Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Electronic Supporting Information

Colorimetric analysis of painting materials using polymer-supported polydiacetylene films

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Table S1. Monosaccharides (%) Composition of natural gums tested in the present study [1]

	Arabinose	Xylose	Rhamnose	Fucose	Glucuronic acid	Galacturonic acid	Glucose	Galactose	Mannose	Other
Arabic	37	-	11	-	7	-	-	45	-	-
Ghatti	47	-	3	-	11	-	-	36	2	1
Guar	35	15	3	7	4	14	11	10	-	1
Karaya	2	-	-	-	-	-	-	34	63	1
Tragacanth	-	-	25	-	4	7	-	64	-	-

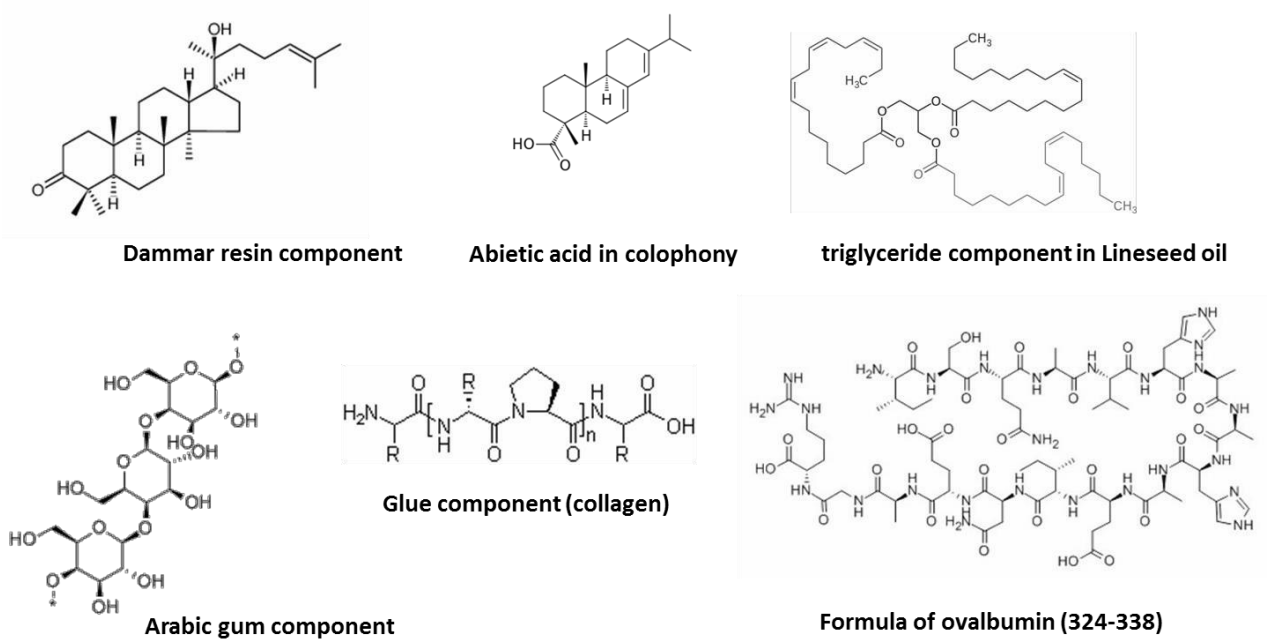
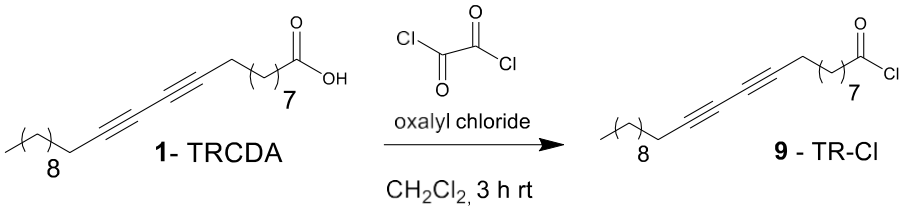


Figure S1. Representative chemical structures of painting materials components

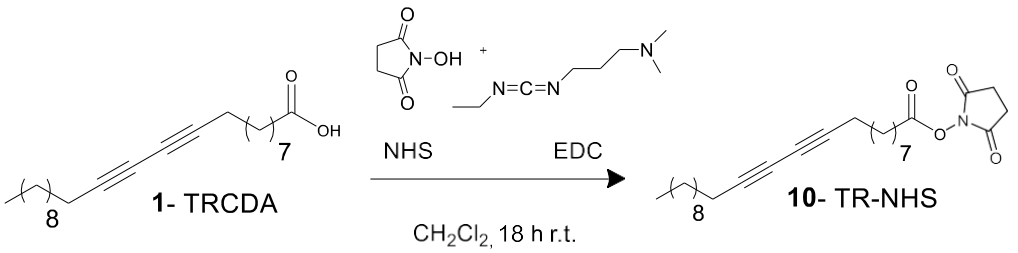
Synthetic Procedures

Synthesis of tricosa-10,12-diynoyl chloride (TR-Cl, 9)



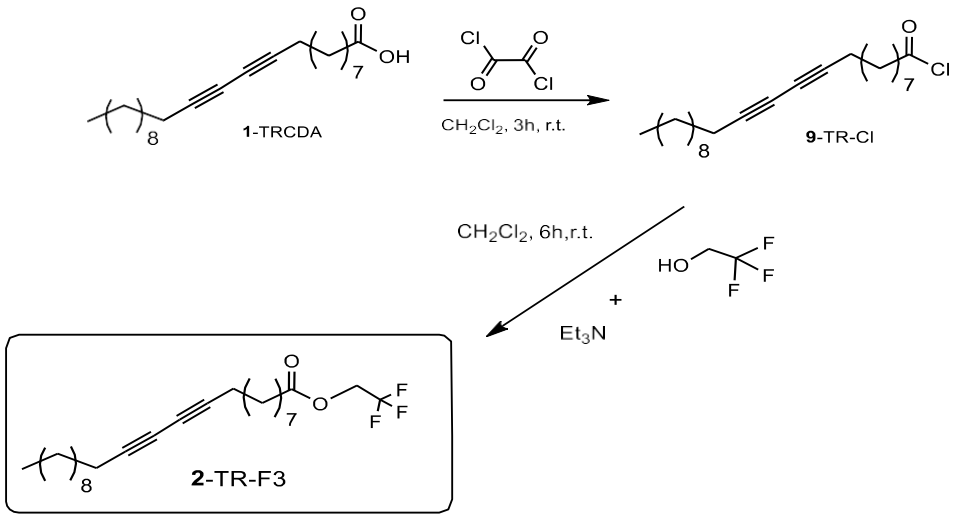
Oxalylchloride (1.2 eq, 1.68 mmol) was added dropwise to a CH_2Cl_2 (15 mL) stirring solution containing **1** (1 eq, 1.40 mmol). The resulting mixture was stirred for 3h at r.t. Removal of the solvent under reduced pressure afforded the desired TR-Cl (**9**) in quantitative yield and the product was used for the next reaction without further purification. **Yield**: oily liquid (97 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.84–0.88 (t, 3H), 1.24–1.40 (m, 22H), 1.46-1.52 (m, 4H), 1.55-1.70 (m, 2H) 2.21-2.24 (t, 4H), 2.32-2.35 (t, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.6, 76.7, 65.3, 53.4, 35.3, 31.9, 29.6, 29.3, 29.1, 29.05, 29.0, 28.95, 28.85, 28.8, 28.80, 28.7, 28.6, 28.3, 24.2, 22.7, 19.2, 19.18, 14.1.

Synthesis of 2,5-dioxopyrrolidin-1-yl tricosa-10,12-diynoate (TR-NHS, 10) [2]



10,12 tricosadiynoic acid (TRCDA, **1**) (1 eq, 0.29 mmol) is solubilized in CH_2Cl_2 (3 mL) in a round bottom flask under a gentle flux of N_2 and avoiding light. N-Hydroxysuccinimide (NHS, 1.2 eq, 0.35 mmol) and 1-ethyl-3-3-dimethylaminopropyl)carbodiimide (EDC, 2 eq, 0.55 mmol) are solubilized in CH_2Cl_2 (5 mL) and mixed with a solution of **1** under stirring at rt. After 20 h, the solvent is evaporated under reduced pressure. The mixture is extracted from water with diethyl ether (x2, 100 mL). The organic layers are recovered, dried with anhydrous Na_2SO_4, filtered and evaporated. TR-NHS is used in the next step without further purification. **Yield**: white powder (98 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.84-0.87 (t,3H), 1.24-1.40 (m, 22H), 1.45-1.52 (m, 4H), 1.68-1.75 (m, 2H), 2.20-2.23 (t, 2H), 2.56-2.59 (t, 4H), 2.81 (s, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ =169.1, 168.6, 77.0, 76.7, 65.3, 65.2, 31.9, 30.9, 29.5, 29.4, 29.3, 29.1, 28.9, 28.8, 28.8, 28.7, 28.6, 28.3, 28.2, 25.6, 24.51, 22.6, 19.2, 19.1, 14.1.

Synthesis of 2,2,2-trifluoroethyl tricosa-10,12-diynoate (TR-F3, 2)

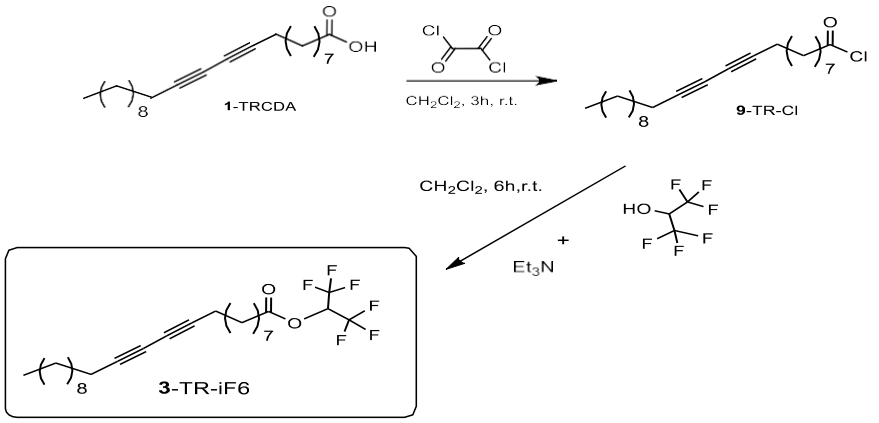


Step 1. Synthesis of ***tricosa-10,12-diynoyl chloride*** (TR-Cl, **9**).

Step 2. Synthesis of ***2,2,2-trifluoroethyl tricosa-10,12-diynoate*** (TR-F3, **2**).

To a stirring solution of **9** (1 eq, 0.30 mmol) in CH_2Cl_2 (15 mL) was added 2,2,2-trifluoroethanol (2 eq, 0.60 mmol) and Et_3N (1.2 eq, 0.36 mmol); the resulting solution is stirred at r.t. for 6 h. The mixture is extracted from water with CH_2CL_2 (x2, 50 mL). The organic layers are recovered, dried with anhydrous Na_2SO_4 and filtered. Evaporation of the solvent left a white solid, that was purified by column chromatography (AcOEt : cyclohexane = 1 : 9). **Yield**: white solid (88 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.84–0.88 (t, 3H), 1.24–1.39 (m, 22H), 1.46-1.53 (m, 4H), 1.60-1.65(m, 2H) 2.20–2.24 (t, 4H), 2.37–2.41 (t, 2H), 4.41-4.48 (q, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 172.1, 77.0, 76.6, 65,2, 60,3, 33.6, 31.9, 29.6, 29.5, 29.3, 29.1, 29.0, 28.9, 28.85, 28.8, 28.7, 28.3, 28.25, 24.6, 22.7, 19.2, 19.1, 14.1. ^{19}F NMR (377 MHz, $CDCl_3$): δ = -73.9 (q).

Synthesis of 1,1,1,3,3,3-hexafluoropropan-2-yl tricosa-10,12-diynoate (TR-iF6, 3)

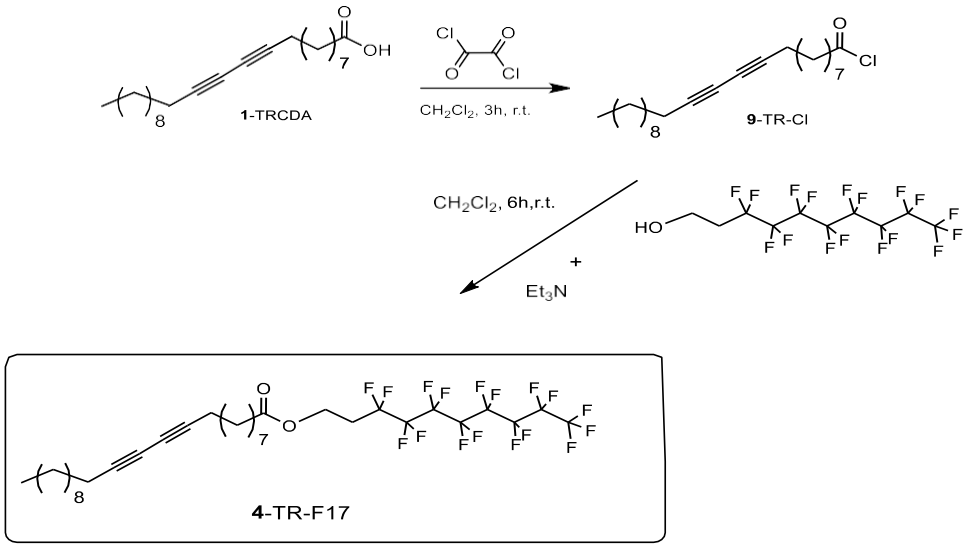


Step 1. Synthesis of ***tricosa-10,12-diynoyl chloride*** (TR-Cl, **9**).

Step 2. Synthesis of ***1,1,1,3,3,3-hexafluoropropan-2-yl tricosa-10,12-diynoate*** (TR-iF6, **3**).

To a stirring solution of **9** (1 eq, 0.27 mmol) in CH_2Cl_2 was added 1,1,1,3,3,3-hexafluoropropanol (1.8 eq, 0.49 mmol) and Et_3N (1.2 eq, 0.36 mmol); the resulting solution is stirred at rt for 5 h. The mixture is extracted from water with CH_2Cl_2 (x2, 50 mL). The organic layers are recovered, dried with anhydrous Na_2SO_4 and filtered. Evaporation of the solvent left a liquid, that was purified by column chromatography (AcOEt: cyclohexane = 1: 9). **Yield**: liquid (85 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.83-0.86 (t, 3H), 1.22-1.37 (m, 20H), 1.44-1.47(m, 6H) 1.61-1.67 (m, 2H), 2.19-2.22 (t, 4H), 2.45-2.49 (t, 2H), 5.70-5.76(m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 109.9, 76.9, 76.65, 76.6, 65.1, 33.2, 31.8, 29.5, 29.4, 29.3, 29.05, 28.9, 28.8, 28.76, 28.65, 28.6, 28.3, 28.2, 24.5, 22.6, 19.2, 19.1. ^{19}F NMR (377 MHz, $CDCl_3$): δ = -73.4.

Synthesis of 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl tricosa-10,12-diynoate (TR-F17, 4)

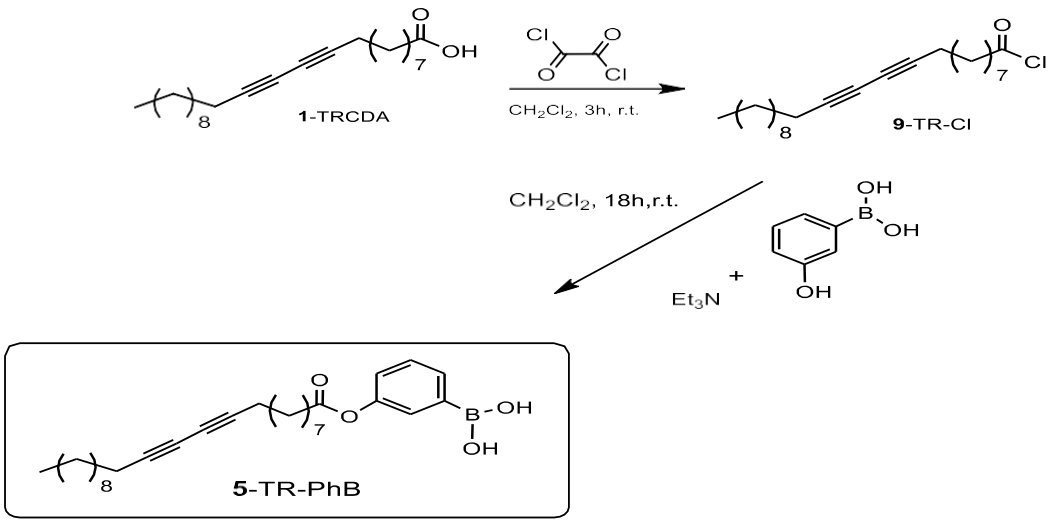


Step 1. Synthesis of ***tricosa-10,12-diynoyl chloride*** (TR-Cl, **9**).

Step 2. Synthesis of ***3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl tricosa-10,12-diynoate*** (TR-F17, **4**).

To a stirring solution of **9** (1 eq, 0.27 mmol) in CH_2Cl_2 (10 mL) was added 1H, 1H, 2H, 2H, perfluoro-1-decanol (1.6 eq, 0.43 mmol) and Et_3N (1.2 eq, 0.32 mmol); the resulting solution is stirred at rt for 5 h. The mixture is extracted from water with CH_2Cl_2 (x2, 50 mL). The organic layers are recovered, dried with anhydrous Na_2SO_4 and filtered. Evaporation of the solvent left a liquid, that was purified by column chromatography (AcOEt : cyclohexane = 1 : 9). **Yield**: white solid (60 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.84-0.86 (t, 3H), 1.24-1.41 (m, 22H), 1.47-1.49(m, 4H), 1.53-1.55 (m, 2H), 2.20-2.24 (t, 4H), 2.28-2.32 (t, 2H), 2.39-2.51 (m, 2H) 4.34-4.37 (t, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 173.3, 124.8, 76.6, 65.25, 65.15, 56.1, 34.0, 31.8, 29.65, 29.5, 29.4, 29.25, 29.0, 29.0, 28.9, 28.8, 28.81, 28.7, 28.3, 28.2, 24.7, 22.6, 19.2, 19.1, 14.05. ^{19}F NMR (377 MHz, $CDCl_3$): δ = -80.74 (t), -113.5, -113.65, -121.68, -121.92,- 122.72, -123.57, -126.11.

Synthesis of (3-(tricosa-10,12-diynoyloxy)phenyl)boronic acid (TR-PhB, 5)

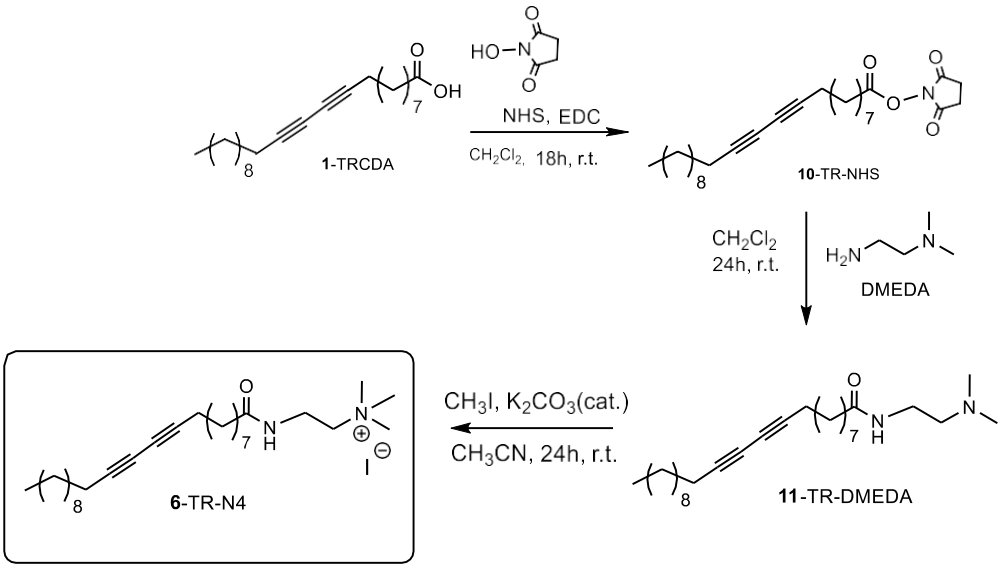


Step 1. Synthesis of ***tricosa-10,12-diynoyl chloride*** (TR-Cl, **9**).

Step 2. Synthesis of ***(3-(tricosa-10,12-diynoyloxy)phenyl)boronic acid*** (TR-PhB, **5**).

Procedure was adapted from a previously reported one.[3] 3-Hydroxyphenylboronic acid (1.5 eq, 2.10 mmol) and Et_3N (3.4 eq, 4.70 mmol) were dissolved in CH_2Cl_2 and **9** (1 eq, 1.40 mmol) was dissolved in a small amount of anhydrous THF. The THF solution containing **9** was added dropwise into the CH_2Cl_2 solution. The resultant solution was stirred at room temperature overnight and concentrated in vacuo at rt. The crude residue was dissolved in a small amount of MeOH. Addition of small amount of HCl water solution to MeOH solution resulted in the formation of white precipitates. The precipitates formed were collected and dried to give the desired product. **Yield**: white solid (76 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.84–0.88 (t, 3H), 1.24–1.41 (m, 22H), 1.46-1.53 (m, 4H),1.65-1.81(m, 2H) 2.20–2.25 (m, 4H), 2.31–2.35 (t, 1H),2.52-2.56 (t, 2H), 7.14-7.16 (d, 1H), 7.29-7.31 (d, 1H), 7.37-7.43 (m, 2H), 7.51-7.58 (d, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 178.8, 172.7, 150.6, 133, 129.2, 128.1, 126.2, 76.7, 65.3, 34.4, 33.8, 31.9, 30.3, 29.7, 29.5, 29.3, 29.1, 29.0, 28.9, 28.8, 28.7, 28.6, 28.3, 24.9, 24.6, 22.6, 19.2, 14.1.

Synthesis of N,N,N-trimethyl-2-(tricosa-10,12-diynamido)ethan-1-aminium iodide (TR-N4, 6)



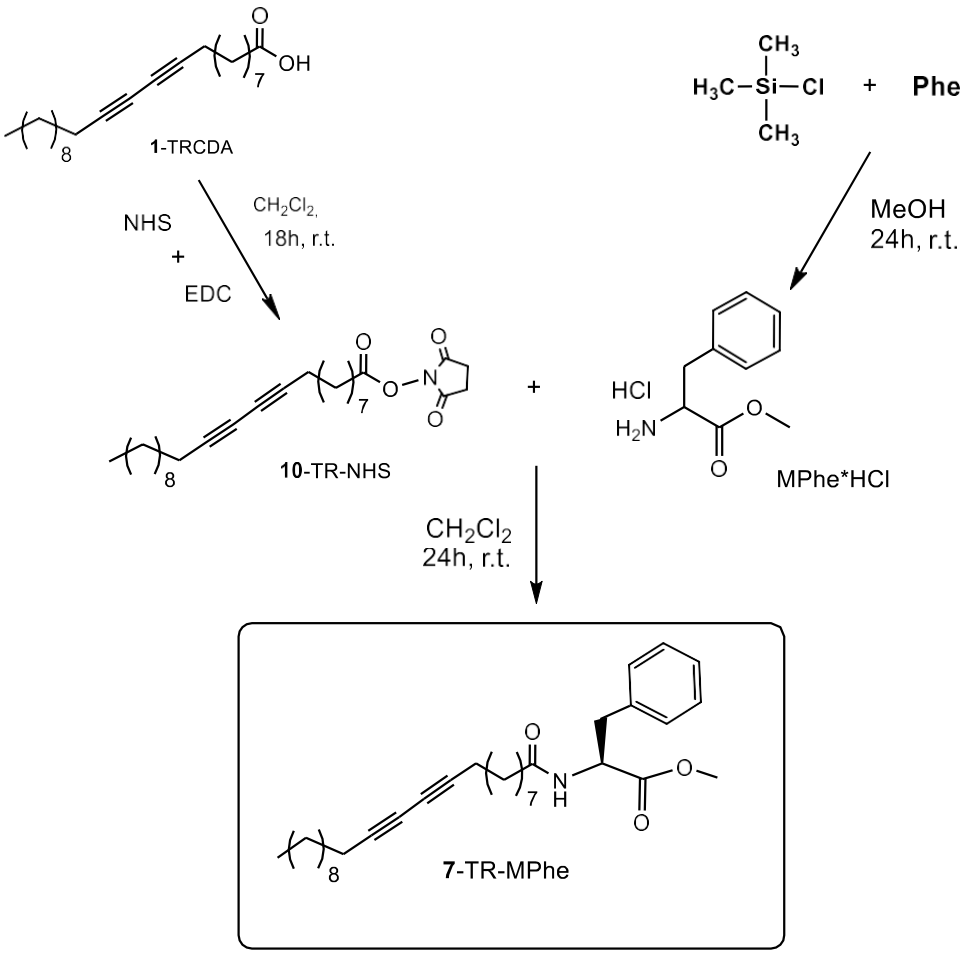
Step 1. Synthesis of ***2,5-dioxopyrrolidin-1-yl tricosa-10,12-diynoate*** (TR-NHS, **10**).

Step 2. Synthesis of ***N-(2-(dimethylamino)ethyl)tricosa-10,12-diynamide*** (TR-DMEDA, **11**). Procedure was adapted from a previously reported one.[4] TR-NHS was added to a solution of N,N-dimethylethylenediamine (DMEDA, 2 eq, 0.45 mmol) in CH_2Cl_2 (10 mL). The resulting mixture was stirred for 24 h. After the solvent was evaporated, the residue was purified by a silica gel column (CH_2Cl_2 : CH_3OH = 20 : 1) to give TR-DMEDA. **Yield:** white solid (96 %).

Step 3. Synthesis of ***N,N,N-trimethyl-2-(tricosa-10,12-diynamido)ethan-1-aminium*** **iodide (**TR-N4, **6).**

To a solution containing TR-DMEDA (1 eq, 0.24 mmol) in CH_3CN (10 mL), CH_3I (5.5 eq, 1.32 mmol) and K_2CO_3 (1.2 eq, 0.29 mmol) were added. The resulting suspension was stirred at r.t. for 24 h and filtered. After evaporation, the quantitative product TR-N4 was obtained. **Yield**: white solid (80%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.83–0.87 (t, 3H), 1.23–1.33 (m, 22H), 1.42-1.50 (t, 4H), 1.55-1.62 (t, 2H), 2.19–2.27 (m, 6H), 3.41 (s, 9H), 3.77–3.80 (m, 2H), 3.84-3.87 (m, 2H), 7.61 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 172.8, 76.7, 65.3, 66.2, 52.2, 50.5, 41.8, 36.5, 31.9, 29.5, 29.4, 29.3, 29.1, 29.05, 28.9, 28.8, 28.7, 28.3, 28.2, 25.5, 24.9, 22.8, 22.6, 19.2, 19.1, 14.1.

Synthesis of methyl tricosa-10,12-diynoylphenylalaninate (TR-MPhe, 7)



Step 1. Synthesis of ***phenylalanine methylester * HCl*** **(MPhe * HCl)** [5]

Phenylalanine (Phe, eq, 3 mmol) and trimethylsilyl chloride (TMSCl, 2 eq, 6 mmol) are stirred in MeOH (10 mL) at rt for 24 h. The solvent is evaporated under reduced pressure and the crude (white powder) is used in the 3rd step with TR-NHS without further purifications. **Yield**: white powder (99 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.29-3.13 (m, 2H), 3.77 (s, 3H), 4.36 (t, 1H), 7.21

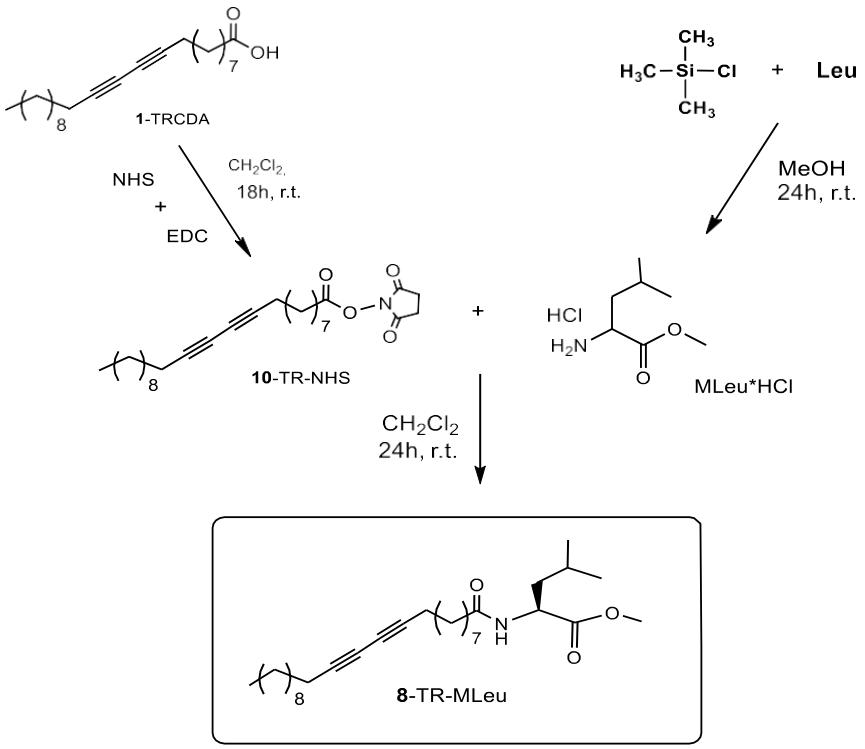
(d, 1H), 7.23 (d, 1H), 7.37-7.34 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 35.7, 53.7, 54.2, 128.2, 129.5, 133.8, 170.1.

Step 2. Synthesis of ***2,5-dioxopyrrolidin-1-yl tricosa-10,12-diynoate*** (TR-NHS - **10**)

Step 3. Synthesis of ***methyl tricosa-10,12-diynoylphenylalaninate*** *(*TR-MPhe - 7)

TR-NHS crude (1 eq, 0.24 mmol) is solubilized in CH_2Cl_2 (15 mL) in a round bottom flask under a gentle flux of N_2 and avoiding light contact (wrapping the flask with an aluminum foil). MPhe*HCl (2 eq, 0.49 mmol) is added to the mixture followed by dropwise addition of triethylamine (Et_3N, 1.2 eq, 0.29 mmol). The reaction is stirred at rt for 24 h. After checking in TLC, extracted with CH_2Cl_2/Brine solution and then the mixture is purified by column chromatography (ethylacetate : cyclohexane = 1 : 5 to 1 : 2 gradient elution) to yield the product. The solvent is removed under a gentle flux of N_2. **Yield**: white powder (85 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.84–0.87 (t, 3H), 1.24–1.41 (m, 22H), 1.45-1.57 (m, 6H), 2.12–2.23 (m, 6H), 3.04-3.16 (m, 2H), 3.71 (s, 3H), 4.84-4.91 (q, 1H), 5.82-5.84 (d, 1H), 7.06-7.08 (d, 2H), 7.24-7.29 (d, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 172.6, 172.1, 135.8, 129.2, 128.5, 127.1, 76.7, 65.2, 52.8, 52.3, 37.9, 36.5, 31.8, 29.5, 29.3, 29.1, 28.8, 28.3, 25.5, 22.6, 19.2, 14.1.

Synthesis of methyl tricosa-10,12-diynoylleucinate (TR-MLeu, 8)



Step 1. Synthesis of ***leucine methylester * HCl*** (**MLeu * HCl**). [5]

Leucine (Leu, 1 eq, 3 mmol) and TMSCl (trimethylsilyl chloride, 2 eq, 6 mmol) are stirred in MeOH (10 mL) at rt for 24 h. The solvent is evaporated under reduced pressure and the crude (white powder) is used in the 3rd step with TR-NHS without further purifications. **Yield**: white solid (98 %). ^{1}H NMR (400 MHz, $CDCl_3$). δ = 0.89 (m, 6H), 1.65 (m, 2H), 1.82 (m, 1H), 3.78 (s, 3H), 4.10 (t, 1H).^{13}C NMR (100 MHz, $CDCl_3$). δ = 21.2, 21.6, 24.0, 38.9, 51.6, 53.6, 171.4.

Step 2. Synthesis of ***2,5-dioxopyrrolidin-1-yl tricosa-10,12-diynoate*** (TR-NHS - **10**).

Step 3. Synthesis of ***Methyl tricosa-10,12*****-diynoylleucinate** (TR-MLeu - **8**).

TR-NHS crude (1 eq, 0.24 mmol) is solubilized in CH_2Cl_2 (15 mL) in a round bottom flask under a gentle flux of N_2 and avoiding light contact. MLeu*HCl (2 eq, 0.49 mmol) is added to the mixture followed by dropwise addition of triethylamine (1.2 eq, 0.29 mmol). The reaction is stirred at rt for 24 h. After checking in Thin Layer Chromatography (TLC), the mixture is extracted with CH_2Cl_2/Brine solution and then purified with column chromatography (ethylacetate : cyclohexane = 1 : 5 to 1 : 2 gradient elution) to yield the product. The solvent is removed under a gentle flux of an inert gas. **Yield**: solid (88 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.84–0.88 (t, 3H), 0.91-0.94 (t, 6H), 1.24–1.41 (m, 22H), 1.45-1.52 (m, 6H), 1.55-1.66(m, 3H), 2.15–2.24 (m, 6H), 3.71 (s, 3H), 4.60-4.66 (m, 1H), 5.75-5.78 (d, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 173.7, 172,8, 76.7, 65.2, 52.2, 50.5, 41.8, 36.5, 31.9, 29.5, 29.3, 29.1, 28.8, 28.7, 28.3, 25.5, 24.9, 22.8, 22.7, 19.2, 14.1.

^{1}H, ^{13}C and ^{19}F NMR spectra were recorded with a Varian Mercury 400 spectrometer with a 5 mm probe. All chemical shifts have been quoted relative to deuterated solvent signals, d in ppm, J in Hz.

Figure S2. ^{1}H NMR spectrum of **2**

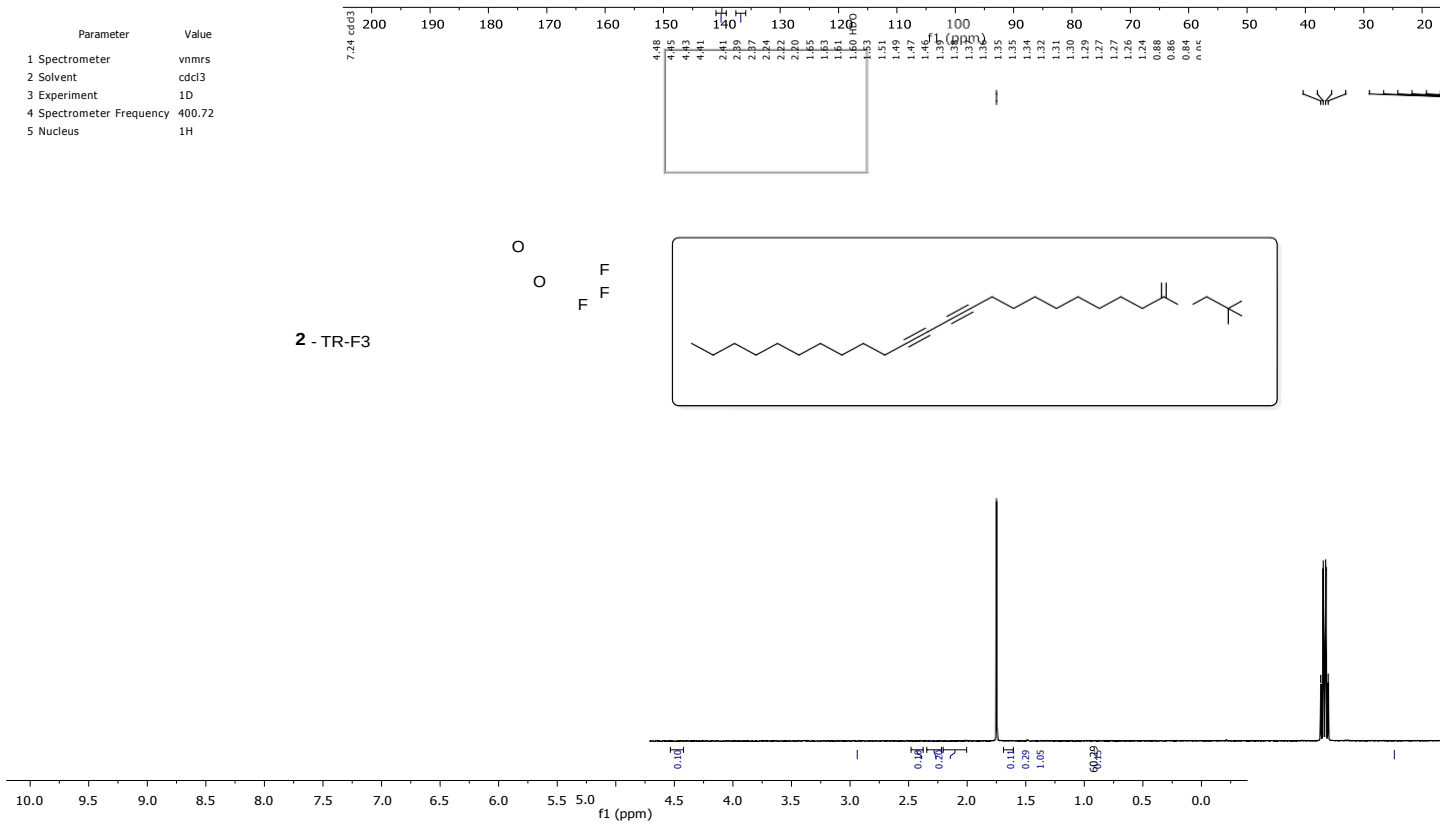


Figure S3. ^{13}C NMR spectrum of **2**

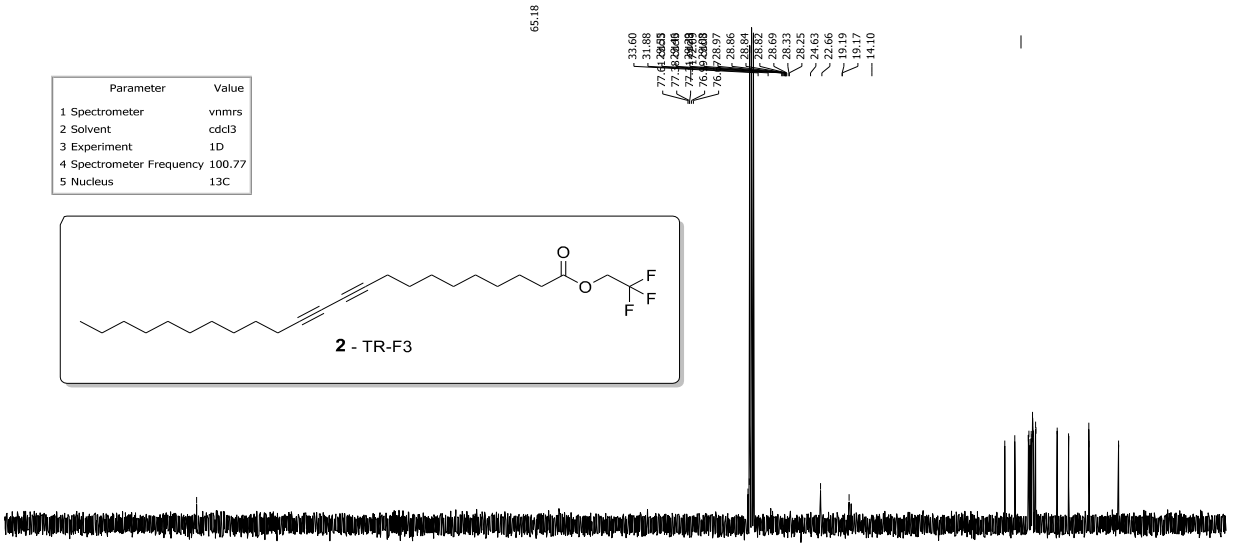


Figure S4. ^{19}F NMR spectrum of **2**

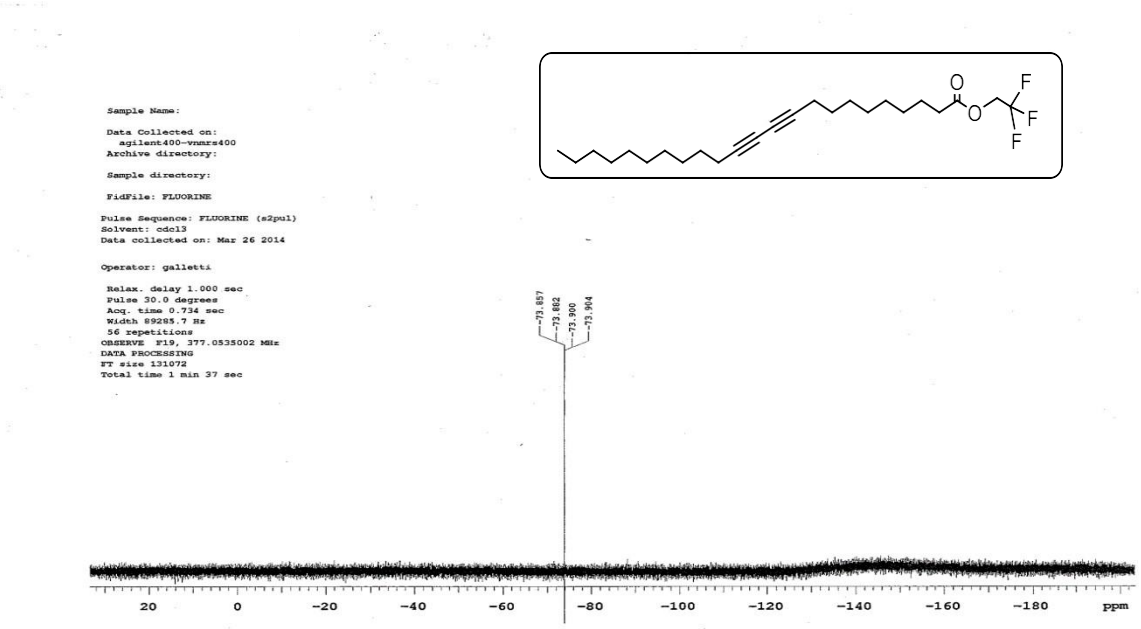


Figure S5. ^{1}H NMR spectrum of **3**

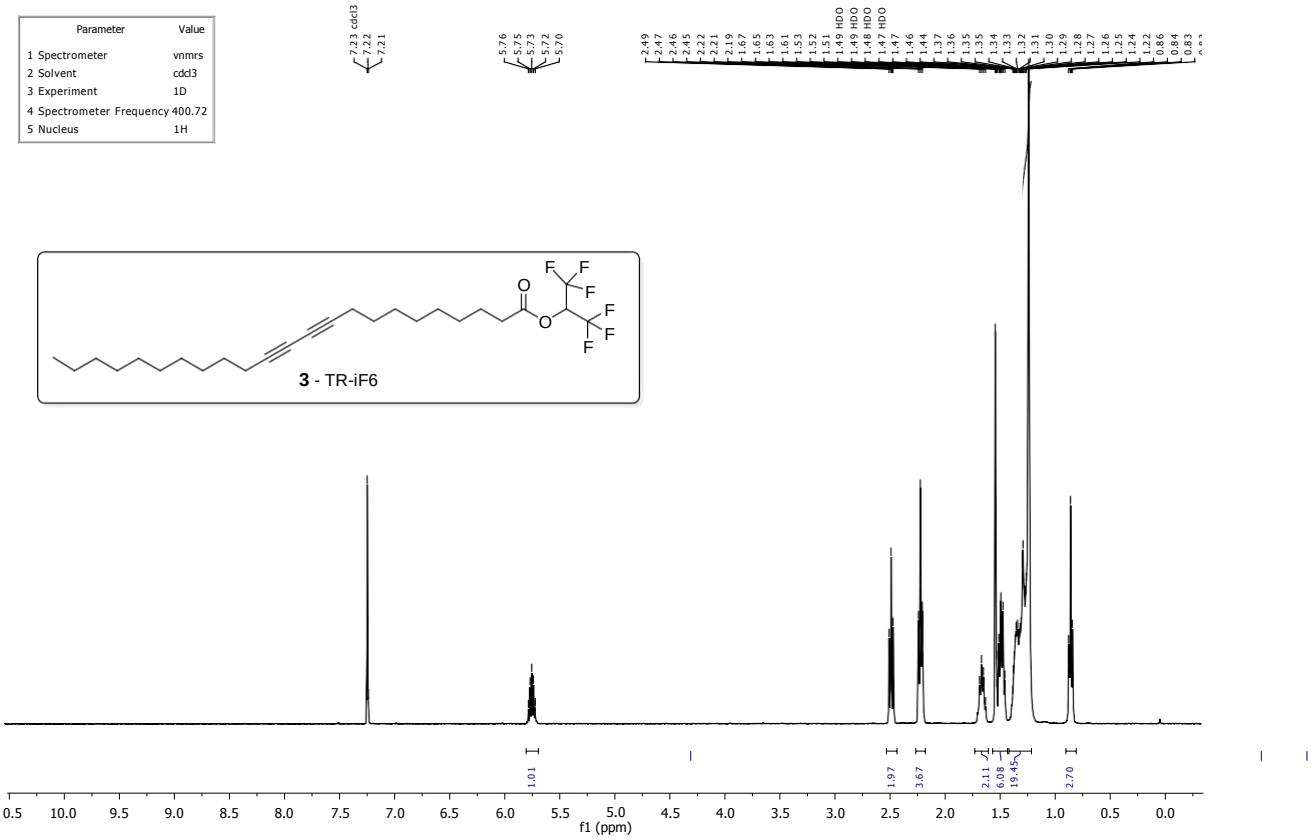


Figure S6. ^{13}C NMR spectrum of **3**

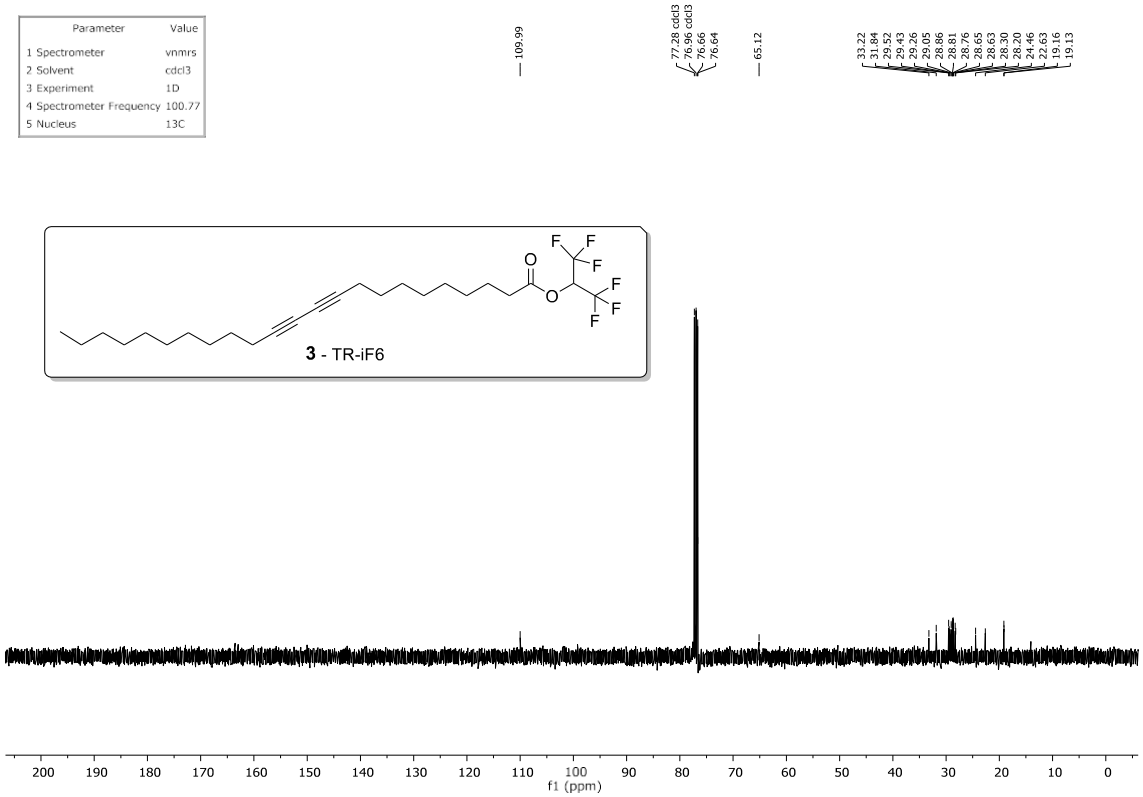


Figure S7. ^{19}F NMR spectrum of **3**

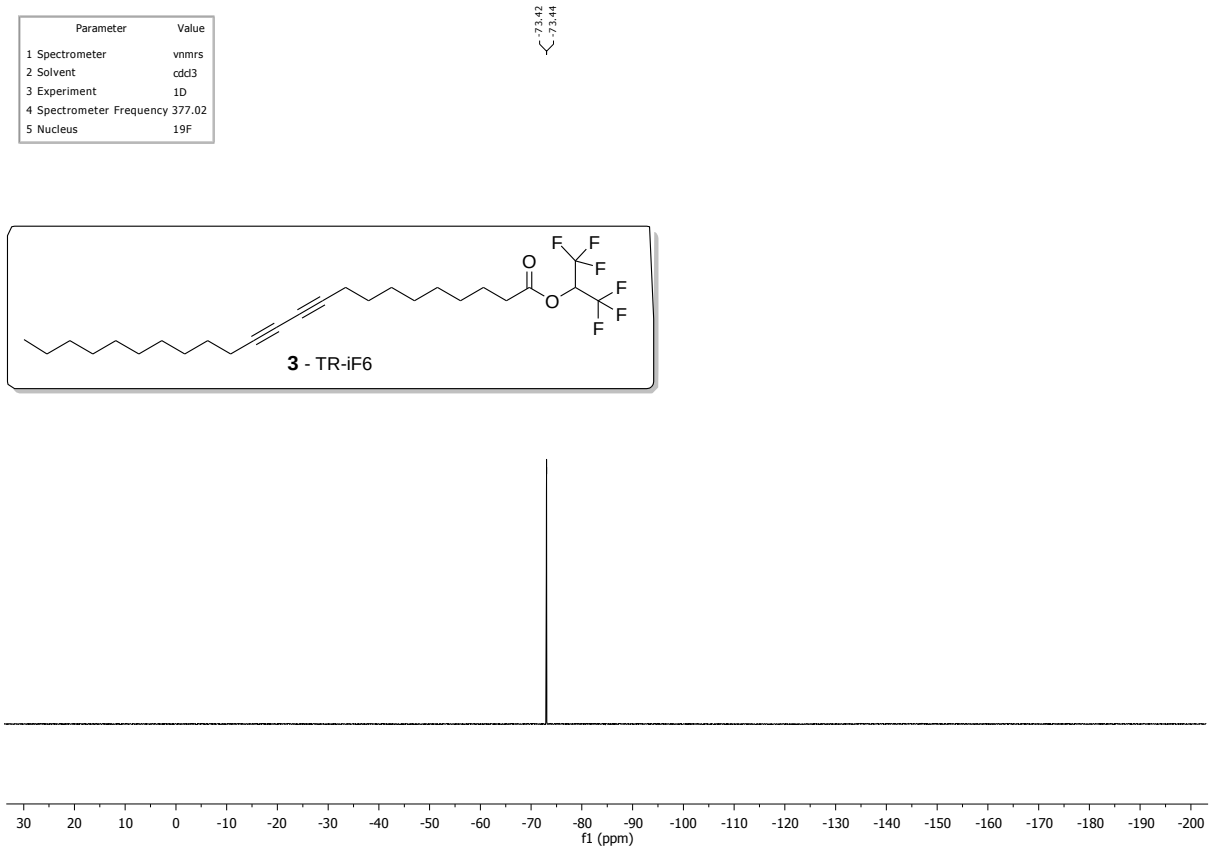
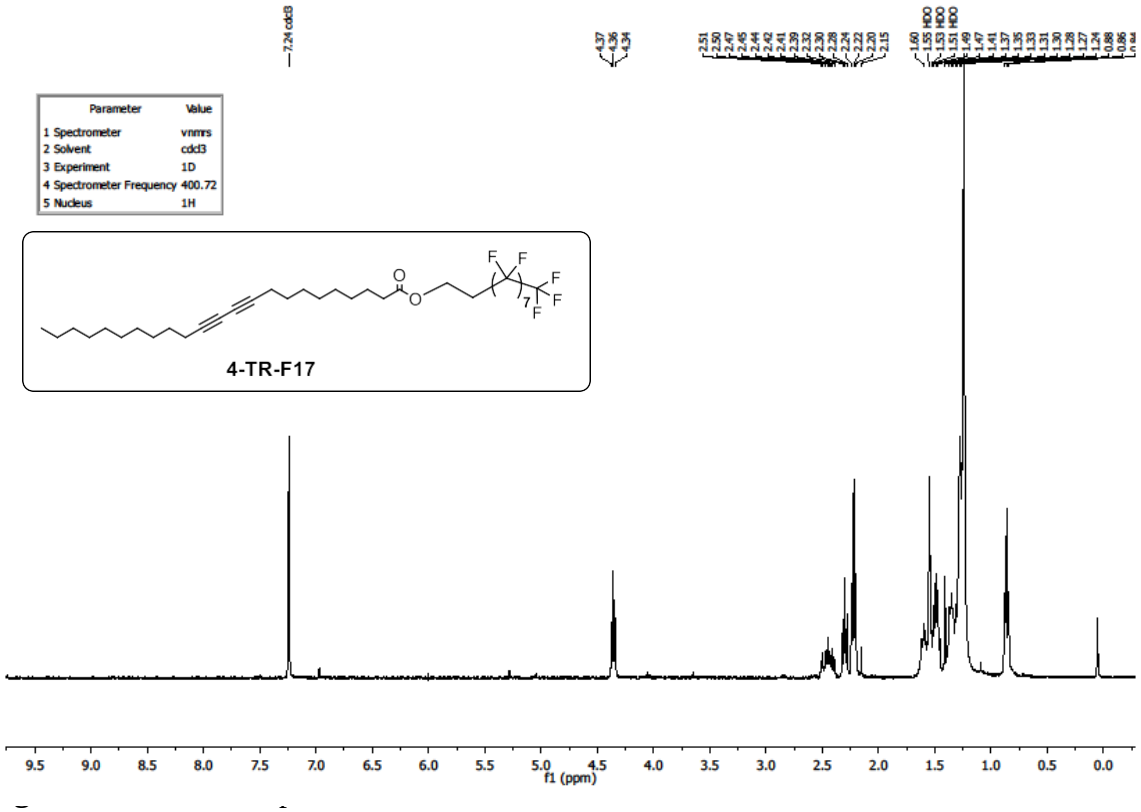


Figure S8. ^{1}H NMR and C13 NMR spectrum of **4**



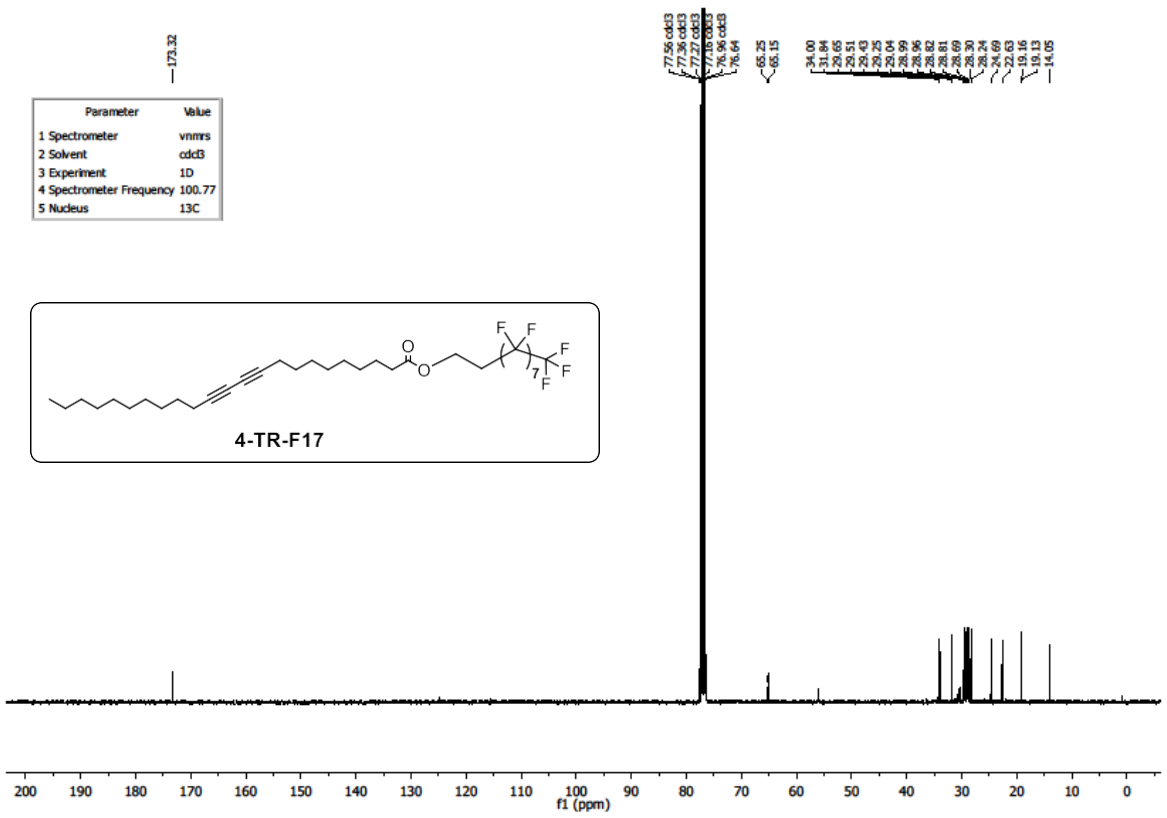


Figure S9. ^{19}F NMR spectrum of **4**

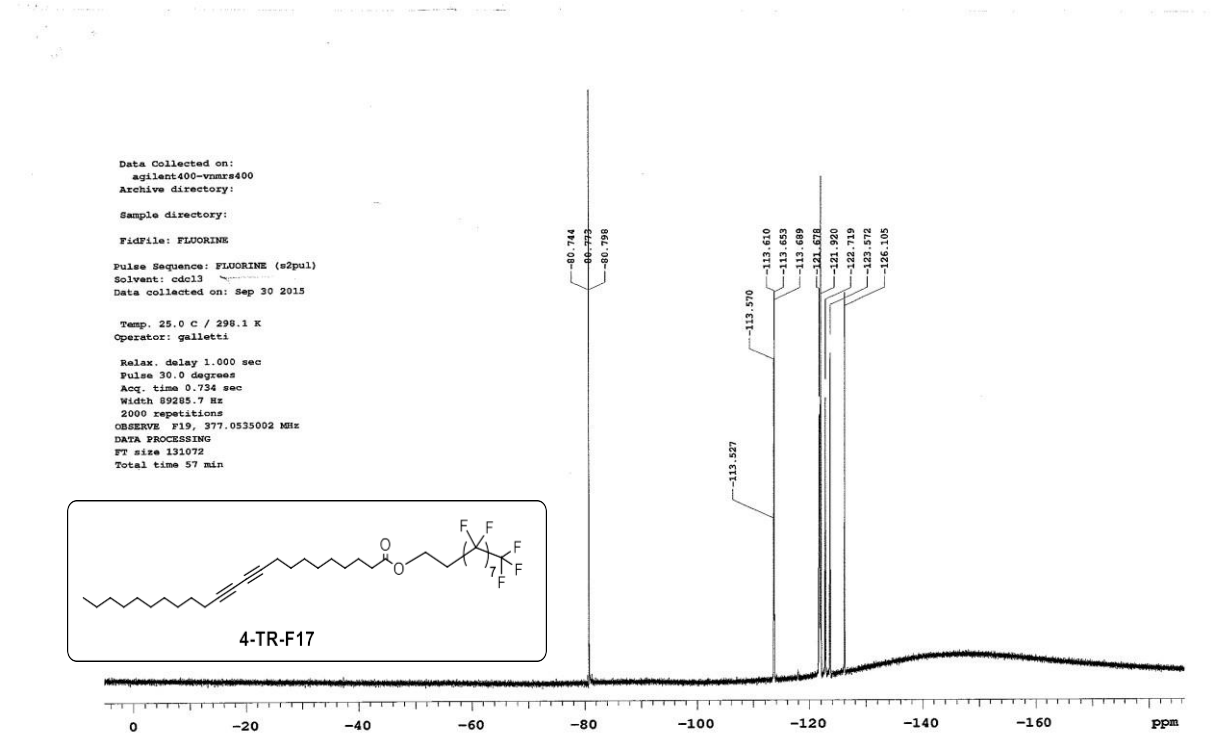


Figure S10. ^{1}H NMR spectrum of **5**

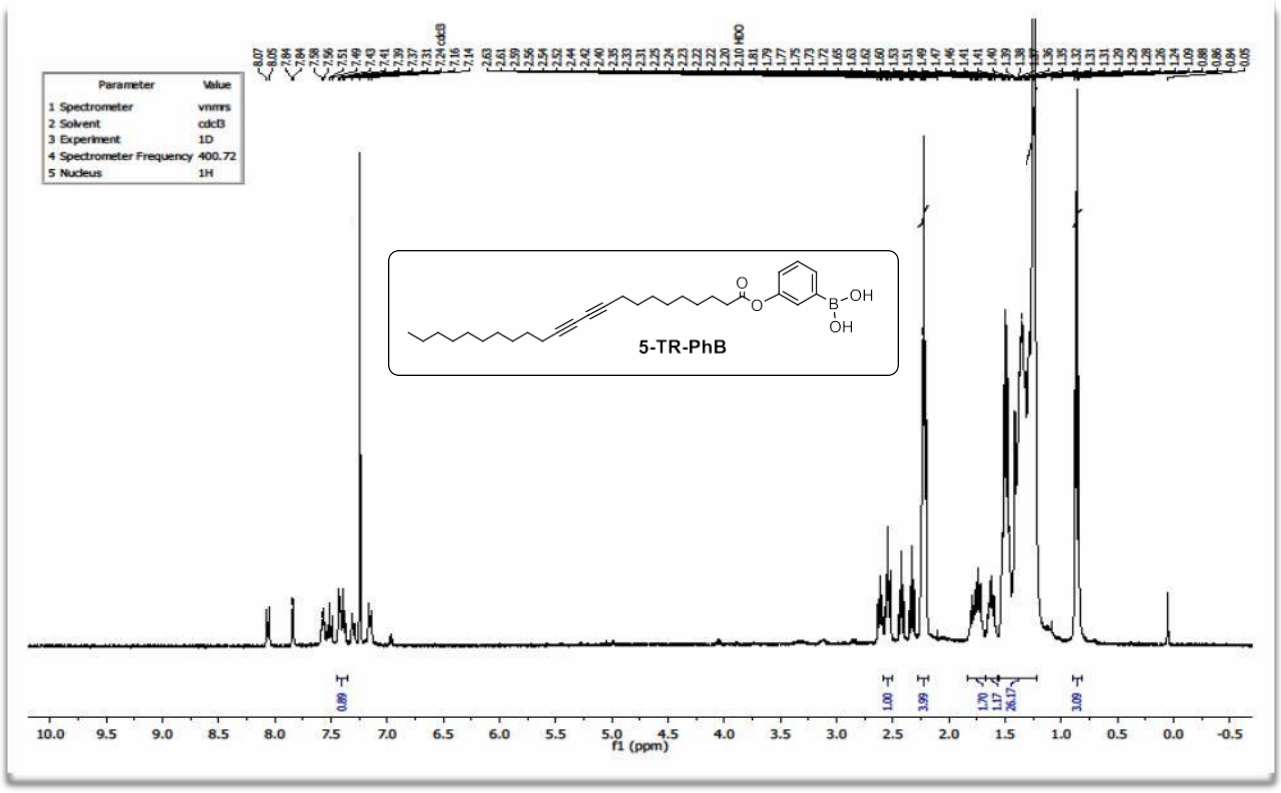


Figure S11. ^{13}C NMR spectrum of **5**

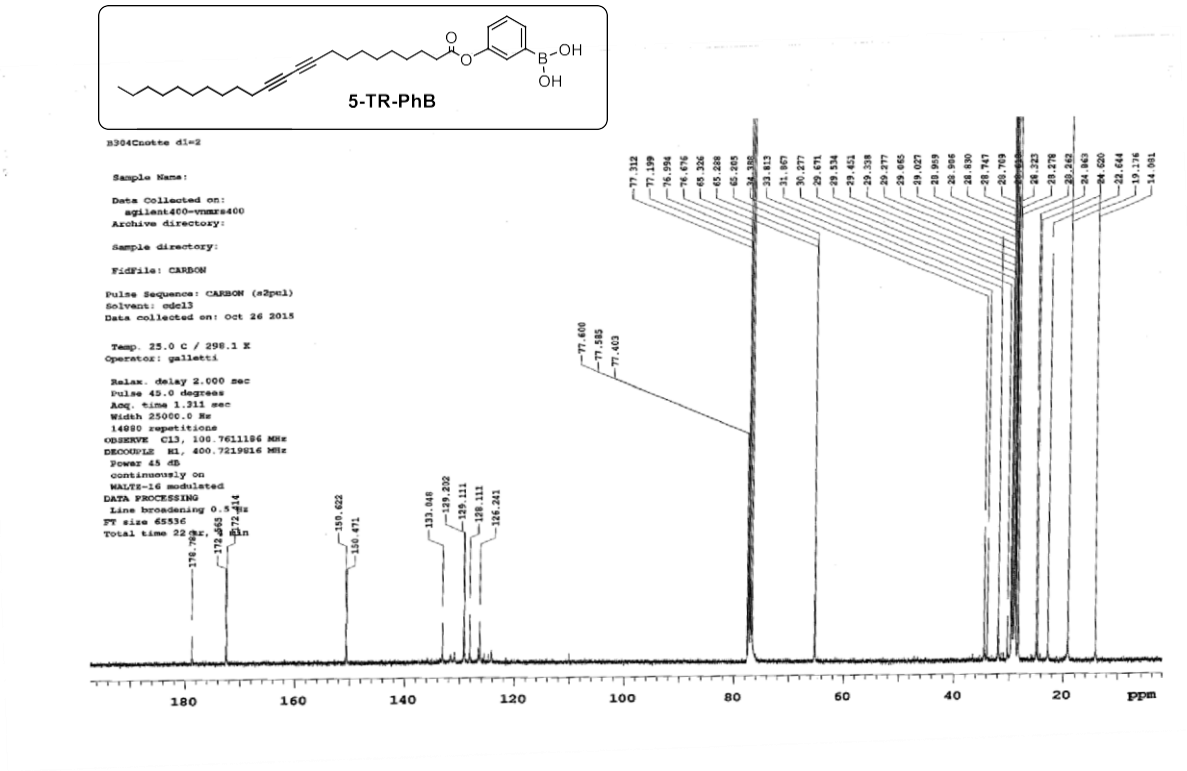


Figure S12. ^{1}H NMR spectrum of **6**

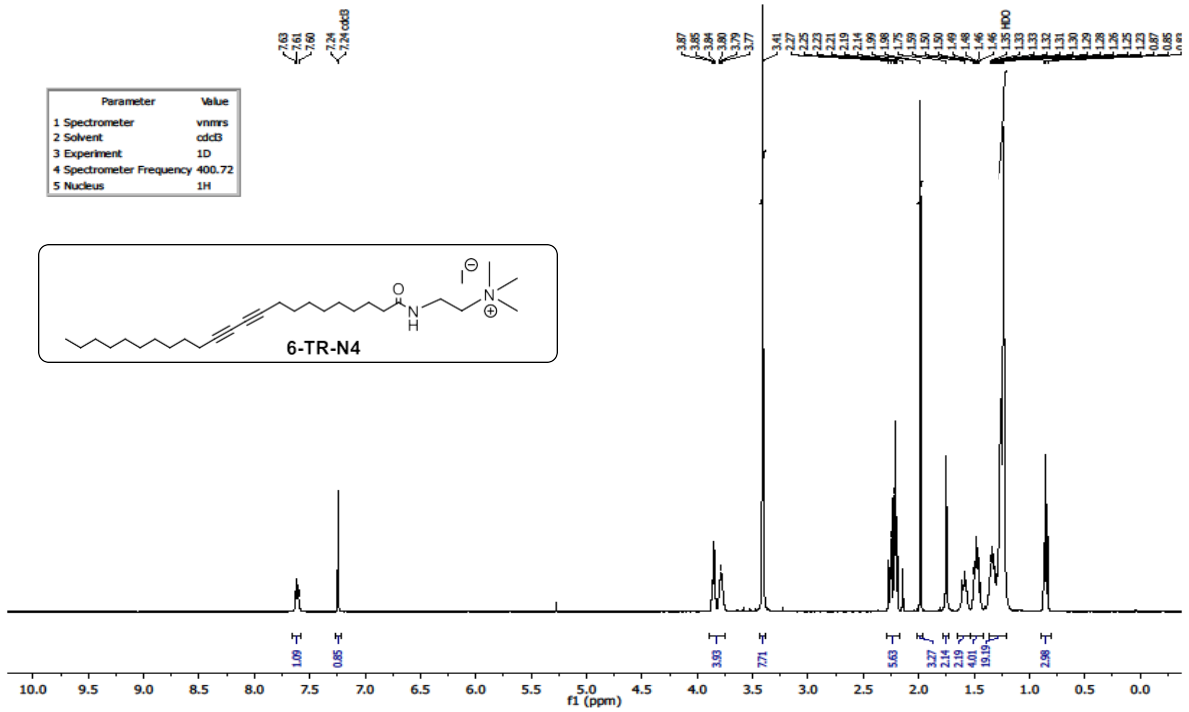


Figure S13. ^{13}C NMR spectrum of **6**

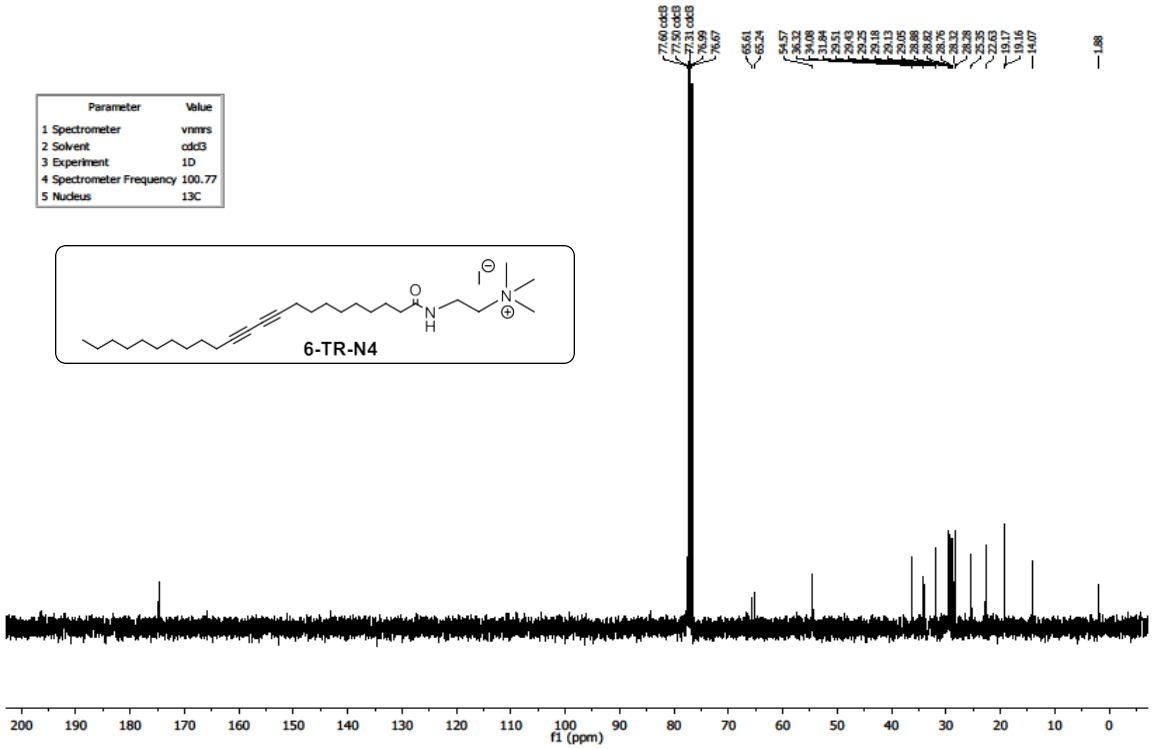


Figure S14. ^{1}H NMR spectrum of **7**

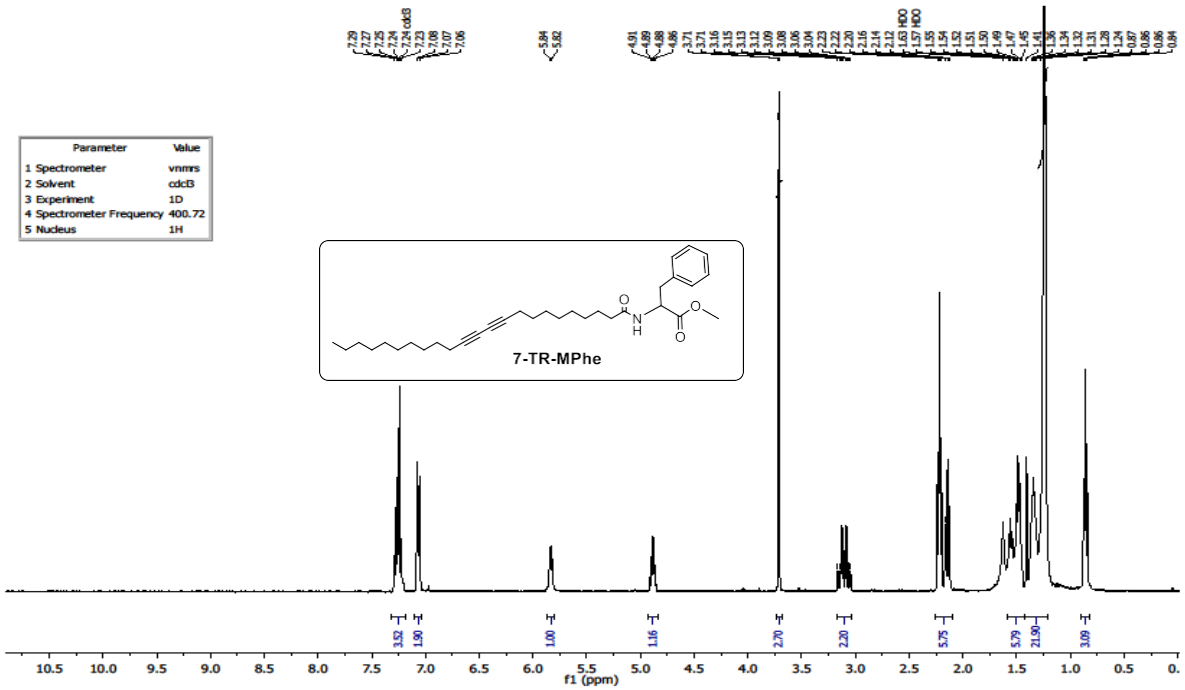


Figure S15. ^{13}C NMR spectrum of **7**

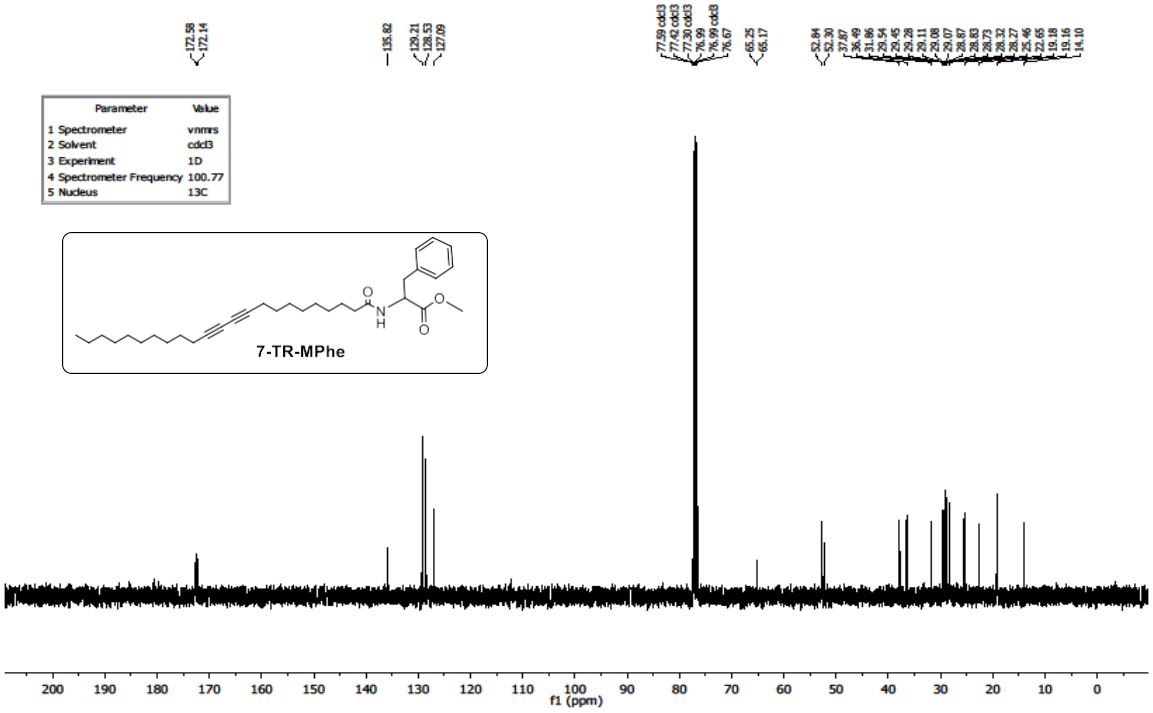


Figure S16. ^{1}H NMR spectrum of **8**

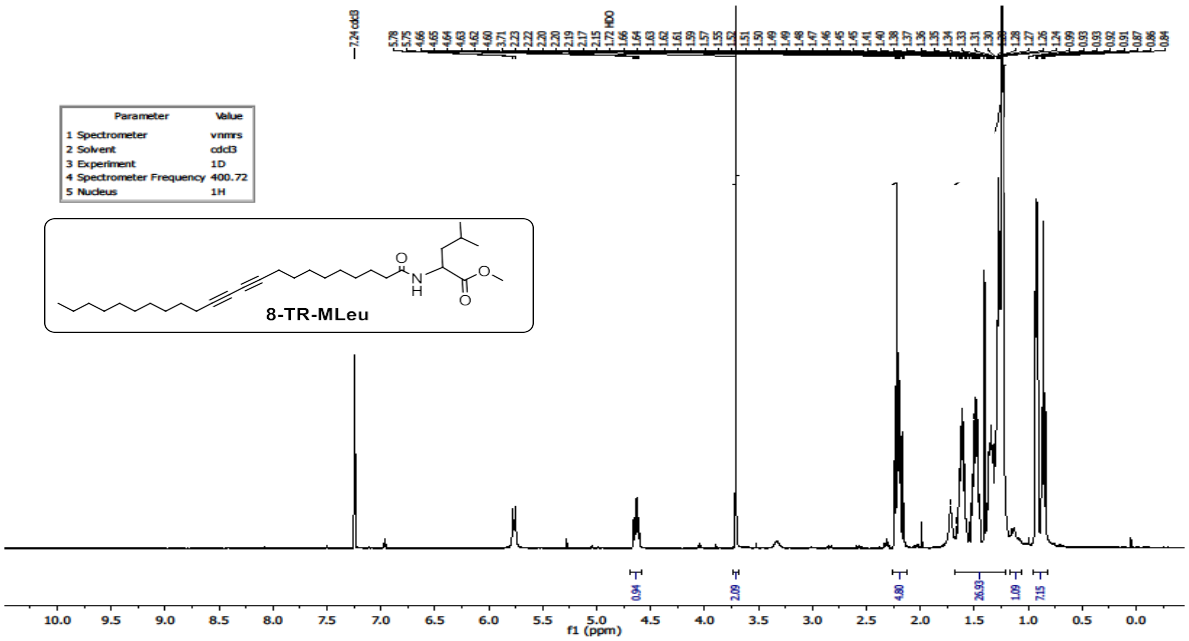


Figure S17. ^{13}C NMR spectrum of **8**

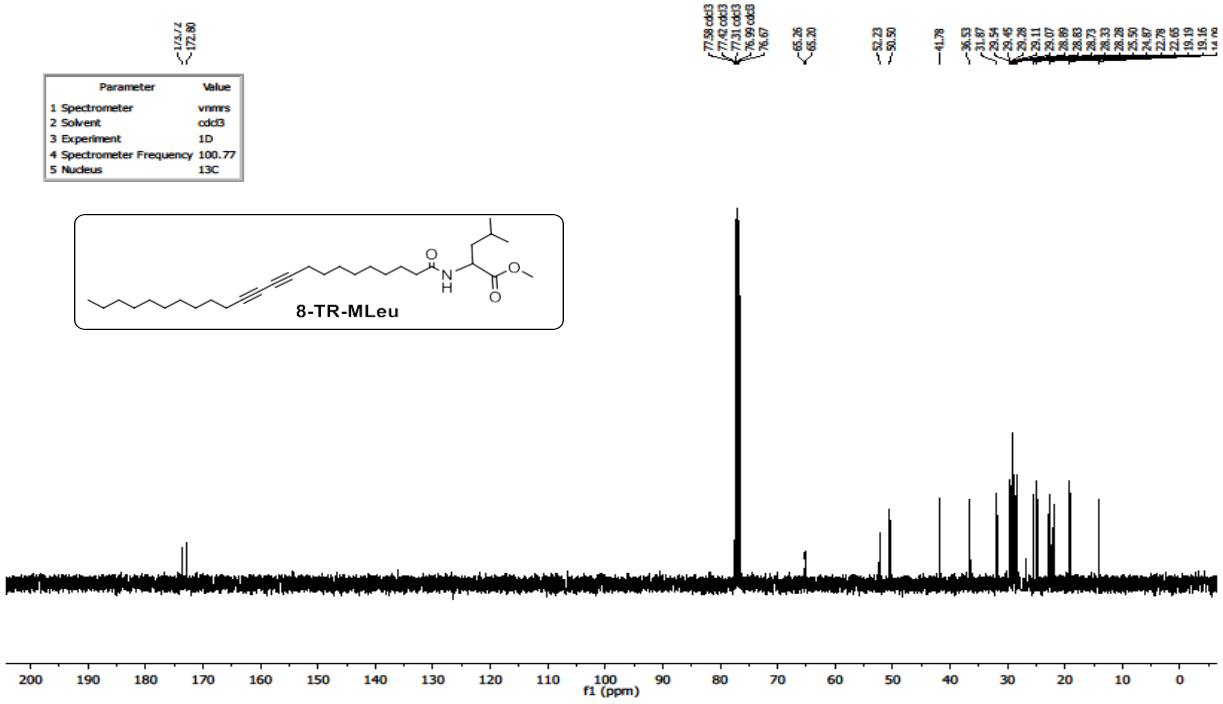


Figure S18. ^{1}H NMR spectrum of **9**

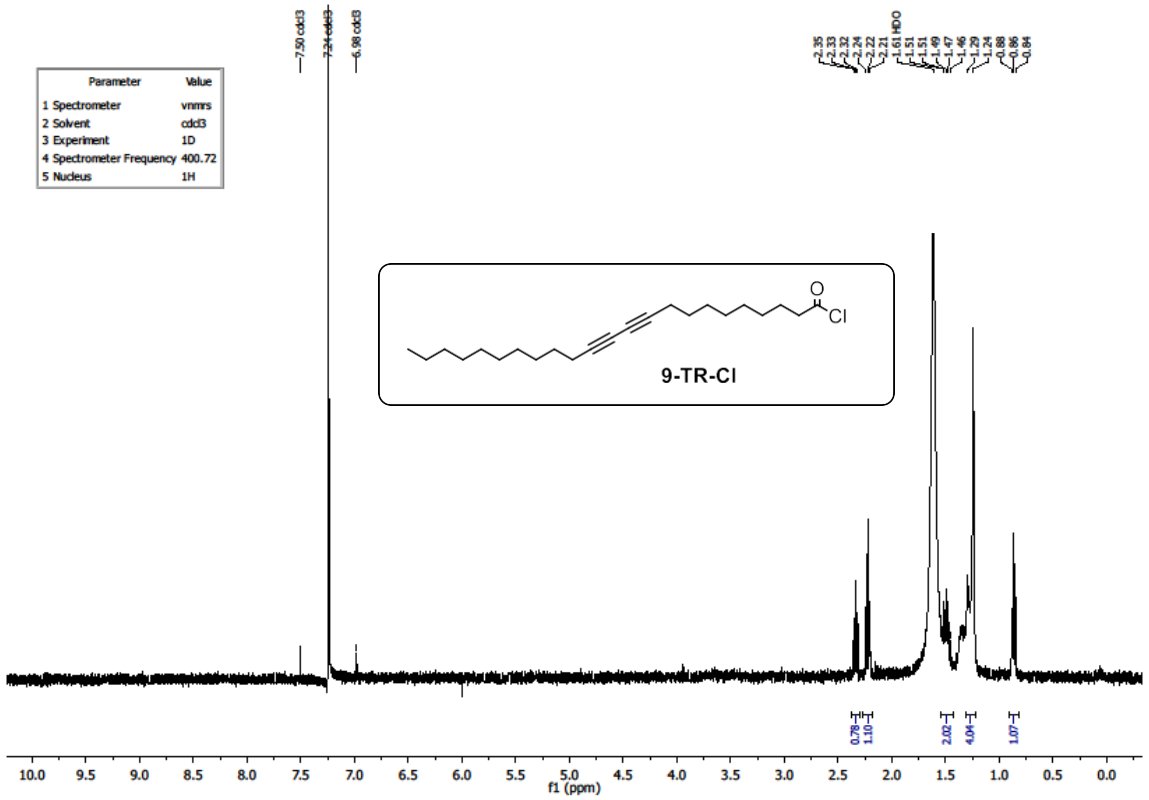


Figure S19. ^{13}C NMR spectrum of **9**

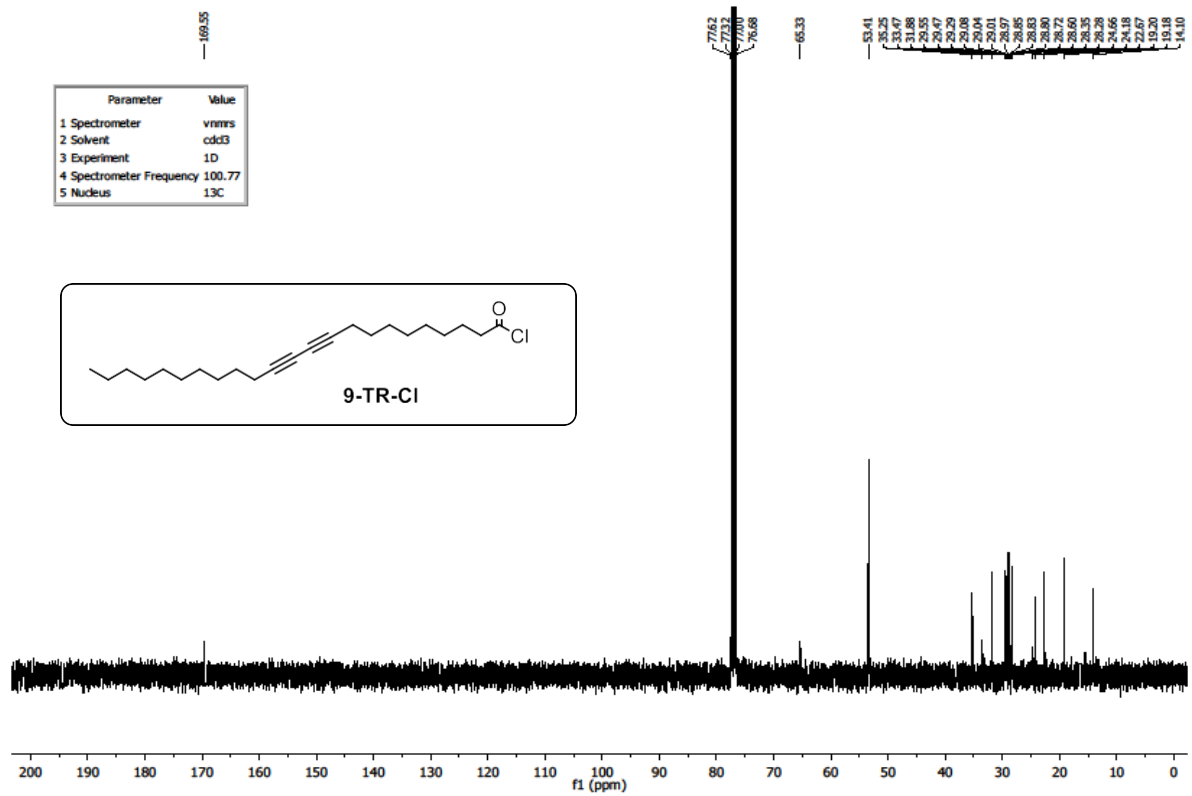


Figure S20. ^{1}H NMR spectrum of **10**

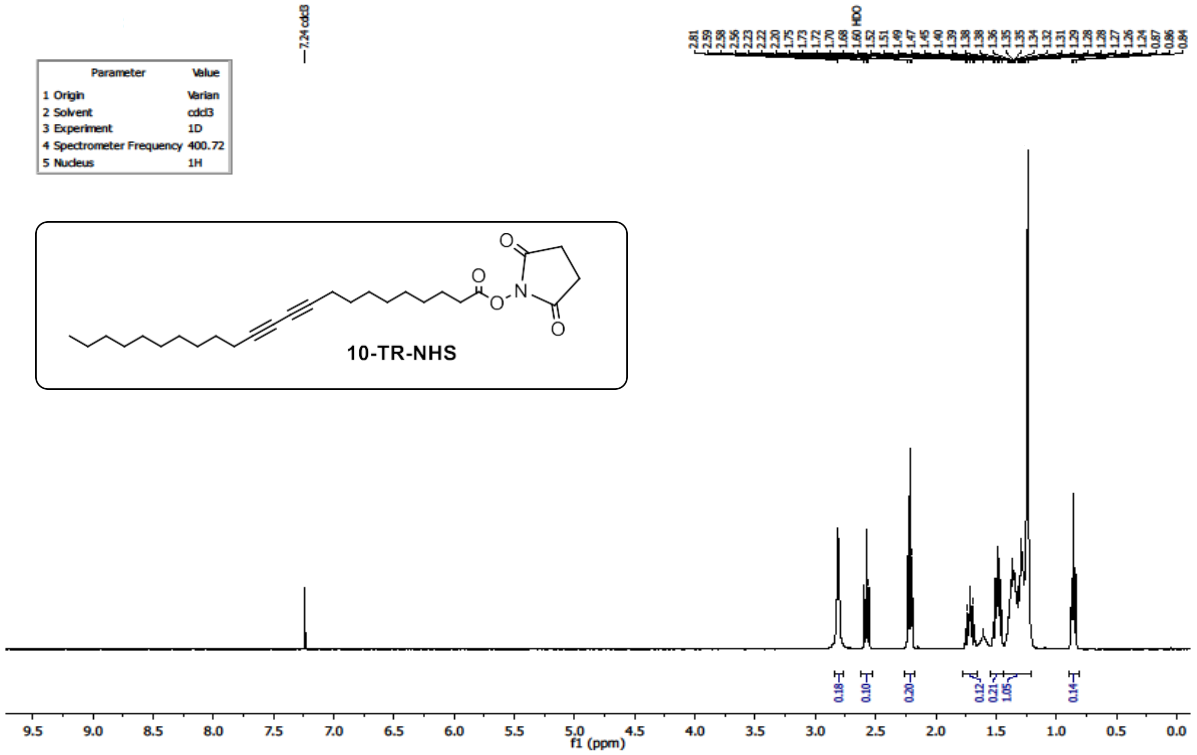
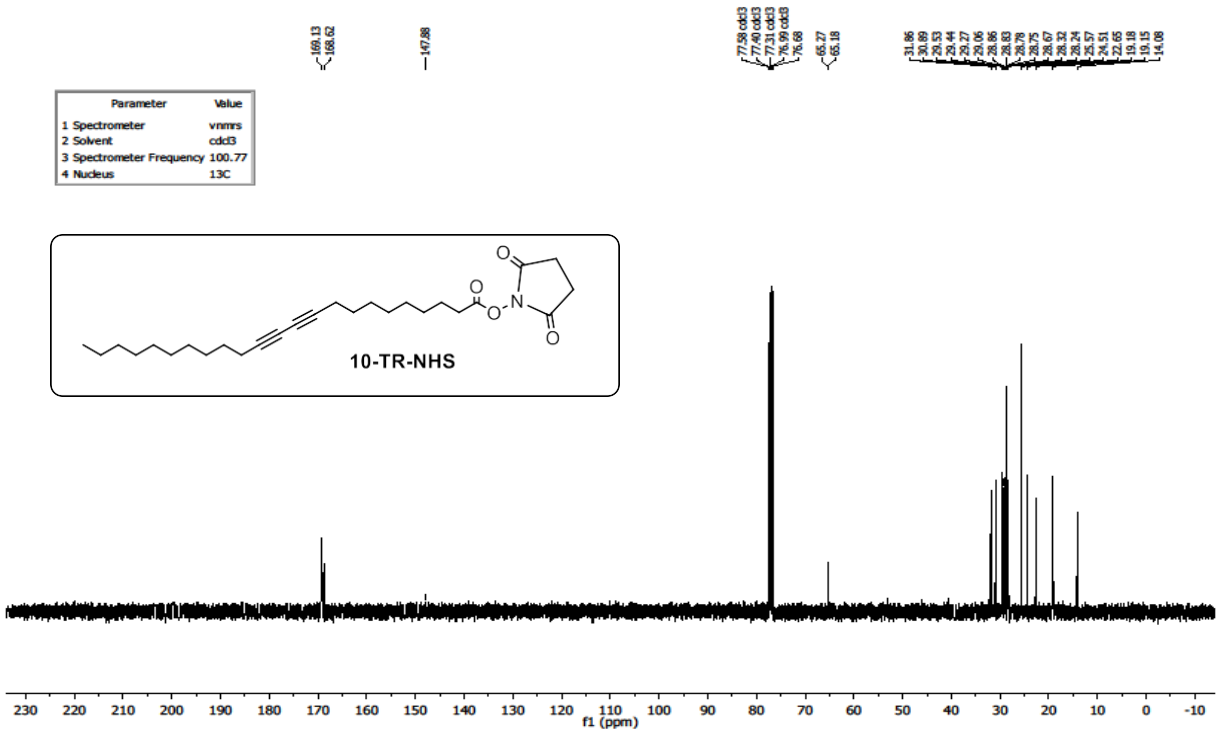


Figure S21. ^{13}C NMR spectrum of **10**



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