

Supporting Information

Phosphine-Catalyzed Domino Reaction: An Efficient Method for the Synthesis of Bicyclo[3.2.0]heptenes Skeleton

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1 General Information

All reactions were carried out with the use of argon atmospheres. Solvents were used from commercially available sources. Yields refer to isolated compounds. Reactions were monitored by TLC using a UV lamp as a visualizing agent. All ^1H , ^{13}C nuclear magnetic resonance spectra were recorded in CDCl_3 . The ^1H NMR was recorded at 400MHz, ^{13}C NMR was recorded at 100MHz. All shifts are reported in ppm as downfield from TMS as standard. Multiplicity is indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), br s (broad singlet). Coupling constants J are reported in Hz. HRMS were obtained on an IonSpec FT-ICR mass spectrometer with ESI resource. Melting points were measured on a RY-I apparatus and are reported uncorrected. Dienes were prepared according to the literature.¹

2 General Procedure for the Synthesis of Bicyclo[3.2.0]heptenes

Trimethyl phosphine (0.5 eq) was added to a mixture of dienic sulfones **1** (1.00 eq) and allenates **2** (3.00 eq) in CH_2Cl_2 (5.0 mL). The resulting suspension was maintained at 25 °C for the desired time under argon atmosphere. The residue was purified by column chromatography on silica gel (gradient eluant: petroleum ether/ethyl acetate 20:1-6:1) to afford bicyclo[3.2.0]heptenes **3**.

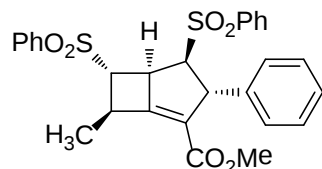
3 Reference

[1] J. J. Murphy, A. Quintard, P. McArdle, A. Alexakis, J. C. Stephens, *Angew. Chem. Int. Ed.* **2011**, 50, 5095-5098.

4 Spectral Data for 3a-3w

(3R,4S,5S,6S,7R)-methyl

7-methyl-3-phenyl-4,6-bis(phenylsulfonyl)bicyclo[3.2.0]hept-1-ene-2-carboxylate (3a)



White solid; mp: 207-208 °C;

^1H NMR (400 MHz, CDCl_3) δ 7.97 (d, J = 7.4 Hz, 2H), 7.84 (d, J = 7.4 Hz, 2H), 7.74 (t, J = 7.5 Hz, 1H), 7.69 (t, J = 7.5 Hz, 1H), 7.63 (d, J = 8.0 Hz, 2H), 7.58 (d, J = 7.6 Hz, 2H), 7.19 – 7.09 (m, 3H), 6.60 – 6.51 (m, 2H), 4.48 (t, J = 7.2 Hz, 1H), 4.45 (s, 1H), 4.18 – 4.06 (m, 2H), 3.67 (s, 3H), 3.63 (d, J = 8.3 Hz, 1H), 1.41 (d, J = 6.9 Hz, 3H).

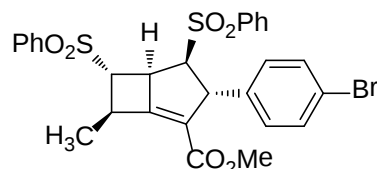
^{13}C NMR (101 MHz, CDCl_3) δ 163.15, 159.54, 139.01, 138.31, 137.19, 134.36, 134.22, 129.60, 129.38, 128.96, 128.82, 128.74, 127.61, 126.35, 125.56, 72.54, 61.21, 57.69, 51.72, 48.23, 44.10, 17.01.

IR (KBr): 3065, 2921, 1714, 1673, 1635, 1446, 1410, 1306, 1145, 1085, 725, 689, 602, 585 cm^{-1} .

HRMS (ESI/[M+Na] $^+$) Calcd. for: $\text{C}_{28}\text{H}_{26}\text{O}_6\text{S}_2\text{Na}$ 545.1063, found 545.1067.

(3R,4S,5S,6S,7R)-methyl

3-(4-bromophenyl)-7-methyl-4,6-bis(phenylsulfonyl)bicyclo[3.2.0]hept-1-ene-2-carboxylate (3b)



White solid; mp: 197-200 °C;

^1H NMR (400 MHz, CDCl_3) δ 7.97 (d, J = 7.6 Hz, 2H), 7.83 (d, J = 7.6 Hz, 2H), 7.77 – 7.71 (m, 1H), 7.69 (d, J = 7.3 Hz, 1H), 7.63 (d, J = 7.9 Hz, 2H), 7.59 (d, J = 7.8 Hz, 2H), 7.26 (d, J = 7.0 Hz, 2H), 6.42 (d, J = 8.1 Hz, 2H), 4.46 (t, J = 7.1 Hz, 1H), 4.41 (s, 1H), 4.15 – 4.06 (m, 2H), 3.67 (s, 3H), 3.59 (d, J = 8.3 Hz, 1H), 1.38 (d, J = 6.8 Hz, 3H).

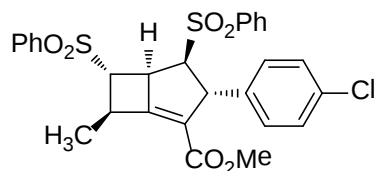
^{13}C NMR (101 MHz, CDCl_3) δ 162.98, 159.79, 138.24, 138.17, 137.10, 134.43, 134.25, 132.06, 129.65, 129.40, 128.77, 128.72, 128.08, 125.22, 121.60, 72.11, 61.12, 57.27, 51.77, 48.29, 44.27, 16.95.

IR (KBr): 3063, 2955, 1715, 1675, 1486, 1446, 1306, 1289, 1145, 1084, 724, 688, 602, 586 cm^{-1} .

HRMS (MALDI/[M+Na] $^+$) Calcd. for: $\text{C}_{28}\text{H}_{25}\text{BrO}_6\text{S}_2\text{Na}$ 623.0168, found 623.0165.

(3R,4S,5S,6S,7R)-methyl

3-(4-chlorophenyl)-7-methyl-4,6-bis(phenylsulfonyl)bicyclo[3.2.0]hept-1-ene-2-carboxylate (3c)



White solid; mp: 203-206 °C;

^1H NMR (400 MHz, CDCl_3) δ 7.97 (d, J = 7.4 Hz, 2H), 7.83 (d, J = 7.4 Hz, 2H), 7.74 (t, J = 7.5 Hz, 1H), 7.70 (t, J = 7.5 Hz, 1H), 7.63 (d, J = 8.2 Hz, 2H), 7.59 (d, J = 7.7 Hz, 2H), 7.11 (d, J = 8.4 Hz, 2H), 6.48 (d, J = 8.4 Hz, 2H), 4.46 (t, J = 7.2 Hz, 1H), 4.42 (s, 1H), 4.16 – 4.06 (m, 2H), 3.67 (s, 3H), 3.59 (d, J = 8.4 Hz, 1H), 1.39 (d, J = 6.9 Hz, 3H).

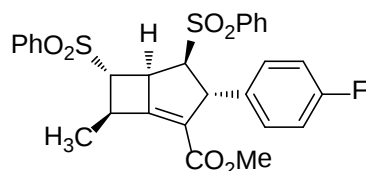
^{13}C NMR (101 MHz, CDCl_3) δ 162.99, 159.76, 138.25, 137.66, 137.11, 134.44, 134.26, 133.49, 129.66, 129.41, 129.10, 128.77, 128.72, 127.76, 125.29, 72.17, 61.13, 57.21, 51.77, 48.28, 44.27, 16.97.

IR (KBr): 3062, 2981, 2960, 1714, 1672, 1490, 1446, 1307, 1291, 1145, 1049, 725, 602, 586 cm^{-1} .

HRMS (MALDI/[$\text{M}+\text{Na}$] $^+$) Calcd. for: $\text{C}_{28}\text{H}_{25}\text{ClO}_6\text{S}_2\text{Na}$ 579.0673, found 579.0681.

(3R,4S,5S,6S,7R)-methyl

3-(4-fluorophenyl)-7-methyl-4,6-bis(phenylsulfonyl)bicyclo[3.2.0]hept-1-ene-2-carboxylate (3d)



White solid; mp: 199-200 °C;

^1H NMR (400 MHz, CDCl_3) δ 7.97 (d, J = 8.2 Hz, 2H), 7.84 (d, J = 7.5 Hz, 2H), 7.74 (t, J = 7.4 Hz, 1H), 7.69 (t, J = 7.4 Hz, 1H), 7.63 (d, J = 8.7 Hz, 2H), 7.59 (d, J = 7.7 Hz, 2H), 6.82 (t, J = 8.5 Hz, 2H), 6.56 – 6.47 (m, 2H), 4.51 – 4.42 (m, 2H), 4.16 – 4.07 (m, 2H), 3.67 (s, 3H), 3.60 (d, J = 8.4 Hz, 1H), 1.39 (d, J = 6.9 Hz, 3H).

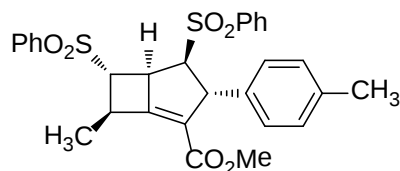
^{13}C NMR (101 MHz, CDCl_3) δ 163.32, 163.05, 160.87, 159.54, 138.28, 137.16, 134.89, 134.86, 134.41, 134.25, 129.64, 129.41, 128.78, 128.72, 128.02, 127.94, 125.52, 115.94, 115.72, 72.32, 61.13, 57.06, 51.75, 48.20, 44.24, 16.96.

IR (KBr): 3064, 2931, 1714, 1675, 1508, 1446, 1306, 1290, 1145, 1085, 726, 688, 602, 586 cm^{-1} .

HRMS (MALDI/[$\text{M}+\text{Na}$] $^+$) Calcd. for: $\text{C}_{28}\text{H}_{25}\text{FO}_6\text{S}_2\text{Na}$ 563.0969, found 563.0972.

(3R,4S,5S,6S,7R)-methyl

7-methyl-4,6-bis(phenylsulfonyl)-3-(p-tolyl)bicyclo[3.2.0]hept-1-ene-2-carboxylate (3e)



White solid; mp: 170-173 °C;

^1H NMR (400 MHz, CDCl_3) δ 7.97 (d, J = 7.5 Hz, 2H), 7.83 (d, J = 7.4 Hz, 2H), 7.76 – 7.71 (m, 1H), 7.68 (t, J = 7.5 Hz, 1H), 7.62 (d, J = 7.7 Hz, 2H), 7.58 (d, J = 7.5 Hz, 2H), 6.94 (d, J = 7.9 Hz, 2H),

6.44 (d, $J = 7.9$ Hz, 2H), 4.48 (t, $J = 7.2$ Hz, 1H), 4.41 (s, 1H), 4.18 – 4.05 (m, 2H), 3.66 (s, 3H), 3.60 (dd, $J = 8.3, 1.0$ Hz, 1H), 2.23 (s, 3H), 1.40 (d, $J = 6.9$ Hz, 3H).

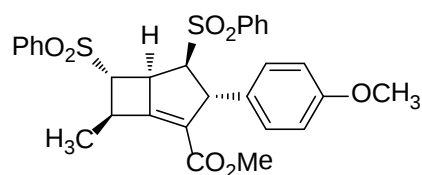
^{13}C NMR (101 MHz, CDCl_3) δ 163.16, 159.27, 138.32, 137.35, 137.24, 136.02, 134.29, 134.19, 129.61, 129.56, 129.36, 128.79, 128.74, 126.22, 125.71, 72.59, 61.23, 57.39, 51.68, 48.21, 44.07, 20.99, 17.00.

IR (KBr): 3062, 2929, 1715, 1675, 1446, 1306, 1145, 1085, 726, 688, 603, 586 cm^{-1} .

HRMS (MALDI/[$\text{M}+\text{Na}$] $^+$) Calcd. for: $\text{C}_{29}\text{H}_{28}\text{O}_6\text{S}_2\text{Na}$ 559.1220, found 559.1221.

(3R,4S,5S,6S,7R)-methyl

3-(4-methoxyphenyl)-7-methyl-4,6-bis(phenylsulfonyl)bicyclo[3.2.0]hept-1-ene-2-carboxylate (3f)



White solid; mp: 190-193 $^{\circ}\text{C}$;

^1H NMR (400 MHz, CDCl_3) δ 7.97 (d, $J = 7.5$ Hz, 2H), 7.83 (d, $J = 7.5$ Hz, 2H), 7.76 – 7.71 (m, 1H), 7.68 (d, $J = 7.5$ Hz, 1H), 7.62 (d, $J = 7.7$ Hz, 2H), 7.58 (d, $J = 7.5$ Hz, 2H), 6.66 (d, $J = 8.4$ Hz, 2H), 6.47 (d, $J = 8.4$ Hz, 2H), 4.47 (t, $J = 7.2$ Hz, 1H), 4.40 (s, 1H), 4.18 – 4.05 (m, 2H), 3.71 (s, 3H), 3.67 (s, 3H), 3.59 (d, $J = 8.2$ Hz, 1H), 1.39 (d, $J = 6.8$ Hz, 3H).

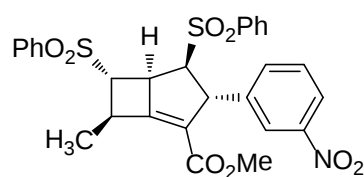
^{13}C NMR (101 MHz, CDCl_3) δ 163.18, 159.09, 158.98, 138.32, 137.26, 134.32, 134.22, 131.03, 129.58, 129.39, 128.77, 128.73, 127.44, 125.81, 114.27, 72.55, 61.21, 57.08, 55.26, 51.69, 48.15, 44.11, 16.99.

IR (KBr): 3063, 2953, 1714, 1674, 1610, 1511, 1446, 1306, 1247, 1145, 1084, 726, 688, 602, 586 cm^{-1} .

HRMS (MALDI/[$\text{M}+\text{Na}$] $^+$) Calcd. for: $\text{C}_{29}\text{H}_{28}\text{O}_7\text{S}_2\text{Na}$ 575.1169, found 575.1170.

(3R,4S,5S,6S,7R)-methyl

7-methyl-3-(3-nitrophenyl)-4,6-bis(phenylsulfonyl)bicyclo[3.2.0]hept-1-ene-2-carboxylate (3h)



White solid; mp: 200-202 $^{\circ}\text{C}$;

^1H NMR (400 MHz, CDCl_3) δ 8.02 (dd, $J = 8.1, 1.1$ Hz, 1H), 7.98 (d, $J = 7.4$ Hz, 2H), 7.87 (d, $J = 7.3$ Hz, 2H), 7.84 – 7.78 (m, 1H), 7.71 (d, $J = 7.4$ Hz, 1H), 7.70 – 7.64 (m, 2H), 7.61 (t, $J = 7.6$ Hz, 2H), 7.35 (t, $J = 7.9$ Hz, 1H), 7.16 (s, 1H), 6.99 (d, $J = 7.6$ Hz, 1H), 4.55 (s, 1H), 4.48 (t, $J = 7.2$ Hz, 1H), 4.19 – 4.10 (m, 2H), 3.69 (s, 3H), 3.63 (dd, $J = 8.5, 1.2$ Hz, 1H), 1.40 (d, $J = 6.9$ Hz, 3H).

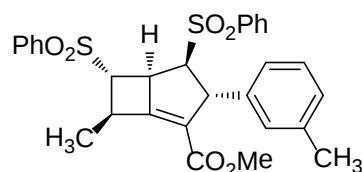
^{13}C NMR (101 MHz, CDCl_3) δ 162.84, 160.80, 148.49, 141.43, 138.18, 136.75, 134.87, 134.31, 132.28, 130.00, 129.87, 129.43, 128.74, 124.34, 122.70, 121.53, 71.88, 61.01, 57.47, 51.88, 48.42, 44.58, 16.96.

IR (KBr): 3065, 2952, 1714, 1674, 1530, 1446, 1350, 1307, 1146, 1084, 726, 688, 603, 585 cm^{-1} .

HRMS (ESI/[$\text{M}+\text{Na}$] $^+$) Calcd. for: $\text{C}_{28}\text{H}_{25}\text{NO}_8\text{S}_2\text{Na}$ 590.0914, found 590.0912.

(3R,4S,5S,6S,7R)-methyl

7-methyl-4,6-bis(phenylsulfonyl)-3-(m-tolyl)bicyclo[3.2.0]hept-1-ene-2-carboxylate (3i)



White solid; mp: 154-157 °C;

^1H NMR (400 MHz, CDCl_3) δ 7.99 – 7.94 (m, 2H), 7.86 – 7.81 (m, 2H), 7.74 (t, J = 7.5 Hz, 1H), 7.69 (t, J = 7.5 Hz, 1H), 7.64 – 7.60 (m, 2H), 7.59 (t, J = 5.5 Hz, 2H), 7.01 (t, J = 7.5 Hz, 1H), 6.95 (d, J = 7.6 Hz, 1H), 6.32 (d, J = 7.5 Hz, 1H), 6.27 (s, 1H), 4.48 (t, J = 7.2 Hz, 1H), 4.41 (s, 1H), 4.13 (m, 2H), 3.67 (s, 3H), 3.60 (dd, J = 8.4, 1.3 Hz, 1H), 2.17 (s, 3H), 1.41 (d, J = 6.9 Hz, 3H).

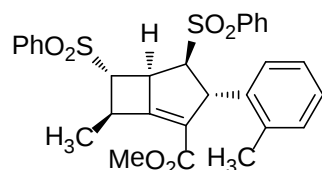
^{13}C NMR (101 MHz, CDCl_3) δ 163.19, 159.49, 138.95, 138.67, 138.33, 137.26, 134.26, 134.20, 129.56, 129.36, 128.88, 128.80, 128.75, 128.35, 126.98, 125.50, 123.31, 72.54, 61.24, 57.71, 51.70, 48.26, 44.14, 21.36, 17.02.

IR (KBr): 3062, 2931, 1714, 1675, 1446, 1306, 1146, 1050, 726, 689, 605, 587, 544 cm^{-1} .

HRMS (MALDI/[$\text{M}+\text{Na}$] $^+$) Calcd. for: $\text{C}_{29}\text{H}_{28}\text{O}_6\text{S}_2\text{Na}$ 559.1220, found 559.1215.

(3R,4S,5S,6S,7R)-methyl

7-methyl-4,6-bis(phenylsulfonyl)-3-(o-tolyl)bicyclo[3.2.0]hept-1-ene-2-carboxylate (3j)



White solid; mp: 187-190 °C;

^1H NMR (400 MHz, CDCl_3) δ 7.96 (d, J = 7.3 Hz, 2H), 7.83 (d, J = 7.3 Hz, 2H), 7.69 (td, J = 7.4, 3.5 Hz, 2H), 7.62 – 7.58 (m, 2H), 7.56 (d, J = 7.6 Hz, 2H), 7.17 – 7.05 (m, 3H), 6.96 (d, J = 7.3 Hz, 1H), 4.72 (s, 1H), 4.54 (t, J = 7.1 Hz, 1H), 4.21 (t, J = 7.4 Hz, 1H), 4.12 (p, J = 6.8 Hz, 1H), 3.72 (d, J = 8.3 Hz, 1H), 3.65 (s, 3H), 1.58 (s, 3H), 1.37 (d, J = 6.9 Hz, 3H).

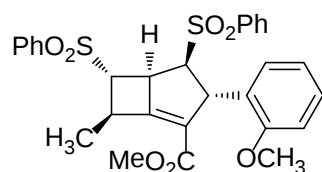
^{13}C NMR (101 MHz, CDCl_3) δ 163.09, 158.64, 138.36, 137.82, 136.96, 135.72, 134.36, 134.21, 130.88, 129.68, 129.40, 128.78, 128.67, 127.70, 127.61, 126.64, 126.47, 72.24, 61.36, 52.84, 51.69, 48.56, 43.66, 18.54, 16.86.

IR (KBr): 3064, 2984, 1714, 1675, 1446, 1306, 1289, 1145, 1085, 726, 688, 649, 603, 586, 538 cm^{-1} .

HRMS (ESI/[$\text{M}+\text{Na}$] $^+$) Calcd. for: $\text{C}_{29}\text{H}_{28}\text{O}_6\text{S}_2\text{Na}$ 559.1220, found 559.1220.

(3R,4S,5S,6S,7R)-methyl

3-(2-methoxyphenyl)-7-methyl-4,6-bis(phenylsulfonyl)bicyclo[3.2.0]hept-1-ene-2-carboxylate (3k)



White solid; mp: 121-124 °C;

¹H NMR (400 MHz, CDCl₃) δ 7.98 (d, *J* = 7.5 Hz, 2H), 7.85 (d, *J* = 7.5 Hz, 2H), 7.68 (t, *J* = 7.2 Hz, 2H), 7.61 – 7.54 (m, 4H), 7.19 – 7.13 (m, 1H), 6.91 (dd, *J* = 7.5, 1.2 Hz, 1H), 6.79 (t, *J* = 7.4 Hz, 1H), 6.66 (d, *J* = 8.2 Hz, 1H), 4.69 (s, 1H), 4.58 (t, *J* = 7.2 Hz, 1H), 4.12 (p, *J* = 6.9 Hz, 1H), 4.04 (t, *J* = 7.4 Hz, 1H), 3.69 (s, 3H), 3.66 (d, *J* = 7.9 Hz, 1H), 3.21 (s, 3H), 1.42 (d, *J* = 6.9 Hz, 3H).

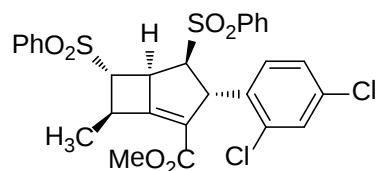
¹³C NMR (101 MHz, CDCl₃) δ 163.33, 160.11, 156.71, 138.54, 138.35, 134.07, 133.79, 129.31, 129.22, 129.12, 128.98, 128.70, 128.02, 125.96, 125.24, 120.55, 110.45, 71.56, 61.53, 54.95, 52.11, 51.62, 48.37, 43.62, 16.90.

IR (KBr): 2951, 1714, 1491, 1446, 1306, 1145, 1084, 731, 602, 587 cm⁻¹.

HRMS (ESI/[M+NH₄]⁺) Calcd. for: C₂₉H₃₂NO₇S₂ 570.1615, found 570.1619.

(3S,4S,5S,6S,7R)-methyl

3-(2,4-dichlorophenyl)-7-methyl-4,6-bis(phenylsulfonyl)bicyclo[3.2.0]hept-1-ene-2-carboxylate (3l)



White solid; mp: 107-110 °C;

¹H NMR (400 MHz, CDCl₃) δ 7.98 (d, *J* = 7.4 Hz, 2H), 7.84 (d, *J* = 7.4 Hz, 2H), 7.71 (d, *J* = 7.5 Hz, 1H), 7.69 – 7.65 (m, 1H), 7.63 – 7.53 (m, 4H), 7.18 (d, *J* = 2.0 Hz, 1H), 7.14 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.03 (d, *J* = 8.4 Hz, 1H), 4.77 (s, 1H), 4.61 (t, *J* = 7.1 Hz, 1H), 4.19 – 4.06 (m, 2H), 3.68 (s, 3H), 3.66 (d, *J* = 8.0 Hz, 1H), 1.43 (d, *J* = 6.9 Hz, 3H).

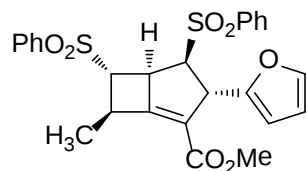
¹³C NMR (101 MHz, CDCl₃) δ 162.79, 160.64, 138.29, 137.38, 134.45, 134.35, 134.29, 134.26, 133.89, 129.93, 129.59, 129.48, 129.41, 129.26, 128.68, 127.55, 125.63, 71.39, 61.31, 53.57, 51.85, 48.35, 43.74, 16.90.

IR (KBr): 3065, 2986, 2952, 1715, 1675, 1446, 1307, 1145, 1085, 727, 688, 602, 587 cm⁻¹.

HRMS (ESI/[M+Na]⁺) Calcd. for: C₂₈H₂₄Cl₂O₆S₂Na 613.0284, found 613.0282.

(3S,4S,5S,6S,7R)-methyl

3-(furan-2-yl)-7-methyl-4,6-bis(phenylsulfonyl)bicyclo[3.2.0]hept-1-ene-2-carboxylate (3m)



White solid; mp: 155-157 °C;

¹H NMR (400 MHz, CDCl₃) δ 7.98 (d, *J* = 7.5 Hz, 2H), 7.83 (d, *J* = 7.5 Hz, 2H), 7.73 – 7.66 (m, 2H), 7.63 – 7.56 (m, 4H), 7.17 (d, *J* = 0.8 Hz, 1H), 6.17 – 6.13 (m, 1H), 5.73 (d, *J* = 3.1 Hz, 1H), 4.49 (s, 1H), 4.45 (t, *J* = 7.2 Hz, 1H), 4.18 (t, *J* = 7.6 Hz, 1H), 4.05 (p, *J* = 7.0 Hz, 1H), 3.88 – 3.84 (m, 1H), 3.71 (s, 3H), 1.35 (d, *J* = 6.9 Hz, 3H).

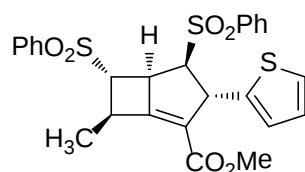
¹³C NMR (101 MHz, CDCl₃) δ 162.93, 160.09, 151.63, 142.42, 138.33, 137.14, 134.28, 134.20, 129.51, 129.39, 128.70, 128.53, 123.62, 110.45, 106.52, 69.70, 61.27, 51.73, 50.96, 48.52, 44.00, 16.82.

IR (KBr): 2953, 1716, 1446, 1306, 1145, 1084, 727, 688, 598, 584 cm^{-1} .

HRMS (ESI/[M+NH₄]⁺) Calcd. for: C₂₆H₂₈NO₇S₂ 530.1302, found 530.1303.

(3R,4R,5S,6S,7R)-methyl

7-methyl-4,6-bis(phenylsulfonyl)-3-(thiophen-2-yl)bicyclo[3.2.0]hept-1-ene-2-carboxylate (3n)



White solid; mp: 210-211 °C;

¹H NMR (400 MHz, CDCl₃) δ 8.00 – 7.95 (m, 2H), 7.87 – 7.82 (m, 2H), 7.76 – 7.67 (m, 2H), 7.65 – 7.57 (m, 4H), 7.06 (dd, J = 5.1, 1.0 Hz, 1H), 6.77 (dd, J = 5.1, 3.5 Hz, 1H), 6.27 (d, J = 3.4 Hz, 1H), 4.69 (s, 1H), 4.45 (t, J = 7.2 Hz, 1H), 4.19 – 4.06 (m, 2H), 3.75 – 3.69 (m, 4H), 1.39 (d, J = 6.9 Hz, 3H).

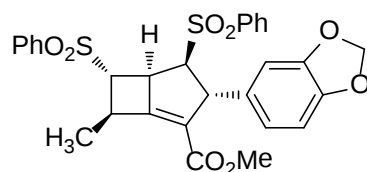
¹³C NMR (101 MHz, CDCl₃) δ 162.93, 159.62, 142.63, 138.28, 137.08, 134.44, 134.25, 129.68, 129.40, 128.76, 128.71, 127.27, 125.61, 124.92, 124.36, 72.57, 61.15, 52.78, 51.83, 48.08, 44.16, 16.93.

IR (KBr): 3063, 2982, 2952, 1715, 1674, 1446, 1306, 1290, 1146, 1084, 726, 689, 605, 587 cm^{-1} .

HRMS (ESI/[M+Na]⁺) Calcd. for: C₂₆H₂₄O₆S₃Na 551.0627, found 551.0630.

(3R,4S,5S,6S,7R)-methyl

3-(benzo[d][1,3]dioxol-5-yl)-7-methyl-4,6-bis(phenylsulfonyl)bicyclo[3.2.0]hept-1-ene-2-carboxylate (3o)



White solid; mp: 187-188 °C;

¹H NMR (400 MHz, CDCl₃) δ 7.97 (d, J = 7.4 Hz, 2H), 7.84 (d, J = 7.5 Hz, 2H), 7.74 (t, J = 7.4 Hz, 1H), 7.69 (t, J = 7.6 Hz, 1H), 7.65 – 7.56 (m, 4H), 6.55 (d, J = 7.9 Hz, 1H), 6.01 (d, J = 8.0 Hz, 1H), 5.96 (s, 1H), 5.87 (s, 2H), 4.46 (t, J = 7.2 Hz, 1H), 4.37 (s, 1H), 4.15 – 4.05 (m, 2H), 3.68 (s, 3H), 3.58 (d, J = 8.3 Hz, 1H), 1.38 (d, J = 6.9 Hz, 3H).

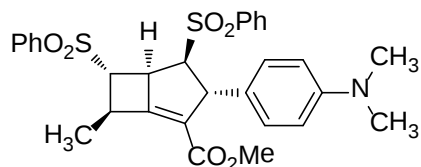
¹³C NMR (101 MHz, CDCl₃) δ 163.13, 159.41, 148.11, 147.03, 138.29, 137.13, 134.39, 134.23, 132.77, 129.62, 129.39, 128.79, 128.73, 125.58, 119.47, 108.50, 106.73, 101.18, 72.45, 61.14, 57.49, 51.74, 48.11, 44.16, 16.97.

IR (KBr): 3063, 2982, 2952, 1714, 1673, 1488, 1445, 1306, 1146, 1085, 1038, 931, 727, 688, 653 cm^{-1} .

HRMS (ESI/[M+Na]⁺) Calcd. for: C₂₉H₂₆O₈S₂Na 589.0961, found 589.0956.

(3R,4S,5S,6S,7R)-methyl

3-(4-(dimethylamino)phenyl)-7-methyl-4,6-bis(phenylsulfonyl)bicyclo[3.2.0]hept-1-ene-2-carboxylate (3p)



White solid; mp: 112-115 °C;

^1H NMR (400 MHz, CDCl_3) δ 7.96 (d, J = 7.6 Hz, 2H), 7.82 (d, J = 7.5 Hz, 2H), 7.75 – 7.66 (m, 2H), 7.63 – 7.55 (m, 4H), 6.48 (d, J = 8.6 Hz, 2H), 6.41 (d, J = 8.6 Hz, 2H), 4.47 (t, J = 7.2 Hz, 1H), 4.37 (s, 1H), 4.18 – 4.04 (m, 2H), 3.66 (s, 3H), 3.58 (d, J = 8.2 Hz, 1H), 2.86 (s, 6H), 1.40 (d, J = 6.9 Hz, 3H).

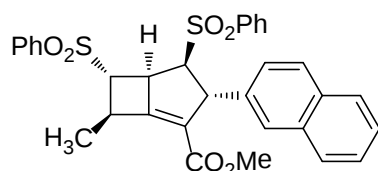
^{13}C NMR (101 MHz, CDCl_3) δ 163.28, 158.70, 149.88, 138.36, 137.39, 134.17, 129.51, 129.34, 128.78, 128.76, 127.07, 126.40, 126.02, 112.68, 72.77, 61.27, 57.05, 51.65, 48.10, 43.97, 40.50, 17.02.

IR (KBr): 3063, 2951, 1715, 1613, 1521, 1446, 1306, 1145, 1085, 726, 602, 586 cm^{-1} .

HRMS (ESI/[M+H] $^+$) Calcd. for: $\text{C}_{30}\text{H}_{32}\text{NO}_6\text{S}_2$ 566.1666, found 566.1673.

(3R,4S,5S,6S,7R)-methyl

7-methyl-3-(naphthalen-2-yl)-4,6-bis(phenylsulfonyl)bicyclo[3.2.0]hept-1-ene-2-carboxylate (3q)



White solid; mp: 204-205 °C;

^1H NMR (400 MHz, CDCl_3) δ 7.97 (d, J = 7.8 Hz, 2H), 7.86 (d, J = 7.7 Hz, 2H), 7.81 – 7.70 (m, 2H), 7.70 – 7.56 (m, 7H), 7.47 – 7.39 (m, 2H), 7.02 (s, 1H), 6.55 (d, J = 8.3 Hz, 1H), 4.61 (s, 1H), 4.51 (t, J = 7.1 Hz, 1H), 4.24 – 4.10 (m, 2H), 3.69 (d, J = 8.5 Hz, 1H), 3.66 (s, 3H), 1.44 (d, J = 6.8 Hz, 3H).

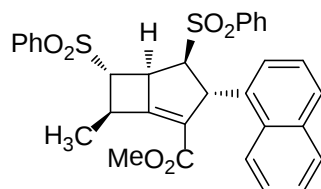
^{13}C NMR (101 MHz, CDCl_3) δ 163.19, 159.80, 138.30, 137.29, 136.44, 134.35, 134.23, 133.27, 132.67, 129.67, 129.39, 128.96, 128.90, 128.77, 127.77, 127.58, 126.49, 126.15, 125.47, 125.09, 124.34, 72.35, 61.25, 57.97, 51.76, 48.39, 44.28, 17.05.

IR (KBr): 3060, 2951, 1714, 1674, 1446, 1306, 1145, 1085, 726, 688, 600, 585 cm^{-1} .

HRMS (MALDI/[M+Na] $^+$) Calcd. for: $\text{C}_{32}\text{H}_{28}\text{O}_6\text{S}_2\text{Na}$ 595.1220, found 595.1215.

(3R,4S,5S,6S,7R)-methyl

7-methyl-3-(naphthalen-1-yl)-4,6-bis(phenylsulfonyl)bicyclo[3.2.0]hept-1-ene-2-carboxylate (3r)



White solid; mp: 132-135 °C;

^1H NMR (400 MHz, CDCl_3) δ 7.93 – 7.88 (m, 4H), 7.80 (t, J = 8.0 Hz, 2H), 7.74 (d, J = 7.8 Hz, 1H), 7.70 – 7.62 (m, 3H), 7.57 (t, J = 7.7 Hz, 2H), 7.41 – 7.33 (m, 3H), 7.02 (t, J = 7.6 Hz, 1H), 6.83 (d, J = 8.6 Hz, 1H), 5.30 (s, 1H), 4.59 (t, J = 7.0 Hz, 1H), 4.17 (p, J = 6.9 Hz, 1H), 4.02 (t, J = 7.1 Hz, 1H),

3.71 (d, $J = 7.4$ Hz, 1H), 3.66 (s, 3H), 1.45 (d, $J = 6.9$ Hz, 3H).

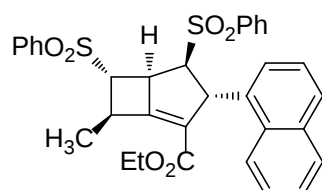
^{13}C NMR (101 MHz, CDCl_3) δ 163.13, 160.34, 138.26, 137.93, 134.56, 134.24, 134.21, 133.52, 130.94, 129.96, 129.45, 129.06, 128.93, 128.75, 128.60, 126.45, 125.71, 125.53, 124.50, 122.35, 72.62, 61.40, 52.24, 51.82, 47.74, 43.46, 16.82.

IR (KBr): 3060, 2987, 2951, 1715, 1678, 1446, 1307, 1145, 1084, 730, 688, 599, 587, 544 cm^{-1} .

HRMS (ESI/[$\text{M}+\text{Na}$] $^+$) Calcd. for: $\text{C}_{32}\text{H}_{28}\text{O}_6\text{S}_2\text{Na}$ 595.1220, found 595.1219.

(3R,4S,5S,6S,7R)-ethyl

7-methyl-3-(naphthalen-1-yl)-4,6-bis(phenylsulfonyl)bicyclo[3.2.0]hept-1-ene-2-carboxylate (3s)



White solid; mp: 196-199 $^{\circ}\text{C}$;

^1H NMR (400 MHz, CDCl_3) δ 7.91 (t, $J = 7.3$ Hz, 4H), 7.79 (t, $J = 8.3$ Hz, 2H), 7.73 (d, $J = 7.4$ Hz, 1H), 7.70 – 7.61 (m, 3H), 7.57 (t, $J = 7.7$ Hz, 2H), 7.41 – 7.33 (m, 3H), 7.00 (t, $J = 7.3$ Hz, 1H), 6.80 (d, $J = 8.6$ Hz, 1H), 5.29 (s, 1H), 4.60 (t, $J = 7.1$ Hz, 1H), 4.21 – 4.07 (m, 3H), 4.04 (t, $J = 7.3$ Hz, 1H), 3.70 (d, $J = 7.5$ Hz, 1H), 1.46 (d, $J = 6.9$ Hz, 3H), 1.20 (t, $J = 7.1$ Hz, 3H).

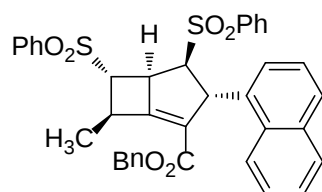
^{13}C NMR (101 MHz, CDCl_3) δ 162.71, 159.45, 138.30, 137.94, 134.48, 134.17, 133.66, 130.92, 129.90, 129.40, 129.09, 128.86, 128.64, 128.60, 126.93, 126.33, 125.62, 125.49, 124.45, 122.35, 72.55, 61.35, 60.80, 52.34, 47.89, 43.36, 16.94, 14.15.

IR (KBr): 3061, 2983, 1710, 1447, 1306, 1145, 1084, 729, 688, 652, 599, 586, 544 cm^{-1} .

HRMS (MALDI/[$\text{M}+\text{Na}$] $^+$) Calcd. for: $\text{C}_{33}\text{H}_{30}\text{O}_6\text{S}_2\text{Na}$ 609.1376, found 609.1380.

(3R,4S,5S,6S,7R)-benzyl

7-methyl-3-(naphthalen-1-yl)-4,6-bis(phenylsulfonyl)bicyclo[3.2.0]hept-1-ene-2-carboxylate (3t)



White solid; mp: 139-142 $^{\circ}\text{C}$;

^1H NMR (400 MHz, CDCl_3) δ 7.90 (t, $J = 7.6$ Hz, 4H), 7.81 – 7.76 (m, 2H), 7.74 (dd, $J = 7.1, 1.9$ Hz, 1H), 7.66 (t, $J = 7.5$ Hz, 1H), 7.61 (t, $J = 7.8$ Hz, 2H), 7.56 (t, $J = 7.7$ Hz, 2H), 7.41 – 7.33 (m, 3H), 7.26 – 7.21 (m, 3H), 7.15 – 7.10 (m, 2H), 6.98 (t, $J = 7.5$ Hz, 1H), 6.77 (d, $J = 8.5$ Hz, 1H), 5.33 (s, 1H), 5.09 (s, 2H), 4.58 (t, $J = 7.0$ Hz, 1H), 4.17 – 4.08 (m, 1H), 4.05 (t, $J = 7.1$ Hz, 1H), 3.72 (d, $J = 7.5$ Hz, 1H), 1.35 (d, $J = 6.9$ Hz, 3H).

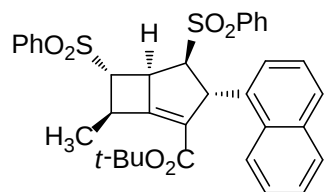
^{13}C NMR (101 MHz, CDCl_3) δ 162.43, 160.51, 138.29, 137.90, 135.49, 134.51, 134.20, 133.59, 130.92, 129.92, 129.42, 129.12, 128.89, 128.72, 128.60, 128.49, 128.18, 127.99, 126.65, 126.38, 125.67, 125.51, 124.56, 122.31, 72.47, 66.50, 61.31, 52.36, 47.87, 43.53, 16.92.

IR (KBr): 3063, 2958, 2930, 1711, 1677, 1447, 1306, 1144, 1084, 784, 727, 688, 599, 586, 544 cm^{-1} .

HRMS (ESI/[M+Na]⁺) Calcd. for: C₃₈H₃₂O₆S₂Na 671.1533, found 671.1536.

(3R,4S,5S,6S,7R)-tert-butyl

7-methyl-3-(naphthalen-1-yl)-4,6-bis(phenylsulfonyl)bicyclo[3.2.0]hept-1-ene-2-carboxylate (3u)



White solid; mp: 210-213 °C;

¹H NMR (400 MHz, CDCl₃) δ 7.94 – 7.88 (m, 4H), 7.82 – 7.76 (m, 2H), 7.73 (dd, *J* = 7.3, 1.8 Hz, 1H), 7.69 – 7.61 (m, 3H), 7.56 (t, *J* = 7.7 Hz, 2H), 7.42 – 7.32 (m, 3H), 7.02 – 6.95 (m, 1H), 6.79 (d, *J* = 8.5 Hz, 1H), 5.26 (s, 1H), 4.58 (t, *J* = 7.1 Hz, 1H), 4.14 (p, *J* = 6.9 Hz, 1H), 4.01 (t, *J* = 7.2 Hz, 1H), 3.65 (d, *J* = 7.6 Hz, 1H), 1.46 (d, *J* = 6.9 Hz, 3H), 1.38 (s, 9H).

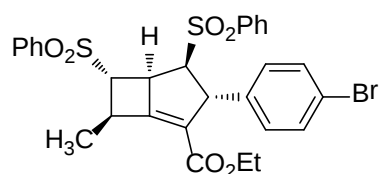
¹³C NMR (101 MHz, CDCl₃) δ 162.13, 157.81, 138.35, 138.06, 134.43, 134.17, 134.14, 133.90, 130.96, 129.87, 129.38, 129.13, 128.81, 128.60, 128.57, 128.53, 126.29, 125.57, 125.50, 124.33, 122.36, 81.51, 72.47, 61.40, 52.46, 47.77, 43.16, 28.16, 17.10.

IR (KBr): 3061, 2978, 2932, 1704, 1675, 1447, 1307, 1146, 1085, 729, 688, 599, 586, 544 cm⁻¹.

HRMS (ESI/[M+Na]⁺) Calcd. for: C₃₅H₃₄O₆S₂Na 637.1689, found 637.1685.

(3R,4S,5S,6S,7R)-ethyl

3-(4-bromophenyl)-7-methyl-4,6-bis(phenylsulfonyl)bicyclo[3.2.0]hept-1-ene-2-carboxylate (3v)



White solid; mp: 204-207 °C;

¹H NMR (400 MHz, CDCl₃) δ 7.97 (d, *J* = 7.4 Hz, 2H), 7.83 (d, *J* = 7.4 Hz, 2H), 7.76 – 7.66 (m, 2H), 7.62 (d, *J* = 7.4 Hz, 2H), 7.59 (d, *J* = 7.4 Hz, 2H), 7.26 (d, *J* = 7.2 Hz, 2H), 6.43 (d, *J* = 8.3 Hz, 2H), 4.47 (t, *J* = 7.2 Hz, 1H), 4.41 (s, 1H), 4.23 – 4.02 (m, 4H), 3.59 (d, *J* = 7.5 Hz, 1H), 1.39 (d, *J* = 6.9 Hz, 3H), 1.22 (t, *J* = 7.1 Hz, 3H).

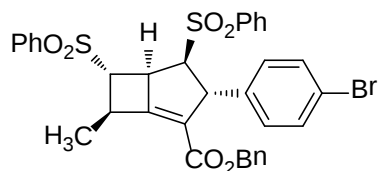
¹³C NMR (101 MHz, CDCl₃) δ 162.55, 158.98, 138.28, 138.24, 137.09, 134.39, 134.21, 131.99, 129.60, 129.37, 128.74, 128.70, 128.08, 125.63, 121.50, 71.95, 61.06, 60.83, 57.37, 48.36, 44.17, 17.08, 14.09.

IR (KBr): 3063, 2978, 2929, 1709, 1674, 1446, 1306, 1145, 1084, 724, 688, 602, 586 cm⁻¹.

HRMS (MALDI/[M+Na]⁺) Calcd. for: C₂₉H₂₇BrO₆S₂Na 637.0325, found 637.0323.

(3R,4S,5S,6S,7R)-benzyl

3-(4-bromophenyl)-7-methyl-4,6-bis(phenylsulfonyl)bicyclo[3.2.0]hept-1-ene-2-carboxylate (3w)



White solid; mp: 202-203 °C;

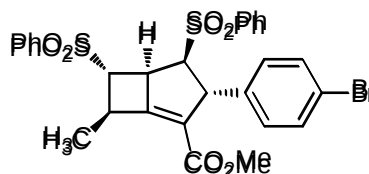
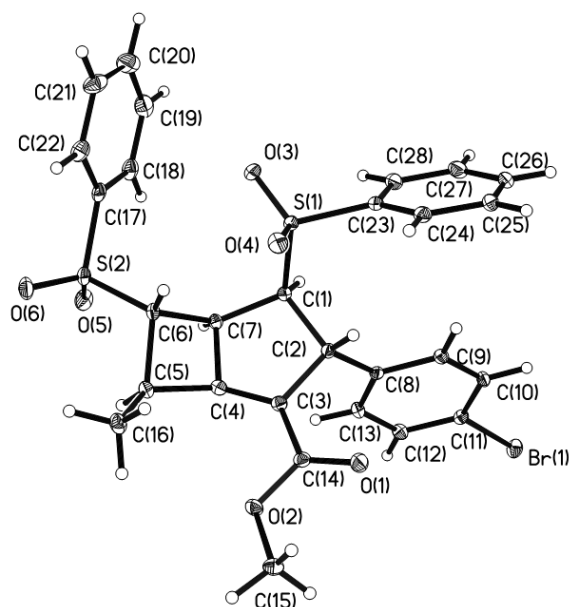
^1H NMR (400 MHz, CDCl_3) δ 7.98 – 7.92 (m, 2H), 7.83 (d, J = 7.3 Hz, 2H), 7.73 (t, J = 7.5 Hz, 1H), 7.68 (t, J = 7.6 Hz, 1H), 7.61 (d, J = 7.6 Hz, 2H), 7.57 (d, J = 7.4 Hz, 2H), 7.33 – 7.28 (m, 3H), 7.25 (d, J = 7.1 Hz, 2H), 7.18 – 7.13 (m, 2H), 6.42 (d, J = 8.4 Hz, 2H), 5.14 (d, J = 12.4 Hz, 1H), 5.04 (d, J = 12.4 Hz, 1H), 4.44 (t, J = 7.2 Hz, 2H), 4.14 – 4.00 (m, 2H), 3.61 (dd, J = 8.4, 1.3 Hz, 1H), 1.27 (d, J = 6.9 Hz, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 162.27, 160.03, 138.22, 137.07, 135.30, 134.40, 134.21, 132.03, 129.61, 129.37, 128.76, 128.67, 128.51, 128.31, 128.12, 125.29, 121.56, 71.86, 66.59, 61.00, 57.41, 48.31, 44.37, 17.04.

IR (KBr): 3063, 2954, 2927, 1710, 1673, 1486, 1447, 1306, 1145, 1084, 725, 688, 601, 586 cm^{-1} .

HRMS (MALDI/[$\text{M}+\text{Na}$] $^+$) Calcd. for: $\text{C}_{34}\text{H}_{29}\text{BrO}_6\text{S}_2\text{Na}$ 699.0481, found 699.0479.

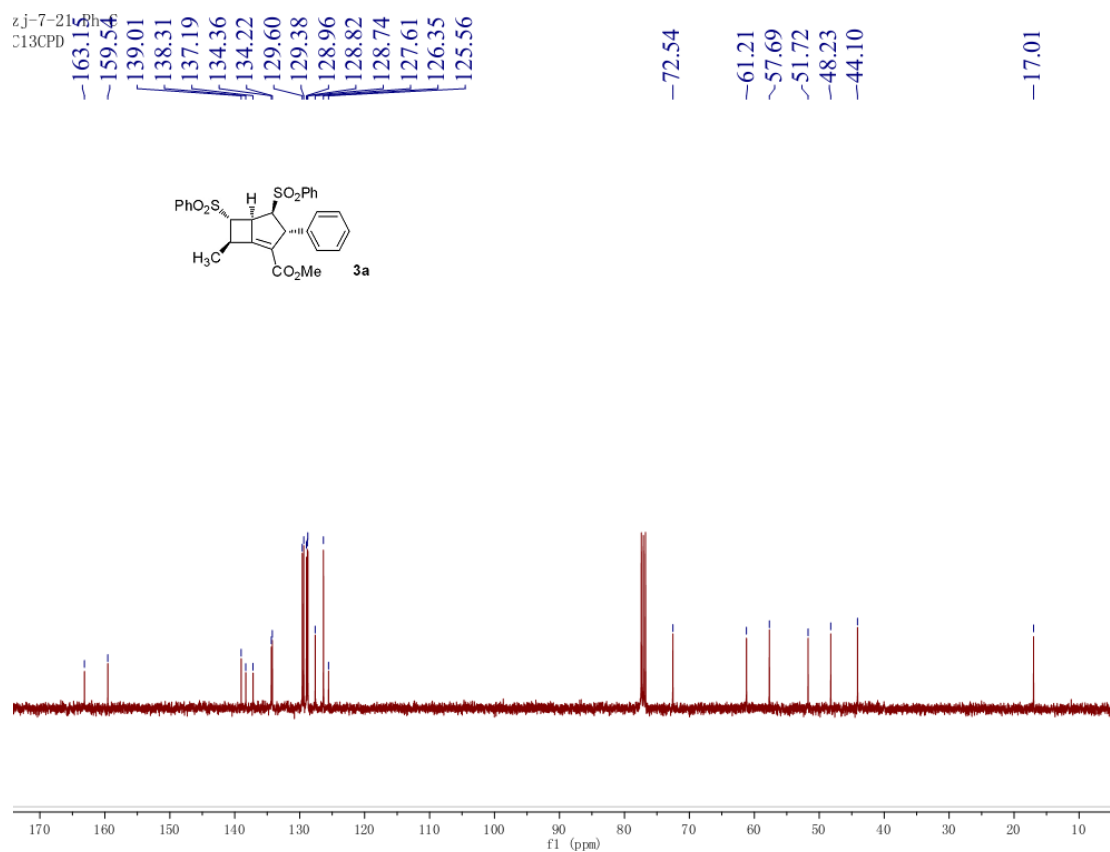
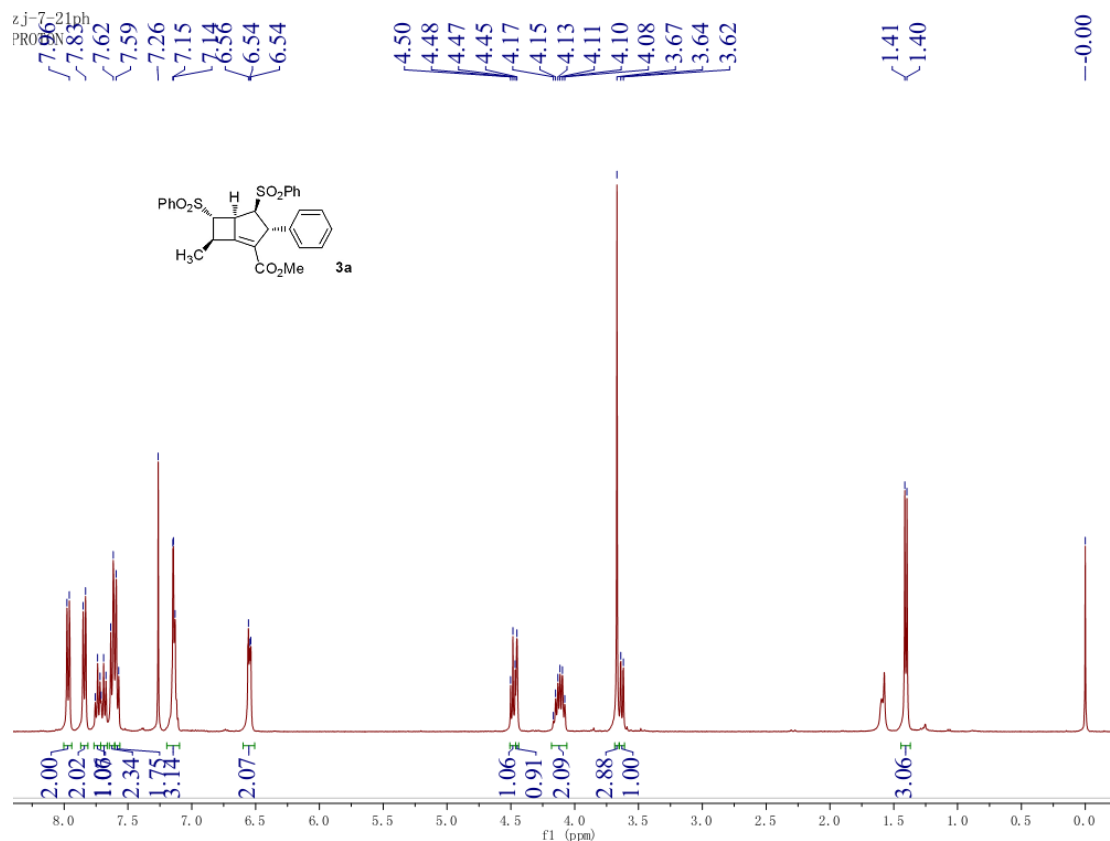
5 X-Ray Crystallography Data

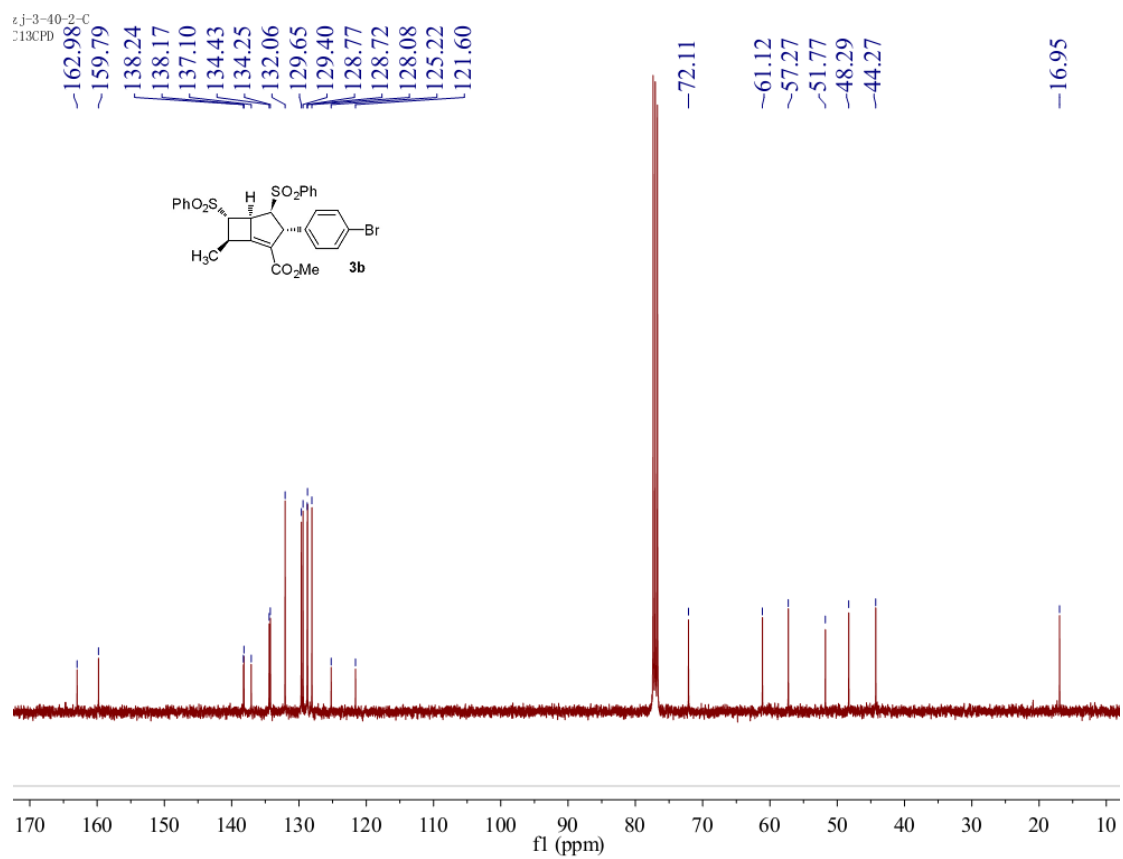
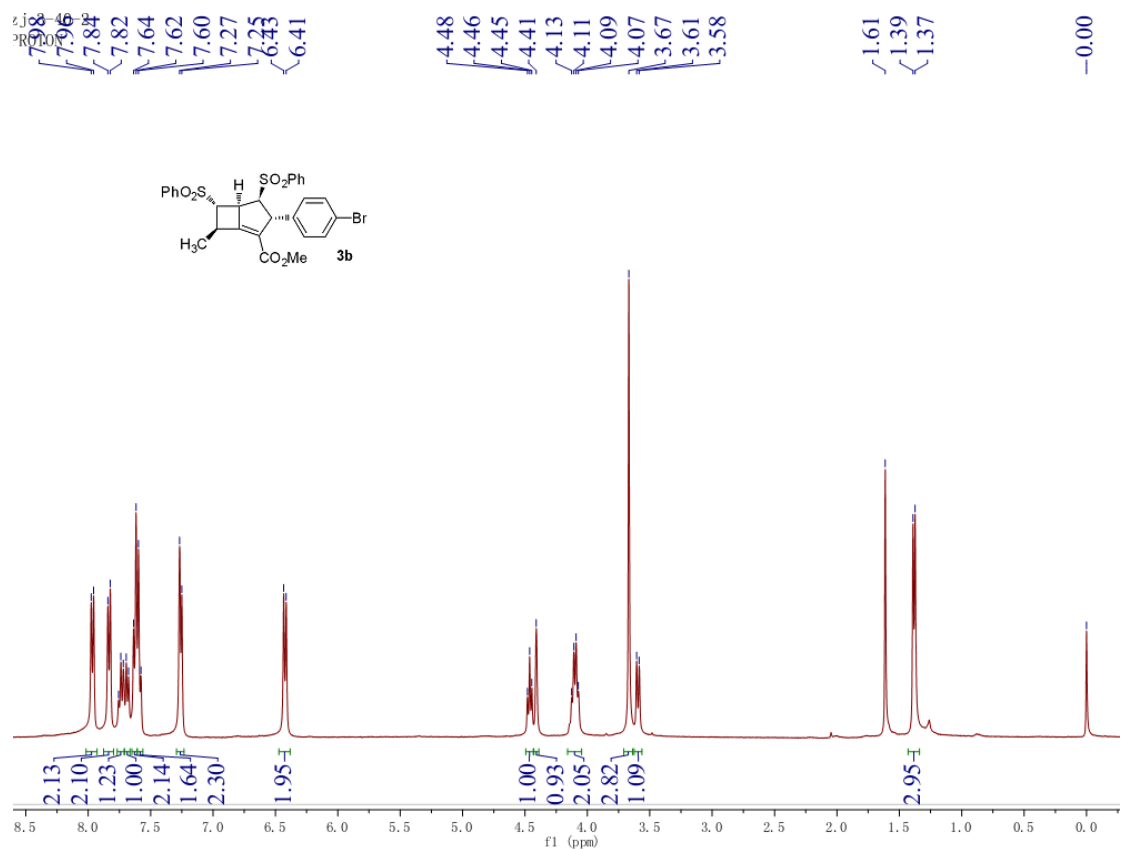


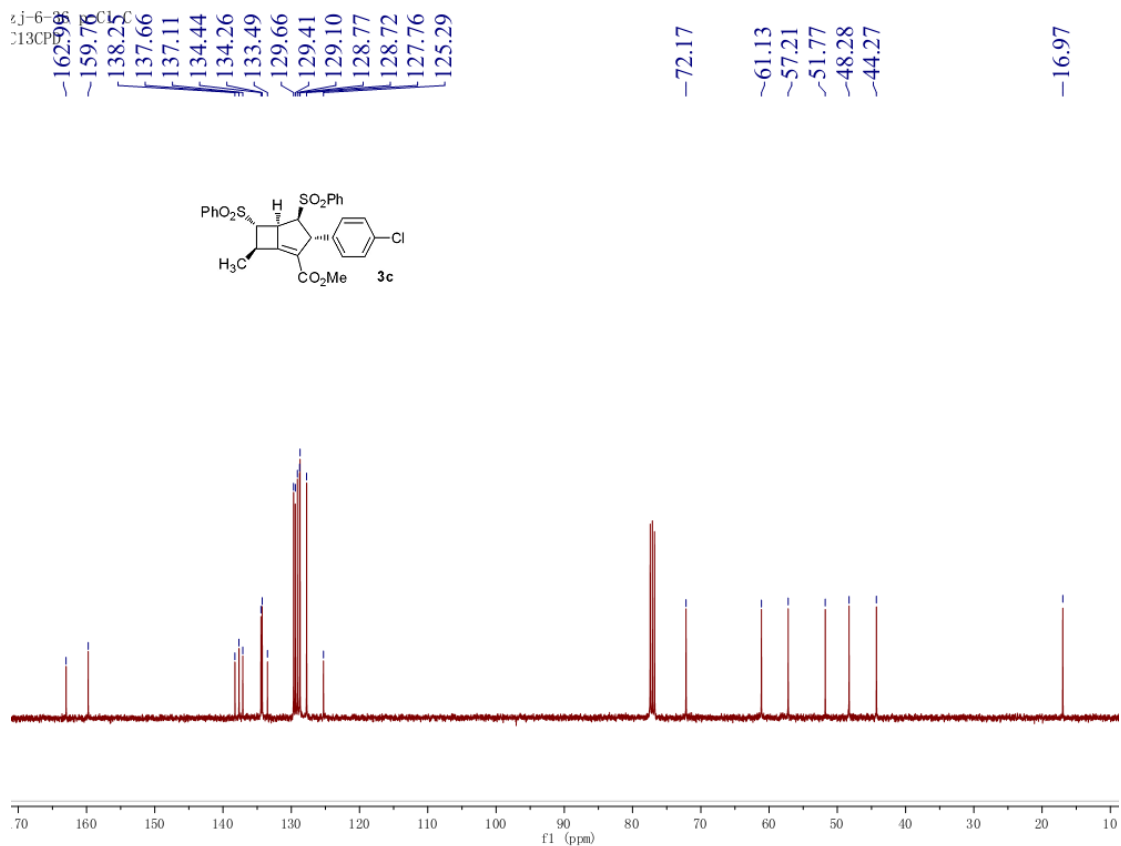
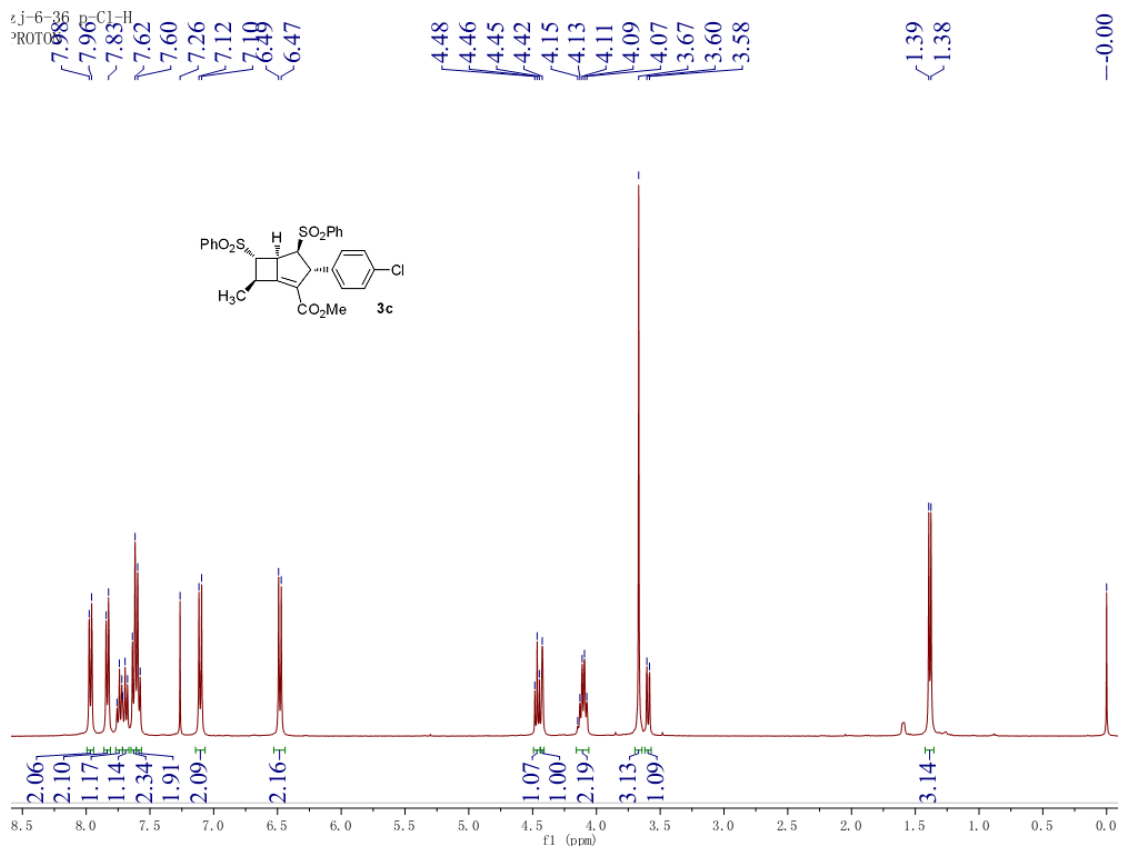
CCDC 921601

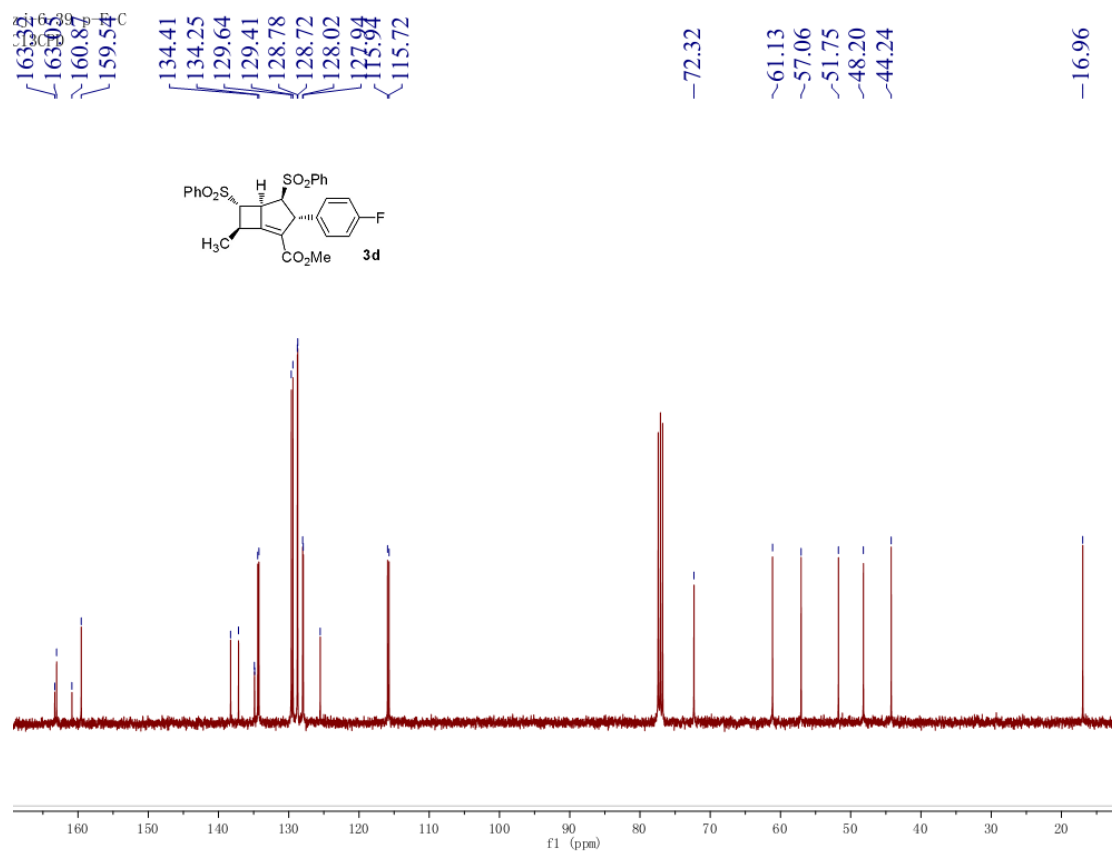
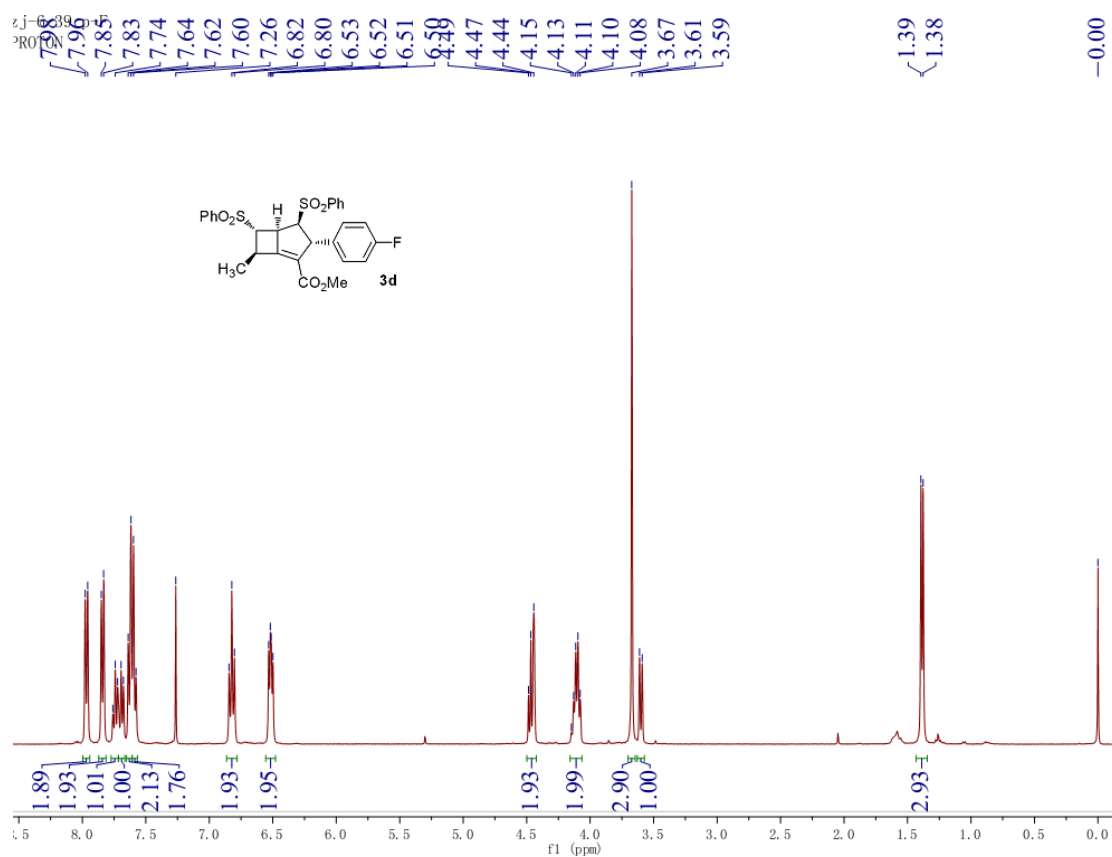
X-ray chromatograph of compound **3b**

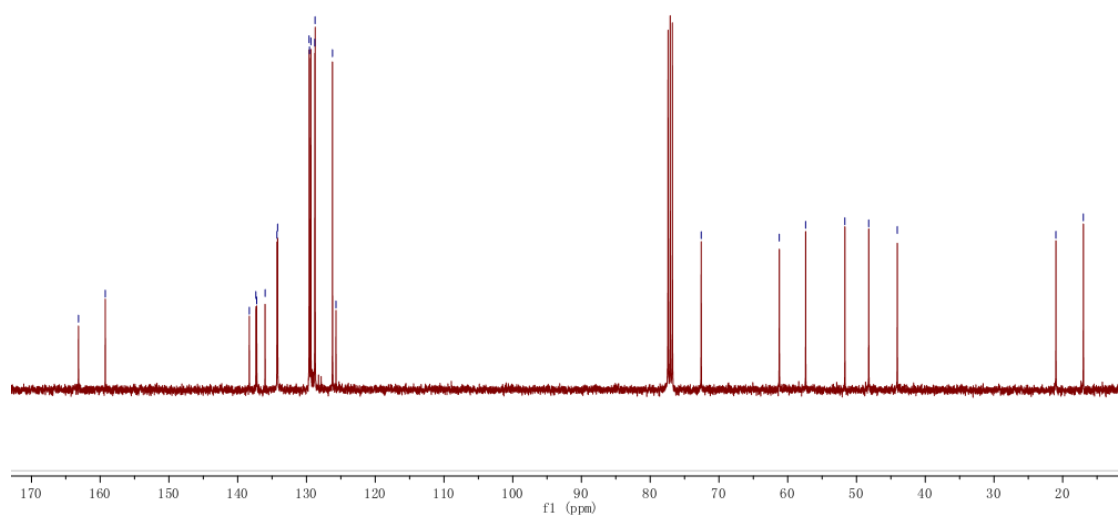
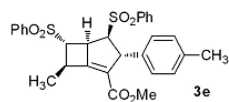
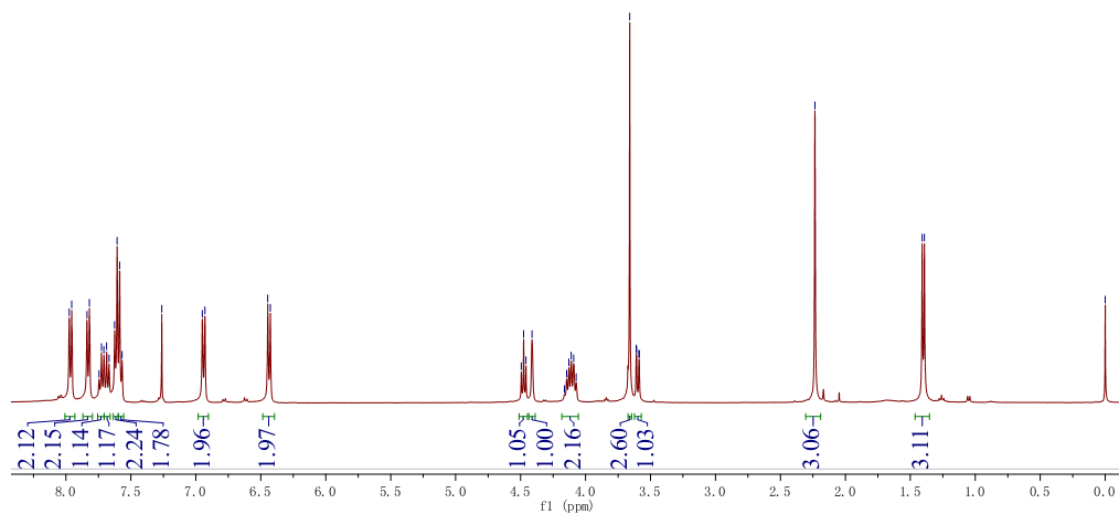
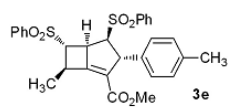
^1H and ^{13}C Spectra of Compound 3a-3w

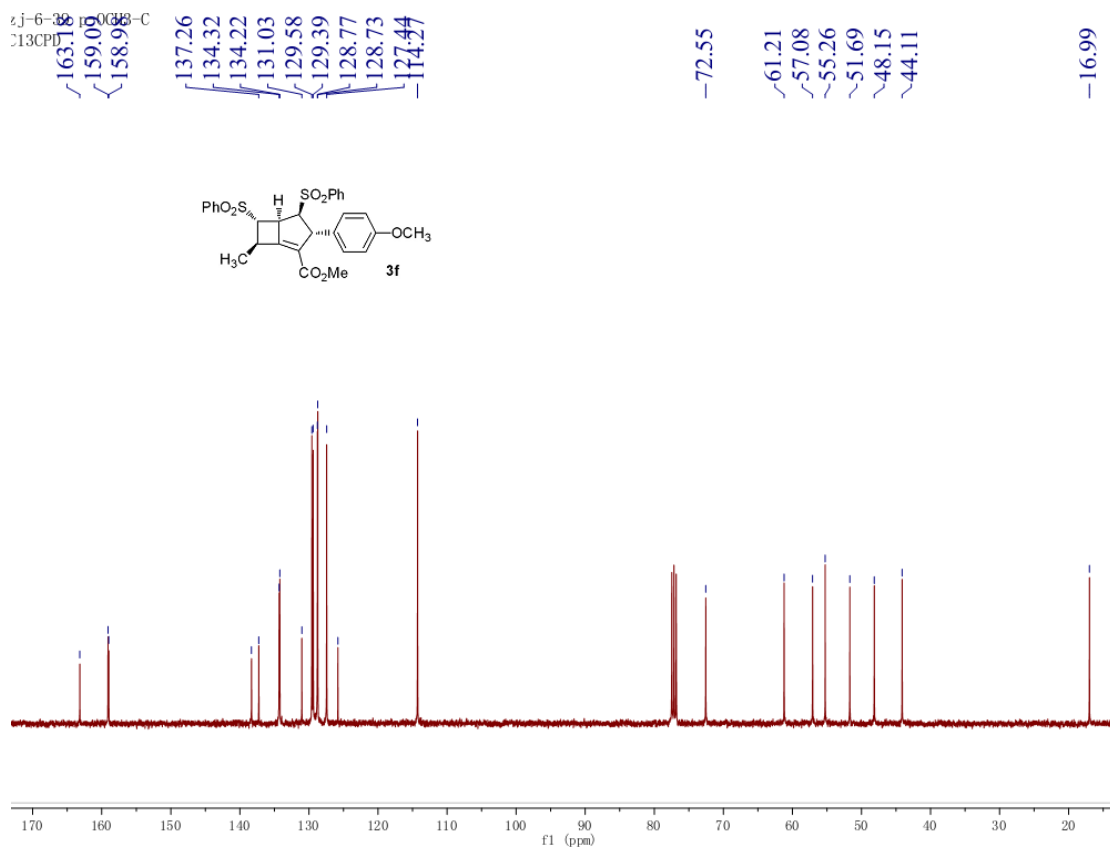
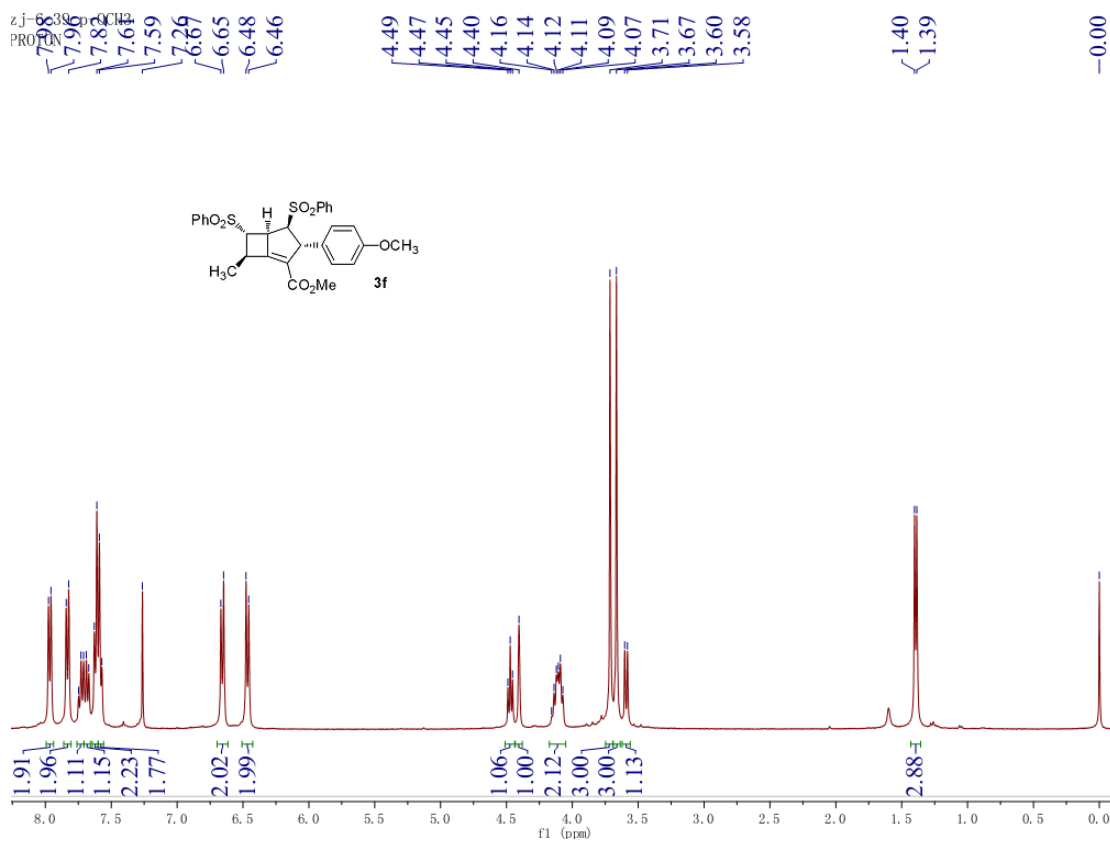


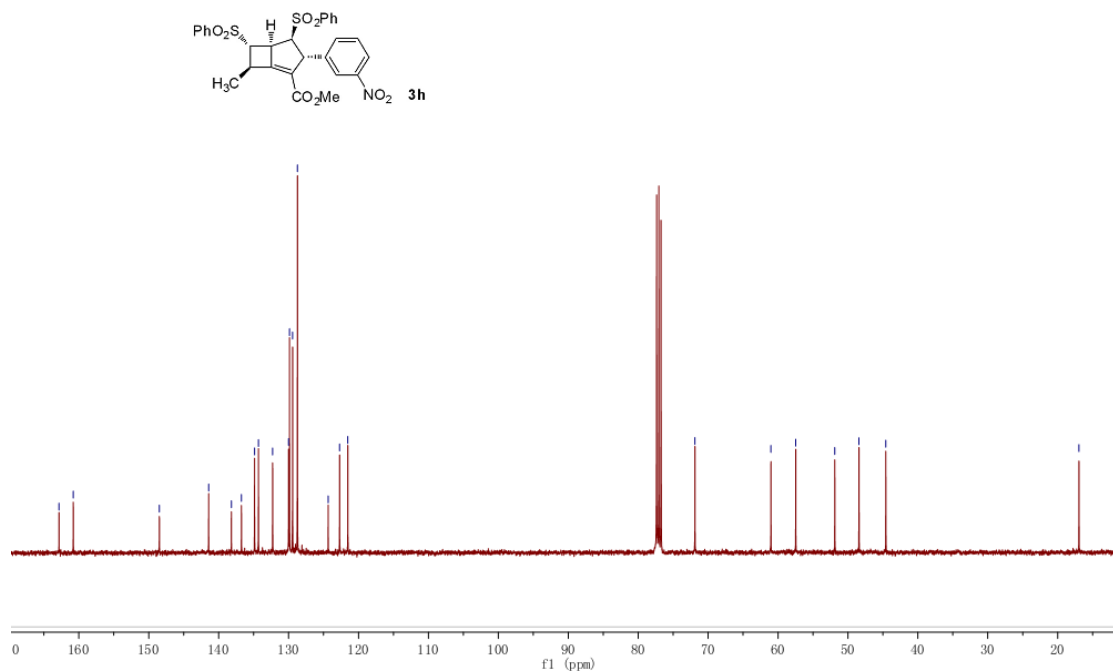
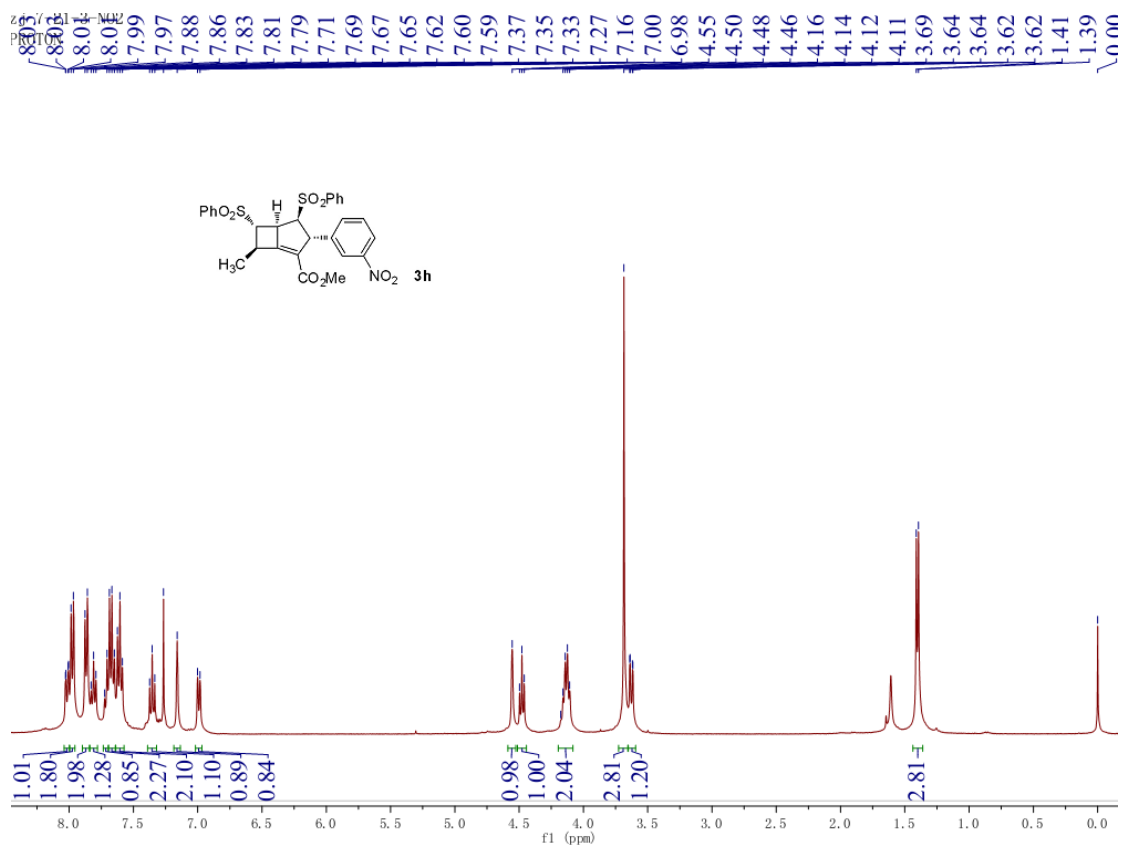


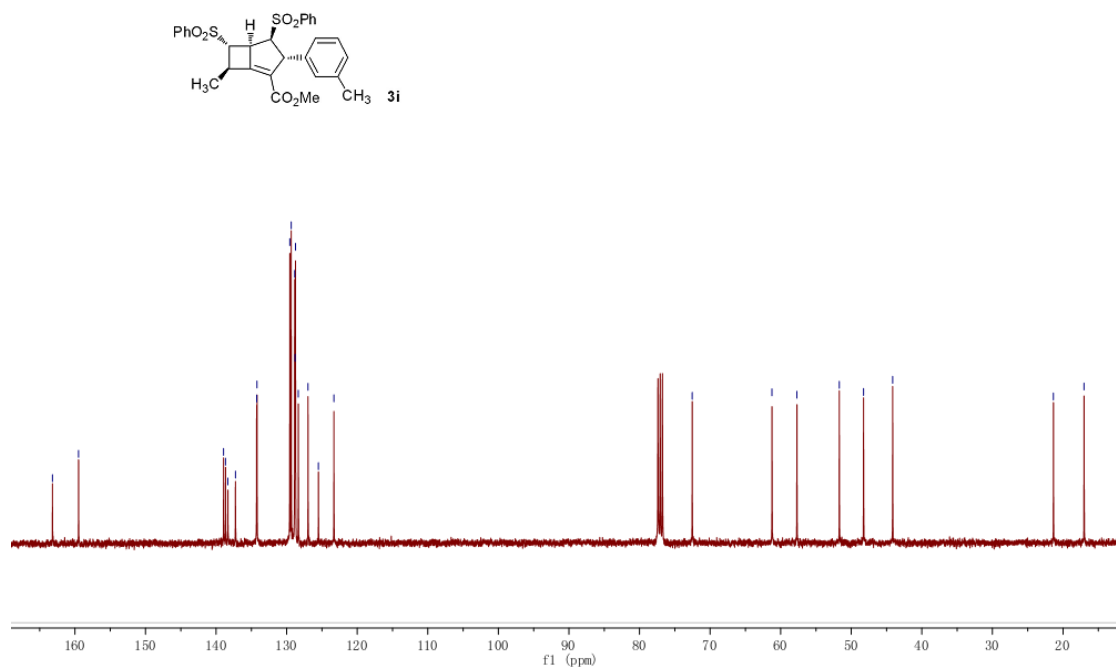
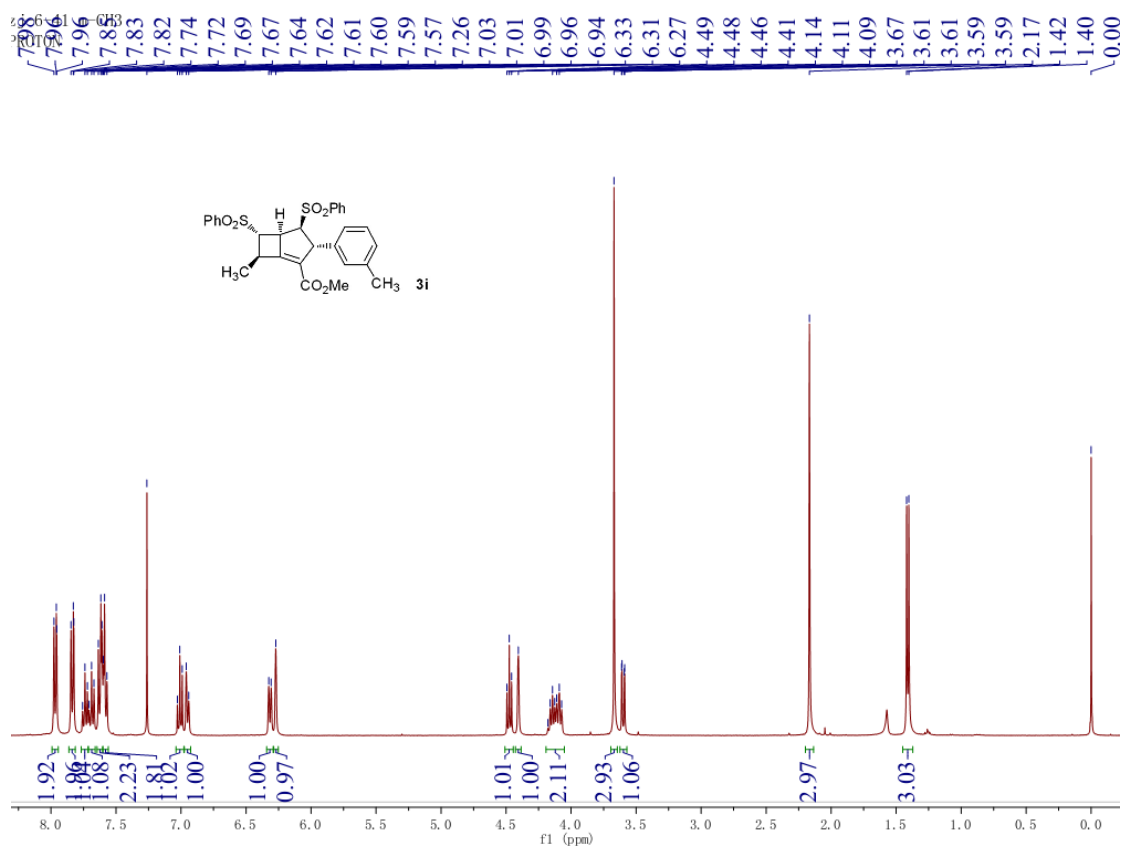


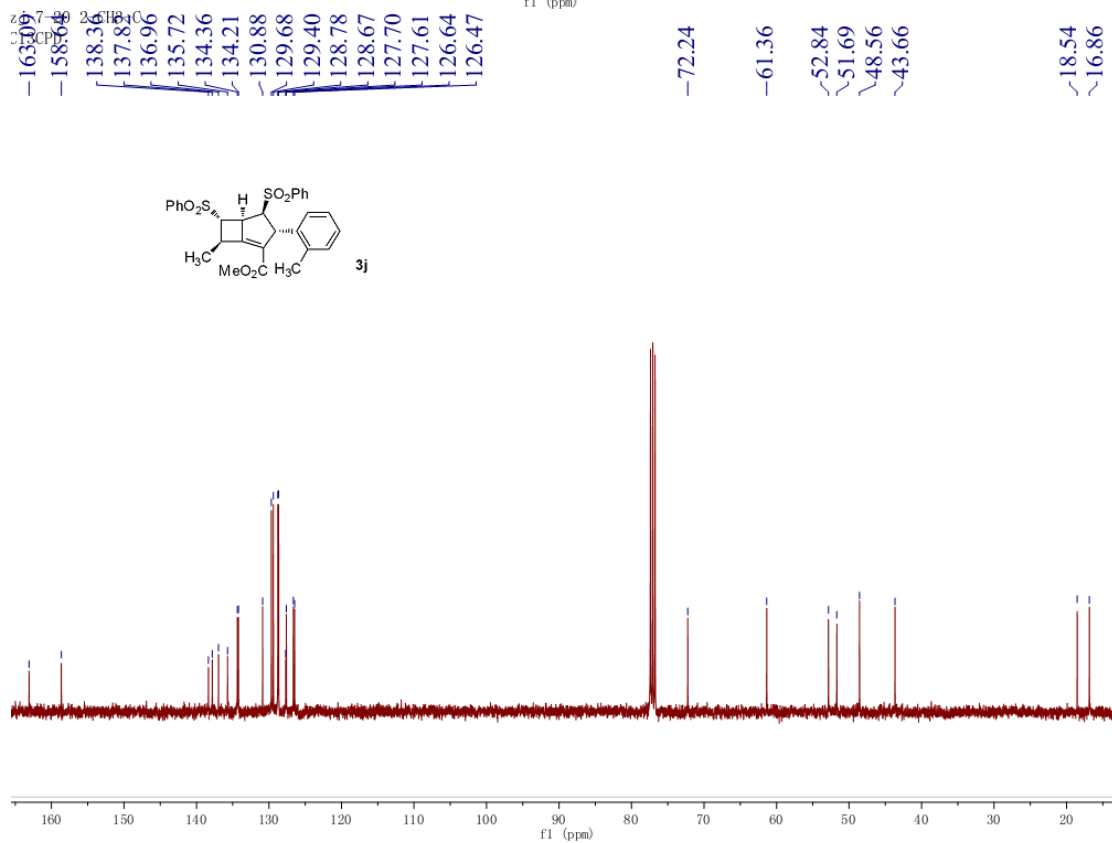
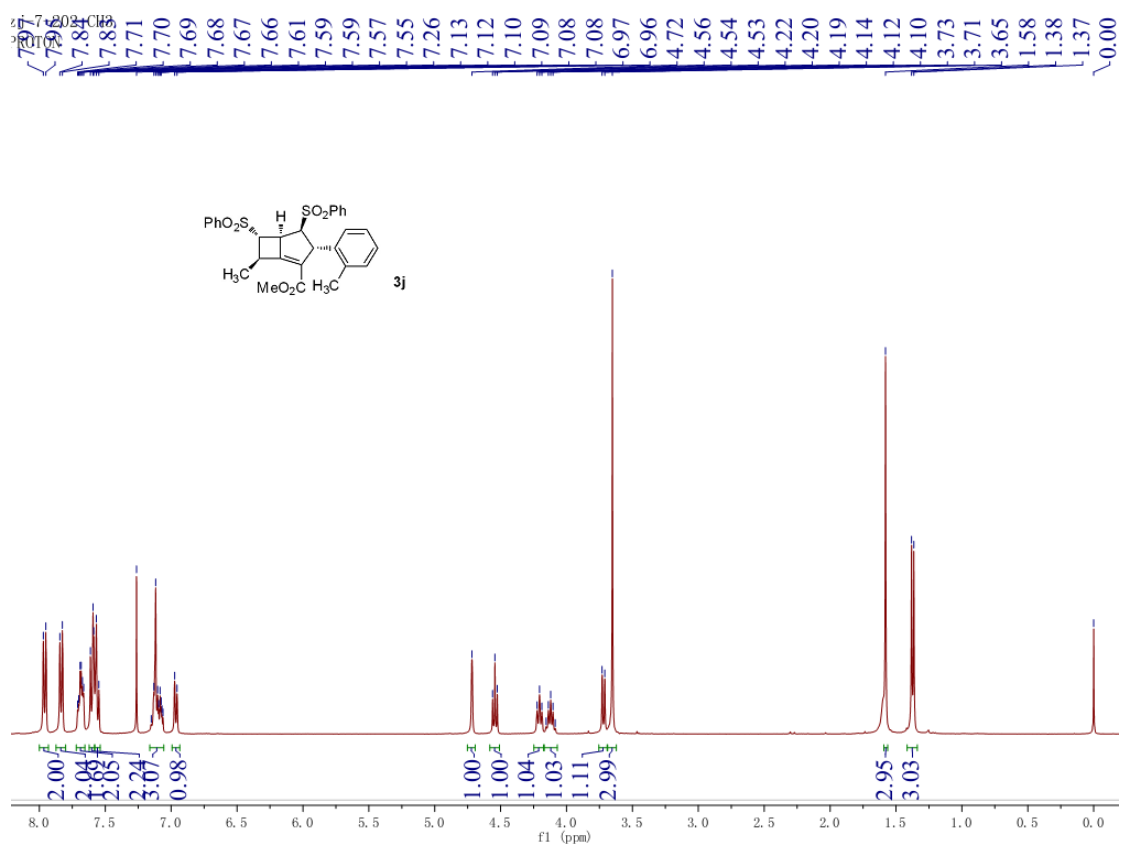


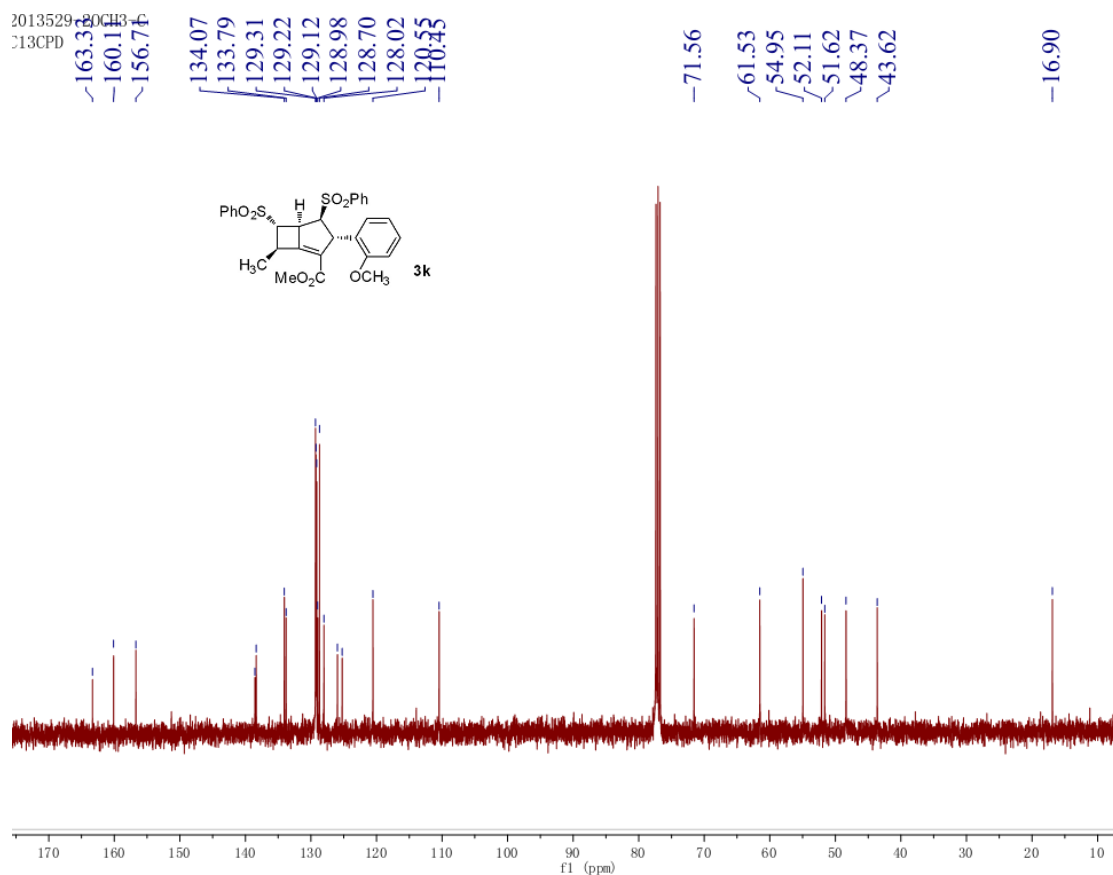
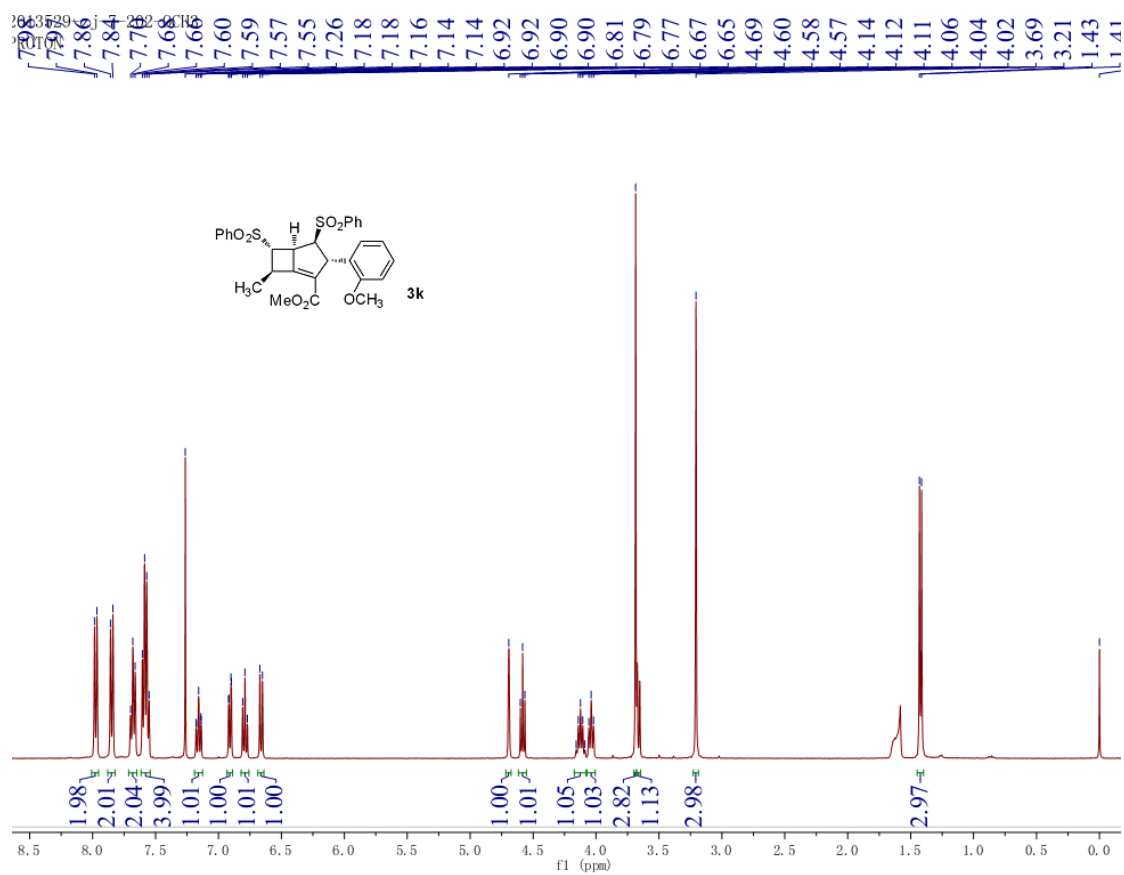


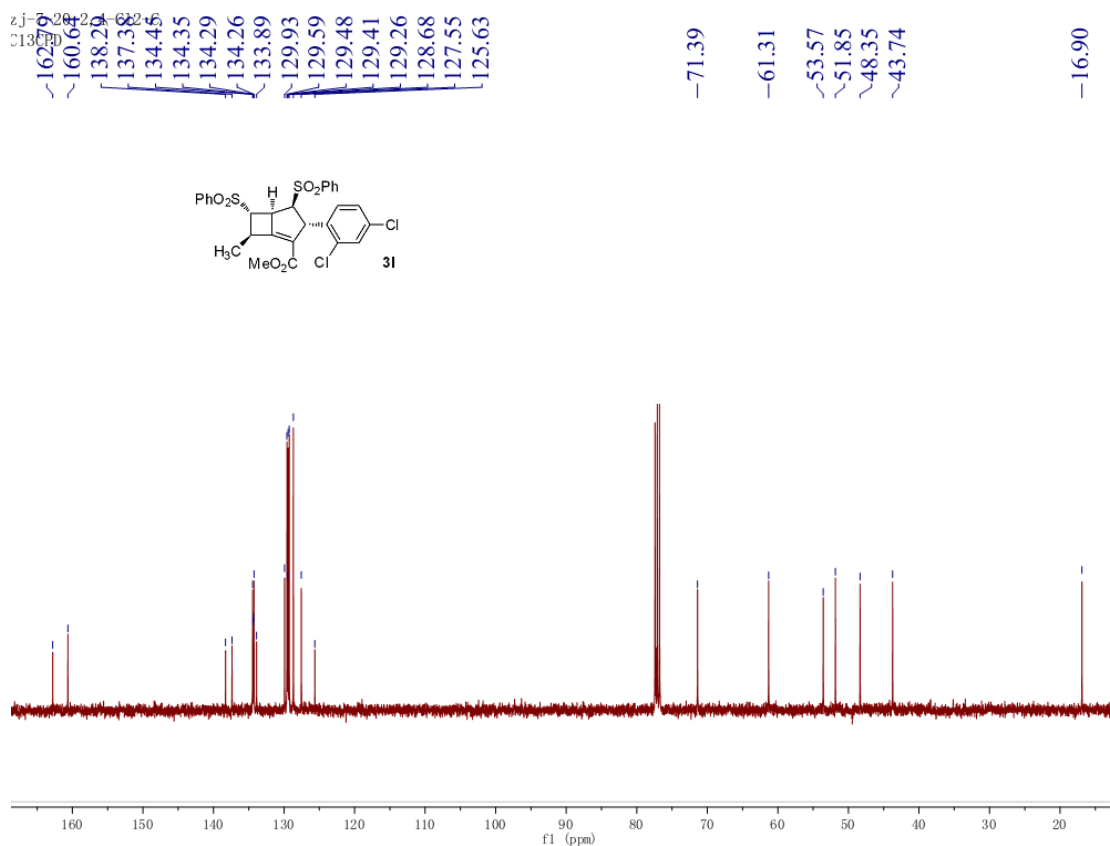
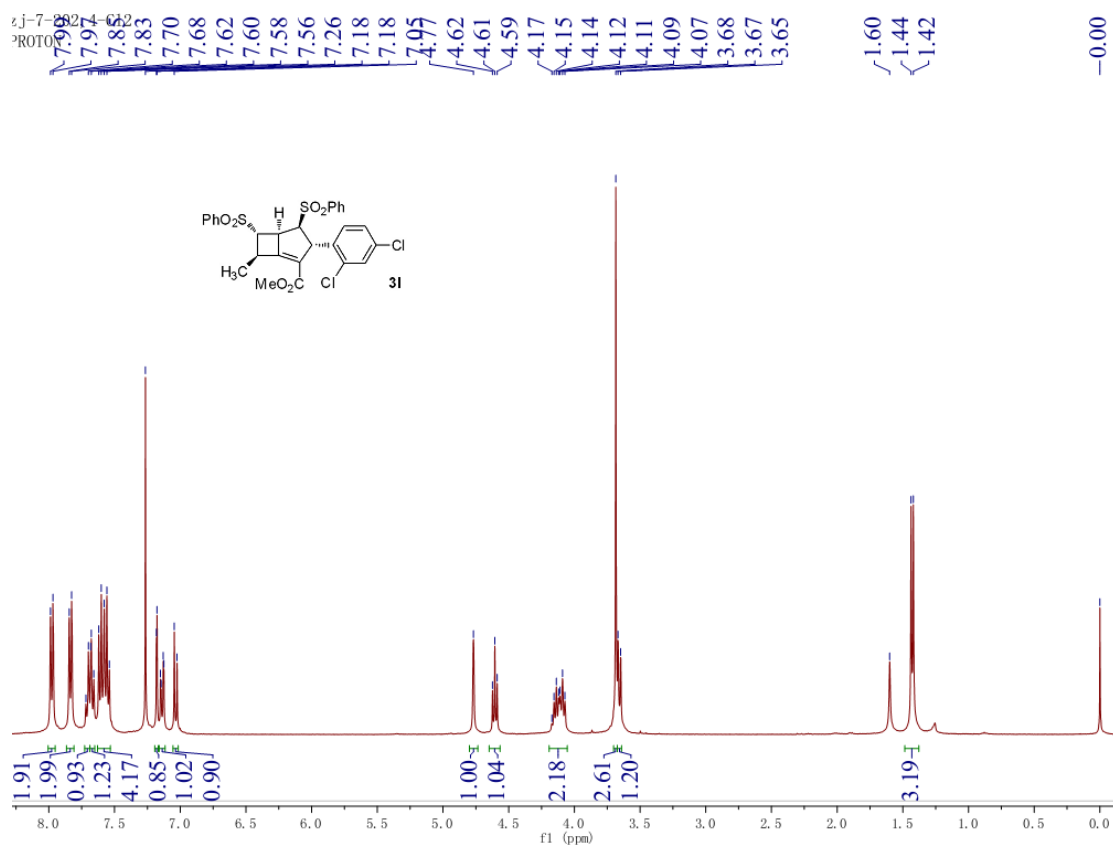


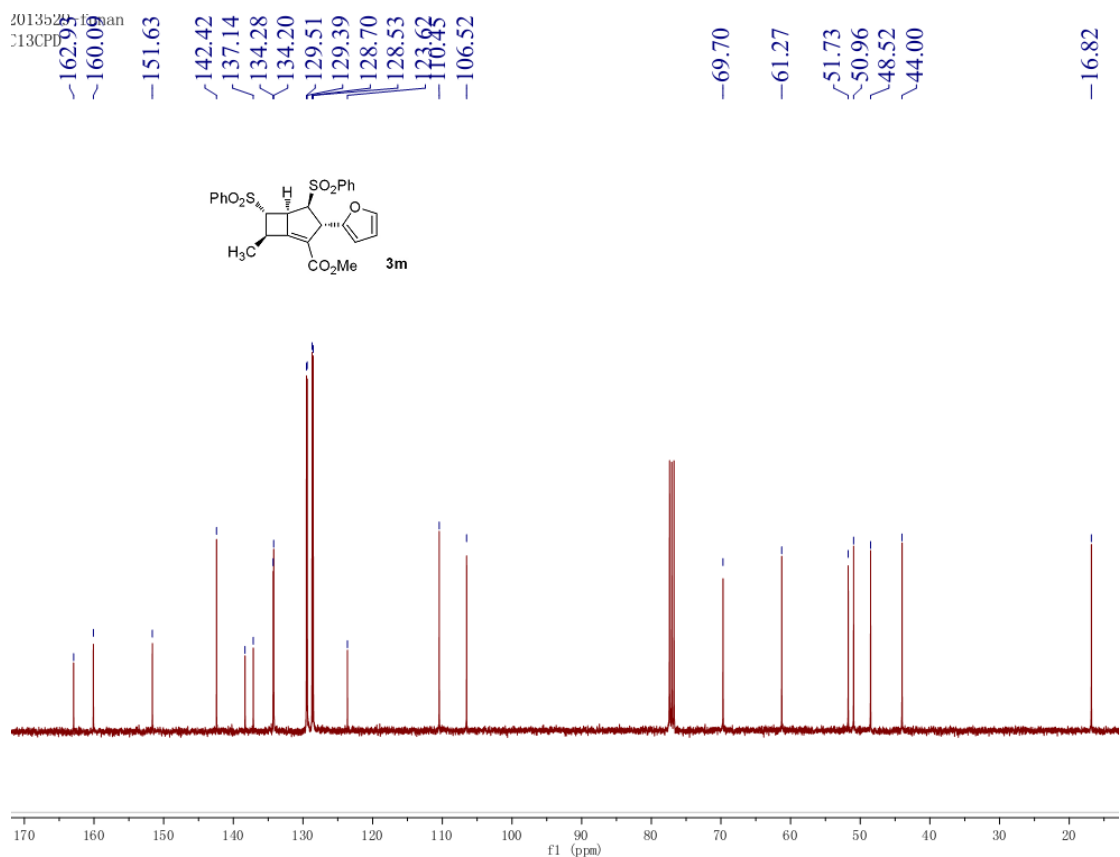
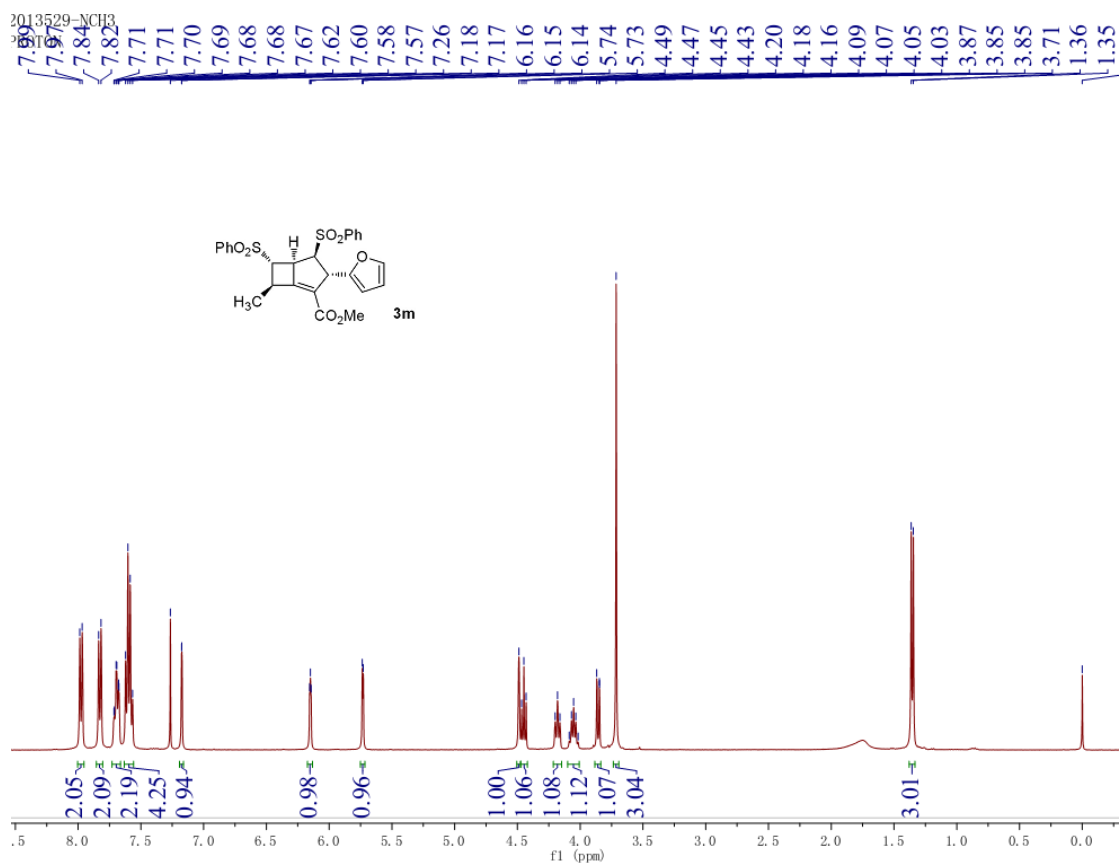


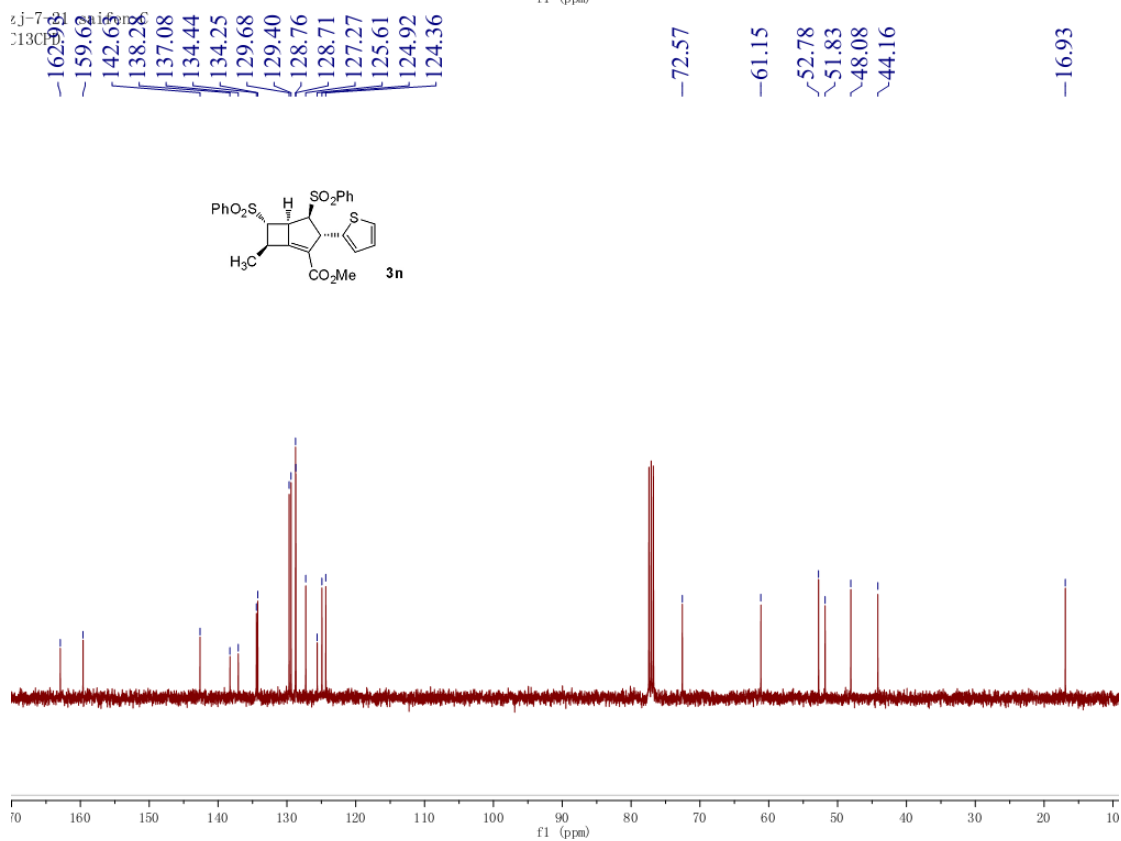
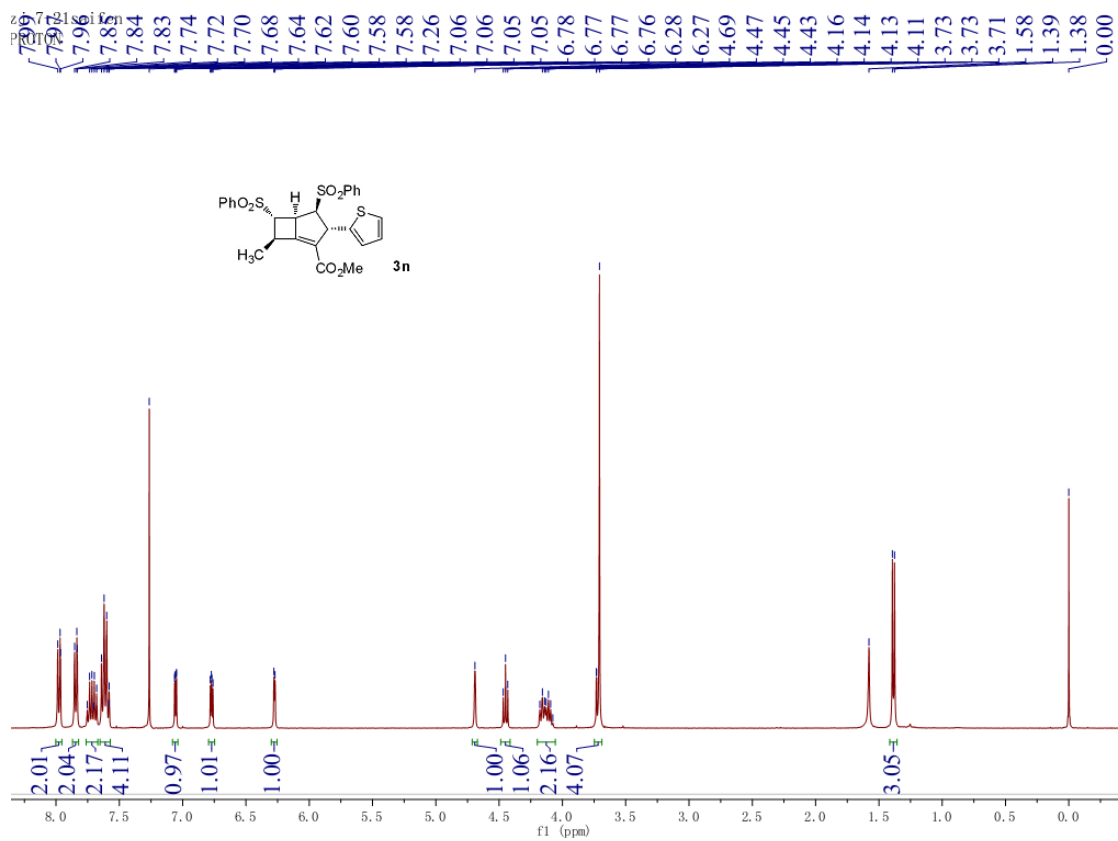




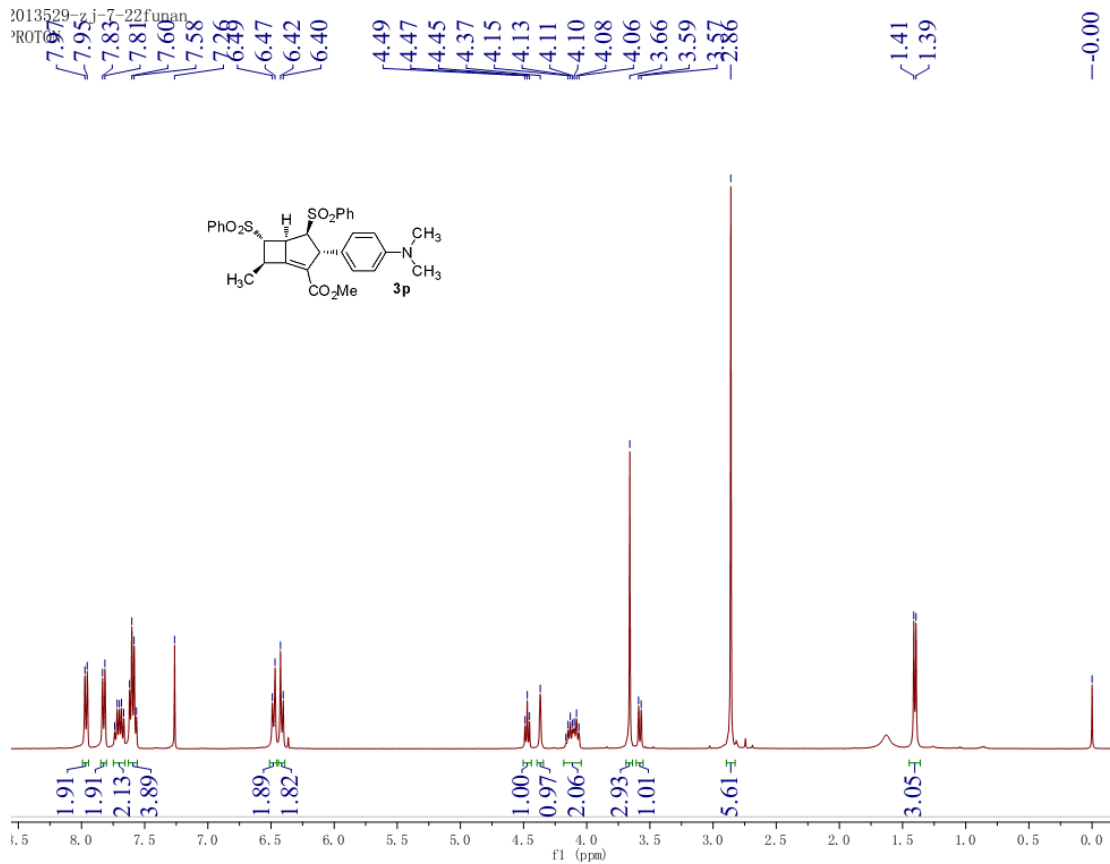








2013529-zj-7-22funan
 1H NMR



2013529-zj-7-22funan
 13C NMR

