

## **DyI<sub>2</sub> Initiated Mild and Highly Selective Silyl Radical-catalyzed Cyclotrimerization of Terminal Alkynes and Polymerization of MMA**

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### **Supporting Information**

All reactions were carried out under argon atmosphere using the standard schlenk techniques. DyI<sub>2</sub> was prepared by the literature procedures.<sup>[1]</sup> The solvents were refluxed and distilled over sodium benzophenone ketyl under nitrogen immediately prior to use. All alkynes were purchased from Aldrich. MMA was dried over CaH<sub>2</sub> and distilled under Ar atmosphere at reduced pressure. <sup>1</sup>H NMR spectra were recorded at 500 MHz using CDCl<sub>3</sub> as solvent. The molecular weight of the polymers was analyzed by an HP series 1100 gel permeation chromatograph (GPC) equipped with Zorbax columns and refractive index detector. GC-MS were obtained on a Hewlett Packard 6890/5973 instrument. X-ray structural analysis was carried out on a Bruker SMART Apex CCD diffractometer using graphite-monochromated MoK<sub>α</sub> (λ = 0.71073 Å) radiation.

#### **1. General procedure for the Cyclotrimerization of alkynes catalyzed by DyI<sub>2</sub>**

To a dark green solution of DyI<sub>2</sub> (0.210g, 0.5 mmol) in THF was added alkynes (5 mmol). The reaction mixture was allowed to reflux for 48h and then was quenched with saturated sodium bicarbonate. The mixture was extracted with ether. The organic layer was separated, dried over anhydrous MgSO<sub>4</sub>, concentrated under reduced pressure, and purified by flash column chromatography to afford desired substituted benzenes.

#### **2. General procedure for the Cyclotrimerization of alkynes catalyzed by DyI<sub>2</sub>/SiCl<sub>4</sub>**

To a dark green solution of DyI<sub>2</sub> (0.210g, 0.5 mmol) in DME was added SiCl<sub>4</sub> (0.06 ml, 0.5 mmol). The solution changed immediately into a pale grey suspension. Then alkyne (1.5 mmol) was added to the suspension. The reaction mixture was allowed to stir at 70°C (oil bath) or reflux for 3 days and then was quenched with saturated sodium bicarbonate. The mixture was extracted with ether. The organic layer was separated, dried over anhydrous MgSO<sub>4</sub>, concentrated under reduced pressure, and purified by flash column chromatography to afford desired substituted benzenes.

**1,2,4-Ph<sub>3</sub>C<sub>6</sub>H<sub>3</sub> (2a):** A solution of 0.16 ml (1.5 mmol) of phenylacetylene, 0.06 ml (0.5 mmol) of SiCl<sub>4</sub>, and 0.210 g (0.5 mmol) of DyI<sub>2</sub> in 15 ml DME was stirred at 70 °C for 3 days to obtain 0.145 g product which was identified as 97% 1,2,4-Ph<sub>3</sub>C<sub>6</sub>H<sub>3</sub> and 3% 1,3,5-Ph<sub>3</sub>C<sub>6</sub>H<sub>3</sub> on the basis of GC-MS (m/z: 306[M<sup>+</sup>]). <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ: 7.64-7.69 (m, 4H), 7.46-7.52 (m, 4H), 7.17-7.25 (m, 10H).

**1,2,4-(*p*-Tol)<sub>3</sub>C<sub>6</sub>H<sub>3</sub> (2b):** A solution of 0.19 ml (1.5 mmol) of *p*-tolylacetylene, 0.06 ml (0.5 mmol) of SiCl<sub>4</sub> and 0.210 g (0.5 mmol) DyI<sub>2</sub> in 15 ml DME was allowed to reflux for 3 days to obtain 0.151 g product which was identified as 97% 1,2,4-(*p*-Tol)<sub>3</sub>-C<sub>6</sub>H<sub>3</sub> and 3% 1,3,5-(*p*-Tol)<sub>3</sub>C<sub>6</sub>H<sub>3</sub> on the basis of GC-MS (m/z: 348[M<sup>+</sup>]). <sup>1</sup>H NMR(CDCl<sub>3</sub>) δ: 7.55-7.62 (m, 4H), 7.46 (d, 1H), 7.27 (d, 2H), 7.03-7.10 (m, 8H), 2.40 (s, 3H, Me), 2.32 (br s, 6H, Me). Recrystallized from ether to give needle crystals, its structure is determined through X-ray single crystal diffraction analysis.

**1,2,4-tris-(4-bromophenyl)benzene (2c):** A solution of 0.271 g (1.5 mmol) of (4-bromophenyl)acetylene, 0.06 ml (0.5 mmol) of SiCl<sub>4</sub>, and 0.210 g (0.5 mmol) DyI<sub>2</sub> in 15 ml DME was allowed to reflux for 3 days to obtain 0.163 g product which was identified as 95% 1,2,4-tri (4-bromophenyl)benzen and 5% 1,3,5-tri (4-bromophenyl)benzen on the basis of HPLC. EI MS (m/z: 543 [M<sup>+</sup>]); <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ: 7.55-7.60 (m, 4H), 7.46-7.51 (m, 3H), 7.37-7.40 (m, 4H), 7.00-7.05 (m, 4H).

**1,2,4-tris-(4-fluorophenyl)benzene (2d):** A solution of 0.17 ml (1.5 mmol) 4-fluorophenylacetylene, 0.06 ml (0.5 mmol) SiCl<sub>4</sub> and 0.210 g DyI<sub>2</sub> in 15 ml DME was stirred at 70°C for about 3 days to obtain 0.119 g product which was identified as 97% 1,2,4-tris-(4-fluorophenyl)benzene and 3% 1,3,5-tris-(4-fluorophenyl)benzene on the basis of GC-MS (m/z 360[M<sup>+</sup>]). <sup>1</sup>H NMR(CDCl<sub>3</sub>) δ: 7.56-7.60 (t, 4H), 7.46 (s, 1H), 7.10-7.15 (t, 6H), 6.93-6.95 (t, 4H).

**1,2,4-(*o*-Tol)<sub>3</sub>-C<sub>6</sub>H<sub>3</sub> (2e) and 1,3,5-(*o*-Tol)<sub>3</sub>-C<sub>6</sub>H<sub>3</sub> (3e):** A solution of 0.19 ml (1.5 mmol) 2-ethynyltoluene, 0.06 ml (0.5 mmol) SiCl<sub>4</sub> and 0.210 g DyI<sub>2</sub> in 15 ml DME was stirred at 70°C for 3 days to obtain 0.074 g product which was identified as 80% 1,2,4-(*o*-Tol)<sub>3</sub>-C<sub>6</sub>H<sub>3</sub> (**a**) and 20% 1,3,5-(*o*-Tol)<sub>3</sub>-C<sub>6</sub>H<sub>3</sub> (**b**) on the basis of GC-MS (m/z: 348[M<sup>+</sup>]). <sup>1</sup>H NMR(CDCl<sub>3</sub>) δ: 6.97-7.35 (m, 30H, **a+b**), 2.38 (s, 3H, **a**), 2.19 (s, 3H, **a**), 2.10 (s, 3H, **a**), 2.37 (s, 9H, **b**).

**1,2,4-tris-(4-methoxyphenyl)benzene (2f):** A solution of 0.19 ml (1.5 mmol) 4-methoxyphenylacetylene, 0.06 ml (0.5 mmol) SiCl<sub>4</sub> and 0.210 g DyI<sub>2</sub> in 15 ml THF was stirred at 70°C for about 3 days to obtain 0.050 g product which was identified as 1,2,4-tris-(4-methoxyphenyl)benzene on the basis of GC-MS (m/z 396[M<sup>+</sup>]). <sup>1</sup>H NMR(CDCl<sub>3</sub>) δ: 7.62 (d, 2H), 7.61 (s, 1H), 7.58(dd, 1H), 7.46 (d, 1H), 7.15 (d, 2H), 7.12 (d, 2H), 7.01 (d, 2H), 6.81 (d, 2H), 6.80 (d, 2H), 3.86 (s, 3H), 3.80 (s, 3H), 3.79 (s,3H).

### 3. Polymerization of MMA catalyzed by DyI<sub>2</sub>/SiCl<sub>4</sub>

The polymerization reaction was carried out at 0°C in THF (8 mL), To a dark green solution of DyI<sub>2</sub> (0.210 g, 0.5 mmol) in THF was added SiCl<sub>4</sub>(0.06 ml, 0.5 mmol). The solution changed immediately into a pale grey suspension. Then the MMA monomer (5 ml) was injected to the suspension. The reaction mixture was allowed to stir at 0°C for 10 hours and was filtered. The filtrate was quenched and washed by methanol. The obtained PMMA was dried and the stereochemical triad analysis was carried out by <sup>1</sup>H NMR (500 MHz) experiments at 25 °C, using PMMA (50-60 mg) in CDCl<sub>3</sub> solutions. CH<sub>3</sub>: mr (δ: 1.02, 29%), rr (δ: 0.85, 71%). Molecular weights and polydispersities of the PMMA polymers were obtained by GPC. Mn: 1.78\*10<sup>5</sup>, Mw/Mn: 1.74.

### 4. Polymerization of MMA catalyzed by AIBN

To a solution of AIBN (18 mg, 0.11 mmol) in THF (3ml) was added MMA monomer (1ml). The reaction mixture was allowed to stir at 70°C (oil bath) for 15h, then quenched and washed by methanol. The obtained PMMA was dried and the stereochemical triad analysis was carried out by <sup>1</sup>H NMR (500 MHz) experiments at 25 °C, using PMMA (50-60 mg) in CDCl<sub>3</sub> solutions. CH<sub>3</sub>: mr (δ: 1.02, 37%), rr (δ: 0.85, 63%). Molecular weights and polydispersities of the PMMA polymers were obtained by GPC. Mn: 1.56\*10<sup>4</sup>, Mw/Mn: 2.17.

### 5. Polymerization of MMA catalyzed by AIBN/DyCl<sub>3</sub>

To a solution of AIBN (18 mg, 0.11 mmol) and DyCl<sub>3</sub> (30 mg, 0.11 mmol) in THF (3 ml) was added MMA monomer (1.0 ml). The reaction mixture was allowed to stir at 70°C (oil bath) for 15h, then quenched and washed by methanol. The obtained PMMA was dried and the stereochemical triad analysis was carried out by <sup>1</sup>H NMR (500 MHz) experiments at 25 °C, using PMMA (50-60 mg) in CDCl<sub>3</sub> solutions. CH<sub>3</sub>: mr (δ: 1.02, 36%), rr (δ: 0.85, 64%). Molecular weights and polydispersities of the PMMA polymers were obtained by GPC. Mn: 1.45\*10<sup>4</sup>, Mw/Mn: 1.75.

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[1] Evans, W. J.; Allen, N. T.; Workman, P. S.; Meyer, J. C. *Inorg. Chem.* **2003**, *42*, 3097.