Supporting Information

Rhodium-Catalyzed Cross-Coupling Reaction of Arylboronates and Diazoesters and Tandem Alkylation Reaction for the Synthesis of Quaternary α,α-Heterodiaryl Carboxylic Esters

Yuk-Tai Tsoi, Zhongyuan Zhou and Wing-Yiu Yu*

State Key Laboratory for Chirosciences and Open Laboratory of Chirotechnology of the Institute of Molecular Technology for Drug Discovery and Synthesis, Department of Applied Biology and Chemical Technology, Hong Kong Polytechnic University, Hung Hom, Kowloon, Hong Kong

Email: bcwyyu@inet.polyu.edu.hk

Table of Content

1. General Experimental Section:

All catalytic reactions were carried out under a nitrogen atmosphere. All diazoesters were prepared according to the literature.[1] Boronates **2a** and **2h** were obtained commercially and used as received without purification. Other arylboronic pinacol esters were prepared by reacting the corresponding arylboronic acids with pinacol in acetone at room temperature. Bromides **3b** and **3c** were prepared according to the literature.[1b] Other halides were obtained commercially and used as received without purification. $[Rh(cod)Cl]_2$,[2a] $[Rh(cod)OH]_2$[2b] and $[Rh(cod)OMe]_2$[2c] were prepared according to the literature.

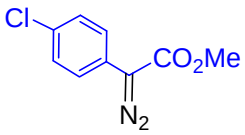
Thin layer chromatography was performed on silica gel plates. Silica gel (Merck, 230-400 mesh) was used for flash column chromatography. ^1H and ^{13}C NMR spectra were recorded on a Brüker (400 MHz) NMR spectrometer. The chemical shift (δ) values are given in ppm and are referenced to residual solvent peaks. Coupling constants (*J*) were reported in hertz (Hz). Mass spectra and high resolution mass spectra (HRMS) were obtained on a VG MICROMASS Fison VG platform, a Finnigan Model Mat 95 ST instrument, or a Brüker APEX 47e FT-ICR mass spectrometer. Melting points were measured on a Büchi Melting Point B-545 machine. Infra-red spectra were obtained by a Brüker Vector 22 FT-IR spectrometer. X-ray crystal structure of **4p** was obtained by a Brüker CCD area detector diffractometer.

2. General Experimental Procedures and Physical Characterization:

2.1 Preparation of diazoesters:[1]

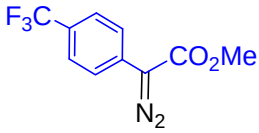
α-Aryldiazoesters were prepared by reaction of α-arylacetate (10 mmol) with *p*-acetamidobencenesulfonylazide (12 mmol) and DBU (14 mmol) in CH_3CN at room temperature. The reaction was monitored by TLC. Upon complete consumption of the starting materials, the reaction mixture was diluted with distilled water (20 mL), followed by extraction with diethyl ether (3 × 10 mL). After washing with 10% $NaHCO_3$ solution (3 × 10 mL) and brine (3 × 10 mL), the combined organic extracts were dried over $MgSO_4$ and concentrated by rotary evaporation. The residue was purified by flash chromatography to afford the diazoesters.

Methyl 4-chlorophenyldiazoacetate (1a)[3b]



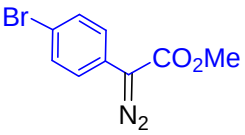
Eluant: 90% *n*-Hexane/10% diethyl ether. The product was obtained as an orange solid (90% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.42 (d, J = 8.4 Hz, 2H), 7.35 (d, J = 8.8 Hz, 2H), 3.87 (s, 3H) ^{13}C NMR (100 MHz, $CDCl_3$):δ_C 165.2, 131.5, 129.1, 125.0, 124.1, 52.0 IR (neat, cm^{-1}): 2096.6, 1698.2

Methyl 4-(trifluoromethyl)phenyldiazoacetate (1b)[3b]



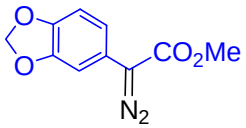
Eluant: 90% *n*-Hexane/10% diethyl ether. The product was obtained as a yellow solid (91% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.61 (s, 4H), 3.89 (s, 3H) ^{13}C NMR (100 MHz, $CDCl_3$):δ_C 164.7, 130.0, 125.8, 125.8, 125.7, 123.3, 52.1 ^{19}F NMR (400 MHz, $CDCl_3$):δ_F –62.5. IR (neat, cm^{-1}): 2106.7, 1689.4.

Methyl 4-bromophenyldiazoacetate (1c)[3b]



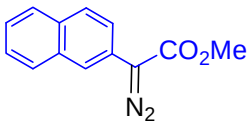
Eluant: 90% *n*-Hexane/10% diethyl ether. The product was obtained as an orange solid (82% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.49 (d, J = 8.0 Hz, 2H), 7.35 (d, J = 8.8 Hz, 2H), 3.86 (s, 3H) ^{13}C NMR (100 MHz, $CDCl_3$):δ_C 165.1, 132.0, 125.3, 124.6, 119.3, 52.1 IR (neat, cm^{-1}): 2094.8, 1698.0

Methyl (1,3-benzodioxole)diazoacetate (1d) [3a]



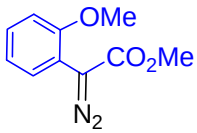
Eluant: 90% *n*-Hexane/10% diethyl ether. The product was obtained as an orange solid (45% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.05 (s, 1H), 6.84-6.85 (m, 2H), 5.97 (s, 2H), 3.85 (s, 3H) ^{13}C NMR (100 MHz, $CDCl_3$):δ_C 165.9, 148.4, 146.1, 118.5, 117.9, 108.8, 105.8, 101.3, 52.0 IR (neat, cm^{-1}): 2086.0, 1703.0.

Methyl 2-naphthyldiazoacetate (1e) [3a]



Eluant: 90% *n*-Hexane/10% diethyl ether. The product was obtained as an orange solid (75% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 8.02 (s, 1H), 7.79-7.87 (m, 3H), 7.43-7.55 (m, 3H), 3.91 (s, 3H) ^{13}C NMR (100 MHz, $CDCl_3$):δ_C 165.7, 133.6, 131.5, 128.7, 127.6, 127.6, 126.6, 125.8, 122.6, 122.6, 121.9, 52.0 IR (neat, cm^{-1}): 2101.8, 1701.0.

Methyl 2-Methoxyphenyldiazoacetate (1f) [1b]

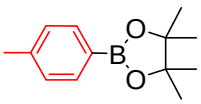


Eluant: 90% *n*-Hexane/10% ethyl acetate. The product was obtained as an orange liquid (80% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.55 (d, J = 7.7 Hz, 1H), 7.26 (t, J = 7.8 Hz, 1H), 7.02 (t, J = 7.6 Hz, 1H), 6.89 (d, J = 8.2 Hz, 1H), 3.86 (s, 3H), 3.84 (s, 3H) ^{13}C NMR (100 MHz, $CDCl_3$):δ_C 169.1, 157.9, 132.6, 131.1, 123.6, 116.1, 113.3, 58.0, 54.4. IR (neat, cm^{-1}): 2093.6, 1697.2.

2.2 Preparation of arylboronic pinacol esters 2b-2g, 2i:

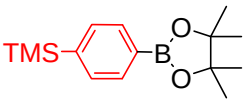
Arylboronic pinacol esters **2b-2g, 2i** were prepared by reacting the corresponding arylboronic acids (10 mmol) with pinacol (15 mmol) in acetone (20 mL) at room temperature for overnight. The reaction mixture was concentrated under reduced pressure and was purified by flash chromatography to afford the arylboronic pinacol esters.

4-tolylboronic pinacol ester (2b)



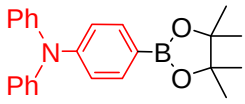
Eluant: 90% *n*-Hexane/10% diethyl ether. The product was obtained as a white solid (91% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.71 (d, J = 7.6 Hz, 2H), 7.19 (d, J = 7.6 Hz, 2H), 2.37 (s, 3H), 1.34 (s, 12H) ^{13}C NMR (100 MHz, $CDCl_3$):δ_C 141.4, 134.8, 128.5, 83.6, 24.8, 21.7

4-(trimethylsilyl)phenylboronic pinacol ester (2c)



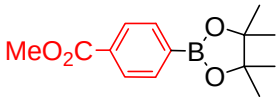
Eluant: 90% *n*-Hexane/10% diethyl ether. The product was obtained as a white solid (90% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.79 (d, J = 7.6 Hz, 2H), 7.53 (d, J = 7.6 Hz, 2H), 1.34 (s, 12H), 0.27 (s, 9H) ^{13}C NMR (100 MHz, $CDCl_3$):δ_C 144.2, 133.8, 132.6, 83.7, 24.8, -1.26

4-(diphenylamino)phenylboronic pinacol ester (2d)



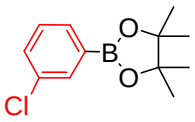
Eluant: 90% *n*-Hexane/10% diethyl ether. The product was obtained as a colorless gummy liquid (82% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.67 (d, J = 8.4 Hz, 2H), 7.24-7.28 (m, 4H), 7.10-7.12 (m, 4H), 7.03-7.07 (m, 4H), 1.34 (s, 12H) ^{13}C NMR (100 MHz, $CDCl_3$):δ_C 150.6, 147.4, 135.8, 129.3, 125.0, 123.4, 121.8, 83.6, 24.9

4-(methoxycarbonyl)phenylboronic pinacol ester (2e)



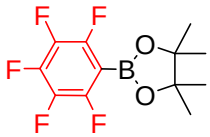
Eluant: 90% *n*-Hexane/10% ethyl acetate. The product was obtained as a white solid (88% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 8.02 (d, J = 8.0 Hz, 2H), 7.87 (d, J = 8.4 Hz, 2H), 3.92 (s, 3H), 1.36 (s, 12H) ^{13}C NMR (100 MHz, $CDCl_3$):δ_C 167.1, 134.7, 132.3, 128.6, 84.2, 52.1, 24.9

3-chlorophenylboronic pinacol ester (2f)



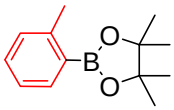
Eluant: 90% *n*-Hexane/10% diethyl ether. The product was obtained as a white solid (92% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.77 (s, 1H), 7.66 (d, J = 7.2 Hz, 1H), 7.40-7.43 (m, 1H), 7.27-7.31 (m, 1H), 1.34 (s, 12H) ^{13}C NMR (100 MHz, $CDCl_3$):δ_C 134.5, 134.0, 132.6, 131.2, 129.2, 84.1, 24.8

pentafluorophenylboronic pinacol ester (2g)



Eluant: 90% *n*-Hexane/10% diethyl ether. The product was obtained as a white solid (90% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 1.38 (s, 12H) ^{13}C NMR (100 MHz, $CDCl_3$):δ_C 84.9, 24.7 ^{19}F NMR (400 MHz, $CDCl_3$):δ_F –129.5 (m), –149.8 (m), –162.0 (m)

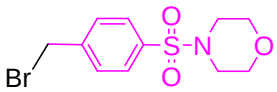
2-methylphenylboronic pinacol ester (2i)



Eluant: 90% *n*-Hexane/10% diethyl ether. The product was obtained as a colorless liquid (87% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.76-7.78 (m, 1H), 7.32 (t, J = 6.4 Hz, 1H), 7.15-7.18 (m, 2H), 2.55 (s, 3H), 1.35 (s, 12H) ^{13}C NMR (100 MHz, $CDCl_3$):δ_C 144.8, 135.8, 130.6, 129.7, 124.7, 83.4, 24.9, 22.2

2.3 Preparation of 4-(bromomethyl)benzene-1-sulfonylmorpholine (3b)[1b]:

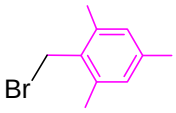
Morpholine (10 mmol) and Et_3N (11 mmol) were dissolved in Et_2O (10 mL), and the solution was stirred at 0°C. To the Et_2O solution, 4-(bromomethyl)benzene-1-sulfonyl chloride (11 mmol) in Et_2O (10 mL) was slowly added. After stirring for 6 h at room temperature, the reaction mixture was filtered and the solvent was removed by rotary evaporation. The residue was purified by flash column chromatography.



Eluant: 80% *n*-Hexane/20% ethyl acetate. The product was obtained as a white solid (80% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.73 (d, J = 7.8 Hz, 2H), 7.57 (d, J = 7.7 Hz, 2H), 4.51 (s, 2H), 3.75 (bs, 4H), 3.02 (bs, 4H) ^{13}C NMR (100 MHz, $CDCl_3$):δ_C 145.4(C), 137.5(C), 132.1(C-H), 130.8(C-H), 68.5(CH_2), 48.4(CH_2), 33.8(CH_2).

2.4 Preparation of (1,3,5-trimethylphenyl)methyl bromide (3c) [1b]:

Benzyl bromides **3c** were prepared by reacting the corresponding alcohols (25 mmol) with PBr_3 (10 mmol) in THF at 0°C. The reaction was monitored by TLC, when the starting materials were completely consumed, the reaction mixture was diluted with distilled water (20 mL), followed by extraction with DCM (3 × 10 mL). The combined organic extracts were dried over $MgSO_4$ and concentrated by rotary evaporation. The residue was purified by distillation to afford the aryl bromides.



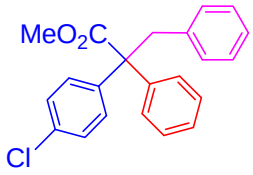
The product was obtained as a white solid (84% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 6.90 (s, 2H), 4.60 (s, 2H), 2.42 (s, 6H), 2.31 (s, 3H) ^{13}C NMR (100 MHz, $CDCl_3$):δ_C 140.9, 139.9, 133.5, 131.7, 32.2, 23.5, 21.6.

2.5 A general procedure for the rhodium-catalyzed three-component coupling reaction of arylboronates, diazoesters and alkyl halides for the synthesis of α,α-heterodiaryl carboxylic esters

All the catalytic reactions were carried out under a nitrogen atmosphere. In a 8 mL-reaction vial with a Teflon-lined cap, $[Rh(cod)OH]_2$ (1 mol %) and KO*t*Bu (3 equiv) were pre-mixed in MTBE (0.5 mL) at room temperature for 2 min. Afterwards, arylboronic pinacol ester (3 equiv) dissolved in a minimum amount of MTBE was added to the reaction vial, and the mixture was stirred for 2 min. Then diazoester (0.2 mmol, 1 equiv) and benzyl/alkyl halide (3 equiv) dissolved in a minimum amount of MTBE separately were added to the reaction vial. The reaction mixture (c.a. 1 – 2 mL) was heated in a 40 °C oil bath for 4 h. The reaction mixture was cooled down to room temperature and the organic mixture was extracted with ethyl acetate. The combined organic layers were dried over Na_2SO_4 and evaporated. The mixture was passed through a short plug of silica with 50 mL of the eluant used for flash chromatography. The filtrate was concentrated by rotary evaporation. For separation of arylboronic pinacol ester

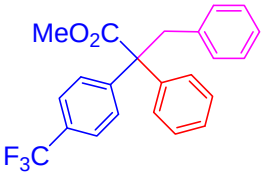
from the crude mixture, methanol (2 mL) was added to the mixture with 4.5 M aqueous potassium hydrogen fluoride (5.7 equiv) in a reaction vial for 20 min to react all unconsumed arylboronic pinacol ester as potassium aryltrifluoroborate for separation.[4] The organic mixture was extracted with DCM. The combined organic layers were dried over Na_2SO_4 and evaporated. The mixture was purified by flash chromatography on a silica gel column to give the desired product.

methyl 2-(4-chlorophenyl)-2,3-diphenylpropanoate (4a)



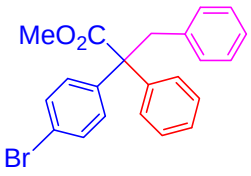
Eluant: 95% *n*-hexane/ 5% diethyl ether. The product was obtained as a white solid (86%). Melting point:100.5 – 101.4 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.28 (s, 3H), 7.20-7.23 (m, 4H), 7.06-7.15 (m, 5H), 6.70 (d, J = 7.2 Hz, 2H), 3.82 (d, J = 12.8 Hz, 1H), 3.73 (s, 3H), 3.62 (d, J = 12.8 Hz, 1H) ^{13}C NMR (100 MHz, $CDCl_3$):δ_C 173.6(C=O), 142.4(C), 141.2(C), 136.9(C), 132.8(C), 130.8(C-H), 130.7(C-H), 128.9(C-H), 127.9(C-H), 127.6(C-H), 127.6(C-H), 127.1(C-H), 126.4(C-H), 61.6(C), 52.3(CH_3), 44.3(CH_2). IR (KBr, cm^{-1}): 1721.4. LRMS (EI): 91.1, 165.1, 178.1, 199.0, 231.0, 259.0, 291.1, 350.1. HRMS (ESI): calcd. for $C_{22}H_{19}O_2NaCl$: 373.0971, found: 373.0986.

methyl 2-(4-(trifluoromethyl)phenyl)-2,3-diphenylpropanoate (4b)



Eluant: 95% *n*-hexane/ 5% diethyl ether. The product was obtained as a white solid (85%). Melting point: 55.2 – 56.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.48 (d, J = 8.0 Hz, 2H), 7.22-7.31 (m, 7H), 7.07-7.15 (m, 3H), 6.69 (d, J = 7.2 Hz, 2H), 3.92 (d, J = 12.8 Hz, 1H), 3.75 (s, 3H), 3.61 (d, J = 12.8 Hz, 1H) ^{13}C NMR (100 MHz, $CDCl_3$):δ_C 173.4(C=O), 146.7(C), 142.1(C), 136.7(C), 130.6(C-H), 129.9(C-H), 128.8(C-H), 128.0(C-H), 127.7(C-H), 127.3(C-H), 126.6(C-H), 124.4(C), 124.4(C-H), 124.3(C-H), 124.3(C), 62.0(C), 52.4(CH_3), 44.3(CH_2). ^{19}F NMR (400 MHz, $CDCl_3$):δ_F –62.5. IR (KBr, cm^{-1}): 1726.6. LRMS (EI): 91.1, 165.1, 178.1, 233.0, 265.1, 293.1, 325.1, 384.2. HRMS (ESI): calcd. for $C_{23}H_{19}O_2NaF_3$: 407.1235, found: 407.1239.

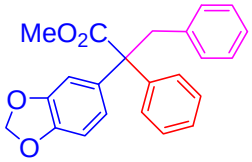
methyl 2-(4-bromophenyl)-2,3-diphenylpropanoate (4c)



Eluant: 95% *n*-hexane/ 5% diethyl ether. The product was obtained as a white solid (84%). Melting point: 101.7 – 102.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.36 (d, J = 7.6 Hz, 2H), 7.28 (bs,

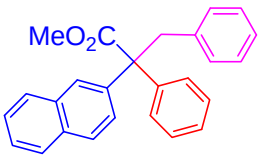
3H), 7.22 (bs, 2H), 7.07-7.15 (m, 3H), 7.01 (d, J = 7.2 Hz, 2H), 6.70 (d, J = 7.2 Hz, 2H), 3.81 (d, J = 12.8 Hz, 1H), 3.72 (s, 3H), 3.61 (d, J = 12.8 Hz, 1H) ^{13}C NMR (100 MHz, $CDCl_3$):δ_C 173.5(C=O), 142.3(C), 141.8(C), 136.8(C), 131.2(C-H), 130.7(C-H), 130.6(C-H), 128.9(C-H), 127.9(C-H), 127.6(C-H), 127.1(C-H), 126.4(C-H), 120.9(C), 61.7(C), 52.3(CH_3), 44.3(CH_2). IR (KBr, cm^{-1}): 1724.7. LRMS (EI): 91.1, 165.1, 178.1, 275.0, 303.0, 335.0, 394.0. HRMS (ESI): calcd. for $C_{22}H_{19}O_2NaBr$: 417.0466, found: 417.0469.

methyl 2-(benzo[d][1,3]dioxol-6-yl)-2,3-diphenylpropanoate (4d)



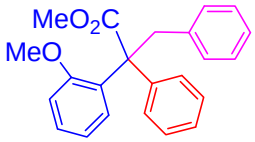
Eluant: 95% *n*-hexane/ 5% diethyl ether. The product was obtained as a colorless gummy liquid (88%). ^{1}H NMR (400 MHz, $CDCl_3$): 7.24-7.25 (m, 3H), 7.78-7.84 (m, 5H), 6.72-6.75 (m, 5H), 5.95 (s, 2H), 3.73-3.78 (m, 4H), 3.64 (d, J = 12.8 Hz, 1H) ^{13}C NMR (100 MHz, $CDCl_3$):δ_C 173.9(C=O), 147.1(C), 146.3(C), 142.7(C), 137.2(C), 136.7(C), 130.8(C-H), 129.2(C-H), 127.6(C-H), 127.4(C-H), 126.8(C-H), 126.3(C-H), 122.4(C-H), 110.1(C-H), 107.3(C-H), 101.0(CH_2), 61.7(C), 52.2(CH_3), 44.6(CH_2). IR (KBr, cm^{-1}): 1730.9. LRMS (EI): 91.1, 152.1, 209.0, 241.1, 269.1, 291.1, 301.1, 360.1. HRMS (ESI): calcd. for $C_{23}H_{20}O_4Na$: 383.1259, found: 383.1274.

methyl 2-(naphthalen-2-yl)-2,3-diphenylpropanoate (4e)



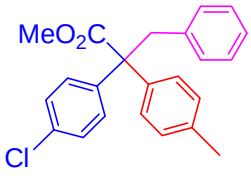
Eluant: 95% *n*-hexane/ 5% diethyl ether. The product was obtained as a colorless gummy liquid (85%). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.78-7.84 (m, 3H), 7.72 (d, J = 8.4 Hz, 1H), 7.49-7.51 (m, 2H), 7.26-7.29 (m, 4H), 7.11-7.19 (m, 3H), 7.04-7.07 (m, 2H), 6.72 (d, J = 7.2 Hz, 2H), 3.98 (d, J = 12.8 Hz, 1H), 3.77 (d, J = 12.8 Hz, 1H), 3.74 (s, 3H) ^{13}C NMR (100 MHz, $CDCl_3$):δ_C 173.9(C=O), 142.5(C), 140.1(C), 137.2(C), 132.8(C), 132.2(C), 130.8(C-H), 129.4(C-H), 128.3(C-H), 127.7(C-H), 127.7(C-H), 127.6(C-H), 127.5(C-H), 127.3(C-H), 127.1(C-H), 126.8(C-H), 126.3(C-H), 126.1(C-H), 126.0(C-H), 62.1(C), 52.2(CH_3), 44.4(CH_2). IR (KBr, cm^{-1}): 1730.8. LRMS (EI): 91.1, 215.1, 275.1, 307.1, 366.1. HRMS (ESI): calcd. for $C_{26}H_{22}O_2Na$: 389.1517, found: 389.1524.

methyl 2-(2-methoxyphenyl)-2,3-diphenylpropanoate (4f)



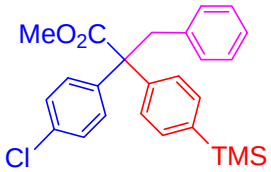
Eluant: 90% *n*-hexane/ 10% diethyl ether. The product was obtained as a white solid (61%). Melting point: 96.5 – 97.9 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.61 (d, J = 7.6 Hz, 2H), 7.22-7.33 (m, 4H), 6.99-7.07 (m, 4H), 6.85 (t, J = 7.4 Hz, 1H), 6.74-6.78 (m, 3H), 4.03 (d, J = 13.2 Hz, 1H), 3.62 (s, 3H), 3.50 (d, J = 13.2 Hz, 1H), 3.37 (s, 3H) ^{13}C NMR (100 MHz, $CDCl_3$):δ_C 174.4(C=O), 157.4(C), 141.6(C), 137.9(C), 131.8(C), 130.9(C-H), 129.8(C-H), 129.4(C-H), 128.2(C-H), 127.6(C-H), 127.1(C-H), 126.8(C-H), 125.9(C-H), 119.3(C-H), 111.7(C-H), 58.4(C), 55.0(CH_3), 51.8(CH_3), 42.6(CH_2). IR (KBr, cm^{-1}): 1726.1. LRMS (EI): 91.1, 152.1, 165.1, 195.1, 255.1, 287.1, 346.1. HRMS (ESI): calcd. for $C_{23}H_{22}O_3Na$: 369.1467, found: 369.1483.

methyl 2-(4-chlorophenyl)-3-phenyl-2-p-tolylpropanoate (4g)



The reaction was run for 3 h. Eluant: 95% *n*-hexane/ 5% diethyl ether. The product was obtained as a white solid (81%). Melting point: 120.4 – 121.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.09-7.18 (m, 9H), 7.01 (d, J = 8.4 Hz, 2H), 6.70 (d, J = 7.2 Hz, 2H), 3.86 (d, J = 12.8 Hz, 1H), 3.71 (s, 3H), 3.52 (d, J = 12.8 Hz, 1H), 2.36 (s, 3H) ^{13}C NMR (100 MHz, $CDCl_3$):δ_C 173.7(C=O), 141.3(C), 139.5(C), 137.0(C), 136.8(C), 132.6(C), 130.9(C-H), 130.8(C-H), 128.7(C-H), 127.6(C-H), 127.5(C-H), 126.4(C-H), 61.3(C), 52.2(CH_3), 44.3(CH_2), 20.9(CH_3). IR (KBr, cm^{-1}): 1724.7. LRMS (EI): 91.1, 178.1, 213.0, 245.1, 273.1, 305.1, 364.1. HRMS (ESI): calcd. for $C_{23}H_{21}O_2NaCl$: 387.1128, found: 387.1115.

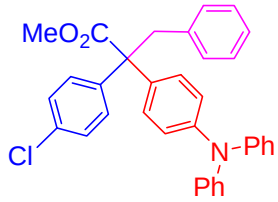
methyl 2-(4-chlorophenyl)-2-(4-(trimethylsilyl)phenyl)-3-phenylpropanoate (4h)



Eluant: 95% *n*-hexane/ 5% diethyl ether. The product was obtained as a colorless gummy liquid (81%). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.46 (d, J = 7.6 Hz, 2H), 7.04-7.26 (m, 9H), 6.71 (d, J = 7.6 Hz, 2H), 3.90 (d, J = 12.8 Hz, 1H), 3.74 (s, 3H), 3.56 (d, J = 12.8 Hz, 1H), 0.32 (s, 9H) ^{13}C NMR (100 MHz, $CDCl_3$):δ_C 173.6(C=O), 142.8(C), 141.1(C), 139.3(C), 136.9(C), 133.0(C-H), 132.6(C), 130.9(C-H), 130.7(C-H), 128.0(C-H), 127.6(C-H), 127.5(C-H), 126.4(C-H), 61.6(C), 52.2(CH_3), 44.2(CH_2),

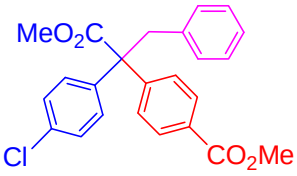
-1.16(CH_3). IR (KBr, cm^{-1}): 1733.3. LRMS (EI): 73.1, 91.1, 199.0, 303.1, 316.1, 331.1, 363.1, 422.2. HRMS (ESI): calcd. for $C_{25}H_{27}O_2NaSiCl$: 445.1367, found: 445.1375.

methyl 2-(4-(diphenylamino)phenyl)-2-(4-chlorophenyl)-3-phenylpropanoate (4i)



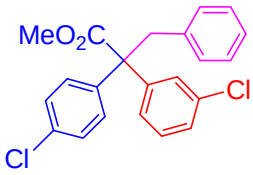
Eluant: 95% *n*-hexane/ 5% diethyl ether. The product was obtained as a white solid (67%). Melting point: 182.7 – 183.7 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.24-7.31 (m, 6H), 7.13-7.18 (m, 9H), 7.03-7.08 (m, 4H), 6.97-6.99 (m, 2H), 6.77 (d, J = 6.8 Hz, 2H), 3.73-3.76 (m, 4H), 3.66 (d, J = 12.8 Hz, 1H) ^{13}C NMR (100 MHz, $CDCl_3$):δ_C 173.7(C=O), 147.5(C), 146.6(C), 141.3(C), 137.1(C), 136.0(C), 132.7(C), 130.8(C-H), 130.7(C-H), 129.7(C-H), 129.2(C-H), 127.7(C-H), 127.6(C-H), 126.4(C-H), 124.4(C-H), 122.9(C-H), 122.6(C-H), 61.2(C), 52.3(CH_3), 44.5(CH_2). IR (KBr, cm^{-1}): 1724.3. HRMS (ESI): calcd. for $C_{34}H_{29}NO_2Cl$: 518.1887, found: 518.1865.

methyl 4-(1-(methoxycarbonyl)-1-(4-chlorophenyl)-2-phenylethyl)benzoate (4j)



The reaction was run for 9 h. Eluant: 90% *n*-hexane/ 10% ethyl acetate. The product was obtained as a light yellow gummy liquid (81%). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.92 (d, J = 8.0 Hz, 2H), 7.21-7.25 (m, 4H), 7.08-7.12 (m, 5H), 6.68 (d, J = 7.2 Hz, 2H), 3.92 (s, 3H), 3.66-3.78 (m, 5H) ^{13}C NMR (100 MHz, $CDCl_3$):δ_C 173.0(C=O), 166.7(C=O), 147.4(C), 140.7(C), 136.3(C), 133.1(C), 130.6(C-H), 130.5(C-H), 129.2(C-H), 128.9(C-H), 128.8(C), 127.9(C-H), 127.7(C-H), 126.6(C-H), 61.7(C), 52.4(CH_3), 52.0(CH_3), 44.1(CH_2). IR (KBr, cm^{-1}): 1724.9. LRMS (EI): 91.1, 289.0, 317.1, 349.1, 408.1. HRMS (ESI): calcd. for $C_{24}H_{22}O_4Cl$: 409.1207, found: 409.1217.

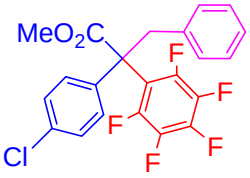
methyl 2-(3-chlorophenyl)-2-(4-chlorophenyl)-3-phenylpropanoate (4k)



Eluant: 95% *n*-hexane/ 5% diethyl ether. The product was obtained as a colorless gummy liquid (83%). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.01-7.25 (m, 11H), 6.67 (d, J = 7.2 Hz, 2H), 3.72 (s, 3H), 3.66-3.67 (m, 2H) ^{13}C NMR (100 MHz, $CDCl_3$):δ_C 173.1(C=O), 144.4(C), 140.6(C), 136.4(C), 133.8(C), 133.1(C),

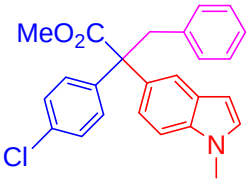
130.6(C-H), 130.5(C-H), 129.2(C-H), 129.0(C), 127.9(C-H), 127.7(C-H), 127.3(C-H), 127.3(C-H), 126.7(C-H), 61.5(C), 52.5(CH_3), 44.3(CH_2). IR (KBr, cm^{-1}): 1734.6. LRMS (EI): 91.1, 139.0, 199.0, 265.0, 293.1, 325.1, 384.1.

methyl 2-(4-chlorophenyl)-2-(perfluorophenyl)-3-phenylpropanoate (4l)



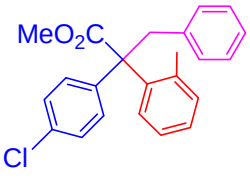
The reaction was run for 8 h. Eluant: 95% *n*-hexane/ 5% diethyl ether. The product was obtained as a white solid (66%). Melting point: 155.3 – 156.7 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.47 (d, J = 8.4 Hz, 2H), 7.33 (d, J = 8.8 Hz, 2H), 7.11-7.14 (m, 3H), 6.95-6.97 (m, 2H), 4.38 (d, J = 12.8 Hz, 1H), 3.65 (s, 3H), 3.26 (d, J = 13.2 Hz, 1H) ^{13}C NMR (100 MHz, $CDCl_3$):δ_C 171.2(C=O), 139.1(C), 135.8(C), 133.8(C), 130.2(C-H), 128.6(C-H), 128.5(C-H), 127.9(C-H), 127.2(C-H), 57.1(C), 53.0(CH_3), 40.9(CH_2). ^{19}F NMR (400 MHz, $CDCl_3$):δ_F –133.37 (d, J = 20 Hz), –154.70 (t, J = 24 Hz), –162.40 (t, J = 20 Hz) IR (KBr, cm^{-1}): 1738.4. LRMS (EI): 91.1, 321.0, 349.0, 381.0, 440.1.

methyl 2-(4-chlorophenyl)-2-(1-methyl-1H-indol-5-yl)-3-phenylpropanoate (4m)



Eluant: 90% *n*-hexane/ 10% ethyl acetate. The product was obtained as a yellow gummy liquid (57%). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.73 (s, 1H), 7.26 (d, J = 9.2 Hz, 1H), 7.10-7.16 (m, 7H), 6.98 (d, J = 7.2 Hz, 2H), 6.74 (d, J = 7.2 Hz, 2H), 6.51 (s, 1H), 4.15 (d, J = 12.8 Hz, 1H), 3.82 (s, 3H), 3.73 (s, 3H), 3.49 (d, J = 12.8 Hz, 1H) ^{13}C NMR (100 MHz, $CDCl_3$):δ_C 174.2(C=O), 142.0(C), 137.3(C), 135.7(C), 133.6(C), 132.2(C), 131.2(C-H), 130.8(C-H), 129.3(C-H), 128.0(C), 127.6(C-H), 127.2(C-H), 126.3(C-H), 122.8(C-H), 120.5(C-H), 108.8(C-H), 101.4(C-H), 61.4(C), 52.1(CH_3), 44.7(CH_2), 32.8(CH_3). IR (KBr, cm^{-1}): 1729.6. HRMS (ESI): calcd. for $C_{25}H_{23}NO_2Cl$: 404.1417, found: 404.1431.

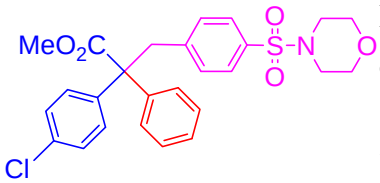
methyl 2-(4-chlorophenyl)-3-phenyl-2-o-tolylpropanoate (4n)



Eluant: 95% *n*-hexane/ 5% diethyl ether. The product was obtained as a colorless gummy liquid (76%). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.56 (s, 1H), 7.27-7.28 (m, 2H), 7.12-7.22 (m, 8H), 6.64 (d, J = 6.8 Hz, 1H), 3.91 (d, J = 12.4 Hz, 1H), 3.72 (s, 3H),

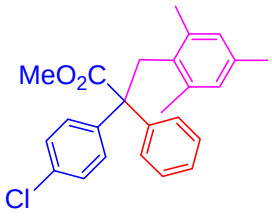
3.53 (d, J = 12.4 Hz, 1H), 1.79 (s, 3H) ^{13}C NMR (100 MHz, $CDCl_3$):δ_C 173.2(C=O), 141.3(C), 140.6C), 137.6(C), 136.2(C), 132.4(C), 132.3(C-H), 130.6(C-H), 130.6(C-H), 127.6(C), 127.6(C-H), 127.4(C-H), 127.3(C-H), 126.7(C-H), 125.7(C-H), 59.7(C), 52.1(CH_3), 46.4(CH_2), 20.9(CH_3). IR (KBr, cm^{-1}): 1728.9. LRMS (EI): 91.1, 178.1, 213.0, 245.1, 273.1, 305.1, 364.1. HRMS (ESI): calcd. for $C_{23}H_{21}O_2NaCl$: 387.1128, found: 387.1112.

methyl 2-(4-chlorophenyl)-2-phenyl-3-(phenyl-4-sulfonyl morpholino)propanoate (4p)



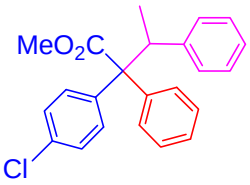
Eluant: 50% *n*-hexane/ 50% ethyl acetate. The product was obtained as a white solid (76%). Melting point: 176.2 – 177.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.42 (d, J = 8.0 Hz, 2H), 7.20-7.26 (m, 5H), 7.14 (s, 2H), 7.07 (d, J = 8.0 Hz, 2H), 6.89 (d, J = 8.0 Hz, 2H), 3.83 (d, J = 12.8 Hz, 1H), 3.72-3.75 (m, 8H), 2.90 (bs, 4H) ^{13}C NMR (100 MHz, $CDCl_3$):δ_C 173.3(C=O), 143.2(C), 141.6(C), 140.7(C), 133.1(C), 132.6(C), 131.3(C-H), 130.5(C-H), 128.9(C-H), 128.0(C-H), 127.9(C-H), 127.4(C-H), 127.0(C-H), 66.0(CH_2), 61.7(C), 52.8(CH_3), 46.0(CH_2), 44.1(CH_2). IR (KBr, cm^{-1}): 1719.8. HRMS (ESI): calcd. for $C_{26}H_{27}NO_5SCl$: 500.1298, found: 500.1297.

methyl 2-(4-chlorophenyl)-3-mesityl-2-phenylpropanoate (4q)



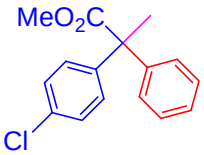
Eluant: 95% *n*-hexane/ 5% diethyl ether. The product was obtained as a white solid (61%). Melting point: 113.2 – 114.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.12-7.28 (m, 7H), 6.92-6.94 (m, 2H), 6.68 (s, 2H), 3.93 (dd, J = 12.8, 14 Hz, 2H), 3.67 (s, 3H), 2.22 (s, 3H), 1.75 (s, 6H) ^{13}C NMR (100 MHz, $CDCl_3$):δ_C 175.1(C=O), 142.1(C), 140.5(C), 138.5(C), 136.0(C), 132.7(C), 131.4(C), 131.3(C-H), 129.0(C-H), 127.7(C-H), 127.2(C-H), 127.0(C-H), 60.6(C), 52.4(CH_3), 37.2(CH_2), 20.7(CH_3), 20.4(CH_3). IR (KBr, cm^{-1}): 1733.9. LRMS (EI): 91.1, 133.1, 165.1, 259.0, 333.1, 392.1. HRMS (ESI): calcd. for $C_{25}H_{25}O_2NaCl$: 415.1441, found: 415.1459.

methyl 2-(4-chlorophenyl)-2,3-diphenylbutanoate (4r)



The product is a mixture of diastereomers in 1:1 NMR ratio. Eluant: 95% *n*-hexane/ 5% diethyl ether. The product was obtained as a yellow gummy liquid (61%). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.47 (m, 1H), 7.22-7.41 (m, 6H), 7.11-7.17 (m, 3H), 7.05 (d, J = 7.6 Hz, 1H), 6.98 (d, J = 7.2 Hz, 1H), 6.80 (d, J = 7.6 Hz, 1H), 6.75 (d, J = 7.6 Hz, 1H), 4.53-4.65 (m, 1H), 3.55, 3.58 (two set of s, 3H), 1.24 (t, J = 5.2 Hz, 3H) ^{13}C NMR (100 MHz, $CDCl_3$):δ_C 173.7(C=O), 173.6(C=O), 141.6(C), 141.5(C), 141.3(C), 140.0(C), 138.2(C), 137.0(C), 133.6(C-H), 133.0(C), 132.8(C), 131.8(C-H), 131.6(C-H), 130.6(C-H), 130.5(C-H), 129.8(C-H), 128.0(C-H), 127.8(C-H), 127.2(C-H), 127.2(C-H), 127.1(C-H), 127.0(C-H), 126.8(C-H), 126.6(C-H), 126.4(C-H), 65.9(C), 65.9(C), 52.1(CH_3), 52.0(CH_3), 42.6(CH), 42.1(CH), 17.4(CH_3), 17.0(CH_3). IR (KBr, cm^{-1}): 1731.6. LRMS (EI): 77.1, 105.1, 165.1, 199.0, 231.0, 260.0, 303.1, 364.1. HRMS (ESI): calcd. for $C_{23}H_{21}O_2NaCl$: 387.1128, found: 387.1147.

methyl 2-(4-chlorophenyl)-2-phenylpropanoate (4s)

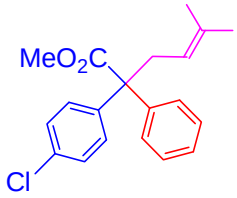


Eluant: 95% *n*-hexane/ 5% diethyl ether. The product was obtained as a light yellow gummy liquid (79%). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.27-7.33 (m, 5H), 7.16-7.22 (m, 4H), 3.74 (s, 3H), 1.93 (s, 3H) ^{13}C NMR (100 MHz, $CDCl_3$):δ_C 175.1(C=O), 144.0(C), 142.9(C), 132.7(C), 129.5(C-H), 128.2(C-H), 128.1(C-H), 127.7(C-H), 127.0(C-H), 56.1(C), 52.5(CH_3), 27.0(CH_3). IR (KBr, cm^{-1}): 1731.6. LRMS (EI): 77.1, 103.1, 165.1, 179.1, 215.1, 274.1. HRMS (ESI): calcd. for $C_{16}H_{15}O_2NaCl$: 297.0658, found: 297.0650.

2.6 A modified procedure for the synthesis of 4t

The catalytic reaction was carried out under a nitrogen atmosphere. In a 8 mL-reaction vial with a Teflon-lined cap, $[Rh(cod)OH]_2$ (10 mol % Rh) and KO*t*Bu (3 equiv) were pre-mixed in MTBE (0.5 mL) at room temperature for 2 min. Afterwards, **2a** (3 equiv) dissolved in a minimum amount of MTBE was added to the reaction vial, and the mixture was stirred for 2 min. Then, **1a** (0.2 mmol, 1 equiv) dissolved in a minimum amount of MTBE and was added to the reaction vial. 3,3-Dimethylallyl bromide (**3f**) dissolved in 1 mL of MTBE for syringe addition to the reaction vial over 1 h. The reaction mixture (ca. 1 – 2 mL) was placed in a 40 °C oil bath for 2 h. The work-up procedure was same as the standard procedure.

methyl 2-(4-chlorophenyl)-5-methyl-2-phenylhex-4-enoate (4t)

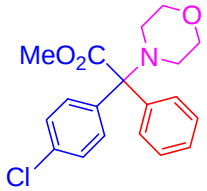


Eluant: 95% *n*-hexane/ 5% diethyl ether. The product was obtained as a colourless gummy liquid (57%). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.23-7.29 (m, 7H), 7.16-7.18 (m, 2H), 4.98 (t, J = 7.2 Hz, 1H) 3.68 (s, 3H), 2.98-3.11 (m, 2H), 1.57 (s, 3H), 1.26 (s, 3H) ^{13}C NMR (100 MHz, $CDCl_3$):δ_C 174.4(C=O), 142.3(C), 141.2(C), 135.2(C), 132.6(C), 130.5(C-H), 128.7(C-H), 127.9(C-H), 127.7(C-H), 126.9(C-H), 119.1(C-H), 60.2(C), 52.4(CH_3), 36.8(CH_2), 25.8(CH_3), 17.5(CH_3). IR (KBr, cm^{-1}): 1731.8. LRMS (EI): 69.1, 105.0, 139.0, 165.1, 199.0, 231.0, 259.0. HRMS (ESI): calcd. for $C_{20}H_{22}O_2Cl$: 329.1319, found: 329.1308.

2.7 A modified procedure for the synthesis of 4u

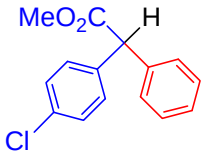
The catalytic reaction was carried out under a nitrogen atmosphere. In a 8 mL-reaction vial with a Teflon-lined cap, $[Rh(cod)Cl]_2$ (10 mol % Rh) and KO*t*Bu (3 equiv) were pre-mixed in MTBE (0.5 mL) at room temperature for 2 min. Afterwards, **2a** (3 equiv) dissolved in a minimum amount of MTBE was added to the reaction vial, and the mixture was stirred for 2 min. Then, **1a** (0.2 mmol, 1 equiv) dissolved in minimum amount of MTBE was added to the reaction vial. After 2 h, *N*-chloromorpholine (**3g**) was added neat to the reaction vial. The reaction mixture (c.a. 1 – 2 mL) was placed in a 40 °C oil bath for 24 h. The work-up procedure was same as the standard procedure.

methyl 2-(4-chlorophenyl)-2-morpholino-2-phenylacetate (4u)



Eluant: 80% *n*-hexane/ 20% ethyl acetate. The product was obtained as a light yellow gummy liquid (25%). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.36-7.40 (m, 4H), 7.22-7.30 (m, 5H), 3.80 (t, *J* = 4.6 Hz, 4H) 3.75 (s, 3H), 2.45 (bs, 4H) ^{13}C NMR (100 MHz, $CDCl_3$):δ_C 170.6(C=O), 138.6(C), 137.9(C), 132.9(C), 130.1(C-H), 128.6(C-H), 128.0(C-H), 127.9(C-H), 127.3(C-H), 78.5(C), 67.5(CH_2), 51.9(CH_3), 48.9(CH_2). IR (KBr, cm^{-1}): 1727.8. LRMS (EI): 105.0, 139.0, 165.1, 286.1. HRMS (ESI): calcd. for $C_{19}H_{21}NO_3Cl$: 346.1210, found: 346.1198.

methyl 2-(4-chlorophenyl)-2-phenylacetate (5a)



Eluant: 95% *n*-hexane/ 5% diethyl ether. The product was obtained as a colorless liquid (95%). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.26-7.37 (m, 9H), 5.03 (s, 1H), 3.77 (s, 3H) ^{13}C NMR (100 MHz, $CDCl_3$):δ_C 172.5(C=O), 138.1(C), 137.1(C), 133.2(C), 129.9(C-H), 128.7(C-H), 128.4(C-H), 127.4(C-H), 56.3(C), 52.4(CH_3). IR (KBr, cm^{-1}): 1737.0. LRMS (EI): 82.3, 165.1, 201.1, 260.0. HRMS (ESI): calcd. for $C_{15}H_{13}O_2NaCl$: 283.0502, found: 283.0505.

3. X-ray crystallographic data:

Table S1. Crystal data and structure refinement for 4p

Empirical formula	C_{26} H_{26} Cl N O_5 S	
Formula weight	499.99	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	Pbca	
Unit cell dimensions	a = 13.4805(6) Å	α = 90°
	b = 18.6319(8) Å	β = 90°
	c = 19.8561(9) Å	γ = 90°
Volume	4987.2(4) $Å^3$	
Z	8	
Density (calculated)	1.332 Mg/m^3	
Absorption coefficient	0.274 mm^{-1}	
F(000)	2096	
Crystal size	0.38 x 0.20 x 0.18 mm^3	
Theta range for data collection	2.05 to 26.98°.	
Index ranges	-16<=h<=16, -23<=k<=21, -25<=l<=25	
Reflections collected	34128	
Independent reflections	4810 [R(int) = 0.0550]	
Completeness to theta = 26.98°	88.5 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7454 and 0.6201	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4810 / 0 / 307	
Goodness-of-fit on F^2	1.005	
Final R indices [I>2sigma(I)]	R1 = 0.0629, wR2 = 0.1893	
R indices (all data)	R1 = 0.1313, wR2 = 0.2332	
Largest diff. peak and hole	0.786 and -0.460 $e.Å^{-3}$	

Figure S1 . **methyl 2-(4-chlorophenyl)-2-phenyl-3-(phenyl-4-sulfonyl morpholino)propanoate** (**4p**)

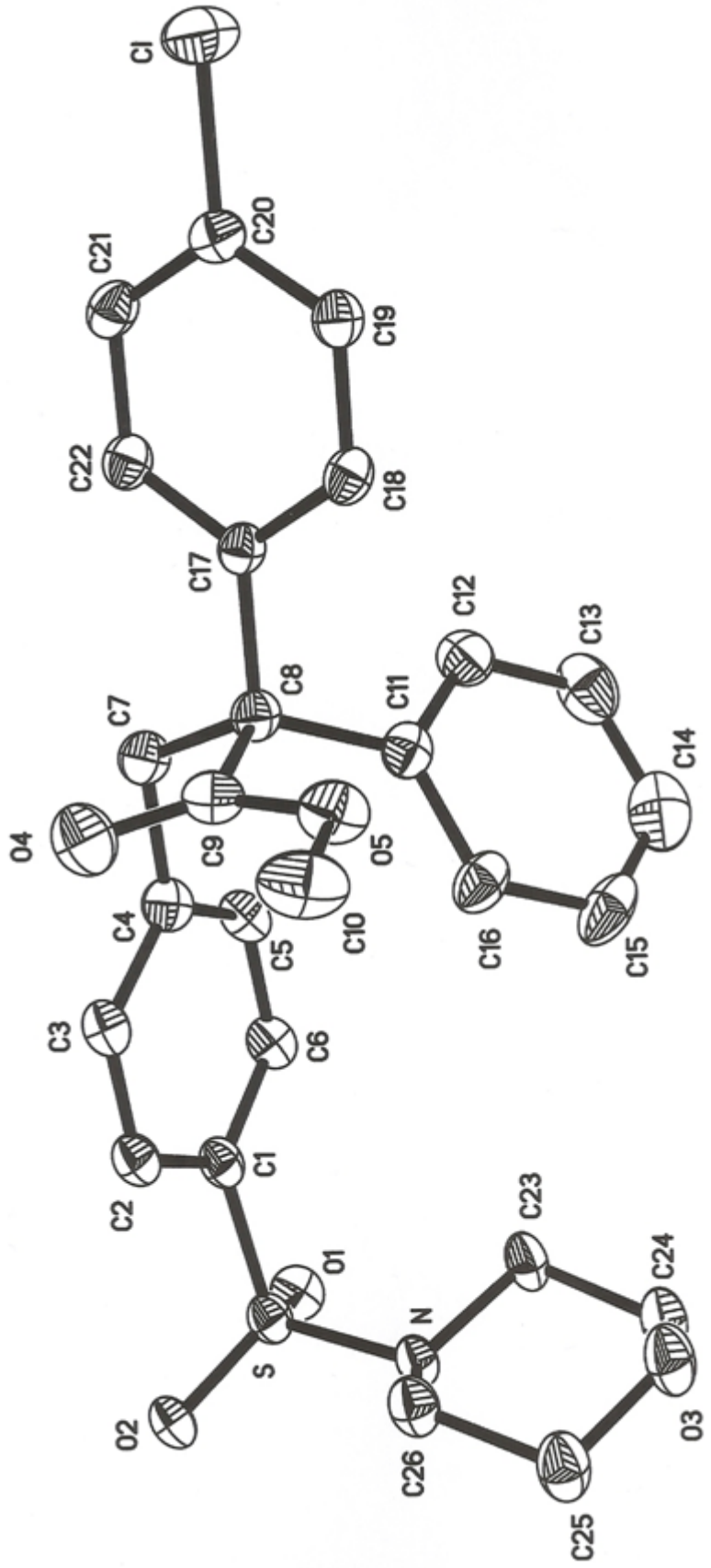


Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for 4p. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Cl(1)	2568(1)	1070(1)	5896(1)	98(1)
S(1)	1116(1)	1456(1)	-411(1)	60(1)
O(1)	744(1)	2146(1)	-592(1)	74(1)
O(2)	719(1)	832(1)	-721(1)	72(1)
O(3)	4392(1)	1422(1)	-409(1)	87(1)
O(4)	1943(2)	-265(1)	2656(1)	90(1)
O(5)	3504(1)	112(1)	2680(1)	80(1)
N(1)	2316(2)	1466(1)	-570(1)	57(1)
C(1)	1012(2)	1362(1)	466(1)	57(1)
C(2)	961(2)	674(1)	749(1)	61(1)
C(3)	973(2)	604(1)	1440(1)	62(1)
C(4)	1071(2)	1203(1)	1854(1)	61(1)
C(5)	1072(2)	1882(1)	1568(1)	63(1)
C(6)	1057(2)	1957(1)	875(1)	61(1)
C(7)	1165(2)	1120(2)	2612(1)	64(1)
C(8)	2240(2)	999(1)	2857(1)	56(1)
C(9)	2526(2)	216(2)	2707(1)	67(1)
C(10)	3848(3)	-618(2)	2597(2)	100(1)
C(11)	2905(2)	1562(1)	2528(1)	61(1)
C(12)	2920(2)	2244(2)	2785(2)	77(1)
C(13)	3438(3)	2797(2)	2478(2)	102(1)
C(14)	3964(3)	2679(2)	1896(2)	114(1)
C(15)	3946(2)	2003(2)	1619(2)	99(1)
C(16)	3431(2)	1439(2)	1929(2)	75(1)
C(17)	2306(2)	1033(1)	3634(1)	52(1)
C(18)	3230(2)	1010(1)	3953(1)	56(1)
C(19)	3316(2)	1019(1)	4643(1)	58(1)
C(20)	2476(2)	1054(1)	5032(1)	59(1)
C(21)	1546(2)	1086(1)	4737(1)	63(1)
C(22)	1479(2)	1073(1)	4041(1)	59(1)
C(23)	2855(2)	2070(2)	-266(2)	70(1)
C(24)	3899(2)	2082(2)	-532(2)	81(1)
C(25)	3883(2)	857(2)	-732(2)	90(1)
C(26)	2834(2)	778(2)	-461(2)	72(1)

Table S3. Bond lengths [Å] and angles [°] for 4p

Cl(1)-C(20)	1.721(3)
S(1)-O(2)	1.4215(19)
S(1)-O(1)	1.4258(19)
S(1)-N(1)	1.649(2)
S(1)-C(1)	1.755(3)
O(3)-C(25)	1.411(4)
O(3)-C(24)	1.418(3)
O(4)-C(9)	1.196(3)
O(5)-C(9)	1.333(3)
O(5)-C(10)	1.448(4)
N(1)-C(23)	1.470(3)
N(1)-C(26)	1.475(3)
C(1)-C(6)	1.376(4)
C(1)-C(2)	1.402(4)
C(2)-C(3)	1.378(4)
C(2)-H(2B)	0.9300
C(3)-C(4)	1.392(4)
C(3)-H(3A)	0.9300
C(4)-C(5)	1.387(4)
C(4)-C(7)	1.519(4)
C(5)-C(6)	1.382(4)
C(5)-H(5A)	0.9300
C(6)-H(6A)	0.9300
C(7)-C(8)	1.546(3)
C(7)-H(7A)	0.9700
C(7)-H(7B)	0.9700
C(8)-C(11)	1.526(4)
C(8)-C(9)	1.539(4)
C(8)-C(17)	1.546(4)
C(10)-H(10A)	0.9600
C(10)-H(10B)	0.9600
C(10)-H(10C)	0.9600
C(11)-C(12)	1.370(4)
C(11)-C(16)	1.404(4)
C(12)-C(13)	1.386(4)
C(12)-H(12A)	0.9300

C(13)-C(14)	1.374(5)
C(13)-H(13A)	0.9300
C(14)-C(15)	1.373(5)
C(14)-H(14A)	0.9300
C(15)-C(16)	1.402(4)
C(15)-H(15A)	0.9300
C(16)-H(16A)	0.9300
C(17)-C(22)	1.380(3)
C(17)-C(18)	1.398(3)
C(18)-C(19)	1.376(4)
C(18)-H(18A)	0.9300
C(19)-C(20)	1.372(4)
C(19)-H(19A)	0.9300
C(20)-C(21)	1.384(4)
C(21)-C(22)	1.385(4)
C(21)-H(21A)	0.9300
C(22)-H(22A)	0.9300
C(23)-C(24)	1.503(4)
C(23)-H(23A)	0.9700
C(23)-H(23B)	0.9700
C(24)-H(24A)	0.9700
C(24)-H(24B)	0.9700
C(25)-C(26)	1.520(4)
C(25)-H(25A)	0.9700
C(25)-H(25B)	0.9700
C(26)-H(26A)	0.9700
C(26)-H(26B)	0.9700

O(2)-S(1)-O(1)	119.74(12)
O(2)-S(1)-N(1)	107.12(11)
O(1)-S(1)-N(1)	106.63(11)
O(2)-S(1)-C(1)	108.57(12)
O(1)-S(1)-C(1)	108.27(12)
N(1)-S(1)-C(1)	105.66(11)
C(25)-O(3)-C(24)	110.0(2)
C(9)-O(5)-C(10)	117.2(2)
C(23)-N(1)-C(26)	111.8(2)
C(23)-N(1)-S(1)	114.48(17)

C(26)-N(1)-S(1)	115.28(17)
C(6)-C(1)-C(2)	120.2(3)
C(6)-C(1)-S(1)	120.1(2)
C(2)-C(1)-S(1)	119.6(2)
C(3)-C(2)-C(1)	119.0(2)
C(3)-C(2)-H(2B)	120.5
C(1)-C(2)-H(2B)	120.5
C(2)-C(3)-C(4)	120.8(2)
C(2)-C(3)-H(3A)	119.6
C(4)-C(3)-H(3A)	119.6
C(5)-C(4)-C(3)	119.4(3)
C(5)-C(4)-C(7)	119.9(2)
C(3)-C(4)-C(7)	120.7(2)
C(6)-C(5)-C(4)	120.0(2)
C(6)-C(5)-H(5A)	120.0
C(4)-C(5)-H(5A)	120.0
C(1)-C(6)-C(5)	120.4(2)
C(1)-C(6)-H(6A)	119.8
C(5)-C(6)-H(6A)	119.8
C(4)-C(7)-C(8)	113.9(2)
C(4)-C(7)-H(7A)	108.8
C(8)-C(7)-H(7A)	108.8
C(4)-C(7)-H(7B)	108.8
C(8)-C(7)-H(7B)	108.8
H(7A)-C(7)-H(7B)	107.7
C(11)-C(8)-C(9)	115.0(2)
C(11)-C(8)-C(17)	111.4(2)
C(9)-C(8)-C(17)	102.6(2)
C(11)-C(8)-C(7)	108.4(2)
C(9)-C(8)-C(7)	108.2(2)
C(17)-C(8)-C(7)	111.2(2)
O(4)-C(9)-O(5)	122.6(3)
O(4)-C(9)-C(8)	124.2(3)
O(5)-C(9)-C(8)	113.1(2)
O(5)-C(10)-H(10A)	109.5
O(5)-C(10)-H(10B)	109.5
H(10A)-C(10)-H(10B)	109.5
O(5)-C(10)-H(10C)	109.5

H(10A)-C(10)-H(10C)	109.5
H(10B)-C(10)-H(10C)	109.5
C(12)-C(11)-C(16)	117.4(3)
C(12)-C(11)-C(8)	119.1(2)
C(16)-C(11)-C(8)	123.2(2)
C(11)-C(12)-C(13)	122.2(3)
C(11)-C(12)-H(12A)	118.9
C(13)-C(12)-H(12A)	118.9
C(14)-C(13)-C(12)	120.7(3)
C(14)-C(13)-H(13A)	119.6
C(12)-C(13)-H(13A)	119.6
C(15)-C(14)-C(13)	118.3(4)
C(15)-C(14)-H(14A)	120.8
C(13)-C(14)-H(14A)	120.8
C(14)-C(15)-C(16)	121.3(3)
C(14)-C(15)-H(15A)	119.3
C(16)-C(15)-H(15A)	119.3
C(15)-C(16)-C(11)	120.0(3)
C(15)-C(16)-H(16A)	120.0
C(11)-C(16)-H(16A)	120.0
C(22)-C(17)-C(18)	117.2(2)
C(22)-C(17)-C(8)	122.7(2)
C(18)-C(17)-C(8)	120.1(2)
C(19)-C(18)-C(17)	121.7(2)
C(19)-C(18)-H(18A)	119.2
C(17)-C(18)-H(18A)	119.2
C(20)-C(19)-C(18)	119.5(2)
C(20)-C(19)-H(19A)	120.3
C(18)-C(19)-H(19A)	120.3
C(19)-C(20)-C(21)	120.7(3)
C(19)-C(20)-Cl(1)	120.2(2)
C(21)-C(20)-Cl(1)	119.1(2)
C(20)-C(21)-C(22)	118.7(2)
C(20)-C(21)-H(21A)	120.6
C(22)-C(21)-H(21A)	120.6
C(17)-C(22)-C(21)	122.2(2)
C(17)-C(22)-H(22A)	118.9
C(21)-C(22)-H(22A)	118.9

N(1)-C(23)-C(24)	109.3(2)
N(1)-C(23)-H(23A)	109.8
C(24)-C(23)-H(23A)	109.8
N(1)-C(23)-H(23B)	109.8
C(24)-C(23)-H(23B)	109.8
H(23A)-C(23)-H(23B)	108.3
O(3)-C(24)-C(23)	111.4(2)
O(3)-C(24)-H(24A)	109.3
C(23)-C(24)-H(24A)	109.3
O(3)-C(24)-H(24B)	109.3
C(23)-C(24)-H(24B)	109.3
H(24A)-C(24)-H(24B)	108.0
O(3)-C(25)-C(26)	111.3(3)
O(3)-C(25)-H(25A)	109.4
C(26)-C(25)-H(25A)	109.4
O(3)-C(25)-H(25B)	109.4
C(26)-C(25)-H(25B)	109.4
H(25A)-C(25)-H(25B)	108.0
N(1)-C(26)-C(25)	107.7(2)
N(1)-C(26)-H(26A)	110.2
C(25)-C(26)-H(26A)	110.2
N(1)-C(26)-H(26B)	110.2
C(25)-C(26)-H(26B)	110.2
H(26A)-C(26)-H(26B)	108.5

Symmetry transformations used to generate equivalent atoms:

Table S4. Anisotropic displacement parameters ($Å^2$x 10^3)for 4p. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Cl(1)	111(1)	121(1)	63(1)	-6(1)	4(1)	8(1)
S(1)	47(1)	66(1)	66(1)	-1(1)	-10(1)	-1(1)
O(1)	62(1)	77(1)	82(1)	7(1)	-14(1)	17(1)
O(2)	60(1)	82(1)	74(1)	-12(1)	-14(1)	-18(1)
O(3)	51(1)	78(1)	132(2)	-5(1)	-13(1)	1(1)
O(4)	94(1)	68(1)	107(2)	0(1)	-8(1)	0(1)
O(5)	76(1)	77(1)	87(1)	-13(1)	-4(1)	27(1)
N(1)	46(1)	50(1)	74(1)	-5(1)	-8(1)	-2(1)
C(1)	42(1)	60(2)	69(2)	-4(1)	-11(1)	1(1)
C(2)	55(2)	60(2)	70(2)	-5(1)	-9(1)	-3(1)
C(3)	55(2)	55(2)	76(2)	0(1)	-9(1)	-3(1)
C(4)	43(1)	71(2)	70(2)	-1(1)	-7(1)	13(1)
C(5)	57(1)	54(2)	78(2)	-11(1)	-13(1)	10(1)
C(6)	57(2)	53(2)	72(2)	1(1)	-13(1)	9(1)
C(7)	50(1)	72(2)	70(2)	-3(1)	1(1)	8(1)
C(8)	46(1)	65(2)	57(2)	-1(1)	1(1)	6(1)
C(9)	76(2)	68(2)	58(2)	-2(1)	-3(1)	6(2)
C(10)	113(2)	91(2)	95(2)	-23(2)	-10(2)	49(2)
C(11)	48(1)	69(2)	66(2)	11(1)	-7(1)	8(1)
C(12)	88(2)	72(2)	71(2)	9(2)	-7(2)	-6(2)
C(13)	117(3)	73(2)	115(3)	20(2)	-22(2)	-21(2)
C(14)	97(3)	113(3)	130(3)	47(2)	-23(2)	-14(2)
C(15)	54(2)	164(3)	79(2)	52(2)	9(2)	18(2)
C(16)	52(2)	103(2)	70(2)	18(2)	7(1)	15(2)
C(17)	48(1)	49(1)	58(2)	-1(1)	4(1)	3(1)
C(18)	45(1)	59(2)	63(2)	7(1)	6(1)	6(1)
C(19)	52(1)	54(2)	68(2)	1(1)	0(1)	1(1)
C(20)	67(2)	52(1)	56(2)	0(1)	4(1)	5(1)
C(21)	60(2)	59(2)	70(2)	-1(1)	16(1)	4(1)
C(22)	50(1)	62(2)	65(2)	4(1)	4(1)	3(1)
C(23)	54(2)	51(2)	106(2)	-8(2)	-7(2)	-9(1)
C(24)	56(2)	67(2)	120(3)	1(2)	-9(2)	-8(2)
C(25)	61(2)	68(2)	141(3)	-14(2)	2(2)	2(2)
C(26)	59(2)	56(2)	101(2)	-6(2)	-6(2)	2(1)

Table S5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for 4p.

	x	y	z	U(eq)
H(2B)	919	270	475	74
H(3A)	916	151	1633	74
H(5A)	1082	2287	1842	76
H(6A)	1077	2413	684	73
H(7A)	760	717	2755	76
H(7B)	903	1547	2827	76
H(10A)	4560	-624	2586	149
H(10B)	3593	-810	2183	149
H(10C)	3620	-905	2968	149
H(12A)	2571	2339	3179	92
H(13A)	3429	3253	2668	122
H(14A)	4322	3047	1694	136
H(15A)	4283	1919	1218	119
H(16A)	3438	984	1737	90
H(18A)	3802	988	3691	67
H(19A)	3938	1002	4845	69
H(21A)	978	1114	5001	76
H(22A)	855	1091	3842	71
H(23A)	2864	2019	220	84
H(23B)	2525	2518	-376	84
H(24A)	3887	2175	-1012	97
H(24B)	4264	2469	-317	97
H(25A)	4242	412	-663	108
H(25B)	3858	949	-1212	108
H(26A)	2491	394	-695	86
H(26B)	2851	664	15	86

Table S6. Torsion angles [°] for 4p.

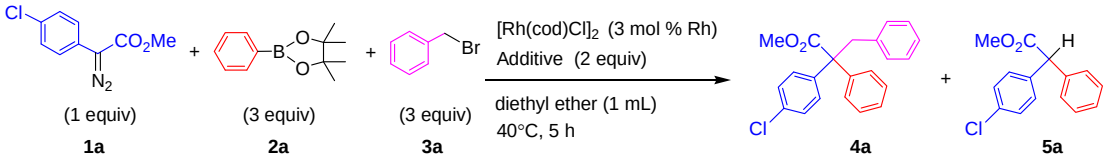
O(2)-S(1)-N(1)-C(23)	-178.25(19)
O(1)-S(1)-N(1)-C(23)	52.4(2)
C(1)-S(1)-N(1)-C(23)	-62.6(2)
O(2)-S(1)-N(1)-C(26)	-46.5(2)
O(1)-S(1)-N(1)-C(26)	-175.82(19)
C(1)-S(1)-N(1)-C(26)	69.1(2)
O(2)-S(1)-C(1)-C(6)	-160.4(2)
O(1)-S(1)-C(1)-C(6)	-29.0(2)
N(1)-S(1)-C(1)-C(6)	85.0(2)
O(2)-S(1)-C(1)-C(2)	24.5(2)
O(1)-S(1)-C(1)-C(2)	155.9(2)
N(1)-S(1)-C(1)-C(2)	-90.1(2)
C(6)-C(1)-C(2)-C(3)	-1.1(4)
S(1)-C(1)-C(2)-C(3)	173.98(19)
C(1)-C(2)-C(3)-C(4)	-2.3(4)
C(2)-C(3)-C(4)-C(5)	5.4(4)
C(2)-C(3)-C(4)-C(7)	-175.2(2)
C(3)-C(4)-C(5)-C(6)	-5.2(4)
C(7)-C(4)-C(5)-C(6)	175.5(2)
C(2)-C(1)-C(6)-C(5)	1.3(4)
S(1)-C(1)-C(6)-C(5)	-173.77(19)
C(4)-C(5)-C(6)-C(1)	1.9(4)
C(5)-C(4)-C(7)-C(8)	-94.3(3)
C(3)-C(4)-C(7)-C(8)	86.4(3)
C(4)-C(7)-C(8)-C(11)	48.6(3)
C(4)-C(7)-C(8)-C(9)	-76.7(3)
C(4)-C(7)-C(8)-C(17)	171.4(2)
C(10)-O(5)-C(9)-O(4)	-1.2(4)
C(10)-O(5)-C(9)-C(8)	175.0(2)
C(11)-C(8)-C(9)-O(4)	-146.6(3)
C(17)-C(8)-C(9)-O(4)	92.3(3)
C(7)-C(8)-C(9)-O(4)	-25.3(4)
C(11)-C(8)-C(9)-O(5)	37.2(3)
C(17)-C(8)-C(9)-O(5)	-83.8(3)
C(7)-C(8)-C(9)-O(5)	158.5(2)
C(9)-C(8)-C(11)-C(12)	-159.8(2)

C(17)-C(8)-C(11)-C(12)	-43.6(3)
C(7)-C(8)-C(11)-C(12)	79.0(3)
C(9)-C(8)-C(11)-C(16)	27.0(4)
C(17)-C(8)-C(11)-C(16)	143.1(2)
C(7)-C(8)-C(11)-C(16)	-94.2(3)
C(16)-C(11)-C(12)-C(13)	-0.6(4)
C(8)-C(11)-C(12)-C(13)	-174.3(3)
C(11)-C(12)-C(13)-C(14)	-0.1(5)
C(12)-C(13)-C(14)-C(15)	1.3(5)
C(13)-C(14)-C(15)-C(16)	-1.8(5)
C(14)-C(15)-C(16)-C(11)	1.1(5)
C(12)-C(11)-C(16)-C(15)	0.2(4)
C(8)-C(11)-C(16)-C(15)	173.5(2)
C(11)-C(8)-C(17)-C(22)	128.9(2)
C(9)-C(8)-C(17)-C(22)	-107.6(3)
C(7)-C(8)-C(17)-C(22)	7.8(3)
C(11)-C(8)-C(17)-C(18)	-52.5(3)
C(9)-C(8)-C(17)-C(18)	71.0(3)
C(7)-C(8)-C(17)-C(18)	-173.5(2)
C(22)-C(17)-C(18)-C(19)	0.6(4)
C(8)-C(17)-C(18)-C(19)	-178.2(2)
C(17)-C(18)-C(19)-C(20)	-0.2(4)
C(18)-C(19)-C(20)-C(21)	-0.5(4)
C(18)-C(19)-C(20)-Cl(1)	-179.73(19)
C(19)-C(20)-C(21)-C(22)	0.7(4)
Cl(1)-C(20)-C(21)-C(22)	179.98(19)
C(18)-C(17)-C(22)-C(21)	-0.3(4)
C(8)-C(17)-C(22)-C(21)	178.4(2)
C(20)-C(21)-C(22)-C(17)	-0.3(4)
C(26)-N(1)-C(23)-C(24)	55.1(3)
S(1)-N(1)-C(23)-C(24)	-171.5(2)
C(25)-O(3)-C(24)-C(23)	60.4(4)
N(1)-C(23)-C(24)-O(3)	-56.6(3)
C(24)-O(3)-C(25)-C(26)	-61.7(3)
C(23)-N(1)-C(26)-C(25)	-55.4(3)
S(1)-N(1)-C(26)-C(25)	171.6(2)
O(3)-C(25)-C(26)-N(1)	58.6(3)

Symmetry transformations used to generate equivalent atoms:

4. Results for Optimization Studies:

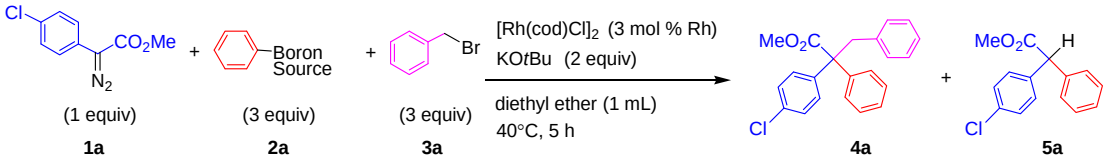
Table S7: Additive screening

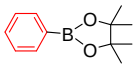
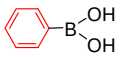
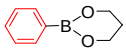
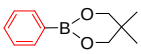
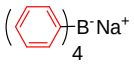
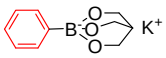


entry[a]	additive	**4a** (%)	**5a** (%)
1	KO*t*Bu	59	<1
2	NaO*t*Bu	<1	99
3	LiO*t*Bu	4	<1
4	NaOMe	0	100
5	KOMe	0	100
6	K_2CO_3	7	<1
7	K_3PO_4	8	<1
8	KOH	2	72
9[b, c]	none	0	0
10[d, e]	none	0	7

[a] The reactions were carried out in a 0.2 mmol-scale of **1a**. Yields were determined by GC/FID using dodecane (0.1 mmol) as internal standard. [b] 65% of **1a** remained, yield was determined by NMR using dibromomethane (0.1 mmol) as internal standard. [c] 0.578 mmol of **2a** remained, 0.535 mmol of **3a** remained, yields were determined by GC/FID using dodecane (0.1 mmol) as internal standard. [d] $[Rh(cod)OH]_2$ (3 mol% of Rh) was used. [e] 61% of **1a** remained, yield was determined by NMR using dibromomethane (0.1 mmol) as internal standard.

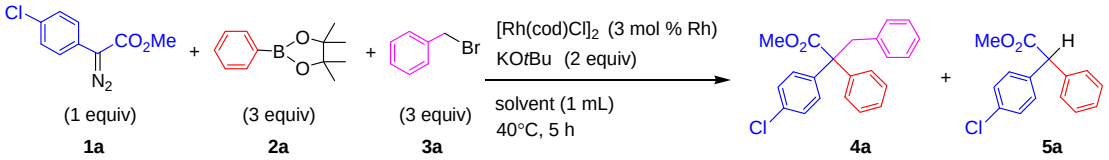
Table S8: Boron source screening



entry[a]	boron source	**4a** (%)	**5a** (%)
1		59	<1
2		0	78
3		2	94
4		18	70
5		<1	0
6		<1	0

[a] The reactions were carried out in a 0.2 mmol-scale of **1a**. Yields were determined by GC/FID using dodecane (0.1 mmol) as internal standard.

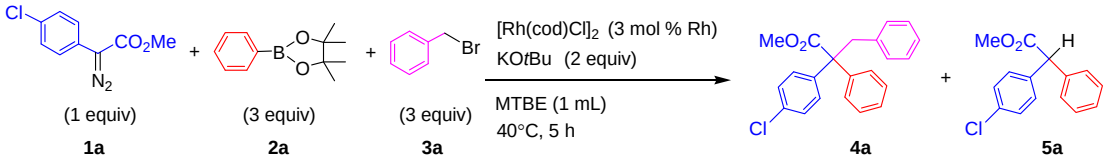
Table S9: Solvent screening



entry[a]	solvent	**4a** (%)	**5a** (%)
1	diethyl ether	59	<1
2	MTBE	68	5
3	1,4-dioxane	58	3
4	THF	50	0
5	toluene	4	6
6	acetone	2	4
7	DMF	2	1
8	DMA	3	<1
9	CH_3CN	0	<1
10	DCM	2	3

[a] The reactions were carried out in a 0.2 mmol-scale of **1a**. Yields were determined by GC/FID using dodecane (0.1 mmol) as internal standard.

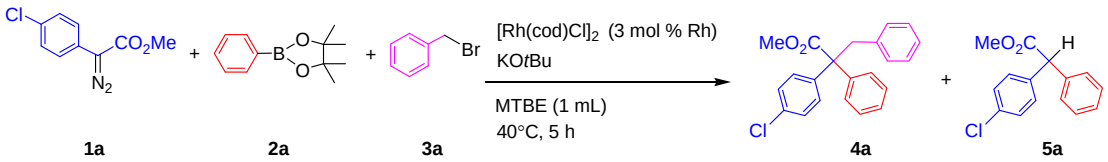
Table S10: Screening of addition method for the diazo reagent



entry[a]	addition method	**1a** remained[d] (%)	**4a** (%)	**5a** (%)
1	one pot	0	68	5
2	syringe addition 5 h	40	7	0
3	2 batches	35	21	<1
4	3 batches	38	22	2
5	2 batches[b]	0	64	5
6	2 batches[c]	0	55	10

[a] The reactions were carried out in a 0.2 mmol-scale of **1a**. Yields were determined by GC/FID using dodecane (0.1 mmol) as internal standard. [b] second batch (0.1 mmol) was syringe added for 3 h. [c] second batch (0.134 mmol) was syringe added for 3 h. [d] **1a** was determined by NMR using dibromomethane (0.1 mmol) as internal standard.

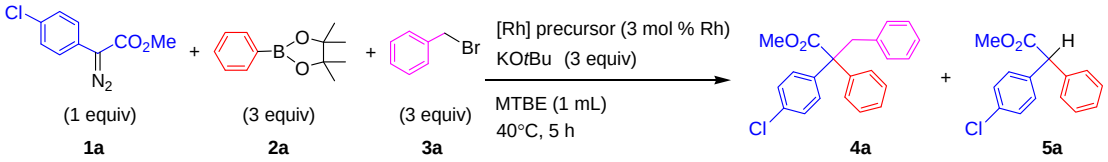
Table S11: Substrate ratios study



entry[a]	Substrate ratio **1a**:**2a**:**3a**:base	limiting reagent remained[b] (%)	**4a** (%)	**5a** (%)
1	1:3:3:2	0	68	5
2	2:3:1:2	0	77	24
3[c]	2:3:1:2	4	74	12
4	2:1:3:2	46	0	0
5	1:3:3:3	0	68	0
6	1:5:3:2	0	73	3

[a] The reactions were carried out in a 0.2 mmol-scale of the limiting reagent. Yields were determined by GC/FID using dodecane (0.1 mmol) as internal standard. [b] **1a** was determined by NMR using dibromomethane (0.1 mmol) as internal standard, other limited reagent were determined by GC/FID. [c] MS4Å (0.1g) was added.

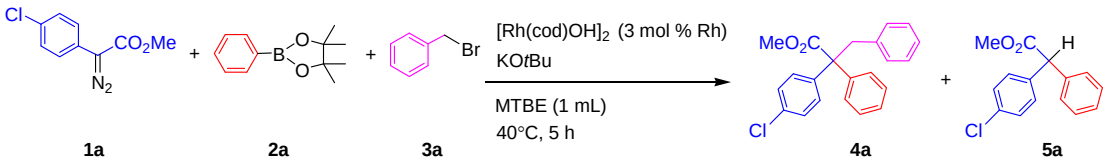
Table S12: Catalyst precursor screening



entry[a]	Rh precursor	**1a** remained[b] (%)	**4a** (%)	**5a** (%)
1	$[Rh(cod)Cl]_2$	0	68	0
2	$[Rh(cod)OH]_2$	0	84	0
3	$[Rh(dppe)Cl]_2$	70	<1	0
4	$Rh(PPh)_3Cl$	40	0	0

[a] The reactions were carried out in a 0.2 mmol-scale of **1a**. Yields were determined by GC/FID using dodecane (0.1 mmol) as internal standard. [b] **1a** was determined by NMR using dibromomethane (0.1 mmol) as internal standard.

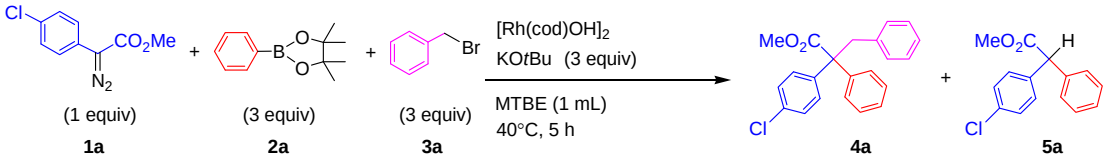
Table S13: Substrate ratios study 2



entry[a]	Substrate ratio **1a**:**2a**:**3a**:base	**1a** remained[b] (%)	**4a** (%)	**5a** (%)
1	1:3:3:3	0	84	0
2	1:3:2:3	0	80	0
4	1:3:1.5:3	0	74	0
6	1:2.5:1.5:3	30	3	0
7	1:3:1.5:2	0	65	1
8	1:3:1.5:1.5	0	48	23
9	1:2:1.5:2	0	76	0
10	1:1.51.5:1.5	0	58	12
11	1:2:3:2	0	70	2
12	1:3:3:2	0	76	0

[a] The reactions were carried out in a 0.2 mmol-scale of **1a**. Yields were determined by GC/FID using dodecane (0.1 mmol) as internal standard. [b] **1a** was determined by NMR using dibromomethane (0.1 mmol) as internal standard.

Table S14: Catalyst loading screening



entry[a]	Rh loading	**1a** remained[b] (%)	**4a** (%)	**5a** (%)
1	3 mol %	0	84	0
2	2 mol %	0	85	0
3[c]	2 mol %	0	86[d]	0
4	1 mol %	20	47	0
5[e]	none	85	0	0

[a] The reactions were carried out in a 0.2 mmol-scale of **1a**. Yields were determined by GC/FID using dodecane (0.1 mmol) as internal standard. [b] **1a** was determined by NMR using dibromomethane (0.1 mmol) as internal standard. [c] The reaction was run 4 h. [d] Isolated yield. [e] 0.195 mmol of **2a** remained, 0.492 mmol of **3a** remained, yields were determined by GC/FID using dodecane (0.1 mmol) as internal standard..

5. Figures of ^{1}H, ^{13}C and ^{19}F NMR spectra:

Figure S1a. ^{1}H NMR of **4a**

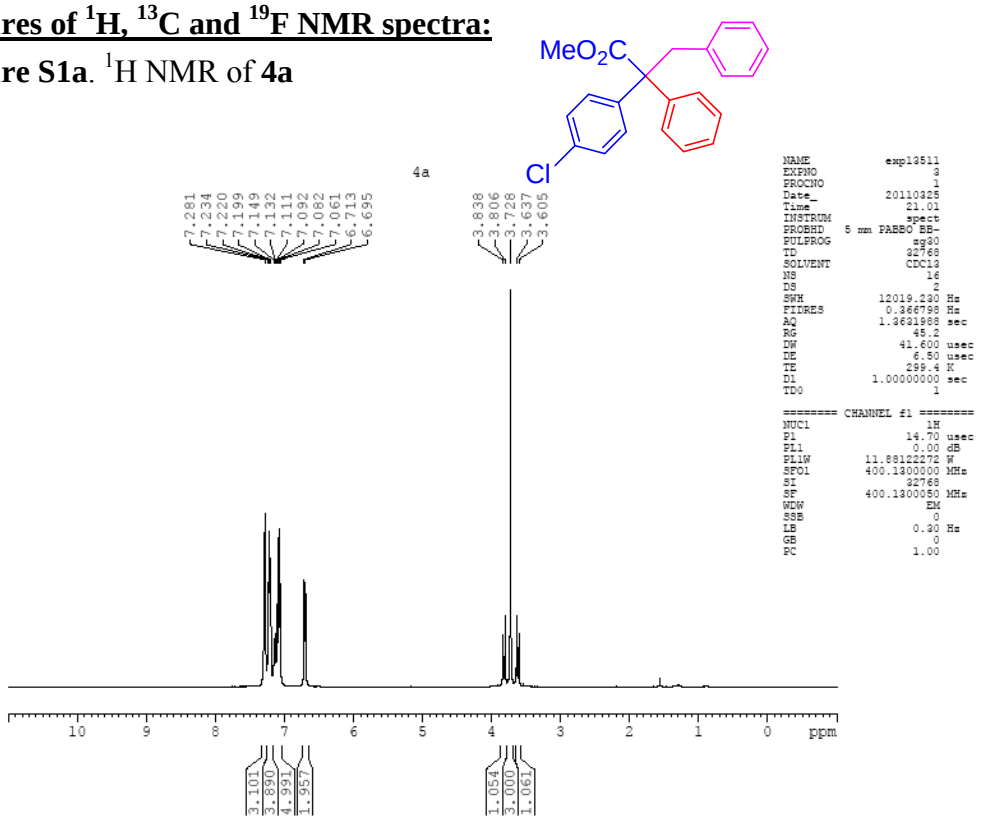


Figure S1b. ^{13}C NMR of **4a**

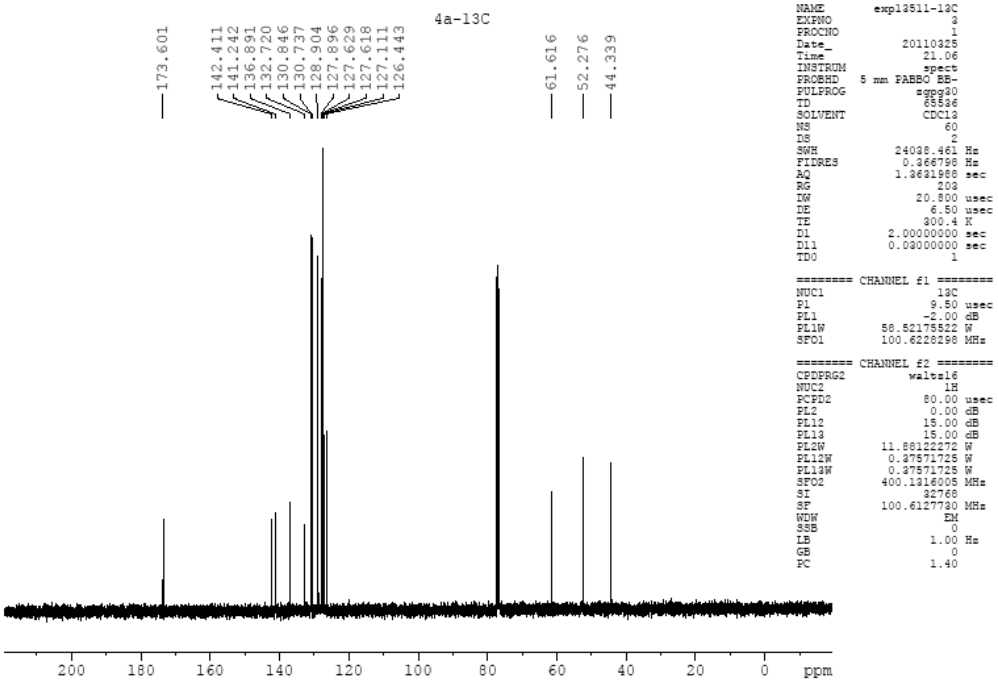


Figure S2a. ^{1}H NMR of **4b**

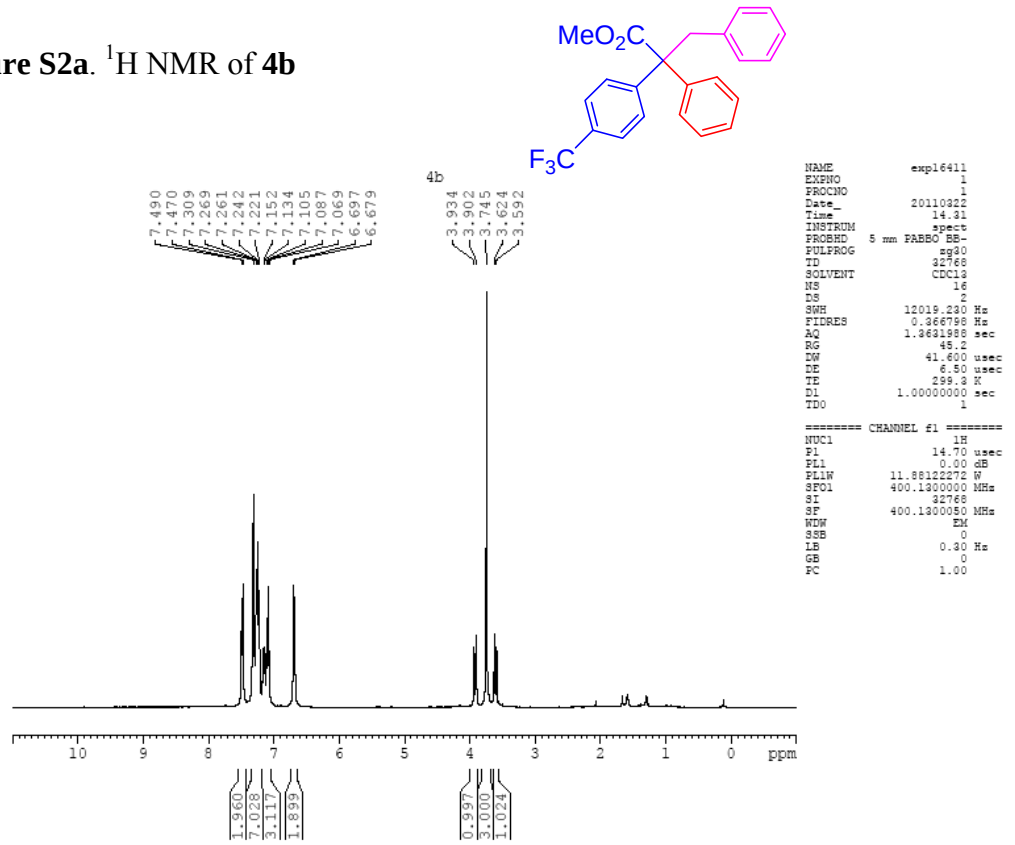


Figure S2b. ^{13}C NMR of **4b**

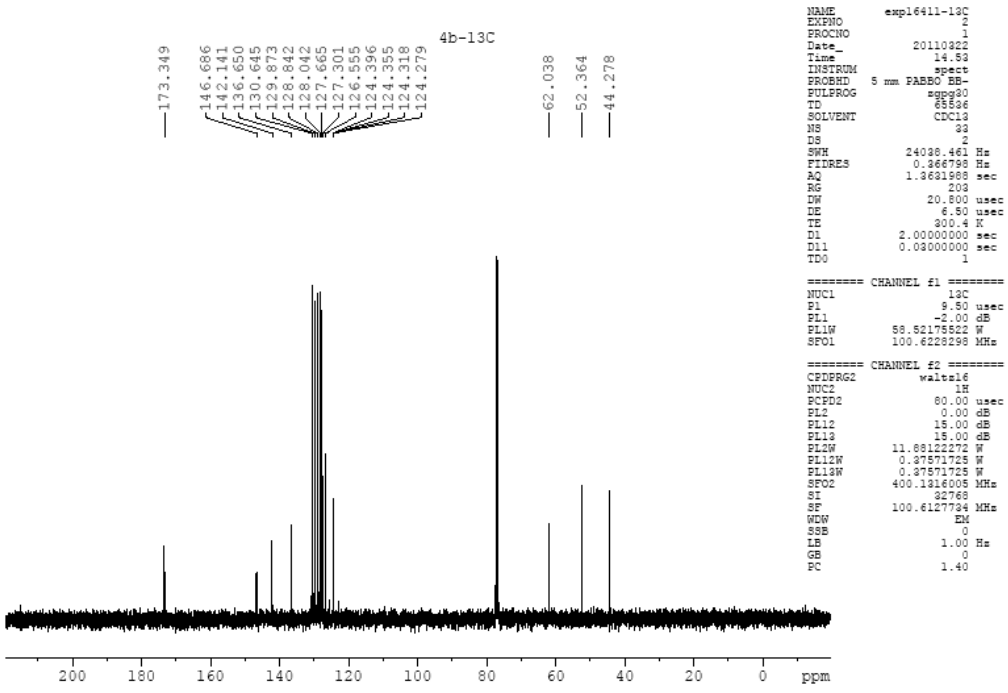
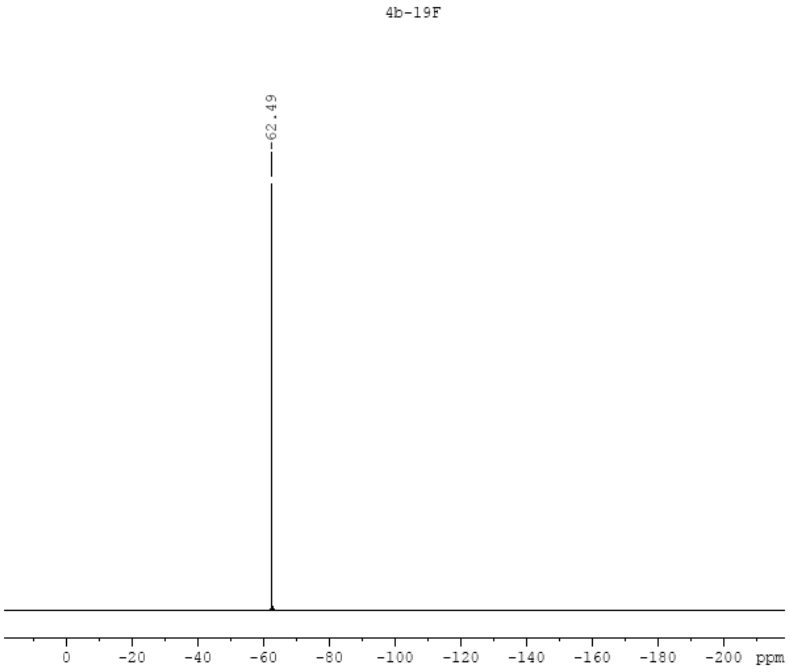


Figure S2c. ^{19}F NMR of **4b**




```
NAME            exp16411-19F
EXPNO                      1
PROCNO                     1
Date_           20110322
Time                   15.29
INSTRUM                spect
PROBHD     5 mm PABBO BB-
PULPROG             zgfhigqn
TD                    131072
SOLVENT                CDCl3
NS                        16
DS                         4
SWH              89285.711 Hz
FIDRES           0.681196 Hz
AQ               0.7340532 sec
RG                      45.2
DW                     5.600 usec
DE                     6.50 usec
TE                    300.0 K
D1               1.00000000 sec
D11              0.03000000 sec
D12              0.00002000 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                   19F
P1                   14.20 usec
PL1                  -3.00 dB
PL1W          18.69428444 W
SFO1          376.4607164 MHz

======== CHANNEL f2 ========
CPDPRG2             waltz16
NUC2                   1H
PCPD2                80.00 usec
PL2                   0.00 dB
PL12                 15.00 dB
PL2W          11.88122272 W
PL12W          0.37571725 W
SFO2          400.1316005 MHz
SI                    65536
SF            376.4982660 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    1.00
```

Figure S3a. ^{1}H NMR of **4c**

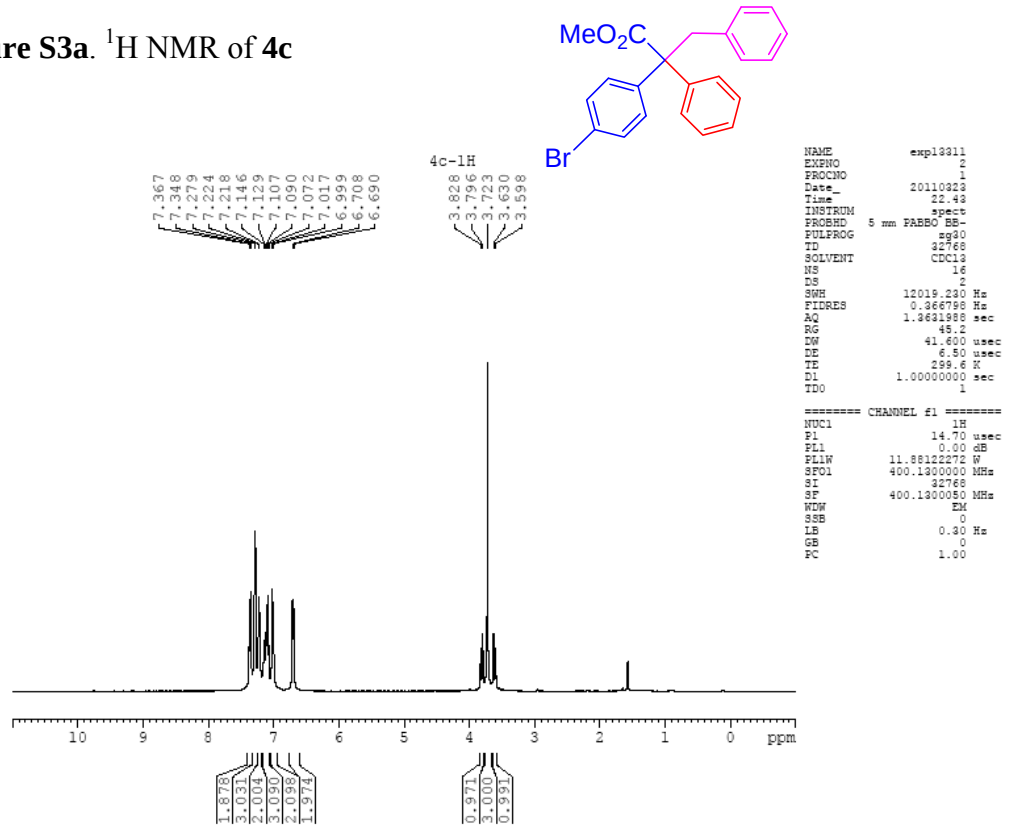


Figure S3b. ^{13}C NMR of **4c**

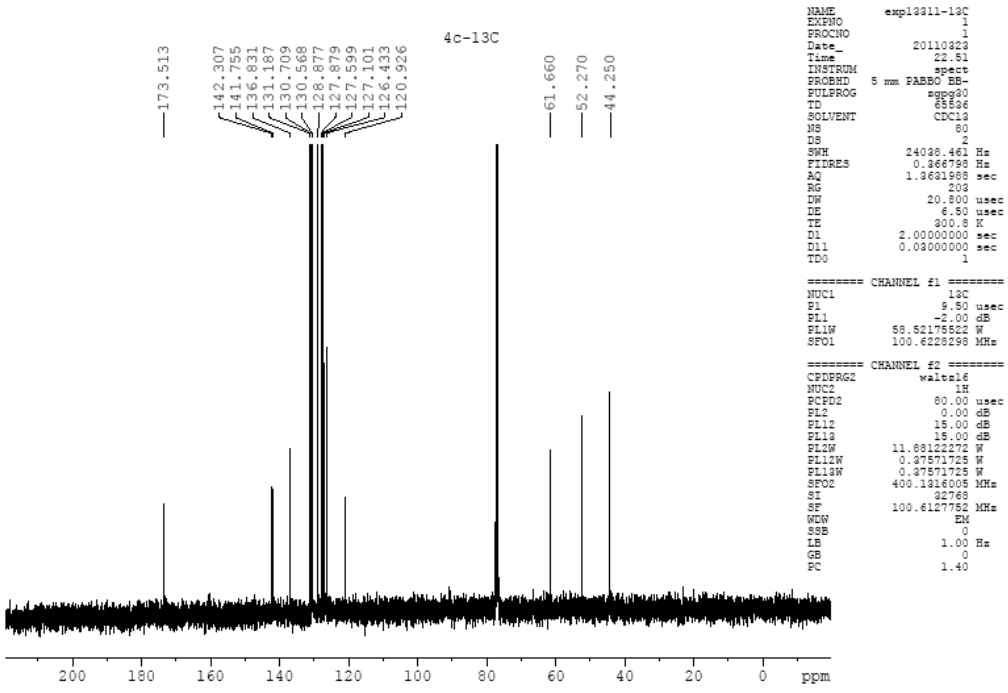


Figure S4a. ^{1}H NMR of **4d**

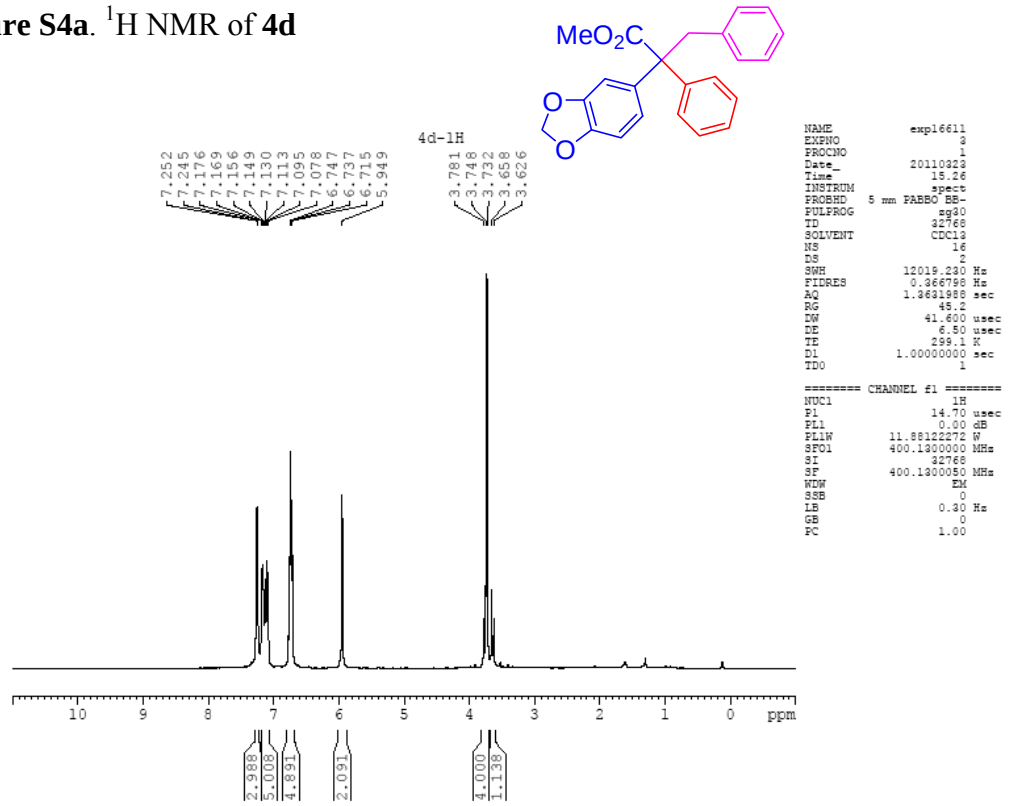


Figure S4b. ^{13}C NMR of **4d**

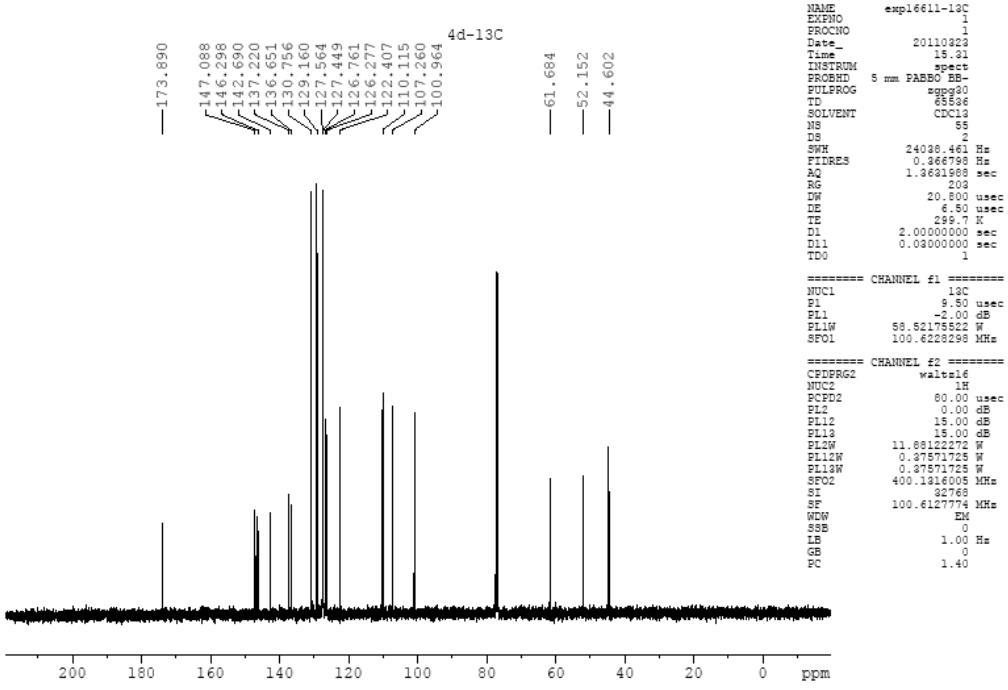


Figure S5a. ^{1}H NMR of **4e**

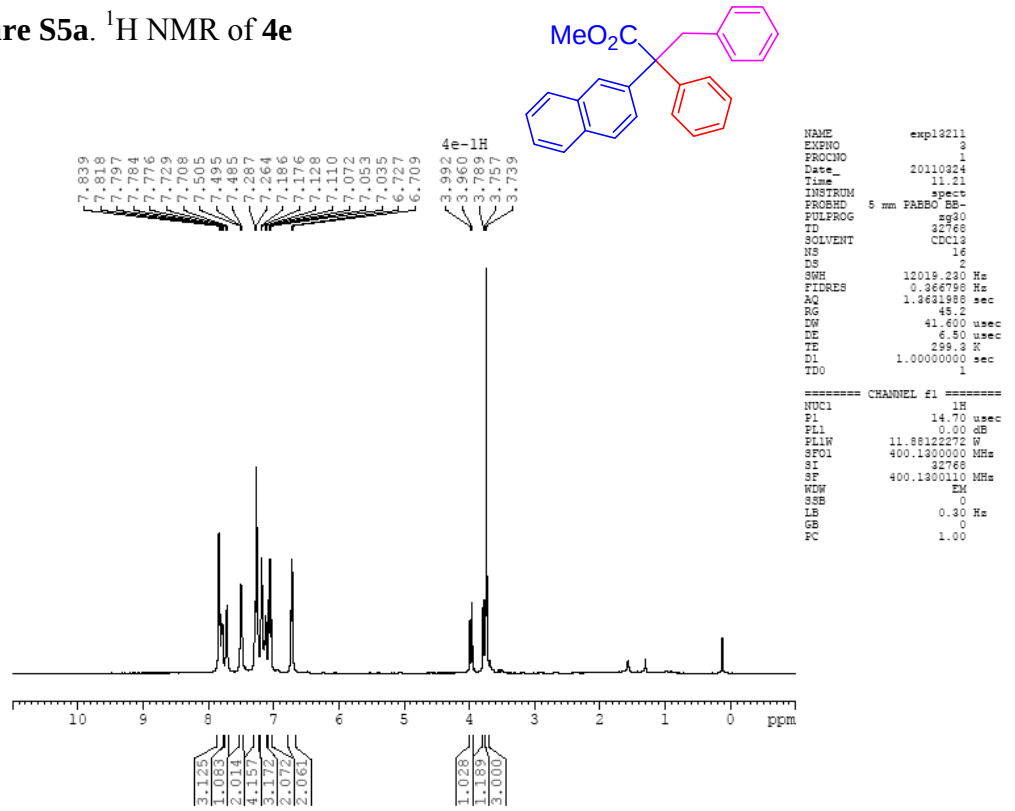


Figure S5b. ^{13}C NMR of **4e**

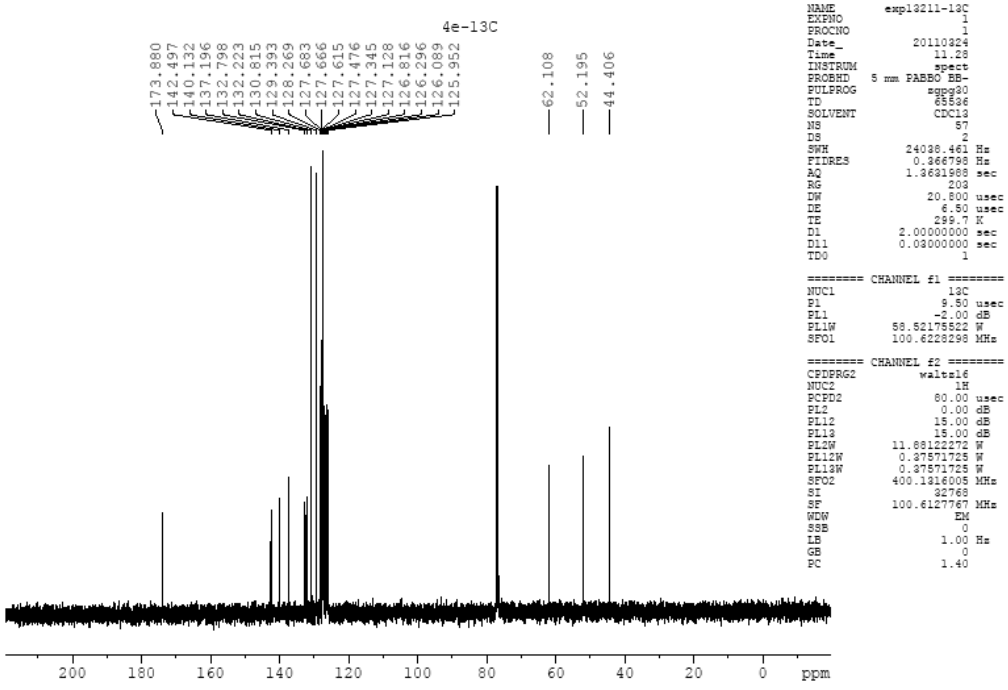


Figure S6a. ^{1}H NMR of **4f**

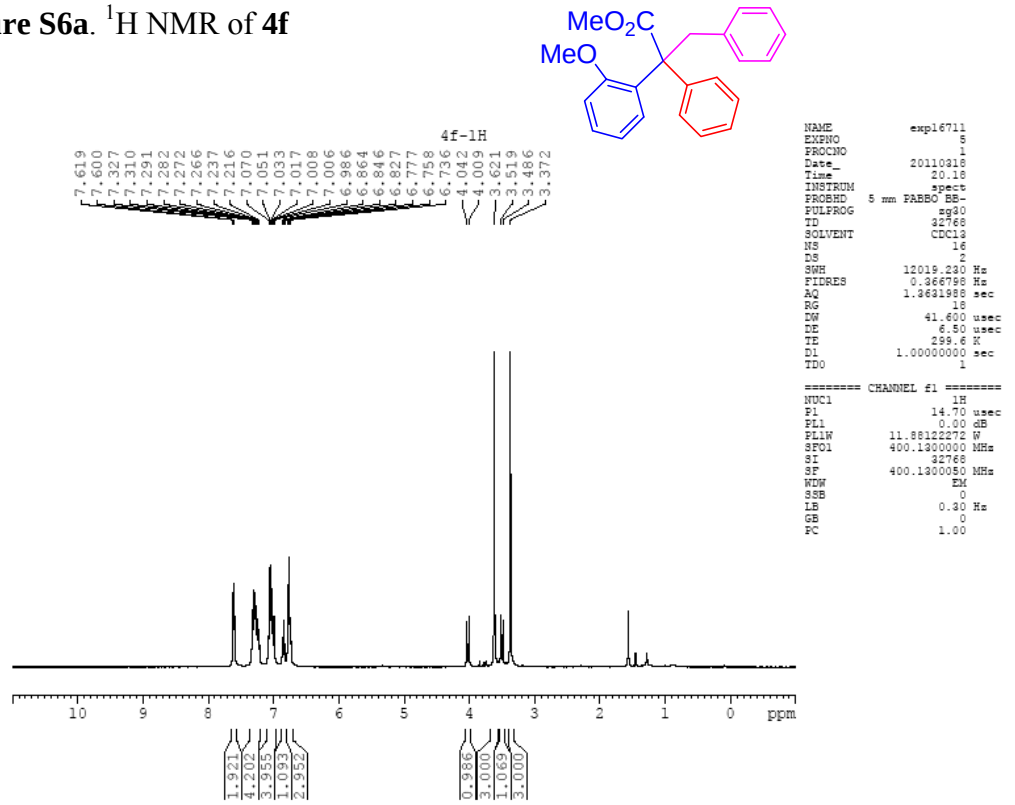


Figure S6b. ^{13}C NMR of **4f**

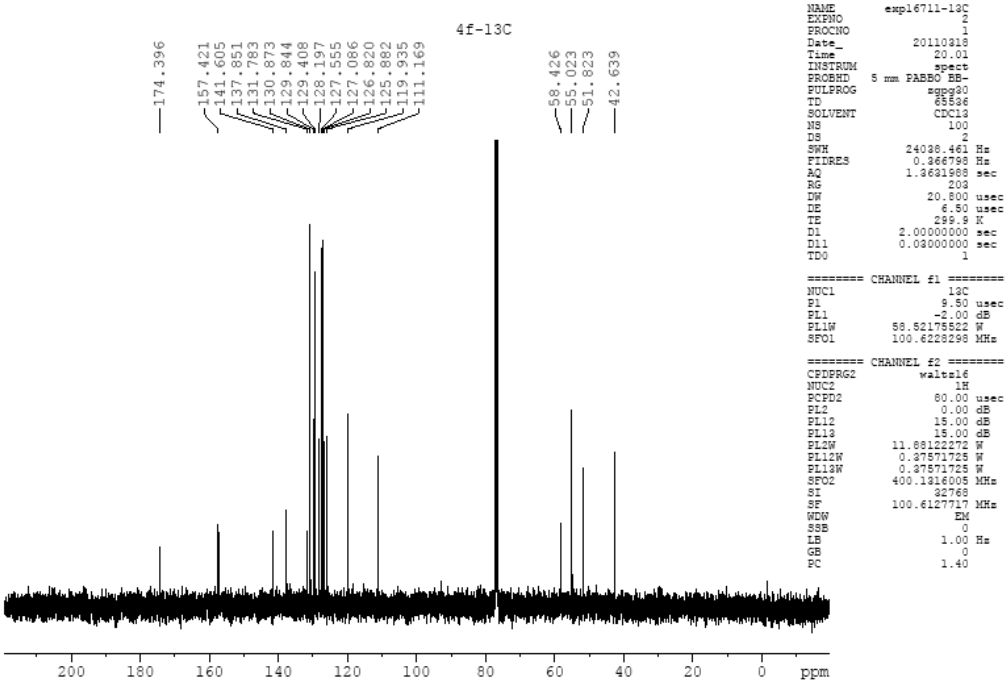


Figure S7a. ^{1}H NMR of **4g**

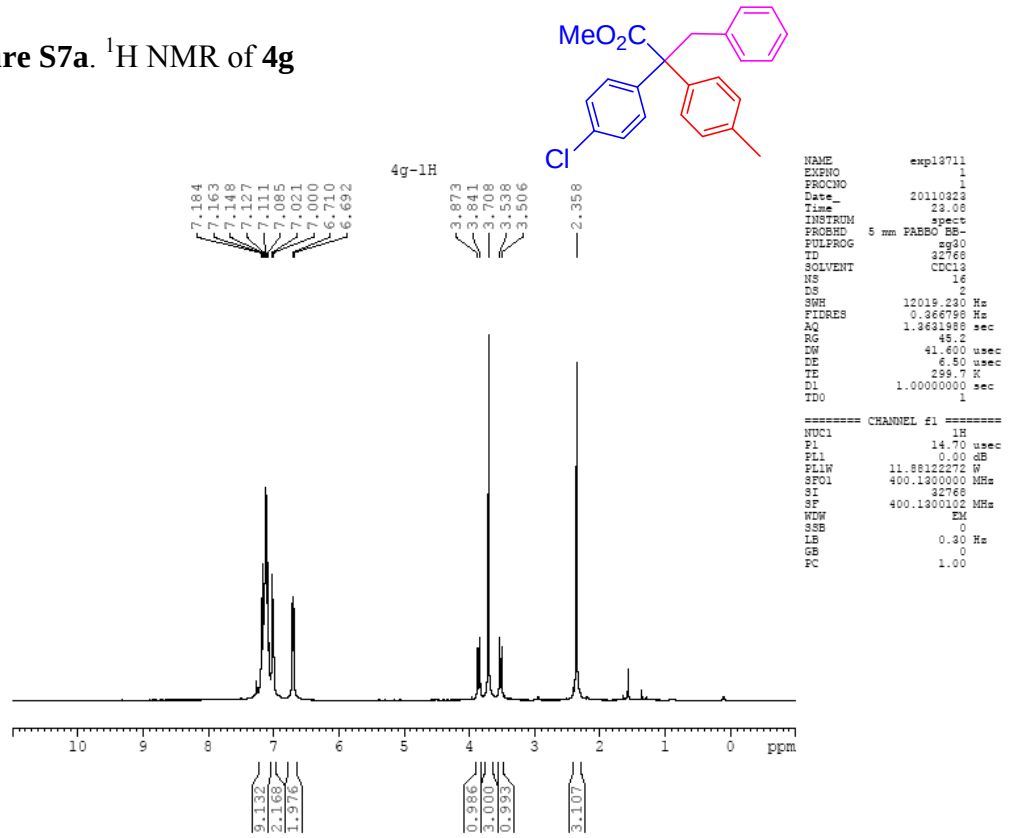


Figure S7b. ^{13}C NMR of **4g**

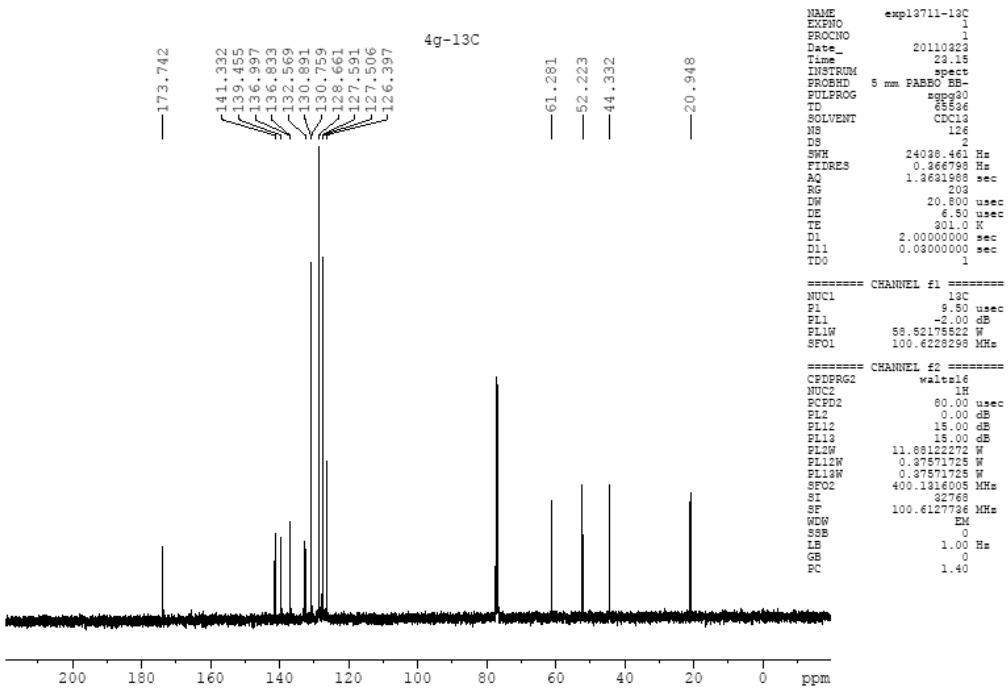


Figure S8a. ^{1}H NMR of **4h**

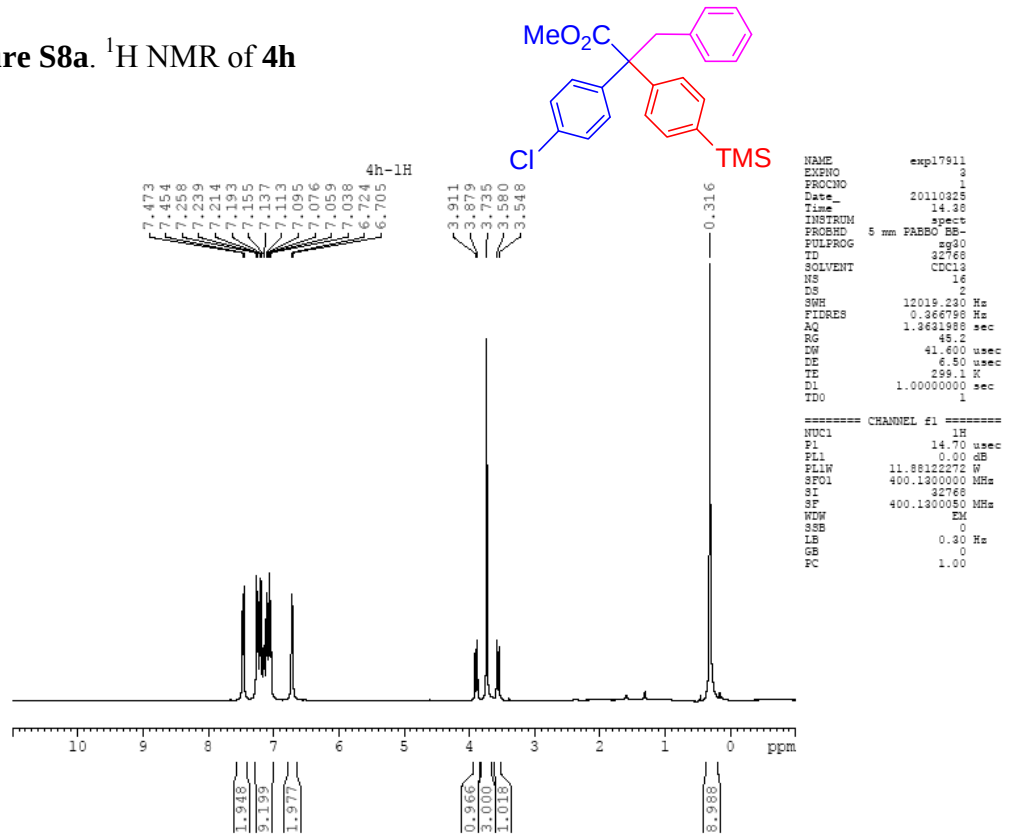


Figure S8b. ^{13}C NMR of **4h**

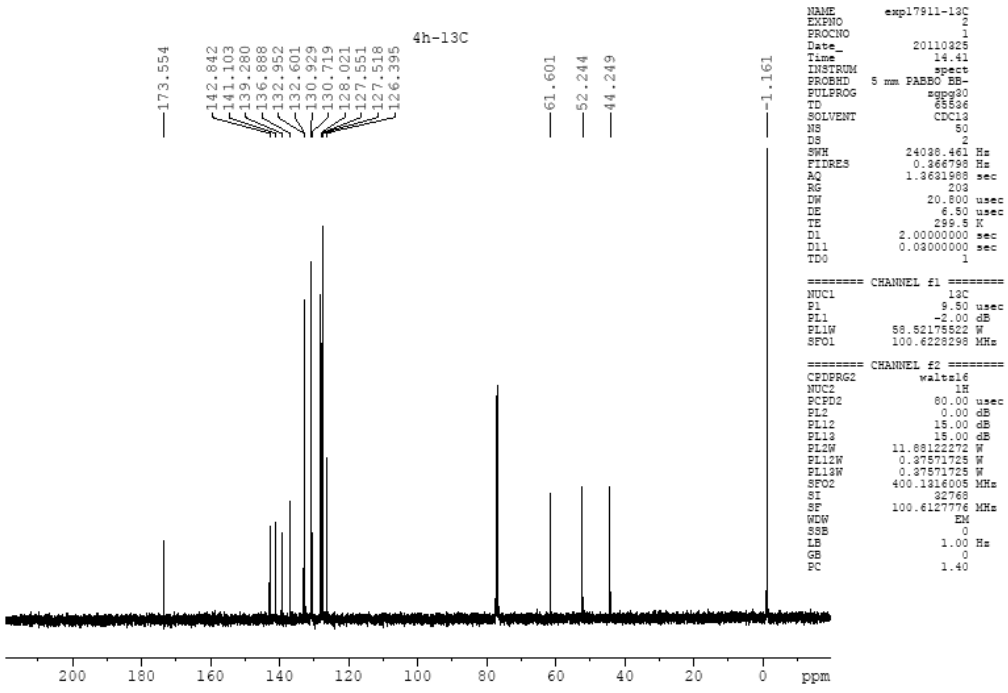


Figure S9a. ^{1}H NMR of **4i**

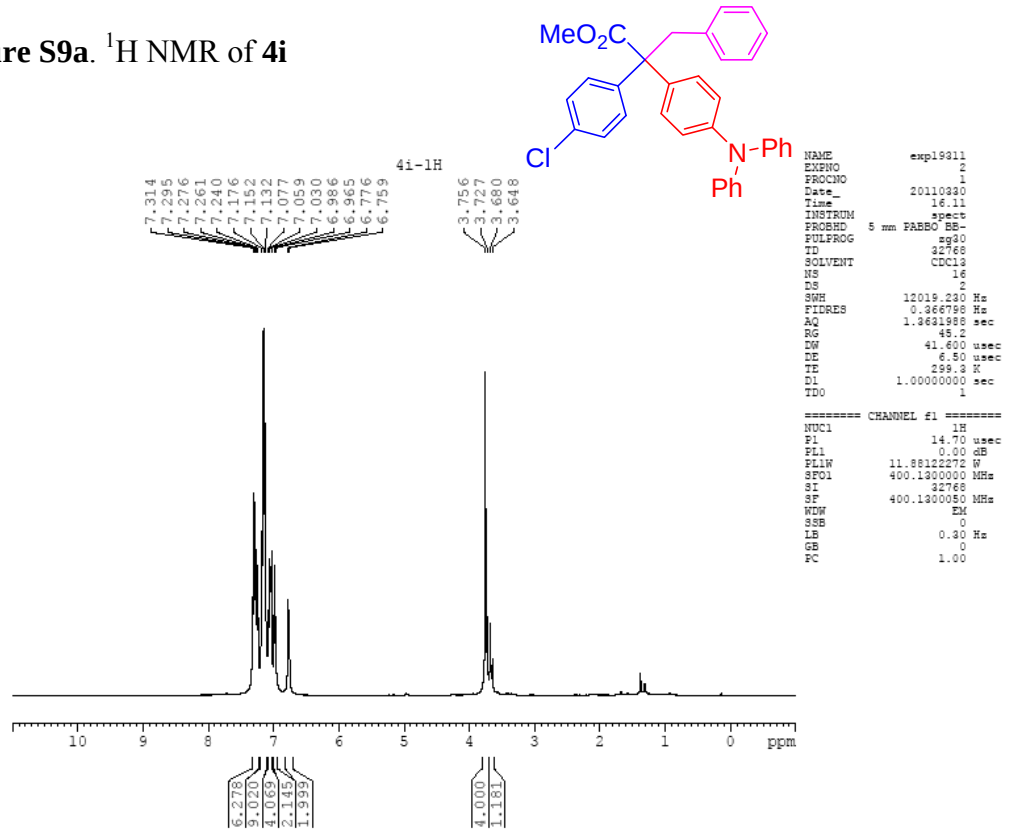


Figure S9b. ^{13}C NMR of **4i**

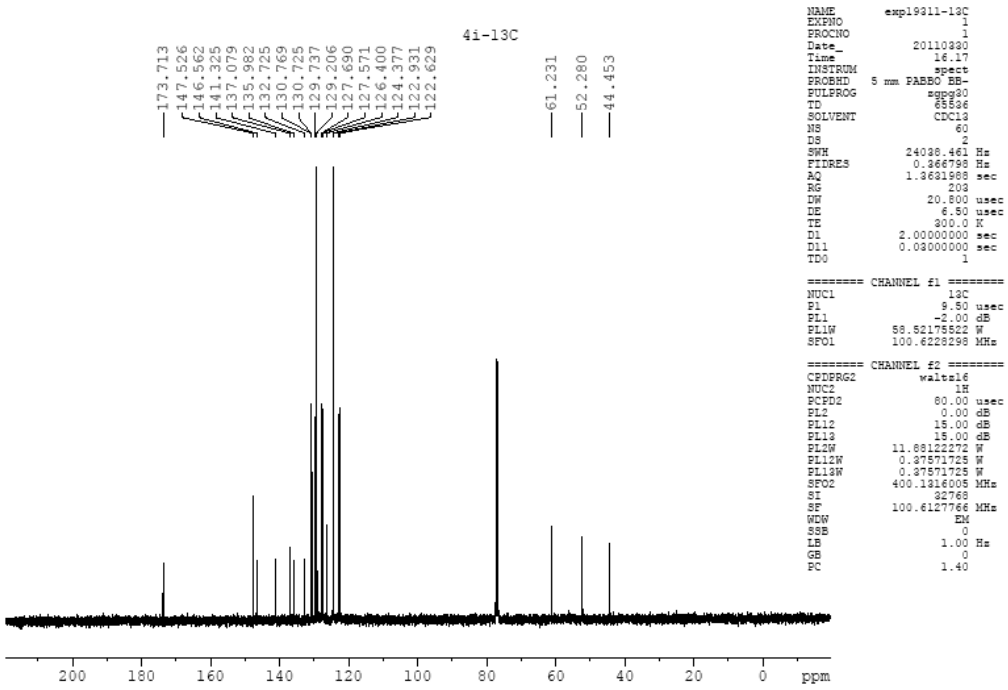
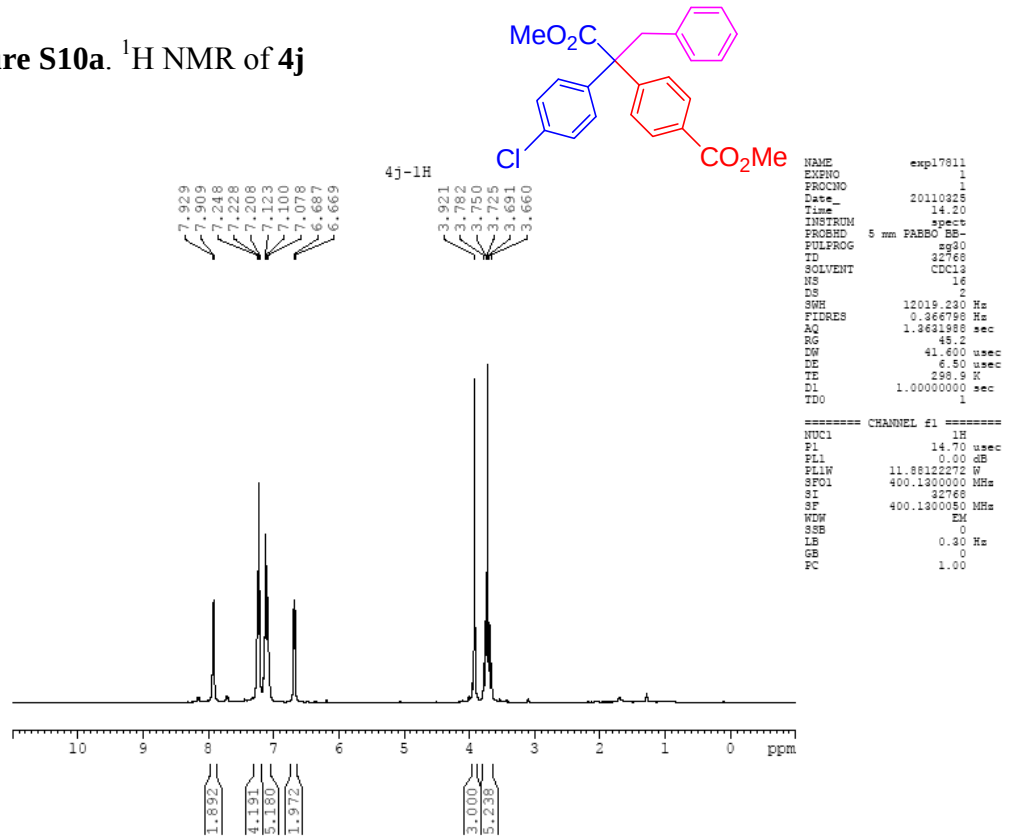


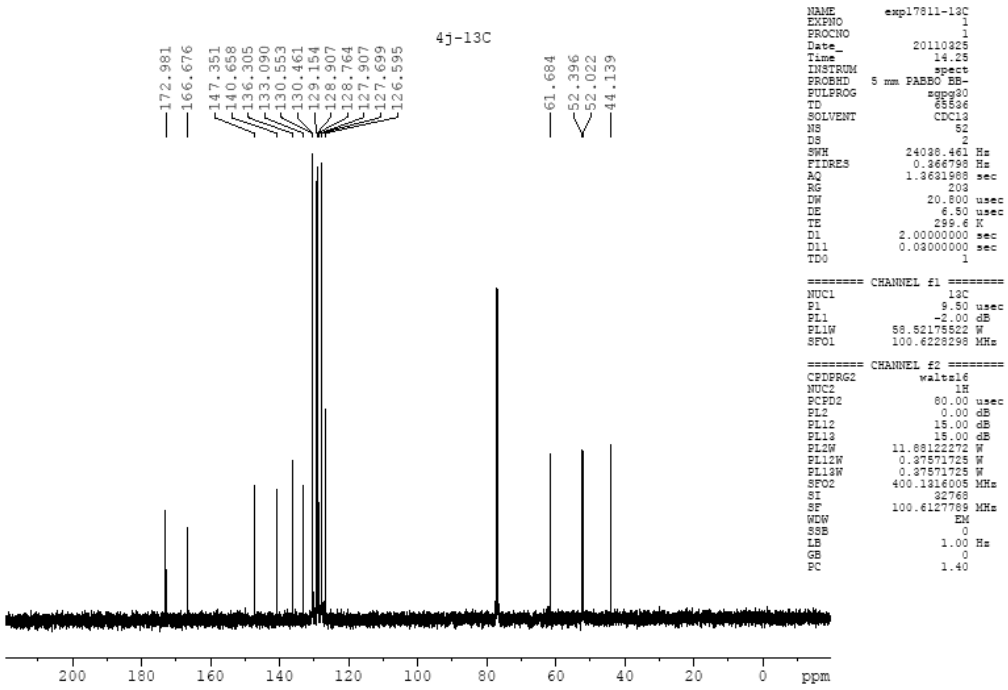
Figure S10a. ^{1}H NMR of **4j**




```
NAME                exp17811
EXPNO                      1
PROCNO                     1
Date_               20110325
Time                   14.20
INSTRUM                spect
PROBHD   5 mm PABBO BB-
PULPROG                zg30
TD                    32768
SOLVENT               CDCl3
NS                        16
DS                         2
SWH               12019.230 Hz
FIDRES             0.366798 Hz
AQ                 1.3621986 sec
RG                      45.2
DW                    41.600 usec
DE                     6.50 usec
TE                    298.9 K
D1                 1.00000000 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                      1H
P1                     14.70 usec
PL1                     0.00 dB
PL1W              11.88122272 W
SFO1             400.1300000 MHz
SI                        32768
SF               400.1300050 MHz
WDW                       EM
SSB                        0
LB                      0.30 Hz
GB                         0
PC                      1.00
```

Figure S10b. ^{13}C NMR of **4j**




```
NAME           exp17811-13C
EXPNO                      1
PROCNO                     1
Date_               20110325
Time                   14.25
INSTRUM                spect
PROBHD   5 mm PABBO BB-
PULPROG            zgpg30
TD                    65536
SOLVENT               CDCl3
NS                        52
DS                         2
SWH               24038.461 Hz
FIDRES             0.366798 Hz
AQ                 1.3631988 sec
RG                       203
DW                    20.800 usec
DE                     6.50 usec
TE                    299.6 K
D1                 2.00000000 sec
D11                0.03000000 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                      13C
P1                      9.50 usec
PL1                    -2.00 dB
PL1W              58.52175522 W
SFO1             100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2                waltz16
NUC2                       1H
PCPD2                  80.00 usec
PL2                     0.00 dB
PL12                   15.00 dB
PL13                   15.00 dB
PL2W              11.88122272 W
PL12W              0.37571725 W
PL13W              0.37571725 W
SFO2             400.1316005 MHz
SI                        32768
SF               100.6127789 MHz
WDW                       EM
SSB                        0
LB                      1.00 Hz
GB                         0
PC                      1.40
```

Figure S11a. ^{1}H NMR of **4k**

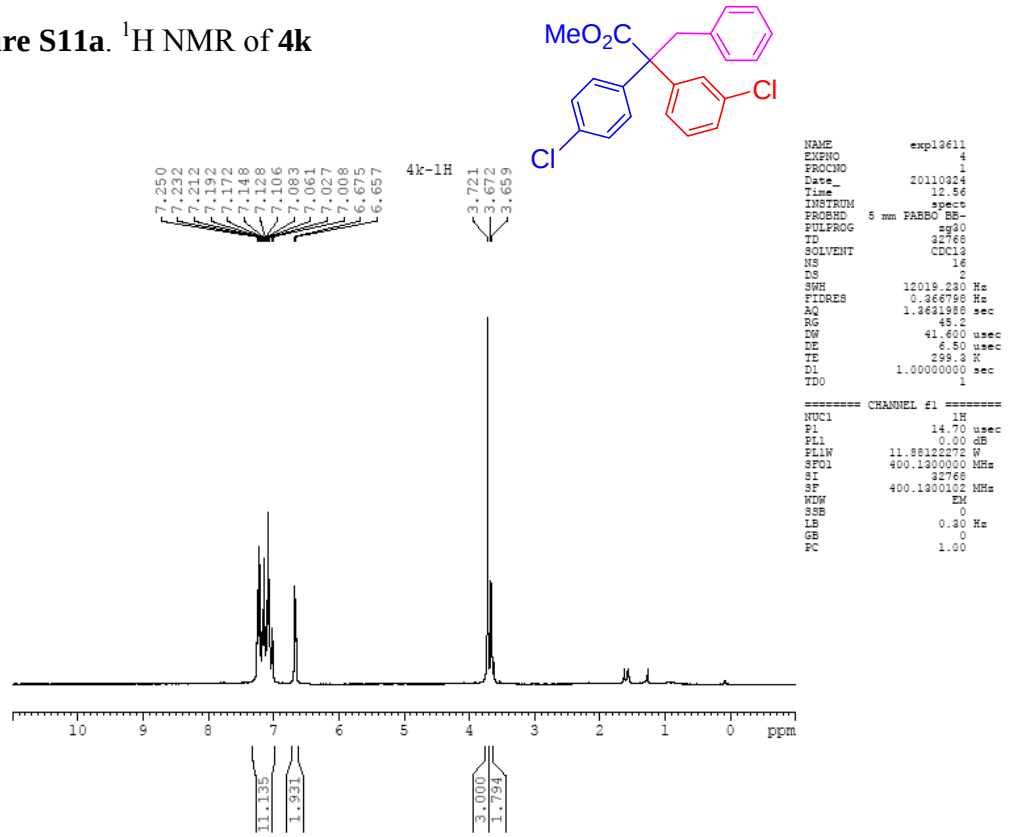


Figure S11b. ^{13}C NMR of **4k**

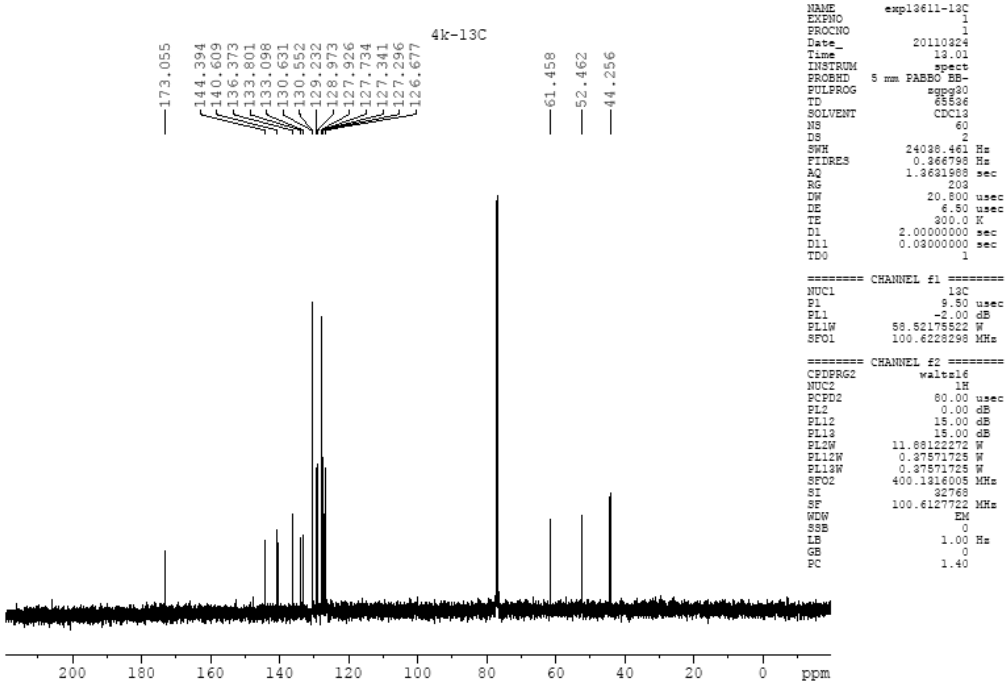


Figure S12a. ^{1}H NMR of **4l**

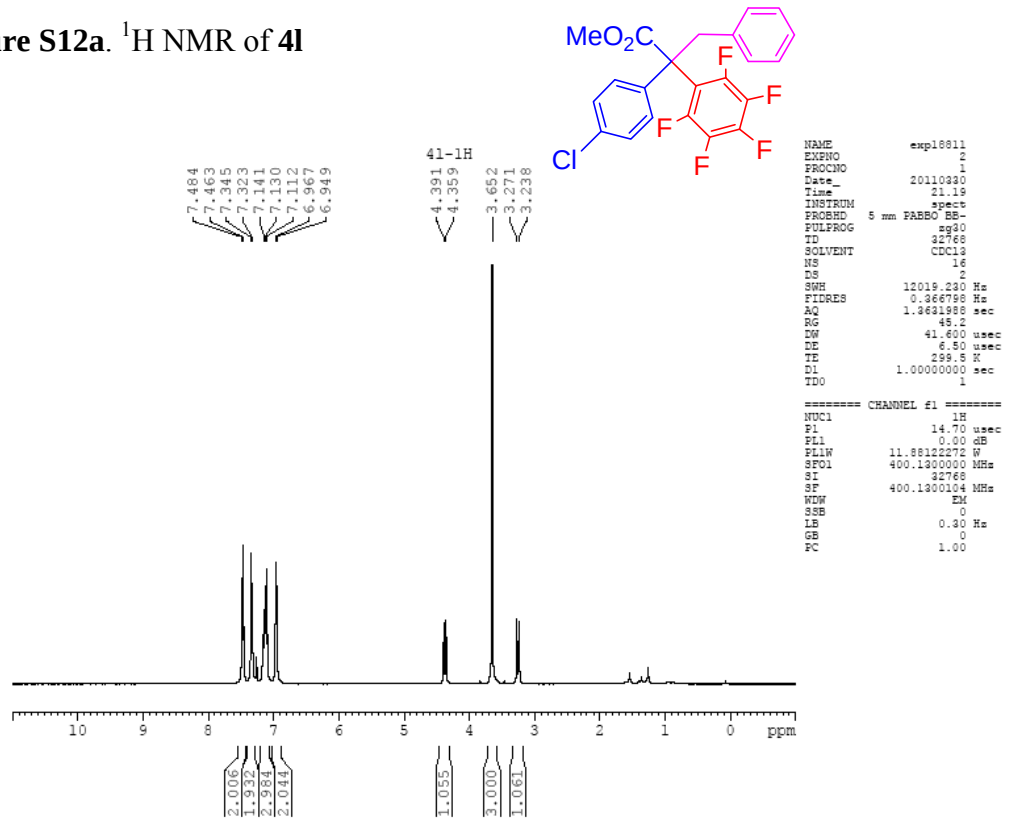


Figure S12b. ^{13}C NMR of **4l**

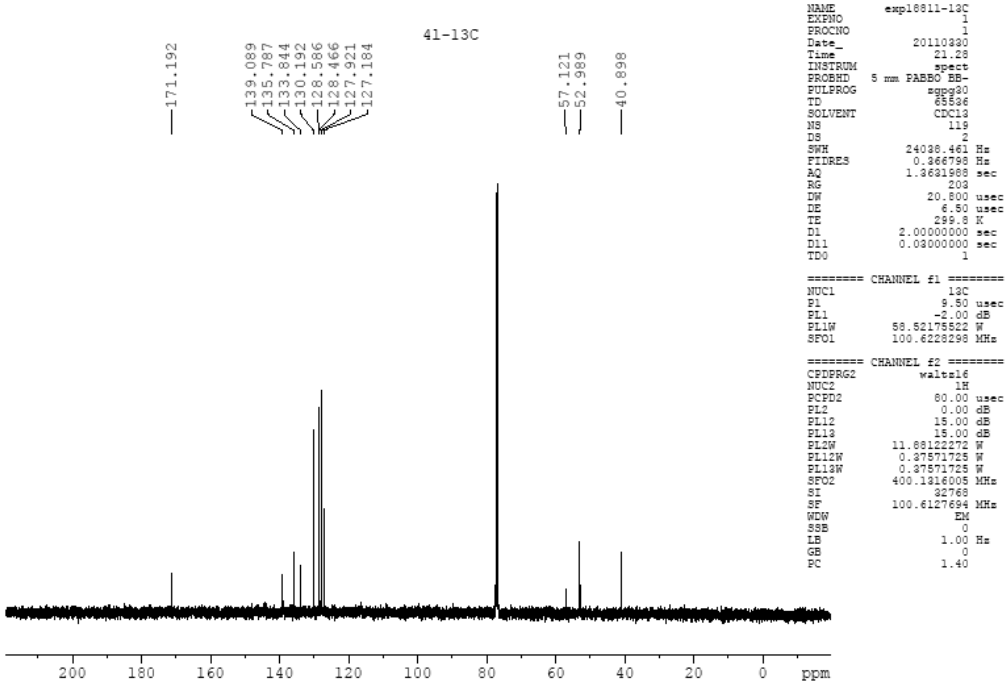


Figure S12c. ^{19}F NMR of **4l**

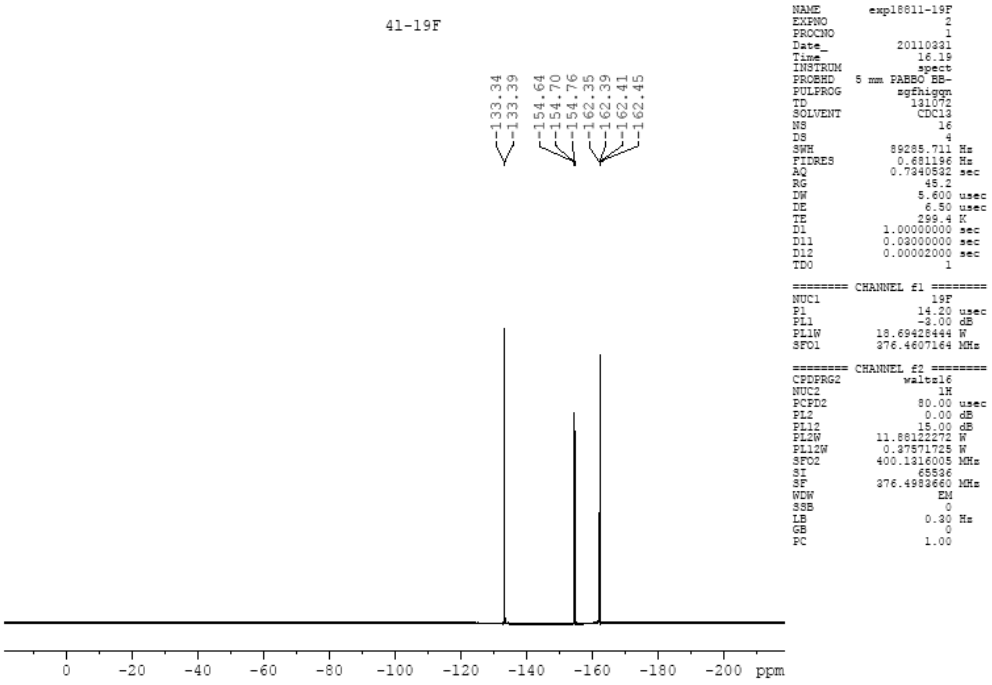


Figure S13a. ^{1}H NMR of **4m**

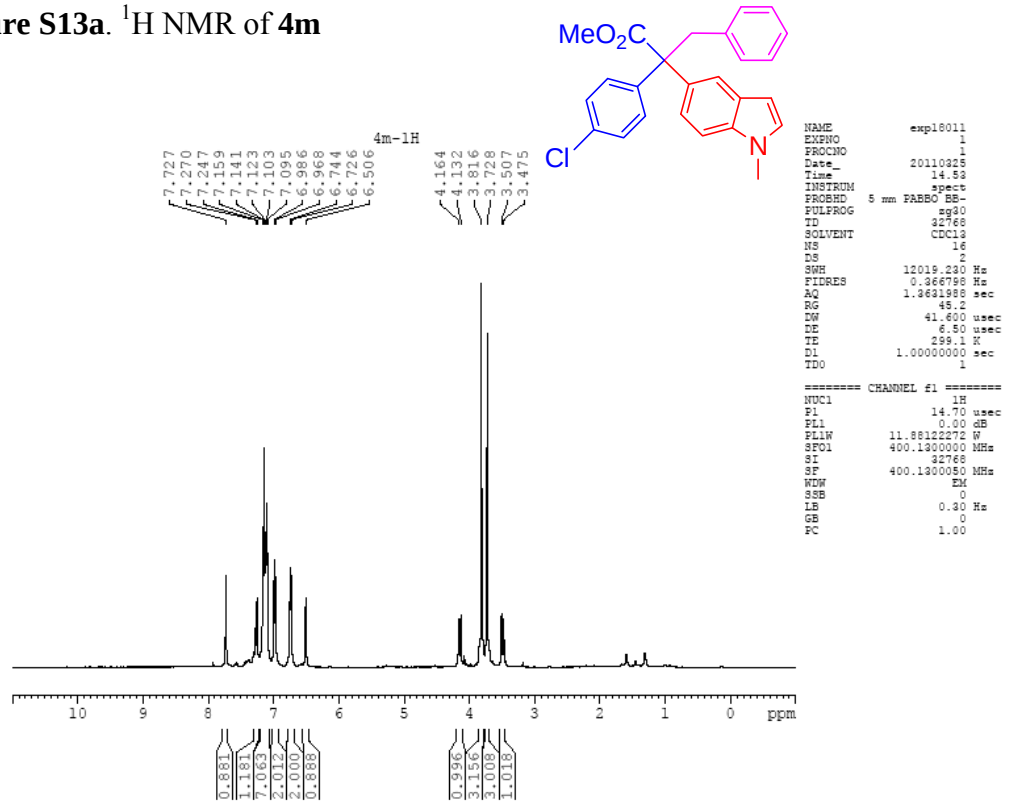


Figure S13b. ^{13}C NMR of **4m**

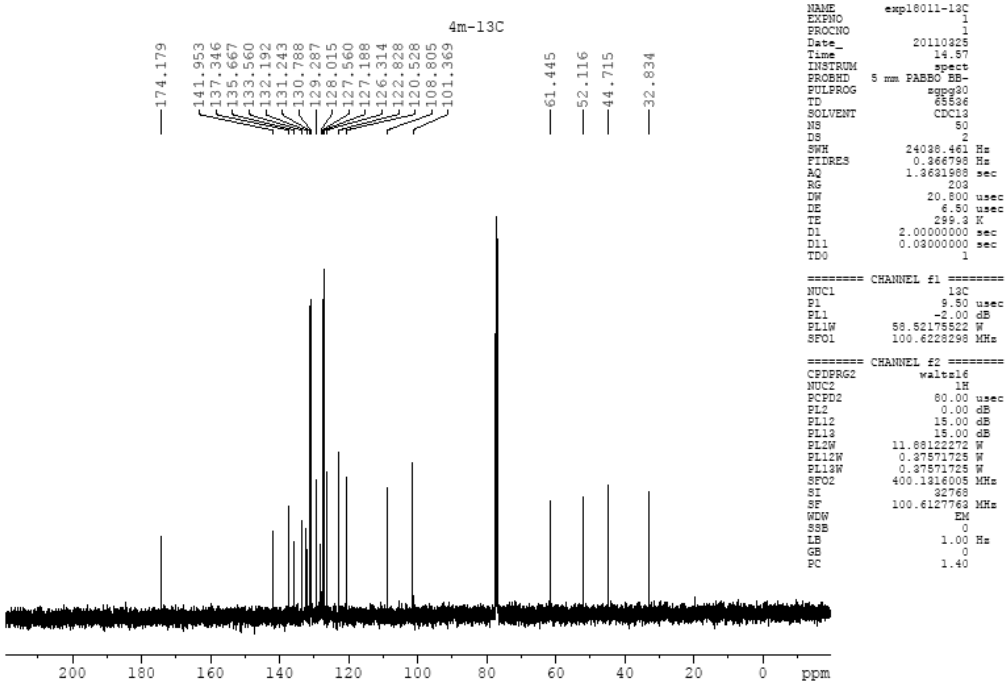


Figure S14a. ^{1}H NMR of **4n**

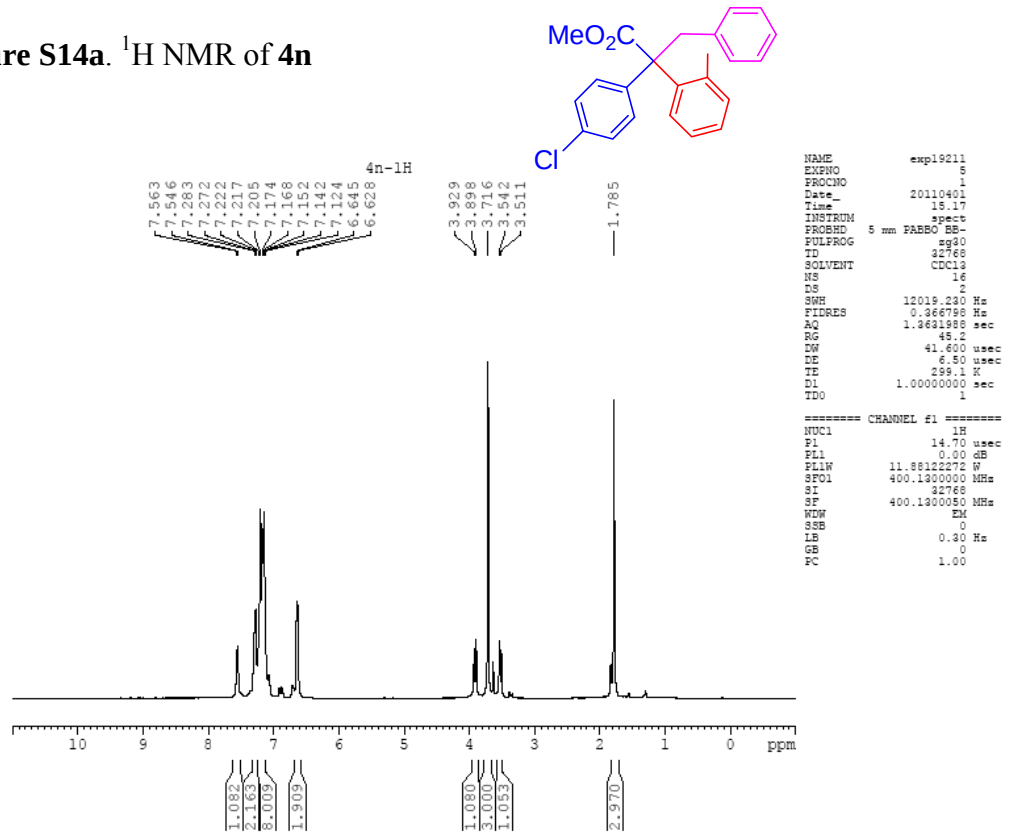


Figure S14b. ^{13}C NMR of **4n**

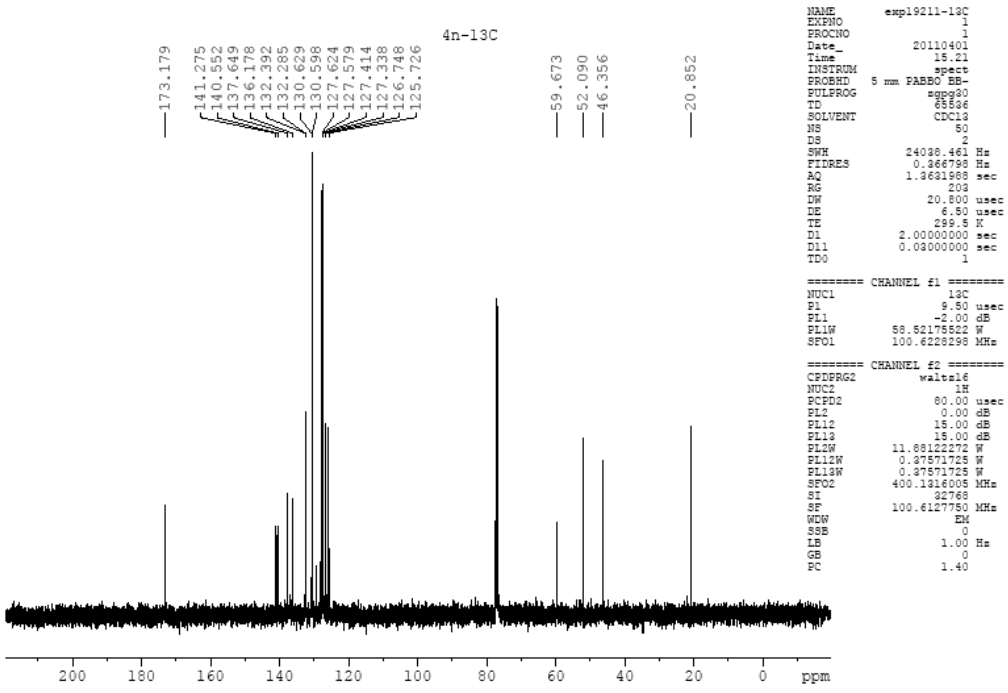


Figure S15a. ^{1}H NMR of **4p**

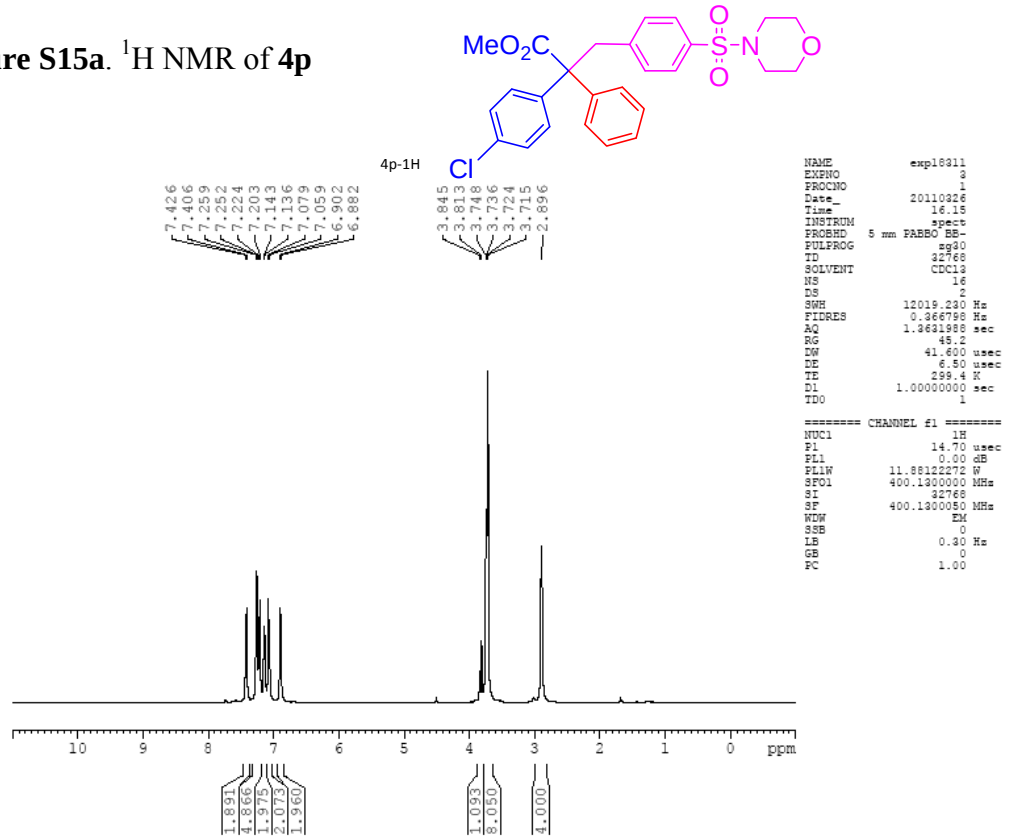


Figure S15b. ^{13}C NMR of **4p**

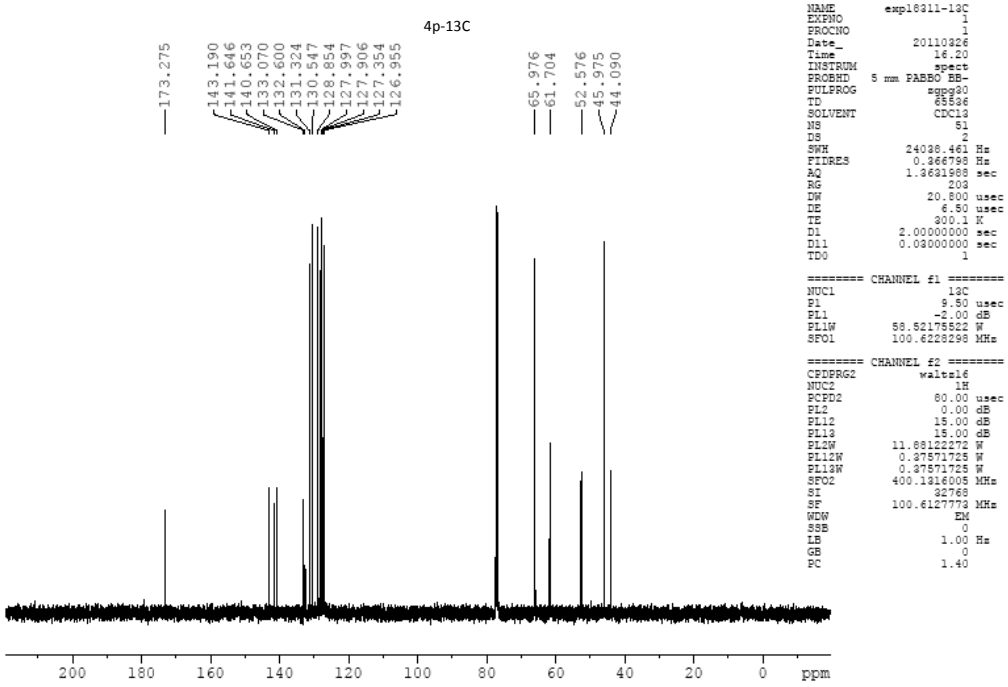


Figure S16a. ^{1}H NMR of **4q**

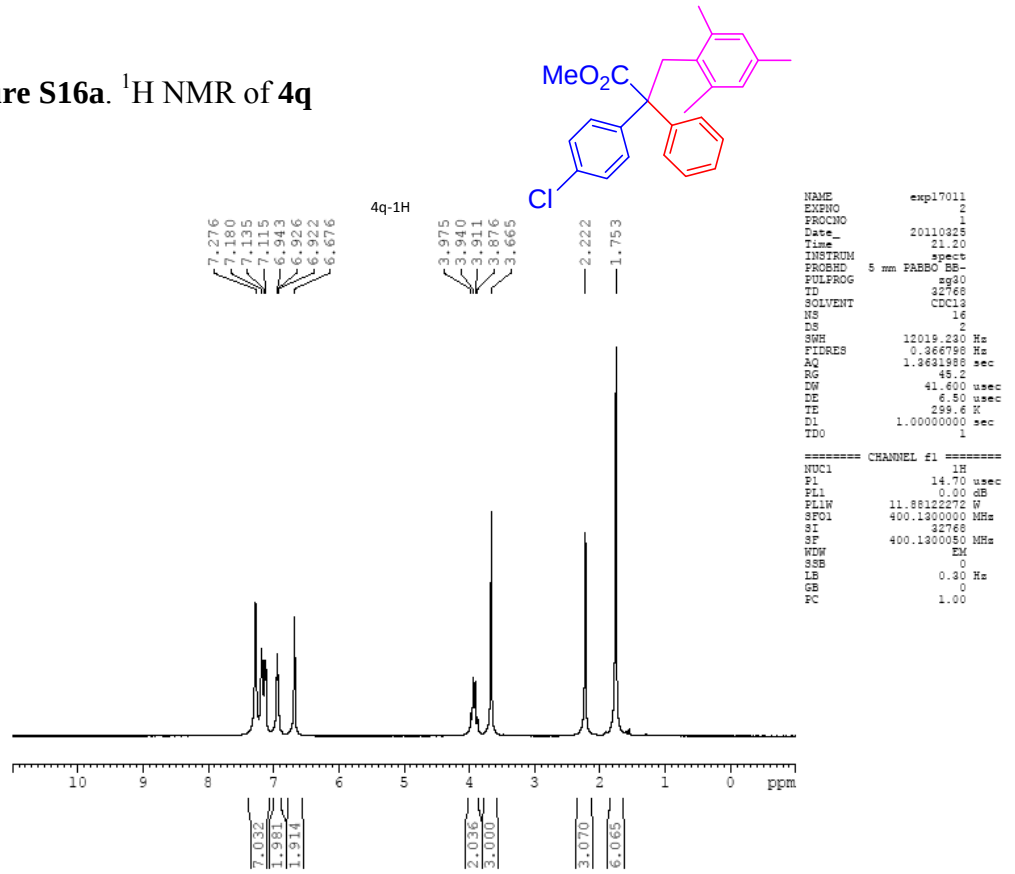


Figure S16b. ^{13}C NMR of **4q**

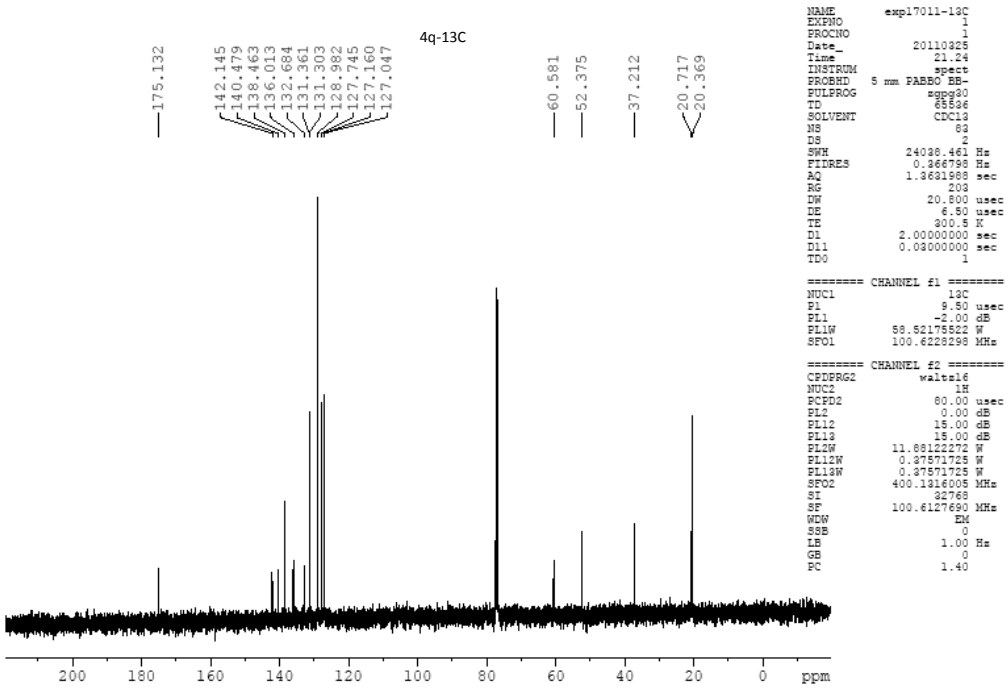


Figure S17a. ^{1}H NMR of **4r**

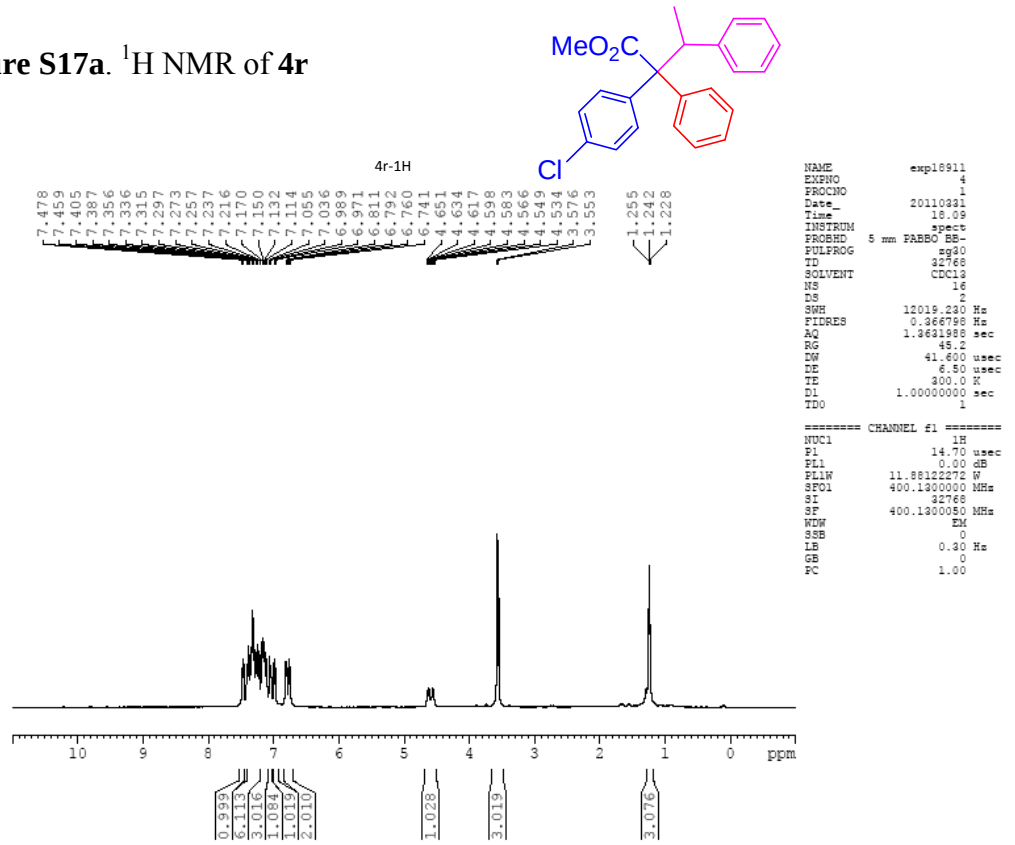


Figure S17b. ^{13}C NMR of **4r**

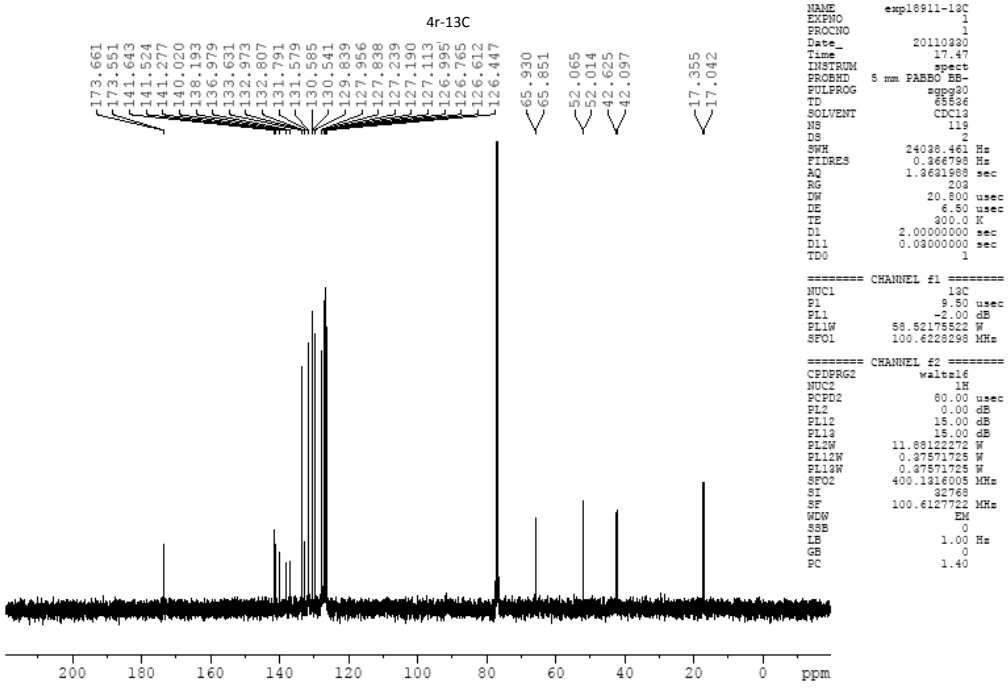


Figure S18a. ^{1}H NMR of **4s**

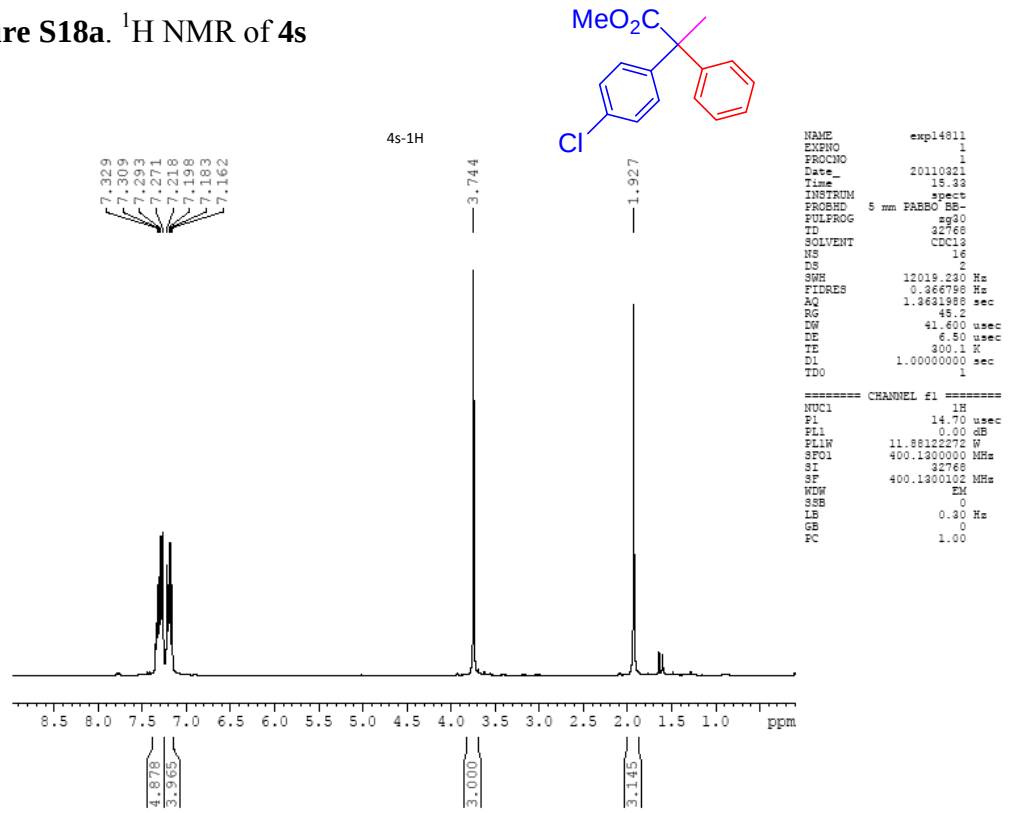


Figure S18b. ^{13}C NMR of **4s**

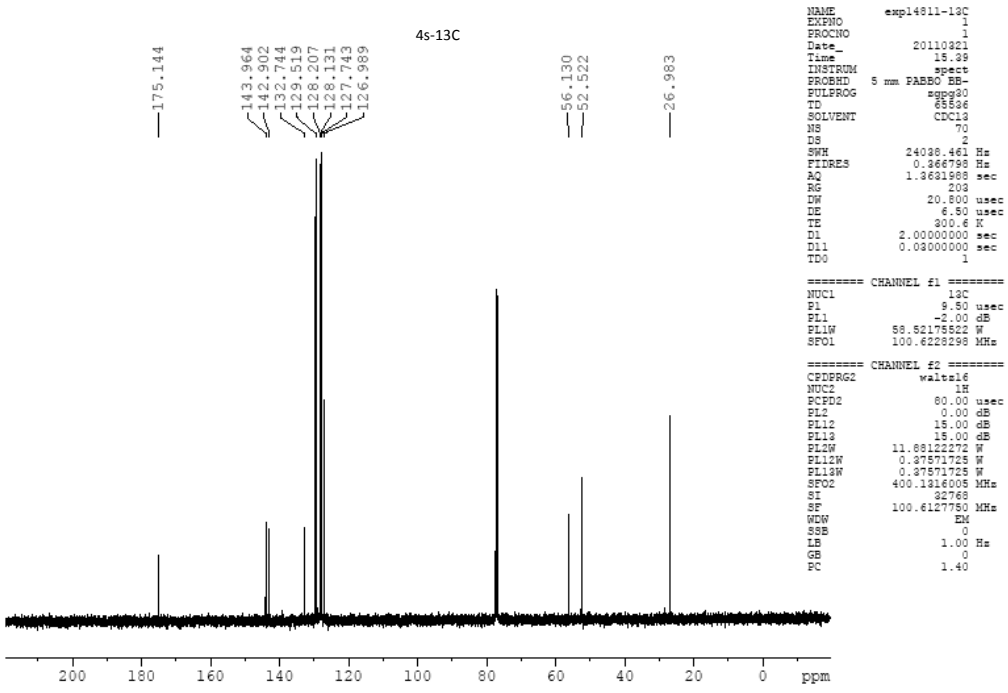


Figure S19a. ^{1}H NMR of **4t**

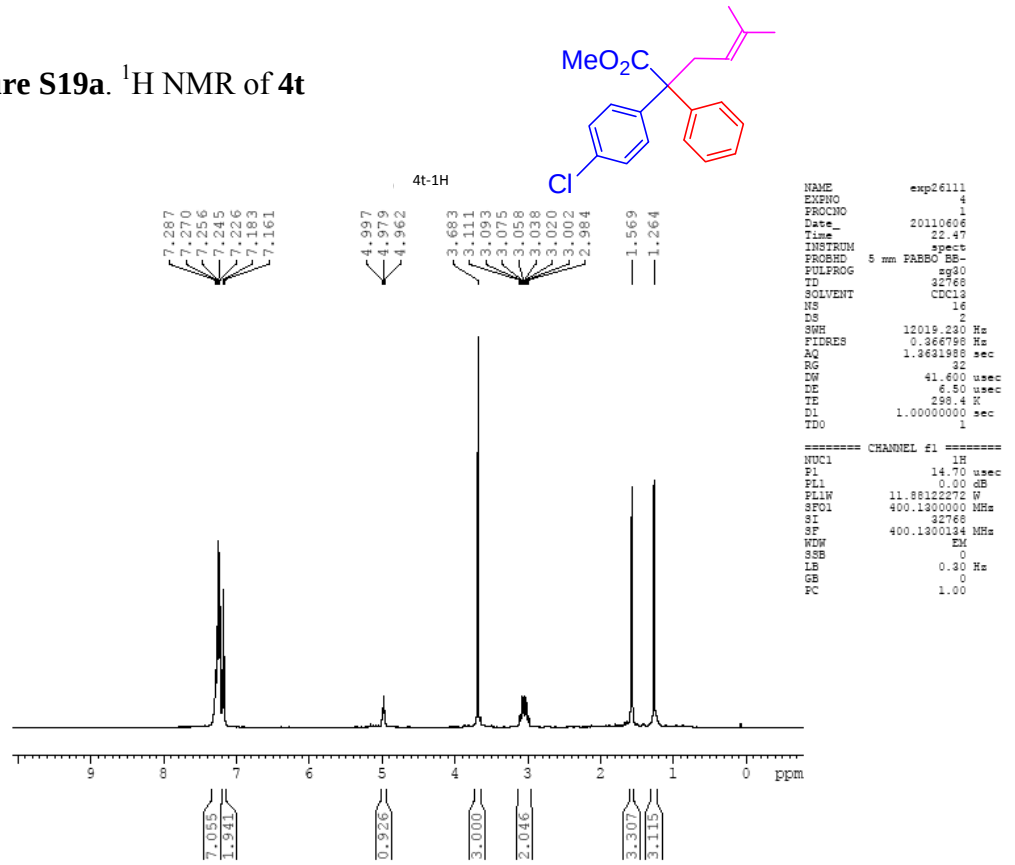


Figure S19b. ^{13}C NMR of **4t**

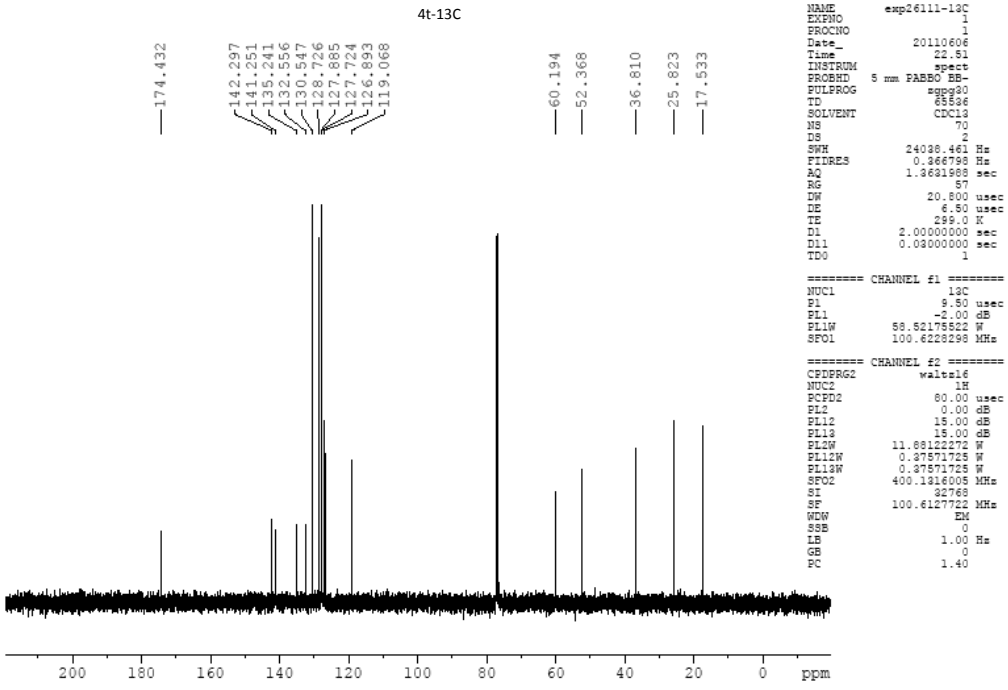


Figure S20a. ^{1}H NMR of **4u**

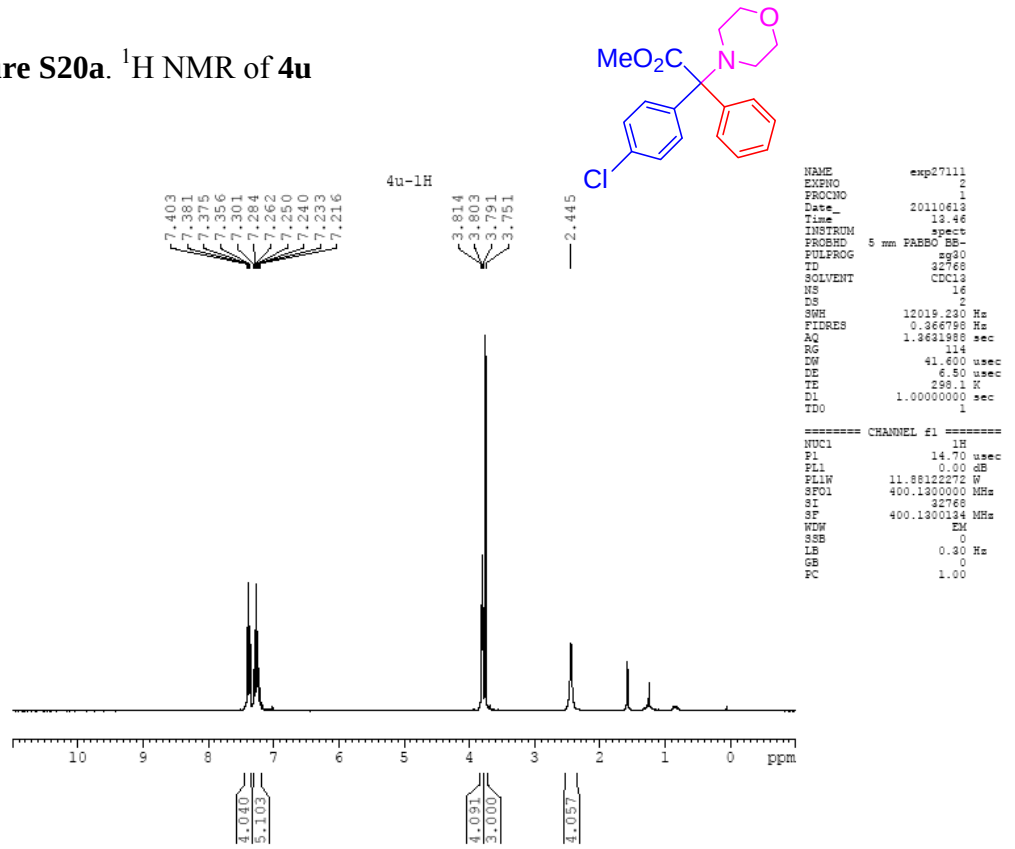


Figure S20b. ^{13}C NMR of **4u**

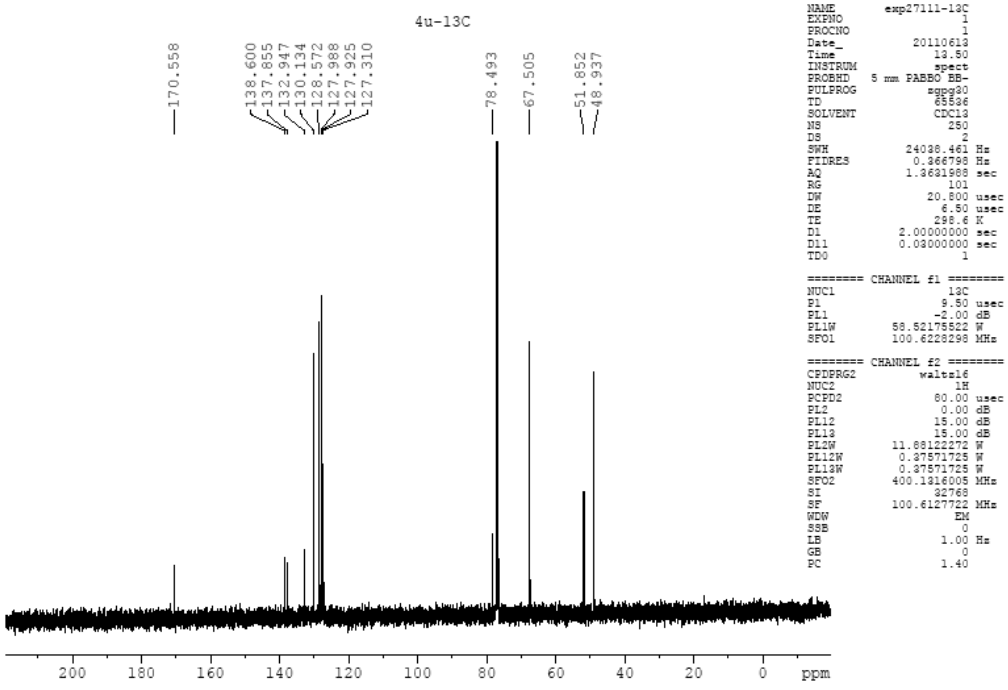


Figure S21a. ^{1}H NMR of **5a**

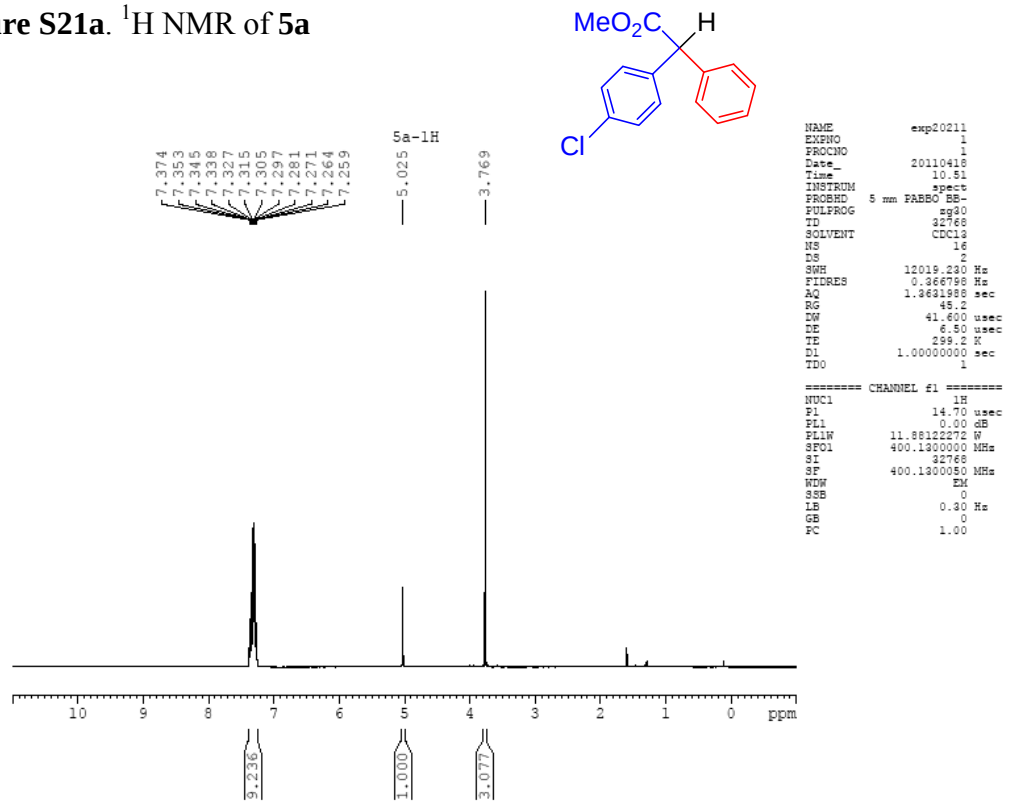


Figure S21b. ^{13}C NMR of **5a**

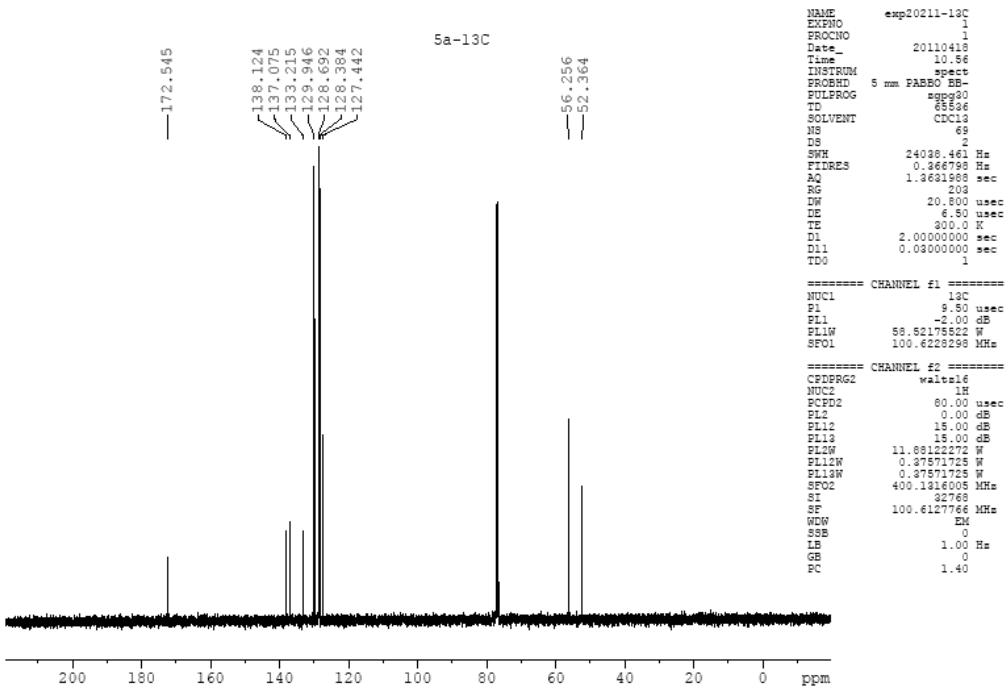


Figure S22a. ^{1}H NMR of **1a**

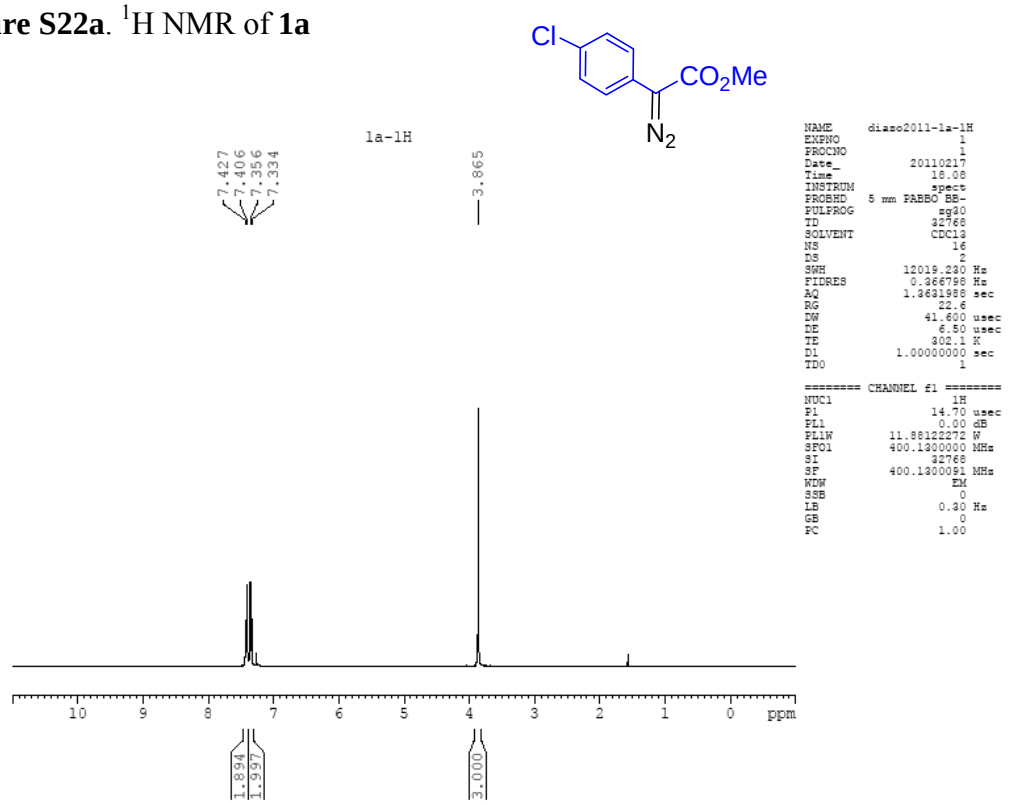


Figure S22b. ^{13}C NMR of **1a**

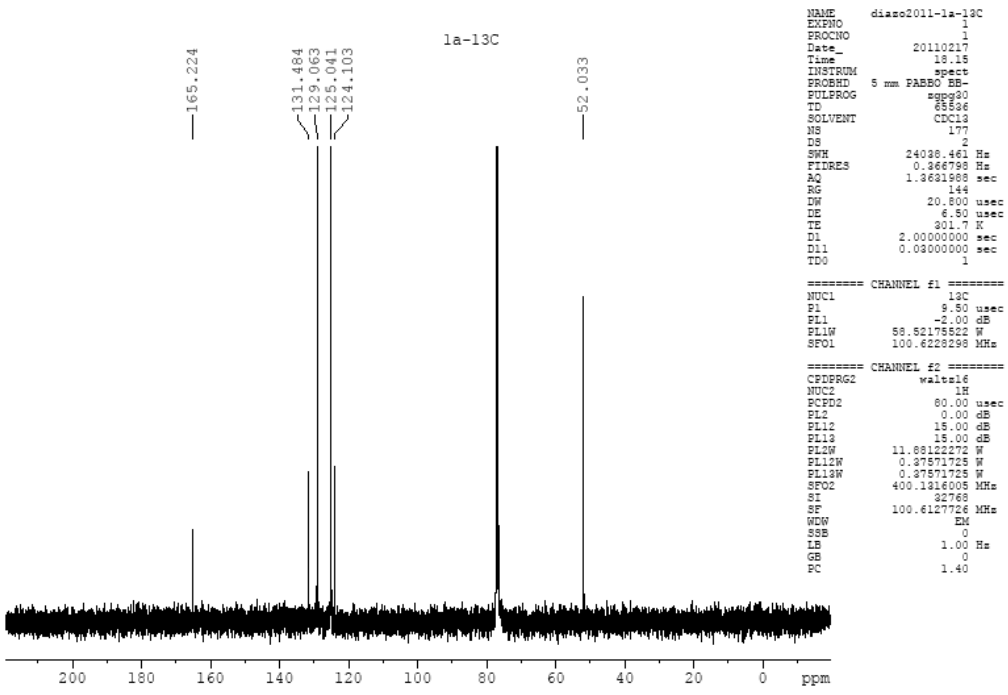


Figure S23a. ^{1}H NMR of **1b**

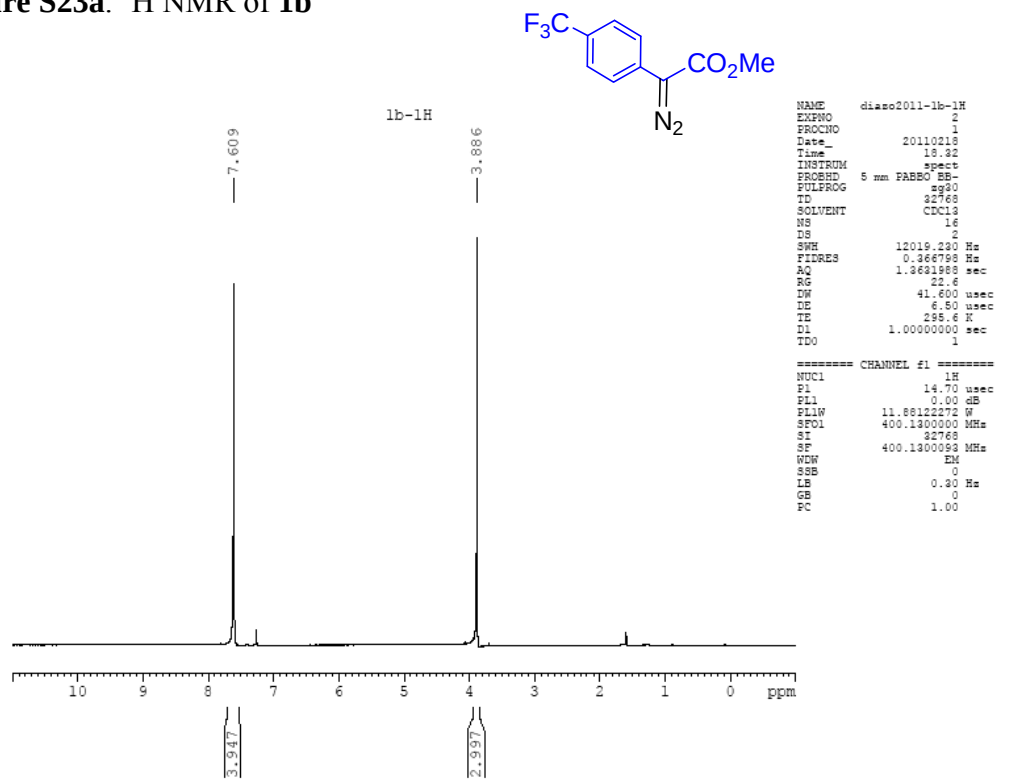


Figure S23b. ^{13}C NMR of **1b**

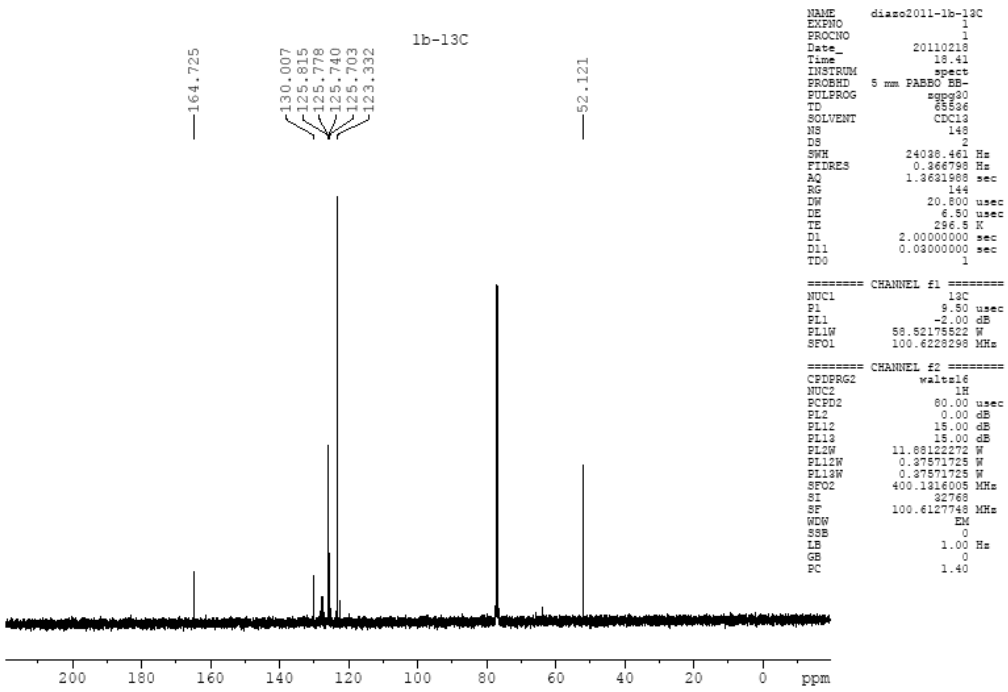


Figure S23c. ^{19}F NMR of **1b**

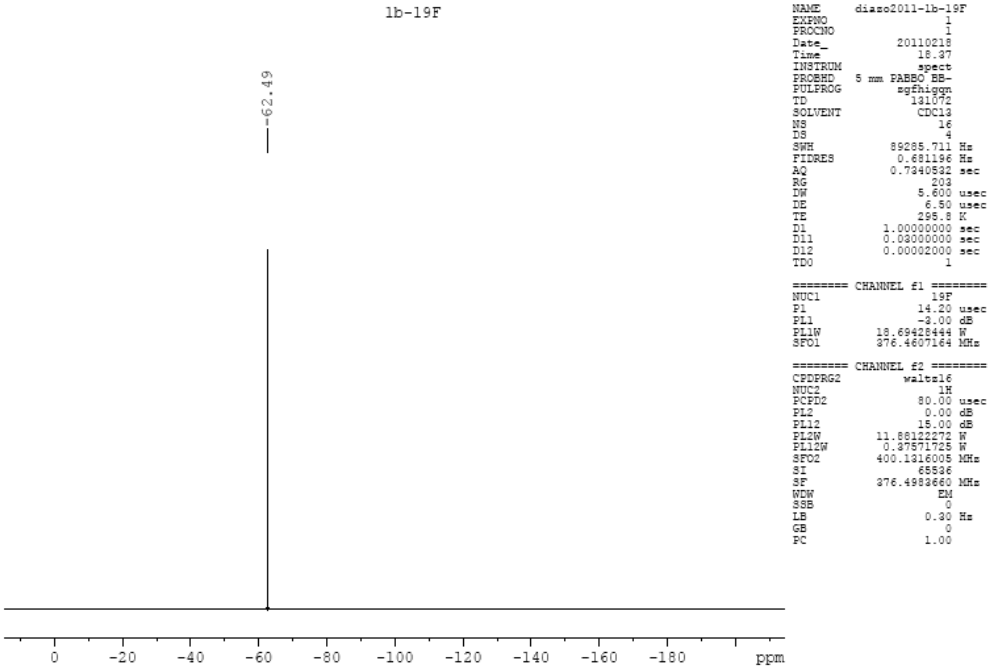


Figure S24a. ^{1}H NMR of **1c**

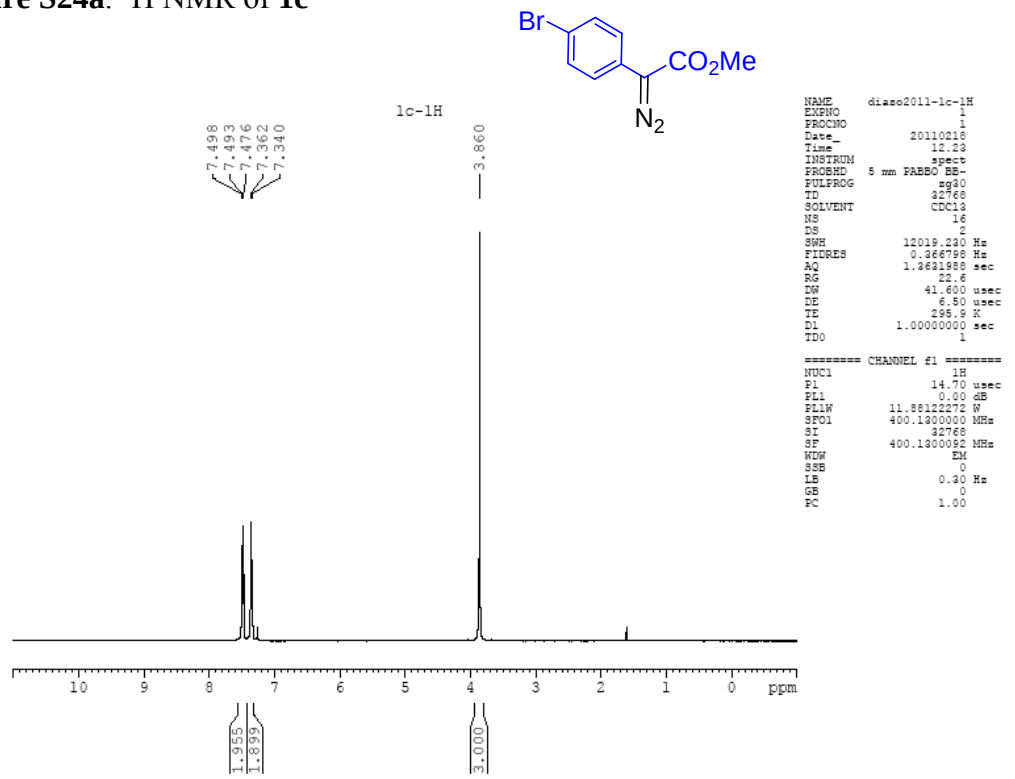


Figure S24b. ^{13}C NMR of **1c**

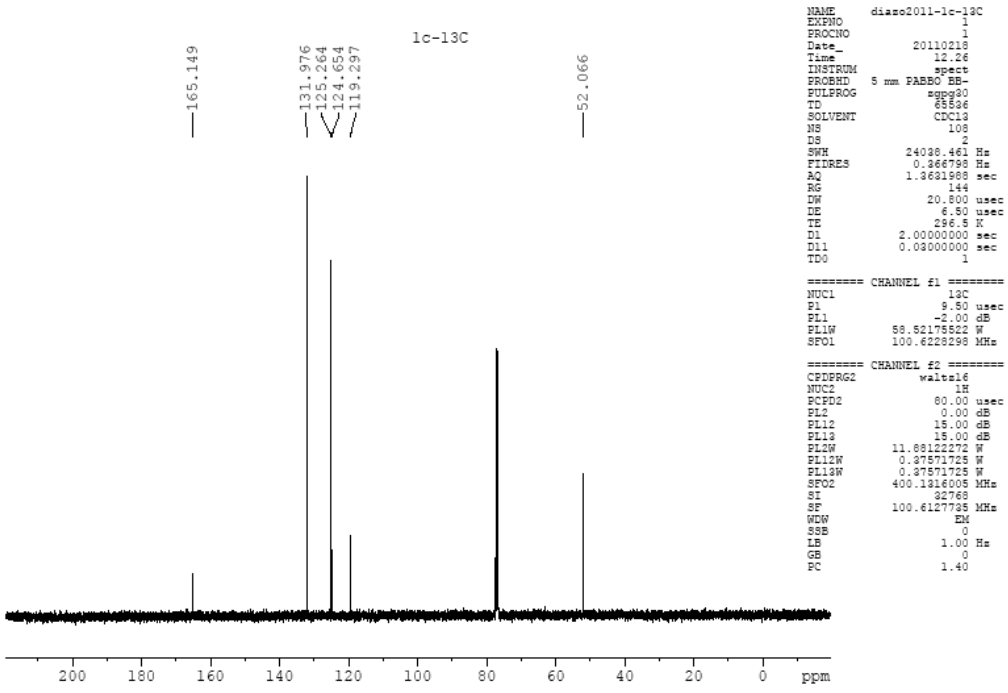


Figure S25a. ^{1}H NMR of **1d**

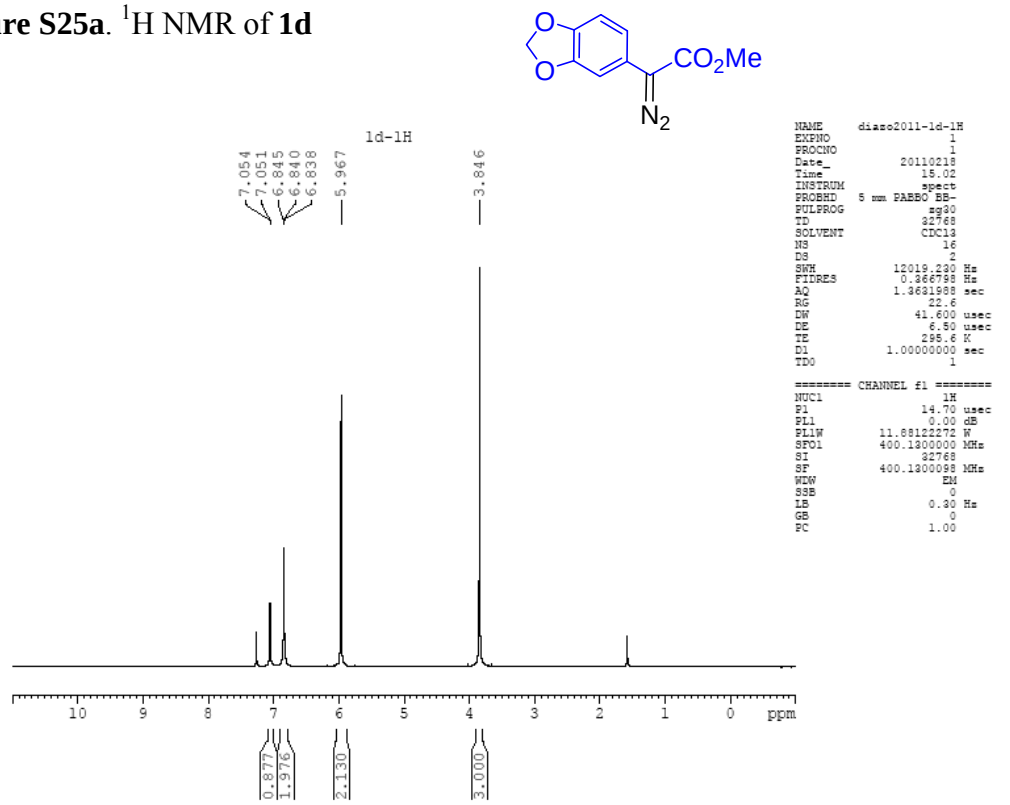


Figure S25b. ^{13}C NMR of **1d**

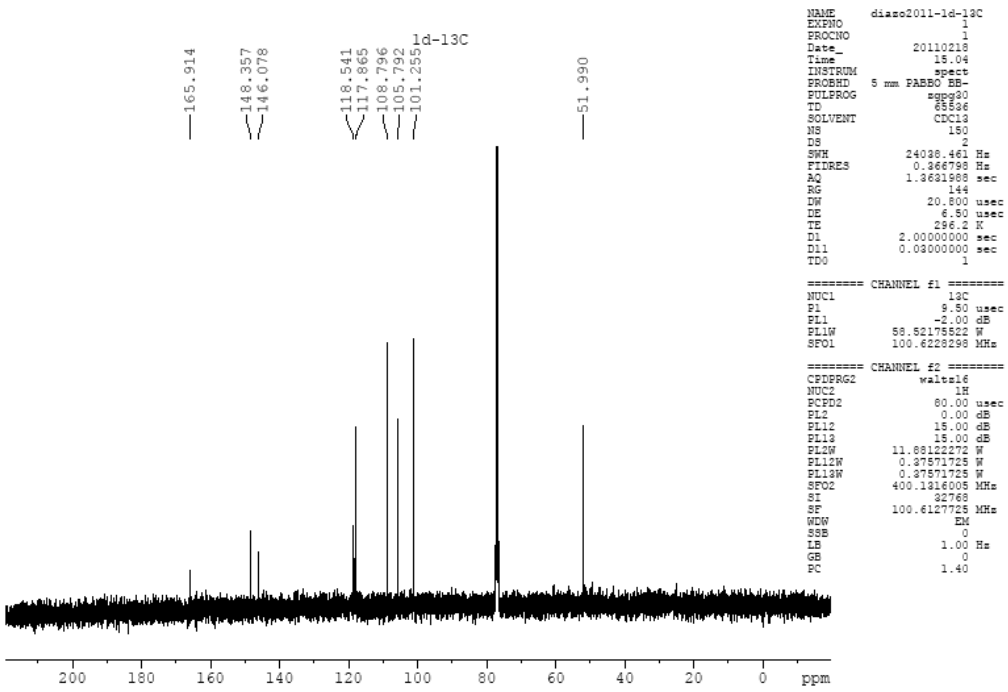


Figure S26a. ^{1}H NMR of **1e**

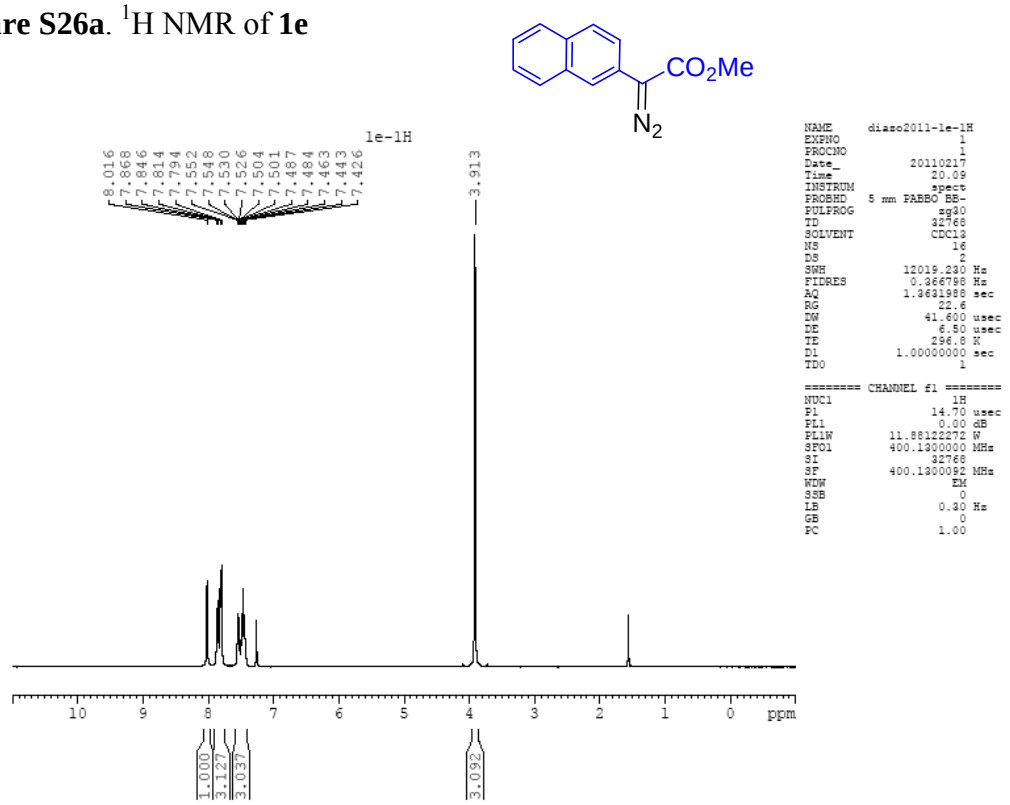


Figure S26b. ^{13}C NMR of **1e**

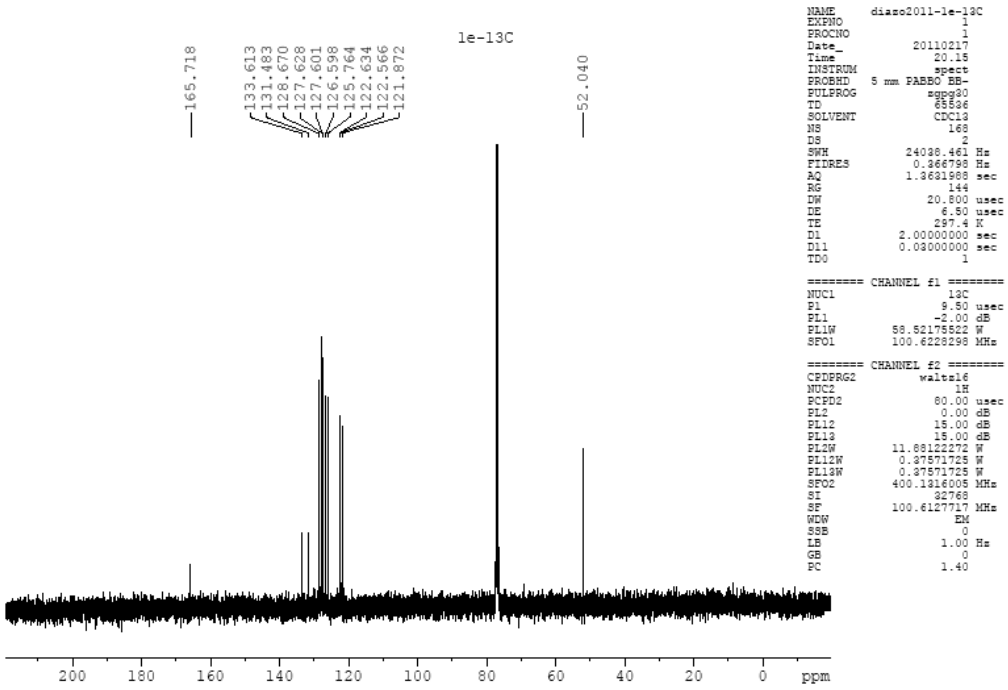


Figure S27a. ^{1}H NMR of **1f**

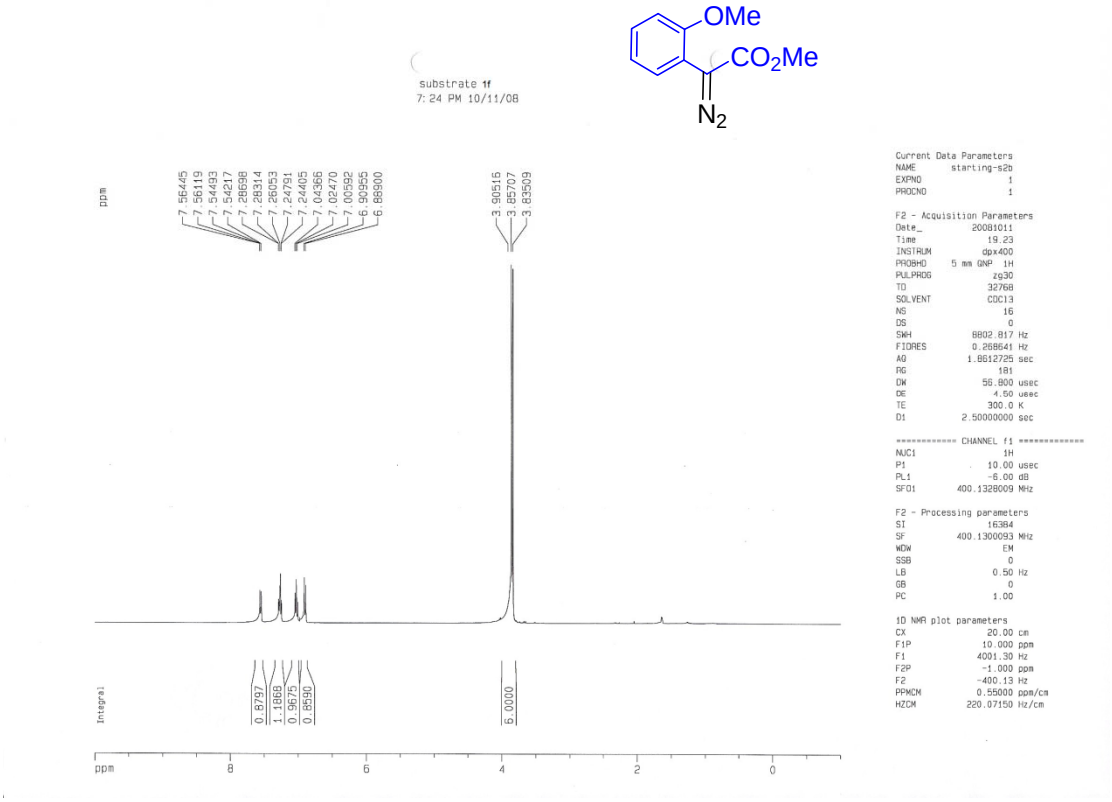


Figure S27b. ^{13}C NMR of **1f**

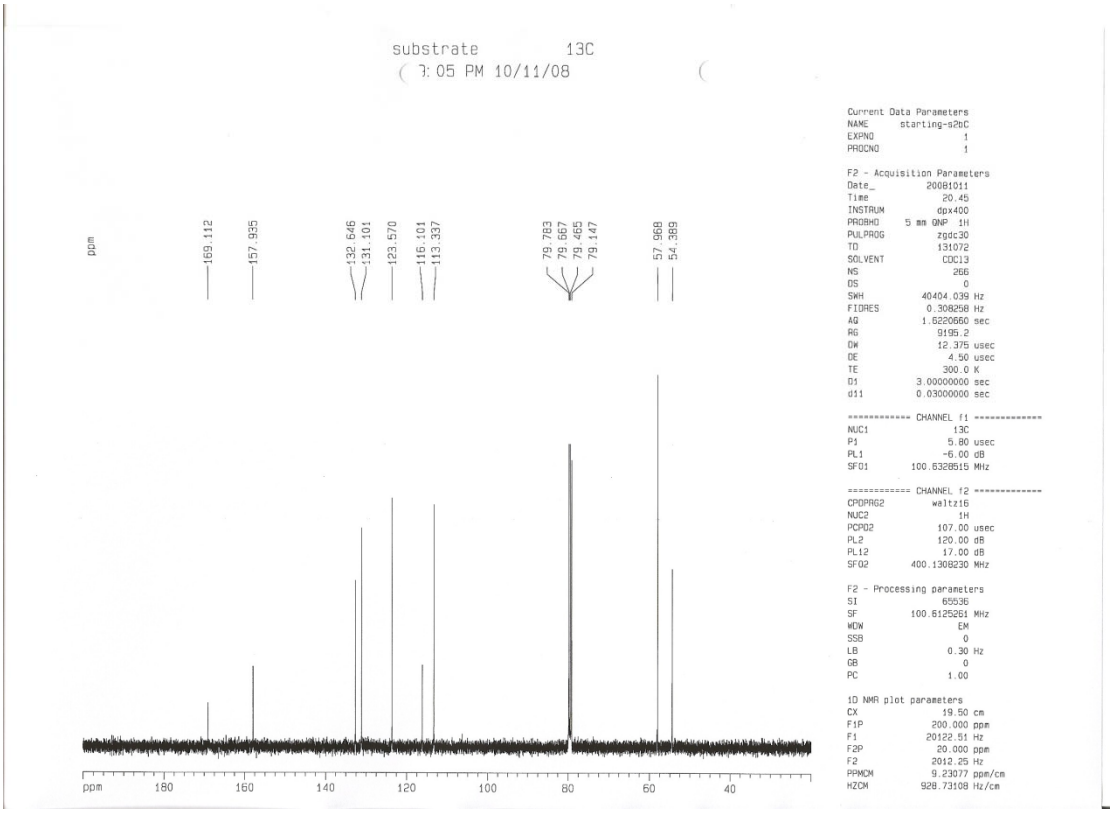
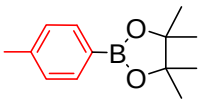
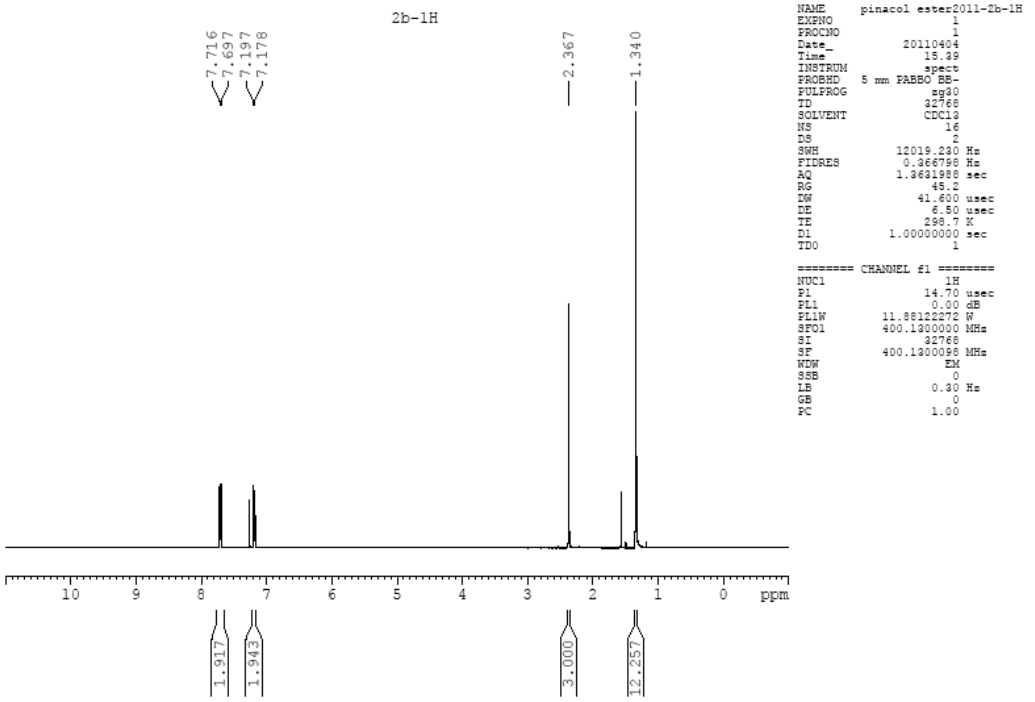


Figure S28a. ^{1}H NMR of **2b**

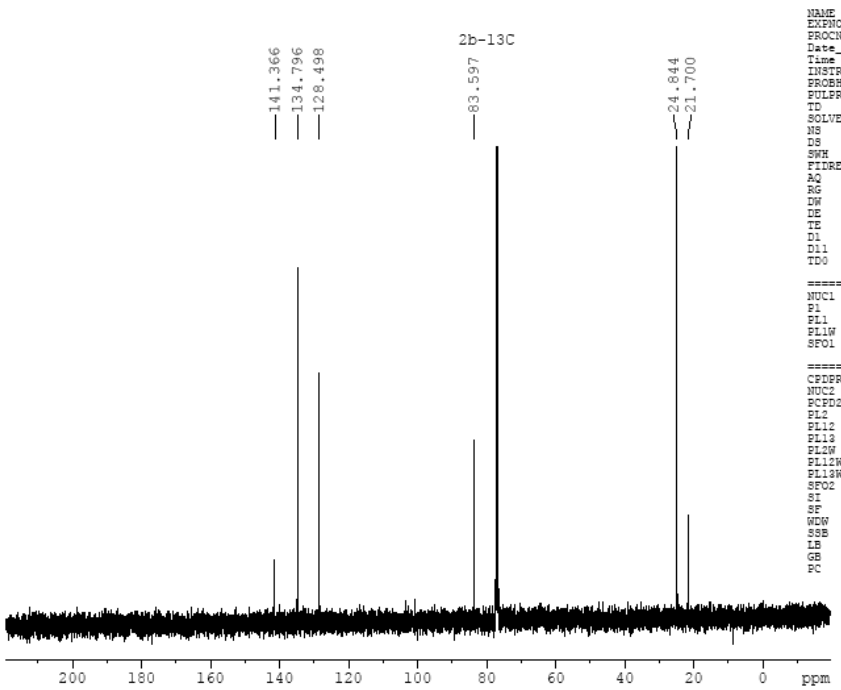





```
NAME            pinacol ester2011-2b-1H
EXPNO                     1
PROCNO                    1
Date_              20110404
Time                  15.39
INSTRUM               spect
PROBHD     5 mm PABBO BB-
PULPROG               zg30
TD                   32768
SOLVENT              CDCl3
NS                      16
DS                       2
SWH              12019.230 Hz
FIDRES            0.366798 Hz
AQ                1.3621986 sec
RG                     45.2
DW                  41.600 usec
DE                   6.50 usec
TE                  298.7 K
D1                1.00000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                    1H
P1                   14.70 usec
PL1                   0.00 dB
PL1W           11.88122272 W
SFO1          400.1300000 MHz
SI                   32768
SF            400.1300098 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    1.00
```

Figure S28b. ^{13}C NMR of **2b**

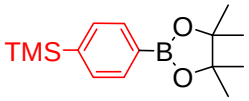



```
NAME            pinacol ester2011-2b-13C
EXPNO                     1
PROCNO                    1
Date_              20110404
Time                  15.43
INSTRUM               spect
PROBHD     5 mm PABBO BB-
PULPROG           zgpg30
TD                   65536
SOLVENT              CDCl3
NS                     103
DS                       2
SWH              24038.461 Hz
FIDRES            0.366798 Hz
AQ                1.3631988 sec
RG                     161
DW                  20.800 usec
DE                   6.50 usec
TE                  299.2 K
D1                2.00000000 sec
D11               0.03000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                   13C
P1                    9.50 usec
PL1                  -2.00 dB
PL1W           58.52175522 W
SFO1          100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2             waltz16
NUC2                    1H
PCPD2                80.00 usec
PL2                   0.00 dB
PL12                 15.00 dB
PL13                 15.00 dB
PL2W           11.88122272 W
PL12W           0.37571725 W
PL13W           0.37571725 W
SFO2          400.1316005 MHz
SI                   32768
SF            100.6127702 MHz
WDW                     EM
SSB                      0
LB                    1.00 Hz
GB                       0
PC                    1.40
```

Figure S29a. ^{1}H NMR of **2c**



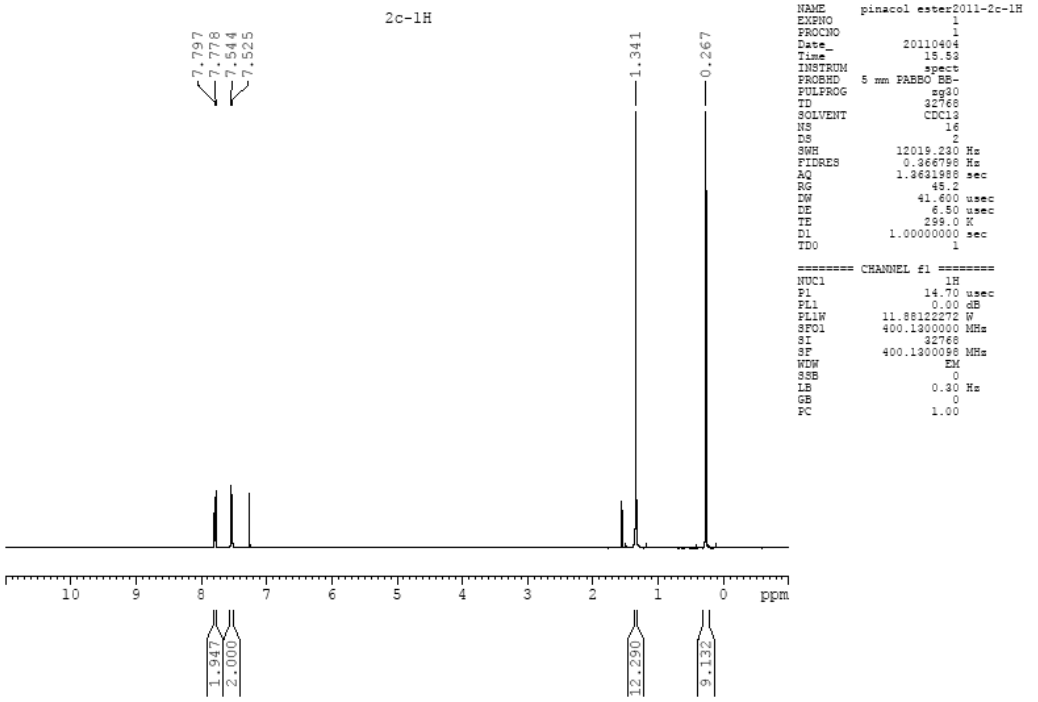


Figure S29b. ^{13}C NMR of **2c**

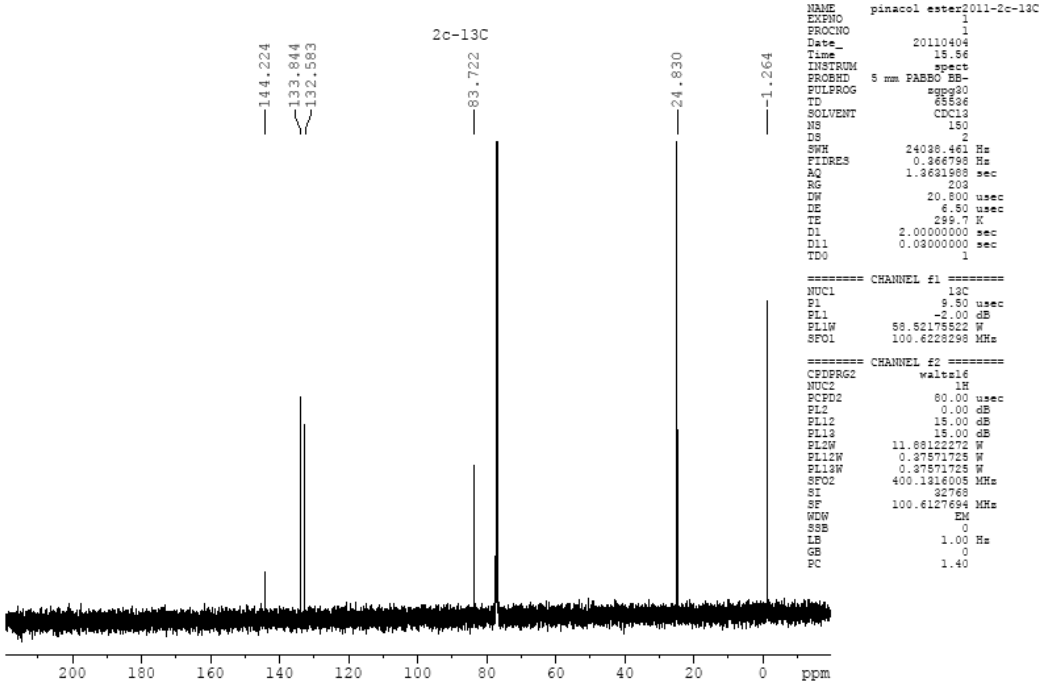
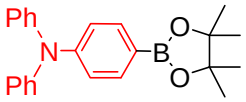


Figure S30a. ^{1}H NMR of **2d**



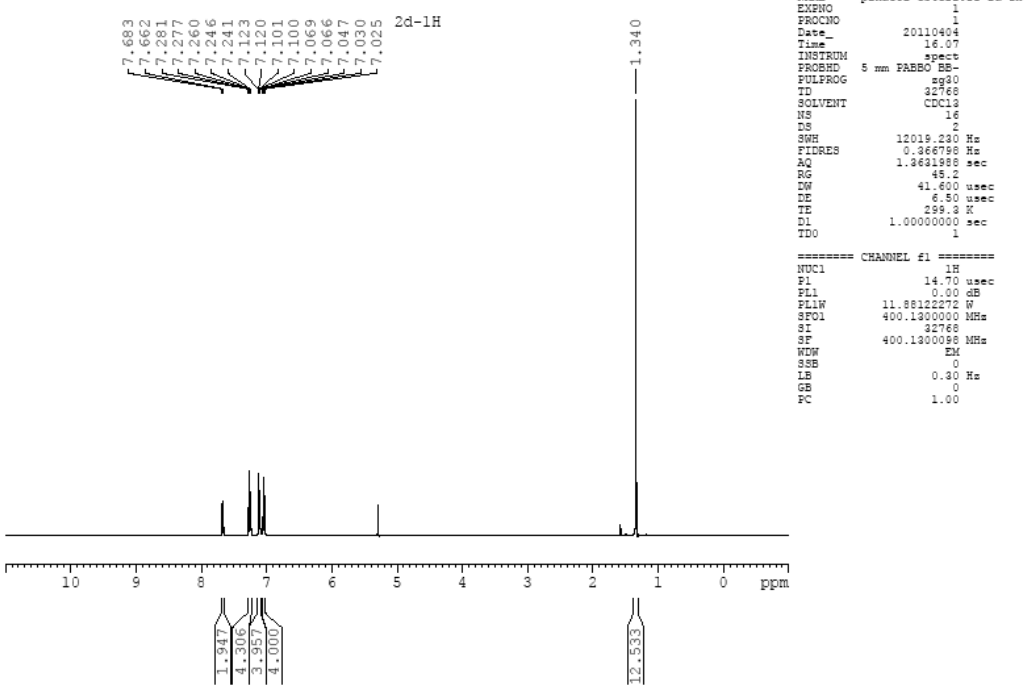


Figure S30b. ^{13}C NMR of **2d**

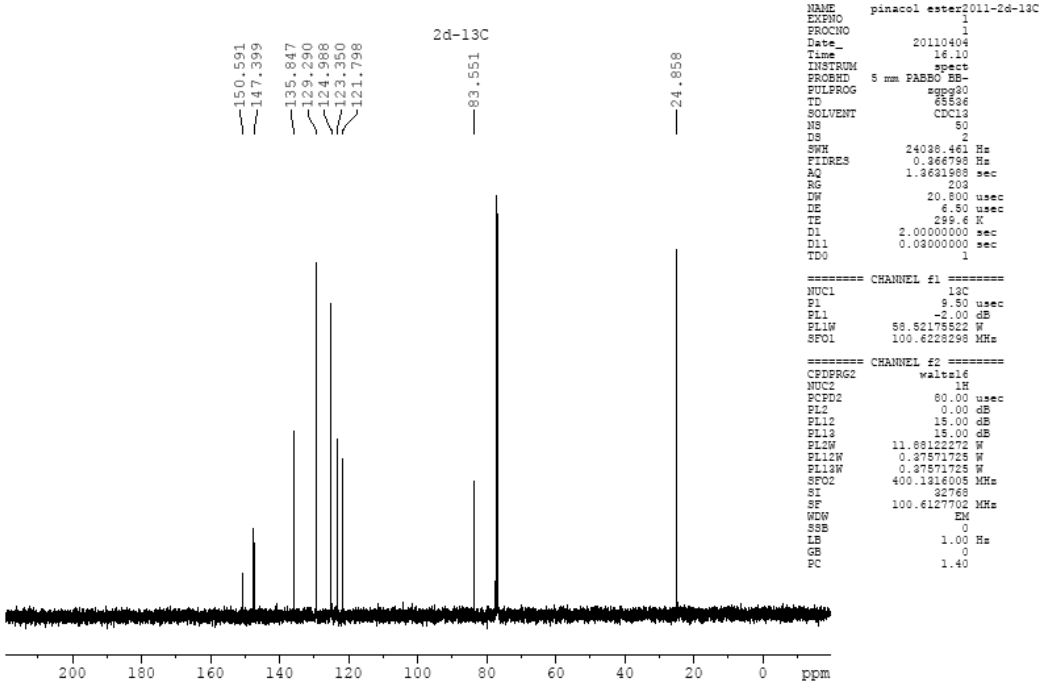
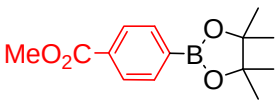


Figure S31a. ^{1}H NMR of **2e**



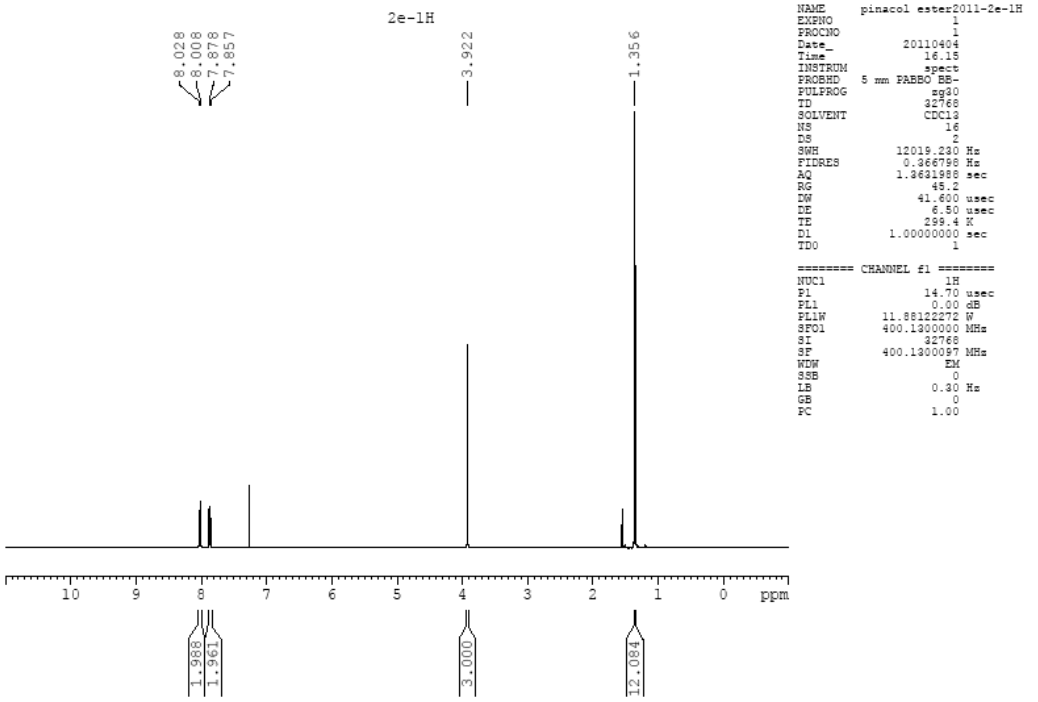


Figure S31b. ^{13}C NMR of **2e**

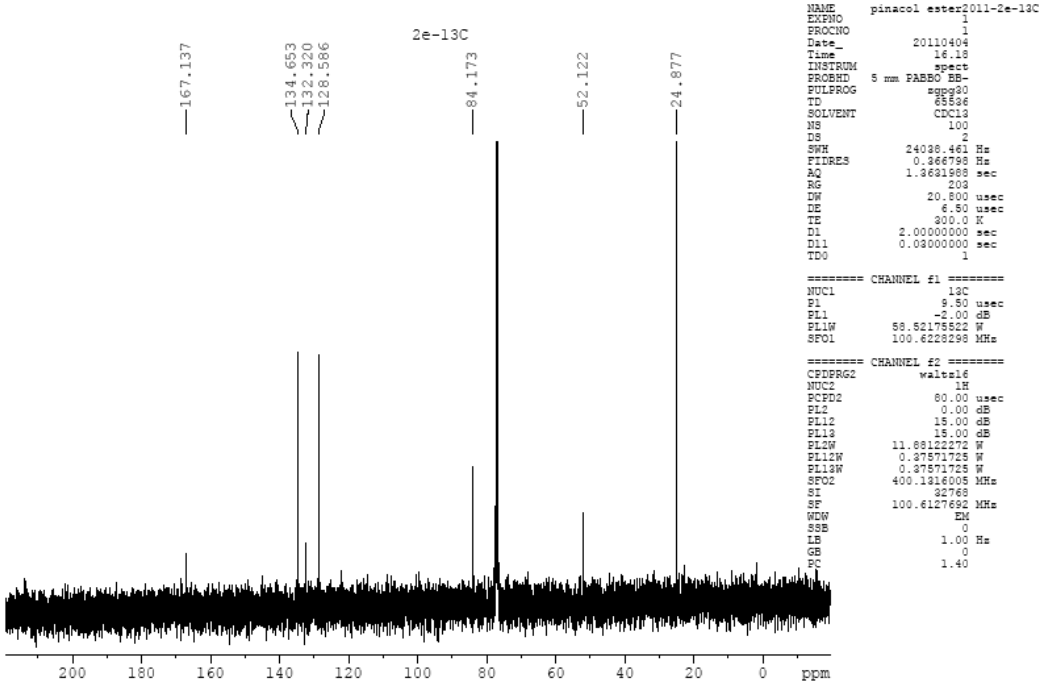


Figure S32a. ^{1}H NMR of **2f**

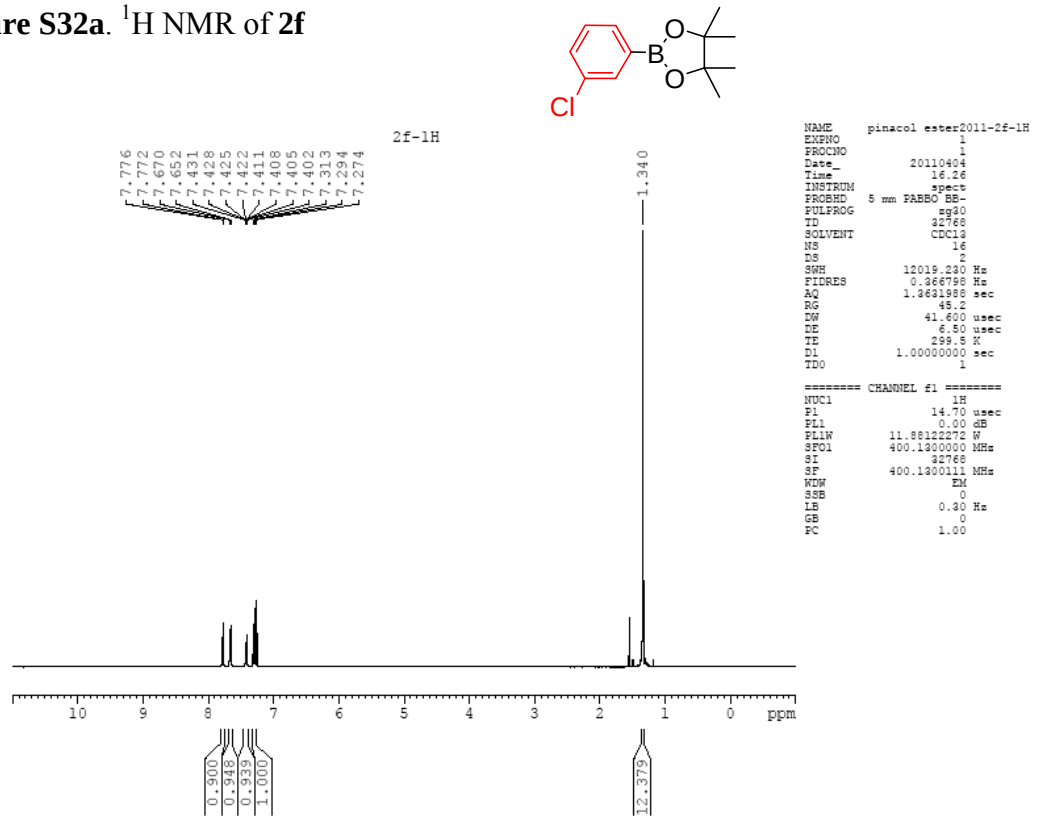


Figure S32b. ^{13}C NMR of **2f**

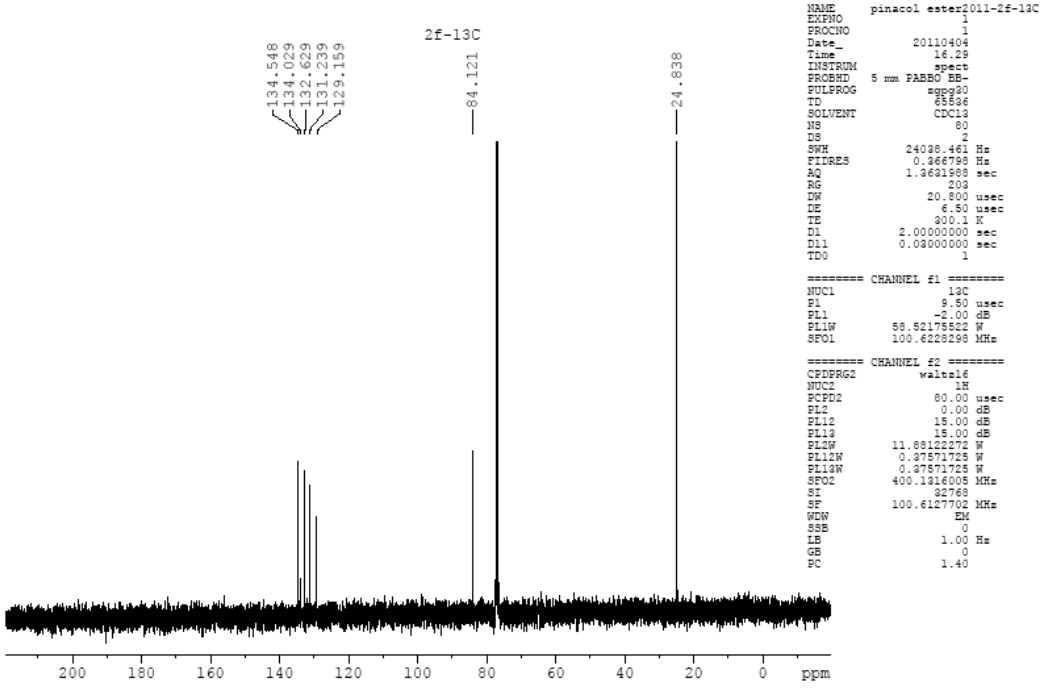


Figure S33a. ^{1}H NMR of **2g**

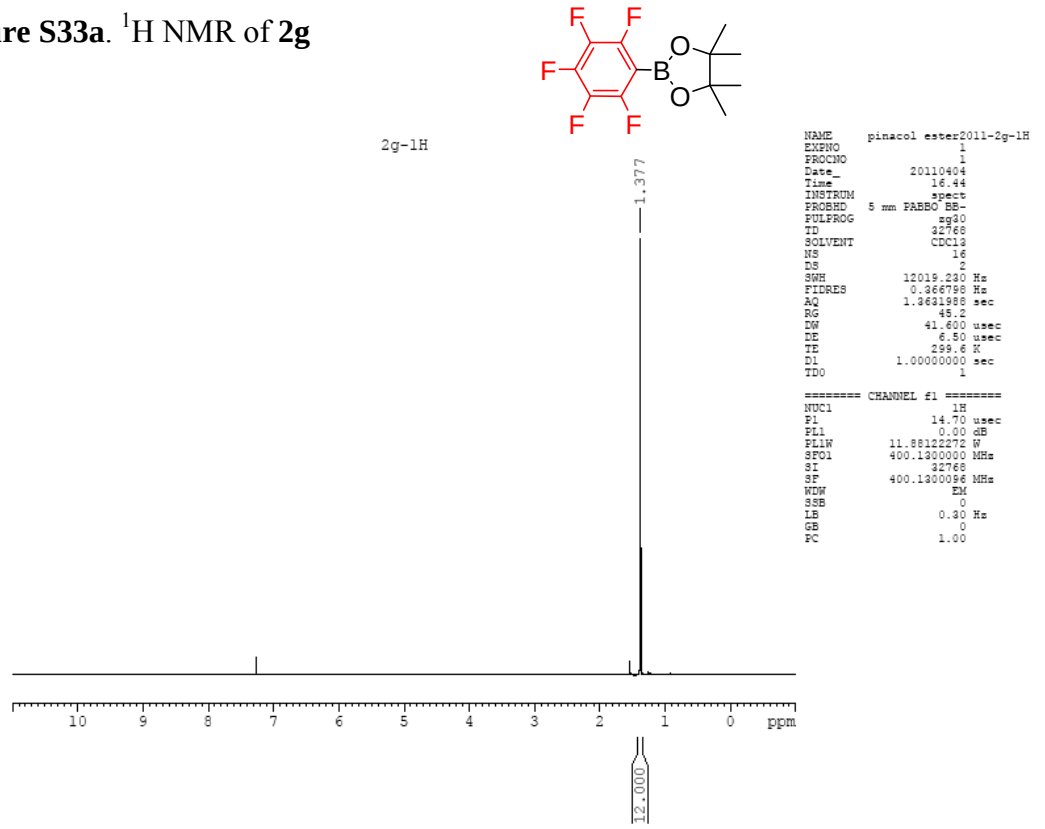


Figure S33b. ^{13}C NMR of **2g**

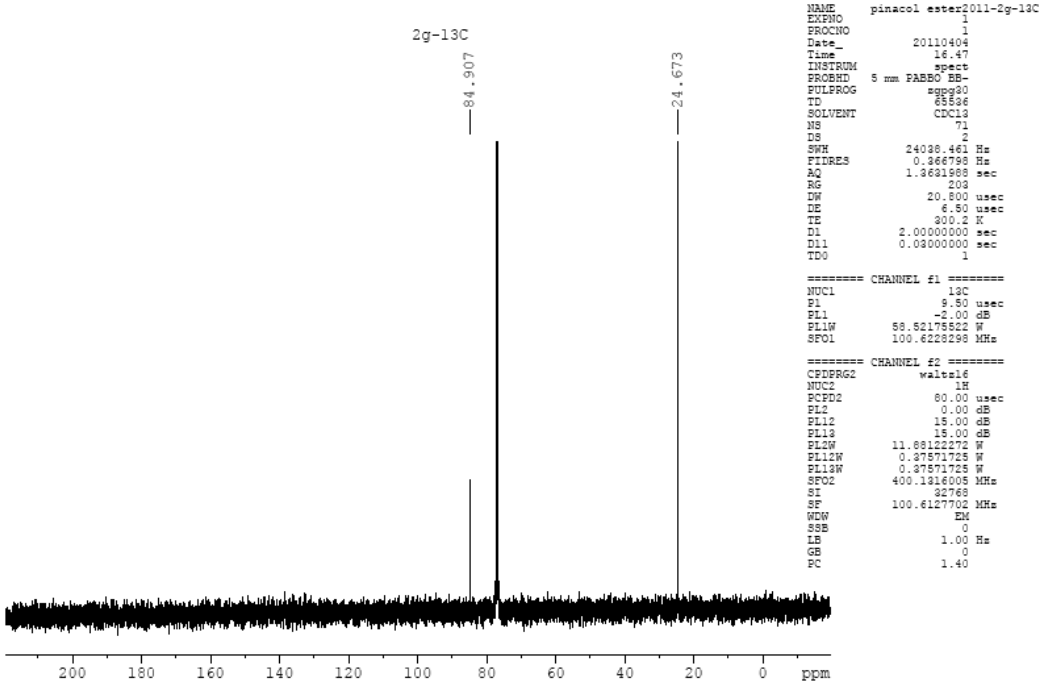


Figure S33c. ^{19}F NMR of **2g**

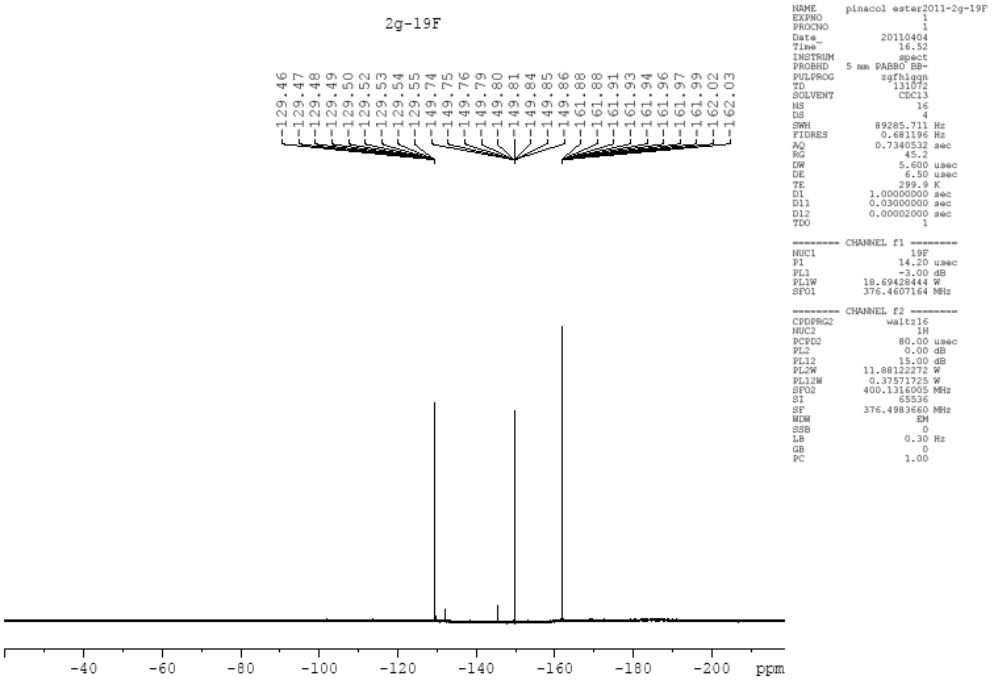


Figure S34a. ^{1}H NMR of **2i**

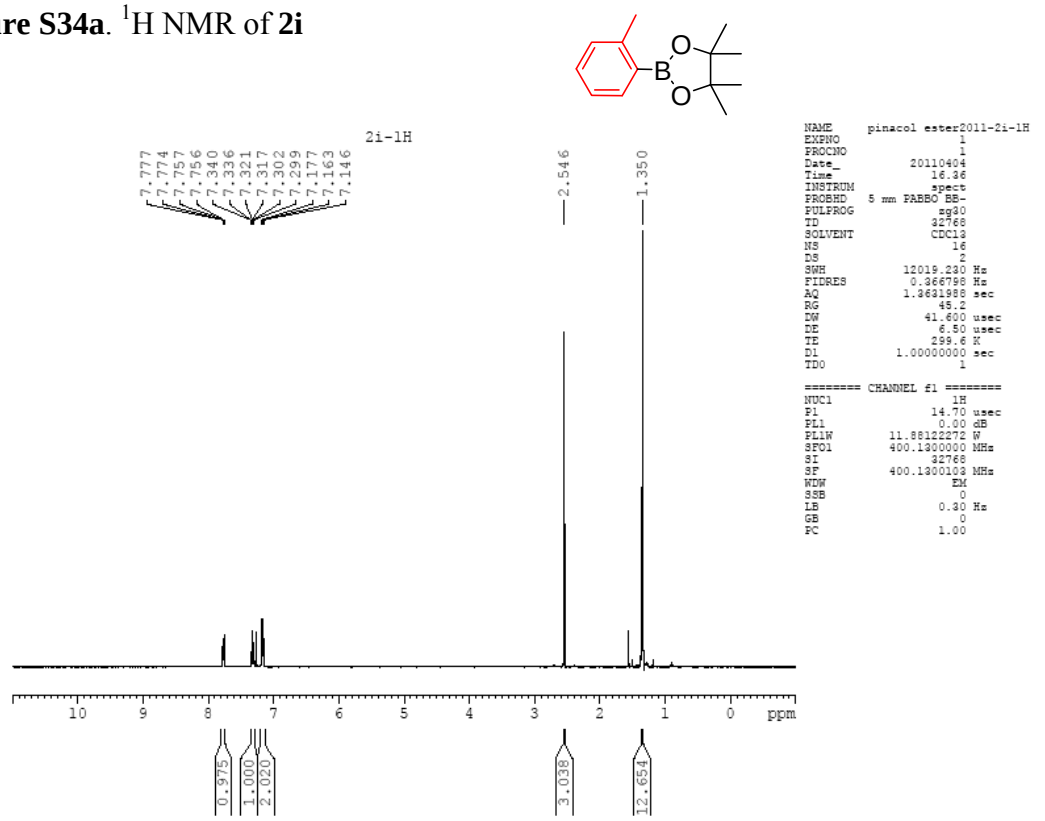


Figure S34b. ^{13}C NMR of **2i**

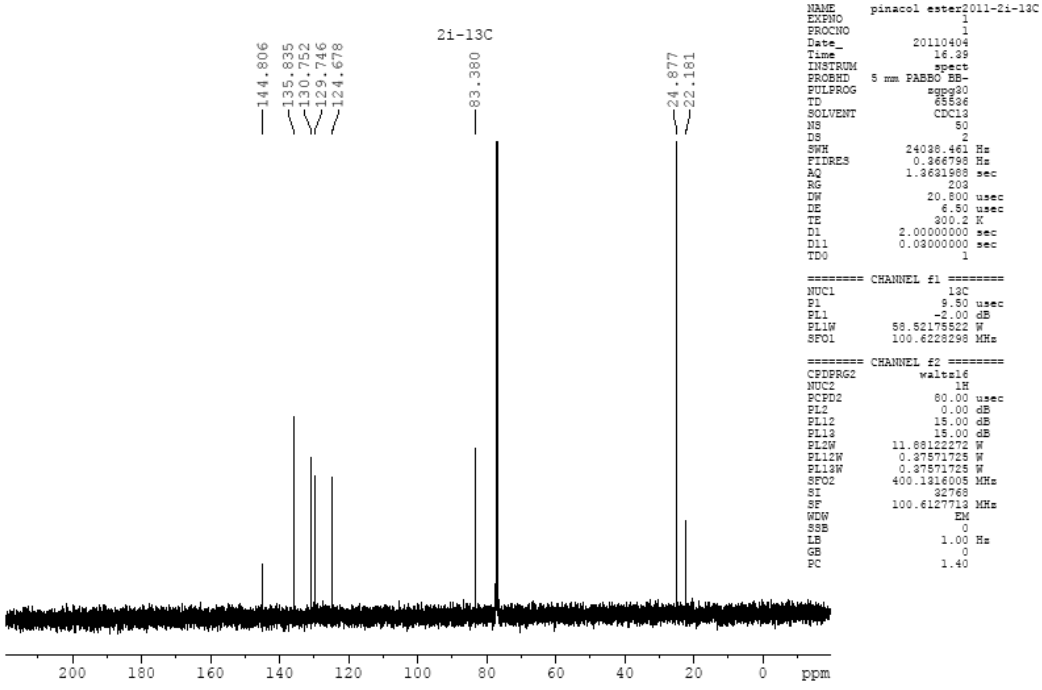


Figure S35a. ^{1}H NMR of **3b**

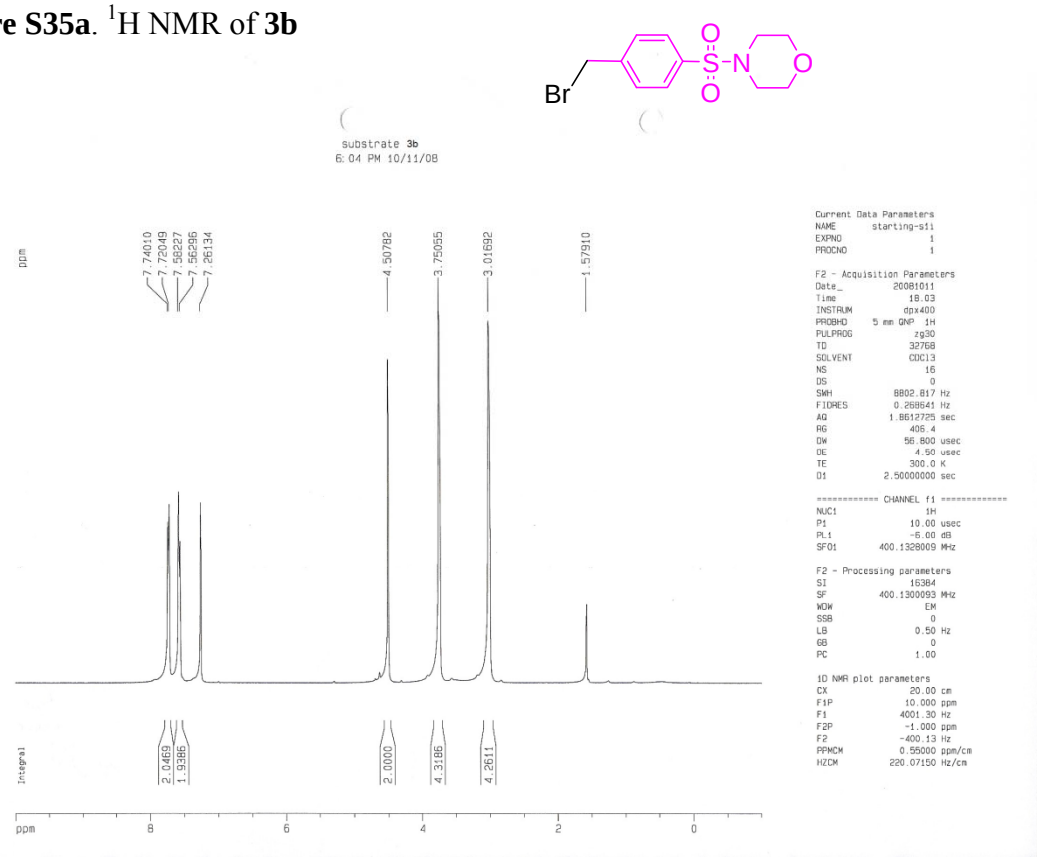


Figure S35b. ^{13}C NMR of **3b**

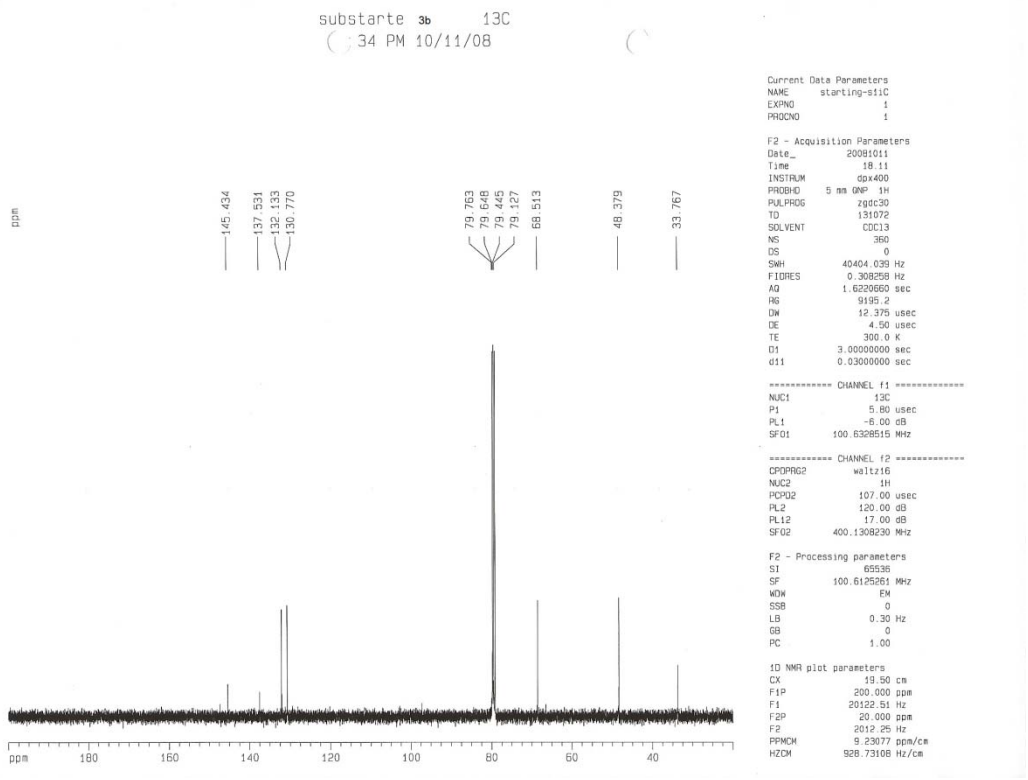
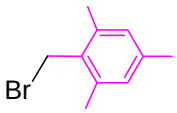


Figure S36a. ^{1}H NMR of **3c**



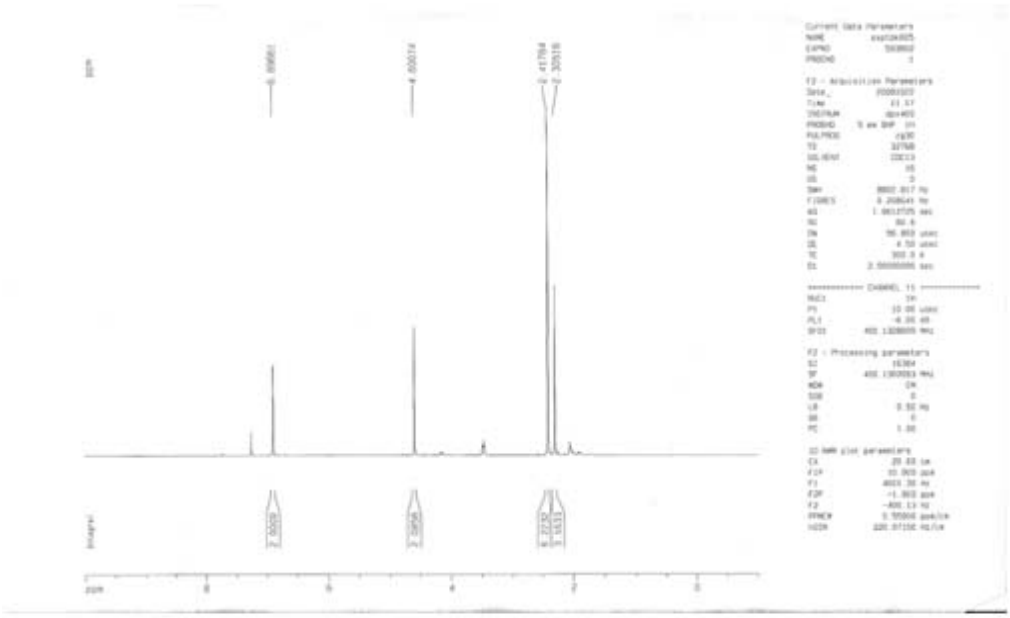
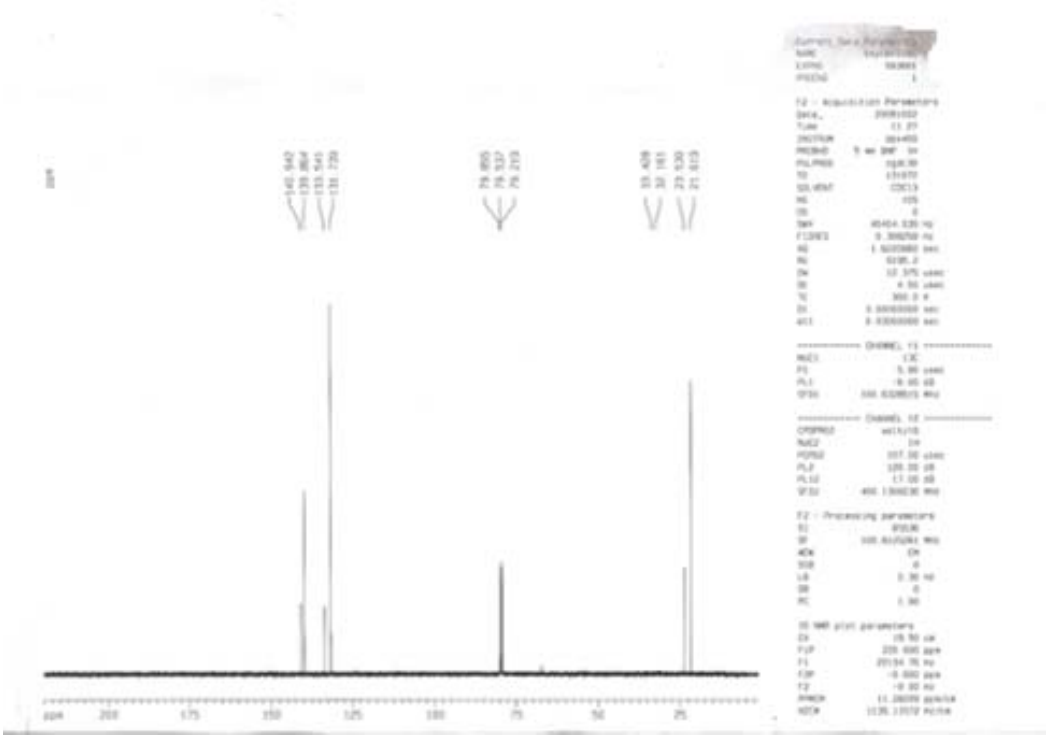


Figure S36b. ^{13}C NMR of **3c**



6. References:

1. (a) Chan, W.-W.; Yeung, S.-H.; Zhou, Z.; Chan, A. S. C.; Yu, W.-Y. *Org. Lett.* **2010,** *12,* 604. (b) Yu, W.-Y.; Tsoi, Y.-T.; Zhou, Z.; Chan, A. S. C. *Org. Lett.* **2009,** *11,* 469. (c) Starmans, W. A. J.; Thijs, L.; Zwanenburg, B. *Tetrahedron* **1998,** *54,* 629.
2. (a) Giordano, G.; Crabtree, R. H. *Inorganic Syntheses, vol 28*; Angelici, R. J., Ed.; Wiley-Interscience: New York, 1990; 88-90. (b) Uson, R.; Oro, L. A.; Cabeza, J. A. *Inorganic Syntheses, vol 23*; Kirschner, S., Ed.; Wiley-Interscience: New York, 1985; 129-130. (c) Uson, R.; Oro, L. A.; Cabeza, J. A. *Inorganic Syntheses, vol 23*; Kirschner, S., Ed.; Wiley-Interscience: New York, 1985; 127-128.
3. (a) Davies, H. M. L.; Townsend, R. J. *J. Org. Chem.* **2001,** *66,* 6595. (b) Davies, H. M. L.; Hansen, T.; Churchill, M. R. *J. Am. Chem. Soc.* **2000,** *122,* 3063.
4. Yuen, A. K. L.; Hutton, C. A. *Tetrahedron Lett.* **2005,** *46,* 7899.