Supplementary Information (SI) for Green Chemistry.

Establishing Parameters for Resonant Acoustic Mixing (RAM) Chemistry using Buchwald-Hartwig Amination as a model

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S1. Experimental section

S1.1 Materials and Methods

All reagents and solvents were obtained from commercial sources and were used without further purification. The catalysts XPhos PdG1 was obtained from Signa Aldrich, as were bromobenzene, 2-, 3- and 4-bromobenzonitrile, 2-, 3- and 4-bromotoluene, 4-bromoanisole, 1-bromo-4-nitrobenzene, 1-bromo-4-fluorobenzene, methyl 4-bromo-2-methoxybenzoate, 2-bromopyridine, 1- and 2-bromonaphthalene, *N*-methylaniline, 4-(methylamino)benzonitrile, *N*-methyl-p-toluidine, 3,5-dimethoxyaniline, and morpholine. 9-bromoanthracene was obtained from Apollo Scientific, and 1-bromopyrene from TCI Chemicals. Diphenylamine and NaO*t*Bu were obtained from Thermo Fisher Scientific. Solid starting materials that were visibly chunky were briefly ground using a mortar and pestle before use.

S1.2 Solution nuclear magnetic resonance (NMR) spectroscopy

^{1}H and ^{13}C NMR spectra were recorded on a Bruker 400 MHz NMR spectrometer. Chemical shifts are reported relative to $CDCl_3$ (δ = 7.26 ppm for ^{1}H NMR and δ = 77.16 ppm for ^{13}C NMR) or d_6-DMSO (δ = 2.50 ppm for ^{1}H NMR and δ = 39.52 ppm for ^{13}C NMR) and data is presented as chemical shifts, and integration.

S1.3 High resolution mass spectrometry (HR-MS)

The molecular weight of the purified products was obtained by high-resolution mass spectrometry using a Waters SYNAPT G2-S.

S1.5 Single crystal X-ray diffraction (scXRD)

Single crystal X-ray diffraction (scXRD) data was measured on an Agilent SuperNova diffractometer equipped with an Atlas detector and an Oxford Cryostream cooling system, using mirror-monochromated CuK_α (λ = 1.54184 Å) or MoK_α (λ = 0.71073 Å) radiation from a microfocus source. Measurements were carried out at 200 K. Data was collected in a series of ω-scans. The data collection was driven, processed and an absorption correction was applied using CrysAlisPro.[64] Single crystals were coated with a thin layer of Paratone oil before mounting on a diffractometer, and structure solution was carried out using the SHELXTL package. The parameters were refined for all data by full-matrix-least-squares refinement of F^2 using SHELXL. All the non-hydrogen atoms were refined with anisotropic thermal parameters, and the coordinates of all carbon-bonded hydrogen atoms were included in the model using a riding model.[65] The hydrogen atom H1 connected to the nitrogen atom N1 in the structure of **1v** was located in the residual map of electron density.

Crystallographic data in CIF format for all herein determined crystal structures can be accessed using the joint CCDC/FIZ Karlsruhe online deposition service, under the deposition numbers 2373258 and 2373259.

S1.6 Differential scanning calorimetry (DSC)

Differential scanning calorimetry (DSC) measurements were carried out on a PerkinElmer DSC 7 instrument using 60 µL stainless-steel pressure-resistant pans equipped with covers and O-rings (product code 03190218). The pans were sealed with a quick-press tool (product code 09908467). All DSC experiments were performed between 20 °C and either 150 °C or 200 °C at heating rates of either 1, 2 or 20 °C min^{-1}. The amounts of material placed in the DSC pans were determined as accurately as possible, although this was challenging due to the very small quantities of material that had to be added directly into the pan. In a typical experiment, a reaction mixture was prepared in the DSC pan containing diphenylamine (1 equiv, ca. 5.2 mg), 1-bromopyrene (1 equiv, ca. 8.7 mg), NaO*t*Bu (2 equiv, ca. 6 mg), XPhos Pd G1 (3 mol %, ca. 0.7 mg), and an amount of THF as close as possible to achieve an η-value of 0.25 µL/mg (typically resulting in a value between 0.18 and 0.23 µL/mg), was analyzed to determine the total heat release (Q). The target amounts were higher in one of the DSC experiments (the test 2 for heating rate of 1 °C/min), to benchmark the robustness of the experiment. A non-reactive mixture that was as similar as possible was also prepared without the catalyst and analyzed using 20°C/min to approximate the heat capacity (C_p) of the reactive system. A sapphire disk (sapphire calibrant, Ø 0.187 in × 0.034 in thick, (product code 915079.903, TA Instruments, 61.70 mg) was used as a reference standard for C_p calibration. After completion of the DSC runs, the pans were punctured and the reaction mixtures were immediately analyzed by ^{1}H NMR spectroscopy in $CDCl_3$ to determine the conversion. In case of the C_p measurements, the NMR analysis confirmed no reaction of 1-bromopyrene.

S1.7 Resonant Acoustic Mixing (RAM)

Experiments were carried out in a LabRAM II (Resodyn) instrument using either 2.5 mL polypropylene vials from Sigma-Aldrich (product code 27425) and, for the purpose of reaction and temperature monitoring in real time, in 5 mL and 9 mL borosilicate glass vials from Fisherbrand (product codes 11523532 and 11543532, respectively). Although no incidents were encountered in this work, it should be kept in mind that glass vials could represent a hazard in case of shattering. With that in mind, it should be noted that rubber O-rings were placed below each of the vials in order to avoid sliding and mechanical impact on the vials during RAM operation, and additional safety is provided by the sample holder which partially also acts as a secondary container in case of spillage. The scale-up experiment was done using a 100 mL glass jar from VWR (product code 215-1514) (Figure S1a), made from borosilicate glass autoclavable to 140 °C to minimize any risks of shattering. The scale-up reaction was operated safely within the safety enclosure of the LabRAM II instrument. Nevertheless, working with glass equipment should be done with outmost care. A RAM sample holder was 3D printed using a Raise3D pro2 printer with a 0.8 mm brass nozzle with PolyMaker PolyTerra© PLA filament. The 3D models were designed using the TinkerCAD software package and sliced using ideaMaker (Figure S1b). In order to avoid sample holder slippage during RAM operation, thick rubber sheets were placed below and on top of the entire assembly, in that way fastening it in the instrument.

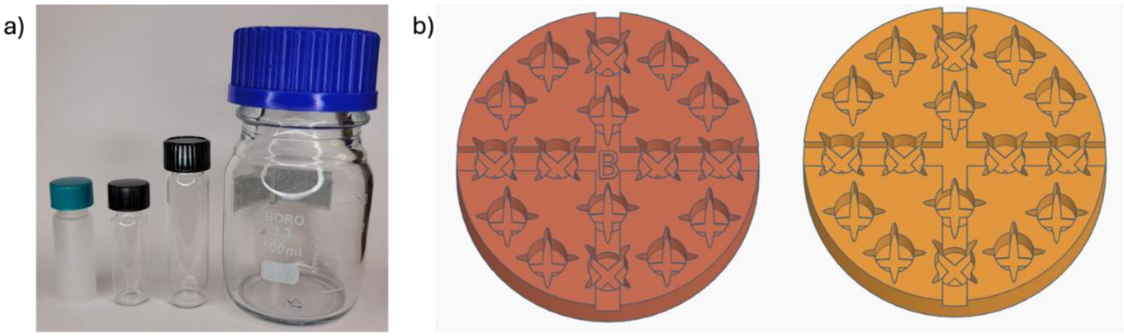


Figure S1. a) Plastic and borosilicate glass vessels used for Buchwald-Hartwig coupling experiments by RAM, in order: 2.5 mL polypropylene vial, 5 mL borosilicate glass vial, 9 mL borosilicate glass vial and 100 mL borosilicate glass vessel; b) in-house developed sample holder design for use on the LabRAM II instrument platform.

S1.8 Real-time Raman spectroscopy and temperature measurement

Real-time Raman monitoring was done using a TR-Coherent probe equipped with an adjustable 1-300 mW 785 nm coherent clean-line laser. To achieve an optimal signal-to-noise ratio, spectra were captured with an integration time of 250 milliseconds and underwent 10 rounds of accumulation. Prior to analysis, all spectra were corrected for darkness and intensity using the OSX software. In a typical experiment, a glass vial with 5 mL capacity was filled with starting materials at 4.5 mmol scale ($\varphi \sim 80$ %) placed in an in-house designed sample holder containing a beam slit. The Raman probe was positioned ca. 30 mm from the center of the vial, and RAM operation was carried out at 60, 80, or 100 g ($g \approx 9.81$ m^2·s^{-1}).

Analysis of real-time data was carried out using MATLAB data treatment functions including background subtraction (msbackadj), and normalization of the area under the curve ($Normalized\ intensity = \frac{Intensity}{\int Intensity}$). Following normalization, selected characteristic signals of the product and the reagent where integrated, normalized on the 0-1 scale, and plotted against time. The Low-frequency/terahertz(THz)-Raman data was analyzed via non-negative linear least-squares (NNLS) fitting, with *in situ* measured spectra fitted as a sum of the normalised component spectra using a non-negative linear least-squares algorithm "lsqnonneg" in MATLAB).[66]

Real-time temperature monitoring was done using a forward-looking infrared thermal camera T400 (FLIR, Teledyne). In a typical experiment, a 5 mL glass vial was placed in an in-house designed sample holder containing a beam slit. The thermal camera was then placed ca. 1 meter from the vial, to minimize any vibration-related effects.

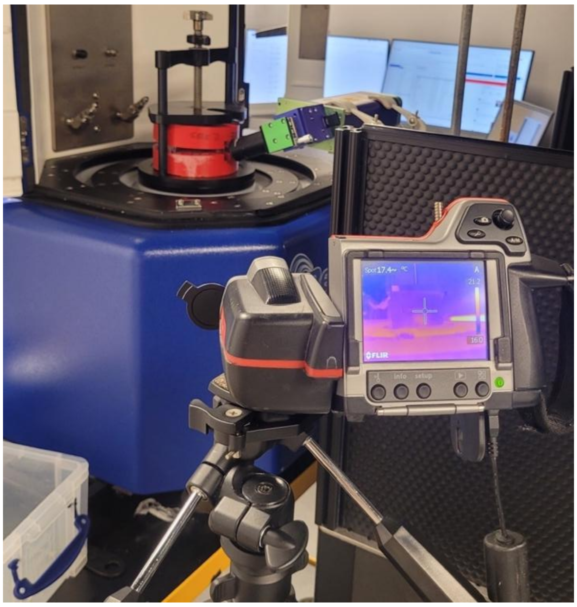


Figure S2. The experimental setup for tandem thermal and Raman spectroscopy monitoring of RAM reactions.

S1.9 General procedure for the RAM synthesis of compounds 1a-1t

For general protocols related to RAM operation, see Section S1.6. In a typical experiment, XPhos Pd G1 (3 mol %), sodium *tert*-butoxide (2 equivalents), the amine (1 equivalent) and the aryl halide (1 equivalent) were added to a 2.5 mL volume polypropylene vial or a 5 mL volume borosilicate glass vial (for purpose of real-time monitoring), followed by the liquid additive (THF). Prior to use, glass vials were washed with a dilute aqueous NaOH solution, rinsed with water and with ethyl acetate and dried in an oven at 130 °C. The reaction mixture was then mixed for a period between 10 minutes to 2 hours at an acceleration of 60, 80 or 100 *g*. All reactions are performed with the LabRAM II safety enclosure closed. The conversion to the Buchwald-Hartwig coupling product was evaluated by solution ^{1}H NMR analysis after quenching the strong butoxide base. Quenching was done by either adding 1 mL of d_6-DMSO with 5 % v/v water (**1c**-**1t**) or, for compounds that are poorly soluble in DMSO (**1a**, **1b**), by adding 1 mL of water, shaking the flask, and then adding $CDCl_3$. Both methods give similar results, as verified by comparing the conversion to **1e** and **1m** using both methods. Upon establishing the reaction conversions, the product isolation procedure was done in separate experiments. Compounds **1a**, **1c**-**1e**, **1g**-**1s**, were mixed for 30 minutes at 100 *g*, and compounds **1b**, **1f** and **1t** for 1.5 hour at 100 *g*. In all cases, except **1a** and **1b**, isolation was achieved by adding CH_2Cl_2 to the reaction mixture, washing with three portions of saturated aqueous NaCl solution, drying over anhydrous $MgSO_4$, followed by rotary evaporation. For **1a** and **1b**, isolation was achieved by adding three portions of saturated aqueous NaCl solution and filtration. Any remaining starting materials were then removed by flash chromatography: the sample was dissolved in CH_2Cl_2, silica was added, and the mixture dried in a rotary evaporator. The solid mixture was then placed in a solid load cartridge and purified by flash chromatography using a gradient from 100 % hexanes to 100 % CH_2Cl_2. For **1a** and **1b**, samples were additionally recrystallized from hexanes.

Table S1. Reaction scale for the reactions conducted in a 2.5 mL polypropylene vial at different φ values (see Figure 2, Table 1).

compound	**approximate φ value**						
	10-15 %	22-27%	30-35 %	37-42%	52-57 %	68-73 %	78-83 %
1a	0.25 mmol	/	0.75 mmol	/	1.25 mmol	1.50 mmol	2.25 mmol
1b	0.25 mmol	/	0.75 mmol	/	1.25 mmol	1.50 mmol	2.00 mmol
1c	0.25 mmol	/	0.75 mmol	/	1.25 mmol	1.50 mmol	2.00 mmol
1d	0.25 mmol	0.75 mmol	/	1.25 mmol	1.75 mmol	2.00 mmol	2.50 mmol
1e	0.25 mmol	/	0.75 mmol	/	1.25 mmol	1.50 mmol	2.00 mmol
1f	0.25 mmol	/	0.75 mmol	/	1.25 mmol	1.50 mmol	2.00 mmol
1g	0.25 mmol	/	/	/	/	/	2.00 mmol
1h	0.25 mmol	/	/	/	/	/	2.00 mmol
1i	0.25 mmol	/	/	/	/	/	2.00 mmol
1j	0.25 mmol	/	/	/	/	/	2.50 mmol
1k	0.25 mmol	/	/	/	/	/	2.50 mmol
1l	0.25 mmol	/	/	/	/	/	2.50 mmol
1m	0.25 mmol	/	/	/	/	/	2.00 mmol
1n	0.25 mmol	/	/	/	/	/	2.50 mmol
1o	0.25 mmol	/	/	/	/	/	2.00 mmol
1p	0.25 mmol	/	/	/	/	/	2.50 mmol
1q	0.25 mmol	/	/	/	/	/	2.50 mmol
1r	0.25 mmol	/	/	/	/	/	2.00 mmol
1s	0.25 mmol	/	/	/	/	/	2.00 mmol
1t	0.25 mmol	/	/	/	/	/	2.00 mmol

Table S2. Reaction scale for reactions conducted in 5 mL glass vials at different φ-values. Values used for *in situ* measurements, thermography and THz-Raman spectroscopy monitoring (see Figures 3-6 in manuscript).

compound	**approximate φ value**	
	10-15 %	78-83 %
1a	0.50 mmol	4.5 mmol
1b	0.50 mmol	4.5 mmol

S10. General procedure for the RAM synthesis of compounds 1u-1x

For general protocols related to RAM operation, see Section S1.6. In a typical procedure, XPhos Pd G1 (5 mol %), sodium *tert*-butoxide (2 or 4 equivalents), 3,5-dimethoxyaniline (1 equivalent) and the aryl bromide (3-bromotoluene or 4-bromobenzonitrile, either 1 or 2 equivalents) were added to a 2.5 mL polypropylene vial, followed by the liquid additive (MeOBz or THF). The reaction mixture was then mixed for a period between 30 min and 2 hours at either 60, 80 or 100 *g*. All reactions are performed with the LabRAM II safety enclosure closed. The conversion to the Buchwald-Hartwig coupling product was established by ^{1}H NMR analysis of a solution obtained by dissolving either the entire crude reaction mixture (for reactions at φ = 10-15 %), or approximately one-half of the sample (for reaction at φ = 30-97 %) in $CDCl_3$.

The RAM reactions for establishing the relative distribution of 1:1 and 2:1 stoichiometric products were conducted with MeOBz as liquid additive (see Figure 7 in the manuscript). For the isolation of compounds **1u**-**1w**, the separation of MeOBz from the products was challenging, so the reactions were also conducted using THF as the liquid additive. In addition, the synthesis of **1u** and **1v** was conducted at 60 *g* for 1 hour, to prevent the potential formation of **1w** and **1x** as a result of longer reaction times or higher accelerations. In all cases, the conversions for the reactions conducted using THF as the liquid additive, as established by ^{1}H NMR analysis of the crude reaction mixture, were similar to those observed with MeOBz as the liquid additive (98 %, 97 %, and 67 % for **1u**, **1v**, and **1w**, respectively). The compounds **1u**-**1w** were isolated by addition of CH_2Cl_2 to the RAM reaction mixture, washing three times with saturated aqueous NaCl solution, after which the organic layer was dried with anhydrous $MgSO_4$, and organic solvent removed using a rotary evaporator. Any remaining starting materials were then removed by dissolving the sample again in CH_2Cl_2, adding silica, and drying with a rotary evaporator. The solid mixture was then placed in a solid loading cartridge and purified by flash chromatography using a gradient from 100 % hexanes to 100 % CH_2Cl_2. In the case of **1x**, an additional purification step was needed to remove MeOBz, involving recrystallization from hexanes.

Table S3. Amount of 3,5-dimethoxyaniline and aryl bromide used with a 2.5 mL polypropylene vial for the synthesis of **1u** and **1v** at different *φ*-values.[a]

compound	**approximate *φ* value**	
	10-15 %	78-83 %
1u	0.25 mmol	2.50 mmol
1v	0.25 mmol	2.00 mmol

a) Reaction conditions: 1 equivalent of 3,5-dimethoxyaniline, 1 equivalent of halogenated compound, 2 equivalents of NaO*t*Bu and 5 mol% of XPhos Pd G1.

Table S4. Amount of 3,5-dimethoxyaniline used for exploring the stoichiometric selectivity of RAM reactions with 3-bromotoluene and 4-bromobenzonitrile at different *φ*-values in a 2.5 mL polypropylene vial (see Figure 8 in the manuscript).[a]

Compound	**approximate *φ* value**			
	12-17%	33-37%	55-60%	78-83%
1u/1w	0.25 mmol	0.75 mmol	1.25 mmol	1.50 mmol
1v/1x	0.25 mmol	0.50 mmol	1.0 mmol	1.25 mmol

a) Reaction conditions: 1 equivalent of 3,5-dimethoxyaniline, 2 equivalents of halogenated compound, 4 equivalents of NaO*t*Bu and 5 mol% of XPhos Pd G1.

S2. Data for optimizing Buchwald-Hartwig coupling by RAM

Reaction conditions: 1 equivalent of 1-bromopyrene (0.25 mmol, 51.8 mg) and diphenylamine (0.25 mmol, 42.3 mg), 2 equivalents of NaO*t*Bu (0.5 mmol, 48.1 mg) and 3 mol% of XPhos Pd G1 (5.5 mg) with THF as liquid additive (Figure S3).

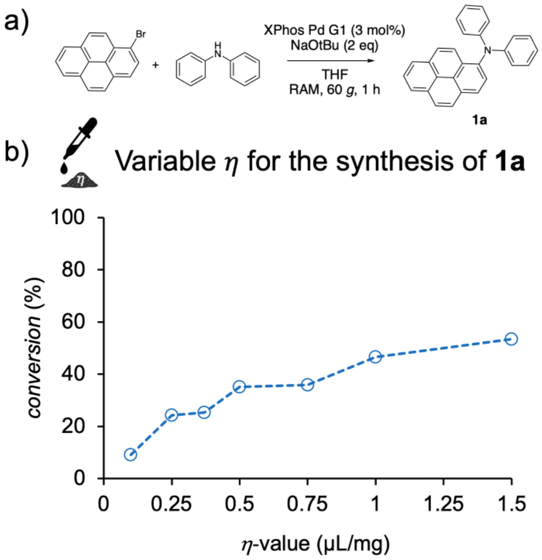


Figure S3. a) Reaction scheme for the reaction between 1-bromopyrene and diphenylamine to form **1a**; b) example results of η-screening in the synthesis of **1a** with THF as liquid additive, after 1 hour of RAM at 60 *g*.

Table S5. Buchwald-Hartwig coupling conversion for the synthesis of **1a** with respect to the η-value, with THF used as liquid additive. The data is presented graphically in Figure S3.

η-value (µL/mg)	0.10	0.25	0.37	0.50	0.75	1.00	1.50
conversion (%)	9	24	25	35	35	47	53

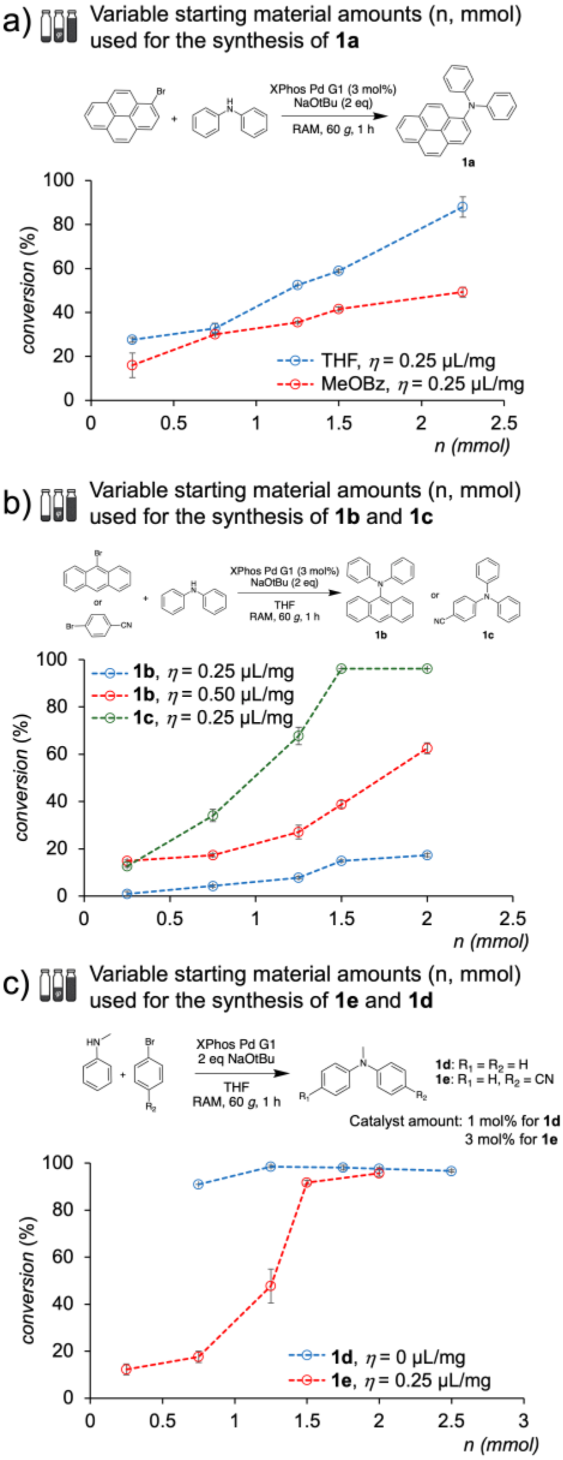


Figure S4. Dependence of the Buchwald-Hartwig amination in RAM on the reagent amount (mmol) for the coupling of: a) 1-bromopyrene (solid) and diphenylamine (solid) to form **1a** in presence of THF or MeOBz (η = 0.25 µL/mg) as the liquid additive; b) diphenylamine and 9-bromoanthracene (solid) or 4-bromobenzonitrile (solid) to form **1b** and **1c**, respectively, at different η-values; c) N-methylaniline (liquid) with bromobenzene (liquid) or 4-bromobenzonitrile (solid) to give products **1d** and **1e**, respectively.

Table S6. Change in ^{1}H NMR conversion for Buchwald-Hartwig coupling in RAM for the synthesis of **1a** with THF or MeOBz as the liquid additive (η = 0.25 µL/mg) after 1 hour of RAM at 60 *g*, with respect to the reagent amount (mmol). This data is represented graphically in Figure S4.

reagent amount (mmol)	0.25	0.75	1.25	1.50	2.25
conversion with THF (%)	28 ± 1	33 ± 2	52 ± 0	59 ± 1	88 ± 5
conversion with MeOBz (%)	10 ± 6	30 ± 0	36 ± 0.5	41 ± 1	51± 2

Table S7. Change in ^{1}H NMR conversion for Buchwald-Hartwig coupling in RAM for the synthesis of **1b** and **1c** with THF as the liquid additive ($\eta = 0.25$ or 0.50 µL/mg) after 1 hour of RAM at 60 *g*, with respect to the reagent amount (mmol). This data is represented graphically in Figure S4.

reagent amount (mmol)	0.25	0.75	1.25	1.50	2.00
conversion of **1b** (%) at $\eta = 0.25$ µL/mg	1 ± 1	4 ± 0.5	8 ± 0.5	15 ± 0	17 ± 1
conversion of **1b** (%) at $\eta = 0.50$ µL/mg	15 ± 0	18 ± 1	27 ± 3	39 ± 2	63 ± 2
conversion of **1c** (%) at $\eta = 0.25$ µL/mg	13 ± 0	34 ± 3	68 ± 4	96 ± 0	96 ± 0

Table S8. Change in ^{1}H NMR conversion for Buchwald-Hartwig coupling in RAM for the synthesis of **1d** and **1e** with THF as the liquid additive ($\eta = 0$ and 0.25 µL/mg) after 1 hour of RAM at 60 *g*, with respect to the filling ratio (φ). This data is represented graphically in Figure S4.

reagent amount (mmol)	0.25	0.75	1.25	1.50	1.75	2.00	2.50
conversion of **1d** (%) at $\eta = 0$ µL/mg	/	91 ± 0	99 ± 0.5	/	98 ± 1	98 ± 0.5	97 ± 0.5
conversion of **1e** (%) at $\eta = 0.25$ µL/mg	15 ± 2	18 ± 2	48 ± 7	91 ± 1	/	97 ± 1	/

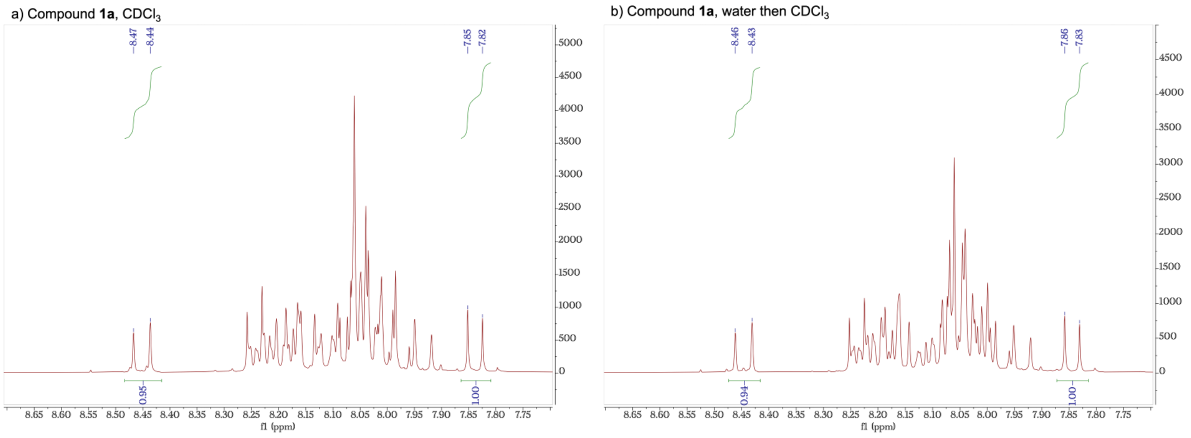


Figure S5. ^{1}H NMR analysis of the crude reaction mixture for the synthesis of compound **1a** (60 g scale, $\varphi \approx 80\%$, MeOBz as liquid additive): comparison of spectra recorded (a) after direct dilution in $CDCl_3$ and (b) after aqueous quench followed by $CDCl_3$ dilution, both indicating a 51% conversion.

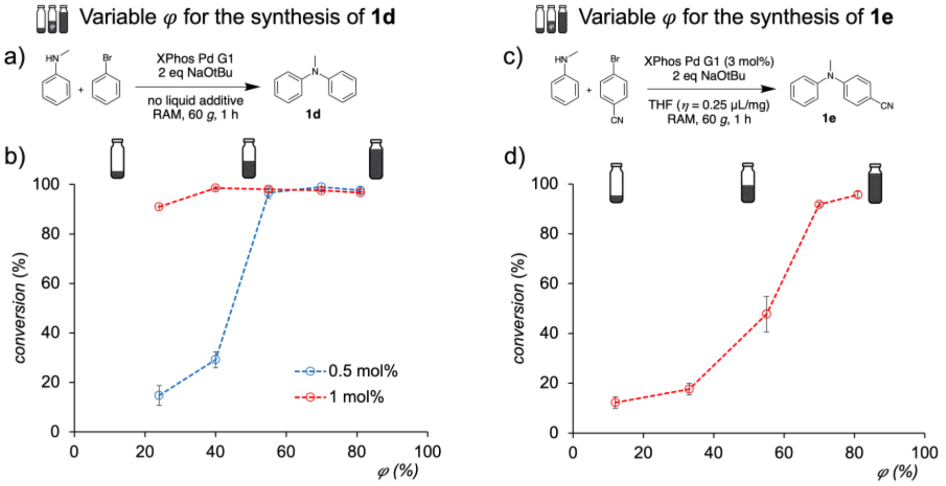


Figure S6. a) Reaction scheme for the coupling of *N*-methylaniline and bromobenzene to form **1d**; b) dependence of the Buchwald-Hartwig amination in RAM to form **1d** on the filling ratio (φ), without any liquid additive, at 0.5 and 1 mol% of catalyst, after 1 hour at 60 *g*. c) Reaction scheme for the coupling of *N*-methylaniline and 4-bromobenzonitrile to form **1e**; b) dependence of the Buchwald-Hartwig amination to form **1e** using RAM on the filling ratio (φ), in the presence of THF ($\eta = 0.25$ µL/mg) and 3 mol% of catalyst, after 1 hour at 60 *g*. Reactions were done in triplicate.

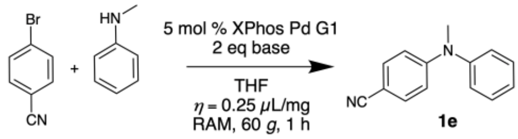
Table S9. Buchwald-Hartwig coupling conversion for the synthesis of **1d** with respect to the φ-value. The data are presented graphically in Figure S5.

approximate φ value (%)		25	40	55	70	80
conversion (%)	0.5 mol% of catalyst	15 ± 4	29 ± 3	97 ± 2	99 ± 0	98 ± 1
	1 mol% of catalyst	91 ± 0	99 ± 0.5	98 ± 1	98 ± 0.5	97 ± 0.5

Table S10. Buchwald-Hartwig coupling conversion for the synthesis of **1e** with respect to the φ-value. The data are presented graphically in Figure S**5**.

approximate φ value (%)	12	33	55	70	80
conversion of **1e** (%) at $\eta = 0.25$ µL/mg	15 ± 2	18 ± 2	48 ± 7	91 ± 1	97 ± 1

Table S11. Comparison of reaction conversions using different bases for the synthesis of **1e**.



base	conversion (%)
NaO*t*Bu	74 ± 4
KO*t*Bu	49 ± 0
LiO*t*Bu	51 ± 1
NaOMe	50 ± 0

Reaction conditions: 4-bromobenzonitrile (0.25 mmol, 45.5 mg) and *N*-methylaniline (0.25 mmol, 27.1 µL), 2 equivalents base (0.5 mmol) and 5 mol% of XPhos Pd G1 (9.2 mg) with THF liquid additive ($\eta = 0.25$ µL/mg).

S3. Comparison between model reactions conducted in a 2.5 mL polypropylene vial and a 5 mL glass vial

Table S12. Comparison of reaction conversions when using a 2.5 mL polypropylene vial and a 5 mL glass vial as the reaction vessel, at approximately the same φ-values.

reactants	**reaction conditions**	**conversion (%)**	
		polypropylene vial	glass vial
diphenylamine & 1-bromopyrene $\eta = 0.25$ µL/mL[a]	φ = 80 %, 60 *g*, 1 hour[b]	90 ± 4	98 ± 0
	φ = 80 %, 80 *g*, 15 min[b]	95 ± 2	92 ± 2
	φ = 80 %, 100 *g*, 10 min[b]	95 ± 1	98 ± 0
diphenylamine & 9-bromoanthracene $\eta = 0.50$ µL/mL[a]	φ = 80 %, 60 *g*, 1 hour[c]	63 ± 2	68 ± 3

a) THF was used as the liquid additive; b) for polypropylene vial: 2.25 mmol of diphenylamine and 1-bromopyrene, NaO*t*Bu (5.0 mmol), and catalyst (3 mol%), for glass vial: 4.5 mmol of diphenylamine and 1-bromopyrene, NaO*t*Bu (9.0 mmol), and catalyst (3 mol%) ; c) for polypropylene vial: 2.0 mmol of diphenylamine and 9-bromoanthracene, NaO*t*Bu (4.0 mmol), and catalyst (3 mol%), for glass vial: 4.5 mmol of diphenylamine and 9-bromoanthracene, NaO*t*Bu (9.0 mmol), and catalyst (3 mol%).

S4. Scale-up of 1a RAM synthesis to 100 mmol

For general protocols related to RAM operation, see Section S1.6. The synthesis of **1a** at 100 mmol scale was conducted by adding XPhos Pd G1 catalyst (3 mol%, 3 mmol, 2.22 g), NaO*t*Bu (2 equivalents, 200 mmol, 19.22 g), diphenylamine (1 equivalent, 100 mmol, 16.92 g) and 1-bromopyrene (1 equivalent, 100 mmol, 28.12 g) to a 100 mL glass jar followed by the liquid additive THF ($\eta = 0.25$ µL/mg, 16.6 mL). The reaction mixture was then mixed for 1 hour at an acceleration of 60 *g*. The LabRAM II safety enclosure was closed during the experiment. Six portions of the sample were analyzed by ^{1}H-NMR in $CDCl_3$, resulting in conversions of 94%, 94%, 94%, 94%, 94%, and 95 %.

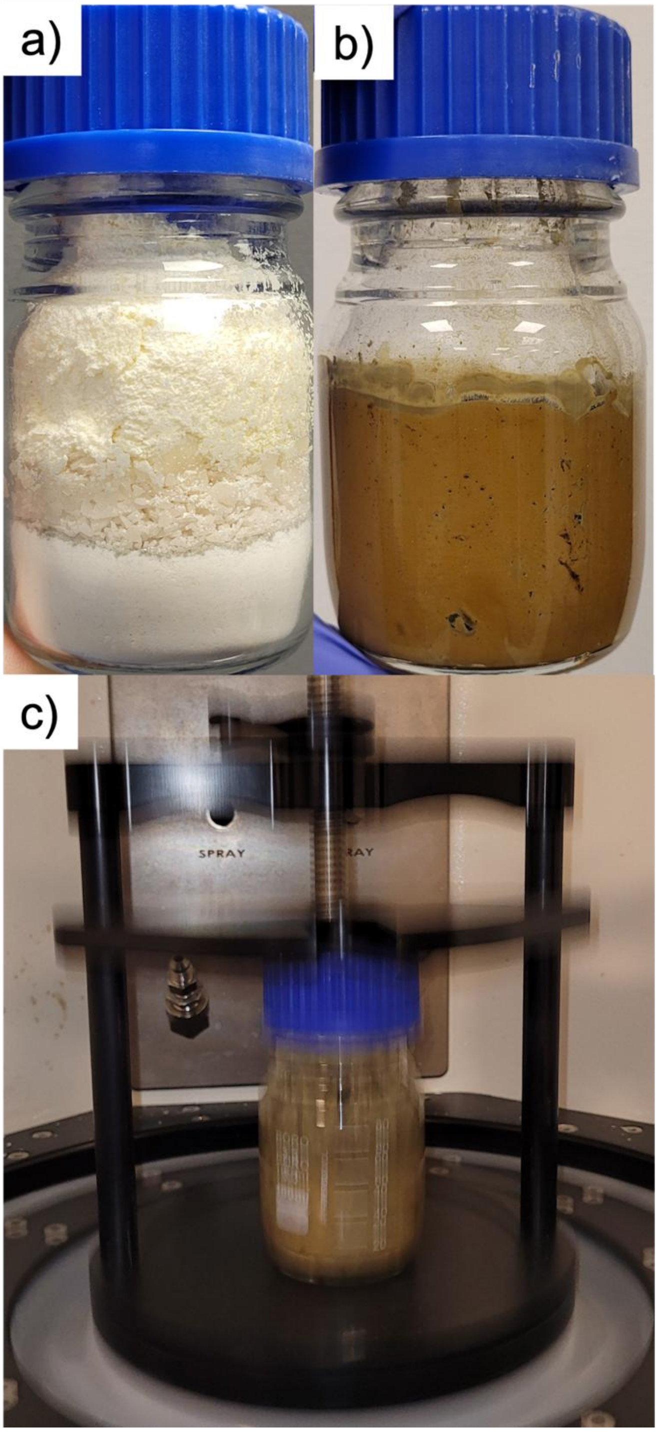


Figure S7. Pictures of the 100 mmol scale experiment for the synthesis of **1a** in a 100 mL glass jar: a) before mixing, b) after 1 h of mixing at 60 *g* and c) during mixing.

S5. Real-time tandem thermal and THz-Raman monitoring for the reaction between diphenylamine and 1-bromopyrene to form 1a

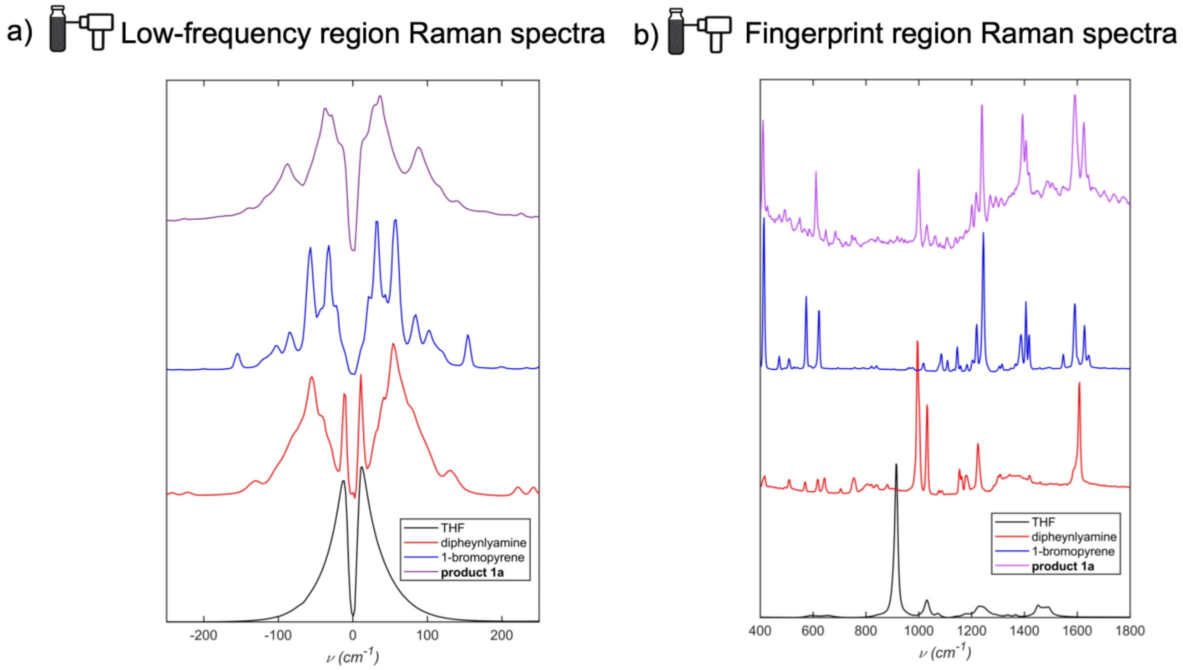


Figure S8. a) Low-frequency and b) fingerprint region Raman spectra of the different reagents and the final product **1a**.

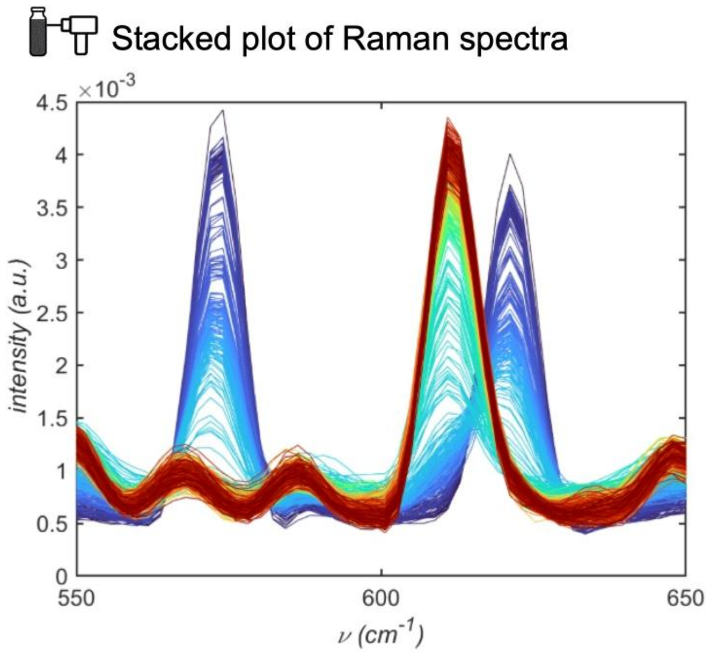


Figure S9. Stacked plot of Raman spectra highlighting the disappearance of 1-bromopyrene bands at 574 and 621 cm^{-1}, with the appearance of product **1a** band at 611 cm^{-1}.

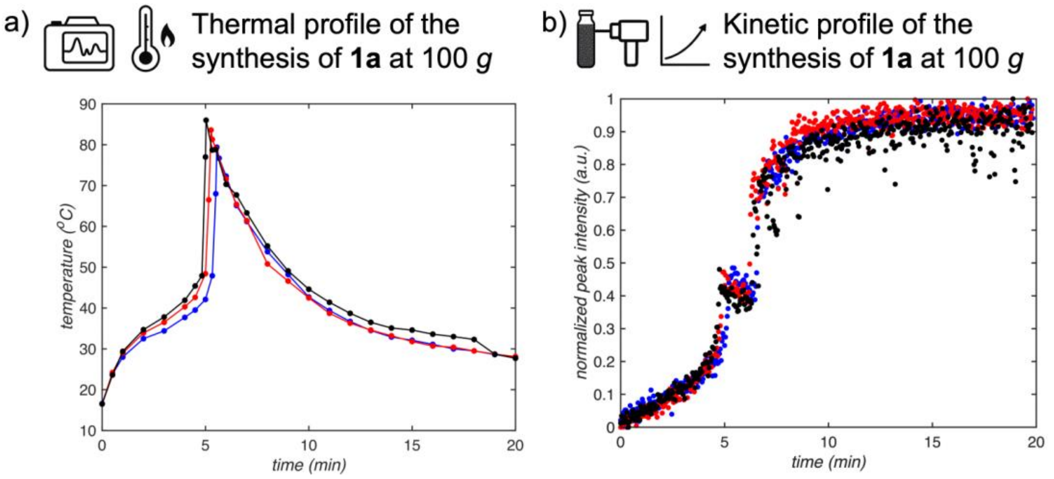


Figure S10. *In situ* real-time monitoring results of experiments run at 100 *g*, showing a) the changes in temperature and b) integrated peak intensity of Raman band at 611 cm^{-1} in triplicate showing reproducibility of the results. The three different colors represent three distinct experiments, and each color represents the same experiments.

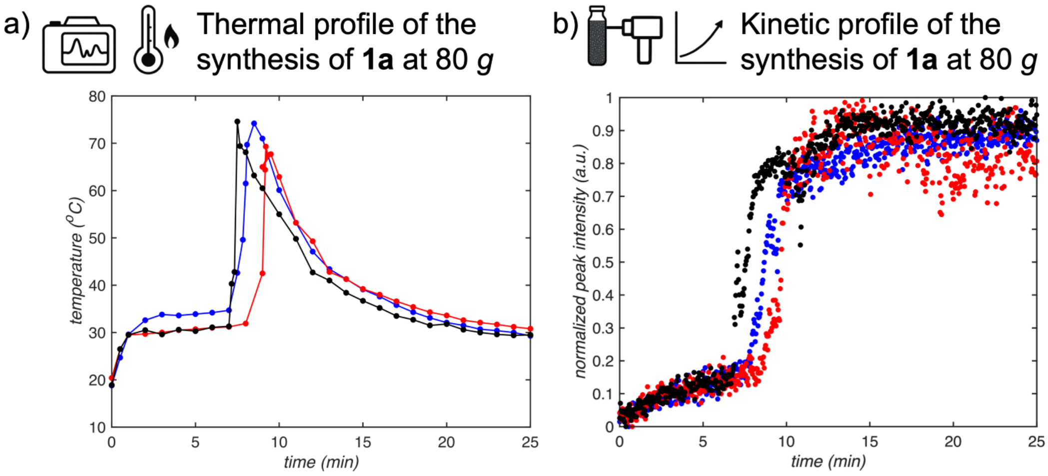


Figure S11. *In situ* real-time monitoring results of experiments run at 80 *g*, showing a) the changes in temperature and b) integrated peak intensity of Raman band at 611 cm^{-1} in triplicate showing reproducibility of the results. The three different colors represent three distinct experiments, and each color represents the same experiments.

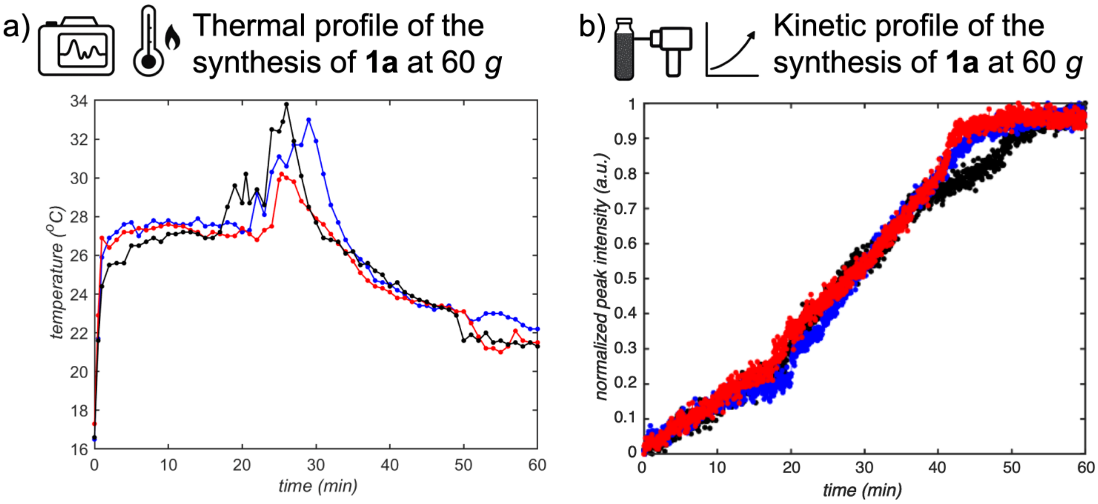


Figure S12. *In situ* real-time monitoring results of experiments run at 60 *g*, showing the changes in temperature (left) and integrated peak intensity of Raman band at 611 cm^{-1} (right) in triplicate showing reproducibility of the results. The three different colors represent three distinct experiments, and each color represents the same experiment.

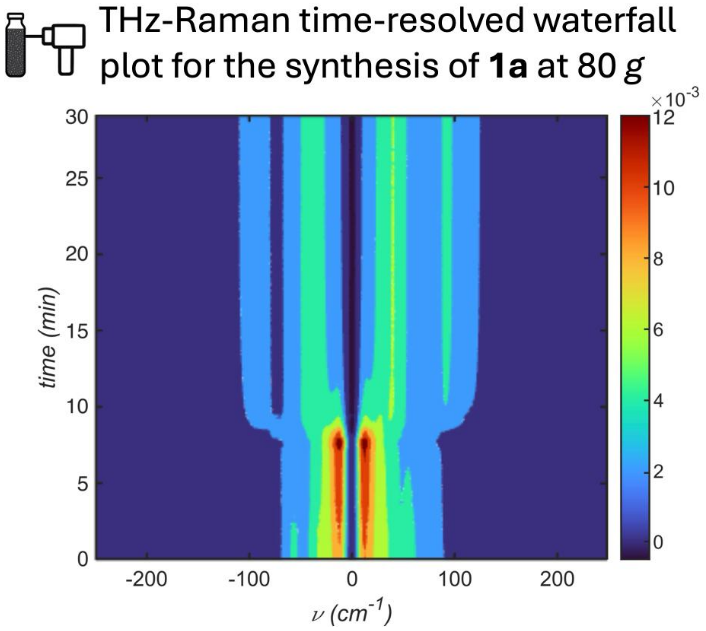


Figure S13. THz-Raman time-resolved waterfall plot for the synthesis of **1a** from 1-bromopyrene and diphenylamine. The reaction was performed at 80 *g*.

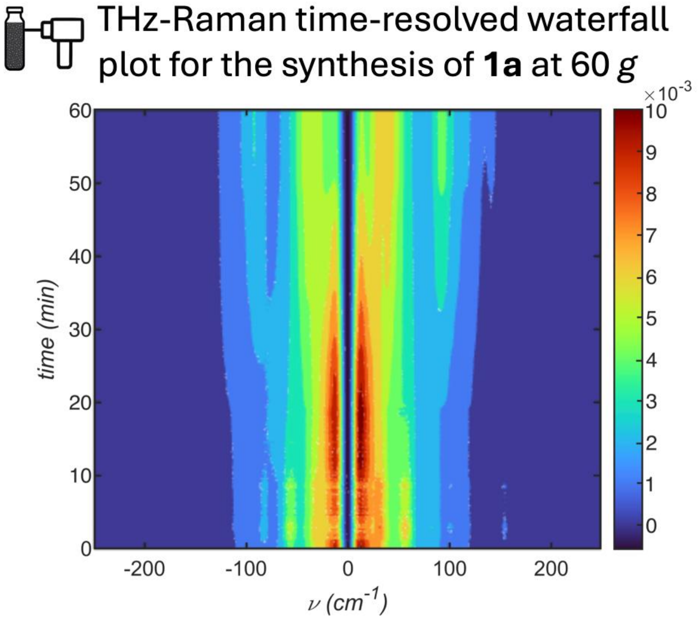


Figure S14. THz-Raman time-resolved waterfall plot for the mechanochemical formation of product **1a** from reactants 1-bromopyrene and diphenylamine. Reaction was performed at 60 *g*.

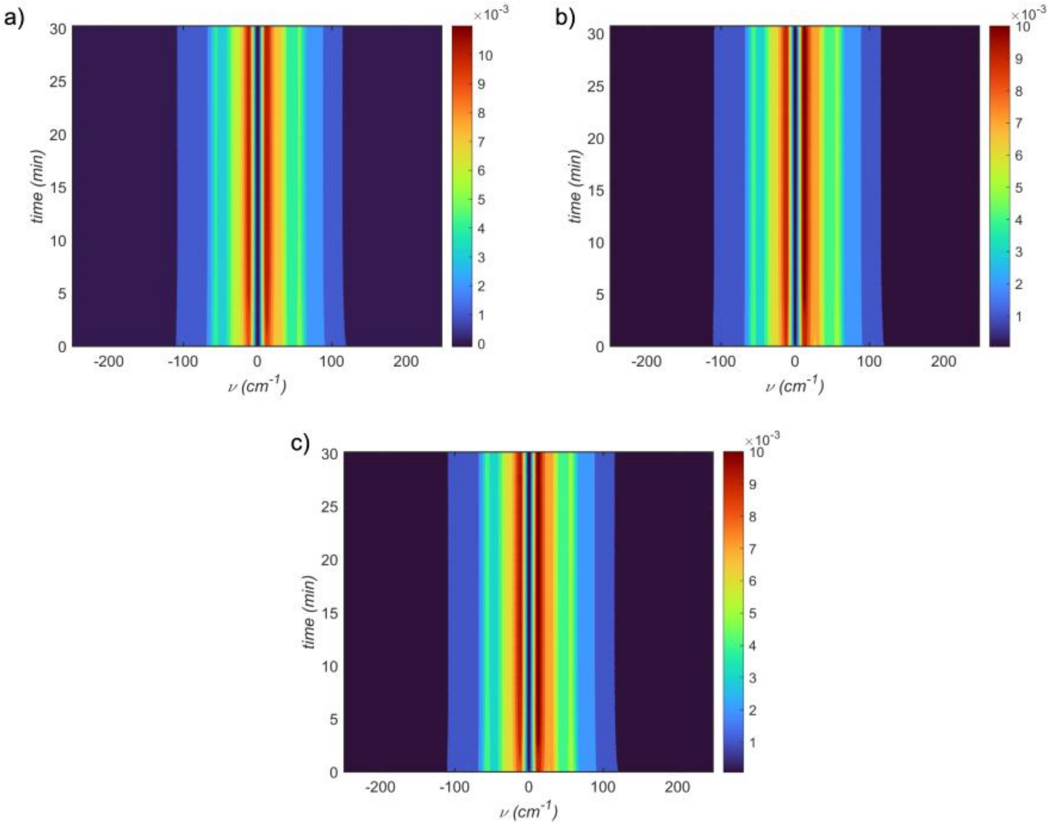


Figure S15. Waterfall plot of *in-situ* THz-Raman following the mixing of diphenylamine, 1-bromopyrene and NaO*t*Bu with THF as the liquid additive (η = 0.25 µL/mg) at 80 *g* repeated 3 times a) trial 1, b) trial 2, c) trial 3. No catalyst was present, no reaction took place and spectroscopic data indicated that the reaction retained crystallinity throughout.

S6. Thermal microscopy images and associated THz-Raman spectra

Thermal microscopy was performed to determine the behavior of mixtures of diphenylamine, 1-bromopyrene and NaO*t*Bu, with and without a XPhos Pd G1 upon exposure to mild temperature increases. The pre-made reaction mixtures were heated at a rate of 10 °C/min, from 20 °C to 70 °C, using a Linkam THMS600 hot-stage equipped with a Leica DM2500 LED microscope. Immediate analysis by ^{1}H NMR analysis found the reaction conversion to be 0 % and 7 %, in the absence and in the presence of the catalyst, respectively.

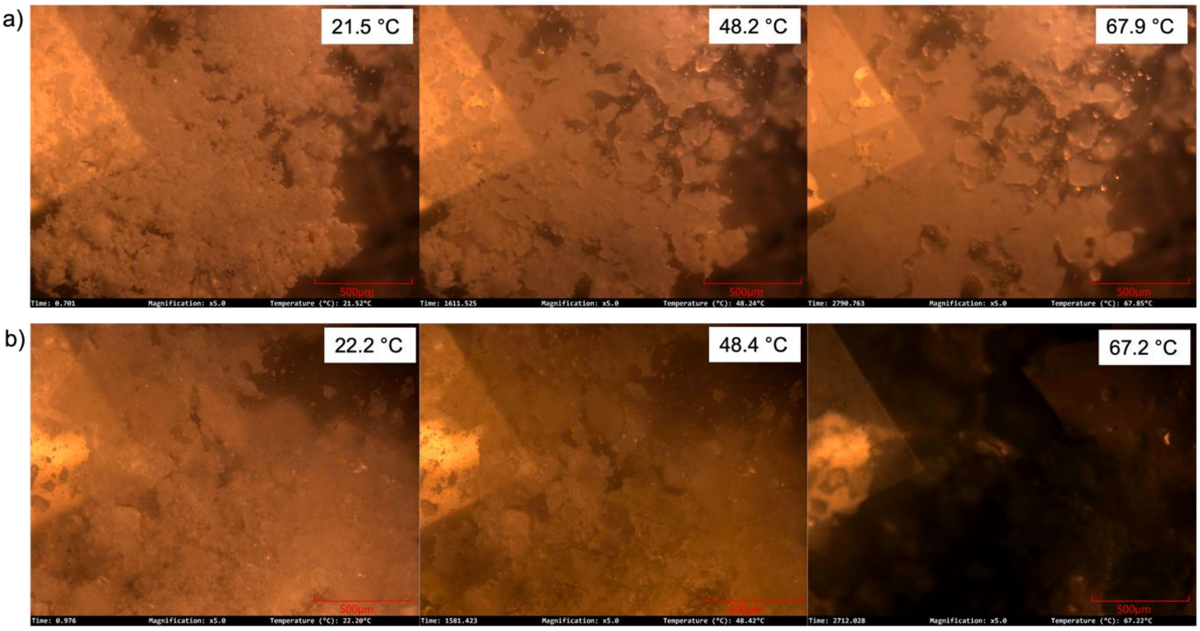


Figure S16. Selected thermal microscopy images of the melting of diphenylamine at 48 °C followed by the dissolution of 1-bromopyrene and NaO*t*Bu at 67 °C. Mixture of diphenylamine (1 equivalent), 1-bromopyrene (1 equivalent) and NaO*t*Bu (2 equivalents): a) without catalyst, b) with 3 mol% of XPhos Pd G1.

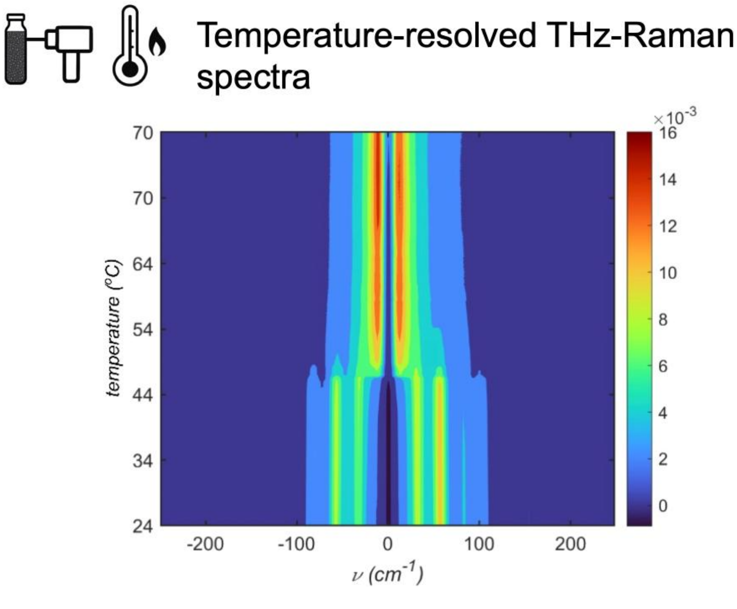


Figure S17. Temperature-resolved THz-Raman spectra recorded during the heating of a mixture of diphenylamine, 1-bromopyrene, NaO*t*Bu and the XPhos Pd G1 catalyst from 24 °C to 70 °C with an observed disappearance of a characteristic THz-Raman signal at ca. 48 ºC.

S7. Temperature profile for the reaction between diphenylamine and 9-bromoanthracene to form 1b, along peak temperature data for the syntheses of 1a and 1b

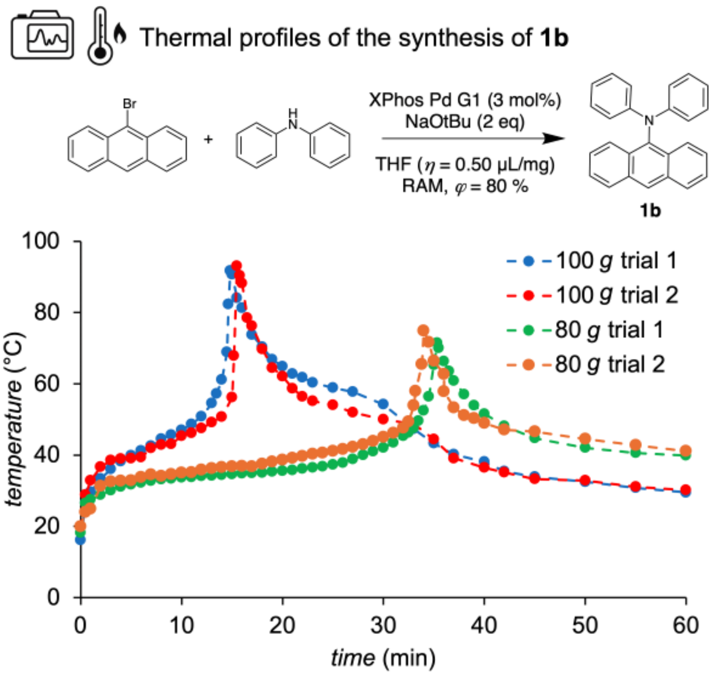


Figure S18. Temperature profile of a) reaction between diphenylamine and 9-bromoanthracene with THF as the liquid additive (η = 0.50 µL/mg) at φ = 80% to form **1b** at 100 *g* and 80 *g*.

Table S13. Peak temperature and the time required to reach peak temperature in the RAM synthesis of **1a** and **1b** at different accelerations. Each value is an average of three separate experiments, with the deviation from the mean shown.

product	**acceleration**		
	100 *g*	80 *g*	60 *g*
1a	82.7 °C (±3.3°C) after 5.4 min (±0.2 min)	71.8 °C (±2.5°C) after 8.4 min (± 0.8 min)	32.0 °C (± 1.8°C) after 27.3 min (± 1.7 min)
1b	91.7°C (± 4.1°C) after 14.8 min (± 1.1 min)	71.5 °C (± 2.8°C) after 35.3 min (± 1.7 min)	Not performed

S8. Thermal analysis and adiabatic temperature rise calculations

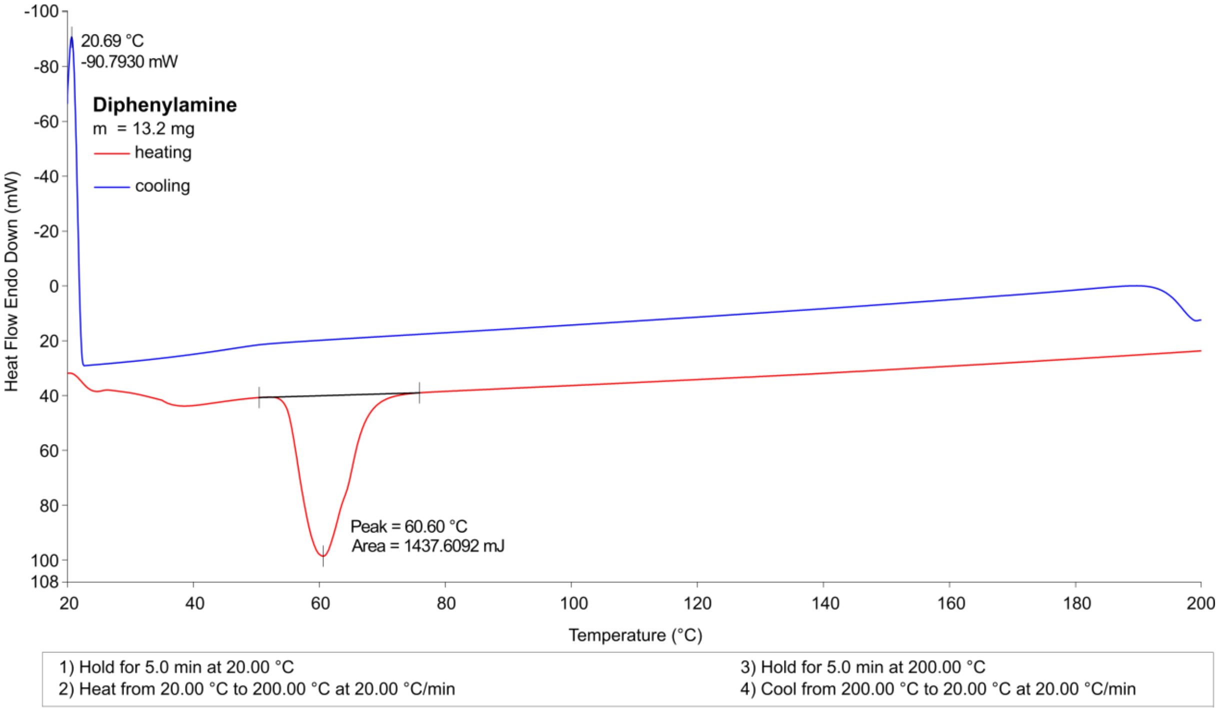


Figure S19. DSC thermogram of commercial diphenylamine reagent (m_{total} = 13.2 mg), recorded using the following temperature program: 5-min isothermal hold at 20 °C, heating from 20 to 200 °C at 20 °C·min⁻¹, 5-min isothermal hold at 200 °C, and cooling from 200 to 20 °C at 20 °C·min⁻¹. Both the heating (red) and cooling (blue) curve are shown.

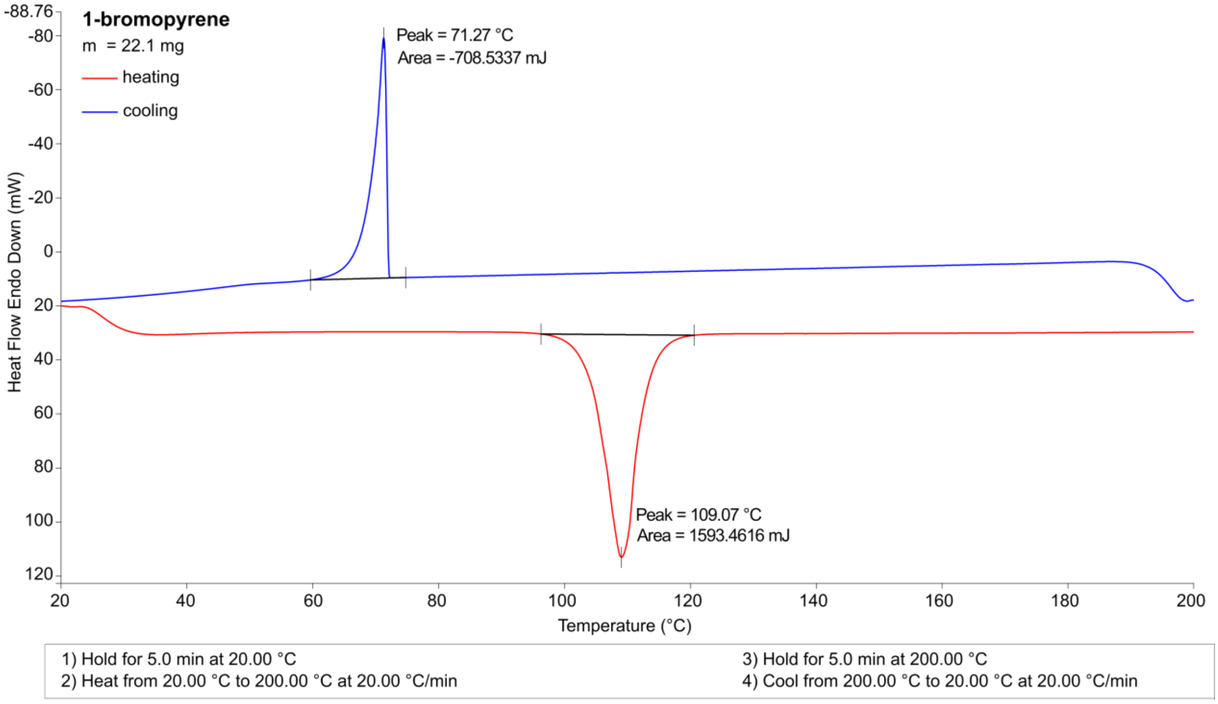


Figure S20. DSC thermogram of commercial 1-bromopyrene reagent (m_{total} = 22.1 mg), recorded using the following temperature program: 5-min isothermal hold at 20 °C, heating from 20 to 200 °C at 20 °C·min⁻¹, 5-min isothermal hold at 200 °C, and cooling from 200 to 20 °C at 20 °C·min⁻¹. Both the heating (red) and cooling (blue) curve are shown.

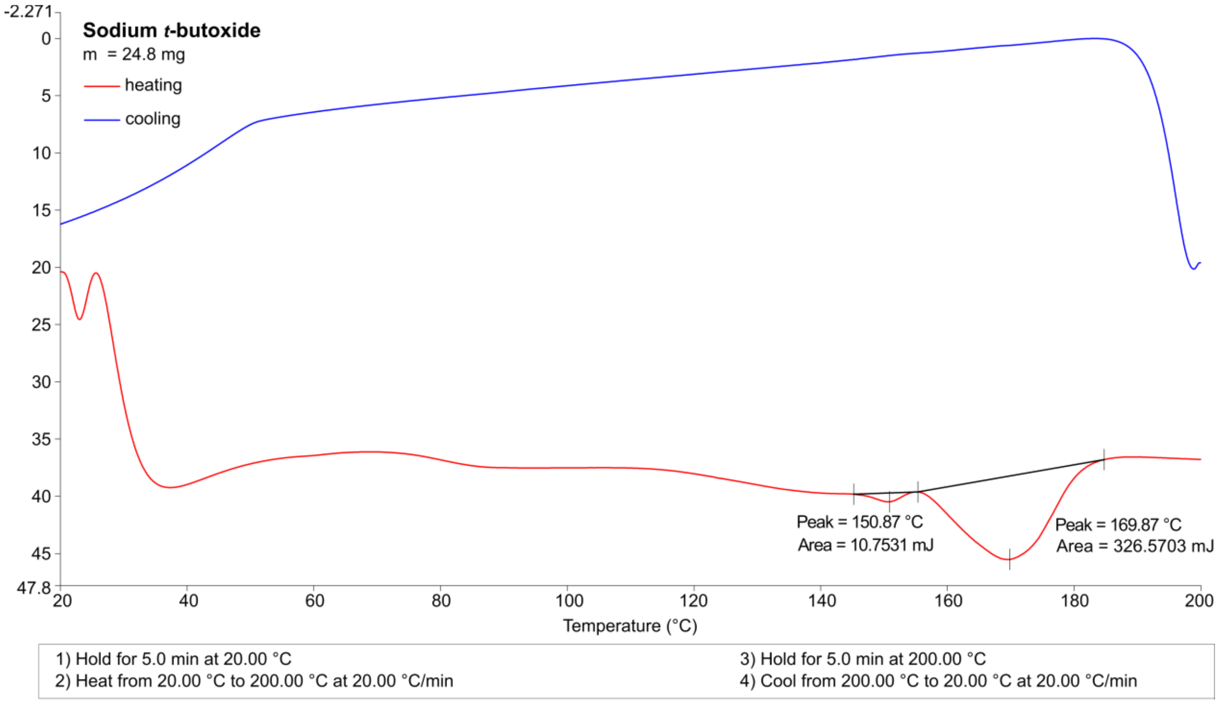


Figure S21. DSC thermogram of commercial sodium *tert*-butoxide (m_{total}= 24.8 mg), recorded using the following temperature program: 5-min isothermal hold at 20 °C, heating from 20 to 200 °C at 20 °C·min⁻¹, 5-min isothermal hold at 200 °C, and cooling from 200 to 20 °C at 20 °C·min⁻¹. Both the heating (red) and cooling (blue) curve are shown.

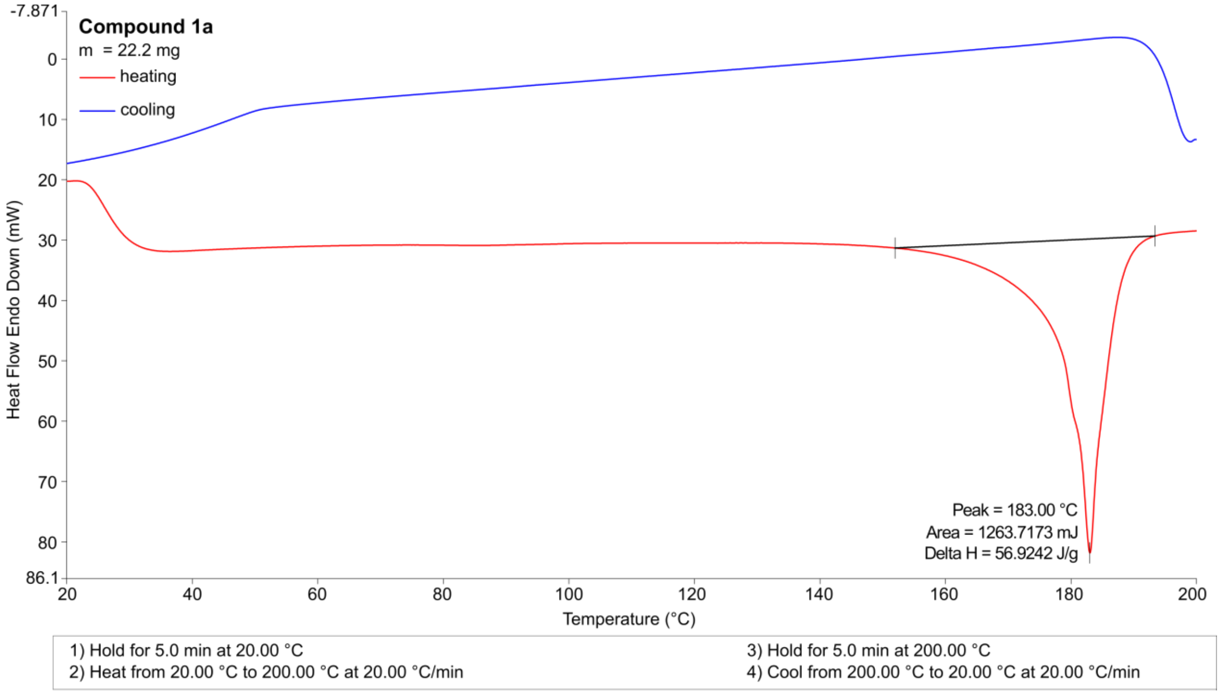


Figure S22. DSC thermogram of the compound **1a** (m_{total} = 22.2 mg), recorded using the following temperature program: 5-min isothermal hold at 20 °C, heating from 20 to 200 °C at 20 °C·min⁻¹, 5-min isothermal hold at 200 °C, and cooling from 200 to 20 °C at 20 °C·min⁻¹. Both the heating (red) and cooling (blue) curve are shown.

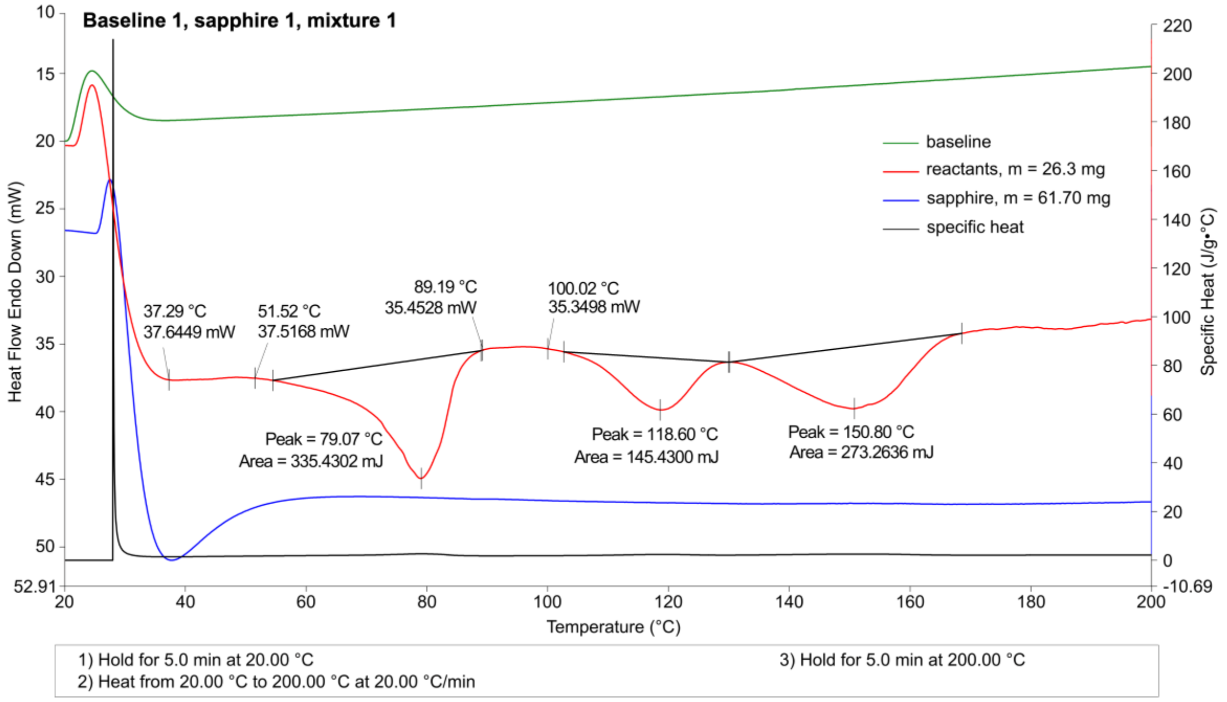


Figure S23. Thermograms for the evaluation of reaction mixture C_p using DSC: baseline (green, baseline 1), sapphire standard (blue, sapphire 1, $m = 61.70$ mg), and reaction mixture (red, mixture 1, $m = 26.3$ mg), along with the calculated specific heat (black). The DSC thermograms were recorded on the same day, following the protocol: 5-min isothermal hold at 20 °C, heating from 20 to 200 °C at 20 °C·min^{-1}, followed by a 5-min isothermal hold at 200 °C. Curves are presented together to illustrate the C_p calculation performed using Pyris software. Six different combinations of duplicate baseline, sapphire standard and reaction mixture measurements were used, shown in Figures S23-S28.

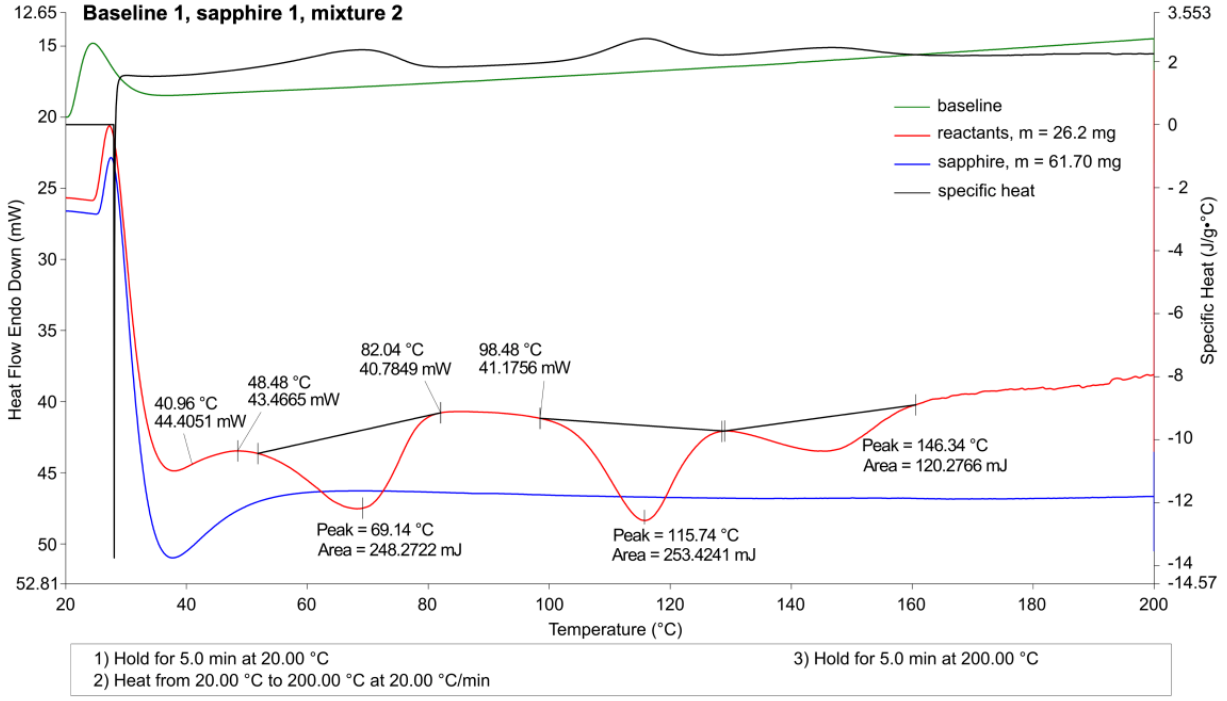


Figure S24. Thermograms for the evaluation of reaction mixture C_p using DSC: baseline (green, baseline 1), sapphire standard (blue, sapphire 1, $m = 61.70$ mg), and reaction mixture (red, mixture 2, $m = 26.2$ mg), along with the calculated specific heat (black). The DSC thermograms were recorded on the same day, following the protocol: 5-min isothermal hold at 20 °C, heating from 20 to 200 °C at 20 °C·min^{-1}, followed by a 5-min isothermal hold at 200 °C. Curves are presented together to illustrate the C_p calculation performed using Pyris software. Six different combinations of duplicate baseline, sapphire standard and reaction mixture measurements were used, shown in Figures S23-S28.

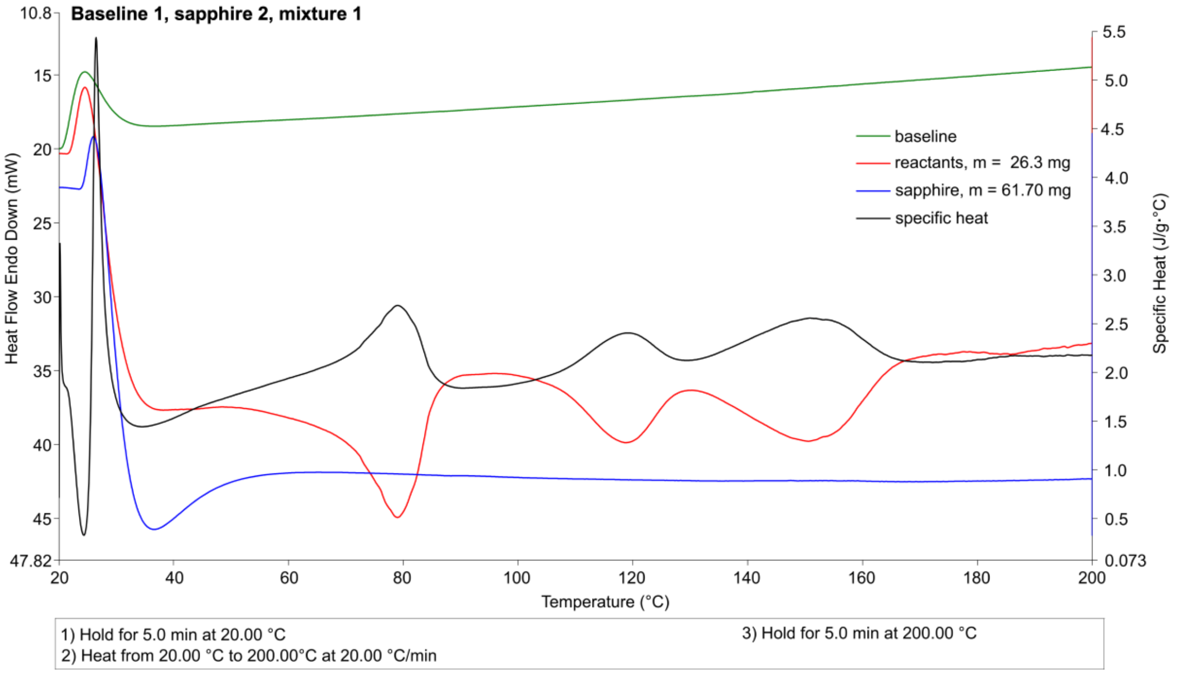


Figure S25. Thermograms for the evaluation of reaction mixture C_p using DSC: baseline (green, baseline 1), sapphire standard (blue, sapphire 2, $m = 61.70$ mg), and reaction mixture (red, mixture 1, $m = 26.3$ mg), along with the calculated specific heat (black). The DSC thermograms were recorded on the same day, following the protocol: 5-min isothermal hold at 20 °C, heating from 20 to 200 °C at 20 °C·min^{-1}, followed by a 5-min isothermal hold at 200 °C. Curves are presented together to illustrate the C_p calculation performed using Pyris software. Six different combinations of duplicate baseline, sapphire standard and reaction mixture measurements were used, shown in Figures S23-S28.

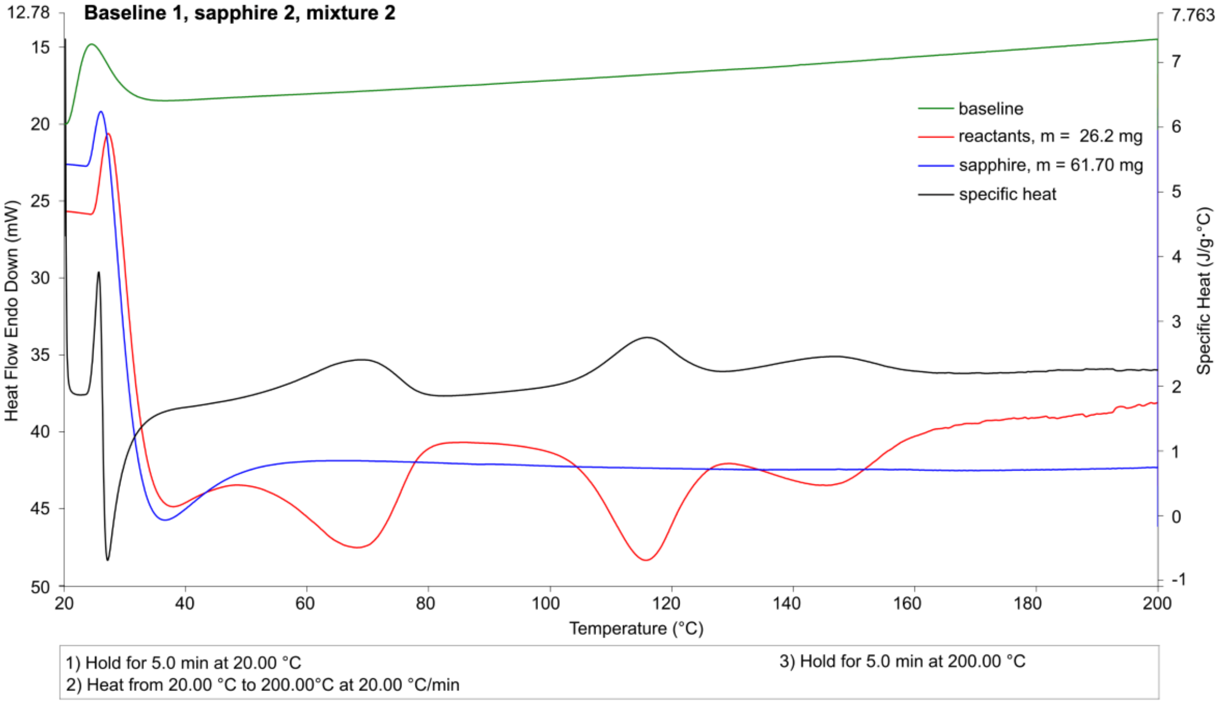


Figure S26. Example thermograms for the evaluation of reaction mixture C_p using DSC: baseline (green, baseline 1), sapphire standard (blue, sapphire 2, $m = 61.70$ mg), and reaction mixture (red, mixture 2, $m = 26.2$ mg), along with the calculated specific heat (black). The DSC thermograms were recorded on the same day, following the protocol: 5-min isothermal hold at 20 °C, heating from 20 to 200 °C at 20 °C·min^{-1}, followed by a 5-min isothermal hold at 200 °C. Curves are presented together to illustrate the C_p calculation performed using Pyris software. Six different combinations of duplicate baseline, sapphire standard and reaction mixture measurements were used, shown in Figures S23-S28.

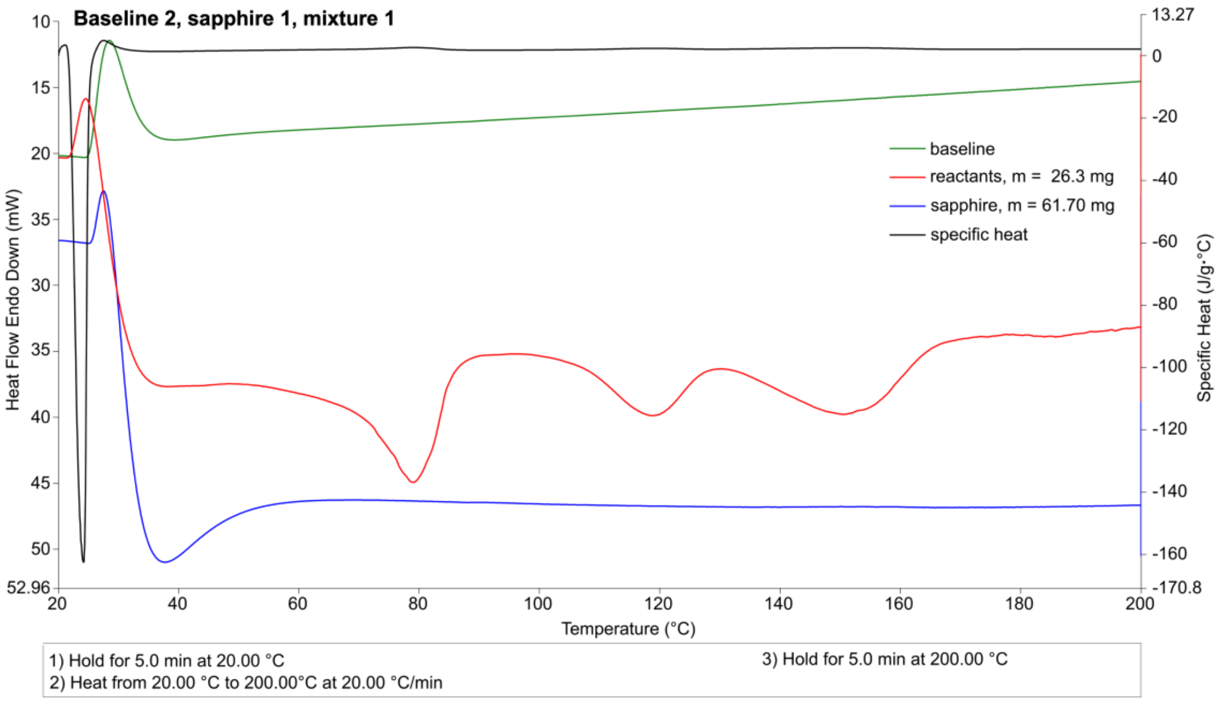


Figure S27. Example thermograms for the evaluation of reaction mixture C_p using DSC: baseline (green, baseline 2), sapphire standard (blue, sapphire 1, m = 61.70 mg), and reaction mixture (red, mixture 1, m = 26.3 mg), along with the calculated specific heat (black). The DSC thermograms were recorded on the same day, following the protocol: 5-min isothermal hold at 20 °C, heating from 20 to 200 °C at 20 °C·min⁻¹, followed by a 5-min isothermal hold at 200 °C. Curves are presented together to illustrate the C_p calculation performed using Pyris software. Six different combinations of duplicate baseline, sapphire standard and reaction mixture measurements were used, shown in Figures S23-S28.

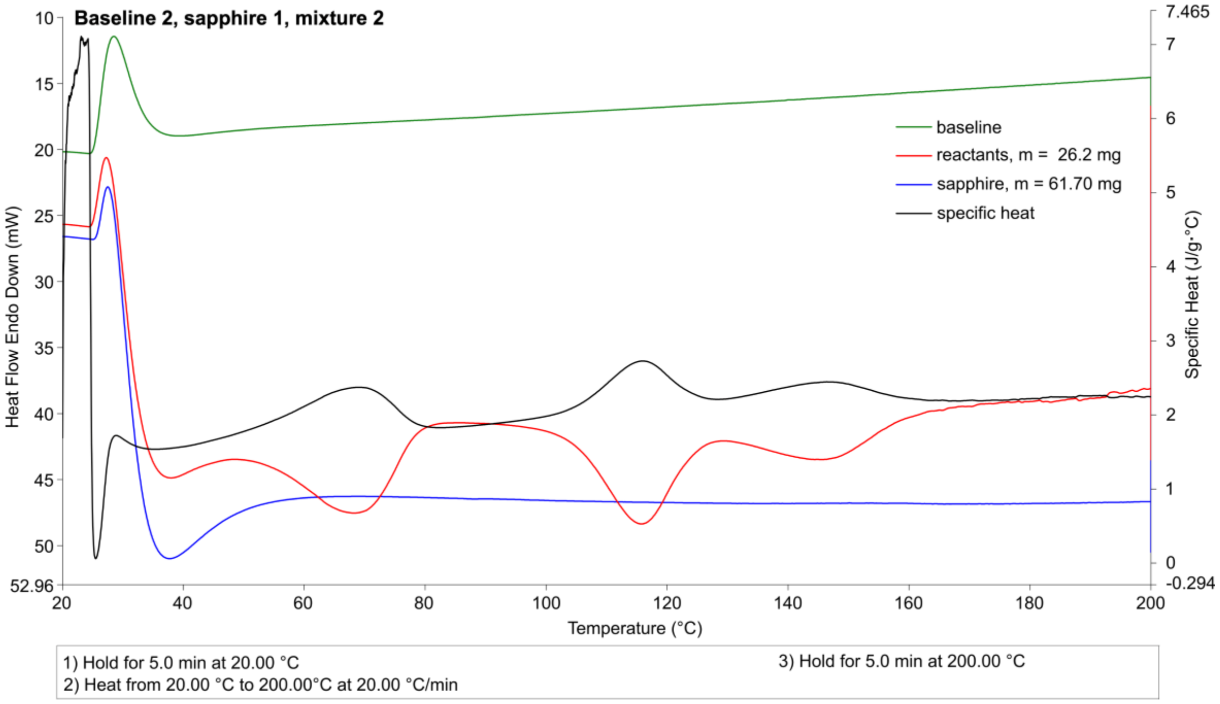


Figure S28. Example thermograms for the evaluation of reaction mixture C_p using DSC: baseline (green, baseline 2), sapphire standard (blue, sapphire 1, m = 61.70 mg), and reaction mixture (red, mixture 2, m = 26.3 mg), along with the calculated specific heat (black). The DSC thermograms were recorded on the same day, following the protocol: 5-min isothermal hold at 20 °C, heating from 20 to 200 °C at 20 °C·min⁻¹, followed by a 5-min isothermal hold at 200 °C. Curves are presented together to illustrate the C_p calculation performed using Pyris software. Six different combinations of duplicate baseline, sapphire standard and reaction mixture measurements were used, shown in Figures S23-S28.

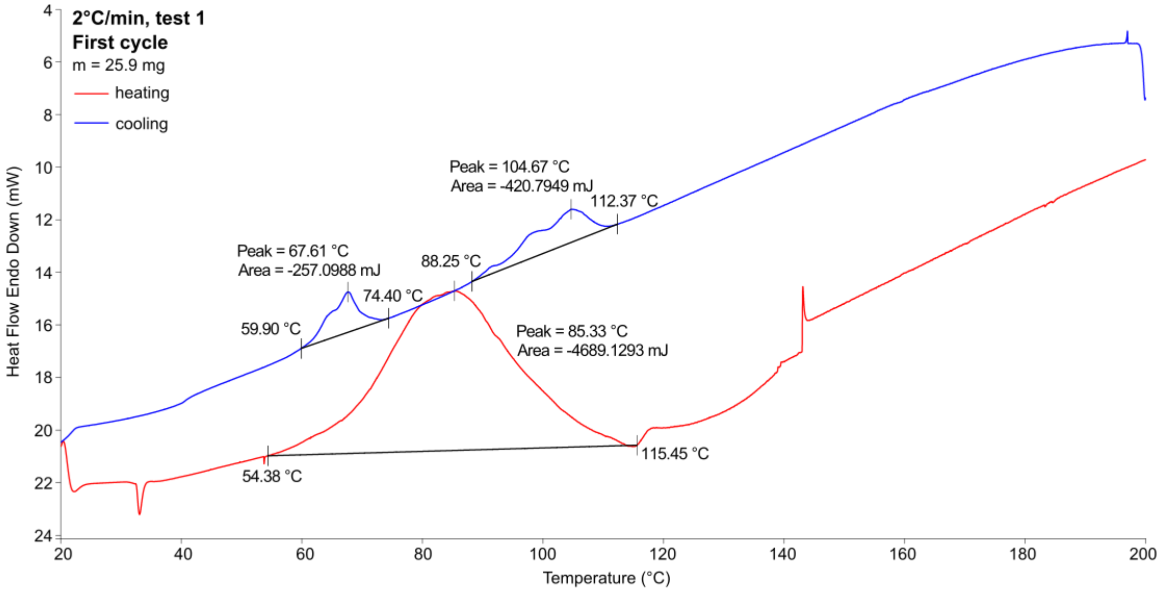
Table S14. The heat capacity (C_p, in $\mathrm{J \cdot g^{-1} \cdot {}^{\circ}C^{-1}}$) of the reaction mixture, as determined from DSC measurements between 21 °C and 200 °C. The C_p values were calculated using six combinations of the baseline, sapphire standard, and reaction mixture experiment data, resulting from having measured twice the baseline (baseline 1 and 2), the sapphire standard (sapphire 1 and 2), and two reaction mixture samples (mixture 1 and 2, each without catalyst present). All measurements were recorded sequentially on the same day, following the standard DSC protocol (5-min isothermal hold at 20 °C, heating from 20 to 200 °C at 20 $\mathrm{{}^{\circ}C \cdot min^{-1}}$, followed by a 5-min hold at 200 °C). The C_p values were calculated using Pyris software.

	Heat capacity (J/g·°C)					
Temperature (°C)	Baseline 1 Sapphire 1 Mixture 1	Baseline 1 Sapphire 1 Mixture 2	Baseline 1 Sapphire 2 Mixture 1	Baseline 1 Sapphire 2 Mixture 2	Baseline 2 Sapphire 1 Mixture 1	Baseline 2 Sapphire 1 Mixture 2
21	0	0	1.874	1.96	3.426	6.201
22	0	0	1.65	1.871	-13.465	6.576
23	0	0	0.947	1.865	-104.183	7.052
24	0	0	0.389	1.924	-160.189	7.029
25	0	0	0.537	2.828	-28.366	0.774
26	0	0	3.631	3.353	0.366	0.183
27	0	0	4.553	-0.629	4.287	0.976
28	0	0	2.749	-0.223	4.696	1.614
29	7.31	1.459	2.042	0.406	3.586	1.722
30	3.301	1.56	1.732	0.82	2.705	1.678
31	2.247	1.553	1.577	1.09	2.152	1.625
32	1.813	1.54	1.498	1.272	1.819	1.583
33	1.604	1.533	1.459	1.395	1.622	1.557
34	1.492	1.53	1.444	1.481	1.506	1.543
35	1.434	1.532	1.443	1.541	1.44	1.536
36	1.407	1.537	1.452	1.585	1.407	1.537
37	1.4	1.545	1.467	1.618	1.397	1.542
38	1.405	1.554	1.485	1.642	1.4	1.55
39	1.419	1.564	1.506	1.659	1.413	1.559
40	1.439	1.575	1.529	1.673	1.433	1.57
41	1.465	1.587	1.556	1.685	1.459	1.583
42	1.493	1.603	1.583	1.699	1.488	1.599
43	1.523	1.622	1.61	1.714	1.518	1.618
44	1.552	1.642	1.635	1.73	1.548	1.639
45	1.579	1.663	1.658	1.746	1.575	1.66
46	1.604	1.683	1.679	1.762	1.601	1.681
47	1.627	1.704	1.698	1.778	1.625	1.702
48	1.65	1.727	1.717	1.797	1.648	1.725
49	1.673	1.751	1.736	1.817	1.672	1.75
50	1.695	1.777	1.754	1.838	1.694	1.776
51	1.718	1.803	1.774	1.862	1.717	1.803
52	1.739	1.831	1.792	1.887	1.738	1.831
53	1.76	1.861	1.81	1.913	1.76	1.86
54	1.781	1.892	1.828	1.942	1.781	1.892
55	1.802	1.925	1.846	1.972	1.801	1.925
56	1.822	1.959	1.865	2.005	1.822	1.959
57	1.843	1.994	1.884	2.039	1.843	1.994
58	1.863	2.032	1.902	2.075	1.862	2.032
59	1.882	2.073	1.919	2.14	1.882	2.073
60	1.902	2.13	1.939	2.154	1.902	2.13
61	1.919	2.154	1.955	2.194	1.919	2.154
62	1.938	2.196	1.973	2.235	1.938	2.196
63	1.957	2.238	1.99	2.277	1.956	2.238
64	1.978	2.278	2.011	2.316	1.978	2.278
65	1.999	2.309	2.032	2.347	1.999	2.31
66	2.021	2.336	2.053	2.373	2.021	2.336
67	2.043	2.354	2.075	2.391	2.043	2.354

68	2.069	2.368	2.1	2.404	2.069	2.368
69	2.097	2.373	2.128	2.408	2.097	2.373
70	2.129	2.369	2.159	2.403	2.128	2.369
71	2.165	2.349	2.196	2.381	2.165	2.349
72	2.208	2.311	2.238	2.343	2.208	2.311
73	2.272	2.257	2.303	2.287	2.272	2.257
74	2.334	2.191	2.364	2.219	2.334	2.191
75	2.397	2.15	2.428	2.142	2.397	2.15
76	2.459	2.034	2.49	2.06	2.459	2.034
77	2.554	1.962	2.586	1.987	2.553	1.962
78	2.612	1.905	2.645	1.929	2.612	1.905
79	2.654	1.867	2.686	1.89	2.653	1.867
80	2.624	1.845	2.656	1.867	2.624	1.845
81	2.549	1.833	2.58	1.855	2.549	1.833
82	2.457	1.828	2.486	1.85	2.457	1.828
83	2.31	1.828	2.336	1.849	2.31	1.828
84	2.121	1.831	2.145	1.852	2.121	1.831
85	1.982	1.836	2.004	1.857	1.982	1.836
86	1.907	1.842	1.928	1.862	1.907	1.842
87	1.863	1.848	1.884	1.868	1.863	1.848
88	1.838	1.855	1.859	1.875	1.838	1.855
89	1.825	1.863	1.844	1.883	1.825	1.863
90	1.819	1.871	1.839	1.891	1.819	1.871
91	1.82	1.879	1.839	1.899	1.82	1.879
92	1.822	1.888	1.842	1.908	1.822	1.888
93	1.826	1.897	1.845	1.917	1.826	1.897
94	1.829	1.906	1.848	1.926	1.829	1.907
95	1.831	1.917	1.85	1.937	1.831	1.917
96	1.835	1.927	1.853	1.947	1.835	1.927
97	1.84	1.939	1.858	1.958	1.84	1.939
98	1.847	1.951	1.865	1.97	1.847	1.951
99	1.856	1.965	1.874	1.984	1.856	1.965
100	1.867	1.981	1.886	2	1.868	1.981
101	1.879	1.999	1.897	2.018	1.879	1.999
102	1.891	2.021	1.909	2.04	1.891	2.021
103	1.907	2.047	1.925	2.067	1.907	2.047
104	1.924	2.08	1.942	2.1	1.924	2.08
105	1.942	2.19	1.959	2.138	1.942	2.19
106	1.961	2.165	1.978	2.184	1.961	2.165
107	1.984	2.219	2.001	2.238	1.984	2.219
108	2.01	2.279	2.028	2.3	2.01	2.279
109	2.042	2.347	2.06	2.368	2.042	2.347
110	2.078	2.418	2.096	2.439	2.078	2.418
11	2.18	2.492	2.137	2.513	2.18	2.491
112	2.161	2.562	2.18	2.585	2.161	2.562
113	2.206	2.628	2.225	2.65	2.206	2.627
114	2.25	2.681	2.27	2.704	2.25	2.68
115	2.291	2.716	2.311	2.739	2.291	2.716
116	2.326	2.729	2.346	2.752	2.326	2.728
117	2.356	2.714	2.375	2.737	2.355	2.714
118	2.376	2.672	2.395	2.694	2.375	2.672
119	2.385	2.609	2.404	2.63	2.384	2.609
120	2.38	2.534	2.399	2.555	2.38	2.534
121	2.361	2.461	2.38	2.481	2.361	2.461
122	2.328	2.396	2.345	2.414	2.327	2.396
123	2.286	2.342	2.304	2.361	2.286	2.342
124	2.239	2.298	2.255	2.315	2.239	2.298
125	2.194	2.261	2.211	2.278	2.194	2.261

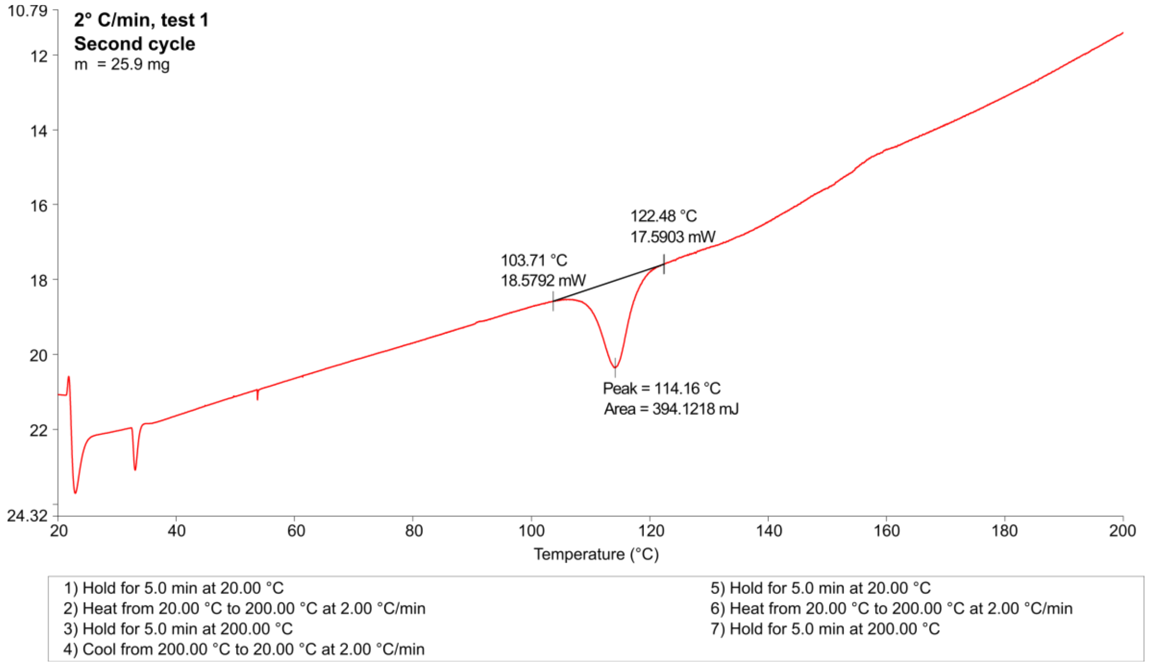
126	2.157	2.234	2.173	2.251	2.157	2.234
127	2.129	2.218	2.145	2.234	2.129	2.218
128	2.13	2.21	2.129	2.226	2.13	2.21
129	2.108	2.211	2.123	2.227	2.108	2.211
130	2.109	2.217	2.124	2.233	2.109	2.217
131	2.15	2.228	2.13	2.243	2.15	2.228
132	2.128	2.242	2.142	2.257	2.128	2.242
133	2.144	2.256	2.159	2.272	2.144	2.256
134	2.164	2.272	2.178	2.287	2.164	2.272
135	2.188	2.289	2.202	2.304	2.188	2.289
136	2.214	2.308	2.228	2.322	2.214	2.308
137	2.239	2.326	2.253	2.341	2.239	2.326
138	2.265	2.344	2.279	2.359	2.265	2.344
139	2.291	2.361	2.305	2.376	2.291	2.361
140	2.317	2.377	2.332	2.392	2.317	2.377
141	2.345	2.392	2.36	2.408	2.345	2.392
142	2.371	2.408	2.386	2.423	2.371	2.408
143	2.397	2.42	2.412	2.435	2.397	2.42
144	2.422	2.43	2.436	2.445	2.422	2.43
145	2.447	2.437	2.461	2.451	2.447	2.437
146	2.471	2.443	2.485	2.457	2.471	2.443
147	2.493	2.444	2.507	2.458	2.493	2.444
148	2.51	2.441	2.525	2.455	2.51	2.441
149	2.524	2.431	2.536	2.443	2.524	2.431
150	2.539	2.417	2.55	2.427	2.539	2.417
151	2.543	2.395	2.556	2.407	2.542	2.395
152	2.539	2.373	2.552	2.385	2.539	2.373
153	2.528	2.351	2.54	2.361	2.528	2.351
154	2.527	2.327	2.538	2.337	2.527	2.327
155	2.513	2.301	2.524	2.311	2.513	2.301
156	2.491	2.281	2.502	2.291	2.491	2.281
157	2.461	2.262	2.472	2.272	2.461	2.262
158	2.425	2.245	2.436	2.254	2.425	2.245
159	2.377	2.233	2.387	2.243	2.377	2.233
160	2.333	2.222	2.342	2.231	2.332	2.222
161	2.289	2.215	2.298	2.223	2.289	2.215
162	2.245	2.207	2.253	2.215	2.245	2.207
163	2.206	2.196	2.213	2.204	2.206	2.197
164	2.173	2.195	2.182	2.204	2.173	2.195
165	2.146	2.195	2.154	2.203	2.146	2.195
166	2.127	2.195	2.135	2.203	2.127	2.195
167	2.13	2.189	2.121	2.196	2.14	2.189
168	2.107	2.188	2.14	2.196	2.107	2.188
169	2.104	2.191	2.1	2.198	2.104	2.191
170	2.1	2.197	2.106	2.203	2.1	2.197
171	2.1	2.194	2.106	2.201	2.1	2.194
172	2.097	2.19	2.104	2.196	2.097	2.19
173	2.098	2.194	2.104	2.201	2.098	2.194
174	2.102	2.199	2.109	2.206	2.103	2.199
175	2.106	2.198	2.12	2.205	2.106	2.198
176	2.107	2.2	2.13	2.206	2.107	2.2
177	2.106	2.207	2.12	2.214	2.106	2.208
178	2.108	2.205	2.14	2.211	2.108	2.205
179	2.14	2.215	2.12	2.221	2.14	2.215
180	2.124	2.219	2.13	2.226	2.124	2.219
181	2.127	2.22	2.132	2.226	2.127	2.22
182	2.138	2.23	2.145	2.237	2.138	2.23
183	2.146	2.236	2.152	2.242	2.146	2.236

184	2.154	2.242	2.16	2.248	2.154	2.242
185	2.157	2.241	2.162	2.247	2.157	2.241
186	2.166	2.241	2.17	2.246	2.166	2.241
187	2.166	2.241	2.17	2.245	2.166	2.241
188	2.164	2.256	2.169	2.261	2.164	2.256
189	2.163	2.256	2.167	2.261	2.163	2.256
190	2.165	2.255	2.169	2.26	2.165	2.255
191	2.162	2.258	2.166	2.262	2.162	2.258
192	2.161	2.259	2.165	2.264	2.161	2.26
193	2.165	2.24	2.168	2.243	2.165	2.24
194	2.167	2.234	2.171	2.237	2.167	2.234
195	2.165	2.249	2.168	2.252	2.165	2.249
196	2.175	2.246	2.178	2.25	2.175	2.247
197	2.169	2.241	2.173	2.244	2.169	2.241
198	2.173	2.248	2.177	2.252	2.173	2.248
199	2.174	2.241	2.178	2.245	2.174	2.241
200	2.172	2.244	2.176	2.248	2.172	2.244



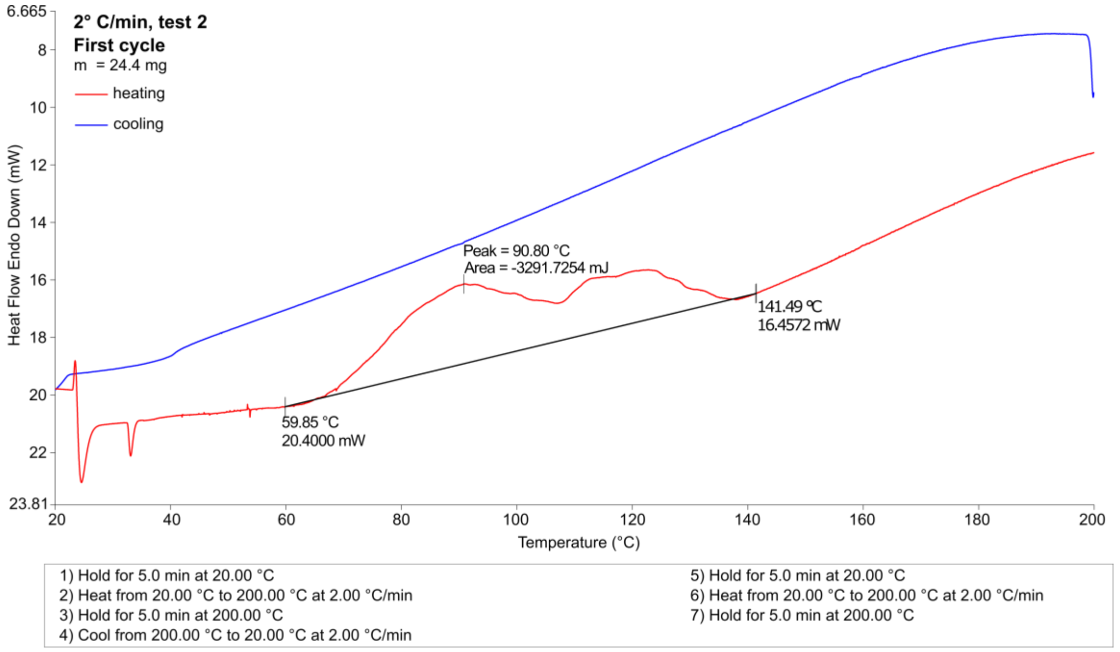
1) Hold for 5.0 min at 20.00 °C
2) Heat from 20.00 °C to 200.00°C at 2.00 °C/min
3) Hold for 5.0 min at 200.00 °C
4) Cool from 200.00 °C to 20.00 °C at 2.00 °C/min
5) Hold for 5.0 min at 20.00 °C
6) Heat from 20.00 °C to 200.00°C at 2.00 °C/min
7) Hold for 5.0 min at 200.00 °C

Figure S29. DSC thermogram of the reactive mixture (experiment: 2 °C/min, test 1) showing the first heating (red) and cooling (blue) cycle. The experiment was performed with a total sample mass (m_{total} = 25.9 mg) including 1 equiv. diphenylamine, 1 equiv. 1-bromopyrene, 2 equiv. NaOtBu, 3 mol% XPhos Pd G1, and THF at 0.21 µL·mg⁻¹, while the reactive mass ($m_{reactive}$ = 18.2 mg) is considered to consist of 1 equiv. diphenylamine, 1 equiv. 1-bromopyrene, and 1 equiv. NaOtBu. The DSC was run following the program: 5-min isothermal hold at 20 °C, heating from 20 to 200 °C at 2 °C·min⁻¹, 5-min hold at 200 °C, and cooling to 20 °C at 2 °C·min⁻¹. This measurement was used to determine the exothermic events of the reaction and to calculate the total enthalpy (ΔH_{total}). A conversion of 99 % was estimated by ^{1}H NMR spectroscopy in $CDCl_3$ directly after two DSC cycles.



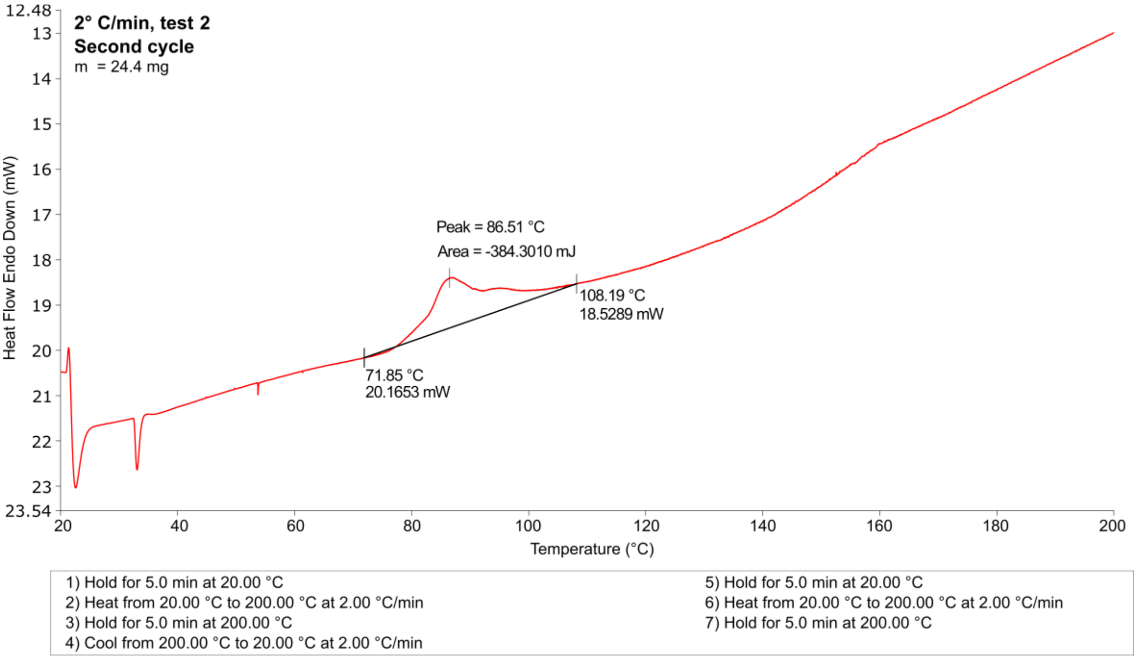
1) Hold for 5.0 min at 20.00 °C
2) Heat from 20.00 °C to 200.00 °C at 2.00 °C/min
3) Hold for 5.0 min at 200.00 °C
4) Cool from 200.00 °C to 20.00 °C at 2.00 °C/min
5) Hold for 5.0 min at 20.00 °C
6) Heat from 20.00 °C to 200.00 °C at 2.00 °C/min
7) Hold for 5.0 min at 200.00 °C

Figure S30. DSC thermogram of the reactive mixture (experiment: 2 °C/min, test 1) showing the second heating cycle. The experiment was performed with a total sample mass (m_{total} = 25.9 mg) including 1 equiv. diphenylamine, 1 equiv. 1-bromopyrene, 2 equiv. NaOtBu, 3 mol% XPhos Pd G1, and THF at 0.21 µL·mg^{-1}, while the reactive mass ($m_{reactive}$ = 18.2 mg) is considered to consist of 1 equiv. diphenylamine, 1 equiv. 1-bromopyrene, and 1 equiv. NaOtBu. The DSC was run following the program: 5-min isothermal hold at 20 °C, heating from 20 to 200 °C at 2 °C·min^{-1}, 5-min hold at 200 °C, and cooling to 20 °C at 2 °C·min^{-1}. This measurement was used to determine the exothermic events of the reaction and to calculate the total enthalpy (ΔH_{total}). A conversion of 99 % was estimated by ^{1}H NMR spectroscopy in $CDCl_3$ directly after two DSC cycles.



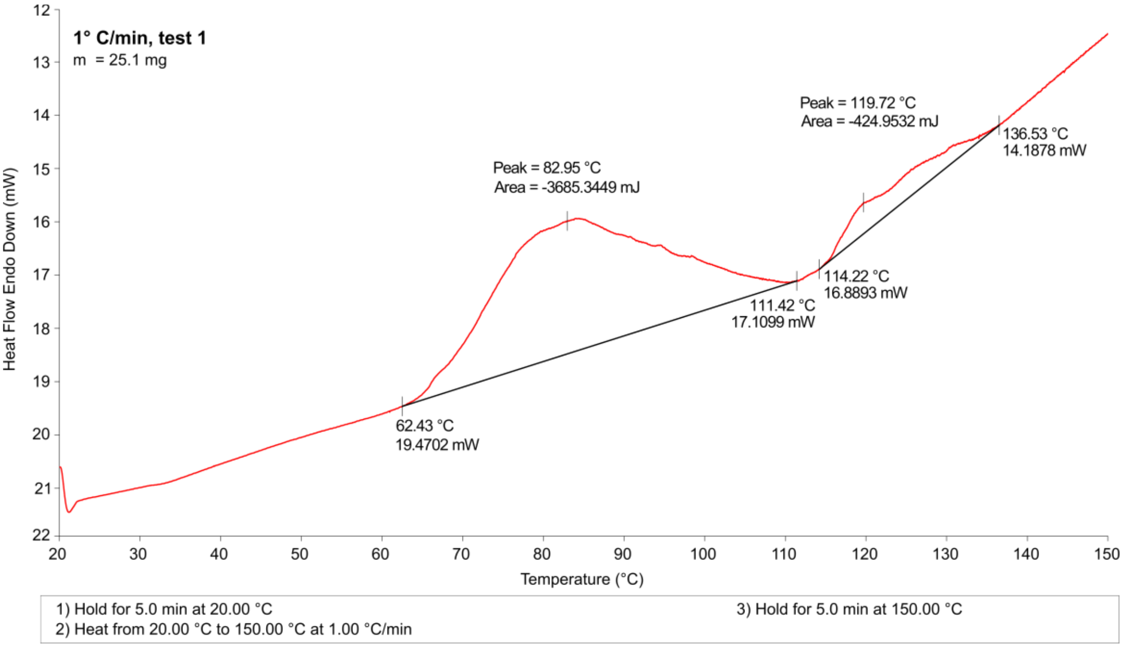
1) Hold for 5.0 min at 20.00 °C
2) Heat from 20.00 °C to 200.00 °C at 2.00 °C/min
3) Hold for 5.0 min at 200.00 °C
4) Cool from 200.00 °C to 20.00 °C at 2.00 °C/min
5) Hold for 5.0 min at 20.00 °C
6) Heat from 20.00 °C to 200.00 °C at 2.00 °C/min
7) Hold for 5.0 min at 200.00 °C

Figure S31. DSC thermogram of the reactive mixture (experiment: 2 °C/min, test 2) showing the first heating (red) and cooling (blue) cycle. The experiment was performed with a total sample mass (m_{total} = 24.4 mg) including 1 equiv. diphenylamine, 1 equiv. 1-bromopyrene, 2 equiv. NaOtBu, 3 mol% XPhos Pd G1, and THF at 0.18 µL·mg^{-1}, while the reactive mass ($m_{reactive}$ = 17.3 mg) is considered to consist of 1 equiv. diphenylamine, 1 equiv. 1-bromopyrene, and 1 equiv. NaOtBu. The DSC was run following the program: 5-min isothermal hold at 20 °C, heating from 20 to 200 °C at 2 °C·min^{-1}, 5-min hold at 200 °C, and cooling to 20 °C at 2 °C·min^{-1}. This measurement was used to determine the exothermic events of the reaction and to calculate the total enthalpy (ΔH_{total}). A conversion of 89 % was estimated by ^{1}H NMR spectroscopy in $CDCl_3$ directly after two DSC cycles.



1) Hold for 5.0 min at 20.00 °C
2) Heat from 20.00 °C to 200.00 °C at 2.00 °C/min
3) Hold for 5.0 min at 200.00 °C
4) Cool from 200.00 °C to 20.00 °C at 2.00 °C/min
5) Hold for 5.0 min at 20.00 °C
6) Heat from 20.00 °C to 200.00 °C at 2.00 °C/min
7) Hold for 5.0 min at 200.00 °C

Figure S32. DSC thermogram of the reactive mixture (experiment: 2 °C/min, test 2) showing the second heating cycle. The experiment was performed with a total sample mass (m_{total} = 24.4 mg) including 1 equiv. diphenylamine, 1 equiv. 1-bromopyrene, 2 equiv. NaOtBu, 3 mol% XPhos Pd G1, and THF at 0.18 µL·mg^{-1}, while the reactive mass ($m_{reactive}$ = 17.3 mg) is considered to consist of 1 equiv. diphenylamine, 1 equiv. 1-bromopyrene, and 1 equiv. NaOtBu. The DSC was run following the program: 5-min isothermal hold at 20 °C, heating from 20 to 200 °C at 2 °C·min^{-1}, 5-min hold at 200 °C, and cooling to 20 °C at 2 °C·min^{-1}. This measurement was used to determine the exothermic events of the reaction and to calculate the total enthalpy (ΔH_{total}). A conversion of 89 % was determined by ^{1}H NMR in $CDCl_3$ directly after the DSC analysis. A conversion of 89 % was estimated by ^{1}H NMR spectroscopy in $CDCl_3$ directly after two DSC cycles.



1) Hold for 5.0 min at 20.00 °C
2) Heat from 20.00 °C to 150.00 °C at 1.00 °C/min
3) Hold for 5.0 min at 150.00 °C

Figure S33. DSC thermogram of the reactive mixture (experiment: 1 °C/min, test 1). The experiment was performed with a total sample mass (m_{total} = 25.1 mg) including 1 equiv. diphenylamine, 1 equiv. 1-bromopyrene, 2 equiv. NaOtBu, 3 mol% XPhos Pd G1, and THF at 0.19 µL·mg^{-1}, while the reactive mass ($m_{reactive}$ = 17.8 mg) is considered to consist of 1 equiv. diphenylamine, 1 equiv. 1-bromopyrene, and 1 equiv. NaOtBu. The DSC was run following the program: 5 min isothermal hold at 20 °C, heating from 20 to 150 °C at 1 °C·min^{-1}, 5-min hold at 150 °C. This measurement was used to determine the exothermic events of the reaction and to calculate the total enthalpy (ΔH_{total}). A conversion of 97 % was estimated by ^{1}H NMR spectroscopy in $CDCl_3$ directly after DSC analysis.

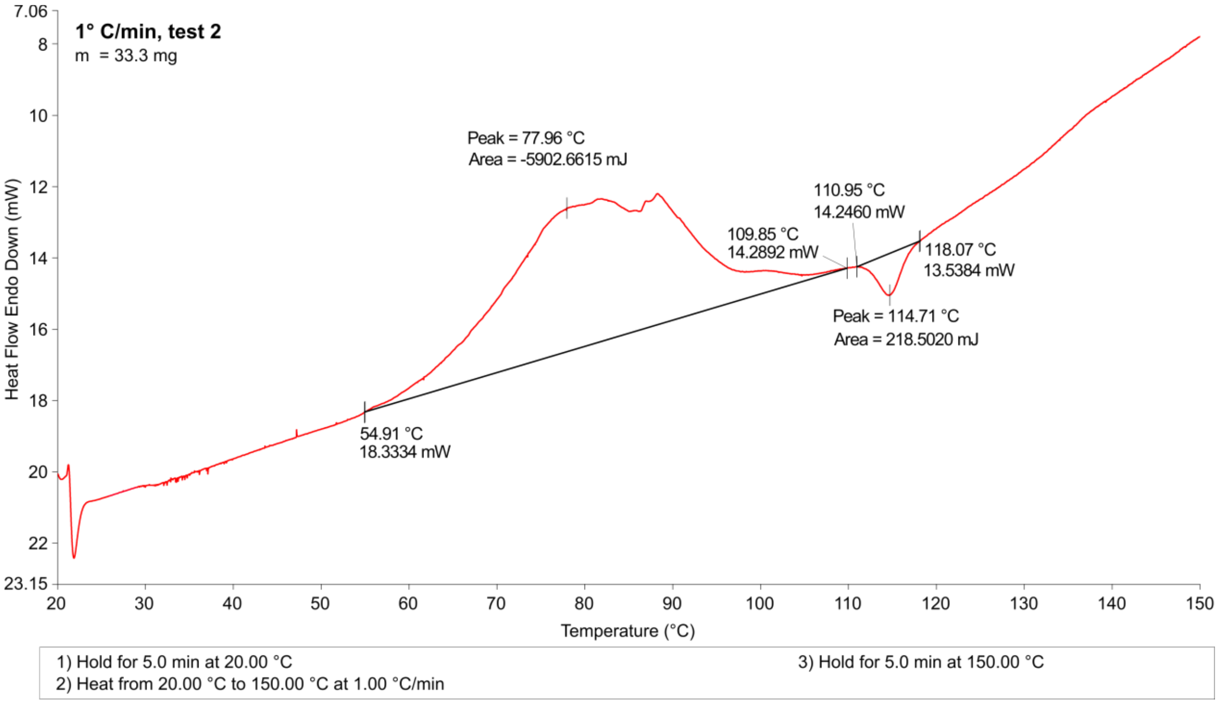


Figure S34. DSC thermogram of the reactive mixture (experiment: 1 °C/min, test 2). The experiment was performed with a total sample mass (m_{total} = 33.3 mg) including 1 equiv. diphenylamine, 1 equiv. 1-bromopyrene, 2 equiv. NaOtBu, 3 mol% XPhos Pd G1, and THF at 0.23 µL·mg⁻¹, while the reactive mass ($m_{reactive}$ = 23.2 mg) is considered to consist of 1 equiv. diphenylamine, 1 equiv. 1-bromopyrene, and 1 equiv. NaOtBu. The DSC was run following the program: 5 min isothermal hold at 20 °C, heating from 20 to 150 °C at 1 °C·min⁻¹, 5-min hold at 150 °C. This measurement was used to determine the exothermic events of the reaction and to calculate the total enthalpy (ΔH_{total}). A conversion of 99 % was estimated by ^{1}H NMR spectroscopy in $CDCl_3$ directly after DSC analysis.

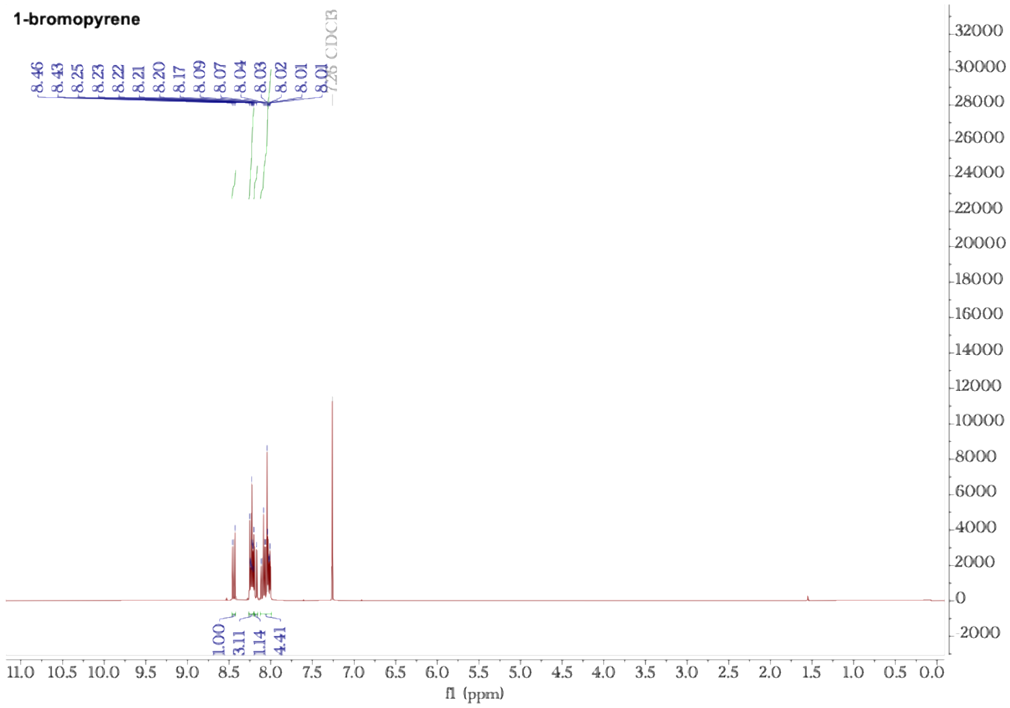


Figure S35. ^{1}H NMR spectrum for reagent 1-bromopyrene in $CDCl_3$.

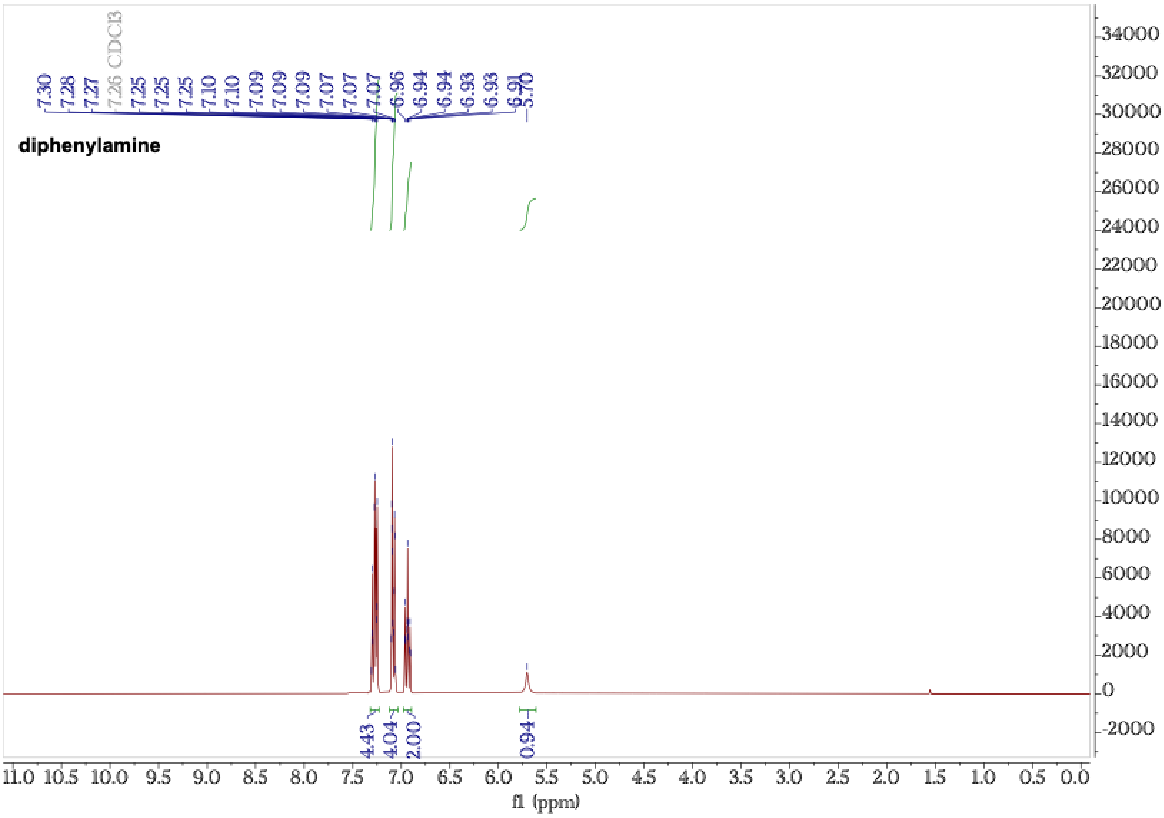


Figure S36. ^{1}H NMR spectrum for reagent diphenylamine in $CDCl_3$.

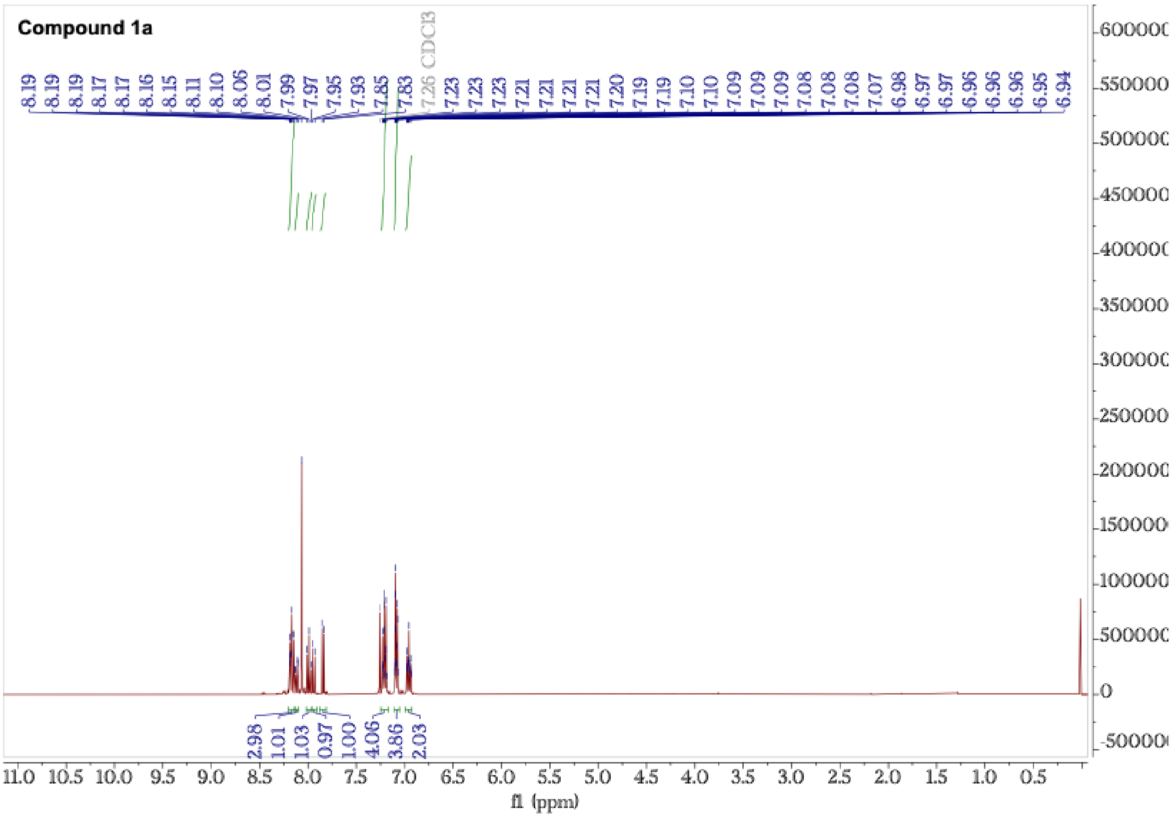


Figure S37. ^{1}H NMR spectrum for the product compound **1a** in $CDCl_3$.

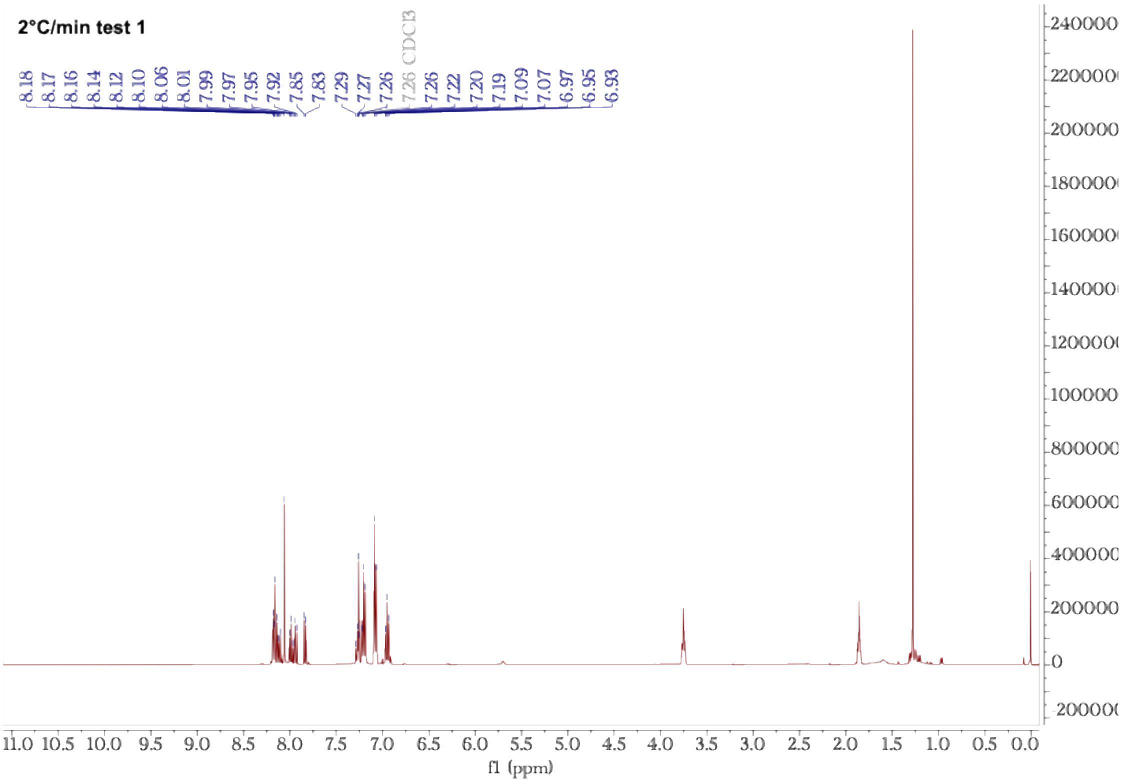


Figure S38. ^{1}H NMR spectra in $CDCl_3$ of the crude reaction mixture obtained immediately after a two-cycle DSC experiment (2 °C·min^{-1}, test 1), showing signals corresponding to compound **1a**, together with residual THF (liquid additive) and *tert*-butanol formed as a byproduct.

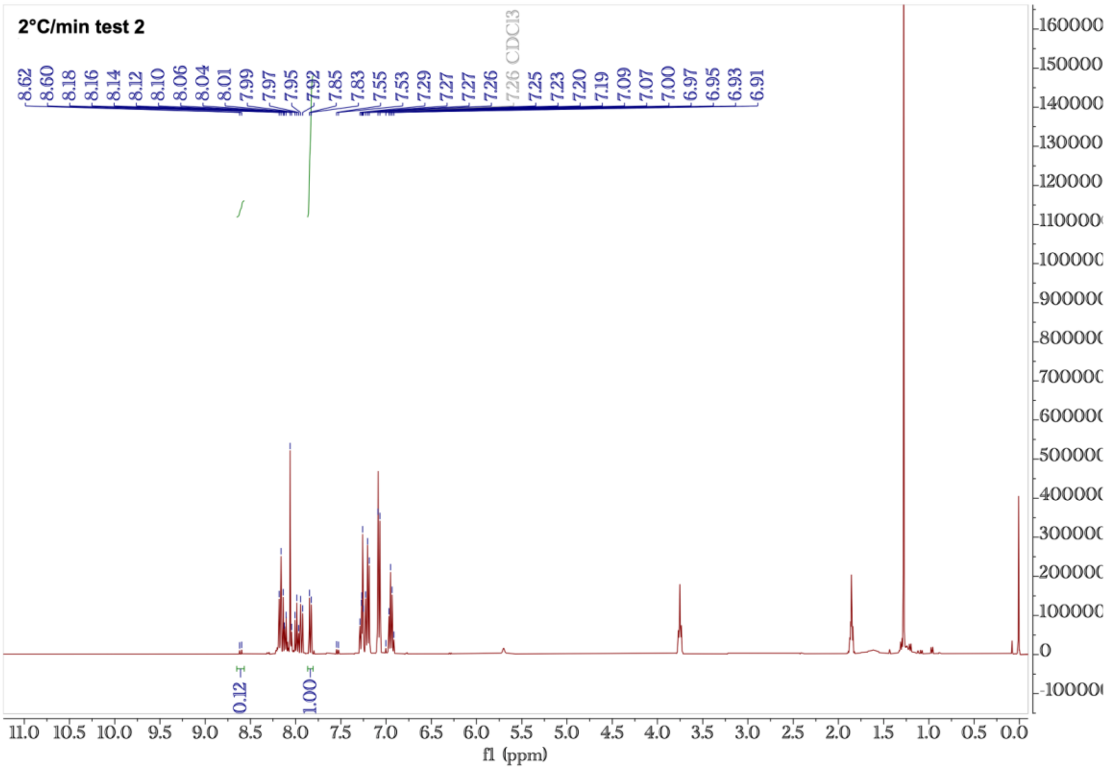


Figure S39. 1H NMR spectrum in $CDCl_3$ of the crude reaction mixture obtained after a two-cycle DSC experiment (2 °C·min^{-1}, test 2). The spectrum shows compound **1a**, residual THF from the liquid additive, *tert*-butanol formed during the reaction, and a minor aromatic byproduct. Integration of the doublets at $\delta = 7.84$ ppm (**1a**) and $\delta = 6.61$ ppm (a not yet identified byproduct) leads to an estimated conversion of 89% to **1a**.

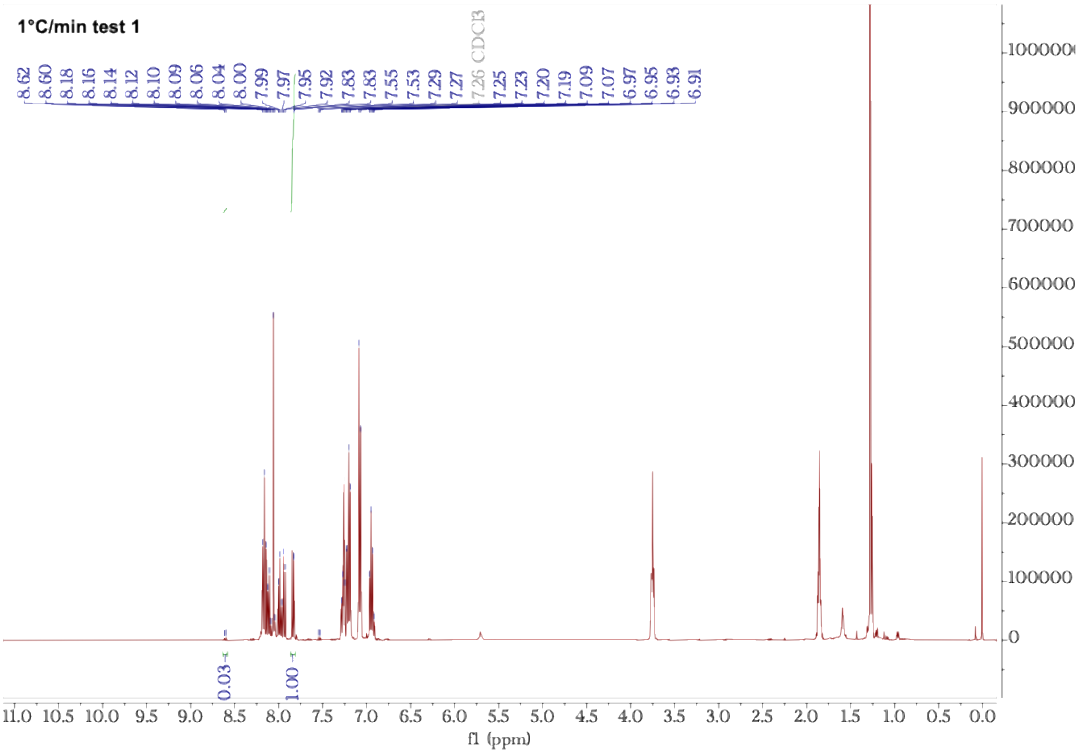


Figure S40. 1H NMR spectrum in $CDCl_3$ of the crude reaction mixture obtained after a one-cycle DSC experiment (1 °C·min^{-1}, test 1). The spectrum shows compound **1a**, residual THF from the liquid additive, *tert*-butanol formed during the reaction, and a minor aromatic byproduct. Integration of the doublets at δ = 7.84 ppm (**1a**) and δ = 6.61 ppm (a not yet identified byproduct) leads to an estimated conversion of 93% to **1a**.

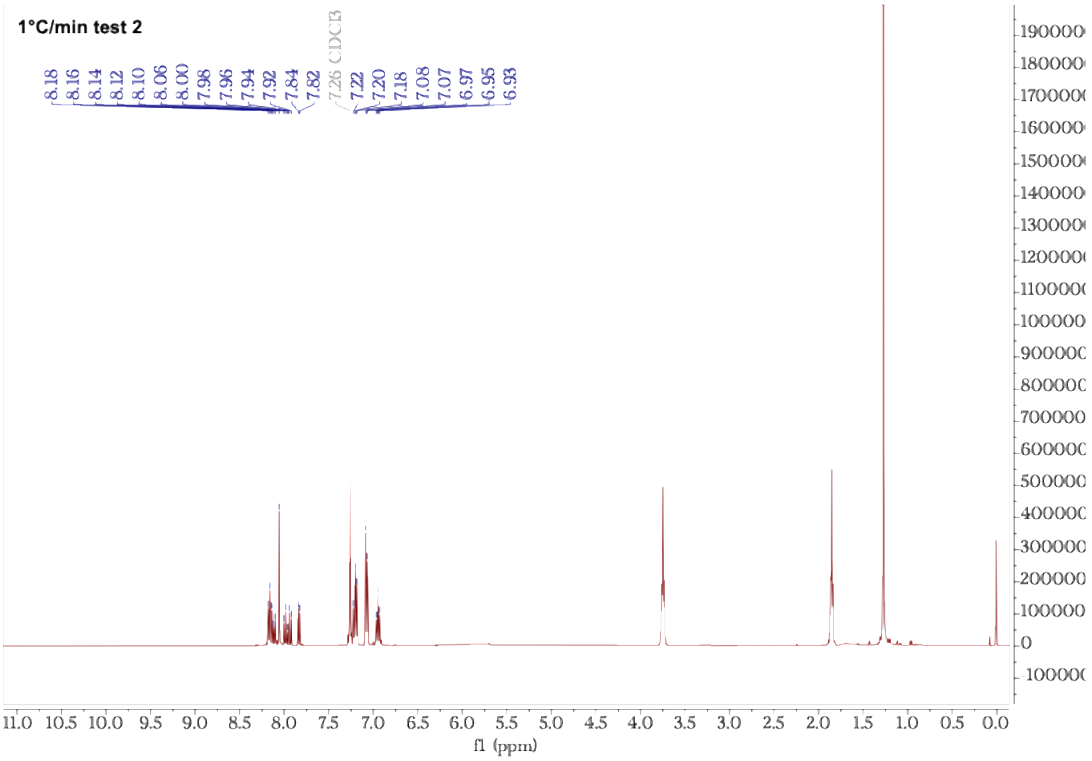


Figure S41. ^1H NMR spectra in $CDCl_3$ of the crude reaction mixture obtained immediately after a one-cycle DSC experiment (1 °C·min^{-1}, test 2), showing signals corresponding to compound **1a**, together with residual THF (liquid additive) and *tert*-butanol formed as a byproduct.

The adiabatic temperature rise (ΔT_{AD}) was calculated using the total heat released during the reaction (Q, in J), the total mass of the reacting mixture (m_{total}, in grams), and the specific heat capacity of the mixture ($C_{p,mixture}$, in J·g^{-1}·K^{-1}). The calculation follows the standard thermodynamic relationship:

$$\Delta T_{AD} = \frac{Q}{m_{\mathrm{total}} \times C_{p,\mathrm{mixture}}}$$

This expression provides the theoretical maximum temperature increase assuming no heat loss to the surroundings, allowing the estimation of the intrinsic thermal hazard of the system. This approach is commonly used in preliminary thermal screening to evaluate potential runaway risks.[67]

The specific heat capacity (C_p) of the reaction system was determined at temperatures of 42 and 90 °C, which were the regions of the DSC trace that were free from exothermic or endothermic events. Measurements included two independent baselines, two sapphire standards, and two separately prepared reaction mixtures (1 equiv. diphenylamine, 1 equiv. 1-bromopyrene, 2 equiv. NaOtBu, and THF in an amount as close to 0.25 µL·mg^{-1} as could be achieved by adding the liquid directly into the DSC pan before sealing). This leads to six baseline–sapphire–mixture combinations, which were all explored to calculate the average specific heat capacity (C_p). At 42 °C, C_p values ranged from 1.488 to 1.699 J·g^{-1}·K^{-1}, giving an average of 1.578 ± 0.0788 J·g^{-1}·K^{-1}. At 90 °C, the measured C_p values ranged from 1.819 to 1.8911 J·g^{-1}·K^{-1}, resulting in an average of 1.852 ± 0.030 J·g^{-1}·K^{-1}. These C_p values were subsequently used for calculating the adiabatic temperature rise and assessing the thermal profile of the reaction. The C_p measurements were conducted using the following thermal program: a 5-min isothermal hold at 20 °C, heating from 20 to 200 °C at 20 °C·min^{-1}, followed by a 5-min hold at 200 °C.

To determine the total heat release (Q) associated with the exothermic events of the coupling reaction, DSC experiments were carried out at two heating rates (1 and 2 °C min^{-1}) and using samples of different total masses. The heating rates were slower than for the calculation of C_p, with the intention to provide more time for the reaction to proceed – attempts to perform the experiments at a faster heating rates led to observation of interfering endothermic event of melting of the 1-bromopyrene reactant. At heating rates of 1 and 2 °C min^{-1} this event was also observable, but was less pronounced. The reaction mixture consisted of 1 equiv. diphenylamine, 1 equiv. 1-bromopyrene, 2 equiv. NaO*t*Bu, 3 mol% XPhos Pd G1, and THF in the amount as close as possible to 0.25 µL·mg^{-1}. A total of four independent DSC runs were performed (two cycles at 2 °C min^{-1}, 2 experiments; one cycles at 1 °C min^{-1}, 2 experiments). The total sample mass in each experiment ranged from 24.4 to 33.3 mg (see Table S15). The measured enthalpy of reaction (ΔH_{total}) varied from 236.7 to 254.4 J·g^{-1}, corresponding to total heat release (Q) in the range 4.13–5.90 J, depending on sample mass.

The total heat release was determined using one of two DSC methods:
(1) a full heat–cool–heat cycle consisting of:

- 5-min hold at 20 °C,
- heating from 20 to 200 °C at 2 °C·min^{-1},
- 5-min hold at 200 °C,
- cooling to 20 °C at 2 °C·min^{-1},
- 5-min hold at 20 °C,
- heating from 20 to 200 °C at 2 °C·min^{-1},
- 5-min hold at 200 °C.

Or (2) a single-heating program consisting of:

- 5-min hold at 20 °C,
- heating from 20 to 150 °C at 1 °C·min^{-1},
- 5-min hold at 150 °C.

Using the average C_p at 42 °C (1.578 ± 0.0788 J·g^{-1}·K^{-1}), the calculated average adiabatic temperature rise (ΔT_{AD}) was 110.3 ± 3.8 K. When using the average C_p at 90 °C (1.852 ± 0.030 J·g^{-1}·K^{-1}), ΔT_{AD} decreased to 94.0 ± 3.3 K (individual values are reported in Table S15).

Table S15. Summary of DSC measurements for the reactive mixture. The total sample mass (m_{total}) includes all components of the reaction mixture (1 equiv. diphenylamine, 1 equiv. 1-bromopyrene, 2 equiv. NaOtBu and THF in the amount as close as possible to η = 0.25 µL/mg), while the reactive mass ($m_{reactive}$) corresponds only to the stoichiometric reactants responsible for the exothermic reaction (1 equiv. diphenylamine, 1 equiv. 1-bromopyrene, 1 equiv. NaOtBu). The table reports the total reaction enthalpy (ΔH_{total}, J·g^{-1}), total heat release (Q, J), and the calculated adiabatic temperature rise (ΔT_{AD}) using the average C_p at 42 °C and 90 °C for four independent DSC experiments: 2 °C·min^{-1} test 1, 2 °C·min^{-1} test 2, 1 °C·min^{-1} test 1, and 1 °C·min^{-1} test 2.

Experiment	2°C/min test 1	2°C/min test 2	1°C/min test 1	1°C/min test 2	Mean
m_{total} (mg)	25.9	24.4	25.1	33.3	
$m_{reactive}$ (mg)	18.3	17.4	17.9	23.2	
ΔH_{total} (J/g)	256.2	237.4	236.7	254.4	241.3 $\pm$ 7.6 J/g
Q (J)	4.69	4.13	4.24	5.90	
ΔT_{AD} (K) (at 42 °C)	114.7	107.3	107.0	112.3	110.3 $\pm$ 3.8 K
ΔT_{AD} (K) (at 90 °C)	97.8	91.4	91.2	95.7	94.0 $\pm$ 3.3 K

S9. Buchwald-Hartwig coupling of 3,5-dimethoxyaniline with 2 equivalents of either 3-bromotoluene or 4-bromobenzonitrile

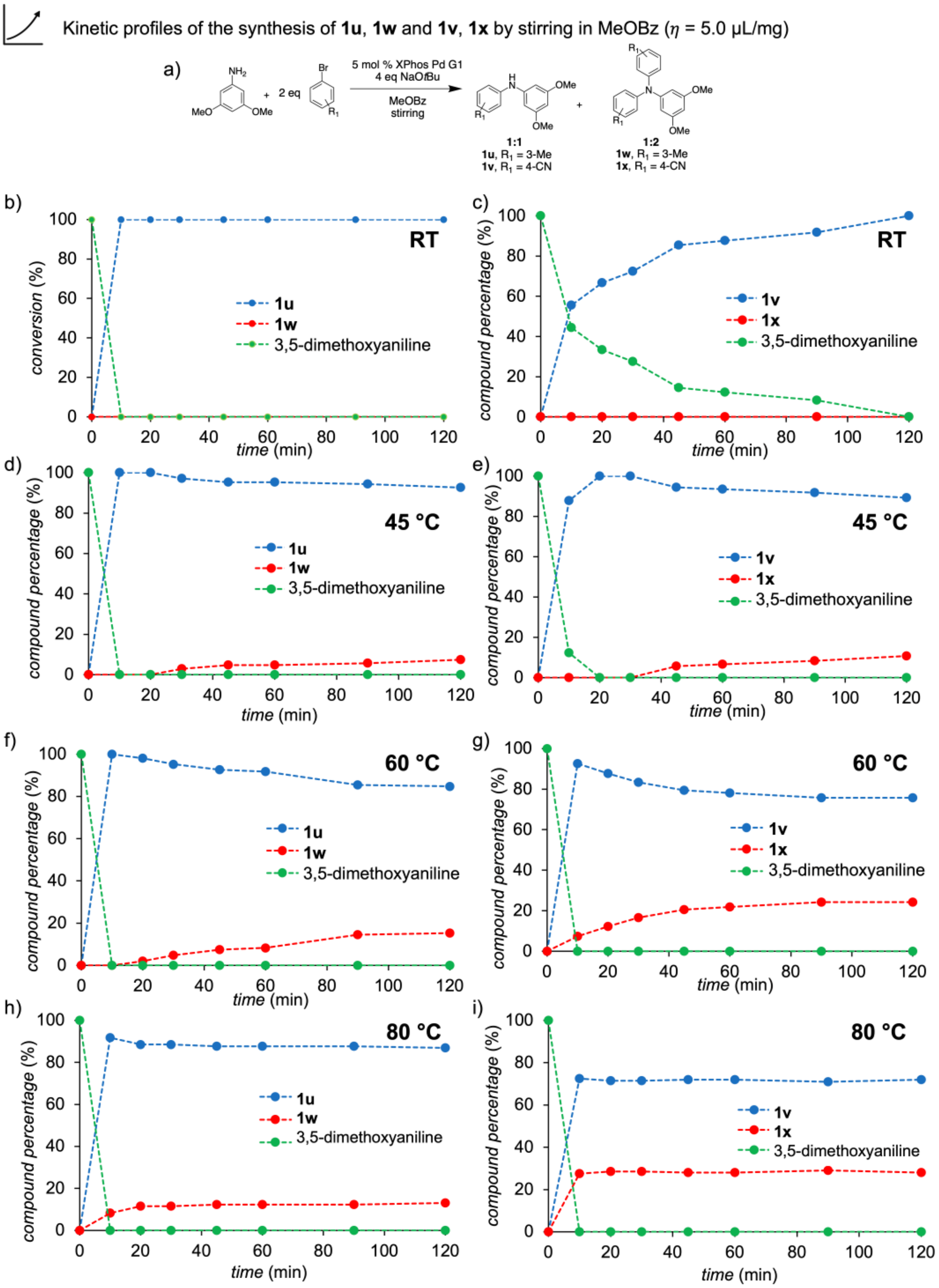


Figure S42. a) Buchwald-Hartwig coupling between 3,5-dimethoxyaniline and 2 equivalents 3-bromotoluene or 4-bromobenzonitrile for the synthesis of **1u**-**1x** by stirring with a magnetic bar at 600 rpm in MeOBz ($\eta = 5.0$ µL/mg) at b,c) room temperature, d,e) 45 °C, f,g) 60 °C. and h,i) 80 °C.

After one day:

- 45 °C: 81 % of **1u** and 19 % of **1w**, 68 % of **1v** and 32 % of **1x**
- 60 °C: 85 % of **1u** and 15 % of **1w**, 76 % of **1v** and 24 % of **1x**

Table S16. Relative amount of 3,5-dimethoxyaniline, **1u** and **1w** for the Buchwald-Hartwig coupling by stirring (600 rpm) in MeOBz (η = 5.0 µL/mg) at room temperature. This data is represented graphically in Figure S18a.

time (min)	0	10	20	30	45	60	90	120
3,5-dimethoxyaniline (%)	100	0	0	0	0	0	0	0
1u (%)	0	100	100	100	100	100	100	100
1w (%)	0	0	0	0	0	0	0	0

Table S17. Relative amount of 3,5-dimethoxyaniline, **1v** and **1x** for the Buchwald-Hartwig coupling by stirring (600 rpm) in MeOBz (η = 5.0 µL/mg) at room temperature. This data is represented graphically in Figure S18b.

time (min)	0	10	20	30	45	60	90	120
3,5-dimethoxyaniline (%)	100	44	33	28	15	12	8	0
1v (%)	0	56	67	72	85	88	92	100
1x (%)	0	0	0	0	0	0	0	0

Table S18. Relative amount of 3,5-dimethoxyaniline, **1u** and **1w** for the Buchwald-Hartwig coupling by stirring (600 rpm) in MeOBz (η = 5.0 µL/mg) at 45 °C. This data is represented graphically in Figure S18c.

time (min)	0	10	20	30	45	60	90	120
3,5-dimethoxyaniline (%)	100	0	0	0	0	0	0	0
1u (%)	0	100	100	97	95	95	94	93
1w (%)	0	0	0	3	5	5	6	7

Table S19. Relative amount of 3,5-dimethoxyaniline, **1v** and **1x** for the Buchwald-Hartwig coupling by stirring (600 rpm) in MeOBz (η = 5.0 µL/mg) at 45 °C. This data is represented graphically in Figure S18d.

time (min)	0	10	20	30	45	60	90	120
3,5-dimethoxyaniline (%)	100	12	0	0	0	0	0	0
1v (%)	0	88	100	100	94	93	92	89
1x (%)	0	0	0	0	6	7	8	11

Table S20. Relative amount of 3,5-dimethoxyaniline, **1u** and **1w** for the Buchwald-Hartwig coupling by stirring (600 rpm) in MeOBz (η = 5.0 µL/mg) at 60 °C. This data is represented graphically in Figure S18e.

time (min)	0	10	20	30	45	60	90	120
3,5-dimethoxyaniline percentage (%)	100	0	0	0	0	0	0	0
1u percentage (%)	0	100	98	95	93	92	85	85
1w percentage (%)	0	0	2	5	7	8	15	15

Table S21. Relative amount of 3,5-dimethoxyaniline, **1v** and **1x** for the Buchwald-Hartwig coupling by stirring (600 rpm) in MeOBz (η = 5.0 µL/mg) at 60 °C. This data is represented graphically in Figure S18f.

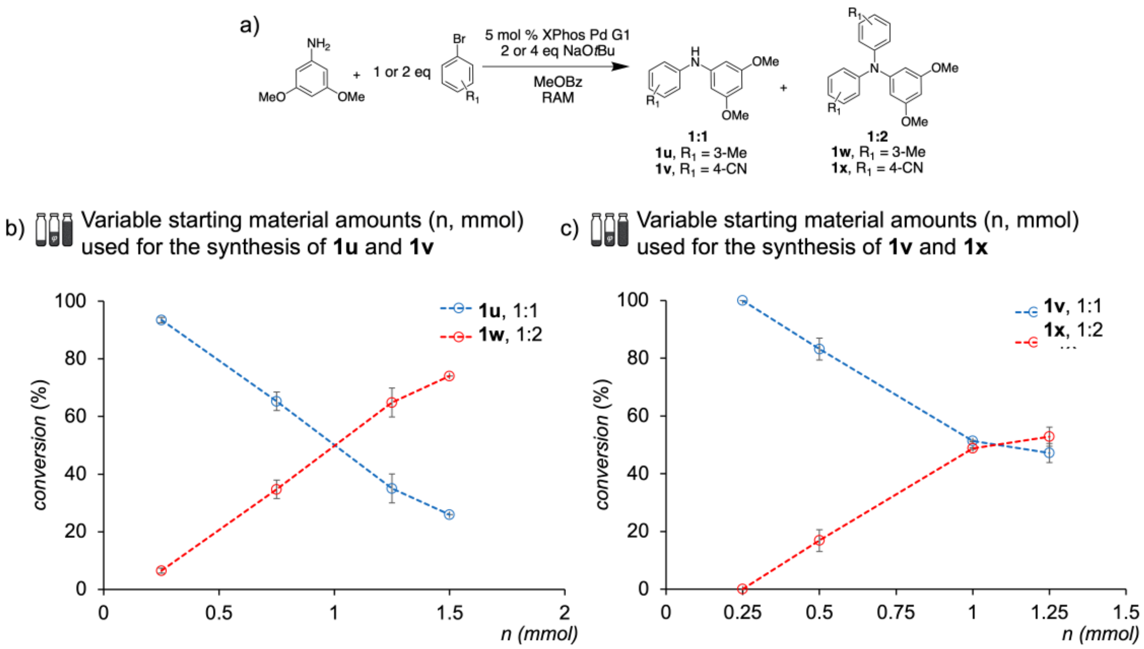
time (min)	0	10	20	30	45	60	90	120
3,5-dimethoxyaniline (%)	100	0	0	0	0	0	0	0
1v (%)	0	93	88	83	79	78	76	76
1x (%)	0	7	12	17	21	22	24	24

Table S22. Relative amount of 3,5-dimethoxyaniline, **1u** and **1w** for the Buchwald-Hartwig coupling by stirring (600 rpm) in MeOBz (η = 5.0 µL/mg) at 80 °C. This data is represented graphically in Figure S18g.

time (min)	0	10	20	30	45	60	90	120
3,5-dimethoxyaniline (%)	100	0	0	0	0	0	0	0
1u (%)	0	92	88	88	88	88	88	87
1w (%)	0	8	12	12	12	12	12	13

Table 23. Relative amount of 3,5-dimethoxyaniline, **1v** and **1x** for the Buchwald-Hartwig coupling by stirring (600 rpm) in MeOBz (η = 5.0 µL/mg) at 80 °C. This data is represented graphically in Figure S18h.

time (min)	0	10	20	30	45	60	90	120
3,5-dimethoxyaniline (%)	100	0	0	0	0	0	0	0
1v (%)	0	72	71	71	71	71	71	71
1x (%)	0	28	29	29	29	29	29	29



b) Variable starting material amounts (n, mmol) used for the synthesis of **1u** and **1v**

c) Variable starting material amounts (n, mmol) used for the synthesis of **1v** and **1x**

Figure S43. Stoichiometric selectivity of the Buchwald-Hartwig amination reaction using RAM: a) the model coupling reaction and b) formation of the 1:1 or 2:1 coupling products with 3,5-dimethoxyaniline as a function of the amount of reagents (mmol), following RAM at 100 *g* for 2 hours with MeOBz as liquid additive for: b) 3-bromotoluene at η = 0.25 µL/mg, and: c) 4-bromobenzonitrile at η = 0.75 µL/mg.

Table S24. Change in ^{1}H NMR for Buchwald-Hartwig coupling in RAM for the synthesis of **1u** and **1w** with MeOBz (η = 0.25 µL/mg) after 2 hours at 100 *g*, with respect to the amount of reagents (mmol). This data is represented graphically in Figure S19b.

amount of reagents (mmol)	0.25	0.75	1.25	1.50
conversion **1u**/**1w** (%)	93/7 ± 1	65/35 ± 3	35/65 ± 5	26/74 ± 0

Table S25. Change in ^{1}H NMR for Buchwald-Hartwig coupling in RAM for the synthesis of **1v** and **1x** with MeOBz (η = 0.75 µL/mg) after 2 hours at 100 *g*, with respect to the amount of reagents (mmol). This data is represented graphically in Figure S19c.

amount of reagents (mmol)	0.25	0.50	1.00	1.25
conversion **1v**/**1x** (%)	100/0 ± 0	83/17 ± 4	51/49 ± 0	47/53 ± 3

S10. Single-crystal X-ray diffraction

Table 26. Crystal data and structure refinement for compounds **1v** and **1x**.

CCDC code	**2372359** (compound **1x**)	**2372358** (compound **1v**)
Empirical formula	$C_{30}H_{28}N_4O_4$	$C_{22}H_{17}N_3O_2$
Formula weight	508.56	355.399
Temperature/K	200.15	200
Crystal system	orthorhombic	monoclinic
Space group	*Pbca*	$P2_1/n$
a (Å)	16.1961(6)	8.30331(16)
b (Å)	8.0577(3)	18.9779(3)
c (Å)	19.9095(7)	11.9497(2)
α (°)	90	90
β (°)	90	106.553(2)
γ (°)	90	90
V/Å^3	2598.26(16)	1804.99(6)
Z	4	4
ρ_{calc} (g/cm^3)	1.300	1.308
μ (mm^{-1})	0.712	0.086
F(000)	1072.0	744.5
Radiation	CuK_α (λ = 1.54184 Å)	MoK_α (λ = 0.71073 Å)
Independent reflections	2675 [R_{int} = 0.0239, R_{sigma} = 0.0239]	3607 [R_{int} = 0.0273, R_{sigma} = 0.0179]
Data/restraints/parameters	2675/0/176	3607/0/269
Goodness-of-fit on F^2	1.038	1.043
Final R indices [I>=2σ (I)]	R_1 = 0.0364, wR_2 = 0.0906	R_1 = 0.0374, wR_2 = 0.0985
Final R indices [all data]	R_1 = 0.0473, wR_2 = 0.0984	R_1 = 0.0399, wR_2 = 0.1004
Largest diff. peak/hole / e Å^{-3}	0.15/-0.17	0.19/-0.23

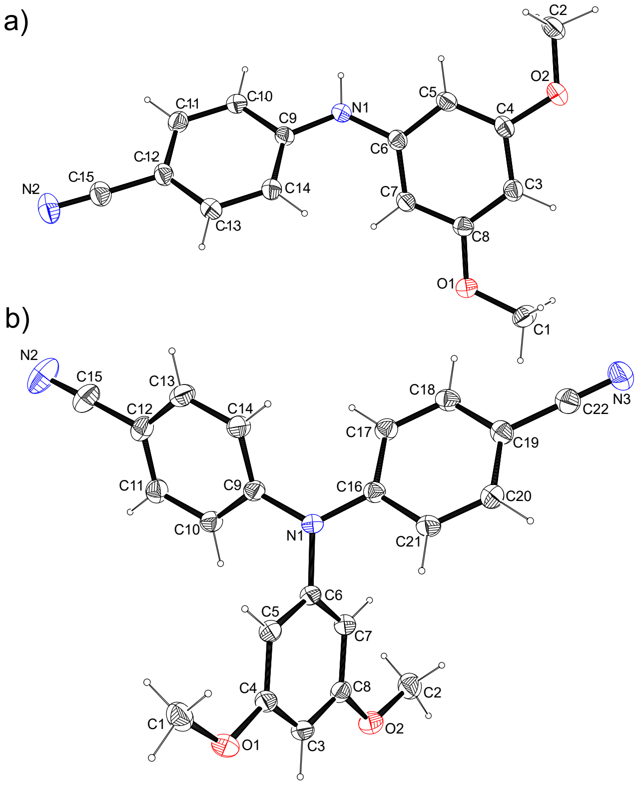


Figure 44. ORTEP representation of the asymmetric unit of a) **1v** and b) **1w** with atoms shown as thermal ellipsoids corresponding to 30 % probability of electron density.

S11. Reaction data for studies illustrated in the manuscript

Table S27. Change in ^{1}H NMR conversion for Buchwald-Hartwig coupling in RAM for the synthesis of **1a** with THF and MeOBz as the liquid additive ($\eta = 0.25$ µL/mg) after 1 hour of RAM at 60 *g*, with respect to the filling ratio (φ). This data is represented graphically in the manuscript, Figure 2a.

approximate φ (%)	12	33	55	70	80
conversion with THF (%)	28 ± 1	33 ± 2	52 ± 0	59 ± 1	88 ± 5
conversion with MeOBz (%)	10 ± 6	30 ± 0	36 ± 0.5	41 ± 1	51± 2

Table S28. Change in ^{1}H NMR conversion for Buchwald-Hartwig coupling in RAM for the synthesis of **1b** with THF as the liquid additive ($\eta = 0.25$ or 0.50 µL/mg) after 1 hour of RAM at 60 *g*, with respect to the filling ratio (φ). This data is represented graphically in the manuscript, Figure 2b.

approximate φ (%)	12	33	55	70	80
conversion of **1b** (%) at $\eta = 0.25$ µL/mg	1 ± 1	4 ± 0.5	8 ± 0.5	15 ± 0	17 ± 1
conversion of **1b** (%) at $\eta = 0.50$ µL/mg	15 ± 0	18 ± 1	27 ± 3	39 ± 2	63 ± 2

Table S29. Change in ^{1}H NMR conversion for Buchwald-Hartwig coupling in RAM for the synthesis of **1c** with THF as the liquid additive ($\eta = 0.25$ µL/mg) after 1 hour of RAM at 60 *g*, with respect to the filling ratio (φ). This data is represented graphically in the manuscript, Figure 2c.

approximate φ (%)	12	33	55	70	80
conversion of **1c** (%) at $\eta = 0.25$ µL/mg	13 ± 0	34 ± 3	68 ± 4	96 ± 0	96 ± 0

Table S30. Change in ^{1}H NMR for Buchwald-Hartwig coupling in RAM for the synthesis of **1u** and **1w** with MeOBz ($\eta = 0.25$ µL/mg) after 2 hours at 100 *g*, with respect to the filling ratio (φ). This data is represented graphically in the manuscript, Figure 8b.

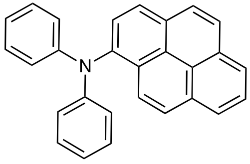
approximate φ (%)	15	35	57	80
conversion **1u**/**1w** (%)	93/7 ± 1	65/35 ± 3	35/65 ± 5	26/74 ± 0

Table S31. Change in ^{1}H NMR for Buchwald-Hartwig coupling in RAM for the synthesis of **1v** and **1x** with MeOBz ($\eta = 0.75$ µL/mg) after 2 hours at 100 *g*, with respect to the filling ratio (φ). This data is represented graphically in the manuscript, Figure 8c.

approximate φ (%)	12	35	57	80
conversion **1v**/**1x** (%)	100/0 ± 0	83/17 ± 4	51/49 ± 0	47/53 ± 3

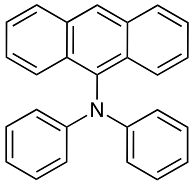
S12. Summary of ^{1}H and ^{13}C NMR and HR-MS Data

N,*N*-diphenylpyren-1-amine **1a**



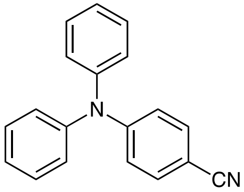
Green solid, isolated yield = 93 %. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.17 (dd, *J* = 8.8, 6.8 Hz, 3H), 8.12 (dd, *J* = 7.7, 1.1 Hz, 1H), 8.07 (s, 2H), 7.99 (t, *J* = 7.6 Hz, 1H), 7.94 (d, *J* = 9.2 Hz, 1H), 7.85 (d, *J* = 8.2 Hz, 1H), 7.24 – 7.19 (m, 4H), 7.11-7.07 (m, 4H), 6.96 (tt, *J* = 7.3, 1.2 Hz, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 148.8, 141.1, 131.4, 131.2, 129.7, 129.3, 128.4, 128.0, 127.8, 127.4, 127.2, 126.5, 126.3, 126.1, 125.3, 125.2, 125.0, 123.5, 122.2, 121.9. HR-MS ESI (+): calculated for $C_{28}H_{20}N$ $[M + H]^+$: 370.1596; measured: 370.1602.

N,*N*-diphenylanthracen-9-amine **1b**



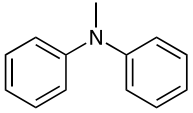
Green-yellow solid, isolated yield = 92 %. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.51 (s, 1H), 8.12 (d, *J* = 8.7 Hz, 2H), 8.06 (d, *J* = 8.3 Hz, 2H), 7.47 – 7.37 (m, 4H), 7.15 (tt, *J* = 7.2, 2.1 Hz, 4H), 7.09 – 7.06 (m, 4H), 6.87 (tt, *J* = 7.2, 1.2 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.9, 137.4, 132.9, 130.8, 129.3, 129.0, 127.0, 126.9, 125.6, 124.5, 121.3, 120.4. HR-MS ESI (+): calculated for $C_{26}H_{20}N$ $[M + H]^+$: 346.1596; measured: 346.1623.

4-(diphenylamino)benzonitrile **1c**



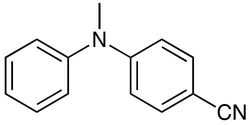
White solid, isolated yield = 90 %. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.43 – 7.40 (m, 2H), 7.36 – 7.31 (m, 4H), 7.18 – 7.13 (m, 6H), 6.98 – 6.94 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 151.8, 146.1, 133.3, 129.9, 126.3, 125.3, 119.9, 119.9, 102.6. HR-MS ESI (+): calculated for $C_{19}H_{15}N_2$ $[M + H]^+$: 271.1235; measured: 271.1264.

N-methyl-*N*-phenylaniline **1d**



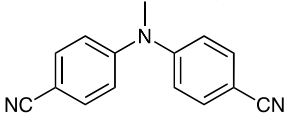
Yellow oil, isolated yield = 90 %. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.31 – 7.27 (m, 4H), 7.06 – 7.02 (m, 4H), 6.97 (tt, *J* = 7.3, 1.1 Hz, 2H), 3.33 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 149.2, 129.3, 121.4, 120.6, 40.4. HR-MS ESI (+): calculated for $C_{13}H_{14}N$ $[M + H]^+$: 184.1126; measured: 184.1125.

4-(methyl(phenyl)amino)benzonitrile **1e**



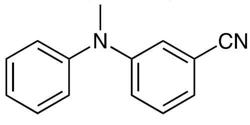
Yellow oil, isolated yield = 92 %. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.45 – 7.40 (m, 4H), 7.28 – 7.24 (m, 1H), 7.22 – 7.18 (m, 2H), 6.72 (d, *J* = 9.1 Hz, 2H), 3.35 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 152.1, 146.9, 133.4, 130.2, 126.6, 126.3, 120.5, 114.0, 99.5, 40.3. HR-MS ESI (+): calculated for $C_{14}H_{13}N_2$ $[M + H]^+$: 209.1079; measured: 209.1087.

4,4'-(methylazanediyl)dibenzonitrile **1f**



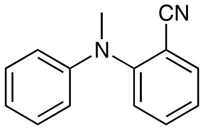
White solid, isolated yield = 44 %. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.60 – 7.57 (m, 4H), 7.13 – 7.09 (m, 4H), 3.42 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 150.8, 133.8, 120.8, 119.2, 105.3, 40.1. HR-MS ESI (+): calculated for $C_{15}H_{12}N_3$ [M + H]$^+$: 234.1031; measured: 234.1044.

3-(methyl(phenyl)amino)benzonitrile **1g**



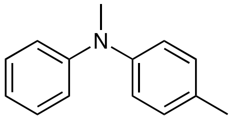
Yellow oil, isolated yield = 92 %. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.41 – 7.36 (m, 2H), 7.25 (t, *J* = 8.1 Hz, 1H), 7.21 – 7.13 (m, 3H), 7.07 – 7.02 (m, 3H), 3.32 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 149.5, 147.6, 130.0, 129.8, 125.0, 124.9, 122.0, 120.2, 119.5, 118.8, 112.9, 40.3. HR-MS ESI (+): calculated for $C_{14}H_{13}N_2$ [M + H]$^+$: 209.1079; measured: 209.1087.

2-(methyl(phenyl)amino)benzonitrile **1h**



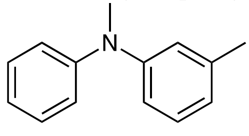
Yellow oil, isolated yield = 89 %. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.64 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.54 (ddd, *J* = 8.3, 7.4, 1.7 Hz, 1H), 7.31 – 7.24 (m, 3H), 7.18 (td, *J* = 7.6, 1.1 Hz, 1H), 6.96 (tt, *J* = 7.4, 1.1 Hz, 1H), 6.90 – 6.88 (m, 2H), 3.41 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 152.6, 148.6, 134.7, 134.0, 129.4, 125.8, 124.1, 121.2, 118.2, 117.7, 109.4, 41.0. HR-MS ESI (+): calculated for $C_{14}H_{13}N_2$ [M + H]$^+$: 209.1079; measured: 209.1087.

N,4-dimethyl-*N*-phenylaniline **1i**



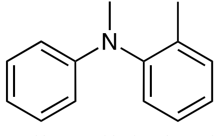
Yellow oil, isolated yield = 90 %. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.25 – 7.20 (m, 2H), 7.14 – 7.10 (m, 2H), 7.02 – 6.98 (m, 2H), 6.94 – 6.91 (m, 2H), 6.87 (tt, *J* = 7.3, 1.1 Hz, 1H), 3.29 (s, 3H), 2.33 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 149.5, 146.7, 132.2, 130.1, 129.2, 122.7, 119.9, 118.3, 40.5, 20.9. HR-MS ESI (+): calculated for $C_{14}H_{16}N$ [M + H]$^+$: 198.1283; measured: 198.1308.

N,3-dimethyl-*N*-phenylaniline **1j**



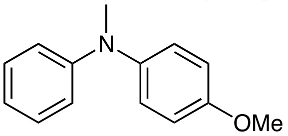
Yellow oil, isolated yield = 92 %. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.32 – 7.27 (m, 2H), 7.19 (t, *J* = 7.7 Hz, 1H), 7.05 – 7.02 (m, 2H), 6.97 (tt, *J* = 7.2, 1.1 Hz, 1H), 6.89 – 6.86 (m, 2H), 6.83 – 6.81 (m, 1H), 3.33 (s, 3H), 2.33 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 149.3, 149.2, 139.1, 129.3, 129.2, 122.5, 121.6, 121.1, 120.2, 118.1, 40.4, 21.7. HR-MS ESI (+): calculated for $C_{14}H_{16}N$ [M + H]$^+$: 198.1283; measured: 198.1304.

N,2-dimethyl-*N*-phenylaniline **1k**



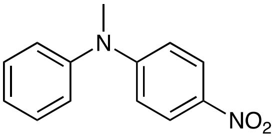
Yellow oil, isolated yield = 91 %. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.33 – 7.15 (m, 6H), 6.73 (tdt, *J* = 7.3, 2.6, 1.1 Hz, 1H), 6.58 – 6.54 (m, 2H), 3.25 (s, 3H), 2.17 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 149.3, 146.9, 137.0, 131.5, 129.1, 128.5, 127.6, 126.5, 116.9, 113.0, 39.2, 18.0. HR-MS ESI (+): calculated for $C_{14}H_{16}N$ [M + H]$^+$: 198.1283; measured: 198.1256.

4-methoxy-*N*-methyl-*N*-phenylaniline **1l**



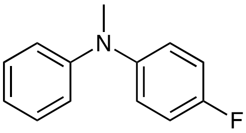
Yellow oil, isolated yield = 93 %. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.25 – 7.19 (m, 2H), 7.14 – 7.10 (m, 2H), 6.94 – 6.90 (m, 2H), 6.83 – 6.79 (m, 3H), 3.83 (s, 3H), 3.28 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 156.4, 149.9, 142.4, 129.0, 126.3, 118.5, 115.9, 114.9, 55.6, 40.6. HR-MS ESI (+): calculated for $C_{14}H_{16}NO$ $[M + H]^+$: 214.1232; measured: 214.1239.

N-methyl-4-nitro-*N*-phenylaniline **1m**



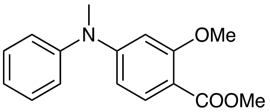
Yellow solid, isolated yield = 91 %. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.08 – 8.04 (m, 2H), 7.48 – 7.43 (m, 2H), 7.33 – 7.29 (m, 1H), 7.25 – 7.21 (m, 2H), 6.69 – 6.65 (m, 2H), 3.41 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 153.9, 146.5, 138.3, 130.4, 126.9, 126.8, 125.9, 112.6, 40.7. HR-MS ESI (+): calculated for $C_{13}H_{13}N_2O_2$ $[M + H]^+$: 229.0977; measured: 229.0968.

4-fluoro-*N*-methyl-*N*-phenylaniline **1n**



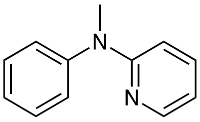
Yellow oil, isolated yield = 87 %. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.27 – 7.21 (m, 2H), 7.06 – 6.97 (m, 4H), 6.90 – 6.86 (m, 3H), 3.27 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 160.0, 157.6, 149.4, 145.4, 145.4, 129.3, 124.4, 124.3, 120.2, 118.2, 116.2, 116.0, 40.7. HR-MS ESI (+): calculated for $C13H_{13}FN$ $[M + H]^+$: 202.1032; measured: 202.1003.

methyl 2-methoxy-4-(methyl(phenyl)amino)benzoate **1o**



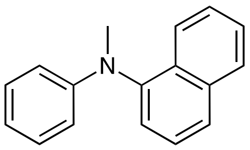
White solid, isolated yield= 75 %. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.75 (d, *J* = 8.8 Hz, 1H), 7.42 – 7.37 (m, 2H), 7.23 – 7.19 (m, 3H), 6.35 (dd, *J* = 8.8, 2.3 Hz, 1H), 6.29 (d, *J* = 2.3 Hz, 1H), 3.83 (s, 3H), 3.78 (s, 3H), 3.36 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.4, 161.4, 153.9, 147.5, 133.6, 129.9, 126.1, 125.5, 108.8, 106.7, 98.2, 55.9, 51.6, 40.4. HR-MS ESI (+): calculated for $C_{16}H_{18}NO_3$ $[M + H]^+$: 272.1287; measured: 272.1334.

N-methyl-*N*-phenylpyridin-2-amine **1p**



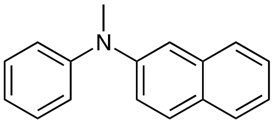
Colorless oil, isolated yield = 84 %. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.22 (ddd, *J* = 5.0, 2.0, 0.9 Hz, 1H), 7.41 – 7.36 (m, 2H), 7.31 – 7.23 (m, 3H), 7.22 – 7.18 (m, 1H), 6.59 (ddd, *J* = 7.1, 5.0, 0.9 Hz, 1H), 6.52 (dt, *J* = 8.6, 0.9 Hz, 1H), 3.47 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 159.0, 147.9, 147.0, 136.7, 129.8, 126.5, 125.6, 113.2, 109.3, 38.5. HR-MS ESI (+): calculated for $C_{12}H_{13}N_2$ $[M + H]^+$: 185.1079; measured: 185.1079.

N-methyl-*N*-phenylnaphthalen-1-amine **1q**



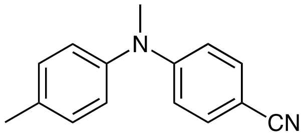
Yellow oil, isolated yield = 89 %. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.92 (tdt, *J* = 9.2, 1.6, 0.8 Hz, 2H), 7.81 (dt, *J* = 8.3, 1.1 Hz, 1H), 7.54 – 7.50 (m, 2H), 7.45 (ddd, *J* = 8.2, 6.8, 1.4 Hz, 1H), 7.39 (dd, *J* = 7.3, 1.2 Hz, 1H), 7.21 – 7.16 (m, 2H), 6.76 (tt, *J* = 7.3, 1.1 Hz, 1H), 6.68 – 6.61 (m, 2H), 3.42 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 150.2, 145.5, 135.3, 131.5, 129.1, 128.6, 126.8, 126.6, 126.5, 126.4, 125.4, 124.0, 117.3, 113.7, 40.3. HR-MS ESI (+): calculated for $C_{17}H_{16}N$ [M + H]$^+$: 234.1283; measured: 234.1311.

N-methyl-*N*-phenylnaphthalen-2-amine **1r**



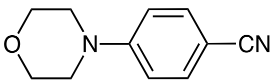
Yellow oil, isolated yield = 90 %. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.79 – 7.70 (m, 3H), 7.45 (ddd, *J* = 8.3, 6.8, 1.3 Hz, 1H), 7.38 – 7.32 (m, 4H), 7.25 (dd, *J* = 8.9, 2.3 Hz, 1H), 7.16 – 7.13 (m, 2H), 7.09 – 7.02 (m, 1H), 3.46 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 149.2, 146.7, 134.8, 129.4, 129.3, 128.7, 127.7, 126.9, 126.4, 123.8, 122.1, 121.9, 121.5, 114.7, 40.7. HR-MS ESI (+): calculated for $C_{17}H_{16}N$ [M + H]$^+$: 234.1283; measured: 234.1245.

4-(methyl(*p*-tolyl)amino)benzonitrile **1s**



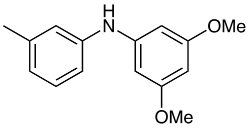
Yellow oil, isolated yield = 93 %. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.42 – 7.38 (m, 2H), 7.25 – 7.21 (m, 2H), 7.10 – 7.07 (m, 2H), 6.70 – 6.66 (m, 2H), 3.32 (s, 3H), 2.38 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 152.3, 144.3, 136.4, 133.3, 130.8, 126.7, 120.6, 113.5, 99.0, 40.3, 21.1. HR-MS ESI (+): calculated for $C_{15}H_{15}N_2$ [M + H]$^+$: 223.1252; measured: 234.1311.

4-morpholinobenzonitrile **1t**



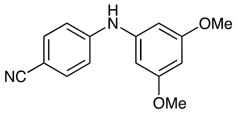
Yellow solid, isolated yield = 39 %. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.52 – 7.49 (m, 2H), 6.87 – 6.84 (m, 2H), 3.86 – 3.83 (m, 4H), 3.28 – 3.26 (m, 4H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 153.6, 133.6, 120.0, 114.2, 101.1, 66.6, 47.4. HR-MS ESI (+): calculated for $C_{11}H_{13}N_2O$ [M + H]$^+$: 189.1028; measured: 189.1015.

3,5-dimethoxy-*N*-(*m*-tolyl)aniline **1u**



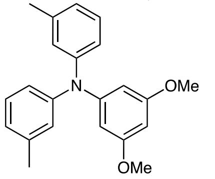
Yellow oil, isolated yield = 94 %. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.18 – 7.14 (m, 1H), 6.94 – 6.91 (m, 2H), 6.79 – 6.77 (m, 1H), 6.23 (d, *J* = 2.2 Hz, 2H), 6.06 (t, *J* = 2.2 Hz, 1H), 3.76 (s, 6H), 2.32 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 161.8, 145.5, 142.7, 139.4, 129.3, 122.5, 119.7, 116.0, 96.0, 93.0, 55.4, 21.7. HR-MS ESI (+): calculated for $C_{15}H_{18}NO_2$ [M + H]$^+$: 244.1338; measured: 244.1389.

4-((3,5-dimethoxyphenyl)amino)benzonitrile **1v**



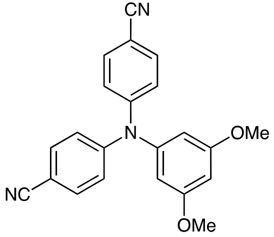
White solid, isolated yield = 92 %. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.51 – 7.47 (m, 2H), 7.03 – 7.00 (m, 2H), 6.31 (d, *J* = 2.2 Hz, 2H), 6.22 (t, *J* = 2.2 Hz, 1H), 6.00 (s, 1H), 3.78 (s, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 161.9, 147.7, 142.1, 133.9, 130.3, 128.6, 119.9, 115.8, 102.1, 99.3, 95.8, 55.6. HR-MS ESI (+): calculated for $C_{15}H_{15}N_2O_2$ [M + H]$^+$: 255.1134; measured: 255.1154.

3,5-dimethoxy-*N*,*N*-di-*m*-tolylaniline **1w**



Yellow oil, yield = 60%, ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.14 (t, *J* = 7.7 Hz, 2H), 6.94 – 6.89 (m, 4H), 6.86 – 6.83 (m, 2H), 6.21 (d, *J* = 2.2 Hz, 2H), 6.14 (t, *J* = 2.2 Hz, 1H), 3.70 (s, 6H), 2.27 (s, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 161.3, 150.1, 147.7, 139.1, 129.1, 125.5, 124.0, 122.1, 102.2, 94.6, 55.4, 21.6. HR-MS ESI (+): calculated for $C_{22}H_{24}NO_2$ [M + H]$^+$: 334.1807; measured: 334.1857.

4,4'-((3,5-dimethoxyphenyl)azanediyl)dibenzonitrile **1x**



White solid, yield = 50%, ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.54 – 7.51 (m, 4H), 7.14 – 7.10 (m, 4H), 6.36 (t, *J* = 2.2 Hz, 1H), 6.23 (d, *J* = 2.2 Hz, 2H), 3.73 (s, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 162.2, 150.1, 146.8, 133.6, 123.1, 119.0, 106.0, 105.4, 98.5, 55.7. HR-MS ESI (+): calculated for $C_{22}H_{18}N_3O_2$ [M + H]$^+$: 356.1399; measured: 356.1392.

S13. ^{1}H and ^{13}C NMR data for isolated products 1a-1x

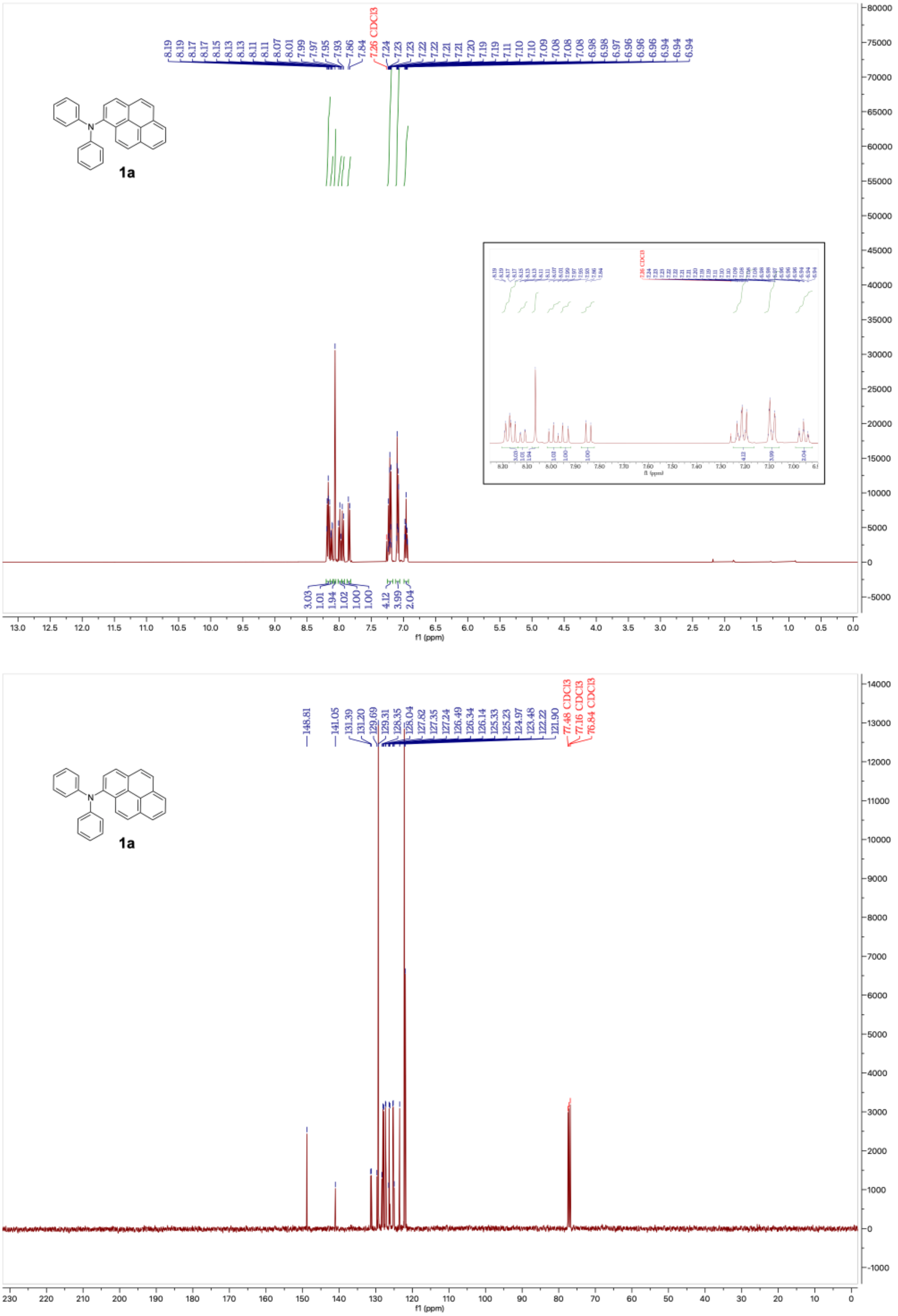


Figure 45. (top) ^{1}H and (bottom) ^{13}C NMR spectra for isolated compound **1a**, synthesized by RAM.

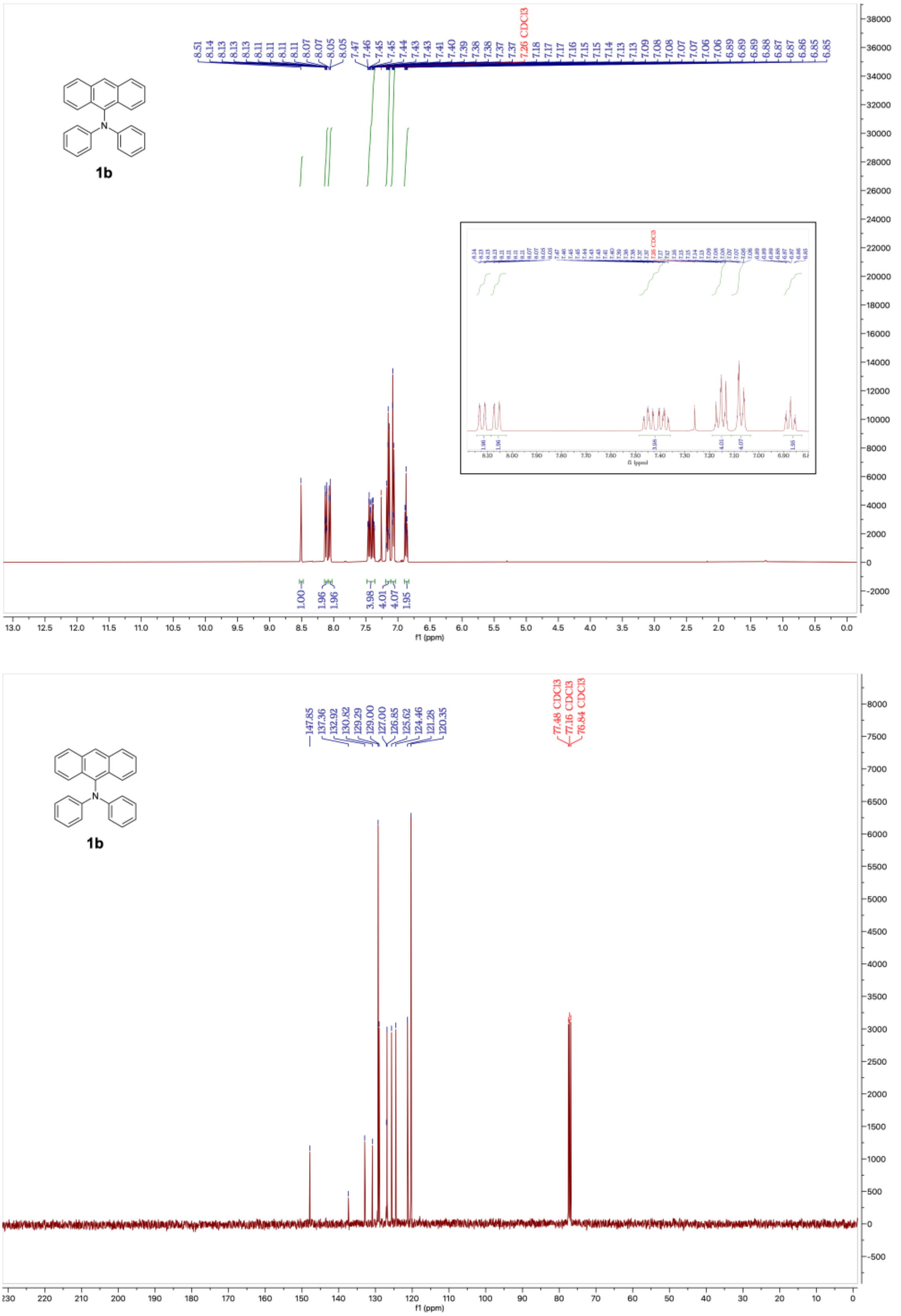


Figure S46. (top) ^{1}H and (bottom) ^{13}C NMR spectra for isolated compound **1b**, synthesized by RAM.

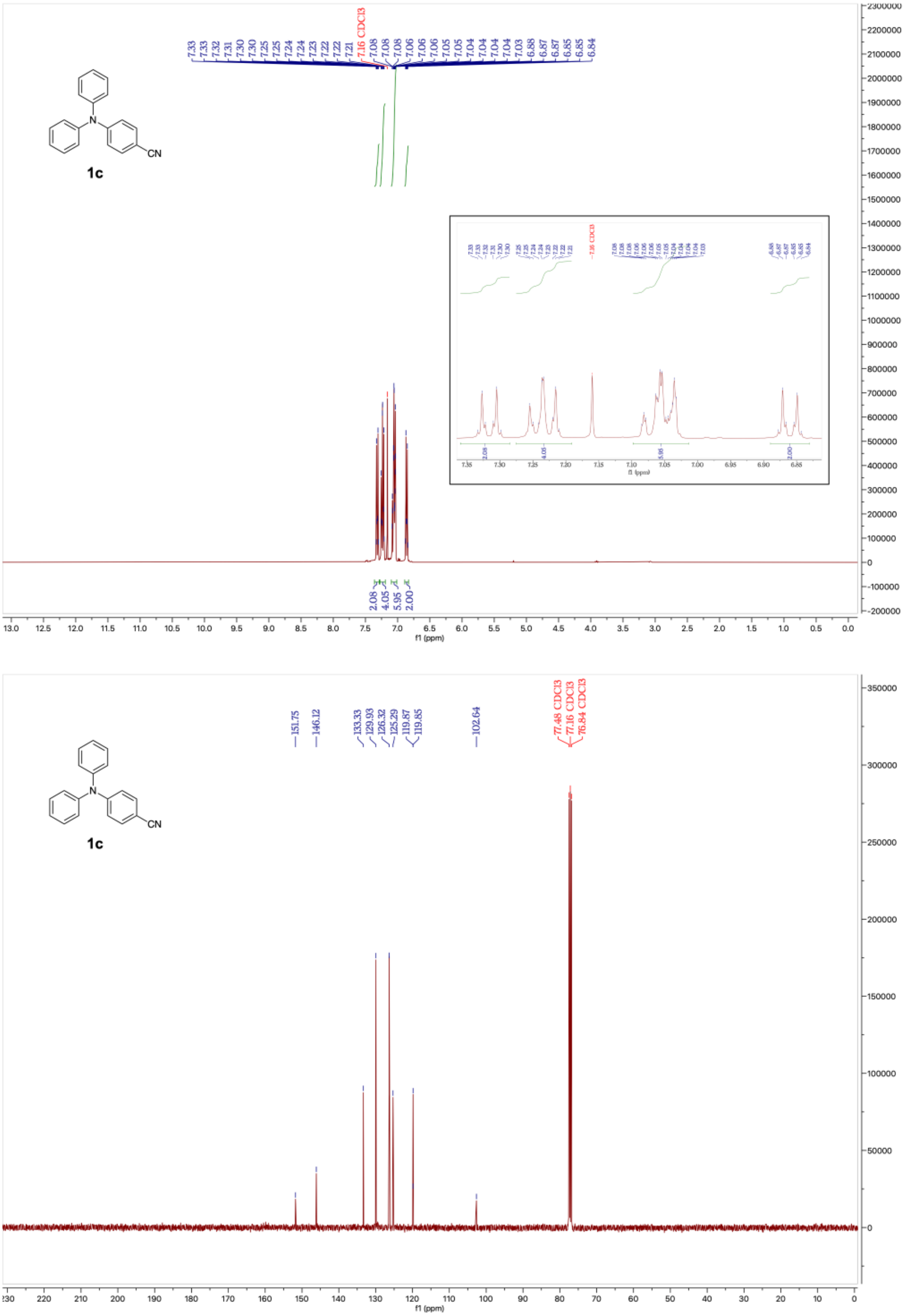


Figure 47. (top) ^{1}H and (bottom) ^{13}C NMR spectra for isolated compound **1c**, synthesized by RAM.

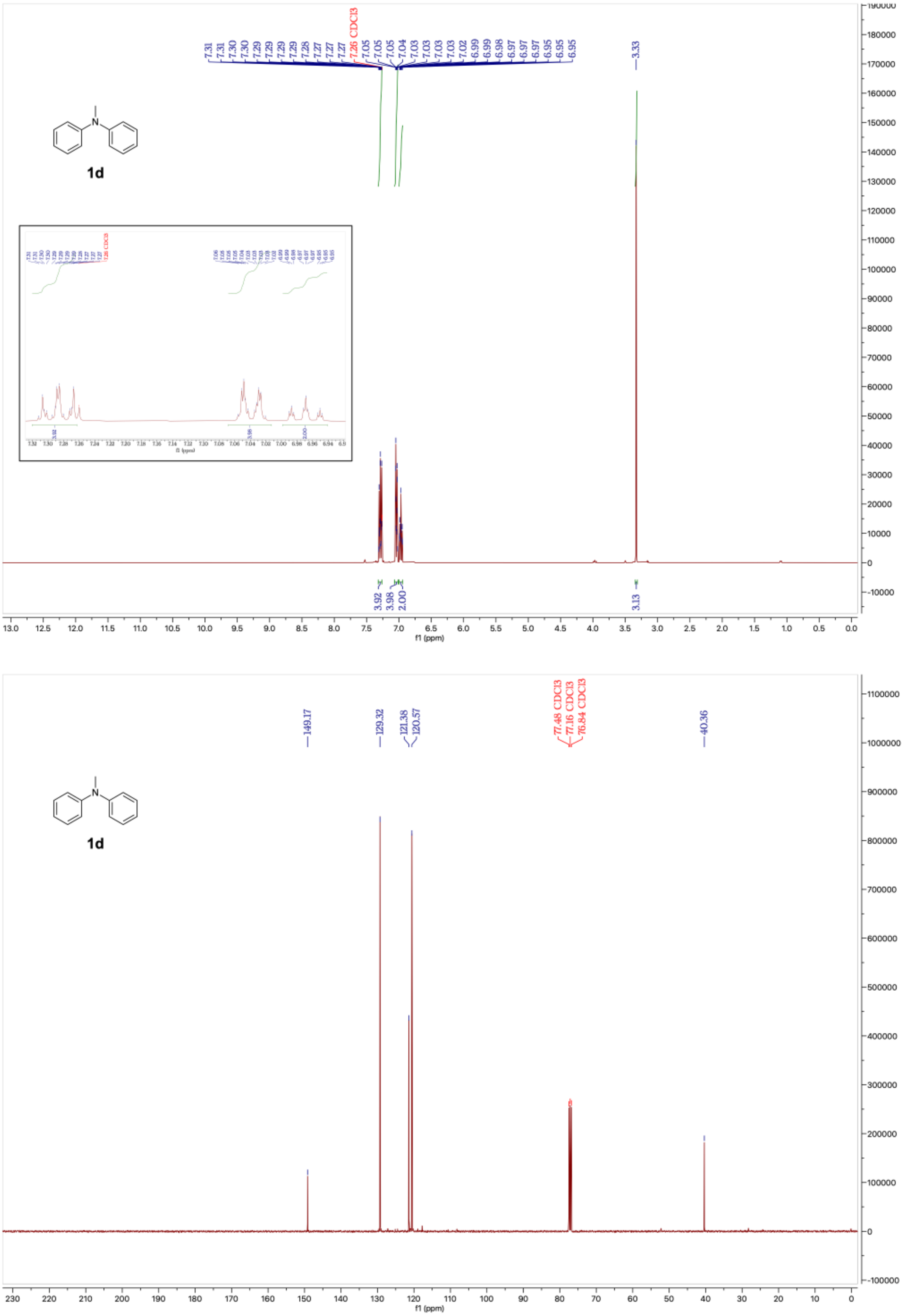


Figure S48. (top) ^{1}H and (bottom) ^{13}C NMR spectra for isolated compound **1d**, synthesized by RAM.

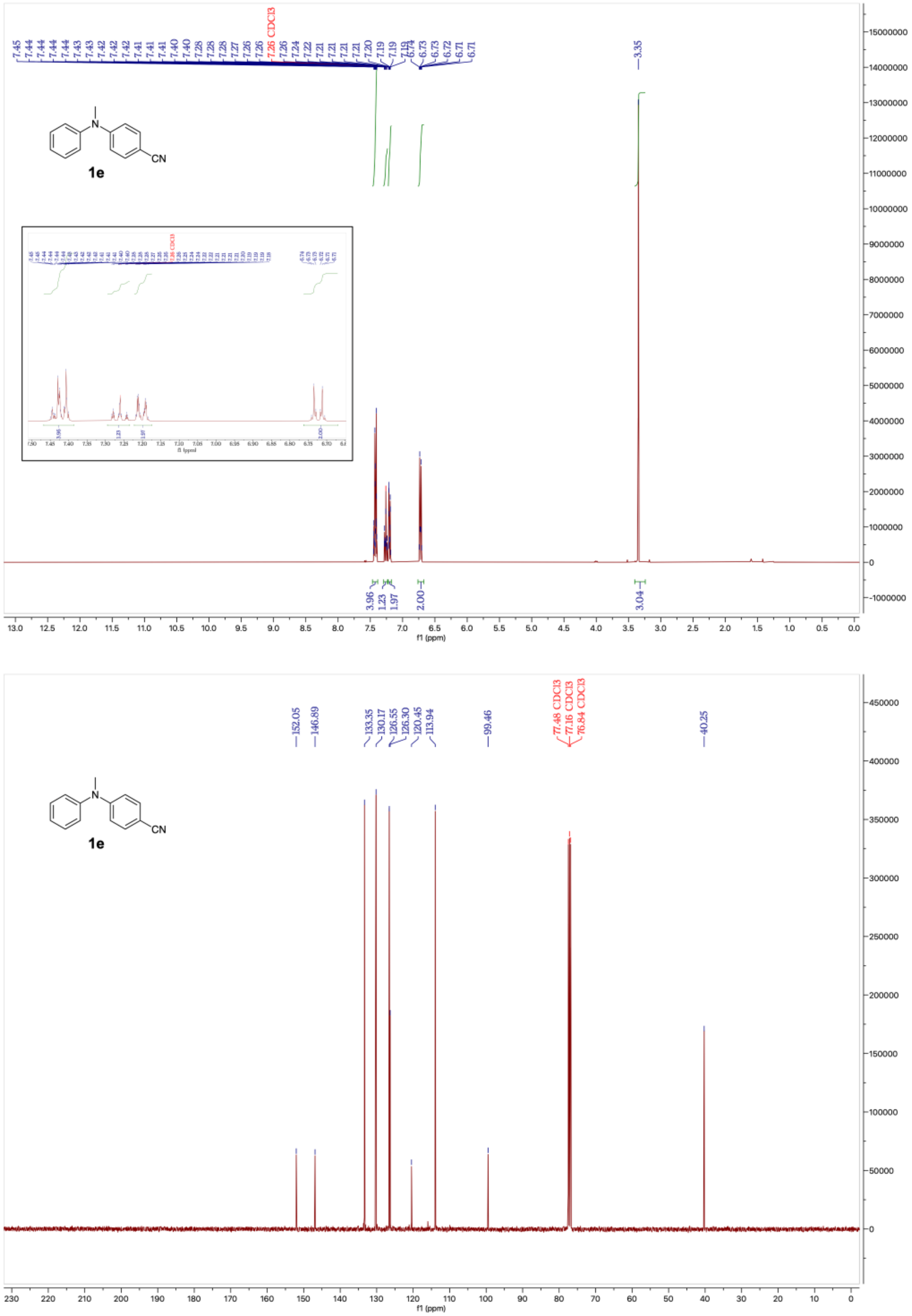


Figure S49. (top) ^{1}H and (bottom) ^{13}C NMR spectra for isolated compound **1e**, synthesized by RAM.

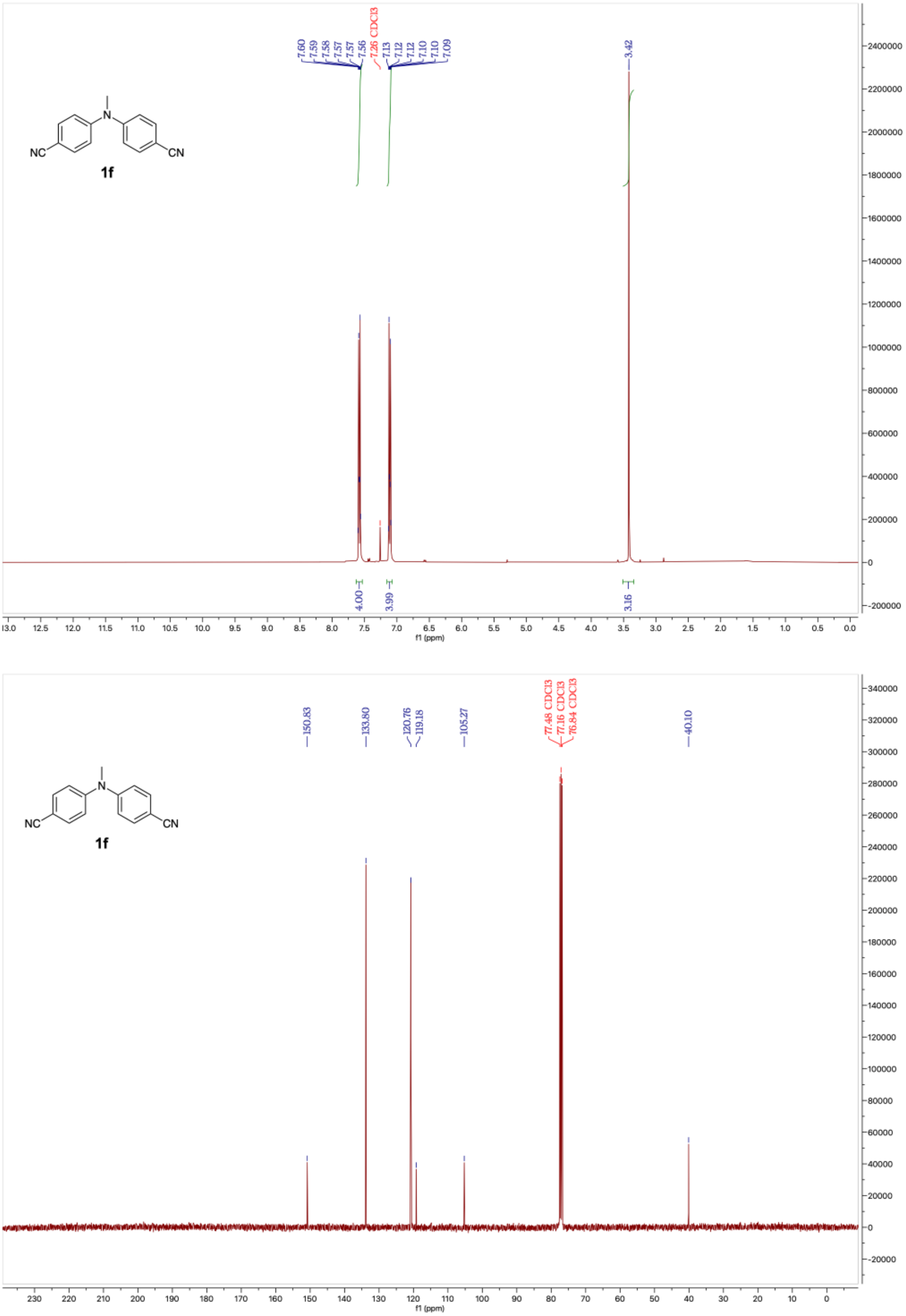


Figure S50. (top) ^{1}H and (bottom) ^{13}C NMR spectra for isolated compound **1f**, synthesized by RAM.

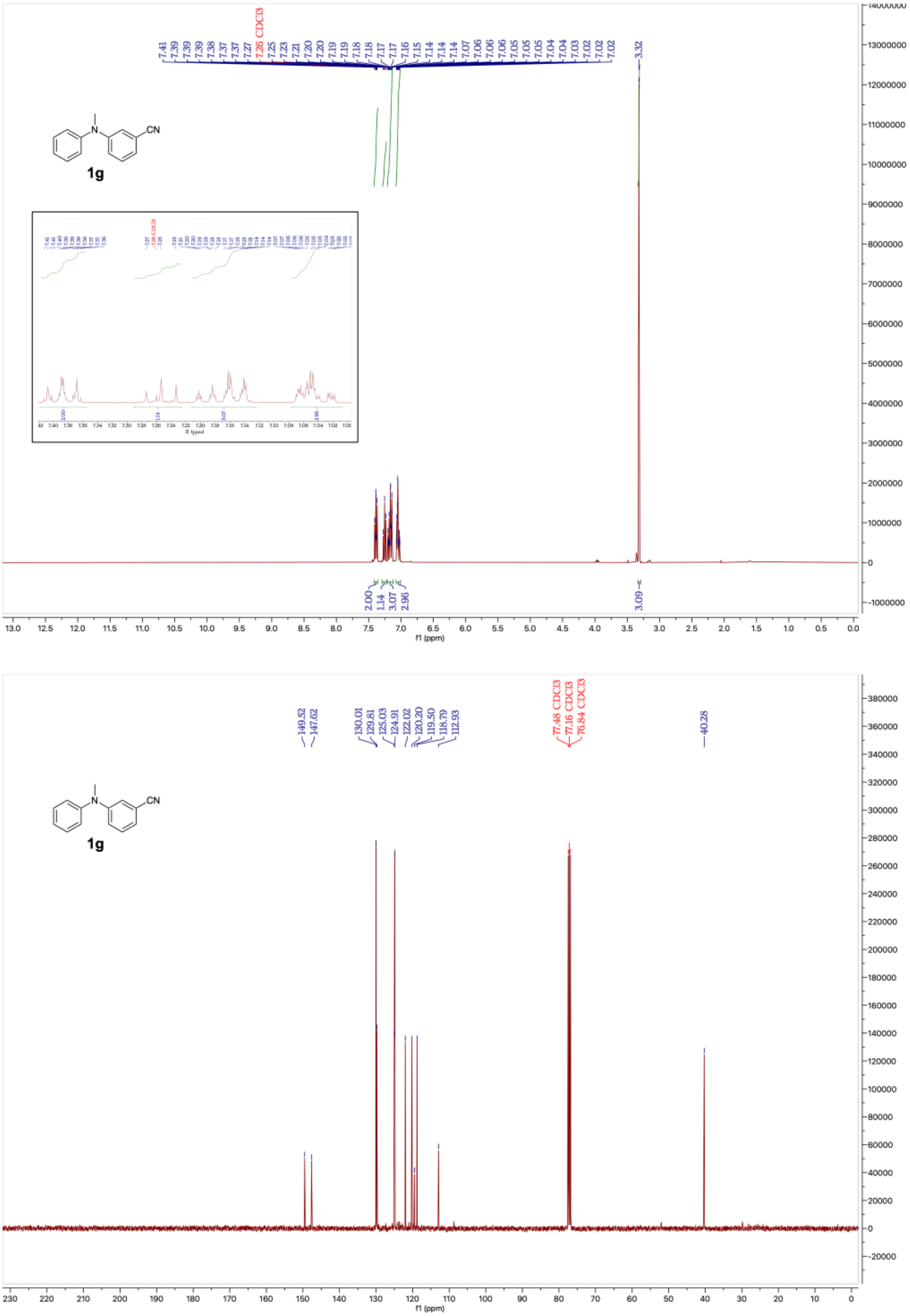


Figure S51. (top) ^{1}H and (bottom) ^{13}C NMR spectra for isolated compound **1g**, synthesized by RAM.

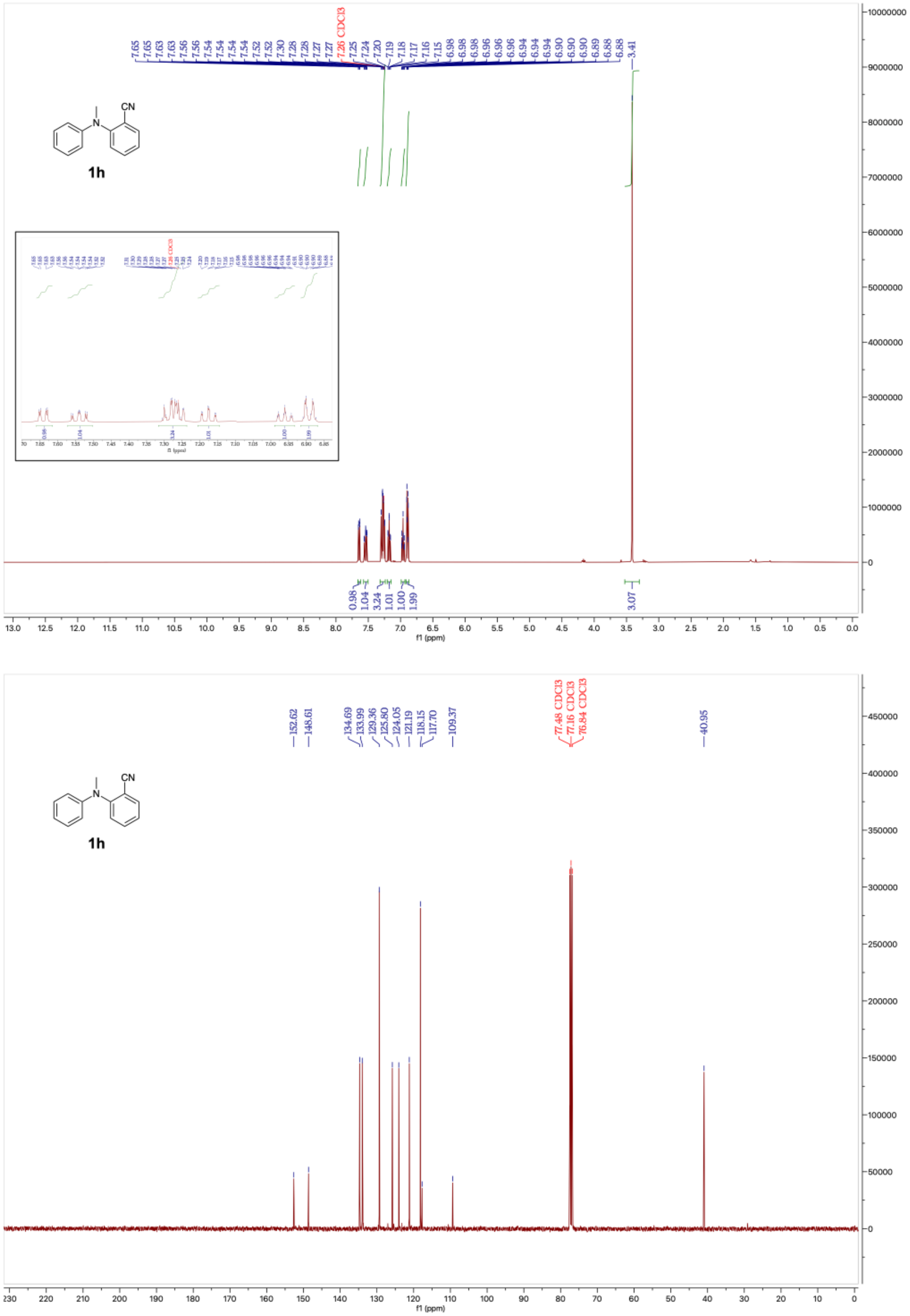


Figure S52. (top) ^{1}H and (bottom) ^{13}C NMR spectra for isolated compound **1h**, synthesized by RAM.

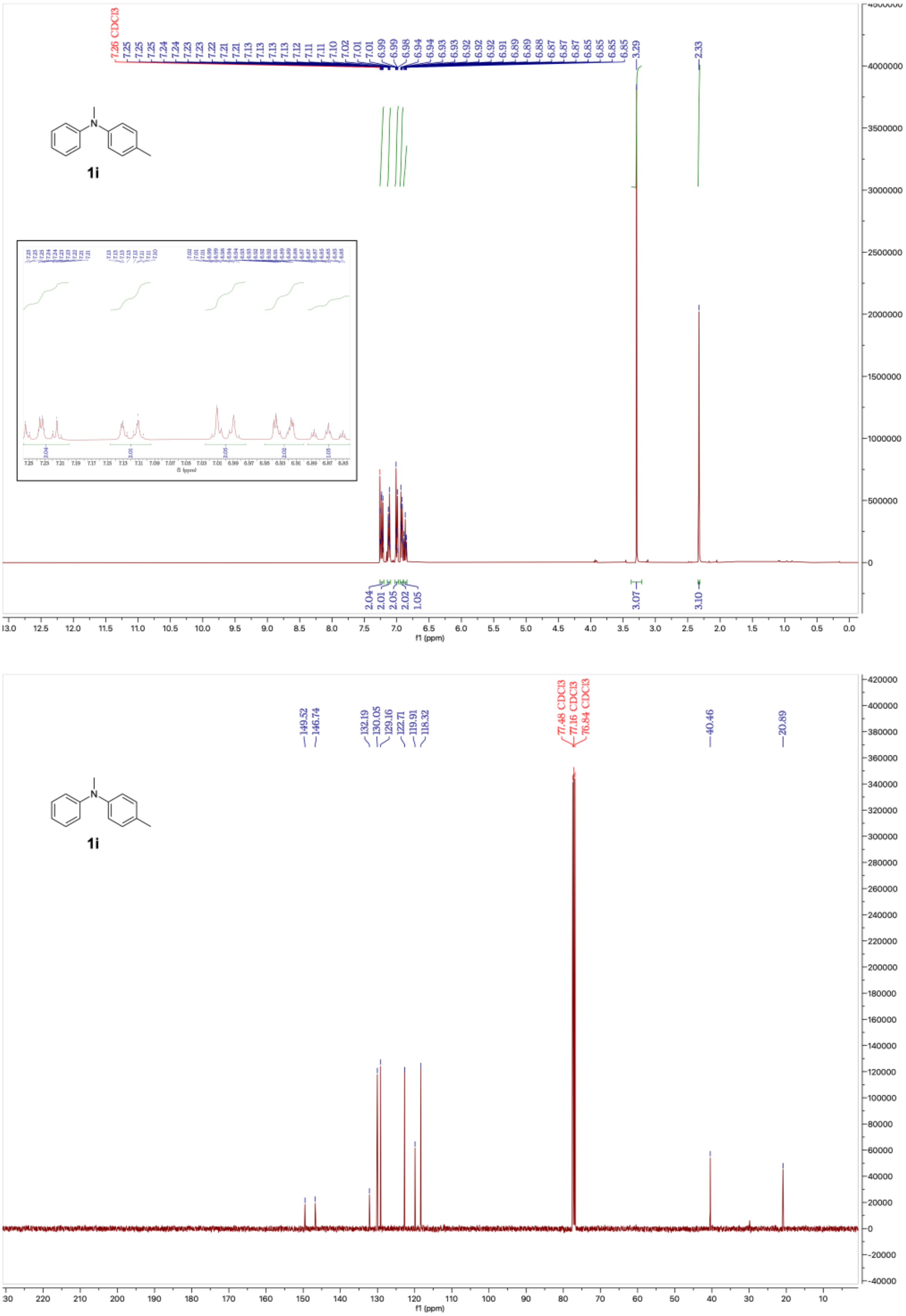


Figure S53. (top) ^{1}H and (bottom) ^{13}C NMR spectra for isolated compound **1i**, synthesized by RAM.

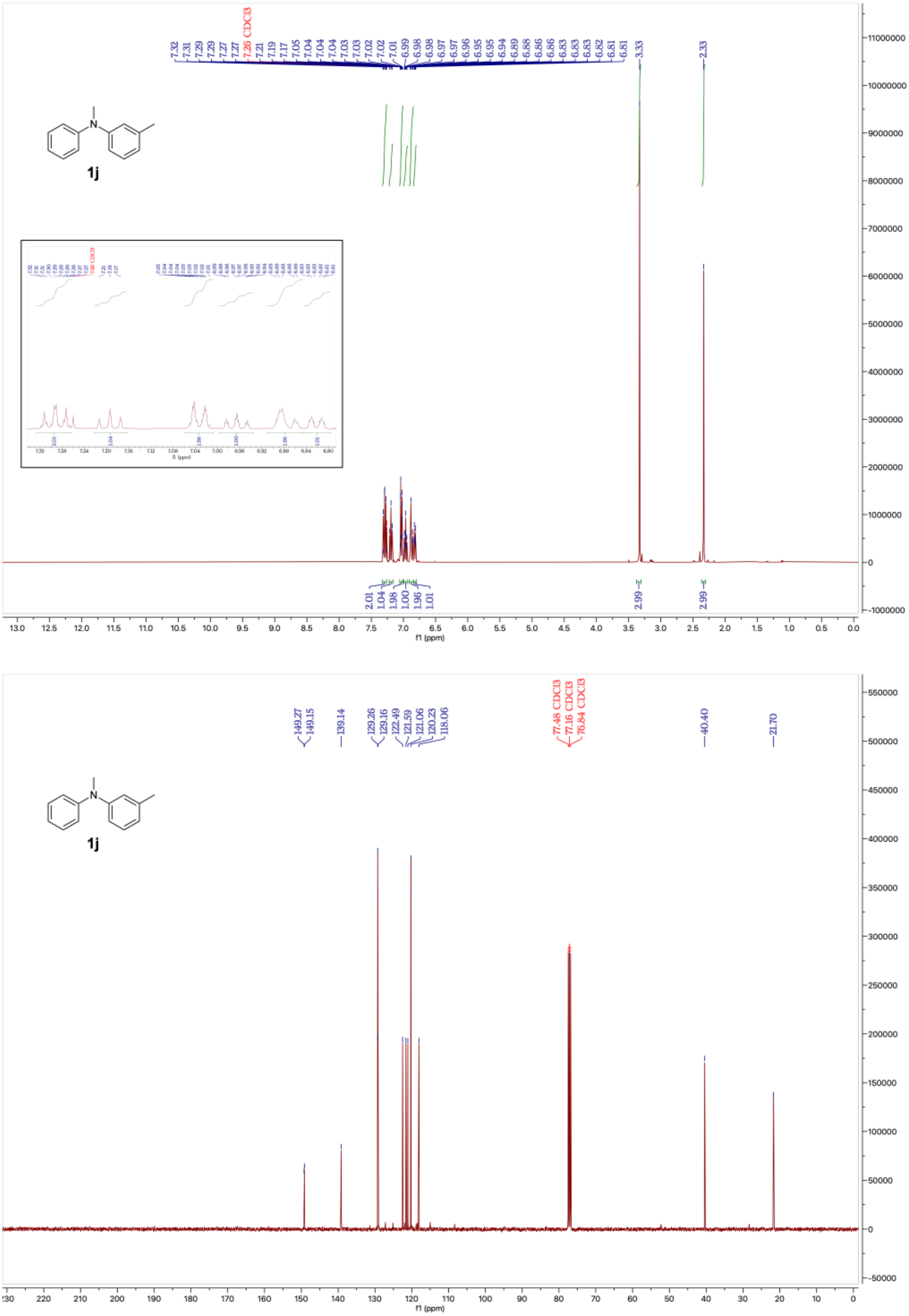


Figure S54. (top) ^{1}H and (bottom) ^{13}C NMR spectra for isolated compound **1j**, synthesized by RAM.

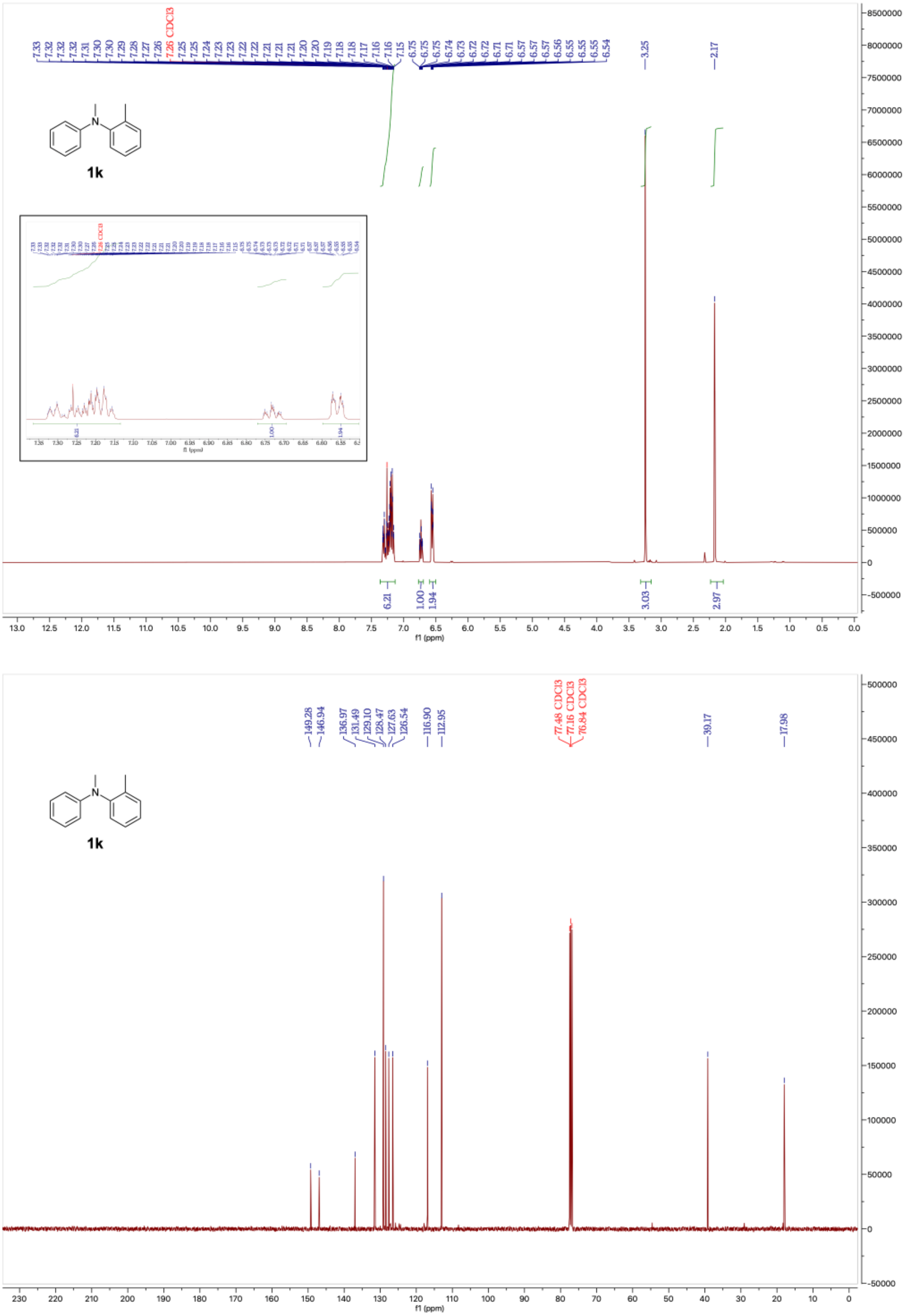


Figure S55. (top) ^{1}H and (bottom) ^{13}C NMR spectra for isolated compound **1k**, synthesized by RAM.

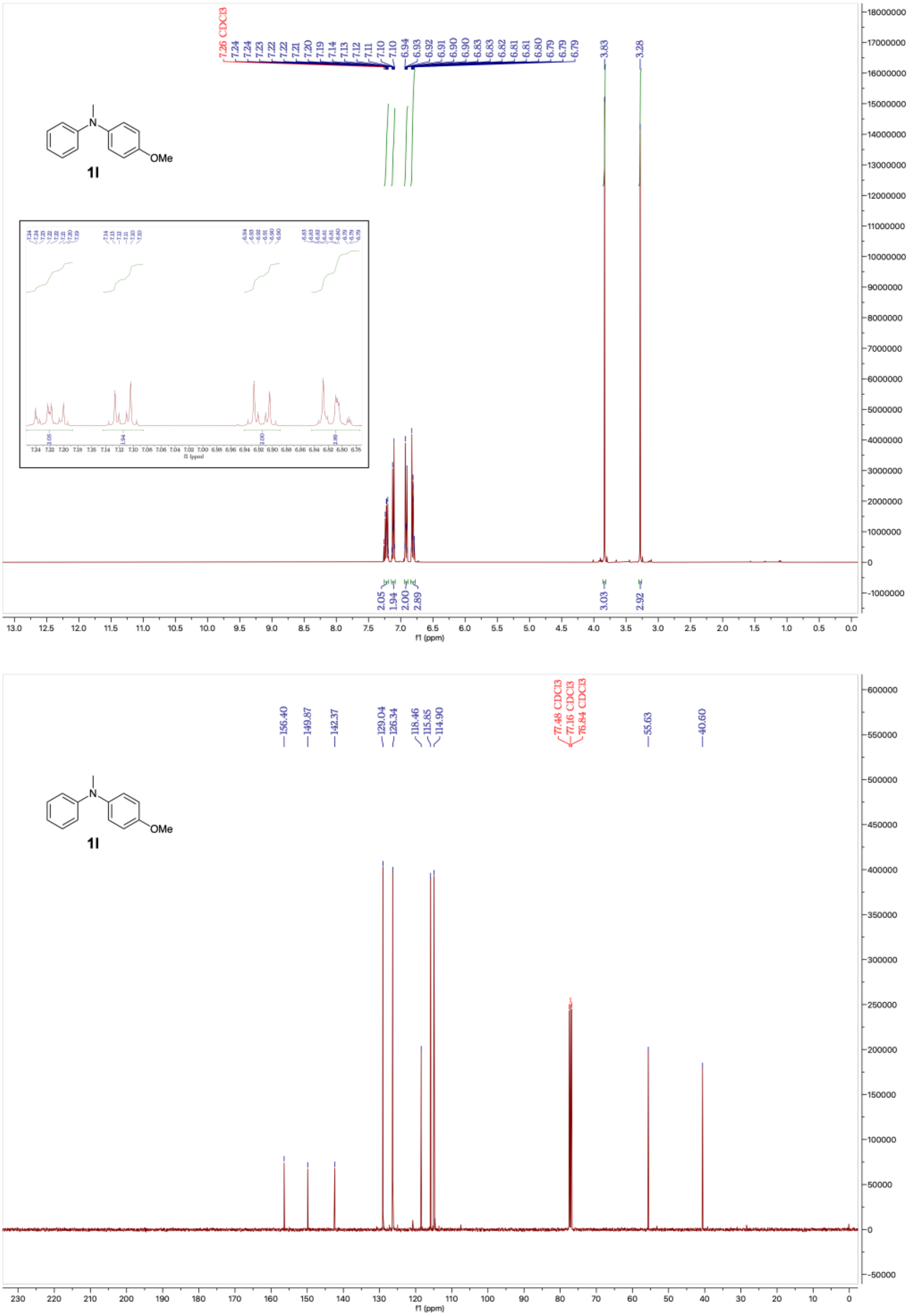


Figure S56. (top) ^{1}H and (bottom) ^{13}C NMR spectra for isolated compound **1l**, synthesized by RAM.

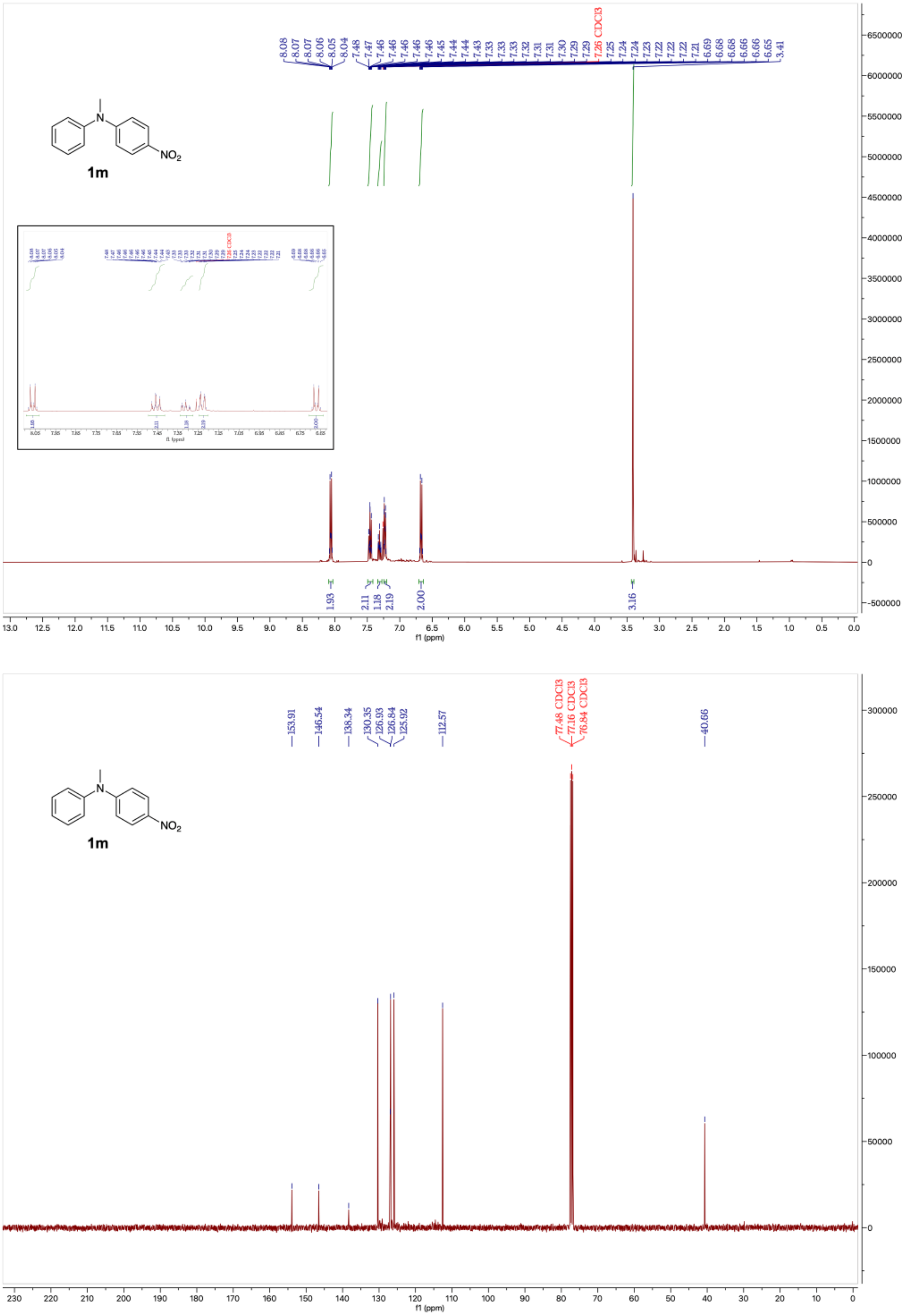


Figure S57. (top) ^{1}H and (bottom) ^{13}C NMR spectra for isolated compound **1m**, synthesized by RAM.

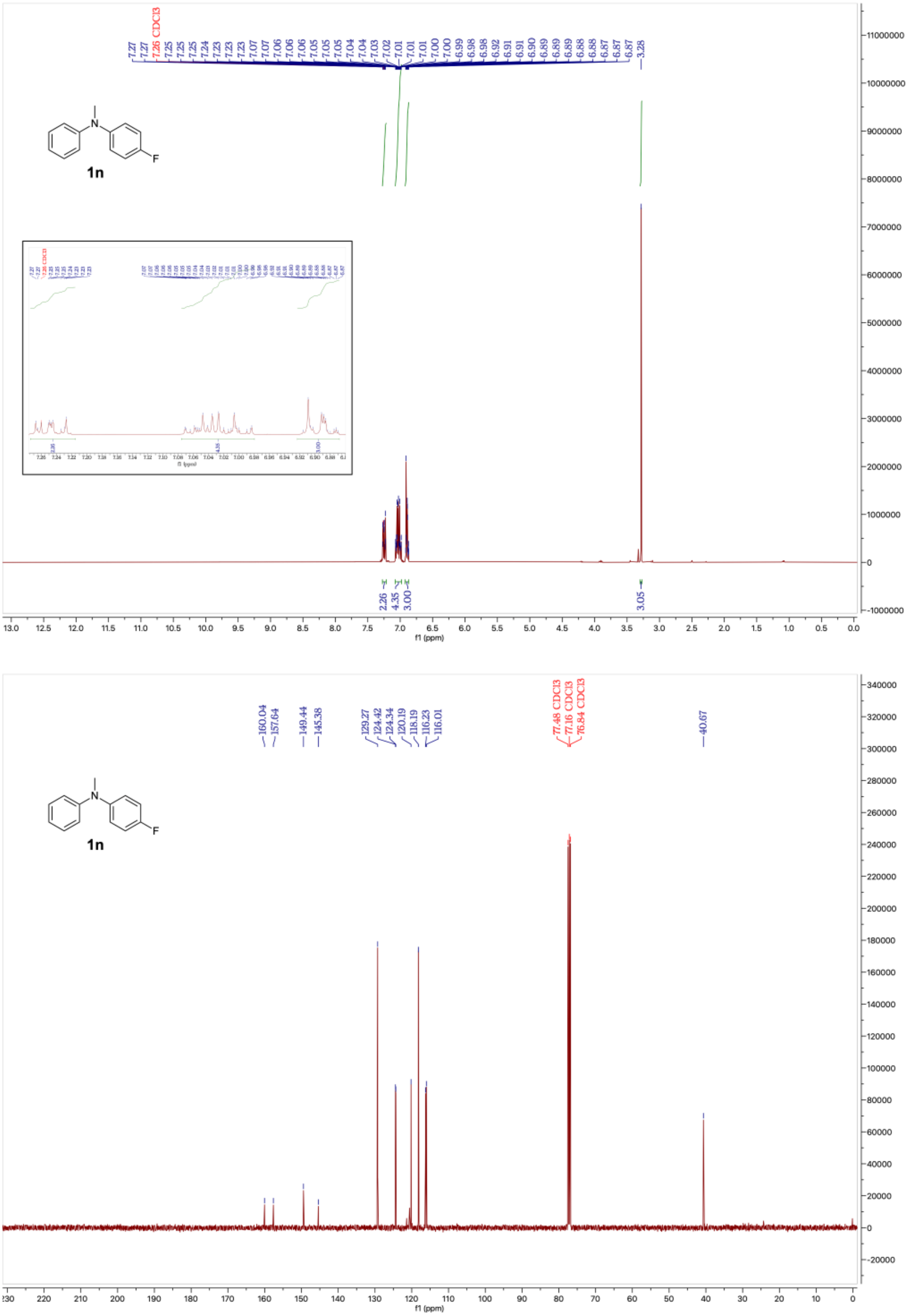


Figure S58. (top) ^{1}H and (bottom) ^{13}C NMR spectra for isolated compound **1n**, synthesized by RAM.

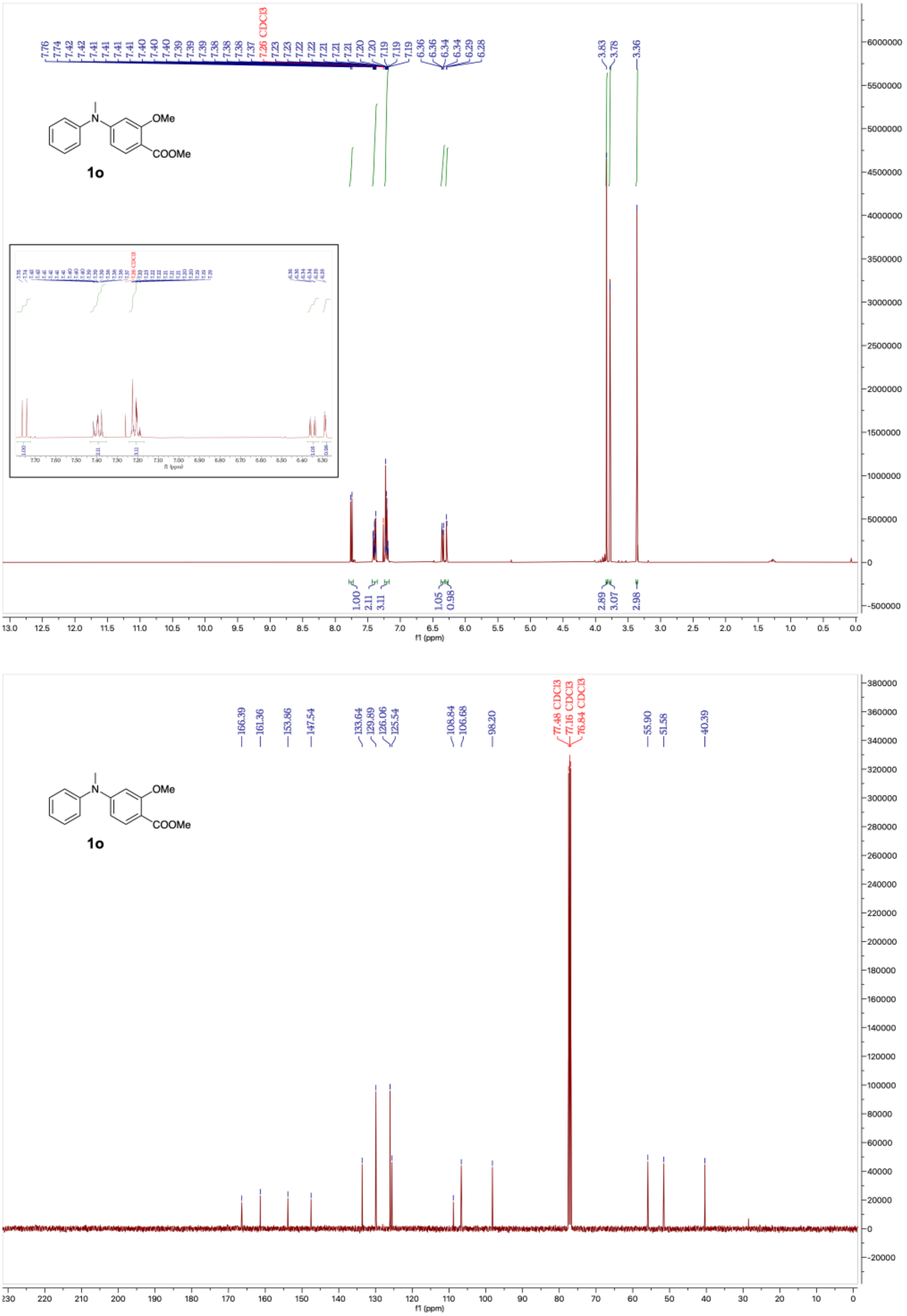


Figure S59. (top) ^{1}H and (bottom) ^{13}C NMR spectra for isolated compound **1o**, synthesized by RAM.

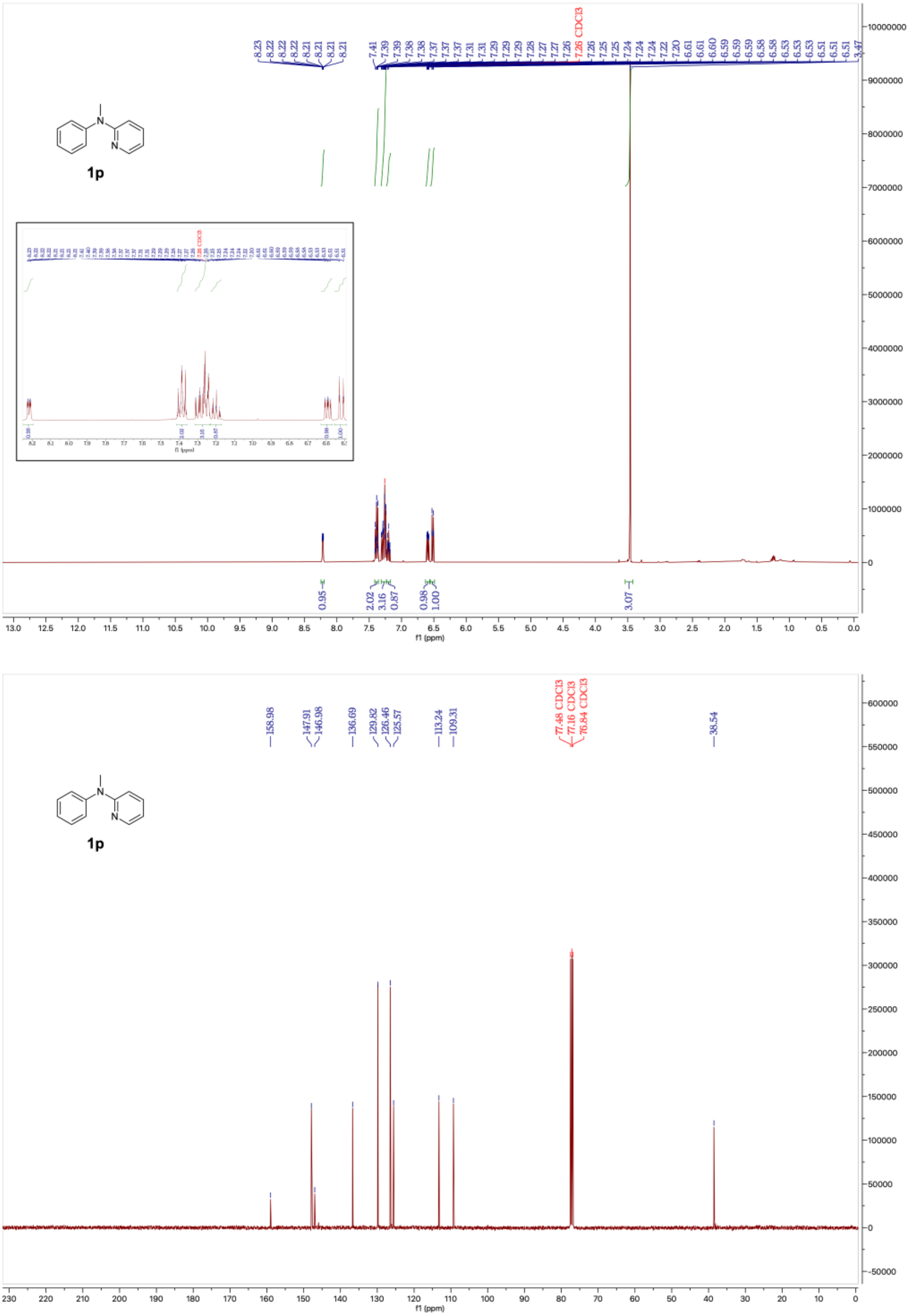


Figure S60. (top) ^{1}H and (bottom) ^{13}C NMR spectra for isolated compound **1p**, synthesized by RAM.

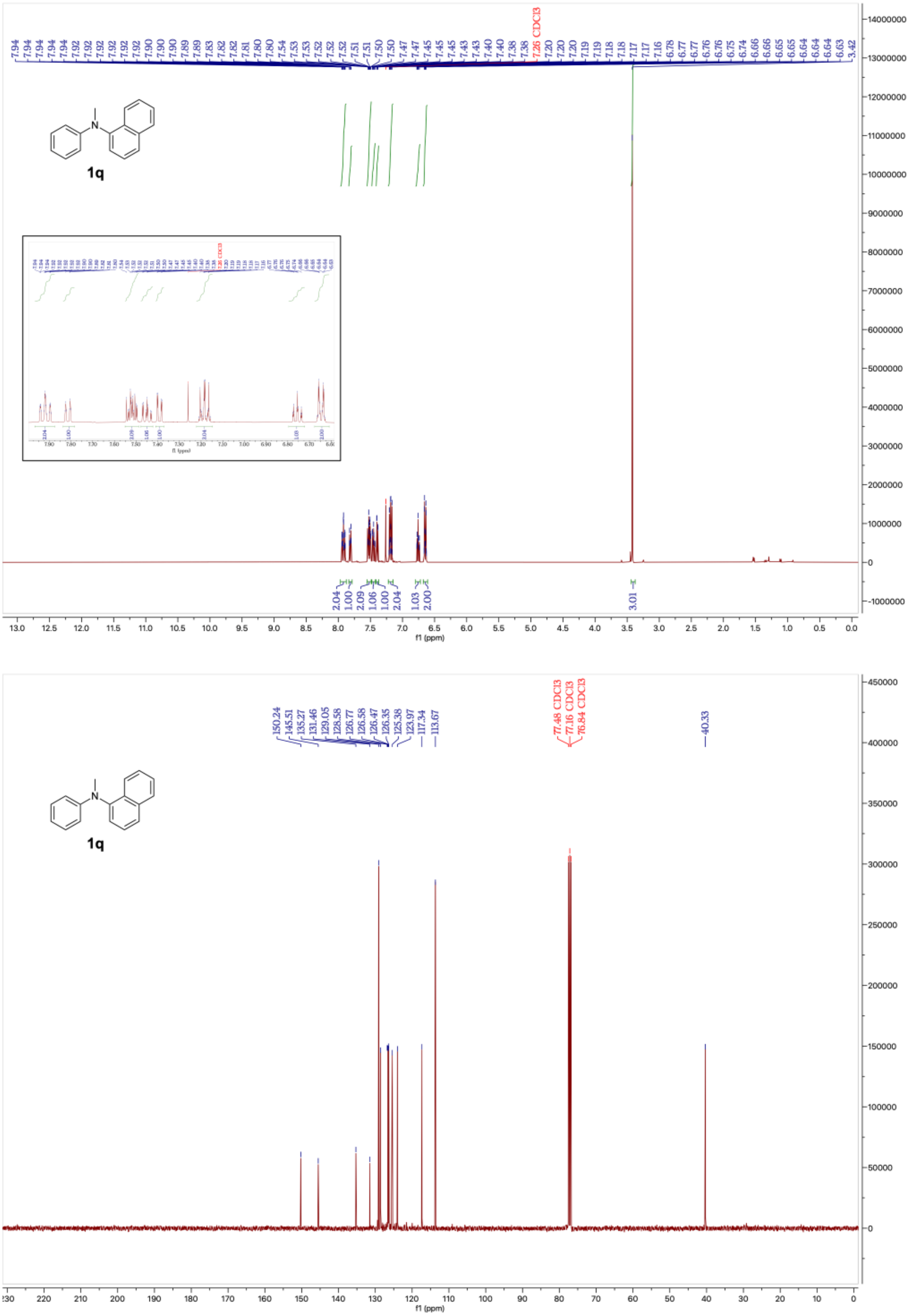


Figure S61. (top) ^{1}H and (bottom) ^{13}C NMR spectra for isolated compound **1q**, synthesized by RAM.

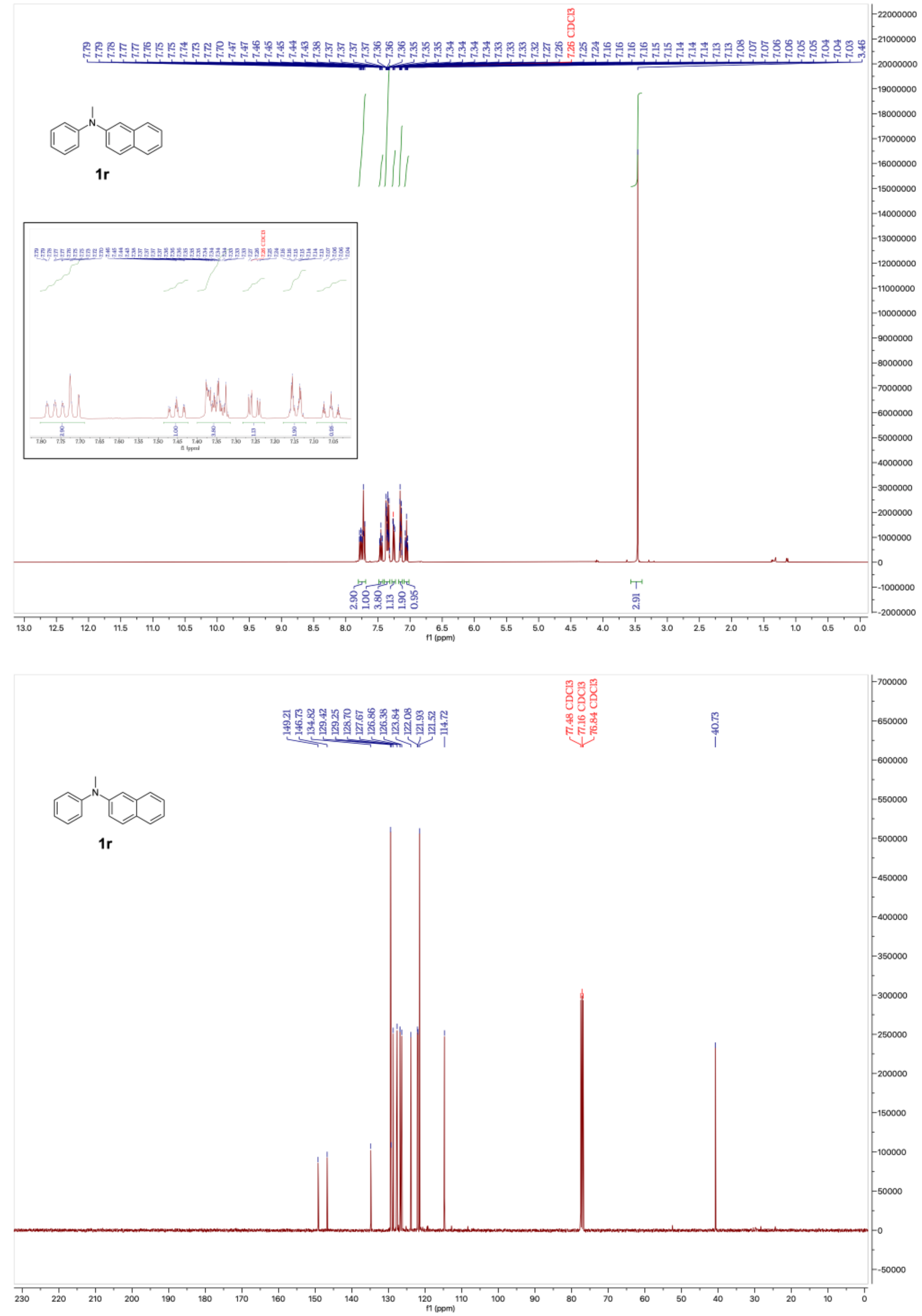


Figure S62. (top) ^{1}H and (bottom) ^{13}C NMR spectra for isolated compound **1r**, synthesized by RAM.

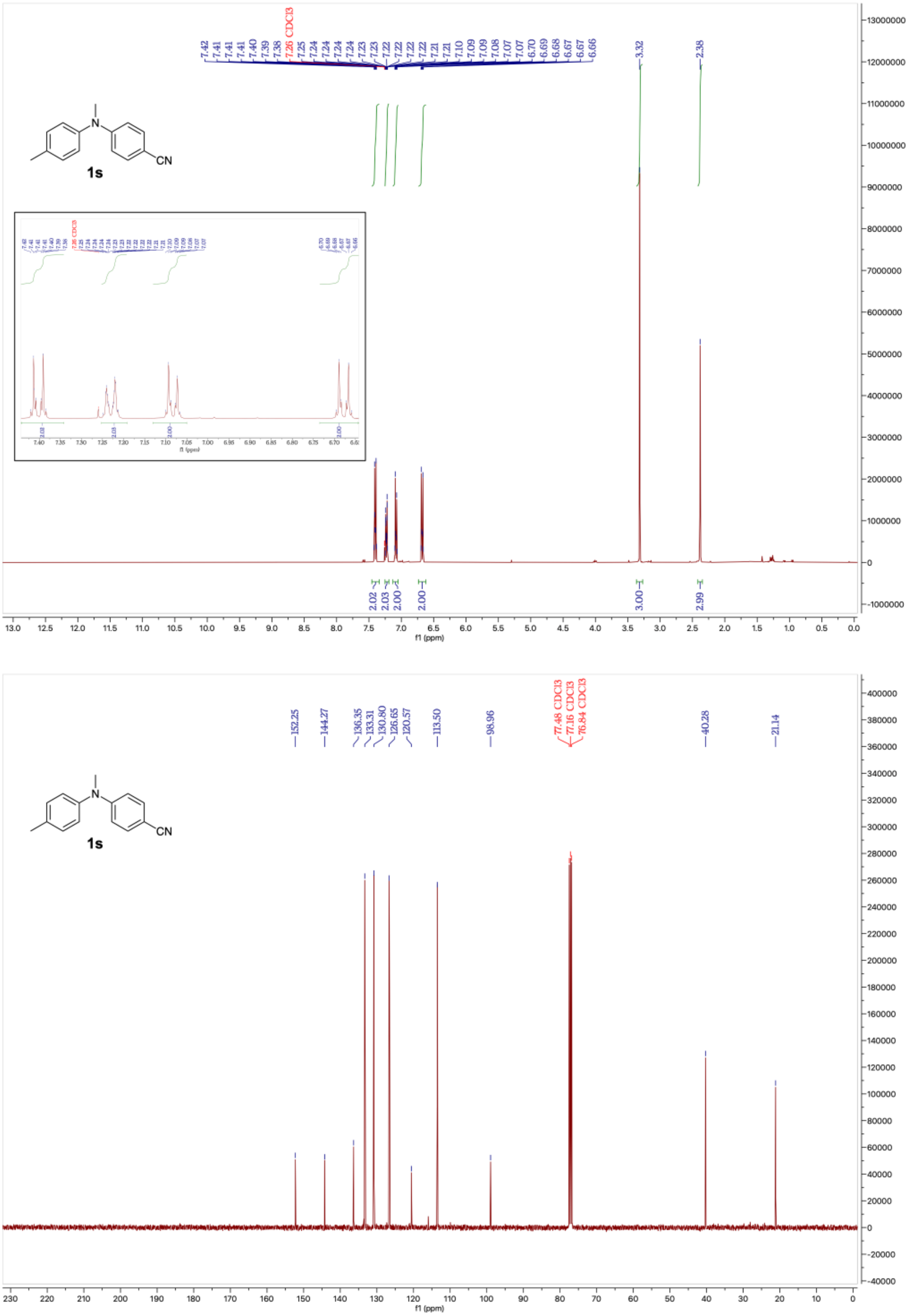


Figure S63. (top) ^{1}H and (bottom) ^{13}C NMR spectra for isolated compound **1s**, synthesized by RAM.

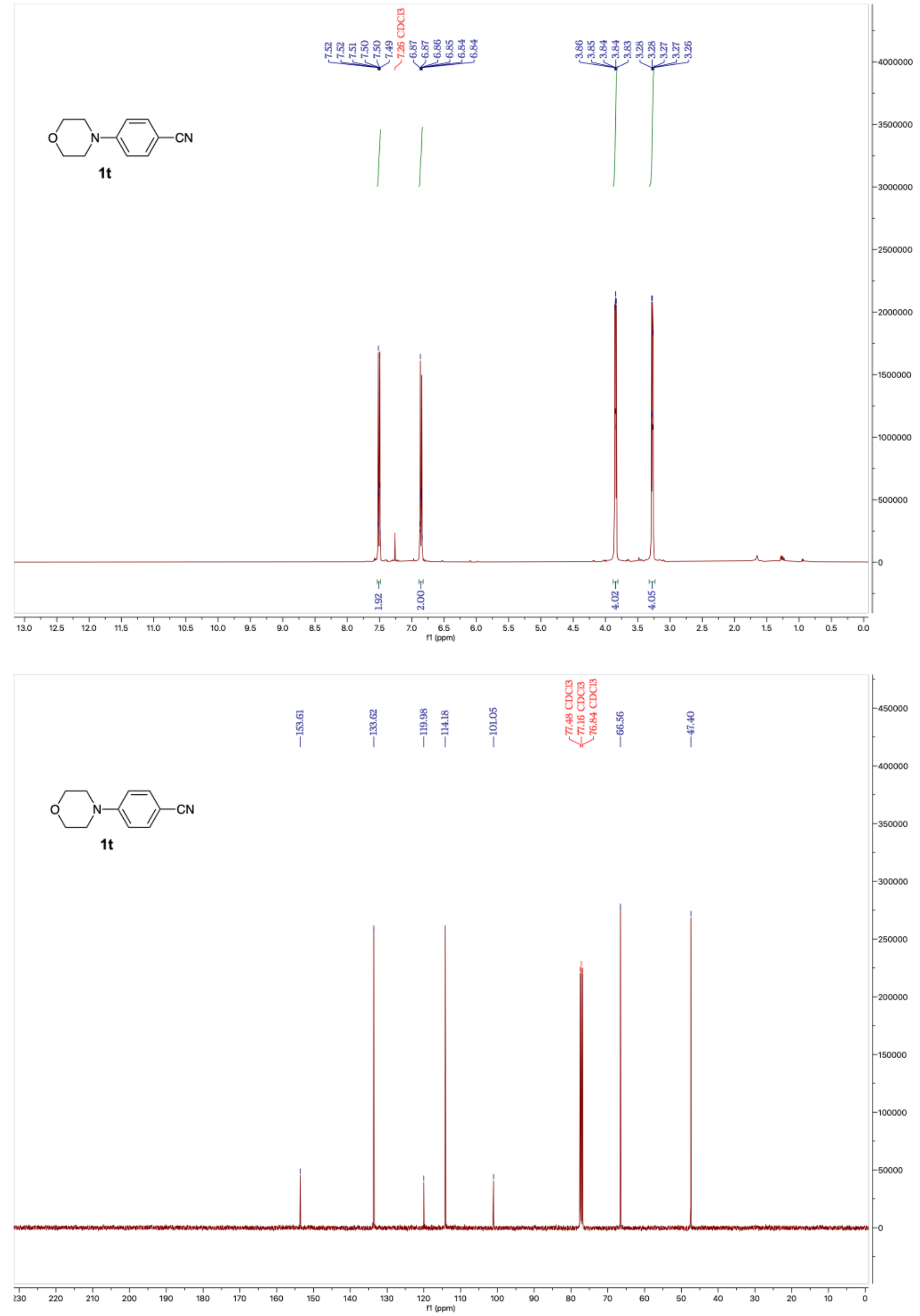


Figure S64. (top) ^{1}H and (bottom) ^{13}C NMR spectra for isolated compound **1t**, synthesized by RAM.

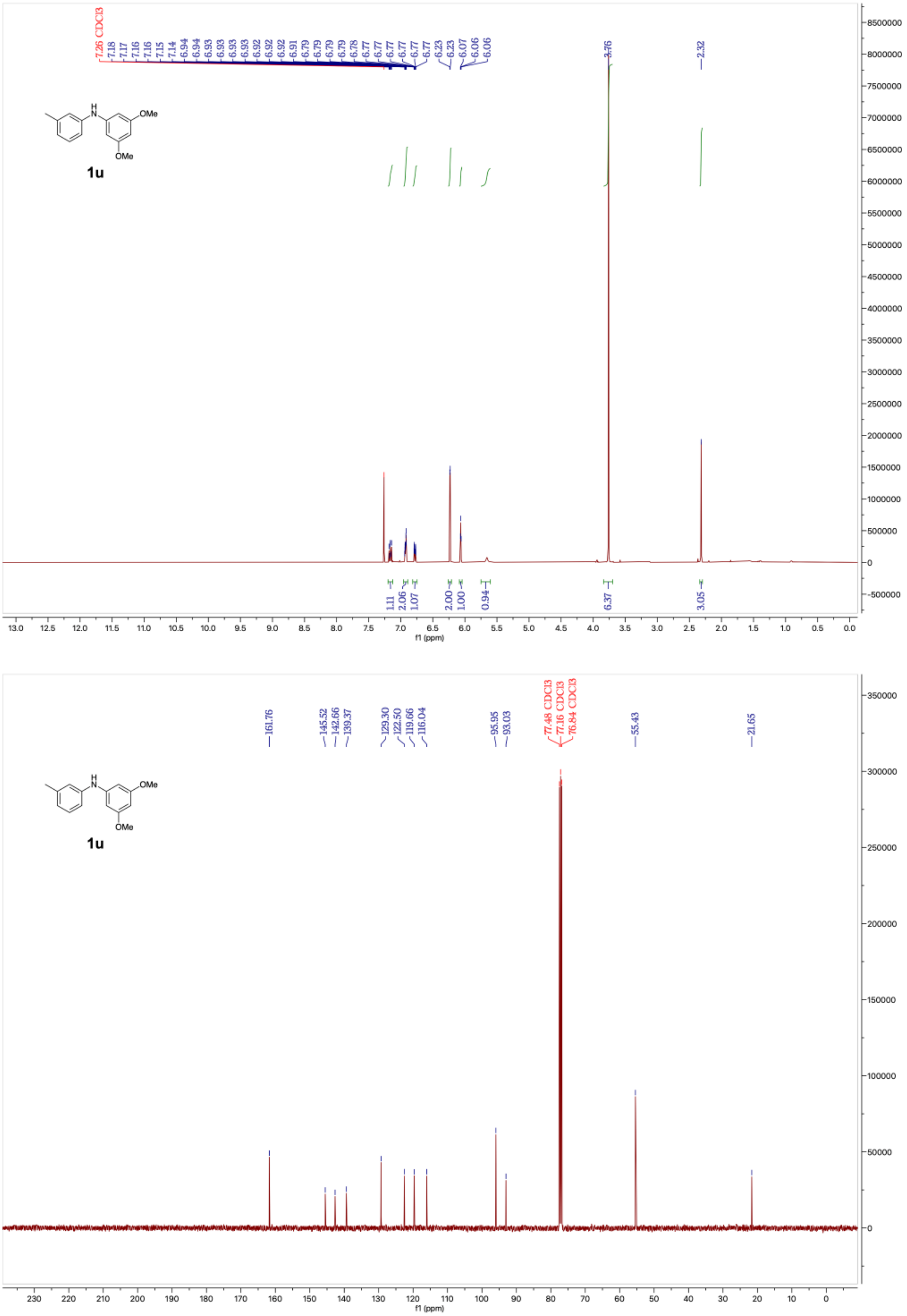


Figure S65. (top) ^{1}H and (bottom) ^{13}C NMR spectra for isolated compound **1u**, synthesized by RAM.

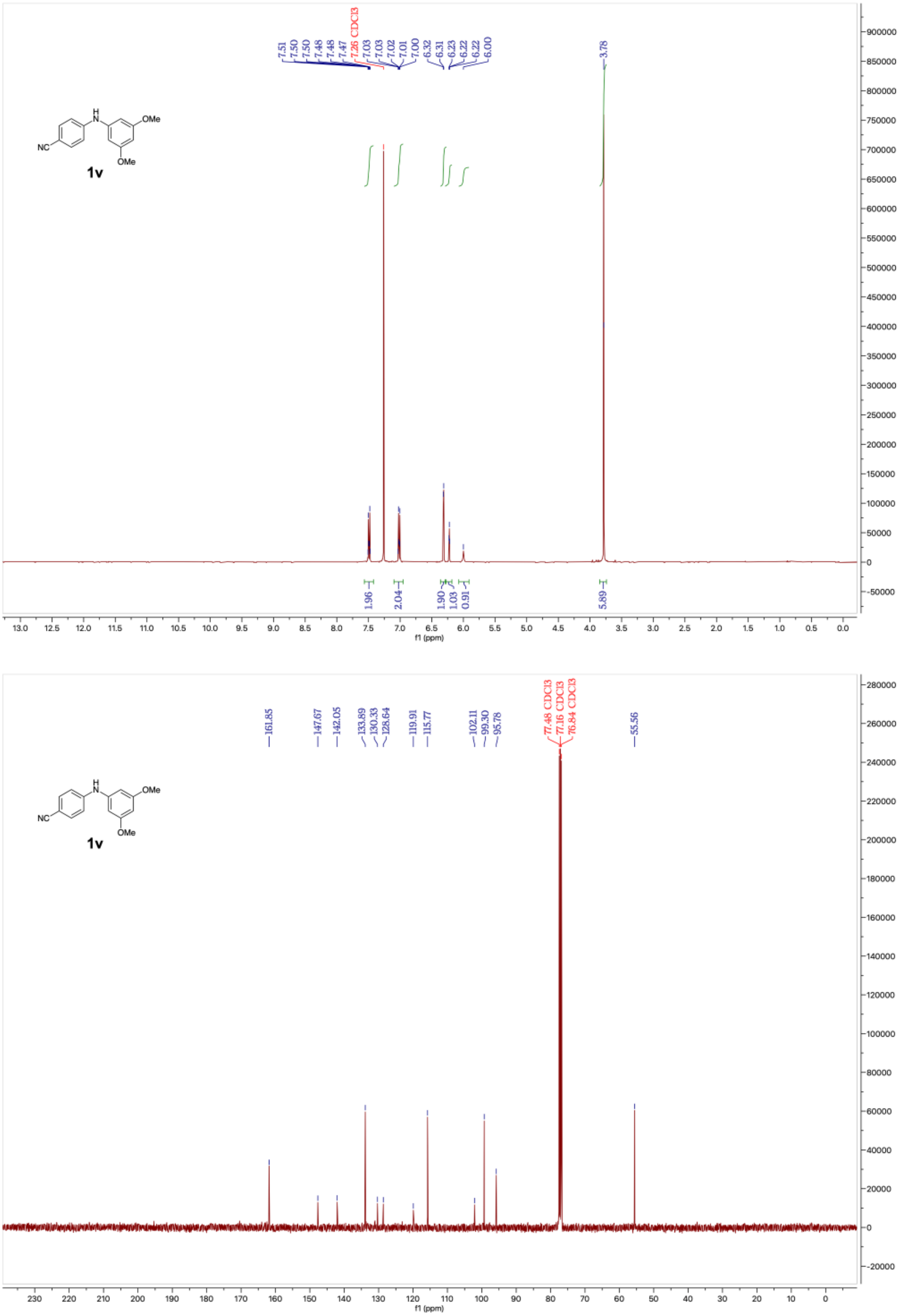


Figure S66. (top) ^{1}H and (bottom) ^{13}C NMR spectra for isolated compound **1v**, synthesized by RAM.

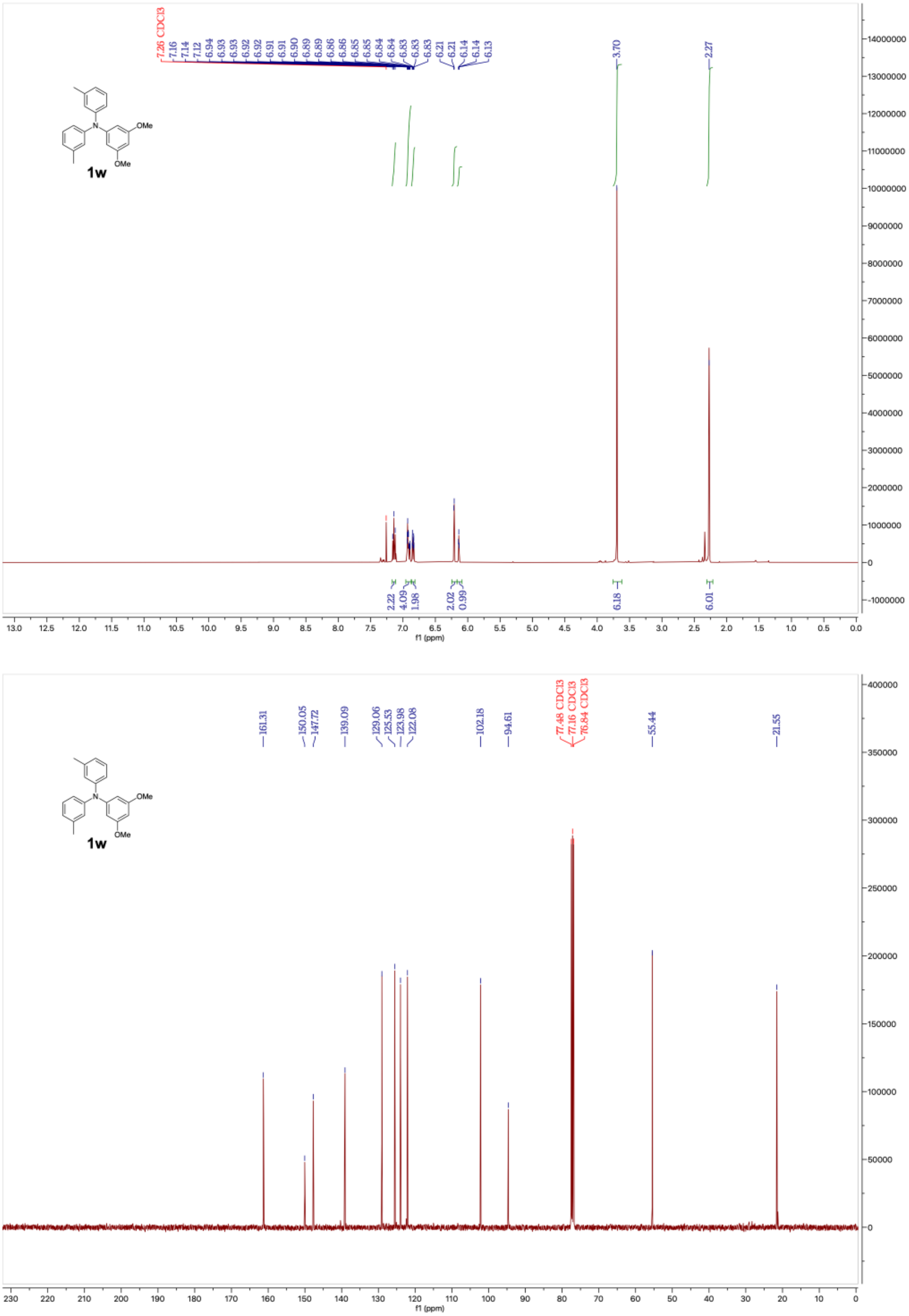


Figure S67. (top) ^{1}H and (bottom) ^{13}C NMR spectra for isolated compound **1w**, synthesized by RAM.

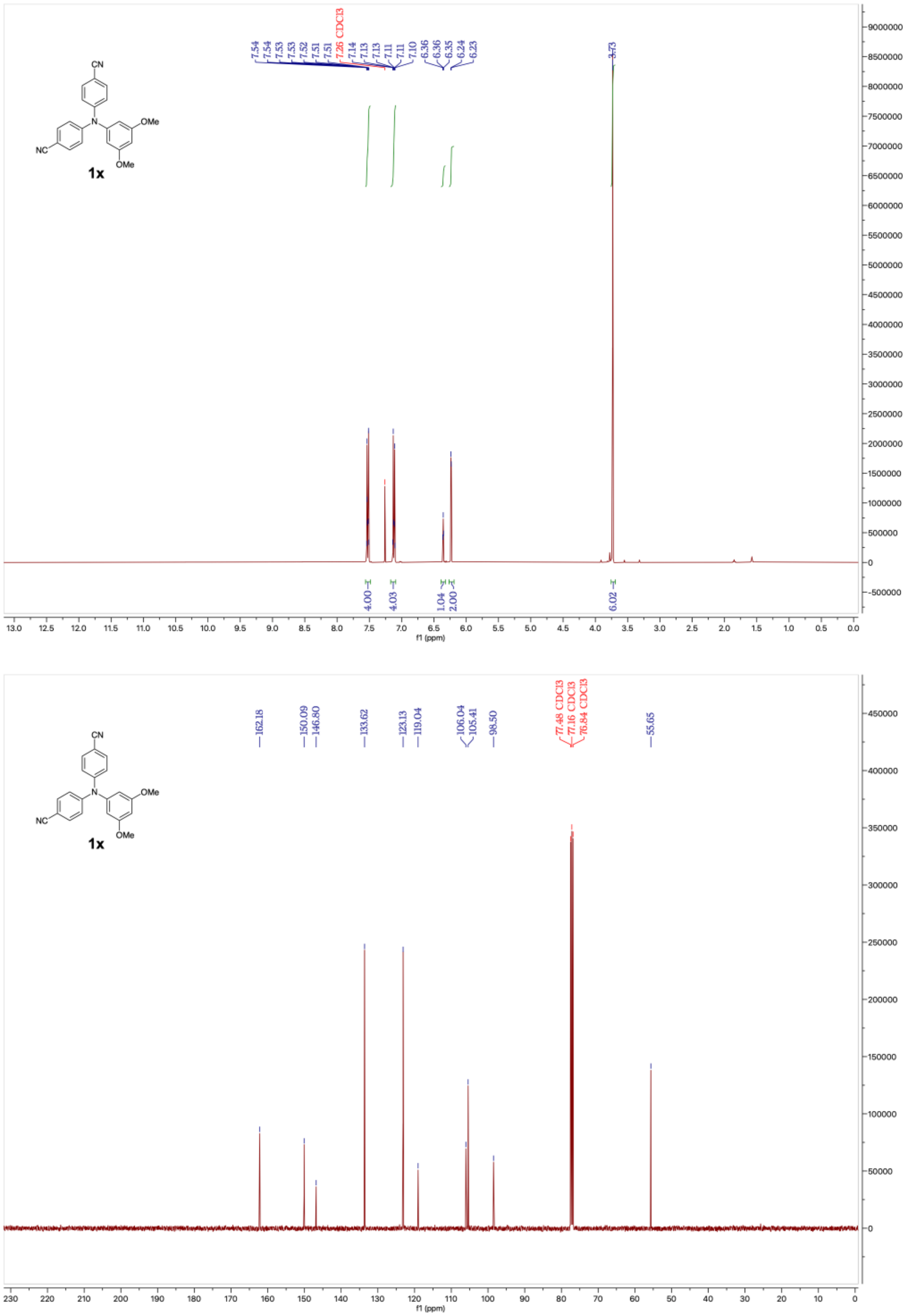


Figure S68. (top) ^{1}H and (bottom) ^{13}C NMR spectra for isolated compound **1x**, synthesized by RAM.

S14. References

[64] CrysAlisPRO, Oxford Diffraction /Agilent Technologies UK Ltd, Yarnton, England.

[65] C. B. Hubschle, G. M. Sheldrick and B. Dittrich, *J. Appl. Crystallogr.*, 2011, **44**, 1281-1284.

[66] C. L. Lawson, and R. J. Hanson, Solving Least-Squares Problems, *Upper Saddle River, NJ: Prentice Hall*. 1975, **23**, 161.

[67] F. Stoessel, *Thermal Safety of Chemical Processes: Risk Assessment and Process Design*, Wiley-VCH, Weinheim, 2008.