Supporting information

End-groups of Poly(*p*-phenylene sulfide) Characterized by DNP NMR Spectroscopy

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1. General

Poly(p-phenylene) sulfide (PPS) was purchased from Sigma-Aldrich (powder, MW ~10,000). Organic compounds and solvents were purchased from chemical suppliers and used without further purification. TEKPol was purchased from Cortechnet. Solution NMR was measured with Bruker Avance III spectrometer (600 MHz for ^{1}H nuclei) using cryo-probe. High resolution mass spectroscopy (HRMS) was measured by Bruker micrOTOF II using electrospray ionization (ESI) positive mode. Atomic absorption spectroscopy (AAS) was measured using Hitachi High-Tech Z-2300.

2. DNP-NMR measurement

All experiments were performed with a Bruker Avance NEO 400 MHz/263 GHz 9.4 T DNP system. TEKPol was used as a polarizing agent (PA). Incipient wetness impregnation of PPS (powder form) with 16 mM TEKPol in TCE was performed to prepare the samples for DNP experiments. Typically, ca. 10 mg of PPS was loaded directly into a 3.2 mm sapphire rotor, and ca. 10 μL of PA solution was added over PPS. The samples were mixed with a fine stick, and sealed with a teflon insert and closed with a zirconia cap. The NMR rotor was stood at an appropriate temperature using temperature-controlled oven. For DNP-NMR measurement, the sample was frozen at ca. 100 K inside the precooled low temperature 3.2 mm MAS probe head and degassed by freeze-thaw cycles according to a literature procedure.[1] The sweep coil of the main magnetic field was tuned so that microwave irradiation occurred at the ^{1}H positive DNP enhancement maximum of the nitroxide biradicals. Standard ramped cross polarization (CP) was used to transfer polarization from the ^{1}H nuclei to the nucleus of interest (^{13}C, ^{15}N). CP contact time was 3000 μs for ^{13}C and ^{15}N. SPINAL-64 ^{1}H heteronuclear decoupling was applied during acquisition.

To determine ε_H and ε_C values, Hahn-echo and CP experiment were applied for ^{1}H and ^{13}C, respectively. A recycle delay was based on DNP build-up time, T_{DNP}, determined by ^{1}H saturation recovery experiment under microwave irradiation, and set as T_{DNP} x 1.3 s. Intensities of ^{1}H signal at 1-10 ppm or ^{13}C signal due to an aromatic part at 130-160 ppm or solvent (TCE) part at 70-100 ppm under microwave (MW) on/off accumulated by 16 scans (for MW on measurement) and 64 scans (for MW off measurement) were utilized for the determination of ε_H and ε_C values. The sample spinning frequency was set to 10 kHz and a sample temperature was 110-112 K under MW on, and 99-100 K under MW off condition. ^{13}C chemical shifts were referenced to tetramethylsilane at 0 ppm using adamantane as an external standard (38.52 ppm). ^{15}N chemical shifts were referenced to liq. NH_3 at 0 ppm using $^{15}NH_4Cl$ as an external standard (39.3 ppm).[2]

DNP enhancement factors (ε, θ, Σ) were collected similarly to the reported procedure.[3] DNP enhancement (ε) is defined as the ratio between the signal intensity per scan attained from the sample under MW irradiation condition ($I_{mw, on}$) and normal condition ($I_{mw, off}$), and calculated according to following formula (eq 1):

$$\varepsilon = \frac{I_{\text{mw on}}}{I_{\text{mw off}}} \qquad (1)$$

The contribution factor (θ) describes the signal quenching effect caused by paramagnetic compounds and defined as ratio between the intensity of signal with PA solution ($I_{\text{mw off, with radical}}$) and without radical ($I_{\text{mw off, without radical}}$). θ was calculated according to following formula (eq 2):

$$\theta = \frac{I_{\text{mw off, with radical}}}{I_{\text{mw off, without radical}}} \qquad (2)$$

The overall sensitivity gain (Σ) describes the actual gain of signal intensity compared to a conventional NMR experiment at the same temperature. It takes into account the DNP enhancement ε, the contribution factor θ and the difference between the DNP build-up time (T_{DNP}) of the sample with a radical containing solution and longitudinal relaxation time of the sample (T_1). Σ was calculated according to following formula (eq 3):

$$\Sigma = \varepsilon \cdot \theta \cdot \sqrt{\frac{T_1}{T_{DNP}}} \qquad (3)$$

Regarding the treatment of errors for each factor, we selected the conditions with 60 °C for 19 hours using TEKPol/TCE as representative model, and repeated the measurement three times to determine the standard error for ε, $T_{DNP,}$ θ and Σ. The percentage of standard error were applied for measurements in other conditions.

3. Time profiles of T_{DNP}, θ, and Σ

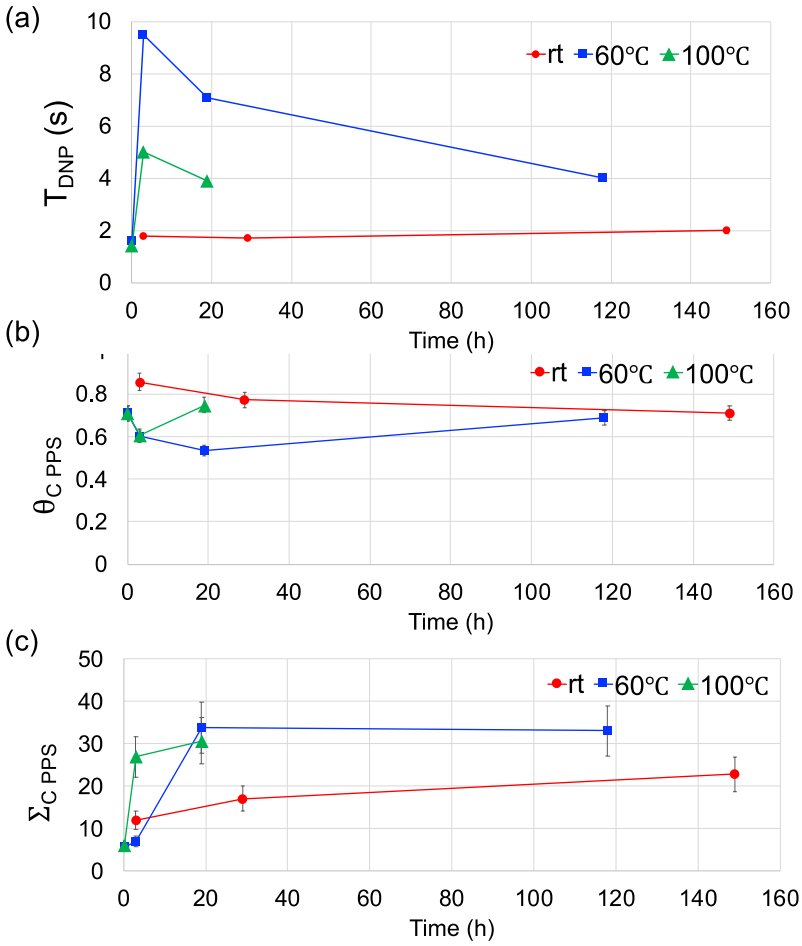


Figure S1. Time-course study of T_{DNP} (a), $\theta_{C,PPS}$ (b), $\Sigma_{C,PPS}$ (c) determined with PPS samples treated at rt, 60 °C, and 100 °C

4. EPR measurement

Continuous Wave (CW) EPR spectra were recorded on a Bruker EMXNano X-band spectrometer (9.5 GHz microwave frequency). The conversion time was set to 15 ms and the time constant to 1.28 ms. 2000 data points were recorded. The modulation frequency was 100 kHz and the modulation amplitude was 1 G. For spin counting experiment, the NMR sample rotor packed with PPS and PA solution prepared by same procedure as DNP-NMR measurement was directly charged in quartz tube. The spectra were recorded at room temperature with a sweep width of 200 G and an attenuation of 25 dB. Quantitative spin amounts were directly obtained via the built-in EMXnano reference-free spin counting module (Xenon software, Bruker). The concentrations are determined by dividing the counted spin with a total weight of sample (Figure S4). Errors were based on measurements using three individual as-prepared samples (before heating). The percentage of standard error was applied for other measurements at each interval.

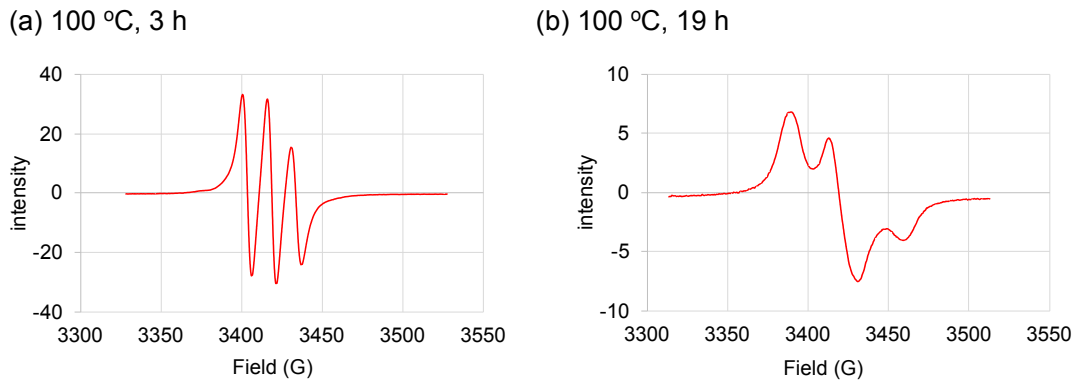


Figure S2. EPR spectra of PPS samples impregnated with TEKPol/TCE solution recorded at room temperature. Spectra were obtained from the sample heated at 100 °C for 3 hours (a), 19 hours (b).

5. SEM analysis

Scanning electron microscopy (SEM) was acquired with JEOL JSM7800F. The sample after thermal treatment was prepared by same procedure as for DNP NMR measurements. The sample was dried under reduced pressure at ambient temperature before SEM analysis. EDX was performed using Oxford X-MAX80mm^2. The SEM-EDX analysis for multi-site on surface was depicted in Figure S5. The elemental composition of surface were mostly identical among several sites, indicating fiber-like structure is derived from PPS after thermal treatment.

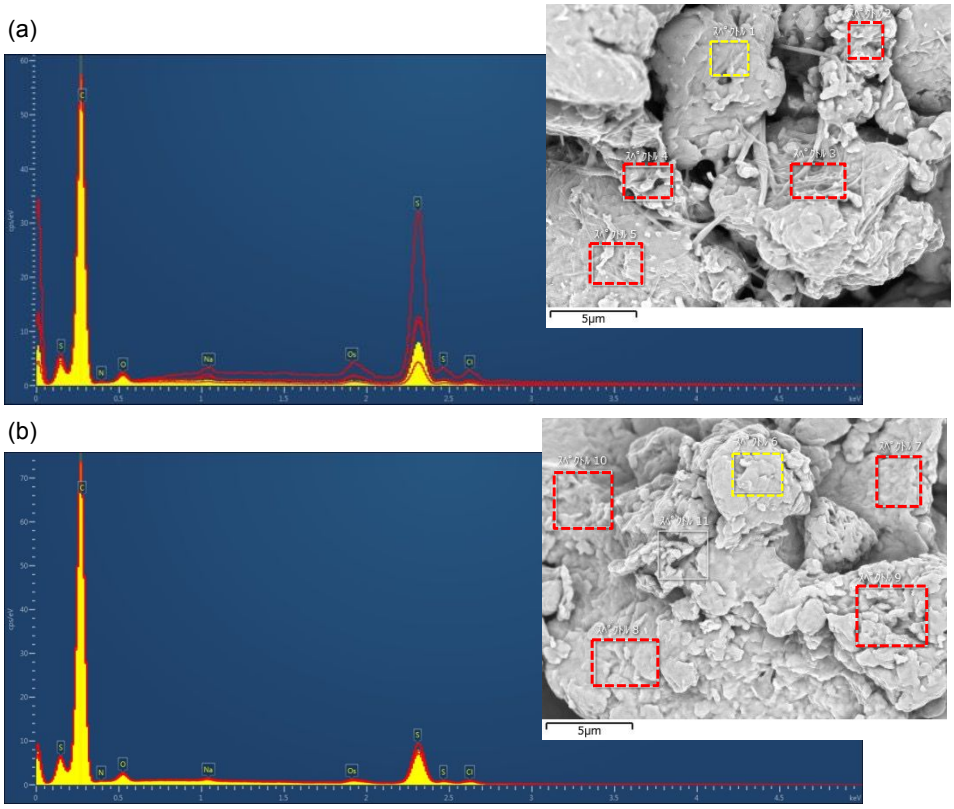


Figure S3. SEM-EDX analysis of PPS after thermal treatment (60 °C, 19 h). Analysis focused on fiber-like surface (a) and flat surface (b) were shown.

6. Time-course of radical concentration

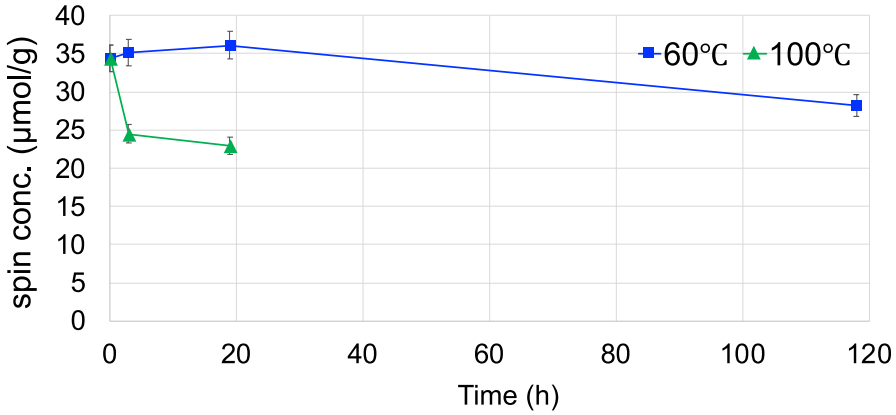


Figure S4. Time-course of spin concentration (μmol/g) under heating conditions

7. Characterization of decomposed product of TEKPol

The sample rotor charged with PPS (ca. 10 mg) and TEKPol/TCE (16 mM, ca. 10 μL) was sealed with Teflon insert and ZrO_2 cap, followed by heating at 100 °C for 3 hours. The mixture was extracted with excess THF at room temperature. The resulting solution was concentrated under reduced pressure. The residue was dissolved in CH_3CN, and employed for ESI-MS measurement. TEKPol in CH_3CN was also analyzed by ESI-MS (Figure S6(a)), which clearly displayed peaks assignable to $[TEKPol]^+$. The decomposed product displayed peaks at m/z 890.55953 (Figure S6(b)). The observed peak pattern was well-matched with mono-radical form of TEKPol where one nitroxide radical was reduced to NH and another one was kept intact (calcd for formula $C_{59}H_{73}N_2O_5$: 890.55922). The presence of nitroxide radical was confirmed by EPR analysis, which exhibited sharp triplet signal typical for mono-nitroxide species.

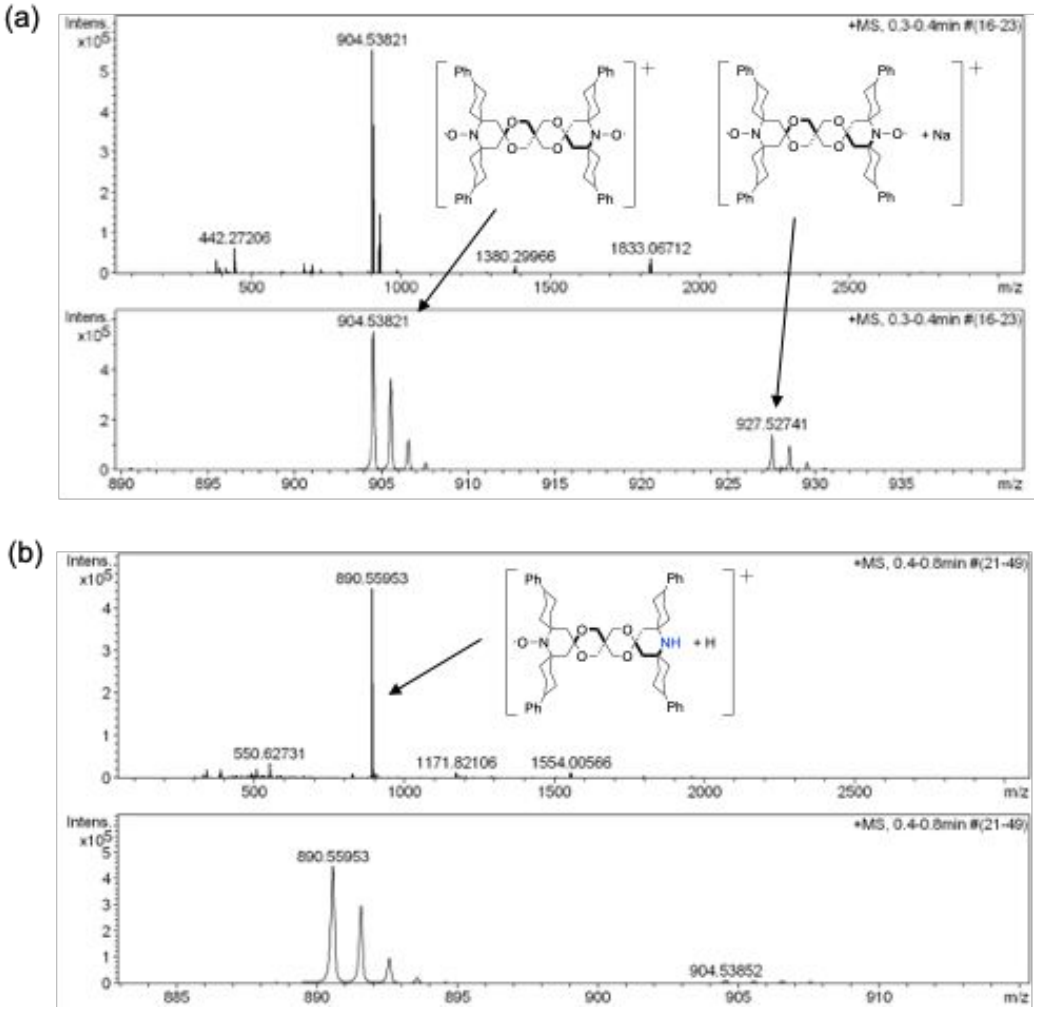


Figure S5. ESI-mass spectra (positive mode) of TEKPol (a) and a decomposed product from TEKPol (b) dissolved in CH_3CN.

8. Screening of solvent of PA solution

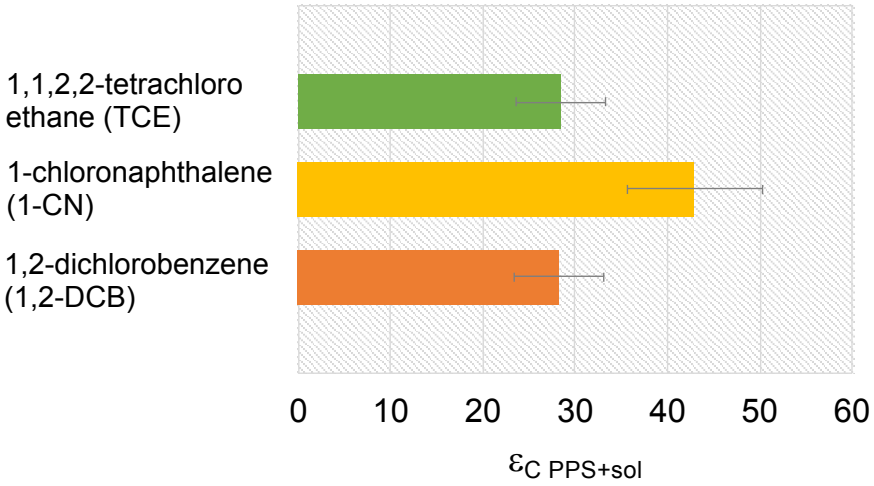


Figure S6. Screening of solvent of PA solution

9. DNP NMR of blank solution

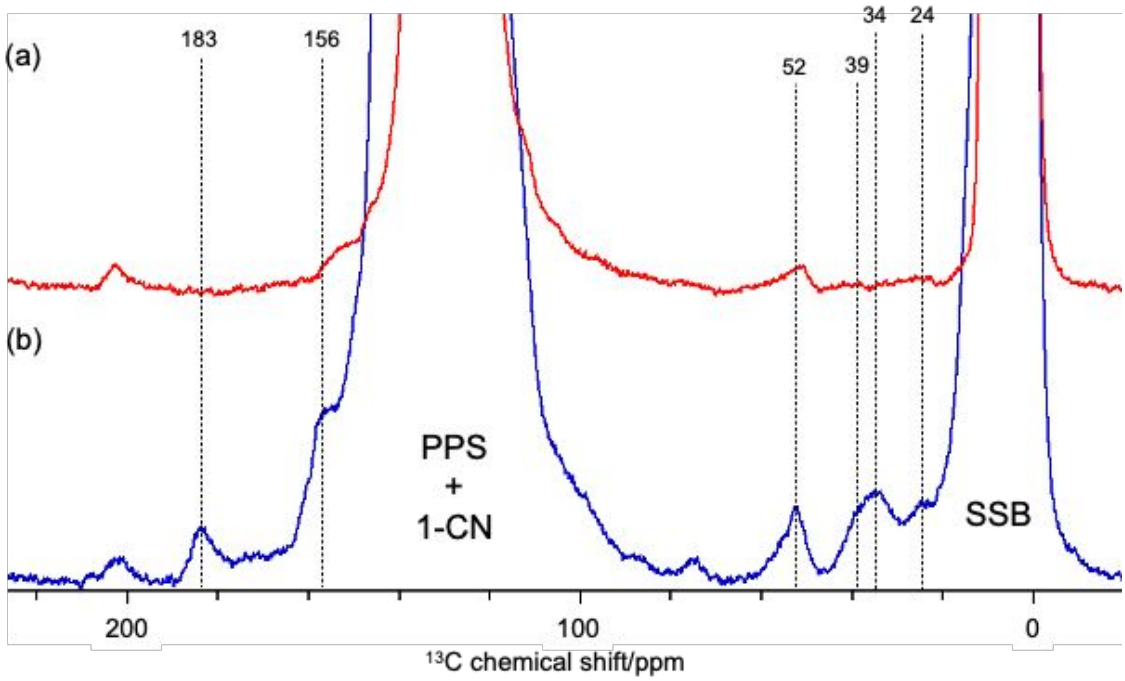


Figure S7. DNP-enhanced ^{13}C CPMAS NMR of TEKPol/1-CN solution (a), PPS with TEKPol/1-CN solution (b). Both samples were heated at 60 ^{o}C for 19 h before measurement. All spectra were recorded at 110–112 K. SSB represents spinning side band of PPS and 1-CN.

10. DNP ^{15}N NMR of model compounds

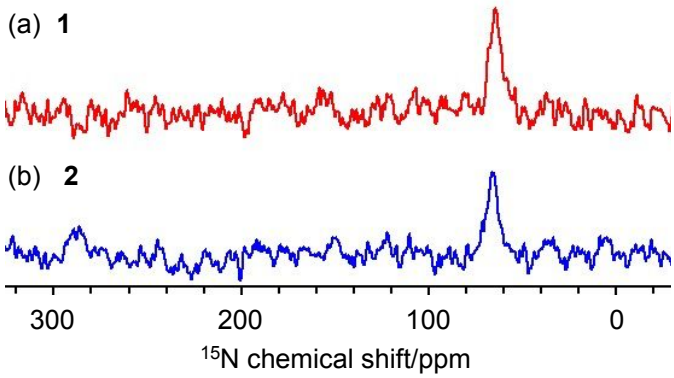
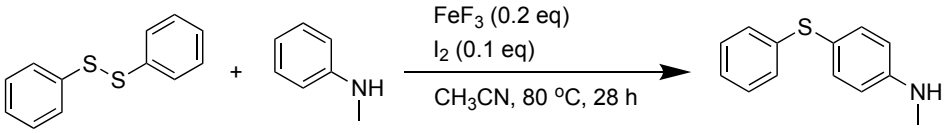


Figure S8. DNP-enhanced ^{15}N CPMAS NMR of **1** (a) and **2** (b) using AMUPol/DMSO-d_6 solution. All spectra were recorded at 110–112 K.

11. Preparation of model compounds

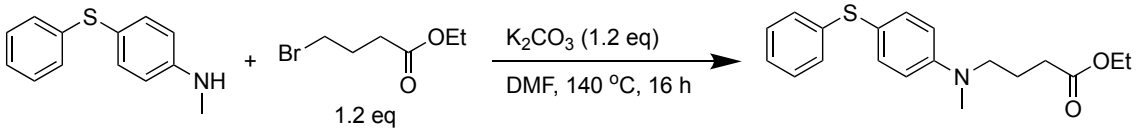
Preparation of N-methyl-4-(phenylthio)aniline[4]



Under N_2 atmosphere, diphenyldisulfide (2.2 g, 10 mmol, 1 eq) and N-methylaniline (1.1 g, 10 mmol, 1 eq) were dissolved in CH_3CH (25 mL). FeF_3 (0.23 g, 2.0 mmol, 0.2 eq) and I_2 (0.26 g, 1.0 mmol, 0.1 eq) were added successively to the solution, and resulting mixture was stirred at 80 °C for 28 hours. After cooling to rt, the solution was diluted by EtOAc (25 mL) and washed with brine. The organic layer was dried over $MgSO_4$, and volatiles are removed under reduced pressure. The residue was purified by Silica-gel column chromatography using Hexane/EtOAc (10/1) as eluent. The title compound was obtained as colorless oil (1.1 g, 51% yield).

^{1}H NMR (600 MHz, $CDCl_3$, rt), δ/ppm: 2.87 (s, 3H, Me), 4.75 (br, s, 1H, NH), 6.64-6.68 (m, 2H), 7.08-7.14 (m, 2H), 7.19-7.23 (m, 2H), 7.34-7.37 (m, 2H).

Preparation of Ethyl 4-(methyl(4-(phenylthio)phenyl)amino)butanoate[5]



Under N_2 atmosphere, N-methyl-4-(phenylthio)aniline (1.0 g, 4.6 mmol, 1 eq) and ethyl 4-bromobutanoate (1.1 g, 5.5 mmol, 1.2 eq) were dissolved in DMF (20 mL). K_2CO_3 (0.76 g, 5.5 mmol, 1.2 eq) were added, and resulting mixture was stirred at 140 °C for 16 hours. After cooling to rt, the solution was diluted by H_2O (100 mL) and extracted with EtOAc (30 mL x 2). The organic layer was washed with brine and dried over $MgSO_4$, and volatiles are removed under reduced pressure. The residue was purified by Silica-gel column chromatography using Hexane/EtOAc (10/1) as eluent. The title compound was obtained as colorless oil (0.25 g, 16% yield).

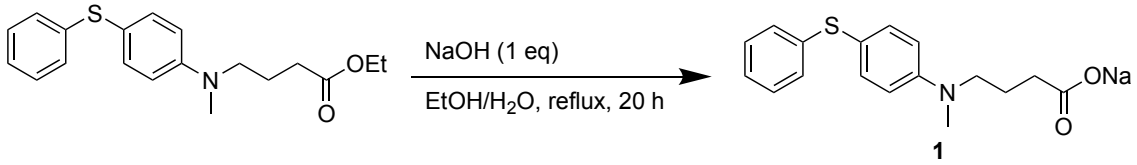
^{1}H NMR (600 MHz, $CDCl_3$, rt), δ/ppm: 1.25 (t, J = 7.2 Hz, 3H, Et), 1.93 (quintet, 2H, J = 7.2 Hz, -$NMeCH_2C\mathit{H}_2CH_2CO_2Et$), 2.36 (t, J = 7.2 Hz, 2H, -$NMeCH_2CH_2C\mathit{H}_2CO_2Et$), 2.97 (s, 3H, -NMe), 3.40 (t, J = 7.2Hz, 2H, -$NMeC\mathit{H}_2CH_2CH_2CO_2Et$), 4.13 (q, J = 7.2 Hz, 2H, Et), 6.71 (br, s, 2H, Ar), 7.06-7.15 (m, 3H, Ar), 7.20-7.22 (m, 2H, Ar), 7.37(d, J = 8.7 Hz, 2H, Ar).

^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$, rt), δ/ppm: 14.2 (s, Et), 22.1 (s, -$NMeCH_2CH_2\mathit{C}H_2CO_2Et$), 31.4 (s, -$NMeCH_2\mathit{C}H_2CH_2CO_2Et$), 38.3 (s, -$NMe\mathit{C}H_2CH_2CH_2CO_2Et$), 51.7 (s, -$N\mathit{Me}CH_2CH_2CH_2CO_2Et$),

60.5 (s, -NMe$CH_2CH_2CH_2CO_2$*Et*), 112.7 (s, Ar), 117.1 (s, Ar), 125.0 (s, Ar), 126.8 (s, Ar), 128.7 (s, Ar), 136.3 (s, Ar), 140.3 (s, Ar), 149.4 (s, Ar), 173.1 (s, Ar).

HRMS (ESI positive, MeOH, m/z) calcd for $[C_{19}H_{23}NO_2S + Na]^+$: 352.1342, observed 352.1346

Synthesis of Sodium 4-(methyl(4-(phenylthio)phenyl)amino)butanoate (**1**)



1

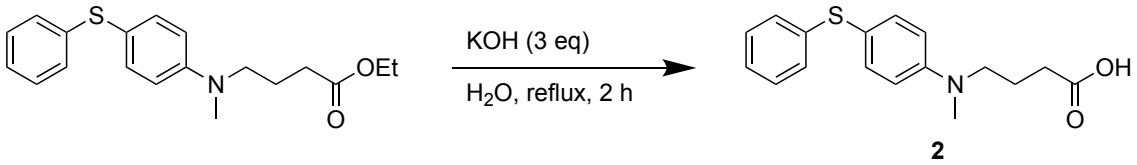
Under N_2 atmosphere, NaOH (48 mg, 1.2 mmol) in H_2O (2.5 mL) was added to the solution of (ethyl 4-(methyl(4-(phenylthio)phenyl)amino)butanoate (0.40 g, 1.2 mmol, 1 eq) in EtOH (2.5 mL). The mixture was refluxed for 20 hours. After cooling to rt, all volatiles are removed under reduced pressure. The resulting solid was rinsed by Hexane for several times and dried at 50 °C under reduced pressure. The title compound was obtained as colorless solid (0.30 g, 77% yield).

^{1}H NMR (600 MHz, DMSO-d_6, rt), δ/ppm: 1.65 (quinted, J = 7.1 Hz, 2H, -NMe$CH_2C\mathit{H}_2CH_2CO_2Na$), 1.89 (t like, 2H, -NMe$CH_2CH_2C\mathit{H}_2CO_2Na$), 2.91 (s, 3H, NMe), 3.32 (t like, 2H, -NMe$C\mathit{H}_2CH_2CH_2CO_2Et$), 6.80 (d, J = 8.9 Hz, 2H, Ar), 7.00-7.03 (m, 2H, Ar), 7.09 (t like, 1H, Ar), 7.24 (t, J = 7.7 Hz, 2H, Ar), 7.27 (d, J = 8.9 Hz, 2H, Ar).

^{13}C{^{1}H} NMR (150 MHz, DMSO-d_6, rt), δ/ppm: 23.1 (s, -NMe$CH_2CH_2\mathit{C}H_2CO_2Na$), 35.0 (s, -NMe$CH_2\mathit{C}H_2CH_2CO_2Na$), 37.9 (s, -NM*e*$\mathit{C}H_2CH_2CH_2CO_2Na$), 52.0 (s, -N*Me*$CH_2CH_2CH_2CO_2Na$), 112.6 (s, Ar), 114.2 (s, Ar), 125.0 (s, Ar), 126.1 (s, Ar), 129.0 (s, Ar), 136.2 (s, Ar), 140.0 (s, Ar), 149.6 (s, Ar), 176.5 (s, Ar).

HRMS (ESI positive, MeOH, m/z) calcd for $[C_{17}H_{18}NO_2SNa + Na]^+$: 346.0848, observed 346.0827

Synthesis of 4-(methyl(4-(phenylthio)phenyl)amino)butanoic acid (**2**)



2

Under N_2 atmosphere, KOH (0.13 g, 2.3 mmol, 3 eq) and **1** (0.25 g, 0.75 mmol, 1 eq) dissolved in H_2O (5 mL) was refluxed for 2 hours. After cooling to rt, H_2O (10 mL) was added. Aqueous solution was washed with Et_2O (10 mL x 2). After pH was tuned as 3-4 using HCl aq., the aqueous solution was extracted by EtOAc (10 mL x 2). Organic layer was washed with brine and dried over $MgSO_4$,

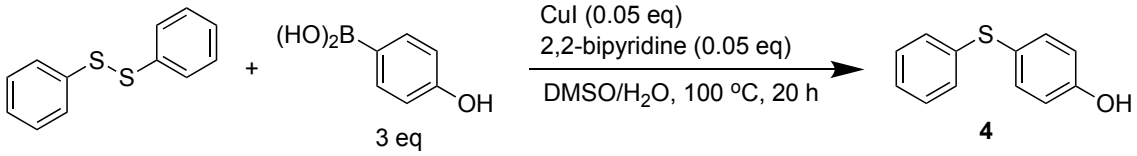
and all volatiles are removed under reduced pressure. The residue was purified by Silica-gel column chromatography using $CHCl_3$/MeOH (95/5) as eluent. The title compound was obtained as colorless oil (0.10 g, 44% yield).

^{1}H NMR (600 MHz, CD_2Cl_2, rt), δ/ppm: 1.92 (quin, *J* = 7.4 Hz, 2H, -NMeCH$_2$C*H*$_2$CH$_2$CO$_2$H), 2.42 (t, *J* = 7.2 Hz, 2H, -NMeCH$_2$CH$_2$C*H*$_2$CO$_2$H), 2.96 (s, 3H, NMe), 3.40 (t, *J* = 7.4 Hz, 2H, -NMeC*H*$_2$CH$_2$CH$_2$CO$_2$H), 6.71 (d, *J* = 9.0 Hz, 2H, Ar), 7.06-7.10 (m, 3H, Ar), 7.18-7.22 (m, 2H, Ar), 7.35 (d, 2H, Ar).

^{13}C{^{1}H} NMR (150 MHz, CD_2Cl_2, rt), δ/ppm: 21.8 (s, -NMeCH$_2$CH$_2$*C*H$_2$CO$_2$H), 30.9 (s, -NMeCH$_2$*C*H$_2$CH$_2$CO$_2$H), 38.2 (s, -NMe*C*H$_2$CH$_2$CH$_2$CO$_2$H), 51.6 (s, -N*Me*CH$_2$CH$_2$CH$_2$CO$_2$H), 112.8 (s, Ar), 117.0 (s, Ar), 125.0 (s, Ar), 126.9 (s, Ar), 128.7 (s, Ar), 136.2 (s, Ar), 140.3 (s, Ar), 149.6 (s, Ar), 176.6 (s, Ar).

HRMS (ESI positive, MeOH, m/z) calcd for $[C_{17}H_{19}NO_2S + H]^+$: 302.1209, observed 302.1210

Synthesis of 4-(phenylthio)phenol (**4**)[6]

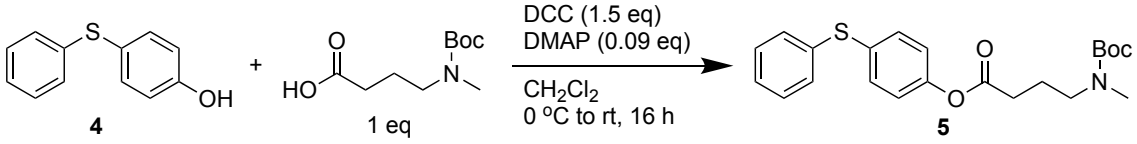


Under N_2 atmosphere, diphenyldisulfide (2.2 g, 10 mmol, 1 eq), 4-hydroxyphenylbronic acid (3.2 g, 30 mmol, 3 eq) and CuI (0.19 mg, 0.10 mmol, 0.05 eq) were dissolved in mixture of DMSO and H_2O (10 mL + 5 mL). The reaction mixture was stirred at 100 °C for 20 hours. After cooling to rt, the solution was diluted by H_2O (200 mL) and extracted with EtOAc (100 mL, 50 mL). The organic layer was washed with brine and dried over $MgSO_4$, and volatiles are removed under reduced pressure. The residue was purified by Silica-gel column chromatography using Hexane/EtOAc (10/1) as eluent. The title compound was obtained as colorless oil (0.50 g, 12% yield).

^{1}H NMR (600 MHz, $CDCl_3$, rt): δ/ppm: 5.07 (br, s, 1H, OH), 6.84-6.88 (m, 2H, Ar), 7.15-7.22 (m, 3H, Ar), 7.24-7.28 (m, 2H, Ar), 7.38-7.41 (m, 2H, Ar).

^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$, rt): δ/ppm: 116.5 (s, Ar), 124.6 (s, Ar), 125.8 (s, Ar), 128.3 (s, Ar), 128.9 (s, Ar), 135.5 (s, Ar), 138.4 (s, Ar), 155.8 (s, Ar)

Synthesis of *N*-Boc-4'-(phenylthio)phenyl 4-methylaminobutanoate (**5**)[7]



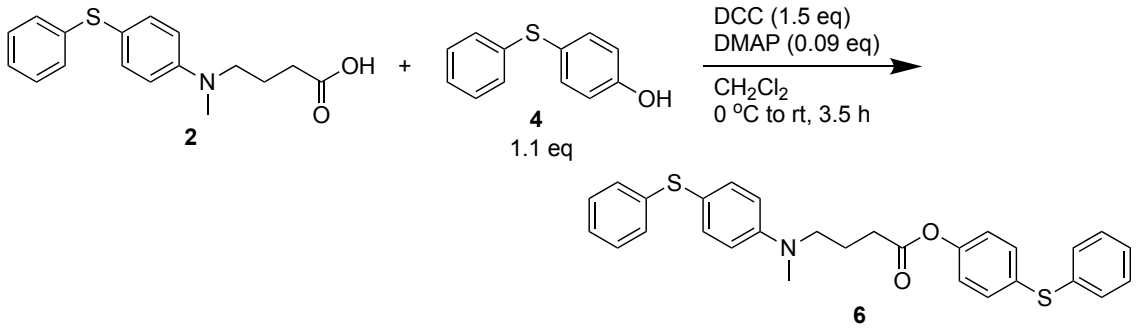
Under N_2 atmosphere, **4** (0.20 g, 0.98 mmol, 1.2 eq), *N*-Boc-4-methylaminobutanoic acid (0.18 g, 0.82 mmol, 1 eq) and DMAP (9.1 mg, 0.074 mmol, 0.09 eq) were dissolved in CH_2Cl_2 (15 mL). To the solution, the solution of DCC (0.31 g, 1.5 mmol, 1.5 eq) in CH_2Cl_2 (2 mL) was added dropwise at 0 °C, and the resulting mixture was further stirred for 16 hours. After the addition of 1M HCl aq (10 mL) and stirring for a while, CH_2Cl_2 layer was separated, dried over $MgSO_4$, and volatiles are removed under reduced pressure. The residue was purified by Silica-gel column chromatography using toluene/EtOAc (5/1) as eluent. The title compound was obtained as colorless oil (0.20 g, 60% yield).

^{1}H NMR (600 MHz, $CDCl_3$, rt): δ/ppm: 1.46 (s, 9H, ^{t}Bu), 1.95 (quintet, J = 7.1 Hz, 2H, -$O_2CCH_2CH_2CH_2NMeBoc$), 2.56 (t, J = 7.3 Hz, 2H, -$O_2CCH_2CH_2CH_2NMeBoc$), 2.87 (s, 3H, NMe), 3.34 (t, J = 7.0 Hz, 2H, -$O_2CCH_2CH_2CH_2NMeBoc$), 7.05 (d, J = 8.8 Hz, 2H, Ar), 7.22-7.27 (m, 2H, Ar), 7.28-7.37 (m, 6H, Ar).

^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$, rt), δ/ppm: 22.9 (s, -$OCOCH_2CH_2CH_2NMeBoc$), 28.5 (s, Boc), 31.4 (s, -$OCOCH_2CH_2CH_2NMeBoc$), 34.2 (s, -$OCOCH_2CH_2CH_2NMeBoc$), 47.8 (s, -$OCOCH_2CH_2CH_2NMeBoc$), 79.6 (s, Boc), 127.1 (s, Ar), 129.2 (s, Ar), 130.8 (s, Ar), 132.4 (s, Ar), 132.8 (s, Ar), 135.8 (s, Ar), 149.9 (s, Ar), 155.8 (s, Ar), 171.6 (s, Ar).

HRMS (ESI positive, MeOH, m/z) calcd for $[C_{22}H_{27}NO_4S + Na]^+$: 424.1553, observed 424.1560

Synthesis of 4-(phenylthio)phenyl 4-(methyl(4-(phenylthio)phenyl)amino)butanoate (**6**)



Under N_2 atmosphere, **4** (49 mg, 0.24 mmol, 1.8 eq), **2** (39 mg, 0.13 mmol, 1 eq) and DMAP (1.4 mg, 0.011 mmol, 0.09 eq) were dissolved in CH_2Cl_2 (15 mL). To the solution, the solution of DCC (40 mg, 0.19 mmol, 1.5 eq) in CH_2Cl_2 (2 mL) was added dropwise at 0 °C, and the resulting mixture was further stirred for 3.5 hours. After the addition of 1M HCl aq (10 mL) and stirring for a while, CH_2Cl_2 layer was separated, dried over $MgSO_4$, and volatiles are removed under reduced pressure. The residue was purified by Silica-gel column chromatography using $CHCl_3$/Hexane (3/2) as eluent. The title compound was obtained as colorless oil (40 mg, 63% yield).

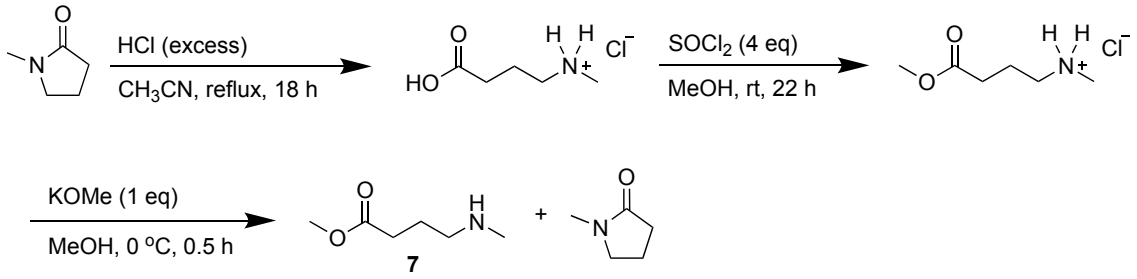
^{1}H NMR (600 MHz, CD_2Cl_2, rt): δ/ppm: 2.02 (quintet, J = 7.3 Hz, 2H, -$MeNCH_2CH_2CH_2CO_2$-), 2.62

(t, J = 7.1 Hz, 2H, -MeNCH$_2$CH$_2$CH_2CO$_2$-), 2.98 (s, 3H, NMe), 3.46 (br t, J = 7.2 Hz, 2H, -MeNCH_2CH$_2$CH$_2$CO$_2$-), 6.75 (br, s, 2H, Ar), 7.00 (d, J = 8.8 Hz, 2H, Ar), 7.06-7.11 (m, 3H, Ar), 7.19 (t, J = 7.8 Hz, 2H, Ar), 7.24-7.28 (m, 2H, Ar), 7.30-7.37 (m, 8H, Ar).

^{13}C{^{1}H} NMR (150 MHz, CD_2Cl_2, rt), δ/ppm: 22.4 (s, -OCOCH$_2$CH$_2$CH$_2$NMe-), 31.8 (s, -OCOCH$_2$$CH_2CH_2$NMe-), 38.6 (s, -OCOCH$_2CH_2CH_2NMe$-), 51.9 (s, -OCOCH$_2CH_2$$CH_2$NMe-), 113.1 (s, Ar), 117.4 (br s, Ar), 122.9 (s, Ar), 125.5 (br s, Ar), 127.3 (br s, Ar), 127.6 (s, Ar), 129.1 (s, Ar), 129.7 (s, Ar), 131.3 (s, Ar), 132.6 (s, Ar), 133.4 (s, Ar), 136.1 (s, Ar), 136.6 (br s, Ar), 140.6 (br s, Ar), 150.0 (br s, Ar), 150.3 (s, Ar), 171.9 (s, Ar).

HRMS (ESI positive, MeOH, m/z) calcd for [$C_{29}H_{27}NO_2S_2$ + H]$^+$: 486.1556, observed 486.1540

Synthesis of methyl 4-(methylamino)butanoate (**7**)[8]



NMP (9.9 g mg, 99 mmol, 1 eq) was mixed with conc. HCl (20 mL), and was refluxed for 18 hours. After cooling the mixture, CH_3CN (30 mL) was added to give colorless crystals, which was collected by filtration. 3-carboxypropylmethylammonium chloride was obtained as colorless hydroscopic crystals (11.4 g, 73%). To the solution of ammonium salt (5.1 g, 30 mmol) in MeOH (100 mL), $SOCl_2$ (8.7 mL, 0.12 mol, 4 eq) was added dropwise at 0 °C, and resulting mixture was further stirred for 22 hours at ambient temperature. After removal of volatiles under reduced pressure, the residue was washed with Et_2O (20 mL), dried at 50 °C under reduced pressure. The methyl ester of ammonium salt was obtained as colorless hydroscopic crystals (5.1 g, 93%). To the solution of this crystal (0.30 g, 1.8 mmol) in MeOH (2 mL), KOMe (0.13 g, 1.8 mmol, 1 eq) was added at 0 °C and the mixture was stirred for 0.5 hours. The solution was concentrated at less than 20 °C under reduced pressure. The residue was extracted with Et_2O (4 mL x 3), and the combined Et_2O solution was concentrated to give colorless oil (0.15 g), which is identified as mixture of **7** and NMP.

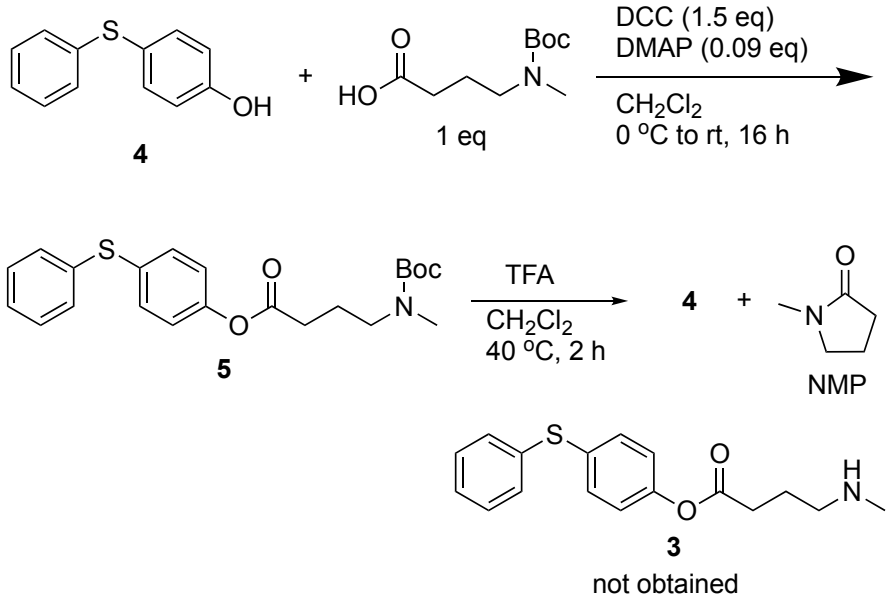
NMR signals for **7**:

^{1}H NMR (600 MHz, $CDCl_3$, rt): δ/ppm: 1.80 (quintet, J = 7.4 Hz, 2H, MeO$_2$CCH$_2$CH_2CH$_2$NHMe), 2.35-2.40 (m, 5H, MeO$_2$CCH$_2$CH$_2$CH$_2$NHMe + MeO$_2$CCH_2CH$_2$CH$_2$NHMe), 2.56 (t, J = 7.4 Hz, 2H, MeO$_2$CCH$_2$CH$_2$CH_2NHMe), 3.66 (s, 3H, MeO$_2$CCH$_2$CH$_2$CH$_2$NHMe).

^{13}C{^{1}H} NMR (150 MHz, CD_2Cl_2, rt), δ/ppm: 25.4 (s, MeO$_2$CCH$_2$CH$_2$CH$_2$NHMe), 32.4 (s,

$MeO_2CCH_2CH_2CH_2NHMe$), 35.9 (s, $MeO_2CCH_2CH_2CH_2NH\mathit{Me}$), 51.8 (s, $\mathit{Me}O_2CCH_2CH_2CH_2NHMe$), 52.0 (s, $MeO_2\mathit{C}CH_2CH_2CH_2NHMe$), 175.4 (s, $MeO_2CCH_2CH_2CH_2NH\mathit{Me}$).

12. Attempt for the synthesis of ester 3

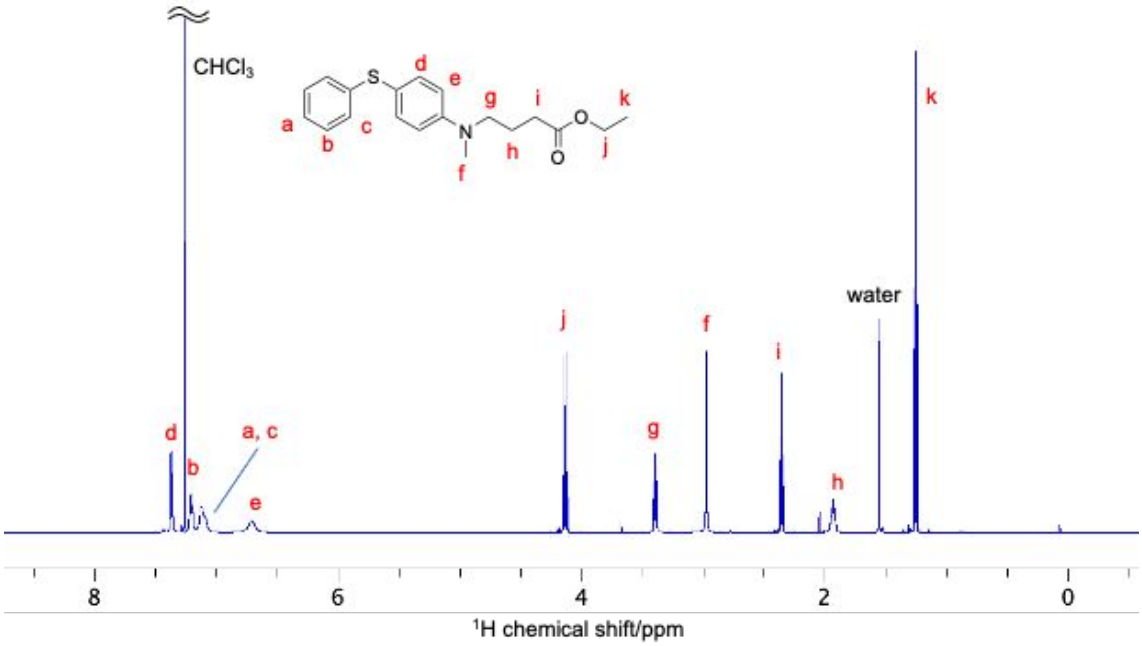


Scheme S1. Attempt for the synthesis of ester **3**

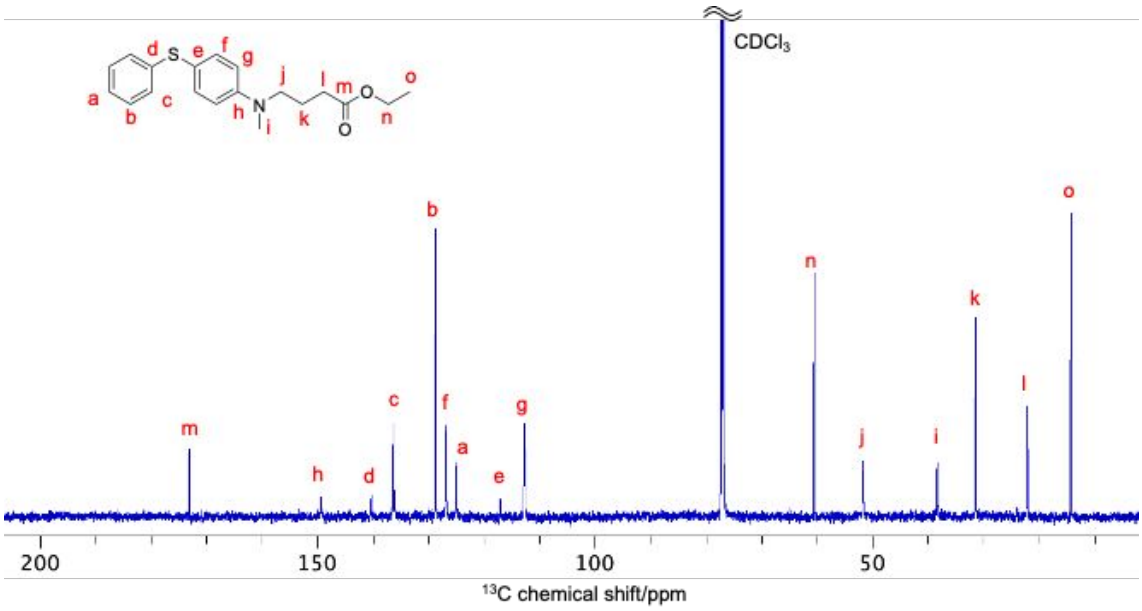
13. Solution ^{1}H and ^{13}C NMR of model compounds

Ethyl 4-(methyl(4-(phenylthio)phenyl)amino)butanoate

^{1}H NMR (600 MHz, $CDCl_3$, rt)

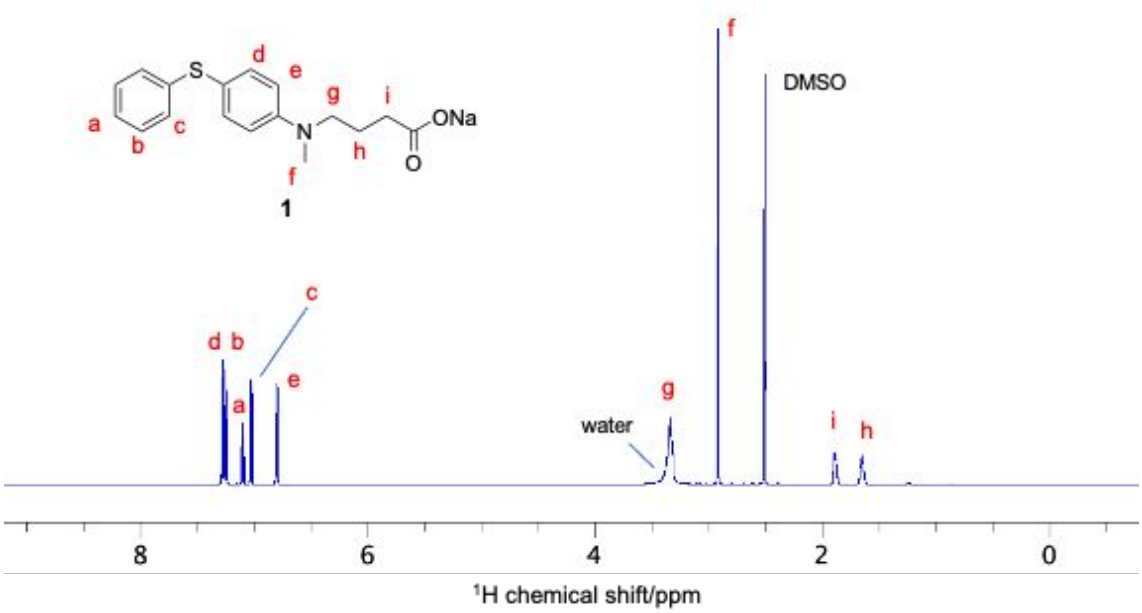


$^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$, rt)

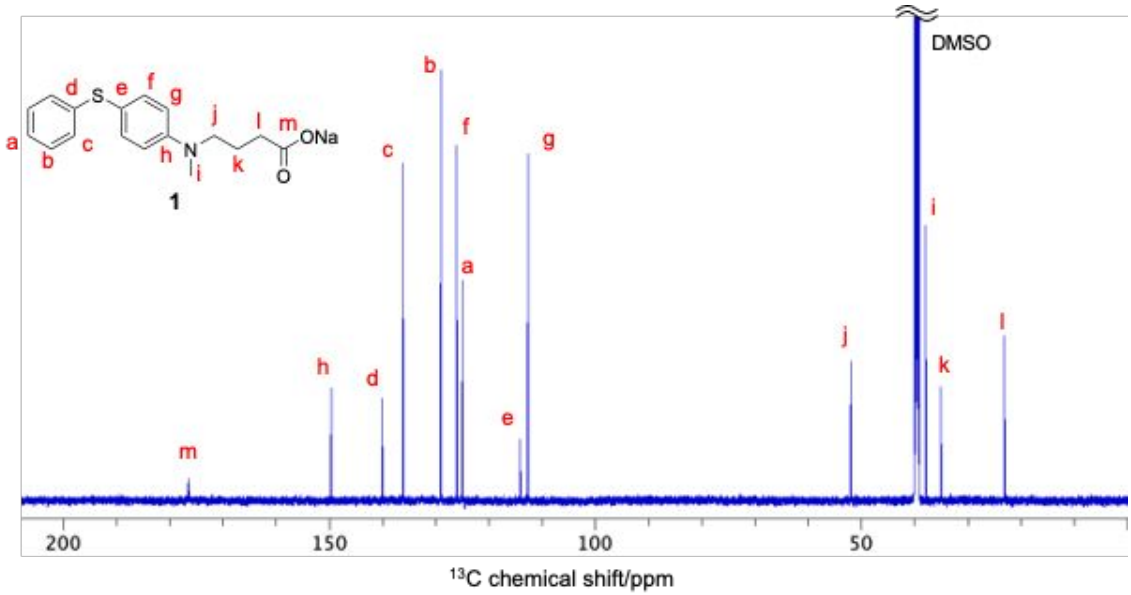


Sodium 4-(methyl(4-(phenylthio)phenyl)amino)butanoate (**1**)

^{1}H NMR (600 MHz, DMSO-d_6, rt)

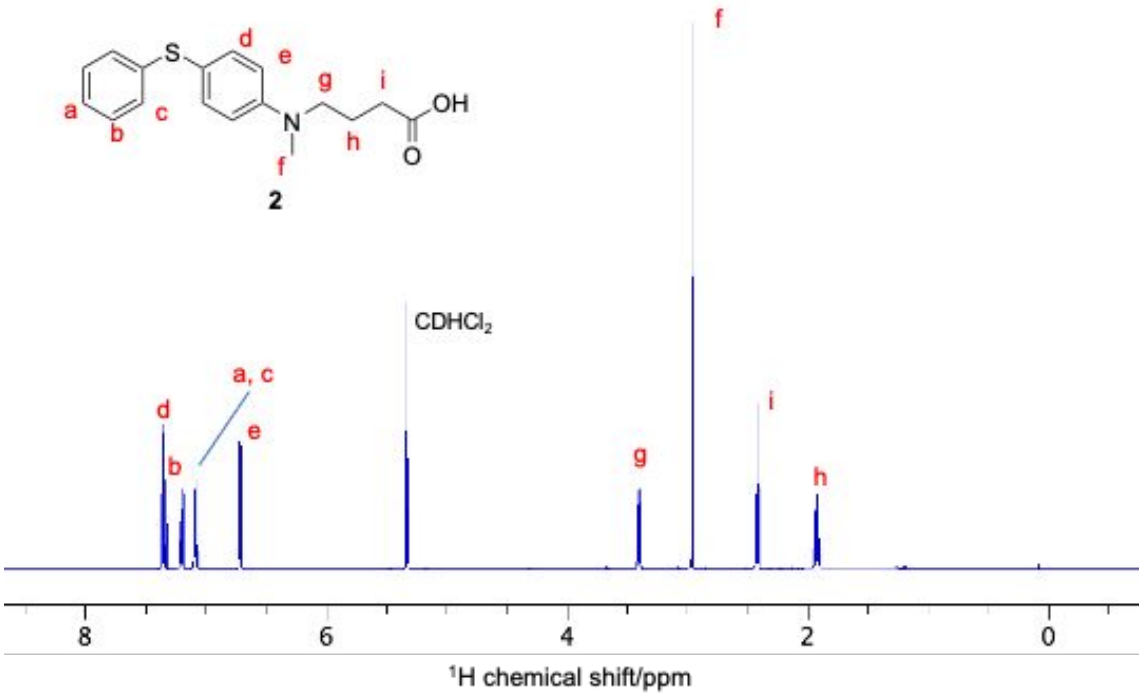


^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$, rt)

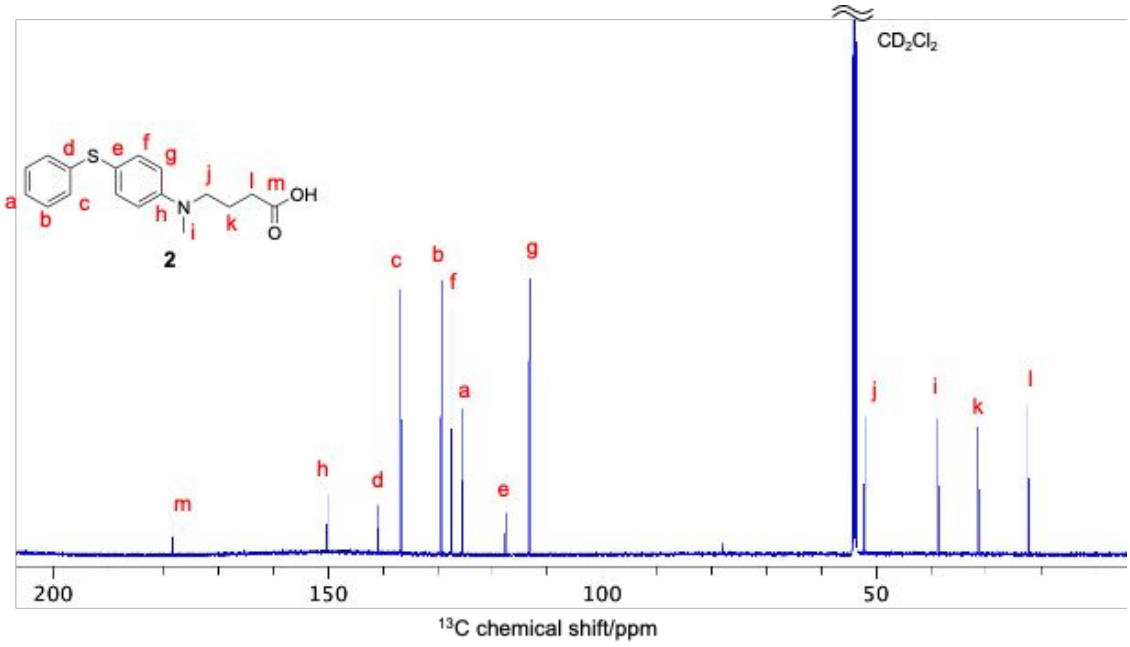


4-(methyl(4-(phenylthio)phenyl)amino)butanoic acid (**2**)

^{1}H NMR (600 MHz, CD_2Cl_2, rt)

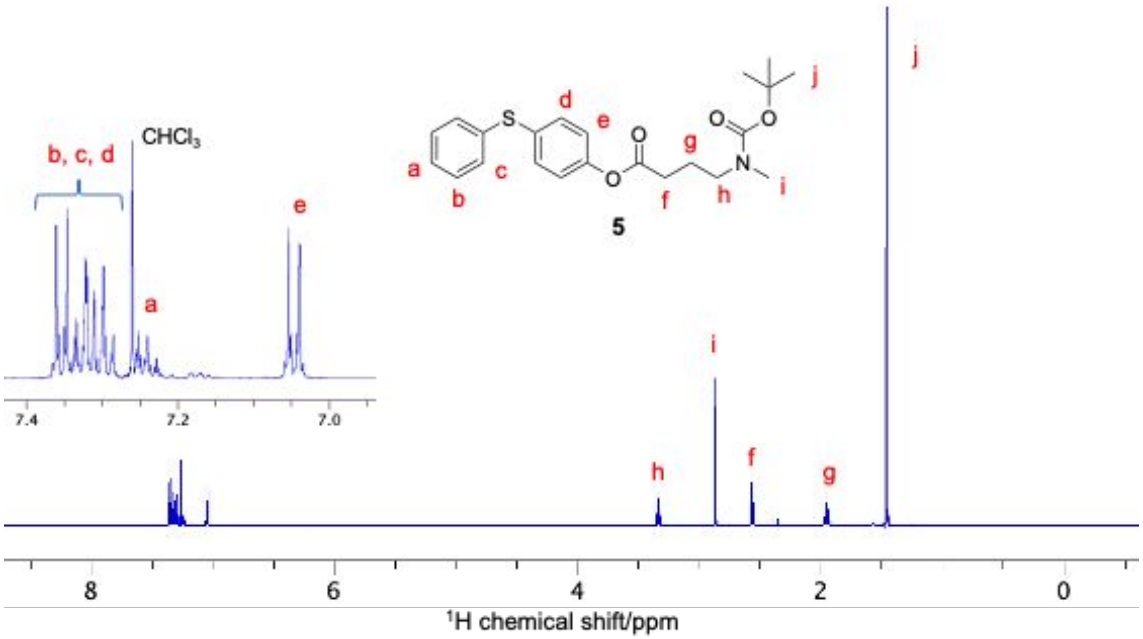


^{13}C{^{1}H} NMR (150 MHz, CD_2Cl_2, rt)

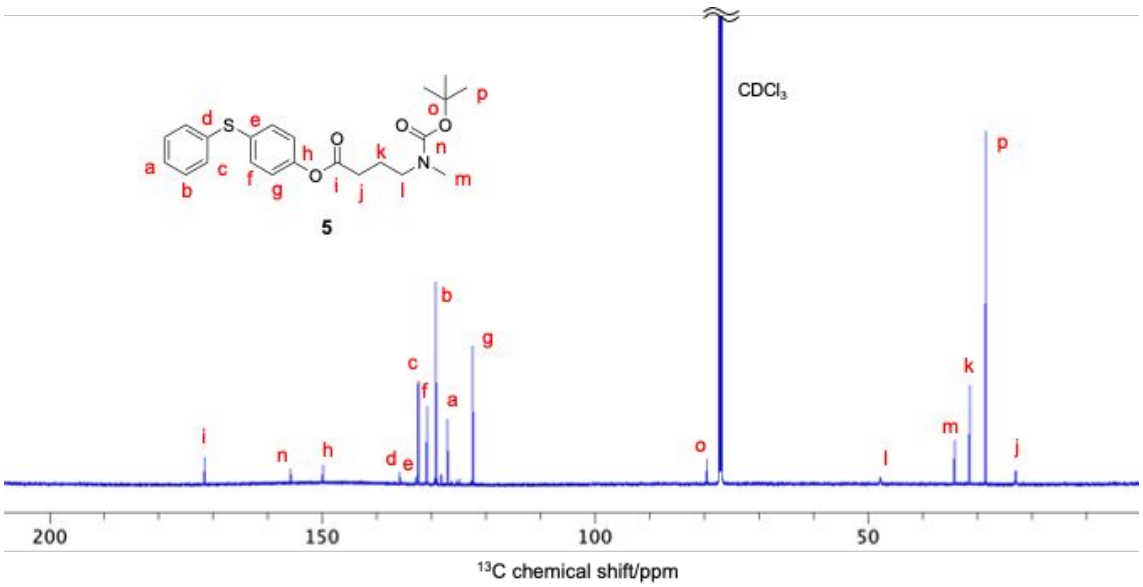


N-Boc-4'-(phenylthio)phenyl 4-methylaminobutanoate (**5**)

^{1}H NMR (600 MHz, CD_2Cl_2, rt)

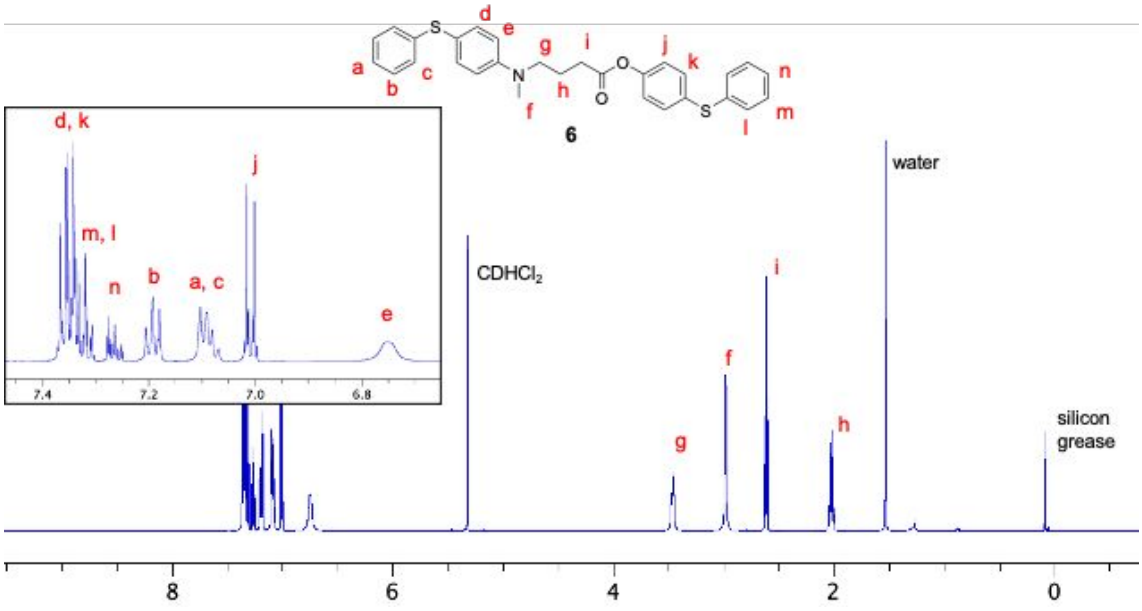


^{13}C{^{1}H} NMR (150 MHz, CD_2Cl_2, rt)

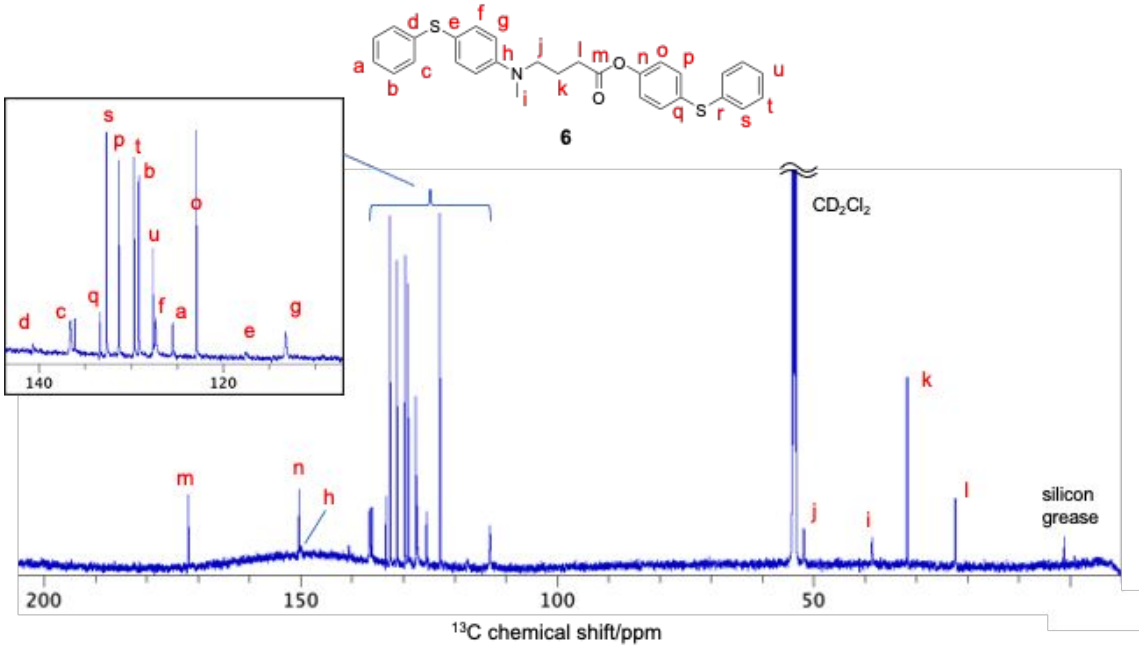


4-(phenylthio)phenyl 4-(methyl(4-(phenylthio)phenyl)amino)butanoate (**6**)

^{1}H NMR (600 MHz, CD_2Cl_2, rt)



^{13}C{^{1}H} NMR (150 MHz, CD_2Cl_2, rt)



14. References

1. Le, D.; Ziarelli, F.; Phan, T. N. T.; Mollica, G.; Thureau, P.; Aussenac, F.; Ouari, O.; Gigmes, D.; Tordo, P.; Viel, S. *Macromol. Rapid Commum.,* **2015**, 36, 1416-1421.
2. Bertani, P.; Raya, J.; Bechinger, B. *Solid State Nucl. Mag.,* **2014**, 61-62, 15-18.
3. Rossini, A. J.; Zagdoun, A.; Lelli, M.; Gajan, D.; Rascón, F.; Rosay, M.; Maas, W. E.; Copéret, C.; Lesage, A.; Emsley, L. *Chem. Sci*., **2012**, 3, 108−115.
4. Li, J.-H.; Zhang, X.-G.; Fang, X.-L.; Tang, R.-Y. *Synthesis* **2011**, *7*, 1099-1105.
5. Egloff, C.; Jacques, S. A.; Nothisen, M.; Weltin, D.; Calligaro, C.; Mosser, M.; Remy, J. S.; Wagner, A. *Chem. Commun.* **2014,** *50*, 10049-10051.
6. Taniguchi, N. *J. Org. Chem.* **2007,** *72*, 1241-1245.
7. DeWit, M. A.; Gillies, E. R., *Org. Biomol. Chem.* **2011,** *9*, 1846-1854.
8. Kane, B. E.; Grant, M. K. O.; El-Fakahany, E. E.; Ferguson, D. M. *Bioorg. Med.Chem.* **2008,** *16*, 1376-1392.