Supporting Information

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1. General

New compounds were characterized by ^{1}H NMR, $^{13}C\{^{1}H\}$ NMR, $^{19}F\{^{1}H\}$ NMR, IR, and HRMS. ^{1}H, $^{13}C\{^{1}H\}$, and $^{19}F\{^{1}H\}$ NMR spectra were recorded on a JEOL JMTC-400/54/SS spectrometer (^{1}H NMR, 400 MHz; $^{13}C\{^{1}H\}$ NMR, 100 MHz, $^{19}F\{^{1}H\}$ NMR, 377 MHz). ^{1}H NMR chemical shifts were determined relative to Me_4Si (0.0 ppm) as an internal standard in $CDCl_3$ and the signals of residual undeuterated DMSO (2.50 ppm) in DMSO-d_6. $^{13}C\{^{1}H\}$ NMR chemical shifts were determined relative to $CDCl_3$ (77.16 ppm) or DMSO-d_6 (39.50 ppm). $^{19}F\{^{1}H\}$ NMR chemical shifts were determined relative to C_6F_6 (−164.9 ppm) as an external standard. Infrared spectra were recorded on a SHIMADZU IRAffinity-1 FT-IR Spectrometer. High-resolution mass spectra were obtained on a JEOL JMS-700 mass spectrometer (magnetic sector type mass spectrometer) and JMS-T100LP. Melting points were determined on a Stanford Research Systems MPA100 OptiMelt Automated Melting Point System. Cyclic voltammetry (CV) was performed with ALS-610E (BAS Inc.) system. UV-vis spectra were recorded on a Shimadzu UV-2550 spectrophotometer. The X-ray diffraction data of the single crystal were collected on a two-dimensional X-ray detector (PILATUS 200K/R) equipped in Rigaku XtaLAB PRO diffractometer using thin multi-layer mirror monochromated Cu-Kα radiation (λ =1.54187 Å). Submicrosecond laser flash photolysis (LFP) is performed with a 355 or 266 nm yttrium aluminum garnet (YAG) laser (6 mJ/pulse, 12 ns pulse width). The monitoring system consists of a 150 W Xenon arc lamp as light source, a Unisoku MD200 monochromator detection and a photomultiplier. All reactions were carried out under nitrogen. Products were purified by chromatography on silica gel BW-300 (Fuji Silysia Chemical Ltd.) or Chromatorex NH (Fuji Silysia Chemical Ltd.). Light irradiation was performed by using LEDs (Kessil PR160L 390 nm (max 40W), Kessil PR160L 467 nm (max 40W), and Kessil PR160L 525 nm (max 40W)). The emission spectra of the LEDs were recorded on a HAMAMATSU Quantaurus-QY C11347-01 spectrometer. The light intensities of the LEDs were measured using Optical Power Meter PM100D (THORLABS Inc.). Analytical thin-layer chromatography (TLC) was performed on pre-coated silica gel glass plates (Merck silica gel 60 F_{254} and Fuji Silysia Chromatorex NH, 0.25 mm thickness). Compounds were visualized with UV lamp or treatment with an ethanolic solution of phosphomolybdic acid followed by heating.

2. Materials

Alkenes **1a**–**1m**, **1o** and **1r** were prepared according to the reported procedure.[1,7–9] Carboxylic acids **2e**, **2j**, **2k**, and **2p** were prepared according to the reported procedure.[10,11] Hypervalent iodine reagents **3a**–**3g** and **13** were prepared according to the reported procedure.[12–14] Dehydrated THF and toluene were used from a solvent purification system. All other solvents and reagents were purchased and used as obtained.

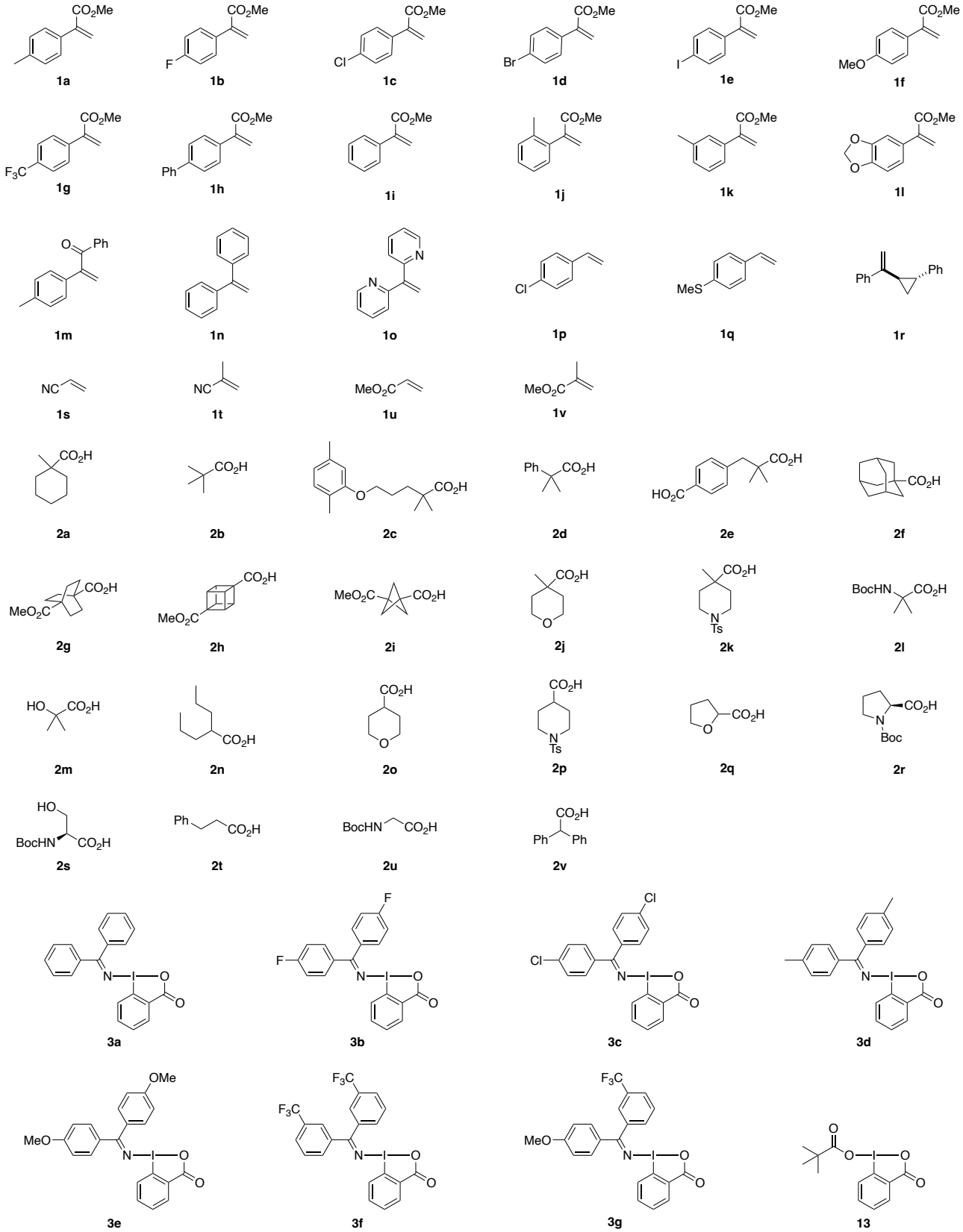
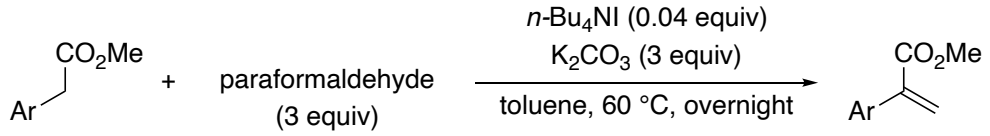


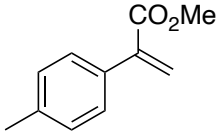
Figure S1. List of substrates and iodine reagents

3. Preparation of alkenes



General procedure I: According to the reported procedure[1], to a solution of ester (1 equiv) in toluene, paraformaldehyde (3 equiv), *n*-Bu_4NI (0.04 equiv), and K_2CO_3 (3 equiv) were added at room temperature. The resulting mixture was stirred at 60 °C overnight. After cooling to room temperature, the suspension was filtered through Celite, and the filtrate was eluted with EtOAc and water. Then, the mixture was extracted with EtOAc. The combined organic layers were dried over Na_2SO_4, filtered, and concentrated under reduced pressure to give the crude mixture, which was purified by flash column chromatography on silica gel gave the desired alkene.

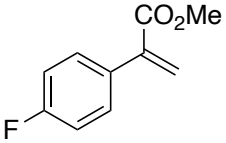
methyl 2-(*p*-tolyl)acrylate (1a)



^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.30 (d, *J* = 8.4 Hz, 2H), 7.16 (d, *J* = 8.4 Hz, 2H), 6.31 (d, *J* = 1.2 Hz, 1H), 5.85 (d, *J* = 1.2 Hz, 1H), 3.81 (s, 3H), 2.36 (s, 3H); ^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$) δ 167.6, 141.3, 138.2, 134.0, 129.0, 128.3, 126.3, 52.3, 21.3

The analytical data for this compound were in excellent agreement with the reported data.[2]

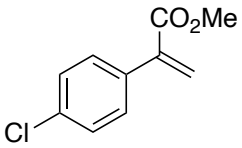
methyl 2-(4-fluorophenyl)acrylate (1b)



^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.43–7.35 (m, 2H), 7.09–6.97 (m, 2H), 6.36 (d, *J* = 1.2 Hz, 1H), 5.87 (d, *J* = 1.2 Hz, 1H), 3.82 (s, 3H); ^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$) δ 167.2, 162.8 (d, $J_{C–F}$ = 246.1 Hz), 140.3, 132.8 (d, $J_{C–F}$ = 4.1 Hz), 130.22 (d, $J_{C–F}$ = 8.2 Hz), 127.1, 115.2 (d, $J_{C–F}$ = 21.4 Hz), 52.4

The analytical data for this compound were in excellent agreement with the reported data.[2]

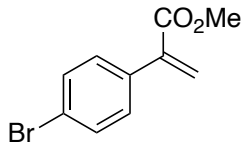
methyl 2-(4-chlorophenyl)acrylate (1c)



^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.38–7.29 (m, 4H), 6.38 (d, *J* = 1.2 Hz, 1H), 5.89 (d, *J* = 1.2 Hz, 1H), 3.82 (s, 3H); $^{13}C\{^1H\}$ NMR: (100 MHz, $CDCl_3$) δ 166.9, 140.3, 135.2, 134.4, 129.8, 128.4, 127.5, 52.4

The analytical data for this compound were in excellent agreement with the reported data.[2]

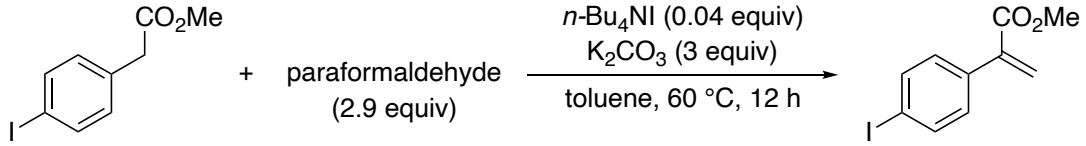
methyl 2-(4-bromophenyl)acrylate (1d)



^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.47 (d, *J* = 8.4 Hz, 2H), 7.28 (d, *J* = 8.4 Hz, 2H), 6.38 (d, *J* = 0.8 Hz, 1H), 5.89 (d, *J* = 0.8 Hz, 1H), 3.81 (s, 3H); $^{13}C\{^1H\}$ NMR: (100 MHz, $CDCl_3$) δ 166.8, 140.3, 135.6, 131.3, 130.1, 127.5, 122.5, 52.4

The analytical data for this compound were in excellent agreement with the reported data.[2]

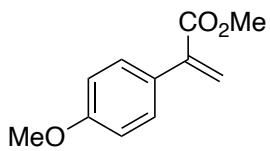
methyl 2-(4-iodophenyl)acrylate (1e)



According to the general procedure **I**, to a solution of methyl 2-(4-iodophenyl)acetate (1.64 g, 5.9 mmol) in toluene, paraformaldehyde (517.3 mg, 17 mmol), *n*-Bu_4NI (87.9 mg, 0.23 mmol), and K_2CO_3 (2.50 g, 18 mmol) were added. The resulting mixture was stirred at 60 °C for 12 h. After cooling to room temperature, the suspension was filtered through Celite, and the filtrate was eluted with EtOAc and water. Then, the mixture was extracted with EtOAc. The combined organic layers were dried over Na_2SO_4, filtered, and concentrated under reduced pressure to give the crude product, which was purified by flash column chromatography on silica gel (hexane/EtOAc = 95:5) gave the product as colorless oil (586.3 mg, 34% yield).

^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.8 Hz, 2H), 7.16 (d, *J* = 8.8 Hz, 2H), 6.38 (d, *J* = 0.8 Hz, 1H), 5.90 (d, *J* = 0.8 Hz, 1H), 3.81 (s, 3H); $^{13}C\{^1H\}$ NMR: (100 MHz, $CDCl_3$) δ 166.7, 140.3, 137.3, 136.2, 130.2, 127.6, 94.3, 52.4; IR: (ATR) 2947, 1717, 1485, 1433, 1389, 1200, 1175, 1057, 1003, 826, 810 cm^{-1}; HRMS (EI) *m*/*z*: (M^+) Calculated for $C_{10}H_9O_2I$ 287.9647; Found 287.9646

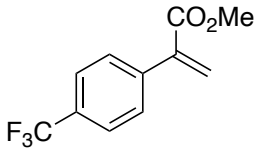
methyl 2-(4-methoxyphenyl)acrylate (1f)



^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.36 (d, J = 8.8 Hz, 2H), 6.89 (d, J = 8.8 Hz, 2H), 6.28 (d, J = 1.2 Hz, 1H), 5.84 (d, J = 1.2 Hz, 1H), 3.83 (s, 3H), 3.82 (s, 3H); ^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$) δ 167.7, 159.7, 140.7, 129.6, 129.3, 125.6, 113.7, 55.4, 52.3

The analytical data for this compound were in excellent agreement with the reported data.[2]

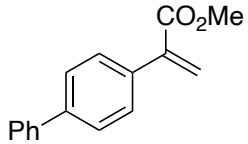
methyl 2-(4-(trifluoromethyl)phenyl)acrylate (1g)



^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.62 (d, J = 8.8 Hz, 2H), 7.53 (d, J = 8.8 Hz, 2H), 6.48 (s, 1H), 5.97 (s, 1H), 3.84 (s, 3H); ^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$) δ 166.6, 140.4, 140.3, 130.3 (q, $J_{C–F}$ = 32.1 Hz), 128.9, 128.8, 125.2 (q, $J_{C–F}$ = 3.2 Hz), 124.2 (q, $J_{C–F}$ = 270.8 Hz), 52.5

The analytical data for this compound were in excellent agreement with the reported data.[2]

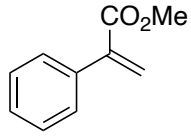
methyl 2-([1,1'-biphenyl]-4-yl)acrylate (1h)



^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.62–7.55 (m, 4H), 7.49 (d, J = 8.8 Hz, 2H), 7.48–7.40 (m, 2H), 7.35 (t, J = 7.6 Hz, 1H), 6.38 (d, J = 1.2 Hz, 1H), 5.95 (d, J = 1.2 Hz, 1H), 3.84 (s, 3H); ^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$) δ 167.4, 141.3, 141.1, 140.8, 135.8, 128.9, 128.8, 127.6, 127.2, 127.0, 126.9, 52.4

The analytical data for this compound were in excellent agreement with the reported data.[3]

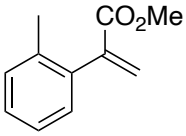
methyl 2-phenylacrylate (1i)



^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.46–7.33 (m, 4H), 6.37 (d, J = 0.8 Hz, 1H), 5.90 (d, J = 0.8 Hz, 1H), 3.83 (s, 3H); ^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$) δ 167.4, 141.5, 136.9, 128.4, 128.33, 128.27, 127.0, 52.3

The analytical data for this compound were in excellent agreement with the reported data.[2]

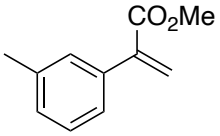
methyl 2-(*o*-tolyl)acrylate (1j)



^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.30–7.08 (m, 4H), 6.52 (d, *J* = 1.6 Hz, 1H), 5.71 (d, *J* = 1.6 Hz, 1H), 3.76 (s, 3H), 2.20 (s, 3H); ^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$) δ 167.3, 141.8, 137.3, 136.2, 130.0, 129.6, 128.8, 128.3, 125.8, 52.4, 19.9

The analytical data for this compound were in excellent agreement with the reported data.[4]

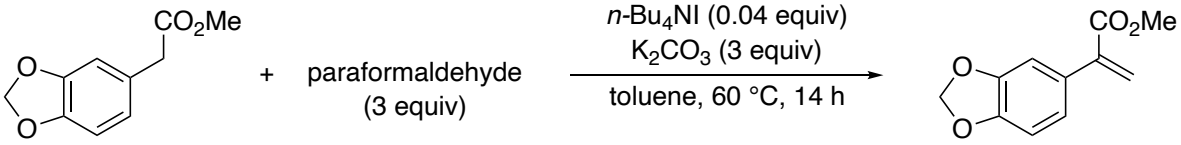
methyl 2-(*m*-tolyl)acrylate (1k)



^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.28–7.10 (m, 4H), 6.33 (d, *J* = 1.2 Hz, 1H), 5.86 (d, *J* = 1.2 Hz, 1H), 3.82 (s, 3H), 2.37 (s, 3H); ^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$) δ 167.6, 141.6, 137.9, 136.8, 129.12, 129.10, 128.2, 126.7, 125.5, 52.3, 21.6

The analytical data for this compound were in excellent agreement with the reported data.[5]

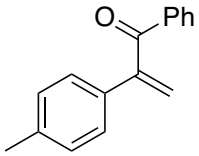
methyl 2-(benzo[*d*][1,3]dioxol-5-yl)acrylate (1l)



According to the general procedure **I**, to a solution of methyl 2-(benzo[*d*][1,3]dioxol-5-yl)acetate (1.93 g, 10 mmol) in toluene, paraformaldehyde (917.6 mg, 31 mmol), *n*-Bu_4NI (162.8 mg, 0.41 mmol), and K_2CO_3 (4.24 g, 31 mmol) were added. The resulting mixture was stirred at 60 °C for 14 h. After cooling to room temperature, the suspension was filtered through Celite, and the filtrate was eluted with EtOAc and water. Then, the mixture was extracted with EtOAc. The combined organic layers were dried over Na_2SO_4, filtered, and concentrated under reduced pressure to give the crude product, which was purified by flash column chromatography on silica gel (hexane/EtOAc = 85:15) gave the product as yellow oil (782.4 mg, 38% yield).

^{1}H NMR: (400 MHz, $CDCl_3$) δ 6.93–6.86 (m, 2H), 6.78 (d, *J* = 8.0 Hz, 1H), 6.25 (s, 1H), 5.95 (s, 2H), 5.81 (s, 1H), 3.80 (s, 3H); ^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$) δ 167.4, 147.7, 147.5, 140.8, 130.7, 125.9, 122.1, 108.9, 108.0, 101.2, 52.2; IR: (ATR) 3001, 2953, 2913, 1711, 1489, 1433, 1236, 1200, 1148, 1109, 1034, 916, 816 cm^{-1}; HRMS (CI) *m/z*: ([M+H]$^+$) Calculated for $C_{11}H_{11}O_4$ 207.0657; Found 207.0652

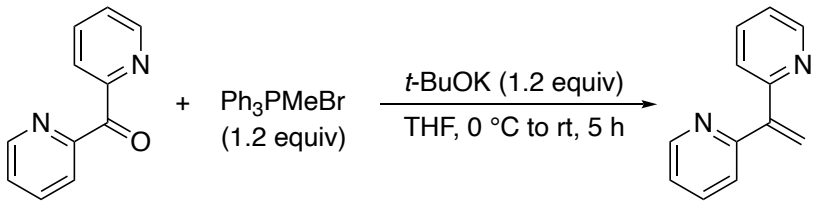
1-phenyl-2-(*p*-tolyl)prop-2-en-1-one (1m)



^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 7.6 Hz, 2H), 7.53 (t, *J* = 7.2 Hz, 1H), 7.41 (dd, *J* = 8.0, 7.2 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.14 (d, *J* = 7.6 Hz, 2H), 6.01 (s, 1H), 5.57 (s, 1H), 2.33 (s, 3H); ^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$) δ 197.9, 148.2, 138.5, 137.2, 134.2, 133.1, 130.1, 129.4, 128.5, 127.0, 120.0, 21.3

The analytical data for this compound were in excellent agreement with the reported data.[6]

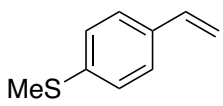
2,2'-(ethene-1,1-diyl)dipyridine (1o)



According to the reported procedure[7], a heat-gun-dried round-bottom flask containing a magnetic stir bar was charged with Ph_3PMeBr (2.15 g, 6 mmol) and dry THF (17 mL). The suspension was cooled to 0 °C, *t*-BuOK (0.56 g, 5 mmol) was added, and the resulting yellow suspension was stirred at 0 °C for 30 min. To this suspension, a solution of di(pyridin-2-yl)methanone (0.91 g, 5 mmol) in THF (5 mL) was added slowly. The mixture was stirred at 0 °C for 4 h before being quenched with water (10 mL). The aqueous layer was extracted with AcOEt (3 × 10 mL), and the combined organic layers were dried over Na_2SO_4. The solution was concentrated under reduced pressure to give the crude product, which was purified by flash column chromatography on NH silica gel (hexane/EtOAc = 90:10) gave the product as red oil (498.1 mg, 55% yield).

^{1}H NMR: (400 MHz, $CDCl_3$) δ 8.65 (dd, *J* = 4.0, 0.8 Hz, 2H), 7.68 (ddd, *J* = 7.6, 7.6, 2.0 Hz, 2H), 7.39 (dd, *J* = 7.6, 0.8 Hz, 2H), 7.21 (ddd, *J* = 7.6, 4.0, 0.8 Hz, 2H), 6.06 (s, 2H); ^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$) δ 158.0, 149.5, 148.7, 136.5, 123.3, 122.7, 120.6; IR: (ATR) 3049, 3001, 1582, 1562, 1470, 1429, 991, 924, 797, 745 cm^{-1}; HRMS (CI) *m/z*: ([M+H]$^+$) Calculated for $C_{12}H_{11}N_2$ 183.0922; Found 183.0924

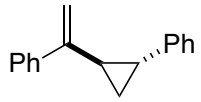
methyl(4-vinylphenyl)sulfane (1q)



^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.33 (d, *J* = 8.4 Hz, 2H), 7.21 (d, *J* = 8.4 Hz, 2H), 6.67 (dd, *J* = 17.6, 10.8 Hz, 1H), 5.70 (d, *J* = 17.6 Hz, 1H), 5.21 (d, *J* = 10.8 Hz, 1H), 2.49 (s, 3H); ^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$) δ 138.1, 136.3, 134.7, 126.7, 113.3, 15.9 (one sp^2 signal was not observed

because of overlapping)
The analytical data for this compound were in excellent agreement with the reported data.[8]

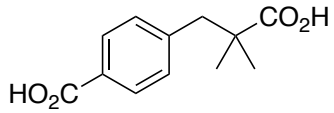
***trans*-(1-(2-phenylcyclopropyl)vinyl)benzene (1r)**



^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.54–7.47 (m, 2H), 7.34–7.12 (m, 8H), 5.37 (s, 1H), 5.04 (s, 1H), 2.04–1.88 (m, 2H), 1.44–1.32 (m, 1H), 1.31–1.20 (m, 1H); ^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$) δ 148.4, 142.7, 141.1, 128.6, 128.4, 127.7, 126.2, 125.87, 125.86, 109.5, 28.0, 26.6, 16.0
The analytical data for this compound were in excellent agreement with the reported data.[9]

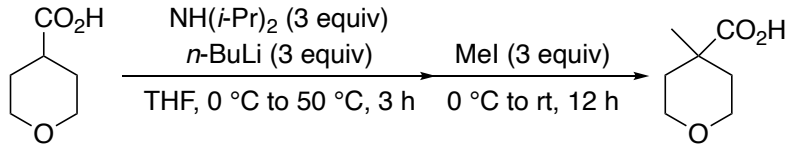
4. Preparation of carboxylic acids

4-(2-carboxy-2-methylpropyl)benzoic acid (2e)



^{1}H NMR: (400 MHz, DMSO-d_6) δ 12.6 (brs, 2H), 7.84 (d, J = 8.4 Hz, 2H), 7.26 (d, J = 7.6 Hz, 2H), 2.85 (s, 2H), 1.07 (s, 6H); ^{13}C{^{1}H} NMR: (100 MHz, DMSO-d_6) δ 178.1, 167.3, 143.4, 130.2, 128.9, 45.2, 42.6, 24.8 (one sp^2 signal was not observed because of overlapping)
The analytical data for this compound were in excellent agreement with the reported data.[10]

4-methyltetrahydro-2*H*-pyran-4-carboxylic acid (2j)

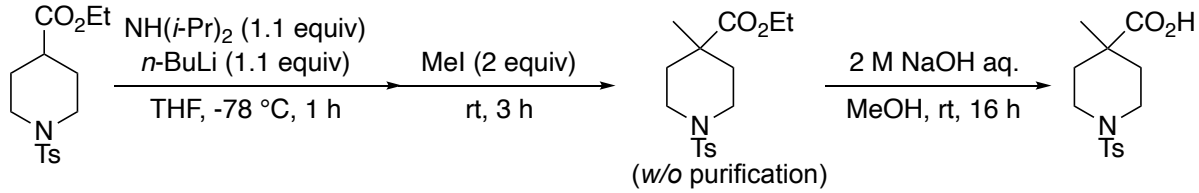


A heat-gun-dried round-bottom flask containing a magnetic stir bar was charged with dry THF (30 mL) and cooled to −78 °C. Diisopropylamine (4.63 g, 46 mmol) and *n*-BuLi (1.6 M in hexane, 28 mL, 45 mmol) were added, and the solution was allowed to stir at −78 °C for 30 min. Tetrahydro-2*H*-pyran-4-carboxylic acid (1.94 g, 15 mmol) in THF (10 mL) was then added dropwise over 10 min, and the resulting solution was stirred an additional 30 min. The resulting mixture was heated at 50 °C for 3 h. The reaction mixture was cooled to 0 °C and methyl iodide (6.27 g, 44 mmol) was added dropwise. The mixture was stirred for 12 h before being quenched with water (20 mL). The aqueous layer was washed with Et_2O (3 × 20 mL). Then, the combined aqueous layers were acidified with sat. 2 M HCl aq. until pH = 2. The mixture was extracted with Et_2O (3 x 20 mL), and the collected organic layers were dried over Na_2SO_4, filtrated, and concentrated under reduced pressure. Recrystallization from hexane/Et_2O gave the product **2j** as a

brown solid (1.25 g, 58% yield).

mp: 67.8–68.7 °C; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 3.86–3.78 (m, 2H), 3.60–3.50 (m, 2H), 2.12–2.03 (m, 2H), 1.59–1.48 (m, 2H), 1.30 (s, 3H); $^{13}C\{^{1}H\}$ NMR: (100 MHz, $CDCl_3$) δ 183.0, 65.3, 40.9, 35.2, 26.3; IR: (ATR) 2955, 2922, 2872, 1715, 1454, 1304, 1207, 1161, 1020, 880, 820 cm^{-1}; HRMS (CI) *m/z*: ($[M+H]^+$) Calculated for $C_7H_{13}O_3$ 145.0865; Found 145.0869

4-methyl-1-tosylpiperidine-4-carboxylic acid (2k)

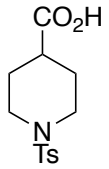


Step 1: A heat-gun-dried round-bottom flask containing a magnetic stir bar was charged with dry THF (15 mL) and cooled to −78 °C. Diisopropylamine (893.4 mg, 8.8 mmol) and *n*-BuLi (1.6 M in hexane, 5.5 mL, 8.8 mmol) were added, and the solution was allowed to stir at −78 °C for 30 min. Ethyl 1-tosylpiperidine-4-carboxylate (2.49 g, 8.0 mmol) in THF (8 mL) was then added, and the solution was stirred an additional 1 h. Methyl iodide (2.41 g, 17 mmol) was added dropwise over 10 min, and the reaction mixture was stirred at this temperature for 1 h and then allowed to warm to room temperature. The mixture was stirred for 3 h before being quenched with water (20 mL). The aqueous layer was extracted with Et_2O (3 × 20 mL), and the combined organic layers were dried over Na_2SO_4. The solution was concentrated under reduced pressure to give the crude product, which was directly used for the next step.

Step 2: The crude product was dissolved in the mixture of MeOH (15 mL) and aqueous NaOH aq. (2 M, 40 mL), and the solution was stirred at rt for 16 h. Then, the solution was concentrated under reduced pressure, and the resulting aqueous layer was washed with Et_2O (2 × 20 mL) to remove impurities and acidified with 2 M HCl aq. The aqueous layer was extracted with Et_2O (3 × 20 mL), and the collected organic layers were dried over Na_2SO_4, filtrated, and concentrated under reduced pressure. Recrystallization from hexane/Et_2O gave the product **2k** as a white solid (1.72 g, 72% yield).

mp: 164.2–166.5 °C; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.63 (d, J = 8.4 Hz, 2H), 7.31 (d, J = 8.4 Hz, 2H), 3.47–3.38 (m, 2H), 2.69–2.58 (m, 2H), 2.43 (s, 3H), 2.19–2.09 (m, 2H), 1.61–1.51 (m, 2H), 1.20 (s, 3H); $^{13}C\{^{1}H\}$ NMR: (100 MHz, $CDCl_3$) δ 181.8, 143.6, 133.8, 129.8, 127.8, 43.6, 41.0, 34.0, 25.8, 21.7; IR: (ATR) 2978, 2936, 2862, 1688, 1346, 1329, 1207, 1173, 1157, 1090, 1057, 935, 719 cm^{-1}; HRMS (DRAT) *m/z*: ($[M+H]^+$) Calculated for $C_{14}H_{20}NO_4S$ 298.1113; Found 298.1100

1-tosylpiperidine-4-carboxylic acid (2p)

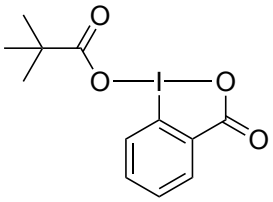


^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.0 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 3.73–3.60 (m, 2H), 2.55–2.40 (m, 5H), 2.37–2.25 (m, 1H), 2.10–1.95 (m, 2H), 1.93–1.75 (m, 2H); ^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$) δ 180.0, 143.8, 133.1, 129.8, 127.8, 45.5, 39.9, 27.3, 21.6

The analytical data for this compound were in excellent agreement with the reported data.[11]

5. Preparation of a hypervalent iodine reagent

1-pivaloyloxy-1,2-benziodoxol-3-(1*H*)-one (60)



According to the reported procedure[12], a reaction flask containing a magnetic stir bar was charged with pivalic anhydride (5 mL) and 1-hydroxy-1,2-benziodoxol-3-(1*H*)-one (1.32 g, 5 mmol) under nitrogen. The reaction mixture was heated up to 150 °C, while stirring vigorously until complete dissolution of the starting material (approx. 1 h). The resulting mixture was allowed to cool to room temperature and then left to settle in a freezer overnight. The white crystals were filtered, washed with Et_2O (3×5 mL) and dried, affording 1-pivaloyloxy-1,2-benziodoxol-3-(1*H*)-one as a white crystalline solid (1.08 g, 62%).

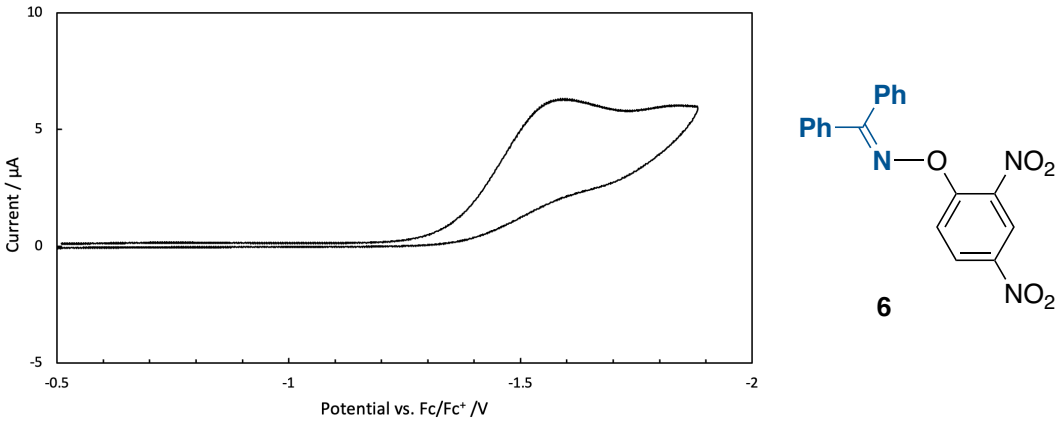
^{1}H NMR: (400 MHz, $CDCl_3$) δ 8.27 (d, *J* = 6.8 Hz, 1H), 8.00–7.90 (m, 2H), 7.72 (dd, *J* = 7.6, 7.6 Hz, 1H), 1.33 (s, 9H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 184.0, 168.4, 136.3, 133.3, 131.4, 129.4, 129.3, 118.7, 39.7, 27.9

The analytical data for this compound were in excellent agreement with the reported data.[12]

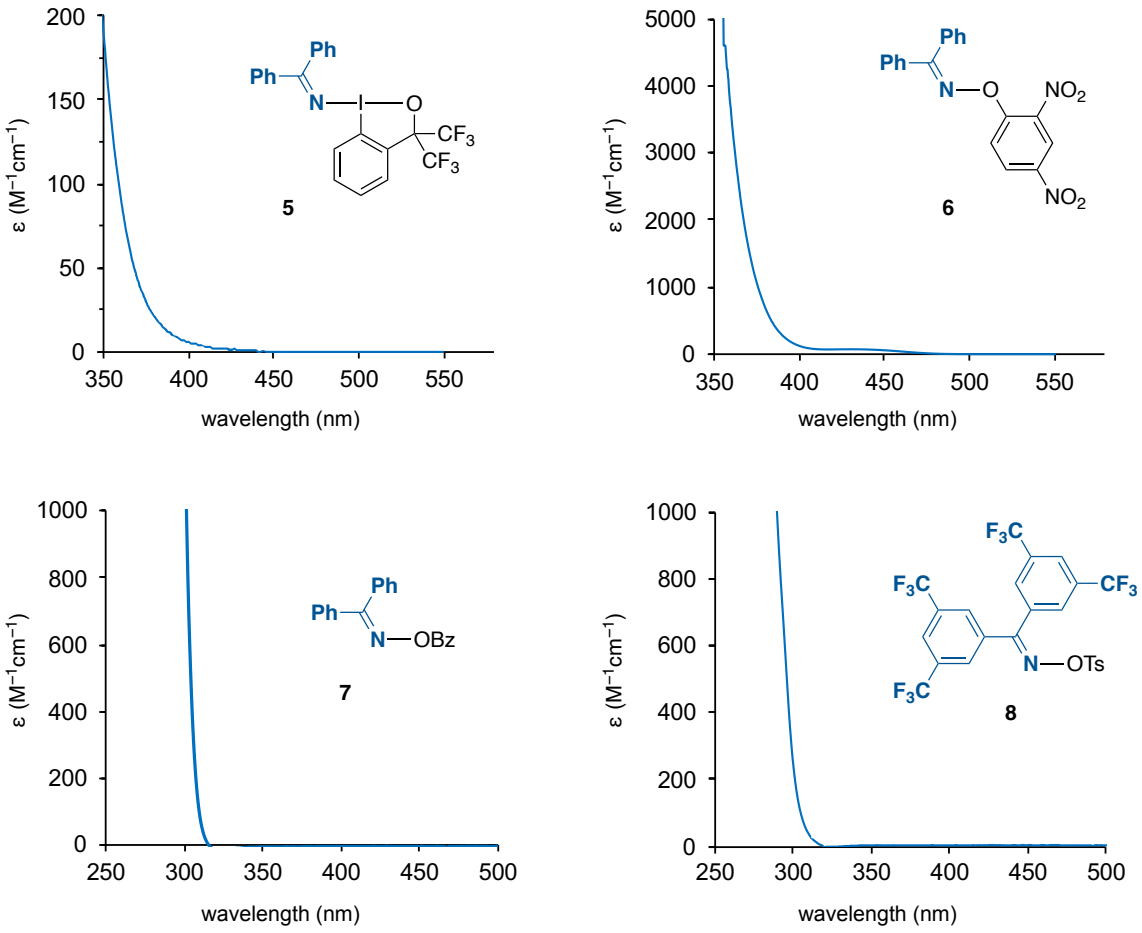
6. Cyclic voltammetry (CV) and UV-vis absorption analyses of aminating reagents

CV measurements: Cyclic voltammetry (CV) was performed with ALS-610E (BAS Inc.) system using a one-component cell equipped with a Ag working electrode, a platinum wire counter electrode, and Ag/Ag^+ reference electrode, and all the measurements were carried out in an dichloromethane solution (1 x 10^{-3} M), which was prepared from distilled and degassed dichloromethane, containing tetra-*n*-butylammonium hexafluorophosphate ($TBAPF_6$, 0.1 M) as the supporting electrolyte at room temperature under the Ar atmosphere at the scanning rate of 0.1 V/s. The potential values were corrected against the Fc/Fc^+ (Fc = ferrocene) redox potential.

No reduction wave of reagents **5**, **7**, and **8** was observed under the conditions used.



UV-vis absorption analyses: All samples were prepared using dry DMSO which were degassed by bubbling with N_2 gas for 30 min before use. A 10 mL volumetric flask was charged with **5**–**8** (0.01 mmol) and DMSO (10 mL). The solution was transferred to 1 cm^2 quartz cuvette. The resulting UV-vis absorption spectra are shown below.



7. Alkylamination: experimental procedures, unsuccessful substrates, and product data

General procedure II: A reaction vial containing a magnetic stir bar was charged with alkene, carboxylic acid, iodine reagent, K_2CO_3, and DMSO. After the vial was purged with nitrogen and sealed with a screw cap, the mixture was stirred and irradiated with a Kessil lamp 467 nm (40W, 100% intensity, 2 cm away (The measured light intensity is >480 mW.)) with a cooling fun (The reaction temperature within the reaction vial was maintained around 27 °C). After 12 h of irradiation, the reaction was then quenched with H_2O. The mixture was extracted with EtOAc. The combined organic extracts were dried over Na_2SO_4, filtrated, and concentrated under reduced pressure to give the crude product. Purification by flash column chromatography on NH silica gel (hexane/EtOAc) gave the product.

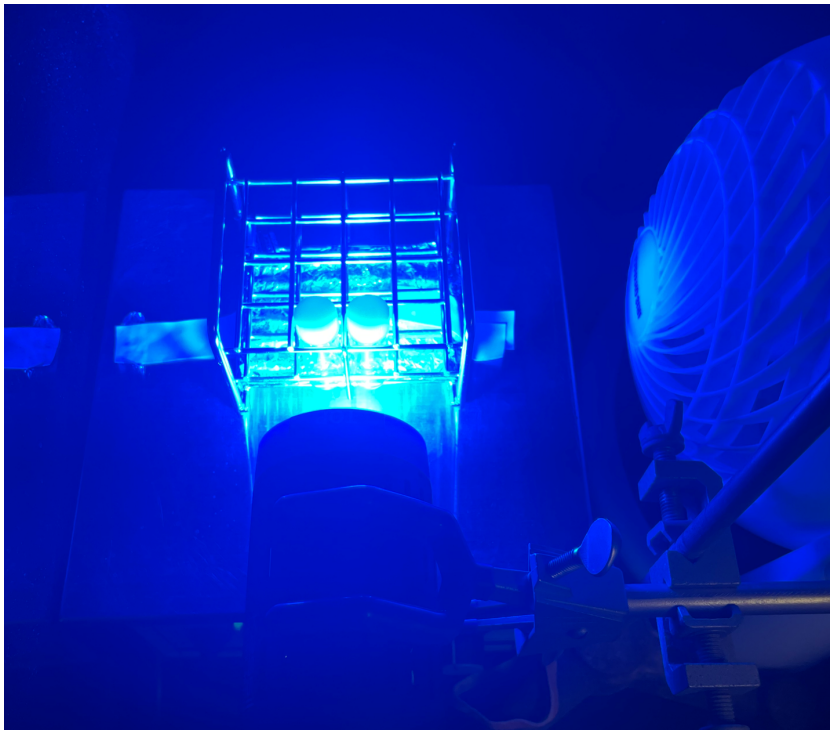
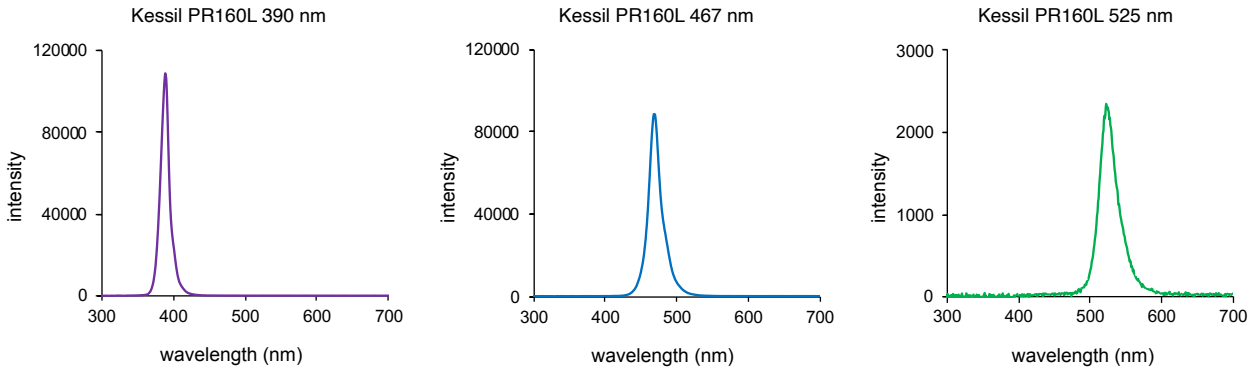


Figure S2. Reaction setup

General procedure III: A reaction vial containing a magnetic stir bar was charged with alkene, carboxylic acid, iodine reagent, KOAc, and acetone. After the vial was purged with nitrogen and sealed with a screw cap, the mixture was stirred and irradiated with a Kessil lamp 390 nm (40W, 100% intensity, 2 cm away, (The measured light intensity is >480 mW.)) with a cooling fun (The reaction temperature within the reaction vial was maintained around 27 °C). After 2 h of irradiation, the reaction was then quenched with H_2O. The mixture was extracted with EtOAc. The combined organic extracts were dried over Na_2SO_4, filtrated, and concentrated under reduced pressure to give the crude product. Purification by flash column chromatography on NH silica gel (hexane/EtOAc) gave the product.

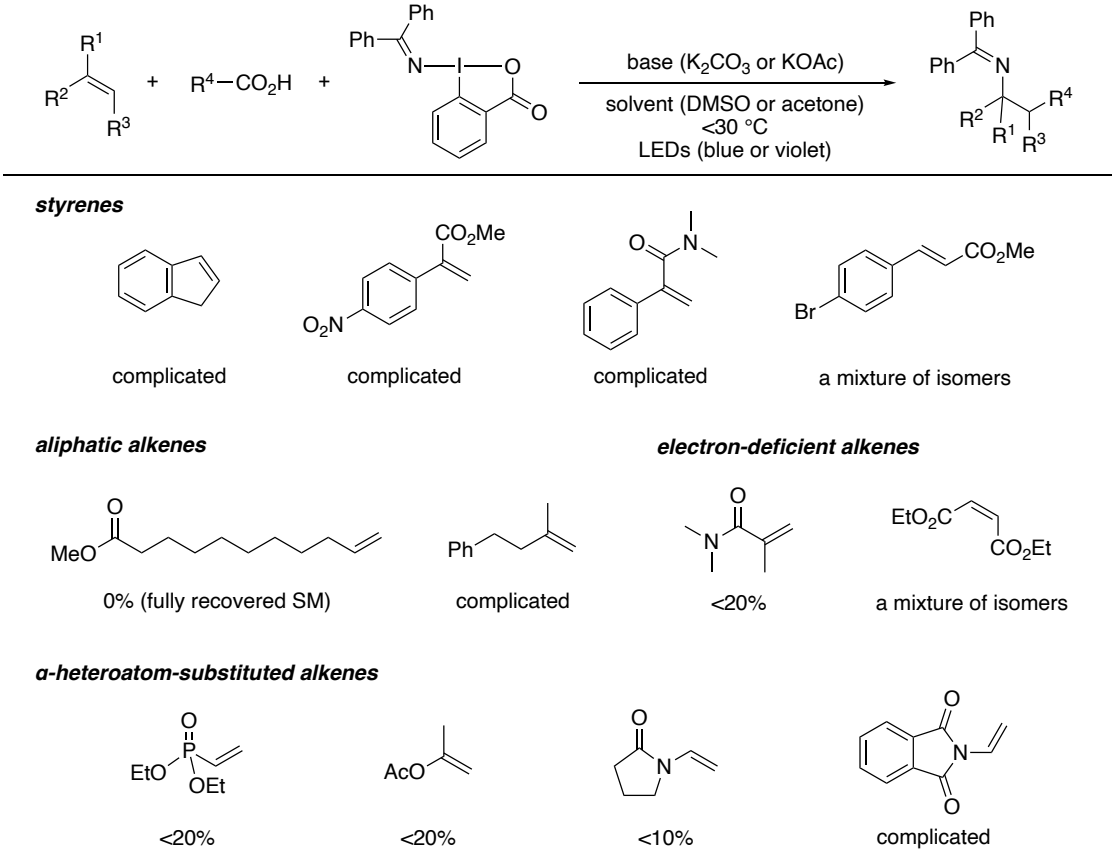
Emission spectra of the LEDs used in the reaction



Unsuccessful Substrates

According to general procedure **II** or **III**, the reactions using alkenes listed below were examined.

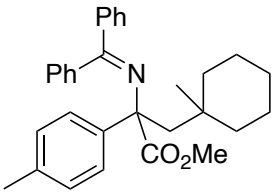
Scheme S1. List of Unsuccessful Substrates[a]



[a] Yields are determined by ^{1}H NMR analysis of the crude mixtures.

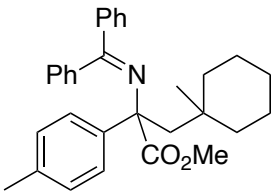
Product data

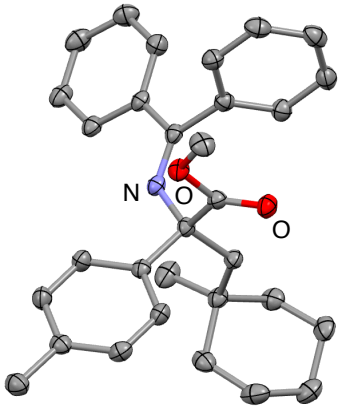
methyl 2-((diphenylmethylene)amino)-3-(1-methylcyclohexyl)-2-(*p*-tolyl)propanoate (4)



According to general procedure **II**, the reaction using alkene **1a** (72.9 mg, 0.41 mmol), carboxylic acid **2a** (57.2 mg, 0.40 mmol), iodine reagent **3a** (204.8 mg, 0.48 mmol), K_2CO_3 (54.7 mg, 0.40 mmol), and DMSO (4 mL) was conducted for 12 h. Purification by flash column chromatography on NH silica gel (hexane/EtOAc = 98:2) and gel permeation chromatography (GPC, $CHCl_3$ as an eluent) gave the product as a white solid (153.3 mg, 84% yield). Recrystallization from hexane/$CHCl_3$ gave a single crystal suitable for X-ray analysis.

mp: 96.5–99.8 °C; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.4 Hz, 2H), 7.60–7.45 (m, 2H), 7.43–7.30 (m, 6H), 7.16–7.04 (m, 4H), 3.17 (s, 3H), 2.46 (d, *J* = 14.8 Hz, 1H), 2.33 (d, *J* = 14.8 Hz, 1H), 2.32 (s, 3H), 1.42–0.99 (m, 10H), 0.76 (s, 3H); ^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$) δ 174.9, 165.1, 142.3, 141.4, 137.2, 136.3, 130.0, 128.9, 128.8, 128.6, 128.3, 128.1, 127.6, 126.2, 71.5, 53.1, 51.7, 40.2, 39.5, 34.3, 26.4, 25.3, 22.2, 22.1, 21.2; IR: (ATR) 2924, 2843, 1728, 1628, 1445, 1221, 1020, 820, 770 cm^{-1}; HRMS (FAB+) *m/z*: ([M+H]$^+$) Calculated for $C_{31}H_{36}NO_2$ 454.2746; Found 454.2753



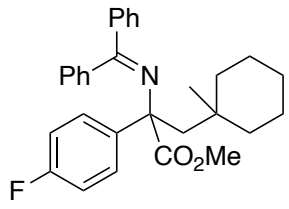


The structure of **4** was determined by X-ray structural analysis. Thermal elipsoids are drawn at the 50% probability level. CCDC 2286656 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

CCDC number	2286656
Empirical formula	$C_{31}H_{35}NO_2$
Formula weight	453.60
Temperature/K	123.15

Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	9.6712(2)
b/Å	10.1319(2)
c/Å	25.4616(4)
α/°	90
β/°	96.565(2)
γ/°	90
Volume/Å^3	2478.56(8)
Z	4
ρ_{calc}g/cm^3	1.216
μ/mm^{-1}	0.580
F(000)	976.0
Crystal size/mm^3	0.23 × 0.214 × 0.187
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	6.99 to 148.678
Index ranges	-12 ≤ h ≤ 12, -12 ≤ k ≤ 12, -31 ≤ l ≤ 25
Reflections collected	31136
Independent reflections	4975 [R_{int} = 0.0489, R_{sigma} = 0.0307]
Data/restraints/parameters	4975/0/310
Goodness-of-fit on F^2	1.046
Final R indexes [I>=2σ (I)]	R_1 = 0.0406, wR_2 = 0.1060
Final R indexes [all data]	R_1 = 0.0433, wR_2 = 0.1086
Largest diff. peak/hole / e Å^{-3}	0.21/-0.23

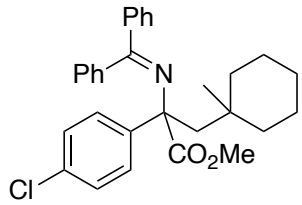
methyl 2-((diphenylmethylene)amino)-2-(4-fluorophenyl)-3-(1-methylcyclohexyl)propanoate (9)



According to general procedure **II**, the reaction using alkene **1b** (74.2 mg, 0.41 mmol), carboxylic acid **2a** (56.3 mg, 0.40 mmol), iodine reagent **3a** (207.0 mg, 0.49 mmol), K_2CO_3 (55.4 mg, 0.40 mmol), and DMSO (4 mL) was conducted for 12 h. Purification by flash column chromatography on NH silica gel (hexane/EtOAc = 95:5) and gel permeation chromatography (GPC, $CHCl_3$ as an

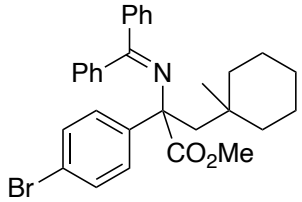
eluent) gave the product as a white solid (168.3 mg, 92% yield).
mp: 121.4–123.2 °C; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.69 (d, J = 8.0 Hz, 2H), 7.67–7.59 (m, 2H), 7.45–7.31 (m, 6H), 7.17–7.06 (m, 2H), 6.97 (dd, J = 9.2, 8.4 Hz, 2H), 3.18 (s, 3H), 2.45 (d, J = 15.2 Hz, 1H), 2.35 (d, J = 15.2 Hz, 1H), 1.44–0.97 (m, 10H), 0.77 (s, 3H); ^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$) δ 174.6, 165.6, 161.6 (d, $J_{C–F}$ = 243.7 Hz), 141.2, 141.1 (d, $J_{C–F}$ = 3.3 Hz), 137.0, 130.2, 128.8, 128.54, 128.50, 128.1, 128.0 (d, $J_{C–F}$ = 8.2 Hz), 127.7, 114.9 (d, $J_{C–F}$ = 21.4 Hz), 71.3, 53.4, 51.8, 40.2, 39.5, 34.4, 26.3, 25.3, 22.2, 22.0; ^{19}F{^{1}H} NMR: (100 MHz, $CDCl_3$) δ −119.0; IR: (ATR) 2928, 1732, 1630, 1504, 1215, 1155, 1030, 841 cm^{-1}; HRMS (FAB+) m/z: ([M+H]$^+$) Calculated for $C_{30}H_{33}FNO_2$ 458.2495; Found 458.2489

methyl 2-(4-chlorophenyl)-2-((diphenylmethylene)amino)-3-(1-methylcyclohexyl)propanoate (10)



According to general procedure **II**, the reaction using alkene **1c** (79.2 mg, 0.40 mmol), carboxylic acid **2a** (56.4 mg, 0.40 mmol), iodine reagent **3a** (204.8 mg, 0.48 mmol), K_2CO_3 (58.8 mg, 0.43 mmol), and DMSO (4 mL) was conducted for 12 h. Purification by flash column chromatography on NH silica gel (hexane/EtOAc = 95:5) and gel permeation chromatography (GPC, $CHCl_3$ as an eluent) gave the product as a white solid (145.7 mg, 77% yield).
mp: 121.7–127.4 °C; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.69 (d, J = 6.8 Hz, 2H), 7.66–7.54 (m, 2H), 7.44–7.30 (m, 6H), 7.26 (d, J = 8.8 Hz, 2H), 7.12–7.05 (m, 2H), 3.17 (s, 3H), 2.44 (d, J = 14.8 Hz, 1H), 2.34 (d, J = 14.8 Hz, 1H), 1.44–0.99 (m, 10H), 0.76 (s, 3H); ^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$) δ 174.5, 165.7, 144.1, 141.1, 137.0, 132.6, 130.3, 128.8, 128.6, 128.3, 128.2, 127.9, 127.7, 71.4, 53.4, 51.8, 40.2, 39.5, 34.4, 26.3, 25.3, 22.2, 22.1 (one sp^2 signal was not observed because of overlapping); IR: (ATR) 2916, 1728, 1634, 1489, 1443, 1209, 1030, 1013, 772, 758 cm^{-1}; HRMS (FAB+) m/z: ([M+H]$^+$) Calculated for $C_{30}H_{33}ClNO_2$ 474.2200; Found 474.2187

methyl 2-(4-bromophenyl)-2-((diphenylmethylene)amino)-3-(1-methylcyclohexyl)propanoate (11)

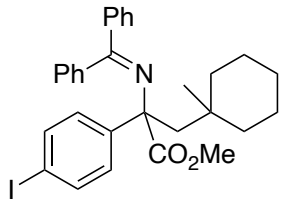


According to general procedure **II**, the reaction using alkene **1d** (98.6 mg, 0.41 mmol), carboxylic acid **2a** (56.8 mg, 0.40 mmol), iodine reagent **3a** (206.0 mg, 0.48 mmol), K_2CO_3 (54.8 mg, 0.40

mmol), and DMSO (4 mL) was conducted for 12 h. Purification by flash column chromatography on NH silica gel (hexane/EtOAc = 95:5) and gel permeation chromatography (GPC, $CHCl_3$ as an eluent) gave the product as a white solid (155.5 mg, 75% yield).

mp: 133.2–134.4 °C; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 7.2 Hz, 2H), 7.62–7.51 (m, 2H), 7.50–7.30 (m, 8H), 7.16–7.06 (m, 2H), 3.17 (s, 3H), 2.44 (d, *J* = 15.2 Hz, 1H), 2.34 (d, *J* = 15.2 Hz, 1H), 1.43–0.97 (m, 10H), 0.76 (s, 3H); ^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$) δ 174.4, 165.7, 144.6, 141.1, 137.0, 131.3, 130.3, 128.8, 128.6, 128.3, 128.2, 127.7, 120.8, 71.4, 53.3, 51.8, 40.2, 39.5, 34.4, 26.3, 25.3, 22.2, 22.1 (one sp^2 signal was not observed because of overlapping); IR: (ATR) 2924, 1732, 1485, 1445, 1213 cm^{-1}; HRMS (FAB+) *m*/*z*: ([M+H]$^+$) Calculated for $C_{30}H_{33}BrNO_2$ 518.1695; Found 518.1688

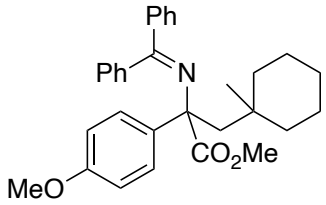
methyl 2-((diphenylmethylene)amino)-2-(4-iodophenyl)-3-(1-methylcyclohexyl)propanoate (12)



According to general procedure **II**, the reaction using alkene **1e** (117.0 mg, 0.41 mmol), carboxylic acid **2a** (56.6 mg, 0.40 mmol), iodine reagent **3a** (205.8 mg, 0.48 mmol), K_2CO_3 (55.2 mg, 0.40 mmol), and DMSO (4 mL) was conducted for 12 h. Purification by flash column chromatography on NH silica gel (hexane/EtOAc = 95:5) and gel permeation chromatography (GPC, $CHCl_3$ as an eluent) gave the product as a white solid (161.8 mg, 72% yield).

mp: 128.2–130.9 °C; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 6.8 Hz, 2H), 7.60 (d, *J* = 8.4 Hz, 2H), 7.47–7.29 (m, 8H), 7.13–7.05 (m, 2H), 3.17 (s, 3H), 2.43 (d, *J* = 14.8 Hz, 1H), 2.34 (d, *J* = 14.8 Hz, 1H), 1.43–0.97 (m, 10H), 0.76 (s, 3H) ; ^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$) δ 174.4, 165.7, 145.4, 141.1, 137.2, 137.0, 130.3, 128.8, 128.6, 128.5, 128.2, 127.7, 92.5, 71.5, 53.2, 51.8, 40.2, 39.6, 34.4, 26.3, 25.3, 22.2, 22.1 (one sp^2 signal was not observed because of overlapping); IR: (ATR) 2922, 1732, 1628, 1445, 1213, 1001 cm^{-1}; HRMS (FAB+) *m*/*z*: ([M+H]$^+$) Calculated for $C_{30}H_{33}NO_2I$ 566.1556; Found 566.1567

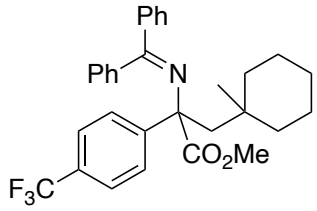
methyl 2-((diphenylmethylene)amino)-2-(4-methoxyphenyl)-3-(1-methylcyclohexyl)propanoate (13)



According to general procedure **II**, the reaction using alkene **1f** (76.4 mg, 0.40 mmol), carboxylic acid **2a** (56.8 mg, 0.40 mmol), iodine reagent **3a** (204.6 mg, 0.48 mmol), K_2CO_3 (55.3 mg, 0.40 mmol), and DMSO (4 mL) was conducted for 12 h. Purification by flash column chromatography on NH silica gel (hexane/EtOAc = 95:5) gave the product as a pale yellow solid (149.7 mg, 80% yield).

mp: 168.9–171.7 °C; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.70 (d, J = 6.8 Hz, 2H), 7.61–7.49 (m, 2H), 7.43–7.29 (m, 6H), 7.13–7.05 (m, 2H), 6.82 (d, J = 9.2 Hz, 2H), 3.80 (s, 3H), 3.19 (s, 3H), 2.45 (d, J = 14.4 Hz, 1H), 2.32 (d, J = 14.4 Hz, 1H), 1.44–0.99 (m, 10H), 0.78 (s, 3H); ^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$) δ 175.0, 165.2, 158.4, 141.4, 137.5, 137.3, 130.1, 128.8, 128.6, 128.4, 128.1, 127.7, 127.5, 113.5, 71.2, 55.3, 53.2, 51.7, 40.2, 39.5, 34.4, 26.4, 25.3, 22.2, 22.1; IR: (ATR) 2926, 1719, 1636, 1506, 1248, 1219, 1173, 1030, 829 cm^{-1}; HRMS (FAB+) *m*/*z*: ([M+H]$^+$) Calculated for $C_{31}H_{36}NO_3$ 470.2695; Found 470.2692

methyl 2-((diphenylmethylene)amino)-3-(1-methylcyclohexyl)-2-(4-(trifluoromethyl)phenyl)propanoate (14)

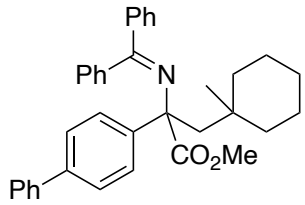


According to general procedure **II**, the reaction using alkene **1g** (92.6 mg, 0.40 mmol), carboxylic acid **2a** (56.5 mg, 0.40 mmol), iodine reagent **3a** (204.2 mg, 0.48 mmol), K_2CO_3 (54.9 mg, 0.40 mmol), and DMSO (4 mL) was conducted for 12 h. Purification by flash column chromatography on NH silica gel (hexane/EtOAc = 95:5) and gel permeation chromatography (GPC, $CHCl_3$ as an eluent) gave the product as a white solid (150.1 mg, 74% yield).

mp: 117.8–118.9 °C; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.85–7.76 (m, 2H), 7.70 (d, J = 8.0 Hz, 2H), 7.54 (d, J = 8.0 Hz, 2H), 7.45–7.31 (m, 6H), 7.13–7.08 (m, 2H), 3.19 (s, 3H), 2.49 (d, J = 14.8 Hz, 1H), 2.40 (d, J = 14.8 Hz, 1H), 1.45–0.96 (m, 10H), 0.76 (s, 3H); ^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$) δ 174.2, 166.0, 149.6, 141.0, 136.9, 130.4, 129.1 (q, $J_{C–F}$ = 32.1 Hz), 128.8, 128.6, 128.5, 128.2, 127.8, 126.8, 125.1 (q, $J_{C–F}$ = 4.1 Hz), 124.4 (q, $J_{C–F}$ = 270.8 Hz), 71.7, 53.4, 51.9, 40.2, 39.6, 34.4, 26.3, 25.2, 22.1, 22.0; ^{19}F{^{1}H} NMR: (377 MHz, $CDCl_3$) δ −64.9; IR: (ATR) 2926, 1734, 1628, 1325, 1163, 1115, 1065, 851 cm^{-1}; HRMS (FAB+) *m*/*z*: ([M+H]$^+$) Calculated for

$C_{31}H_{33}F_3NO_2$ 508.2463; Found 508.2469

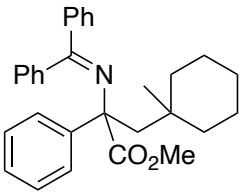
methyl 2-([1,1'-biphenyl]-4-yl)-2-((diphenylmethylene)amino)-3-(1-methylcyclohexyl)propanoate (15)



According to general procedure **II**, the reaction using alkene **1h** (96.2 mg, 0.40 mmol), carboxylic acid **2a** (57.0 mg, 0.40 mmol), iodine reagent **3a** (205.2 mg, 0.48 mmol), K_2CO_3 (55.2 mg, 0.40 mmol), and DMSO (4 mL) was conducted for 12 h. Purification by flash column chromatography on NH silica gel (hexane/EtOAc = 95:5) and gel permeation chromatography (GPC, $CHCl_3$ as an eluent) gave the product as a white solid (180.7 mg, 88% yield).

mp: 137.2–139.6 °C; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 6.8 Hz, 2H), 7.70–7.65 (m, 2H), 7.61 (d, *J* = 7.2 Hz, 2H), δ 7.51 (d, *J* = 8.8 Hz, 2H), 7.47–7.29 (m, 9H), 7.10 (d, *J* = 7.2 Hz, 2H), 3.23 (s, 3H), 2.52 (d, *J* = 15.2 Hz, 1H), 2.40 (d, *J* = 15.2 Hz, 1H), 1.45–1.02 (m, 10H), 0.82 (s, 3H); ^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$) δ 174.8, 165.5, 144.5, 141.3, 141.0, 139.5, 137.3, 130.2, 128.9, 128.8, 128.6, 128.3, 128.1, 127.7, 127.3, 127.1, 126.8, 71.6, 53.2, 51.8, 40.2, 39.5, 34.4, 26.4, 25.3, 22.2, 22.1 (one sp^2 signal was not observed because of overlapping); IR: (ATR) 2920, 1728, 1628, 1443, 1215 cm^{-1}; HRMS (FAB+) *m/z*: ($[M+H]^+$) Calculated for $C_{36}H_{38}NO_2$ 516.2903; Found 516.2900

methyl 2-((diphenylmethylene)amino)-3-(1-methylcyclohexyl)-2-phenylpropanoate (16)

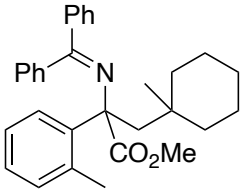


According to general procedure **II**, the reaction using alkene **1i** (66.2 mg, 0.41 mmol), carboxylic acid **2a** (56.8 mg, 0.40 mmol), iodine reagent **3a** (206.2 mg, 0.48 mmol), K_2CO_3 (56.2 mg, 0.41 mmol), and DMSO (4 mL) was conducted for 12 h. Purification by flash column chromatography on NH silica gel (hexane/EtOAc = 95:5) and gel permeation chromatography (GPC, $CHCl_3$ as an eluent) gave the product as a viscous oil (87.3 mg, 50% yield).

^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.77–7.63 (m, 2H), 7.72 (d, *J* = 7.2 Hz, 2H), 7.44–7.33 (m, 6H), 7.33–7.27 (m, 2H), 7.25–7.18 (m, 1H), 7.15–7.06 (m, 2H), 3.18 (s, 3H), 2.49 (d, *J* = 14.8 Hz, 1H), 2.35 (d, *J* = 14.8 Hz, 1H), 1.42–0.98 (m, 10H), 0.76 (s, 3H); ^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$) δ 174.8, 165.3, 145.3, 141.3, 137.2, 130.1, 128.8, 128.6, 128.4, 128.2, 128.1, 127.7, 126.9, 126.4, 71.7, 53.3, 51.7, 40.2, 39.4, 34.4, 26.4, 25.3, 22.2, 22.1; IR: (ATR) 2922, 1728, 1628, 1445, 1213,

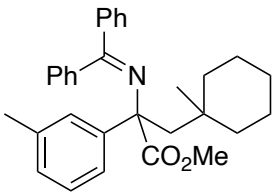
1030, 764 cm^{-1}; HRMS (FAB+) *m*/*z*: ([M+H]$^+$) Calculated for $C_{30}H_{34}NO_2$ 440.2590; Found 440.2587

methyl 2-((diphenylmethylene)amino)-3-(1-methylcyclohexyl)-2-(*o*-tolyl)propanoate (17)



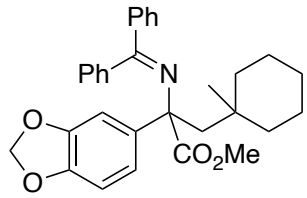
According to general procedure **II**, the reaction using alkene **1j** (72.2 mg, 0.41 mmol), carboxylic acid **2a** (57.8 mg, 0.41 mmol), iodine reagent **3a** (206.2 mg, 0.48 mmol), K_2CO_3 (55.2 mg, 0.40 mmol), and DMSO (4 mL) was conducted for 12 h. Purification by flash column chromatography on NH silica gel (hexane/EtOAc = 95:5) and gel permeation chromatography (GPC, $CHCl_3$ as an eluent) gave the product as a white solid (128.7 mg, 71% yield).
mp: 104.1–105.2 °C; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 6.8 Hz, 2H), 7.41–7.26 (m, 4H), 7.25–6.10 (m, 8H), 3.55 (s, 3H), 2.47 (d, *J* = 14.0 Hz, 1H), 2.36 (d, *J* = 14.0 Hz, 1H), 2.20 (s, 3H), 1.54–1.10 (m, 10H), 0.98 (s, 3H); ^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$) δ 175.6, 163.8, 143.6, 141.3, 137.5, 136.4, 131.7, 129.9, 128.6, 128.0, 127.4, 127.3, 126.8, 126.4, 125.3, 70.6, 52.0, 51.6, 40.4, 38.7, 34.3, 26.4, 24.5, 22.3, 22.1, 21.4 (one sp^2 signal was not observed because of overlapping); IR: (ATR) 2940, 1749, 1626, 1445, 1204, 1140, 1059 cm^{-1}; HRMS (FAB+) *m*/*z*: ([M+H]$^+$) Calculated for $C_{31}H_{36}NO_2$ 454.2746; Found 454.2750

methyl 2-((diphenylmethylene)amino)-3-(1-methylcyclohexyl)-2-(*m*-tolyl)propanoate (18)



According to general procedure **II**, the reaction using alkene **1k** (70.2 mg, 0.40 mmol), carboxylic acid **2a** (57.0 mg, 0.40 mmol), iodine reagent **3a** (206.3 mg, 0.48 mmol), K_2CO_3 (56.3 mg, 0.41 mmol), and DMSO (4 mL) was conducted for 12 h. Purification by flash column chromatography on NH silica gel (hexane/EtOAc = 95:5) gave the product as a white solid (143.3 mg, 79% yield).
mp: 152.5–153.7 °C; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 6.8 Hz, 2H), 7.50–7.28 (m, 8H), 7.16 (dd, *J* = 7.6, 7.2 Hz, 1H), 7.12–7.03. (m, 2H), 7.01 (d, *J* = 7.6 Hz, 1H), 3.21 (s, 3H), 2.47 (d, *J* = 14.4 Hz, 1H), 2.36–2.25 (m, 4H), 1.43–0.96 (m, 10H), 0.78 (s, 3H); ^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$) δ 174.9, 165.2, 145.1, 141.4, 137.6, 137.3, 130.1, 128.8, 128.5, 128.3, 128.1, 127.6, 127.0, 123.5, 71.6, 52.9, 51.8, 40.2, 39.4, 34.4, 26.4, 25.3, 22.2, 22.1, 21.9 (two sp^2 signals were not observed because of overlapping); IR: (ATR) 2920, 1724, 1636, 1443, 1211 cm^{-1}; HRMS (FAB+) *m*/*z*: ([M+H]$^+$) Calculated for $C_{31}H_{36}NO_2$ 454.2746; Found 454.2754

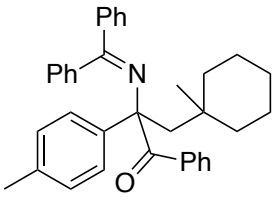
methyl 2-(benzo[*d*][1,3]dioxol-5-yl)-2-((diphenylmethylene)amino)-3-(1-methylcyclohexyl)propanoate (19)



According to general procedure **II**, the reaction using alkene **1l** (42.3 mg, 0.21 mmol), carboxylic acid **2a** (28.3 mg, 0.20 mmol), iodine reagent **3a** (102.7 mg, 0.24 mmol), K_2CO_3 (27.9 mg, 0.20 mmol), and DMSO (2 mL) was conducted for 12 h. Purification by flash column chromatography on NH silica gel (hexane/EtOAc = 85:15) gave the product as a pale yellow solid (67.4 mg, 70% yield).

mp: 174.3–177.4 °C; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.68 (dd, *J* = 8.4, 1.6 Hz, 2H), 7.42–7.30 (m, 6H), 7.24–7.18 (m, 1H), 7.17–7.05 (m, 3H), 6.72 (d, *J* = 8.4 Hz, 1H), 5.97–5.92 (m, 2H), 3.20 (s, 3H), 2.41 (d, *J* = 14.8 Hz, 1H), 2.31 (d, *J* = 14.8 Hz, 1H), 1.45–1.05 (m, 10H), 0.80 (s, 3H); ^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$) δ 174.8, 165.3, 147.7, 146.4, 141.3, 139.5, 137.2, 130.1, 128.8, 128.6, 128.4, 128.1, 127.7, 119.7, 108.0, 107.5, 101.0, 71.4, 53.3, 51.8, 40.2, 39.5, 34.4, 26.4, 25.3, 22.2, 22.1; IR: (ATR) 2916, 2860, 1719, 1630, 1487, 1431, 1240, 1211, 1032, 934, 770 cm^{-1}; HRMS (DRAT) *m*/*z*: ([M+H]$^+$) Calculated for $C_{31}H_{34}NO_4$ 484.2488; Found 484.2465

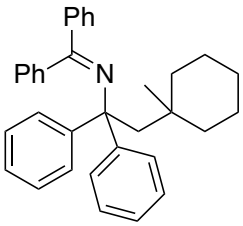
2-((diphenylmethylene)amino)-3-(1-methylcyclohexyl)-1-phenyl-2-(*p*-tolyl)propan-1-one (20)



According to general procedure **II**, the reaction using alkene **1m** (90.1 mg, 0.41 mmol), carboxylic acid **2a** (56.5 mg, 0.40 mmol), iodine reagent **3a** (205.3 mg, 0.48 mmol), K_2CO_3 (56.2 mg, 0.41 mmol), and DMSO (4 mL) was conducted for 12 h. Purification by flash column chromatography on NH silica gel (hexane/EtOAc = 95:5) and recrystallization from hexane/$CHCl_3$ gave the product as a white solid (132.9 mg, 67% yield).

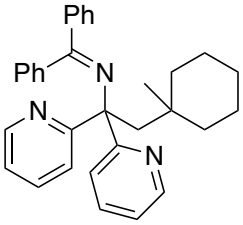
mp: 70.7–73.2 °C; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 8.72 (brs, 1H), 7.72 (dd, *J* = 8.0, 1.6 Hz, 2H), 7.65 (d, *J* = 7.3 Hz, 2H), 7.51–7.27 (m, 4H), 7.25–6.31 (m, 10H), 2.51 (d, *J* = 15.2 Hz, 1H), 2.28 (s, 3H), 2.24 (d, *J* = 15.2 Hz, 1H), 1.45–0.99 (m, 8H), 0.93–0.76 (m, 2H), 0.73 (s, 3H); ^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$) δ 198.0, 165.1, 141.9, 141.4, 137.3, 136.4, 134.3, 131.7, 131.3, 130.0, 129.3, 128.8, 128.6, 128.5, 128.1, 127.8, 127.4, 127.0, 75.7, 53.7, 40.9, 39.0, 34.2, 26.4, 25.7, 22.3, 22.0, 21.2; IR: (ATR) 2928, 2859, 1676, 1624, 1445, 1217, 1179, 779, 762 cm^{-1}; HRMS (CI) *m*/*z*: ([M+H]$^+$) Calculated for $C_{36}H_{38}NO$ 500.2953; Found 500.2949

***N*-(2-(1-methylcyclohexyl)-1,1-diphenylethyl)-1,1-diphenylmethanimine (21)**

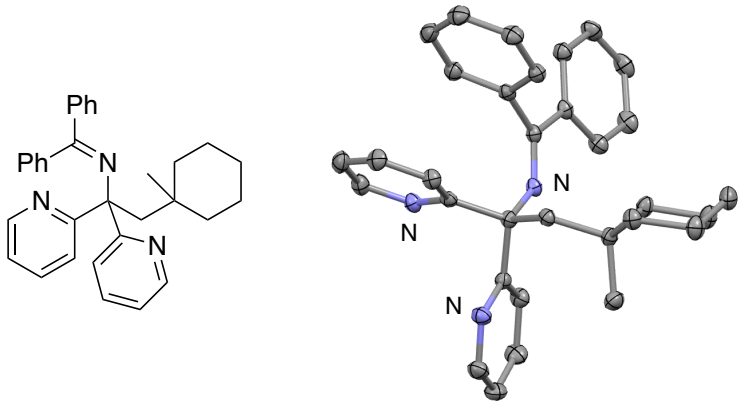


According to general procedure **II**, the reaction using alkene **1n** (72.9 mg, 0.40 mmol), carboxylic acid **2a** (57.1 mg, 0.40 mmol), iodine reagent **3a** (205.1 mg, 0.48 mmol), K_2CO_3 (54.9 mg, 0.40 mmol), and DMSO (4 mL) was conducted for 12 h. Purification by flash column chromatography on NH silica gel (hexane/EtOAc = 99:1) gave the product as a white solid (125.8 mg, 69% yield).
mp: 104.5–107.1 °C; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 7.2 Hz, 2H), 7.60–7.20 (m, 5H), 7.17–6.95 (m, 11H), 6.70–6.30 (m, 2H), 2.47 (s, 2H), 1.46–0.97 (m, 10H), 0.78 (s, 3H); ^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$) δ 164.5, 151.6, 142.4, 139.0, 129.7, 128.5, 128.1, 127.64, 127.59, 127.2, 126.6, 125.6, 68.8, 52.9, 40.1, 34.6, 26.5, 25.6, 22.3 (one sp^2 signal was not observed because of overlapping); IR: (ATR) 2920, 2859, 1626, 1489, 1445, 1263, 1028, 777, 762 cm^{-1}; HRMS (EI) *m*/*z*: (M^+) Calculated for $C_{34}H_{35}N$ 457.2770; Found 457.2764

***N*-(2-(1-methylcyclohexyl)-1,1-di(pyridin-2-yl)ethyl)-1,1-diphenylmethanimine (22)**



According to general procedure **II**, the reaction using alkene **1o** (40.4 mg, 0.22 mmol), carboxylic acid **2a** (56.5 mg, 0.40 mmol), iodine reagent **3a** (170.4 mg, 0.40 mmol), K_2CO_3 (56.0 mg, 0.41 mmol), and DMSO (2 mL) was conducted for 12 h. Purification by flash column chromatography on NH silica gel (hexane/EtOAc = 90:10) gave the product as a white solid (56.1 mg, 55% yield). Recrystallization from hexane/$CHCl_3$ gave a single crystal suitable for X-ray analysis.
mp: 136.1–138.4 °C; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 8.29 (d, *J* = 4.0 Hz, 2H), 8.10–7.20 (br, 2H), 7.68 (d, *J* = 6.4 Hz, 2H), 7.53–7.40 (m, 2H), 7.40–7.31 (m, 3H), 7.12–7.08 (m, 1H), 7.08–6.98 (m, 2H), 6.97–6.87 (m, 2H), 6.80–6.40 (m, 2H), 2.81 (brs, 2H), 1.45–1.05 (m, 10H), 0.77 (s, 3H); ^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$) δ 168.5, 165.1, 148.6, 141.6, 139.2, 135.8, 129.8, 128.6, 128.0, 127.4, 126.8, 122.6, 120.8, 73.4, 52.4, 39.9, 34.6, 26.4, 25.3, 22.3 (one sp^2 signal was not observed because of overlapping); IR: (ATR) 2920, 2855, 1632, 1584, 1460, 1427, 1261, 993, 768 cm^{-1}; HRMS (DRAT) *m*/*z*: ($[M+H]^+$) Calculated for $C_{32}H_{34}N_3$ 460.2753; Found 460.2758

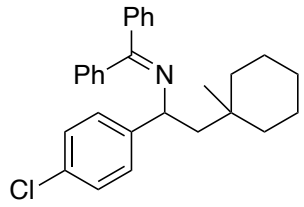


The structure of **22** was determined by X-ray structural analysis. Thermal elipsoids are drawn at the 50% probability level. CCDC 2286658 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

CCDC number	2286658
Empirical formula	$C_{32}H_{33}N_3$
Formula weight	459.61
Temperature/K	123.15
Crystal system	triclinic
Space group	P-1
a/Å	10.3382(2)
b/Å	15.2358(2)
c/Å	17.3918(2)
α/°	107.1090(10)
β/°	95.8940(10)
γ/°	102.6390(10)
Volume/Å^3	2513.40(7)
Z	4
ρ_{calc}g/cm^3	1.215
μ/mm^{-1}	0.544
F(000)	984.0
Crystal size/mm^3	0.093 × 0.078 × 0.039
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	6.29 to 155.14
Index ranges	-12 ≤ h ≤ 13, -19 ≤ k ≤ 18, -19 ≤ l ≤ 22
Reflections collected	33725

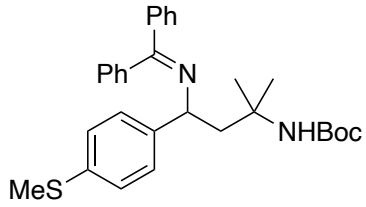
Independent reflections	10284 [R_{int} = 0.0472, R_{sigma} = 0.0478]
Data/restraints/parameters	10284/0/633
Goodness-of-fit on F^2	1.038
Final R indexes [I>=2σ (I)]	R_1 = 0.0402, wR_2 = 0.1011
Final R indexes [all data]	R_1 = 0.0477, wR_2 = 0.1058
Largest diff. peak/hole / e Å^{-3}	0.23/-0.24

_N_-(1-(4-chlorophenyl)-2-(1-methylcyclohexyl)ethyl)-1,1-diphenylmethanimine (23)



According to general procedure **II**, the reaction using alkene **1p** (63.2 mg, 0.46 mmol), carboxylic acid **2a** (57.0 mg, 0.40 mmol), iodine reagent **3a** (206.7 mg, 0.48 mmol), K_2CO_3 (56.5 mg, 0.41 mmol), and DMSO (4 mL) was conducted for 12 h. Purification by flash column chromatography on NH silica gel (hexane/EtOAc = 95:5) and gel permeation chromatography (GPC, $CHCl_3$ as an eluent) gave the product as a viscous oil (67.9 mg, 41% yield).
^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 7.2 Hz, 2H), 7.48–7.28 (m, 6H), 7.26–7.13 (m, 4H), 7.03–6.93 (m, 2H), 4.48 (dd, *J* = 7.6, 4.0 Hz, 1H), 2.12 (dd, *J* = 14.4, 7.6 Hz, 1H), 1.71 (dd, *J* = 14.4, 4.0 Hz, 1H), 1.52–1.01 (m, 10H), 0.72 (s, 3H); ^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$) δ 165.8, 145.9, 140.1, 137.3, 131.9, 130.0, 128.7, 128.6, 128.5, 128.4, 128.2, 127.8, 63.1, 51.7, 38.8, 38.5, 33.6, 26.5, 26.0, 22.11, 22.05 (one sp^2 signal was not observed because of overlapping); IR: (ATR) 2922, 2847, 1616, 1487, 1445, 1281, 1088, 1015, 829, 779 cm^{-1}; HRMS (FAB+) *m*/*z*: ([M+H]$^+$) Calculated for $C_{28}H_{31}ClN$ 416.2145; Found 416.2147

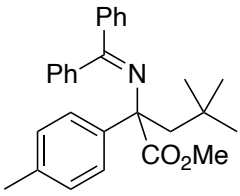
***tert*-butyl (4-((diphenylmethylene)amino)-2-methyl-4-(4-(methylthio)phenyl)butan-2-yl)carbamate (24)**



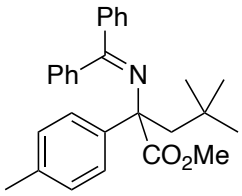
According to general procedure **II**, the reaction using alkene **1q** (30.6 mg, 0.20 mmol), carboxylic acid **2l** (81.2 mg, 0.40 mmol), iodine reagent **3a** (170.4 mg, 0.40 mmol), K_2CO_3 (54.9 mg, 0.40 mmol), and DMSO (2 mL) was conducted for 12 h. Purification by flash column chromatography on NH silica gel (hexane/EtOAc = 90:10) gave the product as a white solid (45.2 mg, 45% yield).
mp: 62.2–66.4 °C; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.0 Hz, 2H), 7.47–7.28 (m, 6H), 7.15

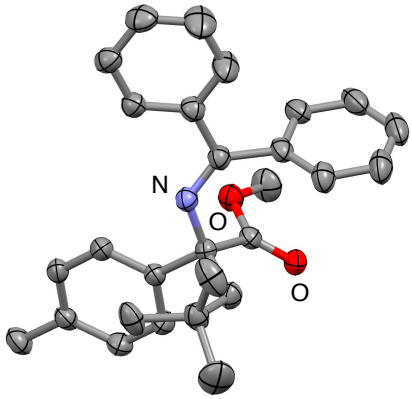
(d, J = 8.4 Hz, 2H), 7.09 (d, J = 8.4 Hz, 2H), 6.94 (d, J = 5.6 Hz, 2H), 5.48 (brs, 1H), 4.51 (dd, J = 10.4, 2.4 Hz, 1H), 2.46 (s, 3H), 2.34 (dd, J = 14.8, 10.4 Hz, 1H), 1.89 (dd, J = 14.8, 2.4 Hz, 1H), 1.28 (s, 9H), 1.27 (s, 3H), 1.23 (s, 3H); $^{13}C\{^{1}H\}$ NMR: (100 MHz, $CDCl_3$) δ 168.0, 154.6, 143.3, 139.5, 137.1, 136.4, 130.3, 128.7, 128.6, 128.4, 128.2, 127.54, 127.48, 127.1, 78.2, 63.4, 52.6, 51.7, 28.7, 28.5, 25.8, 16.2; IR: (ATR) 3366, 2974, 2920, 1713, 1489, 1447, 1364, 1275, 1165, 1072, 781, 770 cm^{-1}; HRMS (ESI) m/z: ($[M+H]^+$) Calculated for $C_{30}H_{37}N_2O_2S$ 489.2576; Found 489.2557

methyl 2-((diphenylmethylene)amino)-4,4-dimethyl-2-(*p*-tolyl)pentanoate (25)



According to general procedure **II**, the reaction using alkene **1a** (71.3 mg, 0.40 mmol), carboxylic acid **2b** (40.9 mg, 0.40 mmol), iodine reagent **3a** (206.7 mg, 0.48 mmol), K_2CO_3 (56.2 mg, 0.41 mmol), and DMSO (4 mL) was conducted for 12 h. Purification by flash column chromatography on NH silica gel (hexane/EtOAc = 95:5) and gel permeation chromatography (GPC, $CHCl_3$ as an eluent) gave the product as a white solid (134.9 mg, 82% yield). Recrystallization from hexane/$CHCl_3$ gave a single crystal suitable for X-ray analysis.
mp: 142.1–144.3 °C; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.71 (dd, J = 8.0, 2.0 Hz, 2H), 7.58–7.49 (m, 2H), 7.43–7.31 (m, 6H), 7.13–7.06 (m, 4H), 3.18 (s, 3H), 2.45 (d, J = 14.4 Hz, 1H), 2.37 (d, J = 14.4 Hz, 1H), 2.33 (s, 3H), 0.79 (s, 9H); $^{13}C\{^{1}H\}$ NMR: (100 MHz, $CDCl_3$) δ 174.9, 165.4, 142.1, 141.3, 137.3, 136.4, 130.1, 128.9, 128.8, 128.6, 128.4, 128.1, 127.6, 126.3, 71.5, 52.3, 51.7, 32.0, 31.8, 21.2; IR: (ATR) 2947, 1728, 1628, 1217, 773 cm^{-1}; HRMS (FAB+) m/z: ($[M+H]^+$) Calculated for $C_{28}H_{32}NO_2$ 414.2433; Found 414.2431

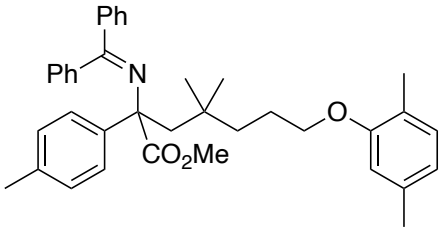




The structure of **25** was determined by X-ray structural analysis. Thermal elipsoids are drawn at the 50% probability level. CCDC 2286657 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

CCDC number	2286657
Empirical formula	$C_{28}H_{31}NO_2$
Formula weight	413.54
Temperature/K	123.15
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	9.07670(10)
b/Å	10.2335(2)
c/Å	25.6684(3)
α/°	90
β/°	96.5420(10)
γ/°	90
Volume/Å^3	2368.72(6)
Z	4
ρ_{calc}g/cm^3	1.160
μ/mm^{-1}	0.560
F(000)	888.0
Crystal size/mm^3	0.145 × 0.113 × 0.082
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	6.932 to 154.934
Index ranges	$-11 \leq h \leq 10$, $-12 \leq k \leq 12$, $-32 \leq l \leq 32$
Reflections collected	35672
Independent reflections	4963 [R_{int} = 0.0382, R_{sigma} = 0.0232]
Data/restraints/parameters	4963/0/317
Goodness-of-fit on F^2	1.056
Final R indexes [I>=2σ (I)]	R_1 = 0.0413, wR_2 = 0.1051
Final R indexes [all data]	R_1 = 0.0472, wR_2 = 0.1107
Largest diff. peak/hole / e Å^{-3}	0.22/-0.18

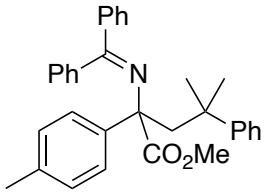
methyl 7-(2,5-dimethylphenoxy)-2-((diphenylmethylene)amino)-4,4-dimethyl-2-(*p*-tolyl)heptanoate (26)



According to general procedure **II**, the reaction using alkene **1a** (74.2 mg, 0.42 mmol), carboxylic acid **2c** (101.2 mg, 0.40 mmol), iodine reagent **3a** (206.2 mg, 0.48 mmol), K_2CO_3 (56.4 mg, 0.41 mmol), and DMSO (4 mL) was conducted for 12 h. Purification by flash column chromatography on NH silica gel (hexane/EtOAc = 95:5) and gel permeation chromatography (GPC, $CHCl_3$ as an eluent) gave the product as a white solid (194.9 mg, 87% yield).

mp: 48.8–50.2 °C; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.0 Hz, 2H), 7.62–7.47 (m, 2H), 7.43–7.24 (m, 6H), 7.16–7.05 (m, 4H), 6.98 (d, *J* = 8.0 Hz, 1H), 6.63 (d, *J* = 7.6 Hz, 1H), 6.48 (s, 1H), 3.61 (t, *J* = 6.8 Hz, 2H), 3.14 (s, 3H), 2.51 (d, *J* = 14.4 Hz, 1H), 2.38 (d, *J* = 14.4 Hz, 1H), 2.302 (s, 3H), 2.296 (s, 3H), 2.14 (s, 3H), 1.74–1.53 (m, 2H), 1.27 (t, *J* = 7.6 Hz, 2H), 0.82 (s, 3H), 0.74 (s, 3H); ^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$) δ 174.8, 165.3, 157.2, 142.0, 141.4, 137.1, 136.44, 136.42, 130.3, 130.1, 129.0, 128.8, 128.6, 128.4, 128.1, 127.7, 126.2, 123.6, 120.5, 112.0, 71.5, 68.6, 51.7, 51.0, 40.9, 34.1, 29.1, 24.4, 21.5, 21.1, 15.9 (one sp^3 signal was not observed because of overlapping); IR: (ATR) 2947, 1728, 1628, 1508, 1445, 1265, 1219, 1128 cm^{-1}; HRMS (FAB+) *m*/*z*: ($[M+H]^+$) Calculated for $C_{38}H_{44}NO_3$ 562.3321; Found 562.3317

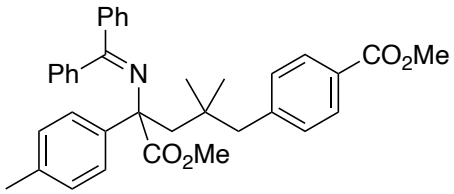
methyl 2-((diphenylmethylene)amino)-4-methyl-4-phenyl-2-(*p*-tolyl)pentanoate (27)



According to general procedure **II**, the reaction using alkene **1a** (72.4 mg, 0.41 mmol), carboxylic acid **2d** (66.0 mg, 0.40 mmol), iodine reagent **3a** (207.0 mg, 0.48 mmol), K_2CO_3 (56.0 mg, 0.40 mmol), and DMSO (4 mL) was conducted for 12 h. Purification by flash column chromatography on NH silica gel (hexane/EtOAc = 95:5) gave the product as a white solid (71.9 mg, 38% yield).

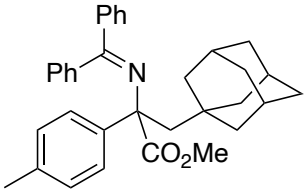
mp: 111.4–113.8 °C; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 7.2 Hz, 2H), 7.43–7.28 (m, 8H), 7.20 (d, *J* = 8.4 Hz, 2H), 7.02–6.85 (m, 7H), 2.99 (s, 3H), 2.88 (d, *J* = 14.8 Hz, 1H), 2.80 (d, *J* = 14.8 Hz, 1H), 2.29 (s, 3H), 1.26 (s, 3H), 1.21 (s, 3H); ^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$) δ 174.4, 165.6, 150.4, 141.7, 141.4, 137.1, 136.2, 130.0, 129.0, 128.8, 128.5, 128.3, 127.9, 127.7, 127.5, 126.3, 126.1, 124.9, 71.4, 53.7, 51.6, 37.9, 31.2, 30.2, 21.2; IR: (ATR) 2968, 1724, 1664, 1223, 1045 cm^{-1}; HRMS (FAB+) *m*/*z*: ($[M+H]^+$) Calculated for $C_{33}H_{34}NO_2$ 476.2590; Found *m*/*z* 476.2593

methyl 4-(4-((diphenylmethylene)amino)-5-methoxy-2,2-dimethyl-5-oxo-4-(*p*-tolyl)pentyl)benzoate (28)



According to general procedure **II**, the reaction using alkene **1a** (71.1 mg, 0.40 mmol), carboxylic acid **2e** (89.1 mg, 0.40 mmol), iodine reagent **3a** (205.4 mg, 0.48 mmol), K_2CO_3 (112.3 mg, 0.81 mmol), and DMSO (4 mL) was conducted for 12 h. To the reaction mixture, methyl iodide (298.1 mg, 2.10 mmol) was added, and the reaction mixture was stirred at room temperature for an additional 3 h. The reaction was then quenched with H_2O (10 mL), and extracted with EtOAc (3 × 10 mL). The combined organic extracts were dried over Na_2SO_4, filtrated, and concentrated under reduced pressure to give the crude product. Purification by flash column chromatography on NH silica gel (hexane/EtOAc = 85:15) gave the product as a white solid (165.1 mg, 75% yield).
mp: 68.1–70.2 °C; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.4 Hz, 2H), 7.67 (d, *J* = 8.4 Hz, 2H), 7.56–7.43 (m, 2H), 7.42–7.23 (m, 6H), 7.13 (d, *J* = 8.4 Hz, 2H), 7.09 (d, *J* = 8.4 Hz, 2H), 6.87 (d, *J* = 6.8 Hz, 2H), 3.90 (s, 3H), 3.16 (s, 3H), 2.58–2.45 (m, 3H), 2.44 (d, *J* = 14.4 Hz, 1H), 2.32 (s, 3H), 0.84 (s, 3H), 0.63 (s, 3H); ^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$) δ 174.7, 167.4, 165.6, 145.0, 142.0, 141.1, 136.9, 136.5, 131.1, 130.2, 129.1, 129.0, 128.8, 128.4, 128.1, 127.8, 127.6, 126.2, 71.3, 52.1, 51.7, 51.6, 51.5, 35.7, 28.7, 28.5, 21.2 (one sp^2 signal was not observed because of overlapping); IR: (ATR) 2949, 1719, 1628, 1433, 1277, 1221, 1180, 1111, 772 cm^{-1}; HRMS (EI) *m*/*z*: (M^+) Calculated for $C_{36}H_{37}NO_4$ 547.2723; Found 547.2720

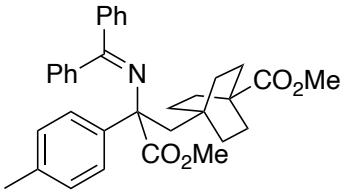
methyl 2-((diphenylmethylene)amino)-3-(1-methylcyclohexyl)-2-(*p*-tolyl)propanoate (29)



According to general procedure **II**, the reaction using alkene **1a** (71.8 mg, 0.41 mmol), carboxylic acid **2f** (72.1 mg, 0.40 mmol), iodine reagent **3a** (206.0 mg, 0.48 mmol), K_2CO_3 (55.9 mg, 0.40 mmol), and DMSO (4 mL) was conducted for 12 h. Purification by flash column chromatography on NH silica gel (hexane/EtOAc = 95:5) and gel permeation chromatography (GPC, $CHCl_3$ as an eluent) gave the product as a white solid (158.8 mg, 81% yield).
mp: 191.3–193.0 °C; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 6.4 Hz, 2H), 7.62–7.44 (m, 2H), 7.43–7.28 (m, 6H), 7.17–7.03 (m, 4H), 3.19 (s, 3H), 2.44–2.27 (m, 4H), 2.22 (d, *J* = 14.4 Hz, 1H), 1.86–1.65 (m, 3H), 1.65–1.17 (m, 12H); ^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$) δ 174.9, 165.2, 142.3, 141.2, 137.3, 136.3, 130.1, 128.9, 128.8, 128.6, 128.3, 128.1, 127.6, 126.2, 71.2, 53.9, 51.8, 44.3,

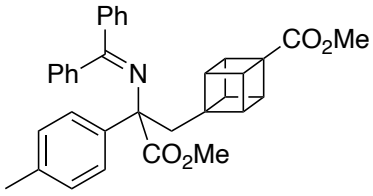
37.0, 34.0, 29.0, 21.2; IR: (ATR) 2895, 1721, 1624, 1219 cm^{-1}; HRMS (FAB+) *m/z*: ($[M+H]^+$) Calculated for $C_{34}H_{38}NO_2$ 492.2903; Found 492.2889

methyl 4-(2-((diphenylmethylene)amino)-3-methoxy-3-oxo-2-(*p*-tolyl)propyl)bicyclo[2.2.2]octane-1-carboxylate (30)



According to general procedure **II**, the reaction using alkene **1a** (71.5 mg, 0.41 mmol), carboxylic acid **2g** (85.4 mg, 0.40 mmol), iodine reagent **3a** (205.3 mg, 0.48 mmol), K_2CO_3 (55.5 mg, 0.40 mmol), and DMSO (4 mL) was conducted for 12 h. Purification by flash column chromatography on NH silica gel (hexane/EtOAc = 95:5) gave the product as a white solid (156.3 mg, 75% yield).
mp: 75.6–83.1 °C; ^1H NMR: (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.4 Hz, 2H), 7.53–7.32 (m, 8H), 7.13–7.05 (m, 4H), 3.55 (s, 3H), 3.16 (s, 3H), 2.37 (d, *J* = 14.4 Hz, 1H), 2.33 (s, 3H), 2.28 (d, *J* = 14.4 Hz, 1H), 1.64–1.52 (m, 6H), 1.42–1.21 (m, 6H); $^{13}C\{^1H\}$ NMR: (100 MHz, $CDCl_3$) δ 178.7, 174.7, 165.7, 142.0, 141.2, 137.2, 136.5, 130.2, 129.0, 128.8, 128.6, 128.4, 128.2, 127.7, 126.2, 71.2, 51.7, 51.6, 51.2, 38.6, 32.1, 31.8, 28.9, 21.2; IR: (ATR) 2947, 2866, 1724, 1628, 1433, 1219, 1067, 1042, 1013, 752 cm^{-1}; HRMS (DART) *m/z*: ($[M+H]^+$) Calculated for $C_{34}H_{38}NO_4$ 524.2801; Found 524.2782

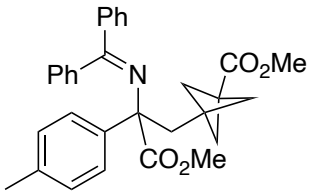
methyl (1*s*,2*R*,3*r*,8*S*)-4-(2-((diphenylmethylene)amino)-3-methoxy-3-oxo-2-(*p*-tolyl)propyl)cubane-1-carboxylate (31)



According to general procedure **II**, the reaction using alkene **1a** (53.5 mg, 0.30 mmol), carboxylic acid **2h** (62.1 mg, 0.30 mmol), iodine reagent **3a** (154.1 mg, 0.36 mmol), K_2CO_3 (43.0 mg, 0.30 mmol), and DMSO (3 mL) was conducted for 12 h. Purification by flash column chromatography on NH silica gel (hexane/EtOAc = 95:5) gave the product as a white solid (52.7 mg, 34% yield).
mp: 76.3–78.3 °C; ^1H NMR: (400 MHz, $CDCl_3$) δ 7.69 (dd, *J* = 8.4, 1.6 Hz, 2H), 7.55 (d, *J* = 8.0 Hz, 2H), 7.44–7.33 (m, 6H), 7.14 (d, *J* = 8.0 Hz, 2H), 7.11–7.07 (m, 2H), 3.92–3.86 (m, 3H), 3.61 (s, 3H), 3.35–3.27 (m, 3H), 3.21 (s, 3H), 2.62 (d, *J* = 14.8 Hz, 1H), 2.53 (d, *J* = 14.8 Hz, 1H), 2.34 (s, 3H); $^{13}C\{^1H\}$ NMR: (100 MHz, $CDCl_3$) δ 174.2, 173.2, 166.4, 141.6, 141.1, 137.0, 136.9, 130.4, 129.1, 128.8, 128.7, 128.5, 128.2, 127.8, 126.0, 71.4, 55.5, 51.8, 51.5, 47.3, 46.5, 44.2, 21.2; IR: (ATR) 2990, 1721, 1433, 1317, 1198, 1086, 1061, 770 cm^{-1}; HRMS (DART) *m/z*: ($[M+H]^+$)

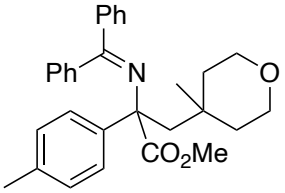
Calculated for $C_{34}H_{32}NO_4$ 518.2331; Found 518.2311

methyl 3-(2-((diphenylmethylene)amino)-3-methoxy-3-oxo-2-(*p*-tolyl)propyl)bicyclo[1.1.1]pentane-1-carboxylate (32)



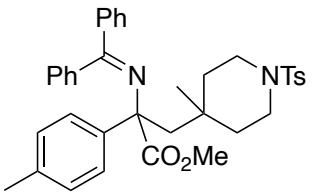
According to general procedure **II**, the reaction using alkene **1a** (69.8 mg, 0.4 mmol), carboxylic acid **2h** (67.7 mg, 0.4 mmol), iodine reagent **3a** (205.4 mg, 0.48 mmol), K_2CO_3 (53.9 mg, 0.39 mmol), and DMSO (4 mL) was conducted for 12 h. Purification by flash column chromatography on NH silica gel (hexane/EtOAc = 95:5) gave the product as a white solid (64.2 mg, 33% yield).
mp: 78.4–82.1 °C; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 6.8 Hz, 2H), 7.54 (d, *J* = 8.0 Hz, 2H), 7.49–7.31 (m, 6H), 7.13 (d, *J* = 7.6 Hz, 2H), 7.10–7.01 (m, 2H), 3.55 (s, 3H), 3.28 (s, 3H), 2.54 (d, *J* = 15.2 Hz, 1H), 2.47 (d, *J* = 15.2 Hz, 1H), 2.34 (s, 3H), 1.75 (dd, *J* = 9.6, 2.0 Hz, 3H), 1.67 (dd, *J* = 9.6, 2.0 Hz, 3H); ^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$) δ 174.1, 170.5, 167.0, 140.9, 140.5, 137.1, 136.8, 130.4, 129.0, 128.7, 128.6, 128.4, 128.2, 127.9, 126.4, 70.5, 53.6, 52.0, 51.5, 41.1, 38.8, 37.1, 21.2; IR: (ATR) 2949, 2914, 2876, 1728, 1628, 1435, 1229, 1200, 1177, 1063 cm^{-1}; HRMS (FAB+) *m*/*z*: ([M+H]$^+$) Calculated for $C_{31}H_{32}NO_4$ 482.2331; Found 482.2320

methyl 2-((diphenylmethylene)amino)-3-(4-methyltetrahydro-2*H*-pyran-4-yl)-2-(*p*-tolyl)propanoate (33)



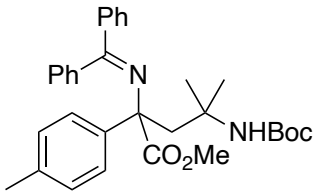
According to general procedure **II**, the reaction using alkene **1a** (71.5 mg, 0.41 mmol), carboxylic acid **2j** (57.9 mg, 0.40 mmol), iodine reagent **3a** (206.2 mg, 0.48 mmol), K_2CO_3 (55.0 mg, 0.40 mmol), and DMSO (4 mL) was conducted for 12 h. Purification by flash column chromatography on NH silica gel (hexane/EtOAc = 95:5) gave the product as a white solid (135.8 mg, 75% yield).
mp: 128.4–131.0 °C; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.0 Hz, 2H), 7.61–7.46 (m, 2H), 7.45–7.30 (m, 6H), 7.18–7.05 (m, 4H), 3.62–3.36 (m, 4H), 3.13 (s, 3H), 2.54 (d, *J* = 14.8 Hz, 1H), 2.38 (d, *J* = 14.8 Hz, 1H), 2.32 (s, 3H), 1.52–1.49 (m, 1H), 1.42–1.28 (m, 2H), 1.07–0.97 (m, 1H), 0.86 (s, 3H); ^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$) δ 174.6, 165.5, 141.9, 141.3, 137.0, 136.5, 130.2, 129.0, 128.8, 128.6, 128.5, 128.1, 127.7, 126.2, 71.3, 63.84, 63.76, 53.6, 51.7, 40.0, 39.2, 32.1, 24.1, 21.2; IR: (ATR) 2949, 1728, 1628, 1443, 1215, 1180, 1020 cm^{-1}; HRMS (FAB+) *m*/*z*: ([M+H]$^+$) Calculated for $C_{30}H_{34}NO_3$ 456.2539; Found 456.2547

methyl 2-((diphenylmethylene)amino)-3-(4-methyl-1-tosylpiperidin-4-yl)-2-(*p*-tolyl)propanoate (34)



According to general procedure **II**, the reaction using alkene **1a** (69.7 mg, 0.40 mmol), carboxylic acid **2l** (120.1 mg, 0.40 mmol), iodine reagent **3a** (205.3 mg, 0.48 mmol), K_2CO_3 (55.6 mg, 0.40 mmol), and DMSO (4 mL) was conducted for 12 h. Purification by flash column chromatography on NH silica gel (hexane/EtOAc = 80:20) gave the product as a white solid (195.3 mg, 80% yield). mp: 126.7–131.3 °C; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 6.8 Hz, 2H), 7.57–7.28 (m, 10H), 7.23 (d, *J* = 8.0 Hz, 2H), 7.08 (d, *J* = 8.4 Hz, 2H), 6.99 (d, *J* = 6.8 Hz, 2H), 3.12–2.93 (m, 2H), 3.06 (s, 3H), 2.60–2.50 (m, 2H), 2.42–2.25 (m, 2H), 2.38 (s, 3H), 2.33 (s, 3H), 1.70–1.61 (m, 1H), 1.47–1.35 (m, 2H), 1.22–1.14 (m, 1H), 0.55 (s, 3H); ^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$) δ 174.5, 165.7, 143.3, 141.7, 141.2, 136.8, 133.2, 130.4, 129.7, 129.2, 128.8, 128.60, 128.57, 128.2, 127.8, 127.7, 126.1, 71.4, 52.3, 51.7, 42.4, 42.2, 38.1, 38.0, 32.2, 24.6, 21.6, 21.2 (one sp^2 signal was not observed because of overlapping); IR: (ATR) 2949, 2942, 2859, 1728, 1346, 1221, 1182, 1092, 930, 725 cm^{-1}; HRMS (DART) *m*/*z*: ([M+H]$^+$) Calculated for $C_{37}H_{41}N_2O_4S$ 609.2787; Found 609.2766

methyl 4-((*tert*-butoxycarbonyl)amino)-2-((diphenylmethylene)amino)-4-methyl-2-(*p*-tolyl)pentanoate (35)

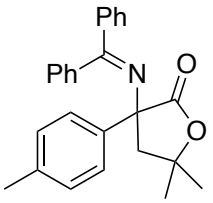


According to general procedure **II**, the reaction using alkene **1a** (71.1 mg, 0.40 mmol), carboxylic acid **2l** (81.4 mg, 0.40 mmol), iodine reagent **3a** (207.3 mg, 0.49 mmol), K_2CO_3 (56.3 mg, 0.41 mmol), and DMSO (4 mL) was conducted for 12 h. Purification by flash column chromatography on NH silica gel (hexane/EtOAc = 90:10) gave the product as a white solid (184.1 mg, 89% yield). mp: 101.9–105.3 °C; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 7.2 Hz, 2H), 7.49–7.28 (m, 8H), 7.15–7.05 (m, 4H), 5.46 (brs, 1H), 3.13 (s, 3H), 2.79 (d, *J* = 14.8 Hz, 1H), 2.64 (d, *J* = 14.8 Hz, 1H), 2.33 (s, 3H), 1.33 (s, 3H), 1.24 (s, 9H), 1.01 (s, 3H); ^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$) δ 173.9, 167.5, 154.5, 141.1, 141.0, 136.75, 136.71, 130.4, 129.1, 129.0, 128.8, 128.5, 128.2, 127.6, 126.5, 78.1, 71.6, 53.0, 51.8, 50.8, 29.7, 28.9, 28.5, 21.2; IR: (ATR) 3387, 2976, 1724, 1697, 1530, 1364, 1279, 1229, 1171, 1080, 1047, 770 cm^{-1}; HRMS (EI) *m*/*z*: (M^+) Calculated for $C_{32}H_{38}N_2O_4$ 514.2832; Found 514.2829

Gram-scale reaction

According to general procedure, the reaction using alkene **1a** (496.8 mg, 2.8 mmol), carboxylic acid **2l** (570.4 mg, 2.8 mmol), iodine reagent **3a** (1.44 g, 3.4 mmol), K_2CO_3 (389.2 mg, 2.8 mmol), and DMSO (20 mL) was conducted for 12 h. Purification by flash column chromatography on NH silica gel (hexane/EtOAc = 90:10) gave the product as a white solid (1.21 g, 84% yield).

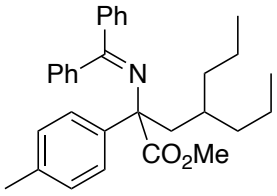
3-((diphenylmethylene)amino)-5,5-dimethyl-3-(*p*-tolyl)dihydrofuran-2(3*H*)-one (36)



According to general procedure **II**, the reaction using alkene **1a** (35.8 mg, 0.20 mmol), carboxylic acid **2m** (21.0 mg, 0.20 mmol), iodine reagent **3a** (103.0 mg, 0.24 mmol), K_2CO_3 (28.2 mg, 0.20 mmol), and DMSO (2 mL) was conducted for 12 h. Purification by flash column chromatography on NH silica gel (hexane/EtOAc = 95:5) gave the product as colorless oil (46.5 mg, 61% yield).

^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 7.6 Hz, 2H), 7.42–7.20 (m, 4H), 7.19–7.05 (m, 4H), 6.91 (d, *J* = 8.4 Hz, 2H), 6.67 (d, *J* = 7.6 Hz, 2H), 2.73 (d, *J* = 13.6 Hz, 1H), 2.62 (d, *J* = 13.6 Hz, 1H), 2.26 (s, 3H), 1.50 (s, 3H), 1.26 (s, 3H); ^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$) δ 176.7, 170.0, 140.7, 137.74, 137.67, 137.2, 130.5, 128.71, 128.69, 128.1, 128.0, 127.8, 127.53, 127.47, 81.0, 71.6, 48.0, 29.9, 28.5, 21.1; IR: (ATR) 2974, 2924, 2872, 1763, 1622, 1445, 1267, 1138, 816, 756 cm^{-1}; HRMS (FAB+) *m*/*z*: ([M+H]$^+$) Calculated for $C_{26}H_{26}NO_2$ 384.1964; Found 384.1973

methyl 2-((diphenylmethylene)amino)-4-propyl-2-(*p*-tolyl)heptanoate (38)

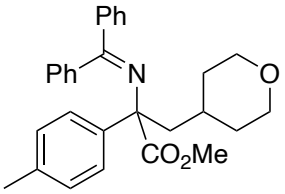


According to general procedure **II**, the reaction using alkene **1a** (71.1 mg, 0.40 mmol), carboxylic acid **2n** (58.3 mg, 0.40 mmol), iodine reagent **3a** (205.8 mg, 0.48 mmol), K_2CO_3 (56.2 mg, 0.41 mmol), and DMSO (4 mL) was conducted for 12 h. Purification by flash column chromatography on NH silica gel (hexane/EtOAc = 95:5) and gel permeation chromatography (GPC, $CHCl_3$ as an eluent) gave the product as a viscous oil (76.5 mg, 42% yield).

^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 6.8 Hz, 2H), 7.52 (d, *J* = 8.4 Hz, 2H), 7.44–7.30 (m, 6H), 7.17–7.05 (m, 4H), 3.17 (s, 3H), 2.33 (s, 3H), 2.28 (dd, *J* = 14.4, 4.4 Hz, 1H), 2.13 (dd, *J* = 14.4, 6.8 Hz, 1H), 1.52–0.89 (m, 9H), 0.72–0.56 (m, 6H); ^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$) δ 174.7, 165.9, 141.5, 141.4, 137.1, 136.3, 130.1, 128.9, 128.7, 128.54, 128.48, 128.0, 127.7, 126.4, 71.9, 51.6, 45.9, 37.0, 36.6, 32.6, 21.2, 19.5, 19.2, 14.4, 14.3; IR: (ATR) 2953, 2926, 2870, 1732,

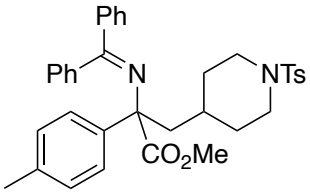
1630, 1445, 1221, 770 cm^{-1}; HRMS (FAB+) *m/z*: ([M+H]$^+$) Calculated for $C_{31}H_{38}NO_2$ 456.2903; Found 456.2907

methyl 2-((diphenylmethylene)amino)-3-(tetrahydro-2*H*-pyran-4-yl)-2-(*p*-tolyl)propanoate (39)



According to general procedure **II**, the reaction using alkene **1a** (72.3 mg, 0.41 mmol), carboxylic acid **2o** (53.0 mg, 0.41 mmol), iodine reagent **3a** (206.0 mg, 0.48 mmol), K_2CO_3 (56.0 mg, 0.41 mmol), and DMSO (4 mL) was conducted for 12 h. Purification by flash column chromatography on NH silica gel (hexane/EtOAc = 95:5) and gel permeation chromatography (GPC, $CHCl_3$ as an eluent) gave the product as a white solid (65.9 mg, 37% yield).
mp: 78.4–81.6 °C; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 6.8 Hz, 2H), 7.52 (d, *J* = 8.0 Hz, 2H), 7.43–7.32 (m, 6H), 7.14 (d, *J* = 7.6 Hz, 2H), 7.06 (d, *J* = 7.6 Hz, 2H), 3.82–3.70 (m, 2H), 3.24 (s, 3H), 3.27–3.11 (m, 2H), 2.35 (s, 3H), 2.26 (dd, *J* = 14.0, 5.6 Hz, 1H), 2.19 (dd, *J* = 14.8, 6.8 Hz, 1H), 1.70–1.60 (m, 1H), 1.32–1.10 (m, 4H); ^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$) δ 174.5, 166.7, 141.3, 141.2, 137.1, 136.7, 130.3, 129.1, 128.7, 128.6, 128.4, 128.2, 127.8, 126.3, 71.3, 68.1, 51.8, 47.6, 34.6, 34.4, 31.1, 21.2 (one sp^3 signal was not observed because of overlapping); IR: (ATR) 2949, 2916, 2837, 1728, 1628, 1443, 1221, 1130 cm^{-1}; HRMS (FAB+) *m/z*: ([M+H]$^+$) Calculated for $C_{29}H_{32}NO_3$ 442.2382; Found 442.2371

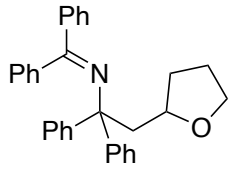
methyl 2-((diphenylmethylene)amino)-2-(*p*-tolyl)-3-(1-tosylpiperidin-4-yl)propanoate (40)



According to general procedure **II**, the reaction using alkene **1a** (69.8 mg, 0.40 mmol), carboxylic acid **2p** (112.8 mg, 0.40 mmol), iodine reagent **3a** (204.4 mg, 0.48 mmol), K_2CO_3 (54.9 mg, 0.40 mmol), and DMSO (4 mL) was conducted for 12 h. Purification by flash column chromatography on NH silica gel (hexane/EtOAc = 80:20) gave the product as a white solid (110.8 mg, 47% yield).
mp: 92.6–94.3 °C; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 7.2 Hz, 2H), 7.54 (d, *J* = 8.4 Hz, 2H), 7.46 (d, *J* = 8.4 Hz, 2H), 7.43–7.30 (m, 6H), 7.26 (d, *J* = 8.4 Hz, 2H), 7.10 (d, *J* = 8.4 Hz, 2H), 7.00 (d, *J* = 7.6 Hz, 2H), 3.62–3.47 (m, 2H), 3.20 (s, 3H), 2.40 (s, 3H), 2.33 (s, 3H), 2.25 (dd, *J* = 14.4, 4.0 Hz, 1H), 2.14 (dd, *J* = 14.4, 6.4 Hz, 1H), 2.09–1.96 (m, 2H), 1.87–1.76 (m, 1H), 1.41–1.11 (m, 4H); ^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$) δ 174.2, 166.9, 143.4, 141.1, 141.0, 136.9, 136.7, 133.3,

130.4, 129.6, 129.1, 128.7, 128.4, 128.2, 127.82, 127.79, 126.2, 71.2, 51.8, 46.8, 46.43, 46.39, 32.8, 32.7, 31.2, 21.6, 21.1 (one sp^2 signal was not observed because of overlapping); IR: (ATR) 2920, 2843, 1728, 1445, 1339, 1225, 1163, 1092, 934, 725 cm^{-1}; HRMS (DART) *m*/*z*: ($[M+H]^+$) Calculated for $C_{36}H_{39}N_2O_4S$ 595.2631; Found 595.2630

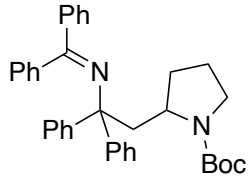
_N_-(1,1-diphenyl-2-(tetrahydrofuran-2-yl)ethyl)-1,1-diphenylmethanimine (41)



According to general procedure **II**, the reaction using alkene **1n** (71.2 mg, 0.40 mmol), carboxylic acid **2q** (56.1 mg, 0.48 mmol), iodine reagent **3a** (205.8 mg, 0.48 mmol), K_2CO_3 (64.9 mg, 0.48 mmol), and DMSO (4 mL) was conducted for 12 h. Purification by flash column chromatography on NH silica gel (hexane/EtOAc = 95:5) and gel permeation chromatography (GPC, $CHCl_3$ as an eluent) gave the product as a white solid (106.8 mg, 62% yield).

mp: 61.4–69.1 °C; ^1H NMR: (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 7.6 Hz, 2H), 7.43–7.28 (m, 5H), 7.25–7.17 (m, 1H), 7.17–6.93 (m, 10H), 6.52 (d, *J* = 7.6 Hz, 2H), 3.79–3.67 (m, 2H), 3.51 (ddd, *J* = 8.0, 8.0, 8.0 Hz, 1H), 2.92 (dd, *J* = 13.2, 3.2 Hz, 1H), 2.40 (dd, *J* = 13.2, 9.2 Hz, 1H), 1.80–1.57 (m, 2H), 1.57–1.42 (m, 1H), 1.07–0.93 (m, 1H); $^{13}C\{^1H\}$ NMR: (100 MHz, $CDCl_3$) δ 166.8, 149.9, 149.8, 142.1, 138.7, 129.9, 128.5, 128.2, 128.1, 127.9, 127.8, 127.5, 127.3, 126.8, 125.93, 125.88, 76.9, 67.9, 66.8, 46.8, 32.6, 26.4 (one sp^2 signal was not observed because of overlapping); IR: (ATR) 3055, 2864, 1624, 1489, 1445, 1273, 1063, 764 cm^{-1}; HRMS (DART) *m*/*z*: ($[M+H]^+$) Calculated for $C_{31}H_{30}NO$ 432.2327; Found 432.2338

***tert*-butyl 2-(2-((diphenylmethylene)amino)-2,2-diphenylethyl)pyrrolidine-1-carboxylate (42)**

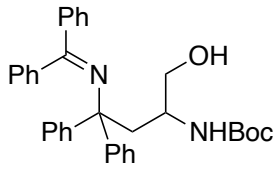


According to general procedure **II**, the reaction using alkene **1n** (71.4 mg, 0.40 mmol), carboxylic acid **2r** (103.6 mg, 0.48 mmol), iodine reagent **3a** (205.5 mg, 0.48 mmol), K_2CO_3 (68.3 mg, 0.49 mmol), and DMSO (4 mL) was conducted for 12 h. Purification by flash column chromatography on NH silica gel (hexane/EtOAc = 95:5) and gel permeation chromatography (GPC, $CHCl_3$ as an eluent) gave the product as a white solid (111.6 mg, 53% yield).

mp: 72.1–76.2 °C; ^1H NMR: (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 7.6 Hz, 2H), 7.60–7.27 (m, 4H), 7.20–6.40 (m, 14H), 3.74–2.93 (m, 4H), 2.43–2.21 (m, 1H), 1.93–1.50 (m, 4H), 1.39 (s, 9H); $^{13}C\{^1H\}$ NMR: (100 MHz, $CDCl_3$) δ 166.4, 154.6, 150.1, 149.3, 142.1, 138.8, 129.9, 128.5, 128.3, 128.14, 128.06, 127.8, 127.7, 127.5, 127.3, 126.5, 125.8, 79.3, 68.5, 55.4, 46.4, 44.9, 31.0, 28.8,

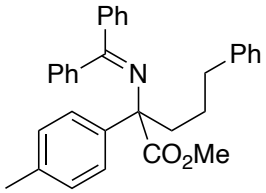
23.7 (one sp^2 signal was not observed because of overlapping); IR: (ATR) 2972, 1686, 1626, 1445, 1391, 1364, 1165, 1099, 762, 731 cm^{-1}; HRMS (DART) *m*/*z*: ($[M+H]^+$) Calculated for $C_{36}H_{39}N_2O_2$ 531.3012; Found 531.3023

tert-butyl (4-((diphenylmethylene)amino)-1-hydroxy-4,4-diphenylbutan-2-yl)carbamate (43)



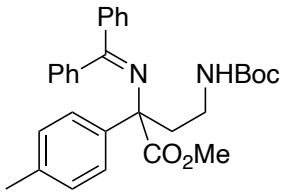
According to general procedure **II**, the reaction using alkene **1n** (72.9 mg, 0.40 mmol), carboxylic acid **2s** (82.8 mg, 0.40 mmol), iodine reagent **3a** (206.1 mg, 0.48 mmol), K_2CO_3 (54.9 mg, 0.40 mmol), and DMSO (4 mL) was conducted for 12 h. Purification by flash column chromatography on NH silica gel (hexane/EtOAc = 70:30) gave the product as a white solid (103.6 mg, 50% yield).
mp: 99.1–101.5 °C; ^1H NMR: (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 7.2 Hz, 2H), 7.41–7.28 (m, 5H), 7.23–6.99 (m, 9H), 6.94 (t, *J* = 8.0 Hz, 2H), 6.52 (d, *J* = 7.8 Hz, 2H), 5.60 (brs, 1H), 3.53–3.44 (m, 2H), 3.44–3.24 (m, 2H), 2.71 (dd, *J* = 14.0, 8.8 Hz, 1H), 2.62–2.47 (m, 1H), 1.33 (s, 9H); $^{13}C\{^1H\}$ NMR: (100 MHz, $CDCl_3$) δ 168.7, 157.0, 148.0, 147.7, 141.5, 138.4, 130.4, 128.6, 128.2, 128.1, 128.01, 127.94, 127.8, 127.4, 127.2, 126.9, 126.4, 126.2, 79.4, 69.2, 67.0, 51.5, 43.3, 28.4 (one sp^2 signal was not observed because of overlapping); IR: (ATR) 3441, 3055, 2972, 2930, 2870, 1688, 1491, 1445, 1366, 1246, 1165, 1028, 764 cm^{-1}; HRMS (ESI) *m*/*z*: ($[M+Na]^+$) Calculated for $C_{34}H_{36}N_2O_3Na$ 543.2624; Found 543.2617

methyl 2-((diphenylmethylene)amino)-5-phenyl-2-(*p*-tolyl)pentanoate (44)



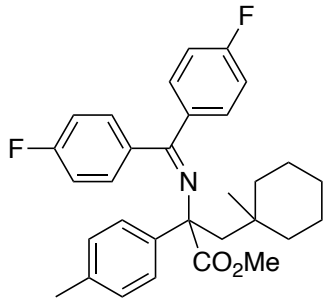
According to general procedure **II**, the reaction using alkene **1a** (71.6 mg, 0.41 mmol), carboxylic acid **2t** (61.4 mg, 0.41 mmol), iodine reagent **3a** (205.0 mg, 0.48 mmol), K_2CO_3 (56.8 mg, 0.41 mmol), and DMSO (4 mL) was conducted for 12 h. Purification by flash column chromatography on NH silica gel (hexane/EtOAc = 95:5) gave the product as a white solid (67.9 mg, 36% yield).
mp: 146.0–148.3 °C; ^1H NMR: (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 7.6 Hz, 2H), 7.52 (d, *J* = 8.4 Hz, 2H), 7.42–7.28 (m, 4H), 7.28–7.09 (m, 7H), 7.06 (d, *J* = 6.8 Hz, 2H), 6.80 (d, *J* = 7.6 Hz, 2H), 3.28 (s, 3H), 2.60–2.36 (m, 2H), 2.34 (s, 3H), 2.21–2.08 (m, 2H), 1.77–1.35 (m, 2H); $^{13}C\{^1H\}$ NMR: (100 MHz, $CDCl_3$) δ 174.4, 167.1, 142.3, 141.22, 141.19, 137.1, 136.5, 130.2, 129.0, 128.72, 128.70, 128.5, 128.3, 128.1, 127.8, 126.4, 125.8, 71.4, 51.8, 40.2, 36.0, 25.0, 21.2 (one sp^2 signal was not observed because of overlapping); IR: (ATR) 2945, 1726, 1634, 1223 cm^{-1}; HRMS (FAB+) *m*/*z*: ($[M+H]^+$) Calculated for $C_{32}H_{32}NO_2$ 462.2433; Found 462.2424

methyl 4-((*tert*-butoxycarbonyl)amino)-2-((diphenylmethylene)amino)-2-(*p*-tolyl)butanoate (45)



According to general procedure **II**, the reaction using alkene **1a** (71.1 mg, 0.40 mmol), carboxylic acid **2u** (70.4 mg, 0.40 mmol), iodine reagent **3a** (205.8 mg, 0.48 mmol), K_2CO_3 (56.2 mg, 0.41 mmol), and DMSO (4 mL) was conducted for 12 h. Purification by flash column chromatography on NH silica gel (hexane/EtOAc = 85:15) gave the product as a white solid (73.2 mg, 38% yield).
mp: 68.2–72.5 °C; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.68 (d, J = 8.4 Hz, 2H), 7.49 (d, J = 7.2 Hz, 2H), 7.44–7.30 (m, 6H), 7.20–7.09 (m, 4H), 4.84 (brs, 1H), 3.21 (s, 3H), 3.22–2.95 (m, 2H), 2.55–2.30 (m, 2H), 2.35 (s, 3H), 1.29 (s, 9H); ^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$) δ 173.8, 168.0, 155.9, 141.1, 140.1, 137.0, 136.8, 130.5, 129.3, 128.9, 128.8, 128.5, 128.2, 127.8, 126.3, 78.7, 71.4, 51.9, 41.6, 36.4, 28.4, 21.2; IR: (ATR) 3408, 2924, 2853, 1732, 1709, 1506, 1229, 1167, 779, 770 cm^{-1}; HRMS (ESI) *m*/*z*: ([M+Na]$^+$) Calculated for $C_{30}H_{34}N_2O_4Na$ 509.2416; Found 509.2425

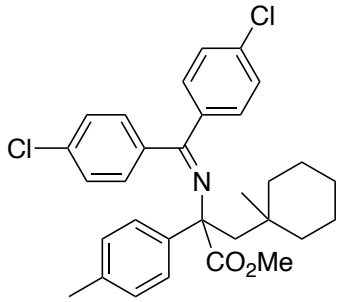
methyl 2-((bis(4-fluorophenyl)methylene)amino)-3-(1-methylcyclohexyl)-2-(*p*-tolyl)propanoate (46)



According to general procedure **II**, the reaction using alkene **1a** (71.6 mg, 0.41 mmol), carboxylic acid **2a** (57.0 mg, 0.40 mmol), iodine reagent **3b** (223.2 mg, 0.48 mmol), K_2CO_3 (57.3 mg, 0.41 mmol), and DMSO (4 mL) was conducted for 12 h. Purification by flash column chromatography on NH silica gel (hexane/EtOAc = 95:5) and gel permeation chromatography (GPC, $CHCl_3$ as an eluent) gave the product as a white solid (160.1 mg, 82% yield).
mp: 59.7–62.9 °C; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.69–7.62 (m, 2H), 7.46–7.37 (m, 2H), 7.10–6.96 (m, 8H), 3.24 (s, 3H), 2.43 (d, J = 14.4 Hz, 1H), 2.33–2.27 (m, 4H), 1.47–1.02 (m, 10H), 0.78 (s, 3H); ^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$) δ 174.9, 164.3 (d, $J_{C–F}$ = 249.4 Hz), 163.3, 162.4 (d, $J_{C–F}$ = 247.0 Hz), 142.0, 137.5 (d, $J_{C–F}$ = 3.3 Hz), 136.5, 133.0 (d, $J_{C–F}$ = 3.3 Hz), 130.7 (d, $J_{C–F}$ = 8.2 Hz), 130.3 (d, $J_{C–F}$ = 8.2 Hz), 129.0, 126.2, 115.1 (d, $J_{C–F}$ = 22.3 Hz), 114.9 (d, $J_{C–F}$ = 23.0 Hz), 71.5, 53.1, 51.8, 40.1, 39.5, 34.4, 26.4, 25.1, 22.2, 22.1, 21.2; ^{19}F{^{1}H} NMR: (377 MHz, $CDCl_3$) δ −113.7, −114.7; IR: (ATR) 2924, 1730, 1628, 1599, 1503, 1223, 1152, 835 cm^{-1}; HRMS (FAB+)

m/*z*: ([M+H]$^+$) Calculated for $C_{31}H_{34}F_2NO_2$ 490.2558; Found 490.2570

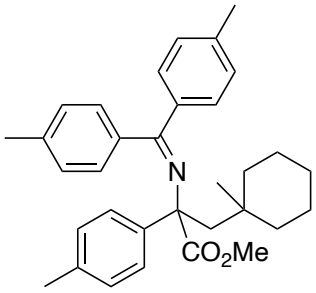
methyl 2-((bis(4-chlorophenyl)methylene)amino)-3-(1-methylcyclohexyl)-2-(*p*-tolyl)propanoate (47)



According to general procedure **II**, the reaction using alkene **1a** (53.3 mg, 0.30 mmol), carboxylic acid **2a** (42.5 mg, 0.30 mmol), iodine reagent **3c** (179.2 mg, 0.36 mmol), K_2CO_3 (42.3 mg, 0.31 mmol), and DMSO (3 mL) was conducted for 12 h. Purification by flash column chromatography on NH silica gel (hexane/EtOAc = 95:5) and gel permeation chromatography (GPC, $CHCl_3$ as an eluent) gave the product as a white solid (105.9 mg, 68% yield).

mp: 78.7–81.1 °C; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 8.8 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.31 (d, *J* = 8.8 Hz, 2H), 7.27 (d, *J* = 8.4 Hz, 2H), 7.04 (d, *J* = 8.0 Hz, 2H), 6.93 (d, *J* = 8.4 Hz, 2H), 3.26 (s, 3H), 2.43 (d, *J* = 14.8 Hz, 1H), 2.31 (s, 3H), 2.31 (d, *J* = 14.8 Hz, 1H), 1.47–1.01 (m, 10H), 0.78 (s, 3H); ^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$) δ 174.8, 163.2, 141.8, 139.5, 136.64, 136.57, 135.3, 134.5, 130.0, 129.8, 129.0, 128.4, 128.0, 126.2, 71.7, 53.0, 51.9, 40.0, 39.6, 34.4, 26.4, 25.1, 22,2, 22.1, 21.2; IR: (ATR) 2922, 1730, 1628, 1585, 1487, 1211, 1090, 1013, 818, 746 cm^{-1}; HRMS (DART) *m*/*z*: ([M+H]$^+$) Calculated for $C_{31}H_{34}NO_2Cl_2$ 522.1967; Found 522.1962

methyl 2-((di-*p*-tolylmethylene)amino)-3-(1-methylcyclohexyl)-2-(*p*-tolyl)propanoate (48)

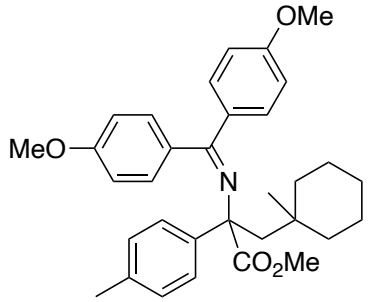


According to general procedure **II**, the reaction using alkene **1a** (53.7 mg, 0.30 mmol), carboxylic acid **2a** (42.9 mg, 0.30 mmol), iodine reagent **3d** (164.3 mg, 0.36 mmol), K_2CO_3 (43.0 mg, 0.31 mmol), and DMSO (3 mL) was conducted for 12 h. Purification by flash column chromatography on NH silica gel (hexane/EtOAc = 95:5) and gel permeation chromatography (GPC, $CHCl_3$ as an eluent) gave the product as a white solid (74.1 mg, 51% yield).

mp: 65.3–67.1 °C; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.62–7.49 (m, 2H), 7.59 (d, *J* = 7.6 Hz, 2H), 7.21–7.12 (m, 4H), 7.09 (d, *J* = 8.4 Hz, 2H), 6.99 (d, *J* = 8.0 Hz, 2H), 3.16 (s, 3H), 2.45 (d, *J* = 14.4

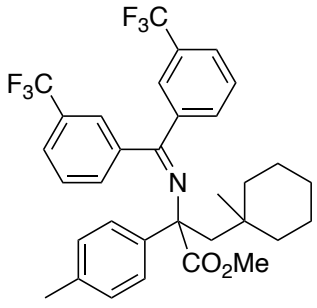
Hz, 1H), 2.39 (s, 3H), 2.37 (s, 3H), 2.33 (s, 3H), 2.30 (d, J = 14.4 Hz, 1H), 1.44–0.97 (m, 10H), 0.74 (s, 3H); $^{13}C\{^{1}H\}$ NMR: (100 MHz, $CDCl_3$) δ 175.1, 165.3, 142.6, 140.1, 139.2, 138.0, 136.2, 134.5, 128.85, 128.79, 128.6, 128.3, 126.3, 71.4, 53.1, 51.7, 40.3, 39.5, 34.4, 26.4, 25.4, 22.3, 22.1, 21.52, 21.46, 21.2 (one sp^2 signal was not observed because of overlapping); IR: (ATR) 2920, 1730, 1605, 1508, 1443, 1211, 1180, 1038, 814, 731cm^{-1}; HRMS (DART) m/z: ([M+H]$^+$) Calculated for $C_{33}H_{40}NO_2$ 482.3059; Found 482.3040

methyl 2-((bis(4-methoxyphenyl)methylene)amino)-3-(1-methylcyclohexyl)-2-(*p*-tolyl)propanoate (49)



According to general procedure **II**, the reaction using alkene **1a** (56.6 mg, 0.32 mmol), carboxylic acid **2a** (43.2 mg, 0.30 mmol), iodine reagent **3e** (178.5 mg, 0.37 mmol), K_2CO_3 (43.6 mg, 0.32 mmol), and DMSO (3 mL) was conducted for 12 h. Purification by flash column chromatography on NH silica gel (hexane/EtOAc = 90:10) and gel permeation chromatography (GPC, $CHCl_3$ as an eluent) gave the product as a white solid (61.4 mg, 40% yield).
mp: 89.3–92.7 °C; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.65 (d, J = 8.8 Hz, 2H), 7.62–7.46 (m, 2H), 7.09 (d, J = 8.8 Hz, 2H), 7.02 (d, J = 8.8 Hz, 2H), 6.90–6.79 (m, 4H), 3.84 (s, 3H), 3.83 (s, 3H), 3.18 (s, 3H), 2.45 (d, J = 14.8 Hz, 1H), 2.33 (s, 3H), 2.30 (d, J = 14.8 Hz, 1H), 1.42–0.97 (m, 10H), 0.74 (s, 3H); ^{13}C $\{^{1}H\}$ NMR: (100 MHz, $CDCl_3$) δ 175.3, 164.5, 161.2, 159.3, 142.6, 136.2, 134.9, 130.4, 130.0, 129.7, 128.9, 126.3, 113.3, 113.0, 71.3, 55.4, 55.3, 53.2, 51.8, 40.2, 39.5, 34.4, 26.4, 25.3, 22.2, 22.1, 21.2; IR: (ATR) 2924, 1726, 1599, 1506, 1246, 1173, 1032, 831 cm^{-1}; HRMS (FAB+) m/z: ([M+H]$^+$) Calculated for $C_{33}H_{40}NO_4$ 514.2957; Found 514.2940

methyl 2-((bis(3-(trifluoromethyl)phenyl)methylene)amino)-3-(1-methylcyclohexyl)-2-(*p*-tolyl)propanoate (50)

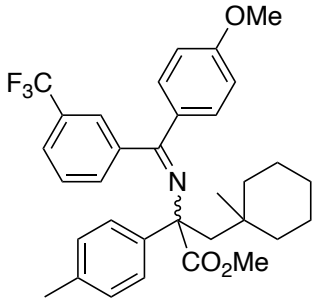


According to general procedure **II**, the reaction using alkene **1a** (53.9 mg, 0.31 mmol), carboxylic

acid **2a** (42.4 mg, 0.30 mmol), iodine reagent **3f** (204.6 mg, 0.36 mmol), K_2CO_3 (41.5 mg, 0.30 mmol), and DMSO (3 mL) was conducted for 12 h. Purification by flash column chromatography on NH silica gel (hexane/EtOAc = 95:5) and gel permeation chromatography (GPC, $CHCl_3$ as an eluent) gave the product as a viscous oil (105.8 mg, 60% yield).

^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.95 (s, 1H), 7.73 (d, J = 7.6 Hz, 1H), 7.66 (d, J = 7.2 Hz, 1H), 7.57 (d, J = 7.6 Hz, 1H), 7.47 (dd, J = 8.0, 7.6 Hz, 1H), 7.42 (dd, J = 8.0, 7.2 Hz, 1H), 7.29–7.11 (m, 3H), 7.08 (s, 1H), 6.98 (d, J = 8.0 Hz, 2H), 3.37 (s, 3H), 2.42 (d, J = 14.4 Hz, 1H), 2.37 (d, J = 14.4 Hz, 1H), 2.28 (s, 3H), 1.51–0.99 (m, 10H), 0.87 (s, 3H); ^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$) δ 174.5, 162.8, 141.4, 141.3, 137.6, 137.0, 131.9, 131.3, 130.9 (q, $J_{C–F}$ = 32.1 Hz), 130.2 (q, $J_{C–F}$ = 32.1 Hz), 129.1, 128.9, 128.4, 127.0 (q, $J_{C–F}$ = 3.3 Hz), 126.2, 125.2 (q, $J_{C–F}$ = 3.2 Hz), 125.1 (q, $J_{C–F}$ = 3.3 Hz), 124.1 (q, $J_{C–F}$ = 270.9 Hz), 123.8 (q, $J_{C–F}$ = 270.8 Hz), 71.8, 53.0, 52.0, 39.8, 39.6, 34.4, 26.3, 24.9, 22.2, 22.1, 21.0 (one sp^2 signal was not observed because of overlapping); ^{19}F{^{1}H} NMR: (100 MHz, $CDCl_3$) δ −65.3, −65.4; IR: (ATR) 2926, 1732, 1327, 1240, 1213, 1165, 1123, 1072, 806 cm^{-1}; HRMS (FAB+) m/z: ([M+H]$^+$) Calculated for $C_{33}H_{34}F_6NO_2$ 590.2494; Found 590.2499

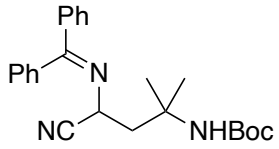
methyl 2-(((4-methoxyphenyl)(3-(trifluoromethyl)phenyl)methylene)amino)-3-(1-methylcyclohexyl)-2-(*p*-tolyl)propanoate (51)



According to general procedure **II**, the reaction using alkene **1a** (55.1 mg, 0.31 mmol), carboxylic acid **2a** (42.6 mg, 0.30 mmol), iodine reagent **3g** (190.1 mg, 0.36 mmol), K_2CO_3 (41.7 mg, 0.30 mmol), and DMSO (3 mL) was conducted for 12 h. Purification by flash column chromatography on NH silica gel (hexane/EtOAc = 95:5) and gel permeation chromatography (GPC, $CHCl_3$ as an eluent) gave the product as a white solid (129.1 mg, 78% yield). The product was obtained as a mixture of *E*/*Z* isomers.

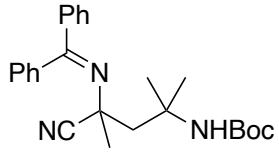
mp: 73.6–77.8 °C; ^{1}H NMR of a mixture of *E*/*Z* isomers: (400 MHz, $CDCl_3$) δ 7.95 (s, 0.4H), 7.89 (d, J = 7.6 Hz, 0.4H), 7.67–7.37 (m, 4H), 7.36–7.20 (m, 2H), 7.15 (s, 0.6H), 7.10 (d, J = 8.4 Hz, 0.6H), 7.04–6.96 (m, 2H), 6.90–6.83 (m, 2H), 3.85 (s, 1.2H), 3.82 (s, 1.8H), 3.30 (s, 1.8H), 3.21 (s, 1.2H), 2.55–2.20 (m, 5H), 1.49–1.00 (m, 10H), 0.85 (s, 1.8H), 0.75 (s, 1.2H); ^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$) complicated due to mixture of *E*/*Z* isomers and C–F coupling; ^{19}F{^{1}H} NMR: (100 MHz, $CDCl_3$) δ −65.2, −65.3; IR: (ATR) 2926, 1730, 1599, 1508, 1331, 1250, 1165, 1125, 1072, 1032, 804 cm^{-1}; HRMS (FAB+) m/z: ([M+H]$^+$) Calculated for $C_{33}H_{37}F_3NO_3$ 552.2726; Found 552.2729

tert-butyl (4-cyano-4-((diphenylmethylene)amino)-2-methylbutan-2-yl)carbamate (52)



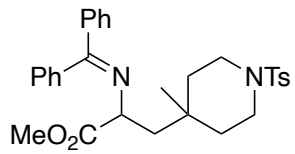
According to general procedure **III**, the reaction using alkene **1s** (11.3 mg, 0.21 mmol), carboxylic acid **2l** (40.6 mg, 0.20 mmol), iodine reagent **3a** (128.5 mg, 0.30 mmol), KOAc (23.2 mg, 0.24 mmol), and acetone (3 mL) was conducted for 2 h. Purification by flash column chromatography on NH silica gel (hexane/EtOAc = 90:10) gave the product as colorless oil (51.6 mg, 66% yield). ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 7.2 Hz, 2H), 7.58–7.48 (m, 3H), 7.45 (t, *J* = 7.2 Hz, 1H), 7.36 (dd, *J* = 7.2, 7.2 Hz, 2H), 7.32–7.20 (m, 2H), 4.83 (brs, 1H), 4.36 (dd, *J* = 7.2, 5.6 Hz, 1H), 2.41 (dd, *J* = 14.4, 5.6 Hz, 1H), 2.33 (dd, *J* = 14.4, 7.2 Hz, 1H), 1.32 (s, 9H), 1.28 (s, 6H); ^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$) δ 173.3, 154.3, 138.4, 135.3, 131.4, 129.6, 129.19, 129.15, 128.4, 127.4, 119.9, 79.0, 51.8, 50.1, 44.4, 28.5, 28.3, 27.2; IR: (ATR) 3364, 2974, 2930, 1713, 1493, 1447, 1366, 1246, 1159, 1074, 772 cm^{-1}; HRMS (DART) *m*/*z*: ([M+H]$^{+}$) Calculated for $C_{24}H_{30}N_3O_2$ 392.2338; Found 392.2319

tert-butyl (4-cyano-4-((diphenylmethylene)amino)-2-methylpentan-2-yl)carbamate (53)



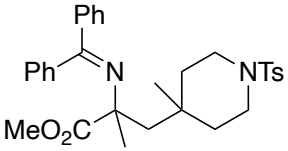
According to general procedure **III**, the reaction using alkene **1t** (13.7 mg, 0.20 mmol), carboxylic acid **2l** (40.3 mg, 0.20 mmol), iodine reagent **3a** (128.3 mg, 0.30 mmol), KOAc (23.1 mg, 0.24 mmol), and acetone (3 mL) was conducted for 2 h. Purification by flash column chromatography on NH silica gel (hexane/EtOAc = 90:10) gave the product as colorless oil (56.7 mg, 70% yield).
^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 7.2 Hz, 2H), 7.57–7.46 (m, 3H), 7.42 (t, *J* = 7.2 Hz, 1H), 7.35 (dd, *J* = 7.2, 7.2 Hz, 2H), 7.30–7.22 (m, 2H), 5.70 (brs, 1H), 2.46 (d, *J* = 14.8 Hz, 1H), 2.28 (d, *J* = 14.8 Hz, 1H), 1.65 (s, 3H), 1.50 (s, 3H), 1.44 (s, 3H), 1.36 (s, 9H); ^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$) δ 168.3, 154.5, 139.4, 135.0, 131.0, 129.8, 128.7, 128.4, 120.7, 78.7, 55.5, 53.7, 52.9, 31.6, 28.9, 28.6, 26.8 (two sp^2 signals were not observed because of overlapping); IR: (ATR) 3360, 2976, 2928, 1715, 1497, 1447, 1364, 1271, 1163, 1067, 773 cm^{-1}; HRMS (DART) *m*/*z*: ([M+H]$^{+}$) Calculated for $C_{25}H_{32}N_3O_2$ 406.2495; Found 406.2478

methyl 2-((diphenylmethylene)amino)-3-(4-methyl-1-tosylpiperidin-4-yl)propanoate (54)



According to general procedure **III**, the reaction using alkene **1u** (17.6 mg, 0.20 mmol), carboxylic acid **2k** (59.9 mg, 0.20 mmol), iodine reagent **3a** (128.3 mg, 0.30 mmol), KOAc (23.9 mg, 0.24 mmol), and acetone (6 mL) was conducted for 2 h. Purification by flash column chromatography on NH silica gel (hexane/EtOAc = 90:10) gave the product as a viscous oil (26.2 mg, 25% yield).
^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 8.0 Hz, 2H), 7.56 (d, *J* = 7.2 Hz, 2H), 7.53–7.38 (m, 4H), 7.38–7.28 (m, 4H), 7.21–7.08 (m, 2H), 4.15 (dd, *J* = 6.8, 4.8 Hz, 1H), 3.68 (s, 3H), 3.18–3.02 (m, 2H), 2.92–2.77 (m, 2H), 2.44 (s, 3H), 1.98 (dd, *J* = 14.4, 4.8 Hz, 1H), 1.86 (dd, *J* = 14.4, 6.8 Hz, 1H), 1.54–1.38 (m, 2H), 1.38–1.21 (m, 2H), 0.62 (s, 3H); ^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$) δ 173.4, 170.1, 143.6, 139.3, 136.3, 133.3, 130.7, 129.8, 129.1, 128.9, 128.7, 128.3, 127.8, 127.7, 62.6, 52.5, 44.4, 42.22, 42.19, 37.1, 36.3, 31.1, 24.0, 21.7; IR: (ATR) 2920, 2855, 1732, 1447, 1344, 1325, 1092, 928, 721 cm^{-1}; HRMS (DART) *m*/*z*: ([M+H]$^+$) Calculated for $C_{30}H_{35}N_2O_4S$ 519.2318; Found 519.2307

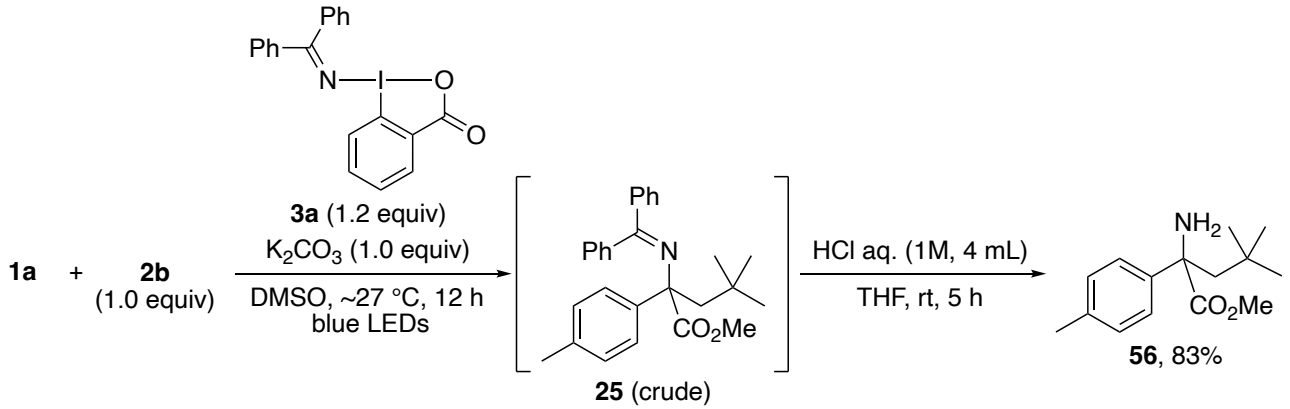
methyl 2-((diphenylmethylene)amino)-2-methyl-3-(4-methyl-1-tosylpiperidin-4-yl)propanoate (55)



According to general procedure **III**, the reaction using alkene **1v** (21.1 mg, 0.21 mmol), carboxylic acid **2k** (59.6 mg, 0.20 mmol), iodine reagent **3a** (128.1 mg, 0.30 mmol), KOAc (23.1 mg, 0.24 mmol), and acetone (6 mL) was conducted for 2 h. Purification by flash column chromatography on NH silica gel (hexane/EtOAc = 90:10) gave the product as a viscous oil (53.1 mg, 50% yield).
^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 8.0 Hz, 2H), 7.50 (d, *J* = 7.2 Hz, 2H), 7.45–7.28 (m, 8H), 7.17–7.04 (m, 2H), 3.35 (s, 3H), 3.42–3.26 (m, 2H), 2.74–2.56 (m, 2H), 2.42 (s, 3H), 2.10 (d, *J* = 14.8 Hz, 1H), 1.91 (d, *J* = 14.8 Hz, 1H), 1.84–1.65 (m, 2H), 1.59–1.47 (m, 2H), 1.34 (s, 3H), 0.92 (s, 3H); ^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$) δ 175.9, 165.7, 143.5, 141.2, 137.7, 133.2, 130.1, 129.7, 128.6, 128.5, 128.1, 127.9, 127.8, 66.8, 55.1, 51.7, 42.3, 37.8, 37.7, 32.1, 26.9, 22.8, 21.7 (one sp^2 and one sp^3 signals were not observed because of overlapping); IR: (ATR) 3671, 2972, 2901, 1728, 1445, 1342, 1161, 1092, 926, 725 cm^{-1}; HRMS (DART) *m*/*z*: ([M+H]$^+$) Calculated for $C_{31}H_{37}N_2O_4S$ 533.2474; Found 533.2475

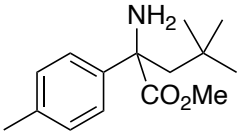
8. Transformation of products

Hydrolysis of 25



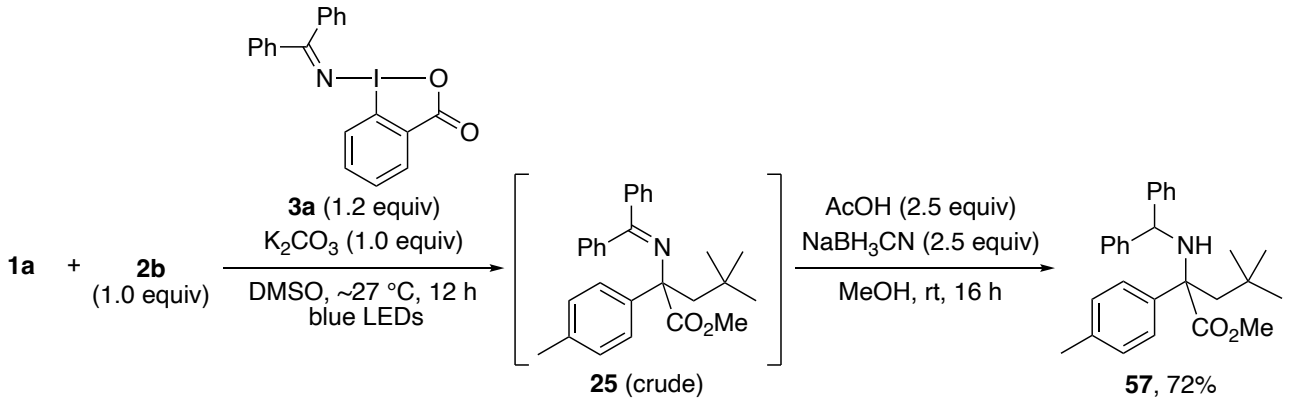
A reaction vial containing a magnetic stir bar was charged with alkene **1a** (73.0 mg, 0.41 mmol), carboxylic acid **2b** (41.3 mg, 0.40 mmol), iodine reagent **3a** (205.5 mg, 0.48 mmol), K_2CO_3 (55.6 mg, 0.41 mmol), and DMSO (4 mL). After the vial was purged with nitrogen and sealed with a screw cap, the mixture was stirred and irradiated with a Kessil lamp 467 nm (40W, 100% intensity, 2 cm away (The measured light intensity is >480 mW.)) with a cooling fun (The reaction temperature within the reaction vial was maintained around 27 °C). After 12 h of irradiation, the reaction was then quenched with H_2O (10 mL). The mixture was extracted with EtOAc (3 × 10 mL). The combined organic extracts were dried over Na_2SO_4, filtrated, and concentrated under reduced pressure to give the crude product. After THF (10 mL), and HCl (1 M in Et_2O, 10 mL) was added to the residue with a magnetic stir bar, the mixture was stirred at room temperature for 12 h. The reaction mixture was diluted with H_2O, washed with Et_2O (3 x 10 mL), and the collected water layers were concentrated under reduced pressure. Then, the residue was basified with sat. $NaHCO_3$ aq. until pH = 9. The mixture was extracted with EtOAc (3 x 10 mL), and the collected organic layers were dried over Na_2SO_4, filtrated, and concentrated under reduced pressure to give the product **56** as a yellow oil (82.8 mg, 83% yield).

methyl 2-amino-4,4-dimethyl-2-(*p*-tolyl)pentanoate (56)



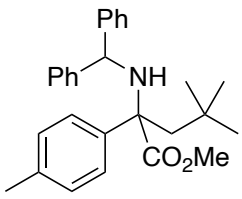
^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.43 (d, J = 8.4 Hz, 2H), 7.13 (d, J = 8.4 Hz, 2H), 3.68 (s, 3H), 2.33 (d, J = 14.8 Hz, 1H), 2.32 (s, 3H), 2.01 (brs, 2H), 1.97 (d, J = 14.8 Hz, 1H), 0.96 (s, 9H); ^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$) δ 177.0, 142.1, 137.0, 129.1, 125.3, 63.8, 52.4, 51.5, 31.7, 31.3, 21.0; IR: (ATR) 2951, 1728, 1510, 1435, 1194, 1177, 820, 756 cm^{-1}; HRMS (FAB+) m/z: ([M+H]$^+$) Calculated for $C_{15}H_{24}NO_2$ 250.1807; Found 250.1803

Hydride reduction of 25



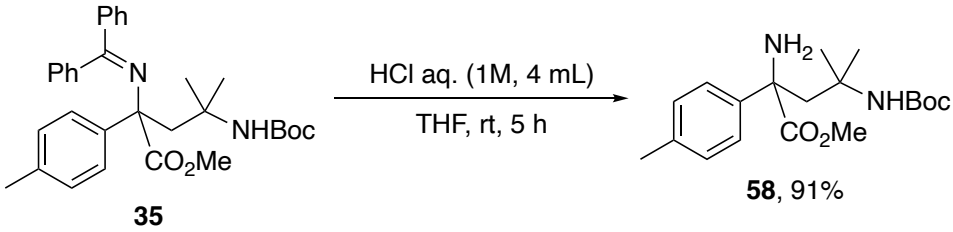
A reaction vial containing a magnetic stir bar was charged with alkene **1a** (72.8 mg, 0.41 mmol), carboxylic acid **2b** (40.6 mg, 0.40 mmol), iodine reagent **3a** (205.5 mg, 0.48 mmol), K_2CO_3 (56.2 mg, 0.41 mmol), and DMSO (4 mL). After the vial was purged with nitrogen and sealed with a screw cap, the mixture was stirred and irradiated with a Kessil lamp 467 nm (40W, 100% intensity, 2 cm away (The measured light intensity is >480 mW.)) with a cooling fun (The reaction temperature within the reaction vial was maintained around 27 °C). After 12 h of irradiation, the reaction was then quenched with H_2O (10 mL). The mixture was extracted with EtOAc (3 × 15 mL). The combined organic extracts were dried over Na_2SO_4, filtrated, and concentrated under reduced pressure to give the crude product. After MeOH (4 mL), $NaCNBH_3$ (63.4 mg, 1.0 mmol), and AcOH (61.2 mg, 1.0 mmol) were added to the residue with a magnetic stir bar under N_2, the mixture was stirred at room temperature for 16 h. The reaction was quenched with H_2O, and the mixture was extracted with EtOAc (3 × 10 mL). The combined organic layers were washed with sat. $NaHCO_3$ aq., dried over Na_2SO_4, filtrated, and concentrated under reduced pressure to give the crude product. Purification by flash column chromatography on NH silica gel (hexane/EtOAc = 60:40) gave the product **57** as a colorless oil (119.0 mg, 72% yield).

methyl 2-(benzhydrylamino)-4,4-dimethyl-2-(*p*-tolyl)pentanoate (57)



^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.31 (d, *J* = 8.0 Hz, 2H), 7.28–7.15 (m, 8H), 7.15–7.06 (m, 2H), 7.00 (d, *J* = 8.0 Hz, 2H), 4.81 (s, 1H), 3.15 (s, 3H), 2.28 (s, 3H), 2.22 (d, *J* = 14.8 Hz, 1H), 2.15 (d, *J* = 14.8 Hz, 1H), 0.72 (s, 9H); ^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$) δ 175.5, 145.52, 145.47 138.6, 136.8, 128.5, 128.24, 128.20, 127.7, 127.5, 127.3, 126.4, 67.7, 61.5, 51.3, 50.2, 31.3, 31.2, 21.1 (one sp^2 signal was not observed because of overlapping); IR: (ATR) 2949, 2922, 1728, 1450, 1169, 820, 743 cm^{-1}; HRMS (FAB+) *m*/*z*: ([M+H]$^+$) Calculated for $C_{28}H_{34}NO_2$ 416.2590; Found 416.2588

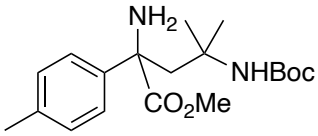
Deprotection of 35



35 **58**, 91%

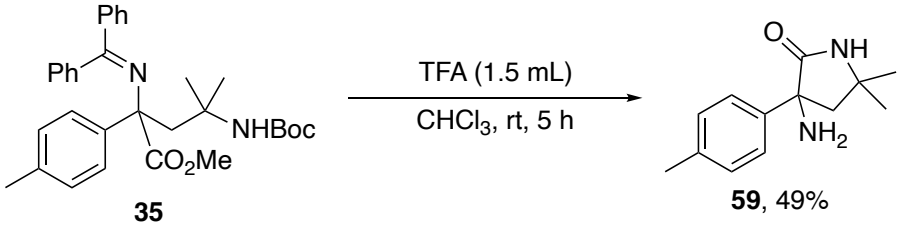
A 10 mL reaction vial containing a magnetic stir bar was charged with **35** (103.2 mg, 0.20 mmol), THF (4 mL), and HCl aq. (1 M, 4 mL). The mixture was stirred at room temperature for 5 h, diluted with H_2O (10 mL), and washed with Et_2O (3 x 10 mL). Then, the combined aqueous layers were basified with sat. $NaHCO_3$ aq. until pH = 9. The mixture was extracted with EtOAc (3 x 10 mL), and the collected organic layers were dried over Na_2SO_4, filtrated, and concentrated under reduced pressure to give the product **58** as colorless oil (64.1 mg, 91% yield).

methyl 2-amino-4-((*tert*-butoxycarbonyl)amino)-4-methyl-2-(*p*-tolyl)pentanoate (58)



^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 8.4 Hz, 2H), 7.14 (d, *J* = 8.4 Hz, 2H), 6.48 (brs, 1H), 3.69 (s, 3H), 2.46 (d, *J* = 15.2 Hz, 1H), 2.33 (s, 3H), 2.32 (d, *J* = 15.2 Hz, 1H), 2.12 (brs, 2H), 1.42 (s, 9H), 1.31 (s, 3H), 1.23 (s, 3H); ^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$) δ 176.3, 154.9, 141.2, 137.4, 129.4, 125.1, 78.5, 63.0, 53.0, 52.7, 48.5, 29.0, 28.7, 27.2, 21.0; IR: (ATR) 3292, 2974, 2928, 1713, 1506, 1363, 1234, 1165, 1065, 822 cm^{-1}; HRMS (ESI) *m*/*z*: ([M+H]$^+$) Calculated for $C_{19}H_{31}N_2O_4$ 351.2284; Found 351.2283

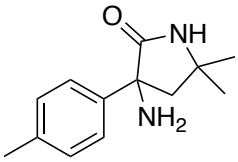
Deprotection and cyclization of 35



35 **59**, 49%

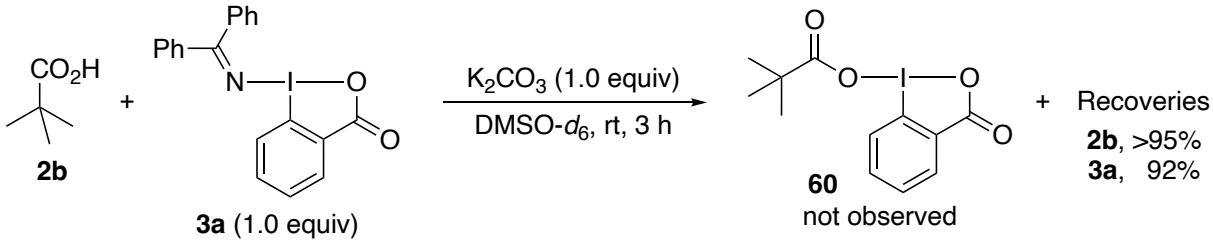
A 10 mL reaction vial containing a magnetic stir bar was charged with **35** (101.7 mg, 0.20 mmol), $CHCl_3$ (3 mL), and trifluoroacetic acid (1.5 mL). The mixture was stirred at room temperature for 5 h, diluted with H_2O (10 mL), and washed with Et_2O (3 x 10 mL). Then, the combined aqueous layers were basified with sat. $NaHCO_3$ aq. until pH = 9. The mixture was extracted with EtOAc (3 x 10 mL), and the collected organic layers were dried over Na_2SO_4, filtrated, and concentrated under reduced pressure to give the product **59** as an off-white solid (21.6 mg, 49% yield).

3-amino-5,5-dimethyl-3-(*p*-tolyl)pyrrolidin-2-one (59)



mp: 178.2–180.5 °C; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 8.0 Hz, 2H), 7.15 (d, *J* = 8.0 Hz, 2H), 6.38 (brs, 1H), 2.52 (d, *J* = 14.0 Hz, 1H), 2.33 (s, 3H), 2.17 (d, *J* = 14.0 Hz, 1H), 1.90 (brs, 2H), 1.38 (s, 3H), 1.10 (s, 3H); ^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$) δ 178.7, 141.8, 137.2, 129.3, 126.1, 63.9, 53.0, 52.8, 31.3, 29.5, 21.2; IR: (ATR) 3343, 3088, 2968, 2920, 1692, 1647, 1508, 1186, 814, 723 cm^{-1}; HRMS (EI) *m*/*z*: (M^+) Calculated for $C_{13}H_{18}N_2O$ 218.1419; Found 218.1421

9. NMR monitoring of the mixture of 2b and 3a and DFT calculations for the ligand exchange



A 3 mL reaction vial containing a magnetic stir bar was charged with pivalic acid **2b** (5.3 mg, 0.05 mmol), iodine reagent **3a** (21.6 mg, 0.05 mmol), K_2CO_3 (6.8 mg, 0.05 mmol), and DMSO-d_6 (1 mL). After the vial was purged with N_2 and sealed with a screw cap, the mixture was stirred at room temperature for 3 h. Mesitylene was added to the mixture as an internal standard before the mixture was transferred into an NMR tube. The resulting ^{1}H NMR spectrum is shown in Figure S3.

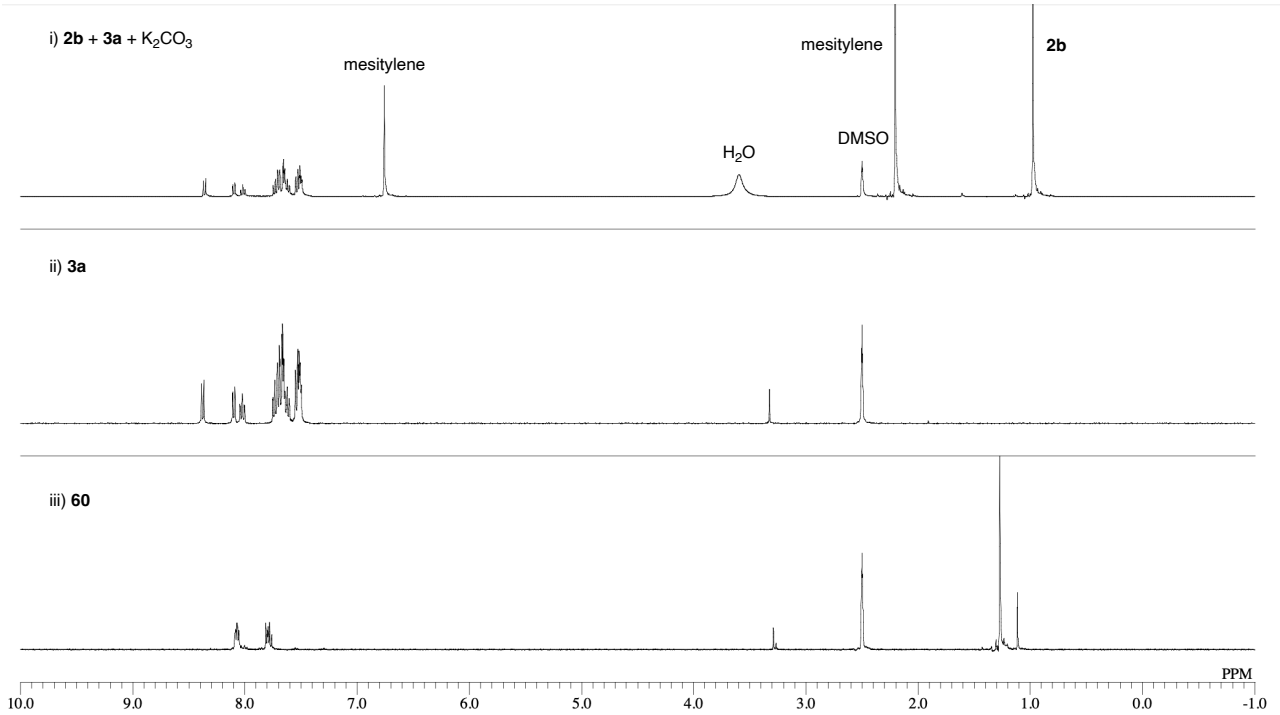


Figure S3. ^{1}H NMR spectra in DMSO-d_6: i) A mixtute of **2b**, **3a**, and K_2CO_3, ii) **3a**, iii) **60**

DFT calculations of the ligand exchange between 2b and 3a

Density functional theory (DFT) computations were performed in Gaussian 16, Revision C.01.[15] Molecular geometries were optimized using M06-2X density functional in the 6-311++G(d,p)-SDD(I) basis set with the SMD solvation model (DMSO). Frequency calculations were performed at the same level of theory as that used for geometry optimization to characterize the stationary points as either minima (no imaginary frequencies) or first-order saddle points (one imaginary frequency). The thermal energy corrections were calculated for the optimized geometry at M06-2X level of theory in the 6-311++G(d,p)-SDD(I) basis set with the SMD solvation model (DMSO).

Calculated energies and thermochemical parameters

structure	*E* [hartree]	*H* [hartree]	*TS* [hartree]	*G* [hartree]
2b	-346.989396	-346.833147	0.041467	-346.874615
3a	-986.927007	-986.618354	0.073565	-986.691919
60	-777.244516	-776.996057	0.066475	-777.062532
benzophenone imine	-556.667961	-556.451282	0.049391	-556.500673

Cartesian coordinates of computed structures

2b

C	0.93699	-0.18877	-0.00003
O	1.51012	-1.24922	-0.00002
C	-0.56842	0.01261	-0.00001
O	1.61172	0.97509	-0.00003
H	2.55995	0.77055	-0.00002
C	-0.95715	0.80388	-1.25766
H	-0.64882	0.27653	-2.16472
H	-2.04364	0.92044	-1.28250
H	-0.50352	1.79644	-1.25948
C	-1.25846	-1.34873	-0.00011
H	-0.98865	-1.92884	0.88500
H	-2.34123	-1.20180	-0.00012
H	-0.98860	-1.92871	-0.88528
C	-0.95706	0.80366	1.25784
H	-0.50352	1.79626	1.25974
H	-2.04356	0.92009	1.28285
H	-0.64853	0.27621	2.16478

3a

I	-1.00050	-0.76495	-0.30870
O	-3.17737	-1.76301	-0.20644
O	-5.33013	-1.20965	0.04902
N	0.58226	0.62408	-0.37742
C	-2.35188	0.85814	0.04921
C	-1.89334	2.15552	0.19127
H	-0.84012	2.39017	0.12609
C	-2.84001	3.15184	0.42325
H	-2.50713	4.17676	0.53900
C	-4.19400	2.83840	0.50706
H	-4.92046	3.62186	0.68747
C	-4.61361	1.52222	0.36207
H	-5.66182	1.25502	0.42729
C	-3.68887	0.50450	0.12917
C	-4.13605	-0.94127	-0.01941
C	1.76732	0.21751	-0.14381
C	2.85066	1.24839	-0.13148
C	2.53452	2.59414	0.08392
H	1.50384	2.87502	0.26572
C	3.53507	3.55572	0.07768
H	3.28473	4.59507	0.25628
C	4.85963	3.18586	-0.15441
H	5.63974	3.93865	-0.16136
C	5.17914	1.84989	-0.37278
H	6.20679	1.55818	-0.55563
C	4.17998	0.88078	-0.35491
H	4.43687	-0.15816	-0.52711
C	2.15494	-1.20148	0.11426
C	1.94367	-2.16941	-0.86845
H	1.53394	-1.88197	-1.83197
C	2.27920	-3.49709	-0.61654
H	2.12315	-4.24616	-1.38400
C	2.81688	-3.85735	0.61503
H	3.07322	-4.89192	0.81216
C	3.03264	-2.88873	1.59387
H	3.45319	-3.16912	2.55260
C	2.71608	-1.55908	1.34170
H	2.89295	-0.79925	2.09549

60

I	-0.29531	-1.08794	-0.00009
O	-4.47646	-1.22492	0.00053
C	-1.43520	0.71151	-0.00010
C	-0.88403	1.97845	-0.00025
H	0.18513	2.13560	-0.00039
C	-1.77350	3.05253	-0.00023
H	-1.37609	4.06069	-0.00035
C	-3.15115	2.84467	-0.00006
H	-3.82419	3.69350	-0.00004
C	-3.66441	1.55423	0.00009
H	-4.73237	1.37016	0.00022
C	-2.79656	0.46471	0.00006
O	1.38830	0.21244	0.00005
C	2.54776	-0.41744	-0.00023
O	2.61962	-1.63149	-0.00054
C	3.74154	0.53355	0.00012
C	-3.29558	-0.95259	0.00017
O	-2.33894	-1.84389	-0.00013
C	5.03698	-0.27305	-0.00118
H	5.10662	-0.90802	-0.88696
H	5.88692	0.41428	-0.00097
H	5.10744	-0.90956	0.88342
C	3.65894	1.41231	-1.25521
H	3.66847	0.80307	-2.16346
H	2.75108	2.01856	-1.25171
H	4.52342	2.08089	-1.28309
C	3.65988	1.40974	1.25731
H	2.75205	2.01605	1.25571
H	3.67003	0.79866	2.16433
H	4.52441	2.07822	1.28594

benzophenone imine

C	-0.00884	1.15127	0.01764
C	1.27683	0.38806	0.04190
C	2.37826	0.85611	-0.68017
C	1.40626	-0.77012	0.81404
C	3.59110	0.17779	-0.62930
H	2.28091	1.74308	-1.29766
C	2.62535	-1.43658	0.87828
H	0.55724	-1.14125	1.37757
C	3.71791	-0.96708	0.15342
H	4.43543	0.54085	-1.20394
H	2.72067	-2.32495	1.49196
H	4.66433	-1.49400	0.19567
C	-1.28912	0.38437	-0.03397
C	-1.37494	-0.83393	-0.71361
C	-2.43307	0.90963	0.57458
C	-2.58980	-1.50800	-0.79507
H	-0.49641	-1.25036	-1.19375
C	-3.64183	0.22780	0.50563
H	-2.36319	1.84996	1.10878
C	-3.72346	-0.98123	-0.18285
H	-2.64923	-2.44552	-1.33581
H	-4.52060	0.63788	0.99016
H	-4.66718	-1.51184	-0.23914
N	-0.06357	2.42615	0.04215
H	0.87525	2.82459	0.10797

10. UV-vis absorption spectra of 3a and the reaction mixture in DMSO

All samples were prepared using dry DMSO which were degassed by bubbling with N_2 gas for 30 min before use. Sample A: A 10 mL volumetric flask was charged with **3a** (213.8 mg, 0.50 mmol) and DMSO (10 mL). The solution was transferred to 1 cm^2 quartz cuvette. Sample B: A 10 mL volumetric flask was charged with **1a** (90.3 mg, 0.51 mmol), **2a** (71.3 mg, 0.50 mmol), **3a** (213.2 mg, 0.50 mmol), K_2CO_3 (70.2 mg, 0.51 mmol), and DMSO (10 mL). The solution was transferred to 1 cm^2 quartz cuvette. The resulting UV-vis absorption spectra are shown in Figure S4.

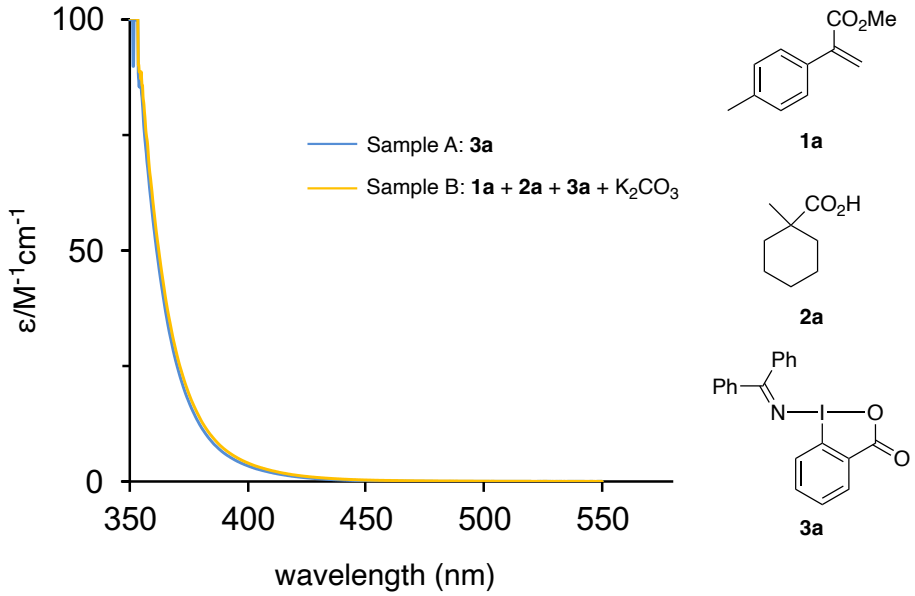


Figure S4.

11. Fluorescence emission analysis and sub-nanosecond transient absorption (TA) spectroscopy measurement of 3a in DMSO

To investigate the photochemical reactivity of DABX **3a**, fluorescence emission analysis of **3a** in DMSO at room temperature was performed, but no significant emission signal was observed as observed from DMSO (Figure S5). In addition, no signal corresponding to the singlet excited state was observed by sub-nanosecond transient absorption (TA) spectroscopy measurements of **3a** in DMSO (Figure S6), while *ortho*-iodobenzoyloxy radical (**62**) with λ_{max} ~410 nm was observed within the time resolution of ~200 ps even though no rise signal at 410 nm was observed. These results indicate that the singlet electronically excited state, ^{1}[**3a**]*, is chemically very reactive and/or that the intersystem crossing process is fast to produce the triplet state ^{3}[**3a**]*. Thus, the lifetime of the singlet excited state of **3a**, ^{1}[**3a**]*, would be too short to participate in the intermolecular reaction (redox process).

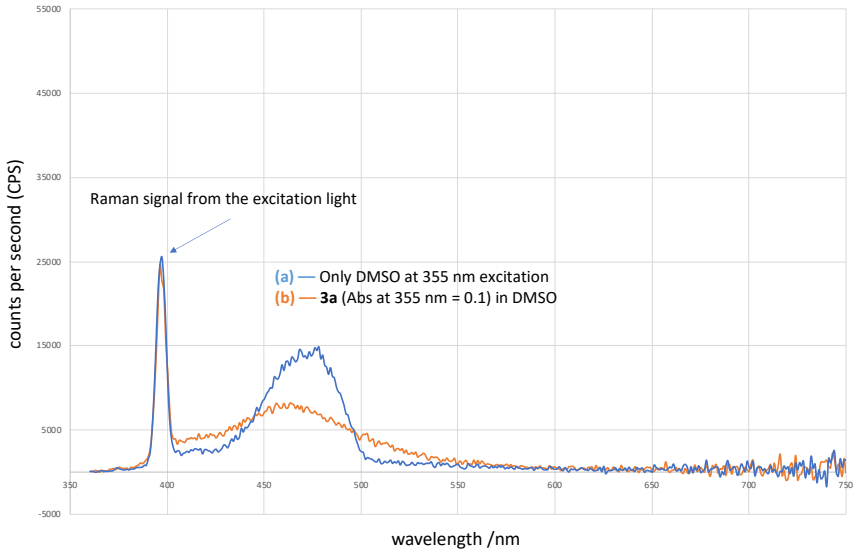


Figure S5. Emission signals from (a) DMSO and (b) **3a** in DMSO at 355 nm excitation.

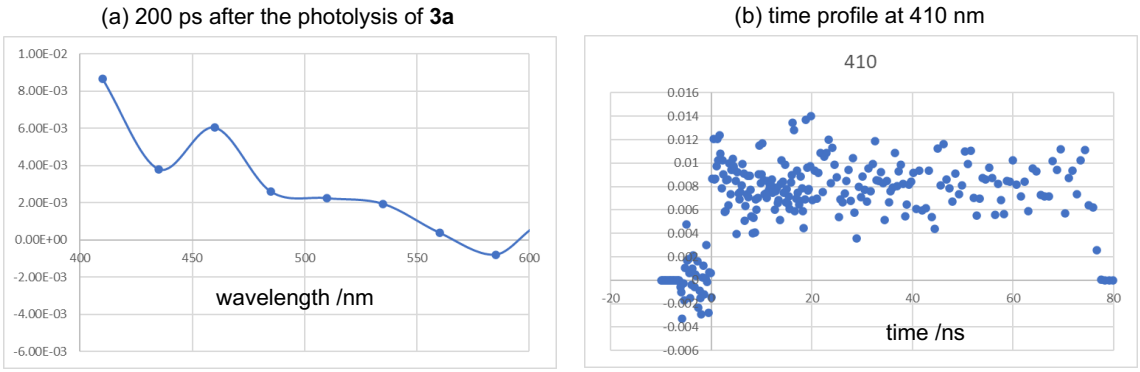


Figure S6. Sub-nanosecond transient absorption spectroscopy in the photolysis of **3a**; (a) Transient absorption spectrum right after the photolysis. (b) The time profile at 410 nm.

12. Sub-microsecond transient absorption (TA) spectroscopy measurement of 3a in DMSO using laser flash photolysis (LFP) method

A 25 mL of stock solution of **3a** (1.7 x 10^{-4} M) in DMSO was prepared for the transient absorption (TA) spectroscopy measurements using laser flash photolysis (LFP) method with Nd-YAG laser (266 or 355 nm, 6 mJ, 12 ns pulse width). The sub-microsecond TA spectra were measured using 1.5 mL of the solution under an air or argon atmosphere at 298 K (Scheme 7a). The time profiles at the monitored wavelengths were measured from 300 nm to 680 nm at every 20 nm. The recovering signal of **3a** at 300 nm was well reproduced by the second-order kinetics (Figure S7). The second-order kinetic equation could reproduce the decay signal of **62** at 420 nm (Figure S8).

The quenching experiments of **62** by RCO_2K were performed in the presence of different concentration of RCO_2K (5 mM, 25 mM, 50 mM, and 100 mM) (Scheme 7b). The observed decay rate-constants were determined by the pseudo-first order analysis.

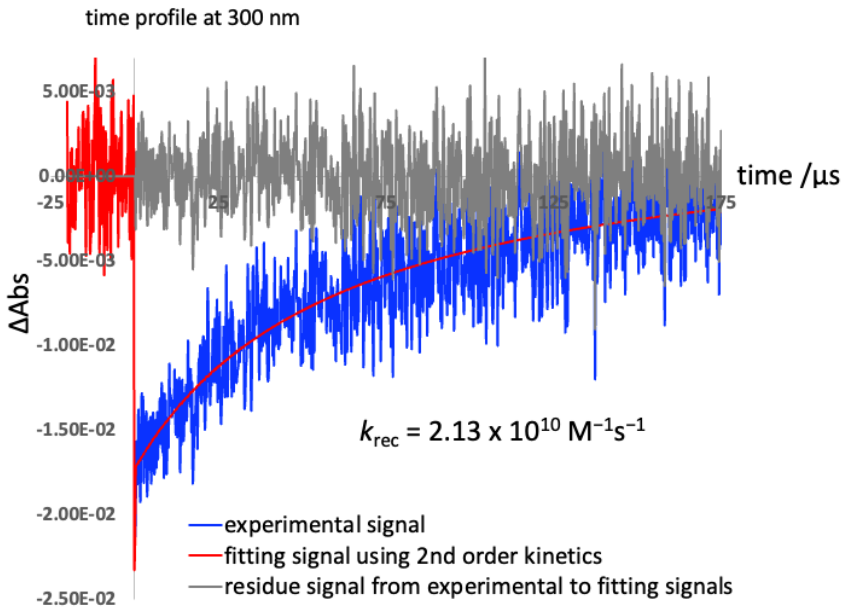


Figure S7.

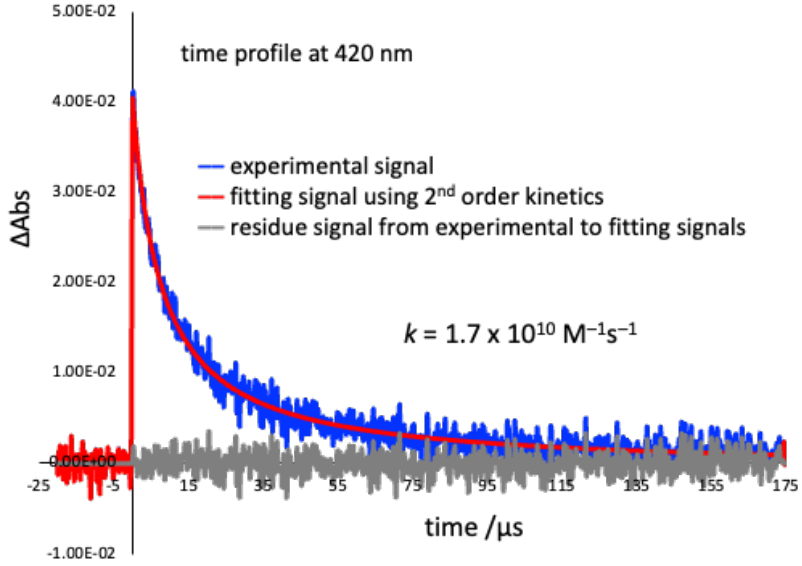


Figure S8.

13. TD-DFT calculations: absorption spectra of 3a, 61a, 62, and 2-iodobenzoate (62 anion)

Density functional theory (DFT) computations were performed in Gaussian 16, Revision C.01.[15] Molecular geometries were optimized using UB3LYP density functional in the 6-31G(d)-LANL2DZ(I) basis set with the SMD solvation model (DMSO). Frequency calculations were performed at the same level of theory as that used for geometry optimization to characterize the stationary points as either minima (no imaginary frequencies) or first-order saddle points (one

imaginary frequency). The thermal energy corrections were calculated for the optimized geometry at UB3LYP level of theory in the 6-31G(d)-LANL2DZ(I) basis set with the SMD solvation model (DMSO).

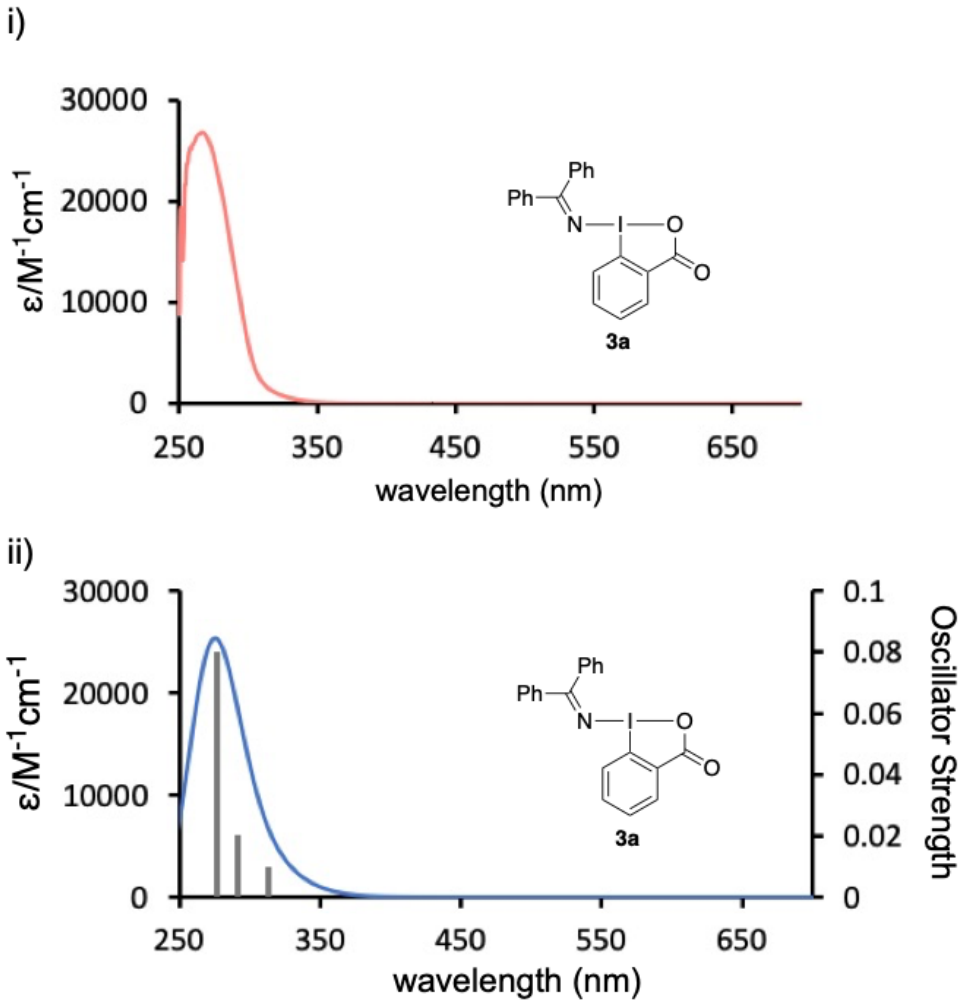


Figure S9. i) UV-vis absorption spectra of **3a** in DMSO. ii)TD-DFT absorption spectrum of **3a**.

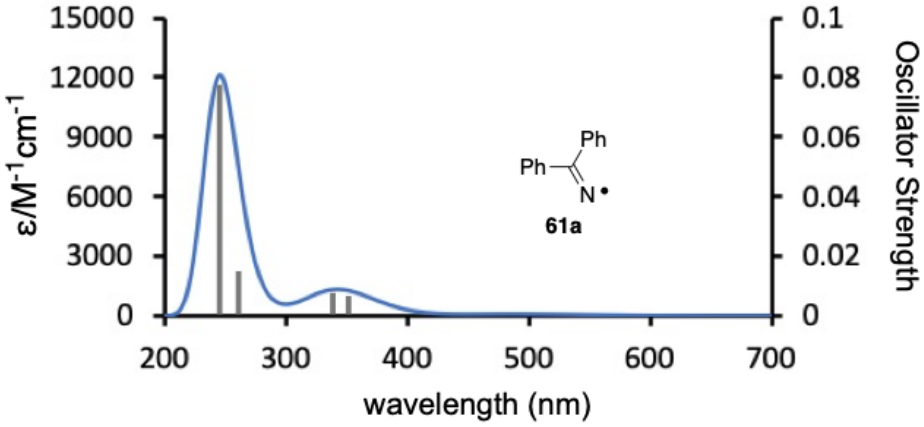


Figure S10. TD-DFT absorption spectrum of **61a**.

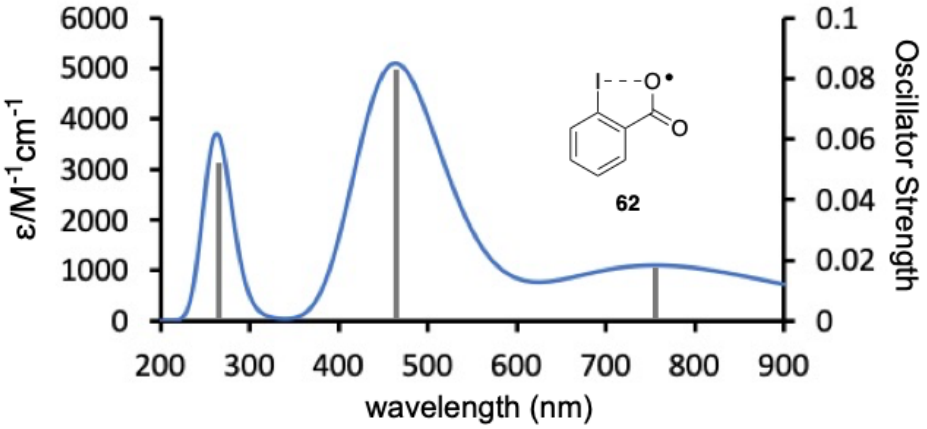


Figure S11. TD-DFT absorption spectrum of **62**.

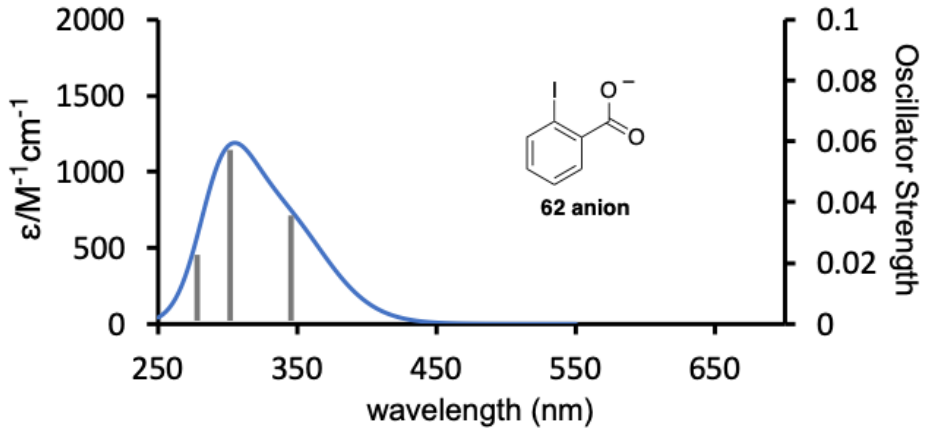


Figure S12. TD-DFT absorption spectrum of **62 anion**.

14. DFT calculations for the reaction of radical 62 with O_2

Density functional theory (DFT) computations were performed in Gaussian 16, Revision C.01.[15] Molecular geometries were optimized using UB3LYP density functional in the 6-31G(d)-LANL2DZ(I) basis set. Frequency calculations were performed at the same level of theory as that used for geometry optimization to characterize the stationary points as either minima (no imaginary frequencies) or first-order saddle points (one imaginary frequency). The thermal energy corrections were calculated for the optimized geometry at UB3LYP level of theory in the 6-31G(d)-LANL2DZ(I) basis set. Molecular structure visualizations were obtained using CYLview.[16]

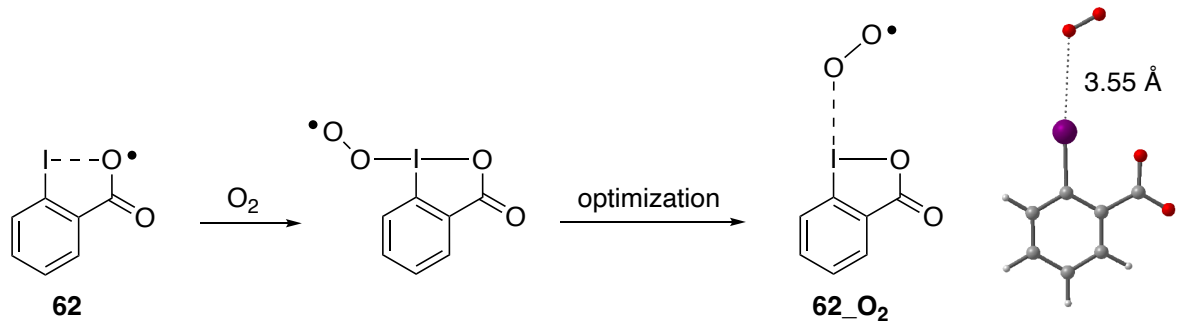


Figure S13.

Calculated energies and thermochemical parameters

structure	*E* [hartree]	*H* [hartree]	*TS* [hartree]	*G* [hartree]
62	-430.916699	-430.815605	0.045810	-430.861415
O_2	-150.320040	-150.312951	0.023286	-150.336237
62_O_2	-581.234092	-581.124480	0.063954	-581.188434

Cartesian coordinates of computed structures

62

C	-0.42020	-0.61928	0.00000
C	-3.16060	-1.09429	-0.00001
C	-1.29966	0.46502	-0.00002
C	-0.88426	-1.93190	0.00003
C	-2.26211	-2.16377	0.00003
C	-2.67849	0.21054	-0.00003
H	-0.18953	-2.76446	0.00006
H	-2.62798	-3.18658	0.00006
H	-3.34845	1.06505	-0.00006
H	-4.23038	-1.27897	-0.00001
C	-0.86380	1.89248	-0.00006
O	0.39093	2.20236	0.00008
O	-1.65908	2.84198	0.00002
I	1.69729	-0.27816	-0.00001

O_2

O	0.00000	0.00000	0.60719
O	0.00000	0.00000	-0.60719

62_O_2

C	1.17413	-0.58071	-0.00035
C	3.95681	-0.63177	-0.00406
C	1.87943	0.62460	-0.00052
C	1.83479	-1.80676	-0.00200
C	3.23174	-1.82585	-0.00386
C	3.28103	0.58404	-0.00240
H	1.27544	-2.73596	-0.00184
H	3.74935	-2.78105	-0.00516
H	3.81276	1.53094	-0.00250
H	5.04238	-0.65092	-0.00551
C	1.23040	1.96779	0.00119
O	-0.05682	2.08277	0.00297
O	1.87010	3.02856	0.00101
I	-0.96867	-0.56784	0.00250
O	-4.50901	-0.29907	0.00478
O	-5.06311	0.78079	-0.01448

15. Determination of computed reduction potentials

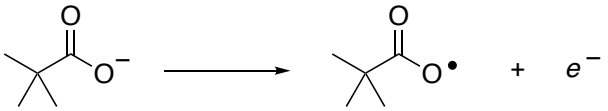
Density functional theory (DFT) computations were performed in Gaussian 16, Revision C.01.[15] Molecular geometries were optimized using M06-2X density functional in the 6-31+G(d,p)-LANL2DZ(I) basis set with the CPCM solvation model (DMSO) and M06 density functional in the Def2-TZVPP basis set with the CPCM or SMD solvation model (DMSO). Frequency calculations were performed at the same level of theory as that used for geometry optimization to characterize the stationary points as either minima (no imaginary frequencies) or first-order saddle points (one imaginary frequency). The thermal energy corrections were calculated for the optimized geometry at M06-2X level of theory in the 6-31+G(d,p)-LANL2DZ(I) basis set

with the CPCM solvation model (DMSO) and M06 level of theory in the Def2-TZVPP basis set with the CPCM or SMD solvation model (DMSO).[17]

The redox potentials were determined according to the following equation:[18]

$$E^{o}_{1/2} = -\frac{G_{(red)} - G_{(ox)}}{nF} - E^{o,SHE}_{1/2} + E^{o,SCE}_{1/2}$$

Where n is the number of electrons transferred (n = 1 in this case), F is Faraday's constant (23.061 kcal mol^{-1} V^{-1}), $E^{o,SHE}_{1/2}$ is the absolute value for the standard hydrogen electrode (SHE, value = 4.281 V), and $E^{o,SCE}_{1/2}$ is the potential of the saturated calomel electrode (SCE) relative to SHE in DMSO (value = −0.279 V).[19] $G_{(red)}$ and $G_{(ox)}$ are the Gibbs free energies in DMSO as gathered from DFT calculations.



(red) **Piv_anion** (ox) **Piv_radical**

M06-2X/6-31+G(d,p)-LANL2DZ(I),CPCM(DMSO)

$G_{(red)}$ = −346.327593 Hartree, $G_{(ox)}$ = −346.109512 Hartree

$G_{(red)} - G_{(ox)}$ = {(−346.327593) − (−346.109512)} × 627.51 = −136.85 kcal mol^{-1}

$E^{o}_{1/2}$ = 1.37 V vs. SCE

M06/Def2-TZVPP,CPCM(DMSO)

$G_{(red)}$ = −346.378721 Hartree, $G_{(ox)}$ = −346.173045 Hartree

$G_{(red)} - G_{(ox)}$ = {(−346.378721) − (−346.173045)} × 627.51 = −129.06 kcal mol^{-1}

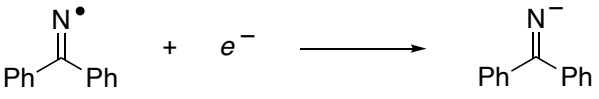
$E^{o}_{1/2}$ = 1.03 V vs. SCE

M06/Def2-TZVPP,SMD(DMSO)

$G_{(red)}$ = −346.369398 Hartree, $G_{(ox)}$ = −346.175856 Hartree

$G_{(red)} - G_{(ox)}$ = {(−346.369398) − (−346.175856)} × 627.51 = −121.45 kcal mol^{-1}

$E^{o}_{1/2}$ = 0.71 V vs. SCE



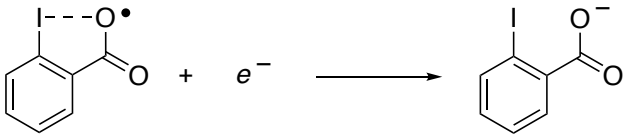
(ox) **61a** (red) **61a anion**

$G_{(red)}$ = −555.86733 Hartree

$G_{(ox)}$ = −555.74103 Hartree

$G_{(red)} - G_{(ox)}$ = {(−555.86733) − (−555.74103)} × 627.51 = −79.25 kcal mol^{-1}

$E^{o}_{1/2}$ = −1.12 V vs. SCE



(ox) **62** (red) **62 anion**

M06-2X/6-31+G(d,p)-LANL2DZ(I),CPCM(DMSO)

$G_{(red)}$ = −430.884557 Hartree, $G_{(ox)}$ = −430.672886 Hartree

$G_{(red)} - G_{(ox)}$ = {(−430.884557) − (−430.672886)} × 627.51 = −132.83 kcal mol^{-1}

$E^{o}_{1/2}$ = 1.20 V vs. SCE

M06/Def2-TZVPP,CPCM(DMSO)

$G_{(red)}$ = −717.358364 Hartree, $G_{(ox)}$ = −717.163607 Hartree

$G_{(red)} - G_{(ox)}$ = {(−717.358364) − (−717.163607)} × 627.51 = −122.21 kcal mol^{-1}

$E^{o}_{1/2}$ = 0.74 V vs. SCE

M06/Def2-TZVPP,SMD(DMSO)

$G_{(red)}$ = −717.353173 Hartree, $G_{(ox)}$ = −717.170068 Hartree

$G_{(red)} - G_{(ox)}$ = {(−717.353173) − (−717.170068)} × 627.51 = −114.90 kcal mol^{-1}

$E^{o}_{1/2}$ = 0.42 V vs. SCE

The value of the reduction potential of radical **62** was found to be highly dependent on the basis set and a solvation model used. As described in the manuscript (Scheme 7b), we have investigated the dynamic quenching of radical **62** with a carboxylate prepared from 2,2-diphenylacetic acid (**2v**) with K_2CO_3, and the quenching rate constant k_q was found to be 2.9 x 10^7 $M^{-1}s^{-1}$. Based on the redox potentials obtained by DFT calculations at the M062X/6-31G+(d,g)-LanL2DZ(I) level of theory, the electron transfer process from pivalate (**Piv_anion**) to radical **62** is endergonic by 0.17 eV. In this case, according to the Rehm-Weller equation, the estimated quenching rate constant is ~1.8 x 10^7 $M^{-1}s^{-1}$ (*J. Am. Chem. Soc.* **2011**, *133*, 11580.), which is in excellent agreement with the experimentally obtained value of k_q = 2.9 x 10^7 $M^{-1}s^{-1}$. Meanwhile, if the electron transfer process is endergonic by 0.29 eV as calculated at the M06/Def2-TZVPP level of theory, the quenching rate constant is estimated to be ~10^6 $M^{-1}s^{-1}$. Furthermore, the reduction potential of pivalate (**Piv_anion**) has been experimentally determined to be +1.29 V in acetonitrile vs SCE (*J. Am. Chem. Soc.* **2015**, *137*, 11340.), which is also in good agreement with the calculated reduction potential of +1.37 V at the M062X/6-31G+(d,g)-LanL2DZ(I),CPCM(DMSO) level of theory.

Therefore, we conclude that the calculated reduction potentials at the M062X/6-31G+(d,g)-LanL2DZ(I),CPCM(DMSO) level of theory are reasonable.

Calculated energies and thermochemical parameters

structure	*E* [hartree]	*H* [hartree]	*TS* [hartree]	*G* [hartree]
Piv_anion	-346.430955	-346.288871	0.038722	-346.327593
Piv_radical	-346.211418	-346.069620	0.039892	-346.109512
61a	-555.894277	-555.690403	0.050627	-555.741030
61a anion	-556.021413	-555.819685	0.046728	-555.867331
62	-430.730447	-430.628101	0.044784	-430.672886
62 anion	-430.942846	-430.841586	0.042971	-430.884557

Cartesian coordinates of computed structures

Piv_anion

C	0.51682	0.00740	-0.00001
C	0.99091	-0.74368	1.25183
H	2.08623	-0.79514	1.27205
H	0.66033	-0.23377	2.16431
H	0.59329	-1.76170	1.26414
C	1.10880	1.41638	-0.00080
H	2.20421	1.36197	-0.00070
H	0.79208	1.97719	-0.88493
H	0.79195	1.97823	0.88262
C	0.99106	-0.74515	-1.25090
H	0.59351	-1.76321	-1.26202
H	0.66050	-0.23636	-2.16402
H	2.08639	-0.79654	-1.27100
C	-1.04016	0.03173	-0.00005
O	-1.61436	-1.09175	-0.00004
O	-1.61978	1.15040	-0.00006

Piv_radical

C	0.53874	-0.00588	-0.00007
C	0.99321	-0.75287	1.26351
H	2.08636	-0.79731	1.27005
H	0.66446	-0.23629	2.16997
H	0.60171	-1.77283	1.27507
C	1.07472	1.43007	-0.00377
H	2.16796	1.39751	-0.00322
H	0.75451	1.97811	-0.89474
H	0.75381	1.98299	0.88394
C	0.99485	-0.76014	-1.25869
H	0.60318	-1.78008	-1.26497
H	0.66742	-0.24867	-2.16851
H	2.08800	-0.80481	-1.26347
C	-0.98450	-0.03351	-0.00073
O	-1.69208	-1.02385	-0.00030
O	-1.56912	1.15078	-0.00041

61a

N	0.00000	2.41247	0.00006
C	0.00001	1.15013	0.00004
C	-1.29917	0.40537	0.03645
C	-3.74912	-0.92618	0.16615
C	-1.41455	-0.77845	0.77321
C	-2.41325	0.91946	-0.63628
C	-3.63399	0.25204	-0.57287
C	-2.63985	-1.43845	0.83991
H	-0.55130	-1.17716	1.29774
H	-2.31314	1.83203	-1.21557
H	-4.49336	0.64882	-1.10353
H	-2.72703	-2.35357	1.41651
H	-4.70053	-1.44620	0.21413
C	1.29918	0.40536	-0.03642
C	3.74911	-0.92623	-0.16621
C	2.41333	0.91950	0.63616
C	1.41449	-0.77854	-0.77307
C	2.63977	-1.43856	-0.83981
C	3.63406	0.25207	0.57270
H	2.31328	1.83213	1.21537
H	0.55118	-1.17729	-1.29748
H	2.72689	-2.35374	-1.41633
H	4.49348	0.64890	1.10324
H	4.70051	-1.44625	-0.21422

61a anion

N	0.00004	2.53186	0.00022
C	0.00004	1.27224	0.00010
C	-1.27979	0.43332	0.02845
C	-3.71502	-0.98310	0.18704
C	-1.38908	-0.73041	0.80174
C	-2.41388	0.86767	-0.66872
C	-3.61649	0.16639	-0.60146
C	-2.59661	-1.42568	0.89376
H	-0.51986	-1.09254	1.34625
H	-2.33498	1.77548	-1.26129
H	-4.47947	0.51448	-1.16249
H	-2.66298	-2.31466	1.51488
H	-4.65265	-1.52735	0.24831
C	1.27984	0.43327	-0.02841
C	3.71496	-0.98333	-0.18716
C	2.41419	0.86792	0.66813
C	1.38881	-0.73084	-0.80118
C	2.59628	-1.42621	-0.89327
C	3.61675	0.16657	0.60079
H	2.33551	1.77603	1.26027
H	0.51939	-1.09320	-1.34522
H	2.66240	-2.31550	-1.51398
H	4.47995	0.51490	1.16133
H	4.65254	-1.52765	-0.24849

62

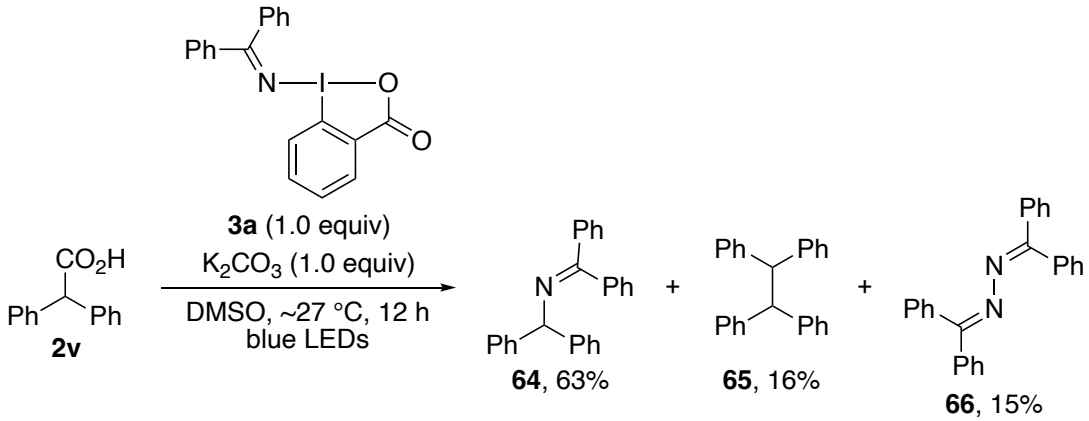
C	-0.48462	-0.61230	-0.00009
C	-3.23692	-0.81243	-0.00001
C	-1.24330	0.55104	-0.00001
C	-1.05683	-1.87676	-0.00016
C	-2.44976	-1.96533	-0.00013
C	-2.63549	0.44174	0.00006

H	-0.44747	-2.77365	-0.00021	H	0.20791	-2.66631	0.00004
H	-2.91638	-2.94471	-0.00017	H	-2.12274	-3.46273	-0.00003
H	-3.22413	1.35344	0.00014	H	-3.45943	0.62678	-0.00009
H	-4.31816	-0.89466	0.00003	H	-3.99578	-1.80272	-0.00009
C	-0.59326	1.90288	0.00002	C	-1.18347	1.91170	-0.00010
O	0.71101	1.92760	-0.00033	O	-0.01911	2.36986	-0.00020
O	-1.25431	2.93576	0.00028	O	-2.25229	2.57219	0.00013
I	1.61233	-0.36642	0.00005	I	1.76606	-0.13083	0.00005

62 anion

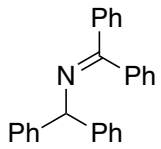
C	-0.32257	-0.57654	-0.00000
C	-2.96261	-1.47035	-0.00006
C	-1.34951	0.37498	-0.00004
C	-0.60399	-1.94687	0.00001
C	-1.92103	-2.39624	-0.00003
C	-2.66680	-0.11294	-0.00006

16. Product analysis of the reaction of 2v with 3a



A 3 mL reaction vial containing a magnetic stir bar was charged with carboxylic acid **2v** (63.9 mg, 0.20 mmol), iodine reagent **3a** (129.0 mg, 0.30 mmol), K_2CO_3 (42.4 mg, 0.31 mmol), and DMSO (3 mL). After the vial was purged with N_2 and sealed with a screw cap, the mixture was stirred and irradiated with a Kessil lamp 467 nm (40W, 100% intensity, 2 cm away (The measured light intensity is >480 mW.)) with a cooling fun (The reaction temperature within the reaction vial was maintained around 27 °C). After 12 h of irradiation, the reaction was then quenched with H_2O (10 mL). The mixture was extracted with EtOAc (3 × 10 mL). The combined organic extracts were dried over Na_2SO_4, filtrated, and concentrated under reduced pressure to give the crude product, which was analyzed by ^{1}H NMR spectroscopy using 1,1,2,2-tetrachloroethane as an internal standard.

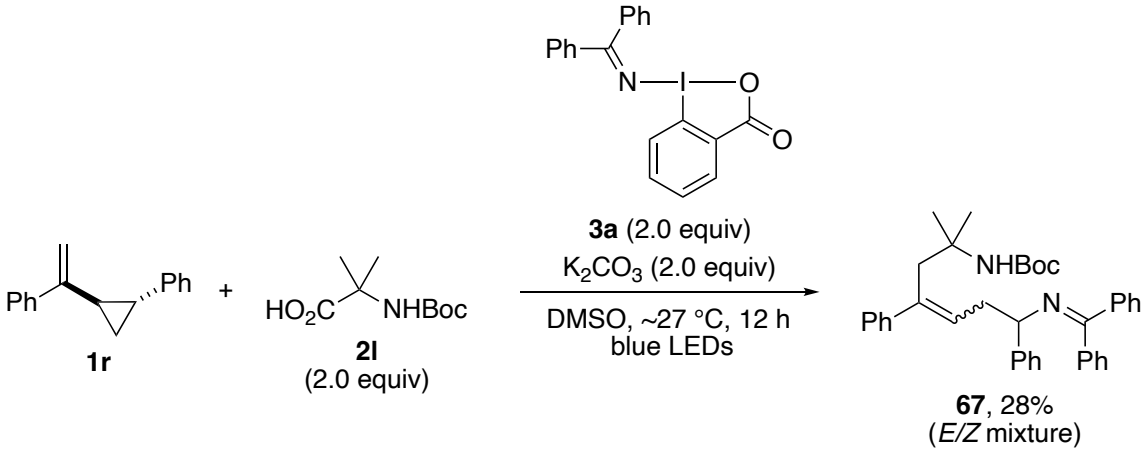
N-benzhydryl-1,1-diphenylmethanimine (64)



^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.75 (dd, *J* = 8.2, 1.6 Hz, 2H), 7.49–7.23 (m, 14H), 7.23–7.16 (m,

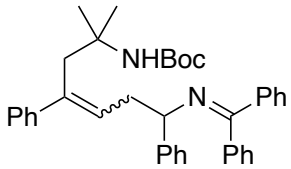
2H), 7.15–6.98 (m, 2H), 5.55 (s, 1H); $^{13}C\{^{1}H\}$ NMR: (100 MHz, $CDCl_3$) δ 167.1, 145.0, 140.0, 136.9, 130.2, 128.9, 128.61, 128.55, 128.5, 128.1, 127.9, 127.7, 126.8, 70.0;
The analytical data for this compound were in excellent agreement with the reported data.[20]

17. Cyclopropane ring-opening experiment



A reaction vial containing a magnetic stir bar was charged with alkene **1r** (67.0 mg, 0.30 mmol), carboxylic acid **2l** (122.4 mg, 0.60 mmol), iodine reagent **3a** (257.0 mg, 0.60 mmol), K_2CO_3 (82.6 mg, 0.60 mmol), and DMSO (3 mL). After the vial was purged with nitrogen and sealed with a screw cap, the mixture was stirred and irradiated with a Kessil lamp 467 nm (40W, 100% intensity, 2 cm away (The measured light intensity is >480 mW.)) with a cooling fun (The reaction temperature within the reaction vial was maintained around 27 °C). After 12 h of irradiation, the reaction was then quenched with H_2O (10 mL). The mixture was extracted with EtOAc (3 × 15 mL). The combined organic extracts were dried over Na_2SO_4, filtrated, and concentrated under reduced pressure to give the crude product. Purification by flash column chromatography on NH silica gel (hexane/EtOAc = 90:10) gave the product **67** as a viscous oil (46.2 mg, 28% yield). The product was obtained as a mixture of *E*/*Z* isomers.

methyl 2-(benzhydrylamino)-4,4-dimethyl-2-(*p*-tolyl)pentanoate (67)

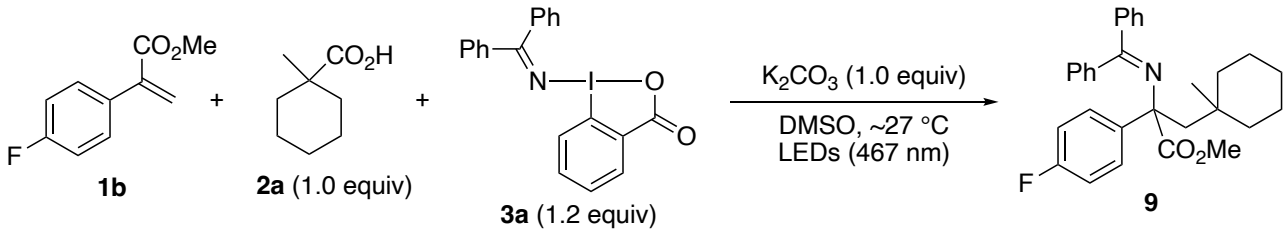


^{1}H NMR signals assigned from a mixture of *E*/*Z* isomers: (400 MHz, $CDCl_3$) δ 7.73–7.56 (m, 2H), 7.56–7.26 (m, 9H), 7.24–7.06 (m, 6H), 7.06–6.89 (m, 3H), 5.48 (dd, *J* = 7.6, 7.2 Hz, 0.7H), 5.43 (dd, *J* = 8.0, 7.2 Hz, 0.3H), 4.47 (dd, *J* = 7.7, 5.8 Hz, 0.7H), 4.36 (dd, *J* = 6.8, 6.8 Hz, 0.3H), 4.17 (brs, 0.7H), 4.12 (brs, 0.3H), 2.90–2.50 (m, 4H), 1.41–1.17 (m, 9H), 1.17–0.92 (m, 6H); $^{13}C\{^{1}H\}$ NMR signals assigned from a mixture of *E*/*Z* isomers (observable signals): (100 MHz, $CDCl_3$) δ 166.9, 166.5, 154.2, 145.4, 144.6, 144.4, 141.6, 140.03, 140.0, 139.4, 139.3, 137.13, 137.09, 130.4, 130.0,

128.71, 128.67, 128.6, 128.43, 128.41, 128.35, 128.30, 128.2, 128.09, 128.06, 127.92, 127.89, 127.4, 127.3, 126.9, 126.8, 126.7, 126.5, 126.4, 78.4, 67.0, 66.8, 53.5, 52.9, 49.3, 39.4, 39.0, 28.5, 27.9; IR: (ATR) 2972, 2930, 1715, 1491, 1364, 1165, 1074, 777 cm^{-1}; HRMS (ESI) *m*/*z*: ($[M+H]^+$) Calculated for $C_{38}H_{43}N_2O_2$ 559.3325; Found 559.3326

18. Light on/off experiments

A 10 mL 0.1 M stock solution of alkene **1b** (236.5 mg, 1.31 mmol) were prepared in DMSO. A 3 mL reaction vial containing a magnetic stir bar was charged with carboxylic acid **2a** (0.20 mmol), iodine reagent **3a** (0.24 mmol), K_2CO_3 (0.20 mmol), and the stock solution (2 mL). Five parallel reaction mixtures in five vials were prepared. After the vials were purged with N_2 and sealed with a screw cap, the mixtures were stirred and irradiated with a Kessil lamp 467 nm (40W, 100% intensity, 2 cm away (The measured light intensity is >480 mW.)) with a cooling fun (The reaction temperature within the reaction vial was maintained around 27 °C). After 30 min of irradiation, the lamp was turned off and one vial was quenched. After another 30 min in dark, another vial was quenched. Then, the lamp was turned on for another 30 min. Repeat the same procedure until the last vial was quenched. The crudes were analyzed by ^1H NMR spectroscopy using 1,1,1,2-tetrachloroethane as an internal standard.



entry	time (min)	light	yield of **9** (%)
1	30	on	9
2	60	off	9
3	90	on	22
4	120	off	22
5	150	on	39

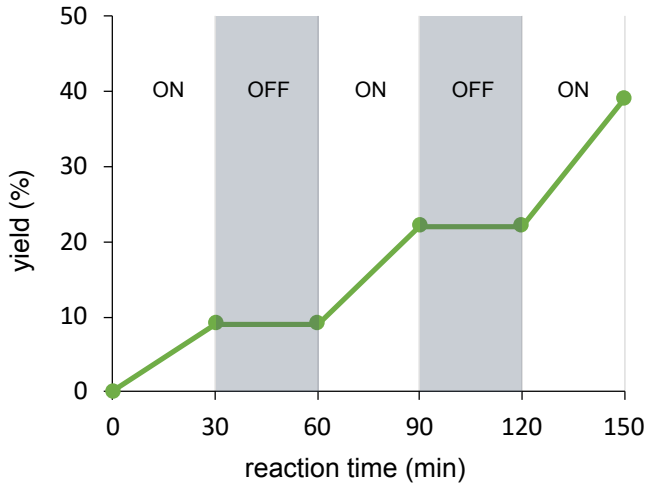
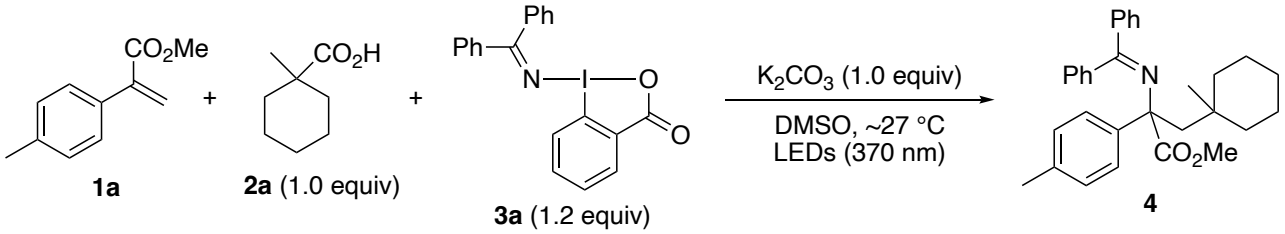


Figure S14.

A 10 mL 0.1 M stock solution of alkene **1a** (178.1 mg, 1.0 mmol) were prepared in DMSO. A 3 mL reaction vial containing a magnetic stir bar was charged with carboxylic acid **2a** (0.10 mmol), iodine reagent **3a** (0.12 mmol), K_2CO_3 (0.10 mmol), and the stock solution (1 mL). Four parallel reaction mixtures in Four vials were prepared. After the vials were purged with N_2 and sealed with a screw cap, the mixtures were stirred and irradiated with a Kessil lamp 370 nm (40W, 100% intensity, 2 cm away with a cooling fun (The reaction temperature within the reaction vial was maintained around 27 °C). After 10 min of irradiation, the lamp was turned off and one vial was quenched. After another 30 min in dark, another vial was quenched. Then, the lamp was turned on for another 10 min. Repeat the same procedure until the last vial was quenched. The crudes were analyzed by ^{1}H NMR spectroscopy using 1,1,2,2-tetrachloroethane as an internal standard.



entry	time (min)	light	yield of **4** (%)
1	10	on	21
2	40	off	20
3	50	on	34
4	120	on	38

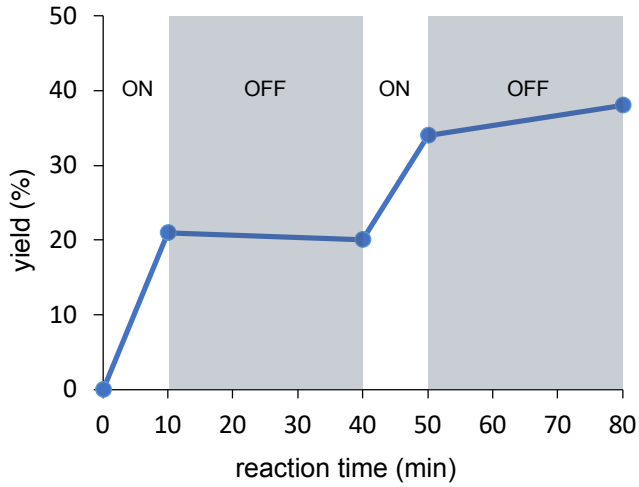


Figure S15.

19. Quantum yield experiments

Chemical actinometer for quantum yield measurement

One of the most reliable and widely used chemical actinometers to measure photon fluxes is ferrioxalate, which upon irradiation decomposes according to the following equations:

$$Fe(C_2O_4)_3^{3+} \xrightarrow{hv} Fe^{2+} + C_2O_4^{-} + 2C_2O_4^{2-}$$

$$Fe^{2+} + 3\,phen \longrightarrow Fe(phen)_3^{2+}$$

The number of ferrous ions generated during the photochemical reaction is determined by conversion to the colored tris-phenanthroline complex, which absorbs the light at 510 nm (ε = 11100 M^{-1} cm^{-1}). The complexation between ferric ions and phenanthroline is not considerable, and their complex does not have absorption at 510 nm.

Procedure for measurement:

1. 120 mg of $K_3[Fe(C_2O_4)_3]\bullet 3H_2O$ was dissolved in 20 mL of 0.05 M H_2SO_4 (1).
2. 5 mg of 1,10-phenanthroline monohydrate and 1.12 g of $CH_3COONa\bullet 3H_2O$ were dissolved in 5 mL of 0.5 M H_2SO_4 (2).
3. 3 mL of solution (1) was taken and irradiated with Xe lamp 365 nm for 0, 10, 20 and 30 s, respectively. After each irradiation, 0.5 mL of solution (2) was added and the absorption spectra were measured.
4. The changes in absorbance at 510 nm with respect to irradiation time were used to calculate the amount of light as the equation below:

$$I\,(mol/s) = \frac{\text{moles of } Fe^{2+}}{\Phi_\lambda \times t \times F} = \frac{V_1 \times V_3 \times \Delta A_{510}}{10^3 \times V_2 \times 1 \times \varepsilon_{510} \times \Phi_\lambda \times t}$$

V_1: irradiated volume (3 mL)

V_2: aliquot of irradiated solution taken for determining ferrous ions (3 mL)

V_3: final volume (3.5 mL)

ΔA_{510}: absorbance difference between solutions before and after irradiation

l: optical pathlength of irradiation cell (1 cm)

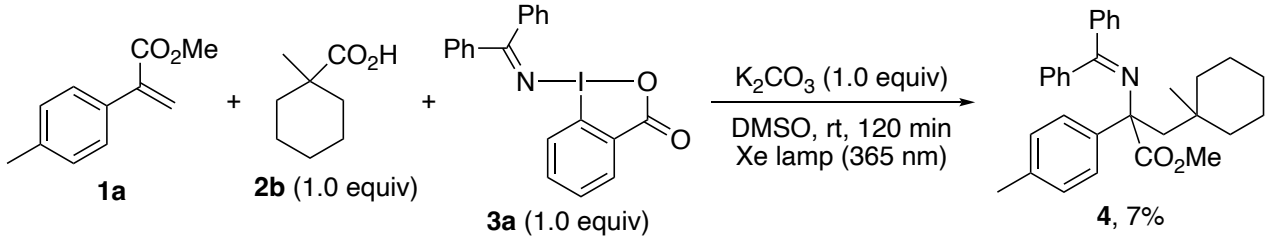
ε_{510}: molar extinction coefficient of $Fe(phen)_3^{2+}$ at 510 nm (11100 $M^{-1}cm^{-1}$)

Φ_λ: quantum yield of ferrous ions generation at the irradiation wavelength (Φ_{365} = 1.21)

t: irradiation time

F: mean function of light absorbed by the ferrioxalate solution

Time (s)	A_{510}	ΔA_{510}	I (mol/s)	I (mol/min)	I_{avg} (mol/min)
0	0	-	-	-	3.8×10^{-7}
10	0.25	0.25	6.5×10^{-9}	3.9×10^{-7}	
20	0.48	0.48	6.3×10^{-9}	3.8×10^{-7}	
30	0.71	0.71	6.2×10^{-9}	3.7×10^{-7}	



A reaction vial containing a magnetic stir bar was charged with alkene **1a** (20.3 mg, 0.12 mmol), carboxylic acid **2a** (14.6 mg, 0.10 mmol), iodine reagent **3a** (42.1 mg, 0.10 mmol), K_2CO_3 (13.8 mg, 0.10 mmol), and DMSO (3 mL). After the vial was purged with nitrogen and sealed with a screw cap, the mixture was stirred and irradiated with a Xe lamp (2 cm away). After 120 min of irradiation, the reaction was then quenched with H_2O (10 mL). The mixture was extracted with EtOAc (3 × 10 mL). The combined organic extracts were dried over Na_2SO_4, filtrated, and concentrated under reduced pressure to give the crude product which was analyzed by ^1H NMR spectroscopy using 1,1,1,2-tetrachloroethane as an internal standard (**4**, 7% yield). The quantum yield (Φ) was determined according to the following equation:

$$\Phi = \frac{0.007\ (\text{mmol})}{3.8\times10^{-7}\ (\text{mol/min}) \times 120\ (\text{min})} = 0.154$$

20. DFT calculations and energy level diagram of the radical addition to 3a

Density functional theory (DFT) computations were performed in Gaussian 16, Revision C.01.[15] Molecular geometries were optimized using M06-2X density functional in the

6-31+G(d,p)-LANL2DZ(I) basis set with the CPCM solvation model (DMSO). Frequency calculations were performed at the same level of theory as that used for geometry optimization to characterize the stationary points as either minima (no imaginary frequencies) or first-order saddle points (one imaginary frequency). Intrinsic Reaction Coordinate (IRC) calculations were performed to confirm that the first-order saddle points found were real transition states connecting the reactants and the products. The thermal energy corrections were calculated for the optimized geometry at M06-2X level of theory in the 6-31+G(d,p)-LANL2DZ(I) basis set with the CPCM solvation model (DMSO). Molecular structure visualizations were obtained using CYLview.[16]

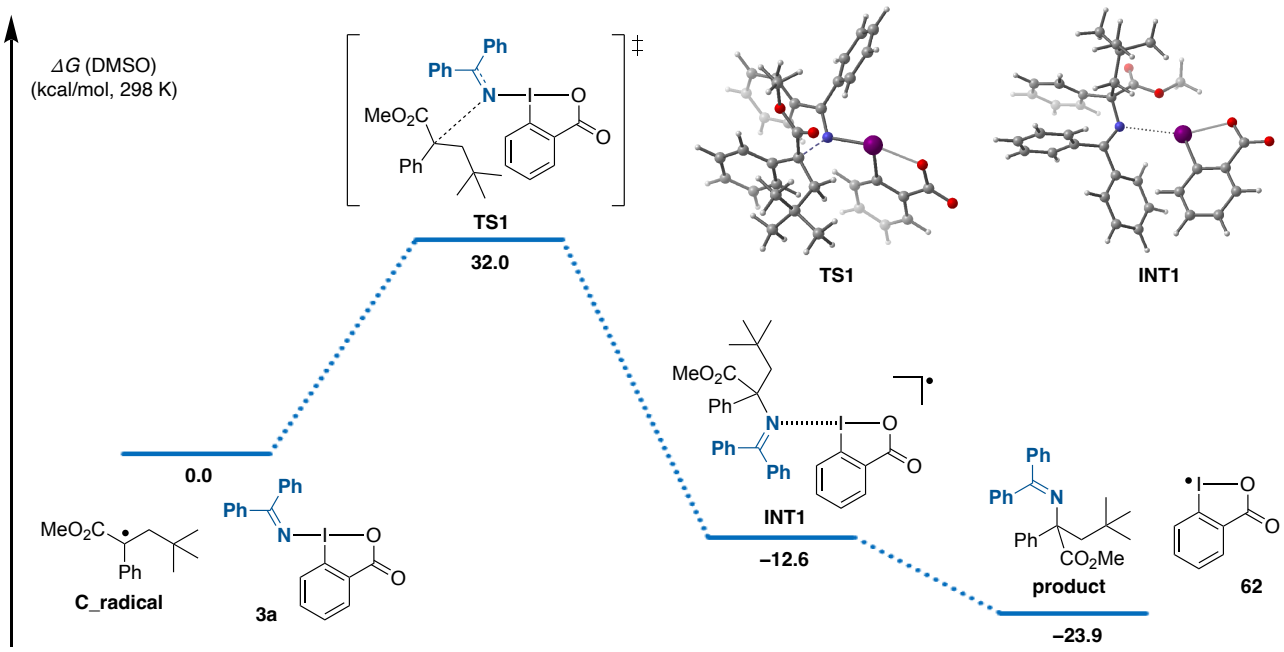


Figure S16. Calculated free energy profile for the radical addition to **3a**. Free energies (kcal/mol) are computed at the M06-2X/6-31+G(d,p)-LANL2DZ(I),CPCM(DMSO) level of theory.

Calculated energies and thermochemical parameters

structure	*E* [hartree]	*H* [hartree]	*TS* [hartree]	*G* [hartree]
C_radical	-695.096153	-694.776539	0.062448	-694.838987
3a	-986.664392	-986.354526	0.074327	-986.428854
TS1	-1681.738508	-1681.108154	0.108722	-1681.216876
INT1	-1681.809131	-1681.175714	0.112212	-1681.287927
product	-1251.075380	-1250.546786	0.086210	-1250.632996
62	-430.730447	-430.628101	0.044784	-430.672886

Cartesian coordinates of computed structures

C_radical

C	3.50565	-1.61450	0.20557
C	2.65331	-2.03844	-0.81501
C	1.45006	-1.38013	-1.04313
C	1.07195	-0.26190	-0.27002
C	1.95096	0.15562	0.75358
C	3.14366	-0.51767	0.99034
H	4.44037	-2.13441	0.38929
H	2.92540	-2.88651	-1.43534

H	0.80685	-1.72673	-1.84472
H	1.67901	0.99640	1.38043
H	3.79289	-0.18689	1.79489
C	-0.21723	0.38437	-0.49180
C	-0.42098	1.82563	-0.30749
O	-1.51674	2.36871	-0.35826
O	0.71094	2.53008	-0.12277
C	0.54445	3.94148	0.03832
H	1.54661	4.33999	0.18216
H	0.08511	4.37292	-0.85317
H	-0.08085	4.15346	0.90771
C	-1.41956	-0.39524	-0.92633
H	-1.13729	-1.13376	-1.68531
H	-2.13515	0.29287	-1.38508
C	-2.16148	-1.16085	0.21296
C	-2.58702	-0.19184	1.32058
H	-3.15867	-0.72630	2.08728
H	-1.71595	0.26327	1.80620
H	-3.20883	0.61480	0.92001
C	-3.40728	-1.79954	-0.41172
H	-3.13205	-2.49524	-1.21238
H	-3.97017	-2.35776	0.34420
H	-4.06953	-1.03616	-0.83449
C	-1.27936	-2.26310	0.80947
H	-0.39961	-1.85085	1.31370
H	-1.85198	-2.83666	1.54681
H	-0.93268	-2.95603	0.03411

3a

I	-0.97503	-0.73992	-0.12865
O	-3.08101	-1.79629	0.00675
O	-5.26811	-1.32464	0.16196
N	0.55954	0.66342	-0.21788
C	-2.37526	0.85986	-0.01301
C	-1.97027	2.18503	-0.03035
H	-0.92334	2.44924	-0.10259
C	-2.96305	3.16445	0.04963
H	-2.67254	4.20972	0.03912
C	-4.30904	2.80956	0.14070
H	-5.06955	3.58054	0.20201
C	-4.67654	1.46731	0.15257
H	-5.71581	1.16358	0.22187
C	-3.70361	0.46900	0.07435
C	-4.08214	-0.99707	0.08438
C	1.76420	0.24858	-0.09377
C	2.85036	1.27195	-0.06106
C	2.54883	2.60853	0.23379
H	1.52336	2.88212	0.45823
C	3.55706	3.56528	0.25184
H	3.31806	4.59664	0.48998
C	4.87601	3.19898	-0.03018
H	5.66208	3.94719	-0.01585
C	5.18185	1.87130	-0.32361
H	6.20440	1.58235	-0.54312
C	4.17410	0.90757	-0.33370
H	4.41772	-0.12529	-0.56228
C	2.15579	-1.19087	0.02415
C	1.96328	-2.05803	-1.05677
H	1.57384	-1.67561	-1.99711
C	2.29390	-3.40724	-0.93149
H	2.15114	-4.07662	-1.77319
C	2.80895	-3.89020	0.27088
H	3.06151	-4.94093	0.36875
C	3.00653	-3.02296	1.34719
H	3.41034	-3.39825	2.28170
C	2.69203	-1.67184	1.22319
H	2.85384	-0.99070	2.05385

TS1

C	2.62818	-0.26648	-1.19714
C	3.87158	-1.85020	-3.06918
C	4.01394	-0.31632	-1.20537
C	1.83899	-0.94571	-2.10744
C	2.47976	-1.75082	-3.05135
C	4.63521	-1.13006	-2.15431
H	0.76200	-0.84692	-2.08120
H	1.88138	-2.29543	-3.77440
H	5.71938	-1.17464	-2.16071
H	4.35954	-2.47991	-3.80515
C	4.81047	0.52545	-0.23545
O	4.08639	1.28680	0.50859
O	6.03923	0.45637	-0.21611
I	1.78393	0.99426	0.28895
C	-1.03481	1.30701	-0.51719
C	-0.91810	2.70636	-0.06121
C	-0.63629	5.39737	0.72304
C	-0.46436	3.03999	1.22776
C	-1.23976	3.75373	-0.94511
C	-1.09376	5.08118	-0.55889
C	-0.32554	4.37125	1.61437
H	-0.25081	2.25862	1.95423
H	-1.58876	3.51628	-1.94555
H	-1.33410	5.87302	-1.26108
H	0.01627	4.60307	2.61800
H	-0.52639	6.43405	1.02374
C	-2.22363	0.95128	-1.32016
C	-4.49528	0.31353	-2.84384
C	-2.13374	0.06465	-2.40209
C	-3.47246	1.52245	-1.02011
C	-4.59803	1.20336	-1.77217
C	-3.25802	-0.25153	-3.15755
H	-1.17339	-0.36992	-2.65453
H	-3.55725	2.20510	-0.17953
H	-5.55718	1.64451	-1.51991
H	-3.16796	-0.94031	-3.99183
H	-5.37322	0.06379	-3.43129
N	-0.14714	0.33399	-0.21996
C	-3.34384	-3.46313	-1.48057
C	-1.97459	-3.36626	-1.73410
C	-1.17454	-2.56672	-0.92982
C	-1.70951	-1.83076	0.14176
C	-3.08476	-1.94437	0.38981
C	-3.88942	-2.75349	-0.41365
H	-3.97571	-4.08620	-2.10578
H	-1.52877	-3.91612	-2.55730
H	-0.11103	-2.52101	-1.13537
H	-3.53877	-1.40887	1.21290
H	-4.95101	-2.82531	-0.19774
C	-0.76179	-1.05426	0.99652
C	-1.24869	-0.12451	2.05967
O	-0.58585	0.19661	3.03499
O	-2.43559	0.42626	1.79259
C	-2.97805	1.30484	2.78746
H	-3.97065	1.56992	2.42824
H	-3.04067	0.78748	3.74629
H	-2.35903	2.19778	2.88908
C	0.47788	-1.81863	1.43099
H	1.08587	-1.15195	2.04420
H	1.07091	-2.08948	0.54810
C	0.27814	-3.11288	2.28616
C	-0.21601	-4.31993	1.47541
H	-0.13841	-5.21937	2.09649
H	-1.25927	-4.21695	1.16677
H	0.39321	-4.47527	0.57795
C	1.66948	-3.45531	2.84162
H	2.05157	-2.64625	3.47330
H	1.62457	-4.36749	3.44569

H	2.38532	-3.62155	2.02838
C	-0.68155	-2.88128	3.45912
H	-1.69279	-2.63887	3.10931
H	-0.75167	-3.79532	4.05871
H	-0.33775	-2.06732	4.10286

INT1

C	-3.71902	0.43159	0.36634
C	-5.85308	2.00196	1.14213
C	-4.96273	-0.16131	0.54037
C	-3.50568	1.78745	0.57481
C	-4.59098	2.57275	0.96490
C	-6.03789	0.63838	0.93300
H	-2.52389	2.23041	0.43869
H	-4.44277	3.63537	1.12903
H	-7.00789	0.17056	1.06770
H	-6.69016	2.62135	1.44524
C	-5.14240	-1.63606	0.31726
O	-4.08122	-2.29745	-0.03885
O	-6.23607	-2.17537	0.46961
I	-2.13547	-0.81069	-0.25339
C	1.10207	1.34496	-0.23504
C	0.05908	2.31154	-0.71108
C	-1.90207	4.10211	-1.61643
C	-0.69721	2.02051	-1.85675
C	-0.16996	3.51660	-0.03413
C	-1.15021	4.40363	-0.48174
C	-1.67142	2.90806	-2.30456
H	-0.50002	1.09740	-2.39248
H	0.41203	3.76050	0.84920
H	-1.32463	5.32872	0.05821
H	-2.24727	2.67218	-3.19385
H	-2.66264	4.79331	-1.96553
C	2.18212	1.93308	0.62435
C	4.18227	3.07979	2.20217
C	2.16464	1.76335	2.01028
C	3.17734	2.71924	0.03462
C	4.18185	3.27721	0.81944
C	3.16623	2.33388	2.79737
H	1.36288	1.19687	2.47578
H	3.17647	2.86893	-1.04187
H	4.96717	3.86352	0.35253
H	3.14860	2.19585	3.87384
H	4.96625	3.51561	2.81333
N	0.97666	0.13118	-0.61311
C	1.93221	-0.95589	-0.32833
C	3.37553	-0.51013	-0.58665
C	4.33869	-0.38740	0.41398
C	3.71238	-0.11269	-1.88746
C	5.61089	0.10838	0.12407
H	4.10743	-0.64695	1.44026
C	4.97655	0.38847	-2.18105
H	2.97263	-0.18801	-2.68069
C	5.93579	0.49842	-1.17225
H	6.34075	0.20211	0.92245
H	5.21282	0.69330	-3.19584
H	6.92326	0.89000	-1.39577
C	1.63082	-1.48993	1.10791
H	2.11519	-0.79183	1.79498
H	0.55332	-1.35379	1.25676
C	1.96292	-2.93772	1.56287
C	3.41051	-3.36922	1.29113
H	3.53228	-4.41746	1.58637
H	3.66910	-3.28269	0.23164
H	4.12514	-2.77886	1.87135
C	1.72446	-2.94679	3.08220
H	0.68526	-2.69109	3.31872
H	1.93131	-3.94063	3.49264
H	2.37753	-2.22662	3.58732
C	1.01551	-3.97627	0.93742
H	1.08923	-4.91488	1.49657
H	-0.02767	-3.64131	0.97005
H	1.27765	-4.20459	-0.09846
C	1.57502	-2.07341	-1.33470
O	2.37964	-2.77207	-1.90866
O	0.25513	-2.23538	-1.47108
C	-0.16192	-3.28030	-2.36119
H	0.23497	-3.09795	-3.36077
H	0.18546	-4.24927	-1.99749
H	-1.25023	-3.24482	-2.36817

product

C	1.40492	-0.37317	-0.16823
C	2.70530	-1.12425	-0.14401
C	5.11814	-2.55651	-0.10742
C	2.77658	-2.38494	0.46652
C	3.85957	-0.58855	-0.72797
C	5.05747	-1.30437	-0.71482
C	3.97252	-3.09391	0.48623
H	1.88211	-2.79319	0.92468
H	3.82550	0.38725	-1.20214
H	5.94203	-0.87935	-1.17846
H	4.01527	-4.06572	0.96808
H	6.05126	-3.11089	-0.09176
C	1.50739	1.08747	-0.50315
C	1.75034	3.80660	-1.10404
C	1.21988	1.55021	-1.78876
C	1.96338	1.98461	0.46818
C	2.07052	3.34017	0.17276
C	1.33690	2.90880	-2.08682
H	0.91351	0.84913	-2.56018
H	2.20903	1.62025	1.46224
H	2.39980	4.03433	0.93984
H	1.10708	3.26190	-3.08726
H	1.83342	4.86429	-1.33349
N	0.35203	-1.04089	0.10438
C	-1.01587	-0.49894	0.17813
C	-1.06455	0.81618	0.96304
C	-1.35818	2.05085	0.38486
C	-0.69671	0.78700	2.31472
C	-1.29888	3.22534	1.13609
H	-1.60835	2.12251	-0.66716
C	-0.62938	1.95529	3.06759
H	-0.45200	-0.16262	2.78393
C	-0.93519	3.18390	2.47942
H	-1.52385	4.17474	0.65952
H	-0.33841	1.90659	4.11245
H	-0.88307	4.09837	3.06214
C	-1.56709	-0.44459	-1.28152
H	-1.12966	0.44928	-1.73418
H	-1.11082	-1.29783	-1.79707
C	-3.08475	-0.47676	-1.61646
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C	-3.69335	-1.87596	-1.41813
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H	-3.87170	-2.10293	-0.36419
C	-1.83146	-1.56719	0.94342
O	-2.69818	-1.32227	1.75540

O	-1.52211	-2.80688	0.56805	H	-3.22413	1.35344	0.00014
C	-2.26546	-3.85666	1.19817	H	-4.31816	-0.89466	0.00003
H	-2.12564	-3.81792	2.27976	C	-0.59326	1.90288	0.00002
H	-3.32841	-3.76424	0.96483	O	0.71101	1.92760	-0.00033
H	-1.86581	-4.78305	0.79165	O	-1.25431	2.93576	0.00028
				I	1.61233	-0.36642	0.00005

62

C	-0.48462	-0.61230	-0.00009
C	-3.23692	-0.81243	-0.00001
C	-1.24330	0.55104	-0.00001
C	-1.05683	-1.87676	-0.00016
C	-2.44976	-1.96533	-0.00013
C	-2.63549	0.44174	0.00006
H	-0.44747	-2.77365	-0.00021
H	-2.91638	-2.94471	-0.00017

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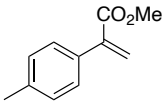
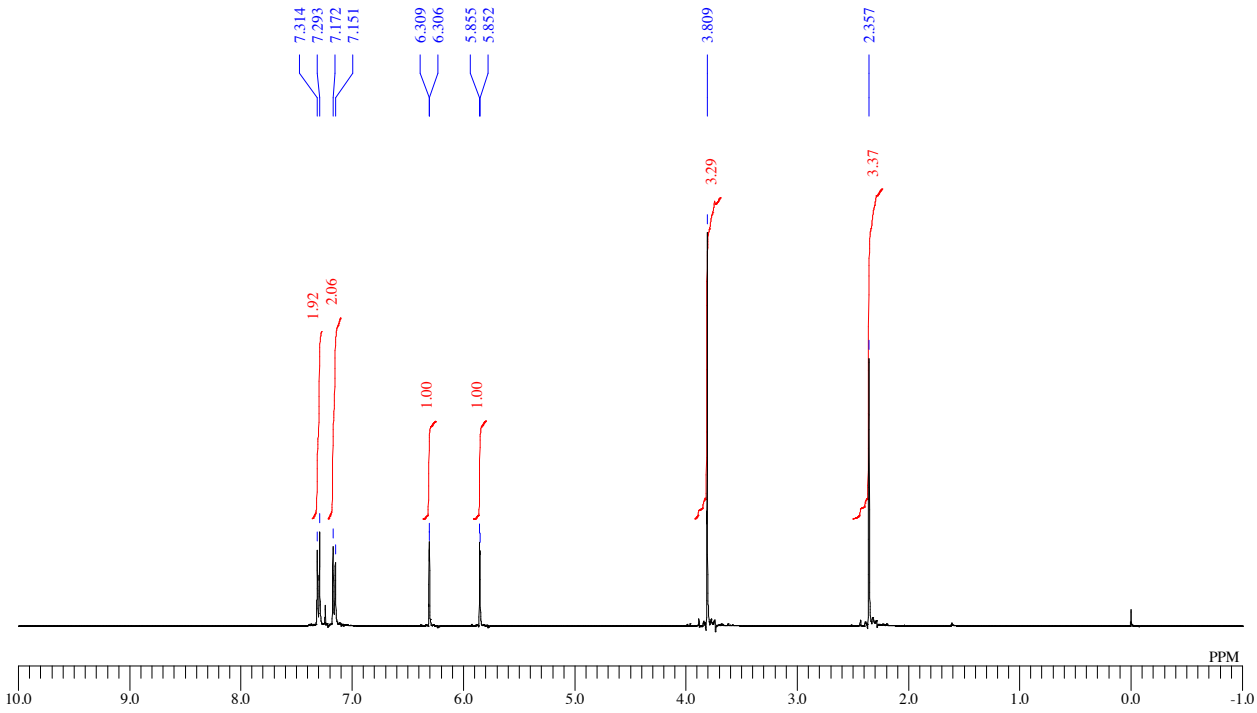
22. NMR spectra



1a

^{1}H NMR: (400 MHz, $CDCl_3$)



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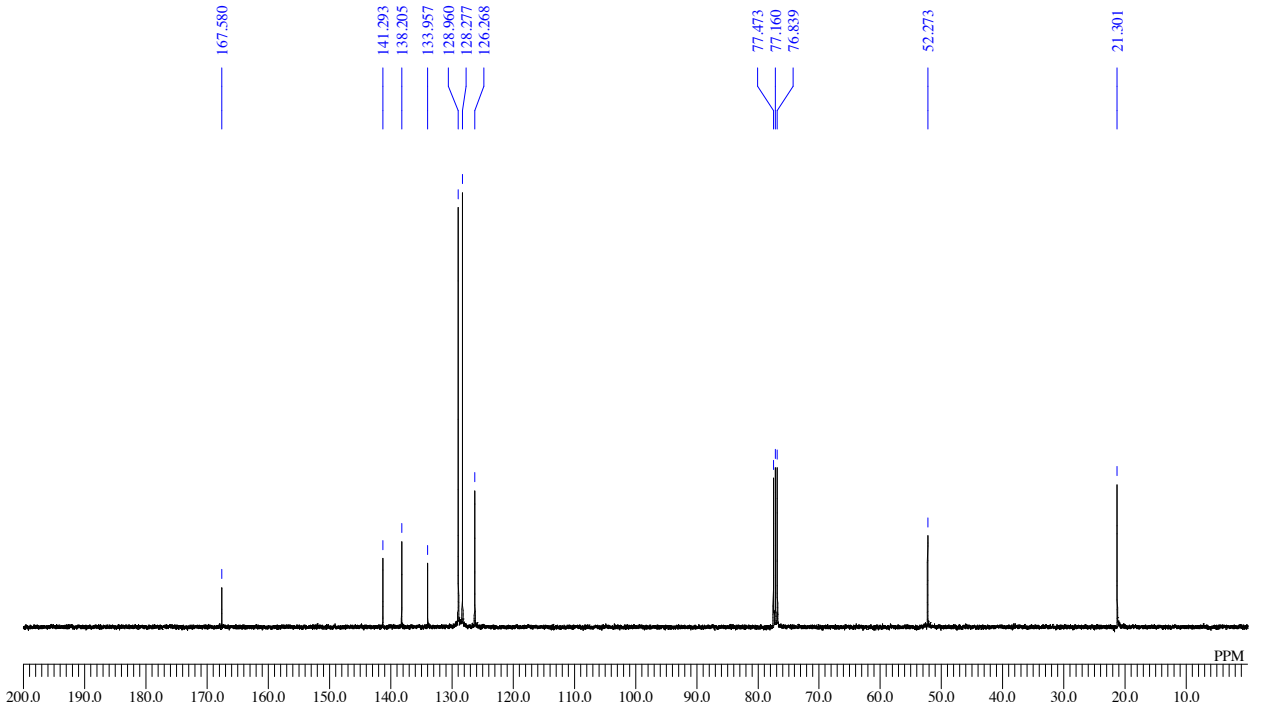

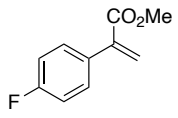

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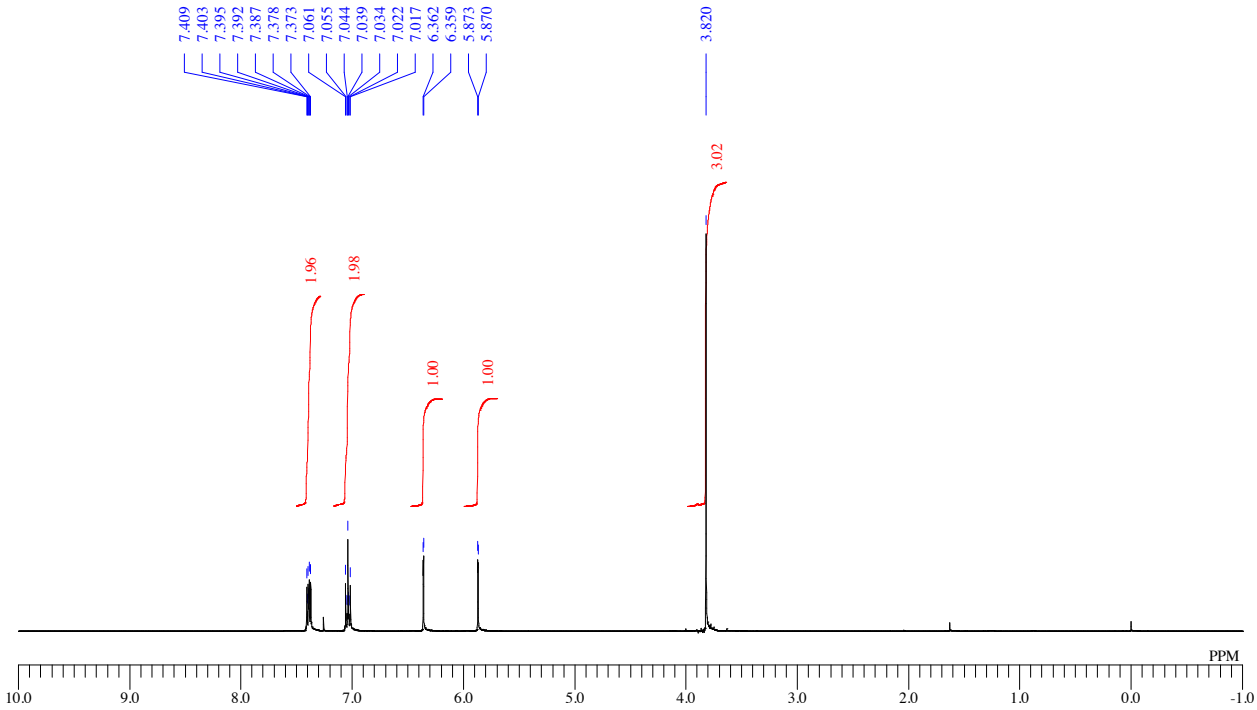

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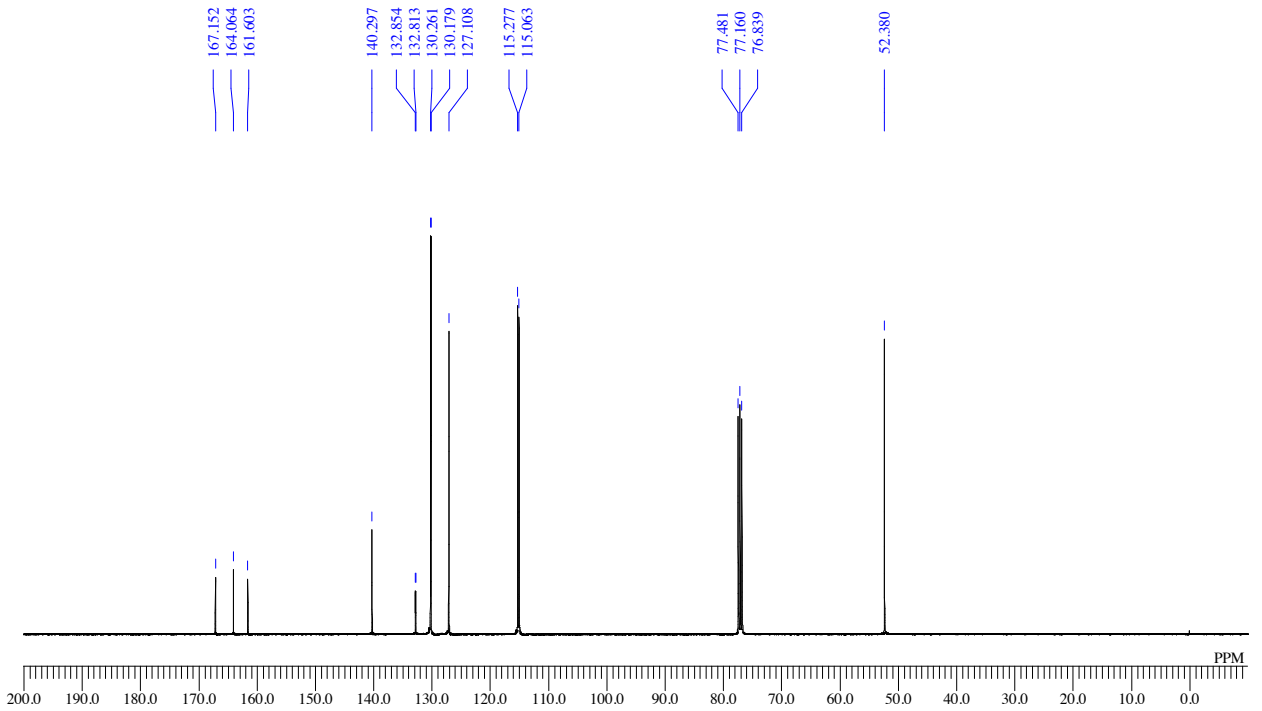

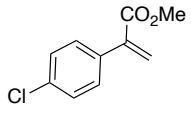

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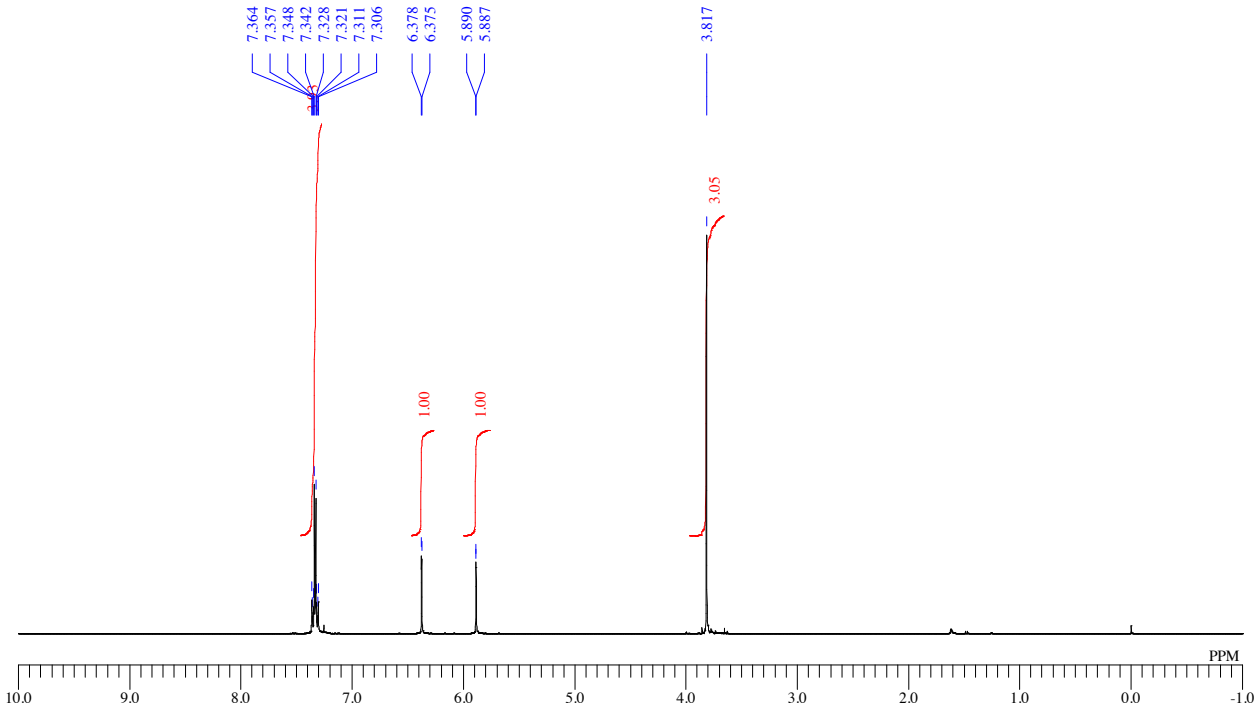

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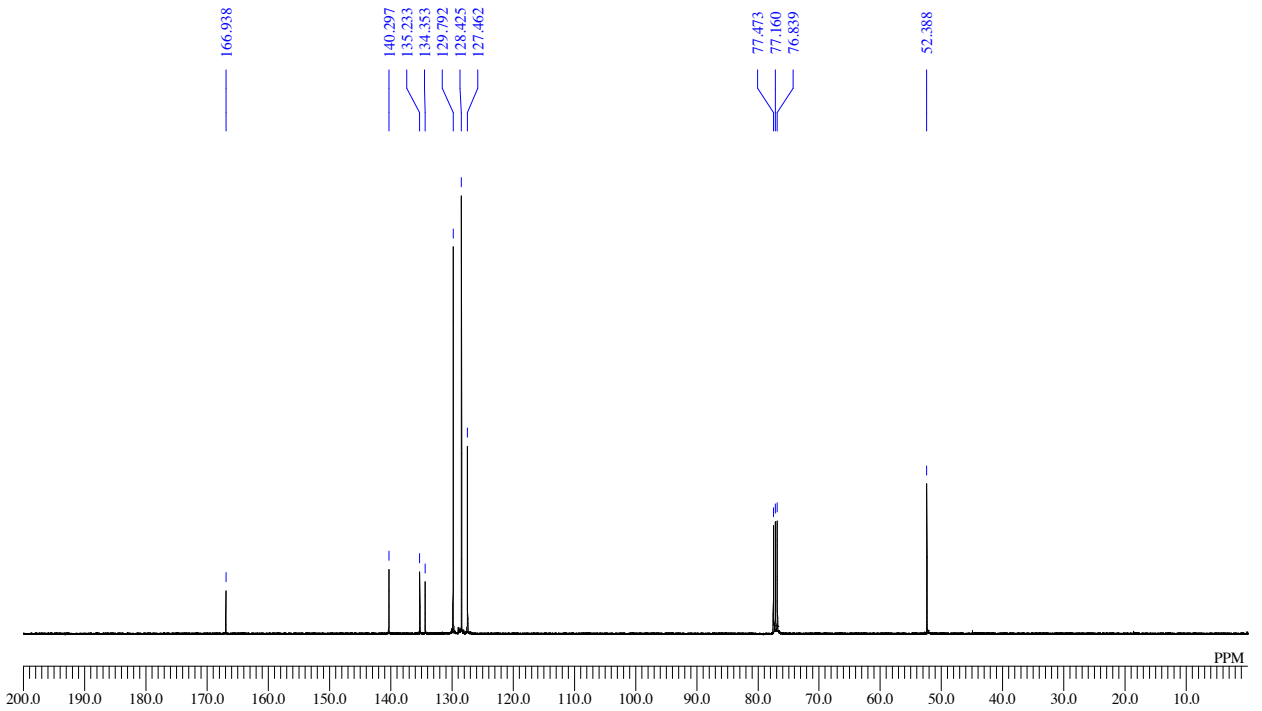

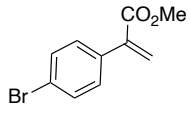

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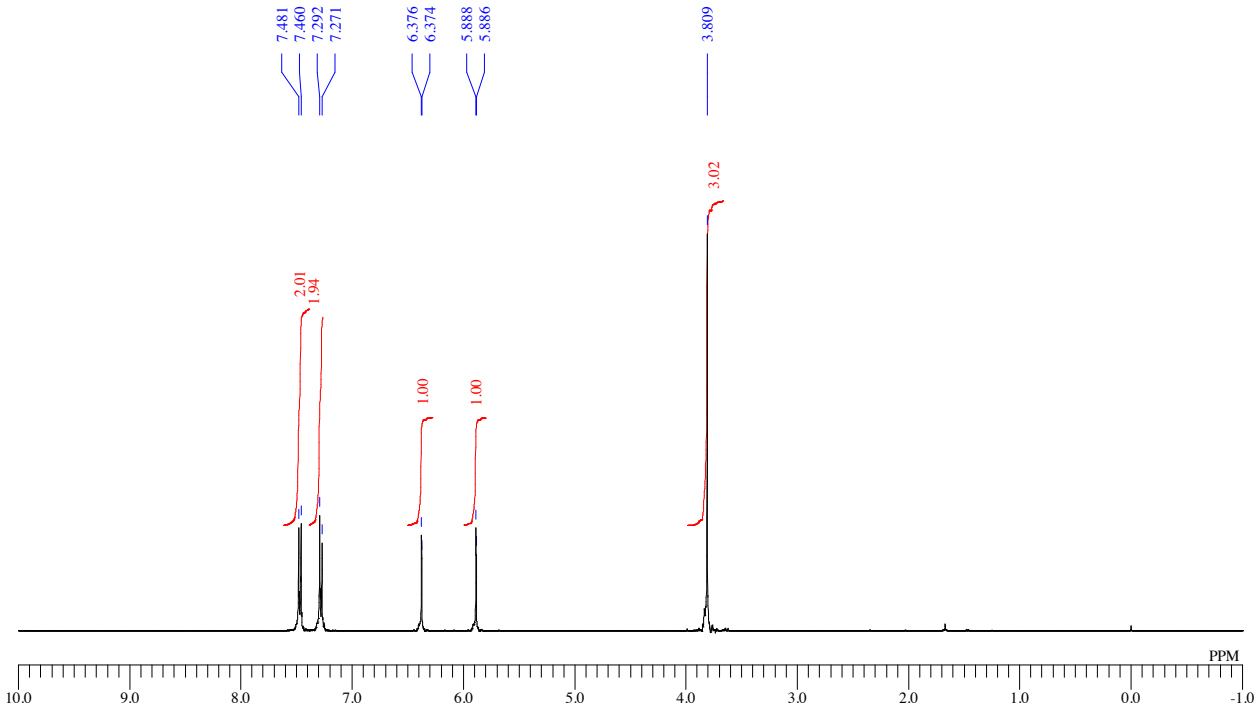

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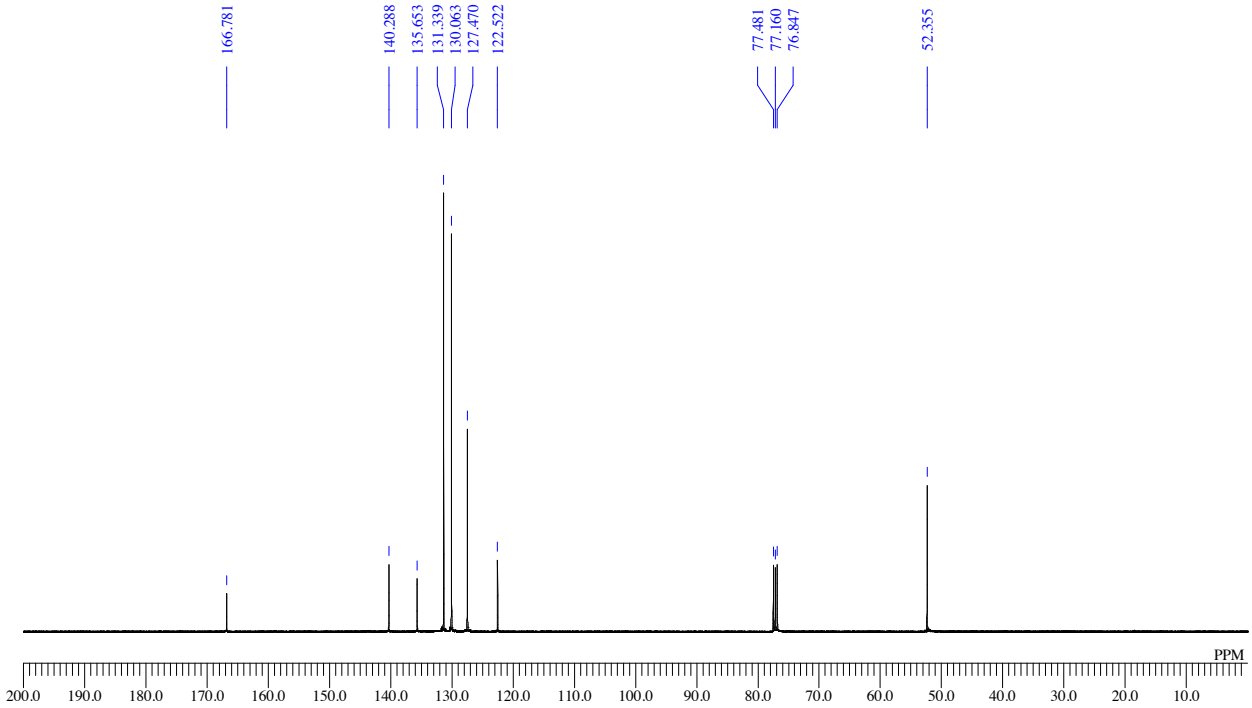

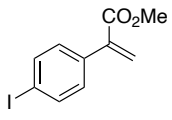

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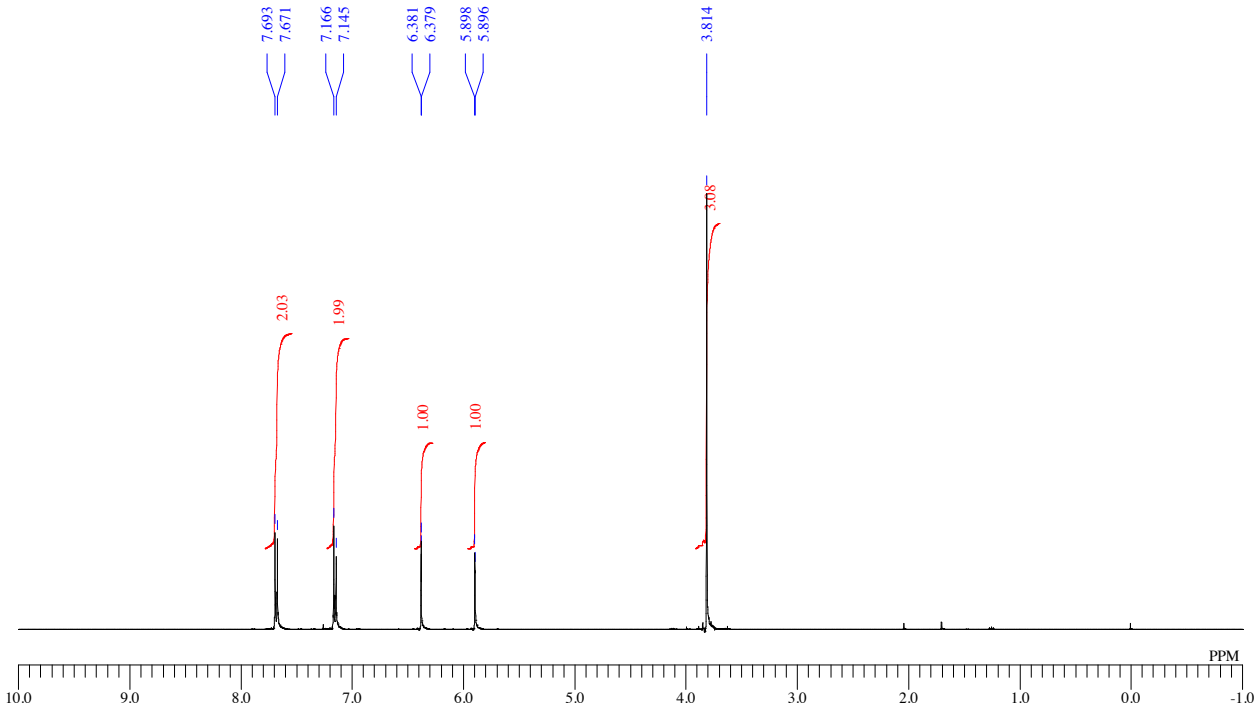

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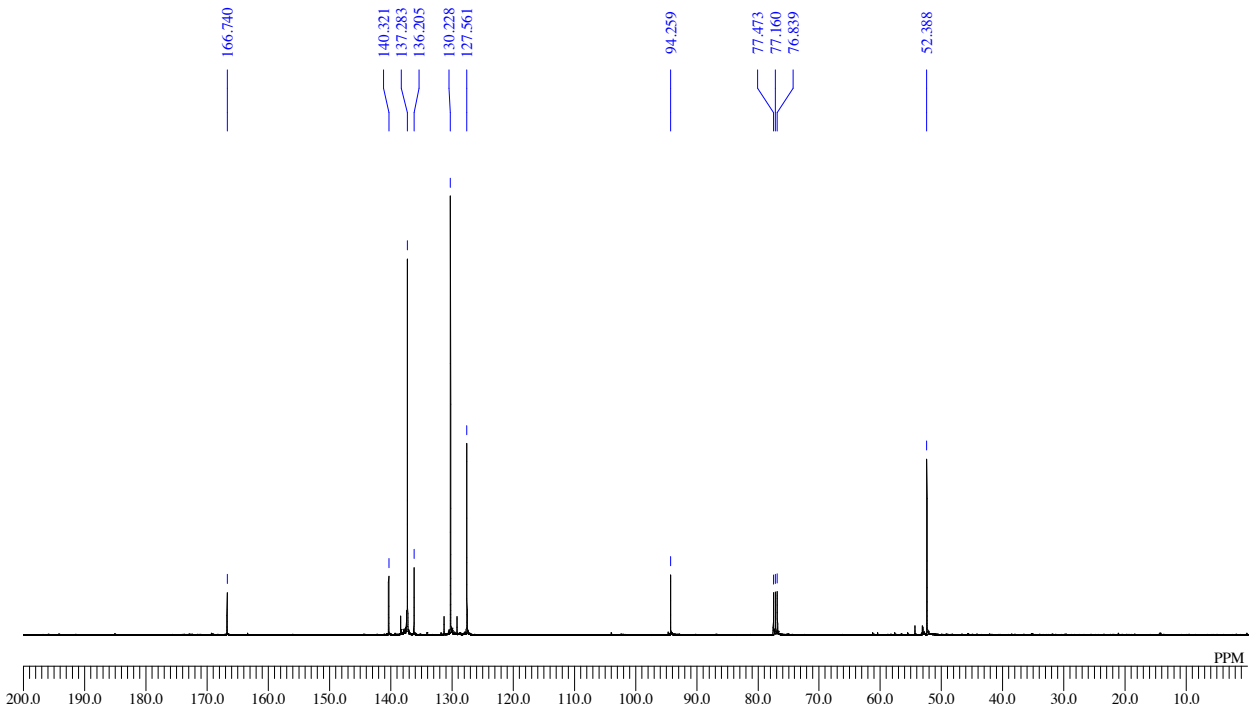

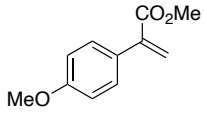

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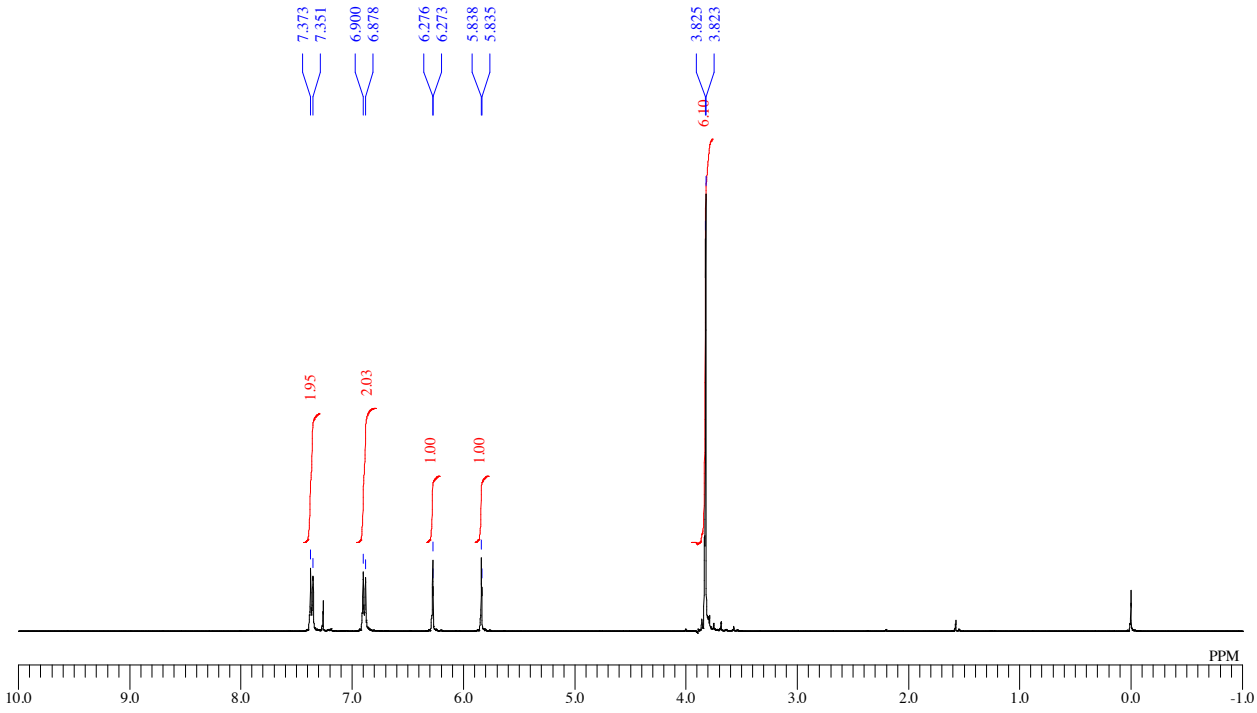

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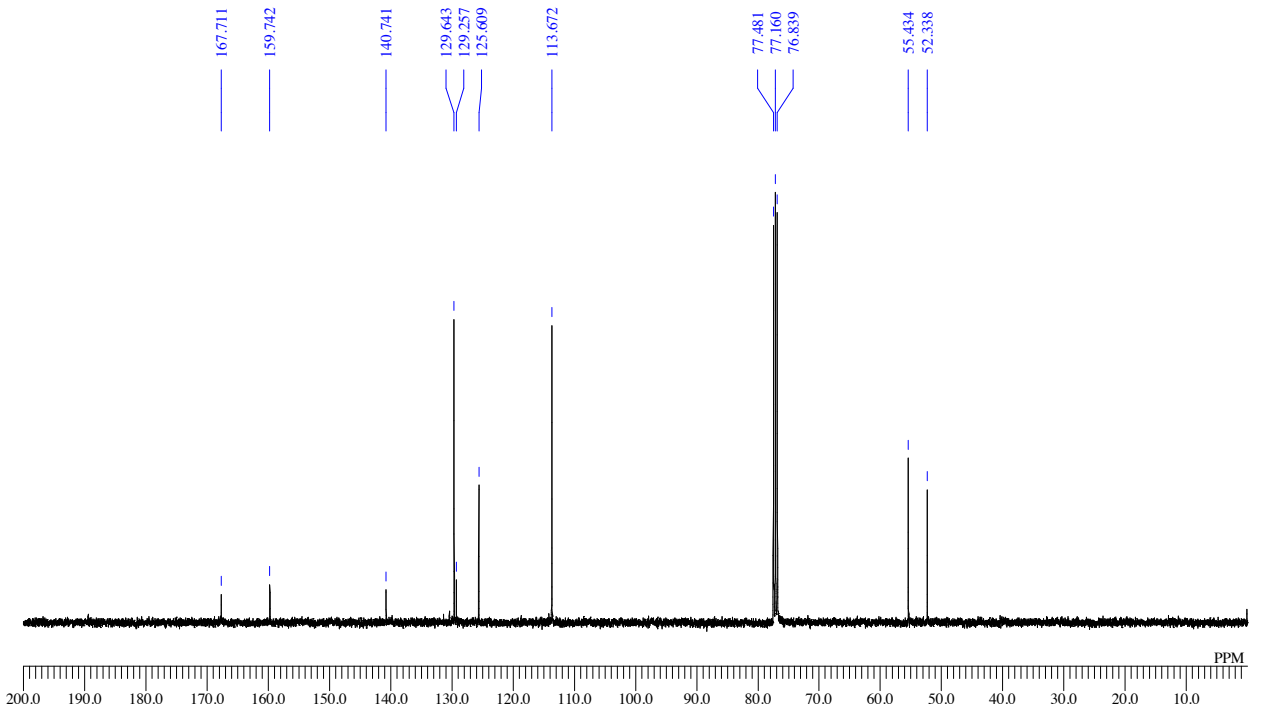

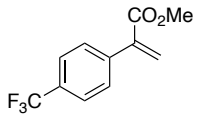

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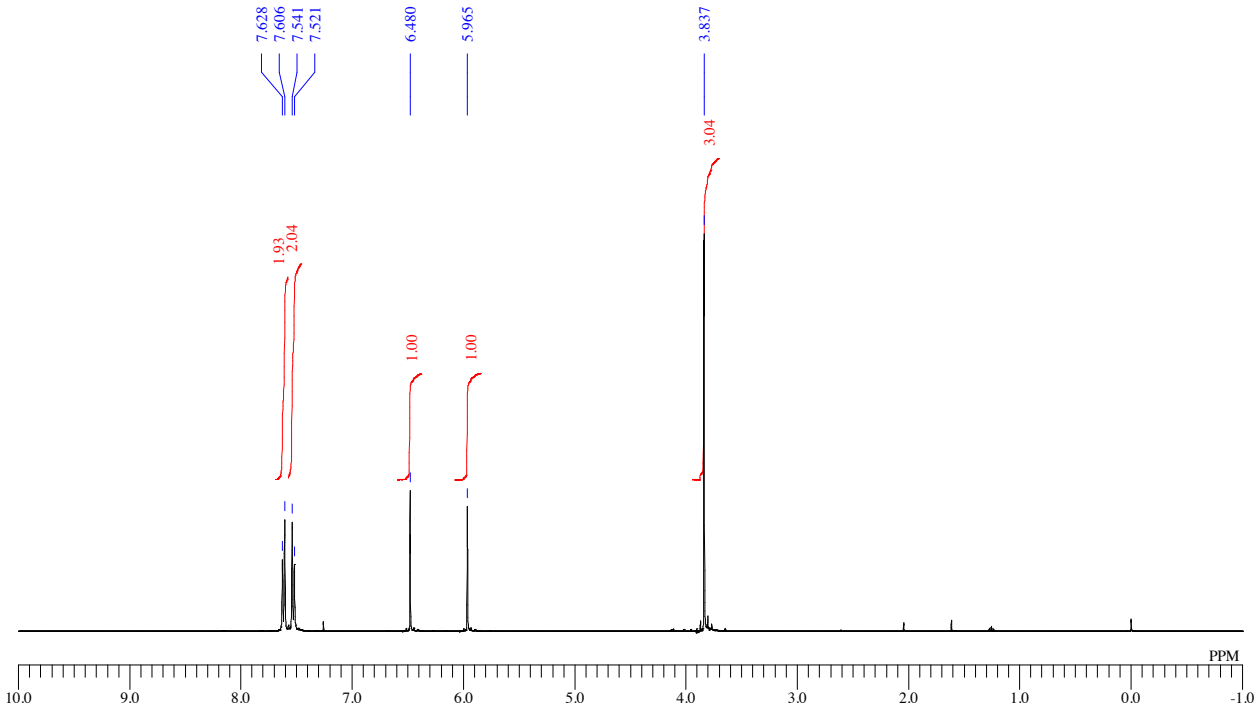

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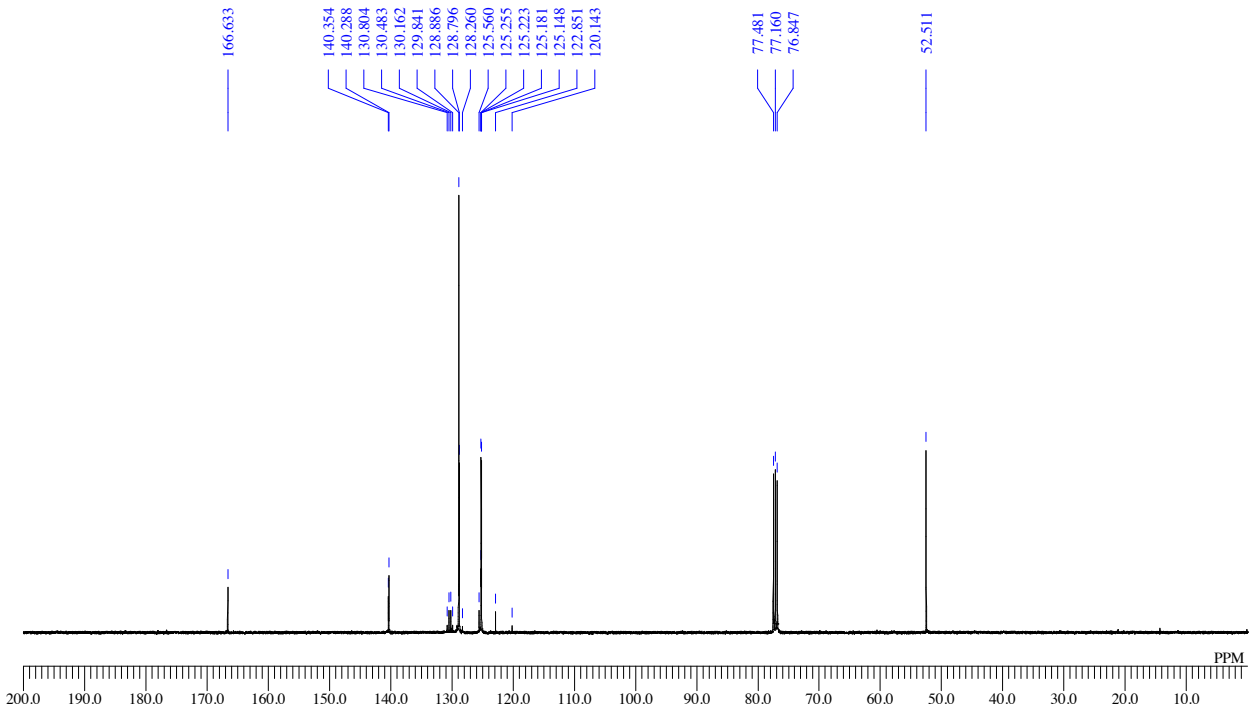

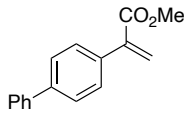

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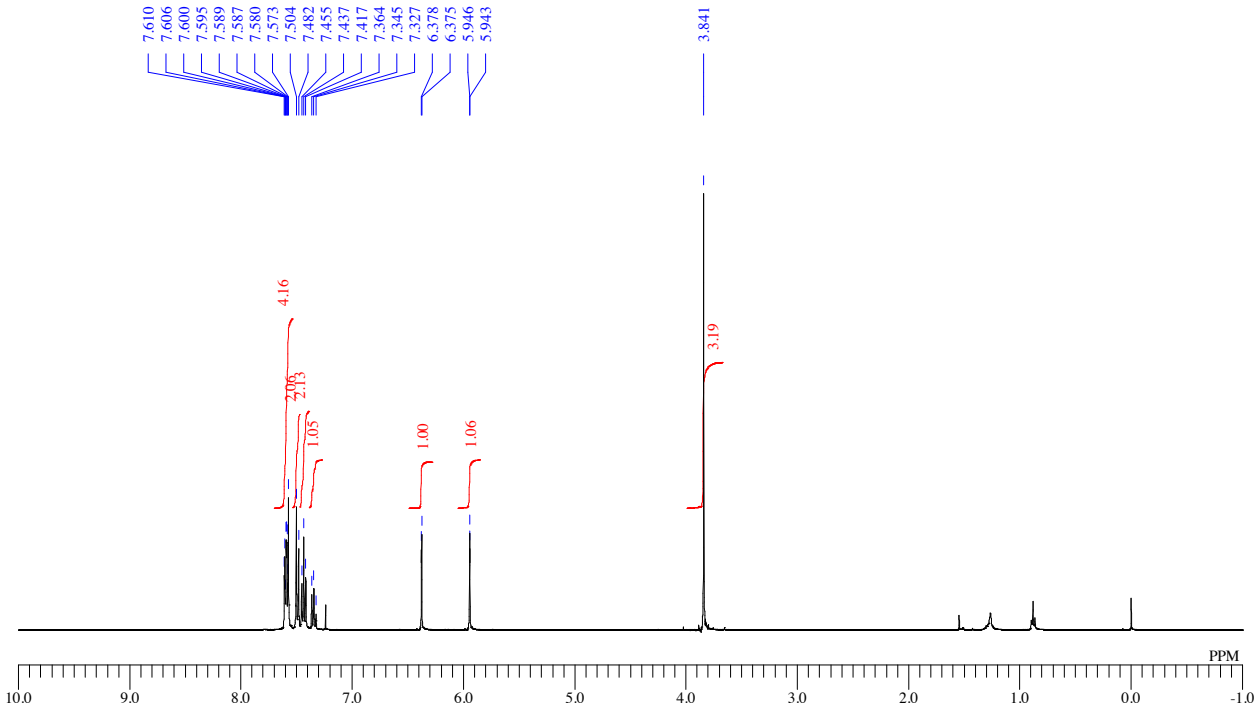

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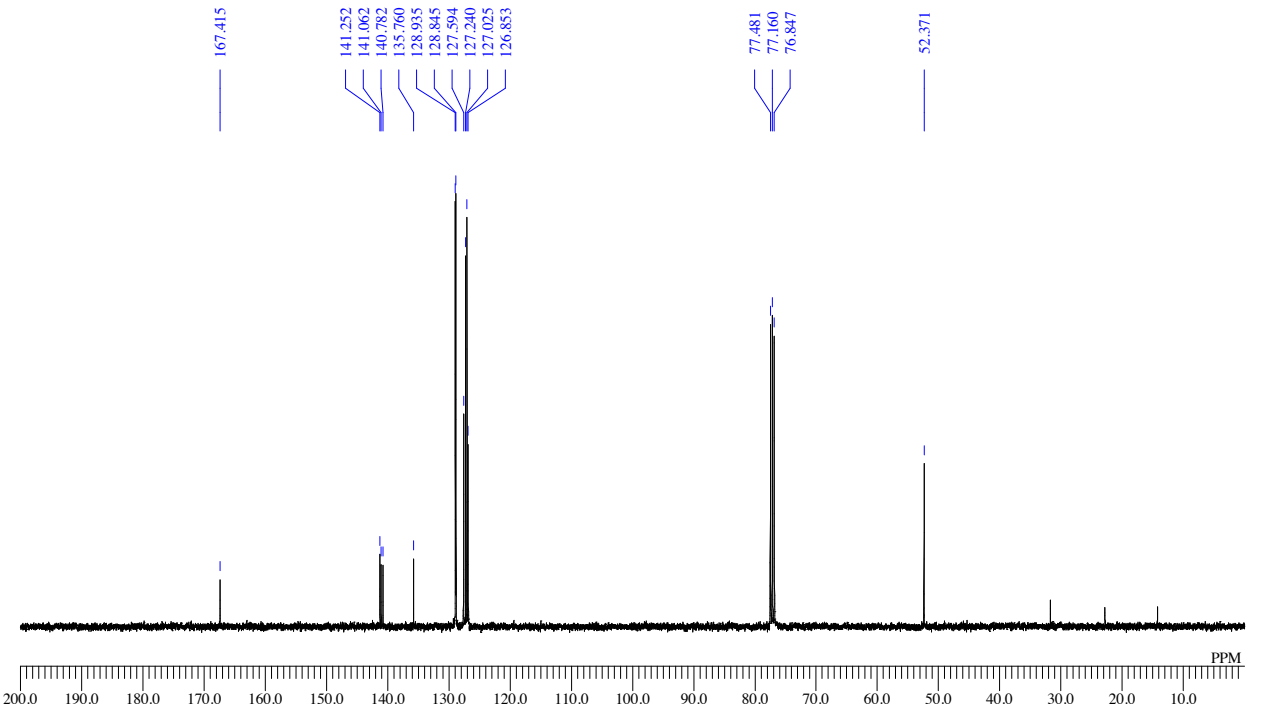

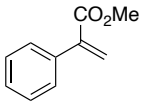

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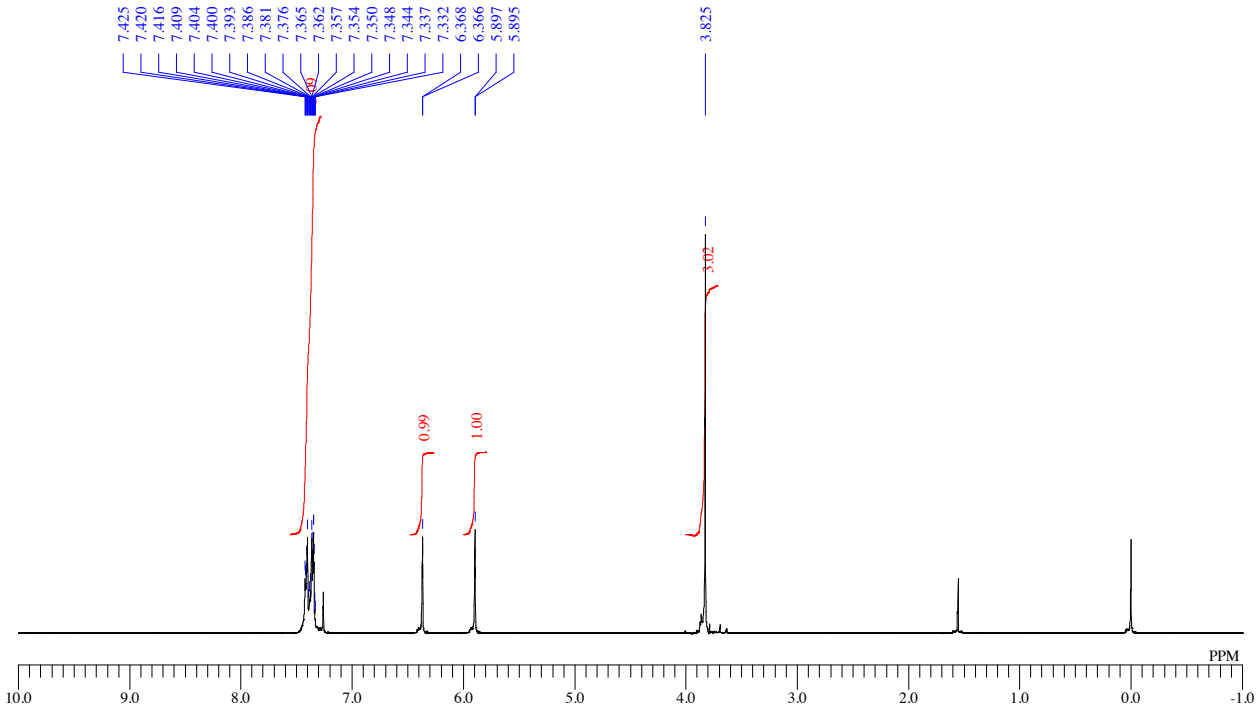

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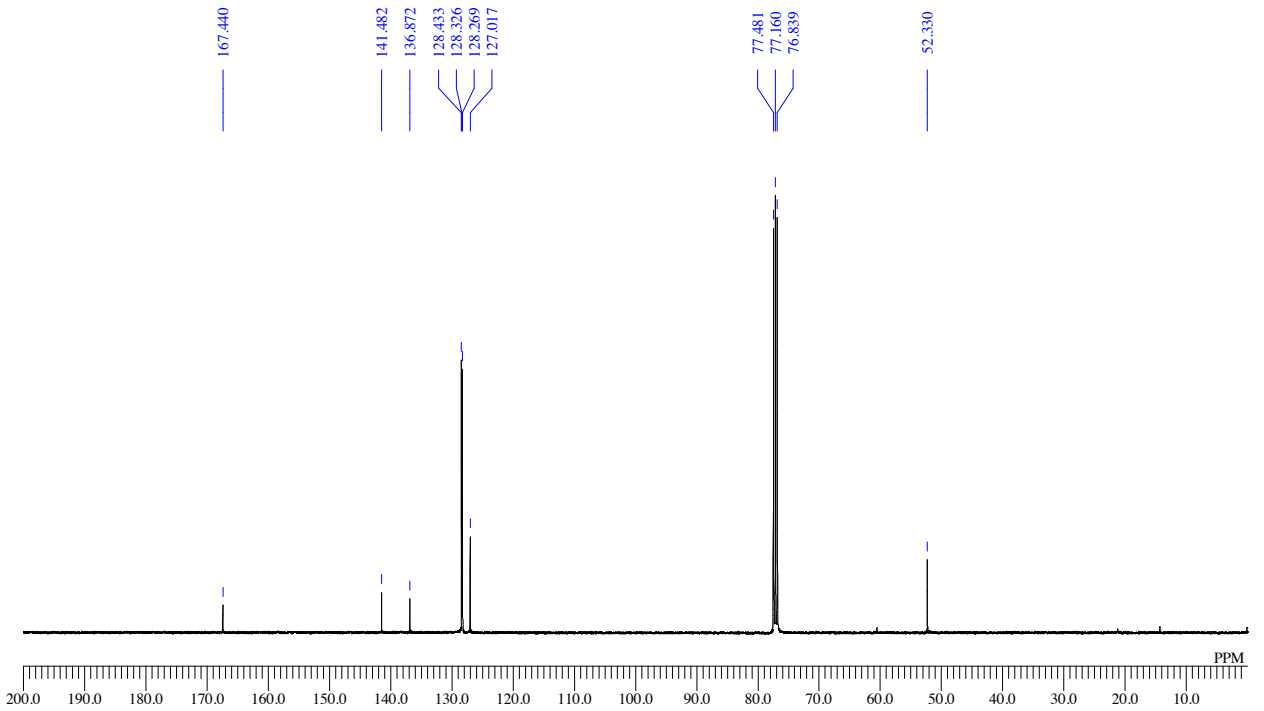

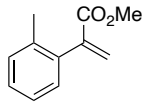

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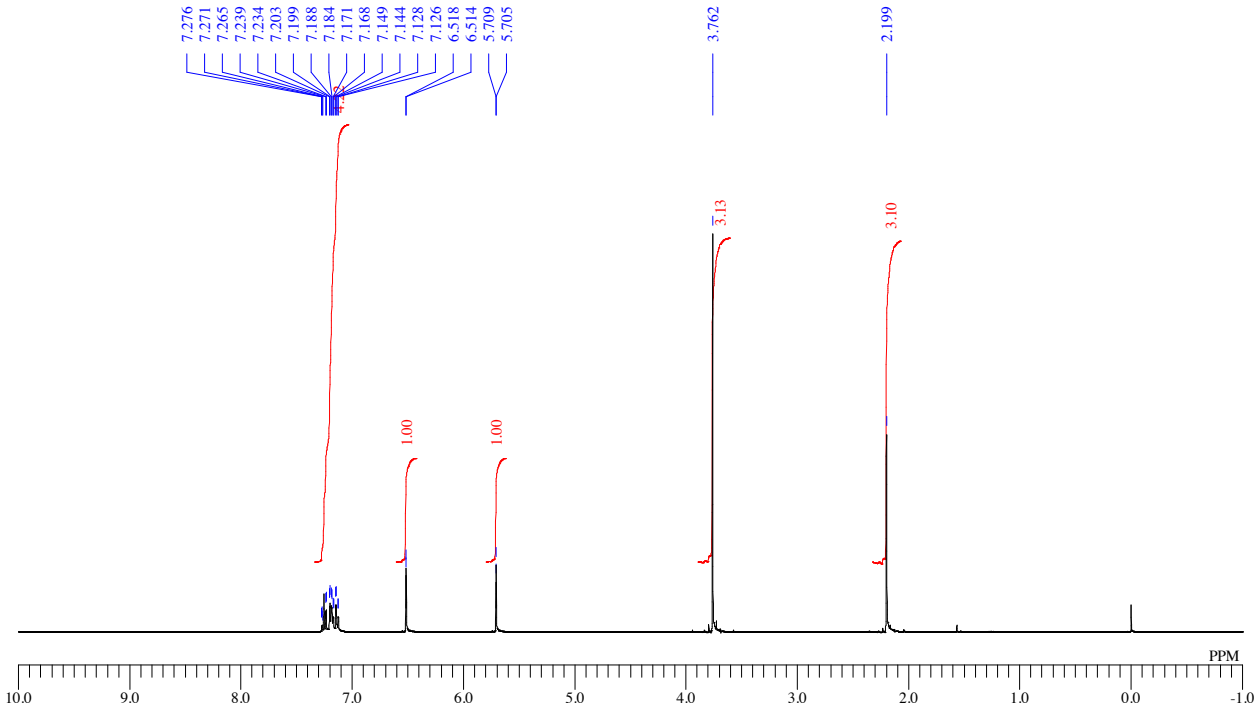

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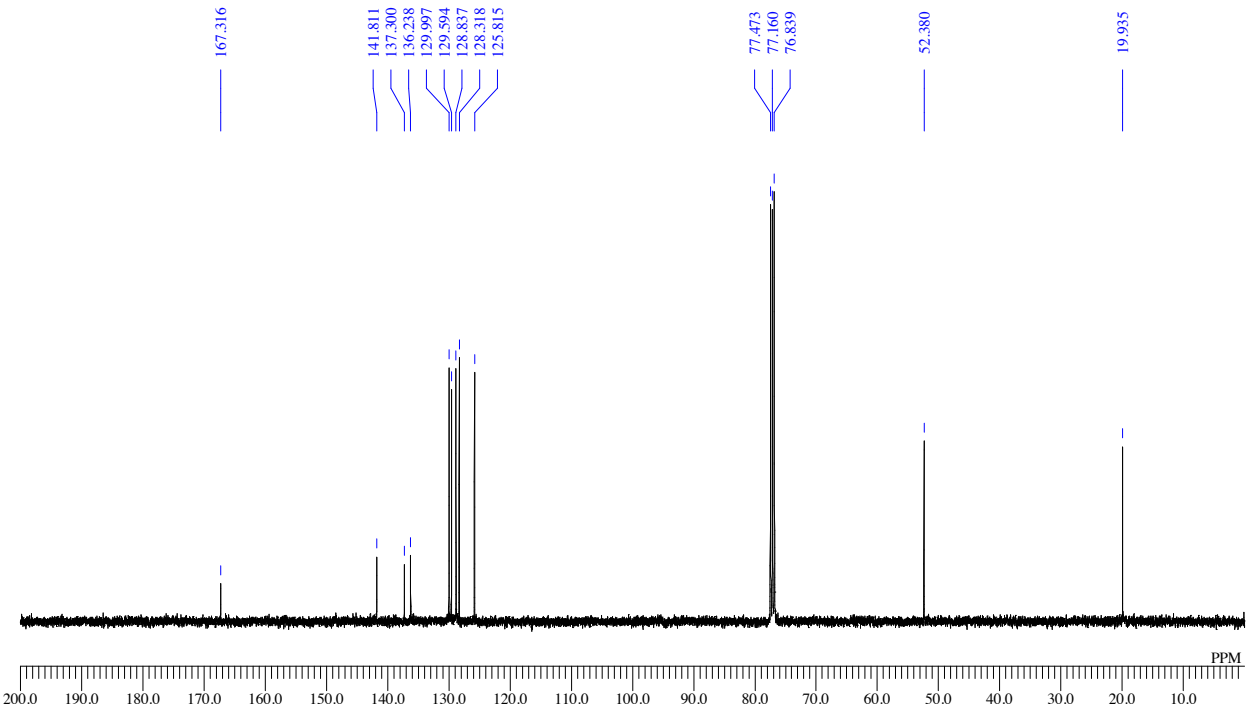

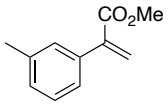

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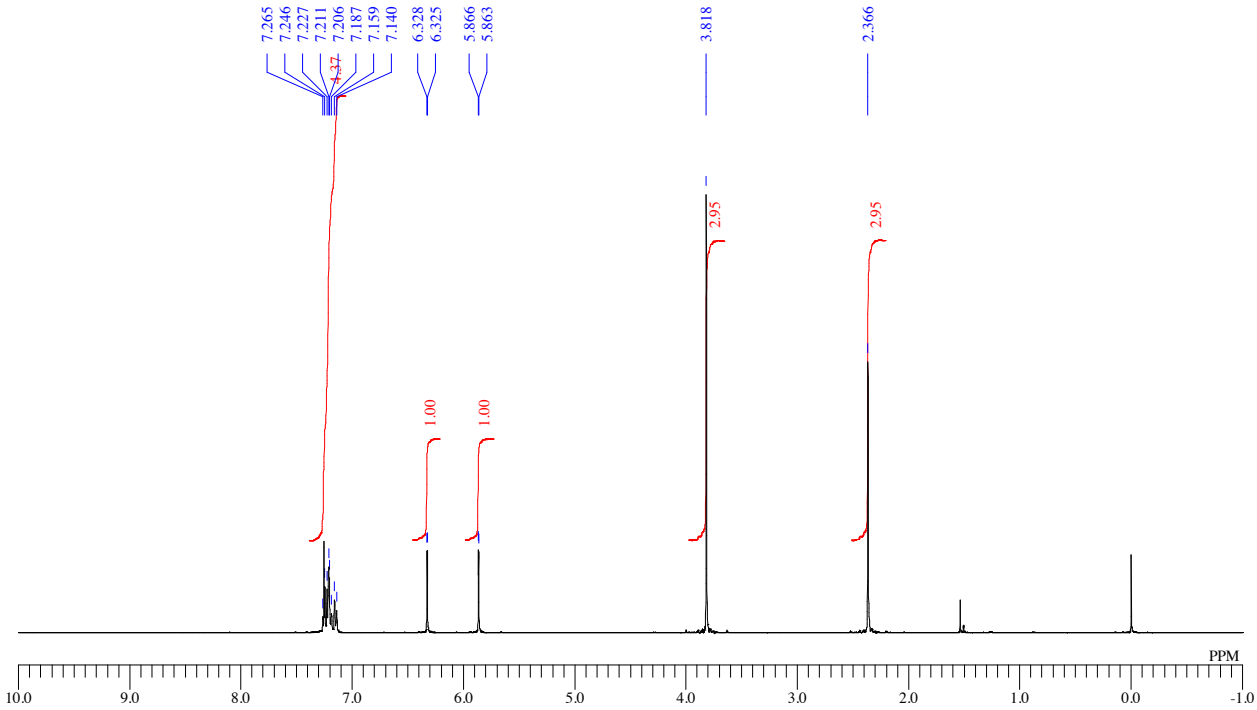
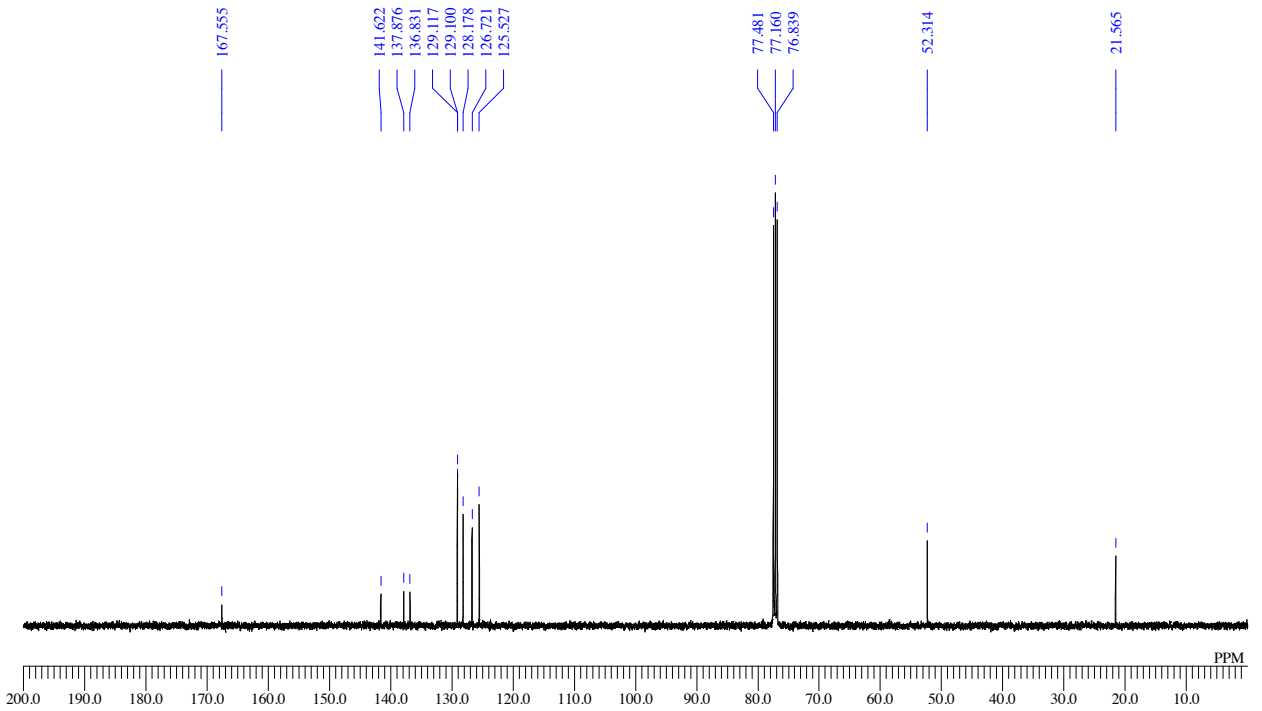
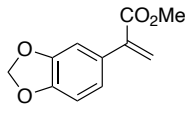


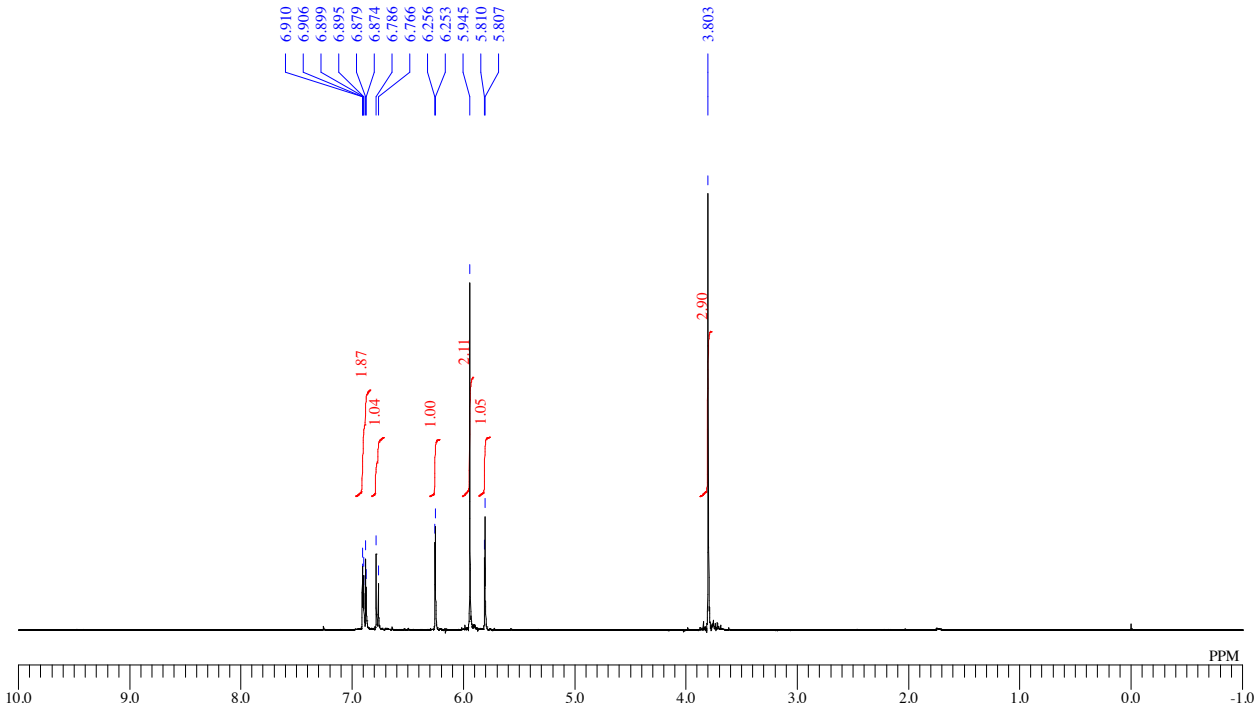
^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$)



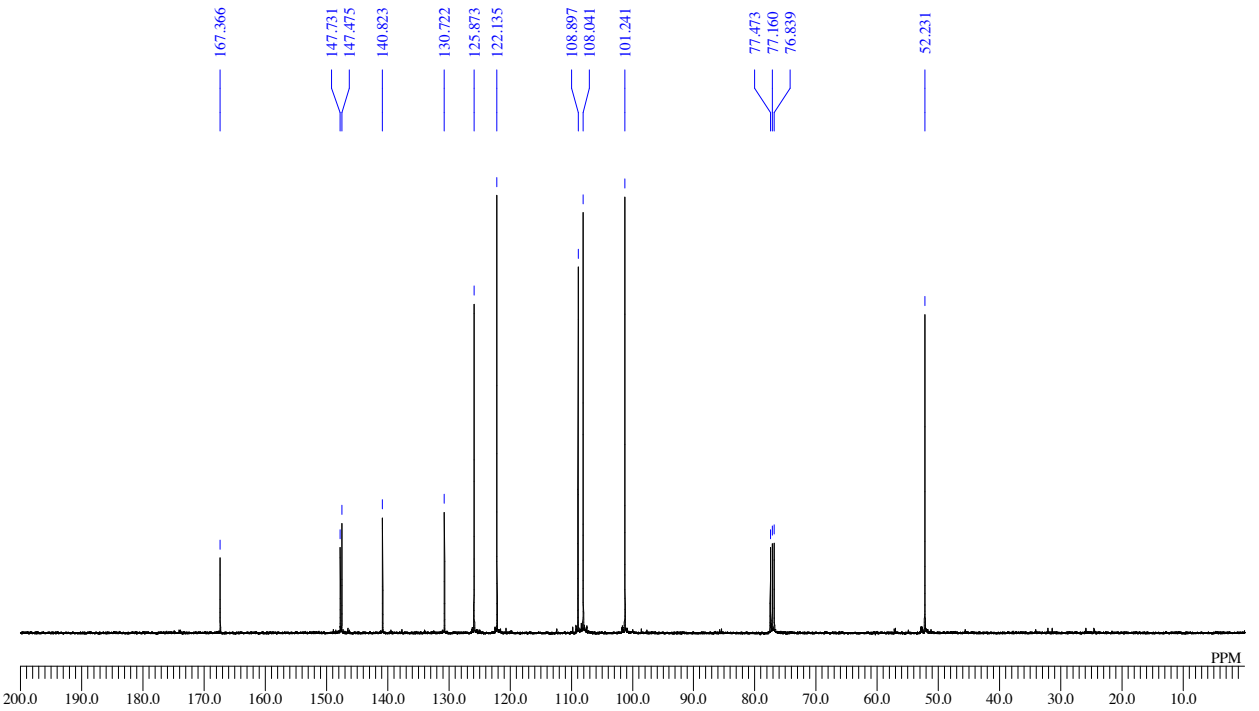


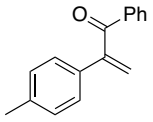
1l

^{1}H NMR: (400 MHz, $CDCl_3$)



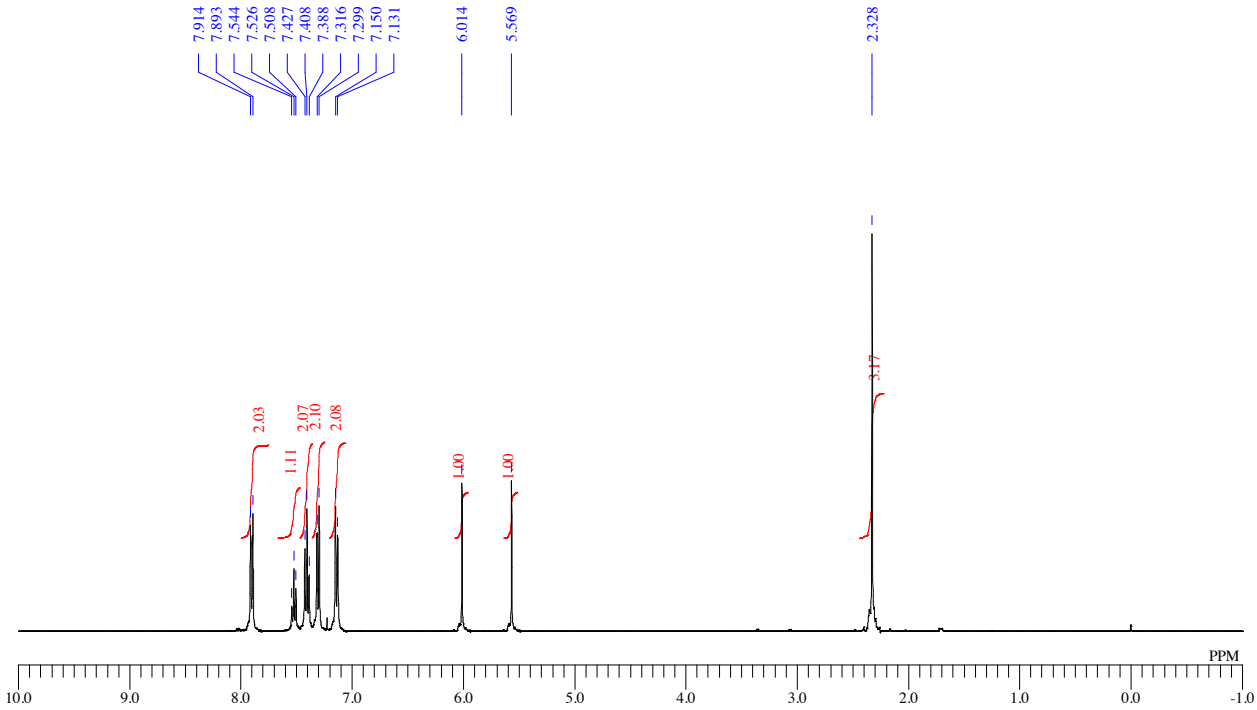
^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$)



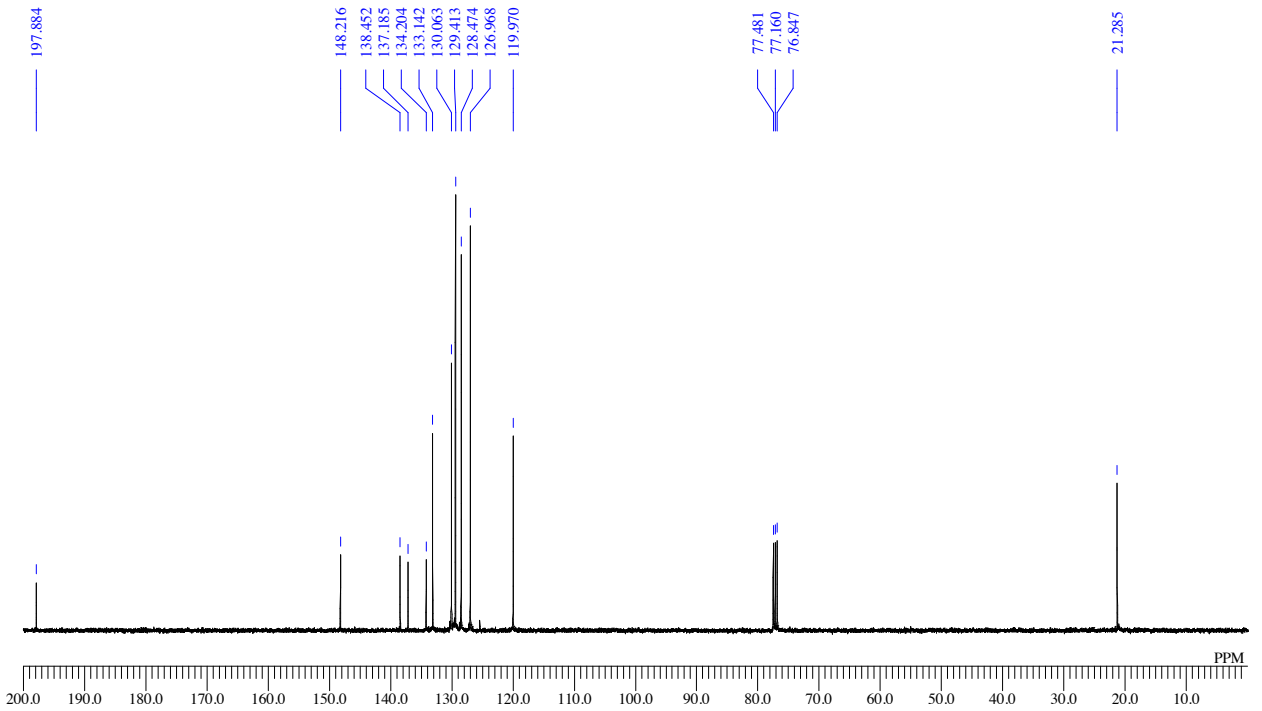


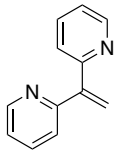
1m

^{1}H NMR: (400 MHz, $CDCl_3$)



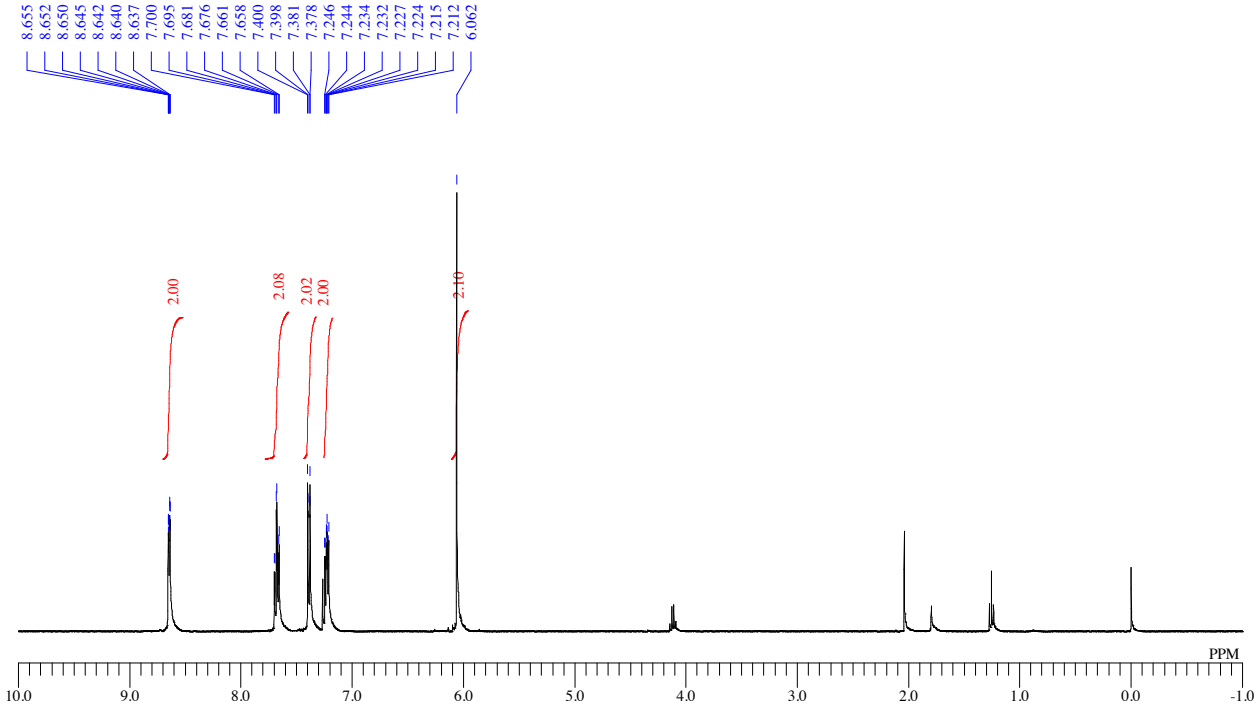
^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$)



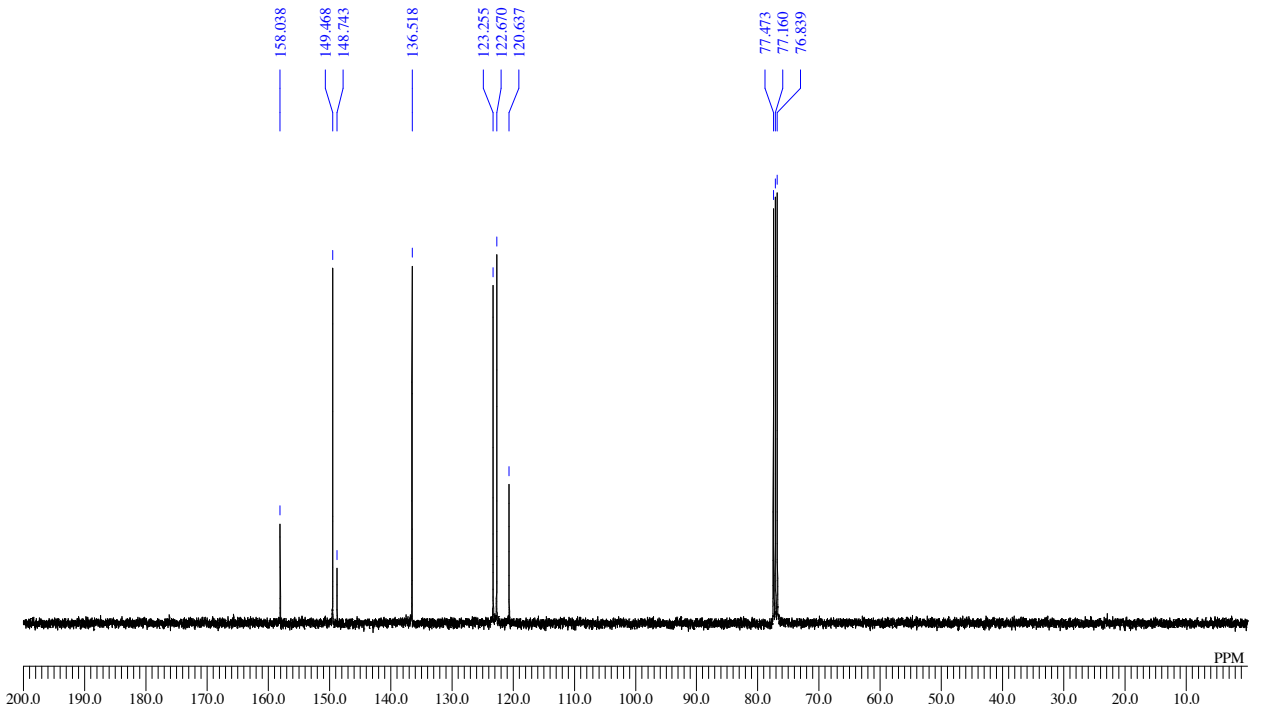


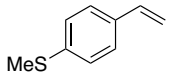
1o

^{1}H NMR: (400 MHz, $CDCl_3$)



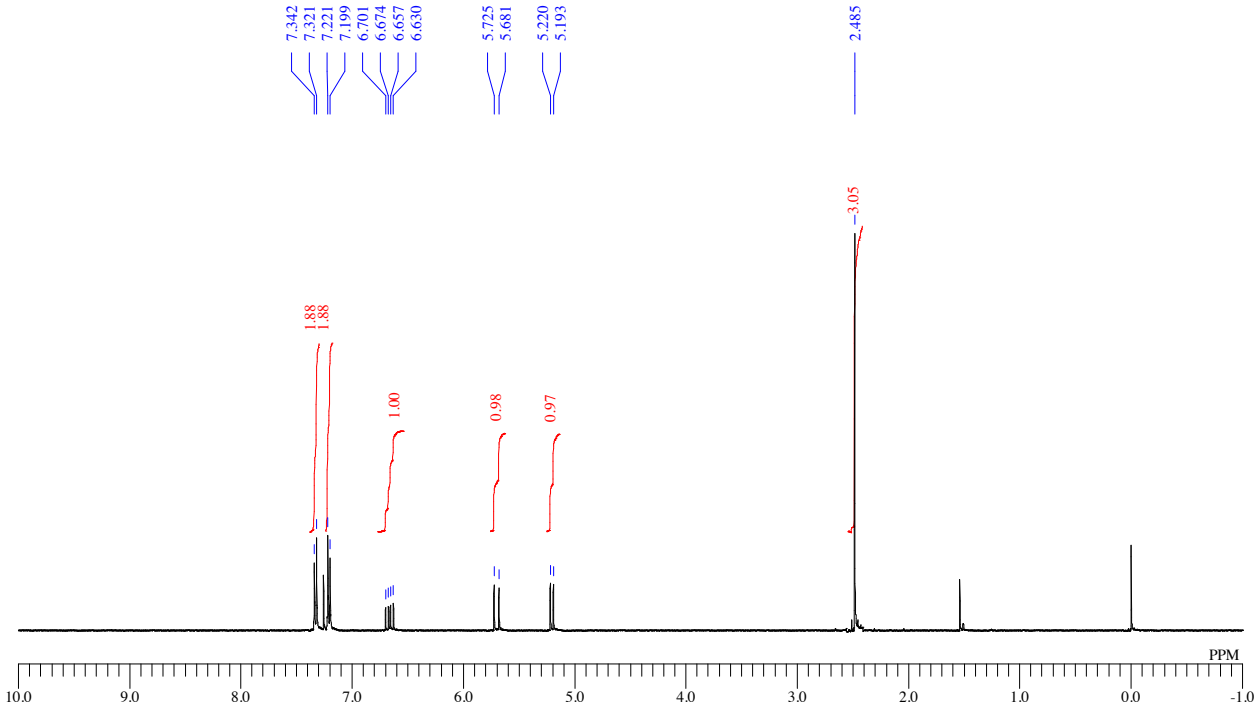
$^{13}C\{^{1}H\}$ NMR: (100 MHz, $CDCl_3$)



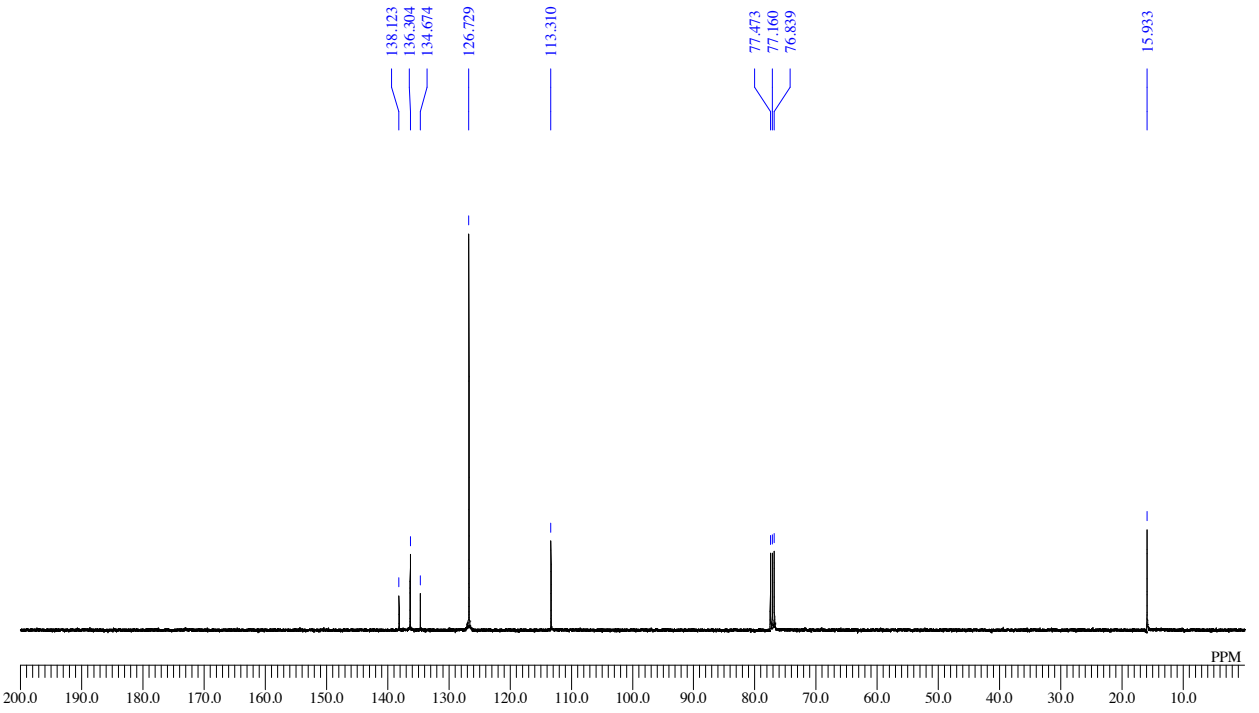


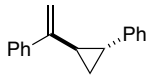
1q

^{1}H NMR: (400 MHz, $CDCl_3$)



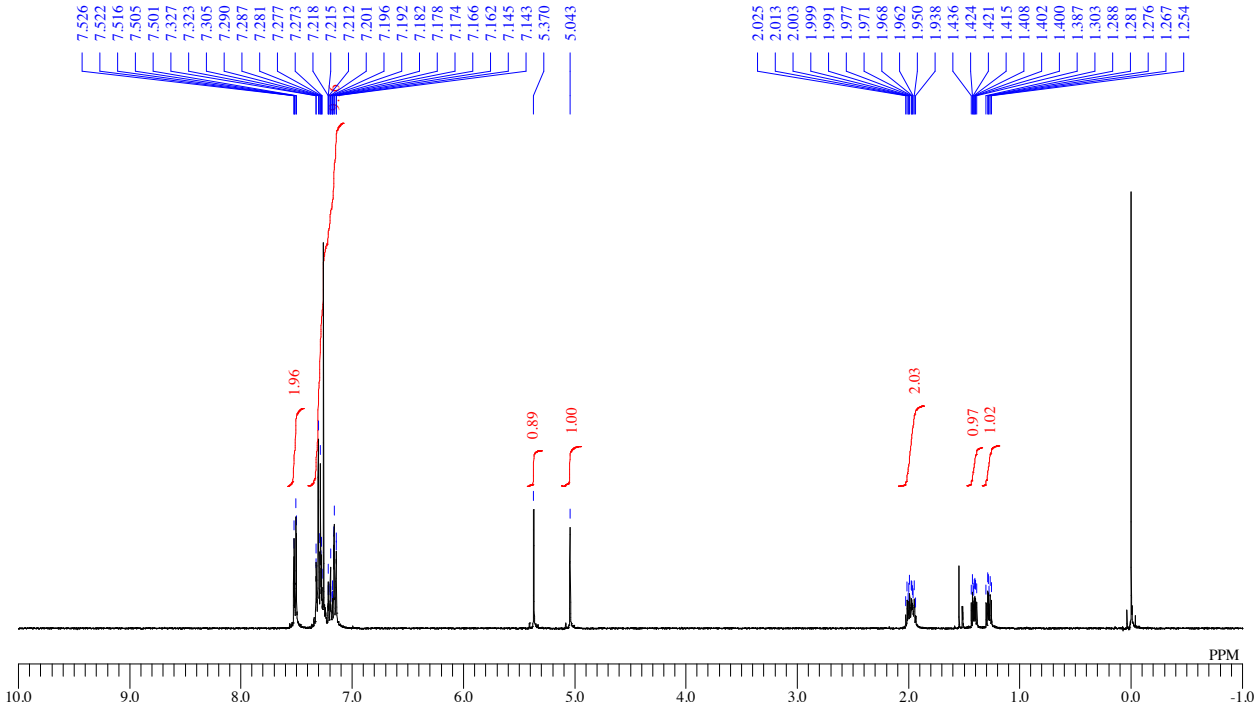
^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$)



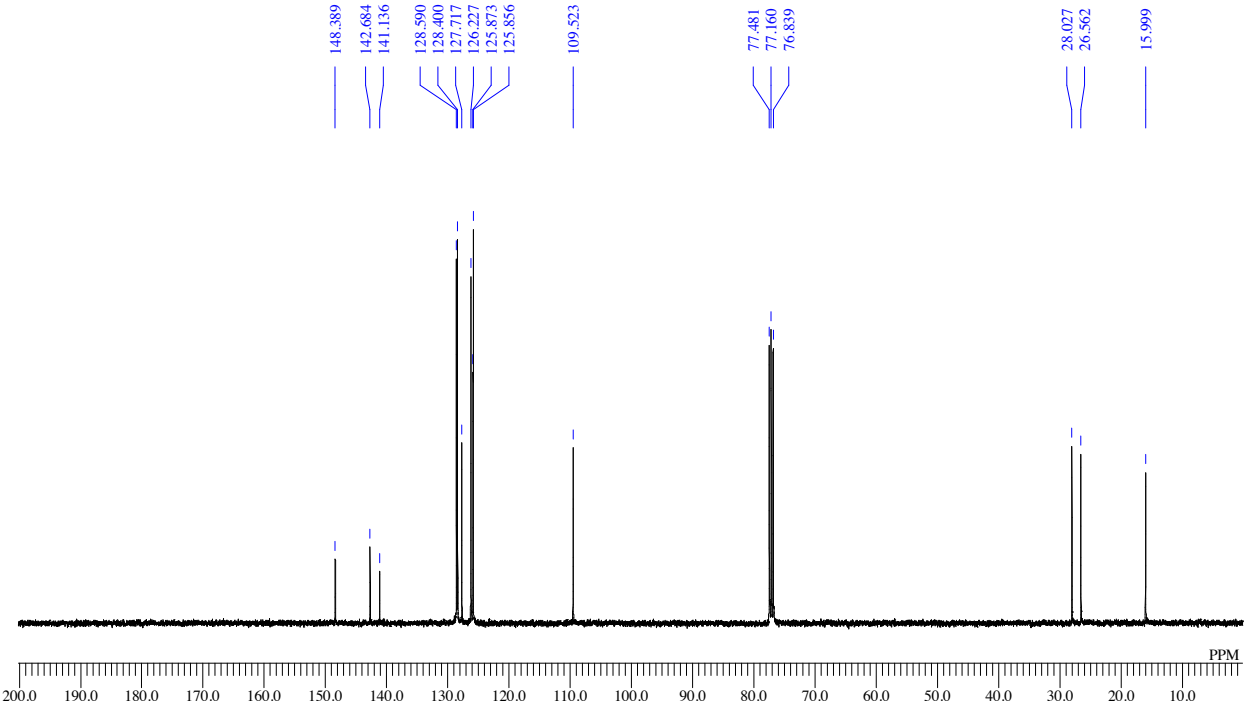


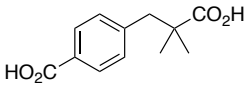
1r

^{1}H NMR: (400 MHz, $CDCl_3$)



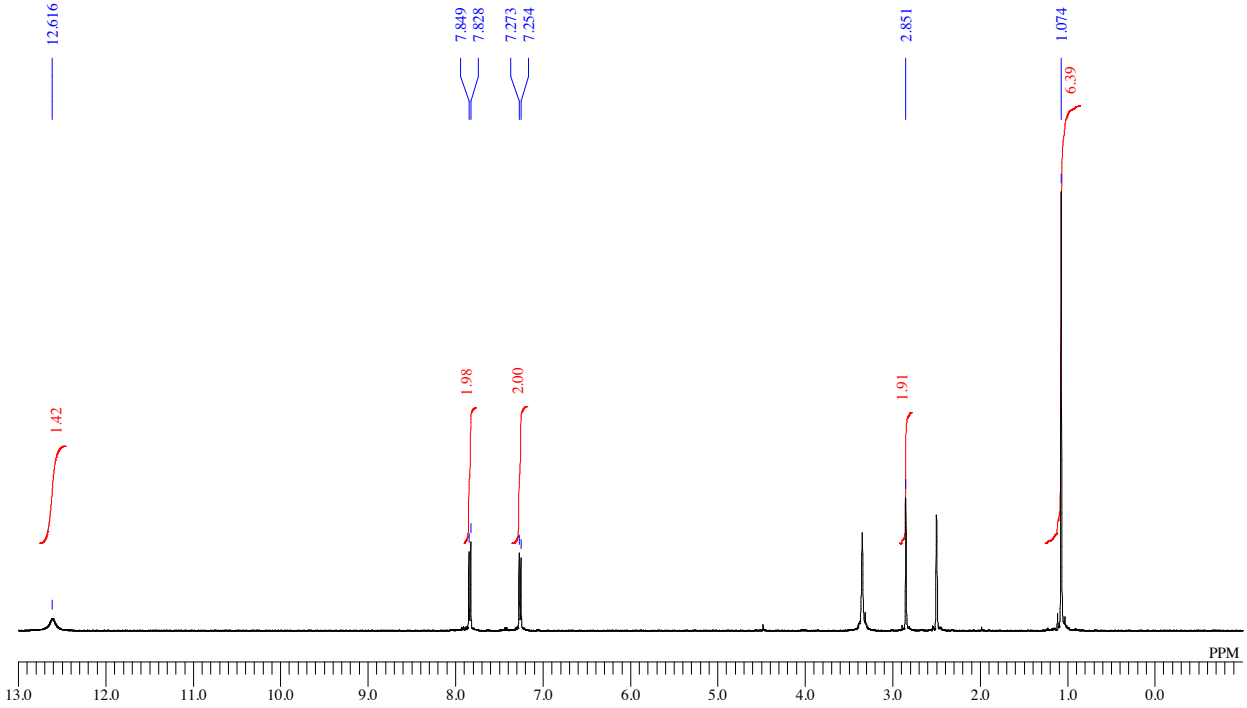
^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$)



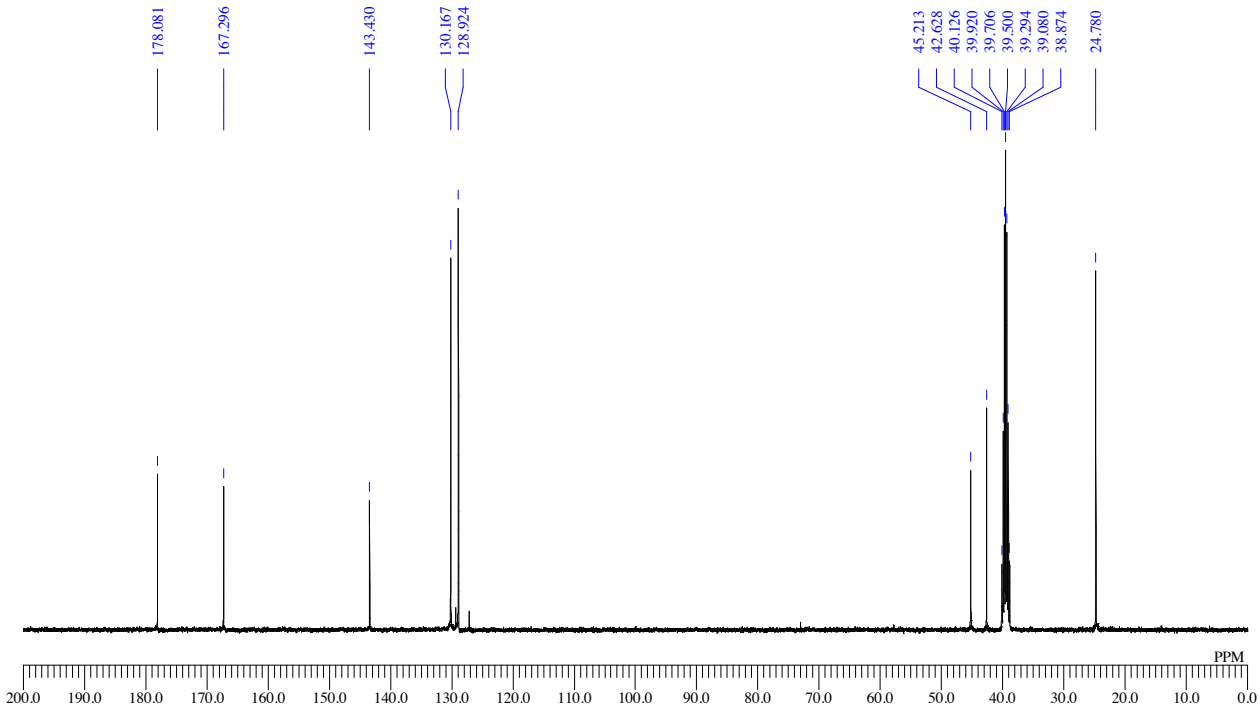


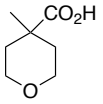
2e

^{1}H NMR: (400 MHz, DMSO-d_6)



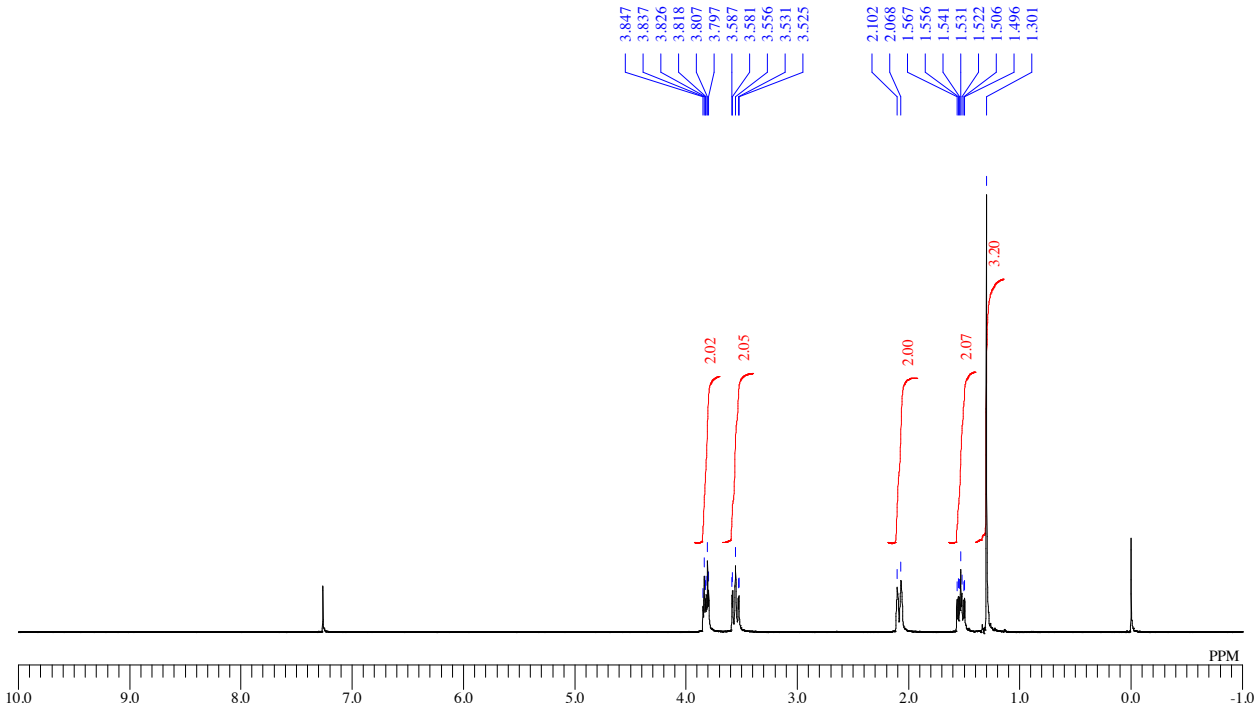
^{13}C{^{1}H} NMR: (100 MHz, DMSO-d_6)



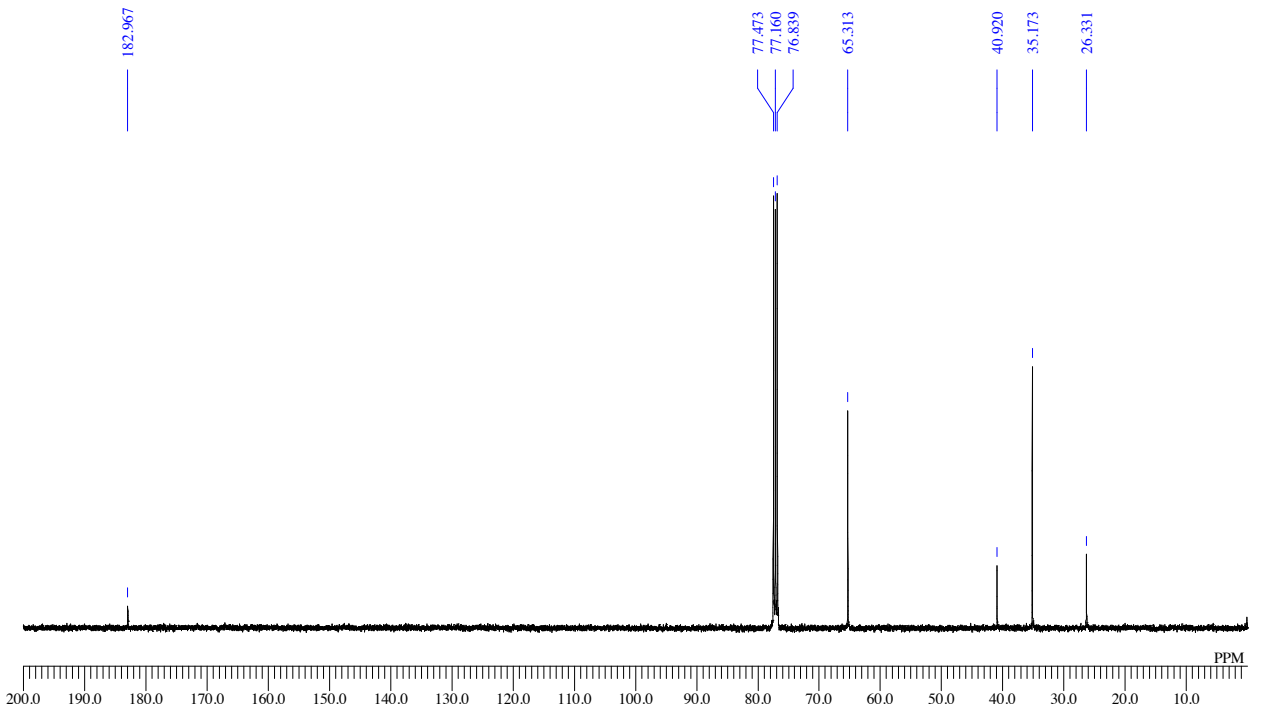


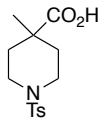
2j

^{1}H NMR: (400 MHz, $CDCl_3$)



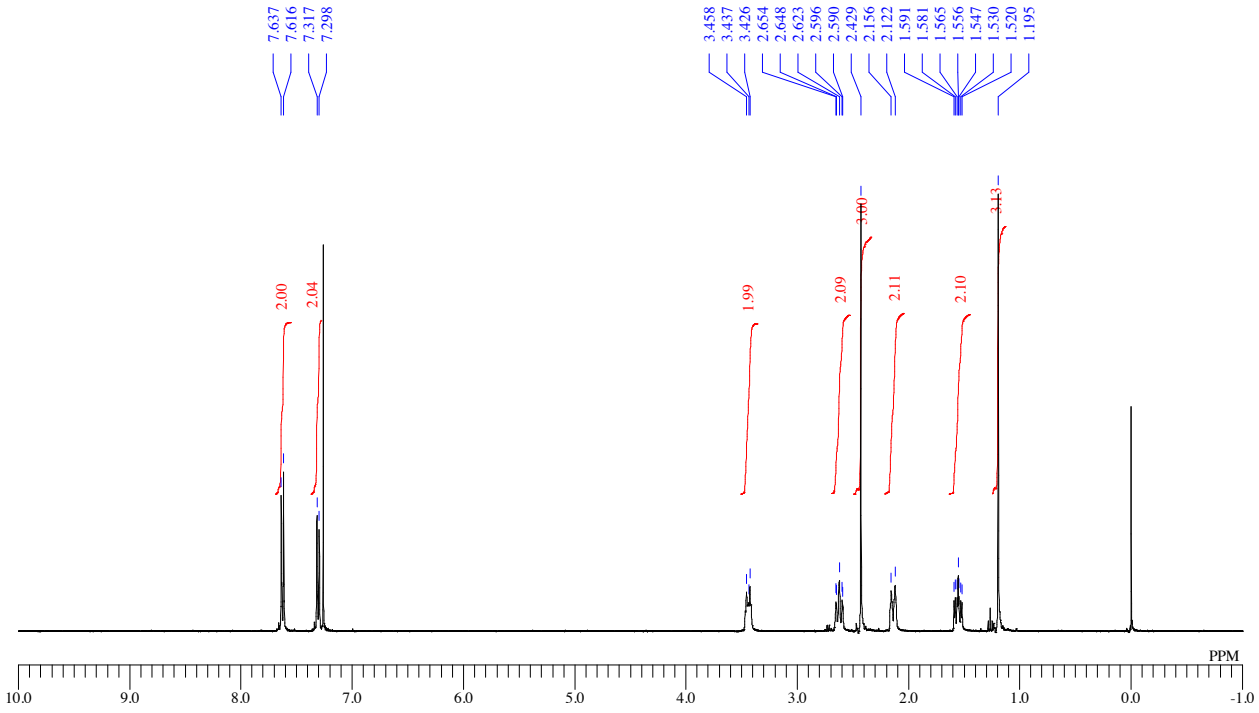
^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$)



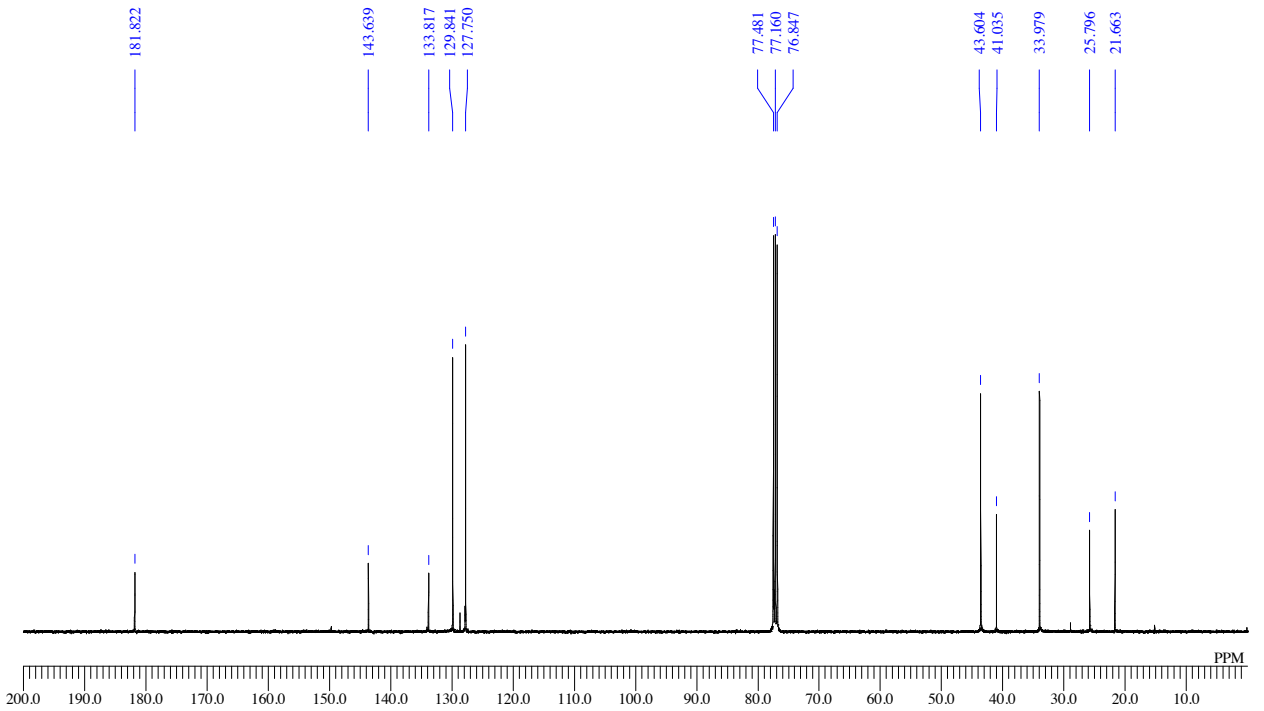


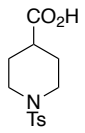
2k

^{1}H NMR: (400 MHz, $CDCl_3$)



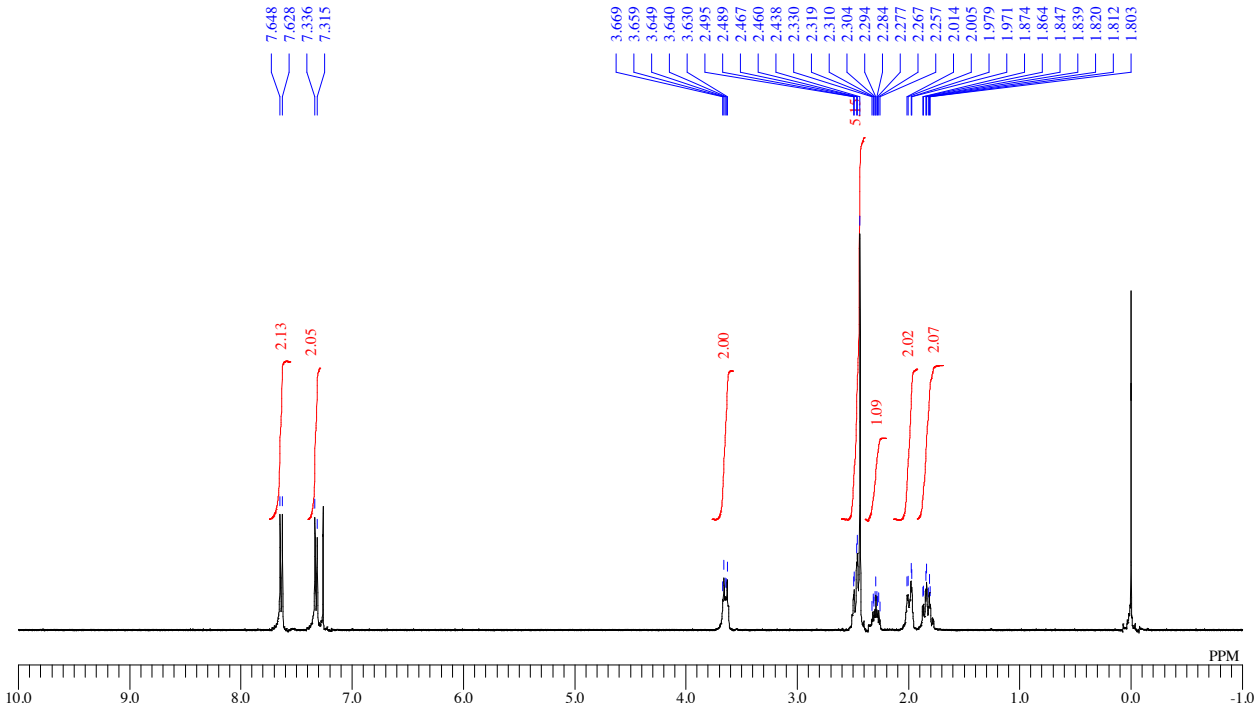
^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$)



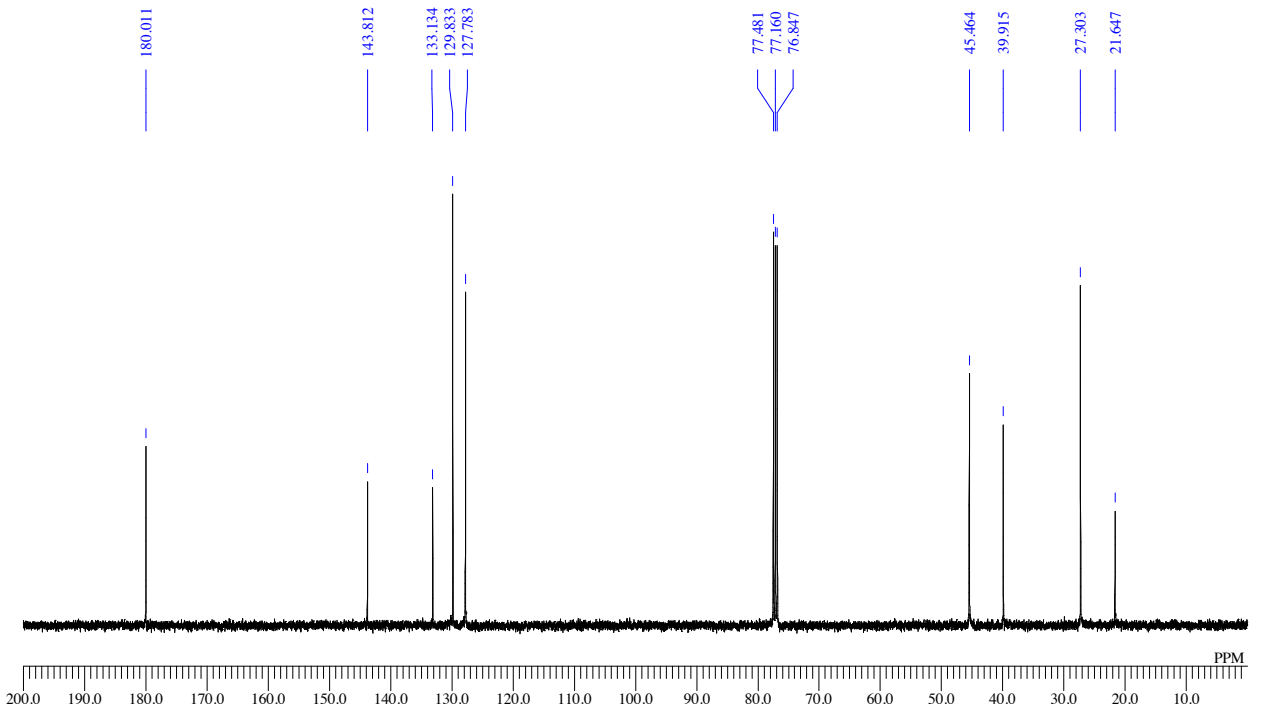


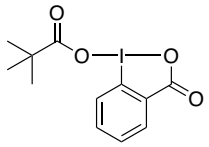
2p

^{1}H NMR: (400 MHz, $CDCl_3$)



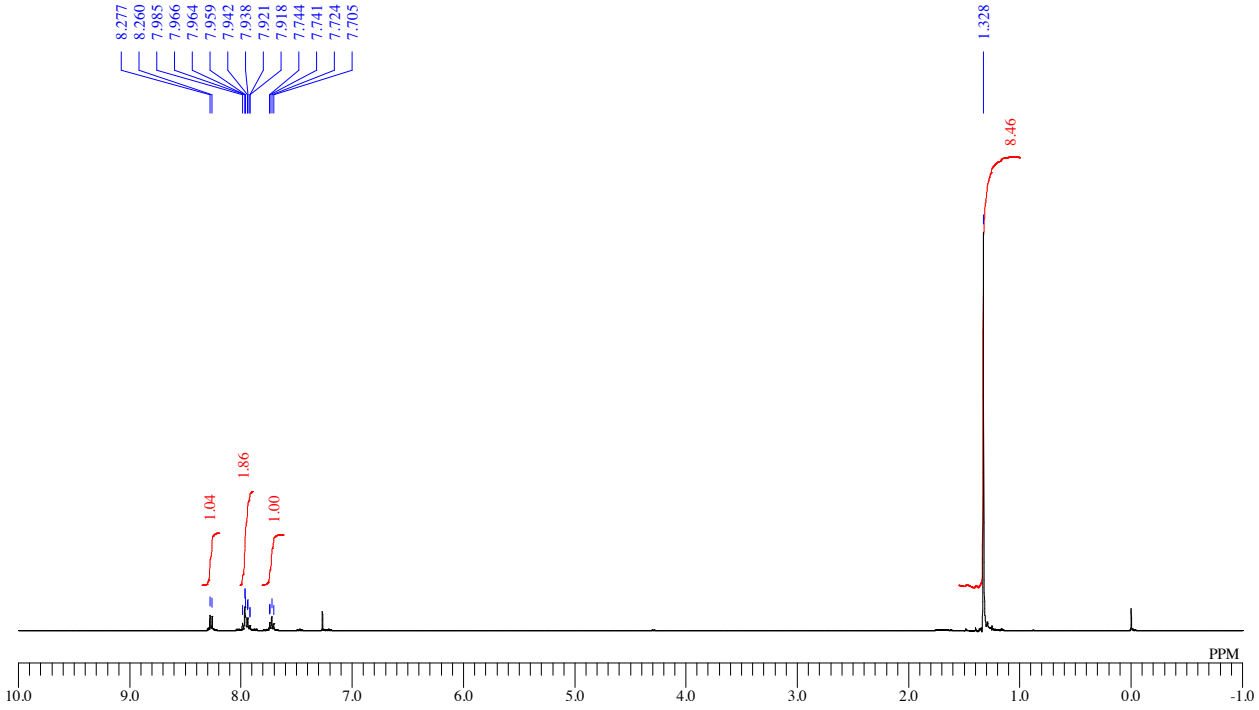
$^{13}C\{^{1}H\}$ NMR: (100 MHz, $CDCl_3$)



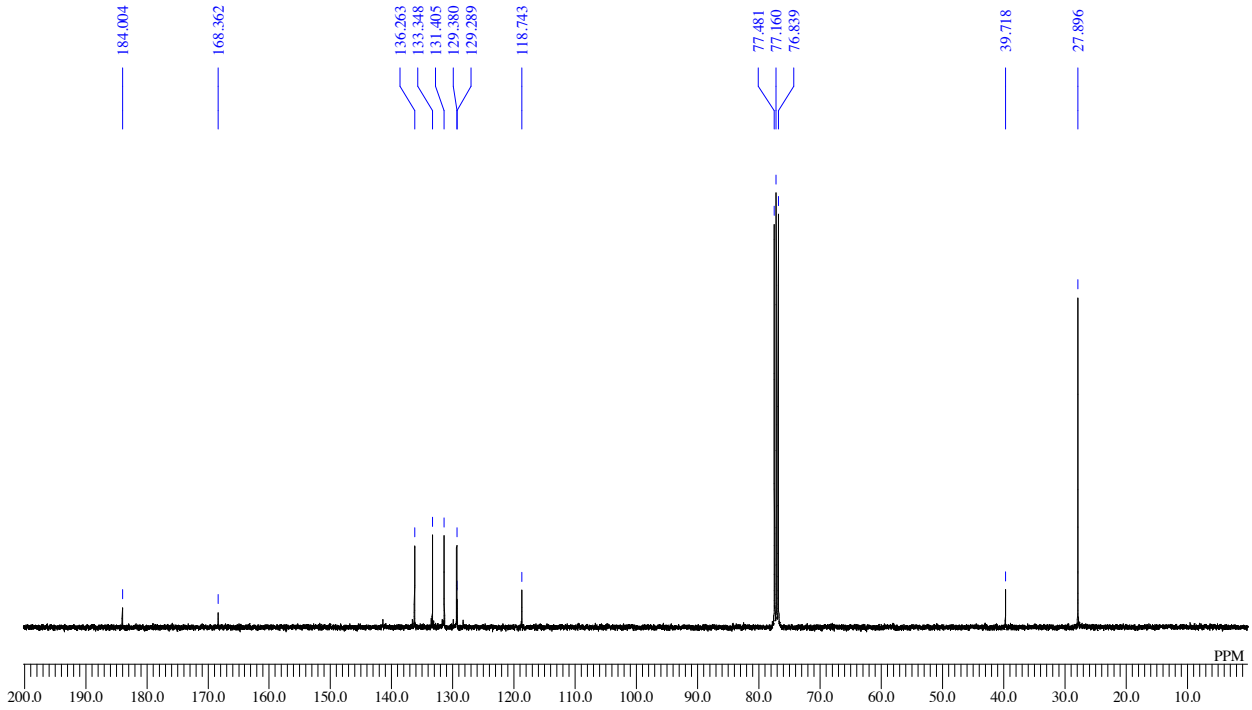


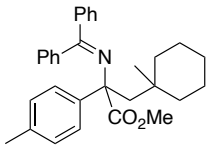
60

^{1}H NMR: (400 MHz, $CDCl_3$)



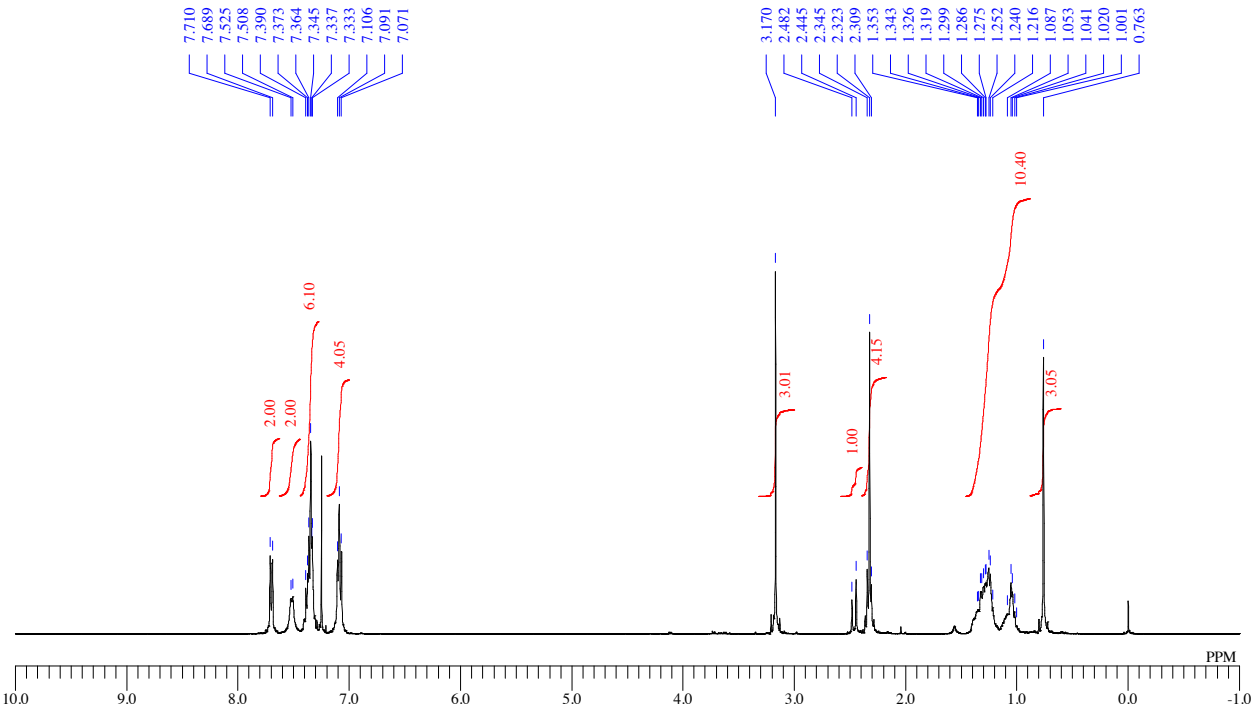
^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$)



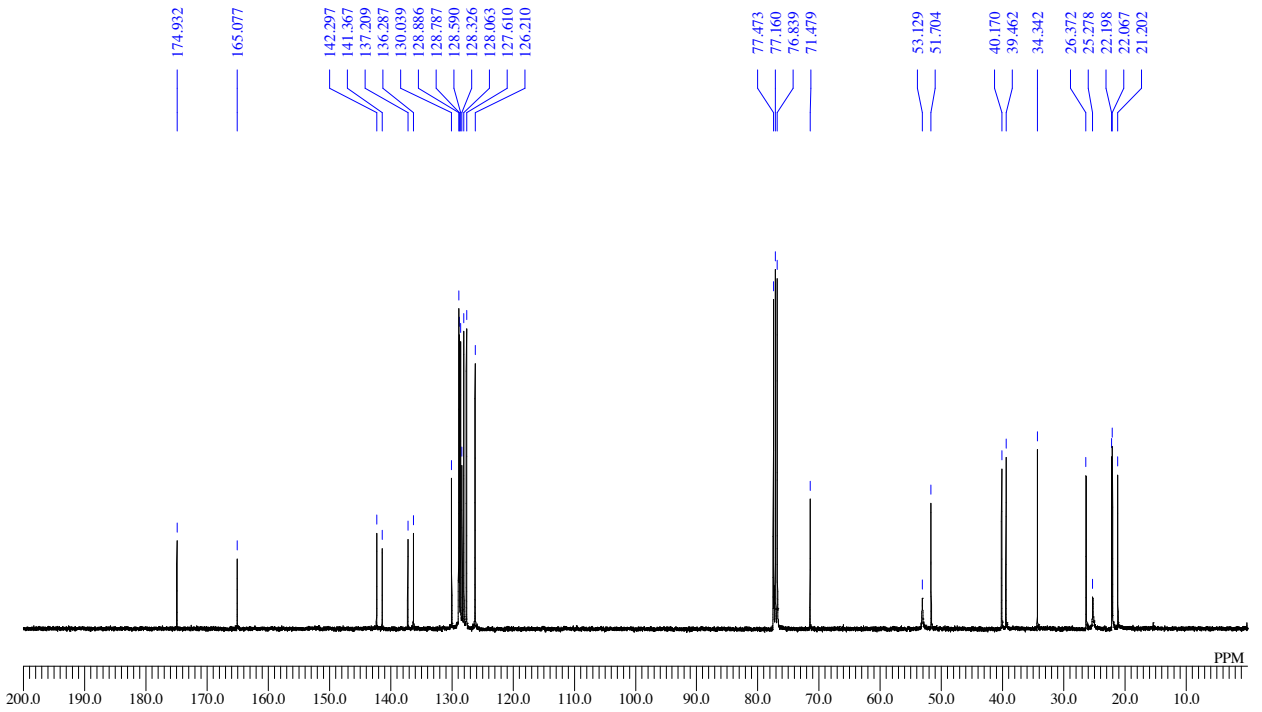


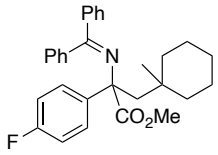
4

^{1}H NMR: (400 MHz, $CDCl_3$)



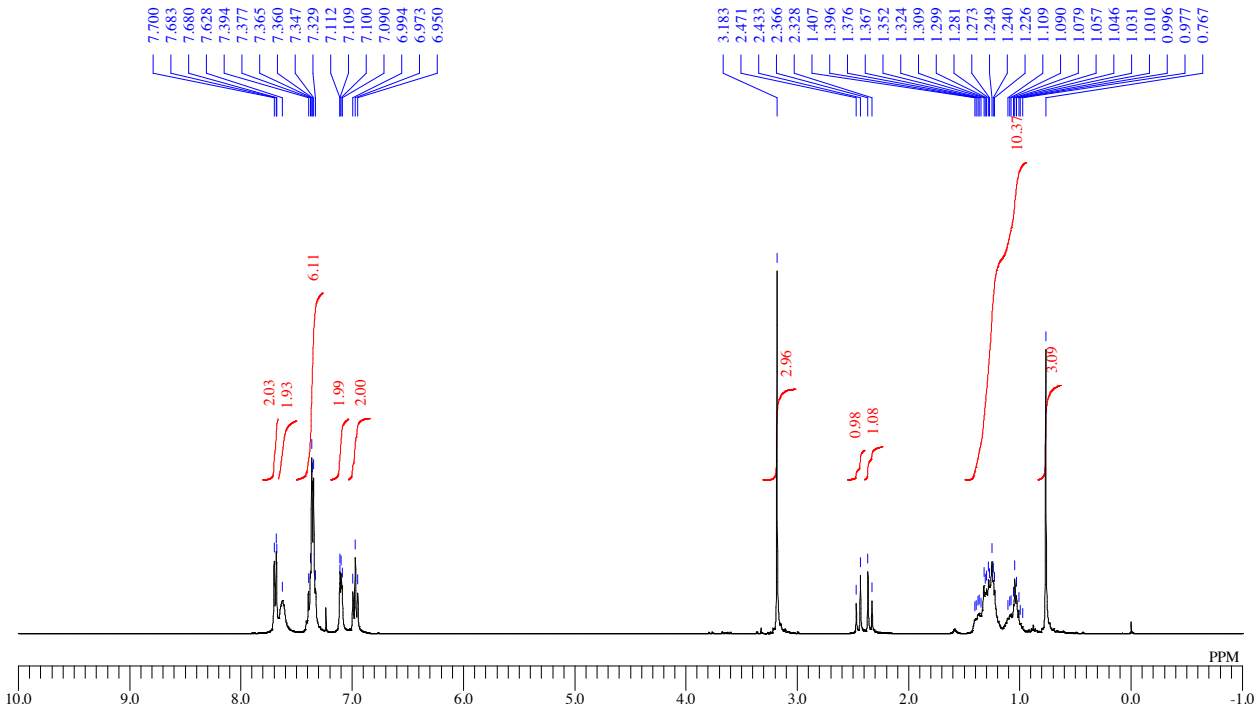
^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$)



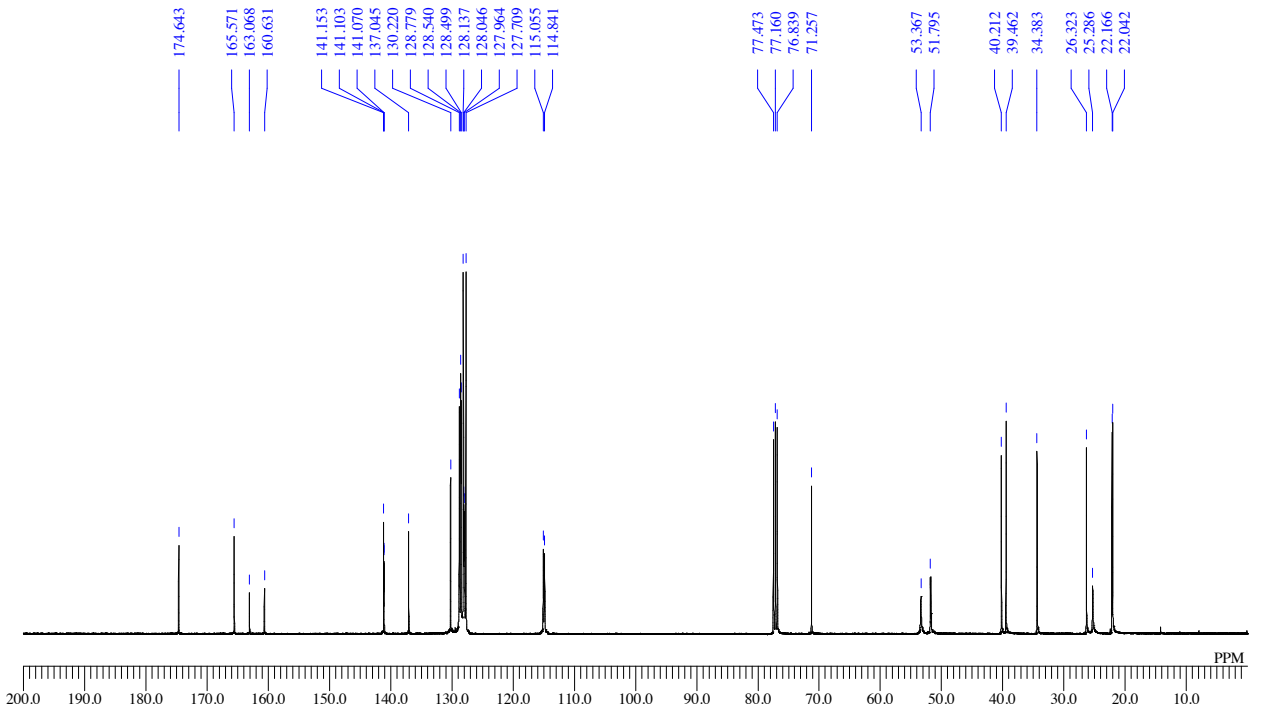


9

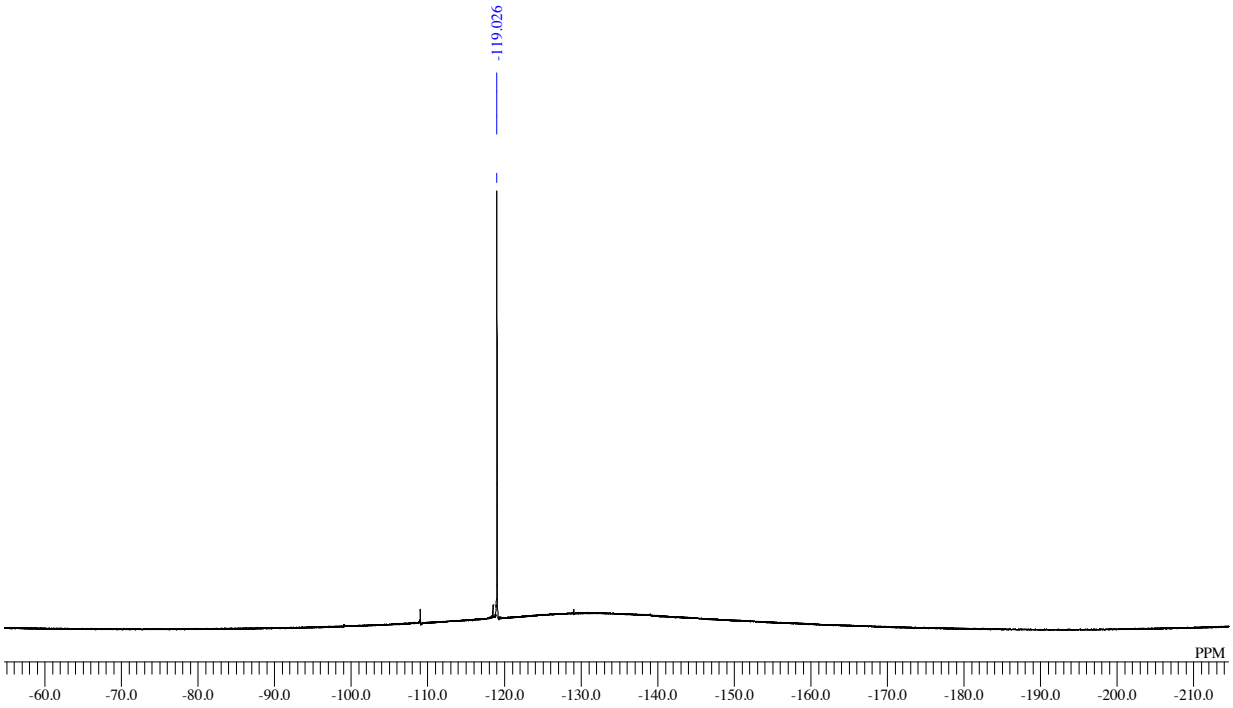
^{1}H NMR: (400 MHz, $CDCl_3$)

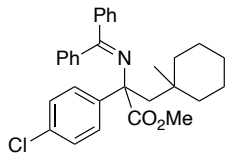


^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$)



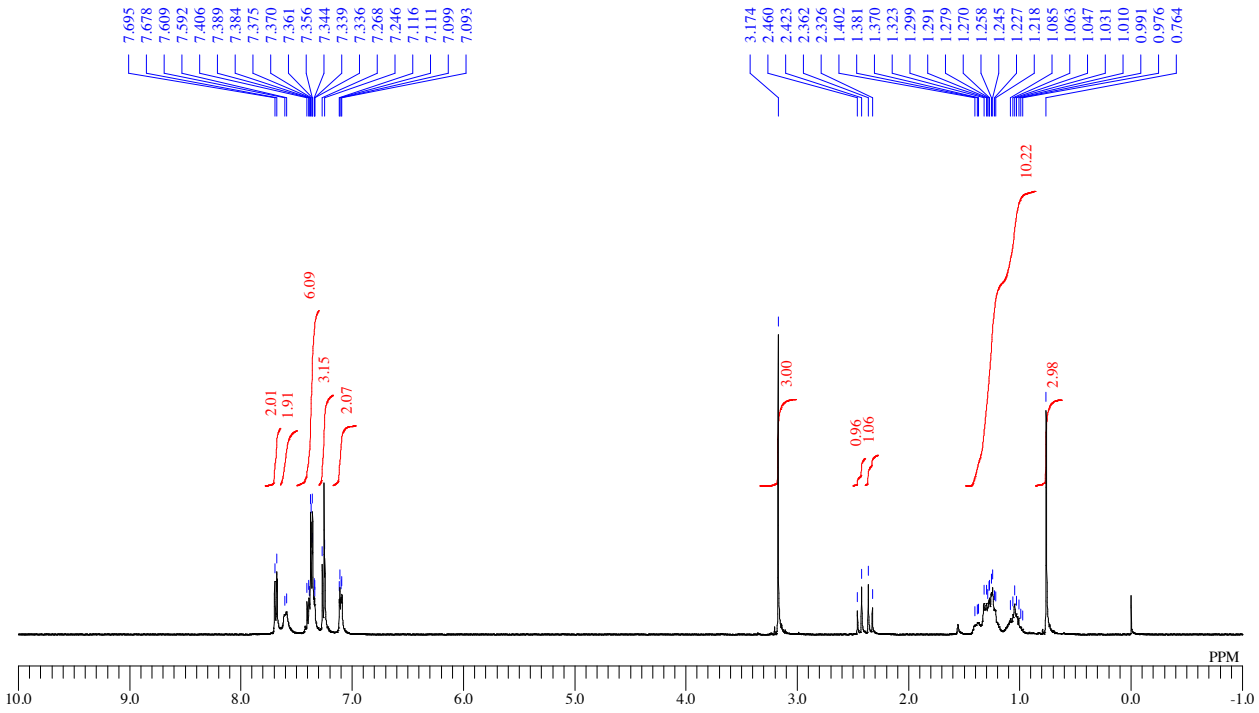
$^{19}F\{^{1}H\}$ NMR: (377 MHz, $CDCl_3$)



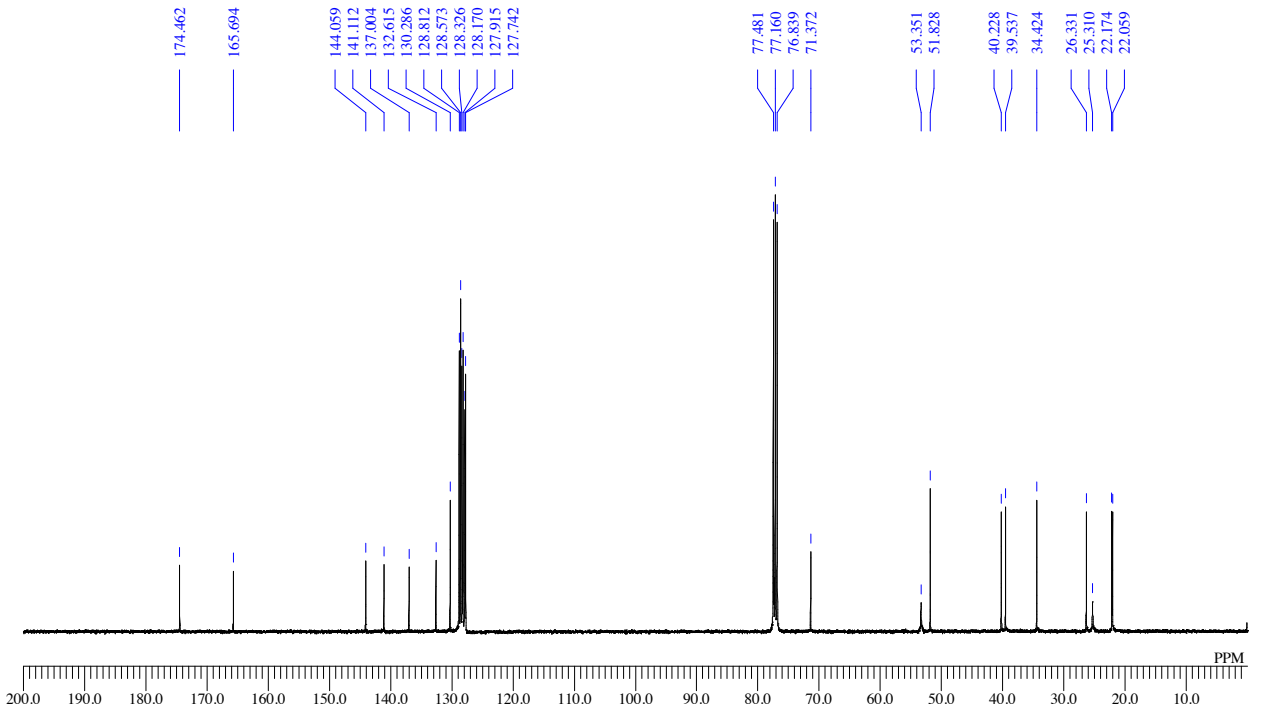


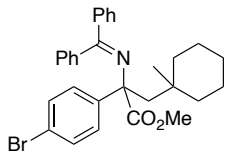
10

^{1}H NMR: (400 MHz, $CDCl_3$)



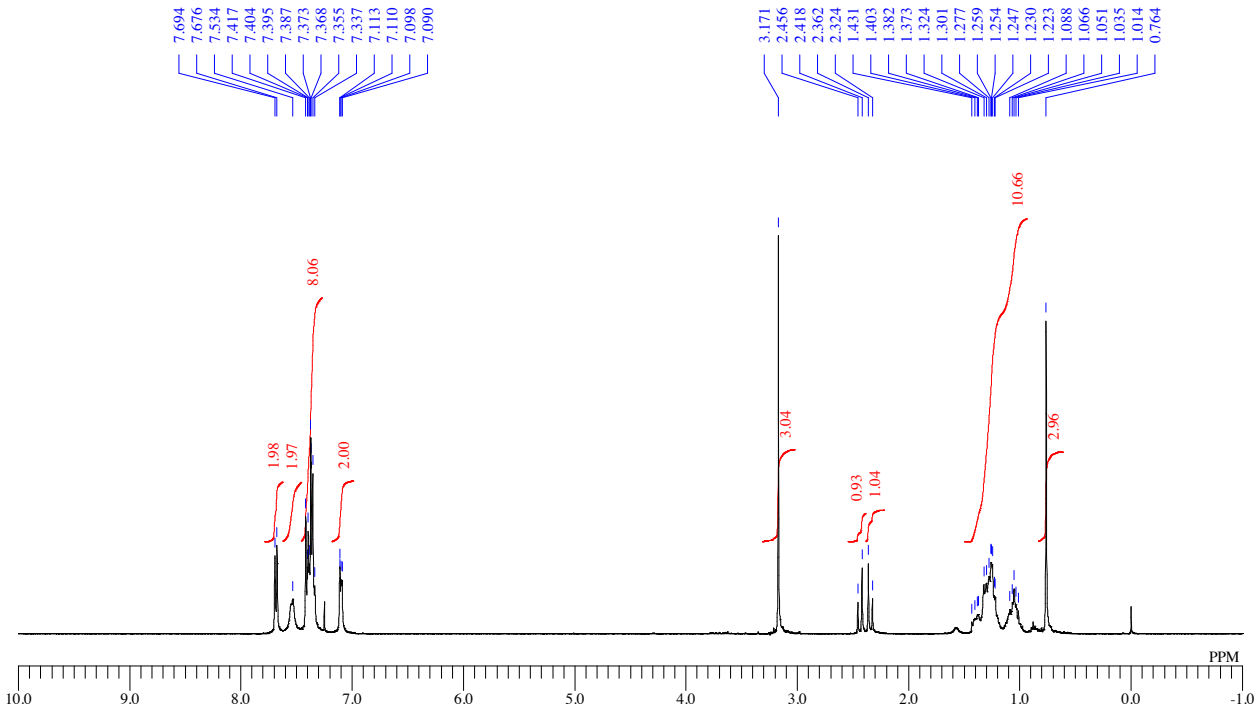
^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$)



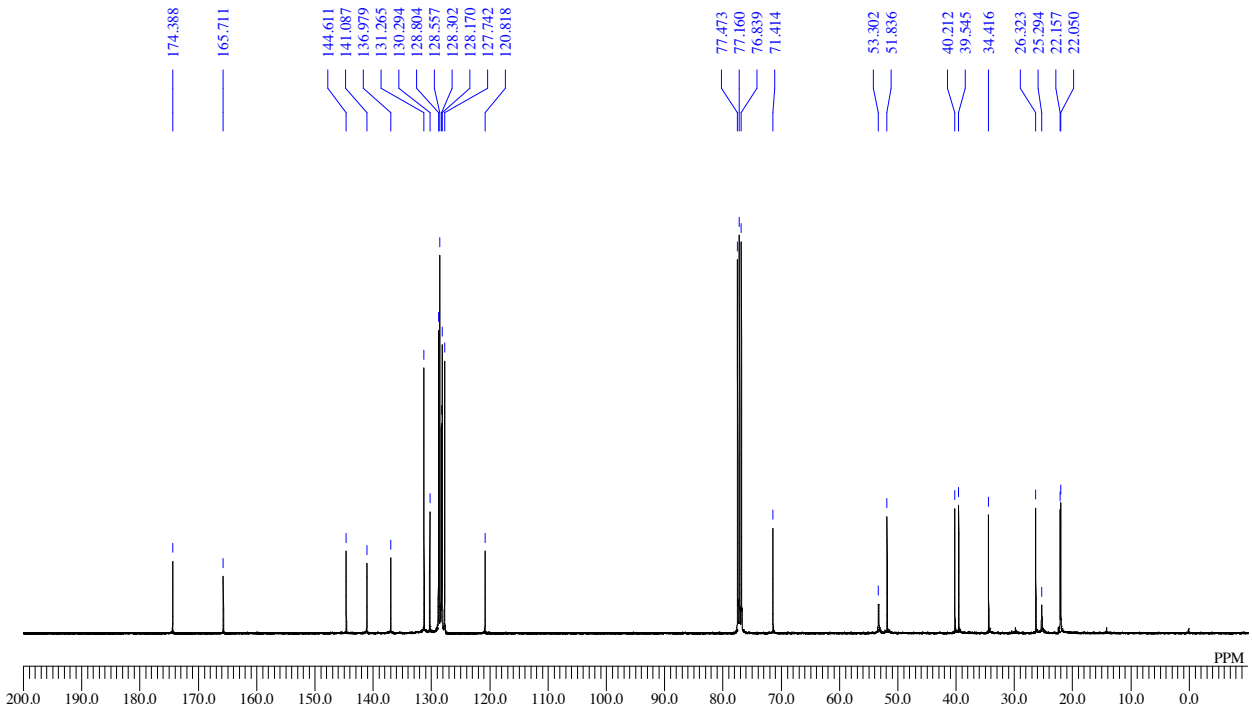


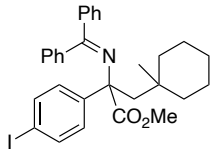
11

^{1}H NMR: (400 MHz, $CDCl_3$)



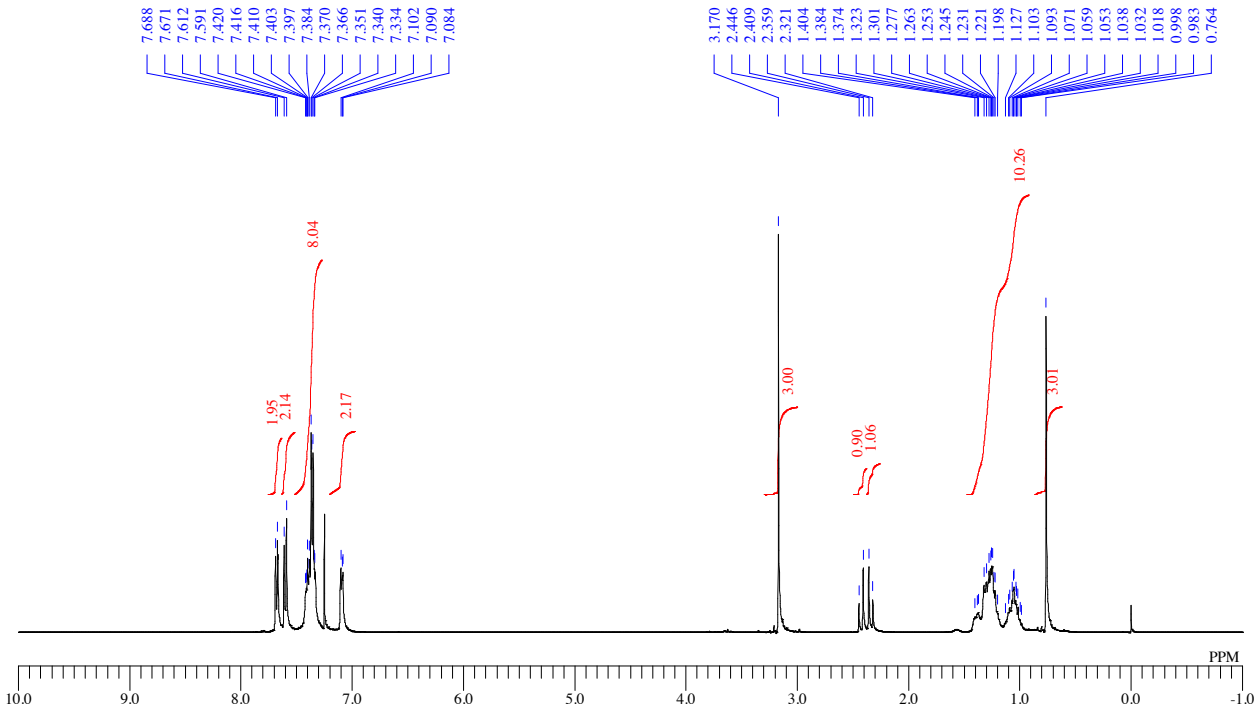
^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$)



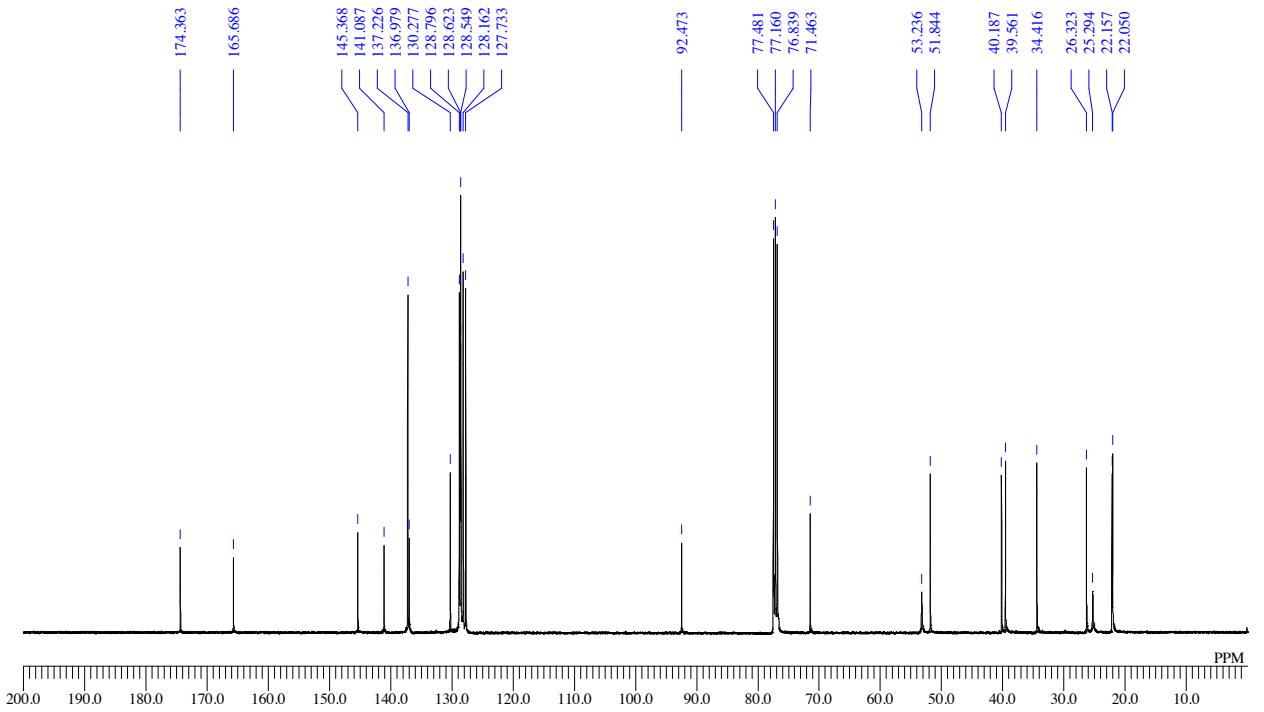


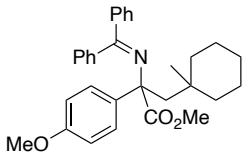
12

^{1}H NMR: (400 MHz, $CDCl_3$)



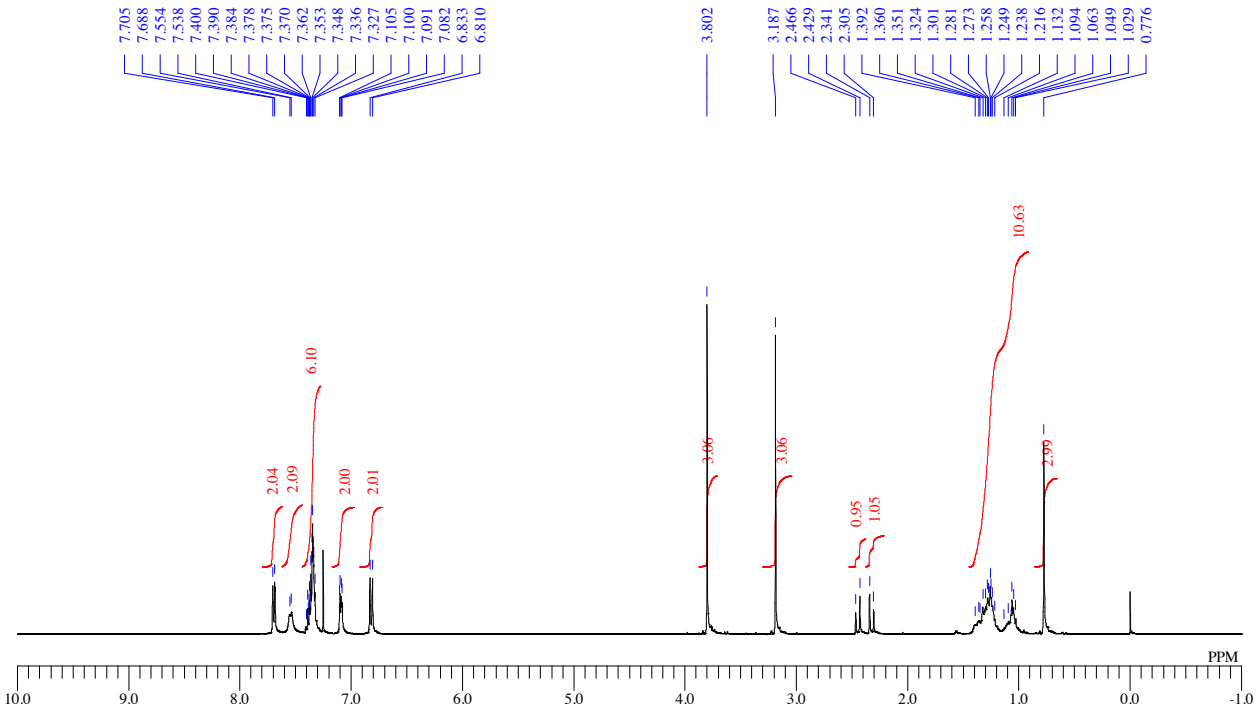
^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$)



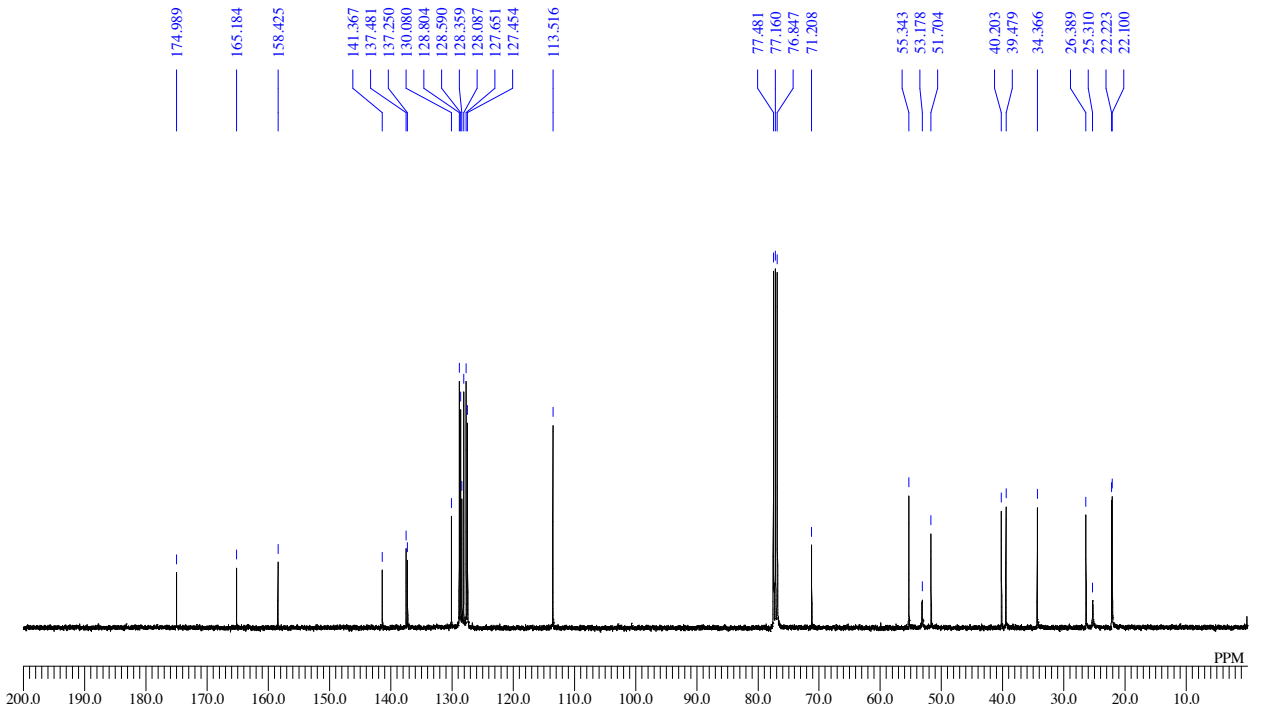


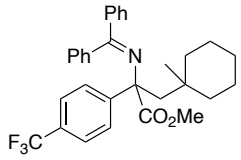
13

^{1}H NMR: (400 MHz, $CDCl_3$)



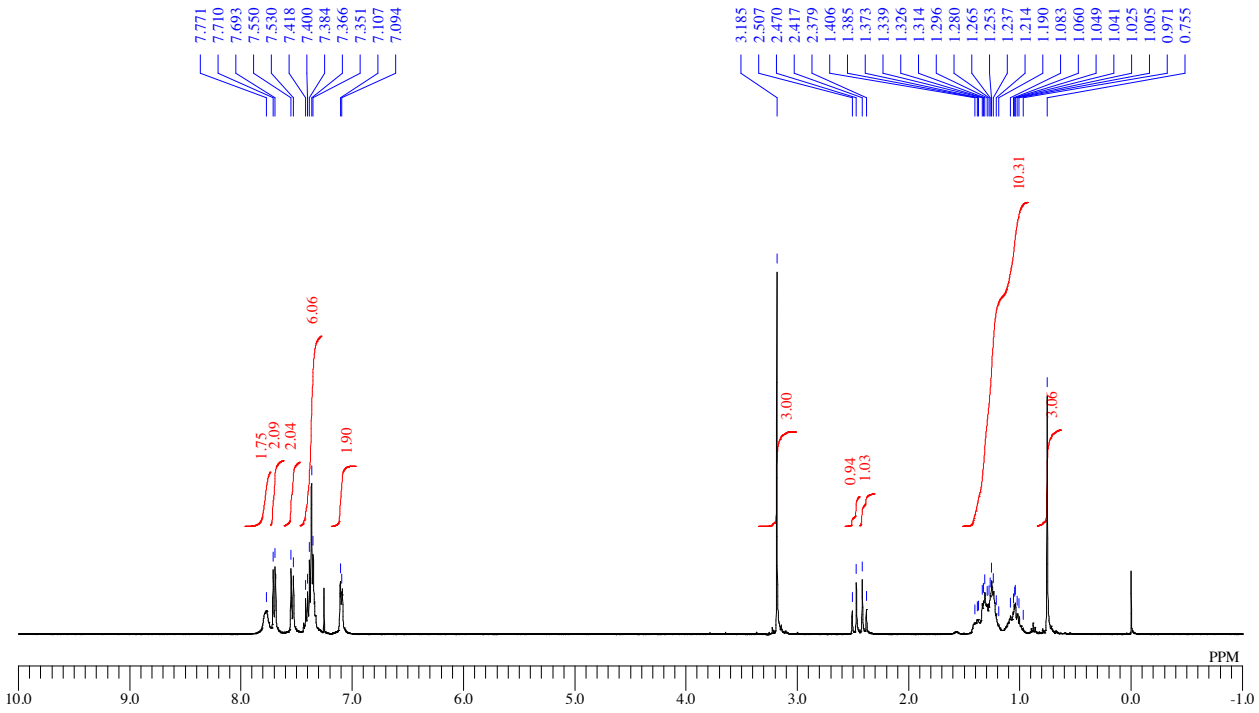
^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$)



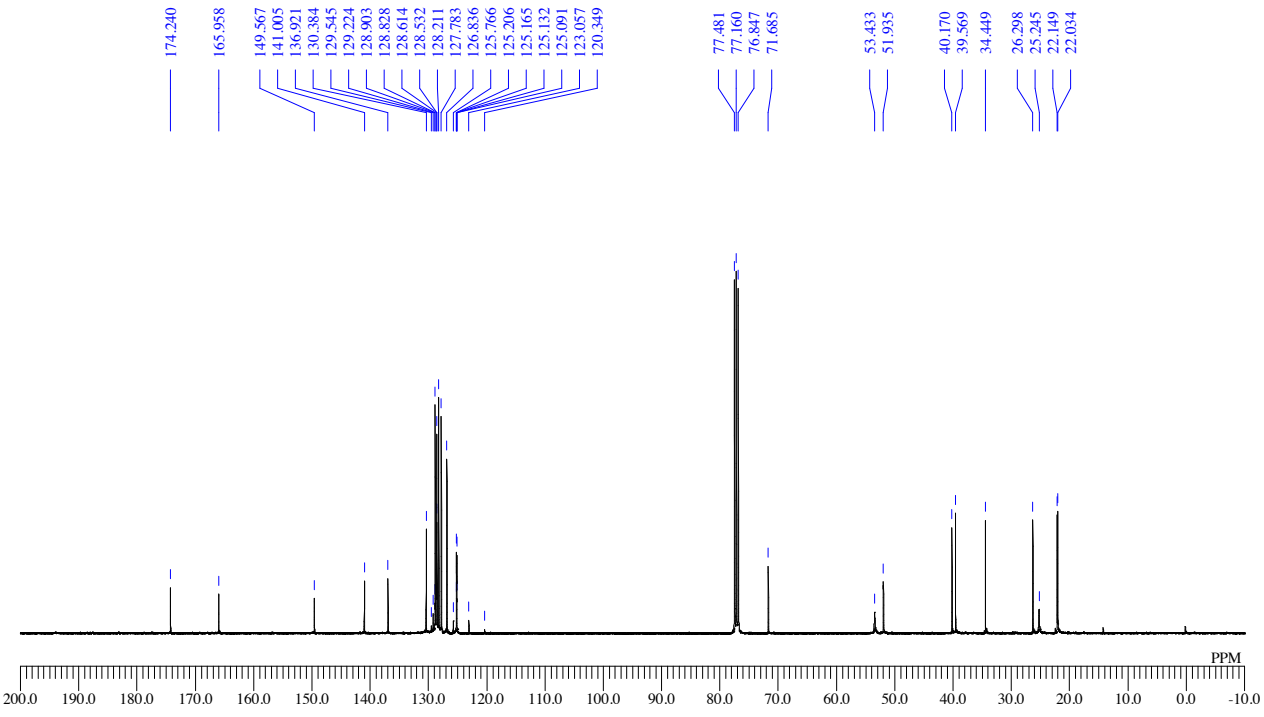


14

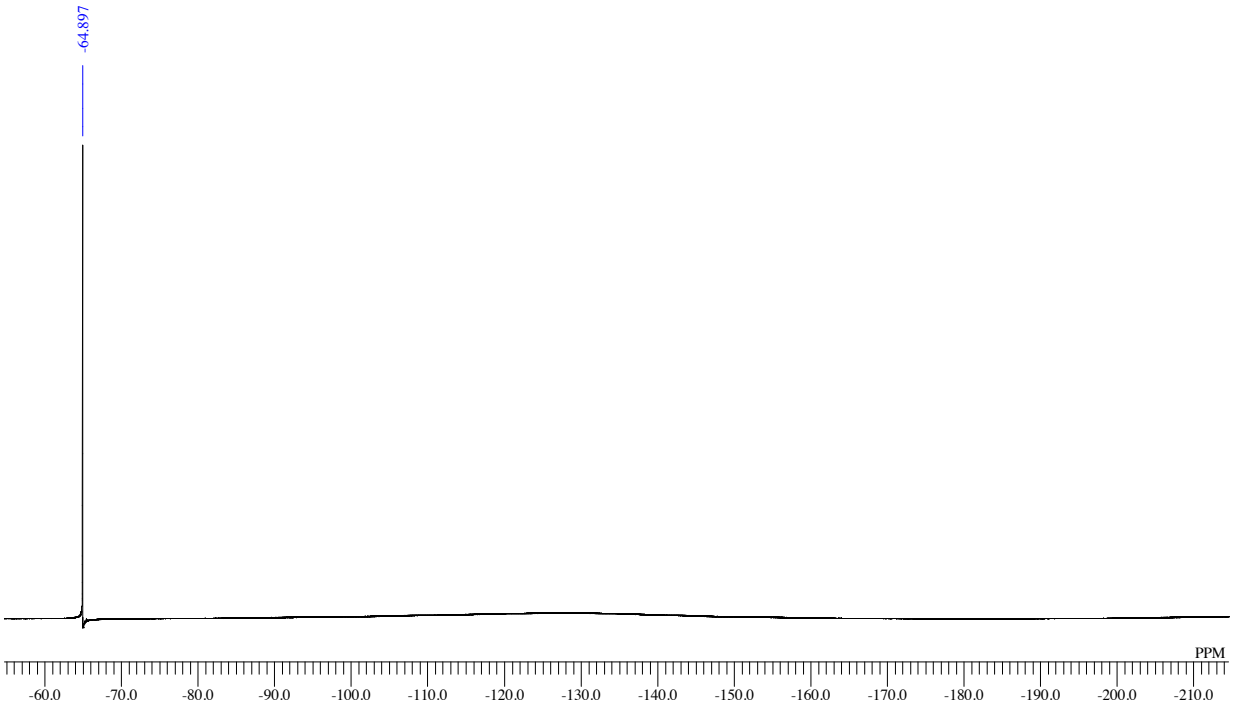
^{1}H NMR: (400 MHz, $CDCl_3$)

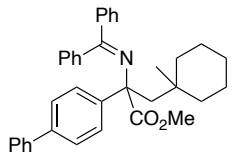


^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$)



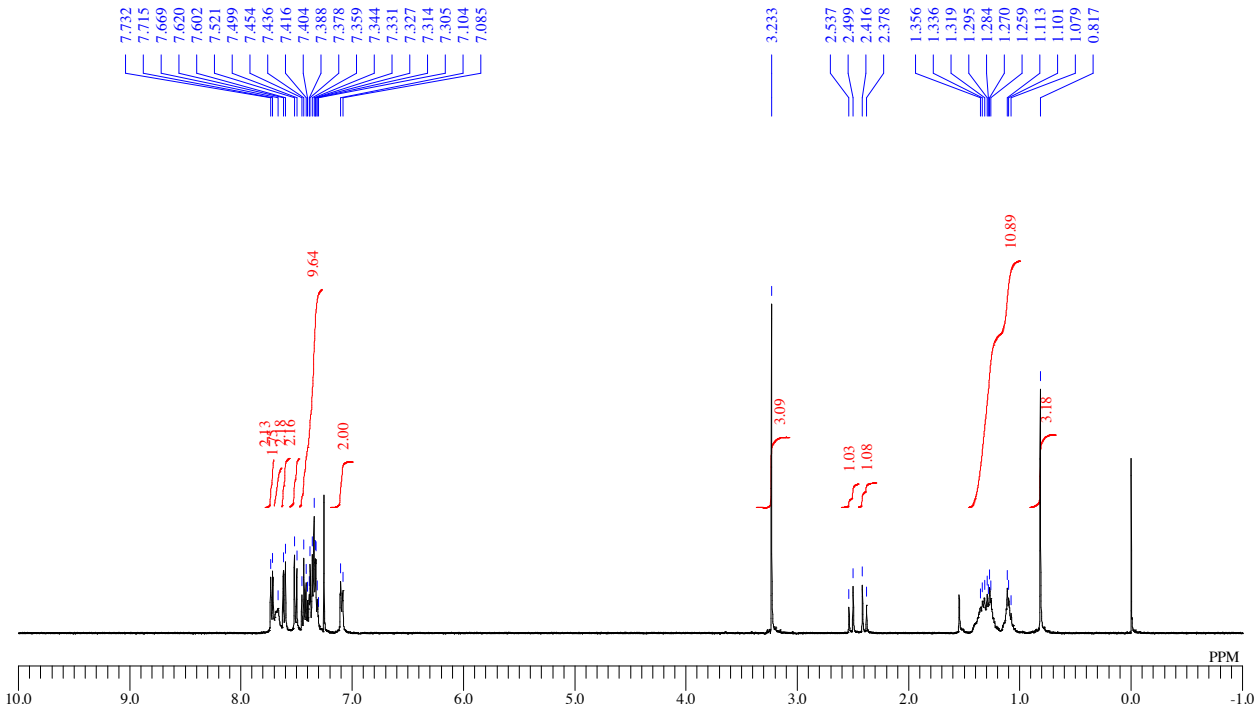
$^{19}F\{^{1}H\}$ NMR: (377 MHz, $CDCl_3$)



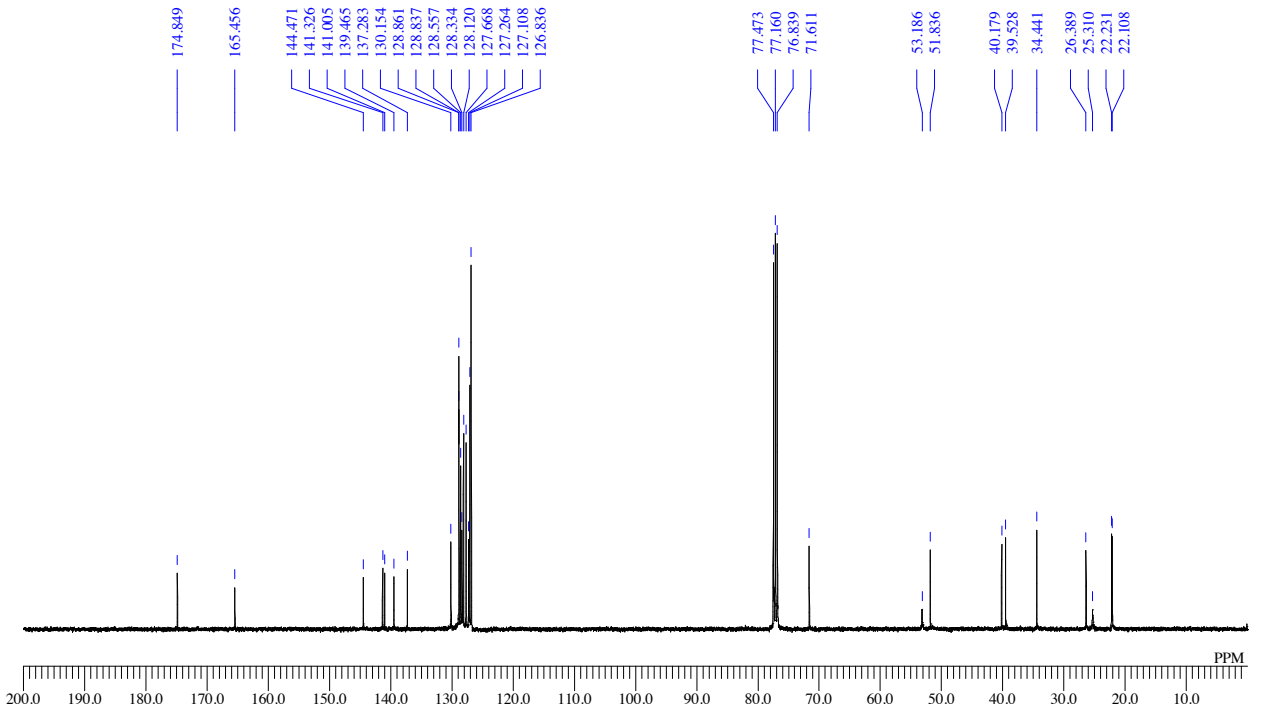


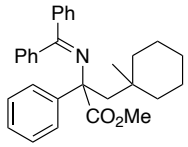
15

^{1}H NMR: (400 MHz, $CDCl_3$)



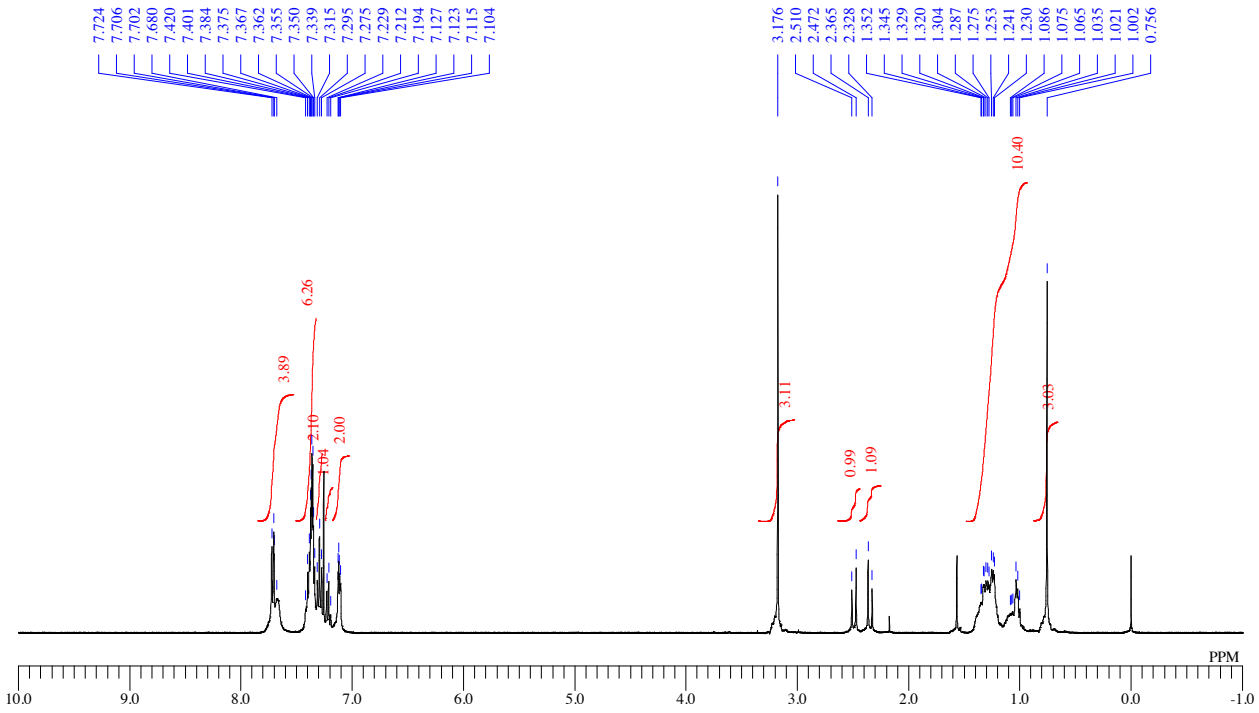
^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$)



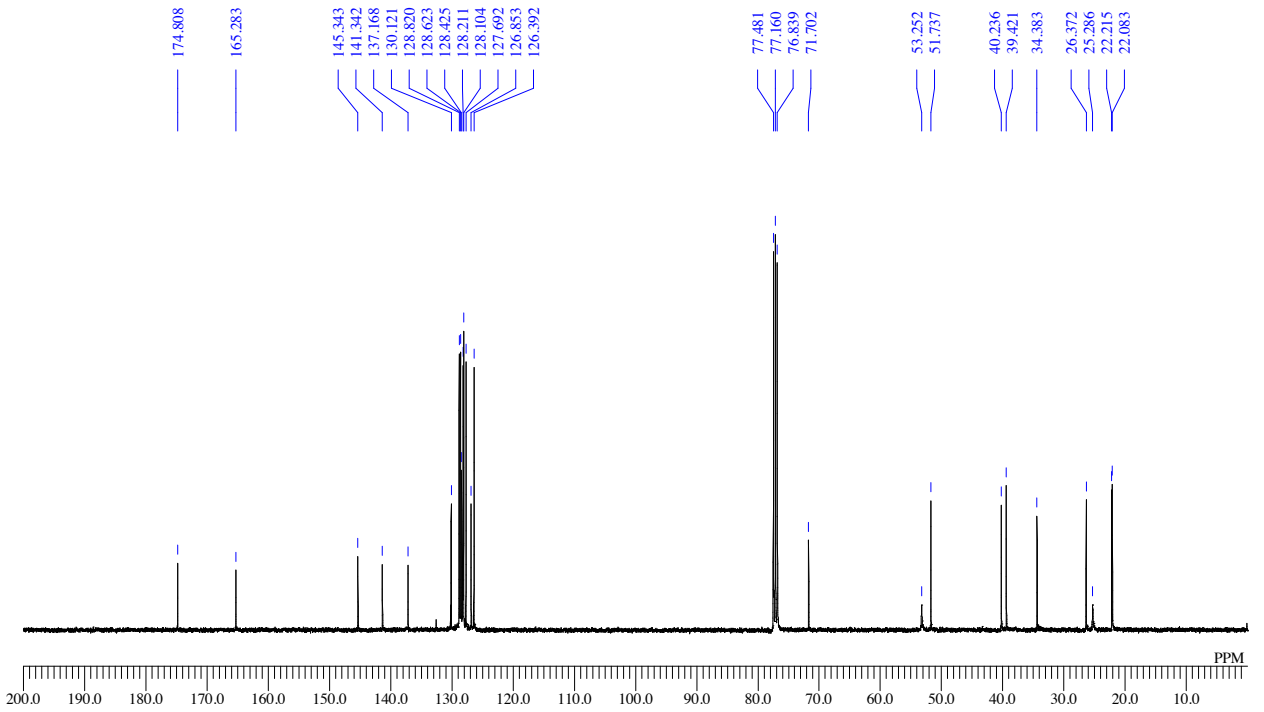


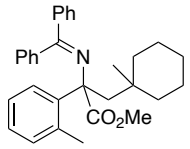
16

^{1}H NMR: (400 MHz, $CDCl_3$)



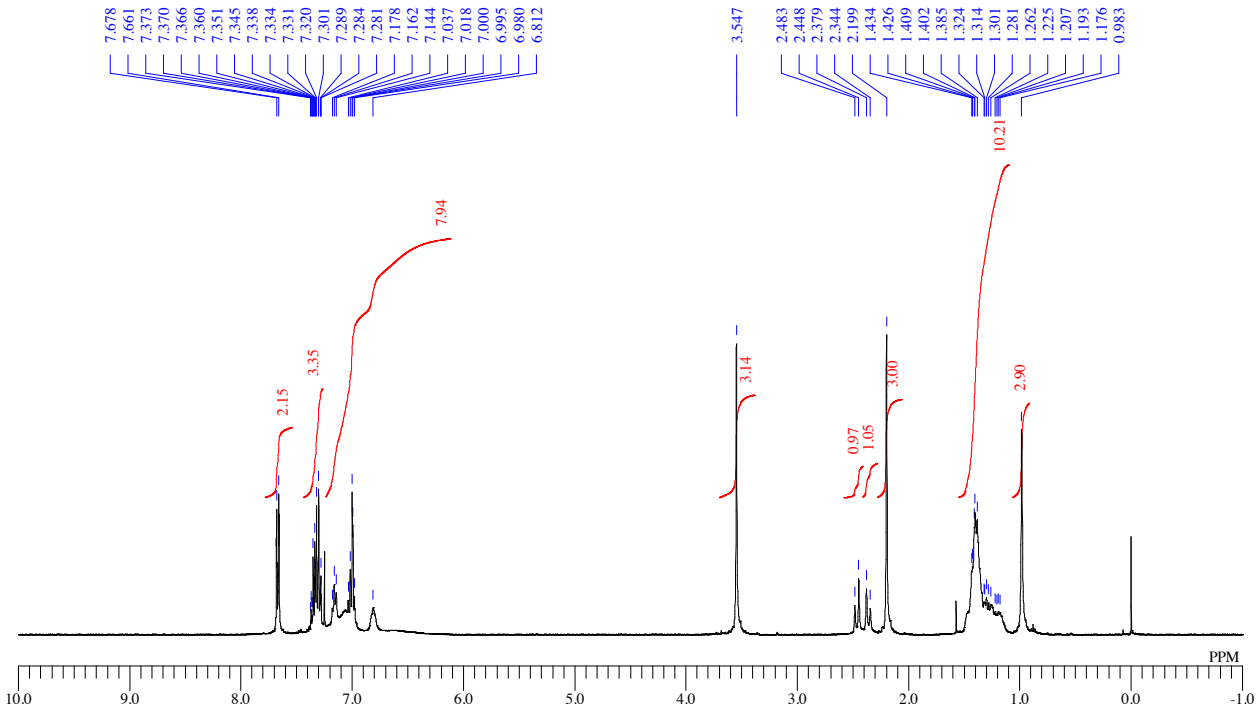
^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$)



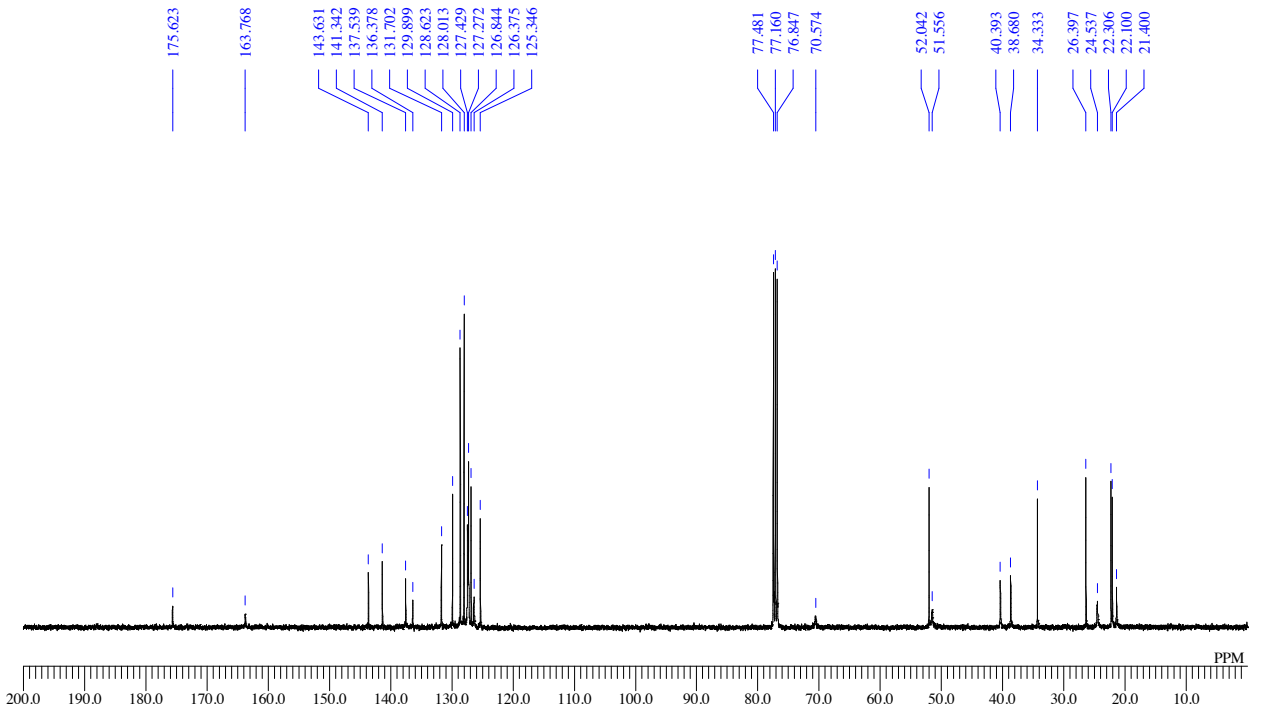


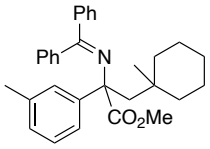
17

^{1}H NMR: (400 MHz, $CDCl_3$)



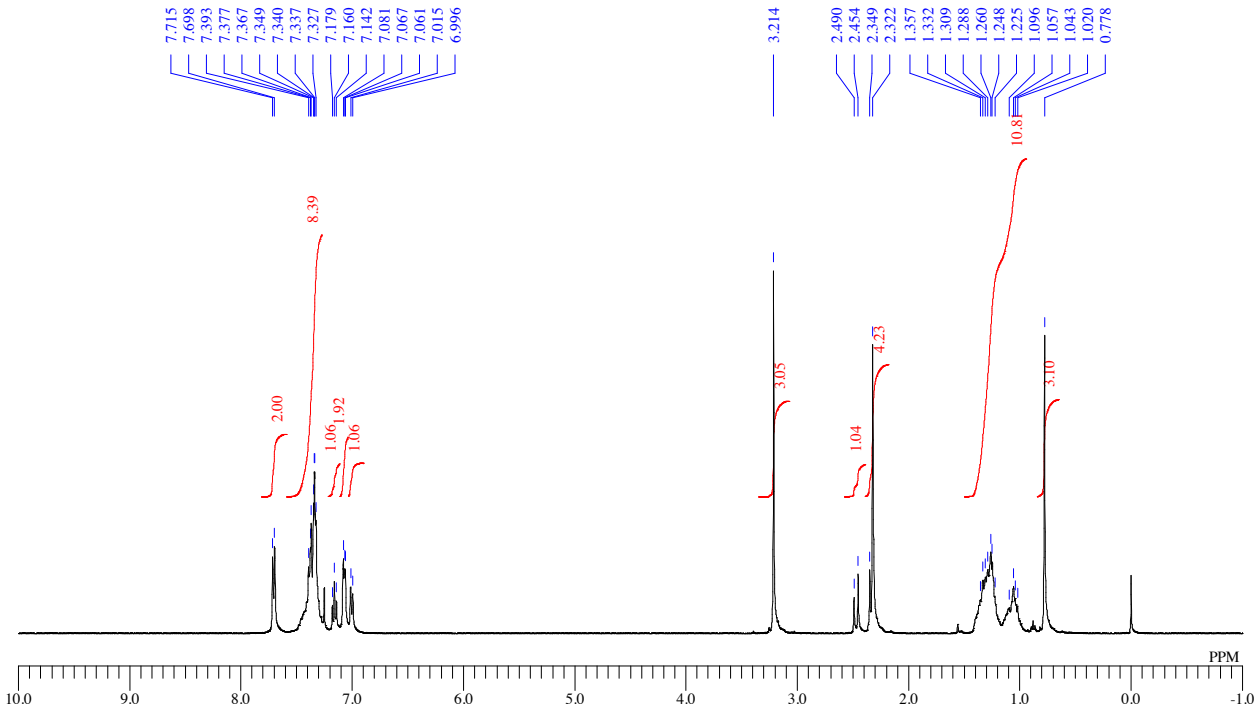
^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$)



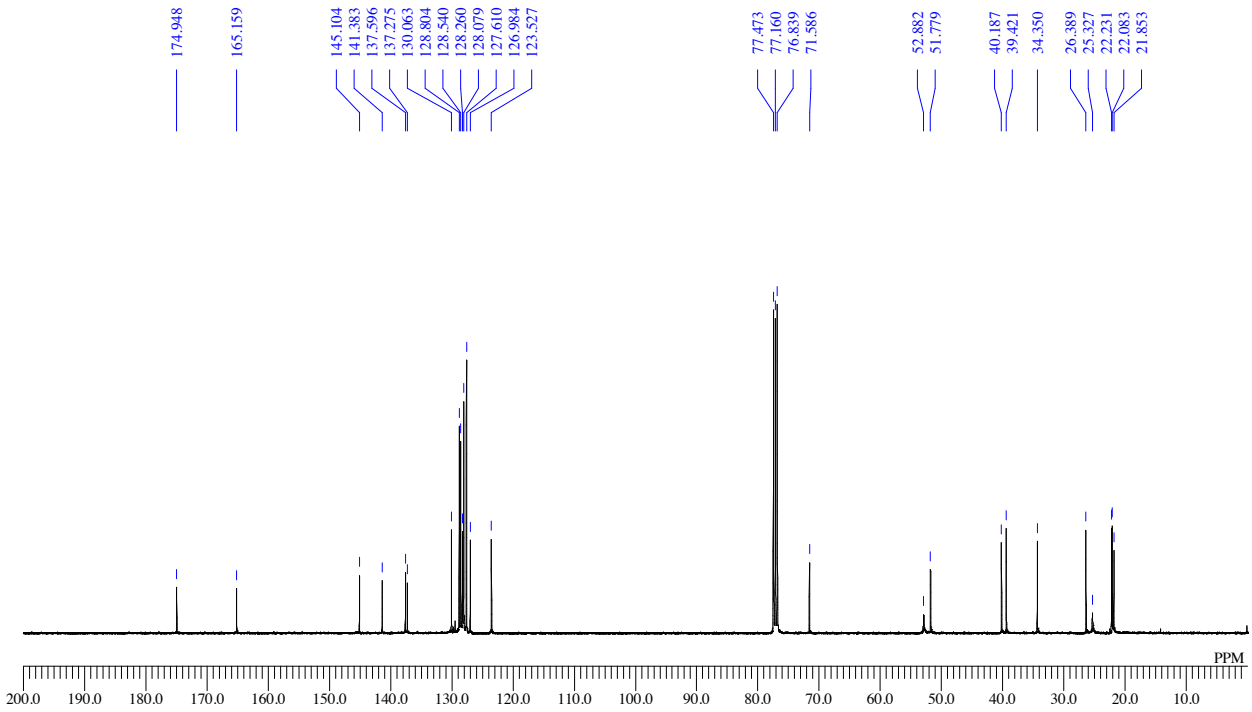


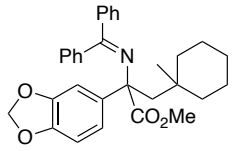
18

^{1}H NMR: (400 MHz, $CDCl_3$)



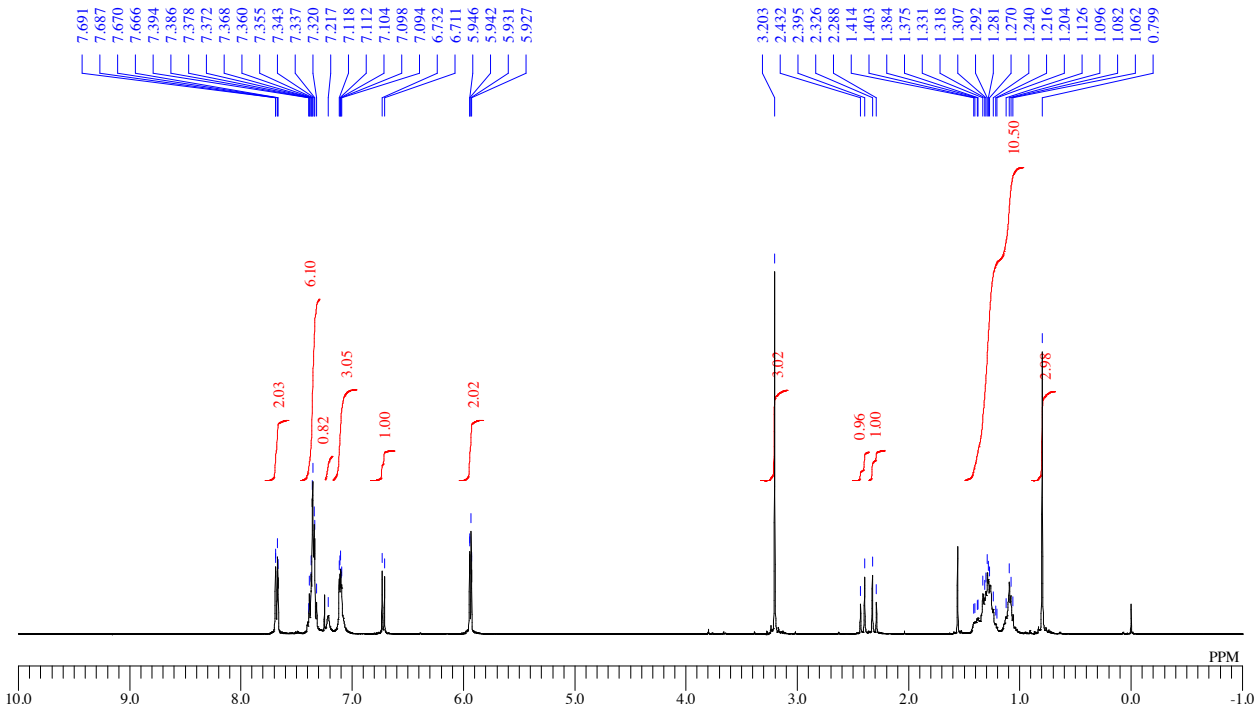
^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$)



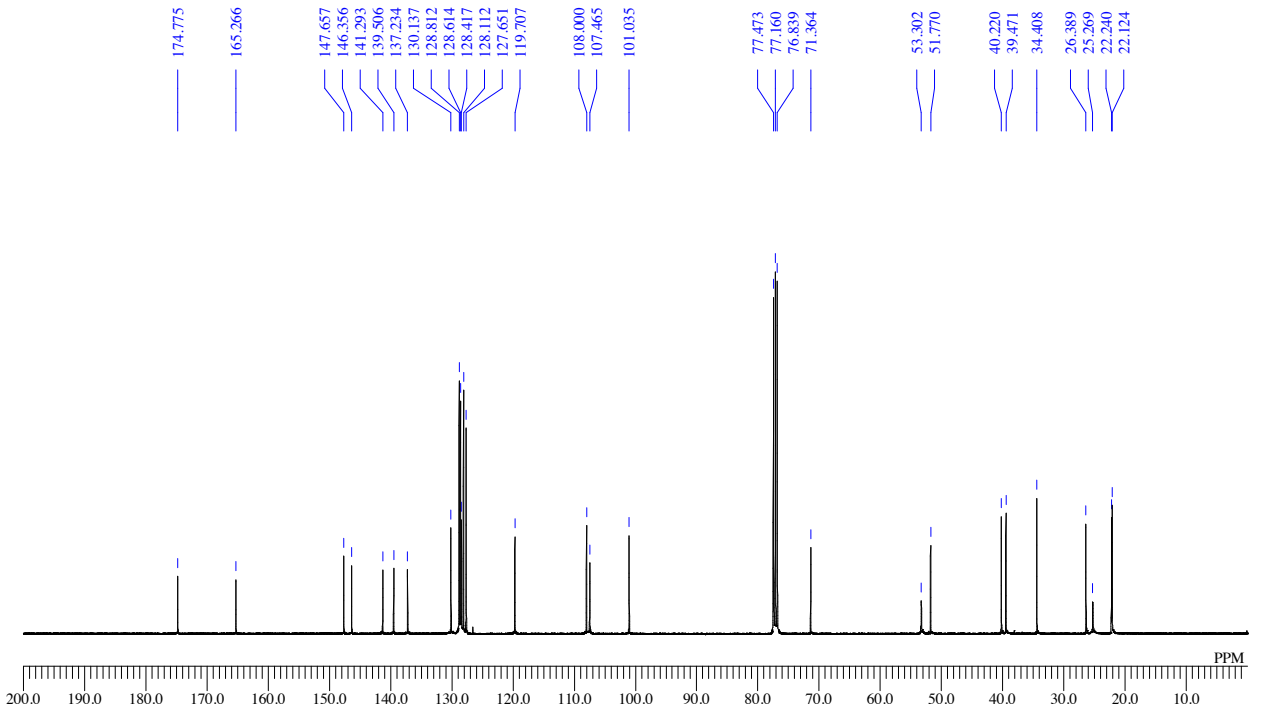


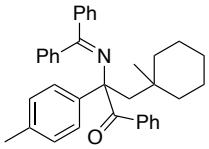
19

^{1}H NMR: (400 MHz, $CDCl_3$)



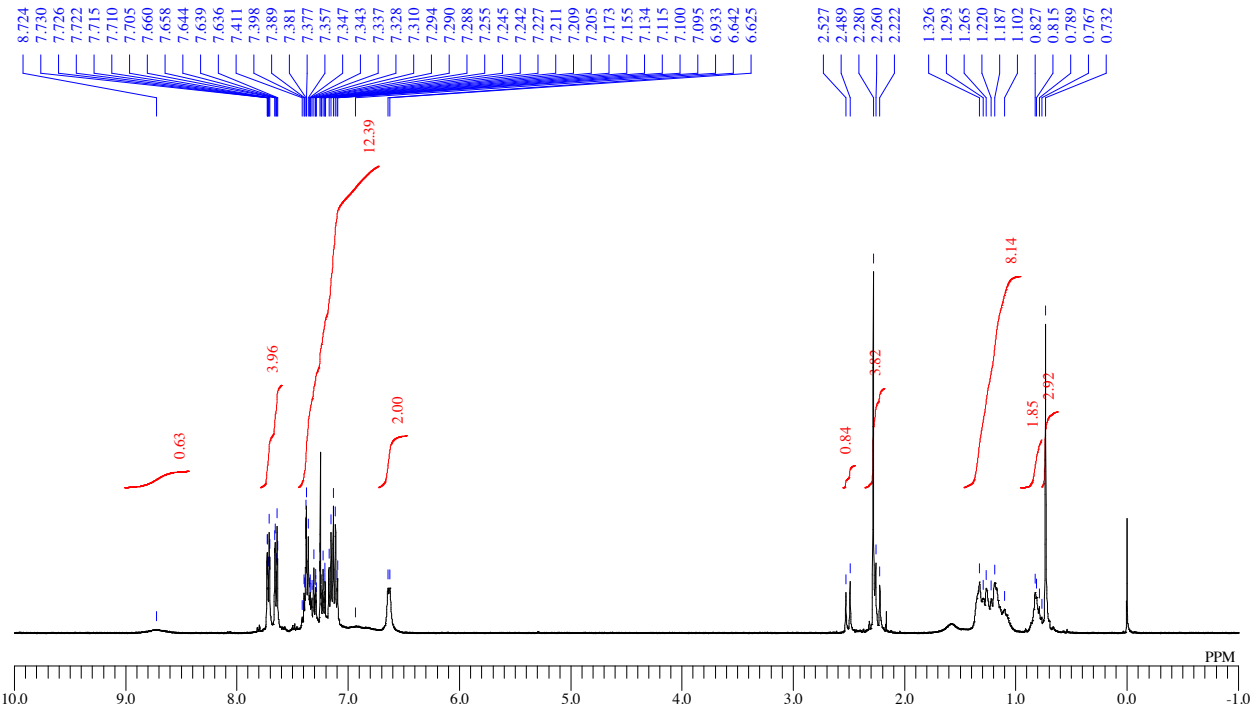
^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$)



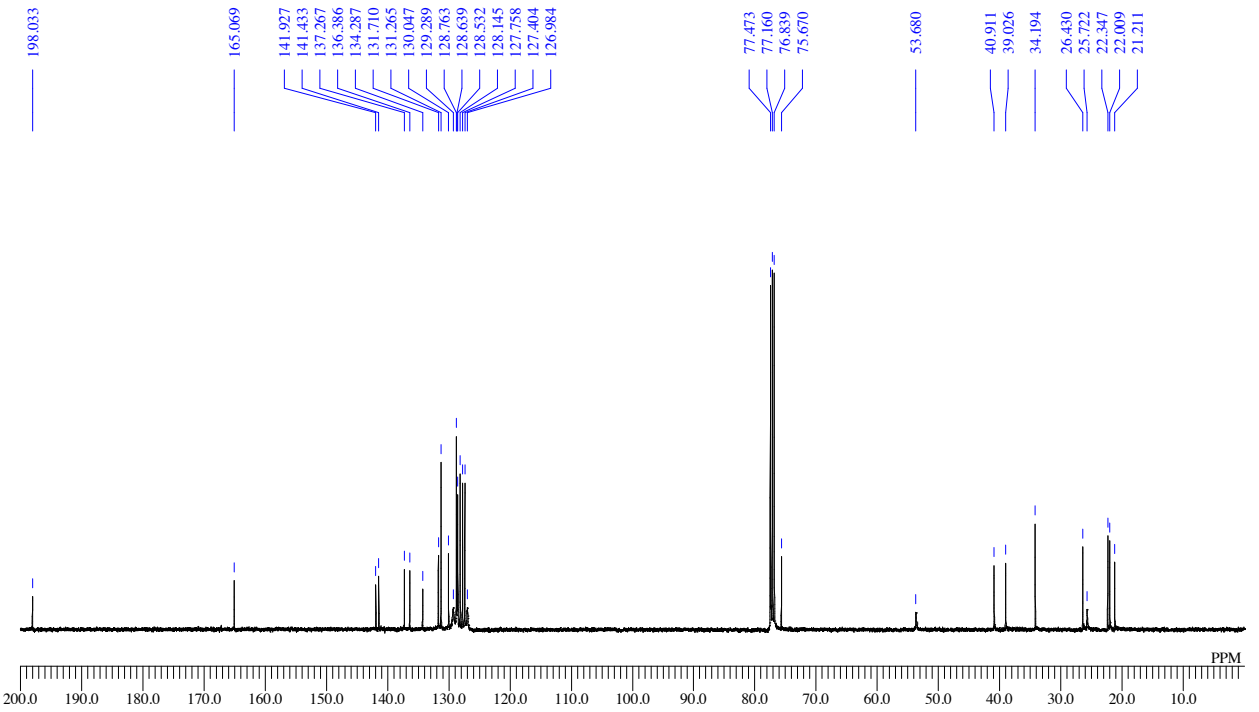


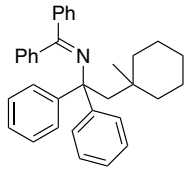
20

^{1}H NMR: (400 MHz, $CDCl_3$)



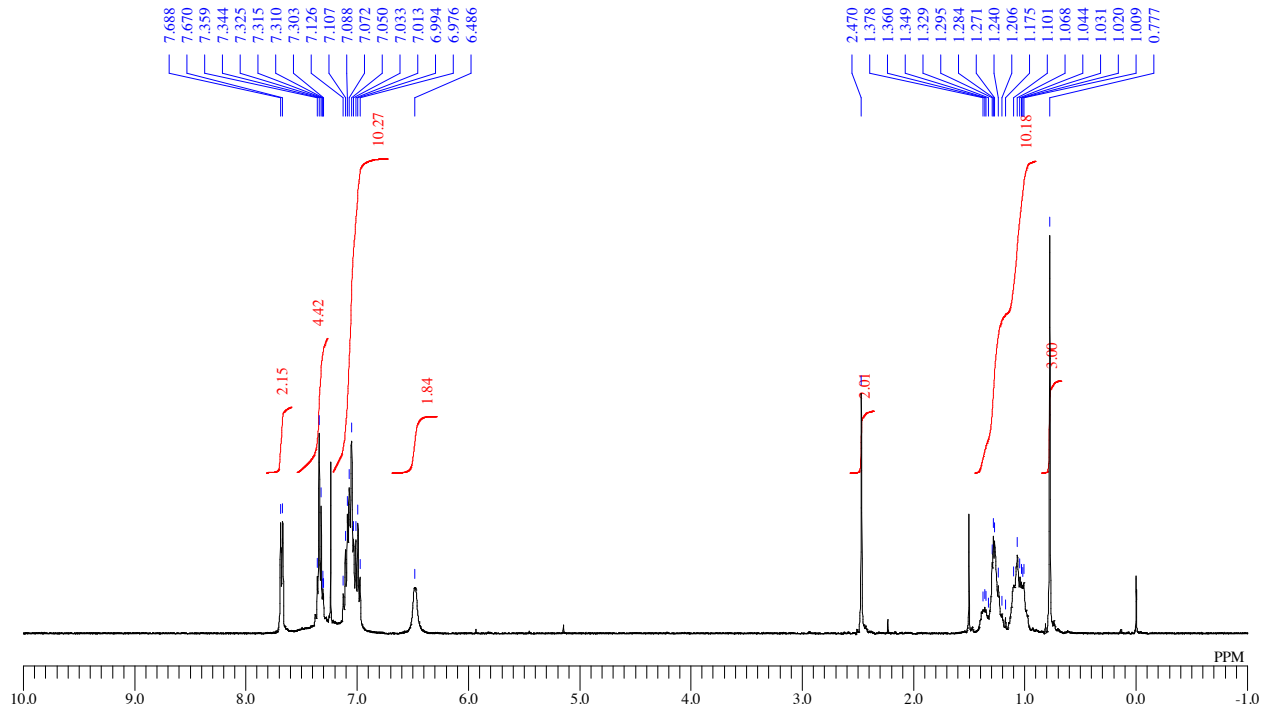
^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$)



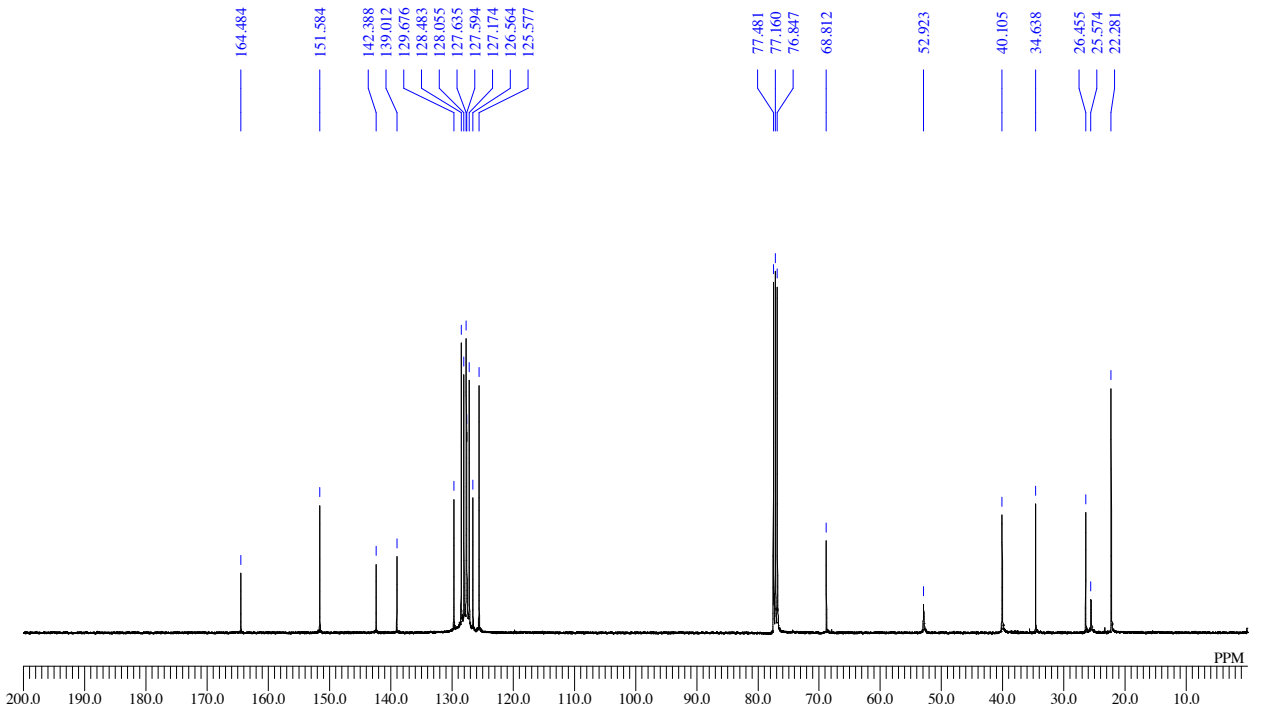


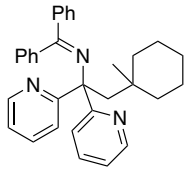
21

^{1}H NMR: (400 MHz, $CDCl_3$)



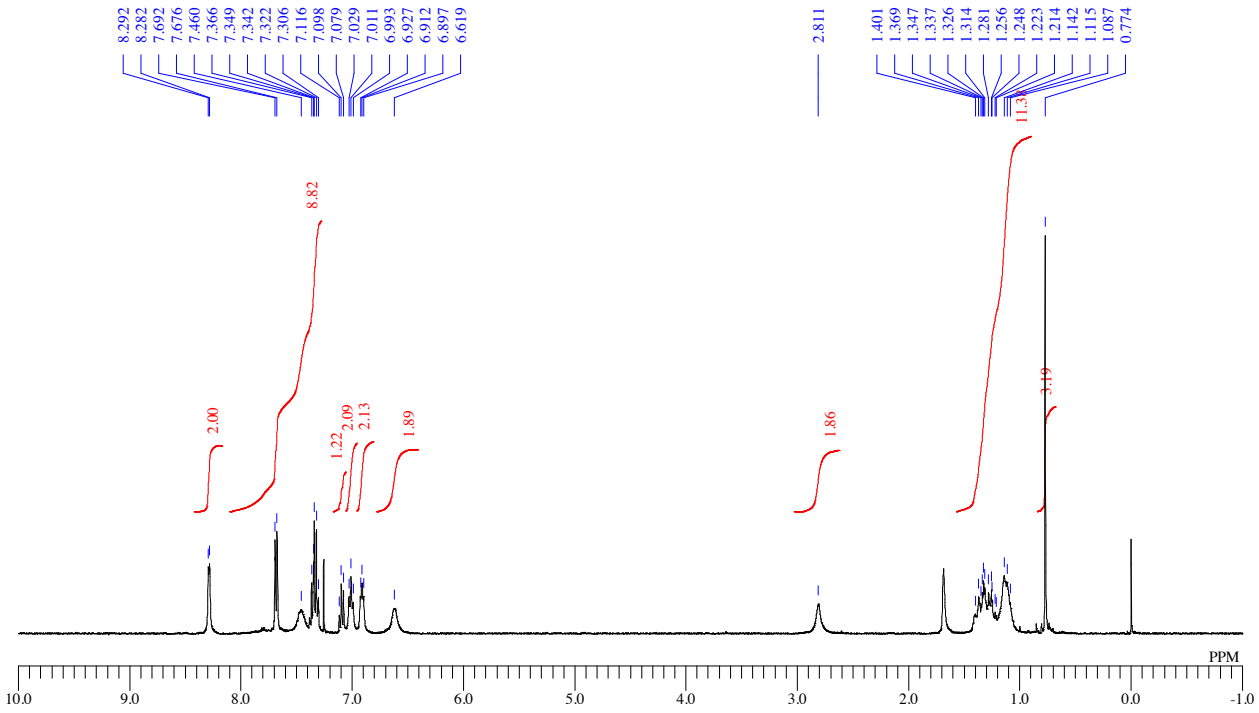
^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$)



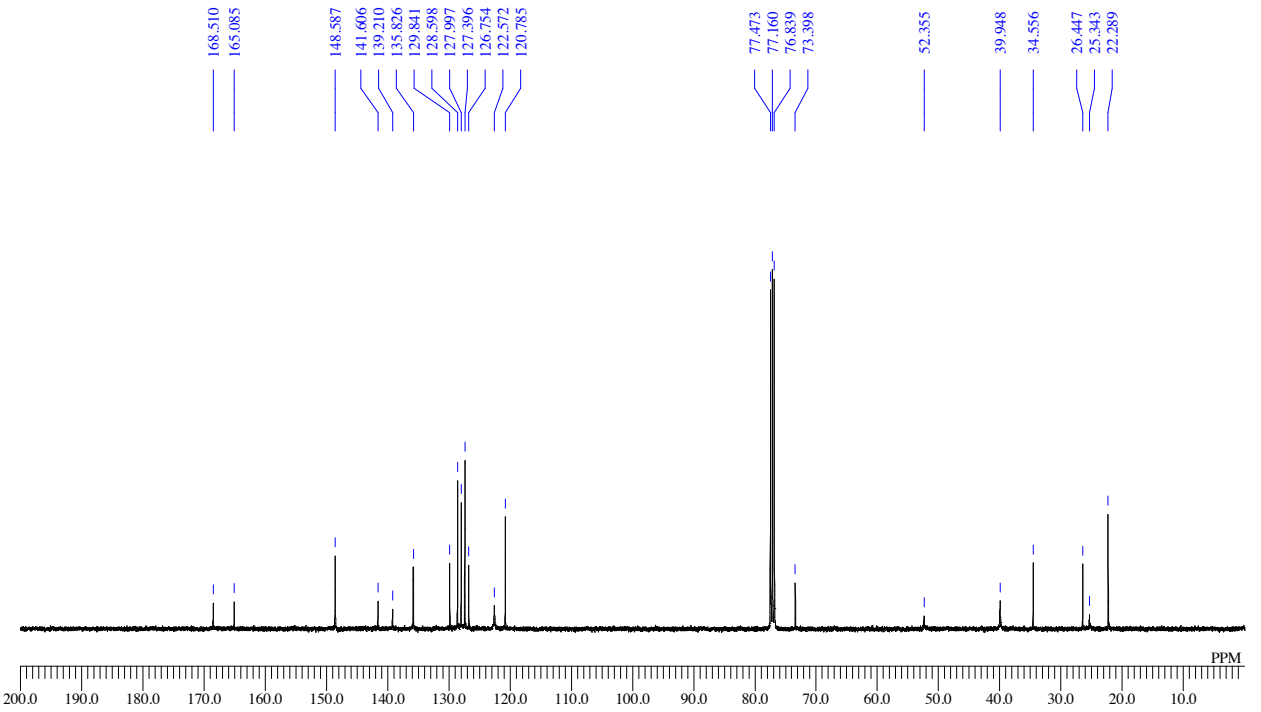


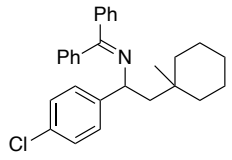
22

^{1}H NMR: (400 MHz, $CDCl_3$)



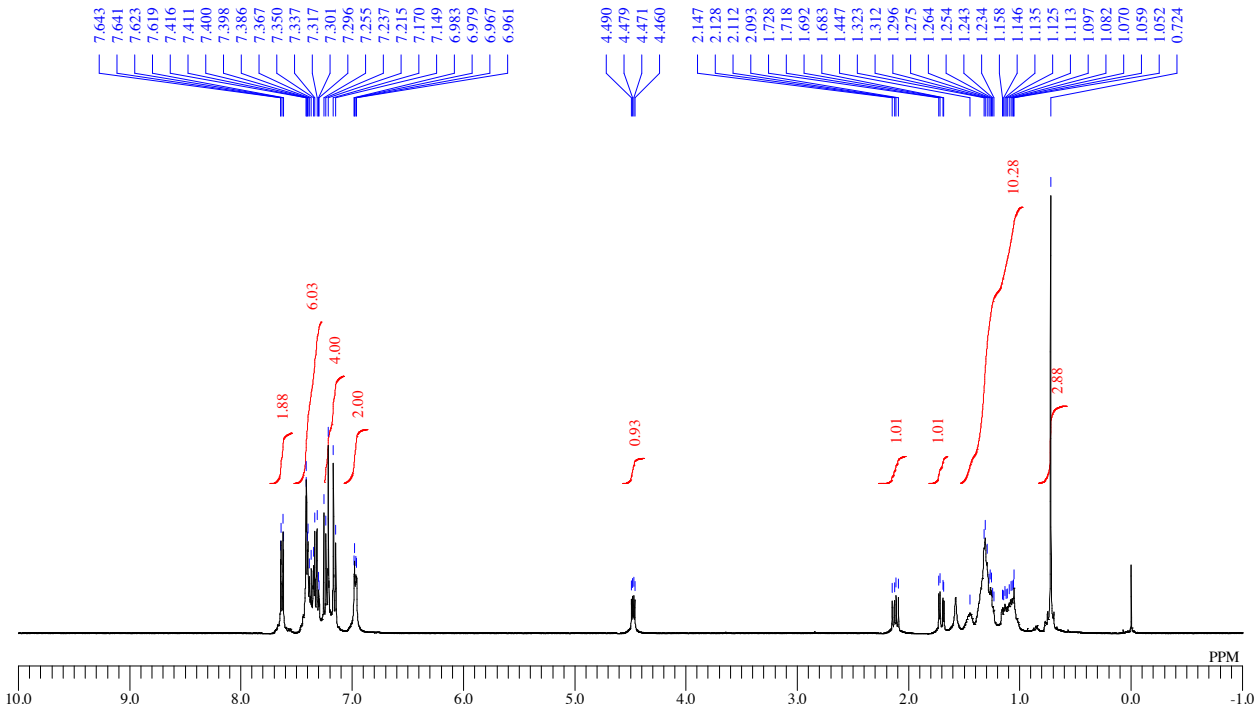
^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$)



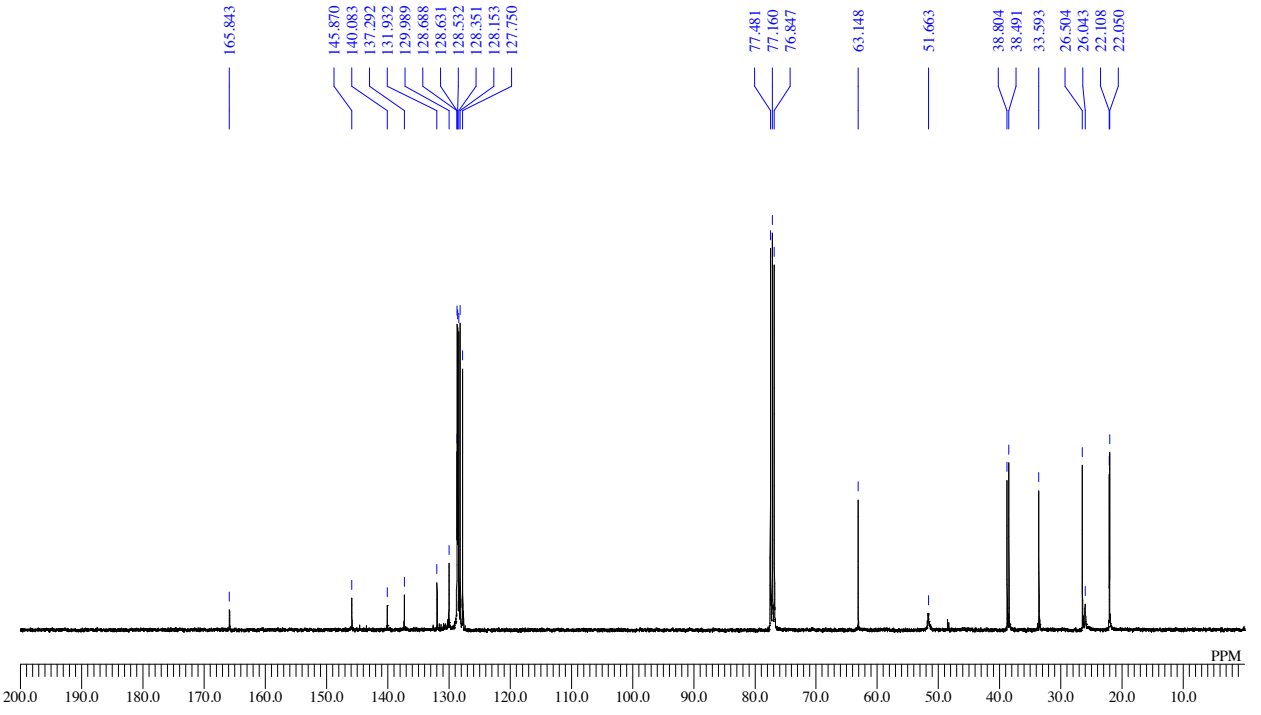


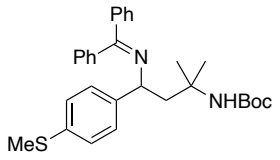
23

^{1}H NMR: (400 MHz, $CDCl_3$)



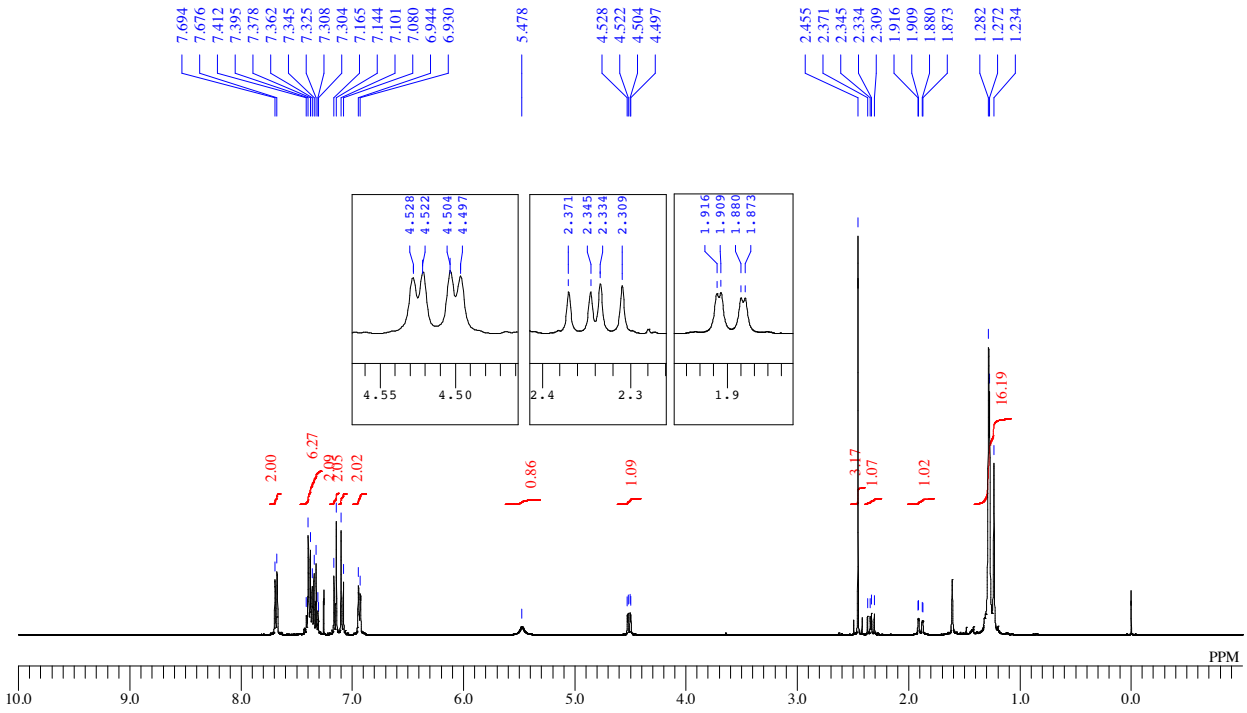
^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$)



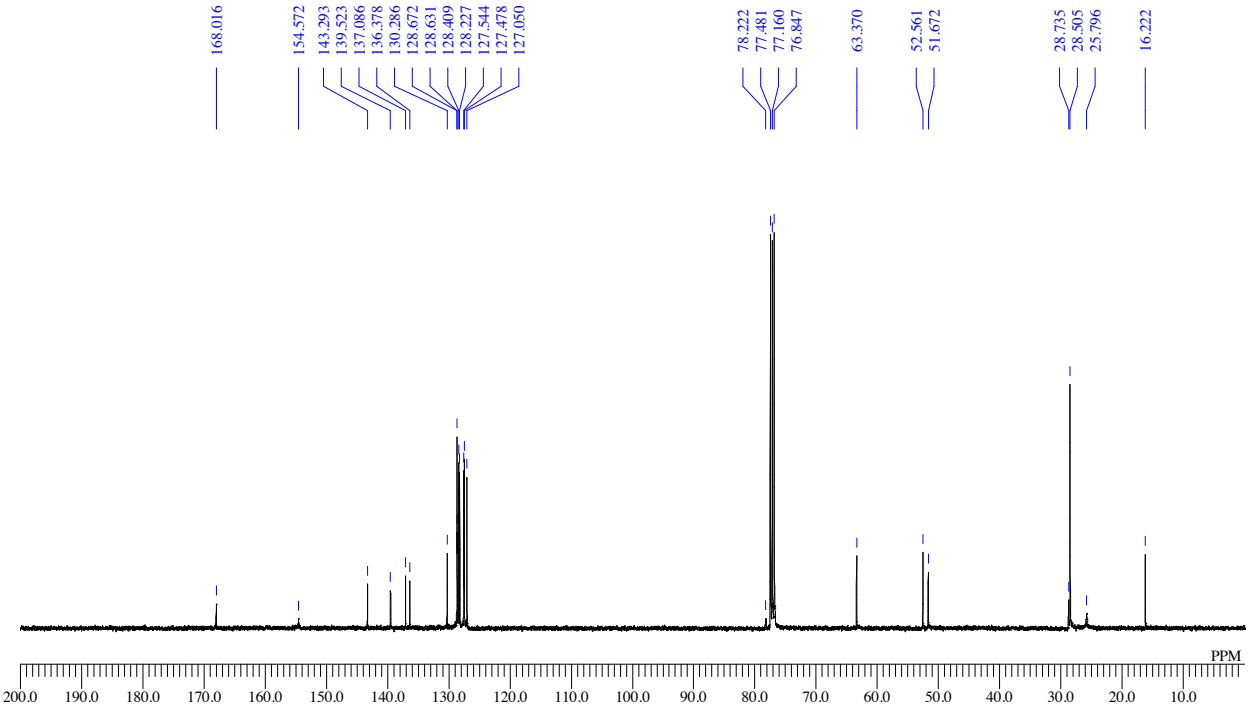


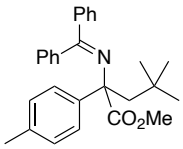
24

^{1}H NMR: (400 MHz, $CDCl_3$)



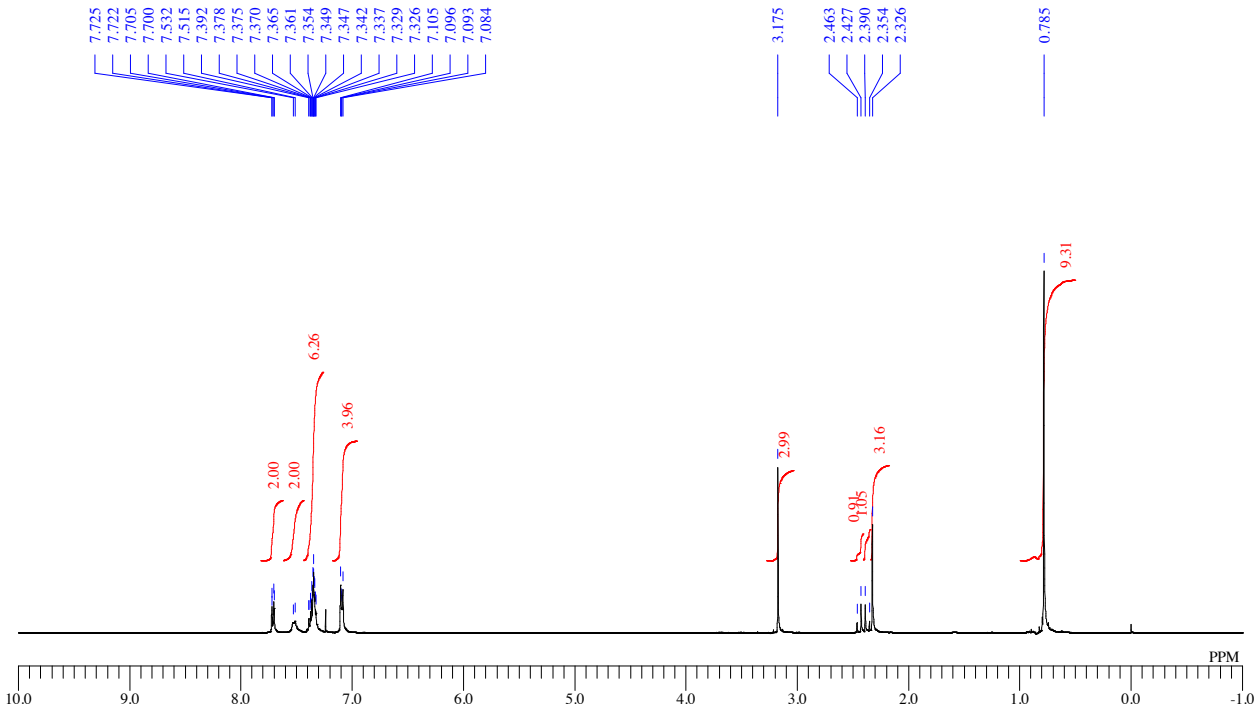
^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$)



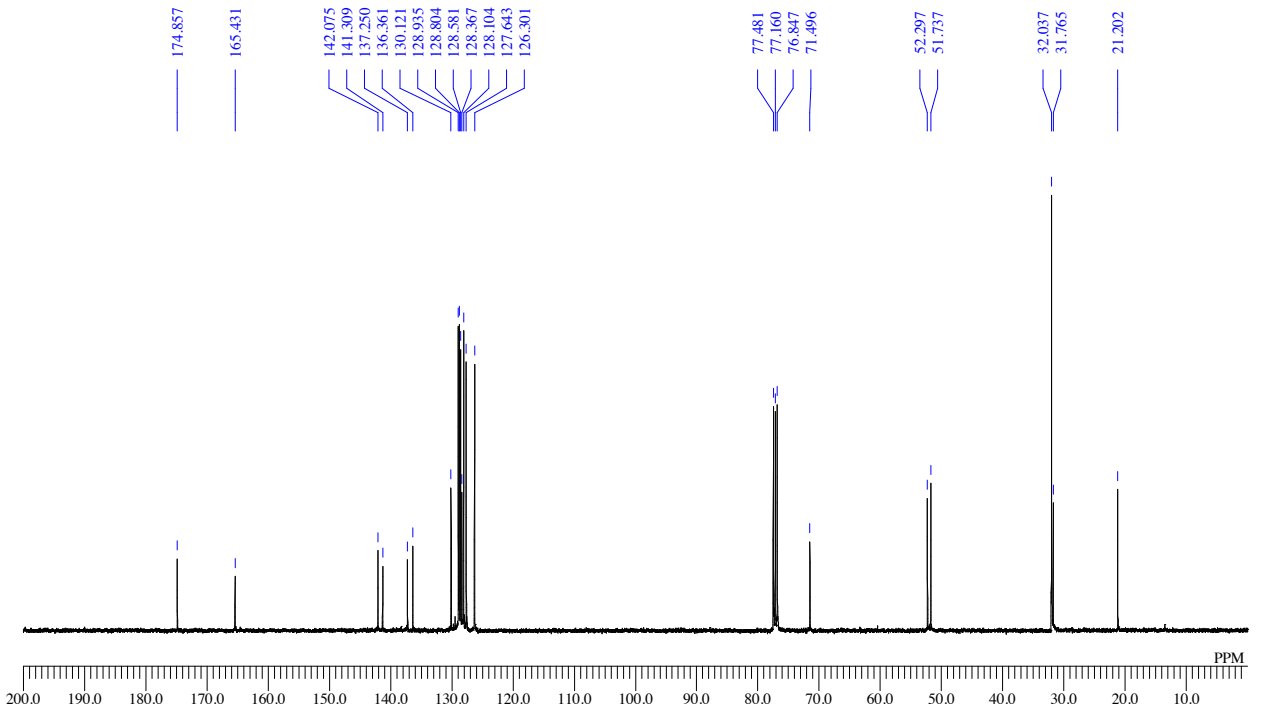


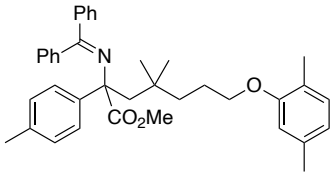
25

^{1}H NMR: (400 MHz, $CDCl_3$)



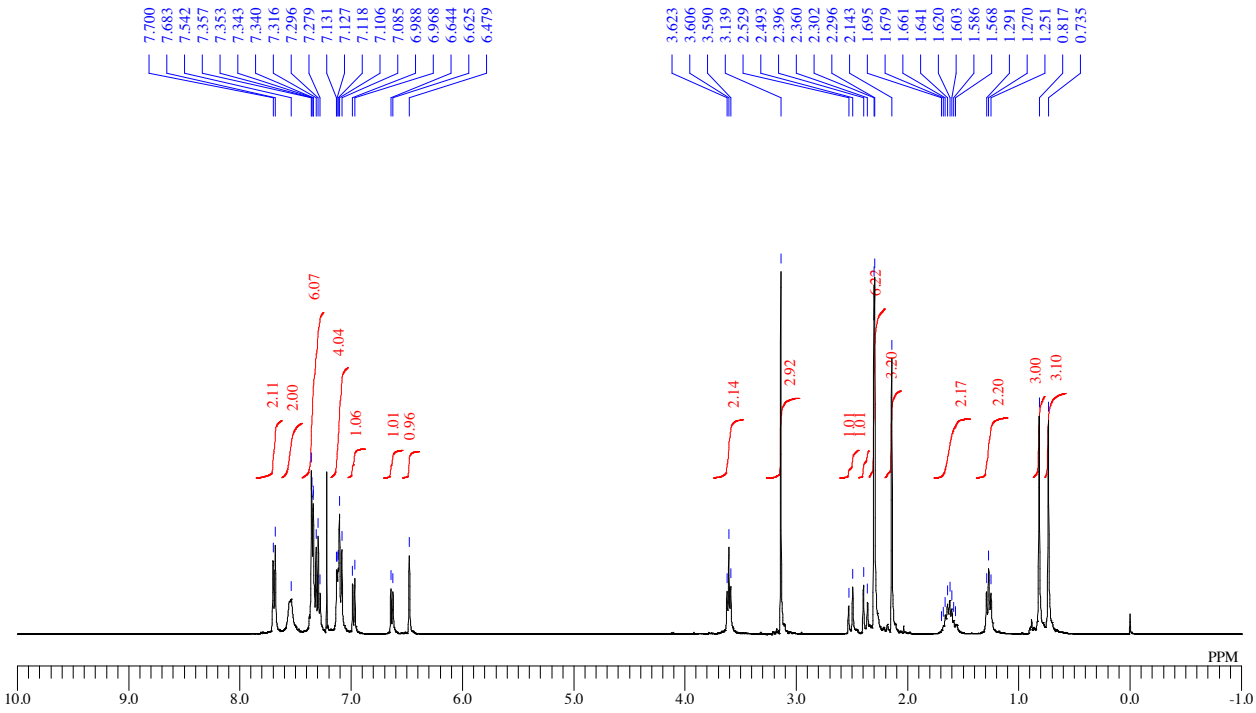
^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$)



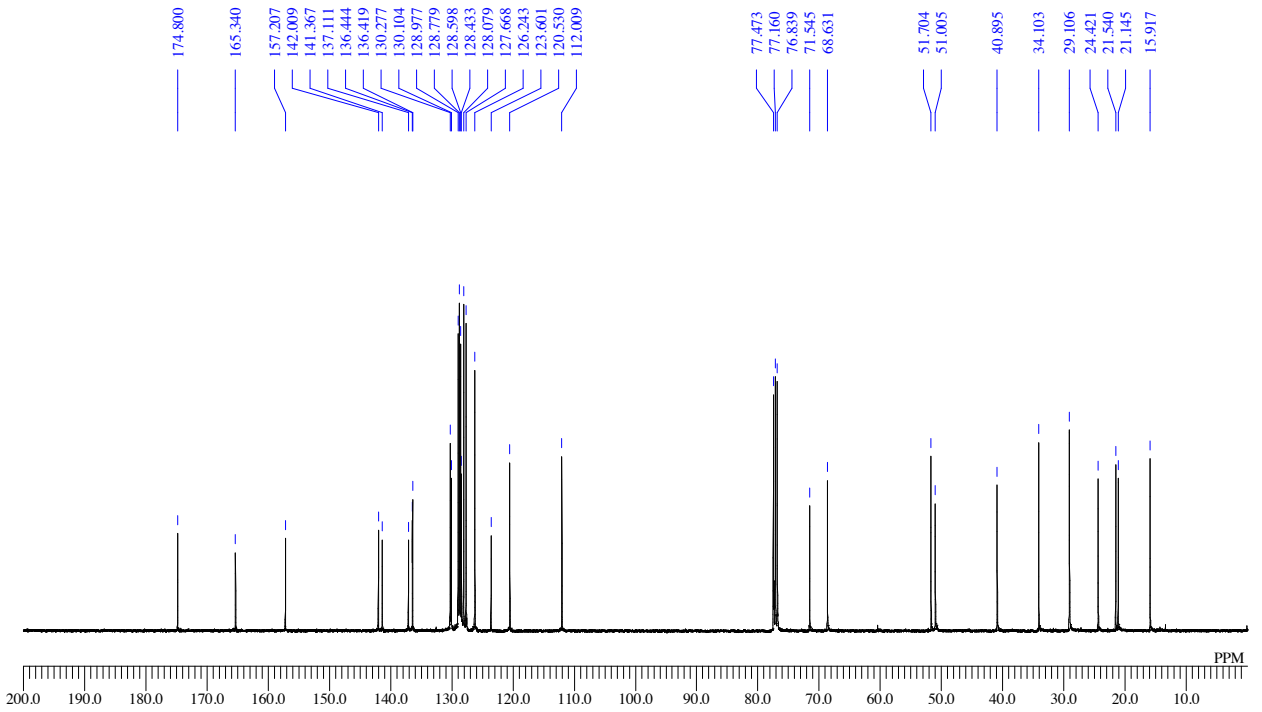


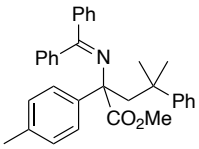
26

^{1}H NMR: (400 MHz, $CDCl_3$)



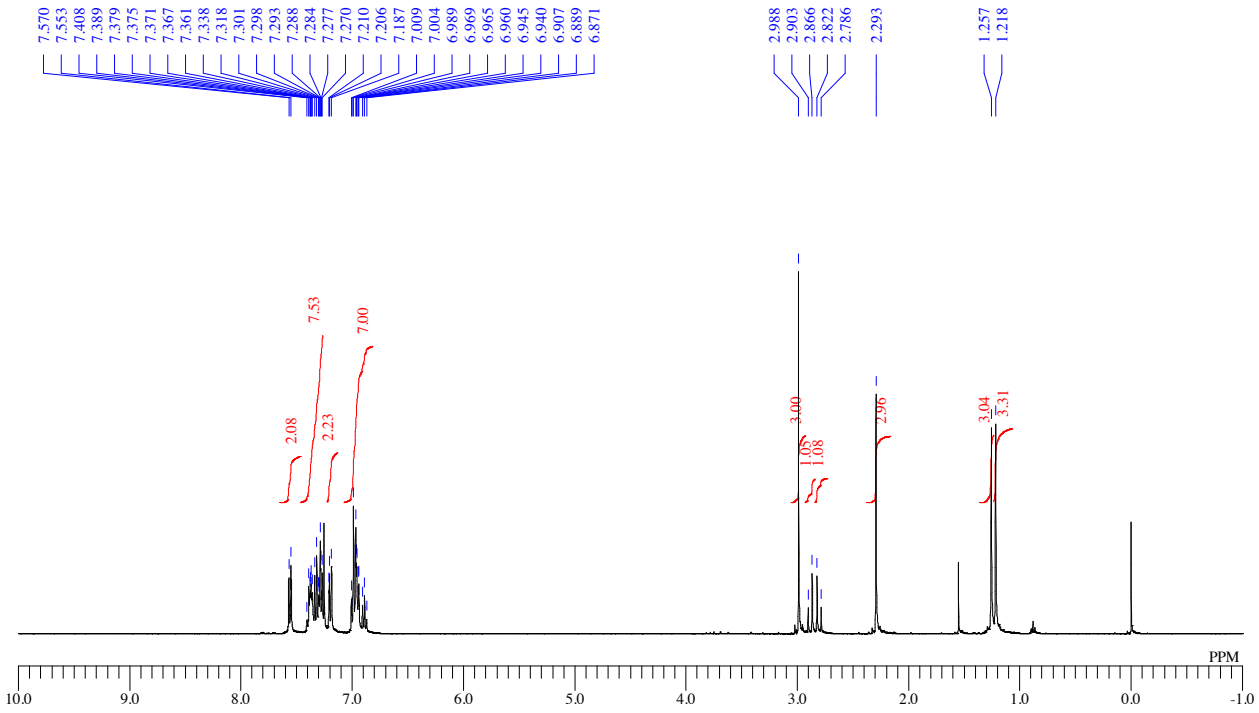
^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$)



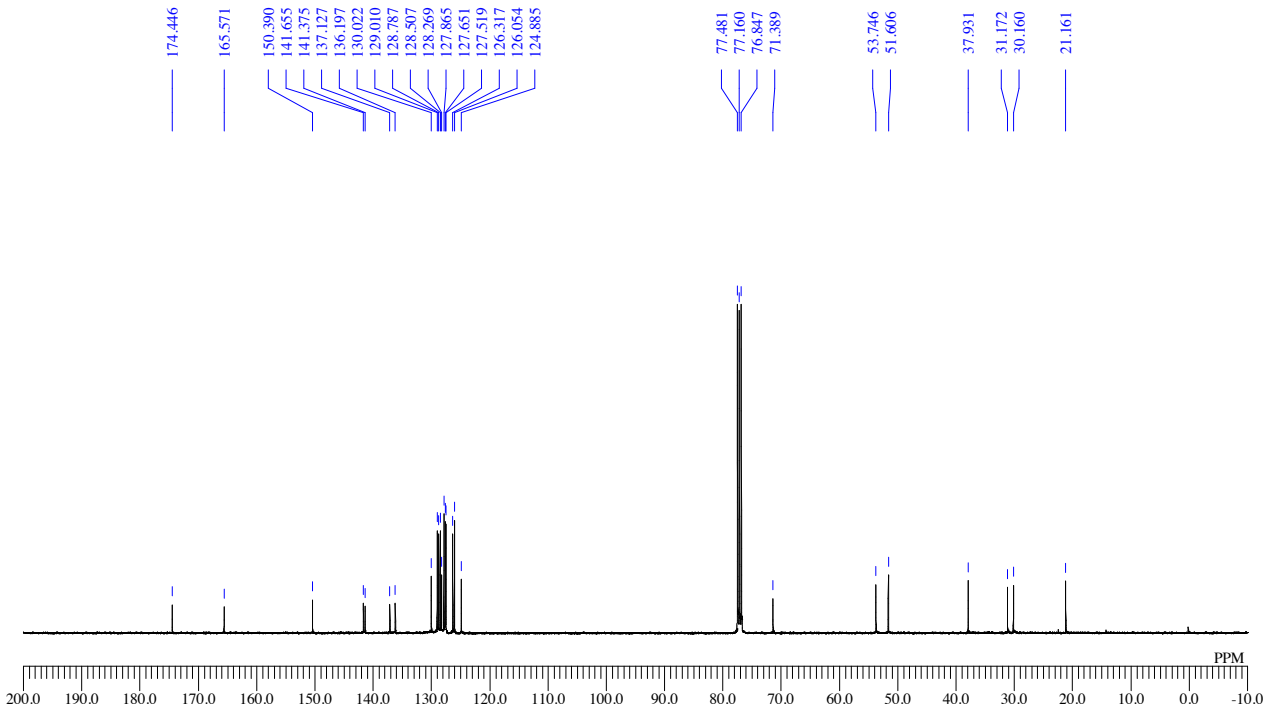


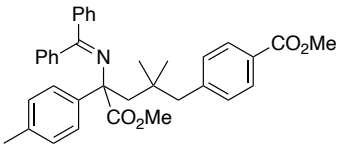
27

^{1}H NMR: (400 MHz, $CDCl_3$)



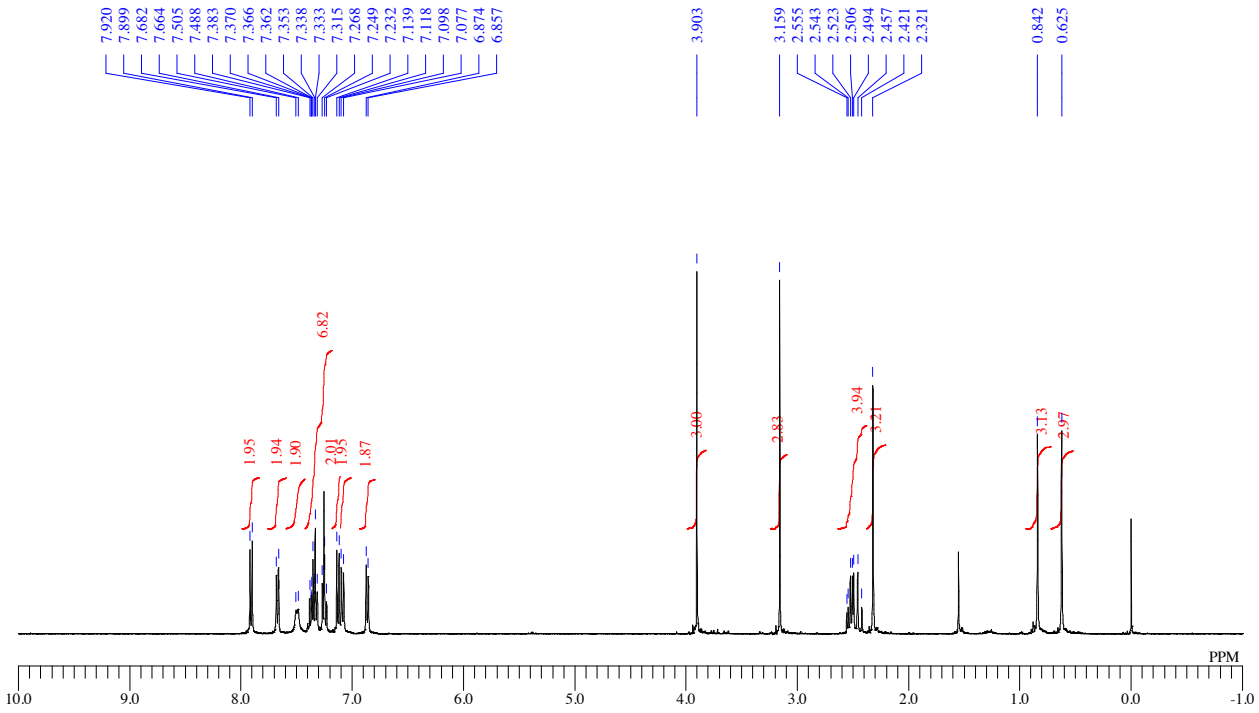
^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$)



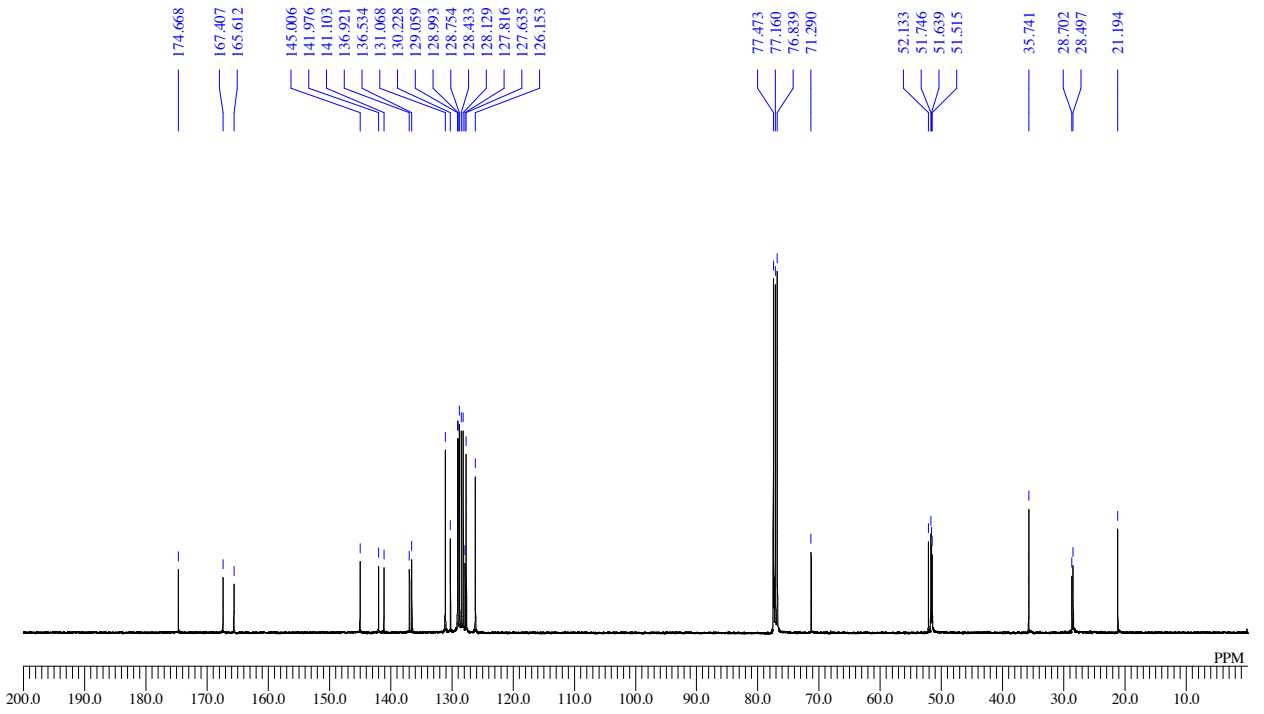


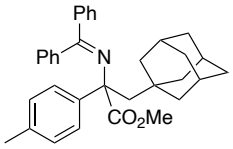
28

^{1}H NMR: (400 MHz, $CDCl_3$)



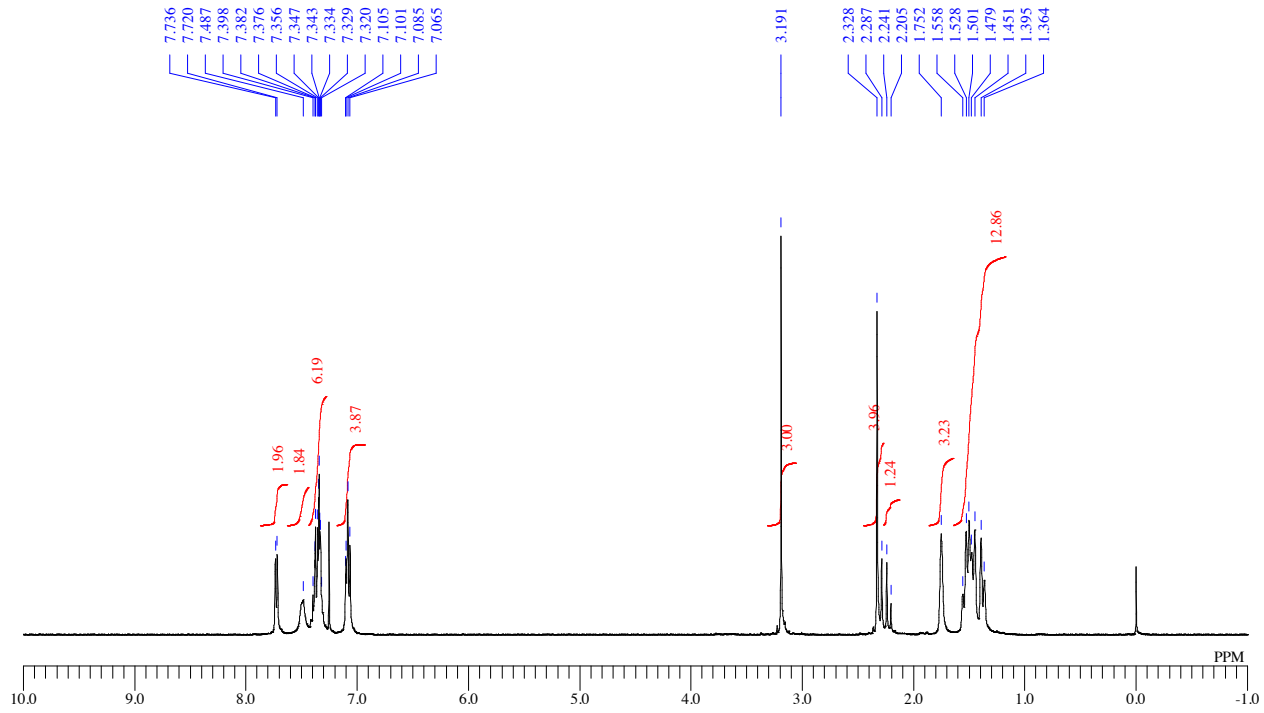
^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$)



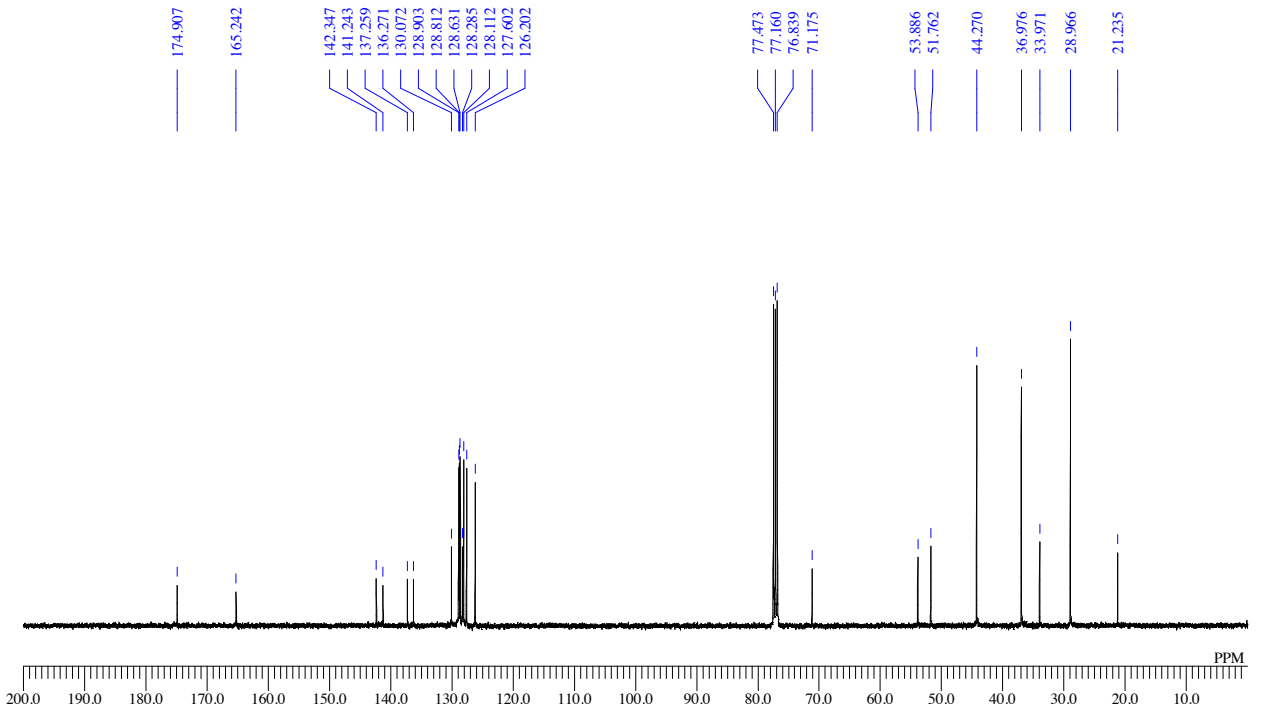


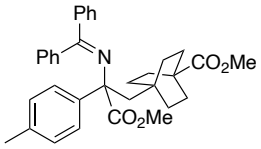
29

^{1}H NMR: (400 MHz, $CDCl_3$)



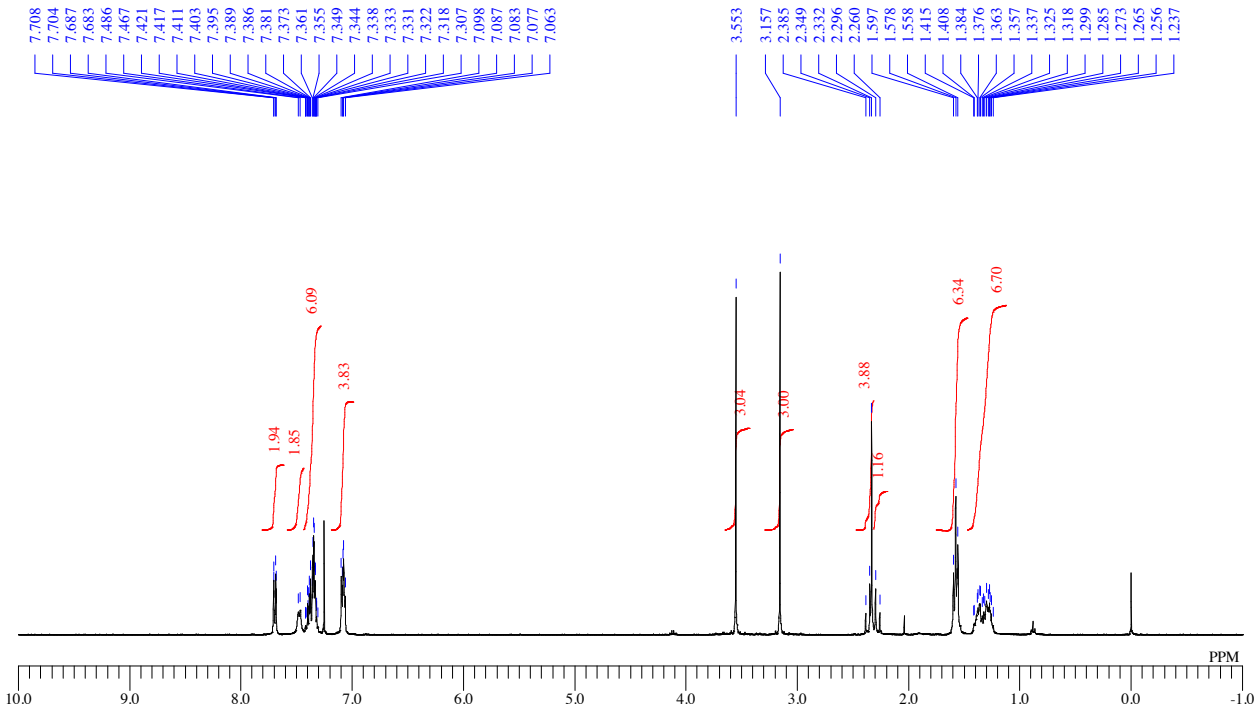
^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$)



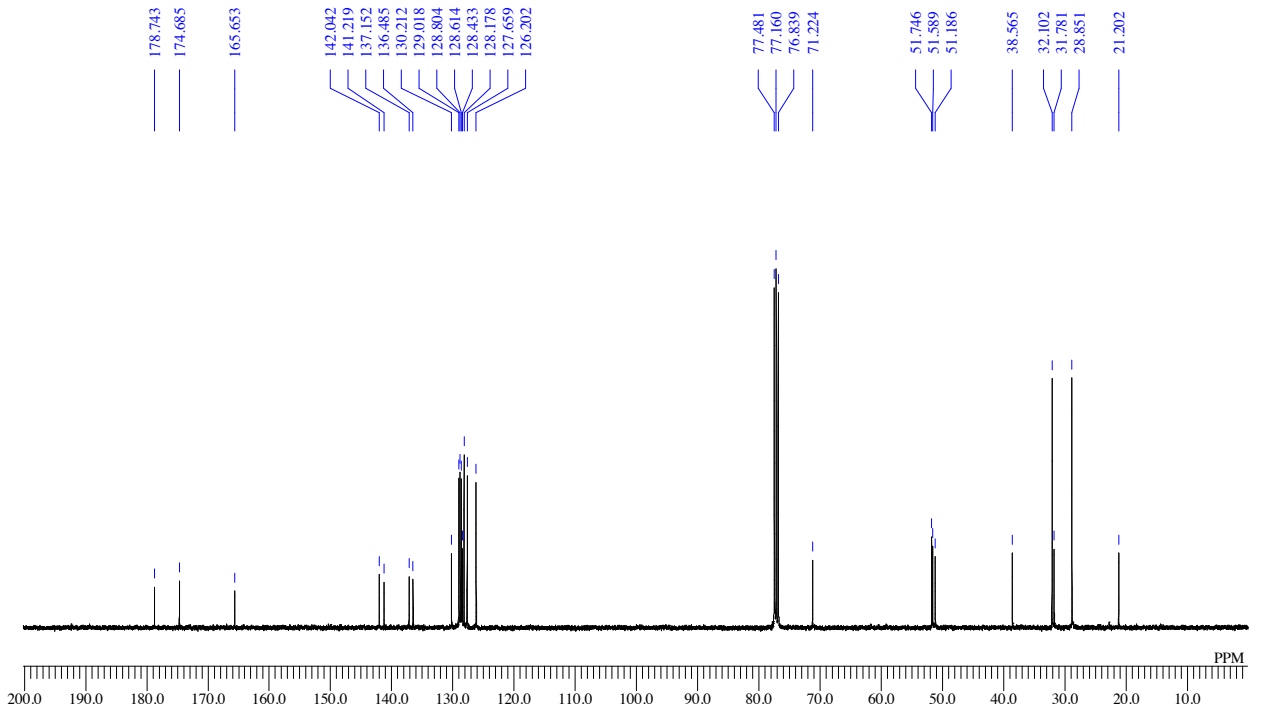


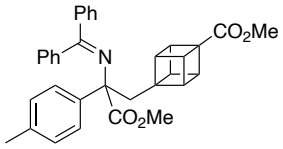
30

^{1}H NMR: (400 MHz, $CDCl_3$)



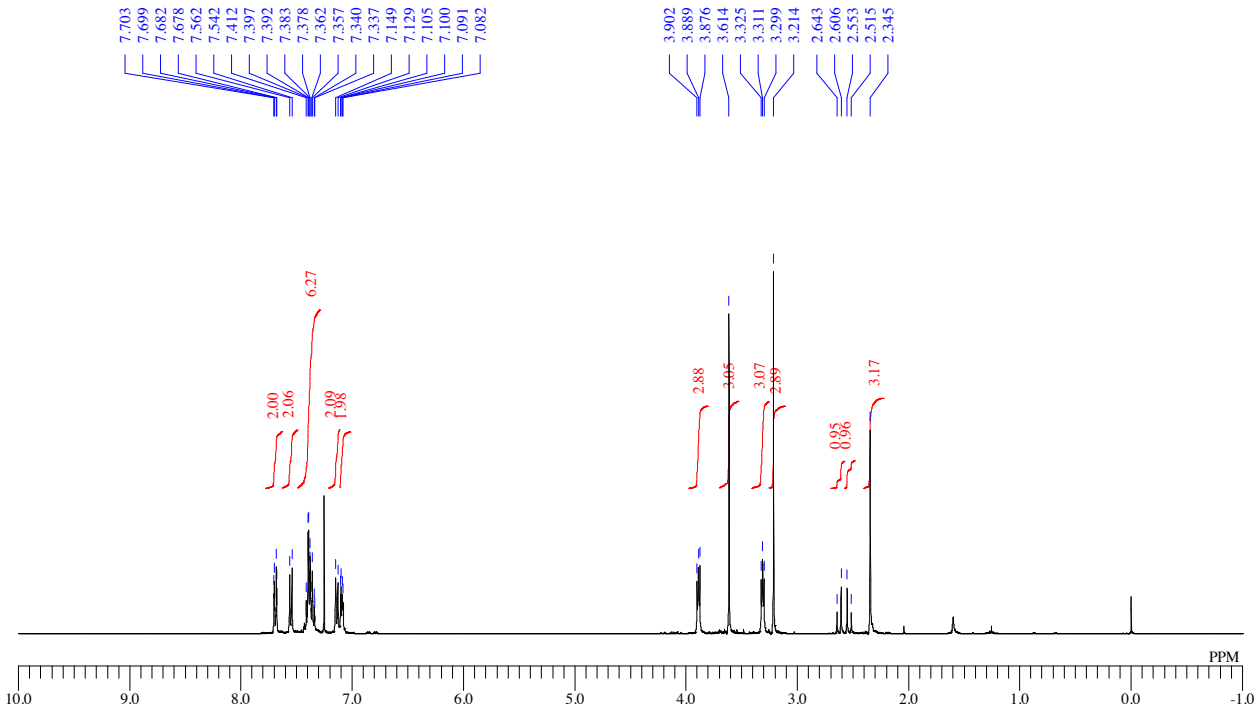
^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$)



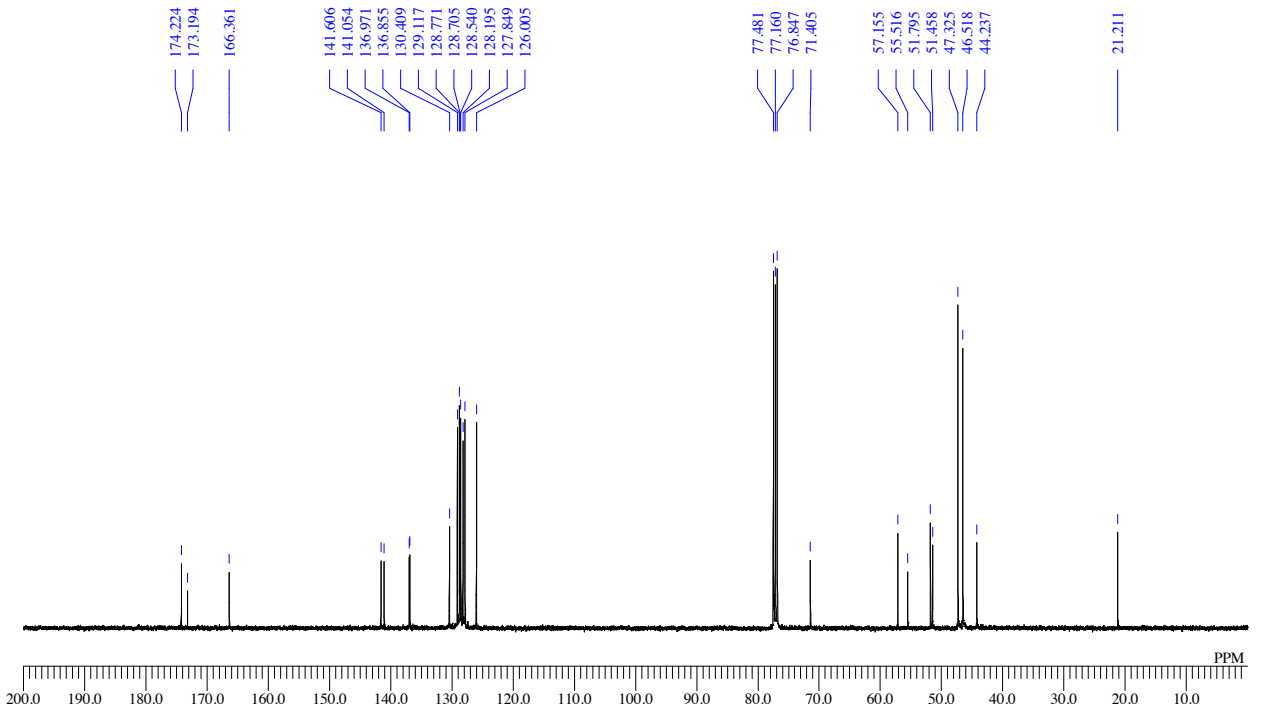


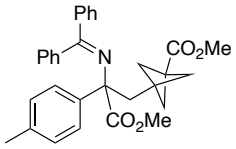
31

^{1}H NMR: (400 MHz, $CDCl_3$)



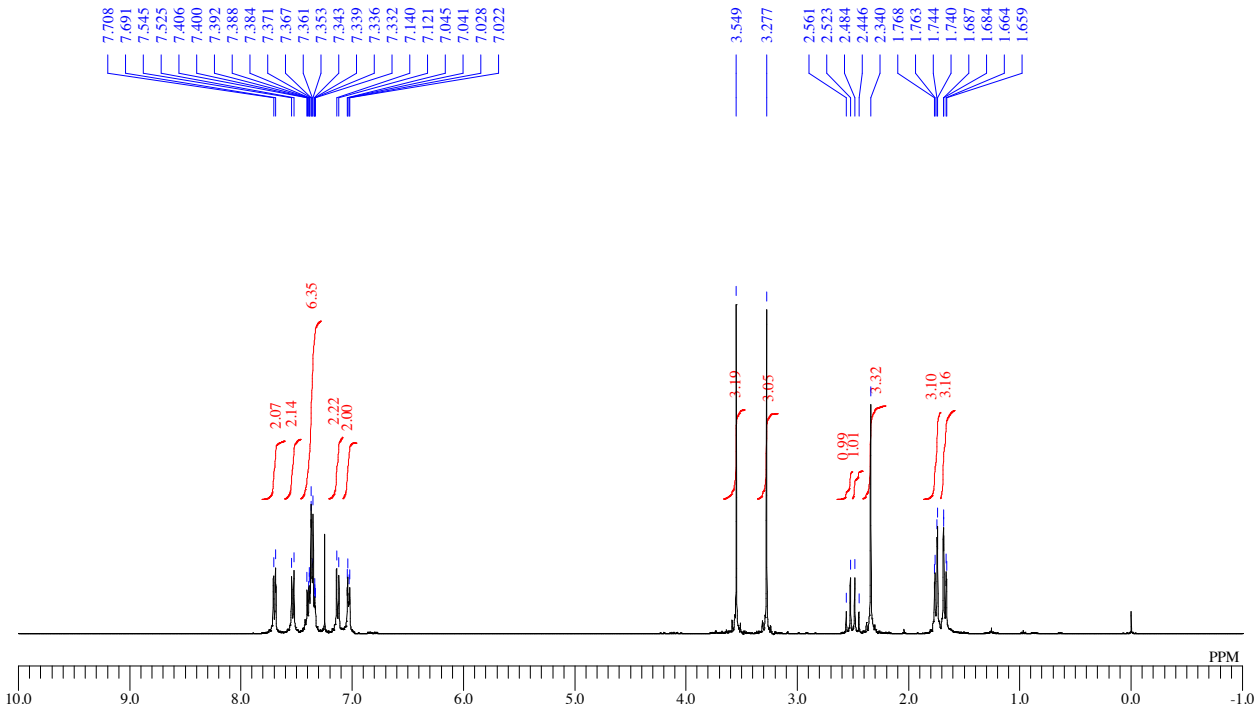
^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$)



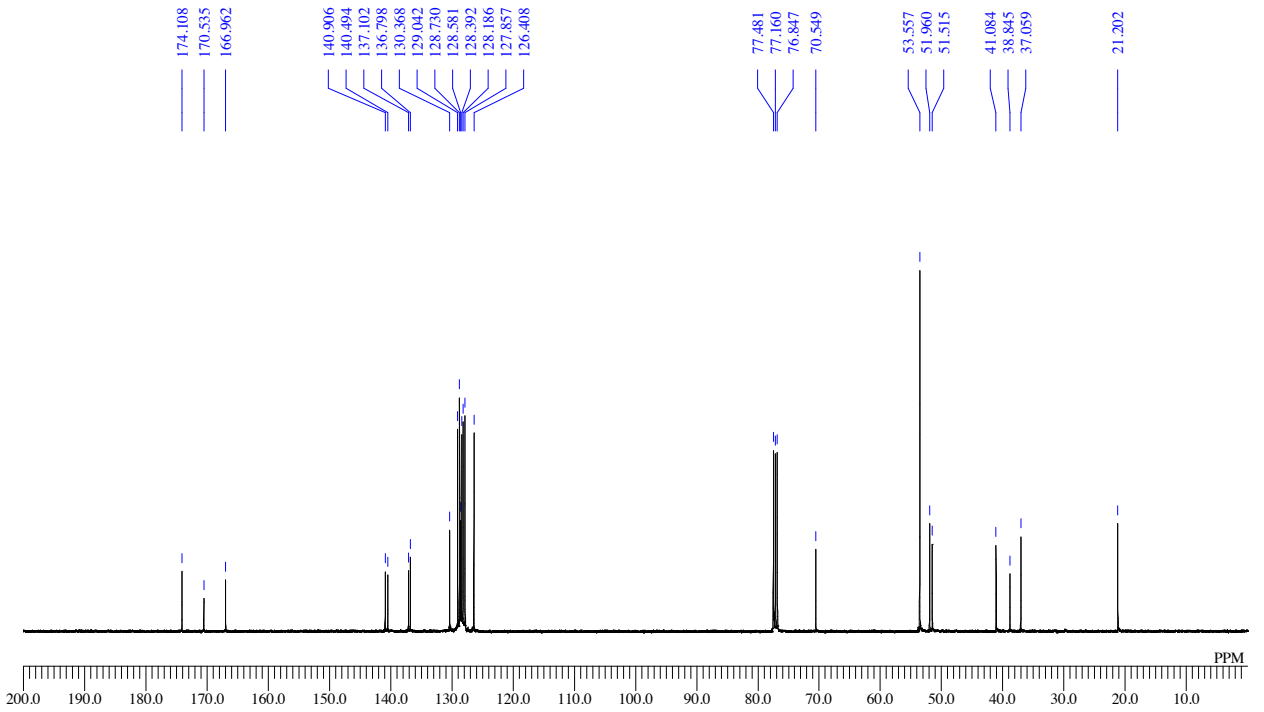


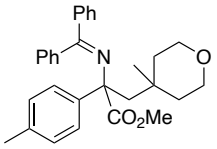
32

^{1}H NMR: (400 MHz, $CDCl_3$)



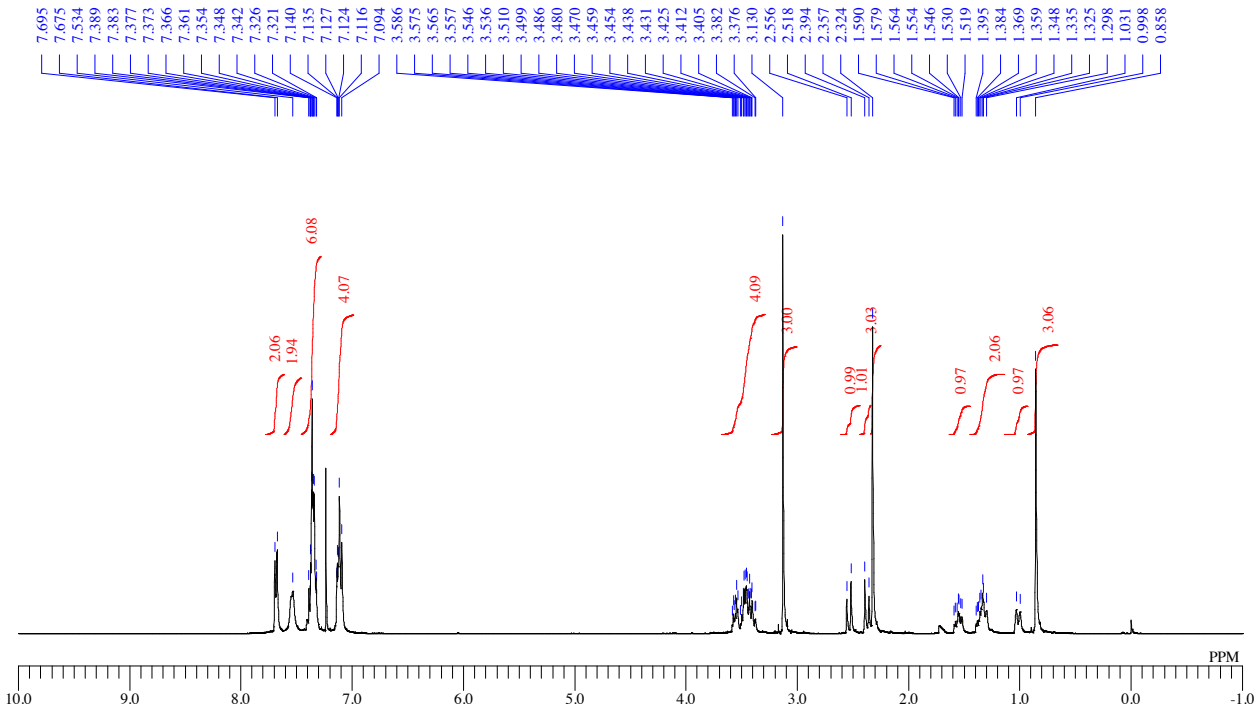
^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$)



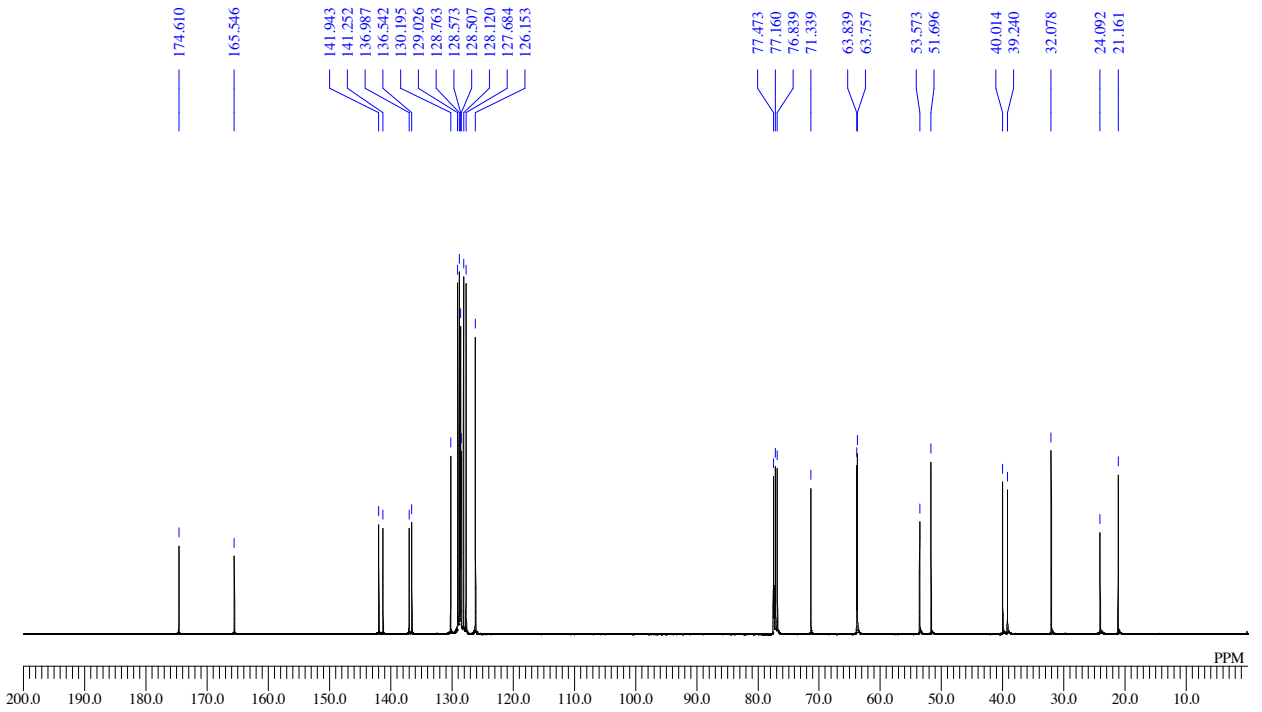


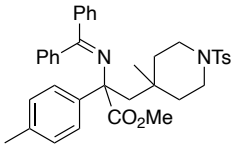
33

^{1}H NMR: (400 MHz, $CDCl_3$)



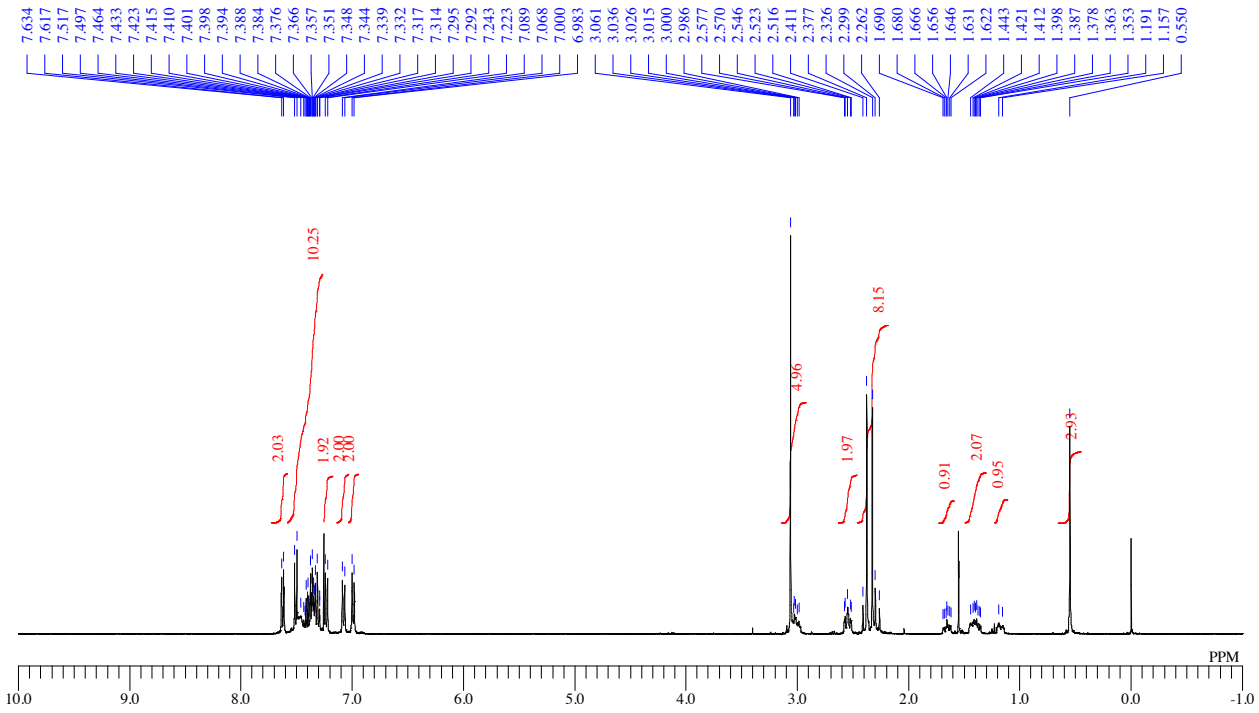
^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$)



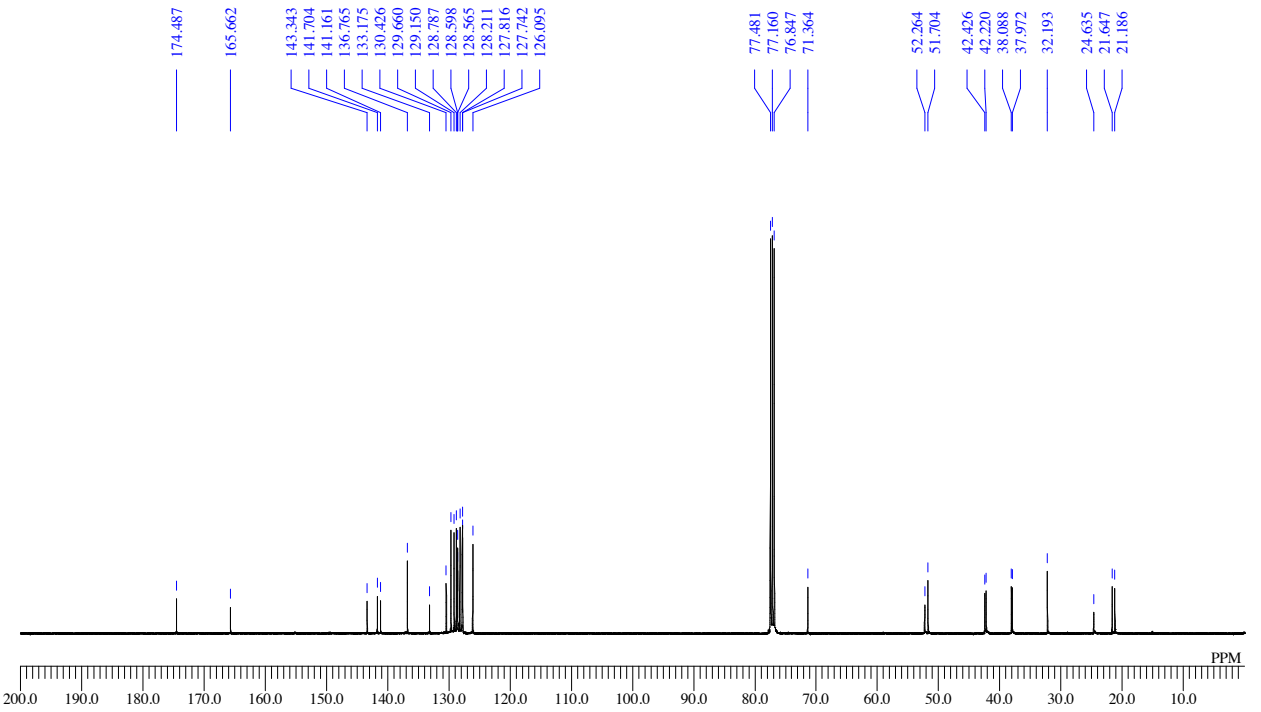


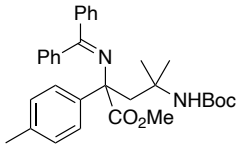
34

^{1}H NMR: (400 MHz, $CDCl_3$)



^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$)





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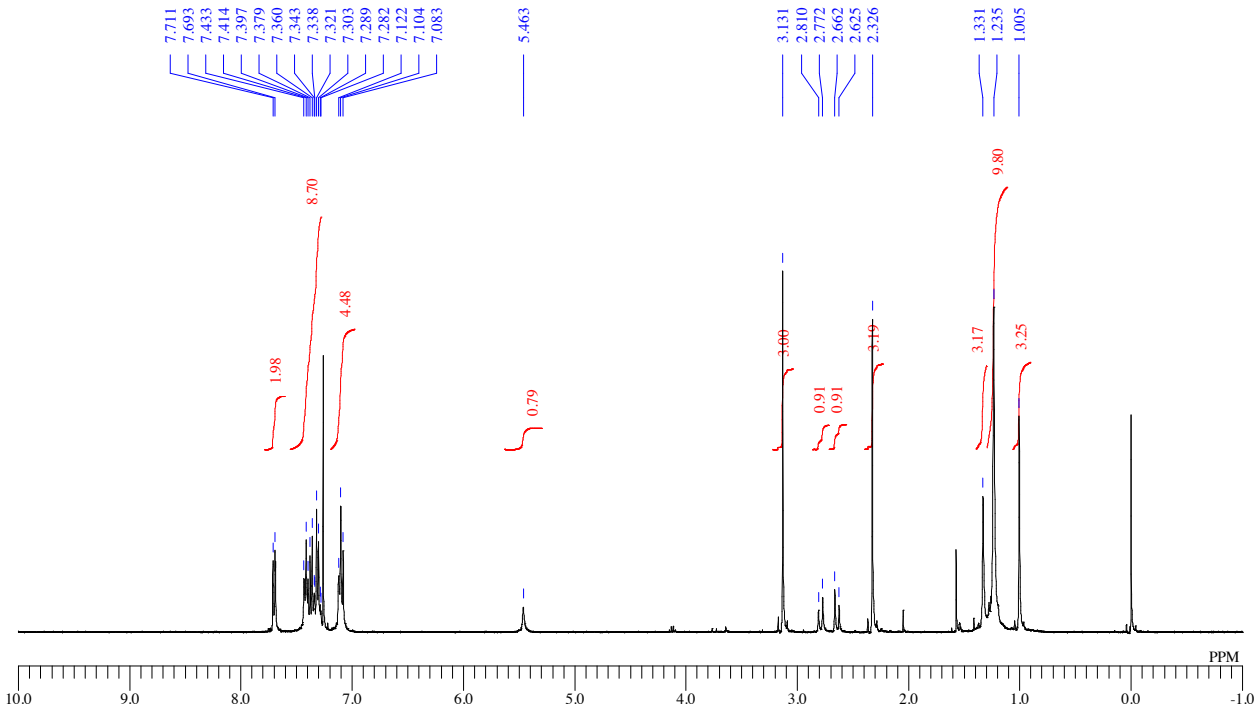
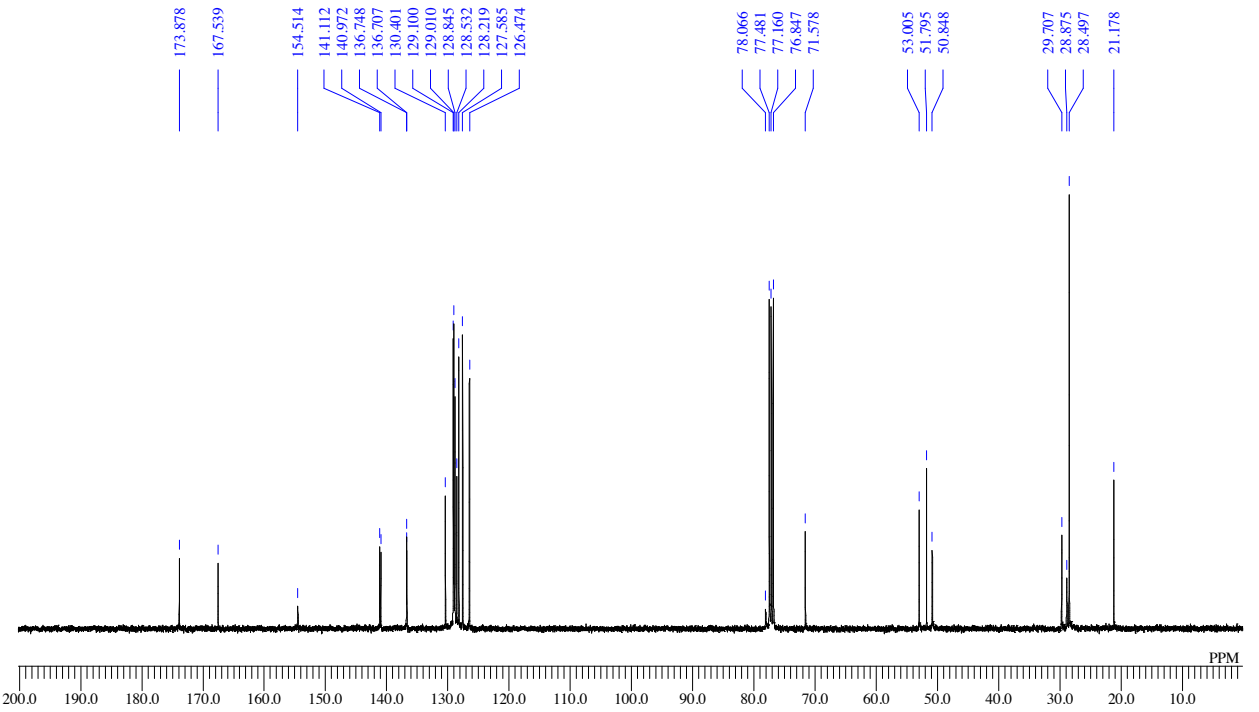
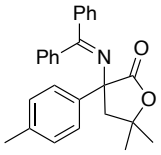
^{1}H NMR: (400 MHz, $CDCl_3$)



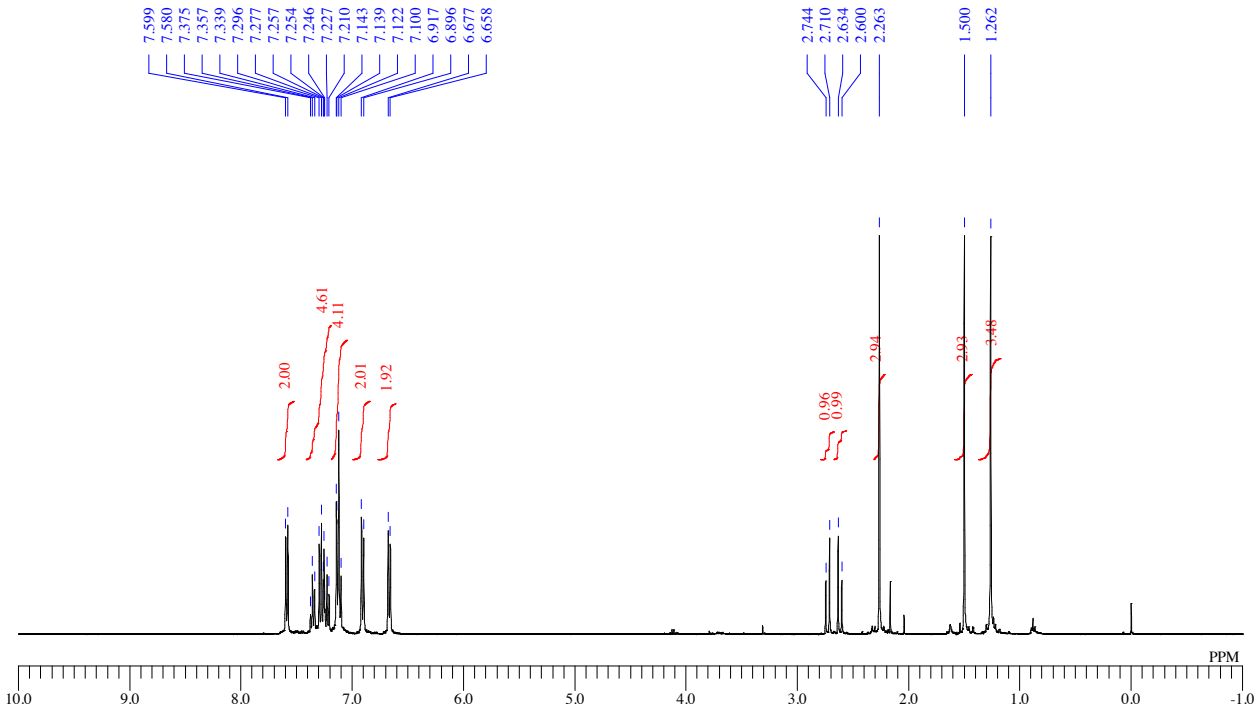
^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$)



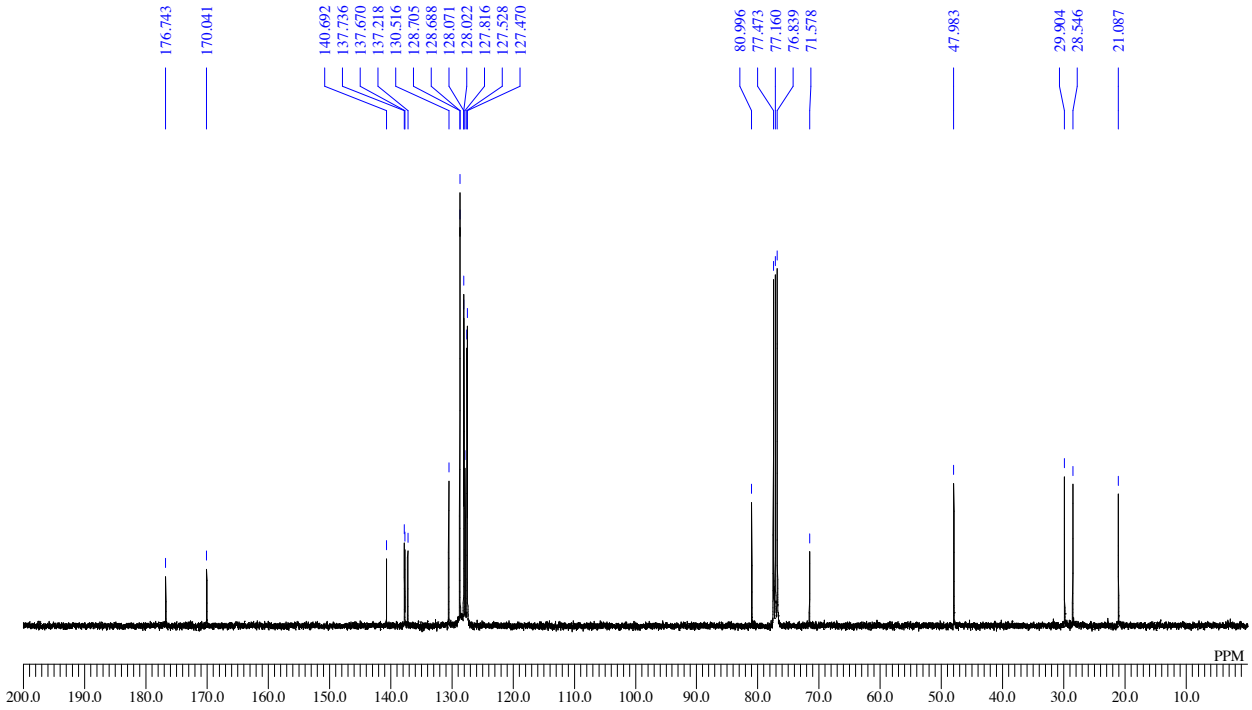


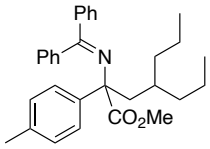
36

^{1}H NMR: (400 MHz, $CDCl_3$)



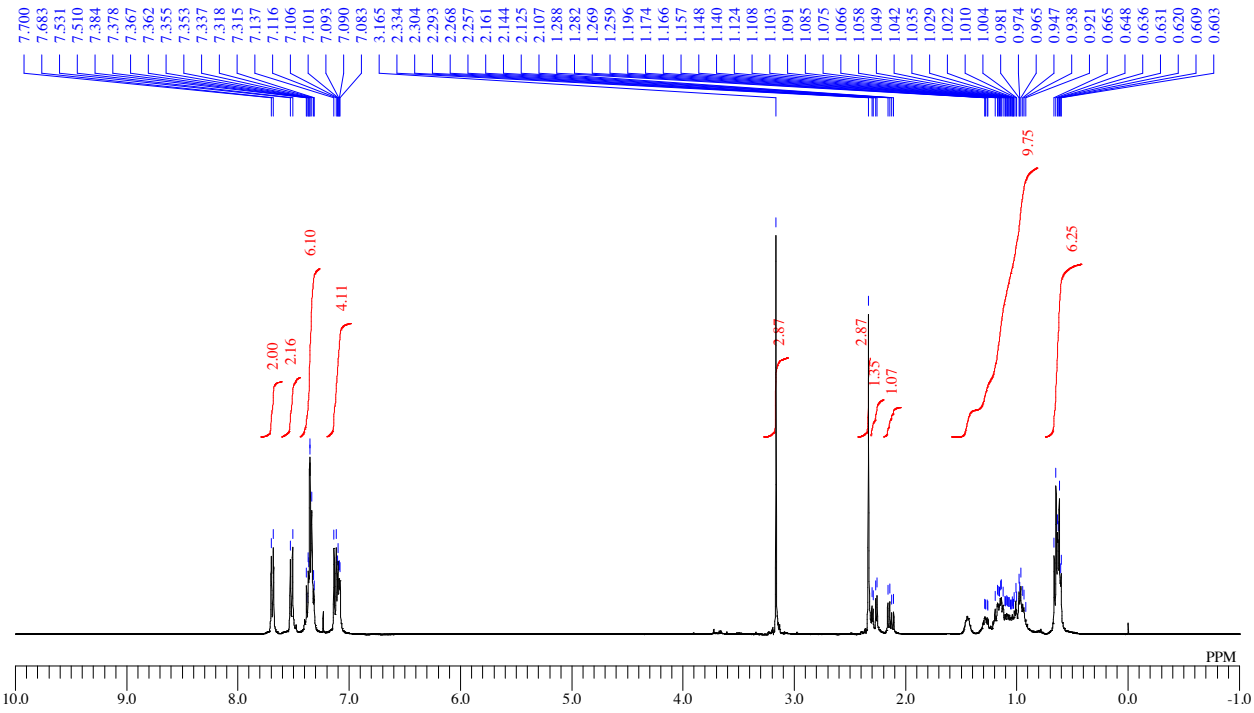
^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$)



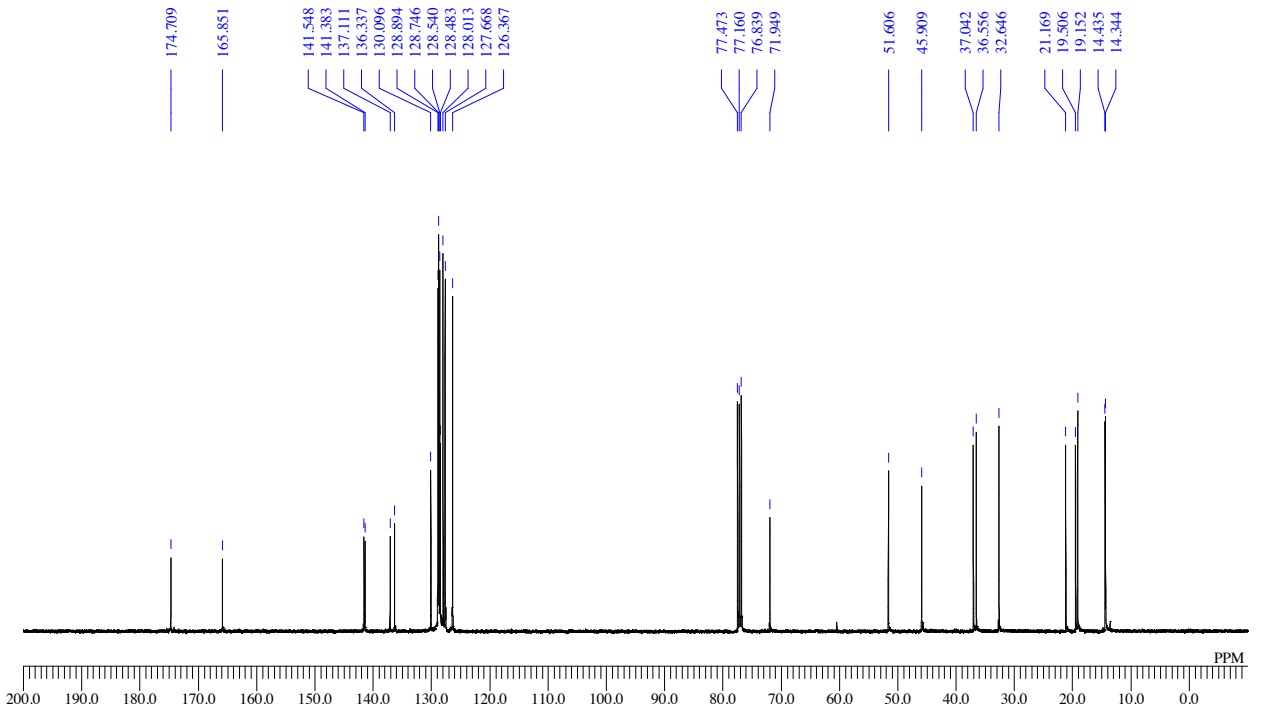


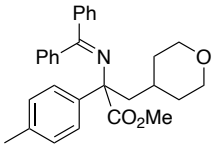
38

^{1}H NMR: (400 MHz, $CDCl_3$)



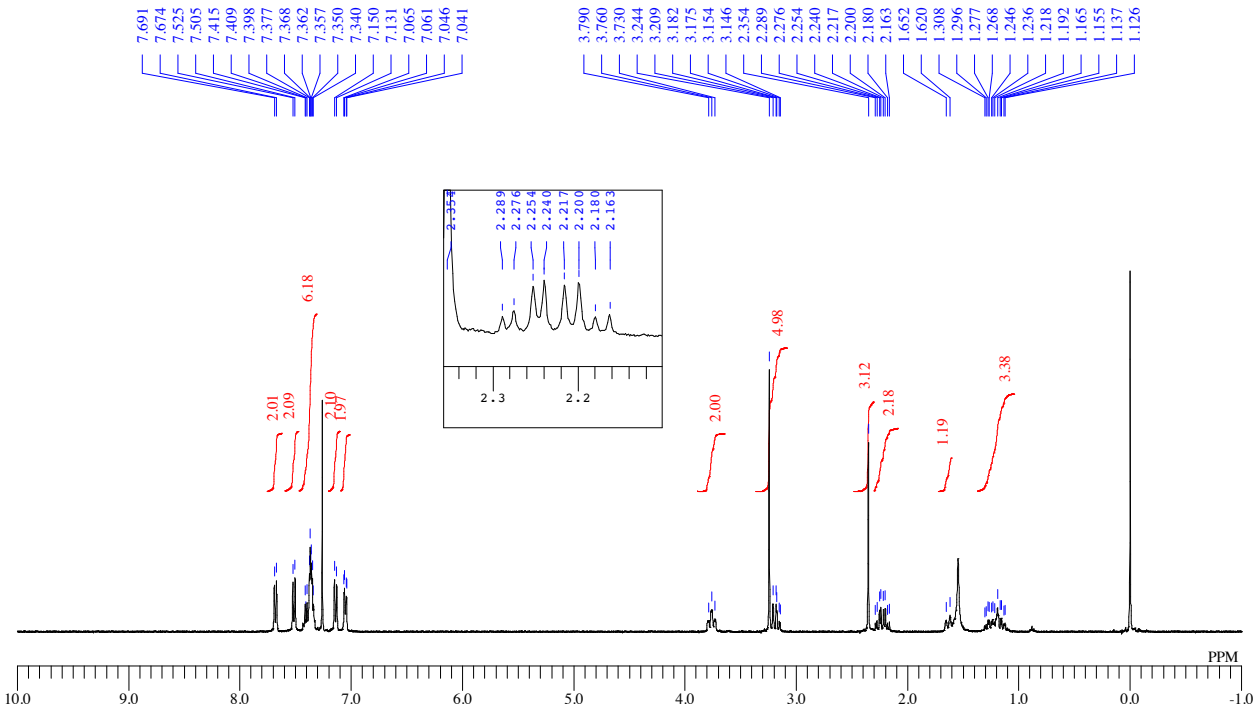
^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$)



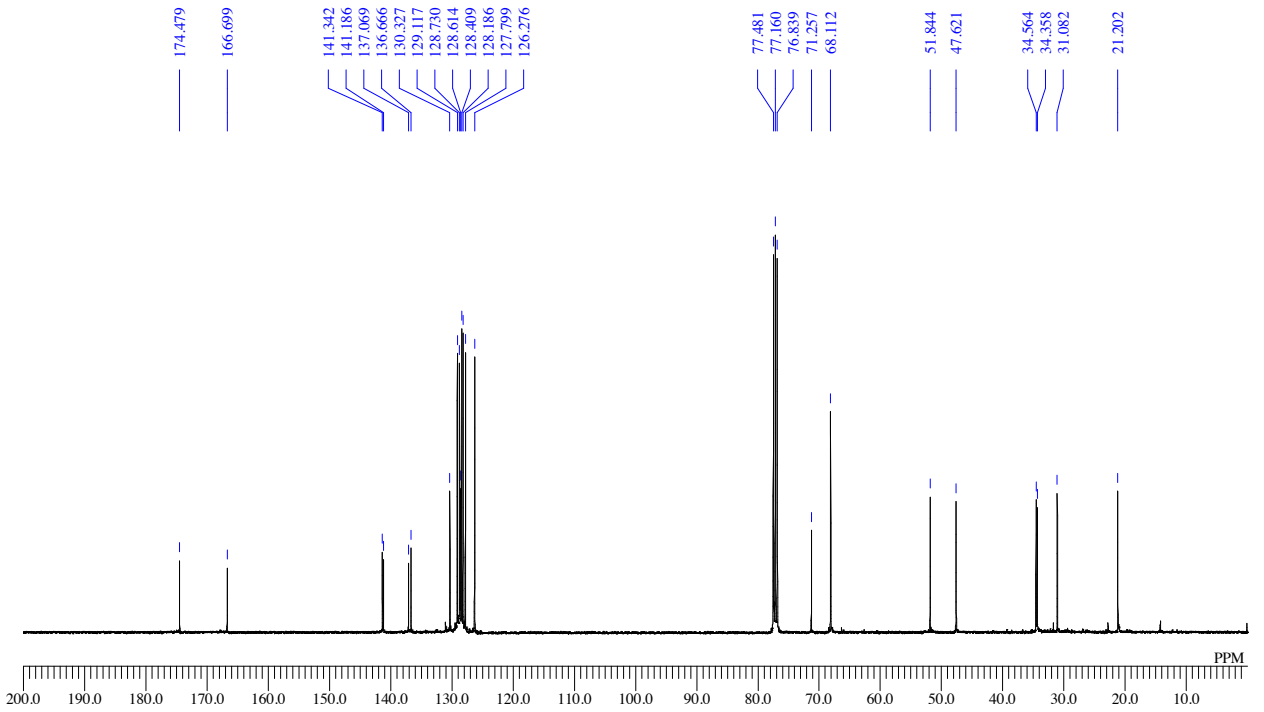


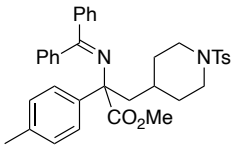
39

^{1}H NMR: (400 MHz, $CDCl_3$)



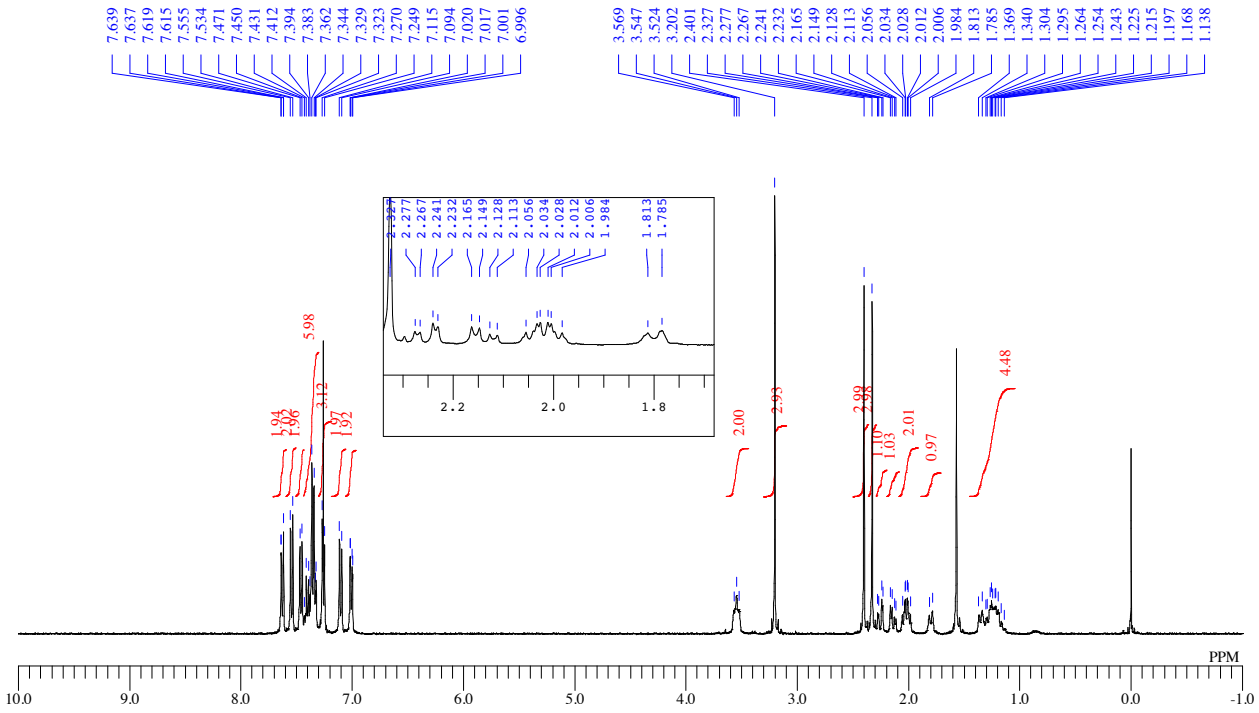
^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$)



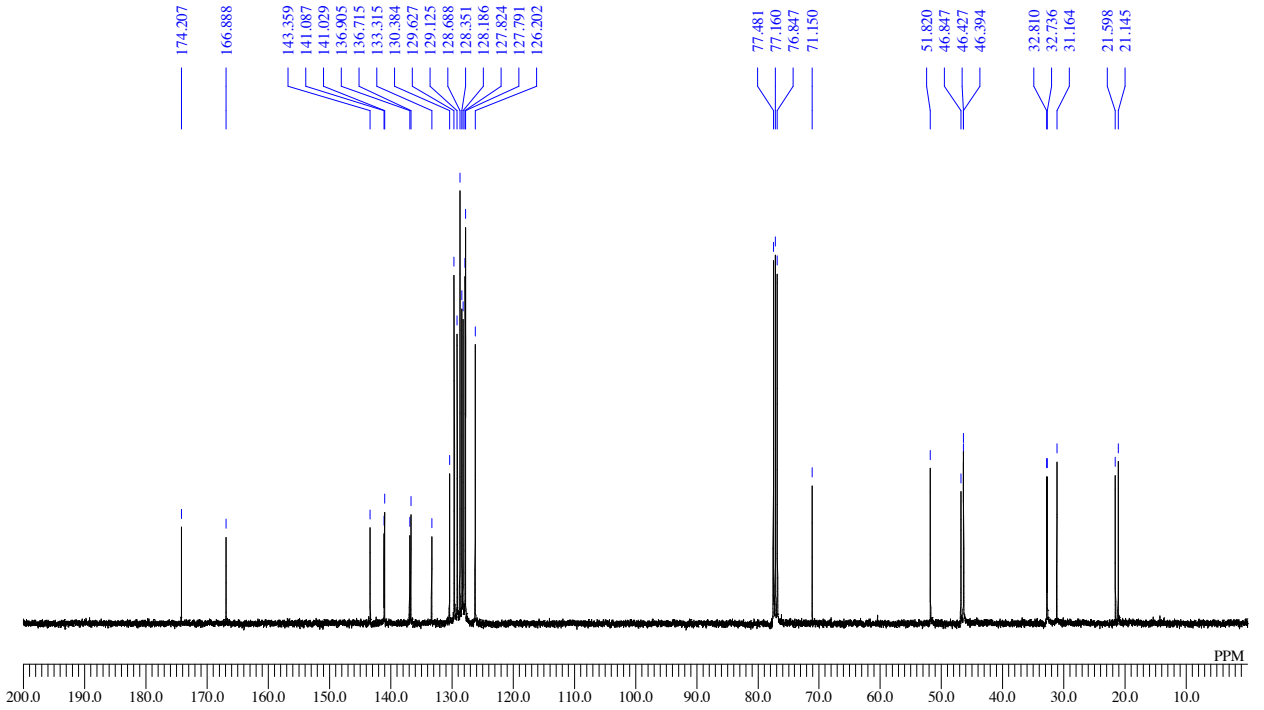


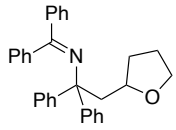
40

^{1}H NMR: (400 MHz, $CDCl_3$)



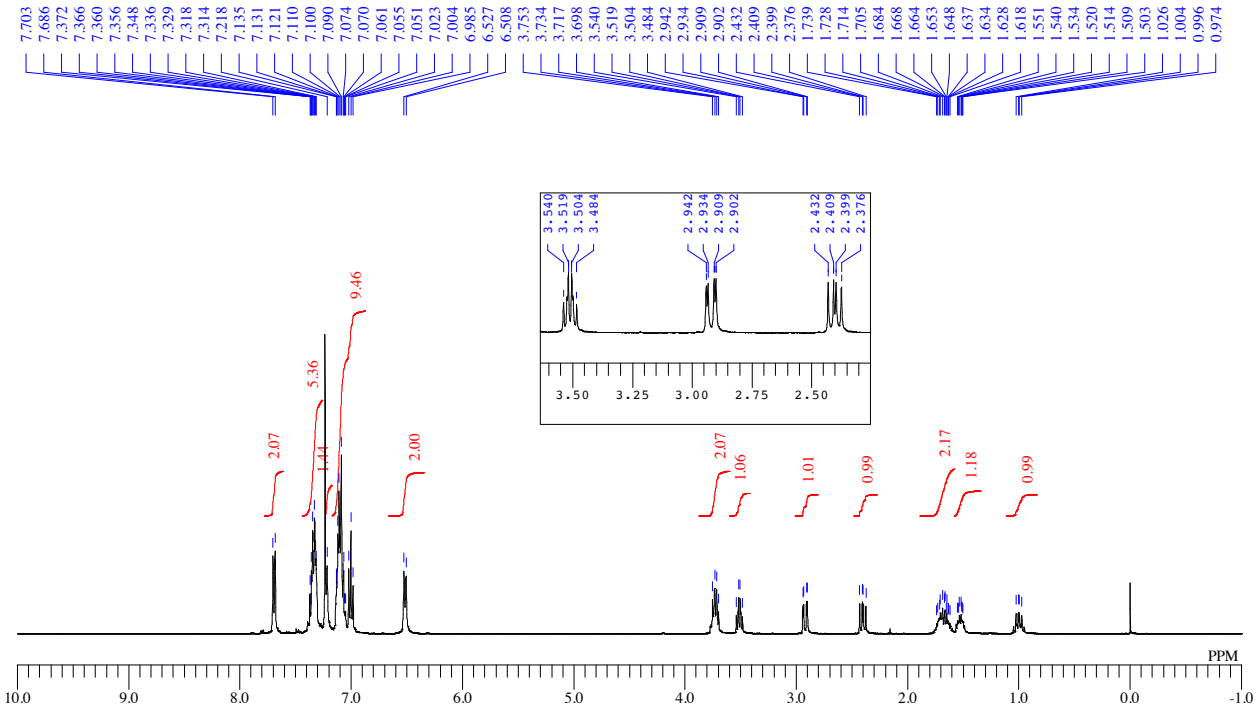
^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$)



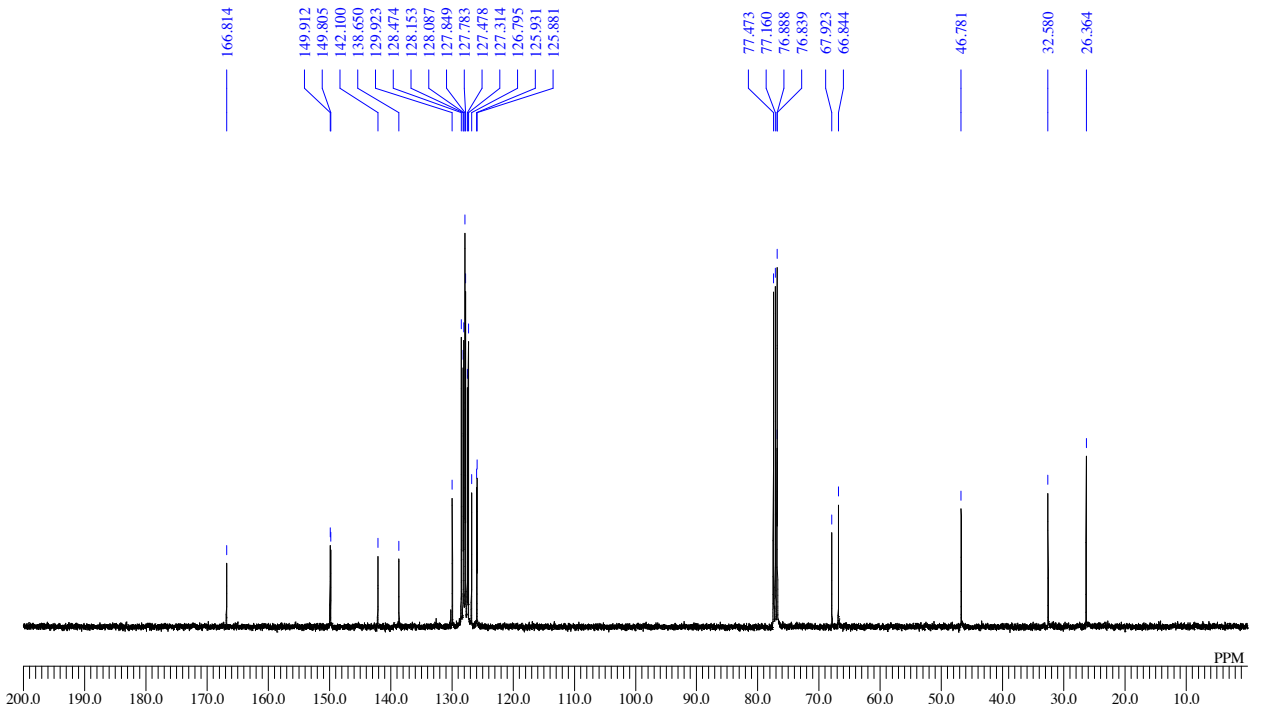


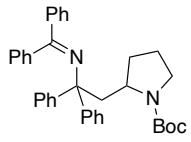
41

^{1}H NMR: (400 MHz, $CDCl_3$)



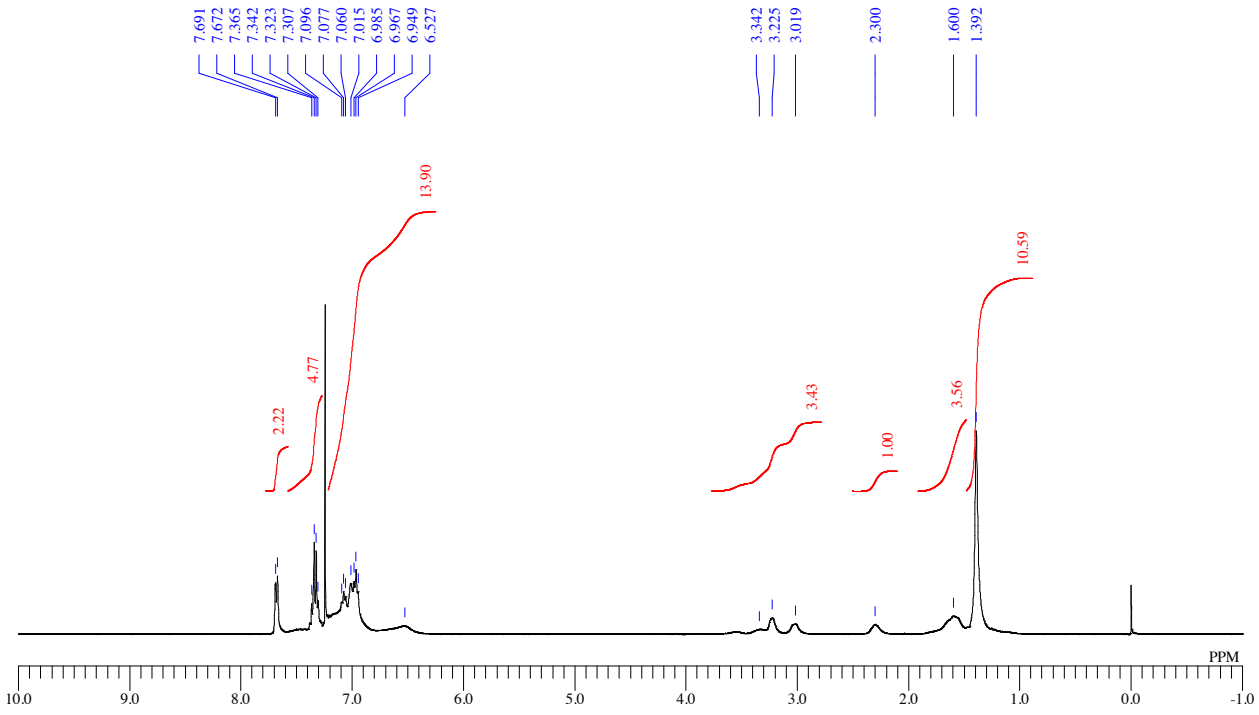
^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$)



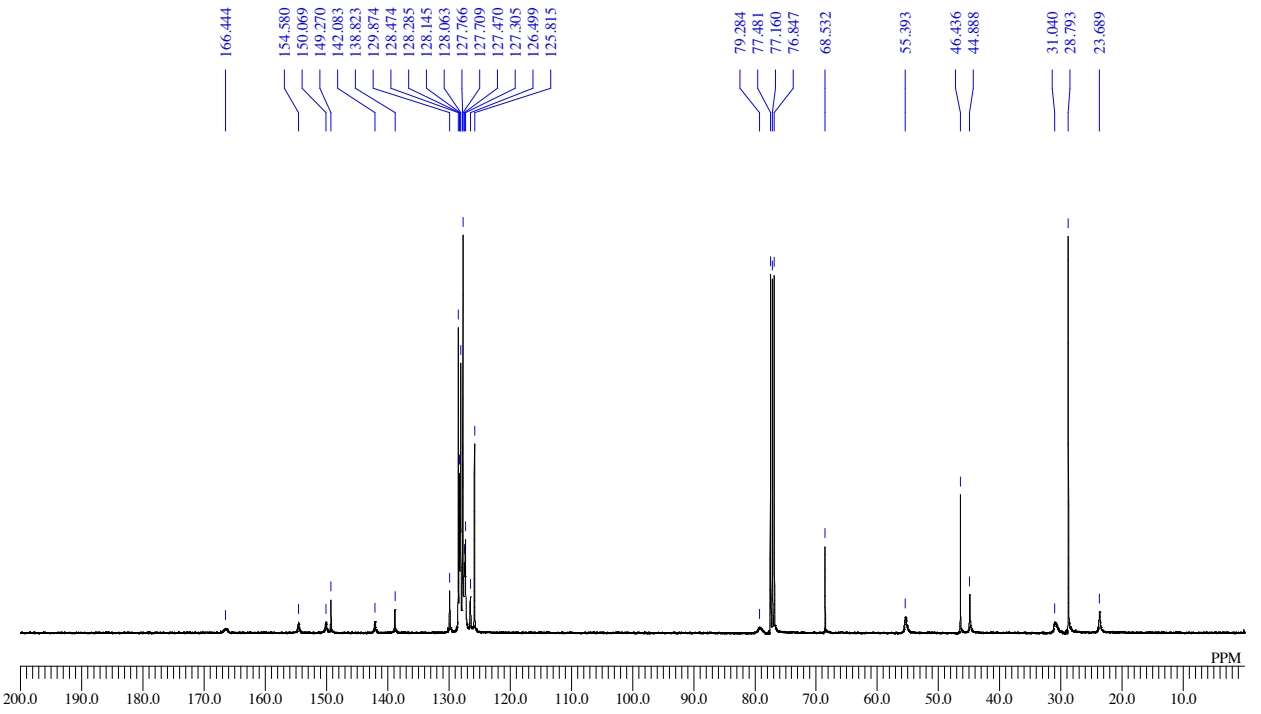


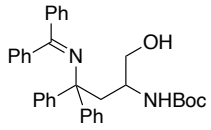
42

^{1}H NMR: (400 MHz, $CDCl_3$)



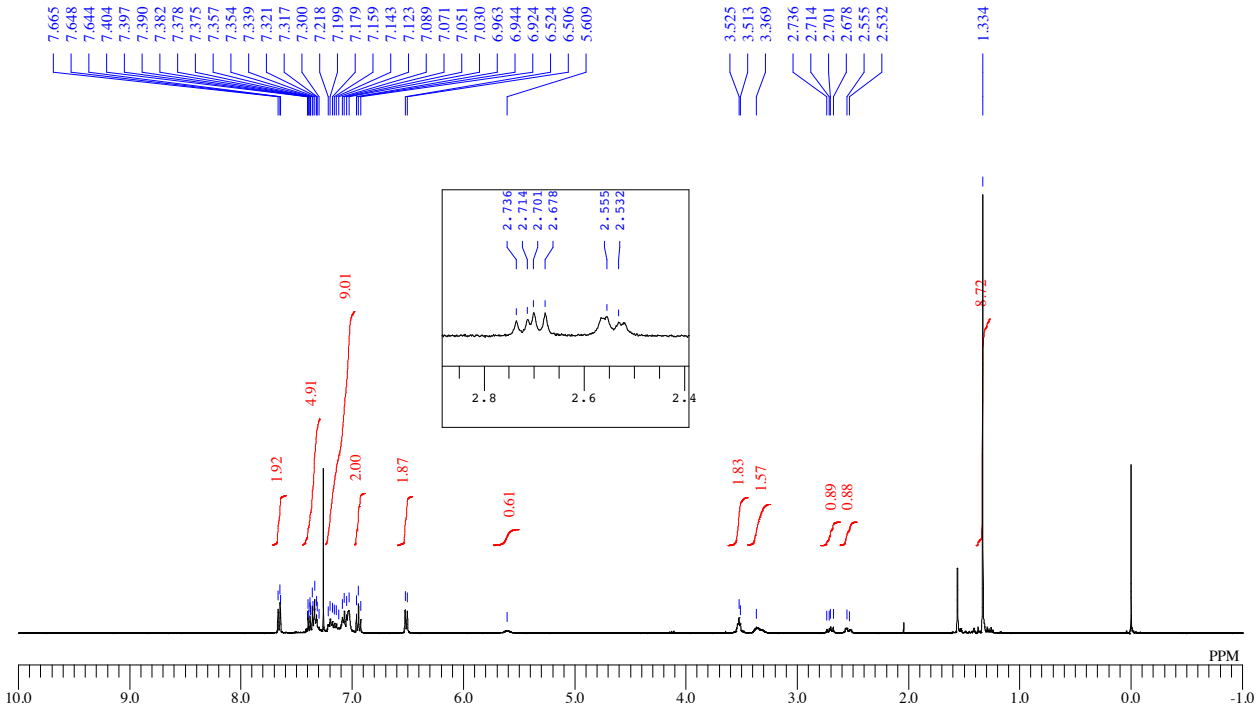
^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$)



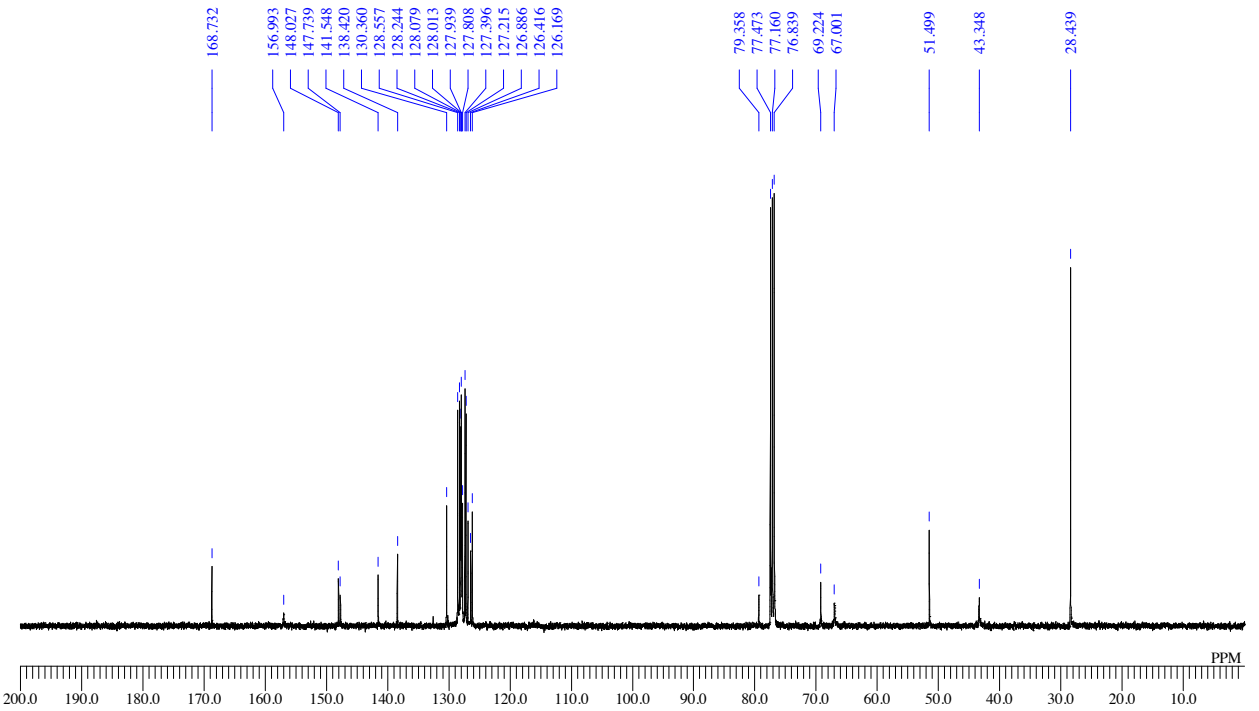


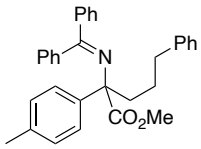
43

^{1}H NMR: (400 MHz, $CDCl_3$)



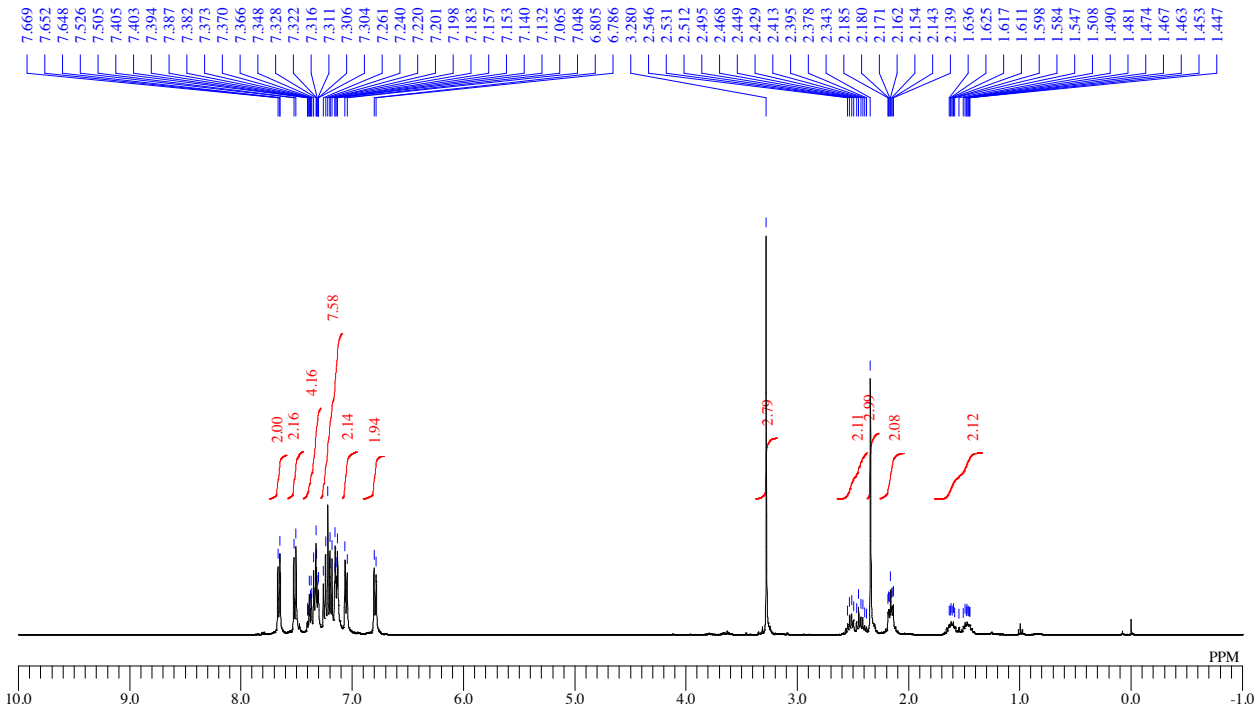
^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$)



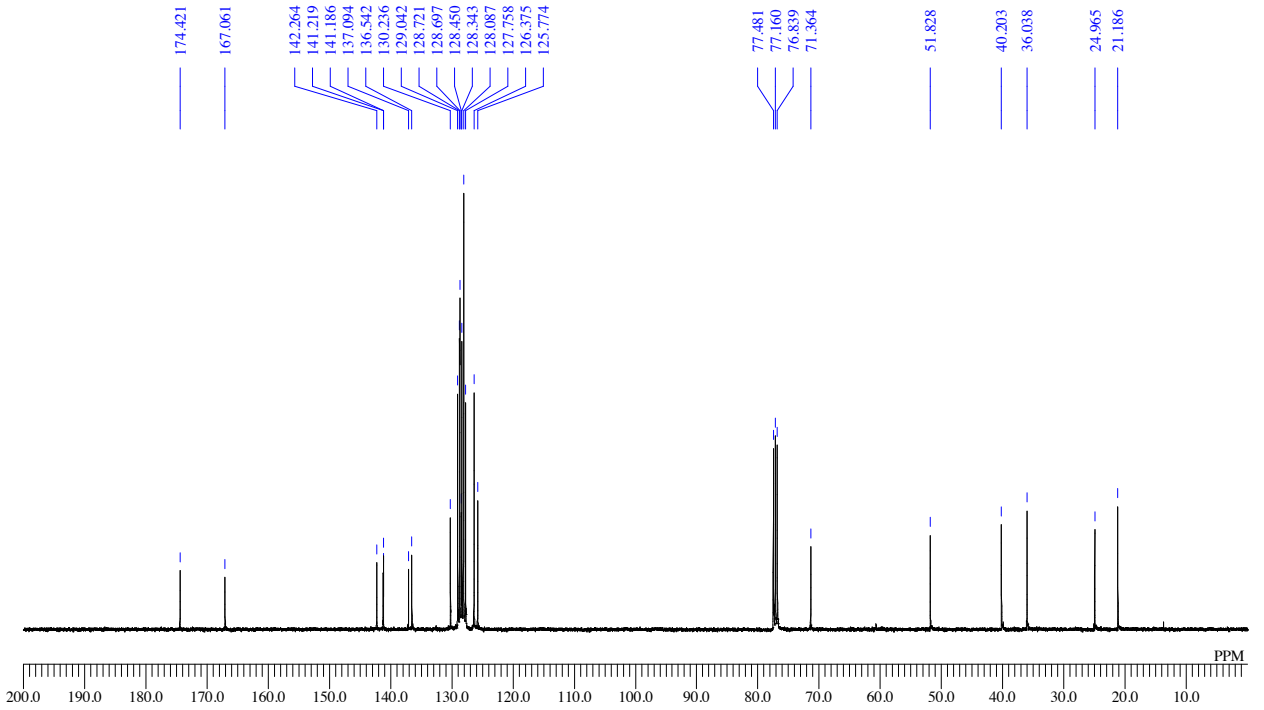


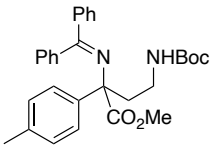
44

^{1}H NMR: (400 MHz, $CDCl_3$)



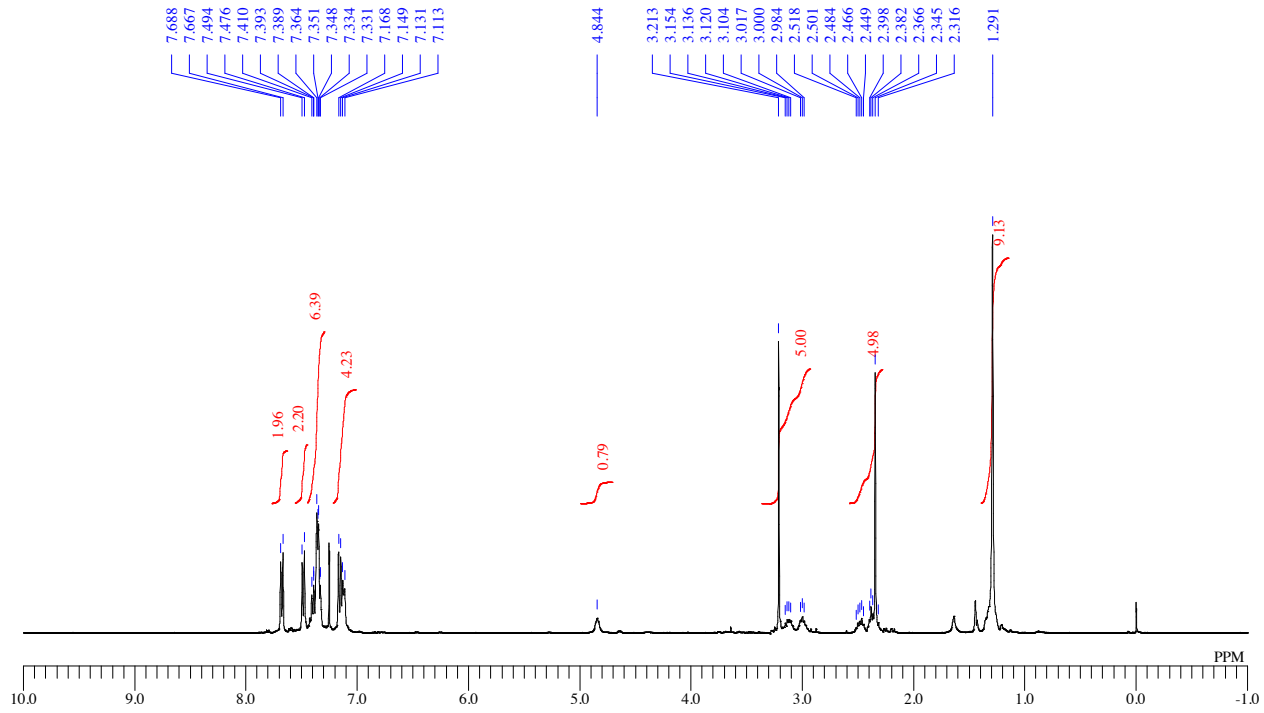
^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$)



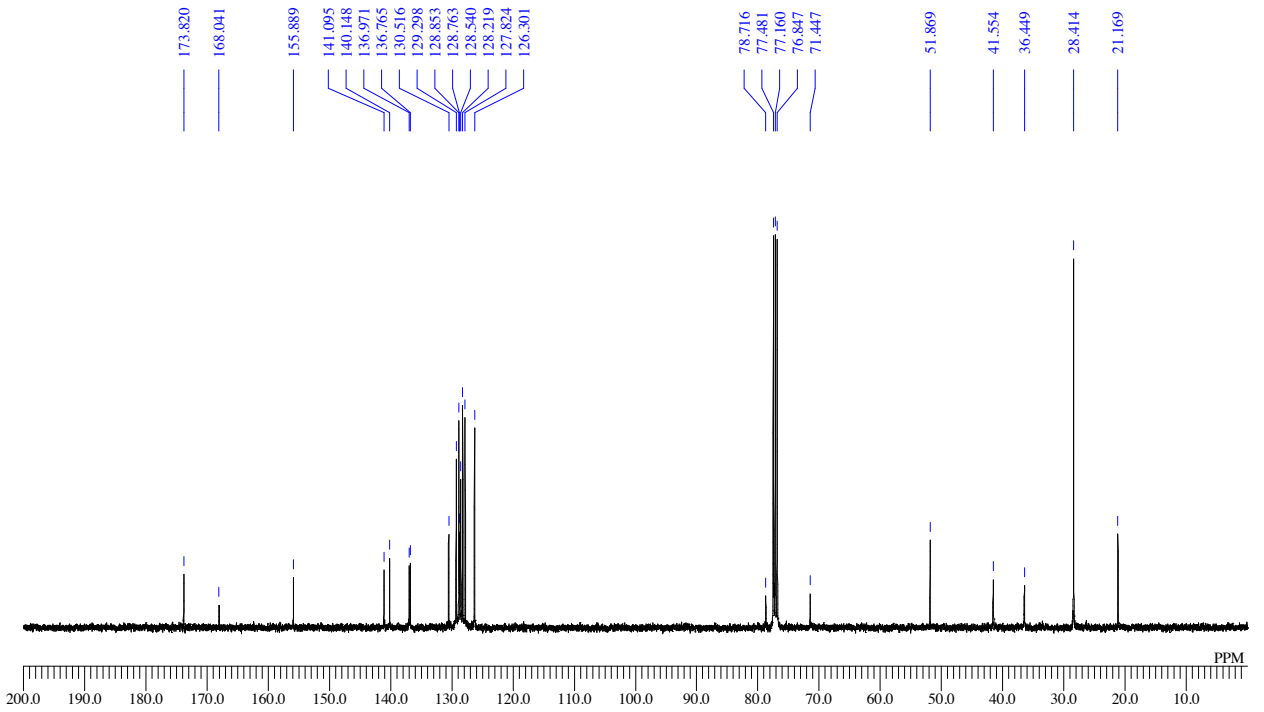


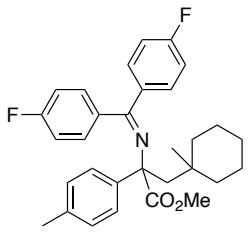
45

^{1}H NMR: (400 MHz, $CDCl_3$)



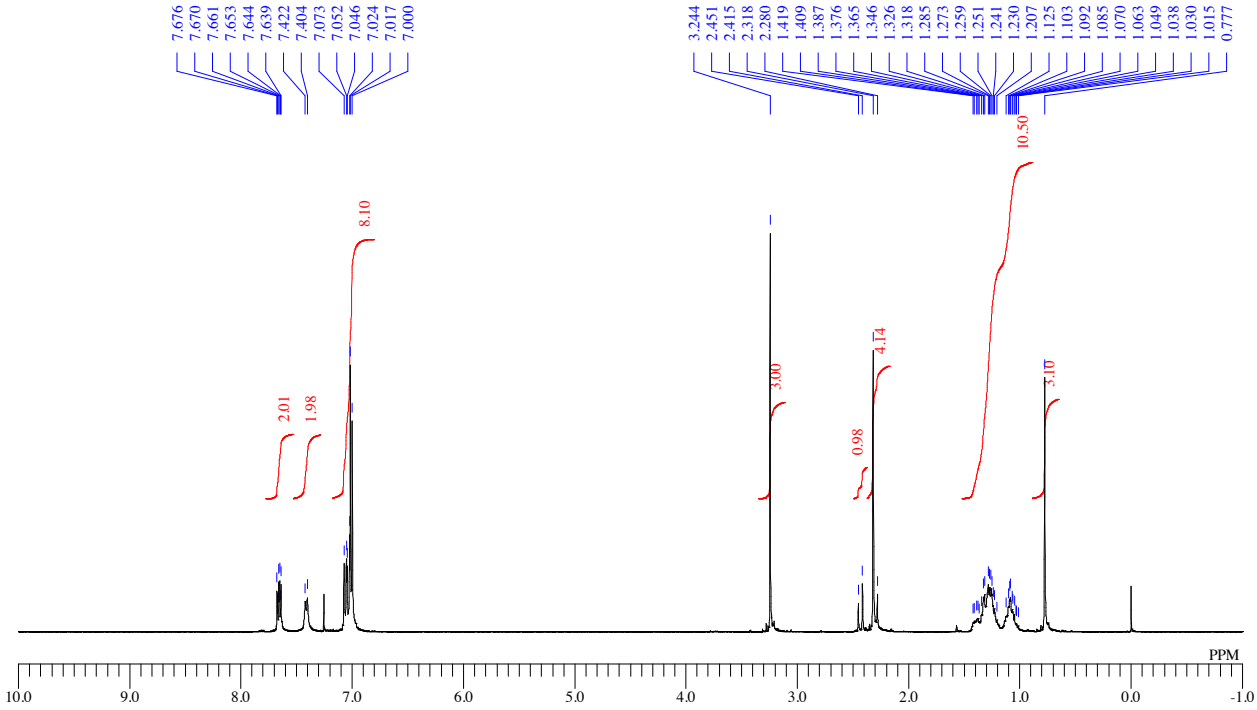
^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$)



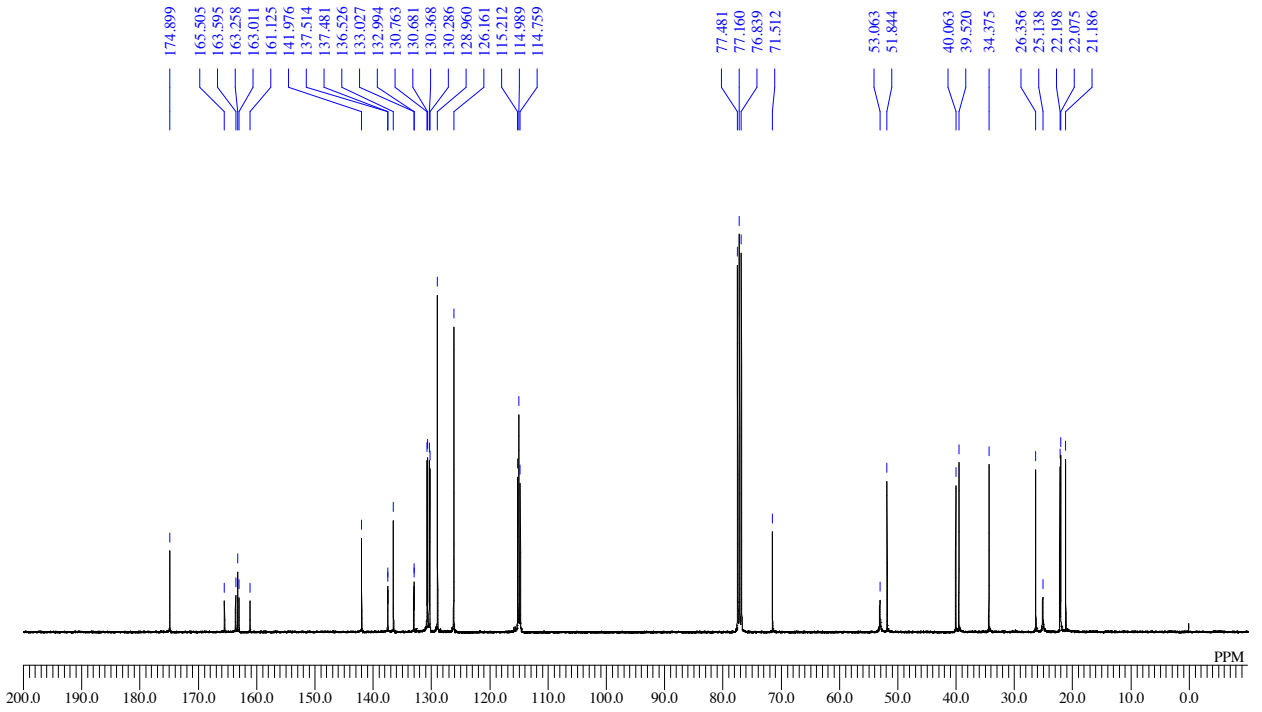


46

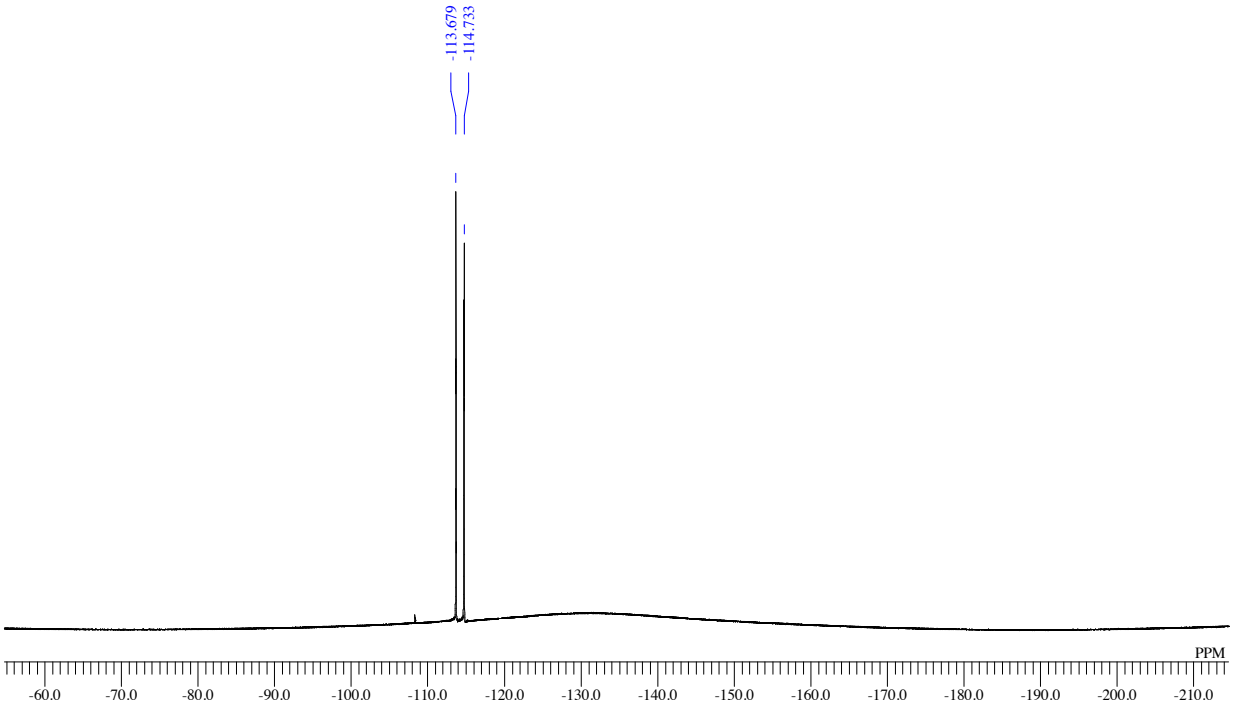
^{1}H NMR: (400 MHz, $CDCl_3$)

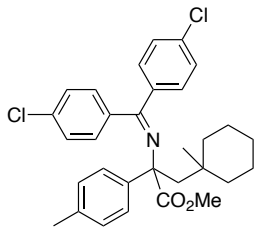


^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$)



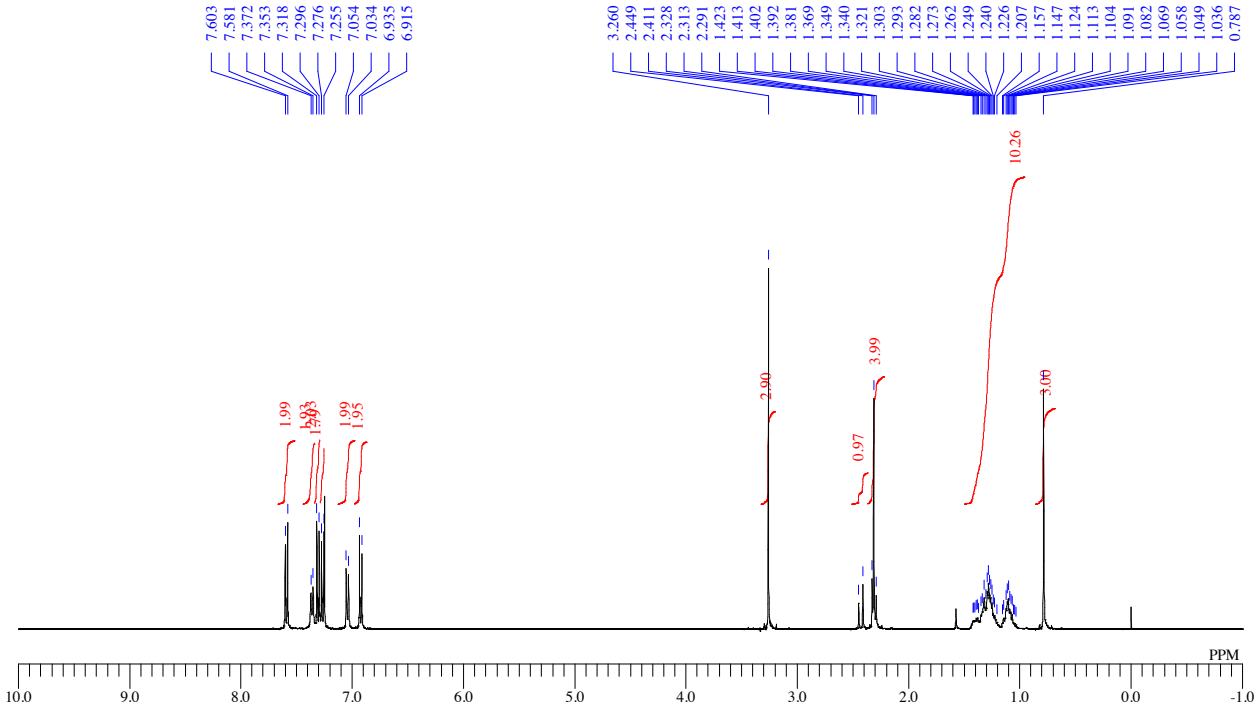
$^{19}F\{^{1}H\}$ NMR: (377 MHz, $CDCl_3$)



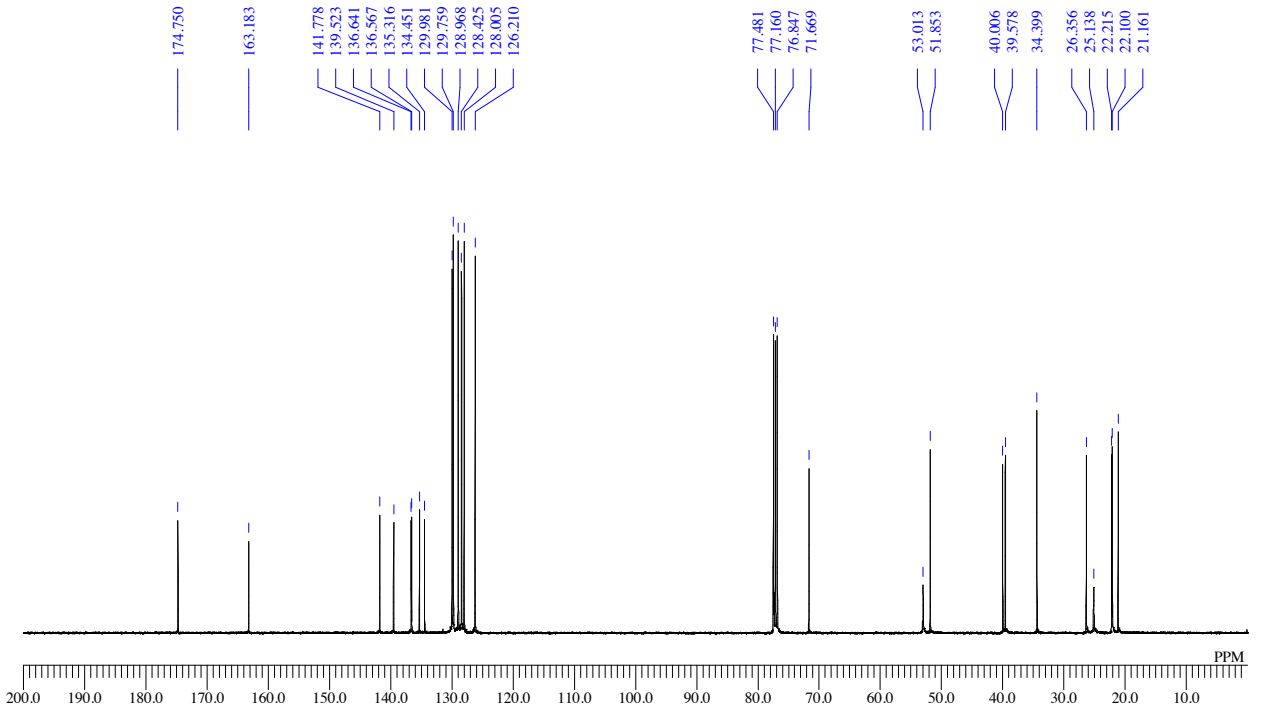


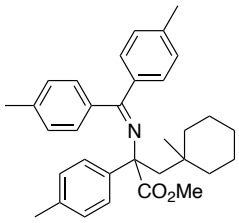
47

^{1}H NMR: (400 MHz, $CDCl_3$)



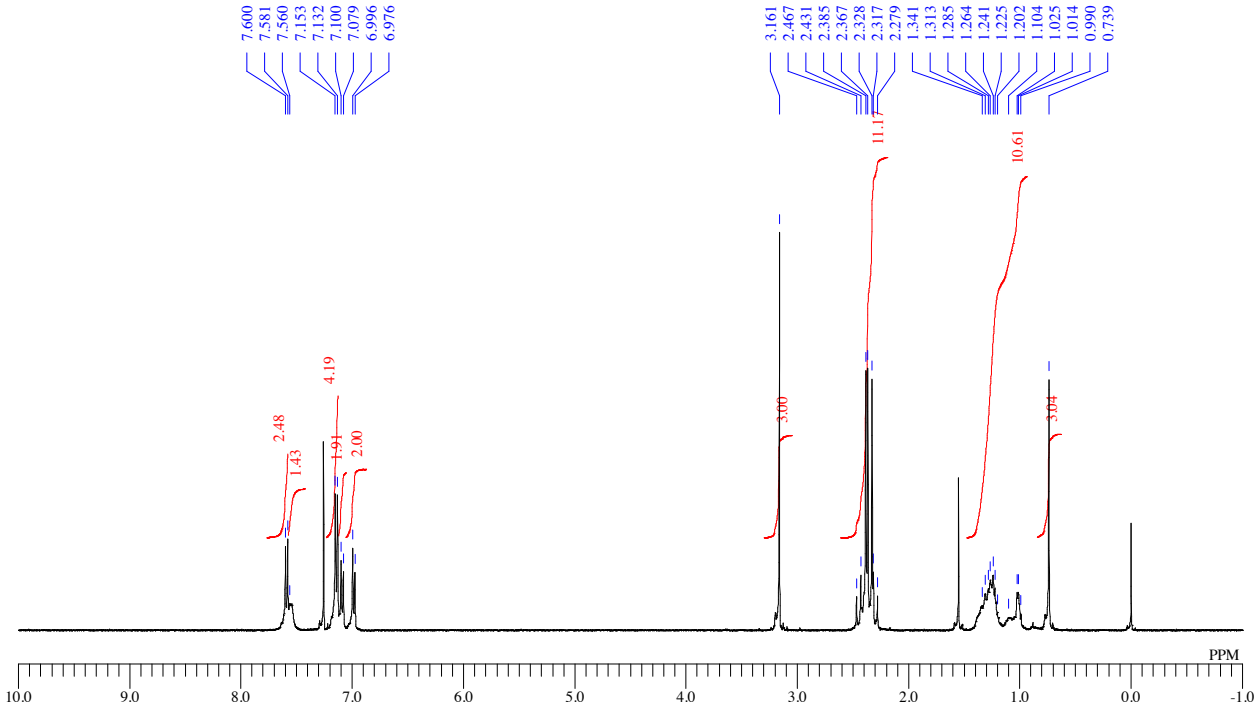
^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$)



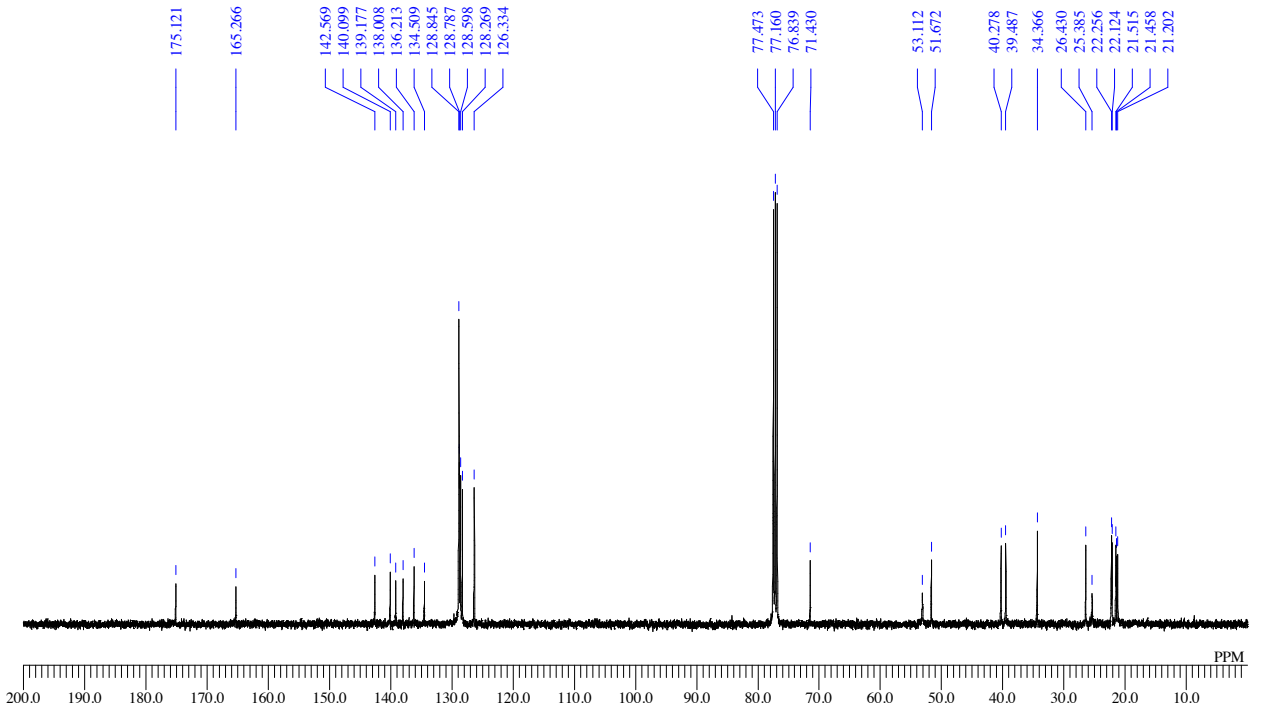


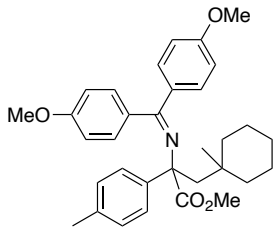
48

^{1}H NMR: (400 MHz, $CDCl_3$)



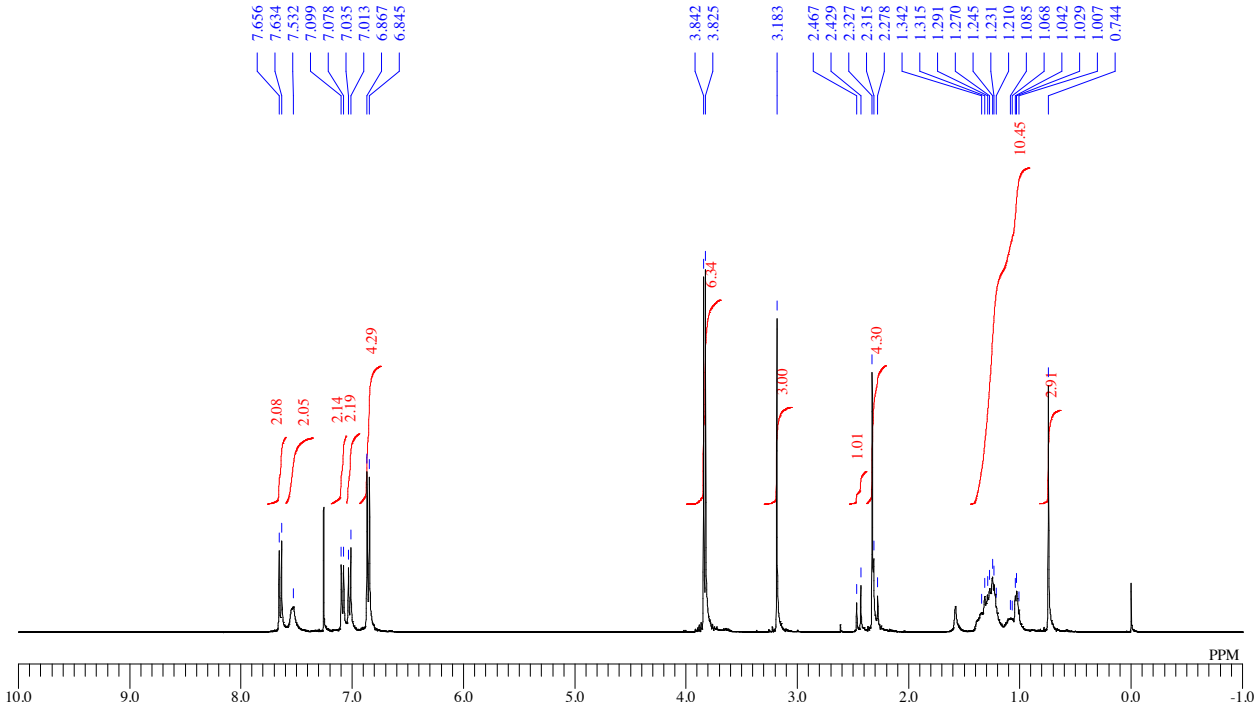
^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$)



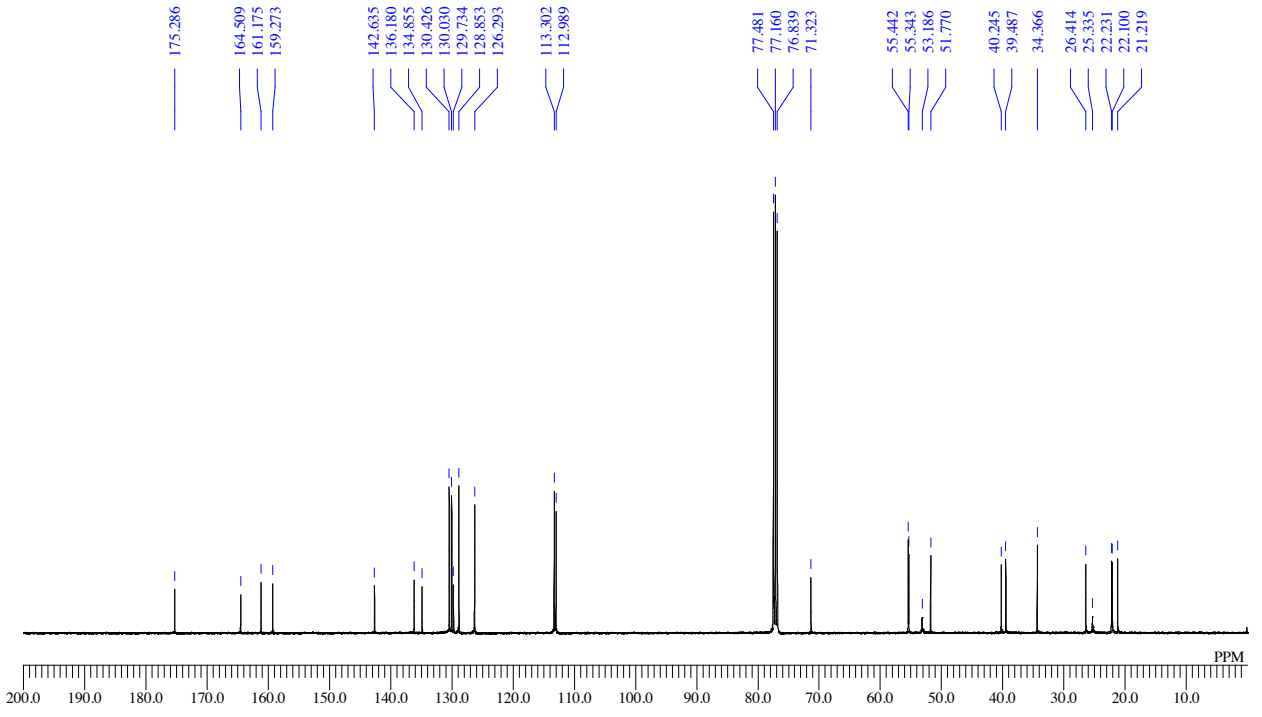


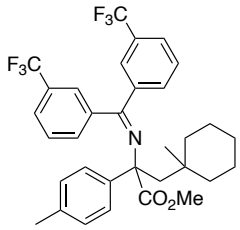
49

^{1}H NMR: (400 MHz, $CDCl_3$)



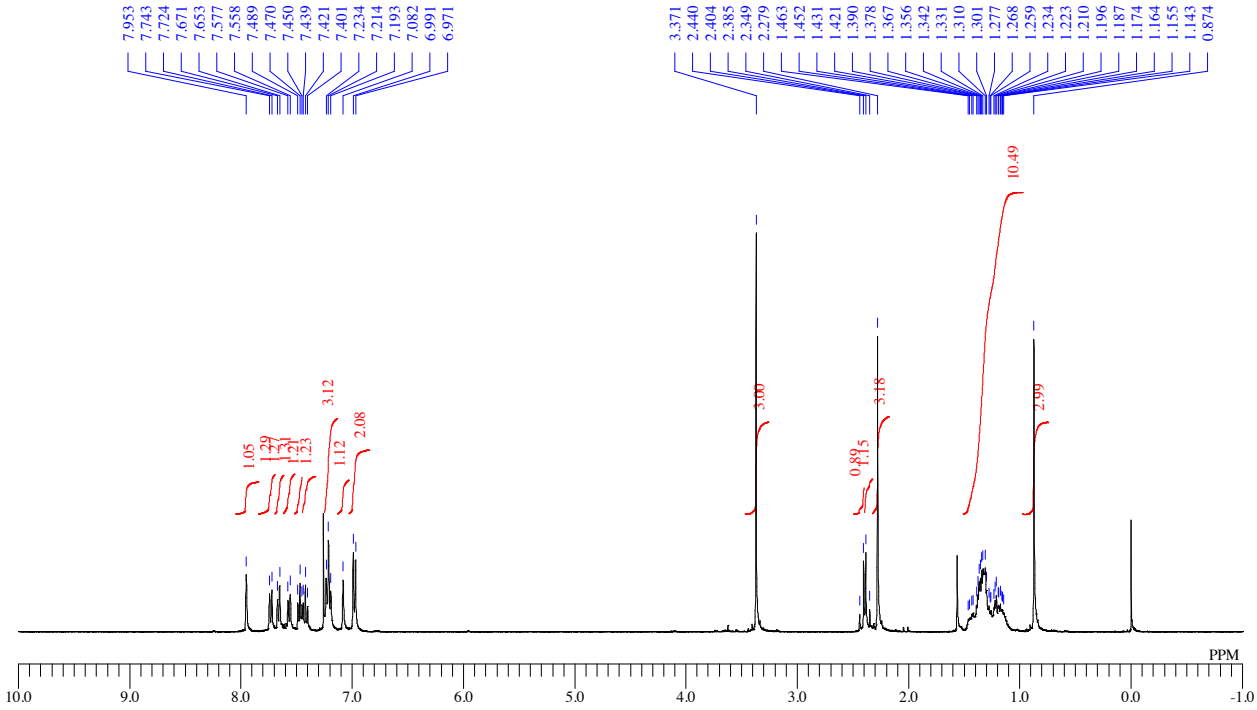
^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$)



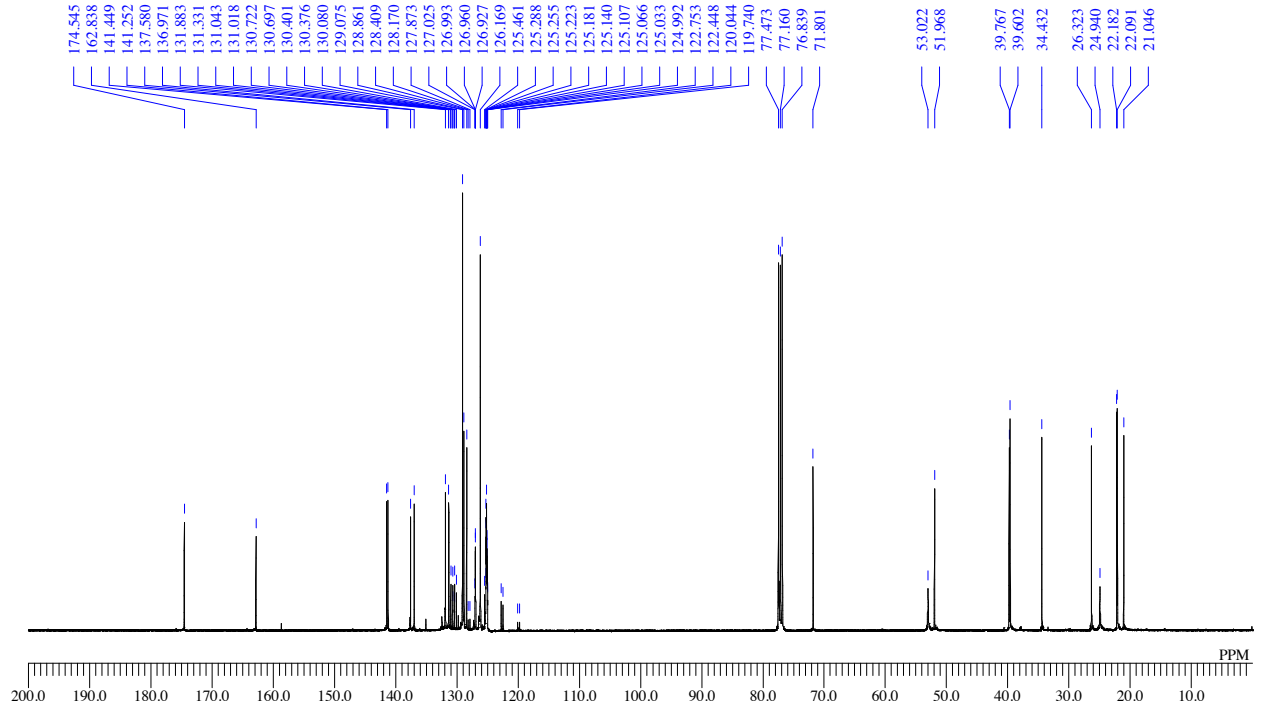


50

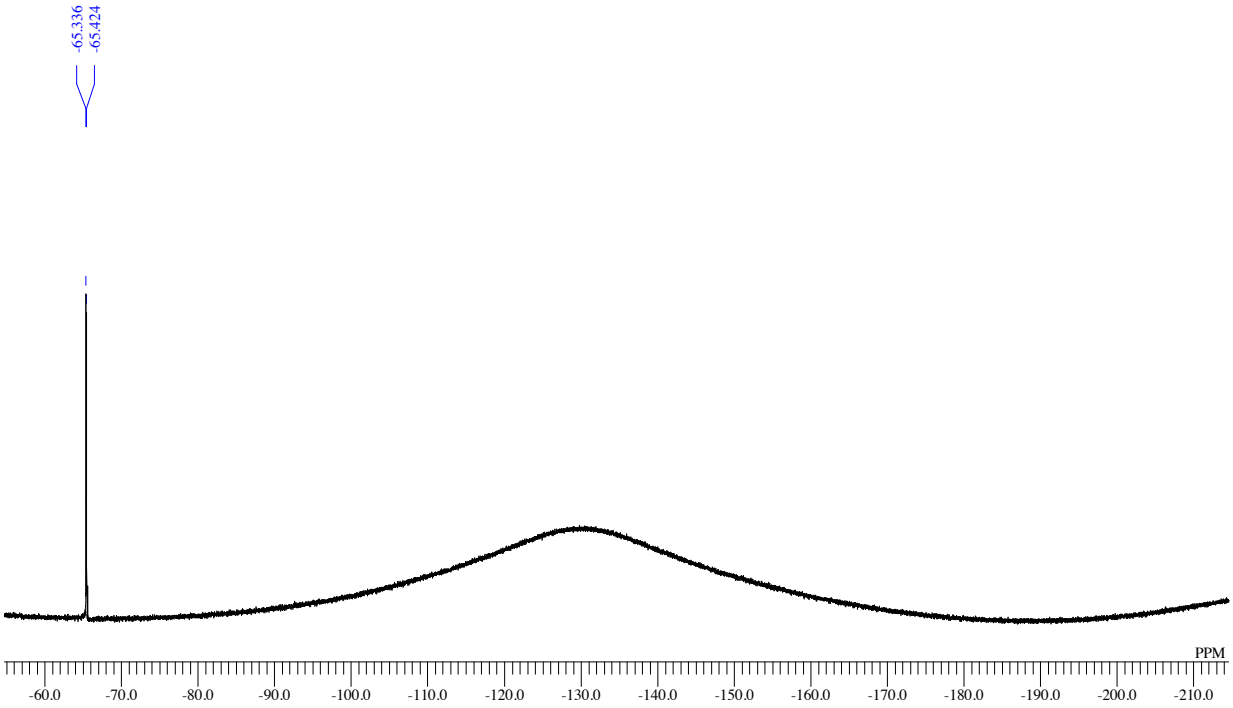
^{1}H NMR: (400 MHz, $CDCl_3$)

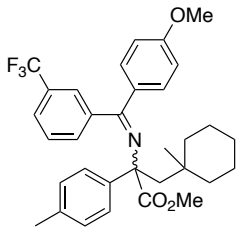


^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$)



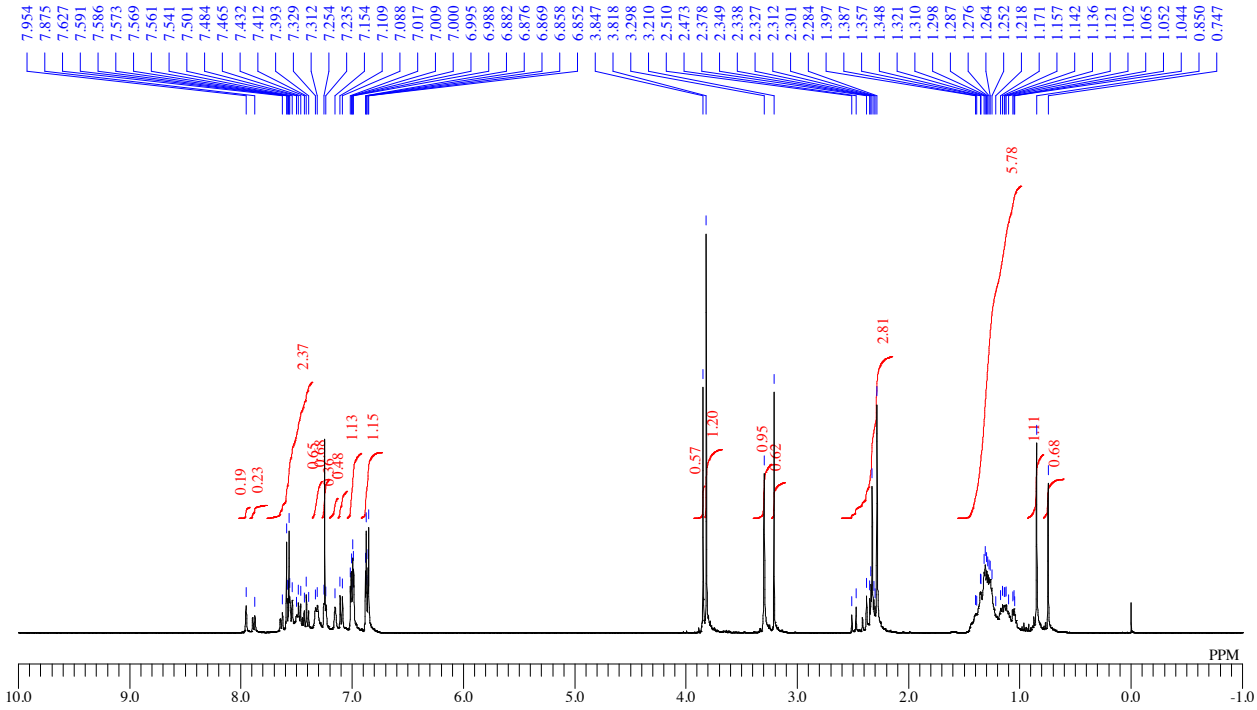
$^{19}F\{^{1}H\}$ NMR: (377 MHz, $CDCl_3$)



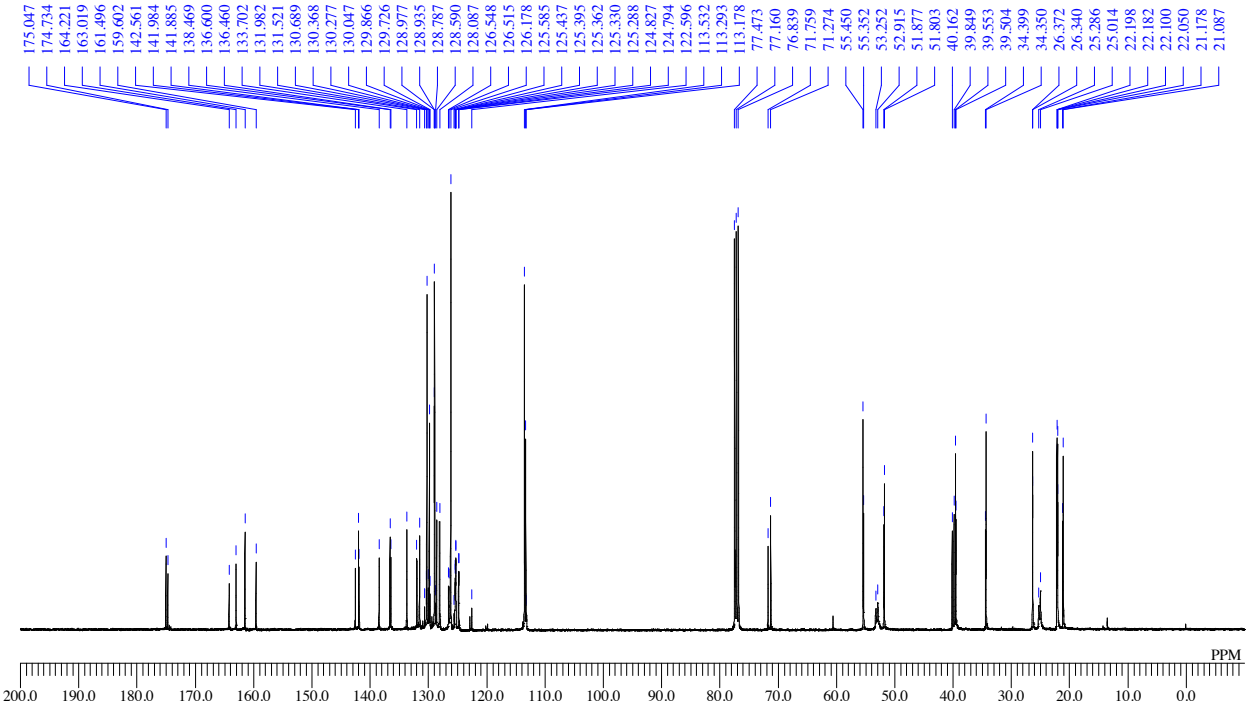


51

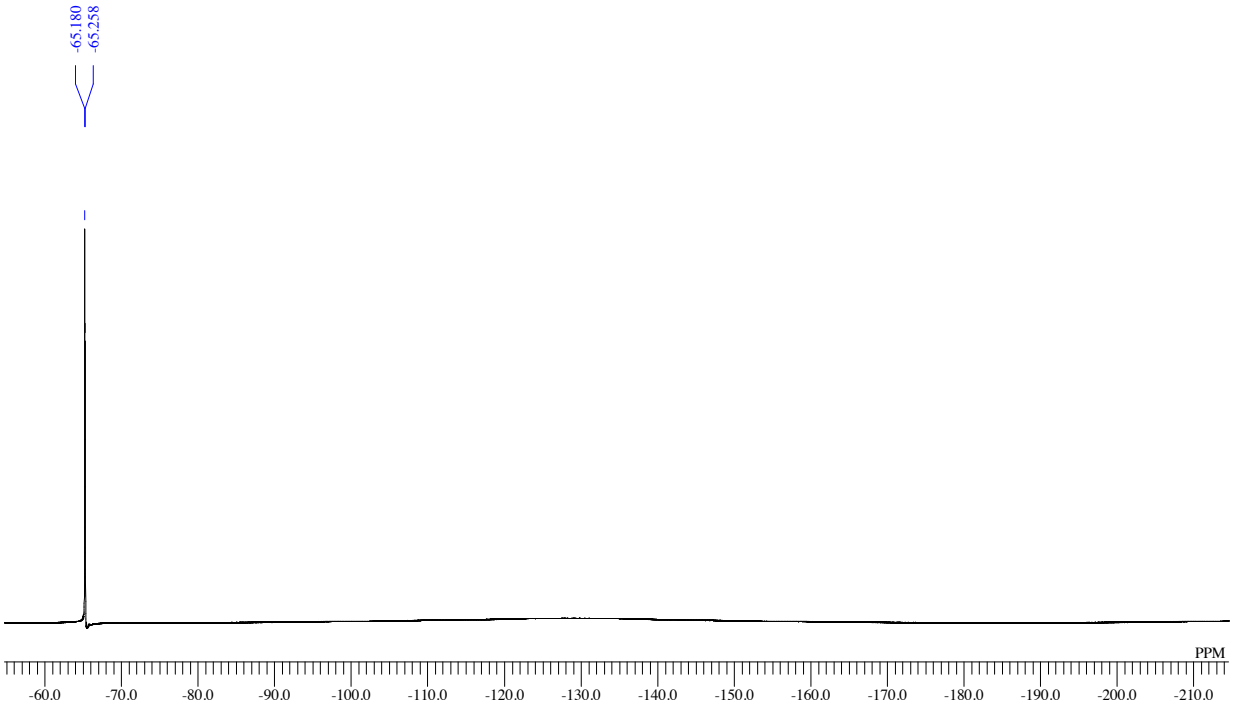
^{1}H NMR: (400 MHz, $CDCl_3$)

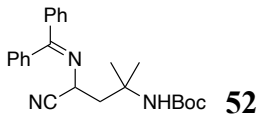


^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$)



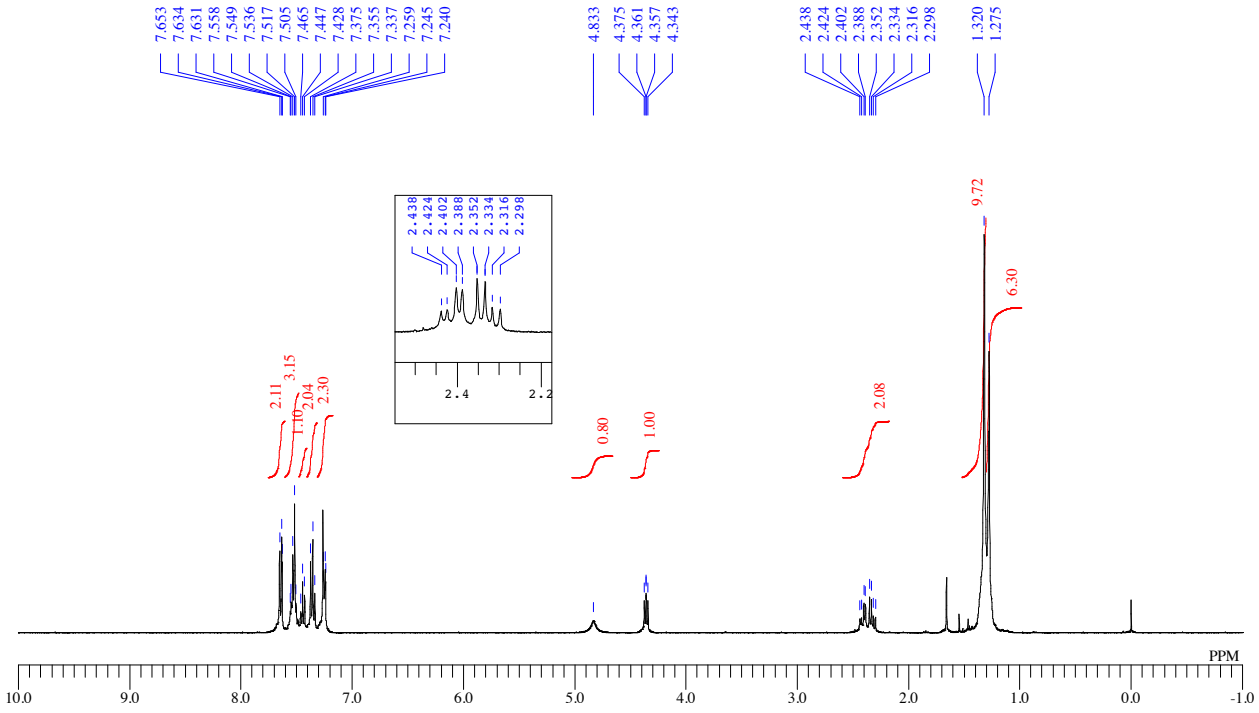
$^{19}F\{^{1}H\}$ NMR: (377 MHz, $CDCl_3$)



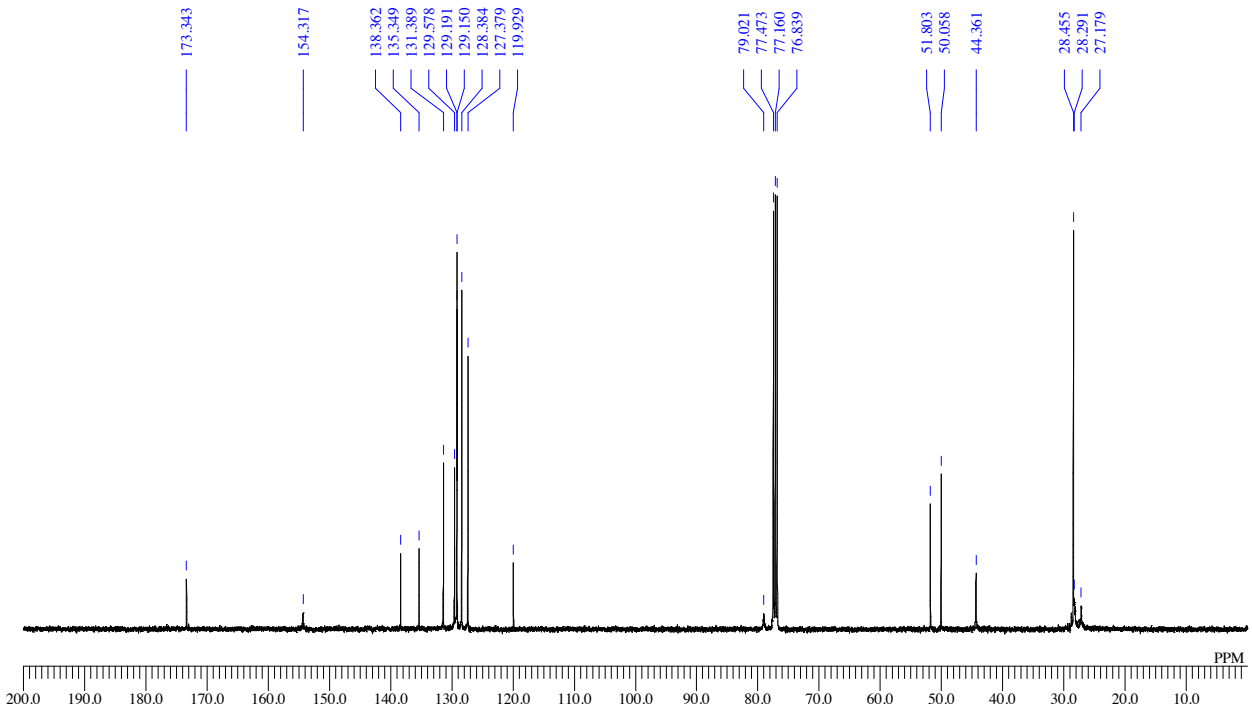


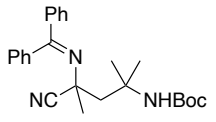
52

^{1}H NMR: (400 MHz, $CDCl_3$)



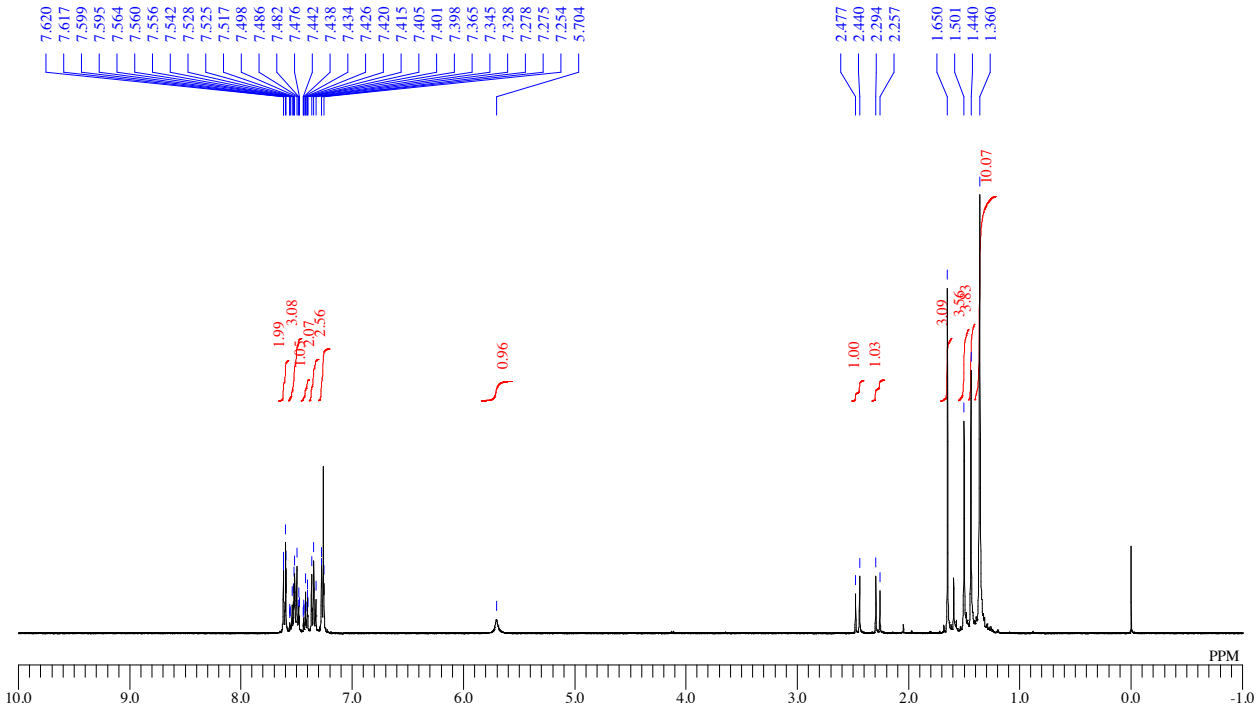
^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$)



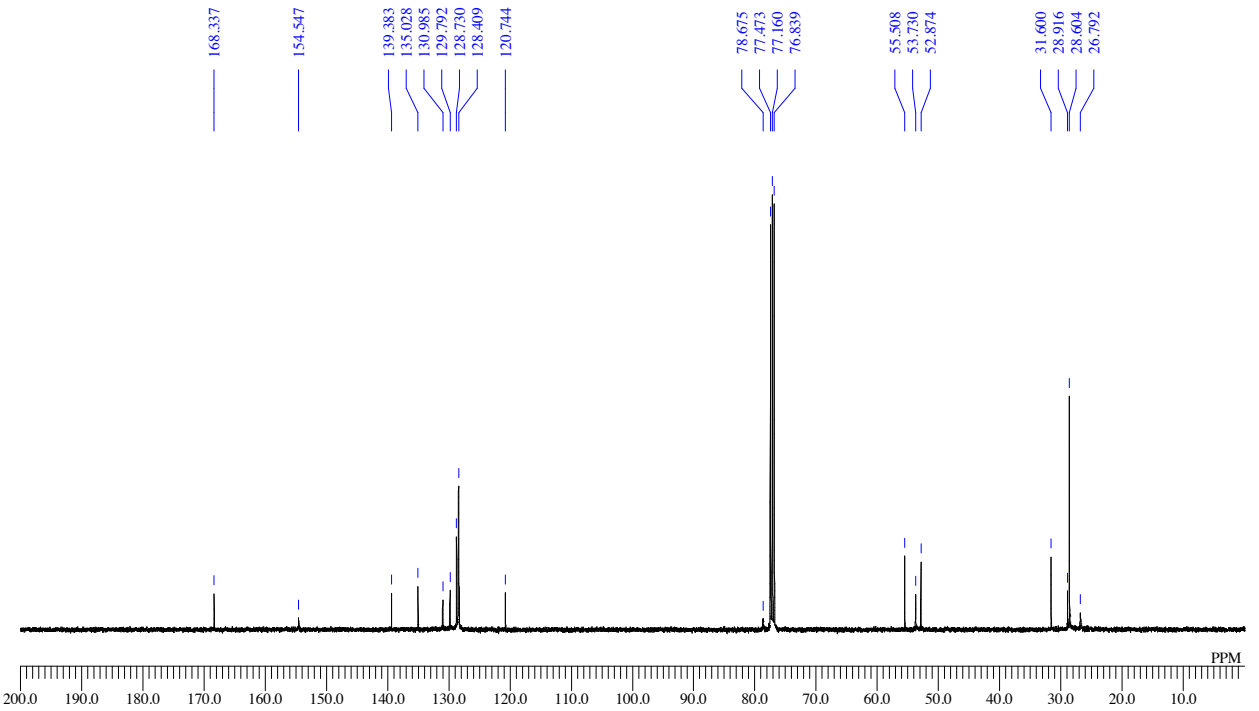


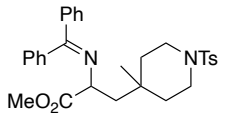
53

^{1}H NMR: (400 MHz, $CDCl_3$)



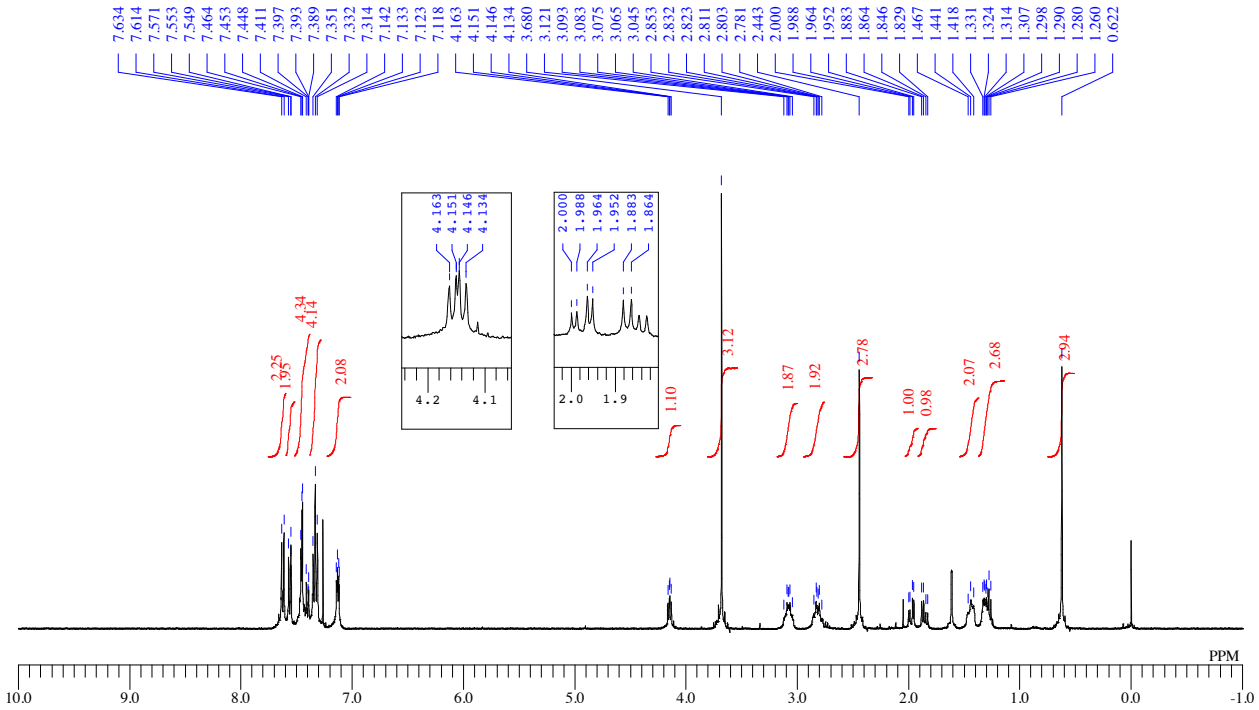
^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$)



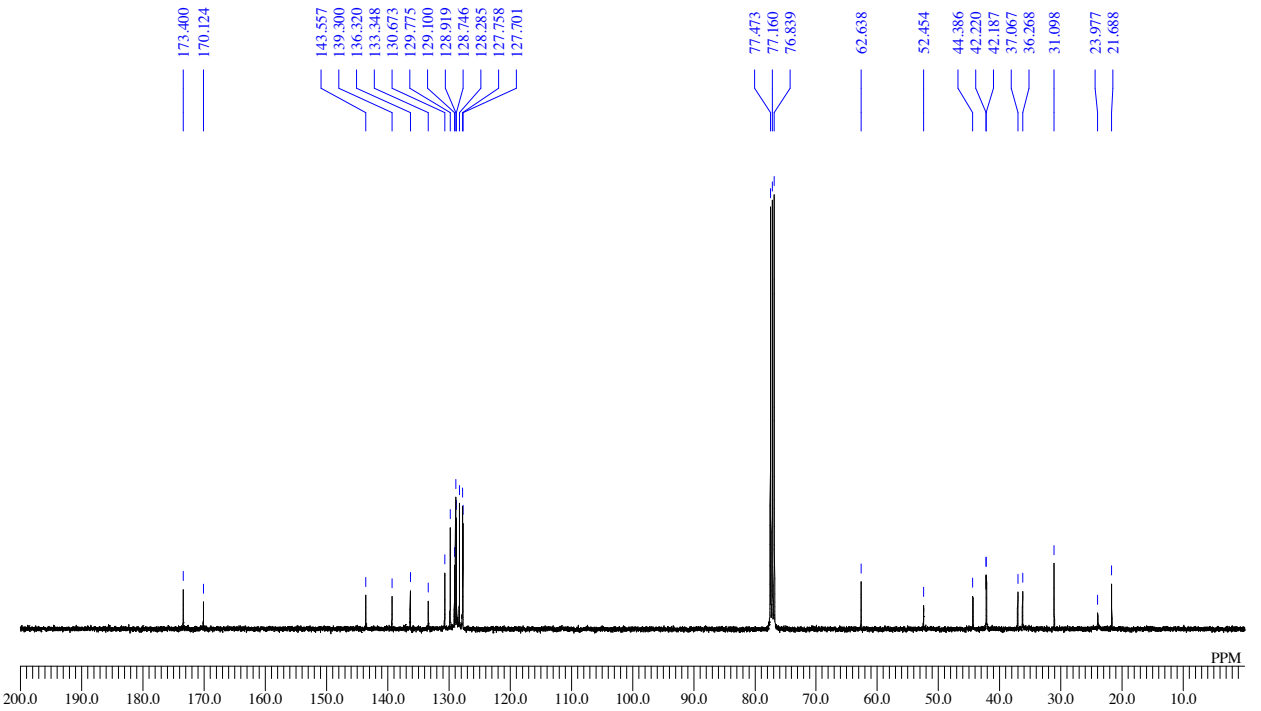


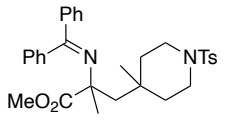
54

^{1}H NMR: (400 MHz, $CDCl_3$)



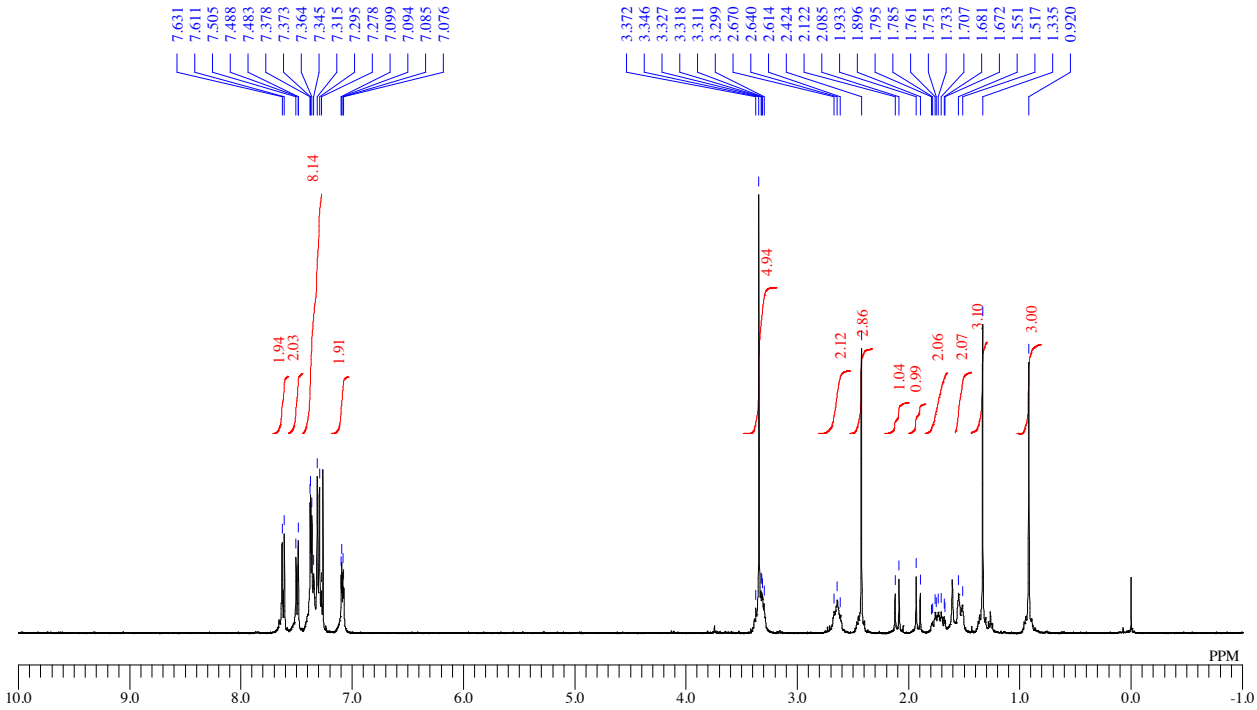
^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$)



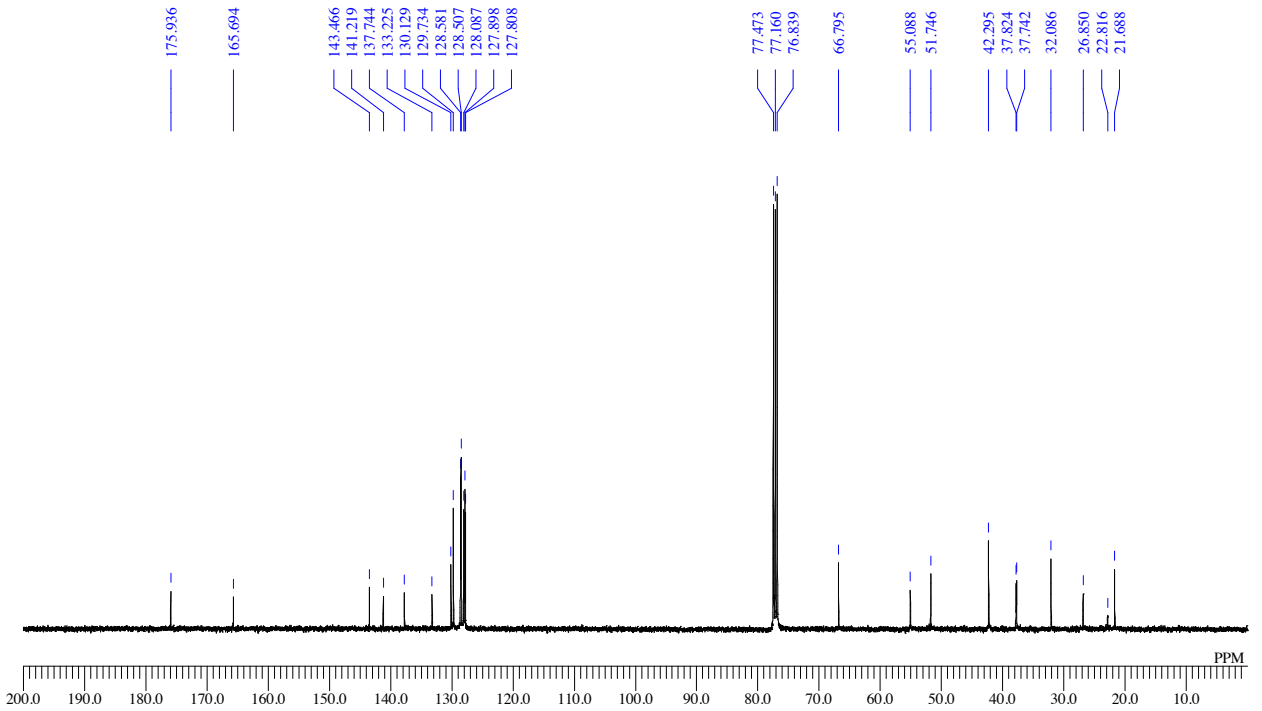


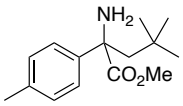
55

^{1}H NMR: (400 MHz, $CDCl_3$)



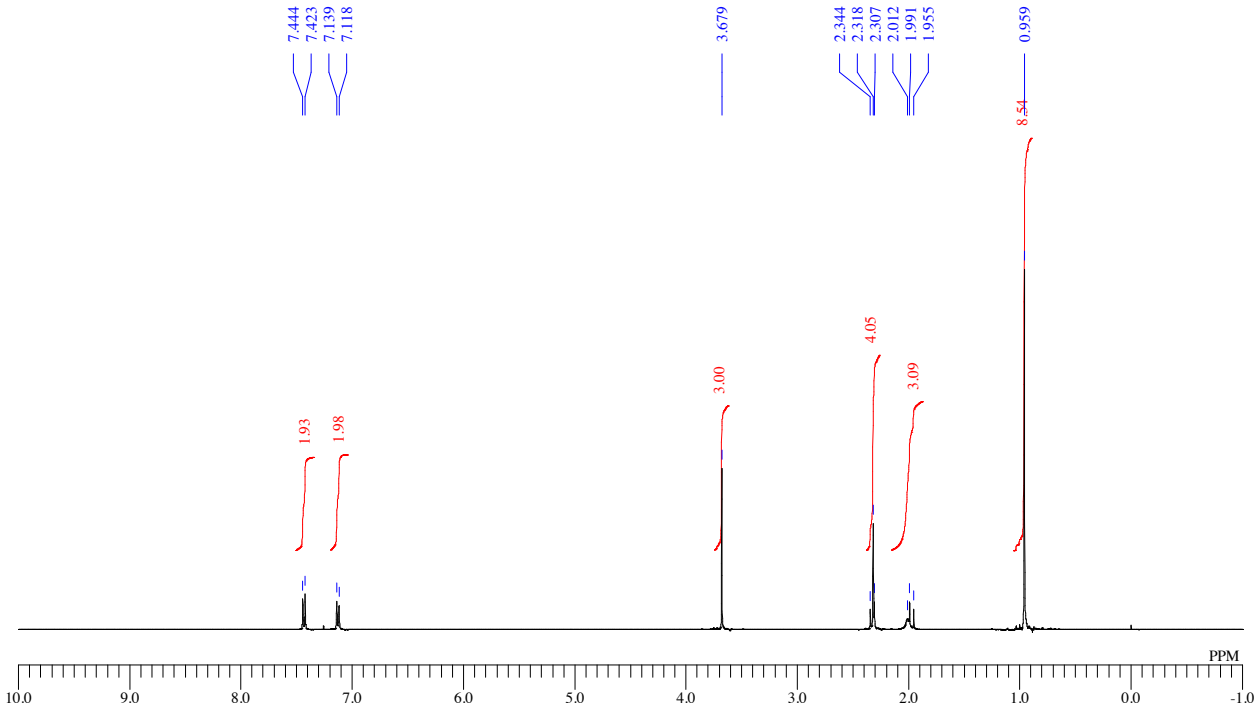
^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$)



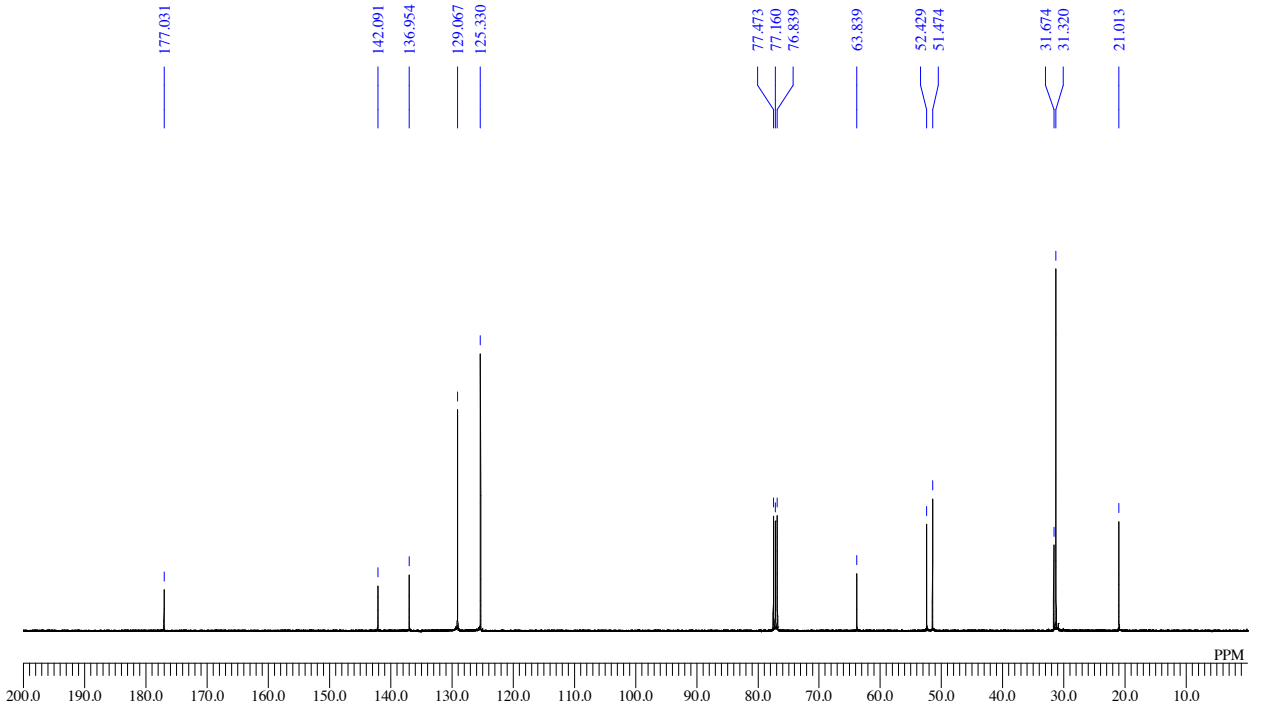


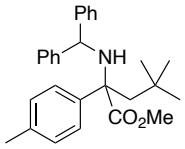
56

^{1}H NMR: (400 MHz, $CDCl_3$)



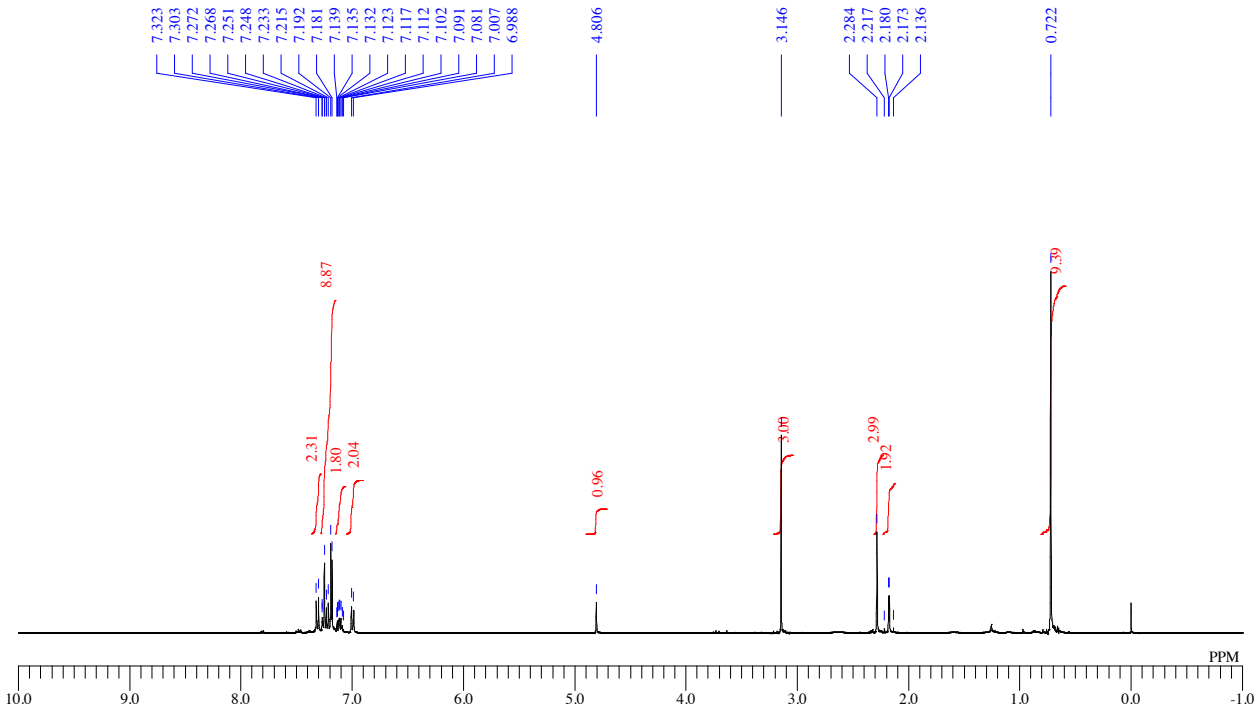
^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$)



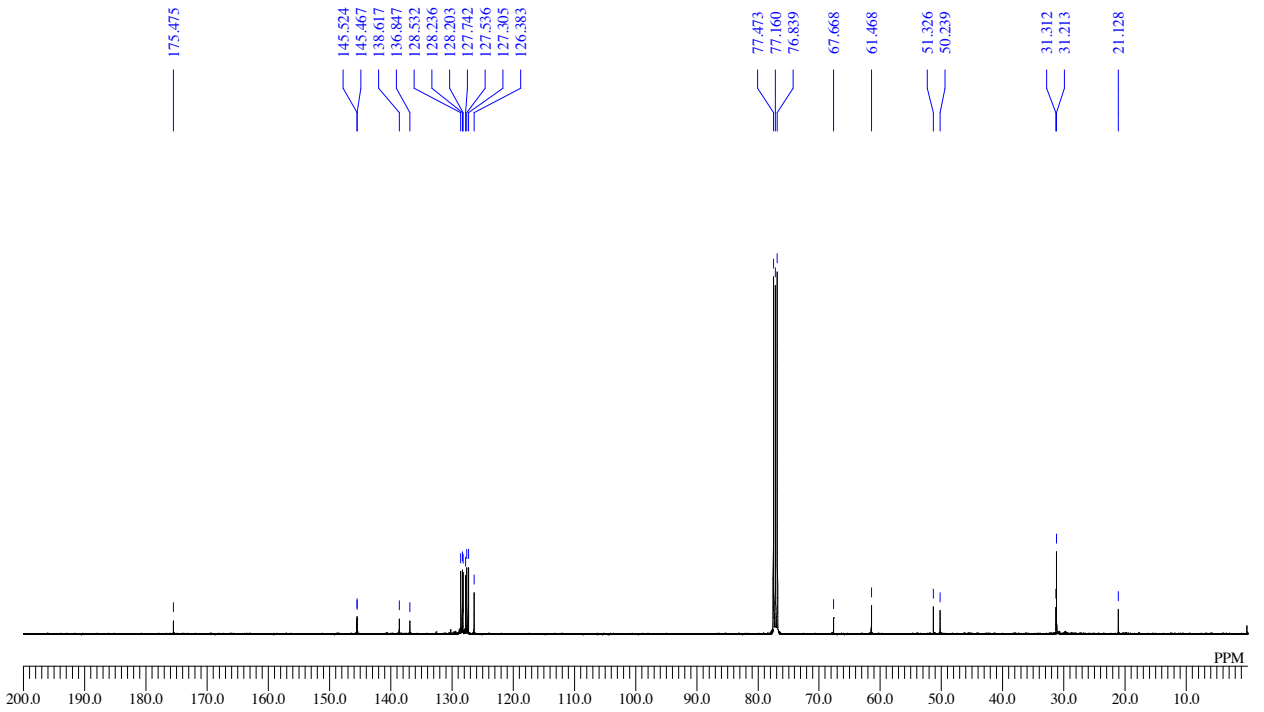


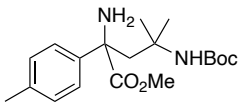
57

^{1}H NMR: (400 MHz, $CDCl_3$)



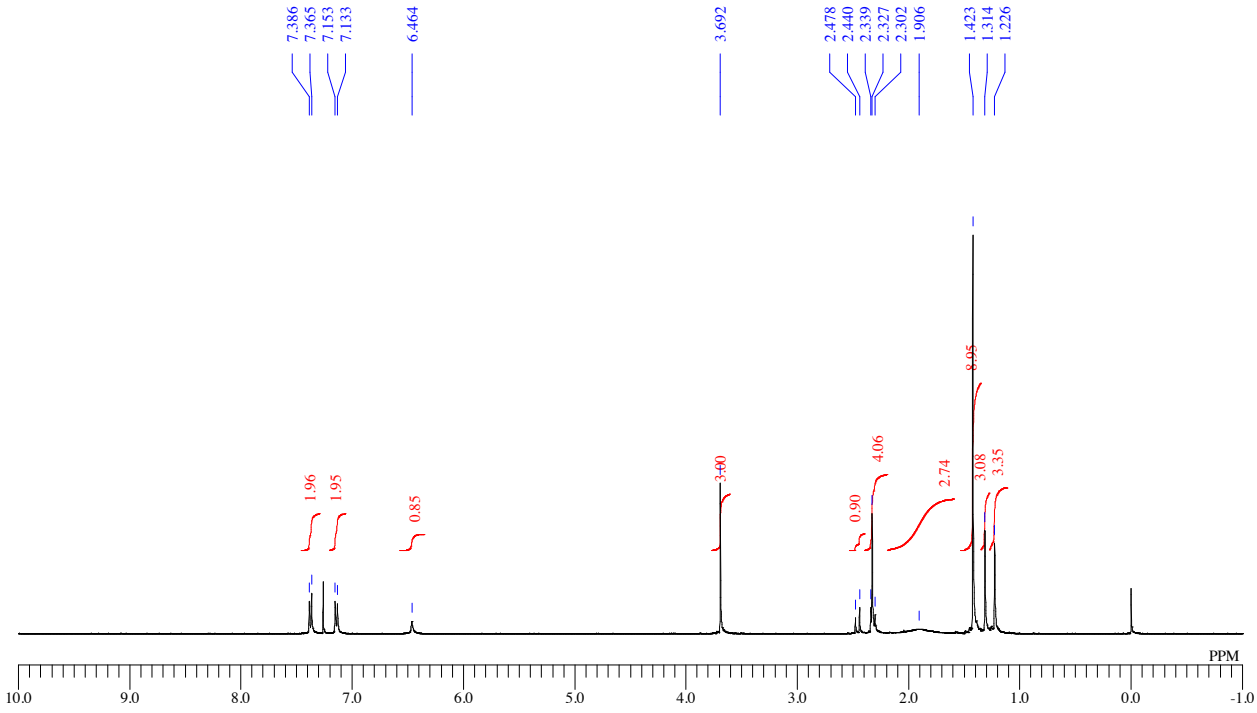
^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$)



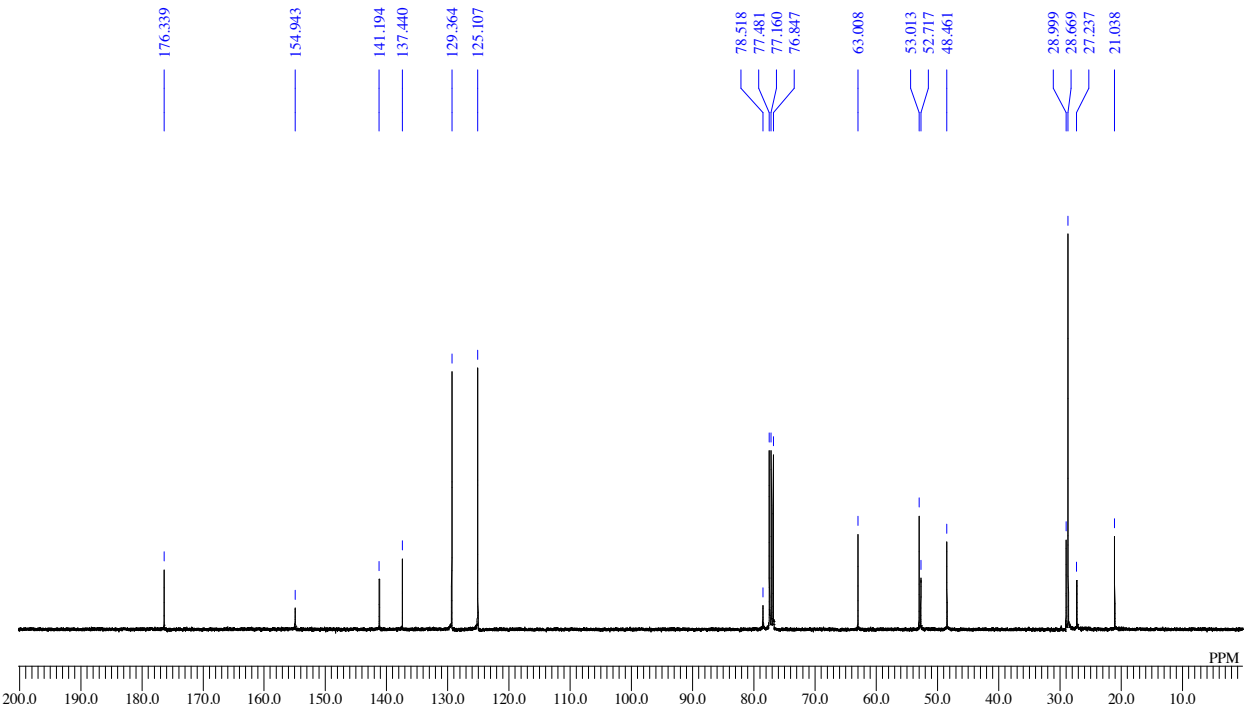


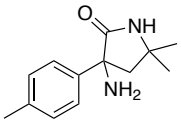
58

^{1}H NMR: (400 MHz, $CDCl_3$)



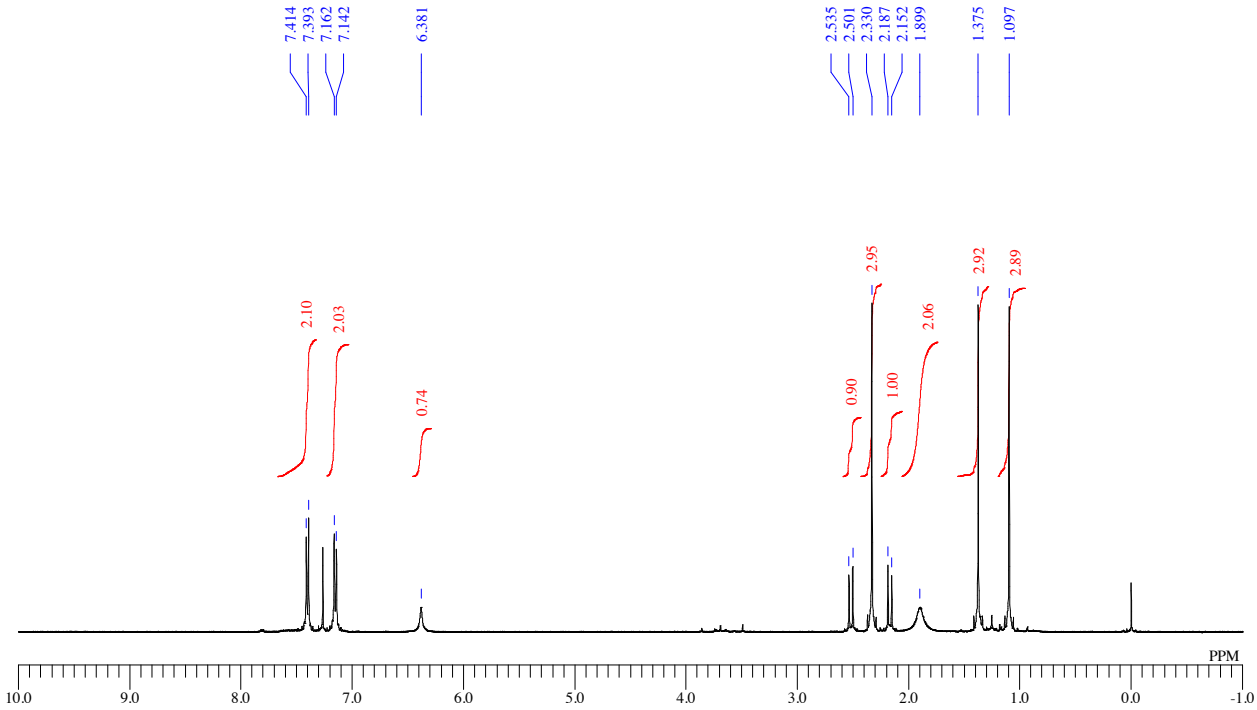
^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$)



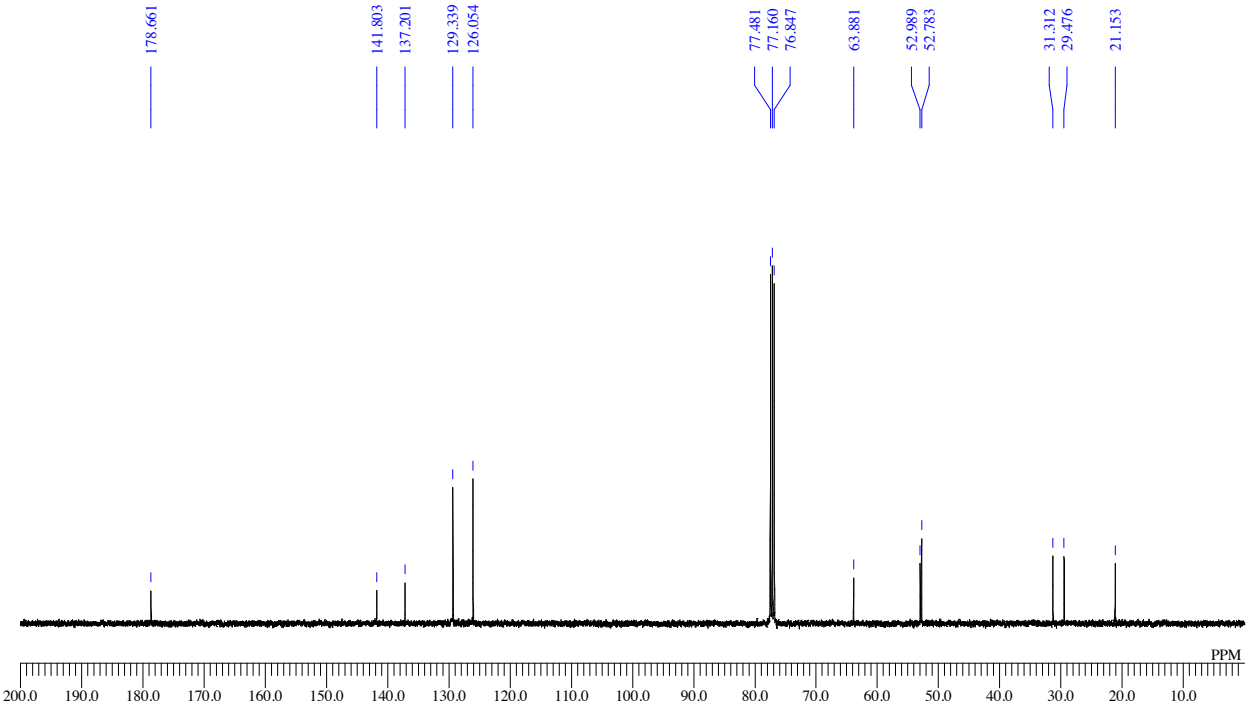


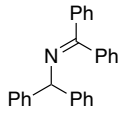
59

^{1}H NMR: (400 MHz, $CDCl_3$)



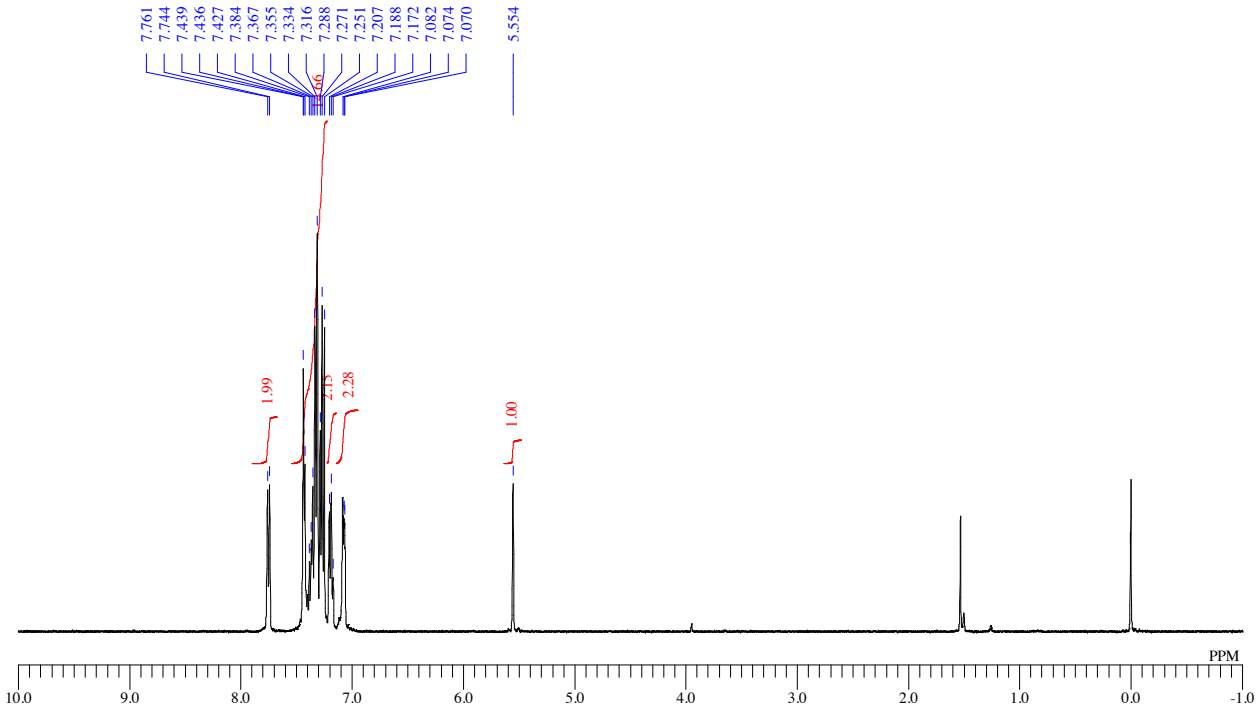
^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$)



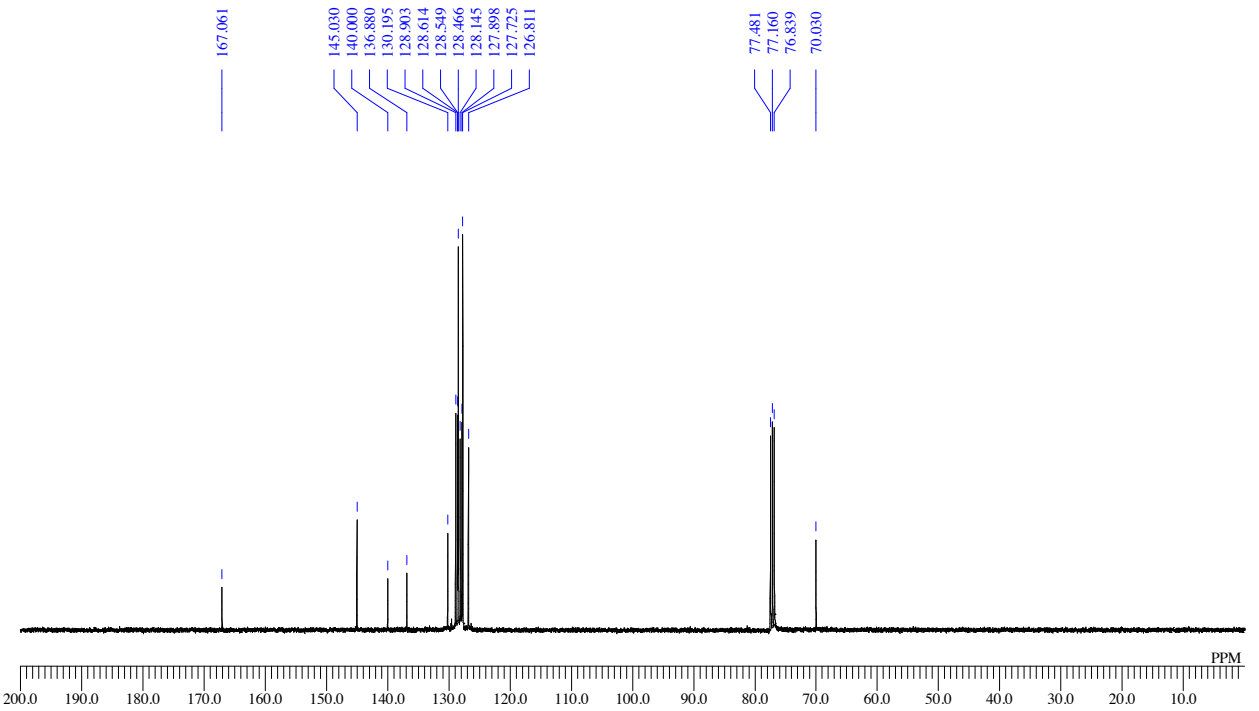


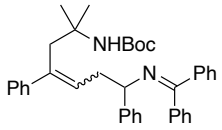
64

^{1}H NMR: (400 MHz, $CDCl_3$)



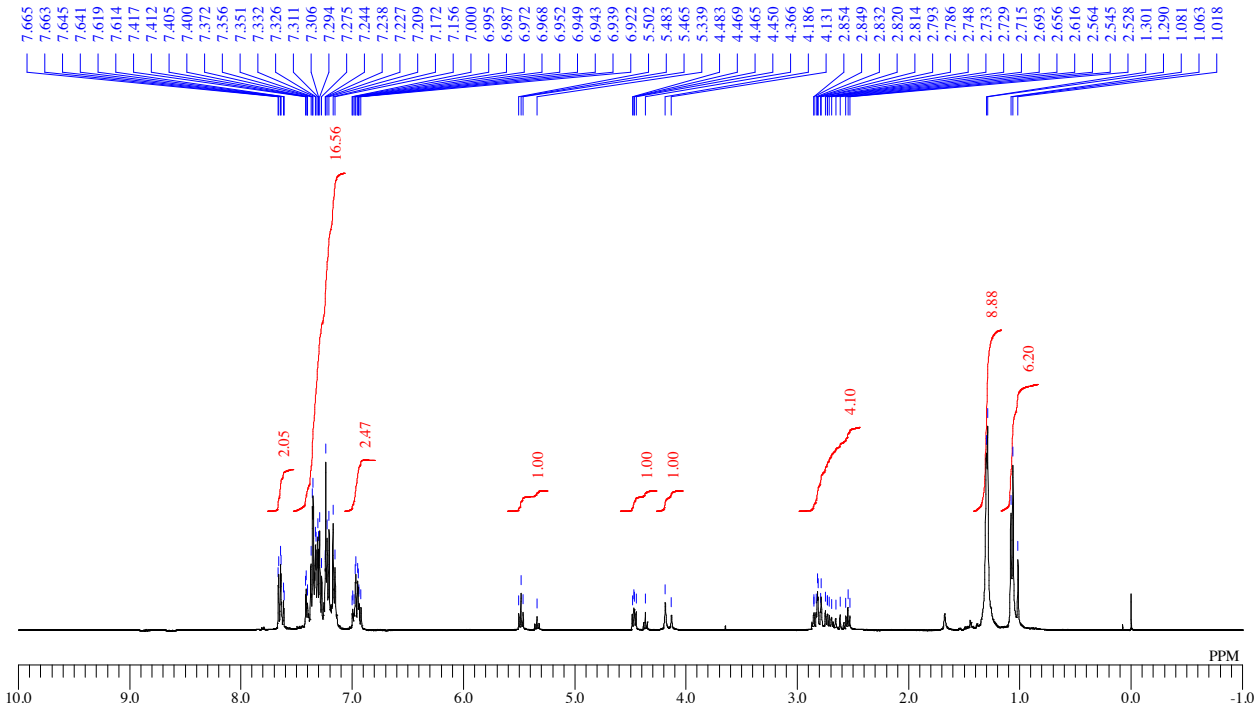
$^{13}C\{^{1}H\}$ NMR: (100 MHz, $CDCl_3$)





67

^{1}H NMR: (400 MHz, $CDCl_3$)



^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$)