Supporting Information

Rhodium-catalyzed triazole-directed C-H bond functionalization of arenes with diazo compounds

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Contents

1. General information

Unless otherwise noted, all chemicals were obtained from commercial resources and were used without further purification. All reactions were carried out in a glass thick-wall tube with magnetic stirring under the atmosphere of N_2. Thin layer chromatography (TLC) was performed on Huanghai GF254 silica gel coated plates and visualized by exposure to UV light (254 nm). Flash column chromatography was carried out using 200-300 mesh silica gel at increased pressure. ^{1}H NMR and ^{13}C NMR were recorded on Bruker spectrometers with $CDCl_3$ as solvent and tetramethylsilane (TMS) as internal standard. Chemical shifts are referenced to residual solvent peaks ($CHCl_3$ in $CDCl_3$: 7.26 ppm for ^{1}H, 77.00 ppm for ^{13}C). Data for ^{1}H NMR spectra are reported as follows: chemical shift (ppm, referenced to TMS; s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, dt = doublet of triplets, m = multiplet), coupling constant (Hz), and integration. High-resolution mass spectra (HRMS) were recorded on a Bruker Apex IV FTMS mass spectrometer (ESI+). All triazoles **1**[1] and diazo compounds **2**[2] were prepared according to the published procedures.

Reference

[1] (a) J. Raushel, V. V. Fokin, *Org. Lett.,* 2010, **12**, 4952-4955; (b) T. Slagbrand, A. Volkov, P. Trillo, F. Tinnis, H. Adolfsson, ACS *Catal.,* 2017, **7**, 1771−1775.

[2] P. Sun, S. Gao, C. Yang, S. Guo, A. Lin, H. Yao, *Org. Lett.,* 2016, **18**, 6464-6467.

2. General procedure of Rh(III)-catalyzed alkylation of triazoles

1) General procedure for the synthesis of 3

1,2,3-Triazole **1** (0.2 mmol, 1.0 equiv), diazo compound **2** (0.44 mmol, 2.2 equiv), $[Cp^*RhCl_2]_2$ (0.005 mmol, 2.5 mol %), $AgSbF_6$ (0.02 mmol, 10 mol %), and 1,2-dichloroethane (2.0 mL) were added into an oven-dried 15 mL tube with a Teflon screw cap. The sealed tube was heated at 40 ^{o}C for 12 h. The solvent was then removed under reduced pressure, and the residue was purified by silica gel chromatography using petroleum ether/ethyl acetate to afford the desired products **3**.

2) General procedure for the synthesis of 4

1,2,3-Triazole **1** (0.2 mmol, 1.0 equiv), diazo compound **2** (0.24 mmol, 1.2 equiv),

$[Cp^*RhCl_2]_2$ (0.005 mmol, 2.5 mol%), $AgSbF_6$ (0.02 mmol, 10 mol%), and 1,2-dichloroethane (2.0 mL) were added into an oven-dried 15 mL tube with a Teflon screw cap. The sealed tube was heated at 40 °C for 2 h. The solvent was then removed under reduced pressure, and the residue was purified by silica gel chromatography using petroleum ether/ethyl acetate to afford the desired products **4**.

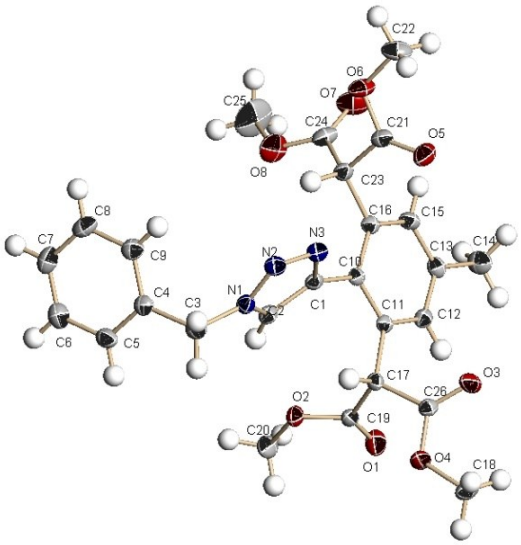
3. X-ray diffraction analysis

The single crystals of compounds were grown by slow diffusion of their hexane solutions for **3a** and **3x**, methanol solution for **A**. Single-crystal X-ray diffraction data were collected at 150 K for **3x**, and 273 K for **3a** and **A** on a Siemens Smart/CCD area-detector diffractometer with a MoKα radiation (λ = 0.71073 Å) by using an ω-2θ scan mode. Unit-cell dimensions were obtained with least-squares refinement. Data collection and reduction were performed using the SMART and SAINT software.[1] All structures were solved by direct methods and refined against F^2 by the full-matrix least squares techniques.[2] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were introduced in their calculated positions. The octyl group is severely disordered, which are not treated. CCDC Nos. 1844325 (**A**), 1844326 (**3a**), and 1844334 (**3x**).

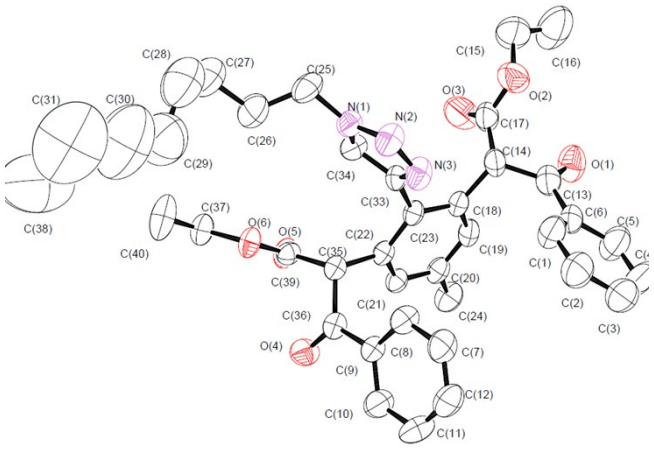
(1) SMART-CCD Software, version 4.05; Siemens Analytical X-ray Instruments, Madison, WI, 1996.

(2) G. K. Sheldrick, SHELXS-97 and SHELXL-97, Program for X-ray Crystal Structure Refinement; University of Götingen: Götingen, Germany 1997.

4. Molecular structures of 3a and 3x



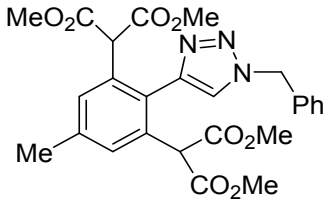
3a



3x

Figure S1. Molecular structures of 3a and 3x. Thermal ellipsoid plot drawn at 40% probability.

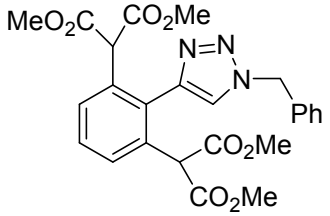
5. Characterization of data for the products



3a

tetramethyl 2,2'-(2-(1-benzyl-1*H*-1,2,3-triazol-4-yl)-5-methyl-1,3-phenylene) -dimalonate (3a)

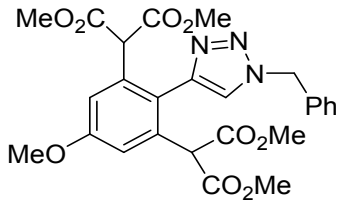
White solid (89.5 mg, 88 %); mp 139-141 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (s, 1H), 7.43-7.37 (m, 3H), 7.36 (s, 2H), 7.32-7.30 (m, 2H), 5.62 (s, 2H), 4.57 (s, 2H), 3.64 (s, 12H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.6, 143.2, 139.4, 134.5, 133.0, 129.8, 129.2, 128.8, 128.3, 128.0, 124.7, 54.5, 54.3, 52.8, 21.6; HRMS (ESI+) calcd for $C_{26}H_{27}N_3O_8$ $[M+Na]^+$ 532.1696, found 532.1690.



3b

tetramethyl 2,2'-(2-(1-benzyl-1*H*-1,2,3-triazol-4-yl)-1,3-phemylene)dimalonate (3b)

White solid (91.0 mg, 92 %); mp 166-169 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, J = 1.2 Hz, 1H), 7.56 (s, 1H), 7.48-7.45 (m, 2H), 7.41-7.37 (m, 3H), 7.33-7.30 (m, 2H), 5.63 (s, 2H), 4.59 (s, 2H), 3.64 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.5, 143.1, 134.5, 133.3, 131.1, 129.3, 129.2, 129.1, 128.8, 128.0, 124.7, 54.7, 54.3, 52.8; HRMS (ESI+) calcd for $C_{25}H_{25}N_3O_8$ $[M+Na]^+$ 518.1540, found 518.1534.

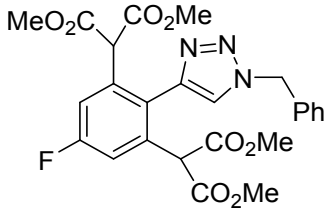


3c

tetramethyl 2,2'-(2-(1-benzyl-1*H*-1,2,3-triazol-4-yl)-5-methoxy-1,3-phemylene)

-dimalonate (3c)

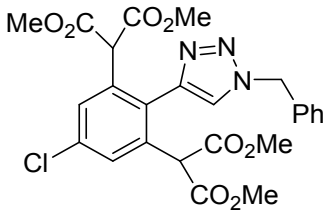
White solid (100.8 mg, 96 %); mp 126-127 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (s, 1H), 7.42-7.37 (m, 3H), 7.31-7.29 (m, 2H), 7.12 (s, 2H), 5.62 (s, 2H), 4.57 (s, 2H), 3.84 (s, 3H), 3.64 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.4, 159.7, 143.1, 134.6, 134.4, 129.2, 128.8, 128.0, 124.8, 123.5, 114.9, 55.5, 54.6, 54.3, 52.8; HRMS (ESI+) calcd for $C_{26}H_{27}N_3O_9$ $[M+Na]^+$ 548.1645, found 548.1640.



3d

tetramethyl 2,2'-(2-(1-benzyl-1*H*-1,2,3-triazol-4-yl)-5-fluoro-1,3-phemylene) -dimalonate (3d)

White solid (86.2 mg, 84 %); mp 136-168 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (s, 1H), 7.44-7.38 (m, 3H), 7.35 (s, 1H), 7.33-7.30 (m, 3H), 5.63 (s, 2H), 4.56 (s, 2H), 3.65 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.9, 162.5 (d, $J_{C\text{-}F}$ = 253.5 Hz), 142.4, 135.4 (d, $J_{C\text{-}F}$ = 8.4 Hz), 134.4, 129.2, 128.9, 128.0, 127.3 (d, $J_{C\text{-}F}$ = 3.4 Hz), 124.8, 116.7 (d, $J_{C\text{-}F}$ = 23.2 Hz), 54.5, 54.4, 53.0; ^{19}F NMR ($CDCl_3$, 376 MHz) δ -110.1; HRMS (ESI+) calcd for $C_{25}H_{24}FN_3O_8$ $[M+Na]^+$ 536.1445, found 536.1440.

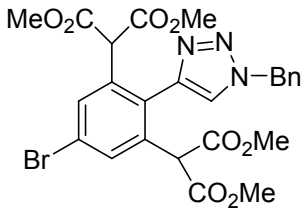


3e

tetramethyl 2,2'-(2-(1-benzyl-1*H*-1,2,3-triazol-4-yl)-5-chloro-1,3-phemylene) -dimalonate (3e)

White solid (64.2 mg, 61 %); mp 134-136 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (s, 1H), 7.48 (s, 1H), 7.43-7.38 (m, 3H), 7.32-7.29 (m, 2H), 7.12 (s, 2H), 5.63 (s, 2H), 4.56

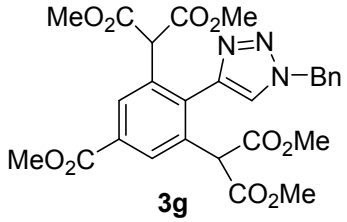
(s, 2H), 3.67 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.9, 142.2, 135.3, 134.8, 134.3, 129.7, 129.5, 129.2, 128.9, 128.0, 124.8, 54.4, 54.3, 53.0; HRMS (ESI+) calcd for $C_{25}H_{24}ClN_3O_8$ $[M+Na]^+$ 552.1150, found 552.1144.



3f

tetramethyl 2,2'-(2-(1-benzyl-1*H*-1,2,3-triazol-4-yl)-5-bromo-1,3-phenylene)-dimalonate (3f)

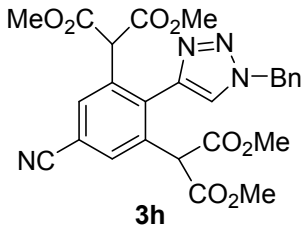
White solid (90.5 mg, 79 %); mp 140-142 °C**;** ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 (s, 2H), 7.48 (s, 1H), 7.41-7.36 (m, 3H), 7.30-7.28 (m, 2H), 5.61 (s, 2H), 5.53 (s, 2H), 3.63 (s, 12H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.9, 142.2, 134.9, 134.3, 132.3, 130.3, 129.2, 128.9, 128.0, 124.8, 123.4, 54.4, 54.3, 53.0; HRMS (ESI+) calcd for $C_{25}H_{24}BrN_3O_8$ $[M+Na]^+$ 596.0639, found 596.0632.



3g

tetramethyl 2,2'-(2-(1-benzyl-1*H*-1,2,3-triazol-4-yl)-5-(methoxycarbonyl)-1,3-phenylene)dimalonate (3g)

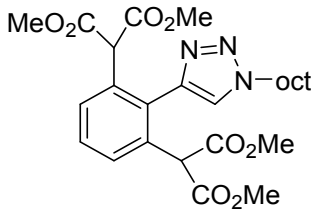
White solid (59.7 mg, 54 %); mp 123-125 °C**;** ^{1}H NMR ($CDCl_3$, 600 MHz) δ 8.21 (s, 2H), 7.53 (s, 1H), 7.42-7.36 (m, 3H), 7.31 (d, J = 7.8 Hz, 2H), 5.63 (s, 2H), 4.63 (s, 2H), 3.92 (s, 3H), 3.65 (s, 12H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 170.7, 168.5, 145.0, 138.2, 136.9, 136.5, 133.7, 133.0, 131.9, 131.5, 130.7, 127.5, 57.4, 57.1, 55.6, 55.1; HRMS (ESI+) calcd for $C_{27}H_{27}N_3O_{10}$ $[M+Na]^+$ 576.1589, found 576.1584.



3h

tetramethyl 2,2'-(2-(1-benzyl-1*H*-1,2,3-triazol-4-yl)-5-cyano-1,3-phenylene)dimalonate (3h)

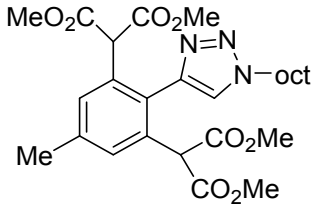
White solid (26.0 mg, 25 %); mp 156-159 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.90 (s, 2H), 7.54 (s, 1H), 7.42-7.38 (s, 3H), 7.31 (d, J = 7.2 Hz, 2H), 5.63 (s, 2H), 4.60 (s, 2H), 3.67 (s, 12H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.2, 144.1, 138.5, 137.3, 136.7, 135.5, 131.9, 131.8, 130.7, 127.6, 120.4, 116.1, 57.2, 56.9, 55.8; HRMS (ESI+) calcd for $C_{26}H_{24}N_4O_8$ $[M+Na]^+$ 543.1486, found 543.1474.



3i

tetramethyl 2,2'-(2-(1-octyl-1*H*-1,2,3-triazol-4-yl)-1,3-phemylene) dimalonate (3i)

White solid (80.9 mg, 78 %); mp 86-87 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (s,1H), 7.60 (d, J = 2.4 Hz, 2H), 7.51-7.47 (m, 1H), 4.62 (s, 2H), 4.44 (t, J = 7.2 Hz, 2H), 3.70 (s, 12H), 2.00-1.93 (m, 2H), 1.35-1.27 (m, 10H), 0.88 (t. J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.6, 142.6, 133.2, 131.3, 129.3, 129.2, 124.5, 54.7, 52.9, 50.6, 31.7, 30.3, 29.1, 29.0, 26.4, 22.6, 14.1; HRMS (ESI+) calcd for $C_{26}H_{35}N_3O_8$ $[M+Na]^+$ 540.2322, found 540.2315.

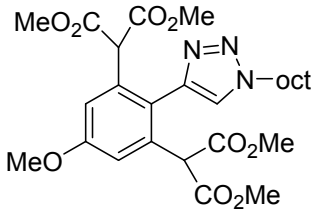


3j

tetramethyl 2,2'-(5-methyl-2-(1-octyl-1*H*-1,2,3-triazol-4-yl)-1,3-phemylene)-

dimalonate (3j)

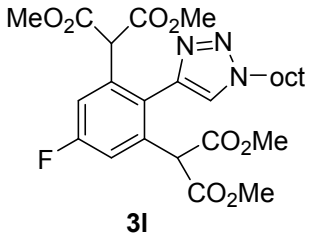
White solid (94.6 mg, 89 %); mp 78-79 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (s, 1H), 7.40 (s, 2H), 4.60 (s, 2H), 4.43(t, J = 6.8 Hz, 2H), 3.70 (s, 12H), 2.43 (s, 3H), 1.98-1.94 (m, 2H), 1.35-1.27 (m, 10H), 0.88 (t, J = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.7, 142.6, 139.2, 132.9, 132.9, 128.5, 124.5, 54.5, 52.9, 50.5, 31.7, 30.3, 29.1, 29.0, 26.4, 22.6, 21.6, 14.1; HRMS (ESI+) calcd for $C_{27}H_{37}N_3O_8$ $[M+Na]^+$ 554.2478, found 554.2473.



3k

tetramethyl 2,2-(5-methoxy-2-(1-octyl-1*H*-1,2,3-triazol-4-yl)-1,3-phenylene)-dimalinate (3k)

White solid (103.7 mg, 95 %); mp 78-80 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (s, 1H), 7.16 (s, 2H), 4.60 (s, 2H), 4.43 (t, J = 7.2 Hz, 2H), 3.86 (s, 3H), 3.70 (s, 12H), 1.99-1.94 (m, 2H), 1.35-1.27 (m, 10H), 0.88 (t, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.4, 159.6, 142.5, 134.3, 124.6, 123.7, 114.9, 55.5, 54.6, 52.9, 50.5, 31.7, 30.3, 29.1, 28.9, 26.4, 22.6, 14.0; HRMS (ESI+) calcd for $C_{27}H_{37}N_3O_9$ $[M+Na]^+$ 570.2428, found 570.2422.

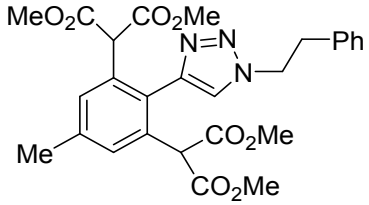


3l

tetramethyl 2,2-(5-fuoro-2-(1-octyl-1*H*-1,2,3-triazol-4-yl)-1,3-phenylene)-dimalinate (3l)

White solid (78.4 mg, 73 %); mp 92-94 °C**;** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (s, 1H), 7.37 (s, 1H), 7.34 (s, 1H), 4.58 (s, 2H), 4.43 (t, J = 7.2 Hz, 2H), 3.69 (s, 12H), 1.96-1.93

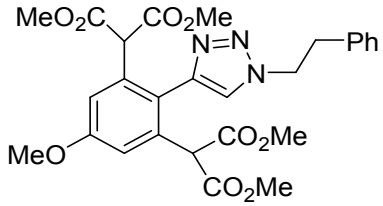
(m, 2H), 1.33-1.25 (m, 10H), 0.86 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.0, 162.4 (d, $J_{C\text{-}F}$ = 247.2 Hz), 141.8, 135.3 (d, $J_{C\text{-}F}$ = 8.4 Hz), 127.5 (d, $J_{C\text{-}F}$ = 3.4 Hz), 124.7, 116.7 (d, $J_{C\text{-}F}$ = 23.0 Hz); ^{19}F NMR ($CDCl_3$, 376 MHz) δ -110.3; HRMS (ESI+) calcd for $C_{26}H_{34}FN_3O_8$ $[M+Na]^+$ 558.2222, found 558.2215.



3m

tetramethyl 2,2-(5-methyl-2-(1-phenethl-1*H*-1,2,3-triazol-4-yl)-1,3-phenylene)-dimalomate (3m)

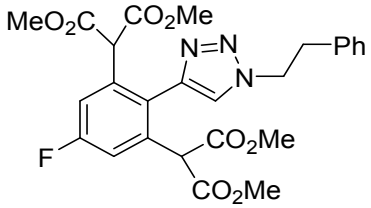
White solid (97.3 mg, 93 %); mp 116-118 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (s, 2H), 7.29-7.27 (m, 3H), 7.23-7.19 (m, 1H), 7.12-7.10 (2H), 4.68 (t, J = 6.8 Hz, 2H), 4.48 (s, 2H), 3.69 (s, 12H), 3.28 (t, J = 6.8 Hz, 2H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.6, 142.3, 139.2, 137.0, 132.9, 129.9, 128.9, 128.7, 128.3, 127.1, 124.9, 54.4, 52.8, 51.9, 36.7, 21.5; HRMS (ESI+) calcd for $C_{27}H_{29}N_3O_8$ $[M+Na]^+$ 546.1847, found 546.1842.



3n

tetramethyl 2,2-(5-methoxy-2-(1-phenethl-1*H*-1,2,3-triazol-4-yl)-1,3-phenylene)-dimalomate (3n)

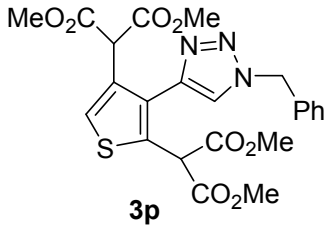
White solid (102.3 mg, 95 %); mp 137-138 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29-7.26 (m, 3H), 7.23-7.20 (m, 1H), 7.14 (s, 2H), 7.11 (d, J = 6.8 Hz, 2H) 4.68 (t, J = 6.8 Hz, 2H), 4.47 (s, 2H), 3.84 (s, 3H), 3.69 (s, 12H), 3.28 (t, J = 6.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.4, 159.6, 142.2, 137.0, 134.3, 128.9, 128.7, 127.1, 125.0, 123.5, 114.9, 58.4, 555.4, 54.5, 52.9, 51.9, 36.7, 18.4; HRMS (ESI+) calcd for $C_{27}H_{29}N_3O_9$ $[M+Na]^+$ 562.1802, found 562.1796.



3o

tetramethyl 2,2-(5-fluoro-2(1-phenethyl-1*H*-1,2,3-triazol-4-yl)-1,3-phenylene)-dimalonate (3o)

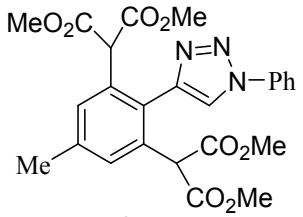
White solid (70.0 mg, 66 %); mp 118-119 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, J = 9.2 Hz, 2H), 7.31 (s, 1H), 7.30-7.26 (m, 2H), 7.24-7.20 (m, 1H), 7.11 (d, J = 7.2, 2H), 4.70 (t, J = 6.8, 2H), 4.46 (s, 2H), 3.71 (s, 12H), 3.29 (t, J = 6.8 Hz , 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.0, 162.3 (d, $J_{C\text{-}F}$ = 247 Hz), 141.5, 136.9, 135.3 (d, $J_{C\text{-}F}$ = 8.0 Hz), 128.9, 128.8 (d, $J_{C\text{-}F}$ = 24.0 Hz), 127.3 (d, $J_{C\text{-}F}$ = 3.0 Hz), 127.1, 125.1, 116.7 (d, $J_{C\text{-}F}$ = 23.0 Hz), 54.4, 53.1, 52.0, 36.7; ^{19}F NMR ($CDCl_3$, 376 MHz) δ -110.4; HRMS (ESI+) calcd for $C_{26}H_{26}FN_3O_8$ $[M+Na]^+$ 550.1602, found 550.1596.



3p

tetramethyl 2,2'-(3-(1-benzyl-1*H*-1,2,3-triazol-4-yl)thiophene-2,4-diyl)-dimalonate (3p)

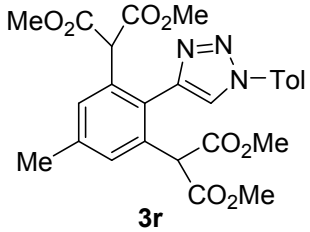
White solid (73.1 mg, 73 %); mp 140-142 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (s, 1H), 7.59 (s, 1H), 7.43-7.37 (m, 3H), 7.33-7.31 (m, 2H), 5.60 (s, 2H), 5.11 (s, 1H), 4.87 (s, 1H), 3.72 (s, 6H), 3.68 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.2, 167.5, 140.9, 134.5, 132.1, 130.8, 130.6, 129.2, 128.8, 128.1, 126.2, 123.5, 54.3, 53.2, 52.9, 51.7, 51.6; HRMS (ESI+) calcd for $C_{23}H_{23}N_3O_8S$ $[M+Na]^+$ 524.1104, found 524.1098.



3q

tetramethyl 2,2'-(2-(1-phenyl-1*H*-1,2,3-triazol-4-yl-1,3-phenylene)dimalonate (3q)

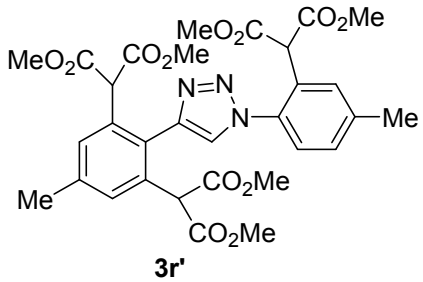
White solid (58.1 mg, 59 %); mp 190-193 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.10 (s, 1H), 7.83-7.80 (m, 2H), 7.59-7.55 (m, 2H), 7.50-7.46 (m, 1H), 7.45 (s, 2H), 4.70 (s, 2H), 3.72 (s, 12H), 2.45 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 168.63, 143.41, 139.53, 136.86, 133.0, 129.9, 129.0, 127.9, 122.9, 120.5, 54.7, 52.9, 21.6; HRMS (ESI+) calcd for $C_{25}H_{25}N_3O_8$ $[M+Na]^+$ 518.1534, found 518.1528**.**



3r

tetramethyl 2,2'-(5-methyl-2-(1-(*p*-tolyl)-1*H*-1,2,3-triazol-4-yl)-1,3-phenylene)-dimalonate (3r)

White solid (62.7 mg, 62 %); mp 198-200 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.04 (s, 1H), 7.68 (d, J = 8.4 Hz, 2H), 7.44 (s, 2H), 7.36 (d, J = 8.0 Hz, 2H), 4.70 (s, 2H), 3.71 (s, 12H), 2.45 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 168.7, 143.3, 139.5, 139.2, 134.6, 133.0, 130.4, 130.1, 128.0, 122.8, 120.4, 54.6, 52.9, 21.6, 21.2; HRMS (ESI+) calcd for $C_{26}H_{27}N_3O_8$ $[M+Na]^+$ 532.1696, found 532.1690.

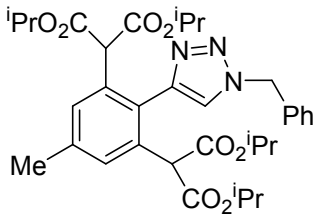


3r'

tetramethyl 2,2'-(2-(1-(2-(1,3-dimethoxy-1,3-dioxopropan-2-yl)-4-methylphenyl)-

1*H*-1,2,3-triazol-4-yl)-5-methyl-1,3-phenylene)dimalonate (3r')

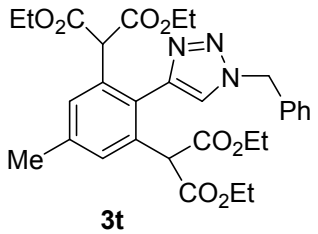
White solid (28.6 mg, 22 %); mp 178-179 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.88 (s, 1H), 7.52 (s, 1H), 7.41(s, 2H), 7.34 (s, 2H), 4.79 (s, 1H), 4.70 (s, 2H), 3.74 (s, 3H), 3.71 (s, 12H), 2.48 (s, 3H), 2.44 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 168.6, 168.0, 142.8, 140.9, 139.6, 133.7, 133.3, 131.1, 130.1, 128.5, 127.8, 127.3, 126.3, 54.8, 53.1, 52.9, 52.0, 21.6, 21.4; HRMS (ESI+) calcd for $C_{31}H_{33}N_3O_{12}$ $[M+Na]^+$ 662.1962, found 662.1954.



3s

tetraisopropyl 2,2'-(2-(1-benzyl-1*H*-1,2,3-triazol-4-yl)-5-methyl-1,3-phenylene)dimalonate (3s)

White solid (77 mg, 62 %); mp 119-121 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 (s, 1H), 7.38-7.34 (m, 5H), 7.30-7.28 (m, 2H), 5.60 (s, 2H), 5.50-4.93 (m, 4H), 4.48 (s, 2H), 2.38 (s, 3H), 1.18 (d, J = 6.0 Hz, 12H), 1.13 (d, J = 6.0 Hz, 12H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.8, 143.4, 138.7, 134.6, 133.1, 129.6, 129.2, 128.7, 128.3, 127.9, 124.7, 69.2, 55.2, 54.2, 21.6, 21.5, 21.4; HRMS (ESI+) calcd for $C_{34}H_{43}N_3O_8$ $[M+Na]^+$ 644.2942, found 644.2938.

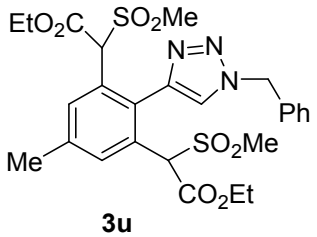


3t

tetraethyl 2,2'-(2-(1-benzyl-1*H*-1,2,3-triazol-4-yl)-5-methyl-1,3-phenylene)-dimalonate (3t)

White solid (101.4 mg, 90 %); mp 95-97 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.48 (s, 1H), 7.42-7.37 (m, 5H), 7.32-7.30 (m, 2H), 5.62 (s, 2H), 4.54 (s, 2H), 4.15-4.03 (m,

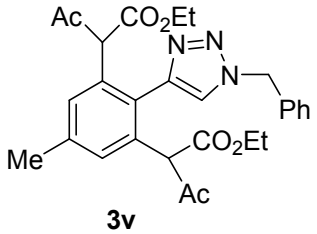
8H), 2.40 (s, 3H), 1.18 (t, J = 7.2 Hz, 12H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 168.2, 143.3, 139.1, 134.5, 133.1, 129.2, 128.8, 128.3, 128.0, 124.7, 61.7, 54.9, 54.3, 21.6, 13.9; HRMS (ESI+) calcd for $C_{30}H_{35}N_3O_8$ [M+Na]$^+$ 588.2316, found 588.2309.



3u

diethyl 2,2'-(2-(1-benzyl-1*H*-1,2,3-triazol-4-yl)-5-methyl-1,3-phenylene)bis(2-(methylsulfonyl)acetate (3u)

Tautomer (1:1.6); white solid (90.6 mg, 78 %); mp 168-171 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.93 (s, 1H), 7.87 (s, 1H), 7.86, 7.78 (both s, 1H), 7.42-7.31 (m, 5H), 5.65 (s, 2H), 4.93, 4.92 (both s, 2H), 4.31-4.09 (both m, 4H), 2.89, 2.85 (both s, 6H), 2.49, 2.48 (both s, 3H), 1.24, 1.21 (both t, J = 7.2 Hz, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 164.9, 164.5, 142.2, 142.1, 140.1, 139.9, 134.6, 134.4, 131.6, 131.5, 131.3, 131.0, 129,3, 129.2, 129.0, 128.9, 128.0, 127.1, 126.7, 69.6, 69.4, 63.0, 54.6, 54.5, 40.1, 39.6, 21.7, 21.6, 13.9 ; HRMS (ESI+) calcd for $C_{26}H_{31}N_3O_8S_2$ [M+Na]$^+$ 600.1451, found 600.1445.



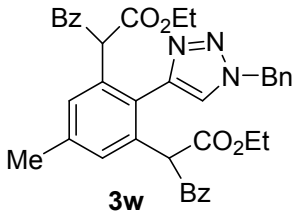
3v

diethyl 2,2'-(2-(1-benzyl-1*H*-1,2,3-triazol-4-yl)-5-methyl-1,3-phenylene)bis(3-oxobutanoate) (3v)

^{1}H NMR spectrum is complicated due to tautomerization (The ratio of two tautomers: 1/7).

Light yellow oil (82.0 mg, 81 %); ^{1}H NMR (400 MHz, $CDCl_3$) for the major tautomer: δ 12.80, 12.77 (both s, 2H), 7.43-7.33 (m, 3H), 7.19-7.17 (m, 1H), 7.11-7.08 (m, 2H), 7.00 (s, 2H), 5.52 (s, 1H), 5.52 (s, 1H), 4.02-3.87 (m, 4H), 2.40 (s, 3H), 1.78, 1.77 (both s, 3H), 1.75, 1.66 (both s, 3H); 1.01 (t, J = 7.2 Hz, 3H), 0.98 (t, J = 7.2 Hz, 3H); ^{1}H

NMR (400 MHz, $CDCl_3$) for the minor tautomer: δ 7.29 (s, 3H), 7.15 (s, 1H), 6.95 (d, J = 6.8 Hz, 4H), 5.57, 5.56 (both s, 2H), 5.22 (s, 1H), 5.26 (s, 1H), 4.24-4.09 (m, 4H), 2.40 (s, 3H), 2.25 (s, 3H), 2.23 (s, 3H), 1.23 (t, J = 7.2 Hz, 3H), 1.22 (t, J = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 202.7, 202.4, 174.4, 174.0, 173.5, 173.3, 172.0, 171.8, 169.1, 168.9, 146.0, 145.9, 145.0, 144.9, 138.8, 138.7 138.2, 138.0, 135.7, 135.6, 135.5, 135.2, 135.1, 134.7, 134.6, 132.6, 132.4, 132.3, 131.8, 130.6, 130.5, 129.2, 129.1, 128.5, 127.6, 127.6, 127.5, 127.3, 123.2, 123.1, 103.6, 103.5, 103.1, 103.0, 61.9, 61.8, 61.4, 60.6, 60.4, 60.3, 60.1, 54.1, 53.8, 53.7, 29.7, 29.6, 29.4, 26.9, 21.3, 21.2, 20.1, 20.0, 19.8, 14.2, 14.1, 14.0, 13.9; HRMS (ESI+) calcd for $C_{28}H_{31}N_3O_6$ $[M+Na]^+$ 528.2105, found 528.2096.



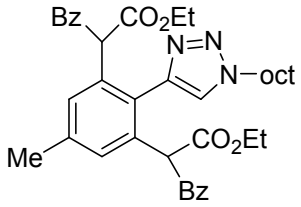
3w

diethyl 2,2'-(2-(1-benzyl-1*H*-1,2,3-triazol-4-yl)-5-methyl-1,3-phenylene)bis(3-oxo-3-phenylpropanoate) (3w).

^{1}H NMR spectrum is complicated due to tautomerization (The ratio of two tautomers: 1/7).

Yellow solid (108.8 mg, 86 %); mp 106-109 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) for the major tautomer: 7.86 (d, J = 6.8 Hz, 2H), 7.64 (d, J = 7.6 Hz, 1H), 7.43-7.39 (m, 2H), 7.65 (s, 1H), 7.33-7.24 (m, 6H), 7.22-7.17 (m, 2H), 7.11-7.09 (m, 3H), 7.01 (s, 1H), 5.51 (s, 1H), 5.42, 5.41 (both s, 2H), 4.14-3.78 (m, 4H), 2.18, 2.11 (both s, 3H), 1.03 (t, J = 6.8 Hz, 6H); ^{1}H NMR (400 MHz, $CDCl_3$) for the minor tautomer: δ 13.37 (s, 1H), 13.36 (s, 1H), 8.00 (d, J = 8.0 Hz, 2H), 7.74 (d, J = 7.6 Hz, 2H), 7.64 (d, J = 7.6 Hz, 1H), 7.33-7.24 (m, 2H), 7.14 (s, 3H), 7.00-6.97 (m, 2H), 6.94-6.88 (m, 4H), 6.78 (s, 1H), 6.72 (s, 1H), 6.02, 5.85 (both s, 2H), 5.39, 5.38 (both s, 2H), 4.14-3.78 (m, 4H), 2.06 (s, 3H), 2.05 (s, 3H), 0.88 (t, J = 7.2 Hz, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 194.9, 194.8, 194.0, 193.9, 172.8, 172.7, 170.4, 169.5, 169.2, 168.8, 145.0, 143.9, 143.8, 139.9, 139.7, 138.9, 135.1, 134.1, 134.0, 133.4, 133.2, 133.0, 130.0, 129.2,

128.9, 128.7, 127.9, 127.8, 127.3, 124.7, 124.6, 123.1, 123.0, 103.4, 103.4, 77.4, 77.1, 76.8, 61.6, 61.4, 61.3, 61.1, 60.9, 57.8, 54.4, 54.2, 54.1, 54.0, 29.7, 26.9, 21.5, 21.4, 21.2, 14.1, 14.0; HRMS (ESI+) calcd for $C_{38}H_{35}N_3O_6$ $[M+Na]^+$ 652.2418, found 652.2416.

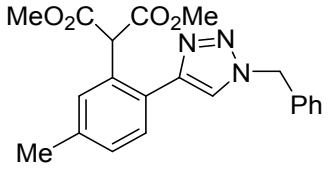


3x

diethyl 2,2'-(5-methyl-2-(1-octyl-1*H*-1,2,3-triazol-4-yl)-1,3-phenylene)bis(3-oxo-3-phenylpropanoate) (3x).

^{1}H NMR spectrum is complicated due to tautomerization (The ratio of two tautomers: 1/5.3).

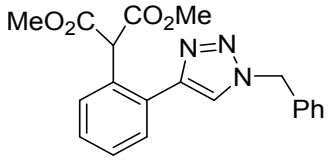
White solid (98.9 mg, 76 %); mp 104-106 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) for the major tautomer: δ 7.80 (d, J = 7.2 Hz, 2H), 7.69 (d, J = 7.6 Hz, 1H), 7.45-7.40 (m, 2H), 7.35-7.29 (m, 4H), 7.21-7.12 (m, 3H), 7.04 (s, 1H), 6.26, 5.93, 5.45 (s, 2H), 4.33 (t, J = 7.2 Hz, 1H), 4.26-3.93 (m, 5H), 2.23, 2.16, 2.09 (all s, 3H), 1.83-1.71 (m, 2H), 0.80 (t, J = 6.4 Hz, 3H); ^{1}H NMR (400 MHz, $CDCl_3$) for the minor tautomer: δ 13.43 (s, 1H), 13.41 (s, 1H), 8.07 (d, J = 7.6 Hz, 2H), 7.75 (d, J = 7.6 Hz, 2H), 7.69 (d, J = 7.6 Hz, 2H), 7.45-7.40 (m, 1H), 7.35-7.29 (m, 2H), 7.00-6.95 (m, 4H), 6.76 (d, J = 14.0 Hz, 2H), 4.26-3.93 (m, 6H), 2.08 (s, 3H), 1.61-1.55 (m, 3H), 0.78 (t, J = 6.4 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 195.1, 194.8, 194.0, 193.9, 172.9, 172.8, 170.1, 169.4, 169.3, 169.2, 168.9, 168.8, 144.6, 144.4, 143.5, 139.9, 139.7, 138.8, 135.8, 135.4, 135.1, 134.1, 133.5, 133.2, 133.0, 132.9, 129.3, 129.0, 128.9, 128.8, 128.7, 128.6, 128.5, 127.9, 127.8, 127.5, 127.4, 124.5, 122.8, 122.7, 103.8, 103.6, 61.7, 61.6, 61.4, 61.3, 61.1, 61.0, 58.2, 58.1, 57.9, 57.8, 50.6, 50.4, 50.2, 31.8, 31.7, 30.2, 28.9, 26.4, 26.3, 22.6, 21.6, 21.5, 21.2, 14.1, 14.0; HRMS (ESI+) calcd for $C_{39}H_{45}N_3O_6$ $[M+Na]^+$ 674.3201, found 674.3203.



4a

dimethyl 2-(2-(1-benzyl-1*H*-1,2,3-triazol-4-yl)-5-methylphenyl)malonate (**4a**)

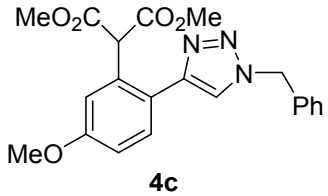
Pale yellow oil (28.8 mg, 38 %); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.62 (s, 1H), 7.38-7.35 (m, 4H), 7.34-7.30 (m, 3H), 7.16 (dd, J = 8.0 Hz, 1.2 Hz, 1H), 5.57 (s, 2H), 5.54 (s, 1 H), 3.72 (s, 6H), 2.37 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 169.3, 147.1, 138.6, 134.6, 130.6, 130.3, 129.5, 129.2, 129.1, 128.8, 128.2, 127.5, 122.0, 54.2, 54.1, 52.8, 21.3. HRMS (ESI+) calcd for $C_{21}H_{21}N_3O_4$ $[M+Na]^+$ 402.1424, found 402.1411.



4b

dimethyl 2-(2-(1-benzyl-1*H*-1,2,3-triazol-4-yl)phenyl)malonate (**4b**)

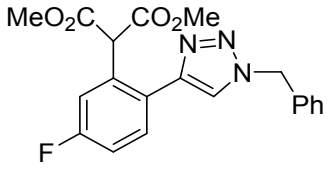
Pale yellow oil (23.4 mg, 32 %); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.66 (s, 1H), 7.57-7. 54 (m, 1H), 7.50-7.48 (m, 1H), 7.40-7.34 (m, 5H), 7.32-7.31 (s, 2H), 5.59 (s, 2H), 5.54 (s, 1H), 3.72 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 169.1, 147.0, 134.5, 130.8, 130.3, 129.9, 129.6, 129.2, 128.8, 128.6, 128.3, 128.1, 122.2, 54.3, 54.2, 52.8; HRMS (ESI+) calcd for $C_{20}H_{19}N_3O_4$ $[M+Na]^+$ 388.1268, found 388.1260.



4c

dimethyl 2-(2-(1-benzyl-1*H*-1,2,3-triazol-4-yl)-5-methoxyphenyl)malonate (**4c**)

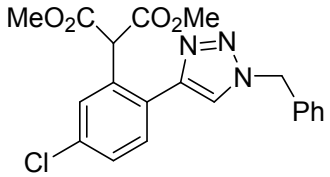
Yellow oil (26.9 mg, 34 %); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.58 (s, 1H), 7.42-7.37 (m, 4H), 7.33-7.31 (m, 2H), 7.10-7.09 (d, J = 1.2 Hz, 1H), 6.92-6.88 (d, J = 8.8 Hz, 2.8 Hz, 1H), 5.57 (s, 2H), 5.51 (s, 1H), 3.83 (s, 3H), 3.72 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 169.1, 159.6, 146.9, 130.8, 129.1, 128.8, 128.2, 121.7, 115.1, 114.1, 55.4, 54.3, 54.2, 52.8; HRMS (ESI+) calcd for $C_{21}H_{21}N_3O_5$ $[M+Na]^+$ 418.1373, found 418.1360.



4d

dimethyl 2-(2-(1-benzyl-1*H*-1,2,3-triazol-4-yl)-5-fluorophenyl)malonate (4d)

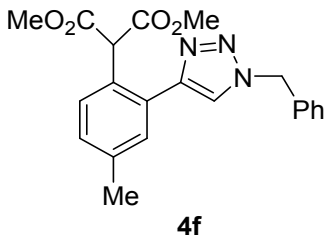
Pale yellow oil (24.5 mg, 32 %); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.63 (s, 1H), 7.48-7.44 (m, 1H), 7.43-7.38 (m, 3H), 7.36-7.30 (m, 3H), 7.06 (td, J = 8.4, 2.8 Hz, 1H), 5.58 (s, 2H), 5.49 (s, 1H), 3.73 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 168.6, 162.4 (d, $J_{C\text{-}F}$ = 246.6 Hz), 146.2, 134.4, 133.0 (d, $J_{C\text{-}F}$ = 8.3 Hz), 131.4 (d, $J_{C\text{-}F}$ = 8.3 Hz), 129.2, 128.9, 128.2, 126.6 ($J_{C\text{-}F}$ = 3.2 Hz), 122.2, 117.0 (d, $J_{C\text{-}F}$ = 22.9 Hz), 115.6 (d, $J_{C\text{-}F}$ = 21.4 Hz), 54.3, 54.1, 53.0; ^{19}F NMR ($CDCl_3$, 376 MHz) δ -112.1; HRMS (ESI+) calcd for $C_{20}H_{18}FN_3O_4$ $[M+Na]^+$ 406.1179, found 406.1174.



4e

dimethyl 2-(2-(1-benzyl-1*H*-1,2,3-triazol-4-yl)-5-chlorophenyl)malonate (4e)

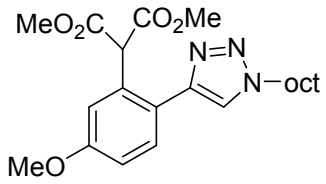
Pale yellow oil (31.9 mg, 40 %); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.66 (s, 1H), 7.57-7.56 (d, J = 2.4 Hz, 1H), 7.44-7.38 (m, 4H), 7.34-7.32 (m, 3H), 5.58 (s, 2H), 5.53 (s, 1H), 3.74 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 168.6, 146.1, 134.5, 134.3, 132.4, 130.7, 130.1, 129.2, 129.0, 128.9, 128.6, 128.2, 122.3, 54.3, 54.0, 53.0; HRMS (ESI+) calcd for $C_{20}H_{18}ClN_3O_4$ $[M+Na]^+$ 422.0884, found 422.0878.



4f

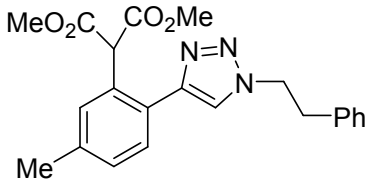
dimethyl 2-(2-(1-benzyl-1*H*-1,2,3-triazol-4-yl)-4-methylphenyl)malonate (4f)

White solid (72.0 mg, 95 %); mp 112-114 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.66 (s, 1H), 7.45-7.37 (m, 4H), 7.33-7.32 (m, 3H), 7.20 (d, J = 8.0 Hz, 1H), 5.58 (s, 2H), 5.47 (s, 1H), 3.71 (s, 6H), 2.34 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 169.3, 147.1, 138.2, 134.5, 130.3, 129.7, 129.5, 129.2, 128.8, 128.2, 127.8, 122.2, 54.2, 53.9, 52.8, 21.0; HRMS (ESI+) calcd for $C_{21}H_{21}N_3O_4$ $[M+Na]^+$ 402.1424, found 402.1399.



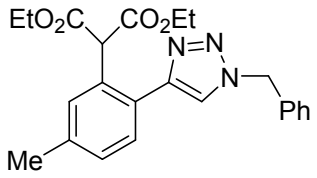
4g

dimethyl 2-(5-methyl-2-(1-octanoyl-1*H*-1,2,3-triazol-4-yl)phenyl)malonate (4g) Yellow oil (29.0 mg, 35 %); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.67 (s, 1H), 7.47 (d, J = 8.8 Hz), 7.13 (d, J = 2.8 Hz, 1H), 6.93 (dd, J = 8.8, 2.8 Hz, 1H), 5.50 (s, 1H), 4.39 (t, J = 7.2 Hz), 3.84 (s, 3H), 3.74 (s, 6H), 1.96-1.91 (m, 2H), 1.35-1.25 (m, 10 H), 0.88 (t, J = 6.4 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 169.0, 159.5, 146.4, 132.0, 130.9, 123.3, 121.7, 115.1, 114.2, 55.4, 54.2, 52.9, 50.4, 31.7, 30.3, 29.1, 29.0, 26.5, 22.6, 14.1; HRMS (ESI+) calcd for $C_{22}H_{31}N_3O_5$ $[M+Na]^+$ 440.2156, found 440.2148.



4h

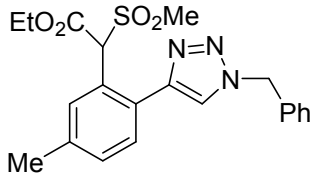
dimethyl 2-(5-methyl-2-(1-phenethyl-1*H*-1,2,3-triazol-4-yl)phenyl)malonate (4h) Yellow oil (22.8 mg, 29 %); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.34 (s, 1H), 7.37-7.28 (m, 4H), 7.25-7.23 (m, 1H), 7.18 (dd, J = 8, 0.8 Hz, 1H), 5.36 (s,1H), 4.65 (t, J = 6.8 Hz, 2H), 3.74 (s, 6H), 3.26 (t, J = 6.8 Hz, 2H), 2.38 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 169.2, 146.2, 138.5, 137.1, 130.2, 129.6, 129.3, 128.9, 128.8, 127.7, 127.1, 122.5, 53.9, 52.8, 51.8, 36.8, 21.4; HRMS (ESI+) calcd for $C_{22}H_{23}N_3O_4$ $[M+Na]^+$ 416.1587, found 416.1581.



4i

diethyl 2-(2-(1-benzyl-1*H*-1,2,3-triazol-4-yl)-5-methylphenyl)malonate (4i)

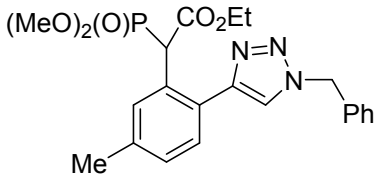
Yellow liquid (35.0 mg, 43 %); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.64 (s, 1H), 7.41-7.36 (m, 5H), 7.33-7.30 (m, 2H), 5.57 (s, 2H), 5.40 (s, 1H), 4.20-4.12 (m, 4H), 2.37 (s, 3H), 1.22 (t, J = 7.2 Hz, 6H) ; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 168.7, 147.1, 138.5, 134.6, 130.7, 130.3, 129.5, 129.2, 129.1, 128.8, 127.6, 122.0, 61.7, 54.5, 54.2, 21.3, 14.0; HRMS (ESI+) calcd for $C_{23}H_{25}N_3O_4$ $[M+Na]^+$ 430.1737, found 430.1743.



4j

ethyl 2-(2-(1-benzyl-1*H*-1,2,3-triazol-4-yl)-5-methylphenyl)-2-(methylsulfonyl) acetate (4j)

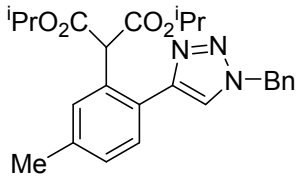
Yellow oil (33.9 mg, 41 %); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.78 (s, 1H), 7.73 (s, 1H), 7.41-7.32 (m, 6H), 7.24 (d, J = 8.0 Hz, 1H), 6.58 (d, 1H), 5.60 (d, J = 14.8 Hz, 1H), 5.57 (d, J = 14.8 Hz, 1H), 4.35-4.18 (m, 2H), 3.05 (s, 3H), 2.41 (s, 3H), 1.27 (t, J = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 165.5, 147.2, 138.8, 134.4, 131.0, 130.6, 129.9, 129.2, 128.9, 128.7, 128.2, 125.8, 122.6, 68.6, 62.7, 54.4, 40.3, 21.4, 13.9; HRMS (ESI+) calcd for $C_{21}H_{23}N_3O_4S$ $[M+Na]^+$ 436.1307, found 436.1301.



4k

ethyl 2-(2-(1-benzyl-1*H*-1,2,3-triazol-4-yl)-5-methylphenyl)-2-(dimethoxy-phosphoryl) acetate (4k)

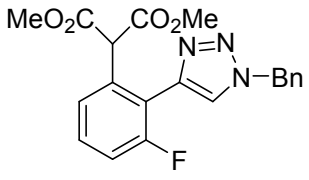
Yellow solid (23.9 mg, 27 %); mp 134-136 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.75 (s, 1H), 7.71 (s, 1H), 7.40-7.31 (m, 6H), 7.15 (d, J = 8.0 Hz, 1H), 5.61, 5.56 (d, J = 14.8 Hz, both 1H), 5.30 (d, J_{HP} = 8.0 Hz, 2H), 4.23-4.41 (m, 2H), 3.69 (d, $^3J_{HP}$ = 10.8 Hz, 3H), 3.56 (d, $^3J_{HP}$ = 10.8 Hz, 3H), 2.38 (s, 3H), 1.20 (t, J = 7.6 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 167.8,146.9, 138.6 (d, J_{CP} = 3.0 Hz), 134.5, 131.1 (d, J_{CP} = 5.0 Hz), 130.0, 129.2, 129.1 (d, J_{CP} = 3.0 Hz), 128.9, 128.4 (d, J_{CP} = 8.0 Hz) 128.2, 127.5 (d, J_{CP} = 8.0 Hz), 122.5, 62.0, 58.4, 53.8(d, J_{CP} = 6.0 Hz), 53.7 (d, J_{CP} = 6.0 Hz), 46.7 (d, J_{CP} = 136.0 Hz), 21.4, 14.0; ^{31}P NMR ($CDCl_3$, 162 MHz) δ 22.2; HRMS (ESI+) calcd for $C_{22}H_{26}N_3O_5P$ $[M+Na]^+$ 466.1502, found 466.1491.



4l

diisopropyl 2-(2-(1-benzyl-1*H*-1,2,3-triazol-4-yl)-5-methylphenyl)malonate (4l)

Yellow oil (22.6 mg, 26 %); ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.65 (s, 1H), 7.41 (d, J = 7.8 Hz, 1H), 7.40-7.39 (m, 4H), 7.31 (d, J = 6.6 Hz, 2H), 7.15 (d, J = 7.8 Hz, 1H), 5.57 (s, 2H), 5.27 (s, 1H), 5.08-5.02 (m, 2H), 2.37 (s, 3H), 1.23 (t, J = 6.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 168.7, 147.1, 138.5, 134.6, 130.7, 130.3, 129.5, 129.2, 129.1, 128.8, 127.6, 122.0, 61.7, 54.5, 54.2, 21.3, 14.0; HRMS (ESI+) calcd for $C_{25}H_{29}N_3O_4$ $[M+Na]^+$ 458.2050, found 458.2045.

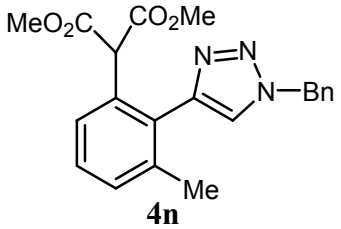


4m

dimethyl 2-(2-(1-benzyl-1H-1,2,3-triazol-4-yl)-3-fluorophenyl)malonate (4m)

White solid (40.6 mg, 53 %); mp 94-96 °C**;** ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.77 (s, J = 3.0 Hz, 1H), 7.39-7.30 (m, 7H), 7.12-7.09 (s, 1H), 5.77 (s, 1H), 5.59 (s, 2H), 3.73 (s, 6H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 171.6, 162.5 (d, J_{C-F} = 245.9 Hz), 142.5, 137.1,

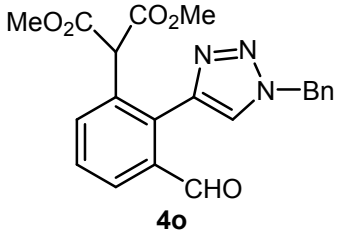
136.4 (d, $J_{C\text{-}F}$ = 2.3 Hz), 132.1 (d, $J_{C\text{-}F}$ = 9.3 Hz), 131.8, 131.4, 130.7, 128.2 (d, $J_{C\text{-}F}$ = 3.2 Hz), 127.3 (d, $J_{C\text{-}F}$ = 10.1 Hz), 121.4 (d, $J_{C\text{-}F}$ = 14.4 Hz), 118.0, (d, $J_{C\text{-}F}$ = 23.1 Hz), 57.2 (d, $J_{C\text{-}F}$ = 2.3 Hz), 56.9, 55.5; ^{19}F NMR ($CDCl_3$, 376 MHz) δ -112.3; HRMS (ESI+) calcd for $C_{20}H_{18}FN_3O_4$ $[M+Na]^+$ 406.1174, found 406.1169.



4n

dimethyl 2-(2-(1-benzyl-1*H*-1,2,3-triazol-4-yl)-3-methylphenyl)malonate (4n)

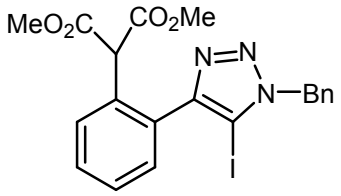
Pale yellow oil (54.6 mg, 72 %); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.43 (s, 1H), 7.41-7.35 (m, 4H), 7.33-7.29 (m, 3H), 7.25-7.23 (s, 1H), 5.62 (s, 2H), 4.65 (s, 1H), 3.63 (s, 6H), 2.11 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.8, 144.5, 138.5, 134.7, 132.8, 130.5, 130.0, 129.2, 128.9, 128.8, 127.9, 126.5, 123.5, 54.8, 54.2, 52.7, 21.0; HRMS (ESI+) calcd for $C_{21}H_{21}N_3O_4$ $[M+Na]^+$ 402.1430, found 402.1424.



4o

dimethyl 2-(2-(1-benzyl-1H-1,2,3-triazol-4-yl)-3-formylphenyl)malonate (4o)

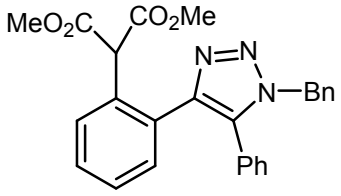
Pale yellow oil (35.4 mg, 45 %); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 9.73 (s, 1H), 8.00 (dd, J = 8.0, 1.2 Hz, 1H), 7.85 (dd, J = 8.0, 1.2 Hz, 1H), 7.61 (s, 1H), 7.44-7.38 (m, 4H), 7.35-7.31 (m, 2H), 5.66 (s, 2H), 4.79 (s, 1H), 3.67 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.2, 168.3, 141.1, 135.8, 134.9, 134.2, 133.6, 133.5, 129.5, 129.3, 129.0, 128.1, 128.0,125.2, 54.5, 53.7, 53.0; HRMS (ESI+) calcd for $C_{21}H_{19}N_3O_5$ $[M+Na]^+$ 416.1228, found 416.1217.



4p

dimethyl 2-(2-(1-benzyl-5-iodo-1*H*-1,2,3-triazol-4-yl)phenyl)malonate (4p)

White solid (51.1 mg, 52 %); mp 159-162 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.62 (d, J = 8.0 Hz, 1H), 7.48-7.44 (m, 1H), 7.36-7.26 (m, 7H), 5.68 (s, 2H), 5.08 (s, 1H), 3.68 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.8, 150.7, 134.2, 132.6, 130.7, 130.1, 129.7, 129.5, 129.0, 128.8, 128.6, 128.1, 127.8, 54.6, 54.1, 52.8; HRMS (ESI+) calcd for $C_{20}H_{18}IN_3O_4$ $[M+Na]^+$ 514.0238, found 514.0234.

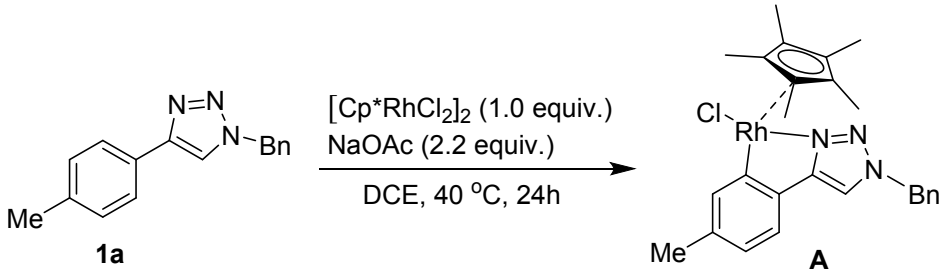


4q

White solid (42.4 mg, 48 %); mp 131-133 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.46-7.44 (m, 1H), 7.31-7.18 (m, 7H), 7.07 (td, J = 8.0, 1.2 Hz, 1H), 7.02-6.94 (m, 5H), 5.44 (s, 2H), 5.37 (s, 1H), 3.58 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.0, 144.2, 135.8, 135.4, 132.3, 130.8, 130.6, 129.8, 129.5, 129.4, 129.0, 128.8, 128.6, 128.2, 127.9, 127.4, 126.8, 54.2, 52.7, 52.2; HRMS (ESI+) calcd for $C_{26}H_{23}N_3O_4$ $[M+Na]^+$ 464.1582, found 464.1581.

6. Mechanistic experiments

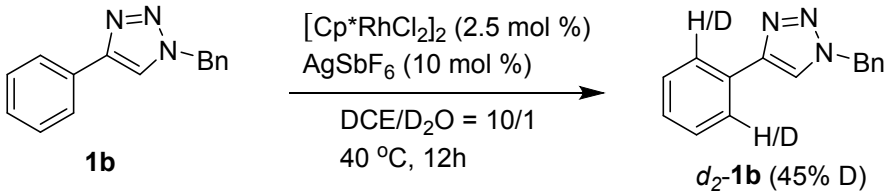
6.1 Synthesis of 1,2,3-triazole coordinated cyclometalated intermediate A



1a **A**

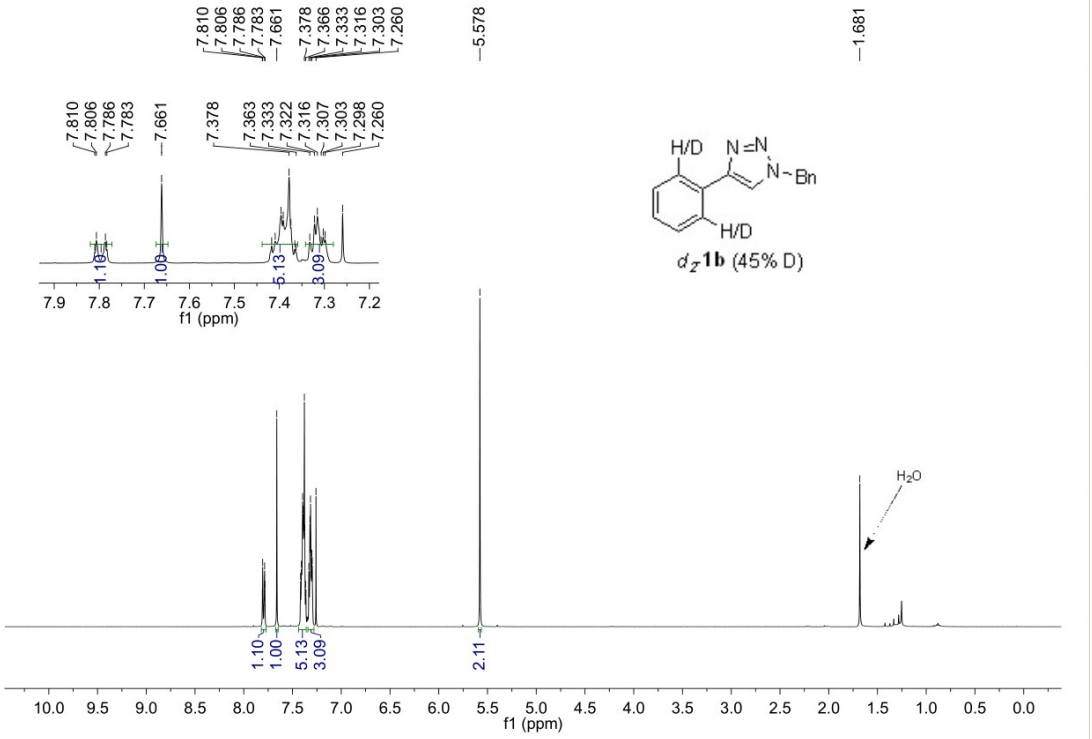
A mixture of $[Cp^*RhCl_2]_2$ (0.05 mmol, 1.0 equiv.), **1a** (0.2 mmol, 2.0 equiv.), NaOAc (0.11 mmol, 2.2 equiv.) and 1,2-dichloroethane (2.0 mL) were added into an oven-dried 15 mL tube with a Teflon screw cap. The sealed tube was heated at 40 °C for 24 h. The reaction mixture was then cooled to room temperature and filtered through Celite pad. The solid residue was washed with DCM three times. The combined filtrate was concentrated under reduced pressure and the crude mixture was kept for recrystallization from DCM/Et_2O at room temperature to obtain a red orange crystal A identified by x-ray diffraction study.

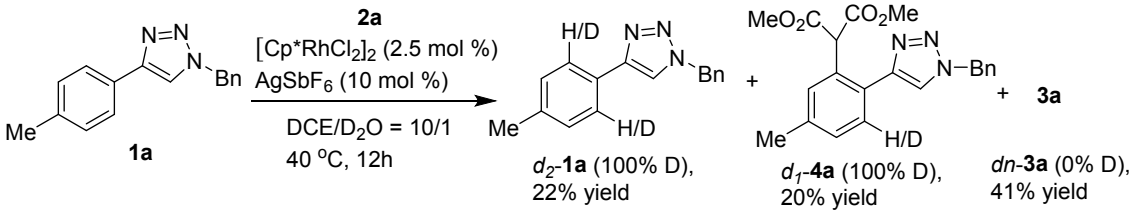
6.2 H/D exchange experiment



1-benzyl-4-phenyl-1*H*-1,2,3-triazole **1b** (0.2 mmol, 1.0 equiv.), $[Cp^*RhCl_2]_2$ (0.005 mmol, 2.5 mol %), $AgSbF_6$ (0.02 mmol, 10 mol %), 1,2-dichloroethane (2.0 mL) and D_2O (0.2 mL) were added into an oven-dried 15 mL tube with a Teflon screw cap. The sealed tube was heated at 40 °C for 12 h. The solvent was then removed under reduced pressure, and the residue was purified by silica gel chromatography using petroleum ether/ethyl acetate to afford a mixture of **1b** and *d_2*-**1b**. The deuterated ratio was calculated based on ^{1}H NMR analysis.

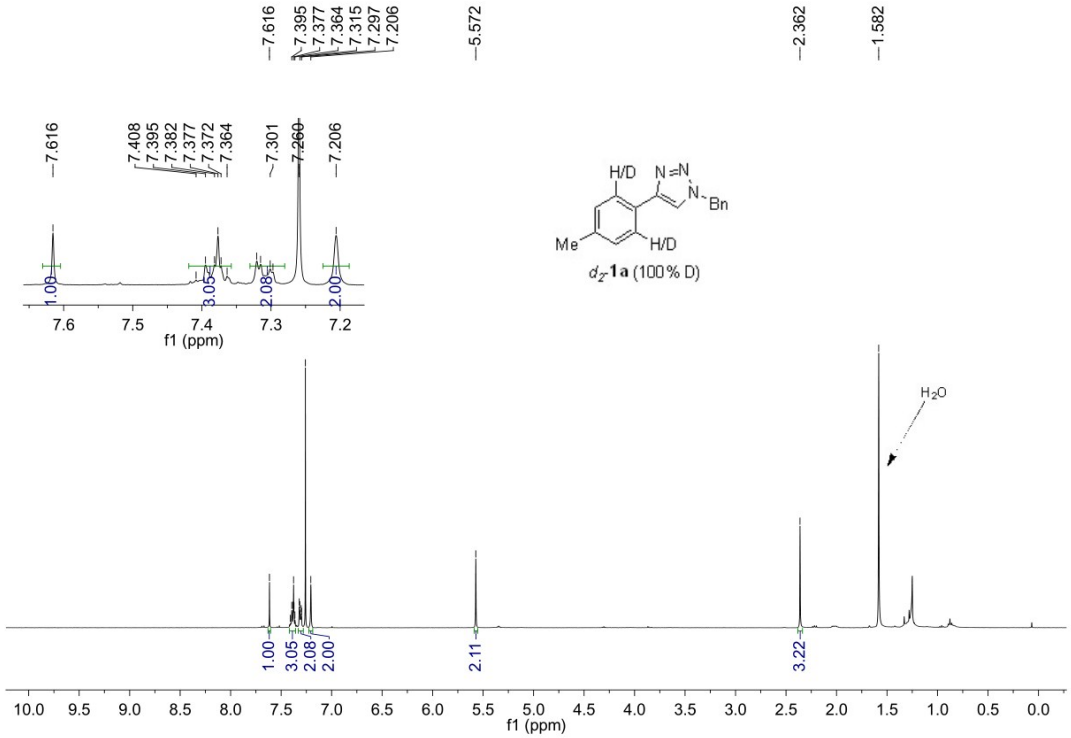
^{1}H NMR Spectrum of 1b and *d_2*-**1b in $CDCl_3$ at 400 MHz**



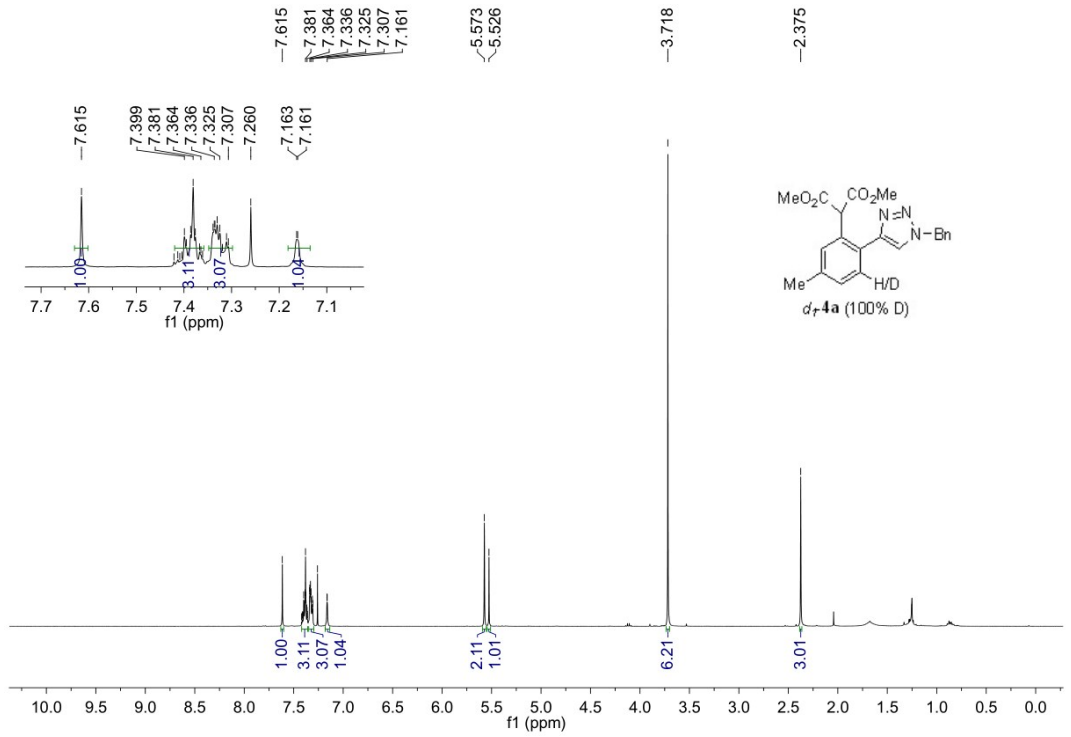


1-benzyl-4-phenyl-1*H*-1,2,3-triazole **1a** (0.2 mmol, 1.0 equiv.), dimethyl 2-diazomalonate (0.3 mmol, 1.5 equiv.), $[Cp^*RhCl_2]_2$ (0.005 mmol, 2.5 mol %), $AgSbF_6$ (0.02 mmol, 10 mol %), 1,2-dichloroethane (2.0 mL) and D_2O (0.2 mL) were added into an oven-dried 15 mL tube with a Teflon screw cap. The sealed tube was heated at 40 °C for 12 h. The solvent was then removed under reduced pressure, and the residue was purified by silica gel chromatography using petroleum ether/ethyl acetate to afford the isolated product d_2-**1a**, d_1-**4a** and d_n-**3a**. The deuterated ratio was calculated from ^{1}H NMR analysis.

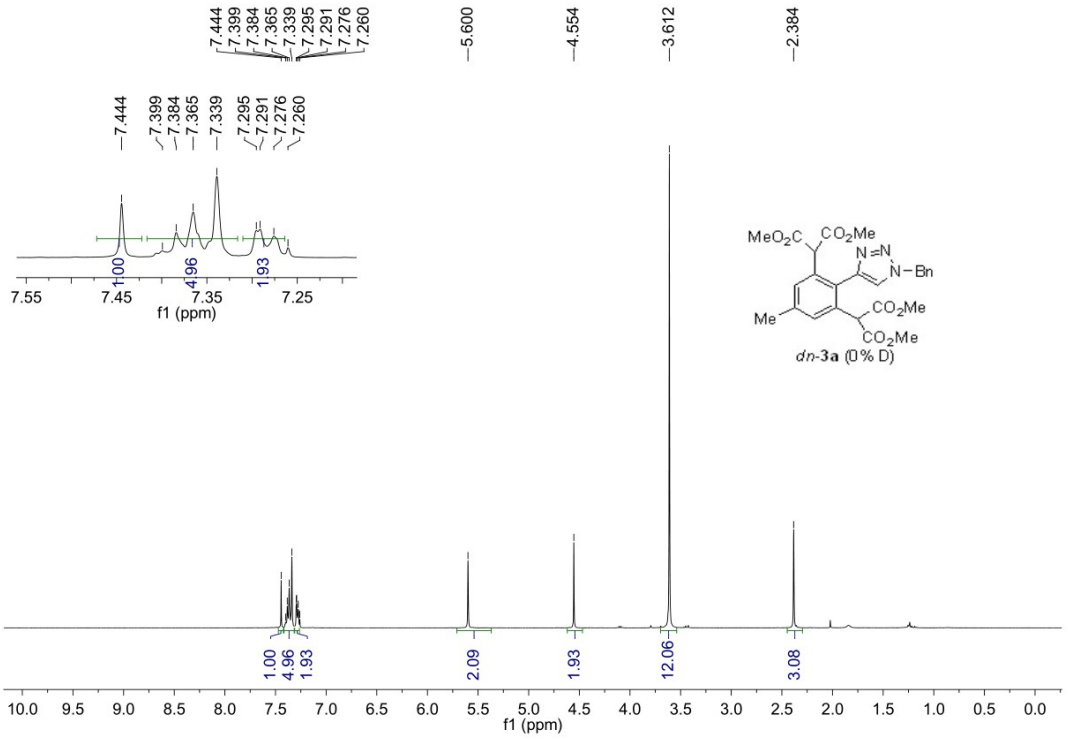
^{1}H NMR Spectrum of d_2-1a in $CDCl_3$ at 400 MHz



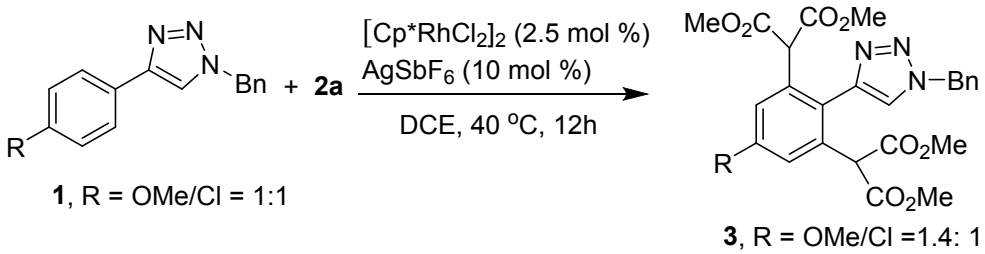
^{1}H NMR Spectrum of d_1-4a in $CDCl_3$ at 400 MHz



^{1}H NMR Spectrum of d_n-3a in $CDCl_3$ at 400 MHz

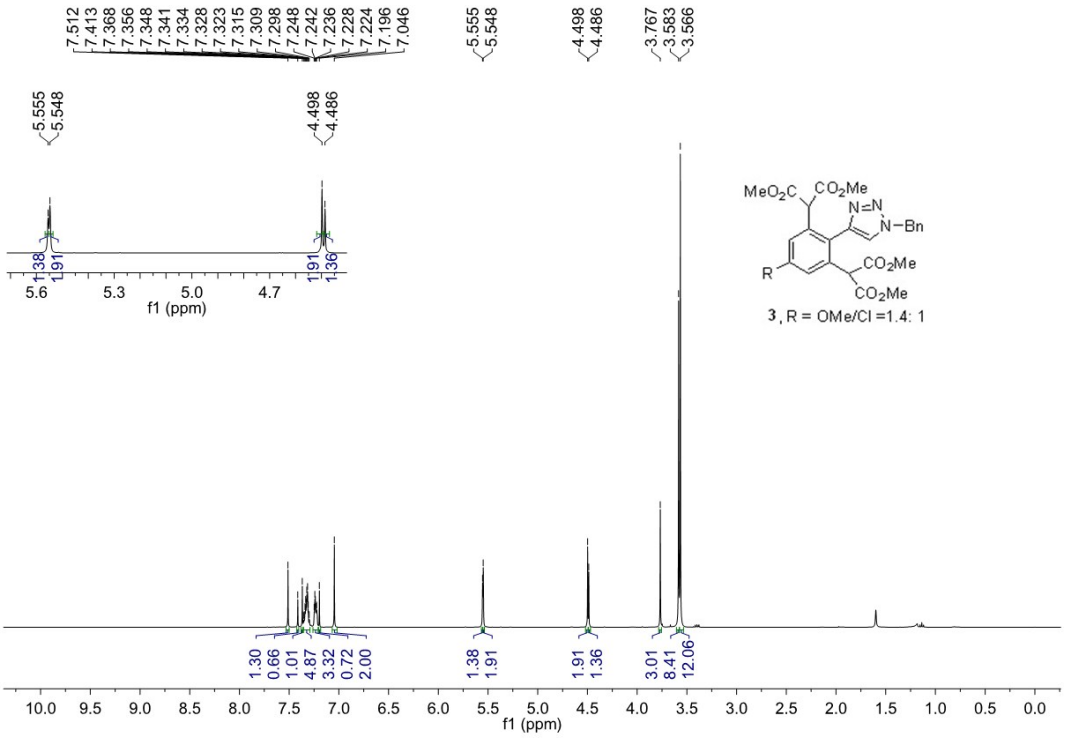


6.3 Intermolecular competition experiments between 1c and 1e



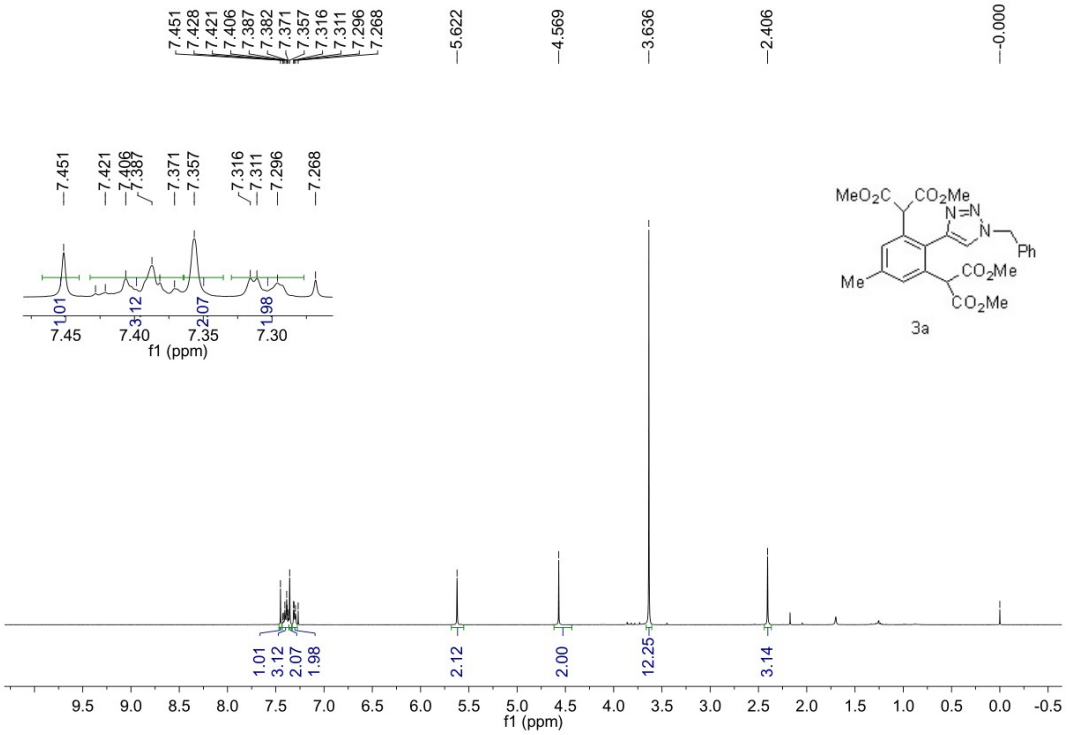
1-benzyl-4-(4-methoxyphenyl)-1*H*-1,2,3-triazole **1c** (0.1 mmol, 1.0 equiv.), 1-benzyl-4-(4-chlorophenyl)-1*H*-1,2,3-triazole **1e** (0.1 mmol, 1.0 equiv.), dimethyl 2-diazomalonate (0.22 mmol, 2.2 equiv.), $[Cp^*RhCl_2]_2$ (0.005 mmol, 2.5 mol %), $AgSbF_6$ (0.02 mmol, 10 mol %), 1,2-dichloroethane (2.0 mL) were added into an oven-dried 15 mL tube with a Teflon screw cap. The sealed tube was heated at 40 °C for 12 h. The solvent was then removed under reduced pressure, and the residue was purified by silica gel chromatography using petroleum ether/ethyl acetate to afford a mixture of **3e** and **3c**. The ratio was calculated from ^{1}H NMR analysis.

^{1}H NMR Spectrum of 3c and **3e in $CDCl_3$ at 400 MHz**

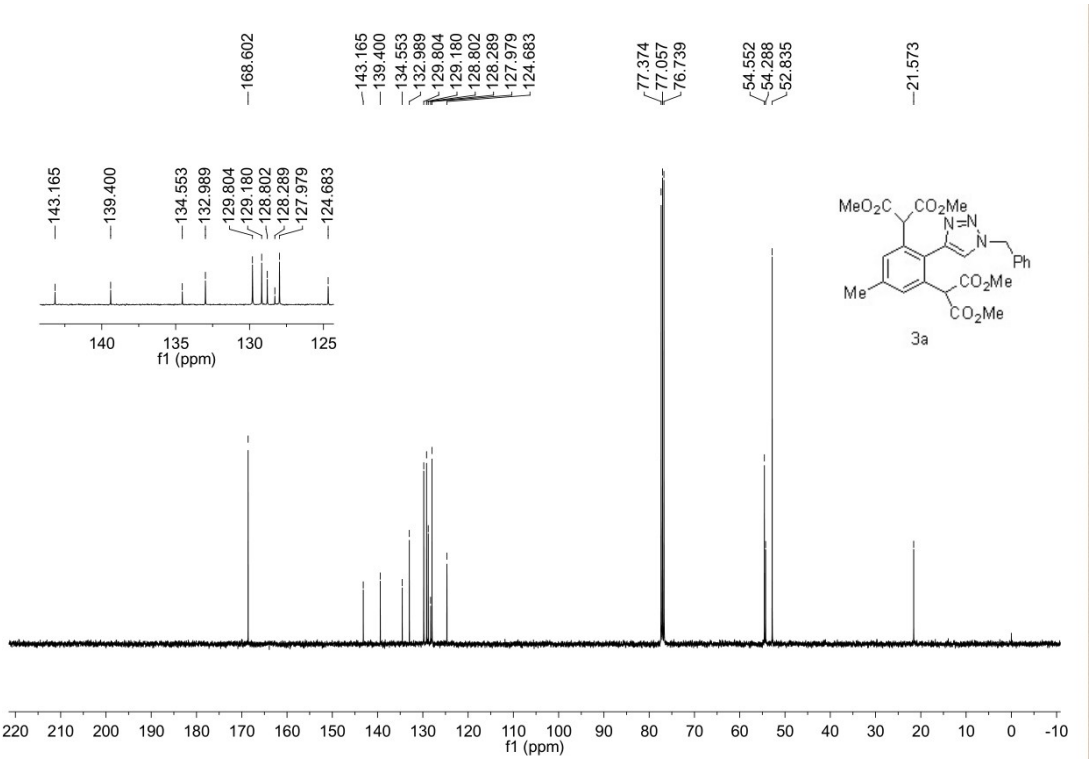


7. ^{1}H and ^{13}C NMR Spectra of products

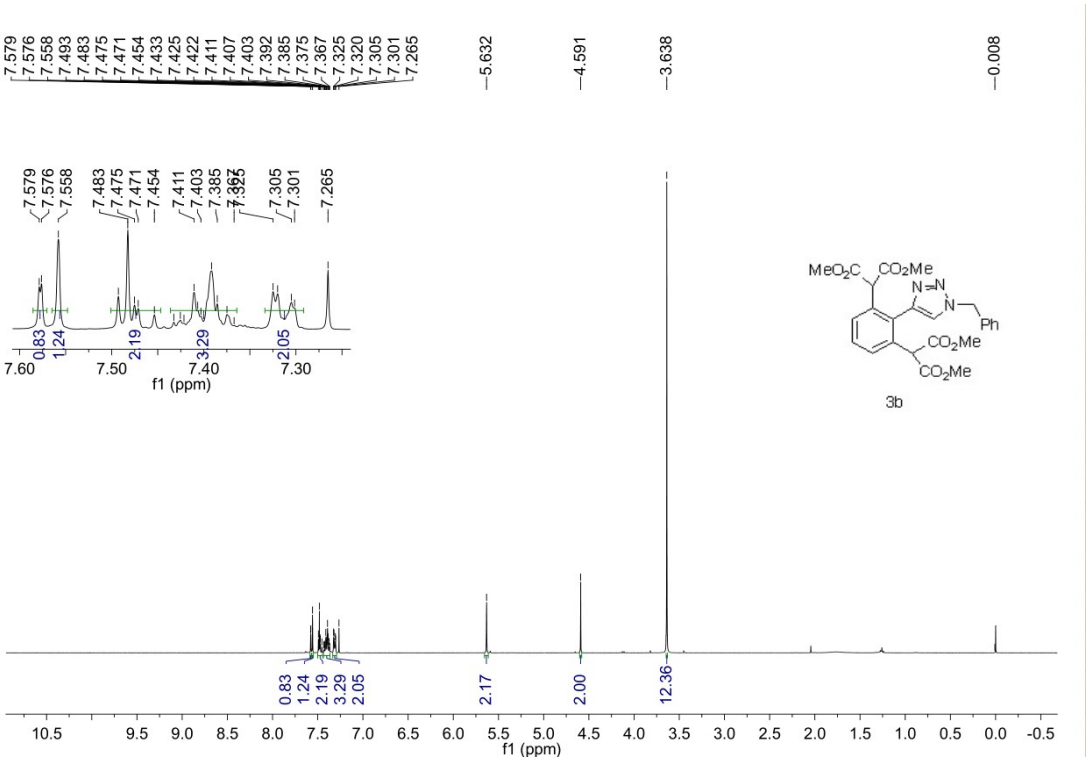
^{1}H NMR Spectrum of 3a in $CDCl_3$ at 400 MHz



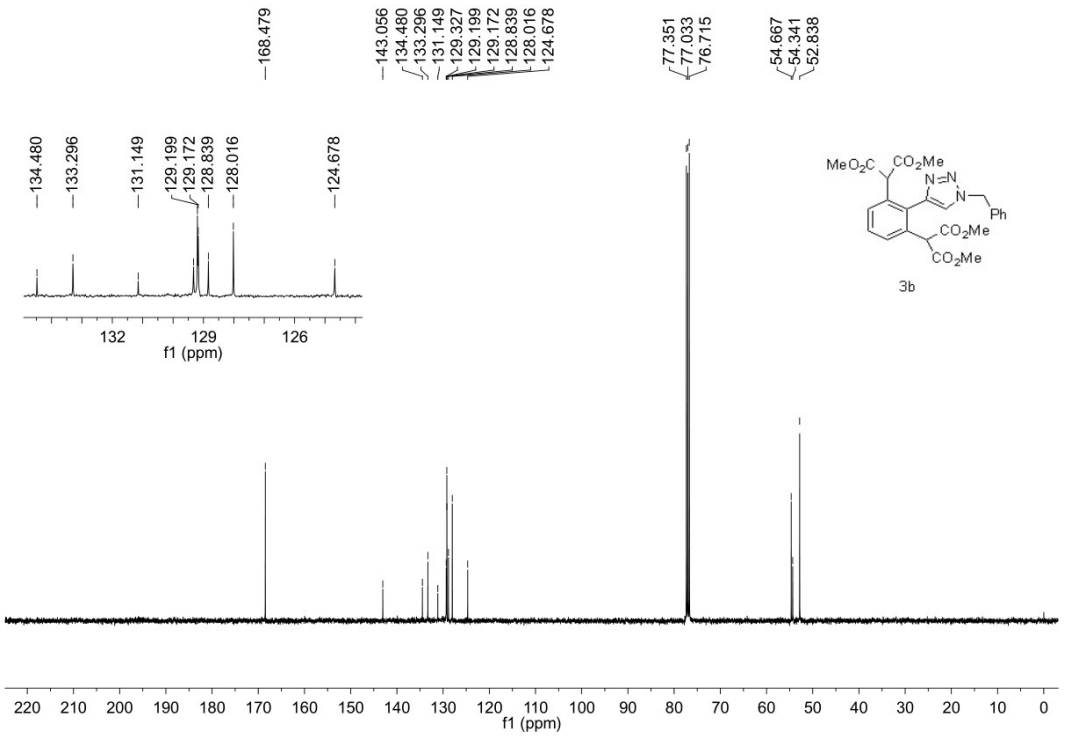
^{13}C NMR Spectrum of 3a in $CDCl_3$ at 100 MHz



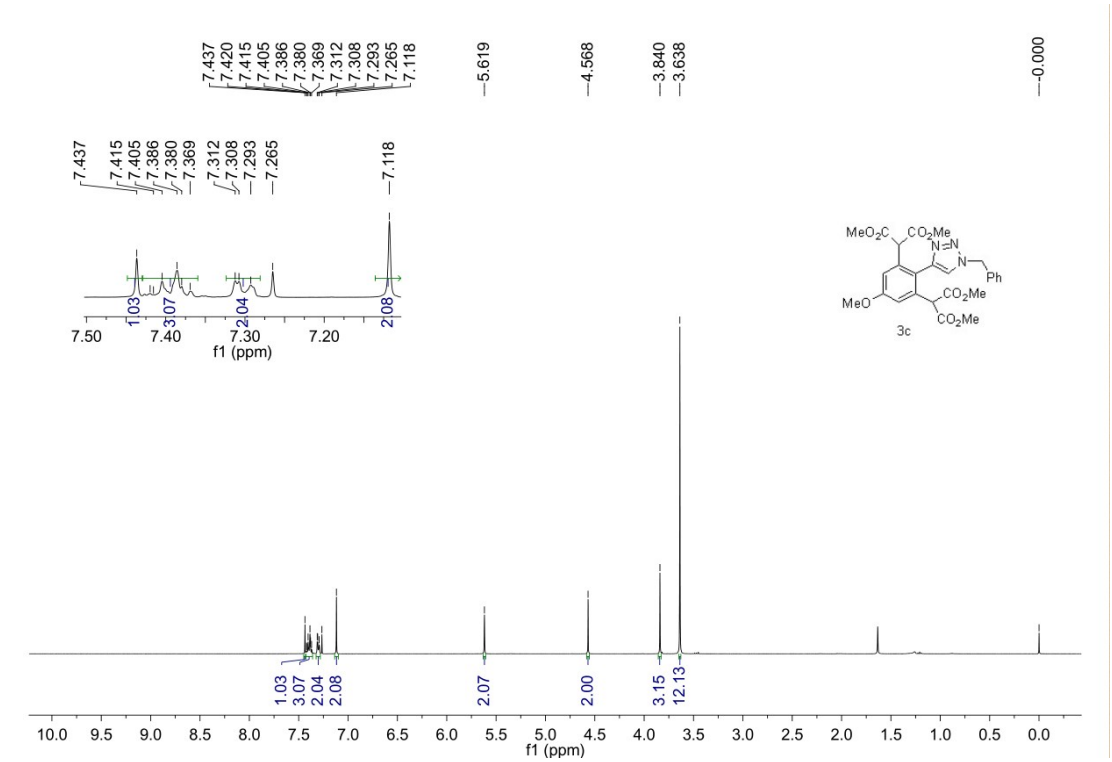
^{1}H NMR Spectrum of 3b in $CDCl_3$ at 400 MHz



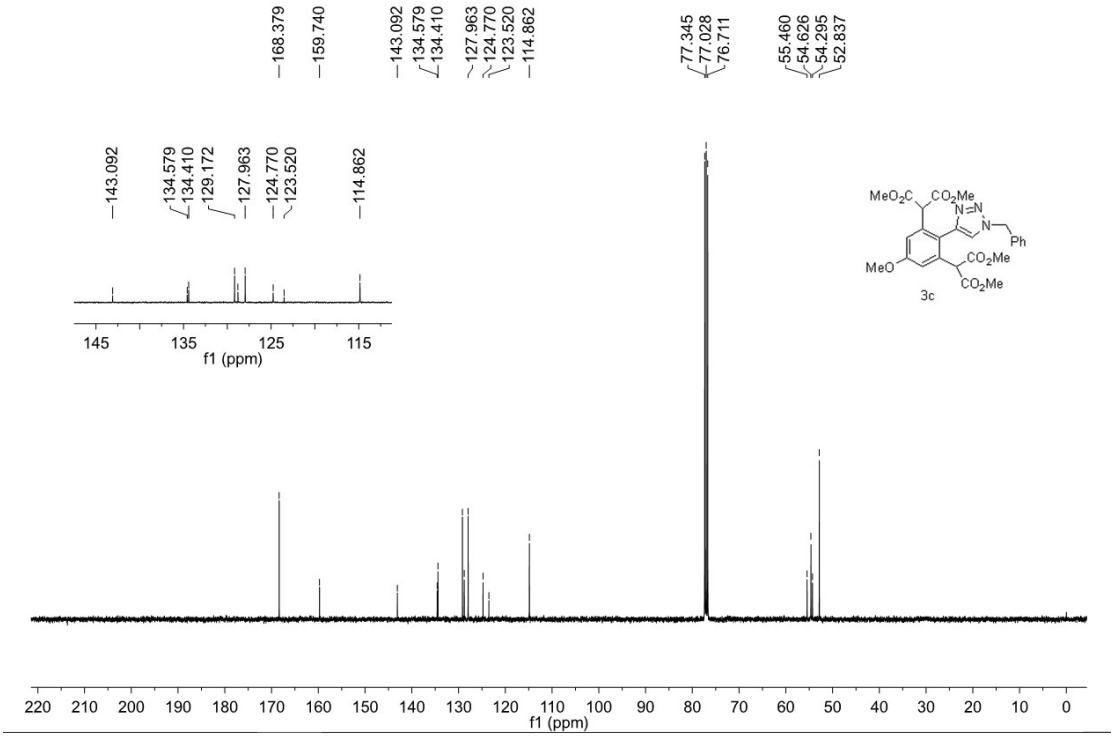
^{13}C NMR Spectrum of 3b in $CDCl_3$ at 100 MHz



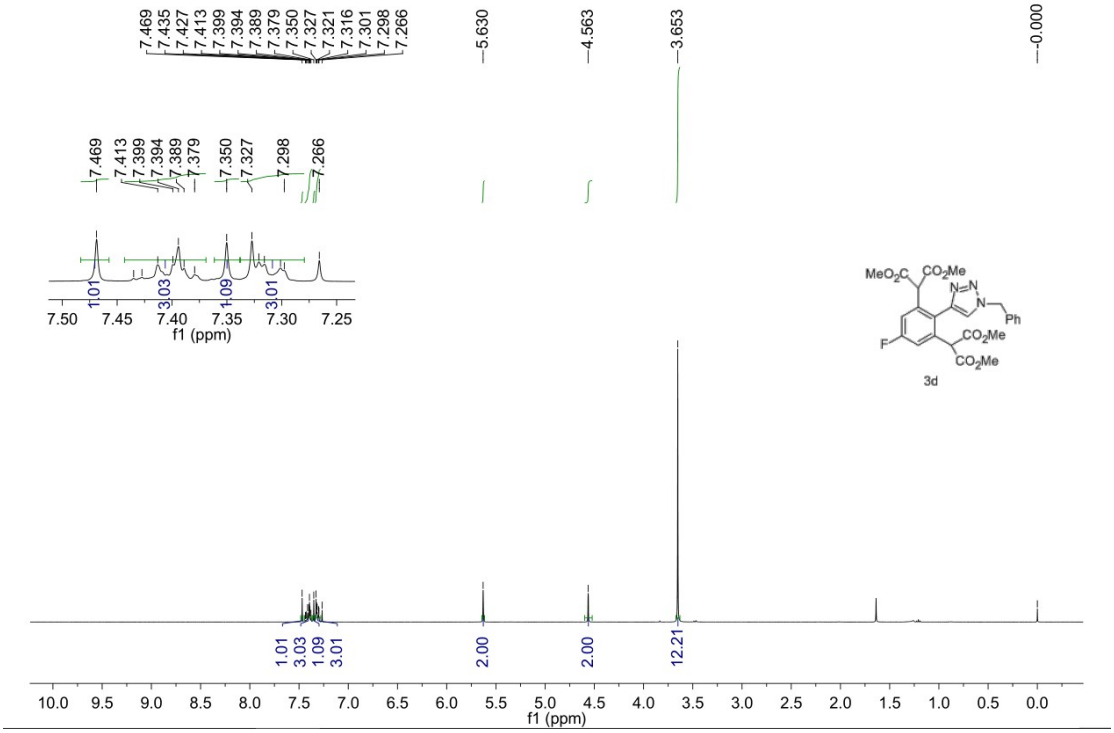
^{1}H NMR Spectrum of 3c in $CDCl_3$ at 400 MHz



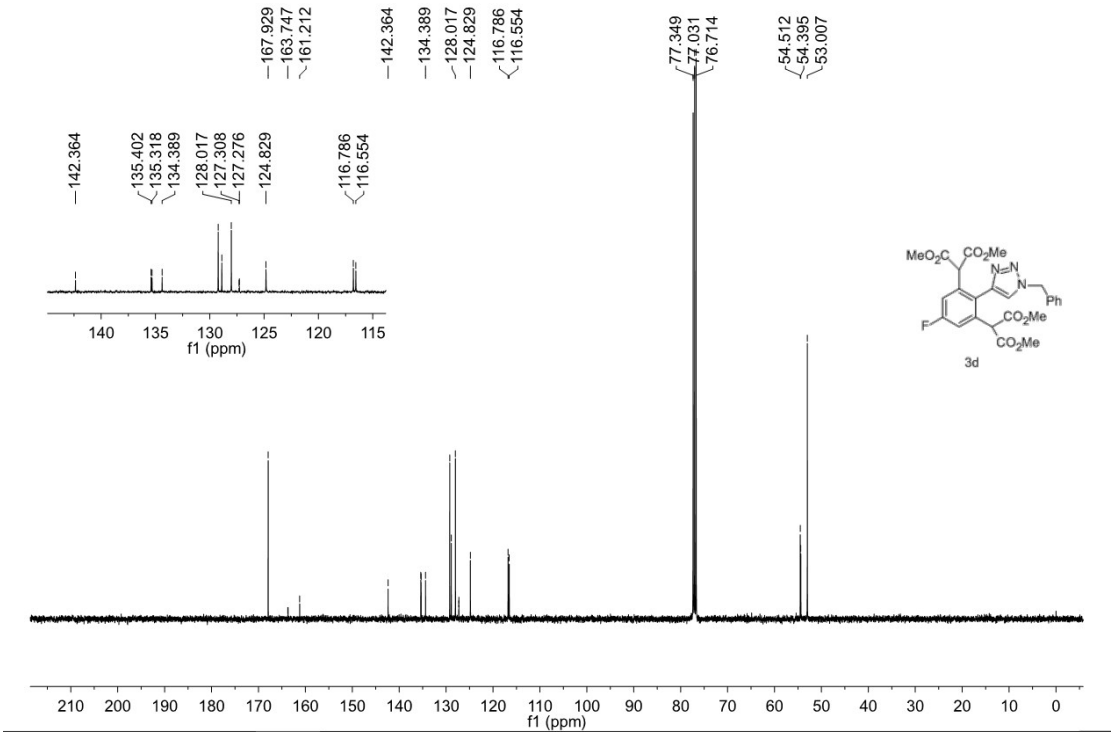
^{13}C NMR Spectrum of 3c in $CDCl_3$ at 100 MHz



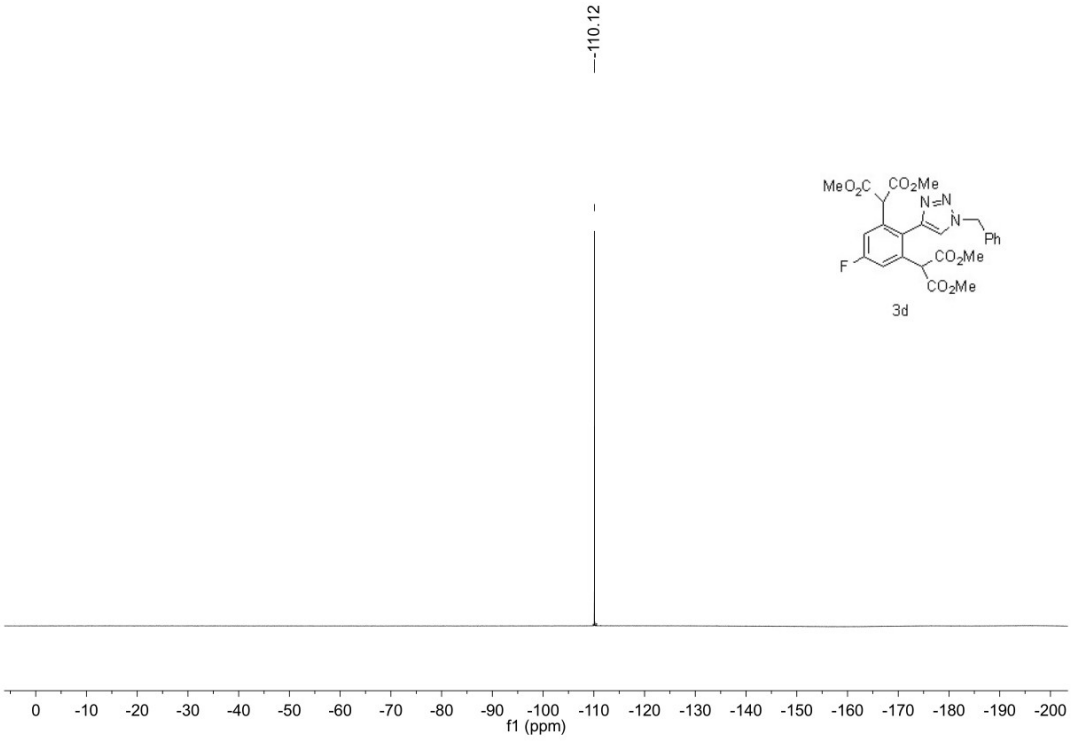
^{1}H NMR Spectrum of 3d in $CDCl_3$ at 400 MHz



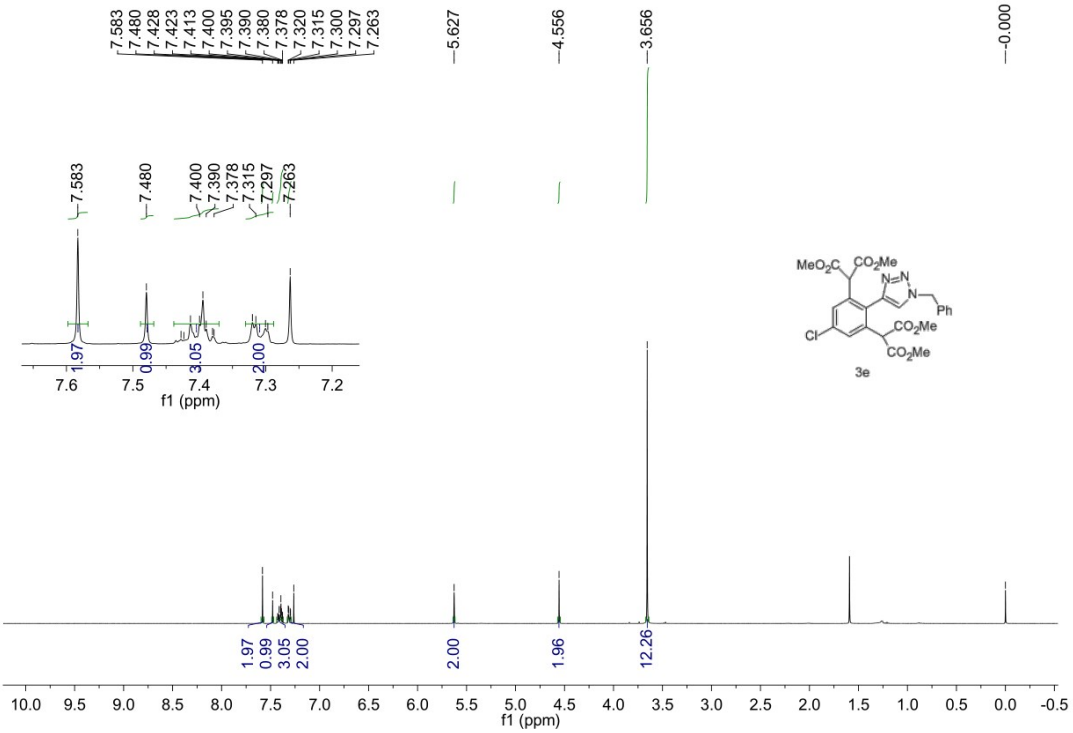
^{13}C NMR Spectrum of 3d in $CDCl_3$ at 100 MHz



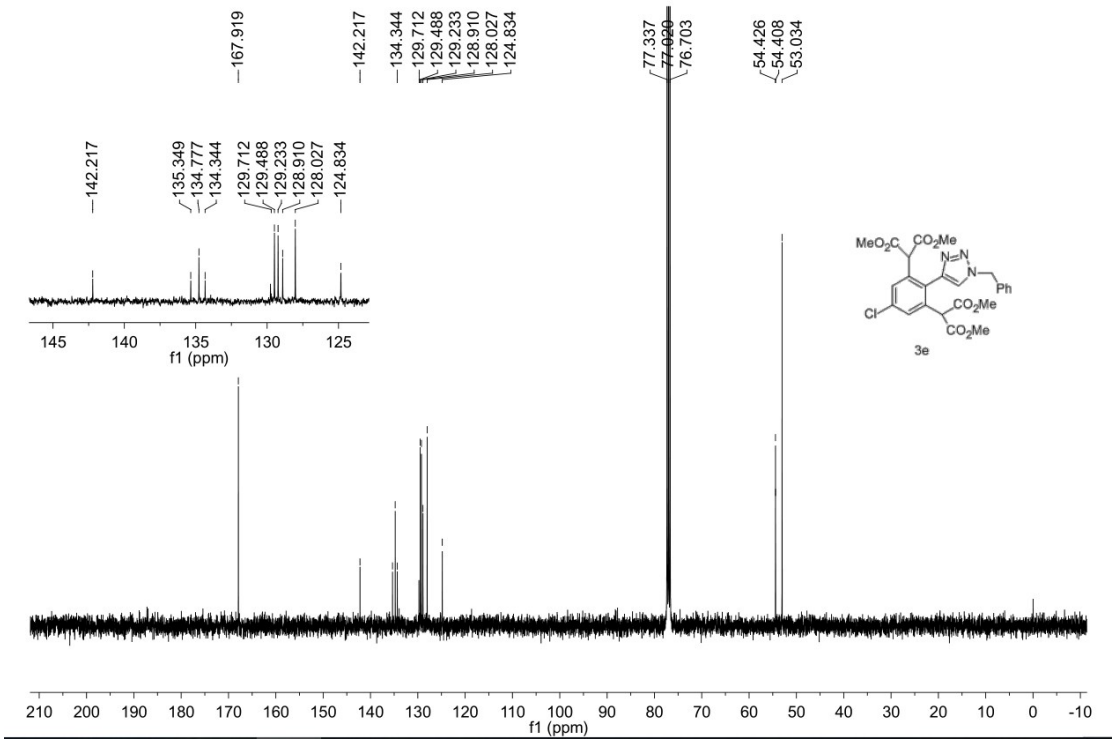
^{19}F NMR Spectrum of 3d in $CDCl_3$ at 376 MHz



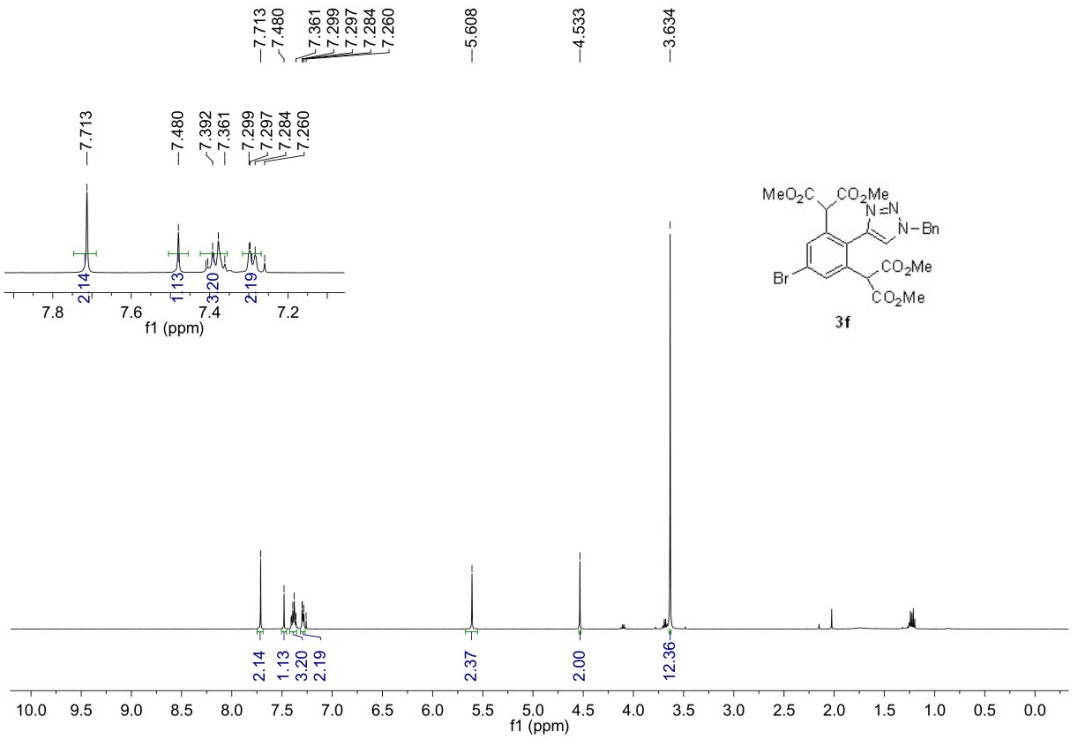
^{1}H NMR Spectrum of 3e in $CDCl_3$ at 400 MHz



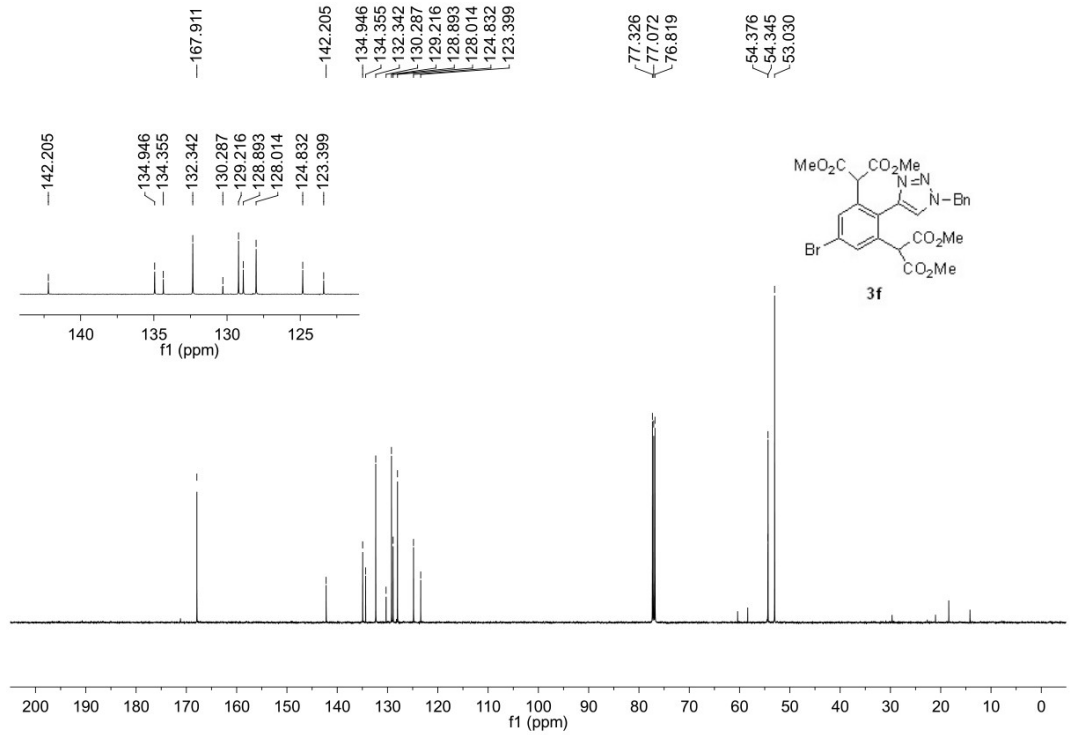
^{13}C NMR Spectrum of 3e in $CDCl_3$ at 100 MHz



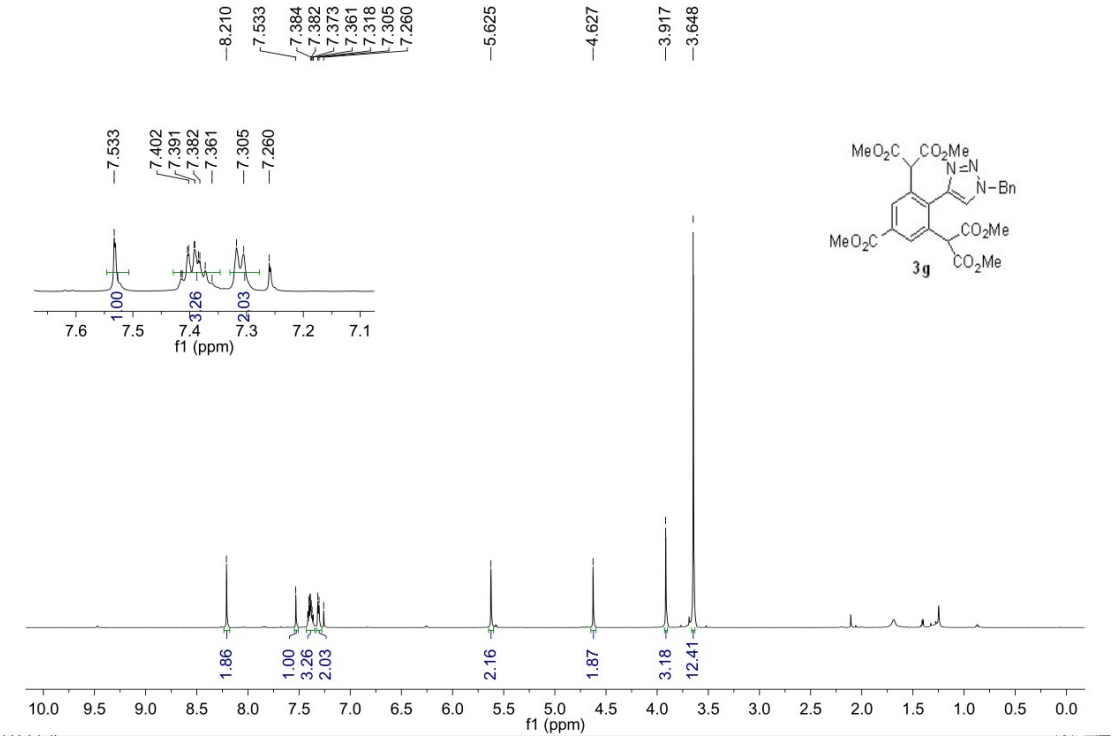
^{1}H NMR Spectrum of 3f in $CDCl_3$ at 500 MHz



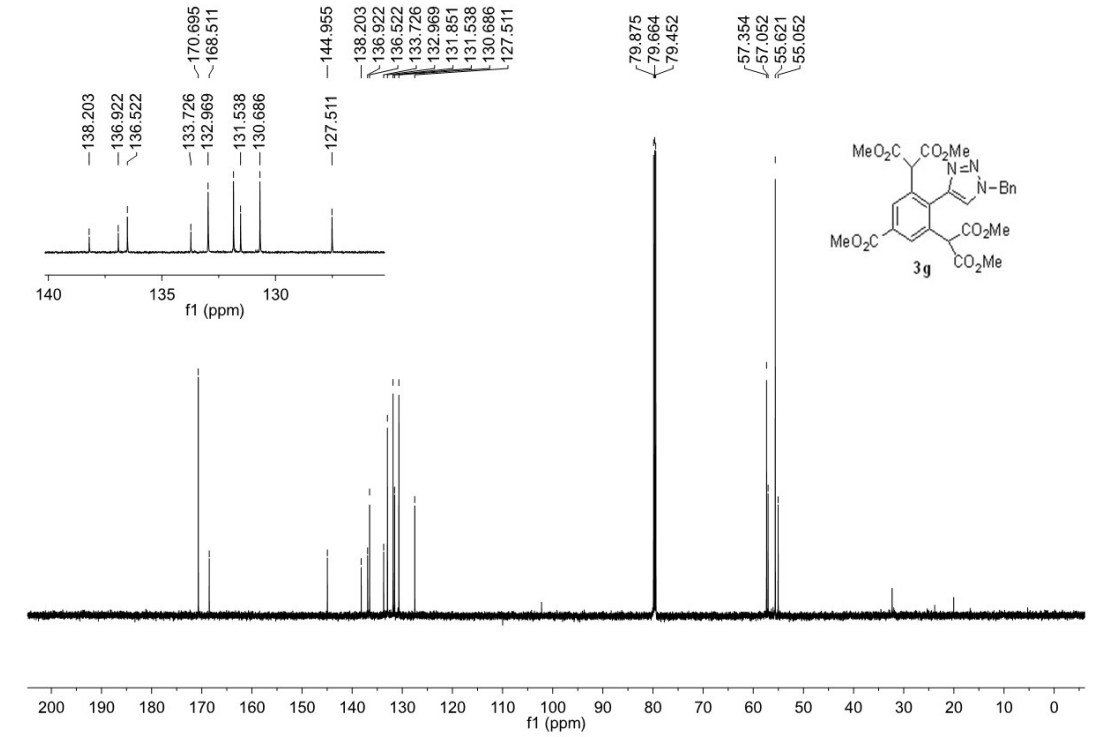
^{13}C NMR Spectrum of 3f in $CDCl_3$ at 125 MHz



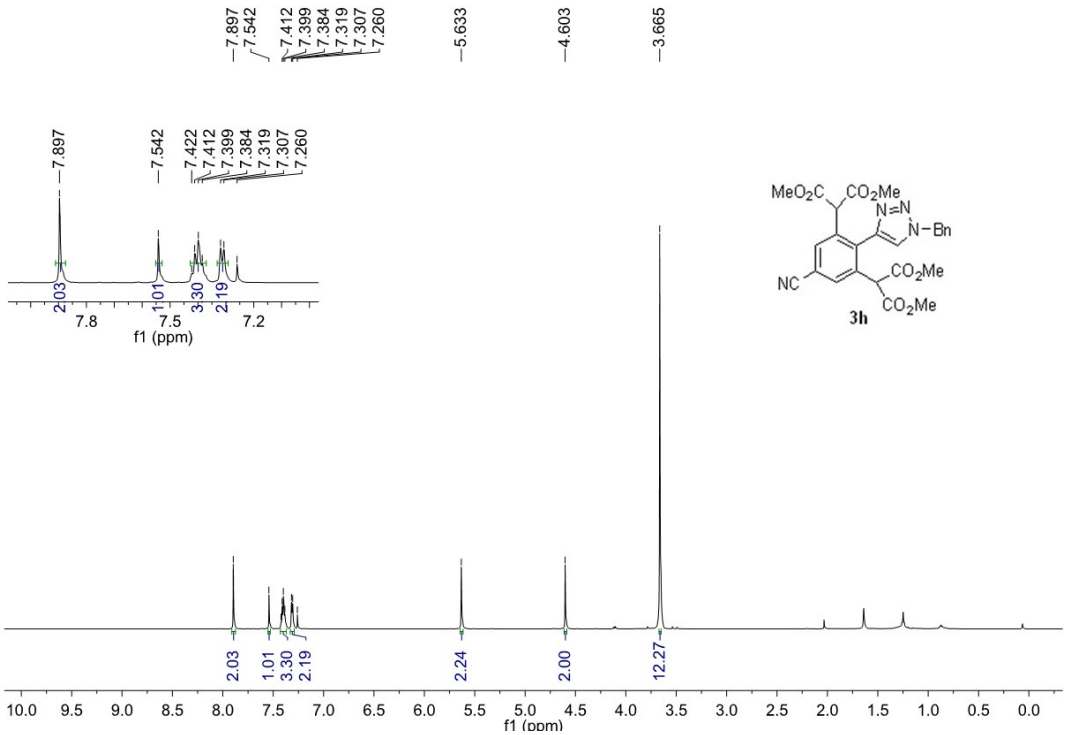
^{1}H NMR Spectrum of 3g in $CDCl_3$ at 600 MHz



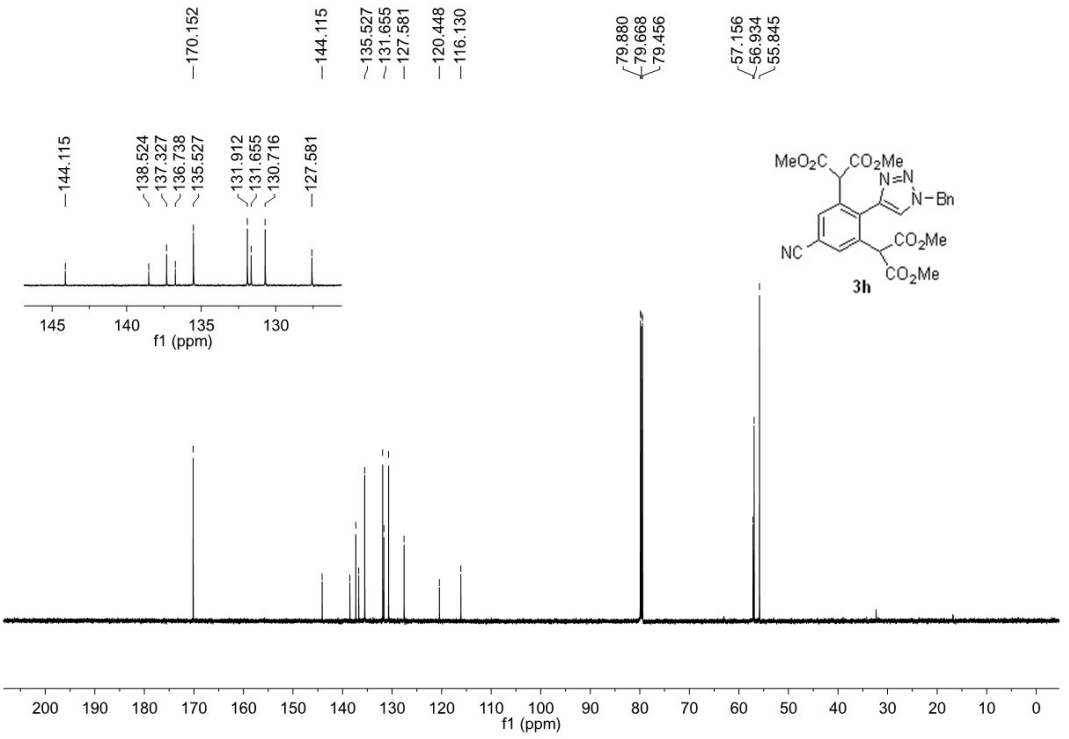
^{13}C NMR Spectrum of 3g in $CDCl_3$ at 150 MHz



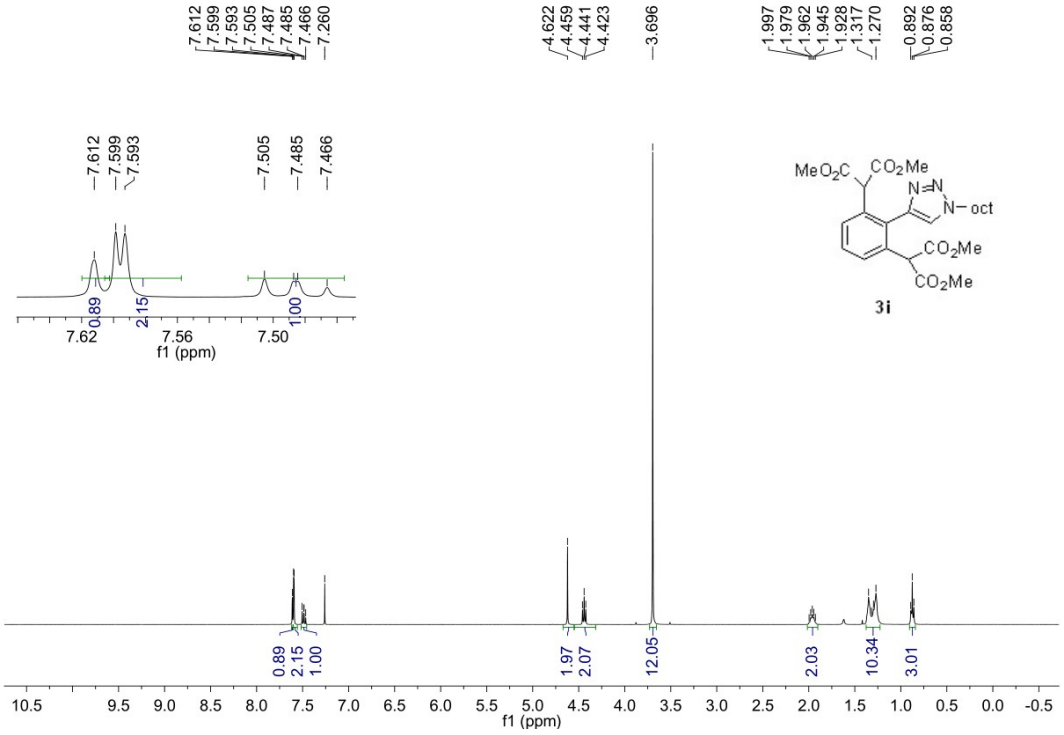
^{1}H NMR Spectrum of 3h in $CDCl_3$ at 600 MHz



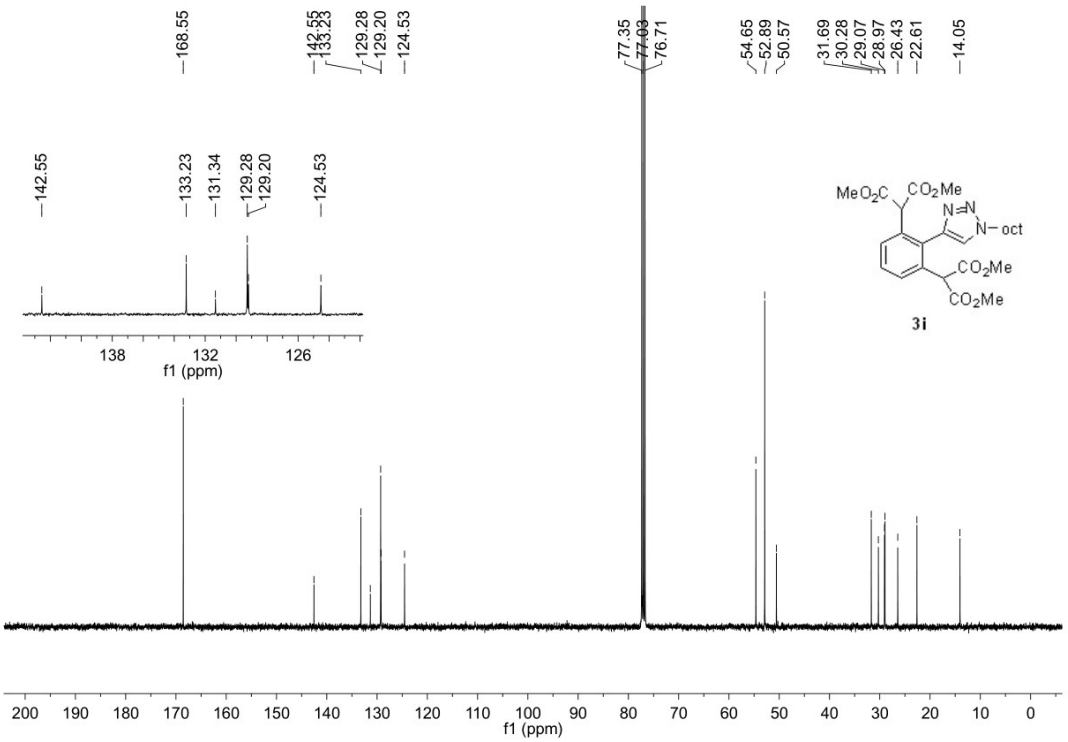
^{13}C NMR Spectrum of 3h in $CDCl_3$ at 150 MHz



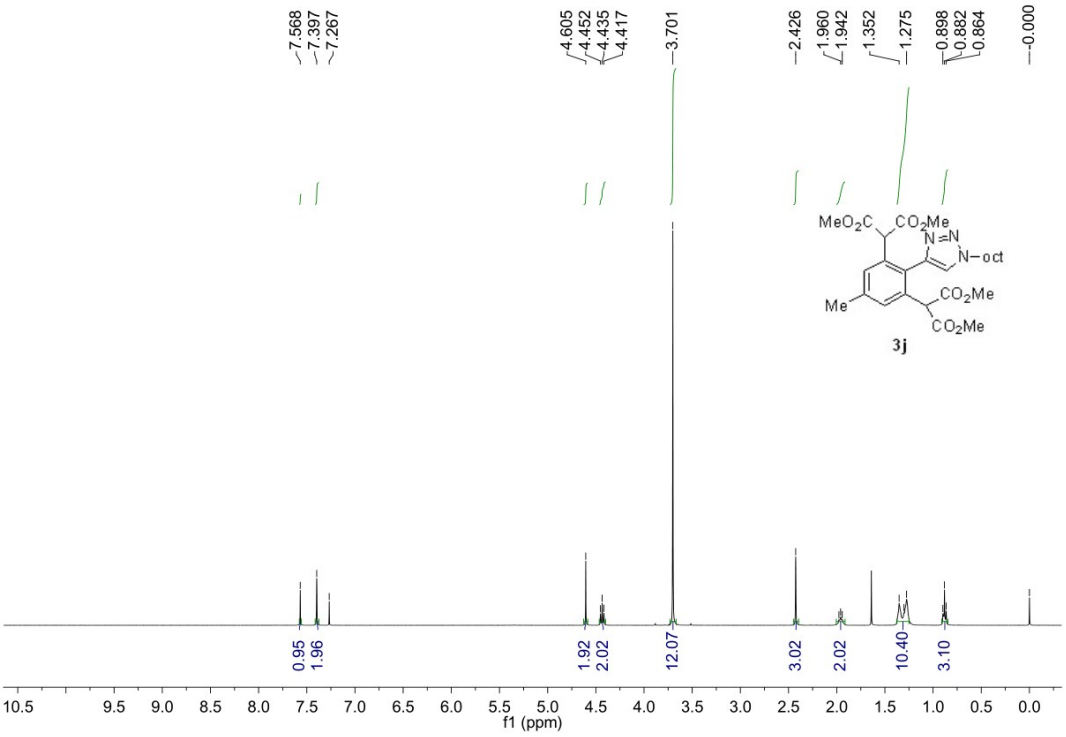
^{1}H NMR Spectrum of 3i in $CDCl_3$ at 400 MHz



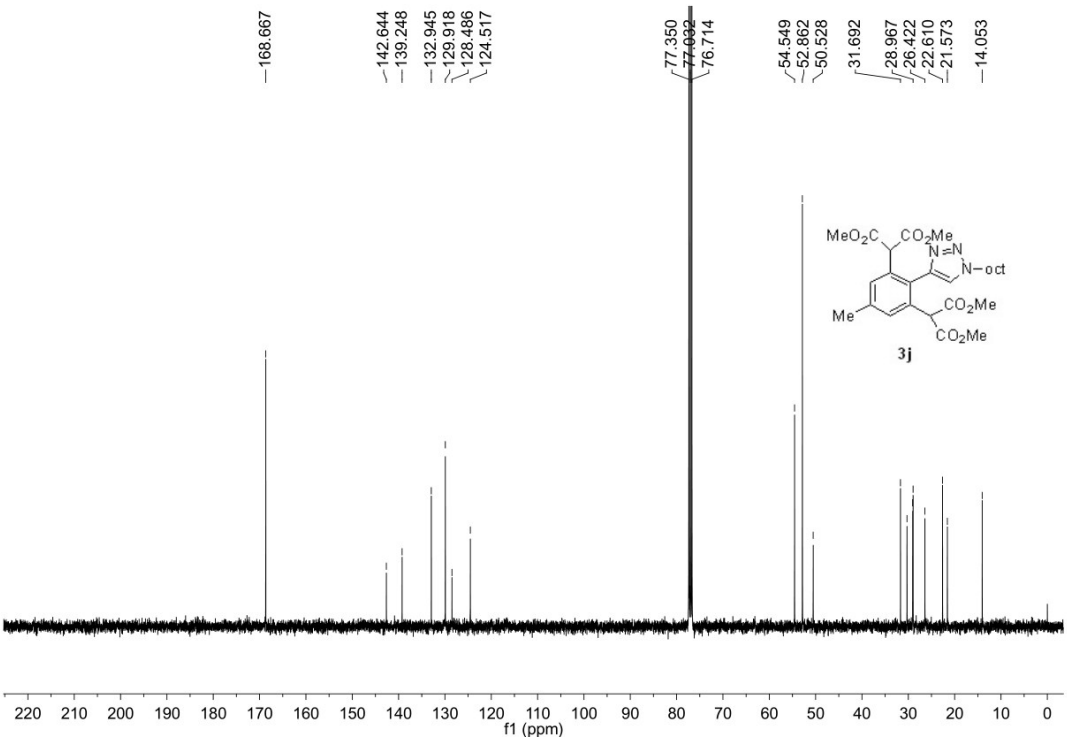
^{13}C NMR Spectrum of 3i in $CDCl_3$ at 100 MHz



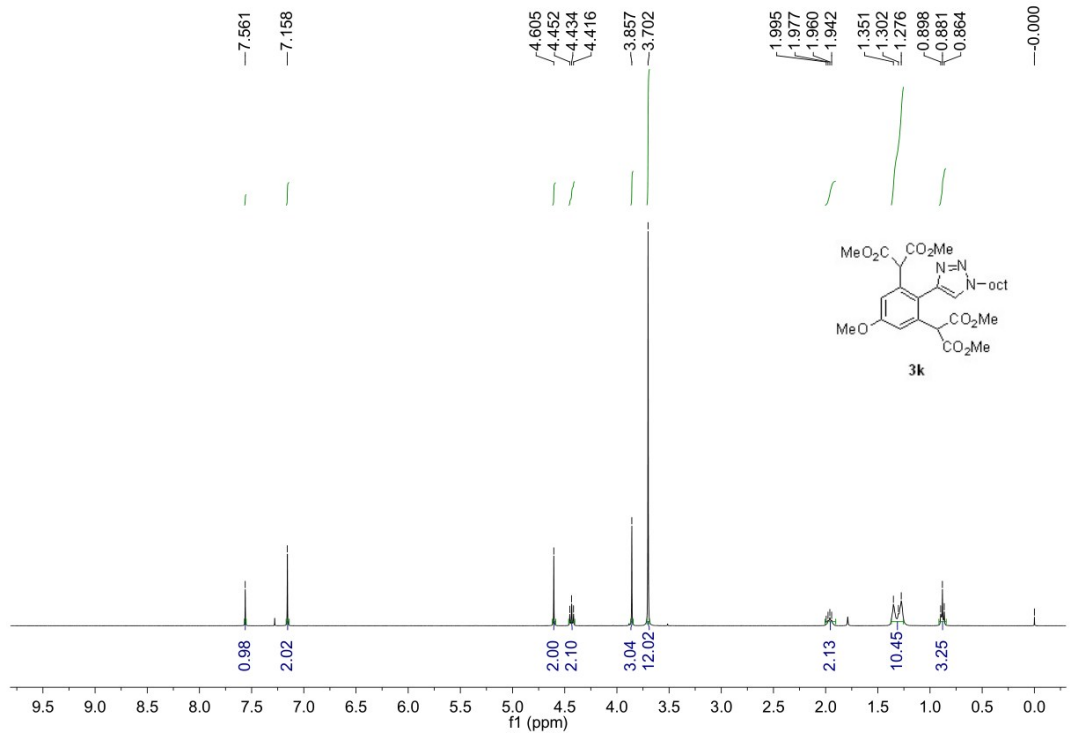
^{1}H NMR Spectrum of 3j in $CDCl_3$ at 400 MHz



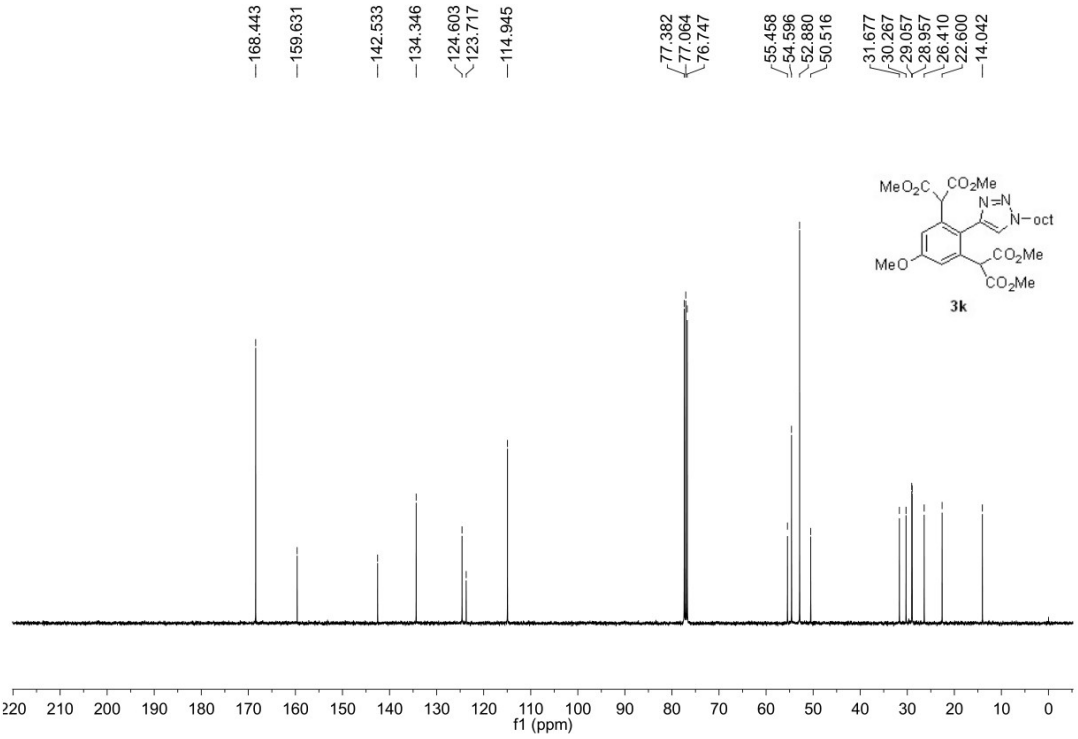
^{13}C NMR Spectrum of 3j in $CDCl_3$ at 100 MHz



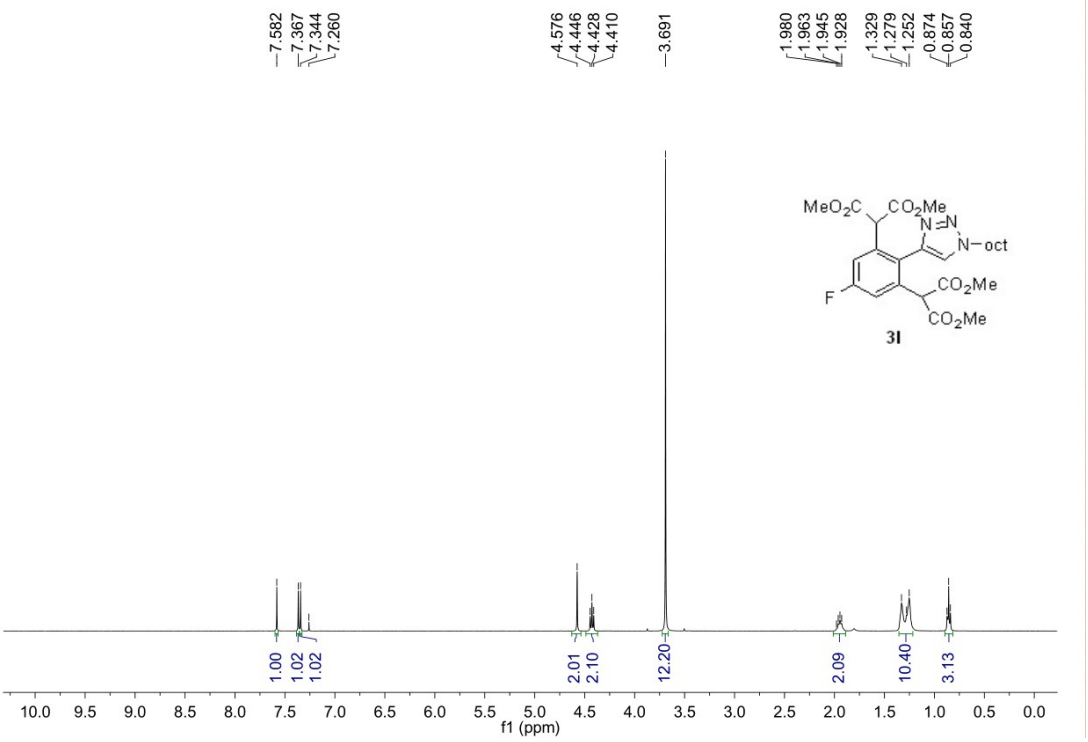
^{1}H NMR Spectrum of 3k in $CDCl_3$ at 400 MHz



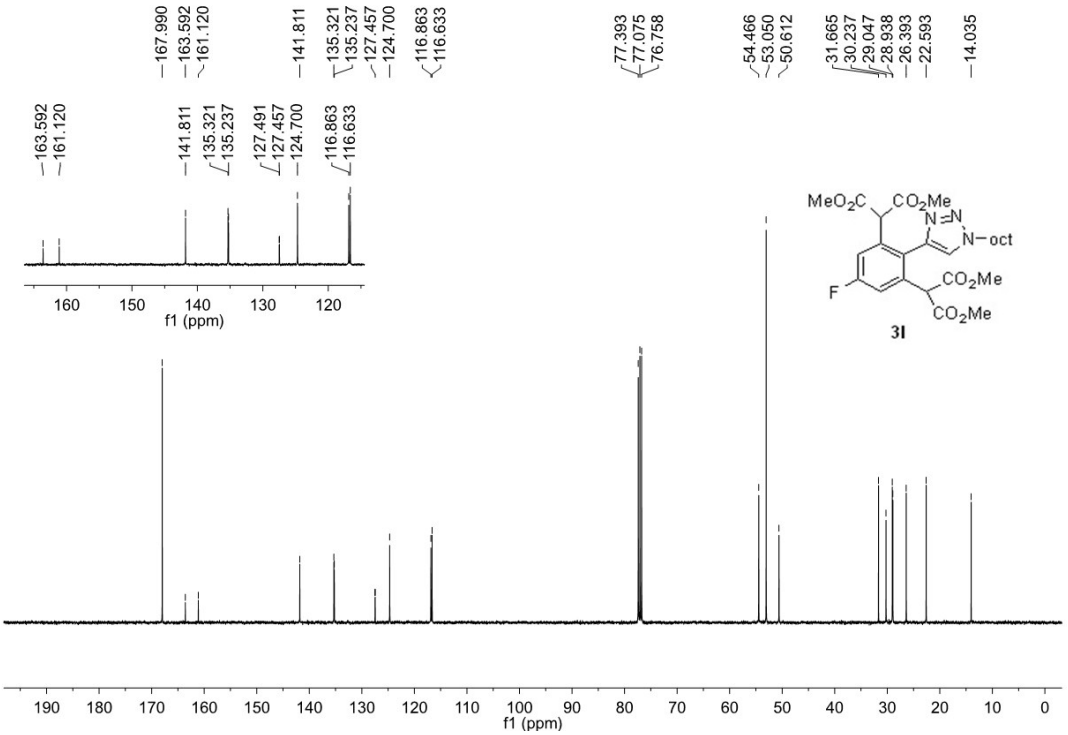
^{13}C NMR Spectrum of 3k in $CDCl_3$ at 100 MHz



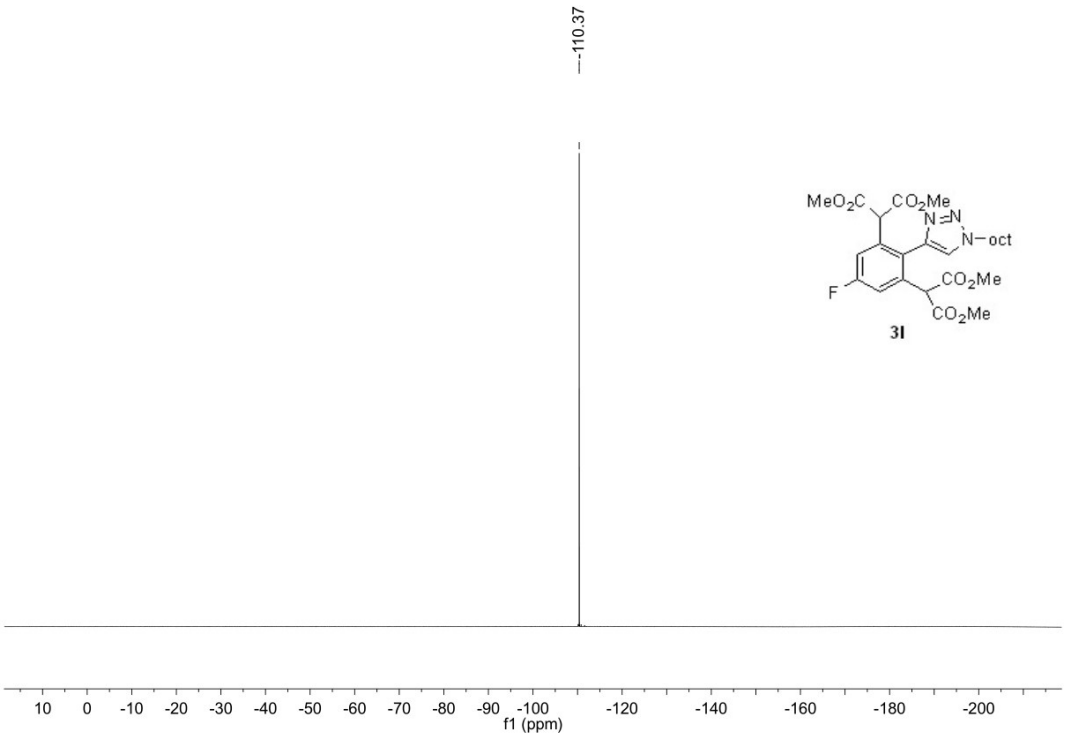
^{1}H NMR Spectrum of 3l in $CDCl_3$ at 400 MHz



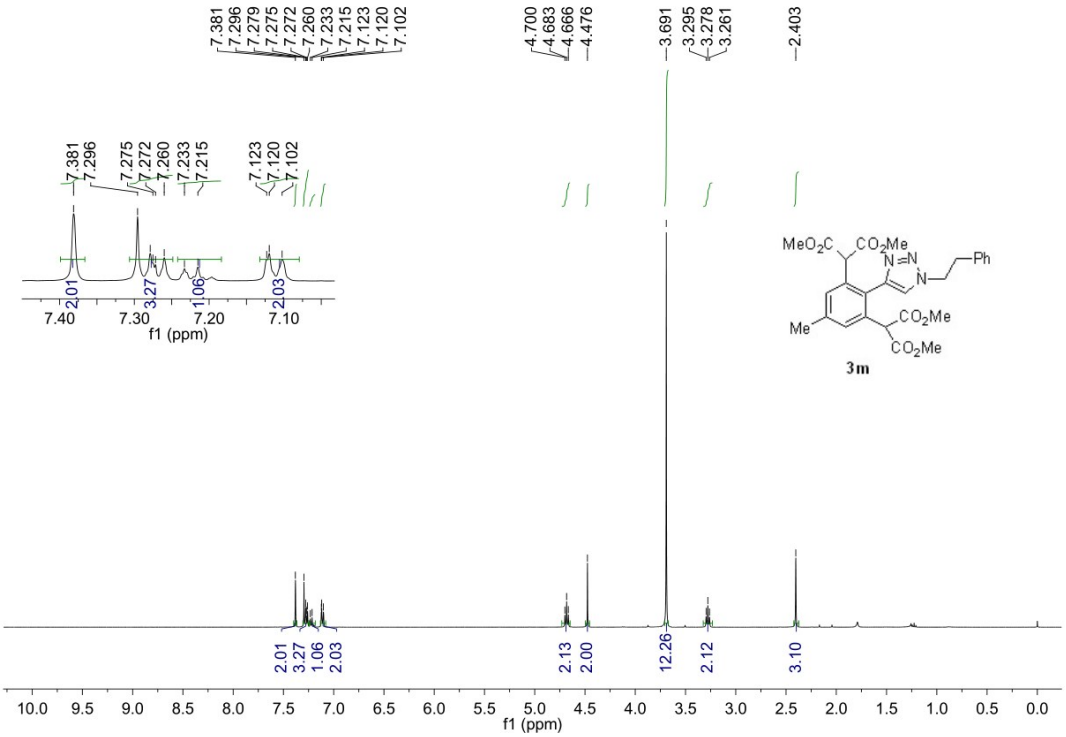
^{13}C NMR Spectrum of 3l in $CDCl_3$ at 100 MHz



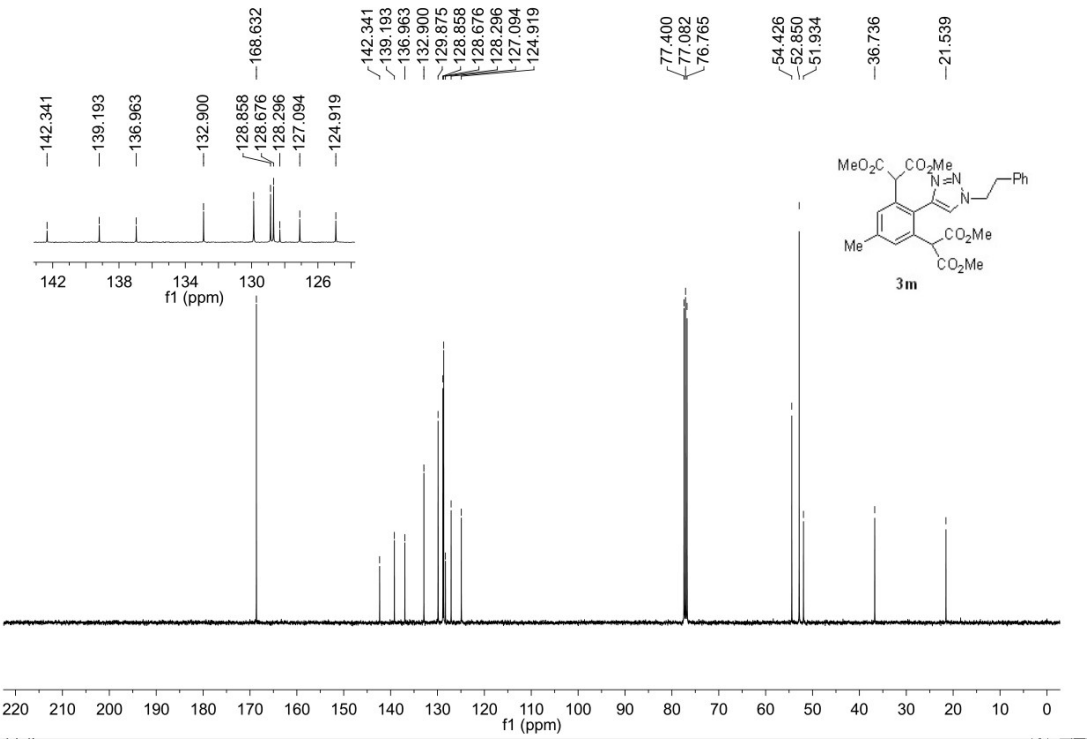
^{19}F NMR Spectrum of 3l in $CDCl_3$ at 376 MHz



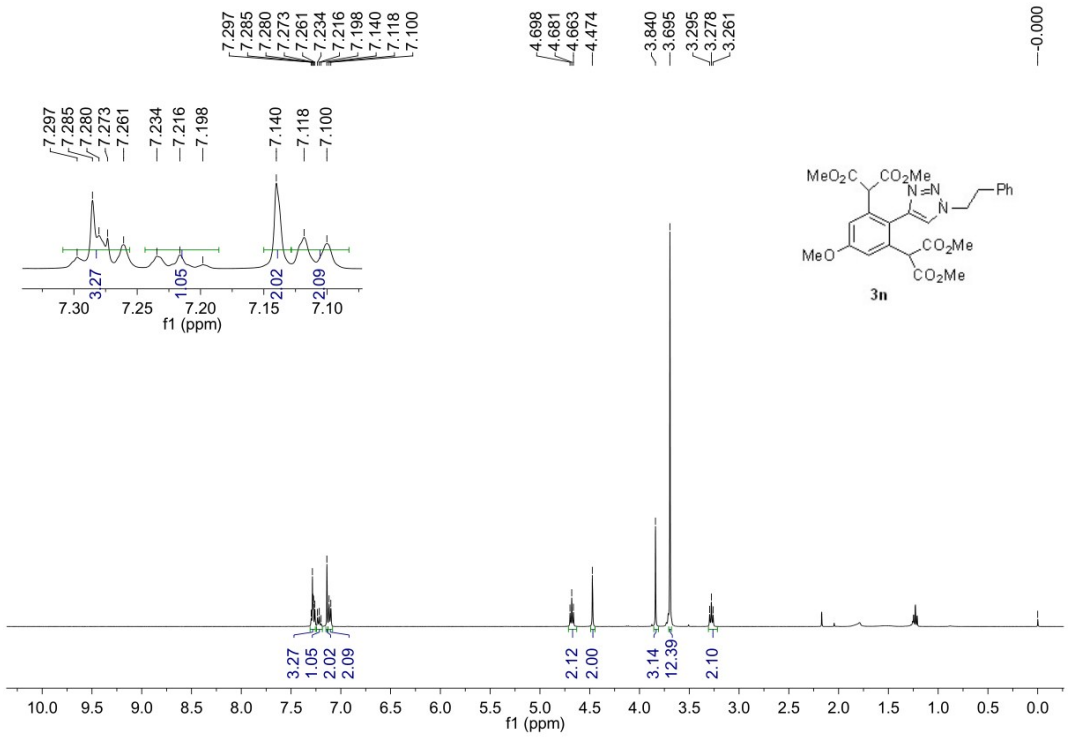
^{1}H NMR Spectrum of 3m in $CDCl_3$ at 400 MHz



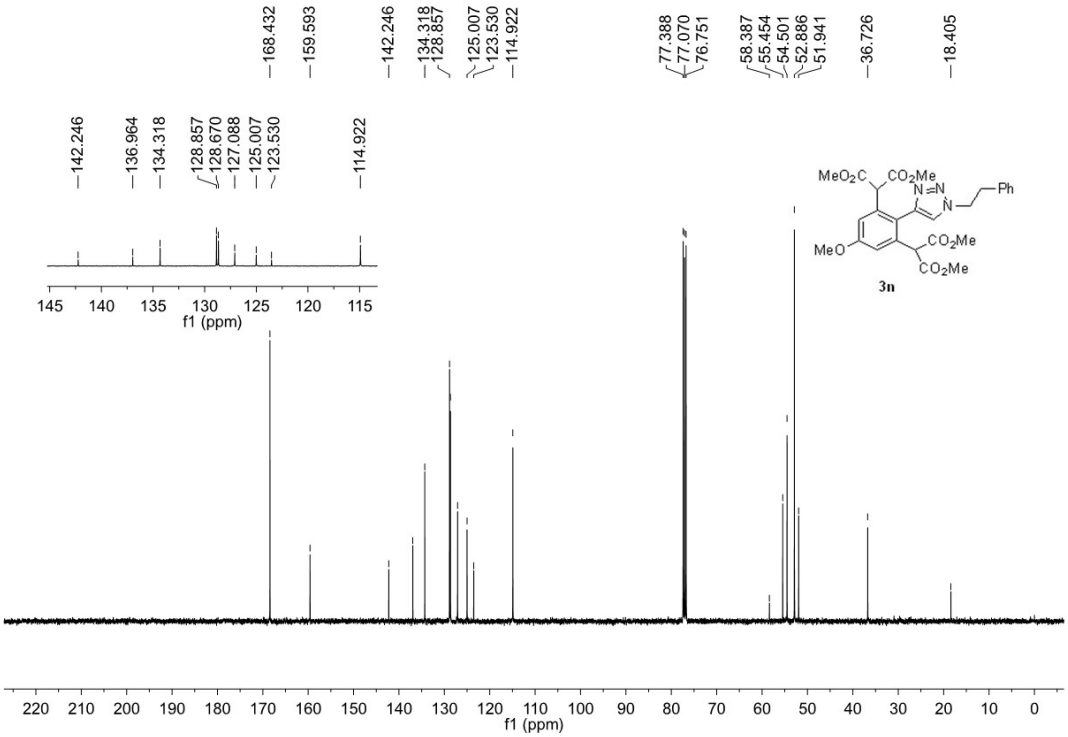
^{13}C NMR Spectrum of 3m in $CDCl_3$ at 100 MHz



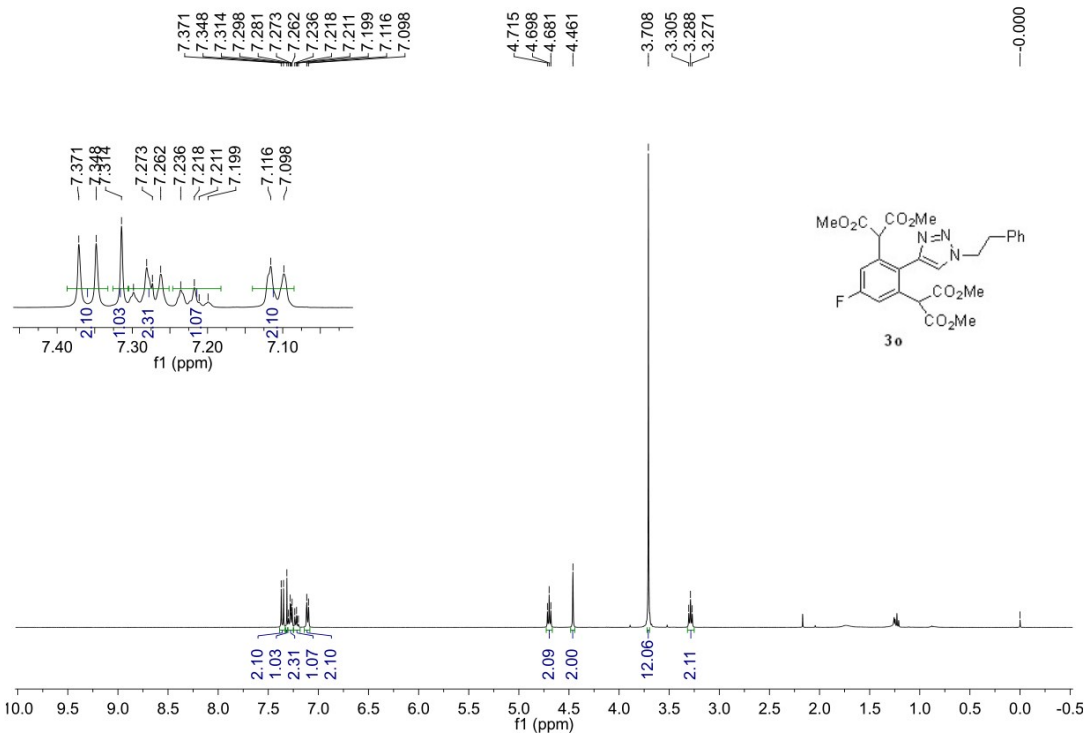
^{1}H NMR Spectrum of 3n in $CDCl_3$ at 400 MHz



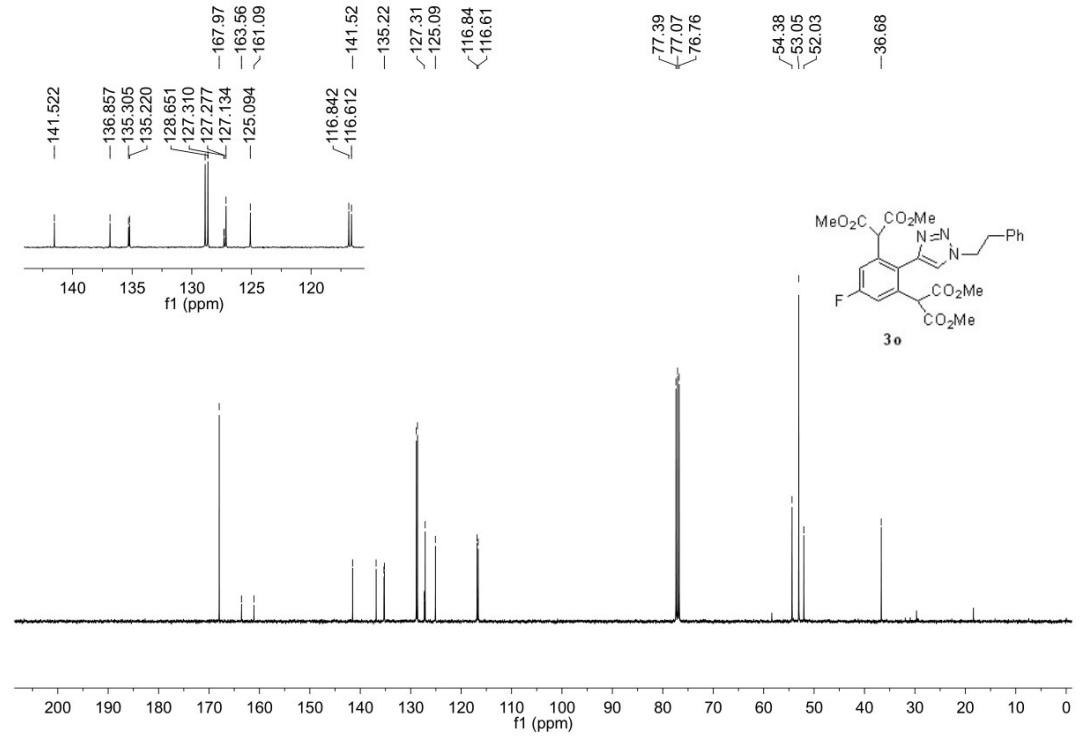
^{13}C NMR Spectrum of 3n in $CDCl_3$ at 100 MHz



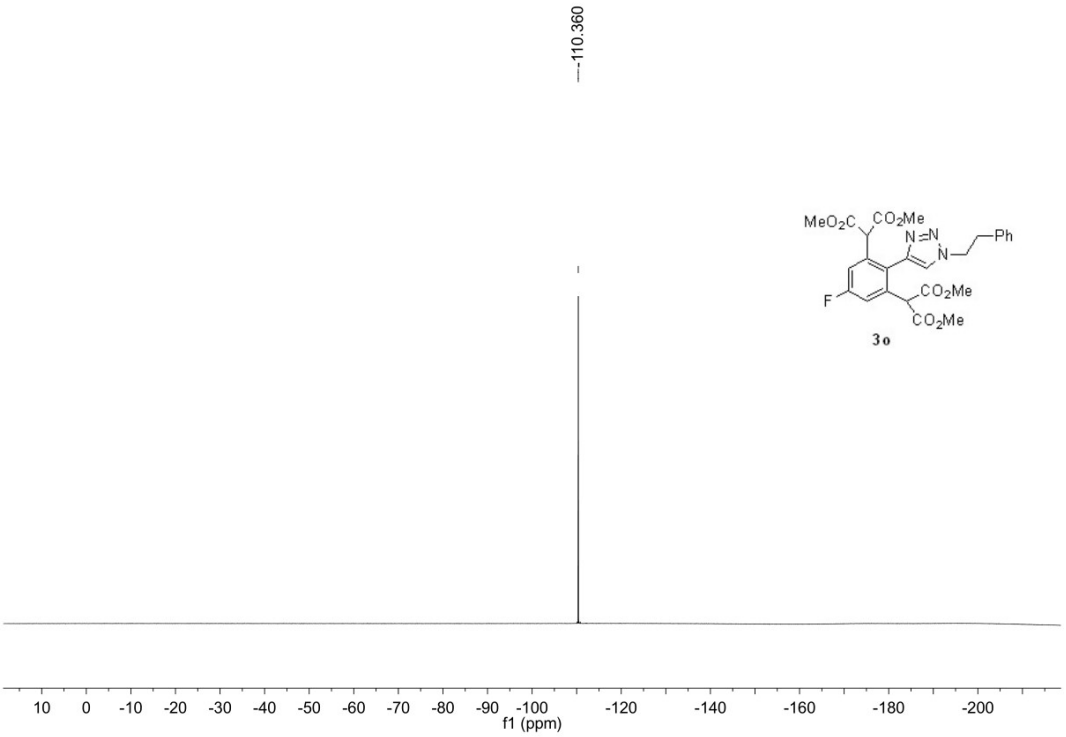
^{1}H NMR Spectrum of 3o in $CDCl_3$ at 400 MHz



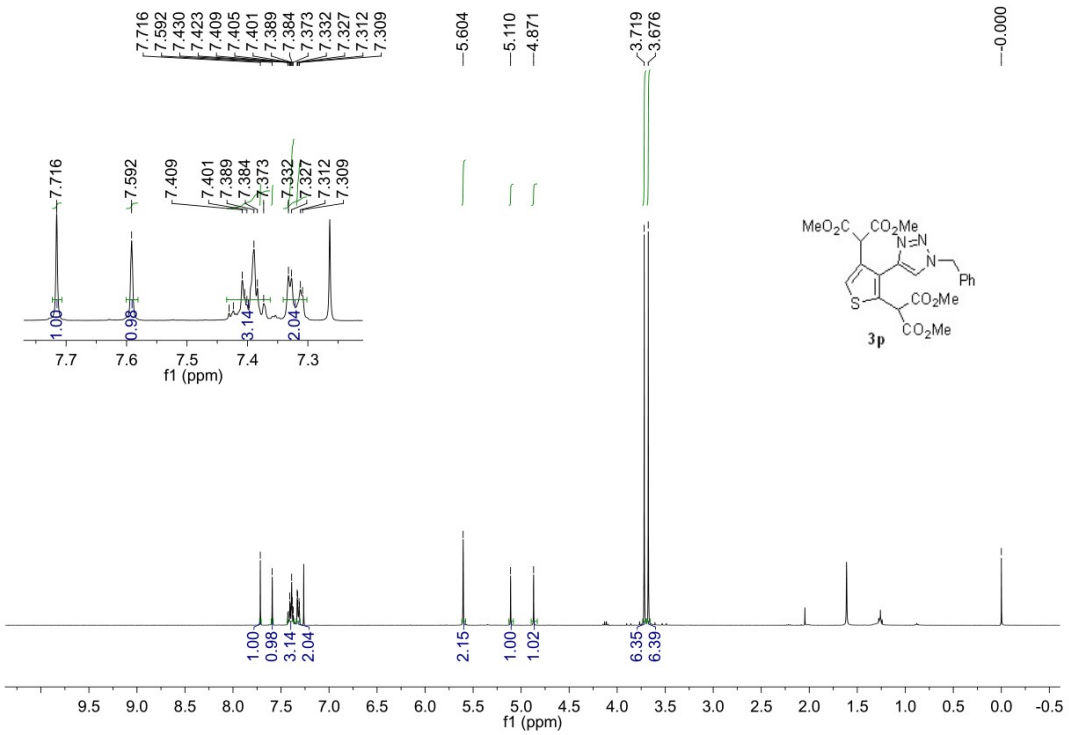
^{13}C NMR Spectrum of 3o in $CDCl_3$ at 100 MHz



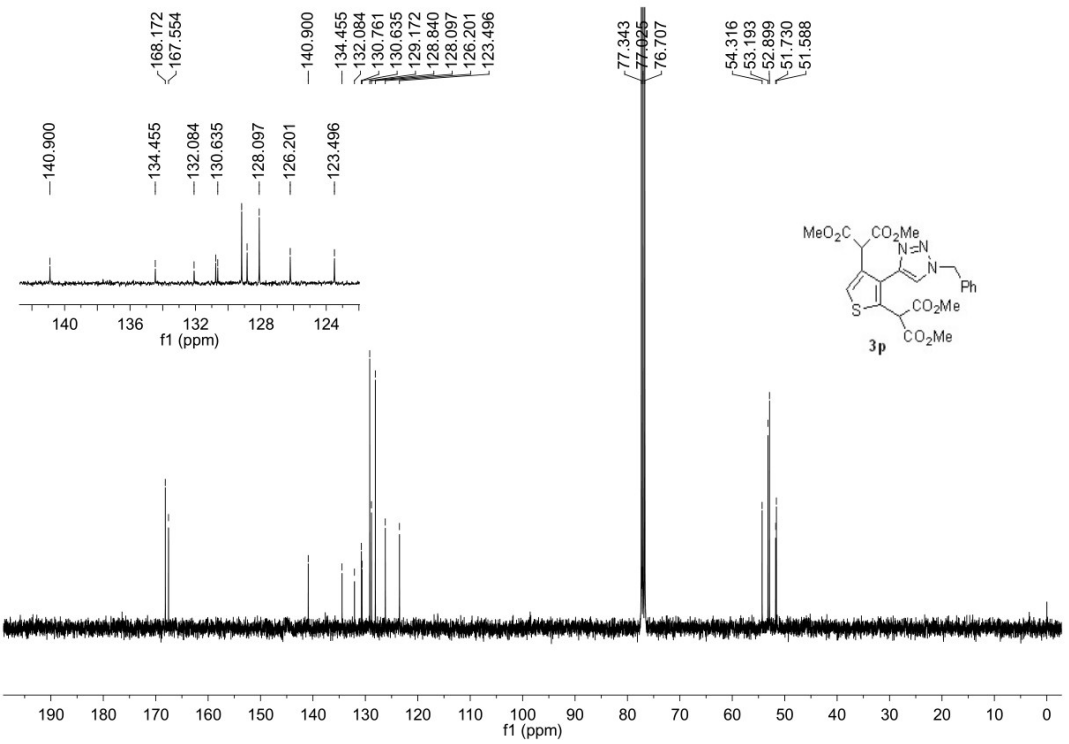
^{19}F NMR Spectrum of 3o in $CDCl_3$ at 376 MHz



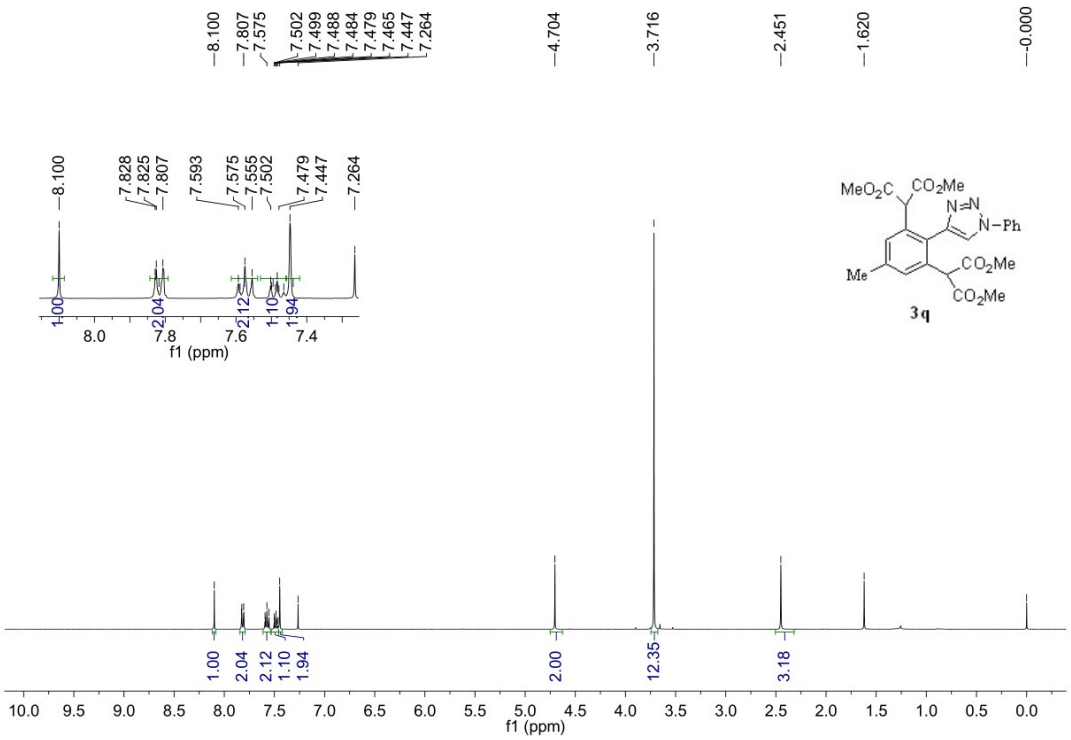
^{1}H NMR Spectrum of 3p in $CDCl_3$ at 400 MHz



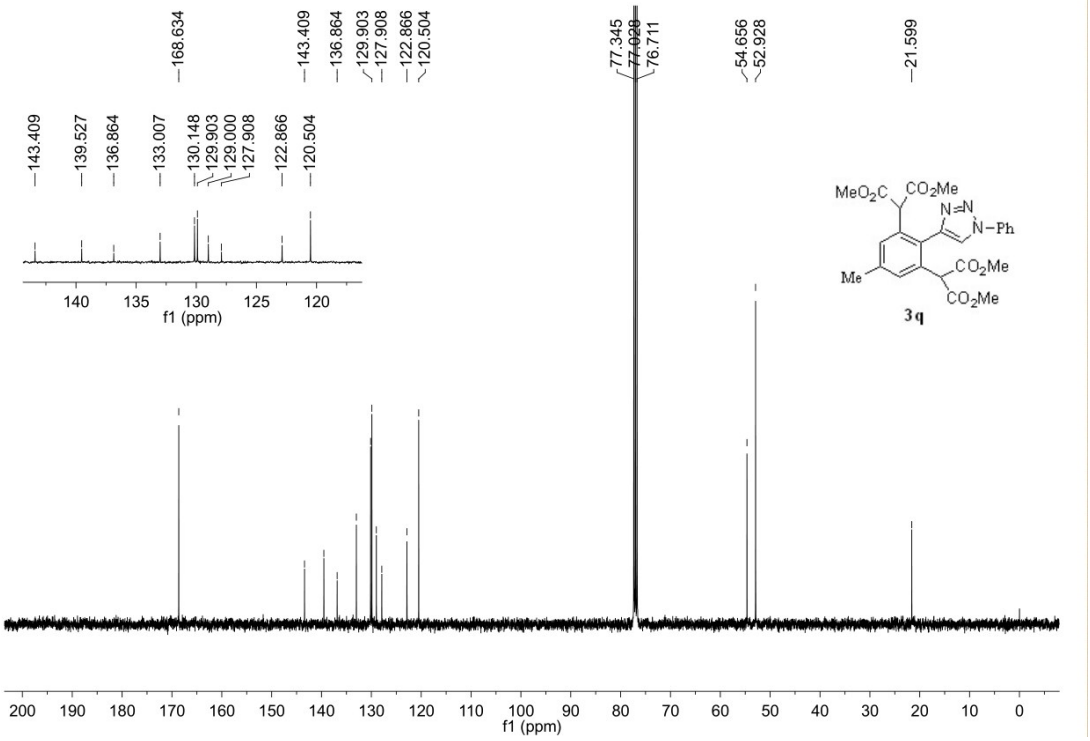
^{13}C NMR Spectrum of 3p in $CDCl_3$ at 100 MHz



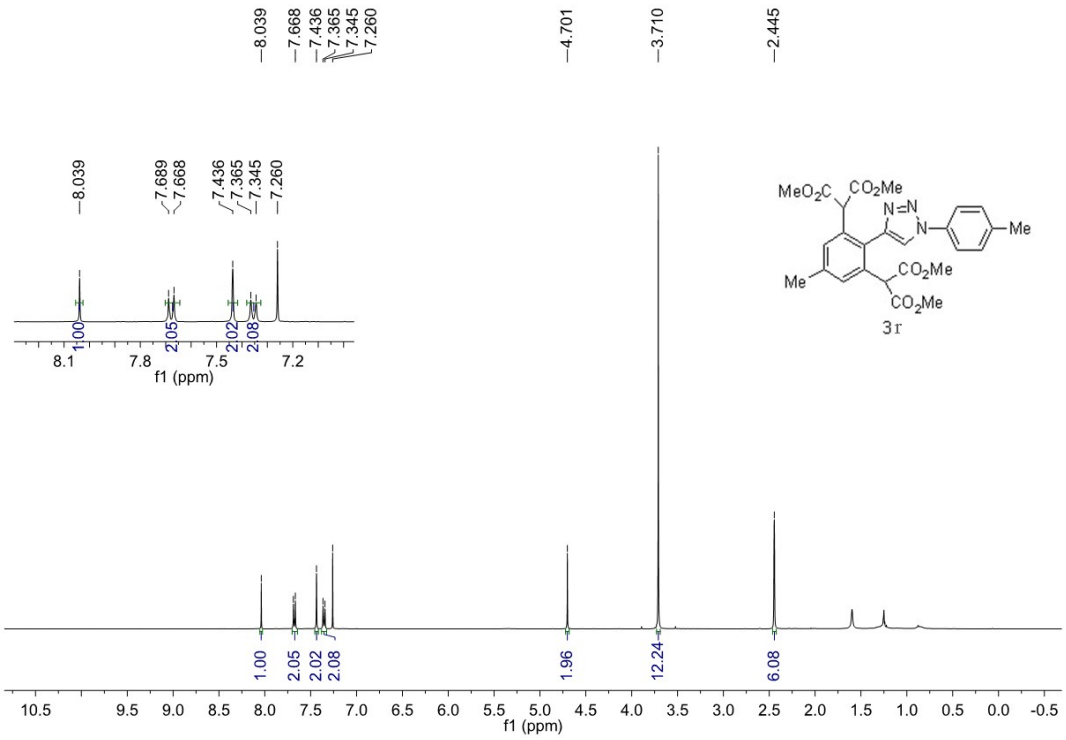
^{1}H NMR Spectrum of 3q in $CDCl_3$ at 400 MHz



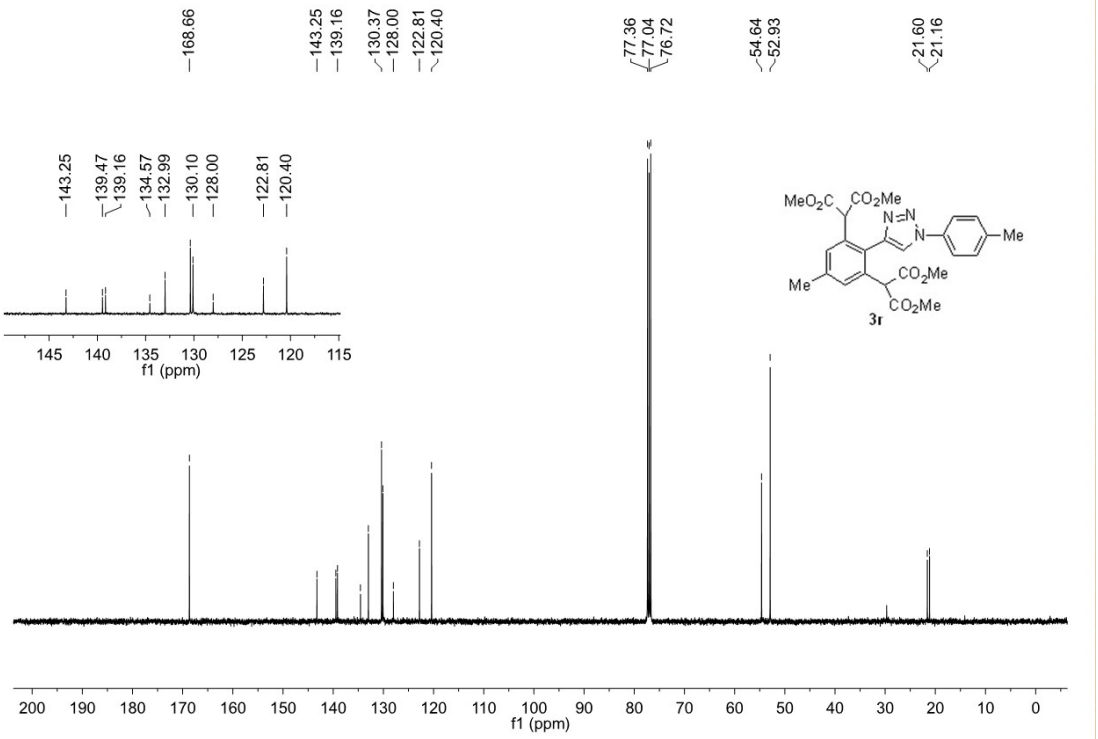
^{13}C NMR Spectrum of 3q in $CDCl_3$ at 100 MHz



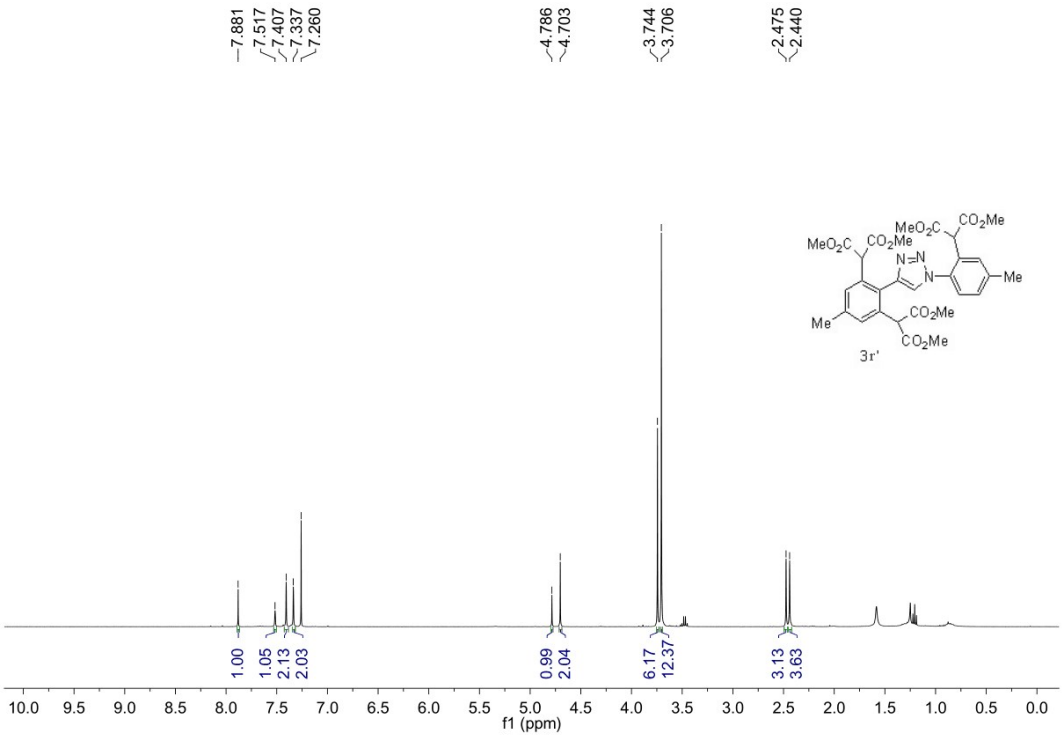
^{1}H NMR Spectrum of 3r in $CDCl_3$ at 400 MHz



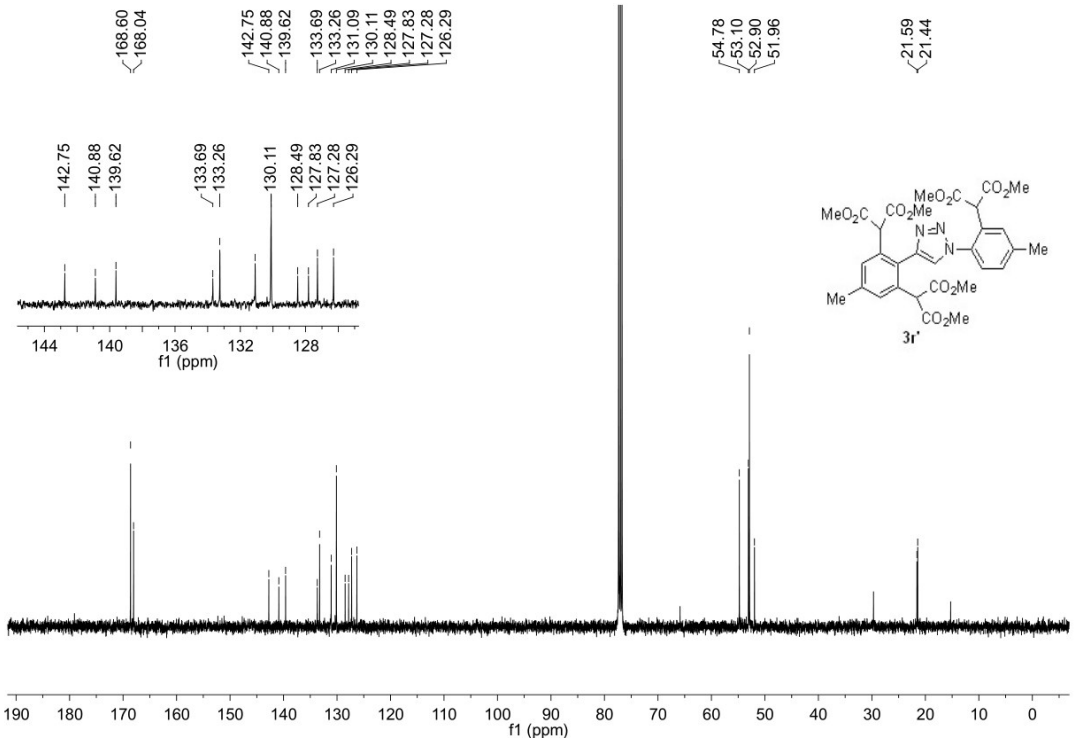
^{13}C NMR Spectrum of 3r in $CDCl_3$ at 100 MHz



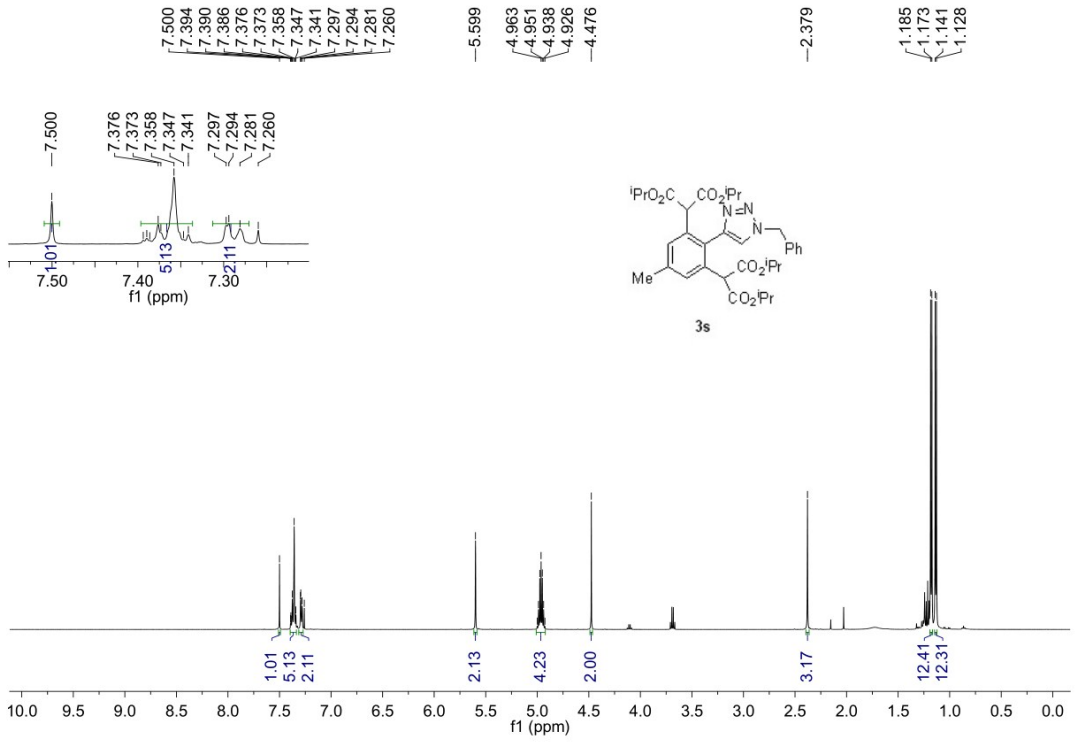
^{1}H NMR Spectrum of 3r' in $CDCl_3$ at 400 MHz



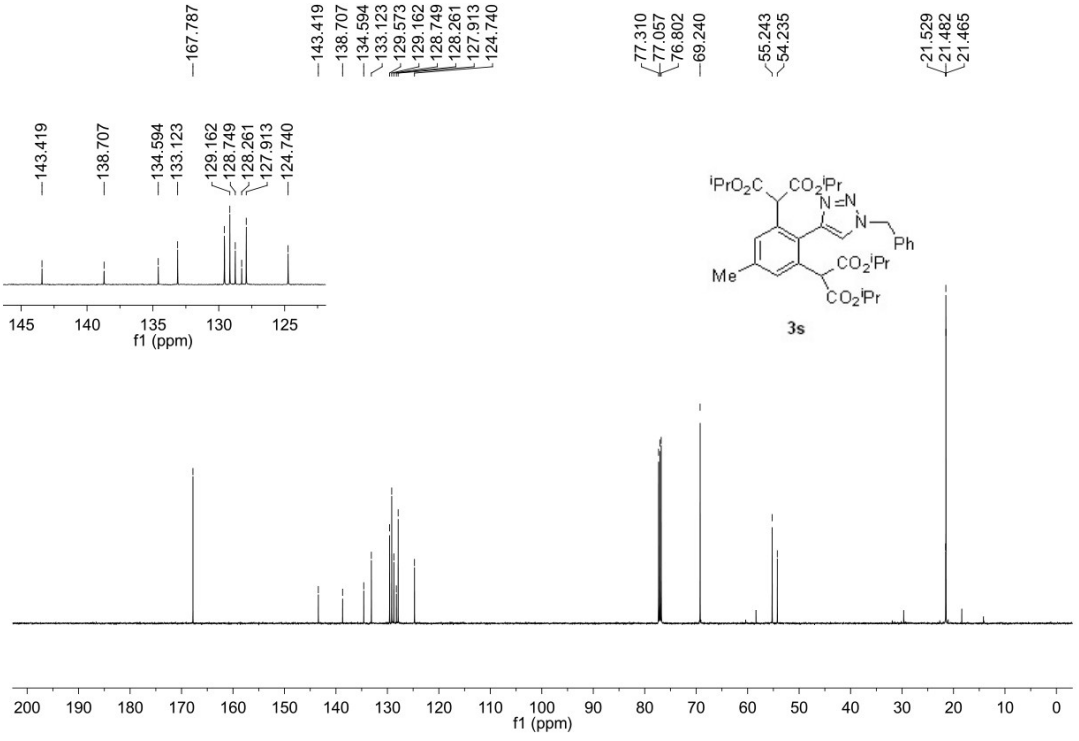
^{13}C NMR Spectrum of 3r' in $CDCl_3$ at 100 MHz



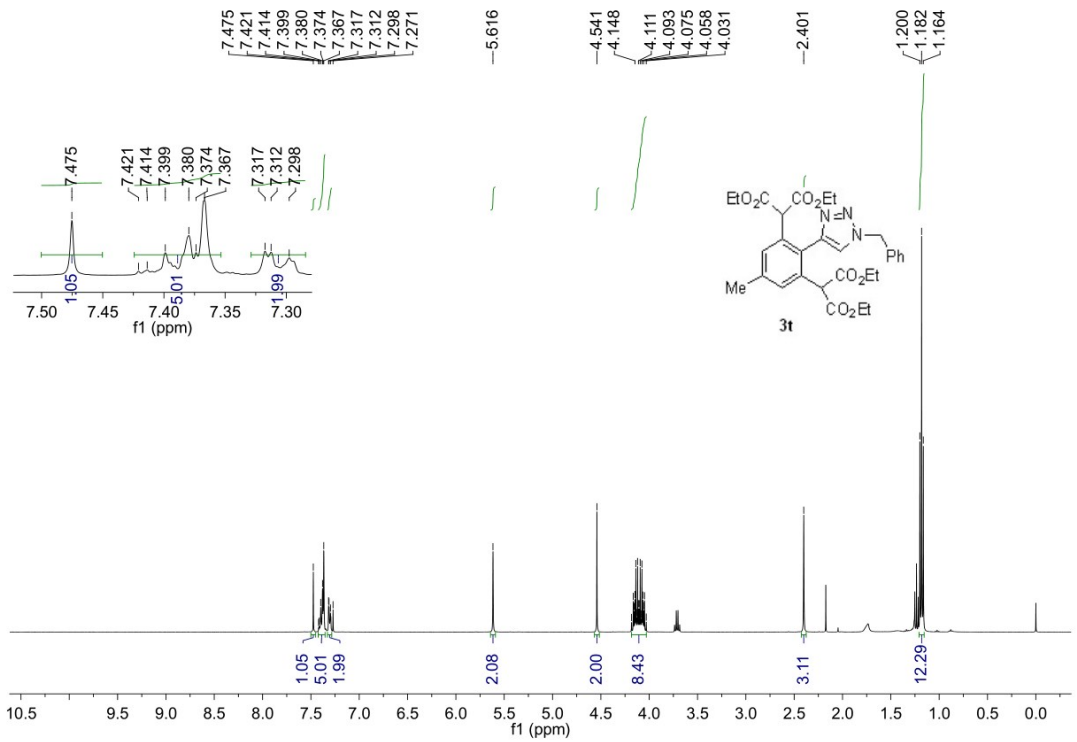
^{1}H NMR Spectrum of 3s in $CDCl_3$ at 400 MHz



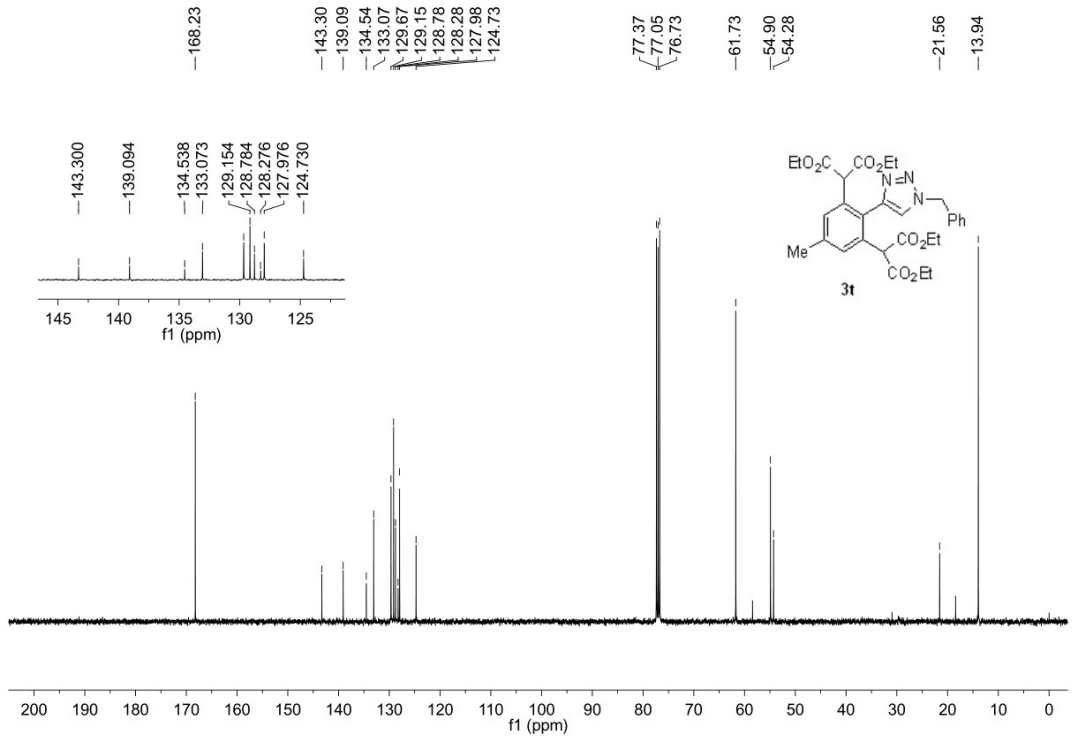
^{13}C NMR Spectrum of 3s in $CDCl_3$ at 100 MHz



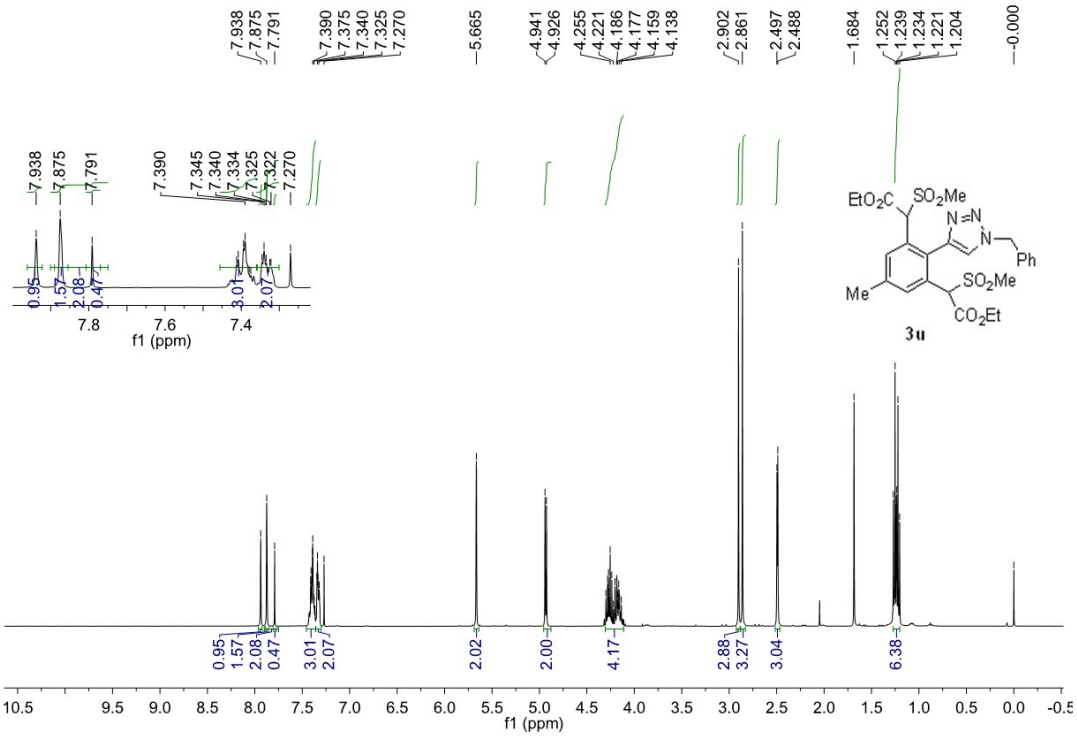
^{1}H NMR Spectrum of 3t in $CDCl_3$ at 400 MHz



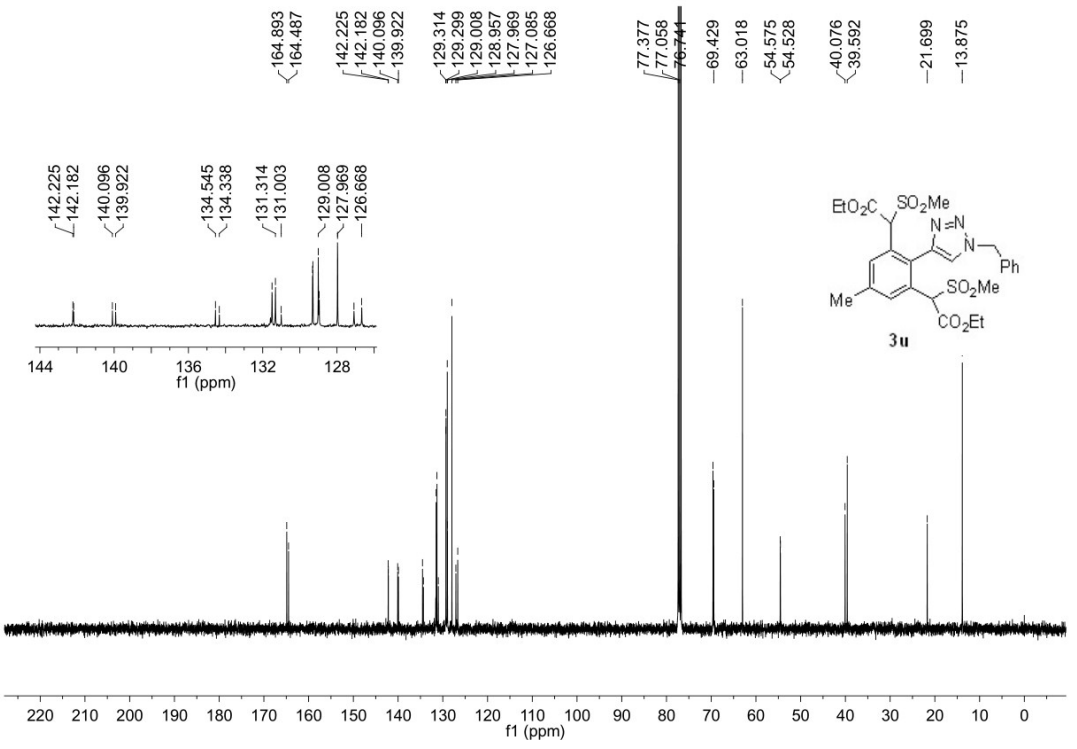
^{13}C NMR Spectrum of 3t in $CDCl_3$ at 100 MHz



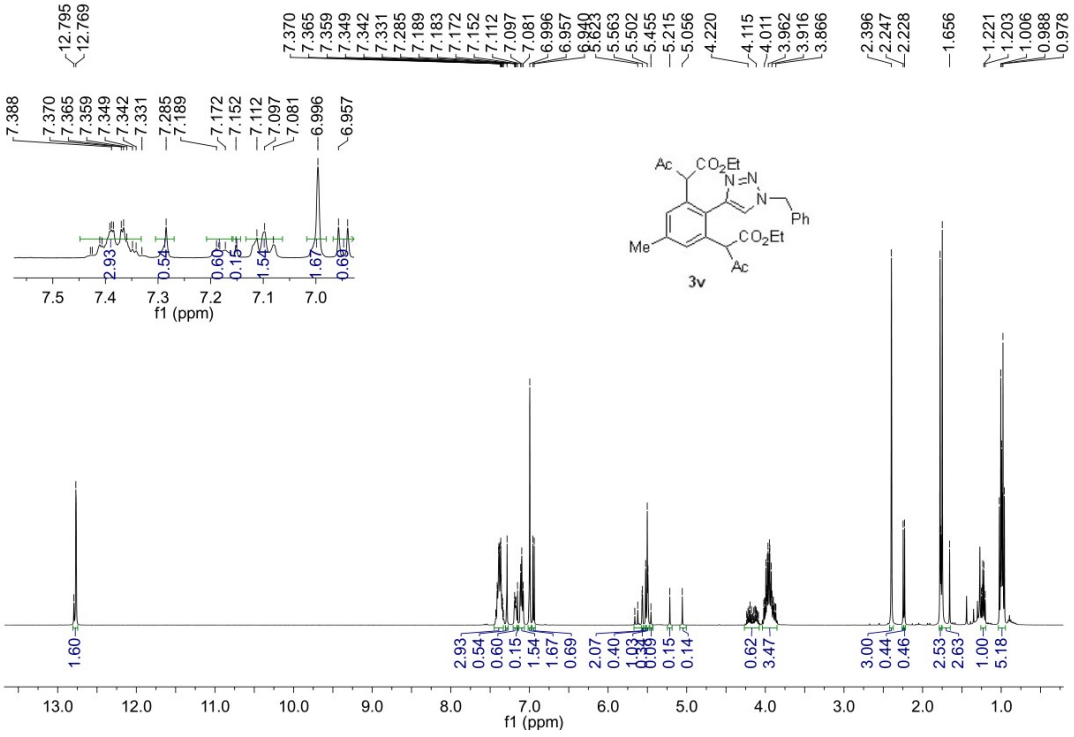
^{1}H NMR Spectrum of 3u in $CDCl_3$ at 400 MHz



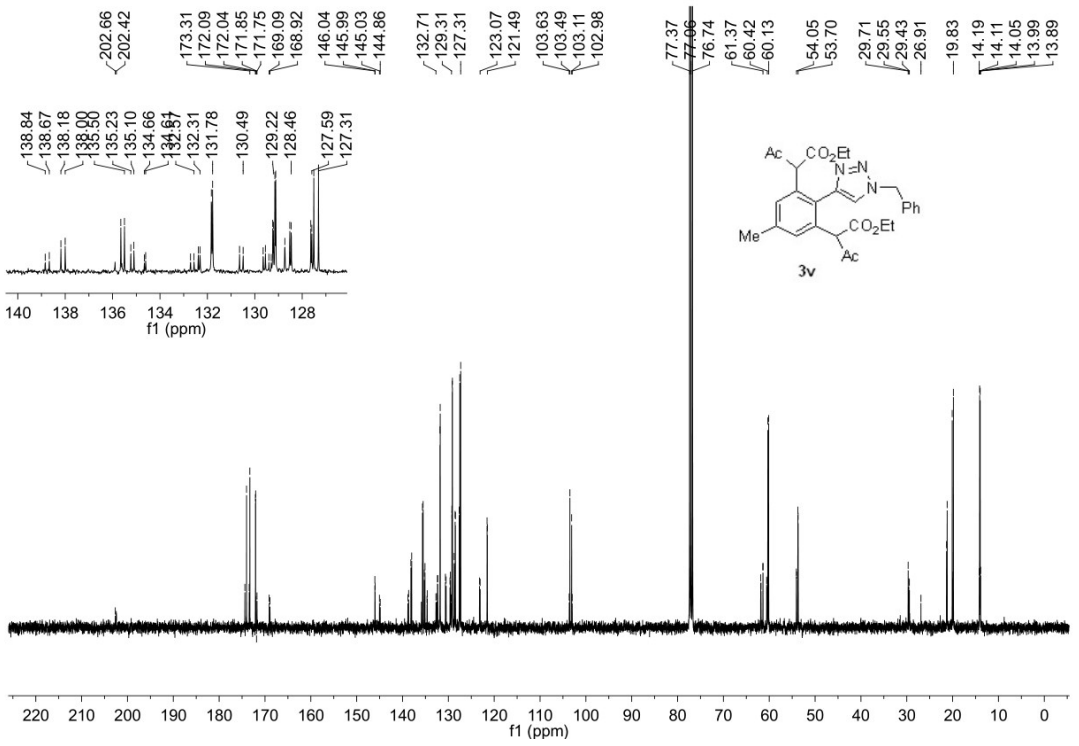
^{13}C NMR Spectrum of 3u in $CDCl_3$ at 100 MHz



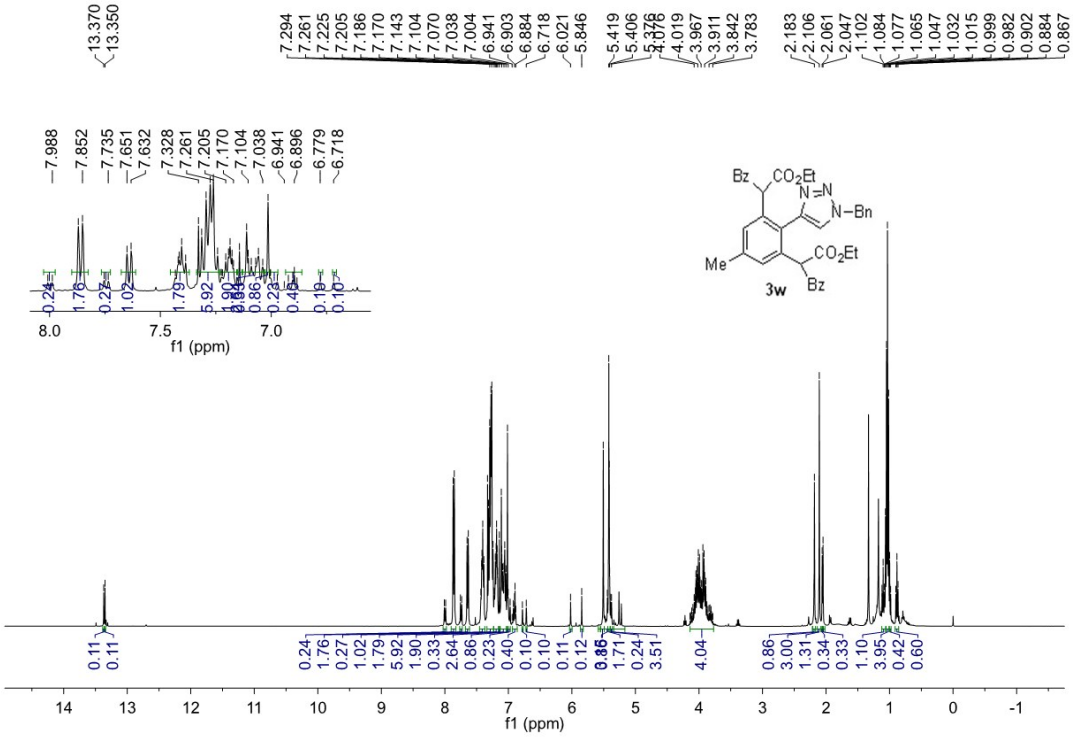
^{1}H NMR Spectrum of 3v in $CDCl_3$ at 400 MHz



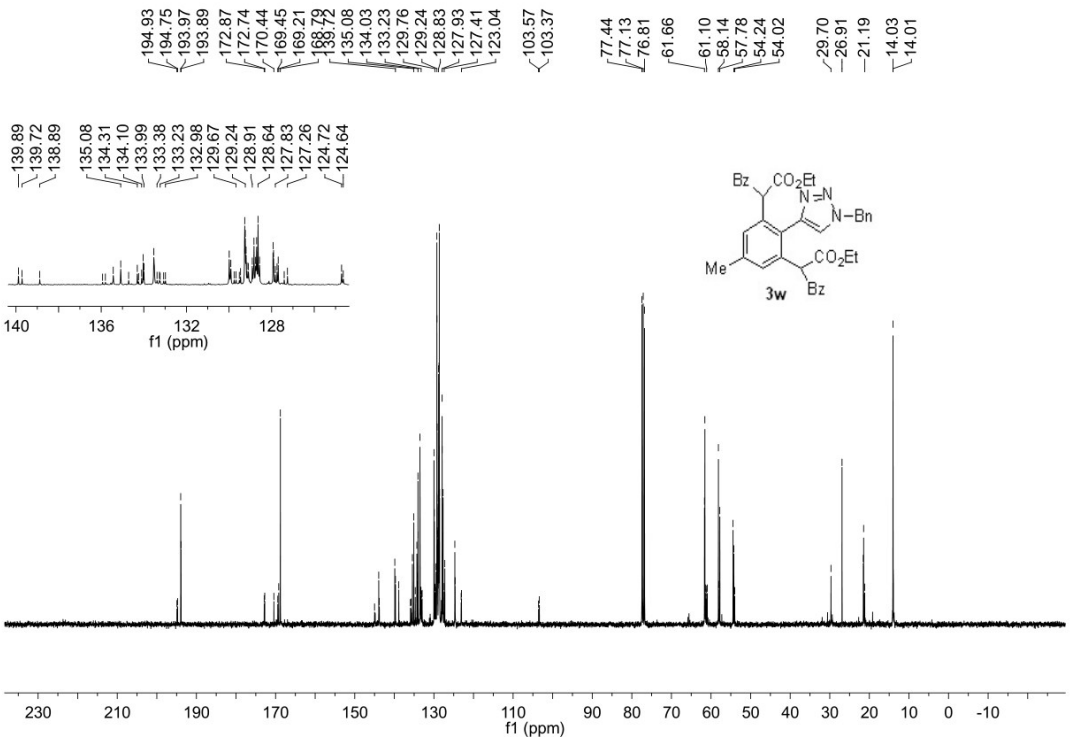
^{13}C NMR Spectrum of 3v in $CDCl_3$ at 100 MHz



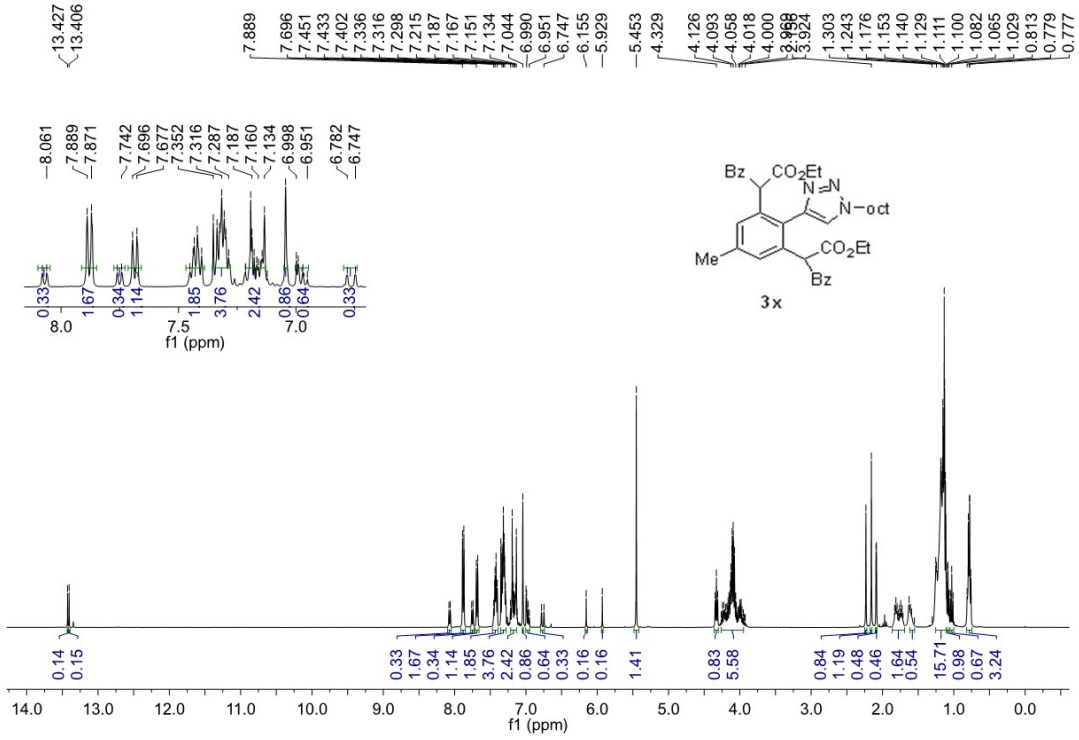
^{1}H NMR Spectrum of 3w in $CDCl_3$ at 400 MHz



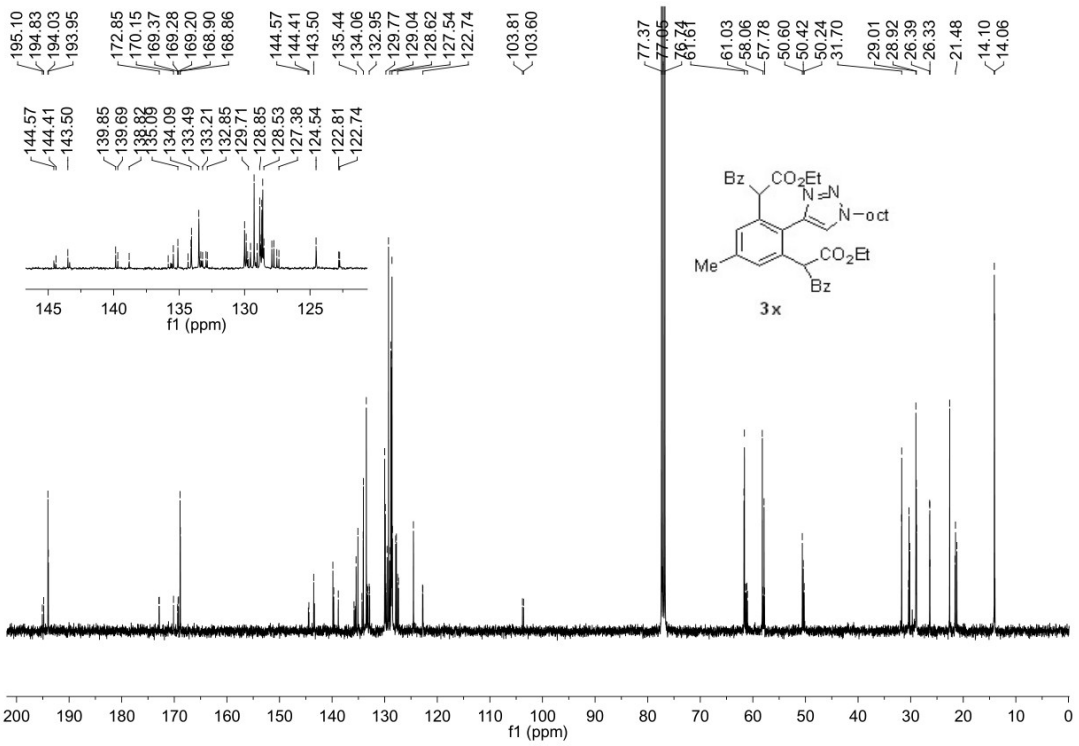
^{13}C NMR Spectrum of 3w in $CDCl_3$ at 100 MHz



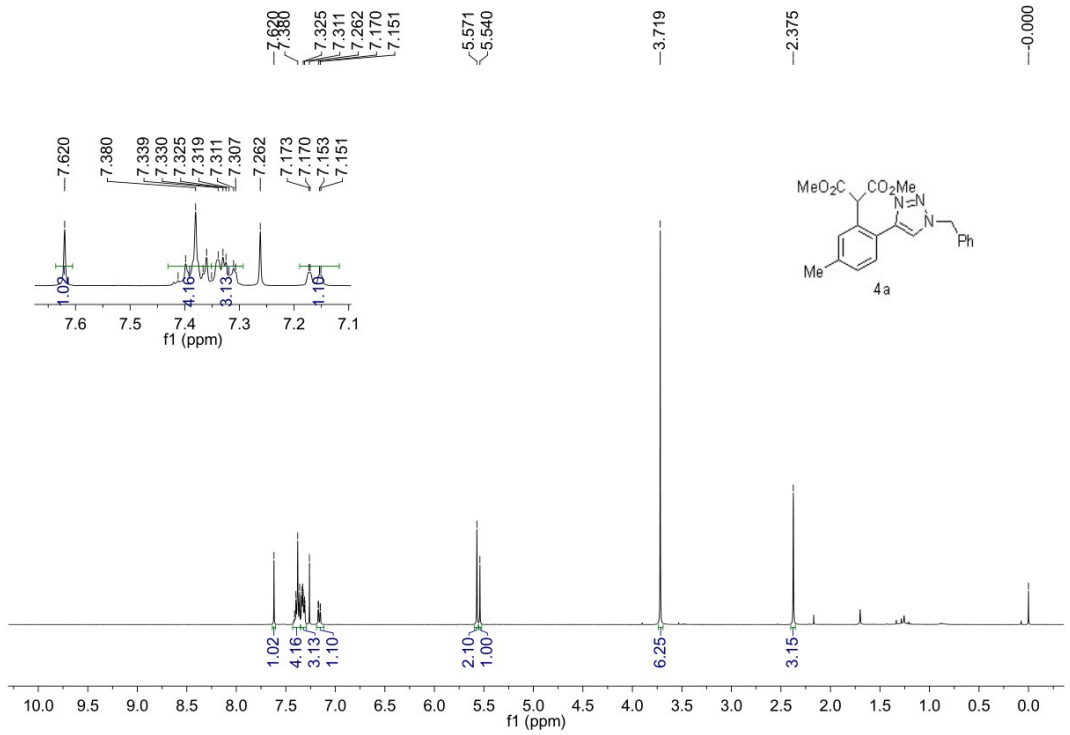
^{1}H NMR Spectrum of 3x in $CDCl_3$ at 400 MHz



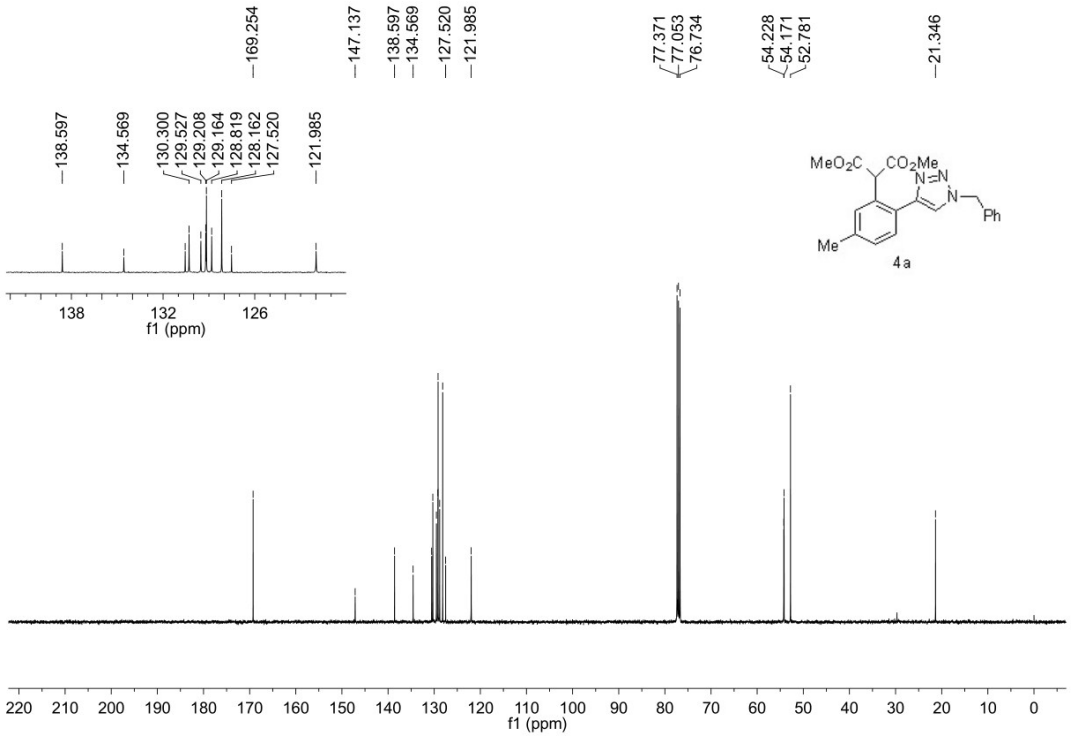
^{13}C NMR Spectrum of 3x in $CDCl_3$ at 100 MHz



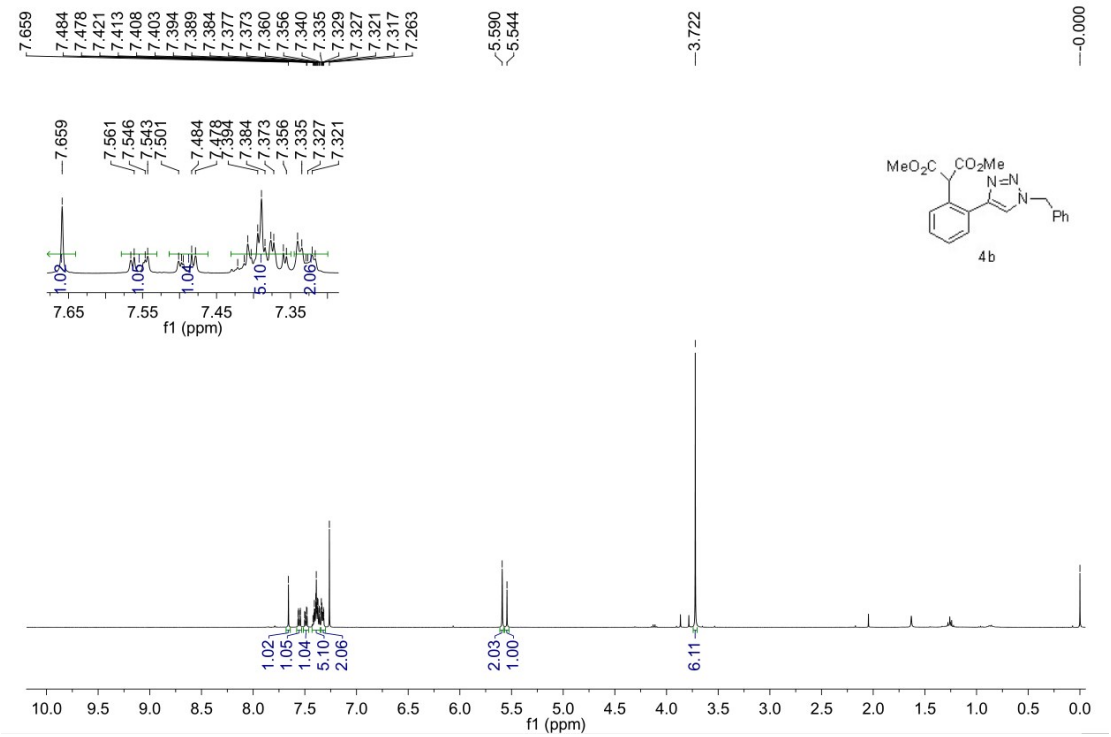
^{1}H NMR Spectrum of 4a in $CDCl_3$ at 400 MHz



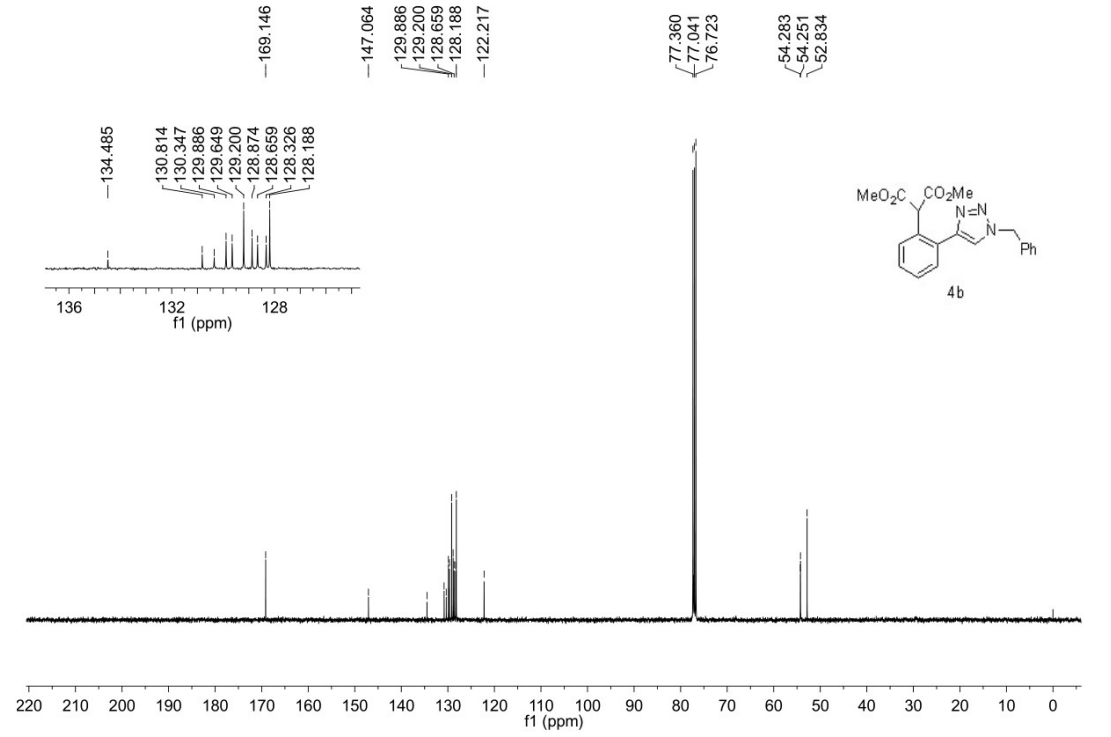
^{13}C NMR Spectrum of 4a in $CDCl_3$ at 100 MHz



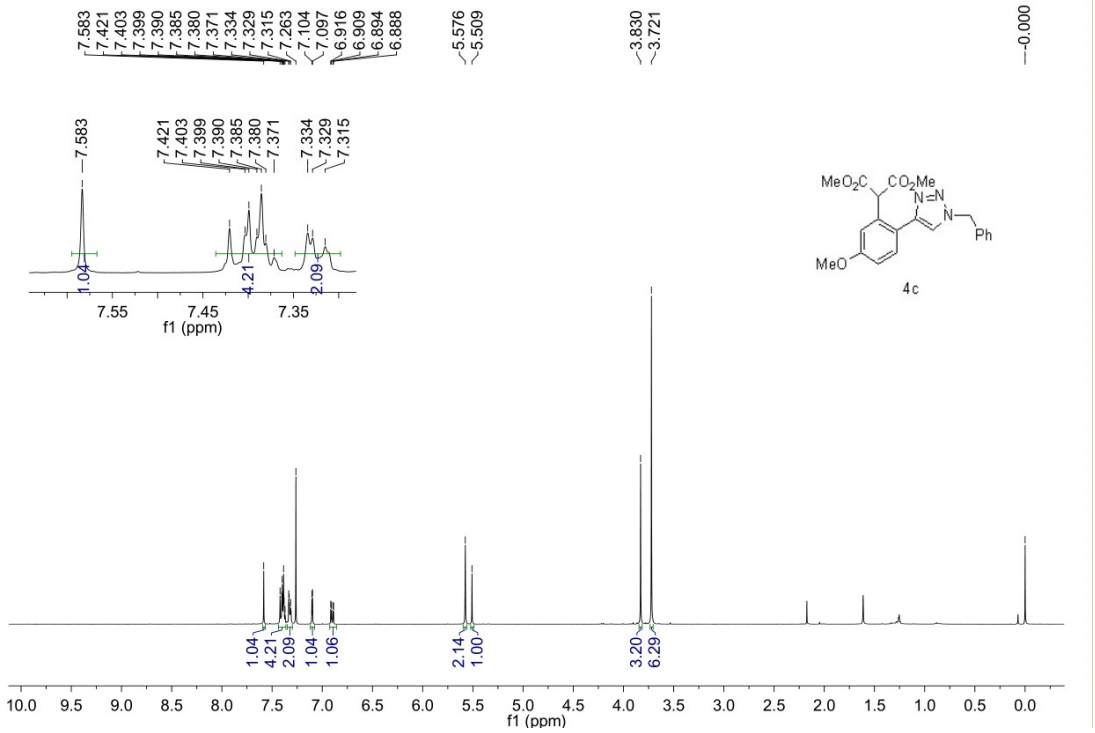
^{1}H NMR Spectrum of 4b in $CDCl_3$ at 400 MHz



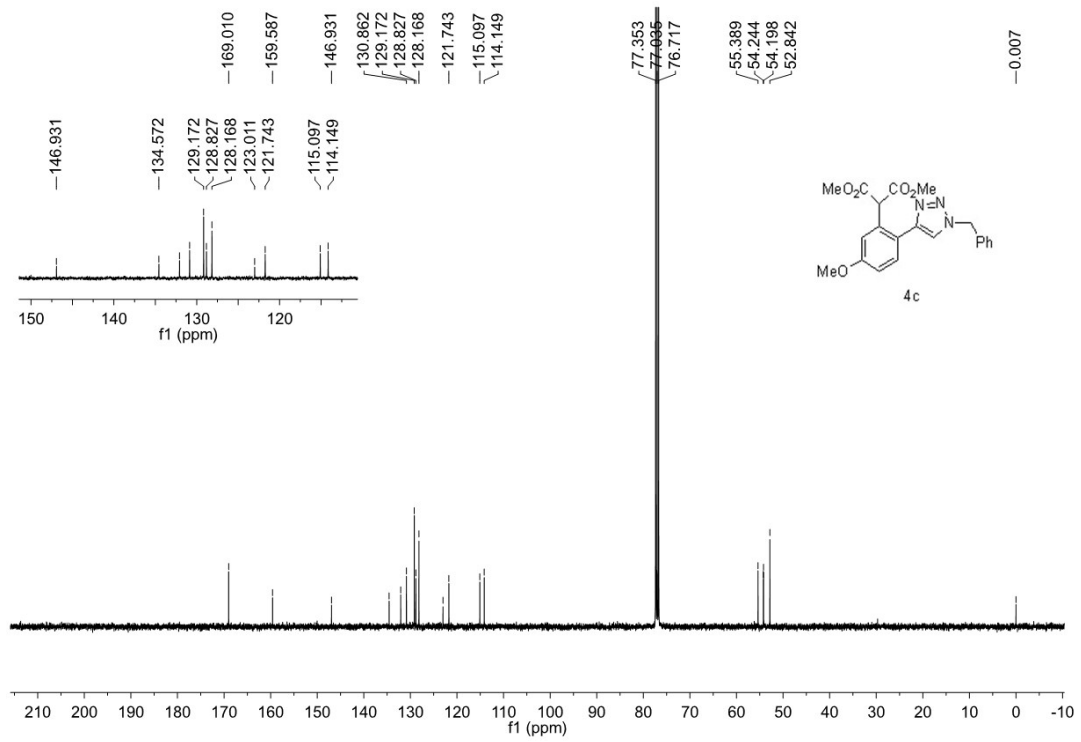
^{13}C NMR Spectrum of 4b in $CDCl_3$ at 100 MHz



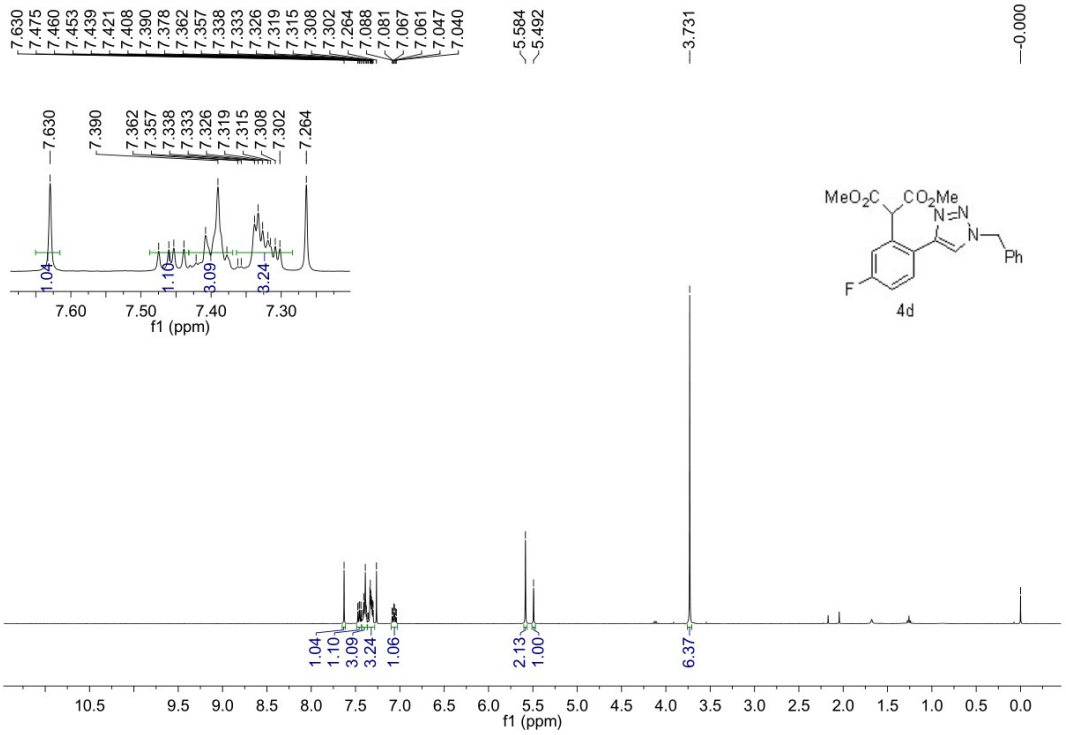
^{1}H NMR Spectrum of 4c in $CDCl_3$ at 400 MHz



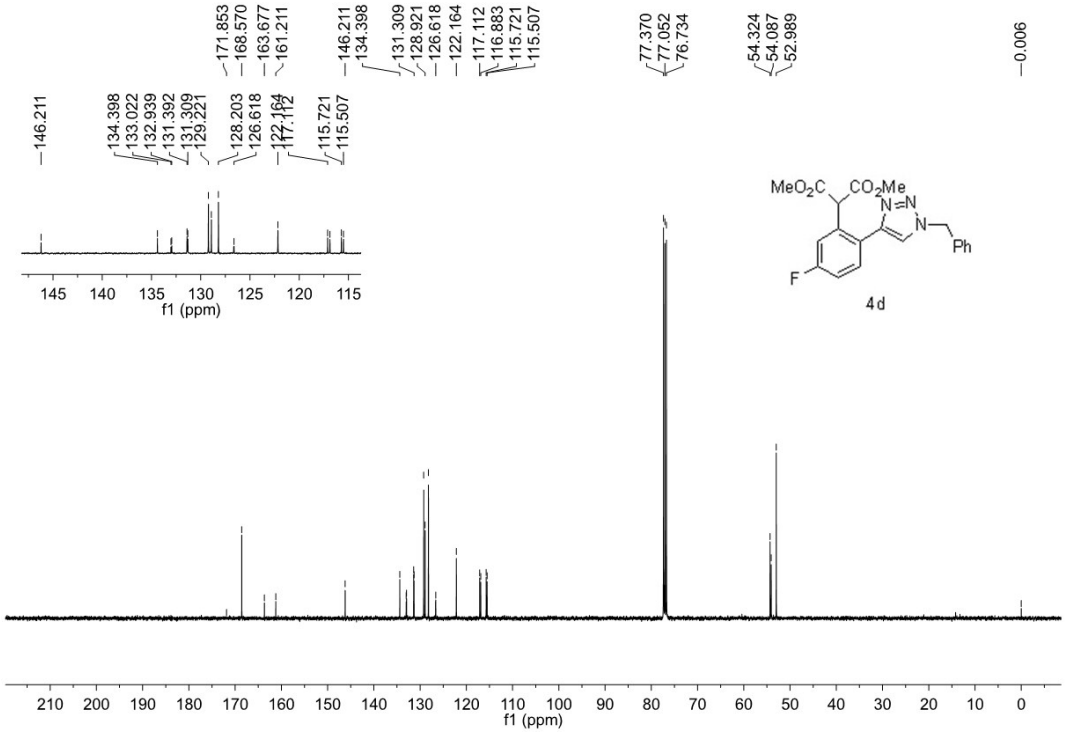
^{13}C NMR Spectrum of 4c in $CDCl_3$ at 100 MHz



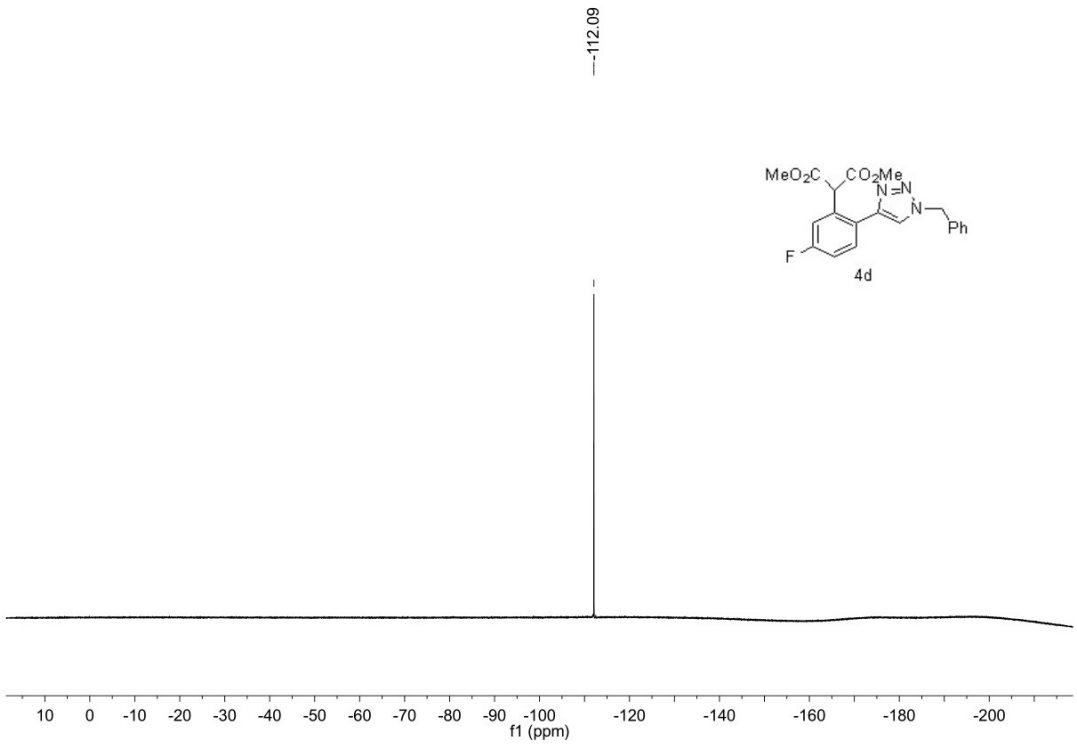
^{1}H NMR Spectrum of 4d in $CDCl_3$ at 400 MHz



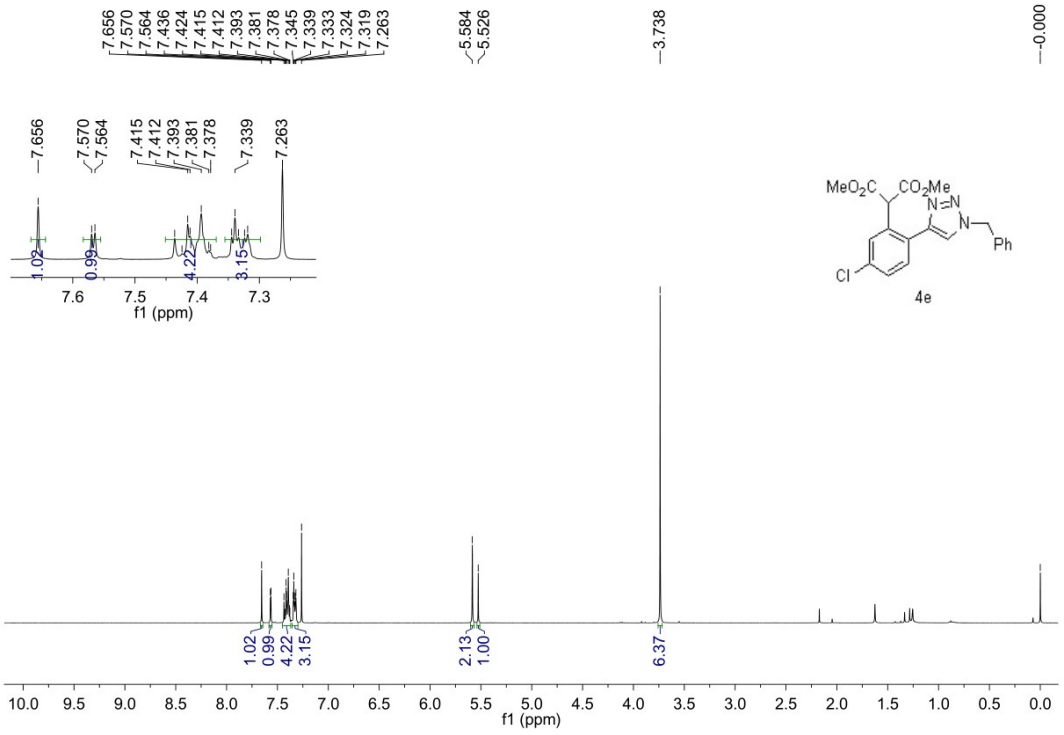
^{13}C NMR Spectrum of 4d in $CDCl_3$ at 100 MHz



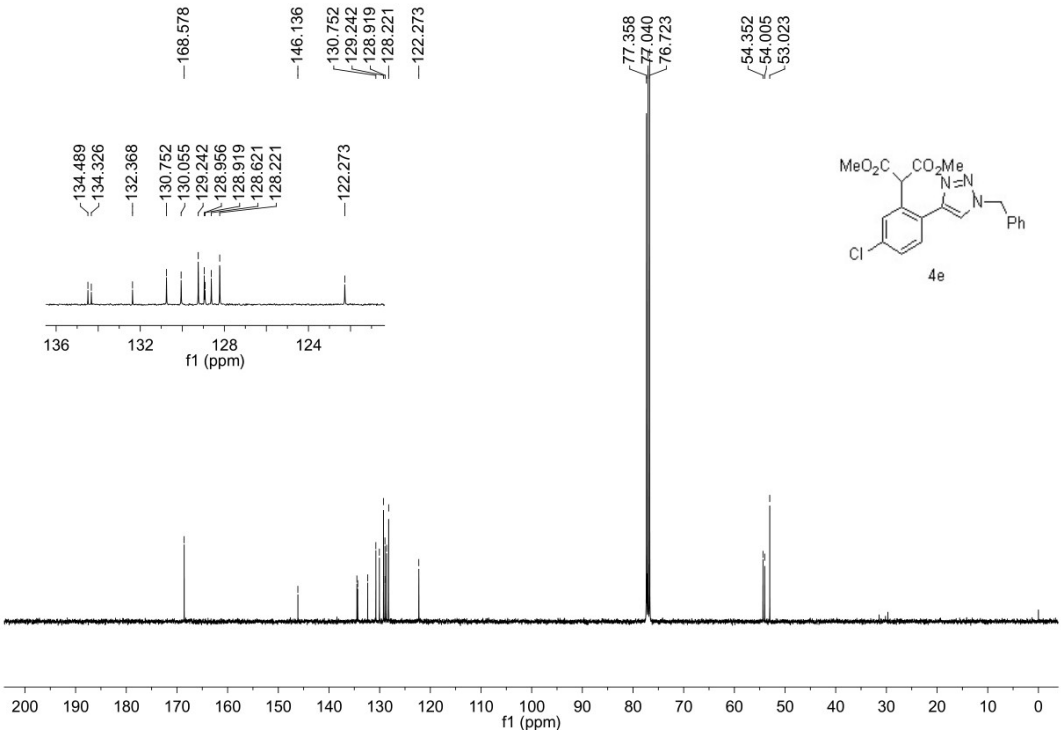
^{19}F NMR Spectrum of 4d in $CDCl_3$ at 376 MHz



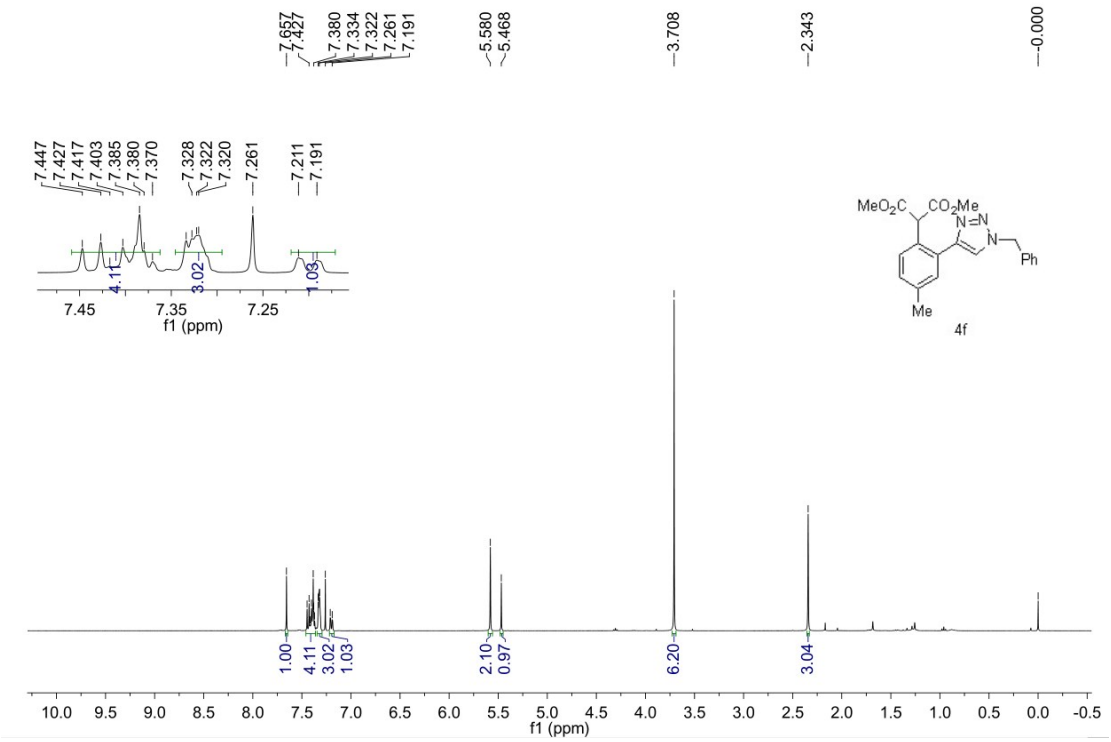
^{1}H NMR Spectrum of 4e in $CDCl_3$ at 400 MHz



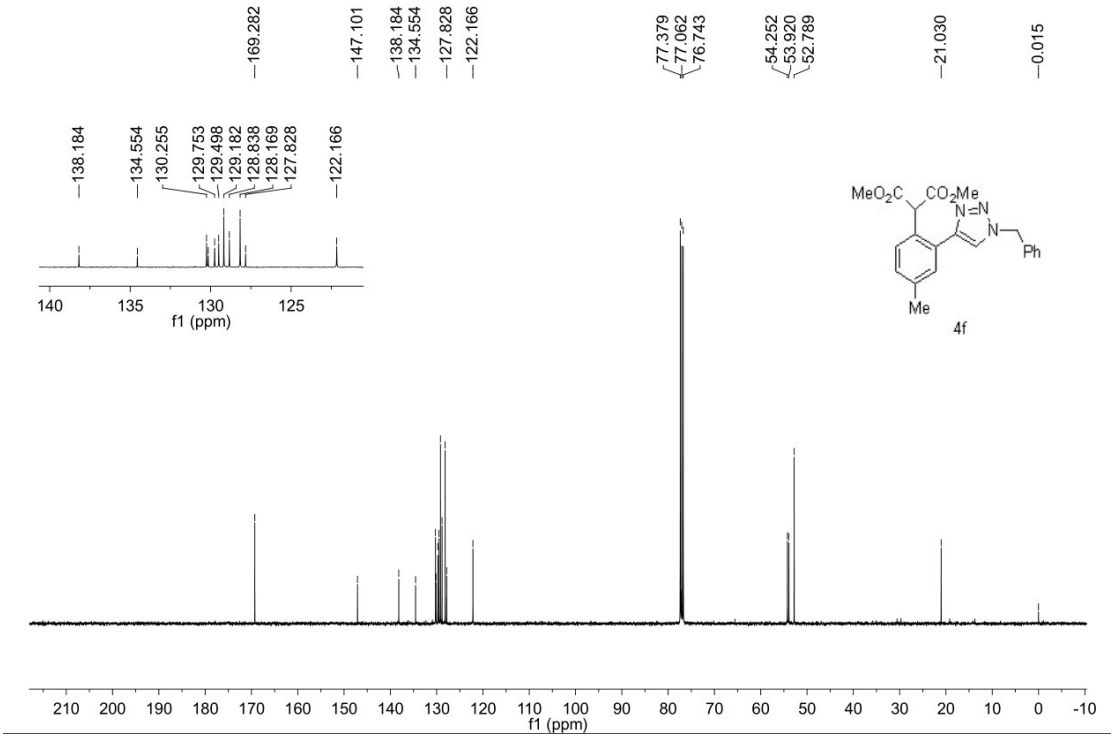
^{13}C NMR Spectrum of 4e in $CDCl_3$ at 100 MHz



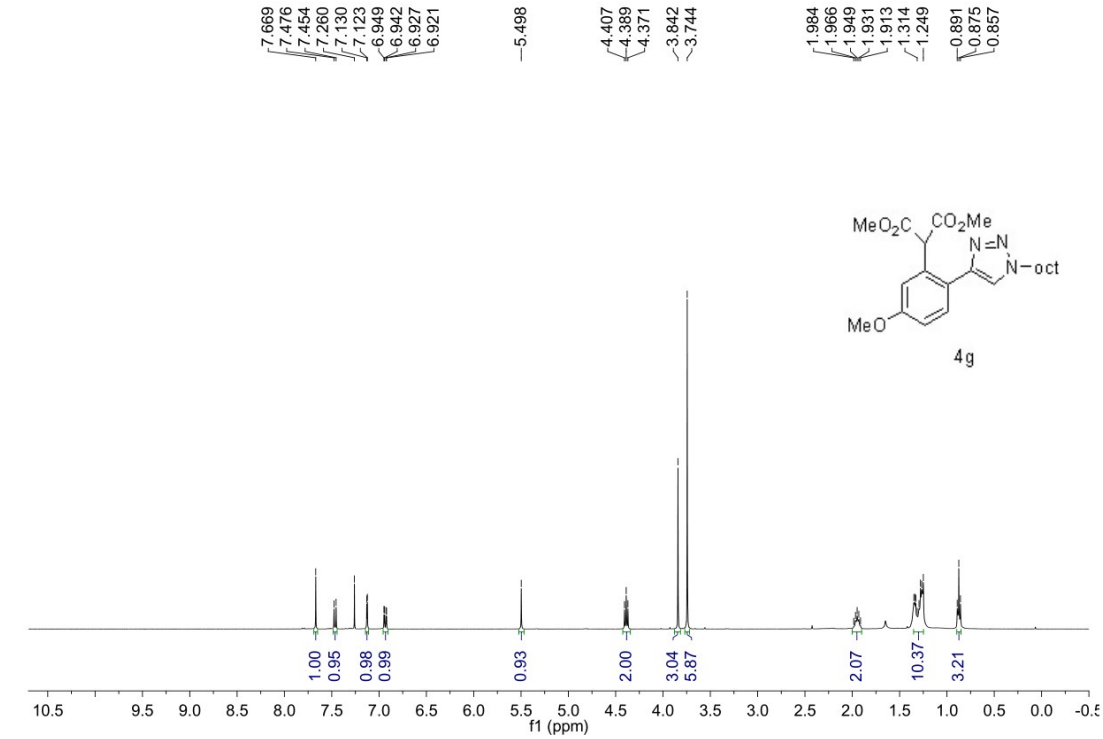
^{1}H NMR Spectrum of 4f in $CDCl_3$ at 400 MHz



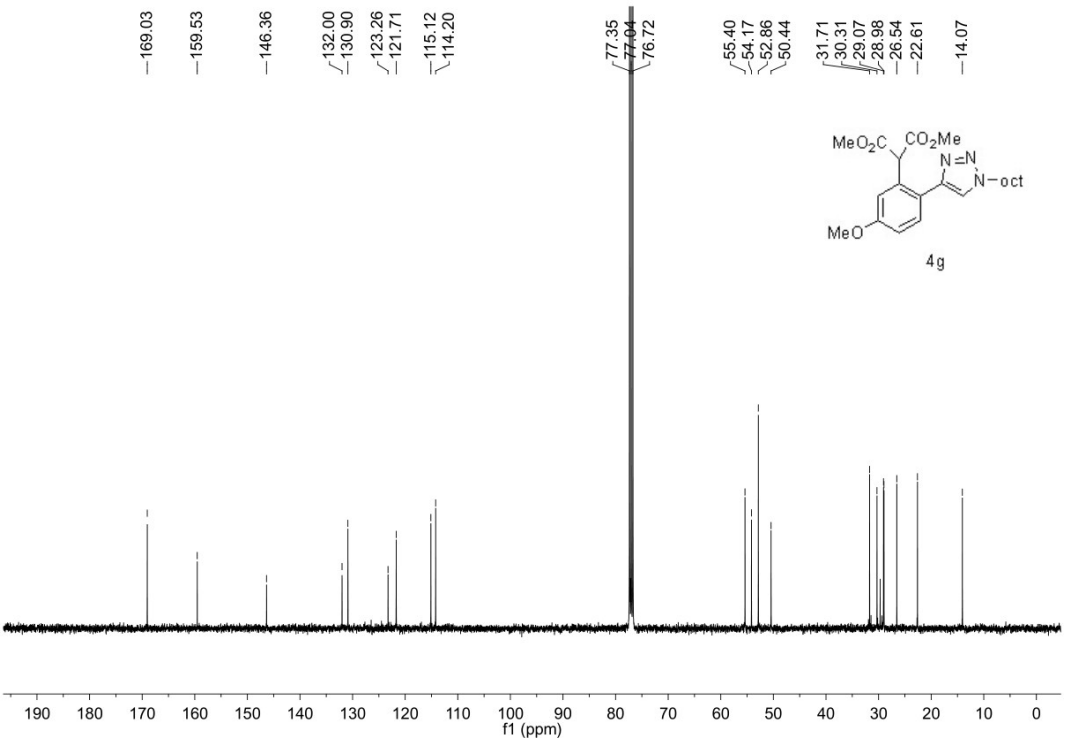
^{13}C NMR Spectrum of 4f in $CDCl_3$ at 100 MHz



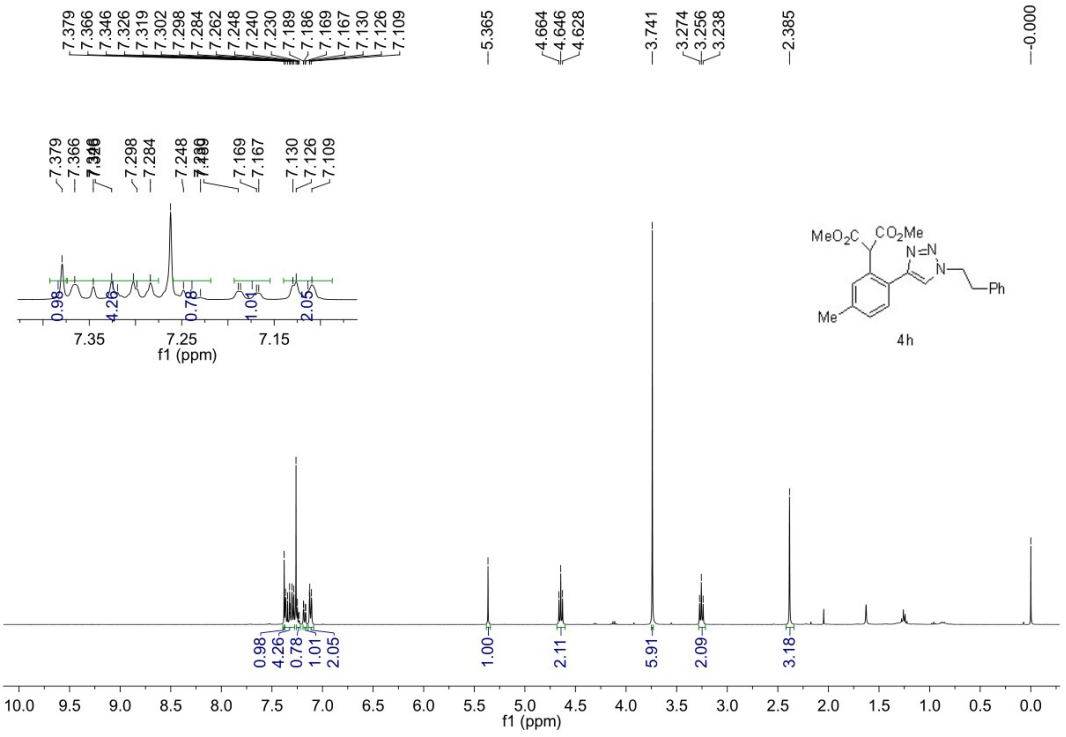
^{1}H NMR Spectrum of 4g in $CDCl_3$ at 400 MHz



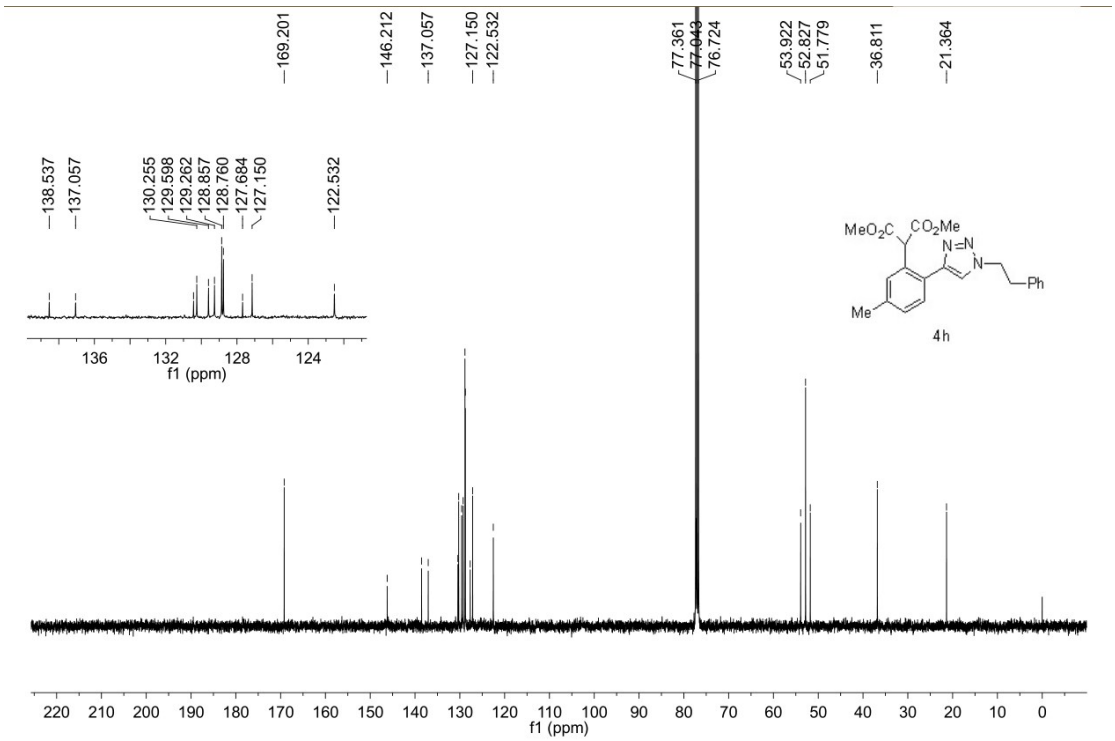
^{13}C NMR Spectrum of 4g in $CDCl_3$ at 100 MHz



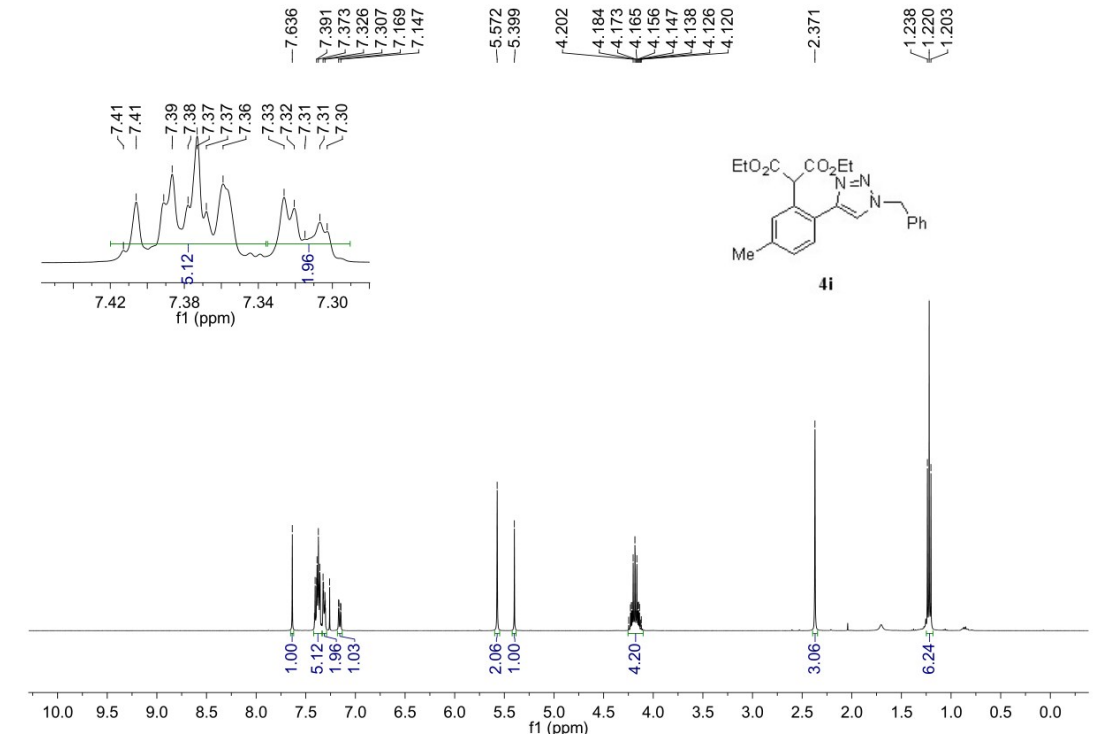
^{1}H NMR Spectrum of 4h in $CDCl_3$ at 400 MHz



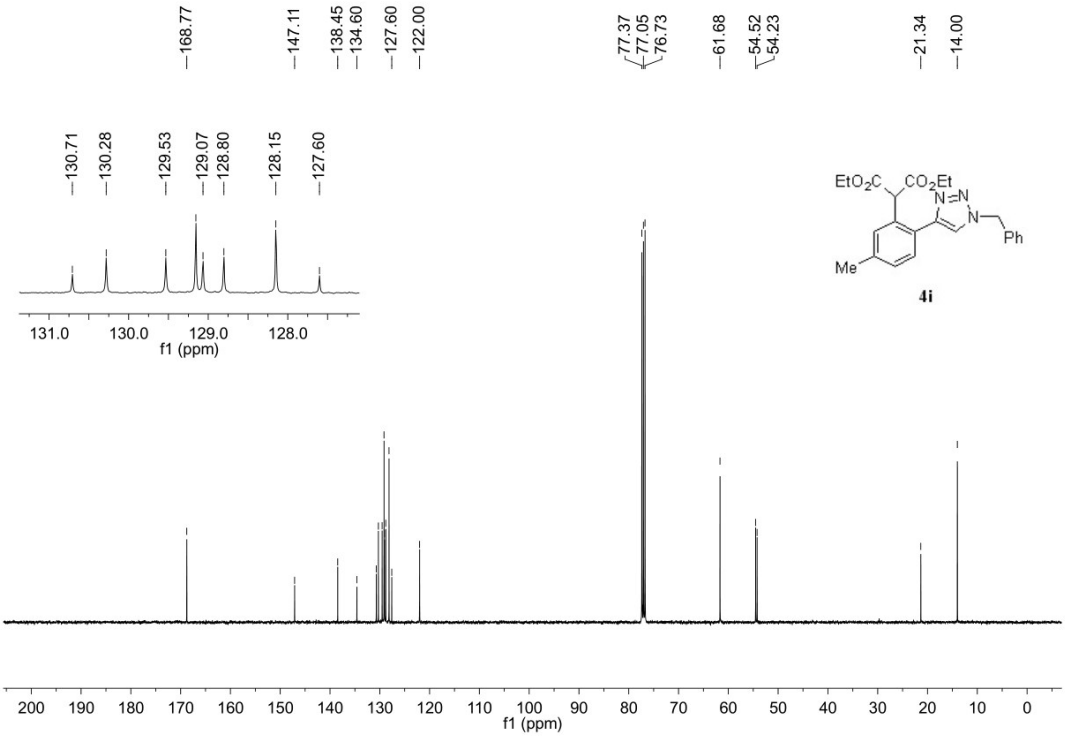
^{13}C NMR Spectrum of 4h in $CDCl_3$ at 100 MHz



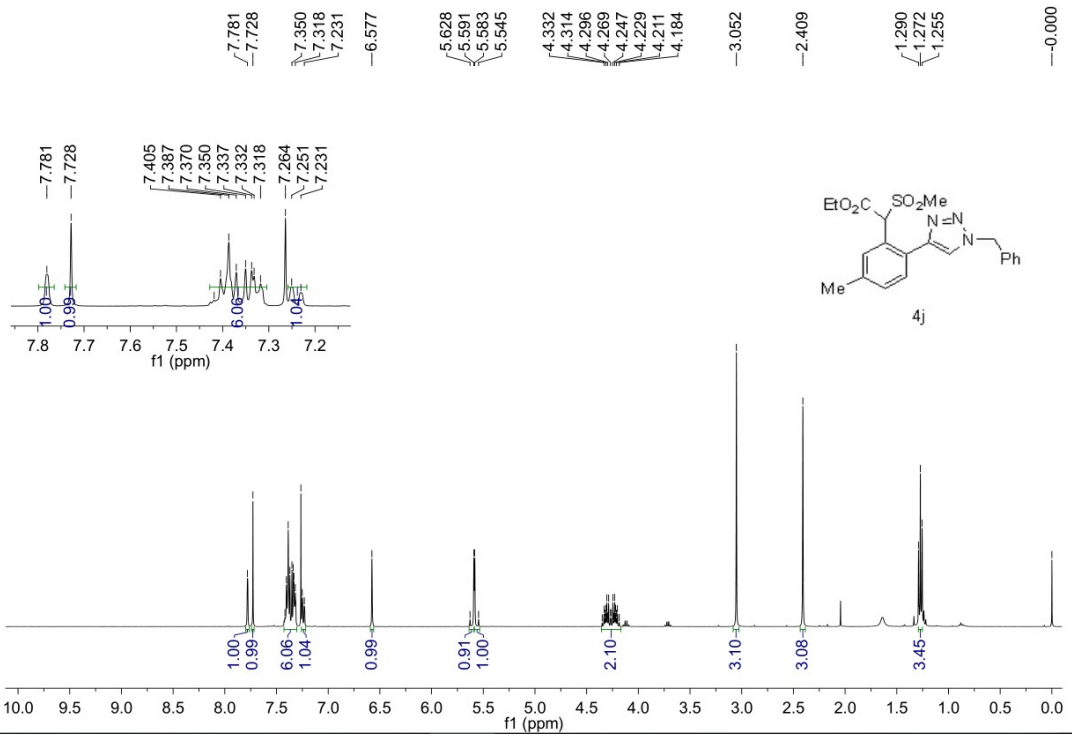
^{1}H NMR Spectrum of 4i in $CDCl_3$ at 400 MHz



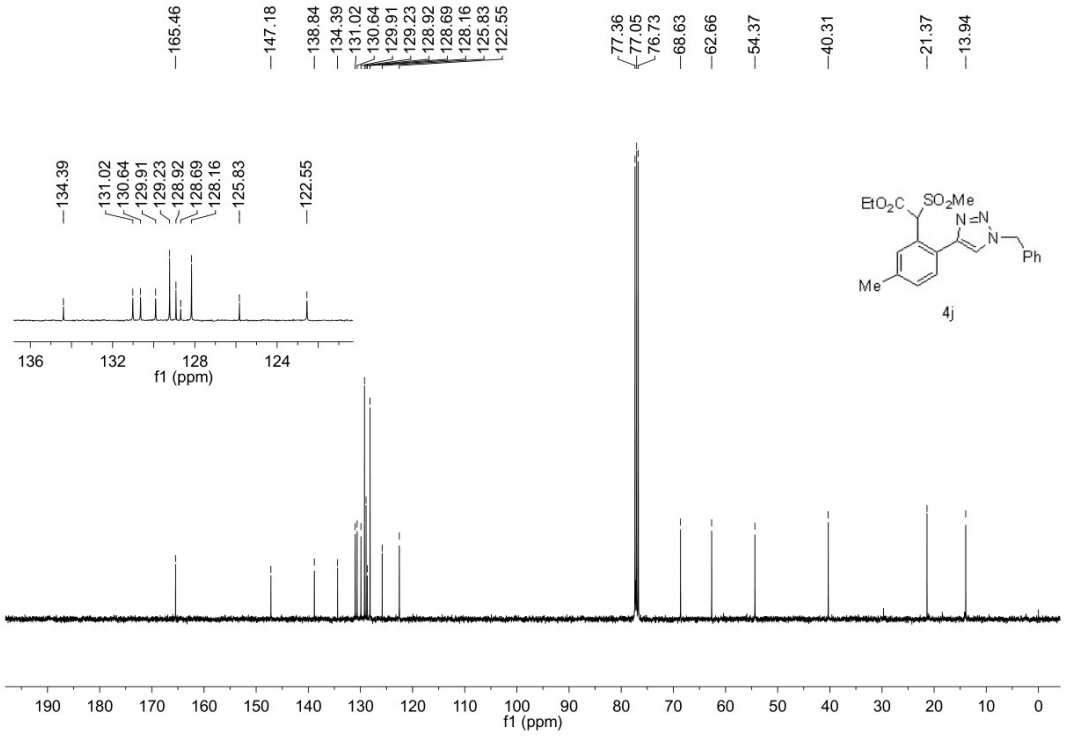
^{13}C NMR Spectrum of 4i in $CDCl_3$ at 100 MHz



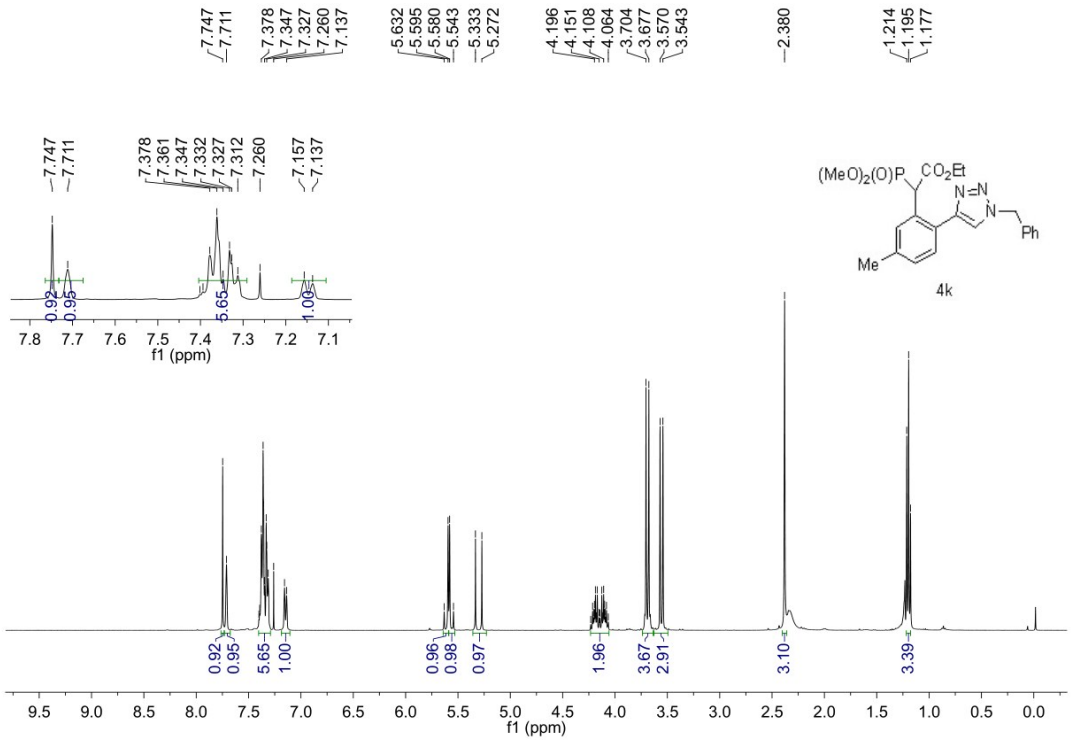
^{1}H NMR Spectrum of 4j in $CDCl_3$ at 400 MHz



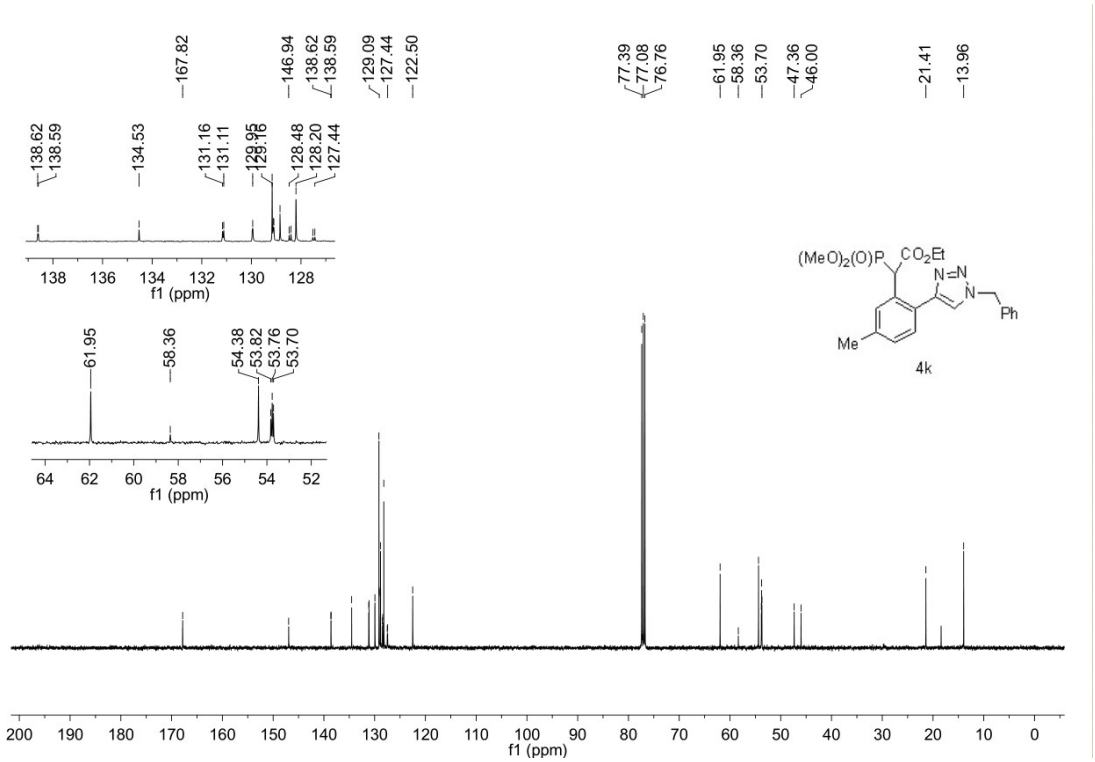
^{13}C NMR Spectrum of 4j in $CDCl_3$ at 100 MHz



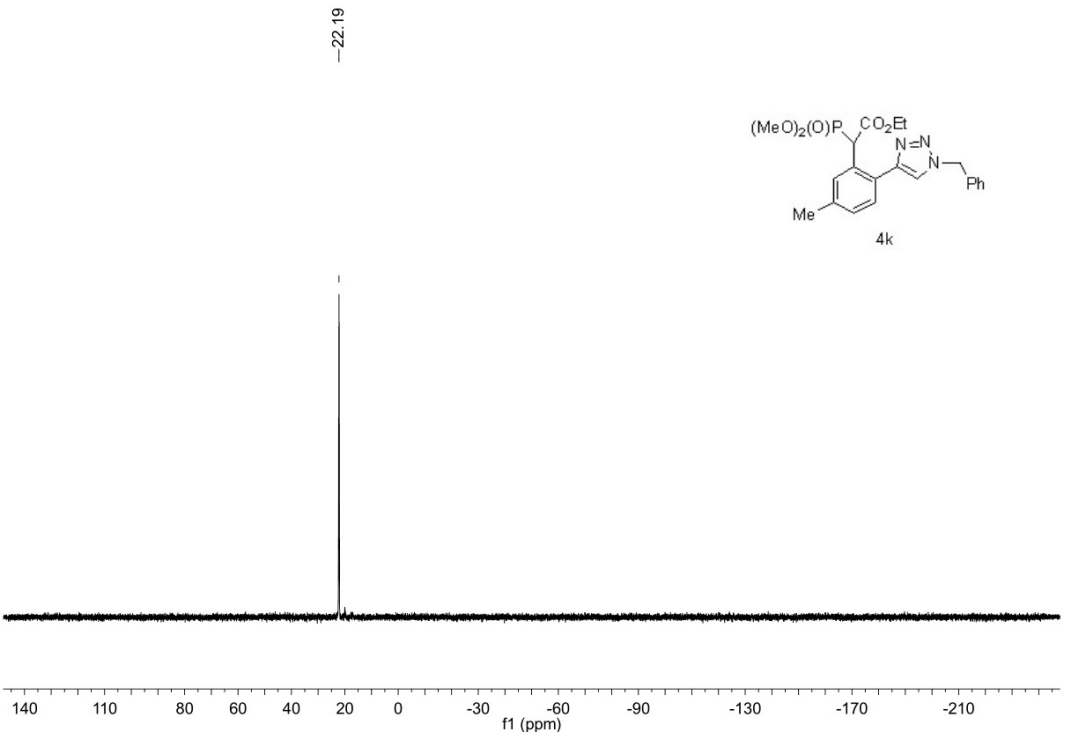
^{1}H NMR Spectrum of 4k in $CDCl_3$ at 400 MHz



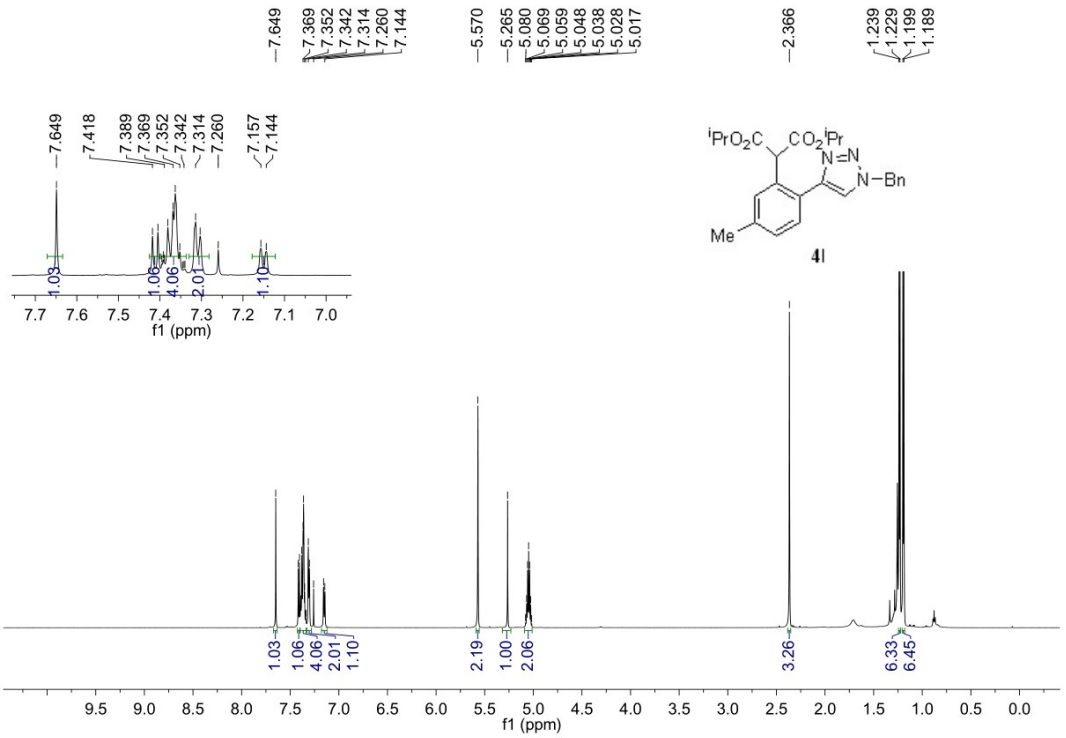
^{13}C NMR Spectrum of 4k in $CDCl_3$ at 100 MHz



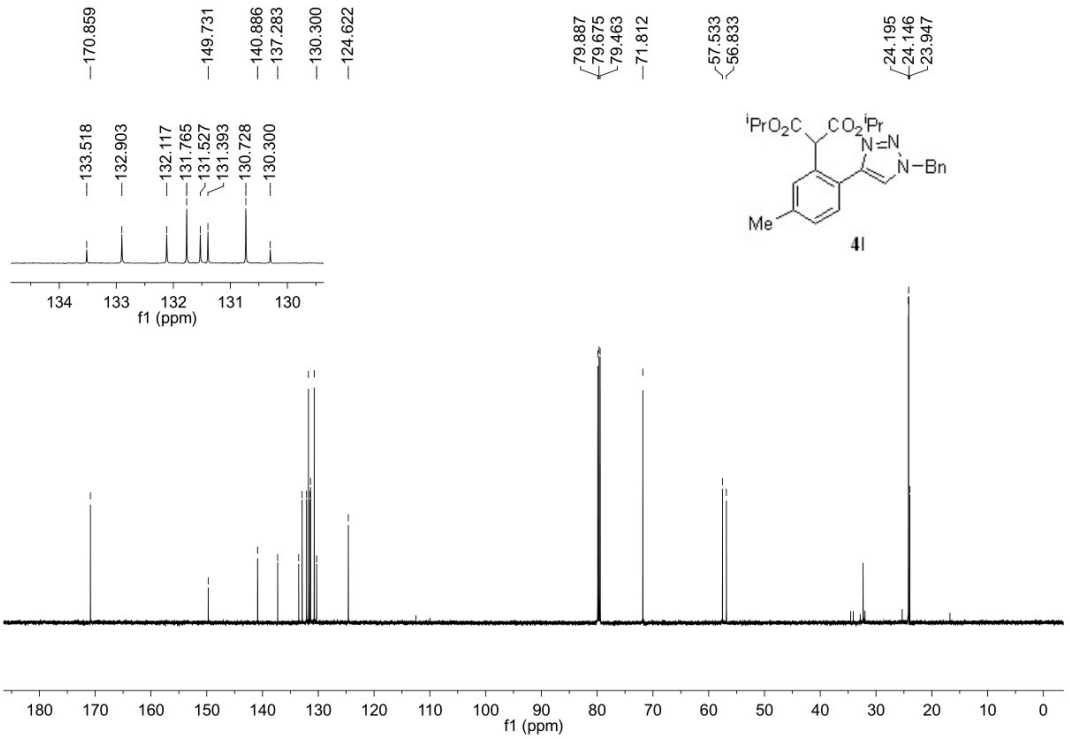
^{31}P NMR Spectrum of 4k in $CDCl_3$ at 162 MHz


22.19
(MeO)2(O)P
CO2Et
N=N
N
Ph
Me
4k
140
110
80
60
40
20
0
-30
-60
-90
-130
-170
-210
f1 (ppm)

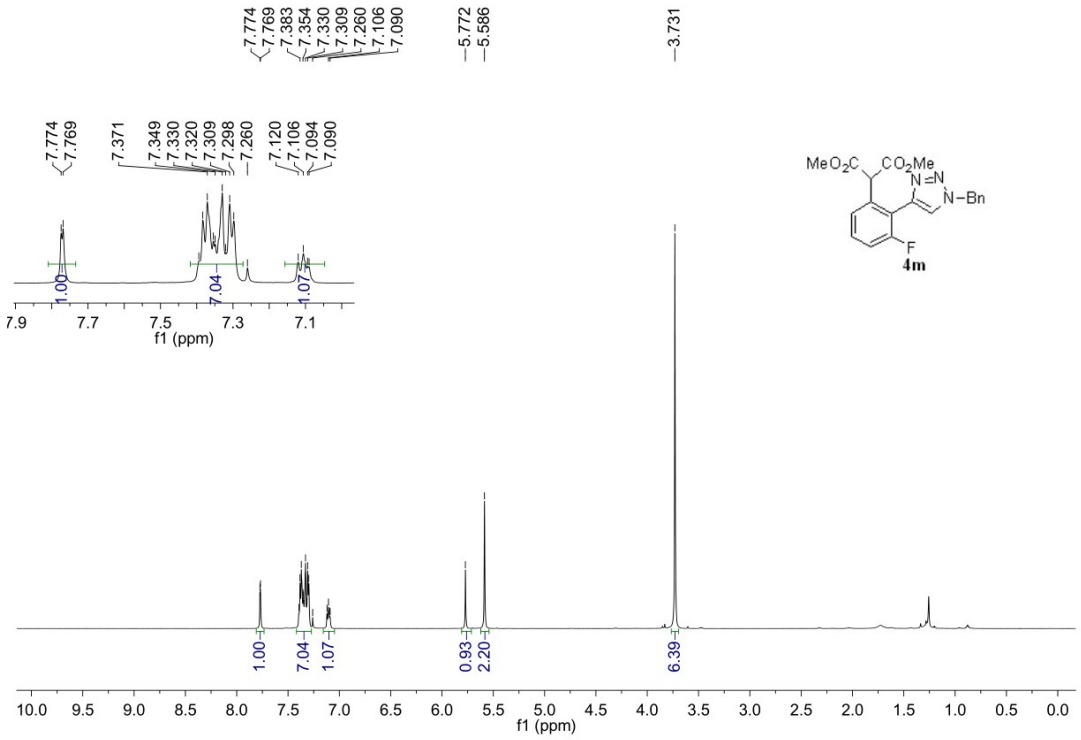
^{1}H NMR Spectrum of 4l in $CDCl_3$ at 400 MHz



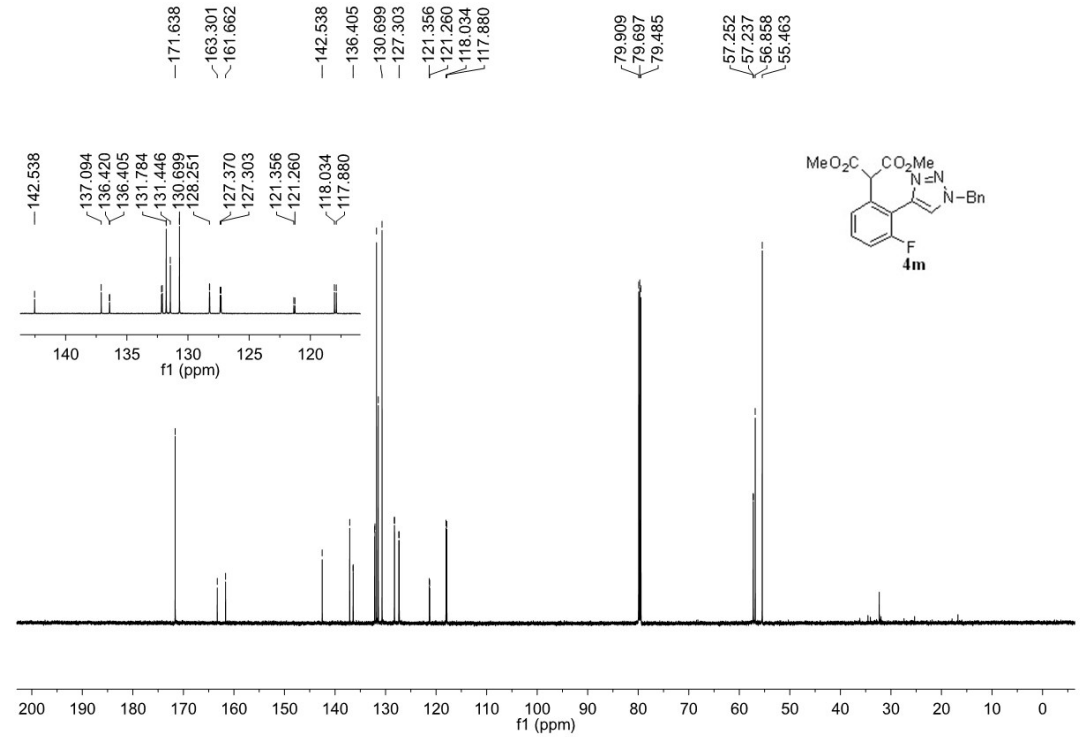
^{13}C NMR Spectrum of 4l in $CDCl_3$ at 100 MHz



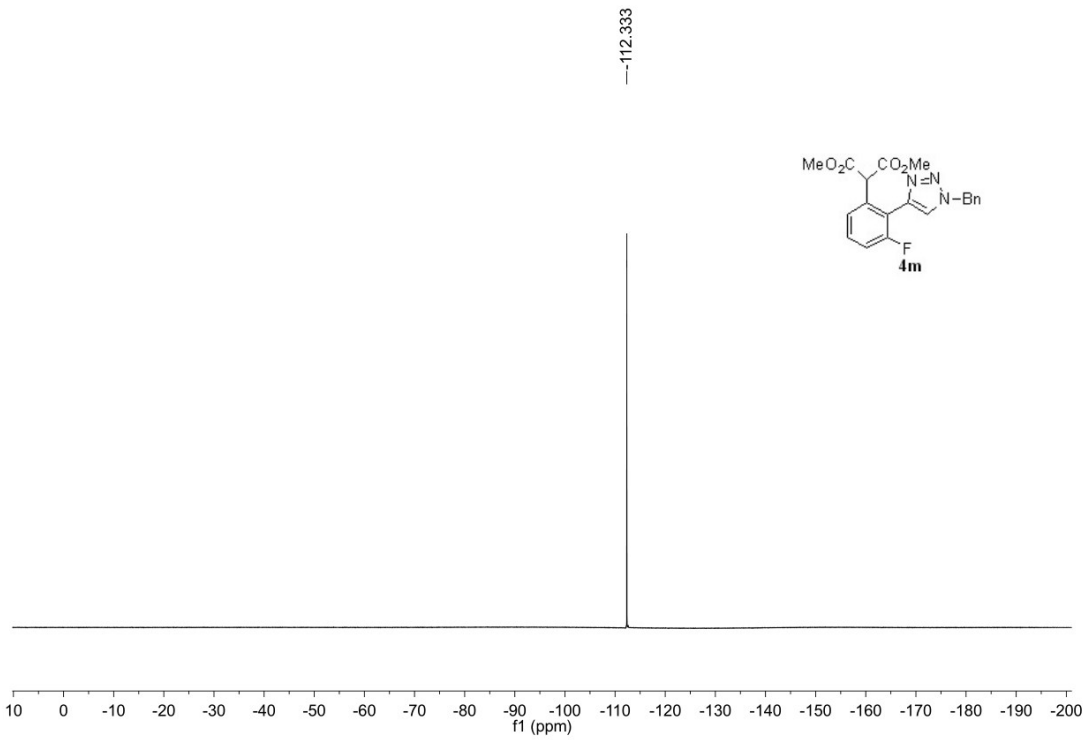
^{1}H NMR Spectrum of 4m in $CDCl_3$ at 600 MHz



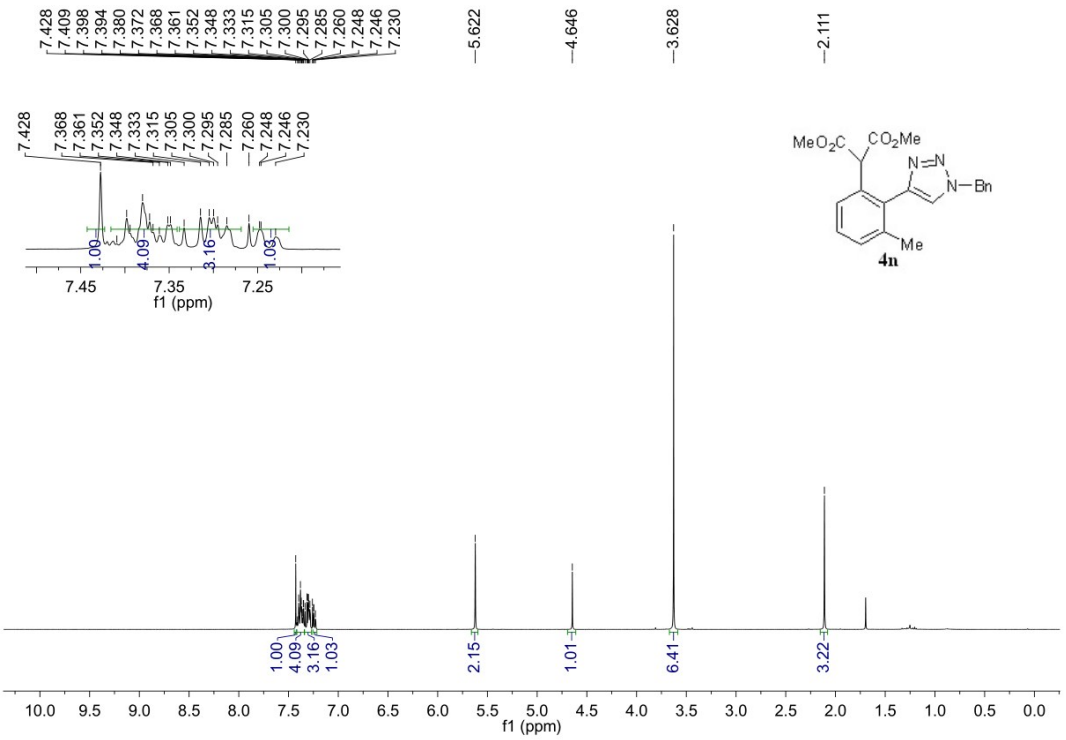
^{13}C NMR Spectrum of 4m in $CDCl_3$ at 150 MHz



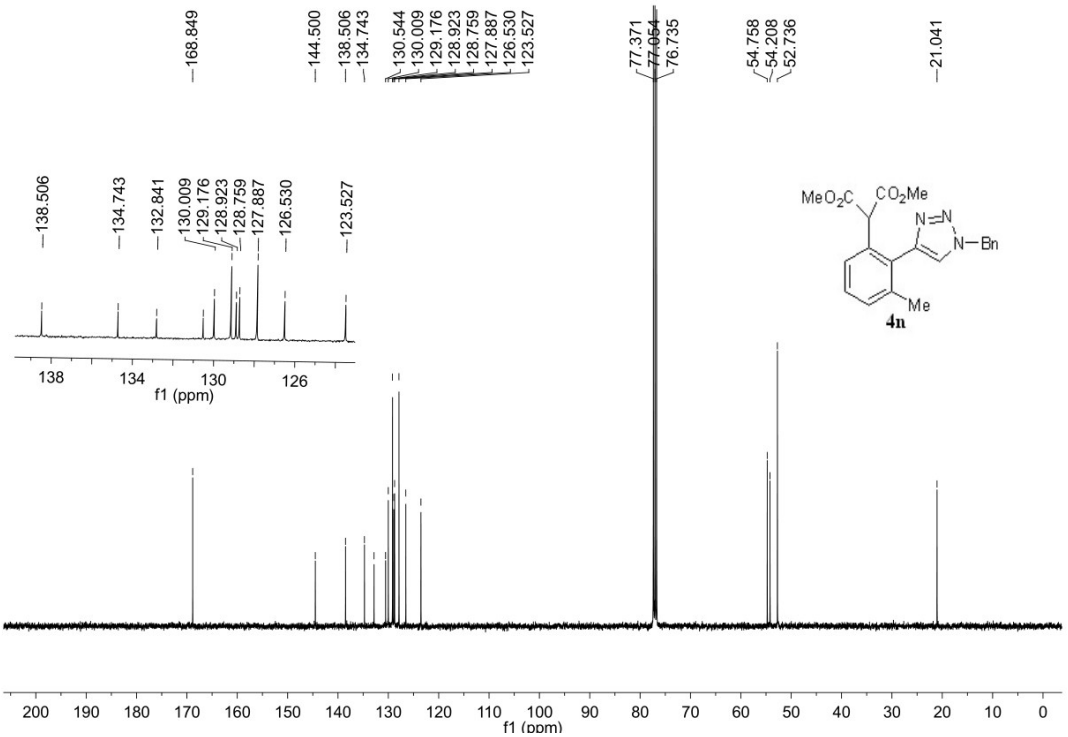
^{19}F NMR Spectrum of 4m in $CDCl_3$ at 376 MHz



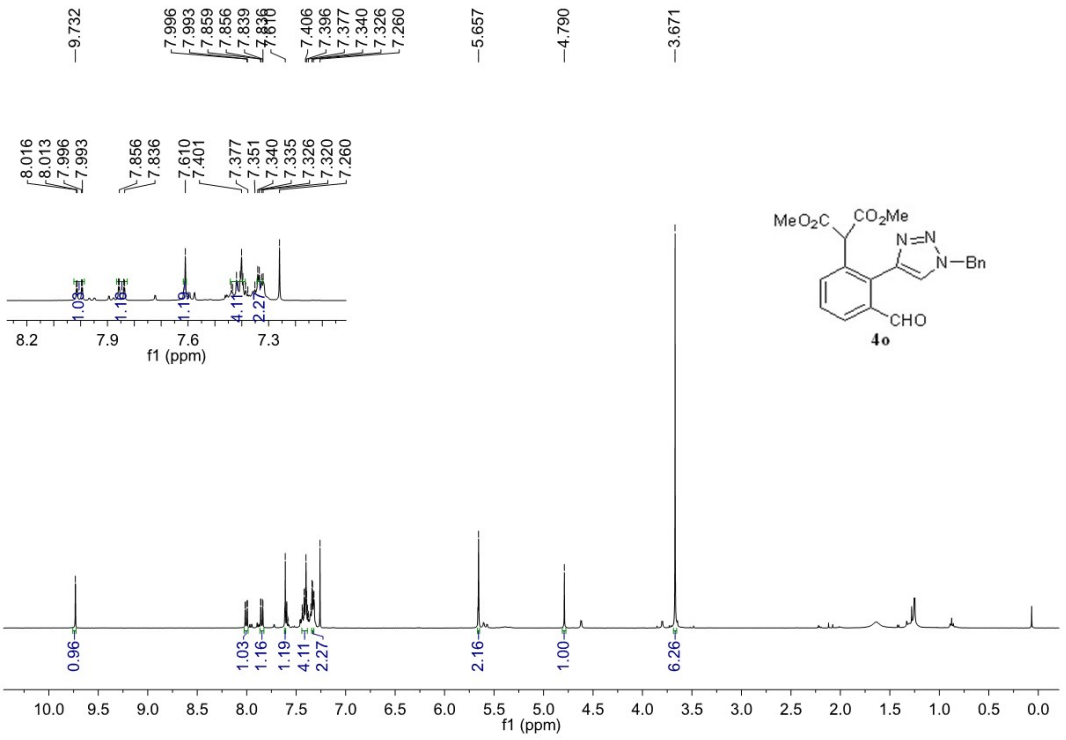
^{1}H NMR Spectrum of 4n in $CDCl_3$ at 400 MHz



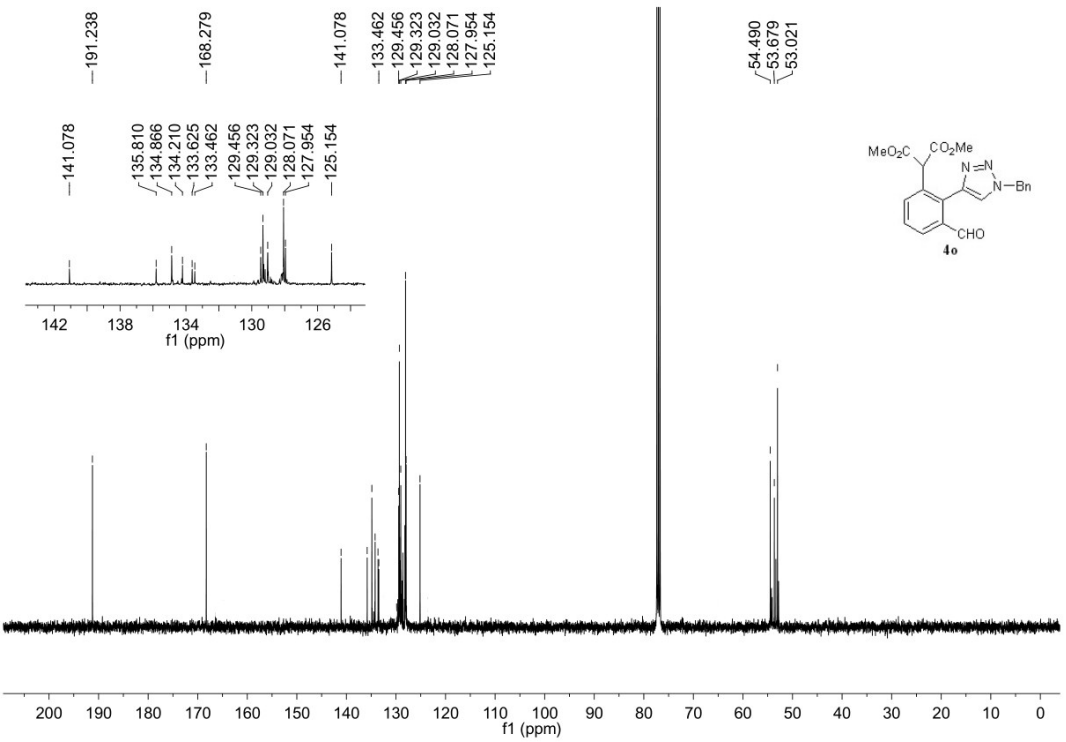
^{13}C NMR Spectrum of 4n in $CDCl_3$ at 100 MHz



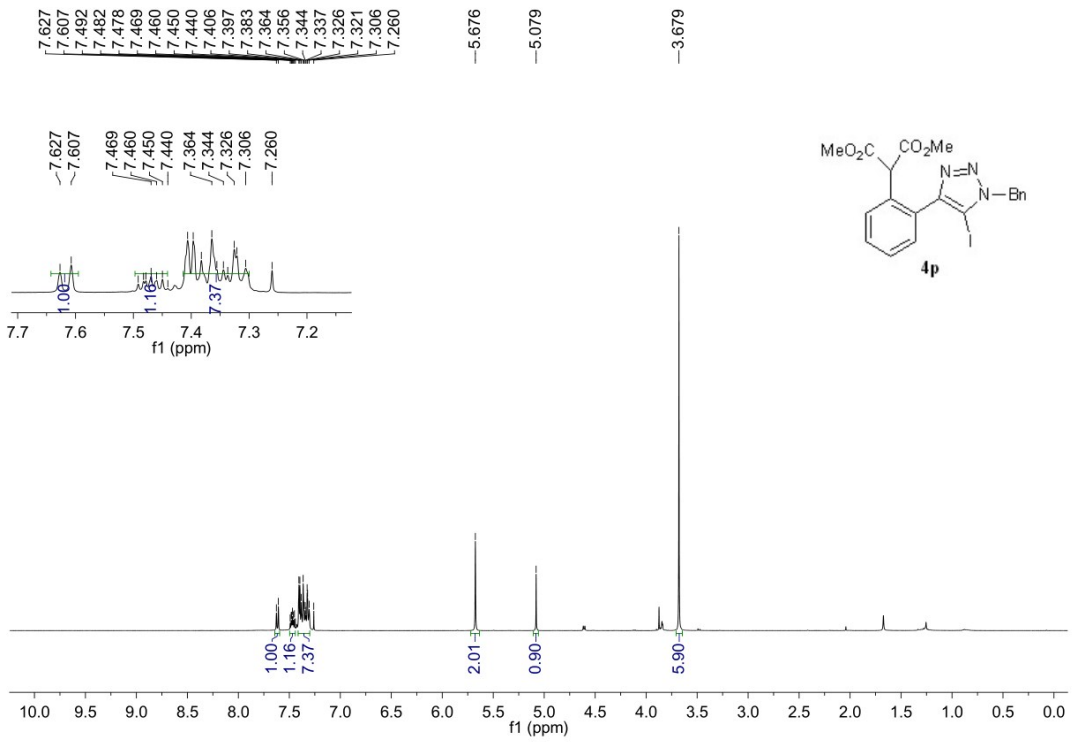
^{1}H NMR Spectrum of 4o in $CDCl_3$ at 400 MHz



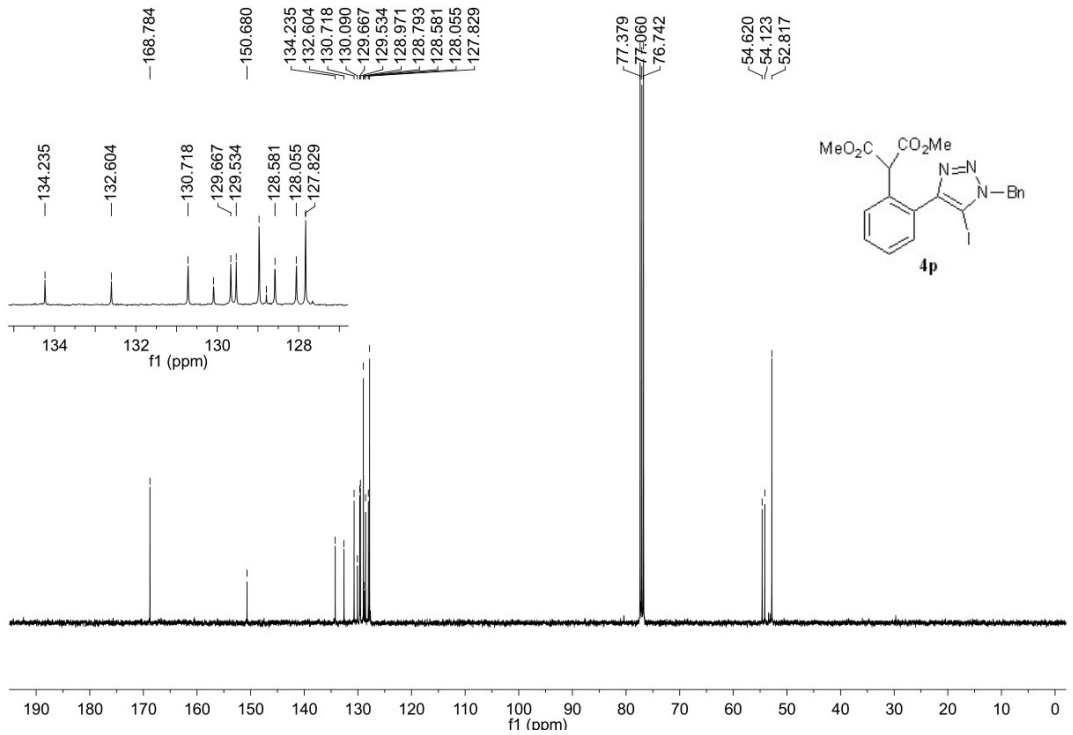
^{13}C NMR Spectrum of 4o in $CDCl_3$ at 100 MHz



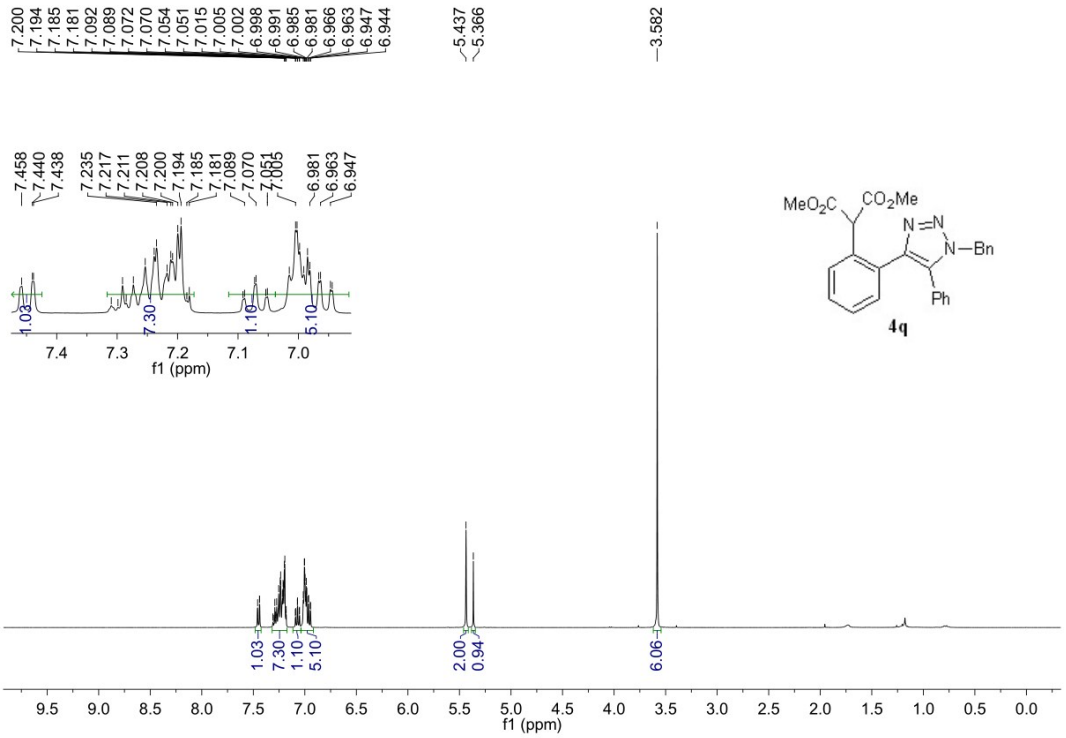
^{1}H NMR Spectrum of 4p in $CDCl_3$ at 400 MHz



^{13}C NMR Spectrum of 4p in $CDCl_3$ at 100 MHz



^{1}H NMR Spectrum of 4q in $CDCl_3$ at 400 MHz



^{13}C NMR Spectrum of 4q in $CDCl_3$ at 100 MHz