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Ruthenium-Catalyzed Synthesis of 1,5-Dichlorides by Sequential Intermolecular Kharasch Reactions

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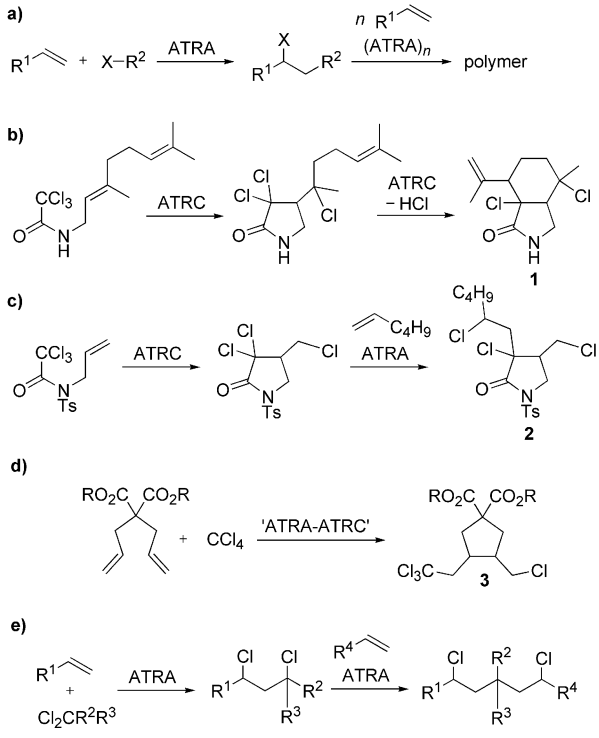
Sequential intermolecular atom transfer radical addition reactions of activated dichlorides Cl_2CRR' (R = CN, CO_2Et, R′ = H, CN, CO_2Et) with two olefins catalyzed by $[Cp^*RuCl_2(PPh_3)]$ in the presence Mg allow the synthesis of linear 1,5-dichlorides. Different olefins can be employed in the first and in the second addition reaction. The reaction products are interesting synthetic precursors as demonstrated by the synthesis of two cyclopentanes by Mg-induced dechlorination. The structure of *trans*-3,4-diphenylcyclopentanecarbonitrile was determined by single-crystal X-ray diffraction.

Introduction

The anti-Markovnikov addition of halogenated compounds to olefins via a radical mechanism (Kharasch reaction)[1] can be achieved by photochemical activation, with radical initiators, or with transition metal catalysts.[2] The latter method is particularly appealing because the reactions can be carried out under mild conditions with good selectivity. Numerous transition metal complexes are able to catalyze atom transfer radical addition (ATRA) reactions. The best performance is typically observed for Cu[3] and Ru[4] catalysts, in particular if the catalysts are used in conjunction with reducing agents such as diazo initiators[5] or Mg.[6]

An interesting feature of ATRA reactions is that they can be performed in a sequential fashion. The ultimate sequential reaction is a polymerization (Scheme 1, a). Atom transfer radical polymerization (ATRP) reactions have been studied extensively over the last years because they allow to obtain polymers with good control over molecular weight, structure, and composition.[7] In the context of synthetic organic chemistry, sequential ATRA reactions have been used to build complex molecules. The group of Itoh, for example, has shown that a bicyclic lactam (**1**) can be obtained by double atom transfer radical cyclizations (ATRC) followed by elimination of HCl (Scheme 1, b).[8,9] The intramolecular cyclization can also be combined with an intermolecular ATRA reactions as demonstrated the successful synthesis of lactam **2** (Scheme 1, c).[10] Intermolecular Kharasch reactions of 1,6-dienes with $CXCl_3$ (X = Br, Cl) have been investigated by several groups.[5b,6c,11] These reactions provide cyclopentanes (**3**) as a mixture of stereoisomers (Scheme 1, d). Formally, these reactions can be regarded as ATRA-ATRC sequences, but the reactions proceed likely via a single ATRA step which is intercepted by an intramolecular radical cyclization.



Scheme 1. Sequential atoms transfer radical addition (ATRA) and cyclization (ATRC) reactions.

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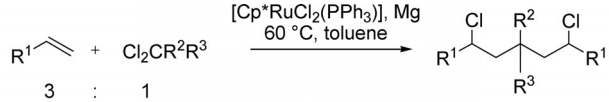
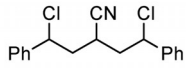
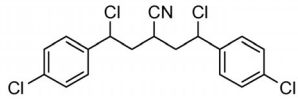
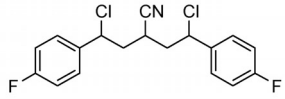
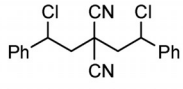
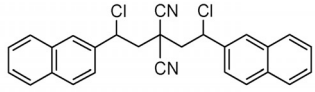
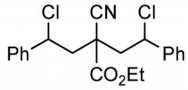
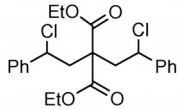
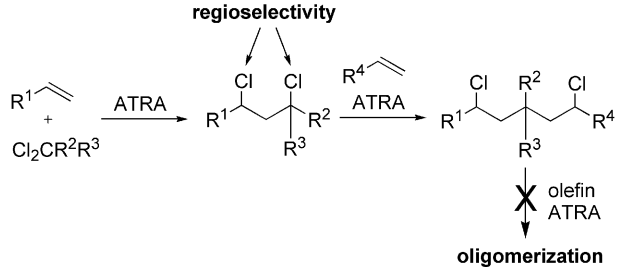
Table 1. Sequential ATRA reactions catalyzed by [Cp*$RuCl_2(PPh_3)$] in the presence of Mg.[a]



#	Olefin	Cl_2CRR'	Product		t [h]	Yield [%][b]
1	Styrene	Cl_2CHCN		**4**	48	91
2	*p*-Chlorostyrene	Cl_2CHCN		**5**	48	90
3	*p*-Fluorostyrene	Cl_2CHCN		**6**	48	92
4	Styrene	$Cl_2C(CN)_2$		**7**	24	88
5[d]	2-Vinylnaphthalene	$Cl_2C(CN)_2$		**8**	24	90
6	Styrene	$Cl_2C(CO_2Et)CN$		**9**	24	90
7	Styrene	$Cl_2C(CO_2Et)_2$		**10**	48	70

[a] Reaction conditions: [chlorinated substrate] 0.50 M, [olefin] 1.50 M, [Ru] 5.0 mM (1.0 mol-%), [Mg] 30 equiv. with respect to the chlorinated substrate, toluene, 60 °C. [b] Isolated yields with respect to the chlorinated substrate. [c] Ratio [styrene]/[Cl_2CHCO_2Et] 2.5:1. [d] Conditions: [$Cl_2C(CN)_2$] 0.30 M, [2-vinylnaphthalene] 0.90 M, [Ru] 3.0 mM (1.0 mol-%), [Mg] 30 equiv.

Below we report that it is possible to perform double Kharasch reactions with dichlorinated compounds in a purely *intermolecular* fashion (Scheme 1, e). The ATRA-ATRA reaction sequence can be performed with one or with two types of olefins allowing the efficient preparation of structurally diverse 1,5-dichlorides. The latter are interesting synthetic precursors as demonstrated by the synthesis if cyclopentanes by Mg-induced reductive coupling (Table 1).



Scheme 2. Regio- and chemoselectivity need to be controlled for sequential ATRA reactions.

Results and Discussion

Double ATRA reactions involving 1,1-dichlorides face two synthetic challenges (Scheme 2). On one hand, oligomerization has to be suppressed, i.e. the reaction has to be stopped after two ATRA steps. The second difficulty is to achieve a good regioselectivity. The reaction product after the first ATRA is a 1,3-dichloride and both halides could react in the second step.

We hypothesized that it should be possible to solve both problems by using appropriate electron-withdrawing substituents on the dichlorinated substrate. These substituents (R^2 and R^3) should selectively activate the adjacent chloride of the intermediate 1,3-dichloride. Furthermore, they should render the intermediate 1,3-dichloride more reactive than the 1,5-dichloride product, which would allow to avoid problems with oligomerization.

The addition of dichloroacetonitrile to styrene was used as a test reaction. As a catalyst, we decided to employ the Ru complex [Cp*$RuCl_2(PPh_3)$] in combination with Mg. Mg reduces the Ru^{III} precursor in situ to a catalytically active Ru^{II} species, and it helps to avoid the accumulation of undesired Ru^{III} complexes during the course of the reaction.[6a] Screening of different reaction conditions revealed

that the double Kharasch adduct **4** could be obtained in 91% isolated yield when styrene and dichloroacetonitrile were used in a ratio of 3:1 (Table 1, entry 1). The high yield of the desired 1,5-dichloride shows that the second ATRA reaction proceeds with good regioselectivity at the chloro atom next to the electron-withdrawing nitrile group. The one-pot reaction proceeds in a step-wise fashion via an 1,3-dichloride intermediate. The latter could be identified when reaction mixtures were analyzed after shorter times by gas chromatography (GC). *p*-Chloro- and *p*-fluorostyrene could be coupled in a similar fashion to give the chlorinated nitriles **5** and **6** in good yields after 48 h (Table 1, entries 2 and 3). Clean reactions were observed as well with the doubly activated chlorides $Cl_2C(CN)_2$ and $Cl_2C(CN)(CO_2Et)$ (Table 1, entries 4–6). For the reaction of styrene with $Cl_2C(CO_2Et)_2$, however, a lower yield of 70% was obtained due to the formation of side products, which were hard to separate (Table 1, entry 7). For all cases listed in Table 1, the products were obtained as a mixture of two or more diastereoisomers. The isomer ratios are given in the experimental part.

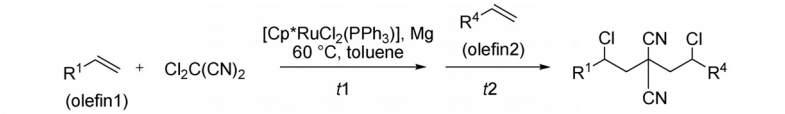
Next, we have investigated the possibility to perform double ATRA reactions with *two different olefins*. First, the less reactive olefin (1.1 equiv.) was allowed to react with $Cl_2C(CN)_2$ to give the mono Kharasch adduct. After time t_1, olefin 2 was added to the mixture and the reaction was stirred for another period t_2. Using this one-pot, two-step procedure it was possible to obtain the corresponding 1,5-dichlorides **11**–**14** as a mixture of stereoisomers in moderate to good yield (Table 2).

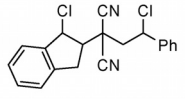
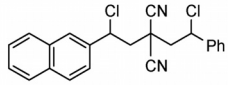
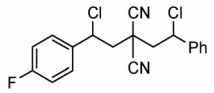
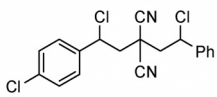
We have recently reported that cyclopropanes can be synthesized from 1,3-dichlorides (the reaction products of single ATRA and ATRC reactions) by Mg-induced dechlorination in THF.[6b] We were thus interested to see whether 1,5-dichlorides could be cyclized in a similar fashion to give cyclopentanes. It should be noted that the reductive cyclization of alkyl 1,5-dihalides has been reported before, but previous attempts have focused on the more reactive bromides and iodides.[12]

When a mixture of 4-chloro-2-(2-chloro-2-phenylethyl)-4-phenylbutanenitrile (**4**), Mg (10 equiv., activated with 5 mol-% of DIBAL-H) and LiCl[13] in THF was stirred for 2 h at room temperature, the desired cyclopentane **15** could indeed be detected by GC–MS (Scheme 3, a). In a reaction on preparative scale, **15** was obtained with an isolated yield of 49% as a mixture of three stereoisomers (ratio: 4:1:1). Interestingly, the entire ATRA-ATRA-dechlorination reaction sequence could also be performed in one pot (Scheme 3, b). After the second ATRA reaction had completed, the toluene solution was diluted with THF containing LiCl to induce cyclization. The yield for this one-pot reaction was 60%, which is higher than what was obtained in the two-step procedure (presumably because only one isolation step was involved). A similar behavior was observed for 4-chloro-2-[2-chloro-2-(4-fluorophenyl)ethyl]-4-(4-fluorophenyl)butanenitrile (**6**). A Mg-induced cyclization gave cyclopentane **16** in 39% yield as a mixture of isomers. A one-pot reaction according to Scheme 3 (b) gave slightly better results (42%). Attempts to cyclize more reactive dicyano compounds such as **7** were not successful.

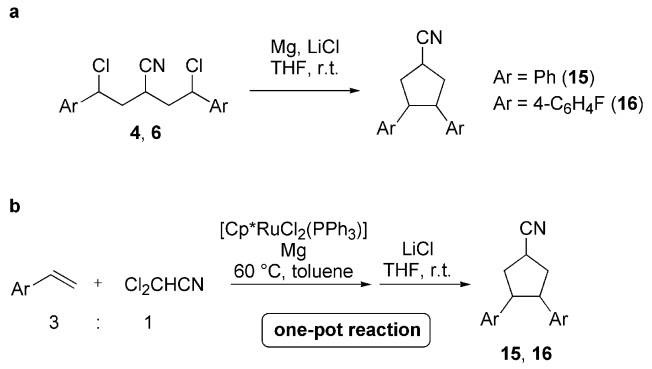
The main isomer of **15** (**15C**, see Exp. Section) was characterized by single-crystal X-ray crystallography. The two phenyl groups of **15C** show a *trans* configuration (Figure 1), which is expected to be more stable than the *cis* configuration because repulsive interactions between the phenyl rings are minimized.

Table 2. Sequential ATRA reactions with two different olefins catalyzed by [Cp*$RuCl_2(PPh_3)$] in the presence of Mg.[a]



#	Olefin 1	Olefin 2	Product		*t*1 [h]	*t*2 [h]	Yield [%][b]
1	Indene	Styrene		**11**	24	24	75
2[c]	2-Vinylnaphthalene	Styrene		**12**	24	24	76
3	*p*-Fluorostyrene	Styrene		**13**	24	48	70
3	*p*-Chlorostyrene	Styrene		**14**	24	48	72

[a] Reaction conditions: [olefin 1] 0.55 M, [chlorinated substrate] 0.50 M, [olefin 2] 1.00 M, [Ru] 5.0 mM (1.0 mol-%), [Mg] 30 equiv. with respect to the chlorinated substrate, toluene, 60 °C. [b] Isolated yields with respect to the chlorinated substrate. [c] Conditions: [olefin 1] 0.44 M, [chlorinated substrate] 0.40 M, [olefin 2] 0.80 M, [Ru] 4.0 mM (1.0 mol-%), [Mg] 30 equiv.



Scheme 3. Regio- and chemoselectivity for sequential ATRA reactions.

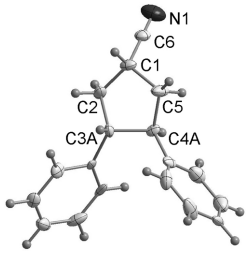


Figure 1. Molecular structure of cyclopentane **15C** in the crystal, shown with 40% thermal probability ellipsoids. Selected bond lengths [Å] and angles [°]: N1–C6 1.139(4), C1–C6 1.471(5), C1–C2 1.542(4), C1–C5 1.547(4), C2–C3A 1.522(6), C3A-C4A 1.543(7), C4A–C5 1.554(6); C6–C1–C2 112.5(3), C6–C1–C5 113.3(3), N1–C6–C1 178.9(5).

Conclusions

We have demonstrated that it is possible to perform sequential intermolecular atom transfer radical addition reactions of activated dichlorides to olefins with the help of a Ru catalyst.[14] Different chlorinated substrates and olefins can be used to give selectively 1,5-dichlorides in good yields. The stereo-control of the reactions is poor, which is not unexpected for this type of radical addition reaction. However, this one-pot three-component reaction provides easy access to a diverse set of linear 1,5-dichlorides, which are difficult to prepare otherwise. An interesting perspective is the utilization of 1,5-dichlorides as precursors for cyclopentanes. The successful synthesis of compounds **15** and **16** demonstrates that a reductive coupling is possible, but further optimization of the reaction conditions is needed to improve yields and substrate scope.

Experimental Section

General: All reactions were performed under an atmosphere of dry dinitrogen using a glovebox or standard Schlenk and vacuum-line techniques. The solvents and liquid substrates were distilled from appropriate drying agents according to the literature and stored under nitrogen. The olefinic substrates were stored at a temperature of –18 °C. The solvents and the chlorinated esters as well as the solids were kept at room temperature. Before use, commercial chemicals were put under an atmosphere of dry nitrogen. The Mg powder was agitated by a stirring bar under an atmosphere of dry dinitrogen for 5 d before use. LiCl was dried under vacuum at 140 °C for 5 h.[13] Catalyst $[Cp^*RuCl_2(PPh_3)]$[15] and the substrates $Cl_2C(CO_2Et)CN$[16] and $Cl_2C(CO_2Et)_2$[16] were synthesized according to literature procedures. The ^1H and ^{13}C spectra were recorded on a Bruker Avance DPX 400 spectrometer with the residual solvents as internal standards. All spectra were recorded at room temperature. Column chromatography was performed using Silica Gel 60 (230–400 mesh, 0.04–0.063 nm) from Fluka. Plates with Silica Gel 60 F245 from Merck were used for thin-layer chromatography. Elemental analyses were performed on a EA 1110 CHN instrument.

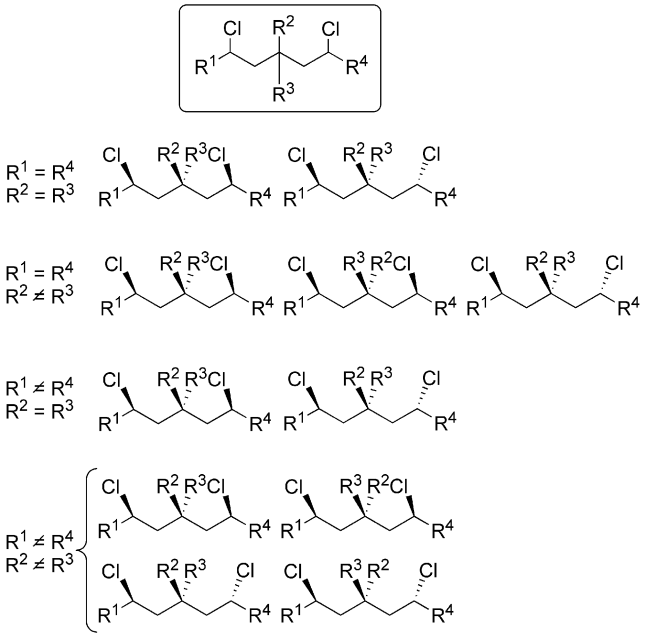
General Procedure for Sequential ATRA Reactions with One Olefin: Mg powder (30 equiv.) and toluene were added to a flask containing the desired amount of the Ru catalyst. The olefin (3.0 or 2.5 equiv.) and the chlorinated substrate (1.0 equiv.) were added ([chlorinated substrate] 0.5 M) and the mixture was stirred at 60 °C. After the given time, the crude reaction mixture was filtered and the solvent was removed under reduced pressure. The product was purified by flash chromatography.

General Procedure for Sequential ATRA Reactions with Two Different Olefins: Mg powder (30 equiv.) and toluene were added to a flask containing the desired amount of the Ru catalyst. Olefin 1 (1.1 equiv.) and the chlorinated substrate (1.0 equiv.) were added ($[\text{chlorinated substrate}]_{final}$ 0.5 M) and the mixture was stirred at 60 °C. After time t_1, olefin 2 (2.0 equiv.) was added and the reaction was stirred again at 60 °C. After time t_2, the crude reaction mixture was filtered and the solvent was removed under reduced pressure. The product was purified by flash chromatography.

General Procedure for Mg-Induced Reductive Cyclopentanations. Method A: Mg powder (231 mg, 10 equiv.), LiCl (201 mg, 5 equiv.) and DIBAL-H (48 μL of a 1 M solution in hexanes, 5 mol-% with respect to substrate) were added to a flask containing THF (5 mL). The mixture was stirred for 5 min and then a THF solution (4.5 mL) of the chlorinated substrate (0.95 mmol) was added ($[\text{chlorinated substrate}]_{final}$ 0.5 M). After stirring for 2 h at room temp., the reaction mixture was filtered under an inert atmosphere and Et_2O and a saturated aqueous solution of NH_4Cl were added. After biphasic separation, the aqueous phase was extracted again with Et_2O. The organic phases were mixed, washed with brine, dried with $MgSO_4$, and the solvents were removed under reduced pressure.

Method B: Mg powder (1.82 g, 30 equiv.) and toluene were added to a flask containing the Ru catalyst (14.2 mg, 1 mol-%). The olefin (3.0 equiv.) and dichloroacetonitrile (200 μL, 1.0 equiv.) were added ($[Cl_2CHCN]_{final}$ 0.5 M) and the mixture was stirred at 60 °C. After 48 h, the reaction mixture was cooled to room temperature and diluted to four times the original volume using a 0.5 M solution of LiCl in THF. After stirring for 2 h at room temp. the mixture was filtered under an inert atmosphere and Et_2O and a saturated aqueous solution of NH_4Cl were added. After biphasic separation, the aqueous phase was extracted again with Et_2O. The organic phases were mixed, washed with brine, dried with $MgSO_4$, and the solvents were removed under reduced pressure. In both cases (Methods A and B) the product was purified by flash chromatography.

Characterization of Products: All products except for **16** were obtained as a mixture of isomers. For the assignment of the ^1H NMR spectra, the different isomers were labeled as A, B, and C. Due to overlap of peaks in the ^{13}C NMR spectra, the correct number of peaks could not always be observed.



4-Chloro-2-(2-chloro-2-phenylethyl)-4-phenylbutanenitrile (4): Flash chromatography on silica gel: hexane/ethyl acetate, 9:1. The product (1.45 g, 91%) was obtained as a mixture of 3 diastereoisomers (ratio from ^{1}H NMR: δ = A:B:C = 1.0:1.0:1.8). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.19–2.41 (m, CH_2, 7 H, A, B, 3 H, C), 2.47–2.62 (m, CH_2, 1 H, A or B, 1 H, C, CHCN, 1 H, A or B), 2.87–2.97 (m, CHCN, 1 H, C), 3.52–3.62 (m, CHCN, 1 H, A or B), 4.99–5.15 (m, CHCl, 6 H, A, B, C), 7.25–7.39 (m, aromatic, 30 H, A, B, C). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 27.33, 27.99, 28.71 (*C*HCN), 41.10, 41.89, 41.94, 42.41 (CH_2), 59.33, 59.36, 60.58, 60.80 (CHCl), 119.92, 120.02, 120.09 (CN), 126.81, 126.83 (br), 126.94 (br), 127.01, 129.04 (br), 129.12, 129.21 (br), 129.28, 139.10, 139.21, 140.091, 140.24 (aromatic) ppm. $C_{18}H_{17}Cl_2N$ (318.25): calcd. C 67.93, H 5.38, N 4.40; found C 68.05, H 5.32, N 4.46.

4-Chloro-2-[2-chloro-2-(4-chlorophenyl)ethyl]-4-(4-chlorophenyl)-butanenitrile (5): Flash chromatography on silica gel: hexane/ethyl acetate, 9:1. The product (1.75 g, 90%) was obtained as a mixture of 3 diastereoisomers (ratio from ^{1}H NMR A:B:C = 1.0:1.7:2.3). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.19–2.40 (m, CH_2, 3 H, A, 4 H, B, 3 H, C), 2.43–2.59 (m, C*H*$_2$, 1 H, A, 1 H, C, CHCN, 1 H, A), 2.85–2.94 (m, CHCN, 1 H, C), 3.50–3.58 (m, CHCN, 1 H, B), 4.93–5.09 (m, CHCl, 6 H, A, B, C), 7.25–7.41 (m, aromatic, 24 H, A, B, C) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 27.20, 27.91, 28.63 (*C*HCN), 40.89, 41.77, 41.86, 42.35 (CH_2), 58.30, 58.36, 59.63, 59.84 (CHCl), 119.63, 119.67, 119.78 (CN), 128.16, 128.18, 128.31, 128.37, 129.23 (br), 129.35, 129.44, 134.87, 134.89, 135.14, 135.15, 137.51, 136.64, 138.50, 138.66 (aromatic) ppm. $C_{18}H_{15}Cl_4N$ (387.14): calcd. C 55.84, H 3.91, N 3.62; found C 55.76, H 3.94, N 3.57.

4-Chloro-2-[2-chloro-2-(4-fluorophenyl)ethyl]-4-(4-fluorophenyl)-butanenitrile (6): Flash chromatography on silica gel: hexane/ethyl acetate, 9:1. The product (1.31 g, 92%)was obtained as a mixture of 3 diastereoisomers (ratio from ^{1}H NMR: A:B:C = 1.0:1.7:2.3). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.17–2.37 (m, CH_2, 3 H, A, 4 H, B, 3 H, C), 2.44–2.60 (m, CH_2, 1 H, A, 1 H, C, CHCN, 1 H, A), 2.85–2.94 (m, CHCN 1 H, C), 3.48–3.59 (m, CHCN, 1 H, B), 4.96–5.07 (m, CHCl, 6 H, A, B, C), 7.25–7.41 (m, aromatic, 24 H, A, B, C). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 27.24, 27.97, 28.69 (*C*HCN), 41.06, 41.95, 42.02, 42.49 (CH_2), 58.39, 58.45, 59.75, 59.93 (CHCl), 115.90–116.34 (m, aromatic), 119.70, 119.74, 119.86 (CN), 128.58–136.12 (m, aromatic), 161.55–164.16 (m, C-F). $C_{18}H_{15}Cl_2F_2N$ (354.23): calcd. C 61.03, H 4.27, N 3.95; found C 61.05, H 4.33, N 4.01.

2,2-Bis(2-chloro-2-phenylethyl)malononitrile (7): Flash chromatography on silica gel: hexane/ethyl acetate, 88:12. The product (1.51 g, 88%) was obtained as a mixture of 2 diastereoisomers (ratio from GC: A:B = 1.0:1.1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.60–2.83 (m, CH_2, 8 H, A, B), 5.15–5.21 (m, CHCl, 4 H, A, B), 7.35–7.50 (m, aromatic, 20 H, A, B). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 34.08 [*C*(CN)$_2$], 47.12, 47.19 (CH_2), 57.83, 57.88 (CHCl), 112.49, 113.23, 114.05 (CN), 127.24 (br), 129.28 (br), 129.82 (br), 138.45 (aromatic). $C_{19}H_{16}Cl_2N_2$ (343.26): calcd. C 66.48, H 4.70, N 8.16; found C 66.36, H 4.78, N 8.17.

2,2-Bis[2-chloro-2-(naphthalen-2-yl)ethyl]malononitrile (8): Flash chromatography on silica gel: hexane/ethyl acetate, 88:12. The product (2.00 g, 90%) was obtained as a mixture of 2 diastereoisomers (ratio from GC: A:B = 1.0:1.0). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.64–2.94 (m, CH_2, 8 H, A, B), 5.33–5.38 (m, CHCl, 4 H, A, B), 7.43–7.57 (m, aromatic, 6 H, A, 6 H, B), 7.77–7.90 (m, aromatic, 8 H, A, 8 H, B). ^{13}C NMR ($CDCl_3$, 100 MHz): δ; 34.23 [*C*(CN)$_2$], 46.76, 46.86 (CH_2), 58.26, 58.35 (CHCl), 112.66, 113.44, 114.23 (CN), 123.80, 123.84, 126.86, 126.91, 127.01, 127.22, 127.86, 128.26, 128.28, 129.58, 129.59, 132.91, 133.66, 135.52, 135.60 (aromatic). $C_{27}H_{20}Cl_2N_2$ (443.38): calcd. C 73.14, H 4.55, N 6.32; found C 72.84, H 4.54, N 6.29.

Ethyl 4-Chloro-2-(2-chloro-2-phenylethyl)-2-cyano-4-phenylbutanoate (9): Flash chromatography on silica gel: hexane/ethyl acetate, 85:15. The product (1.77 g, 90%), was obtained as a mixture of 3 diastereoisomers (ratio from ^{1}H NMR A:B:C = 1.0:2.0:3.0). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 0.87, (t, J = 7.2 Hz, CH_3, 3 H, B), 1.16 (dd, J = 7.2, 7.2 Hz, CH_3, 3 H, C), 1.43 (t, J = 7.2 Hz, CH_3, 3 H, A), 2.26–2.31 (m, CH_2, 2 H, A), 2.43–2.47 (m, CH_2, 1 H, B), 2.52–2.57 (m, CH_2, 1 H, B), 2.67–2.72 (m, CH_2, 2 H, B), 2.84–3.00 (m, CH_2, 2 H, A, 4 H, C, OCH_2, 2 H, B), 3.57–3.84 (m, OCH_2, 2 H, C), 4.36 (q, J = 7.2 Hz, OCH_2, 2 H, A), 5.08–5.18 (m, CHCl, 6 H, A, B, C), 7.24–7.45 (m, aromatic, 30 H, A, B, C). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 13.17, 13.53, 13.82 (CH_3), 46.86 (CH_2), 46.97 (*C*CN), 47.09 (CH_2), 47.31 (*C*CN), 47.51 (CH_2), 47.55 (*C*CN), 47.82 (CH_2), 58.49, 58.62, 58.93, 58.96 (CHCl), 62.93, 63.26, 63.66 (OCH_2), 116.93, 117.11, 117.21 (CN), 126.92, 127.8, 127.89, 128.60, 128.69, 128.99, 129.03, 129.11, 129.14, 129.18, 129.21, 138.6, 138.7, 140.2 (aromatic), 166.26, 167.06, 167.79 (*C*OOEt). IR (film): $\tilde{\nu}$ = 1737 (C=O) cm^{-1}. $C_{21}H_{21}Cl_2NO_2$ (390.31): calcd. C 64.92, H 5.42, N 3.59; found C 65.03, H 5.70, N 3.58.

Diethyl 2,2-Bis(2-chloro-2-phenylethyl)malonate (10): Flash chromatography on silica gel: hexane/ethyl acetate, 9:1. The product (1.23 g, 70%) was obtained as a mixture of 2 diastereoisomers (ratio from ^{1}H NMR: A:B = 1.0:1.4). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.14 (t, J = 7.1 Hz, CH_3, 3 H, B), 1.18 (dd, J = 7.1, 7.1 Hz, CH_3, 6 H, A), 1.28 (t, J = 7.1 Hz, CH_3, 3 H, B), 2.83–3.05 (m, CH_2, 8 H, A, B), 3.84–4.03 (m, OCH_2, 4 H, A, 2 H, B), 4.16 (q, J = 7.14 Hz, OCH_2, 2 H, B), 4.86–4.90 (m, CHCl, 2 H, A), 4.97–5.00 (m, CHCl, 2 H, B), 7.29–7.41 (m, aromatic, 20 H, A, B). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 13.58, 13.79, 13.82, 13.92 (CH_3), 42.03, 42.19 (CH_2), 55.72, 55.74 [*C*(CO_2Et)$_2$], 58.86, 59.07 (CHCl), 61.64, 61.83, 61.91 (OCH_2), 127.06, 127.16, 128.65, 128.71, 128.75, 128.76, 141.39, 141.56 (aromatic), 169.54, 169.81, 170.40 (*C*OOEt). IR (film): $\tilde{\nu}$ = 1728 (C=O) cm^{-1}. $C_{23}H_{26}Cl_2O_4$ (437.36): calcd. C 63.16, H 5.99; found C 63.37, H 6.47.

2-(1-Chloro-2,3-dihydro-1*H*-indan-2-yl)-2-(2-chloro-2-phenylethyl)-malononitrile (11): Flash chromatography on silica gel: hexane/ethyl

acetate, 4:1. The product (1.06 g, 75%) was obtained as a mixture of 2 diastereoisomers (ratio from NMR: A:B = 1.0:1.0). δ = 2.76–2.80 (m, CH_2, 1 H), 2.90–3.02 (m, CH_2, 2 H), 3.06–3.31 (m, CH_2, 5 H), 3.42–3.58 (m, CH, 2 H), 5.24–5.34 (m, CHCl, 2 H), 5.45 (d, J = 6.7 Hz, CHCl, 1 H), 5.50 (d, J = 6.8 Hz, CHCl, 1 H), 7.20–7.60 (m, aromatic, 20 H, A, B). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 35.10, 35.8 [$C(CN)_2$], 39.35, 39.46 (CH_2Ar), 45.11, 45.14 (CH_2CCl), 56.39, 56.44 (*C*HCCl), 58.47 (br) (*C*HClCH$_2$), 62.04, 62.10 (*C*HClCH), 112.50, 112.95, 113.48, 113.70 (CN), 124.54, 125.3, 127.36, 127.4, 128.42, 129.33, 129.36, 129.83, 129.93, 137.76, 137.80, 138.41, 138.61, 140.31 (Ph). $C_{20}H_{16}Cl_2N_2$ (355.27): calcd. C 67.62, H 4.54, N 7.89; found C 67.35, H 4.68, N 7.82.

2-[2-Chloro-2-(naphthalene-2-yl)ethyl]-2-(2-chloro-2-phenylethyl)-malononitrile (12): Flash chromatography on silica gel: hexane/ethyl acetate, 4:1. The product (1.20 g, 76%) was obtained as a mixture of 2 diastereoisomers (ratio from GC: A:B = 1.0:1.0). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.56–2.98 (m, CH_2, 8 H), 5.14–5.21 (m, CHCl, 2 H), 5.36–5.42 (m, CHCl, 2 H), 7.32–7.58 (m, aromatic, 8 H, A, 8 H, B), 7.80–7.94 (m, aromatic, 4 H, A, 4 H, B). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 34.16 [$C(CN)_2$], 46.83, 46.92, 47.07, 47.16 (CH_2), 57.84, 57.91, 58.24, 58.31 (CHCl), 112.57, 113.31, 113.34, 114.13 (CN), 123.78, 123.83, 126.90, 126.93,127.02, 127.22, 127.87, 128.25, 129.26, 129.28, 129.61, 129.79, 132.92, 133.69, 135.53, 135.56, 138.43, 138.48 (aromatic). $C_{23}H_{18}Cl_2N_2$ (393.32): calcd. C 70.24, H 4.61, N 7.12; found C 70.39, H 4.33, N 7.18.

2-[2-Chloro-2-(4-fluorophenyl)ethyl]-2-(2-chloro-2-phenylethyl)-malononitrile (13): Flash chromatography on silica gel: hexane/ethyl acetate, 12:1. The product (501 mg, 70%) was obtained as a mixture of 2 diastereoisomers (ratio from GC: A:B = 1.0:1.5). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.57–2.90 (m, CH_2, 8 H, A, B), 5.19–5.24 (m, CHCl, 4 H, A, B), 7.10–7.14 (m, aromatic, 2 H, A, 2 H, B), 7.42–7.46 (m, aromatic, 7 H, A, 7 H, B). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 34.01 [$C(CN)_2$], 47.04, 47.11, 47.18 (CH_2), 57.13, 57.16, 57.84, 57.90 (CHCl), 112.51, 113.19, 114.01 (CN), 116.24–116.46 (m, aromatic), 127.23–138.48 (m, aromatic), 162.06–164.55 (m, C-F). $C_{24}H_{15}Cl_2FN_2$ (421.30): calcd. C 63.17, H 4.19, N 7.75; found C 63.16, H 4.67, N 7.40.

2-[2-Chloro-2-(4-chlorophenyl)ethyl]-2-(2-chloro-2-phenylethyl)-malononitrile (14): Flash chromatography on silica gel: hexane/ethyl acetate, 15:1. The product (709 mg, 72%) was obtained as a mixture of 2 diastereoisomers (ratio from GC: A:B = 1.0:1.2). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.57–2.90 (m, CH_2, 8 H, A, B), 5.14–5.21 (m, CHCl, 4 H, A, B), 7.34–7.38 (m, aromatic, 9 H, A, B). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 34.01 [$C(CN)_2$], 46.84, 46.92, 47.08, 47.15 (CH_2), 57.06, 57.11, 57.84, 57.88 (CHCl), 112.52, 113.19, 113.26, 113.99 (CN), 127.24, 128.65, 129.31, 129.33, 129.50, 129.54, 129.86, 135.71, 136.95, 136.96, 138.43 (aromatic). $C_{24}H_{15}Cl_3N_2$ (437.76): calcd. C 60.42, H 4.00, N 7.42; found C 60.01, H 4.06, N 7.04.

3,4-Diphenylcyclopentanecarbonitrile (15): Flash chromatography on silica gel: hexane/ethyl acetate, 9:1. The product (115 mg, 49% by method A; 371 mg, 60% by method B) was obtained as a mixture of 3 diastereoisomers (ratio from GC: A:B:C = 1.0:1.0:4.0). The NMR spectroscopic data of the main product (C) is given. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.22–2.35 (m, CH_2, 2 H), 2.56–2.63 (m, CH_2, 1 H), 2.67–2.74 (m, CH_2, 1 H), 3.10–3.22 (m, CHCN or C*H*Ph, 1 H), 3.35–3.43 (m, CHCN or C*H*Ph, 2 H), 7.07–7.26 (m, aromatic, 10 H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 26.56 (*C*HCN), 39.16, 39.14 (CH_2), 52.2, 53.33 (*C*HPh), 123.32 (CN), 126.80, 126.85, 127.29, 127.38, 128.59, 128.61, 141.08, 141.37 (aromatic). $C_{18}H_{17}N$ (247.34): calcd. C 87.41, H 6.93, N 5.51; found C 87.42, H 6.84, N 5.66.

3,4-Bis(4-fluorophenyl)cyclopentanecarbonitrile (16): Flash chromatography on silica gel: hexane/ethyl acetate, 12:1. The product (68 mg, 39% by method A; 140 mg, 42% by method B) was obtained as a single diastereoisomer. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.20–2.32 (m, CH_2, 2 H), 2.56–2.63 (m, CH_2, 1 H), 2.67–2.75 (m, CH_2, 1 H), 3.05–3.12 (m, C*H*Ar, 1 H), 3.16–3.24 (m, C*H*CN, 1 H), 3.28–3.36 (m, C*H*Ar, 1 H), 6.92–7.09 (m, aromatic, 9 H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 26.56 (*C*HCN), 39.16, 39.14 (CH_2), 52.2, 53.33 (*C*HPh), 115.38–115.61 (m, aromatic), 123.11 (CN), 128.56–136.51 (m, aromatic), 160.48–162.95 (m, C-F). $C_{18}H_{15}F_2N$ (283.32): calcd. C 76.31, H 5.34, N 4.94; found C 76.62, H 5.63, N 4.56.

Crystallographic Analyses: Single crystals of **15C** were obtained by slow evaporation of a CH_2Cl_2/hexane solution. Intensity data for **15C** were collected using an Oxford Diffraction KM-4 CCD diffractometer having kappa geometry and using graphite monochromatized Mo-K_α radiation (λ = 0.71073 Å) at low temperature. A summary of the crystallographic data, the data collection parameters, and the refinement parameters are given in Table 3. Data reduction was carried out with CrysAlis PRO.[17] Structure solution and refinement were performed with the SHELXTL software package.[18] The structures were refined using the full-matrix least-squares routines on F^2. All non-hydrogen atoms were refined with anisotropic displacement parameters. H atoms were included to the models in calculated positions using the riding model. Disorder problems have been observed for the carbon atoms next to the phenyl groups (C3 and C4).

Table 3. Crystallographic data for cyclopentane **15C**.

Formula	$C_{18}H_{17}N$
FW	247.33
Crystal size [mm^3]	0.20 × 0.11 × 0.09
Crystal system	orthorhombic
Space group	*Pbca*
a [Å]	5.981(2)
b [Å]	18.648(6)
c [Å]	24.581(7)
$\alpha = \beta = \gamma$ [°]	90
V [A^3]	2741.7(15)
Z	8
ρ calcd. [g cm^{-3}]	1.198
T [K]	140(2)
θ range [°]	3.31 to 26.36
Reflections collected	22582
Independent reflections	2805
Absorption correction	semiempirical
Max. / min. transmission	1.00000 / 0.47460
Data / restraints / parameters	2805 / 21 / 179
Goodness of fit on F^2	0.934
Final R indices [$I < 2\sigma(I)$]	R_1 = 0.0922, wR_2 = 0.0683
R indices (all data)	R_1 = 0.2845, wR_2 = 0.0994
Max. peak / hole [e Å^{-3}]	0.182 / –0.152

CCDC-790832 contains the supplementary crystallographic data for **15C**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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