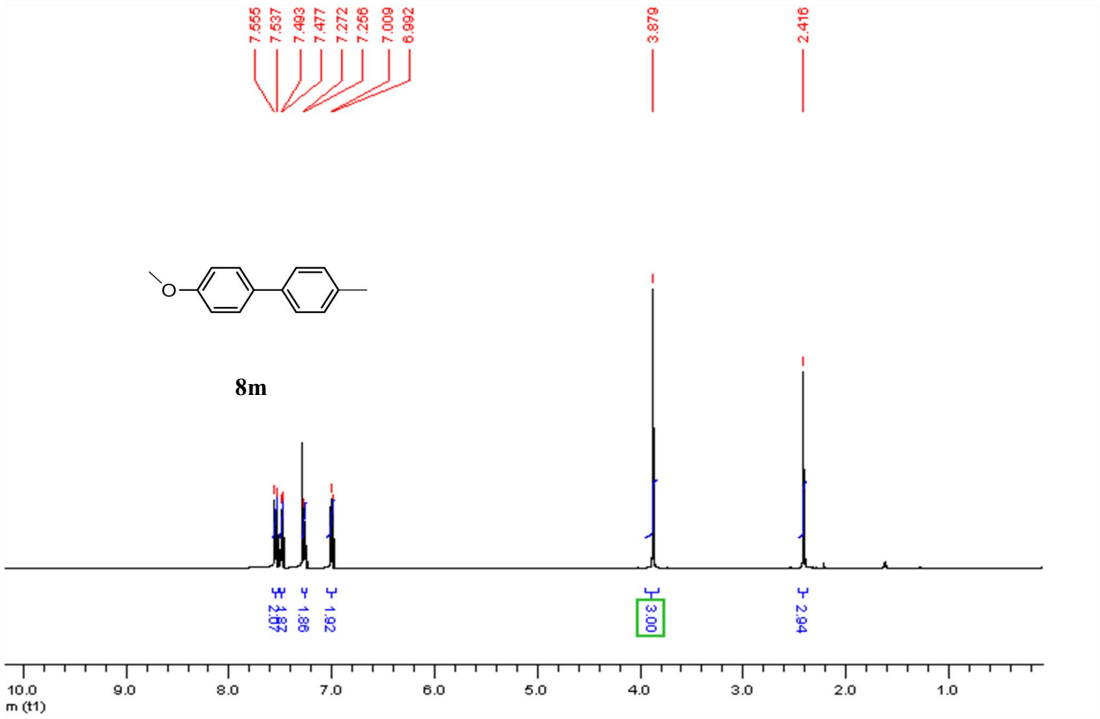
7.493
6.993
6.975
3.871
8l
4.04
3.95
6.00
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)

^{1}H NMR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7.493
7.477
7.272
7.256
7.009
6.992
3.879
2.416
8m
1.87
1.86
1.92
3.00
2.94
10.0
9.0
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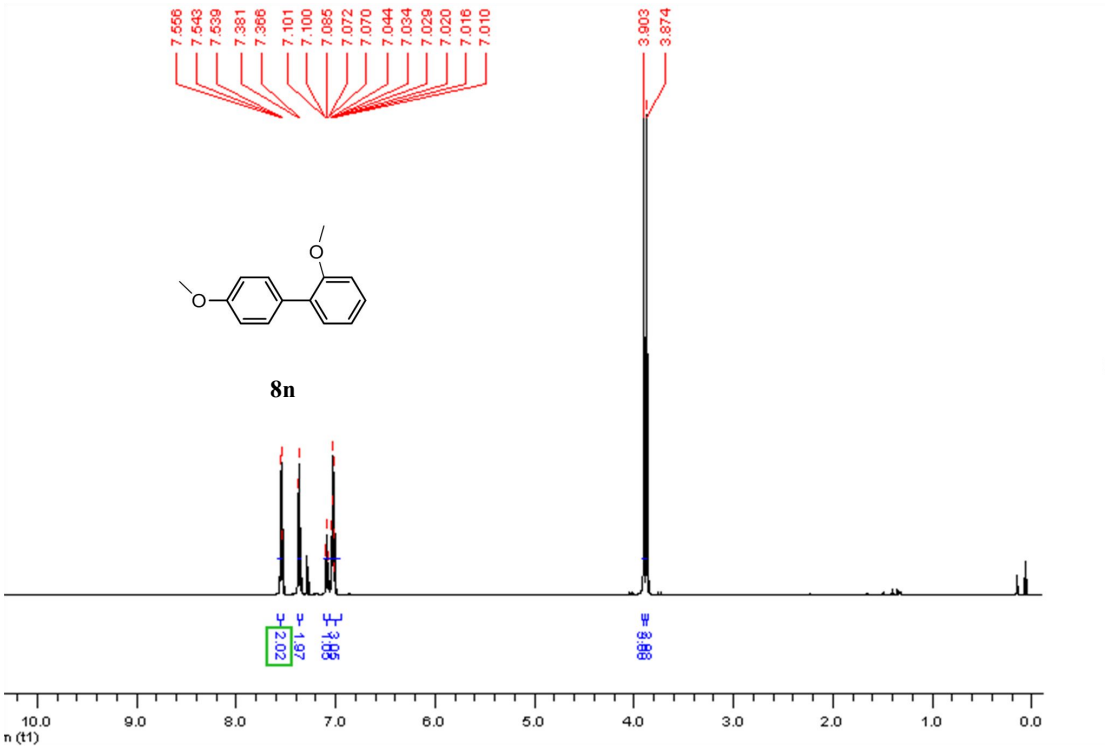
7.0
6.0
5.0
4.0
3.0
2.0
1.0
m (t1)

^{1}H NMR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7.100
7.085
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7.070
7.044
7.034
7.029
7.020
7.016
7.010
3.903
3.874
8n
2.02
1.97
3.05
8.88
10.0
9.0
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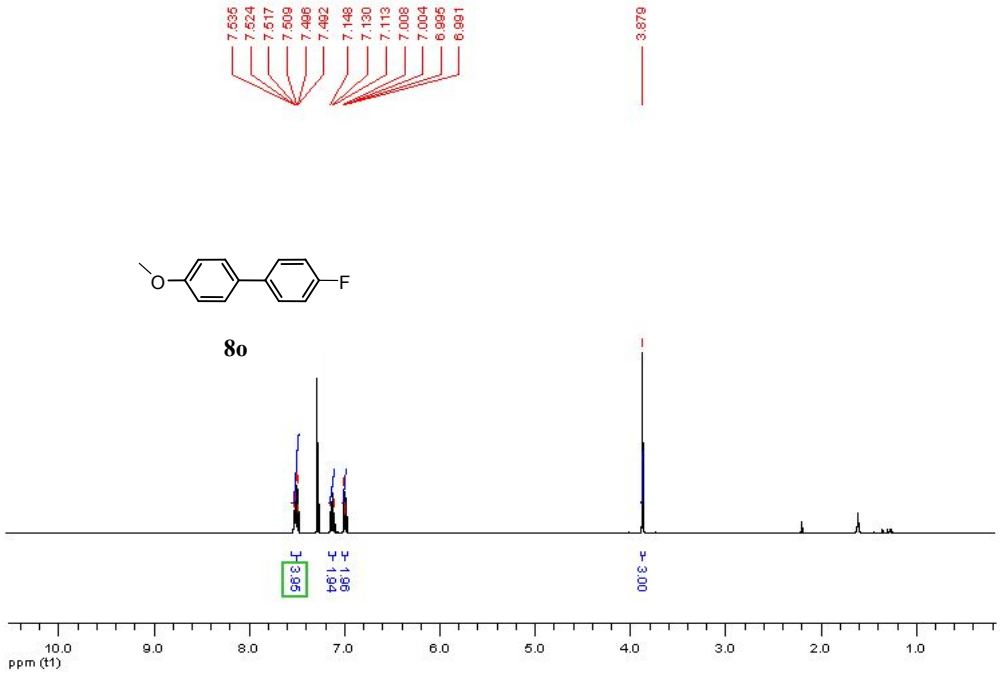
6.0
5.0
4.0
3.0
2.0
1.0
0.0
n (t1)

^{1}H NMR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7.492
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7.130
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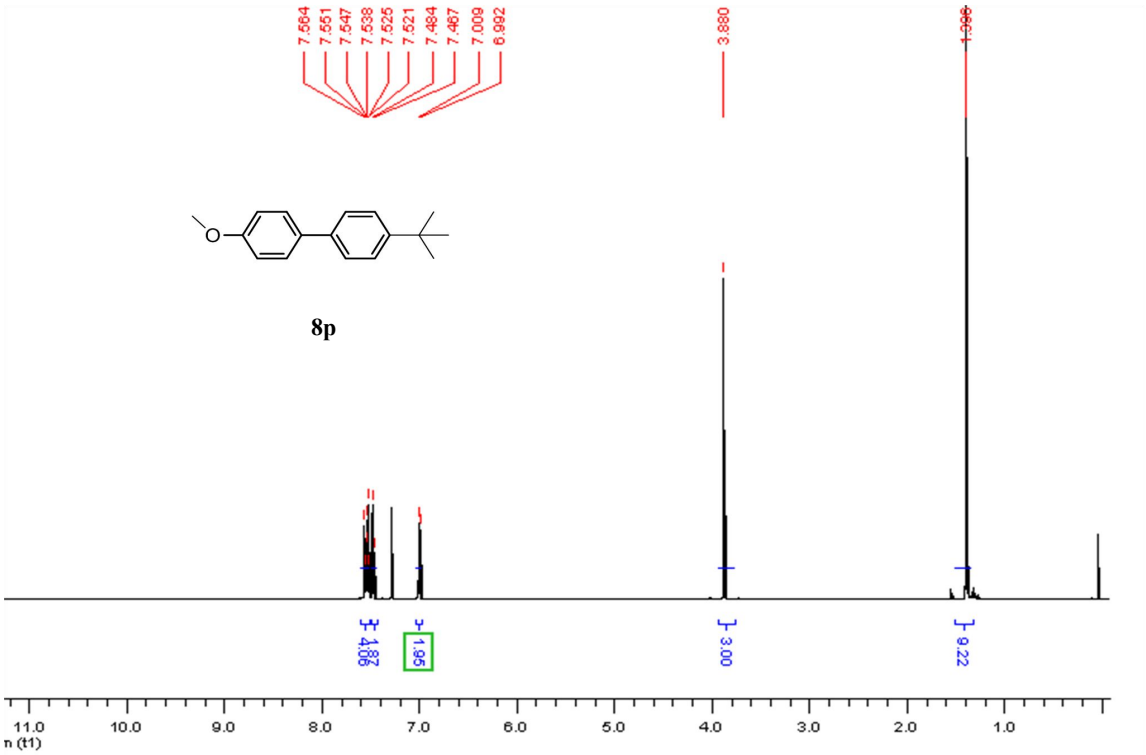
F
3.95
1.96
1.94
3.00
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)

8o

^{1}H NMR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7.521
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7.467
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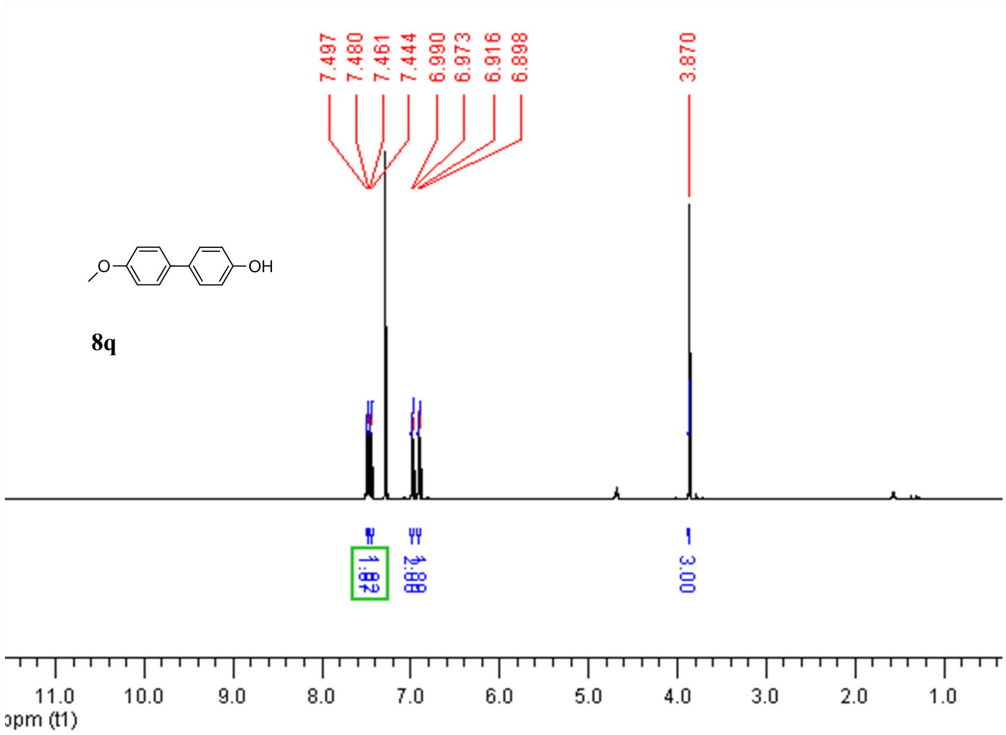
4.86
1.95
3.00
9.22
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
n (t1)

8p

^{1}H NMR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6.916
6.898
3.870
O
OH
8q
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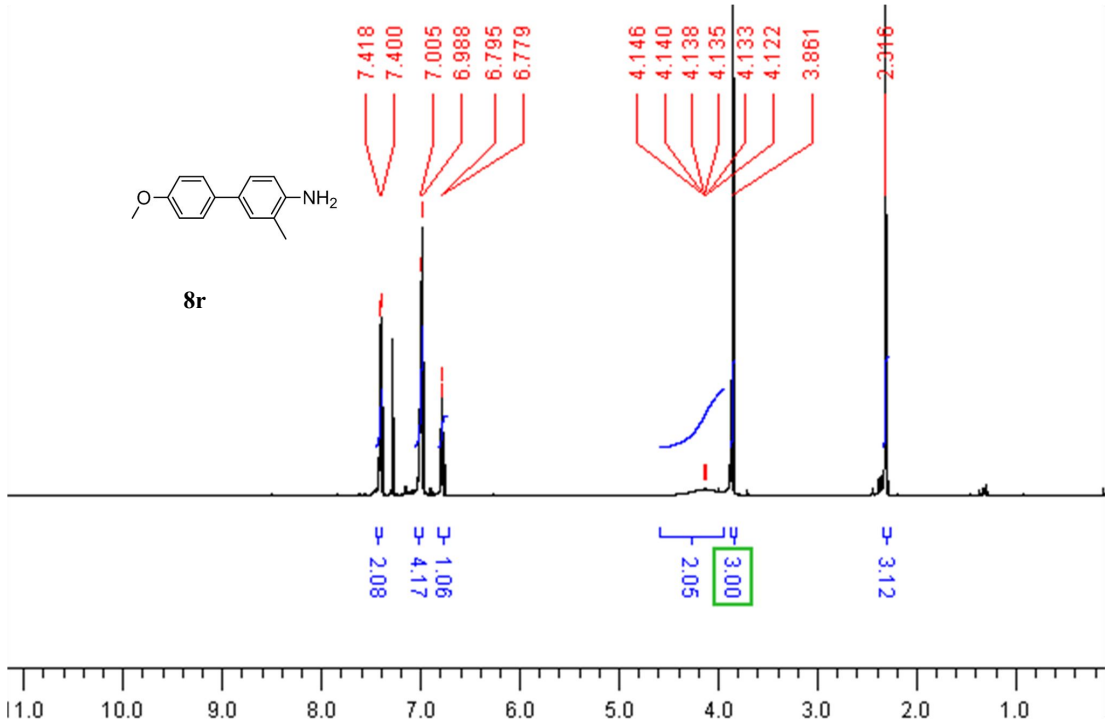
2.88
3.00
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)

^{1}H NMR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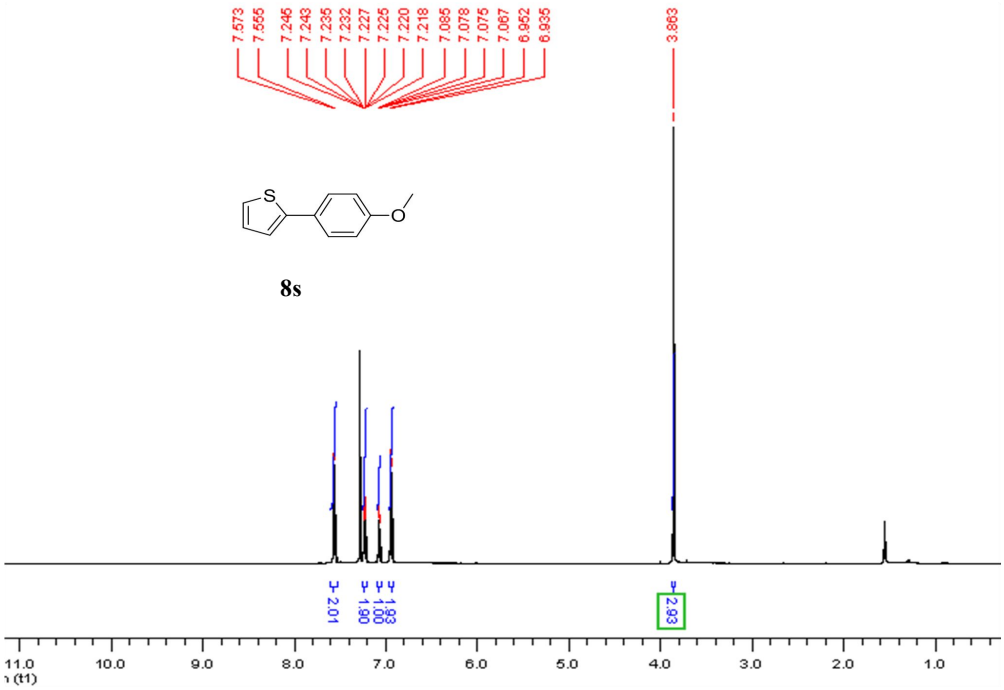
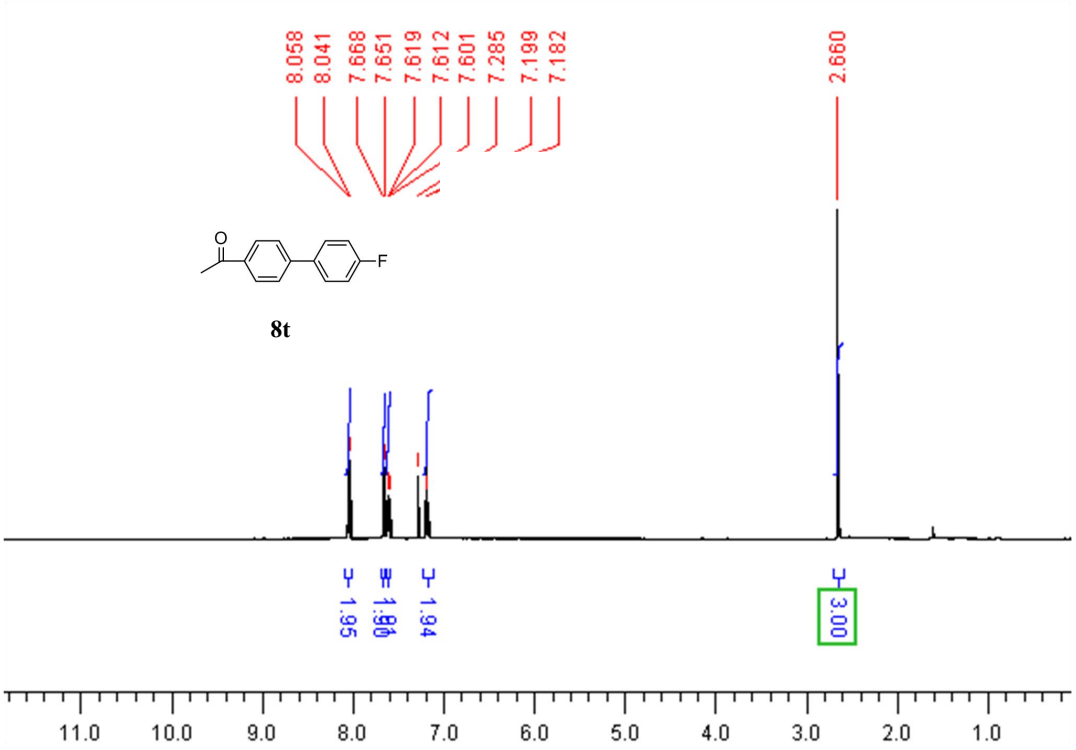
7.005
6.988
6.795
6.779
4.146
4.140
4.138
4.135
4.133
4.122
3.861
2.316
O
NH2
8r
2.08
4.17
1.06
2.05
3.00
3.12
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0

^{1}H NMR



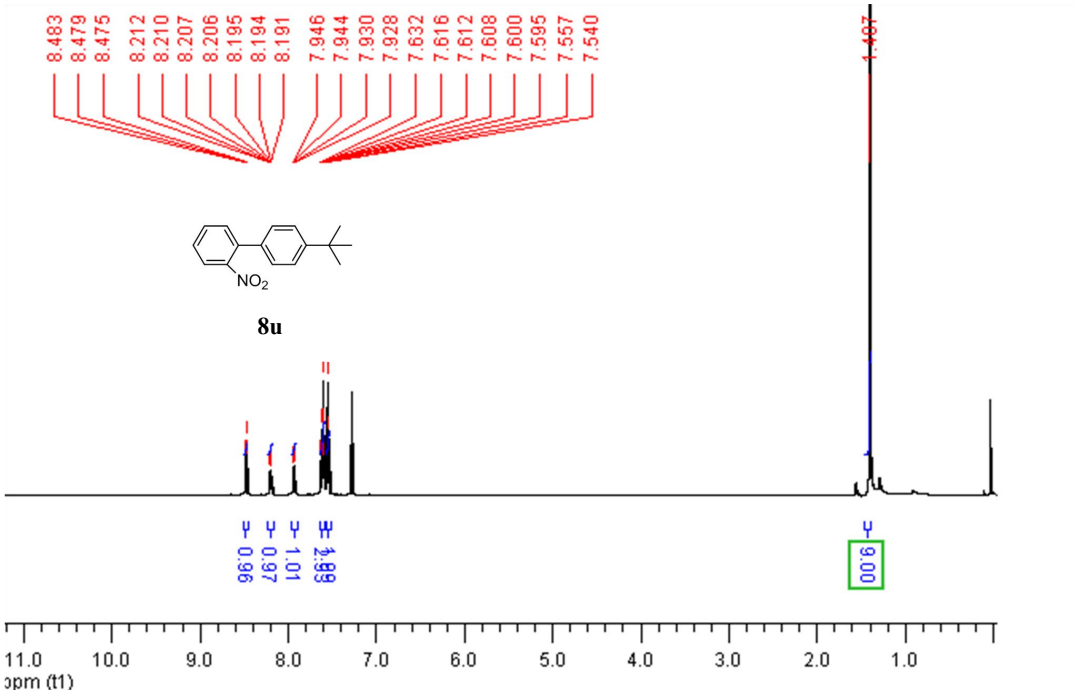
8s

^{1}H NMR



8t

^{1}H NMR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8.210
8.207
8.206
8.195
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8.191
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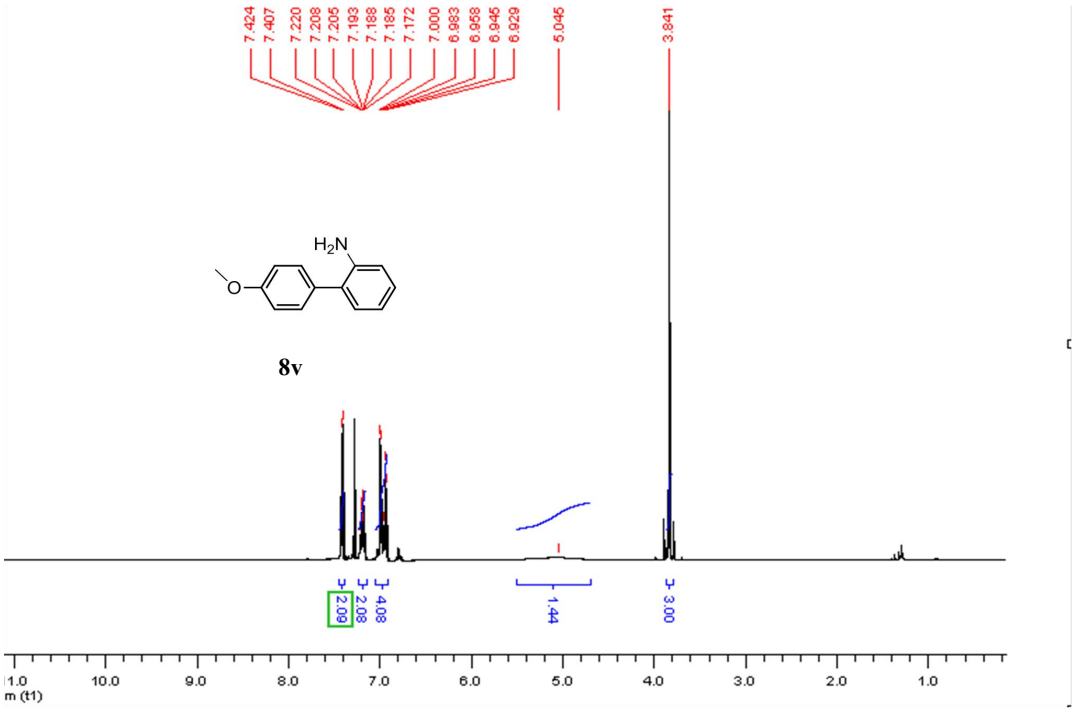
7.930
7.928
7.632
7.616
7.612
7.608
7.600
7.595
7.557
7.540
1.407
NO2
8u
0.96
0.97
1.01
1.99
9.00
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)

^{1}H NMR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7.205
7.193
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7.185
7.172
7.000
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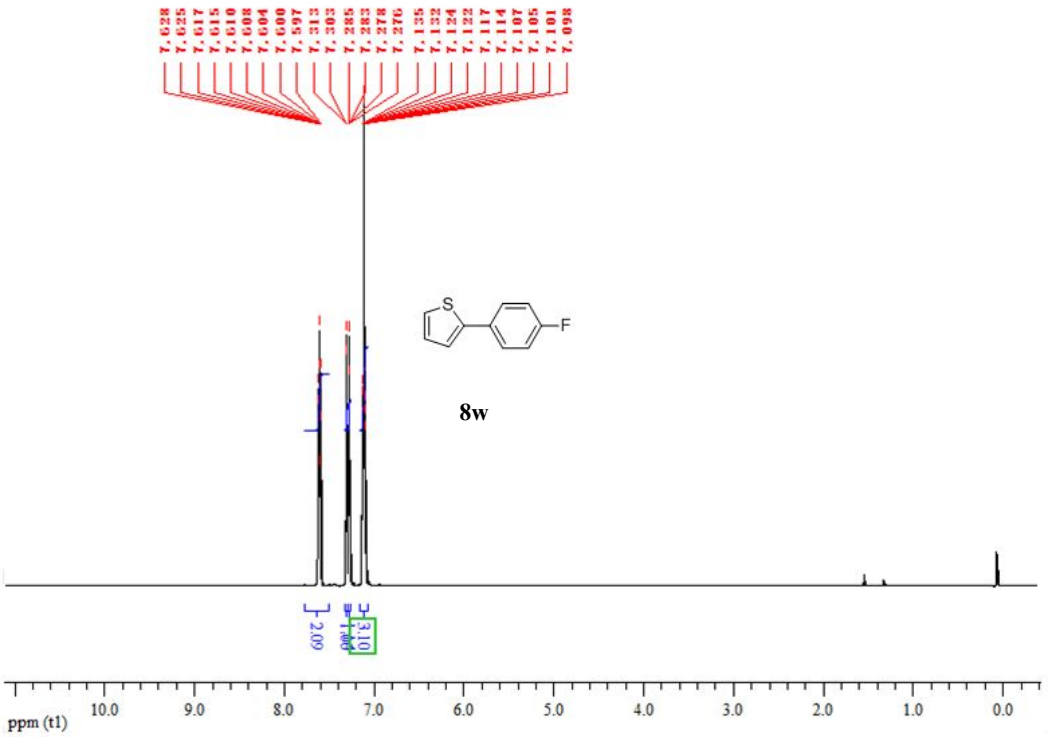
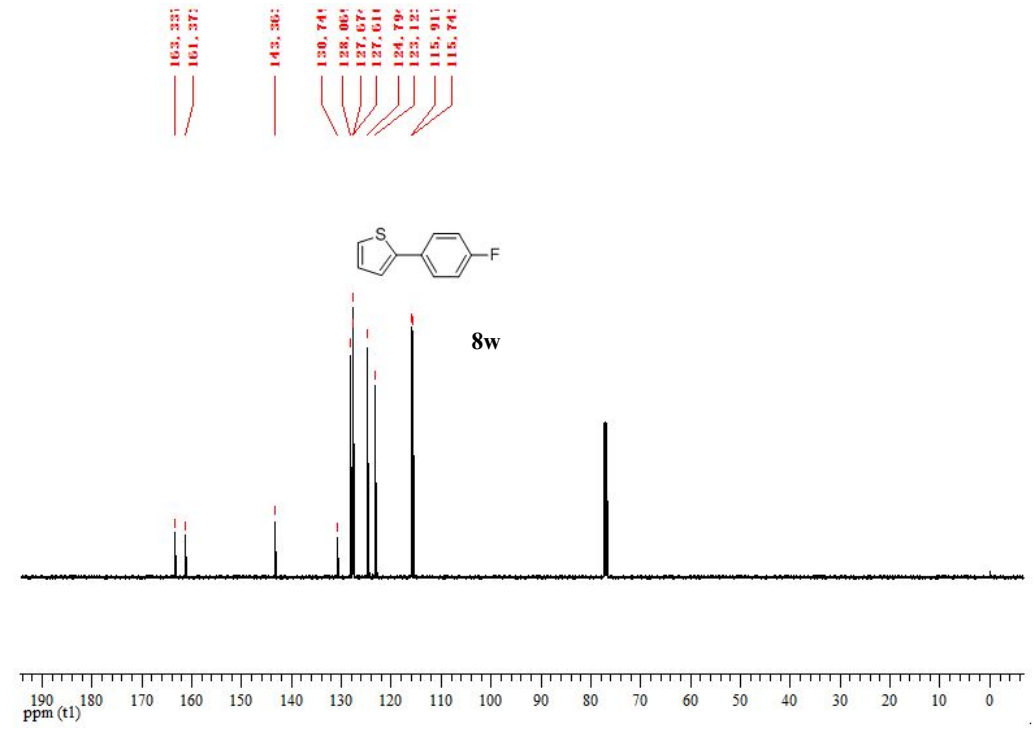
6.929
5.045
3.841
H2N
O
8v
2.09
2.08
4.08
1.44
3.00
1.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
m (t1)

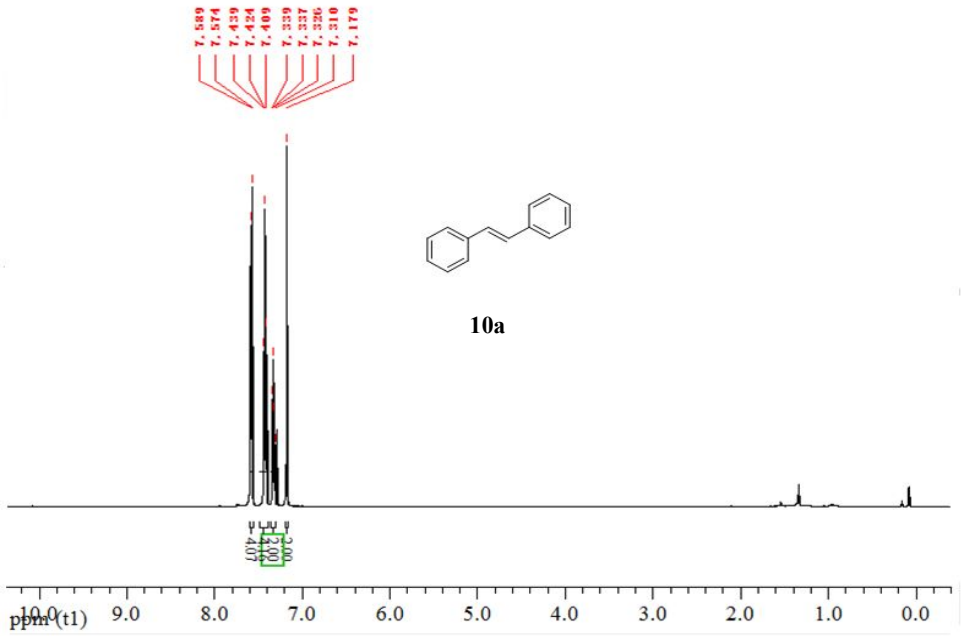
^{1}H NMR



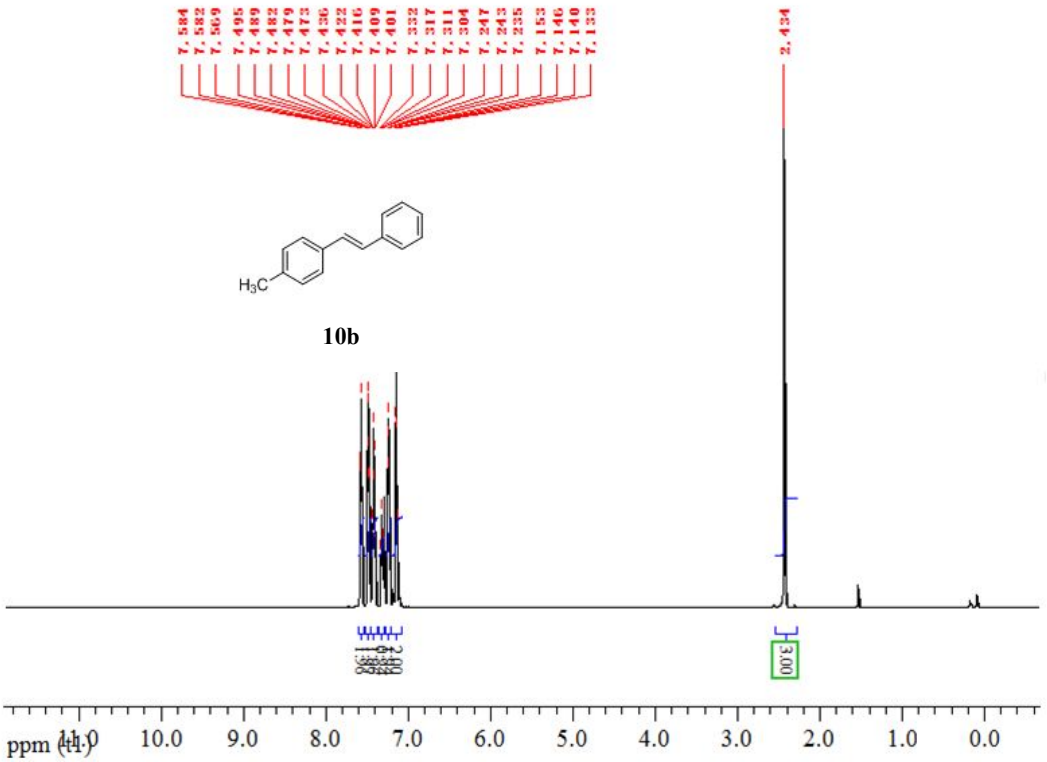
^{13}C NMR



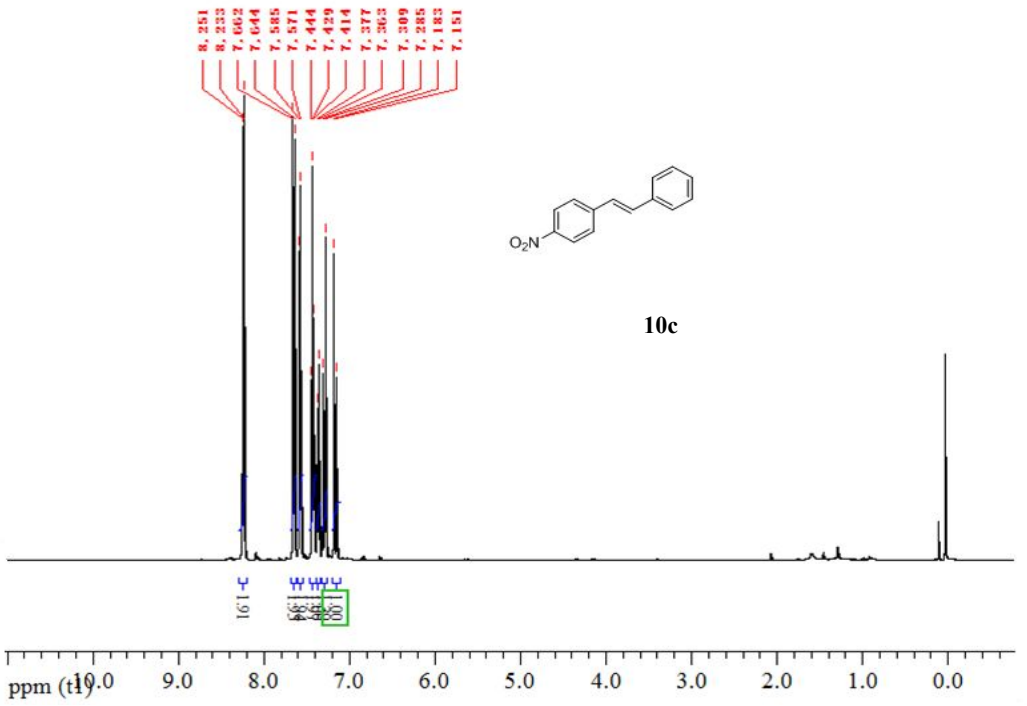
^{1}H NMR


7.589
7.574
7.439
7.424
7.409
7.339
7.337
7.326
7.310
7.179
10a
ppm (t1)

^{1}H NMR

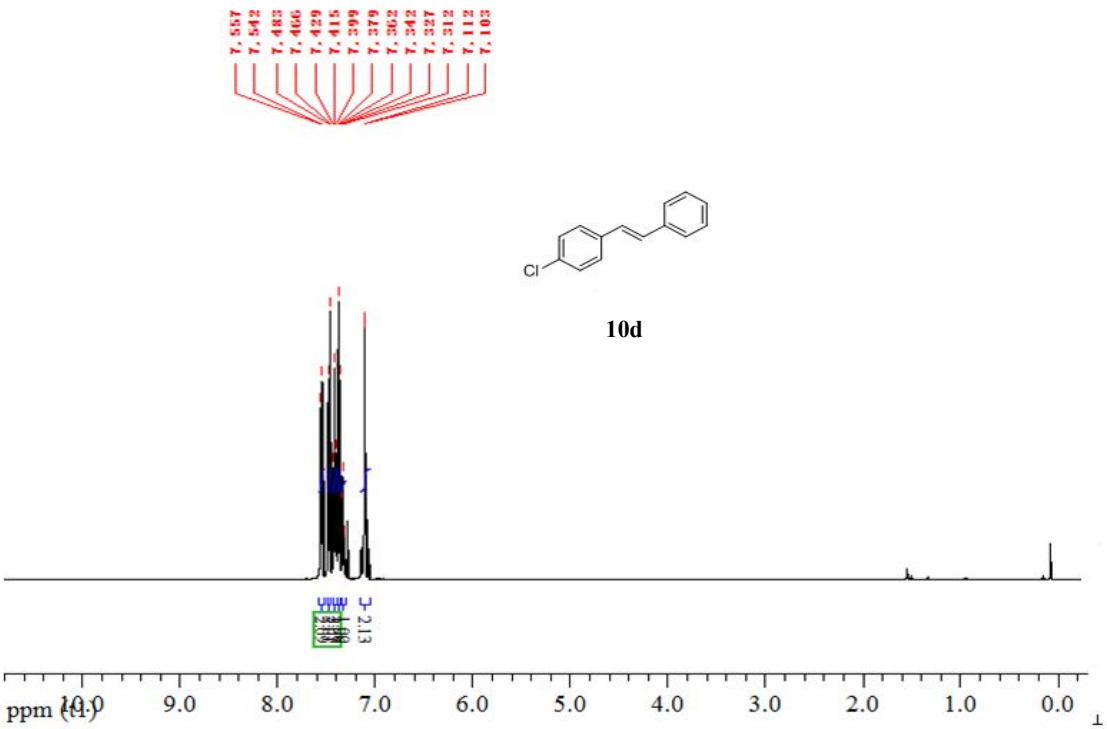

7.584
7.582
7.569
7.495
7.489
7.482
7.479
7.473
7.436
7.422
7.416
7.409
7.401
7.332
7.317
7.311
7.304
7.247
7.243
7.235
7.153
7.146
7.140
7.133
2.434
H3C
10b
ppm (t1)

^{1}H NMR



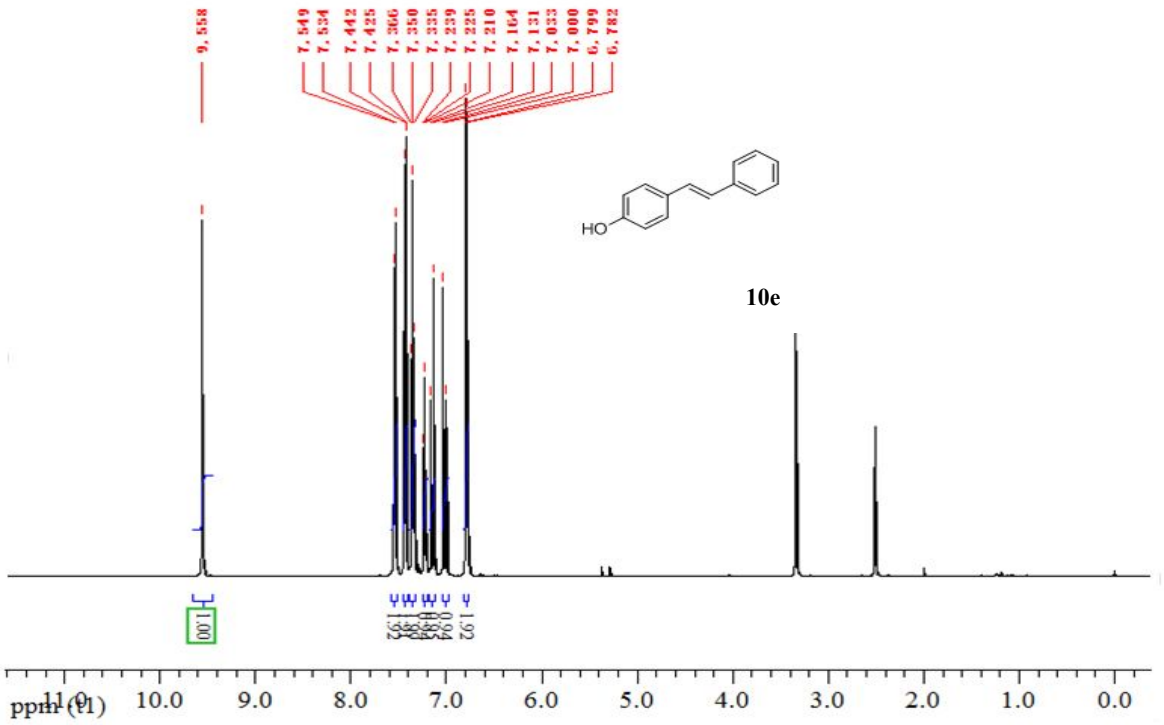
10c

^{1}H NMR

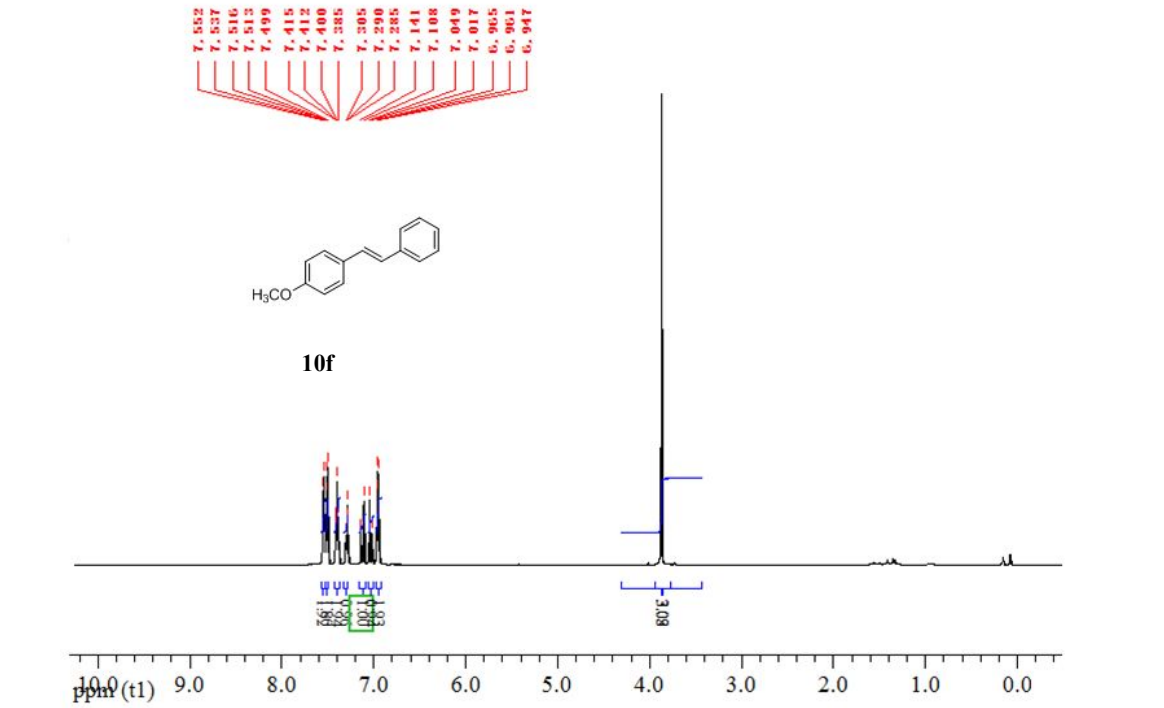


10d

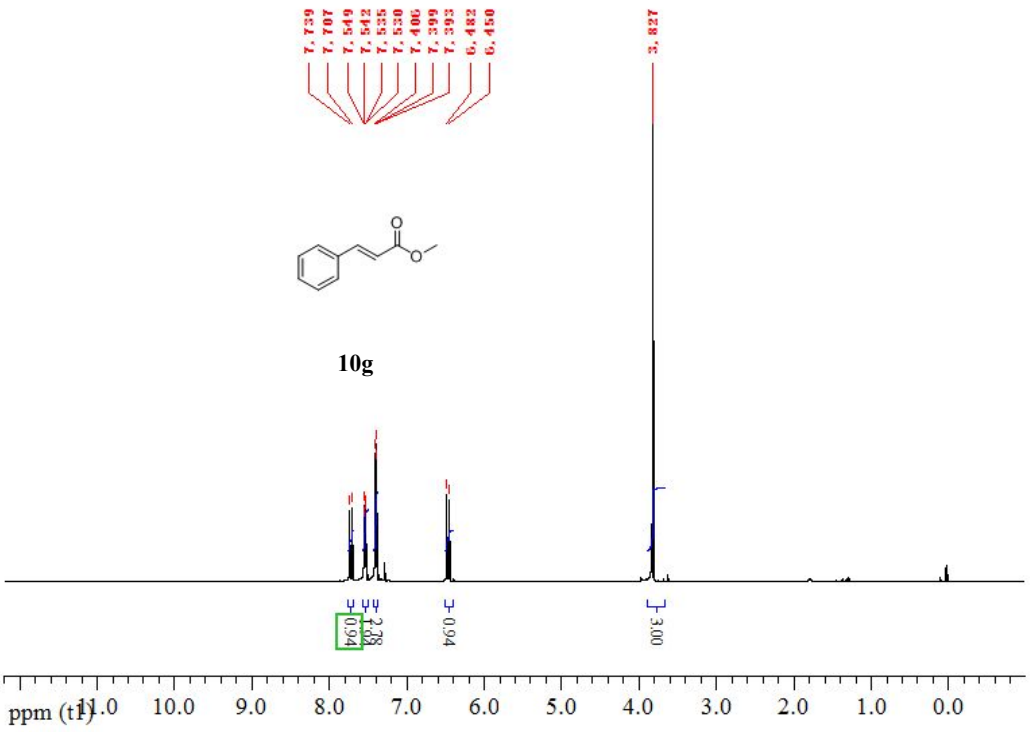
^{1}H NMR


9.558
7.549
7.534
7.442
7.425
7.366
7.350
7.335
7.239
7.225
7.210
7.164
7.131
7.033
7.000
6.799
6.782
HO
10e
1.00
1.92
ppm (t1)
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0

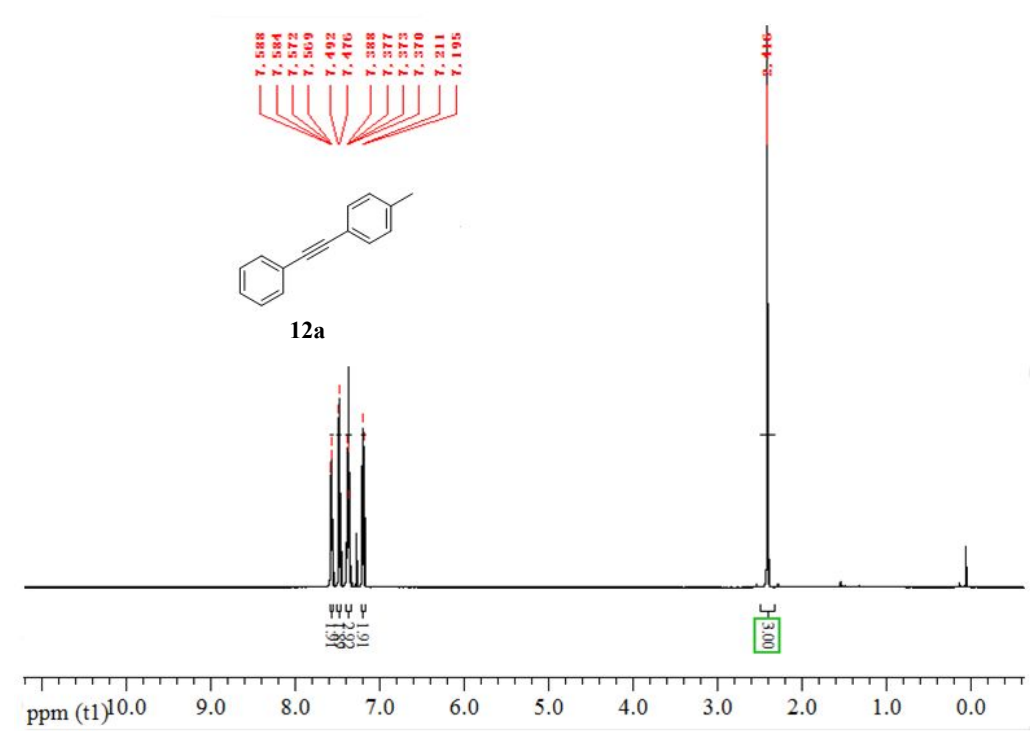
^{1}H NMR


7.552
7.537
7.516
7.513
7.499
7.415
7.412
7.400
7.385
7.305
7.290
7.285
7.141
7.108
7.049
7.017
6.965
6.961
6.947
H3CO
10f
3.09
ppm (t1)
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0

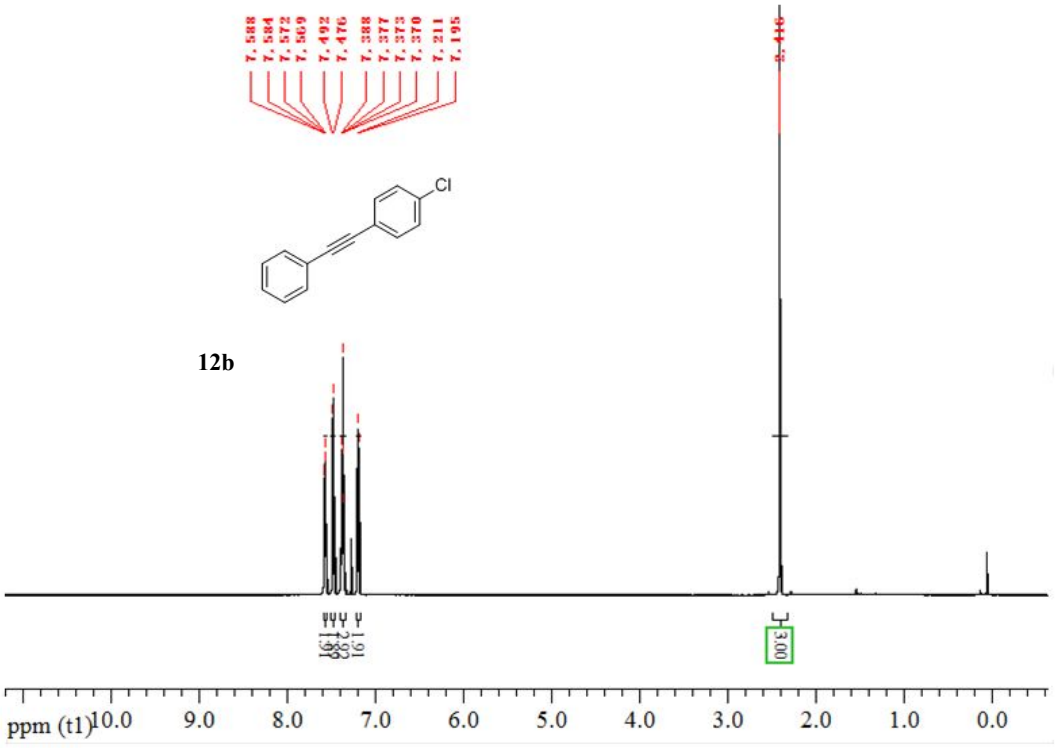
^{1}H NMR


7.739
7.707
7.549
7.542
7.535
7.530
7.406
7.399
7.393
6.482
6.450
3.827
10g
0.94
2.28
0.94
3.00
ppm (t1)
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0

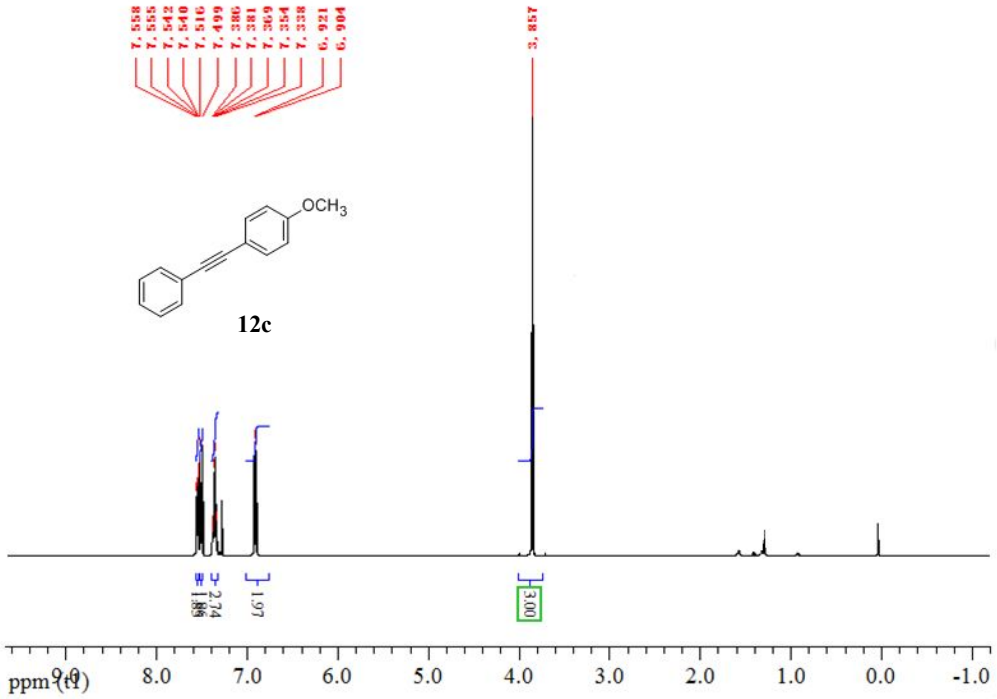
^{1}H NMR


7.588
7.584
7.572
7.569
7.492
7.476
7.388
7.377
7.373
7.370
7.211
7.195
3.416
12a
1.91
2.00
1.97
3.00
ppm (t1)
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0

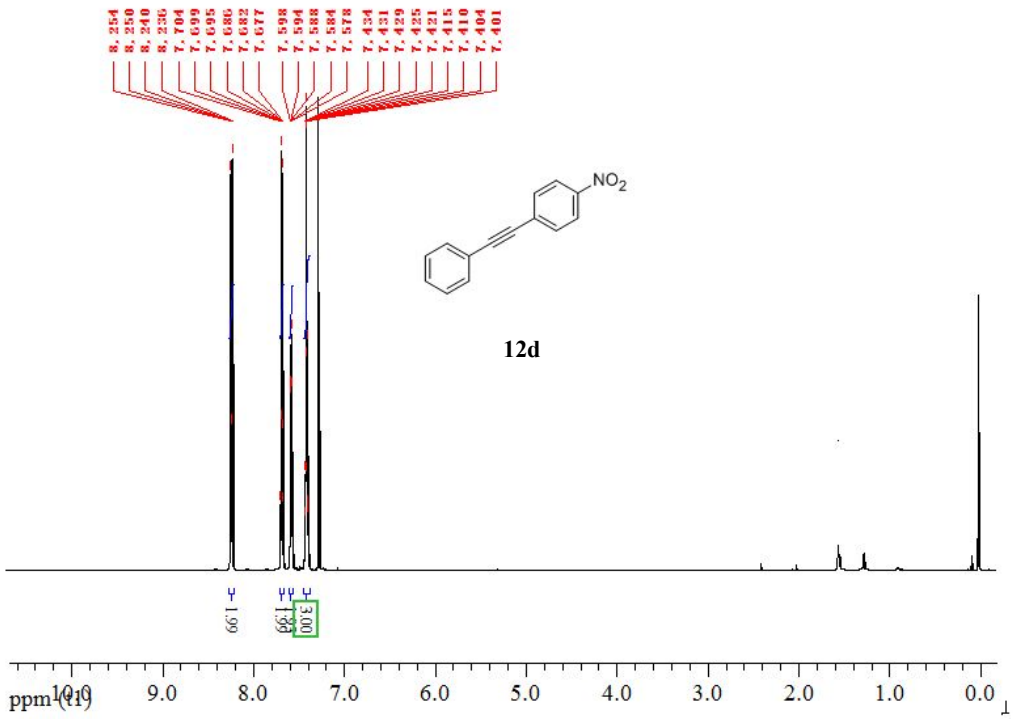
^{1}H NMR


7.588
7.584
7.572
7.569
7.492
7.476
7.388
7.377
7.373
7.370
7.211
7.195
2.416
Cl
12b
1.91
2.00
1.97
3.00
ppm (t1)
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0

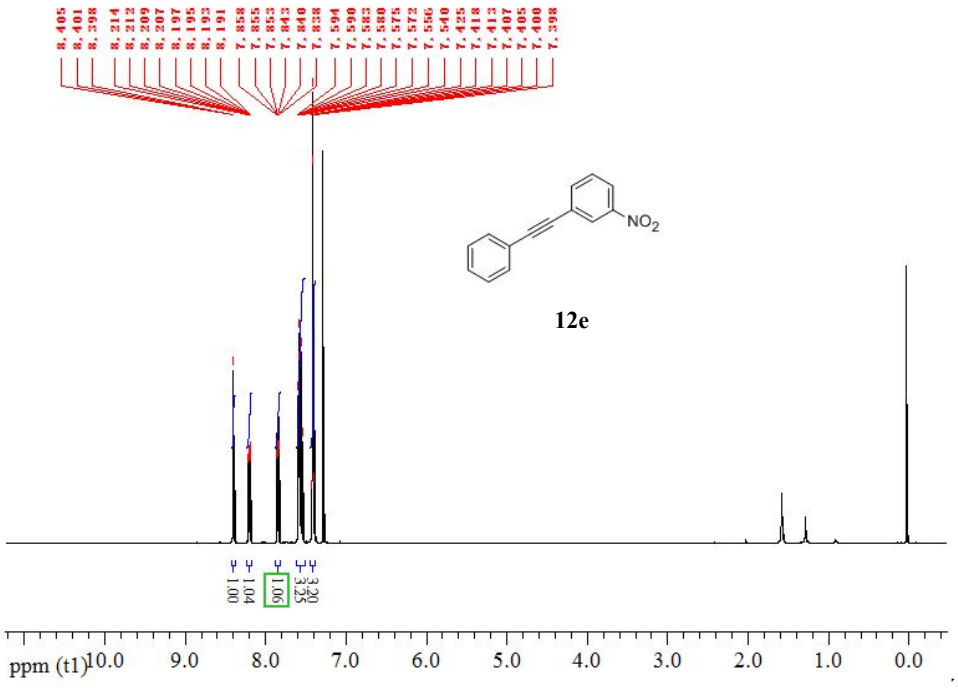
^{1}H NMR


7.558
7.555
7.542
7.540
7.516
7.499
7.386
7.381
7.369
7.354
7.338
6.921
6.904
3.857
OCH3
12c
2.74
1.89
1.97
3.00
ppm (t1)
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0

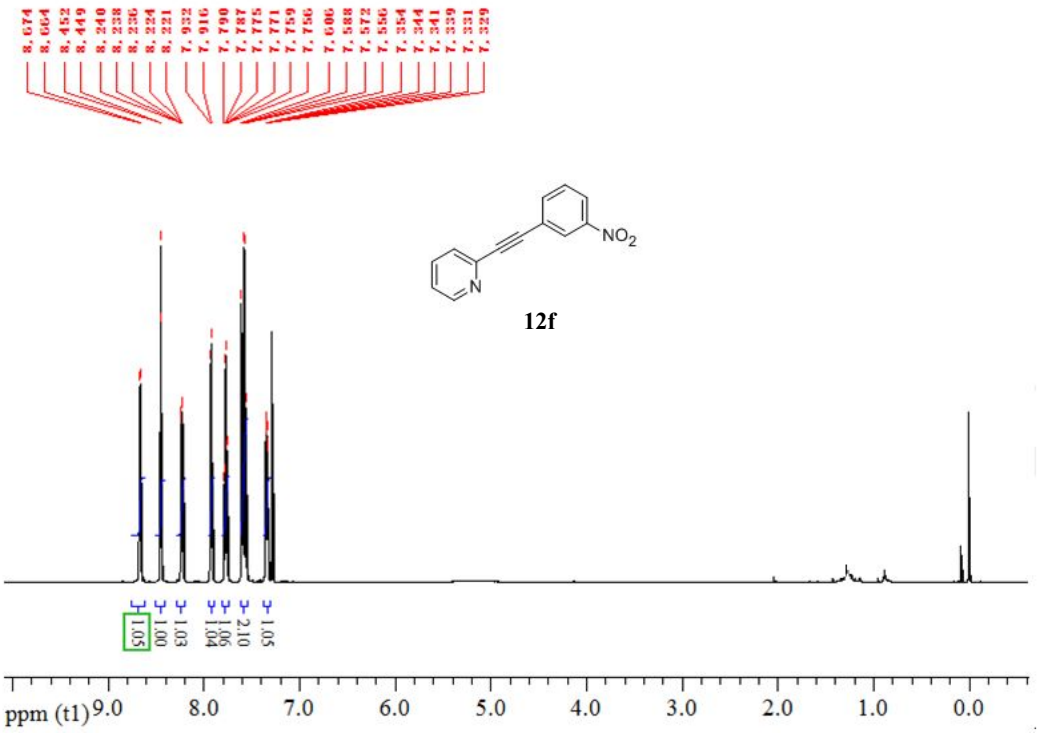
^{1}H NMR



^{1}H NMR

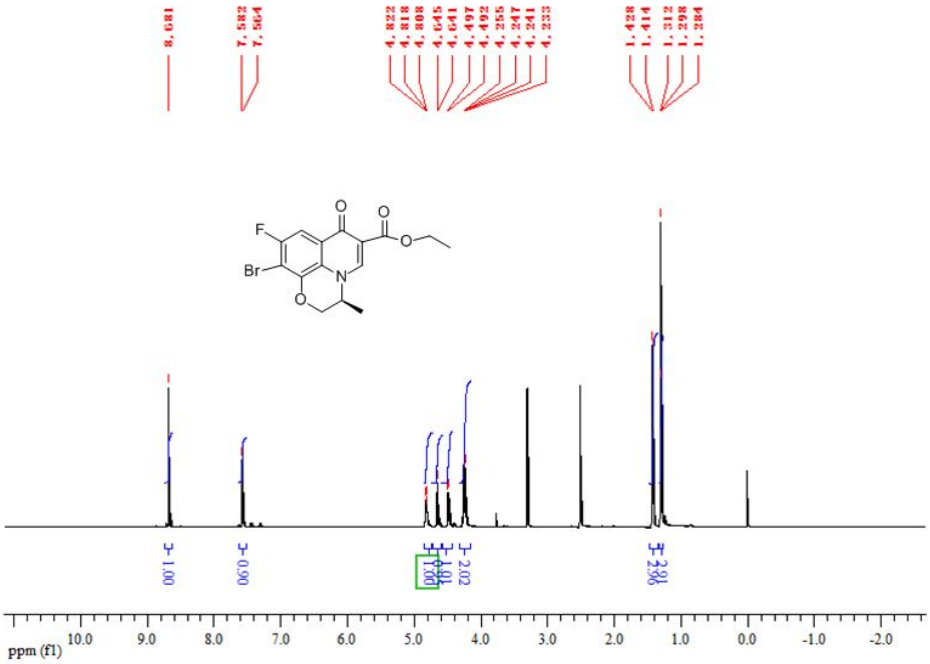


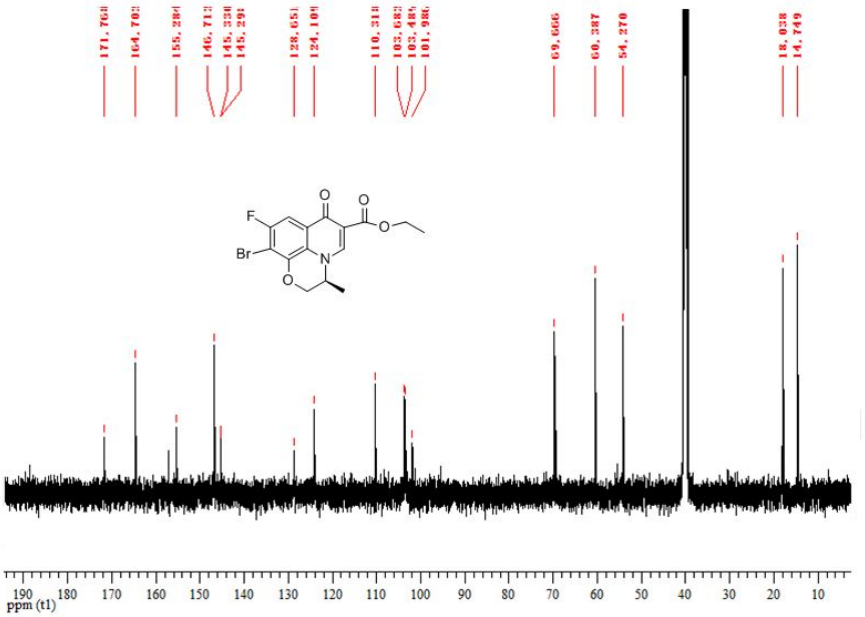
^{1}H NMR

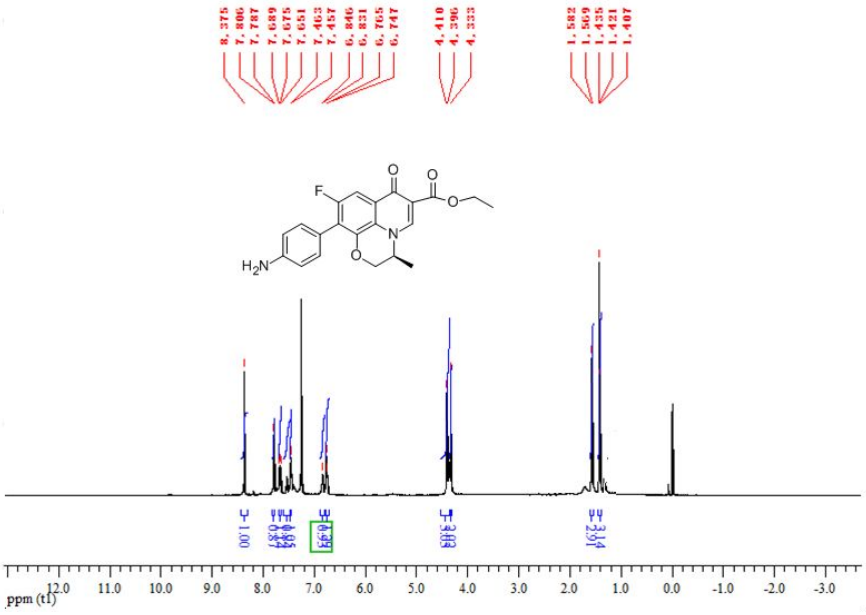


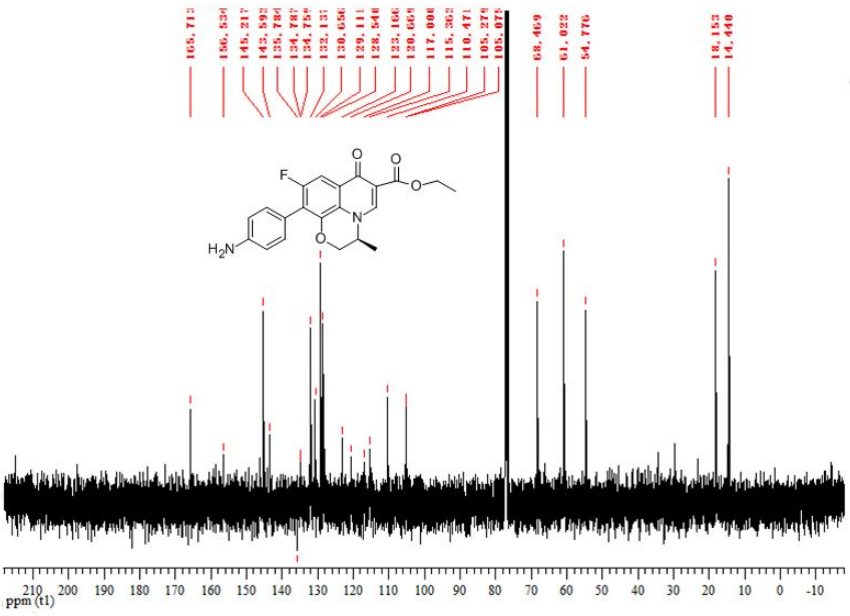
12f

Quinolone bromides:



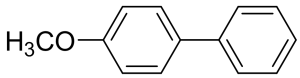

171.768
164.702
155.284
146.713
145.330
145.291
128.651
124.109
110.318
103.682
103.485
101.988
69.666
60.387
54.270
18.038
14.749
F
Br
O
O
O
N
O
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
ppm (t1)

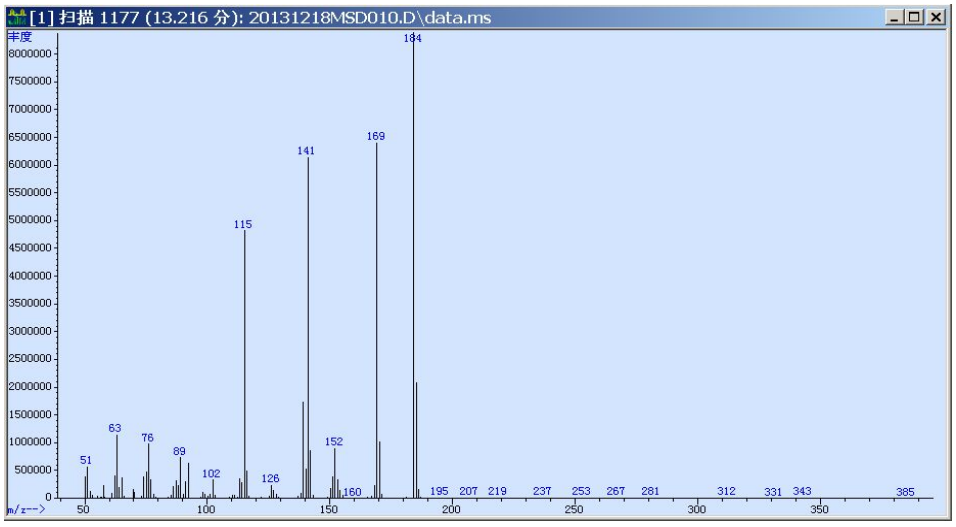

8.375
7.806
7.787
7.689
7.675
7.651
7.463
7.457
6.846
6.831
6.765
6.747
4.410
4.396
4.333
1.582
1.569
1.435
1.421
1.407
F
O
O
O
N
O
H2N
1.00
0.87
0.93
3.03
2.91
12.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 -1.0 -2.0 -3.0
ppm (t1)



The selected GC-MS chromatogram of products:
4-methoxybiphenyl 8a:

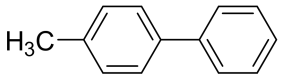
GC-MS (EI) [M]+: m/z calcd. for $C_{13}H_{12}O$: 184.0, found: 184.

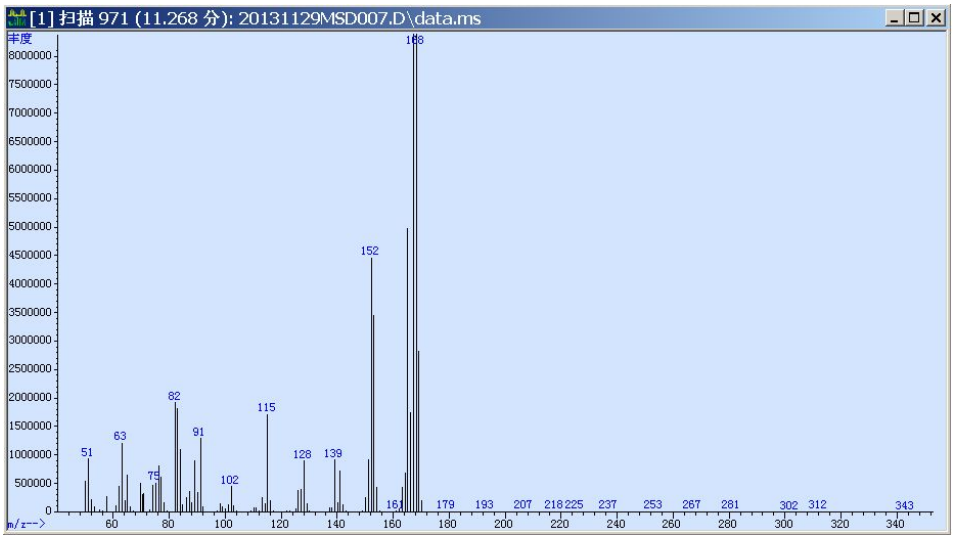




4-methylbiphenyl 8b:

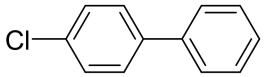
GC-MS (EI) [M]+: m/z calcd. for $C_{13}H_{12}$: 168.0, found: 168.

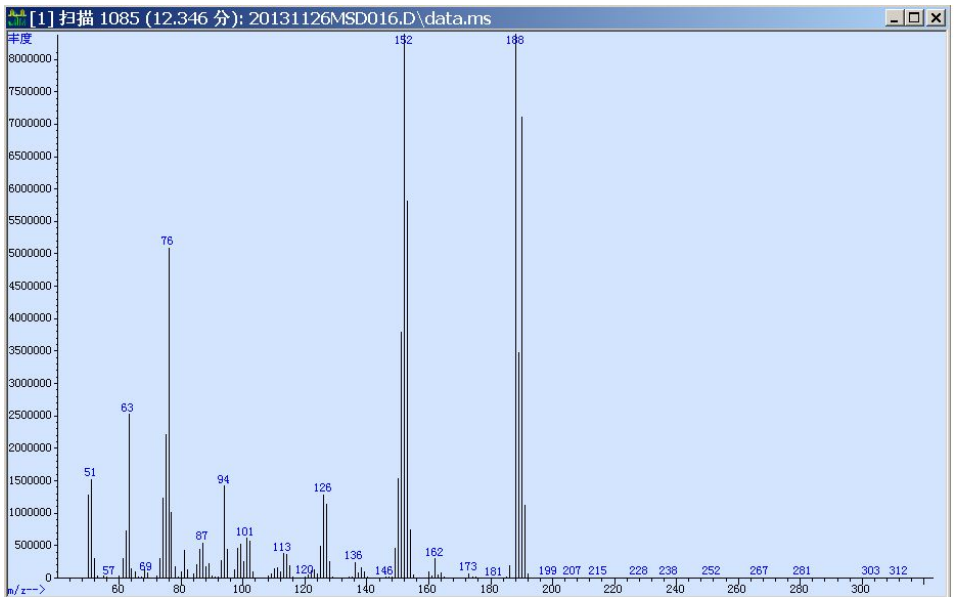




4-chlorobiphenyl 8c:

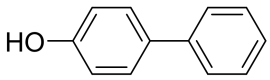
GC-MS (EI) [M]+: m/z calcd. for $C_{12}H_9Cl$: 188.0, found: 188.

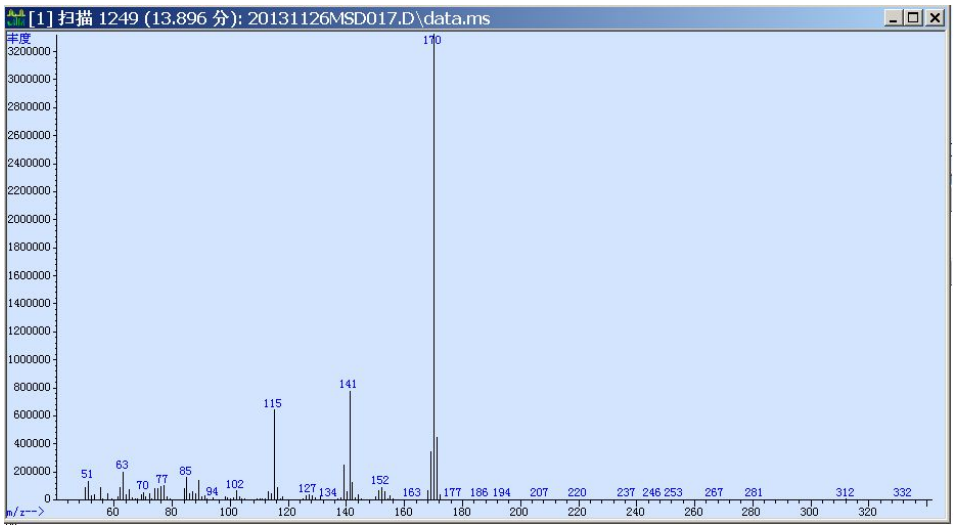




biphenyl-4-ol 8d:

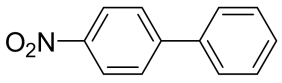
GC-MS (EI) [M]+: m/z calcd. for $C_{12}H_{10}O$: 170.0, found: 170.

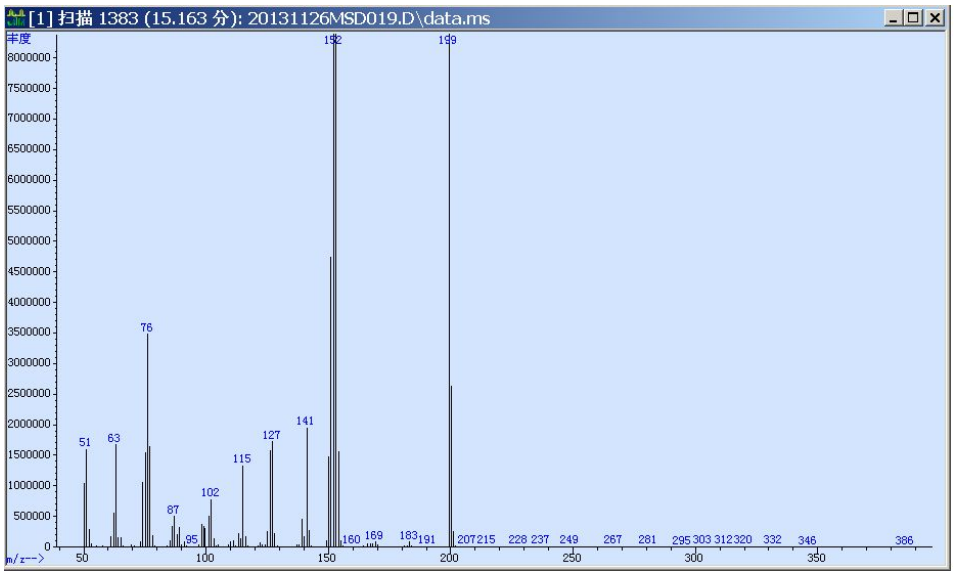




4-nitrobiphenyl 8e:

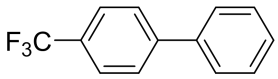
GC-MS (EI) [M]+: m/z calcd. for $C_{12}H_9NO_2$: 199.0, found: 199.

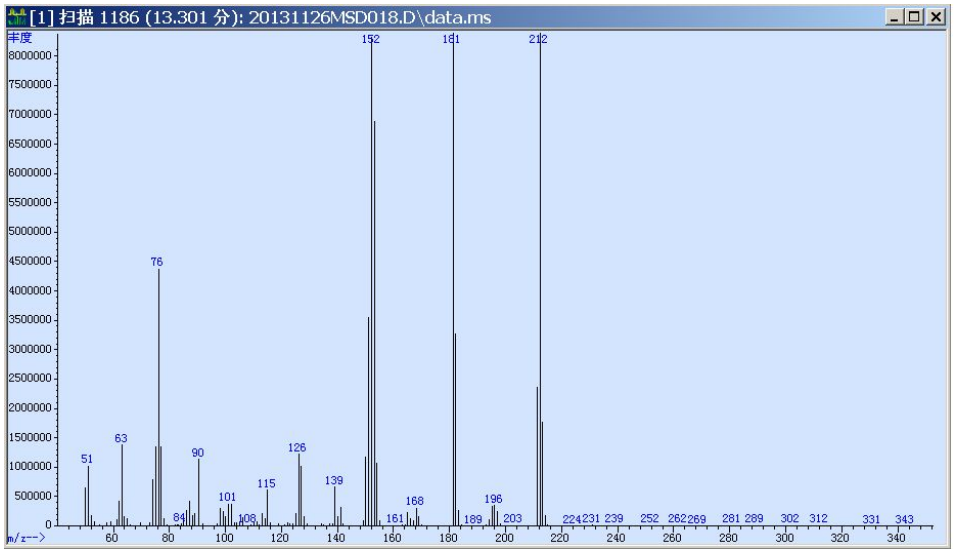




4-(trifluoromethyl)biphenyl 8f:

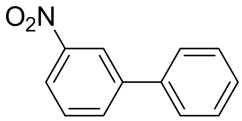
GC-MS (EI) [M]+: m/z calcd. for $C_{13}H_9F_3$: 222.0, found: 222.

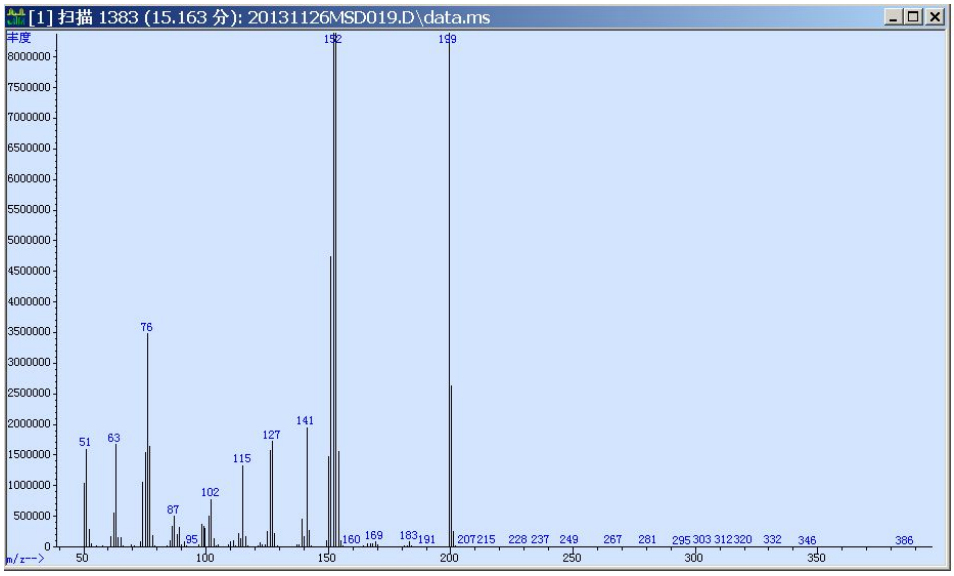




3-nitrobiphenyl 8h:

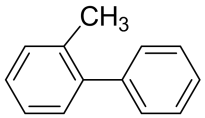
GC-MS (EI) [M]+: m/z calcd. for $C_{12}H_9NO_2$: 199.0, found: 199.

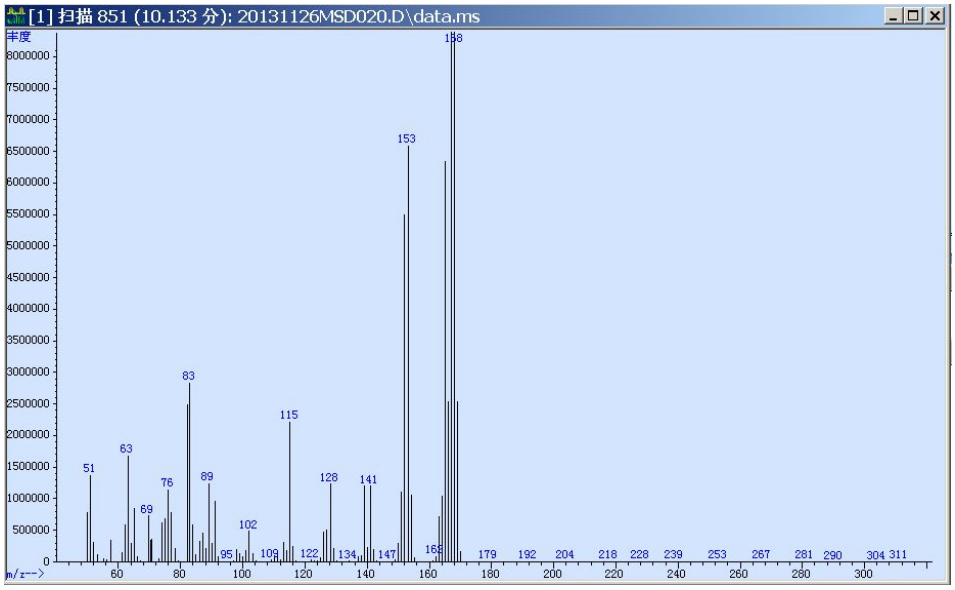




2-methylbiphenyl 8j:

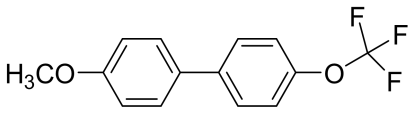
GC-MS (EI) [M]+: m/z calcd. for $C_{13}H_{12}$: 168.0, found: 168.

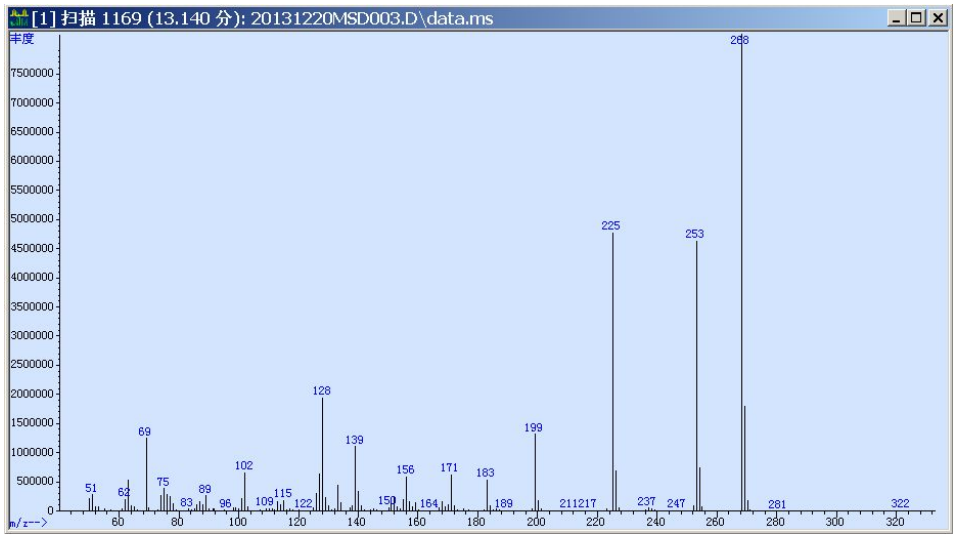




4-methoxy-4'-(trifluoromethoxy)biphenyl 8k:

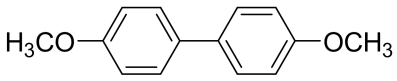
GC-MS (EI) [M]+: m/z calcd. for $C_{14}H_{11}F_3O_2$: 268.0, found: 268.

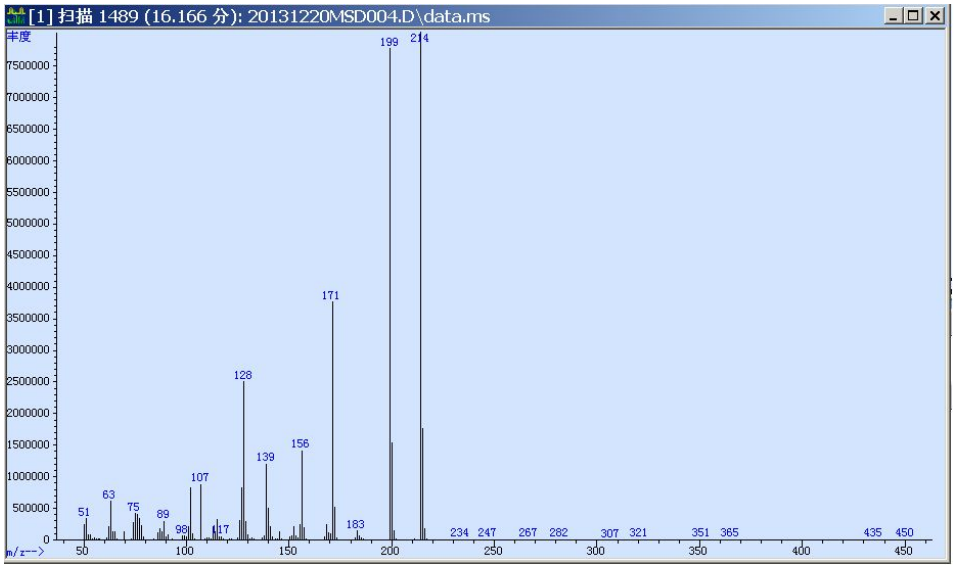




4,4'-dimethoxybiphenyl 8l:

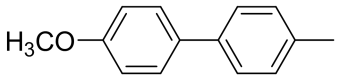
GC-MS (EI) [M]+: m/z calcd. for $C_{14}H_{14}O_2$: 214.0, found: 214.

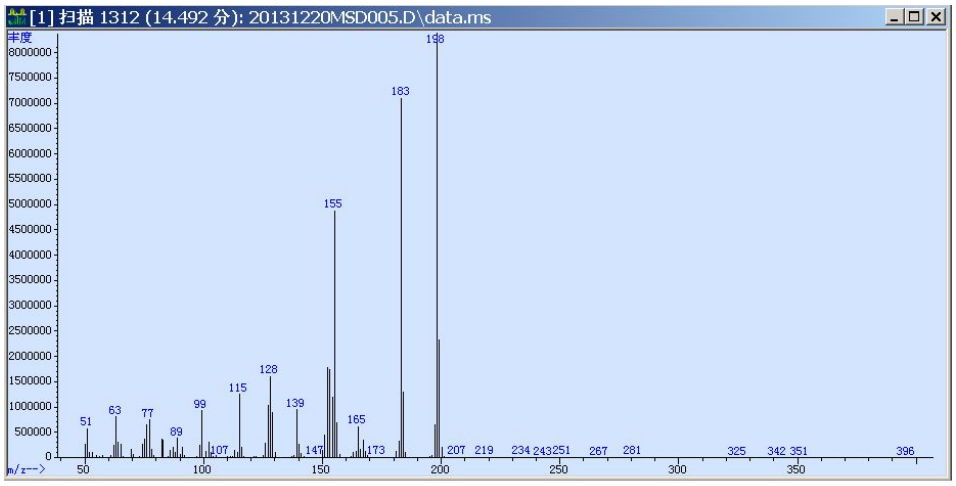




4-methoxy-4'-methylbiphenyl 8m:

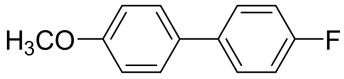
GC-MS (EI) [M]+: m/z calcd. for C14H14O: 198.0, found: 198.

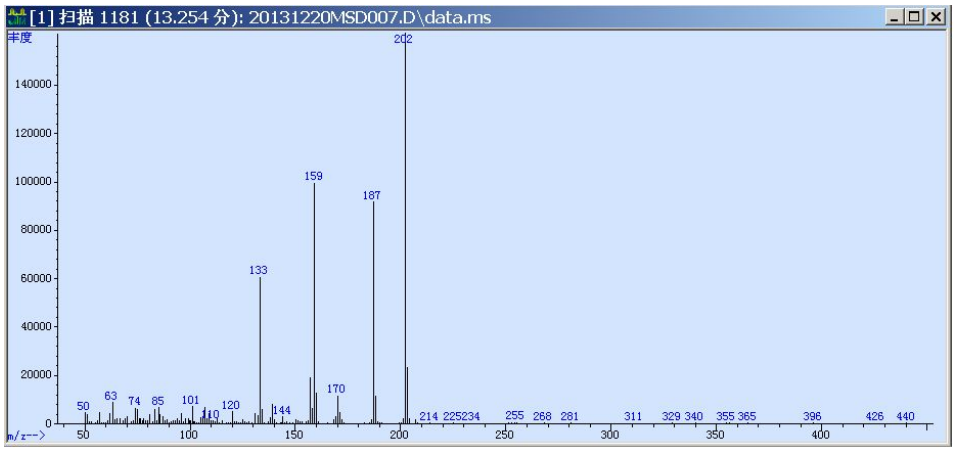




2,4'-dimethoxybiphenyl 8n:

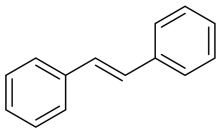
GC-MS (EI) [M]+: m/z calcd. for $C_{13}H_{11}FO$: 202.0, found: 202.

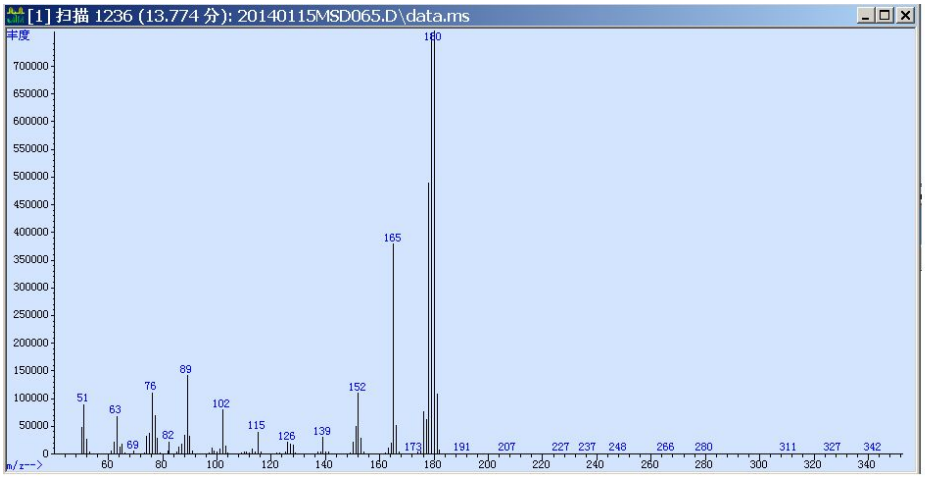




(*E*)-1,2-diphenylethene 10a:

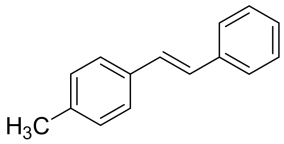
GC-MS (EI) [M]+: m/z calcd. for $C_{14}H_{12}$: 180.0, found: 180.

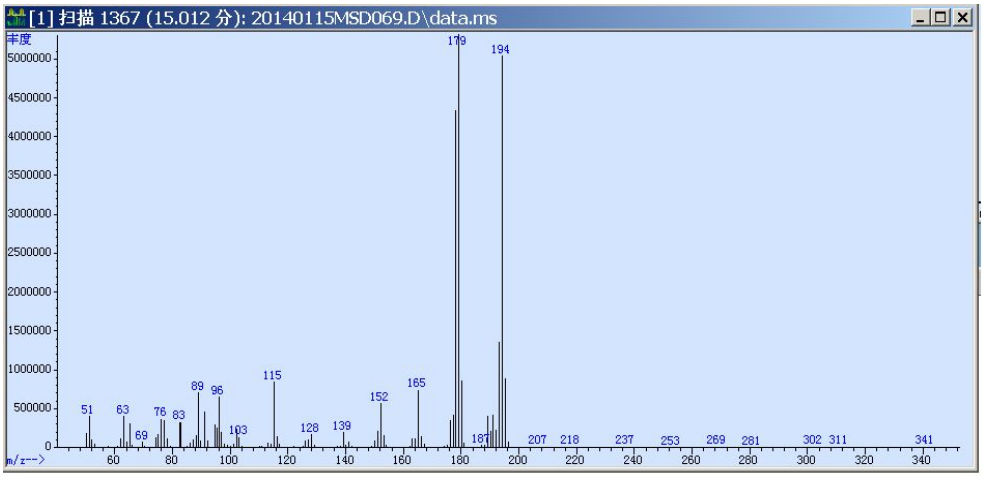




***E*)-1-methyl-4-styrylbenzene 10b:**

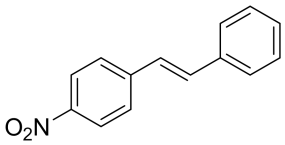
GC-MS (EI) [M]+: m/z calcd. for $C_{15}H_{14}$: 194.0, found: 194.

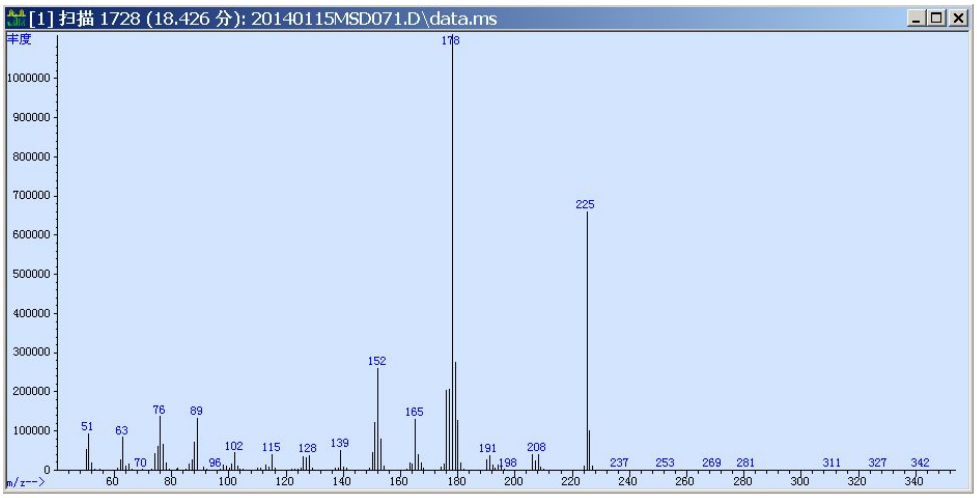




(*E*)-1-nitro-4-styrylbenzene 10c:

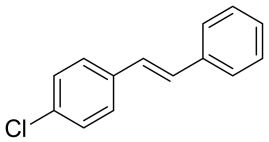
GC-MS (EI) [M]+: m/z calcd. for $C_{14}H_{11}NO_2$: 225.0, found: 225.

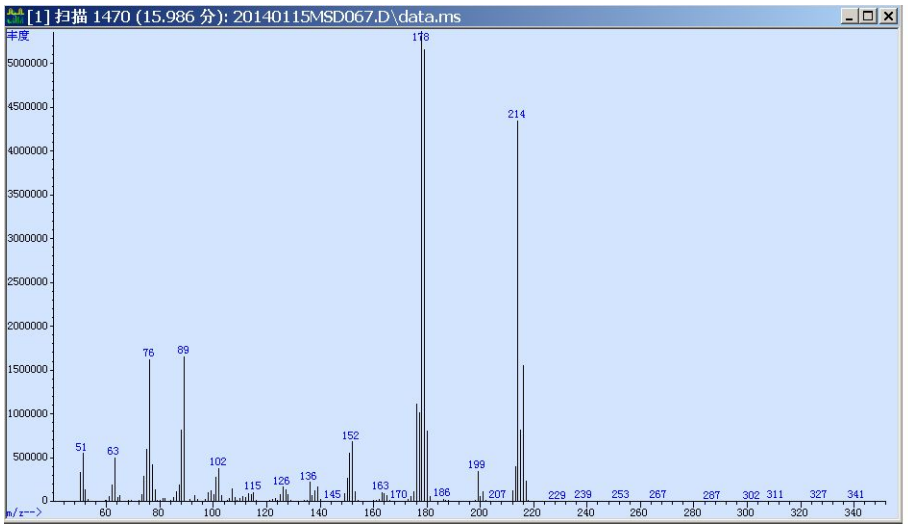




(*E*)-1-chloro-4-styrylbenzene 10d:

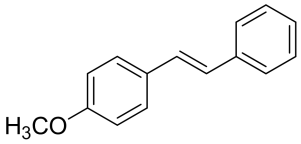
GC-MS (EI) [M]+: m/z calcd. for $C_{14}H_{11}Cl$: 214.0, found: 214.

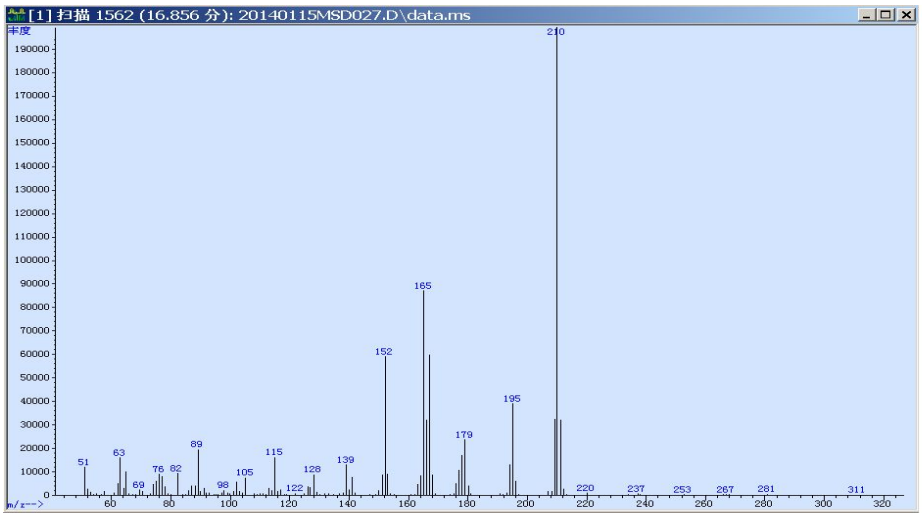




(*E*)-1-methoxyl-4-styrylbenzene 10f:

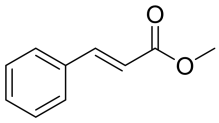
GC-MS (EI) [M]+: m/z calcd. for $C_{15}H_{14}O$: 210.0, found: 210.

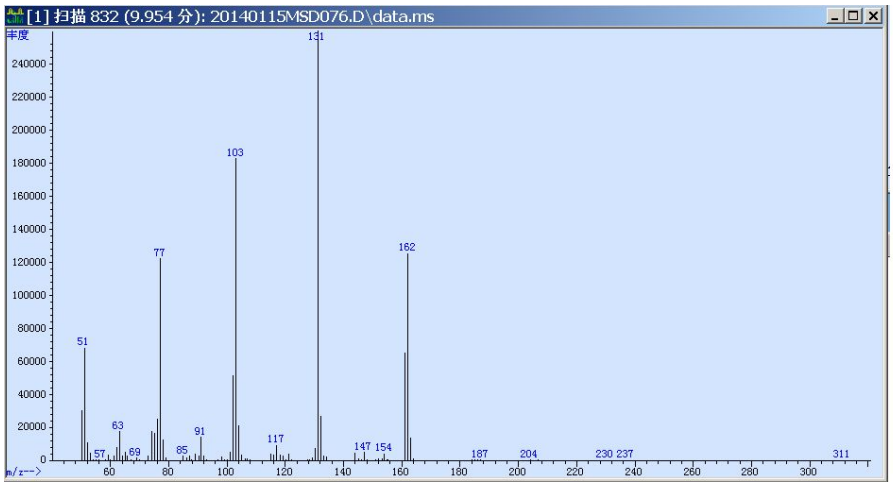




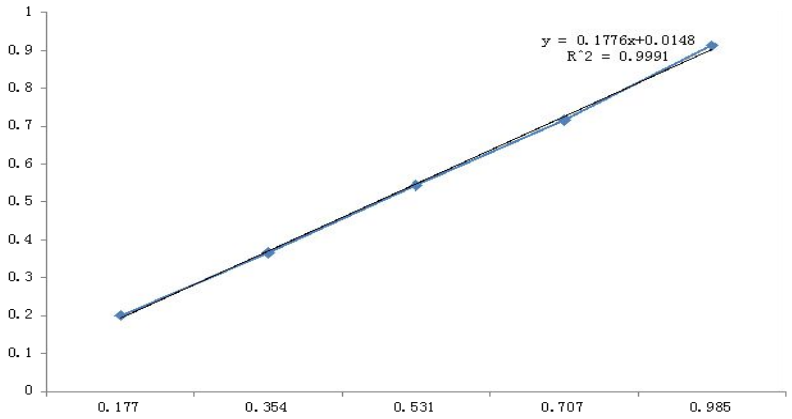
Methyl cinnamate 10g:

GC-MS (EI) [M]+: m/z calcd. for $C_{10}H_{10}O_2$: 162.0, found: 162.





The selected GC-analysis of products:



calibration curve

[General procedure: 分别将产物标准溶液稀释成20 mg/10 mL, 40 mg/10 mL, 60 mg/10 mL, 80 mg/10 mL, 100 mg/10mL 的梯度质量浓度, 取梯度质量浓度的产物标准溶液100 μL于20 ml 试管中, 加人500 μL 22.6 mg/10 mL 内标溶液,气相色谱测定以产物的峰面积与内标物的峰面积比($A_{产物}/A_{内标}$) 为纵坐标Y, 其质量比($M_{产物}/M_{内标}$)为横坐标X, 绘制标准曲线。]

NO.	1	2	3	4	5	average
$S_i/_s$	0.886	0.967	0.958	0.988	0.969	0.9536

response factor：$S_{i/s} = S_i/S_s = A_i\ m_s\ /（A_s\ m_i）$

$S_{i/s}$=0.9536

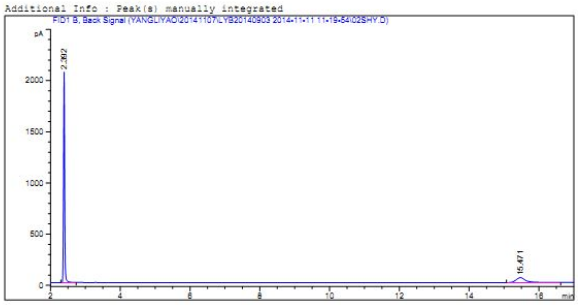
relative quality correcting factor：$f_{i/s} = f'_i/f'_s = m_iA_s/(m_sA_i)$

$m_i =（A_i\ /A_s）*m_s * f'_i/f'_s =（A_i\ /A_s\ ）*m_s\ / S_{i/s}$

= 0.9469*184/ 0.9536

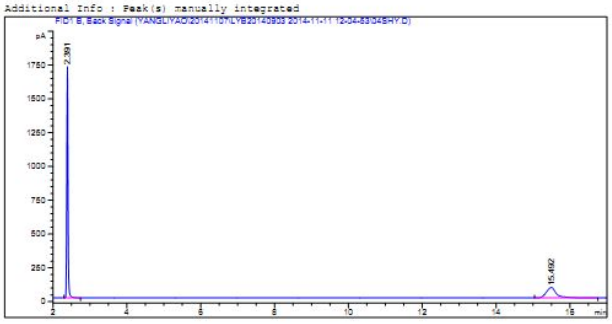
= 182.72

NO. 1:




```
---------------------------------------------------------------------
                        Area Percent Report
---------------------------------------------------------------------

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: FID1 B, Back Signal

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]         %
----|--------|----|-------|----------|----------|--------|
   1  2.392 BV    0.0357 4718.49170 2063.63037 83.34396
   2  15.471 BB    0.2502  942.97632   48.63651 16.65604
```

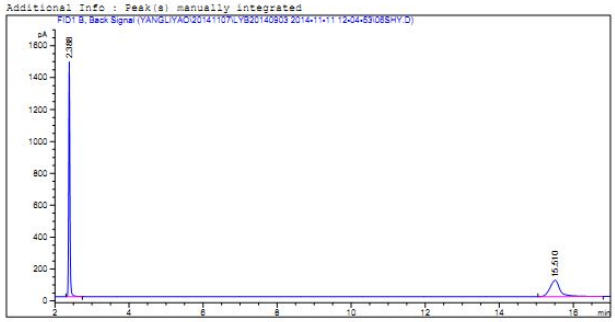
NO. 2:




```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: FID1 B, Back Signal

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]         %
----|--------|----|-------|----------|----------|--------|
   1  2.391 BV    0.0365 4036.02808 1711.79004 73.21147
   2  15.492 BB    0.2349 1476.80737   77.28842 26.78853
```

NO.3:

Additional Info : Peak(s) manually integrated



Area Percent Report

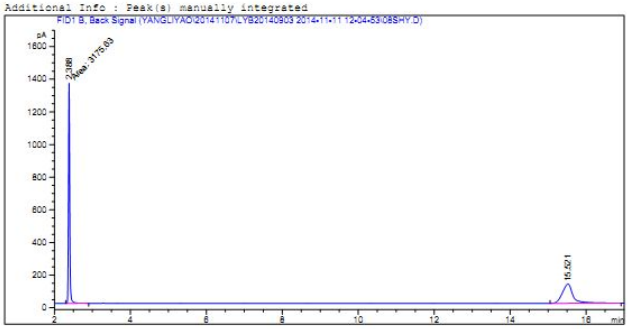
Sorted By : Signal
Multiplier: : 1.0000
Dilution: : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: FID1 B, Back Signal

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	2.388	BV	0.0365	3486.69653	1477.79114	64.34264
2	15.510	BB	0.2333	1932.25537	102.77600	35.65736

NO.4:

Additional Info : Peak(s) manually integrated



Area Percent Report

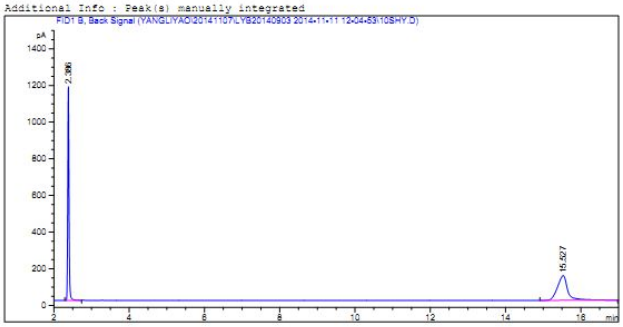
Sorted By : Signal
Multiplier: : 1.0000
Dilution: : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: FID1 B, Back Signal

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	2.388	MM	0.0391	3175.63428	1353.98901	58.27015
2	15.521	BB	0.2599	2274.21338	117.95347	41.72985

NO.5:

Additional Info : Peak(s) manually integrated



Area Percent Report

Sorted By : Signal
Multiplier: : 1.0000
Dilution: : 1.0000
Use Multiplier & Dilution Factor with ISTDs

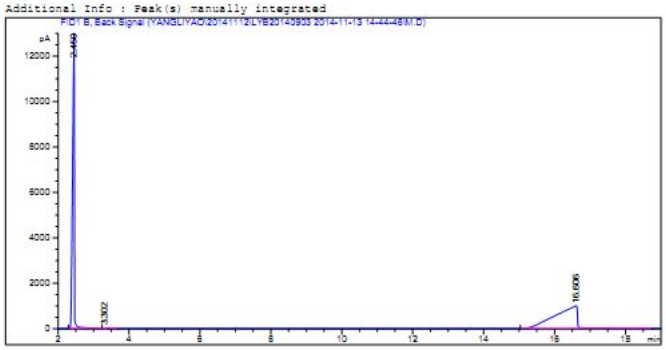
Signal 1: FID1 B, Back Signal

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	2.386	BV	0.0367	2772.67261	1168.34900	52.25565
2	15.527	BB	0.2300	2533.30371	134.94049	47.74435

Table 1, entry 5, 84% of GC yield:

Table 1, entry 6, 99% of GC yield:

Additional Info : Peak(s) manually integrated



Area Percent Report

Sorted By : Signal
Multiplier: : 1.0000
Dilution: : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: FID1 B, Back Signal

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	2.450	VB S	0.0463	4.51632e4	1.30856e4	51.34093
2	3.302	BB X	0.0502	35.78336	10.93300	0.04068
3	16.606	BB	0.5242	4.27694e4	981.87457	48.61849

4. X-ray Crystal Data for GPT-Pd catalyst 5c

Crystals of GPT-Pd catalyst **5c** ($C_{33}H_{48}Cl_2N_4O_9Pd$) were recrystallized from a acetonitrile-dichloromethane solution. A single white needle crystal which was suitable for X-ray diffraction measurements was mounted on a glass fiber. Unit cell measurements and intensity data collections were performed on a Rigaku AFC7R diffractometer with graphite monochromated Mo Ka. The data reduction included a correction for Lorentz and polarization effects, with an applied multi-scan absorption correction (SADABS). The crystal structure was solved and refined using the SHELXTL-97 program suite. Direct methods yielded all non-hydrogen atoms which were refined with anisotropic thermal parameters. The reflection data were consistent with a monoclinic system: P2(1)/c. The obtained crystal structure has been deposited at the Cambridge Crystallographic Data Centre and allocated the deposition number: 790566 (CCDC NO). The crystallographic data and refinement parameters of **5c** are listed in Table S1.

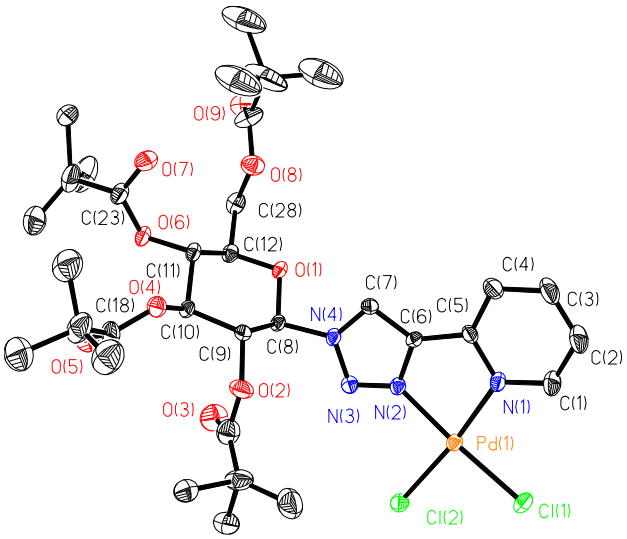


Table S1. Crystallographic data and structure refinement for **5c.**

Identification code	140414_cc2014_2_b
Empirical formula	C_{66} $H_{96}Cl_4$ N8 O_{18} Pd_2
Formula weight	1644.11
Temperature, K	293(2) K
Wavelength, Å	0.71073 Å
Crystal system	Orthorhombic
Space group	P212121
Cell dimensions	
a, *b*, *c*, Å	9.6866(3) Å, 11.4036(5) Å, 41.7046(15)Å
α, β, γ, ^{o}	90^o, 90^o, 90^o
Volume, $Å^3$	4606.8(3) $Å^3$
Z	2
Calculated density, g/cm^3	1.185
Absorption coefficient, mm^{-1}	0.564
F (000)	1704
Crystal size, mm	0.32 x 0.28 x 0.16 mm
Theta range for data collection, ^{o}	3.03 to 25.01 deg
Limiting indices	-10<=h<=11, -13<=k<=10, -47<=l<=49
Completeness to theta = 25.01 ^{o}	99.7 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.00000 and 0.91960
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	8108 / 64 / 465
Goodness of fit on F^2	1.140
R indices [$I > 2\sigma(I)$]	R1 = 0.0606, wR2 = 0.1644
R indices (all data)	R1 = 0.0645, wR2 = 0.1676
Absolute structure parameter	0.02(5)
Largest diff. peak and hole, e $Å^{-3}$	0.782 and -0.827 e.A^-3

6.References

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