Supporting Information

D–π–A–π–D initiators based on benzophenone conjugate extension for two-photon polymerization additive manufacturing

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I. General remarks

All reagents were obtained from commercial suppliers and used without further purification.

Table S1 Reagents

Reagents	1-Bromo-hexane	Aladdin Industrial Corporation
	1-Bromo-dodecane	Aladdin Industrial Corporation
	7-Bromomethyl-pentadecane	Aladdin Industrial Corporation
	9-Bromomethyl-icosane	Aladdin Industrial Corporation
	Diphenyl-amine	Aladdin Industrial Corporation
	NaH	Shanghai Macklin Biochemical Co., Ltd.
	Na_2SO_4	Chengdu Kelong Co., Ltd.
	NBS	Aladdin Industrial Corporation
	$Pd(PPh_3)_2Cl_2$	Ark Pharm
	PPh_3	Aladdin Industrial Corporation
	KOH	Aladdin Industrial Corporation
	CuI	Adamas-Beta
	Et_3N	Shanghai Macklin Biochemical Co., Ltd.

	Bis-(4-bromo-phenyl)-methanone	Shanghai Macklin Biochemical Co., Ltd.
	Ethynyltrimethylsilane	Aladdin Industrial Corporation
	K_2CO_3	Aladdin Industrial Corporation
Solvent	Petroleum ether	Shanghai Titan Scientific Co., Ltd.
	EA	Aladdin Industrial Corporation
	DMF	Aladdin Industrial Corporation
	THF	Aladdin Industrial Corporation
	DCM	Shanghai Macklin Biochemical Co., Ltd.
	MeOH	Aladdin Industrial Corporation
Resin	TMPTA	Aladdin Industrial Corporation
	PETA	Aladdin Industrial Corporation

II. Synthesis

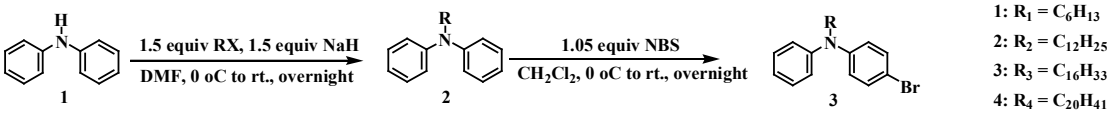


Figure S1. Intermediate product **3** synthesis route.

Substrate **1** (10 mmol) and NaH (in 60% mineral oil, 0.6 g, 15 mmol) were added to DMF (30 mL) at 0 ℃, and the resulting mixture was stirred for 15 min. Subsequently, bromoalkyl **RX** (15 mmol) was slowly added at 0 ℃. The resulting solution was then stirred overnight at room temperature. The reaction solution was quenched with water (100 mL), extracted with EA (100 mL), washed with brine (50 mL×3), and dried over anhydrous Na_2SO_4. Then the solvent was evaporated, and the residue was purified by silica-gel-column chromatography to provide the desired intermediate product **2**.

NBS (1.87 g, 10.5 mmol) solution in DCM (150 mL) was slowly added to (10 mmol) solution **2** in DCM (100 mL) at 0 ℃. The resulting mixture was then stirred overnight at room temperature. The reaction was stopped with water (100 mL), washed with brine (100 mL), and dried on anhydrous Na_2SO_4. The solvent was evaporated, and the residue was purified by silica gel column chromatography to provide the desired intermediate product **3**.

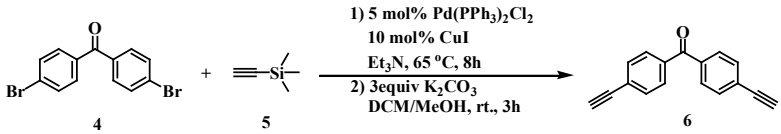


Figure S2. Intermediate product **6** synthesis route.

$Pd(PPh_3)_2Cl_2$ (350 mg, 0.5 mmol), PPh_3 (262 mg, 1.0 mmol), CuI (190 mg, 1.0

mmol), bromine material **4** (5 mmol), ethynyltrimethylsilane **5** (1.47 g, 15 mmol), and Et_3N (50.0 mL) were loaded into a flame-drying sealable tube with a magnetic stirring rod in an Ar atmosphere. The tube was sealed, and the reaction was stirred at 65 °C for 8 h. After cooling to ambient temperature, the reaction solution was diluted with 100 mL of ethyl acetate (EA), filtered through a diatomite pad and washed with EA (50 mL). The solvent was evaporated and the residue added to K_2CO_3 (4.15 g, 30 mmol), DCM (50 mL) and MeOH (50 mL). The resulting mixture was then stirred at room temperature for 3 h. The reaction solution was filtered through a diatomite pad and washed with 30 mL DCM. The filtrate was evaporated, and the residue was purified by silica-gel-column chromatography to provide the desired intermediate product **6**.

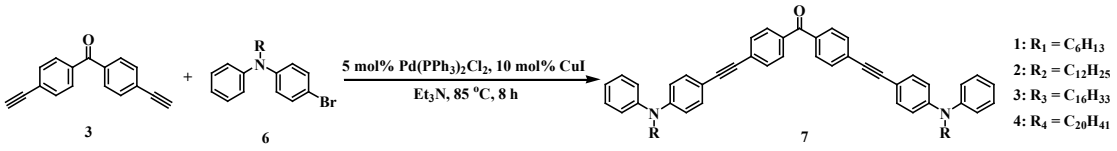


Figure S3. Final product **7** synthesis route.

$Pd(PPh_3)_2Cl_2$ (35 mg, 0.05 mmol), PPh_3 (26 mg, 0.10 mmol), CuI (19 mg, 0.10 mmol), bromine material **6** (1.5 mmol), terminal alkyne **3** (230 mg, 0.5 mmol), Et_3N (5.0 mL) and DMF (10.0 mL) were filled into a flame-drying sealable tube with a magnetic stirring rod in an Ar atmosphere. The tube was sealed, and the reaction was stirred at 90 ° C for 8 h. After cooling to ambient temperature, the reaction solution was diluted with 50 mL of ethyl acetate (EA), filtered through a diatomite pad, washed with EA (30 mL) and brine (50 mL×2), and dried on anhydrous Na_2SO_4. The solvent was evaporated, and the residue was purified by silica-gel-column chromatography to

provide the desired product **7**.

III. Copies of images

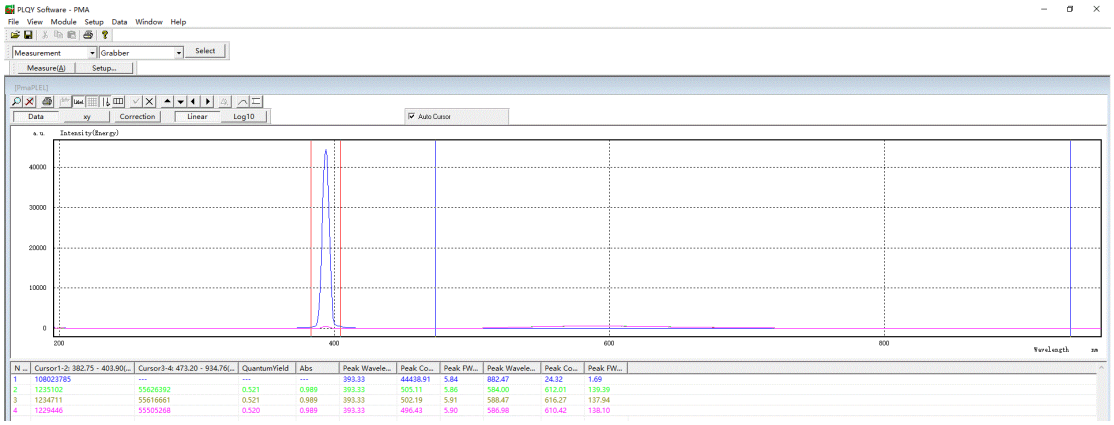


Figure S4. The fluorescence quantum yield of BM-PPPM-C6.

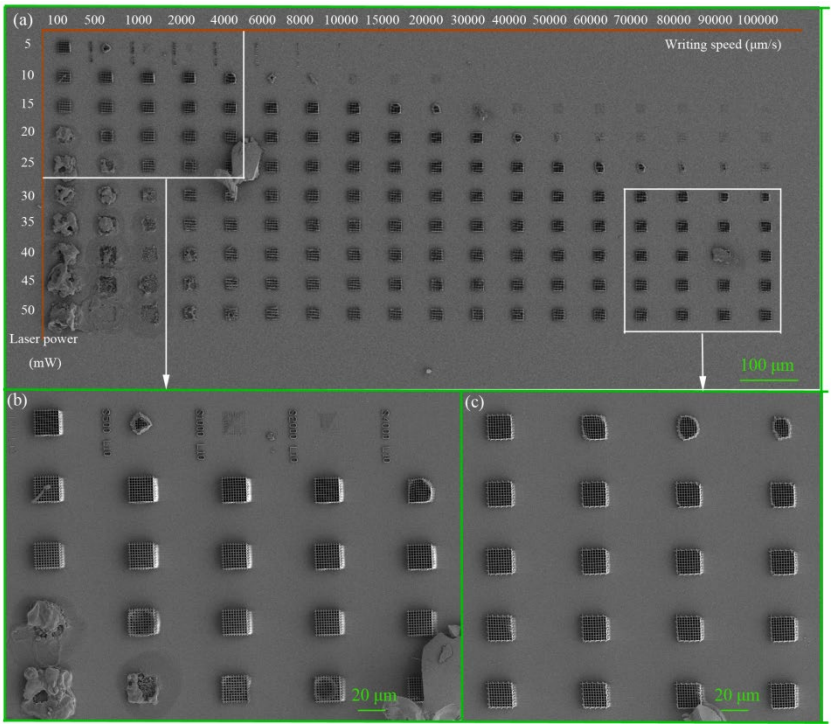


Figure S5. SEM images of structures with initiator BM-PPPM-C12 in PMPTA, 10 μmol/g.

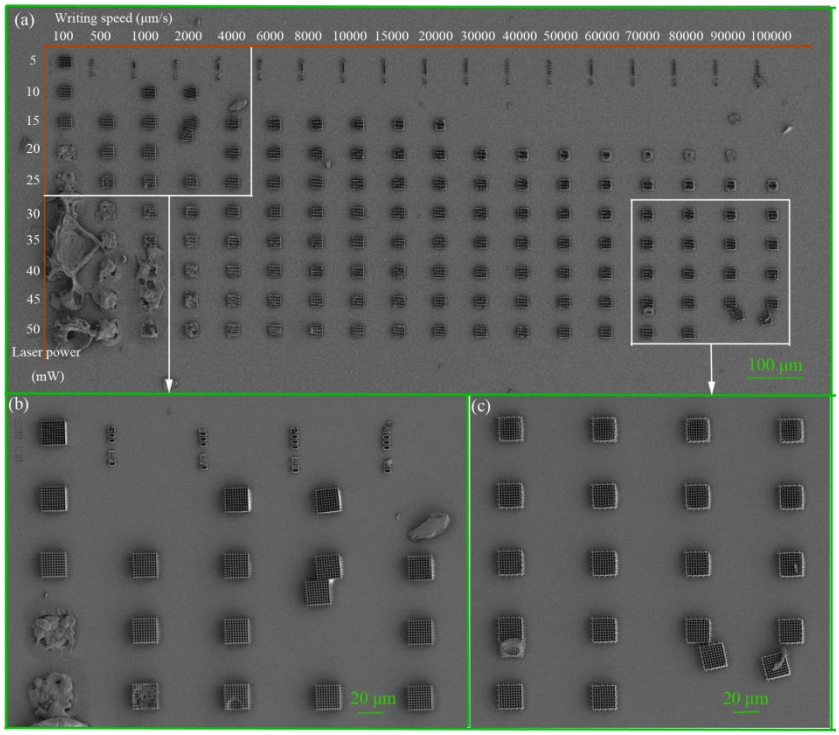


Figure S6. SEM images of structures with initiator BM-PPPM-C16 in PMPTA, 10 μmol/g.

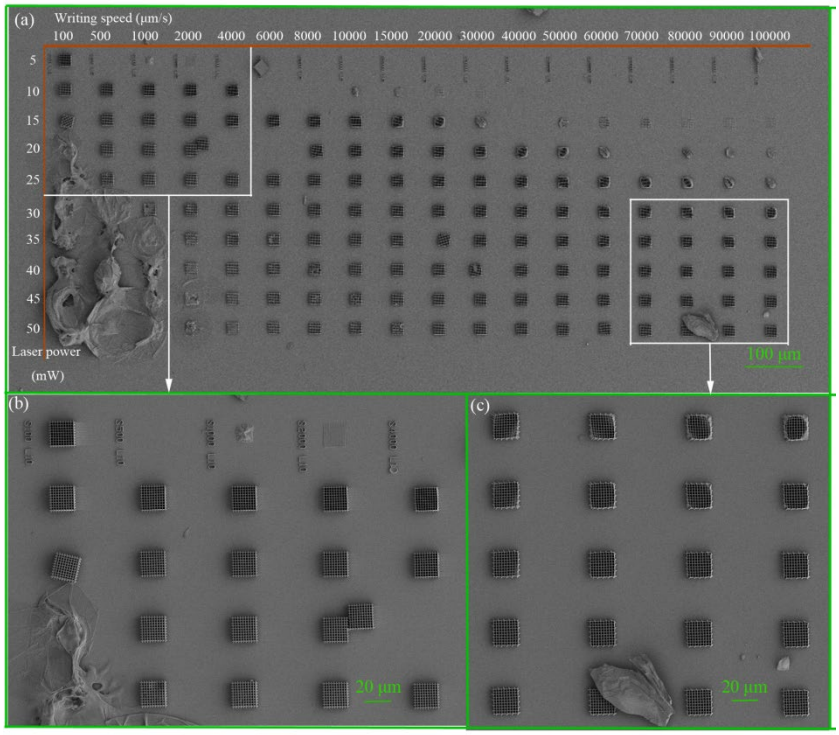


Figure S7. SEM images of structures with initiator BM-PPPM-C20 in PMPTA, 10

μmol/g.

IV. Copies of photos

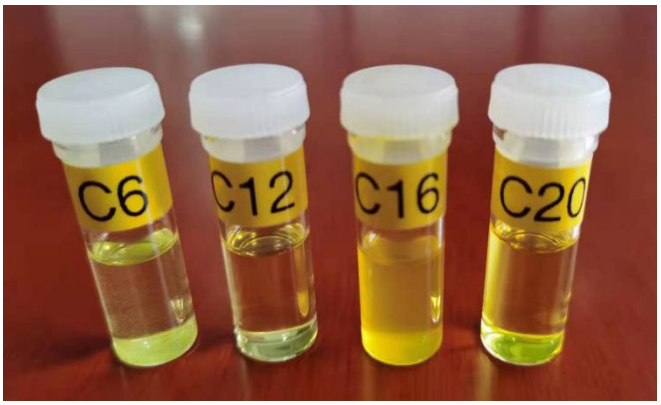
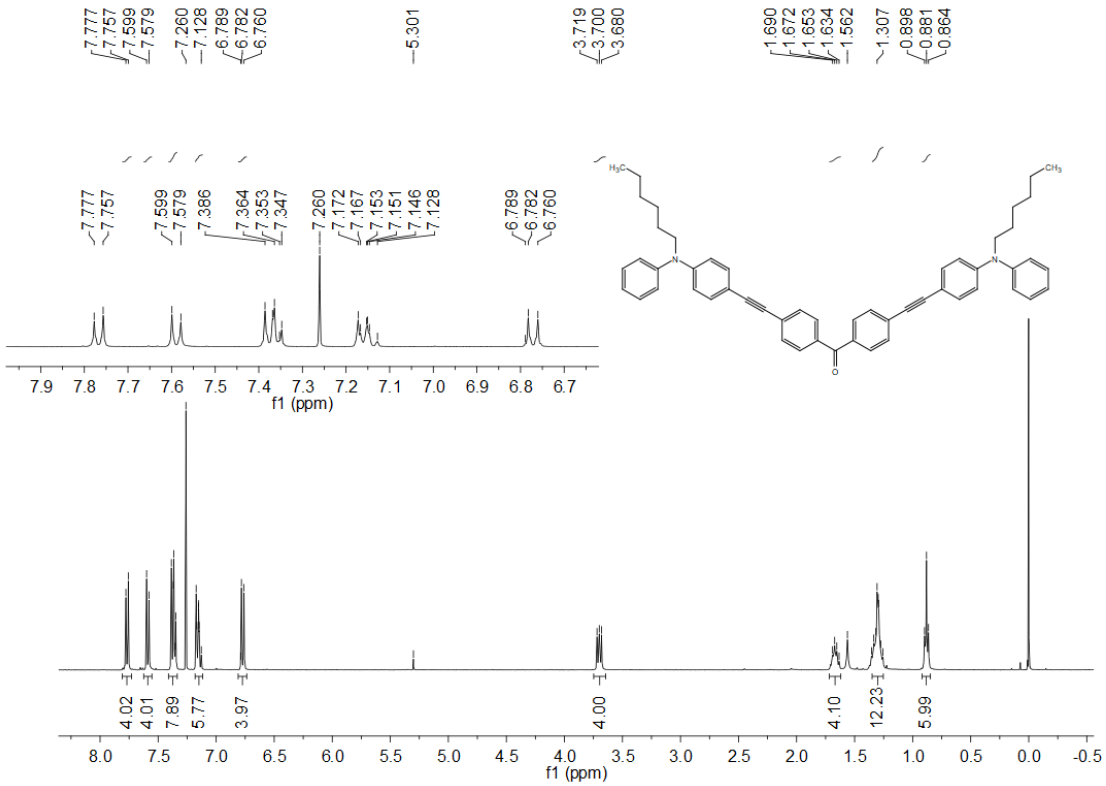
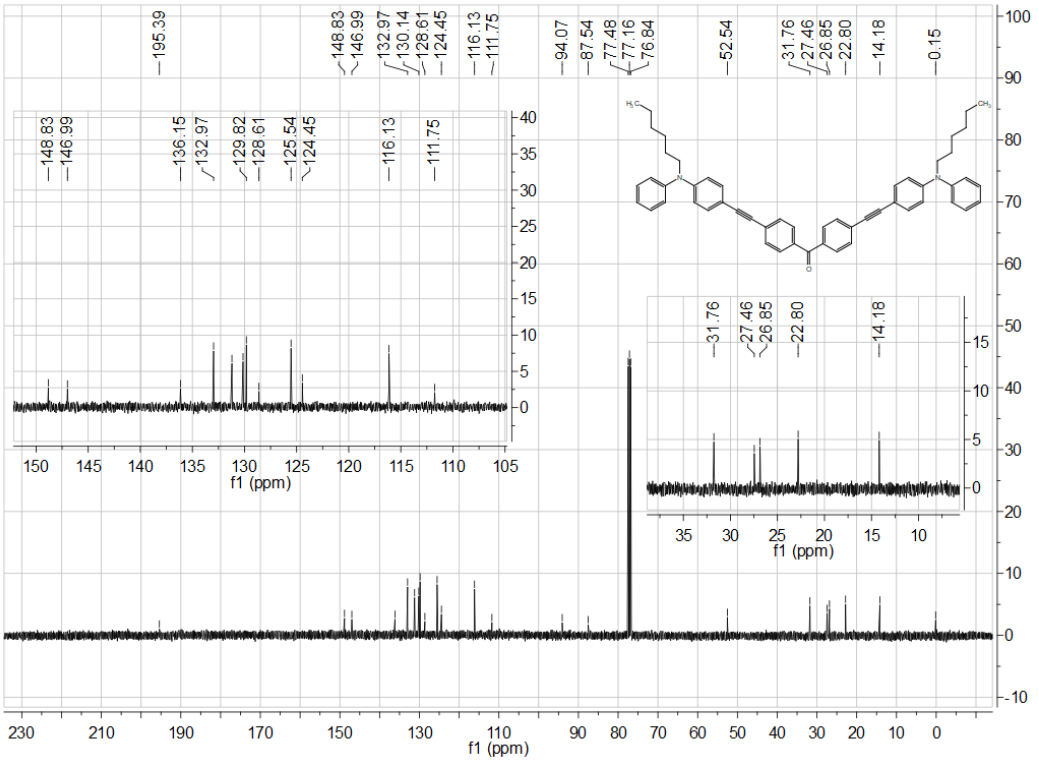


Figure S8. Photos showing differences in solubility of different molecules

V. Copies of ^{1}H, and ^{13}C NMR spectra

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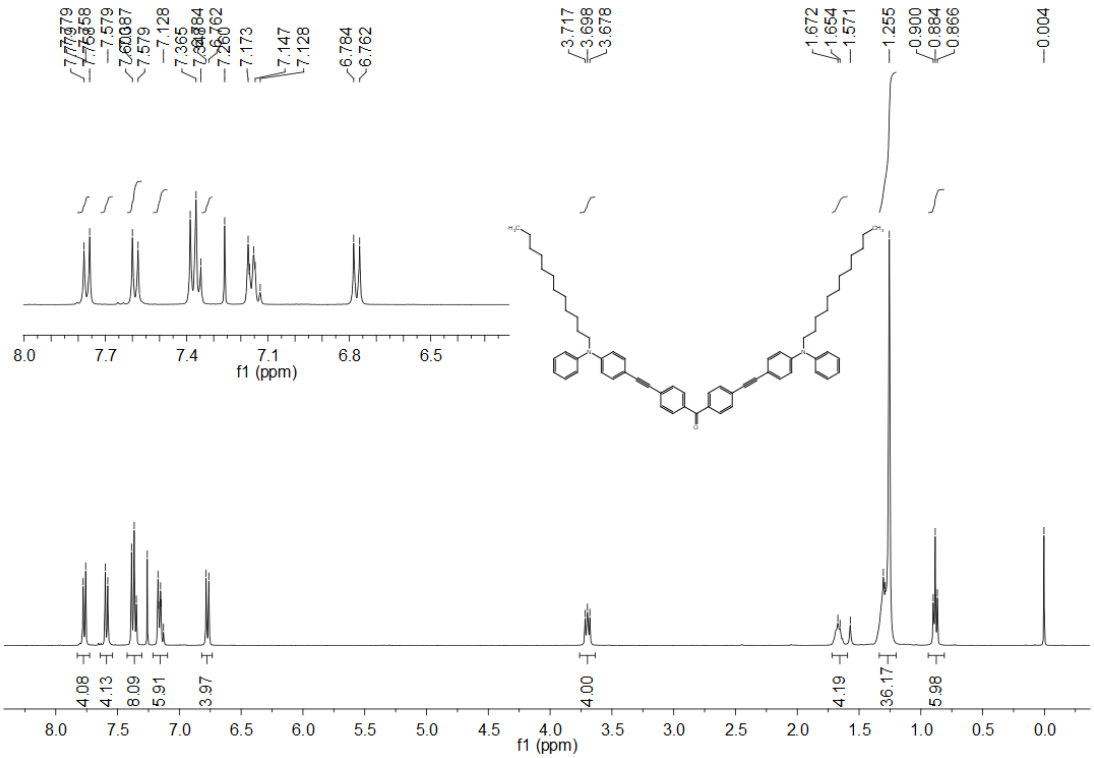
125.54
f1 (ppm)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1.654
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0.884
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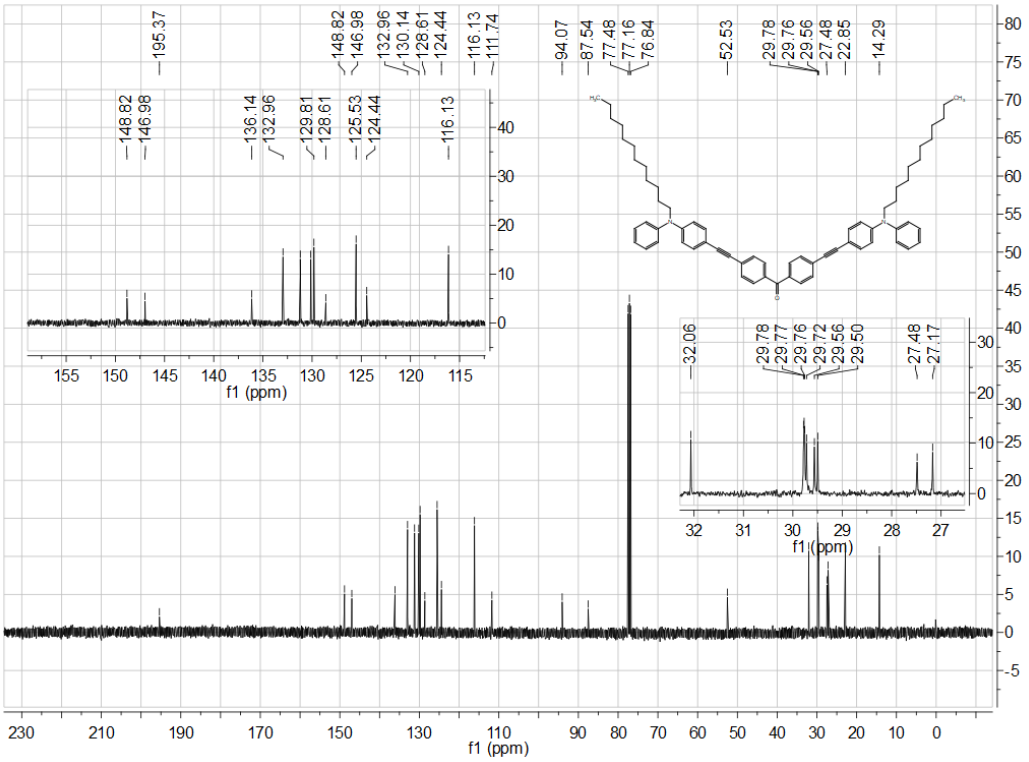
f1 (ppm)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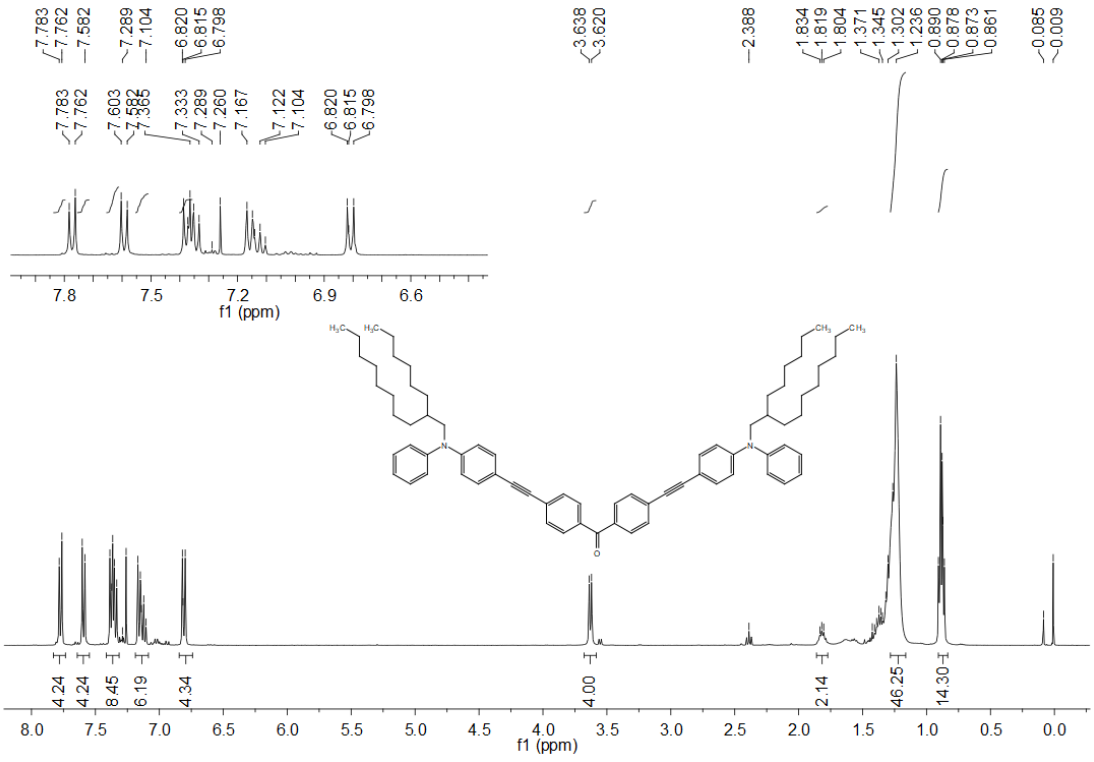
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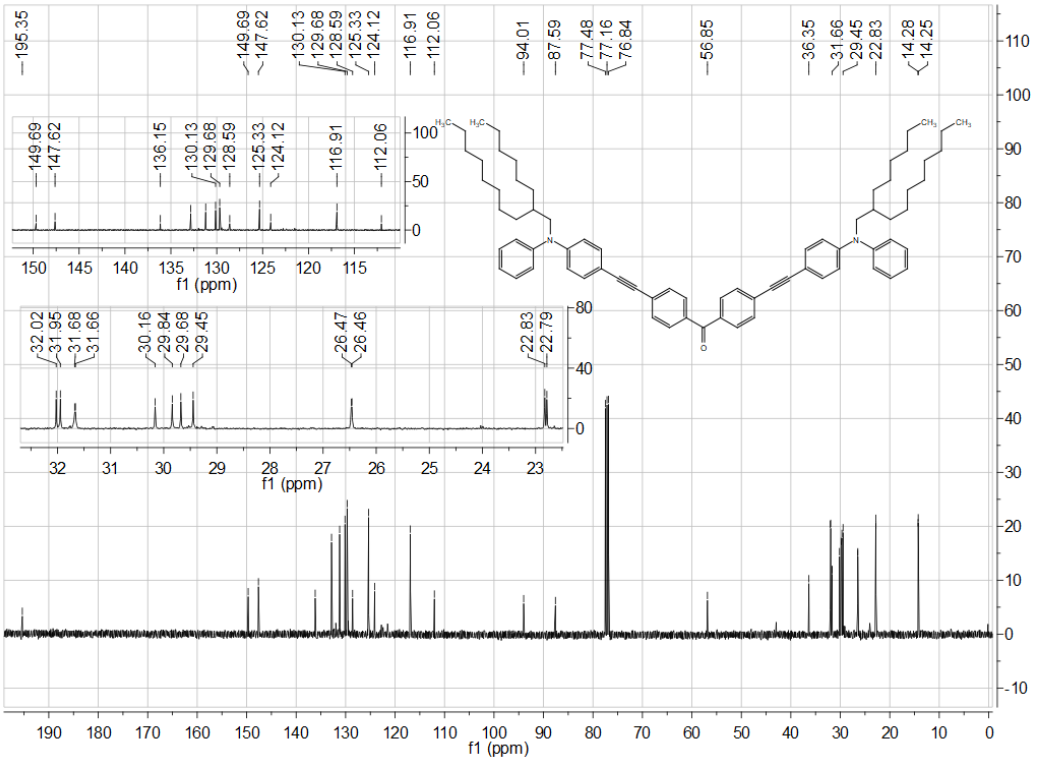
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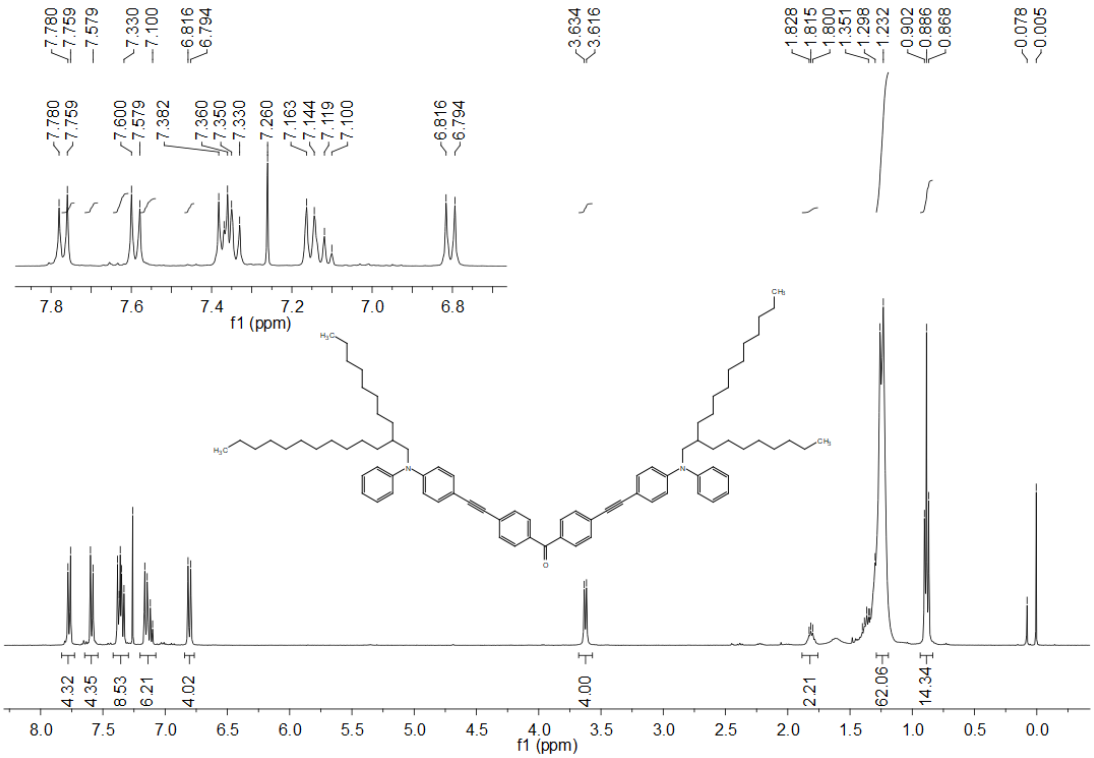
f1 (ppm)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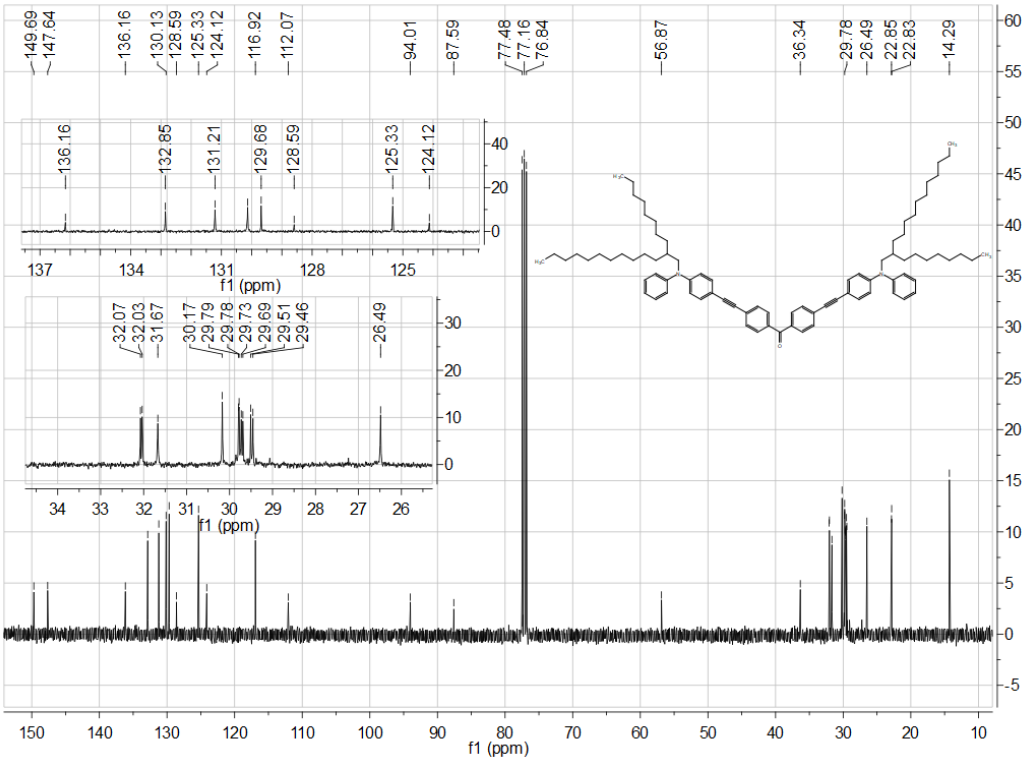
f1 (ppm)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f1 (ppm)