# Iron-catalyzed Carboarylation of Alkynes *via* Activation of π-activated Alcohols: Rapid Synthesis of Substituted Benzofused Six-membered Heterocycles

Rupsa Chanda, Abhisek Kar, Aniruddha Das, Baitan Chakraborty, Umasish Jana*

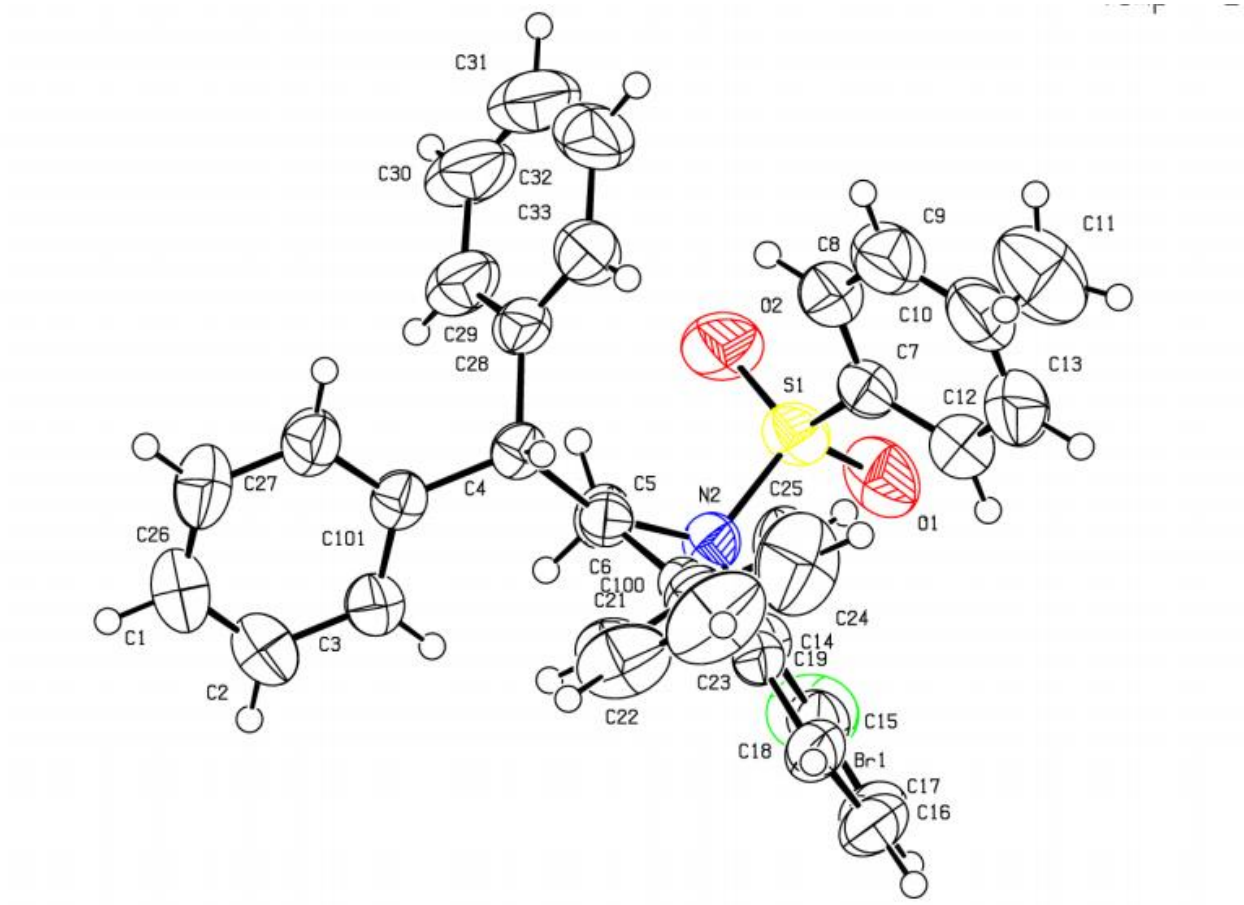
Department of Organic Chemistry, Jadavpur University, Jadavpur, Kolkata-700032, India
Email:jumasish2004@yahoo.co.in; umasish@gmail.com

**Table of content**

**General information:**

All $^{1}H$ NMR spectra were recorded with Bruker Avance III (300, 400 or 500 MHz) spectrometers in deuterated solvents ($CDCl_3$). Chemical shifts are reported in parts per million (ppm, δ) relative to tetramethylsilane (TMS) and the solvent resonance were referenced to internal standard $CDCl_3$ (δ 7.26 ppm). All coupling constants are absolute values and are expressed in Hz. The descriptions of the signals are reported as follows: s = singlet, d = doublet, dd = double of doublet, t = triplet, m = multiplet and dt = doublet of triplets. $^{13}C$ NMR spectra were recorded with Bruker Avance III 300 (75 MHz), 400 (100 MHz) and 500 (125 MHz) spectrometers as solutions in $CDCl_3$ with complete proton decoupling. Chemical shifts are reported in parts per million (ppm, δ) and are referenced to internal standard $CHCl_3$ (δ = 77.16 ppm). High resolution mass spectra were taken using Q-Tof micro MS system by electron spray ionization (ESI) technique. Crystallographic data were collected at room temperature on a Bruker $D_8$ quest microfocus single crystal XRD machine. The routine monitoring of the reaction was performed with silica gel coated glass slides (Merck, silica gel G for TLC) and pre-coated Al plates which were analyzed with iodine and UV-light respectively. Solvents, reagents, and chemicals were purchased from Aldrich, Alfa aesar, Merck, SRL, Spectrochem, and Process Chemicals. $FeCl_3$ (98%, purity) and $Fe(OTf)_3$ (90%, purity) catalysts were purchased from Alfa Aesar and were directly used. The final products were purified by column chromatography on Merck silica gel (100–200 mesh). All reactions involving moisture-sensitive reactants were executed with oven-dried glass ware.

**Figure 1. ORTEP diagram for the crystal structure of compound 3c (Thermal ellipsoid contour at 50% probability level)**




**CCDC no. 1982134**

**Sample preparation and crystal structure determination for 3c**

The single crystal Suitable for X-ray of compound **3c** was mounted on the tip of a thin glass fiber with commercially available glue. The X-ray single crystal data collection of **3c** crystal was performed at room temperature using a Bruker APEX III $D_8$ Quest smart diffractometer, equipped with a microfocus and a sealed tube Xray source with graphite monochromated Mo-Kα radiation (λ = 0.71073 Å). The data were integrated using the SAINT1 program, and the absorption corrections were made with SADABS.2 The structure was solved by SHELXS 20173 using the Patterson method and followed by successive Fourier and difference Fourier synthesis. Full matrix least-squares refinements were performed on F2 using SHELXL-20174 with anisotropic displacement parameters for all non-hydrogen atoms. All hydrogen atoms were fixed geometrically by HFIX command and placed in ideal positions. All calculations were carried out using SHELXS-2017, 3 SHELXL-2017, PLATON v1.15,4 ORTEP-3v2,5 and WinGX system Ver-1.80.6 The data collection and the structure refinement parameters and crystallographic data for the compound are given in Table S1.

**References:**


1. SMART (V 5.628), SAINT (V 6.45a), XPREP, SHELXTL, Bruker AXS Inc., Madison, WI, 2004.

2. M. S. George, SADABS (Version 2.03), University of Göttingen, Germany, 2002.

3. M. S. George, *Acta Crystallogr*. *A*., 2008, **64**, 112.

4. L. S. Anthony, *Acta Crystallogr. D. Biol. Crystallogr.*, 2009, **65**, 148.

5. J. F. Louis, *J. Appl. Crystallogr.*, 1997, **30**, 565.

6. J. F. Louis, *J. Appl. Crystallogr.*, 1999, **32**, 837.

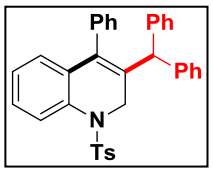
**Table S1. Table for crystallographic data and structural refinement parameters for 3c**

| | |
|---|---|
| Empirical formula | $C_{35}H_{28}BrNO_2S$ |
| Formula weight | 606.57 |
| Temperature/K | 273(2) |
| Crystal system | monoclinic |
| Space group | 'C 2/c' |
| a/Å | 31.598(3) |
| b/Å | 11.6057(9) |
| c/Å | 21.0251(17) |
| α/° | 90 |
| β/° | 129.356(2) |
| γ/° | 90 |
| Volume/Å$^3$ | 5961.7(8) |
| Z | 8 |
| $\rho_{calc}$g/cm$^3$ | 1.360 |
| μ/mm$^{-1}$ | 1.483 |
| F(000) | 2512 |
| Crystal size/mm$^3$ | .3 × .2 × .1 |
| Radiation | MoK\a (λ = 0.71073) |
| θ range/° | 2.5825 to 24.6152 |
| Index ranges | -39 ≤ h ≤ 39, -14 ≤ k ≤ 14, -26 ≤ l ≤ 26 |
| Data/restraints/parameters | 6126/0/362 |
| Goodness-of-fit on $F^2$ | 1.056 |
| Largest diff. peak/hole / e Å$^{-3}$ | 0.44/-0.609 |

All the starting materials **1a-1i** were prepared by Sonogashira coupling of corresponding propargylated anilines according to previous reports.[1]

## 1. Representative Experimental Procedure for the Synthesis and Characterization of 3a-3h:

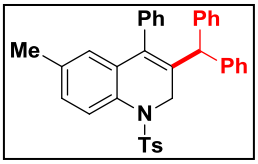
### 3-Benzhydryl-4-phenyl-1-tosyl-1,2-dihydroquinoline (3a):




In an oven-dried round-bottom flask, 4-methyl-*N*-phenyl-*N*-(3-phenylprop-2-yn-1-yl)benzenesulfonamide (**1a**) (54 mg, 0.15 mmol) and diphenylmethanol (**2a**) (27 mg, 0.15 mmol) were taken in dry nitromethane (2 mL) and $Fe(OTf)_3$ (7.5 mg, 0.015 mmol) was added to the mixture under argon atmosphere and stirred for 2 h at 80 °C. After the completion of the reaction (monitored by TLC), the crude reaction mixture was extracted with EtOAc (15 mL, twice) and the combined organic layer was washed with water (15 mL, two times), dried over anhydrous $Na_2SO_4$ and concentrated under reduced pressure. The product was purified by column chromatography on silica gel (100−200 mesh), eluted by petroleum ether/ethyl acetate (95:5 v/v), to afford the desired product **3a** (35.5 mg, 0.06 mmol, 71%) as a light yellow solid, m.p. 184–188 °C. **$^1$H NMR (400 MHz, $CDCl_3$)** δ 7.80 (dd, *J* = 8.1, 1.2 Hz, 1H), 7.39 – 7.15 (m, 10H), 7.12 – 7.01 (m, 5H), 6.89 (d, *J* = 8.0 Hz, 2H), 6.54 (t, *J* = 8.4 Hz, 5H), 4.93 (s, 1H), 4.68 (s, 2H), 2.37 (s, 3H) ppm. **$^{13}$C NMR (75 MHz, $CDCl_3$)** δ 142.7, 140.5, 136.9, 135.8, 134.8, 134.1, 134.0, 132.3, 130.4, 129.7, 129.4, 129.3, 129.2, 129.1, 128.9, 128.6, 128.5, 127.6, 127.5, 127.3, 126.9, 126.7, 126.6, 126.2, 125.8, 53.0, 45.8, 21.4 ppm. **HRMS:** m/z calcd for $C_{35}H_{29}NO_2SNa$ $[M + Na]^+$, 550.1817; found, 550.1818.

The above procedure was followed for all the reactions listed in Table 2. These compounds are not reported earlier and were characterized properly by their spectroscopic data ($^1$H NMR, $^{13}$C NMR, and HRMS).

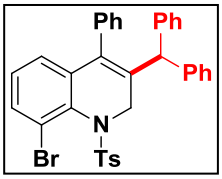
### 3-Benzhydryl-6-methyl-4-phenyl-1-tosyl-1,2-dihydroquinoline (3b):




white solid (49 mg, 0.09 mmol, 89%) m.p. 175–178 °C. **$^1$H NMR (400 MHz, $CDCl_3$)** δ 7.69 (d, *J* = 8.1 Hz, 1H), 7.38 – 7.28 (m, 9H), 7.12 – 7.03 (m, 5H), 6.90 (d, *J* = 8.0 Hz, 2H), 6.56 (d, *J* = 8.0 Hz, 2H), 6.54 – 6.50 (m, 2H), 6.33 (d, *J* = 2.0 Hz, 1H), 4.90 (s, 1H), 4.65 (s, 2H), 2.38 (s, 3H), 2.18 (s, 3H) ppm. **$^{13}$C NMR (100 MHz, $CDCl_3$)** δ 142.7, 140.7, 137.1, 136.1, 135.9, 135.0, 134.1, 132.2, 131.6, 129.5, 129.5, 129.3, 128.9, 128.7, 128.6, 128.5, 127.6,

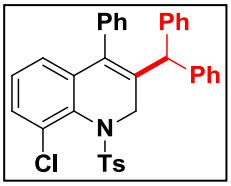
127.4, 127.3, 127.0, 125.9, 53.1, 46.0, 21.5, 21.3 ppm. **HRMS:** m/z calcd for $C_{36}H_{31}NO_2SNa$ $[M + Na]^+$, 564.1973; found, 564.1974.

**3-Benzhydryl-8-bromo-4-phenyl-1-tosyl-1,2-dihydroquinoline (3c):**



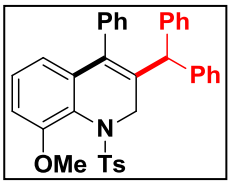

Eluted by petroleum ether/ethyl acetate (95:5 v/v), white solid (58 mg, 0.095 mmol, 88%) m.p. 192–194 °C. **$^1$H NMR (300 MHz, $CDCl_3$)** δ 7.56 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.44 (d, *J* = 6.9 Hz, 3H), 7.39 – 7.11 (m, 6H), 7.05 (dd, *J* = 8.9, 3.4 Hz, 3H), 6.99 (d, *J* = 7.5 Hz, 5H), 6.78 (d, *J* = 8.1 Hz, 2H), 6.54 (dd, *J* = 7.8, 1.3 Hz, 1H), 6.16 (s, 1H), 4.90 (s, 1H), 4.85 (d, *J* = 18.6 Hz, 1H), 4.20 (d, *J* = 18.6 Hz, 1H), 2.42 (s, 3H) ppm. **$^{13}$C NMR (75 MHz, $CDCl_3$)** δ 143.9, 143.4, 141.0, 140.5, 136.8, 136.7, 136.3, 135.3, 135.2, 132.9, 132.7, 132.4, 130.7, 129.7, 129.5, 129.4, 129.2, 128.7, 128.6, 128.57, 128.5, 128.48, 128.4, 128.3, 128.2, 127.8, 127.6, 127.4, 127.3, 126.6, 125.6, 123.1, 53.3, 47.0, 21.6 ppm. **HRMS:** m/z calcd for $C_{35}H_{28}BrNO_2SNa$ $[M + Na]^+$, 628.0922; found, 628.0922.

**3-Benzhydryl-8-chloro-4-phenyl-1-tosyl-1,2-dihydroquinoline (3d):**




Eluted by petroleum ether/ethyl acetate (95:5 v/v), white solid (48 mg, 0.085 mmol, 81%) m.p. 165–167 °C. **$^1$H NMR (400 MHz, $CDCl_3$)** δ 7.44 (d, *J* = 7.8 Hz, 3H), 7.38 (dd, *J* = 8.1, 1.4 Hz, 1H), 7.38 – 7.15 (m, 5H), 7.10 – 6.97 (m, 9H), 6.83 – 6.75 (m, 2H), 6.51 (dd, *J* = 7.8, 1.4 Hz, 1H), 6.18 (s, 1H), 4.92 (s, 1H), 4.86 (d, *J* = 18.6 Hz, 1H), 4.19 (d, *J* = 18.6 Hz, 1H), 2.42 (s, 3H) ppm. **$^{13}$C NMR (100 MHz, $CDCl_3$)** δ 143.4, 141.1, 140.5, 136.9, 136.5, 136.4, 135.4, 135.2, 133.2, 131.0, 130.8, 129.7, 129.5, 129.2, 128.8, 128.6, 128.5, 128.4, 128.3, 127.9, 127.8, 127.3, 126.7, 125.0, 53.3, 47.0, 21.6 ppm. **HRMS:** m/z calcd for $C_{35}H_{28}ClNO_2SNa$ $[M + Na]^+$, 584.1427, found 584.1426.

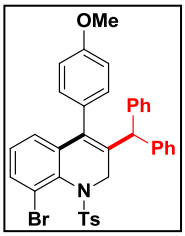
**3-Benzhydryl-8-methoxy-4-phenyl-1-tosyl-1,2-dihydroquinoline (3e):**




Eluted by petroleum ether/ethyl acetate (95:5 v/v), white solid (43 mg, 0.077 mmol, 74%) m.p. 185–188 °C. **$^1$H NMR (300 MHz, $CDCl_3$)** δ 7.27 – 7.36 (m, 9H), 7.11 – 6.96 (m, 7H), 6.95 – 6.83 (m, 3H), 6.65 (s, 2H), 6.22 (dd, *J* = 7.8, 1.3 Hz, 1H), 4.94 (s, 1H), 4.51 (s, 2H), 3.86 (s, 3H), 2.41 (s, 3H) ppm. **$^{13}$C NMR (75 MHz, $CDCl_3$)** δ 155.3,

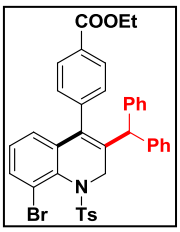
142.7, 140.9, 137.0, 136.7, 136.1, 135.5, 135.2, 129.6, 129.5, 129.0, 128.5, 128.5, 127.9, 127.6, 127.5, 126.9, 122.6, 119.1, 112.3, 56.3, 53.2, 46.9, 21.6 ppm. **HRMS:** m/z calcd for $C_{36}H_{31}NO_3SNa$ $[M + Na]^+$, 580.1922, found 580.1923.

**3-Benzhydryl-8-bromo-4-(4-methoxyphenyl)-1-tosyl-1,2-dihydroquinoline (3f):**



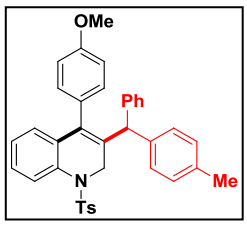

white solid (64 mg, 0.1 mmol, 92%) m.p 200–202 °C. **$^1$H NMR (400 MHz, $CDCl_3$)** δ 7.59 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.53 – 7.40 (m, 3H), 7.20 – 7.29 (m, 3H), 7.14 – 7.07 (m, 2H), 7.03 (dd, *J* = 8.1, 2.4 Hz, 5H), 6.85 (d, *J* = 8.0 Hz, 3H), 6.81 (d, *J* = 8.1 Hz, 2H), 6.62 (dd, *J* = 7.8, 1.4 Hz, 1H), 6.13 (s, 1H), 4.99 (s, 1H), 4.88 (d, *J* = 18.7 Hz, 1H), 4.22 (d, *J* = 18.6 Hz, 1H), 3.86 (s, 3H), 2.45 (s, 3H) ppm. **$^{13}$C NMR (125 MHz, $CDCl_3$)** δ 159.2, 143.4, 141.3, 140.7, 137.09, 137.1, 135.4, 134.9, 132.8, 132.5, 130.8, 130.7, 129.2, 128.8, 128.5, 128.4, 128.3, 127.3, 126.6, 125.7, 123.1, 113.9, 55.4, 53.4, 47.2, 21.6 ppm. **HRMS:** m/z calcd for $C_{36}H_{30}BrNO_3SNa$ $[M + Na]^+$, 658.1027; found, 658.1025.

**Ethyl 4-(3-benzhydryl-8-bromo-1-tosyl-1,2-dihydroquinolin-4-yl)benzoate (3g):**




white solid (43 mg, 0.06 mmol, 57%) m.p 194–196 °C. **$^1$H NMR (300 MHz, $CDCl_3$)** δ 7.97 (d, *J* = 7.9 Hz, 2H), 7.58 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.50 – 7.35 (m, 3H), 7.25 – 7.13 (m, 3H), 7.08 – 6.94 (m, 8H), 6.89 – 6.75 (m, 2H), 6.47 (dd, *J* = 7.8, 1.4 Hz, 1H), 6.30 (s, 1H), 4.83 (d, *J* = 18.6 Hz, 1H), 4.83 (s, 1H), 4.40 (q, *J* = 7.1 Hz, 2H), 4.20 (d, *J* = 18.7 Hz, 1H), 2.44 (s, 3H), 1.41 (t, *J* = 7.1 Hz, 3H) ppm. **$^{13}$C NMR (125 MHz, $CDCl_3$)** δ 166.4, 143.6, 141.3, 140.9, 140.3, 137.4, 136.1, 135.2, 134.4, 133.2, 132.5, 130.7, 130.1, 129.9, 129.7, 129.3, 128.9, 128.65, 128.58, 128.5, 128.3, 127.4, 126.8, 125.4, 123.3, 61.3, 53.5, 47.1, 21.7, 14.5 ppm. **HRMS:** m/z calcd for $C_{38}H_{32}BrNO_4SNa$ $[M + Na]^+$, 700.1133; found, 700.1133.

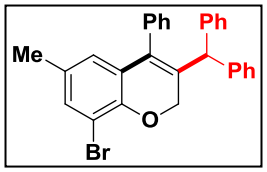
**8-Bromo-4-(4-methoxyphenyl)-3-(phenyl(p-tolyl)methyl)-1-tosyl-1,2-dihydroquinoline (3h):**



Eluted by petroleum ether/ethyl acetate (95:5 v/v), white solid (54 mg, 0.083 mmol, 93%) m.p 138–140 °C. **$^1$H NMR (500 MHz, $CDCl_3$)** δ 7.67 (d, *J* = 8.1 Hz, 1H), 7.34 (t, *J* = 7.3 Hz, 4H), 7.32 – 7.27 (m, 2H), 7.06 (dt, *J* = 8.4, 2.5 Hz, 5H), 6.89 (d, *J* = 8.0 Hz, 2H), 6.86 – 6.80 (m, 2H), 6.63 – 6.53 (m, 2H), 6.48 – 6.42 (m, 2H), 6.36 (d, *J* = 2.1 Hz, 1H), 4.96 (s, 1H), 4.63 (s, 2H), 3.83 (s, 3H), 2.37 (s, 3H), 2.19 (s, 3H). **$^{13}$C NMR (75 MHz, $CDCl_3$)** δ 158.9, 142.7, 140.8, 136.1, 134.7, 134.2, 132.5, 131.6, 130.6, 129.5, 129.1, 128.9, 128.7, 128.4, 127.4, 127.3, 126.9, 125.9, 114.0, 55.4, 53.1, 46.0, 21.6, 21.3. **HRMS:** m/z calcd for $C_{37}H_{33}NO_3SNa$ $[M + Na]^+$, 594.2079; found, 594.2076.

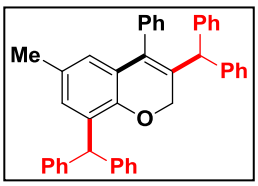
**2. Representative Experimental Procedure for the Synthesis and Characterization of 4a-4f:**

**3-Benzhydryl-8-bromo-6-methyl-4-phenyl-2*H*-chromene (4a):**




In an oven-dried round-bottom flask, 2-bromo-4-methyl-1-((3-phenylprop-2-yn-1-yl)oxy)benzene (45 mg, 0.15 mmol) and diphenylmethanol (**2a**) (27 mg, 0.15 mmol) were taken in dry nitromethane (2 mL) and $Fe(OTf)_3$ (7.5 mg, 0.015 mmol) was added to the mixture under an Ar atmosphere and stirred for 2 h at 80 °C. After the completion of the reaction (monitored by TLC), the crude reaction mixture was extracted with EtOAc (15 mL, twice) and the combined organic layer was washed with water (15 mL, two times), dried over anhydrous $Na_2SO_4$ and concentrated under reduced pressure. The product was purified by column chromatography on silica gel (100−200 mesh), eluted by petroleum ether to afford the desired product **4a** (53 mg, 0.11 mmol, 76%) as a white solid, m.p. 180–185 °C. **$^1$H NMR (500 MHz, $CDCl_3$)** δ 7.46 – 7.44 (m, 1H), 7.43 – 7.38 (m, 2H), 7.36 (d, *J* = 7.4 Hz, 1H), 7.33 (d, *J* = 1.4 Hz, 1H), 7.33 – 7.30 (m, 2H), 7.29 (s, 1H), 7.27 (d, *J* = 5.1 Hz, 1H), 7.25 – 7.21 (m, 2H), 7.18 (d, *J* = 2.0 Hz, 1H), 7.17 – 7.14 (m, 4H), 6.42 (d, *J* = 2.0 Hz, 1H), 5.10 (s, 1H), 4.76 (s, 2H), 2.14 (s, 3H). **$^{13}$C NMR (100 MHz, $CDCl_3$)** δ 148.2, 142.4, 141.3, 136.6, 133.6, 132.97, 132.5, 132.2, 132.0, 131.8, 129.9, 129.8, 129.2, 129.1, 129.06, 129.0, 128.9, 128.7, 128.6, 128.5, 128.4, 128.3, 127.9, 127.6, 127.4, 126.8, 126.7, 126.3, 109.5, 67.1, 51.9, 20.6 ppm. Anal. calcd. for $C_{29}H_{23}BrO$: C, 74.52; H, 4.96; found: C, 74.81; H, 5.23 %.

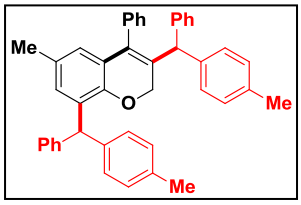
**3,8-Dibenzhydryl-6-methyl-4-phenyl-2*H*-chromene (4b):**




In an oven-dried round-bottom flask, 1-methyl-4-((3-phenylprop-2-yn-1-yl)oxy)benzene (33 mg, 0.15 mmol) and diphenylmethanol (**2a**) (55 mg, 0.3 mmol) were taken in dry nitromethane (2 mL) and to it $Fe(OTf)_3$ (7.5 mg, 0.015 mmol) was added to the mixture under an Ar atmosphere and stirred for 3 h at 80 °C. After the completion of the reaction (monitored by TLC), the crude reaction mixture was extracted with EtOAc (15 mL, twice) and the

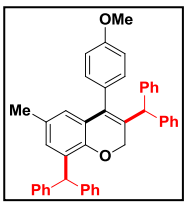
combined organic extract was washed with water (15 mL, two times), dried over anhydrous $Na_2SO_4$ and concentrated under reduced pressure. The product was purified by column chromatography on silica gel (100−200 mesh), eluted by petroleum ether to afford the desired product **4b** (65 mg, 0.11 mmol, 79%) as a white solid, m.p. 165–169 °C. **$^1$H NMR (500 MHz, $CDCl_3$)** δ 7.47 – 7.39 (m, 3H), 7.36 – 7.28 (m, 9H), 7.28 – 7.20 (m, 4H), 7.20 – 7.12 (m, 9H), 6.59 (d, *J* = 2.4 Hz, 1H), 6.41 (d, *J* = 2.2 Hz, 1H), 5.92 (s, 1H), 5.09 (s, 1H), 4.48 (d, *J* = 1.4 Hz, 2H), 2.07 (s, 3H). **$^{13}$C NMR (100 MHz, $CDCl_3$)** δ 149.0, 144.1, 141.72, 141.7, 137.3, 134.3, 131.3, 131.0, 130.6, 130.3, 129.9, 129.8, 129.7, 129.6, 129.3, 129.1, 129.0, 128.75, 128.7, 128.6, 128.5, 128.2, 127.7, 127.6, 126.9, 126.7, 126.6, 126.1, 125.4, 125.3, 66.3, 52.0, 49.5, 21.1 ppm. **HRMS:** m/z calcd for $C_{42}H_{34}ONa$ $[M + Na]^+$, 577.2507; found, 577.2509.

**6-Methyl-4-phenyl-3,8-bis(phenyl(p-tolyl)methyl)-2*H*-chromene (4c):**




In an oven-dried round-bottom flask, 1-methyl-4-((3-phenylprop-2-yn-1-yl)oxy)benzene (33 mg, 0.15 mmol) and phenyl(p-tolyl)methanol (**2b**) (59 mg, 0.3 mmol) were taken in dry nitromethane (2 mL) and $Fe(OTf)_3$ (7.5 mg, 0.015 mmol) was added to the mixture under an Ar atmosphere and stirred for 3 h at 80 °C. After the completion of the reaction (monitored by TLC), the crude reaction mixture was extracted with EtOAc (15 mL, twice) and the combined organic extract was washed with water (15 mL, two times), dried over anhydrous $Na_2SO_4$ and concentrated under reduced pressure. The product was purified by column chromatography on silica gel (100−200 mesh), eluted by petroleum ether to afford the desired product **4c** (72 mg, 0.12 mmol, 84%) as a white solid, m.p. 150–155 °C. **$^1$H NMR (300 MHz, $CDCl_3$)** δ 7.36 – 7.44 (m, 3H), 7.33 – 7.14 (m, 7H), 7.16 – 7.05 (m, 9H), 6.99 (dd, *J* = 9.1, 7.0 Hz, 4H), 6.54 (d, *J* = 2.1 Hz, 1H), 6.34 (d, *J* = 2.1 Hz, 1H), 5.83 (s, 1H), 5.00 (s, 1H), 4.44 (d, *J* = 1.2 Hz, 2H), 2.32 (s, 6H), 2.03 (s, 3H) ppm. **$^{13}$C NMR (100 MHz, $CDCl_3$)** 149.0, 144.4, 141.9, 141.1, 138.6, 137.4, 136.2, 135.6, 134.1, 131.5, 131.1, 130.3, 129.9, 129.7, 129.5, 129.4, 129.3, 129.2, 129.1, 128.9, 128.7, 128.6, 128.5, 128.2, 127.5, 126.5, 126.0, 125.4, 125.2, 66.3, 51.6, 48.9, 21.2, 21.14, 21.10 ppm. **HRMS:** m/z calcd for $C_{44}H_{38}ONa$ $[M + Na]^+$, 605.2820; found, 605.2820.

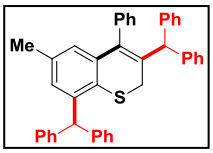
**3,8-Dibenzhydryl-4-(4-methoxyphenyl)-6-methyl-2*H*-chromene (4d):**




In an oven-dried round-bottom flask 1-methoxy-4-(3-(p-tolyloxy)prop-1-yn-1-yl)benzene (38 mg, 0.15 mmol) and diphenylmethanol (**2b**) (56 mg, 0.3 mmol) were taken in dry nitromethane (2 mL) and $Fe(OTf)_3$ (7.5 mg, 0.015

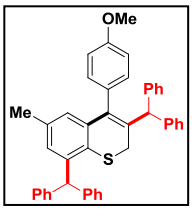
mmol) was added to the mixture under an Ar atmosphere and stirred for 2 h at 80 °C. After the completion of the reaction (monitored by TLC), the crude reaction mixture was extracted with EtOAc (15 mL, twice) and the combined organic layer was washed with water (15 mL, two times), dried over anhydrous $Na_2SO_4$ and concentrated under reduced pressure. The product was purified by column chromatography on silica gel (100−200 mesh), eluted by petroleum ether/ethyl acetate (99:1 v/v), to afford the desired product **4d** (66 mg, 0.11 mmol, 74%) as a yellow gummy liquid. **$^1$H NMR (400 MHz, $CDCl_3$)** δ 7.29 – 7.27 (m, 3H), 7.24 (s, 3H), 7.22 (d, *J* = 1.6 Hz, 1H), 7.20 (s, 2H), 7.19 (s, 2H), 7.14 – 7.13 (m, 3H), 7.13 – 7.10 (m, 6H), 7.09 (s, 2H), 6.94 (d, *J* = 8.8 Hz, 2H), 6.53(d, *J* = 2.0 Hz, 1H), 6.39 (d, *J* = 1.6 Hz, 1H) 5.86 (s, 1H), 5.09 (s, 1H), 4.43 (s, 2H), 3.85 (s, 3H), 2.04 (s, 3H) ppm. **$^{13}$C NMR (75 MHz, $CDCl_3$)** 158.9, 148.9, 143.9, 141.7, 133.7, 131.3, 130.8, 130.7, 129.7, 129.4, 129.2, 128.9, 128.5, 128.4, 128.3, 128.1, 126.5, 126.0, 125.6, 125.2, 113.9, 66.1, 55.2, 51.9, 49.3, 20.99 ppm. **HRMS:** m/z calcd for $C_{43}H_{36}O_2Na$ $[M + Na]^+$, 607.2613; found, 607.2609

**3,8-Dibenzhydryl-6-methyl-4-phenyl-2*H*-thiochromene (4e):**




In an oven-dried round-bottom flask, (3-phenylprop-2-yn-1-yl)(p-tolyl)sulfane (35 mg, 0.15 mmol) and diphenylmethanol (**2a**) (55 mg, 0.30 mmol) were taken in dry nitromethane (2 mL) and to $Fe(OTf)_3$ (7.5 mg, 0.015 mmol) was added to the mixture under an Ar atmosphere and stirred for 3 h at 80 °C. After the completion of the reaction (monitored by TLC), the crude reaction mixture was extracted with EtOAc (15 mL, twice) and the combined organic layer was washed with water (15 mL, two times), dried over anhydrous $Na_2SO_4$ and concentrated under reduced pressure. The product was purified by column chromatography on silica gel (100−200 mesh), eluted by petroleum ether to afford the desired product **4d** (60 mg, 0.1 mmol, 72%) as a light yellow semisolid. **$^1$H NMR (400 MHz, $CDCl_3$)** δ 7.29 (s, 2H), 7.28 (d, *J* = 1.2 Hz, 4H), 7.24 (d, *J* = 7.6 Hz, 3H), 7.19 – 7.22 (m, 2H), 7.16 – 7.18 (m, 6H), 7.13 (s, 1H), 7.11 (s, 2H), 7.09 (d, *J* = 1.6 Hz, 1H), 7.08 (d, *J* = 2.8 Hz, 3H), 6.99 (d, *J* = 8 Hz, 2H), 6.94 (dd, *J* = 7.6, 1.2 Hz, 1H), 6.03 (s, 1H), 5.52 (s, 1H), 3.42 (s, 2H), 2.28 (s, 3H) ppm. **$^{13}$C NMR (100 MHz, $CDCl_3$)** δ 155.7, 144.3, 143.2, 142.7, 142.5, 141.2, 135.7, 131.9, 130.6, 129.9, 129.8, 129.6, 129.4, 129.2, 129.1, 129.08, 128.7, 128.6, 128.5, 128.4, 128.1, 126.6, 126.4, 124.8, 120.7, 57.0, 50.9, 39.7, 21.1 ppm. **HRMS:** m/z calcd for $C_{42}H_{35}S$ $[M + H]^+$, 571.2459; found, 571.2460.

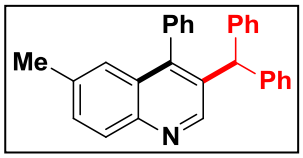
**3,8-Dibenzhydryl-4-(4-methoxyphenyl)-6-methyl-2*H*-thiochromene (4f):**



In an oven-dried round-bottom flask, (3-(4-methoxyphenyl)prop-2-yn-1-yl)(p-tolyl)sulfane (27 mg, 0.10 mmol) and diphenylmethanol (**2a**) (37 mg, 0.20 mmol) were taken in dry nitromethane (2 mL) and $Fe(OTf)_3$ (7.5 mg, 0.015 mmol) was added to the mixture under an Ar atmosphere and stirred for 2 h at 80 °C. After the completion of the reaction (monitored by TLC), the crude reaction mixture was extracted with EtOAc (15 mL, twice) and the combined organic layer was washed with water (15 mL, two times), dried over anhydrous $Na_2SO_4$ and concentrated under reduced pressure. The product was purified by column chromatography on silica gel (100−200 mesh), eluted by petroleum ether/ethyl acetate (98:2 v/v), to afford the desired product **4f** (46 mg, 0.07 mmol, 76%) as a white solid, m.p. 166–168 °C. **$^1$H NMR (300 MHz, $CDCl_3$)** δ 7.29 – 7.34 (m, 3H), 7.23 – 7.27 (m, 4H), 7.21 (s, 2H), 7.16 – 7.18 (m, 6H), 7.02 (d, *J* = 8.7 Hz, 2H), 6.96 (s, 2H), 6.90 (d, *J* = 7.8 Hz, 6H), 6.62 (s, 1H), 6.01 (s, 1H), 5.82 (s, 1H), 3.67 (s, 3H), 3.43 (s, 2H), 2.30 (s, 3H) ppm. **$^{13}$C NMR (75 MHz, $CDCl_3$)** δ 155.4, 151.3, 143.8, 143.3, 141.8, 136.2, 135.8, 131.1, 130.9, 129.8, 129.7, 129.6,129.3, 129.0, 128.5, 128.4, 127.9, 126.4, 125.8, 123.0, 107.2, 56.0, 50.7, 49.4, 39.5, 21.1 ppm. **HRMS:** m/z calcd for $C_{43}H_{36}OSNa$ $[M + Na]^+$, 623.2385; found, 623.2383.

**3. Representative Experimental Procedure for the Synthesis and Characterization of 5a-5f:**

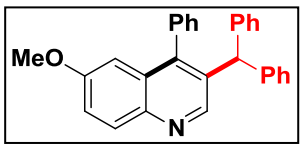
**3-Benzhydryl-6-methyl-4-phenylquinoline (5a):**




In an oven-dried round-bottom flask, 4-methyl-*N*-(3-phenylprop-2-yn-1-yl)-*N*-(p-tolyl)benzenesulfonamide (**1b**) (56 mg, 0.15 mmol) and diphenylmethanol (**2a**) (27 mg, 0.15 mmol) were taken in dry DCE (2 mL) and anhydrous $FeCl_3$ (48 mg, 0.3 mmol) was added to the mixture under an Ar atmosphere and stirred for 2 h at 80 °C. After the completion of the reaction (monitored by TLC), the crude reaction mixture was extracted with EtOAc (15 mL, twice) and the combined organic layer was washed with water (15 mL, two times), dried over anhydrous $Na_2SO_4$ and concentrated under reduced pressure. The product was purified by column chromatography on silica gel (100−200 mesh), eluted by petroleum ether/ethyl acetate (95:5 v/v), to afford the desired product **5a** (48 mg, 0.12 mmol, 87%) as a light yellow solid, m.p. 130–135 °C. **$^1$H NMR (300 MHz, $CDCl_3$)** δ 8.70 (s, 1H), 8.09 (d, *J* = 8.4 Hz, 1H), 7.43 – 7.54 (m, 4H), 7.25 – 7.28 (m, 6H), 7.10 – 7.23 (m, 3H), 6.99 (d, *J* = 6.9 Hz, 4H), 5.47 (s, 1H), 2.40 (s, 3H) ppm. **$^{13}$C NMR (75 MHz, $CDCl_3$)** δ 151.1, 143.1, 136.9, 136.4, 134.2, 131.5, 129.5, 129.4, 128.8, 128.6, 128.2, 127.9, 126.6, 125.5, 51.8, 21.9 ppm. **HRMS:** m/z calcd for $C_{29}H_{24}N$ $[M + H]^+$, 386.1909; found, 386.1890.

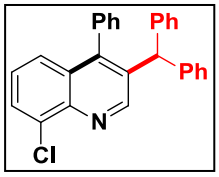
The above procedure was followed for all the reactions listed in Table 3. These compounds are not reported earlier and were characterized properly by their spectroscopic data ($^1$H NMR, $^{13}$C NMR, HRMS and elemental analysis).

**3-Benzhydryl-6-methoxy-4-phenylquinoline (5b):**



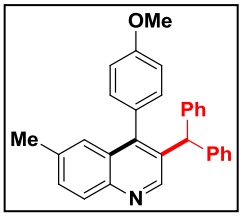

Eluted by petroleum ether/ethyl acetate (95:5 v/v), yellow gummy liquid (34 mg, 0.08 mmol, 89%). **$^1$H NMR (300 MHz, $CDCl_3$)** δ 8.59 (s, 1H),7.53 – 7.49 (m, 4H), 7.31 – 7.26 (m, 5H), 7.23 (d, J = 2.1 Hz, 1H), 7.12 (dd, *J* = 7.6, 1.8 Hz, 2H), 6.96 – 6.94 (m, 5H), 6.71 (d, J = 2.4 Hz, 1H), 5.54 (s, 1H), 3.72 (s, 3H) ppm. **$^{13}$C NMR (75 MHz, $CDCl_3$)** δ 160.4, 154.9, 140.5, 136.9, 133.7, 130.8, 129.7, 129.1, 129.0, 128.4, 128.2, 127.6, 126.6, 104.8, 55.8, 51.8 ppm. **HRMS:** m/z calcd for $C_{29}H_{24}NO$ $[M + H]^+$, 402.1858; found, 402.1853.

**3-Benzhydryl-8-chloro-4-phenylquinoline (5c):**



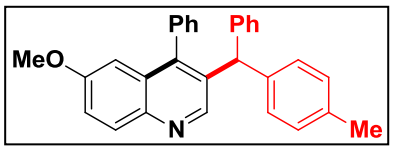

Eluted by petroleum ether/ethyl acetate (95:5 v/v), yellow gummy liquid (25 mg, 0.06 mmol, 63%). **$^1$H NMR (300 MHz, $CDCl_3$)** δ 8.96 (s, 1H), 7.82 (dd, *J* = 5.7, 3.0 Hz, 1H), 7.54 – 7.51 (m, 3H), 7.49 – 7.44 (m, 2H), 7.38 – 7.34 (m, 3H), 7.31 – 7.24 (m, 2H), 7.22 – 7.19 (m, 1H), 7.15 – 7.12 (m, 2H), 7.06 – 7.01 (m, 4H), 5.51 (s, 1H) ppm. **$^{13}$C NMR (75 MHz, $CDCl_3$)** δ 152.4, 148.5, 142.4, 141.7, 135.5, 135.4, 132.8, 129.6, 129.4, 129.3, 129.2, 128.6, 126.9, 126.8, 125.9, 51.7 ppm. Anal. calcd. for $C_{28}H_{20}ClN$: C, 82.85; H, 4.97; N, 3.45; found: C, 82.99; H, 5.15; N, 3.51%.

**3-Benzhydryl-4-(4-methoxyphenyl)-6-methylquinoline (5d):**



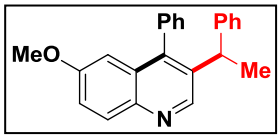

Eluted by petroleum ether/ethyl acetate (95:5 v/v), yellow solid (36 mg, 0.09 mmol, 92%), m.p. 145–147 °C. **$^1$H NMR (500 MHz, $CDCl_3$)** δ 8.72 (s, 1H), 8.02 (d, *J* = 8.5 Hz, 1H), 7.52 (dd, *J* = 8.5, 1.9 Hz, 1H), 7.28 (d, *J* = 7.5 Hz, 3H), 7.25 – 7.20 (m, 3H), 7.09 – 7.00 (m, 9H), 5.55 (s, 1H), 3.93 (s, 3H), 2.43 (s, 3H) ppm. **$^{13}$C NMR (100 MHz, $CDCl_3$)** δ 159.5, 151.3, 143.3, 136.8, 134.5, 131.4, 130.7, 129.4, 128.9, 128.7, 128.5, 128.4, 128.3, 126.6, 125.6, 114.0, 55.5, 51.8, 21.9 ppm. Anal. calcd. for $C_{30}H_{25}NO$: C, 86.71; H, 6.06; N, 3.37; found: C, 86.80; H, 5.50; N, 3.52%.

**6-Methoxy-4-phenyl-3-(phenyl(p-tolyl)methyl)quinoline (5e):**



Eluted by petroleum ether/ethyl acetate (95:5 v/v), light yellow gummy liquid (35 mg, 0.08, 93%). **$^1$H NMR (300 MHz, $CDCl_3$)** δ 8.58 (s, 1H),7.54 – 7.49 (m, 5H), 7.31 – 7.26 (m, 2H), 7.14 (d, *J* = 6.9 Hz, 2H) 7.09 (d, *J* = 7.8 Hz, 3H), 6.94 – 6.92 (m, 2H), 6.83 (d, *J* = 8.1 Hz, 2H), 6.71 (d, *J* = 2.4 Hz, 1H), 5.49 (s, 1H), 3.72 (s, 3H), 2.34 (s, 3H) ppm. **$^{13}$C NMR (75 MHz, $CDCl_3$)** δ 158.9, 142.3 138.9, 138.5, 136.7, 135.6, 135.2, 129.9, 129.8, 129.7, 129.4, 129.2, 129.1, 129.0, 128.8, 128.7, 128.6, 128.5, 127.8, 127.5, 126.9, 104.8, 55.5, 51.4, 21.0 ppm. **HRMS:** m/z calcd for $C_{30}H_{26}NO$ $[M + H]^+$, 416.2014; found, 416.2009.

**6-Methoxy-4-phenyl-3-(1-phenylethyl)quinoline (5f):**

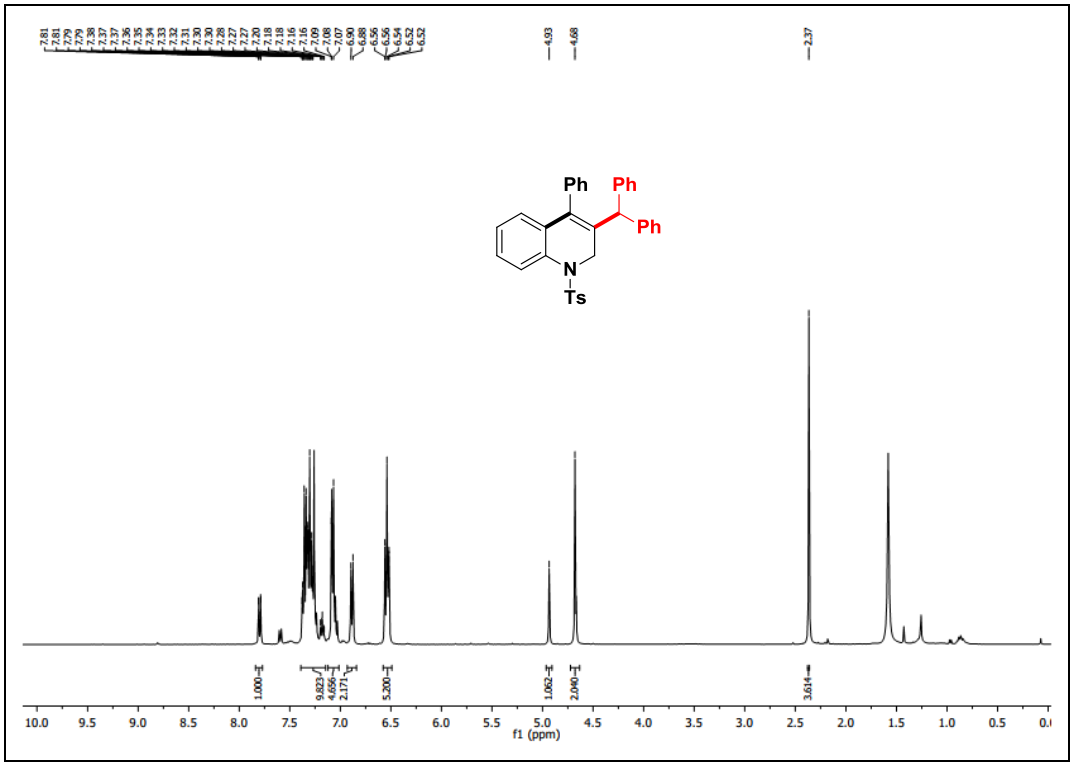



Eluted by petroleum ether/ethyl acetate (95:5 v/v), yellow solid (31 mg, 0.09 mmol,79%), m.p. 98 °C. **$^1$H NMR (500 MHz, $CDCl_3$)** δ 8.70 (s, 1H), 8.09 (d, *J* = 9.2 Hz, 1H), 7.60 – 7.54 (m, 1H), 7.52 – 7.46 (m, 2H), 7.36 – 7.31 (m, 2H), 7.25 – 7.21 (m, 2H), 7.20 – 7.14 (m, 2H), 7.12 – 7.07 (m, 2H), 6.62 (d, *J* = 2.7 Hz, 1H), 4.18 (q, *J* = 7.3 Hz, 1H), 3.68 (s, 3H), 1.64 (d, *J* = 7.2 Hz, 3H). **$^{13}$C NMR (125 MHz, $CDCl_3$)** δ 144.7, 137.2, 136.4, 129.5, 129.2, 128.9, 128.8, 128.6, 128.4, 127.6, 126.5, 126.4, 121.8, 104.9, 55.5, 39.5, 21.7 ppm. **HRMS:** m/z calcd for $C_{24}H_{22}NO$ $[M + H]^+$, 340.1701; found, 340.1703.

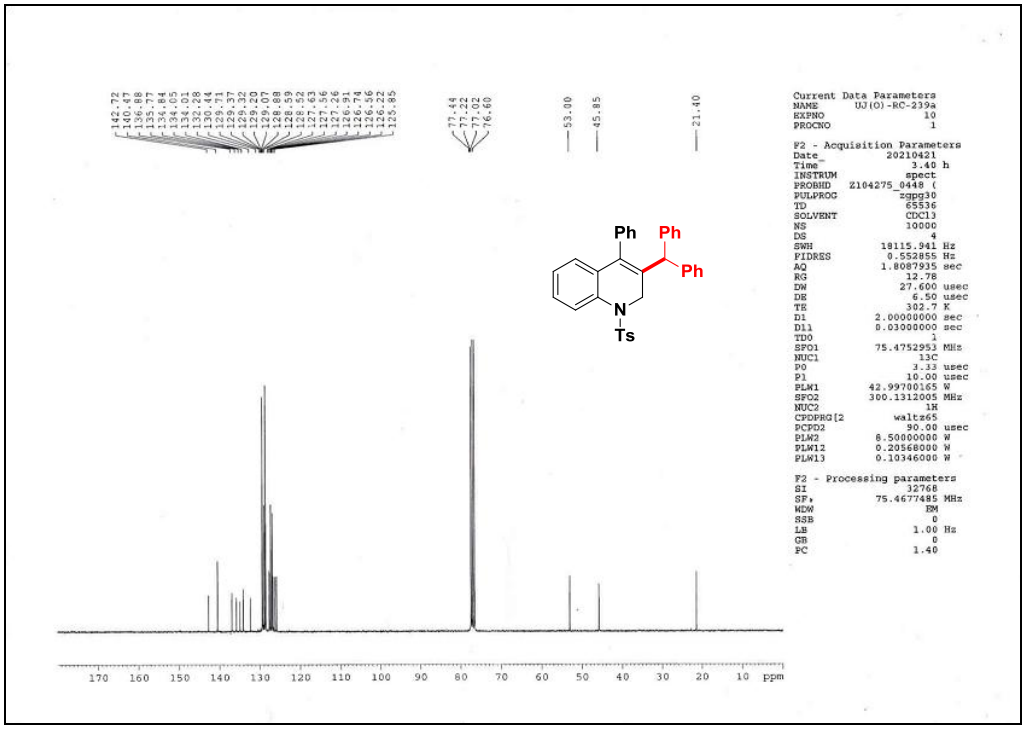
## REFERENCE:

1 (a) P. Kartick, B. Krishnendu, J. Swapnadeep, S. Soumen and J. Umasish, *Org. Lett.*, 2014, **16**, 2166; (b) P. Kartick, J. Swapnadeep, K. Sandip and J. Umasish, *J. Org. Chem.*, 2016, **81**, 1164.

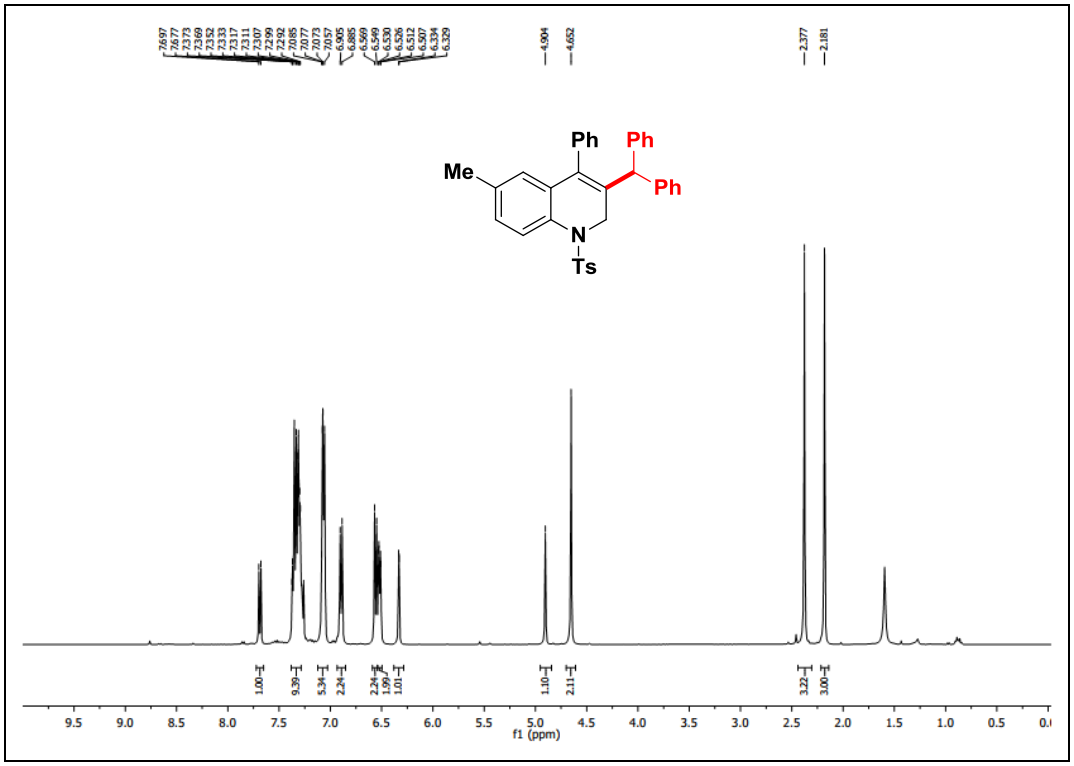
$^{1}$H NMR spectrum of compound **3a**, $CDCl_3$, 400 MHz



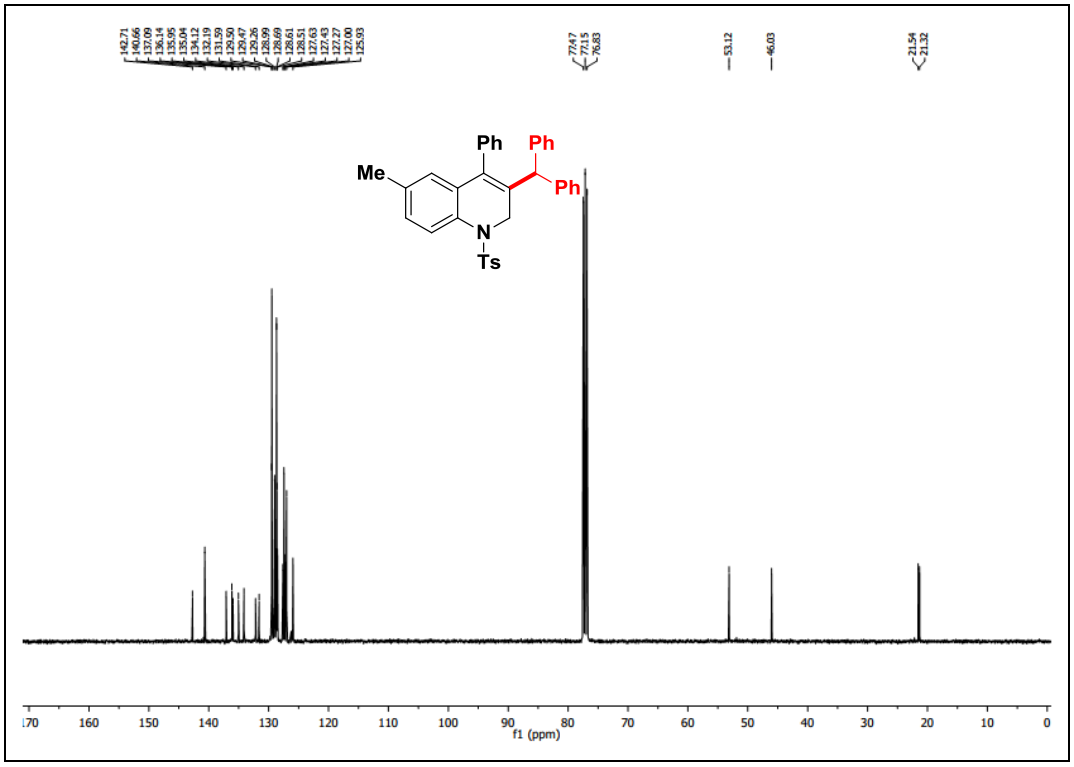

$^{13}$C NMR spectrum of compound **3a**, $CDCl_3$, 75 MHz



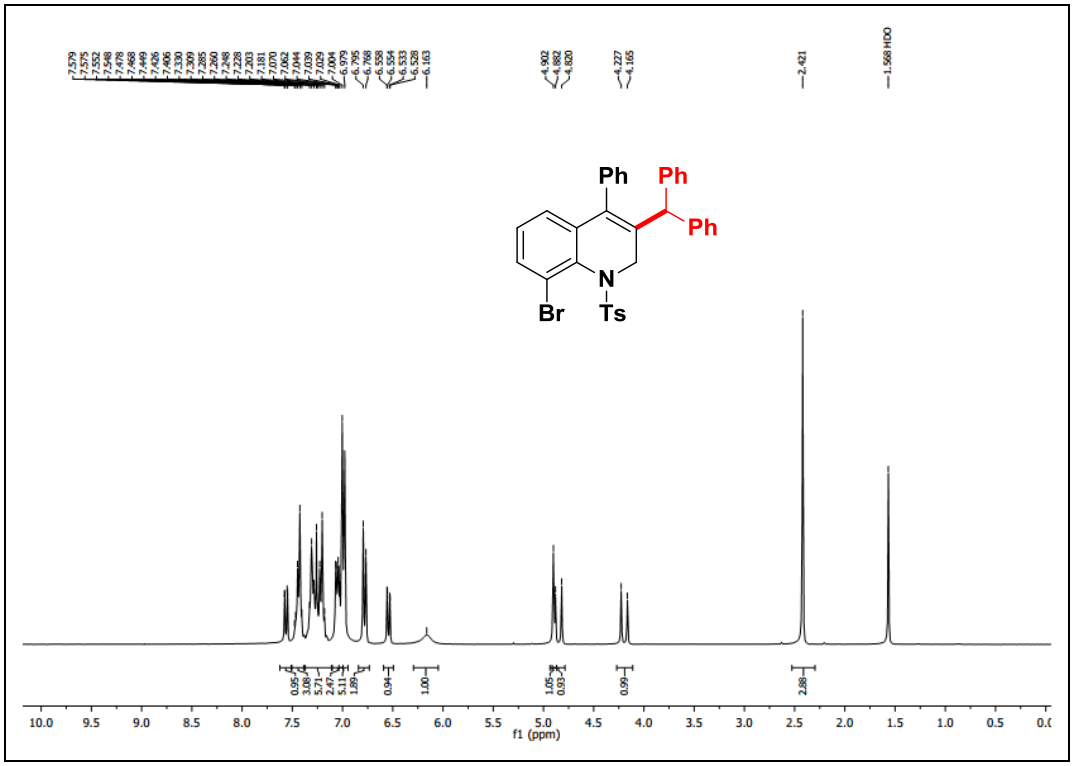
$^{1}$H NMR spectrum of compound **3b**, $CDCl_3$, 400 MHz



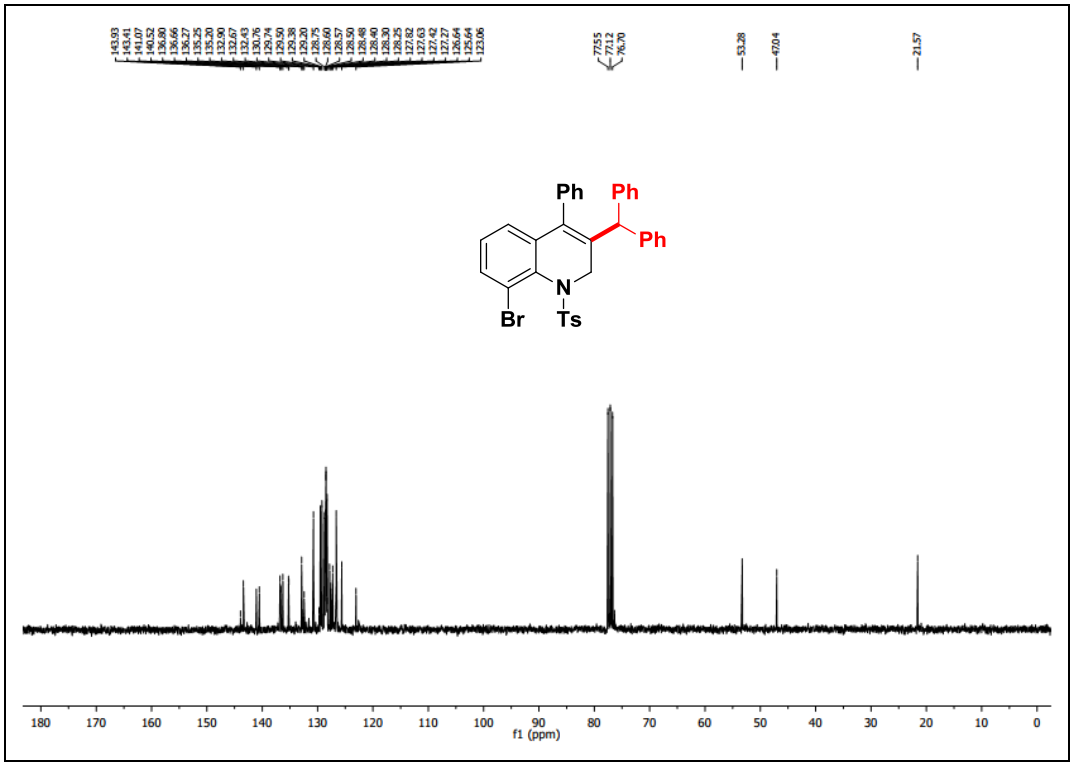

$^{13}$C NMR spectrum of compound **3b**, $CDCl_3$, 100 MHz



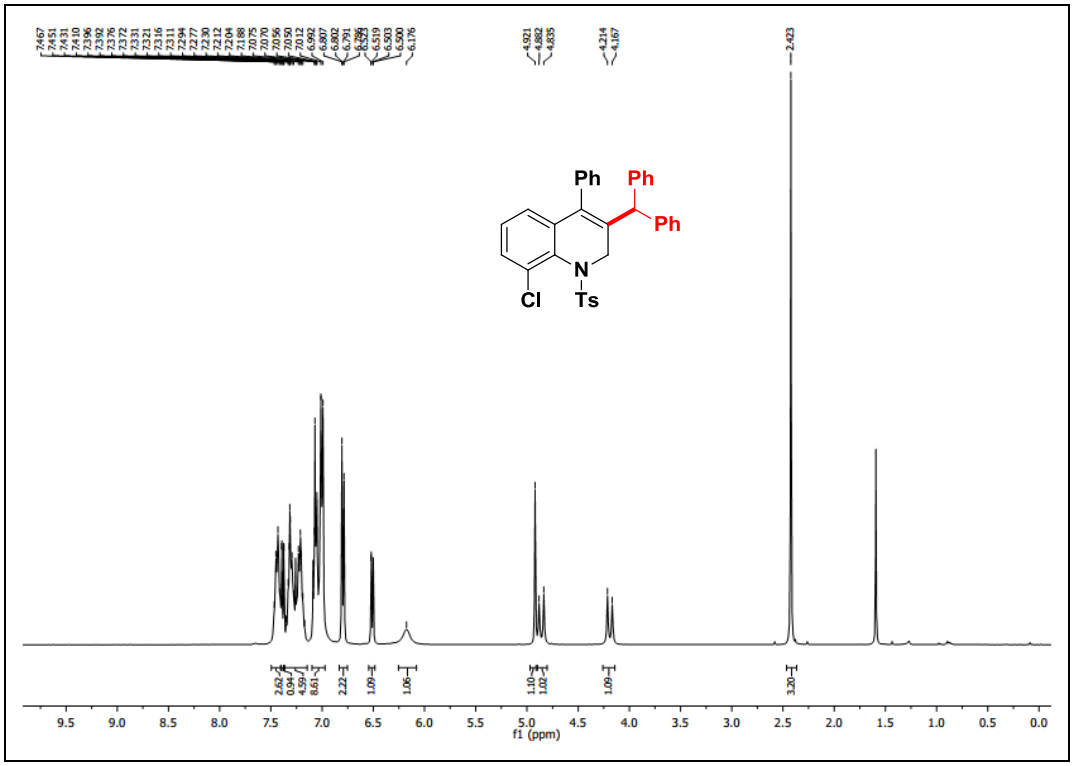
$^{1}$H NMR spectrum of compound **3c**, $CDCl_3$, 300 MHz



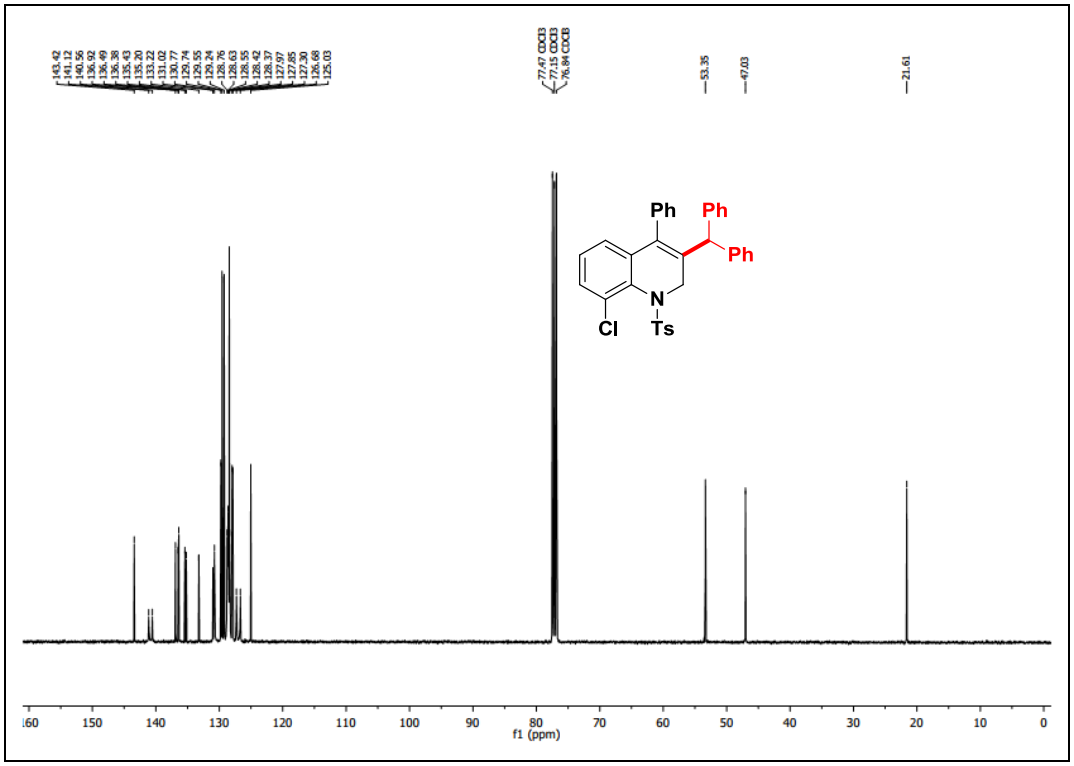

$^{13}$C NMR spectrum of compound **3c**, $CDCl_3$, 75 MHz



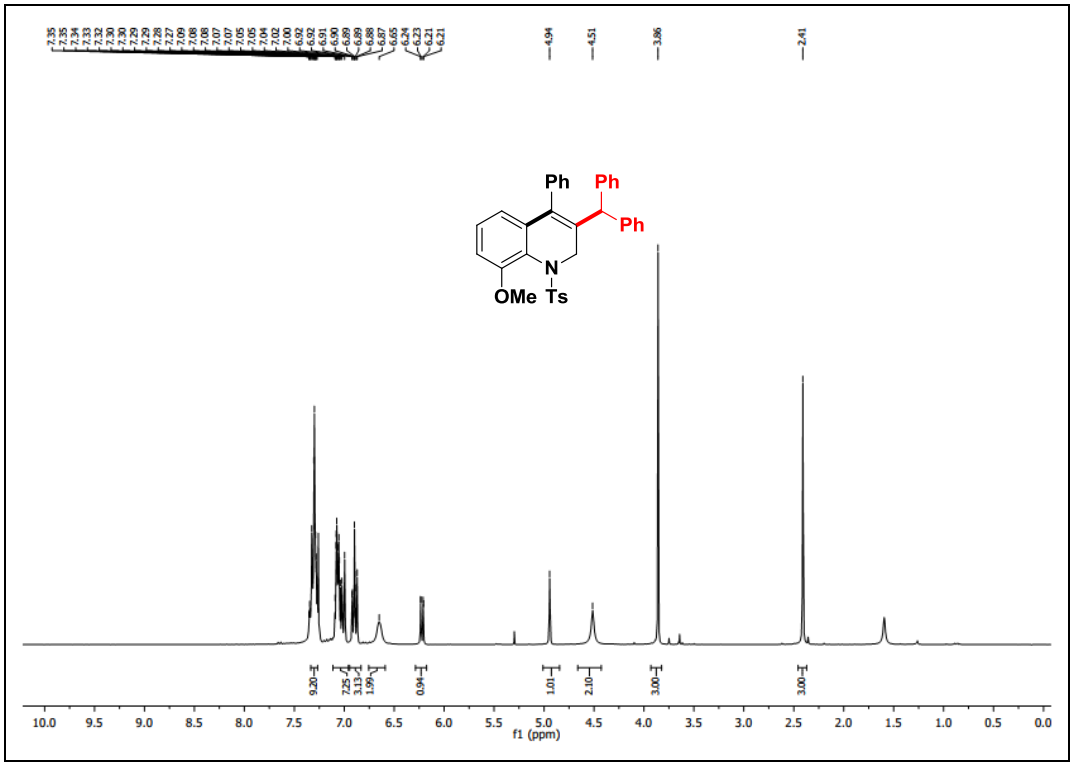
$^{1}$H NMR spectrum of compound **3d**, $CDCl_3$, 400 MHz



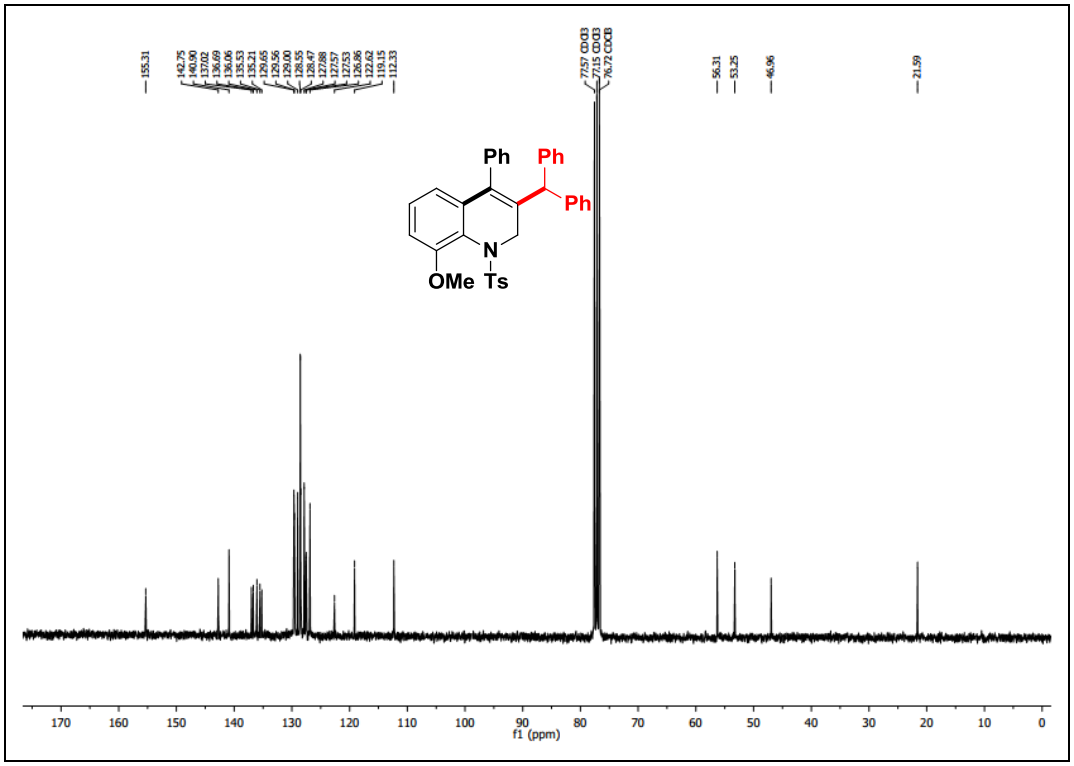

$^{13}$C NMR spectrum of compound **3d**, $CDCl_3$, 100 MHz



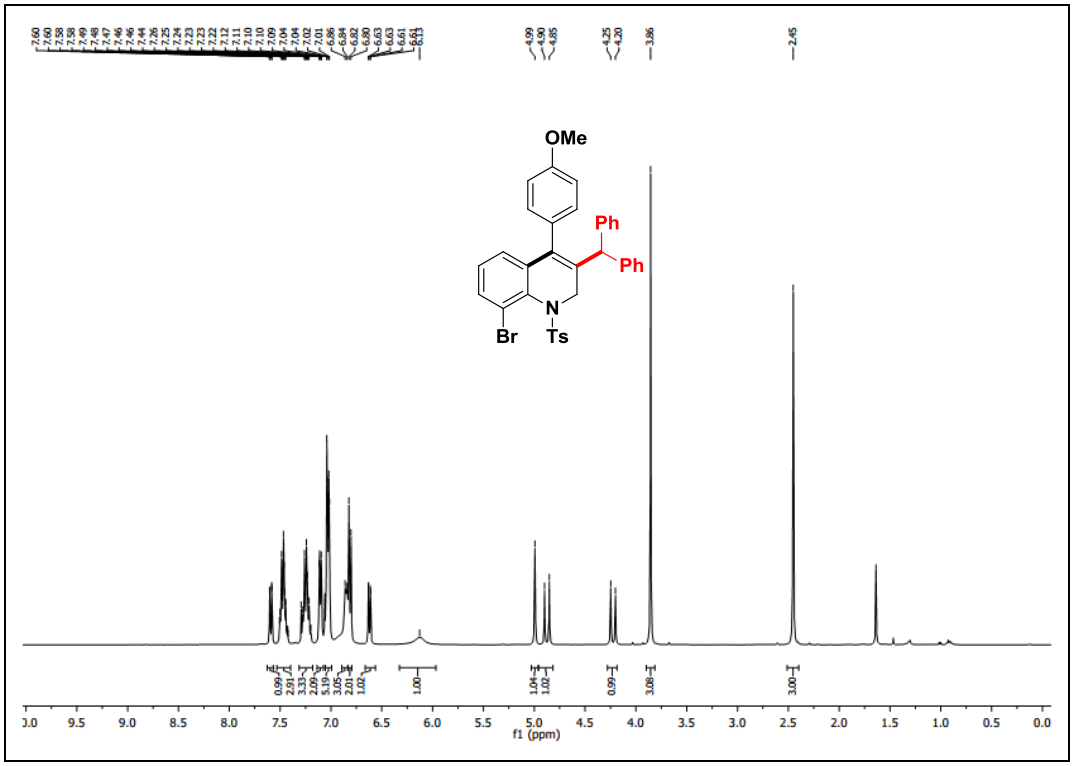
$^{1}$H NMR spectrum of compound **3e**, $CDCl_3$, 300 MHz



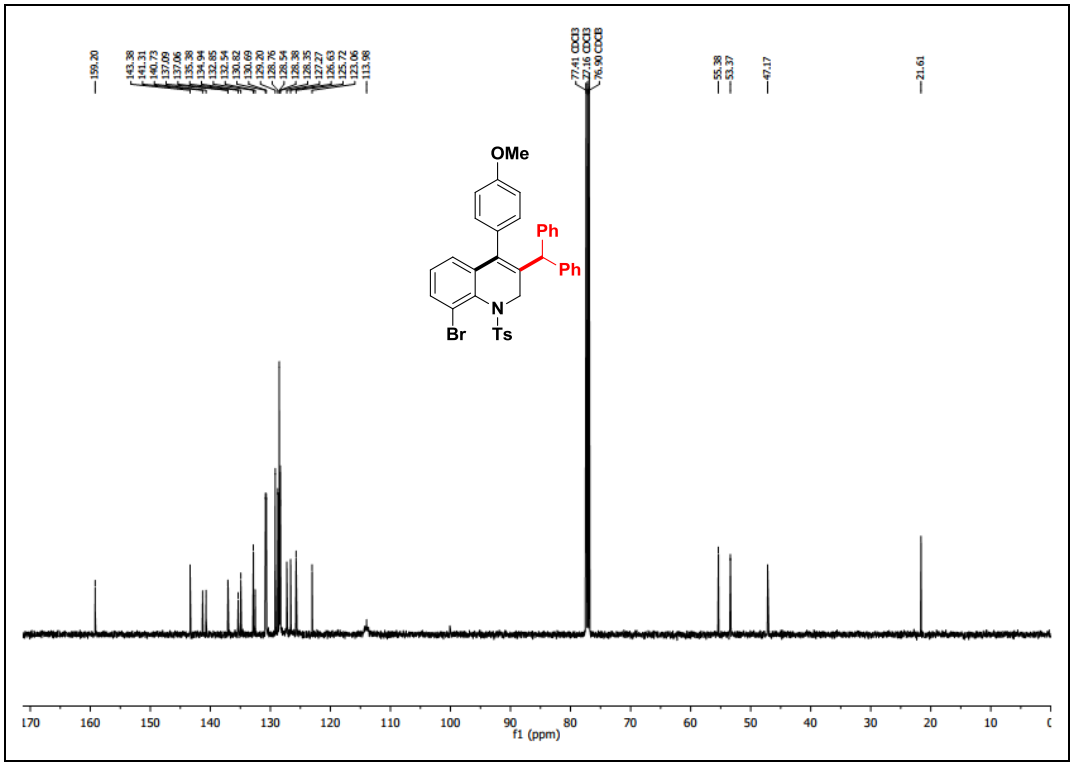

$^{13}$C NMR spectrum of compound **3e**, $CDCl_3$, 75 MHz



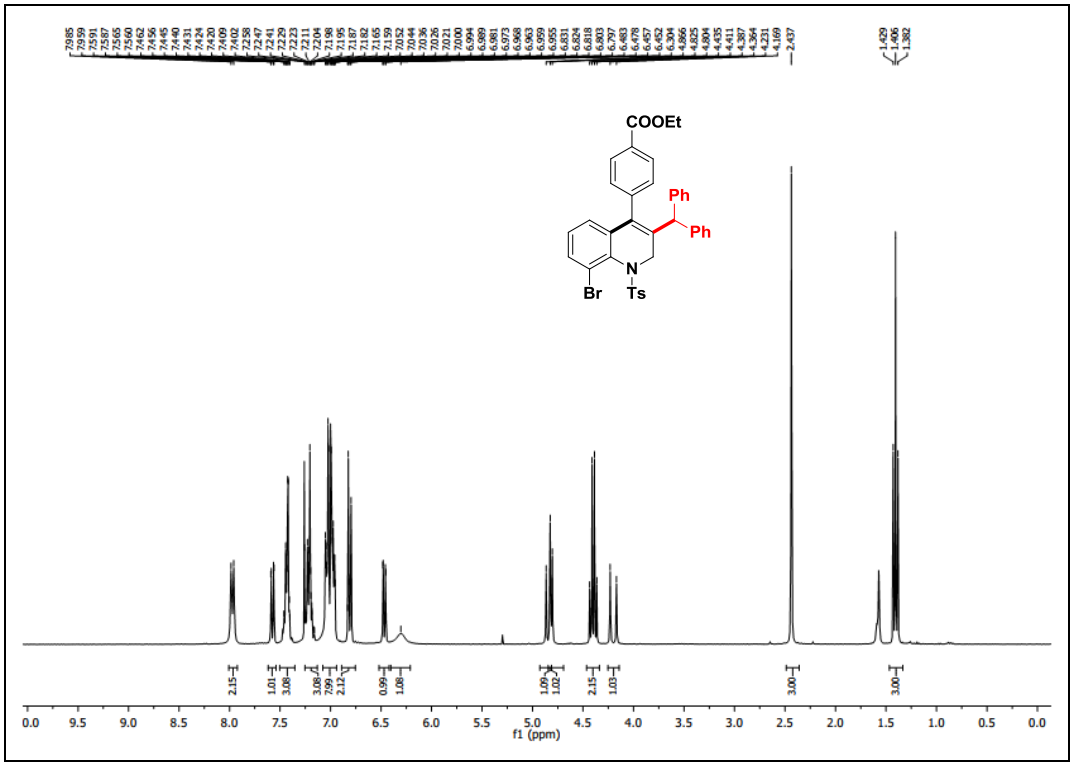
$^{1}$H NMR spectrum of compound **3f**, $CDCl_3$, 400 MHz



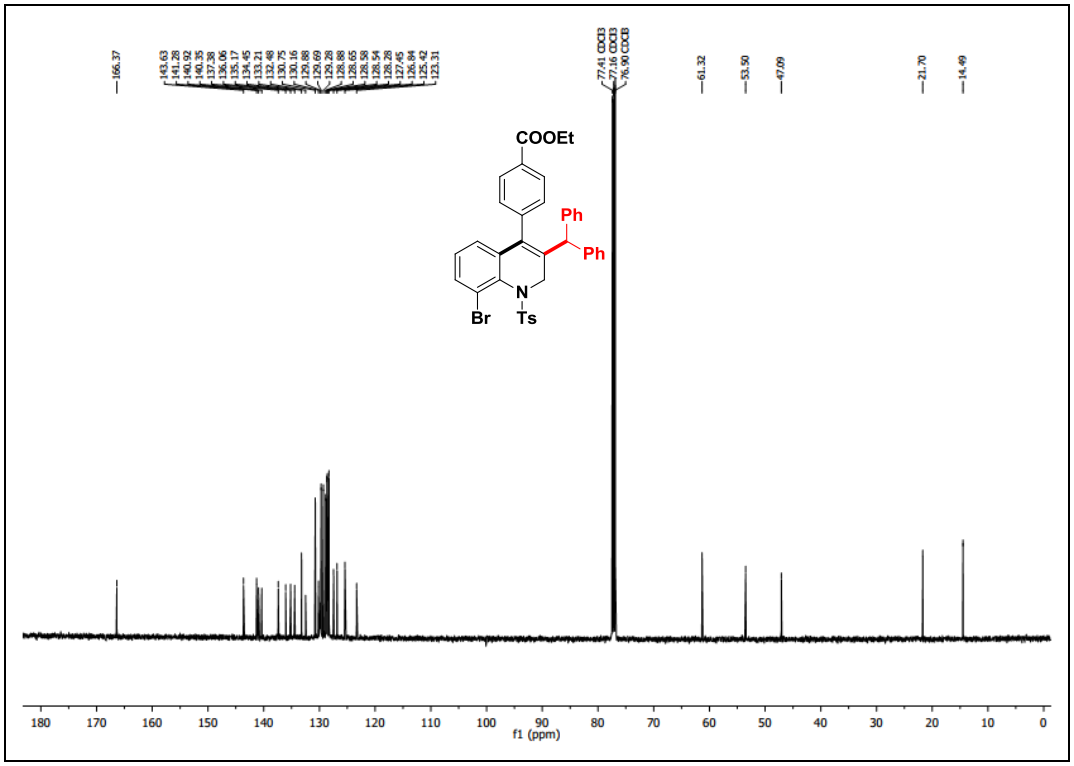

$^{13}$C NMR spectrum of compound **3f**, $CDCl_3$, 125 MHz



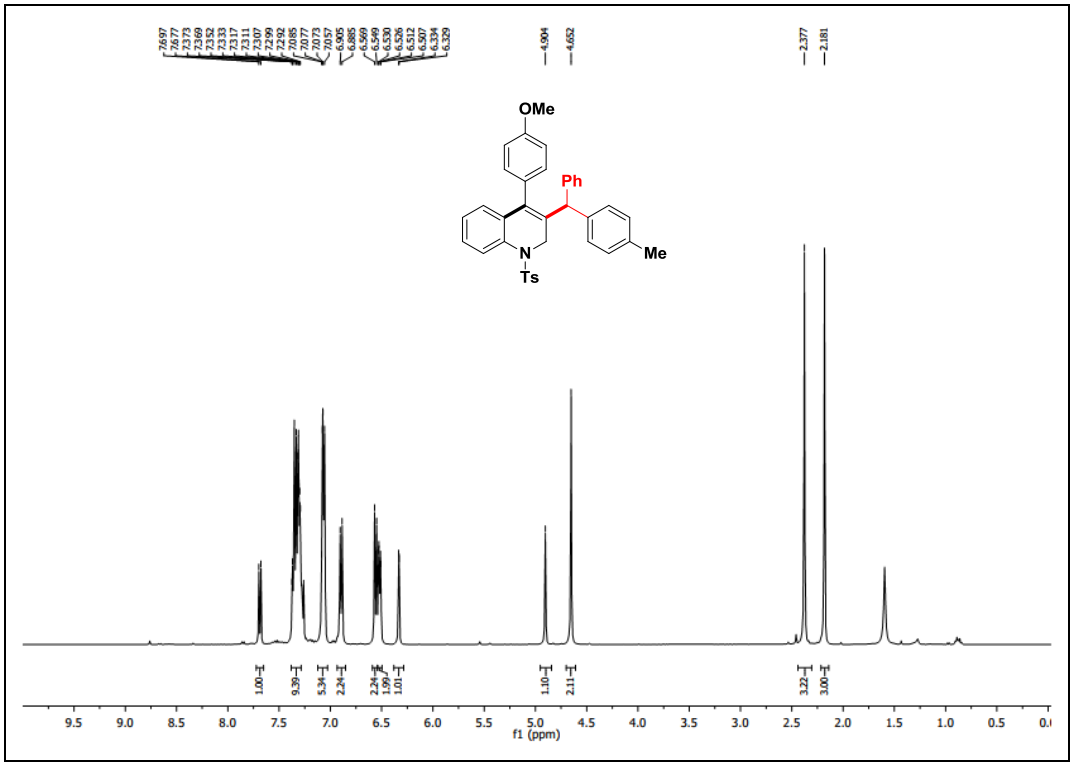
$^{1}$H NMR spectrum of compound **3g**, $CDCl_3$, 300 MHz



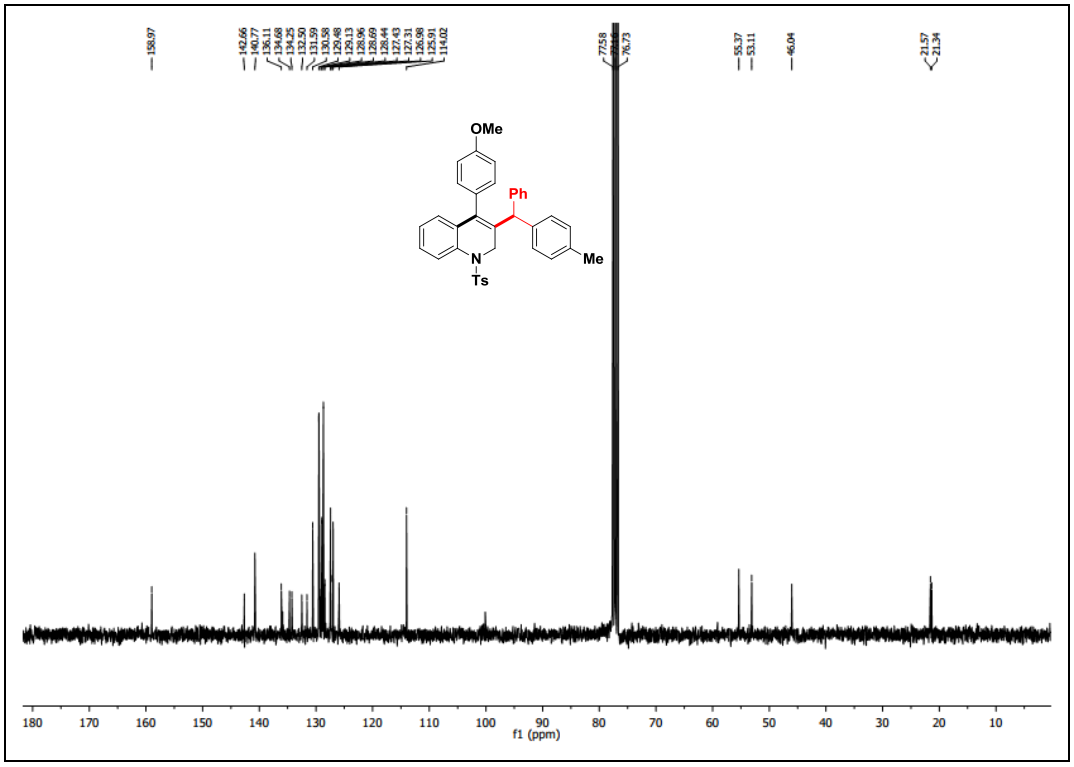

$^{13}$C NMR spectrum of compound **3g**, $CDCl_3$, 125 MHz



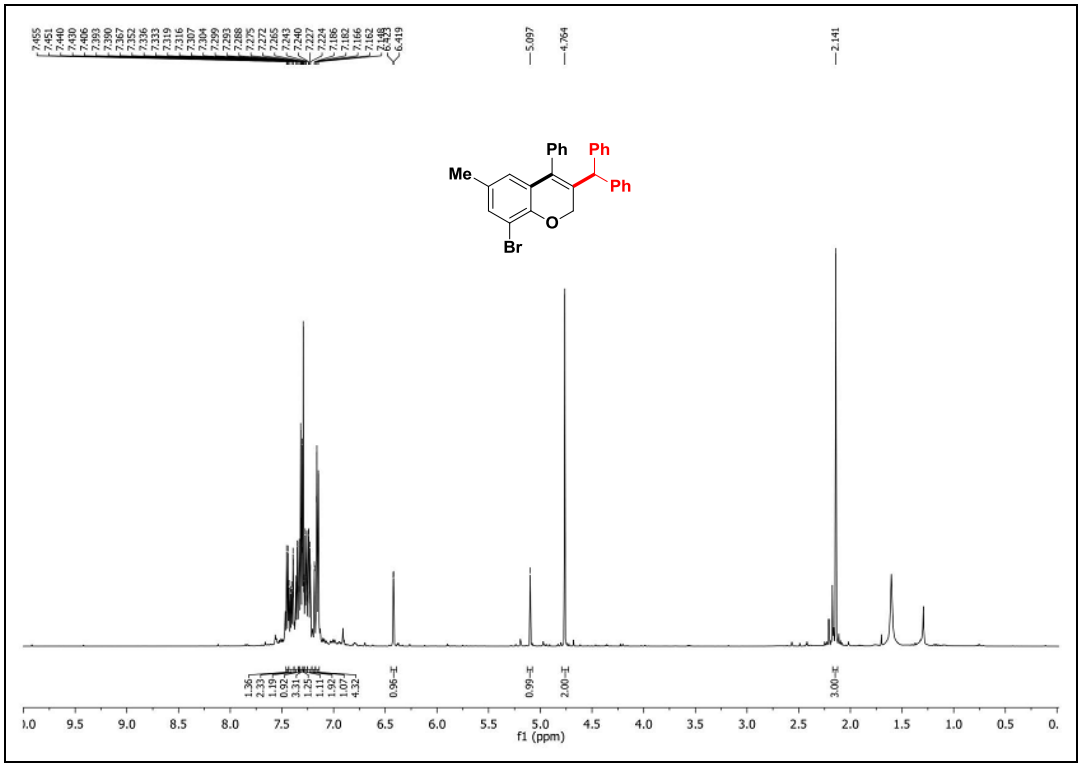
$^{1}$H NMR spectrum of compound **3h**, $CDCl_3$, 500 MHz



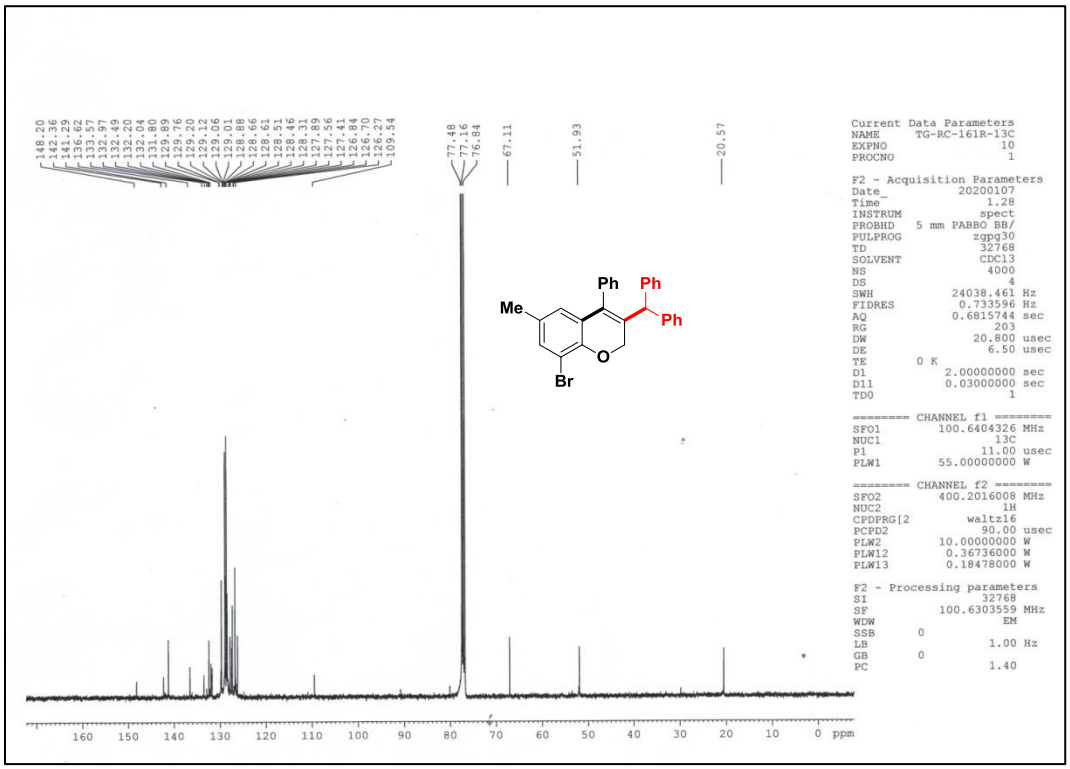

$^{13}$C NMR spectrum of compound **3h**, $CDCl_3$, 75 MHz



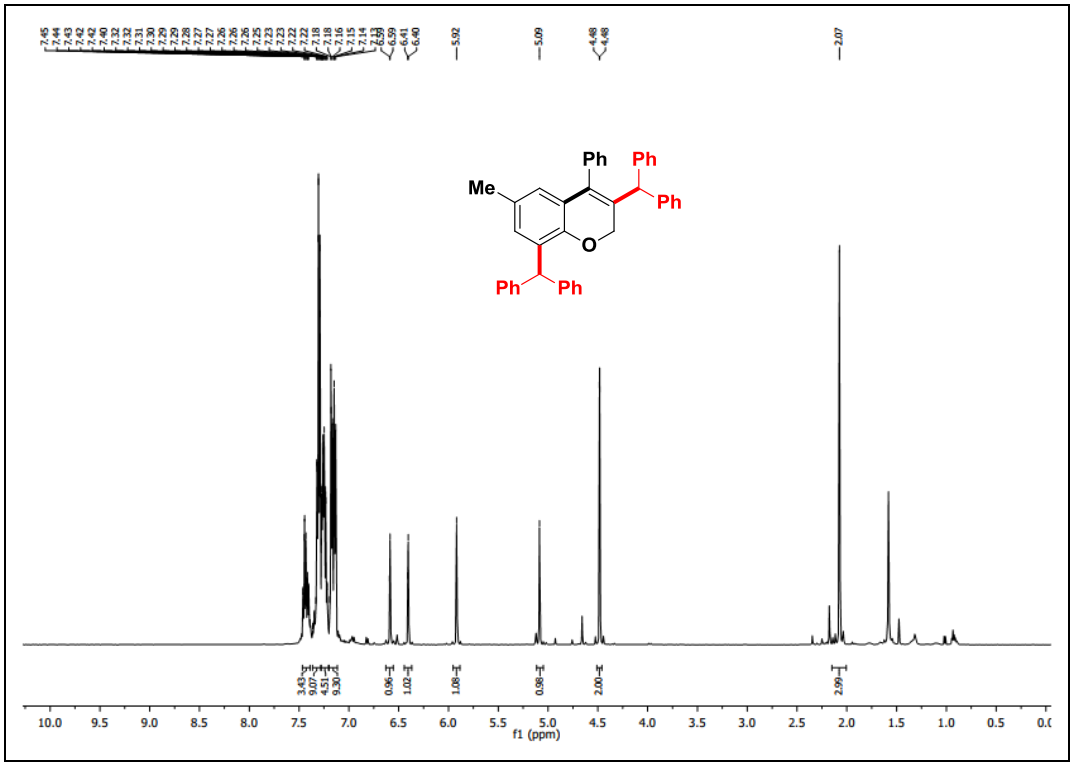
$^{1}$H NMR spectrum of compound **4a**, $CDCl_3$, 500 MHz



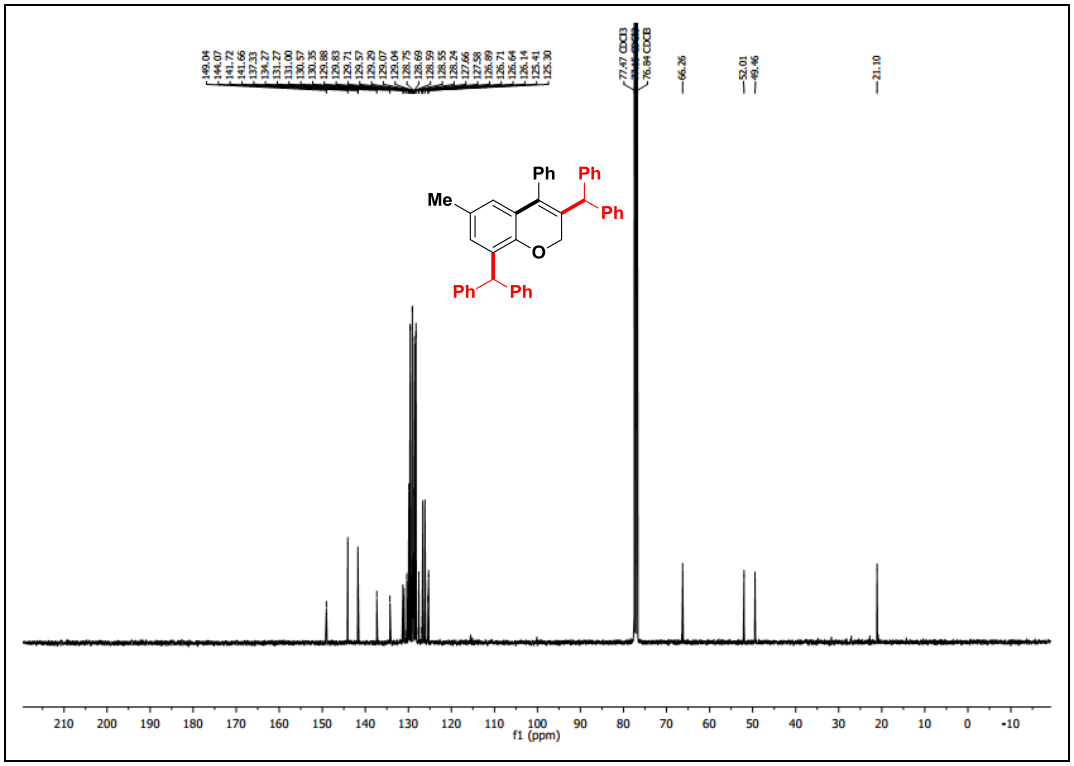

$^{13}$C NMR spectrum of compound **4a**, $CDCl_3$, 100 MHz



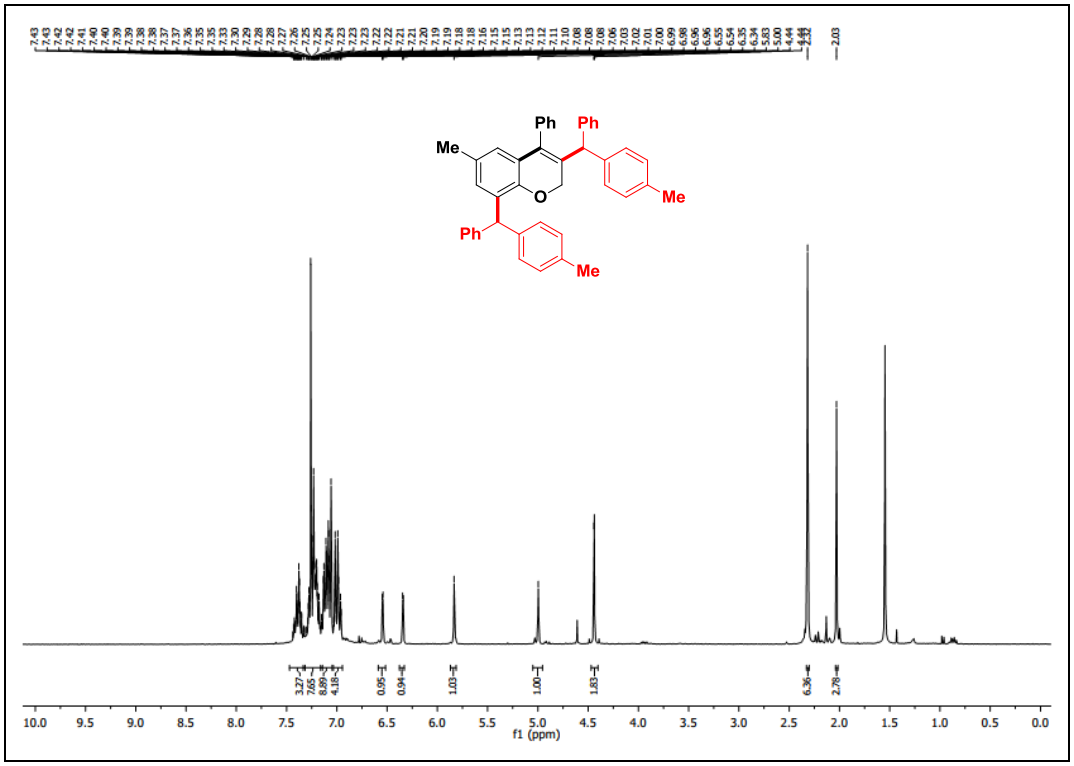
$^{1}$H NMR spectrum of compound **4b**, $CDCl_3$, 500 MHz



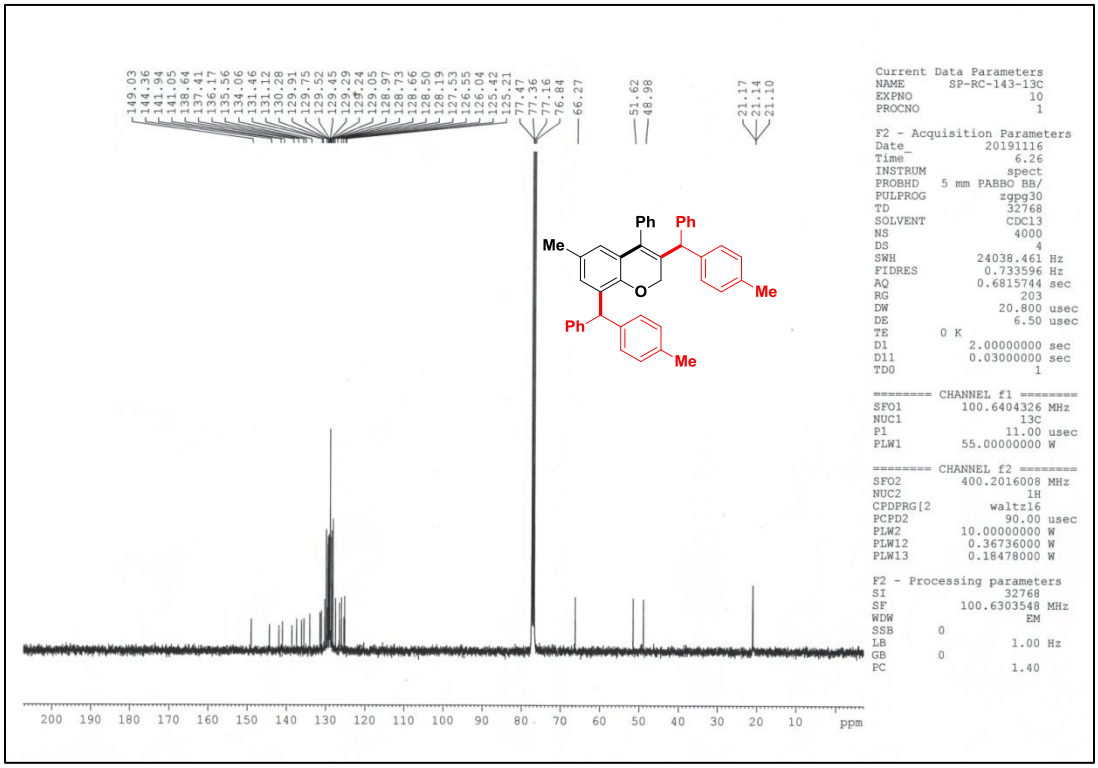

$^{13}$C NMR spectrum of compound **4b**, $CDCl_3$, 100 MHz



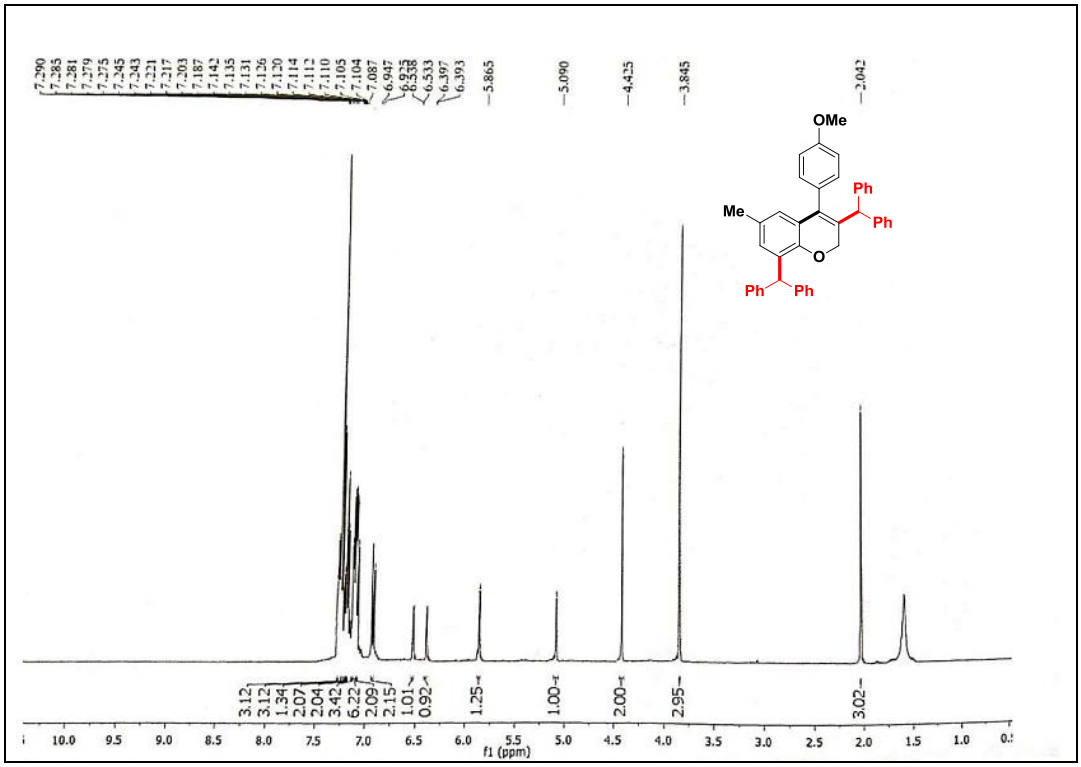
$^{1}$H NMR spectrum of compound **4c**, $CDCl_3$, 300 MHz



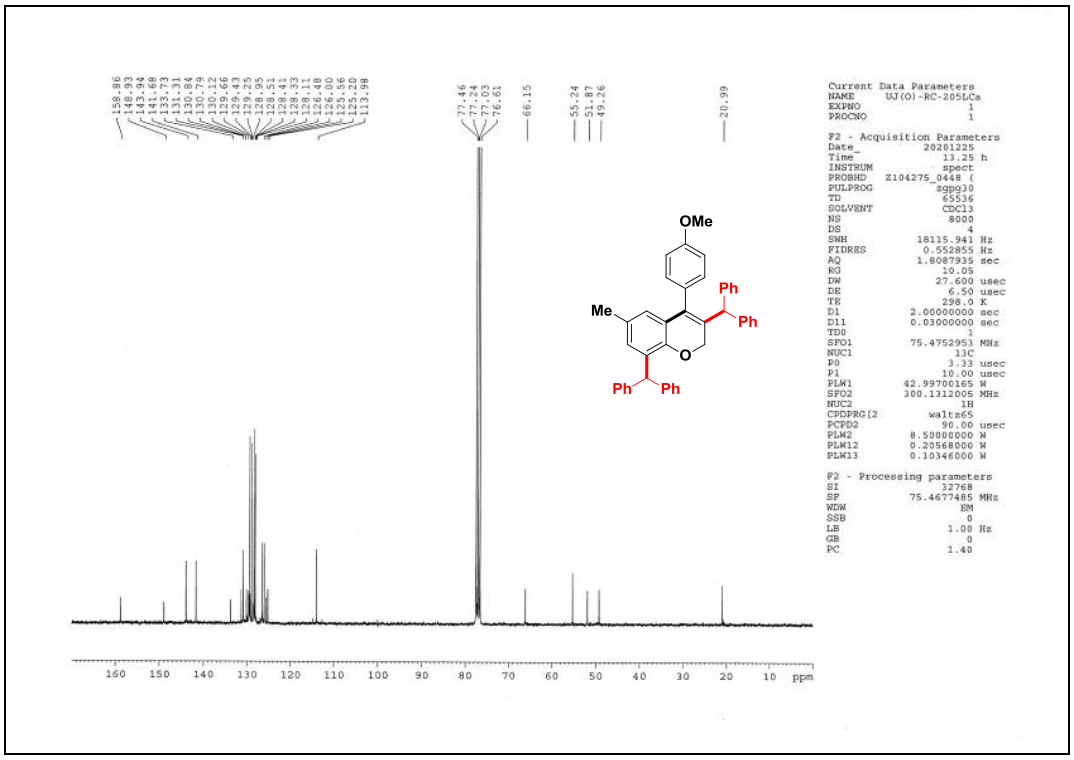

$^{13}$C NMR spectrum of compound **4c**, $CDCl_3$, 100 MHz



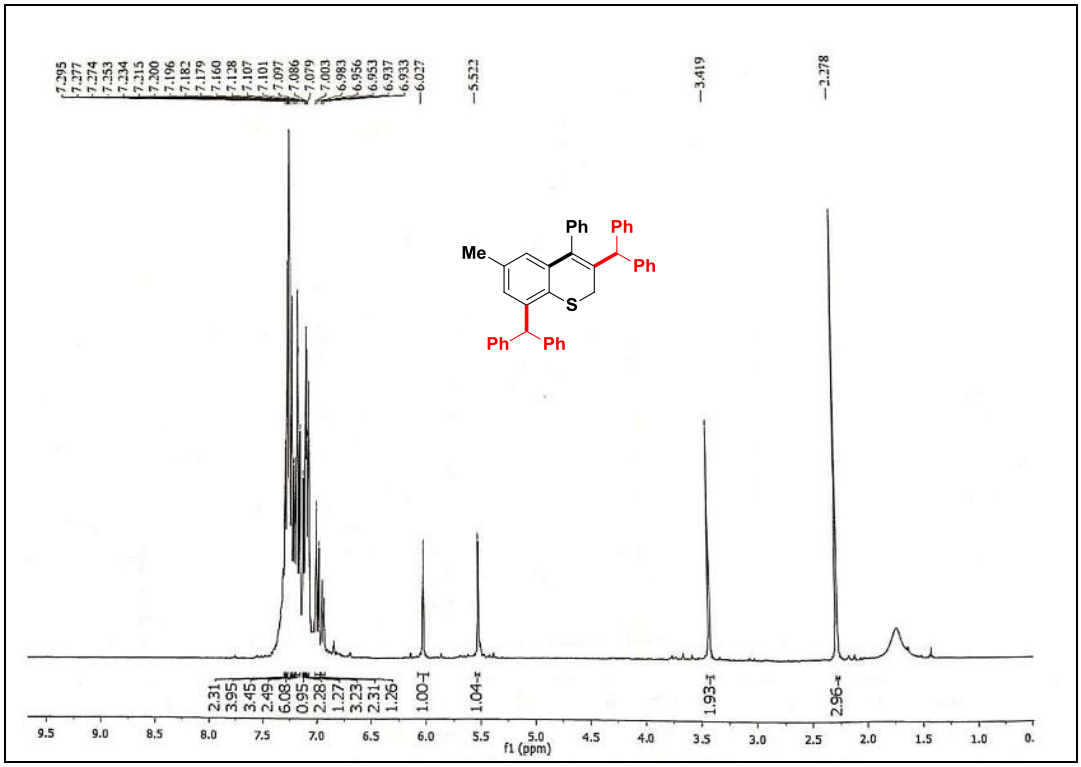
$^{1}$H NMR spectrum of compound **4d**, $CDCl_3$, 400 MHz



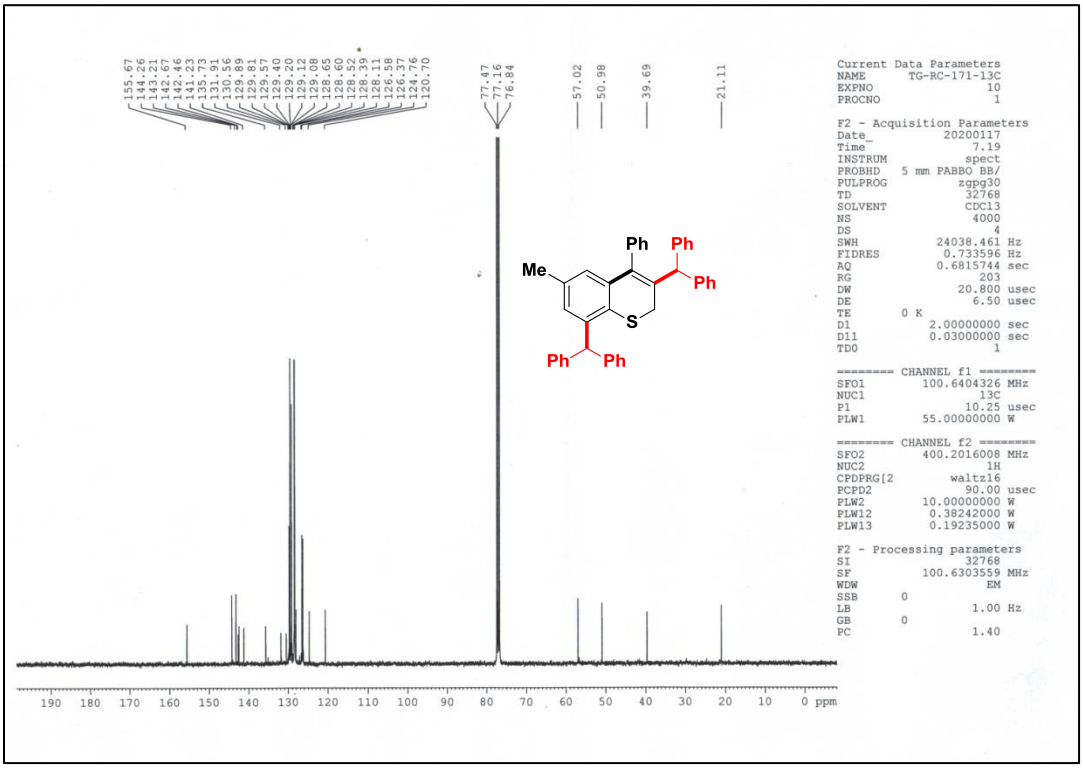

$^{13}$C NMR spectrum of compound **4d**, $CDCl_3$, 75 MHz



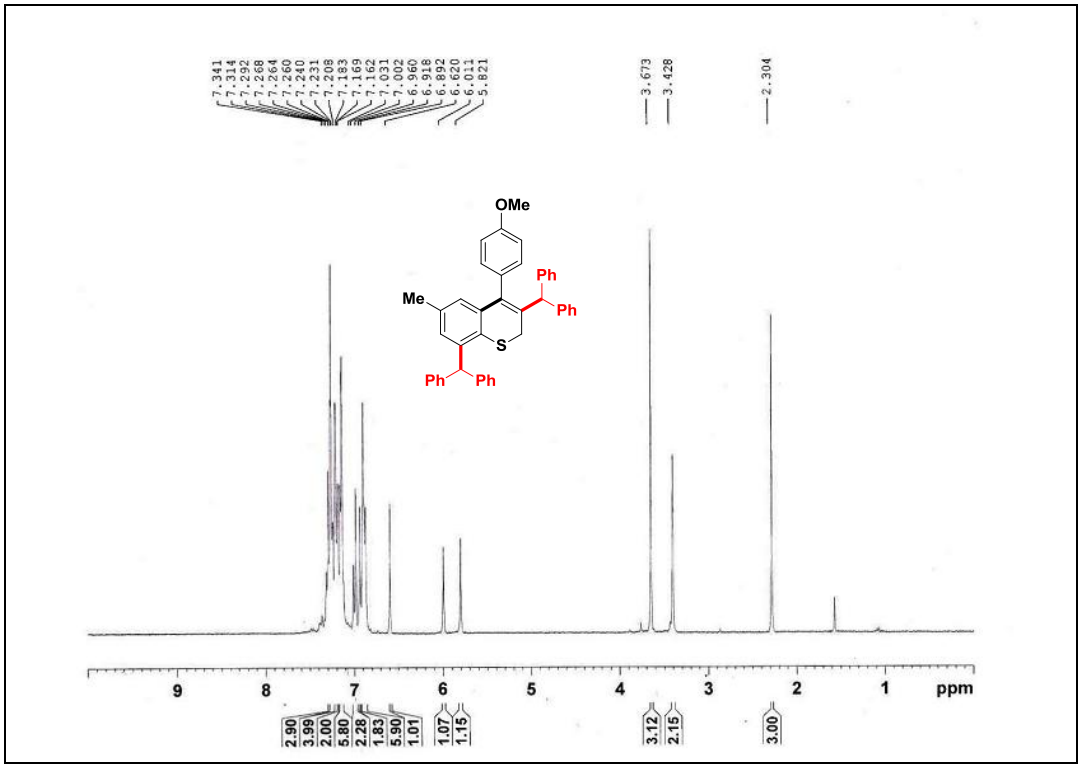
$^{1}$H NMR spectrum of compound **4e**, $CDCl_3$, 400 MHz



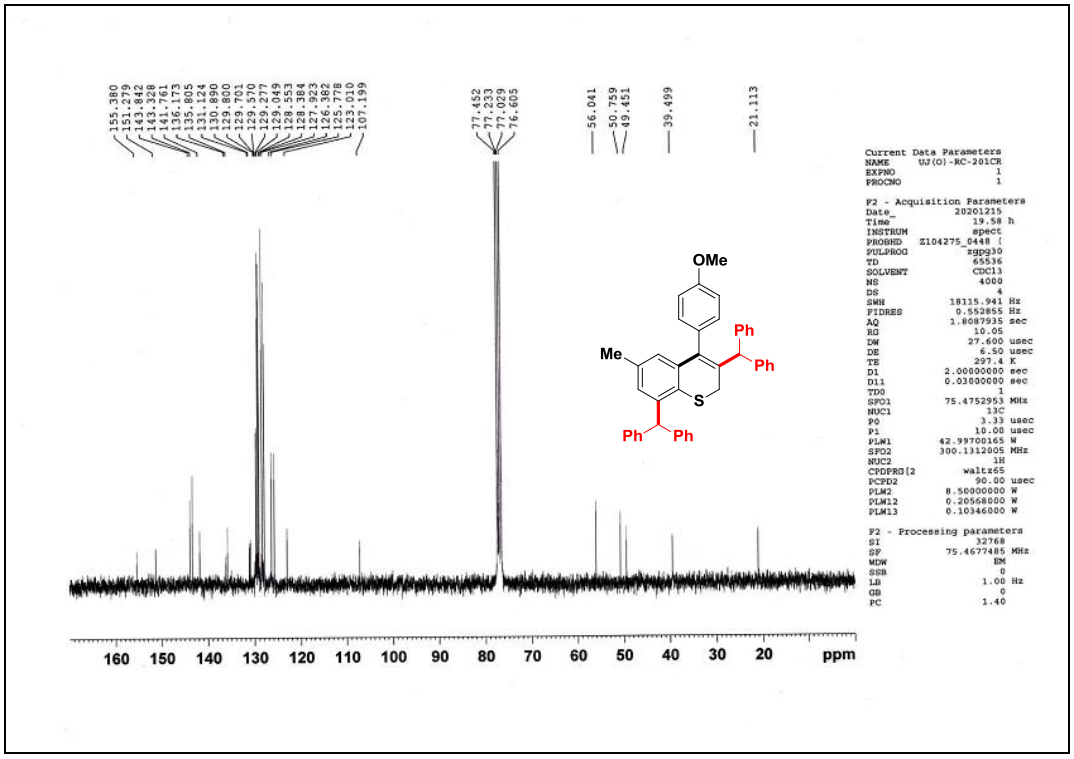

$^{13}$C NMR spectrum of compound **4e**, $CDCl_3$, 100 MHz



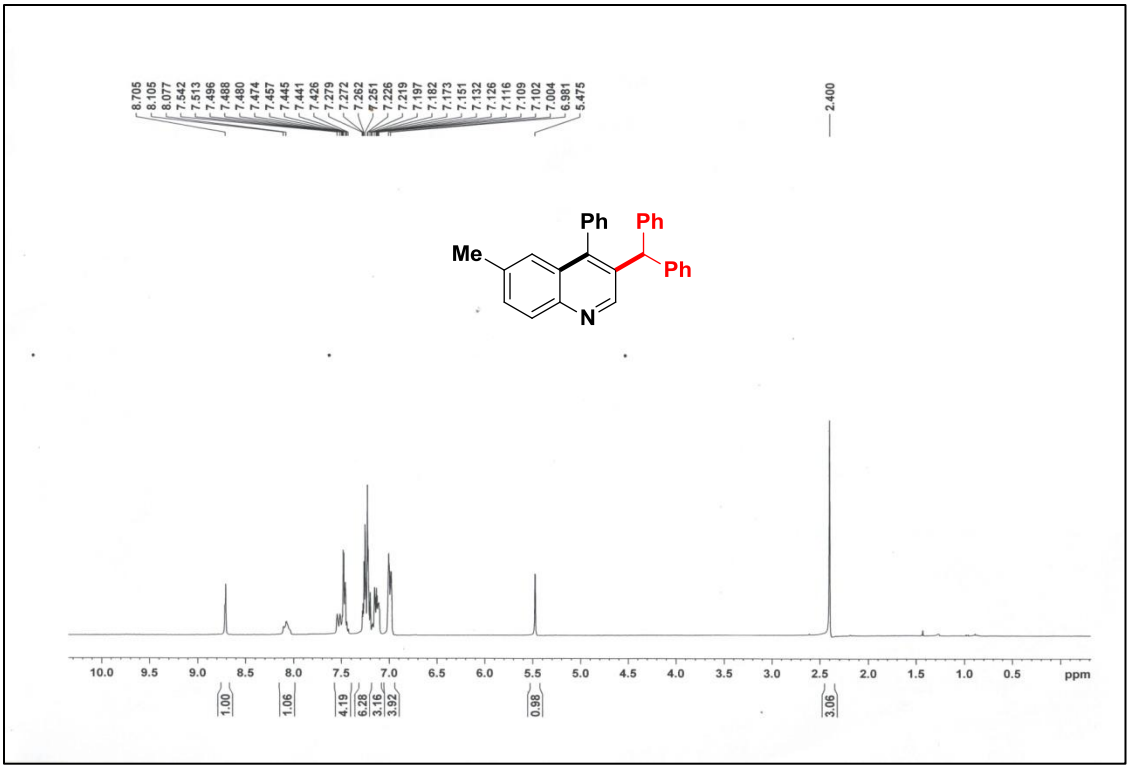
$^{1}$H NMR spectrum of compound **4f**, $CDCl_3$, 300 MHz



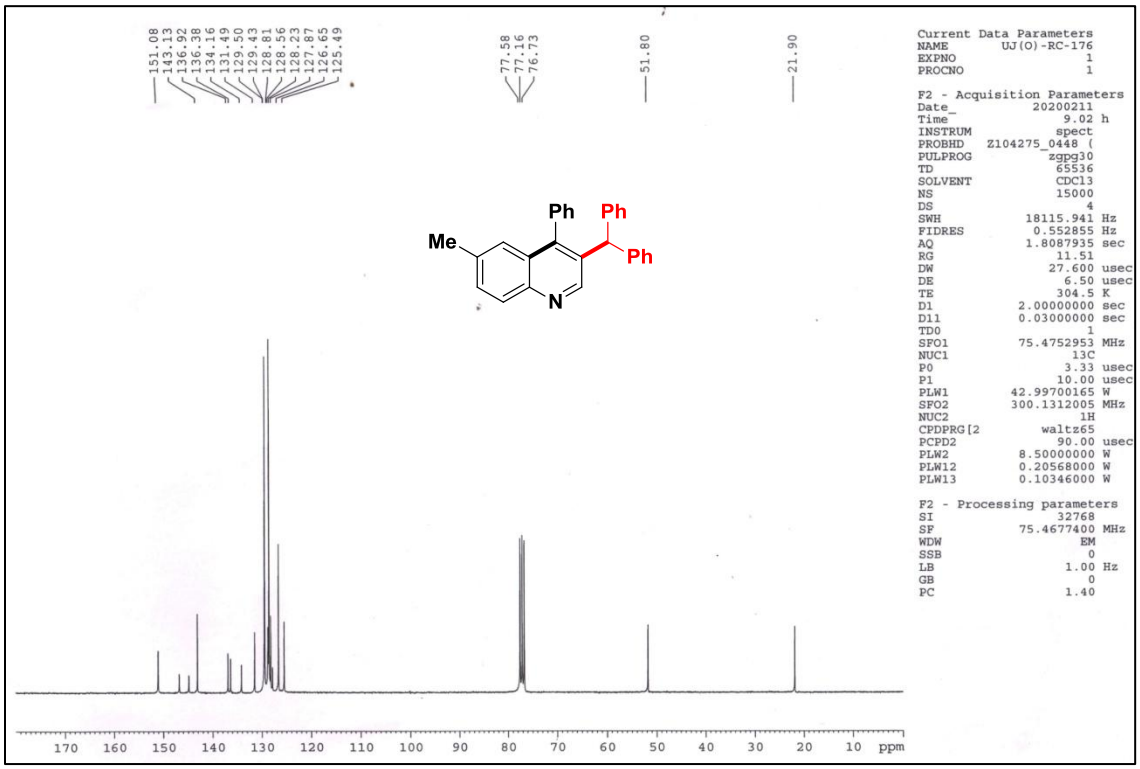

$^{13}$C NMR spectrum of compound **4f**, $CDCl_3$, 75 MHz



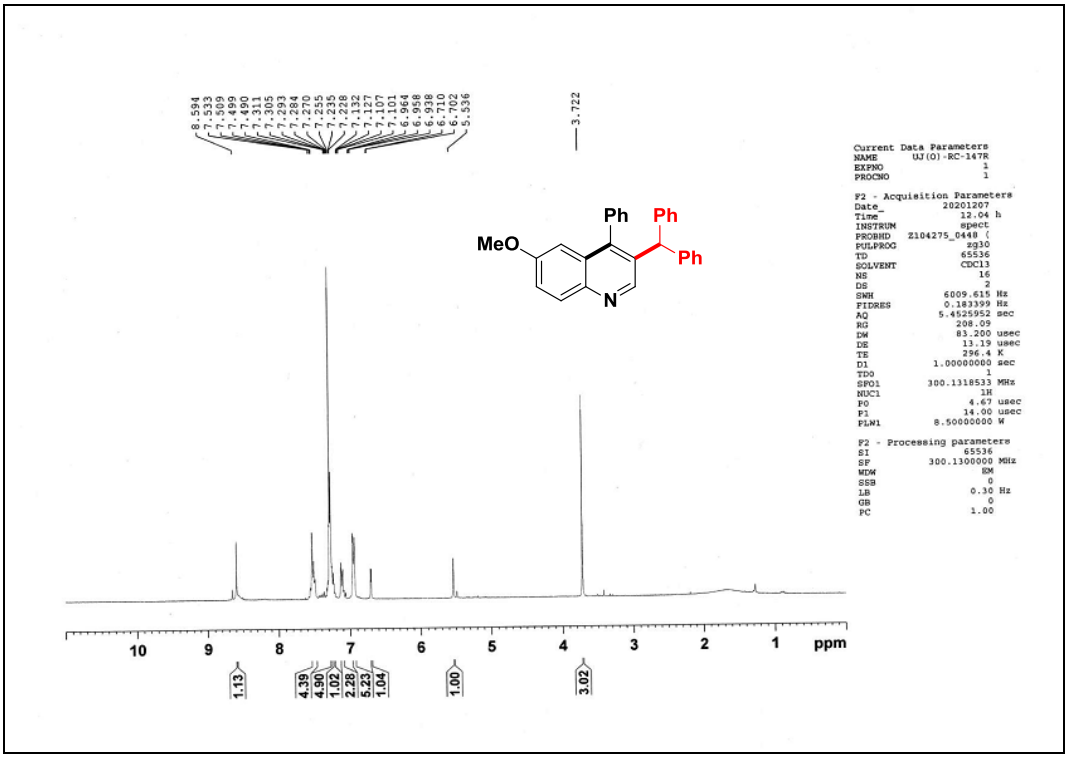
$^{1}$H NMR spectrum of compound **5a**, $CDCl_3$, 300 MHz



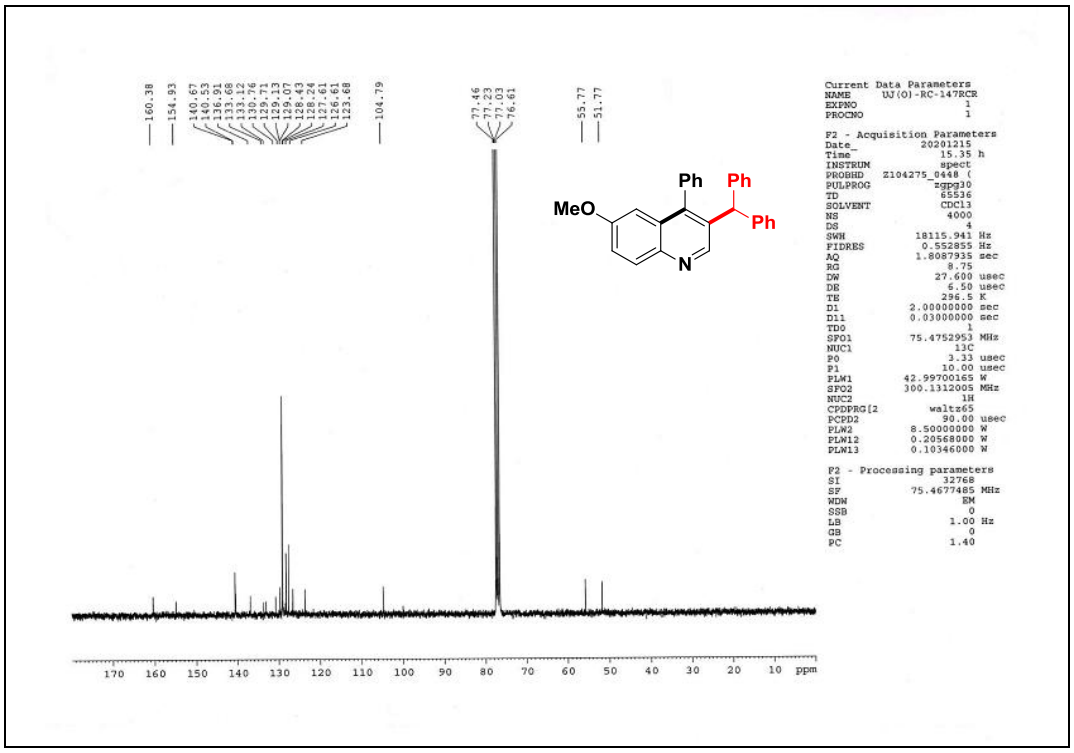

$^{13}$C NMR spectrum of compound **5a**, $CDCl_3$, 75 MHz



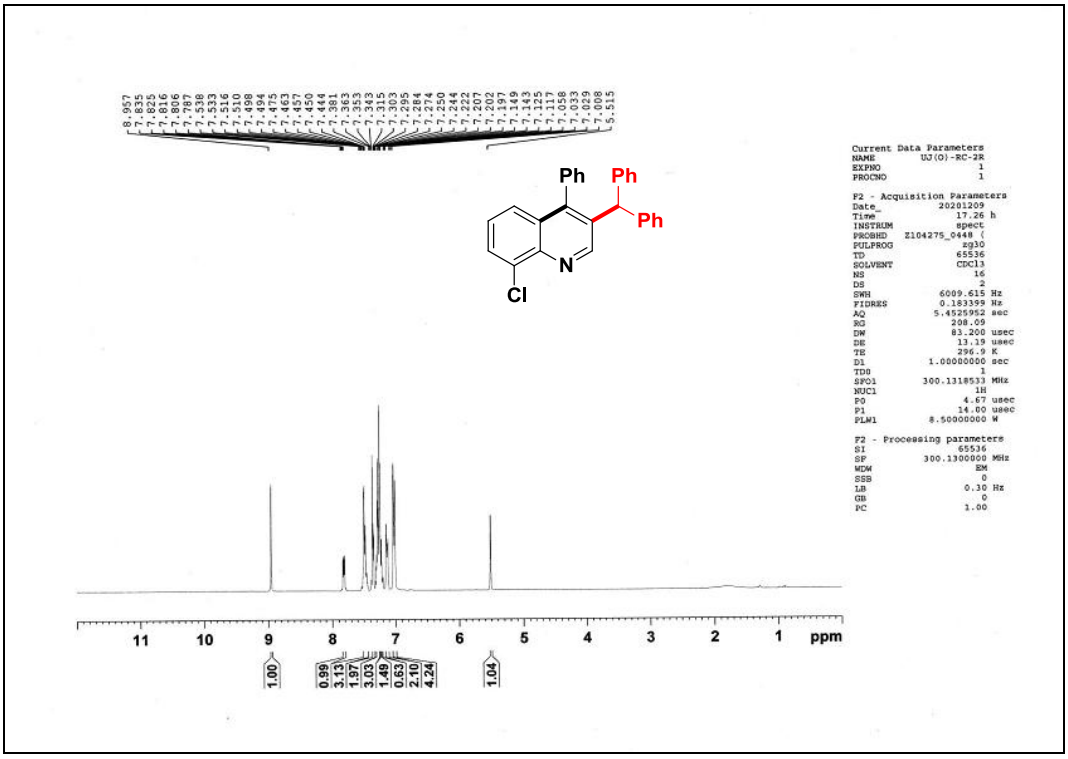
$^{1}$H NMR spectrum of compound **5b**, $CDCl_3$, 300 MHz



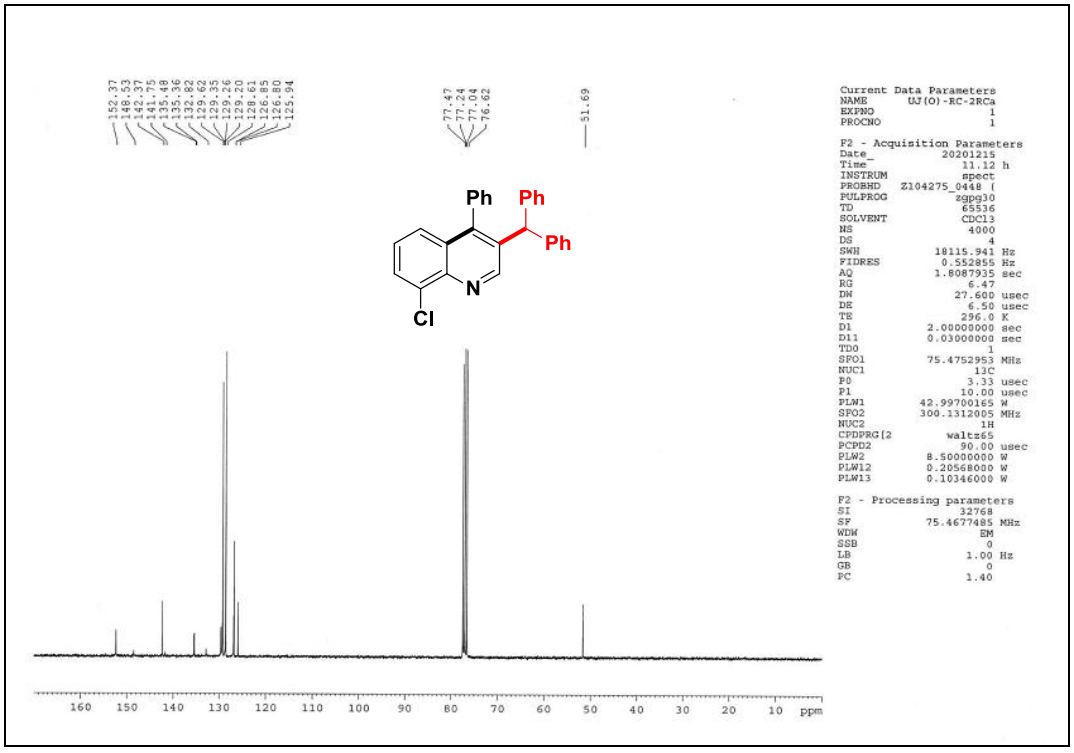

$^{13}$C NMR spectrum of compound **5b**, $CDCl_3$, 75 MHz



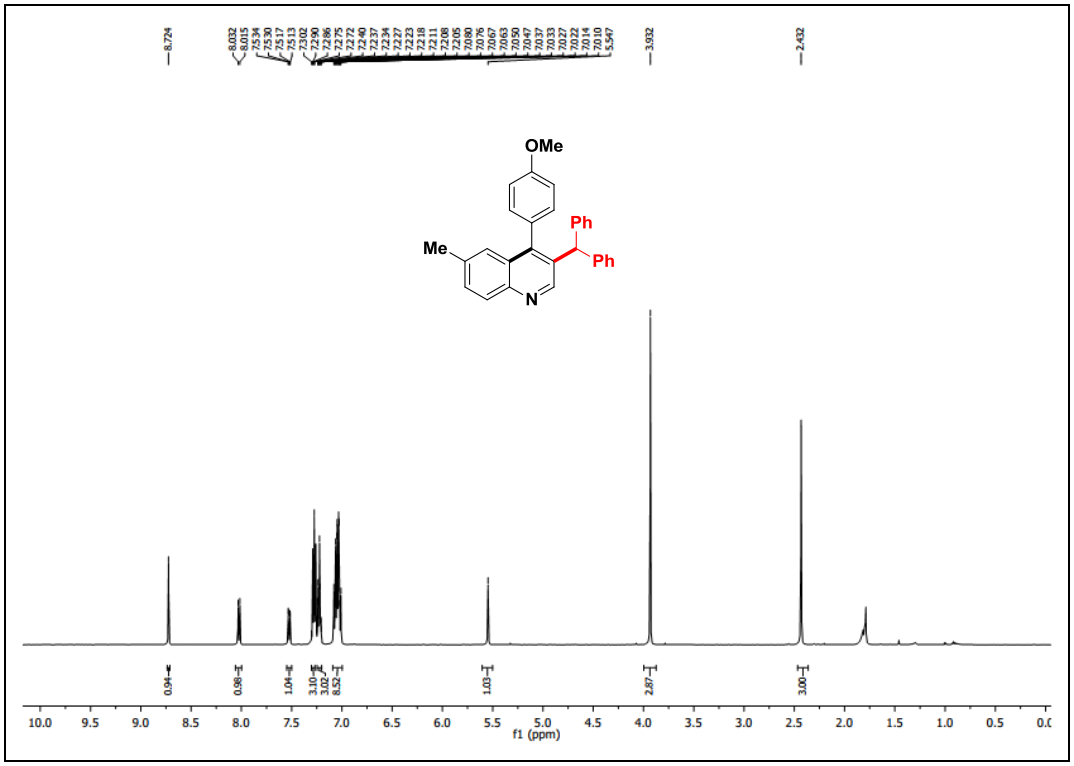
$^{1}$H NMR spectrum of compound **5c**, $CDCl_3$, 300 MHz



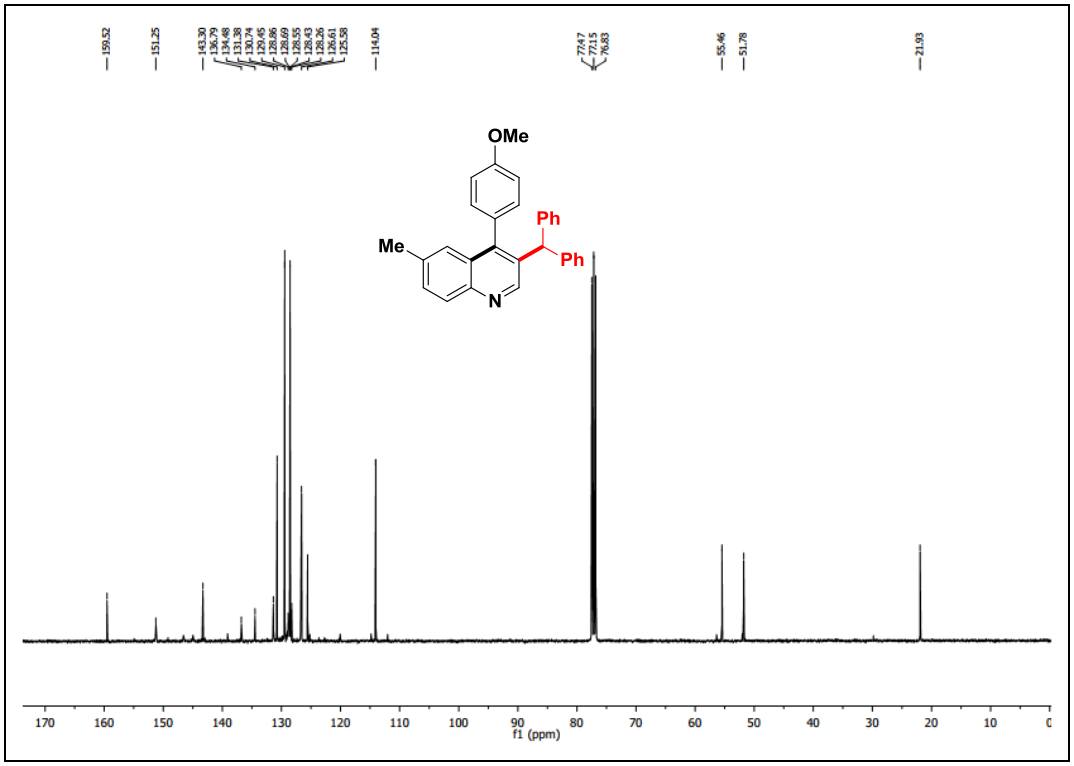

$^{13}$C NMR spectrum of compound **5c**, $CDCl_3$, 75 MHz



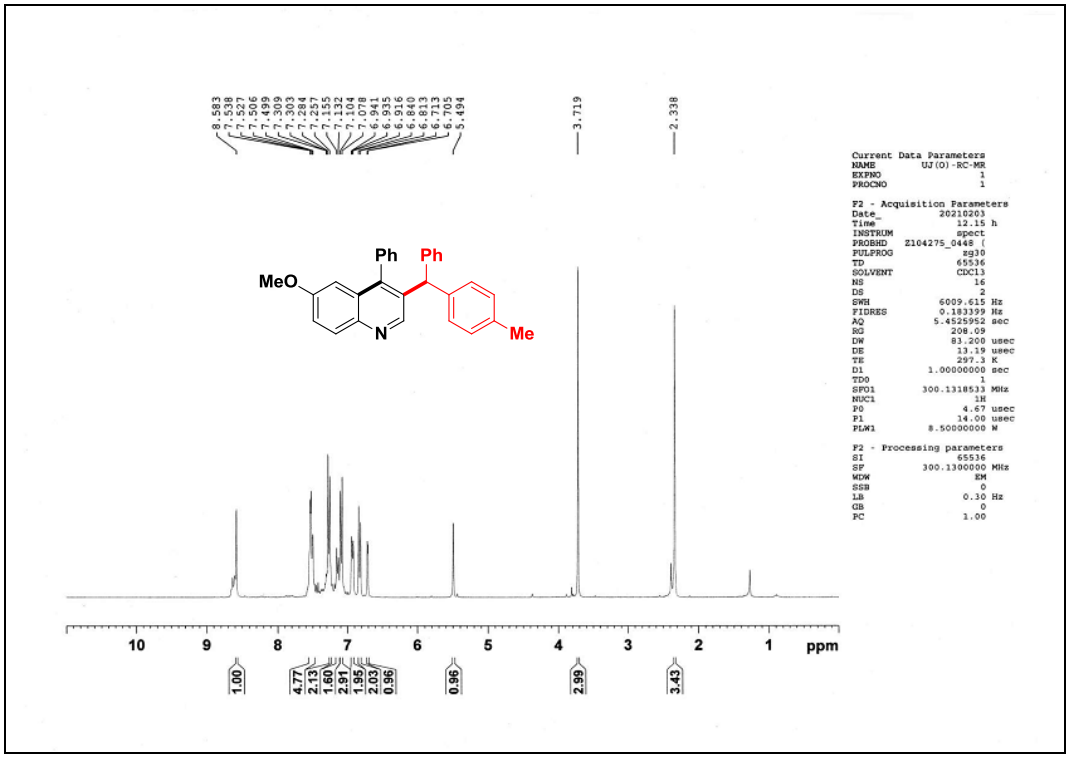
$^{1}$H NMR spectrum of compound **5d**, $CDCl_3$, 500 MHz



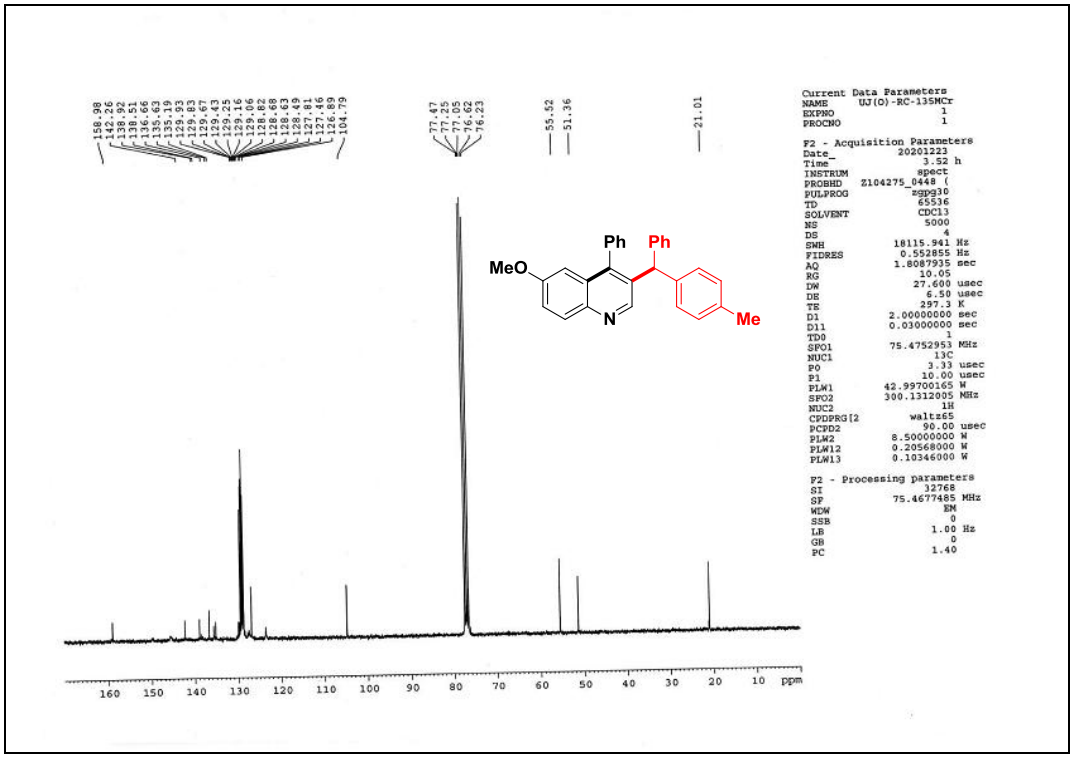

$^{13}$C NMR spectrum of compound **5d**, $CDCl_3$, 100 MHz



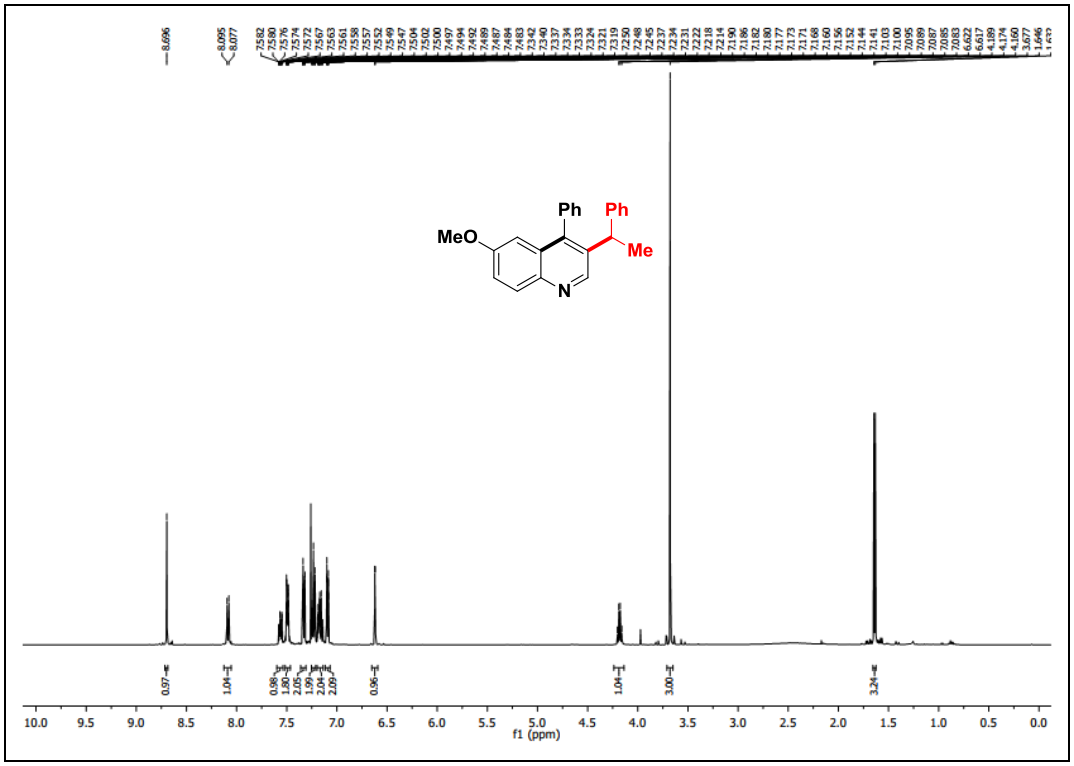
$^{1}$H NMR spectrum of compound **5e**, $CDCl_3$, 300 MHz




$^{13}$C NMR spectrum of compound **5e**, $CDCl_3$, 75 MHz



$^{1}$H NMR spectrum of compound **5f**, $CDCl_3$, 500 MHz




$^{13}$C NMR spectrum of compound **5f**, $CDCl_3$, 125 MHz