Electronic Supporting Information

Promoting Halogen-Bonding Catalyzed Living Radical Polymerization through Ion-Pair Strain

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1. Materials and Methods.

Materials:

All chemical reagents were purchased from commercial suppliers (Energy Chemical, TCI, Inno-chem). All reagents and solvents were used as supplied without further purification. MMA, OMA, AN, BzMA, TFMA, MEMA, BA, and BzA were purified through an alumina column to remove the stabilizer.

Instruments & Methods:

Gel permeation chromatography (GPC). The GPC analysis with a dimethyl formamide (DMF) eluent was made on a P3100 liquid chromatograph pump (Elite, China) equipped with three Shodex mixed gel columns (KD801, KD802.5 and KD804; 300*8.0 mm; bead size = 7 μm; pore size = 20~200 Å). The flow rate of 1.0 mL/min (40 ℃). Sample detection and quantification were made with a Shodex differential refractometer RI-201 calibrated with known concentrations of polymer in solvent. The GPC analysis with a tetrahydrofuran(THF) eluent were made on a liquid chromatograph pump (Waters ACQUITY) equipped with three mixed gel columns (ACQUITY APC XT 125, 2.5μm, 4.6*150mm, ACQUITY APC XT 200, 2.5μm, 4.6*150mm, ACQUITY APC, XT 450, 2.5μm, 4.6*150mm). The flow rate of 0.5 mL/min (40 ℃). Sample detection and quantification were made with a differential refractometer calibrated with known concentrations of polymer in solvent.

Nuclear magnetic resonance (NMR). The NMR data was performed on JEOL 500 MHz spectrometer at 298 K.

Electrospray mass spectrometry (ESI-MS). The synthetic compounds were firstly dissolved in methanol with a concentration of 5 mg/L, and then subjected to Agilent1290/Bruker maXis spectrometer to collect the mass information.

Gas chromatography (GC). The GC equipped with an MXT-1 15 m*0.53 mm i.d., 3μm column was used for chromatographic separation from Nitrogen (99.99% purities) was used as carrier gas with a flow of 0.1 L/min. The sample was injected through a sample loop of 1 μL volume. The temperature was ranged from 50℃ to 250℃ and the rate was 40℃/min.

Fourier Transform Infrared Spectroscopy (FT-IR). FI-IR spectra were collected on a Bruker Vector 33 FT-IR spectrometer in the 500~4000 cm^{-1} region. The samples were dispersed in

anhydrous KBr powder, piled into thin tablets, and then subjected to the FT-IR spectrometer. The raw data was processed using Win-IR software.

Cyclic voltammetry. Cyclic voltammograms were recorded on a CHI600E electrochemical workstation using 0.5 M solutions of tetrabutylammonium hexafluorophosphate as the supporting electrolyte and ferrocene as an external standard (Fc/Fc$^+$ = 0.428 V). All experiments were run at a scan rate of 100 mV/s in acetonitrile (Energy Chemical, anhydrous 99.9%). Cyclic voltammetry was carried out in a three-electrode electrochemical cell, consisting of a glassy carbon disk working electrode (Gaoss Union), an Ag/Ag$^+$ quasi-reference electrode (Gaoss Union), and a platinum wire counter electrode (Gaoss Union).

DFT calculation: The geometries of the cations were optimized at the hybrid Meta-GGA level using TPSSh functional[1, 2] with def2-TZVP basis sets of the Karlsruhe group, as implemented in Orca program (Orca 5.0.3)[3, 4]. The solvent effects of toluene toward the cations were treated by the Conductor-like Polarizable Continuum Model (CPCM)[5].

2. Synthetic procedures and characterization.
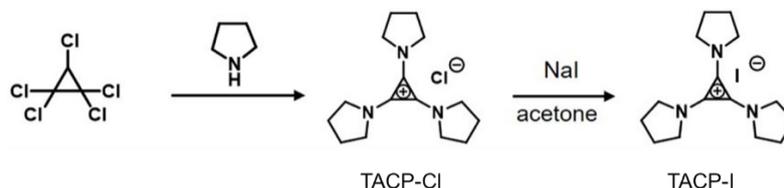
Scheme S1: Synthesis route of TACP-Cl and TACP-I

TACP-Cl：A 500 mL round bottom flask was charged with 40 mL of DCM and pentachlorocyclopropane (1.00 mL, 7.00 mmol). The flask was cooled to 0 °C and pyrrolidine (4.7mL, 56 mmol) was added dropwise. The reaction was stirred for 1 h at 0 °C and then for 24 h at room temperature. The reaction was transferred to a separatory funnel and washed with twice with 1M HCl (20 mL) and brine (20 mL). The organic layer was dried over anhydrous Na$_2$SO$_4$ and concentrated in vacuo to give TACP-Cl as a white solid, which was carried to the next step without further purification (1.87 g, 6.58 mmol, 94% yield). ^{1}H NMR (500 MHz, CDCl$_3$): δ(ppm) = 3.52~3.55(m, 12H), 2.02~2.06(m, 12H); ^{13}C NMR (125 MHz, CDCl$_3$): δ(ppm) = -113.88, -50.99, -25.88; MS (ESI-MS, m/z): Calc. for C$_{15}$H$_{24}$N$_3^+$: 246.20. Found: 246.197.

TACP-I: Anion exchange was accomplished by mixing an acetone (15 mL) solution of the corresponding TACP-Cl (1.87 g, 6.58 mmol) with an acetone (15 mL) solution of sodium iodide (2.0 g, 13.16 mmol). The reaction mixture was stirred at room temperature for 2 h. as sodium chloride was allowed to precipitate. The reaction mixture was then filtered, and an additional equivalent of sodium iodide was added to the filtrate. No further precipitation was observed over the course of 2 h. The reaction solution was then concentrated in vacuo to a solid mixture of cyclopropenium iodide and sodium iodide. Cyclopropenium iodide was extracted in pure form from this solid mixture with dichloromethane followed by a water wash to remove trace sodium iodide. The title cyclopropenium salt TACP-I was isolated as a white solid in 98% yield (2.42 g, 6.45 mmol).

^{1}H NMR (500 MHz, CDCl$_3$): δ(ppm) = 3.52~3.55(m, 12H), 2.02~2.06(m, 12H); ^{13}C NMR (125 MHz, CDCl$_3$): δ(ppm) = -113.88, -50.99, 25.88; MS (ESI-MS, m/z): Calc. for C$_{15}$H$_{24}$N$_3{}^+$: 246.20, Found: 246.196.

Scheme S2: Synthesis route of **TACE-I.**

TAC-Cl: TAC-Cl was synthesized according to the reported procedure1. [6]

TACE-Cl: A 500mL round bottom flask was charged with DCM (250 mL), TAC-Cl (1.55 g, 5 mmol) and N, N-Diisopropylethylamine (DIPEA) (969.4 mg, 7.5 mmol,). The flask was cooled to 0°C and N-Ethyl methylamine (354.7 mg, 6 mmol) was added slowly. The reaction was stirred for 4 h at 0°C, then the DCM layer was washed with 1M HCl (100 mL). The combined organic extracts were dried over sodium sulfate and concentrated. The residue was purified by flash chromatography on silica gel, using DCM: MeOH (10: 1) as eluent. TACE-Cl was isolated as a yellow solid in 75% yield (1.43 g, 4.316 mmol). ^{1}H NMR (500 MHz, CDCl$_3$): δ(ppm) = 3.95~3.83 (m, 4H), 3.60 (q, J = 7.0 Hz, 2H), 3.29 (s, 3H), 1.38 (dd, J = 6.9 Hz, 24H), 1.31 (t, J = 7.2 Hz, 3H). ^{13}C NMR (125 MHz, CDCl$_3$): δ(ppm)=119.06, 116.83, 51.53, 49.63, 39.65, 22.06, 13.47. MS (ESI-MS, m/z): Calc. for

$C_{18}H_{36}N_3^+$: 294.29. Found: 294.2926.

TACE-I: Anion exchange was accomplished by mixing an acetone (15 mL) solution of the corresponding 1b (1.43 g, 4.316 mmol) with an acetone (15 mL) solution of sodium iodide (1.3 g, 8.632 mmol). The reaction mixture was stirred at room temperature for 2 h. as sodium chloride was allowed to precipitate. The reaction mixture was then filtered, and an additional equivalent of sodium iodide was added to the filtrate. No further precipitation was observed over the course of 2 h. The reaction solution was then concentrated in vacuo to a solid mixture of cyclopropenium iodide and sodium iodide. Cyclopropenium iodide was extracted in pure form from this solid mixture with dichloromethane followed by a water wash to remove trace sodium iodide. The title cyclopropenium salt was isolated as a light-yellow solid in 98% yield (1.76 g, 2.95 mmol). ^{1}H-NMR (500 MHz, CDCl$_3$): δ(ppm) = 3.90 (p, J = 6.9 Hz, 4H), 3.61 (q, J = 7.2 Hz, 2H), 3.29 (s, 3H), 1.40 (d, J = 6.9 Hz, 24H), 1.32 (t, J = 7.2 Hz, 3H). ^{13}C NMR (125 MHz, CDCl$_3$): δ(ppm) = 119.29, 117.12, 51.54, 49.79, 39.65, 22.25, 13.59. MS (ESI-MS, m/z): Calc. for $C_{18}H_{36}N_3^+$: 294.29. Found: 294.2917.
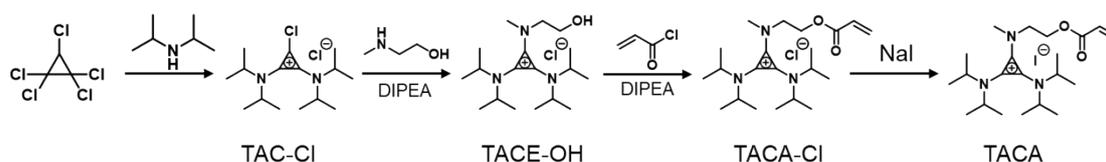
Scheme S3: Synthesis route of **TACA.**

TACA: A 500 mL round bottom flask was charged with DCM (250 mL), TAC-Cl (1.55 g, 5 mmol) and DIPEA (969.4 mg, 7.5 mmol). The flask was cooled to 0°C and 2-Methylaminoethanol (450.66 mg, 6 mmol) was added slowly. The reaction was stirred for 24 h at 0°C, then the DCM layer was washed with 1M HCl (100 mL). The combined organic extracts were dried over sodium sulfate and concentrated. The residue was purified by flash chromatography on silica gel, using DCM: MeOH (10: 1) as eluent. The TACE-OH was isolated as a yellow solid in 70% yield (1.39 g, 4 mmol). Then a 500ml round bottom flask was charged with DCM (200 mL), TACE-OH (1.39 g, 4 mmol) and DIPEA (775.52 mg, 6 mmol). The flask was cooled to 0°C and acrylylchloride (543 mg, 6 mmol) was added slowly. The reaction was stirred for 24 h at 0°C, then the DCM layer was washed with 1M HCl. The combined organic extracts were dried over sodium sulfate and concentrated. The

residue was purified by flash chromatography on silica gel, using DCM: MeOH (10: 1) as eluent. TACA-Cl was isolated as a yellow solid in 75% yield (1.2 g, 3 mmol). Anion exchange was accomplished by the procedure similar to TACP-I. The TACA was a light-yellow solid in 98% yield (1.76 g, 2.94 mmol). ^{1}H NMR (500 MHz, CDCl$_3$) δ(ppm) 6.36 (d, J = 17.3 Hz, 1H), 6.04 (dd, J = 17.3, 10.4 Hz, 1H), 5.87 (d, J = 10.4 Hz, 1H), 4.46 (t, J = 5.2 Hz, 2H), 3.95~3.80 (m, 6H), 3.33 (s, 3H), 1.35 (d, J = 6.9 Hz, 24H). ^{13}C NMR (125 MHz, CDCl$_3$): δ(ppm)=165.67, 132.12, 127.69, 119.67, 117.71, 60.73, 54.08, 51.69, 40.67, 22.28. MS (ESI-MS, m/z): Calc. for C$_{21}$H$_{38}$O$_2$N$_3^+$: 364.30. Found: 364.2972.

TPFI: TPFI was synthesized according to the reported procedure. [7]

3. Experimental Conditions.

Radical-Generation Reaction:

A mixture of toluene-d_8 (0.9 mL), acetonitrile-d_3 (0.1 mL), CP-I (10 mM), an organic salt catalyst (80 mM), and TEMPO (20 mM) in a sealed NMR tube was heated at a certain temperature for 1~5 h under argon atmosphere. The reactions were monitored by ^{1}H-NMR spectroscopy.
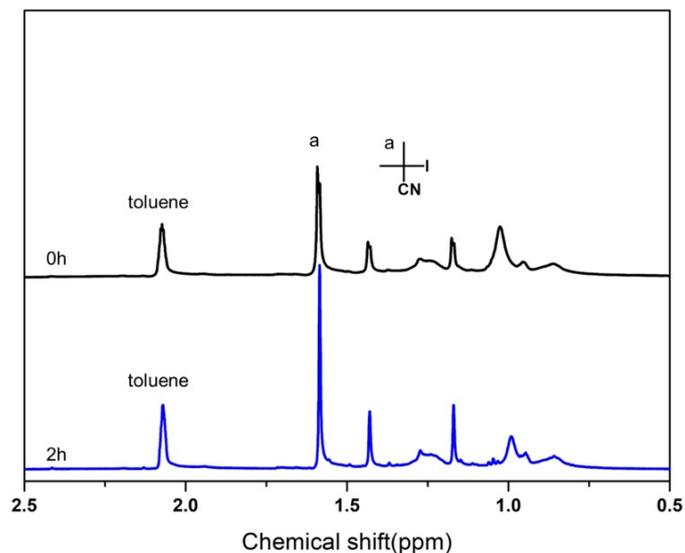
Figure S1: ^{1}H NMR spectrum of the radical-generation reaction with TACP-I as catalyst and TPFI as inhibitor.
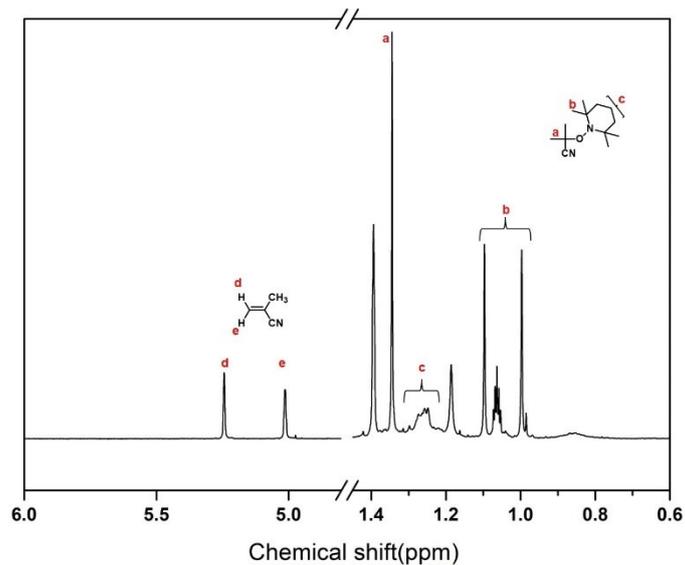
Figure S2: ^{1}H NMR spectrum of the radical-generation reaction catalyzed by TACP-Cl.

Bulk Polymerization of MMA:

In a typical run, a mixture of MMA (3 mL, 28.3mmol), CP-I (27.5mg, 0.141mmol), and a catalyst (26.5mg, 0.071mmol) in a 25 mL Schlenk flask was heated at 60°C under argon atmosphere with magnetic stirring. After certain reaction time, an aliquot (0.1 mL) of the solution was taken out by a syringe, quenched, and analyzed by ^{1}H-NMR.
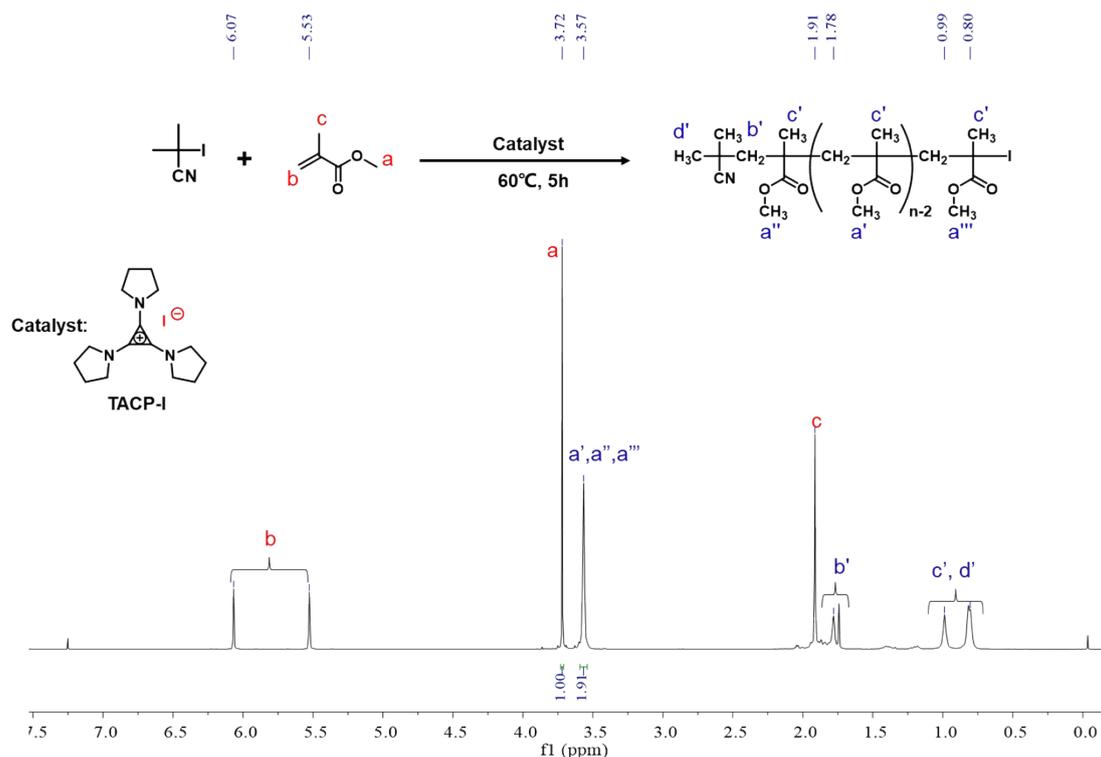
Figure S3. ^{1}H NMR spectrum of the polymerization catalyzed by TACP-I after 5 h of reaction.
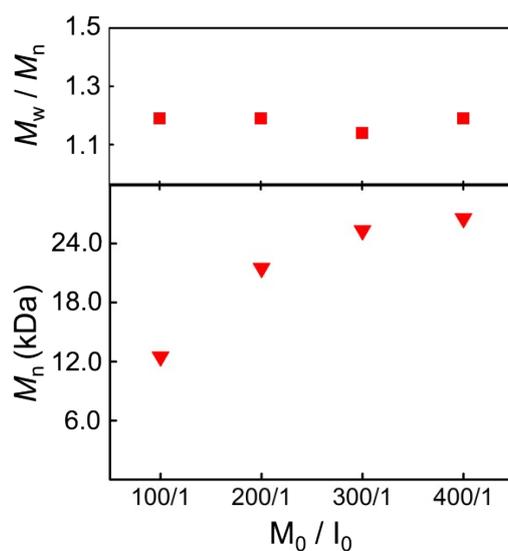
Figure S4. The plots of M_n and Đ against $[M]_0/[I]_0$. The polymerizations were performed in bulk with $[MMA]_0/[CP\text{-}I]_0/[TACP\text{-}I]_0 = X/1/0.5$ (X = 100,200,300,400) at 60 °C for 6 h.

Chain-End Fidelity:

A mixture of MMA (3mL, 28.3mmol), CP-I (27,5mg, 0.141mmol), and TACP-I (26.5mg, 0.071mmol) in 25mL Schlenk flask was heated at 60°C for 2 h under argon atmosphere with magnetic stirring. The desired PMMA-I was obtained after purification by reprecipitation from hexane and methanol. GPC (DMF): M_n = 15.3 kDa, $Đ$ = 1.11. Monomer conversion (%): 50% (Target DP=200). The peak at 3.7~ 3.75 ppm was assigned as the ω-terminal chain-end unit (a′), and the main peak at 3.55–3.63 ppm and its side peak at 3.63–3.65 ppm is assigned to the monomer units (a) in the middle of the chain.[8] In this case, the fraction of iodine chain end was calculated to be larger than 95%.
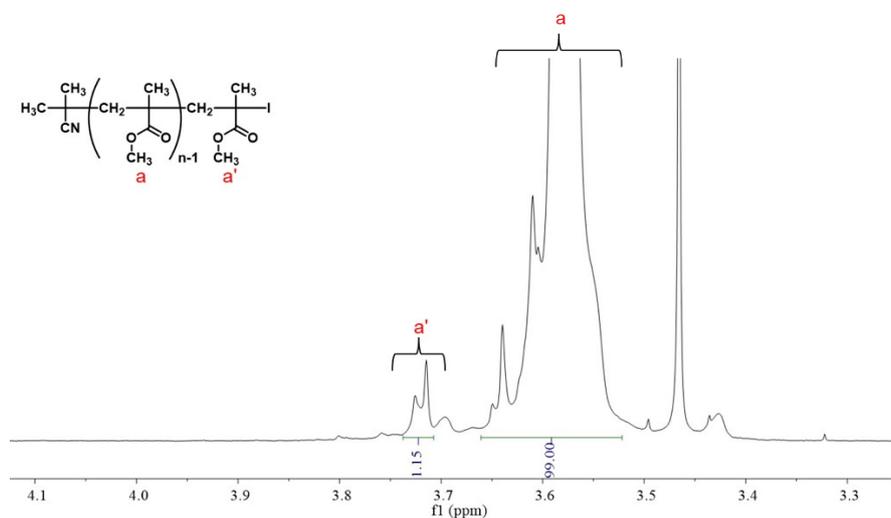
Figure S5: ^{1}H NMR spectrum (in the range of 3.3~4.10 ppm, CDCl$_3$) of PMMA–I(M_n =15.3 kDa and $Đ$ of 1.11 with DMF as eluent and PMMA as standard).
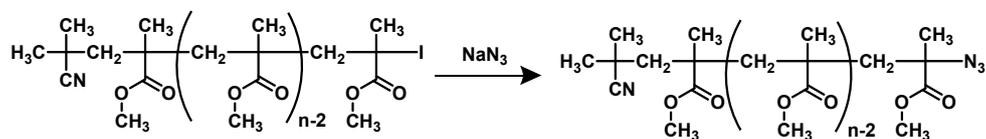
Scheme S4: Synthesis route of **PMMA-N$_3$.**

PMMA-N$_3$: A 50 mL round bottom flask was charged with PMMA-I(M_n=10000) (200mg, 0.02mmol) and DMF(5mL). The flask was cooled to 0 °C and NaN$_3$ (5mg, 0.07mmol) dissolved in DMF was added dropwise. The mixture was heated at 45°C for 12 h under with magnetic stirring before DI water was added. Then the reaction mixture was extracted with ethyl acetate (EA, 100

mL) and washed by water (2 x 100 mL). The organic layer was dried over with anhydrous Na_2SO_4. After purification by reprecipitation from methanol, a PMMA-N_3 was isolated. The polymer (Figure S6) displayed signals at 3.74~3.80 ppm, indicates the transformation of -I to -N_3. The infrared (IR) spectrum (Figure S7) of the polymer after the chain-end transformation showed a characteristic absorption band for azido moiety at 2120 cm^{-1}, demonstrating the successful generation of PMMA−N_3.
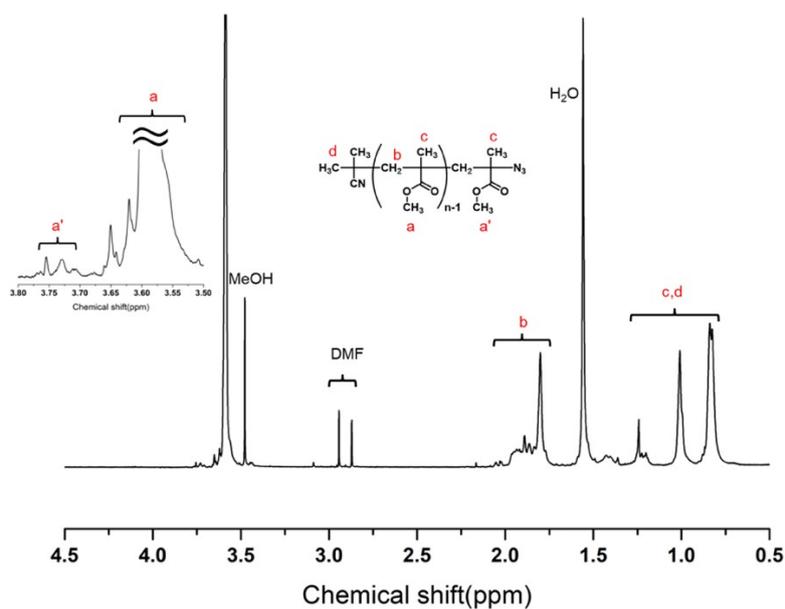
Figure S6: ^{1}H NMR spectrum (in the range of 4.5~0.5 ppm, CDCl$_3$) of PMMA–N_3.
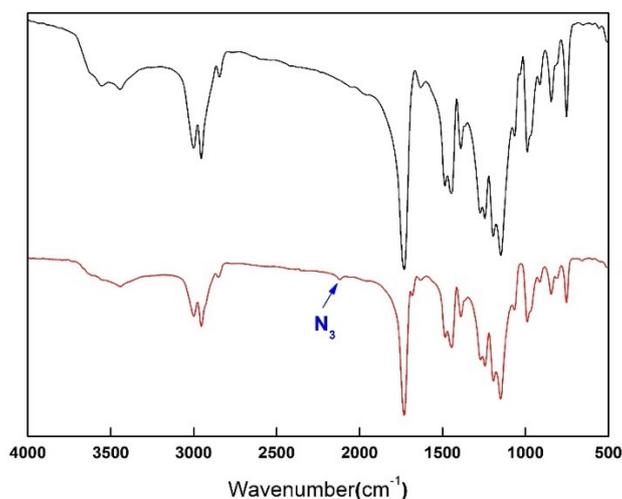
Figure S7: IR spectra of PMMA-I (black line) and PMMA–N_3 (red line).

Self-Catalyzed Polymerization:

In a typical run, a mixture of BzA (170 μL, 1.134 mmol), TACA(62.5 mg, 0.126 mmol), CP-I (2.5 mg，0.0126 mmol) in a 25 mL Schlenk flask was heated at 110°C under argon atmosphere with magnetic stirring. The conversion of BzA and TACA were calculated using ^{1}H NMR to be 37.5% and 34.3%, respectively. The desired polymer was obtained after purification by reprecipitation twice from a mixture of hexane/ethanol (7/3(v/v)).
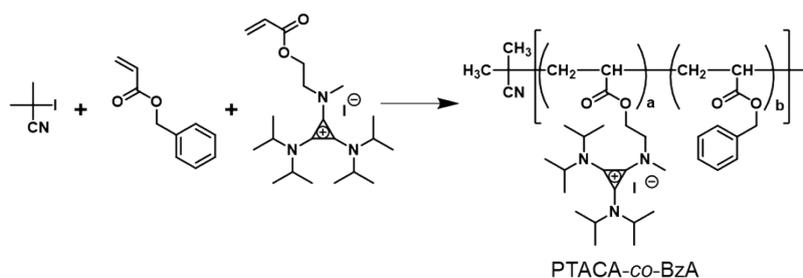
Scheme S3: Polymerization of PTACA-*co*-BzA.
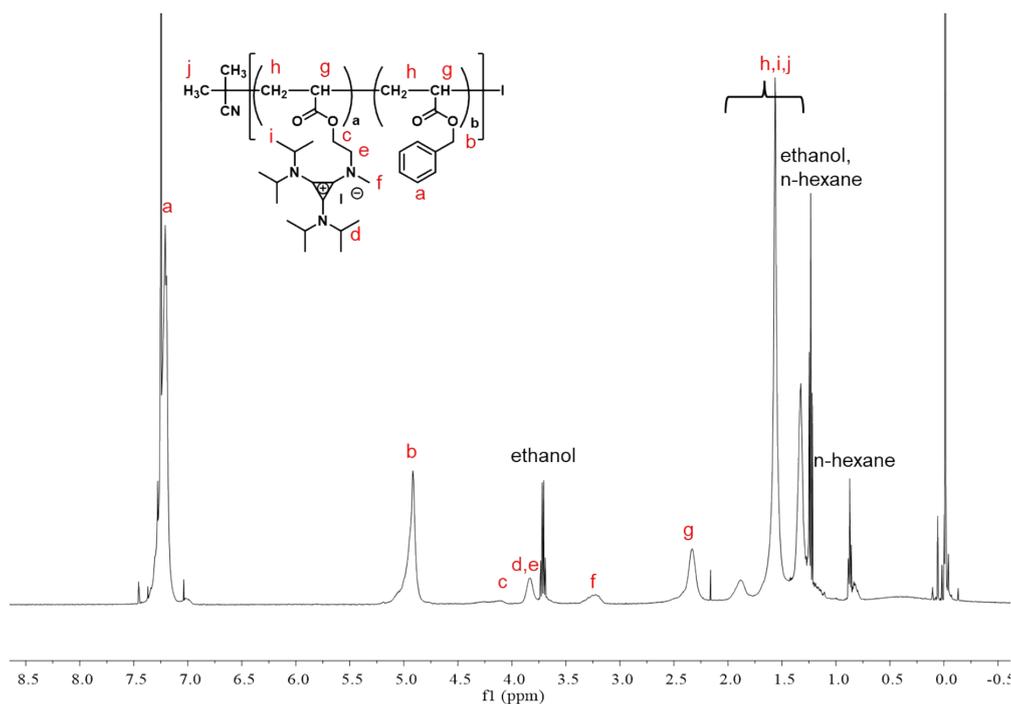
Figure S8: ^{1}H NMR spectrum of the polymer PTACA-*co*-BzA after purification.

Chain-Extension Experiment and Block Copolymerization

Preparation of the Macroinitiator PMMA-I: A mixture of MMA (3mL, 28.3mmol), CP-I (27.5mg, 0.141mmol), and TACP-I (26.5mg, 0.071mmol) in a 25mL Schlenk flask was heated at 60°C for 2 h under argon atmosphere with magnetic stirring. The desired PMMA-I was obtained after purification by reprecipitation from hexane and methanol. GPC (DMF): M_n = 15.3 kDa, $Đ$ = 1.11.

Chain-Extension Polymerization:

Polymerization of PMMA with Macroinitiator PMMA-I: A mixture of PMMA-I (GPC with DMF eluent: M_n = 15.3 kDa, $Đ$ = 1.11, 90.5 mg, 0.00905 mmol of iodine chain end), MMA (1 mL, 9.43 mmol) and TACP-I (47 mg, 0.126 mmol) in a 100 mL round-bottom flask was heated at 60°C under argon atmosphere with magnetic stirring. After a prescribed time t, an aliquot (0.1 mL) of the solution was taken out by a syringe, quenched to room temperature, diluted by DMF to a known concentration, and analyzed by GPC.

Block Copolymerization of PMMA-*b*-PBzMA: A mixture of PMMA-I (GPC with DMF eluent: M_n = 15.3 kDa, $Đ$ = 1.11, 90mg, 0.009 mmol of iodine chain end), BzMA (0.3mL,1.764mmol) and TACP-I (13.4mg, 0.036mmol) in a 25mL Schlenk flask was heated at 60°C for 6 h under argon atmosphere with magnetic stirring. The desired product was obtained after purification by reprecipitation from hexane and methanol.

Block Copolymerization of PMMA-*b*-PTFMA: A mixture of PMMA-I (GPC with DMF eluent: M_n = 15.3 kDa, $Đ$ = 1.11, 100 mg, 0.01 mmol of iodine chain end), TFMA (0.3mL, 2.1 mmol) and TACP-I (7.4 mg, 0.02mmol) in a 25mL Schlenk flask was heated at 60°C for 6 h under argon atmosphere with magnetic stirring. The desired product was obtained after purification by reprecipitation from hexane and methanol.
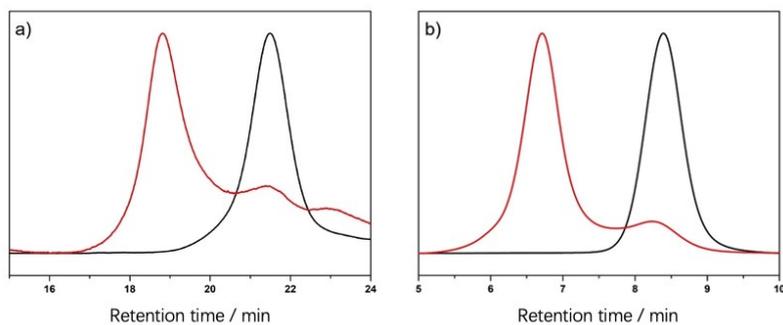
Figure S9: The GPC chromatograms of chain-extension block polymerization (macroinitiator: black; block copolymer of PMMA-b-PTFMA: red; characterized by GPC with (a) DMF as eluent and PMMA as standard and (b) THF as eluent and PS as standard).
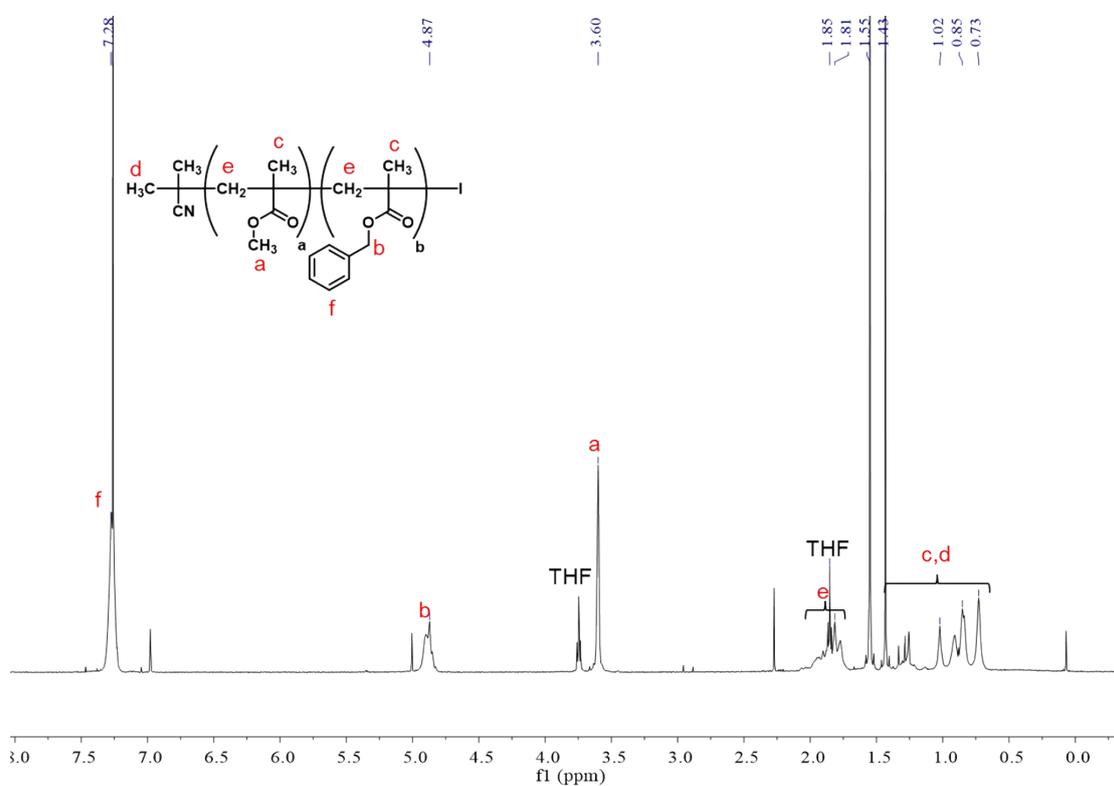
Figure S10: ^{1}H NMR spectrum of block copolymer of PMMA-*b*-PBzMA after purification.
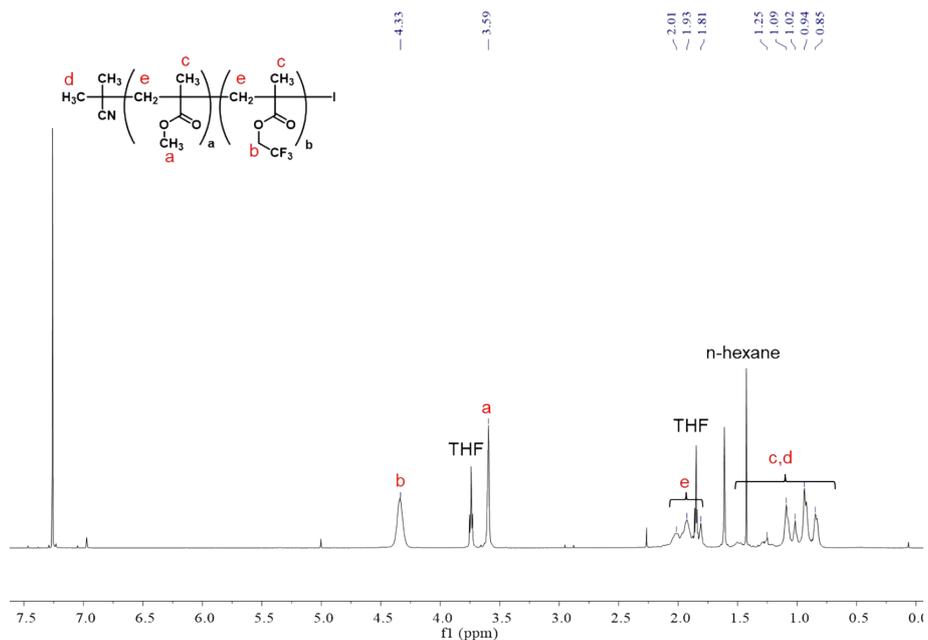
Figure S11: ^{1}H NMR spectrum of block copolymer of PMMA-*b*-PTFMA after purification.
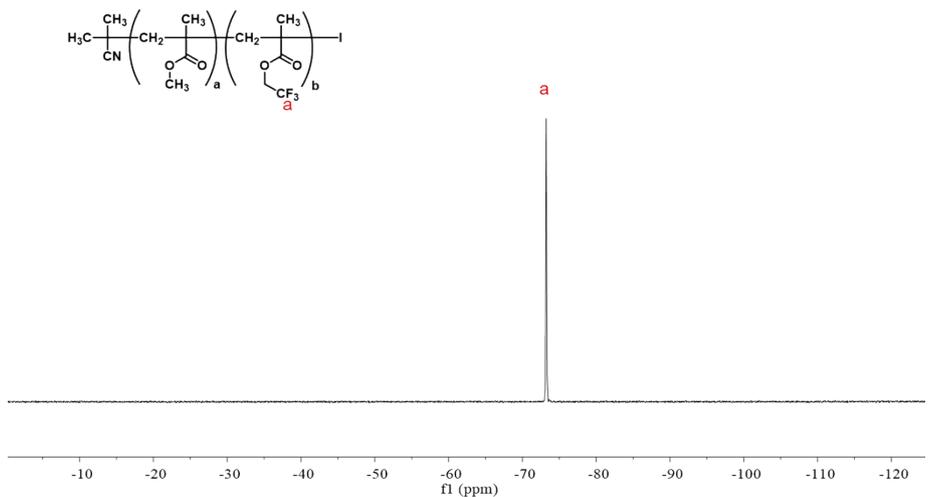
Figure S12: ^{19}F NMR spectrum of block copolymer of PMMA-*b*-PTFMA after purification.

XB-Catalyzed Depolymerization

Preparation of the PMMA-I for depolymerization: A mixture of MMA (3mL, 28.3mmol), CP-I (27.5mg, 0.141mmol), and TBMP-I (24.4mg, 0.071mmol) in a 25mL Schlenk flask was heated at 60°C for 4 h under argon atmosphere with magnetic stirring. The desired PMMA-I was obtained by reprecipitation from hexane and methanol. GPC (DMF): M_n = 10.2 kDa, Đ = 1.15.

Depolymerization: In a 25 mL Schlenk flask, a catalyst (320mM) and 10 mg of PMMA-I (3.2 mM of iodine chain end) was dissolved in 0.5 mL tetraglyme. The Schlenk flask was then put into a 120 °C oil bath under argon atmosphere with magnetic stirring. the reaction was periodically removed from the oil bath and quickly added to an ice bath until the solution cooled to room temperature. The sample was diluted by DMF to a known concentration, and analyzed by GPC.
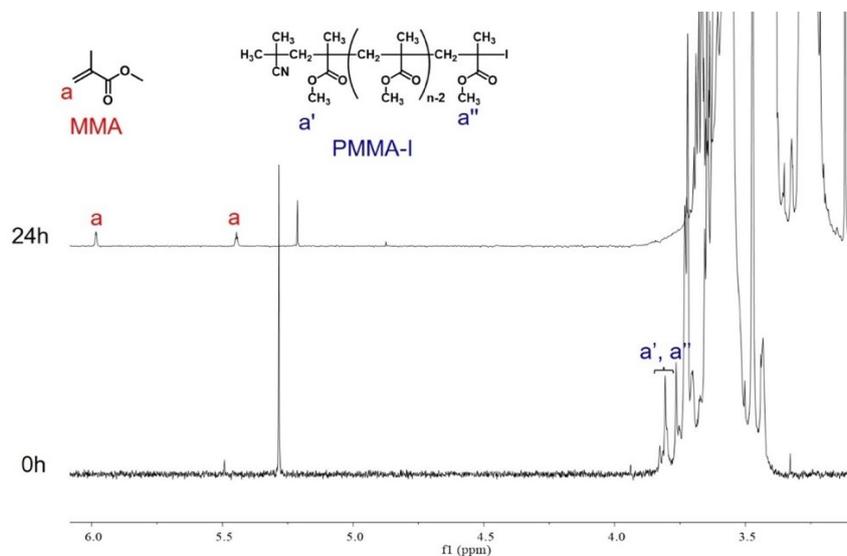
Figure S13: ^{1}H-NMR spectra of depolymerization of PMMA-I with TACP-I catalyst: [PMMA-I]$_0$/ [TACP-I] = 1/100 in tetraglyme at 120°C for 24h.
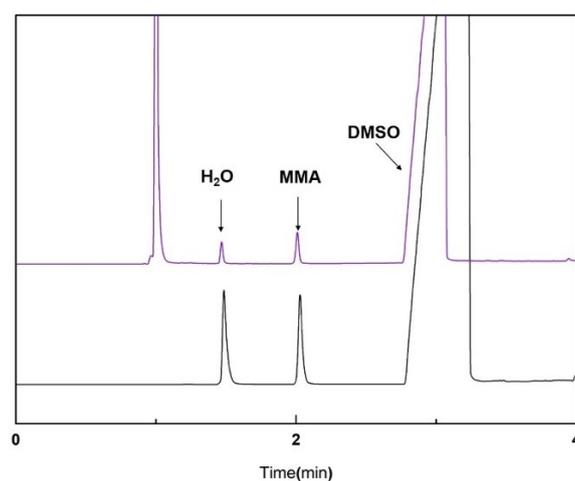
Figure S14: Gas chromatography for characterization of MMA generation through depolymerization of PMMA-I: [PMMA-I]$_0$: [TACP-I] = 1/100 in tetraglyme at 120°C for 24h. (MMA in DMSO: black; depolymerizing product: purple).
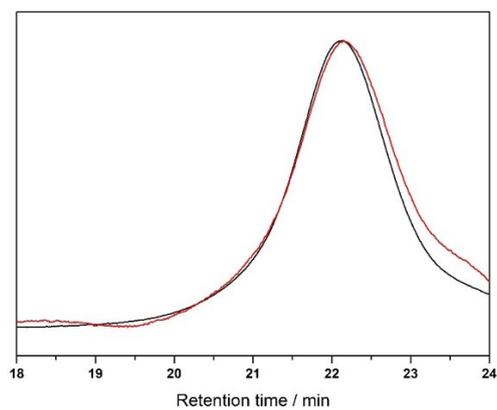
Figure S15: GPC characterization for [PMMA-I]$_0$ (3.2mM) in tetraglyme at 120°C without

catalyst for 0 h (black line) and 24 h (red line).
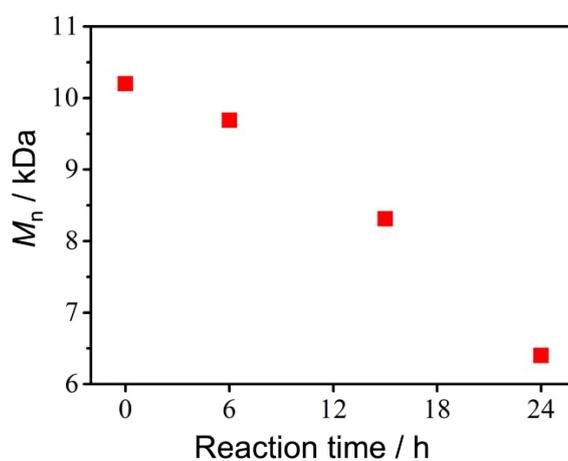
Figure S16: The plot of $M_{n,GPC}$ against reaction time.

(Depolymerization of [PMMA-I]$_0$ (3.2mM) at 120 °C in tetraglyme with TACP-I as catalyst.)
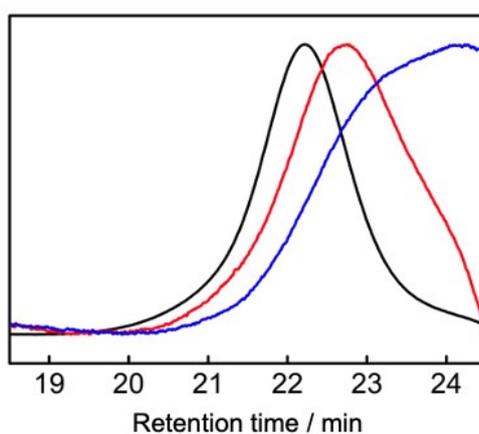
Figure S17: Depolymerization of [PMMA-I]$_0$ (3.2mM) in tetraglyme. GPC traces obtained from

the samples: before reaction (black line); reacted at 120 °C for 24 h with TACP-I as catalyst (red

line); reacted at 150 °C for 24 h with TACP-I as catalyst (blue line).

4. Appendix.
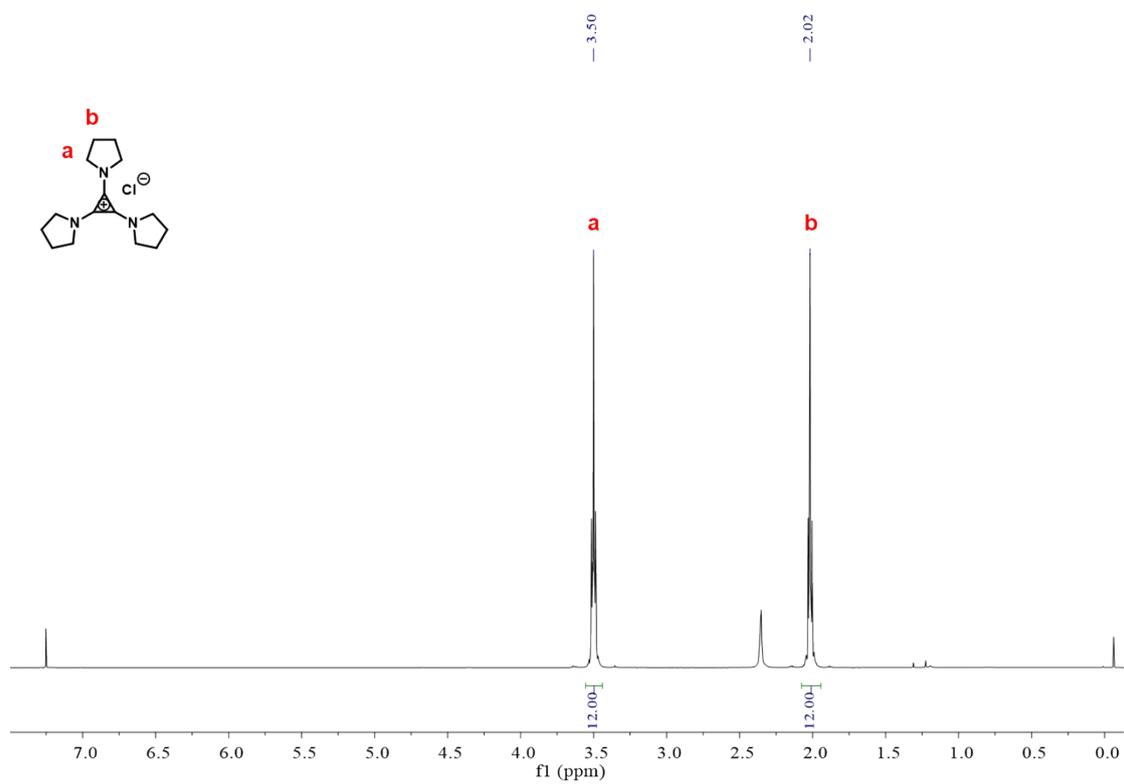
Figure S18: ^{1}H NMR (500 MHz, CDCl$_3$) spectrum of **TACP-Cl**.
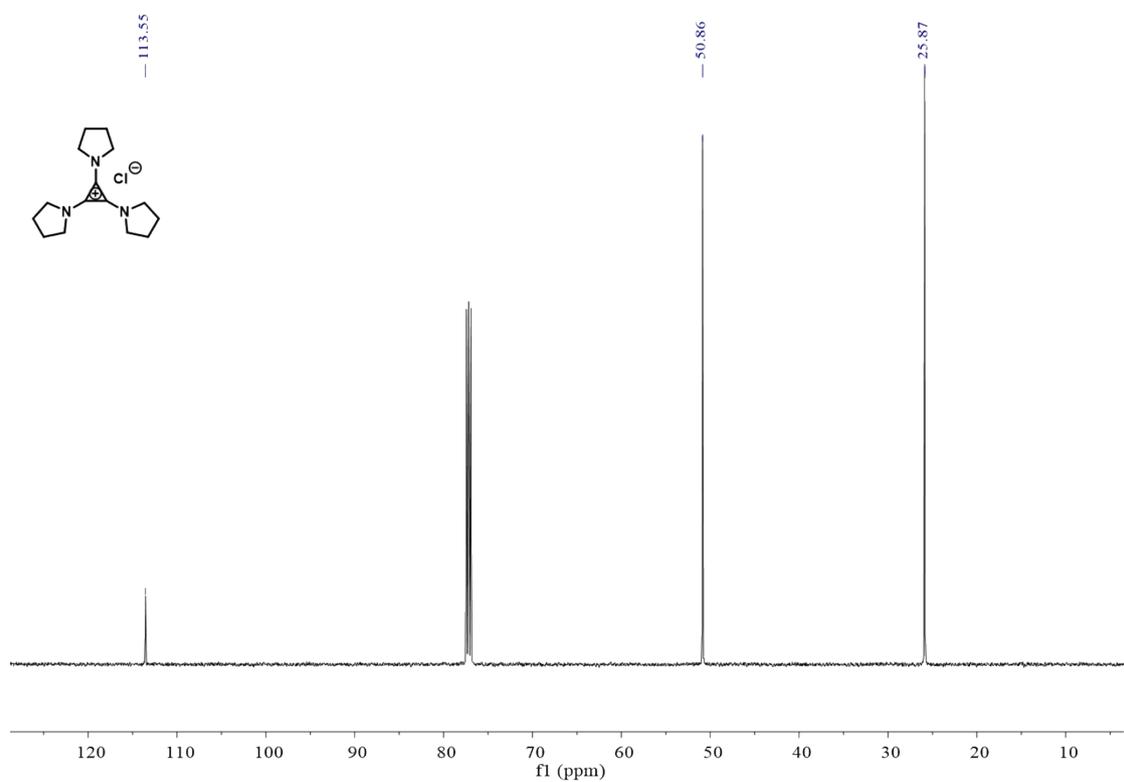
Figure S19: ^{13}C NMR (125MHz, CDCl$_3$) spectrum of **TACP-Cl**.
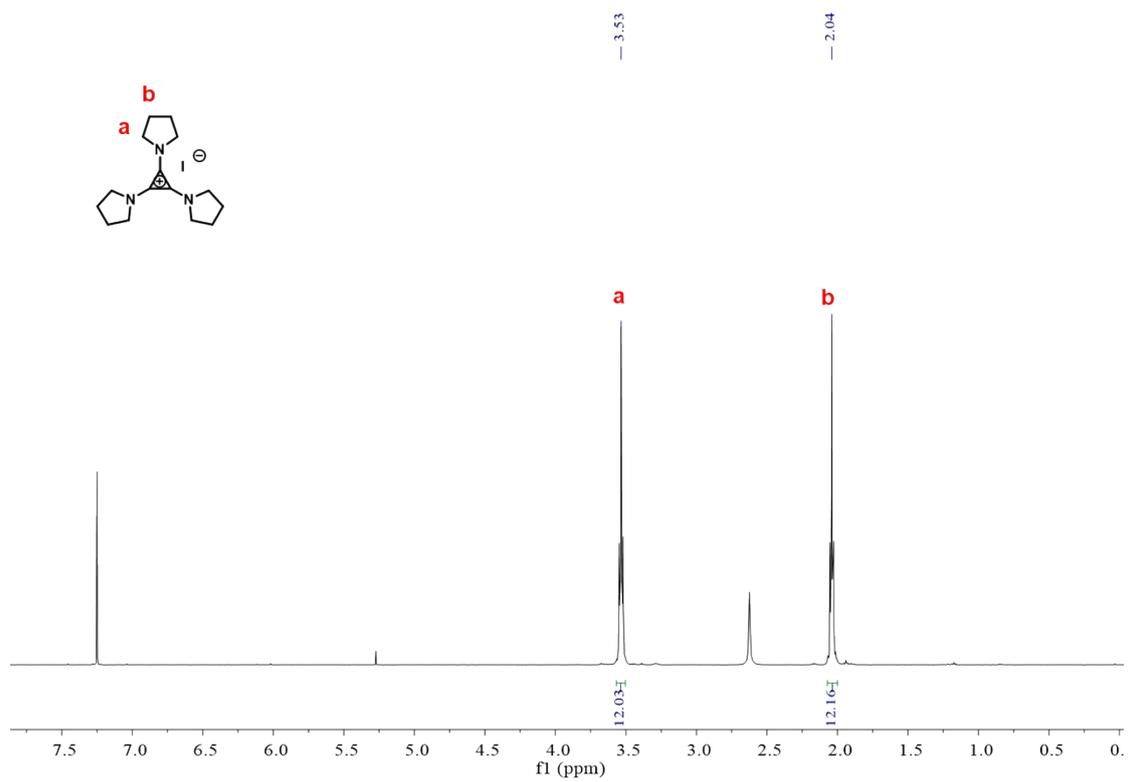
Figure S20: ^{1}H NMR (500 MHz, CDCl$_3$) spectrum of **TACP-I**.
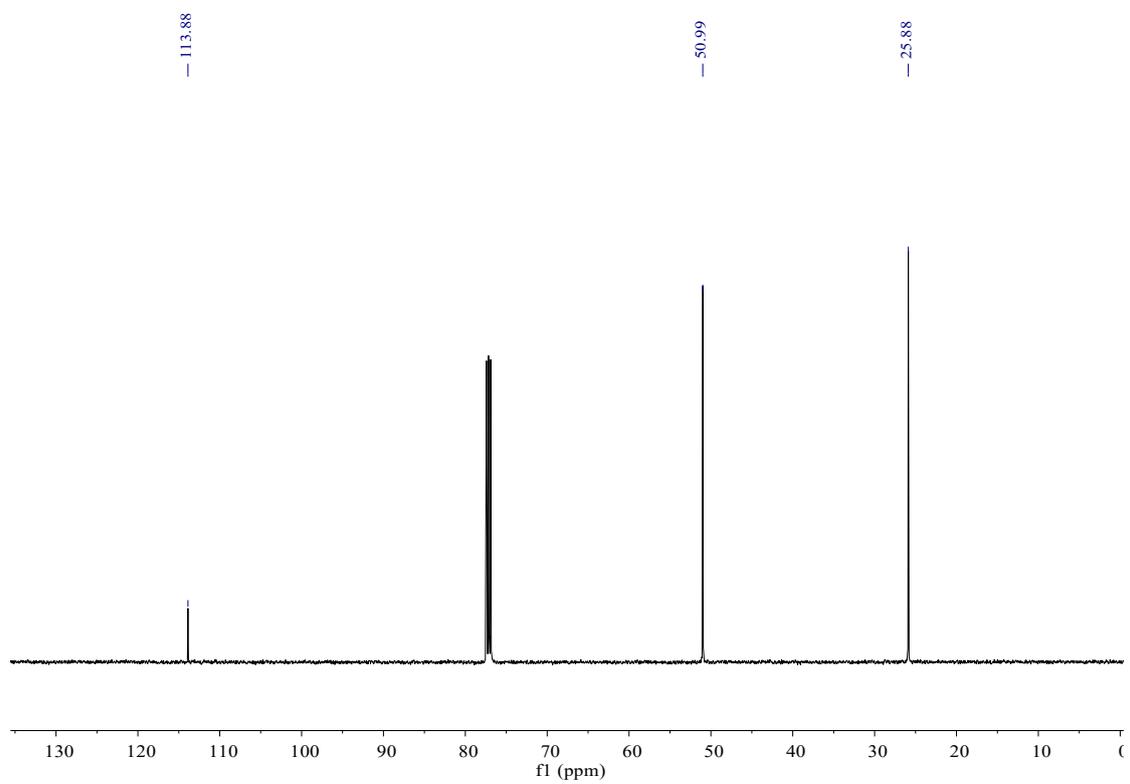
Figure S21: ^{13}C NMR (125MHz, CDCl$_3$) spectrum of **TACP-I**.
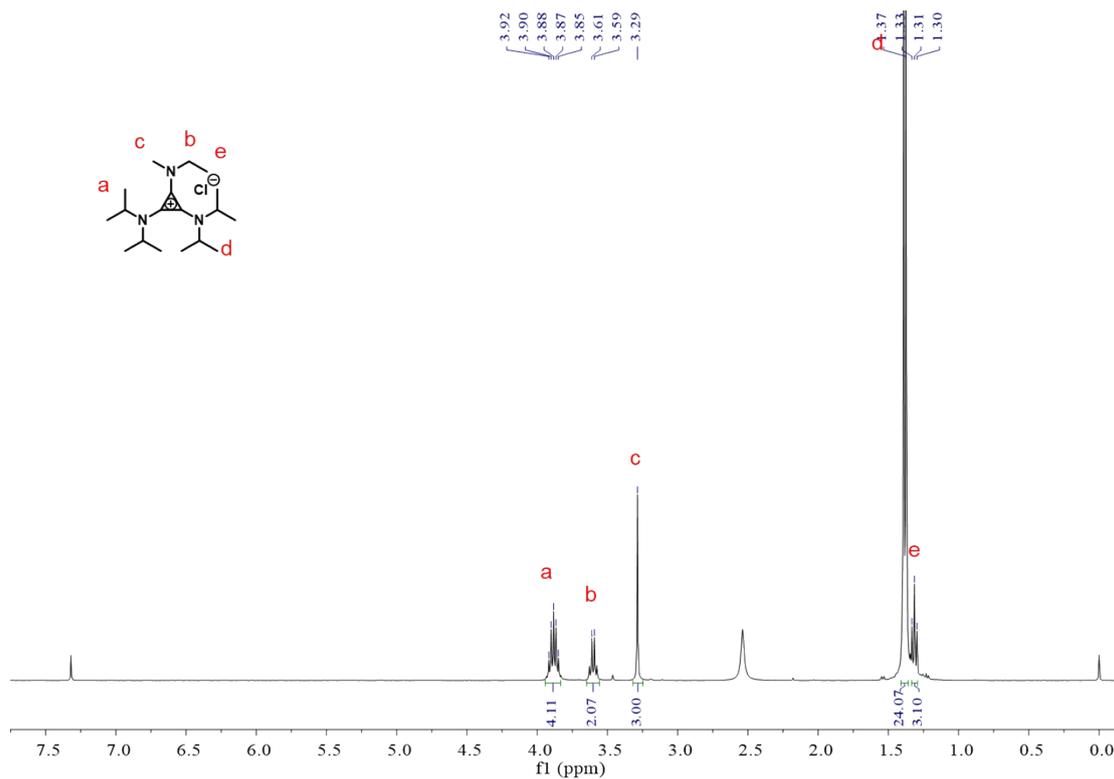
Figure S22: ^{1}H NMR (500 MHz, CDCl$_3$) spectrum of **TACE-Cl**.
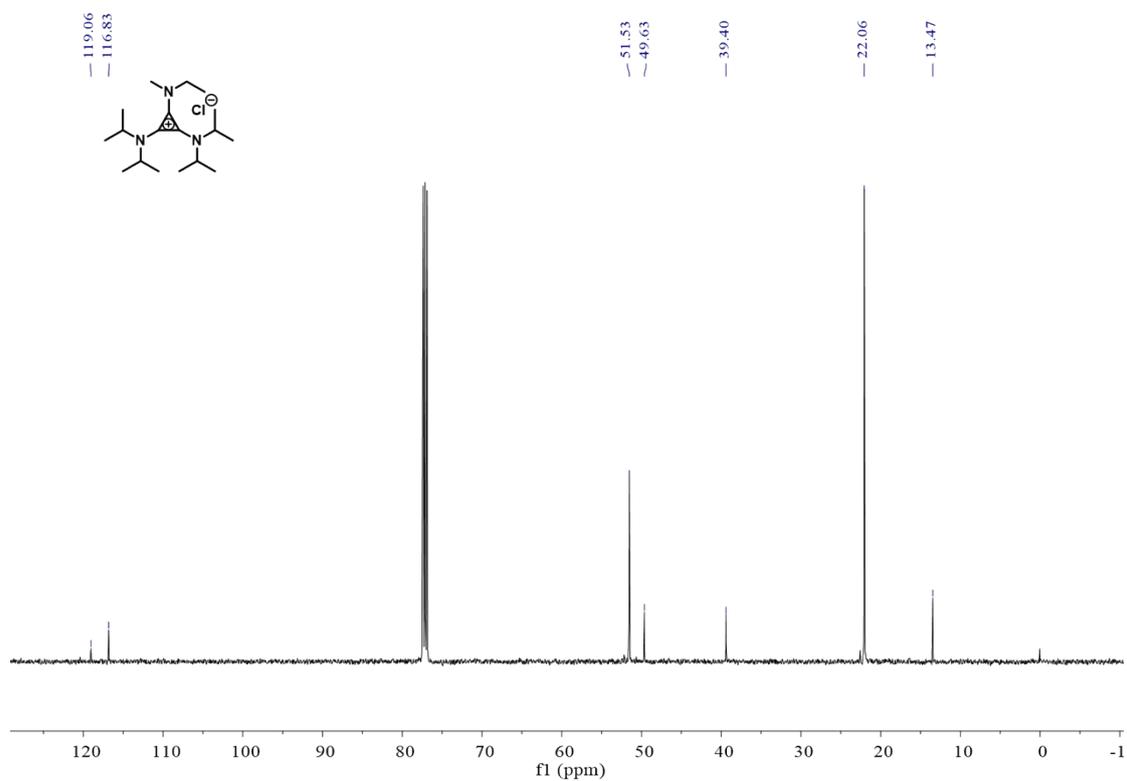
Figure S23: ^{13}C NMR (125MHz, CDCl$_3$) spectrum of **TACE-Cl**.
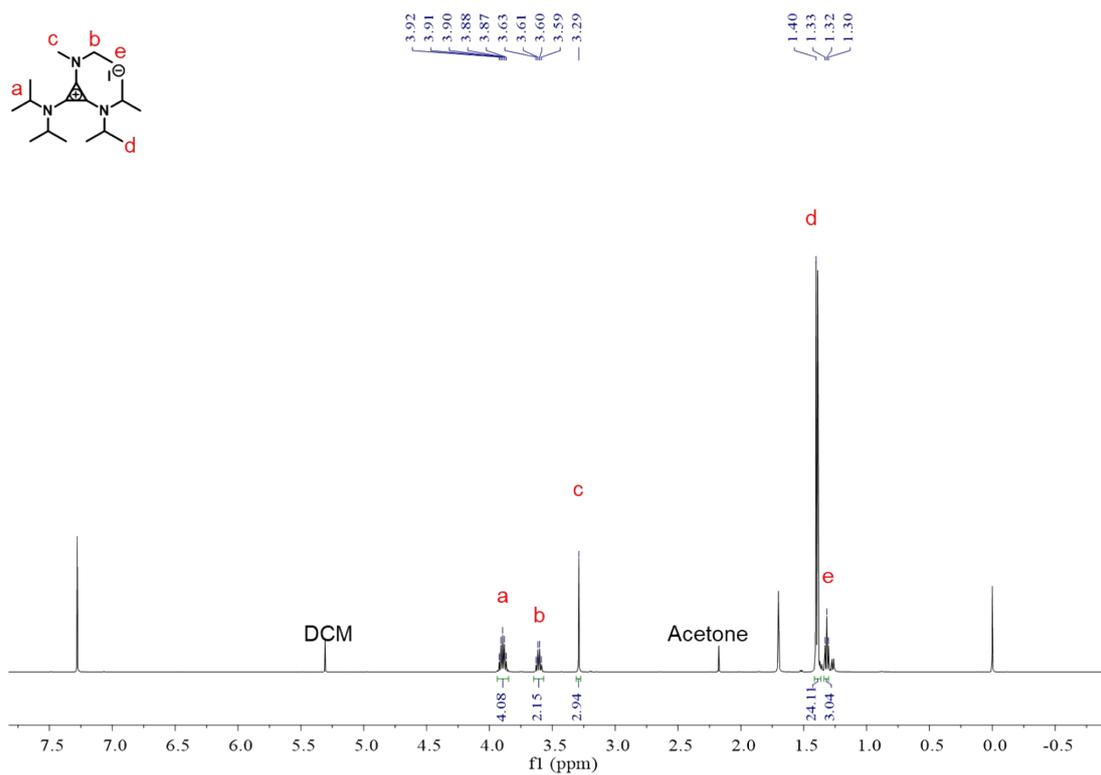
Figure S24: ^{1}H NMR (500 MHz, CDCl$_3$) spectrum of **TACE-I**.
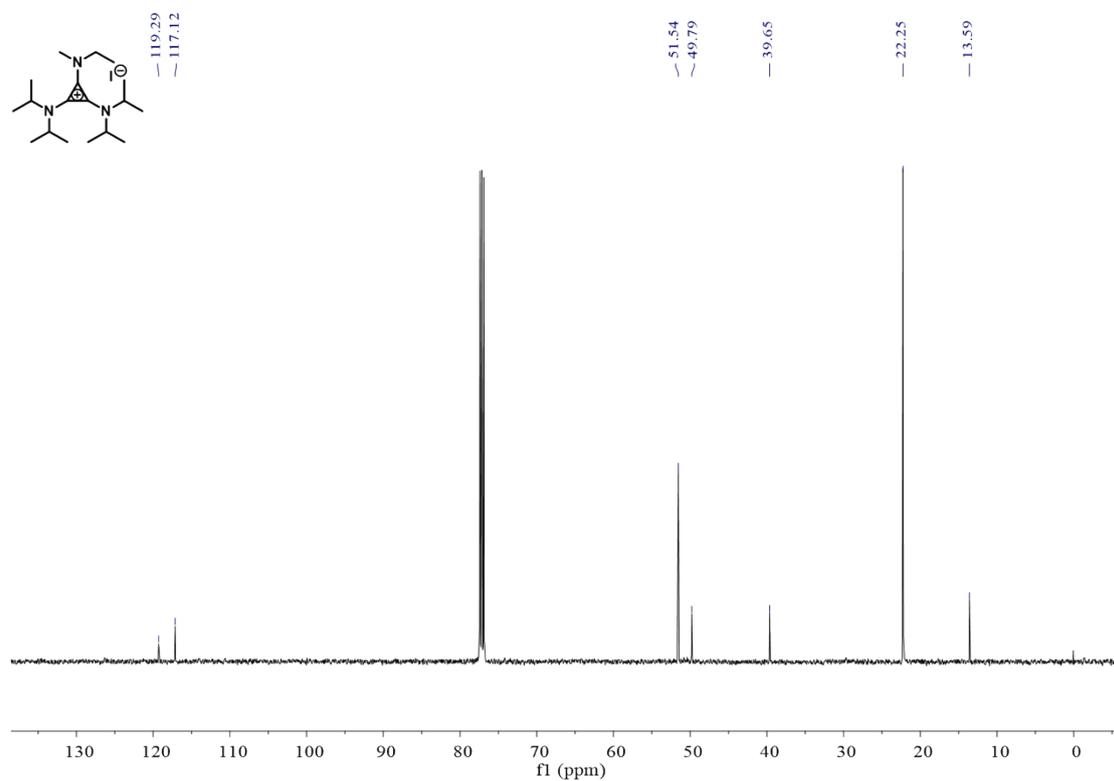
Figure S25: ^{13}C NMR (125MHz, CDCl$_3$) spectrum of **TACE-I**.
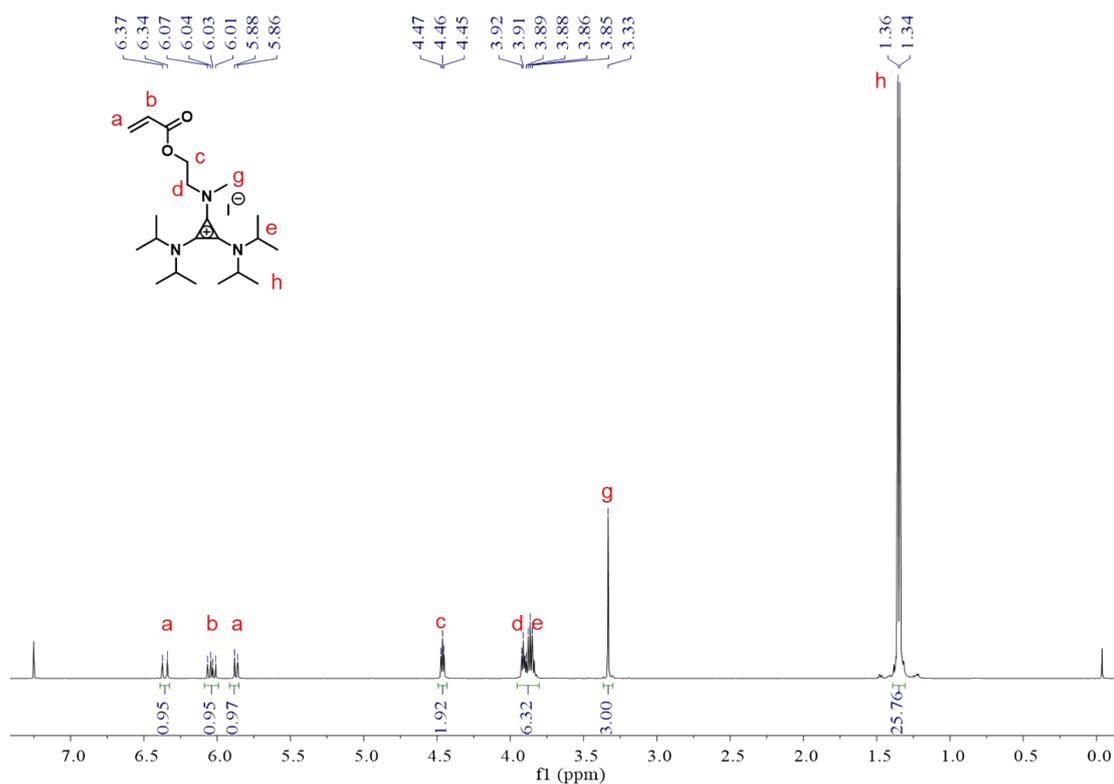
Figure S26: ^{1}H NMR (500 MHz, CDCl$_3$) spectrum of **TACA**.
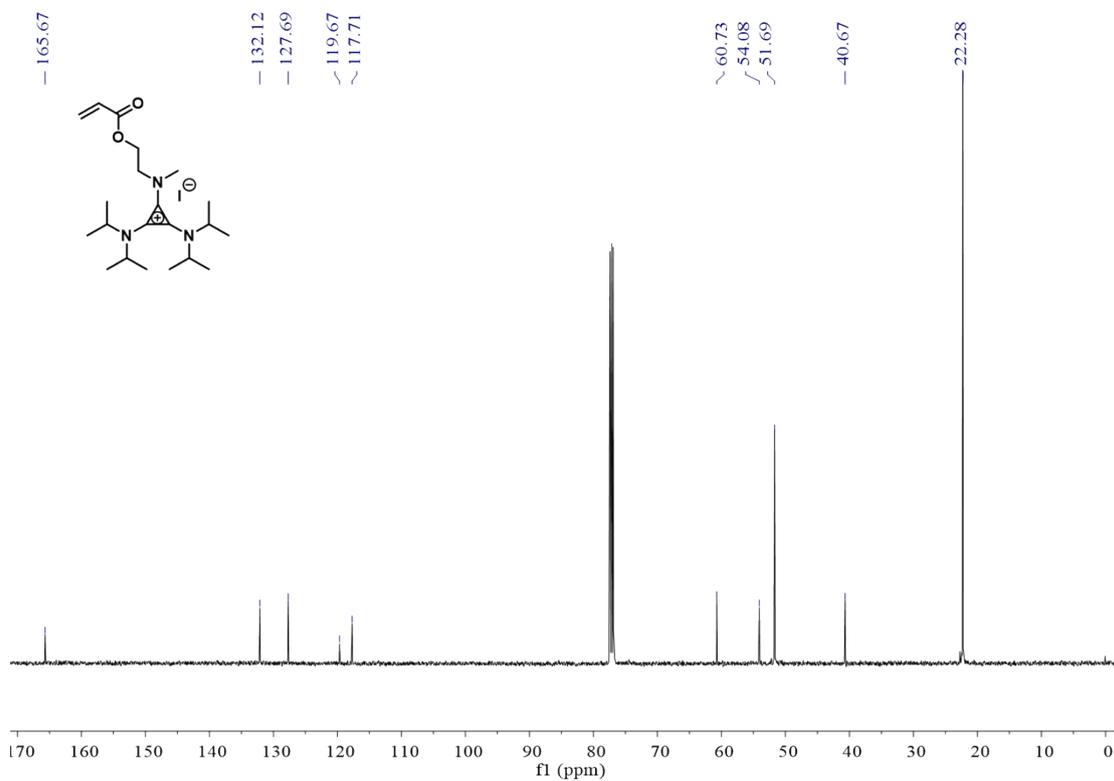
Figure S27: ^{13}C NMR (125MHz, CDCl$_3$) spectrum of **TACA**.

5. References.

[1] Tao, J.; Perdew, J. P.; Staroverov, V. N.; Scuseria, G. E. Climbing the Density Functional Ladder: Nonempirical Meta--Generalized Gradient Approximation Designed for Molecules and Solids. *Phys. Rev. Lett.* **2003,** *91*, 146401.

[2] Staroverov, V. N.; Scuseria, G. E.; Tao, J.; Perdew, J. P. Comparative assessment of a new nonempirical density functional: Molecules and hydrogen-bonded complexes. *J. Chem. Phys.* **2003,** *119*, 12129-12137.

[3] Neese, F. The ORCA program system. *WIREs Comput. Mol. Sci.* **2012,** *2*, 73-78.

[4] Neese, F. Software update: the ORCA program system, version 4.0. *WIREs Comp. Mol. Sci.* **2018,** *8*, e1327.

[5] Barone, V.; Cossi, M., Quantum Calculation of Molecular Energies and Energy Gradients in Solution by a Conductor Solvent Model. *J. Phy. Chem. A* **1998,** *102*, 1995-2001.

[6] Zack, M. S.; Michael, R.; Steffen, J.; Lambert, T. H. Oxidizable Ketones: Persistent Radical Cations from the Single-Electron Oxidation of 2,3-Diaminocyclopropenones. *Angew. Chem. Int. Ed.* **2019**, *58*, 8049-8052.

[7] Florian K.; Stefan H. J.; Zhang, Q.; Sebastian. M. W.; Severin, S.; Ingo, S.; Eberhardt, H., Stefan, M. H. Organocatalysis by Neutral Multidentate Halogen-Bond Donors. *Angew. Chem. Int. Ed.* **2013**, *52*, 7028-7032.

[8] Goto, A.; Ohtsuki, A.; Tanishima, M.; Kaji, H. Reversible Generation of a Carbon-Centered Radical from Alkyl Iodide Using Organic Salts and Their Application as Organic Catalysts in Living Radical Polymerization. *J. Am. Chem. Soc.* **2013**, *135*, 11131-11139.