Bond-Weakening Catalysis: Conjugate Aminations Enabled by the Soft Homolysis of Strong N-H Bonds

Kyle T. Tarantino, David C. Miller, Ted A. Callon, Robert R. Knowles*

Department of Chemistry, Princeton University, Princeton, New Jersey 08540

correspondence to: rknowles@princeton.edu

Supporting Information

Table of Contents ***Page***

I. Materials and Methods

General Information

Commercial reagents were purified prior to use following the guidelines of Perrin and Armarego.[1] All solvents were purified according to the method of Grubbs.[2] Organic solutions were concentrated under reduced pressure on a Büchi rotary evaporator. Chromatographic purification of products was accomplished by flash chromatography on Silicycle F60 silica gel according to the method of Still.[3] Thin-layer chromatography (TLC) was performed on Silicycle 250 μm silica gel plates. Visualization of the developed chromatogram was performed by fluorescence quenching, and potassium permanganate or ceric ammonium molybdate stain. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker 500 (500 and 125 MHz) instrument, and are internally referenced to residual solvent signals (note: CDCl3 referenced at δ 7.27 and 77.0 ppm respectively). Data for ^{1}H NMR are reported as follows: chemical shift (δ ppm), integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constant (Hz) and assignment. Data for ^{13}C NMR are reported in terms of chemical shift and no special nomenclature is used for equivalent carbons. IR spectra were recorded on a Perkin Elmer Paragon 1000 spectrometer and are reported in terms of frequency of absorption (cm^{-1}). High-resolution mass spectra were obtained at Princeton University mass spectrometry facilities using an Agilent 6210 TOF LC/MS. Gas chromatography-mass spectrometry (GC-MS) was performed on an Agilent 6890 GC-5975C MSD.

General Procedure for Bond Weakening Reactions

Method A (reaction optimization):

An oven-dried 2-dram vial in an inert atmosphere glovebox was charged with a magnetic stir bar, substrate (0.05 mmol, 1.0 equiv), $Cp^*_2Ti^{III}Cl$ (0.005 mmol, 0.1 equiv), TEMPO (0.005 mmol, 0.1 equiv). The flask was closed with a septa and sealed with electrical tape. 1 mL degassed anhydrous solvent was added and the reaction was stirred at room temperature. The reaction removed from the glovebox and quenched by addition of 1 mL H_2O. The reaction was extracted with 2 mL ethyl acetate, filtered through a pipette containing ¾ inch of silica gel, and rinsed with ethyl acetate. The solvent was removed by rotary evaporation under reduced pressure to give a crude residue, which was purified by preparative silica gel thin layer chromatography.

Method B (preparative scale):

A flame-dried round bottom flask (25 mL) was charged with a magnetic stir bar, starting material (0.5 mmol, 1.0 equiv), and pumped into a glovebox. $Cp^*_2Ti^{III}Cl$ (0.005 mmol, 0.01 equiv), and TEMPO (0.005 mmol, 0.01 equiv) was added and the flask was capped with a septum. 10 mL of degassed anhydrous MeCN was added and the reaction was stirred at room temperature. After 1 h the reaction was removed from the glovebox. The reaction was concentrated under reduced pressure on a rotary evaporator. The crude material was purified by silica gel column chromatography (gradient from 100% hexane to 50% EtOAc/hexane) to obtain the named products.

---

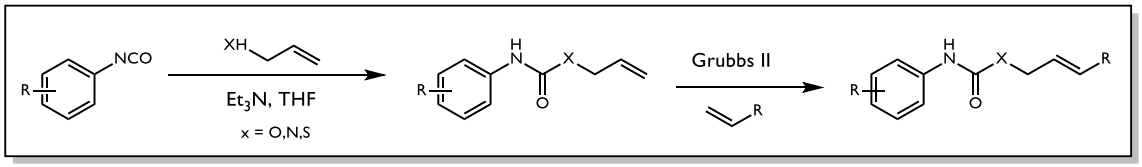
[1] D. D. Perrin, W. L. F. Amarego, *Purification of Laboratory Chemicals* (Pergamon, Press, © Oxford, ed. 3, 1988).

[2] A. B. Pangborn, M. A. Giardello, R. H. Grubbs, R. K. Rosen, F. J. Timmers, *Organometallics* 1996, *15*, 1518.

[3] Still, W. C.; Khan, M.; Mitra, A.; *J. Org. Chem.* **1978**, *43*, 2923.

II. Synthesis and Characterization of Substrates

General procedure for the synthesis of carbamate substrates

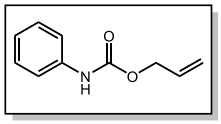


Nucleophile additions to aryl isocyanates

A flame dried round bottom flask was charged with phenyl isocyanate (1.75 g, 14.7 mmol, 1.0 equiv), allyl alcohol (0.854 g, 14.7 mmol, 1.0 equiv) in THF (30 mL), flushed with Ar, and cooled to 0 ^{o}C. Triethylamine (1.48g, 2.05 mL, 14.7 mmol, 1.0 equiv) was added to the flask by syringe over 5 minutes. The homogeneous mixture was stirred for 90 minutes. After the reaction was complete, solvent was removed under reduced pressure to afford the desired products as crystalline white solids which were used without further purification.

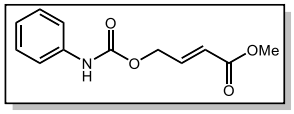
Olefin Metathesis

A flame dried round bottom flask was charged with allyl phenylcarbamate (2.46 g, 13.8 mmol, 1.0 equiv) in DCM (28 mL), methyl acrylate (6.29 mL, 69.4 mmol, 5.0 eq) and flushed with Ar. Grubbs second generation catalyst (0.589 g, 0.69 mmol, 0.05 equiv) was added in one portion and the reaction was stirred at room temperature under an atmosphere of Ar. The homogeneous solution was stirred for 6 hours. Once the reaction was complete, the reaction was concentrated to dryness under reduced pressure on a rotary evaporator. The crude material was purified by silica gel column chromatography (gradient from 100% hexane to 30% EtOAc/hexane) to obtain the desired substrates.



Allyl phenylcarbamate

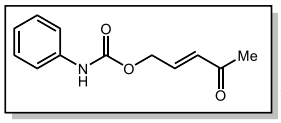
Followed general procedure using phenylisocyanate and allyl alcohol on 14.7 mmol scale and used without purification to give 2.46 g (94% yield) of Allyl phenylcarbamate as a white solid. ^{1}H NMR (500 MHz, Chloroform-d) δ 7.41 (d, *J* = 8.0 Hz, 2H), 7.34 (t, *J* = 7.9 Hz, 2H), 7.10 (t, *J* = 7.4 Hz, 1H), 6.67 (s, 1H), 6.00 (ddt, *J* = 17.3, 10.9, 5.7 Hz, 1H), 5.40 (dd, *J* = 17.3, 1.6 Hz, 1H), 5.29 (dd, *J* = 10.5, 1.6 Hz, 1H), 4.70 (d, *J* = 5.7 Hz, 3H).; ^{13}C NMR (126 MHz, $CDCl_3$) δ 137.75, 132.43, 129.33, 129.09, 123.53, 118.29, 65.87.; IR(Neat): 3303, 1722, 1701, 1596, 1534, 1501, 1488, 1442, 1315, 1301, 1224, 1161, 1054, 1027, 993, 936, 907, 743, 693 cm^{-1}; MS (ESI) exact mass calculated for $[M+H]^+$ ($C_{10}H_{12}O_2N$) requires *m/z* 178.1, found *m/z* 178.1.



1- methyl (E)-4-((phenylcarbamoyl)oxy)but-2-enoate

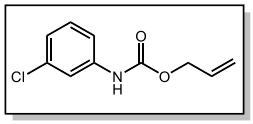
Followed general procedure from allyl phenylcarbamate on 13.8 mmol scale and purified using silica gel chromatography to give 1.2 g (37% yield) of methyl (E)-4-((phenylcarbamoyl)oxy)but-2-enoate as a white solid. ^{1}H NMR (500 MHz, Chloroform-d) δ 7.39 (d, *J* = 8.1 Hz, 2H),

7.33 (t, *J* = 7.6 Hz, 2H), 7.09 (t, *J* = 7.3 Hz, 1H), 7.00 (dt, *J* = 15.8, 4.2 Hz, 1H), 6.74 - 6.63 (m, 1H), 6.08 (d, *J* = 15.8 Hz, 1H), 4.85 (d, *J* = 4.1 Hz, 2H), 3.76 (s, 3H).; ^{13}C NMR (75 MHz, $CDCl_3$) δ 141.79, 129.12, 123.82, 121.69, 118.81, 63.25, 51.77.; IR(Neat) 3375, 2952, 1727, 1707, 1668, 1598, 1525, 1439, 1311, 1201, 1176, 1095, 1024, 957, 832, 754, 692 cm^{-1}; MS (ESI) exact mass calculated for $[M+H]^+$ ($C_{12}H_{14}O_4N$) requires *m/z* 236.1, found *m/z* 219.1.



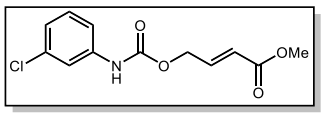
(E)-4-oxopent-2-en-1-yl phenylcarbamate

Followed general procedure from allyl phenylcarbamate and methyl vinyl ketone on 2.25 mmol scale and purified using silica gel chromatography to give 250 mg (51% yield) of E-4-oxopent-2n-1-yl phenylcarbamate as a white solid. ^{1}H NMR (500 MHz, Chloroform-d) δ 7.42 (d, *J* = 7.9 Hz, 2H), 7.36 (t, *J* = 7.9 Hz, 2H), 7.13 (t, *J* = 7.3 Hz, 1H), 6.84 (dt, *J* = 16.1, 4.6 Hz, 1H), 6.72 (s, 1H), 6.33 (dt, *J* = 16.2, 1.9 Hz, 1H), 4.90 (dd, *J* = 4.6, 2.0 Hz, 2H), 2.32 (s, 3H).; ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.75, 140.23, 130.82, 129.17, 123.88, 63.34, 27.36.; IR(Neat): 3365, 1710, 1664, 1597, 1529, 1442, 1366, 1315, 1227, 1103, 1014, 963, 746, 689 cm^{-1}; MS (ESI) exact mass calculated for $[M+H]^+$ ($C_{12}H_{14}O_3N$) requires *m/z* 219.1, found *m/z* 219.1.



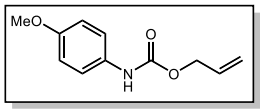
allyl (3-chlorophenyl)carbamate

Followed general procedure using 3-chlorophenylisocyanate and allyl alcohol on 16.4 mmol scale and used without purification to give 3.10 g (89% yield) of the titled compound as a clear oil. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.51 (s, 1H), 7.23 - 7.19 (m, 2H), 7.07 - 7.01 (m, 1H), 6.66 (s, 1H), 5.96 (ddt, *J* = 17.2, 10.4, 5.8 Hz, 1H), 5.37 (dq, *J* = 17.2, 1.5 Hz, 1H), 5.28 (dq, *J* = 10.4, 1.3 Hz, 1H), 4.67 (dt, *J* = 5.8, 1.4 Hz, 2H).; ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.91, 138.97, 134.81, 132.17, 130.04, 123.56, 118.55, 66.10.; IR(Neat) 3315, 1705, 1593, 1527, 1484, 1425, 1273, 1212, 1054, 995, 876, 768, 678 cm^{-1}; MS (ESI) exact mass calculated for $[M+H]^+$ ($C_{10}H_{11}ClO_2N$) requires *m/z* 212.1, found *m/z* 212.1.



methyl (E)-4-(((3-chlorophenyl)carbamoyl)oxy)but-2-enoate

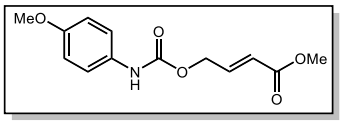
Followed general procedure from allyl (3-chlorophenyl)carbamate on 14.2 mmol scale and purified using silica gel chromatography to give 1.8 g (47% yield) of the titled compound as a white solid. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.51 (s, 1H), 7.25 - 7.21 (m, 2H), 7.09 - 7.04 (m, 1H), 6.98 (dt, *J* = 15.8, 4.6 Hz, 1H), 6.74 (s, 1H), 6.07 (dt, *J* = 15.8, 2.0 Hz, 1H), 4.84 (dd, *J* = 4.6, 2.0 Hz, 2H), 3.76 (s, 3H).; ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.29, 152.45, 141.58, 138.70, 134.83, 130.10, 123.82, 121.82, 118.83, 116.66, 63.43, 51.85.; IR(Neat) 3317, 2953, 1728, 1699, 1661, 1596, 1537, 1478, 1426, 1286, 1274, 1215, 1197, 1052, 1024, 942, 897, 869, 783, 766, 670 cm^{-1}; MS (ESI) exact mass calculated for $[M+H]^+$ ($C_{12}H_{13}ClO_4N$) requires *m/z* 270.1, found *m/z* 270.1.



allyl (4-methoxyphenyl)carbamate

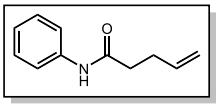
Followed general procedure using 4-methoxyphenylisocyanate and allyl alcohol on 15.4 mmol scale and used without purification to give 2.95 g (92% yield) of allyl (4-methoxyphenyl)carbamate as a white solid. ^{1}H NMR (500 MHz, Chloroform-

d) δ 7.31 (d, *J* = 8.5 Hz, 2H), 6.88 (d, *J* = 8.8 Hz, 2H), 6.61 (s, 1H), 5.99 (ddt, *J* = 16.4, 11.0, 5.7 Hz, 1H), 5.38 (d, *J* = 17.2 Hz, 1H), 5.28 (d, *J* = 10.4 Hz, 1H), 4.68 (d, *J* = 5.6 Hz, 2H), 3.81 (s, 3H).; ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.01, 132.56, 130.78, 120.64, 118.14, 114.25, 65.78, 55.52.; IR (Neat) 3331, 2962, 2946, 1699, 1516, 1459, 1411, 1244, 1221, 1172, 1061, 1026, 995, 935, 818, 784, 769 cm^{-1}; MS (ESI) exact mass calculated for $[M+H]^+$ ($C_{11}H_{13}O_3N$) requires *m/z* 208.1, found *m/z* 208.1.



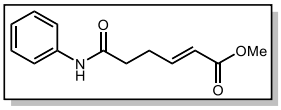
methyl (E)-4-(((4-methoxyphenyl)carbamoyl)oxy)but-2-enoate

Followed general procedure from allyl (4-methoxyphenyl)carbamate and methyl acrylate on 2.43 mmol scale and purified using silica gel chromatography to give 621 mg (97% yield) of methyl (E)-4-(((4-methoxyphenyl)carbamoyl)oxy)but-2-enoate as a white solid. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.37 - 7.30 (m, 2H), 7.01 (dt, *J* = 15.8, 4.5 Hz, 1H), 6.89 (d, *J* = 8.9 Hz, 2H), 6.60 (s, 1H), 6.10 (d, *J* = 15.7 Hz, 1H), 4.85 (dd, *J* = 4.5, 2.0 Hz, 2H), 3.82 (s, 3H), 3.78 (s, 3H).; ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.30, 156.22, 152.99, 141.98, 130.46, 121.56, 120.80, 114.31, 63.16, 55.52, 51.78.; IR(Neat) 3379, 3010, 1719, 1705, 1667, 1530, 1511, 1444, 1319, 1244, 1224, 1180, 1061, 1019, 953, 808, 761 cm^{-1}; MS (ESI) exact mass calculated for $[M+H]^+$ ($C_{13}H_{15}O_5N$) requires *m/z* 266.1, found *m/z* 266.1.



N-phenylpent-4-enamide

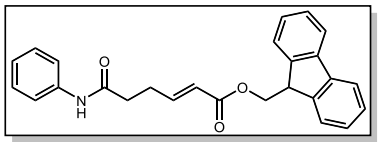
A flame dried 500 mL round bottom flask was chaged with 50 mL anhydrous Et_2O. MeMgBr (17.5 mL, 3.0 M, 52.6 mmol, 2 equiv.) was added to the flask. Freshly distilled aniline (4.79 mL, 52.6 mmol, 2 equiv.) was dissolved in 50 mL Et_2O and added to the reaction dropwise via addition funnel over 30 min to rapidly stirred MeMgBr solution at room temperature. Once all aniline had been added, methyl pent-4-enoate (3.0 g, 26.3 mmol, 1.0 equiv.) was dissolved in 50 mL Et_2O and added via addition funnel over 30 minutes at room temperature. After addition was complete the reaction was allowed to stir at room temperature under Ar for 2 h. Once complete, the reaction was quenched by slow addition of 200 mL H_2O, followed by 50 mL 1 N HCl(aq). Organics were extracted with 3 x 150 mL ethyl acetate. Combined organics were dried over Na_2SO_4 and concentrated. The titled compound was obtained as a beige solid and used without further purification. (3.95 g, 86%). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.50 (d, *J* = 7.9 Hz, 2H), 7.32 (t, *J* = 7.9 Hz, 2H), 7.21 (s, 1H), 7.10 (t, *J* = 7.4 Hz, 1H), 5.89 (ddt, *J* = 16.7, 10.4, 6.0 Hz, 1H), 5.13 (d, *J* = 16.7 Hz, 1H), 5.06 (d, *J* = 10.4 Hz, 1H), 2.54 - 2.41 (m, 4H).; ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.46, 137.81, 136.87, 129.02, 124.29, 119.79, 116.00, 36.87, 29.46.; IR(Neat) 3317, 1664, 1601, 1534, 1488, 1439, 1315, 1242, 1176, 919, 755 cm^{-1}; MS (ESI) exact mass calculated for $[M+H]^+$ ($C_{11}H_{14}ON$) requires *m/z* 176.1, found *m/z* 176.1.



Methyl (E)-6-oxo-6-(phenylamino)hex-2-enoate

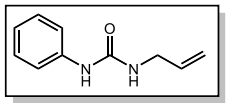
Followed general cross metathesis procedure from N-phenylpent-4-enamide on 5.71 mmol scale and purified using silica gel chromatography to give 1.22 g (92% yield) of the titled compound as a biege solid. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.50 (d, *J* = 7.9 Hz, 2H), 7.32 (t, *J* = 7.7 Hz, 2H), 7.23

- 7.17 (m, 1H), 7.11 (t, *J* = 7.5 Hz, 1H), 7.00 (dt, *J* = 15.7, 6.8 Hz, 1H), 5.91 (d, *J* = 15.7 Hz, 1H), 3.73 (s, 3H), 2.65 (q, *J* = 7.1 Hz, 3H), 2.51 (t, *J* = 7.4 Hz, 2H).; ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.35, 166.83, 147.03, 137.61, 129.06, 124.47, 122.02, 119.84, 51.57, 35.60, 27.63.; IR(Neat) 3295, 3261, 1721, 1658, 1600, 1543, 1498, 1431, 1309, 1284, 1262, 1209, 1183, 1090, 1020, 969, 746, 717, 689 cm^{-1}; MS (ESI) exact mass calculated for $[M+H]^+$ ($C_{13}H_{16}O_3N$) requires *m/z* 234.1, found *m/z* 234.1.



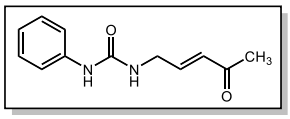
(9H-fluoren-9-yl)methyl (E)-6-oxo-6-(phenylamino)hex-2-enoate

(E)-methyl 6-oxo-6-(phenylamino)hex-2-enoate (500 mg, 2.14 mmol, 1.0 equiv), (9H-fluoren-9-yl)methanol (4.21 g, 21.4 mmol, 10 equiv), and Otera's Catalyst (51 mg, 0.043 mmol, 0.02 equiv) was added to 50 mL round bottom flask. Toluene (11 mL, 0.2 M) was added and the reaction was heated to reflux for 16 h. After, the reaction was cooled to room temperature, and concentrated to dryness under reduced pressure on a rotary evaporator. The crude solid was purified by flash column chromatography eluting with 30% EtOAc in Hexanes to afford the titled compound as a white solid. (220 mg, 26%) ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.79 (d, *J* = 7.6 Hz, 2H), 7.61 (d, *J* = 7.5 Hz, 2H), 7.53 (d, *J* = 7.9 Hz, 2H), 7.42 (t, *J* = 7.5 Hz, 2H), 7.39 - 7.29 (m, 4H), 7.24 (s, 1H), 7.15 (t, *J* = 7.4 Hz, 1H), 7.09 (dt, *J* = 15.6, 6.8 Hz, 1H), 6.04 (d, *J* = 15.7 Hz, 1H), 4.45 (d, *J* = 7.4 Hz, 2H), 4.27 (t, *J* = 7.3 Hz, 1H), 2.72 (q, *J* = 7.6, 7.1 Hz, 2H), 2.57 (t, *J* = 7.5 Hz, 2H).; ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.33, 166.27, 147.59, 143.80, 141.28, 137.59, 129.09, 127.79, 127.11, 125.09, 124.51, 122.11, 120.04, 119.86, 66.44, 46.78, 35.60, 27.72.; IR(Neat) 3060, 1732, 1696, 1597, 1497, 1389, 1292, 1171, 758, 741 cm^{-1}; MS (ESI) exact mass calculated for $[M+H]^+$ ($C_{26}H_{23}O_3N$) requires *m/z* 398.1, found *m/z* 398.1.



1-allyl-3-phenylurea

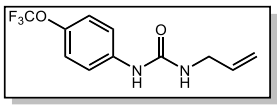
Followed general procedure using phenylisocyanate and allyl amine on 14.7 mmol scale and used without purification to give 2.22 g (86% yield) of allyl 1-allyl-3-phenylurea carbamate as a white solid. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.59 (s, 1H), 7.35 – 7.20 (m, 4H), 7.10 – 6.99 (m, 1H), 5.83 (ddt, *J* = 14.7, 10.3, 5.3 Hz, 1H), 5.19 (d, *J* = 17.1 Hz, 1H), 5.10 (d, *J* = 10.0 Hz, 1H), 3.81 (d, *J* = 5.3 Hz, 2H).; ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.52, 138.79, 134.99, 129.07, 123.30, 120.48, 115.61, 42.53.; IR(Neat) 3340, 3293, 1631, 1561, 1506, 1238, 1039, 827, 679 cm^{-1}; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{10}H_{13}N_2O$) requires *m/z* 176.09496, found *m/z* 176.09582 difference 0.81 ppm.



(E)-1-(4-oxopent-2-en-1-yl)-3-phenylurea

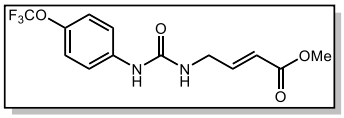
Followed the general cross metathesis procedure using 1-allyl-3-phenylurea (1.0 g, 5.67 mmol) to furnish 260 mg (20% yield) of the titled compound as a beige solid. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.49 (d, *J* = 7.7 Hz, 2H), 7.38 (t, *J* = 8.0 Hz, 2H), 7.23 (s, 1H), 7.17 (t, *J* = 7.4 Hz, 1H), 7.06 – 7.03 (m, 1H), 6.21 (t, *J* = 3.1 Hz, 1H), 6.04 – 6.00 (m, 1H), 2.52 (d, *J* = 1.1 Hz, 3H).; ^{13}C NMR (126 MHz, $CDCl_3$) δ 129.25, 124.81, 120.16, 117.66, 111.77, 111.15, 14.68.; IR(Neat) 3316, 1722, 1634, 1598, 1546, 1499, 1443, 1434, 1314, 1300,

1280, 1192, 1167, 1013, 754, 662 cm^{-1}; MS (ESI) exact mass calculated for $[M+H]^+$ ($C_{13}H_{17}O_2N_2$) requires *m/z* 233.1, found *m/z* 233.1.



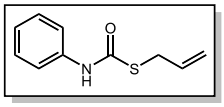
1-allyl-3-(4-(trifluoromethoxy)phenyl)urea

Followed general procedure using 4-trifluoromethoxy-phenylisocyanate and allyl amine on 6.63 mmol scale and used without purification to give 940 mg (54% yield) of 1-allyl-3-(4-(trifluoromethoxy)phenyl)urea as a white solid. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.30 (d, *J* = 8.9 Hz, 2H), 7.08 (d, *J* = 8.5 Hz, 2H), 5.84 (ddt, *J* = 17.7, 10.5, 5.3 Hz, 1H), 5.19 (d, *J* = 17.2 Hz, 1H), 5.11 (d, *J* = 10.3 Hz, 1H), 3.83 (d, *J* = 5.3 Hz, 2H).; ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.54, 144.95, 137.14, 134.65, 121.96, 121.58, 116.27, 42.88.; IR(Neat: 3316, 1631, 1214, 1203, 1151, 1103, 933 cm^{-1}; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{11}H_{12}F_3N_2O_2$) requires *m/z* 260.00726, found *m/z* 260.07745 difference 0.73 ppm.



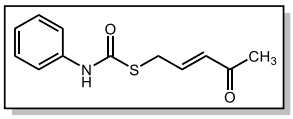
methyl (E)-4-(3-(4-(trifluoromethoxy)phenyl)ureido)but-2-enoate

Followed the general cross metathesis procedure using 1-allyl-3-(4-(trifluoromethoxy)phenyl)urea (0.922 g, 3.54 mmol) to furnish 350 mg (31% yield) of the titled compound as a beige solid. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.36 (d, *J* = 9.0 Hz, 2H), 7.18 (d, *J* = 8.4 Hz, 2H), 6.97 (dt, *J* = 15.7, 4.9 Hz, 1H), 6.77 (s, 1H), 5.99 (dd, *J* = 15.7, 1.8 Hz, 1H), 4.08 (d, *J* = 4.8 Hz, 2H), 3.76 (s, 3H).; ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.63, 155.05, 145.03, 136.89, 122.04, 121.75, 121.19, 51.80, 40.98.; IR(Neat) 3361, 1717, 1664, 1655, 1559, 1503, 1248, 1226, 1199, 1155, 841, 708 cm^{-1}; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{13}H_{14}F_3N_2O_4$) requires *m/z* 318.08274, found *m/z* 318.08317 difference 1.35 ppm.



S-allyl phenylcarbamothioate

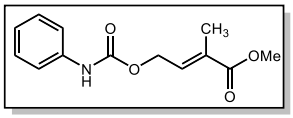
Followed general procedure using phenylisocyanate and allyl mercaptan on 14.7 mmol scale and used without purification to give 2.74 g (96% yield) of S-allyl phenylcarbamothioate as a white solid. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.34 (d, *J* = 7.8 Hz, 2H), 7.24 (t, *J* = 7.9 Hz, 2H), 7.04 (t, *J* = 7.3 Hz, 1H), 7.02 (s, 1H), 5.83 (ddt, *J* = 16.9, 10.0, 6.9 Hz, 1H), 5.21 (dd, *J* = 17.0, 1.5 Hz, 1H), 5.06 (dd, *J* = 10.0, 1.4 Hz, 1H), 3.57 (d, *J* = 7.1 Hz, 2H).; ^{13}C NMR (126 MHz, $CDCl_3$) δ 133.65, 129.17, 124.55, 117.90, 33.10.; IR(Neat) 3325, 1657, 1596, 1522, 1497, 1440, 1308, 1235, 1156, 742, 687, 671 cm^{-1}; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{10}H_{12}NOS$) requires *m/z* 193.05613, found *m/z* 193.05625 difference 0.03 ppm.



(E)-S-(4-oxopent-2-en-1-yl) phenylcarbamothioate

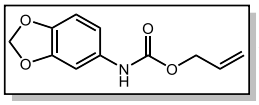
Followed the general cross metathesis procedure using S-allyl phenylcarbamothioate (0.500 g, 2.59 mmol) to furnish 260 mg (43% yield) of the titled compound as a beige solid. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.43 (d, *J* = 7.7 Hz, 2H), 7.39 – 7.34 (m, 2H), 7.17 (t, *J* = 7.5 Hz, 1H), 7.08 (s, 1H), 6.80 (dt, *J* = 15.8, 7.1 Hz, 1H), 6.27 (d, *J* = 15.8 Hz, 1H), 3.78 (dd, *J* = 7.1, 1.4 Hz, 2H), 2.29 (s, 3H).; ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.82, 132.67, 129.45, 129.26, 121.55, 31.30, 27.23.; IR(Neat) 3325, 1673, 1659, 1598, 1535, 1497,

1442, 1434, 1257, 1235, 1148, 972, 880, 748, 687 cm-[1]; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{12}H_{14}NO_2S$) requires *m/z* 235.0667, found *m/z* 235.06708 difference 1.62 ppm.



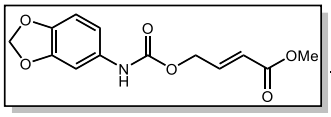
(E)-S-(4-oxopent-2-en-1-yl) phenylcarbamothioate

Followed the general cross metathesis procedure using allyl phenylcarbamate (0.500 g, 2.80 mmol) and methyl methacrylate to furnish 23 mg (3% yield) of the titled compound as a beige solid. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.31 (d, *J* = 8.0 Hz, 2H), 7.24 (t, *J* = 7.9 Hz, 2H), 7.01 (tt, *J* = 7.1, 1.2 Hz, 1H), 6.73 (tq, *J* = 6.2, 1.4 Hz, 1H), 6.66 (s, 1H), 4.78 (dd, *J* = 6.3, 1.4 Hz, 2H), 3.69 (s, 3H), 1.85 (d, *J* = 1.4 Hz, 3H).; IR(Neat) 2983, 1721, 1696, 1597, 1536, 1442, 1315, 1229, 1085, 1047, 1026, 987, 744, 693 cm^{-1}; MS (ESI) exact mass calculated for $[M+H]^+$ ($C_{13}H_{15}O_4N$) requires *m/z* 250.1, found *m/z* 250.1.



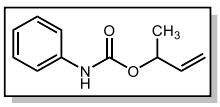
allyl benzo[d][1,3]dioxol-5-ylcarbamate

Followed general procedure using 5-isocyanatobenzo[d][1,3]dioxole and allyl alcohol on 6.13 mmol scale and used without purification to give 1.33 g (98% yield) of allyl benzo[d][1,3]dioxol-5-ylcarbamate as a white solid. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.11 (s, 1H), 6.75 (d, *J* = 8.4 Hz, 1H), 6.70 (d, *J* = 8.5 Hz, 1H), 6.54 (s, 1H), 6.04 - 5.92 (m, 3H), 5.38 (dd, *J* = 17.3, 1.3 Hz, 1H), 5.28 (dd, *J* = 10.3, 1.3 Hz, 1H), 4.67 (d, *J* = 5.7 Hz, 2H).; ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.97, 132.45, 118.26, 108.11, 101.26, 65.86.; IR(Neat) 3317, 1701, 1540, 1502, 1488, 1450, 1435, 1202, 1140, 1103, 1034, 926, 792 cm^{-1}; MS (ESI) exact mass calculated for $[M+H]^+$ ($C_{11}H_{12}O_4N$) requires *m/z* 222.1, found *m/z* 222.1.



methyl (E)-4-((benzo[d][1,3]dioxol-5-ylcarbamoyl)oxy)but-2-enoate

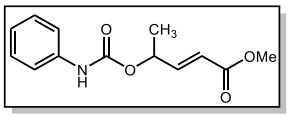
Followed general cross metathesis procedure using allyl benzo[d][1,3]dioxol-5-ylcarbamate and methyl acrylate on 6.03 mmol scale to give 0.500 g (30% yield) of allyl benzo[d][1,3]dioxol-5-ylcarbamate as a white solid. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.08 (s, 1H), 6.98 (dt, *J* = 15.8, 4.5 Hz, 1H), 6.74 (d, *J* = 8.3 Hz, 1H), 6.69 (d, *J* = 8.1 Hz, 1H), 6.63 (s, 1H), 6.06 (d, *J* = 15.8 Hz, 1H), 5.95 (s, 2H), 4.82 (dd, *J* = 4.7, 2.0 Hz, 2H), 3.76 (s, 3H).; ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.28, 152.87, 148.02, 141.85, 121.63, 112.08, 108.16, 101.32, 63.24, 51.80.; IR(Neat) 3314, 3095, 2901, 1730, 1702, 1667, 1558, 1493, 1447, 1431, 1320, 1259, 1215, 1201, 1183, 1143, 1049, 1034, 929, 858, 791, 685 cm^{-1}; MS (ESI) exact mass calculated for $[M+H]^+$ ($C_{13}H_{14}O_6N$) requires *m/z* 280.1, found *m/z* 280.1.



but-3-en-2-yl phenylcarbamate

Followed general procedure using phenylisocyanate and but-3-en-2-ol on 18.3 mmol scale and purified by flash column chromatography (2% EtOAc in Hexanes to 20% EtOAc in Hexanes over 10 column volumes) to give 1.25 g (36% yield) of but-3-en-2-yl phenylcarbamate as a white solid. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.38 (d, *J* = 8.0 Hz, 2H), 7.33 - 7.28 (m, 2H), 7.06 (tt, *J* = 7.4, 1.2 Hz, 1H), 6.60 (s, 1H), 5.90 (ddd, *J* = 17.3, 10.5, 5.9 Hz, 1H), 5.40 - 5.33 (m, 1H), 5.30 (dt, *J* = 17.3, 1.3 Hz, 1H), 5.17 (dt, *J* = 10.6, 1.2 Hz, 1H), 1.38 (d, *J* = 6.5 Hz, 3H).; ^{13}C NMR

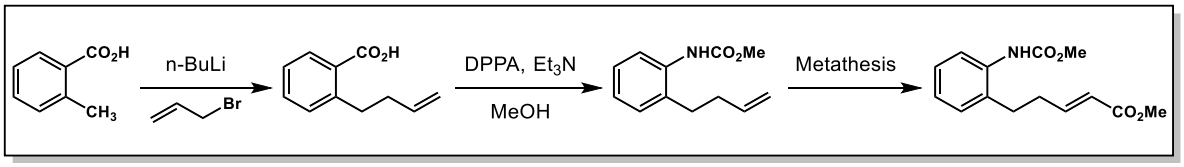
(126 MHz, $CDCl_3$) δ 152.85, 137.90, 137.82, 129.05, 123.38, 118.57, 115.91, 71.97, 20.16.; IR(Neat) 3303, 2983, 1721, 1696, 1597, 1536, 1442, 1315, 1229, 1085, 1047, 1026, 987, 744, 693 cm^{-1}; MS (ESI) exact mass calculated for $[M+H]^+$ ($C_{11}H_{14}O_2N$) requires *m/z* 192.1, found *m/z* 192.1.

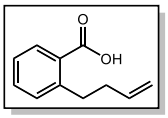


methyl (E)-4-((phenylcarbamoyl)oxy)pent-2-enoate

Followed general cross metathesis procedure using but-3-en-2-yl phenylcarbamate and methyl acrylate on 2.61 mmol scale to give 0.260 g (40% yield) of methyl (E)-4-((phenylcarbamoyl)oxy)pent-2-enoate as a white solid. ^1H NMR (500 MHz, Chloroform-d) δ 7.38 (d, *J* = 8.0 Hz, 2H), 7.31 (t, *J* = 7.9 Hz, 2H), 7.08 (td, *J* = 7.3, 1.2 Hz, 1H), 6.94 (dd, *J* = 15.8, 4.9 Hz, 1H), 6.67 (s, 1H), 6.03 (dd, *J* = 15.7, 1.6 Hz, 1H), 5.55 - 5.48 (m, 1H), 3.75 (s, 3H), 1.42 (d, *J* = 6.7 Hz, 3H).; ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.55, 152.36, 146.78, 137.54, 129.12, 123.69, 120.59, 118.67, 69.77, 51.78, 19.90.; IR(Neat) 3303, 2983, 1721, 1696, 1597, 1536, 1442, 1315, 1229, 1085, 1047, 1026, 987, 744, 693 cm^{-1}; MS (ESI) exact mass calculated for $[M+H]^+$ ($C_{13}H_{16}O_4N$) requires *m/z* 250.1, found *m/z* 250.1.

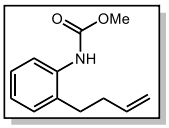
Synthesis of methyl (E)-5-(2-((methoxycarbonyl)amino)phenyl)pent-2-enoate





2-(but-3-en-1-yl)benzoic acid

Followed literature procedure.[4] 1.36 g 2-methylbenzoic acid gave 430 mg 2-(but-3-en-1-yl)benzoic acid (24% yield) as a white solid. Spectra matched literature reported values.

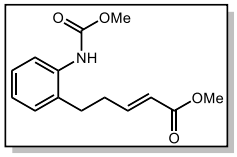


methyl (2-(but-3-en-1-yl)phenyl)carbamate

To a 100 mL flame dried round bottom flask charged with magnetic stir bar topped with reflux condenser was added 2-(but-3-en-1-yl)benzoic acid (425 mg, 2.41 mmol, 1 equiv.), 1,4-dioxane (4.8 mL, 0.5 M), triethylamine (0.672 mL, 4.82 mmol, 2 equiv.), methanol (0.976 mL, 24.12 mmol, 10 equiv.) and the reaction was heated to 100 °C. Diphenyl phosphorazidate (1.56 mL, 7.24 mmol, 3 equiv) was added dropwise over 10 minutes by syringe to the refluxing solution. The reaction was heated to 100 °C for 10 h. Once all starting material was consumed by TLC analysis (10% EtOAc/Hexanes) the reaction was cooled to room temperature and quenched by addition of 50 mL sat. aq. $NaHCO_3$. Organics were extracted 3 x 50 mL EtOAc. Combined organics were washed with 50 mL sat. aq. $NaHCO_3$, dried over Na_2SO_4 and concentrated. Crude oil was purified by flash column chromatography (1% EtOAc/Hexanes to 10% EtOAc/Hexanes over 15 column volumes) to yield 257 mg (52% yield) of a colorless oil.

(4) Cheng, Y. A.; Chen, T. Tan, C. K.; Heng, J. J.; Yeung, Y. *J. Am. Chem .Soc.* **2012**, *134*, 16492

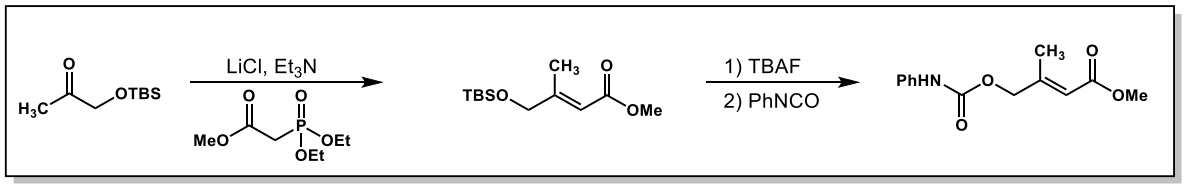
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.25 - 7.20 (m, 2H), 7.17 (t, *J* = 6.7 Hz, 2H), 7.09 (t, *J* = 7.4 Hz, 1H), 5.86 (ddt, *J* = 16.9, 10.2, 6.7 Hz, 1H), 5.08 (dd, *J* = 17.1, 1.7 Hz, 1H), 5.03 (dd, *J* = 10.3, 1.5 Hz, 1H), 3.78 (s, 3H), 2.69 - 2.63 (m, 2H), 2.39 - 2.31 (m, 2H).; ^{13}C NMR (126 MHz, $CDCl_3$) δ 137.45, 135.20, 129.50, 127.02, 120.22, 115.77, 115.28, 52.46, 33.84, 30.81.; IR(Neat) 3317, 2953, 2172, 1708, 1639, 1589, 1522, 1453, 1352, 1296, 1220, 1184, 1064, 1046, 912, 768, 752 cm^{-1}; MS (ESI) exact mass calculated for $[M+H]^+$ ($C_{12}H_{16}O_2N$) requires *m/z* 206.1, found *m/z* 206.1.

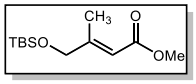


methyl (E)-5-(2-((methoxycarbonyl)amino)phenyl)pent-2-enoate

Followed the general cross metathesis procedure using ethyl (2-(but-3-en-1-yl)phenyl)carbamate (0.257 g, 1.25 mmol) and methyl acrylate to furnish 260 mg (79% yield) of the titled compound as a beige solid. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.58 (s, 1H), 7.19 – 7.14 (m, 1H), 7.12 – 7.07 (m, 1H), 7.04 (t, *J* = 7.5 Hz, 1H), 6.92 (dtd, *J* = 15.4, 6.9, 1.4 Hz, 1H), 6.30 (d, *J* = 29.9 Hz, 1H), 5.79 (dd, *J* = 15.7, 1.7 Hz, 1H), 3.70 (s, 3H), 3.66 (s, 3H), 2.66 (dd, *J* = 8.9, 6.8 Hz, 2H), 2.43 (tdd, *J* = 9.8, 5.5, 2.3 Hz, 2H).; ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.86, 154.69, 147.67, 135.11, 135.09, 129.30, 127.37, 127.34, 121.86, 121.82, 52.54, 51.55, 32.14, 29.77.; IR(Neat) 2952, 1734,1696, 1492, 1437, 1318, 1282, 1191, 1130, 763 cm^{-1}; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{14}H_{18}NO_4$) requires *m/z* 263.11576, found *m/z* 263.11599 difference 0.80 ppm.

Synthesis of methyl (E)-3-methyl-4-((phenylcarbamoyl)oxy)but-2-enoate

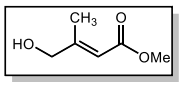




methyl (E)-4-((tert-butyldimethylsilyl)oxy)-3-methylbut-2-enoate

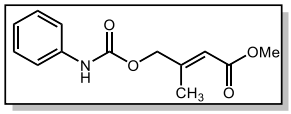
To a flame dried 250 mL round bottom flask charged with magnetic stirbar was added 1-((tert-butyldimethylsilyl)oxy)propan-2-one (5.0 g, 26.5 mmol, 1.0 equiv), methyl 2-(diethoxyphosphoryl)acetate (5.77 mL, 6.70 g, 31.9 mmol, 1.2 equiv.), lithium chloride (5.63 g, 133 mmol, 5.0 equiv.), and triethylamine (18.5 mL, 13.4 g, 133 mmol, 5 equiv.). THF (53 mL, 0.5 M) was added and the mixture was stirred at room temperature under an Ar atmosphere for 12 h. The reaction was quenched by addition of 50 mL H_2O. Organics were extracted 3 x 100 mL ethyl acetate. Combined organics were dried over Na_2SO_4 and concentrated to dryness on a rotary evaporator. Crude oil was purified by flash column chromatography (50 g silica gel cartridge, gradient from 1% EtOAc in hexanes to 10% EtOAc in hexanes over 20 column volumes) to afford the titled compound as a 2:1 E:Z mixture of olefin isomers. The Z isomer is removed following TBS deprotection in a subsequent step. The product was obtained as a colorless oil (2.91 g, 44.8% yield). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 6.01 (s, 1H), 4.11 (s, 2H), 3.70 (s, 3H), 2.05 (s, 3H), 0.92 (s, 9H), 0.08 (s, 6H).; ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.60, 157.81, 112.95, 67.15, 51.03, 31.74, 26.00, 15.58, -5.32.;

IR(Neat) 3331, 2118, 1635, 1381 cm^{-1}; MS (ESI) exact mass calculated for $[M+H]^+$ ($C_{12}H_{24}O_3Si$) requires *m/z* 245.1, found *m/z* 245.1.



methyl (E)-4-hydroxy-3-methylbut-2-enoate

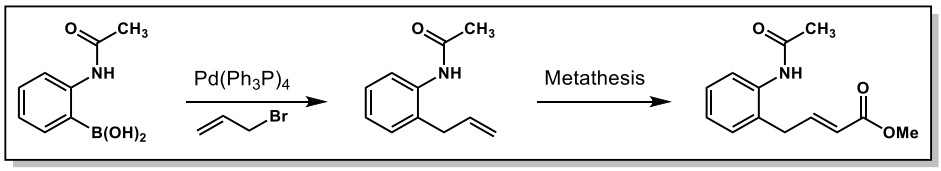
To a flame dried 100 mL round bottom flask charged with magnetic stirbar was added methyl (E)-4-((tert-butyldimethylsilyl)oxy)-3-methylbut-2-enoate (1.0 g, 4.09 mmol, 1.0 equiv.) and THF (12 mL, 0.35 M). The reaction was cooled to 0 °C and TBAF (8.18 mL, 1.0 M in THF, 2 equiv), was added via syringe. The reaction was allowed to stir for 1 h at 0 °C. After, the reaction was quenched by addition of 10 mL of aq. 1 M HCl. Organics were extracted 3 x 50 mL EtOAc, dried over Na_2SO_4 and concentrated to dryness. Crude oil was dissolved in minimal hexanes and purified by flash column chromatography (5% EtOAc in hexanes to 40% EtOAc in hexanes) to afford a colorless oil. Spectra are consistent with literature reported values: *J. Org. Chem.* **2001**, *66*, 2506-2508

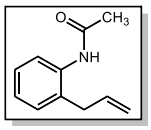


methyl (E)-3-methyl-4-((phenylcarbamoyl)oxy)but-2-enoate

Followed general procedure using phenylisocyanate and methyl (E)-4-hydroxy-3-methylbut-2-enoate on 2.29 mmol scale and purified by flash column chromatography (2% EtOAc in Hexanes to 30% EtOAc in Hexanes over 10 column volumes) to give 0.248 g (43% yield) of the titled compound as a white solid. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.39 (d, *J* = 7.7 Hz, 2H), 7.35 - 7.29 (m, 2H), 7.09 (t, *J* = 7.3 Hz, 1H), 6.72 (s, 1H), 5.91 (q, *J* = 1.5 Hz, 1H), 4.70 - 4.63 (m, 2H), 3.72 (s, 3H), 2.17 (dd, *J* = 1.4, 0.7 Hz, 3H).; ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.19, 166.65, 152.46, 137.44, 129.14, 128.61, 123.80, 115.00, 67.80, 51.16, 15.75.; IR(Neat) 3327, 2950, 1706, 1662, 1600, 1536, 1501, 1441, 1332, 1312, 1211, 1152, 1085, 1048, 1029, 852, 752, 691 cm^{-1}; MS (ESI) exact mass calculated for $[M+H]^+$ ($C_{13}H_{16}O_4N$) requires *m/z* 250.1, found *m/z* 250.1.

Synthesis of methyl (E)-4-(2-acetamidophenyl)but-2-enoate

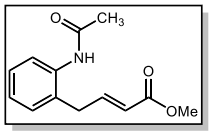




N-(2-allylphenyl)acetamide

To a 100 mL round bottom flask charged with magnetic stir bar 2-acetamidophenylboronic acid (0.93 g, 5.20 mmol, 1.0 equiv) was added. A reflux condenser was attached to the round bottom flask and the entire reaction apparatus was evacuated and backfilled with Ar 10 times. Anhydrous, degassed dimethoxyethane (22.6 mL, 0.23 M) was added, followed by allyl bromide (0.67 mL, 7.79 mmol, 1.5 equiv). Na_2CO_3 (1.1 g, 10.4 mmol, 2.0 equiv) was dissolved in H_2O (5 mL) and degassed by sparging with Ar for 5 minutes. Sodium carbonate solution was added via syringe to degassed reaction mixture and the reaction was heated to reflux for

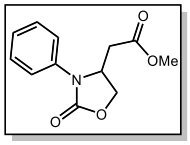
16 h. After, the reaction was cooled to room temperature and quenched by addition of 100 mL H_2O. Organics were extracted with ethyl acetate (100 mL x 3), dried over Na_2SO_4 and concentrated. Crude solid was dissolved in minimal DCM and purified by silica gel column chrotography (2% EtOAc in Hexanes to 40% EtOAc in Hexanes) to afford the titled compound as a beige solid. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.84 (d, *J* = 8.0 Hz, 1H), 7.29 - 7.23 (m, 1H), 7.18 (d, *J* = 7.5 Hz, 1H), 7.11 (t, *J* = 7.5 Hz, 1H), 5.98 (ddt, *J* = 16.6, 10.2, 6.1 Hz, 1H), 5.19 (dd, *J* = 10.2, 2.3 Hz, 1H), 5.10 (dd, *J* = 16.6, 2.3 Hz, 1H), 3.39 (d, *J* = 6.1 Hz, 2H), 2.15 (s, 3H).; ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.25, 136.39, 136.08, 130.22, 129.78, 127.53, 125.32, 123.75, 116.57, 37.03, 24.36.; IR(Neat) 3276, 1654, 1585, 1530, 1481, 1447, 1368, 1295, 1269, 993, 914, 751, 710, 693 cm^{-1}; MS (ESI) exact mass calculated for $[M+H]^+$ ($C_{11}H_{14}NO$) requires *m/z* 176.1, found *m/z* 176.1.



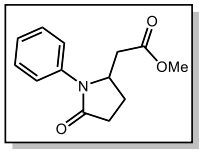
methyl (E)-4-(2-acetamidophenyl)but-2-enoate

Followed the general cross metathesis procedure N-(2-allylphenyl)acetamide (0.67 g, 3.71 mmol) and methyl acrylate to furnish 280 mg (23% yield) of the titled compound as a beige solid. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.62 (d, *J* = 7.9 Hz, 1H), 7.32 - 7.27 (m, 1H), 7.18 (d, *J* = 4.5 Hz, 2H), 7.10 (dt, *J* = 15.6, 6.2 Hz, 1H), 6.93 (s, 1H), 5.76 (d, *J* = 15.7 Hz, 1H), 3.72 (s, 3H), 3.51 (dd, *J* = 6.1, 2.0 Hz, 2H), 2.17 (s, 3H).; ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.56, 166.59, 146.29, 135.33, 130.34, 130.31, 128.01, 126.40, 125.34, 122.36, 51.67, 34.75, 24.16.; IR(Neat) 3260, 1721, 1651, 1532, 1432, 1332, 1268, 1204, 1149, 1008, 980, 762, 705 cm^{-1}; MS (ESI) exact mass calculated for $[M+H]^+$ ($C_{13}H_{15}NO_3$) requires *m/z* 234.1, found *m/z* 234.1.

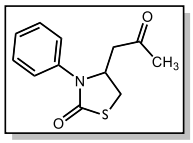
III. Characterization of Products



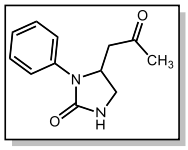
5- methyl 2-(2-oxo-3-phenyloxazolidin-4-yl)acetate
Followed Method B using ((E)-methyl 4-((phenylcarbamoyl)oxy)but-2-enoate (118 mg, 0.5 mmol) for 20 min and purified using silica gel chromatography to give 110 mg (94% yield) of the titled compound as a white solid. IR (Neat): 3061, 3028, 2961, 2873, 1767, 1447, 1192, 1178, 984, 755, 698 cm^{-1}; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.45 - 7.38 (m, 4H), 7.22 (tt, *J* = 7.0, 1.7 Hz, 1H), 4.80 (dddd, *J* = 9.9, 8.2, 4.9, 3.3 Hz, 1H), 4.70 (t, *J* = 8.6 Hz, 1H), 4.23 (dd, *J* = 9.1, 4.8 Hz, 1H), 3.68 (s, 3H), 2.88 (dd, *J* = 16.8, 3.4 Hz, 1H), 2.57 (dd, *J* = 16.8, 10.0 Hz, 1H).; ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.43, 155.37, 135.97, 129.45, 125.78, 122.05, 67.42, 53.07, 52.21, 36.80.; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{12}H_{13}NO_2$) required *m/z* 235.08446, found *m/z* 235.08436 difference 0.42 ppm.



6- methyl 2-(5-oxo-1-phenylpyrrolidin-2-yl)acetate
Followed Method B using (E)-methyl 6-oxo-6-(phenylamino)hex-2-enoate (117 mg, 0.5 mmol) for 30 min and purified using silica gel chromatography to give 101 mg (87% yield) of the titled compound as a white solid. IR(Neat) 2953, 1731, 1691, 1596, 1497, 1457, 1436, 1386, 1290, 1193, 1171, 1116, 1073, 1055, 1007, 901, 828, 756, 693, 657 cm^{-1}; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.42 - 7.34 (m, 4H), 7.22 (tt, *J* = 7.2, 2.0 Hz, 1H), 4.62 (tdd, *J* = 8.5, 6.2, 4.1 Hz, 1H), 3.62 (s, 3H), 2.74 - 2.67 (m, 1H), 2.64 (dd, *J* = 9.5, 7.2 Hz, 1H), 2.59 (dd, *J* = 9.7, 6.0 Hz, 1H), 2.55 - 2.43 (m, 1H), 2.38 (dd, *J* = 15.7, 9.3 Hz, 1H), 1.96 - 1.86 (m, 1H).; ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.02, 170.97, 136.94, 129.23, 126.30, 124.20, 56.56, 51.86, 38.38, 30.82, 24.47.; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{13}H_{16}NO_3$) required *m/z* 233.10519, found *m/z* 233.10493 difference 1.13 ppm.

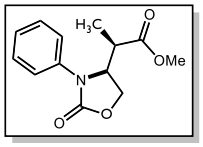


7- 4-(2-oxopropyl)-3-phenylthiazolidin-2-one
Followed Method B using (E)-S-(4-oxopent-2-en-1-yl) phenylcarbamothioate (118 mg, 0.5 mmol) for 30 min and purified using silica gel chromatography to give 81 mg (69% yield) of the titled compound as a white solid. IR(Neat) 3056, 1712, 1660, 1594, 1493, 1385, 1364, 1266, 1157, 1098, 836, 755, 751, 705, 694 cm^{-1}; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.34 (t, *J* = 7.9 Hz, 2H), 7.24 (d, *J* = 7.5 Hz, 2H), 7.23 - 7.18 (m, 1H), 4.73 (ddt, *J* = 10.2, 7.0, 3.4 Hz, 1H), 3.73 (dd, *J* = 11.4, 7.3 Hz, 1H), 2.97 - 2.94 (m, 1H), 2.94 - 2.89 (m, 1H), 2.67 (dd, *J* = 18.3, 2.8 Hz, 1H), 2.04 (s, 3H).; ^{13}C NMR (126 MHz, $CDCl_3$) δ 205.79, 170.86, 137.28, 129.51, 127.07, 125.47, 57.58, 44.95, 31.67, 30.56.; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{12}H_{14}NO_2S$) required *m/z* 235.00670, found *m/z* 235.00638 difference 1.36 ppm.

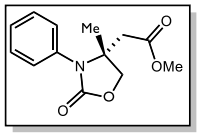


8- 5-(2-oxopropyl)-1-phenylimidazolidin-2-one
Followed Method B using (E)-1-(4-oxopent-2-en-1-yl)-3-phenylurea (109 mg, 0.5 mmol) for 30 min and purified using silica gel chromatography to give 105 mg (96% yield) of the titled compound as a white solid. IR(Neat) 3241, 3105, 1710, 1683, 1599, 1497, 1455, 1440, 1406, 1366, 1258, 1137, 801, 752, 688 cm^{-1}; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.40 (d, *J* = 7.6 Hz, 2H), 7.36 (t, *J* = 7.9 Hz,

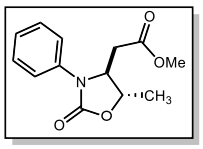
2H), 7.13 (t, *J* = 7.2 Hz, 1H), 4.82 - 4.75 (m, 1H), 4.73 (s, 1H), 3.87 (t, *J* = 8.8 Hz, 1H), 3.15 (dd, *J* = 9.1, 4.7 Hz, 1H), 2.96 (dd, *J* = 18.5, 2.8 Hz, 1H), 2.75 (dd, *J* = 18.5, 10.1 Hz, 1H), 2.12 (s, 3H).; ^{13}C NMR (126 MHz, $CDCl_3$) δ 206.48, 137.73, 129.20, 124.35, 121.51, 109.99, 52.36, 46.02, 44.25, 30.57; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{12}H_{14}N_2O_2$) required *m/z* 218.10553, found *m/z* 218.10528 difference 1.14 ppm.



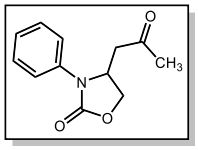
9- methyl (R)-2-((S)-2-oxo-3-phenyloxazolidin-4-yl)propanoate
Followed Method B using (E)-methyl 2-methyl-4-((phenylcarbamoyl)oxy)but-2-enoate (25 mg, 0.1 mmol) for 30 min and purified using silica gel preprative TLC to give 24.5 mg (98% yield) of the titled compound as a white solid. IR (Neat) 2984, 2952, 1749, 1732, 1598, 1502, 1409, 1298, 1209, 1140, 759, 695, 675 cm^{-1}; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.46 - 7.37 (m, 4H), 7.21 (tt, *J* = 7.1, 1.5 Hz, 1H), 4.68 (dt, *J* = 8.9, 3.7 Hz, 1H), 4.54 (t, *J* = 8.9 Hz, 1H), 4.36 (dd, *J* = 9.0, 3.8 Hz, 1H), 2.82 (qd, *J* = 7.2, 3.6 Hz, 1H), 1.15 (d, *J* = 7.2 Hz, 3H).; ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.78, 155.66, 136.43, 129.23, 125.95, 123.04, 64.44, 58.79, 52.18, 40.39, 12.12.; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{13}H_{15}NO_4$) required *m/z* 249.10011, found *m/z* 249.10035 difference 0.98 ppm.



10- methyl 2-(4-methyl-2-oxo-3-phenyloxazolidin-4-yl)acetate
Followed Method B using (E)-methyl 3-methyl-4-((phenylcarbamoyl)oxy)but-2-enoate (125 mg, 0.50 mmol) for 30 min and purified using silica gel chromatography to give 110 mg (88% yield) of the titled product as a white solid. IR(Neat) 2963, 1743, 1722, 1596, 1500, 1435, 1394, 1382, 1367, 1328, 1277, 1233, 1208, 1155, 1126, 1061, 1004, 965, 699, 654 cm^{-1}; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.37 (t, *J* = 7.4 Hz, 2H), 7.32 (t, *J* = 7.4 Hz, 1H), 7.18 (d, *J* = 7.3 Hz, 2H), 4.56 (d, *J* = 9.1 Hz, 1H), 4.23 (d, *J* = 9.1 Hz, 1H), 3.63 (s, 3H), 2.68 (d, *J* = 15.5 Hz, 1H), 2.48 (d, *J* = 15.5 Hz, 1H), 1.38 (s, 3H).; ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.99, 156.84, 134.34, 129.54, 129.40, 128.60, 73.42, 61.02, 52.10, 42.71.; HRMS (ESI) exact mass calculated for $[M+Na]^+$ ($C_{13}H_{15}NO_4Na$) requires *m/z* 249.10011, found *m/z* 249.10012 difference 0.04 ppm.

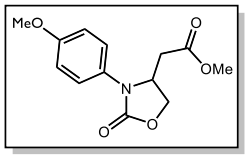


11- methyl 2-(5-methyl-2-oxo-3-phenyloxazolidin-4-yl)acetate
Followed Method B using (E)-methyl 4-((phenylcarbamoyl)oxy)pent-2-enoate (125 mg, 0.5 mmol) for 30 min and purified using silica gel chromatograhpy to give 115 mg (92% yield) of the titled compound as a white solid. IR (Neat) 2984, 2952, 1749, 1732, 1598, 1502, 1409, 1298, 1209, 1140, 759, 695, 675 cm^{-1}; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.41 - 7.36 (m, 2H), 7.35 - 7.30 (m, 2H), 7.13 (tt, *J* = 7.2, 1.3 Hz, 1H), 4.42 (qd, *J* = 6.3, 3.7 Hz, 1H), 4.30 (dt, *J* = 9.8, 3.7 Hz, 1H), 2.75 (dd, *J* = 16.6, 3.4 Hz, 1H), 2.49 (dd, *J* = 16.6, 9.8 Hz, 1H), 1.50 (d, *J* = 6.3 Hz, 3H).; ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.48, 154.61, 136.23, 129.39, 125.55, 121.84, 75.64, 59.57, 52.10, 36.61, 20.90.; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{13}H_{16}NO_4$) required *m/z* 249.10011, found *m/z* 249.10029 difference 0.75 ppm.



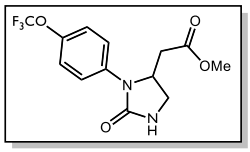
12- 4-(2-oxopropyl)-3-phenyloxazolidin-2-one

Followed Method B using (E)-4-oxopent-2-en-1-yl phenylcarbamate (110 mg, 0.5 mmol) for 30 min and purified using silica gel chromatography to give 104 mg (95% yield) of the titled compound as a white solid. IR(Neat) 3060, 2919., 1746, 1708, 1598, 1499, 1399, 1365, 1215, 1165, 1091, 1037, 757, 732, 693, 673 cm^{-1}; ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.36 - 7.31 (m, 4H), 7.18 - 7.10 (m, 1H), 4.81 - 4.71 (m, 1H), 4.66 (ddd, *J* = 9.1, 8.3, 0.9 Hz, 1H), 3.98 (dd, *J* = 8.8, 4.8 Hz, 1H), 2.99 (dd, *J* = 18.5, 2.8 Hz, 1H), 2.64 (dd, *J* = 18.5, 10.0 Hz, 1H), 2.07 (s, 3H).; ^{13}C NMR (126 MHz, $CDCl_3$) δ 205.78, 155.42, 136.22, 129.44, 125.59, 121.84, 67.91, 52.32, 46.09, 30.35.; HRMS (ESI) exact mass calculated for $[M+Na]^+$ ($C_{12}H_{13}NNaO_3$) required *m/z* 219.08954, found *m/z* 219.08986 difference 1.45 ppm.



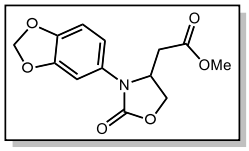
13- methyl 2-(3-(4-methoxyphenyl)-2-oxooxazolidin-4-yl)acetate

Followed Method B using (E)-methyl 4-(((4-methoxyphenyl)carbamoyl)oxy)but-2-enoate (133 mg, 0.5 mmol) for 30 min and purified using silica gel chromatography to give 127 mg (96% yield) of the titled compound as a white solid. IR(Neat) 3012, 2955, 2839, 1733, 1512, 1438, 1407, 1367, 1327, 1297, 1246, 1200, 1171, 1126, 1030, 969, 831, 748 cm^{-1}; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.29 (d, *J* = 8.9 Hz, 1H), 6.92 (d, *J* = 8.9 Hz, 1H), 4.72 - 4.63 (m, 2H), 4.23 - 4.17 (m, 1H), 3.80 (s, 3H), 3.66 (s, 3H), 2.80 (dd, *J* = 16.6, 3.5 Hz, 1H), 2.58 - 2.50 (m, 1H).; ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.37, 157.90, 155.94, 128.63, 125.00, 114.70, 67.48, 55.53, 53.92, 52.13, 37.08.; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{13}H_{15}NO_5$) required *m/z* 265.09502, found *m/z* 265.09470 difference 1.22 ppm.



14- methyl 2-(2-oxo-3-(4-(trifluoromethoxy)phenyl)imidazolidin-4-yl)acetate

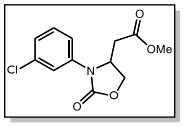
Followed Method B using (E)-methyl 4-(3-(4-(trifluoromethoxy)phenyl)ureido)but-2-enoate (159 mg, 0.5 mmol) for 30 min and purified using silica gel chromatography to give 155 mg (97% yield) of the titled compound as a white solid. IR(Neat) 3226, 3115, 1731, 1703, 1508, 1431, 1276, 1256, 1207, 1142, 1007, 985, 943, 922, 900, 848, 810, 753 cm^{-1}; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.47 (d, *J* = 9.0 Hz, 2H), 7.22 (d, *J* = 9.0 Hz, 2H), 5.02 (s, 1H), 4.72 (dddd, *J* = 9.7, 8.2, 4.4, 3.4 Hz, 1H), 3.85 (t, *J* = 8.9 Hz, 1H), 3.32 (dd, *J* = 9.1, 4.5 Hz, 1H), 2.79 (dd, *J* = 16.3, 3.4 Hz, 1H), 2.58 (dd, *J* = 16.3, 9.8 Hz, 1H).; ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.81, 159.06, 145.42, 136.31, 122.59, 121.91, 120.47 (d, J = 257 Hz), 53.24, 52.04, 43.77, 36.84..; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{13}H_{14}F_3N_2O_4$) required *m/z* 318.08274, found *m/z* 318.08240 difference 1.09 ppm.



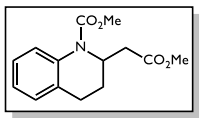
15- methyl 2-(3-(benzo[d][1,3]dioxol-5-yl)-2-oxooxazolidin-4-yl)acetate

Followed Method B using (E)-methyl 4-((benzo[d][1,3]dioxol-5-ylcarbamoyl)oxy)but-2-enoate (140 mg, 0.5 mmol) for 30 min and purified using silica gel chromatography to give 132 mg (95% yield)

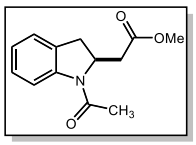
of the titled compound as a white solid. IR(Neat) 2956, 1731, 1632, 1504, 1488, 1408, 1218, 1174, 1093, 1032, 930, 808, 719 cm^{-1}; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 6.96 (d, *J* = 2.2 Hz, 1H), 6.81 (d, *J* = 8.3 Hz, 1H), 6.75 (dd, *J* = 8.3, 2.2 Hz, 1H), 5.98 (s, 2H), 4.69 (t, *J* = 8.5 Hz, 1H), 4.63 (dddd, *J* = 9.6, 8.4, 4.9, 3.4 Hz, 1H), 4.19 (dd, *J* = 8.7, 4.9 Hz, 1H), 3.67 (s, 3H), 2.82 (dd, *J* = 16.7, 3.4 Hz, 1H), 2.54 (dd, *J* = 16.7, 9.5 Hz, 1H).; ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.31, 155.80, 148.37, 146.05, 129.80, 116.83, 108.43, 105.55, 101.68, 67.46, 54.06, 52.16, 36.96.; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{13}H_{14}NO_6$) required *m/z* 279.07429, found *m/z* 279.07467 difference 1.36 ppm.



16- methyl 2-(3-(3-chlorophenyl)-2-oxooxazolidin-4-yl)acetate
Followed Method B using (E)-methyl 4-(((3-chlorophenyl)carbamoyl)oxy)but-2-enoate (135 mg, 0.50 mmol) for 30 min and purified using silica gel chromatography to give 133 mg (99% yield) of the titled compound as a white solid. IR(Neat) 2955, 1730, 1594, 1576, 1484, 1437, 1400, 1369, 1196, 1174, 1127, 1095, 982, 874, 779, 751, 682 cm^{-1}; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.51 (s, 1H), 7.35 - 7.29 (m, 2H), 7.21 - 7.16 (m, 1H), 4.83 - 4.74 (m, 1H), 4.69 (ddd, *J* = 9.1, 8.2, 0.7 Hz, 1H), 4.24 (dd, *J* = 9.1, 4.5 Hz, 1H), 3.70 (s, 3H), 2.87 (dd, *J* = 16.8, 3.3 Hz, 1H), 2.58 (dd, *J* = 16.8, 9.9 Hz, 1H).; ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.19, 154.89, 137.34, 135.16, 130.38, 125.64, 121.66, 119.43, 67.36, 52.84, 52.27, 36.56.; HRMS (ESI) exact mass calculated for $[M+Na]^+$ ($C_{12}H_{12}ClNO_4Na$) requires *m/z* 269.04549, found *m/z* 269.04521 difference 1.01 ppm.

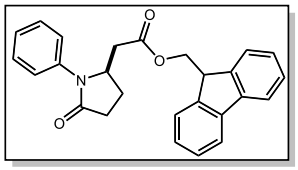


17- methyl 2-(2-methoxy-2-oxoethyl)-3,4-dihydroquinoline-1(2H)-carboxylate
Followed Method B using ((E)-methyl 5-(2-((methoxycarbonyl)amino)phenyl)pent-2-enoate (132 mg, 0.5 mmol) for 30 min and purified using silica gel chromatography to give 113 mg (86% yield) of the titled compound as a white solid. IR(Neat) 3327, 3006, 2957, 1729, 1704, 1529, 1456, 1430, 1293, 1213, 1192, 1160, 1061, 1047, 753, 724, 714 cm^{-1}; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.48 (d, *J* = 7.8 Hz, 1H), 7.18 (t, *J* = 7.7 Hz, 1H), 7.10 (d, *J* = 7.2 Hz, 1H), 7.05 (t, *J* = 7.3 Hz, 1H), 4.92 (p, *J* = 6.5 Hz, 1H), 3.77 (s, 3H), 3.64 (s, 3H), 2.71 - 2.62 (m, 3H), 2.41 (dd, *J* = 14.9, 8.0 Hz, 1H), 2.33 (dq, *J* = 13.1, 6.6 Hz, 1H), 1.67 (dq, *J* = 13.5, 6.7 Hz, 1H).; ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.48, 155.13, 136.26, 131.54, 127.83, 126.23, 125.56, 124.49, 53.01, 51.70, 50.47, 38.30, 28.98, 24.85.; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{14}H_{18}NO_4$) required *m/z* 264.11576, found *m/z* 264.11540 difference 1.37 ppm.



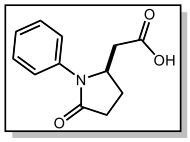
18- methyl 2-(1-acetylindolin-2-yl)acetate
Followed Method B using (E)-methyl 4-(2-acetamidophenyl)but-2-enoate (117 mg, 0.50 mmol) for 30 min and purified using silica gel chromatography to give 114 mg (98% yield) of the titled compound as a white solid. IR (Neat) 2984, 2952, 1749, 1732, 1598, 1502, 1409, 1298, 1209, 1140, 759, 695, 675 cm^{-1}; IR (Neat) 2984, 2952, 1749, 1732, 1598, 1502, 1409, 1298, 1209, 1140, 759, 695, 675 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6, 80°C) δ 7.70 (s, 1H), 7.22 (d, *J* = 7.4 Hz, 1H), 7.14 (t, *J* = 7.8 Hz, 1H), 6.98 (t, *J* = 7.4 Hz, 1H), 4.83 (tdd, *J* = 9.0, 4.1, 1.7 Hz, 1H), 3.56 (s, 3H), 3.37 (dd, *J* = 16.2, 8.9 Hz, 1H), 2.79 (d, *J* = 16.3 Hz, 1H), 2.70 (dd, *J* = 15.2, 4.0 Hz, 1H), 2.48 (dd, *J* = 15.1, 9.2 Hz, 1H), 2.24 (s, 3H).; ^{13}C NMR (100 MHz,

DMSO-d_6, 80°C) δ 171.13, 168.41, 142.27, 131.42, 127.68, 125.84, 124.02, 116.92, 57.27, 51.96, 39.63, 34.63, 23.92.; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{13}H_{16}NO_3$) requires *m/z* 233.10519, found *m/z* 233.10548 difference 1.24 ppm.



19- (9H-fluoren-9-yl)methyl (R)-2-(5-oxo-1-phenylpyrrolidin-2-yl)acetate

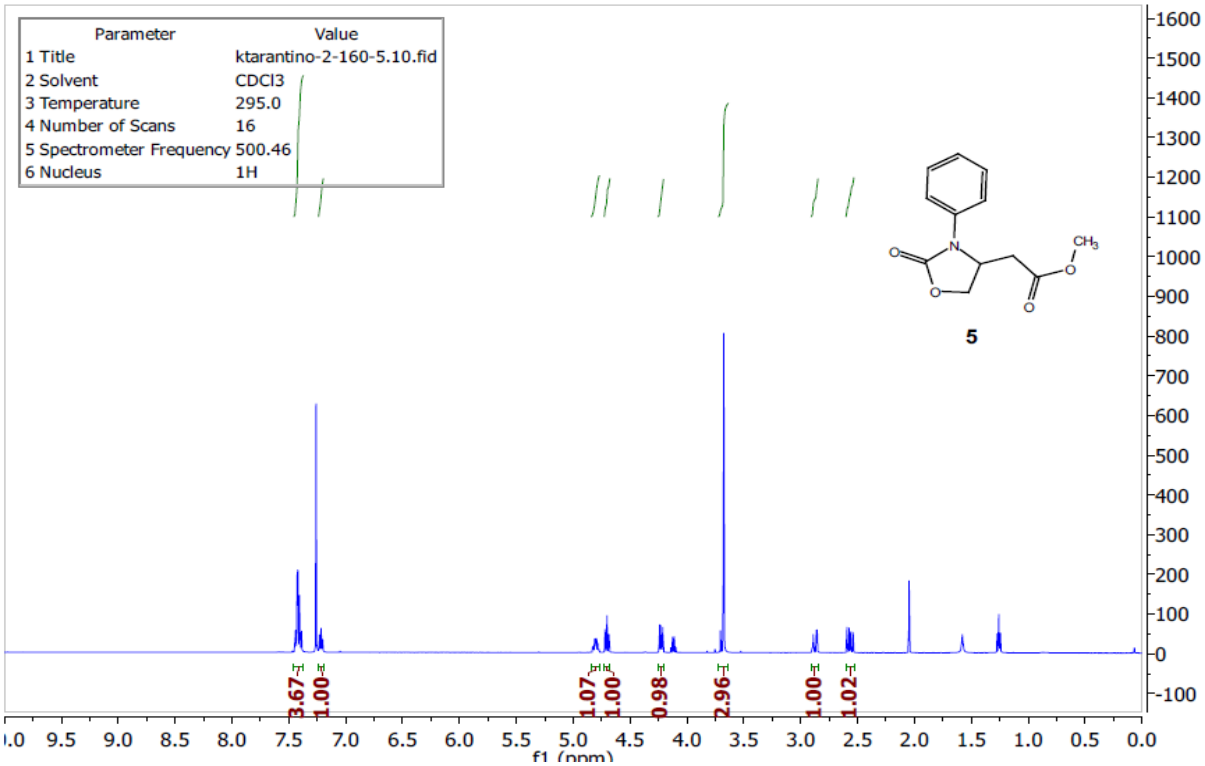
Followed Method B using (E)-(9H-fluoren-9-yl)methyl 6-oxo-6-(phenylamino)hex-2-enoate (199 mg, 0.5 mmol) for 30 min and purified using silica gel chromatograhpy to give 184 mg (93% yield) of the titled compound as a white solid. IR (Neat) 2984, 2952, 1749, 1732, 1598, 1502, 1409, 1298, 1209, 1140, 759, 695, 675 cm^{-1}; ^1H NMR (500 MHz, Chloroform-*d*) δ 7.78 (d, *J* = 7.5 Hz, 2H), 7.54 - 7.51 (m, 2H), 7.42 (td, *J* = 7.5, 3.4 Hz, 2H), 7.39 - 7.29 (m, 6H), 7.20 (t, *J* = 7.2 Hz, 1H), 4.45 (d, *J* = 6.3 Hz, 2H), 4.41 (tt, *J* = 8.2, 4.6 Hz, 1H), 4.15 (t, *J* = 6.3 Hz, 1H), 2.68 (dd, *J* = 15.5, 3.7 Hz, 1H), 2.59 (ddd, *J* = 17.1, 9.5, 7.3 Hz, 1H), 2.51 (dd, *J* = 9.7, 6.1 Hz, 1H), 2.33 (dd, *J* = 15.6, 9.7 Hz, 1H), 2.28 - 2.20 (m, 1H), 1.76 - 1.67 (m, 1H).; ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.96, 170.35, 143.49, 141.40, 136.88, 129.23, 127.93, 127.17, 126.16, 124.80, 123.87, 120.11, 66.06, 56.41, 46.83, 38.54, 30.82, 24.25.; HRMS (ESI) exact mass calculated for $[M+Na]^+$ ($C_{26}H_{23}NNaO_3$) required *m/z* 420.15701, found *m/z* 420.15743 difference 1.05 ppm.

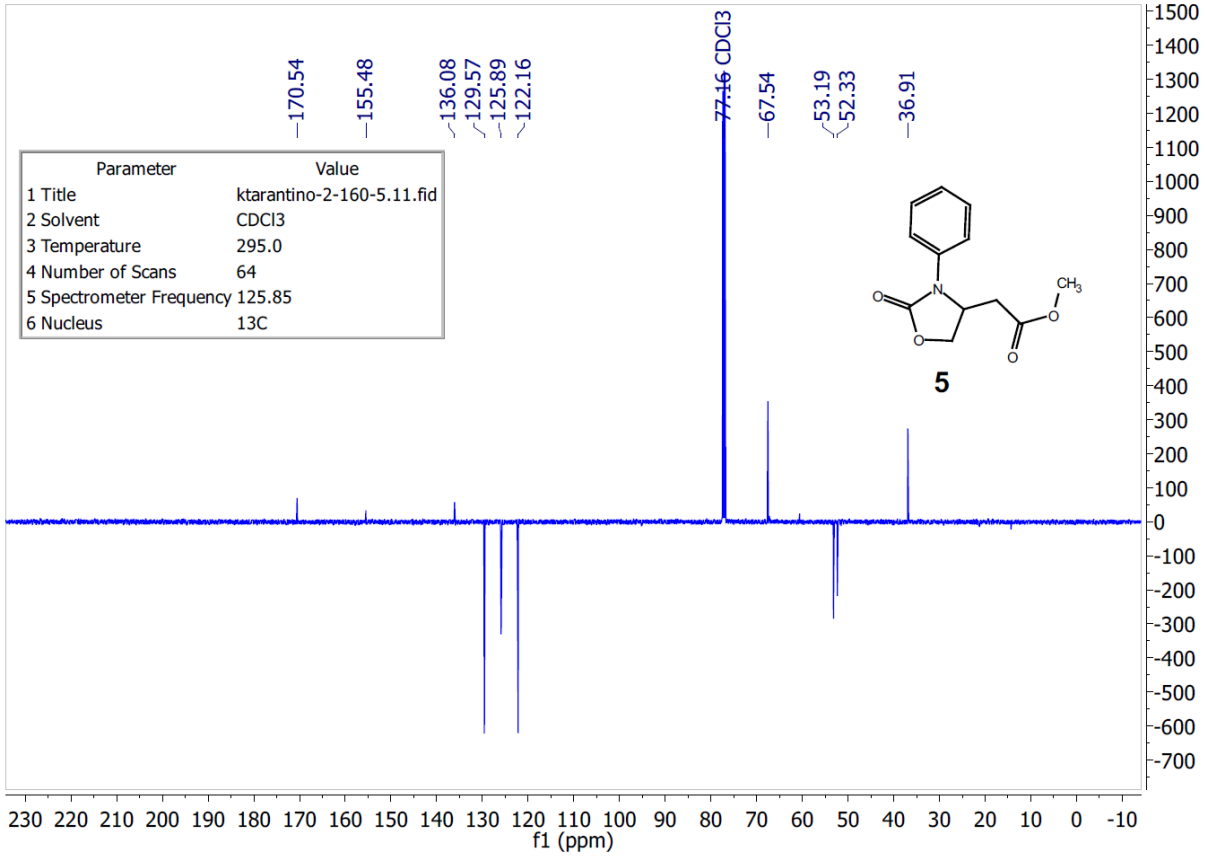


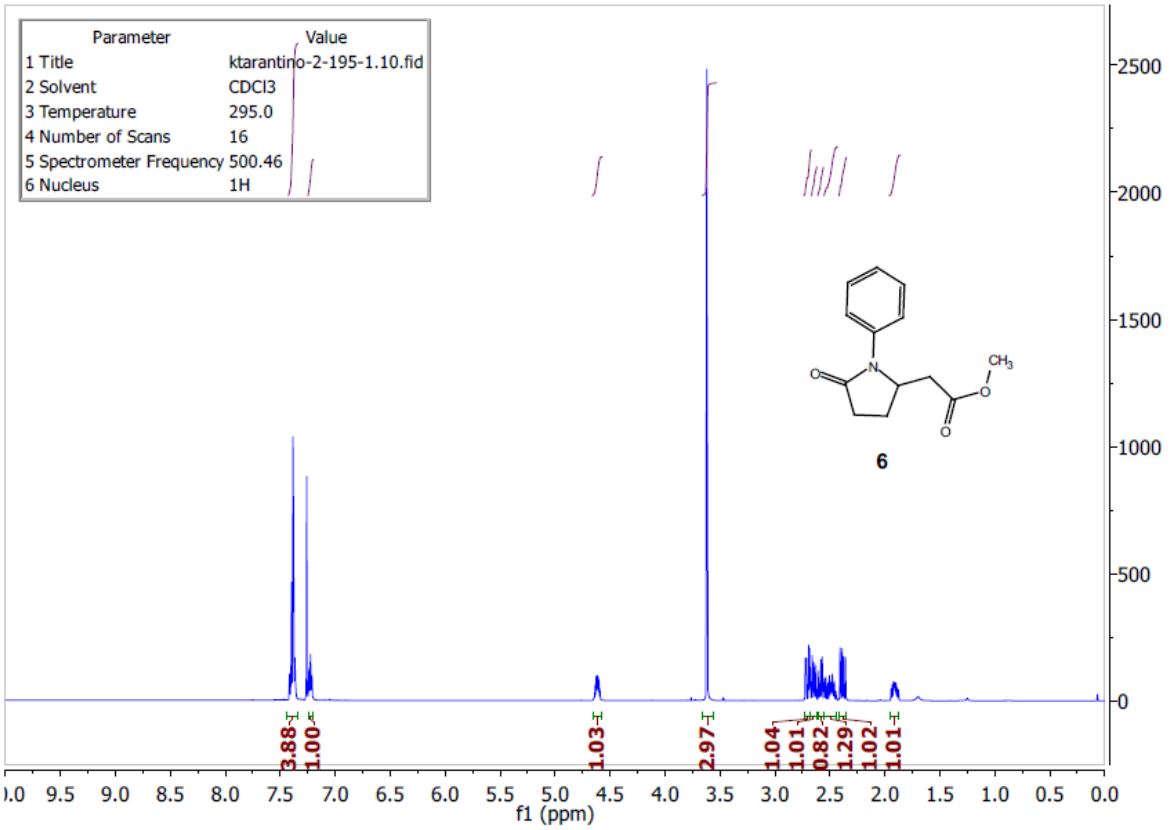
2-(5-oxo-1-phenylpyrrolidin-2-yl)acetic acid

(E)-(9H-fluoren-9-yl)methyl 6-oxo-6-(phenylamino)hex-2-enoate (199 mg, 0.5 mmol) and potassium *tert*-butoxide (84 mg, 0.75 mmol, 1.5 equiv.) and THF (10 mL) was added to 50 mL rbf and stirred at room temperature for 30 min. Rx was quenched with H_2O, extracted with EtOAc, dried over Na_2SO_4 and concentrated. Crude material was purified using silica gel chromatograhpy to give 100 mg (91% yield) of the titled compound as a white solid. IR(Neat) 2994, 1656, 1596, 1546, 1498, 1409, 1296, 1190, 758, 695 cm^{-1}; ^1H NMR (500 MHz, Chloroform-*d*) δ 7.42 - 7.34 (m, 4H), 7.26 - 7.21 (m, 1H), 4.60 (ddt, *J* = 11.2, 9.6, 3.8 Hz, 1H), 2.74 (dd, *J* = 16.1, 3.5 Hz, 1H), 2.72 - 2.65 (m, 1H), 2.63 - 2.56 (m, 1H), 2.56 - 2.47 (m, 1H), 2.41 (dd, *J* = 16.2, 9.5 Hz, 1H), 1.99 - 1.91 (m, 1H).; ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.84, 174.36, 136.69, 129.33, 126.53, 124.28, 56.45, 37.97, 30.79, 24.36.; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{12}H_{14}NO_3$) required *m/z* 219.08954, found *m/z* 219.08945 difference 0.43 ppm.

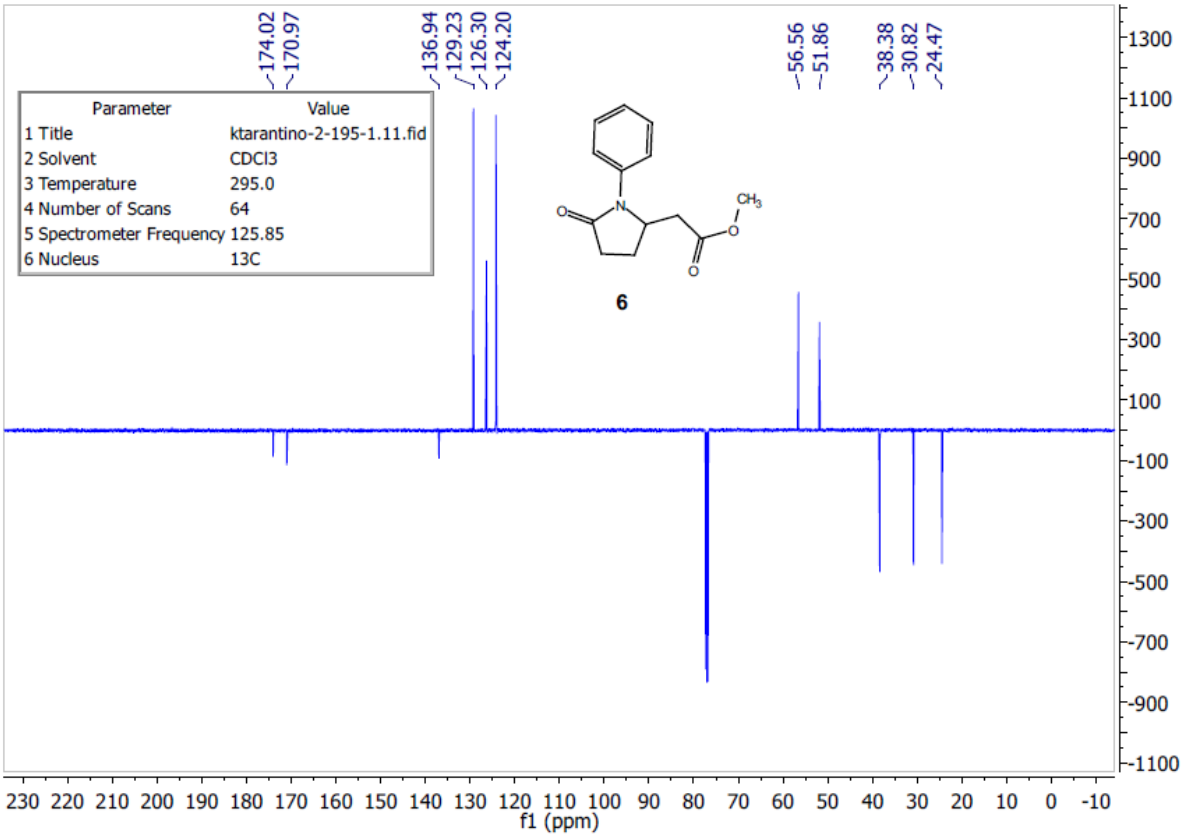
IV. ^{1}H and ^{13}C NMR Spectra of Products



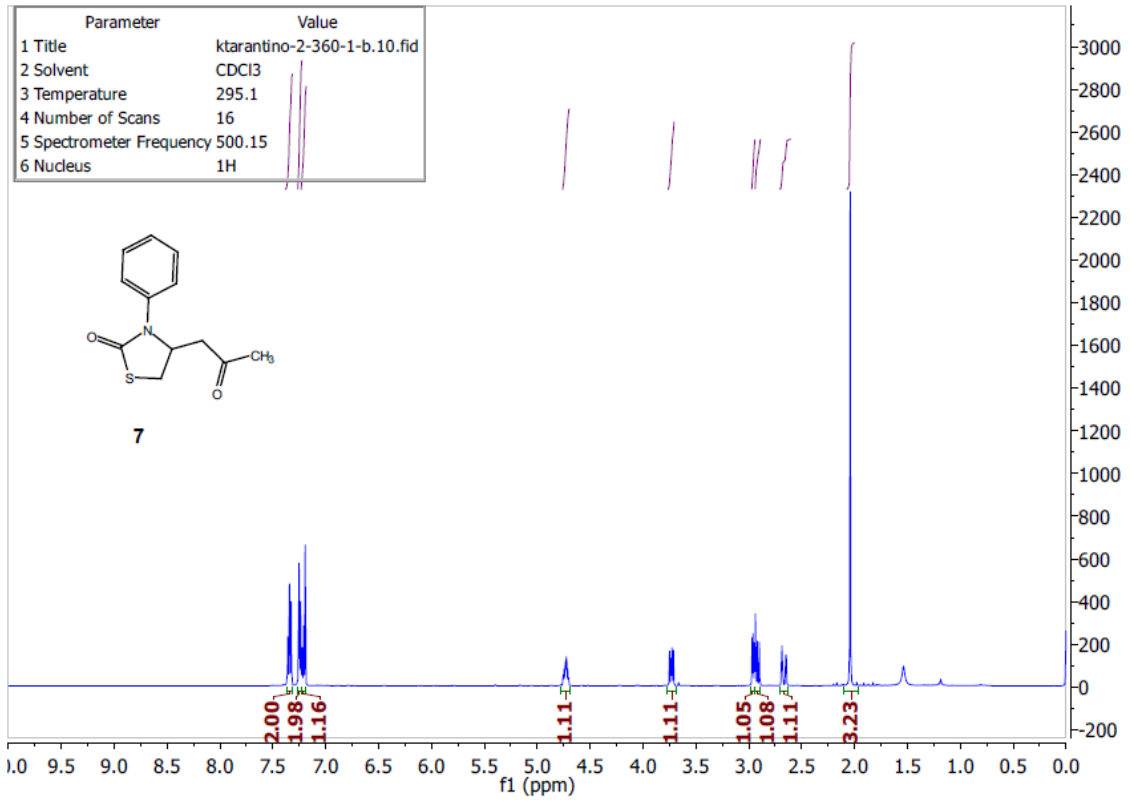


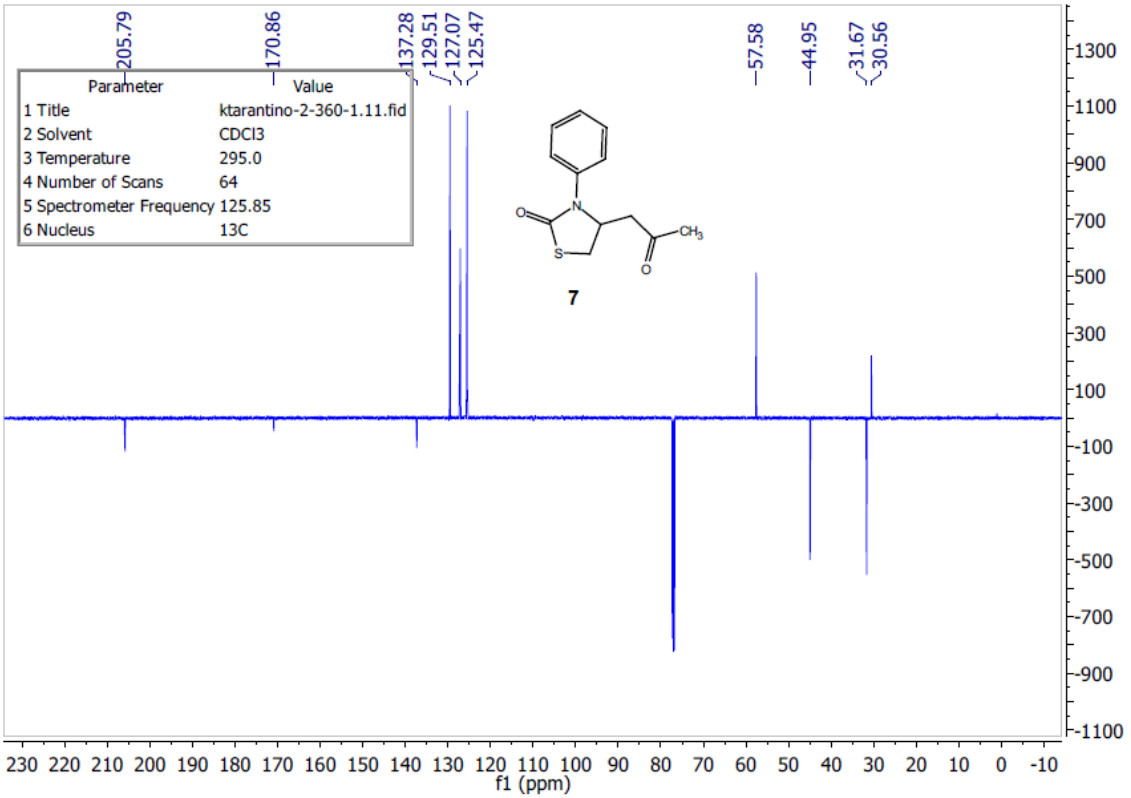

Parameter Value
1 Title ktarantino-2-195-1.10.fid
2 Solvent CDCl3
3 Temperature 295.0
4 Number of Scans 16
5 Spectrometer Frequency 500.46
6 Nucleus 1H
3.88
1.00
1.03
2.97
1.04
1.01
0.82
1.29
1.02
1.01
f1 (ppm)

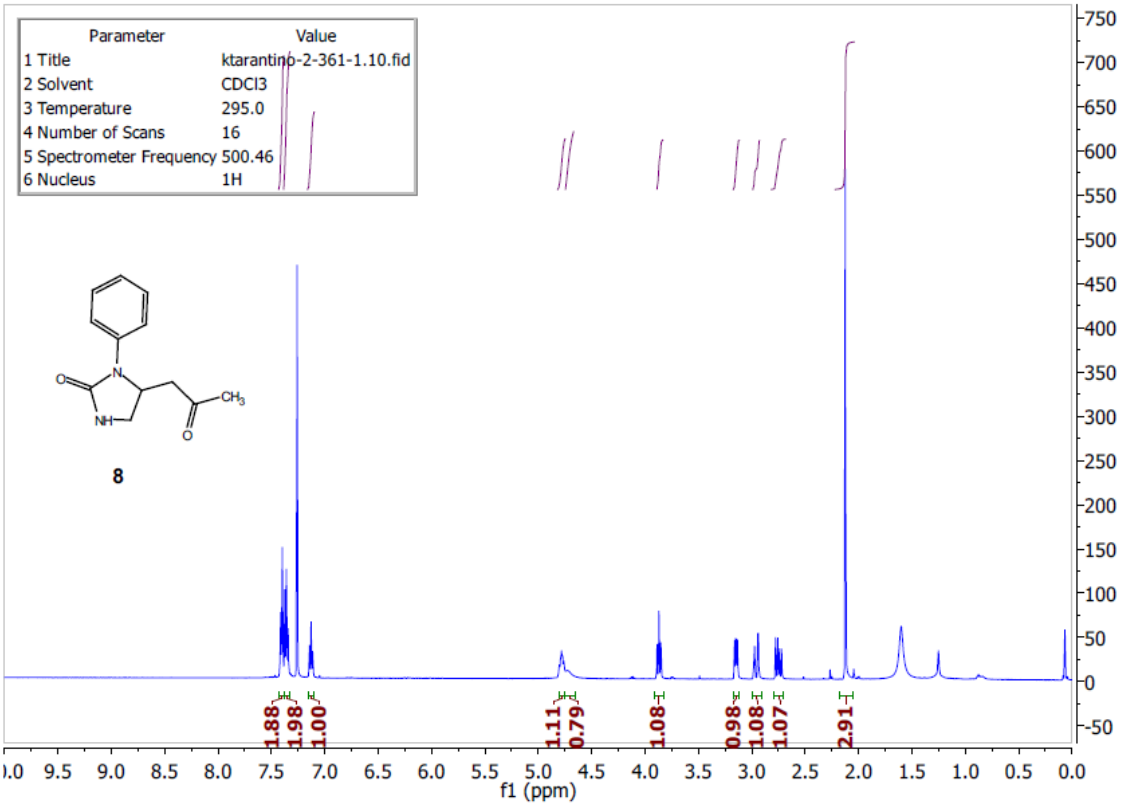
6

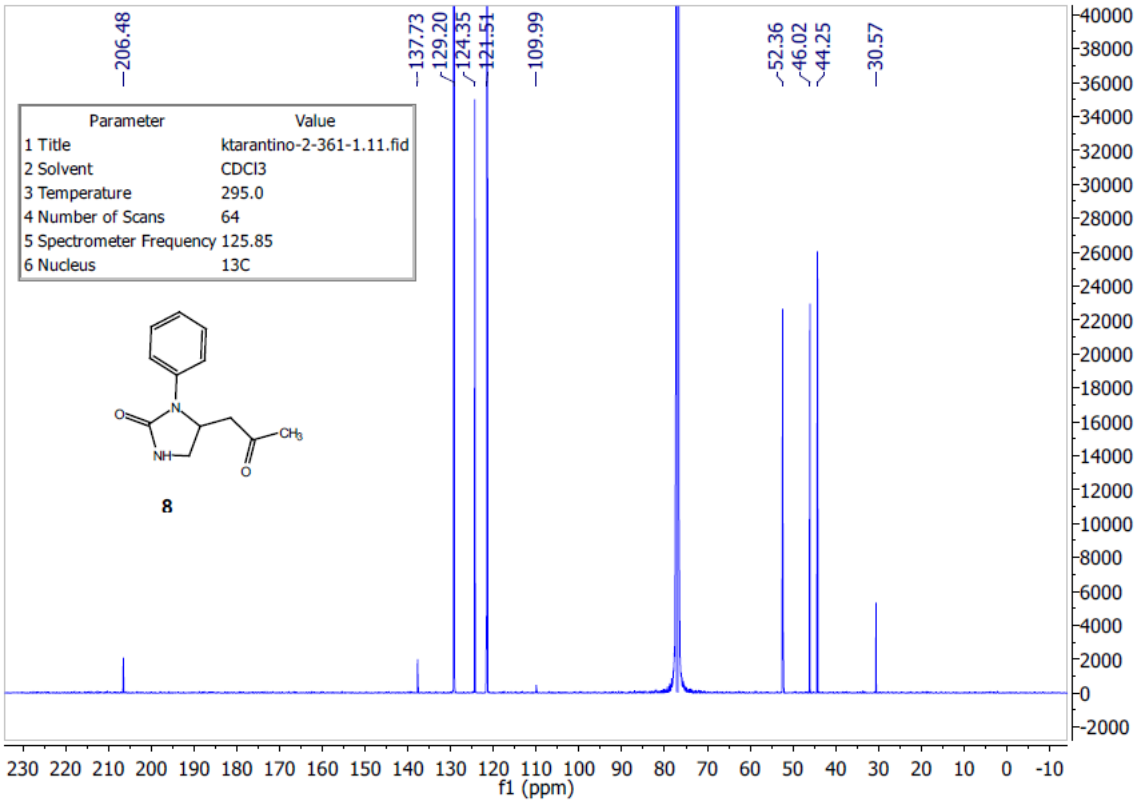

174.02
170.97
136.94
129.23
126.30
124.20
56.56
51.86
38.38
30.82
24.47
Parameter Value
1 Title ktarantino-2-195-1.11.fid
2 Solvent CDCl3
3 Temperature 295.0
4 Number of Scans 64
5 Spectrometer Frequency 125.85
6 Nucleus 13C
f1 (ppm)

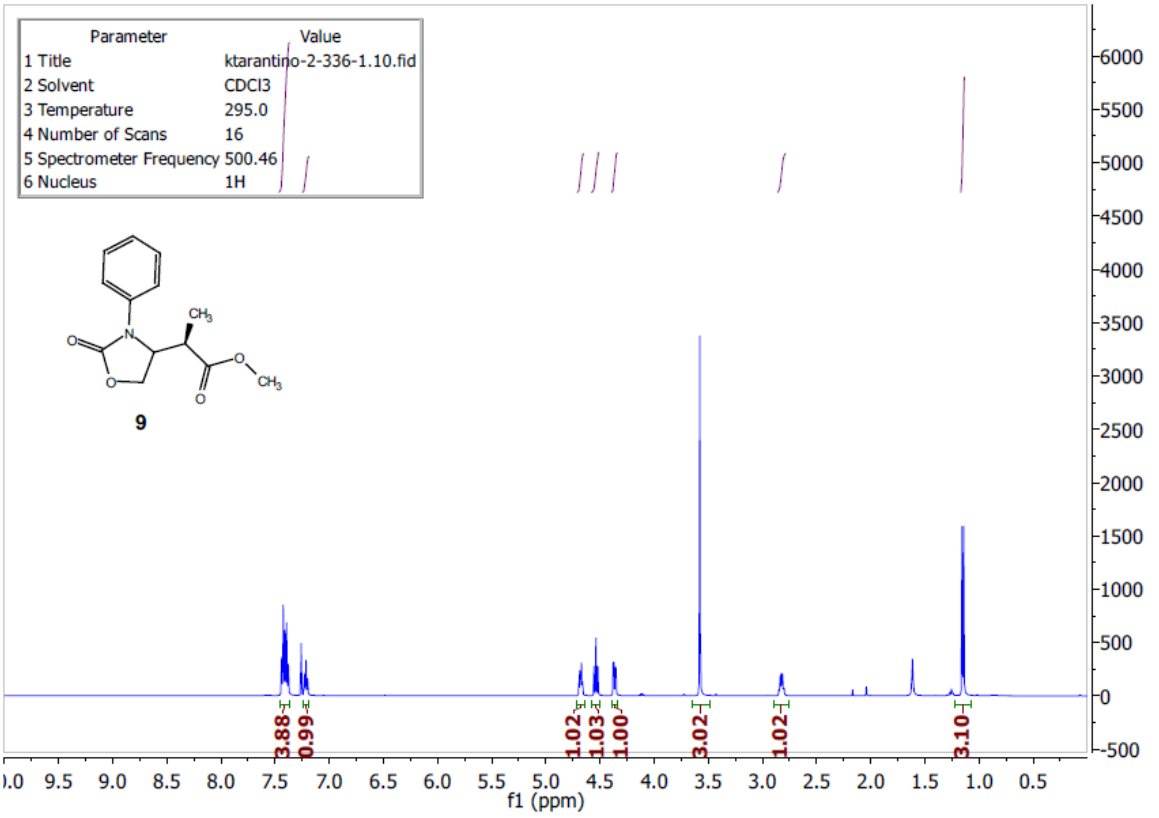
6

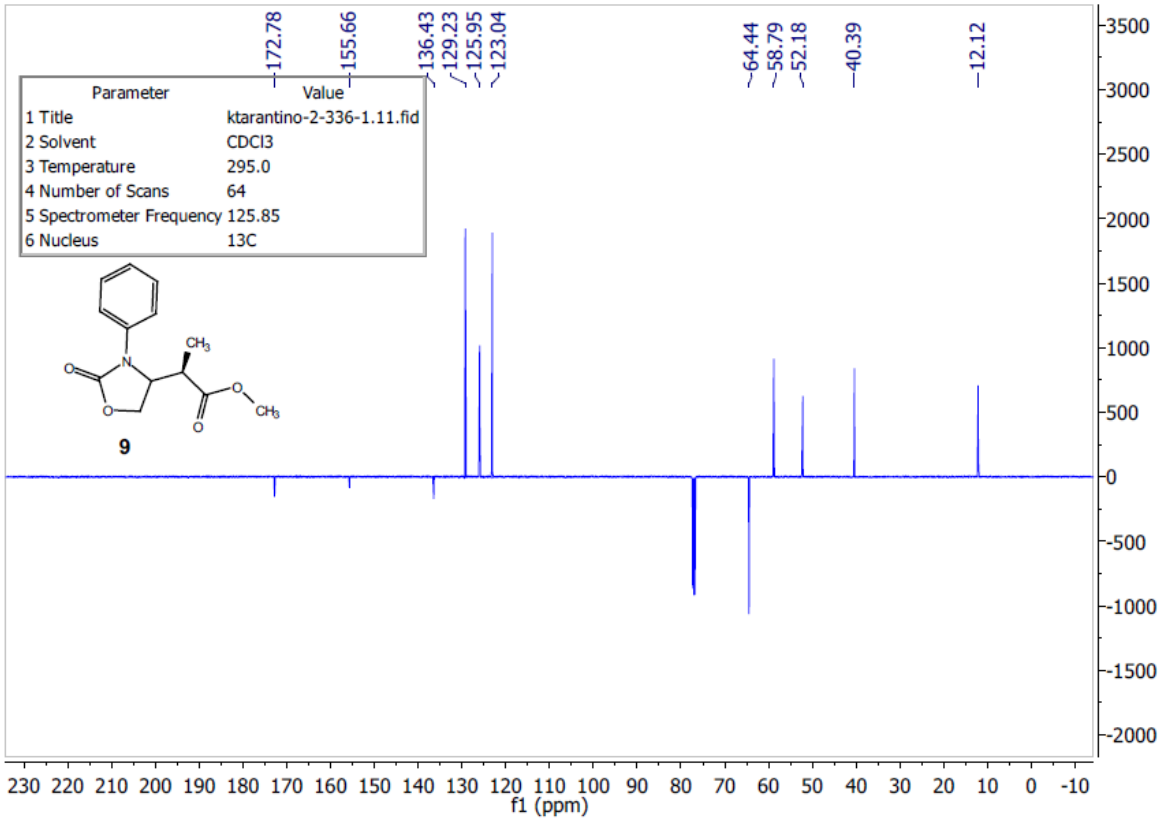

Parameter Value
1 Title ktarantino-2-360-1-b.10.fid
2 Solvent CDCl3
3 Temperature 295.1
4 Number of Scans 16
5 Spectrometer Frequency 500.15
6 Nucleus 1H
7
2.00
1.98
1.16
1.11
1.11
1.05
1.08
1.11
3.23
f1 (ppm)

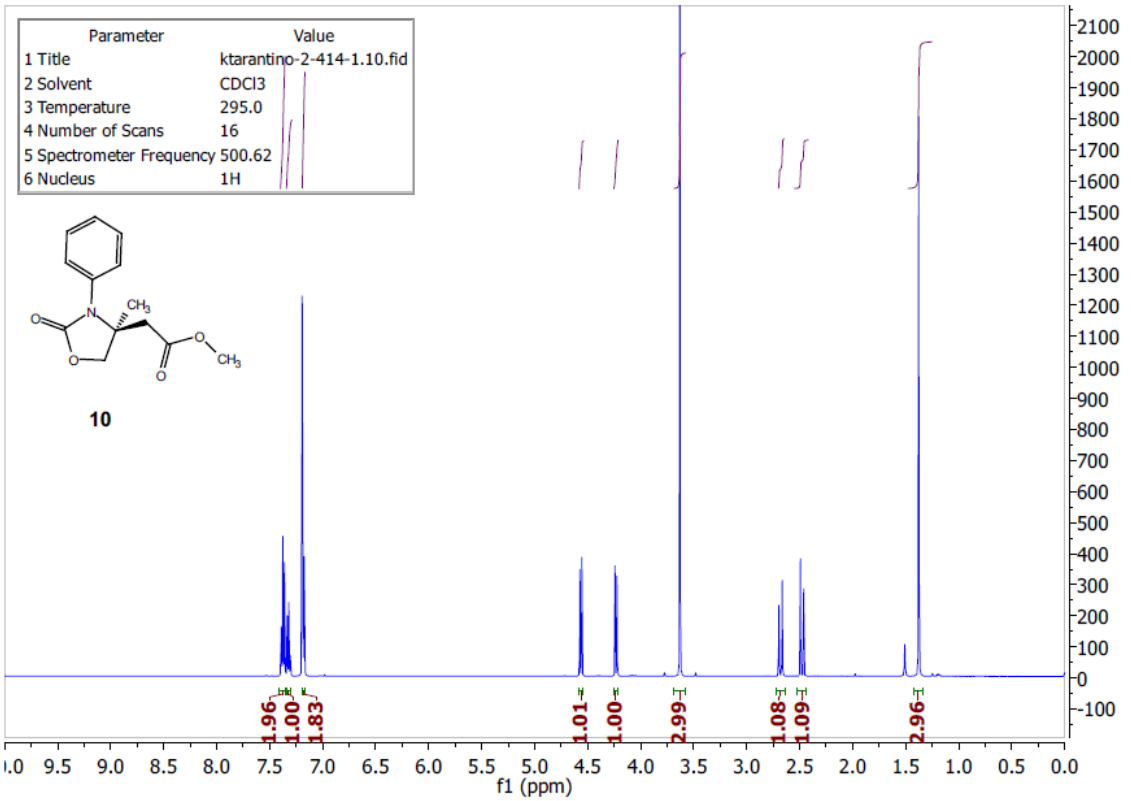

205.79
170.86
137.28
129.51
127.07
125.47
57.58
44.95
31.67
30.56
Parameter Value
1 Title ktarantino-2-360-1.11.fid
2 Solvent CDCl3
3 Temperature 295.0
4 Number of Scans 64
5 Spectrometer Frequency 125.85
6 Nucleus 13C
7
f1 (ppm)

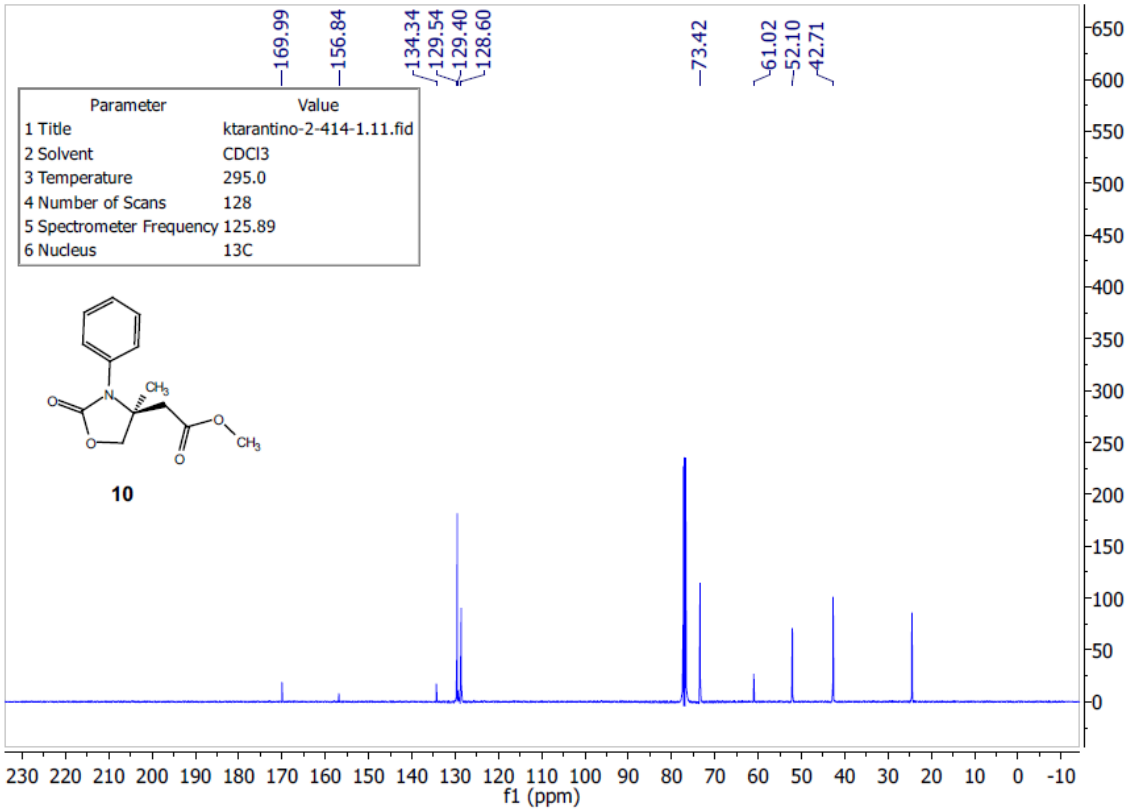

Parameter Value
1 Title ktarantino-2-361-1.10.fid
2 Solvent CDCl3
3 Temperature 295.0
4 Number of Scans 16
5 Spectrometer Frequency 500.46
6 Nucleus 1H
8
1.88
1.98
1.00
1.11
0.79
1.08
0.98
1.08
1.07
2.91
f1 (ppm)

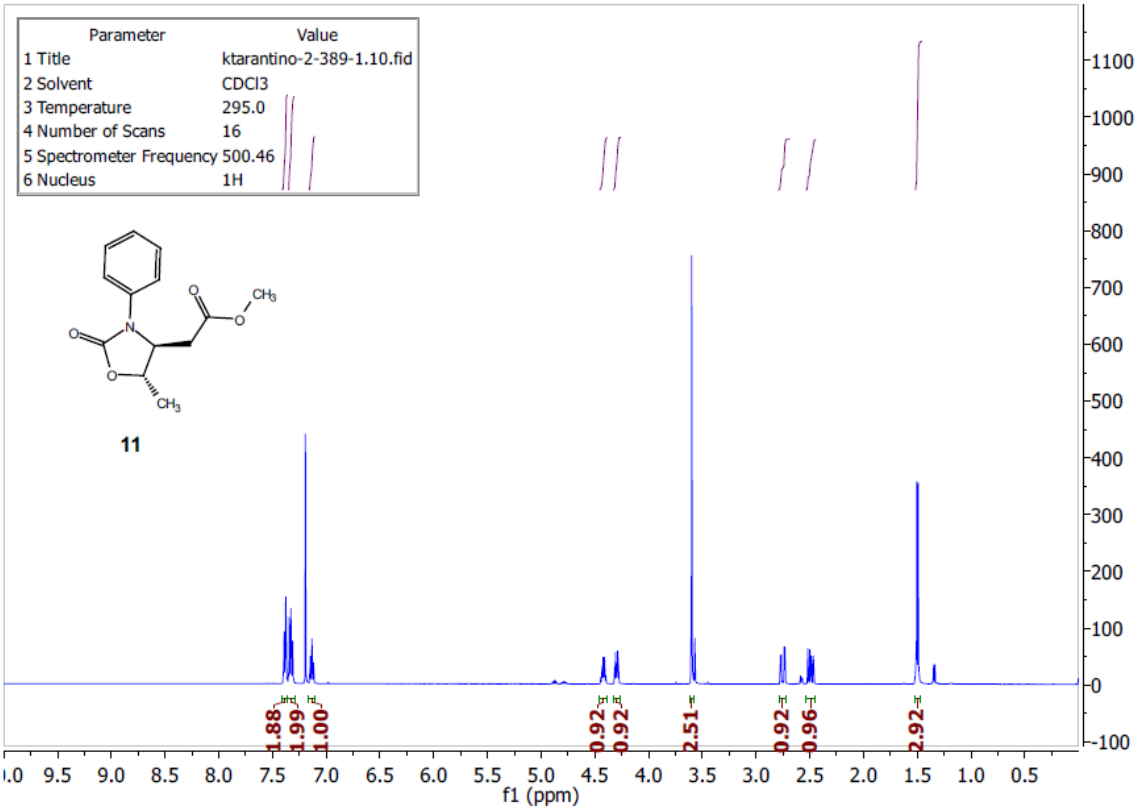

206.48
137.73
129.20
124.35
121.51
109.99
52.36
46.02
44.25
30.57
Parameter Value
1 Title ktarantino-2-361-1.11.fid
2 Solvent CDCl3
3 Temperature 295.0
4 Number of Scans 64
5 Spectrometer Frequency 125.85
6 Nucleus 13C
8
f1 (ppm)

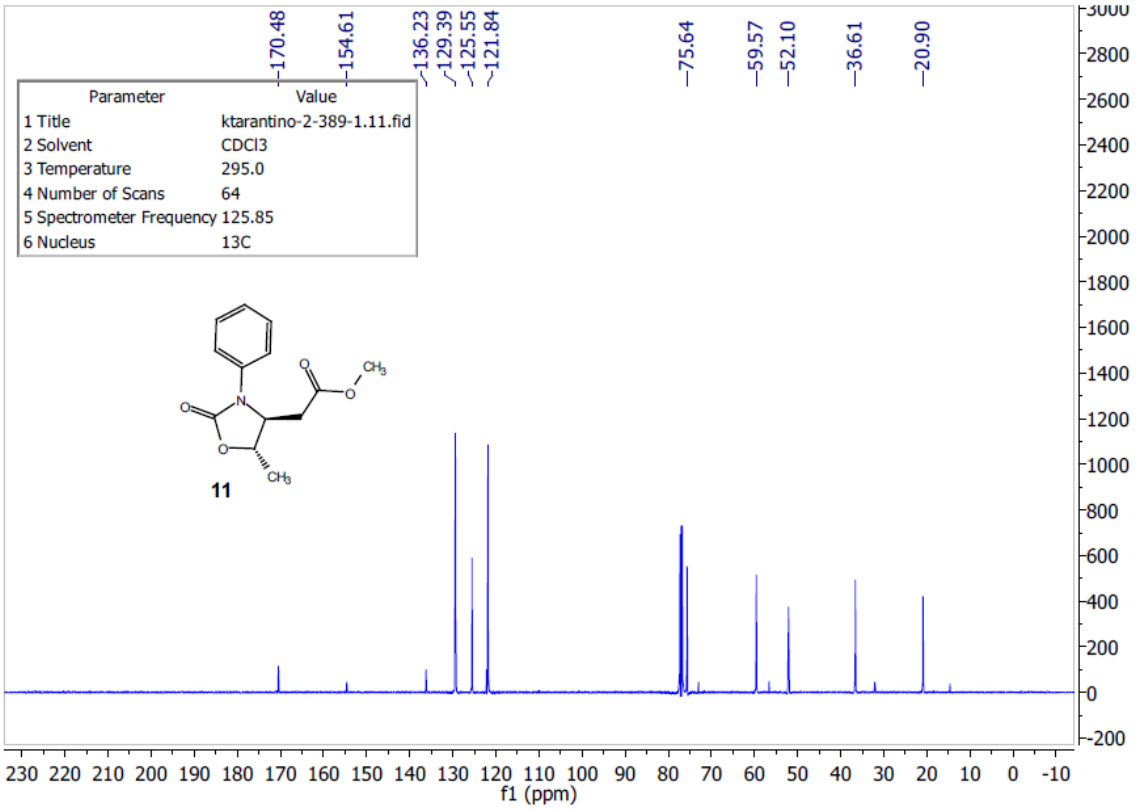

Parameter Value
1 Title ktarantino-2-336-1.10.fid
2 Solvent CDCl3
3 Temperature 295.0
4 Number of Scans 16
5 Spectrometer Frequency 500.46
6 Nucleus 1H
9
3.88
0.99
1.02
1.03
1.00
3.02
1.02
3.10
f1 (ppm)

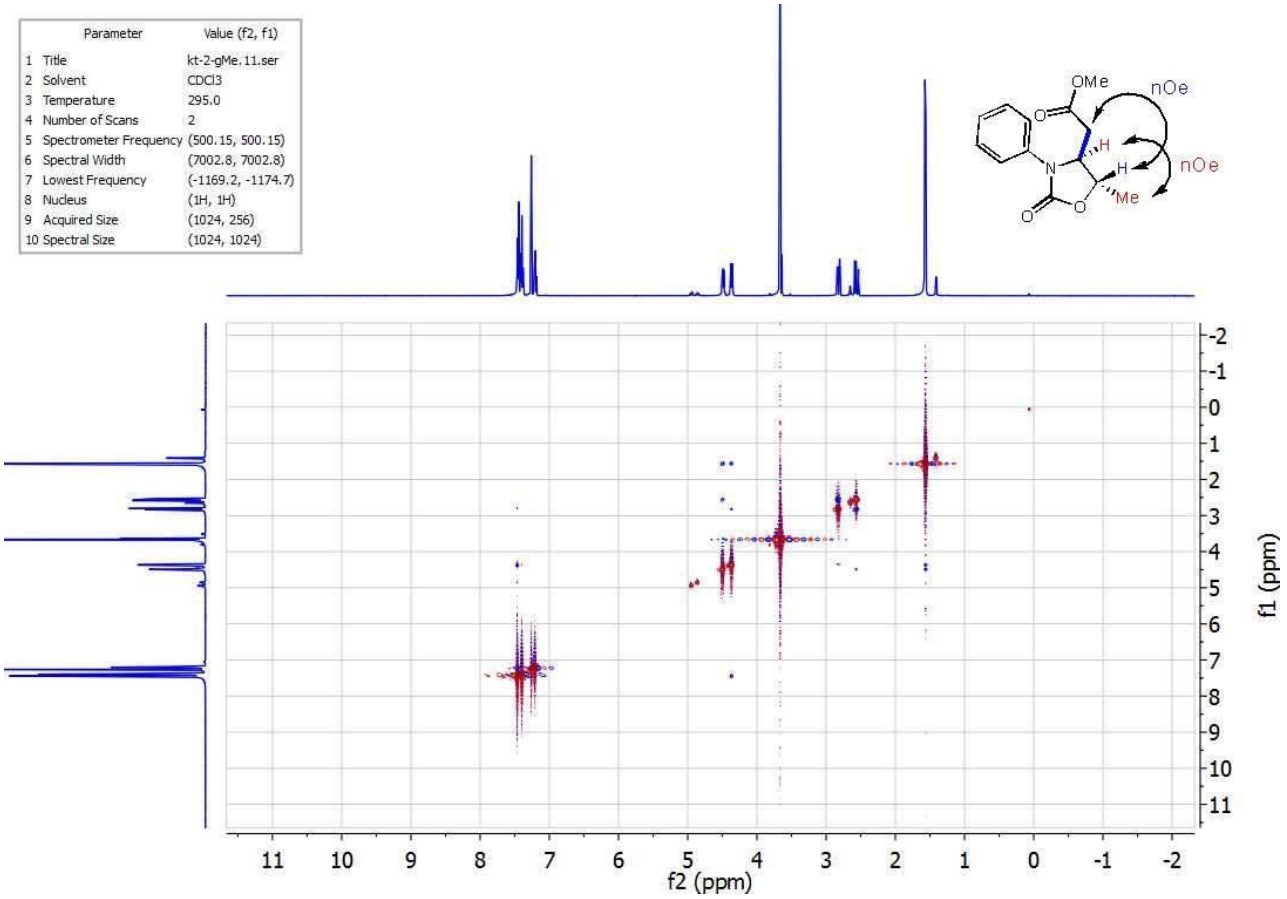

172.78
155.66
136.43
129.23
125.95
123.04
64.44
58.79
52.18
40.39
12.12
Parameter Value
1 Title ktarantino-2-336-1.11.fid
2 Solvent CDCl3
3 Temperature 295.0
4 Number of Scans 64
5 Spectrometer Frequency 125.85
6 Nucleus 13C
9
f1 (ppm)

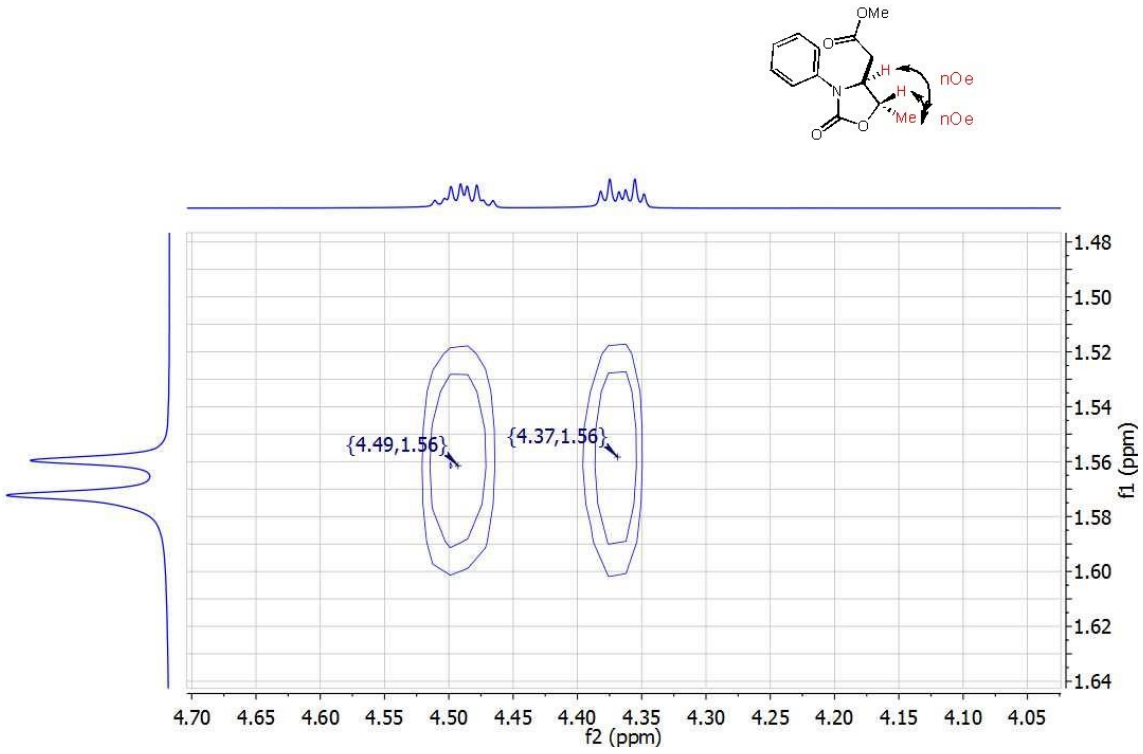

Parameter Value
1 Title ktarantino-2-414-1.10.fid
2 Solvent CDCl3
3 Temperature 295.0
4 Number of Scans 16
5 Spectrometer Frequency 500.62
6 Nucleus 1H
10
1.96
1.00
1.83
1.01
1.00
2.99
1.08
1.09
2.96
f1 (ppm)

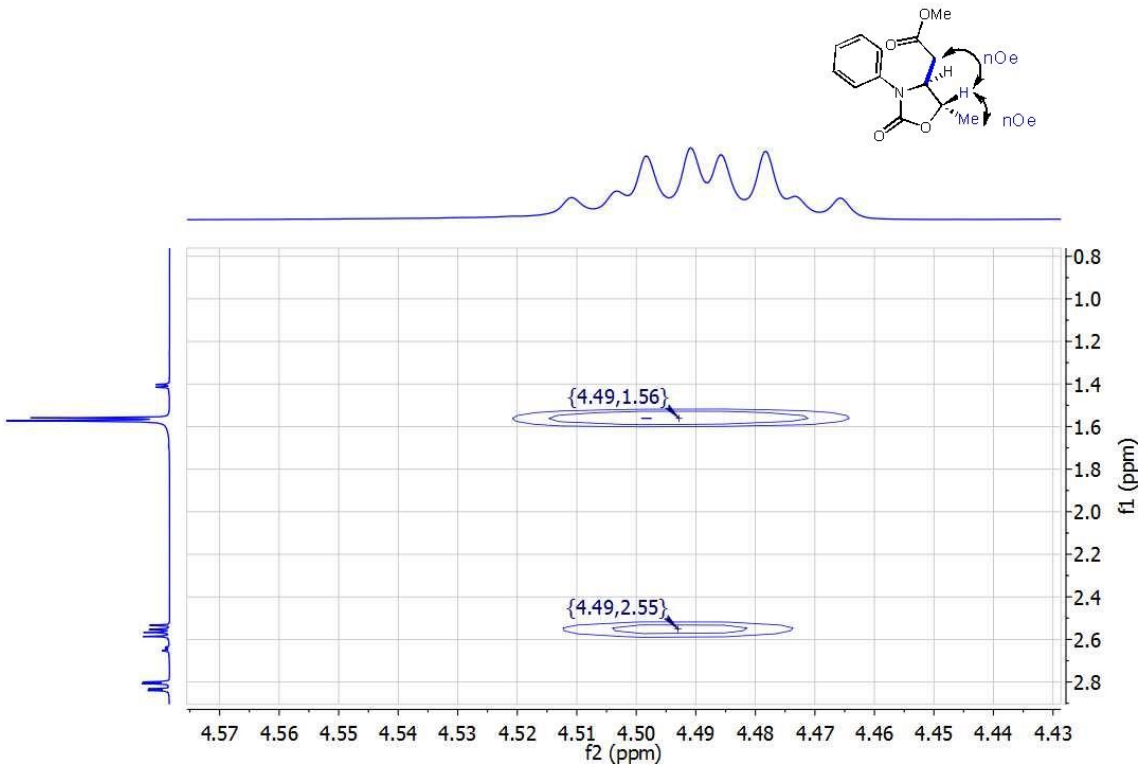

169.99
156.84
134.34
129.54
129.40
128.60
73.42
61.02
52.10
42.71
Parameter Value
1 Title ktarantino-2-414-1.11.fid
2 Solvent CDCl3
3 Temperature 295.0
4 Number of Scans 128
5 Spectrometer Frequency 125.89
6 Nucleus 13C
10
f1 (ppm)

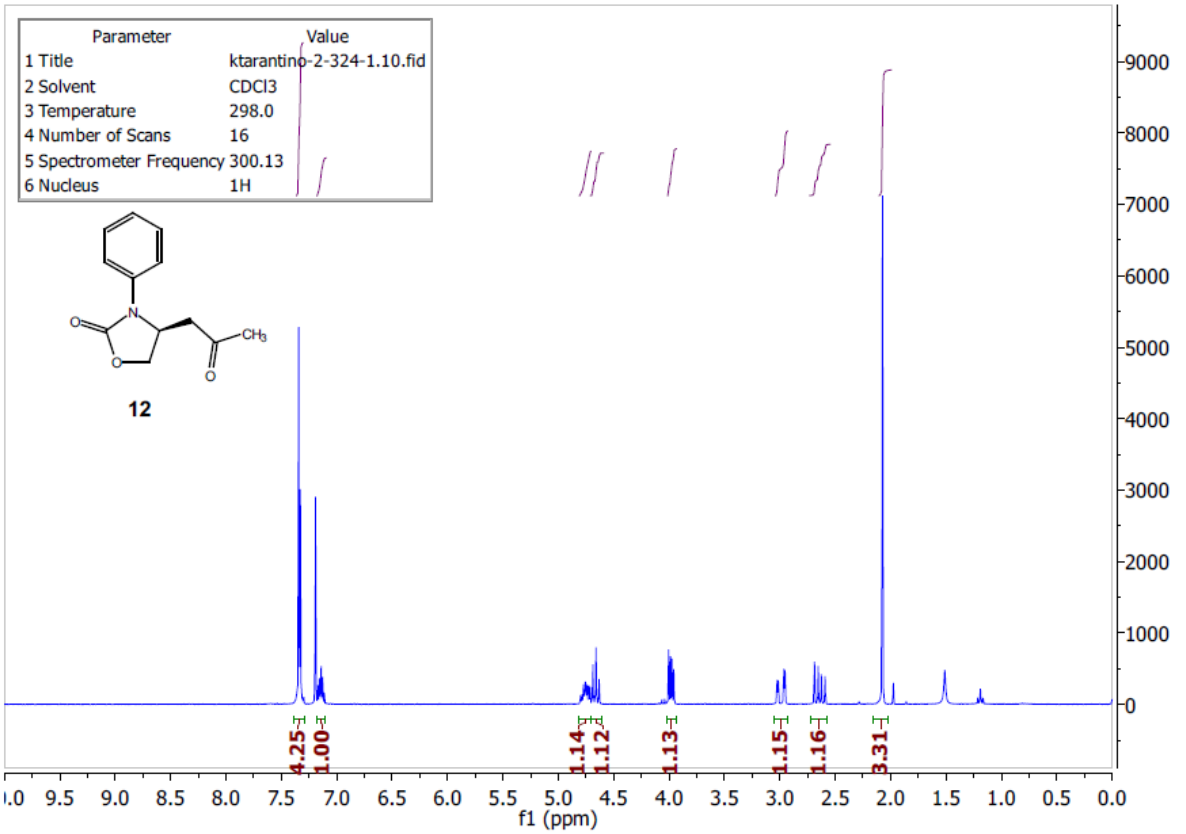

Parameter Value
1 Title ktarantino-2-389-1.10.fid
2 Solvent CDCl3
3 Temperature 295.0
4 Number of Scans 16
5 Spectrometer Frequency 500.46
6 Nucleus 1H
11
1.88
1.99
1.00
0.92
0.92
2.51
0.92
0.96
2.92
f1 (ppm)

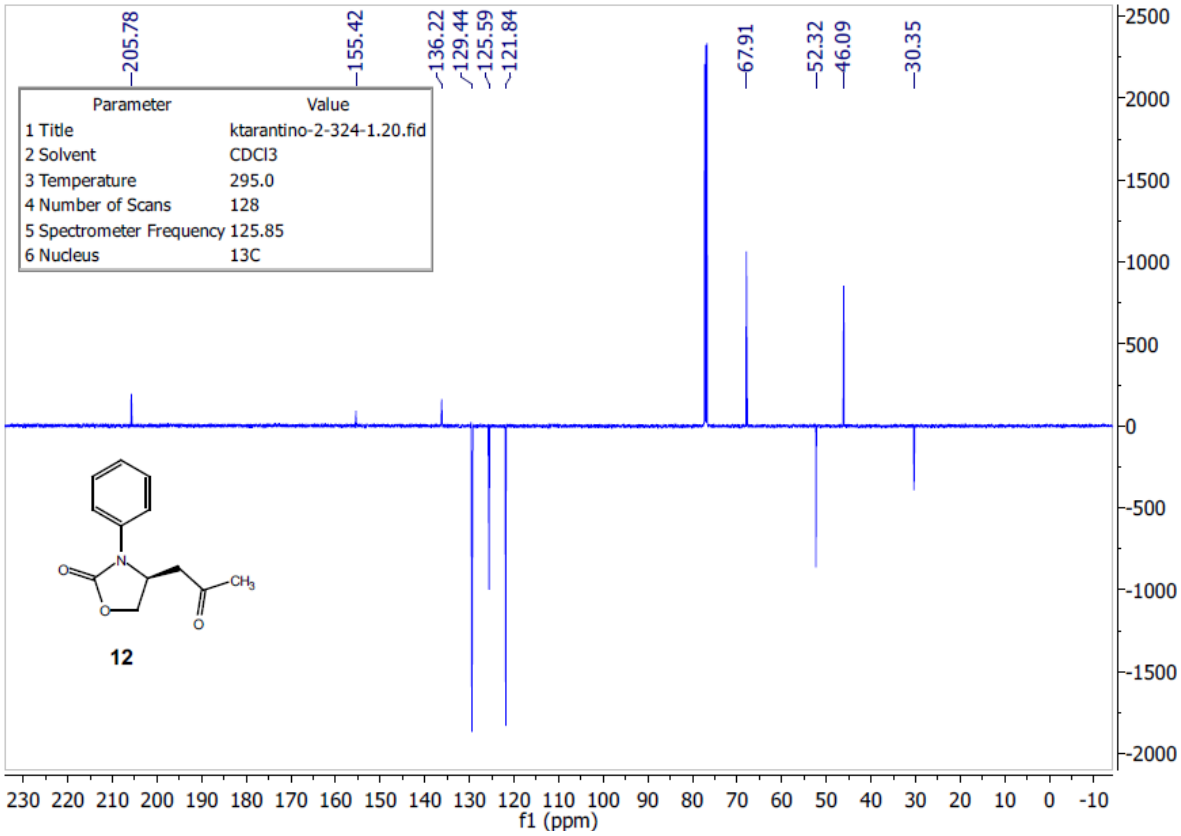

170.48
154.61
136.23
129.39
125.55
121.84
75.64
59.57
52.10
36.61
20.90
Parameter Value
1 Title ktarantino-2-389-1.11.fid
2 Solvent CDCl3
3 Temperature 295.0
4 Number of Scans 64
5 Spectrometer Frequency 125.85
6 Nucleus 13C
11
f1 (ppm)

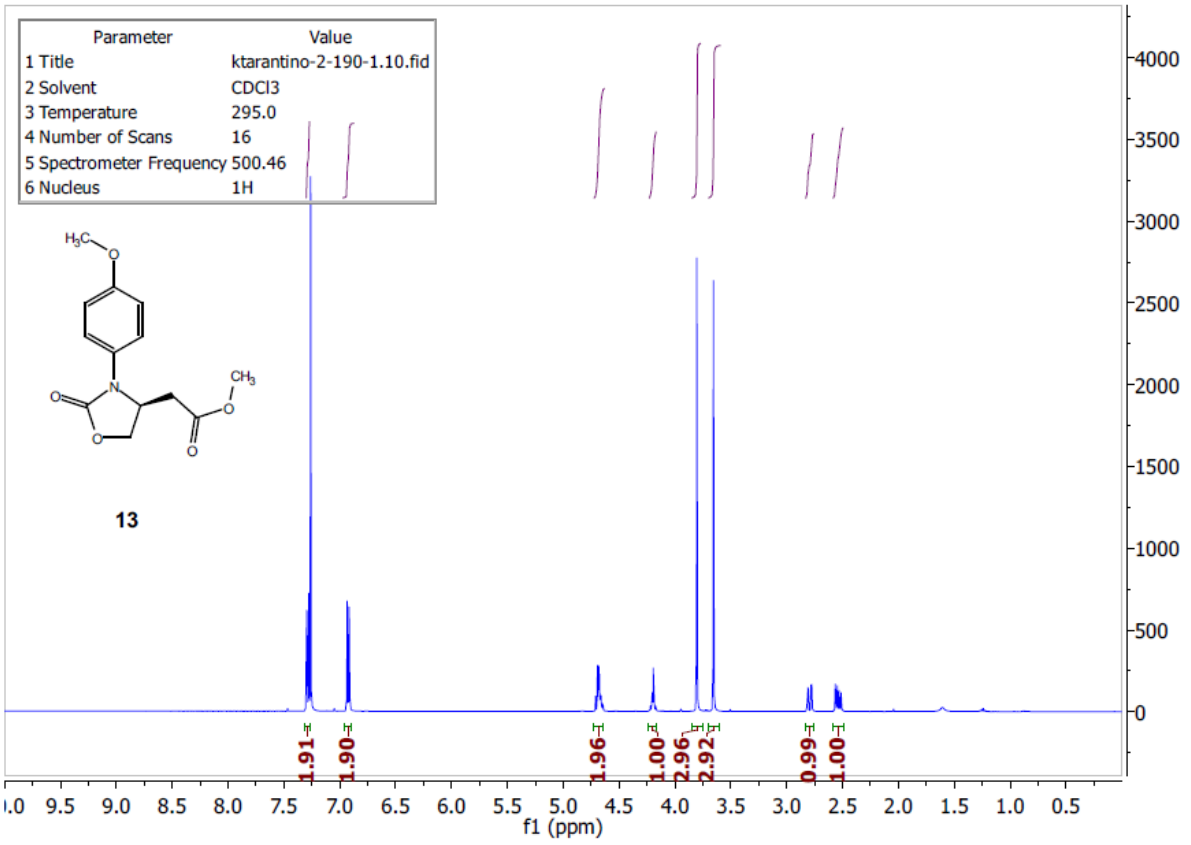

Parameter Value (f2, f1)
1 Title kt-2-gMe.11.ser
2 Solvent CDCl3
3 Temperature 295.0
4 Number of Scans 2
5 Spectrometer Frequency (500.15, 500.15)
6 Spectral Width (7002.8, 7002.8)
7 Lowest Frequency (-1169.2, -1174.7)
8 Nucleus (1H, 1H)
9 Acquired Size (1024, 256)
10 Spectral Size (1024, 1024)
OMe
nOe
nOe
H
H
Me
N
O
O
O
f2 (ppm)
f1 (ppm)

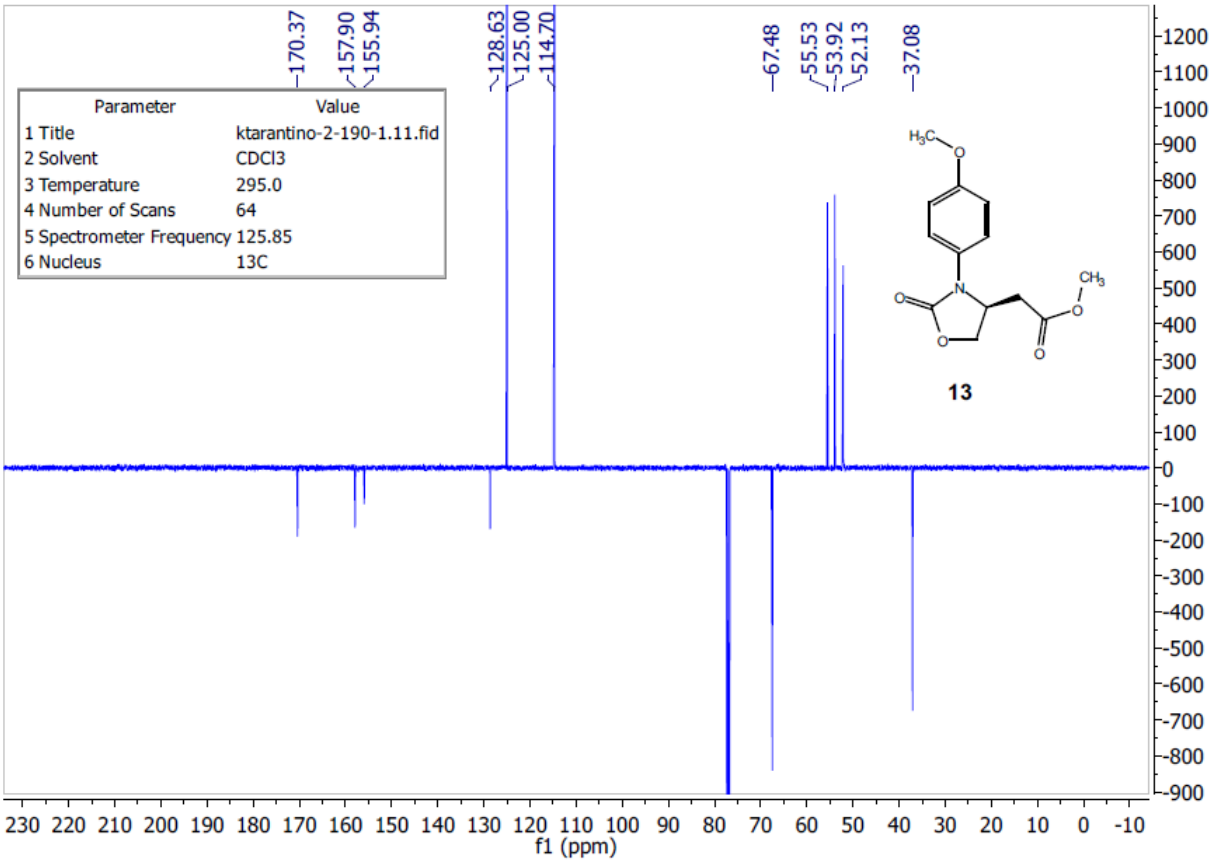

OMe
O
H
N
H
Me
O
O
nOe
nOe
{4.49,1.56}
{4.37,1.56}
1.48
1.50
1.52
1.54
1.56
1.58
1.60
1.62
1.64
f1 (ppm)
4.70 4.65 4.60 4.55 4.50 4.45 4.40 4.35 4.30 4.25 4.20 4.15 4.10 4.05
f2 (ppm)

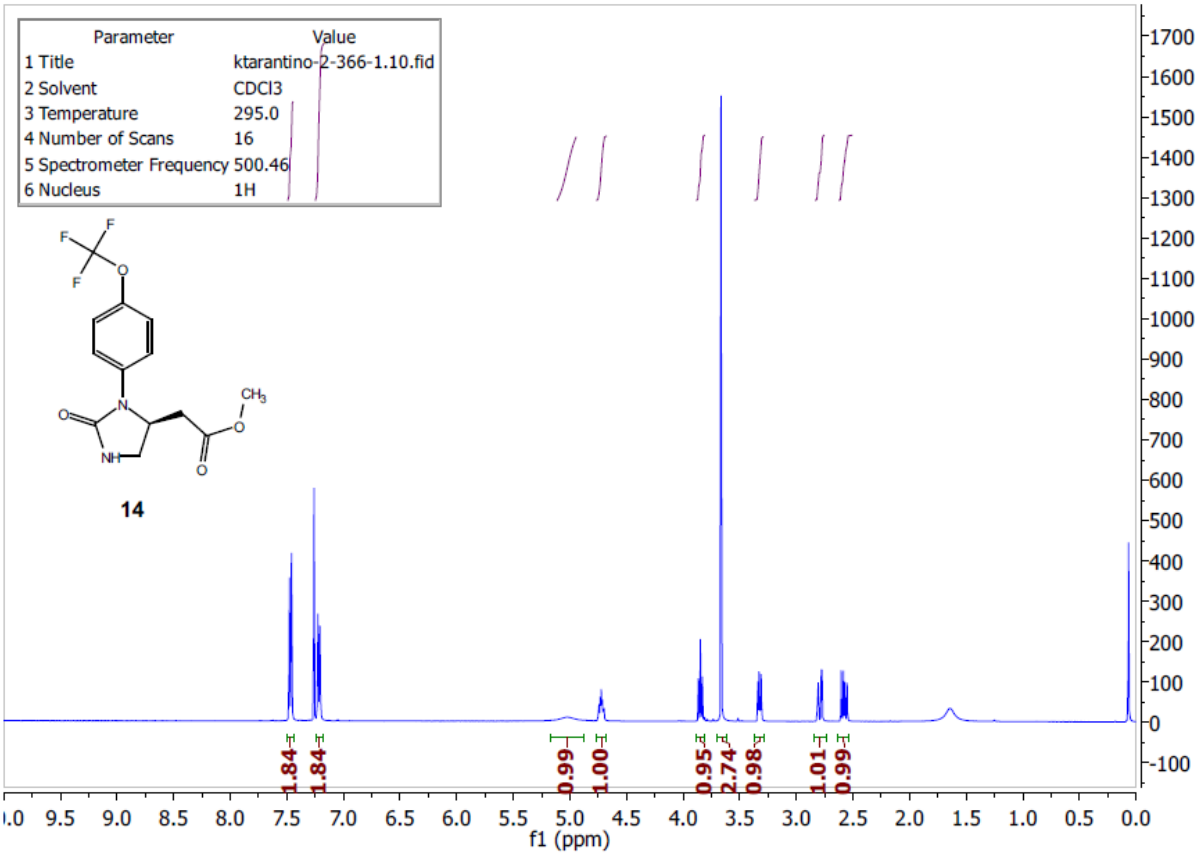

OMe
O
H
N
H
Me
O
O
nOe
nOe
{4.49,1.56}
{4.49,2.55}
0.8
1.0
1.2
1.4
1.6
1.8
2.0
2.2
2.4
2.6
2.8
f1 (ppm)
4.57 4.56 4.55 4.54 4.53 4.52 4.51 4.50 4.49 4.48 4.47 4.46 4.45 4.44 4.43
f2 (ppm)

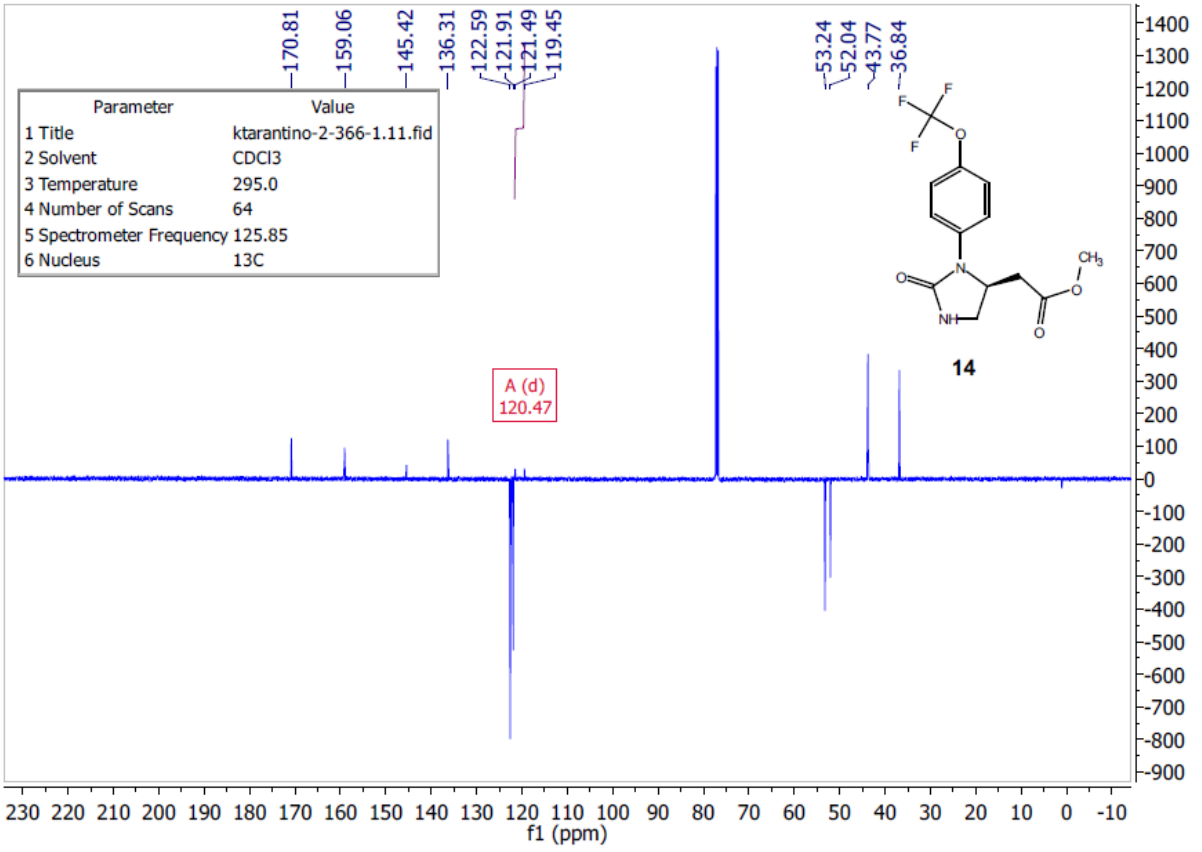

Parameter Value
1 Title ktarantino-2-324-1.10.fid
2 Solvent CDCl3
3 Temperature 298.0
4 Number of Scans 16
5 Spectrometer Frequency 300.13
6 Nucleus 1H
12
4.25
1.00
1.14
1.12
1.13
1.15
1.16
3.31
f1 (ppm)

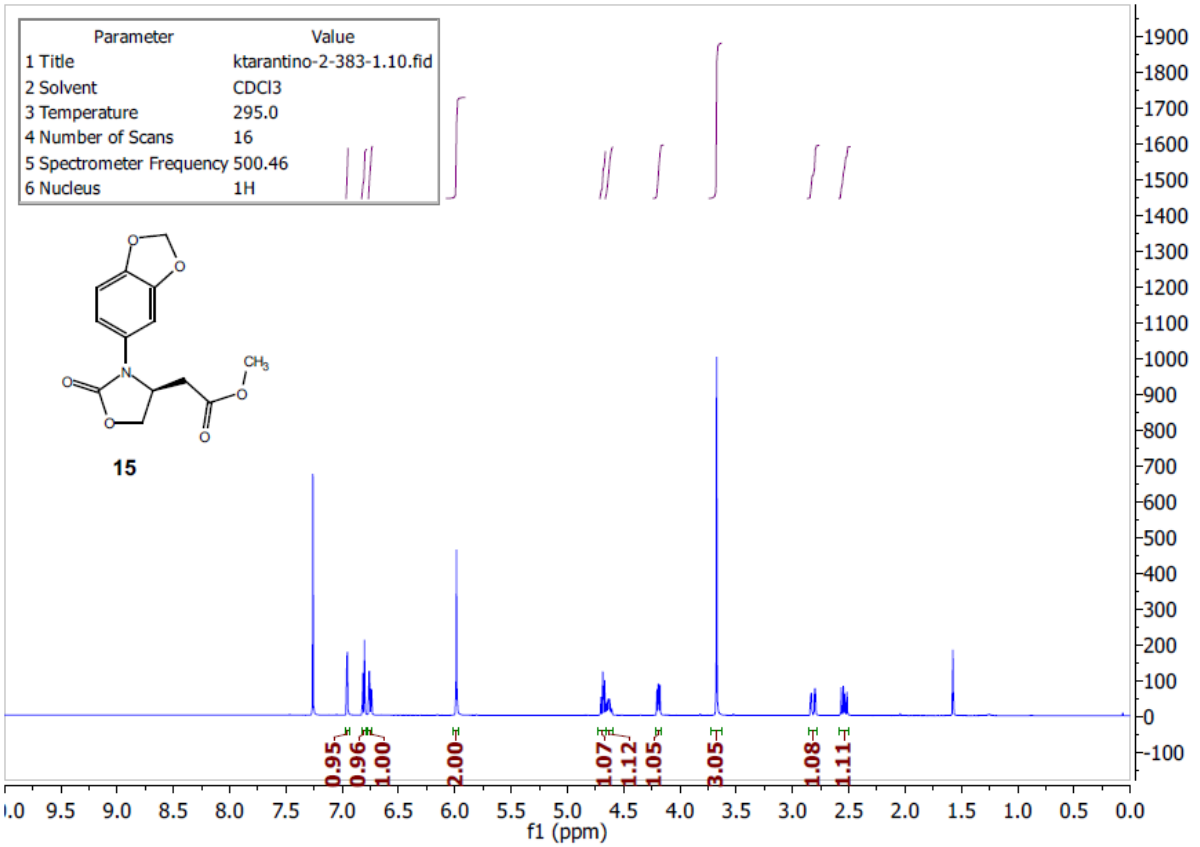

205.78
155.42
136.22
129.44
125.59
121.84
67.91
52.32
46.09
30.35
Parameter Value
1 Title ktarantino-2-324-1.20.fid
2 Solvent CDCl3
3 Temperature 295.0
4 Number of Scans 128
5 Spectrometer Frequency 125.85
6 Nucleus 13C
12
f1 (ppm)

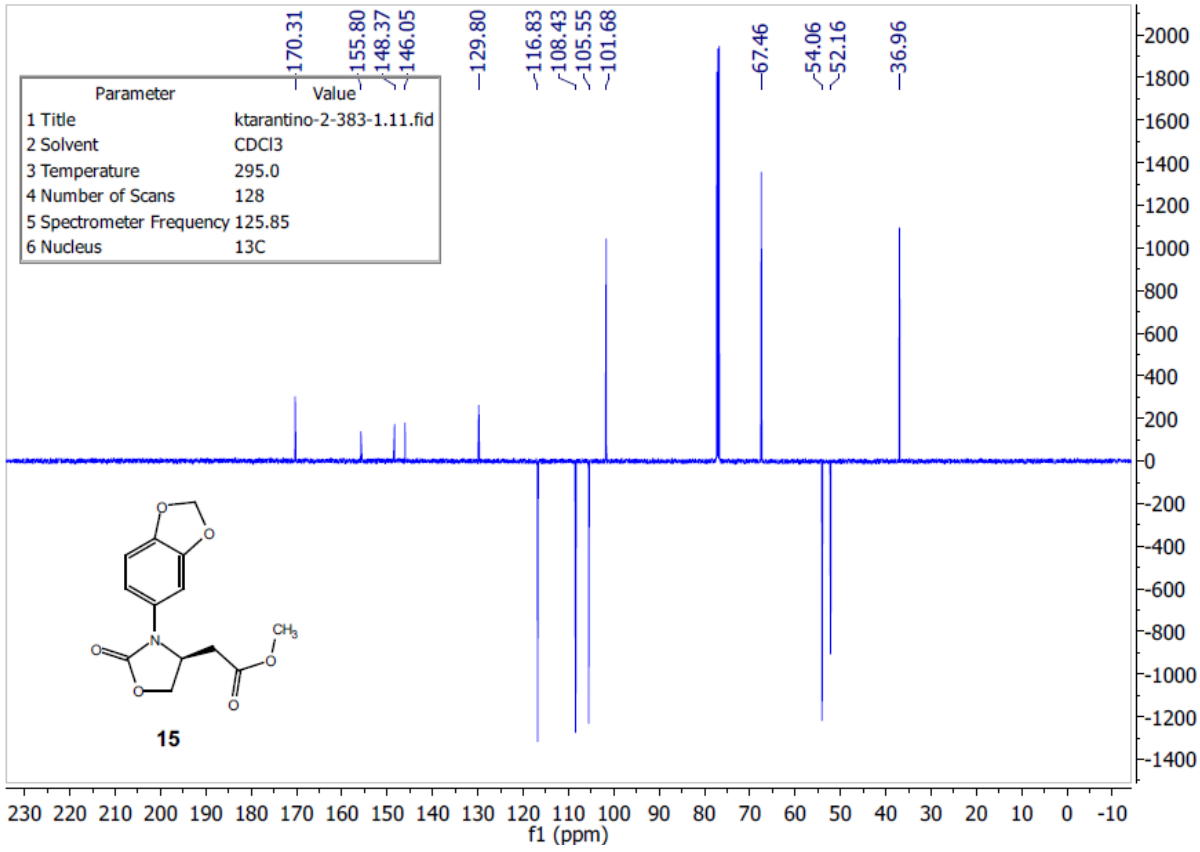

Parameter Value
1 Title ktarantino-2-190-1.10.fid
2 Solvent CDCl3
3 Temperature 295.0
4 Number of Scans 16
5 Spectrometer Frequency 500.46
6 Nucleus 1H
13
1.91
1.90
1.96
1.00
2.96
2.92
0.99
1.00
f1 (ppm)

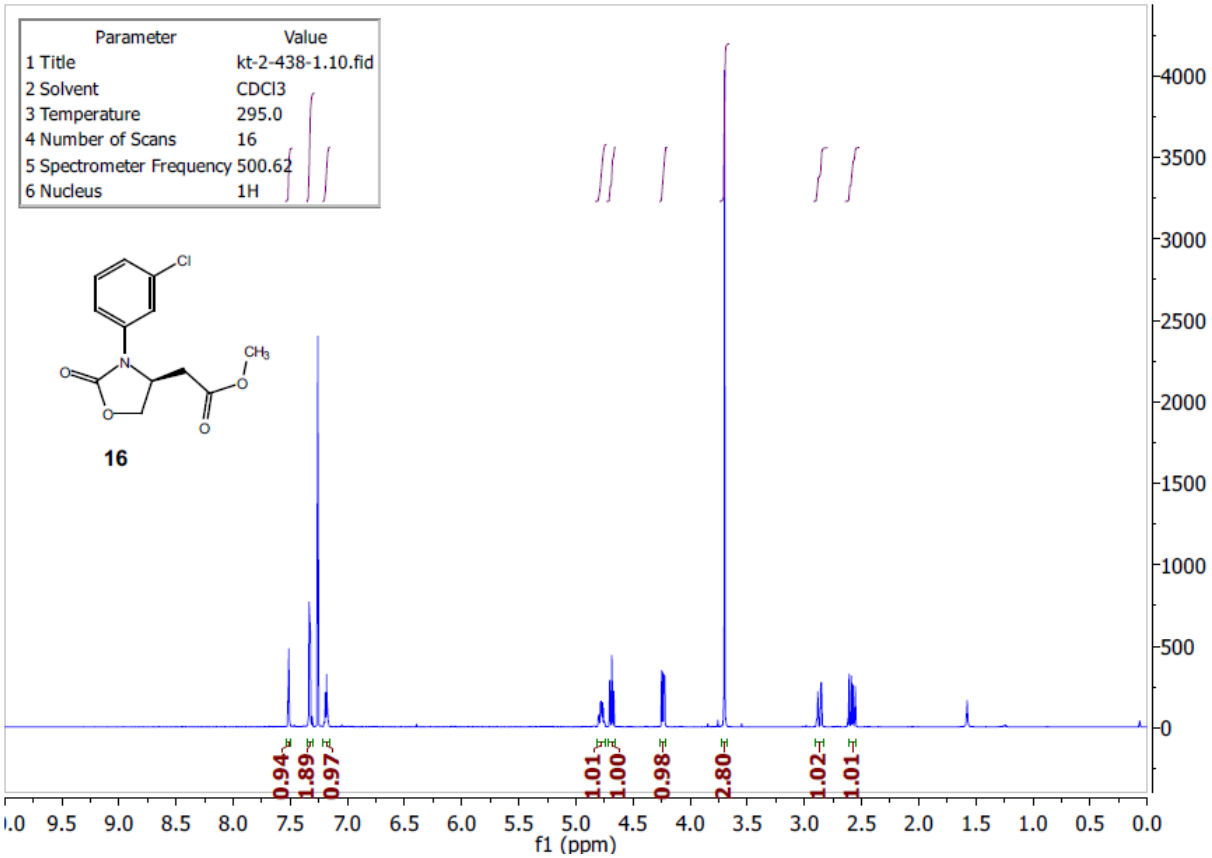

170.37
157.90
155.94
128.63
125.00
114.70
67.48
55.53
53.92
52.13
37.08
Parameter Value
1 Title ktarantino-2-190-1.11.fid
2 Solvent CDCl3
3 Temperature 295.0
4 Number of Scans 64
5 Spectrometer Frequency 125.85
6 Nucleus 13C
13
f1 (ppm)

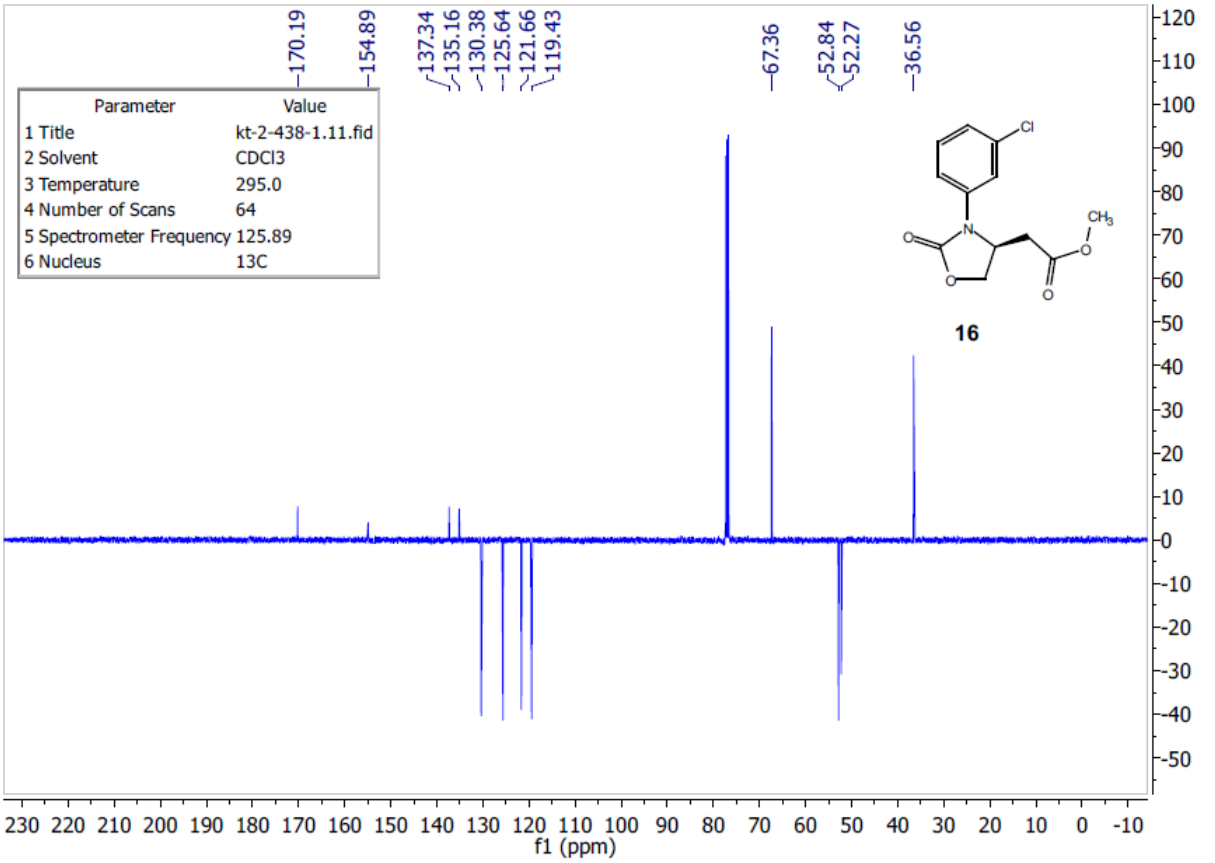

Parameter Value
1 Title ktarantino-2-366-1.10.fid
2 Solvent CDCl3
3 Temperature 295.0
4 Number of Scans 16
5 Spectrometer Frequency 500.46
6 Nucleus 1H
14
1.84
1.84
0.99
1.00
0.95
2.74
0.98
1.01
0.99
f1 (ppm)

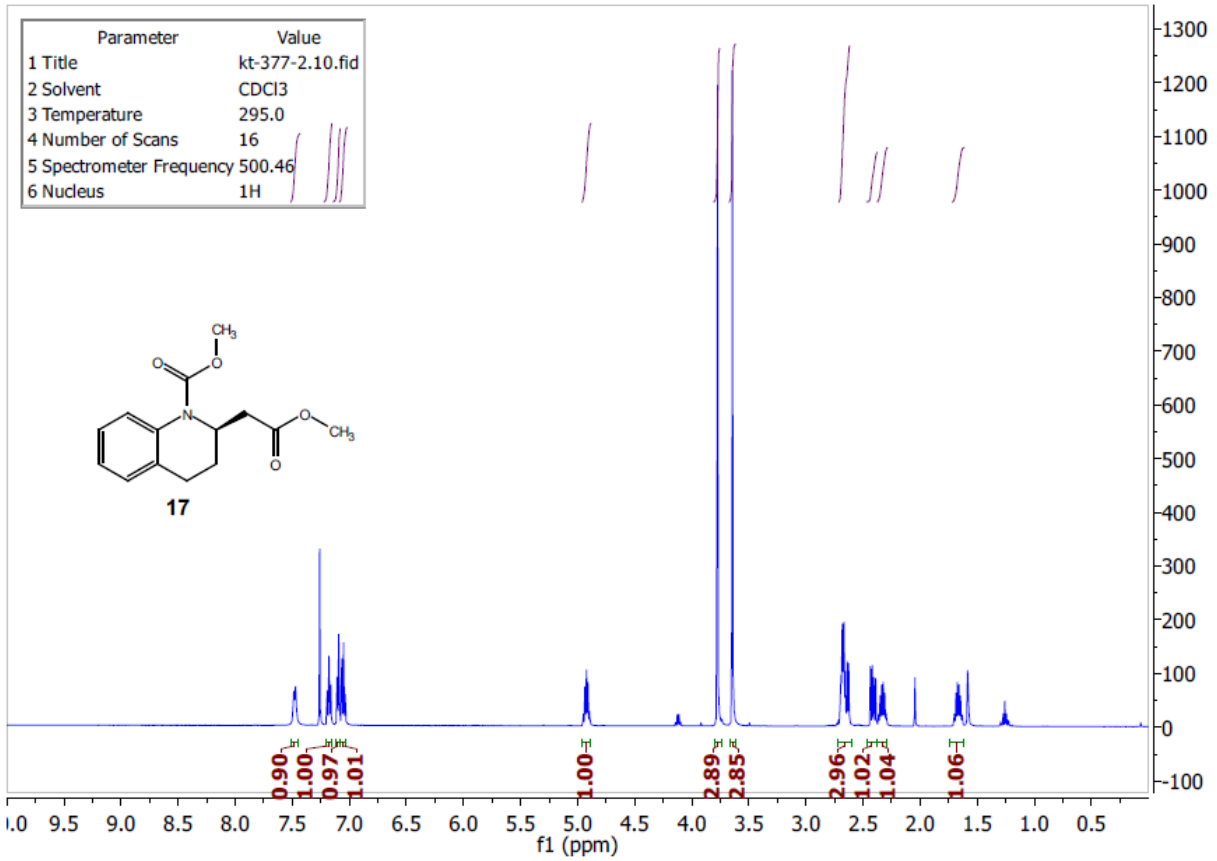

170.81
159.06
145.42
136.31
122.59
121.91
121.49
119.45
53.24
52.04
43.77
36.84
Parameter Value
1 Title ktarantino-2-366-1.11.fid
2 Solvent CDCl3
3 Temperature 295.0
4 Number of Scans 64
5 Spectrometer Frequency 125.85
6 Nucleus 13C
A (d)
120.47
14
f1 (ppm)

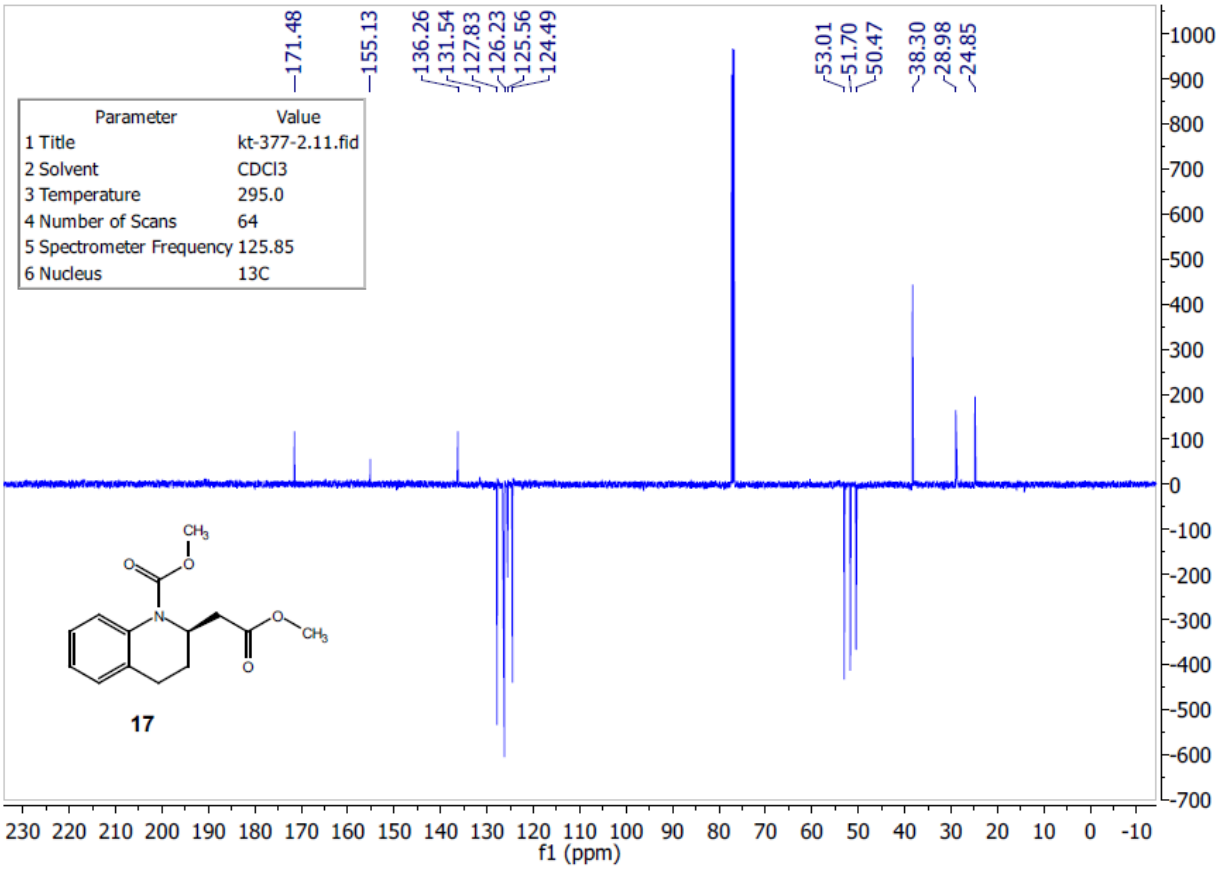

Parameter Value
1 Title ktarantino-2-383-1.10.fid
2 Solvent CDCl3
3 Temperature 295.0
4 Number of Scans 16
5 Spectrometer Frequency 500.46
6 Nucleus 1H
15
0.95
0.96
1.00
2.00
1.07
1.12
1.05
3.05
1.08
1.11
f1 (ppm)

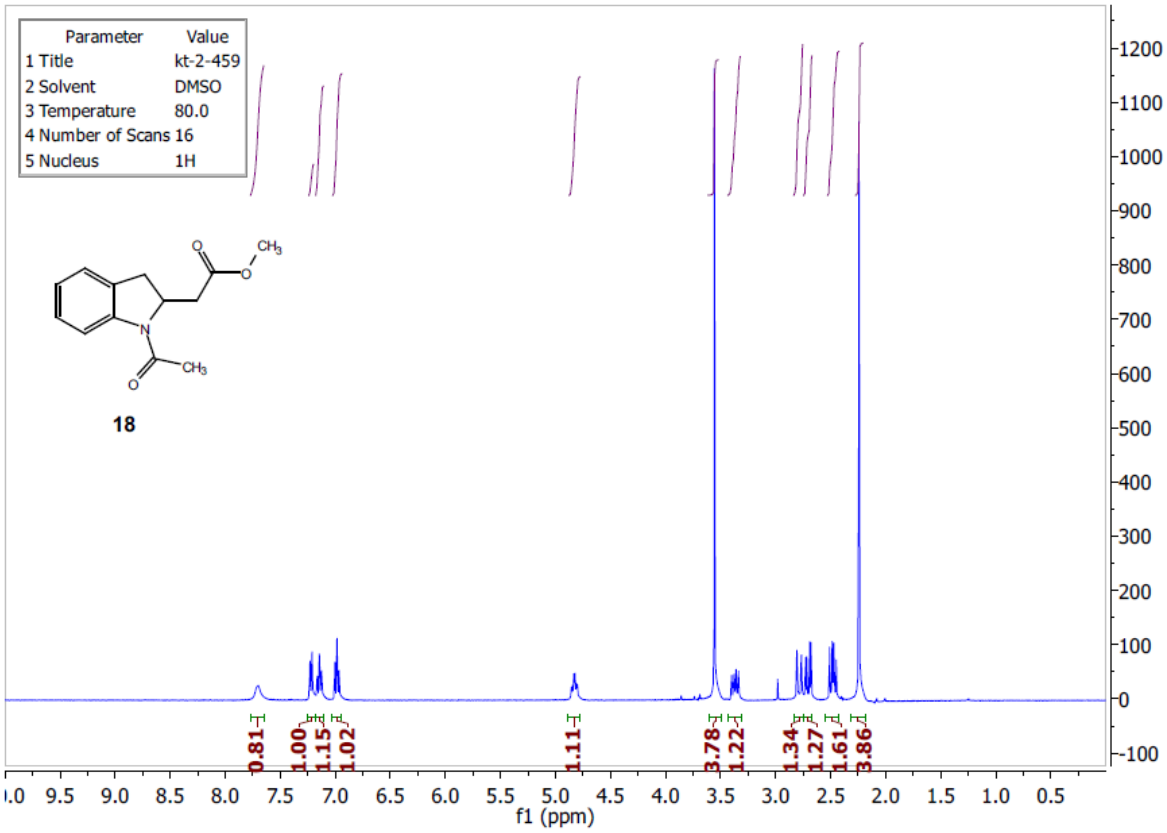

170.31
155.80
148.37
146.05
129.80
116.83
108.43
105.55
101.68
67.46
54.06
52.16
36.96
Parameter Value
1 Title ktarantino-2-383-1.11.fid
2 Solvent CDCl3
3 Temperature 295.0
4 Number of Scans 128
5 Spectrometer Frequency 125.85
6 Nucleus 13C
15
f1 (ppm)

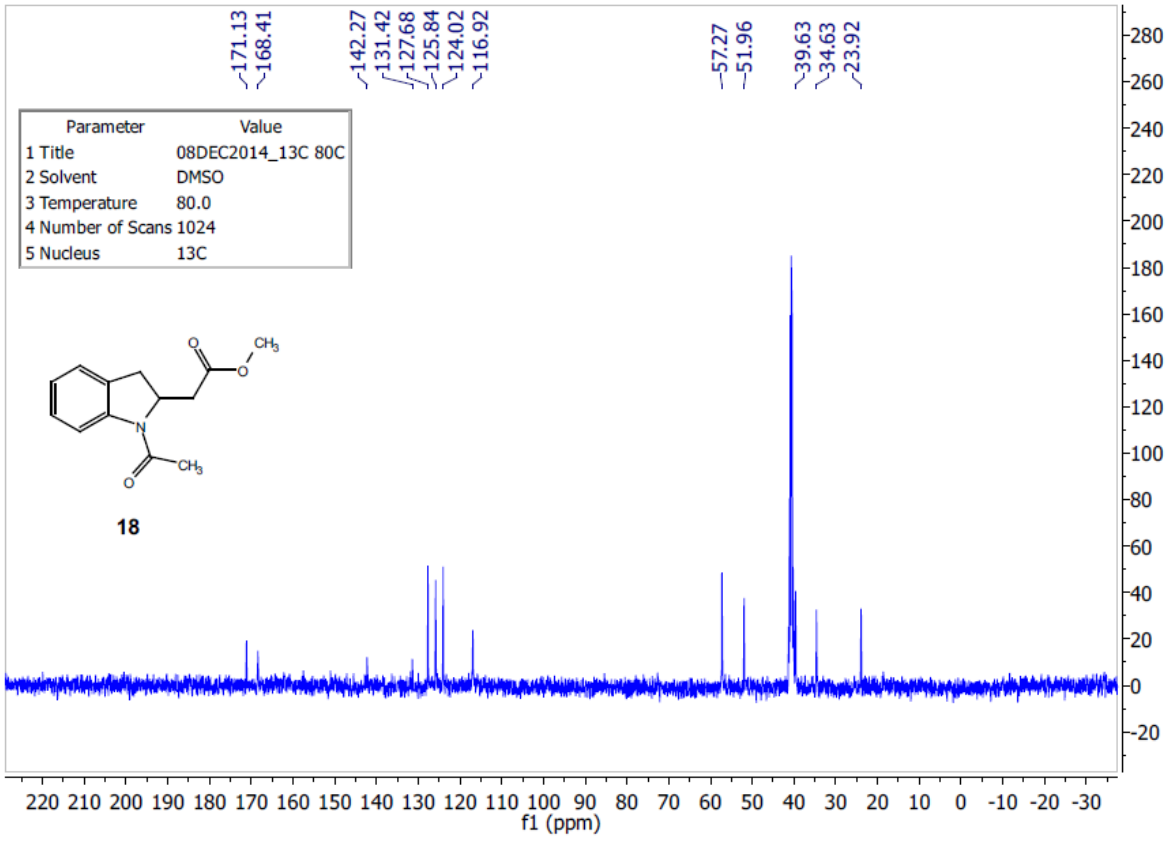

Parameter Value
1 Title kt-2-438-1.10.fid
2 Solvent CDCl3
3 Temperature 295.0
4 Number of Scans 16
5 Spectrometer Frequency 500.62
6 Nucleus 1H
16
0.94
1.89
0.97
1.01
1.00
0.98
2.80
1.02
1.01
f1 (ppm)

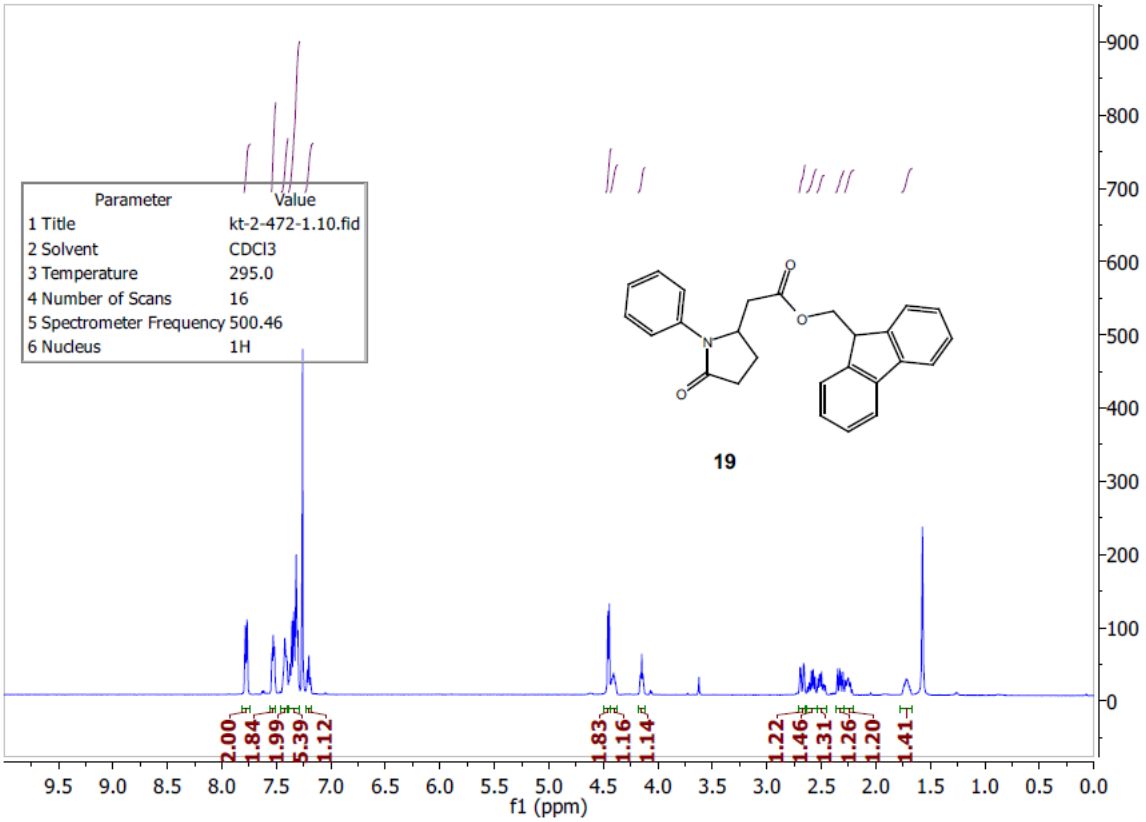

170.19
154.89
137.34
135.16
130.38
125.64
121.66
119.43
67.36
52.84
52.27
36.56
Parameter Value
1 Title kt-2-438-1.11.fid
2 Solvent CDCl3
3 Temperature 295.0
4 Number of Scans 64
5 Spectrometer Frequency 125.89
6 Nucleus 13C
16
f1 (ppm)

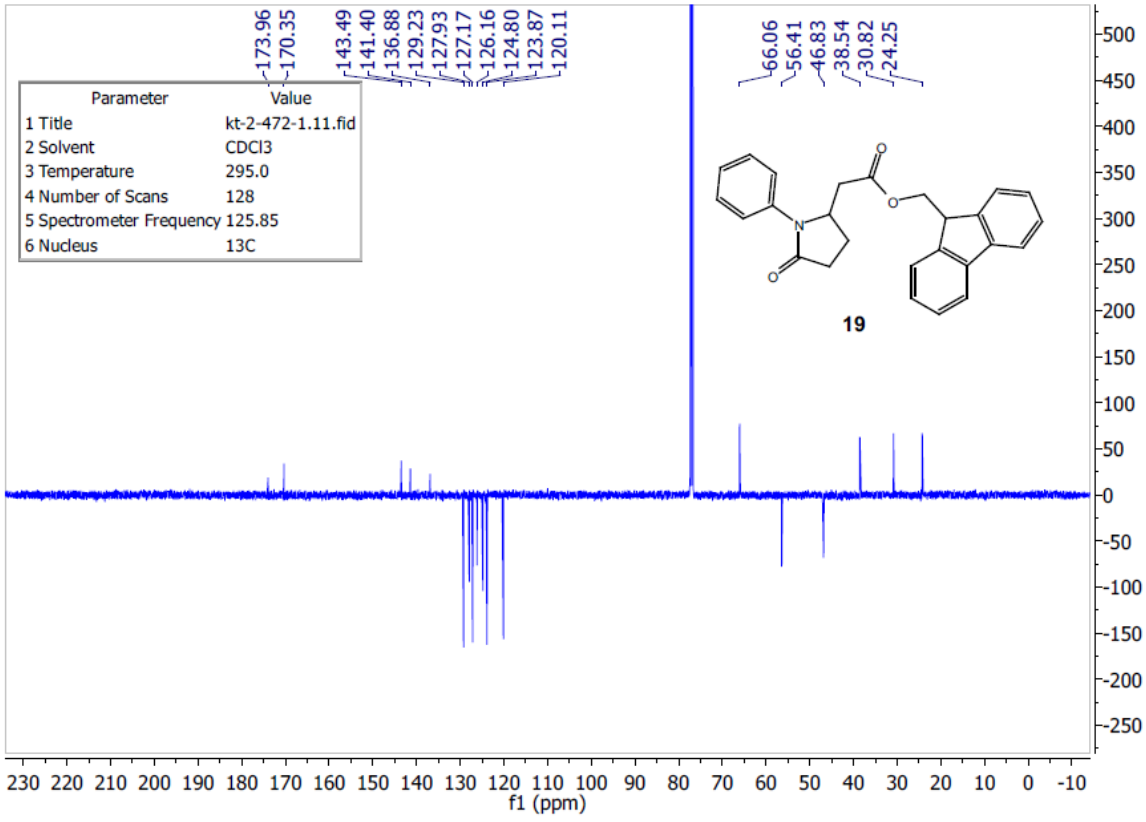

Parameter Value
1 Title kt-377-2.10.fid
2 Solvent CDCl3
3 Temperature 295.0
4 Number of Scans 16
5 Spectrometer Frequency 500.46
6 Nucleus 1H
17
0.90
1.00
0.97
1.01
1.00
2.89
2.85
2.96
1.02
1.04
1.06
f1 (ppm)


171.48
155.13
136.26
131.54
127.83
126.23
125.56
124.49
53.01
51.70
50.47
38.30
28.98
24.85
Parameter Value
1 Title kt-377-2.11.fid
2 Solvent CDCl3
3 Temperature 295.0
4 Number of Scans 64
5 Spectrometer Frequency 125.85
6 Nucleus 13C
17
f1 (ppm)


Parameter Value
1 Title kt-2-459
2 Solvent DMSO
3 Temperature 80.0
4 Number of Scans 16
5 Nucleus 1H
18
0.81
1.00
1.15
1.02
1.11
3.78
1.22
1.34
1.27
1.61
3.86
f1 (ppm)


171.13
168.41
142.27
131.42
127.68
125.84
124.02
116.92
57.27
51.96
39.63
34.63
23.92
Parameter Value
1 Title 08DEC2014_13C 80C
2 Solvent DMSO
3 Temperature 80.0
4 Number of Scans 1024
5 Nucleus 13C
18
f1 (ppm)

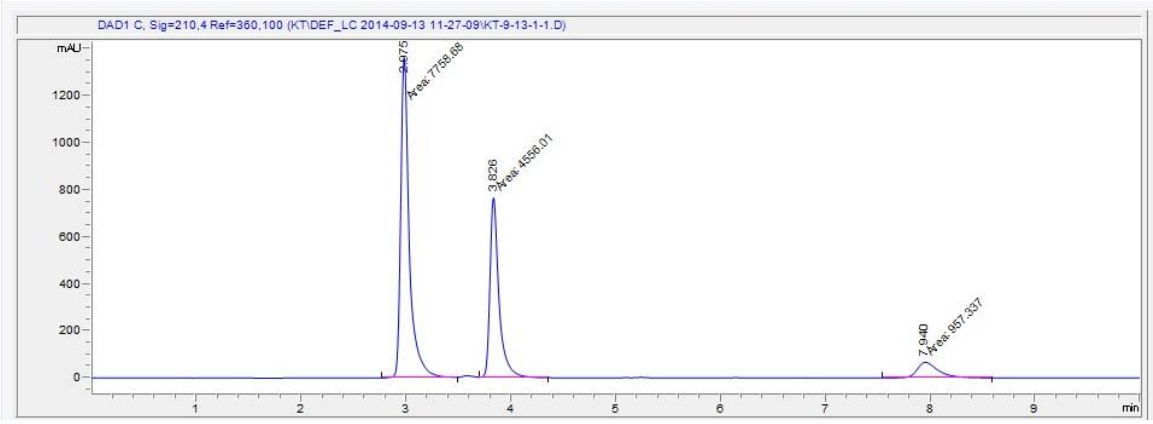

Parameter Value
1 Title kt-2-472-1.10.fid
2 Solvent CDCl3
3 Temperature 295.0
4 Number of Scans 16
5 Spectrometer Frequency 500.46
6 Nucleus 1H
19
2.00 1.84 1.99 5.39 1.12 1.83 1.16 1.14 1.22 1.46 1.31 1.26 1.20 1.41
f1 (ppm)


173.96 170.35 143.49 141.40 136.88 129.23 127.93 127.17 126.16 124.80 123.87 120.11
66.06 56.41 46.83 38.54 30.82 24.25
Parameter Value
1 Title kt-2-472-1.11.fid
2 Solvent CDCl3
3 Temperature 295.0
4 Number of Scans 128
5 Spectrometer Frequency 125.85
6 Nucleus 13C
19
f1 (ppm)

V. Kinetic Experiments

Kinetics experiments were run in a glovebox on a 0.25 mmol scale using substrate **I** as a model substrate in anhydrous, degassed MeCN at 23 °C. In an illustrative example, **1** (62 mg, 0.25 mmol, 1 equiv) and diphenyl ether (42.5 mg, 0.25 mmol, 1 equiv, internal standard) was dissolved in anhydrous, degassed MeCN (10 mL, 0.025 M). $Cp^*_2Ti^{III}Cl$ (4.4 mg, 0.0125 mmol, 0.05 equiv) was added and the mixture was pre–stirred for 3 minutes. Then, 0.1 mL of a stock solution of TEMPO (3.9 mg per mL MeCN) containing (0.39 mg, 0.0025 mmol, 0.01 equiv) was added and timing commenced. 0.1 mL aliquots were taken and quenched by addition to 0.1 mL a solution of $Cp_2Fe(BF_4)$ (3 mg/mL MeCN, 10.9 mM). Once all time points were obtained, the vials were removed from the glovebox and filtered through ~2 cm of neutral alumina in a glass pipette and eluted with 40% isopropanol in hexanes. Samples were analyzed on a Agilent 1260 Infinity HPLC using a Zorbax – Rx Sil 5μm 4.6 x 250 mm column using a 10 minute method with 20% IPA 80% Hexanes as the eluent. UV absorbances were measured at 210 nm. Starting material conversions and yields obtained by peak area integration relative to Ph_2O internal standard. All experiments were run in triplicate.

A sample HPLC trace is shown below, the peaks are: 2.975 min - Ph_2O (internal standard), 3.826 min – substrate **1**, 7.940 min – product **5**.



Time(min)	Area Ph2O	Area SUB	% Conversion	Asub/AIS	%SM	Ln[SM]	[SM]
0.00	6204	4335	0.1	0.698742747	100	-3.688879	0.0250
0.50	6235	3597	17.5	0.576904571	82.51384	-3.881084	0.0206
1.00	6469	2693	40.5	0.41629309	59.54181	-4.207371	0.0149
1.50	5963	1681	59.7	0.281905081	40.32048	-4.59719	0.0101
2.00	7065	1506	69.5	0.213163482	30.48847	-4.876701	0.0076
2.50	6361	846	81.0	0.132997956	19.02251	-5.348427	0.0048
3.00	8342	912	84.4	0.109326301	15.63678	-5.544424	0.0039
3.50	6749	541	88.5	0.080160024	11.46517	-5.854736	0.0029
4.00	7568	521	90.2	0.068842495	9.846444	-6.006939	0.0025
4.50	6749	362	92.3	0.053637576	7.671706	-6.256511	0.0019
5.00	7139	309	93.8	0.043283373	6.190759	-6.470992	0.0015
6.00	7837	255	95.3	0.032537961	4.653858	-6.756353	0.0012
7.00	7852	208	96.2	0.026490066	3.788836	-6.961991	0.0009
8.00	7554	162	96.9	0.021445592	3.067332	-7.173241	0.0008
9.00	6541	116	97.5	0.017734291	2.53651	-7.36326	0.0006
10.00	7212	112	97.8	0.015529673	2.221187	-7.496008	0.0006

Table S1 5 mol% Cp*2TiCl, 2 mol% TEMPO, 0.025 M substrate **1** in MeCN – Run 1

Time(min)	Area Ph2O	Area SUB	% Conversion	Asub/AIS	%SM	Ln[SM]	[SM]
0.00	6696	4683	6.8	0.69937276	100	-3.688879	0.0250
0.50	7656	4770	16.9	0.623040752	83.0721	-3.874341	0.0208
1.00	7225	3422	36.8	0.473633218	63.1511	-4.148519	0.0158
1.50	6856	2235	56.5	0.325991832	43.46558	-4.52208	0.0109
2.00	6979	1856	64.5	0.265940679	35.45876	-4.725679	0.0089
2.50	6819	1251	75.5	0.183457985	24.46106	-5.096967	0.0061
3.00	7594	1149	79.8	0.151303661	20.17382	-5.289664	0.0050
3.50	6561	737	85.0	0.112330437	14.97739	-5.587508	0.0037
4.00	7016	595	88.7	0.084806157	11.30749	-5.868585	0.0028
4.50	7329	540	90.2	0.073679902	9.823987	-6.009223	0.0025
5.00	6337	381	92.0	0.060123087	8.016412	-6.212559	0.0020
6.00	7108	339	93.6	0.047692741	6.359032	-6.444173	0.0016
7.00	7687	315	94.5	0.040978275	5.46377	-6.595911	0.0014
8.00	6991	228	95.7	0.03261336	4.348448	-6.824231	0.0011
9.00	7561	189	96.7	0.024996694	3.332892	-7.090209	0.0008
10.00	6400	142	97.0	0.0221875	2.958333	-7.209424	0.0007

Table S2 5 mol% Cp*2TiCl, 2 mol% TEMPO, 0.025 M substrate **1** in MeCN – Run 2

Time(min)	Area Ph2O	Area SUB	% Conversion	Asub/AIS	%SM	Ln[SM]	[SM]
0.00	6594	4400	0.3	0.66727328	100	-3.688879	0.0250
0.50	6275	4069	14.7	0.64844622	85.32187	-3.847619	0.0213
1.00	5614	3116	27.0	0.55504097	73.03171	-4.003156	0.0183
1.50	5016	1906	50.0	0.37998405	49.9979	-4.382069	0.0125
2.00	6490	2150	56.4	0.33127889	43.58933	-4.519237	0.0109
2.50	5150	1209	69.1	0.23475728	30.88912	-4.863646	0.0077
3.00	5412	890	78.4	0.16444937	21.63808	-5.219595	0.0054
3.50	6157	858	81.7	0.13935358	18.336	-5.385183	0.0046
4.00	5782	666	84.8	0.11518506	15.15593	-5.575658	0.0038
4.50	6218	609	87.1	0.09794146	12.88703	-5.737828	0.0032
5.00	5687	442	89.8	0.07772112	10.22646	-5.969071	0.0026
6.00	7514	495	91.3	0.06587703	8.66803	-6.134408	0.0022
7.00	5257	197	95.1	0.03747384	4.930769	-6.698555	0.0012
8.00	6310	273	94.3	0.04326466	5.692718	-6.554862	0.0014
9.00	6998	265	95.0	0.03786796	4.982627	-6.688092	0.0012
10.00	4797	172	95.3	0.03585574	4.717861	-6.742694	0.0012

Table S3 5 mol% Cp*2TiCl, 2 mol% TEMPO, 0.025 M substrate **1** in MeCN – Run 3

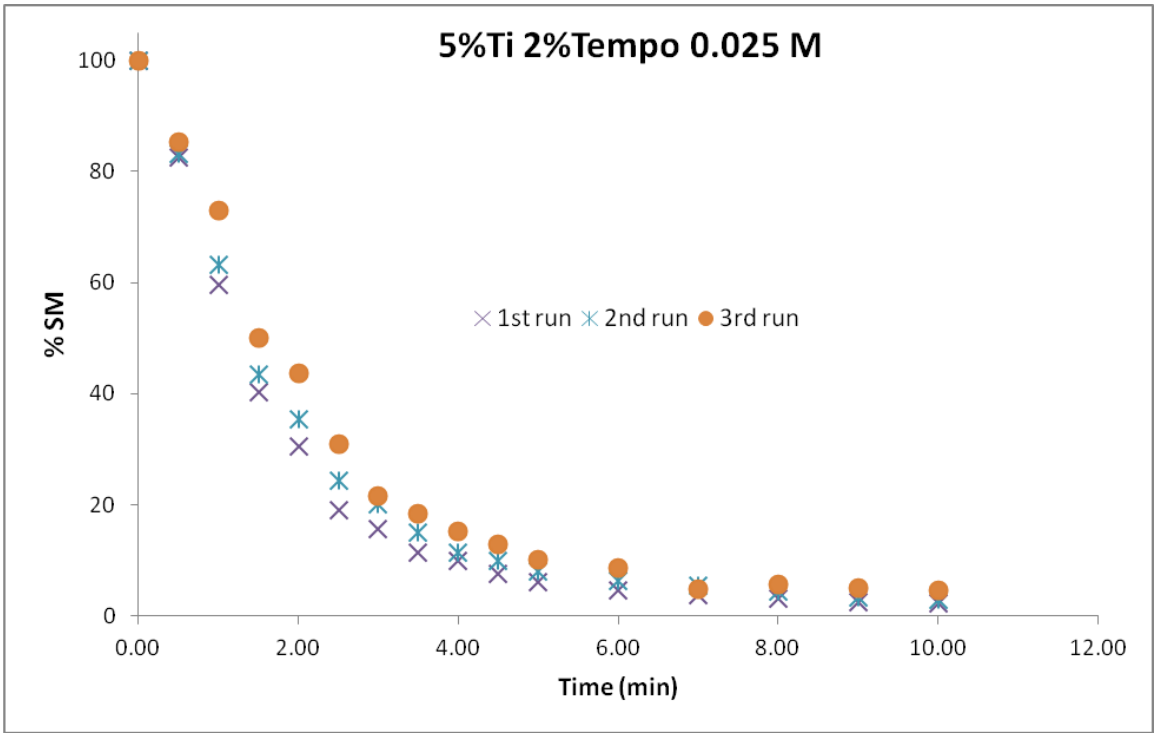


Figure S1 Overlay of 3 kinetic runs using 5 mol% Cp^*_2TiCl, 2 mol% TEMPO and 0.025 M substrate **1** in MeCN.

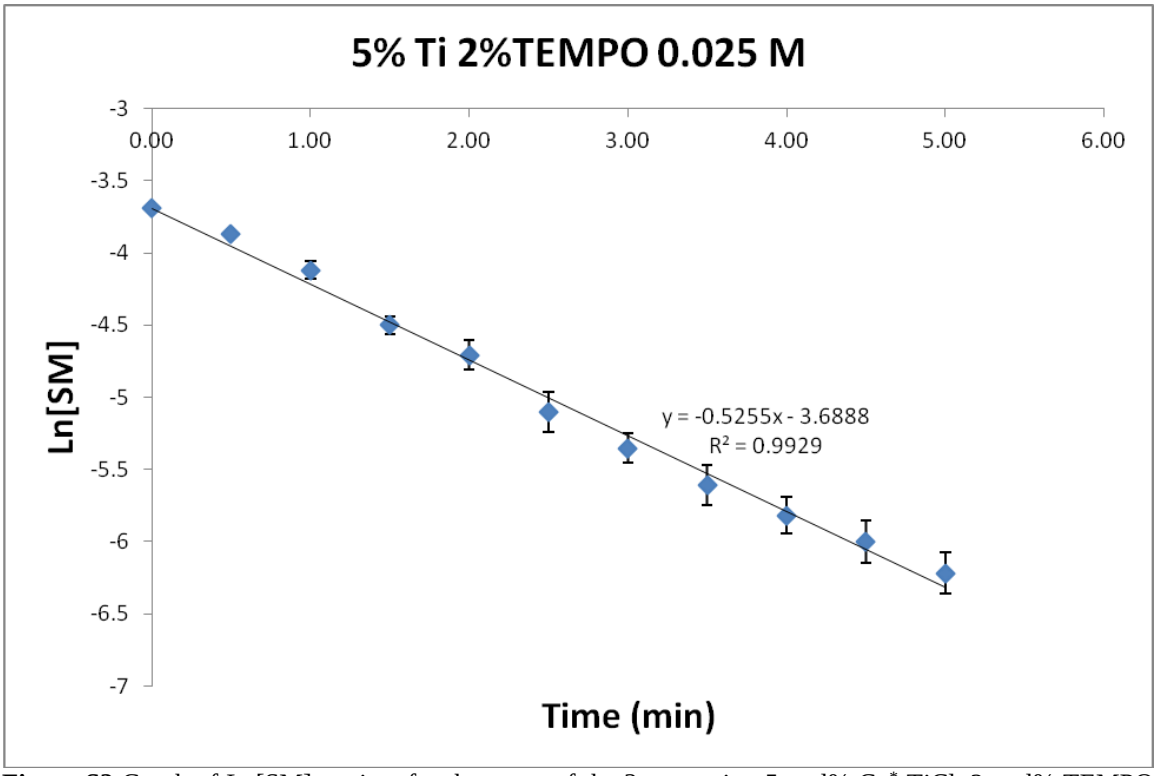


Figure S2 Graph of Ln[SM] vs time for the mean of the 3 runs using 5 mol% Cp^*_2TiCl, 2 mol% TEMPO and 0.025 M substrate **1** in MeCN. Error bars calculated using standard error of the mean (standard deviation / sqrt(n))

Time (min)	Area Ph2O	Area SUB	% Conversion	Asub/AIS	%SM	Ln[SM]	[SM]
0.00	4629	410	1.6	0.643551523	100	-3.688879	0.0250
0.50	6170	4746	14.5	0.769205835	85.46731	-3.845916	0.0214
1.00	4941	2834	36.3	0.573568104	63.72979	-4.139398	0.0159
1.50	5777	2919	43.9	0.505279557	56.14217	-4.266162	0.0140
2.00	5837	2125	59.5	0.364056879	40.45076	-4.593964	0.0101
2.50	7076	2106	66.9	0.297625777	33.06953	-4.795437	0.0083
3.00	7364	1677	74.7	0.227729495	25.30328	-5.063116	0.0063
3.50	5756	1035	80.0	0.17981237	19.97915	-5.29936	0.0050
4.00	5313	722	84.9	0.135893092	15.09923	-5.579406	0.0038
4.50	6773	844	86.2	0.124612432	13.84583	-5.666066	0.0035
5.00	5237	491	89.6	0.093755967	10.41733	-5.950579	0.0026
6.00	5096	335	92.7	0.065737834	7.304204	-6.3056	0.0018
7.00	6833	386	93.7	0.056490561	6.276729	-6.457201	0.0016
8.00	6366	306	94.7	0.048067861	5.340873	-6.61866	0.0013
9.00	6077	263	95.2	0.043277933	4.808659	-6.723631	0.0012
10.00	6181	221	96.0	0.035754732	3.972748	-6.914592	0.0010

Table S4 4 mol% Cp*2TiCl, 2 mol% TEMPO, 0.025 M Substrate **1** in MeCN – Run 1

Time (min)	Area Ph2O	Area SUB	% Conversion	Asub/AIS	%SM	Ln[SM]	[SM]
0.00	5376	4810	0.6	0.670572917	100	-3.688879	0.0250
0.50	6149	4750	18.7	0.772483331	81.31403	-3.895731	0.0203
1.00	5942	3863	31.6	0.650117805	68.43345	-4.068188	0.0171
1.50	5869	3604	35.4	0.614073948	64.63936	-4.125226	0.0162
2.00	7373	3200	54.3	0.434016004	45.6859	-4.47226	0.0114
2.50	5959	2300	59.4	0.3859708	40.62851	-4.58958	0.0102
3.00	7227	2600	62.1	0.359762004	37.86968	-4.659899	0.0095
3.50	7693	2513	65.6	0.326660601	34.38533	-4.75642	0.0086
4.00	5860	1300	76.6	0.221843003	23.3519	-5.143371	0.0058
4.50	6256	2030	65.8	0.324488491	34.15668	-4.763091	0.0085
5.00	5853	1554	72.1	0.265504869	27.94788	-4.963708	0.0070
6.00	6038	1369	76.1	0.226730706	23.86639	-5.121578	0.0060
7.00	6011	1175	79.4	0.195474963	20.57631	-5.269909	0.0051
8.00	7301	1526	78.0	0.209012464	22.00131	-5.202948	0.0055
9.00	5100	818	83.1	0.160392157	16.88338	-5.46772	0.0042
10.00	6573	1199	80.8	0.182412901	19.20136	-5.339069	0.0048

Table S5 4 mol% Cp*2TiCl, 2 mol% TEMPO, 0.025 M Substrate **1** in MeCN – Run 2

Time (min)	Area Ph2O	Area SUB	% Conversion	Asub/AIS	%SM	Ln[SM]	[SM]
0.00	5171	4800	-3.1	0.92825372	100	-3.688879	0.0250
0.50	7149	5505	18.1	0.77003777	81.91891	-3.88832	0.0205
1.00	6756	4285	32.5	0.63425104	67.47351	-4.082314	0.0169
1.50	6236	3538	39.6	0.56735087	60.35648	-4.193781	0.0151
2.00	6347	3097	48.1	0.48794706	51.90926	-4.344552	0.0130
2.50	6655	2840	54.6	0.42674681	45.3986	-4.478568	0.0113
3.00	5156	1614	66.7	0.31303336	33.30142	-4.78845	0.0083
3.50	5600	1634	69.0	0.29178571	31.04103	-4.85874	0.0078
4.00	6483	1607	73.6	0.24787907	26.37011	-5.021818	0.0066
4.50	6852	1715	73.4	0.25029189	26.6268	-5.012132	0.0067
5.00	6422	1345	77.7	0.20943631	22.28046	-5.19034	0.0056
6.00	6596	1162	81.3	0.17616737	18.74121	-5.363325	0.0047
7.00	7161	1134	83.2	0.15835777	16.84657	-5.469902	0.0042
8.00	6850	942	85.4	0.13751825	14.6296	-5.611003	0.0037
9.00	6376	679	88.7	0.1064931	11.32905	-5.866679	0.0028
10.00	6830	786	87.8	0.11508053	12.24261	-5.789127	0.0031

Table S6 4 mol% Cp*2TiCl, 2 mol% TEMPO, 0.025 M Substrate **1** in MeCN – Run 3

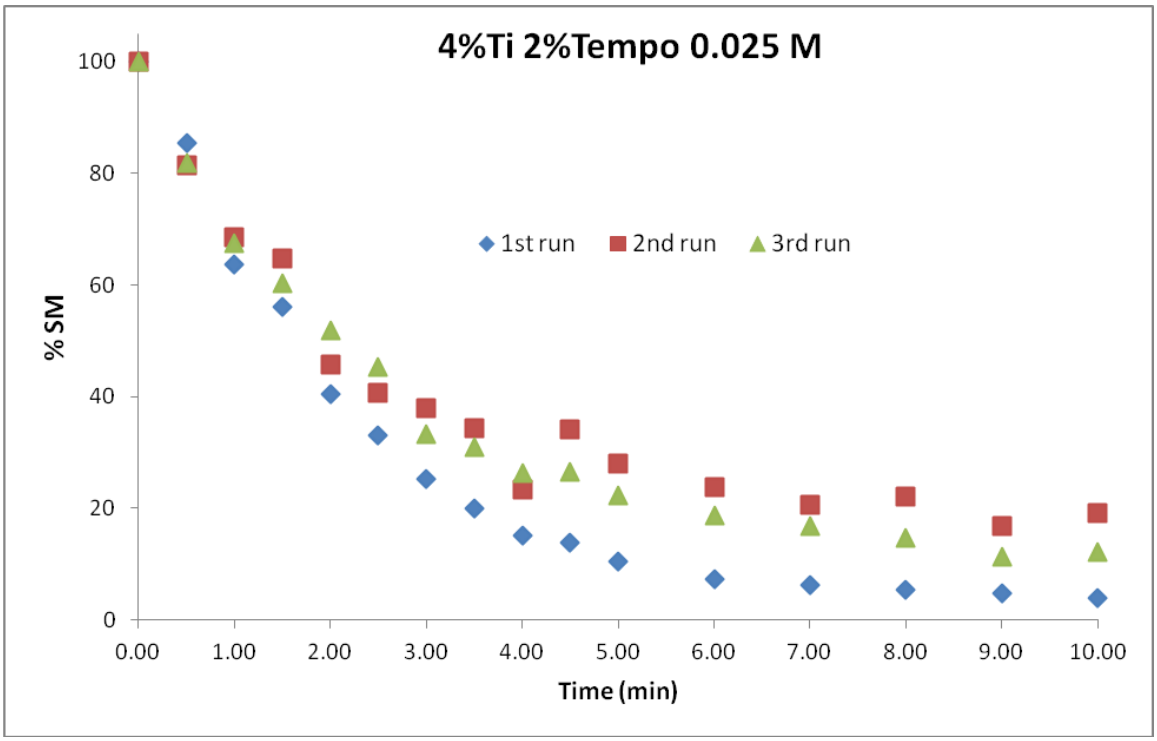


Figure S3 Overlay of 3 independent kinetic runs with 4 mol% Cp*2TiCl, 2 mol% TEMPO, 0.025 M substrate **1** in MeCN.

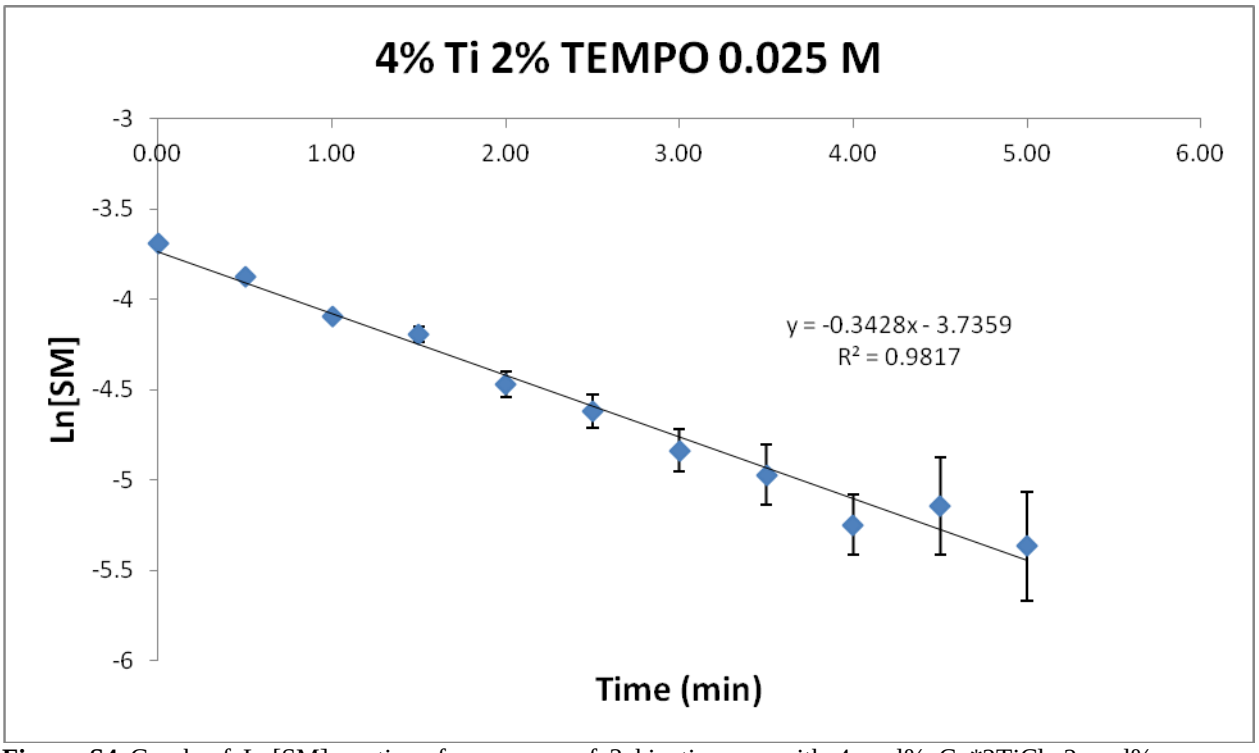


Figure S4 Graph of Ln[SM] vs time for average of 3 kinetic runs with 4 mol% Cp*2TiCl, 2 mol% TEMPO, 0.025 M substrate **1** in MeCN. Error bars calculated using standard error of the mean (standard deviation / sqrt(n))

Time (min)	Area Ph2O	Area SUB	% Conversion	Asub/AIS	%SM	Ln[SM]	[SM]
0.00	4590	3910	0.9	0.851851852	100	-3.68887945	0.0250
0.50	3973	2890	15.4	0.727410018	84.58256	-3.85632154	0.0211
1.00	5924	3900	23.4	0.65833896	76.55104	-3.95609191	0.0191
1.50	5345	3100	32.6	0.579981291	67.43968	-4.082816	0.0169
2.00	5552	2898	39.3	0.521974063	60.69466	-4.18819394	0.0152
2.50	6334	3027	44.4	0.477897063	55.56943	-4.27641648	0.0139
3.00	6136	2388	54.7	0.389178618	45.25333	-4.48177343	0.0113
3.50	6821	2407	59.0	0.352880809	41.03265	-4.57968149	0.0103
4.00	5402	1572	66.2	0.291003332	33.8376	-4.77247713	0.0085
4.50	5634	1437	70.3	0.255058573	29.65797	-4.90431863	0.0074
5.00	6224	1381	74.2	0.221883033	25.80035	-5.04366148	0.0065
6.00	6508	1124	79.9	0.17271051	20.08262	-5.294195	0.0050
7.00	6747	998	82.8	0.147917593	17.19972	-5.44915653	0.0043
8.00	5932	747	85.4	0.125927175	14.64269	-5.61010808	0.0037
9.00	6246	690	87.2	0.110470701	12.84543	-5.7410615	0.0032
10.00	4904	435	89.7	0.0887031	10.31431	-5.96051701	0.0026

Table S7 3 mol% Cp*2TiCl, 2 mol% TEMPO, 0.025 M substrate **1** in MeCN – Run 1

Time (min)	Area Ph2O	Area SUB	% Conversion	Asub/AIS	%SM	Ln[SM]	[SM]
0.00	4621	3613	2.3	0.781865397	100	-3.688879454	0.0250
0.50	4944	3363	15.0	0.680218447	85.027306	-3.85107719	0.0213
1.00	4725	2900	23.3	0.613756614	76.719577	-3.953892727	0.0192
1.50	4813	2571	33.2	0.534178267	66.772283	-4.092761565	0.0167
2.00	5626	2523	43.9	0.448453608	56.056701	-4.267685943	0.0140
2.50	4936	1984	49.8	0.401944895	50.243112	-4.377176181	0.0126
3.00	5766	2057	55.4	0.356746445	44.593306	-4.496465891	0.0111
3.50	3771	961	68.1	0.254839565	31.854946	-4.832856991	0.0080
4.00	5465	1508	65.5	0.275937786	34.492223	-4.753315755	0.0086
4.50	7000	1532	72.6	0.218857143	27.357143	-4.985071981	0.0068
5.00	6412	1104	78.5	0.172177168	21.522146	-5.22496719	0.0054
6.00	4751	622	83.6	0.130919806	16.364976	-5.498906211	0.0041
7.00	5496	675	84.6	0.122816594	15.352074	-5.562799046	0.0038
8.00	6151	620	87.4	0.100796618	12.599577	-5.760386374	0.0031
9.00	4548	284	92.2	0.062445031	7.8056288	-6.23920452	0.0020
10.00	5007	374	90.7	0.074695426	9.3369283	-6.060072318	0.0023

Table S8 3 mol% Cp*2TiCl, 2 mol% TEMPO, 0.025 M substrate **1** in MeCN – Run 2

(min)	Area Ph2O	Area SUB	% Conversion	Asub/AIS	%SM	Ln[SM]	[SM]
0.00	5999	4881	-1.7	0.813635606	100	-3.688879454	0.0250
0.50	5945	4100	13.8	0.689655172	86.2068966	-3.837299459	0.0216
1.00	4727	2849	24.7	0.602707849	75.3384811	-3.972058599	0.0188
1.50	5620	2693	40.1	0.479181495	59.8976868	-4.201411753	0.0150
2.00	6300	2642	47.6	0.419365079	52.4206349	-4.33474933	0.0131
2.50	3687	864	70.7	0.234336859	29.2921074	-4.916731532	0.0073
3.00	4218	796	76.4	0.188715031	23.5893789	-5.133253078	0.0059
3.50	5524	1019	76.9	0.184467777	23.0584721	-5.156016384	0.0058
4.00	5430	872	79.9	0.160589319	20.0736648	-5.294640892	0.0050
4.50	6312	854	83.1	0.135297845	16.9122307	-5.466012572	0.0042
5.00	4327	422	87.8	0.097527155	12.1908944	-5.793360329	0.0030
6.00	7032	630	88.8	0.089590444	11.1988055	-5.878242523	0.0028
7.00	6269	422	91.6	0.067315361	8.41442016	-6.16410272	0.0021
8.00	5541	328	92.6	0.059195091	7.39938639	-6.292652563	0.0018
9.00	5646	292	93.5	0.05171803	6.46475381	-6.427684709	0.0016
10.00	6448	308	94.0	0.047766749	5.97084367	-6.507161404	0.0015

Table S9 3 mol% Cp*2TiCl, 2 mol% TEMPO, 0.025 M substrate **1** in MeCN – Run 3

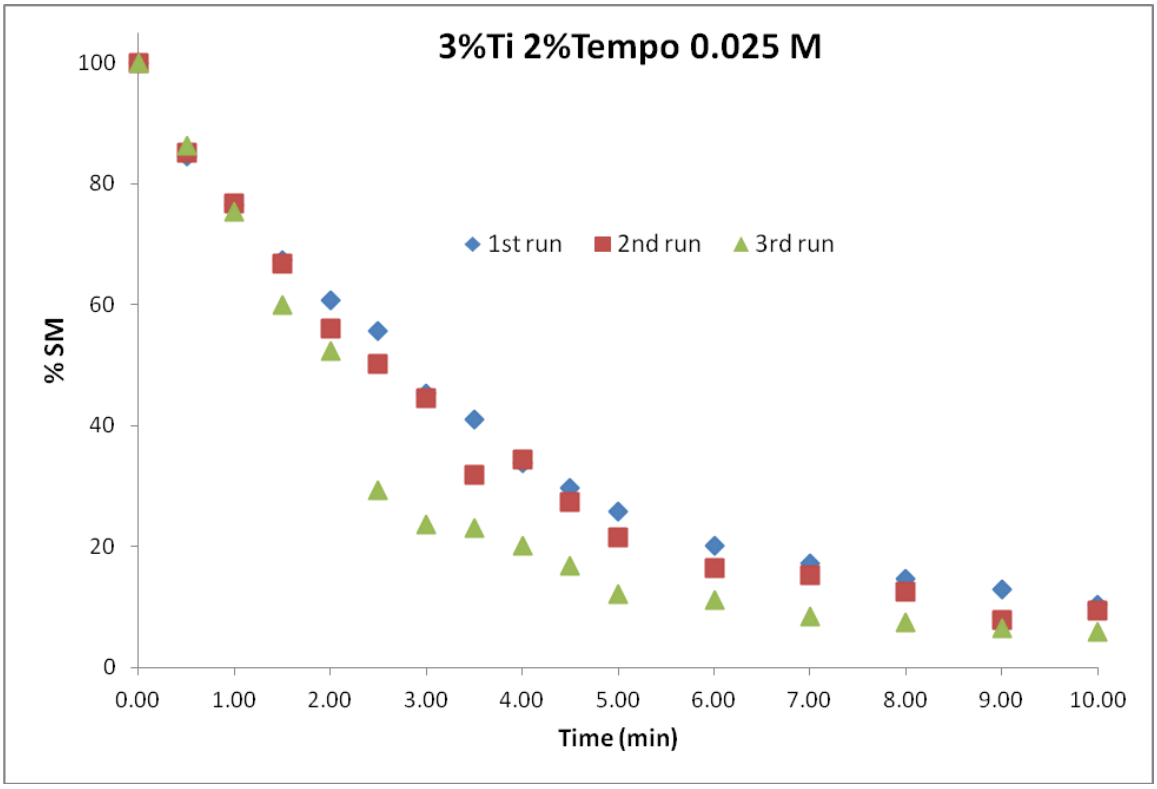


Figure S5 Overlay of 3 kinetics experiments with 3 mol% Cp*2TiCl, 2 mol% TEMPO, 0.025 M substrate **1** in MeCN

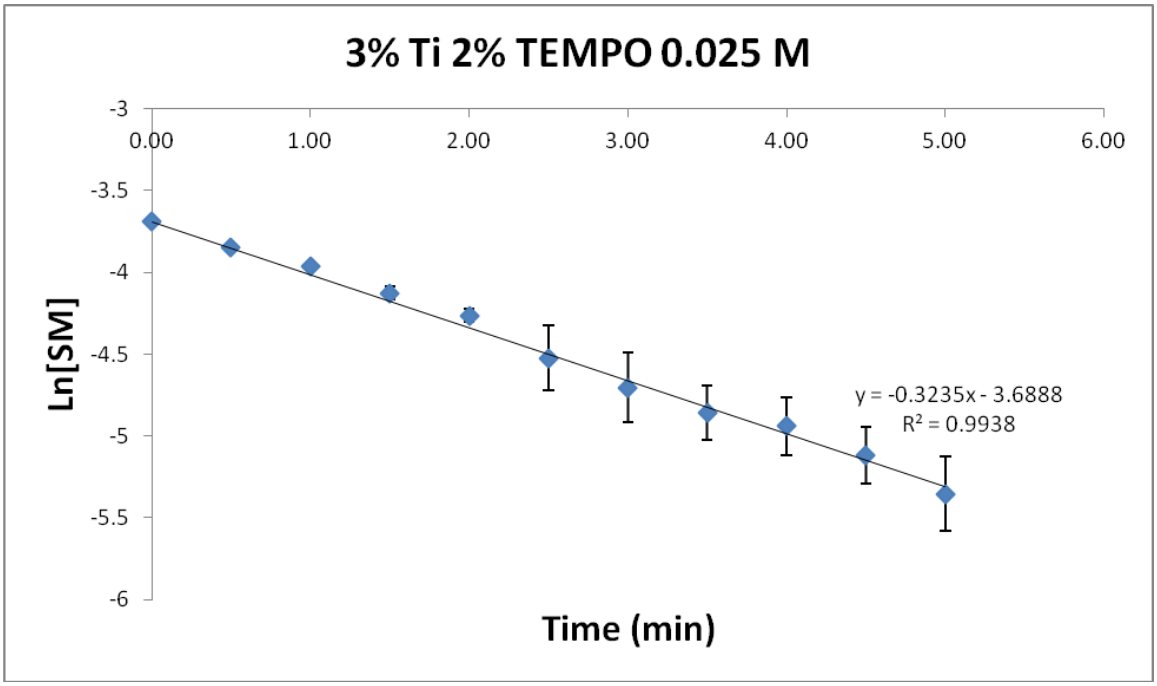


Figure S6 Graph of Ln[SM] vs time for average of 3 kinetic runs with 3 mol% Cp*2TiCl, 2 mol% TEMPO, 0.025 M substrate **1** in MeCN. Error bars calculated using standard error of the mean (standard deviation / sqrt(n))

Time (min)	Area Ph2O	Area SUB	% Conversion	Asub/AIS	%SM	Ln[SM]	[SM]
0.00	5399	3807	0.0	0.70513058	100	-3.68887945	0.0250
0.50	6413	4022	11.1	0.627163574	88.9429	-3.80605507	0.0222
1.00	5873	3300	20.3	0.561893411	79.68643	-3.91595029	0.0199
1.50	6051	3080	27.8	0.509006776	72.18617	-4.01480113	0.0180
2.00	7675	3653	32.5	0.475960912	67.49968	-4.08192673	0.0169
2.50	8388	3729	37.0	0.444563662	63.047	-4.15016919	0.0158
3.00	8542	3168	47.4	0.370873332	52.5964	-4.33140188	0.0131
3.50	7410	2395	54.2	0.323211876	45.83717	-4.46895439	0.0115
4.00	8134	2269	60.4	0.278952545	39.56041	-4.61622078	0.0099
4.50	7574	1756	67.1	0.231845788	32.87984	-4.80119001	0.0082
5.00	7589	1512	71.7	0.199235736	28.25515	-4.95277373	0.0071
6.00	8018	1328	76.5	0.165627338	23.48889	-5.13752214	0.0059
7.00	9335	1396	78.8	0.149544724	21.20809	-5.23966695	0.0053
8.00	8366	1009	82.9	0.12060722	17.10424	-5.45472331	0.0043
9.00	7872	764	86.2	0.097052846	13.76381	-5.67200683	0.0034
10.00	7763	699	87.2	0.090042509	12.76962	-5.74698057	0.0032

Table S10 2 mol% Cp*2TiCl, 2% TEMPO 0.025 M Substrate 1 in MeCN – Run 1

Time (min)	Area Ph2O	Area SUB	% Conversion	Asub/AIS	%SM	Ln[SM]	[SM]
0.00	3883	3289	0.3	0.847025496	100	-3.688879454	0.0250
0.50	7609	5703	11.8	0.749507163	88.177313	-3.81469993	0.0220
1.00	6268	4106	22.9	0.655073389	77.067457	-3.949368531	0.0193
1.50	6808	3933	32.0	0.577702703	67.965024	-4.075056422	0.0170
2.00	7919	4666	30.7	0.58921581	69.319507	-4.055323286	0.0173
2.50	8237	4234	39.5	0.514022095	60.473188	-4.191849552	0.0151
3.00	6728	2529	55.8	0.375891795	44.222564	-4.50481448	0.0111
3.50	7596	2592	59.9	0.341232227	40.144968	-4.601552539	0.0100
4.00	7437	2151	66.0	0.289229528	34.027003	-4.766895216	0.0085
4.50	8186	2426	65.1	0.296359638	34.86584	-4.742542092	0.0087
5.00	7257	1680	72.8	0.23150062	27.235367	-4.989533251	0.0068
6.00	7075	1296	78.4	0.183180212	21.550613	-5.22364537	0.0054
7.00	7141	1051	82.7	0.147178266	17.31509	-5.442471255	0.0043
8.00	7580	991	84.6	0.130738786	15.381034	-5.560914469	0.0038
9.00	8231	995	85.8	0.120884461	14.221701	-5.63928058	0.0036
10.00	6954	617	89.6	0.088725913	10.438343	-5.948563813	0.0026

Table S11 2 mol% Cp*2TiCl, 2% TEMPO 0.025 M Substrate 1 in MeCN – Run 2

Time (min)	Area Ph2O	Area SUB	% Conversion	Asub/AIS	%SM	Ln[SM]	[SM]
0.00	5632	4206	-0.9	0.746803977	100	-3.688879454	0.0250
0.50	4790	3100	12.5	0.647181628	87.4569768	-3.822902661	0.0219
1.00	5818	3582	16.8	0.61567549	83.1993905	-3.872809618	0.0208
1.50	7300	4000	26.0	0.547945205	74.0466494	-3.989354348	0.0185
2.00	6920	3641	28.9	0.526156069	71.1021715	-4.029931762	0.0178
2.50	5409	2492	37.7	0.460713625	62.258598	-4.162752993	0.0156
3.00	6563	2403	50.5	0.366143532	49.4788557	-4.39250422	0.0124
3.50	7262	2559	52.4	0.352382264	47.6192248	-4.430813077	0.0119
4.00	8158	2780	54.0	0.340769797	46.0499725	-4.464322475	0.0115
4.50	4729	959	72.6	0.202791288	27.4042281	-4.983352329	0.0069
5.00	6558	1304	73.1	0.19884111	26.8704203	-5.003023576	0.0067
6.00	7142	1048	80.2	0.146737609	19.8294066	-5.306883625	0.0050
7.00	6318	660	85.9	0.104463438	14.1166808	-5.646692508	0.0035
8.00	5323	459	88.3	0.08622957	11.6526446	-5.838516484	0.0029
9.00	7556	762	86.4	0.100847009	13.6279742	-5.681925034	0.0034
10.00	7056	564	89.2	0.079931973	10.8016179	-5.914353708	0.0027

Table S12 2 mol% Cp*2TiCl, 2% TEMPO 0.025 M Substrate 1 in MeCN – Run 3

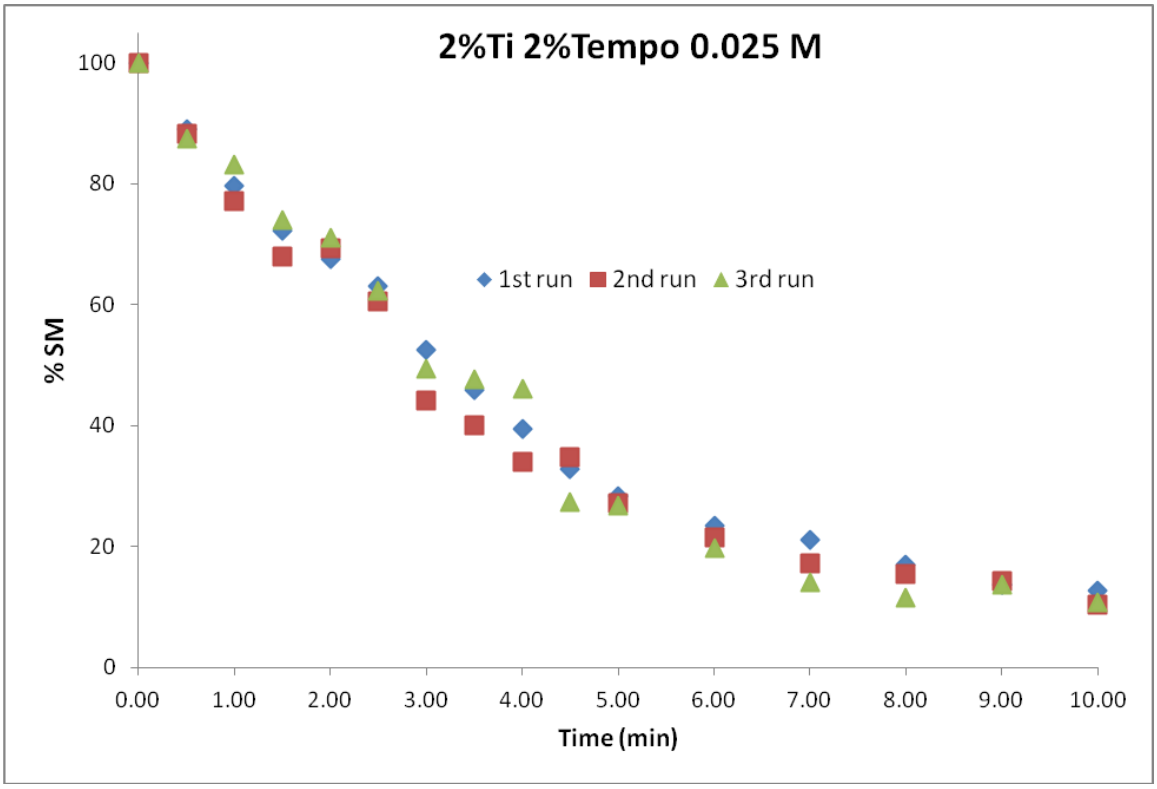


Figure S7 Overlay of 3 kinetics experiments with 2 mol% Cp*2TiCl, 2 mol% TEMPO, 0.025 M substrate **1** in MeCN

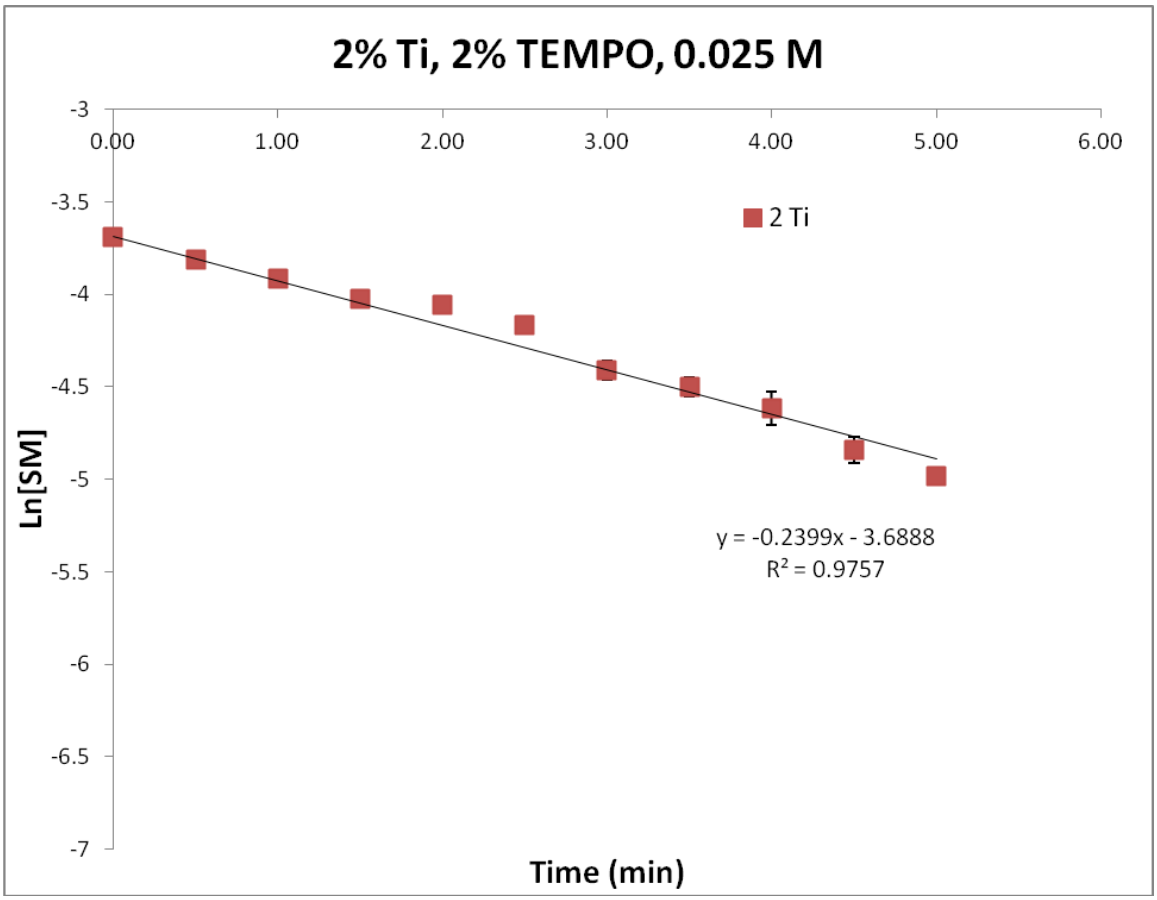


Figure S8 Graph of Ln[SM] vs time for average of 3 kinetic runs with 2 mol% Cp*2TiCl, 2 mol% TEMPO, 0.025 M substrate **1** in MeCN. Error bars calculated using standard error of the mean (standard deviation / sqrt(n))

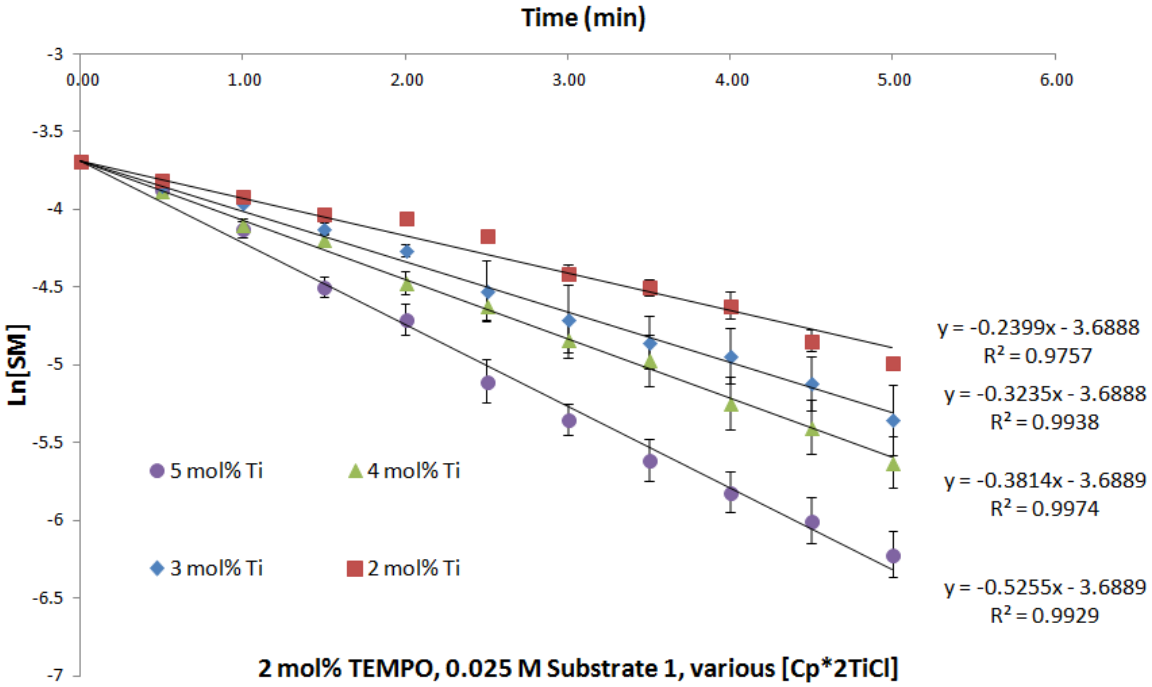


Figure S9 Graph of Ln[SM] vs time. Each dataset is the average of 3 runs (shown above). Experiments were run with 2 mol% TEMPO, 0.025 M substrate **1**, and varying mol% Cp*2TiCl from 2 mol% to 5 mol%. Experiments were run in MeCN at 23 °C. Error bars were calculated using standard error (standard deviation / square root (n))

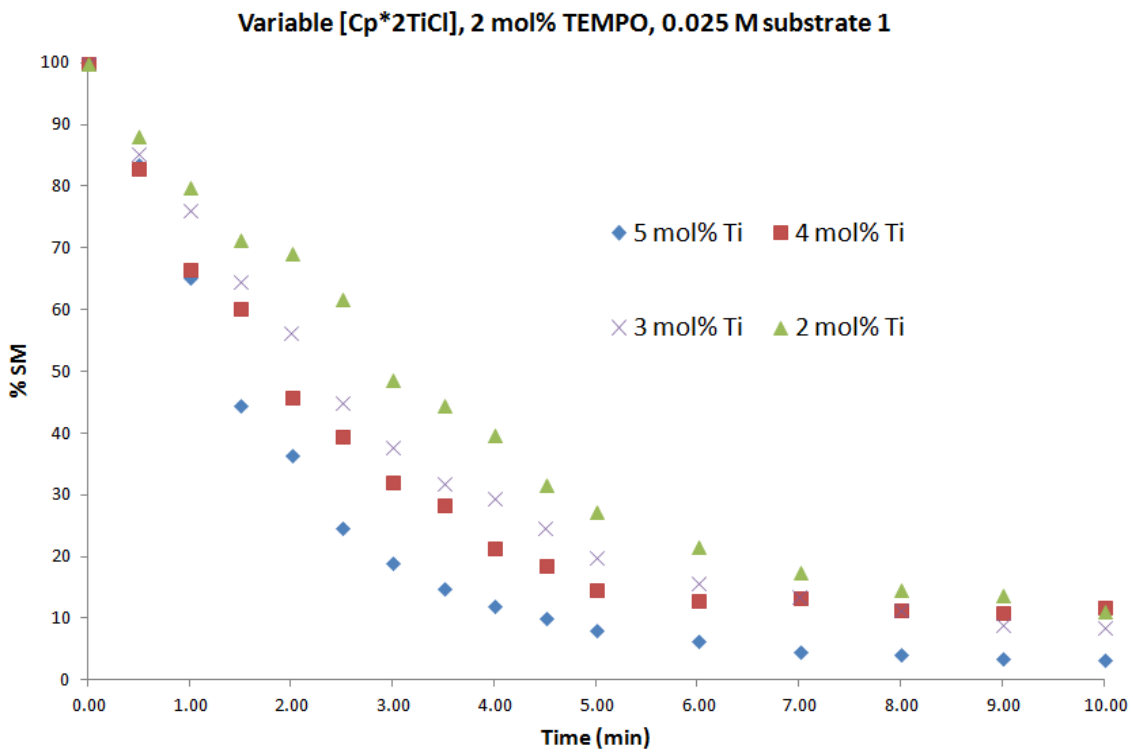


Figure S10 Graph of %SM vs time. Each dataset is an average of 3 kinetic experiments using 2 mol% TEMPO, 0.025 M substrate **1** in MeCN at 23 °C. Mol% of Cp*2TiCl was varied in each dataset from 2 mol% to 5 mol%.

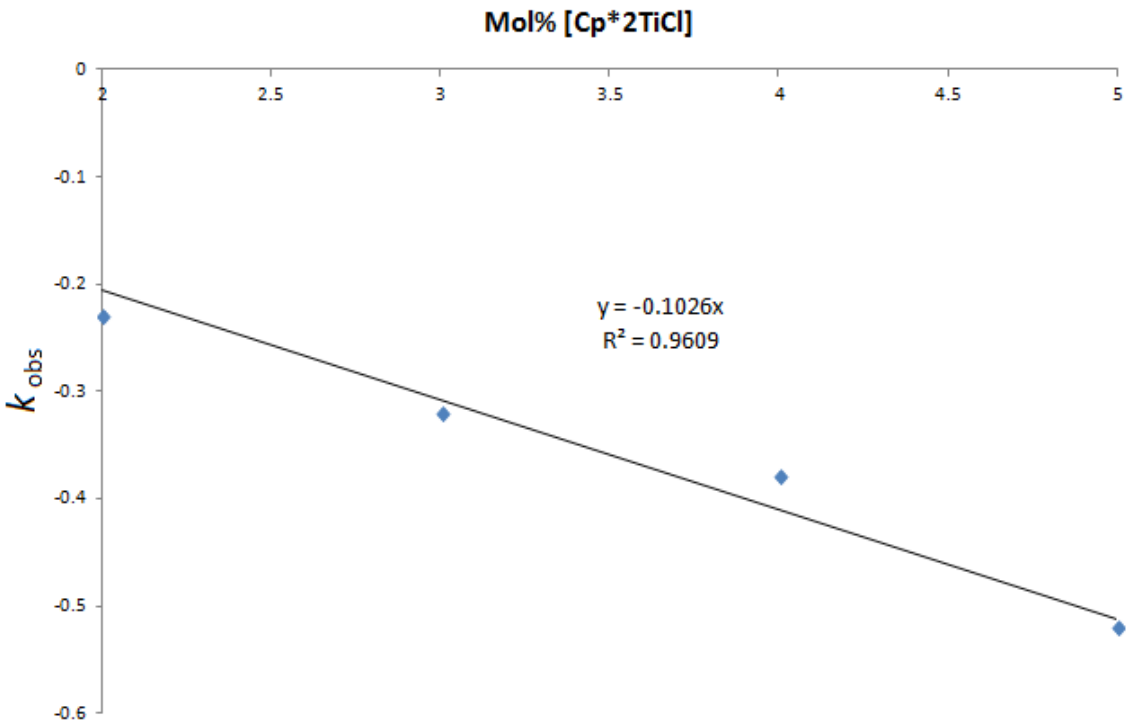


Figure S11 Graph of k_{obs} vs mol% Cp*2TiCl. Experiments were all run with 2 mol% TEMPO and 0.025 M substrate **1** in MeCN at 23 °C. k_{obs} was calculated from the slope of Ln[SM] vs time plots. Each data point is the average of 3 experiments.

Time (min)	Area Ph2O	Area SUB	% Conversion	Asub/AIS	%SM	Ln[SM]	[SM]
0.00	5399	3807	0.0	0.70513058	100	-3.68887945	0.0250
0.50	6413	4022	11.1	0.62716357	88.9429	-3.80605507	0.0222
1.00	5873	3300	20.3	0.56189341	79.68643	-3.91595029	0.0199
1.50	6051	3080	27.8	0.50900678	72.18617	-4.01480113	0.0180
2.00	7675	3653	32.5	0.47596091	67.49968	-4.08192673	0.0169
2.50	8388	3729	37.0	0.44456366	63.047	-4.15016919	0.0158
3.00	8542	3168	47.4	0.37087333	52.5964	-4.33140188	0.0131
3.50	7410	2395	54.2	0.32321188	45.83717	-4.46895439	0.0115
4.00	8134	2269	60.4	0.27895254	39.56041	-4.61622078	0.0099
4.50	7574	1756	67.1	0.23184579	32.87984	-4.80119001	0.0082
5.00	7589	1512	71.7	0.19923574	28.25515	-4.95277373	0.0071
6.00	8018	1328	76.5	0.16562734	23.48889	-5.13752214	0.0059
7.00	9335	1396	78.8	0.14954472	21.20809	-5.23966695	0.0053
8.00	8366	1009	82.9	0.12060722	17.10424	-5.45472331	0.0043
9.00	7872	764	86.2	0.09705285	13.76381	-5.67200683	0.0034
10.00	7763	699	87.2	0.09004251	12.76962	-5.74698057	0.0032

Table S13 2 mol% Cp*2TiCl, 2% TEMPO 0.025 M Substrate **1** in MeCN – Run 1

Time (min)	Area Ph2O	Area SUB	% Conversion	Asub/AIS	%SM	Ln[SM]	[SM]
0.00	3883	3312	-0.3	0.94514551	100	-3.688879	0.0250
0.50	7609	5703	11.8	0.74950716	88.17731	-3.8147	0.0220
1.00	6268	4106	22.9	0.65507339	77.06746	-3.949369	0.0193
1.50	6808	3933	32.0	0.5777027	67.96502	-4.075056	0.0170
2.00	7919	4666	30.7	0.58921581	69.31951	-4.055323	0.0173
2.50	8237	4234	39.5	0.5140221	60.47319	-4.19185	0.0151
3.00	6728	2529	55.8	0.3758918	44.22256	-4.504814	0.0111
3.50	7596	2910	54.9	0.38309637	45.07016	-4.485829	0.0113
4.00	7437	2612	58.7	0.35121689	41.31963	-4.572712	0.0103
4.50	8186	2910	58.2	0.35548497	41.82176	-4.560633	0.0105
5.00	7257	2100	66.0	0.28937578	34.04421	-4.76639	0.0085
6.00	7075	1296	78.4	0.18318021	21.55061	-5.223645	0.0054
7.00	7141	1051	82.7	0.14717827	17.31509	-5.442471	0.0043
8.00	7580	991	84.6	0.13073879	15.38103	-5.560914	0.0038
9.00	8231	995	85.8	0.12088446	14.2217	-5.639281	0.0036
10.00	6954	617	89.6	0.08872591	10.43834	-5.948564	0.0026

Table S14 2 mol% Cp*2TiCl, 2% TEMPO 0.025 M Substrate **1** in MeCN – Run 2

Time (min)	Area Ph2O	Area SUB	% Conversion	Asub/AIS	%SM	Ln[SM]	[SM]
0.00	5231	3912	-1.1	0.74784936	100	-3.688879	0.0250
0.50	4790	3100	12.5	0.64718163	87.45698	-3.822903	0.0219
1.00	5818	3582	16.8	0.61567549	83.19939	-3.87281	0.0208
1.50	7300	4000	26.0	0.54794521	74.04665	-3.989354	0.0185
2.00	6920	3641	28.9	0.52615607	71.10217	-4.029932	0.0178
2.50	5409	2492	37.7	0.46071363	62.2586	-4.162753	0.0156
3.00	6563	2710	44.2	0.41292092	55.80012	-4.272274	0.0140
3.50	7262	2832	47.3	0.38997521	52.69935	-4.329446	0.0132
4.00	8158	2930	51.5	0.35915666	48.53468	-4.411771	0.0121
4.50	4729	1210	65.4	0.25586805	34.57676	-4.750868	0.0086
5.00	6558	1810	62.7	0.27599878	37.29713	-4.675133	0.0093
6.00	7142	1048	80.2	0.14673761	19.82941	-5.306884	0.0050
7.00	6318	660	85.9	0.10446344	14.11668	-5.646693	0.0035
8.00	5323	459	88.3	0.08622957	11.65264	-5.838516	0.0029
9.00	7556	762	86.4	0.10084701	13.62797	-5.681925	0.0034
10.00	7056	564	89.2	0.07993197	10.80162	-5.914354	0.0027

Table S15 2 mol% Cp*2TiCl, 2% TEMPO 0.025 M Substrate **1** in MeCN – Run 3

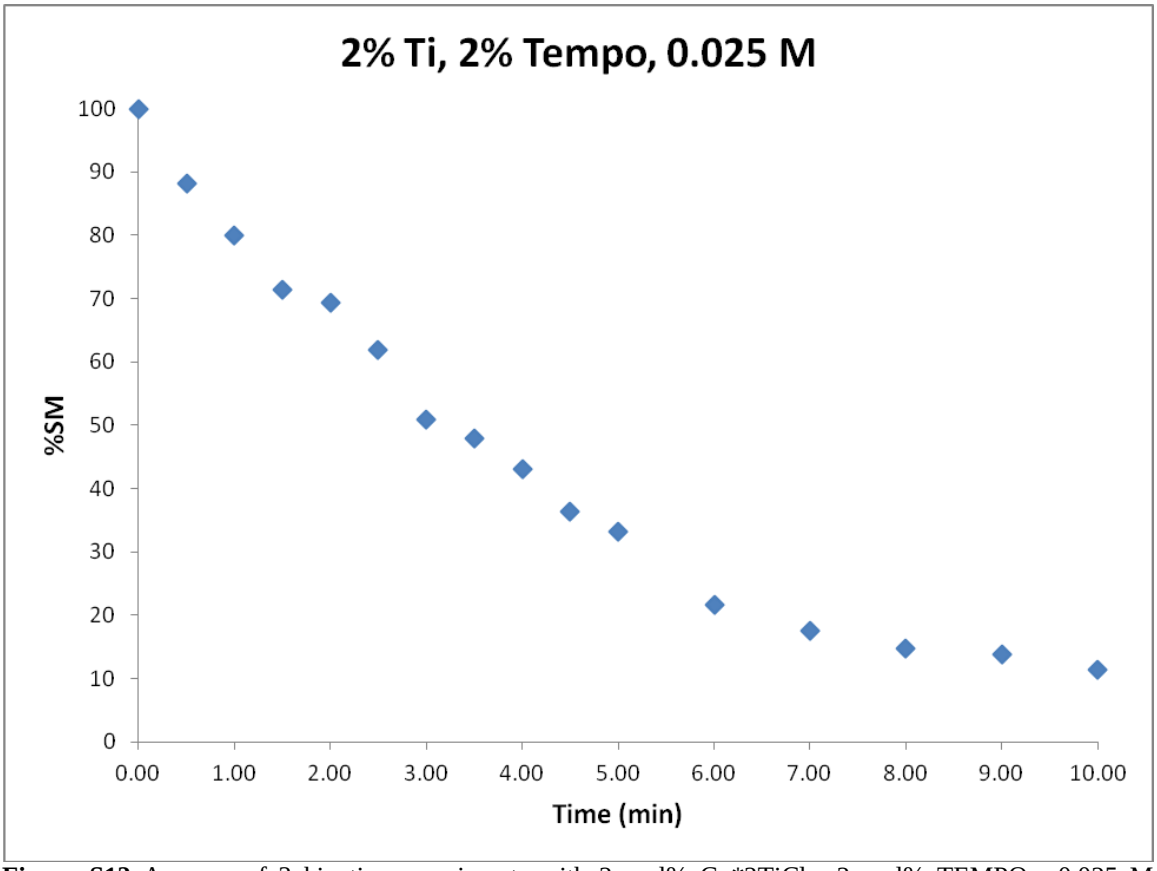


Figure S12 Average of 3 kinetics experiments with 2 mol% Cp*2TiCl, 2 mol% TEMPO, 0.025 M substrate **1** in MeCN

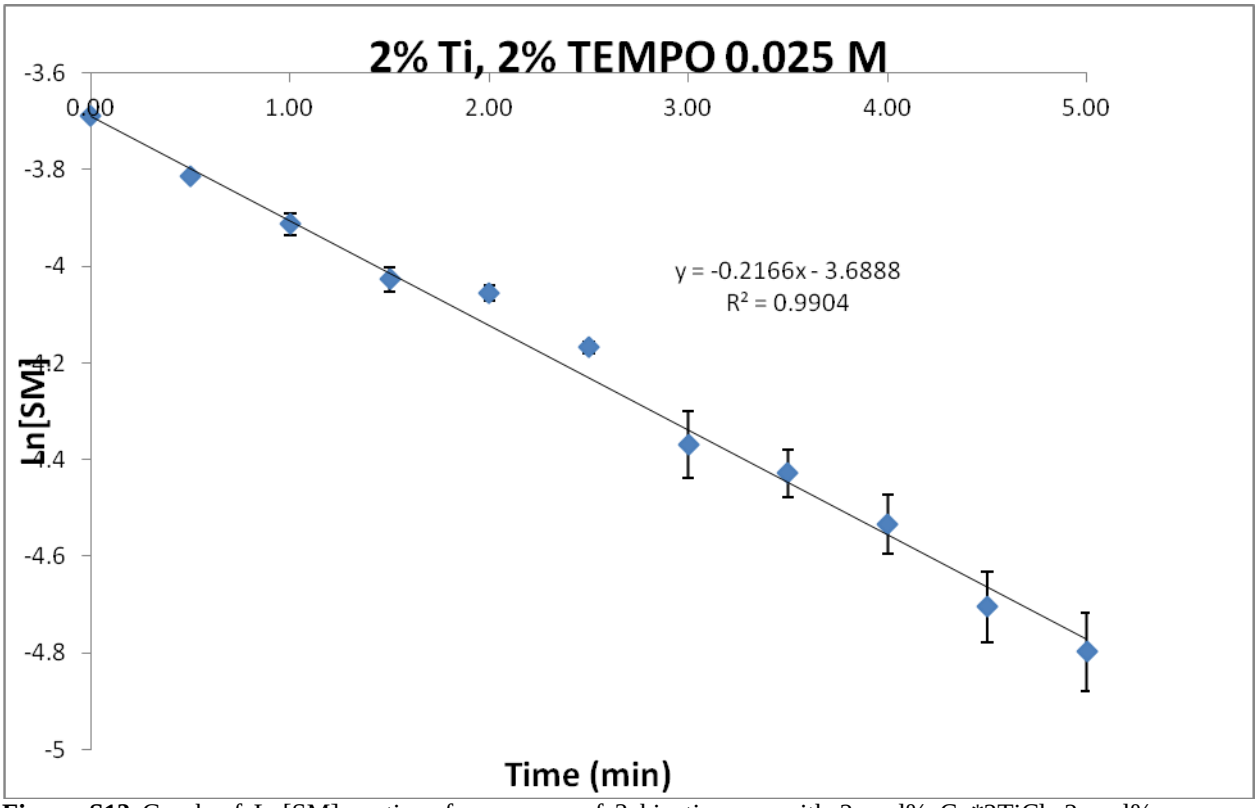


Figure S13 Graph of Ln[SM] vs time for average of 3 kinetic runs with 2 mol% Cp*2TiCl, 2 mol% TEMPO, 0.025 M substrate **1** in MeCN. Error bars calculated using standard error of the mean (standard deviation / sqrt(n))

Time (min)	Area Ph2O	Area SUB	% Conversion	Asub/AIS	%SM	Ln[SM]	[SM]
0.00	4997	4513	2.9	0.90314189	100	-3.68887945	0.0250
0.50	5725	4613	19.4	0.80576419	80.57642	-3.9048436	0.0201
1.00	6301	4400	30.2	0.69830186	69.83019	-4.04798326	0.0175
1.50	5899	3612	38.8	0.61230717	61.23072	-4.17940066	0.0153
2.00	6090	2990	50.9	0.4909688	49.09688	-4.40025415	0.0123
2.50	6531	2388	63.4	0.36564079	36.56408	-4.69498333	0.0091
3.00	6125	1725	71.8	0.28163265	28.16327	-4.95603116	0.0070
3.50	5675	1304	77.0	0.22977974	22.97797	-5.15951355	0.0057
4.00	5948	1151	80.6	0.19351042	19.35104	-5.33130335	0.0048
4.50	5405	823	84.8	0.15226642	15.22664	-5.57100298	0.0038
5.00	7105	1044	85.3	0.14693878	14.69388	-5.60661873	0.0037
6.00	6155	614	90.0	0.0997563	9.97563	-5.99390456	0.0025
7.00	5087	323	93.7	0.06349518	6.349518	-6.44567068	0.0016
8.00	5524	340	93.8	0.0615496	6.15496	-6.47679135	0.0015
9.00	5978	344	94.2	0.05754433	5.754433	-6.54407914	0.0014
10.00	6820	361	94.7	0.05293255	5.293255	-6.62761625	0.0013

Table S16 2 mol% Cp*2TiCl, 3% TEMPO 0.025 M Substrate **1** in MeCN – Run 1

Time (min)	Area Ph2O	Area SUB	% Conversion	Asub/AIS	%SM	Ln[SM]	[SM]
0.00	3952	4210	3.2	1.0652834	100	-3.688879	0.0250
0.50	4405	3815	21.3	0.86606129	78.73284	-3.927989	0.0197
1.00	5796	4686	26.5	0.80848861	73.49896	-3.996778	0.0184
1.50	5461	3945	34.3	0.72239517	65.67229	-4.109373	0.0164
2.00	6732	3812	48.5	0.56625074	51.47734	-4.352908	0.0129
2.50	5220	2300	59.9	0.44061303	40.05573	-4.603778	0.0100
3.00	4897	1987	63.1	0.40575863	36.88715	-4.686186	0.0092
3.50	4973	1566	71.4	0.31490046	28.62731	-4.939688	0.0072
4.00	5503	1415	76.6	0.25713247	23.37568	-5.142354	0.0058
4.50	5146	1224	78.4	0.23785464	21.62315	-5.220285	0.0054
5.00	5357	1078	81.7	0.20123203	18.29382	-5.387486	0.0046
6.00	5706	941	85.0	0.16491413	14.99219	-5.58652	0.0037
7.00	6048	865	87.0	0.14302249	13.00204	-5.728943	0.0033
8.00	5214	538	90.6	0.10318374	9.38034	-6.055434	0.0023
9.00	6758	642	91.4	0.09499852	8.636229	-6.138084	0.0022
10.00	5321	427	92.7	0.08024807	7.295279	-6.306822	0.0018

Table S17 2 mol% Cp*2TiCl, 3% TEMPO 0.025 M Substrate **1** in MeCN – Run 2

Time (min)	Area Ph2O	Area SUB	% Conversion	Asub/AIS	%SM	Ln[SM]	[SM]
0.00	5441	5791	3.2	1.06432641	100	-3.688879	0.0250
0.50	6232	5412	21.1	0.86842105	78.94737	-3.925268	0.0197
1.00	6092	4464	33.4	0.73276428	66.61493	-4.095121	0.0167
1.50	6462	4345	38.9	0.67239245	61.12659	-4.181103	0.0153
2.00	6501	3878	45.8	0.59652361	54.22942	-4.300826	0.0136
2.50	6677	3324	54.7	0.49782837	45.25712	-4.48169	0.0113
3.00	5883	2337	63.9	0.3972463	36.1133	-4.707388	0.0090
3.50	5709	2012	68.0	0.35242599	32.03873	-4.827104	0.0080
4.00	5728	1856	70.5	0.32402235	29.45658	-4.911132	0.0074
4.50	6045	1755	73.6	0.29032258	26.39296	-5.020952	0.0066
5.00	6734	1663	77.5	0.24695575	22.45052	-5.182736	0.0056
6.00	7203	1466	81.5	0.20352631	18.50239	-5.37615	0.0046
7.00	6797	988	86.8	0.14535825	13.21439	-5.712744	0.0033
8.00	5571	617	89.9	0.11075211	10.06837	-5.98465	0.0025
9.00	6940	753	90.1	0.10850144	9.863767	-6.005181	0.0025
10.00	6773	637	91.5	0.0940499	8.549991	-6.148119	0.0021

Table S18 2 mol% Cp*2TiCl, 3% TEMPO 0.025 M Substrate **1** in MeCN – Run 3

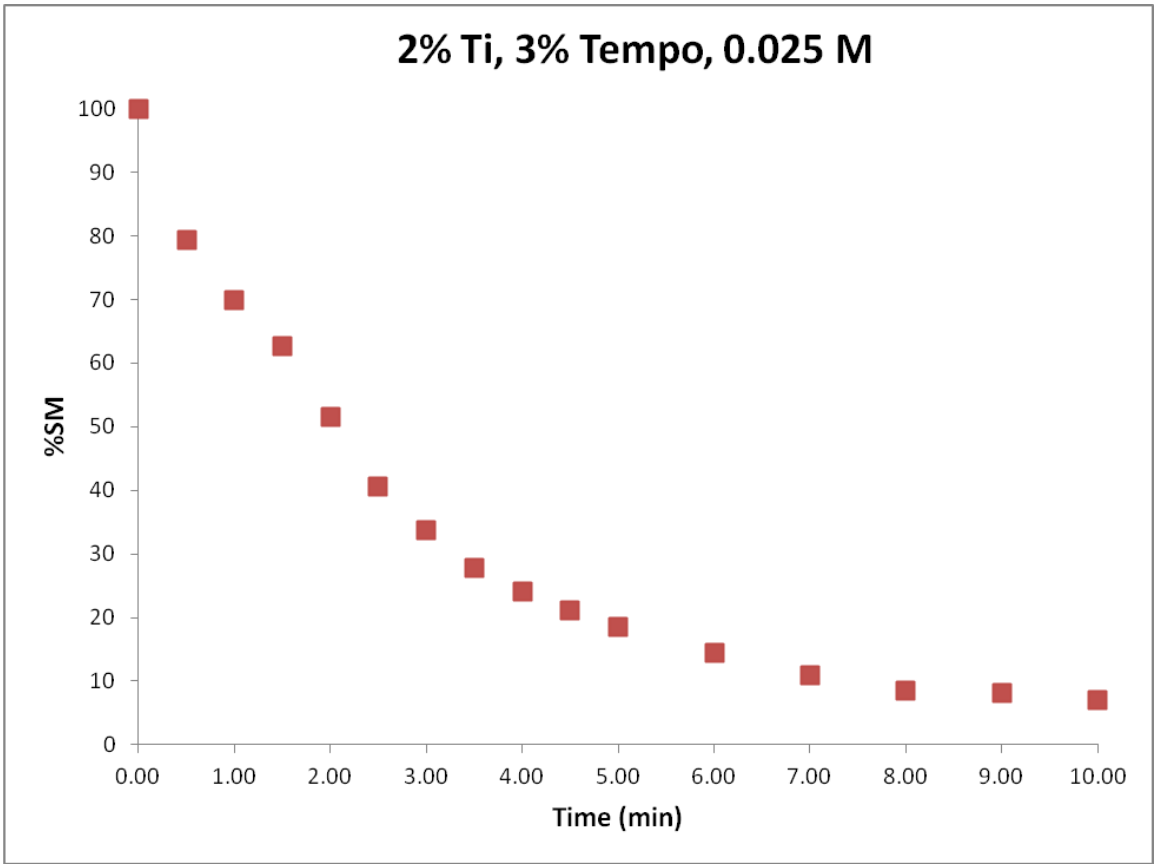


Figure S14 Overlay of 3 kinetics experiments with 2 mol% Cp*2TiCl, 3 mol% TEMPO, 0.025 M substrate **1** in MeCN

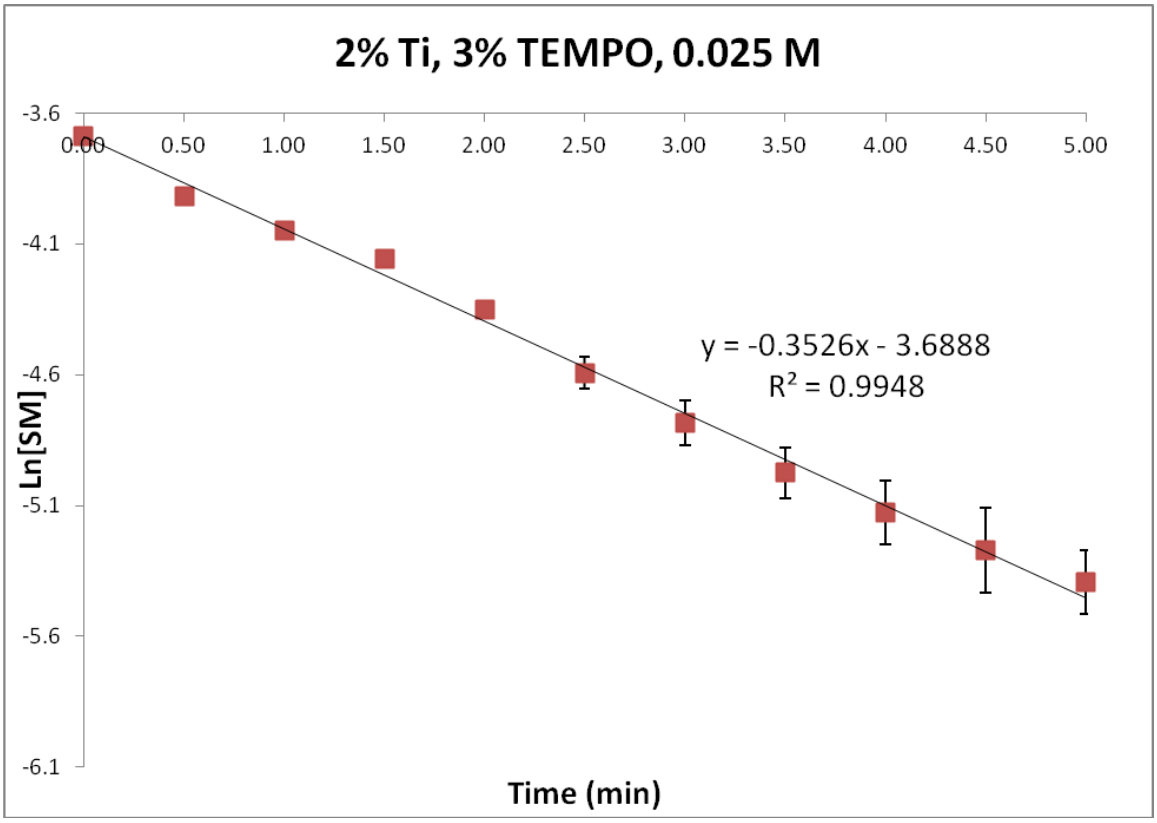


Figure S15 Graph of Ln[SM] vs time for average of 3 kinetic runs with 2 mol% Cp*2TiCl, 3 mol% TEMPO, 0.025 M substrate **1** in MeCN. Error bars calculated using standard error of the mean (standard deviation / sqrt(n))

Time (min)	Area Ph2O	Area SUB	% Conversion	Asub/AIS	%SM	Ln[SM]	[SM]
0.00	4182	3932	-1.1	0.94021999	100	-3.68887945	0.0250
0.50	4665	3700	20.7	0.79314041	79.31404	-3.92063447	0.0198
1.00	6406	4363	31.9	0.68108024	68.10802	-4.07295461	0.0170
1.50	5719	3227	43.6	0.56425949	56.42595	-4.26112051	0.0141
2.00	5744	2330	59.4	0.40564067	40.56407	-4.59116702	0.0101
2.50	6966	2126	69.5	0.30519667	30.51967	-4.87567835	0.0076
3.00	6963	1668	76.0	0.23955192	23.95519	-5.11786457	0.0060
3.50	7176	1369	80.9	0.1907748	19.07748	-5.34554103	0.0048
4.00	6661	938	85.9	0.1408197	14.08197	-5.64915441	0.0035
4.50	5951	638	89.3	0.10720887	10.72089	-5.92185572	0.0027
5.00	7301	651	91.1	0.08916587	8.916587	-6.10613642	0.0022
6.00	6919	431	93.8	0.06229224	6.229224	-6.46479789	0.0016
7.00	6149	257	95.8	0.04179541	4.179541	-6.86384812	0.0010
8.00	7070	267	96.2	0.03776521	3.776521	-6.96524655	0.0009
9.00	7466	244	96.7	0.03268149	3.268149	-7.10982589	0.0008
10.00	6544	169	97.4	0.02582518	2.582518	-7.34528462	0.0006

Table S19 2 mol% Cp*2TiCl, 4 mol% TEMPO 0.025 M Substrate **1** in MeCN – Run 1

Time (min)	Area Ph2O	Area SUB	% Conversion	Asub/AIS	%SM	Ln[SM]	[SM]
0.00	4340	4632	3.0	1.06728111	100	-3.688879	0.0250
0.50	5942	4015	24.9	0.67569842	75.0776	-3.975527	0.0188
1.00	6505	3968	32.2	0.60999231	67.77692	-4.077828	0.0169
1.50	6115	3215	41.6	0.52575634	58.41737	-4.226436	0.0146
2.00	6185	2573	53.8	0.41600647	46.22294	-4.460573	0.0116
2.50	6962	2410	61.5	0.3461649	38.46277	-4.644359	0.0096
3.00	6832	1738	71.7	0.2543911	28.26568	-4.952401	0.0071
3.50	6352	1108	80.6	0.17443325	19.38147	-5.329732	0.0048
4.00	7710	1183	83.0	0.15343709	17.04857	-5.457984	0.0043
4.50	6624	905	84.8	0.1366244	15.18049	-5.574039	0.0038
5.00	6199	635	88.6	0.10243588	11.38176	-5.862037	0.0028
6.00	6470	515	91.2	0.07959815	8.844238	-6.114283	0.0022
7.00	5211	288	93.9	0.0552677	6.140856	-6.479086	0.0015
8.00	6481	346	94.1	0.05338682	5.931869	-6.51371	0.0015
9.00	4892	197	95.5	0.04026983	4.474425	-6.795672	0.0011
10.00	6642	233	96.1	0.0350798	3.897755	-6.933649	0.0010

Table S20 2 mol% Cp*2TiCl, 4 mol% TEMPO 0.025 M Substrate **1** in MeCN – Run 2

Time (min)	Area Ph2O	Area SUB	% Conversion	Asub/AIS	%SM	Ln[SM]	[SM]
0.00	4147	4509	1.2	1.08729202	100	-3.688879	0.0250
0.50	6668	3973	25.5	0.59583083	74.47885	-3.983534	0.0186
1.00	6288	3206	36.3	0.50986005	63.73251	-4.139355	0.0159
1.50	2671	1103	48.4	0.41295395	51.61924	-4.350155	0.0129
2.00	5906	1994	57.8	0.33762276	42.20284	-4.551562	0.0106
2.50	6269	1945	61.2	0.31025682	38.7821	-4.636091	0.0097
3.00	6055	1284	73.5	0.21205615	26.50702	-5.01664	0.0066
3.50	5552	1098	75.3	0.19776657	24.72082	-5.086404	0.0062
4.00	6870	1251	77.2	0.18209607	22.76201	-5.168957	0.0057
4.50	6129	958	80.5	0.15630609	19.53826	-5.321675	0.0049
5.00	6548	772	85.3	0.11789859	14.73732	-5.603666	0.0037
6.00	5224	419	90.0	0.08020674	10.02584	-5.988884	0.0025
7.00	7367	528	91.0	0.07167097	8.958871	-6.101405	0.0022
8.00	6697	406	92.4	0.06062416	7.57802	-6.268798	0.0019
9.00	7108	345	93.9	0.04853686	6.067107	-6.491168	0.0015
10.00	5623	244	94.6	0.04339321	5.424151	-6.603188	0.0014

Table S21 2 mol% Cp*2TiCl, 4 mol% TEMPO 0.025 M Substrate **1** in MeCN – Run 3

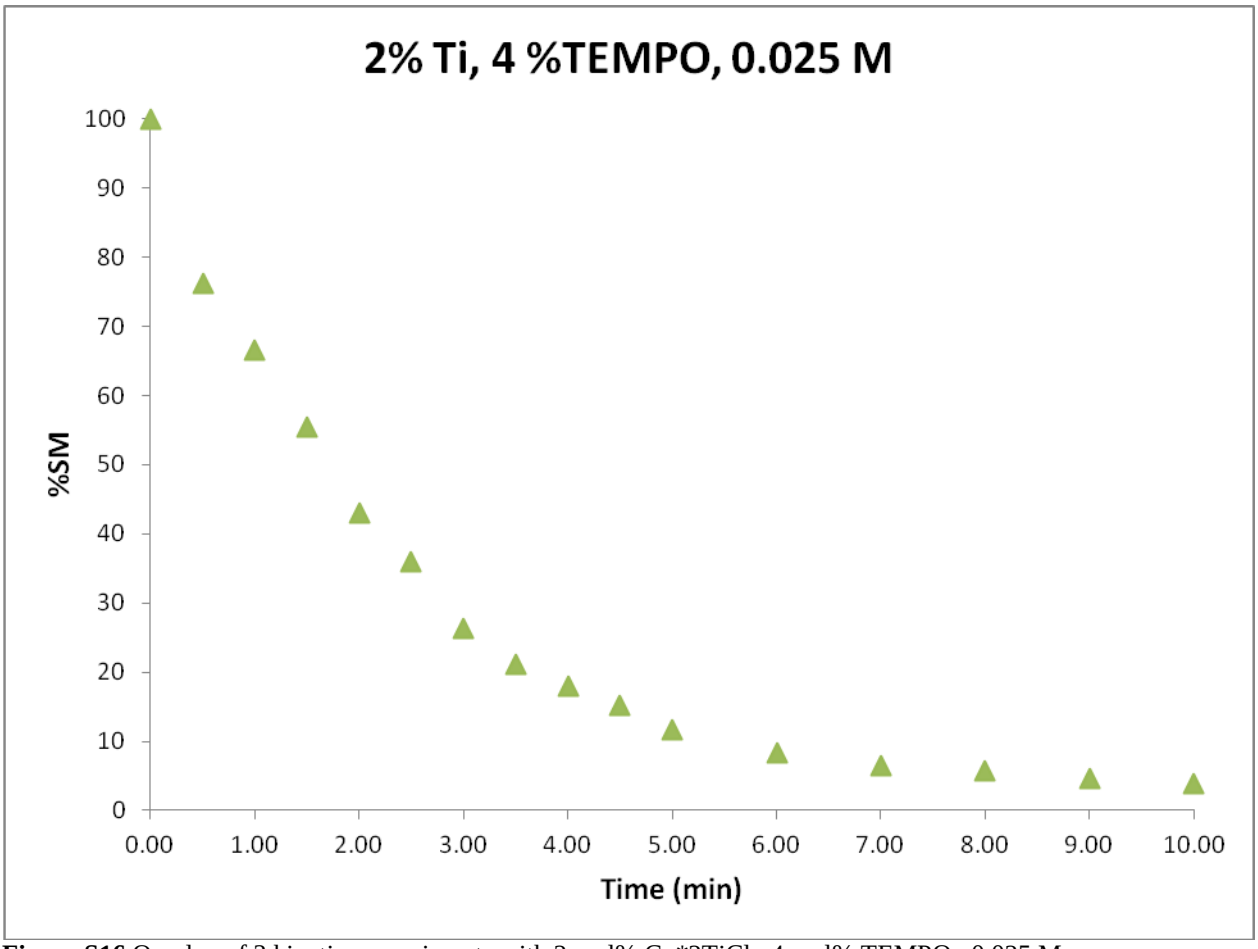


Figure S16 Overlay of 3 kinetics experiments with 2 mol% Cp*2TiCl, 4 mol% TEMPO, 0.025 M substrate **1** in MeCN

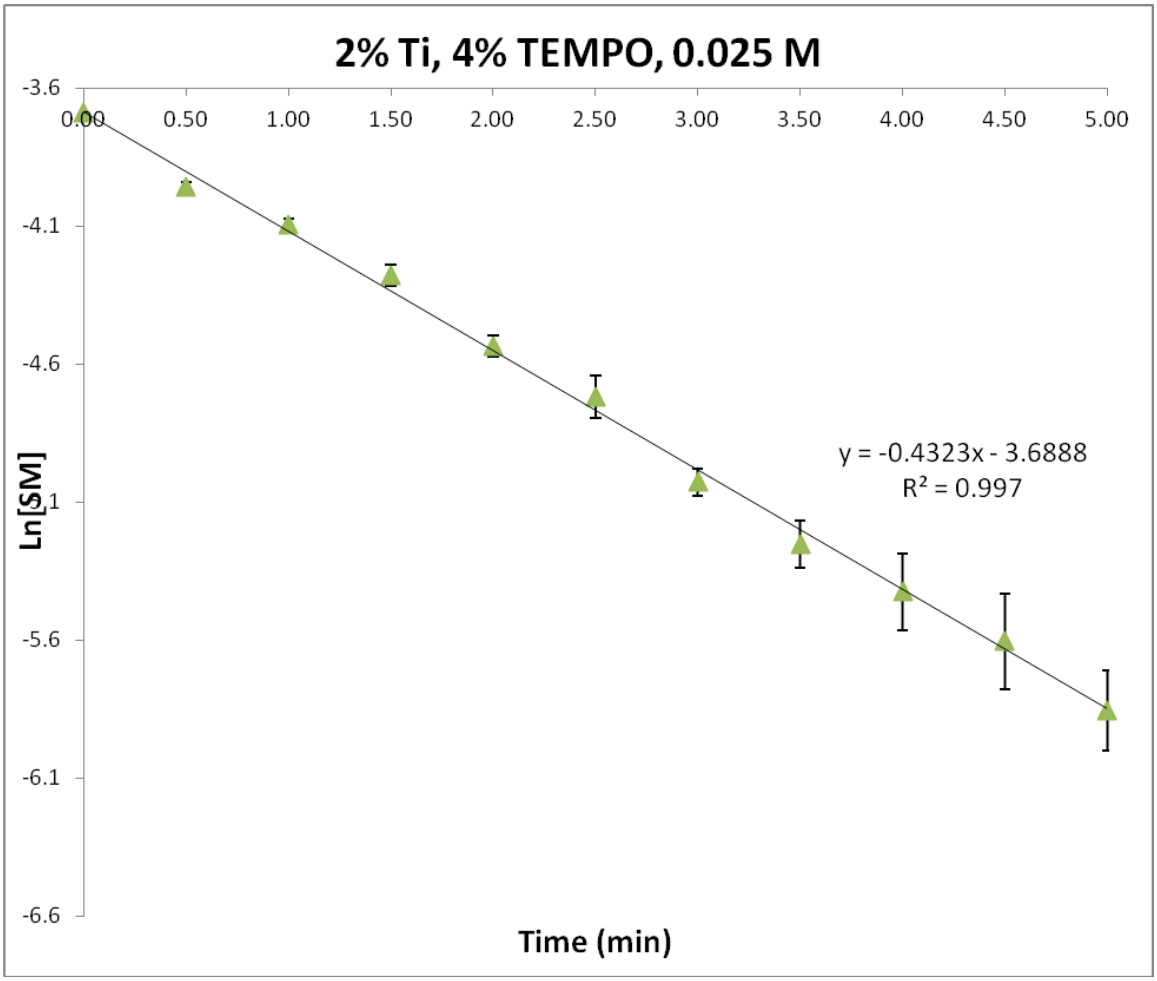


Figure S17 Graph of Ln[SM] vs time for average of 3 kinetic runs with 2 mol% Cp*2TiCl, 4 mol% TEMPO, 0.025 M substrate **1** in MeCN. Error bars calculated using standard error of the mean (standard deviation / sqrt(n))

Time (min)	Area Ph2O	Area SUB	% Conversion	Asub/AIS	%SM	Ln[SM]	[SM]
0.00	4019	4800	0.5	1.19432695	100	-3.68887945	0.0250
0.50	5181	4900	21.2	0.94576337	78.81361	-3.92696389	0.0197
1.00	5751	4139	40.0	0.71970092	59.97508	-4.20012055	0.0150
1.50	5827	3589	48.7	0.61592586	51.32716	-4.35582969	0.0128
2.00	4726	1907	66.4	0.40351248	33.62604	-4.77874886	0.0084
2.50	6089	2300	68.5	0.37773033	31.47753	-4.84477575	0.0079
3.00	6210	1806	75.8	0.29082126	24.2351	-5.10624745	0.0061
3.50	6086	1300	82.2	0.213605	17.80042	-5.4148278	0.0045
4.00	5182	920	85.2	0.17753763	14.7948	-5.5997737	0.0037
4.50	6688	1095	86.4	0.16372608	13.64384	-5.68076152	0.0034
5.00	6208	796	89.3	0.12822165	10.68514	-5.92519589	0.0027
6.00	5965	1028	85.6	0.17233864	14.36155	-5.6294949	0.0036
7.00	6483	853	89.0	0.13157489	10.96457	-5.89938011	0.0027
8.00	6512	808	89.7	0.12407862	10.33989	-5.95804086	0.0026
9.00	7167	816	90.5	0.11385517	9.487931	-6.04402909	0.0024
10.00	5975	543	92.4	0.09087866	7.573222	-6.26943107	0.0019

Table S22 2 mol% Cp*2TiCl, 5 mol% TEMPO 0.025 M Substrate **1** in MeCN – Run 1

Time (min)	Area Ph2O	Area SUB	% Conversion	Asub/AIS	%SM	Ln[SM]	[SM]
0.00	5682	6100	2.4	1.07356565	100	-3.688879	0.0250
0.50	5694	4102	20.0	0.72040745	80.04527	-3.911457	0.0200
1.00	5266	2725	42.5	0.51747057	57.49673	-4.242322	0.0144
1.50	5756	2563	50.5	0.4452745	49.47494	-4.392583	0.0124
2.00	6699	2200	63.5	0.32840722	36.48969	-4.69702	0.0091
2.50	4805	1396	67.7	0.2905307	32.28119	-4.819565	0.0081
3.00	6948	1500	76.0	0.21588946	23.98772	-5.116508	0.0060
3.50	5919	903	83.0	0.15255955	16.95106	-5.463719	0.0042
4.00	7605	1000	85.4	0.13149244	14.61027	-5.612325	0.0037
4.50	6881	900	88.1	0.13079494	11.89045	-5.818314	0.0030
5.00	6962	800	89.6	0.11490951	10.44632	-5.9478	0.0026
6.00	6394	600	91.5	0.09383797	8.530725	-6.150375	0.0021
7.00	6426	500	92.9	0.0778089	7.073536	-6.337689	0.0018
8.00	6576	557	92.3	0.08470195	7.700177	-6.252806	0.0019
9.00	6558	480	93.3	0.07319305	6.653913	-6.398844	0.0017
10.00	2825	221	92.9	0.07823009	7.111826	-6.332291	0.0018

Table S23 2 mol% Cp*2TiCl, 5 mol% TEMPO 0.025 M Substrate **1** in MeCN – Run 2

Time (min)	Area Ph2O	Area SUB	% Conversion	Asub/AIS	%SM	Ln[SM]	[SM]
0.00	5011	6284	3.5	1.25404111	100	-3.688879	0.0250
0.50	6562	6533	23.4	0.99558062	76.58312	-3.955673	0.0191
1.00	6547	4820	43.4	0.73621506	56.63193	-4.257477	0.0142
1.50	6282	4135	49.4	0.65822986	50.63307	-4.369445	0.0127
2.00	7157	3720	60.0	0.51977085	39.98237	-4.605611	0.0100
2.50	5551	2669	63.0	0.48081427	36.98571	-4.683518	0.0092
3.00	5955	1500	80.6	0.25188917	19.37609	-5.33001	0.0048
3.50	6481	1508	82.1	0.23268014	17.89847	-5.409334	0.0045
4.00	6930	1100	87.8	0.15873016	12.21001	-5.791793	0.0031
4.50	6708	900	89.7	0.13416816	10.32063	-5.959905	0.0026
5.00	5631	960	89.3	0.17048482	10.6553	-5.927992	0.0027
6.00	6844	1299	88.1	0.18980129	11.86258	-5.820661	0.0030
7.00	6208	990	90.0	0.15947165	9.966978	-5.994772	0.0025
8.00	6043	876	90.9	0.14496111	9.06007	-6.090173	0.0023
9.00	6480	860	91.7	0.13271605	8.294753	-6.178426	0.0021
10.00	6557	700	93.3	0.10675614	6.672259	-6.396091	0.0017

Table S24 2 mol% Cp*2TiCl, 5 mol% TEMPO 0.025 M Substrate **1** in MeCN – Run 3

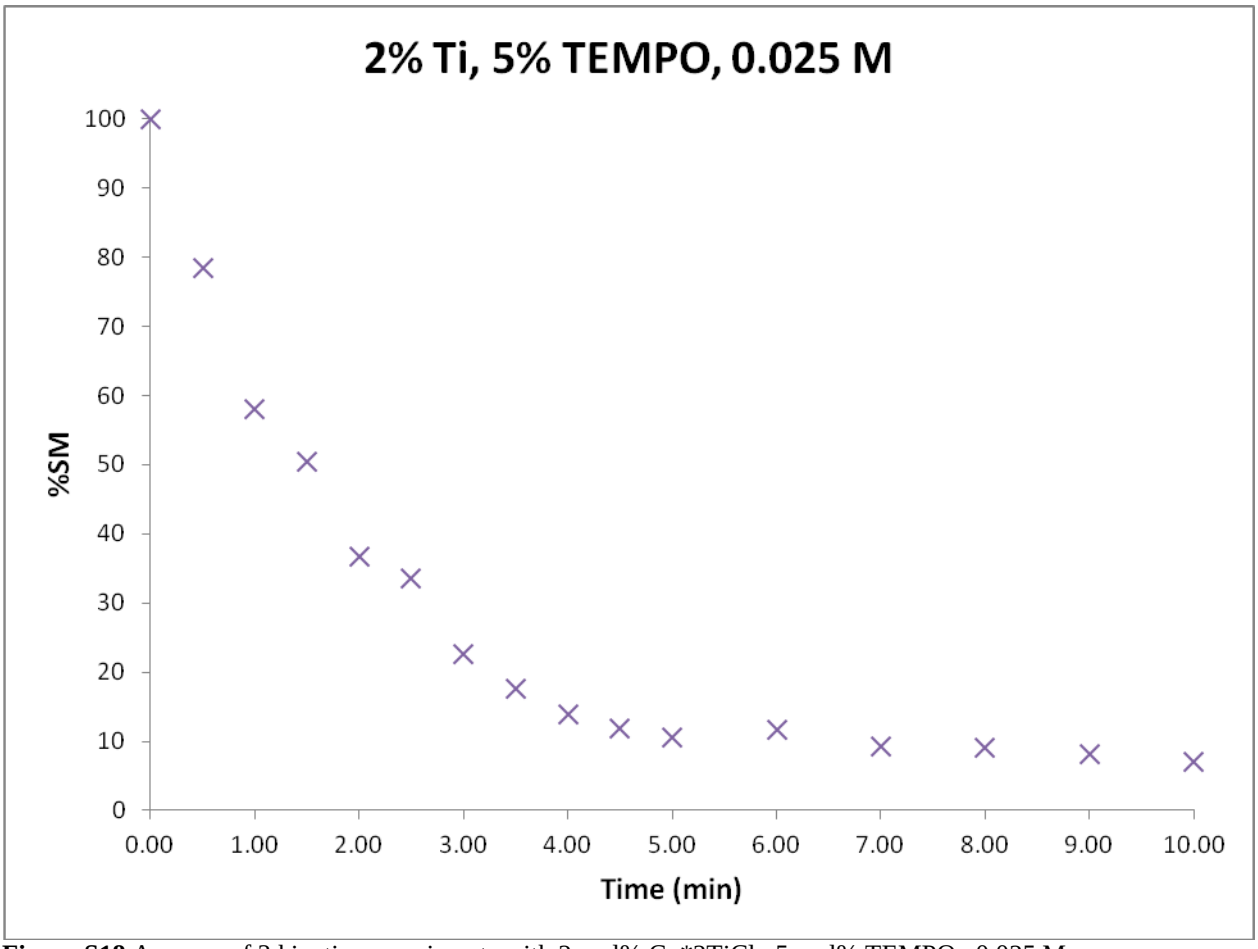


Figure S18 Average of 3 kinetics experiments with 2 mol% Cp*2TiCl, 5 mol% TEMPO, 0.025 M substrate **1** in MeCN

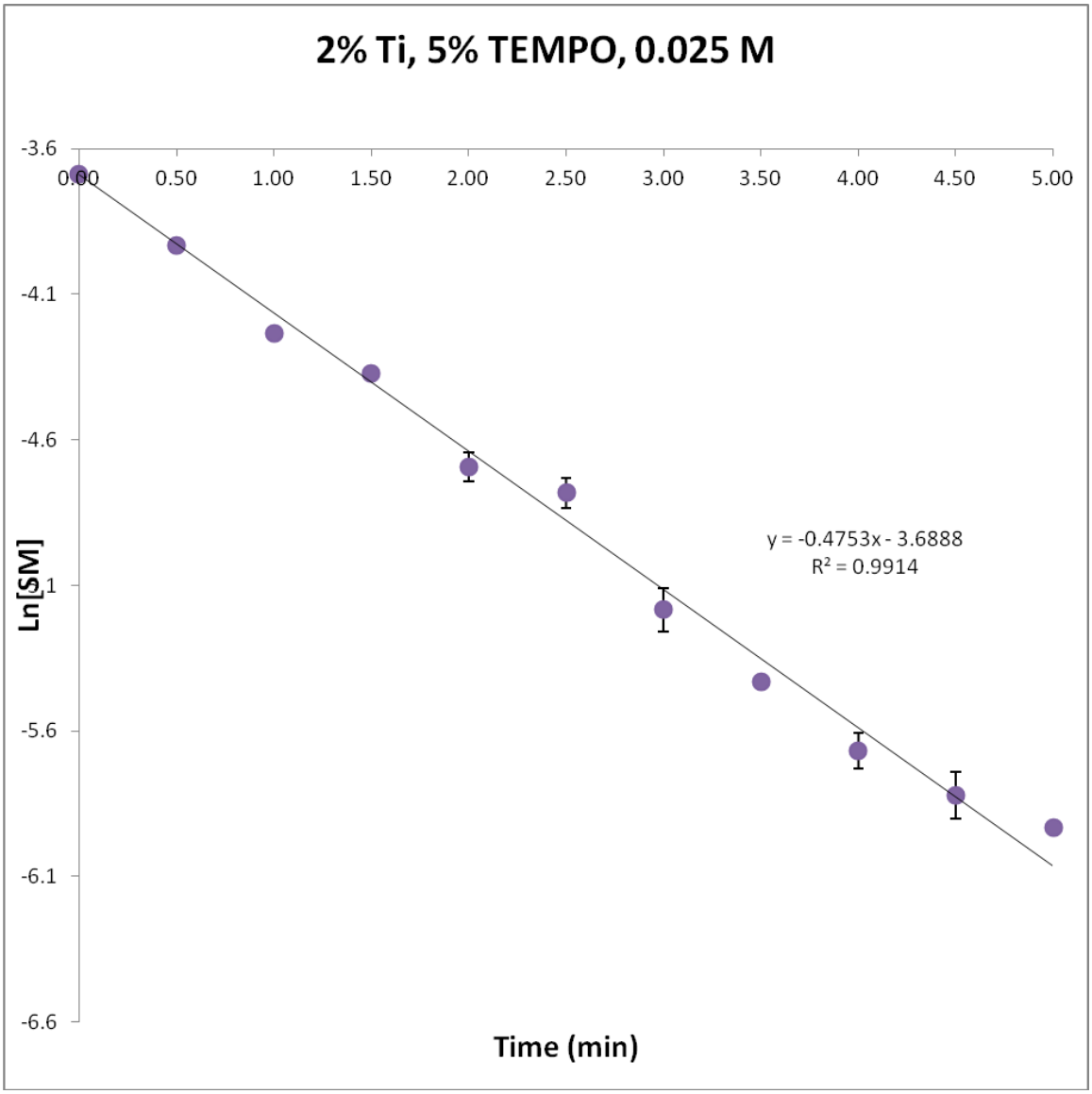


Figure S19 Graph of Ln[SM] vs time for average of 3 kinetic runs with 2 mol% Cp*2TiCl, 5 mol% TEMPO, 0.025 M substrate **1** in MeCN. Error bars calculated using standard error of the mean (standard deviation / sqrt(n))

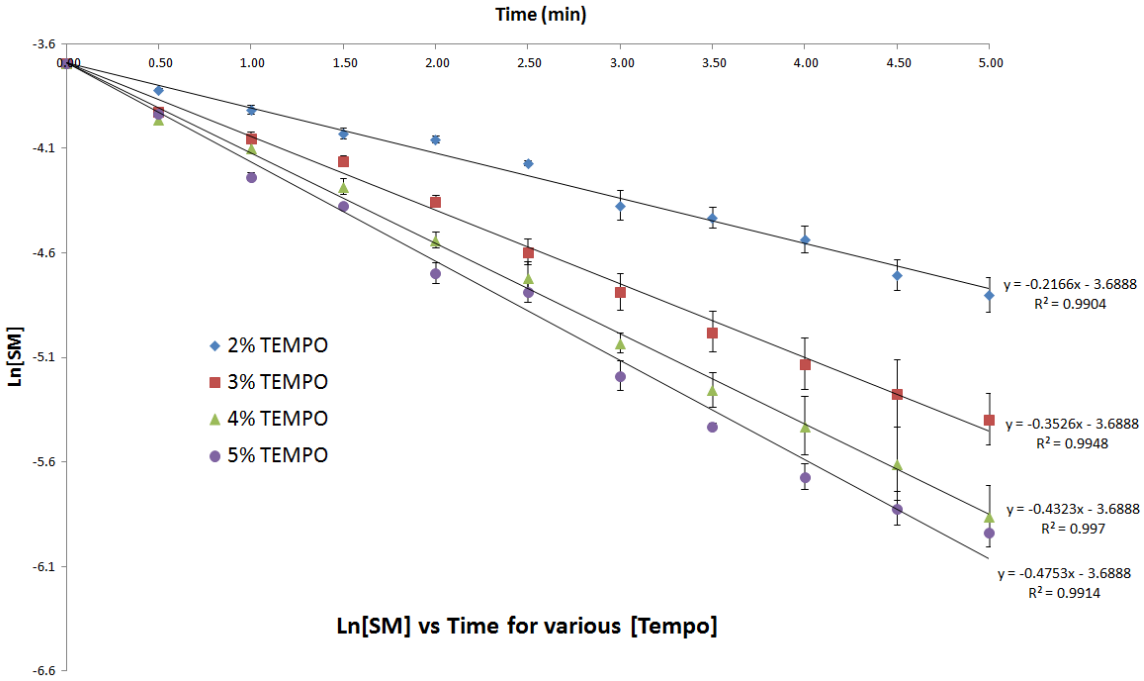


Figure S20 Overlay of Ln[SM] vs time for various [TEMPO], 2 mol% Cp*2TiCl, 0.025 M substrate **1** in MeCN at 23 °C. Each experiment was run in triplicate, data shown is the mean of the 3 values. Error bars were calculated by the standard error (standard deviation/square root(n))

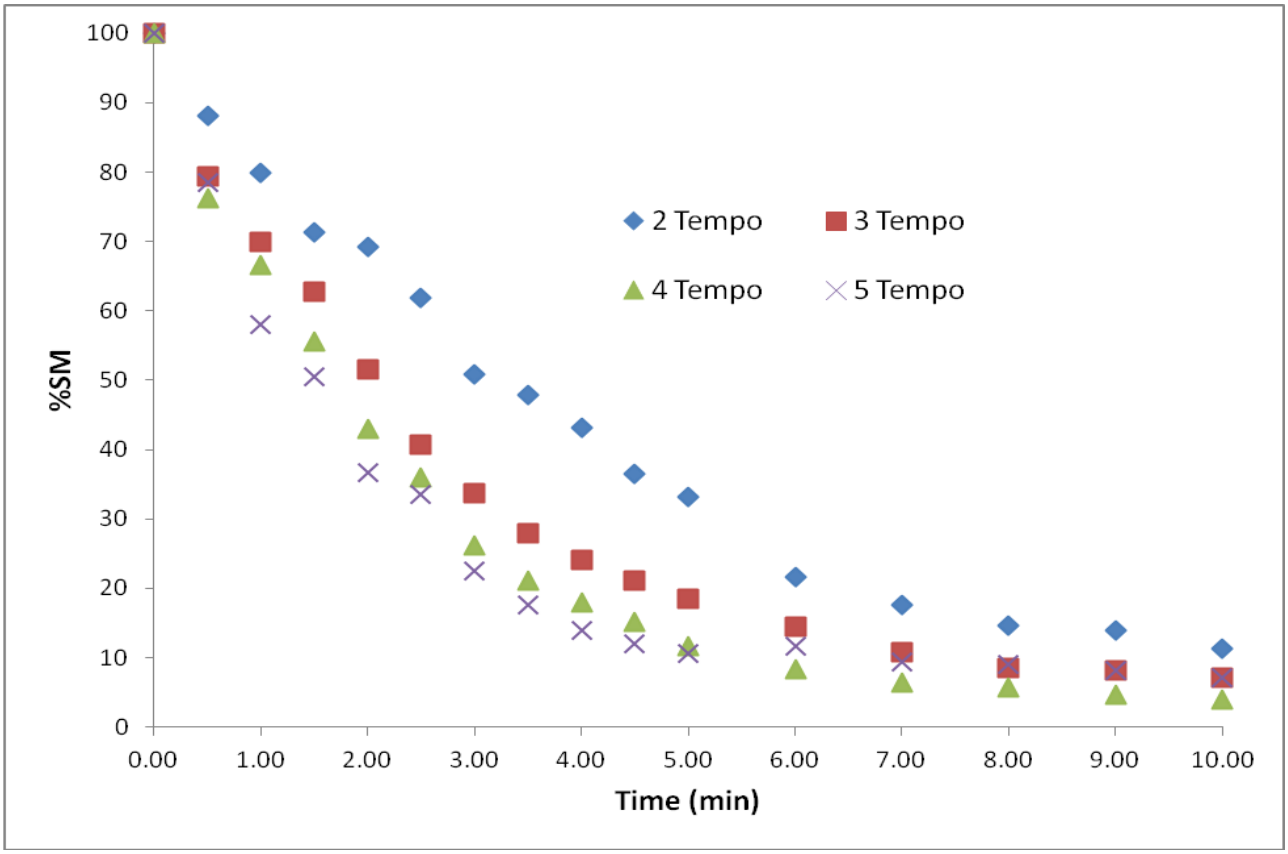


Figure S21 Overlay of average of 3 runs of %SM vs time for various [TEMPO] (from 5 mol% to 2 mol%), 2 mol% Cp*2TiCl, 0.025 M substrate **1** in MeCN at 23 °C.

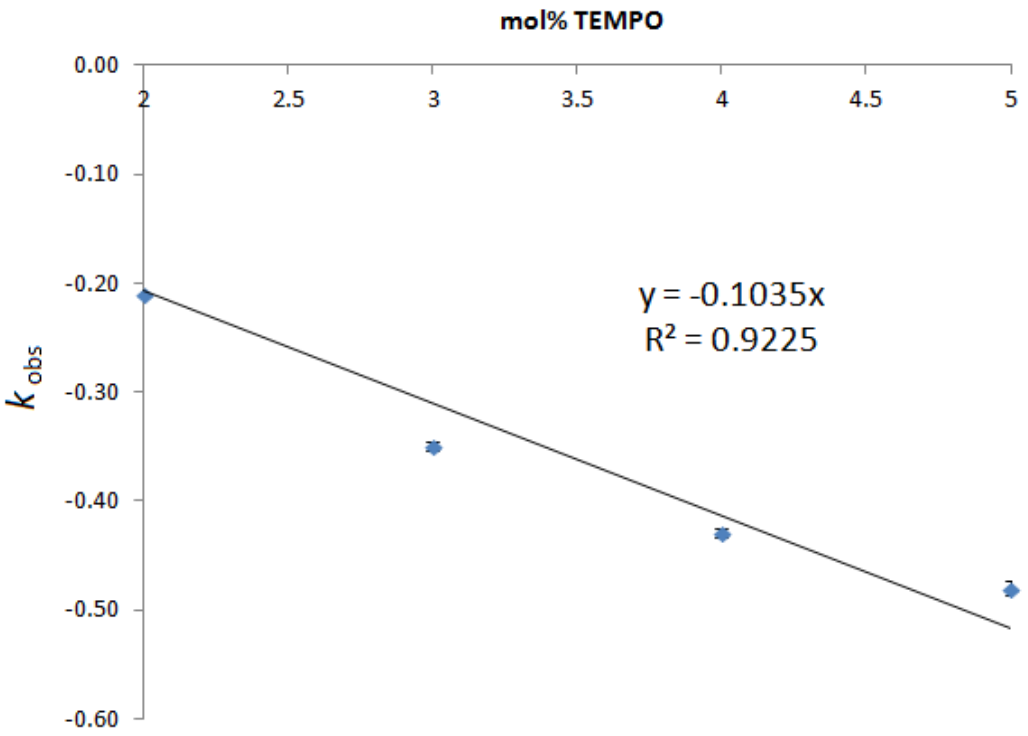


Figure S22 Plot of k_{obs} vs [TEMPO]. Experiments all run with 2 mol% Cp*2TiCl, 0.025 M substrate **1** in MeCN at 23 °C. k_{obs} was calculated from the slope of Ln[SM] vs time plots. Each data point is the average of 3 experiments.

Time (min)	Area Ph2O	Area SUB	% Conversion	Asub/AIS	%SM	Ln[SM]	[SM]
0.00	5816	6841	2.0	0.879470426	100	-3.283414	0.0375
0.50	6374	6210	18.8	0.974270474	81.18920615	-3.491802	0.0304
1.00	7351	6012	31.8	0.817847912	68.15399265	-3.666815	0.0256
1.50	6091	4307	41.1	0.707108849	58.92573743	-3.812307	0.0221
2.00	6184	4014	45.9	0.649094437	54.0912031	-3.897913	0.0203
2.50	6657	3585	55.1	0.53853087	44.87757248	-4.084646	0.0168
3.00	6452	2843	63.3	0.440638562	36.71988014	-4.285266	0.0138
3.50	7083	3006	64.6	0.424396442	35.36637018	-4.322823	0.0133
4.00	5310	1639	74.3	0.3086629	25.72190835	-4.641241	0.0096
4.50	5562	1545	76.9	0.277777778	23.14814815	-4.74667	0.0087
5.00	7144	1801	79.0	0.252099664	21.00830534	-4.843667	0.0079
6.00	7699	1600	82.7	0.207819197	17.31826644	-5.036823	0.0065
7.00	7814	1300	86.1	0.166368057	13.86400478	-5.259289	0.0052
8.00	7522	1180	86.9	0.156873172	13.07276434	-5.318054	0.0049
9.00	7645	1000	89.1	0.130804447	10.90037061	-5.499788	0.0041
10.00	6577	800	89.9	0.121636004	10.13633369	-5.572458	0.0038

Table S25 5 mol% Cp*2TiCl, 2 mol% TEMPO, 0.0375 M substrate **1** – Run 1

Time (min)	Area Ph2O	Area SUB	% Conversion	Asub/AIS	%SM	Ln[SM]	[SM]
0.00	4995	6113	5.9	0.793193193	100	-3.283414	0.0375
0.50	5964	6100	21.3	1.022803488	78.67719135	-3.523231	0.0295
1.00	5411	4541	35.4	0.839216411	64.55510854	-3.721065	0.0242
1.50	4606	3203	46.5	0.695397308	53.4921006	-3.909051	0.0201
2.00	6266	4369	46.4	0.697255027	53.63500209	-3.906383	0.0201
2.50	6853	4560	48.8	0.665402014	51.18477029	-3.953142	0.0192
3.00	6963	3946	56.4	0.566709752	43.59305781	-4.113687	0.0163
3.50	7092	4112	55.4	0.579808235	44.60063343	-4.090836	0.0167
4.00	6013	3006	61.5	0.499916847	38.45514206	-4.239092	0.0144
4.50	6918	2900	67.8	0.4191963	32.24586919	-4.415195	0.0121
5.00	7144	2800	69.9	0.39193729	30.14902231	-4.482432	0.0113
6.00	7699	2500	75.0	0.324717496	24.97826891	-4.670578	0.0094
7.00	7814	2200	78.3	0.281545943	21.65738024	-4.813238	0.0081
8.00	7522	1800	81.6	0.239298059	18.407543	-4.975824	0.0069
9.00	7645	1500	84.9	0.196206671	15.09282085	-5.174365	0.0057
10.00	6577	1000	88.3	0.152045005	11.69576964	-5.429357	0.0044

Table S26 5 mol% Cp*2TiCl, 2 mol% TEMPO, 0.0375 M substrate **1** – Run 2

Time (min)	Area Ph2O	Area SUB	% Conversion	Asub/AIS	%SM	Ln[SM]	[SM]
0.00	6684	7461	7.0	1.041741472	100	-3.283414	0.0375
0.50	5140	4800	22.2	0.93385214	77.82101	-3.534173	0.0292
1.00	7296	5873	32.9	0.804961623	67.08014	-3.682697	0.0252
1.50	6855	5132	37.6	0.74865062	62.38755	-3.755219	0.0234
2.00	6355	4209	44.8	0.662313139	55.19276	-3.877753	0.0207
2.50	6042	3099	57.3	0.512909633	42.74247	-4.133392	0.0160
3.00	6954	3371	59.6	0.484756974	40.39641	-4.189844	0.0151
3.50	6705	2497	69.0	0.37240865	31.03405	-4.453499	0.0116
4.00	7661	2361	74.3	0.30818431	25.68203	-4.642793	0.0096
4.50	9191	2895	73.8	0.314982048	26.2485	-4.620976	0.0098
5.00	6451	1431	81.5	0.221826073	18.48551	-4.971598	0.0069
6.00	6399	1027	86.6	0.160493827	13.37449	-5.295236	0.0050
7.00	6511	901	88.5	0.138381201	11.53177	-5.443479	0.0043
8.00	6704	763	90.5	0.113812649	9.484387	-5.638938	0.0036
9.00	7188	669	92.2	0.093071786	7.755982	-5.84012	0.0029
10.00	6830	639	92.2	0.093557833	7.796486	-5.834911	0.0029

Table S27 5 mol% Cp*2TiCl, 2 mol% TEMPO, 0.0375 M substrate **1** – Run 3

Time (min)	Area Ph2O	Area SUB	% Conversion	Asub/AIS	%SM	Ln[SM]	[SM]
0.00	5157	3713	2.7	0.719992244	100	-3.688879	0.0250
0.50	6535	3900	19.4	0.596786534	80.64682893	-3.90397	0.0202
1.00	6694	3300	33.4	0.492978787	66.618755	-4.095063	0.0167
1.50	7144	3191	39.6	0.446668533	60.36061257	-4.193713	0.0151
2.00	6835	2583	48.9	0.377907827	51.06862532	-4.360879	0.0128
2.50	7476	2683	51.5	0.358881755	48.49753445	-4.412537	0.0121
3.00	7922	2429	58.6	0.306614491	41.43439071	-4.569938	0.0104
3.50	6982	1874	63.7	0.268404469	36.27087414	-4.703035	0.0091
4.00	6229	1445	68.7	0.231979451	31.34857445	-4.848881	0.0078
4.50	6858	1533	69.8	0.223534558	30.20737273	-4.885964	0.0076
5.00	7203	1352	74.6	0.18769957	25.36480671	-5.060687	0.0063
6.00	6642	972	80.2	0.146341463	19.77587343	-5.309587	0.0049
7.00	7180	900	83.1	0.125348189	16.93894452	-5.464434	0.0042
8.00	7589	943	83.2	0.124258796	16.79172914	-5.473163	0.0042
9.00	7279	799	85.2	0.109767825	14.8334899	-5.597162	0.0037
10.00	6088	551	87.8	0.090505913	12.23052882	-5.790114	0.0031

Table S28 5 mol% Cp*2TiCl, 2 mol% TEMPO, 0.025 M substrate **1** – Run 1

Time (min)	Area Ph2O	Area SUB	% Conversion	Asub/AIS	%SM	Ln[SM]	[SM]
0.00	5561	3910	5.0	0.703110951	100	-3.688879	0.0250
0.50	5887	3400	22.0	0.57754374	78.04645141	-3.936745	0.0195
1.00	6846	3578	29.4	0.522640958	70.62715652	-4.036635	0.0177
1.50	7011	3100	40.2	0.442162316	59.75166437	-4.203853	0.0149
2.00	5597	2213	46.6	0.395390388	53.43113347	-4.315656	0.0134
2.50	6165	2070	54.6	0.335766423	45.37384099	-4.479114	0.0113
3.00	8280	2400	60.8	0.289855072	39.16960439	-4.626149	0.0098
3.50	5953	1577	64.2	0.26490845	35.79843912	-4.716145	0.0089
4.00	6007	1329	70.1	0.221241884	29.89755196	-4.896273	0.0075
4.50	6920	1270	75.2	0.183526012	24.80081237	-5.083173	0.0062
5.00	7567	1200	78.6	0.158583322	21.43017869	-5.229249	0.0054
6.00	7213	1000	81.3	0.138638569	18.73494179	-5.363659	0.0047
7.00	6854	800	84.2	0.116720163	15.77299506	-5.53575	0.0039
8.00	6594	700	85.7	0.106157113	14.34555575	-5.630609	0.0036
9.00	7727	650	88.6	0.084120616	11.36765081	-5.863278	0.0028
10.00	6655	600	87.8	0.090157776	12.18348326	-5.793968	0.0030

Table S29 5 mol% Cp*2TiCl, 2 mol% TEMPO, 0.025 M substrate **1** – Run 2

Time (min)	Area Ph2O	Area SUB	% Conversion	Asub/AIS	%SM	Ln[SM]	[SM]
0.00	6132	4152	8.5	0.677103718	100	-3.688879	0.0250
0.50	6411	3800	19.9	0.592731243	80.09882	-3.910789	0.0200
1.00	6896	3606	29.3	0.522911833	70.66376	-4.036117	0.0177
1.50	5593	2410	41.8	0.430895763	58.22916	-4.229663	0.0146
2.00	6212	2148	53.3	0.345782357	46.72735	-4.44972	0.0117
2.50	5802	1680	60.9	0.289555326	39.1291	-4.627183	0.0098
3.00	6318	1565	66.5	0.24770497	33.47364	-4.783291	0.0084
3.50	6041	1439	67.8	0.238205595	32.18995	-4.822395	0.0080
4.00	5456	1134	71.9	0.207844575	28.0871	-4.958739	0.0070
4.50	6749	1250	75.0	0.185212624	25.02873	-5.074025	0.0063
5.00	6904	1180	76.9	0.170915411	23.09668	-5.154361	0.0058
6.00	6074	890	80.2	0.146526177	19.80083	-5.308326	0.0050
7.00	7181	890	83.3	0.12393817	16.7484	-5.475747	0.0042
8.00	6843	764	84.9	0.111646938	15.08742	-5.580188	0.0038
9.00	6153	599	86.8	0.097350886	13.15553	-5.717208	0.0033
10.00	6215	508	89.0	0.081737731	11.04564	-5.892014	0.0028

Table S30 5 mol% Cp*2TiCl, 2 mol% TEMPO, 0.025 M substrate **1** – Run 3

Time (min)	Area Ph2O	Area SUB	% Conversion	Asub/AIS	%SM	Ln[SM]	[SM]
0.00	4679	3516	-1.5	0.751442616	100	-3.976562	0.0188
0.50	4093	2700	10.9	0.659662839	89.14362689	-4.091483	0.0167
1.00	4586	2649	21.9	0.577627562	78.05777867	-4.224282	0.0146
1.50	5442	2679	33.5	0.492282249	66.52462827	-4.384159	0.0125
2.00	5269	2195	43.7	0.416587588	56.29561997	-4.551115	0.0106
2.50	5679	1890	55.0	0.332805071	44.97365829	-4.775655	0.0084
3.00	5775	1428	66.6	0.247272727	33.41523342	-5.07272	0.0063
3.50	5527	1250	69.4	0.226162475	30.56249664	-5.161958	0.0057
4.00	5166	885	76.8	0.171312427	23.15032803	-5.439723	0.0043
4.50	5196	729	81.0	0.140300231	18.95949067	-5.639427	0.0036
5.00	6037	756	83.1	0.125227762	16.92267056	-5.753078	0.0032
6.00	6687	657	86.7	0.098250336	13.2770725	-5.995693	0.0025
7.00	6914	475	90.7	0.068701186	9.283944054	-6.353445	0.0017
8.00	6122	356	92.1	0.058150931	7.858233928	-6.52017	0.0015
9.00	6818	352	93.0	0.051628043	6.976762624	-6.639147	0.0013
10.00	6343	305	93.5	0.048084503	6.497905757	-6.710252	0.0012

Table S31 5 mol% Cp*2TiCl, 2 mol% TEMPO, 0.01875 M substrate **1** – Run 1

Time (min)	Area Ph2O	Area SUB	% Conversion	Asub/AIS	%SM	Ln[SM]	[SM]
0.00	3966	2795	-3.6	0.704740292	100	-3.976562	0.0188
0.50	5470	2988	19.7	0.546252285	80.33121841	-4.195573	0.0151
1.00	5794	2821	28.4	0.486882982	71.60043859	-4.310631	0.0134
1.50	5400	2260	38.5	0.418518519	61.54684096	-4.461933	0.0115
2.00	5757	2101	46.3	0.364947021	53.66867956	-4.598902	0.0101
2.50	4944	1380	59.0	0.279126214	41.04797259	-4.86699	0.0077
3.00	5036	1040	69.6	0.206513106	30.36957436	-5.16829	0.0057
3.50	5860	1266	68.2	0.216040956	31.77072877	-5.123186	0.0060
4.00	5244	894	74.9	0.170480549	25.070669	-5.360033	0.0047
4.50	4742	705	78.1	0.148671447	21.86344804	-5.496916	0.0041
5.00	5302	680	81.1	0.128253489	18.86080724	-5.644646	0.0035
6.00	4771	406	87.5	0.085097464	12.51433292	-6.054857	0.0023
7.00	4773	314	90.3	0.065786717	9.674517198	-6.312236	0.0018
8.00	6276	470	89.0	0.074888464	11.01300941	-6.182654	0.0021
9.00	7020	528	88.9	0.075213675	11.06083459	-6.178321	0.0021
10.00	5960	364	91.0	0.061073826	8.981444927	-6.386571	0.0017

Table S32 5 mol% Cp*2TiCl, 2 mol% TEMPO, 0.01875 M substrate **1** – Run 2

Time (min)	Area Ph2O	Area SUB	% Conversion	Asub/AIS	%SM	Ln[SM]	[SM]
0.00	2893	2091	2.3	0.722779122	100	-3.976562	0.0188
0.50	5510	3506	14.0	0.636297641	85.98617	-4.127545	0.0161
1.00	5965	3220	27.1	0.539815591	72.94805	-4.291984	0.0137
1.50	5460	2432	39.8	0.445421245	60.19206	-4.484191	0.0113
2.00	5616	2025	51.3	0.360576923	48.72661	-4.695506	0.0091
2.50	6711	2412	51.4	0.359409924	48.56891	-4.698748	0.0091
3.00	5335	1365	65.4	0.255857545	34.57534	-5.038591	0.0065
3.50	6408	1647	65.3	0.257022472	34.73277	-5.034048	0.0065
4.00	5748	1083	74.5	0.188413361	25.46127	-5.344573	0.0048
4.50	5750	973	77.1	0.169217391	22.86722	-5.452027	0.0043
5.00	5086	752	80.0	0.147856862	19.98066	-5.586967	0.0037
6.00	5377	636	84.0	0.11828157	15.984	-5.810144	0.0030
7.00	4429	438	86.6	0.098893655	13.36401	-5.989167	0.0025
8.00	5823	546	87.3	0.0937661	12.67109	-6.042408	0.0024
9.00	5175	362	90.5	0.069951691	9.452931	-6.335407	0.0018
10.00	5072	397	89.4	0.078272871	10.57741	-6.223011	0.0020

Table S33 5 mol% Cp*2TiCl, 2 mol% TEMPO, 0.01875 M substrate **1** – Run 3

Sample	Area Ph2O	Area SUB	% Conversion	Asub/AIS	%SM	Ln[SM]	[SM]
0.00	3688	2219	-0.3	0.601681128	100	-4.382027	0.0125
0.50	3413	1758	26.4	0.515089364	73.58419	-4.688767	0.0092
1.00	4710	2268	31.2	0.481528662	68.78981	-4.756141	0.0086
1.50	4669	2088	36.1	0.447204969	63.88642	-4.83009	0.0080
2.00	4306	1530	49.2	0.355318161	50.75974	-5.060093	0.0063
2.50	4143	1171	59.6	0.282645426	40.37792	-5.288914	0.0050
3.00	5624	1214	69.2	0.215860597	30.83723	-5.558474	0.0039
3.50	3937	690	75.0	0.175260351	25.03719	-5.766834	0.0031
4.00	4842	832	75.5	0.171829822	24.54712	-5.786602	0.0031
4.50	4418	631	79.6	0.142824808	20.40354	-5.971488	0.0026
5.00	5152	530	85.3	0.102872671	14.6961	-6.299615	0.0018
6.00	4018	290	89.7	0.072175212	10.31074	-6.65401	0.0013
7.00	4780	251	92.5	0.05251046	7.501494	-6.972095	0.0009
8.00	4752	263	92.1	0.055345118	7.906445	-6.919519	0.0010
9.00	4523	250	92.1	0.055273049	7.89615	-6.920822	0.0010
10.00	4095	147	94.9	0.035897436	5.128205	-7.352441	0.0006

Table S34 5 mol% Cp*2TiCl, 2 mol% TEMPO, 0.0125 M substrate **1** – Run 1

Sample	Area Ph2O	Area SUB	% Conversion	Asub/AIS	%SM	Ln[SM]	[SM]
0.00	3410	2199	5.2	0.644868035	100	-4.382027	0.0125
0.50	3617	2000	18.7	0.552944429	81.31536	-4.588862	0.0102
1.00	4611	2100	33.0	0.455432661	66.97539	-4.782872	0.0084
1.50	3857	1592	39.3	0.412756028	60.69942	-4.881263	0.0076
2.00	4052	1221	55.7	0.301332675	44.31363	-5.195905	0.0055
2.50	3907	1027	61.3	0.262861531	38.65611	-5.332492	0.0048
3.00	3456	764	67.5	0.221064815	32.50953	-5.505663	0.0041
3.50	4252	752	74.0	0.176857949	26.00852	-5.728773	0.0033
4.00	5139	862	75.3	0.167736914	24.66719	-5.781723	0.0031
4.50	2899	400	79.7	0.137978613	20.29097	-5.977021	0.0025
5.00	4529	611	80.2	0.134908368	19.83947	-5.999524	0.0025
6.00	4730	499	84.5	0.105496829	15.51424	-6.245439	0.0019
7.00	4801	444	86.4	0.092480733	13.60011	-6.377119	0.0017
8.00	4942	382	88.6	0.077296641	11.36715	-6.556469	0.0014
9.00	4849	287	91.3	0.059187461	8.704038	-6.82341	0.0011
10.00	4721	275	91.4	0.058250371	8.566231	-6.839369	0.0011

Table S35 5 mol% Cp*2TiCl, 2 mol% TEMPO, 0.0125 M substrate **1** – Run 2

Sample	Area Ph2O	Area SUB	% Conversion	Asub/AIS	%SM	Ln[SM]	[SM]
0.00	2652	3094	2.8	1.16666667	100	-4.382027	0.0125
0.50	3221	2942	23.9	0.91338094	76.11508	-4.65495	0.0095
1.00	3333	2857	28.6	0.85718572	71.43214	-4.718449	0.0089
1.50	2380	1700	40.5	0.71428571	59.52381	-4.90082	0.0074
2.00	2566	1624	47.3	0.63289166	52.74097	-5.021804	0.0066
2.50	2798	1376	59.0	0.49177984	40.98165	-5.274072	0.0051
3.00	3312	1384	65.2	0.4178744	34.82287	-5.436923	0.0044
3.50	2848	1000	70.7	0.3511236	29.2603	-5.610965	0.0037
4.00	3152	989	73.9	0.31376904	26.14742	-5.723446	0.0033
4.50	2878	830	76.0	0.28839472	24.03289	-5.807773	0.0030
5.00	2686	785	75.6	0.29225614	24.35468	-5.794473	0.0030
6.00	2479	513	82.8	0.20693828	17.24486	-6.139683	0.0022
7.00	3247	749	80.8	0.23067447	19.22287	-6.031096	0.0024
8.00	2249	439	83.7	0.19519787	16.26649	-6.19809	0.0020
9.00	2864	687	80.0	0.2398743	19.98953	-5.991988	0.0025
10.00	2882	558	83.9	0.19361554	16.13463	-6.206229	0.0020

Table S36 5 mol% Cp*2TiCl, 2 mol% TEMPO, 0.0125 M substrate **1** – Run 3

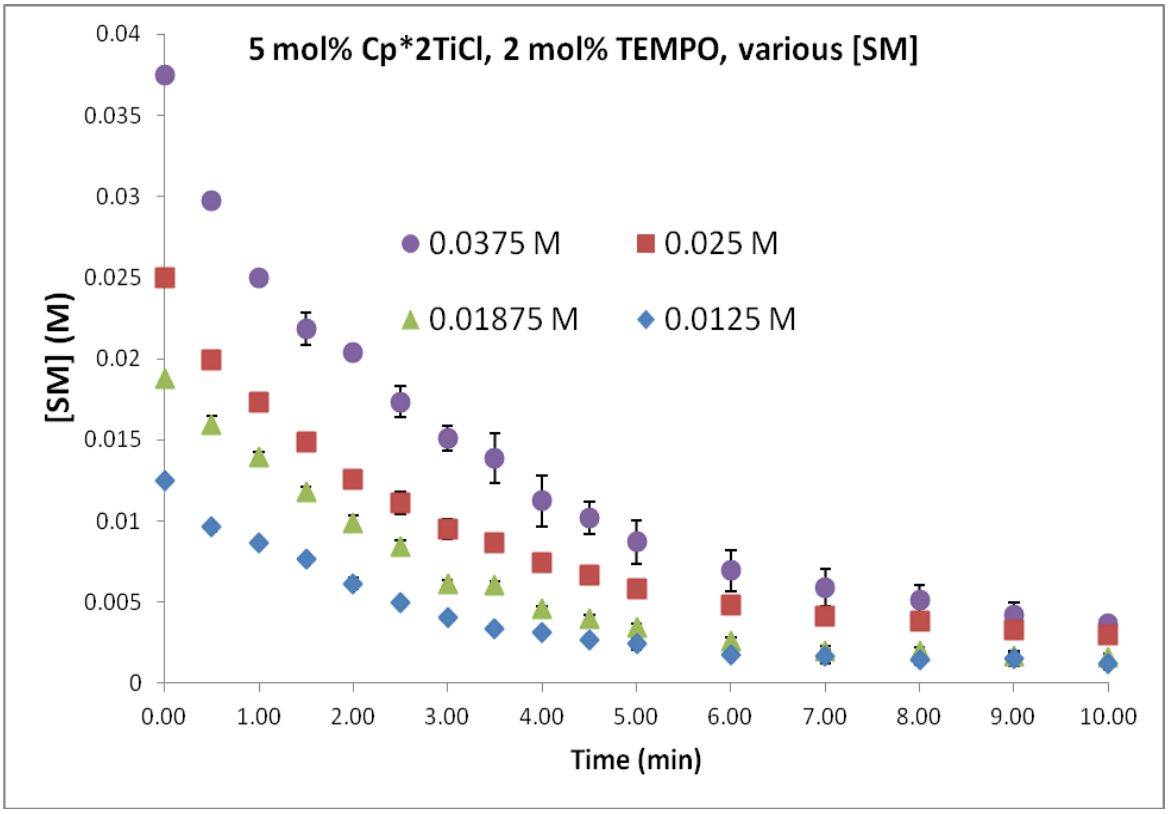


Figure S23 Each data set is an average of 3 kinetic runs with 5 mol% Cp*2TiCl, 2 mol% TEMPO, various starting concentration of substrate **1**. Error bars were calculated by the standard error of the means. (stdev / sqrt (n))

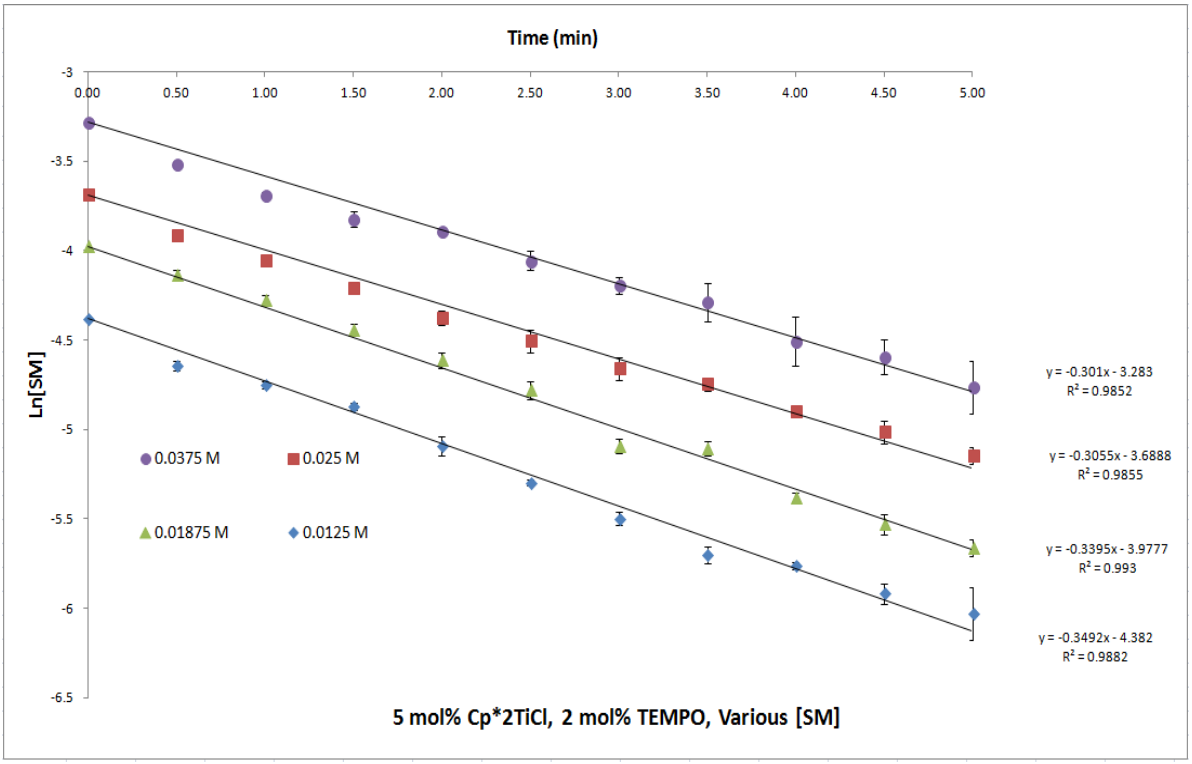


Figure S24 Each data set is an average of 3 kinetic runs using 5 mol% Cp*2TiCl, 2 mol% TEMPO, various starting concentration of substrate **1**. Error bars were calculated by the standard error of the means. (stdev / sqrt (n))

Time (min)	Area Ph2O	Area SUB	% Conversion	Asub/AIS	%SM	Ln[SM]	[SM]
0.00	5234	3241	0.0	0.619220481	100	-3.6888	0.0250
0.50	5747	3314	7.0	0.576648686	93.00785	-3.761366	0.0233
1.00	4581	2424	14.7	0.529142109	85.3455	-3.847342	0.0213
1.50	6038	3583	4.3	0.593408413	95.71103	-3.732716	0.0239
2.00	5629	3061	12.3	0.543791082	87.70824	-3.820034	0.0219
2.50	5791	3041	15.3	0.525125194	84.69761	-3.854962	0.0212
3.00	4463	2220	19.8	0.497423258	80.22956	-3.909158	0.0201
3.50	5834	3199	11.6	0.548337333	88.44151	-3.811708	0.0221
4.00	5308	3103	5.7	0.584589299	94.2886	-3.747689	0.0236
4.50	6086	3461	8.3	0.568682221	91.72294	-3.775277	0.0229
5.00	5268	2900	11.2	0.550493546	88.78928	-3.807784	0.0222
6.00	5374	2877	13.7	0.535355415	86.34765	-3.835668	0.0216
7.00	5192	2520	21.7	0.485362096	78.28421	-3.933704	0.0196
8.00	5445	2589	23.3	0.475482094	76.69066	-3.95427	0.0192
9.00	5925	2922	20.5	0.493164557	79.54267	-3.917756	0.0199
10.00	4504	2080	25.5	0.461811723	74.48576	-3.983442	0.0186
15.00	5134	2160	32.1	0.420724581	67.8588	-4.076621	0.0170

Table S37 5 mol% Cp*2TiCl, 2 mol% TEMPO, 0.025 M Deuterated **1** – Run 1

Time (min)	Area Ph2O	Area SUB	% Conversion	Asub/AIS	%SM	Ln[SM]	[SM]
0.00	5132	3810	0.0	0.742400624	100	-3.68888	0.0250
0.50	4769	3200	9.3	0.67100021	90.6757	-3.78676	0.0227
1.00	5468	3558	12.1	0.650694952	87.93175	-3.817489	0.0220
1.50	6339	4453	5.1	0.702476731	94.92929	-3.740917	0.0237
2.00	5900	3728	14.6	0.631864407	85.38708	-3.846855	0.0213
2.50	5946	4016	8.7	0.675412042	91.2719	-3.780207	0.0228
3.00	6134	3935	13.3	0.641506358	86.69005	-3.831711	0.0217
3.50	5026	2991	19.6	0.595105452	80.41966	-3.906791	0.0201
4.00	4597	2843	16.4	0.618446813	83.57389	-3.868318	0.0209
4.50	4738	2695	23.1	0.568805403	76.8656	-3.951991	0.0192
5.00	4545	2777	17.4	0.6110011	82.56772	-3.880431	0.0206
6.00	5101	2892	23.4	0.566947657	76.61455	-3.955263	0.0192
7.00	4689	2600	25.1	0.55448923	74.93098	-3.977482	0.0187
8.00	5391	2743	31.2	0.508810981	68.75824	-4.063453	0.0172
9.00	5597	2946	28.9	0.526353404	71.12884	-4.029557	0.0178
10.00	4730	2361	32.5	0.499154334	67.45329	-4.082614	0.0169
15.00	5877	2931	32.6	0.498723839	67.39511	-4.083477	0.0168

Table S38 5 mol% Cp*2TiCl, 2 mol% TEMPO, 0.025 M Deuterated – Run 2

Time (min)	Area Ph2O	Area SUB	% Conversion	Asub/AIS	%SM	Ln[SM]	[SM]
0.00	4891	3610	0.0	0.73809037	100	-3.6888	0.0250
0.50	5182	3725	2.9	0.71883443	97.13979	-3.717899	0.0243
1.00	5770	4206	1.5	0.72894281	98.50578	-3.703934	0.0246
1.50	5268	3393	13.0	0.64407745	87.03749	-3.827711	0.0218
2.00	5227	3449	10.8	0.65984312	89.16799	-3.803528	0.0223
2.50	4126	2588	15.2	0.62724188	84.76242	-3.854197	0.0212
3.00	6040	4072	8.9	0.67417219	91.10435	-3.782044	0.0228
3.50	4583	2892	14.7	0.63102771	85.27402	-3.84818	0.0213
4.00	5562	3520	14.5	0.63286588	85.52242	-3.845271	0.0214
4.50	5846	3535	18.3	0.60468697	81.71445	-3.890819	0.0204
5.00	4567	2804	17.0	0.61396978	82.96889	-3.875584	0.0207
6.00	5465	3530	12.7	0.64592864	87.28765	-3.824841	0.0218
7.00	5015	2969	20.0	0.59202393	80.00323	-3.911983	0.0200
8.00	5661	3444	17.8	0.60837308	82.21258	-3.884741	0.0206
9.00	4174	2351	23.9	0.56324868	76.11469	-3.961808	0.0190
10.00	5284	2987	23.6	0.56529145	76.39074	-3.958188	0.0191
15.00	5224	2830	26.8	0.54173047	73.20682	-4.000761	0.0183

Table S39 5% Ti, 2% TEMPO, 0.025 M Deuterated – Run 3

Time (min)	Area Ph2O	Area SUB	% Conversion	Asub/AIS	%SM	Ln[SM]	[SM]
0.50	5871	3612	0.0	0.61522739	100	-3.688879	0.0250
1.00	6162	3609	5.5	0.58568647	94.46556	-3.745814	0.0236
1.50	6648	3920	4.9	0.58965102	95.105	-3.739068	0.0238
2.00	6097	3289	13.0	0.53944563	87.00736	-3.828057	0.0218
2.50	5100	2685	15.1	0.52647059	84.91461	-3.852403	0.0212
3.00	6584	3424	16.1	0.5200486	83.87881	-3.864677	0.0210
3.50	6384	3204	19.1	0.5018797	80.94834	-3.900238	0.0202
4.00	7294	4066	10.1	0.55744447	89.9104	-3.795236	0.0225
4.50	6428	3382	15.1	0.52613566	84.86059	-3.85304	0.0212
5.00	6506	3505	13.1	0.53873348	86.8925	-3.829378	0.0217
6.00	6428	3223	19.1	0.50140012	80.87099	-3.901194	0.0202
7.00	5780	2607	27.3	0.45103806	72.74807	-4.007047	0.0182
8.00	5303	2174	33.9	0.40995663	66.12204	-4.102548	0.0165
9.00	5902	2527	30.9	0.42815995	69.05806	-4.059102	0.0173
10.00	6799	3231	23.4	0.47521694	76.64789	-3.954828	0.0192
15.00	6213	2377	38.3	0.3825849	61.70724	-4.171648	0.0154

Table S40 5% Ti, 2% TEMPO, 0.025 M Deuterated – Run 4

Time(min)	Area Ph2O	Area SUB	% Conversion	Asub/AIS	%SM	Ln[SM]
0.00	5157	3784	0.0	0.73375994	100	-3.688879454
0.50	6535	3900	19.4	0.59678653	80.64683	-3.903970155
1.00	6694	3300	33.4	0.49297879	66.61875	-4.095063496
1.50	7144	3191	39.6	0.44666853	60.36061	-4.193712858
2.00	6835	2583	48.9	0.37790783	51.06863	-4.360879317
2.50	7476	2683	51.5	0.35888175	48.49753	-4.412536679
3.00	7922	2429	58.6	0.30661449	41.43439	-4.569938411
3.50	6982	1874	63.7	0.26840447	36.27087	-4.703034586
4.00	6229	1445	68.7	0.23197945	31.34857	-4.848880846
4.50	6858	1533	69.8	0.22353456	30.20737	-4.885963615
5.00	7203	1352	74.6	0.18769957	25.36481	-5.06068699
6.00	6642	972	80.2	0.14634146	19.77587	-5.309586959
7.00	7180	900	83.1	0.12534819	16.93894	-5.46443426
8.00	7589	943	83.2	0.1242588	16.79173	-5.473163188
9.00	7279	799	85.2	0.10976783	14.83349	-5.597162185
10.00	6088	551	87.8	0.09050591	12.23053	-5.790114452

Table S41 5% Ti, 2% TEMPO, 0.025 M Proteated – Run 1

Time (min)	Area Ph2O	Area SUB	% Conversion	Asub/AIS	%SM	Ln[SM]
0.00	5561	4113	0.0	0.73961518	100	-3.688879
0.50	5887	3400	22.0	0.57754374	78.04645	-3.936745
1.00	6846	3578	29.4	0.52264096	70.62716	-4.036635
1.50	7011	3100	40.2	0.44216232	59.75166	-4.203853
2.00	5597	2213	46.6	0.39539039	53.43113	-4.315656
2.50	6165	2070	54.6	0.33576642	45.37384	-4.479114
3.00	8280	2400	60.8	0.28985507	39.1696	-4.626149
3.50	5953	1577	64.2	0.26490845	35.79844	-4.716145
4.00	6007	1329	70.1	0.22124188	29.89755	-4.896273
4.50	6920	1270	75.2	0.18352601	24.80081	-5.083173
5.00	7567	1200	78.6	0.15858332	21.43018	-5.229249
6.00	7213	1000	81.3	0.13863857	18.73494	-5.363659
7.00	6854	800	84.2	0.11672016	15.773	-5.53575
8.00	6594	700	85.7	0.10615711	14.34556	-5.630609
9.00	7727	650	88.6	0.08412062	11.36765	-5.863278
10.00	6655	600	87.8	0.09015778	12.18348	-5.793968

Table S42 5% Ti, 2% TEMPO, 0.025 M Proteated – Run 2

Time (min)	Area Ph2O	Area SUB	% Conversion	Asub/AIS	%SM	Ln[SM]
0.00	6132	4687	0.0	0.76435095	100	-3.688879
0.50	6411	3800	19.9	0.59273124	80.09882	-3.910789
1.00	6896	3606	29.3	0.52291183	70.66376	-4.036117
1.50	5593	2410	41.8	0.43089576	58.22916	-4.229663
2.00	6212	2148	53.3	0.34578236	46.72735	-4.44972
2.50	5802	1680	60.9	0.28955533	39.1291	-4.627183
3.00	6318	1565	66.5	0.24770497	33.47364	-4.783291
3.50	6041	1439	67.8	0.2382056	32.18995	-4.822395
4.00	5456	1134	71.9	0.20784457	28.0871	-4.958739
4.50	6749	1250	75.0	0.18521262	25.02873	-5.074025
5.00	6904	1180	76.9	0.17091541	23.09668	-5.154361
6.00	6074	890	80.2	0.14652618	19.80083	-5.308326
7.00	7181	890	83.3	0.12393817	16.7484	-5.475747
8.00	6843	764	84.9	0.11164694	15.08742	-5.580188
9.00	6153	599	86.8	0.09735089	13.15553	-5.717208
10.00	6215	508	89.0	0.08173773	11.04564	-5.892014

Table S43 5% Ti, 2% TEMPO, 0.025 M Proteated – Run 3

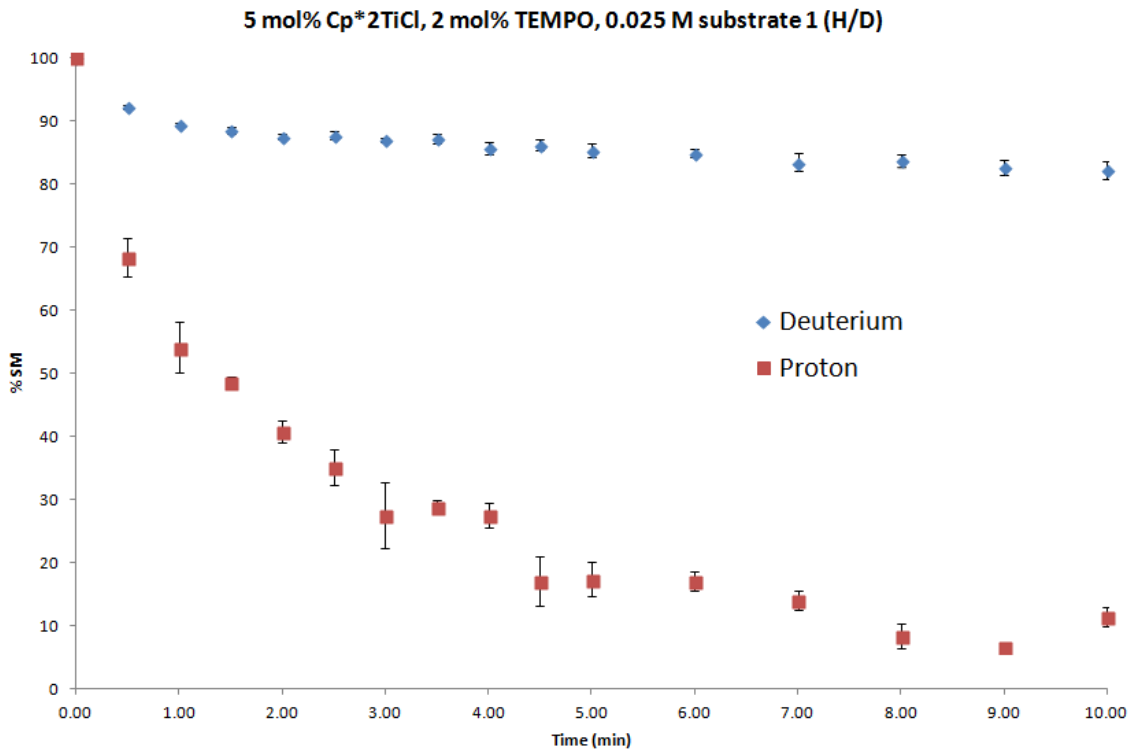


Figure S25 Chart comparing %yield of product vs time using 5 mol% Cp*2TiCl, 2 mol% TEMPO, 0.025 M substrate **1** (N-H and N-D isotopologs). The deuterium dataset is the average of 4 runs (Tables S37 – S40), the proton dataset is the average of 3 runs (Tables S41 – S43). Error bars were calculated by the standard error of the means {standard deviation / sqrt (number of expts)}.

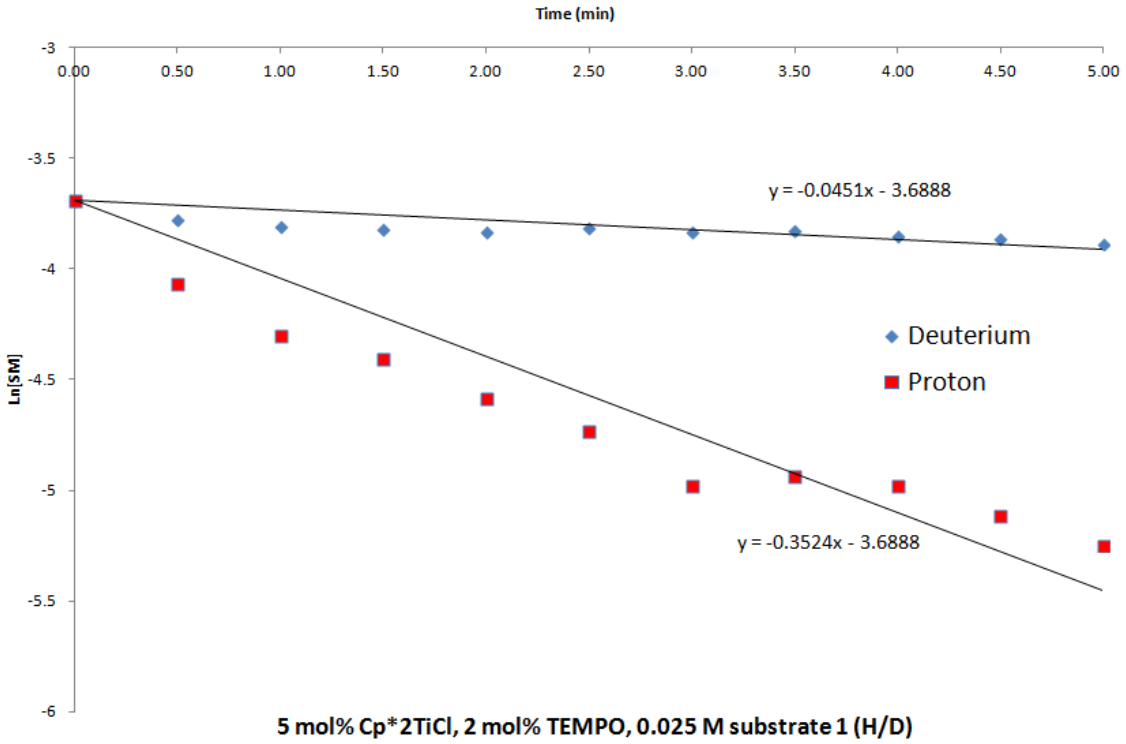


Figure S26 Ln[SM] vs time. Reactions run with 5 mol% Cp*2TiCl, 2 mol% TEMPO, 0.025 M substrate **1** (N-H and N-D isotopologs). The deuterium dataset is the average of 4 runs (Tables S37 – S40), the proton dataset is the average of 3 runs (Tables S41 – S43). The slopes of these plots are k_{obs} and are used to calculate the KIE (S105)

The KIE was obtained by taking the ratio of k_{obs} for the proteated and deuterated isotopologs of **1** obtained through independent kinetic experiments using 5 mol% Cp^*_2TiCl, and 2 mol% TEMPO at 0.025 M in MeCN at 23 °C (See tables S37 – S43 for raw data, Figs. S25, S26 for averages). k_{obs} was calculated independently for each kinetic experiment by calculating the slope from the plot of Ln[SM] vs time. The error of the slopes was calculated by LINEST analysis. The data is shown below. The error in the average slopes and in the KIE was calculated by standard propagation of error methods.

$$k_{H} = [(k_{obs(run\ 1)} \pm \text{error}) + (k_{obs(run\ 2)} \pm \text{error}) + (k_{obs(run\ 3)} \pm \text{error})] / (3 \pm 0)$$

$$k_{H} = [(-0.26 \pm 0.01) + (-0.308 \pm 0.004) + (-0.322 \pm 0.009)] / (3 \pm 0)$$

$$k_{Haverage} = (-0.92 \pm 0.02) / (3 \pm 0)$$

$$k_{Haverage} = -0.305 \pm 0.007$$

$$k_{D} = [(k_{obs(run\ 1)} \pm \text{error}) + (k_{obs(run\ 2)} \pm \text{error}) + (k_{obs(run\ 3)} \pm \text{error}) + (k_{obs(run\ 4)} \pm \text{error})] / (4 \pm 0)$$

$$k_{D} = [(-0.034 \pm 0.007) + (-0.050 \pm 0.004) + (-0.043 \pm 0.004) + (-0.041 \pm 0.005)] / (4 \pm 0)$$

$$k_{Daverage} = (-0.168 \pm 0.02) / (4 \pm 0)$$

$$k_{Daverage} = -0.042 \pm 0.005$$

$$KIE = k_H/k_D$$

$$KIE = (-0.305 \pm 0.007) / (-0.042 \pm 0.005)$$

$$KIE = 7 \pm 1$$

VI. DFT Computational Information

Computational Details

All calculations used DFT methodology[5] as implemented in the Gaussian 09 series of computer programs.[6] We employed the unrestricted B3LYP functional.[7-11] All-electron, split-valence double-ζ plus polarization function 6-31G(d) basis sets were used.[12-15] For some calculations, the LANL2DZ basis set which includes a relativistic effective core potential developed by Hay and Wadt and includes a double- ζ basis set was employed.[16] Where applicable, solvation is described using the CPCM polarizable conductor calculation model designating acetonitrile as the solvent;[17] otherwise calculations were performed in the gas phase. All complexes underwent geometry optimization, and stationary points were subjected to normal mode analysis.

---

(5) Parr, R. G.; Yang, W. *Density-Functional Theory of Atoms and Molecules*; University Press: Oxford, 1989.

(6) Gaussian 09, Revision C.01, Frisch, M. J. T., G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Keith, T.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, N. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J., Gaussian, Inc., Wallingford, CT.

(7) Parr, R. G.; Yang, W. *Annu. Rev. Phys. Chem.* **1995**, *46*, 701.

(8) Stephens, P. J.; Devlin, F. J.; Chabalowski, C. F.; Frisch, M. J. *J. Phys. Chem.* **1994**, *98*, 11623.

(9) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.

(10) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098.

(11) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

(12) Clark, T.; Chandrasekhar, J.; Spitznagel, G. W.; Schleyer, P. v. R. *J. Comput. Chem.* **1983**, *4*, 294.

(13) Hariharan, P. C.; Pople, J. A. *Mol. Phys.* **1974**, *27*, 209

(14) Ditchfield, R.; Hehre, W. J.; Pople, J. A. *J. Chem. Phys.* **1971**, *54*, 724.

(15) Krishnan, R.; Binkley, J. S.; Seeger, R.; Pople, J. A. *J. Chem. Phys.* **1980**, *72*, 650.

(16) (a) Hay, P.J.; Wadt, W.R. *J. Chem. Phys.*, **1985**, *82*, 270-283. (b) Hay, P.J.; Wadt, W.R. *J. Chem. Phys.*, **1985**, *82*, 299-310. (c) Wadt, W.R.; Hay, P.J. *J. Chem. Phys.*, **1985**, *82*, 284-298.

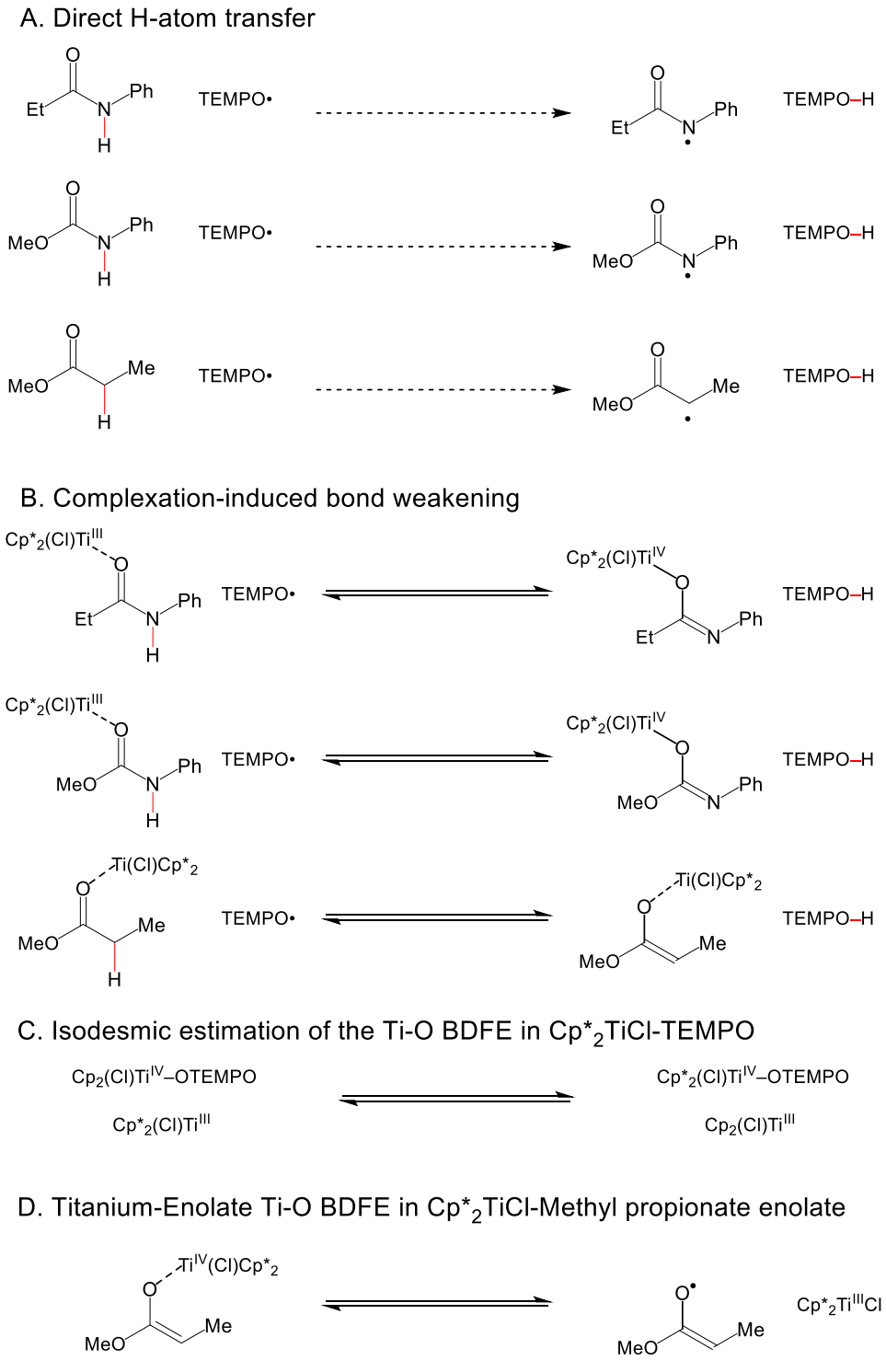
(17) (a) Barone, V.; Cossi, M. *J. Phys. Chem. A.*, **1998**, *102*, 1995. (b) Cossi, M.; Rega, N.; Scalmani, G.; Barone, V. *J. Comp. Chem.*, **2003**, *24*, 669.

Table S44: Thermodynamic parameters; for entries 1 – 14 and 41 – 44, geometries and frequencies were calculated with UB3LYP/6-31G(d) in all cases except for Cp^*_2TiCl-Methyl *N*-phenylcarbamate, which was optimized at UB3LYP/6-31G and subject to a subsequent frequency calculation at UB3LYP/6-31G(d). Entries 15-22 were calculated treating all atoms at UB3LYP/6-31G(d) except for titanium, which was treated with UB3LYP/LANL2DZ. Entries 23-40 are calculated the same level of theory as 1-14 with exception of the addition of the CPCM (solvent = acetonitrile) solvation model. Energies are given in hartree particle^{-1}.

Entry	Job Name	E+ZPE	G	H	S
1	*N*-phenyl propanamide	-479.395171	-479.432628	-479.383862	102.637
2	*N*-phenyl propanamidyl radical	-478.753041	-478.790670	-478.741793	102.871
3	Methyl *N*-phenylcarbamate	-515.329375	-515.365746	-515.318413	99.620
4	Methyl *N*-phenylcarbamyl radical	-514.686035	-514.722956	-514.675243	100.421
5	TEMPO	-483.456450	-483.493199	-483.443466	104.672
6	$Cp^*_2Ti^{III}Cl$	-2089.520656	-2089.577003	-2089.491607	179.732
7	$Cp^*_2Ti^{IV}Cl$-TEMPO	-2572.970135	-2573.036017	-2572.928550	225.551
8	$Cp^*_2Ti^{III}Cl$-amide	-2568.912610	-2568.984186	-2568.871884	233.807
9	$Cp^*_2Ti^{IV}Cl$-azaenolate	-2568.326993	-2568.395384	-2568.287094	227.914
10	$Cp^*_2Ti^{III}Cl$-carbamate	-2604.836304	-2604.905329	-2604.795852	230.414
11	$Cp^*_2Ti^{IV}Cl$-carbazaenolate	-2604.258278	-2604.326757	-2604.218635	227.562
12	$Cp_2Ti^{III}Cl$	-1696.638602	-1696.679639	-1696.626365	112.123
13	$Cp_2Ti^{IV}Cl$-TEMPO	-2180.122650	-2180.173505	-2180.097702	159.541
14	TEMPOH	-484.050688	-484.086313	-484.037641	102.439
	LANL2DZ Jobs				
15	$Cp^*_2Ti^{III}Cl$	-1298.163586	-1298.220037	-1298.134471	180.090
16	$Cp^*_2Ti^{IV}Cl$-TEMPO	-1781.602205	-1781.668502	-1781.560767	226.748
17	$Cp^*_2Ti^{III}Cl$-amide	-1777.527720	-1777.619055	-1777.506958	235.928
18	$Cp^*_2Ti^{IV}Cl$-azaenolate	-1776.957255	-1777.025892	-1776.917210	228.740
19	$Cp^*_2Ti^{III}Cl$-carbamate	-1813.466497	-1813.536870	-1813.426052	233.234
20	$Cp^*_2Ti^{IV}Cl$-carbazaenolate	-1812.887399	-1812.955703	-1812.847722	227.265
21	$Cp_2Ti^{III}Cl$	-905.288895	-905.326301	-905.277527	102.654
22	$Cp_2Ti^{IV}Cl$-TEMPO	-1388.760424	-1388.811318	-1388.735415	159.752
Entry	**Job Name**	**E+ZPE**	**G**	**H**	**S**
	CPCM Jobs (Solvent = Acetonitrile)				
23	*N*-phenyl propanamide	-479.404590	-479.442034	-479.393259	102.656
24	*N*-phenyl propanamidyl radical	-478.760870	-478.798749	-478.749575	103.495
25	Methyl *N*-phenylcarbamate	-515.337573	-515.374528	-515.326530	101.020
26	Methyl *N*-phenylcarbamyl radical	-514.694928	-514.731904	-514.684112	100.587
27	TEMPO	-483.461947	-483.498652	-483.448961	104.583
28	$Cp^*_2Ti^{III}Cl$	-2089.531049	-2089.587055	-2089.501925	179.171
29	$Cp^*_2Ti^{IV}Cl$-TEMPO	-2572.978018	-2573.044012	-2572.936624	226.019
30	$Cp^*_2Ti^{III}Cl$-amide	-2568.928292	-2568.998805	-2568.887663	233.917
31	$Cp^*_2Ti^{IV}Cl$-azaenolate	-2568.339036	-2568.408065	-2568.298920	229.715

32	$Cp^*_2Ti^{III}Cl$-carbamate	-2604.851645	-2604.921991	-2604.811058	233.480
33	$Cp^*_2Ti^{IV}Cl$-carbazaenolate	-2604.272153	-2604.341402	-2604.232226	229.779
34	$Cp_2Ti^{III}Cl$	-1696.651225	-1696.690550	-1696.638970	108.558
35	$Cp_2Ti^{IV}Cl$-TEMPO	-2180.133521	-2180.184514	-2180.108484	160.019
36	TEMPOH	-484.054477	-484.090159	-484.041378	102.669
37	$Cp^*_2Ti^{III}Cl$-ester	-2397.113294	-2397.180238	-2397.075618	220.190
38	$Cp^*_2Ti^{IV}Cl$-esterenolate	-2396.501910	-2396.566425	-2396.464952	84.672
39	Methyl propionate	-307.589501	-307.621368	-307.581138	84.672
40	Methyl propionate radical	-306.948674	-306.980632	-306.940374	84.731
	Other Gas Phase Calculations				
41	*N*-phenyl propanamide - BF_3	-803.957459	-804.001082	-803.942100	124.137
42	*N*-phenyl propanamidyl rad. - BF_3	-803.313592	-803.25786	-803.298223	125.516
43	$Cp^*_2Ti^{III}Cl$ – MeCN	-2222.23391	-2222.296788	-2222.199911	203.895
44	$Cp_2Ti^{III}Cl$ – MeCN	-1829.257744	-1829.404347	-1829.340499	124.379
	Other Solvated Calculations (Solvation = CPCM with Acetonitrile Solvent)				
45	$Cp^*_2Ti^{III}Cl$ – MeCN	-2222.25132	-2222.312946	-2222.217664	200.538
46	MeCN	-132.717002	-132.739660	-132.712486	57.823

Figure S27. Isodesmic reactions used for our thermochemical analyses of bond weakening. Explicit calculations are shown below in Table S45.



T**able S45.** Analysis of the reactions above. Energies are provided in kcal mol^{-1} using the conversion factor 627.51 kcal mol^{-1} per hartree and are rounded off after the third decimal place. Entropies are provided in e.u. and are rounded off after the third decimal place.

Rxn	Entries for Δ	ΔE+ZPE	ΔG	ΔH	ΔS
6-31G(d) -- Gas Phase					
A-Amide	=(2+14)-(1+5)	30.053	30.650	30.054	-1.999
A-Carbamate	=(4+14)-(3+5)	30.812	31.172	30.745	-1.432
B-Amide	=(9+14)-(5+8)	-5.410	-2.706	-5.889	-10.680
B-Carbamate	=(11+14)-(5+10)	-10.173	-9.125	-10.641	-5.085
C	=(7+12)-(6+13)	21.692	21.870	21.394	-1.599
C (Explicit MeCN)	=(7+44)-(13+43)	17.998	18.781	17.736	-3.506
LANL2DZ on Titanium, 6-31G(d) on all other atoms – Gas Phase					
B-Amide	=(18+14)-(5+17)	-2.368	0.031	-2.778	-9.421
B-Carbamate	=(20+14)-(19+5)	-9.501	-7.500	-9.943	-8.202
C	=(16+21)-(15+22)	20.651	22.937	19.824	-10.44
6-31G(d) – CPCM (Solvent = Acetonitrile)					
A-Amide	=(24+36)-(23+27)	32.122	32.491	32.171	-1.075
A-Carbamate	=(26+36)-(25+27)	31.448	32.076	31.376	-2.347
A-Ester	=(40+36)-(39+27)	30.307	30.892	30.338	-1.855
B-Amide	=(31+36)-(30+27)	-2.054	-0.481	-2.305	-6.116
B-Carbamate	=(33+36)-(32+27)	-8.181	-6.851	-8.525	-5.615
B-Ester	=(38+36)-(37+27)	11.831	13.997	30.338	-1.855
C	=(29+34)-(28+35)	22.168	23.222	21.847	-4.613
D	=(38)-(40+28)	13.923	-0.792	14.215	50.335

Titanium-TEMPO BDFE (Figure S27, Reaction C)

Using the value of 25 kcal mol^{-1} for the Cp_2TiCl-TEMPO BDFE (cf. reference 9(a) in the main text), we can estimate that the Cp^*_2TiCl-TEMPO BDFE is 3.3 kcal mol^{-1} or 2.1 kcal mol^{-1} using the ΔG value from the table above for 6-31G(d) and LANL2DZ entries for Reaction C respectively. Using the solvation model CPCM, this value is 1.8 kcal mol^{-1}. If MeCN is explicity bound (Entires 43 and 44) to the titanium, this value can be estimated as 6.2 kcal mol^{-1}.

Computed values for the bond weakening of *N*-phenyl propanamide and Methyl *N*-phenylcarbamate can be furnished by taking the ΔΔ of the Reactions A and B above; the results are shown below:

Quantity	ΔΔE+ZPE	ΔΔG	ΔΔH	ΔΔS
6-31G(d) Only – Gas Phase				
Amide Bond Weakening	35.462	33.356	35.943	8.681
Carbamate Bond Weakening	40.985	40.297	41.386	3.653
6-31G(d) – CPCM (Solvent = Acetonitrile)				
Amide Bond Weakening	34.177	32.973	34.476	5.041

Carbamate Bond Weakening	39.629	38.928	39.901	3.268
Ester Bond Weakening	18.476	16.894	18.887	6.682
LANL2DZ on Titanium, 6-31G(d) on all other atoms – Gas Phase				
Amide Bond Weakening	32.420	30.619	32.832	7.422
Carbamate Bond Weakening	40.312	38.669	40.688	6.770

Bond Weakening of Carbamates and Amides (cf. Figure S27 B)
Taking a value of 98 kcal mol^{-1} as the BDFE of the N-H bond in *N*-phenyl propanamide and Methyl *N*-phenylcarbamate, tabulated ΔG values at 6-31G(d) predicts amide and carbamate BDFEs of ~63 and ~57 kcal mol^{-1} respectively. Using the ΔG values furnished from the 6-31G(d)/LANL2DZ jobs, the BDFEs predicted for amides and carbamates are ~66 and ~58 kcal mol^{-1} respectively. Adding a CPCM solvent model to the 6-31G(d) level of theory furnishes ~65 and ~59 kcal mol^{-1} respectively for amides and carbamates. All three are in excellent agreement.

PCET to the Titanium Enolate Complex (cf. Figure S27 B)
A reviewer proposed concerted PCET from TEMPO-H to the titanium-bound ester enolate as means to regenerate TEMPO• and the active Ti(II) catalyst. Using the same thermochemical analysis at the 6-31G(d) level of theory with a CPCM (solvent = acetonitrile) solvation model, we estimate that the ester C-H BDFE is weaked by 17 kcal mol^{-1}. Using a BDFE of ~96 (based on that of ethyl propionate) for the alpha C-H bond, we estimate a weakened ester C-H BDFE of about 79 kcal mol^{-1}. Using 67 kcal mol^{-1} for the O-H BDFE of TEMPO-H, based solely on differential BDFEs this process should be 12 kcal mol^{-1} favorable. This is in excellent agreement with our DFT estimate (Isodesmic Reaction B, Ester, CPCM model included).

Titanium-Enolate Homolysis and Abstraction from TEMPO-H (cf. Figure S27 D)
The reviewers also indicated that it's possible the titanium-bound ester enolate propsed at the end of our catalytic cycle could also homolyze and do an H-atom transfer to TEMPO-H in solution. The calculated BDE (ΔE) from that process is ~14 kcal mol^{-1}. While we favor the idea of concerted PCET given its favorability (approx. 12 kcal mol^{-1} favorable, *vide supra*) and that it avoids the generation of the high-energy enolate radical, we cannot definitively rule out the homolysis-abstraction pathway and consequently present it as an alternative mechanism.

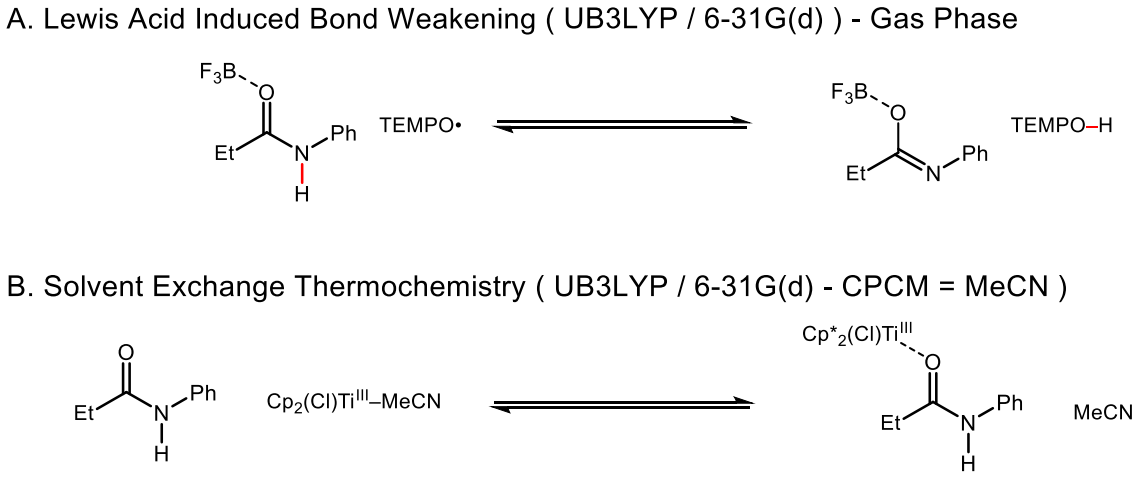
Compuations on titanium complexes of this sort have been done at both the 6-31G(d) and 6-31G(d)/LANL2DZ basis sets by Waymouth (ref. 8(a) in the main text) and Cuerva[18] respectively. We evaluated both methods on our complexes and found that both furnish energies in reasonable accord with each other; given both precedent and our results we believe both accurately describe the species studied in this work.

---

(18) Paradas, M.; Campana; A.G.; Jimenez, T.; Robles, R.; Oltra, J.E.; Bunuel, E.; Justica, J.; Cardenas, D.J.; Cuerva, J.M. *J. Am. Chem. Soc.*, **2010**, *132*, 12748.

Lewis Acidity is Not Responsible for Bond Weakening

Figure S28: Evaluation of the N-H BDFE of the BF3-adduct of *N*-phenyl propanamide as well as binding of the amide substrate.



T**able S46.** Analysis of the reaction above. Energies are provided in kcal mol^{-1} using the conversion factor 627.51 kcal mol^{-1} per hartree and are rounded off after the third decimal place. Entropies are provided in e.u. and are rounded off after the third decimal place.

Rxn	Entries for Δ	ΔE+ZPE	ΔG	ΔH	ΔS
6-31G(d) -- Gas Phase					
A from Fig. S28	=(14+42)-(5+41)	31.143	31.443	31.189	-0.854
6-31G(d) – CPCM (Solvent = Acetonirile)					
B from Fig. S28	=(30+46)–(23+45)	6.662	10.175	6.761	-11.454

A reviewer suggested that strictly Lewis acidity, responsible for a decrease of the pKa of alpha protons upon binding to a carbonyl group, could also be the root source for bond weakening in these complexes. To examine this effect we calculated the estimated BDFE of the BF3-adduct of *N*-phenyl propanamide. This reaction is significantly uphill (~31 kcal mol^{-1}) and demonstrates a slight *increase* of the BDFE (Table S27, A-Amide) by ~ 1.1 kcal mol^{-1} to furnish an effective BDFE of 99 kcal mol^{-1} (Figure S28, A and Table S46). We believe this supports our claim that only a *redox active* Lewis acid is competent to affect bond weakening in the appropriate substrates.

Another reviewer pointed out that we should include the energy of the amide binding to the titanium species. We calculated the thermodynamics of exchange between a discrete acetonitrile molecule and *N*-phenyl propanamide (Figure S28, B.) to the Cp*$_2$TiCl species: this is calculated to be endergonic by 6.8, 10.2, and 6.7 kcal mol^{-1} for ΔE, ΔG, and ΔH respectively (Table S46).

S47: Optimized geometries in Cartesian coordinates (Å) and energies (hartree) for stationary points. All energies and frequencies calculated at UB3LYP/6-31G(d); all geometries optimized at UB3LYP/6-31G except for Cp^*_2TiCl-Methyl *N*-phenylcarbamate, which was optimized at UB3LYP/6-31G with frequencies calculated at UB3LYP/6-31G(d).

N-phenyl propanamide (Entry 1)

```
 E(UB3LYP)                                          -479.579852
 Zero-point correction=                           0.184681
 Thermal correction to Energy=                    0.195046
 Thermal correction to Enthalpy=                  0.195990
 Thermal correction to Gibbs Free Energy=         0.147224
 Sum of electronic and zero-point Energies=          -479.395171
 Sum of electronic and thermal Energies=             -479.384806
 Sum of electronic and thermal Enthalpies=           -479.383862
 Sum of electronic and thermal Free Energies=        -479.432628

Charge = 0; Multiplicity = 1
 C                  0.78975300    0.29880600   -0.01463900
 C                  1.21392800   -1.03906700   -0.02020400
 C                  1.74600500    1.32603200    0.03200400
 C                  2.57948000   -1.32223300    0.01938400
 H                  0.47790000   -1.82953700   -0.05481200
 N                 -0.56873000    0.68228800   -0.05262100
 C                  3.10462200    1.02579700    0.07163000
 H                  1.42059600    2.36506100    0.03665600
 C                  3.53164200   -0.30330600    0.06534100
 H                  2.89794100   -2.36146200    0.01439100
 C                 -1.69755300   -0.10571800   -0.12648000
 H                 -0.72640200    1.68107600   -0.04644300
 H                  3.82895700    1.83518000    0.10710200
 H                  4.59126600   -0.54010200    0.09624900
 C                 -3.00188000    0.68875900   -0.23567000
 O                 -1.67878600   -1.32867600   -0.13371000
 C                 -4.19019700   -0.07545100    0.35022700
 H                 -2.89681500    1.67148400    0.24284500
 H                 -3.17399100    0.88298700   -1.30424100
 H                 -5.12493300    0.46382700    0.16580700
 H                 -4.07885000   -0.20845500    1.43155600
 H                 -4.25907200   -1.06838700   -0.10064300
```

N-phenyl propanamidyl radical (Entry 2)

```
 E(UB3LYP)                                             -478.923437
 Zero-point correction=                           0.170396
 Thermal correction to Energy=                    0.180700
 Thermal correction to Enthalpy=                  0.181644
 Thermal correction to Gibbs Free Energy=         0.132766
 Sum of electronic and zero-point Energies=           -478.753041
 Sum of electronic and thermal Energies=              -478.742737
 Sum of electronic and thermal Enthalpies=            -478.741793
 Sum of electronic and thermal Free Energies=         -478.790670

Charge = 0; Multiplicity = 2
 C                 -1.64970500   -0.09667800   -0.30856200
 O                 -1.72978600    0.87098800   -1.05575200
 N                 -0.51236500   -0.89615900   -0.20501400
 C                  0.72494500   -0.38448800   -0.08329300
 C                  1.03095600    0.99823400    0.14360000
 C                  1.81371300   -1.31189000   -0.14405300
 C                  2.34460800    1.40432800    0.29329200
 H                  0.22132700    1.71708200    0.17372000
 C                  3.12040100   -0.88603100    0.00826300
 H                  1.56957100   -2.35574300   -0.31321000
 C                  3.39508200    0.47337000    0.22837600
 H                  2.56682500    2.45446600    0.46215800
 H                  3.93557400   -1.60243500   -0.04162200
 H                  4.42195300    0.80690700    0.34880900
 C                 -2.82758900   -0.62076500    0.50063900
 H                 -3.04985700   -1.63248300    0.13562600
 H                 -2.49385900   -0.75827100    1.53890000
 C                 -4.05815500    0.28052700    0.42338300
 H                 -4.88118100   -0.14223900    1.00922100
 H                 -3.84015100    1.28138000    0.80956600
 H                 -4.39088700    0.39690600   -0.61191500
```

Methyl *N*-phenylcarbamate (Entry 3)

```
E(UB3LYP)                                             -515.490646
Zero-point correction=                           0.161271
Thermal correction to Energy=                    0.171288
Thermal correction to Enthalpy=                  0.172233
Thermal correction to Gibbs Free Energy=         0.124900
Sum of electronic and zero-point Energies=          -515.329375
Sum of electronic and thermal Energies=             -515.319358
Sum of electronic and thermal Enthalpies=           -515.318413
Sum of electronic and thermal Free Energies=        -515.365746

Charge = 0; Multiplicity = 1
C                 -1.71722300    0.09514100    0.00036900
O                 -1.75959900    1.31037100    0.00096700
C                  0.75464100   -0.30536900    0.00054000
C                  1.16667700    1.03545400    0.00010600
C                  1.71881700   -1.32551200    0.00034200
C                  2.53011200    1.33052500   -0.00045900
H                  0.42489200    1.82218100    0.00030200
C                  3.07533700   -1.01301400   -0.00019500
H                  1.40082300   -2.36646000    0.00078000
C                  3.49169200    0.31941200   -0.00058500
H                  2.83919600    2.37258200   -0.00088700
H                  3.80678600   -1.81673100   -0.00031400
H                  4.54972500    0.56484300   -0.00105600
C                 -4.06798300   -0.01105900   -0.00083700
H                 -4.83293300   -0.78849400   -0.00113600
H                 -4.16155700    0.61703300    0.88919100
H                 -4.16104300    0.61723000   -0.89077700
O                 -2.81619700   -0.70969900   -0.00050800
N                 -0.59860000   -0.69835500    0.00068000
H                 -0.78172800   -1.69254200   -0.00022400
```

Methyl *N*-phenylcarbamyl radical (Entry 4)

E(UB3LYP)	-514.833459
Zero-point correction=	0.147424
Thermal correction to Energy=	0.157272
Thermal correction to Enthalpy=	0.158216
Thermal correction to Gibbs Free Energy=	0.110503
Sum of electronic and zero-point Energies=	-514.686035
Sum of electronic and thermal Energies=	-514.676187
Sum of electronic and thermal Enthalpies=	-514.675243
Sum of electronic and thermal Free Energies=	-514.722956

Charge = 0; Multiplicity = 2

C	-1.67112600	-0.08570100	-0.27514600
O	-1.80626100	0.88012300	-1.00824300
N	-0.55310100	-0.90758400	-0.19215900
C	0.68075000	-0.38806200	-0.08069000
C	0.98974900	0.99668400	0.13074200
C	1.76808900	-1.31779200	-0.14059000
C	2.30422800	1.40183900	0.27110400
H	0.18116700	1.71731300	0.15419900
C	3.07561000	-0.89253000	0.00365000
H	1.52056700	-2.36238600	-0.29916700
C	3.35318400	0.46832400	0.21100800
H	2.52898800	2.45323700	0.42821100
H	3.88937600	-1.61064200	-0.04308700
H	4.38097700	0.80156700	0.32383600
C	-3.89139200	0.14614300	0.45128800
H	-4.55371700	-0.35745000	1.15627300
H	-3.74790100	1.19138700	0.73976000
H	-4.30888300	0.11225300	-0.55875700
O	-2.65291600	-0.57582500	0.51020000

TEMPO (Entry 5)

E(UB3LYP)	-483.719770
Zero-point correction=	0.263320
Thermal correction to Energy=	0.275360
Thermal correction to Enthalpy=	0.276304
Thermal correction to Gibbs Free Energy=	0.226571
Sum of electronic and zero-point Energies=	-483.456450
Sum of electronic and thermal Energies=	-483.444410
Sum of electronic and thermal Enthalpies=	-483.443466
Sum of electronic and thermal Free Energies=	-483.493199

Charge = 0; Multiplicity = 2

C	-2.12443800	0.14154900	0.00000000
C	-1.36048100	0.59024900	1.24708700
C	0.07141700	0.02335400	1.33162300
C	0.07141700	0.02335400	-1.33162300
C	-1.36048100	0.59024900	-1.24708700
H	-1.30581200	1.68759400	1.24608700
H	-1.89510500	0.30424300	2.16132800
H	-2.26657200	-0.94654700	0.00000000
H	-3.12873200	0.58244100	0.00000000
H	-1.30581200	1.68759400	-1.24608700
H	-1.89510500	0.30424300	-2.16132800
N	0.75704100	0.14868300	0.00000000
O	2.01832100	-0.10014300	0.00000000
C	0.89197900	0.84302400	2.34112800
H	0.40891700	0.80557400	3.32396900
H	1.90612200	0.44896100	2.42690700
H	0.95596200	1.89028100	2.02694700
C	0.07141700	-1.45936500	1.76153100
H	1.08582800	-1.86107300	1.68659600
H	-0.26423900	-1.54899500	2.80099500
H	-0.58962900	-2.07256900	1.14146600
C	0.89197900	0.84302400	-2.34112800
H	1.90612200	0.44896100	-2.42690700
H	0.40891700	0.80557400	-3.32396900
H	0.95596200	1.89028100	-2.02694700
C	0.07141700	-1.45936500	-1.76153100
H	1.08582800	-1.86107300	-1.68659600
H	-0.58962900	-2.07256900	-1.14146600

$Cp^*_2Ti^{III}Cl$ (Entry 6)

E(UB3LYP)	-2089.970393
Zero-point correction=	0.449737
Thermal correction to Energy=	0.477841
Thermal correction to Enthalpy=	0.478786
Thermal correction to Gibbs Free Energy=	0.393389
Sum of electronic and zero-point Energies=	-2089.520656
Sum of electronic and thermal Energies=	-2089.492551
Sum of electronic and thermal Enthalpies=	-2089.491607
Sum of electronic and thermal Free Energies=	-2089.577003

Charge = 0; Multiplicity = 2

Ti	-0.00002800	-0.32518400	-0.00021600
C	-2.35874000	-0.71970000	0.46848000
C	-1.95003500	0.44384900	1.18236900
C	-1.63901600	1.45628200	0.22277500
C	-1.79387200	0.89420900	-1.08379400
C	-2.24183100	-0.44980200	-0.92819300
C	2.24097100	-0.44879500	0.92968200
C	1.79344900	0.89562900	1.08286000
C	1.63959400	1.45568500	-0.22468700
C	1.95092100	0.44166400	-1.18247200
C	2.35884300	-0.72088600	-0.46648600
Cl	-0.00036200	-2.69548300	-0.00025700
C	2.94178900	-1.96148900	-1.08044600
H	4.01810100	-1.82219700	-1.25603600
H	2.81321200	-2.83270800	-0.43567400
H	2.47883100	-2.20030100	-2.04267200
C	2.60179300	-1.39322900	2.04306100
H	2.35647400	-2.42746800	1.78627200
H	3.67746000	-1.34690300	2.26367600
H	2.07133300	-1.14843600	2.96921000
C	1.69832300	1.63700400	2.38979800
H	1.31786500	1.00118400	3.19607800
H	2.68574100	2.00094000	2.70706000
H	1.04236000	2.50944900	2.32130900
C	2.04424000	0.63406400	-2.67324300
H	1.32528700	1.37461800	-3.03739000
H	3.04469000	0.98316800	-2.96711300
H	1.85894500	-0.29984000	-3.21373100
C	-1.53035600	2.91979600	0.55284400
H	-2.53109400	3.31616700	0.77695300
H	-0.91199500	3.11343900	1.43473500
H	-1.13248400	3.50916600	-0.27487900
C	-1.69911400	1.63352700	-2.39193000
H	-2.68638900	1.99809800	-2.70891200
H	-1.04209200	2.50533500	-2.32532600
H	-1.32005000	0.99606800	-3.19756800
C	-2.60379700	-1.39579400	-2.03986100
H	-3.67951500	-1.34897900	-2.26011900
H	-2.07349900	-1.15296100	-2.96661900
H	-2.35913500	-2.42977500	-1.78146500
C	-2.94116100	-1.95935600	1.08484400
H	-4.01732000	-1.81984300	1.26118100
H	-2.81311900	-2.83156700	0.44130200

H	-2.47736700	-2.19666700	2.04704900
C	-2.04245000	0.63856100	2.67289600
H	-3.04314100	0.98681400	2.96694600
H	-1.85549300	-0.29418300	3.21482900
H	-1.32422000	1.38068000	3.03523900
C	1.53126300	2.91864100	-0.55731400
H	1.13351900	3.50953900	0.26937800
H	2.53207000	3.31441800	-0.78215600
H	0.91290900	3.11085100	-1.43953200

$Cp^*_2Ti^{IV}Cl(TEMPO)$ (Entry 7)

E(UB3LYP)	-2573.686945
Zero-point correction=	0.716809
Thermal correction to Energy=	0.757150
Thermal correction to Enthalpy=	0.758094
Thermal correction to Gibbs Free Energy=	0.650928
Sum of electronic and zero-point Energies=	-2572.970135
Sum of electronic and thermal Energies=	-2572.929795
Sum of electronic and thermal Enthalpies=	-2572.928850
Sum of electronic and thermal Free Energies=	-2573.036017

Charge = 0; Multiplicity = 1

Ti	0.77233700	0.05833800	-0.16772000
C	0.85778600	2.63151900	-0.13708400
C	0.19281500	2.23879900	1.04421400
C	1.10603300	1.45487000	1.82595200
C	2.37932100	1.49664300	1.17314500
C	2.20792100	2.13612800	-0.07601300
C	0.98207200	-2.34916600	-0.99405700
C	0.90634200	-2.45915100	0.41405400
C	2.06480300	-1.84094100	0.97566200
C	2.91139300	-1.43727800	-0.10770800
C	2.23607200	-1.73162700	-1.31348400
Cl	0.76085000	0.60200400	-2.51671700
O	-1.06362600	-0.26637700	-0.06299800
C	-4.56408100	0.93743200	-0.76436500
C	-4.51186800	-0.26456400	1.39372400
C	-5.32420100	-0.04216100	0.12239800
H	-5.08841500	1.10007600	-1.71408700
H	-4.53258600	1.90966900	-0.25415100
H	-5.00062600	-0.98721000	2.05990800
H	-4.44981700	0.68369900	1.94448200
H	-6.31326300	0.36345000	0.37043700
H	-5.50445300	-0.98815000	-0.40230800
C	-2.45747100	1.77865900	-1.71456000
H	-2.45063500	2.59522000	-0.98823600
H	-1.44206900	1.58776600	-2.05364700
H	-3.04683200	2.10396800	-2.58036600
C	-3.14111600	-2.23555200	0.60503600
H	-2.24446700	-2.47399600	0.03804300
H	-3.21248000	-2.93368400	1.44659300
H	-4.00583700	-2.41554600	-0.03775800
C	-3.07788300	-0.77699900	1.11761700
C	-2.31958000	-0.72285500	2.45445900
H	-1.27803800	-1.01902000	2.33315100
H	-2.34155300	0.29184400	2.86363100
H	-2.79056800	-1.39445400	3.18122000
N	-2.40380000	0.19199000	0.18506000
C	-3.10733900	0.52670400	-1.10774700
C	-3.07483100	-0.59527700	-2.16626000
H	-3.46205700	-0.20825500	-3.11581800
H	-2.04726100	-0.92216400	-2.33381700
H	-3.67931500	-1.46349300	-1.89446800
C	-0.00507500	-3.35372600	1.20516800
H	0.58965900	-4.16444600	1.65075300

H	-0.51984600	-2.85312800	2.02929400
H	-0.76210500	-3.82346600	0.57640100
C	0.03984600	-2.92876200	-2.00868000
H	0.42728200	-3.87610900	-2.41000900
H	-0.94603700	-3.13227300	-1.58389700
H	-0.09747700	-2.24677800	-2.85356200
C	2.86313600	-1.67288600	-2.67515900
H	3.51074100	-2.55154000	-2.81776800
H	2.11579800	-1.67286000	-3.46985400
H	3.48248700	-0.78104500	-2.80762800
C	4.38243600	-1.12597800	-0.05471400
H	4.94338400	-1.96126600	-0.49733300
H	4.65727300	-0.23242200	-0.62495100
H	4.74859900	-1.00337000	0.96528100
C	2.46638300	-2.05437400	2.40999000
H	2.73533300	-3.10973300	2.56685100
H	3.33559100	-1.46301900	2.70287100
H	1.65484000	-1.83143500	3.10962900
C	0.88862300	1.08504000	3.26929200
H	0.96010300	1.97828000	3.90792000
H	-0.09624800	0.64587600	3.44350500
H	1.63832100	0.37624300	3.62795000
C	3.69375400	1.31734100	1.87844300
H	3.86016600	2.20174900	2.51111800
H	3.72691100	0.45180200	2.54115900
H	4.53668800	1.25717500	1.19001000
C	3.27451400	2.49893200	-1.06931200
H	3.52015800	3.56825800	-0.99929800
H	4.20077400	1.94204700	-0.90278400
H	2.94083700	2.30303600	-2.09295400
C	0.38945400	3.61149400	-1.17178100
H	1.04015300	4.49686300	-1.16401300
H	0.42696700	3.18640100	-2.17933100
H	-0.63181200	3.94821500	-0.98437000
C	-1.13728000	2.73666700	1.53559900
H	-1.37939600	3.69880900	1.07268000
H	-1.94664700	2.03828200	1.30908900
H	-1.10439200	2.89611300	2.62004400

$Cp^*_2Ti^{III}Cl$-*N*-phenyl propanamide (Entry 8)

E(UB3LYP)	-2569.548823
Zero-point correction=	0.636213
Thermal correction to Energy=	0.675995
Thermal correction to Enthalpy=	0.676939
Thermal correction to Gibbs Free Energy=	0.564636
Sum of electronic and zero-point Energies=	-2568.912610
Sum of electronic and thermal Energies=	-2568.872828
Sum of electronic and thermal Enthalpies=	-2568.871884
Sum of electronic and thermal Free Energies=	-2568.984186

Charge = 0; Multiplicity = 2

Ti	-1.13705700	0.13485000	0.00849300
C	-1.27094900	0.87353400	-2.38803400
C	-0.20102600	-0.05704000	-2.34483400
C	-0.72226800	-1.32511500	-1.95982200
C	-2.13833200	-1.18092400	-1.80880500
C	-2.47240200	0.18804100	-2.03180800
C	-1.06698600	0.20528300	2.44172800
C	-0.46619300	-1.03999700	2.08381300
C	-1.46818700	-1.86268000	1.50617200
C	-2.70170900	-1.13120500	1.52516700
C	-2.45375200	0.13588900	2.11159400
Cl	-1.63162700	2.56418300	0.22948800
C	0.91409400	-1.48921400	2.47175600
H	0.91185800	-1.89133700	3.49552600
H	1.29177100	-2.28172300	1.81906300
H	1.63938100	-0.67214800	2.44650300
C	-0.40668600	1.31475400	3.21045600
H	-0.58760800	1.20826600	4.28982000
H	0.67919700	1.31369700	3.06772100
H	-0.78820000	2.29145000	2.90030900
C	-3.51051500	1.13388600	2.49140200
H	-3.92582000	0.88925300	3.48064500
H	-3.11164100	2.14897300	2.52865100
H	-4.34288300	1.13926200	1.78044900
C	-4.08101200	-1.68274700	1.28167400
H	-4.59600200	-1.83789000	2.24044600
H	-4.70967100	-1.00426400	0.69457600
H	-4.05984300	-2.64685600	0.77011300
C	-1.30752700	-3.33635200	1.24804200
H	-1.39689300	-3.89761100	2.18985800
H	-2.06894300	-3.73291600	0.57250400
H	-0.32822800	-3.58215500	0.82589200
C	0.02927400	-2.62808000	-2.03047000
H	0.10255600	-2.98156900	-3.06980800
H	1.05535500	-2.53990400	-1.65690800
H	-0.46300500	-3.41860200	-1.45910500
C	-3.12361600	-2.31718400	-1.82283200
H	-3.27638300	-2.64872600	-2.86046800
H	-2.78200900	-3.18993700	-1.26183800
H	-4.10221500	-2.02831100	-1.43514900
C	-3.85045900	0.79115300	-2.05940400
H	-4.21469900	0.91360900	-3.08956600
H	-4.57788800	0.16504400	-1.53292500

H	-3.85463000	1.77664800	-1.58295200
C	-1.18912000	2.27449400	-2.92257700
H	-1.31761700	2.26837500	-4.01528100
H	-1.95762100	2.91755000	-2.49091600
H	-0.22131100	2.74145100	-2.71224500
C	1.20069900	0.20914900	-2.81476500
H	1.27361300	0.05603100	-3.90125700
H	1.51346300	1.24042000	-2.62059900
H	1.93101400	-0.45558800	-2.34674300
O	1.09080600	0.67253200	0.18962900
C	1.97292800	1.54669200	0.24062700
C	3.97764100	0.00001400	0.10827600
C	2.79137200	4.03667700	0.25358000
C	5.37899200	0.04157200	0.17718000
C	3.33103200	-1.23009000	-0.07055800
H	2.38472900	5.05116300	0.30550100
H	3.50919200	3.94485400	1.07955000
H	3.33638400	3.95788800	-0.69528000
C	6.12543700	-1.12775700	0.06790300
H	5.88487900	0.99500100	0.31809000
C	4.09317500	-2.39442100	-0.17925400
H	2.25315100	-1.26456200	-0.11519200
C	5.48569000	-2.35579200	-0.11167600
H	7.20914800	-1.07616700	0.12398800
H	3.58275700	-3.34364100	-0.31853700
H	6.06611600	-3.26960300	-0.19720000
N	3.30104600	1.23868100	0.21566400
H	3.91953500	2.03497900	0.28218500
C	1.64296100	3.02743800	0.35063000
H	1.10055300	3.15255200	1.29368900
H	0.88224500	3.22838500	-0.40889500

$Cp^*_2Ti^{IV}Cl$-*N*-phenyl propanamide aza-enolate (Entry 9)

```
 E(UB3LYP)                                          -2568.951203
 Zero-point correction=                           0.624210
 Thermal correction to Energy=                    0.663165
 Thermal correction to Enthalpy=                  0.664109
 Thermal correction to Gibbs Free Energy=         0.555819
 Sum of electronic and zero-point Energies=          -2568.326993
 Sum of electronic and thermal Energies=             -2568.288038
 Sum of electronic and thermal Enthalpies=           -2568.287094
 Sum of electronic and thermal Free Energies=        -2568.395384

Charge = 0; Multiplicity = 1
 Ti                  0.94336000    0.08062300    0.13800800
 C                   1.34473700   -1.10495600    2.33088000
 C                  -0.02048500   -1.25176700    1.98288500
 C                  -0.09097000   -2.03357500    0.78875000
 C                   1.23950800   -2.38988400    0.42111700
 C                   2.13468100   -1.75804600    1.33609400
 C                   1.78481700    1.80817500   -1.52608200
 C                   0.66310400    1.17531000   -2.10147300
 C                   0.96551500   -0.21240900   -2.27443200
 C                   2.33398200   -0.40345700   -1.88530400
 C                   2.81502500    0.82358500   -1.36468200
 Cl                  1.93925900    1.71591600    1.55720200
 C                  -0.56985600    1.87116900   -2.59327100
 H                  -0.32351300    2.49648100   -3.46202600
 H                  -1.32984500    1.15608800   -2.91090800
 H                  -1.01975600    2.52341800   -1.83997400
 C                   1.95325900    3.28223000   -1.30860100
 H                   2.55802600    3.71394100   -2.11884700
 H                   0.99195700    3.80375700   -1.30536800
 H                   2.45688600    3.49740500   -0.36292100
 C                   4.22371100    1.11590600   -0.93497700
 H                   4.78568000    1.58881600   -1.75310300
 H                   4.24412800    1.79758100   -0.08011200
 H                   4.76222600    0.20640300   -0.65300900
 C                   3.22846000   -1.53445200   -2.31254500
 H                   3.80992200   -1.20650300   -3.18579200
 H                   3.95180500   -1.82840800   -1.54757300
 H                   2.67172000   -2.42049000   -2.61671600
 C                   0.09809900   -1.17531800   -3.04171300
 H                   0.09924800   -0.92660600   -4.11228700
 H                   0.44934700   -2.20605800   -2.95495600
 H                  -0.94304800   -1.15125400   -2.70436100
 C                  -1.34246800   -2.58640400    0.17012600
 H                  -1.69910200   -3.45539500    0.74134200
 H                  -2.15074300   -1.85354800    0.15300200
 H                  -1.17391700   -2.92212100   -0.85680100
 C                   1.56853800   -3.54764900   -0.48009700
 H                   1.27599300   -4.47579400    0.03106300
 H                   1.02493500   -3.53092700   -1.42791600
 H                   2.63445500   -3.62539900   -0.69590800
 C                   3.62563800   -1.93205300    1.43174900
 H                   3.88681000   -2.59072500    2.27151400
```

H	4.04896200	-2.37983900	0.52914400
H	4.13331700	-0.97668400	1.60336100
C	1.86541300	-0.55180500	3.62230800
H	1.91200200	-1.35987800	4.36737900
H	2.86838600	-0.13355600	3.51563100
H	1.22133000	0.23519700	4.02079600
C	-1.18107700	-0.78663300	2.81041200
H	-1.35544200	-1.47999200	3.64505500
H	-1.00426800	0.20321300	3.24348700
H	-2.09971500	-0.73986800	2.22410000
O	-0.82737100	0.78510900	0.23024800
C	-1.78388900	1.65110600	0.56912500
C	-3.69036000	0.34229500	-0.06392400
C	-2.39372700	3.93582500	1.56930100
C	-4.46374800	-0.46074400	0.79791600
C	-3.72548400	0.05555900	-1.44140600
H	-1.95223300	4.84453600	1.99501800
H	-3.00822300	4.21761100	0.70906800
H	-3.06294400	3.49370300	2.31288900
C	-5.19610900	-1.53988600	0.30587600
H	-4.48751800	-0.21292100	1.85533500
C	-4.46948600	-1.01907300	-1.92873100
H	-3.19112300	0.70508500	-2.12528800
C	-5.20057500	-1.83225000	-1.06013000
H	-5.77767200	-2.14837000	0.99442700
H	-4.48307100	-1.21615000	-2.99839200
H	-5.77906800	-2.66823900	-1.44328600
N	-3.04812100	1.46851300	0.45483100
C	-1.29122100	2.95698800	1.16903000
H	-0.60484700	3.42323100	0.45049800
H	-0.65680200	2.71078300	2.02880500

$Cp^*_2Ti^{III}Cl$-Methyl *N*-phenyl carbamate (Entry 10)

N.B.: coordinates optimized at UB3LYP/6-31G; frequency at UB3LYP/6-31G(d.

E(UB3LYP)	-2605.447196
Zero-point correction=	0.610892
Thermal correction to Energy=	0.650401
Thermal correction to Enthalpy=	0.651345
Thermal correction to Gibbs Free Energy=	0.541868
Sum of electronic and zero-point Energies=	-2604.836304
Sum of electronic and thermal Energies=	-2604.796796
Sum of electronic and thermal Enthalpies=	-2604.795852
Sum of electronic and thermal Free Energies=	-2604.905329

Charge = 0; Multiplicity = 2

Ti	1.07358100	0.09229100	0.00076900
C	1.37226200	0.57505300	2.45295600
C	0.11599100	-0.10092700	2.37724500
C	0.34718300	-1.42668700	1.89378600
C	1.76484100	-1.57848700	1.70050400
C	2.39722300	-0.33309700	2.02005700
C	1.11535400	0.41963500	-2.43346700
C	0.16798600	-0.63862900	-2.22711500
C	0.86999400	-1.76829600	-1.70999000
C	2.26854900	-1.42076500	-1.63766600
C	2.41737500	-0.07924900	-2.09420500
Cl	2.20735900	2.35118300	-0.02064600
C	-1.25052600	-0.62244700	-2.72050300
H	-1.26995000	-0.74915500	-3.81299300
H	-1.85037000	-1.42837100	-2.29167800
H	-1.75996700	0.32017100	-2.49905600
C	0.82526700	1.73284800	-3.10197900
H	0.97587200	1.66320100	-4.18943900
H	-0.21166500	2.04786800	-2.94080600
H	1.47878200	2.52142000	-2.71945200
C	3.72956100	0.60374000	-2.35221300
H	4.12123300	0.31895300	-3.34066500
H	3.62862100	1.68966300	-2.32180100
H	4.48451300	0.33061700	-1.60778400
C	3.42086800	-2.37255200	-1.46249000
H	3.87849900	-2.58346500	-2.44015700
H	4.21361700	-1.96404400	-0.82569700
H	3.11015800	-3.32934100	-1.03948900
C	0.29846100	-3.15318000	-1.57257700
H	0.36950800	-3.69688800	-2.52653500
H	0.82581800	-3.75325000	-0.82567500
H	-0.76038200	-3.13547600	-1.29460900
C	-0.63296300	-2.56873500	1.94191000
H	-0.45228100	-3.18896300	2.83310300

H	-1.66598300	-2.21735200	2.00556700
H	-0.55729500	-3.23269600	1.07484800
C	2.46092100	-2.90780800	1.61176200
H	2.49514400	-3.36489200	2.61263100
H	1.94611000	-3.61739700	0.95874300
H	3.49252800	-2.81792100	1.26685800
C	3.87644400	-0.06616400	2.07573800
H	4.26519000	-0.18654000	3.09755300
H	4.43675200	-0.75357200	1.43295200
H	4.10531200	0.95209600	1.74652400
C	1.59996200	1.91240500	3.09637300
H	1.68709400	1.79739400	4.18748700
H	2.51012200	2.38592000	2.72597800
H	0.77625600	2.60916500	2.90702800
C	-1.18306300	0.44412200	2.89914400
H	-1.26943500	0.26181500	3.98032300
H	-1.25877800	1.52714500	2.75474000
H	-2.05206900	-0.01948000	2.42436000
O	-0.96425900	1.20094200	-0.08865300
C	-1.96182800	1.96060700	-0.09084100
C	-3.90482500	0.32356200	-0.07160900
C	-0.62664800	4.03654700	-0.11562100
C	-5.30940300	0.31142100	-0.16057200
C	-3.20610600	-0.88658700	0.04895200
H	-0.90131700	5.08307700	0.00262200
H	0.01921700	3.69061100	0.68824900
H	-0.12482500	3.85994700	-1.06593000
C	-6.00678400	-0.89616500	-0.13176400
H	-5.85140200	1.24883600	-0.25410200
C	-3.91931300	-2.09091700	0.07559900
H	-2.12824900	-0.88381800	0.11231500
C	-5.31456100	-2.10752500	-0.01444000
H	-7.08953200	-0.88903200	-0.20156800
H	-3.37140100	-3.02262000	0.17087300
H	-5.85477500	-3.04768400	0.00759100
N	-3.27982400	1.59351100	-0.10043200
H	-3.90403600	2.38901000	-0.12329700
O	-1.91887700	3.32650700	-0.08814400

$Cp^*_2Ti^{IV}Cl$-Methyl *N*-phenyl carbamate aza-enolate (Entry 11)

E(UB3LYP)	-2604.858731
Zero-point correction=	0.600453
Thermal correction to Energy=	0.639152
Thermal correction to Enthalpy=	0.640096
Thermal correction to Gibbs Free Energy=	0.531974
Sum of electronic and zero-point Energies=	-2604.258278
Sum of electronic and thermal Energies=	-2604.219580
Sum of electronic and thermal Enthalpies=	-2604.218635
Sum of electronic and thermal Free Energies=	-2604.326757

Charge = 0; Multiplicity = 1

Ti	-0.97039400	0.01417700	-0.16817500
C	-1.32857300	-1.74423400	-1.93645500
C	0.04182000	-1.74280100	-1.56940100
C	0.13405100	-2.17112300	-0.20956900
C	-1.18431500	-2.43658500	0.25751300
C	-2.09829400	-2.12055200	-0.79762000
C	-1.84452300	2.12579900	0.85366800
C	-0.77997700	1.68039400	1.66841200
C	-1.13726500	0.41547700	2.22989100
C	-2.47728600	0.12415200	1.81730100
C	-2.88963500	1.14538400	0.92057500
Cl	-1.72769200	1.20389000	-2.05781900
C	0.44382800	2.46330000	2.03360400
H	0.28188000	2.98222300	2.98916700
H	1.31733600	1.81900800	2.15735900
H	0.68262900	3.21781600	1.28198800
C	-1.92861700	3.46255900	0.17792200
H	-2.16156200	4.24207100	0.91730200
H	-0.98548800	3.71999900	-0.30919300
H	-2.70820100	3.47719300	-0.58539300
C	-4.25782500	1.29266200	0.31735200
H	-4.86061800	2.00789500	0.89429800
H	-4.20203400	1.65849000	-0.71191700
H	-4.80114400	0.34319200	0.30752100
C	-3.41522500	-0.84469700	2.48109500
H	-4.04066500	-0.29159600	3.19598400
H	-4.09658100	-1.33508400	1.78205000
H	-2.89082000	-1.61493900	3.04662000
C	-0.33314900	-0.28105000	3.29462700
H	-0.29644300	0.32863300	4.20811700
H	-0.76288500	-1.24608800	3.57200900
H	0.70268700	-0.45232700	2.98236500
C	1.40117200	-2.47341200	0.53530000
H	1.79022000	-3.45923200	0.24374900
H	2.18022300	-1.73759400	0.33031300
H	1.24096400	-2.49651200	1.61746800

C	-1.48729200	-3.27945200	1.46570100
H	-1.17918200	-4.31369000	1.25692100
H	-0.94261900	-2.96645000	2.35988800
H	-2.55113300	-3.30630600	1.70335600
C	-3.57558800	-2.40282000	-0.84840900
H	-3.77696300	-3.26769600	-1.49555000
H	-3.98792800	-2.63803300	0.13506900
H	-4.14299400	-1.56080700	-1.25975500
C	-1.86604100	-1.58434700	-3.32584800
H	-1.92832800	-2.57326900	-3.80387500
H	-2.86602300	-1.14397200	-3.33318400
H	-1.22358700	-0.95201300	-3.94188300
C	1.18441500	-1.44705200	-2.49479100
H	1.35740500	-2.29266500	-3.17481900
H	0.98323000	-0.56481300	-3.11164900
H	2.10921500	-1.27000300	-1.94367500
O	0.89834900	0.58061100	-0.27496300
C	1.74216300	1.50864500	-0.65202600
N	3.02454700	1.49395200	-0.58881700
C	3.76913900	0.45029100	-0.03245100
C	1.97121300	3.61705100	-1.71861400
C	4.53307200	-0.38415500	-0.87075600
C	3.88761700	0.27548100	1.35918600
H	1.29270600	4.36604300	-2.13180400
H	2.59595000	4.05200600	-0.93255400
H	2.62342200	3.21809400	-2.50020100
C	5.34771200	-1.38227300	-0.33775500
H	4.47901800	-0.22761900	-1.94448100
C	4.70916100	-0.72038500	1.88728200
H	3.34514000	0.94387700	2.02134500
C	5.43876100	-1.56175600	1.04457800
H	5.92125300	-2.01830100	-1.00797300
H	4.78334500	-0.83490600	2.96640700
H	6.07880800	-2.33593100	1.45872700
O	1.12468300	2.59196700	-1.19222400

$Cp_2Ti^{III}Cl$ (Entry 12)

E(UB3LYP)	-1696.809033
Zero-point correction=	0.170431
Thermal correction to Energy=	0.181723
Thermal correction to Enthalpy=	0.182667
Thermal correction to Gibbs Free Energy=	0.129394
Sum of electronic and zero-point Energies=	-1696.638602
Sum of electronic and thermal Energies=	-1696.627310
Sum of electronic and thermal Enthalpies=	-1696.626365
Sum of electronic and thermal Free Energies=	-1696.679639

Charge = 0; Multiplicity = 1

Ti	-0.00033200	0.11126800	-0.00285900
C	2.32856600	0.35718200	0.53297800
C	1.83943500	-0.79206700	1.20621100
C	1.47495500	-1.74478300	0.21785200
C	1.71765800	-1.17556300	-1.06154400
C	2.25139500	0.12165500	-0.86221400
C	-2.21717700	0.08246400	0.93739800
C	-1.70975200	-1.23811500	1.00579400
C	-1.52171000	-1.70069600	-0.32445700
C	-1.89632700	-0.66030500	-1.21490300
C	-2.33534900	0.43774800	-0.42982900
H	2.65396500	1.27694400	0.99896200
H	1.78202500	-0.92922000	2.27877700
H	1.08427900	-2.73497700	0.40908200
H	1.53843200	-1.65322900	-2.01676500
H	2.51289500	0.83091800	-1.63696900
H	-2.44154000	0.72524200	1.77921400
H	-1.50595300	-1.79811600	1.90998900
H	-1.15834800	-2.67798400	-0.61248500
H	-1.87774800	-0.70637300	-2.29661200
H	-2.65754000	1.39889500	-0.80490400
Cl	0.02862800	2.45264000	0.00064100

$Cp_2Ti^{IV}Cl(TEMPO)$ (Entry 13)

```
 E(UB3LYP)                                          -2180.559534
 Zero-point correction=                           0.436884
 Thermal correction to Energy=                    0.460888
 Thermal correction to Enthalpy=                  0.461832
 Thermal correction to Gibbs Free Energy=         0.386029
 Sum of electronic and zero-point Energies=          -2180.122650
 Sum of electronic and thermal Energies=             -2180.098646
 Sum of electronic and thermal Enthalpies=           -2180.097702
 Sum of electronic and thermal Free Energies=        -2180.173505

Charge = 0; Multiplicity = 1
 Ti                  1.45754400    0.05028100   -0.00149200
 C                   1.41164800    1.77478500    1.70829300
 C                   0.64005900    0.69724600    2.18118900
 C                   1.50119100   -0.42010800    2.34334300
 C                   2.82306100    0.00098900    2.03318300
 C                   2.76609000    1.34205500    1.60874200
 C                   1.68087500   -1.32959700   -2.06082700
 C                   1.45893300   -2.22197800   -0.99146600
 C                   2.55294300   -2.12221000   -0.09859100
 C                   3.48452600   -1.19581900   -0.65088400
 C                   2.94168600   -0.70874300   -1.85587600
 H                   1.04293500    2.74910800    1.42554600
 H                  -0.43618100    0.68187700    2.28028300
 H                   1.20826600   -1.40273000    2.68871700
 H                   3.71181500   -0.61224700    2.08447800
 H                   3.59516700    1.93918600    1.25350800
 H                   1.00043900   -1.12419000   -2.87604700
 H                   0.58194300   -2.83592000   -0.84691300
 H                   2.68218700   -2.69324300    0.81136800
 H                   4.43646300   -0.90956000   -0.22468500
 H                   3.38751400    0.03885600   -2.49473400
 Cl                  1.77019500    2.01543900   -1.34994500
 O                  -0.35280900   -0.16009800   -0.27150200
 C                  -3.76647100    1.28541200    0.15461800
 C                  -3.77101800   -1.09400200    0.85485000
 C                  -4.55055700   -0.02283300    0.09626500
 H                  -4.28019900    2.07892200   -0.40168500
 H                  -3.71633900    1.61572400    1.20124300
 H                  -4.28729200   -2.06155500    0.82115900
 H                  -3.71029200   -0.80261900    1.91221000
 H                  -5.54160300    0.11179000    0.54745300
 H                  -4.72571100   -0.32724600   -0.94297000
 C                  -1.60377300    2.48747400    0.01582600
 H                  -1.53610000    2.56239400    1.10632600
 H                  -0.60406500    2.55556900   -0.41427100
```

H	-2.18182100	3.34685400	-0.34389700
C	-2.36638900	-2.04318000	-1.03918400
H	-1.40348400	-1.95481800	-1.54554900
H	-2.57579000	-3.10723900	-0.87806500
H	-3.13606800	-1.66070100	-1.71307300
C	-2.33572800	-1.30445700	0.31939700
C	-1.59153400	-2.18300500	1.34414900
H	-0.58041500	-2.42682000	1.01247900
H	-1.52568600	-1.67184700	2.31026200
H	-2.13558800	-3.12295000	1.49140800
N	-1.64546900	0.03331400	0.29797600
C	-2.32262700	1.18988500	-0.39515900
C	-2.31381100	1.10328800	-1.93675900
H	-2.65567600	2.05675100	-2.35522300
H	-1.29946600	0.92377100	-2.30050000
H	-2.96809300	0.32060300	-2.32741700

TEMPOH (Entry 14)

```
 E(UB3LYP)                                                -484.325986
 Zero-point correction=                           0.275298
 Thermal correction to Energy=                    0.287401
 Thermal correction to Enthalpy=                  0.288346
 Thermal correction to Gibbs Free Energy=         0.239674
 Sum of electronic and zero-point Energies=           -484.050688
 Sum of electronic and thermal Energies=              -484.038585
 Sum of electronic and thermal Enthalpies=            -484.037641
 Sum of electronic and thermal Free Energies=         -484.086313

Charge = 0; Multiplicity = 1
 C                     0.00000000    2.17007900    0.02032000
 C                     1.25168100    1.43458200   -0.46577500
 C                     1.29486000   -0.04858600   -0.03259100
 C                    -1.29486000   -0.04858600   -0.03259100
 C                    -1.25168200    1.43458200   -0.46577500
 H                     1.28029800    1.47672000   -1.56304000
 H                     2.16248500    1.92819300   -0.10405200
 H                     0.00000000    2.24859400    1.11470200
 H                    -0.00000100    3.19946700   -0.35968300
 H                    -1.28029800    1.47671900   -1.56304000
 H                    -2.16248500    1.92819300   -0.10405200
 N                     0.00000000   -0.66173100   -0.44703600
 C                     2.39353400   -0.76494800   -0.84232400
 H                     3.35844300   -0.26475800   -0.70069200
 H                     2.50155300   -1.80538000   -0.52193400
 H                     2.14983700   -0.75128400   -1.91032300
 C                     1.63464900   -0.18756400    1.46918500
 H                     1.46862700   -1.21657700    1.79849600
 H                     2.69093100    0.05665200    1.63253100
 H                     1.04445100    0.47670500    2.10469400
 C                    -2.39353400   -0.76494800   -0.84232400
 H                    -2.50155200   -1.80538100   -0.52193400
 H                    -3.35844300   -0.26475800   -0.70069300
 H                    -2.14983700   -0.75128400   -1.91032300
 C                    -1.63464900   -0.18756400    1.46918500
 H                    -1.46862600   -1.21657700    1.79849600
 H                    -1.04445200    0.47670500    2.10469300
 H                    -2.69093100    0.05665100    1.63253100
 O                     0.00000000   -2.03835200    0.00819300
 H                     0.00000300   -2.53194300   -0.82652100
```

$Cp^*_2Ti^{III}Cl$-LANL2DZ (Entry 15)

E(UB3LYP)	-1298.613131
Zero-point correction=	0.449545
Thermal correction to Energy=	0.477716
Thermal correction to Enthalpy=	0.478661
Thermal correction to Gibbs Free Energy=	0.393094
Sum of electronic and zero-point Energies=	-1298.163586
Sum of electronic and thermal Energies=	-1298.135415
Sum of electronic and thermal Enthalpies=	-1298.134471
Sum of electronic and thermal Free Energies=	-1298.220037

Charge = 0; Multiplicity = 2

Ti	-0.00001900	-0.32384600	-0.00015600
C	-2.34972300	-0.72170500	0.46667200
C	-1.94302600	0.44031100	1.18434000
C	-1.63565800	1.45629400	0.22815500
C	-1.78790300	0.89762800	-1.08060600
C	-2.23381000	-0.44719600	-0.92930400
C	2.23320300	-0.44639800	0.93038000
C	1.78756400	0.89870100	1.07992800
C	1.63601700	1.45589700	-0.22954000
C	1.94364400	0.43878000	-1.18441100
C	2.34981500	-0.72249400	-0.46522400
Cl	-0.00021300	-2.68867500	-0.00020000
C	2.93017800	-1.96493700	-1.07717400
H	4.00522000	-1.82336200	-1.26002500
H	2.80744100	-2.83302500	-0.42710600
H	2.46044200	-2.20791200	-2.03499100
C	2.58682500	-1.39053100	2.04610300
H	2.34396900	-2.42448200	1.78626400
H	3.66102700	-1.34179500	2.27405000
H	2.04794300	-1.14681900	2.96765100
C	1.69264400	1.64311600	2.38505400
H	1.31524400	1.00780200	3.19322600
H	2.68053700	2.00959300	2.69846600
H	1.03475500	2.51402100	2.31563900
C	2.02752300	0.62160400	-2.67682900
H	1.32400400	1.37878400	-3.03673200
H	3.03417400	0.94319300	-2.98110700
H	1.81187200	-0.31009000	-3.20999700
C	-1.52810500	2.91906300	0.56092200
H	-2.52980400	3.31282800	0.78607300
H	-0.90959000	3.11131100	1.44295700
H	-1.13178200	3.50987200	-0.26651800
C	-1.69326200	1.64055900	-2.38660200
H	-2.68104900	2.00751400	-2.69979400
H	-1.03459300	2.51099300	-2.31856600
H	-1.31689700	1.00405200	-3.19431700

C	-2.58823300	-1.39246200	-2.04380200
H	-3.66246800	-1.34338400	-2.27151900
H	-2.04944500	-1.15016000	-2.96577600
H	-2.34585300	-2.42622200	-1.78280300
C	-2.92961900	-1.96349500	1.08039000
H	-4.00449700	-1.82172600	1.26404100
H	-2.80745500	-2.83225400	0.43111000
H	-2.45906200	-2.20549400	2.03805800
C	-2.02626300	0.62480700	2.67658800
H	-3.03308000	0.94571300	2.98103000
H	-1.80935500	-0.30601600	3.21078300
H	-1.32334400	1.38315200	3.03518200
C	1.52865100	2.91825400	-0.56415800
H	1.13241400	3.51015700	0.26253800
H	2.53038200	3.31162100	-0.78985700
H	0.91011600	3.10944000	-1.44641800

$Cp^*_2Ti^{IV}Cl(TEMPO)$-LANL2DZ (Entry 16)

E(UB3LYP)	-1782.318671
Zero-point correction=	0.716466
Thermal correction to Energy=	0.756959
Thermal correction to Enthalpy=	0.757903
Thermal correction to Gibbs Free Energy=	0.650168
Sum of electronic and zero-point Energies=	-1781.602205
Sum of electronic and thermal Energies=	-1781.561711
Sum of electronic and thermal Enthalpies=	-1781.560767
Sum of electronic and thermal Free Energies=	-1781.668502

Charge = 0; Multiplicity = 1

Ti	0.76843700	0.05780600	-0.15262000
C	0.86606900	2.62727000	-0.09527500
C	0.19455800	2.21563900	1.07410100
C	1.10067400	1.41018200	1.84409900
C	2.37977300	1.46842000	1.20368100
C	2.21487600	2.12367600	-0.03750200
C	0.99383000	-2.30430500	-1.04364700
C	0.90993100	-2.45656600	0.35948600
C	2.06696200	-1.85707300	0.94576100
C	2.92491100	-1.43221800	-0.12048000
C	2.25482800	-1.68502900	-1.33753800
Cl	0.75376500	0.64590000	-2.49950100
O	-1.07146200	-0.26890200	-0.05189200
C	-4.56309900	0.95640800	-0.75124500
C	-4.52892100	-0.29839100	1.37698800
C	-5.33080800	-0.04482000	0.10456800
H	-5.08007600	1.14357700	-1.70048600
H	-4.53355600	1.91551800	-0.21647000
H	-5.02275900	-1.03753100	2.02092600
H	-4.47221200	0.63627800	1.95122300
H	-6.32221900	0.35404200	0.35424600
H	-5.50520300	-0.97760200	-0.44510400
C	-2.44750800	1.81277600	-1.67108400
H	-2.44635200	2.61615000	-0.93017700
H	-1.42928500	1.62529500	-2.00428300
H	-3.02885500	2.15409800	-2.53633100
C	-3.14836500	-2.25057200	0.55446600
H	-2.25350600	-2.46803900	-0.02412300
H	-3.20907400	-2.96937300	1.37940300
H	-4.01627800	-2.42077000	-0.08694200
C	-3.09202400	-0.80334300	1.10084400
C	-2.34556100	-0.77720900	2.44570700
H	-1.30345900	-1.07473800	2.33014200
H	-2.36809600	0.22974200	2.87397900
H	-2.82642800	-1.46110200	3.15452700
N	-2.41096500	0.18490900	0.19499100

C	-3.10499500	0.55039400	-1.09424100
C	-3.06913600	-0.54921900	-2.17656400
H	-3.45010600	-0.13967200	-3.11938500
H	-2.04134300	-0.87473200	-2.34567000
H	-3.67790900	-1.42138500	-1.92741500
C	-0.00966400	-3.36714000	1.12120000
H	0.58144900	-4.18427200	1.56004700
H	-0.53630200	-2.88130300	1.94643300
H	-0.75679600	-3.82663000	0.47330300
C	0.05551700	-2.84671000	-2.08143300
H	0.46016300	-3.76155900	-2.53760900
H	-0.92188900	-3.09368400	-1.66000200
H	-0.10144300	-2.11870300	-2.88354300
C	2.88928100	-1.58190800	-2.69320000
H	3.56952100	-2.43432200	-2.84474500
H	2.14705000	-1.59620200	-3.49238900
H	3.47548400	-0.66507900	-2.80628300
C	4.39624100	-1.12806800	-0.05012600
H	4.95601000	-1.95243700	-0.51472400
H	4.67520800	-0.21933900	-0.59347800
H	4.75738800	-1.03699600	0.97505500
C	2.45496800	-2.10735700	2.37760300
H	2.71627500	-3.16801500	2.51107200
H	3.32476200	-1.52789800	2.69221500
H	1.63713700	-1.89591000	3.07331400
C	0.87145800	1.01089900	3.27725300
H	0.94916100	1.88946000	3.93550000
H	-0.11969600	0.57962800	3.43372900
H	1.61103400	0.28553400	3.62347200
C	3.68814200	1.27234100	1.91485300
H	3.84913500	2.14294500	2.56815500
H	3.71413200	0.39272100	2.55910700
H	4.53640700	1.22672400	1.23197000
C	3.28275800	2.48811600	-1.02798500
H	3.50708000	3.56320600	-0.97647000
H	4.21729600	1.95141600	-0.84281500
H	2.95812000	2.26573200	-2.04941300
C	0.40652600	3.62403900	-1.11679900
H	1.05985400	4.50745300	-1.09117800
H	0.45104300	3.21084800	-2.12907100
H	-0.61533600	3.96002700	-0.93133200
C	-1.13713800	2.70321000	1.56924700
H	-1.39044500	3.66209500	1.10581600
H	-1.93921600	1.99536700	1.34498300
H	-1.10155100	2.86360000	2.65375100

$Cp^*_2Ti^{III}Cl$-*N*-phenyl propanamide-LANL2DZ (Entry 17)

E(UB3LYP)	-1778.183839
Zero-point correction=	0.636119
Thermal correction to Energy=	0.675937
Thermal correction to Enthalpy=	0.676881
Thermal correction to Gibbs Free Energy=	0.564784
Sum of electronic and zero-point Energies=	-1777.547720
Sum of electronic and thermal Energies=	-1777.507902
Sum of electronic and thermal Enthalpies=	-1777.506958
Sum of electronic and thermal Free Energies=	-1777.619055

Charge = 0; Multiplicity = 2

Ti	1.13321200	0.12574000	0.00712600
C	2.46038000	0.13401400	2.09806200
C	1.07343600	0.19719900	2.42933100
C	0.47915500	-1.05346800	2.07827600
C	1.48289800	-1.87045700	1.49695100
C	2.71308000	-1.13123400	1.51082200
C	1.25026900	0.87737200	-2.37611100
C	0.18984600	-0.06432400	-2.33516900
C	0.72450400	-1.32858200	-1.95768600
C	2.14089000	-1.17228500	-1.81702100
C	2.46046800	0.20094500	-2.03124000
Cl	1.64533800	2.56376900	0.23308000
C	-1.21707800	0.19108700	-2.79427600
H	-1.29521300	0.03790900	-3.88058100
H	-1.93818800	-0.48020900	-2.32135100
H	-1.53562000	1.21980200	-2.59659100
C	1.15054700	2.28018600	-2.90194100
H	1.26323300	2.27963300	-3.99664800
H	0.18195600	2.73716600	-2.67426700
H	1.92049200	2.92600900	-2.47729300
C	3.83163900	0.81878500	-2.05471300
H	4.18960400	0.95966200	-3.08486000
H	3.82440600	1.79647200	-1.56272400
H	4.56695700	0.19256000	-1.53940300
C	3.13639100	-2.29906600	-1.83791300
H	3.28502600	-2.62745000	-2.87736800
H	4.11440800	-2.00066600	-1.45605300
H	2.80547300	-3.17517600	-1.27582500
C	-0.01858900	-2.63641300	-2.02249100
H	-0.10647200	-2.98446600	-3.06268100
H	0.48919100	-3.42559000	-1.46311900
H	-1.03866400	-2.55617700	-1.63089700
C	-0.89997200	-1.50744700	2.46383000
H	-0.89674600	-1.91200300	3.48677900
H	-1.62654900	-0.69162200	2.43944700
H	-1.27414400	-2.29918500	1.80807800

C	1.32960000	-3.34403800	1.23561100
H	1.43089300	-3.90692500	2.17545200
H	0.34802300	-3.59354400	0.82112900
H	2.08808200	-3.73317700	0.55238400
C	4.09476200	-1.67279700	1.26027700
H	4.61602000	-1.82100100	2.21700700
H	4.07799400	-2.63848600	0.75141900
H	4.71347500	-0.98958200	0.66801000
C	3.51480300	1.13720500	2.46985800
H	3.97198000	0.86520400	3.43343800
H	4.31670900	1.18208000	1.72608600
H	3.10086900	2.14279100	2.55757000
C	0.40911100	1.30392200	3.19801200
H	0.60403900	1.20560200	4.27585100
H	0.77651100	2.28206100	2.87542100
H	-0.67799900	1.28843000	3.06640000
O	-1.09266000	0.65201400	0.19996100
C	-1.96540700	1.53573700	0.25111700
C	-3.98535000	0.00836200	0.11500900
C	-2.75875000	4.03324400	0.24981500
C	-5.38712700	0.06442800	0.17318900
C	-3.35035900	-1.22955100	-0.05420000
H	-2.34210800	5.04370500	0.30327900
H	-3.29161100	3.95587600	-0.70613000
H	-3.48887600	3.95269400	1.06631800
C	-6.14515100	-1.09766800	0.06275800
H	-5.88421800	1.02354400	0.30667000
C	-4.12398800	-2.38658000	-0.16427900
H	-2.27255900	-1.27604500	-0.09004900
C	-5.51682000	-2.33331500	-0.10740000
H	-7.22864500	-1.03454000	0.11055300
H	-3.62256600	-3.34171500	-0.29591800
H	-6.10606800	-3.24137300	-0.19380900
C	-1.62180300	3.01272600	0.36613900
H	-0.84474400	3.20590400	-0.37860100
H	-1.09470500	3.13202100	1.31874100
N	-3.29715100	1.24040100	0.22409200
H	-3.90804700	2.04261700	0.28898600

$Cp^*_2Ti^{IV}Cl$-*N*-phenyl propanamide aza-enolate-LANL2DZ (Entry 18)

E(UB3LYP)	-1777.581158
Zero-point correction=	0.623903
Thermal correction to Energy=	0.663004
Thermal correction to Enthalpy=	0.663948
Thermal correction to Gibbs Free Energy=	0.555266
Sum of electronic and zero-point Energies=	-1776.957255
Sum of electronic and thermal Energies=	-1776.918154
Sum of electronic and thermal Enthalpies=	-1776.917210
Sum of electronic and thermal Free Energies=	-1777.025892

Charge = 0; Multiplicity = 1

Ti	0.93667100	0.07898400	0.12601200
C	1.34572300	-1.03401800	2.35387100
C	-0.01670900	-1.19137400	2.00258800
C	-0.08033800	-2.00791300	0.83109300
C	1.25257100	-2.37578800	0.48301800
C	2.14175000	-1.71095600	1.37977400
C	1.78772600	1.76499700	-1.57017200
C	0.66468300	1.11808100	-2.12477000
C	0.96513700	-0.27501700	-2.25904600
C	2.33727400	-0.45437000	-1.87526900
C	2.81881800	0.78436100	-1.38557200
Cl	1.93309900	1.75175000	1.50205000
C	-0.57128900	1.80030000	-2.62616700
H	-0.33387400	2.39063100	-3.52178900
H	-1.33864300	1.07717900	-2.90520100
H	-1.00654800	2.48225600	-1.89094100
C	1.95604000	3.24335000	-1.38851500
H	2.56253400	3.65449700	-2.20845000
H	0.99437200	3.76409400	-1.39963700
H	2.45798600	3.47997400	-0.44707700
C	4.22434400	1.08675700	-0.95410000
H	4.77830800	1.58134500	-1.76488000
H	4.23500100	1.75386000	-0.08730600
H	4.77329400	0.17867600	-0.68850800
C	3.22823300	-1.59884500	-2.27142400
H	3.81104300	-1.29534000	-3.15277300
H	3.94941500	-1.87401600	-1.49754700
H	2.66805100	-2.49030400	-2.55237800
C	0.09392800	-1.25988300	-2.99267100
H	0.10444300	-1.05399300	-4.07245900
H	0.43488400	-2.28934800	-2.86057600
H	-0.94855700	-1.21208000	-2.66205600
C	-1.32961000	-2.57427800	0.22107700
H	-1.70749400	-3.40808900	0.82996900
H	-2.12621700	-1.83100700	0.15507500

H	-1.14914100	-2.96277300	-0.78490400
C	1.58896900	-3.56008000	-0.37982500
H	1.29804200	-4.47190400	0.16122300
H	1.04783100	-3.57593200	-1.32898600
H	2.65599500	-3.64035300	-0.58904600
C	3.63392700	-1.86594800	1.48068100
H	3.90192800	-2.49135200	2.34361000
H	4.06172200	-2.34075800	0.59410800
H	4.12846000	-0.89811300	1.61732000
C	1.85969400	-0.43983400	3.62899300
H	1.90905500	-1.22604900	4.39734700
H	2.86036500	-0.01898000	3.51143100
H	1.20879100	0.35416900	4.00158500
C	-1.18165400	-0.70607600	2.81152800
H	-1.34465900	-1.36636400	3.67504600
H	-1.01608600	0.30356800	3.20123800
H	-2.10152500	-0.69693000	2.22547500
O	-0.83440100	0.78403200	0.20210000
C	-1.78776800	1.65974300	0.52992000
C	-3.69729100	0.33971800	-0.06998700
C	-2.38634900	3.96364600	1.49081400
C	-4.46784700	-0.44581800	0.81075900
C	-3.73463100	0.02325400	-1.44115500
H	-1.93999900	4.87858300	1.89811300
H	-3.00297500	4.23181700	0.62764000
H	-3.05440600	3.53781200	2.24502600
C	-5.20075500	-1.53582100	0.34331800
H	-4.48934000	-0.17557200	1.86271400
C	-4.47960900	-1.06179600	-1.90416500
H	-3.20127300	0.65769300	-2.13965500
C	-5.20830100	-1.85705100	-1.01662100
H	-5.78042000	-2.12989500	1.04587600
H	-4.49543400	-1.28157600	-2.96936400
H	-5.78760000	-2.70094600	-1.38071600
N	-3.05280500	1.47596500	0.42417200
C	-1.28807000	2.97399800	1.10469900
H	-0.60186800	3.42439500	0.37601300
H	-0.65165100	2.73966500	1.96626600

$Cp^*_2Ti^{III}Cl$-Methyl *N*-phenyl carbamate-LANL2DZ (Entry 19)

E(UB3LYP)	-1814.079024
Zero-point correction=	0.612527
Thermal correction to Energy=	0.652027
Thermal correction to Enthalpy=	0.652971
Thermal correction to Gibbs Free Energy=	0.542154
Sum of electronic and zero-point Energies=	-1813.466497
Sum of electronic and thermal Energies=	-1813.426997
Sum of electronic and thermal Enthalpies=	-1813.426052
Sum of electronic and thermal Free Energies=	-1813.536870

Charge = 0; Multiplicity = 2

Ti	1.08397300	-0.03442800	0.13493000
C	1.16082500	-1.72725300	1.96003600
C	-0.12326000	-1.74282100	1.33906400
C	0.04261000	-2.22064800	0.00072500
C	1.42373200	-2.48555900	-0.19974200
C	2.11877300	-2.15968000	1.01018800
C	1.93905000	2.15256200	-0.69104800
C	1.32320400	1.52712200	-1.80837400
C	2.04282800	0.33686400	-2.10909000
C	3.13754500	0.24609800	-1.19077800
C	3.04400100	1.34042000	-0.28476900
Cl	0.69223600	1.36976200	2.17732200
C	0.20764900	2.07117900	-2.65588800
H	0.60872500	2.52074200	-3.57610300
H	-0.49174600	1.28481300	-2.95977200
H	-0.36275400	2.84264400	-2.13395500
C	1.66178100	3.52574900	-0.15097000
H	2.49679900	4.19814600	-0.39518100
H	0.75496700	3.95467100	-0.58386600
H	1.54548500	3.50732700	0.93652700
C	4.02455600	1.70587900	0.79563700
H	4.74852400	2.45418900	0.43985800
H	3.50865200	2.12334300	1.66572200
H	4.59783000	0.83717900	1.13596300
C	4.35997000	-0.61258300	-1.36020000
H	5.08284800	-0.08764000	-2.00212200
H	4.86476300	-0.81306500	-0.41301300
H	4.14754700	-1.56969600	-1.84027100
C	1.83064800	-0.47822000	-3.35724700
H	2.04521000	0.12346200	-4.25244000
H	2.48570400	-1.35141200	-3.39355300
H	0.79761700	-0.83439500	-3.45724800
C	-1.04306200	-2.59125500	-0.97074200
H	-1.16215900	-3.68374600	-1.02109300
H	-2.00509400	-2.17069700	-0.67720500
H	-0.82865800	-2.24559800	-1.98974100

C	1.95408800	-3.30346700	-1.34465800
H	1.74117800	-4.36793000	-1.16371100
H	1.48319100	-3.04509200	-2.29663800
H	3.03580200	-3.21572100	-1.46624700
C	3.55288100	-2.46598500	1.35049300
H	3.60206800	-3.28276600	2.08455900
H	4.12679900	-2.78313400	0.47702300
H	4.06812900	-1.60835300	1.79909000
C	1.45194100	-1.46933800	3.41028500
H	1.56931600	-2.42430600	3.94530800
H	2.37414000	-0.89591100	3.54495800
H	0.65041600	-0.90466600	3.88855700
C	-1.41773700	-1.45894100	2.04818900
H	-1.65116900	-2.25884200	2.76503200
H	-1.35967600	-0.51755100	2.60483700
H	-2.25595200	-1.39172600	1.35050800
O	-1.16378400	0.56327400	-0.37730900
C	-1.86916300	1.49174000	0.01797600
C	-4.09159100	0.33881300	-0.14320000
C	-1.86736700	3.59845700	1.21290000
C	-5.21828000	0.12868000	0.66101100
C	-3.89553300	-0.43685900	-1.29077300
H	-1.10347600	4.36279100	1.34987100
H	-2.79008500	4.07676600	0.85519500
H	-2.02836100	3.08102600	2.16218800
C	-6.14549100	-0.85474400	0.31943500
H	-5.36147700	0.73098900	1.55489000
C	-4.82217500	-1.42854600	-1.61480700
H	-3.02656100	-0.26476200	-1.91354500
C	-5.94874400	-1.64065300	-0.81779200
H	-7.01697100	-1.01011800	0.94904100
H	-4.66335600	-2.03161800	-2.50435600
H	-6.66785200	-2.41071000	-1.08120100
N	-3.22204200	1.41258700	0.19461000
H	-3.68133100	2.23778400	0.55206700
O	-1.32899400	2.69858500	0.23977000

$Cp^*_2Ti^{IV}Cl$-Methyl *N*-phenyl carbamate aza-enolate-LANL2DZ (Entry 20)

E(UB3LYP)	-1813.487695
Zero-point correction=	0.600296
Thermal correction to Energy=	0.639029
Thermal correction to Enthalpy=	0.639973
Thermal correction to Gibbs Free Energy=	0.531992
Sum of electronic and zero-point Energies=	-1812.887399
Sum of electronic and thermal Energies=	-1812.848666
Sum of electronic and thermal Enthalpies=	-1812.847722
Sum of electronic and thermal Free Energies=	-1812.955703

Charge = 0; Multiplicity = 1

Ti	0.96548000	0.01318000	0.15853000
C	1.30357800	-1.70775300	1.96625400
C	-0.05984300	-1.70968000	1.57589200
C	-0.13025500	-2.16306300	0.22300800
C	1.19545200	-2.43915800	-0.21683600
C	2.09216200	-2.10063100	0.84595800
C	1.85952100	2.10467800	-0.87142300
C	0.80247000	1.64938700	-1.68920500
C	1.16328500	0.37536600	-2.22843000
C	2.50147200	0.09132900	-1.80367700
C	2.90479900	1.12259800	-0.91501500
Cl	1.69939500	1.22959300	2.03442000
C	-0.41757900	2.42757400	-2.07531900
H	-0.25016900	2.92500600	-3.04157200
H	-1.29237400	1.78284600	-2.18798200
H	-0.65583400	3.19846700	-1.34029800
C	1.93631800	3.44869700	-0.21033800
H	2.15278300	4.22252200	-0.96095100
H	0.99474900	3.69879100	0.28354900
H	2.72433000	3.47922800	0.54383400
C	4.26251100	1.27382000	-0.29042100
H	4.86893200	1.99766400	-0.85283300
H	4.18597700	1.63133000	0.74062900
H	4.81088600	0.32736400	-0.27933800
C	3.44319600	-0.88826400	-2.44538700
H	4.06691700	-0.34697800	-3.17104300
H	4.12574800	-1.36055200	-1.73504600
H	2.92223300	-1.67197300	-2.99521700
C	0.36509000	-0.33785000	-3.28637200
H	0.31887100	0.26615900	-4.20332500
H	0.80621500	-1.29935300	-3.55850700
H	-0.66749700	-0.51935300	-2.96881400
C	-1.38565600	-2.47601000	-0.53632600
H	-1.79493500	-3.44424400	-0.21463900
H	-2.15745800	-1.72142200	-0.37565500
H	-1.20226000	-2.54290300	-1.61298000

C	1.51855000	-3.30373700	-1.40405900
H	1.19436900	-4.33121900	-1.18576300
H	0.99961900	-2.99962000	-2.31640600
H	2.58792600	-3.34475600	-1.61355200
C	3.57072000	-2.36734300	0.92228800
H	3.77231800	-3.21145900	1.59637000
H	3.99624400	-2.62574100	-0.04958700
H	4.12262200	-1.50662700	1.31558100
C	1.81845900	-1.51769100	3.35969400
H	1.87539600	-2.49676100	3.85883900
H	2.81713800	-1.07449700	3.37223700
H	1.16391700	-0.87451700	3.95133600
C	-1.21616100	-1.39539100	2.47732400
H	-1.38453000	-2.21846600	3.18582500
H	-1.03143400	-0.48828500	3.06276700
H	-2.13717300	-1.25076800	1.91060500
O	-0.90266700	0.57831400	0.23896000
C	-1.74005700	1.51458200	0.61338700
C	-3.77446000	0.45189300	0.02250700
C	-1.95721400	3.63057200	1.66445300
C	-4.56922100	-0.34400500	0.87020700
C	-3.86732700	0.23547200	-1.36559700
H	-1.27385900	4.38423000	2.06127900
H	-2.59518500	4.05862800	0.88520200
H	-2.59642700	3.23666200	2.45939500
C	-5.39213800	-1.34298300	0.35133400
H	-4.53184100	-0.15647100	1.93967300
C	-4.69861500	-0.75994400	-1.88001700
H	-3.29680900	0.87076400	-2.03663000
C	-5.46071300	-1.56178900	-1.02711900
H	-5.98980500	-1.94830400	1.02883000
H	-4.75391100	-0.90593300	-2.95648300
H	-6.10790400	-2.33555800	-1.43074500
N	-3.02383100	1.49817800	0.56515900
O	-1.11749400	2.60315500	1.13378000

$Cp_2Ti^{III}Cl$-LANL2DZ (Entry 21)

E(UB3LYP)	-905.459237
Zero-point correction=	0.170342
Thermal correction to Energy=	0.180766
Thermal correction to Enthalpy=	0.181710
Thermal correction to Gibbs Free Energy=	0.132935
Sum of electronic and zero-point Energies=	-905.288895
Sum of electronic and thermal Energies=	-905.278471
Sum of electronic and thermal Enthalpies=	-905.277527
Sum of electronic and thermal Free Energies=	-905.326301

Charge = 0; Multiplicity = 1

Ti	-0.00038200	0.10977400	-0.00257600
C	2.31899900	0.36140200	0.53130100
C	1.83506700	-0.78900700	1.20622900
C	1.47163900	-1.74306300	0.21919400
C	1.71045300	-1.17409100	-1.06156300
C	2.24116000	0.12453000	-0.86404600
C	-2.20709200	0.08301300	0.94030400
C	-1.70218900	-1.23859500	1.00438200
C	-1.51794200	-1.69834400	-0.32810600
C	-1.89187400	-0.65526500	-1.21505100
C	-2.32548700	0.44224100	-0.42623300
H	2.63253000	1.28573700	0.99575700
H	1.76978800	-0.92126300	2.27884100
H	1.07744500	-2.73136600	0.41205200
H	1.52387800	-1.64985100	-2.01615800
H	2.48994000	0.83762600	-1.63918000
H	-2.41870800	0.72772300	1.78370900
H	-1.49155100	-1.79863000	1.90679300
H	-1.15116500	-2.67315300	-0.61957200
H	-1.86499200	-0.69439800	-2.29674600
H	-2.63560900	1.40830500	-0.79799100
Cl	0.02826200	2.44219500	0.00062900

$Cp_2Ti^{IV}Cl(TEMPO)$-LANL2DZ (Entry 22)

```
 E(UB3LYP)                                          -1389.197149
 Zero-point correction=                           0.436726
 Thermal correction to Energy=                    0.460790
 Thermal correction to Enthalpy=                  0.461734
 Thermal correction to Gibbs Free Energy=         0.385831
 Sum of electronic and zero-point Energies=          -1388.760424
 Sum of electronic and thermal Energies=             -1388.736359
 Sum of electronic and thermal Enthalpies=           -1388.735415
 Sum of electronic and thermal Free Energies=        -1388.811318

Charge = 0; Multiplicity = 1
 Ti                   1.45991100    0.04211200    0.00402900
 C                    1.41832900    1.75813400    1.70934800
 C                    0.64228000    0.68110300    2.17509300
 C                    1.50025100   -0.44006700    2.33305600
 C                    2.82536000   -0.01986500    2.03422100
 C                    2.77245700    1.32258800    1.61235600
 C                    1.68314600   -1.29079700   -2.06635300
 C                    1.45838000   -2.20246700   -1.01411800
 C                    2.55338200   -2.12283500   -0.11988900
 C                    3.49113100   -1.19353300   -0.65844600
 C                    2.94996400   -0.68288400   -1.85415400
 H                    1.05214400    2.73030500    1.41759300
 H                   -0.43525700    0.66357400    2.25795700
 H                    1.20230700   -1.42586400    2.66460300
 H                    3.71127500   -0.63745000    2.07919100
 H                    3.60149900    1.91545400    1.25046600
 H                    0.99659100   -1.05474800   -2.86777600
 H                    0.57408600   -2.80635200   -0.87383600
 H                    2.67586000   -2.70389900    0.78456300
 H                    4.44126000   -0.91329100   -0.22475600
 H                    3.39464600    0.08064800   -2.47417800
 Cl                   1.76394300    2.02044000   -1.32851000
 O                   -0.35736000   -0.16886400   -0.27309600
 C                   -3.76176700    1.29152600    0.16449000
 C                   -3.77944100   -1.09352800    0.84391500
 C                   -4.55237900   -0.01229300    0.09249000
 H                   -4.27025000    2.09282700   -0.38542800
 H                   -3.71195000    1.61164600    1.21438200
 H                   -4.30030500   -2.05826000    0.80144400
 H                   -3.71920500   -0.81077600    1.90375400
 H                   -5.54389500    0.12312400    0.54248200
 H                   -4.72591800   -0.30675200   -0.94990900
 C                   -1.59280800    2.48444300    0.04039700
 H                   -1.52779700    2.55027700    1.13173000
 H                   -0.59154500    2.55019800   -0.38684600
```

H	-2.16588400	3.34948300	-0.31411400
C	-2.37609300	-2.03510900	-1.05547400
H	-1.41272200	-1.94483900	-1.56094000
H	-2.58823900	-3.09994200	-0.90226800
H	-3.14486900	-1.64541400	-1.72641800
C	-2.34405200	-1.30672000	0.30906800
C	-1.60657700	-2.19730800	1.32916300
H	-0.60001500	-2.45628700	0.99367600
H	-1.52941100	-1.68858200	2.29582600
H	-2.16333000	-3.12988900	1.47684100
N	-1.64680400	0.02707300	0.29853000
C	-2.31726500	1.19379600	-0.38349000
C	-2.30490100	1.12156500	-1.92616800
H	-2.65135400	2.07745100	-2.33572100
H	-1.28844200	0.95128200	-2.28875900
H	-2.95420900	0.33902900	-2.32548800

N-phenyl propanamide-CPCM (Entry 23)

```
 E(UB3LYP)                                            -479.589123
 Zero-point correction=                           0.184534
 Thermal correction to Energy=                    0.194920
 Thermal correction to Enthalpy=                  0.195864
 Thermal correction to Gibbs Free Energy=         0.147089
 Sum of electronic and zero-point Energies=           -479.404590
 Sum of electronic and thermal Energies=              -479.394203
 Sum of electronic and thermal Enthalpies=            -479.393259
 Sum of electronic and thermal Free Energies=         -479.442034

Charge = 0; Multiplicity = 1
 C                 -0.79297500   -0.29823800   -0.00710100
 C                 -1.21785600    1.04054800   -0.01975700
 C                 -1.75330900   -1.32423600    0.02742200
 C                 -2.58407400    1.32867200    0.00056700
 H                 -0.48291200    1.83204800   -0.04477600
 N                  0.56355100   -0.68663400   -0.02676800
 C                 -3.11207800   -1.01989000    0.04757400
 H                 -1.42995300   -2.36270400    0.03813000
 C                 -3.53863400    0.31081700    0.03424700
 H                 -2.90014000    2.36861100   -0.01007600
 C                  1.69650200    0.09022000   -0.06688400
 H                  0.71711600   -1.68753900   -0.03049000
 H                 -3.83777200   -1.82819100    0.07375900
 H                 -4.59819500    0.54900000    0.04998600
 C                  2.99160200   -0.71754300   -0.14750200
 O                  1.68289500    1.31939500   -0.06026000
 C                  4.22817800    0.11065600    0.19807500
 H                  2.91773400   -1.59500200    0.50698500
 H                  3.07262700   -1.10941100   -1.17129600
 H                  5.13308000   -0.49368800    0.08022300
 H                  4.18872100    0.46814500    1.23234500
 H                  4.30753700    0.98397000   -0.45517500
```

N-phenyl propanamidyl radical-CPCM (Entry 24)

```
 E(UB3LYP)                                          -478.931093
 Zero-point correction=                           0.170223
 Thermal correction to Energy=                    0.180573
 Thermal correction to Enthalpy=                  0.181517
 Thermal correction to Gibbs Free Energy=         0.132344
 Sum of electronic and zero-point Energies=          -478.760870
 Sum of electronic and thermal Energies=             -478.750520
 Sum of electronic and thermal Enthalpies=           -478.749575
 Sum of electronic and thermal Free Energies=        -478.798749


Charge = 0; Multiplicity = 2
 C                  1.65012900   -0.14307000    0.33382500
 O                  1.77142800    0.70403600    1.21548000
 N                  0.50654600   -0.92007200    0.19155100
 C                 -0.72497400   -0.39716300    0.07459500
 C                 -1.00525500    0.99464300   -0.13451100
 C                 -1.83029700   -1.30760200    0.11913900
 C                 -2.31033700    1.42824700   -0.27838400
 H                 -0.18298900    1.69998100   -0.16929100
 C                 -3.12849200   -0.85417100   -0.02544700
 H                 -1.61103200   -2.35962600    0.27143300
 C                 -3.37806900    0.51438200   -0.22497400
 H                 -2.51319900    2.48339200   -0.43676100
 H                 -3.95664700   -1.55543400    0.01331400
 H                 -4.39810900    0.86799500   -0.34092300
 C                  2.77565000   -0.53023000   -0.61142800
 H                  2.98911300   -1.59527200   -0.45183400
 H                  2.38808600   -0.46380500   -1.63756900
 C                  4.03470900    0.31728000   -0.43977500
 H                  4.80702600   -0.00391900   -1.14597800
 H                  3.82640100    1.37684600   -0.61945400
 H                  4.43571800    0.22416000    0.57411700
```

Methyl *N*-phenylcarbamate-CPCM (Entry 25)

```
E(UB3LYP)                                          -515.498507
Zero-point correction=                           0.160934
Thermal correction to Energy=                    0.171033
Thermal correction to Enthalpy=                  0.171977
Thermal correction to Gibbs Free Energy=         0.123979
Sum of electronic and zero-point Energies=          -515.337573
Sum of electronic and thermal Energies=             -515.327474
Sum of electronic and thermal Enthalpies=           -515.326530
Sum of electronic and thermal Free Energies=        -515.374528

Charge = 0; Multiplicity = 1
C                  1.71827700    0.09214700   -0.00017600
O                  1.75549400    1.31288200   -0.00003800
C                 -0.75325800   -0.30420500   -0.00011000
C                 -1.17046500    1.03600000    0.00004000
C                 -1.71686200   -1.32679000   -0.00016600
C                 -2.53528000    1.33062900    0.00013600
H                 -0.43323100    1.82661200    0.00007300
C                 -3.07430700   -1.01548700   -0.00006800
H                 -1.39729400   -2.36628000   -0.00029200
C                 -3.49491700    0.31701600    0.00008500
H                 -2.84586000    2.37221000    0.00025500
H                 -3.80370900   -1.82083500   -0.00011200
H                 -4.55343800    0.55997000    0.00016100
C                  4.07652900   -0.01220300    0.00030200
H                  4.83429200   -0.79547500    0.00034400
H                  4.17493900    0.61117100   -0.89189300
H                  4.17470300    0.61103100    0.89262300
O                  2.81619600   -0.70342300    0.00007900
N                  0.59982500   -0.69757500   -0.00022600
H                  0.77900400   -1.69369700   -0.00015400
```

Methyl *N*-phenylcarbamyl radical-CPCM (Entry 26)

```
E(UB3LYP)                                          -514.842259
Zero-point correction=                           0.147331
Thermal correction to Energy=                    0.157202
Thermal correction to Enthalpy=                  0.158147
Thermal correction to Gibbs Free Energy=         0.110354
Sum of electronic and zero-point Energies=          -514.694928
Sum of electronic and thermal Energies=             -514.685056
Sum of electronic and thermal Enthalpies=           -514.684112
Sum of electronic and thermal Free Energies=        -514.731904

Charge = 0; Multiplicity = 2
C                  1.67006700   -0.11333600    0.29015500
O                  1.82257900    0.77905800    1.11188800
N                  0.54972400   -0.92434900    0.16639600
C                 -0.68166100   -0.39754500    0.06539400
C                 -0.97426100    0.99339100   -0.13529200
C                 -1.78039300   -1.31640200    0.12124300
C                 -2.28359800    1.41700300   -0.26346600
H                 -0.15827700    1.70552300   -0.17500700
C                 -3.08294300   -0.87259700   -0.00794300
H                 -1.55077900   -2.36681000    0.26857400
C                 -3.34429800    0.49485200   -0.20100500
H                 -2.49616100    2.47102100   -0.41582800
H                 -3.90541300   -1.57988100    0.03838300
H                 -4.36800900    0.84166100   -0.30392300
C                  3.88084500    0.18447100   -0.47332000
H                  4.51767300   -0.25956200   -1.23796900
H                  3.73191000    1.24873700   -0.67154500
H                  4.32701100    0.05773100    0.51615100
O                  2.63135000   -0.52743300   -0.55666300
```

TEMPO-CPCM (Entry 27)

E(UB3LYP) -483.724963
Zero-point correction= 0.263016
Thermal correction to Energy= 0.275057
Thermal correction to Enthalpy= 0.276001
Thermal correction to Gibbs Free Energy= 0.226310
Sum of electronic and zero-point Energies= -483.461947
Sum of electronic and thermal Energies= -483.449906
Sum of electronic and thermal Enthalpies= -483.448961
Sum of electronic and thermal Free Energies= -483.498652

Charge = 0; Multiplicity = 2

C	-2.12281100	0.13477100	0.00000000
C	-1.36007900	0.58495500	1.24680200
C	0.07292500	0.02057200	1.33293000
C	0.07292500	0.02057200	-1.33293000
C	-1.36007900	0.58495500	-1.24680200
H	-1.30695100	1.68211100	1.24616500
H	-1.89219300	0.29612300	2.16102500
H	-2.26633400	-0.95294200	0.00000000
H	-3.12569400	0.57768100	0.00000000
H	-1.30695100	1.68211100	-1.24616500
H	-1.89219300	0.29612300	-2.16102500
N	0.75919000	0.14825500	0.00000000
O	2.02850300	-0.06749400	0.00000000
C	0.88490600	0.84172200	2.34803600
H	0.37926700	0.81864800	3.31932400
H	1.89199700	0.43722900	2.46710400
H	0.96473700	1.88578100	2.02655200
C	0.07292500	-1.46277600	1.76033600
H	1.08750000	-1.86718100	1.69706000
H	-0.27176800	-1.54979100	2.79658900
H	-0.58338600	-2.07535600	1.13551600
C	0.88490600	0.84172200	-2.34803600
H	1.89199700	0.43722900	-2.46710400
H	0.37926700	0.81864800	-3.31932400
H	0.96473700	1.88578100	-2.02655200
C	0.07292500	-1.46277600	-1.76033600
H	1.08750000	-1.86718100	-1.69706000
H	-0.58338600	-2.07535600	-1.13551600
H	-0.27176800	-1.54979100	-2.79658900

$Cp^*_2Ti^{III}Cl$-CPCM (Entry 28)

```
 E(UB3LYP)                                          -2089.979981
 Zero-point correction=                              0.448932
 Thermal correction to Energy=                       0.477112
 Thermal correction to Enthalpy=                     0.478056
 Thermal correction to Gibbs Free Energy=            0.392926
 Sum of electronic and zero-point Energies=          -2089.531049
 Sum of electronic and thermal Energies=             -2089.502869
 Sum of electronic and thermal Enthalpies=           -2089.501925
 Sum of electronic and thermal Free Energies=        -2089.587055

Charge = 0; Multiplicity = 2
 Ti                -0.00003200   -0.32474400   -0.00021600
 C                 -2.35940100   -0.71497000    0.46307400
 C                 -1.95349900    0.44813900    1.17976200
 C                 -1.63693400    1.46049300    0.22178400
 C                 -1.78829100    0.89954100   -1.08699600
 C                 -2.23932300   -0.44330600   -0.93372500
 C                  2.23866400   -0.44275800    0.93477200
 C                  1.78802800    0.90039800    1.08636500
 C                  1.63746500    1.45999300   -0.22309100
 C                  1.95419000    0.44653700   -1.17981500
 C                  2.35940700   -0.71593700   -0.46167700
 Cl                -0.00039800   -2.75251400   -0.00018200
 C                  2.95514100   -1.94925600   -1.07918400
 H                  4.02174700   -1.78570900   -1.28865900
 H                  2.87322200   -2.81513300   -0.41931100
 H                  2.47346000   -2.20855000   -2.02721300
 C                  2.59886300   -1.37827200    2.05597300
 H                  2.43407100   -2.42264400    1.77723900
 H                  3.65699400   -1.27120900    2.33285500
 H                  2.00875900   -1.17645400    2.95619100
 C                  1.68419000    1.63826400    2.39463800
 H                  1.29767200    0.99948600    3.19550700
 H                  2.67019900    1.99946800    2.71900900
 H                  1.03077000    2.51179600    2.32395000
 C                  2.04915600    0.63676000   -2.67066800
 H                  1.33396000    1.38029400   -3.03485400
 H                  3.05144000    0.98159100   -2.96302700
 H                  1.86011600   -0.29678600   -3.21051100
 C                 -1.52772700    2.92403000    0.55273300
 H                 -2.52981000    3.31809600    0.77429600
 H                 -0.91299400    3.11737900    1.43663800
 H                 -1.12906600    3.51316700   -0.27430400
 C                 -1.68466300    1.63598500   -2.39609000
 H                 -2.67053800    1.99777300   -2.72022100
 H                 -1.03037500    2.50898300   -2.32671700
 H                 -1.29923000    0.99602700   -3.19653700
 C                 -2.60035500   -1.37987200   -2.05377200
 H                 -3.65842200   -1.27228300   -2.33069100
 H                 -2.01015800   -1.17961000   -2.95428100
 H                 -2.43634200   -2.42402800   -1.77380700
 C                 -2.95482200   -1.94758900    1.08227100
 H                 -4.02126600   -1.78375900    1.29234000
 H                 -2.87342000   -2.81416900    0.42325400
```

H	-2.47249100	-2.20591900	2.03023900
C	-2.04780600	0.63994400	2.67045300
H	-3.05023100	0.98423700	2.96295800
H	-1.85766300	-0.29281800	3.21127200
H	-1.33306500	1.38450900	3.03339600
C	1.52861400	2.92315700	-0.55579300
H	1.13005800	3.51337400	0.27052300
H	2.53078400	3.31673800	-0.77782000
H	0.91393100	3.11556900	-1.43994500

$Cp^*_2Ti^{IV}Cl(TEMPO)$-CPCM (Entry 29)

E(UB3LYP)	-2573.693774
Zero-point correction=	0.715756
Thermal correction to Energy=	0.756206
Thermal correction to Enthalpy=	0.757151
Thermal correction to Gibbs Free Energy=	0.649762
Sum of electronic and zero-point Energies=	-2572.978018
Sum of electronic and thermal Energies=	-2572.937568
Sum of electronic and thermal Enthalpies=	-2572.936624
Sum of electronic and thermal Free Energies=	-2573.044012

Charge = 0; Multiplicity = 1

Ti	0.77092500	0.05665500	-0.16555100
C	0.85413500	2.61723200	-0.15063500
C	0.19323400	2.23573800	1.03734700
C	1.11217000	1.46508500	1.82572500
C	2.38350900	1.50269900	1.16971900
C	2.20643400	2.12595000	-0.08743900
C	0.98633100	-2.35042700	-0.98607700
C	0.90211400	-2.45359900	0.42143800
C	2.05595400	-1.82816800	0.98769900
C	2.91156300	-1.43307700	-0.09221900
C	2.24332000	-1.73288700	-1.30040000
Cl	0.75874700	0.59434500	-2.56721000
O	-1.06492800	-0.26205000	-0.07533700
C	-4.57045000	0.93738300	-0.76024100
C	-4.50703900	-0.25876800	1.40179000
C	-5.32648900	-0.03838300	0.13447400
H	-5.09803500	1.09544200	-1.70909400
H	-4.53702100	1.91164200	-0.25419600
H	-4.99276100	-0.97964300	2.07164000
H	-4.44091400	0.69058600	1.95014300
H	-6.31210500	0.37195900	0.38757500
H	-5.51343800	-0.98538300	-0.38584700
C	-2.46449900	1.77445200	-1.71691200
H	-2.46814800	2.59626600	-0.99661600
H	-1.44239800	1.58515000	-2.03701000
H	-3.04615600	2.09053700	-2.59167300
C	-3.14370300	-2.23283100	0.60850200
H	-2.24889600	-2.47640900	0.04059400
H	-3.21595400	-2.92859400	1.45157400
H	-4.01057500	-2.41004400	-0.03221100
C	-3.07501700	-0.77457800	1.12048700
C	-2.31015400	-0.71840600	2.45321300
H	-1.26700600	-1.00670800	2.32718900
H	-2.33722400	0.29496900	2.86546100
H	-2.77328100	-1.39555300	3.17948500
N	-2.40533400	0.19327200	0.18213400
C	-3.11499300	0.52464200	-1.10627000
C	-3.08951900	-0.60327600	-2.15976300
H	-3.45408600	-0.21406800	-3.11771000
H	-2.06693900	-0.95756700	-2.30311600
H	-3.71789600	-1.45519400	-1.89148500
C	-0.01114300	-3.34711400	1.21159000
H	0.58506100	-4.15429400	1.66123500

H	-0.52650400	-2.84427700	2.03334500
H	-0.76572900	-3.81981100	0.58207900
C	0.05464300	-2.94927700	-1.99978900
H	0.43782700	-3.91187500	-2.36764700
H	-0.93970800	-3.13065900	-1.58492100
H	-0.06168500	-2.29247100	-2.86748100
C	2.88779400	-1.69600000	-2.65485700
H	3.53291400	-2.57928500	-2.77654100
H	2.15085800	-1.70772100	-3.45941100
H	3.51810500	-0.81191100	-2.78967600
C	4.38372100	-1.12806700	-0.02982500
H	4.94230600	-1.97114700	-0.46058700
H	4.66928800	-0.24199700	-0.60599000
H	4.74160100	-0.99863800	0.99173200
C	2.44440700	-2.02835500	2.42751300
H	2.71068600	-3.08271200	2.59364900
H	3.31093800	-1.43534300	2.72331900
H	1.62528800	-1.79994500	3.11584900
C	0.89552500	1.10134000	3.27054000
H	0.93839500	2.00305400	3.89906300
H	-0.07816200	0.63725400	3.44239800
H	1.66239400	0.41743100	3.63959200
C	3.70044900	1.33218300	1.87238800
H	3.86318400	2.22272900	2.49702100
H	3.73763900	0.47354400	2.54323900
H	4.54196600	1.27032900	1.18269900
C	3.27716700	2.49708500	-1.07370200
H	3.55202200	3.55588400	-0.96348000
H	4.18888500	1.90977200	-0.93594700
H	2.93352700	2.35285900	-2.10226500
C	0.38496700	3.60192600	-1.18138700
H	1.03090900	4.49061000	-1.16354800
H	0.43038500	3.18600600	-2.19218300
H	-0.63885400	3.93169200	-0.99577200
C	-1.13581600	2.73570300	1.52944300
H	-1.37818700	3.69777100	1.06611600
H	-1.94486000	2.03670900	1.30386800
H	-1.10163300	2.89305000	2.61385400

$Cp^*_2Ti^{III}Cl$-*N*-phenyl propanamide-CPCM (Entry 30)

E(UB3LYP)	-2569.564138
Zero-point correction=	0.635846
Thermal correction to Energy=	0.675531
Thermal correction to Enthalpy=	0.676475
Thermal correction to Gibbs Free Energy=	0.565333
Sum of electronic and zero-point Energies=	-2568.928292
Sum of electronic and thermal Energies=	-2568.888607
Sum of electronic and thermal Enthalpies=	-2568.887663
Sum of electronic and thermal Free Energies=	-2568.998805

Charge = 0; Multiplicity = 2

Ti	1.12075300	0.13861500	0.00087900
C	1.38792600	0.64256700	2.44847300
C	0.26218900	-0.21862200	2.36370700
C	0.69497300	-1.47415900	1.84876500
C	2.10989600	-1.39515700	1.65104900
C	2.53366600	-0.07313700	1.98368300
C	1.03871700	0.46698500	-2.41342700
C	0.35513500	-0.76618500	-2.18868000
C	1.29522000	-1.71183500	-1.70265600
C	2.57810300	-1.07064900	-1.65585100
C	2.41833300	0.26688000	-2.10107600
Cl	1.72524900	2.61718900	-0.00382900
C	-1.05286900	-1.06960600	-2.61536800
H	-1.07622500	-1.32802600	-3.68422200
H	-1.47753700	-1.91693800	-2.07117000
H	-1.72239000	-0.21745900	-2.47439900
C	0.45013600	1.68260600	-3.07284300
H	0.55764300	1.62758100	-4.16610400
H	-0.61976500	1.78011600	-2.86241900
H	0.94216200	2.59778900	-2.73450400
C	3.54752800	1.21362700	-2.39687400
H	3.97032700	1.00548300	-3.39117500
H	3.21544700	2.25334800	-2.38371800
H	4.36516600	1.11706300	-1.67449200
C	3.91708400	-1.74085500	-1.50018700
H	4.40861100	-1.81931000	-2.48050600
H	4.59912200	-1.17897300	-0.85291400
H	3.83378600	-2.75346200	-1.10194200
C	1.02896300	-3.18750800	-1.57544200
H	1.10774600	-3.67526800	-2.55814500
H	1.74126200	-3.68976700	-0.91721200
H	0.02311000	-3.39553300	-1.19867500
C	-0.11772700	-2.74182100	1.83555600
H	-0.07830900	-3.23736400	2.81712900
H	-1.17392800	-2.55605700	1.61957500
H	0.24942700	-3.46257900	1.10092600
C	3.02224200	-2.58513400	1.53231800
H	3.15785200	-3.03310100	2.52795600
H	2.62304300	-3.37169600	0.88818900
H	4.01531100	-2.31792100	1.16699100
C	3.95545100	0.41751300	2.04075600
H	4.39383800	0.26329500	3.03756600
H	4.59681800	-0.10657100	1.32469300

H	4.01733700	1.48719200	1.81873000
C	1.39760200	1.98512400	3.12260500
H	1.45030200	1.85746800	4.21413600
H	2.25417300	2.58656700	2.81383100
H	0.49549900	2.56626300	2.90700500
C	-1.10545700	0.09369900	2.90193300
H	-1.15373100	-0.13688800	3.97606100
H	-1.35882900	1.15304400	2.79398700
H	-1.88863100	-0.48940200	2.41149300
O	-1.05379000	0.73137300	-0.05775500
C	-1.95529600	1.59390400	-0.05262900
C	-3.93392500	0.01545900	-0.04633600
C	-2.79946400	4.07290900	-0.15788700
C	-5.33536400	0.04434800	-0.13275000
C	-3.27273700	-1.21552800	0.06102200
H	-2.40224600	5.09247100	-0.15238800
H	-3.34568000	3.94430300	-1.09964200
H	-3.51052300	4.00496400	0.67418800
C	-6.06543000	-1.14110900	-0.11137700
H	-5.85230900	0.99725100	-0.21722800
C	-4.01827700	-2.39654300	0.08080600
H	-2.19531600	-1.23995400	0.11784100
C	-5.41080000	-2.37109600	-0.00456900
H	-7.14874600	-1.10016700	-0.17926100
H	-3.49588800	-3.34582100	0.16275700
H	-5.97954500	-3.29601100	0.01131500
N	-3.27267300	1.26757500	-0.06145700
H	-3.90322800	2.05847800	-0.07868600
C	-1.64051000	3.08106900	-0.02229200
H	-0.89538800	3.24785500	-0.80406700
H	-1.09837600	3.25551200	0.91389200

$Cp^*_2Ti^{IV}Cl$-*N*-phenyl propanamide aza-enolate – CPCM (Entry 31)

```
 E(UB3LYP)                                          -2568.962201
 Zero-point correction=                           0.623164
 Thermal correction to Energy=                    0.662336
 Thermal correction to Enthalpy=                  0.663281
 Thermal correction to Gibbs Free Energy=         0.554136
 Sum of electronic and zero-point Energies=          -2568.339036
 Sum of electronic and thermal Energies=             -2568.299864
 Sum of electronic and thermal Enthalpies=           -2568.298920
 Sum of electronic and thermal Free Energies=        -2568.408065

Charge = 0; Multiplicity = 1
 Ti                  0.95044400    0.08934400    0.12782900
 C                   1.38420000   -1.00830800    2.35470300
 C                   0.01659300   -1.17505400    2.02612500
 C                  -0.05925900   -2.00042300    0.86065600
 C                   1.26926700   -2.36453100    0.49430900
 C                   2.16918000   -1.69098200    1.37460700
 C                   1.75953000    1.75168300   -1.59187800
 C                   0.63303200    1.09704300   -2.13462600
 C                   0.93926900   -0.29498000   -2.26687100
 C                   2.31260300   -0.46879900   -1.88822000
 C                   2.79481100    0.77591800   -1.40972900
 Cl                  1.95126400    1.81122400    1.49539000
 C                  -0.60056100    1.77865900   -2.64391500
 H                  -0.35292800    2.37644400   -3.53112600
 H                  -1.36181400    1.05625600   -2.94105900
 H                  -1.04487800    2.45735200   -1.91069200
 C                   1.92266300    3.23514100   -1.44446300
 H                   2.41657300    3.64410400   -2.33723600
 H                   0.95918300    3.74299100   -1.34496700
 H                   2.53437200    3.49357500   -0.57754800
 C                   4.21249300    1.08016900   -1.01965500
 H                   4.77638700    1.44586900   -1.88938300
 H                   4.25700600    1.85270900   -0.24746300
 H                   4.73300000    0.19476200   -0.64421000
 C                   3.20735500   -1.60726300   -2.29243300
 H                   3.76260500   -1.30148400   -3.19019300
 H                   3.95365100   -1.86279900   -1.53638600
 H                   2.65411900   -2.50887900   -2.55207100
 C                   0.07216100   -1.28850900   -2.99357700
 H                   0.10249000   -1.10281000   -4.07599000
 H                   0.40211500   -2.31744800   -2.83663400
 H                  -0.97584400   -1.22518200   -2.68460600
 C                  -1.31129000   -2.59070800    0.27912600
 H                  -1.62812600   -3.46325900    0.86806000
 H                  -2.13649200   -1.87643600    0.27974100
 H                  -1.15948500   -2.93286600   -0.74809300
 C                   1.59752000   -3.55617000   -0.36155200
 H                   1.32092600   -4.46081700    0.19794600
 H                   1.03905000   -3.58916000   -1.29971400
 H                   2.66051400   -3.63406000   -0.58846300
 C                   3.66011300   -1.86587000    1.46737700
 H                   3.91814800   -2.51952800    2.31173100
```

H	4.08141800	-2.32059500	0.56816600
H	4.17150100	-0.91181000	1.63328700
C	1.91332000	-0.42172000	3.62784500
H	1.97202300	-1.21359800	4.38863900
H	2.91491500	-0.00469000	3.50376700
H	1.26565900	0.36678800	4.01820500
C	-1.13950200	-0.70001700	2.85456900
H	-1.30318700	-1.37939400	3.70241100
H	-0.96509400	0.29776500	3.27026100
H	-2.06319200	-0.66964600	2.27500600
O	-0.84413100	0.79444800	0.22178800
C	-1.79988200	1.65480700	0.54296500
C	-3.70198000	0.31870500	-0.05638300
C	-2.41082400	3.97595400	1.48691900
C	-4.45785500	-0.48275800	0.82341900
C	-3.75473000	0.01886100	-1.43111400
H	-1.96055700	4.89355900	1.88306500
H	-3.02234200	4.24234200	0.61915500
H	-3.07984100	3.56660400	2.24990900
C	-5.19420400	-1.56929400	0.35091700
H	-4.46399800	-0.23402500	1.88121500
C	-4.49971000	-1.06465500	-1.89945200
H	-3.22968600	0.66026000	-2.12993800
C	-5.21758100	-1.87237500	-1.01341600
H	-5.76087500	-2.17580100	1.05329600
H	-4.52294800	-1.27277800	-2.96654200
H	-5.79680100	-2.71465400	-1.38123400
N	-3.06936900	1.46441500	0.44001700
C	-1.31571700	2.97879400	1.11287000
H	-0.62854300	3.42628900	0.38425000
H	-0.68775400	2.75127100	1.98238900

$Cp^*_2Ti^{III}Cl$-Methyl *N*-phenyl carbamate - CPCM (Entry 32)

```
 E(UB3LYP)                                          -2605.463499
 Zero-point correction=                              0.611854
 Thermal correction to Energy=                       0.651497
 Thermal correction to Enthalpy=                     0.652441
 Thermal correction to Gibbs Free Energy=            0.541507
 Sum of electronic and zero-point Energies=          -2604.851645
 Sum of electronic and thermal Energies=             -2604.812002
 Sum of electronic and thermal Enthalpies=           -2604.811058
 Sum of electronic and thermal Free Energies=        -2604.921991

Charge = 0; Multiplicity = 2
 Ti                  1.09730500    0.09628200    0.00506800
 C                   1.35365100    0.54523100    2.44092300
 C                   0.11321200   -0.14172000    2.33472400
 C                   0.36887300   -1.45324300    1.84532700
 C                   1.78431300   -1.58429400    1.67547300
 C                   2.39266400   -0.34149700    2.01812900
 C                   1.12519100    0.45718800   -2.40583900
 C                   0.20151700   -0.61409700   -2.20697100
 C                   0.92115600   -1.73205900   -1.70741000
 C                   2.30669200   -1.36280400   -1.63439200
 C                   2.42946700   -0.02087500   -2.07627400
 Cl                  2.21247800    2.37171800    0.02307000
 C                  -1.21727400   -0.61926600   -2.70264700
 H                  -1.22811800   -0.71261800   -3.79823900
 H                  -1.79313100   -1.45627800   -2.30275000
 H                  -1.75246800    0.30112800   -2.45434400
 C                   0.80208500    1.76891600   -3.06420900
 H                   0.91424000    1.69844100   -4.15600200
 H                  -0.22983900    2.07581100   -2.86671400
 H                   1.46132500    2.56533500   -2.71009400
 C                   3.73436500    0.67510600   -2.34088600
 H                   4.14673400    0.35369100   -3.30886900
 H                   3.61462700    1.75932300   -2.36852600
 H                   4.48468800    0.44293800   -1.57770800
 C                   3.48013900   -2.29069200   -1.46433300
 H                   3.95246100   -2.47001900   -2.44077500
 H                   4.25747500   -1.87789600   -0.81188600
 H                   3.18831200   -3.26335000   -1.06606200
 C                   0.37076300   -3.12783900   -1.58886300
 H                   0.40581900   -3.63576900   -2.56362700
 H                   0.93980800   -3.74690600   -0.89102700
 H                  -0.67361300   -3.13566400   -1.26398500
 C                  -0.60058400   -2.60505100    1.86492600
 H                  -0.48724000   -3.17787100    2.79745100
 H                  -1.63937700   -2.26979300    1.82395200
 H                  -0.44261700   -3.30823900    1.04301800
 C                   2.50257800   -2.90182800    1.57822200
 H                   2.54152800   -3.36197200    2.57677400
 H                   1.99905300   -3.61759100    0.92444700
 H                   3.53374100   -2.79577300    1.23690300
 C                   3.87008600   -0.06821200    2.10649800
 H                   4.25326300   -0.26472300    3.11826600
 H                   4.44224800   -0.69874900    1.41787800
```

H	4.09481000	0.97456300	1.86402900
C	1.54653200	1.87368400	3.11625400
H	1.54793100	1.74251300	4.20849800
H	2.49225400	2.33691000	2.83130800
H	0.74776600	2.58349900	2.87780900
C	-1.20085100	0.37833800	2.84672500
H	-1.30136300	0.16441000	3.92060000
H	-1.28564700	1.46304900	2.73010500
H	-2.05605000	-0.08188100	2.34602200
O	-1.01517100	1.23793600	-0.08810300
C	-2.01089600	1.96435200	-0.07918200
C	-3.92621900	0.29829400	-0.07247100
C	-0.73106600	3.99201800	-0.07132700
C	-5.33002700	0.27240600	-0.12018000
C	-3.21576200	-0.90626000	-0.00888000
H	-0.98725800	5.05101300	-0.03605700
H	-0.13474800	3.70685900	0.79426200
H	-0.17386600	3.75855200	-0.97828600
C	-6.01185000	-0.94140400	-0.10663900
H	-5.88446700	1.20637700	-0.16911900
C	-3.91371300	-2.11670700	0.00183300
H	-2.13580900	-0.89278800	0.02075500
C	-5.30769400	-2.14681700	-0.04674900
H	-7.09749400	-0.94128800	-0.14407300
H	-3.35221200	-3.04558900	0.04866200
H	-5.83809900	-3.09424200	-0.03759500
N	-3.31937400	1.57077500	-0.08747700
H	-3.96309700	2.35239200	-0.09501200
O	-1.99768800	3.30883500	-0.06465000

$Cp^*_2Ti^{IV}Cl$-Methyl *N*-phenyl carbamate aza-enolate – CPCM (Entry 33)

E(UB3LYP)	-2604.871469
Zero-point correction=	0.599316
Thermal correction to Energy=	0.638299
Thermal correction to Enthalpy=	0.639243
Thermal correction to Gibbs Free Energy=	0.530067
Sum of electronic and zero-point Energies=	-2604.272153
Sum of electronic and thermal Energies=	-2604.233170
Sum of electronic and thermal Enthalpies=	-2604.232226
Sum of electronic and thermal Free Energies=	-2604.341402

Charge = 0; Multiplicity = 1

Ti	-0.97383600	0.01655500	-0.17000400
C	-1.40129900	-1.75534800	-1.90429500
C	-0.02012500	-1.75650100	-1.57761900
C	0.10742600	-2.16813800	-0.21479600
C	-1.19817300	-2.42373200	0.29302700
C	-2.14034800	-2.11420900	-0.73892900
C	-1.79068500	2.14095500	0.84545900
C	-0.72704100	1.67749200	1.65225200
C	-1.10591800	0.42283400	2.22496300
C	-2.45563900	0.15720700	1.82697400
C	-2.85428200	1.18031400	0.92551700
Cl	-1.75201900	1.21728300	-2.09696300
C	0.50855800	2.44125200	2.01784100
H	0.34734900	2.96762400	2.96898100
H	1.36852400	1.78213300	2.15657300
H	0.76491700	3.18936700	1.26550600
C	-1.86712600	3.48723700	0.18863200
H	-2.14546300	4.24764400	0.93181100
H	-0.90741500	3.77449100	-0.24693400
H	-2.61672900	3.50513400	-0.60433100
C	-4.23177100	1.35440200	0.35194600
H	-4.83045200	2.01895200	0.99031700
H	-4.19860500	1.79686200	-0.64720400
H	-4.76682800	0.40311900	0.28256600
C	-3.40931300	-0.78826400	2.50101400
H	-4.02629300	-0.21146500	3.20397000
H	-4.09729400	-1.27648500	1.80794700
H	-2.89921300	-1.55659600	3.08136800
C	-0.31388900	-0.27597100	3.29732500
H	-0.24381100	0.35992600	4.19008800
H	-0.77702800	-1.21429700	3.60734100
H	0.71157400	-0.49462700	2.98077300
C	1.39241300	-2.47899300	0.49486900
H	1.73647300	-3.48882200	0.22997600
H	2.18263800	-1.77628400	0.22604200
H	1.27367400	-2.45400800	1.58212700
C	-1.46807300	-3.24860500	1.52067200
H	-1.18109500	-4.28783800	1.30771300
H	-0.88409400	-2.93501200	2.38861400
H	-2.52177400	-3.25961700	1.79844300
C	-3.61779000	-2.40087400	-0.74910900
H	-3.83237000	-3.24441300	-1.41892900
H	-3.99512400	-2.67274900	0.23817600

H	-4.20493700	-1.55087100	-1.11369400
C	-1.98242400	-1.62833700	-3.27939800
H	-2.08198100	-2.63148200	-3.71893800
H	-2.97531200	-1.17202700	-3.26731500
H	-1.34677500	-1.03576700	-3.94050800
C	1.10097300	-1.49866900	-2.53996900
H	1.30280500	-2.39378500	-3.14418900
H	0.85899300	-0.68582800	-3.23269100
H	2.02260800	-1.23654100	-2.01774100
O	0.91199300	0.57321200	-0.34411400
C	1.76260000	1.50086700	-0.68701000
N	3.04736000	1.48367700	-0.59814500
C	3.77594400	0.42311600	-0.04504300
C	2.01790600	3.65115300	-1.68304000
C	4.49576500	-0.44589400	-0.88828300
C	3.93232300	0.27422300	1.34627400
H	1.34797200	4.41245600	-2.08651400
H	2.60375900	4.06089600	-0.85535300
H	2.70104900	3.29602200	-2.45938400
C	5.30606600	-1.45092300	-0.35875100
H	4.41222700	-0.31595700	-1.96397900
C	4.74698600	-0.73012300	1.87135600
H	3.42232700	0.96426300	2.01208500
C	5.43478200	-1.60366900	1.02458700
H	5.84437700	-2.11348200	-1.03225300
H	4.84794100	-0.82564900	2.94986600
H	6.06968400	-2.38345700	1.43590700
O	1.16348500	2.59398500	-1.23208200

$Cp_2Ti^{III}Cl$ – CPCM (Entry 34)

E(UB3LYP)	-1696.821490
Zero-point correction=	0.170235
Thermal correction to Energy=	0.181576
Thermal correction to Enthalpy=	0.182520
Thermal correction to Gibbs Free Energy=	0.130940
Sum of electronic and zero-point Energies=	-1696.651255
Sum of electronic and thermal Energies=	-1696.639914
Sum of electronic and thermal Enthalpies=	-1696.638970
Sum of electronic and thermal Free Energies=	-1696.690550

Charge = 0; Multiplicity = 1

Ti	-0.00174700	0.11140200	-0.01105100
C	2.32286200	0.26191800	0.59109100
C	1.78146100	-0.90046800	1.19786000
C	1.40500700	-1.79168900	0.15694900
C	1.69856200	-1.17304800	-1.08962300
C	2.27141400	0.09395800	-0.81643100
C	-2.15676400	-0.01655100	1.03979400
C	-1.67879900	-1.34218100	0.90760800
C	-1.57092400	-1.63293400	-0.48065100
C	-1.97392900	-0.48467100	-1.20781700
C	-2.33765400	0.51486700	-0.26507600
H	2.67605700	1.14270700	1.11031100
H	1.68451500	-1.08247300	2.26073900
H	0.97360600	-2.77392700	0.29233700
H	1.51939100	-1.59612100	-2.07004200
H	2.57736600	0.82562700	-1.55344500
H	-2.32834000	0.50889600	1.97115400
H	-1.42719000	-2.01273500	1.71945300
H	-1.23313800	-2.56662700	-0.91017900
H	-2.00388500	-0.38891700	-2.28600800
H	-2.67350200	1.51515700	-0.49940900
Cl	0.10036100	2.51778600	0.00035200

$Cp_2Ti^{IV}Cl(TEMPO)$ – CPCM (Entry 35)

```
 E(UB3LYP)                                          -2180.569887
 Zero-point correction=                           0.436366
 Thermal correction to Energy=                    0.460459
 Thermal correction to Enthalpy=                  0.461403
 Thermal correction to Gibbs Free Energy=         0.385373
 Sum of electronic and zero-point Energies=          -2180.133521
 Sum of electronic and thermal Energies=             -2180.109428
 Sum of electronic and thermal Enthalpies=           -2180.108484
 Sum of electronic and thermal Free Energies=        -2180.184514

Charge = 0; Multiplicity = 1
 Ti                  1.45694700    0.04289900    0.00655800
 C                   1.41065400    1.72147800    1.74736400
 C                   0.62868500    0.63800600    2.19109300
 C                   1.48200000   -0.48862300    2.33338800
 C                   2.80954900   -0.06915200    2.04440700
 C                   2.76452500    1.28134000    1.64903300
 C                   1.71085200   -1.25881300   -2.09717000
 C                   1.44943200   -2.18366400   -1.06589000
 C                   2.52161100   -2.12949200   -0.14038600
 C                   3.48388500   -1.20292100   -0.63960200
 C                   2.97760300   -0.66467300   -1.83790900
 H                   1.04871800    2.70656200    1.49378200
 H                  -0.44793900    0.62718400    2.28452900
 H                   1.18203900   -1.47824400    2.65132300
 H                   3.69341600   -0.68918300    2.09070500
 H                   3.60531700    1.87866100    1.32222700
 H                   1.05755700   -1.02461500   -2.92722000
 H                   0.56213800   -2.79120000   -0.96538500
 H                   2.61832000   -2.73190500    0.75295200
 H                   4.42858000   -0.94731500   -0.17971300
 H                   3.45722300    0.08989900   -2.44367400
 Cl                  1.79918100    2.08599200   -1.32212300
 O                  -0.34997300   -0.13346300   -0.28807100
 C                  -3.77128800    1.27787900    0.20586500
 C                  -3.76067300   -1.12358500    0.83068600
 C                  -4.55240700   -0.03045600    0.11740400
 H                  -4.29279100    2.08657900   -0.32053700
 H                  -3.70798100    1.57656900    1.26109400
 H                  -4.27387400   -2.09099500    0.76916400
 H                  -3.68976700   -0.86835600    1.89665100
 H                  -5.53597900    0.08823700    0.58841200
 H                  -4.74354100   -0.30220500   -0.92791600
 C                  -1.61118900    2.48661300    0.07170000
 H                  -1.54333800    2.54043100    1.16317500
 H                  -0.60813700    2.55329700   -0.35106000
 H                  -2.18389100    3.35545900   -0.27339900
 C                  -2.37205300   -2.00905900   -1.10606200
 H                  -1.41353800   -1.90796700   -1.61876300
 H                  -2.57972500   -3.07706200   -0.97411500
 H                  -3.14872500   -1.60620900   -1.75977000
 C                  -2.32984200   -1.31467700    0.27464100
 C                  -1.57685700   -2.22254500    1.26629800
```

H	-0.56942600	-2.46208100	0.92131600
H	-1.50272300	-1.74195100	2.24736900
H	-2.12306000	-3.16455100	1.38819200
N	-1.64659700	0.02866900	0.28883000
C	-2.33453100	1.20027100	-0.36489900
C	-2.35295800	1.15328400	-1.90892200
H	-2.68134600	2.12418100	-2.29721100
H	-1.35097000	0.95526100	-2.29728100
H	-3.03149700	0.39563500	-2.30649000

TEMPOH - CPCM (Entry 36)

```
 E(UB3LYP)                                          -484.329235
 Zero-point correction=                           0.274758
 Thermal correction to Energy=                    0.286912
 Thermal correction to Enthalpy=                  0.287856
 Thermal correction to Gibbs Free Energy=         0.239075
 Sum of electronic and zero-point Energies=          -484.054477
 Sum of electronic and thermal Energies=             -484.042322
 Sum of electronic and thermal Enthalpies=           -484.041378
 Sum of electronic and thermal Free Energies=        -484.090159

Charge = 0; Multiplicity = 1
 C                  0.00000000    2.16955700    0.01389700
 C                  1.25173800    1.43258700   -0.46976400
 C                  1.29553400   -0.04962800   -0.03226500
 C                 -1.29553400   -0.04962800   -0.03226500
 C                 -1.25173800    1.43258700   -0.46976400
 H                  1.28086000    1.47236700   -1.56724500
 H                  2.16260900    1.92651700   -0.10930100
 H                  0.00000000    2.25256600    1.10784000
 H                  0.00000000    3.19687800   -0.37107400
 H                 -1.28086100    1.47236700   -1.56724500
 H                 -2.16260900    1.92651700   -0.10930100
 N                  0.00000000   -0.66542100   -0.44436500
 C                  2.39588100   -0.76730900   -0.83865800
 H                  3.36031000   -0.26819300   -0.69099400
 H                  2.49996900   -1.80932600   -0.52202000
 H                  2.15812100   -0.75215700   -1.90805400
 C                  1.63656500   -0.17933800    1.47015700
 H                  1.48103200   -1.20814300    1.80596400
 H                  2.69080600    0.07493200    1.63026700
 H                  1.04138200    0.48329300    2.10246300
 C                 -2.39588100   -0.76730900   -0.83865800
 H                 -2.49996900   -1.80932600   -0.52202000
 H                 -3.36031000   -0.26819300   -0.69099400
 H                 -2.15812100   -0.75215700   -1.90805400
 C                 -1.63656500   -0.17933800    1.47015700
 H                 -1.48103200   -1.20814300    1.80596400
 H                 -1.04138200    0.48329300    2.10246300
 H                 -2.69080600    0.07493200    1.63026700
 O                  0.00000000   -2.04297400    0.00982500
 H                  0.00000000   -2.53936300   -0.82397700
```

$Cp^*_2Ti^{III}Cl$-Methyl Propionate – CPCM (Entry 37)

```
 E(UB3LYP)                                          -2397.683273
 Zero-point correction=                              0.569978
 Thermal correction to Energy=                       0.606710
 Thermal correction to Enthalpy=                     0.607654
 Thermal correction to Gibbs Free Energy=            0.503035
 Sum of electronic and zero-point Energies=          -2397.113294
 Sum of electronic and thermal Energies=             -2397.076563
 Sum of electronic and thermal Enthalpies=           -2397.075618
 Sum of electronic and thermal Free Energies=        -2397.180238

Charge = 0; Multiplicity = 2
 Ti                  0.43090700    0.04044200   -0.19579200
 C                   0.03572500    2.51801600   -0.47380800
 C                  -0.55898900    2.15520000    0.76156100
 C                   0.46453100    1.68043300    1.63456100
 C                   1.70835300    1.78946900    0.93708200
 C                   1.43594200    2.25975100   -0.38577300
 C                   0.52006400   -2.34340600   -0.59749900
 C                   0.69423400   -2.17529900    0.81225500
 C                   1.94818700   -1.54589200    1.02929900
 C                   2.55887000   -1.32301100   -0.24818600
 C                   1.68637300   -1.83180000   -1.24402500
 Cl                 -0.36229900    0.21060300   -2.59798900
 C                  -0.16257200   -2.75483500    1.90295200
 H                   0.33278100   -3.62477000    2.35801900
 H                  -0.35622400   -2.04030100    2.71052500
 H                  -1.12558000   -3.09794600    1.51870300
 C                  -0.59453500   -3.09115100   -1.27574500
 H                  -0.31827400   -4.14115500   -1.44845800
 H                  -1.50795300   -3.09430800   -0.67360400
 H                  -0.83645100   -2.64859400   -2.24627700
 C                   2.04539700   -1.98624100   -2.69455600
 H                   2.66659200   -2.88322600   -2.83695500
 H                   1.15884400   -2.08872900   -3.32273700
 H                   2.62079600   -1.13302600   -3.06899000
 C                   3.97801900   -0.89686800   -0.51762000
 H                   4.55864200   -1.74310200   -0.91056100
 H                   4.04685600   -0.09737000   -1.26388000
 H                   4.48507100   -0.55478100    0.38704200
 C                   2.61040200   -1.46496400    2.37807200
 H                   2.85982400   -2.47734900    2.72758200
 H                   3.54253000   -0.89748900    2.35414900
 H                   1.96330700   -1.02173500    3.14124300
 C                   0.26547400    1.36802800    3.09477800
 H                  -0.03363600    2.26595100    3.65326500
 H                  -0.51652600    0.61703700    3.25827200
 H                   1.18037600    0.99195200    3.55896400
 C                   3.07269900    1.79639200    1.57106600
 H                   3.34574400    2.83140200    1.82339200
 H                   3.10998900    1.22451200    2.49933500
 H                   3.85266000    1.41837000    0.90767800
 C                   2.45575300    2.64231700   -1.42462500
 H                   2.68772700    3.71644900   -1.38095600
 H                   3.39911200    2.10584400   -1.28685700
```

H	2.09724100	2.42994600	-2.43729000
C	-0.65488400	3.24360600	-1.59220800
H	-0.65784000	4.32517600	-1.39094800
H	-0.15566400	3.08261000	-2.54984100
H	-1.69689200	2.93070600	-1.70715300
C	-1.98443200	2.42273400	1.15320900
H	-2.09311300	3.45612500	1.51236600
H	-2.67779000	2.30883400	0.31332000
H	-2.31996300	1.76996200	1.96323500
O	-1.72402900	-0.49048400	0.36733900
C	-2.92658800	-0.51669000	0.10003100
C	-4.96030300	0.28331100	-1.26045800
H	-5.28730000	0.44799000	-2.29197800
H	-5.66018500	-0.40972100	-0.78652900
H	-5.01979800	1.24063800	-0.73179700
C	-3.43738200	-1.10860500	2.36446400
H	-4.36243300	-1.17188500	2.93590000
H	-2.90539000	-2.05967300	2.39357900
H	-2.80023700	-0.31451600	2.75610200
C	-3.52977400	-0.26597500	-1.26185500
H	-3.49893300	-1.23125800	-1.78698900
H	-2.83831700	0.38204000	-1.80359900
O	-3.84895300	-0.81097900	1.01367900
H	-2.34585300	-2.42622200	-1.78280300
C	-2.92961900	-1.96349500	1.08039000
H	-4.00449700	-1.82172600	1.26404100
H	-2.80745500	-2.83225400	0.43111000
H	-2.45906200	-2.20549400	2.03805800
C	-2.02626300	0.62480700	2.67658800
H	-3.03308000	0.94571300	2.98103000
H	-1.80935500	-0.30601600	3.21078300
H	-1.32334400	1.38315200	3.03518200
C	1.52865100	2.91825400	-0.56415800
H	1.13241400	3.51015700	0.26253800
H	2.53038200	3.31162100	-0.78985700
H	0.91011600	3.10944000	-1.44641800

$Cp^*_2Ti^{IV}Cl$-Methyl Propionate Enolate – CPCM (Entry 38)

```
E(UB3LYP)                                          -2397.059822
Zero-point correction=                              0.557912
Thermal correction to Energy=                       0.593926
Thermal correction to Enthalpy=                     0.594870
Thermal correction to Gibbs Free Energy=            0.493397
Sum of electronic and zero-point Energies=          -2396.501910
Sum of electronic and thermal Energies=             -2396.465896
Sum of electronic and thermal Enthalpies=           -2396.464952
Sum of electronic and thermal Free Energies=        -2396.566425

Charge = 0; Multiplicity = 1
Ti                  0.27368400    0.02169400   -0.17913900
C                  -0.46852800    2.40896600   -0.18486700
C                  -0.66544100    1.91247900    1.12487800
C                   0.60918000    1.57111800    1.67508900
C                   1.60881700    1.94122500    0.71456100
C                   0.94490800    2.41131800   -0.44417900
C                   0.55935400   -2.42156300   -0.47918100
C                   0.88011500   -2.11652500    0.87669600
C                   2.08357100   -1.35304800    0.88729700
C                   2.48540600   -1.14699000   -0.46777000
C                   1.56251400   -1.84211500   -1.30297400
Cl                 -0.12386900    0.33206000   -2.55200500
C                   0.22956400   -2.69923500    2.09815200
H                   0.86111600   -3.49540200    2.51682500
H                   0.08275400   -1.96023300    2.89284800
H                  -0.73995300   -3.14076200    1.86482300
C                  -0.56403300   -3.29699800   -0.94889400
H                  -0.27980200   -4.35718800   -0.90444600
H                  -1.45563400   -3.16493900   -0.33158200
H                  -0.83930100   -3.07445900   -1.98417600
C                   1.77479500   -2.10695200   -2.76279600
H                   2.44623500   -2.97042800   -2.87776600
H                   0.84223900   -2.33838500   -3.28129600
H                   2.23869000   -1.25750200   -3.27009100
C                   3.79540700   -0.58932700   -0.95558800
H                   4.40259800   -1.39073700   -1.39770300
H                   3.66788400    0.17359600   -1.73241200
H                   4.38118400   -0.15067700   -0.14595100
C                   2.94823100   -1.20037100    2.10694100
H                   3.47447200   -2.15038800    2.27969900
H                   3.71405300   -0.43135900    2.00014500
H                   2.37165700   -0.99310500    3.01019100
C                   0.82131700    1.26579500    3.13422100
H                   0.48340700    2.11472100    3.74405300
H                   0.25442900    0.39112100    3.47223100
H                   1.87306800    1.09826200    3.37024900
C                   3.07180900    2.15310200    0.98313700
H                   3.22889000    3.20652800    1.25546700
H                   3.44532400    1.55378200    1.81356900
H                   3.69459200    1.95772000    0.10789000
C                   1.61197500    3.02687200   -1.64021200
H                   1.82777000    4.08766700   -1.44908400
H                   2.56347200    2.53982400   -1.87596400
```

H	0.97730900	2.96825300	-2.52679600
C	-1.50437700	3.03540300	-1.07262800
H	-1.45777500	4.13022200	-0.98794700
H	-1.34105900	2.77700700	-2.12204100
H	-2.51397500	2.71796700	-0.80376300
C	-1.94406700	1.91319900	1.90750000
H	-1.98045200	2.80738000	2.54585300
H	-2.82225600	1.92946700	1.26054600
H	-2.02566500	1.04224400	2.56274600
O	-1.49117400	-0.63398700	0.18084000
C	-2.79525200	-0.42446000	-0.00868100
C	-4.84986800	0.13922900	-1.37451100
H	-5.14625800	-0.33301800	-2.32199100
H	-5.41747200	-0.33583900	-0.56968700
H	-5.18136300	1.18747300	-1.43775000
C	-3.24377900	-1.75126900	1.95176000
H	-4.07035100	-1.84620300	2.65977900
H	-3.11991200	-2.70186700	1.41776800
H	-2.32566000	-1.51961800	2.49675200
C	-3.36813700	0.02553900	-1.14567100
H	-2.69861600	0.33742600	-1.93780900
O	-3.61280100	-0.69891100	1.06644600

Methyl Propionate – CPCM (Entry 39)

E(UB3LYP)	-307.708334
Zero-point correction=	0.118833
Thermal correction to Energy=	0.126252
Thermal correction to Enthalpy=	0.127196
Thermal correction to Gibbs Free Energy=	0.086966
Sum of electronic and zero-point Energies=	-307.589501
Sum of electronic and thermal Energies=	-307.582082
Sum of electronic and thermal Enthalpies=	-307.581138
Sum of electronic and thermal Free Energies=	-307.621368

Charge = 0; Multiplicity = 1

O	-0.10688200	1.30417700	-0.00004500
C	-0.05209000	0.08925900	0.00001000
C	-2.41557500	-0.02123500	0.00001400
H	-3.16869300	-0.80891500	-0.00021600
H	-2.51668700	0.60251500	0.89172100
H	-2.51647900	0.60285300	-0.89147800
O	-1.14562300	-0.70069200	0.00004200
C	2.48780600	0.10741400	0.00006400
H	2.53379400	0.75068000	-0.88417800
H	2.53380700	0.75037500	0.88452800
H	3.37141400	-0.53837000	-0.00005100
C	1.21673500	-0.73925200	-0.00007700
H	1.18083200	-1.40193400	-0.87394100
H	1.18079800	-1.40220100	0.87357900

Methyl Propionate Enolate Radical – CPCM (Entry 40)

```
 E(UB3LYP)                                             -307.053823
 Zero-point correction=                           0.105149
 Thermal correction to Energy=                    0.112505
 Thermal correction to Enthalpy=                  0.113449
 Thermal correction to Gibbs Free Energy=         0.073190
 Sum of electronic and zero-point Energies=           -306.948674
 Sum of electronic and thermal Energies=              -306.941318
 Sum of electronic and thermal Enthalpies=            -306.940374
 Sum of electronic and thermal Free Energies=         -306.980632

Charge = 0; Multiplicity = 2
 O                 -0.10897100    1.31817300    0.00001900
 C                 -0.02379000    0.09215700    0.00000300
 C                 -2.38497300   -0.06054600   -0.00003500
 H                 -3.13041800   -0.85587700   -0.00086300
 H                 -2.49618300    0.56330500    0.89123000
 H                 -2.49546000    0.56454600   -0.89050600
 O                 -1.11135300   -0.72377300    0.00004100
 C                  2.53834000    0.00196700   -0.00001500
 H                  3.12812000   -0.29905000    0.87817400
 H                  3.12811400   -0.29907300   -0.87820000
 H                  2.43441500    1.08936800   -0.00002800
 C                  1.21206500   -0.66235500   -0.00000300
 H                  1.14415600   -1.74575900    0.00001600
```

N-Phenyl Propanamide – BF_3 Adduct (Entry 41)

```
 E(UB3LYP)                                          -804.157683
 Zero-point correction=                           0.200225
 Thermal correction to Energy=                    0.214639
 Thermal correction to Enthalpy=                  0.215583
 Thermal correction to Gibbs Free Energy=         0.156601
 Sum of electronic and zero-point Energies=          -803.957459
 Sum of electronic and thermal Energies=             -803.943045
 Sum of electronic and thermal Enthalpies=           -803.942100
 Sum of electronic and thermal Free Energies=        -804.001082

Charge = 0; Multiplicity = 1
 C                 -0.67200700   -0.80461700    0.26948200
 N                  0.61686300   -1.18827300    0.31152700
 H                  0.76529200   -2.17116500    0.50149600
 C                  1.81367100   -0.43901500    0.12364300
 C                  3.00943600   -1.17017900    0.16556500
 C                  1.84388800    0.94747200   -0.08196700
 C                  4.23165400   -0.52548100    0.00236000
 H                  2.98218100   -2.24655400    0.32533000
 C                  3.07920100    1.57652200   -0.24339800
 H                  0.92807100    1.51948200   -0.11417600
 C                  4.27197300    0.85458200   -0.20375200
 H                  5.15019800   -1.10413200    0.03656500
 H                  3.09943500    2.65086900   -0.40195500
 H                  5.22405000    1.36106100   -0.33151300
 C                 -1.71177000   -1.88014000    0.47991100
 H                 -1.28170300   -2.69377800    1.07619300
 H                 -2.52234100   -1.42920600    1.05557100
 C                 -2.25258300   -2.42170400   -0.86041400
 H                 -3.00809300   -3.18816200   -0.66280700
 H                 -2.71499700   -1.61446600   -1.43051100
 H                 -1.45662400   -2.87492200   -1.46192800
 O                 -0.95125100    0.39656300    0.02454300
 F                 -2.07675700    2.43898600   -0.04185600
 F                 -3.07416500    0.63831900   -1.07361100
 F                 -3.00550900    0.75185000    1.22191000
 B                 -2.42927800    1.12986800    0.03282700
```

N-Phenyl Propanamidyl Radical – BF_3 Adduct (Entry 42)

```
 E(UB3LYP)                                          -803.499472
 Zero-point correction=                           0.185880
 Thermal correction to Energy=                    0.200305
 Thermal correction to Enthalpy=                  0.201249
 Thermal correction to Gibbs Free Energy=         0.141612
 Sum of electronic and zero-point Energies=           -803.313592
 Sum of electronic and thermal Energies=              -803.299167
 Sum of electronic and thermal Enthalpies=            -803.298223
 Sum of electronic and thermal Free Energies=         -803.357860

Charge = 0; Multiplicity = 2
 C                 -0.61237800   -0.71580400    0.15898400
 N                  0.63010900   -1.19717100   -0.07398900
 C                  1.76940400   -0.49269700   -0.02741100
 C                  2.93965300   -1.10653900   -0.57947100
 C                  1.89422700    0.80104500    0.58160000
 C                  4.15625700   -0.45463700   -0.54393800
 H                  2.82860300   -2.08890100   -1.02642700
 C                  3.12172900    1.43336900    0.60800700
 H                  1.01545100    1.27665500    1.00120000
 C                  4.25535900    0.81663000    0.04854000
 H                  5.03765300   -0.92268300   -0.97183500
 H                  3.21191100    2.41505300    1.06331200
 H                  5.21435700    1.32566500    0.07689700
 C                 -1.54231300   -1.63300800    0.91039300
 H                 -0.94960500   -2.17845300    1.65292000
 H                 -2.28349100   -1.01904200    1.42400200
 C                 -2.22938600   -2.63526600   -0.04300000
 H                 -2.86991300   -3.30465200    0.53970300
 H                 -2.84838500   -2.10005300   -0.76496600
 H                 -1.48961800   -3.24135100   -0.57510500
 O                 -0.95786200    0.38580400   -0.34738200
 F                 -2.26489900    2.26717400   -0.87827500
 F                 -3.32186700    0.22342100   -0.79701100
 F                 -2.62202600    1.23595000    1.14701300
 B                 -2.45020600    1.10281300   -0.21010000
```

$Cp^*_2Ti^{III}Cl$-Explicitly Bound MeCN (Entry 43)

```
 E(UB3LYP)                                          -2222.730504
 Zero-point correction=                           0.496593
 Thermal correction to Energy=                    0.529649
 Thermal correction to Enthalpy=                  0.530593
 Thermal correction to Gibbs Free Energy=         0.433716
 Sum of electronic and zero-point Energies=          -2222.233911
 Sum of electronic and thermal Energies=             -2222.200855
 Sum of electronic and thermal Enthalpies=           -2222.199911
 Sum of electronic and thermal Free Energies=        -2222.296788

Charge = 0; Multiplicity = 2
 Ti                  0.02316900    0.02111200   -0.16281700
 C                   0.99864000   -2.17610500   -0.64190100
 C                   0.98961400   -2.07335700    0.77968500
 C                  -0.35995600   -2.02542000    1.21730000
 C                  -1.19730200   -2.12237400    0.06025200
 C                  -0.35915500   -2.20074300   -1.08898700
 C                  -0.23684900    2.43539800    0.06084500
 C                  -0.53301800    1.85049600    1.33560900
 C                  -1.73641000    1.10515500    1.20165600
 C                  -2.17410400    1.21177000   -0.15929900
 C                  -1.26320800    2.05105200   -0.84878900
 Cl                  1.01747300    0.51146600   -2.39661000
 C                   0.18313900    2.13100000    2.62933600
 H                  -0.23267800    3.01800200    3.12860700
 H                   0.09985300    1.29701000    3.33446500
 H                   1.24938500    2.32102000    2.47357500
 C                   0.85650500    3.41956000   -0.24951800
 H                   0.44947900    4.43551200   -0.34649300
 H                   1.60964400    3.45179100    0.54391600
 H                   1.36057200    3.17070200   -1.18929100
 C                  -1.45187700    2.57320900   -2.24360800
 H                  -2.11078800    3.45451300   -2.23001400
 H                  -0.50267600    2.86001100   -2.69905100
 H                  -1.91038100    1.82769600   -2.89999600
 C                  -3.49966700    0.76743700   -0.71685600
 H                  -4.18091300    1.62501100   -0.81198200
 H                  -3.40213700    0.32895400   -1.71638000
 H                  -3.99343600    0.03366600   -0.07674400
 C                  -2.57267600    0.61539200    2.35129800
 H                  -3.24356900    1.41897100    2.68911000
 H                  -3.20755100   -0.23362800    2.08621500
 H                  -1.96715600    0.32370000    3.21271000
 C                  -0.77904100   -2.17836800    2.65493300
 H                  -0.54780000   -3.19285800    3.01130700
 H                  -0.25714700   -1.48404300    3.32408000
 H                  -1.85096900   -2.02793500    2.79223800
 C                  -2.67023600   -2.42626900    0.06691600
 H                  -2.82394500   -3.51370200    0.12318700
 H                  -3.19003700   -1.98883800    0.92296200
 H                  -3.17143500   -2.08062200   -0.84056000
 C                  -0.81077800   -2.43071000   -2.50522400
 H                  -0.76618900   -3.49820300   -2.76509400
```

H	-1.84425300	-2.10276300	-2.65857500
H	-0.18497800	-1.88062600	-3.21292100
C	2.21079700	-2.40888200	-1.49758500
H	2.45198600	-3.48103000	-1.53991100
H	2.05331700	-2.04969100	-2.51578500
H	3.09297200	-1.89021200	-1.10776500
C	2.17779100	-2.18792600	1.69344800
H	2.25933700	-3.20884000	2.09330900
H	3.11484600	-1.97300000	1.17198900
H	2.10586800	-1.51171400	2.55287500
N	2.04551500	0.58639900	0.41748700
C	3.14650000	0.91002800	0.57102500
C	4.53638400	1.32448100	0.71420800
H	4.99558700	1.41624500	-0.27558200
H	4.59265500	2.29356800	1.21996300
H	5.09661400	0.58821300	1.29911800

$Cp_2Ti^{III}Cl$-Explicitly Bound MeCN (Entry 44)

```
 E(UB3LYP)                                          -1829.575434
 Zero-point correction=                           0.217690
 Thermal correction to Energy=                    0.233991
 Thermal correction to Enthalpy=                  0.234935
 Thermal correction to Gibbs Free Energy=         0.171087
 Sum of electronic and zero-point Energies=          -1829.357744
 Sum of electronic and thermal Energies=             -1829.341443
 Sum of electronic and thermal Enthalpies=           -1829.340499
 Sum of electronic and thermal Free Energies=        -1829.404347

Charge = 0; Multiplicity = 2
 Ti                -0.34219000    0.00103600    0.03531000
 C                 -0.17180400    2.37234200    0.36266800
 C                 -0.08991800    2.18176200   -1.04055500
 C                 -1.31839200    1.64461300   -1.48464500
 C                 -2.17391000    1.52390800   -0.35422900
 C                 -1.46857700    1.97537900    0.78529100
 C                  0.04429200   -2.36262400   -0.20707500
 C                 -0.43345300   -1.86970800   -1.45701800
 C                 -1.76658400   -1.44371400   -1.26558500
 C                 -2.11248100   -1.66433400    0.09860100
 C                 -1.00011500   -2.25174900    0.73983300
 Cl                 0.58052800   -0.04796000    2.31816100
 N                  1.79953000    0.01228500   -0.47866200
 C                  2.95004800    0.00652400   -0.60193100
 C                  4.40294500   -0.00471100   -0.71387100
 H                  4.75704400    0.93705700   -1.14468400
 H                  4.84591400   -0.12884600    0.27962500
 H                  4.72814600   -0.83078400   -1.35403700
 H                 -3.06441000   -1.43505300    0.56059000
 H                 -2.41354900   -1.02138000   -2.02272800
 H                  0.12030600   -1.83803700   -2.38714700
 H                  1.03609200   -2.74511600   -0.00717600
 H                 -0.92799400   -2.49732100    1.78927400
 H                  0.61831200    2.72677600    1.00920700
 H                  0.77331200    2.38435600   -1.66140700
 H                 -1.56479000    1.37877800   -2.50457700
 H                 -3.18879700    1.14809600   -0.36535400
 H                 -1.82940700    1.98190700    1.80459500
```

$Cp^*_2Ti^{III}Cl$-Explicitly Bound MeCN – CPCM (Solvent = Acetonitrile) (Entry 45)

```
 E(UB3LYP)                                          -2222.748010
 Zero-point correction=                           0.496689
 Thermal correction to Energy=                    0.529401
 Thermal correction to Enthalpy=                  0.530346
 Thermal correction to Gibbs Free Energy=         0.435064
 Sum of electronic and zero-point Energies=          -2222.251320
 Sum of electronic and thermal Energies=             -2222.218608
 Sum of electronic and thermal Enthalpies=           -2222.217664
 Sum of electronic and thermal Free Energies=        -2222.312946

Charge = 0; Multiplicity = 2
 Ti                  -0.01232600   -0.02485500   -0.18679500
 C                   -1.27715000    2.00445900   -0.66963700
 C                   -1.30197100    1.88680000    0.75234700
 C                    0.02290000    2.03871900    1.23633700
 C                    0.87793000    2.26935900    0.11070900
 C                    0.07598200    2.24534400   -1.06620100
 C                    0.56439100   -2.38170300    0.05672400
 C                    0.69529200   -1.76692700    1.34562000
 C                    1.79369200   -0.86433200    1.28517700
 C                    2.32835300   -0.90214700   -0.04428600
 C                    1.58626500   -1.85585600   -0.78582900
 Cl                  -0.75363900   -0.61749200   -2.56868800
 C                   -0.06229100   -2.13977000    2.59202800
 H                    0.45210300   -2.94014800    3.14284000
 H                   -0.16320100   -1.29166500    3.27723100
 H                   -1.06947500   -2.50048300    2.36546500
 C                   -0.35426100   -3.51346700   -0.31209700
 H                    0.18873600   -4.46895600   -0.31920500
 H                   -1.17925600   -3.61829500    0.39774700
 H                   -0.78354500   -3.37189200   -1.30913800
 C                    1.95179500   -2.35139300   -2.15529400
 H                    2.73953100   -3.11608900   -2.08177700
 H                    1.09676000   -2.79608800   -2.66750500
 H                    2.33756900   -1.54818500   -2.79111600
 C                    3.61864900   -0.28530200   -0.51487000
 H                    4.40608100   -1.05007300   -0.57586400
 H                    3.53031300    0.15720800   -1.51359100
 H                    3.97708100    0.49145100    0.16317100
 C                    2.48333600   -0.26970200    2.48217600
 H                    3.23515600   -0.97763800    2.86075300
 H                    3.01278700    0.65771200    2.25162700
 H                    1.79347700   -0.06813700    3.30445800
 C                    0.35912700    2.23414100    2.69062300
 H                   -0.06913800    3.18128400    3.04880600
 H                   -0.05150200    1.44343200    3.32844700
 H                    1.43493200    2.28132300    2.86740300
 C                    2.29682000    2.76517400    0.16488100
 H                    2.30767400    3.86434000    0.19559200
 H                    2.83100600    2.41796900    1.05239900
```

H	2.87461000	2.46548300	-0.71302900
C	0.54336900	2.59971900	-2.45137200
H	0.46080700	3.68202600	-2.62851300
H	1.59249800	2.32780400	-2.60908200
H	-0.04923900	2.08922500	-3.21432900
C	-2.48830900	2.06981100	-1.55713000
H	-2.92527700	3.07871800	-1.54131900
H	-2.23762000	1.82739700	-2.59143900
H	-3.27021100	1.37343100	-1.23614800
C	-2.52518300	1.81212700	1.62352200
H	-2.75687600	2.80235700	2.04121000
H	-3.40583000	1.48404100	1.06531600
H	-2.39065800	1.13113300	2.47092700
N	-1.97078100	-0.87435600	0.25735400
C	-3.01925600	-1.32509300	0.45590200
C	-4.33838800	-1.89195400	0.70121700
H	-4.92182000	-1.89146300	-0.22427100
H	-4.24053700	-2.92076900	1.05994300
H	-4.86499200	-1.29981300	1.45540600

$Cp^*_2Ti^{III}Cl$-Explicitly Bound MeCN – CPCM (Solvent = Acetonitrile) (Entry 45)

```
 E(UB3LYP)                                          -132.762631
 Zero-point correction=                           0.045629
 Thermal correction to Energy=                    0.049200
 Thermal correction to Enthalpy=                  0.050145
 Thermal correction to Gibbs Free Energy=         0.022671
 Sum of electronic and zero-point Energies=          -132.717002
 Sum of electronic and thermal Energies=             -132.713431
 Sum of electronic and thermal Enthalpies=           -132.712486
 Sum of electronic and thermal Free Energies=        -132.739960

Charge = 0; Multiplicity = 1
 C                    0.00000000    0.00000000    0.27890300
 C                    0.00000000    0.00000000   -1.18049100
 H                    0.00000000    1.02719900   -1.55675000
 H                    0.88958000   -0.51360000   -1.55675000
 H                   -0.88958000   -0.51360000   -1.55675000
 N                    0.00000000    0.00000000    1.43996800
```

VII. EPR Experiments

Experiment was run in anhydrous, degassed MeCN in sealed microcapillaries. g_{iso} = 2.003, A_{iso} = 44, lwpp = 0.455, microwave frequency = 9.764 GHz, power, = 0.6325 mW, modulation amplitude = 0.1 mT/100 kHz, temperature = 23 °C.

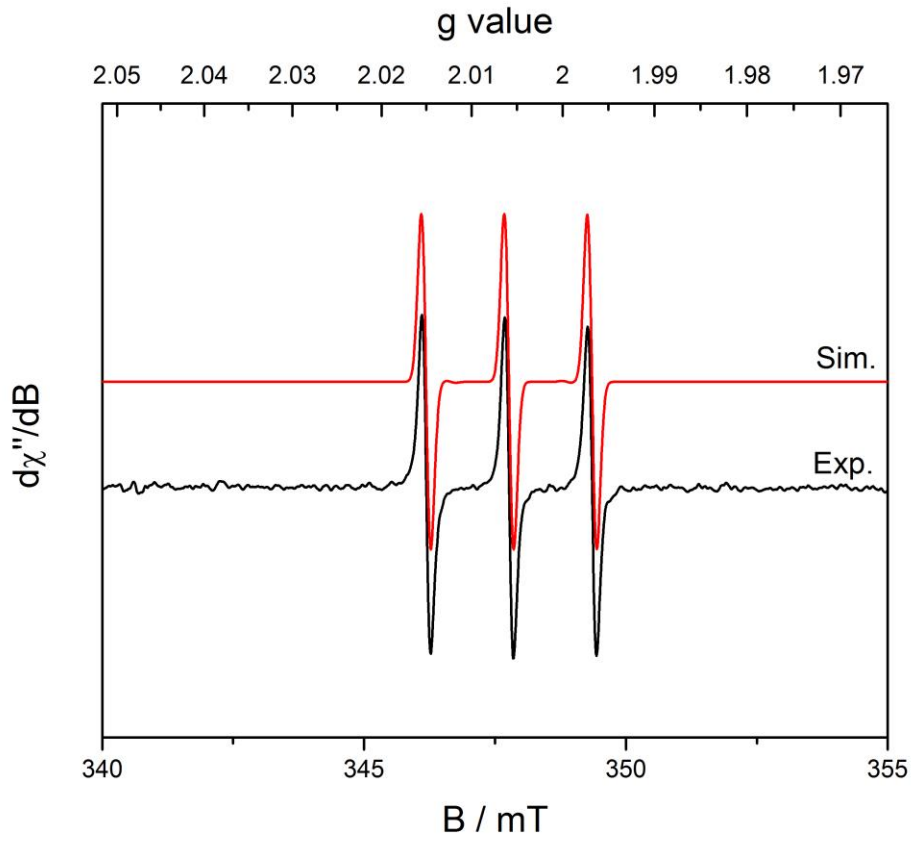


Figure S29 EPR of TEMPO in MeCN

Experiment was run in anhydrous, degassed MeCN in sealed microcapillaries. g_{iso} = 1.98, lwpp = 0.455, microwave frequency = 9.384 GHz, power, = 0.6325 mW, modulation amplitude = 0.1 mT/100 kHz, temperature = 23 °C.

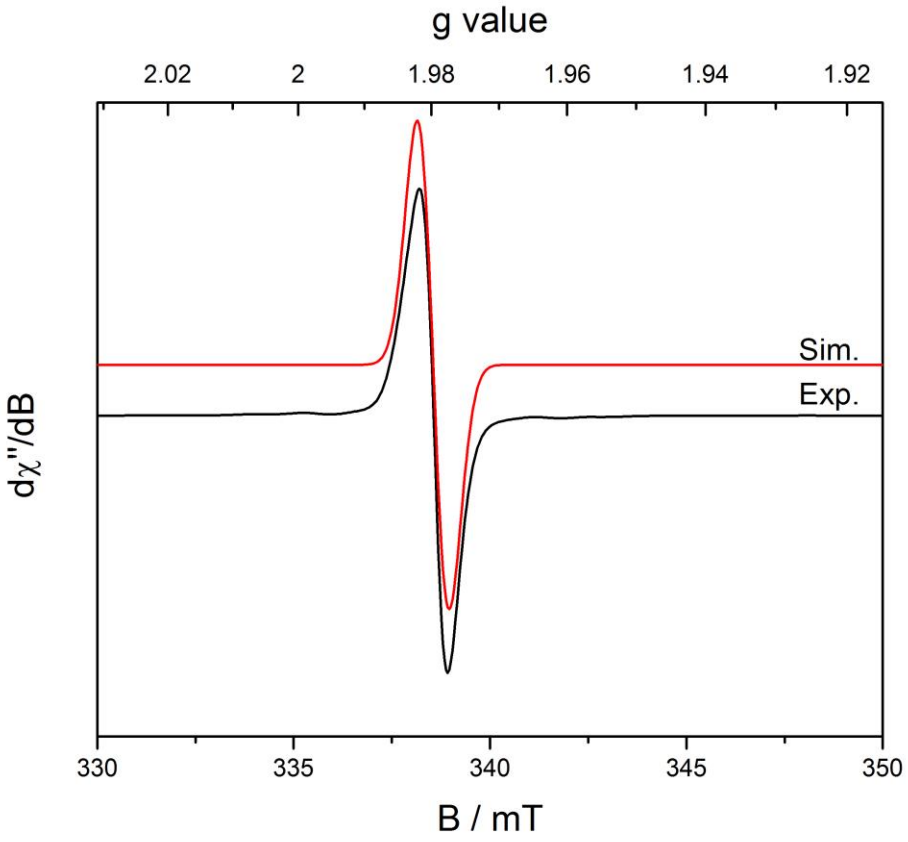


Figure S30 EPR of Cp^*_2TiCl in MeCN

Experiment was run in anhydrous, degassed MeCN in sealed microcapillaries. Microwave frequency = 9.763 GHz, power, = 0.6325 mW, modulation amplitude = 0.1 mT/100 kHz, temperature = 23 °C. TEMPO g_{iso} = 2.003, TEMPO A_{iso} = 44, TEMPO lwpp = 0.455; Cp*$_2$TiCl g_{iso} = 1.98, Ti lwpp = 0.455. Values for both Cp$^*_2$TiCl and TEMPO are unchanged in the presence of each other.

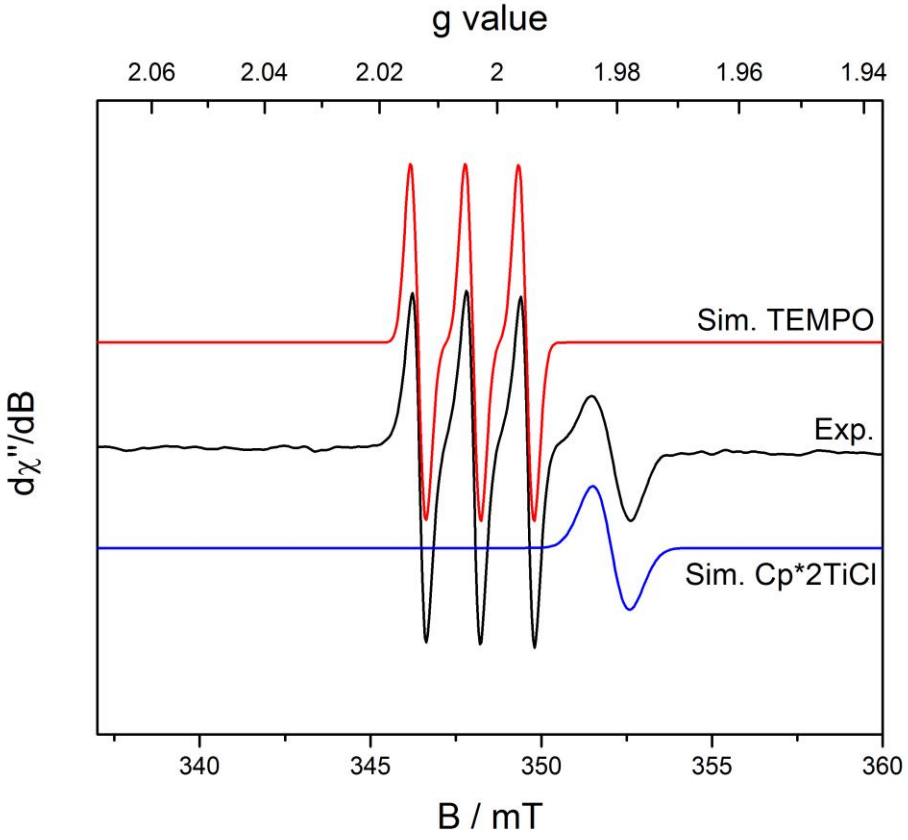


Figure S31 EPR of 1:1 TEMPO, Cp$^*_2$TiCl

VIII. CV Experiments

Experiment was performed at 23 °C in MeCN at 1 mM of $Cp^*_2TiCl_2$ using 0.1 M NBu_4PF_6 as supporting electrolyte. Scan rate (V/s) = 0.05. Platinum mesh electrode was used for a counter electrode. SCE reference electrode, glassy carbon working electrode.

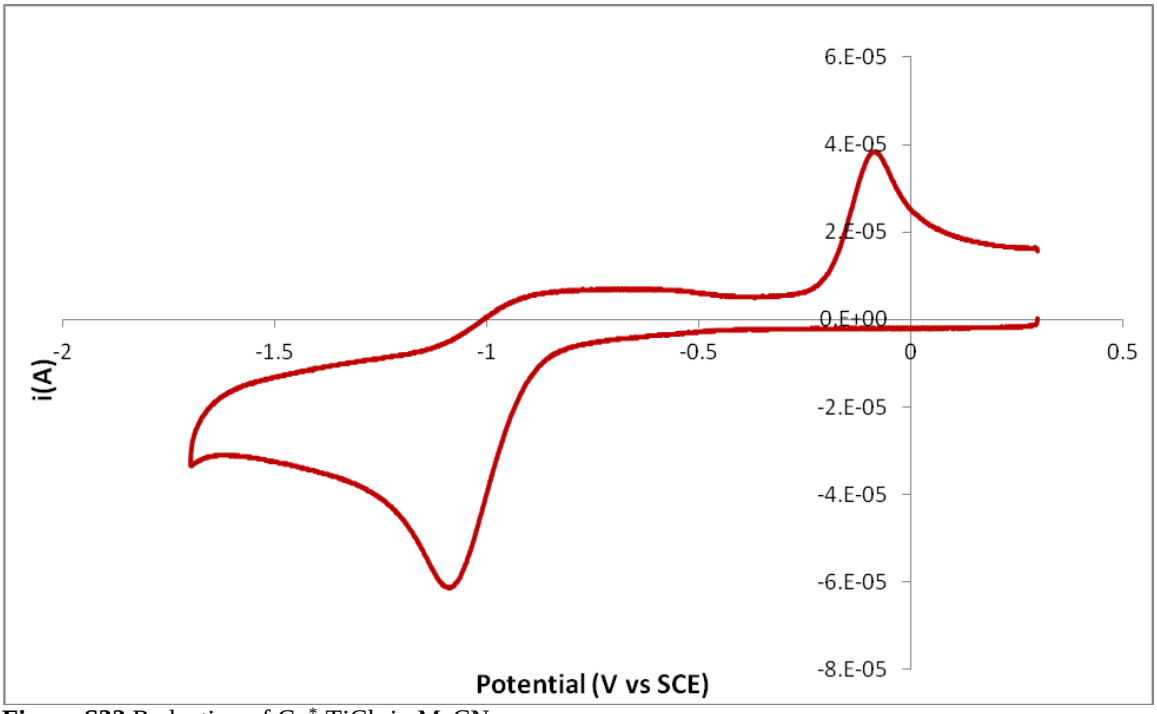


Figure S32 Reduction of $Cp^*_2TiCl_2$ in MeCN